

MONKI: a three-dimensional Monte Carlo simulator for transfer of polarised light in planetary atmospheres

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Abstract.

Spectropolarimetry is a powerful tool for characterising planetary atmospheres and surfaces. For the design and operation of spectro(polari)metric instrumentation, numerically simulated signals of the measured radiation are essential. ~~Here we~~ We present MONKI (Monte Carlo KNMI), an efficient and accurate Monte Carlo radiative transfer code written in Fortran, ~~based on the Monte Carlo method~~. MONKI computes ~~both total and total, linearly polarised, and circularly~~ polarised radiances reflected ~~and transmitted by a planetary atmosphere~~ by and transmitted through planetary atmospheres, fully accounting for the polarisation of light in all orders of scattering. ~~MONKI can handle atmospheres that are horizontally homogeneous;~~ Unlike classical Monte Carlo approaches that rely on post-sampling weight corrections and can therefore produce rare but disproportionately large photon weights, MONKI samples scattering directions from the full polarisation-dependent distribution,
10 consistently in both forward and backward Monte Carlo modes. We provide the corresponding theoretical framework in the appendices. Because of this exact polarised sampling approach, the code converges robustly for optically thick and/or strongly polarising atmospheres. MONKI can handle horizontally homogeneous atmospheres as well as ~~those atmospheres~~ with horizontal inhomogeneities, such as three-dimensional (3D) patchy clouds. We validate MONKI through comparisons with ~~various other radiative transfer codes and demonstrate that it converges reliably even for optically thick and strongly~~
15 ~~polarising atmospheres~~. Finally, we present sample simulations of sunlight reflected by the Earth and Venus, and explain the total and polarised radiance features by analysing the altitudes at which ~~the~~ photons are scattered. We conclude that MONKI is a versatile and accurate tool ~~, suitable~~ for simulations and detailed analyses of ~~locally reflected light by the total and polarised light emerging from the atmospheres of the~~ Earth, Venus, and, in principle, any other planet.

1 Introduction

20 Sunlight and, more generally, starlight ~~of from~~ solar-type stars, can be considered to be unpolarised when integrated over the disk (Kemp et al., 1987). This light becomes (partially) polarised when it is scattered by the particles constituting a planetary atmosphere. Measuring the degree of polarisation, P , of the scattered light, i.e., the ~~amount~~ fraction of polarised radiance ~~w.r.t.~~

with respect to the total radiance, is a powerful tool to characterise planetary atmospheres because the scattering angle and wavelength dependence of P is ~~are~~ very sensitive to the ~~scattering angles, the wavelength of the light, and the~~ composition, size, and shape of the scattering particles (Hansen and Travis, 1974). If a planetary atmosphere is bounded below by a surface, light that has been reflected by the surface can also influence the polarisation of the light that is reflected by the planet at the top of ~~at~~ the atmosphere (TOA), depending on optical properties of the surface. In particular, Fresnel reflection by liquid surfaces (water on Earth, but ~~methane~~ hydrocarbons on Titan) or leaves of vegetation can strongly polarise the light (see e.g. Mishchenko and Travis, 1997; Vanderbilt et al., 1985). Additionally, since P is a relative measure, it is insensitive to various instrumental errors and to uncertainties in the total flux of the light that is incident at TOA.

An example of an Earth-observation satellite instrument dedicated to measuring the degree of polarisation was the POLarisation and Directionality of the Earth's Reflectances (POLDER) imager (Deschamps et al., 1994). With multi-angular polarisation observations across three spectral bands, it provided an alternative for ~~cloud droplet size retrieval compared the retrieval of cloud droplet sizes~~ to traditional methods ~~relying that relied~~ solely on total radiances (Breon and Doutriaux-Boucher, 2005), and improved the capability to characterise aerosols above liquid water clouds (Waquet et al., 2013). In February 2024, NASA launched the Plankton, Aerosol, Cloud, Ocean Ecosystem (PACE) satellite (Werdell et al., 2019), carrying the Hyper-Angular Rainbow Polarimeter-2 (HARP-2) (McBride et al., 2024) and the SPEXone spectropolarimeter (van Amerongen et al., 2019), enabling accurate global polarisation measurements of aerosols and clouds to better quantify their impact on radiative forcing. ~~Upcoming spaceborne Earth observation polarimeters are the Multi-Viewing Multi-Channel Multi-polarisation Imaging mission (3MI) on METOP-SG (On 13 August 2025, the MetOp-SG-A1~~ (Meteorological Operational Satellite - Second Generation ~~) planned for 2025 A1~~ was launched successfully carrying the Multi-Viewing Multi-Channel Multi-Polarisation Imaging (3MI) instrument (Marbach et al., 2015), and the Multi-Angle Polarimeter (MAP) on the Copernicus Anthropogenic Carbon Dioxide Monitoring (CO2M) mission ~~that~~ is scheduled for launch in ~~2026-2027~~ (Spilling and Thales, 2021).

Polarimetry has also proven its strength in characterising other solar system bodies than the Earth (see Bagnulo et al., 2024, and references therein). A famous example is the characterisation of Venus's main cloud deck by Hansen and Hovenier (1974), who found that the droplets consist of a ~~~~~ ~75% H_2SO_4 mixture with water, and that their sizes are described by a narrow distribution and effective radii of $\sim 1 \mu\text{m}$ ~~radius~~. They achieved this characterisation using ground-based polarisation measurements of Venus (spatially unresolved, thus integrated across the planet's disk) at a number of wavelengths and a range of planetary phase angles (that is, the angles between Earth, Venus and the Sun) collected over decades by several different observers. ESA's upcoming Venus orbiter EnVision (Ghail et al., 2021), planned for launch in 2032, will carry VenSpec-H (Neefs et al., 2025), a near-infrared spectrometer that will include polarisation filters. These filters will be used to correct for VenSpec-H's polarisation sensitivity (i.e. like with many spectrometers, the instrument response depends on the polarisation of the observed light) and can also be used to characterise Venus's clouds and hazes in unprecedented detail. Beyond our solar system, polarimetry has been proposed to detect liquid water clouds (Stam, 2008; Karalidi et al., 2011; Rossi et al., 2022) and liquid water oceans (Trees and Stam, 2019, 2022) on exoplanets, for example with NASA's upcoming space-borne Habitable Worlds Observatory (HWO) (Vaughan et al., 2023).

Radiative transfer simulations of reflected (polarised) light are essential for spectro(polari)meters on space missions. Simulations (1) help explore the observational parameter space during the design phase, (2) serve as sample signals for the development of end-to-end data simulations, and (3) form the core of atmospheric retrieval algorithms during space mission operations. For instruments that are polarisation sensitive, simulations are used to estimate the impact of the sensitivity on the total radiance measurements. Even for instruments with a polarisation scrambler, such as TROPOMI (Veefkind et al., 2012), accounting for polarisation in radiative transfer simulations remains important for accurate total radiance estimations. This is because atmospheric scattering is only properly described by a (phase) matrix multiplication of the Stokes vector, not by a scalar (phase function) multiplication of the radiance (see Chandrasekhar, 1960; van de Hulst, 1981; Hovenier et al., 2004). Neglecting (linear) polarisation can cause errors of more than 9% in the computed geometric albedo of planets with Rayleigh scattering atmospheres (Stam and Hovenier, 2005), and up to 10% in the computed locally reflected radiance for cloud-free atmospheres (Mishchenko et al., 1994) and 8% in patchy cloudy conditions (Emde and Mayer, 2018), depending on the wavelength and scattering geometry.

Several types of radiative transfer algorithms can simulate both the total and polarised radiances reflected by scattering planetary atmospheres. Classical radiative transfer codes divide the atmosphere into horizontally homogeneous, plane-parallel layers, computing the signal at the top of the atmosphere (TOA) using e.g. the doubling-adding method (de Haan et al., 1987) or the discrete-ordinates method (Chandrasekhar, 1960). Despite advances in radiative transfer simulations and computing power, most satellite retrieval algorithms for aerosols, clouds and trace gases still rely on this horizontally homogeneous approach, due to its simplicity, efficiency, and the limited availability of knowledge about the scene’s inhomogeneity. For instance, the aerosol retrieval algorithm of SPeXone applies an independent pixel approximation (IPA), modelling the signal of a partly cloudy pixel as a weighted sum of horizontally homogeneous cloud-free and fully cloudy scenes (see Hasekamp, 2010; Hasekamp et al., 2019).

In reality, planetary atmospheres are usually horizontally inhomogeneous. In particular, 3D cloud structures can cast shadows onto the surface or lower atmospheric layers, and/or scatter light towards cloud-free regions (see, e.g. Marchand and Ackerman, 2004; Marshak and Davis, 2005; Marshak et al., 2006), thus affecting observations from imagers such as MODIS (Wen et al., 2013; Várnai et al., 2013). Furthermore, 3D cloud effects can introduce significant errors in aerosol retrievals, as shown by Stap et al. (2016a, b) and Cornet et al. (2018) for POLDER observations over broken cloud decks. Although spectro(polari)meters typically have larger pixels than imagers, Trees et al. (2022) detected cloud shadows in radiance measurements by the TROPOMI spectrometer which has a pixel size of $5.5 \times 3.5 \text{ km}^2$ in the nadir viewing direction. As the spatial resolution of spectro(polari)metric instruments continues to increase, understanding and correcting for these 3D effects becomes increasingly important.

Examples of radiative transfer codes capable of simulating both total and polarised radiances while accounting for the 3D structure of the atmosphere are 3DMCPOL (Cornet et al., 2010; Fauchez et al., 2014), MSCART (Wang et al., 2017), MYSTIC (Mayer, 2009; Emde et al., 2010), SHDOM (Evans, 1998), and SPARTA (Barlakas et al., 2016). Most of these codes (except SHDOM) use the Monte Carlo method, simulating light as the statistical propagation of photon packets through a model atmosphere. Their simulated total and polarised radiances have been compared (Emde et al.,

2018). We note that these codes have primarily been applied to model scenarios on Earth. An example of a polarised 3D radiative transfer code for simulating sunlight reflected by other planets than ~~the~~ Earth is the Preconditioned Backward Monte Carlo (PBMC) algorithm of García Muñoz and Mills (2015). Unlike classical Monte Carlo codes, PBMC converges even in
95 optically thick and strongly polarising atmospheres, such as that of Venus, by fully ~~accounting for the photon’s polarisation state history along its path.~~ taking into account polarisation of light when sampling scattering directions. Other Monte Carlo codes that also take into account polarisation-dependent sampling of scattering directions are 3DMCPOL (Cornet et al., 2010), SMART-G (Ramon et al., 2019), and the code of Bartel and Hielscher (2000), but only do so in forward mode.

In this paper, we present MONKI (Monte Carlo KNMI), a 3D Monte Carlo code for simulating total and linearly and
100 circularly polarised radiances that are locally reflected or transmitted by planetary atmospheres. MONKI can perform simulations in both forward and backward modes (with reversed photon directions) for horizontally homogeneous and inhomogeneous (3D cloudy) ~~scenes~~ plane-parallel atmospheres. MONKI is designed for versatility, accepting input model atmospheres and surfaces for any planet. For Earth-based applications, MONKI computes atmospheric optical properties identically to DAK (Doubling Adding KNMI) (de Haan et al., 1987; Stammes, 2001) and has already been used to simulate cloud
105 shadow effects in TROPOMI’s Absorbing Aerosol Index product (Trees et al., 2025), as well as 3D cloud-radiation effects in satellite-based global horizontal irradiance retrievals (Wiltink et al., 2026). By fully tracking the polarisation state history of photons along their ~~paths,~~ MONKI also converges in trajectories and sampling scattering directions from the corresponding polarisation-dependent distribution. MONKI converges in both forward and backward modes, including for optically thick and strongly polarising planetary atmospheres. The code has been written in ~~Fortran-90.~~ modern Fortran. In addition to presenting
110 the code itself, this paper provides, we believe for the first time, a complete derivation of the underlying forward and backward Monte Carlo equations and polarisation-dependent sampling formulae, thereby offering a unified theoretical framework for readers who wish to understand, validate, or extend polarised Monte Carlo radiative transfer methods.

This paper is organised as follows. In Sect. 2, we describe the MONKI algorithm. In Sect. 3, we validate MONKI through comparisons with results of other radiative transfer codes. In Sect. 4, we show sample simulations of total radiances and the
115 degree of polarisation for locally reflected light from Earth and Venus. In Sect. 5, finally, we provide a summary, discussion, and outlook. The appendices contain ~~derivations and~~ detailed explanations of the formulae implemented in MONKI, together with the derivation of the forward and backward Monte Carlo equations for polarised radiative transfer.

2 Method

2.1 Definitions of ~~TOA~~ radiance, reflectance and polarisation

120 The radiance and polarisation state of a light beam can be described by a Stokes vector (see, e.g., Hansen and Travis, 1974; Hovenier et al., 2004)

$$\mathbf{I} = [I, Q, U, V]^T, \quad (1)$$

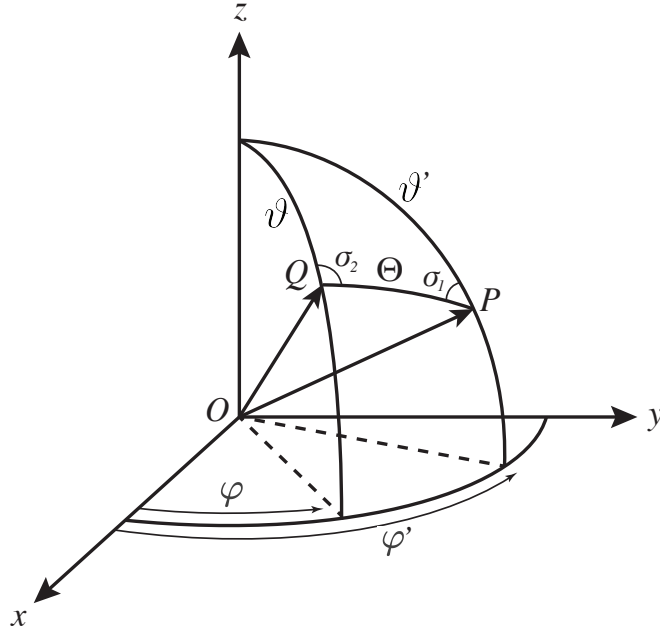


Figure 1. The reference system used in MONKI. The z -axis points towards the zenith. The incident light with propagation direction OP is scattered at O into direction OQ over scattering angle Θ . The azimuthal angles for the incident and scattered light are denoted by φ' and φ , respectively. The zenith angles of the incident and scattered light are ϑ' and ϑ , respectively. Angles σ_1 and σ_2 are the angles between the meridian planes of the incident and scattered light, respectively, with OPQ the scattering plane.

where I is the total radiance (or intensity), Q and U are the linearly polarised radiances, and V is the circularly polarised radiance. All radiances are expressed in units of $\text{W m}^{-2} \text{nm}^{-1} \text{sr}^{-1}$, where nm^{-1} indicates the dependence on the wavelength of light, λ , and sr^{-1} indicates the dependence on the solid angle, Ω . The linearly polarised radiances, Q and U , are defined relative to a reference plane. For example, for light that is reflected locally by the planet, the local meridian plane can be used, which contains the local zenith direction and the direction of light propagation towards the observer (see de Haan et al., 1987). In particular, for $Q > 0$ ($Q < 0$), the direction of polarisation is parallel (perpendicular) to the reference plane. For $U > 0$ ($U < 0$), the direction of polarisation is rotated by $+45^\circ$ (-45°) from the direction parallel to the reference plane, with positive rotations defined as anti-clockwise when looking in the propagation direction of the light. For $V > 0$, there is an excess of right-handed circular polarisation, that is, the electric field vector rotates clockwise when looking in the propagation direction of the light.

The sunlight that is incident at the top of the atmosphere (TOA) of a planet is assumed to be unpolarised (Kemp et al., 1987), and is represented by the following Stokes vector flux Stokes vector $\underline{E}_0(\lambda) = E_0(\lambda)\underline{1}$, with

$$\underline{1} = \begin{bmatrix} E_0(\lambda)\underline{1}, 0, 0, 0 \end{bmatrix}^T, \quad (2)$$

and where $E_0(\lambda)$ is the wavelength-dependent total incident solar flux, measured perpendicular to the propagation direction of the light, expressed in $\text{W m}^{-2} \text{nm}^{-1}$. In Earth observation studies, ~~the wavelength-dependent total solar flux, $E_0(\lambda)$~~ ; is commonly known as the 'irradiance spectrum'. The incident sunlight is ~~also~~ assumed to be unidirectional, leading to the following expression for the radiance Stokes vector of the light that is locally reflected by the planetary atmosphere-surface system (thus at TOA) (see Hansen and Travis, 1974)¹

$$\mathbf{I}(\mu, \mu_0, \varphi, \varphi_0, \lambda) = \frac{\mu_0}{\pi} \mathbf{R}(\mu, \mu_0, \varphi, \varphi_0, \lambda) \mathbf{E}_0(\lambda), \quad (3)$$

where $\mathbf{R}$ denotes the 4×4 reflectance matrix of the local atmosphere-surface system. We use the quantities ~~$\mu = |\cos \theta|$ and $\mu_0 = |\cos \theta_0|$, where θ ($0 \leq \theta \leq \pi$) and θ_0 ($0 \leq \theta_0 \leq \pi$)~~ $\mu = |\cos \vartheta|$ and $\mu_0 = |\cos \vartheta_0|$, where ϑ ($0 \leq \vartheta \leq \pi$) and ϑ_0 ($0 \leq \vartheta_0 \leq \pi$) represent the ~~local viewing and solar zenith angles~~ zenith angles of the propagation directions of the reflected light and the incident direct solar beam, respectively, measured positively from the local zenith (i.e., the z -axis). ~~see Fig. 1.~~ Angles φ ($0 \leq \varphi \leq 2\pi$) and φ_0 ($0 \leq \varphi_0 \leq 2\pi$) are the ~~local viewing and solar~~ corresponding azimuth angles, respectively. They are defined relative to the x -axis of the local Cartesian coordinate system, ~~and are measured in the clockwise sense when looking in the local zenith direction, as illustrated in Fig. 1 with the sign convention shown in Fig. 1.~~ For (scattered or unscattered) light that is incident on a particle, we use the notations ϑ' and φ' instead of ϑ_0 and φ_0 . In addition, we use $\theta = \arccos(\mu)$ and $\theta_0 = \arccos(\mu_0)$ for the viewing and solar zenith angles, defined between 0 and $\pi/2$ with respect to the local normal.

~~The reference system used in MONKI. The incident light with propagation direction OP is scattered at O into direction OQ over scattering angle Θ . The azimuthal angles for the incident and scattered light are denoted by φ' and φ , respectively. The zenith angles of the incident and scattered light are ϑ' and ϑ , respectively. In the case of incident and reflected (or transmitted) light at TOA (or BOA), the solar and viewing azimuth and zenith angles are defined as $\varphi_0 = \varphi'$, $\theta_0 = 180^\circ - \vartheta'$, $\varphi = \varphi$, and $\theta = \vartheta$. Angles σ_1 and σ_2 are the angles between the meridian planes of the incident and scattered light, respectively, with OPQ the scattering plane.~~

Light in the local atmosphere-surface system usually becomes polarised upon scattering, leading to non-zero values of Q , U , and/or V . From Eq. 3 it follows that the assumption of ~~the~~ unpolarised incident sunlight implies that only the first column of $\mathbf{R}$, thus $[R_{11}, R_{21}, R_{31}, R_{41}]^T$, contributes to $\mathbf{I}$. ~~Combining Eqs. 2 and Substituting $E_0 = E_0 \mathbf{1}$ into Eq. 3,~~ and omitting the explicit dependencies on angles and wavelengths, we arrive at

$$\begin{bmatrix} R_{11} \\ R_{21} \\ R_{31} \\ R_{41} \end{bmatrix} = \frac{\pi}{\mu_0 E_0} \begin{bmatrix} I \\ Q \\ U \\ V \end{bmatrix}, \quad (4)$$

where the element R_{11} is referred to as the total TOA reflectance, R_{21} and R_{31} as the linearly polarised TOA reflectances, and R_{41} as the circularly polarised TOA reflectance. Those TOA reflectances are independent of E_0 , and their (angular and ~~wavelength-dependent~~) values are determined by the composition wavelength-dependent values depend on the composition

¹Hansen and Travis (1974) used the notation $\pi \mathbf{F}_0$ instead of $\mathbf{E}_0$ for the solar flux vector.

165 and structure of the local atmosphere and surface. Similar definitions can be derived for the transmittance at the bottom of the atmosphere (BOA), by replacing $\mathbf{R}$ in Eq. 3 with $\mathbf{T}$, the 4×4 transmission matrix of the local ~~atmosphere~~atmosphere-surface system (note that light that is reflected by the surface can be scattered downwards again by the atmosphere - the atmospheric transmission matrix will thus also depend on the properties of the surface, if present).

The polarisation of the reflected or transmitted light beam ~~can be~~is quantified by its degree of polarisation P :

$$170 \quad P = \frac{\sqrt{Q^2 + U^2 + V^2}}{I}. \quad (5)$$

The degree of polarisation is independent of the choice of reference plane. ~~When~~For observations in the principal plane, i.e. the vertical plane containing the local zenith direction and the incident solar beam, the viewing direction lies in the same vertical plane as the incident radiation. In this case (with relative azimuth angles of 0° or 180°), the principal plane coincides with the scattering plane. If the local atmosphere-surface system is horizontally homogeneous, symmetry implies that $U = 0$, and we
 175 can use ~~an alternative definition that includes the direction of polarisation:~~ the signed degree of linear polarisation

$$P_s = -Q/I. \quad (6)$$

When P_s is positive (negative), the light is polarised perpendicularly (parallel) to the reference plane. Because P and P_s are relative measures, they are both independent of the incoming solar flux E_0 .

2.2 Model grid and ~~coordinate system~~geometrical notation

180 The ~~local atmosphere-surface coordinate system~~coordinate system used in MONKI is Cartesian, with the positive z -axis pointing towards the local zenith and the x - and y -axes oriented horizontally, as shown in Fig. 1. The ~~model~~computational domain of the atmosphere-surface system is discretised on a 3D ~~domain~~rectangular grid that is composed of N_x ~~and~~ N_y columns in the x ~~and~~direction, N_y columns in the y ~~directions~~direction, and N_z layers in the z direction. ~~The domain is cyclic~~, as illustrated in Fig. 2. All columns have the same horizontal dimensions, which may be square or rectangular, while the layer
 185 thicknesses may vary with altitude. Each grid cell may contain a different number and type of scattering particles, as described in Appendix A. The computational domain is periodic in the horizontal directions: light emerging from one horizontal boundary re-enters the domain through the opposite boundary. ~~The observer and light source are considered infinitely~~

To indicate in our Monte Carlo simulations the location and direction of a photon that travels through the computational domain, we use the vectors $\mathbf{x}$ and $\boldsymbol{\omega}$, that denote position and propagation direction, respectively:

$$190 \quad \mathbf{x} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}, \quad \boldsymbol{\omega} = \begin{bmatrix} \sin \vartheta \cos \varphi \\ \sin \vartheta \sin \varphi \\ \cos \vartheta \end{bmatrix}. \quad (7)$$

Here, ϑ and φ are the local zenith and azimuth angles, respectively, as defined in Sect. 2.1 and shown in Fig. 1. Throughout the description of the method, $\boldsymbol{\omega}$ denotes a generic photon propagation direction. At a scattering event, we use $\boldsymbol{\omega}'$ for the

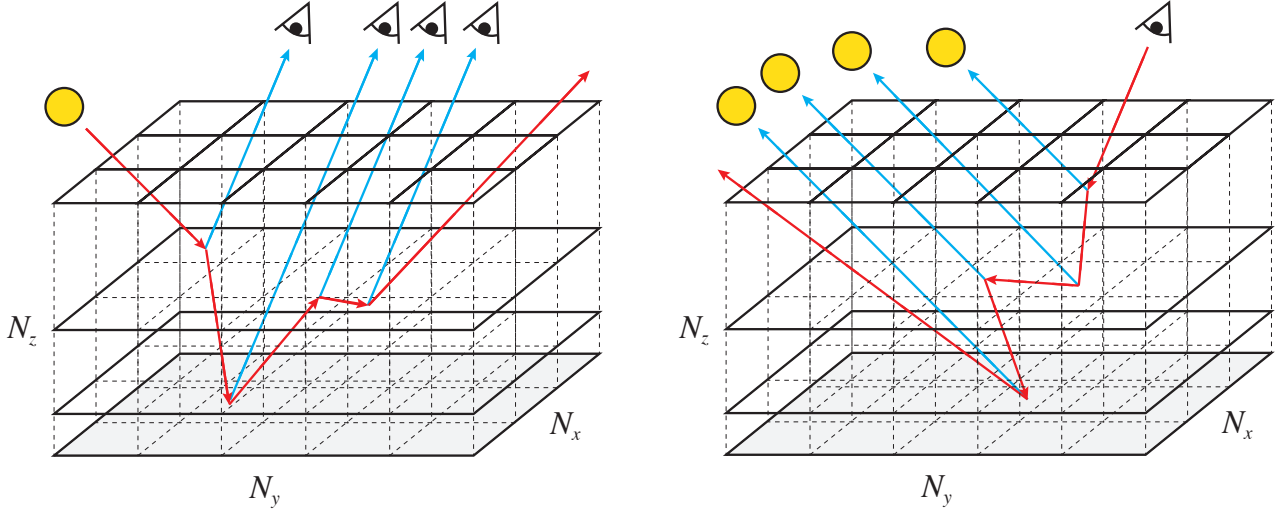


Figure 2. Sketches of the 3D computational domain of MONKI with a photon trajectory (red arrows) in forward mode (left) and backward mode (right). Here, the numbers of columns in the x and y directions are $N_x = 3$ and $N_y = 5$, respectively, while $N_z = 3$ is the number of layers. The domain is periodic in the horizontal directions. At every scattering event (i.e. each change in direction of the red arrow), the probability of scattering towards the detector/eye (in forward mode) or towards the light source/Sun (in backward mode) is computed according to the local estimation method (blue arrows).

propagation direction of the photon incident on the scattering particle, and ω for the propagation direction after scattering, consistent with the angular notation in Fig. 1.

195 The light source (the Sun) and the observer (the detector) are assumed to be sufficiently far from the domain, resulting in identical values of θ , θ_0 , φ , and φ_0 for all grid cells computational domain that the incident solar beam and the rays towards the detector can be treated as collimated. We denote the entry point of a photon of the incident sunlight at TOA by x_0 , and its direction of propagation by ω_0 . Similarly, $x^\bullet$ denotes the point where a photon travelling in the detector direction intersects the TOA or BOA boundary, and $\omega^\bullet$ denotes the propagation direction of light towards the detector. The directions ω_0 and $\omega^\bullet$ are therefore constant throughout the domain. When needed, O denotes the horizontal area of a selected detector grid column at TOA or BOA.

200

2.3 Calculating the reflected and transmitted sunlight

Flow diagram of a photon trajectory in MONKI. The boxes in the grey area pertain to the path of the photon through the atmosphere-surface domain, while the boxes in the blue and green areas represent interactions with the atmosphere and surface, respectively.

Given an atmosphere-surface system, MONKI computes the total and polarised TOA reflectances and BOA transmittances of an atmosphere-surface system radiances reflected at TOA, or transmitted at BOA, using the Monte Carlo method (see, e.g.,

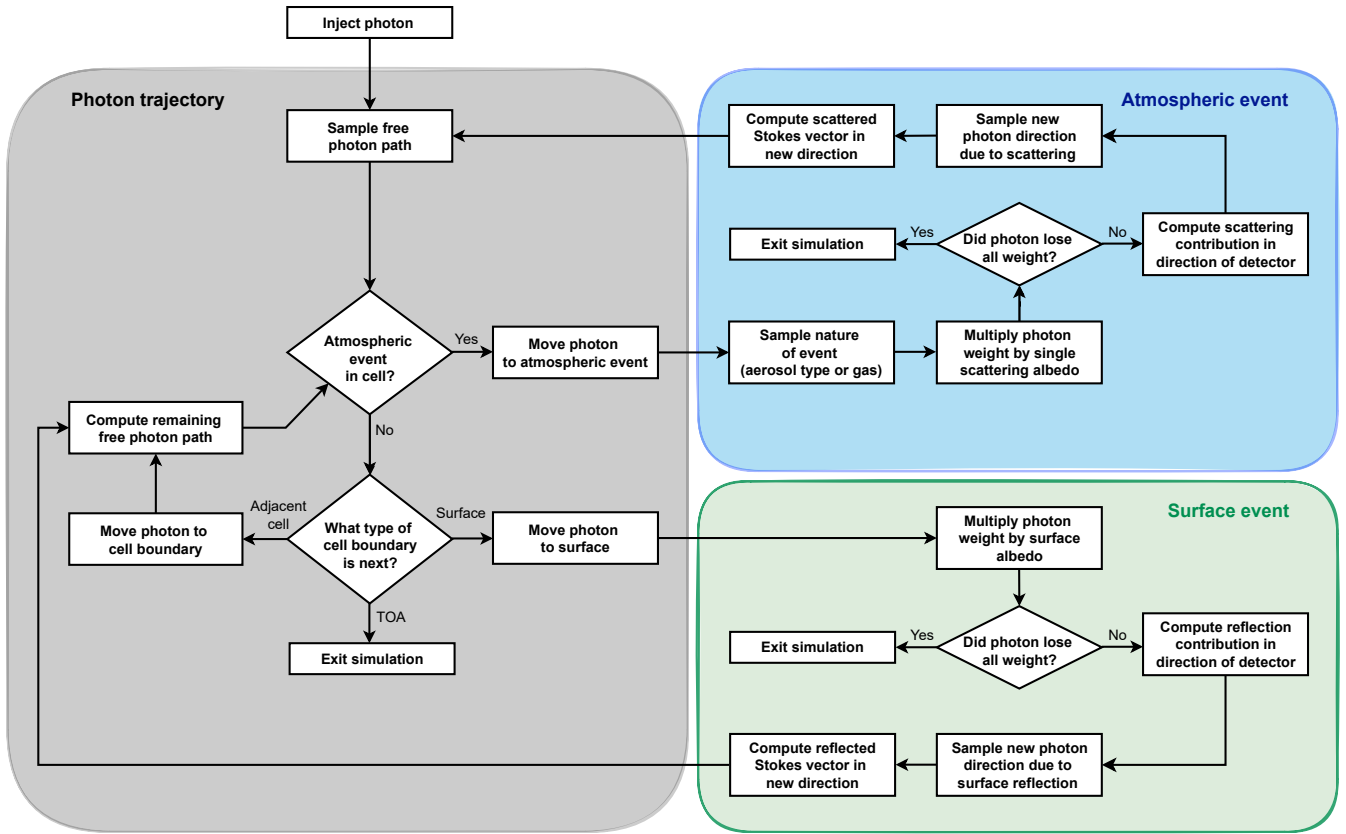


Figure 3. Flow diagram of a photon trajectory in MONKI in forward mode. The boxes in the grey area pertain to the trajectory of the photon through the atmosphere-surface domain, while the boxes in the blue and green areas represent interactions with the atmosphere and surface, respectively.

Marshak and Davis, 2005): "~~photons~~ photons" are traced through the system.² Since MONKI fully accounts for the polarisation of light, a photon is represented by a normalised Stokes vector, $\vec{I} = [1, \bar{Q}, \bar{U}, \bar{V}]^T$ $\vec{I} = [1, \bar{Q}, \bar{U}, \bar{V}]^T$, carrying a weight, w , representing that represents the probability of 'survival' of the photon (i.e., w will become zero upon total absorption). Since $\vec{I}$ changes along the photon trajectory, its dependence on position, direction, and previous events is omitted for readability. The trajectory of a photon in the forward mode is summarised in the flow diagram in Fig. 3, which is explained below. We refer to Appendices G1 to G7 for the derivation of the forward Monte Carlo equations for polarised light as used in this section. A similar diagram applies for the backward mode, by replacing 'detector' with 'the Sun' (see Sect. 2.4).

The photons begin their trajectory as solar irradiance photons (with $\bar{Q} = \bar{U} = \bar{V} = 0$ and $w = 1$) at TOA where they are injected into the direction of propagation of the sunlight at random x, y -locations into the grid cells

²Note that what we refer to as photons in a Monte Carlo radiative transfer simulation ~~do are~~ not represent actual quanta of the electromagnetic field, but rather ~~are~~ numerical entities used to simulate the light path in a statistical manner.

At the start of a forward simulation for light with a given wavelength λ , photons are injected at TOA at randomly sampled entry points x_0 , with propagation direction ω_0 , normalised Stokes vector $\bar{I} = 1$, and weight $w = 1$. Before a photon moves through the domain, the free photon path length d , that is, the straight photon path length through the grid cell (the straight geometrical distance travelled) until an atmospheric event (i.e., a, i.e. scattering or absorption, occurs) is sampled as follows (see App-Appendix B):

$$d = \frac{-\ln(\xi_1)}{\beta}, \quad (8)$$

where ξ_1 is a random number in the open interval $(0, 1)$, drawn from a uniform distribution. Quantity β is the atmospheric extinction coefficient in m^{-1} , which depends on the vertical optical thickness b and the vertical extent Δz of the grid cell via $\beta = b/\Delta z$. The wavelength dependence and spatial distribution of b throughout across the 3D grid depend on the scattering and absorption optical thicknesses of the gases and aerosol particles in the grid cells (see Appendix A for a description of the model atmosphere). Although all optical properties and radiances generally depend on the wavelength, we omit the λ -notation here. In the current version of MONKI, we only consider elastic scattering processes, that is, for which the wavelength of the light remains invariant.

Next, the free path length d is compared with the distance along the straight photon path to the boundary of the grid cell, to check whether the atmospheric event occurs in the current cell. If so, the photon is moved to the atmospheric event location. If not, the photon is moved along its straight path to the grid cell boundary. The grid cell boundary may be (1) the surface, (2) TOA where the photon leaves the simulation, or (3) the boundary of an adjacent grid cell. In the latter case, the free photon path distance-path length that remains after reaching the boundary is rescaled using the β value of the adjacent grid cell-grid cell that the photon enters.

If an atmospheric event occurs, the photon interacts with an atmospheric particle, which can be either a gas molecule or an aerosol particle of one of the atmospheric constituents present in the grid cell: either the gas or one of the n_c types found in the grid cell N_c aerosol types. To determine which particle-type-constituent is encountered, we draw a uniformly distributed random number ξ_2 between 0 and 1 and solve the following equation-for- j -inequality for the constituent type index t (see, e.g., Eq. 18 of Barker et al., 2003):

$$\sum_{i=1}^{j-1} \frac{\beta_{i,t-1}}{\beta} \frac{\beta_{t'}}{\beta} \leq \xi_2 < \sum_{i=1}^j \frac{\beta_{i,t}}{\beta} \frac{\beta_{t'}}{\beta}, \quad (9)$$

where β_i where $\beta_{t'}$ is the total extinction coefficient of a certain aerosol type ($i = 1, \dots, n_c$) or of the mixture of scattering gas molecules ($i = n_c + 1$) constituent t' in the grid cell. Here, β is again the constituents comprise the gas and the N_c aerosol types, and $\beta = \sum_{i=1}^{n_c+1} \beta_i$ is the total extinction of all aerosols and the gas in the grid cell: $\beta = \sum_{i=1}^{n_c+1} \beta_i$ coefficient of the grid cell. Appendix A explains how this constituent-wise treatment is related to the effective optical properties of a grid cell that contains gas molecules and one or more aerosol types.

In an atmospheric event, the photon is either absorbed or scattered by the constituent that it encounters. The probability of scattering is, by definition, equal to the single-scattering albedo. Therefore, instead of single-scattering albedo a_t of that

constituent, and that of absorption equals $(1 - a_t)$. Instead of removing the photon from the cell-simulation upon absorption, we apply a more efficient approach: multiplying the photon weight w by the single-scattering albedo. For molecular scattering, a_t . Thus, if the gas is selected, w is multiplied by the molecular single-scattering albedo a^m (see Appendix A). For aerosol scattering; if aerosol type c is selected, w is multiplied by the single-scattering albedo a^c of the type of aerosol a^a (see Appendix A). If the photon lost all its weight has lost virtually all of its weight³, the photon exits-is removed from the simulation. Otherwise, its contribution to the TOA reflectance-or-BOA-transmittance-or BOA signal measured by the detector for this scattering event is computed, as explained below.

Instead of collecting photons within the narrow solid angle subtended by the detector, MONKI uses the more efficient 'local estimation method' (Marchuk et al., 1980; Marshak and Davis, 2005), a standard approach in Monte Carlo radiative transfer algorithms (see, e.g., Spada et al., 2006; Mayer, 2009; Deutschmann et al., 2011). In this method, the photon is used to simulate the signal contributions of all atmospheric scattering and surface reflection events along the photon's trajectory.

The contribution of an event Suppose that we have a detector towards the direction $\omega^\bullet$. For an atmospheric event involving constituent type t , the contribution to the TOA reflectance-or-BOA-transmittance-or BOA signal measured by the detector is expressed by the column vector Φ : W :

$$W(\omega^\bullet) = w \cdot \frac{1}{4\pi} Z_t(x, \omega^\bullet, \omega') \cdot \bar{I}' \cdot \exp \left(- \int_0^{s_{\text{det}}} \beta(x + s' \omega^\bullet) ds' \right), \quad (10)$$

where the exponential term represents the direct transmittance along the straight path s' from the event location ($s=0$ in direction $\omega^\bullet$, from the location x of the considered event ($s'=0$) to the detector ($s=s_{\text{det}}$ boundary ($s'=s^\bullet$), and χ is the 4×4 normalised phase matrix, representing the probability density function of the photon scattering (or surface reflection) direction. $Z_t/(4\pi)$ is the normalised 4×4 phase matrix of the selected constituent type, describing the scattering of the event's incident normalised Stokes vector $\bar{I}'$ in direction ω' towards the detector -in direction $\omega^\bullet$. The extinction coefficient β in the transmittance term is the total extinction coefficient of the atmospheric mixture along the path. MONKI can, in practice, compute the result of Eq. 10 simultaneously for multiple viewing zenith angles, that is, for multiple detector locations as seen from the event location $\theta^\bullet$ given a viewing azimuth angle $\varphi^\bullet$.

In the case of an atmospheric event, χ For the selected atmospheric constituent type t , the phase matrix is computed as $\div$

$$Z_t(x, \omega^\bullet, \omega') = \frac{1}{4\pi} L(-\sigma_2) F_t(\Theta x, \lambda \Theta) L(-\sigma_1), \quad (11)$$

where F is the single scattering where F_t is the single-scattering matrix of the gas-or-the-aerosol-type-selected constituent, i.e. the gas or one of the aerosol types at x (see Appendix A), and A . Matrix F_t depends on the scattering angle $\Theta = \arccos(\omega^\bullet \cdot \omega')$ (see Fig. 1) and on λ . Matrix L is the 4×4 rotation matrix that transforms the Stokes vector between different reference planes

³We set $w = 10^{-16}$ as the minimum allowable-weight for a photon to continue in the simulation.

(see Hovenier and van der Mee, 1983):

$$\mathbf{L}(\alpha) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos 2\alpha & \sin 2\alpha & 0 \\ 0 & -\sin 2\alpha & \cos 2\alpha & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \quad (12)$$

The ~~rotation~~ Rotation angle α is positive in the anti-clockwise direction when viewed along the ~~direction of light propagation~~ propagation direction of the light. Specifically, angles $-\sigma_1$ and $-\sigma_2$ in Eq. 11 are the angles required to rotate the reference plane from the local meridian plane of the incident beam ~~, through the scattering plane,~~ to the local meridian plane of the scattered beam (see Fig. 1). ~~Matrix χ~~ For a given incident photon direction and selected atmospheric constituent, matrix $\mathbf{Z}_t$ thus generally depends on the two angles that describe the ~~new direction of the photon: ϑ and φ (see Fig. 1).~~ detector direction $\omega^\bullet$, namely $\vartheta^\bullet$ and $\varphi^\bullet$.

If the photon reaches the surface, w is multiplied by the surface albedo, A_s , which equals the probability of reflection by the Lambertian surface. The value of A_s can depend on λ . If the photon retains ~~weight and the observer is not at BOA~~ enough weight (see footnote 3) and the detector is at TOA, the surface reflection contribution to the TOA ~~reflectance~~ signal is computed, again using Eq. ~~??~~. ~~For reflection by a Lambertian surface, matrix χ is given by:~~ 10. For $A_s > 0$, the atmospheric scattering factor $\mathbf{Z}_t/(4\pi)$ in Eq. 10 is replaced by:

$$\frac{\mu_\bullet}{\pi} \frac{1}{A_s} \mathbf{R}_L = \begin{pmatrix} \mu_\bullet/\pi & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (13)$$

where ~~μ/π~~ $\mu_\bullet = |\cos \vartheta^\bullet|$, with $\vartheta^\bullet$ the zenith angle corresponding to the detector direction $\omega^\bullet$. The factor $\mu_\bullet/\pi$ corresponds to the probability density function of the Lambertian surface reflection direction (see Eq. C3), and $\mathbf{R}_L$ is the 4×4 Lambertian surface reflection matrix, which is filled with zeros except for its upper left element which equals A_s (see Eq. 13). The division by A_s is necessary because, as explained above, the multiplication by A_s is already included in w .

After computing the event's contribution to the TOA ~~reflectance or BOA transmittance~~ or BOA signal, the new propagation direction of the photon, ~~$(\vartheta, \varphi)\omega$~~ , is sampled from the probability density function of the ~~scattering~~ (atmospheric scattering or surface reflection) direction. To sample this new direction, we apply either the inverse transform method or the acceptance-rejection method, depending on the type of event, fully accounting for the photon's state of polarisation along its trajectory (see Appendices C, D, ??, E, and F for details on those methods and the choice of method). For the continuation of the photon's trajectory ~~in its new direction~~ after an atmospheric event, its Stokes vector is adjusted as follows ~~:(see Appendix G7):~~

$$\bar{\mathbf{I}} = \frac{\vartheta}{\left[\frac{\mathbf{Z}_t(x, \omega, \omega') \bar{\mathbf{I}}'}{\left[\mathbf{Z}_t(x, \omega, \omega') \bar{\mathbf{I}}' \right]_1} \right]}, \varphi, \quad (14)$$

where $\bar{\mathbf{I}}$ where $\bar{\mathbf{I}}$ is the normalised Stokes vector of the photon before the event and matrix χ is now, and Z_t is computed for the new direction of the photon, (ϑ, φ) . Subsequently, the scattered (or reflected) vector is normalised again by its first element: $\bar{\mathbf{I}} = \mathbf{I}/I$ newly sampled propagation direction ω and the incident direction ω' . The division by the first element, indicated by $[\dots]_1$, of the scattered Stokes vector is necessary for normalisation. Indeed, in this way the first element of $\bar{\mathbf{I}}$ remains equal to 1.0, as the directional dependence of I is already taken care of in the sampling of the new photon direction, while the probability of scattering (or surface reflection) instead of absorption at each atmospheric event is captured by w . For a surface event, we set $\bar{\mathbf{I}} = 1$, because the Lambertian reflection fully depolarises the photon, while the probability of surface reflection instead of absorption is captured by the multiplication of w by A_s .

Next, a new free photon path length d is sampled using Eq. 8 in case of an atmospheric event, or the remaining free photon path length is computed in case of a surface event. The photon continues its trajectory, where it again may be (partially) absorbed, scattered by an atmospheric particle or scattered, or reflected by the surface.

Finally, the TOA reflectance column vector of a given (x, y) -grid column is computed as

$$[R_{11}, R_{21}, R_{31}, R_{41}]^T = \frac{\pi}{\mu} \frac{\sum_{i=1}^N \sum_{j=1}^M \Phi_{i,j}}{N},$$

detector radiance Stokes vector in the direction $\omega^\bullet$ and at wavelength λ , for a given grid column and averaged over its horizontal area O at TOA or BOA, is computed using the unbiased estimator (see also Appendix G10):

$$I(O, \omega^\bullet; \omega_0) \approx \frac{\mu_0}{\mu_\bullet} \frac{E_0}{N} \sum_{j=1}^{N_x N_y} \sum_{i=1}^N \sum_{n=1}^{M_{i,j}} \mathbf{W}_{n,i,j} \chi_{n,i,j}, \quad \text{where} \quad \chi_{n,i,j} = \begin{cases} 1, & \text{if } \mathbf{x}_{n,i,j}^\bullet \in O, \\ 0, & \text{otherwise.} \end{cases} \quad (15)$$

where the summation is performed over all M scattering events (including $M_{i,j}$ scattering and surface reflection events) of all N photons that were injected into the column injected into each of the $N_x \times N_y$ grid columns at TOA. A similar equation applies for the transmittance at BOA, which is obtained by replacing R with T . By default, MONKI assumes $E_0 = \pi$. Vector $\mathbf{W}_{n,i,j}$ denotes the local-estimation contribution of event n of photon i injected in source column j towards the detector direction $\omega^\bullet$ (Eq. 10), and the indicator function $\chi_{n,i,j}$ selects only those contributions whose straight detector path intersects TOA or BOA within the horizontal area O of the considered grid column, at location $\mathbf{x}_{n,i,j}^\bullet$. Thus, photons injected in grid columns other than the considered one can also contribute to its signal. The factor $\mu_0/\mu_\bullet$ accounts for the conversion between the horizontal source and detector areas associated with the same scattering volume element (see Appendix G6). The explicit dependence of I on the horizontal area O is only relevant for horizontally inhomogeneous scenes, where the estimator yields the radiance Stokes vector averaged over that area. For horizontally homogeneous scenes, this dependence vanishes because the same radiance is obtained everywhere within O .

2.4 Backward Monte Carlo simulation

MONKI can be used in both forward and backward modes. In backward mode, photon paths are traced from the detector towards the light source (the Sun), as illustrated in Fig. 2. The detector radiance Stokes vector is again computed using the

local estimation method, here with the option to evaluate multiple solar zenith angles ϑ_0 at a fixed solar azimuth angle φ_0 simultaneously.

The backward mode is particularly useful when the detector is at a finite distance from, or even inside, the atmosphere-surface system. Although this application is not treated in the present paper, it is important for future extensions of MONKI to spherical atmospheres in combination with a detector at a finite distance. In such cases, the path from a scattering event to the detector depends on the location of the event, and the detector cannot be represented by a single collimated viewing direction throughout the domain. Consequently, in forward mode, only a small fraction of photons launched from the source would reach the detector's field of view, severely limiting the code's efficiency. In backward mode, by contrast, photons are launched from the detector, so that all traced photon paths lie within its field of view. Assuming collimated illumination from a light source at infinite distance, every backward-traced photon that is not completely absorbed can, in principle, be connected to the source direction and therefore contributes to the local estimate. We refer to Appendix G8 for the derivation of the backward Monte Carlo equations for polarised light as used in this section.

According to the reciprocity principle (see Sect. 2.4 of Hovenier et al., 2004), reversing a light path through a medium preserves the reflectance and transmittance along the original path. In practice, this principle allows swapping the light source and detector in a radiative transfer simulation and launching photons in the reverse direction. In the following, we continue to use ω' and ω for the incident and scattered propagation directions in the associated forward trajectory. Thus, along the backward trajectory, the photon arrives at the current event from the detector side with propagation direction $-\omega$, and leaves the event towards the source side with propagation direction $-\omega'$. Reversing both propagation directions leaves the scattering angle $\Theta = \arccos((- \omega) \cdot (- \omega')) = \arccos(\omega \cdot \omega')$ unchanged.

At atmospheric events in the backward mode, the interacting constituent type t is selected in the same way as in the forward mode, and the photon weight is multiplied by the corresponding single-scattering albedo a_t . Because MONKI accounts for polarisation, the orientation of the Stokes vector must be mirrored relative to the reference plane when tracing the reversed photon trajectory. That is, the phase matrices used in the reversed light path do not give the desired result (which is the scattered radiance in the forward light path), and must be corrected as follows (see Eq. 3.37 of Hovenier et al., 2004)⁴:

$$\mathbf{Z}_t(x, \omega, \omega') = \Delta_3 \mathbf{Z}_t(x, -\omega', -\omega)^T \Delta_3, \quad (16)$$

where the minus signs indicate reversed propagation directions, the superscript T denotes the transpose, and Δ_3 is given by

$$\Delta_3 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \quad (17)$$

⁴The relation of Eq. 16 is only valid for particles very small compared to the wavelength, or particles accompanied by their mirror particles in equal numbers and in random orientation, or particles with a plane of symmetry (such as spheres, spheroids, ellipsoids, cylinders and cubes) that are randomly oriented (see Hovenier et al., 2004, Sects. 2.4, 2.7 and 3.3).

In the backward mode, the normalised unpolarised incident Stokes vector, $\mathbf{1} = [1, 0, 0, 0]^T$, must be multiplied by the phase matrices at the end of the photon trajectory. That is, the event's contribution to the TOA or BOA signal measured by the detector is computed as follows:

$$\mathbf{W}^{\text{bw}}(\omega_0) = w \cdot \overline{\mathbf{M}} \cdot \frac{1}{4\pi} \mathbf{Z}_t(\mathbf{x}, \omega_1, \omega_0) \cdot \mathbf{1} \cdot \exp\left(-\int_0^{s_0} \beta(\mathbf{x} - s' \omega_0) ds'\right), \quad (18)$$

where the direct transmittance is calculated in direction $-\omega_0$ from the event location $\mathbf{x}$ ($s' = 0$) to the entry location of the solar beam ($s' = s_0$). Matrix $\overline{\mathbf{M}}$ is the 4×4 normalised detector-response matrix, which contains the cumulative polarisation transformation between the current event and the detector, and its path dependence is omitted from the notation. The phase matrix $\mathbf{Z}_t(\mathbf{x}, \omega_1, \omega_0)$ in Eq. 18 describes the first scattering event of the associated forward trajectory, from the sunlight direction ω_0 into the direction ω_1 . Along the backward trajectory, this same event is encountered in reverse, from $-\omega_1$ towards $-\omega_0$. Therefore the phase matrix is obtained from the reversed one using the reciprocity correction of Eq. 16. For a surface event, the atmospheric phase-matrix factor π arises from the definition of the TOA reflectance, while μ accounts for the angle between the direction of the reflected light and the horizontal grid at TOA. $\mathbf{Z}_t/(4\pi)$ is replaced by the corresponding Lambertian surface-reflection factor, analogous to Eq. 13.

After computing the event's contribution to the TOA or BOA signal, the new upstream direction of the backward-traced photon, $-\omega'$, is sampled from the polarisation-dependent probability density function of the scattering direction, now using the propagated matrix $\overline{\mathbf{M}}$ (see Appendix G8). At the start of the backward simulation at the detector, $\overline{\mathbf{M}}$ is initialised as the identity matrix. It is updated at each event to retain the full polarisation history accumulated along the backward photon trajectory as follows (Appendix G8):

$$\overline{\mathbf{M}}' = \frac{\overline{\mathbf{M}} \mathbf{Z}_t(\mathbf{x}, \omega, \omega')}{[\overline{\mathbf{M}} \mathbf{Z}_t(\mathbf{x}, \omega, \omega') \mathbf{1}]_1}. \quad (19)$$

Here, $-\omega$ is the propagation direction of the backward-traced photon on the detector side of the current event, and $\overline{\mathbf{M}}'$ denotes the updated detector-response matrix after sampling the new upstream propagation direction on the source side, $-\omega'$. Note that the right-multiplications by $\mathbf{Z}_t$ in Eq. 19 for all events are applied before the multiplication by $\mathbf{1}$ in Eq. 18 (see also Collins et al., 1972). For a surface event, the detector-response matrix is updated analogously, using the corresponding Lambertian surface-reflection matrix instead of the atmospheric phase matrix.

Finally, the detector radiance Stokes vector in the direction $\omega^\bullet$ and at wavelength λ , for a given grid column and averaged over its horizontal area O at TOA or BOA, is computed by the unbiased estimator (see Appendix G10):

$$I(O, \omega^\bullet; \omega_0) \approx \frac{E_0}{N} \sum_{i=1}^N \sum_{n=1}^{M_i} \mathbf{W}_{n,i}^{\text{bw}}, \quad (20)$$

where the summation is performed over all M_i scattering and surface reflection events of all N photons launched uniformly over the horizontal area O of the considered grid column at TOA or BOA, and again $E_0 = \pi$ by default. Here, $\mathbf{W}_{n,i}^{\text{bw}}$ denotes

the backward local-estimation contribution of event n of photon i (Eq. 18). In contrast to the forward mode (Eq. 15), no factor $\mu_0/\mu_\bullet$, no indicator function χ , and no additional sum over the $N_x \times N_y$ source columns appear, because in backward mode the estimator is written directly for photons launched from and averaged over the same detector area O of the considered grid column (see Appendix G10). In Appendix ??, we use a simple example to validate the inclusion of π and μ .

2.5 Precomputation of optical paths to the detector

The extinction coefficient β in Eq. ??-10 depends on the position s' along the path of the photon straight path between the event location and the detector boundary. Coefficient β may vary across grid cells within the 3D domain. Moreover, the lengths of the different path segments within each grid cell depend on both the location of the event and the viewing geometry detector direction $\omega^\bullet$. The integral in Eq. ??-10 can be numerically evaluated by propagating the photon from the event's location to the detector boundary, obtaining β and the path segment length for each grid cell.

This evaluation is computationally expensive, as it must be performed for all events of each photon and every viewing zenith angle of the detector. However, if the path to the detector passes through atmospheric grid cells that have the same optical properties in the horizontal directions, the horizontal cell boundaries can be neglected along this path, as only the extinction coefficient β and the path segment length per layer are relevant. If the event occurs at the surface or exactly at the bottom boundary of a layer, while the detector is above TOA, then Eq. ??-10 simplifies to:

$$W(\omega^\bullet) = w \cdot \frac{1}{4\pi} Z_t(x, \omega^\bullet, \omega') \cdot \bar{I}' \cdot \exp \left(-\frac{1}{\mu} \frac{1}{\mu_\bullet} \sum_{k=k^*}^{N_z} \beta_k \Delta z_k \right), \quad (21)$$

where k^* denotes the index of the layer where the event happens and $\Delta z_k/\mu \Delta z_k/\mu_\bullet$ is the path segment length through layer k in the direction from the event to the detector. Note that $\frac{1}{\mu} \sum_{k=k^*}^{N_z} \beta_k \Delta z_k \frac{1}{\mu_\bullet} \sum_{k=k^*}^{N_z} \beta_k \Delta z_k$ can be computed for each k^* and $\mu_\bullet$ prior to simulating the photon trajectories. If the event occurs within the atmosphere and not exactly at a layer boundary (as is most often the case), the photon is first propagated by a distance Δs toward towards the detector until it reaches the nearest layer boundary. The term $\beta_{k^*} \Delta s$ is then added to $\frac{1}{\mu} \sum_{k=k^*+1}^{N_z} \beta_k \Delta z_k \frac{1}{\mu_\bullet} \sum_{k=k^*+1}^{N_z} \beta_k \Delta z_k$. A similar approach applies for a detector below BOA. An analogous expression can be derived for the backward mode, by precomputing the optical path from the event towards the sunlight-entry boundary.

In 3D cloudy scenes, there are still many cloud-free paths between atmospheric or surface events and the detector, for example, when events occur in atmospheric layers above the clouds or between patchy clouds. For every grid cell, we precompute whether straight paths to the detector are cloud- and aerosol-free from all cell corners as well as for several points within each cell. If these paths pass through gas only, the grid cell is flagged. Assuming that the gas is horizontally homogeneously distributed homogeneous, we use Eq. ??-21 for events in the flagged cells, eliminating the need for photon propagations to propagate photons between the event locations and the detector boundary. This approach is computationally more efficient compared to evaluating Eq. ??-10, while its results are identical.⁵

⁵The computation speed increases with the number of cloud-free grid cells and viewing directions. For example, for the cloudy Earth sample signal of Fig. 12, for $\theta_0 = \varphi = \varphi_0 = 0^\circ$ and 90 viewing zenith angles, the speed improvement is a factor 1.9.

2.6 Simulation rounds and noise estimation

The computation of the ~~TOA-reflectance or BOA-transmittance~~ detector radiance Stokes vector with Eq.?? and 15, or Eq. 20 in backward mode, using N photons ~~represents per column is called~~ one simulation round. In practice, we perform N_r independent simulation rounds. As an example, consider the simulation of the TOA reflectance R_r estimated with N photons as in Eq. ?? (we have omitted the notation of the matrix element indices for readability and introduced the subscript r indicating the simulation round number). The final result that we report rounds, so that in total $N_r N$ photons per column are used. Let I_r denote the estimate of the first Stokes component obtained in round r . The value reported in this paper is the mean ~~TOA reflectance estimated from all simulation rounds; over all rounds,~~

$$\langle I \rangle = \frac{\sum_{r=1}^{N_r} R_r}{N_r}, \frac{1}{N_r} \sum_{r=1}^{N_r} I_r. \quad (22)$$

We compute the noise as the standard deviation of the mean (see Eq. 4.46 of Marshak and Davis, 2005). The Monte Carlo noise of this reported mean is estimated from the scatter between the independent round estimates:

$$\sigma_{\bar{R}} = \sqrt{\frac{1}{N_r - 1} \left[\frac{1}{N_r} \sum_{r=1}^{N_r} R_r^2 - \left(\frac{\sum_{r=1}^{N_r} R_r}{N_r} \right)^2 \right]}.$$

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$$\sigma_{\langle I \rangle} = \sqrt{\frac{1}{N_r - 1} \left[\frac{1}{N_r} \sum_{r=1}^{N_r} I_r^2 - \left(\frac{1}{N_r} \sum_{r=1}^{N_r} I_r \right)^2 \right]}. \quad (23)$$

To ensure a reliable estimate of $\sigma_{\bar{R}}$, we impose that $N_r \geq 30$. This quantity estimates the standard error of the mean $\langle I \rangle$, not the standard deviation of the individual round estimates I_r .⁶ To obtain a reliable estimate of $\sigma_{\langle I \rangle}$, we require $N_r \geq 30$. In this paper, we use $N_r = 100$. The same procedure is applied to the other Stokes components Q , U , and V .

2.7 Backward Monte Carlo simulation

MONKI can be used both in the forward and in the backward mode, where photon paths are traced from the detector to the light source. The backward mode is significantly more efficient than the forward mode in case the detector is at a finite distance from the atmosphere-surface system. The reason is that in forward mode, only a small fraction of the photons from the source end up in the detector's field of view. In the backward mode, every photon that is not completely absorbed contributes to the result, assuming that the light source is at an infinite distance.

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⁶Equation 23 is obtained by first estimating the scatter between the independent round estimates I_r (cf. Eq. 4.46 of Marshak and Davis, 2005), and then dividing by $\sqrt{N_r}$ to obtain the standard error of their mean. Since each round contains the same number of photons, averaging over N_r rounds is statistically equivalent to using one simulation with $N_r N$ independent photons.

According to the reciprocity principle (see Sect. 2.4 of Hovenier et al., 2004), reversing a light path through a medium preserves the reflectance and transmittance along the original path. In practice, this principle allows swapping the light source and detector in a radiative transfer simulation: $\theta \rightarrow \theta_0$, $\theta_0 \rightarrow \theta$, $\varphi \rightarrow \varphi_0 + 180^\circ$, and $\varphi_0 \rightarrow \varphi + 180^\circ$. To compute the TOA reflectance in backward mode, photons are injected downward into the domain at TOA along the reversed viewing direction.

445 For the BOA transmittance, photons are injected upward from the surface, also along the reversed viewing direction.

Because MONKI accounts for polarisation, the orientation of the Stokes vector must be mirrored relative to the reference plane when tracing the reversed photon trajectory. Consequently, in the backward mode, the χ matrices must be modified as follows (see Eq. 3.37 of Hovenier et al., 2004)⁷:

$$\chi_{\text{bw}}(-\mu, -\mu_0, \varphi_0 - \varphi) = \Delta_3 \chi^T(\mu, \mu_0, \varphi - \varphi_0) \Delta_3,$$

450 with χ^T the transpose of χ and with Δ_3 given by

$$\Delta_3 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

Finally, in the backward mode, the incident Stokes vector $I_0 = [1, 0, 0, 0]^T$ must be multiplied by the χ matrices at the end of the photon trajectory. That is, the event's contribution to the TOA reflectance or the BOA transmittance is computed as follows:

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$$\Phi_{\text{bw}} = w \cdot \overline{W} \cdot \chi_{\text{bw}} \cdot I_0 \cdot \exp\left(-\int_0^{s_{\text{sun}}} \beta(s') ds'\right),$$

where the direct transmittance is calculated from the event location ($s = 0$) to the light source ($s = s_{\text{sun}}$). Here, $\overline{W}$ is the 4×4 normalised 'weight matrix', which starts as the identity matrix at the beginning of the simulation. It is updated at each event to account for the continuation of the photon's trajectory in the new direction (ϑ, φ) , as follows:

$$\underline{W} = \overline{W} \cdot \chi_{\text{bw}}(\vartheta, \varphi),$$

460 after which it is normalised by its upper left element: $\overline{W} = \underline{W} / W_{11}$. Note that the right-multiplications by χ_{bw} in Eq. 19 for all scattering (and reflection) events are applied before the multiplication by I_0 in Eq. ?? (see also Collins et al., 1972).

3 Validation results

In this section, we present the validation of MONKI. In Sect. 3.1, we validate MONKI's total and polarised radiances for horizontally homogeneous scenes by comparing them with results from the widely used doubling-adding method. In Sect. 3.2,

⁷The relation of Eq. 16 is only valid for particles very small compared to the wavelength, or particles accompanied by their mirror particles in equal numbers and in random orientation, or particles with a plane of symmetry (such as spheres, spheroids, ellipsoids, cylinders and cubes) that are randomly oriented (see Hovenier et al., 2004, Sects. 2.4, 2.7 and 3.3).

Table 1. Comparison of the TOA radiances computed with MONKI, using 10^7 photons in forward mode, with the benchmark results of de Haan et al. (1987) for an atmosphere consisting of two plane-parallel layers with a total optical thickness $b = 0.6$ (see text), and an underlying Lambertian reflecting surface with $A_s = 0.1$. The direction of the incident unpolarised light beam is $(\mu_0, \varphi_0) = (0.5, 0.0)$. The reported uncertainties in the MONKI results refer to twice the standard error of the mean, evaluated separately for each Stokes component using Eq. 23.

		$\mu = 0.1$		$\mu = 0.5$		$\mu = 1.0$	
		de Haan	MONKI	de Haan	MONKI	de Haan	MONKI
$\mu_0 = 0.5$ $\varphi = 0^\circ$	I	0.532950	0.532497±0.000605	0.208430	0.208432±0.000225	0.093680	0.093679±0.000077
	Q	-0.028340	-0.028361±0.000137	-0.036299	-0.036337±0.000069	-0.024156	-0.024158±0.000038
	U	0.000000	0.000040±0.000125	0.000000	-0.000033±0.000049	0.000000	-0.000008±0.000023
	V	0.000000	-0.000007±0.000011	0.000000	-0.000001±0.000006	0.000000	0.000000±0.000002
$\mu_0 = 0.5$ $\varphi = 30^\circ$	I	0.418140	0.417873±0.000489	0.184970	0.185024±0.000206	0.093680	0.093679±0.000077
	Q	-0.000058	-0.000067±0.000130	-0.019649	-0.019663±0.000064	-0.012078	-0.012072±0.000028
	U	-0.073705	-0.073144±0.000156	-0.041401	-0.041470±0.000077	-0.020920	-0.020925±0.000034
	V	0.000106	0.000107±0.000011	0.000040	0.000044±0.000006	0.000000	0.000000±0.000002

we validate MONKI's total and polarised radiances against benchmark results for thick Rayleigh-scattering atmospheres. In Sect. 3.3, we validate MONKI for scenes with 3D cloud structures. In what follows, all results that we present are for a detector at TOA or BOA. Therefore, we omit the $\bullet$ notation for the detector direction, and use ϑ , φ and μ instead of $\vartheta^\bullet$, $\varphi^\bullet$ and $\mu_\bullet$.

3.1 Comparison with de Haan et al. (1987)

Here, we present a comparison of total and polarised radiances that emerge from a horizontally homogeneous atmosphere-surface system (i.e., $N_x = N_y = 1$) with the benchmark results of de Haan et al. (1987), who used an efficient doubling-adding algorithm that included full polarisation for all orders of scattering.

The paper by de Haan et al. (1987) lists benchmark results for different atmosphere-surface systems. We compare with their results for an atmosphere with a total optical thickness $b = 0.6$ that consists of two plane-parallel layers. Both layers contain gaseous molecules with a scattering optical thickness $b_{\text{sca}}^{\text{m}} = 0.1$. The bottom layer also contains water-haze L aerosols (Deirmendjian, 1969), with a scattering optical thickness $b_{\text{sca}}^{\text{c}} = 0.4$, $b_{\text{sca}}^{\text{a}} = 0.4$. The aerosol characteristics and expansion coefficients at $\lambda = 0.70 \mu\text{m}$ are provided by de Rooij and van der Stap (1984). There is no absorption of light ($b_{\text{abs}}^{\text{m}} = b_{\text{abs}}^{\text{c}} = 0$, $b_{\text{abs}}^{\text{m}} = b_{\text{abs}}^{\text{a}} = 0$), and the depolarisation factor of the gaseous molecules is 0.0279, a typical value for terrestrial air. The atmosphere is illuminated from above by unidirectional, unpolarised light propagating in the direction $(\mu_0, \varphi_0) = (0.5, 0^\circ)$ with a total flux E_0 equal to π . The Lambertian reflecting surface has an albedo A_s of 0.1.

Table 1 shows the results of both codes for the radiances at TOA benchmark results and simulated TOA radiances with MONKI for six viewing geometries: $\mu = \{0.1, 0.5, 1.0\}$ and $\varphi = \{0^\circ, 30^\circ\}$ (see Table 9 of de Haan et al., 1987). The

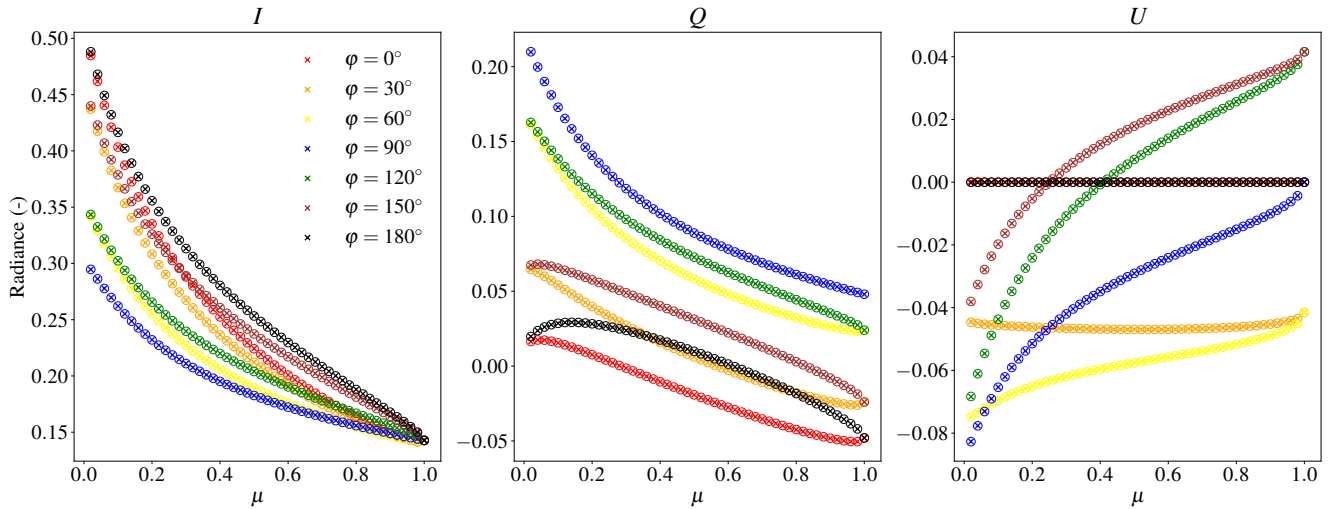


Figure 4. Comparison of the TOA radiances I , Q and U computed using with MONKI using 10^7 photons in forward mode (crosses) with the benchmark results of de Haan et al. (1987) from Natraj and Hovenier (2012) (circles), for an a Rayleigh-scattering atmosphere consisting of two plane-parallel layers with a total an optical thickness $b = 0.6$ (see text). The direction $b = 16$, a single scattering albedo of the incident unpolarised light beam is $(\mu_0, \varphi_0) = (0.5, 0.0)$ 1.0, a depolarisation factor of 0.0, and a black surface below. The reported uncertainties in the MONKI results refer to two times the standard deviation different colours indicate different values of φ (Eq.?? $\varphi_0 = 0^\circ$).

MONKI simulations simulations were done in forward mode and used 10^7 photons in total, distributed over 100 rounds. The listed errors represent twice the standard deviation of the results, computed error of the mean, evaluated separately for each Stokes component using Eq.?? 23. The results agree excellently: almost all differences between the MONKI results and those of de Haan et al. (1987) fall within the two standard deviationstwice the standard error of the mean. The magnitude of these differences is comparable to that reported by MYSTIC for simulations with 10^7 photons, as shown in Table 2 of Emde et al. (2010), and would further decrease if more photons were used. The MONKI results for a solar geometry with $(\mu_0, \varphi_0) = (0.1, 0)$ and those for an observer a detector on the surface (not in Table 1) also show excellent agreement, too (see Tables S1, S2, and S3). Using MONKI's backward mode, we find similar results (see Tables S4, S5, S6, and S7).

3.2 Comparison with Natraj and Hovenier (2012)

The model atmospheres used by de Haan et al. (1987) are optically relatively thin. Here, we compare with the benchmark results of Natraj and Hovenier (2012), who reported total and polarised radiances of light that is reflected and transmitted by optically thick Rayleigh-scattering atmospheres, computed using the method of X and Y X and Y functions (Chandrasekhar, 1960; Natraj et al., 2009). According to Natraj and Hovenier (2012), their results are accurate up to eight decimal places.

We compare to their Tables 1, 3, and 5, which list the Stokes parameters I , Q and U of light that is reflected by a homogeneous atmospheric layer with an optical thickness of $b = 16$. The layer contains only gas, which does not absorb and which has a depolarisation factor of zero. The surface below the layer is black. The atmosphere is illuminated from the

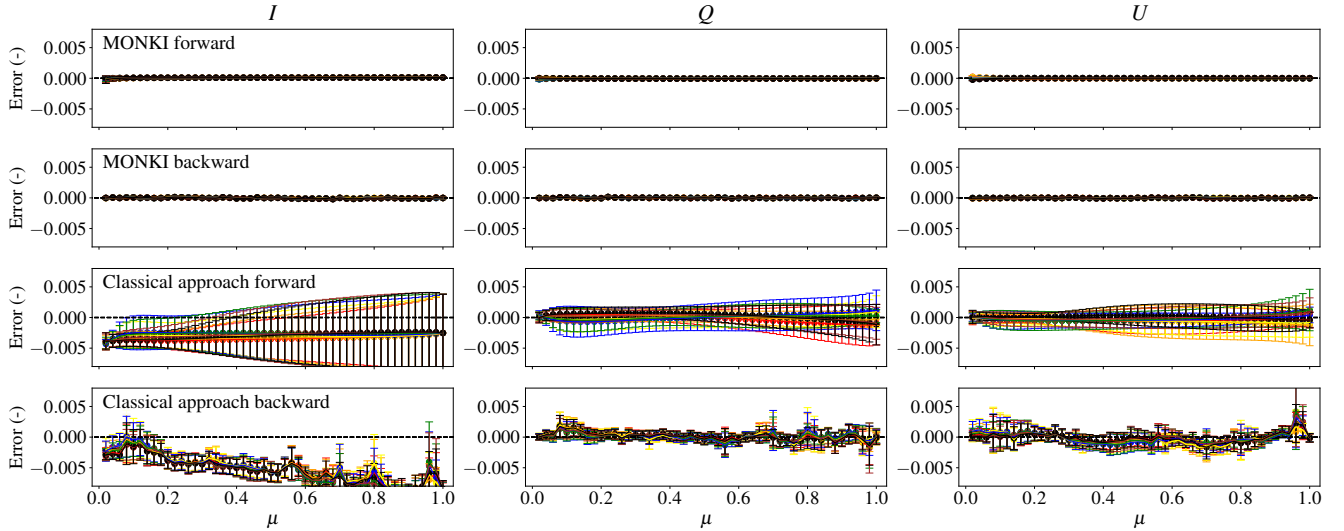


Figure 5. Similar to Fig. 4, but presented as differences (MONKI results minus Natraj and Hovenier results), for MONKI in the forward mode (first row) and in the backward mode (second row), fully taking into account polarisation of light when sampling scattering directions. The third and fourth rows show the results when using instead the classical scattering direction sampling approach in MONKI, as used by, e.g., MYSTIC (see Appendix G9). The error bars indicate the ± 2 standard errors of the mean of the simulated results (Eq. 23). Those error bars, and the seven different colours referring to the different values of φ , are virtually indistinguishable for the MONKI forward and backward modes.

top by a beam of unpolarised light with $E_0 = \pi$, with ~~directions~~ $\mu_0 = 0.2$ and $\varphi_0 = 0^\circ$. Under these conditions ~~direction~~ $(\mu_0, \varphi_0) = (0.2, 0^\circ)$. Because there is only Rayleigh scattering in the model atmosphere, no circularly polarised light will emerge (see Hansen and Travis, 1974, and Eq. A2), thus $V = 0$ ~~(it is not included in the tables)~~ for all geometries. Figure 4 shows ~~Stokes parameters~~ I , Q and U computed by MONKI in forward mode using ~~10^8 photons~~ 10^7 photons distributed over 100 simulation rounds, and as listed by Natraj and Hovenier (2012). Viewing direction μ ranges from 0 to 1.0 ~~(nadir-viewing direction)~~, and φ from 0° to 180° . As can be seen in Fig. 5, the agreement between the results of MONKI and those of Natraj and Hovenier (2012) is excellent for all geometries. ~~Indeed, the maximum differences in I , Q , and U are 1.2×10^{-4} , 5.4×10^{-5} , and 5.3×10^{-5} , respectively. They fall within the 2 standard deviation noise values for I , Q , and U : 1.6×10^{-4} , 8.0×10^{-5} , 5.6×10^{-5} , respectively. Additionally, our numerical tests show that the differences decrease further when increasing the number of photons in both forward and backward mode.~~

Note that Garc a Mu oz and Mills (2015) wrote that for thick, strongly polarising⁷ atmospheres, such as those used by Natraj and Hovenier (2012), some Monte Carlo codes may fail to converge. For examples of such codes, Garc a Mu oz and Mills (2015) referred to MYSTIC (Emde et al., 2010) and the integral-vector Monte Carlo method (IVMCM) (Gay et al., 2010). As shown

⁷Note that for such atmospheres, the radiation that is observed emerging at TOA or BOA will generally have a low degree of polarisation because it comprises light with a broad range of polarisation states:

by García Muñoz and Mills (2015) (in their MONKI fully accounts for the photon's polarisation history when sampling scattering directions. However, when the classical scattering-direction sampling approach is used in MONKI instead, Fig. 8), the non-convergence arises from neglecting the 5 (two bottom rows) shows clear deviations and a much larger variance. The classical approach (see Collins et al., 1972) neglects the polarisation state of the incident photon when sampling a new scattering direction, and by then correcting for the corrects for this neglect by adjusting the photon's weighting factor (see, e.g., Collins et al., 1972) (see Appendix G9). Examples of codes that use this approach are MYSTIC (Emde et al., 2010), MSCART (Wang et al., 2017, 2019), SPARTA (Barlakas et al., 2016), IVMCM (Gay et al., 2010), and the backward mode of SMART-G (Ramon et al., 2019). García Muñoz and Mills (2015) pointed out that for thick, strongly polarising⁷ atmospheres, such as those used by Natraj and Hovenier (2010), those codes may fail to converge. This is because, upon multiple scattering, these correction factors are multiplied repeatedly. In the unlikely event that a photon path contains several strongly polarising scattering directions, this can produce infrequent but very large photon weights (see Appendix G9).

Comparison of the TOA radiances I , Q and U computed with MONKI (crosses) with the benchmark results from Natraj and Hovenier (2010) (circles), for a Rayleigh-scattering atmosphere with an optical thickness $b = 16$, a single scattering albedo of 1.0, a depolarisation factor of 0.0, and a black surface below. The colours indicate different values of φ ($\varphi_0 = 0^\circ$). In optically thick atmospheres where photons are on average scattered multiple times, this correction procedure leads to a significantly poorer sampling of certain scattering directions.

Because MONKI fully accounts for the photon's polarisation history and it thus does not include such variance-producing corrections (see Appendices D, E, and F), and MONKI indeed converges for thick Rayleigh-scattering atmospheres in both its forward and backward mode. Figure 6 shows MONKI's convergence history when computing the TOA reflectance R_{11} in both the forward and the backward mode, for photon numbers up to 10^7 , for $\mu = 1.0$, $\varphi = 0^\circ$, and $\varphi_0 = 0^\circ$, different solar angles values of μ_0 , and different optical thicknesses b (the single scattering albedo is 1.0). The surface is black.

The lines in Fig. 6 clearly show MONKI's convergence with increasing photon numbers. Indeed, for $\mu = 1.0$ with the two cases with $\mu_0 = 1.0$, namely $b = 16$ and with $b = 4$, the lines pertaining to MONKI's forward and the backward mode are virtually the same (those cases were also used by García Muñoz and Mills (2015) to demonstrate non-convergence when one corrects for the negligence of polarisation of the classical approach, see their Fig. 8). This was also to be expected, as for this solar and viewing geometry ($\mu = \mu_0$), the photon paths in the forward and backward direction modes are identical. For $\mu = 1.0$ and $\mu_0 = 0.5$, the photon paths in the forward mode differ from those in the backward mode, and consequently, although MONKI converges to the same values, its convergence history is different for the forward and backward modes. These results demonstrate the convergence of MONKI show that, unlike classical Monte Carlo codes (right figure in Fig. 6), MONKI converges well for optically thick atmospheres and polarising atmospheres in both its forward and backward modes.

⁷Note that for such atmospheres, the radiation that emerges at TOA or BOA will generally have a relatively low degree of polarisation because it comprises light with a broad range of polarisation states.

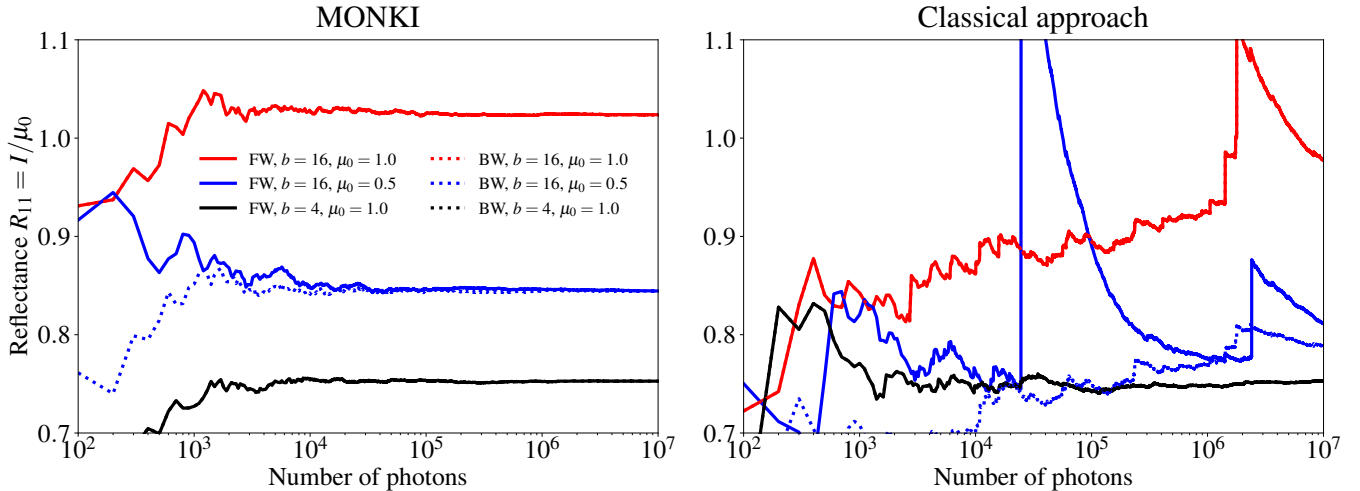


Figure 6. Left: convergence history of the TOA reflectance, R_{11} , by MONKI in forward mode (solid lines) and backward mode (dotted lines) for a Rayleigh scattering atmosphere with $b = 4$ and $\mu_0 = 1.0$ (black), $b = 16$ and $\mu_0 = 0.5$ (blue), and $b = 16$ and $\mu_0 = 1.0$ (red). The viewing geometry is nadir ($\mu = 1.0$). For $\mu_0 = 1.0$, the solid and dotted lines overlap. Right: similar, but using the classical scattering direction sampling approach in MONKI, as used by, e.g., MYSTIC (see Appendix G9). The jumps are caused by infrequent but large photon weights.

3.3 Comparison with Emde et al. (2018)

In the previous sections, we validated MONKI for horizontally homogeneous atmosphere-surface systems. Here, we validate MONKI for horizontally inhomogeneous (3D) cloudy atmospheres by comparing MONKI's results with benchmarks from the polarised radiative transfer model intercomparison project (IPRT) (Emde et al., 2018).

Convergence history of the TOA reflectance, R_{11} , by MONKI in forward mode (solid lines) and backward mode (dotted lines) for a Rayleigh scattering atmosphere with $b = 4$ and $\mu_0 = 1.0$ (black), $b = 16$ and $\mu_0 = 0.5$ (blue), and $b = 16$ and $\mu_0 = 1.0$ (red). The viewing zenith angle $\mu = 1.0$. For $\mu_0 = 1.0$, the dashed and dotted lines overlap.

MONKI results (columns 1 and 2) of the radiance I divided by E_0 (top row) and degree of polarisation P in % (bottom row), for a cubic cloud inside a Rayleigh scattering atmosphere, and the differences between the MONKI results and those of MYSTIC (columns 3 and 4). Results are shown for 2 of the 9 cases described by Emde et al. (2018). In case 4 (columns 1 and 3), the detector is on the surface (BOA), and in case 9 (columns 2 and 4), the detector is at TOA. The sunlight is incident from left to right along the x -direction. The solar and viewing angles are given in Table S8. Because of the horizontal periodicity, the cloud shadow crosses the right domain boundary and re-enters the domain on the left hand side.

Results of MONKI in forward ('MONKI-F') and backward mode ('MONKI-B') for the cubic cloud scenario of Emde et al. (2018), cases 4 (rows 1 and 2) and 9 (rows 3 and 4), for a cross-section through the domain at $y = 3.95$ km (see Fig. 7). Stokes parameters I , Q , U and V are shown in four columns, also for the other codes in the IPRT project, with the absolute differences

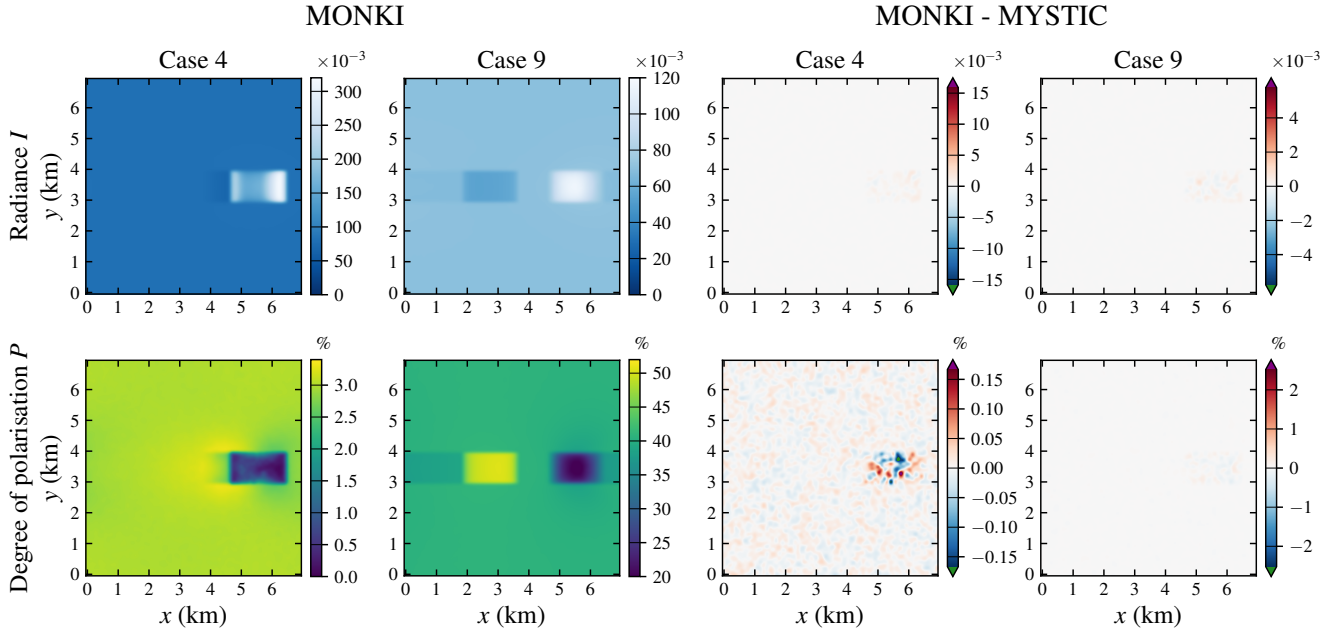


Figure 7. MONKI results (columns 1 and 2) of the radiance I divided by E_0 (top row) and degree of polarisation P in % (bottom row), for a cubic cloud inside a Rayleigh scattering atmosphere, and the differences between the MONKI results and those of MYSTIC (columns 3 and 4). Results are shown for 2 of the 9 cases described by Emde et al. (2018). In case 4 (columns 1 and 3), the detector is on the surface (BOA), and in case 9 (columns 2 and 4), the detector is at TOA. The sunlight is incident from left to right along the x -direction. The solar and viewing angles are given in Table S8. Because of the horizontal periodicity, the cloud shadow crosses the right domain boundary and re-enters the domain on the left-hand side.

of all codes with MYSTIC below. The grey area in the difference plots corresponds to 2 standard deviations of 3DMCPOL. The Stokes parameters are divided by $1000/E_0$.

560 MONKI results (columns 1 and 2) of the radiance I (row 1) and P (row 2), for a 3D cumulus cloud field inside a scattering and absorbing gaseous atmosphere (Emde et al., 2018), for 2 different solar and viewing geometries with an observer at TOA (cases 5 and 9 in Table S8). The sunlight is incident from left to right along the x -direction. Radiance I is divided by E_0 , and P is in %. Columns 3 and 4 show the differences between MONKI and MYSTIC.

Our first comparison with ~~results from the IPRT~~ IPRT results is for a homogeneous Rayleigh scattering atmosphere with
565 $b = 0.5$, that has a cubic-shaped cloud with an optical thickness of 10 embedded (see Sect. 5 of Emde et al., 2018). The single scattering albedo of the gaseous molecules is 1.0 and the depolarisation factor is ~~set to~~ 0.0. The cloud droplets are spherical with their sizes described by a gamma distribution with effective radii of $10 \mu\text{m}$ ~~and have a gamma size distribution with~~ and an effective variance of 0.1. Their single scattering albedo is 1.0. We use their single scattering matrices at $\lambda = 800 \text{ nm}$ as provided by the IPRT. The surface reflects Lambertian with an albedo of 0.2.

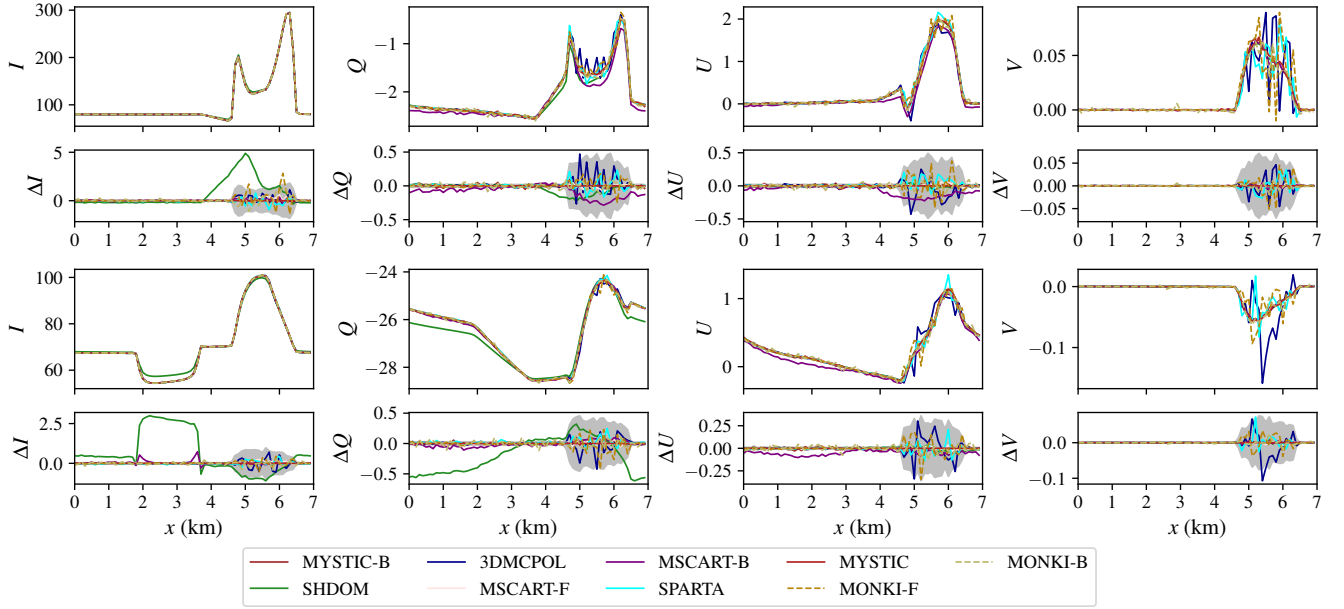


Figure 8. Results of MONKI in forward ('MONKI-F') and backward mode ('MONKI-B') for the cubic cloud scenario of Emde et al. (2018), cases 4 (rows 1 and 2) and 9 (rows 3 and 4), for a cross-section through the domain at $y = 3.95$ km (see Fig. 7). Stokes parameters I , Q , U and V are shown in four columns, also for the other codes in the IPRT project, with the absolute differences of all codes with MYSTIC below. The grey area in the difference plots corresponds to 2 standard deviations of 3DMCPOL. The Stokes parameters are divided by $1000/E_0$.

570 The cloud has dimensions of $1 \times 1 \times 1$ km³, and extends from 2 to 3 km altitude. The computational domain extends to an altitude of 5 km. Horizontally, the domain spans 7 km in both directions, with periodic boundary conditions. Both the light source and the detector are at infinite distances from the atmosphere-surface system: the solar and viewing geometries are the same across the domain. The horizontal area of 7×7 km² is covered by 70×70 pixels. MONKI used 10^7 photons per pixel, matching the number of photons used in the IPRT (Emde et al., 2018).

575 Figure 7 shows the results of MONKI (in forward mode) for the radiance I and degree of polarisation P , for IPRT-cases 4 and 9, that differ in solar and viewing geometries (see Table 4 of Emde et al., 2018). Because MONKI defines the angles slightly different-differently from Emde et al. (2018), we have listed the geometries in Table S8 in the Supplementary Material. Figure S1 in the Supplementary Material shows the results for all 9 cases and all Stokes parameters, with cases 1 to 4 pertaining to light transmitted through the atmosphere, thus at BOA, and cases 5 to 9 pertaining to reflected light, thus at TOA. Results
580 for cases 1 to 4 are stored on the x, y -grid at the surface, whereas results for cases 5 to 9 are stored on the x, y -grid at TOA.⁸

⁸MONKI can also map the reflected light at TOA on the x, y -grid at the surface, making MONKI suitable for air- and spaceborne applications which typically store measurements on ground-based pixel grids.

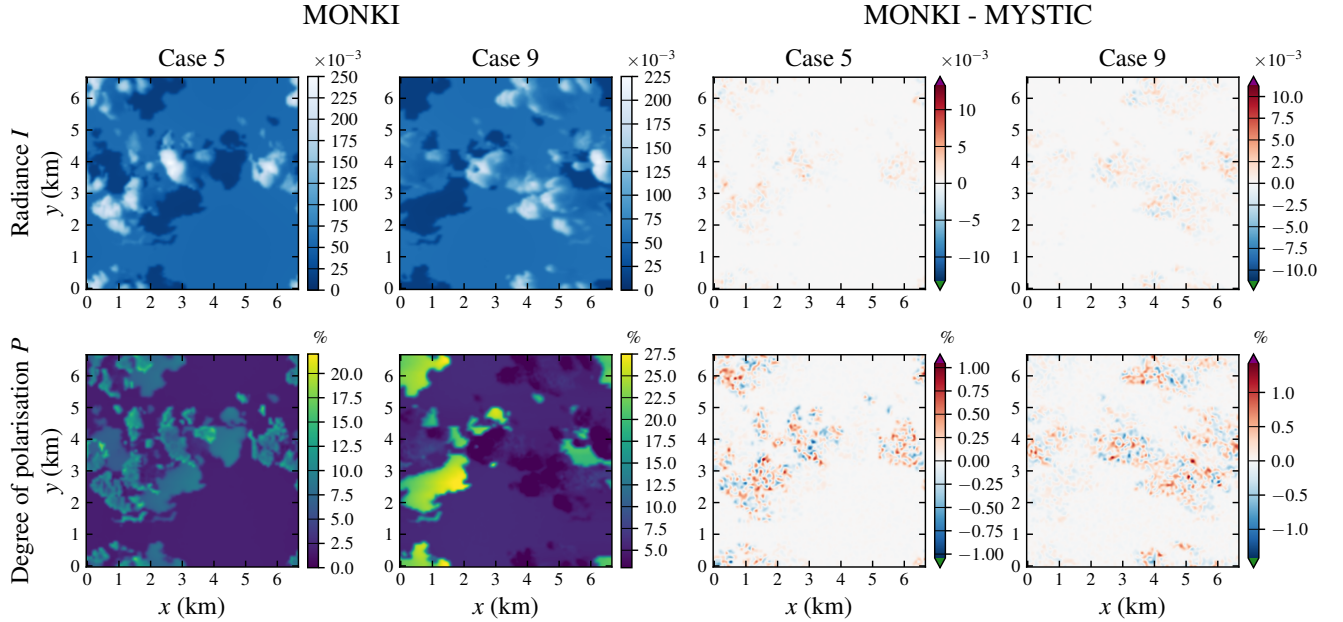


Figure 9. MONKI results (columns 1 and 2) of the radiance I (row 1) and P (row 2), for a 3D cumulus cloud field inside a scattering and absorbing gaseous atmosphere (Emde et al., 2018), for 2 different solar and viewing geometries with a detector at TOA (cases 5 and 9 in Table S8). The sunlight is incident from left to right along the x -direction. Radiance I is divided by E_0 , and P is in %. Columns 3 and 4 show the differences between MONKI and MYSTIC.

The radiance I in the cloud-free regions of cases 1 to 4 (BOA) is smaller than in cases 5 to 9 (TOA), due to the larger contribution of the surface reflection in the latter cases (see Fig. S1). Cases 5 to 9 (TOA) show shadows on the surface, while cases 1 to 4 (BOA) only show subtle shadows in the sky. Note that due to horizontal periodicity, the shadow of the cloud stretches outside the right-hand-right-hand side of the domain and back into the domain on the left-hand-left-hand side. The difference between the surface and sky shadows are is, for instance, evident in P for case 9 (see Fig. 7), where P to the right on the right-hand side of the cloud is relatively low due to the atmospheric shadow: in this part of the atmosphere, the direct sunlight is attenuated by the cloud. Instead, this part of the atmosphere is mostly illuminated by diffuse light with generally a lower degree of polarisation due to randomisation (see Fig. 7 of Trees et al., 2025). Above the cloud shadow on the surface, P is high because the shadow suppresses the unpolarised contribution of light that has been reflected by the Lambertian surface.

590 For a detailed discussion of the features in Figs. 7 and S1, see Sect. 5 of Emde et al. (2018).

MONKI's results closely match the benchmark results (cf. Fig. A2 of Emde et al., 2018). Figure 7 shows the differences between MONKI and MYSTIC for test cases 4 and 9 for I and P , and Fig. S2 in the Supplementary Material shows the differences for all nine cases and all Stokes parameters. In the cloud-free regions, the differences in I , Q , U , and V are nearly zero. Small, random differences in P remain below 0.07% and are centred around zero. In cloudy pixels, the differences are

595 larger, as expected because of increased simulation noise. This effect is common in Monte Carlo codes due to infrequent but

significant contributions in the local estimation method associated with strongly forward-peaked Mie scattering phase functions of the cloud droplets (see, e.g., Barker et al., 2003). Nevertheless, these differences remain below 2.82×10^{-3} , 0.66×10^{-3} , 0.63×10^{-3} , 10.98×10^{-5} , and 0.49 % for I , Q , U , V , and P , respectively, and are centred around zero for all cases. Increasing the number of photons would reduce this random noise. We find no systematic biases between MONKI and MYSTIC.

600 To demonstrate how MONKI performs compared to other codes, Fig. 8 shows cross-sections ~~of the results of cases 4 and 9~~ at $y = 3.95$ km ~~in Fig. 8, of of the results of~~ MONKI in both forward and backward ~~modemodes for cases 4 and 9~~, together with results of the codes used in the ~~IPRT-project~~ IPRT project (Emde et al., 2018). Also, the differences with MYSTIC are shown, ~~on top of the 2 standard deviation of the results of~~ together with the ± 2 standard deviation range of the 3DMCPOL : results. The results for all nine cases are shown in Fig. S5 in the Supplementary Material. Unlike some other codes, MONKI

605 shows excellent agreement with MYSTIC in all cases, in both its forward and backward ~~modemodes~~.

Emde et al. (2018) also provide test cases for a more realistic scenario: a 3D cumulus cloud field that has been generated by a Large Eddy Simulation (LES) code (Stevens et al., 1999), embedded within a scattering and absorbing gaseous atmosphere. The domain size is $6.7 \times 6.7 \times 30$ km³. The cloud’s optical thickness and droplet effective radius vary across the $100 \times 100 \times 53$ grid cells (the 12 top layers are cloud-free). For a detailed description of the model, see Emde et al. (2018). Figure 9 shows I and

610 P as computed with MONKI for the solar and viewing geometries of cases 5 and 9 (see Table S8), along with their differences from MYSTIC benchmark results. We used 10^6 photons per pixel. Once again, we find no systematic biases. Numerical tests showed that the remaining differences decrease when increasing the number of photons.

~~Model settings used in the sample simulations of the Earth and Venus at $\lambda = 550$ nm: Setting Earth Venus Altitude-range 0–100 km (33 layers) 0–100 km (40 layers) Surface albedo A_s 0.05 0.0 Vertical temperature-pressure profile MLS VIRA~~

615 ~~Gravitational acceleration g 9.81 m s⁻² (not used) 8.87 m s⁻² Real refractive index n of the gas Peek and Reeder (1972) Wilmouth and Sayres (2020)~~

~~Depolarisation factor δ 0.0283 for air 0.0789 for CO₂ Absorbing gases O₃ (MLS profile) None Absorption cross-sections σ_{abs}^m Bass and Paur (1985) — Cloud altitude range 1–2 km 50–70 km Cloud optical thickness b^c 5–30 Cloud particle type Liquid water Liquid 75% H₂SO₄ solution Particle size distribution Two-parameter gamma Two-parameter gamma Effective~~

620 ~~radius r_{eff} 10 μ m 1.05 μ m Effective variance v_{eff} 0.1 0.07 Real refractive index of the liquid droplets 1.33 1.43 Imaginary refractive index of the liquid droplets 0 0~~

4 Sample signals for the Earth and Venus

The model atmosphere-surface systems of the Earth (in blue) and Venus (in orange). From left to right: the pressure profiles, temperature profiles, the ozone volume mixing ratio profile for the Earth, the cloud model for the Earth, the cloud model for

625 ~~Venus. Below the latter two graphs, the surface albedo, A_s , is also given.~~

In this section, we present sample simulations with MONKI of sunlight that is locally reflected by the atmospheres of the Earth and Venus. The model atmospheres ~~were~~ are horizontally homogeneous (i.e., $N_x = N_y = 1$), as illustrated in Fig. 10. These simulations demonstrate MONKI’s versatility in handling different types of atmospheres, following the formulae pro-

Table 2. Model settings used in the sample simulations of the Earth and Venus at $\lambda = 550$ nm.

<u>Setting</u>	<u>Earth</u>	<u>Venus</u>
<u>Altitude range</u>	<u>0–100 km (33 layers)</u>	<u>0–100 km (40 layers)</u>
<u>Surface albedo A_s</u>	<u>0.05</u>	<u>0.0</u>
<u>Vertical temperature-pressure profile</u>	<u>MLS</u>	<u>VIRA</u>
<u>Gravitational acceleration g</u>	<u>9.81 m s^{-2} (not used)</u>	<u>8.87 m s^{-2}</u>
<u>Refractive index n of the gas</u>	<u>Peck and Reeder (1972)</u>	<u>Sneep and Ubachs (2005); Wilmouth and Sayres (2020)</u>
<u>Depolarisation factor ρ</u>	<u>0.0283 for air</u>	<u>0.0789 for CO_2</u>
<u>Absorbing gases</u>	<u>O_3 (MLS profile)</u>	<u>None</u>
<u>Absorption cross-sections $\sigma_{\text{abs}}^{\text{m}}$</u>	<u>Bass and Paur (1985)</u>	<u>—</u>
<u>Cloud altitude range</u>	<u>1–2 km</u>	<u>50–70 km</u>
<u>Cloud optical thickness b^{a}</u>	<u>5</u>	<u>30</u>
<u>Cloud particle type</u>	<u>Liquid water</u>	<u>Liquid 75% H_2SO_4 solution</u>
<u>Particle size distribution</u>	<u>Two-parameter gamma</u>	<u>Two-parameter gamma</u>
<u>Effective radius r_{eff}</u>	<u>$10 \mu\text{m}$</u>	<u>$1.05 \mu\text{m}$</u>
<u>Effective variance v_{eff}</u>	<u>0.1</u>	<u>0.07</u>
<u>Real refractive index of the liquid droplets n_{r}</u>	<u>1.33</u>	<u>1.43</u>
<u>Imaginary refractive index of the liquid droplets n_{i}</u>	<u>0</u>	<u>0</u>

vided in Appendix A. Below, we first describe the model setting and then the results. The model settings are also summarized in Tab. summarised in Table 2.

~~The atmosphere of the Earth’s model~~ The Earth model atmosphere consists of 33 plane-parallel, horizontally homogeneous layers from 0 to 100 km altitude. The surface reflects Lambertian with an albedo A_s of 0.05. The only absorbing gas is ozone (O_3). The wavelength- and temperature-dependent O_3 absorption cross-sections, $\sigma_{\text{abs}}^{\text{m}}(\lambda, T)$, are taken from Bass and Paur (1985). Pressure, temperature, and ozone volume mixing ratios (VMRs) vary with altitude according to the standard Mid-Latitude Summer profile (Anderson et al., 1986). We assume that the pressure-to-temperature ratio decreases exponentially with altitude within each layer (see Eq. A10). The refractive index of air, n , is computed with the dispersion formula of Peck and Reeder (1972). The King correction factor F_K of the air (Eq. A9) is the sum of the values for N_2 , O_2 , Ar, and CO_2 as given by Bates (1984), weighted by the respective mixing ratios of those gases on Earth: 78.084%, 20.9476%, 0.934%, and 0.0375%. At $\lambda = 550$ nm, this yields a depolarisation factor ~~$\delta = 0.0283$~~ $\rho = 0.0283$.

~~The Earth scenario~~ In the Earth scenario, the cloud extends from 1 to 2 km, with a vertically homogeneous optical thickness ~~$b = b^{\text{a}}$~~ b^{a} of 5. We assume a two-parameter gamma distribution for cloud droplet sizes (Hansen and Travis, 1974), with an effective radius $r_{\text{eff}} = 10 \mu\text{m}$ and an effective variance $v_{\text{eff}} = 0.1$. The droplets are composed of liquid water with a real refractive index of 1.33 (Hale and Querry, 1973) and an imaginary refractive index of zero (i.e., the single scattering albedo of the cloud droplets is 1.0).

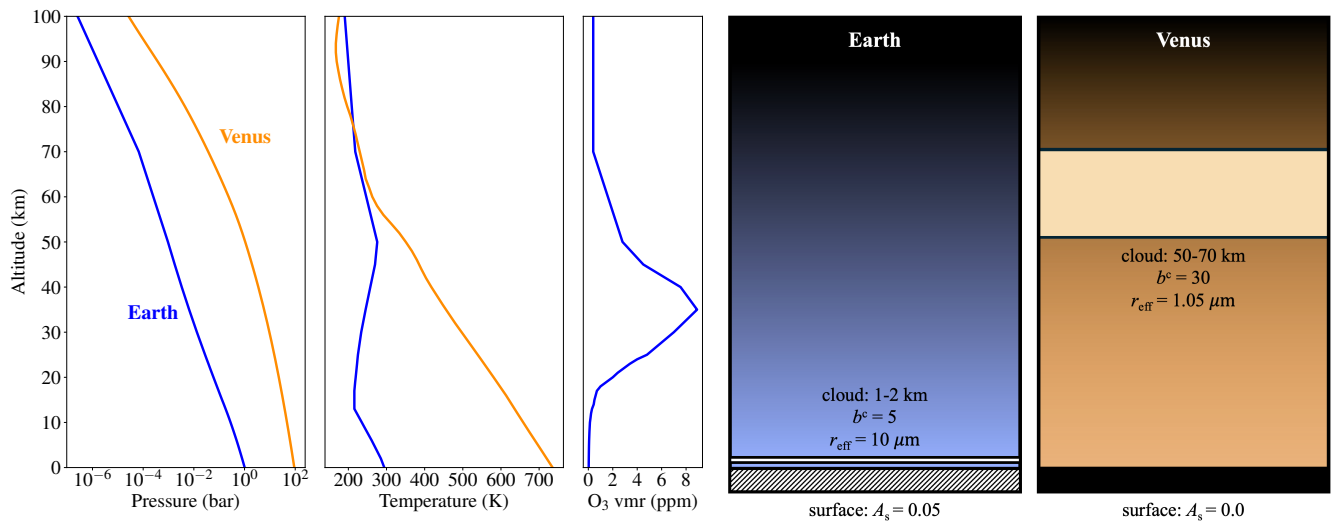


Figure 10. Sample signals. The model atmosphere-surface systems of the TOA reflectance R_{TT} Earth (top in blue) and degree of polarisation $P_s = -Q/I$ Venus (bottom in orange). From left to right: the pressure profiles, temperature profiles, the ozone volume mixing ratio profile for the Earth (left) and Venus (right), computed with MONKI. Note the different y-scales cloud model for P_s . The signals are presented as functions of viewing angle θ the Earth, and the cloud model for solar zenith angles $\theta_0 = 0^\circ$ (solid line) Venus. Below the latter two graphs, 45° (dashed line) the surface albedo, and 75° (dotted line). The solar azimuth angle φ_0 A_s is 0° also given.

645 The Venus model atmosphere consists of 40 plane-parallel, horizontally homogeneous layers from 0 to 100 km altitude. At $\lambda = 550$ nm, the reflected light at TOA is virtually insensitive to Venus's lower atmosphere and surface albedo. Therefore, we use 4 km thick layers from the surface to 40 km and 2 km thick layers above 40 km. The surface is assumed black. We neglect gaseous absorption, which is a reasonable assumption for Venus at $\lambda = 550$ nm (Moroz, 1981; Haus et al., 2015). Pressure profiles follow the Venus International Reference Atmosphere (VIRA) for latitudes up to 30° , based on Seiff et al. (1985),
650 which incorporates data from four Pioneer Venus Probes, the Pioneer Venus Orbiter, and the Venera 10, 12, and 13 landers. We assume hydrostatic equilibrium (Eq. A11), a gravitational acceleration of $g = 8.87$ m s $^{-2}$, and the background gas molecular molar mass M is computed by the weighted sum of 96.5% CO $_2$ (44.01 g mol $^{-1}$) and 3.5% N $_2$ (28.0134 g mol $^{-1}$). The values for n and F_K at $\lambda = 550$ nm are computed with the parametrisations for CO $_2$ stated in Sneep and Ubachs (2005)⁹, leading to a depolarisation factor $\delta = 0.0789$ $\rho = 0.0789$.

655 Contributions to the computed TOA reflectances at $\theta_0 = 0^\circ$, for Earth (left) and Venus (right), plotted at the altitudes of the last scattering event of the photons (in km $^{-1}$), for the total reflectances R_{TT} (top row) and the polarised reflectances $|R_{2T}|$ (bottom row).

The cloud in the Venus model extends from 50 to 70 km, with a vertically homogeneous optical thickness $b^c = 30$ $b^a = 30$ (see Haus et al., 2015, for more detailed Venus cloud models). The cloud particles are liquid droplets and their properties fol-

⁹The refractive index of CO $_2$ stated in Sneep and Ubachs (2005) needs to be divided by 10^3 , see Wilmouth and Sayres (2020).

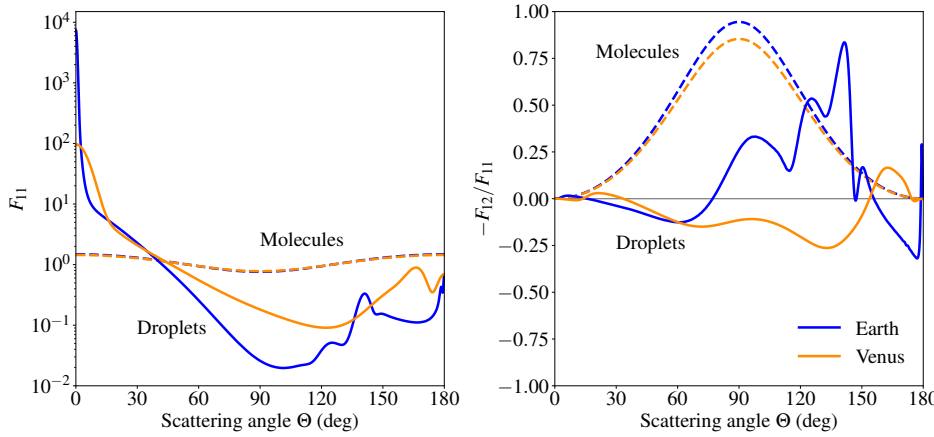


Figure 11. The phase function F_{11} (left) and the degree of linear polarisation ($-F_{12}/F_{11}$) (right) as functions of the scattering angle Θ , for singly scattered light by gaseous molecules (dashed lines) and cloud droplets (solid lines). The blue lines are for Earth-like gas (with a depolarisation factor ρ equal to 0.0283) and cloud particles ($r_{\text{eff}} = 10 \mu\text{m}$), and the orange lines are for Venus-like gas (with $\rho = 0.0789$) and cloud particles ($r_{\text{eff}} = 1.05 \mu\text{m}$). The wavelength of the light is 550 nm.

low those of Hansen and Hovenier (1974): a two-parameter gamma distribution with an effective radius of $1.05 \mu\text{m}$ and an effective variance of 0.07. The droplets are composed of 75% H_2SO_4 solution in water, with a real refractive index of 1.43 at $\lambda = 550 \text{ nm}$ (Palmer and Williams, 1975). Their single scattering albedo is 1.0.

Figure 11 shows the [angular distribution of the](#) singly scattered radiance, F_{11} (the phase function), and the degree of linear polarisation, $-F_{12}/F_{11}$, of the gas and cloud droplets in the Earth and Venus model atmospheres as functions of the scattering angle Θ (see [App. Appendix A](#) for definitions of the single-scattering matrix elements). The large droplets of the Earth cloud produce a strong forward peak in F_{11} due to diffraction (see Hansen and Travis, 1974). The peaks near $\Theta = 142^\circ$ and 122° are the primary and secondary cloudbows, caused by, respectively, one and two internal reflections inside the spherical droplets. The radiance and polarisation enhancement near $\Theta = 180^\circ$ is called the 'glory'. These features are less pronounced or absent in the much smaller cloud droplets on Venus. The features due to Rayleigh scattering by gas molecules are similar on Earth and Venus: F_{11} is [stronger in the forward and backward directions](#) [fairly isotropic](#), while polarisation is strongest around $\Theta = 90^\circ$. For the Venusian gas, the Rayleigh polarisation maximum is lower than for the Earth's gas because it has a larger depolarisation factor.

Figure 12 shows the simulated TOA reflectance, R_{11} , and degree of polarisation, P_s , computed with MONKI for the Earth and Venus model atmosphere–surface systems described above. Simulations were performed for three solar zenith angles: $\theta_0 = 0^\circ, 45^\circ$, and 75° . The viewing zenith angles range from $\theta = 0^\circ$ to $\theta = 89^\circ$ in 1° increments. The [solar azimuth angle is azimuth angle of the sunlight was](#) $\varphi_0 = 0^\circ$. The viewing azimuth angles are $\varphi = 0^\circ$ and 180° ([thus \$U = 0\$](#)). For each combination of the 90 values of θ , and (θ_0, φ) , we used 10^8 photons for the computations for the Earth and 10^5 photons for Venus (the more isotropic scattering by the small Venusian cloud droplets requires fewer photons). In Fig. S6, we provide the comparison of the computations for the Earth with results computed with Doubling-Adding KNMI (DAK), which uses identical formulae for the optical properties of the model atmosphere as MONKI (see Appendix A).

For the Earth model (Fig. 12), the reflectance R_{11} generally increases with θ and θ_0 . With increasing angles, the optical paths through the gas and clouds increase and multiple scattering increases. Cloud droplet single scattering features (Fig. 11) leave

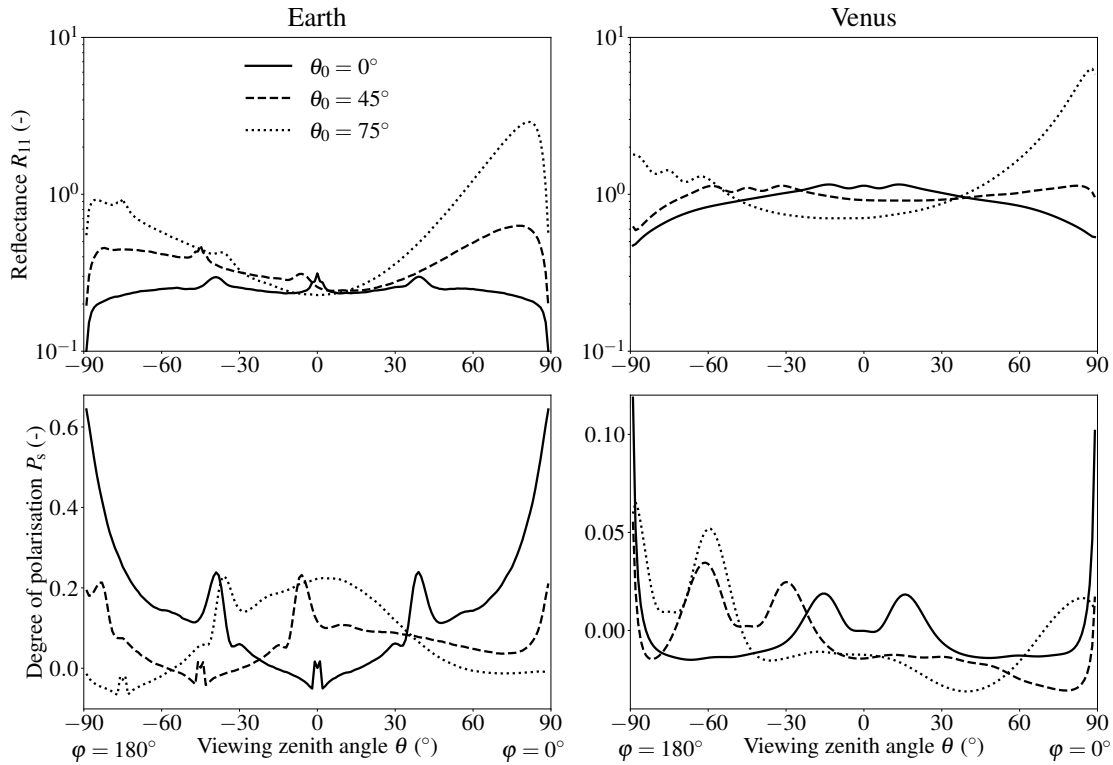


Figure 12. Sample signals of the TOA reflectance R_{11} (top) and degree of polarisation $P_s = -Q/I$ (bottom), for the Earth (left) and Venus (right), computed with MONKI. Note the different y -scales for P_s . The signals are presented as functions of viewing angle θ , and for solar zenith angles $\theta_0 = 0^\circ$ (solid line), 45° (dashed line), and 75° (dotted line). The azimuth angle of the sunlight φ_0 is 0° .

signatures in R_{11} , but show up more distinctly in P_s . The cloudbows emerge near $(\theta, \varphi) = (38^\circ, 0^\circ)$, $(7^\circ, 180^\circ)$, and $(37^\circ, 180^\circ)$, corresponding to the [single](#)-scattering angle $\Theta = 142^\circ$ for $\theta_0 = 0^\circ$, 45° and 75° , respectively.¹⁰ The glory shifts from $\theta = 0^\circ$ to 45° to 75° in the $\varphi = 180^\circ$ direction with increasing θ_0 . Rayleigh scattering, which enhances P_s around $\Theta = 90^\circ$, causes P_s to peak near $\theta = 90^\circ$ for $\theta_0 = 0^\circ$ and near $(\theta, \varphi) = (10^\circ, 0^\circ)$ for $\theta_0 = 75^\circ$. [The latter-This behaviour](#) can be verified with vertical profiles of the layer contributions to the total and polarised TOA reflectances. As an example, Fig. 13 shows those profiles for $\theta_0 = 0^\circ$, demonstrating that, [toward-towards](#) perpendicular scattering geometries, an increasing fraction of the polarised signal originates from the gas above the cloud.

The Venus results in Fig. 12 show that this planet appears much brighter in locally reflected light than Earth. The higher R_{11} values are primarily due to the larger cloud optical thickness. As on Earth, cloud droplet single scattering features leave distinct signatures in P_s of the locally reflected light, which can be seen to shift with increasing θ_0 , as they are characteristic for given scattering angles. However, the increase [of the polarisation that is in polarisation](#) due to Rayleigh scattering around a scattering angle of 90° is less pronounced on Venus than on Earth. For example, for $\theta_0 = 0^\circ$, P_s increases only at the largest

¹⁰As [single scattering angle](#) Θ equals 180° minus the reflection angle (cf. Fig. 1).

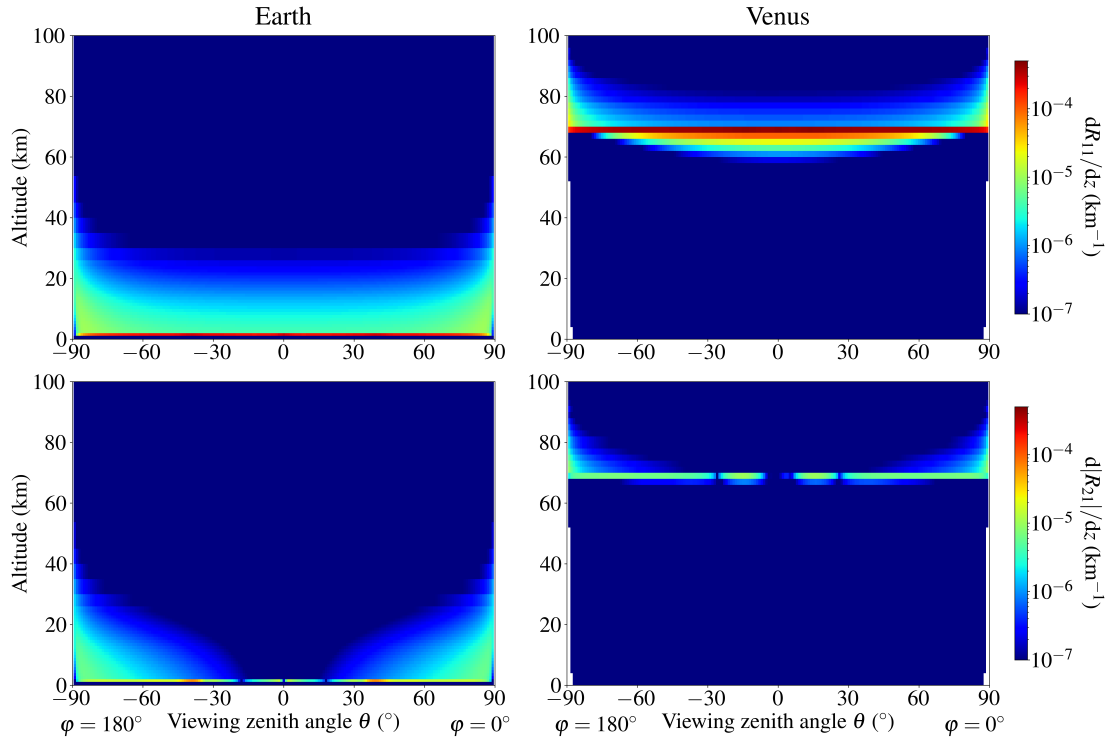


Figure 13. Contributions to the computed TOA reflectances at $\theta_0 = 0^\circ$, for Earth (left) and Venus (right), plotted as functions of the altitude of the last scattering event of the photons. The contribution profiles are expressed per kilometre (km^{-1}) for the total reflectances R_{11} (top row) and the polarised reflectances $|R_{21}|$ (bottom row).

viewing zenith angles. Despite Venus's large atmospheric pressure at surface level, the cloud deck ~~reaches~~ extends up to 70 km ~~of altitude~~ altitude, leaving little gas above the cloud for light to scatter from, as shown in Fig. 13. Instead, the signal is dominated by abundant virtually unpolarised light multiply scattered in the upper parts of the Venusian clouds.

5 Summary, discussion, and outlook

Polarimetry is a powerful tool for characterising planetary atmospheres and surfaces. Radiative transfer simulations of total and polarised radiances are essential for designing, preparing, and operating spectro(polari)metric remote sensing instruments. Even for instruments that do not measure polarisation, accounting for polarisation in simulations is crucial for obtaining accurate total radiance calculations and for assessing potential errors due to an instrument's polarisation sensitivity if no polarisation scrambler is used. With the increasing spatial resolution of current and future Earth observation spectro(polari)meters, simulating 3D radiative transfer effects, such as cloud shadows, becomes increasingly important.

In this paper, we have presented the 3D radiative transfer code MONKI (Monte Carlo KNMI), which fully accounts for the linear and circular polarisation of light at all orders of scattering. MONKI is written in ~~Fortran-90~~ modern Fortran and is based

on the Monte Carlo method. Rather than counting photons at the detector, MONKI uses the more efficient ‘local estimation method,’ which calculates the probability of scattering towards the detector at each scattering event. MONKI can compute both horizontally homogeneous and inhomogeneous (3D cloudy) scenes. It can operate both in forward mode (with photons propagating from the source to the detector) and in backward mode (with photons propagating in the opposite direction). Both modes converge to similar results~~in similar computation times~~, with comparable computation times in the tested cases.

We compared results of MONKI with benchmark results for polarised radiances in horizontally homogeneous atmospheres (de Haan et al., 1987) and thick Rayleigh-scattering atmospheres (Natraj and Hovenier, 2012). Additionally, we validated MONKI’s 3D radiative transfer capabilities using benchmark results for polarised radiances from 3D clouds (Emde et al., 2018). In all cases, MONKI showed excellent agreement with the benchmark results.

Although MONKI is not the first code of its kind, it has ~~subtle-but-fundamental~~ fundamental methodological differences from other Monte Carlo codes. A common limitation of Monte Carlo codes is their failure to converge in optically thick and strongly polarising atmospheres. This issue arises ~~if~~ when approximations are made ~~when propagating the polarisation state of photons during sampling of the scattering direction. MONKI, however, fully tracks in the sampling of scattering directions, by neglecting the photon’s polarisation state and correcting afterwards by weight factors. MONKI instead samples scattering directions from the full polarisation-dependent distribution while fully tracking~~ the polarisation history of each photon along its trajectory, ~~and therefore converges even in optically thick,~~. As demonstrated in this paper, this exact polarised sampling approach converges in both forward and backward modes, including for optically thick and strongly polarising planetary atmospheres. ~~The derivations of our formulae are provided in the appendices~~ In addition, the appendices provide a complete derivation of the corresponding forward and backward Monte Carlo equations and polarisation-dependent sampling formulae, thereby offering a unified theoretical framework for polarised Monte Carlo radiative transfer.

The current version of MONKI does not use variance reduction techniques other than the local estimation method. Although such techniques can reduce the noise (and therefore the computation time needed for convergence), they can introduce biases (see, e.g. Barker et al., 2003) and/or increase code complexity. For example, directional importance sampling, which involves adjusting forward-peaked single scattering phase functions and photon weights, and photon splitting (see, e.g. Buras and Mayer, 2011), are mathematically correct but can reduce a code’s intuitiveness. By omitting those variance reduction techniques, MONKI produces unbiased results while preserving readability and simplicity, and thus adaptability when future extensions of the code are to be implemented. Instead of using such techniques, we increase the number of photons to achieve higher precision when needed.

In order to speed up MONKI’s simulations, we implemented and presented a precomputation approach for optical paths to the detector. By precomputing the optical thickness of the horizontally homogeneous background gas for each atmospheric layer towards the detector, and by identifying grid cells that have cloud- and aerosol-free optical paths to the detector, MONKI avoids repeated photon propagations between the locations of the scattering events and the detector. This approach significantly improves computational efficiency, especially in scenes with low and/or patchy clouds, without compromising the accuracy.

We have presented sample signals of the TOA reflectance and degree of polarisation of light that is locally reflected by the Earth and Venus using horizontally homogeneous cloud models. This exercise demonstrated MONKI’s versatility for

various atmospheric conditions. For Earth applications, MONKI uses the same method as DAK (Doubling-Adding KNMI) to compute the input atmospheric optical properties. MONKI can handle spectral variations of those properties, producing simulated spectra by so-called line-by-line computations. MONKI can import different particle scattering matrices and can, in principle, also simulate light scattered by non-spherical aerosol particles and ice clouds.

Since MONKI uses the Monte Carlo method, it can save-store the locations of photon scattering, also for different orders of scattering, for detailed analyses of features in the simulated signals. Among the planned extensions of MONKI is the implementation of atmospheric sphericity, which would allow computations for scenes with a low sun-Sun and/or large viewing angles. We conclude that MONKI is an accurate radiative transfer code, ready to support the design, preparation, and operations of spectro(polari)metric missions for Earth, Venus, and other planets.

Code availability. The version of MONKI as described in this paper is available from Zenodo under the Creative Commons Attribution 4.0 International licence. The version of the model used to produce the results presented in this paper (Trees, 2025), as well as the required input data, are archived under DOI (<https://doi.org/10.5281/zenodo.15380811>).

Appendix A: Describing the atmosphere and surface

In this appendix, we provide the formulae that describe the optical properties of the atmosphere and surface. ~~Each grid cell in a MONKI simulation used by MONKI.~~ Each atmospheric grid cell can contain gas molecules and multiple aerosol types (e.g., such as cloud or haze droplets) particles. For each cell, ~~the Monte Carlo photon simulation requires the of these constituents,~~ MONKI uses the total optical thickness, b , the single scattering albedo, a , and the single scattering matrix, F , separately for the gas and each aerosol type, the single-scattering albedo, and the single-scattering matrix.

The total optical thickness of a grid cell is the sum of the optical thicknesses of gas, b^m , and aerosols, b^c ; the gas and all aerosol types:

$$b(\lambda) = b^m(\lambda) + \sum_{c=1}^{N_c} b_{-c}^{ca}(\lambda)$$

$$= b_{\text{sca}}^m(\lambda) + b_{\text{abs}}^m(\lambda) + \sum_{c=1}^{N_c} \left[b_{\text{sca}}^{ca}(\lambda) + b_{\text{abs}}^{ca}(\lambda) \right], \quad (\text{A1})$$

~~where subscripts ‘sca’ and ‘abs’ denote~~ where superscripts m and a refer to gas molecules and aerosol particles, respectively, and subscripts “sca” and “abs” refer to scattering and absorption, ~~respectively.~~ The index $c = 1, \dots, N_c$ denotes the aerosol type. For a grid cell with vertical extent Δz , the corresponding total extinction coefficient is $\beta = b/\Delta z$. Analogous relations hold for the scattering and absorption extinction coefficients, and for each constituent type separately; for example, $\beta_t = b_t/\Delta z$ and $\beta_{\text{sca},t} = b_{\text{sca},t}/\Delta z$ for constituent type t .

A1 Gas molecules

770 Single scattering of light by gas molecules is described by the anisotropic Rayleigh scattering matrix $\mathbf{F}^m$ (Hansen and Travis, 1974):

$$\mathbf{F}^m(\Theta, \lambda) = \begin{bmatrix} F_{11}^m(\Theta, \lambda) & F_{12}^m(\Theta, \lambda) & 0 & 0 \\ F_{21}^m(\Theta, \lambda) & F_{22}^m(\Theta, \lambda) & 0 & 0 \\ 0 & 0 & F_{33}^m(\Theta, \lambda) & 0 \\ 0 & 0 & 0 & F_{44}^m(\Theta, \lambda) \end{bmatrix}. \quad (\text{A2})$$

Here, Θ is the scattering angle, defined relative to the propagation direction of the incident light, such that $\Theta = 0^\circ$ corresponds to forward scattering and $\Theta = 180^\circ$ to backward scattering. The matrix elements of $\mathbf{F}^m$ are given by:

775 are

$$F_{11}^m(\Theta, \lambda) = \frac{3}{4}\Delta(\lambda)(1 + \cos^2 \Theta) + 1 - \Delta(\lambda), \quad (\text{A3})$$

$$F_{22}^m(\Theta, \lambda) = \frac{3}{4}\Delta(\lambda)(1 + \cos^2 \Theta), \quad (\text{A4})$$

$$F_{33}^m(\Theta, \lambda) = \frac{3}{2}\Delta(\lambda)\cos \Theta, \quad (\text{A5})$$

$$F_{44}^m(\Theta, \lambda) = \frac{3}{2}\Delta(\lambda)\Delta'(\lambda)\cos \Theta, \quad (\text{A6})$$

$$780 \quad F_{12}^m(\Theta, \lambda) = F_{21}^m(\Theta, \lambda) = -\frac{3}{4}\Delta(\lambda)\sin^2 \Theta, \quad (\text{A7})$$

with

$$\Delta(\lambda) = \frac{1 - \delta(\lambda)}{1 + \delta(\lambda)/2}, \quad \Delta'(\lambda) = \frac{1 - 2\delta(\lambda)}{1 - \delta(\lambda)}. \quad (\text{A8})$$

The depolarisation factor δ is given by (Bodhaine et al., 1999):

$$\delta(\lambda) = \frac{6F_K(\lambda) - 6}{7F_K(\lambda) + 3},$$

785 where F_K is the so-called King correction factor, which F_K according to (Bodhaine et al., 1999)

$$\rho(\lambda) = \frac{6F_K(\lambda) - 6}{7F_K(\lambda) + 3}, \quad (\text{A9})$$

where F_K depends on the mix of atmospheric gases composition of the atmospheric gas mixture.

In the current version of MONKI, gas properties are horizontally homogeneous, varying only with height, and vary only with altitude z . The scattering optical thickness for the gas in atmospheric layer k (between altitudes z_k^{bot} and

790 z_k^{top}), is computed as (Stam et al., 2000) :-

$$b_{\text{sca}}^m(\lambda) = \frac{24\pi^3}{\lambda^4 N_L^2} \frac{(n^2(\lambda) - 1)^2}{(n^2(\lambda) + 2)^2} \frac{24\pi^3}{\lambda^4 N_L^2} \frac{(n^2(\lambda) - 1)^2}{(n^2(\lambda) + 2)^2} F_{\text{KK}}(\lambda) \frac{N_{\text{av}}}{R} \int_{z_k^{\text{bot}}}^{z_k^{\text{top}}} \frac{p(z)}{T(z)} dz, \quad (\text{A10})$$

where N_L is the Loschmidt number, N_{av} is Avogadro's constant, R is the universal gas constant, $n(\lambda)$ is the ~~wavelength dependent~~ wavelength-dependent refractive index of the atmospheric gas under standard conditions, and $p(z)$ and $T(z)$ are the ~~vertical profiles of the ambient~~ vertical profiles-values pressure and temperature ~~profiles~~ in Pa and K, respectively. Given the ~~vertical profiles-values~~ of p and T at the layer boundaries ~~z_k^{bot} and z_k^{top}~~ , the integral is evaluated assuming an exponential decrease of p/T with ~~z~~ altitude within the layer.

Alternatively, if ~~for example~~ for example the temperature profile is unknown, b_{sca}^m can be computed assuming hydrostatic equilibrium:

$$b_{sca}^m(\lambda) = \frac{24\pi^3}{\lambda^4 N_L^2} \frac{(n^2(\lambda) - 1)^2}{(n^2(\lambda) + 2)^2} \frac{24\pi^3}{\lambda^4 N_L^2} \frac{(n^2(\lambda) - 1)^2}{(n^2(\lambda) + 2)^2} F_{kK}(\lambda) \frac{N_{av}}{M} \frac{\Delta p_k}{g}, \quad (A11)$$

800 ~~where $\Delta p_k = p(z_k^{bot}) - p(z_k^{top})$~~ where $\Delta p_k = p(z_k^{bot}) - p(z_k^{top})$, g is the gravitational acceleration, and M is the ~~molecular~~ molar mass of the background gas.

The gaseous absorption optical thickness ~~for all n_g gases in atmospheric~~ of layer k is computed ~~as follows (Stam et al., 2000)~~ by summing over all absorbing gases:

$$b_{abs}^m(\lambda) = \sum_{i=1}^{n_g} \frac{n_g N_g}{R} \int_{z_k^{bot}}^{z_k^{top}} \frac{p(z)}{T(z)} \eta_{ii}(z) \sigma_{abs,i}^m(\lambda, z) dz, \quad (A12)$$

805 ~~where η_i~~ where η_i is the volume mixing ratio of ~~the absorbing gas with index~~ absorbing gas i and ~~$\sigma_{abs,i}^m$~~ and $\sigma_{abs,i}^m$ is its absorption cross section in m^2 . ~~The latter does not only depend on λ and i , but generally also on the ambient temperature and pressure inside the layer, hence the dependence on z . Between z_k^{bot} and z_k^{top} , we assume that η_i and $\sigma_{abs,i}^m$~~ The absorption cross section may depend on wavelength, temperature, and pressure, hence its dependence on altitude. Within each layer, η_i and $\sigma_{abs,i}^m$ are assumed to vary linearly with altitude. The single scattering albedo for the gas in a grid cell is defined as:

810 single-scattering albedo of the gas is

$$a^m(\lambda) = \frac{b_{sca}^m(\lambda)}{b_{sca}^m(\lambda) + b_{abs}^m(\lambda)} \frac{b_{sca}^m(\lambda)}{b_{sca}^m(\lambda) + b_{abs}^m(\lambda)}. \quad (A13)$$

~~A light beam that interacts with an ensemble of aerosol particles is scattered and/or absorbed.~~

A2 Aerosol particles

Aerosol particles are ~~spherical and defined~~ described by their size ~~distributions and refractive index~~ (Hansen and Travis, 1974)

815 ~~For a given wavelength and aerosol particle type, the single scattering albedo a^c , and the single scattering matrix F^c , are computed~~ distribution, refractive index, and number density. In the present version of MONKI, aerosol particles are assumed to be spherical, so their optical properties are pre-computed with Mie theory (de Rooij and van der Stap, 1984):

$$a^c(\lambda) = \frac{b_{sca}^c(\lambda)}{b_{sca}^c(\lambda) + b_{abs}^c(\lambda)},$$

For aerosol type c , the pre-computed single-scattering matrix used by MONKI is

$$820 \quad \mathbf{F}_c^a(\Theta, \lambda) = \begin{bmatrix} F_{11,c}^a(\Theta, \lambda) & F_{12,c}^a(\Theta, \lambda) & 0 & 0 \\ F_{21,c}^a(\Theta, \lambda) & F_{22,c}^a(\Theta, \lambda) & 0 & 0 \\ 0 & 0 & F_{33,c}^a(\Theta, \lambda) & F_{34,c}^a(\Theta, \lambda) \\ 0 & 0 & F_{43,c}^a(\Theta, \lambda) & F_{44,c}^a(\Theta, \lambda) \end{bmatrix}, \quad (\text{A14})$$

and

$$\mathbf{F}^c(\Theta, \lambda) = \begin{bmatrix} F_{11}^c(\Theta, \lambda) & F_{12}^c(\Theta, \lambda) & 0 & 0 \\ F_{21}^c(\Theta, \lambda) & F_{22}^c(\Theta, \lambda) & 0 & 0 \\ 0 & 0 & F_{33}^c(\Theta, \lambda) & F_{34}^c(\Theta, \lambda) \\ 0 & 0 & F_{43}^c(\Theta, \lambda) & F_{44}^c(\Theta, \lambda) \end{bmatrix},$$

respectively, with $F_{12}^c = F_{21}^c$ and $F_{43}^c = -F_{34}^c$. The scattering and absorption optical thicknesses for an aerosol type at a given wavelength are:

$$825 \quad b_{\text{sca}}^c(\lambda) = a^c(\lambda) \sigma^c(\lambda) N^c,$$

$$b_{\text{abs}}^c(\lambda) = (1 - a^c(\lambda)) \sigma^c(\lambda) N^c,$$

with $F_{12}^a = F_{21}^a$ and $F_{43}^a = -F_{34}^a$.

The single-scattering albedo of aerosol type c is

$$a_c^a(\lambda) = \frac{b_{\text{sca},c}^a(\lambda)}{b_{\text{sca},c}^a(\lambda) + b_{\text{abs},c}^a(\lambda)}. \quad (\text{A15})$$

830 ~~where N^c is the aerosol~~ Equivalently, if the extinction cross section $\sigma_c^a(\lambda)$ and the particle column number density $N_{\text{col},c}^a$ are specified, the scattering and absorption optical thicknesses are

$$b_{\text{sca},c}^a(\lambda) = a_c^a(\lambda) \sigma_c^a(\lambda) N_{\text{col},c}^a, \quad (\text{A16})$$

$$b_{\text{abs},c}^a(\lambda) = [1 - a_c^a(\lambda)] \sigma_c^a(\lambda) N_{\text{col},c}^a. \quad (\text{A17})$$

835 ~~Here, $N_{\text{col},c}^a$ is expressed in m^{-2} and σ_c^c the particle extinction cross-section in m^2 , the latter one also being computed with Mie theory σ_c^a in m^2 . Each grid cell can contain multiple aerosol types and number densities, allowing the simulation of 3D cloud structures. MONKI to represent horizontally inhomogeneous aerosol and cloud fields. The total aerosol optical thickness of a grid cell is~~

$$b^a(\lambda) = \sum_{c=1}^{N_c} [b_{\text{sca},c}^a(\lambda) + b_{\text{abs},c}^a(\lambda)]. \quad (\text{A18})$$

Instead of computing optical properties using the equations above, MONKI also allows prescribed input values for

840 A3 Effective single-scattering matrix of a mixture

The vector radiative transfer equation (VRTE) in Appendix G1 is written in terms of an effective single-scattering matrix $\mathbf{F}$ for the local atmospheric mixture. Let the index t denote all scattering constituent types present in a grid cell, for example the gas and the aerosol types. The total scattering coefficient is

$$\beta_{\text{sca}}(\mathbf{x}, \lambda) = \sum_t \beta_{\text{sca},t}(\mathbf{x}, \lambda), \quad (\text{A19})$$

845 and, for $\beta_{\text{sca}} > 0$, the effective single-scattering matrix is

$$\mathbf{F}(\mathbf{x}, \Theta, \lambda) = \frac{\sum_t \beta_{\text{sca},t}(\mathbf{x}, \lambda) \mathbf{F}_t(\mathbf{x}, \Theta, \lambda)}{\beta_{\text{sca}}(\mathbf{x}, \lambda)}. \quad (\text{A20})$$

If $\beta_{\text{sca}} = 0$, the scattering source term in the VRTE vanishes and the choice of $\mathbf{F}$ is irrelevant. For a grid cell containing gas molecules and N_c aerosol types, Eq. A20 becomes

$$\mathbf{F}(\mathbf{x}, \Theta, \lambda) = \frac{\beta_{\text{sca}}^{\text{m}}(\mathbf{x}, \lambda) \mathbf{F}^{\text{m}}(\mathbf{x}, \Theta, \lambda) + \sum_{c=1}^{N_c} \beta_{\text{sca},c}^{\text{a}}(\mathbf{x}, \lambda) \mathbf{F}_c^{\text{a}}(\mathbf{x}, \Theta, \lambda)}{\beta_{\text{sca}}^{\text{m}}(\mathbf{x}, \lambda) + \sum_{c=1}^{N_c} \beta_{\text{sca},c}^{\text{a}}(\mathbf{x}, \lambda)}. \quad (\text{A21})$$

850 This definition is equivalent to summing the scattering source terms of the individual constituents in the VRTE. The reason is that the rotation matrices used to construct the phase matrix from $\mathbf{F}$ depend only on the incident and scattered directions, and not on the constituent type.

The effective matrix in Eq. A20 is useful for writing the VRTE compactly. In the Monte Carlo algorithm, however, MONKI does not explicitly construct this matrix at every atmospheric event. Instead, the distance to the next atmospheric event is sampled using the total extinction coefficient $\beta = \sum_t \beta_t$, where $\beta_t = \beta_{\text{sca},t} + \beta_{\text{abs},t}$ is the total extinction coefficient of constituent type t . At the event location $\mathbf{x}$, the constituent involved in the event is selected according to the probability

$$\text{Pr}(t \mid \mathbf{x}, \lambda) = \frac{\beta_t(\mathbf{x}, \lambda)}{\beta(\mathbf{x}, \lambda)}. \quad (\text{A22})$$

The photon weight is then multiplied by the single-scattering albedo of the selected constituent,

$$a_t(\mathbf{x}, \lambda) = \frac{\beta_{\text{sca},t}(\mathbf{x}, \lambda)}{\beta_t(\mathbf{x}, \lambda)}, \quad (\text{A23})$$

860 and the scattering direction and Stokes-vector update are computed with the corresponding constituent matrix $\mathbf{F}_t$. Averaged over many photon histories, this gives

$$\beta(\mathbf{x}, \lambda) \sum_t \text{Pr}(t \mid \mathbf{x}, \lambda) a_t(\mathbf{x}, \lambda) \mathbf{F}_t(\mathbf{x}, \Theta, \lambda) = \beta(\mathbf{x}, \lambda) a(\mathbf{x}, \lambda) \mathbf{F}(\mathbf{x}, \Theta, \lambda), \quad (\text{A24})$$

where

$$a(\mathbf{x}, \lambda) = \frac{\beta_{\text{sca}}(\mathbf{x}, \lambda)}{\beta(\mathbf{x}, \lambda)} \quad (\text{A25})$$

865 is the single-scattering albedo of the local mixture. Thus, the Monte Carlo treatment of a grid cell containing several constituents reproduces the same effective scattering source term as the VRTE: the total extinction coefficient β is used for path sampling, while the single-scattering albedo and scattering matrix are those of the selected constituent at the atmospheric event. If only one atmospheric constituent is present, then $\Pr(t | \mathbf{x}, \lambda) = 1$, $a = a_t$, and $\mathbf{F} = \mathbf{F}_t$. In that case, the constituent type subscript t may be omitted.

870 A4 Prescribed optical properties

As explained above, the Mie single-scattering matrices $\mathbf{F}_c^a$ for the spherical particles in the model atmosphere are provided as input, while the Rayleigh single-scattering matrix $\mathbf{F}^m$ is determined by the depolarisation factor ρ , which depends on wavelength and atmospheric composition. Instead of computing b_{sca}^m , b_{abs}^m , b^c , and δ . This feature is particularly $b_{\text{sca},c}^a$, $b_{\text{abs},c}^a$ and ρ from the formulae above, MONKI can also use prescribed input values. This option is useful for benchmarking MONKI

875 against other radiative transfer codes.

A5 Surface

In the current version of MONKI, the ~~surface-lower boundary~~ is assumed to ~~reflect Lambertian~~. That is, ~~the be a Lambertian surface~~. The surface reflects isotropically and fully ~~depolarising, with a specified albedo~~, ~~depolarises the incident light~~. It is described by a surface albedo A_s , which may depend on wavelength.

880 Appendix B: Sampling the free photon path length

This appendix, along with Appendices C, ~~??D~~, E, and F, concerns sampling techniques for randomly selecting a continuous variable based on its probability distribution (see, e.g., Dekking et al., 2005, for an introduction to probability theory). In MONKI, we use two techniques: the inverse transform method and the acceptance-rejection method (see Chap. 3 of Kroese et al., 2011).

885 Here, we describe how the inverse transform method is used to sample the free photon path length, d , until an atmospheric event (i.e., scattering or absorption) occurs. The inverse transform method requires (1) the cumulative distribution function (CDF) of d , denoted as $P(s)^{11}$, which gives the probability that the photon interacts within distance s , (2) a random number, ξ , uniformly distributed between 0 and 1, and (3) a solution for $d = P^{-1}(\xi)$, where P^{-1} is the inverse of P .

The direct transmittance, defined as the probability of a photon travelling along a straight distance s through an optically
890 homogeneous medium with total extinction coefficient β , is given by $T_{\text{dir}} = e^{-\beta s}$. In other words, this expression represents the probability that the photon does not encounter an atmospheric event along distance s , or $\Pr(d > s)$ (see, e.g., Marshak and Davis, 2005). The probability that the photon does encounter an atmospheric event before reaching distance s therefore equals

¹¹In the appendices of this paper, P denotes the CDF corresponding to a PDF p , and is not the degree of polarisation as in Sect. 2.1.

÷

$$\Pr(d \leq s) = 1 - e^{-\beta s}. \quad (\text{B1})$$

895 By definition, Eq. B1 is $P(s)$, the CDF for the free ~~photon~~-path length, d . The corresponding probability density function (PDF) is obtained by differentiating $P(s)$ with respect to s :

$$\underline{p_d(s) = \frac{dP(s)}{ds} = \beta e^{-\beta s}, \quad s \geq 0.} \quad (\text{B2})$$

This is the exponential distribution for the distance to the next atmospheric event. To sample d using the inverse transform method, we generate a uniformly distributed random number $\xi \in (0, 1)$ and compute (see also Eq. 9 of Mayer, 2009) ÷

$$900 \quad d = P^{-1}(\xi) = \frac{-\ln(1 - \xi)}{\beta}. \quad (\text{B3})$$

Since ξ is uniformly distributed in $(0, 1)$, ~~the transformation $\ln(1 - \xi) \rightarrow \ln(\xi)$ is valid because both ξ and $1 - \xi$ have identical probability density functions over this interval. Thus $1 - \xi$ has the same probability density function as ξ . Therefore, Eq. B3 simplifies into~~ B3 can equivalently be written as (Eq. 4.39 of Marshak and Davis, 2005) ÷

$$d = \frac{-\ln \xi}{\beta}. \quad (\text{B4})$$

905 Sampling random values of d with Eq. B4 ensures that the sampled free ~~photon path length follows an exponential distribution~~path lengths follow the PDF of Eq. B2, which is consistent with the law of Lambert-Beer for radiative attenuation.

In the finite computational domain, the sampled distance d is compared with the distance to the next grid-cell or domain boundary along the photon direction. If that boundary is reached before the sampled atmospheric event, the photon is moved to the boundary and the remaining optical path is continued in the next grid cell, or the photon leaves the atmosphere or reaches
910 the surface if the domain boundary is TOA or BOA, respectively.

Appendix C: Sampling the surface reflection direction

In this ~~Appendix~~appendix, we show how to sample the ~~direction (μ, φ)~~ propagation direction ω , or equivalently (μ, φ) , of a photon after it has been reflected by the Lambertian surface, that is, an isotropically and fully depolarising surface. ~~Similarly as in App.~~ As in Appendix B, we use the inverse transform method for this.

915 Suppose $\mathbf{I}$ is the radiance Stokes vector that has been reflected by a flat surface that reflects Lambertian. Consequently, only the first element of $\mathbf{I}$, I , is non-zero, and I will be independent of μ and φ . The reflected irradiance, or net flux, that emerges from the Lambertian surface then equals (see, e.g., Liou, 2002):

$$E = \int_0^{2\pi} \int_0^1 I \mu d\mu d\varphi = \pi I. \quad (\text{C1})$$

Dividing both sides by πI gives

$$920 \quad \int_0^{2\pi} \int_0^1 p(\mu, \varphi) d\mu d\varphi = 1, \quad (C2)$$

with

$$p(\mu, \varphi) = \frac{1}{\pi} \mu. \quad (C3)$$

Since $p(\mu, \varphi)$ is a function whose integrals equal 1, it is by definition the joint probability ~~distribution~~-density function (PDF) of μ and φ . For Lambertian reflection, μ and φ are independent due to the symmetry in the azimuthal direction, such that
 925 $p(\mu, \varphi) = p(\mu)p(\varphi)$. Thus, the direction (μ, φ) can be sampled by sampling μ and φ individually from their marginal PDFs (see Sect. 3.2 of Kroese et al., 2011).

The marginal PDF of μ can be obtained by integrating Eq. C3 over φ :

$$p(\mu) = \int_0^{2\pi} p(\mu, \varphi) d\varphi = \int_0^{2\pi} \frac{1}{\pi} \mu d\varphi = 2\mu. \quad (C4)$$

The corresponding CDF is (see also Mayer, 2009, Eq. 18)

$$930 \quad P(\mu) = \int_0^\mu p(\mu') d\mu' = 2 \int_0^\mu \mu' d\mu' = \mu^2. \quad (C5)$$

The sampling expression for μ follows from the inverse of P (see also Mayer, 2009, Eq. 19):

$$\mu = P^{-1}(\xi_1) = \sqrt{\xi_1}, \quad (C6)$$

where ξ_1 is a generated, uniformly distributed random number between 0 and 1.

The marginal PDF of φ can be obtained by integrating Eq. C3 over μ :

$$935 \quad p(\varphi) = \int_0^1 p(\mu, \varphi) d\mu = \int_0^1 \frac{1}{\pi} \mu d\mu = \frac{1}{2\pi}. \quad (C7)$$

The corresponding CDF is:

$$P(\varphi) = \int_0^\varphi p(\varphi') d\varphi' = \int_0^\varphi \frac{1}{2\pi} d\varphi' = \frac{\varphi}{2\pi}. \quad (C8)$$

The sampling expression for φ is then:

$$\varphi = P^{-1}(\xi_2) = 2\pi\xi_2, \quad (C9)$$

940 where ξ_2 is another generated uniformly distributed random number between 0 and 1.

Appendix D: The probability distribution of the atmospheric scattering direction of polarised light

In this [Appendix](#), we derive the probability density function (PDF) of the scattering direction of light in a unit volume of atmosphere.

Let $\mathbf{I}'(\vartheta', \varphi') d\Omega'$ represent the flux vector of incident light in direction ω' at a unit volume in the atmosphere, for a given wavelength λ . Here, we omit the λ -dependence notation. The incident light may be polarised, described by the Stokes vector $\mathbf{I}' = [I', Q', U', V']^T$, where $|Q'| > 0$, $|U'| > 0$ and/or $|V'| > 0$. The radiance Stokes vector of the scattered light is then (Hovenier et al., 2004, Eqs. 4.1 and 4.3) ÷

$$\mathbf{I}(\vartheta, \varphi; \vartheta\omega', \varphi') = \frac{a}{4\pi} \mathbf{Z}(\vartheta\omega, \varphi; \vartheta\omega', \varphi') \mathbf{I}'(\vartheta\omega', \varphi') d\Omega', \quad (\text{D1})$$

whose first element, I , represents the total scattered radiance, or the energy scattered per unit solid angle, per unit wavelength interval, by the unit volume in the direction (ϑ, φ) contribution in the direction ω , for light from the specific incident direction ω' . Here, a is the single scattering albedo, and $\mathbf{Z}(\vartheta, \varphi; \vartheta\omega', \varphi') \mathbf{Z}(\omega, \omega')$ is the phase matrix, given by $\mathbf{Z} = \mathbf{L}(-\sigma_2) \mathbf{F}(\Theta) \mathbf{L}(-\sigma_1)$ $\mathbf{Z} = \mathbf{L}(-\sigma_2) \mathbf{F}(\Theta) \mathbf{L}(-\sigma_1)$ (Hovenier et al., 2004, Eq. 3.7). Matrices $\mathbf{F}$ and $\mathbf{L}$ are the single scattering matrix and the matrix for rotation of the polarisation reference plane, respectively, as in Eqs. 11 and 12. In the Monte Carlo algorithm, the quantities a , $\mathbf{F}$ and $\mathbf{Z}$ in this appendix should be read as a_t , $\mathbf{F}_t$ and $\mathbf{Z}_t$ of the selected constituent type t (here, we omit the t subscript notation).

To sample the scattering direction $(\vartheta, \varphi)\omega$, it is convenient to first consider the scattered radiance vector after the rotation over angle σ_1 only, $\mathbf{I}^\times$, defined with respect to the scattering plane (see, e.g., the notes of Whitney, 2011):

$$\mathbf{I}^\times(\cos\Theta, \sigma_1; \vartheta\omega', \varphi') = \frac{a}{4\pi} \mathbf{F}(\Theta) \mathbf{L}(-\sigma_1) \mathbf{I}'(\vartheta\omega', \varphi') d\Omega'. \quad (\text{D2})$$

Recall that in the case of Rayleigh and Mie scattering (and a few other special cases, see Hansen and Travis, 1974), the single scattering matrix elements $F_{13} = F_{14} = F_{24} = F_{23} = F_{31} = F_{32} = F_{41} = F_{42} = 0$ (see App. $F_{13} = F_{14} = F_{23} = F_{24} = F_{31} = F_{32} = F_{41}$ (see Appendix A)). Substituting those values into Eq. D2 yields the following expression for the first element of $\mathbf{I}^\times$:

$$\begin{aligned} I^\times(\cos\Theta, \sigma_1; \vartheta\omega', \varphi') = \frac{a}{4\pi} & \left[F_{11}(\Theta) I'(\vartheta\omega', \varphi') \right. \\ & \left. + F_{12}(\Theta) (Q'(\vartheta\omega', \varphi') \cos 2\sigma_1 - U'(\vartheta\omega', \varphi') \sin 2\sigma_1) \right] d\Omega'. \end{aligned} \quad (\text{D3})$$

Note that the value of $I^\times$ equals the total scattered radiance I , since the left multiplication by $\mathbf{L}(-\sigma_2)$ in Eq. D1 does not affect the first Stokes component. From inspection of Eq. D3 it is clear that I not only depends on the phase function F_{11} , but also on scattering matrix element F_{12} and on the state of polarisation of the light beam $\mathbf{I}'$ incident at the scattering volume.

Because of the conservation of energy, the total scattered radiance integrated over all scattering directions must equal the fraction a of the incident flux $\mathbf{I}' d\Omega'$ that is being scattered:

$$\int_{-\pi-1}^{\pi} \int_{-1}^1 I^\times(\cos\Theta, \sigma_1; \vartheta\omega', \varphi') d\cos\Theta d\sigma_1 = a I'(\vartheta\omega', \varphi') d\Omega'. \quad (\text{D4})$$

970 Let us now define the normalised incident Stokes vector by

$$\underline{\bar{I}}' = \frac{\underline{I}'(\omega')}{I'(\omega')} = \left[1, \frac{Q'(\omega')}{I'(\omega')}, \frac{U'(\omega')}{I'(\omega')}, \frac{V'(\omega')}{I'(\omega')} \right]^T. \quad (\text{D5})$$

Substituting Eq. D3 into Eq. ~~D4~~ yields:-

$$\frac{aI'(\vartheta', \varphi') d\Omega' \int_{-\pi}^{\pi} \int_{-1}^1 \frac{1}{4\pi} \frac{1}{I'(\vartheta', \varphi')} \left[F_{11}(\Theta) I'(\vartheta', \varphi') \right. \\ \left. + F_{12}(\Theta) (Q'(\vartheta', \varphi') \cos 2\sigma_1 - U'(\vartheta', \varphi') \sin 2\sigma_1) \right]$$

975 $d \cos \Theta d\sigma_1 = aI'(\vartheta', \varphi') d\Omega'$.

~~Dividing~~ D4 and dividing both sides by ~~$aI'(\vartheta', \varphi') d\Omega'$~~ gives $aI'(\omega') d\Omega'$ gives

$$\int_{-\pi}^{\pi} \int_{-1}^1 \frac{1}{4\pi} p(\cos \Theta, \sigma_1) d \cos \Theta d\sigma_1 = 1, \quad (\text{D6})$$

with

$$p(\cos \Theta, \sigma_1) = \frac{1}{4\pi} \frac{1}{I'(\vartheta', \varphi')} \left[F_{11}(\Theta) \underline{I'(\vartheta', \varphi')} + F_{12}(\Theta) \underline{Q'(\vartheta', \varphi')} \left(\frac{Q'(\omega')}{I'(\omega')} \cos 2\sigma_1 - \frac{U'(\vartheta', \varphi')}{I'(\omega')} \frac{U'(\omega')}{I'(\omega')} \sin 2\sigma_1 \right) \right] \\ = \frac{1}{4\pi} \left[\underline{Z(\omega, \omega')} \underline{\bar{I}'} \right]_1. \quad (\text{D7})$$

980

where $[\dots]_1$ indicates the first element of a Stokes vector. Since the integrals in Eq. D6 equal 1, $p(\cos \Theta, \sigma_1)$ is the joint PDF for the scattering direction ~~$(\cos \Theta, \sigma_1)$~~ $(\cos \Theta, \sigma_1)$ of polarised light incident on the scattering volume.¹² Given the functions for $F_{11}(\Theta)$ and $F_{12}(\Theta)$, and the values of the Stokes parameters of the incident beam $\underline{I}'$, the variables $\cos \Theta$ and σ_1 can be sampled with a sampling method using this PDF (see Apps-Appendices E and F).

985 Finally, the scattering direction ω , or equivalently its angles ϑ and φ ~~are~~ is determined from the sampled values $\cos \Theta$ and σ_1 using spherical trigonometry (see Fig. 1):

$$\vartheta = \arccos(\cos \vartheta' \cos \Theta + \sin \vartheta' \sin \Theta \cos \sigma_1), \quad (\text{D8})$$

$$\varphi = \varphi' - \arccos \left(\frac{\cos \Theta - \cos \vartheta' \cos \vartheta}{\sin \vartheta' \sin \vartheta} \frac{\cos \Theta - \cos \vartheta' \cos \vartheta}{\sin \vartheta' \sin \vartheta} \right) \cdot \underline{\text{sign}} \underline{\text{sign}}(\sigma_1), \quad (\text{D9})$$

where the multiplication by the sign of σ_1 is needed for the correct rotation direction of φ .

¹²If the incident light is unpolarised, Eq. ~~??~~ D7 simplifies to the well-known result ~~$p(\cos \Theta, \varphi) = F_{11}(\Theta)/(4\pi)$~~ $p(\cos \Theta, \sigma_1) = F_{11}(\Theta)/(4\pi)$ (see, e.g., Hansen and Travis, 1974).

990 Similarly, we can derive a PDF for the scattering direction in the *backward* Monte Carlo mode. Following the convention introduced in Sect. 2.4, ω' and ω denote the incident and scattered propagation directions in the associated forward trajectory, while $-\omega$ and $-\omega'$ are the corresponding detector-side and source-side directions along the backward trajectory. In contrast to the forward case, the quantity propagated along the trajectory is not a physical Stokes vector of incident radiation, but a normalised 4×4 response matrix $\overline{\mathbf{M}}$, which describes the cumulative polarisation-dependent detector response between
 995 the current scattering event and the detector (see Appendix G8 for a more detailed explanation). Accordingly, the backward analogue of Eq. D1 is

$$\mathcal{I}^{\text{bw}}(\omega; \omega') = \frac{a}{4\pi} \overline{\mathbf{M}} \mathbf{Z}(\omega, \omega') \mathbf{1} d\Omega', \quad (\text{D10})$$

where $\mathbf{1} = [1, 0, 0, 0]^T$. Here, $\mathcal{I}^{\text{bw}}$ is not a physical radiance Stokes vector, but a dimensionless quantity describing how radiation scattered at the current event would contribute to the detector signal along the corresponding forward trajectory.
 1000 In backward mode, $\mathbf{Z}(\omega, \omega')$ is obtained from the phase matrix in the reversed geometry through the reciprocity relation in Eq. 16. Using the same reasoning as in the forward case, we find the following expression for the joint PDF of the backward scattering direction:

$$\begin{aligned} p^{\text{bw}}(\cos \Theta, \sigma_2) &= \frac{1}{4\pi} [F_{11}(\Theta) + \overline{M}_{12} F_{12}(\Theta) \cos 2\sigma_2 + \overline{M}_{13} F_{12}(\Theta) \sin 2\sigma_2] \\ &= \frac{1}{4\pi} [\overline{\mathbf{M}} \mathbf{Z}(\omega, \omega') \mathbf{1}]_1, \end{aligned} \quad (\text{D11})$$

1005 where $\overline{M}_{12}$ and $\overline{M}_{13}$ are the (1,2) and (1,3) elements of $\overline{\mathbf{M}}$. Compared to the forward expression, the sign in front of the $\overline{M}_{13}$ term is positive, and rotation angle σ_2 is used instead of σ_1 .

Finally, once $\cos \Theta$ and σ_2 have been sampled, the source-side direction in the reversed geometry, $(\pi - \vartheta', \varphi' + \pi)$, is obtained from the known detector-side reversed direction $(\pi - \vartheta, \varphi + \pi)$ through

$$\pi - \vartheta' = \arccos(\cos(\pi - \vartheta) \cos \Theta + \sin(\pi - \vartheta) \sin \Theta \cos \sigma_2), \quad (\text{D12})$$

$$1010 \quad \varphi' + \pi = \varphi + \pi - \arccos\left(\frac{\cos \Theta - \cos(\pi - \vartheta) \cos(\pi - \vartheta')}{\sin(\pi - \vartheta) \sin(\pi - \vartheta')}\right) \cdot \text{sign}(\sigma_2), \quad (\text{D13})$$

These are the backward analogues of Eqs. D8 and D9, written for the reversed scattering geometry. In practice, this formulation allows the same direction-reconstruction routine to be used as in the forward mode: the reversed detector-side direction $(\pi - \vartheta, \varphi + \pi)$ is used as the incident direction, the reversed source-side direction $(\pi - \vartheta', \varphi' + \pi)$ is reconstructed as the scattered direction, and σ_2 is used as the corresponding rotation angle in place of σ_1 .

1015 Appendix E: Sampling the Rayleigh scattering direction

In this ~~Appendix~~ ~~appendix~~, we describe how to sample the photon ~~direction~~ ~~(ϑ, φ)~~ propagation direction ω , or equivalently (ϑ, φ) , after Rayleigh scattering of polarised light. Because ~~finding the CDF, and its inverse, corresponding to the CDF~~

1020 corresponding to the PDF $p(\cos \Theta, \sigma_1)$ of the scattering direction (Eq. ??) is not straightforward D7), and its inverse are not readily available, we do not use the inverse transform method. Instead, we use the acceptance-rejection method (see Sect. 3.1.5 of Kroese et al., 2011).

The acceptance-rejection method requires the determination of an envelope function $f(\cos \Theta, \sigma_1) = Cg(\cos \Theta, \sigma_1)$ for some constant $C \geq 1$, such that $f(\cos \Theta, \sigma_1) \geq p(\cos \Theta, \sigma_1)$ for all $\cos \Theta$. $f(\cos \Theta, \sigma_1) = Cg(\cos \Theta, \sigma_1)$, with $C \geq 1$, such that

$$f(\cos \Theta, \sigma_1) \geq p(\cos \Theta, \sigma_1) \quad (\text{E1})$$

1025 for all $\cos \Theta$ and σ_1 . The function $g(\cos \Theta, \sigma_1)$ Here, $g(\cos \Theta, \sigma_1)$ is called the proposal PDF. Then, the acceptance-rejection method is executed in three steps. The method proceeds as follows: (1) randomly sample $\cos \Theta$ and σ_1 from $g(\cos \Theta, \sigma_1)$ sample a candidate pair $(\cos \Theta, \sigma_1)$ from $g(\cos \Theta, \sigma_1)$ using uniformly distributed random numbers $\xi_1, \xi_2 \in (0, 1)$, (2) generate a another uniformly distributed random variable ξ between 0 and 1 number $\xi_3 \in (0, 1)$, and (3) accept the values of $\cos \Theta$ candidate if

$$\xi_3 \cdot f(\cos \Theta, \sigma_1) \leq p(\cos \Theta, \sigma_1); \quad (\text{E2})$$

otherwise, reject it and σ_1 if $\xi f(\cos \Theta, \sigma_1) \leq p(\cos \Theta, \sigma_1)$, otherwise reject and return to step (1).

1030 For Rayleigh scattering, we construct an envelope function by recognizing that $p(\cos \Theta, \sigma_1)$ (Eq. ??) is largest at $\Theta = 0^\circ$, where $F_{12}^m = 0$ (Eq. A7). For simplicity, we set the envelope function equal to this maximum value. To show that this choice is valid, define

$$X = \frac{Q'}{I'} \cos 2\sigma_1 - \frac{U'}{I'} \sin 2\sigma_1. \quad (\text{E3})$$

Because the incident Stokes vector is physically admissible, its degree of polarisation,

$$1035 \quad P' = \frac{\sqrt{Q'^2 + U'^2 + V'^2}}{I'}, \quad (\text{E4})$$

satisfies $P' \leq 1$. Therefore,

$$\left(\frac{Q'}{I'}\right)^2 + \left(\frac{U'}{I'}\right)^2 \leq 1. \quad (\text{E5})$$

Using the Cauchy-Schwarz inequality, it then follows that

$$\begin{aligned} 1040 \quad |X| &= \left| \frac{Q'}{I'} \cos 2\sigma_1 - \frac{U'}{I'} \sin 2\sigma_1 \right| \\ &\leq \sqrt{\left(\frac{Q'}{I'}\right)^2 + \left(\frac{U'}{I'}\right)^2} \sqrt{\cos^2 2\sigma_1 + \sin^2 2\sigma_1} \\ &\leq 1. \end{aligned} \quad (\text{E6})$$

Hence,

$$-1 \leq X \leq 1 \quad \text{for all } \sigma_1. \quad (\text{E7})$$

For Rayleigh scattering (Appendix A),

$$1045 \quad F_{11}^{\text{m}}(\Theta) = \frac{3}{4}\Delta(1 + \cos^2 \Theta) + 1 - \Delta, \quad F_{12}^{\text{m}}(\Theta) = -\frac{3}{4}\Delta \sin^2 \Theta, \quad (\text{E8})$$

so that

$$F_{12}^{\text{m}}(\Theta) \leq 0 \quad \text{for all } \Theta. \quad (\text{E9})$$

Using Eq. D7, the PDF for the scattering direction becomes

$$p(\cos \Theta, \sigma_1) = \frac{1}{4\pi} [F_{11}^{\text{m}}(\Theta) + F_{12}^{\text{m}}(\Theta) X]. \quad (\text{E10})$$

1050 Because $F_{12}^{\text{m}}(\Theta) \leq 0$ and $X \geq -1$, we obtain

$$p(\cos \Theta, \sigma_1) \leq \frac{1}{4\pi} [F_{11}^{\text{m}}(\Theta) - F_{12}^{\text{m}}(\Theta)]. \quad (\text{E11})$$

Substituting the Rayleigh expressions yields

$$\begin{aligned} F_{11}^{\text{m}}(\Theta) - F_{12}^{\text{m}}(\Theta) &= \frac{3}{4}\Delta(1 + \cos^2 \Theta) + 1 - \Delta + \frac{3}{4}\Delta \sin^2 \Theta \\ &= 1 - \Delta + \frac{3}{4}\Delta (1 + \cos^2 \Theta + \sin^2 \Theta) \\ 1055 \quad &= 1 - \Delta + \frac{3}{2}\Delta \\ &= F_{11}^{\text{m}}(0^\circ). \end{aligned} \quad (\text{E12})$$

Combining Eqs. E11 and E12, we find

$$p(\cos \Theta, \sigma_1) \leq \frac{F_{11}^{\text{m}}(0^\circ)}{4\pi} \quad \text{for all } \Theta \text{ and } \sigma_1. \quad (\text{E13})$$

We may therefore choose the constant envelope function

$$1060 \quad f(\cos \Theta, \sigma_1) = \frac{F_{11}^{\text{m}}(0^\circ)}{4\pi} \frac{F_{11}^{\text{m}}(0^\circ)}{4\pi} = \frac{1}{4\pi} \left(\frac{3}{2}\Delta(\lambda) + 1 - \Delta(\lambda) \right). \quad (\text{E14})$$

~~Since f is constant in $\cos \Theta$~~

Since $f(\cos \Theta, \sigma_1)$ is constant on the domain $(\cos \Theta, \sigma_1) \in [-1, 1] \times [-\pi, \pi]$, the normalising constant needed to make g a valid PDF, i.e. such that its double integral over the domain equals 1, is

$$C = \int_{-\pi}^{\pi} \int_{-1}^1 f(\cos \Theta, \sigma_1) d\cos \Theta d\sigma_1 = F_{11}^{\text{m}}(0^\circ), \quad (\text{E15})$$

1065 and the proposal PDF becomes

$$\underline{g(\cos \Theta, \sigma_1) = \frac{f(\cos \Theta, \sigma_1)}{C} = \frac{1}{4\pi}.} \quad (\text{E16})$$

Thus, candidate values can be sampled independently from g as

$$\underline{\cos \Theta = 2\xi_1 - 1, \quad \sigma_1 = \pi(2\xi_2 - 1),} \quad (\text{E17})$$

~~with ξ_1 and σ_1 , the proposal PDF $g = f/C$ is constant and thus follows a uniform distribution in the $\cos \Theta, \sigma_1$ -domain.~~

1070 ~~Therefore, we can sample $\cos \Theta$ and σ_1 independently by generating uniformly distributed random values in the domains $(-1, 1)$ and $(-\pi, \pi)$, respectively. Then ξ_2 independent random numbers uniformly distributed on $(0, 1)$.~~

Next, we generate ξ , another uniformly distributed random number $\xi_3 \in (0, 1)$ and compute $p(\cos \Theta, \sigma_1)$ from the sampled $\cos \Theta$; and σ_1 , $F_{11}^m(\Theta)$, $F_{12}^m(\Theta)$ and I' (Eq ??), thus fully preserving the history of the photon's polarisation state. If $\xi f(\cos \Theta, \sigma_1) \leq p(\cos \Theta, \sigma_1)$ the Rayleigh matrix elements $F_{11}^m(\Theta)$ and σ_1 are accepted. Otherwise, $\cos \Theta$, $F_{12}^m(\Theta)$, and σ_1 are rejected, and the steps

1075 ~~listed above are the incident Stokes vector I' using Eq. D7. The candidate pair $(\cos \Theta, \sigma_1)$ is accepted if~~

$$\underline{\xi_3 \cdot f(\cos \Theta, \sigma_1) \leq p(\cos \Theta, \sigma_1);} \quad (\text{E18})$$

otherwise, it is rejected and the procedure above is repeated. Finally, with the accepted values for once $\cos \Theta$ and σ_1 have been accepted, the angles ϑ and φ are computed with spherical trigonometry (Eqs. using Eqs. D8 and D9).

1080 The same acceptance-rejection scheme can also be used in the backward Monte Carlo mode to sample $-\omega'$. Using Eq. D11, define

$$\underline{Y = \overline{M}_{12} \cos 2\sigma_2 + \overline{M}_{13} \sin 2\sigma_2.} \quad (\text{E19})$$

The normalised detector-response matrix $\overline{M}$ plays the same role in backward sampling as a normalised Stokes vector in forward sampling, so its first-row linear-polarisation components obey $\overline{M}_{12}^2 + \overline{M}_{13}^2 \leq 1$. Therefore $|Y| \leq 1$ by the Cauchy-Schwarz inequality. Hence, for Rayleigh scattering,

$$1085 \quad \underline{p^{\text{bw}}(\cos \Theta, \sigma_2) = \frac{1}{4\pi} [F_{11}^m(\Theta) + F_{12}^m(\Theta) Y] \leq \frac{1}{4\pi} [F_{11}^m(\Theta) - F_{12}^m(\Theta)] = \frac{F_{11}^m(0^\circ)}{4\pi}.} \quad (\text{E20})$$

Therefore, the same constant envelope function and proposal PDF as in the forward case can be used in backward mode as well. The only differences are that $p(\cos \Theta, \sigma_1)$ is replaced by $p^{\text{bw}}(\cos \Theta, \sigma_2)$ and that the sampled direction is reconstructed using the backward geometry from Appendix D.

Appendix F: Sampling the Mie scattering direction

1090 In this ~~Appendix~~ appendix, we describe how to sample the photon ~~direction (ϑ, φ)~~ propagation direction ω , or equivalently (ϑ, φ) , after Mie scattering of polarised light ~~. Similarly as in App. by a specific spherical aerosol type c (in this appendix, we omit the c subscript notation).~~ As in Appendix E, we use the acceptance-rejection method.

For Mie scattering, it is generally inefficient to use a constant ~~value-for-the-envelope-function~~ f . That ~~envelope function~~. This is because Mie scattering phase functions are often strongly peaked in the forward scattering ~~directions~~ direction (see Fig. 11),
 1095 ~~resulting-which would result~~ in a low acceptance rate for the generated scattering angles. Instead, we construct ~~the following~~ envelope function, for which it can be shown that it satisfies $f \geq p$ for all $\cos \Theta$ and σ_1 :

$$\underline{f(\cos \Theta, \sigma_1) = \frac{1}{4\pi} \left(F_{11}^c(\Theta) + |F_{12}^c(\Theta)|\sqrt{2} \right)}.$$

an envelope function that follows the Θ -dependence of the scattering direction PDF $p(\cos \Theta, \sigma_1)$ more closely.

Using Eq. D7, define

$$1100 \quad \underline{X = \frac{Q'}{I'} \cos 2\sigma_1 - \frac{U'}{I'} \sin 2\sigma_1.} \quad (F1)$$

~~Note that here~~ As shown in Appendix E, the physical admissibility of the incident Stokes vector implies that

$$\underline{|X| \leq 1.} \quad (F2)$$

The PDF for the scattering direction can therefore be written as

$$\underline{p(\cos \Theta, \sigma_1) = \frac{1}{4\pi} [F_{11}^a(\Theta) + F_{12}^a(\Theta) X],} \quad (F3)$$

1105 which satisfies

$$\begin{aligned} \underline{p(\cos \Theta, \sigma_1)} &\leq \underline{\frac{1}{4\pi} [F_{11}^a(\Theta) + |F_{12}^a(\Theta)| |X|]} \\ &\leq \underline{\frac{1}{4\pi} [F_{11}^a(\Theta) + |F_{12}^a(\Theta)|]}. \end{aligned} \quad (F4)$$

We may therefore choose the envelope function

$$\underline{f(\cos \Theta, \sigma_1) = \frac{1}{4\pi} [F_{11}^a(\Theta) + |F_{12}^a(\Theta)|].} \quad (F5)$$

1110 Note that f is not constant, but depends on Θ . ~~In fact, f follows the PDF p (Eq. ??), which strongly varies with only.~~
Compared to a constant envelope, this choice follows the Θ , closely. ~~This ensures a high acceptance rate of the generated scattering angles-dependence of $p(\cos \Theta, \sigma_1)$ more closely and thereby improves the acceptance rate.~~

The proposal PDF g ~~can be~~ is obtained from f ~~as follows:-~~

$$\begin{aligned} \underline{g(\cos \Theta, \sigma_1)} &= \underline{\frac{1}{C} f(\cos \Theta, \sigma_1)} \\ 1115 \quad &= \underline{\frac{1}{4\pi C} \left(F_{11}^c(\Theta) + |F_{12}^c(\Theta)|\sqrt{2} \right)}, \end{aligned}$$

through

$$g(\cos \Theta, \sigma_1) = \frac{1}{C} f(\cos \Theta, \sigma_1) = \frac{1}{4\pi C} [F_{11}^a(\Theta) + |F_{12}^a(\Theta)|], \quad (\text{F6})$$

where the ~~normalizing~~ normalising constant C ~~, which makes g a valid PDF whose integrals equal 1,~~ is given by $\div$

$$\begin{aligned} C &= \int_{-\pi}^{\pi} \int_{-1}^1 f(\cos \Theta, \sigma_1) d\cos \Theta d\sigma_1 \\ 1120 \quad &= \frac{1}{2} \int_{-1}^1 \left[F_{11}^c{}^a(\Theta) + \left| F_{12}^c{}^a(\Theta) \sqrt{2} \right| \right] d\cos \Theta. \end{aligned} \quad (\text{F7})$$

~~Quantities $\cos \Theta$~~

Quantities $\cos \Theta$ and σ_1 must be sampled from $g(\cos \Theta, \sigma_1)$. Equivalently, they can be sampled from the marginal PDF $g(\cos \Theta)$ and the conditional PDF ~~$g(\sigma_1 | \cos \Theta)$~~ $g(\sigma_1 | \cos \Theta)$ of σ_1 given $\cos \Theta$ (Kroese et al., 2011, Sect. 3.2). ~~We apply~~ (Kroese et al., 2011, Sect. 3.2). As in Appendix B, we use the inverse transform method for ~~that, which requires determining~~ the CDFs corresponding to these PDFs (see App. B). this.

The marginal PDF ~~$g(\cos \Theta)$~~ can be obtained by integration of $\cos \Theta$ is obtained by integrating over σ_1 :

$$\begin{aligned} g(\cos \Theta) &= \int_{-\pi}^{\pi} g(\cos \Theta, \sigma_1) d\sigma_1 \\ &= \frac{1}{2C} \left[F_{11}^c{}^a(\Theta) + \left| F_{12}^c{}^a(\Theta) \sqrt{2} \right| \right]. \end{aligned} \quad (\text{F8})$$

~~and the conditional PDF $g(\sigma_1 | \cos \Theta)$ is obtained with~~ The conditional PDF of σ_1 given $\cos \Theta$ then follows from the product rule (see, e.g., Rice, 2007, Sect. 3.5.2):

$$g(\sigma_1 | \cos \Theta) = \frac{g(\cos \Theta, \sigma_1)}{g(\cos \Theta)} = \frac{1}{2\pi}. \quad (\text{F9})$$

~~It may be noted that, indeed, $g(\sigma_1 | \cos \Theta)$ does not depend on $\cos \Theta$, such that $g(\sigma_1 | \cos \Theta) = g(\sigma_1)$ with $g(\sigma_1)$ the marginal PDF of σ . That is,~~ Thus, under the proposal PDF g , the variables $\cos \Theta$ and σ_1 are independent in the probability distribution g , and σ_1 is uniformly distributed on $[-\pi, \pi]$.

1135 The CDF corresponding to $g(\cos \Theta)$ is $\div$

$$\begin{aligned} G(\cos \Theta) &= \int_{-1}^{\cos \Theta} g(\cos \Theta') d\cos \Theta' \\ &= \frac{1}{2C} \int_{-1}^{\cos \Theta} \left[F_{11}^c{}^a(\Theta') + \left| F_{12}^c{}^a(\Theta') \sqrt{2} \right| \right] d\cos \Theta'. \end{aligned} \quad (\text{F10})$$

In order to evaluate Eq. F10, we precompute the expression for normalising constant C and generate a lookup table (LUT) for $G(\cos \Theta)$ at on a fine $\cos \Theta$ -grid, using the available data for $F_{11}^c(\Theta)$ and $F_{12}^c(\Theta)$ as computed using values of $F_{11}^a(\Theta)$ and $F_{12}^a(\Theta)$ computed with Mie theory. According to the inverse transform method, the sampling expression for $\cos \Theta$ is ÷

$$\cos \Theta = G^{-1}(\xi_1), \quad (\text{F11})$$

with G^{-1} the inverse of G ,and and where ξ_1 is a uniformly distributed random number between 0 and 1. The value on (0,1). In practice, the value of $\cos \Theta$ in Eq. F11 that corresponds corresponding to ξ_1 can be retrieved directly is retrieved from the LUT using linear interpolation of the G values between 0 and 1. by linear interpolation.

The CDF corresponding to $g(\sigma_1)$ is

$$\begin{aligned} G(\sigma_1) &= \int_{-\pi}^{\sigma_1} g(\sigma'_1) d\sigma'_1 \\ &= \int_{-\pi}^{\sigma_1} \frac{1}{2\pi} d\sigma'_1 = \frac{\sigma_1 + \pi}{2\pi}. \end{aligned} \quad (\text{F12})$$

Hence, the sampling expression for σ_1 is ÷

$$\sigma_1 = G^{-1}(\xi_2) = 2\pi\xi_2 - \pi, \quad (\text{F13})$$

where also ξ_2 is a another uniformly distributed random number between 0 and 1. on (0,1).

Finally Next, we compute $p(\cos \Theta, \sigma_1)$ from the sampled $\cos \Theta$, σ_1 and the Stokes vector of the incident beam, the Mie matrix elements $F_{11}^a(\Theta)$ and $F_{12}^a(\Theta)$, and the incident Stokes vector I' (Eq.??), and generate the using Eq. D7. We then generate a third uniformly distributed random variable $\xi \in (0, 1)$. If $\xi f(\cos \Theta, \sigma_1) \leq p(\cos \Theta, \sigma_1)$, the quantities $\cos \Theta$ and σ_1 are accepted ÷ otherwise, they are number $\xi_3 \in (0, 1)$. The candidate pair $(\cos \Theta, \sigma_1)$ is accepted if

$$\xi_3 \cdot f(\cos \Theta, \sigma_1) \leq p(\cos \Theta, \sigma_1); \quad (\text{F14})$$

otherwise, it is rejected and the above steps are repeated. With the accepted values for Finally, once $\cos \Theta$ and σ_1 ,have been accepted, the angles ϑ and φ are computed using spherical trigonometry (Eqs. with spherical trigonometry using Eqs. D8 and D9).

Appendix G: Validation of the TOA reflectance formula

In this Appendix, we explain the role of π and μ in The same acceptance-rejection scheme can also be used in the backward Monte Carlo mode to sample $-\omega'$. In that case, Eq. D7 is replaced by the backward PDF $p^{\text{bw}}(\cos \Theta, \sigma_2)$ from Eq. D11. Since, analogously to Appendix E, the reflectance estimation formula (Eq.??). This formula follows from the local estimation method (Marchuk et al., 1980), which we use in Sect. 2.3. A mathematical explanation of this method, for unpolarised light and all orders of scattering, is available in factor multiplying $F_{12}^a(\Theta)$ in p^{bw} has absolute value not exceeding 1, the same envelope

1165 function of Eq. F5 also bounds the backward PDF. Therefore, the same proposal PDF, normalising constant C , and lookup table for $G(\cos \Theta)$ can be used in backward mode as well. The only differences are that p is replaced by p^{bw} and the sampled direction is reconstructed using the backward geometry from Appendix D.

Appendix G: Derivation of forward and backward Monte Carlo estimators for polarised radiative transfer

1170 For readers who wish to understand the theoretical basis of our Monte Carlo code using the local estimation method including polarisation of light, we here provide a complete derivation of the radiance Stokes-vector equations in forward and backward Monte Carlo modes, including polarisation-dependent sampling of the scattering direction. We note that related Monte Carlo derivations were presented by Marshak and Davis (2005) and Deutschmann et al. (2011), ~~although the~~ for the scalar case, and by Marchuk et al. (1980), Deutschmann (2015), and Wang et al. (2019) for the polarised case. However, these derivations are spread over multiple chapters ~~and use different notations,~~ or papers, sometimes omit intermediate derivation steps, and do not
1175 always make the consistency of the physical units explicit. In addition, the polarised derivations are generally formulated by extending scalar Monte Carlo expressions to Stokes-vector quantities, and they do not include polarisation-dependent sampling of the scattering direction.

~~For simplicity, consider a horizontally homogeneous, single-layer atmosphere that is illuminated at TOA by a beam of unpolarised light in-~~ To our knowledge, the derivation presented here is the first to start directly from the vector radiative transfer equation (VRTE) for polarised light and to proceed explicitly to the final forward and backward local-estimation formulae, while consistently incorporating polarisation-dependent sampling of the scattering directions. Readers interested only in the practical Monte Carlo method, including polarisation-dependent sampling of the scattering direction, may start with Appendix G7.

G1 Vector radiative transfer equation (VRTE)

1185 Let us consider a light beam with wavelength λ , described by the radiance Stokes vector $\mathbf{I} = [I, Q, U, V]^T$ in $\text{W m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$, propagating through a three-dimensional medium occupying a volume $\mathcal{V}$. We assume the system is in steady state, meaning that neither the radiation field nor the optical properties of the medium vary with time. Let $\mathbf{x} = [x, y, z]^T$ denote position and $\boldsymbol{\omega} = [\sin \vartheta \cos \varphi, \sin \vartheta \sin \varphi, \cos \vartheta]^T$ a propagation direction, with local zenith angle ϑ and azimuth angle φ . Then, the rate of change of $\mathbf{I}$ at $\mathbf{x}$ in the direction of $\boldsymbol{\omega}$ is described by the ~~direction (μ_0, φ_0) . The reflected radiance at TOA in the direction (μ, φ) is $I(\mu, \mu_0, \varphi - \varphi_0)$. The albedo at TOA, A , is the ratio of the outgoing irradiance over the incoming irradiance and~~ steady-state, monochromatic vector radiative transfer equation (VRTE) (Marchuk et al., 1980):

$$\boldsymbol{\omega} \cdot \nabla \mathbf{I}(\mathbf{x}, \boldsymbol{\omega}, \lambda) = -\beta(\mathbf{x}, \lambda) \mathbf{I}(\mathbf{x}, \boldsymbol{\omega}, \lambda) + \frac{\beta_{\text{sca}}(\mathbf{x}, \lambda)}{4\pi} \int_{4\pi} \mathbf{Z}(\mathbf{x}, \boldsymbol{\omega}, \boldsymbol{\omega}', \lambda) \mathbf{I}(\mathbf{x}, \boldsymbol{\omega}', \lambda) d\Omega' + \mathbf{S}_0(\mathbf{x}, \boldsymbol{\omega}, \lambda). \quad (\text{G1})$$

Here, $\nabla = [\partial/\partial x, \partial/\partial y, \partial/\partial z]^T$, $\beta = \beta_{\text{abs}} + \beta_{\text{sca}}$ is the total extinction coefficient, and β_{sca} is the total scattering coefficient, both in m^{-1} . Matrix $\mathbf{Z}$ is dimensionless and describes how light from incident directions $\boldsymbol{\omega}'$ is scattered into the beam along

1195 ω . The factor $1/(4\pi)$ originates from the normalisation of the phase matrix. We neglect inelastic scattering processes, such as Raman scattering, for which λ changes upon scattering.

The phase matrix is written as

$$\mathbf{Z}(\mathbf{x}, \omega, \omega', \lambda) = \mathbf{L}(-\sigma_2) \mathbf{F}(\mathbf{x}, \Theta, \lambda) \mathbf{L}(-\sigma_1), \quad (\text{G2})$$

1200 where $\Theta = \arccos(\omega \cdot \omega')$ is the scattering angle, and $\mathbf{L}$ is the rotation matrix that transforms the Stokes vector's reference plane between the local meridian planes of the incident and scattered light (Eq. 12) via the rotation angles σ_1 and σ_2 (Fig. 1). The single-scattering matrix $\mathbf{F}$ is the effective single-scattering matrix of the local atmospheric mixture. It is equal to the single-scattering matrix of the scattering constituent if only one constituent is present, and to the scattering-coefficient-weighted mixture matrix if several constituents are present. In the Monte Carlo implementation, this effective matrix need not be constructed explicitly at each atmospheric event, because the scattering constituent is sampled first, as described in Appendix A.

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The first term on the right-hand side of the VRTE describes attenuation by extinction, that is, by absorption and scattering out of the beam. The second term accounts for radiation scattered into the beam, using the phase matrix constructed from the effective single-scattering matrix of the local mixture. The final term, S_0 , is the source density in $\text{W m}^{-3} \text{ sr}^{-1} \text{ nm}^{-1}$ due to emission sources. In the current version of MONKI, thermal emission by the atmosphere and surface is neglected, so the Sun is the only emission source.

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G2 Formal solution of the VRTE

To obtain a formal expression for the radiance Stokes vector $\mathbf{I}(\mathbf{x}, \omega, \lambda)$, we start from the VRTE (Eq. G1) written as:

$$(\omega \cdot \nabla + \beta(\mathbf{x}, \lambda)) \mathbf{I}(\mathbf{x}, \omega, \lambda) = \frac{\beta_{\text{sca}}(\mathbf{x}, \lambda)}{4\pi} \int_{4\pi} \mathbf{Z}(\mathbf{x}, \omega, \omega', \lambda) \mathbf{I}(\mathbf{x}, \omega', \lambda) d\Omega' + S_0(\mathbf{x}, \omega, \lambda), \quad (\text{G3})$$

Rearranging Eq. G3 yields:

$$\mathcal{L} \mathbf{I}(\mathbf{x}, \omega, \lambda) = \frac{1}{4\pi} \frac{\beta_{\text{sca}}(\mathbf{x}, \lambda)}{\beta(\mathbf{x}, \lambda)} \int_{4\pi} \mathbf{Z}(\mathbf{x}, \omega, \omega', \lambda) \mathbf{I}(\mathbf{x}, \omega', \lambda) d\Omega' + \frac{S_0(\mathbf{x}, \omega, \lambda)}{\beta(\mathbf{x}, \lambda)}, \quad (\text{G4})$$

where $\mathcal{L}$ is a linear differential operator,

$$\mathcal{L} := 1 + \frac{1}{\beta(\mathbf{x}, \lambda)} \omega \cdot \nabla. \quad (\text{G5})$$

Using this operator in the method of Green's functions, we obtain the following formal solution for the radiance Stokes vector at wavelength λ and position $\mathbf{x}$ in direction $\boldsymbol{\omega}$ (see Appendix H for the derivation):

$$\begin{aligned} \mathbf{I}(\mathbf{x}, \boldsymbol{\omega}, \lambda) = & \int_{\mathcal{V}} \beta(\mathbf{x}^*, \lambda) \exp \left[- \int_0^{\|\mathbf{x} - \mathbf{x}^*\|} \beta(\mathbf{x}^* + s' \boldsymbol{\omega}, \lambda) ds' \right] \\ & \times \mathbf{q}(\mathbf{x}^*, \boldsymbol{\omega}, \lambda) \delta \left(\boldsymbol{\omega} - \frac{\mathbf{x} - \mathbf{x}^*}{\|\mathbf{x} - \mathbf{x}^*\|} \right) \frac{1}{\|\mathbf{x} - \mathbf{x}^*\|^2} d^3 \mathbf{x}^*, \end{aligned} \quad (\text{G6})$$

where the integration extends over the spatial domain $\mathcal{V}$ of the medium. Here, $\mathbf{x}^*$ denotes the position of a local radiation source within the medium, i.e., a point at which radiation is scattered into the beam or where direct solar illumination is represented through the source term. The Dirac delta function ensures that only source points $\mathbf{x}^*$ located upstream of $\mathbf{x}$ along the direction $-\boldsymbol{\omega}$ contribute, and the exponential factor accounts for extinction between $\mathbf{x}^*$ and $\mathbf{x}$. The factor $\|\mathbf{x} - \mathbf{x}^*\|^{-2}$ arises from the Jacobian that converts the line integral in the $-\boldsymbol{\omega}$ -direction to a volume integral (see Eq. H30). Finally, the local source term in Eq. G6 is obtained directly from the right-hand side of Eq. G4:

$$\mathbf{q}(\mathbf{x}, \boldsymbol{\omega}, \lambda) = \frac{1}{4\pi} \frac{\beta_{\text{sca}}(\mathbf{x}, \lambda)}{\beta(\mathbf{x}, \lambda)} \int_{4\pi} \mathbf{Z}(\mathbf{x}, \boldsymbol{\omega}, \boldsymbol{\omega}', \lambda) \mathbf{I}(\mathbf{x}, \boldsymbol{\omega}', \lambda) d\Omega' + \frac{\mathbf{S}_0(\mathbf{x}, \boldsymbol{\omega}, \lambda)}{\beta(\mathbf{x}, \lambda)}. \quad (\text{G7})$$

Equations G6-G7 show that the radiance Stokes vector at point $\mathbf{x}$ in direction $\boldsymbol{\omega}$ is the superposition of contributions from all source points $\mathbf{x}^*$ within the medium lying upstream of $\mathbf{x}$, i.e. along the direction $-\boldsymbol{\omega}$ as seen from $\mathbf{x}$, each weighted by the local source term $\mathbf{q}$ and exponentially attenuated along the optical path between $\mathbf{x}^*$ and $\mathbf{x}$.

G3 Collision density

The collision density, $\mathbf{f}(\mathbf{x}, \boldsymbol{\omega})$ in $\text{W m}^{-3} \text{ sr}^{-1} \text{ nm}^{-1}$, is defined as the product of the extinction coefficient β and the Stokes vector $\mathbf{I}$. It quantifies the rate at which radiant energy interacts with the medium at position $\mathbf{x}$ in direction $\boldsymbol{\omega}$ due to extinction processes. Because polarisation is included, the collision density is itself a Stokes vector. For brevity, the wavelength dependence λ is omitted in the following expressions, but all quantities remain wavelength dependent. Substituting Eq. G7 into Eq. G6, replacing $\beta_{\text{sca}}(\mathbf{x}^*)/\beta(\mathbf{x}^*)$ by the single scattering albedo $a(\mathbf{x}^*)$, and after some rearrangement, the collision density can be expressed in terms of the total TOA reflectance R_{TT} as (Hovenier et al., 2004, Eq. 4.52):

$$A = \frac{1}{\pi} \int_0^{2\pi} \int_0^1 R_{11}(\mu, \mu_0, \varphi - \varphi_0) \mu d\mu d\varphi.$$

1240 as the sum of contributions from radiation scattered into the beam (first term) and from the emitting source (second term):

$$\underline{f(x, \omega)} := \beta(x) \underline{I(x, \omega)} \quad (\text{G8})$$

$$\begin{aligned} &= \int_V \int_{4\pi} \beta(x) \beta(x^*) \frac{a(x^*)}{4\pi} \underline{Z(x^*, \omega, \omega')} \\ &\quad \times \underline{I(x^*, \omega')} \exp \left[- \int_0^{\|x-x^*\|} \beta(x^* + s'\omega) ds' \right] \delta \left(\omega - \frac{x-x^*}{\|x-x^*\|} \right) \frac{d\Omega' d^3x^*}{\|x-x^*\|^2} \\ &\quad + \int_V \beta(x) \underline{S_0(x^*, \omega)} \exp \left[- \int_0^{\|x-x^*\|} \beta(x^* + s'\omega) ds' \right] \\ &\quad \times \delta \left(\omega - \frac{x-x^*}{\|x-x^*\|} \right) \frac{d^3x^*}{\|x-x^*\|^2}. \end{aligned} \quad (\text{G9})$$

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In compact form, Eq. G9 can be written as

$$\underline{f(x, \omega)} = \int_V \int_{4\pi} \underline{k[(x^*, \omega') \rightarrow (x, \omega)]} \underline{f(x^*, \omega')} d\Omega' d^3x^* + \underline{\Psi(x, \omega)}, \quad (\text{G10})$$

where

$$\underline{k[(x^*, \omega') \rightarrow (x, \omega)]} = \beta(x) \frac{a(x^*)}{4\pi} \underline{Z(x^*, \omega, \omega')} \exp \left[- \int_0^{\|x-x^*\|} \beta(x^* + s'\omega) ds' \right] \frac{\delta \left(\omega - \frac{x-x^*}{\|x-x^*\|} \right)}{\|x-x^*\|^2} \quad (\text{G11})$$

1250 represents the *transport kernel* describing the contribution of photons scattered at (x^*, ω') to the collision density at (x, ω) .

The second term in Eq. G10,

$$\underline{\Psi(x, \omega)} = \int_V \beta(x) \underline{S_0(x^*, \omega)} \exp \left[- \int_0^{\|x-x^*\|} \beta(x^* + s'\omega) ds' \right] \frac{\delta \left(\omega - \frac{x-x^*}{\|x-x^*\|} \right)}{\|x-x^*\|^2} d^3x^*, \quad (\text{G12})$$

represents the total contribution from the emitting source, or the *initial collision density*.

For simplicity, Eq. G10 can be written as

$$1255 \quad \underline{f} = \underline{K}[\underline{f}] + \underline{\Psi}, \quad (\text{G13})$$

where the integral operator $\underline{K}$ is defined by

$$\underline{K}[\underline{f}](x, \omega) = \int_V \int_{4\pi} \underline{k[(x^*, \omega') \rightarrow (x, \omega)]} \underline{f(x^*, \omega')} d\Omega' d^3x^*. \quad (\text{G14})$$

The solution of Eq. G13 can be written as a Neumann series:

$$\begin{aligned} \underline{f} &= \underline{\Psi} + K[\underline{\Psi}] + K^2[\underline{\Psi}] + K^3[\underline{\Psi}] + \cdots \\ &= \sum_{n=0}^{\infty} K^n[\underline{\Psi}], \end{aligned} \tag{G15}$$

with $K^2[\underline{\Psi}] = K[K[\underline{\Psi}]]$, $K^3[\underline{\Psi}] = K[K[K[\underline{\Psi}]]]$, etc., which converges for physically realistic media with $0 \leq a \leq 1$ (Sect. 4.2 of Marchuk). As we shall later see, this Neumann series representation is useful because it allows us to express the solution as a superposition of contributions from the various orders of light scattering.

We now introduce the following inner product notation for Stokes-vector-valued functions:

$$(\underline{u}, \underline{v}) = \int_{\mathcal{V}} \int_{4\pi} \underline{u}(\underline{x}, \underline{\omega})^T \underline{v}(\underline{x}, \underline{\omega}) d\Omega d^3 \underline{x}. \tag{G16}$$

Let $\underline{x}^\bullet$ denote the detector location, and let $\underline{\omega}^\bullet$ denote the propagation direction of the detected radiation at the detector. Then, we can evaluate the Neumann series at $\underline{x}^\bullet$ in the direction $\underline{\omega}^\bullet$ by defining

$$\delta_{\underline{x}^\bullet, \underline{\omega}^\bullet} = \delta(\underline{x} - \underline{x}^\bullet) \delta(\underline{\omega} - \underline{\omega}^\bullet),$$

and by introducing the canonical basis vectors

$$\underline{e}_1 = [1, 0, 0, 0]^T, \quad \underline{e}_2 = [0, 1, 0, 0]^T, \quad \underline{e}_3 = [0, 0, 1, 0]^T, \quad \underline{e}_4 = [0, 0, 0, 1]^T.$$

The individual components of the collision density Stokes vector at $(\underline{x}^\bullet, \underline{\omega}^\bullet)$ are then given by

$$\begin{aligned} [\underline{f}(\underline{x}^\bullet, \underline{\omega}^\bullet)]_j &= \int_{\mathcal{V}} \int_{4\pi} \underline{f}(\underline{x}, \underline{\omega})^T \delta_{\underline{x}^\bullet, \underline{\omega}^\bullet} \underline{e}_j d\Omega d^3 \underline{x} \\ &= (\underline{f}(\underline{x}, \underline{\omega}), \delta_{\underline{x}^\bullet, \underline{\omega}^\bullet} \underline{e}_j), \quad j = 1, 2, 3, 4. \end{aligned} \tag{G17}$$

Substituting the Neumann series (Eq. G15) for $\underline{f}$ yields

$$\begin{aligned} [\underline{f}(\underline{x}^\bullet, \underline{\omega}^\bullet)]_j &= \left(\sum_{n=0}^{\infty} K^n[\underline{\Psi}], \delta_{\underline{x}^\bullet, \underline{\omega}^\bullet} \underline{e}_j \right) \\ &= \sum_{n=0}^{\infty} (K^n[\underline{\Psi}], \delta_{\underline{x}^\bullet, \underline{\omega}^\bullet} \underline{e}_j) \\ &= (\underline{\Psi}, \delta_{\underline{x}^\bullet, \underline{\omega}^\bullet} \underline{e}_j) + (K[\underline{\Psi}], \delta_{\underline{x}^\bullet, \underline{\omega}^\bullet} \underline{e}_j) \\ &\quad + (K^2[\underline{\Psi}], \delta_{\underline{x}^\bullet, \underline{\omega}^\bullet} \underline{e}_j) + (K^3[\underline{\Psi}], \delta_{\underline{x}^\bullet, \underline{\omega}^\bullet} \underline{e}_j) + \cdots. \end{aligned} \tag{G18}$$

For the next step, we introduce the adjoint operator K^+ :

$$K^+[g](\underline{x}, \underline{\omega}) = \int_{\mathcal{V}} \int_{4\pi} \underline{k}[(\underline{x}, \underline{\omega}) \rightarrow (\underline{x}^*, \underline{\omega}')]^T \underline{g}(\underline{x}^*, \underline{\omega}') d\Omega' d^3 \underline{x}^*, \tag{G19}$$

for which it can be shown that (see Eqs. S23 to S30 in the Supplementary material)

$$\left(K[\underline{u}], \underline{g}\right) = (\underline{u}, K^+[\underline{g}]) \quad (\text{G20})$$

For arbitrary Stokes-vector-valued functions $\underline{u}$ and $\underline{g}$. Using Eq. G20, Eq. G18 can be written as

$$\begin{aligned} [f(\underline{x}^\bullet, \omega^\bullet)]_j &= (\Psi, \delta_{\underline{x}^\bullet \omega^\bullet} e_j) + (\Psi, K^+[\delta_{\underline{x}^\bullet \omega^\bullet} e_j]) \\ &+ (K[\Psi], K^+[\delta_{\underline{x}^\bullet \omega^\bullet} e_j]) + (K^2[\Psi], K^+[\delta_{\underline{x}^\bullet \omega^\bullet} e_j]) + \dots \end{aligned} \quad (\text{G21})$$

It may be noted that Eq. G21 is the vector analogue of the scalar collision density expression of Marshak and Davis (2005) (their Eq. 4.60), who neglected polarisation of light.

G4 Detector radiance and contribution function

We now consider the radiance Stokes vector $\underline{I}$ in the direction $\omega^\bullet$ reaching a detector located at a given point $\underline{x}^\bullet$. Using the definition of the collision density $\underline{f} = \beta \underline{I}$ and Eq. G21, the individual Stokes vector components of $\underline{I}$ become

$$\begin{aligned} [I(\underline{x}^\bullet, \omega^\bullet)]_j &= \frac{1}{\beta(\underline{x}^\bullet)} [f(\underline{x}^\bullet, \omega^\bullet)]_j \\ &= \frac{1}{\beta(\underline{x}^\bullet)} (\Psi(\underline{x}, \omega), \delta_{\underline{x}^\bullet \omega^\bullet} e_j) \\ &+ \frac{1}{\beta(\underline{x}^\bullet)} (\Psi(\underline{x}, \omega), K^+[\delta_{\underline{x}^\bullet \omega^\bullet} e_j]) \\ &+ \frac{1}{\beta(\underline{x}^\bullet)} (K[\Psi](\underline{x}, \omega), K^+[\delta_{\underline{x}^\bullet \omega^\bullet} e_j]) \\ &+ \frac{1}{\beta(\underline{x}^\bullet)} (K^2[\Psi](\underline{x}, \omega), K^+[\delta_{\underline{x}^\bullet \omega^\bullet} e_j]) + \dots, \end{aligned} \quad (\text{G22})$$

for $j = 1, 2, 3, 4$.

As an intermediate step, let us write out the operator $K^+[\delta_{\underline{x}^\bullet \omega^\bullet} e_j]$, which is a Stokes-vector-valued function of $\underline{x}$ and ω (see Eq. G19). Using also the definition of the transport kernel in Eq. G11, we get:

$$\begin{aligned} K^+[\delta_{\underline{x}^\bullet \omega^\bullet} e_j](\underline{x}, \omega) &= \int_V \int_{4\pi} k[(\underline{x}, \omega) \rightarrow (\underline{x}^*, \omega')]^T \delta(\underline{x}^* - \underline{x}^\bullet) \delta(\omega' - \omega^\bullet) e_j d\Omega' d^3x^* \\ &= k[(\underline{x}, \omega) \rightarrow (\underline{x}^\bullet, \omega^\bullet)]^T e_j \\ &= \beta(\underline{x}^\bullet) \frac{a(\underline{x})}{4\pi} \underline{Z}(\underline{x}, \omega^\bullet, \omega)^T e_j \exp \left[- \int_0^{\|\underline{x}^\bullet - \underline{x}\|} \beta(\underline{x} + s' \omega^\bullet) ds' \right] \frac{\delta\left(\omega^\bullet - \frac{\underline{x}^\bullet - \underline{x}}{\|\underline{x}^\bullet - \underline{x}\|}\right)}{\|\underline{x}^\bullet - \underline{x}\|^2}. \end{aligned} \quad (\text{G23})$$

which describes how photons are transported from point $\underline{x}$ in direction ω to the detector location $(\underline{x}^\bullet, \omega^\bullet)$.

Now, by cancelling out $\beta(\mathbf{x}^\bullet)$ in the second and higher order terms, and taking the single scattering albedo $a(\mathbf{x})$ to the front, Eq. G22 can be rewritten as

$$\begin{aligned}
 1305 \quad [I(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet)]_j &= \frac{1}{\beta(\mathbf{x}^\bullet)} [\Psi(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet)]_j \\
 &+ (a(\mathbf{x}) \Psi(\mathbf{x}, \boldsymbol{\omega}), \Phi_j(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet, \mathbf{x}, \boldsymbol{\omega})) \\
 &+ (a(\mathbf{x}) K[\Psi](\mathbf{x}, \boldsymbol{\omega}), \Phi_j(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet, \mathbf{x}, \boldsymbol{\omega})) \\
 &+ (a(\mathbf{x}) K^2[\Psi](\mathbf{x}, \boldsymbol{\omega}), \Phi_j(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet, \mathbf{x}, \boldsymbol{\omega})) + \dots,
 \end{aligned} \tag{G24}$$

where

$$1310 \quad \Phi_j(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet, \mathbf{x}, \boldsymbol{\omega}) = \frac{1}{4\pi} \mathbf{Z}(\mathbf{x}, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega})^T \mathbf{e}_j \exp \left[- \int_0^{\|\mathbf{x}^\bullet - \mathbf{x}\|} \beta(\mathbf{x} + s' \boldsymbol{\omega}^\bullet) ds' \right] \frac{\delta \left(\boldsymbol{\omega}^\bullet - \frac{\mathbf{x}^\bullet - \mathbf{x}}{\|\mathbf{x}^\bullet - \mathbf{x}\|} \right)}{\|\mathbf{x}^\bullet - \mathbf{x}\|^2} \tag{G25}$$

is the *contribution function* for the j^{th} component of the detector radiance Stokes vector. Equation G24 expresses the radiance Stokes vector at the detector as the superposition of contributions from direct illumination and all scattering events within the medium, i.e. from all event locations $\mathbf{x}$ integrated over the volume $\mathcal{V}$ and all propagation directions $\boldsymbol{\omega}$. Each term in the Neumann expansion corresponds to photons that have undergone a specific number of collisions. The first term accounts for direct illumination and the second for single scattering, while higher-order terms describe multiple scattering, weighted by successive applications of the transport operator K . The contribution function $\Phi_j(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet, \mathbf{x}, \boldsymbol{\omega})$ acts as a detector sensitivity kernel for the j^{th} Stokes component: it quantifies the contribution of radiation present at $(\mathbf{x}, \boldsymbol{\omega})$ to the corresponding component of the detector signal at $(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet)$.

G5 Scattering-order decomposition of the detector radiance

1320 The radiance Stokes vector arriving at the detector, given component-wise by Eq. G24, is a superposition of the direct illumination, or 0^{th} -order scattering contribution, $\mathbf{I}^{(0)}$, the singly scattered contribution $\mathbf{I}^{(1)}$, and higher-order scattered contributions $\mathbf{I}^{(n)}$ with $n = 2, 3, 4, \dots$. Here, those contributions are evaluated.

G5.1 Zeroth-order contribution (direct illumination)

1325 For solar illumination we assume that the Sun is effectively at infinity, which we describe by a plane-parallel (collimated) beam with fixed direction $\boldsymbol{\omega}_0$ and spectral irradiance E_0 (in $\text{W m}^{-2} \text{nm}^{-1}$). Because this incident solar beam is taken to be unpolarised, its Stokes vector equals $E_0 \mathbf{1}$, with $\mathbf{1} = [1, 0, 0, 0]^T$. Since the incident beam is collimated, for every point $\mathbf{x} \in \mathcal{V}$ there is a unique upstream ray in direction $-\boldsymbol{\omega}_0$, and therefore a unique entry point of the incident sunlight on the source boundary. We denote this point by $\mathbf{x}_0(\mathbf{x})$, and define it by

$$\mathbf{x}_0(\mathbf{x}) := \mathbf{x} - s_0(\mathbf{x}) \boldsymbol{\omega}_0, \quad s_0(\mathbf{x}) \geq 0, \tag{G26}$$

1330 where $s_0(\mathbf{x})$ is the unique distance from $\mathbf{x}$ to the sunlight-entry boundary along direction $-\boldsymbol{\omega}_0$.

The initial collision density $\Psi(\mathbf{x}, \boldsymbol{\omega})$ in Eq. G24 represents the part of the collision density $f = \beta I$ generated by sources *before* any scattering occurs. Let us now rewrite the expression for Ψ in Eq. G12 as a line integral along the straight path in the viewing direction.

$$\mathbf{x}^* = \mathbf{x} - s^* \boldsymbol{\omega},$$

1335 from the observation point ($s^* = 0$) to the upstream boundary of the medium ($s^* = s_b$). Equivalently, the upper integration limit may be written as ∞ , with the understanding that all optical coefficients and source terms vanish outside the medium. Using the transformation identity to convert the volume integral in Eq. G12 to a line integral (see Eq. H30),

$$ds^* = \delta\left(\boldsymbol{\omega} - \frac{\mathbf{x} - \mathbf{x}^*}{\|\mathbf{x} - \mathbf{x}^*\|}\right) \frac{1}{\|\mathbf{x} - \mathbf{x}^*\|^2} d^3\mathbf{x}^*,$$

we obtain

$$1340 \quad \Psi(\mathbf{x}, \boldsymbol{\omega}) = \beta(\mathbf{x}) \int_0^\infty S_0(s^*, \boldsymbol{\omega}) \exp\left[-\int_0^{s^*} \beta(\mathbf{x}^* + s' \boldsymbol{\omega}) ds'\right] ds^*. \quad (\text{G27})$$

For a collimated solar beam with irradiance E_0 incident in direction $\boldsymbol{\omega}_0$, we represent the source term in line-integral form as

$$S_0(s^*, \boldsymbol{\omega}) = E_0 \delta(s^* - s_0(\mathbf{x})) \delta(\boldsymbol{\omega} - \boldsymbol{\omega}_0) \mathbf{1},$$

so that the source is located at the unique entry point of the incident sunlight $\mathbf{x}_0(\mathbf{x})$. Substituting this expression into Eq. G27 and dividing by $\beta(\mathbf{x})$ gives the unscattered radiance Stokes vector field at $\mathbf{x}$ and $\boldsymbol{\omega}$:

$$1345 \quad I^{(0)}(\mathbf{x}, \boldsymbol{\omega}) = \frac{\Psi(\mathbf{x}, \boldsymbol{\omega})}{\beta(\mathbf{x})} = \int_0^\infty E_0 \delta(s^* - s_0(\mathbf{x})) \delta(\boldsymbol{\omega} - \boldsymbol{\omega}_0) \mathbf{1} \exp\left[-\int_0^{s^*} \beta(\mathbf{x}^* + s' \boldsymbol{\omega}) ds'\right] ds^* \\ = E_0 \delta(\boldsymbol{\omega} - \boldsymbol{\omega}_0) \exp[-\tau(\mathbf{x}_0(\mathbf{x}) \rightarrow \mathbf{x})] \mathbf{1}. \quad (\text{G28})$$

For this direct beam, only the first Stokes component is nonzero because of the multiplication by $\mathbf{1}$. The Dirac delta functions enforce $s^* = s_0(\mathbf{x})$ and $\boldsymbol{\omega} = \boldsymbol{\omega}_0$, so that $\mathbf{x}^* = \mathbf{x} - s_0(\mathbf{x})\boldsymbol{\omega}_0 = \mathbf{x}_0(\mathbf{x})$, and

$$\tau(\mathbf{x}_0(\mathbf{x}) \rightarrow \mathbf{x}) = \int_0^{s_0(\mathbf{x})} \beta(\mathbf{x}_0(\mathbf{x}) + s' \boldsymbol{\omega}_0) ds'$$

1350 is the optical depth along the straight path from the point where the solar beam enters the computational domain to the point $\mathbf{x}$. Hence, at the detector point $\mathbf{x}^\bullet$ and in the direction $\boldsymbol{\omega}^\bullet$, the unscattered contribution is

$$I^{(0)}(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet) = E_0 \delta(\boldsymbol{\omega}^\bullet - \boldsymbol{\omega}_0) \exp[-\tau(\mathbf{x}_0(\mathbf{x}^\bullet) \rightarrow \mathbf{x}^\bullet)] \mathbf{1}. \quad (\text{G29})$$

This direct-illumination term is nonzero only when the observation direction $-\boldsymbol{\omega}^\bullet$ coincides with the solar direction $-\boldsymbol{\omega}_0$. In the current version of MONKI, this zeroth-order term is not evaluated, because MONKI only computes local estimates at scattering and surface-reflection events (see Appendices G7 and G8). If needed, the direct contribution could be added analytically using Eq. G29. In what follows, only the scattered contributions to the detector signal, i.e. scattering orders $n \geq 1$, are considered.

G5.2 First-order contribution

The ~~prefactor $1/\pi$ ensures that~~ first-order (single-scattering) contribution corresponds to photons that undergo exactly one scattering event before reaching the detector. In Eq. G24, this is the second term in the Neumann expansion. For the j^{th} component of the singly scattered detector radiance Stokes vector, we have

$$[\mathbf{I}^{(1)}(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet)]_j = (a(\mathbf{x}) \boldsymbol{\Psi}(\mathbf{x}, \boldsymbol{\omega}), \boldsymbol{\Phi}_j(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet, \mathbf{x}, \boldsymbol{\omega})), \quad j = 1, 2, 3, 4. \quad (\text{G30})$$

Substituting $\boldsymbol{\Phi}_j$ (Eq. G25) and using the vector inner product definition of Eq. G16 yields

$$[\mathbf{I}^{(1)}(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet)]_j = \int_{\mathcal{V}} \int_{4\pi} a(\mathbf{x}) \boldsymbol{\Psi}(\mathbf{x}, \boldsymbol{\omega})^T \frac{1}{4\pi} \mathbf{Z}(\mathbf{x}, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega})^T \mathbf{e}_j \times \exp[-\tau(\mathbf{x} \rightarrow \mathbf{x}^\bullet)] \frac{\delta\left(\boldsymbol{\omega}^\bullet - \frac{\mathbf{x}^\bullet - \mathbf{x}}{\|\mathbf{x}^\bullet - \mathbf{x}\|}\right)}{\|\mathbf{x}^\bullet - \mathbf{x}\|^2} d\Omega d^3\mathbf{x}, \quad (\text{G31})$$

where

$$\tau(\mathbf{x} \rightarrow \mathbf{x}^\bullet) = \int_0^{\|\mathbf{x}^\bullet - \mathbf{x}\|} \beta(\mathbf{x} + s' \boldsymbol{\omega}^\bullet) ds'.$$

Now use the identity

$$\mathbf{u}^T \mathbf{Z}^T \mathbf{e}_j = (\mathbf{Z} \mathbf{u})^T \mathbf{e}_j = \mathbf{e}_j^T \mathbf{Z} \mathbf{u} = [\mathbf{Z} \mathbf{u}]_j, \quad (\text{G32})$$

which holds for any Stokes vector $\mathbf{u}$. Applying Eq. G32 with $\mathbf{u} = \boldsymbol{\Psi}(\mathbf{x}, \boldsymbol{\omega})$ gives

$$[\mathbf{I}^{(1)}(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet)]_j = \int_{\mathcal{V}} \int_{4\pi} \frac{a(\mathbf{x})}{4\pi} [\mathbf{Z}(\mathbf{x}, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}) \boldsymbol{\Psi}(\mathbf{x}, \boldsymbol{\omega})]_j \times \exp[-\tau(\mathbf{x} \rightarrow \mathbf{x}^\bullet)] \frac{\delta\left(\boldsymbol{\omega}^\bullet - \frac{\mathbf{x}^\bullet - \mathbf{x}}{\|\mathbf{x}^\bullet - \mathbf{x}\|}\right)}{\|\mathbf{x}^\bullet - \mathbf{x}\|^2} d\Omega d^3\mathbf{x}. \quad (\text{G33})$$

Using the direct-beam initial collision term (Eq. G28), or equivalently $\boldsymbol{\Psi}(\mathbf{x}, \boldsymbol{\omega}) = \beta(\mathbf{x}) \mathbf{I}^{(0)}(\mathbf{x}, \boldsymbol{\omega})$, we obtain

$$\boldsymbol{\Psi}(\mathbf{x}, \boldsymbol{\omega}) = \beta(\mathbf{x}) E_0 \delta(\boldsymbol{\omega} - \boldsymbol{\omega}_0) \exp[-\tau(\mathbf{x}_0(\mathbf{x}) \rightarrow \mathbf{x})] \mathbf{1}. \quad (\text{G34})$$

1375 Substituting Eq. G34 into Eq. G33 yields

$$\begin{aligned} \underline{[I^{(1)}(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet)]_j} = & \int_V \int_{4\pi} \frac{a(\mathbf{x}) \beta(\mathbf{x}) E_0}{4\pi} [Z(\mathbf{x}, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}) \mathbf{1}]_j \delta(\boldsymbol{\omega} - \boldsymbol{\omega}_0) \exp[-\tau(\mathbf{x}_0(\mathbf{x}) \rightarrow \mathbf{x})] \\ & \times \exp[-\tau(\mathbf{x} \rightarrow \mathbf{x}^\bullet)] \frac{\delta\left(\boldsymbol{\omega}^\bullet - \frac{\mathbf{x}^\bullet - \mathbf{x}}{\|\mathbf{x}^\bullet - \mathbf{x}\|}\right)}{\|\mathbf{x}^\bullet - \mathbf{x}\|^2} d\Omega d^3\mathbf{x}. \end{aligned} \quad (\text{G35})$$

The angular integration over Ω is straightforward because of the Dirac delta $\delta(\boldsymbol{\omega} - \boldsymbol{\omega}_0)$, and the remaining spatial Dirac delta restricts $\mathbf{x}$ to the backward ray, which extends from the detector to ∞ by again assuming that all optical coefficients and source terms vanish outside the medium,

$$\underline{\mathbf{x} = \mathbf{x}_1(s_1) := \mathbf{x}^\bullet - s_1 \boldsymbol{\omega}^\bullet, \quad s_1 > 0.}$$

For each such scattering point $\mathbf{x}_1(s_1)$, the corresponding entry point of the incident sunlight is denoted by

$$\underline{\mathbf{x}_0(s_1) := \mathbf{x}_0(\mathbf{x}_1(s_1)) = \mathbf{x}_1(s_1) - s_0(s_1) \boldsymbol{\omega}_0, \quad s_0(s_1) \geq 0,} \quad (\text{G36})$$

where $s_0(s_1)$ is the unique distance from $\mathbf{x}_1(s_1)$ to the sunlight-entry boundary along direction $-\boldsymbol{\omega}_0$. Hence,

$$\begin{aligned} \underline{[I^{(1)}(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet)]_j} = & \frac{E_0}{4\pi} \int_0^\infty a(\mathbf{x}_1(s_1)) \beta(\mathbf{x}_1(s_1)) [Z(\mathbf{x}_1(s_1), \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_0) \mathbf{1}]_j \\ & \times \exp[-\tau(\mathbf{x}_0(s_1) \rightarrow \mathbf{x}_1(s_1))] \exp[-\tau(\mathbf{x}_1(s_1) \rightarrow \mathbf{x}^\bullet)] ds_1. \end{aligned} \quad (\text{G37})$$

Finally, collecting the four Stokes components $j = 1, 2, 3, 4$ into a single vector yields

$$\begin{aligned} \underline{I^{(1)}(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet)} = & \frac{E_0}{4\pi} \int_0^\infty a(\mathbf{x}_1(s_1)) \beta(\mathbf{x}_1(s_1)) Z(\mathbf{x}_1(s_1), \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_0) \mathbf{1} \\ & \times \exp[-\tau(\mathbf{x}_0(s_1) \rightarrow \mathbf{x}_1(s_1))] \exp[-\tau(\mathbf{x}_1(s_1) \rightarrow \mathbf{x}^\bullet)] ds_1. \end{aligned} \quad (\text{G38})$$

1390 Equation G38 shows that the singly scattered radiance Stokes vector at the reflected irradiance is normalised by the incident irradiance. The factor μ accounts for the projection effect, as detector is obtained by integrating, along the detector line of sight, the contributions from all possible scattering points illuminated by the solar beam. Each contribution is weighted by the local extinction coefficient $\beta(\mathbf{x}_1(s_1))$, the single-scattering albedo $a(\mathbf{x}_1(s_1))$, the phase matrix for scattering from $\boldsymbol{\omega}_0$ into $\boldsymbol{\omega}^\bullet$, and the transmittances along both the solar and detector paths.

1395 **G5.3** Second-order contribution

Similarly, the second-order scattering contribution corresponds to photons that undergo exactly two scattering events before reaching the detector. Starting with

$$[I^{(2)}(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet)]_j = (a(\mathbf{x})K[\Psi](\mathbf{x}, \boldsymbol{\omega}), \Phi_j(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet, \mathbf{x}, \boldsymbol{\omega}))$$

from Eq. G24, and following the same procedure as for the singly scattered radiance Stokes vector, the spatial integrations collapse onto the detector line of sight and the upstream ray of the preceding scattering event. Introducing the detector-ray parameterisation

$$\mathbf{x}_2(s_2) := \mathbf{x}^\bullet - s_2 \boldsymbol{\omega}^\bullet, \quad s_2 > 0,$$

for the second (last) scattering event, and denoting the location of the first scattering event upstream of $\mathbf{x}_2$ by

$$\mathbf{x}_1(s_2, s_1, \boldsymbol{\omega}_1) := \mathbf{x}_2(s_2) - s_1 \boldsymbol{\omega}_1, \quad s_1 > 0,$$

we define the corresponding entry point of the incident sunlight by

$$\mathbf{x}_0(s_2, s_1, \boldsymbol{\omega}_1) := \mathbf{x}_1(s_2, s_1, \boldsymbol{\omega}_1) - s_0(s_2, s_1, \boldsymbol{\omega}_1) \boldsymbol{\omega}_0,$$

where $s_0(s_2, s_1, \boldsymbol{\omega}_1) \geq 0$ is the unique distance from $\mathbf{x}_1(s_2, s_1, \boldsymbol{\omega}_1)$ to the sunlight-entry boundary along direction $-\boldsymbol{\omega}_0$. We then obtain for the second-order scattered Stokes vector at the detector

$$\begin{aligned} I^{(2)}(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet) = & \frac{E_0}{(4\pi)^2} \int_0^\infty a(\mathbf{x}_2(s_2)) \beta(\mathbf{x}_2(s_2)) \exp[-\tau(\mathbf{x}_2(s_2) \rightarrow \mathbf{x}^\bullet)] \\ & \times \int_{4\pi} \mathbf{Z}(\mathbf{x}_2(s_2), \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_1) \\ & \times \int_0^\infty a(\mathbf{x}_1(s_2, s_1, \boldsymbol{\omega}_1)) \beta(\mathbf{x}_1(s_2, s_1, \boldsymbol{\omega}_1)) \mathbf{Z}(\mathbf{x}_1(s_2, s_1, \boldsymbol{\omega}_1), \boldsymbol{\omega}_1, \boldsymbol{\omega}_0) \mathbf{1} \\ & \times \exp[-\tau(\mathbf{x}_0(s_2, s_1, \boldsymbol{\omega}_1) \rightarrow \mathbf{x}_1(s_2, s_1, \boldsymbol{\omega}_1))] \\ & \times \exp[-\tau(\mathbf{x}_1(s_2, s_1, \boldsymbol{\omega}_1) \rightarrow \mathbf{x}_2(s_2))] ds_1 d\Omega_1 ds_2. \end{aligned} \tag{G39}$$

This expression represents photons that are first scattered from the sunlight direction $\boldsymbol{\omega}_0$ into an intermediate direction $\boldsymbol{\omega}_1$ at $\mathbf{x}_1$, and subsequently scattered at $\mathbf{x}_2$ into the detector direction $\boldsymbol{\omega}^\bullet$.

G5.4 Third- and higher-order contributions

Similarly, the third-order scattering contribution corresponds to photons that undergo exactly three scattering events before reaching the detector. Introducing the detector-ray parameterisation

$$\mathbf{x}_3(s_3) := \mathbf{x}^\bullet - s_3 \boldsymbol{\omega}^\bullet, \quad s_3 > 0,$$

1420 for the third (last) scattering event, and denoting the location of the second scattering event upstream of $\mathbf{x}_3$ by

$$\mathbf{x}_2(s_3, s_2, \boldsymbol{\omega}_2) := \mathbf{x}_3(s_3) - s_2 \boldsymbol{\omega}_2, \quad s_2 > 0,$$

and the location of the first scattering event upstream of $\mathbf{x}_2$ by

$$\mathbf{x}_1(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1) := \mathbf{x}_2(s_3, s_2, \boldsymbol{\omega}_2) - s_1 \boldsymbol{\omega}_1, \quad s_1 > 0,$$

we define the corresponding entry point of the incident sunlight by

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$$\mathbf{x}_0(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1) := \mathbf{x}_1(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1) - s_0(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1) \boldsymbol{\omega}_0,$$

where $s_0(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1) \geq 0$ is the unique distance from $\mathbf{x}_1(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1)$ to the sunlight-entry boundary along direction $-\boldsymbol{\omega}_0$. We then obtain for the third-order scattered Stokes vector at the detector

$$\begin{aligned} \mathbf{I}^{(3)}(\mathbf{x}^\bullet, \boldsymbol{\omega}^\bullet) = & \frac{E_0}{(4\pi)^3} \int_0^\infty a(\mathbf{x}_3(s_3)) \beta(\mathbf{x}_3(s_3)) \exp[-\tau(\mathbf{x}_3(s_3) \rightarrow \mathbf{x}^\bullet)] \\ & \times \int_{4\pi} \mathbf{Z}(\mathbf{x}_3(s_3), \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_2) \\ & \times \int_0^\infty a(\mathbf{x}_2(s_3, s_2, \boldsymbol{\omega}_2)) \beta(\mathbf{x}_2(s_3, s_2, \boldsymbol{\omega}_2)) \exp[-\tau(\mathbf{x}_2(s_3, s_2, \boldsymbol{\omega}_2) \rightarrow \mathbf{x}_3(s_3))] \\ & \times \int_{4\pi} \mathbf{Z}(\mathbf{x}_2(s_3, s_2, \boldsymbol{\omega}_2), \boldsymbol{\omega}_2, \boldsymbol{\omega}_1) \\ & \times \int_0^\infty a(\mathbf{x}_1(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1)) \beta(\mathbf{x}_1(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1)) \\ & \times \mathbf{Z}(\mathbf{x}_1(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1), \boldsymbol{\omega}_1, \boldsymbol{\omega}_0) \mathbf{1} \\ & \times \exp[-\tau(\mathbf{x}_0(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1) \rightarrow \mathbf{x}_1(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1))] \\ & \times \exp[-\tau(\mathbf{x}_1(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1) \rightarrow \mathbf{x}_2(s_3, s_2, \boldsymbol{\omega}_2))] ds_1 d\Omega_1 ds_2 d\Omega_2 ds_3. \end{aligned} \tag{G40}$$

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This expression represents photons that are first scattered from the sunlight direction $\boldsymbol{\omega}_0$ into an intermediate direction $\boldsymbol{\omega}_1$ at $\mathbf{x}_1$, subsequently scattered at $\mathbf{x}_2$ into a second intermediate direction $\boldsymbol{\omega}_2$, and finally scattered at $\mathbf{x}_3$ into the detector direction $\boldsymbol{\omega}^\bullet$. In what follows, for notational simplicity, we omit the explicit dependence of $\mathbf{x}_0, \mathbf{x}_1, \mathbf{x}_2, \dots$ on the free-path variables $s_0, s_1, s_2, \dots$ and on the intermediate directions $\boldsymbol{\omega}_1, \boldsymbol{\omega}_2, \dots$.

1440 Higher-order scattered Stokes vector contributions can be derived using a similar approach.

G6 Forward finite-area formulation of the scattering-order contributions

The radiance Stokes vector expressions derived above for the first few scattering orders, such as Eqs. G38, G39, and G40, are written for a detector at a fixed point $\mathbf{x}^\bullet$ and are parameterised along the detector line of sight. Hence, they can directly be used for the backward Monte Carlo simulation (Appendix G8). In the practical *forward* Monte Carlo simulation, however, photons are launched from the sunlight-entry boundary of a rectangular domain and are traced in the sunlight direction ω_0 . It is therefore useful to rewrite these deterministic expressions in a form that is directly compatible with forward photon tracing. This rewriting is possible because the incident solar beam is collimated, and because in our local-estimation method the contribution towards the detector is computed along collimated rays in the fixed detector direction $\omega^\bullet$. Hence, the same set of scattering points can be parameterised either from the detector side or from the solar-side.

We consider a finite horizontal source area O_0 on the sunlight-entry boundary and a finite horizontal detector area O on the detector boundary. We write $\mathbf{x}_0 \in O_0$ for the entry point of the incident sunlight of a photon and $\mathbf{x}^\bullet \in O$ for the point where the ray towards the detector intersects the detector boundary. Thus, in the present subsection, neither $\mathbf{x}_0$ nor $\mathbf{x}^\bullet$ is a fixed point: both vary over the finite areas O_0 and O , respectively. The detector-area-averaged radiance Stokes vector for scattering order n is defined by

$$\mathbf{I}^{(n)}(O, \omega^\bullet; \omega_0) = \frac{1}{O} \int_O \mathbf{I}^{(n)}(\mathbf{x}^\bullet, \omega^\bullet) dO, \quad (\text{G41})$$

where O denotes the horizontal area of the detector region O . Below, we first derive the corresponding forward formulation for the first-order contribution, and next for the second-order contribution. The third-order expression then follows in complete analogy.

G6.1 First-order contribution

We start from the first-order point-detector expression in Eq. G38 and average it over the detector area O :

$$\begin{aligned} \mathbf{I}^{(1)}(O, \omega^\bullet; \omega_0) = & \frac{E_0}{O 4\pi} \int_O \int_0^\infty a(\mathbf{x}_1(s_1)) \beta(\mathbf{x}_1(s_1)) \mathbf{Z}(\mathbf{x}_1(s_1), \omega^\bullet, \omega_0) \mathbf{1} \\ & \times \exp[-\tau(\mathbf{x}_0(s_1) \rightarrow \mathbf{x}_1(s_1))] \exp[-\tau(\mathbf{x}_1(s_1) \rightarrow \mathbf{x}^\bullet)] ds_1 dO. \end{aligned} \quad (\text{G42})$$

Equation G42 is written as a line integral along the detector path,

$$\mathbf{x}_1 = \mathbf{x}^\bullet - s_1 \omega^\bullet, \quad s_1 > 0, \quad (\text{G43})$$

where $\mathbf{x}_1$ is the single-scattering location. In forward mode it is more natural to parameterise the same scattering point from the solar side:

$$\mathbf{x}_1 = \mathbf{x}_0 + s_0 \omega_0, \quad s_0 > 0, \quad (\text{G44})$$

with $\mathbf{x}_0 \in O_0$. Hence, for the same scattering point $\mathbf{x}_1$,

$$\mathbf{x}_1 = \mathbf{x}^\bullet - s_1 \boldsymbol{\omega}^\bullet = \mathbf{x}_0 + s_0 \boldsymbol{\omega}_0. \quad (\text{G45})$$

1470 To transform the integration from the detector-side parameterisation $(\mathbf{x}^\bullet, s_1)$ to the solar-side parameterisation $(\mathbf{x}_0, s_0)$, we compare the same set of scattering points around $\mathbf{x}_1$. For a horizontal area element dO at the detector boundary and a path-length interval ds_1 along $\boldsymbol{\omega}^\bullet$, the corresponding differential scattering volume is

$$dV = \mu_\bullet dO ds_1, \quad \mu_\bullet = |\cos \vartheta^\bullet|. \quad (\text{G46})$$

1475 Likewise, for a horizontal area element dO_0 at the sunlight-entry boundary and a path-length interval ds_0 along $\boldsymbol{\omega}_0$, the same differential scattering volume is

$$dV = \mu_0 dO_0 ds_0, \quad \mu_0 = |\cos \vartheta_0|. \quad (\text{G47})$$

Hence,

$$\mu_\bullet dO ds_1 = \mu_0 dO_0 ds_0. \quad (\text{G48})$$

1480 Now let $h(\mathbf{x}_1)$ be any integrable function of the scattering point. Then integration over the same scattering volume can be written equivalently as

$$\iint h(\mathbf{x}^\bullet - s_1 \boldsymbol{\omega}^\bullet) \mu_\bullet dO ds_1 = \iint h(\mathbf{x}_0 + s_0 \boldsymbol{\omega}_0) \mu_0 dO_0 ds_0. \quad (\text{G49})$$

1485 In the detector-side formulation, the restriction to the selected detector area O is already contained in the integration over $\mathbf{x}^\bullet \in O$. After rewriting the integral in solar-side variables $(\mathbf{x}_0, s_0)$, this detector selection is no longer part of the integration limits. Since O_0 denotes the full illuminated sunlight-entry boundary, every illuminated scattering point is already represented once on the solar side, and the restriction to the chosen detector area must therefore be written explicitly through the indicator function

$$\chi(\mathbf{x}^\bullet) = \begin{cases} 1, & \text{if } \mathbf{x}^\bullet \in O, \\ 0, & \text{otherwise,} \end{cases} \quad (\text{G50})$$

where on the right-hand side $\mathbf{x}^\bullet$ denotes the point where the ray from the scattering point $\mathbf{x}_1 = \mathbf{x}_0 + s_0 \boldsymbol{\omega}_0$ in direction $\boldsymbol{\omega}^\bullet$ intersects the detector area O . Hence,

$$1490 \quad \int_O \int_0^\infty h(\mathbf{x}^\bullet - s_1 \boldsymbol{\omega}^\bullet) \mu_\bullet ds_1 dO = \int_{O_0} \int_0^\infty h(\mathbf{x}_0 + s_0 \boldsymbol{\omega}_0) \chi(\mathbf{x}^\bullet) \mu_0 ds_0 dO_0. \quad (\text{G51})$$

Dividing by $\mu_\bullet$ gives

$$\int_O \int_0^\infty h(\mathbf{x}^\bullet - s_1 \boldsymbol{\omega}^\bullet) ds_1 dO = \frac{\mu_0}{\mu_\bullet} \int_{O_0} \int_0^\infty h(\mathbf{x}_0 + s_0 \boldsymbol{\omega}_0) \chi(\mathbf{x}^\bullet) ds_0 dO_0. \quad (\text{G52})$$

Equation G52 shows that the factor $\mu_0/\mu_\bullet$ is the Jacobian that appears from rewriting the same scattering-volume integration in solar-side variables instead of detector-side variables.

1495 Using Eqs. G42 and G52, the first-order detector-area-averaged radiance Stokes vector becomes

$$\begin{aligned} \underline{I^{(1)}(O, \boldsymbol{\omega}^\bullet; \boldsymbol{\omega}_0)} = & \frac{\mu_0 E_0}{\mu_\bullet O 4\pi} \int_{O_0} \int_0^\infty a(\mathbf{x}_1) \beta(\mathbf{x}_1) \mathbf{Z}(\mathbf{x}_1, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_0) \mathbf{1} \\ & \times \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)] \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}^\bullet)] \chi(\mathbf{x}^\bullet) ds_0 dO_0, \end{aligned} \quad (\text{G53})$$

where $\mathbf{x}_1 = \mathbf{x}_0 + s_0 \boldsymbol{\omega}_0$, and where $\mathbf{x}^\bullet$ is the intersection point of the ray from $\mathbf{x}_1$ in direction $\boldsymbol{\omega}^\bullet$ with the detector boundary.

G6.2 Second-order contribution

1500 For the second-order contribution, we start from the point-detector expression in Eq. G39 and average it over the detector area O . This gives

$$\begin{aligned} \underline{I^{(2)}(O, \boldsymbol{\omega}^\bullet; \boldsymbol{\omega}_0)} = & \frac{E_0}{O(4\pi)^2} \int_O \int_0^\infty a(\mathbf{x}_2) \beta(\mathbf{x}_2) \exp[-\tau(\mathbf{x}_2 \rightarrow \mathbf{x}^\bullet)] \\ & \times \int_{4\pi} \mathbf{Z}(\mathbf{x}_2, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_1) \int_0^\infty a(\mathbf{x}_1) \beta(\mathbf{x}_1) \mathbf{Z}(\mathbf{x}_1, \boldsymbol{\omega}_1, \boldsymbol{\omega}_0) \mathbf{1} \\ & \times \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)] \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}_2)] ds_1 d\Omega_1 ds_2 dO, \end{aligned} \quad (\text{G54})$$

1505 where

$$\mathbf{x}_2 = \mathbf{x}^\bullet - s_2 \boldsymbol{\omega}^\bullet, \quad \mathbf{x}_1 = \mathbf{x}_2 - s_1 \boldsymbol{\omega}_1. \quad (\text{G55})$$

Thus, in the detector-side parameterisation, the last scattering point $\mathbf{x}_2$ lies on the detector line of sight, while the preceding scattering point $\mathbf{x}_1$ lies upstream of $\mathbf{x}_2$ in direction $-\boldsymbol{\omega}_1$. In forward mode, the same two scattering points are more naturally described by

$$1510 \quad \mathbf{x}_1 = \mathbf{x}_0 + s_0 \boldsymbol{\omega}_0, \quad \mathbf{x}_2 = \mathbf{x}_1 + s_1 \boldsymbol{\omega}_1, \quad (\text{G56})$$

with $\mathbf{x}_0 \in O_0$.

The change of variables is carried out with respect to the *second* scattering point x_2 . For fixed ω_1 and s_1 , the relation between the two scattering points is

$$x_2 = x_1 + s_1 \omega_1, \quad x_1 = x_2 - s_1 \omega_1. \quad (\text{G57})$$

1515 Hence, once x_2 is specified, x_1 is uniquely determined, and vice versa. The map from x_1 to x_2 is therefore a translation, and no additional Jacobian factor is introduced by the relation between the first and second scattering points (i.e., it has Jacobian 1). The only Jacobian arises when the same set of possible second-scattering locations x_2 is parameterised either from the detector side by $(x^\bullet, s_2)$ or from the solar side by (x_0, s_0) . For a horizontal area element dO at the detector boundary and a path-length interval ds_2 along $\omega^\bullet$, the corresponding differential volume of second-scattering locations is

$$1520 \quad dV = \mu_\bullet dO ds_2, \quad \mu_\bullet = |\cos \vartheta^\bullet|. \quad (\text{G58})$$

Likewise, for a horizontal area element dO_0 at the sunlight-entry boundary and a path-length interval ds_0 along ω_0 , the same set of second-scattering locations is described by

$$dV = \mu_0 dO_0 ds_0, \quad \mu_0 = |\cos \vartheta_0|. \quad (\text{G59})$$

Therefore,

$$1525 \quad \mu_\bullet dO ds_2 = \mu_0 dO_0 ds_0, \quad (\text{G60})$$

and hence

$$dO ds_2 = \frac{\mu_0}{\mu_\bullet} dO_0 ds_0. \quad (\text{G61})$$

Exactly as in the first-order case, the indicator function χ is not part of this Jacobian. It only selects those second-scattering points for which the detector ray from x_2 in direction $\omega^\bullet$ intersects the chosen detector area O .

1530 Substituting Eq. G61 into Eq. G54, and using the forward parameterisation in Eq. G56, gives

$$\begin{aligned} I^{(2)}(O, \omega^\bullet; \omega_0) = & \frac{\mu_0 E_0}{\mu_\bullet O (4\pi)^2} \int_{O_0}^{\infty} \int_0^{\infty} a(x_1) \beta(x_1) \exp[-\tau(x_0 \rightarrow x_1)] \\ & \times \int_{4\pi}^{\infty} \int_0^{\infty} a(x_2) \beta(x_2) Z(x_2, \omega^\bullet, \omega_1) Z(x_1, \omega_1, \omega_0) \mathbf{1} \\ & \times \exp[-\tau(x_1 \rightarrow x_2)] \exp[-\tau(x_2 \rightarrow x^\bullet)] \chi(x^\bullet) ds_1 d\Omega_1 ds_0 dO_0, \end{aligned} \quad (\text{G62})$$

with

$$1535 \quad x_1 = x_0 + s_0 \omega_0, \quad x_2 = x_1 + s_1 \omega_1. \quad (\text{G63})$$

Equation G62 is therefore the finite-area forward formulation corresponding to Eq. G39. The factor $\mu_0/\mu_\bullet$ appears because the integration over the second-scattering locations is rewritten from detector-side variables to solar-side variables, whereas the relation between x_1 and x_2 contributes no further Jacobian because it is a translation.

G6.3 Third- and higher-order contributions

1540 For completeness, we also write the third-order contribution first in the detector-side parameterisation. Averaging the point-detector expression of Eq. G40 over the detector area O gives

$$\begin{aligned}
 \underline{I^{(3)}(O, \omega^\bullet; \omega_0)} = & \frac{E_0}{O(4\pi)^3} \int_O \int_0^\infty a(\mathbf{x}_3) \beta(\mathbf{x}_3) \exp[-\tau(\mathbf{x}_3 \rightarrow \mathbf{x}^\bullet)] \\
 & \times \int_{4\pi} \underline{Z(\mathbf{x}_3, \omega^\bullet, \omega_2)} \int_0^\infty a(\mathbf{x}_2) \beta(\mathbf{x}_2) \exp[-\tau(\mathbf{x}_2 \rightarrow \mathbf{x}_3)] \\
 & \times \int_{4\pi} \underline{Z(\mathbf{x}_2, \omega_2, \omega_1)} \int_0^\infty a(\mathbf{x}_1) \beta(\mathbf{x}_1) \underline{Z(\mathbf{x}_1, \omega_1, \omega_0)} \mathbf{1} \\
 & \times \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)] \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}_2)] ds_1 d\Omega_1 ds_2 d\Omega_2 ds_3 dO,
 \end{aligned} \tag{G64}$$

where

$$\underline{\mathbf{x}_3 = \mathbf{x}^\bullet - s_3 \omega^\bullet}, \quad \underline{\mathbf{x}_2 = \mathbf{x}_3 - s_2 \omega_2}, \quad \underline{\mathbf{x}_1 = \mathbf{x}_2 - s_1 \omega_1}. \tag{G65}$$

Thus, in the detector-side parameterisation, the last scattering point $\mathbf{x}_3$ lies on the detector line of sight, while the preceding scattering points $\mathbf{x}_2$ and $\mathbf{x}_1$ lie successively upstream.

1550 For the forward Monte Carlo formulation, the same set of third-scattering locations is instead parameterised from the solar side. As for the second-order contribution, the only Jacobian arises from rewriting the volume element of the last scattering point. The intermediate scattering points are related by translations and therefore introduce no additional Jacobian. This gives

$$\begin{aligned}
 \underline{I^{(3)}(O, \omega^\bullet; \omega_0)} = & \frac{\mu_0 E_0}{\mu_\bullet O(4\pi)^3} \int_{O_0} \int_0^\infty a(\mathbf{x}_1) \beta(\mathbf{x}_1) \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)] \\
 & \times \int_{4\pi} \int_0^\infty a(\mathbf{x}_2) \beta(\mathbf{x}_2) \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}_2)] \\
 & \times \int_{4\pi} \int_0^\infty a(\mathbf{x}_3) \beta(\mathbf{x}_3) \underline{Z(\mathbf{x}_3, \omega^\bullet, \omega_2)} \underline{Z(\mathbf{x}_2, \omega_2, \omega_1)} \underline{Z(\mathbf{x}_1, \omega_1, \omega_0)} \mathbf{1} \\
 & \times \exp[-\tau(\mathbf{x}_2 \rightarrow \mathbf{x}_3)] \exp[-\tau(\mathbf{x}_3 \rightarrow \mathbf{x}^\bullet)] \chi(\mathbf{x}^\bullet) ds_2 d\Omega_2 ds_1 d\Omega_1 ds_0 dO_0,
 \end{aligned} \tag{G66}$$

with

$$\underline{\mathbf{x}_1 = \mathbf{x}_0 + s_0 \omega_0}, \quad \underline{\mathbf{x}_2 = \mathbf{x}_1 + s_1 \omega_1}, \quad \underline{\mathbf{x}_3 = \mathbf{x}_2 + s_2 \omega_2}. \tag{G67}$$

For higher scattering orders, the same pattern continues: one additional scattering direction and one additional free-path variable are introduced for each extra collision. The factor $\mu_0/\mu_\bullet$ appears only once, because only the last scattering location is reparameterised from detector-side variables to solar-side variables. The intermediate collision points are related by translations with Jacobian 1. The indicator function χ likewise remains unchanged, since it always selects whether the ray from the last scattering event intersects the detector area O .

G7 Forward Monte Carlo estimators of the scattered radiance

Up to this point in this appendix, the expressions for the various radiance contributions from different scattering orders have been written in fully deterministic form: they are exact integral representations of the radiance Stokes vector, and no stochastic or Monte Carlo sampling has yet been involved. We now show how those deterministic expressions can be evaluated statistically with Monte Carlo simulations. The basic idea is to interpret the integration variables, such as free-path lengths and scattering directions, as random variables drawn from appropriate probability density functions. In this way, the deterministic radiance integrals are evaluated as sample averages over many independently simulated photon trajectories.

For readability, the derivation below is written for a medium with one atmospheric constituent at each location, described by β , a , and $\mathbf{Z}$. In the actual implementation, a grid cell may contain gas molecules and one or more aerosol types. The free path is then sampled with the total extinction coefficient of the local mixture, after which the interacting constituent is selected with probability β_t/β (Sect. 2.3 and Appendix A). The estimator keeps the same form, but a and $\mathbf{Z}$ are replaced by a_t and $\mathbf{Z}_t$ of the selected constituent type t . Averaged over many photon histories, this is equivalent to using the effective single-scattering matrix of the mixture, see Eq. A24.

G7.1 First-order forward estimator

We first consider the simplest case, namely the first-order scattered radiance. We show how the deterministic first-order radiance leaving TOA at an angle contributes less to outgoing irradiance due to the slanted projection of the horizontal TOA area element. Stokes-vector expression for a finite detector area (Eq. G53) can be evaluated using a forward Monte Carlo simulation.

Now Equation G53 has the form of an integral over the sunlight-entry location $\mathbf{x}_0$ and the first free-path length s_0 . In general, an integral of a vector-valued function $\mathbf{g}_1(\mathbf{x}_0, s_0)$, consider an observer centered at $(\mu^\odot, \varphi^\odot)$, subtending a small solid angle $d\Omega^\odot = d\mu^\odot d\varphi^\odot$. The fraction of the total irradiance at TOA directed towards the observer is given by:

$$dA^\odot = \frac{1}{\pi} R_{11}(\mu^\odot, \mu_0, \varphi^\odot - \varphi_0) \mu^\odot d\mu^\odot d\varphi^\odot.$$

$$\mathbf{J} = \int_{O_0} \int_0^\infty \mathbf{g}_1(\mathbf{x}_0, s_0) ds_0 dO_0, \tag{G68}$$

This quantity also represents the probability that an injected photon at TOA is reflected back to TOA within $d\Omega^\odot$ can be simulated by sampling the random variables $\mathbf{X}_0$ and S_0 from the joint PDF $p(\mathbf{x}_0, s_0)$, and computing the Monte Carlo estimator (see, e.g., Eq. 4.47 of Marshak and Davis, 2005)

$$\mathbf{J} \approx \frac{1}{N} \sum_{i=1}^N \frac{\mathbf{g}_1(\mathbf{X}_{0,i}, S_{0,i})}{p(\mathbf{X}_{0,i}, S_{0,i})}. \quad (\text{G69})$$

The approximation sign indicates that the right-hand side is a finite-sample Monte Carlo estimate of the exact integral. The estimator is unbiased and converges to $\mathbf{J}$ in the limit $N \rightarrow \infty$; for finite N it contains Monte Carlo sampling noise.

In the forward Monte Carlo simulation, photon launch positions are sampled uniformly over O_0 , so that the PDF for the horizontal launch location is

$$p_{O_0}(\mathbf{x}_0) = \frac{1}{O_0}, \quad \mathbf{x}_0 \in O_0. \quad (\text{G70})$$

For a given $\mathbf{x}_0$, the physical probability density for the distance to the first collision along the solar path follows an exponential distribution according to the Lambert-Beer law for radiative attenuation¹³:

$$\Pr(\mu \in d\mu^\odot \wedge \varphi \in d\varphi^\odot) = p(\mu^\odot, \varphi^\odot) d\mu^\odot d\varphi^\odot,$$

$$p_{S_0}(s_0 | \mathbf{x}_0) = \beta(\mathbf{x}_1) \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)], \quad \mathbf{x}_1 = \mathbf{x}_0 + s_0 \boldsymbol{\omega}_0, \quad s_0 \geq 0. \quad (\text{G71})$$

In the simulation, the free path $S_{0,i}$ of photon i is stochastically sampled from $p_{S_0}(s_0 | \mathbf{X}_{0,i})$ using the inverse transform method (see Appendix B). The joint sampling density for a photon trajectory with one scattering event is therefore

$$p(\mathbf{x}_0, s_0) = p_{O_0}(\mathbf{x}_0) p_{S_0}(s_0 | \mathbf{x}_0). \quad (\text{G72})$$

Let $\mathbf{g}_1(\mathbf{x}_0, s_0)$ denote the integrand of Eq. G53. Explicitly,

$$\begin{aligned} \mathbf{g}_1(\mathbf{x}_0, s_0) = & \frac{\mu_0 E_0}{\mu_\bullet O 4\pi} a(\mathbf{x}_1) \beta(\mathbf{x}_1) \mathbf{Z}(\mathbf{x}_1, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_0) \mathbf{1} \\ & \times \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)] \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}^\bullet)] \chi(\mathbf{x}^\bullet). \end{aligned} \quad (\text{G73})$$

Dividing by the sampling densities $p_{O_0}(\mathbf{x}_0) p_{S_0}(s_0 | \mathbf{x}_0)$ yields

$$\begin{aligned} \frac{\mathbf{g}_1(\mathbf{x}_0, s_0)}{p_{O_0}(\mathbf{x}_0) p_{S_0}(s_0 | \mathbf{x}_0)} = & \frac{\mu_0 O_0 E_0}{\mu_\bullet O 4\pi} a(\mathbf{x}_1) \mathbf{Z}(\mathbf{x}_1, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_0) \mathbf{1} \\ & \times \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}^\bullet)] \chi(\mathbf{x}^\bullet). \end{aligned} \quad (\text{G74})$$

¹³In the finite computational domain, this continuous density is accompanied by the probability that the photon reaches the next domain boundary before an atmospheric event occurs.

Thus, the factors $\beta(\mathbf{x}_1)$ and $\exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)]$ cancel with the sampling density and are accounted for implicitly through the stochastic sampling of the free path.

For N simulated photons, each corresponding to an independent realisation of the random pair $(\mathbf{X}_{0,i}, S_{0,i})$, the singly scattered radiance Stokes vector averaged over the detector area O is therefore estimated according to Eq. G69 as

$$\begin{aligned} \mathbf{I}^{(1)}(O, \boldsymbol{\omega}^\bullet; \boldsymbol{\omega}_0) &\approx \frac{\mu_0 O_0 E_0}{\mu_\bullet O 4\pi} \frac{1}{N} \sum_{i=1}^N a(\mathbf{x}_{1,i}) \mathbf{Z}(\mathbf{x}_{1,i}, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_0) \mathbf{1} \\ &\quad \times \exp[-\tau(\mathbf{x}_{1,i} \rightarrow \mathbf{x}_i^\bullet)] \chi(\mathbf{x}_i^\bullet), \end{aligned} \quad (\text{G75})$$

where p is the probability density function (PDF) of the photon reflection towards (μ, φ) . Equating Eqs. ?? and ??, we obtain:

$$\mathbf{x}_{1,i} = \mathbf{X}_{0,i} + S_{0,i} \boldsymbol{\omega}_0$$

denotes the sampled first scattering location of photon i , and $\mathbf{x}_i^\bullet$ is the corresponding detector-boundary intersection point of the ray in direction $\boldsymbol{\omega}^\bullet$.

Equation G75 is the first-order *local estimate* of Marchuk et al. (1980) written in the practical forward Monte Carlo form used here. Photons are launched uniformly over the source area O_0 , the first atmospheric event is sampled along the sunlight direction, and at that event location the contribution towards the detector is evaluated along the collimated direction $\boldsymbol{\omega}^\bullet$.

G7.2 Second-order forward estimator

We now derive the forward Monte Carlo estimator for the second-order radiance Stokes vector contribution. In this case, a photon trajectory contains two scattering events: a first scattering at location $\mathbf{x}_1$, a change of propagation direction to $\boldsymbol{\omega}_1$, and a second scattering at location $\mathbf{x}_2$, at which the contribution towards the detector is computed. We use the finite-area forward formulation derived in Eq. G62.

Equation G62 has the form of an integral over the sunlight-entry location $\mathbf{x}_0$, the first free-path length s_0 , the intermediate propagation direction $\boldsymbol{\omega}_1$, and the second free-path length s_1 . In general, an integral of a vector-valued function $\mathbf{g}_2(\mathbf{x}_0, s_0, \boldsymbol{\omega}_1, s_1)$,

$$R_{11} = \frac{\pi}{\mu^\odot} p(\mu^\odot, \varphi^\odot),$$

$$J = \int_{O_0} \int_0^\infty \int_{4\pi} \int_0^\infty \mathbf{g}_2(\mathbf{x}_0, s_0, \boldsymbol{\omega}_1, s_1) ds_1 d\Omega_1 ds_0 dO_0, \quad (\text{G76})$$

which indeed matches the first element of Eq can be simulated by the Monte Carlo estimator

$$J \approx \frac{1}{N} \sum_{i=1}^N \frac{\mathbf{g}_2(\mathbf{X}_{0,i}, S_{0,i}, \boldsymbol{\Omega}_{1,i}, S_{1,i})}{p(\mathbf{X}_{0,i}, S_{0,i}, \boldsymbol{\Omega}_{1,i}, S_{1,i})}, \quad (\text{G77})$$

where the random quadruples $(\mathbf{X}_{0,i}, S_{0,i}, \boldsymbol{\Omega}_{1,i}, S_{1,i})$ are sampled from the joint density $p(\mathbf{x}_0, s_0, \boldsymbol{\omega}_1, s_1)$ with

$$\mathbf{x}_1 = \mathbf{x}_0 + s_0 \boldsymbol{\omega}_0. \quad (\text{G78})$$

As in the first-order case, photons are launched uniformly over O_0 , so that

$$p_{O_0}(\mathbf{x}_0) = \frac{1}{O_0}, \quad \mathbf{x}_0 \in O_0. \quad (\text{G79})$$

For a given $\mathbf{x}_0$, the first free-path length is sampled from (Appendix B)

$$p_{S_0}(s_0 | \mathbf{x}_0) = \beta(\mathbf{x}_1) \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)], \quad \mathbf{x}_1 = \mathbf{x}_0 + s_0 \boldsymbol{\omega}_0, \quad s_0 \geq 0. \quad (\text{G80})$$

At the first scattering event, the new propagation direction $\boldsymbol{\omega}_1$ is sampled from the angular probability density (Eq. D7)

$$p_{\omega_1}(\boldsymbol{\omega}_1 | \mathbf{x}_1, \mathbf{1}) = \frac{1}{4\pi} [\mathbf{Z}(\mathbf{x}_1, \boldsymbol{\omega}_1, \boldsymbol{\omega}_0) \mathbf{1}]_1. \quad (\text{G81})$$

which reduces to the simple form $F_{11}(\Theta)/(4\pi)$ because the incident solar beam is unpolarised at the first scattering event.

Given $(\mathbf{x}_1, \boldsymbol{\omega}_1)$, the second free-path length is sampled from (Appendix B)

$$p_{S_1}(s_1 | \mathbf{x}_1, \boldsymbol{\omega}_1) = \beta(\mathbf{x}_2) \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}_2)], \quad \mathbf{x}_2 = \mathbf{x}_1 + s_1 \boldsymbol{\omega}_1, \quad s_1 \geq 0. \quad (\text{G82})$$

The joint sampling density for a photon trajectory with two scattering events is therefore

$$p(\mathbf{x}_0, s_0, \boldsymbol{\omega}_1, s_1) = p_{O_0}(\mathbf{x}_0) p_{S_0}(s_0 | \mathbf{x}_0) p_{\omega_1}(\boldsymbol{\omega}_1 | \mathbf{x}_1, \mathbf{1}) p_{S_1}(s_1 | \mathbf{x}_1, \boldsymbol{\omega}_1). \quad (\text{G83})$$

Let $g_2(\mathbf{x}_0, s_0, \boldsymbol{\omega}_1, s_1)$ denote the integrand of Eq. G62. Explicitly,

$$\begin{aligned} g_2(\mathbf{x}_0, s_0, \boldsymbol{\omega}_1, s_1) = & \frac{\mu_0 E_0}{\mu_\bullet O} \frac{1}{(4\pi)^2} a(\mathbf{x}_1) \underbrace{\beta(\mathbf{x}_1) \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)]}_{\text{solar path}} \\ & \times a(\mathbf{x}_2) \underbrace{\beta(\mathbf{x}_2) \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}_2)]}_{\text{inter-collision path}} \mathbf{Z}(\mathbf{x}_2, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_1) \mathbf{Z}(\mathbf{x}_1, \boldsymbol{\omega}_1, \boldsymbol{\omega}_0) \mathbf{1} \\ & \times \exp[-\tau(\mathbf{x}_2 \rightarrow \mathbf{x}^\bullet)] \chi(\mathbf{x}^\bullet). \end{aligned} \quad (\text{G84})$$

Dividing Eq. G84 by the sampling densities shows that the factors

$$\frac{1}{O_0}, \quad \beta(\mathbf{x}_1) \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)], \quad \frac{1}{4\pi} [\mathbf{Z}(\mathbf{x}_1, \boldsymbol{\omega}_1, \boldsymbol{\omega}_0) \mathbf{1}]_1, \quad \beta(\mathbf{x}_2) \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}_2)]$$

cancel with the chosen sampling densities. We define the normalised radiance Stokes vector after the first scattering event as

$$\bar{\mathbf{I}}_1 = \frac{\mathbf{Z}(\mathbf{x}_1, \boldsymbol{\omega}_1, \boldsymbol{\omega}_0) \mathbf{1}}{[\mathbf{Z}(\mathbf{x}_1, \boldsymbol{\omega}_1, \boldsymbol{\omega}_0) \mathbf{1}]_1}. \quad (\text{G85})$$

Using this definition, the remaining contribution becomes

$$\begin{aligned}
 & \frac{g_2(\mathbf{x}_0, s_0, \boldsymbol{\omega}_1, s_1)}{p_{O_0}(\mathbf{x}_0) p_{S_0}(s_0 | \mathbf{x}_0) p_{\omega_1}(\boldsymbol{\omega}_1 | \mathbf{x}_1, \mathbf{1}) p_{S_1}(s_1 | \mathbf{x}_1, \boldsymbol{\omega}_1)} \\
 & = \frac{\mu_0 O_0 E_0}{\mu_\bullet O 4\pi} a(\mathbf{x}_1) a(\mathbf{x}_2) Z(\mathbf{x}_2, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_1) \bar{I}_1 \\
 & \times \exp[-\tau(\mathbf{x}_2 \rightarrow \mathbf{x}^\bullet)] \chi(\mathbf{x}^\bullet).
 \end{aligned} \tag{G86}$$

For N simulated photons, the second-order scattered radiance Stokes vector averaged over the detector area O is therefore estimated as

$$\begin{aligned}
 I^{(2)}(O, \boldsymbol{\omega}^\bullet; \boldsymbol{\omega}_0) & \approx \frac{\mu_0 O_0 E_0}{\mu_\bullet O 4\pi} \frac{1}{N} \sum_{i=1}^N a(\mathbf{x}_{1,i}) a(\mathbf{x}_{2,i}) Z(\mathbf{x}_{2,i}, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_{1,i}) \bar{I}_{1,i} \\
 & \times \exp[-\tau(\mathbf{x}_{2,i} \rightarrow \mathbf{x}_i^\bullet)] \chi(\mathbf{x}_i^\bullet),
 \end{aligned} \tag{G87}$$

where

$$\mathbf{x}_{1,i} = \mathbf{X}_{0,i} + S_{0,i} \boldsymbol{\omega}_0, \quad \mathbf{x}_{2,i} = \mathbf{x}_{1,i} + S_{1,i} \boldsymbol{\Omega}_{1,i},$$

and where $\mathbf{x}_i^\bullet$ is the corresponding detector-boundary intersection point of the ray from $\mathbf{x}_{2,i}$ in direction $\boldsymbol{\omega}^\bullet$. ~~?? if p is simulated with the Monte Carlo estimate $\sum_{j=1}^M \sum_{i=1}^N \Phi_{i,j} / N$, as defined in Sect. 2.3.~~

~~To illustrate the Monte Carlo process with a simple example, assume that the layer consists of vacuum ($\beta = 0$) Equation G87 is the second-order local estimate in the practical forward Monte Carlo form used here: photons are launched uniformly over the source area O_0 , the first and second collision locations are sampled successively along the directions $\boldsymbol{\omega}_0$ and $\boldsymbol{\omega}_1$, and at the second collision point the contribution towards the detector is evaluated along the collimated direction $\boldsymbol{\omega}^\bullet$.~~

G7.3 Third- and higher-order forward estimators

It is useful to evaluate the third-order scattered radiance explicitly, because at this order the polarisation state of the photon starts to affect the sampling of the scattering direction itself. We use the finite-area forward formulation derived in Eq. G66.

Equation G66 has the form of an integral over the sunlight-entry location $\mathbf{x}_0$, the first free-path length s_0 , the first intermediate propagation direction $\boldsymbol{\omega}_1$, the second free-path length s_1 , the second intermediate propagation direction $\boldsymbol{\omega}_2$, and the third free-path length s_2 . In general, an integral of a vector-valued function $g_3(\mathbf{x}_0, s_0, \boldsymbol{\omega}_1, s_1, \boldsymbol{\omega}_2, s_2)$, ~~and that the surface reflects Lambertian with albedo A_s . Consequently, every injected photon reaches the surface, its weight is multiplied by the probability of reflection, A_s (see Sect. 2.3).~~

$$J = \int_{O_0} \int_0^\infty \int_{4\pi} \int_0^\infty \int_{4\pi} \int_0^\infty g_3(\mathbf{x}_0, s_0, \boldsymbol{\omega}_1, s_1, \boldsymbol{\omega}_2, s_2) ds_2 d\Omega_2 ds_1 d\Omega_1 ds_0 dO_0, \tag{G88}$$

can be simulated by the Monte Carlo estimator

$$\underline{J} \approx \frac{1}{N} \sum_{i=1}^N \frac{g_3(\underline{X}_{0,i}, S_{0,i}, \underline{\Omega}_{1,i}, S_{1,i}, \underline{\Omega}_{2,i}, S_{2,i})}{p(\underline{X}_{0,i}, S_{0,i}, \underline{\Omega}_{1,i}, S_{1,i}, \underline{\Omega}_{2,i}, S_{2,i})}. \quad (\text{G89})$$

1685 Here, the random sextuples $(\underline{X}_{0,i}, S_{0,i}, \underline{\Omega}_{1,i}, S_{1,i}, \underline{\Omega}_{2,i}, S_{2,i})$ are sampled from the joint density $p(\underline{x}_0, s_0, \underline{\omega}_1, s_1, \underline{\omega}_2, s_2)$.

As in the first- and ~~subsequently multiplied by~~ second-order cases, photons are launched uniformly over O_0 , so that

$$p_{O_0}(\underline{x}_0) = \frac{1}{O_0}, \quad \underline{x}_0 \in O_0. \quad (\text{G90})$$

For a given $\underline{x}_0$, the first free-path length is sampled from (Appendix B)

$$p_{S_0}(s_0 | \underline{x}_0) = \beta(\underline{x}_1) \exp[-\tau(\underline{x}_0 \rightarrow \underline{x}_1)], \quad \underline{x}_1 = \underline{x}_0 + s_0 \underline{\omega}_0, \quad s_0 \geq 0. \quad (\text{G91})$$

1690 At the first scattering event, the outgoing direction $\underline{\omega}_1$ is sampled from (Eq. D7)

$$p_{\omega_1}(\underline{\omega}_1 | \underline{x}_1, \underline{1}) = \frac{1}{4\pi} [Z(\underline{x}_1, \underline{\omega}_1, \underline{\omega}_0) \underline{1}]_1. \quad (\text{G92})$$

Given $(\underline{x}_1, \underline{\omega}_1)$, the second free-path length is sampled from (Appendix B)

$$p_{S_1}(s_1 | \underline{x}_1, \underline{\omega}_1) = \beta(\underline{x}_2) \exp[-\tau(\underline{x}_1 \rightarrow \underline{x}_2)], \quad \underline{x}_2 = \underline{x}_1 + s_1 \underline{\omega}_1, \quad s_1 \geq 0. \quad (\text{G93})$$

The normalised radiance Stokes vector after the first scattering event is, as in Eq. G85,

$$1695 \quad \bar{\underline{I}}_1 = \frac{Z(\underline{x}_1, \underline{\omega}_1, \underline{\omega}_0) \underline{1}}{[Z(\underline{x}_1, \underline{\omega}_1, \underline{\omega}_0) \underline{1}]_1}. \quad (\text{G94})$$

At the second scattering event, the incident beam is in general already polarised. Therefore, the new direction $\underline{\omega}_2$ must be sampled from the polarisation-dependent angular probability density (Eq. D7)

$$p_{\omega_2}(\underline{\omega}_2 | \underline{x}_2, \bar{\underline{I}}_1, \underline{\omega}_1) = \frac{1}{4\pi} [Z(\underline{x}_2, \underline{\omega}_2, \underline{\omega}_1) \bar{\underline{I}}_1]_1. \quad (\text{G95})$$

The corresponding normalised radiance Stokes vector after the second scattering event is

$$1700 \quad \bar{\underline{I}}_2 = \frac{Z(\underline{x}_2, \underline{\omega}_2, \underline{\omega}_1) \bar{\underline{I}}_1}{[Z(\underline{x}_2, \underline{\omega}_2, \underline{\omega}_1) \bar{\underline{I}}_1]_1}. \quad (\text{G96})$$

Given $(\underline{x}_2, \underline{\omega}_2)$, the third free-path length is sampled from

$$p_{S_2}(s_2 | \underline{x}_2, \underline{\omega}_2) = \beta(\underline{x}_3) \exp[-\tau(\underline{x}_2 \rightarrow \underline{x}_3)], \quad \underline{x}_3 = \underline{x}_2 + s_2 \underline{\omega}_2, \quad s_2 \geq 0. \quad (\text{G97})$$

The joint sampling density for a photon trajectory with three scattering events is therefore

$$p(\underline{x}_0, s_0, \underline{\omega}_1, s_1, \underline{\omega}_2, s_2) = p_{O_0}(\underline{x}_0) p_{S_0}(s_0 | \underline{x}_0) p_{\omega_1}(\underline{\omega}_1 | \underline{x}_1, \underline{1}) p_{S_1}(s_1 | \underline{x}_1, \underline{\omega}_1) \\ \times p_{\omega_2}(\underline{\omega}_2 | \underline{x}_2, \bar{\underline{I}}_1, \underline{\omega}_1) p_{S_2}(s_2 | \underline{x}_2, \underline{\omega}_2). \quad (\text{G98})$$

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Let $g_3(\mathbf{x}_0, s_0, \boldsymbol{\omega}_1, s_1, \boldsymbol{\omega}_2, s_2)$ denote the integrand of Eq. G66. Explicitly,

$$\begin{aligned}
 g_3(\mathbf{x}_0, s_0, \boldsymbol{\omega}_1, s_1, \boldsymbol{\omega}_2, s_2) = & \frac{\mu_0 E_0}{\mu_\bullet O} \frac{1}{(4\pi)^3} a(\mathbf{x}_1) \underbrace{\beta(\mathbf{x}_1) \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)]}_{\text{solar path}} \\
 & \times a(\mathbf{x}_2) \underbrace{\beta(\mathbf{x}_2) \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}_2)]}_{\text{first inter-collision path}} \\
 & \times a(\mathbf{x}_3) \underbrace{\beta(\mathbf{x}_3) \exp[-\tau(\mathbf{x}_2 \rightarrow \mathbf{x}_3)]}_{\text{second inter-collision path}} \mathbf{Z}(\mathbf{x}_3, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_2) \\
 & \times \mathbf{Z}(\mathbf{x}_2, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1) \mathbf{Z}(\mathbf{x}_1, \boldsymbol{\omega}_1, \boldsymbol{\omega}_0) \mathbf{1} \\
 & \times \exp[-\tau(\mathbf{x}_3 \rightarrow \mathbf{x}^\bullet)] \chi(\mathbf{x}^\bullet).
 \end{aligned} \tag{G99}$$

Here,

$$\mathbf{x}_1 = \mathbf{x}_0 + s_0 \boldsymbol{\omega}_0, \quad \mathbf{x}_2 = \mathbf{x}_1 + s_1 \boldsymbol{\omega}_1, \quad \mathbf{x}_3 = \mathbf{x}_2 + s_2 \boldsymbol{\omega}_2. \tag{G100}$$

Dividing Eq. G99 by the sampling densities shows that the factors

$$\begin{aligned}
 \frac{1}{O_0}, \quad \beta(\mathbf{x}_1) \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)], \quad \frac{1}{4\pi} [\mathbf{Z}(\mathbf{x}_1, \boldsymbol{\omega}_1, \boldsymbol{\omega}_0) \mathbf{1}]_1, \\
 \beta(\mathbf{x}_2) \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}_2)], \quad \frac{1}{4\pi} [\mathbf{Z}(\mathbf{x}_2, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1) \bar{\mathbf{I}}_1]_1, \quad \beta(\mathbf{x}_3) \exp[-\tau(\mathbf{x}_2 \rightarrow \mathbf{x}_3)]
 \end{aligned}$$

cancel with the corresponding sampling densities. Using the definition of $\bar{\mathbf{I}}_2$, the remaining contribution becomes

$$\begin{aligned}
 & \frac{g_3(\mathbf{x}_0, s_0, \boldsymbol{\omega}_1, s_1, \boldsymbol{\omega}_2, s_2)}{p_{O_0}(\mathbf{x}_0) p_{S_0}(s_0 | \mathbf{x}_0) p_{\boldsymbol{\omega}_1}(\boldsymbol{\omega}_1 | \mathbf{x}_1, \mathbf{1}) p_{S_1}(s_1 | \mathbf{x}_1, \boldsymbol{\omega}_1) p_{\boldsymbol{\omega}_2}(\boldsymbol{\omega}_2 | \mathbf{x}_2, \bar{\mathbf{I}}_1, \boldsymbol{\omega}_1) p_{S_2}(s_2 | \mathbf{x}_2, \boldsymbol{\omega}_2)} \\
 = & \frac{\mu_0 O_0 E_0}{\mu_\bullet O 4\pi} a(\mathbf{x}_1) a(\mathbf{x}_2) a(\mathbf{x}_3) \mathbf{Z}(\mathbf{x}_3, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_2) \bar{\mathbf{I}}_2 \\
 & \times \exp[-\tau(\mathbf{x}_3 \rightarrow \mathbf{x}^\bullet)] \chi(\mathbf{x}^\bullet).
 \end{aligned} \tag{G101}$$

For N simulated photons, the third-order scattered radiance Stokes vector averaged over the detector area O is therefore estimated as

$$\begin{aligned}
 \mathbf{I}^{(3)}(O, \boldsymbol{\omega}^\bullet; \boldsymbol{\omega}_0) \approx & \frac{\mu_0 O_0 E_0}{\mu_\bullet O 4\pi} \frac{1}{N} \sum_{i=1}^N a(\mathbf{x}_{1,i}) a(\mathbf{x}_{2,i}) a(\mathbf{x}_{3,i}) \mathbf{Z}(\mathbf{x}_{3,i}, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_{2,i}) \bar{\mathbf{I}}_{2,i} \\
 & \times \exp[-\tau(\mathbf{x}_{3,i} \rightarrow \mathbf{x}_i^\bullet)] \chi(\mathbf{x}_i^\bullet),
 \end{aligned} \tag{G102}$$

where

$$\mathbf{x}_{1,i} = \mathbf{X}_{0,i} + S_{0,i}\boldsymbol{\omega}_0, \quad \mathbf{x}_{2,i} = \mathbf{x}_{1,i} + S_{1,i}\boldsymbol{\Omega}_{1,i}, \quad \mathbf{x}_{3,i} = \mathbf{x}_{2,i} + S_{2,i}\boldsymbol{\Omega}_{2,i},$$

and where $\mathbf{x}_i^\bullet$ is the corresponding detector-boundary intersection point of the ray from $\mathbf{x}_{3,i}$ in direction $\boldsymbol{\omega}^\bullet$.

1730 Equation G102 is the third-order local estimate in the practical forward Monte Carlo form used here. In contrast to the first- and second-order cases, the sampling of the second intermediate direction $\boldsymbol{\omega}_2$ is here explicitly polarisation dependent (Eq. G95), because the beam incident on the second scattering event is already polarised.

The pattern that emerges from the third-order case extends directly to all higher scattering orders. Let the normalised Stokes vector, which is initialised as $\bar{\mathbf{I}}_0 = \mathbf{1}$ at injection, after scattering order n be

$$\bar{\mathbf{I}}_n = \frac{\mathbf{Z}(\mathbf{x}_n, \boldsymbol{\omega}_n, \boldsymbol{\omega}_{n-1}) \bar{\mathbf{I}}_{n-1}}{[\mathbf{Z}(\mathbf{x}_n, \boldsymbol{\omega}_n, \boldsymbol{\omega}_{n-1}) \bar{\mathbf{I}}_{n-1}]_1}. \quad (\text{G103})$$

1735 Then the Monte Carlo estimator for the n^{th} -order scattered radiance Stokes vector averaged over the detector area O can be written as

$$\begin{aligned} \bar{I}^{(n)}(O, \boldsymbol{\omega}^\bullet; \boldsymbol{\omega}_0) \approx & \frac{\mu_0 O_0 E_0}{\mu_\bullet O 4\pi} \frac{1}{N} \sum_{i=1}^N w_{n,i} \mathbf{Z}(\mathbf{x}_{n,i}, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_{n-1,i}) \bar{\mathbf{I}}_{n-1,i} \\ & \times \exp[-\tau(\mathbf{x}_{n,i} \rightarrow \mathbf{x}_i^\bullet)] \chi(\mathbf{x}_i^\bullet), \end{aligned} \quad (\text{G104})$$

where

$$1740 \quad w_{n,i} = \prod_{l=1}^n a(\mathbf{x}_{l,i}) \quad (\text{G105})$$

is the weight of photon i at scattering order n .

Finally, the total scattered radiance Stokes vector averaged over the detector area O is obtained by summing over all scattering orders:

$$\begin{aligned} \bar{I}(O, \boldsymbol{\omega}^\bullet; \boldsymbol{\omega}_0) = & \sum_{n=1}^{\infty} \bar{I}^{(n)}(O, \boldsymbol{\omega}^\bullet; \boldsymbol{\omega}_0) \\ 1745 \quad \approx & \frac{\mu_0 O_0 E_0}{\mu_\bullet O 4\pi} \frac{1}{N} \sum_{i=1}^N \sum_{n=1}^{M_i} w_{n,i} \mathbf{Z}(\mathbf{x}_{n,i}, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_{n-1,i}) \bar{\mathbf{I}}_{n-1,i} \\ & \times \exp[-\tau(\mathbf{x}_{n,i} \rightarrow \mathbf{x}_i^\bullet)] \chi(\mathbf{x}_i^\bullet), \end{aligned} \quad (\text{G106})$$

where M_i is the total number of scattering events for photon i . Equation G106 shows that, in the Monte Carlo simulation, a photon can be recycled to simulate the radiance contributions from all scattering orders: after computing the local estimate for scattering event n , the photon continues its trajectory through the domain to scattering event $n+1$, and so on, until it leaves the domain or its weight becomes negligible.

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G8 Backward Monte Carlo estimators for the scattered radiance

In backward Monte Carlo, photons are launched from the detector and traced upstream through the medium. As in the forward case, backward Monte Carlo simulates the same detector radiance Stokes vector, but the sampling strategy is reversed: photon trajectories are sampled from detector to source instead of from source to detector.

1755 To remain consistent with the notation of the forward Monte Carlo derivation, we label the scattering events in *forward order*: $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n$, where $\mathbf{x}_1$ is the first scattering event encountered by the incoming solar beam and $\mathbf{x}_n$ the last scattering event before the detector. Likewise, the propagation directions are labelled as $\omega_0, \omega_1, \dots, \omega_n$, where ω_0 is the incident solar-beam direction before the first scattering event and $\omega_n \equiv \omega^\bullet$ is the detector direction after the last scattering event in the forward trajectory. In backward Monte Carlo, the same physical trajectory is sampled in reverse order, starting at event $\mathbf{x}_n$ and ending
1760 at $\mathbf{x}_1$.

As in Appendix G7, the derivation below is written for a medium with one atmospheric scattering constituent type at each location, determining β , a , and Z . The constituent selection used for mixed grid cells is described in Sect. 2.3 and Appendix A.

For polarised radiative transfer, the phase matrix along the reversed trajectory is not identical to the phase matrix in the
1765 forward trajectory, because the Stokes-vector orientation is mirrored, as explained in Sect. 2.4. At a scattering event that has forward incident and scattered directions ω_{n-1} and ω_n , respectively, the backward simulation samples the same event in the reversed geometry, with directions $-\omega_n$ and $-\omega_{n-1}$. The corresponding forward phase matrix is obtained from the phase matrix in the reversed scattering geometry through the reciprocity relation of Hovenier et al. (2004):

$$Z(\mathbf{x}_n, \omega_n, \omega_{n-1}) = \Delta_3 Z(\mathbf{x}_n, -\omega_{n-1}, -\omega_n)^T \Delta_3, \quad \Delta_3 = \text{diag}(1, 1, -1, 1). \quad (\text{G107})$$

1770 In the derivation below we continue to write the phase matrices as they appear along the associated forward trajectory, with the understanding that in the actual backward simulation they are evaluated through Eq. G107.

To retain the full polarisation history during backward sampling, we introduce a normalised 4×4 matrix $\overline{\mathbf{M}}_m$, which contains the cumulative polarisation-dependent detector response after the m detector-side scattering events closest to the detector have been incorporated. At the detector, this matrix is initialised as

$$1775 \quad \overline{\mathbf{M}}_0 = \text{diag}(1, 1, 1, 1), \quad (\text{G108})$$

which is the 4×4 identity matrix.

G8.1 First-order backward estimator

For the first-order contribution, the only scattering point lies on the detector line of sight. The finite-area expression in Eq. G42 is already written in this detector-side parameterisation: the integration is over detector-boundary points $\mathbf{x}^\bullet \in O$ and over the
1780 distance s_1 along the ray opposite to the detector direction. This is precisely the natural parameterisation for backward tracing.

We therefore take Eq. G42 as the starting point, with

$$\mathbf{x}_1 = \mathbf{x}^\bullet - s_1 \boldsymbol{\omega}^\bullet, \quad s_1 > 0. \quad (\text{G109})$$

Here, $\mathbf{x}^\bullet$ is the detector-boundary launch point of the backward photon, and $\mathbf{x}_0$ is the point where the solar ray through $\mathbf{x}_1$ enters the computational domain in direction $\boldsymbol{\omega}_0$. Since the integration is performed directly over the detector area O , no transformation to a source-area parameterisation is needed. Consequently, no factor $\mu_0/\mu_\bullet$ and no indicator function χ appear in the backward formulation.

Equation G42 has the form of an integral over the detector launch location $\mathbf{x}^\bullet$ and the first free-path length s_1 . In general, an integral of a vector-valued function $\mathbf{g}_1^{\text{bw}}(\mathbf{x}^\bullet, s_1)$,

$$\mathbf{J} = \int_O \int_0^\infty \mathbf{g}_1^{\text{bw}}(\mathbf{x}^\bullet, s_1) ds_1 dO, \quad (\text{G110})$$

can be simulated by sampling the random pair $(\mathbf{X}^\bullet, S_1)$ from the joint PDF $p^{\text{bw}}(\mathbf{x}^\bullet, s_1)$ and computing the Monte Carlo estimator

$$\mathbf{J} \approx \frac{1}{N} \sum_{i=1}^N \mathbf{g}_1^{\text{bw}}(\mathbf{X}_i^\bullet, S_{1,i}). \quad (\text{G111})$$

In backward mode, photons are launched uniformly over the detector area O , so that

$$p_O(\mathbf{x}^\bullet) = \frac{1}{O}, \quad \mathbf{x}^\bullet \in O. \quad (\text{G112})$$

For a given launch point $\mathbf{x}^\bullet$, the first free-path length is sampled from the physical Lambert-Beer distribution along the backward trajectory (again, see Appendix B):

$$p_{S_1}^{\text{bw}}(s_1 | \mathbf{x}^\bullet) = \beta(\mathbf{x}_1) \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}^\bullet)], \quad \mathbf{x}_1 = \mathbf{x}^\bullet - s_1 \boldsymbol{\omega}^\bullet, \quad s_1 \geq 0, \quad (\text{G113})$$

noting that $\tau(\mathbf{x}^\bullet \rightarrow \mathbf{x}_1) = \tau(\mathbf{x}_1 \rightarrow \mathbf{x}^\bullet)$. The joint sampling density for a photon trajectory with one scattering event is therefore

$$p^{\text{bw}}(\mathbf{x}^\bullet, s_1) = p_O(\mathbf{x}^\bullet) p_{S_1}^{\text{bw}}(s_1 | \mathbf{x}^\bullet). \quad (\text{G114})$$

Let $\mathbf{g}_1^{\text{bw}}(\mathbf{x}^\bullet, s_1)$ denote the integrand of Eq. G42. Explicitly,

$$\begin{aligned} \mathbf{g}_1^{\text{bw}}(\mathbf{x}^\bullet, s_1) = & \frac{E_0}{4\pi O} a(\mathbf{x}_1) \beta(\mathbf{x}_1) \mathbf{Z}(\mathbf{x}_1, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_0) \mathbf{1} \\ & \times \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)] \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}^\bullet)]. \end{aligned} \quad (\text{G115})$$

Dividing by the sampling densities $p_O(\mathbf{x}^\bullet) p_{S_1}^{\text{bw}}(s_1 | \mathbf{x}^\bullet)$ yields

$$\frac{g_1^{\text{bw}}(\mathbf{x}^\bullet, s_1)}{p_O(\mathbf{x}^\bullet) p_{S_1}^{\text{bw}}(s_1 | \mathbf{x}^\bullet)} = \frac{E_0}{4\pi} a(x_1) \mathbf{Z}(x_1, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_0) \mathbf{1} \exp[-\tau(x_0 \rightarrow x_1)]. \quad (\text{G116})$$

Thus, the factors $\beta(x_1)$ and $\exp[-\tau(x_1 \rightarrow \mathbf{x}^\bullet)]$ cancel with the sampling density and are accounted for implicitly through the stochastic sampling of the backward free path.

For N simulated photons, the singly scattered detector-area-averaged radiance Stokes vector is therefore estimated as

$$\mathbf{I}^{(1)}(O, \boldsymbol{\omega}^\bullet; \boldsymbol{\omega}_0) \approx \frac{E_0}{4\pi} \frac{1}{N} \sum_{i=1}^N a(x_{1,i}) \mathbf{Z}(x_{1,i}, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_0) \mathbf{1} \exp[-\tau(x_{0,i} \rightarrow x_{1,i})], \quad (\text{G117})$$

where

$$x_{1,i} = X_i^\bullet - S_{1,i} \boldsymbol{\omega}^\bullet. \quad (\text{G118})$$

Here, $X_i^\bullet$ is the sampled detector launch position of photon i , and $x_{0,i}$ is the point where the solar ray through $x_{1,i}$ in direction $-\boldsymbol{\omega}_0$ enters the computational domain. Compared to the first-order forward estimator (Eq. G75), the PDF of the reflection direction towards the observer, μ/π (Eq. G75), has been absorbed into the backward free-path sampling, while the remaining explicit transmittance is the direct solar transmittance from $x_{1,i}$ to the source boundary. Equation G117 is therefore the first-order local estimate in practical backward Monte Carlo form.

G8.2 Second-order backward estimator

For the second-order contribution, the last scattering point of the forward trajectory, x_2 , lies on the detector line of sight, while the preceding scattering point, x_1 , lies upstream of x_2 in direction $-\boldsymbol{\omega}_1$. The finite-area expression in Eq. G54 is already written in this detector-side parameterisation, with

$$x_2 = \mathbf{x}^\bullet - s_2 \boldsymbol{\omega}^\bullet, \quad x_1 = x_2 - s_1 \boldsymbol{\omega}_1, \quad s_2 > 0, \quad s_1 > 0. \quad (\text{G119})$$

We therefore use Eq. G54 as the starting point for the second-order backward estimator. Here, $\mathbf{x}^\bullet \in O$ is the detector-boundary launch point of the backward photon, and x_0 is the point where the solar ray through x_1 enters the computational domain in direction $\boldsymbol{\omega}_0$. ~~(13)~~

Equation G54 has the form of an integral over the detector launch location $\mathbf{x}^\bullet$, the free-path length s_2 from the detector to the last scattering event, the intermediate propagation direction $\boldsymbol{\omega}_1$, and the free-path length s_1 from x_2 to x_1 . In general, an integral of a vector-valued function $g_2^{\text{bw}}(\mathbf{x}^\bullet, s_2, \boldsymbol{\omega}_1, s_1)$, ~~when computing the photon's contribution to~~

$$\mathbf{J} = \int_O \int_0^\infty \int_{4\pi} \int_0^\infty g_2^{\text{bw}}(\mathbf{x}^\bullet, s_2, \boldsymbol{\omega}_1, s_1) ds_1 d\Omega_1 ds_2 dO, \quad (\text{G120})$$

1830 can be simulated by sampling the random quadruple $(\mathbf{X}^\bullet, S_2, \Omega_1, S_1)$ from the joint PDF $p^{\text{bw}}(\mathbf{x}^\bullet, s_2, \omega_1, s_1)$ and computing the Monte Carlo estimator

$$J \approx \frac{1}{N} \sum_{i=1}^N \frac{g_2^{\text{bw}}(\mathbf{X}_i^\bullet, S_{2,i}, \Omega_{1,i}, S_{1,i})}{p^{\text{bw}}(\mathbf{X}_i^\bullet, S_{2,i}, \Omega_{1,i}, S_{1,i})}. \quad (\text{G121})$$

As in the first-order case, the detector launch position is sampled uniformly over O , so that

$$p_O(\mathbf{x}^\bullet) = \frac{1}{O}, \quad \mathbf{x}^\bullet \in O. \quad (\text{G122})$$

For a given launch point $\mathbf{x}^\bullet$, the free-path length to the last scattering point is sampled from (Appendix B)

$$1835 \quad p_{S_2}^{\text{bw}}(s_2 | \mathbf{x}^\bullet) = \beta(\mathbf{x}_2) \exp[-\tau(\mathbf{x}_2 \rightarrow \mathbf{x}^\bullet)], \quad \mathbf{x}_2 = \mathbf{x}^\bullet - s_2 \omega^\bullet, \quad s_2 \geq 0. \quad (\text{G123})$$

At $\mathbf{x}_2$, the preceding direction ω_1 is sampled from the backward angular probability density (Eq. D11)

$$p_{\omega_1}^{\text{bw}}(\omega_1 | \mathbf{x}_2, \omega^\bullet, \overline{M}_0) = \frac{1}{4\pi} [\overline{M}_0 \mathbf{Z}(\mathbf{x}_2, \omega^\bullet, \omega_1) \mathbf{1}]_1 = \frac{1}{4\pi} [\mathbf{Z}(\mathbf{x}_2, \omega^\bullet, \omega_1) \mathbf{1}]_1, \quad (\text{G124})$$

and the detector-response matrix is updated according to

$$\overline{M}_1 = \frac{\overline{M}_0 \mathbf{Z}(\mathbf{x}_2, \omega^\bullet, \omega_1)}{[\overline{M}_0 \mathbf{Z}(\mathbf{x}_2, \omega^\bullet, \omega_1) \mathbf{1}]_1}. \quad (\text{G125})$$

1840 Given $(\mathbf{x}_2, \omega_1)$, the free-path length from $\mathbf{x}_2$ to $\mathbf{x}_1$ is sampled from (Appendix B)

$$p_{S_1}^{\text{bw}}(s_1 | \mathbf{x}_2, \omega_1) = \beta(\mathbf{x}_1) \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}_2)], \quad \mathbf{x}_1 = \mathbf{x}_2 - s_1 \omega_1, \quad s_1 \geq 0. \quad (\text{G126})$$

The joint sampling density for a photon trajectory with two scattering events is therefore

$$p^{\text{bw}}(\mathbf{x}^\bullet, s_2, \omega_1, s_1) = p_O(\mathbf{x}^\bullet) p_{S_2}^{\text{bw}}(s_2 | \mathbf{x}^\bullet) p_{\omega_1}^{\text{bw}}(\omega_1 | \mathbf{x}_2, \omega^\bullet, \overline{M}_0) p_{S_1}^{\text{bw}}(s_1 | \mathbf{x}_2, \omega_1). \quad (\text{G127})$$

Let $g_2^{\text{bw}}(\mathbf{x}^\bullet, s_2, \omega_1, s_1)$ denote the integrand of Eq. G54. Explicitly,

$$1845 \quad g_2^{\text{bw}}(\mathbf{x}^\bullet, s_2, \omega_1, s_1) = \frac{E_0}{O(4\pi)^2} a(\mathbf{x}_2) \underbrace{\beta(\mathbf{x}_2) \exp[-\tau(\mathbf{x}_2 \rightarrow \mathbf{x}^\bullet)]}_{\text{upstream detector path}} \\ \times a(\mathbf{x}_1) \underbrace{\beta(\mathbf{x}_1) \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}_2)]}_{\text{upstream inter-collision path}} \mathbf{Z}(\mathbf{x}_2, \omega^\bullet, \omega_1) \mathbf{Z}(\mathbf{x}_1, \omega_1, \omega_0) \mathbf{1} \\ \times \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)]. \quad (\text{G128})$$

Dividing Eq. G128 by the joint sampling density shows that the factors

$$\frac{1}{O}, \quad \beta(\mathbf{x}_2) \exp[-\tau(\mathbf{x}_2 \rightarrow \mathbf{x}^\bullet)], \quad \frac{1}{4\pi} [\mathbf{Z}(\mathbf{x}_2, \omega^\bullet, \omega_1) \mathbf{1}]_1, \quad \beta(\mathbf{x}_1) \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}_2)]$$

1850 cancel with the chosen sampling densities. The remaining contribution is

$$\frac{g_2^{\text{bw}}(\mathbf{x}^\bullet, s_2, \boldsymbol{\omega}_1, s_1)}{p_O(\mathbf{x}^\bullet) p_{S_2}^{\text{bw}}(s_2 | \mathbf{x}^\bullet) p_{\boldsymbol{\omega}_1}^{\text{bw}}(\boldsymbol{\omega}_1 | \mathbf{x}_2, \boldsymbol{\omega}^\bullet, \overline{\mathbf{M}}_0) p_{S_1}^{\text{bw}}(s_1 | \mathbf{x}_2, \boldsymbol{\omega}_1)} \\ = \frac{E_0}{4\pi} a(\mathbf{x}_2) a(\mathbf{x}_1) \overline{\mathbf{M}}_1 \mathbf{Z}(\mathbf{x}_1, \boldsymbol{\omega}_1, \boldsymbol{\omega}_0) \mathbf{1} \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)]. \quad (\text{G129})$$

For N simulated photons, the second-order scattered detector-area-averaged radiance Stokes vector is therefore estimated as

$$1855 \quad I^{(2)}(O, \boldsymbol{\omega}^\bullet; \boldsymbol{\omega}_0) \approx \frac{E_0}{4\pi} \frac{1}{N} \sum_{i=1}^N a(\mathbf{x}_{2,i}) a(\mathbf{x}_{1,i}) \overline{\mathbf{M}}_{1,i} \mathbf{Z}(\mathbf{x}_{1,i}, \boldsymbol{\omega}_{1,i}, \boldsymbol{\omega}_0) \mathbf{1} \exp[-\tau(\mathbf{x}_{0,i} \rightarrow \mathbf{x}_{1,i})], \quad (\text{G130})$$

where

$$\mathbf{x}_{2,i} = \mathbf{X}_i^\bullet - S_{2,i} \boldsymbol{\omega}^\bullet, \quad \mathbf{x}_{1,i} = \mathbf{x}_{2,i} - S_{1,i} \boldsymbol{\Omega}_{1,i}. \quad (\text{G131})$$

1860 Here, $\mathbf{X}_i^\bullet$ is the sampled detector launch position of photon i , and $\mathbf{x}_{0,i}$ is the point where the solar ray through $\mathbf{x}_{1,i}$ in direction $-\boldsymbol{\omega}_0$ enters the computational domain. Equation G130 is therefore the second-order local estimate in practical backward Monte Carlo form: photons are launched uniformly over the detector area O , the last scattering event is sampled first along the detector line of sight, the preceding direction and preceding scattering point are then sampled upstream, and at the first forward scattering event the contribution from the solar direction is evaluated through the direct transmittance towards the source.

G8.3 Third- and higher-order backward estimators

1865 The advantage of the detector-response matrix formulation becomes particularly clear for the third-order contribution. At this order, the sampling of the upstream direction at the second backward scattering event already depends on the polarisation history accumulated between that event and the detector.

The deterministic starting point is the detector-side finite-area expression in Eq. G64. This expression is already written in the natural variables for backward tracing: the last scattering point of the forward trajectory lies on the detector line of sight, and the preceding scattering points are reached successively upstream.

$$1870 \quad \mathbf{x}_3 = \mathbf{x}^\bullet - s_3 \boldsymbol{\omega}^\bullet, \quad \mathbf{x}_2 = \mathbf{x}_3 - s_2 \boldsymbol{\omega}_2, \quad \mathbf{x}_1 = \mathbf{x}_2 - s_1 \boldsymbol{\omega}_1, \quad s_3 > 0, \quad s_2 > 0, \quad s_1 > 0. \quad (\text{G132})$$

Here, $\mathbf{x}^\bullet \in O$ is the detector-boundary launch point of the backward photon, and $\mathbf{x}_0$ is the point where the solar ray through $\mathbf{x}_1$ enters the computational domain in direction $\boldsymbol{\omega}_0$. Since Eq. G64 is kept in this detector-side parameterisation, no transformation to a source-area formulation is needed in backward mode. Consequently, no factor $\mu_0/\mu_\bullet$ and no detector-selection function χ appear.

1875 As in the lower-order cases, the detector launch position is sampled uniformly over O according to Eq. G112. For a given launch point $\mathbf{x}^\bullet$, the free-path length to the last scattering point is sampled from (Appendix B)

$$p_{S_3}^{\text{bw}}(s_3 | \mathbf{x}^\bullet) = \beta(\mathbf{x}_3) \exp[-\tau(\mathbf{x}_3 \rightarrow \mathbf{x}^\bullet)], \quad \mathbf{x}_3 = \mathbf{x}^\bullet - s_3 \boldsymbol{\omega}^\bullet, \quad s_3 \geq 0. \quad (\text{G133})$$

At $\mathbf{x}_3$, the preceding direction ω_2 is sampled from the backward angular probability density (Eq. D11)

$$p_{\omega_2}^{\text{bw}}(\omega_2 | \mathbf{x}_3, \omega^\bullet, \overline{M}_0) = \frac{1}{4\pi} [\overline{M}_0 \mathbf{Z}(\mathbf{x}_3, \omega^\bullet, \omega_2) \mathbf{1}]_1 = \frac{1}{4\pi} [\mathbf{Z}(\mathbf{x}_3, \omega^\bullet, \omega_2) \mathbf{1}]_1, \quad (\text{G134})$$

1880 and the first detector-response update is again

$$\overline{M}_1 = \frac{\overline{M}_0 \mathbf{Z}(\mathbf{x}_3, \omega^\bullet, \omega_2)}{[\overline{M}_0 \mathbf{Z}(\mathbf{x}_3, \omega^\bullet, \omega_2) \mathbf{1}]_1}, \quad (\text{G135})$$

which is identical in form to Eq. G125.

Given $(\mathbf{x}_3, \omega_2)$, the free-path length from $\mathbf{x}_3$ to $\mathbf{x}_2$ is sampled from (Appendix B)

$$p_{S_2}^{\text{bw}}(s_2 | \mathbf{x}_3, \omega_2) = \beta(\mathbf{x}_2) \exp[-\tau(\mathbf{x}_2 \rightarrow \mathbf{x}_3)], \quad \mathbf{x}_2 = \mathbf{x}_3 - s_2 \omega_2, \quad s_2 \geq 0. \quad (\text{G136})$$

1885 At $\mathbf{x}_2$, the next upstream direction ω_1 is sampled from (Eq. D11)

$$p_{\omega_1}^{\text{bw}}(\omega_1 | \mathbf{x}_2, \omega_2, \overline{M}_1) = \frac{1}{4\pi} [\overline{M}_1 \mathbf{Z}(\mathbf{x}_2, \omega_2, \omega_1) \mathbf{1}]_1. \quad (\text{G137})$$

This density depends explicitly on the accumulated detector response through $\overline{M}_1$; this is the first scattering order at which the backward angular sampling itself becomes explicitly polarisation-dependent. The detector-response matrix is then updated to

$$\overline{M}_2 = \frac{\overline{M}_1 \mathbf{Z}(\mathbf{x}_2, \omega_2, \omega_1)}{[\overline{M}_1 \mathbf{Z}(\mathbf{x}_2, \omega_2, \omega_1) \mathbf{1}]_1}. \quad (\text{G138})$$

1890 Finally, given $(\mathbf{x}_2, \omega_1)$, the free-path length from $\mathbf{x}_2$ to $\mathbf{x}_1$ is sampled from (Appendix B)

$$p_{S_1}^{\text{bw}}(s_1 | \mathbf{x}_2, \omega_1) = \beta(\mathbf{x}_1) \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}_2)], \quad \mathbf{x}_1 = \mathbf{x}_2 - s_1 \omega_1, \quad s_1 \geq 0. \quad (\text{G139})$$

The joint sampling density for a photon trajectory with three scattering events is therefore

$$p^{\text{bw}}(\mathbf{x}^\bullet, s_3, \omega_2, s_2, \omega_1, s_1) = p_O(\mathbf{x}^\bullet) p_{S_3}^{\text{bw}}(s_3 | \mathbf{x}^\bullet) p_{\omega_2}^{\text{bw}}(\omega_2 | \mathbf{x}_3, \omega^\bullet, \overline{M}_0) \\ \times p_{S_2}^{\text{bw}}(s_2 | \mathbf{x}_3, \omega_2) p_{\omega_1}^{\text{bw}}(\omega_1 | \mathbf{x}_2, \omega_2, \overline{M}_1) p_{S_1}^{\text{bw}}(s_1 | \mathbf{x}_2, \omega_1). \quad (\text{G140})$$

1895 Let $g_3^{\text{bw}}(\mathbf{x}^\bullet, s_3, \omega_2, s_2, \omega_1, s_1)$ denote the integrand of Eq. G64. Explicitly,

$$g_3^{\text{bw}}(\mathbf{x}^\bullet, s_3, \omega_2, s_2, \omega_1, s_1) = \frac{E_0}{(4\pi)^3 O} a(\mathbf{x}_3) \underbrace{\beta(\mathbf{x}_3) \exp[-\tau(\mathbf{x}_3 \rightarrow \mathbf{x}^\bullet)]}_{\text{upstream detector path}} \\ \times a(\mathbf{x}_2) \underbrace{\beta(\mathbf{x}_2) \exp[-\tau(\mathbf{x}_2 \rightarrow \mathbf{x}_3)]}_{\text{first upstream inter-collision path}} \\ \times a(\mathbf{x}_1) \underbrace{\beta(\mathbf{x}_1) \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}_2)]}_{\text{second upstream inter-collision path}} \mathbf{Z}(\mathbf{x}_3, \omega^\bullet, \omega_2) \mathbf{Z}(\mathbf{x}_2, \omega_2, \omega_1) \mathbf{Z}(\mathbf{x}_1, \omega_1, \omega_0) \mathbf{1} \\ \times \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)]. \quad (\text{G141})$$

1900 Dividing Eq. G141 by the joint sampling density Eq. G140 shows that the factors

$$\frac{1}{Q}, \quad \beta(\mathbf{x}_3) \exp[-\tau(\mathbf{x}_3 \rightarrow \mathbf{x}^\bullet)], \quad \frac{1}{4\pi} [\mathbf{Z}(\mathbf{x}_3, \boldsymbol{\omega}^\bullet, \boldsymbol{\omega}_2) \mathbf{1}]_1,$$

$$\beta(\mathbf{x}_2) \exp[-\tau(\mathbf{x}_2 \rightarrow \mathbf{x}_3)], \quad \frac{1}{4\pi} [\overline{\mathbf{M}}_1 \mathbf{Z}(\mathbf{x}_2, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1) \mathbf{1}]_1, \quad \beta(\mathbf{x}_1) \exp[-\tau(\mathbf{x}_1 \rightarrow \mathbf{x}_2)]$$

cancel with the chosen sampling densities. The remaining contribution is

$$\begin{aligned} & \frac{g_3^{\text{bw}}(\mathbf{x}^\bullet, s_3, \boldsymbol{\omega}_2, s_2, \boldsymbol{\omega}_1, s_1)}{p_O(\mathbf{x}^\bullet) p_{S_3}^{\text{bw}}(s_3 | \mathbf{x}^\bullet) p_{\omega_2}^{\text{bw}}(\boldsymbol{\omega}_2 | \mathbf{x}_3, \boldsymbol{\omega}^\bullet, \overline{\mathbf{M}}_0) p_{S_2}^{\text{bw}}(s_2 | \mathbf{x}_3, \boldsymbol{\omega}_2) p_{\omega_1}^{\text{bw}}(\boldsymbol{\omega}_1 | \mathbf{x}_2, \boldsymbol{\omega}_2, \overline{\mathbf{M}}_1) p_{S_1}^{\text{bw}}(s_1 | \mathbf{x}_2, \boldsymbol{\omega}_1)} \\ &= \frac{E_0}{4\pi} a(\mathbf{x}_3) a(\mathbf{x}_2) a(\mathbf{x}_1) \overline{\mathbf{M}}_2 \mathbf{Z}(\mathbf{x}_1, \boldsymbol{\omega}_1, \boldsymbol{\omega}_0) \mathbf{1} \exp[-\tau(\mathbf{x}_0 \rightarrow \mathbf{x}_1)]. \end{aligned} \quad (\text{G142})$$

For N simulated photons, the third-order scattered detector-area-averaged radiance Stokes vector is therefore estimated as

$$\mathbf{I}^{(3)}(O, \boldsymbol{\omega}^\bullet; \boldsymbol{\omega}_0) \approx \frac{E_0}{4\pi} \frac{1}{N} \sum_{i=1}^N a(\mathbf{x}_{3,i}) a(\mathbf{x}_{2,i}) a(\mathbf{x}_{1,i}) \overline{\mathbf{M}}_{2,i} \mathbf{Z}(\mathbf{x}_{1,i}, \boldsymbol{\omega}_{1,i}, \boldsymbol{\omega}_0) \mathbf{1} \exp[-\tau(\mathbf{x}_{0,i} \rightarrow \mathbf{x}_{1,i})]. \quad (\text{G143})$$

Here,

$$1910 \quad \mathbf{x}_{3,i} = \mathbf{X}_i^\bullet - S_{3,i} \boldsymbol{\omega}^\bullet, \quad \mathbf{x}_{2,i} = \mathbf{x}_{3,i} - S_{2,i} \boldsymbol{\Omega}_{2,i}, \quad \mathbf{x}_{1,i} = \mathbf{x}_{2,i} - S_{1,i} \boldsymbol{\Omega}_{1,i}, \quad (\text{G144})$$

where $\mathbf{X}_i^\bullet$ is the sampled detector launch position of photon i , and $\mathbf{x}_{0,i}$ is the point where the solar ray through $\mathbf{x}_{1,i}$ in direction $-\boldsymbol{\omega}_0$ enters the computational domain.

The pattern of the third-order derivation extends directly to all higher scattering orders. At each detector-side scattering event, the detector-response matrix is updated according to

$$1915 \quad \overline{\mathbf{M}}_m = \frac{\overline{\mathbf{M}}_{m-1} \mathbf{Z}(\mathbf{x}_{n-m+1}, \boldsymbol{\omega}_{n-m+1}, \boldsymbol{\omega}_{n-m})}{[\overline{\mathbf{M}}_{m-1} \mathbf{Z}(\mathbf{x}_{n-m+1}, \boldsymbol{\omega}_{n-m+1}, \boldsymbol{\omega}_{n-m}) \mathbf{1}]_1}, \quad m = 1, \dots, n-1. \quad (\text{G145})$$

The backward Monte Carlo estimator for the n^{th} -order detector-area-averaged radiance Stokes vector is therefore

$$\mathbf{I}^{(n)}(O, \boldsymbol{\omega}^\bullet; \boldsymbol{\omega}_0) \approx \frac{E_0}{4\pi} \frac{1}{N} \sum_{i=1}^N w_{n,i} \overline{\mathbf{M}}_{n-1,i} \mathbf{Z}(\mathbf{x}_{1,i}, \boldsymbol{\omega}_{1,i}, \boldsymbol{\omega}_0) \mathbf{1} \exp[-\tau(\mathbf{x}_{0,i} \rightarrow \mathbf{x}_{1,i})]. \quad (\text{G146})$$

where

$$w_{n,i} = \prod_{l=1}^n a(\mathbf{x}_{l,i}) \quad (\text{G147})$$

1920 is the photon weight at scattering order n .

In analogy with Eq. ??-G106, the total scattered detector-area-averaged radiance Stokes vector is

$$I(O, \omega^\bullet; \omega_0) = \sum_{n=1}^{\infty} I^{(n)}(O, \omega^\bullet; \omega_0) \approx \frac{E_0}{4\pi} \frac{1}{N} \sum_{i=1}^N \sum_{n=1}^{M_i} w_{n,i} \bar{M}_{n-1,i} \mathbf{Z}(x_{1,i}, \omega_{1,i}, \omega_0) \mathbf{1} \exp[-\tau(x_{0,i} \rightarrow x_{1,i})], \quad (\text{G148})$$

where M_i is the total number of scattering events for photon i . **Finally, a new photon direction-**

1925 It should be noted that the incident polarisation state along the backward trajectory need not be known a priori, because the propagated matrix $\bar{M}$ represents the polarisation-dependent detector response rather than a physical radiance Stokes vector. The actual incident solar Stokes vector, $E_0 \mathbf{1}$, enters the estimator only when the backward trajectory reaches the solar-side scattering event x_1 . Hence, forward and backward Monte Carlo simulate the same detector radiance Stokes vector, while differing only in the way the photon trajectories are sampled.

G9 Classical angular sampling based on unpolarised PDFs

1930 In this section, we discuss an alternative strategy for sampling the scattering direction in Monte Carlo simulations of polarised light, for both forward and backward tracing. The key idea is that the scattering direction can either be sampled from the full polarisation-dependent probability density function (PDF) such as in MONKI, or from a simplified PDF corresponding to unpolarised radiation, combined with an importance-sampling correction (Collins et al., 1972) such as used in MYSTIC (Emde et al., 2010) that we call the classical approach.

1935 In forward Monte Carlo, the scattering direction at a second- or higher-order scattering event depends on the polarisation state of the incident radiation at the scattering particle. For example, at the second scattering event of a photon trajectory that continues to higher order, located at x_2 , the incident direction ω_1 is known, and the outgoing direction ω_2 to the next scattering event must be sampled. As shown in Eq. G95, the physically correct PDF for sampling ω_2 is **sampled-after-reflection-(App.C)**

$$1940 \quad p_{\omega_2}(\omega_2 \mid x_2, \bar{\mathbf{I}}_1, \omega_1) = \frac{1}{4\pi} [Z(x_2, \omega_2, \omega_1) \bar{\mathbf{I}}_1]_1, \quad (\text{G149})$$

where $\bar{\mathbf{I}}_1$ is the normalised radiance Stokes vector immediately before the scattering event. In the classical approach, the scattering direction is instead sampled from the PDF corresponding to unpolarised incident radiation,

$$p_{\omega_2}^{(0)}(\omega_2 \mid x_2, \omega_1) = \frac{1}{4\pi} [Z(x_2, \omega_2, \omega_1) \mathbf{1}]_1. \quad (\text{G150})$$

In that case, the photon's weight w must be multiplied with the correction factor:

$$1945 \quad C_{\omega_2} = \frac{[Z(x_2, \omega_2, \omega_1) \bar{\mathbf{I}}_1]_1}{[Z(x_2, \omega_2, \omega_1) \mathbf{1}]_1}. \quad (\text{G151})$$

In backward Monte Carlo, photons are traced from the detector towards the source. At a scattering event at x_2 , the direction ω_2 towards the detector is known, and the preceding direction ω_1 must be sampled. As shown in Eq. G137, the physically

correct sampling PDF is

$$p_{\omega_1}^{\text{bw}}(\omega_1 | x_2, \omega_2, \bar{M}_1) = \frac{1}{4\pi} [\bar{M}_1 Z(x_2, \omega_2, \omega_1) \mathbf{1}]_1, \quad (\text{G152})$$

1950 where $\bar{M}_1$ is the propagated normalised detector-response matrix. Analogously to the forward case, in the classical approach the unpolarised sampling PDF is used

$$p_{\omega_1}^{\text{bw},(0)}(\omega_1 | x_2, \omega_2) = \frac{1}{4\pi} [Z(x_2, \omega_2, \omega_1) \mathbf{1}]_1. \quad (\text{G153})$$

The corresponding correction factor is then

$$C_{\omega_1}^{\text{bw}} = \frac{[\bar{M}_1 Z(x_2, \omega_2, \omega_1) \mathbf{1}]_1}{[Z(x_2, \omega_2, \omega_1) \mathbf{1}]_1}. \quad (\text{G154})$$

1955 The use of approximate PDFs (Eqs. G150 and G153) yields unbiased estimators only when combined with the corresponding correction factors (Eqs. G151 and G154). However, as demonstrated by García Muñoz and Mills (2015), this classical approach, which neglects the radiation's polarisation state during directional sampling, is not well suited for optically thick and strongly polarising media. In such environments, the scattering direction is strongly influenced by the polarisation state, particularly for Rayleigh scattering at angles near $\Theta \sim 90^\circ$ and for some values of σ_1 (see Fig. 3 of García Muñoz and Mills, 2015). In such
1960 geometries, the polarised probability density ($[Z\bar{I}]_1$ in the numerator) can be significantly larger than the unpolarised density ($[Z\mathbf{1}]_1$ in the denominator) used for sampling. If a photon trajectory contains multiple collisions in such regions, repeated multiplication by correction factors larger than unity leads to large cumulative weight fluctuations (see Fig. 6). This produces infrequent but disproportionately large photon weights that dominate the Monte Carlo variance and may severely degrade the practical convergence of the simulation. MONKI avoids these variance-producing factors by sampling directly from the full
1965 polarisation-dependent distribution.

G10 Multi-column implementation of the scattered-radiance Monte Carlo estimators

In the main text, the simulated detector radiance is written for a horizontally inhomogeneous rectangular domain that is discretised into $N_x \times N_y$ horizontal grid columns of equal area O . In this appendix, we connect the general forward and backward estimators derived in Appendices G7–G8 to that practical multi-column implementation, using the notation introduced
1970 in Sect. 2.2.

We consider one selected detector column with horizontal area O at TOA or BOA, and we denote by $I(O, \omega^\bullet; \omega_0)$ the radiance Stokes vector averaged over that area. The incident solar radiation is represented by collimated parallel beams in direction ω_0 , and the detector local estimations are evaluated along collimated parallel beams in direction $\omega^\bullet$. Here, x_0 denotes a photon injection point at the domain boundary, while $x^\bullet$ denotes the point where a local-estimation ray in direction $\omega^\bullet$
1975 intersects the boundary at TOA or BOA.

As in Appendices G7–G8, we suppress the constituent type index t in the notation below. In the actual implementation, β is the total extinction coefficient of the local mixture, while a and ~~the photon travels upward leaving the domain~~ Z at an

atmospheric event are the single-scattering albedo and phase matrix of the selected constituent. Thus, in a grid cell containing several constituents, a and $\mathbf{Z}$ represent a_t and $\mathbf{Z}_t$. Thus

1980 **G10.1 Forward implementation**

In the present forward implementation, N photons are injected uniformly into each source column. Since the domain contains $N_x N_y$ source columns of equal area O , the total illuminated horizontal domain boundary is $N_x N_y O$ and the total number of injected photons is $N_x N_y N$. Applying the general forward finite-area estimator of Eq. G106 to the full illuminated horizontal domain boundary, the practical forward estimator of the radiance Stokes vector emerging from the specific column with horizontal detector area O is

$$\begin{aligned} \underline{I(O, \omega^\bullet; \omega_0)} &\approx \frac{\mu_0 N_x N_y O}{\mu_\bullet O} \frac{E_0}{N_x N_y N} \sum_{j=1}^{N_x N_y} \sum_{i=1}^N \sum_{n=1}^{M_{i,j}} \mathbf{W}_{n,i,j} \chi_{n,i,j}, \\ &= \frac{\mu_0}{\mu_\bullet} \frac{E_0}{N} \sum_{j=1}^{N_x N_y} \sum_{i=1}^N \sum_{n=1}^{M_{i,j}} \mathbf{W}_{n,i,j} \chi_{n,i,j}, \quad \text{where} \quad \chi_{n,i,j} = \begin{cases} 1, & \text{if } \mathbf{x}_{n,i,j}^\bullet \in O, \\ 0, & \text{otherwise.} \end{cases} \end{aligned} \quad (\text{G155})$$

and

$$\underline{\mathbf{W}_{n,i,j}} = w_{n,i,j} \frac{1}{4\pi} \mathbf{Z}(\mathbf{x}_{n,i,j}, \omega^\bullet, \omega_{n-1,i,j}) \bar{\mathbf{I}}_{n-1,i,j} \exp \left[- \int_0^{s_{n,i,j}^\bullet} \beta(\mathbf{x}_{n,i,j} + s' \omega^\bullet) ds' \right], \quad (\text{G156})$$

1990 with

$$\underline{w_{n,i,j}} = \prod_{l=1}^n a(\mathbf{x}_{l,i,j}). \quad (\text{G157})$$

Here, $\mathbf{x}_{n,i,j}$ is the location of the n^{th} scattering event of photon i injected in source column j , carrying weight $w_{n,i,j}$, and $\mathbf{x}_{n,i,j}^\bullet$ is the intersection point of the local-estimation ray $\mathbf{x}_{n,i,j} + s' \omega^\bullet$ with the detector boundary. The indicator function $\chi_{n,i,j}$ selects only those local-estimation contributions whose detector-boundary intersection point $\mathbf{x}_{n,i,j}^\bullet$ lies inside the selected detector column. Thus, photons injected in columns other than the selected detector column may still contribute to the detector signal, provided that their local-estimation ray intersects the considered detector area O . The factor $\mu_0/\mu_\bullet$ in Eq. G155 is the same factor as in the general forward finite-area expressions (Eqs. G53, G62, and G66), which comes from rewriting the scattering-volume integration in terms of the source area and solar beam, instead of detector area and line of sight.

2000 **G10.2 Backward implementation**

In backward mode, photons are injected uniformly into the selected detector column O in direction $-\omega^\bullet$. Therefore, consistent with the general backward estimator of Eq. G148, the practical backward estimator of the radiance Stokes vector emerging

from the selected column with horizontal detector area O is simply

$$I(O, \omega^\bullet; \omega_0) \approx \frac{E_0}{N} \sum_{i=1}^N \sum_{n=1}^{M_i} \mathbf{W}_{n,i}^{\text{bw}}, \quad (\text{G158})$$

with

$$\mathbf{W}_{n,i}^{\text{bw}} = w_{n,i} \frac{1}{4\pi} \overline{\mathbf{M}}_{n-1,i} \mathbf{Z}(\mathbf{x}_{1,i}, \omega_{1,i}, \omega_0) \mathbf{1} \exp \left[- \int_0^{s_{0,i}} \beta(\mathbf{x}_{1,i} - s' \omega_0) ds' \right], \quad (\text{G159})$$

where

$$w_{n,i} = \prod_{l=1}^n a(\mathbf{x}_{l,i}), \quad (\text{G160})$$

and where $s_{0,i}$ is the distance from the first forward scattering event $\mathbf{x}_{1,i}$ to the entry point of the incident sunlight $\mathbf{x}_{0,i}$. No factor $\mu_0/\mu_\bullet$ appears in Eq. G158, because in backward mode we directly use the line-of-sight formulation of the radiance expressions (e.g., Eqs. G42, G54, and G64). In those expressions, the integration is performed directly over the detector area O and the backward free-path variables. Hence, no sum over the $N_x \times N_y$ source columns and no indicator function are needed.

Appendix H: Derivation of the formal solution of the VRTE using Green's functions

Here, we derive the formal solution of the vector radiative transfer equations (VRTE) as presented in Appendix G2, using the method of Green's functions. We refer to the Supplementary material of this paper for a brief introduction to Green's functions with an example.

H1 Rearranging the VRTE

To derive a formal expression for the radiance Stokes vector $\mathbf{I}(\mathbf{x}, \omega)$, we start from the steady-state, monochromatic VRTE written as (Eq. G3)

$$\mathcal{L} \mathbf{I}(\mathbf{x}, \omega) = \frac{1}{4\pi} \frac{\beta_{\text{sca}}(\mathbf{x})}{\beta(\mathbf{x})} \int_{4\pi} \mathbf{Z}(\mathbf{x}, \omega, \omega') \mathbf{I}(\mathbf{x}, \omega') d\Omega' + \frac{\mathbf{S}_0(\mathbf{x}, \omega)}{\beta(\mathbf{x})}, \quad (\text{H1})$$

where

$$\mathcal{L} := 1 + \frac{1}{\beta(\mathbf{x})} \omega \cdot \nabla \quad (\text{H2})$$

is a linear differential operator. For notational simplicity, we suppress the λ -dependence throughout this appendix. For convenience, we define the local source term

$$\mathbf{q}(\mathbf{x}, \omega) = \frac{1}{4\pi} \frac{\beta_{\text{sca}}(\mathbf{x})}{\beta(\mathbf{x})} \int_{4\pi} \mathbf{Z}(\mathbf{x}, \omega, \omega') \mathbf{I}(\mathbf{x}, \omega') d\Omega' + \frac{\mathbf{S}_0(\mathbf{x}, \omega)}{\beta(\mathbf{x})}, \quad (\text{H3})$$

2025 so that Eq. H1 becomes

$$\mathcal{L} \mathbf{I}(\mathbf{x}, \boldsymbol{\omega}) = \mathbf{q}(\mathbf{x}, \boldsymbol{\omega}). \quad (\text{H4})$$

Because the extinction coefficient $\beta(\mathbf{x})$ is a scalar, the operator $\mathcal{L}$ acts identically on all four components of the Stokes vector. Thus, the propagation and extinction part of the VRTE does not mix the Stokes components, and all polarisation coupling is contained in the scattering term through the phase matrix $\mathbf{Z}$ and is therefore part of the source term $\mathbf{q}$. For this reason, the Green's function associated with $\mathcal{L}$ is a scalar function rather than a 4×4 matrix, and it multiplies each component of the Stokes vector in the same way.

In the derivation below, we assume homogeneous inflow boundary conditions along each ray. Physically, this means that no radiation enters the medium from outside through the upstream boundary in the direction $\boldsymbol{\omega}$. External illumination, such as the direct solar beam, is represented by the source term $\mathbf{S}_0$ rather than by an inhomogeneous boundary condition.

2035 H2 Reduction to one dimension along a straight path

For a fixed observation point $\mathbf{x}$ and propagation direction $\boldsymbol{\omega}$, we parameterise the upstream ray by the distance coordinate s , defined such that points along the ray are given by $\mathbf{x} - s\boldsymbol{\omega}$, with

$$0 \leq s \leq s_b, \quad (\text{H5})$$

where s denotes the distance measured from the observation point backward along the ray, and s_b is the distance from the observation point to the upstream boundary of the medium. Thus, $s = 0$ corresponds to the observation point itself, while larger values of s lie farther upstream. Along this path, we define

$$\mathbf{I}(s, \boldsymbol{\omega}) := \mathbf{I}(\mathbf{x} - s\boldsymbol{\omega}, \boldsymbol{\omega}), \quad \mathbf{q}(s, \boldsymbol{\omega}) := \mathbf{q}(\mathbf{x} - s\boldsymbol{\omega}, \boldsymbol{\omega}). \quad (\text{H6})$$

The directional derivative then becomes

$$\boldsymbol{\omega} \cdot \nabla = - \frac{d}{ds}, \quad (\text{H7})$$

2045 because increasing s moves opposite to the propagation direction $\boldsymbol{\omega}$. Hence, the operator $\mathcal{L}$ reduces to the one-dimensional form

$$\mathcal{L}_s = 1 - \frac{1}{\beta(s)} \frac{d}{ds}. \quad (\text{H8})$$

Accordingly, Eq. H4 becomes

$$\mathcal{L}_s \mathbf{I}(s, \boldsymbol{\omega}) = \mathbf{q}(s, \boldsymbol{\omega}), \quad (\text{H9})$$

2050 with homogeneous inflow boundary condition

$$\mathbf{I}(s_b, \boldsymbol{\omega}) = \mathbf{0}. \quad (\text{H10})$$

Thus, along each fixed ray direction $\boldsymbol{\omega}$, the vector radiative transfer problem reduces to a first-order ordinary differential equation in the upstream distance coordinate s .

H3 Definition of the Green's function

2055 Let an arbitrary evaluation point along the ray be located at s , and let a source point be located at s^* , where both s and s^* are measured as upstream distances from the observation point ($s = 0$). The corresponding Green's function $G(s, s^*)$ satisfies¹⁴ (see Supplementary material)

$$\mathcal{L}_s[G(s, s^*)] = \delta(s - s^*), \quad (\text{H11})$$

or, after multiplying both sides by $\beta(s)$, ~~each photon reflects only once ($M=1$),~~

2060
$$\left(-\frac{d}{ds} + \beta(s)\right)G(s, s^*) = \beta(s)\delta(s - s^*).$$
 (H12)

Once the Green's function is known, the solution of Eq. H9 can be written as

$$I(s, \omega) = \int_0^{s_b} G(s, s^*) \mathbf{q}(s^*, \omega) ds^*. \quad (\text{H13})$$

Because $G(s, s^*)$ is scalar, it multiplies each component of the source vector $\mathbf{q}(s^*, \omega)$ in exactly the same way. Equation H13 therefore expresses the Stokes vector at the evaluation point s as the superposition of contributions from all source points s^* along the ray.

2065

H4 Solution for $s \neq s^*$

For all $s \neq s^*$, the Dirac delta function in Eq. H12 vanishes, and the Green's function satisfies

$$\frac{dG}{ds} = \beta(s)G. \quad (\text{H14})$$

Solving this equation separately on the intervals $s < s^*$ and ~~MONKI computes for all N photons: $s > s^*$ gives~~

2070
$$G(s, s^*) = \begin{cases} C_-(s^*) \exp\left[-\int_s^{s^*} \beta(s') ds'\right], & s < s^*, \\ C_+(s^*) \exp\left[\int_{s^*}^s \beta(s') ds'\right], & s > s^*, \end{cases} \quad (\text{H15})$$

where $C_-(s^*)$ and $C_+(s^*)$ are integration constants that may depend on the source position s^* . The two integration constants differ because the point $s = s^*$ is singular: the Dirac delta function can introduce a discontinuity there, so the solutions on the two sides of s^* must be treated separately.

¹⁴In this appendix, symbol G denotes a Green's function, and is not the CDF of an arbitrary function g as in Appendix F.

H5 Jump condition and causality

2075 To determine these constants, we integrate Eq. H12 across a small interval $[s^* - \epsilon, s^* + \epsilon]$ around the source point:

$$\underline{p} \int_{s^* - \epsilon}^{s^* + \epsilon} \left[-\frac{dG}{ds} + \beta(\underline{\mu^\ominus s}) G(s, \underline{\varphi^\ominus s^*}) \right] ds = \frac{\sum_{i=1}^N \Phi_i}{N} = \frac{\sum_{i=1}^N \frac{\mu^\ominus}{\pi} A_s}{N} = \frac{\mu^\ominus}{\pi} A_s \int_{s^* - \epsilon}^{s^* + \epsilon} \beta(s) \delta(s - s^*) ds. \quad (\text{H16})$$

As $\epsilon \rightarrow 0$, the integral of βG over the vanishingly small interval tends to zero, whereas the derivative term yields the jump condition

$$G(s^{*-}, s^*) - G(s^{*+}, s^*) = \beta(s^*). \quad (\text{H17})$$

2080 Here, s^{*-} denotes a point immediately closer to the observation point than s^* , whereas s^{*+} denotes a point immediately farther upstream. This jump condition reflects the presence of a point source at $s = s^*$, where the Green's function itself is discontinuous.

For a transport equation, radiation propagates from larger values of s toward smaller values, i.e. from upstream towards the observation point. A source located at s^* therefore contributes only to evaluation points with $s < s^*$, while points farther upstream ($s > s^*$) remain unaffected. This causality requirement implies

$$G(s, s^*) = 0 \quad \text{for } s > s^*, \quad (\text{H18})$$

so that

$$G(s^{*+}, s^*) = 0. \quad (\text{H19})$$

Combining the jump condition with the causality condition gives

$$2090 \quad G(s^{*-}, s^*) = \beta(s^*). \quad (\text{H20})$$

Comparing this with Eq. H15 shows that

$$C_-(s^*) = \beta(s^*), \quad C_+(s^*) = 0. \quad (\text{H21})$$

H6 Formal solution along a ray

The complete one-dimensional Green's function is therefore

$$2095 \quad G(s, s^*) = \beta(s^*) H(s^* - s) \exp \left[-\int_s^{s^*} \beta(s') ds' \right], \quad (\text{H22})$$

where H is the Heaviside step function. The factor $H(s^* - s)$ ensures that only source points located upstream of the evaluation point contribute to the solution, while the exponential factor accounts for attenuation along the optical path between s^* and s .

Substituting Eq. ~~??~~ H22 into Eq. ~~??~~ yields the expected result: H13 yields

$$\underline{I(s, \omega)} = \int_0^{s_b} \beta(s^*) H(s^* - s) \exp \left[- \int_s^{s^*} \beta(s') ds' \right] \underline{q(s^*, \omega)} ds^*. \quad (\text{H23})$$

2100 Equation H23 therefore expresses the Stokes vector at the evaluation point s as the cumulative contribution of all local source vectors along the ray, each exponentially attenuated between its point of origin and that evaluation point. In particular, at the observation point ($s = 0$) we obtain

$$\underline{I(0, \omega)} = \int_0^{s_b} \beta(s^*) \exp \left[- \int_0^{s^*} \beta(s') ds' \right] \underline{q(s^*, \omega)} ds^*. \quad (\text{H24})$$

2105 where no Heaviside function appears since for $s = 0$ we have $H(s^* - s) = H(s^*) = 1$ for $s^* \in [0, s_b]$. Equation H24 expresses the Stokes vector at the observation point as the cumulative contribution of all source points along the upstream ray, each exponentially attenuated between its point of origin and the observation point.

H7 Three-dimensional formal solution

We now rewrite Eq. H24 in 3D spatial coordinates. Because s^* is defined as the upstream distance from the observation point, a source point $\underline{x}^*$ along the ray through the observation point $\underline{x}$ in direction ω is written as

$$2110 \quad \underline{x}^* = \underline{x} - s^* \omega, \quad s^* \geq 0. \quad (\text{H25})$$

Hence,

$$s^* = \|\underline{x} - \underline{x}^*\|, \quad \hat{\underline{r}} = \frac{\underline{x} - \underline{x}^*}{\|\underline{x} - \underline{x}^*\|}, \quad (\text{H26})$$

where $\hat{\underline{r}}$ is the unit vector pointing from the source point $\underline{x}^*$ to the observation point $\underline{x}$. In spherical coordinates centered at $\underline{x}$, the differential volume element is

$$2115 \quad \underline{d^3 x^*} = s^{*2} ds^* d\Omega_{\hat{\underline{r}}}, \quad (\text{H27})$$

where $d\Omega_{\hat{\underline{r}}}$ is the differential solid-angle element. The factor s^{*2} arises from the Jacobian of the transformation from Cartesian to spherical coordinates.

To restrict the integration to points lying exactly on the ray in direction ω , we use the Dirac delta distribution on the unit sphere:

$$2120 \quad \underline{R_{11}} \underline{1} = \underline{A_s}, \int_{4\pi} \delta(\omega - \hat{\underline{r}}) \underline{d\Omega_{\hat{\underline{r}}}}. \quad (\text{H28})$$

confirming the correct formulation. Multiplying by this identity collapses the angular integration and leaves only contributions from points $\mathbf{x}^*$ for which $\hat{\mathbf{r}} = \boldsymbol{\omega}$, i.e. source points that lie on the ray through $\mathbf{x}$ with the correct orientation. Hence,

$$ds^* = \delta(\boldsymbol{\omega} - \hat{\mathbf{r}}) \frac{1}{s^{*2}} d^3 \mathbf{x}^*. \quad (\text{H29})$$

Rewriting $\hat{\mathbf{r}}$ and s^* in terms of $\mathbf{x}$ and $\mathbf{x}^*$ gives the desired transformation

$$2125 \quad ds^* = \delta\left(\boldsymbol{\omega} - \frac{\mathbf{x} - \mathbf{x}^*}{\|\mathbf{x} - \mathbf{x}^*\|}\right) \frac{1}{\|\mathbf{x} - \mathbf{x}^*\|^2} d^3 \mathbf{x}^*. \quad (\text{H30})$$

The Dirac delta function ensures that only points $\mathbf{x}^*$ along the ray through $\mathbf{x}$ in direction $\boldsymbol{\omega}$ contribute to the integral, while the factor $1/\|\mathbf{x} - \mathbf{x}^*\|^2$ arises from the Jacobian that converts the line integral into a volume integral.

Using Eq. H30, the one-dimensional formal solution at the observation point can be written in 3D spatial coordinates as

$$2130 \quad \begin{aligned} I(\mathbf{x}, \boldsymbol{\omega}) = & \int_{\mathcal{V}} \beta(\mathbf{x}^*) \exp \left[- \int_0^{\|\mathbf{x} - \mathbf{x}^*\|} \beta(\mathbf{x}^* + s' \boldsymbol{\omega}) ds' \right] \\ & \times q(\mathbf{x}^*, \boldsymbol{\omega}) \delta\left(\boldsymbol{\omega} - \frac{\mathbf{x} - \mathbf{x}^*}{\|\mathbf{x} - \mathbf{x}^*\|}\right) \frac{1}{\|\mathbf{x} - \mathbf{x}^*\|^2} d^3 \mathbf{x}^*, \end{aligned} \quad (\text{H31})$$

where the integration extends over the spatial domain $\mathcal{V}$ of the medium. The local source term follows from Eq. H3:

$$q(\mathbf{x}, \boldsymbol{\omega}) = \frac{1}{4\pi} \frac{\beta_{\text{sca}}(\mathbf{x})}{\beta(\mathbf{x})} \int_{4\pi} \mathbf{Z}(\mathbf{x}, \boldsymbol{\omega}, \boldsymbol{\omega}') I(\mathbf{x}, \boldsymbol{\omega}') d\Omega' + \frac{\mathbf{S}_0(\mathbf{x}, \boldsymbol{\omega})}{\beta(\mathbf{x})}. \quad (\text{H32})$$

Equation H31 shows that the radiance Stokes vector at point $\mathbf{x}$ in direction $\boldsymbol{\omega}$ is the superposition of contributions from all upstream source points $\mathbf{x}^*$ lying on the ray through $\mathbf{x}$. Each contribution is weighted by the local source vector $\mathbf{q}$ and attenuated exponentially along the optical path between $\mathbf{x}^*$ and $\mathbf{x}$. Note that in the 1D formulation (Eq. H24), the Heaviside factor no longer appeared because the solution had been specialised to the observation point $s = 0$, for which $H(s^* - s) = H(s^*) = 1$ over the integration range $s^* \in [0, s_b]$. In the final three-dimensional volume formulation of Eq. ??-H31, the corresponding upstream restriction is already enforced by the Dirac delta function, which selects only source points $\mathbf{x}^*$ lying on the ray through $\mathbf{x}$ with the correct orientation. Therefore, no separate Heaviside function is needed.

2140 *Author contributions.* VT developed MONKI, derived the theoretical framework, performed the simulations unless otherwise stated, and wrote the manuscript. PW was closely involved in the development of MONKI and tested MONKI as a user. JW did the validation of MONKI against the benchmark results of Emde et al. (2018). PS did the simulations with DAK for the comparison with MONKI (Fig. S6). All authors reviewed the manuscript and were involved in the selection of the results presented in this paper.

Competing interests. The authors declare that they have no conflict of interest.

2145 References

- Anderson, G. P., Clough, S. A., Kneizys, F. X., Chetwynd, J. H., and Shettle, E. P.: AFGL Atmospheric Constituent Profiles (0–120 km), AFGL-TR-86-0110, Air Force Geophysics Laboratory, Hanscom Air Force Base, MA, environmental Research Papers, No. 954, 1986.
- Bagnulo, S., Belskaya, I., Cellino, A., Kwon, Y. G., Muñoz, O., and Stam, D. M.: Polarimetry of Solar System minor bodies and planets: Polarimetry of Solar System minor bodies and planets, *The Astronomy and Astrophysics Review*, 32, 7, <https://doi.org/10.1007/s00159-024-00157-w>, 2024.
- 2150 Barker, H. W., Goldstein, R. K., and Stevens, D. E.: Monte Carlo Simulation of Solar Reflectances for Cloudy Atmospheres., *Journal of the Atmospheric Sciences*, 60, 1881–1894, [https://doi.org/10.1175/1520-0469\(2003\)060<1881:MCSOSR>2.0.CO;2](https://doi.org/10.1175/1520-0469(2003)060<1881:MCSOSR>2.0.CO;2), 2003.
- Barlakas, V., Macke, A., and Wendisch, M.: SPARTA - Solver for Polarized Atmospheric Radiative Transfer Applications: Introduction and application to Saharan dust fields, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 178, 77–92, <https://doi.org/10.1016/j.jqsrt.2016.02.019>, 2016.
- 2155 Bartel, S. and Hielscher, A. H.: Monte Carlo Simulations of the Diffuse Backscattering Mueller Matrix for Highly Scattering Media, *Applied Optics*, 39, 1580–1588, <https://doi.org/10.1364/AO.39.001580>, 2000.
- Bass, A. M. and Paur, R. J.: The ultraviolet cross-sections of ozone. I. The measurements. II - Results and temperature dependence, in: *Atmospheric ozone; Proceedings of the Quadrennial*, edited by Zerefos, C. S. and Ghazi, A., pp. 606–616, 1985.
- 2160 Bates, D. R.: Rayleigh scattering by air, *Planetary and Space Science*, 32, 785–790, [https://doi.org/10.1016/0032-0633\(84\)90102-8](https://doi.org/10.1016/0032-0633(84)90102-8), 1984.
- Bodhaine, B. A., Wood, N. B., Dutton, E. G., and Slusser, J. R.: On Rayleigh Optical Depth Calculations, *Journal of Atmospheric and Oceanic Technology*, 16, 1854, [https://doi.org/10.1175/1520-0426\(1999\)016<1854:ORODC>2.0.CO;2](https://doi.org/10.1175/1520-0426(1999)016<1854:ORODC>2.0.CO;2), 1999.
- Breon, F. M. and Doutriaux-Boucher, M.: A Comparison of Cloud Droplet Radii Measured From Space, *IEEE Transactions on Geoscience and Remote Sensing*, 43, 1796–1805, <https://doi.org/10.1109/TGRS.2005.852838>, 2005.
- 2165 Buras, R. and Mayer, B.: Efficient unbiased variance reduction techniques for Monte Carlo simulations of radiative transfer in cloudy atmospheres: The solution, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 112, 434–447, <https://doi.org/10.1016/j.jqsrt.2010.10.005>, 2011.
- Chandrasekhar, S.: *Radiative transfer*, Dover Publications, New York, 1960.
- Collins, D. G., Blättner, W. G., Wells, M. B., and Horak, H. G.: Backward Monte Carlo Calculations of the Polarization Characteristics of the Radiation Emerging from Spherical-Shell Atmospheres, *Applied Optics*, 11, 2684–2696, <https://doi.org/10.1364/AO.11.002684>, 1972.
- 2170 Cornet, C., C-Labonnote, L., and Szczap, F.: Three-dimensional polarized Monte Carlo atmospheric radiative transfer model (3DMCPOL): 3D effects on polarized visible reflectances of a cirrus cloud, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 111, 174–186, <https://doi.org/10.1016/j.jqsrt.2009.06.013>, 2010.
- Cornet, C., -Labonnote, L. C., Waquet, F., Szczap, F., Deaconu, L., Parol, F., Vanbauce, C., Thieuleux, F., and Riédi, J.: Cloud heterogeneity on cloud and aerosol above cloud properties retrieved from simulated total and polarized reflectances, *Atmospheric Measurement Techniques*, 11, 3627–3643, <https://doi.org/10.5194/amt-11-3627-2018>, 2018.
- 2175 de Haan, J. F., Bosma, P. B., and Hovenier, J. W.: The adding method for multiple scattering calculations of polarized light, *Astronomy & Astrophysics*, 183, 371–391, 1987.
- de Rooij, W. A. and van der Stap, C. C. A. H.: Expansion of Mie scattering matrices in generalized spherical functions, *Astronomy and Astrophysics*, 131, 237–248, 1984.
- 2180 Deirmendjian, D.: *Electromagnetic scattering on spherical polydispersions.*, American Elsevier Publishing Company, 1969.

- Dekking, F., Kraaikamp, C., Lopuhaa, H., and Meester, L.: A modern introduction to probability theory and statistics, Springer Londen, <https://doi.org/https://doi.org/10.1007/1-84628-168-7>, 2005.
- Deschamps, P. Y., Breon, F. M., Leroy, M., Podaire, A., Bricaud, A., Buriez, J. C., and Seze, G.: The POLDER mission: instrument characteristics and scientific objectives, *IEEE Transactions on Geoscience and Remote Sensing*, 32, 598–615, <https://doi.org/10.1109/36.297978>, 1994.
- Deutschmann, T.: On Modeling Elastic and Inelastic Polarized Radiation Transport in the Earth Atmosphere with Monte Carlo Methods, Dissertation (dr. rer. nat.), Universität Leipzig, Leipzig, Germany, [https://ul.qucosa.de/landing-page/?tx_dlf\[id\]=https%3A%2F%2Ful.qucosa.de%2Fapi%2Fqucosa%253A13186%2Fmets](https://ul.qucosa.de/landing-page/?tx_dlf[id]=https%3A%2F%2Ful.qucosa.de%2Fapi%2Fqucosa%253A13186%2Fmets), 2015.
- 2190 Deutschmann, T., Beirle, S., Frieß, U., Grzegorski, M., Kern, C., Kritten, L., Platt, U., Prados-Román, C., Puķīte, J., Wagner, T., Werner, B., and Pfeilsticker, K.: The Monte Carlo atmospheric radiative transfer model McArtim: Introduction and validation of Jacobians and 3D features, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 112, 1119–1137, <https://doi.org/10.1016/j.jqsrt.2010.12.009>, 2011.
- Emde, C. and Mayer, B.: Errors induced by the neglect of polarization in radiance calculations for three-dimensional cloudy atmospheres, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 218, 151–160, <https://doi.org/10.1016/j.jqsrt.2018.07.001>, 2018.
- 2195 Emde, C., Buras, R., Mayer, B., and Blumthaler, M.: The impact of aerosols on polarized sky radiance: model development, validation, and applications, *Atmospheric Chemistry and Physics*, 10, 383–396, <https://doi.org/10.5194/acp-10-383-2010>, 2010.
- Emde, C., Barlas, V., Cornet, C., Evans, F., Wang, Z., Labonotte, L. C., Macke, A., Mayer, B., and Wendisch, M.: IPRT polarized radiative transfer model intercomparison project - Three-dimensional test cases (phase B), *Journal of Quantitative Spectroscopy and Radiative Transfer*, 209, 19–44, <https://doi.org/10.1016/j.jqsrt.2018.01.024>, 2018.
- 2200 Evans, K. F.: The Spherical Harmonics Discrete Ordinate Method for Three-Dimensional Atmospheric Radiative Transfer., *Journal of the Atmospheric Sciences*, 55, 429–446, [https://doi.org/10.1175/1520-0469\(1998\)055<0429:TSHDOM>2.0.CO;2](https://doi.org/10.1175/1520-0469(1998)055<0429:TSHDOM>2.0.CO;2), 1998.
- Fauche, T., Cornet, C., Szczap, F., Dubuisson, P., and Rosambert, T.: Impact of cirrus clouds heterogeneities on top-of-atmosphere thermal infrared radiation, *Atmospheric Chemistry and Physics*, 14, 5599–5615, <https://doi.org/10.5194/acp-14-5599-2014>, 2014.
- 2205 García Muñoz, A. and Mills, F. P.: Pre-conditioned backward Monte Carlo solutions to radiative transport in planetary atmospheres. Fundamentals: Sampling of propagation directions in polarising media, *Astronomy and Astrophysics*, 573, A72, <https://doi.org/10.1051/0004-6361/201424042>, 2015.
- Gay, B., Vaillon, R., and Pinar Mengüç, M.: Polarization imaging of multiply-scattered radiation based on integral-vector Monte Carlo method, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 111, 287–294, 2010.
- 2210 Ghail, R., Ansan, V., Bovolo, F., Breuer, D., Campbell, B., and Kiefer, W.: EnVision assessment study report – Understanding why Earth’s closest neighbour is so different (ESA/SCI(2021)1), European Space Agency, <https://sci.esa.int/web/cosmic-vision/-/envision-assessment-study-report-yellow-book>, 2021.
- Hale, G. M. and Query, M. R.: Optical Constants of Water in the 200-nm to 200-μm Wavelength Region, *Applied Optics*, 12, 555–563, <https://doi.org/10.1364/AO.12.000555>, 1973.
- 2215 Hansen, J. E. and Hovenier, J. W.: Interpretation of the polarization of Venus., *Journal of the Atmospheric Sciences*, 31, 1137–1160, [https://doi.org/10.1175/1520-0469\(1974\)031<1137:IOTPOV>2.0.CO;2](https://doi.org/10.1175/1520-0469(1974)031<1137:IOTPOV>2.0.CO;2), 1974.
- Hansen, J. E. and Travis, L. D.: Light scattering in planetary atmospheres, *Space Science Reviews*, 16, 527–610, <https://doi.org/10.1007/BF00168069>, 1974.

- 2220 Hasekamp, O. P.: Capability of multi-viewing-angle photo-polarimetric measurements for the simultaneous retrieval of aerosol and cloud properties, *Atmospheric Measurement Techniques*, 3, 839–851, <https://doi.org/10.5194/amt-3-839-2010>, 2010.
- Hasekamp, O. P., Fu, G., Rusli, S. P., Wu, L., Di Noia, A., Brugh, J. a. d., Landgraf, J., Martijn Smit, J., Rietjens, J., and van Amerongen, A.: Aerosol measurements by SPEXone on the NASA PACE mission: expected retrieval capabilities, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 227, 170–184, <https://doi.org/10.1016/j.jqsrt.2019.02.006>, 2019.
- 2225 Haus, R., Kappel, D., and Arnold, G.: Radiative heating and cooling in the middle and lower atmosphere of Venus and responses to atmospheric and spectroscopic parameter variations, *Planetary and Space Science*, 117, 262–294, <https://doi.org/10.1016/j.pss.2015.06.024>, 2015.
- Hovenier, J. W. and van der Mee, C. V. M.: Fundamental relationships relevant to the transfer of polarized light in a scattering atmosphere, *AAP*, 128, 1–16, 1983.
- 2230 Hovenier, J. W., Van Der Mee, C., and Domke, H., eds.: Transfer of polarized light in planetary atmospheres : basic concepts and practical methods, vol. 318 of *Astrophysics and Space Science Library*, <https://doi.org/10.1007/978-1-4020-2856-4>, 2004.
- Karalidi, T., Stam, D. M., and Hovenier, J. W.: Flux and polarisation spectra of water clouds on exoplanets, *Astronomy and Astrophysics*, 530, A69, <https://doi.org/10.1051/0004-6361/201116449>, 2011.
- Kemp, J., Henson, G., Steiner, C., Beardsley, I., and Powell, E.: The optical polarization of the Sun, measured at a sensitivity of parts in ten million, *Nature*, 328, <https://doi.org/10.1038/328092a0>, 1987.
- 2235 Kroese, D. P., Taimre, T., and Botev, Z. I.: Handbook of Monte Carlo Methods, Wiley Series in Probability and Statistics, John Wiley & Sons, <https://doi.org/10.1002/9781118014967>, 2011.
- Liou, K. N.: An Introduction to Atmospheric Radiation, Academic Press, San Diego, CA, 2nd edn., 2002.
- Marbach, T., Riedi, J., Lacan, A., and Schlüssel, P.: The 3MI mission: multi-viewing-channel-polarisation imager of the EUMETSAT polar system: second generation (EPS-SG) dedicated to aerosol and cloud monitoring, in: Polarization Science and Remote Sensing VII, edited by Shaw, J. A. and LeMaster, D. A., vol. 9613 of *Society of Photo-Optical Instrumentation Engineers (SPIE) Conference Series*, p. 961310, <https://doi.org/10.1117/12.2186978>, 2015.
- 2240 Marchand, R. and Ackerman, T.: Evaluation of radiometric measurements from the NASA Multiangle Imaging Spectroradiometer (MISR): Two- and three-dimensional radiative transfer modeling of an inhomogeneous stratocumulus cloud deck, *Journal of Geophysical Research (Atmospheres)*, 109, D18208, <https://doi.org/10.1029/2004JD004710>, 2004.
- 2245 Marchuk, G. I., Mikhailov, G. A., Nazaraliev, M. A., Darbinjan, R. A., Kargin, B. A., and Elepov, B. S.: The Monte Carlo Methods in Atmospheric Optics, vol. 12 of *Springer Series in Optical Sciences*, Springer-Verlag, Berlin, Heidelberg, <https://doi.org/10.1007/978-3-540-35237-2>, 1980.
- Marshak, A. and Davis, A., eds.: 3D Radiative Transfer in Cloudy Atmospheres, Physics of Earth and Space Environments, Springer, Berlin, Heidelberg, <https://doi.org/10.1007/3-540-28519-9>, 2005.
- 2250 Marshak, A., Platnick, S., Várnai, T., Wen, G., and Cahalan, R. F.: Impact of three-dimensional radiative effects on satellite retrievals of cloud droplet sizes, *Journal of Geophysical Research (Atmospheres)*, 111, D09207, <https://doi.org/10.1029/2005JD006686>, 2006.
- Mayer, B.: Radiative transfer in the cloudy atmosphere, in: European Physical Journal Web of Conferences, vol. 1 of *European Physical Journal Web of Conferences*, p. 75, <https://doi.org/10.1140/epjconf/e2009-00912-1>, 2009.
- 2255 McBride, B. A., Sienkiewicz, N., Xu, X., Puthukkudy, A., Fernandez-Borda, R., and Martins, J. V.: In-flight characterization of the Hyper-Angular Rainbow Polarimeter (HARP2) on the NASA PACE mission, in: Society of Photo-Optical Instrumentation Engineers (SPIE)

- Conference Series, edited by Babu, S. R., Hélière, A., and Kimura, T., vol. 13192 of *Society of Photo-Optical Instrumentation Engineers (SPIE) Conference Series*, p. 131920H, <https://doi.org/10.1117/12.3033680>, 2024.
- 2260 Mishchenko, M. I. and Travis, L. D.: Satellite retrieval of aerosol properties over the ocean using polarization as well as intensity of reflected sunlight, *Journal of Geophysical Research*, 102, 16,989–17,013, <https://doi.org/10.1029/96JD02425>, 1997.
- Mishchenko, M. I., Lacis, A. A., and Travis, L. D.: Errors induced by the neglect of polarization in radiance calculations for Rayleigh-scattering atmospheres., *Journal of Quantitative Spectroscopy and Radiative Transfer*, 51, 491–510, [https://doi.org/10.1016/0022-4073\(94\)90149-X](https://doi.org/10.1016/0022-4073(94)90149-X), 1994.
- Moroz, V. I.: The Atmosphere of Venus, *Space Science Reviews*, 29, 3–127, <https://doi.org/10.1007/BF00177144>, 1981.
- 2265 Natraj, V. and Hovenier, J. W.: Polarized Light Reflected and Transmitted by Thick Rayleigh Scattering Atmospheres, *The Astrophysical Journal*, 748, 28, <https://doi.org/10.1088/0004-637X/748/1/28>, 2012.
- Natraj, V., Li, K.-F., and Yung, Y. L.: Rayleigh Scattering in Planetary Atmospheres: Corrected Tables Through Accurate Computation of X and Y Functions, *The Astrophysical Journal*, 691, 1909–1920, <https://doi.org/10.1088/0004-637X/691/2/1909>, 2009.
- 2270 Neefs, E., Vandaele, A. C., De Cock, R., Erwin, J., Robert, S., Thomas, I. R., Berkenbosch, S., Jacobs, L., Bogaert, P., Beeckman, B., Brassine, A., Messios, N., De Donder, E., Bolsée, D., Pereira, N., Tackley, P., Gerya, T., Kögl, S., Kögl, P., Gröbelbauer, H. P., Wirz, F., Székely, G., Eaton, N., Roibás-Millán, E., Torralbo, I., Rubio-Arnaldo, H., Alvarez, J. M., Navajas Ortega, D., De Vos, L., Sørensen, R., Moelans, W., Algoedt, A., Blau, M., Stam, D., Renotte, E., Klinkenberg, P., Borguet, B., Thomas, S., Vervaeke, M., Thienpont, H., Castro, J. M., and Jimenez, J.: VenSpec-H spectrometer on the ESA EnVision mission: Design, modeling, analysis, *Acta Astronautica*, 226, 178–201, <https://doi.org/10.1016/j.actaastro.2024.10.018>, 2025.
- 2275 Palmer, K. F. and Williams, D.: Optical constants of sulfuric acid; application to the clouds of Venus?, *Applied Optics*, 14, 208–219, <https://doi.org/10.1364/AO.14.000208>, 1975.
- Peck, E. R. and Reeder, K.: Dispersion of Air*, *Journal of the Optical Society of America* (1917-1983), 62, 958, <https://doi.org/10.1364/JOSA.62.000958>, 1972.
- Ramon, D., Steinmetz, F., Jolivet, D., Compiègne, M., and Frouin, R.: Modeling polarized radiative transfer in the ocean-atmosphere system with the GPU-accelerated SMART-G Monte Carlo code, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 222, 89–107, <https://doi.org/10.1016/j.jqsrt.2018.10.017>, 2019.
- 2280 Rice, J. A.: *Mathematical Statistics and Data Analysis*, Cengage Learning, Belmont, CA, 3rd edn., 2007.
- Rossi, L., Berzosa-Molina, J., Desert, J. M., Fossati, L., García Muñoz, A., Haswell, C., Kabath, P., Kislyakova, K., Stam, D., and Vidotto, A.: Spectropolarimetry as a tool for understanding the diversity of planetary atmospheres, *Experimental Astronomy*, 54, 1187–1196, <https://doi.org/10.1007/s10686-021-09813-w>, 2022.
- 2285 Seiff, A., Schofield, J. T., Kliore, A. J., Taylor, F. W., Limaye, S. S., Revercomb, H. E., Sromovsky, L. A., Kerzhanovich, V. V., Moroz, V. I., and Marov, M. Y.: Models of the structure of the atmosphere of Venus from the surface to 100 kilometers altitude, *Advances in Space Research*, 5, 3–58, [https://doi.org/10.1016/0273-1177\(85\)90197-8](https://doi.org/10.1016/0273-1177(85)90197-8), 1985.
- Sneep, M. and Ubachs, W.: Direct measurement of the Rayleigh scattering cross section in various gases, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 92, 293–310, <https://doi.org/10.1016/j.jqsrt.2004.07.025>, 2005.
- 2290 Spada, F., Krol, M. C., and Stammes, P.: McSCIA: application of the Equivalence Theorem in a Monte Carlo radiative transfer model for spherical shell atmospheres, *Atmospheric Chemistry & Physics*, 6, 4823–4842, <https://doi.org/10.5194/acp-6-4823-2006>, 2006.

- Spilling, D. and Thales, A.: The Multi Angle Polarimeter (MAP) on board ESA's Copernicus Carbon Dioxide Monitoring mission (CO2M), in: International Conference on Space Optics — ICSO 2020, edited by Cugny, B., Sodnik, Z., and Karafolas, N., vol. 11852, p. 118520R, 2295 International Society for Optics and Photonics, SPIE, <https://doi.org/10.1117/12.2599174>, 2021.
- Stakgold, I. and Holst, M. J.: Green's Functions and Boundary Value Problems, John Wiley & Sons, 3 edn., <https://doi.org/10.1002/9780470906538>, 2011.
- Stam, D. M.: Spectropolarimetric signatures of Earth-like extrasolar planets, *Astronomy and Astrophysics*, 482, 989–1007, <https://doi.org/10.1051/0004-6361:20078358>, 2008.
- 2300 Stam, D. M. and Hovenier, J. W.: Errors in calculated planetary phase functions and albedos due to neglecting polarization, *Astronomy and Astrophysics*, 444, 275–286, <https://doi.org/10.1051/0004-6361:20053698>, 2005.
- Stam, D. M., de Haan, J. F., Hovenier, J. W., and Stammes, P.: A fast method for simulating observations of polarized light emerging from the atmosphere applied to the oxygen-A band., *Journal of Quantitative Spectroscopy and Radiative Transfer*, 64, 131–149, [https://doi.org/10.1016/S0022-4073\(99\)00009-6](https://doi.org/10.1016/S0022-4073(99)00009-6), 2000.
- 2305 Stammes, P.: Spectral radiance modelling in the UV-visible range, *IRS 2000: Current Problems in Atmospheric Radiation*, edited by: Smith, W.L. and Timofeyev, Y.M., A. Deepak Publishing, Hampton, Virginia, pp. 385–388, 2001.
- Stap, F. A., Hasekamp, O. P., Emde, C., and Röckmann, T.: Influence of 3D effects on 1D aerosol retrievals in synthetic, partially clouded scenes, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 170, 54–68, <https://doi.org/10.1016/j.jqsrt.2015.10.008>, 2016a.
- Stap, F. A., Hasekamp, O. P., Emde, C., and Röckmann, T.: Multiangle photopolarimetric aerosol retrievals in the vicinity of 2310 clouds: Synthetic study based on a large eddy simulation, *Journal of Geophysical Research (Atmospheres)*, 121, 12,914–12,935, <https://doi.org/10.1002/2016JD024787>, 2016b.
- Stevens, B., Moeng, C.-H., and Sullivan, P. P.: Large-Eddy Simulations of Radiatively Driven Convection: Sensitivities to the Representation of Small Scales., *Journal of the Atmospheric Sciences*, 56, 3963–3984, [https://doi.org/10.1175/1520-0469\(1999\)056<3963:LESORD>2.0.CO;2](https://doi.org/10.1175/1520-0469(1999)056<3963:LESORD>2.0.CO;2), 1999.
- 2315 Trees, V.: MONKI (Monte Carlo KNMI), <https://doi.org/10.5281/zenodo.15380811>, in *MONKI: a three-dimensional Monte Carlo simulator of total and polarised radiation reflected by planetary atmospheres* (1.0), 2025.
- Trees, V. J. H. and Stam, D. M.: Blue, white, and red ocean planets. Simulations of orbital variations in flux and polarization colors, *Astronomy and Astrophysics*, 626, A129, <https://doi.org/10.1051/0004-6361/201935399>, 2019.
- Trees, V. J. H. and Stam, D. M.: Ocean signatures in the total flux and polarization spectra of Earth-like exoplanets, *Astronomy and Astro-* 2320 *physics*, 664, A172, <https://doi.org/10.1051/0004-6361/202243591>, 2022.
- Trees, V. J. H., Wang, P., Stammes, P., Tilstra, L. G., Donovan, D. P., and Siebesma, A. P.: DARCLOS: a cloud shadow detection algorithm for TROPOMI, *Atmospheric Measurement Techniques*, 15, 3121–3140, <https://doi.org/10.5194/amt-15-3121-2022>, 2022.
- Trees, V. J. H., Wang, P., Stammes, P., Tilstra, L. G., Donovan, D. P., and Siebesma, A. P.: Cancellation of cloud shadow effects in the absorbing aerosol index retrieval algorithm of TROPOMI, *Atmospheric Measurement Techniques*, 18, 73–91, [https://doi.org/10.5194/amt-](https://doi.org/10.5194/amt-18-73-2025) 2325 [18-73-2025](https://doi.org/10.5194/amt-18-73-2025), 2025.
- van Amerongen, A., Rietjens, J., Campo, J., Dogan, E., Dingjan, J., Nalla, R., Caron, J., and Hasekamp, O.: SPEXone: a compact multi-angle polarimeter, in: International Conference on Space Optics — ICSO 2018, edited by Sodnik, Z., Karafolas, N., and Cugny, B., vol. 11180 of *Society of Photo-Optical Instrumentation Engineers (SPIE) Conference Series*, p. 111800L, <https://doi.org/10.1117/12.2535940>, 2019.
- van de Hulst, H. C.: *Light Scattering by Small Particles*, Dover Publications, New York, 1981.

- 2330 Vanderbilt, V., Grant, L., and Daughtry, C.: Polarization of light scattered by vegetation, *Proceedings of the IEEE*, 73, 1012–1024, <https://doi.org/10.1109/PROC.1985.13232>, 1985.
- Várnai, T., Marshak, A., and Yang, W.: Multi-satellite aerosol observations in the vicinity of clouds, *Atmospheric Chemistry and Physics*, 13, 3899–3908, <https://doi.org/10.5194/acp-13-3899-2013>, 2013.
- Vaughan, S. R., Gebhard, T. D., Bott, K., Casewell, S. L., Cowan, N. B., Doelman, D. S., Kenworthy, M., Mazoyer, J., Millar-Blanchaer, M. A., Trees, V. J. H., Stam, D. M., Absil, O., Altinier, L., Baudoz, P., Belikov, R., Bidot, A., Birkby, J. L., Bonse, M. J., Brandl, B., Carlotti, A., Choquet, E., van Dam, D., Desai, N., Fogarty, K., Fowler, J., van Gorkom, K., Gutierrez, Y., Guyon, O., Haffert, S. Y., Herscovici-Schiller, O., Hours, A., Juanola-Parramon, R., Kleisioti, E., König, L., van Kooten, M., Krasteva, M., Laginja, I., Landman, R., Lebouilleux, L., Mouillet, D., N'Diaye, M., Por, E. H., Pueyo, L., and Snik, F.: Chasing rainbows and ocean glints: Inner working angle constraints for the Habitable Worlds Observatory, *Monthly Notices of the Royal Astronomical Society*, 524, 5477–5485, <https://doi.org/10.1093/mnras/stad2127>, 2023.
- 2340 Veefkind, J. P., Aben, I., McMullan, K., Förster, H., de Vries, J., Otter, G., Claas, J., Eskes, H. J., de Haan, J. F., Kleipool, Q., van Weele, M., Hasekamp, O., Hoogeveen, R., Landgraf, J., Snel, R., Tol, P., Ingmann, P., Voors, R., Kruizinga, B., Vink, R., Visser, H., and Levelt, P. F.: TROPOMI on the ESA Sentinel-5 Precursor: A GMES mission for global observations of the atmospheric composition for climate, air quality and ozone layer applications, *Remote Sensing of Environment*, 120, 70–83, <https://doi.org/10.1016/j.rse.2011.09.027>, 2012.
- 2345 Wang, Z., Cui, S., Yang, J., Gao, H., Liu, C., and Zhang, Z.: A novel hybrid scattering order-dependent variance reduction method for Monte Carlo simulations of radiative transfer in cloudy atmosphere, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 189, 283–302, <https://doi.org/10.1016/j.jqsrt.2016.12.002>, 2017.
- Wang, Z., Cui, S., Zhang, Z., Yang, J., Gao, H., and Zhang, F.: Theoretical extension of universal forward and backward Monte Carlo radiative transfer modeling for passive and active polarization observation simulations, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 235, 81–94, <https://doi.org/10.1016/j.jqsrt.2019.06.025>, 2019.
- 2350 Waquet, F., Cornet, C., Deuzé, J. L., Dubovik, O., Ducos, F., Goloub, P., Herman, M., Lapyonok, T., Labonnote, L. C., Riedi, J., Tanré, D., Thieuleux, F., and Vanbauce, C.: Retrieval of aerosol microphysical and optical properties above liquid clouds from POLDER/PARASOL polarization measurements, *Atmospheric Measurement Techniques*, 6, 991–1016, <https://doi.org/10.5194/amt-6-991-2013>, 2013.
- 2355 Wen, G., Marshak, A., Levy, R. C., Remer, L. A., Loeb, N. G., Várnai, T., and Cahalan, R. F.: Improvement of MODIS aerosol retrievals near clouds, *Journal of Geophysical Research (Atmospheres)*, 118, 9168–9181, <https://doi.org/10.1002/jgrd.50617>, 2013.
- Werdell, P. J., Behrenfeld, M. J., Bontempi, P. S., Boss, E., Cairns, B., Davis, G. T., Franz, B. A., Gliese, U. B., Gorman, E. T., Hasekamp, O., Knobelspiesse, K. D., Mannino, A., Martins, J. V., McClain, C. R., Meister, G., and Remer, L. A.: The Plankton, Aerosol, Cloud, Ocean Ecosystem Mission: Status, Science, Advances, *Bulletin of the American Meteorological Society*, 100, 1775–1794, <https://doi.org/10.1175/BAMS-D-18-0056.1>, 2019.
- 2360 Whitney, B. A.: Monte Carlo radiative transfer, in: *Fluid Flows To Black Holes: A Tribute to S Chandrasekhar on His Birth Centenary*. Edited by D. J. Saikia and Virginia Trimble., edited by Saikia, D. J. and Trimble, V., pp. 151–176, World Scientific Publishing Co. Pte. Ltd, https://doi.org/10.1142/9789814374774_0011, 2011.
- Wilmouth, D. M. and Sayres, D. S.: Determination of Rayleigh scattering cross sections and indices of refraction for Ar, CO₂, SF₆, and CH₄ using BBCES in the ultraviolet, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 255, 107 224, <https://doi.org/https://doi.org/10.1016/j.jqsrt.2020.107224>, 2020.

Wiltink, J. I., Trees, V. J. H., van Heerwaarden, C. C., and Meirink, J. F.: Errors in satellite-based global horizontal irradiance retrievals due to three-dimensional cloud-radiation interactions, *EGUsphere*, 2026, 1–36, <https://doi.org/10.5194/egusphere-2026-723>, 2026.

Supplementary material

2370 Green's functions

Definition of a Green's function

The method of Green's functions is a powerful way to solve an inhomogeneous linear boundary-value problem, that is, an equation of the form (see, e.g., Stakgold and Holst, 2011)

$$\mathcal{L}[u(x)] = q(x), \quad (S1)$$

2375 where u and q are functions of a variable x , and $\mathcal{L}$ is a linear operator acting on x . We consider homogeneous boundary conditions,

$$u(a) = 0,$$

$$u(b) = 0, \quad (S2)$$

where a and b are real values with $a < b$. The objective is to find an expression for $u(x)$.

2380 The Green's function $G(x, x^*)$ for this boundary-value problem is defined as the solution of

$$\mathcal{L}[G(x, x^*)] = \delta(x - x^*), \quad (S3)$$

where δ is the Dirac delta function, with the same homogeneous boundary conditions,

$$G(a, x^*) = 0,$$

$$G(b, x^*) = 0. \quad (S4)$$

2385 Multiplying Eq. S3 by $q(x^*)$ and integrating over x^* gives

$$\int_a^b \mathcal{L}[G(x, x^*)] q(x^*) dx^* = \int_a^b \delta(x - x^*) q(x^*) dx^*. \quad (S5)$$

The right-hand side can be evaluated using the defining property of the Dirac delta function. On the left-hand side, the linear operator $\mathcal{L}$ can be interchanged with the integration over x^* , because $\mathcal{L}$ acts on x and not on x^* . This gives

$$\mathcal{L} \left[\int_a^b G(x, x^*) q(x^*) dx^* \right] = q(x). \quad (S6)$$

2390 Comparing Eq. S6 with Eq. S1, and using the fact that G satisfies the same homogeneous boundary conditions, we obtain

$$u(x) = \int_a^b G(x, x^*) q(x^*) dx^*. \quad (S7)$$

Thus, once the Green's function is known, the solution can be written as a weighted integral over the source term q . The Green's function $G(x, x^*)$ can sometimes be found directly from Eq. S3 and the boundary conditions, as shown in the example below.

2395 **Example**

Let us consider the boundary-value problem

$$-\alpha u''(x) = q(x), \quad (\text{S8})$$

where $u'' \equiv d^2u/dx^2$ is the second derivative of u with respect to x , and α is a positive constant. The boundary conditions are

$$u(0) = 0, \quad (\text{S9})$$

$$u(B) = 0. \quad (\text{S10})$$

Here, the linear operator is

$$\mathcal{L}[u(x)] = -\alpha u''(x). \quad (\text{S11})$$

The Green's function is defined by

$$\mathcal{L}[G(x, x^*)] = \delta(x - x^*), \quad (\text{S12})$$

2405 or equivalently,

$$-\alpha G''(x, x^*) = \delta(x - x^*). \quad (\text{S13})$$

Hence,

$$G''(x, x^*) = -\frac{1}{\alpha} \delta(x - x^*). \quad (\text{S14})$$

Integrating once with respect to x gives

$$2410 \quad G'(x, x^*) = -\frac{1}{\alpha} H(x - x^*) + C_1(x^*), \quad (\text{S15})$$

where H is the Heaviside step function and C_1 may depend on x^* . Thus,

$$G'(x, x^*) = \begin{cases} C_1(x^*), & x < x^*, \\ -\frac{1}{\alpha} + C_1(x^*), & x > x^*. \end{cases} \quad (\text{S16})$$

Integrating once more gives¹⁵

$$G(x, x^*) = \begin{cases} C_1(x^*)x + C_2(x^*), & x < x^*, \\ -\frac{x - x^*}{\alpha} + C_1(x^*)x + C_2(x^*), & x \geq x^*. \end{cases} \quad (\text{S17})$$

¹⁵We include $x = x^*$ in the second branch. At $x = x^*$, both branches reduce to the same value, so $G(x, x^*)$ is continuous there, although its first derivative is discontinuous.

2415 The boundary condition at $x = 0$ gives

$$\underline{G(0, x^*) = 0 \quad \Rightarrow \quad C_2(x^*) = 0.} \quad (\text{S18})$$

The boundary condition at $x = B$ gives

$$\underline{G(B, x^*) = 0 \quad \Rightarrow \quad -\frac{B - x^*}{\alpha} + C_1(x^*)B = 0,} \quad (\text{S19})$$

so that

$$2420 \quad \underline{C_1(x^*) = \frac{B - x^*}{\alpha B}.} \quad (\text{S20})$$

The Green's function is therefore

$$\underline{G(x, x^*) = \begin{cases} \frac{x(B - x^*)}{\alpha B}, & x < x^*, \\ \frac{x^*(B - x)}{\alpha B}, & x \geq x^*. \end{cases}} \quad (\text{S21})$$

The solution of the boundary-value problem is then

$$\underline{u(x) = \int_0^B G(x, x^*) q(x^*) dx^*.} \quad (\text{S22})$$

2425 **Adjoint transport operator identity**

To verify the adjoint identity $(K[\mathbf{u}], \mathbf{g}) = (\mathbf{u}, K^+[\mathbf{g}])$ stated in Eq. G20, we start from the definition of the operator K ,

$$K[\mathbf{u}](\mathbf{x}, \boldsymbol{\omega}) = \int_{\mathcal{V}} \int_{4\pi} \mathbf{k}[(\mathbf{x}^*, \boldsymbol{\omega}') \rightarrow (\mathbf{x}, \boldsymbol{\omega})] \mathbf{u}(\mathbf{x}^*, \boldsymbol{\omega}') d\Omega' d^3\mathbf{x}^*. \quad (\text{S23})$$

and the inner product

$$(\mathbf{u}, \mathbf{v}) = \int_{\mathcal{V}} \int_{4\pi} \mathbf{u}(\mathbf{x}, \boldsymbol{\omega})^T \mathbf{v}(\mathbf{x}, \boldsymbol{\omega}) d\Omega d^3\mathbf{x}. \quad (\text{S24})$$

2430 Then

$$\begin{aligned} (K[\mathbf{u}], \mathbf{g}) &= \int_{\mathcal{V}} \int_{4\pi} (K[\mathbf{u}](\mathbf{x}, \boldsymbol{\omega}))^T \mathbf{g}(\mathbf{x}, \boldsymbol{\omega}) d\Omega d^3\mathbf{x} \\ &= \int_{\mathcal{V}} \int_{4\pi} \left[\int_{\mathcal{V}} \int_{4\pi} \mathbf{k}[(\mathbf{x}^*, \boldsymbol{\omega}') \rightarrow (\mathbf{x}, \boldsymbol{\omega})] \mathbf{u}(\mathbf{x}^*, \boldsymbol{\omega}') d\Omega' d^3\mathbf{x}^* \right]^T \mathbf{g}(\mathbf{x}, \boldsymbol{\omega}) d\Omega d^3\mathbf{x} \\ &= \int_{\mathcal{V}} \int_{4\pi} \int_{\mathcal{V}} \int_{4\pi} \mathbf{u}(\mathbf{x}^*, \boldsymbol{\omega}')^T \mathbf{k}[(\mathbf{x}^*, \boldsymbol{\omega}') \rightarrow (\mathbf{x}, \boldsymbol{\omega})]^T \mathbf{g}(\mathbf{x}, \boldsymbol{\omega}) d\Omega' d^3\mathbf{x}^* d\Omega d^3\mathbf{x}. \end{aligned} \quad (\text{S25})$$

where we used the identity $(\mathbf{A}\mathbf{u})^T = \mathbf{u}^T \mathbf{A}^T$. Reordering the integrations gives

$$2435 \quad (K[\mathbf{u}], \mathbf{g}) = \int_{\mathcal{V}} \int_{4\pi} \mathbf{u}(\mathbf{x}^*, \boldsymbol{\omega}')^T \left[\int_{\mathcal{V}} \int_{4\pi} \mathbf{k}[(\mathbf{x}^*, \boldsymbol{\omega}') \rightarrow (\mathbf{x}, \boldsymbol{\omega})]^T \mathbf{g}(\mathbf{x}, \boldsymbol{\omega}) d\Omega d^3\mathbf{x} \right] d\Omega' d^3\mathbf{x}^*. \quad (\text{S26})$$

Now relabel the dummy integration variables $(\mathbf{x}^*, \boldsymbol{\omega}') \leftrightarrow (\mathbf{x}, \boldsymbol{\omega})$. Then Eq. S26 becomes

$$(K[\mathbf{u}], \mathbf{g}) = \int_{\mathcal{V}} \int_{4\pi} \mathbf{u}(\mathbf{x}, \boldsymbol{\omega})^T \left[\int_{\mathcal{V}} \int_{4\pi} \mathbf{k}[(\mathbf{x}, \boldsymbol{\omega}) \rightarrow (\mathbf{x}^*, \boldsymbol{\omega}')]^T \mathbf{g}(\mathbf{x}^*, \boldsymbol{\omega}') d\Omega' d^3\mathbf{x}^* \right] d\Omega d^3\mathbf{x}. \quad (\text{S27})$$

Recognizing the term in brackets as the definition of $K^+[\mathbf{g}]$,

$$K^+[\mathbf{g}](\mathbf{x}, \boldsymbol{\omega}) = \int_{\mathcal{V}} \int_{4\pi} \mathbf{k}[(\mathbf{x}, \boldsymbol{\omega}) \rightarrow (\mathbf{x}^*, \boldsymbol{\omega}')]^T \mathbf{g}(\mathbf{x}^*, \boldsymbol{\omega}') d\Omega' d^3\mathbf{x}^*. \quad (\text{S28})$$

2440 we obtain

$$\begin{aligned} (K[\mathbf{u}], \mathbf{g}) &= \int_{\mathcal{V}} \int_{4\pi} \mathbf{u}(\mathbf{x}, \boldsymbol{\omega})^T K^+[\mathbf{g}](\mathbf{x}, \boldsymbol{\omega}) d\Omega d^3\mathbf{x} \\ &= (\mathbf{u}, K^+[\mathbf{g}]). \end{aligned} \quad (\text{S29})$$

Hence,

$$(K[\mathbf{u}], \mathbf{g}) = (\mathbf{u}, K^+[\mathbf{g}]), \quad (\text{S30})$$

2445 which proves Eq. G20. It should be noted that reciprocity is not used in the proof above. The transpose in the definition of K^+ follows solely from the Stokes vector inner product.

Additional tables and figures

Table S1. Similar to Table 1, except for $(\mu_0, \varphi_0) = (0.1, 0^\circ)$.

		$\mu = 0.1$		$\mu = 0.5$		de
		de Haan	MONKI	de Haan	MONKI	
$\mu_0 = 0.5$ <u>$\mu_0 = 0.1$</u> $\varphi = 0^\circ$	I	0.522770	0.522889 <u>0.522851</u> ± 0.000698 0.000324	0.106590	0.106610 <u>0.106604</u> ± 0.000126 0.000067	0.0
	Q	0.011506	0.011517 <u>0.011495</u> ± 0.000100 0.000045	-0.005186	-0.005192 <u>-0.005189</u> ± 0.000031 0.000015	-0.0
	U	0.000000	0.000017 <u>0.000018</u> ± 0.000071 0.000032	0.000000	0.000003 <u>0.000003</u> ± 0.000027 0.000014	0.0
	V	0.000000	0.000001 <u>0.000000</u> ± 0.000006 0.000003	0.000000	0.000000 <u>0.000001</u> ± 0.000004 0.000002	0.0
$\mu_0 = 0.5$ <u>$\mu_0 = 0.1$</u> $\varphi = 30^\circ$	I	0.276300	0.276328 <u>0.276336</u> ± 0.000288 0.000153	0.083628	0.083655 <u>0.083659</u> ± 0.000103 0.000054	0.0
	Q	0.034368	0.034374 <u>0.034354</u> ± 0.000098 0.000048	0.003839	0.003844 <u>0.003847</u> ± 0.000031 0.000017	-0.0
	U	-0.016042	-0.016035 <u>-0.016039</u> ± 0.000065 0.000030	-0.014492	-0.014500 <u>-0.014497</u> ± 0.000027 0.000013	-0.0
	V	0.000027	0.000029 <u>0.000028</u> ± 0.000006 0.000003	0.000017	0.000017 <u>0.000018</u> ± 0.000004 0.000002	0.0

Table S2. Similar to Table 1, except for downward **emerging** light at the surface (BOA).

		$\mu = 0.1$		$\mu = 0.5$		de Haan
		de Haan	MONKI	de Haan	MONKI	
$\mu_0 = 0.5$ $\varphi = 0^\circ$	I	1.036450	1.037420 <u>1.036876</u> ± 0.003919 0.001867	2.287330	2.287581 <u>2.287212</u> ± 0.003720 0.001710	0.088417
	Q	0.010451	0.010433 <u>0.010411</u> ± 0.000450 0.000221	0.007210	0.007210 <u>0.007216</u> ± 0.000181 0.000091	-0.023375
	U	0.000000	0.000037 <u>0.000196</u>	0.000000	<u>0.000012</u> ± 0.000086	<u>0.000000</u>
	V	<u>0.000000</u>	<u>0.000015</u> ± 0.000021	<u>0.000000</u>	<u>0.000007</u> ± 0.000008	<u>0.000000</u>
<u>$\mu_0 = 0.5$</u> <u>$\varphi = 30^\circ$</u>	<u>I</u>	<u>0.566020</u>	<u>0.566066</u> ± 0.001217	<u>0.604840</u>	<u>0.604612</u> ± 0.000578	<u>0.088417</u>
	<u>Q</u>	<u>0.013634</u>	<u>0.013609</u> ± 0.000208	<u>0.012593</u>	<u>0.012600</u> ± 0.000087	<u>-0.011687</u>
	<u>U</u>	<u>-0.016244</u>	<u>-0.016223</u> ± 0.000231	<u>-0.002307</u>	<u>-0.002334</u> ± 0.000079	<u>0.020243</u>
	<u>V</u>	<u>0.000084</u>	<u>0.000086</u> ± 0.000025	<u>-0.000137</u>	<u>-0.000135</u> ± 0.000007	<u>0.000000</u>

Table S3. Similar to Table S1, except for downward light at the surface (BOA).

		$\mu = 0.1$		$\mu = 0.5$		$\mu = 1.0$	
		de Haan	MONKI	de Haan	MONKI	de Haan	MONKI
$\mu_0 = 0.1$ $\varphi = 0^\circ$	I	0.191930	0.191924±0.000392	0.129879	0.129944±0.000106	0.022968	0.022975±0.000026
	Q	0.003451	0.003448±0.000062	0.000363	0.000347±0.000025	-0.013424	-0.013432±0.000019
	U	0.000000	-0.000007±0.000052	0.000000	0.000012±0.000019	0.000000	0.000003±0.000008
	V	0.000000	0.000001±0.000005	0.000000	0.000001±0.000002	0.000000	-0.000000±0.000001
$\mu_0 = 0.1$ $\varphi = 30^\circ$	I	0.086631	0.086559±0.000243	0.084823	0.084868±0.000107	0.022968	0.022975±0.000026
	Q	0.006335	0.006333±0.000059	0.005860	0.005843±0.000025	-0.006712	-0.006713±0.000011
	U	0.001320	0.001327±0.000037	0.006928	0.006938±0.000334-0.000021	0.011626	0.011634±0.000017
	V	-0.000010	-0.000006±0.000007	-0.000062	-0.000059±0.000002	0.000000	0.000014-0.000000±0.000000

Table S4. Comparison of the TOA radiances computed with MONKI using 10^7 photons in backward mode with the benchmark results of de Haan et al. (1987) for an atmosphere consisting of two plane-parallel layers with a total optical thickness $b = 0.6$ (see text). The direction of the incident unpolarised light beam is $(\mu_0, \varphi_0) = (0.5, 0^\circ)$. The reported uncertainties in the MONKI results refer to twice the standard error of the mean, evaluated separately for each Stokes component using Eq. 23.

		$\mu = 0.1$		$\mu = 0.5$		$\mu = 1.0$	
		de Haan	MONKI	de Haan	MONKI	de Haan	MONKI
$\mu_0 = 0.5$ $\varphi = 0^\circ$	I	0.532950	0.533025 $\pm$ 0.000329	0.208430	0.208418 $\pm$ 0.000235	0.093680	0.093736 $\pm$ 0.000133
	Q	-0.028340	-0.028370 $\pm$ 0.000085	-0.036299	-0.036337 $\pm$ 0.000076	-0.024156	-0.024202 $\pm$ 0.000062
	U	0.000000	0.000038 $\pm$ 0.000079	0.000000	0.000041 $\pm$ 0.000056	0.000000	0.000032 $\pm$ 0.000041
	V	0.000000	-0.000000 $\pm$ 0.000006	0.000000	-0.000004 $\pm$ 0.000006	0.000000	0.000003 $\pm$ 0.000005
$\mu_0 = 0.5$ $\varphi = 30^\circ$	I	0.418140	0.418242 $\pm$ 0.000268	0.184970	0.184817 $\pm$ 0.000217	0.093680	0.093756 $\pm$ 0.000152
	Q	-0.000058	-0.000077 $\pm$ 0.000085	-0.019649	-0.019652 $\pm$ 0.000062	-0.012078	-0.012128 $\pm$ 0.000052
	U	-0.073705	-0.073111 $\pm$ 0.000084	-0.041401	-0.041354 $\pm$ 0.000083	-0.020920	-0.020920 $\pm$ 0.000057
	V	0.000106	0.000107 $\pm$ 0.000006	0.000040	0.000037 $\pm$ 0.000006	0.000000	0.000005 $\pm$ 0.000005

Table S5. Similar to Table S4, except for $(\mu_0, \varphi_0) = (0.1, 0^\circ)$.

		$\mu = 0.1$		$\mu = 0.5$		de Haan
		de Haan	MONKI	de Haan	MONKI	
$\mu_0 = 0.1$ $\varphi = 0^\circ$	I	0.522770	0.522857 $\pm$ 0.000325	0.106590	0.106499 $\pm$ 0.000121	0.026009
	Q	0.011506	0.011484 $\pm$ 0.000047	-0.005186	-0.005194 $\pm$ 0.000032	-0.014984
	U	0.000000	-0.000021 $\pm$ 0.000034	0.000000	-0.000002 $\pm$ 0.000058-0.000024	0.000000
	V	0.000000	0.0000160.000000 $\pm$ 0.000045-0.000002	0.000000	0.000001-0.000004 $\pm$ 0.000014-0.000003	0.000000
$\mu_0 = 0.1$ $\varphi = 30^\circ$	I	0.276300	0.276342 $\pm$ 0.000168	0.083628	0.083548 $\pm$ 0.000114	0.026009
	Q	0.034368	0.034349 $\pm$ 0.000054	0.003839	0.003826 $\pm$ 0.000029	-0.007492
	U	-0.016042	-0.016057 $\pm$ 0.000036	-0.014492	-0.014488 $\pm$ 0.000032	-0.012976
	V	0.000027	0.000026 $\pm$ 0.000002	0.000017	0.000013 $\pm$ 0.000003	0.000000

Table S6. Similar to Table S4, except for downward light at the surface (BOA).

		$\mu = 0.1$		$\mu = 0.5$		
		de Haan	MONKI	de Haan	MONKI	de Haan
$\mu_0 = 0.5$ $\varphi = 0^\circ$	I	1.036450	1.036884 $\pm$ 0.000626	2.287330	2.287353 $\pm$ 0.001495	0.088417
	Q	0.010451	0.010466 $\pm$ 0.000076	0.007210	0.007229 $\pm$ 0.000070	-0.023375
	U	0.000000	0.000039 $\pm$ 0.000055	0.000000	-0.000027 $\pm$ 0.000058	0.000000
	V	0.000000	0.000007 $\pm$ 0.000008	0.000000	-0.000001 $\pm$ 0.000005	0.000000
$\mu_0 = 0.5$ $\varphi = 30^\circ$	I	0.566020	0.5661750.566619 $\pm$ 0.002438-0.000519	0.604840	0.6047780.604551 $\pm$ 0.001157-0.000530	0.088417
	Q	0.013634	0.0136280.013664 $\pm$ 0.000479-0.000081	0.012593	0.0126050.012595 $\pm$ 0.000189-0.000070	-0.011687
	U	-0.016244	-0.016229-0.016226 $\pm$ 0.000417-0.000064	-0.002307	-0.002332-0.002325 $\pm$ 0.000148-0.000065	0.020243
	V	0.000084	0.0000930.000090 $\pm$ 0.000049-0.000008	-0.000137	-0.000137-0.000139 $\pm$ 0.000015-0.000006	0.000000

Table S7. Similar to Table S4S5, except for downward **emerging** light at the surface (BOA).

		$\mu = 0.1$		$\mu = 0.5$		
		de Haan	MONKI	de Haan	MONKI	de Haan
$\mu_0 = 0.5$ $\varphi = 0^\circ$	I	0.191930	0.1918960.191814 $\pm$ 0.000813-0.000243	0.129879	0.1299070.129851 $\pm$ 0.000243-0.000162	0.02
	Q	0.003451	0.003459 $\pm$ 0.000122-0.000028	0.000363	0.0003570.000366 $\pm$ 0.000046-0.000027	-0.0
	U	0.000000	-0.0000160.000017 $\pm$ 0.000103-0.000025	0.000000	0.000014-0.000026 $\pm$ 0.000035-0.000025	0.00
	V	0.000000	0.0000000.000003 $\pm$ 0.000012-0.000003	0.000000	0.0000020.000001 $\pm$ 0.000004-0.000002	0.00
$\mu_0 = 0.5$ $\varphi = 30^\circ$	I	0.086631	0.0863560.086687 $\pm$ 0.000502-0.000130	0.084823	0.0848070.084820 $\pm$ 0.000222-0.000122	0.02
	Q	0.006335	0.0062870.006345 $\pm$ 0.000127-0.000033	0.005860	0.0058290.005853 $\pm$ 0.000051-0.000031	-0.00
	U	0.001320	0.0013360.001339 $\pm$ 0.000079-0.000025	0.006928	0.0069330.006910 $\pm$ 0.000041-0.000027	0.01
	V	-0.000010	-0.000007 $\pm$ 0.000014-0.000003	-0.000062	-0.000059-0.000062 $\pm$ 0.000004-0.000003	0.00

Table S8. Viewing and solar geometries for the 9 3D cloud test cases of Emde et al. (2018), using the angular definitions of MONKI. The ~~solar~~ azimuth angle of the sunlight is $\varphi_0 = 0^\circ$ for all cases. The solar zenith angle θ_0 is defined with respect to the local zenith. For the cases with ~~$\theta > 90^\circ$~~ $\vartheta > 90^\circ$ the ~~observer~~ detector is at BOA, otherwise the ~~observer~~ detector is at TOA.

No.	θ_0 [$^\circ$]	θ <u>ϑ</u> [$^\circ$]	φ [$^\circ$]
1	20	140	180
2	20	140	240
3	20	140	300
4	20	140	0
5	40	0	180
6	40	40	180
7	40	40	240
8	40	40	300
9	40	40	0

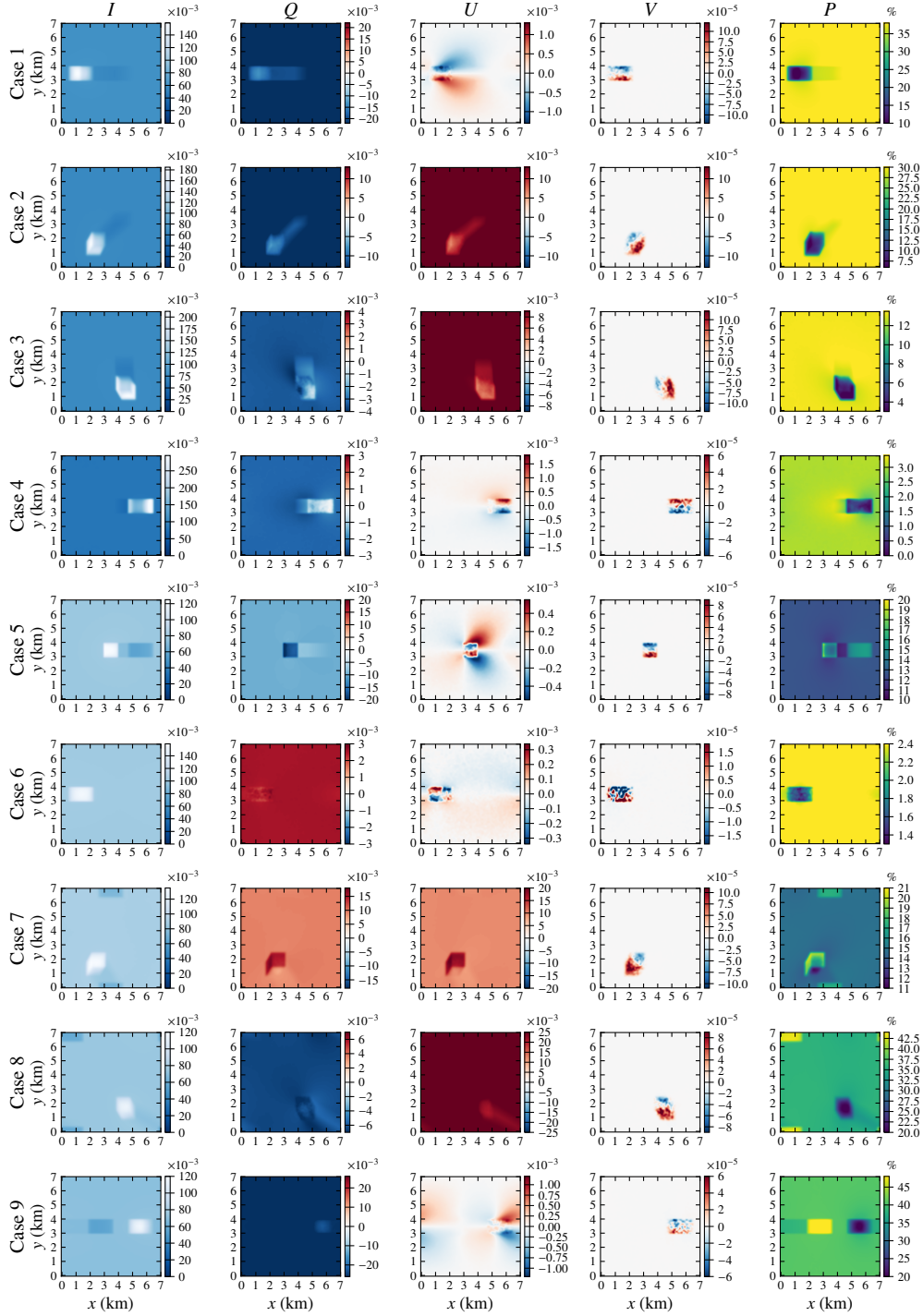


Figure S1. Similar to Fig. 7, except for all Stokes parameters I , Q , U , and V , and for degree of polarisation P (the columns), at all 9 solar and viewing geometry cases (the rows) presented in Table S8.

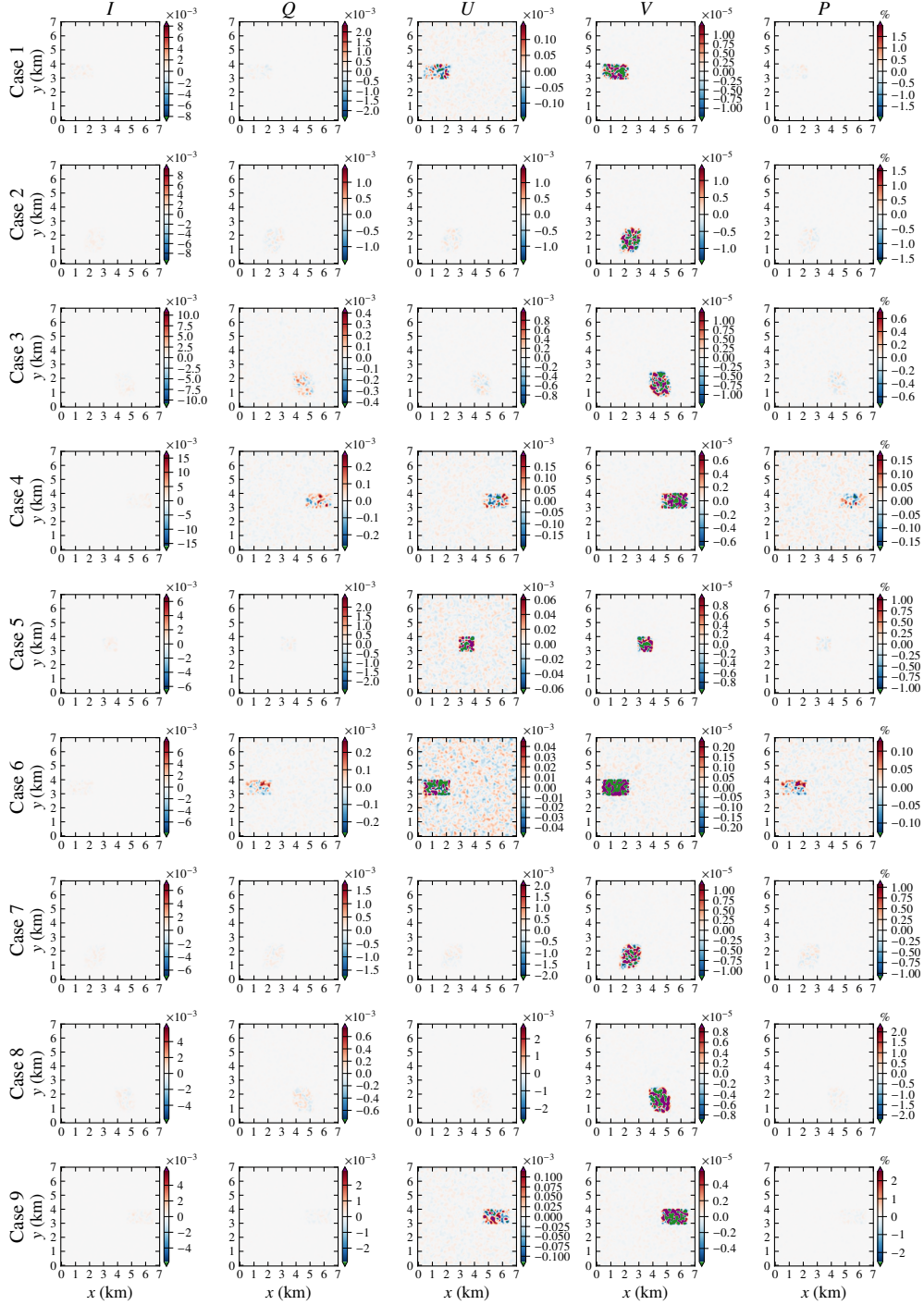


Figure S2. Similar to Fig. S1, except for the differences between MONKI and MYSTIC (see Fig. A2 of Emde et al., 2018). Following Emde et al. (2018), the limits of the colorbars are set to 5% of the maximum values for I and P , and to 10% of the values for $|Q|$ and $|U|$ and $|V|$. Values larger than the upper limit are marked in purple and values smaller than the lower limit are marked in green.

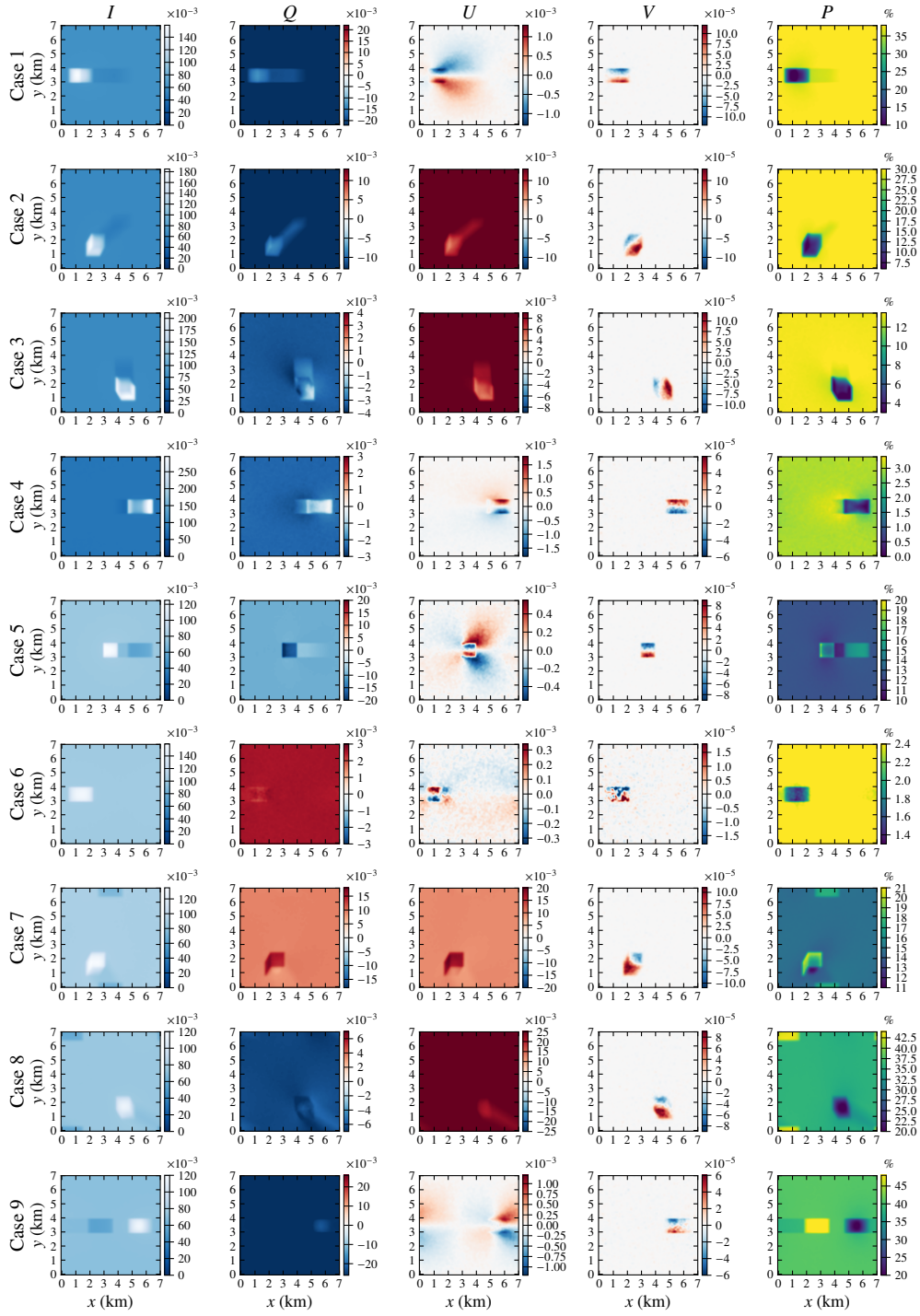


Figure S3. Similar to Fig. ??, except with MONKI in backward mode.

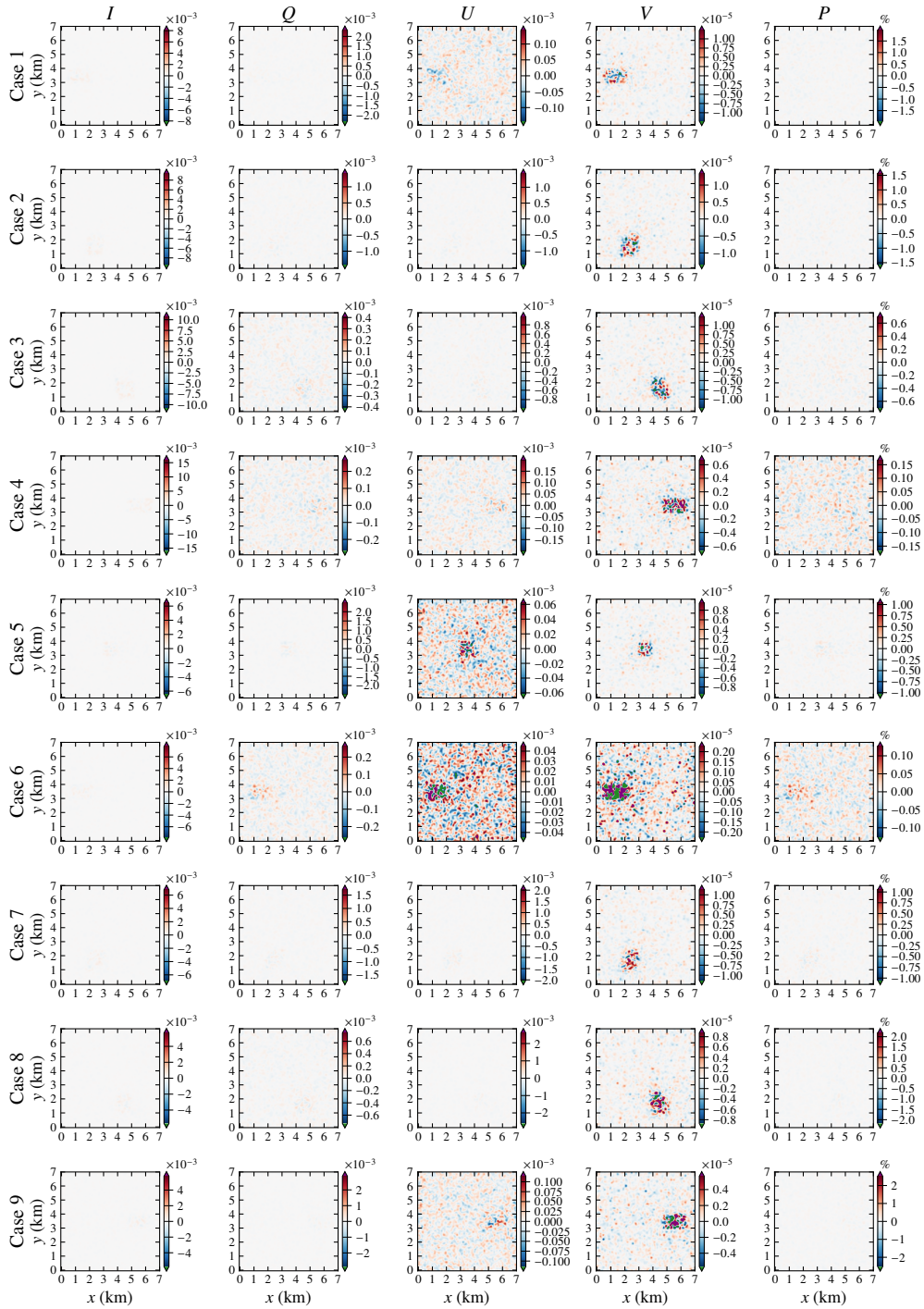


Figure S4. Similar to Fig. S2, except with MONKI in backward mode.

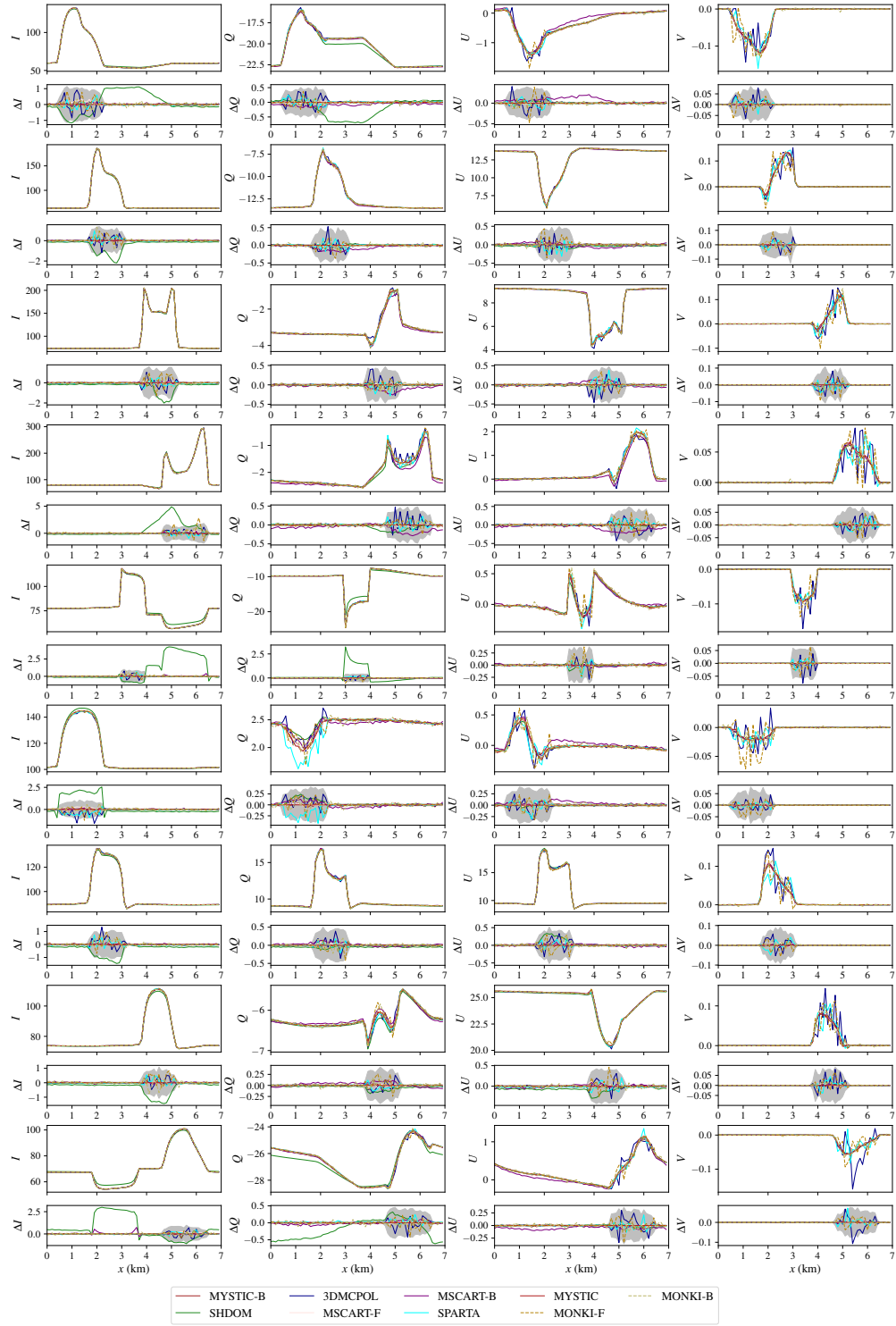


Figure S5. Similar to Fig. 8, except for the cases 1 to 9 (top to bottom row) with the geometries listed in Table S8.

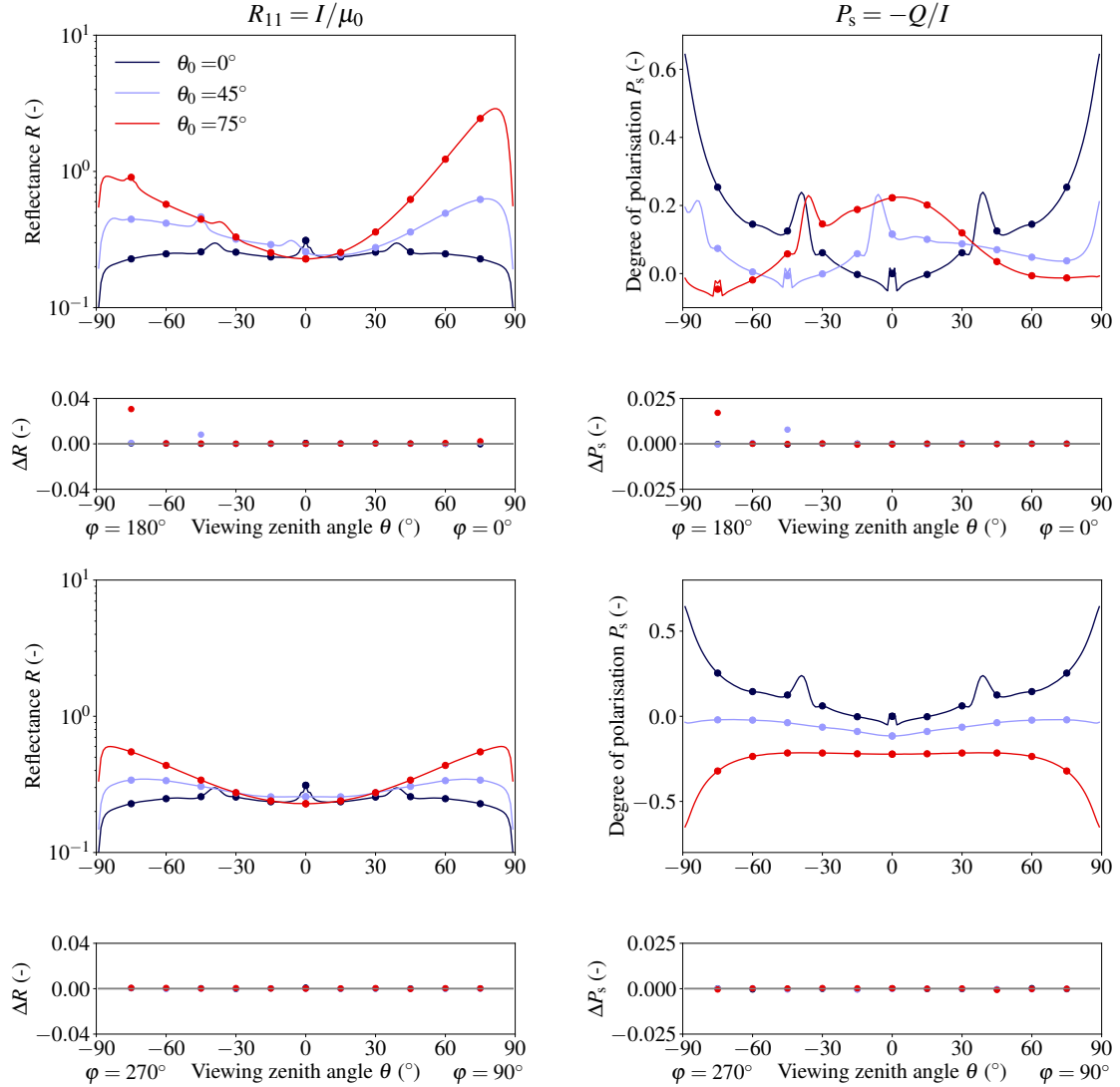


Figure S6. Comparison of the Earth model (see Sect. 4) results of MONKI (solid lines) and DAK (dots) for the TOA reflectance R_{11} and the degree of polarisation $P_s P_s$, at the azimuth directions ($\varphi = 180^\circ$, $\varphi = 0^\circ$) (top row), and ($\varphi = 270^\circ$, $\varphi = 90^\circ$) (bottom row). The **solar** azimuth angle of the sunlight is $\varphi_0 = 0^\circ$. The differences (MONKI–DAK) are also shown. For this comparison, MONKI used 10^9 photons per (θ_0, φ) -combination and 90 viewing zenith angles θ simultaneously. In DAK, 170 Gaussian quadrature points were used for both μ and μ_0 , and 170 Fourier terms for the azimuth direction. This number of Gauss points in DAK explains the remaining differences between DAK and MONKI in the backscattering directions ($\theta_0 = 75^\circ$, $\theta = 75^\circ$, $\varphi = 180^\circ$) and ($\theta_0 = 45^\circ$, $\theta = 45^\circ$, $\varphi = 180^\circ$), where the sharp glory feature of the cloud droplets (at $\Theta \sim 180^\circ$ in Fig. 11) is not fully resolved by DAK’s Gaussian points.

List of symbols

Table S9. Radiometric and polarimetric quantities.

Symbol	Description	Unit
$\underline{I} = [I, Q, U, V]^T$	Radiance Stokes vector	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
$\underline{I}$	Total radiance, or first Stokes component	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
$\underline{Q}$	Linearly polarised radiance defined with respect to the chosen reference plane	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
$\underline{U}$	Linearly polarised radiance at $\pm 45^\circ$ with respect to the chosen reference plane	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
$\underline{V}$	Circularly polarised radiance	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
$\underline{I}' = [I', Q', U', V']^T$	Incident radiance Stokes vector at a scattering event	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
$\underline{I}'$	First component of the incident radiance Stokes vector	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
$\underline{I}^\times$	Scattered Stokes vector after rotation to the scattering plane, used in the angular-PDF derivation	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
$\underline{I}^\times$	First component of $\underline{I}^\times$	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
$\underline{I}(O, \omega^\bullet; \omega_0)$	Detector-area-averaged radiance Stokes vector for detector area O , detector direction $\omega^\bullet$, and sunlight direction ω_0	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
$\underline{I}^{(0)}, \underline{I}^{(1)}, \underline{I}^{(2)}, \dots$	Zeroth-, first-, second-, and higher-order radiance Stokes vector contributions	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
$\underline{I}^{(n)}$	n^{th} -order radiance Stokes vector contribution	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
$\underline{\bar{I}}$	Normalised Stokes vector carried by a Monte Carlo photon	$\sim$
$\underline{\bar{I}}'$	Normalised incident Stokes vector in the angular-PDF derivation	$\sim$
$\underline{\bar{I}}_0$	Initial normalised Stokes vector of a photon in forward mode, equal to $\underline{1}$	$\sim$
$\underline{\bar{I}}_1, \underline{\bar{I}}_2, \dots$	Normalised radiance Stokes vectors after successive forward scattering events	$\sim$
$\underline{E}_0$	Incident solar irradiance	$\text{W m}^{-2} \text{ nm}^{-1}$
$\underline{E}_0$	Incident solar flux Stokes vector	$\text{W m}^{-2} \text{ nm}^{-1}$
$\underline{E}$	Reflected irradiance, or net flux, emerging from a Lambertian surface in Appendix C	$\text{W m}^{-2} \text{ nm}^{-1}$
$\underline{1}$	Unpolarised unit Stokes vector, $[1, 0, 0, 0]^T$	$\sim$
$\underline{e}_i$	Canonical basis vector in Stokes space	$\sim$
$\underline{P}$	Degree of polarisation	$\sim$
$\underline{P}'$	Degree of polarisation of the incident Stokes vector in the sampling derivations	$\sim$
$\underline{P}_s$	Signed degree of linear polarisation, $-Q/I$	$\sim$

Table S10. Geometry, coordinates, and directions, part I.

<u>Symbol</u>	<u>Description</u>	<u>Unit</u>
$\underline{x}, \underline{y}, \underline{z}$	<u>Cartesian coordinates</u>	<u>m</u>
$\underline{x} = [x, y, z]^T$	<u>Position vector</u>	<u>m</u>
$\underline{x}^\bullet$	<u>Detector location or detector-boundary intersection point, depending on context</u>	<u>m</u>
$\underline{x}^*$	<u>Source point or dummy spatial integration variable in the Green-function derivation</u>	<u>m</u>
$\underline{x}_0$	<u>Entry point of the incident sunlight on the domain boundary; in the forward implementation also the photon injection point at the boundary</u>	<u>m</u>
$\underline{x}_0(\underline{x})$	<u>Entry point of the incident sunlight associated with spatial point $\underline{x}$</u>	<u>m</u>
$\underline{x}_{0,i}$	<u>Entry point of the incident sunlight associated with photon i in backward mode</u>	<u>m</u>
$\underline{x}_1, \underline{x}_2, \underline{x}_3, \dots$	<u>Successive scattering locations along a photon path, labelled in forward order</u>	<u>m</u>
$\underline{x}_{1,i}, \underline{x}_{2,i}, \dots$	<u>Sampled scattering locations of photon i</u>	<u>m</u>
$\underline{x}_{n,i,j}$	<u>Location of event n of photon i injected in source column j</u>	<u>m</u>
$\underline{x}_i^\bullet$	<u>Detector-boundary intersection point associated with photon i</u>	<u>m</u>
$\underline{x}_{n,i,j}^\bullet$	<u>Intersection point of the detector ray associated with event (n, i, j) with the boundary at TOA or BOA</u>	<u>m</u>
$\underline{\omega}$	<u>Generic propagation-direction unit vector</u>	<u>–</u>
$\underline{\omega}'$	<u>Incident propagation-direction unit vector at a scattering event or in scattering integrals</u>	<u>–</u>
$\underline{\omega}^\bullet$	<u>Detector/viewing direction</u>	<u>–</u>
$\underline{\omega}_0$	<u>Solar-beam direction</u>	<u>–</u>
$\underline{\omega}_1, \underline{\omega}_2, \dots$	<u>Intermediate photon directions between successive scattering events</u>	<u>–</u>
$\underline{\omega}_{n,i}$	<u>Photon direction associated with event or order n of photon i</u>	<u>–</u>
$\underline{\Omega}_1, \underline{\Omega}_2, \dots$	<u>Randomly sampled propagation directions between successive scattering events</u>	<u>–</u>
$\hat{\underline{r}}$	<u>Unit vector from a source point towards the observation point in the Green-function derivation</u>	<u>–</u>
$\ \underline{x} - \underline{x}^*\ $	<u>Distance between the observation point $\underline{x}$ and source point $\underline{x}^*$</u>	<u>m</u>

Table S11. Geometry, coordinates, and directions, part II.

<u>Symbol</u>	<u>Description</u>	<u>Unit</u>
ϑ, φ	Zenith and azimuth angles of a generic propagation direction	rad or $^{\circ}$
ϑ', φ'	Zenith and azimuth angles of the incident direction at a scattering event	rad or $^{\circ}$
ϑ_0, φ_0	Zenith and azimuth angles of the incident solar beam	rad or $^{\circ}$
$\vartheta^{\bullet}, \varphi^{\bullet}$	Zenith and azimuth angles of the detector direction	rad or $^{\circ}$
ϑ_n, φ_n	Zenith and azimuth angles of the photon direction after scattering event n	rad or $^{\circ}$
θ	Viewing zenith angle, $\arccos(\mu)$, defined between 0 and $\pi/2$ with respect to the local normal	rad or $^{\circ}$
θ_0	Solar zenith angle, $\arccos(\mu_0)$, defined between 0 and $\pi/2$ with respect to the local normal	rad or $^{\circ}$
μ	$ \cos \vartheta $	$-$
μ_0	$ \cos \vartheta_0 $	$-$
$\mu^{\bullet}$	$ \cos \vartheta^{\bullet} $	$-$
Θ	Scattering angle	rad or $^{\circ}$
σ_1, σ_2	Rotation angles between the meridian planes and the scattering plane	rad or $^{\circ}$
Ω	Solid angle	sr
$d\Omega$	Differential solid-angle element	sr
$d\Omega'$	Differential solid-angle element for the incident direction in scattering integrals	sr
O_0	Horizontal source area on the illuminated sunlight-entry boundary in the finite-area forward formulation	m^2
O	Horizontal detector area or grid-column area, depending on context	m^2
dO, dO_0	Differential horizontal detector and source area elements	m^2
dV	Differential scattering volume element	m^3
$d^3\mathbf{x}$	Differential volume element	m^3
$\mathcal{V}$	Spatial domain occupied by the atmosphere	m^3

Table S12. Grid, indices, and model-domain quantities.

<u>Symbol</u>	<u>Description</u>	<u>Unit</u>
<u>N_x, N_y, N_z</u>	<u>Numbers of grid columns in the x and y directions and layers in the z direction</u>	<u>—</u>
<u>i</u>	<u>Photon index; also used as absorbing-gas species index in Appendix A, depending on context</u>	<u>—</u>
<u>j</u>	<u>Source-column index in the multi-column estimator; also used as Stokes-component index in the derivation, depending on context</u>	<u>—</u>
<u>k</u>	<u>Vertical layer index</u>	<u>—</u>
<u>k^*</u>	<u>Index of the layer containing a given event</u>	<u>—</u>
<u>l</u>	<u>Dummy product index over scattering events</u>	<u>—</u>
<u>m</u>	<u>Backward detector-side event counter in the detector-response matrix recursion</u>	<u>—</u>
<u>n</u>	<u>Scattering order or event index</u>	<u>—</u>
<u>r</u>	<u>Simulation-round index</u>	<u>—</u>
<u>c</u>	<u>Aerosol or cloud-particle type index</u>	<u>—</u>
<u>t, t'</u>	<u>Atmospheric constituent type indices, referring to gas molecules or aerosol types</u>	<u>—</u>
<u>z_k^{bot}</u>	<u>Bottom altitude of layer k</u>	<u>m or km</u>
<u>z_k^{top}</u>	<u>Top altitude of layer k</u>	<u>m or km</u>
<u>Δz_k</u>	<u>Thickness of layer k</u>	<u>m or km</u>

Table S13. Optical coefficients, matrices, and surface quantities.

<u>Symbol</u>	<u>Description</u>	<u>Unit</u>
<u>λ</u>	<u>Wavelength</u>	<u>nm or m</u>
<u>β</u>	<u>Total extinction coefficient</u>	<u>m^{-1}</u>
<u>β_{sca}</u>	<u>Total scattering coefficient</u>	<u>m^{-1}</u>
<u>β_{abs}</u>	<u>Total absorption coefficient</u>	<u>m^{-1}</u>
<u>$\beta_t, \beta_{t'}$</u>	<u>Total extinction coefficient of constituent type t or t'</u>	<u>m^{-1}</u>
<u>$\beta_{\text{sca},t}$</u>	<u>Scattering coefficient of constituent type t</u>	<u>m^{-1}</u>
<u>β^{m}</u>	<u>Gas extinction coefficient</u>	<u>m^{-1}</u>
<u>$\beta_{\text{sca}}^{\text{m}}, \beta_{\text{abs}}^{\text{m}}$</u>	<u>Gas scattering and absorption coefficients</u>	<u>m^{-1}</u>
<u>β_c^{a}</u>	<u>Extinction coefficient of aerosol type c</u>	<u>m^{-1}</u>
<u>$\beta_{\text{sca},c}^{\text{a}}, \beta_{\text{abs},c}^{\text{a}}$</u>	<u>Scattering and absorption coefficients of aerosol type c</u>	<u>m^{-1}</u>
<u>β_k</u>	<u>Extinction coefficient of layer k in the precomputation of optical paths</u>	<u>m^{-1}</u>
<u>$\beta_{n,i,j}(s')$</u>	<u>Extinction coefficient encountered along the event-to-detector path associated with event (n, i, j)</u>	<u>m^{-1}</u>
<u>a</u>	<u>Single-scattering albedo of the local mixture</u>	<u>$\sim$</u>
<u>a_t</u>	<u>Single-scattering albedo of selected constituent type t</u>	<u>$\sim$</u>
<u>a^{m}</u>	<u>Single-scattering albedo of the gas</u>	<u>$\sim$</u>
<u>a_c^{a}</u>	<u>Single-scattering albedo of aerosol type c</u>	<u>$\sim$</u>
<u>b</u>	<u>Total optical thickness</u>	<u>$\sim$</u>
<u>b_t</u>	<u>Optical thickness of constituent type t</u>	<u>$\sim$</u>
<u>$b_{\text{sca},t}, b_{\text{abs},t}$</u>	<u>Scattering and absorption optical thicknesses of constituent type t</u>	<u>$\sim$</u>
<u>b^{m}</u>	<u>Gas optical thickness</u>	<u>$\sim$</u>
<u>b^{a}</u>	<u>Aerosol or cloud optical thickness</u>	<u>$\sim$</u>
<u>$b_{\text{sca}}^{\text{m}}, b_{\text{abs}}^{\text{m}}$</u>	<u>Gas scattering and absorption optical thicknesses</u>	<u>$\sim$</u>
<u>$b_{\text{sca},c}^{\text{a}}, b_{\text{abs},c}^{\text{a}}$</u>	<u>Scattering and absorption optical thicknesses of aerosol type c</u>	<u>$\sim$</u>
<u>$\tau(\mathbf{x}_a \rightarrow \mathbf{x}_b)$</u>	<u>Optical depth between two points $\mathbf{x}_a$ and $\mathbf{x}_b$</u>	<u>$\sim$</u>

Table S14. Atmospheric and particle properties.

Symbol	Description	Unit
ρ	Depolarisation factor	-
Δ, Δ'	Rayleigh-scattering coefficients derived from ρ	-
F_K	King correction factor	-
n	Refractive index of the gas	-
n_r, n_i	Real and imaginary parts of the particle refractive index	-
$\sigma_{\text{abs},i}^{\text{m}}$	Absorption cross section of gas species i	m^2
σ_c^{a}	Extinction cross section of aerosol type c	m^2
η_i	Volume mixing ratio of gas species i	-
N_{g}	Number of absorbing gas species	-
N_{c}	Number of aerosol or cloud-particle types	-
$N_{\text{cal},c}^{\text{a}}$	Particle column number density of aerosol type c	m^{-2}
r_{eff}	Effective particle radius	μm
v_{eff}	Effective variance of the particle size distribution	-
$p(z)$	Pressure profile	Pa
$T(z)$	Temperature profile	K
g	Gravitational acceleration	m s^{-2}
M	Molar mass of the background gas	kg mol^{-1}
R	Universal gas constant	$\text{J mol}^{-1} \text{K}^{-1}$
N_{av}	Avogadro constant	mol^{-1}
N_L	Loschmidt number	m^{-3}
Δp_k	Pressure difference across layer k	Pa

Table S15. Monte Carlo path, weight, and estimator quantities, part I.

<u>Symbol</u>	<u>Description</u>	<u>Unit</u>
$\underline{N}$	<u>Number of photons launched per source column in forward mode or per detector column in backward mode</u>	<u>–</u>
$\underline{N_r}$	<u>Number of independent simulation rounds</u>	<u>–</u>
$\underline{M_i}$	<u>Total number of scattering events of photon i</u>	<u>–</u>
$\underline{M_{i,j}}$	<u>Total number of events of photon i launched in source column j</u>	<u>–</u>
$\underline{w}$	<u>Photon weight</u>	<u>–</u>
$\underline{w_{n,i}}$	<u>Photon weight at scattering order or event n of photon i</u>	<u>–</u>
$\underline{w_{n,i,j}}$	<u>Photon weight at event n of photon i launched in source column j</u>	<u>–</u>
$\underline{\mathbf{X}_0}$	<u>Random forward launch position on the source area O_0</u>	<u>m</u>
$\underline{\mathbf{X}^\bullet}$	<u>Random backward launch position on the detector area O</u>	<u>m</u>
$\underline{d}$	<u>Free photon path length to the next atmospheric event</u>	<u>m</u>
$\underline{\Delta s}$	<u>Distance from an event location to the nearest layer boundary along the detector path</u>	<u>m</u>
$\underline{s}$	<u>Generic line-of-sight distance variable</u>	<u>m</u>
$\underline{s'}$	<u>Dummy path-integration variable</u>	<u>m</u>
$\underline{s^*}$	<u>Upstream distance variable in the Green-function derivation</u>	<u>m</u>
$\underline{s_b}$	<u>Distance from the observation point to the upstream boundary along a ray</u>	<u>m</u>
$\underline{s^\bullet}$	<u>Distance from an event location to the detector boundary</u>	<u>m</u>
$\underline{s_{n,i,j}^\bullet}$	<u>Distance from event (n, i, j) to the detector boundary along the detector path</u>	<u>m</u>
$\underline{s_0}$	<u>Solar-side distance from a scattering point to the sunlight-entry boundary along $-\omega_0$; also used as a free-path variable in the forward derivation</u>	<u>m</u>
$\underline{s_{0,i}}$	<u>Solar-side distance from $\mathbf{x}_{1,i}$ to the sunlight-entry boundary in the backward estimators</u>	<u>m</u>
$\underline{s_1, s_2, s_3}$	<u>Path-length variables between successive scattering events in the deterministic derivations</u>	<u>m</u>
$\underline{S_0, S_1, S_2, S_3}$	<u>Random free-path lengths in forward Monte Carlo</u>	<u>m</u>
$\underline{S_{0,i}, S_{1,i}, S_{2,i}, S_{3,i}}$	<u>Realisations of sampled forward free-path lengths for photon i</u>	<u>m</u>
$\underline{\xi, \xi_1, \xi_2, \xi_3}$	<u>Independent random numbers uniformly distributed on $(0, 1)$</u>	<u>–</u>

Table S16. Monte Carlo path, weight, and estimator quantities, part II.

Symbol	Description	Unit
$\underline{W}$	Local-estimation contribution to the detector signal in forward mode	–
$\underline{W}_{n,i,j}$	Forward local-estimation contribution of event n of photon i launched in source column j	–
$\underline{W}^{\text{bw}}$	Local-estimation contribution to the detector signal in backward mode	–
$\underline{W}_{n,i}^{\text{bw}}$	Backward local-estimation contribution of event n of photon i	–
$\underline{\chi}$	Indicator function selecting detector rays that intersect detector area O	–
$\underline{\chi}_{n,i,j}$	Indicator for event (n, i, j) in the practical forward multi-column estimator	–
$\underline{\overline{M}}$	Normalised detector-response matrix in backward Monte Carlo	–
$\underline{\overline{M}}'$	Updated normalised detector-response matrix after a backward-mode event	–
$\underline{\overline{M}_0, \overline{M}_1, \overline{M}_2, \dots}$	Updated detector-response matrices after successive backward events	–
$\underline{\overline{M}_{12}, \overline{M}_{13}}$	Elements (1,2) and (1,3) of $\underline{\overline{M}}$	–
$\underline{[\cdot]}_1$	Operation selecting the first component of a Stokes vector	–
$\underline{I}_r$	Simulated first Stokes parameter in simulation round r	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
$\underline{\langle I \rangle}$	Mean value of I over simulation rounds	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
$\underline{\sigma_{\langle I \rangle}}$	Standard error of the mean of I	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$

Table S17. Probability densities, cumulative distributions, and sampling functions.

<u>Symbol</u>	<u>Description</u>	<u>Unit</u>
$p(\cdot)$	<u>Probability density function, generic notation, including joint PDFs</u>	<u>depends on argument</u>
$P(\cdot)$	<u>Cumulative distribution function in the sampling appendices</u>	<u>–</u>
p_{Qa}	<u>PDF of the forward launch position on the source area O_0</u>	<u>m^{-2}</u>
p_Q	<u>PDF of the backward launch position on the detector area O</u>	<u>m^{-2}</u>
$p_{S_0}, p_{S_1}, p_{S_2}, p_{S_3}$	<u>PDFs of sampled free paths in forward Monte Carlo</u>	<u>m^{-1}</u>
$p_{S_0}^{\text{bw}}, p_{S_1}^{\text{bw}}, p_{S_2}^{\text{bw}}, p_{S_3}^{\text{bw}}$	<u>PDFs of sampled free paths in backward Monte Carlo; the index depends on the scattering order considered</u>	<u>m^{-1}</u>
$p_{\omega_1}, p_{\omega_2}$	<u>PDFs of sampled scattering directions in forward Monte Carlo</u>	<u>sr^{-1}</u>
$p_{\omega_1}^{\text{bw}}, p_{\omega_2}^{\text{bw}}$	<u>PDFs of sampled scattering directions in backward Monte Carlo</u>	<u>sr^{-1}</u>
$p(\mu, \varphi)$	<u>Joint PDF of the Lambertian reflection direction</u>	<u>–</u>
$p(\mu)$	<u>Marginal PDF of μ for Lambertian reflection</u>	<u>–</u>
$p(\varphi)$	<u>Marginal PDF of φ for Lambertian reflection</u>	<u>–</u>
$p(\cos \Theta, \sigma_1)$	<u>Joint PDF of the forward scattering direction of polarised light</u>	<u>–</u>
$p^{\text{bw}}(\cos \Theta, \sigma_2)$	<u>Joint PDF of the backward scattering direction</u>	<u>–</u>
f	<u>Envelope function in acceptance-rejection sampling</u>	<u>same as target PDF</u>
g	<u>Proposal PDF in acceptance-rejection sampling</u>	<u>same as target PDF</u>
C	<u>Normalisation or rejection constant in acceptance-rejection sampling</u>	<u>–</u>
G	<u>CDF of the proposal distribution in the Mie-sampling appendix</u>	<u>–</u>
G^{-1}	<u>Inverse CDF used in inverse-transform sampling, particularly for Mie scattering</u>	<u>depends on argument</u>
X	<u>Auxiliary quantity in the forward sampling derivations</u>	<u>–</u>
Y	<u>Auxiliary quantity in the backward sampling derivations</u>	<u>–</u>

Table S18. Vector radiative transfer equation, collision-density, and operator symbols.

<u>Symbol</u>	<u>Description</u>	<u>Unit</u>
∇	<u>Spatial gradient operator</u>	m^{-1}
$\mathcal{L}$	<u>Linear transport operator in the VRTE derivation</u>	$\sim$
$\mathcal{L}_s$	<u>One-dimensional transport operator along a ray</u>	$\sim$
S_0	<u>Source-density term in the VRTE</u>	$\text{W m}^{-3} \text{ nm}^{-1} \text{ sr}^{-1}$
q	<u>Local source term in the formal VRTE solution</u>	$\text{W m}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$
f	<u>Collision-density Stokes vector</u>	$\text{W m}^{-3} \text{ nm}^{-1} \text{ sr}^{-1}$
Ψ	<u>Initial collision density</u>	$\text{W m}^{-3} \text{ nm}^{-1} \text{ sr}^{-1}$
k	<u>Transport kernel in the collision-density formulation</u>	$\text{m}^{-3} \text{ sr}^{-1}$
K	<u>Integral transport operator acting on the collision density</u>	$\sim$
K^+	<u>Adjoint transport operator</u>	$\sim$
(u, v)	<u>Inner product of Stokes-vector-valued functions</u>	<u>depends on arguments</u>
u, v, g	<u>Generic Stokes-vector-valued functions used in the operator derivations</u>	<u>depends on context</u>
$\delta(\cdot)$	<u>Dirac delta function</u>	<u>inverse of argument unit</u>
$\delta_{\mathbf{x} \bullet \boldsymbol{\omega} \bullet}$	<u>Product Dirac delta function selecting detector point and propagation direction</u>	$\text{m}^{-3} \text{ sr}^{-1}$
Φ_j	<u>Contribution function for the j^{th} detector Stokes component</u>	$\text{m}^{-2} \text{ sr}^{-1}$

Table S19. Scattering-order, finite-area, and parameterised-path symbols.

<u>Symbol</u>	<u>Description</u>	<u>Unit</u>
$\underline{J}$	Generic vector-valued integral used in the Monte Carlo-estimator derivations	depends on context
$\underline{g_1, g_2, g_3}$	Integrands used in the first-, second-, and third-order forward Monte Carlo-estimator derivations	depends on context
$\underline{g_1^{bw}, g_2^{bw}, g_3^{bw}}$	Integrands used in the first-, second-, and third-order backward Monte Carlo-estimator derivations	depends on context
$\underline{h(\boldsymbol{x}_1)}$	Generic integrable function of the scattering point used in the finite-area transformation	depends on context
$\underline{s_0(\boldsymbol{x})}$	Solar-side distance from $\boldsymbol{x}$ to the sunlight-entry boundary along $-\boldsymbol{\omega}_0$	m
$\underline{\boldsymbol{x}_1(s_1)}$	First-scattering location along the detector line of sight in the first-order derivation	m
$\underline{\boldsymbol{x}_0(s_1)}$	Entry point of the incident sunlight associated with $\boldsymbol{x}_1(s_1)$	m
$\underline{\boldsymbol{x}_2(s_2)}$	Second, or last, scattering location along the detector line of sight in the second-order derivation	m
$\underline{\boldsymbol{x}_1(s_2, s_1, \boldsymbol{\omega}_1)}$	First-scattering location in the second-order derivation	m
$\underline{\boldsymbol{x}_0(s_2, s_1, \boldsymbol{\omega}_1)}$	Entry point of the incident sunlight associated with $\boldsymbol{x}_1(s_2, s_1, \boldsymbol{\omega}_1)$	m
$\underline{\boldsymbol{x}_3(s_3)}$	Third, or last, scattering location along the detector line of sight in the third-order derivation	m
$\underline{\boldsymbol{x}_2(s_3, s_2, \boldsymbol{\omega}_2)}$	Second-scattering location in the third-order derivation	m
$\underline{\boldsymbol{x}_1(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1)}$	First-scattering location in the third-order derivation	m
$\underline{\boldsymbol{x}_0(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1)}$	Entry point of the incident sunlight associated with $\boldsymbol{x}_1(s_3, s_2, s_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_1)$	m

Table S20. Classical sampling-approach symbols.

<u>Symbol</u>	<u>Description</u>	<u>Unit</u>
$\tilde{p}_{\omega_2}^{(0)}$	<u>Approximate forward PDF for sampling ω_2 when the incident beam is treated as unpolarised</u>	<u>sr^{-1}</u>
$\tilde{p}_{\omega_1}^{\text{bw},(0)}$	<u>Approximate backward PDF for sampling ω_1 when the incident beam is treated as unpolarised</u>	<u>sr^{-1}</u>
$\tilde{C}_{\omega_2}$	<u>Importance-sampling correction factor in the classical forward approach</u>	<u>$\sim$</u>
$\tilde{C}_{\omega_1}^{\text{bw}}$	<u>Importance-sampling correction factor in the classical backward approach</u>	<u>$\sim$</u>

Table S21. Symbols used in the Green-function discussion.

<u>Symbol</u>	<u>Description</u>	<u>Unit</u>
<u>$u(x)$</u>	<u>Unknown scalar function in the generic boundary-value problem</u>	<u>—</u>
<u>$q(x)$</u>	<u>Source term in the generic boundary-value problem</u>	<u>—</u>
<u>x</u>	<u>One-dimensional coordinate in the generic Green-function example</u>	<u>—</u>
<u>x^*</u>	<u>Source location in the one-dimensional Green-function example</u>	<u>—</u>
<u>a, b</u>	<u>Interval endpoints in the generic boundary-value problem</u>	<u>—</u>
<u>B</u>	<u>Interval length or upper boundary in the worked Green-function example</u>	<u>—</u>
<u>α</u>	<u>Positive constant in the worked Green-function example</u>	<u>depends on context</u>
<u>$G(x, x^*)$</u>	<u>Green's function in the generic one-dimensional example</u>	<u>—</u>
<u>$G(s, s^*)$</u>	<u>Green's function along a ray in the VRTE derivation</u>	<u>m^{-1}</u>
<u>H</u>	<u>Heaviside step function</u>	<u>—</u>
<u>$C_1(x^*), C_2(x^*)$</u>	<u>Integration constants in the worked Green-function example</u>	<u>—</u>
<u>$C_-(s^*), C_+(s^*)$</u>	<u>Integration constants for the Green's function on either side of the source point s^*</u>	<u>depends on context</u>
<u>ϵ</u>	<u>Infinitesimal interval half-width used to derive the Green-function jump condition</u>	<u>same unit as s</u>
<u>s^{*-}, s^{*+}</u>	<u>Points immediately downstream and upstream of the source point s^* in the Green-function derivation</u>	<u>m</u>