A review of “Technical Note: New insights into stomatal oxygen transport viewed as a multicomponent diffusion process” by Vila-Guerau de Arellano et al. (egusphere-2025-2705)

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Synopsis

This study considers the drag exerted by water vapour molecules escaping stomata due to transpiration—the dominant gas exchange process—on oxygen molecules exported from stomata due to photosynthetic production. The issue at hand is the degree to which oxygen transport occurs down its concentration gradient due to Fickian diffusion, versus transport that may be a consequence of mass flow. The study is based on the broadly accepted theory of the Stefan-Maxwell equations, taken to represent the fundamental physics of multicomponent diffusion, and from which a multitude of equations are derived. The authors’ mathematical manipulations appear to be correct; I hardly criticize them (but see Specific comments below). Rather, my doubts regarding these analyses concern their starting point, and specifically whether the Stefan-Maxwell equations do indeed accurately represent the fundamental physics of transport mechanisms.

General assessment

I neither endorse nor oppose publication of this manuscript. I have expressed my assessment that the concentration gradients determining diffusion should be specified, not as molar fractions (as in the Stefan-Maxwell equations) which seem to violate Newton’s laws, but as mass fractions. My justification of this view is available publicly, both as a peer-reviewed article (Kowalski et al., 2021) and a reprint manuscript currently under discussion (Kowalski, 2025), and I invite the authors to join that discussion online as well as here in reply. In short, I believe that inertia, which is fundamental to Newton’s laws of motion including the definition of drag forces, must be considered when partitioning transport between diffusive and non-diffusive mechanisms.

It seems clear that we disagree—in the authors’ words, regarding the definition of uphill and downhill transport—specifically regarding how these directions are defined by whether molar- or mass-based “concentration” gradients orient diffusion. Here my intention is not to oppose the publication of opposing viewpoints, but rather to stimulate further open discussion. Therefore, I recommend “major revision”, and pose ***five questions*** that I ask the authors to address, at least in reply and at best within a revised version of their manuscript. Some of these questions require building up a background context in which to frame them, and I beg the authors’ indulgence in this regard.

Question 1: The authors use "mass" in many instances where I think it either undermines the molar-based description of diffusion, or contradicts their own definitions. For example:

> At line 38, they seem to distinguish diffusive and non-diffusive transport, the latter equated with "mass flow" due to drag exerted by exiting water vapour (I agree);
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> At line 106, however, equation (5) defines the reference velocity (u) based on molar exchanges (I disagree). To simplify, in the static situation where their $u = 0$, the case of opposing/offsetting molar fluxes of water vapour (18 g mol^{-1}) and dry air (29 g mol^{-1}) does not exclude but rather ensures mass flow. Thus, their definition of diffusion is not independent of mass flow, but necessarily includes it;
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> At line 118, the authors note that the total diffusive flux of the mixture is zero, but this is defined on a molar (and not a mass) basis;
>
> At line 230, the authors again appear to make a clear distinction between "diffusive and mass flows", as if these were independent within their molar framework.

Would the authors like to revise their manuscript at lines 38 and 230 (see also lines 68, 99, 101, 116, 321, and 371) to refer to "molar flow" rather than "mass flow"?

Question 2: Similarly, the authors identify "mass balance" as one of the three key elements used in their study (line 67), and begin their derivations with equation (1) that is alleged to represent mass balance, despite having molar units. If this seems trivial, it should be noted that the time derivative of their equation (2) yields

$$\frac{dc_t}{dt} = \sum_{\alpha=1}^{n} \frac{dc_\alpha}{dt}$$

which need not be zero since the number of moles is not conserved through certain chemical reactions (see question 4 below), unlike total mass. ***Would the authors like to revise their manuscript at lines 68, 89, 90, 127, 153, and 326 (perhaps 131 and 405 as well) to refer to "molar balance" instead of "mass balance"?***

Question 3: Regarding drag forces, I think an analogy is worth examining. Suppose a steel ball of 4cm diameter is in equilibrium at rest on a frictionless horizontal plane. Now, if it experiences a drag force caused by collisions with a swarm of balls moving initially with speed U all in the same direction, perhaps we can distinguish two cases:

A. The moving balls that collide with the steel ball are ping-pong balls of negligible mass (or inertia)—and hence momentum—and therefore hardly drag it along even as they lose much of their original momentum; or

B. The moving balls are also 4cm-diameter steel balls, and if there are many of them the initially static ball ultimately joins the group (whose overall velocity is slightly slowed by its initial inertia—since it began as static—conserving total momentum).

Is inertia relevant to the drag forces caused by collisions, and does this apply to large collections of molecules as in fluids?

Question 4: Let us consider an initially static system with no external forces applied, consisting of nitrogen dioxide (NO_2) on the right ($x > 0$) and ethene (ethylene; C_2H_4) on the left ($x < 0$), diffusing in opposite directions with equal flux magnitudes. Since these gases have equal molecular masses (44 g mol^{-1}), at first glimpse the distinction between molar-based and mass-based definitions of diffusion seems moot; the initial reference velocity is zero in either case. But if dimerization of NO_2 to form dinitrogen tetroxide (N_2O_4)

$$2NO_2(g) \rightarrow N_2O_4(g)$$

reduces the number of moles of leftward-diffusing molecules, this proceeding reaction makes the molar-based reference velocity (u) that the authors define in their equation (5) increasingly more rightward ($\frac{du}{dt} > 0$). In their molar-based framework, the authors seem to suggest that the time-derivative of u is governed by the Navier-Stokes equation (line 411). ***Does this mean that the system can accelerate with no external forces acting?***

Question 5: The answer to Question 4 conditions the follow-up question, which I will therefore specify doubly:

> ***2A*: *If no, then do the well-established Stefan-Maxwell equations provide a rigorous physical framework for the analysis of transport mechanisms?***
>
> ***2B: If yes, then do Newton's laws require revision so as not to conflict with the Stefan-Maxwell equations?***

To my mind these questions are revelatory, and I hope the authors will consider them and reply. I furthermore would like to hear the authors' opinions regarding the Kowalski et al. (2021) and Kowalski (2025) analyses that similarly criticise the molar-based framework for representing diffusion as infringing upon Newton's laws. Together with this review, these amount to three documents (ranging from peer-reviewed and published to "grey literature") that provide examples where it seems to me that the molar-based, Stefan-Maxell framework contravenes Newton's laws in defining non-diffusive transport, and therefore in erroneously partitioning net transport and misrepresenting diffusion.

Finally, in case the authors find them to be of use when revising their manuscript, I add the following two specific observations.

Specific comments

1. Beginning at line 324, the authors state that "Although previous studies have recognized that transport of O_2 … could be relevant across scales from the canopy to the atmospheric boundary layer (Kowalski et al., 2021), our analysis of the fundamental mass balance equation demonstrates that the primary effects of Stefan flow emerge at the stomatal scale (see Appendix C)." This misses the point that the Kowalski et al. (2021) paper is principally about *turbulent* diffusion, as its title indicates. Its analysis included within the definition of "diffusion" reordering of mass by both molecular motions and turbulence. Appendix C, which considers only molecular diffusion, defines length and velocity scales that are not relevant to the case of atmospheric boundary layer considered by Kowalski et al. (2021), except within millimeters of the surface.
2. Line 409. Since the molar fraction is dimensionless, equation (C1) has units of s^{-1}.

References

Kowalski, A. S., Serrano-Ortiz, P., Miranda-Garc a, G., and Fratini, G., "Disentangling turbulent gas diffusion from non-diffusive transport in the boundary layer." *Boundary-Layer Meteorology*, **179** (3), 347-367. https://doi.org/10.1007/s10546-021-00605-5, 2021.

Kowalski, A. S.: Comment on "Technical note: An assessment of the relative contribution of the Soret effect to open water evaporation" by Roderick and Shakespeare (2025), EGUsphere [preprint], https://doi.org/10.5194/egusphere-2025-2814, 2025.