

Response to  
Reviewer #2

'Mathematically sound, but please consider elaborating on real-world applicability'

The technical note by Vilà-Guerau de Arellano et al. explores to what extent oxygen transport through stomata is regulated by water fluxes in the context of multicomponent mass transfer. The central thesis is that, under low Reynolds number conditions dominated by molecular diffusion, as water fluxes from the evaporating substomatal cavity are typically much higher than oxygen fluxes, the gradient of oxygen across stomata is proportional to water fluxes according to the Stefan–Maxwell equations, leading to uphill diffusion of oxygen that counterbalances the Stefan flow. As the authors put it, this phenomenon “can strongly affect the interpretation of O<sub>2</sub> exchange on stomatal level”, which I agree on the premise that mass transfer is dominated by multicomponent molecular diffusion and the Stefan flow induced by evaporation. But empirically, it is this premise that I have certain doubts about.

Thanks for reading and commenting on the manuscript. As the referee noted, our starting premise is the use of the Stefan–Maxwell (SM) equations, as they provide both a rigorous mathematical framework and a physically interpretable description of O<sub>2</sub> transport between the substomatal cavity and the atmosphere. In this sense, they offer a theoretical basis for interpreting future observational studies as well as a consistent mathematical representation of O<sub>2</sub> transport. The resulting expressions are readily applicable for both experimentalists and modelers, as shown by equation (26) and the regime identification presented in Table 2, thereby facilitating the interpretation of future laboratory experiments and their implementation in weather, climate, and carbon–oxygen models that explicitly represent leaf-scale processes

A leaf receiving an intermediate to high level of radiation is typically warmer than the ambient air, because it needs to dissipate heat through diffusion (what meteorologists call sensible heat transfer), in addition to outgoing thermal radiation and latent heat transfer through transpiration. As oxygen and water molecules have different molecular weights, this leaf-to-air temperature gradient may create conditions for thermophoresis in which oxygen molecules move down the temperature gradient (from the substomatal cavity to the air) as opposed to the direction of water vapor thermodiffusion. How thermodiffusion compares to the Stefan flow and molecular diffusion in stomatal oxygen transport seems unknown to me, and it bears consequences for how we interpret leaf-level oxygen exchange measurements.

The referee raises a very interesting and valid point that can serve as a natural follow-up to our study. In meteorological terms, our current analysis assumes neutral stability which means that instabilities due to temperature differences at molecular or turbulent scales are omitted. Including thermal (buoyant) effects, such as temperature gradients between the leaf and the surrounding air, would be a logical next step. Our Technical Note focuses solely on the effects of transport driven by velocity differences arising from the molar flux of water vapor without accounting for these temperature differences. As the referee notes, temperature differences between the atmosphere near the leaf and the substomatal cavity could generate thermally driven instabilities that influence O<sub>2</sub> transport.

In the revised manuscript and in the discussion section, we will address the thermodiffusion effect in the Discussion section, citing relevant sources such as Curtiss and Hirschfelder (1949), *Transport Properties of Multicomponent Gas Mixtures (Journal of Chemical Physics, 17)*, as a potential extension of our neutral-condition theoretical framework. We are also aware of the study by Griffani et al., *New Phytologist*, 2024 on the effect of the thermodiffusion to transpiration and a similar kind of analysis can be carried out for O<sub>2</sub>, but we see that it is out of the scope of the present stud

Regarding the interpretation of Stefan–Maxwell diffusion as “the drag forces exerted by all other species,” I concur with my fellow reviewer that the underlying physical picture seems murky. It is clear that the authors are alluding to the kinetic theory of gases. But if Stefan–Maxwell diffusion originates from drag forces at the molecular level, in what sense does it differ from viscosity? It seems that this physical picture (lines 36–54) needs to be clarified to build a robust intuition.

Following the advice of the referee, we will revise this part of the Introduction to better place our research in context. In the revised manuscript, we will specify that “drag” (friction) in the Stefan–Maxwell framework refers to momentum exchange in binary molecular collisions between different species, rather than to shear stress in bulk flow, and its relation with viscosity as expressed by the SM diffusion coefficients. In our case, molecular friction arising from differences in molecular velocities—driven by the molar density flux—gives rise to mole gradients. These gradients, in turn, drive diffusive transport at rates determined by the corresponding diffusion coefficients.

I consider the nondimensional treatment in Appendix C a helpful framework for assessing under which conditions Stefan flow and multicomponent molecular diffusion matter. But it seems that the wind speed range quoted in line 425 is the condition in a greenhouse. Wind experienced by top-canopy leaves in a forest can be quite different. It would help to give a threshold of wind speed at which turbulent diffusion becomes more important than multicomponent molecular diffusion.

In real canopies—particularly at the top of the canopy and away from the leaf surface—the flow regime is typically turbulent, and turbulent transport dominates the exchange of oxygen. In our view, the Stefan–Maxwell equations are valid and applicable only under low Reynolds number conditions (below about  $10^3$ – $10^4$ ), which occur very close to the leaf when wind speeds approach  $0 \text{ m s}^{-1}$ . As a representative example, for large leaves with a characteristic length scale of  $\sim 10 \text{ cm}$ , the Reynolds number would be below  $\sim 10^3$ , still below the critical value for transition to turbulence. The precise threshold is difficult to determine, as it depends on leaf morphology, flow speed, atmospheric stability, and micro-scale turbulence. The wind speeds given in the manuscript ( $0.05$ – $0.15 \text{ m s}^{-1}$ ) are intended as illustrative values, representative of potential laboratory or controlled-environment experiments.

In the revised manuscript (Discussion section and in commenting Appendix C), we will clarify the applicability of the SM equations in relation to wind speed values and, following the referee’s advice, place our study in a clearer real-world context near the leaf surface. Importantly, at the canopy scale (e.g. eddy covariance flux observations), the effects of Stefan flow are negligible; thus, the real-world applicability of our theory lies primarily at the small, near-leaf scale (see Appendix C).

Lastly, Table 1 presents calculations of molar fluxes of water vapor,  $\text{O}_2$ , and  $\text{CO}_2$  and their partition into Stefan flow and diffusive flux components. The calculations assume a water vapor mole fraction of 0.01, but in reality, it is the most variable component in the canopy air. In a desert, this value could be much smaller, whereas in a tropical rainforest at  $35^\circ\text{C}$ , the air could hold 5.5% water vapor (in mole fractions) at saturation. It would be helpful to expand this table (maybe into a figure) to show calculations under a range of realistic water vapor mole fractions.

Our analysis shows that the most relevant variable is the molar flux density of water, as expressed in Eq. (22). In this equation, the water vapor mole fraction  $x_w$  is included in the water vapor gradient (Eq. 22a) but does not appear in the expression for the  $\text{O}_2$  gradient. Our representative value  $x_w = 0.01 \text{ mol mol}^{-1}$  is already relatively high, corresponding to a specific humidity of  $16 \text{ g}_w \text{ kg}_a^{-1}$ . Observed and simulated values studied in the Amazon rainforest (see Fig. 10 in Pedruzo-Bagazgoitia et al., 2023, *Journal of Advances in Modeling Earth Systems*, 15, e2022MS003210, <https://doi.org/10.1029/2022MS003210>) range between 20 and  $25 \text{ g}_w \text{ kg}_a^{-1}$ , corresponding to mole

fractions of 0.012–0.016 mol mol<sup>-1</sup>. Below we present a sensitivity analysis with respect to different values of the water vapor mole fraction.

Following the referee's recommendation, we have carried out a sensitivity analysis on  $x_w$  over the range 0.01 mol mol<sup>-1</sup> (very dry conditions, 16 g<sub>w</sub>kg<sub>a</sub><sup>-1</sup> to 0.016 mol mol<sup>-1</sup> (tropical Amazonia conditions, 25 g<sub>w</sub>kg<sub>a</sub><sup>-1</sup>). For the water vapor gradient, we obtained values of -9.45 m<sup>-1</sup> (dry) and -9.31 (mol mol<sup>-1</sup>) m<sup>-1</sup> (tropical), compared to the value in Table 1 for  $x_w = 0.01$  (-9.37 (mol mol<sup>-1</sup>) m<sup>-1</sup>). The effect is not very important on the gradients. In the revised manuscript, we will retain the table as it stands but include these additional values in the text to provide a clearer sensitivity analysis of our findings.