Supplement of

Determination of water diffusion coefficients in aerosols based on characteristic time analysis

Shuqi Guo[1], Chengyi Fan[1], Chunsheng Zhao[1]

[1]Department of Atmospheric and Oceanic Sciences, School of Physics, Peking University, Beijing, 100871, China

Correspondence to: Chunsheng Zhao (zcs@pku.edu.cn)

S1 Derivation of the D_2O concentration inside a droplet with a non-uniform initial concentration distribution

For a non-uniform initial concentration distribution, the governing equation for D_2O diffusion inside the droplet, together with the initial and boundary conditions, can be written as

$$\frac{\partial C}{\partial t} = D_w\left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right], \tag{S1}$$

$$\left(\frac{\partial C}{\partial r}\right)_{r=0} = 0, \tag{S2}$$

$$C(R,t) = C_s, \tag{S3}$$

$$C(r,0) = Ar^2 + E, \tag{S4}$$

where

$$A = \frac{3(1-\Phi_0)C_s}{2R^2}, \tag{S5}$$

$$E = \frac{(3\Phi_0-1)C_s}{2}. \tag{S6}$$

To convert the boundary condition into a homogeneous form, we introduce the transformation

$$v(r,t) = C(r,t) - C_s. \tag{S7}$$

After this transformation, the diffusion equation, together with the corresponding initial and boundary conditions become

$$\frac{\partial v}{\partial t} = D_w\left[\frac{\partial^2 v}{\partial r^2} + \frac{2}{r}\frac{\partial v}{\partial r}\right], \tag{S8}$$

$$\left(\frac{\partial v}{\partial r}\right)_{r=0} = 0, \tag{S9}$$

$$v(R,t) = 0, \tag{S10}$$

$$v(r,0) = A(r^2 - R^2). \tag{S11}$$

The equation for $v(r,t)$ is solved using separation of variables. We assume that $v(r,t)$ can be expressed as the product of a radial function and a temporal function:

$$v(r,t) = X(r)T(t). \tag{S12}$$

Substitution of this expression into Eq. (S8) gives

$$\frac{T'}{D_w T} = \frac{X'' + \frac{2}{r}X'}{X} = -\lambda^2. \tag{S13}$$

S1.1 Solution of the temporal equation $T(t)$

The temporal part can be written as

$$T' + D_w \lambda^2 T = 0. \tag{S14}$$

The general solution is therefore

$$T(t) = exp(-D_w \lambda^2 t). \tag{S15}$$

S1.2 Solution of the spatial equation $X(r)$

The spatial part can be written as

$$X'' + \frac{2}{r}X' + \lambda^2 X = 0. \tag{S16}$$

We introduce a function $w(r) = rX(r)$, so that $X(r) = \frac{w(r)}{r}$. The first and second derivatives of $X(r)$ are

$$X'(r) = \frac{w'(r)}{r} - \frac{w(r)}{r^2}, \tag{S17}$$

$$X''(r) = \frac{w''(r)}{r} - \frac{2w'(r)}{r^2} + \frac{2w(r)}{r^3}. \tag{S18}$$

Substituting $w(r)$ into the spatial equation gives

$$w'' + \lambda^2 w = 0. \tag{S19}$$

The general solution of this equation is

$$w(r) = C_1 sin(\lambda r) + C_2 cos(\lambda r). \tag{S20}$$

Transforming back to $X(r)$, we obtain

$$X(r) = C_1 \frac{sin(\lambda r)}{r} + C_2 \frac{cos(\lambda r)}{r} . \tag{S21}$$

Applying the boundary conditions for the spatial function,

$$X'(r) = 0, \tag{S22}$$

$$X(R) = 0, \tag{S23}$$

and requiring the concentration at the droplet centre to remain finite, we have

$$C_2 = 0, \tag{S24}$$

$$C_1 \frac{sin(\lambda R)}{R} = 0. \tag{S25}$$

The eigenvalues are therefore

$$\lambda = \frac{n\pi}{R} \quad (n = 1,2,3, \ldots) . \tag{S26}$$

Let $k_n = \frac{n\pi}{R}$. The solution of the spatial equation can then be written as

$$X(r) = C_1 \frac{sin(k_n r)}{r} \quad (n = 1,2,3, \ldots) . \tag{S27}$$

S1.3 General solution of $v(r, t)$

Combining the temporal and spatial solutions gives the general solution for $v(r,t)$:

$$v(r,t) \;=\; \sum_{n=1}^{\infty} B_n \frac{sin(k_n r)}{r} exp(-\frac{n^2\pi^2 D_w t}{R^2}), \tag{S28}$$

where B_n is the expansion coefficient

S1.4 Determination of the expansion coefficient B_n

The coefficient B_n is determined by expanding the initial condition using the orthogonality of the eigenfunctions in spherical coordinates. Substituting t=0 into the general solution gives

$$v(r,0) \;=\; \sum_{n=1}^{\infty} B_n \frac{sin(k_n r)}{r} \;= A(r^2 - R^2)\,. \tag{S29}$$

Here, $\frac{sin(k_n r)}{r}$ is the eigenfunction obtained in spherical coordinates, with the corresponding orthogonal weight function r^2. To determine the expansion coefficient B_n, both sides of the above equation are multiplied by the eigenfunction $\frac{sin(k_m r)}{r}$ and the weight function r^2, and then integrated over the interval $[0, R]$:

$$\sum_{n=1}^{\infty} B_n \int_0^R \frac{sin(k_n r)}{r}\frac{sin(k_m r)}{r} r^2 dr \;=\; \int_0^R A(r^2 - R^2)\frac{sin(k_m r)}{r} r^2 dr. \tag{S30}$$

The integral on the left-hand side can be simplified using the orthogonality of the sine functions:

$$\int_0^R sin(k_n r)\, sin(k_m r) dr \;=\; \begin{cases} 0 & n \neq m \\ \frac{R}{2} & n = m \end{cases}. \tag{S31}$$

Therefore, the left-hand side reduces to $B_n \frac{R}{2}$.

The integral on the right-hand side can then be evaluated as

$$A\int_0^R (r^3 - R^2 r)\, sin(\frac{n\pi r}{R}) dr. \tag{S32}$$

Thus, the expression for B_n is

$$B_n \;=\; \frac{2A}{R}\int_0^R (r^3 - R^2 r)\, sin(\frac{n\pi r}{R}) dr. \tag{S33}$$

Using integration by parts, the two integrals $\int_0^R r^3 sin(\frac{n\pi r}{R})\, dr$ and $\int_0^R r sin(\frac{n\pi r}{R})\, dr$ are evaluated as

$$\int_0^R r^3 sin(\frac{n\pi r}{R}) \;=\; -\frac{R^4}{n\pi}(-1)^n + \frac{6R^4}{n^3\pi^3}(-1)^n, \tag{S34}$$

$$\int_0^R r sin(\frac{n\pi r}{R})\, dr \;=\; -\frac{R^2}{n\pi}(-1)^n. \tag{S35}$$

Therefore,

$$B_n \;=\; \frac{12AR^3}{n^3\pi^3}(-1)^n. \tag{S36}$$

Substituting the expression for A from Eq. (S5) gives

$$B_n = \frac{3(1-\Phi_0)C_s}{2R^2}\frac{12AR^3}{n^3\pi^3}(-1)^n = \frac{18(1-\Phi_0)C_sR}{n^3\pi^3}(-1)^n. \quad \text{(S37)}$$

S1.5 Expression for $C(r,t)$

The complete expression for the transformed variable $v(r,t)$ has been obtained as

$$v(r,t) = \sum_{n=1}^{\infty}\left[\frac{18(1-\Phi_0)C_sR}{n^3\pi^3}(-1)^n\right]\frac{sin(\frac{n\pi r}{R})}{r}exp(-\frac{n^2\pi^2 D_w t}{R^2}). \quad \text{(S38)}$$

Transforming back to the original concentration distribution gives

$$C(r,t) = C_s + \sum_{n=1}^{\infty}\left[\frac{18(1-\Phi_0)C_sR}{n^3\pi^3}(-1)^n\right]\frac{sin(\frac{n\pi r}{R})}{r}exp(-\frac{n^2\pi^2 D_w t}{R^2}). \quad \text{(S39)}$$

S2 Derivation of the D_2O fraction in the droplet

The concentration distribution of D_2O inside the droplet has been derived above. On this basis, a radial averaging method is used to further calculate the D_2O fraction inside the droplet, namely

$$\Phi_{D_2O}(t) = \frac{\overline{C(t)}}{C_s} = \frac{1}{C_s}\frac{1}{R}\int_0^R C(r,t)\,dr. \quad \text{(S40)}$$

Substituting the expression for $C(r,t)$ gives

$$\Phi_{D_2O}(t) = 1 + \sum_{n=1}^{\infty}\frac{18(1-\Phi_0)(-1)^n}{n^3\pi^3}exp(-\frac{n^2\pi^2 D_w t}{R^2})\int_0^R \frac{sin(\frac{n\pi r}{R})}{r}\,dr. \quad \text{(S41)}$$

The integral can be evaluated by a change of variables. Let $x = \frac{n\pi r}{R}$, so that $dr = \frac{R}{n\pi}dx$. When $r = R$, $x = n\pi$. Therefore,

$$\int_0^R \frac{sin(\frac{n\pi r}{R})}{r}\,dr = \int_0^{n\pi}\frac{sinx}{x}\,dx = Si(n\pi). \quad \text{(S42)}$$

This integral is the sine integral. Thus, the final expression for $\Phi_{D_2O}(t)$ is

$$\Phi_{D_2O}(t) = 1 + \sum_{n=1}^{\infty}\frac{18(1-\Phi_0)(-1)^n}{n^3\pi^3}Si(n\pi)exp(-\frac{n^2\pi^2 D_w t}{R^2}). \quad \text{(S43)}$$