I. INTERPARTICLE FLUX

Each transport process is induced by a gradient in its driving potential. Thus, when a system is in an extensive equilibrium state there is no net transport. This does not imply, however, that there is no motion of the mobile particles that would become the carriers if transport were initiated. Indeed, these carrier particles typically transport at the same rate in any specific direction that they do during a net transport process. But when there is no potential gradient, this transport flux is balanced by an equal flux in the opposite direction. The isotropic counterbalancing fluxes prescribe a maximum for each potential transport flux. No matter how large the gradient, the flux cannot exceed this limit. The magnitude of the limit can be determined for carrier particles of known speed distribution.

A. Speed Distributions

In Sect. IIIA of Unit IIIC, we considered the translational mode of molecular gases. This development began with a description of the energy states in terms of their quantum numbers, eqn. IIIA-8. The energy of these states corresponds to that of linear translation. Therefore, each state defines a particle velocity.[5]

$$\varepsilon_{tr} = \frac{h^2}{8m^* V^{2/3}} (\ell^2 + m^2 + n^2) = \frac{m^*}{2} (V_x^2 + V_y^2 + V_z^2) = \frac{m^* \bar{V}^2}{2}$$

Since the quantum numbers are integers, the energy states and their corresponding velocities are quantized. But we had already concluded that the translational mode always satisfies the high temperature limit, $T \gg \theta_{tr}$; thus the velocity distribution can also be approximated as continuous. The velocity distribution is obtained directly from eqn. IIIC-1b (see the following development).

Example 1. Use the distribution of independent translating molecules over their accessible energy states, eqn. IIIC-1b, to derive an expression for the distribution of gaseous molecules as a function of velocity.

The partition function for the translational mode was derived by integration over the accessible energy states in Exmp. 4 of Unit IIIC. Using this result expressed in terms of particle mass and total volume the probability that a particle will be in the n, m, ℓ state is

$$\rho_{tr}(\ell, m, n) = \frac{e^{-\varepsilon(\ell, m, n)/kT}}{Z_{tr}} = \frac{h^3 \, e^{-\left[\frac{h^2(\ell^2+m^2+n^2)}{8m^* V^{2/3} kT}\right]}}{V(2\pi m^* kT)^{3/2}}$$

[5]Velocity is not completely specified by an energy state. A state, $\varepsilon(\ell,m,n)$, may correspond to positive or negative direction for each of the three velocity components,

$$V_x = \pm \left(\frac{h^2}{8m^* V^{2/3}} \ell^2\right)^{\frac{1}{2}}$$