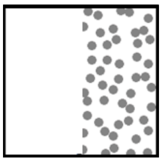
Distinguishing transport types

In the following examples, I will attempt to distinguish clearly between two types of transport, initially in the simplest of situations and then towards increasing complexity. The first type I will call Newtonian transport, whereby conveyance of a fluid constituent occurs because of fluid motion. The second I will call Fickian transport, whereby transport of a fluid constituent occurs independent of, or most simply in the absence of, fluid motion. I present examples of each that are quite clear, but then two cases that may be less intuitive to the authors (or other scientists who specify Fick's 1st law using molar concentration gradients), illustrating that Newton's laws should be kept in mind when specifying Fick's law.

1 Newtonian transport

The first case involves a system composed of two elements: a fluid that is pure xenon gas (Xe) and "Isaac", a cubic container, so named because he will help us to interpret the situation using Newton's laws. Initially, the system and indeed both elements are at rest, and importantly no external forces act on the system, but the Xe occupies only the right half of the container, leaving a vacuum on the left as depicted below.



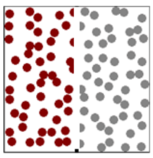
Of course, this situation is not stable, and so the Xe will expand to occupy the whole container. However, if we ask Isaac about the motion of the system and its elements, he would say the following: "Newton's three laws explain the resulting motion:

1. The system stayed stationary (1st Law), with no movement of its centre of mass;
2. The fluid shifted (its centre of mass) left because I pushed it (2nd Law); and
3. I, Isaac, moved right because the fluid pushed me back (reaction; 3rd Law)."

So far, this is all fairly straightforward, first-year physics for a multi-component system with no external forces.

2 Fickian transport

The second case is designed in contrast to the first, to illustrate transport with no fluid motion. Isaac is again present but now two gases, nitrous oxide (N_2O) and carbon dioxide (CO_2) compose the fluid. Each gas type occupies identical volume and are at the same temperature and pressure; hence, there are equal moles of each gas.



Now, if we ask Isaac about the motion of the system and its elements, he might say something quite different, along the following lines:

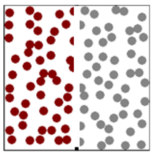
"Except for the mixing of N_2O and CO_2 (about which ask Adolf Fick) this was rather boring and trivial:

1. The system remained stationary (1st Law);
2. *Since the two gases have equal molecular mass (44 g mol^{-1})*, the fluid's centre of mass did not change and it experienced no force (2nd Law); and
3. There was no action, and so no reaction, and I, Isaac, did not move (3rd Law)."

This is again straightforward, but the italics give an indication of where we are heading, into perhaps unfamiliar territory.

3 Discerning types of transport

The third case is designed in demonstrate the difference between kinematic and inertial points of view regarding Fick's law. It is kinematically identical to the second, but now with two gases of very different mass, hydrogen (H_2, 2 g mol^{-1}) and Xe (131.3 g mol^{-1}).



Now, if we ask Isaac about the motion of the system and its elements, he might say something like the following:

"This is very similar to the first case above involving Xe and the vacuum. Since 98% of the fluid mass is Xe, the fluid's centre of mass is initially on the right, very near to where it was at the start of Case 1, and therefore the situation is much the same:

1. The system remained stationary (1st Law);
2. The fluid shifted (its centre of mass) left because I pushed it (2nd Law); and
3. I, Isaac, moved right because the fluid pushed me back (3rd Law)."

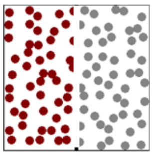
This no longer straightforward, regarding transport of the two gas types. The Xe moved left mostly by Newtonian transport, helped a little bit by Fickian transport. The H_2 had to diffuse upstream in order to achieve the same overall displacement magnitude as the Xe, requiring large Fickian transport to the right to overcome the Newtonian transport to the left.

If the Navier-Stokes equation fails to describe the motion of the fluid due to the lack of a pressure gradient force, then we should interpret this as a shortcoming of the Navier-Stokes equation, and not of the laws that it attempts (and fails, in this case) to represent.

The key point to recognise here is that, although Case 3 is identical to Case 2 kinematically, in *inertial* terms it more closely resembles Case 1, and therefore inertia cannot be neglected when describing diffusion. Respecting Newton's laws, the determinant of diffusion is the gradient in the mass fraction, and not the molar fraction.

4 Newtonian transport that may seem counter-intuitive

The fourth case adds trace amounts of carbon dioxide (CO_2; 44 g mol^{-1}) to Case 3 above, specified so as to demonstrate the error of specifying Fick's law using molar fraction gradients. Again, we have the lighter gas on the left (2 g mol^{-1}) and the heavier gas on the right (131.3 g mol^{-1}), but now each side is "doped" with a tiny mass fraction (1 mg kg^{-1}) of CO_2 that negligibly influences the effective molecular mass of the mixtures. In terms of mass, we can still treat the lighter gas as hydrogen (H_2, 2 g mol^{-1}) and the heavier gas as Xe (131.3 g mol^{-1}), each negligibly contaminated with CO_2.



In inertial terms, this is >99.99% the same as Case 3, and would negligibly change Isaac's description of the situation. If asked about CO_2 transport, Isaac would likely respond that, since he pushed the fluid to the left, and the fluid shifted left, transport of CO_2 is explained by fluid motion: the CO_2 simply went with the flow, with no need to invoke diffusion. Indeed, using a mass-fraction gradient to specify Fick's law, we find that there is no diffusion in this case. However, if we convert the mass fractions to molar fractions (using molecular masses), we find that there is 0.05 ppm CO_2 on the left versus 2.98 ppm CO_2 on the right, suggesting erroneously from Roderick and Shakespeare's version of Fick's law that diffusion is responsible for CO_2 transport.

Conclusion

I believe that these cases demonstrate that the authors have used an incorrect version of Fick's law. And since their goal is to describe water vapour diffusion – from lighter, moister air towards heavier, drier air – they need to specify this correctly before addressing the complicated issue of thermodiffusion.