

UNIT III E  
TRANSPORT PROCESSES

Conserved quantities are transported by mobile carrier particles. These include gas molecules, free electrons, phonons, and photons whose speed distributions and average speeds are developed in the unit. The equilibrium flux of the mobile carrier particles is related to their mean speed and particle density. Two transport limits are identified: the limit dominated by particle-particle collisions, the continuum regime; and the limit dominated by wall-particle collisions, the free particle regime. The Knudsen number is introduced to discriminate between the two regimes. Photon heat transport through a low density gas is analyzed as an example of free particle transport. The result of this analysis is an expression for the limiting black body emission from a surface, the Stefan-Boltzmann law, and an introduction to the concept of surface absorptance and emittance. Molecular heat and momentum transport through a gas are analyzed as examples of continuum transport. The result of this analysis is a prediction of gaseous thermal conductivity and viscosity. Heat and charge transport through a solid are analyzed as a second example of continuum transport. This yields a qualitative description of the dependence of thermal conductivity on temperature in insulators and metals, as well as a description of the temperature dependence of electrical conductivity in metals and semiconductors.

Objectives

1. Determine the mean, most probable, and rms speeds of gaseous molecules, free electrons, phonons, and photons for given equilibrium conditions.
2. Determine the probability that a gaseous particle will have speeds above or below a specified speed.
3. Specify the mean free path, mean free time, or Knudsen number of molecular gas particles under specified conditions.
4. Evaluate the maximum possible, or black body, photon energy flux at a specified temperature.
5. Interpret the distribution of black body radiation, Planck's law, to evaluate the relative emission at different wavelengths.
6. Determine the viscosity or thermal conductivity of a molecular gas. Interpret the effect of temperature and pressure on these properties.
7. Describe the temperature dependence of the thermal conductivity of metallic and nonmetallic solids. Discuss the effect of impurities, defects, and annealing.
8. Differentiate between electrical insulators, conductors, and semiconductors. Discuss the effect of temperature on electrical conductivity in each of these materials.
9. Determine thermal conductivity from the electrical conductivity of a metal using the Wiedemann-Franz law. Discuss the authenticity of this result for specific cases.

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Whenever a gradient in a thermodynamic potential exists between one region and another, it induces heat, work, or the movement of matter between the two regions.<sup>1</sup> Determining the rate at which these *transport processes* proceed under given conditions is a central problem in the practice of each of the various fields of engineering. Specifically, temperature is the potential for heat transport, voltage is the potential for charge transport (i.e., electric current), pressure is the potential for the bulk transport and concentration is the potential for the transport of a specific species of matter, and velocity is the potential for the transport of momentum. In all of these processes the transported quantity is carried by *mobile "carrier" particles*. Different particles act as carriers for one or more transport processes to varying degrees in different substances.

Molecules (or atoms) are relatively mobile in liquids and gases. Thus they act as the principal carrier for heat, mass, momentum, and species. (Electric current is transported by ionized molecules.) In solids, lattice points have very limited mobility. Thus the molecules or atoms that occupy these sites are carriers only in the very limited diffusion processes.<sup>2</sup>

Free Electrons are the principal carriers of electric current. In condensed phase conductors, the highly mobile free electron gas is an important carrier of heat as well as charge.

Phonons Lattice vibrations in a condensed phase result in the generation of acoustical waves. This mobile phonon gas is a contributor to heat transport in condensed phases.<sup>3</sup> In liquids it is often more important than heat transport due to molecular motion.<sup>4</sup> However, in good conductors, phonon transport is often negligible in comparison to free electron transport.

Photons The mobile photon gas occupies all space. Its net contribution to heat transport is dependent on the presence and mobility of other carriers.<sup>4</sup> In their absence, as in a vacuum, photon heat transport is predominant.

If transport effects are to be predicted by microscopic means, one must determine at what rate the proposed carrier will move unimpeded in a given direction, how much of the transported quantity it would carry with it, and how frequently the particles would undergo collisions that inhibit the transport process.

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<sup>1</sup>Each of the intrinsic, fundamentally intensive properties is a thermodynamic potential, see definitions 12 and 16, Unit IA.

<sup>2</sup>There is very limited momentum or mass transport within a solid.

<sup>3</sup>Neither photons nor phonons contribute to mass (or species) transport since they are massless. Their contribution to momentum transport is usually very low when compared to molecular transport.

<sup>4</sup>Recognize that we are comparing to molecular transport within the media, not to energy carried with the bulk motion, convection.

## 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.<sup>5</sup>

$$\epsilon_{tr} = \frac{h^2}{8m^* V^{2/3}} (\ell^2 + m^2 + n^2) = \frac{m^*}{2} (v_x^2 + v_y^2 + v_z^2) = \frac{m^* \bar{v}^2}{2}$$

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  $n, m, \ell$  state is

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

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

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

The transformation of this distribution to velocity must satisfy the conservation of probability condition

$$1 = \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} \rho_{tr}(\ell, m, n) d\ell dm dn = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho_{tr}(V_x, V_y, V_z) dV_x dV_y dV_z$$

Then substituting for  $\ell$  in terms of  $V_x$

$$\left(\frac{h^2}{8m^* V^{2/3}}\right) \ell^2 = \frac{m^*}{2} V_x^2 \quad \text{or} \quad \ell = \pm \left[ \frac{4(m^*)^2 V^{2/3}}{h^2} \right]^{1/2} V_x \quad d\ell = \pm \left[ \frac{4(m^*)^2 V^{2/3}}{h^2} \right]^{1/2} dV_x$$

and  $\ell = 0, V_x = 0; \ell \Rightarrow \infty, V_x \Rightarrow \pm \infty.$

Similarly for  $m$  and  $n$  in terms of  $V_y$  and  $V_z$ , we have

$$1 = \frac{h^3}{V(2\pi m^* kT)^{3/2}} \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} e^{-\frac{m^*}{2kT}(V_x^2 + V_y^2 + V_z^2)} \left| \frac{4(m^*)^2 V^{2/3}}{h^2} \right|^{3/2} dV_x dV_y dV_z$$

$$= \frac{1}{2^3} \left(\frac{2m^*}{\pi kT}\right)^{3/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{m^*}{2kT}(V_x^2 + V_y^2 + V_z^2)} dV_x dV_y dV_z$$

where the factor  $1/2^3$  comes from extending all three limits from zero to  $-\infty$ . The integrand of this probability integral is the velocity distribution,  $\rho(\vec{V})$ . It can be expressed in the simpler form of eqn. IIIE-1 by substituting  $R = \bar{R}/M = N_A k/N_A m^*$ .

In a stationary gas the probability that a particle will have the velocity  $\vec{V}$  is

$$\rho(\vec{V}) = \frac{e^{-\vec{V}^2/2RT}}{(2\pi RT)^{3/2}} \quad \text{(III E-1)}$$

A sketch of the distribution in two of its three directions is shown in Fig. III E-1. Notice that the most probable velocity is zero;  $\rho_{max} = \rho(\vec{V} = 0) = (2\pi RT)^{-3/2}$ . The velocity distribution is symmetric with respect to the origin. Thus, the average of any odd function of velocity over the entire velocity space is zero. This supports our expectation that there is no net transport within a stationary gas in equilibrium.<sup>6</sup> In that respect it is useful to ignore the direction of individual particle motions and consider the *speed distribution*  $V \equiv |\vec{V}|$

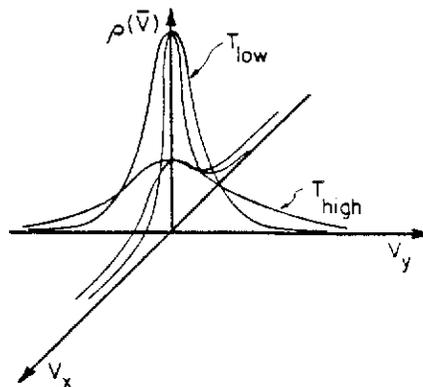


Fig. III E-1. Velocity Distribution in a Molecular Gas

<sup>6</sup>The distribution in an equilibrium gas that is moving with velocity  $\vec{V}_0$  is readily shown to be

$$\rho(\vec{V}) = \frac{e^{-(\vec{V}-\vec{V}_0)^2/2RT}}{(2\pi RT)^{3/2}}$$

This distribution is symmetric with respect to  $\vec{V}_0$ . And there is still no molecular transport except that contributed by the mean particle motion, viz., convection.

$$\rho(V) = \frac{4\pi V^2 e^{-V^2/2RT}}{(2\pi RT)^{3/2}} \quad (\text{IIIE-2})$$

Exercise 1. Express the velocity distribution in a spherical coordinate representation of velocity space ( $0 < V < \infty$ ,  $0 < \theta < \pi$ ,  $0 < \phi < 2\pi$ ) and integrate over all directions to obtain the particle speed distribution.

The speed distribution is sketched in Fig. IIIE-2.

It is not a symmetric curve and its maximum, *the most probable speed*, is not zero.

$$v_{mp} = \sqrt{2RT} \quad (\text{IIIE-3})$$

Exercise 2. Differentiate the speed distribution, eqn. IIIE-2, to derive eqn. IIIE-3 for the most probable speed.

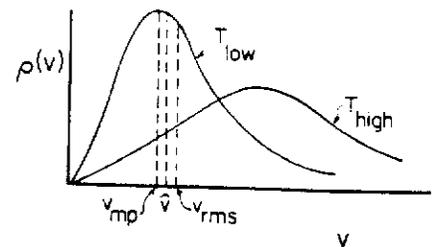


Fig. IIIE-2. Speed Distribution in a Molecular Gas

Exercise 3. We had earlier noted that the most probable velocity is zero, Fig. IIIE-1. We now find that the most probable speed is not zero, Fig. IIIE-2. How can the highest probability be simultaneously a stationary and a moving particle?

The mean of any function of speed,  $\phi(V)$ , is defined by

$$\hat{\phi}(V) \equiv \int_0^{\infty} \phi(V) \rho(V) dV \quad (\text{IIID-4})$$

This definition is applied to determine the average speed as well as the average of the square, cube, and other multiples of the speed that are of physical interest.

Example 2. Use the definition of the mean and the integrals of Table IIIE-1 to determine the average speed of independent molecules of a molecular gas.

The average speed is defined by

$$\hat{V} \equiv \int_0^{\infty} V \rho(V) dV$$

To evaluate the required integral, we express it in terms of the dimensionless argument ( $x^2 = V^2/2RT$ ,  $dx = dV/\sqrt{2RT}$ ) and use Table IIIE-1<sup>7</sup>

$$\hat{V} \equiv \frac{4\pi}{(2\pi RT)^{3/2}} \int_0^{\infty} V^2 e^{-V^2/2RT} dV = \frac{4\pi}{(2\pi RT)^{3/2}} (2RT)^2 \int_0^{\infty} x^3 e^{-x^2} dx = 4 \left(\frac{2RT}{\pi}\right)^{1/2} \left(\frac{1}{2}\right) = \left(\frac{8RT}{\pi}\right)^{1/2}$$

Exercise 4. Determine the average kinetic energy of the particles in a molecular gas,  $\hat{\epsilon}_{ke} = m \hat{V}^2/2$ . Verify that the result is the same as the translational mode's contribution to the internal energy of perfect gases.

In Exer. 4 the average of the square of the speed was determined. The square root of this parameter, the *root mean square speed* provides an energy-based measure of average particle

<sup>7</sup>The parameter  $x (= V/\sqrt{2RT})$  is often called the molecular speed ratio.

speed. Thus we have defined three measures of average particle speed: the most probable, the average, and the root mean square or rms (Exer. 2, Exmp. 2, and Exer. 4, respectively).

$$v_{mp} = \sqrt{2RT} \quad \hat{v} = \sqrt{\frac{8RT}{\pi}} \quad v_{rms} \equiv (\hat{v}^2)^{1/2} = \sqrt{3RT} \quad (\text{IIIE-3,5a,b})$$

These averages are not far apart numerically and are of identical form. Each is directly proportional to the square root of temperature and inversely proportional to the square root of particle molecular weight.

Exercise 5. For purposes of comparison determine  $v_{mp}$  and  $v_{rms}$  for the common, and not so common, constituents of the atmosphere at 300 K: nitrogen,  $N_2$ , water vapor,  $H_2O$ , helium, He, and gasoline (octane) fumes,  $C_8H_{18}$ .

The various average speeds specified by eqn. IIIE-3 provide one measure of the character of the molecular speed distribution. A second approach is the specification of the fraction of particles that have speeds within a certain range. Table IIIE-1 includes a tabulation of the probability integral up to specified dimensionless speeds,  $x^* = v^*/\sqrt{2RT}$ . The fraction of particles with speeds between zero and  $v^*$  is

$$P(0 \rightarrow v^*) = \int_0^{v^*} \rho(v) dv = \frac{4}{\sqrt{\pi}} \int_0^{v^*/\sqrt{2RT}} x^2 e^{-x^2} dx \quad (\text{IIIE-6})$$

Use of this function is illustrated in the following exercises.

Exercise 6. Determine the percentage of oxygen molecules at 600 K whose speeds are above 1000 m/s.

Exercise 7. What fraction of gaseous molecules travel at speeds between  $v_{mp}$  and  $v_{rms}$ ?

The procedure used to derive the speed distribution of molecular gas particles can also be applied to the free electrons of a metallic solid. At normal temperatures free electrons are distributed over their energy levels in a manner that is very similar to their distribution at absolute zero,  $T \ll \theta_F$  (see Fig. IIID-4). Therefore, a good approximation to the free electron speed distribution at all practical temperatures is the distribution they exhibit at absolute zero.

Example 3. Exmp. 8 of Unit IIID used the distribution of free electrons at absolute zero to determine the value of the Fermi level at absolute zero,  $\epsilon_F^0$ . Transform this energy distribution to obtain a speed distribution for free electrons at zero temperature.

At absolute zero the number of free electrons with energy  $\epsilon$  is

$$n_{el}(\epsilon) \Big|_{\substack{T=0 \\ \epsilon < \epsilon_F^0}} = g_{el}(\epsilon) = 4\pi V \left( \frac{2m_e}{h^2} \right)^{3/2} \epsilon^{1/2} \quad \text{and} \quad n_{el}(\epsilon) \Big|_{\substack{T=0 \\ \epsilon > \epsilon_F^0}} = 0$$

Also the total number of electrons was shown to be

$$N_{el} = \frac{8\pi V}{3} \left( \frac{2m_e}{h^2} \right)^{3/2} \epsilon_F^0{}^{3/2}$$

Substitution gives an expression for the probability of an energy level

$$\rho_{el}(\epsilon) \Big|_{\substack{T=0 \\ \epsilon < \epsilon_F}} = \frac{n_{el}(\epsilon)}{N_{el}} = \frac{3}{2} \frac{\epsilon^{\frac{1}{2}}}{(\epsilon_F^0)^{3/2}} \quad \rho_{el}(\epsilon) \Big|_{\substack{T=0 \\ \epsilon > \epsilon_F}} = 0$$

A speed distribution is obtained by substituting

$$\epsilon = \frac{m^* V^2}{2} \quad \epsilon_F^0 = \frac{m^* V_F^2}{2} \quad d\epsilon = m^* V dV$$

into

Ans. 1. To go from Cartesian to spherical velocity coordinates, we express  $dV_x dV_y dV_z \Rightarrow V^2 \sin \theta d\theta d\phi dV$  where  $0 \leq V \leq \infty$ ,  $0 \leq \theta \leq \pi$ , and  $0 \leq \phi \leq 2\pi$ . Then the probability integral is

$$1 = \int_0^\infty \int_0^\pi \int_0^{2\pi} \rho(\vec{V}) V^2 \sin \theta d\phi d\theta dV$$

The speed distribution is obtained by integrating the velocity distribution over  $\theta$  and  $\phi$ .

This gives  $\int_0^{2\pi} \int_0^\pi \sin \theta d\phi d\theta = 4\pi$ . So

$$\rho(V) = 4\pi V^2 \rho(\vec{V}) = \frac{4\pi}{(2\pi RT)^{3/2}} V^2 e^{-V^2/2RT}$$

Ans. 2. The most probable speed is determined by setting

$$\frac{d}{dV} \rho(V) = \frac{4\pi}{(2\pi RT)^{3/2}} \frac{d}{dV} \left[ V^2 e^{-V^2/2RT} \right] = \frac{4\pi e^{-V^2/2RT}}{(2\pi RT)^{3/2}} \left( 2V - \frac{2V^3}{2RT} \right) = 0$$

This gives

$$V_{mp}^2 = 2RT, \quad V_{mp} = \sqrt{2RT}$$

Ans. 3. The velocity distribution specifies direction as well as magnitude of particle translational energy. It corresponds to the probability of each specific energy *state*. The speed distribution specifies only the magnitude of particle energy. It corresponds to the probability of each energy *level*. There are very few states of low energy. Thus the probability of the low energy states (velocities) can be relatively high even while these levels (speeds) are not probable. The most probable level (speed) is achieved when the increasing numbers of states per level can no longer compensate for the decreasing probability of the higher energy states.

Ans. 4. As defined, the average kinetic energy requires a determination of the average speed squared. Transforming to dimensionless form, we find

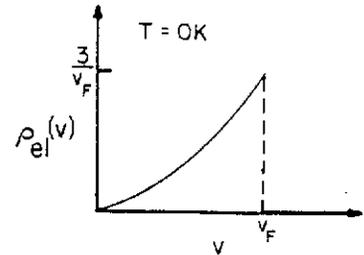
$$\begin{aligned} \overline{V^2} &= \int_0^\infty V^2 \rho(V) dV = \frac{4\pi}{(2\pi RT)^{3/2}} \int_0^\infty V^2 V^2 e^{-V^2/2RT} = \frac{4\pi}{(2\pi RT)^{3/2}} (2RT)^{5/2} \int_0^\infty x^4 e^{-x^2} dx \\ &= \frac{4\pi}{(\pi)^{3/2}} (2RT) \left( \frac{3\sqrt{\pi}}{8} \right) = 3RT \end{aligned}$$

Thus, since  $R = \bar{R}/M = k/m^*$ ,  $\hat{\epsilon}_{ke} = m^* V^2/2 = 3m^* kT/(2m^*) = (3/2) kT$ . And the total energy for a mole of molecules is

$$\bar{u}_{ke} = N_A \hat{\epsilon}_{ke} = \frac{3}{2} N_A kT = \frac{3}{2} \bar{R}T,$$

which is the same as that determined for the translational mode in Unit IIIC.

$$\rho_{el}(\epsilon)d\epsilon = \rho_{el}(V)dV \Big|_{V \leq V_F} = \frac{3 \left( \frac{m_e^* V^2}{2} \right)^{3/2}}{2 \left( \frac{m_e^* V_F^2}{2} \right)^{3/2}} m_e^* V dV = 3 \frac{V^2}{V_F^3} dV$$



$$\text{and } \rho_{el}(V) \Big|_{V > V_F} = 0.$$

In Exmp. 3 we derived the speed distribution for free electrons at zero temperature. This result is a good approximation for the electron speeds at all practical temperatures in a solid,  $T \ll \theta_F$

$$\rho_{el}(V) \Big|_{V \leq V_F} = 3 \frac{V^2}{V_F^3} \quad \rho_{el}(V) \Big|_{V > V_F} = 0 \quad \text{where } V_F \equiv \left( \frac{2k\theta_F}{m_e^*} \right)^{1/2} \quad (\text{IIIE-7})$$

Since the approximate distribution is independent of temperature, the *most probable*, *average*, and *rms speeds of free electrons* are constant for each substance.<sup>3</sup>

$$v_{mp} = V_F \quad \hat{v} = \frac{3}{4} V_F \quad v_{rms} = \sqrt{\frac{3}{5}} V_F \quad (\text{IIIE-8a,b,c})$$

<sup>3</sup>The highest probability is that at the Fermi level (see the figure of Exmp. 3). But the probability curve does not have zero slope at that point.

**Ans. 5.** The variation in the various average speeds are due to different molecular weights:  $M_{N_2} = 28.01$ ,  $M_{H_2O} = 18.02$ ,  $M_{He} = 4.00$ ,  $M_{C_8H_{18}} = 114.2$ . Thus for nitrogen

$$v_{mp} = \sqrt{2RT} = \left[ 2 \cdot \left( \frac{8314}{28.01} \right) \text{ J/(kg K)} \cdot 300 \text{ K} \cdot 1 \text{ kg m}^2 / (\text{J s}^2) \right]^{1/2} = 422.0 \text{ m/s}$$

$$\text{and } v_{rms} = \sqrt{\frac{3}{2}} v_{mp} = 516.8 \text{ m/s}$$

Similarly  $v_{mp}$  and  $v_{rms}$  for the other molecules are respectively:  $H_2O - 526.3 \text{ m/s}$  and  $644.4 \text{ m/s}$ ,  $He - 1117 \text{ m/s}$  and  $1368 \text{ m/s}$ ,  $C_8H_{18} - 209.0 \text{ m/s}$  and  $256.0 \text{ m/s}$ .

**Ans. 6.** For the conditions specified

$$x^* = \frac{v^*}{\sqrt{2RT}} = \frac{1000 \text{ m/s}}{\left[ 2 \cdot \left( \frac{8314}{32.00} \right) \text{ J/(kg K)} \cdot 600 \text{ K} \cdot 1 \text{ kg m}^2 / (\text{J s}^2) \right]^{1/2}} = 1.79$$

Interpolating from Table IIIE-1, we find  $\int_0^{x^*} x^2 e^{-x^2} dx = 0.401$ . And

$$P(0 \rightarrow x^*) = \frac{4}{\sqrt{\pi}} \int_0^{x^*} x^2 e^{-x^2} dx = \frac{4}{\sqrt{\pi}} \cdot 0.401 = 0.906$$

The probability is that 9.4% of the molecules have speeds above 1000 m/s.

**Ans. 7.** In dimensionless form  $x_{mp} = v_{mp} / \sqrt{2RT} = 1$  and  $x_{rms} = v_{rms} / \sqrt{2RT} = \sqrt{3/2} = 1.225$ .

Thus,  $P(0 - x_{mp}) = 0.1895$  and  $P(0 - x_{rms}) = 0.2687$ . So  $(26.9 - 19.0)$  or 7.9% of the particles are between these speeds.

Exercise 8. The average free electron energy was determined in Exmp. 9 of Unit IIID to be  $\bar{\epsilon}_{el} = (3/5)\epsilon_F^0$ . Verify that this result is consistent with eqn. IIIE-7b.

Exercise 9. Use the distribution of free electrons and the definition of a mean, eqns. IIIE-6 and 4, to determine the mean free electron speed, eqn. IIIE-7b.

Exercise 10. The Fermi temperature of the free electrons of solid copper is  $8.44 \cdot 10^4 K$ , see Exer. 17 of Unit IIID. Determine the average, rms, and Fermi speed of these electrons.

Now that we have considered the speed distribution of molecular and free electron gases, the simplicity of the distribution applicable to photons and phonons is readily appreciated. Each electromagnetic and acoustic wave travels at the speed of light and sound respectively.

$$\rho_{\text{pht}}(V) \Big|_{V=c} = 1 \qquad \rho_{\text{pht}}(V) \Big|_{V \neq c} = 0 \qquad \text{(IIIE-9a)}$$

$$\rho_{\text{phn}}(V) \Big|_{V=c_s} = 1 \qquad \rho_{\text{phn}}(V) \Big|_{V \neq c_s} = 0 \qquad \text{(IIIE-9b)}$$

Thus their most probable, mean, and root mean square speeds all have the same value. For photons and phonons, respectively, the values are

$$V_{\text{mp}} = \hat{V} = V_{\text{rms}} = c \qquad V_{\text{mp}} = \hat{V} = V_{\text{rms}} = c_s \qquad \text{(III-10a,b)}$$

In the following section we use the speed distributions developed in this section to determine the maximum possible transport flux.

### B. Interparticle Flux

The preceding section considered the motion of the four principal transport carriers. We found that their speed distributions varied substantially. However, all of these gases share one characteristic—the particles move in random directions. One result of this isotropicity of particle velocities is that there is no *net* transport when the carrier gas is in equilibrium. Another is that all of the gases have the same proportion of their collective speeds directed positively in any single direction.

Example 4. Determine the average velocity component of equilibrium gas particles contributing positively to transport in any single direction. Show that this average can be expressed as a fraction of the mean speed within the isotropically translating particles.

If we represent velocity in spherical coordinates  $0 \leq V < \infty$ ,  $0 \leq \theta \leq \pi$ ,  $0 \leq \phi \leq 2\pi$ , the projection of the general velocity vector in the direction  $\theta = 0$  is  $V \cos \theta$ . The average of these components in the positive sense is determined by restricting the integral limits on  $\theta$  to  $0 \leq \theta \leq \pi/2$ . Thus, the average positive velocity component is written symbolically as

$$\overline{V \cos \theta}_{\text{pos}} = \frac{\int_0^{2\pi} \int_0^{\pi/2} \int_0^{\infty} V \cos \theta \rho(V, \theta, \phi) V^2 \sin \theta \, dV \, d\theta \, d\phi}{\int_0^{2\pi} \int_0^{\pi/2} \int_0^{\infty} \rho(V, \theta, \phi) V^2 \sin \theta \, dV \, d\theta \, d\phi}$$

Note that the denominator is not the total probability but the probability of positive velocities,  $0 \leq \theta \leq \pi/2$ .  $\rho(V, \theta, \phi)$  symbolizes the velocity distribution. However for the isotropic distributions it is independent of direction  $\rho(V, \theta, \phi) \Rightarrow \rho_{\text{vel}}(V)$ . (The subscript vel emphasizes the fact that this is an isotropic velocity distribution, not a speed distribution.) As a result the integral ratio simplifies to

$$\widehat{V \cos \theta}_{\text{pos}} = \frac{\int_0^{2\pi} d\phi \int_0^{\pi/2} \cos \theta \sin \theta d\theta \int_0^{\infty} V^2 \rho_{\text{vel}}(V) dV}{\int_0^{2\pi} d\phi \int_0^{\pi/2} \sin \theta d\theta \int_0^{\infty} V^2 \rho_{\text{vel}}(V) dV} = \frac{2\pi \left(\frac{1}{2}\right) \widehat{V}}{2\pi(1) \widehat{V}} = \frac{\widehat{V}}{2}$$

The solution of Exmp. 4 showed that the average positive velocity component of *any type of translating particles* in equilibrium moving in a single direction is  $V/2$ . Further, since these velocity distributions are isotropic, half of the particles will have positive velocity components and the other half negative. Therefore, the rate at which carrier particles move in a single direction per unit area time in an equilibrium gas is

$$\dot{n}'' = \left(\frac{n_v}{2}\right) \widehat{V \cos \theta}_{\text{pos}} = \frac{n_v \widehat{V}}{4} \quad (\text{III E-11})$$

where  $n_v$  is the number of carrier particles per unit volume, or *carrier particle density*. The particle flux directly governs the *maximum* rate of diffusion of any specific type of particle. Since each transported quantity is carried by a flux of carrier gas particles,  $\dot{n}''$  also sets an upper limit on each transport process equal to the mean value of the transported quantity per particle times  $\dot{n}''$ , see below. However, rather than substitute directly to determine the maximum flux limits, we first consider those processes that reduce transport rates below their respective maxima.

Transport can only occur at its maximum rate when the carrier particles are unimpeded in their motions. Insofar as the carrier particles collide with one another or with other particles present within the transport space, transport is reduced below this maximum.

### C. Interparticle Collisions

A carrier particle has undergone a collision when its momentum is altered by particles or barriers within the system. Collisions with the boundaries of the system are called particle-wall collisions. Collision between particles within the system are particle-particle collisions. We begin our discussion with the consideration of particle-particle collisions. Obviously, particle-particle collision frequencies will depend upon the densities of the colliding particles, the speed with which they move, and the range and distribution of the forces acting between them. The last of these characteristics of the colliding particles is known collectively as their *collision cross section*. In general collision cross section is dependent on the type of particles that collide, the magnitude and relative directions of their momenta, and their angular orientation at

incidence. To simplify our discussion we will model collision cross sections as though they were constant.

This is a reasonably good approximation for collisions between molecular gas particles. It treats the particles as though they are hard spheres of radius  $r^+$ .<sup>9</sup> Hard spheres collide when their centers approach one another to the distance  $d^+ = 2r^+$ . Thus the effective cross section for collisions between like and unlike hard spheres is

$$\sigma^+ = \pi(d^+)^2 \quad \sigma_{12}^+ = \pi\left(\frac{d_1^+ + d_2^+}{2}\right)^2$$

Values for the hard sphere diameter and collision cross section of a number of atoms and molecules are listed in Table IIIE-2 at the end of this unit. The frequency with which collisions occur and the average distance between them can be approximated by studying the motion of a fictitious "collision" particle whose radius equals the molecular diameter.

**Example 5.** Determine the frequency with which a particle of radius  $d^+$  moving at the mean particle speed  $\hat{V}$  would encounter stationary point particles of number density  $n_v$ . What would be the average (or mean free) time and average distance (or mean free length) between these encounters?

The model process for this determination is shown at right. The moving particle encounters the stationary point particles at a frequency equal to the number of points per unit time within the cylinder through which it passes.

$$v_c = \sigma^+ \hat{V} n_v$$



<sup>9</sup>The hard sphere radius can be defined as the minimum in the pair interaction potential, see Unit ICS.

**Ans. 8.** The rms speed is defined in terms of the average energy. Thus,

$$v_{\text{rms}} = \left(\frac{2\hat{\epsilon}_{\text{el}}}{m_e^*}\right)^{\frac{1}{2}} = \left[\frac{2 \cdot (3/5)\epsilon_F^0}{m_e^*}\right]^{\frac{1}{2}} = \left[\frac{2 \cdot (3/5)m_e^* v_F^2}{m_e^* 2}\right]^{\frac{1}{2}} = \left(\frac{3}{5}\right)^{\frac{1}{2}} v_F$$

**Ans. 9.** 
$$\hat{V}_{\text{el}} = \int_0^\infty v \rho_{\text{el}}(v) dv = \frac{3}{v_F} \int_0^{v_F} v v^2 dv = \frac{3}{4} v_F$$

**Ans. 10.** From its definition, with  $\epsilon_F^0 = k\theta_F$

$$v_F = \left(\frac{2k\theta_F}{m_e^*}\right)^{\frac{1}{2}} = \left[\frac{2 \cdot 1.380 \cdot 10^{-23} \text{ J/elect K} \cdot 8.44 \cdot 10^4 \text{ K}}{9.109 \cdot 10^{-31} \text{ kg/elect}}\right]^{\frac{1}{2}} = 1.60 \cdot 10^6 \text{ m/s}$$

$$v_{\text{el}} = \frac{3}{4} v_F = \frac{3}{4} \cdot 1.60 \cdot 10^6 \text{ m/s} = 1.20 \cdot 10^6 \text{ m/s}$$

$$v_{\text{rms,el}} = \left(\frac{3}{5}\right)^{\frac{1}{2}} v_F = \left(\frac{3}{5}\right)^{\frac{1}{2}} \cdot 1.60 \cdot 10^6 \text{ m/s} = 1.24 \cdot 10^6 \text{ m/s}$$

The average time between these encounters is the reciprocal of the frequency  $\tau_c = v_c^{-1} = (\sigma^+ \hat{V} n_v)^{-1}$ . The average distance between encounters is the product of the time between encounters and the particle speed  $\lambda_c = \tau_c \hat{V} = (\sigma^+ n_v)^{-1}$ .

Exmp. 5 considered the motion of an oversize collision particle moving at the mean particle speed through a *stationary* gas of point particles. This is the appropriate model for the consideration of collisions between relatively fast and relatively slow moving particles. Examples of this type include: photons colliding with molecules in a gas or phonons in a solid; phonons colliding with defects or lattice points in a solid, free electrons colliding with phonons in a metal; fast neutrons colliding with fuel or moderator nuclei in a nuclear reactor. The mean free time,  $\tau_{c,1-2}$ , and mean free path,  $\lambda_{c,1-2}$ , for collisions between the fast particles, 1, and slow particles, 2 are

$$\tau_{c,1-2} = \frac{1}{\sigma_{12}^+ \hat{V}_1 n_{v,2}} \quad \lambda_{c,1-2} = \frac{1}{\sigma_{12}^+ n_{v,2}} \quad (\text{IIIE-12a,13a})$$

Exercise 11. A nuclear reactor functions by slowing down the fast neutrons produced in the fission reaction by sequences of collisions with the "moderator." If graphite carbon is employed as the moderator, its cross section for neutron scattering is approximately  $4 \cdot 10^{-24}$  cm<sup>2</sup>. Estimate the neutron mean free path in a graphite moderator. (Graphite density is about 1.6 g/cm<sup>3</sup>.)

A determination of the mean free time and mean free path for collisions between identical particles requires that *relative* particle speeds be accounted for. The result of such a development (see Ref.4, pg. 344) is

$$\tau_c = \frac{1}{\sqrt{2} \sigma^+ n_v \hat{V}} \quad \lambda_c = \frac{1}{\sqrt{2} \sigma^+ n_v} \quad (\text{IIIE-12b,13b})$$

The mean free time and, especially, the mean free path are important in the classification of transport processes. If the distance between the particle-particle collisions is large in comparison to the average transport distance in the system, then particles move relatively unimpeded throughout the container. Such processes are *dominated by wall-particle collisions* and transport within this regime is called *free particle transport*. In the opposite extreme when the mean free path is small in comparison to the container size, then transport processes are *dominated by particle-particle collisions*. This transport regime is called the *continuum*. Thus a formal classification of transport regimes is obtained by comparing the particle-particle mean free path to a characteristic length parameter of transport, most formally  $L \equiv V/A$ . This ratio is called the *Knudsen number*.

$$\text{Kn} = \frac{\lambda_c}{L} \quad (\text{IIIE-14})$$

In molecular gases the continuum regime is usually identified as  $\text{Kn} < 10^{-2}$ , and the free particle regime as  $\text{Kn} > 10$ , the range between them being a transition regime. This

classification scheme can be used in conjunction with eqn. IIIE-13b to determine which flow regime is present under given conditions. When the gas falls within the perfect gas region, eqn. III-13b is adapted to this specific case by substituting  $n_v = p/kT$ . This gives

$$\lambda_c = \frac{kT}{\sqrt{2} \sigma^+ p} \quad (\text{IIIE-15})$$

Exercise 12. Determine the mean free path and mean free time for nitrogen gas at STP.

Example 6. If vacuum insulation is to be at all effective, the pressure level must be below that within the continuum region. It is desirable that it be low enough to establish a free molecular transport regime. For a thermos bottle using nitrogen gas and a 1 cm separation gap, determine the threshold (i.e., continuum limit) pressure level and desired (i.e., free molecule limit) pressure level for operation at room temperature (300 K), liquid nitrogen temperature (77 K), and liquid helium temperature (4.2 K).

The required pressure levels are established by the Knudsen number limits,  $10^{-2}$  and  $10$ . The corresponding pressures are established from eqns. IIIE-14 and 15.

$$p = \frac{kT}{Kn\sqrt{2} L \sigma^+}$$

From Table IIIE-2,  $\sigma_{N_2}^+ = 44.2 \text{ (Å)}^2$ . Thus at 300 K, the threshold pressure is

$$p_1 = \frac{1.380 \cdot 10^{-23} \text{ J/(part K)} \cdot 10^{-5} \text{ bar m}^3/\text{J} \cdot 300 \text{ K}}{10^{-2} \sqrt{2} \cdot 1 \text{ cm} \cdot 44.2 \text{ (Å)}^2 \cdot 10^{-20} \text{ m}^2 \text{ (Å)}^2 \cdot 10^2 \text{ m/cm}} = 6.63 \cdot 10^{-4} \text{ bar}$$

A similar calculation shows that the free particle limit pressure is  $p_2 = 6.63 \cdot 10^{-7} \text{ bar}$ . At 77 K,  $p_1 = 1.70 \cdot 10^{-4} \text{ bar}$ ,  $p_2 = 1.70 \cdot 10^{-7} \text{ bar}$ ; and at 4.2 K,  $p_1 = 9.28 \cdot 10^{-6} \text{ bar}$ ,  $p_2 = 9.28 \cdot 10^{-9} \text{ bar}$ .

The preceding exercises demonstrate that a combination of low pressure and/or small physical dimensions are required to establish the free particle regime in a molecular gas. These conditions are present within most high vacuum systems and on the exterior of extra-atmospheric vehicles. However, an overwhelming majority of molecular gas applications are within the continuum flow regime.

## II. FREE PARTICLE RADIATION TRANSPORT

The rapidly moving photons are an important means of heat transport through gases. Photon-photon collisions are normally overshadowed by photon-molecule scattering. Hence, it is this process that prescribes photon mean free paths. Examining the form of eqn. IIIE-13a, we would expect shorter photon mean free paths in higher density gaseous media. This is indeed the case. However, the greatest variation in photon mean free paths is associated with variations in the collision cross section. Photon-molecule collisions are electromagnetic in character. Thus dipole molecule gases (e.g.,  $H_2O$ ,  $CO$ ) and molecules that can be easily distorted into dipoles (e.g.,  $CO_2$ ) have far bigger cross sections for photon collisions than monatomic or homonuclear diatomic molecule gases. Since the principal constituents in air are homonuclear diatomic, air is relatively transparent to

electromagnetic radiation. That is, photon mean free paths are long and photon transport through air is well approximated by the free particle limit.<sup>10</sup>

Photon energy is independent of photon speed. (All photons travel at the speed of light.) Therefore, the *equilibrium* rate of thermal energy transport by a photon gas is simply the product of equilibrium photon flux,  $\dot{n}_{\text{pht}}''$ , and the mean energy per photon,  $\hat{\epsilon}_{\text{pht}}$ .<sup>11</sup>

$$\dot{e}_{\text{pht}}'' = \dot{n}_{\text{pht}}'' \hat{\epsilon}_{\text{pht}} = \frac{n_{\text{v,pht}} c}{4} \hat{\epsilon}_{\text{pht}} = \frac{u_{\text{v,pht}} c}{4} \quad (\text{IIIE-16a})$$

When we substitute the expression for the photon energy density developed in Unit IIID, eqn. IIID-6b, we obtain the *Stefan-Boltzmann Law*

$$\dot{e}_{\text{pht}}'' = \dot{e}_{\text{b}}''(T) = \sigma T^4 \quad (\text{IIIE-16b})$$

where  $\sigma$  is the Stefan-Boltzmann constant

$$\sigma = \frac{2\pi^5 k^4}{15 h^3 c^2} = 5.668 \cdot 10^{-8} \text{ W}/(\text{m}^2 \text{K}^4) = 1.714 \cdot 10^{-9} \text{ BTU}/(\text{hr ft}^2 \text{R}^4)$$

The Stefan-Boltzmann law represents the rate at which photons will be moving in all directions within an equilibrium enclosure. But heat transport only occurs when temperature differences are present, that is, for nonequilibrium conditions.

Radiant Exchange within an enclosure containing an "optically thin" gas is governed by photon-wall collisions. Net transport results from the different rates at which surfaces emit and absorb photons. The maximum rate at which a surface can emit radiation is set by the Stefan-Boltzmann Law. A surface that emits at the maximum rate is called a *black body (or black surface)*. Since photon transport occurs within all media corresponding to their equilibrium temperature, a real surface emits at less than the black body rate in proportion to the rate at which photons approaching the surface from its interior are reflected back into the body. This percentage is a property of the surface called its *emittance (or emissivity)*.

<sup>10</sup>Not only are photon-molecule collisions limited to certain specific molecules, they are strongly concentrated at certain specific frequencies. The effect of these preferred scattering and absorption bands are evidenced by two natural phenomena. The earth's blue sky is a result of atmospheric scattering of the "blue" from the solar spectrum. Thus the blue photons are incident from all directions, not just from the small solid angle at which the sun is observed. The red sunset is caused by selective absorption of the solar spectrum excluding the red wavelength by the far thicker atmosphere when solar radiation enters tangentially to the earth's surface.

<sup>11</sup>Thermal radiation transport refers to the transport of energy due to temperature differences, radiation heat transport. It excludes the transport of radiation generated by mechanical means, for example, by radio, TV, or microwave transmitters or by a laser. This is radiation work transport.

<p>Ans. 11.</p> $\lambda_{\text{c,n-c}} = \frac{M_{\text{c}}}{\sigma_{\text{n-c}} \rho_{\text{c}} N_{\text{A}}} = \frac{12 \text{ g}/(\text{g mol})}{4 \cdot 10^{-24} \text{ cm}^2/\text{part} \cdot 1.6 \text{ g/gm}^3 \cdot 6.023 \cdot 10^{23} \text{ part}/(\text{g mol})} = 3.1 \text{ cm}$
--

Similarly, photons incident on a surface from its exterior will either be reflected, or will be transmitted into the interior and subsequently absorbed. The proportion that is absorbed is also a property of the surface called the *absorptance* (or *absorptivity*).

Implicit to the preceding discussion is the assumption that photon transmission through the enclosure walls is unlikely; that is, the walls are assumed to be "optically thick." Photon mean free paths are relatively short in most solids.<sup>12</sup> The free electrons of a metallic solid have especially large cross sections for photon collisions. Thus metallic solids are seldom transparent and the probability of photon reflection at the surface is high; metals have low emittance and absorptance coefficients.<sup>13</sup> The bound electrons of nonconducting solids are not as efficient at scattering photons. Thus nonconductors are much more likely to be semitransparent and their emittance and absorptance properties may approach unity.<sup>12</sup>

**Exercise 13.** Determine the magnitude of black body radiant emission at 300, 1000, 3000 and 10,000 K.

**Exercise 14.** A galactic probe coasts at speed with its engine shut down, far from any appreciable radiant source. It expends energy at a rate of 450 W to run its systems. After use, this power is dissipated from a radiator whose area is 2m<sup>2</sup>. The radiator is constructed of aluminum because of its light weight and high thermal conductivity. Its uncoated emittance is 0.05. A design alternative calls for coating the radiator with a nonconducting "nearly" black coating with an emittance of 0.95. What will be the steady state temperature of the radiator for the two conditions? What is your recommendation?

In Unit IIID the photon energy density was obtained by integration of the wavelength distribution of photon energy—Planck's Law, eqn. IIID-5. When this expression is substituted into eqn. IIIE-16a, we obtain the wavelength distribution of black body radiant emission. This expression is also called *Planck's Law*

$$e_{\lambda}''(T) = \frac{u_{\nu\lambda}(T)c}{4} = \frac{2\pi hc^2}{\lambda^5} \frac{1}{[e^{(hc/\lambda kT)} - 1]} \quad (\text{IIIE-18})$$

<sup>12</sup>Photon transport through a solid should be modeled as a continuum. Its contribution to net transport is usually much less than that of the phonons and/or free electrons and is, therefore, neglected.

<sup>13</sup>The process of transmission and subsequent absorption of a photon incident on the surface from the exterior is the reverse of that for transmission of a photon incident on surface from the interior, viz., emission. Thus the emissivity and absorptivity are identical at every point for photons of the same wavelength traveling at the same angle.

Ans. 12. From Table IIIE-2,  $\sigma_{N_2}^+ = 44.2 \text{ } \overset{\circ}{\text{A}}^2/\text{part}$ . Thus

$$\lambda_c = \frac{1.38 \cdot 10^{-23} \text{ J}/(\text{part K}) \cdot 300 \text{ K}}{\sqrt{2} \cdot 44.2 \text{ } \overset{\circ}{\text{A}}^2 \cdot 10^{-20} \frac{\text{m}^2}{\overset{\circ}{\text{A}}^2} \cdot 1.013 \cdot 10^5 \text{ N/m}^2} = 6.54 \cdot 10^{-8} \text{ m}$$

and

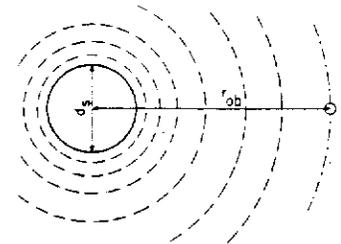
$$\hat{v} = \left(\frac{8RT}{\pi}\right)^{\frac{1}{2}} = \left[\frac{8}{\pi} \cdot \left(\frac{8317}{28.01}\right) \text{ J}/(\text{kg K}) \cdot 300 \text{ K}\right]^{\frac{1}{2}} = 476 \text{ m/s} \quad \tau_c = \frac{\lambda_c}{\hat{v}} = 1.37 \cdot 10^{-10} \text{ s}$$

This function has the same form as that for the energy density, see Fig. IIID-1. Therefore, the position of the maximum radiant emission is determined from *Wein's Law* derived in Unit IIID.

$$\lambda_{\text{max}} T = 2898 \mu\text{m K} \quad (\text{IIID-6})$$

Example 7. Measurements of the wavelength distribution of the solar radiation incident on the outer fringes of the atmosphere indicates that the sun's black body emission temperature is 5600 K. The total solar constant is 1330 W/m<sup>2</sup>. Independent celestial measurements have shown that the average distance from the sun to the earth is 150 · 10<sup>6</sup> km. Use this data to deduce the diameter of the sun.

The sun emits uniformly in all directions at the total rate,  $\dot{Q}_s = A_s \dot{e}_b''(T_s)$ . This total emission is diminished in intensity as it spreads over the increasing area spherical surfaces that it passes through at increasing distances from the sun. The total radiation crossing each larger radius sphere is the same. Finally, at the earth's orbit,  $r_{ob}$ , we have



$$\dot{Q}_s = \pi d_s^2 \dot{e}_b''(T_s) = \pi (2r_{ob})^2 \dot{q}_{solar}''$$

or

$$d_s = \frac{4r_{ob}^2 \dot{q}_{solar}''}{\sigma T_s^4} = \left[ \frac{4 \cdot (1.50 \cdot 10^8 \text{ km})^2 \cdot 1330 \text{ W/m}^2}{5.668 \cdot 10^{-8} \text{ W/(m}^2 \text{K}^4) \cdot (5600 \text{ K})^4} \right]^{1/2} = 1.465 \cdot 10^6 \text{ km}$$

The eyes of earthlings are sensitized to perceive radiation above a threshold intensity in the wavelength range from 0.4 to 0.7 μm that spans the peak emission from the sun. Our vision is based on observing differences between the partial reflection of the available natural light within the visible spectrum. An object is green because it preferentially absorbs radiation from other colors, reflecting a combination of wavelengths that the eye perceives as a particular green hue. For an object to be visible as a result of its own emission, it must be hot enough to *emit* with sufficient intensity in the visible to be above the threshold level of optical sensitivity.

Exercise 15. What is the magnitude of solar emission  $\dot{e}_b''_{\lambda}$  at the maximum and at both extremes of the visible spectrum 0.4 and 0.7 μm? What are the intensities of natural solar radiation incident on the atmosphere at the same wavelengths?

Exercise 16. An object is said to be red hot when its emission at the long wavelength (red) end of the visible is sufficient that the eye can detect its emission. This condition is achieved at about 1200 K. What are  $\lambda_{\text{max}}$  and  $\dot{e}_b''_{\lambda_{\text{max}}}$  at this temperature? What is the magnitude of emission at 0.7 μm?

Our discussion of photon transport in gases has been based on the free particle mode. Molecular transport at very low pressures (see Exmp. 6) and free electron and phonon transport at very low temperatures (discussed briefly below) must also be modeled on this basis. Though these processes are significant to certain engineering designs, we will not consider free particle transport further. Instead we devote the remainder of the unit to the far more typical case—transport within the continuum regime.

### III. CONTINUUM TRANSPORT

The carrier particles of the vast majority of transport processes have sufficiently short mean free paths that they fall within the continuum regime. Transport is induced by difference(s) in thermodynamic potential(s). Thus a region undergoing a transport process cannot be in an extensive equilibrium state.<sup>14</sup> However, the continuum assumption assures that as carrier particles move from region to region and effect transport they will be continuously relaxed through collisions toward an equilibrium value in each local region. Thus the *continuum* assumption is sufficient to assure *local equilibrium states*.<sup>14</sup> The properties of systems undergoing a continuum transport process are equilibrium properties at each point. The spatial property variations are continuous; continuum transport can be described in terms of local property derivatives. Furthermore, most continuum transport processes occur with or without net carrier particle transport. (Mass and charge transport are exceptions, see below.) That is, transport results from the gradient in the transported quantity rather than from a net flux of carrier particles. Consider the following general development.

Continuum Transport without a Net Carrier Particle Flux. Let  $\hat{\Gamma}(x)$  be the mean value of a conserved quantity *per carrier particle* at position  $x$  and  $\dot{n}''(x)$  the flux of carrier particles. Since local equilibrium exists at position  $x$ , the particle flux is isotropic at that point (in a stationary system). Thus the flux of carrier particles in positive  $x$  direction is equal to the flux of carrier particles in the negative  $x$  direction at each point. If the system is in an extensive equilibrium state, the flux of the conserved quantity is the same in all directions.

$$j''_{+x} = j''_{-x} = \dot{n}''(x)\hat{\Gamma}(x)$$

Now consider how this changes when the system is not in extensive equilibrium. Let  $\lambda_x$  be the component of the mean free path in the  $x$  direction for particles moving in either the positive or the negative  $x$  direction at point  $x$ . Then

<sup>14</sup>The distinction between an extensive and an intensive (local) equilibrium state is discussed in Unit IA, see definitions 28 and 31.

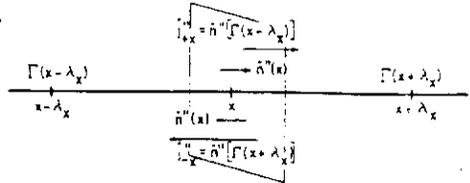
Ans. 13.  $\dot{e}_b''(300 \text{ K}) = \sigma T^4 = 5.668 \cdot 10^{-8} \text{ W}/(\text{m}^2 \text{K}^4) \cdot (300 \text{ K})^4 = 459.1 \text{ W}/\text{m}^2$ ;  $\dot{e}_b''(1000 \text{ K}) = 5.668 \cdot 10^4 \text{ W}/\text{m}^2$ ;  $\dot{e}_b''(3000 \text{ K}) = 4.591 \cdot 10^6 \text{ W}/\text{m}^2$ ,  $\dot{e}_b''(10,000 \text{ K}) = 5.668 \cdot 10^8 \text{ W}/\text{m}^2$ .

Ans. 14. The rate of radiation is governed by the surface temperature and emittance according to  $\dot{Q} = A\epsilon\sigma T^4$ . Thus the respective steady state temperatures are

$$T_1 = \left( \frac{\dot{Q}}{A\epsilon_1\sigma} \right)^{1/4} = \left[ \frac{450 \text{ W}}{2\text{m}^2 \cdot 0.05 \cdot 5.668 \cdot 10^{-8} \text{ W}/(\text{m}^2 \text{K}^4)} \right]^{1/4} = 531 \text{ K}; \quad T_2 = 254 \text{ K}.$$

The higher temperature may be too high for some components. The system may be designed to operate at any desired temperature level between these two by using an appropriate surface treatment or radiator area.

the flux in the positive direction at point  $x$  is governed by the average value of the conserved quantity at the position of the last collision, that is at  $x - \lambda_x$ . Thus,  $j_{+x}'' = \bar{n}''(x) \hat{\Gamma}(x - \lambda_x)$ . Similarly, the flux in the negative direction is  $j_{-x}'' = \bar{n}''(x) \hat{\Gamma}(x + \lambda_x)$ .



The net flux is the difference between these two quantities. And since the system is a continuum we can simplify by expanding  $\hat{\Gamma}(x)$  in a Taylor series. Thus the net transport of the conserved quantity  $\Gamma$  is

$$j_{\Gamma}'' = j_{+x}'' - j_{-x}'' = \bar{n}'' \left[ \hat{\Gamma}(x - \lambda_x) - \hat{\Gamma}(x + \lambda_x) \right] = \bar{n}'' \left\{ \left[ \hat{\Gamma}(x) - \lambda_x \frac{\partial \hat{\Gamma}(x)}{\partial x} \right] - \left[ \hat{\Gamma}(x) + \lambda_x \frac{\partial \hat{\Gamma}(x)}{\partial x} \right] \right\} = -2\bar{n}''(x) \lambda_x \frac{\partial \hat{\Gamma}(x)}{\partial x}$$

This is a general differential expression for the transport flux in a continuum. It is written in terms of the mean free path component in a single direction. This directional mean free path can be related to the general, nondirectional mean free path,  $\lambda_c$ , by integration using a particle's collision probability, see Ref. 1. The result is  $\lambda_x = (2/3) \cdot \lambda_c$ . With this substitution, the *continuum transport flux without net carrier particle flux* is

Ans. 15. The maximum for solar radiation occurs at  $\lambda_{\max} = 2898 \mu\text{mK}/5600 \text{ K} = 0.518 \mu\text{m}$ . At this peak,  $x_{\max} = hc/\lambda_{\max} kT = 4.965$  and

$$\dot{e}_{b,\lambda_{\max}}'' = \frac{2\pi hc^2}{\lambda_{\max}^5} \frac{1}{(e^{x_{\max}} - 1)} = \frac{2\pi \cdot 6.625 \cdot 10^{-34} \text{ Js} (2.998 \cdot 10^8 \text{ m/s})^2 \cdot (10^6 \mu\text{m/m})^4}{(0.518 \mu\text{m})^5 (e^{4.965} - 1)} = 7.05 \cdot 10^7 \text{ W}/(\text{m}^2 \mu\text{m})$$

Similarly, at 0.4 and 0.7  $\mu\text{m}$ ,

$$\dot{e}_{b,0.4\mu\text{m}}'' (5600 \text{ K}) = 5.98 \cdot 10^7 \text{ W}/(\text{m}^2 \mu\text{m}) \quad \dot{e}_{b,0.7\mu\text{m}}'' (5600 \text{ K}) = 5.84 \cdot 10^7 \text{ W}/(\text{m}^2 \mu\text{m})$$

The radiation incident on the atmosphere is attenuated by the factor

$$\left( \frac{d_{\text{sun}}}{d_{\text{orb}}} \right)^2 = \left( \frac{1.465 \cdot 10^6 \text{ km}}{150 \cdot 10^6 \text{ km}} \right)^2 = 9.54 \cdot 10^{-5}$$

So the intensities of natural solar light are

$$i_{\max}'' = 6792 \text{ W}/(\text{m}^2 \mu\text{m}), \quad i_{0.4\mu\text{m}}'' = 5705 \text{ W}/(\text{m}^2 \mu\text{m}), \quad i_{0.7\mu\text{m}}'' = 5571 \text{ W}/(\text{m}^2 \mu\text{m})$$

Ans. 16.  $\lambda_{\max} = 2898 \mu\text{mK}/1200 \text{ K} = 2.416 \mu$ . At this maximum:

$$\dot{e}_{b,\lambda_{\max}}'' = \frac{2\pi hc^2}{\lambda_{\max}^5 (e^{4.965} - 1)} = 3.19 \cdot 10^4 \text{ W}/(\text{m}^2 \mu\text{m})$$

But at  $\lambda = 0.7 \mu\text{m}$ ,  $\lambda T = 840 \mu\text{mK}$  and  $hc/\lambda kT = 17.14$ . Thus

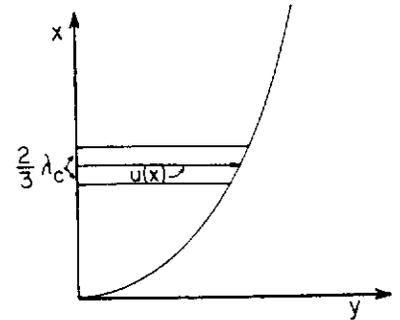
$$\dot{e}_{b,0.7\mu}'' (1200 \text{ K}) = \frac{2\pi hc^2}{\lambda^5 [e^{(hc/\lambda kT)} - 1]} = 80.48 \text{ W}/(\text{m}^2 \mu\text{m})$$

Notice that this threshold level for visibility is about two orders of magnitude less than that of natural light (see Exer. 15,  $i''$ )

$$j_{\Gamma}'' = -\frac{4\dot{n}''}{3} \lambda_c \frac{\partial \hat{\Gamma}(x)}{\partial x} \quad (\text{IIIE-18})$$

We can apply this result to momentum, heat, and species transport.

Momentum Transport. Consider fluid flow parallel to a surface as shown. The particles in contact with the wall are stationary. As a result a velocity defect zone is developed in the vicinity of the surface. The thickness and velocity distribution within this "boundary layer" are governed by momentum transport between the adjacent layers. The average y momentum of the particles at distance x from the wall is  $\hat{\Gamma}(x) = m^* u(x)$ . The momentum flux is predicted by eqn. IIIE-18 and it equals the negative of the shear stress at that point.<sup>15</sup>



$$j_{m^*u}'' = -\frac{4}{3} \dot{n}'' \lambda_c \frac{\partial m^* u(x)}{\partial x} = -\sigma_{xy}$$

The proportionality between the velocity gradient and shear stress is normally reported in terms of the constitutive equation,  $\sigma_{xy} = \mu \partial u / \partial x$ , that defines the Newtonian viscosity of a fluid,  $\mu$ . When we substitute this definition into the previous expression for the momentum flux, we obtain a general expression for the viscosity of a fluid

$$\mu = \frac{4}{3} \dot{n}'' m^* \lambda_c = \frac{\rho \hat{V} \lambda_c}{3} \quad (\text{IIIE-19a})$$

A similar procedure can be used to develop a general expression for thermal conductivity.

Heat Transport. Continuum energy transport by means of any carrier particle,  $i$ , can be obtained by identifying the transported quantity as the average energy per carrier particle,  $\Gamma_i(x) = \bar{u}_i / N_A$ . Application of eqn. IIIE-18 gives the continuum heat flux contribution of each type of carrier particle<sup>16</sup>.

$$j_{th,i}'' = \frac{4}{3} \dot{n}_i'' \lambda_{c,i} \frac{\partial}{\partial x} \left[ \frac{\bar{u}_i(T(x))}{N_A} \right] = -\frac{4}{3} \frac{\dot{n}_i'' \lambda_{c,i}}{N_A} \frac{d\bar{u}_i(T)}{dT} \frac{\partial T}{\partial x} = -\frac{4}{3} \frac{\dot{n}_i'' \lambda_{c,i}}{N_A} \bar{c}_{v,i} \frac{\partial T}{\partial x} = \dot{q}_i''$$

The proportionality between the rate of continuum heat transport and the local temperature gradient is normally reported in terms of the constitutive equation called the *Fourier-Biot Law*,  $\dot{q}_{x,i}'' = -K_i \partial T / \partial x$ , that defines the thermal conductivity component,  $K_i$

$$K_i = \frac{4}{3} \frac{\dot{n}_i''}{N_A} \bar{c}_{v,i} \lambda_{c,i} = \frac{\rho_i \hat{V}_i c_{v,i}}{3} \lambda_{c,i} \quad (\text{IIIE-20a})$$

Note the similarity of the expressions for  $K_i$  and  $\mu$ . In a fluid the carrier particle for both heat and momentum is the molecule. Thus the molecular conductivity of a fluid is

<sup>15</sup>Note that there need be no net particle transport in the x direction in order for the y momentum to be transported in this direction.

<sup>16</sup>We will apply this relationship to molecule, phonon, and free electron carrier particles. The result is equally applicable to a photon continuum, or radiant transport in optically thick media. However, it is unusual for radiation to be an appreciable transport process in media that are optically thick.

predicted by analogy with the thermal conductivity

$$K = \mu c_v \quad (\text{IIIE-21a})$$

A similar procedure can be employed to develop a general expression for the rate of diffusion induced by a concentration gradient within a molecular gas mixture. This expression provides a means to define the diffusion coefficient. However, this development requires consideration of gaseous mixtures; that is, requires techniques of Unit VIA. Since Unit VIA is not a prerequisite to this unit, diffusion is discussed in Appendix A. In the following section we consider momentum and heat transport within molecular gaseous continua.

#### A. The Transport Properties of Molecular Gases

The viscosity of a perfect molecular gas is determined by substituting eqns. IIIE-5a, 11, and 13b into eqn. IIIE-19a. The result is

$$\mu^* = \frac{2}{3\sigma^+} \left( \frac{MkT}{\pi N_A} \right)^{\frac{1}{2}} \quad (\text{IIIE-19b})$$

Exercise 17. Determine the viscosity of oxygen and helium at 100, 300, and 1000 K.

Both the form and numerical results predicted by eqn. IIIE-19b are in satisfactory agreement with data. Similarly, application of eqns. 20a and 21a correctly predicts the form for perfect gases. The numerical predictions, however, are off by a significant factor. This deviation is primarily caused by coupling between the speed, energy and mean free path of the carrier molecules. A more rigorous development would account for the fact that slow moving molecules have less kinetic energy and shorter than average mean free paths and vice versa.<sup>17</sup> These effects have been accounted for by Eucken, whose expression for K has the same form but a different numerical coefficient than that of eqns. IIIE-20a or 21a

$$K^* = \frac{(9\gamma^* - 5)}{4} \mu^* c_v^* = \frac{(9\gamma^* - 5)}{6\sigma^+} \frac{k}{(\gamma^* - 1)} \left( \frac{RT}{\pi} \right)^{\frac{1}{2}} \quad (\text{IIIE-20b})$$

The analogy between heat and momentum transport is further emphasized by the dimensionless property ratio called the *Prandtl number*,  $Pr \equiv \mu c_p / K$ . Eqns. IIIE-19b and 20b predict the Prandtl number of perfect gases to be

$$Pr^* \equiv \frac{\mu^* c_p^*}{K^*} = \frac{4\gamma^*}{9\gamma^* - 5} \quad (\text{IIIE-22})$$

Exercise 18. Extend the results of Exer. 17 to determine the thermal conductivity and Prandtl number of oxygen and helium at 100, 300, and 1000 K.

<sup>17</sup>The transport flux of kinetic energy is enhanced by a factor of four thirds over that predicted using eqn. IIIE-15, viz.,  $\dot{e}_{ke}'' = \dot{n}'' 2kT$  rather than  $\dot{n}'' (3/2) \cdot kT$ , see Ref. 4. This correction is not by itself sufficient to obtain Eucken's result. The mean free path effect must also be accounted for.

Appendix A employs a similar procedure to predict the rate at which one species diffuses through another within a continuum fluid. When applied to a perfect gas the resulting diffusion coefficients have a form similar to that for  $\mu^*$  and  $K^*$ . All of the molecular transport coefficients within a perfect gas continuum are *independent of pressure*.<sup>18</sup> Recognize that this means there is no inherent reduction in viscous drag associated with flight at higher altitudes and there is no inherent reduction in the rate of molecular heat conduction obtained by evacuation.<sup>19</sup> These transport processes are only indirectly affected by pressure as long as the gas remains within the continuum regime, see Exmp. 6.

### B. Transport Properties of Solids

There are two carrier particles that dominate the transport processes that occur in solids— free electrons and phonons.<sup>20</sup> Since phonons are uncharged, only free electrons participate in charge transport. And, to the extent that free electrons are present, they tend to dominate heat transport as well. However, since phonons contribute in a manner similar to heat transport in both conductors and nonconductors, we will first determine the form and magnitude of the phonon conductivity. Ultimately, we will see how both free electron and phonon contributions can be superposed to determine the total heat transport in a solid.

The phonon contribution to thermal conductivity is predicted directly from eqn. IIIE-20a.

$$K_{\text{phn}} = \frac{\rho c \lambda}{3} c_{\text{v,phn}} c_{\text{v,phn}}$$

where  $\rho$  is the lattice density and  $c_{\text{v,phn}}$  is the Debye continuum portion of the specific heat.<sup>21</sup> The difficulty in employing this result is associated with specifying the phonon mean free path.

Phonon Collision Processes. As phonons propagate through the crystal they carry their energy with them. However, if that energy is to be delivered from one region to another, the carrier phonons must exchange energy in different locations of the crystal. Thus, phonon collisions are necessary for phonon heat transport,

<sup>18</sup>The pressure independence is a result of the cancellation of the pressure dependences of the number density and mean free path,  $n_v \lambda_c \sim p^{-1} p \rho^{-1}$ .

<sup>19</sup>Total drag may well be reduced at higher altitudes since density is a factor in the "form" drag associated with separated flow. Similarly, the net rate of heat transport under evacuated conditions changes with pressure since the free convective flow that causes "convective" augmentation is a result of density changes.

<sup>20</sup>Diffusion in solids is very minimal; but atoms or molecules would be the carrier particles. Photon heat transport is also present; but it is almost always negligible in comparison to phonon or free electron processes.

<sup>21</sup>The internal mode components of the specific heat (see Appendix A, Unit IIID) do not participate in phonon transport. This energy is localized within each specific lattice point.

and  $\lambda_{c,phn}$  is a primary factor in determining  $K_{phn}$ . Two types of collisions are important in limiting the phonon mean free path. (Phonon collisions with free electrons and photons are not ordinarily a significant effect.)

Phonon-phonon collisions are dominant at high temperatures,  $T \sim \theta_D$ . However, only a portion of the phonon-phonon collisions limit the rate of heat transport. If two freely translating phonons collide, energy and momentum are conserved; thus there is no net change in the rate or direction of energy transport. In contrast, when a phonon collides with an optical mode vibration in a molecular crystal (see Unit IIID), the rate and direction of energy transport are altered. Similarly a certain fraction of phonon-phonon collisions involve localized lattice point vibrations (atomic or molecular). Such processes also alter the rate and direction of energy transport. Collectively all of the phonon collisions that affect the rate of phonon transport are called *Umklapp processes*. Partially as a result of the necessity to discriminate between the effective and ineffective phonon-phonon collisions, it is difficult to quantitatively predict the magnitude of the effective mean free path. But on a qualitative basis, eqn. IIIE-13a predicts that it is inversely proportional to the phonon density within the crystal,  $\lambda_{c,phn-phn} \propto n_{v,phn}^{-1}$ .

Phonon-Lattice Defect Collisions. Imperfections in the crystalline array are present in all but the most perfect single crystals. These imperfections may be due to strain, mechanical working, or lattice distortions in the region of an impurity or simply the grain boundary where two lattice orientations meet. All of these sources limit the phonon mean free path to a constant that is proportional to the defect spacing,  $\lambda_{c,phn-def} = \delta L$ .

Since we cannot predict the magnitude of  $\lambda_{c,phn}$ , we are prevented from making a quantitative determination of  $K_{phn}$ . However, an understanding of the underlying physical

Ans. 17. From Table IIIE-2,  $\sigma_{O_2}^+ = 40.9 \text{ (Å)}^2$  and  $\sigma_{He}^+ = 14.9 \text{ (Å)}^2$ . This gives for oxygen at 100 K

$$\mu_{O_2}^* (100 \text{ K}) = \frac{2}{3\sigma^+} \left( \frac{MkT}{\pi N_A} \right)^{\frac{1}{2}} = \frac{2}{3 \cdot 40.9 \cdot 10^{-20} \text{ m}^2} \left[ \frac{32.0 \text{ kg/(kg mol)} \cdot 1.38 \cdot 10^{-23} \text{ J/(part K)} \cdot 100 \text{ K}}{\pi \cdot 6.023 \cdot 10^{26} \text{ part/(kg mol)}} \right]^{\frac{1}{2}}$$

$$= 0.787 \cdot 10^{-5} \text{ kg/(m s)}$$

A similar procedure gives the values listed in the table of Ans. 18.

Ans. 18. The values of  $\mu^*$  predicted in Exer. 17, and listed in the table below, can be readily extended to the evaluation of  $K^*$  using Eucken's formula. At 100 K,  $c_{v,O_2}^* = (5/2)R$ .  
 $c_{p,O_2}^* = (5/2 + 1)R$

$$K_{O_2}^* (100 \text{ K}) = \frac{(9\gamma^* - 5)}{4} \mu^* c_v^* = \left( \frac{9 \cdot 1.4 - 5}{4} \right) \cdot 7.87 \cdot 10^{-6} \text{ kg/(m s)} \cdot (5/2) \cdot \left( \frac{8314}{32.0} \right) \text{ J/(kg K)}$$

$$= 9.71 \cdot 10^{-3} \text{ W/(m K)}$$

and

$$P_r^* = \frac{4\gamma^*}{(9\gamma^* - 5)} = \frac{4 \cdot 1.4}{9 \cdot 1.4 - 5} = 0.757.$$

Substance	T (K)	$\mu^* \cdot 10^5$ [kg/(m s)]	$c_p^*$ [J/(kg K)]	$\gamma^*$	$K^* \cdot 10^2$ [W/(m K)]	$P_r^*$
Oxygen	100	0.787	651	1.40	0.973	0.737
	300	1.73	659	1.39	2.14	0.740
	1000	7.87	831	1.51	11.1	0.771
Helium	100	0.764	3120	1.67	5.98	0.667
	300	1.68	3120	1.67	13.1	0.667
	1000	7.64	3120	1.67	59.8	0.667

The results for the remaining conditions as well as the values of  $c_v^*$  (see Unit IIIC) and  $\mu^*$  for Exer. 17 are listed in the table.

process does allow us to achieve considerable insight with respect to how  $K_{phn}$  varies with temperature, see Fig. III E-3.

The Thermal Conductivity of Insulating Solids. Heat transport within an opaque electrical nonconductor is dominated by phonon transport. The thermal conductivity in such crystals is predicted by eqn. III E-20a, where the effective mean free path is determined from

$$\frac{1}{\lambda_{c,phn}} = \frac{1}{\lambda_{c,phn-phn}} + \frac{1}{\lambda_{c,phn-imp}}$$

Thus, phonon heat transport is limited by the most efficient collision process, i.e., the shortest mean free path. This limiting process changes as we go from one region of temperature to another.

The high temperature region is defined by  $T > \theta_D$ . In this range,  $c_{v,phn} = 3R$  in atomic lattices and  $5R$  or  $6R$  in molecular lattices. Also the phonon density is high enough that phonon-phonon collisions dominate;  $n_{v,phn} \propto T$  (see Unit IIID) and  $\lambda_{c,phn-phn} \ll \lambda_{c,phn-imp}$ . Thus thermal conductivity is inversely proportional to temperature.

$$K_{ins}(T > \theta_D) \propto \frac{\rho c_s (3)R}{3n_{v,phn}} \propto \frac{1}{T}$$

The low temperature region,  $T \ll \theta_D$ . At low temperatures  $c_{v,phn} \propto T^3$  and phonon-impurity collisions will dominate  $\lambda_{c,phn-phn} > \lambda_{c,phn-imp} \sim \delta L$ . Thus the conductivity will be proportional to

$$K_{ins}(T \ll \theta_D) \propto \frac{\rho c_s \delta L T^3}{3} \propto T^3$$

The intermediate temperature region,  $T \sim \theta_D$ . The temperature variation of  $K_{ins}$  in this region is strongly dependent on the purity and quality of the crystal. In very pure, carefully grown single crystals  $\lambda_{c,phn-imp}$  approaches the size of the crystal and phonon-phonon collisions continue to dominate to quite low temperatures. This gives relatively large values of  $K_{ins}$  down to quite low temperatures. In ordinary solids with an appreciable impurity concentration,  $\lambda_{c,phn-imp}$  is much shorter and these processes will become dominant at higher temperatures. Below this point, the conductivity follows the Debye specific heat curve.

$$K_{ins}(T \sim \theta_D) \propto \frac{\rho c_s \delta L c_{v,phn}(T)}{3} \propto c_{v,phn}(T)$$

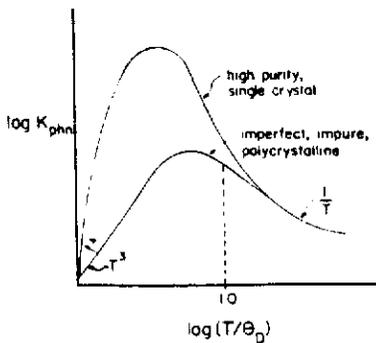


Fig. III E-3. Insulator Thermal Conductivities (Schematic)

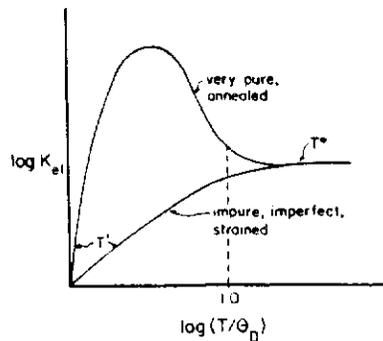


Fig. III E-4. Metallic Thermal Conductivities (Schematic)

The preceding discussion is summarized in Fig. IIIE-4; it illustrates the form of the thermal conductivity of insulating solids. It also represents the phonon component of the total conductivity of an electrical conductor. The free electron contribution to the thermal conductivity of a *metallic conductor* can be discussed in a similar manner. For free electrons, eqn. IIIE-20 takes the form

$$K_{el} = \frac{\rho V_F c_{v,el} \lambda_{c,F}}{3}$$

where  $\rho$  is the crystalline density and  $c_{v,el}$  is the free electron specific heat. In Unit IIID we found that  $c_{v,el} [= (\pi^2/2) \cdot R \cdot (T/\theta_F)]$  was quite low, since only the electrons in the vicinity of the Fermi level are capable of being excited. Therefore, the velocity and mean free path of interest are those of the free electrons *at the Fermi level*,  $V_F$  and  $\lambda_{c,F}$ . Now consider the temperature dependence of  $K_{el}(T)$ .  $\rho$  and  $V_F$  are constant and the temperature dependence of  $c_{v,el} (\propto T)$  is known. Therefore, the variations in  $K_{el}$  to be determined are governed by those in  $\lambda_{c,F}$ .

Free Electron Collision Processes. The important collision processes for free electrons are the same as those for phonons. We can, therefore, separate the form of  $K_{el}$  into low and high temperature regions.

In the high temperature region,  $T > \theta_D$ , the phonon density is sufficient that electron-phonon collisions predominate,  $\lambda_{c,F} \approx \lambda_{c,el-phn} \propto 1/n_{v,phn}$ . The temperature dependence is determined by  $n_{v,phn} \propto T$ . Thus

$$K_{el}(T > \theta_D) = \frac{\rho V_F c_{v,el} \lambda_{c,el-p}}{3} \propto \frac{T}{T} \propto T^0$$

At high temperatures  $K_{el}$  is independent of temperature.

In the low temperature region,  $T < \theta_D$ , the phonon density is sufficiently reduced that  $\lambda_{c,el-phn} > \lambda_{c,el-def} = \delta L$ . Thus

$$K_{el}(T < \theta_D) = \frac{\rho V_F c_{v,el} \delta L}{3} \propto T$$

when the temperature is reduced to the point that defect collisions dominate, then  $K_{el}$  is linearly proportional to temperature. In very pure, carefully annealed conductors this transition is delayed to much lower temperatures.

At low temperature levels the phonon density falls exponentially,  $n_{v,phn} \propto \exp(-\theta_D/T)$ . This causes  $K_{el}$  to increase until the defect scattering limit is reached, see Fig. IIIE-4.

We have noted that heat is carried simultaneously by phonons and electrons, Figs. IIIC-4 and 5. Their effects can be combined on the basis of

$$\frac{1}{K} = \frac{1}{K_{el}} + \frac{1}{K_{phn}} \quad (\text{III E-23})$$

Even though only a small percentage of the free electrons near the Fermi level participate in heat transport, so that  $c_{v,el} > c_{v,phn}$ , the speed of electron motion is so much faster

than that of phonons,  $V_F \gg c_s$ , that  $K_{el}$  dominates the conductivity of good electrical conductors by one and a half to two orders of magnitude. In alloyed materials and poor conductors the ratio is much less and the two contributions may be comparable.

Exercise 19. The following are illustrations of material applications in which the consideration of heat conduction is an essential element in design: (a) aluminum wire for long distance electrical transmission; (b) copper lead wires to a superconducting magnet (these span the temperature range from the  $\sim 10$  K magnet to the 300 K supply); (c) silicon rectifier; (d) the stainless steel tubes of steam boiler; (e) synthetic diamonds used as the cutting edge on a high-speed cutting tool. We are to make a decision based on engineering judgement whether their respective thermal conductivities could be considered constant or must they be treated as a variable for accurate engineering design. If variable conductivity analysis is necessary, will  $K(T)$  have a positive or negative slope?

The second transport process that is of great significance in solids is charge transport. To be a conductor a crystal must contain electrons that are not bound to specific points within the crystal—free electrons. Whether a specific solid is an insulator, conductor, or semiconductor can be discussed in terms of the *band theory* for the electrons of a solid.

Consider the formation of an atomic lattice point solid. The Bohr model for the atom specifies that the states accessible to the electrons are located on spheres of increasing radii (the successively higher energy shells, levels, have 2, 8, 18, etc., states). As these atoms are packed into a crystal, their electron interactions cause a slight shift in the magnitude of the states giving rise to an almost continuous "band" of accessible states clustered around the still discrete Bohr levels, see Fig. IIIE-5. We will examine this model to distinguish the electrical properties of solids.

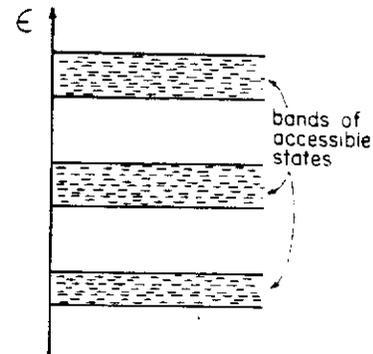


Fig. IIIE-5. Bands Formed by the Splitting of Levels

Insulators. Noble gas atoms have a full outer electron shell. In their crystalline form the band corresponding to the outer shell is full and the next higher band is empty. The Fermi level in such solids is in the *forbidden gap* between the bands. As a result there are no empty states accessible to the electrons; these solids are nonconducting. Molecules are formed by ionic or covalent electron bonding. In that sense they achieve a stable outer electron configuration similar to the rare gases. Molecular crystals are generally electrical insulators. (See Fig. IIIE-6a.)

Conductors. Metals have a relatively small number of electrons in their outer shell. As a result they form atomic crystals in which the outer shell band is only partly full. The Fermi level is within this conduction band. Since there are many empty state accessible to these free electrons, metals are electrical conductors. (See Fig. IIIE-6b.)

Semiconductors. Transition elements like carbon, silicon, and germanium, form atomic crystals in which the valence electrons are shared among the nearest

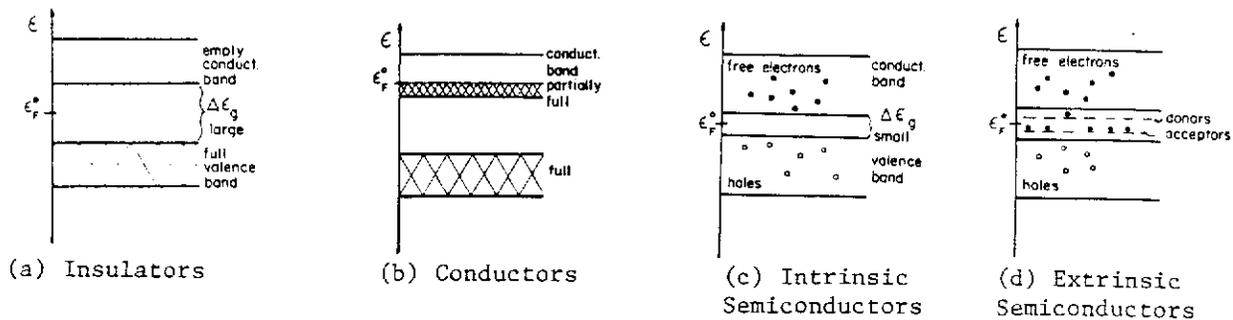


Fig. IIIE-6. Electrical Characteristics

neighbors in a stable covalent bond. This gives a filled valence band that is relatively narrowly separated from the next higher conduction band. The Fermi level is in the forbidden gap. In that respect, semiconductors are like insulators. The difference between them is the magnitude of the gap,  $\Delta\epsilon_g$ . In a semiconductor crystal the gap is smaller than that of an insulator. The energy gap of a semiconductor can be overcome by thermal excitation. When the temperature level in the crystal reaches  $T \sim \theta_g (= \Delta\epsilon_g/k)$ , electrons are excited into the conduction band where they act as *free electrons*. In addition, the empty states in the valence band provide "holes" that allow the bound electrons to change state. (See Fig. IIIE-6c.) Thus, the holes act as *positively charged carrier particles*. A pure substance of this type is called an *intrinsic semiconductor*.

The electrical properties of a semiconductor can be modified by introducing a suitable impurity called a dopant, (Fig. IIIE-6d). Semiconductors with positive carrier particles, "*P type*," formed by introducing an impurity with empty states just above the valence band. These *acceptor states* are readily occupied by electrons at relatively low temperatures. Similarly, semiconductors with negative carrier particles, "*n type*," are formed by doping with an impurity with a full, *donor state* just below the conduction band.

When a potential is imposed on a conductor (or semiconductor), the free electrons are accelerated toward regions of high voltage.<sup>22</sup> Without collisions the electrons would continue to accelerate and very high current densities would result,  $i'' \Rightarrow \infty$ . However, after an electron has been accelerated for a time period that averages a mean free time, it will be scattered by a collision with the lattice.<sup>22</sup> As a result, each electron will, on average, lose the momentum it had acquired in the direction of the applied field. Thus

<sup>22</sup>Each electron that is accelerated shifts to a different energy state. Therefore, it leaves an empty state that is accessible to other electrons. Electrons below the Fermi level accelerate by shifting sequentially into vacant states created by the acceleration of the entire group. Thus, unlike free electron heat transport that involves only electrons near the Fermi level, all of the free electrons participate in charge transport. On the other hand, electron-lattice collisions occur one at a time. A collision must move each electron to an accessible empty state. Thus collisions are limited by the accessibility of empty states and hence by the collision probability of electrons near the Fermi level. Thus, the appropriate mean free time is that of electrons near the Fermi level,  $\tau_{c,F}$ .

the net effect of the potential is to cause the electrons to drift through the lattice at a speed,  $u_{el}$ , that is governed by the field intensity,  $|\bar{E}|$ , and the collision frequency,  $\tau_{c,F}$ . As described by Newton's third law, the relationship is  $|\bar{F}_{el}| = e|\bar{E}| = m_e^* |\bar{a}_{el}| = m_e^* u_{el} / \tau_{c,F}$ , where the electron acceleration is expressed as a ratio of the drift velocity and the mean free time. The current density can also be described in terms of the drift velocity (as well as the free electron number density and the electron charge)  $i'' = n_{v,el} e u_{el}$ . This permits one to eliminate the drift velocity between these two expressions. The result is an expression in the form of *Ohm's Law* that allows the *electrical conductivity*,  $\sigma_{el}$ , to be determined.

$$i'' = \sigma_{el} |\bar{E}| = \left( \frac{n_{v,el} e^2 \tau_{c,F}}{m_e^*} \right) |\bar{E}| \quad \text{or} \quad \sigma_{el} = \frac{n_e N_A \rho e^2 \tau_{c,F}}{m_e^* M V_F} \quad (\text{IIIE-24a, 24b})$$

We have expressed the electrical conductivity in terms of the free electron mean free path. This is the only variable in eqn. IIIE-24b. Thus the temperature dependence of  $\sigma_{el}$  can be deduced from our earlier discussion of free electron collision processes as they related to  $K_{el}$ , Fig. IIIE-6.

The temperature dependence of  $\sigma_{el}$  is governed by  $\lambda_{c,F}$ . In the *high temperature region*,  $T > \theta_D$ , free electron collisions are dominated by electron-phonon interactions,  $\lambda_{c,F} = \lambda_{c,el-phn} \propto 1/n_{v,phn} \propto 1/T$ . Thus,

$$\sigma_{el}(T > \theta_D) \propto \frac{1}{T}$$

In the *low temperature region*,  $T \ll \theta_D$ , the phonon density is sufficiently reduced that  $\lambda_{c,el-phn} \approx \lambda_{c,el-def} = \delta L$ . Thus at low temperatures metallic electrical resistance becomes constant

$$\sigma_{el} \Rightarrow \sigma_{el,0} \propto T^0$$

The temperature level at which the transition from phonon to defect scattering occurs is heavily dependent on the purity and condition (annealing, cold working, etc.) of the conductor.

The analogy between electrical conductivity and the *free electron component* of thermal conductivity in metals can be expressed in an analytic form.

Ans. 19. (a) Aluminum transmission cables will be at temperatures slightly above those of environment. Thus,  $\theta_{D,Al} = 396 \text{ K} > T_0$ . In this excellent conductor, the thermal conductivity will have a slight negative slope. Constant-K analysis should be satisfactory. (b)  $\theta_{D,Cu} = 315 \text{ K}$ . The copper wire's temperature varies from low to intermediate. The slope of  $K(T)$  will be negative throughout. Variable  $K(T)$  analysis is essential to achieve a reasonable solution in this situation. (c) Silicon rectifiers ( $\theta_D = 658 \text{ K}$ ) are at temperatures slightly above their environment. Assuming an environment near 300 K,  $K(T)$  is significantly variable with negative slope. Over the narrow temperature span within the material constant K analysis should be satisfactory. (d) Iron, Chrome, and Nickel are the principal components in stainless steel. Thus,  $\theta_D \sim 450 \text{ K}$ . At the elevated temperatures of operation, K should be constant. (e) Diamond has a high Debye temperature, 1860 K. Even at high cutting temperatures,  $T < \theta_D$ .  $K(T)$  will have a negative slope.

**Example 8.** Formulate the ratio  $K_{el}/\sigma_{el}$  by substitution of all known parameters into eqns. IIIE-20b and 24b. Verify that all unknown parameters cancel and obtain the result in terms of universal constants and temperature.

The ratio of interest is of the general form

$$\frac{K_{el}}{\sigma_{el}} = \frac{\rho v_F \frac{c_{v,el}}{3} \lambda}{n_e N_A e^2 \lambda} \frac{1}{c_{,F}} = \frac{v_F^2 M c_{v,el} m_e^*}{3 n_e N_A e^2 m_e^* M v_F}$$

Then substituting from eqns. IIID-22 and IIIE-7

$$c_{v,el} = \frac{\pi^2}{2} M \bar{R} \left( \frac{T}{\theta_F} \right) \quad v_F = \left( \frac{2k \theta_F}{m_e^*} \right)^{\frac{1}{2}} \quad \bar{R} = N_A k$$

we have

$$\frac{K_{el}}{\sigma_{el}} = \frac{1}{3} \left( \frac{\pi k}{e} \right)^2 T$$

The preceding problem expressed the analogy between the thermal and electrical conductivity of free electrons in a metal in the analytic form known as the *Wiedemann-Franz Law*.

$$\frac{K_{el}}{\sigma_{el} T} = L = \frac{\pi^2}{3} \left( \frac{k}{e} \right)^2 = 2.45 \cdot 10^{-8} \text{ W}\Omega/\text{K}^2 \quad (\text{IIIE-25})$$

where  $L$  is known as the *Lorentz number*. The Wiedemann-Franz law is sufficiently accurate that the relatively easily measured electrical conductivity is often employed to predict the thermal conductivity of good conductors.<sup>23</sup>

**Example 9.** Platinum resistance thermometers are constructed of a carefully wound strain free coil of highly purified platinum wire. A particular thermometer uses a 3 m length of 50  $\mu\text{m}$  diameter wire. Its calibration curve includes the following values:  $T = 10 \text{ K}$ ,  $R = 0.2723 \Omega$ ;  $T = 100 \text{ K}$ ,  $R = 42.36 \Omega$ ; and  $T = 300 \text{ K}$ ,  $R = 151.3 \Omega$ . Use these data and the Wiedemann-Franz law to determine the thermal conductivity of platinum at each of these temperatures. In addition, determine the free electron mean free path at these temperatures.

The resistance of a wire is related to its electrical conductivity by  $R = L/(A_c \sigma_{el})$ . Thus  $\sigma_{el}$  can be determined from

$$\sigma_{el}(10 \text{ K}) = \frac{4 L}{\pi d^2(10 \text{ K})} = \frac{4 \cdot 3 \text{ m}}{\pi \cdot (50 \cdot 10^{-6})^2 \cdot 0.2723 \Omega} = 5.611 \cdot 10^9 / (\Omega \text{ m})$$

Similarly,  $\sigma_{el}(100 \text{ K}) = 3.607 \cdot 10^7 / (\Omega \text{ m})$  and  $\sigma_{el}(300 \text{ K}) = 1.010 \cdot 10^6 / (\Omega \text{ m})$ . The eqn. IIIE-25 gives the corresponding values for  $K_{el}$

<sup>23</sup>The Wiedemann-Franz law only predicts the free electron contribution to thermal conductivity. Its utility is therefore restricted to good conductors in which  $K_{el} \gg K_{phn}$ . The Wiedemann-Franz law is sufficient for engineering accuracy at both low and high temperatures. The relationship is not as accurate at intermediate temperatures in good conductors with relatively large values of  $\lambda_{c,el-def}$ .

$$K(10 \text{ K}) \approx K_{el}(10 \text{ K}) = L \sigma_{el} T = 2.45 \cdot 10^{-8} \text{ W } \Omega / \text{K}^2 \cdot 5.611 \cdot 10^9 / (\Omega \text{ m}) \cdot 10 \text{ K} = 1375 \text{ W}/(\text{mK})$$

$$\text{And } K(100 \text{ K}) \approx 88.37 \text{ W}/(\text{mK}), \quad K(300 \text{ K}) \approx 74.24 \text{ W}/(\text{mK})$$

The carefully measured resistances of the platinum thermometer give an accurate measure of the free electron mean free path based on eqn. III E-21b. For platinum  $n_e = 2$ ,  $\theta_F = 1.14 \cdot 10^5 \text{ K}$ ,  $\rho = 21.5 \text{ g}/\text{cm}^3$  and  $M = 195.0 \text{ kg}/(\text{kg mol})$ . Thus,

$$v_F = \left( \frac{2k\theta_F}{m_e^*} \right)^{\frac{1}{2}} = \left[ \frac{2 \cdot 1.380 \cdot 10^{-23} \text{ J}/(\text{part K}) \cdot 1.14 \cdot 10^5 \text{ K}}{9.109 \cdot 10^{-31} \text{ kg/elect}} \right]^{\frac{1}{2}} = 1.86 \cdot 10^6 \text{ m/s}$$

$$\begin{aligned} \lambda_{c,F}(10 \text{ K}) &= \frac{\sigma_{el}(10 \text{ K}) m_e^* v_F M}{n_e N_A \rho e^2} \\ &= \frac{5.611 \cdot 10^9 / (\text{m}) \cdot 9.109 \cdot 10^{-31} \text{ kg/elect} \cdot 1.86 \cdot 10^6 \text{ m/s} \cdot 195 \text{ kg}/(\text{kg mol})}{2 \cdot 6.023 \cdot 10^{26} \text{ part}/(\text{kg mol}) \cdot 21.5 \cdot 10^3 \text{ kg}/\text{m}^3 \cdot (1.602 \cdot 10^{-19} \text{ C})^2} \\ &= 2.81 \cdot 10^{-6} \text{ m} = 2.81 \cdot 10^4 \text{ \AA} \end{aligned}$$

and

$$\lambda_{c,F}(100 \text{ K}) = 181 \text{ \AA}, \quad \lambda_{c,F}(300 \text{ K}) = 50.6 \text{ \AA}.$$

**Exercise 20.** Nichrome is an alloy that is used extensively in resistance heating elements. At room temperature its conductivity is  $9.7 \cdot 10^5 / (\Omega \text{ m})$ . Use the Wiedemann-Franz law to determine its thermal conductivity. Comment on the authenticity of this procedure for nichrome.

A comparison between Exmp. 9 and Exer. 20 illustrates the very large difference between the electrical conductivities of the relatively good conductor, platinum, and the poor conductor, nichrome. The Wiedemann-Franz law provides a convenient method of predicting the thermal conductivity of metals from rather easily obtained electric resistance data. However, this technique is not satisfactory for poor conductors; in poor conductors—metallic or semiconductor, lattice heat conduction is appreciable. In principle, eqn. III E-24b can be employed to determine the electrical conductivity of semiconductors. However, one must recognize that the free electron number density (or valence) of semiconductors is a variable. Indeed, in intrinsic semiconductors the variation of  $n_{v,el}$  dominates the temperature dependence of the electrical conductivity. As a result  $\sigma_{el}$  increases with temperature for intrinsic semiconductors.

$$\text{Ans. 20. } K \approx K_{el} = L \sigma_{el} T = 2.45 \cdot 10^{-8} \text{ W } \Omega / \text{K}^2 \cdot 9.7 \cdot 10^5 / (\Omega \text{ m}) \cdot 300 \text{ K} = 7.13 \text{ W}/(\text{mK}).$$

The thermal conductivity is an order of magnitude less than that for platinum and nearly two orders of magnitude less than that for copper. The accuracy of the prediction is dependent on phonon heat conduction being negligible for nichrome. This is a questionable assumption.

APPENDIX A

CONTINUUM DIFFUSION

The molar concentrations,  $x_i$ , are fundamentally intensive properties of a single phase mixture. In equilibrium these potentials are uniform. If a gradient exists in one of them, it will result in diffusion of that species.<sup>24</sup> The carrier particles for diffusion are the particles of the diffusing species. In that respect, diffusion is unlike momentum and heat transport which occur even when the carrier particle flux is isotropic. Diffusion is more like charge transport in that it requires a drift, or net unbalanced movement, of the carrier particles.

Diffusion in a Continuum. The mass rate of diffusion of species  $i$  in a single direction is the product of particle mass and the difference between the positive and negative fluxes of that species  $j_i'' = m_i^*(\dot{n}_{i,+}'' - \dot{n}_{i,-}'')$ . The magnitudes of these two interpenetrating particle fluxes are governed by the positive-direction flux leaving position  $z - \lambda_{z,i}$  and the negative-direction flux leaving  $z + \lambda_{z,i}$ . Our development concerns diffusion in a continuum. Thus both fluxes can be expanded in a Taylor series about the position  $z$ .<sup>25</sup>

$$j_i'' = m_i^*(\dot{n}_{i,+}'' - \dot{n}_{i,-}'') = m_i^* \left\{ \left[ \dot{n}_i''(z) - \lambda_{z,i} \frac{\partial \dot{n}_i''(z)}{\partial z} \right] - \left[ \dot{n}_i''(z) + \lambda_{z,i} \frac{\partial \dot{n}_i''(z)}{\partial z} \right] \right\} = -2m_i^* \lambda_{z,i} \frac{\partial \dot{n}_i''(z)}{\partial z}$$

Now the species flux can be expressed in terms of eqn. III E-11,  $\dot{n}_i''(z) = \dot{n}_{v,i}''(z) \hat{V}_i / 4 = n_v \hat{V}_i x_i(z) / 4$ , where only the mole fraction is a function of

position. ( $\hat{V}_i$  varies with temperature and  $n_v$  with temperature or pressure. Such gradients have been considered separately and are ignored in our discussion of diffusion.) In addition, the directional mean free path component can be replaced by the mean free path,  $\lambda_{z,i} = (2/3) \lambda_{c,i}$ . This gives  $j_i'' = -(m_i^* n_v \hat{V}_i \lambda_{c,i}) / 3 \cdot [\partial x_i(z) / \partial z]$ . The standard form is obtained by introducing the mass fraction,  $y_i = M_i x_i / M$  (where  $m_i^* N_A = M_i$  and  $n_v = N_A \rho / M$ ).

$$j_i'' = - \rho \left( \frac{\hat{V}_i \lambda_{c,i}}{3} \right) \frac{\partial y_i(z)}{\partial z} \quad (\text{III E-A1})$$

This constitutive equation, called *Fick's Law*, is normally introduced as a definition of the diffusion coefficient,  $j_i'' = - \rho D_i \partial y_i / \partial z$ . Comparing this to eqn. III E-A1, we obtain

$$D_i = \frac{\hat{V}_i \lambda_{c,i}}{3} \quad (\text{III E-A2a})$$

<sup>24</sup>More correctly, equilibrium implies uniformity of the chemical potential. In single phase mixtures this is equivalent to uniform concentrations. Our discussion also ignores imposed fields. In a gravitational field nonuniform, hydrostatically distributed concentrations is the equilibrium state.

<sup>25</sup>We use  $z$  as the spatial coordinate to avoid confusion with  $x_i$  and  $y_i$ .

This is the general form of the diffusion coefficient.  $\hat{V}_i$  is the mean speed of the diffusing particles and  $\lambda_{c,i}$  is their mean free path considering all collision processes. For example, in a binary mixture in which only molecule-molecule collisions are important

$$D_{12} = \frac{\hat{V}_1 \lambda_{c,1}}{3} \quad \text{where} \quad \frac{1}{\lambda_{c,1}} = \frac{1}{\lambda_{c,1-1}} + \frac{1}{\lambda_{c,1-2}} \quad (\text{IIIE-A2b,A3})$$

where  $D_{12}$  connoted diffusion of species 1 through species 2. In that sense the diffusion coefficient, indeed the whole idea of diffusion, is dependent not only on the diffusing species but also on the species it is diffusing through. From the definitions of eqns. IIIE-A2b and A3, it is recognized that a hypothetical self-diffusion coefficient can be defined as

$$D_{11} = \frac{\hat{V}_1 \lambda_{c,1-1}}{3} \quad (\text{IIIE-A2c})$$

This is a property of the pure substance and it provides a useful guide to the diffusability of the species. ( $D_{12} \Rightarrow D_{11}$ , if species 1 and 2 are very similar.)

For a perfect gas and a perfect gas mixture, the self- and binary diffusion coefficients are obtained by substituting eqns. IIIE-5a, 13b, and A3 into eqn. IIIE-A2a

$$\rho D_{11}^* = \frac{2}{3\sigma_{11}^+} \left( \frac{M_1 kT}{\pi N_A} \right)^{\frac{1}{2}} \quad \rho D_{12}^* = \frac{2 \left( 1 + \frac{y_2}{y_1} \right)}{3 \left[ \sigma_{11}^+ + \left( \frac{y_2 M_1}{y_1 M_2} \right) \sigma_{12}^+ \right]} \left( \frac{M_1 kT}{\pi N_A} \right)^{\frac{1}{2}} \quad (\text{IIIE-A4a,A4b})$$

A comparison between eqn. IIIE-A4a and eqn. IIIE-19b reveals that they are identical. The ratio,  $(u_1/\rho_1 D_{11})$ , is known as the Schmidt number,  $S_c$ .<sup>26</sup> Our theory predicts that it is unity for perfect gases. Data is closer to 0.75. Thus the simple hard sphere theory predicts the correct parametric form for the diffusion coefficients; but like the prediction of thermal conductivity, it is numerically imprecise.

**Exercise A1.** Use eqns. IIIE-A4 to predict the self-diffusion coefficients of nitrogen and oxygen at STP. Compare these results to the binary diffusion coefficients of the nitrogen and oxygen components in air at STP ( $y_{O_2} = 0.23$ ,  $y_{N_2} = 0.77$ ).

TABLE IIIE-1 EXPONENTIAL INTEGRALS

Finite Limit	Infinite Limit	
$\int_0^x x^2 e^{-x^2} dx$	$n = 0, 2, 4, \dots$	$n = 1, 3, 5, \dots$
0	$\int_0^{\infty} x^n e^{-x^2} dx = \frac{(n-1)}{2} \frac{(n-3)}{2} \dots \frac{1}{2} \frac{\sqrt{\pi}}{2}$	$\int_0^{\infty} x^n e^{-x^2} dx = \frac{1}{2} \frac{(n-1)!}{2^{(n-1)/2}}$
0.0016		
0.0194		
0.0583	$\int_0^{\infty} e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$	$\int_0^{\infty} x e^{-x^2} dx = \frac{1}{2}$
0.1179		
0.1895		
0.2612		
0.3234	$\int_0^{\infty} x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{4}$	$\int_0^{\infty} x^3 e^{-x^2} dx = \frac{1}{2}$
0.3708		
0.4030		
0.4227		
0.4336	$\int_0^{\infty} x^4 e^{-x^2} dx = \frac{3\sqrt{\pi}}{8}$	$\int_0^{\infty} x^5 e^{-x^2} dx = 1$
0.4390		
0.4410		
$\sqrt{\pi}/4$	$\int_{-\infty}^{\infty} x^n e^{-x^2} dx = 2 \int_0^{\infty} x^n e^{-x^2} dx$	$\int_{-\infty}^{\infty} x^n e^{-x^2} dx = 0$

TABLE IIIE-2. COLLISION CROSS SECTIONS

Substance	Symbol	$d^+(\text{\AA})$	$\sigma^+(\text{\AA}^2)$
Helium	He	2.18	14.9
Neon	Ne	2.59	21.1
Argon	Ar	3.64	41.6
Krypton	Kr	4.16	54.4
Xenon	Xe	4.85	73.9
Mercury	Hg	4.26	57.0
Hydrogen	H <sub>2</sub>	2.74	23.6
Nitrogen	N <sub>2</sub>	3.75	44.2
Oxygen	O <sub>2</sub>	3.61	40.9
Hydrogen chloride	HCl	4.46	62.5
Carbon dioxide	CO <sub>2</sub>	4.59	66.2
Water	H <sub>2</sub> O	4.60	66.5
Ammonia	NH <sub>3</sub>	4.43	61.7
Methane	CH <sub>4</sub>	4.14	53.8
Ethylene	C <sub>2</sub> H <sub>4</sub>	4.95	77.0
Ethane	C <sub>2</sub> H <sub>6</sub>	5.30	88.2

Extracted from Kennard, E. R., Kinetic Theory of Gases, McGraw Hill (1938).

Ans. 1. The densities of  $N_2$ ,  $O_2$ , and air at STP are

$$\rho_{N_2} = \frac{p}{RT} = \frac{1.013 \cdot 10^5 \text{ N/m}^2}{\left(\frac{8317}{28.00}\right) \text{ J/(kg K)} \cdot 300 \text{ K}} = 1.137 \text{ kg/m}^3$$

$$\rho_{O_2} = 1.299 \text{ kg/m}^3, \quad \rho_m = 1.176 \text{ kg/m}^3$$

From Table IIIE-2,  $\sigma_{N_2}^+ = 44.2(\text{\AA})^2$  and  $\sigma_{O_2}^+ = 42.6(\text{\AA})^2$ .

$$D_{N_2, N_2} = \frac{2}{3\rho_{N_2} \sigma_{N_2}^+} \left( \frac{M_{N_2} kT}{\pi N_A} \right)^{\frac{1}{2}}$$

$$= \frac{2}{3 \cdot 1.137 \text{ kg/m}^3 \cdot 44.2 \cdot 10^{-20} \text{ m}^2} \left[ \frac{28.00 \text{ kg/(kg mol)}}{\pi \cdot 6.023 \cdot 10^{26} \text{ part/(kg mol)}} \left( \frac{1.380 \cdot 10^{-23} \text{ J/(part K)} \cdot 300 \text{ K} \cdot 1 \text{ kg m}^2}{\text{J s}^2} \right)^{\frac{1}{2}} \right] = 1.04 \cdot 10^{-5} \text{ m}^2/\text{s}$$

Similarly,  $D_{O_2, O_2} = 1.01 \cdot 10^{-5} \text{ m}^2/\text{s}$ . Then

$$D_{N_2, O_2} = \frac{2 \left( 1 + \frac{y_{O_2}}{y_{N_2}} \right)}{3\rho \left[ \frac{y_{O_2} M_{N_2}}{\sigma_{N_2}} + \frac{y_{N_2} M_{O_2}}{y_{N_2} M_{O_2} \left( \frac{\sigma_{N_2} + \sigma_{O_2}}{2} \right)} \right]} \left( \frac{M_{N_2} kT}{\pi N_A} \right)^{\frac{1}{2}} = 1.04 \cdot 10^{-5} \text{ m}^2/\text{s}$$

and

$$D_{O_2, N_2} = 0.988 \cdot 10^{-5} \text{ m}^2/\text{s}$$