

EAS327: Appendix on Molecular Transport in a Materially-homogeneous Medium

Consider the case of a medium that is stationary, in the sense that there is nowhere any bulk motion - that is, in any finite region, the atoms or molecules composing the material have no organised (coherent, same-way) velocity.

There is nevertheless a random motion of individual molecules/atoms (I'll call them "particles"), even though the particles may be restrained by bonding forces; individual particles have kinetic energy and potential energy, and they move. The degree of motion, expressed statistically, is related to the temperature. For a gas, the root-mean-square molecular velocity (which is the same as the standard deviation of the velocity) is proportional to the Kelvin temperature.

Molecular Heat Transport, ie. conduction, and Fourier's Law

Suppose now that our medium is not homogeneous in its temperature: let there be a temperature gradient $\partial T/\partial x$.

This means that we have particles with higher temperature (greater r.m.s. velocity, ie. more energy) in contact with those of lower energy. For simplicity, say the "fast ones" are on the right. Statistically, when the fast particles bounce off the slow ones to the left, there is (again, statistically) a trend towards equalization of the sharing of energy; progressively those on the left gain (on average) in energy (get into a more frantic state of motion) while those on the right lose; that is, the gas on the left gets warmer, and that on the right cooler - heat has been transported.

This immensely complex field of motion of individual particles results in a macroscopic law called Fourier's law of conduction, which states that the heat flux density along the x-axis, which we'll call Q_{Hx} (with the x signifying this is the x -component of a vector) and which has units $[\text{J m}^{-2} \text{s}^{-1}]$ is proportional to the temperature gradient:

$$Q_{Hx} = -k \frac{dT}{dx} \quad (1)$$

where the constant of proportionality k (with messy units of $[\text{J s}^{-1} \text{K}^{-1} \text{m}^{-1}]$) is called the "conductivity" of the medium. If we introduce the "grad operator" as a shorthand for the vector gradient (the vector each of whose

components is a spatial derivative) then relative to Cartesian coordinates

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \quad (2)$$

and the vector heat flux density is

$$\vec{Q}_H = -k \nabla T = -k \left(\frac{\partial T}{\partial x}, \frac{\partial T}{\partial y}, \frac{\partial T}{\partial z} \right) \quad (3)$$

where please note that $\partial T/\partial x$ is called a “partial derivative” and indicates the rate of change of T along the x axis.

If the medium has density ρ and specific heat capacity c then the conductivity may be expressed in terms of a “thermal diffusivity” κ [$\text{m}^2 \text{s}^{-1}$] which is defined such that¹

$$k = \rho c \kappa \quad (4)$$

and so then Fourier’s Law reads

$$\boxed{\vec{Q}_H = -\rho c \kappa \nabla T} \quad (5)$$

“Diffusivities” *always* carry the units of [**velocity x length**].

Molecular mixing, ie. diffusion, and Fick’s Law

Now suppose that our medium is a gas or fluid, and that it is composed of a mixture of two species, A and B.

If A and B are uniformly mixed - the state of maximum disorganisation, maximum entropy - things are static. But suppose instead, that B is present at higher concentration C_B [kg m^{-3}] on the right, at large x , that is, we have a concentration gradient $\partial C_B/\partial x$. Then simply as a “law of large numbers” expressing the outcome of the chaotic shiftiness of the molecular positions, since there are more B’s per unit volume on the right than on the left, there is a slow migration of B, on average, towards the left. This fact is expressed by Fick’s law of diffusion, which going straight to the vector form, states that the vector mass flux density \vec{Q}_m [$\text{kg m}^{-2} \text{s}^{-1}$] is given by

$$\boxed{\vec{Q}_H = -\mathcal{D}_{BA} \nabla C_B} \quad (6)$$

where \mathcal{D}_{BA} is called the “molecular diffusivity of B in A” and by symmetry equals \mathcal{D}_{AB} . We often drop the “A in B” words, and speak of the molecular diffusivity of (say) carbon dioxide, it being implicit that we mean in, say, air.

¹Symbols for the thermal diffusivity vary; another common one is \mathcal{D}_H .

How does this relate to our “Ohm’s Law analogy” laws?

In our course we need laws to express the exchange of heat and mass between a fluid, in an arbitrary state of motion (which might be the state of rest - though of course rest can only exist at the macroscopic level), and an immersed body of arbitrary geometry. Thus the exchange process is not necessarily diffusion (in the case of mass transport) or conduction (case of heat transport), for it may well be that along part of the “transport pathway” bulk velocity of the medium plays a role, that is, the transport may be a mix of diffusion/conduction and convection, for example conduction right hard against the body where the fluid is at rest, but convection away from the body.

Our Ohm’s law analogy is a “bulk” formulation that subsumes both types of transport (diffusive and convective), throwing the specifics into the magnitude of the transport resistance. For heat transport (including the effects of “all agencies” but radiation), the Ohm’s Law analogy is

$$Q_H = \rho c \frac{T_1 - T_2}{r_H} \quad (7)$$

If it happened that we knew that we were dealing with purely molecular conduction, and the length of the transport pathway was dx , then clearly, invoking the “true law” (Fourier’s law) we can evaluate the transport resistance as

$$r_H = \frac{dx}{\kappa} \quad (8)$$

which (you can check) is dimensionally consistent. In a purely conductive scenario, the resistance is simply the length of the path, divided by the thermal diffusivity.

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