

## Gas Kinetics

The behavior of vapors and gases on both the macroscopic and the molecular scale is fundamental to an understanding of thin-film deposition from the vapor phase. This chapter will examine the molecular interaction of gases and will relate that behavior to the macroscopic, measurable properties such as temperature and pressure.

### 2.1 Vapors and Gases

It is important at the outset to distinguish between the behaviors of vapors and gases. At a fixed temperature,  $T$ , a vapor can be condensed to a liquid or solid by compressing it sufficiently, whereas a gas cannot. This situation is illustrated by the pressure-volume-temperature ( $p$ - $V$ - $T$ ) diagram of Fig. 2.1. The possible equilibrium states of any pure material can be represented by a surface in  $p$ - $V$ - $T$  space such as the one shown. Here, the  $V$  is that of a fixed amount of material which we will set at one mole ( $6.02 \times 10^{23}$  molecules), so that  $V$  is the molar volume,  $V_m$ . Now visualize a cut through the  $p$ - $V$ - $T$  surface along a  $p$ - $V$  plane positioned at temperature  $T_2$ . The cut intercepts the surface along the line a-b-c-d-e-f, so this line represents the relationship between  $p$  and  $V_m$  for that material at that  $T$ . At the lowest  $p$ , we are at point a, and the material exists in the vapor phase, as labeled. Reducing the volume of the container holding our mole of vapor raises its pressure, and we move along the line a-b. At point b, condensation to the liquid phase begins, and at point c, condensation is complete. During condensation, volume is decreasing at a fixed  $p$  and  $T$ ; that is, the line b-c is perpendicular to the  $p$ - $T$  plane. The  $p$  in this region,  $p_v$ ,

ishes at the "critical" point. Every material has a single such point in  $p$ - $V$ - $T$  space, the coordinates of which are the critical  $p$ ,  $V$ , and  $T$  ( $p_c$ ,  $V_c$ , and  $T_c$ ). Above  $T_c$ , there is no volume discontinuity upon compression and thus no distinction between the two phases. Instead, molar density ( $1/V_m$ ) increases monotonically with increasing  $p$ , as it does at  $T_4$ . Above  $T_c$ , a material cannot be condensed to a liquid, and it is called a gas; below  $T_c$ , it can be condensed and is called a vapor.

A second important aspect of Fig. 2.1 for thin-film work is the  $p$ - $T$  behavior of the surfaces labeled "liquid-vapor" and "solid-vapor," which represent the regions in which condensation is taking place. Since these surfaces, as well as the solid-liquid surface, are perpendicular to the  $p$ - $T$  plane, their projections on that plane are lines, as shown in Fig. 2.2. Note that below a certain  $T$ , the liquid-phase region vanishes so that condensation occurs directly to the solid phase. The vaporization of material in this region is called sublimation. The point where the liquid phase vanishes is called the triple point because it is the only point where all three phases can exist simultaneously in equilibrium. The lines abutting the vapor phase are the vapor pressure ( $p_v$ ) curves. These data are of fundamental importance in controlling thin-film processes, and they will be discussed quantitatively

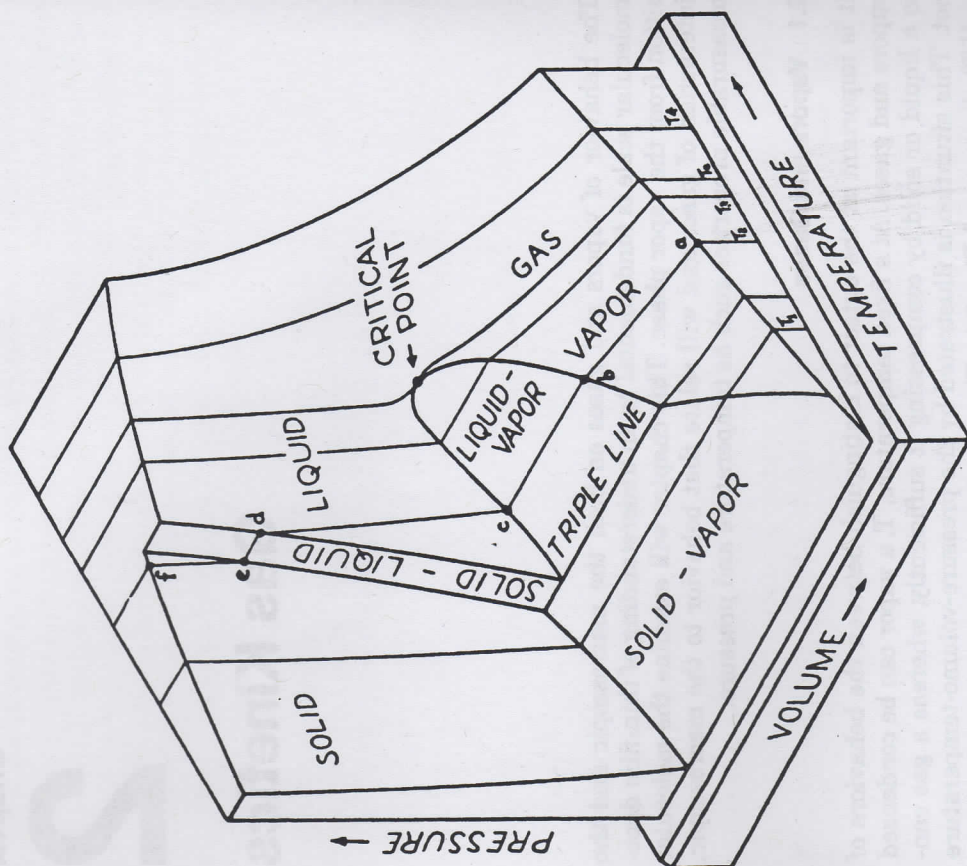


Figure 2.1  $p$ - $V$ - $T$  diagram for a fixed amount of pure material. [Reprinted from Sears (1950) with permission of the publisher. © 1950, 1953 by Addison-Wesley Publishing Co., Inc.]

is called the saturation vapor pressure, or often just the vapor pressure. Of course, an abrupt decrease in  $V$  could be imposed during condensation, which would push the system to a  $p$  above the line  $b$ - $c$ , but this would not be an *equilibrium* situation. In such an instance, the vapor is said to be "supersaturated." Supersaturation is an important driving force in the nucleation and growth of thin films, and it will be discussed in more detail in Chap. 5. The distance  $b$ - $c$  along the  $V$  axis is the volume difference,  $\Delta V$ , between the vapor and liquid phases at  $T_2$ . Note that at higher  $T$  values,  $\Delta V$  becomes smaller and finally van-

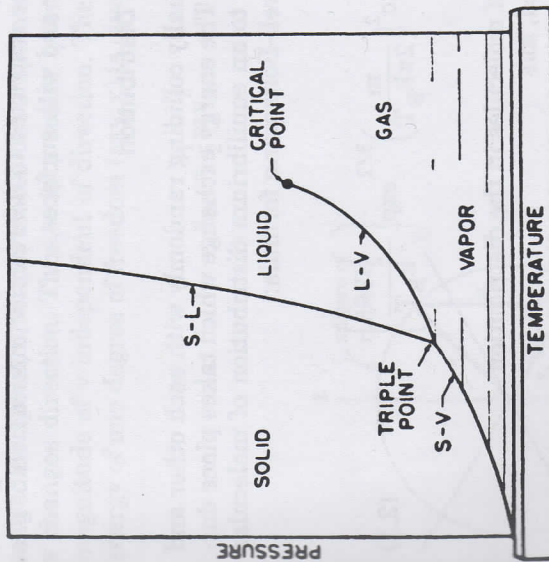


Figure 2.2 Projection of the  $p$ - $V$ - $T$  surface of Fig. 2.1 on the  $p$ - $T$  plane. [Reprinted from Sears (1950) with permission of the publisher; "triple point" label added. © 1950, 1953 by Addison-Wesley Publishing Co., Inc.]

in Sec. 4.1. The  $p_v$  increases exponentially with  $T$ , and at its terminus at the critical point,  $p_v$  is well above one atmosphere. There, the vapor has to be compressed so much to make it condense that its concentration has approached the concentration of the liquid phase, and that is why the phase boundary vanishes. Thin-film processes are carried out at much lower  $p$ , sometimes above and sometimes below the  $p_v$  line. During film deposition, the amount by which the  $p$  of the source vapor exceeds  $p_v$  is the supersaturation, as mentioned above. In the first two steps of the thin-film process (source supply and transport to the substrate), good process control requires that one avoid condensation by keeping  $p$  below the  $p_v$  line. Condensation should also be avoided during the compression that occurs in vacuum pumps (more in Sec. 3.2).

By definition, all vapors are condensable, but sometimes a vapor will not be condensable under conditions encountered in thin-film work, these conditions usually being at or below one atmosphere of  $p$  and at or above room  $T$  (25° C). If the  $p_v$  of a particular vapor is  $> 1$  atm. at 25° C, its condensation will not be encountered, and it may therefore be thought of as a gas for practical purposes. For example, nitrous oxide ( $N_2O$ ) is, strictly speaking, a vapor at 25° C, because its  $T_c$  is 37° C; but since its  $p_v$  at 25° C is 55 atm,  $N_2O$  is considered to be a gas. In this chapter, we will be talking about gases and about vapors in the absence of condensation, so we will refer to them all as gases. Our discussion will also be restricted to *nonreactive* interaction of gas molecules with each other and with surfaces.

## 2.2 Maxwell-Boltzmann Distribution

Gas molecules are continually colliding randomly with each other and with containing surfaces. The energy exchange which takes place during these collisions leads to an equilibrium distribution of molecular speeds given by the Maxwell-Boltzmann formula:

$$\frac{dN/dc}{N} = 4\pi c^2 \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left( -\frac{\frac{1}{2} m c^2}{k_B T} \right) \quad (2.1)$$

where  $N$  = total number of molecules in the distribution

$c$  = molecular speed, m/s

$dN/dc$  = incremental number of molecules  $dN$  within the speed increment  $dc$

$m$  = molecular mass, kg

$k_B$  = Boltzmann's constant =  $1.38 \times 10^{-23}$  J/K

$T$  = absolute temperature, K

Many important properties of gases follow from this formula, as we will see below. Its derivation is too involved to deal with here, but it is worthwhile reviewing its origin in statistical mechanics because of the utility of this thinking in many aspects of thin-film deposition. All particles have various modes, or degrees of freedom, of energy storage. For molecules, they are translational, rotational, vibrational, and electronic, listed here in order of increasing spacing between quantized energy levels. Electronic excitation requires the largest energy jump to reach the first level above ground state, so it is seen only at extremely high  $T$  or when there is a source of high-energy particles. In relation to thin-film processes, electronic and vibrational excitation are important in plasmas and in deposition activated by UV photons. Rotational excitation usually increases in degree over the  $T$  range of thermal film deposition, and this affects gas heat capacity, as we will see in Sec. 2.4. Translational energy levels have the closest spacing, and their distribution can be considered as a continuum at ordinary  $T$  values.

There are three translational-energy degrees of freedom or components, corresponding to the three orthogonal directions of velocity:  $v_x$ ,  $v_y$ , and  $v_z$ . The total velocity,  $v$ , of a molecule is the vector sum of these three components, and it may be represented as a vector in velocity space as shown in Fig. 2.3. The absolute magnitude of  $v$  is called the molecular speed,  $c$ , which traces out a spherical surface of radius  $c$  as  $v$  changes direction. Thus,  $c$  is a scalar quantity that represents the magnitude of  $v$  independent of direction. The molecular translational energy of one degree of freedom (say,  $x$ ) is given by

$$\epsilon_{tx} = \frac{1}{2} m v_x^2 \quad (2.2)$$

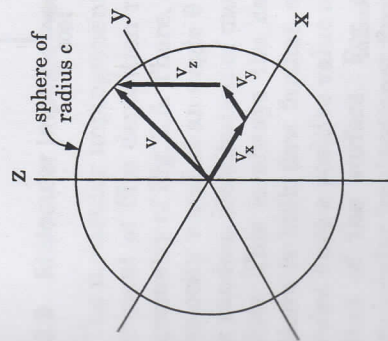
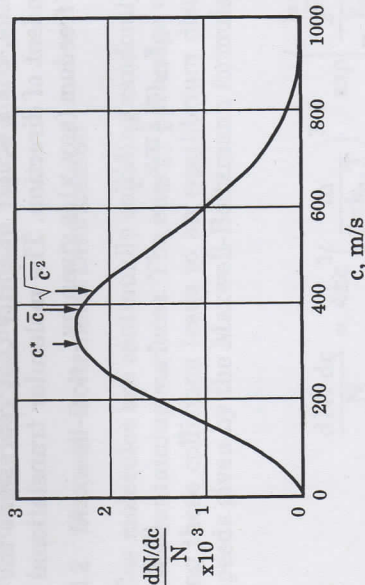


Figure 2.3 Representation of molecular velocity,  $v$ , in velocity space. Molecular speed is represented by  $c$ .

Now, at thermal equilibrium, it is known from Boltzmann statistics that, for each degree of freedom, the probability of finding a molecule at energy level  $\epsilon$  is exponentially distributed in energy according to the Boltzmann factor,  $\exp(-\epsilon/k_B T)$ , where  $k_B$  is Boltzmann's constant. This is the equilibrium distribution in  $\epsilon$  because it provides the *maximum number of ways of arranging a group of molecules among the available quantum states to yield the same total energy for the group*. Each of the three translational-energy degrees of freedom is distributed in this way. The product of these terms gives the exponential term in Eq. (2.1), since we know from Pythagorus that  $v^2 = v_x^2 + v_y^2 + v_z^2$ , and we know furthermore that  $v^2 \equiv c^2$ . In addition, the probability of finding a molecule at speed  $c$  and energy  $(1/2)mc^2$  will be proportional to the number of ways of distributing the energy among the  $x$ ,  $y$ , and  $z$  components to arrive at this speed; that is, the probability is proportional to what is called the "degeneracy" of this translational energy level. The degeneracy is proportional to the surface area of the sphere of radius  $c$  in velocity space,  $4\pi c^2$ , which is the first term in Eq. (2.1). Finally, the middle term in Eq. (2.1) is a normalizing factor that makes the integral of the distribution over all speeds come out to unity.

The  $c^2$  and exponential terms together lead to a peak in the speed distribution, as shown in Fig. 2.4 for Ar at 25° C. In this chapter, we



$N$  = number of atoms in the distribution

$\bar{c}$  = mean speed

$\sqrt{\bar{c}^2}$  = root-mean-square (rms) speed

$c^*$  = speed of sound

Figure 2.4 Maxwell-Boltzmann distribution of molecular speeds for Ar at room T.

will be expressing various properties of the gas in terms of the mean speed in the distribution,

$$\bar{c} = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} \quad (2.3)$$

or the root-mean-square (rms) speed,

$$\sqrt{\bar{c}^2} = \sqrt{\frac{3k_B T}{\pi m}} = \sqrt{\frac{3RT}{M}} \quad (2.4)$$

Here, the speeds have also been expressed in terms of the molar quantities  $R$  and  $M$ , where

$$R = k_B N_A = \text{gas constant} = 8.31 \text{ J/mol}\cdot\text{K} \text{ or } \text{Pa}\cdot\text{m}^3/\text{mol}\cdot\text{K}$$

(J = joules = N·m)

$$N_A = \text{Avogadro's number} = 6.02 \times 10^{23} \text{ mc/mol}$$

(mc = molecule)

$$M = mN_A = \text{molar mass ("molecular weight")} \text{ in kg/mol}$$

The above equations, obtained by integrating over the Maxwell-Boltzmann distribution, relate the molecular speeds to the measurable quantity  $T$ . The rms speed differs slightly from the mean speed because of the skew of the distribution. Both quantities are shown in Fig. 2.4, along with the speed of sound,  $c^*$ , which is close in value because it is, after all, molecular collisions that carry sound pressure waves through a gas. All three speeds are seen to be near the peak of the distribution (see Exercise 2.2). Whether the mean or the rms speed is called for will depend on whether we are dealing with a quantity that is proportional to  $c$  or to  $c^2$ .

### 2.3 Molecular Impingement Flux

The molecular impingement flux at a surface is a fundamental determinant of film deposition rate. We can calculate this flux using the geometry of Fig. 2.5. There, a molecule at point A is shown moving at a velocity  $v$  and at an angle  $\theta$  to the surface normal. We are considering a random distribution of molecular directions; that is, there is no bulk flow. This is always the case immediately above a surface, even if there is bulk flow farther away. With no bulk flow, half of the molecules have a positive value of the velocity component  $v_x(\theta)$  in the direction of the surface. For a given value of  $v_x$ , the corresponding molecular impingement flux ( $\text{mc/m}^2\cdot\text{s}$ ) would be given by

$$J_i = \frac{1}{2} n v_x \quad (2.5)$$

where  $n$  is the molecular concentration ( $\text{mc}/\text{m}^3$ ). Now we need to determine the average value of  $v_x$  as  $\theta$  ranges from  $0^\circ$  to  $90^\circ$ . For this purpose, imagine that the molecules originating at point  $A$  and having positive  $v_x(\theta)$  pass through the surface of a hemisphere of unit radius ( $r = 1$ ) having its origin at  $A$ . For random motion, the same molecular flux will pass through every differential area on the surface of this hemisphere. At an angle  $\theta$ , the  $x$  component of velocity is given by  $v_x(\theta) = v \cos \theta$ . Molecules traveling at that angle pass through the dashed circle shown in Fig. 2.5, which has circumference ( $2\pi \sin \theta$ ) and differential area ( $2\pi \sin \theta d\theta$ ). Integrating over the hemisphere and normalizing by dividing by the area of the hemisphere,  $A = 2\pi$ , we have for the average value of  $v_x$  over the hemisphere of impingement directions:

$$\bar{v}_x = \frac{\int v_x(\theta) dA}{\int dA} = \frac{1}{2\pi} \int_0^\pi (v \cos \theta) (2\pi \sin \theta) d\theta = v \cdot \frac{1}{2} \sin^2 \theta \Big|_0^{\pi/2} = \frac{1}{2} v \quad (2.6)$$

Substituting into Eq. (2.5) gives

$$J_i = \frac{1}{4} n v$$

We must now average over the Maxwell-Boltzmann distribution of speeds. First, we may substitute  $c$  for  $v$ , since the distribution of magnitudes of these two quantities within the hemisphere of positive  $x$  is

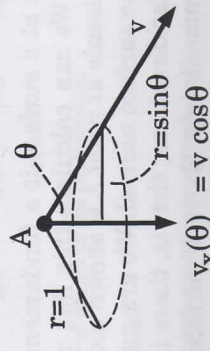


Figure 2.5 Geometry of molecular impingement.

the same. Next, since  $J_i$  is linearly proportional to  $c$ , we may average over  $c$  simply by substituting the mean speed,  $\bar{c}$ . Thus,

$$J_i = \frac{1}{4} n \bar{c} \quad (2.7)$$

where  $J_i$  ( $\text{mc}/\text{m}^2 \cdot \text{s}$ ) is the molecular impingement flux, and  $\bar{c}$  is the mean molecular speed from Eq. (2.3). We next need an expression for the molecular concentration,  $n$ , in terms of  $p$  and  $T$ , to be able to express  $J_i$  entirely in terms of macroscopic quantities; so we will proceed to derive one.

## 2.4 Ideal-Gas Law

The ideal-gas law is an "equation of state" which expresses the relationship between pressure, volume, and temperature ( $p$ ,  $V$ , and  $T$ ) in the high-volume vapor and gas regions of Fig. 2.1. We can approach its derivation by considering the meaning of pressure. Pressure is the force per unit area exerted on a surface by the momentum reversal that occurs when molecules impinge on it and bounce back off. For specular reflection, the momentum change per molecule would be  $2mv_x$ , using the geometry of Fig. 2.5. Even though molecules bounce off of surfaces in random directions rather than specularly, the momentum reversal has the same magnitude when averaged over the hemisphere, because the molecules are *approaching* in random directions as well. Newton tells us that the force exerted in a collision process is equal to the *rate* of momentum change, which is proportional to the impingement flux given by Eq. (2.5); that is,

$$F/A = J_i (2mv_x) = nmv_x^2 \quad (2.8)$$

where  $F/A$  = force/area. Now, since  $v^2 = v_x^2 + v_y^2 + v_z^2$ , and because the distribution of directions is random, the three orthogonal components on the right are all the same. Thus,

$$v_x^2 = \frac{1}{3} v^2 \quad (2.9)$$

and



To finally obtain the pressure, we need to average this expression for  $F/A$  over the Maxwell-Boltzmann distribution. Since  $F/A$  is proportional to  $v^2$  and thus to  $c^2$ , we average by substituting the mean square speed, which is the square of Eq. (2.4). Thus,

$$p = \frac{1}{3} n m \bar{c}^2 = n k_B T = n_m \frac{RT}{V} = \frac{N_m RT}{V} = \frac{RT}{V_m} \quad (2.10)$$

where  $p$  = pressure,  $N/m^2$  [ $N/m^2$  = Pa (pascals);  $N$  = newtons =  $kg \cdot m/s^2$ ]

$n$  = molecular concentration,  $mc/m^3 = N/V$

$n_m$  = molar concentration,  $mol/m^3$   
 $= n/N_A (= 2.4 \times 10^{14} p \text{ mc/cm}^3 \text{ at } 25^\circ \text{C})$

$N_m$  =  $N/N_A$  = number of moles of gas  
 $V$  = volume,  $m^3$

$V_m$  = molar volume =  $22,400 \text{ cm}^3/\text{mol}$  at  $0^\circ \text{C}$  and  $1 \text{ atm}$  ("standard" conditions)

The last equality is the familiar form of the ideal gas law.

The ideal gas law is obeyed when the volume of the *molecules* in the gas is much smaller than the volume of the gas and when the cohesive forces between the molecules can be neglected. Both of these assumptions are valid when the concentration  $n$  is low enough that the spacing between molecules is much larger than the molecular diameter. This is always the case in thin-film deposition from the vapor phase, where  $T$  is at or above room  $T$  and  $p$  is at or below  $1 \text{ atm}$ . These conditions place molar concentration,  $n_m$ , well away from the critical point on Fig. 2.2, since most materials have  $p_c \gg 1 \text{ atm}$ , and those that do not, have  $T_c \ll 25^\circ \text{C}$ .

We now consider the ideal gas law in connection with the energy content of the gas. Note that Eq. (2.10) contains the molecular translational energy,  $\epsilon_t = (1/2)mc^2$ . In fact, inspection shows that  $\epsilon_t$  is proportional to the pressure-volume product  $pV$ , which has the units of energy ( $N \cdot m$ ). By rearranging Eq. (2.10), we obtain

$$\epsilon_t = \frac{3}{2} k_B T \quad (2.11)$$

This important result is an expression of the equipartition theorem of classical statistical mechanics, and it will be very useful when we are

discussing chemical reactions. The classical (as opposed to the quantum mechanical) statistical treatment assumes that the quantized energy levels of molecules are close enough together so that they may be approximated as a continuum. This is a good assumption for *translational* energy when  $T$  is well above absolute zero  $K$ , although it is not a good one for rotational, vibrational and electronic energy in gases. According to the equipartition theorem, energy is distributed equally among all degrees of freedom, and each one contains  $(1/2)k_B T$  of energy. There are three degrees of freedom of translational energy, corresponding to the  $x$ ,  $y$ , and  $z$  directions; thus we obtain Eq. (2.11). For *atomic* gases,  $\epsilon_t$  also represents the total kinetic energy content. For *molecular* gases, there is additional kinetic energy in various rotational degrees of freedom at ordinary  $T$  and also in vibrational degrees of freedom at very high  $T$ . This energy must be included when estimating gas heat capacity,  $c_v$ , which is the rate of increase in total molecular kinetic energy with  $T$ . Thus,

$$\frac{c_v}{N_A} = \frac{d\epsilon_m}{dT} = \frac{d(\epsilon_t + \epsilon_r + \epsilon_v)}{dT} \quad (2.12)$$

where  $c_v$  = molar heat capacity at constant volume,  $J/\text{mol} \cdot K$

$\epsilon_m$  = total kinetic energy content per molecule

$\epsilon_r, \epsilon_v$  = rotational, vibrational energy content

Thus, it is found experimentally that  $c_v$  for *atomic* gases is equal to  $(3/2)R$  and is independent of  $T$ . Conversely,  $c_v$  for *molecular* gases is larger, the amount depending on the complexity of the molecule. For small diatomic molecules at room  $T$ , the two rotational degrees of freedom are excited, but the vibrational ones are not, so that  $c_v = (5/2)R$ . For all molecules,  $c_v$  increases with  $T$  as more of the rotational and vibrational quantum levels become accessible.

The heat capacity of any gas is larger when measured at constant pressure ( $c_p$ ) rather than at constant volume ( $c_v$ ), because then the heat input is doing  $pV$  work on the surroundings in addition to adding kinetic energy to the molecules. From the ideal gas law, it is seen that this work is  $RdT$  per mole, so that the added heat capacity is  $R$ ; thus,

$$c_p = c_v + R \quad (2.13)$$

where  $c_p$  is the molar heat capacity at constant pressure ( $J/\text{mol} \cdot K$ ). The distinction between these two heat capacities may also be expressed in thermodynamic terms; thus,

$$c_v = \left( \frac{\partial U_m}{\partial T} \right)_v \quad (2.14)$$

where  $U_m$  = internal energy per mole, =  $\epsilon_m N_A$  [see Eq. (2.12)] except at extreme  $T$  when electronic excitation is also involved. The notation in Eq. (2.14) indicates a partial derivative,  $\partial$ , at constant  $V$ . On the other hand, at constant  $p$  we have

$$c_p = \left( \frac{\partial H_m}{\partial T} \right)_p \quad (2.15)$$

where  $H_m$  = *enthalpy* per mole. The enthalpy function is defined as

$$H_m = U_m + pV_m \quad (2.16)$$

Therefore, by differentiation,

$$\left( \frac{\partial H_m}{\partial T} \right)_p = \left( \frac{\partial U_m}{\partial T} \right)_p + p \left( \frac{\partial V_m}{\partial T} \right)_p \quad (2.17)$$

For the ideal-gas case, the second term on the right is just  $R$ , and the first term on the right is  $c_v$ , since for that case  $U_m$  is a function only of  $T$ . Thus, Eq. (2.17) is equivalent to Eq. (2.13).

In dealing with heat *transfer* in gases,  $c_v$  is the quantity to use, even though the system under study may be operating at constant  $p$ . This is because heat is transferred only by way of the internal energy; that is,  $pV$  does not contribute to the thermal conductivity. However, the heat *content* of a gas being raised in  $T$  at constant  $p$  is measured by  $c_p$ . Note also that here we have been working with heat capacity per *mole*, whereas heat capacity per *gram* is the quantity usually reported in data tables. Finally, the term "specific heat" refers to  $c_p$  per gram relative to water. It is important to keep in mind the distinctions between these various expressions of heat capacity.

## 2.5 Units of Measurement

In all of the above, we have used SI (Système International) units, which are based on m, kg, and s. This is the easiest way to avoid errors in any calculation, since these units and those derived from them (such as J, N, Pa) are self-consistent; that is, all conversion factors are unity. To demonstrate this point, insert SI units for the terms on the right-hand side of Eq. (2.10) and show that they cancel to yield pressure in Pa.

Unfortunately, other units are frequently encountered in thin-film technology either for historical reasons or for convenience of size. Pressure is frequently measured either in torr, where 1 torr = 133 Pa = 1 mm of rise on a mercury manometer (mm Hg); in millitorr or microns ( $\mu\text{m Hg}$ ); or in bar, where 1 bar = 750 Torr =  $1.0 \times 10^5$  Pa = 0.99 standard atmosphere (atm). (The difference between 1 bar and 1 atm is negligible for practical calculations in thin-film work.) Also,  $\text{cm}^3$  and  $\text{cm}^3$  are often used because they are more convenient in size than m and  $\text{m}^3$ .

The "standard" conditions of  $T$  and  $p$  ("stp") are  $0^\circ\text{C}$  and 1 atm (760 torr). From the ideal gas law, Eq. (2.10), it may be found that at stp the molecular density,  $n$ , is  $2.69 \times 10^{19}$   $\text{mc}/\text{cm}^3$ , and the molar volume,  $V_m$ , is 22,400  $\text{cm}^3$ . Note that these conditions are different from the standard conditions to which thermodynamic data are referenced: those are  $25^\circ\text{C}$  and 1 bar.

The term usually encountered in gas supply monitoring is the "mass" flow rate measured in standard  $\text{cm}^3$  per minute or per second or liters per minute ("sccm," "secs," or "slm"), "standard" meaning at 1 atm and  $0^\circ\text{C}$ . Mass flow rate thus has the units of (pressure  $\times$  volume/time), which can be seen from Eq. (2.10) to be actually proportional to *molecular* or *molar* flow rate,  $dN/dt$ , rather than to "mass" flow rate, the conversion being 1 sccm =  $4.48 \times 10^{17}$   $\text{mc}/\text{s}$ . In vacuum pumping, mass flow rate (pump "throughput") is often measured in  $\text{torr}\cdot\text{l}/\text{s}$  or  $\text{Pa}\cdot\text{l}/\text{s}$  ( $l$  = liters).

## 2.6 Knudsen Equation

So far we have developed expressions for molecular energy, speed, concentration and flow rate in terms of macroscopic quantities. We can do the same for the molecular impingement flux given by Eq. (2.7), now that we have expressions for both the mean speed,  $\bar{c}$ , in Eq. (2.3) and the molecular concentration,  $n$ , in Eq. (2.10). Thus, in SI units, we have:

$$J_i \left( \frac{\text{mc}}{\text{m}^2 \cdot \text{s}} \right) = \frac{N_A p}{\sqrt{2\pi M R T}} \quad (2.18)$$

However, it is more common to use  $\text{cm}^2$  rather than  $\text{m}^2$  for flux, and g rather than kg for molecular weight, in which case we obtain

$$J_i \left( \frac{\text{mc}}{\text{cm}^2 \cdot \text{s}} \right) = 2.63 \times 10^{20} \frac{p}{\sqrt{M T}} \quad (2.19)$$

where the units of  $p$ ,  $M$ , and  $T$  are Pa, g, and K. For  $p$  in torr, the proportionality factor changes to  $3.51 \times 10^{22}$ .

Equation (2.19), the Knudsen equation, is one of the most important relationships in thin-film technology. It is valid in both the vacuum and fluid regimes of operating  $p$ , and it can also be used to calculate effusion flux through an orifice if  $p$  is low enough, as will be discussed in Sec. 3.3. To get a feeling for impingement flux magnitudes, consider that for an  $M$  of 40, 25°C C and  $10^{-3}$  Pa,  $J_i = 2.4 \times 10^{15}$   $\text{mc/cm}^2\text{-s}$ . If all of this impinging gas is adsorbing and sticking on the surface in a thin-film deposition process, how rapidly does it accumulate? For a typical molecular diameter of 0.3 nm, there are about  $10^{15}$  molecules per monomolecular layer ("monolayer" or ML), so the accumulation rate is 2.4 ML/s or 2.6  $\mu\text{m/h}$ , which is a typical thin-film deposition rate (although rates can be much faster). This means that only  $10^{-8}$  atm of reactant gas  $p$  is needed to achieve this deposition rate if all the gas impinging on the surface deposits. It also means that if this gas is a background impurity in the deposition chamber rather than a constituent of the desired film, the film is likely to incorporate a high level of contamination. To deposit a 99.9 percent pure film at 2.6  $\mu\text{m/h}$ , the  $p$  of reactive impurity gases must be kept below  $10^{-6}$  Pa, which is considered to be in the range of "ultra-high" vacuum (UHV). On the other hand, the  $p$  of inert background gases or of carrier gases used in CVD, such as  $\text{H}_2$ , can be much higher without compromising film purity. Indeed, CVD processes are often run at 1 atm. The impurity impingement flux is determined by the *partial*  $p$  of the impurity gas(es), not the total  $p$ . The key quantity to keep in mind is the *ratio* of film molecular deposition flux to reactive impurity impingement flux, or what one might think of as the "goodies-to-crud" ratio or the purity ratio. To improve film purity, this ratio needs to be increased, either by increasing deposition rate or by decreasing impurity partial  $p$  values.

In any thin-film process, the linear deposition rate,  $dh/dt$ , is easily determined from film thickness,  $h$ , and deposition time. The molecular deposition flux may be found from this rate if the film density is known. In SI units,

$$J_r = \frac{dh}{dt} \left( \frac{\rho_m N_A}{M} \right) \quad (2.20)$$

where  $J_r$  = molecular deposition flux,  $\text{mc/m}^2\text{-s}$

$\rho_m$  = film density,  $\text{kg/m}^3$

or in more conventional units,

$$J_r \left( \frac{\text{mc}}{\text{cm}^2\text{-s}} \right) = 1.67 \times 10^{16} \frac{dh}{dt} (\mu\text{m/h}) \rho_m (\text{g/cm}^3)}{M (\text{g/mol})} \quad (2.21)$$

It is worth remembering that, for most solids, the molecular concentration,  $(\rho_m N_A/M)$ , is of the order of  $5 \times 10^{22}$   $\text{mc/cm}^3$ .

Another quantity encountered in the study of gas adsorption is the langmuir, L, which refers to the amount of exposure to a gas that a surface has seen, in  $\text{mc/cm}^2$ . Exposure is proportional to  $pt$ , and  $1 \text{ L} = 10^{-6}$  torr-s. If all the impinging gas adsorbs, 1 L represents a surface accumulation of about 1/3 monolayer. Note that the term "adsorption," which refers to gas accumulation on a surface, differs from the term "absorption," which refers to the takeup of a gas into the bulk of a liquid or solid.

## 2.7 Mean Free Path

The mean free path,  $l$ , is the mean distance that a particle travels in a gas before encountering a collision with a gas molecule. We need to estimate  $l$  for gas molecules and also for electrons and ions, since all of these particles are involved in various deposition processes. We begin with the simplest case—the electron. Consider an electron passing through an array of gas molecules of effective collision diameter  $a$  as shown in Fig. 2.6a, directly into the plane of the drawing. Since electrons are much smaller than molecules, the collision cross section,  $\sigma_m$ , is just the projected area of the gas molecule,  $(\pi/4)a^2$ . For a gas concentration of  $n$   $\text{mc/cm}^3$ , the total projected area of gas molecules per  $\text{cm}^2$  of gas cross section and per cm length of electron travel is  $n\sigma_m$ . This is the fractional area that is "filled" by collisions per cm of travel, and its inverse is the distance that the electron needs to travel before the projected area of collision cross section just fills one  $\text{cm}^2$ . This distance is the electron's mean free path,  $l_e$ . Thus,



Figure 2.6 Geometry for mean-free-path calculation showing a particle traveling into the plane of the drawing and encountering gas molecules of diameter  $a$ ; the particle is an electron in part (a) and an ion in (b).



$$l_e = \frac{1}{\sigma_m n} = \frac{1}{(\pi/4) a^2 n} \quad (2.22)$$

(This equation is an approximation, since  $\sigma_m$  is actually a function of electron kinetic energy, as we will see in Sec. 9.1.) In considering instead the passage of a molecular ion, which has a radius about the same as that of a molecule, the collision diameter becomes doubled to the dashed circle shown in Fig. 2.6b, because the ion and molecule need only touch at their peripheries to collide. Thus,

$$l_i = \frac{1}{\pi a^2 n} \quad (2.23)$$

In the above two cases, we have been able to assume that the molecules are standing still while the electrons or ions are moving through them, because the charged particles encountered in thin-film work travel much faster than molecules. However, in the case of molecule-molecule collisions, the molecules are sometimes heading straight at each other and sometimes sideswiping each other, so that on average they approach each other at  $90^\circ$ . Thus, the mean speed of mutual approach is  $\sqrt{2} \bar{c}$  rather than  $\bar{c}$ , which shortens  $l$  by  $1/\sqrt{2}$ ; thus,

$$l = \frac{1}{\sqrt{2} \pi a^2 n} \quad (2.24)$$

Let us estimate the mean free path of a typical 0.3 nm diameter molecule at 1 Pa and  $25^\circ\text{C}$ . We first need to find  $n$  from the ideal gas law, Eq. (2.10). Working in SI units, we have

$$n = \frac{p N_A}{RT} = \frac{1 \times 6.02 \times 10^{23}}{8.31 \times 298} = 2.43 \times 10^{20} \text{ mc/m}^3$$

Inserting this into Eq. (2.24) gives

$$l = \frac{1}{\sqrt{2} \pi (0.3 \times 10^{-9})^2 (2.43 \times 10^{20})} = 1.03 \times 10^{-2} \text{ m} = 1.03 \text{ cm}$$

Unless  $T$  is extremely high,  $p$  is the main determinant of  $l$ , and the above example shows that  $l \propto 1/p$ . It is worth remembering that the mean free path at 1 Pa and room  $T$  is about 1 cm for small molecules. The order of magnitude of  $l$  is very important in film deposition,

because it determines whether the process is operating in the high-vacuum regime or the fluid-flow regime. The regime is determined by the value of the Knudsen number,

$$\text{Kn} = l/L \quad (2.25)$$

where  $L$  is a characteristic dimension in the process, such as the distance between the source and the substrate. For  $\text{Kn} > 1$ , the process is in high vacuum. This is also known as the molecular flow regime, since the molecules flow independently of each other and collide only with the walls. Conversely, for  $\text{Kn} < 0.01$ , the process is in fluid flow. Intermediate values of  $\text{Kn}$  constitute a transition regime where the equations applicable to either of the limiting regimes are not strictly valid. Plasma processes often operate in the transition regime. High-vacuum processes require  $p < 10^{-2}$  Pa for typical chamber sizes to ensure  $\text{Kn} > 1$ .

$\text{Kn}$  is the first and most elementary of several dimensionless numbers that we will encounter in this book. Dimensionless numbers are very useful for characterizing a process, because a particular magnitude of such a number has the same meaning irrespective of the scale or operating conditions of the process. Thus, a  $\text{Kn}$  of 1 represents the high-vacuum edge of the transition regime whether one has a 1 meter chamber at  $10^{-2}$  Pa or a 1 cm chamber at 1 Pa.

2.8 Transport Properties

The remaining macroscopic properties that we wish to relate to molecular interaction are the transport properties, which quantify the rate of transport of mass (diffusion), momentum (viscous shear), and energy (heat conduction) through a fluid, where here again we mean a gaseous fluid. The transport to be discussed here occurs by random molecular motion through a gas which has no bulk flow in the direction of the transport. Mass and heat can be transported by bulk flow as well, but these topics will be deferred to Chap. 7. Table 2.1 summarizes the quantities and equations describing the transport properties, and they will be dealt with in turn below. Also shown in the table are the quantities relating to the flow of electricity, because that is sometimes a helpful analogy.

Transport is always described by an equation of the form

$$(\text{flux of } A) = - (\text{proportionality factor}) \times (\text{gradient in } A) \quad (2.26)$$

The general form of such equations is three-dimensional, but in this book we will always be using the simpler one-dimensional form, where the flux is in the  $x$  direction and the gradient is  $dA/dx$ . To make an example of the electrical analog, current density,  $j(A/cm^2)$ , is driven by a gradient in electrical potential,  $dV/dx$  (V/cm), and the proportionality factor is the electrical conductivity,  $s$ , or inverse resistivity,  $1/\rho$  ( $1/\Omega\cdot\text{cm}$  or  $A/V\cdot\text{cm}$ ), as shown in Table 2.1. This is just the familiar Ohm's law.

2.8.1 Diffusion

The behavior of molecular diffusion will be described using Fig. 2.7a. Here, the concentration of the black A molecules in a mixture with the B molecules is decreasing from  $n_A$  to  $(n_A - \Delta n_A)$  in the  $x$  direction over a distance of one mean free path,  $l$ . Diffusion of A occurs in the direction of decreasing  $n_A$ . A rough estimate of the diffusion flux can be made by calculating the net flux through an imaginary slab of thickness  $l$ , using Eq. (2.7) for the fluxes in opposite directions. Thus,

$$J_A(\text{net}) = J(\text{down at } x) - J(\text{up at } x + l) = \frac{1}{4}\Delta n_A \bar{c}$$

Since  $\Delta n_A = l(-dn_A/dx)$ , we have

$$J_A = -\left(\frac{1}{4}\bar{c}l\right)\frac{dn_A}{dx} = -D_{AB}\frac{dn_A}{dx} \tag{2.27}$$

which shows that the diffusivity or diffusion coefficient of A through B,  $D_{AB}$ , is proportional to  $\bar{c}$  and  $l$ . We will see that this is also the case for momentum and energy transport.

Inserting expressions for  $\bar{c}$  and  $l$  from Eqs. (2.3) and (2.24), we find that  $D_{AB}$  should be proportional to  $T^{3/2}/\sqrt{M_A^2}$ . Empirically, the  $T$  dependence is found to be  $T^{7/4}$ , which is given in Table 2.1 along with

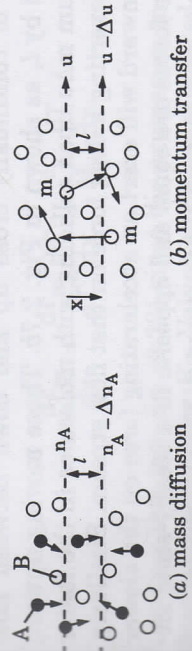


Figure 2.7 Illustration of transport properties on a molecular scale. Flux is downward in the  $x$  direction.

Transported quantity	Describing equation	Derivation from elementary kinetic theory	Typical value at 300 K, 1 atm
Mass	Diffusing flux = $J_A \left(\frac{dn_A}{dx}\right) = -D_{AB} \left(\frac{dn_A}{dx}\right)$ (Fick's law)	Diffusivity = $D_{AB} \left(\frac{cm^2}{s}\right) = \frac{1}{3} \bar{c} l \propto \frac{1}{3} \sqrt{\frac{8kT}{\pi M}} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{-1/2} \frac{p(a_A + a_B)}{2}$	Ar-He: $0.19 \text{ cm}^2/\text{s}$ Ar-He: 0.72
Momentum	Shear stress = $\tau \left(N/m^2\right) = \eta \frac{du}{dx}$	Viscosity = $\eta \left(\text{Poise}\right) = \frac{1}{3} n m \bar{c} l \propto \sqrt{\frac{M}{T}}$	Ar: $2.26 \times 10^{-4} \text{ Poise}$ He: $2.02 \times 10^{-4}$
Energy (heat)	Conductive heat flux = $\Phi \left(\frac{W}{cm^2}\right) = -K_T \frac{dT}{dx}$ (Fourier's law)	Thermal conductivity = $K_T \left(\frac{W}{cm \cdot K}\right) = \frac{1}{2} n \left(\frac{N_A}{c_v}\right) \bar{c} l \propto \sqrt{\frac{T}{M}}$	Ar: $0.176 \text{ W/cm} \cdot K$ He: 1.52
Charge	Current density = $j \left(\frac{A}{cm^2}\right) = -s \frac{dV}{dx} = -s \frac{d\psi}{dx}$ (Ohm's law)		

\*cm-g-s (cgs) units appear here instead of SI units when they are commonly used for these quantities.  
†1 Poise = 1 g/cm·s = 0.1 kg/m·s or N·s/m<sup>2</sup> or Pa·s.

the  $M$  and  $\alpha$  averaging factors that account for the A-B mixture. The numerical constant is not given, because the quantitative values of  $D_{AB}$  need to be determined empirically. An empirical correlation for many binary mixtures is available [1]. For rough calculations satisfactory for thin-film deposition work, the 1 atm values given for Ar-Ar and Ar-He in Table 2.1 can be extrapolated to other  $T$ ,  $p$ , and  $M$  with factor-of-two or so accuracy.  $T$  and  $p$  are the main determinants of  $D_{AB}$ .  $p$  is particularly important, since it can be lower than 1 atm by many orders of magnitude in deposition processes, with a correspondingly large increase in  $D_{AB}$ . When  $p$  is reduced so far that  $Kn > 1$ , diffusion no longer occurs. Instead, molecules travel from wall to wall in molecular flow, without encountering each other in the gas phase.

Note that  $D_{AB}$  is not dependent upon the ratio of  $n_A$  to  $n_B$ , which may seem strange at first. However, consider a very dilute mixture of A in B. Total  $p$  is constant along the  $n_A$  gradient, meaning that  $(n_A + n_B)$  does not vary with  $x$ . Therefore,  $dn_B/dx$  must be equal in magnitude and opposite in sign to  $dn_A/dx$ . In addition, for  $(n_A + n_B)$  not to increase with time at one end or the other, the diffusion flux of B through A must be equal and opposite to that of A through B; that is,  $J_A = -J_B$ . Thus, in accordance with the transport equation [Eq. (2.27)],  $D_{BA} = D_{AB}$  even though  $n_B \gg n_A$ . On the other hand, the coefficient of self-diffusion of B through B ( $D_{BB}$ ) is different from  $D_{BA}$  and  $D_{AB}$ . This is because  $D_{BB}$  involves the scattering of molecules of B by other molecules of B with no regard for what the dilute A constituent is doing.

### 2.8.2 Viscosity

Gas viscosity is the result of molecular momentum transport along a gradient in bulk flow velocity  $u$ . In Fig. 2.7b, gas is flowing to the right with velocity  $u$  at level  $x$  and  $(u - \Delta u)$  at level  $(x + l)$ . The  $u$  gradient is along the  $x$  axis and perpendicular to the bulk flow. This situation is encountered in fluid flow whenever the flow stream approaches a boundary, since  $u$  must go to zero at the boundary. Superimposed upon the bulk flow is the random molecular motion at velocity  $\bar{c}$ , which causes molecules to continually cross up and down between flow streams separated by  $l$ , as shown in Fig. 2.7b. Those moving upward will gain momentum  $m\Delta u$  upon colliding with molecules in the faster flow stream, thus exerting a drag force on that flow stream. Similarly, those moving downward will exert an accelerating force on the slower flow stream. These forces are equal and opposite in a steady-state situation. They appear as a viscous shear stress,  $\tau(N/m^2)$ , between the two flow streams, and  $\tau$  is equal to the rate of momentum transfer per unit area perpendicular to  $x$ . This rate is equal to the molecular flux times the momentum gain/loss per molecule; thus,

$$\tau = J(m\Delta u) = \frac{1}{4}n\bar{c}ml \frac{du}{dx} = \eta \frac{du}{dx} \quad (2.28)$$

where  $\eta$  = viscosity (kg/m·s = N·s/m<sup>2</sup> = Pa·s in SI units; g/cm·s = Poise in cgs units).

Substituting for  $n$  from the ideal gas law and for  $\bar{c}$  and  $l$  as we did for diffusion, we find that  $\eta \propto \sqrt{MT}/a^2$ . There are two surprises here. First,  $\eta$  increases with  $T$ , which is the opposite of liquid behavior. Second,  $\eta$  is independent of  $p$ . The latter is because, although the molecules are traveling longer distances along the  $u$  gradient at lower  $p$ , there are fewer of them doing so, so these trends cancel out. As in the case of diffusion, viscosity has no meaning for  $Kn > 1$ , where molecules no longer collide with each other. In that regime, flow is still limited by the proximity of boundaries, but not due to viscous drag. Flow is limited instead by the fact that molecules bounce off of surfaces randomly rather than in specular reflection, so that they are just as likely to be scattered back in the direction from which they came as to be scattered forward. This behavior accounts for pumping in the "molecular drag" vacuum pump, which operates across the transition flow regime (see Sec. 3.1).

### 2.8.3 Heat conduction

Gaseous heat conduction occurs by transfer of energy in molecular collisions downward along a gradient in molecular kinetic energy  $\epsilon_m$ . Its equation is analogous to that for momentum transfer, with  $m\Delta u$  replaced by  $2\Delta\epsilon_m$ . The reason for the 2 is that the average energy of molecules crossing a plane is twice the average over all directions [2], because the faster ones cross the plane more often. Thus,

$$\Phi = \frac{1}{4}n\bar{c} \left( l \frac{d\epsilon_m}{dx} \right) \cdot 2 \quad (2.29)$$

where  $\Phi$  = heat flux, J/(s·cm<sup>2</sup>) (= W/cm<sup>2</sup>). We can substitute  $T$  for  $\epsilon_m$  using Eq. (2.12) for the heat capacity; thus,

$$\frac{d\epsilon_m}{dx} = \frac{d\epsilon_m}{dT} \frac{dT}{dx} = \frac{c_v}{N_A} \frac{dT}{dx} \quad (2.30)$$

Inserting this into Eq. (2.29) gives the expression in Table 2.1 for the thermal conductivity,  $K_T$ . Values of  $K_T$  are tabulated in various handbooks [3]. As in the case of  $D$  and  $\eta$ , the derivation of  $K_T$  here has been simplified to focus on the physical process rather than on obtaining the exact quantitative value. Consequently, the fractions appearing in

the equations for these quantities, such as the 1/4 in Eq. (2.29), are not to be considered exact, although the dependencies on  $n$  and the other molecular quantities are quite close to what is observed experimentally.

Note that in terms of the macroscopic quantities, we have  $K_T \propto c_v \sqrt{M} \alpha^2$ . Thus, small, light molecules generally have higher  $K_T$ , although this trend is sometimes reversed by the higher  $c_v$  of more complex molecules, which have more rotational and vibrational modes of energy storage. Note also that  $K_T$ , like  $\eta$ , is independent of  $p$ , and for the same reasons: as  $p$  decreases, the molecular flux is lower, but the molecules travel farther between collisions. However, as  $p$  decreases into the molecular flow regime, the situation changes, as we shall see below.

Consider heat transfer by gas conduction between two parallel plates as shown in Fig. 2.8. This is a common situation in film deposition, where one plate is a heated platform at temperature  $T_h$ , and the other is a substrate for film deposition that is being raised to  $T_s$  by heat transfer from the platform. For a gap of  $b$  between the plates, the appropriate Knudsen number is  $l/b$ . At higher  $p$  where  $Kn \ll 1$  (Fig. 2.8a), the heat flux is given by

$$\Phi = -K_T \frac{dT}{dx} = \frac{K_T}{b} (T_h - T_s) \quad (2.31)$$

Now consider instead the case where  $Kn > 1$  (Fig. 2.8b). Here, gas molecules are bouncing back and forth from plate to plate without encountering any collisions along the way, so the use of  $K_T$ , which is a bulk fluid property, is no longer appropriate. Instead, the heat flux between plates is proportional to the flux of molecules across the gap times the amount of heat carried per molecule, or

$$\begin{aligned} \Phi &= \left[ J_1 \gamma' \frac{c_v}{N_A} \right] (T_h - T_s) \\ &= \left[ 4.37 \times 10^{-4} \frac{p}{\sqrt{MT}} \gamma' c_v \right] (T_h - T_s) = h_c (T_h - T_s) \end{aligned} \quad (2.32)$$

where  $J_1$  = molecular impingement flux,  $mc/cm^2 \cdot s$ , from Eq. (2.19)  
 $\gamma'$  = thermal accommodation factor ( $\approx$  unity except for He)

$h_c$  = heat transfer coefficient,  $W/cm^2 \cdot K$

Here we have introduced two new quantities,  $\gamma'$  and  $h_c$ .  $\gamma'$  will be discussed below. The heat transfer coefficient,  $h_c$ , is given by the

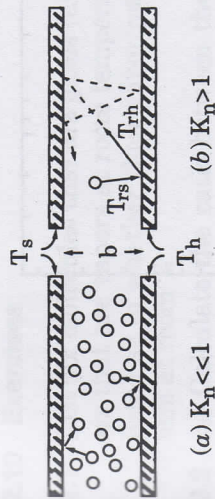


Figure 2.8 Gas-conductive heat transfer between parallel plates at (a) low and (b) high Knudsen numbers,  $Kn$ .

quantity in square brackets in Eq. (2.32). Note that  $h_c$  contains *no dependence on the distance* over which heat is being transferred. Note also that  $h_c$  appears, rather than  $K_T$ , whenever heat transfer is taking place across an interface rather than through a bulk fluid or other material. This applies to the situation of Fig. 2.8b, because there are no gas-gas collisions.

We can see that there are two fundamental differences between the Eq. (2.31) and Eq. (2.32) expressions for  $\Phi$ . In the first ( $Kn \ll 1$ ),  $\Phi$  is independent of  $p$ , because  $K_T$  is independent of  $p$ ; also,  $\Phi$  is inversely proportional to  $b$ . In the second ( $Kn > 1$ ),  $\Phi$  is proportional to  $p$  and independent of  $b$ . These relationships and the transition region between them are illustrated in Fig. 2.9 for the case of Ar at 25°C. Here, the effective  $h_c$  in the  $Kn \ll 1$  regime is  $K_T/b$ . One important conclusion which can be drawn from Fig. 2.9 is that heat transfer to a substrate from a platform can be increased by increasing the gas  $p$  between them, but only if the gap is kept small enough that  $Kn > 1$ .

Helium is often chosen to improve heat transfer to substrates because of its high  $K_T$ , but in fact it is not the best choice when  $Kn > 1$ , because of the thermal accommodation factor in Eq. (2.32). Referring again to Fig. 2.8, consider the molecule approaching the heated platform. It has the temperature  $T_{rs}$ , which it acquired by being reflected from the substrate. Upon being reflected from the platform, it will have temperature  $T_{rh}$ , and the thermal accommodation coefficient is defined as

$$\gamma = \frac{T_{rs} - T_{rh}}{T_{rs} - T_h} \quad (2.33)$$

Gamma ( $\gamma$ ) represents the degree to which the molecule accommodates itself to the temperature  $T_h$  of the surface from which it is reflected. For most molecule-surface combinations,  $\gamma$  is close to unity, but for He it is 0.1 to 0.4, depending on the surface [4]. If  $\gamma$  is less than unity and

the equations for these quantities, such as the 1/4 in Eq. (2.29), are not to be considered exact, although the dependencies on  $n$  and the other molecular quantities are quite close to what is observed experimentally.

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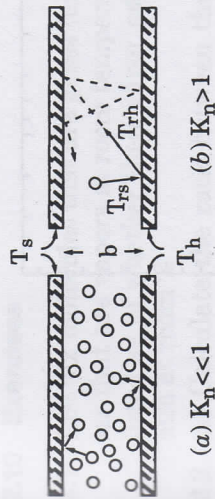


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quantity in square brackets in Eq. (2.32). Note that  $h_c$  contains *no dependence on the distance* over which heat is being transferred. Note also that  $h_c$  appears, rather than  $K_T$ , whenever heat transfer is taking place across an interface rather than through a bulk fluid or other material. This applies to the situation of Fig. 2.8b, because there are no gas-gas collisions.

We can see that there are two fundamental differences between the Eq. (2.31) and Eq. (2.32) expressions for  $\Phi$ . In the first ( $Kn \ll 1$ ),  $\Phi$  is independent of  $p$ , because  $K_T$  is independent of  $p$ ; also,  $\Phi$  is inversely proportional to  $b$ . In the second ( $Kn > 1$ ),  $\Phi$  is proportional to  $p$  and independent of  $b$ . These relationships and the transition region between them are illustrated in Fig. 2.9 for the case of Ar at 25°C. Here, the effective  $h_c$  in the  $Kn \ll 1$  regime is  $K_T/b$ . One important conclusion which can be drawn from Fig. 2.9 is that heat transfer to a substrate from a platform can be increased by increasing the gas  $p$  between them, but only if the gap is kept small enough that  $Kn > 1$ .

Helium is often chosen to improve heat transfer to substrates because of its high  $K_T$ , but in fact it is not the best choice when  $Kn > 1$ , because of the thermal accommodation factor in Eq. (2.32). Referring again to Fig. 2.8, consider the molecule approaching the heated platform. It has the temperature  $T_{rs}$ , which it acquired by being reflected from the substrate. Upon being reflected from the platform, it will have temperature  $T_{rh}$ , and the thermal accommodation coefficient is defined as

$$\gamma = \frac{T_{rs} - T_{rh}}{T_{rs} - T_h} \quad (2.33)$$

Gamma ( $\gamma$ ) represents the degree to which the molecule accommodates itself to the temperature  $T_h$  of the surface from which it is reflected. For most molecule-surface combinations,  $\gamma$  is close to unity, but for He it is 0.1 to 0.4, depending on the surface [4]. If  $\gamma$  is less than unity and

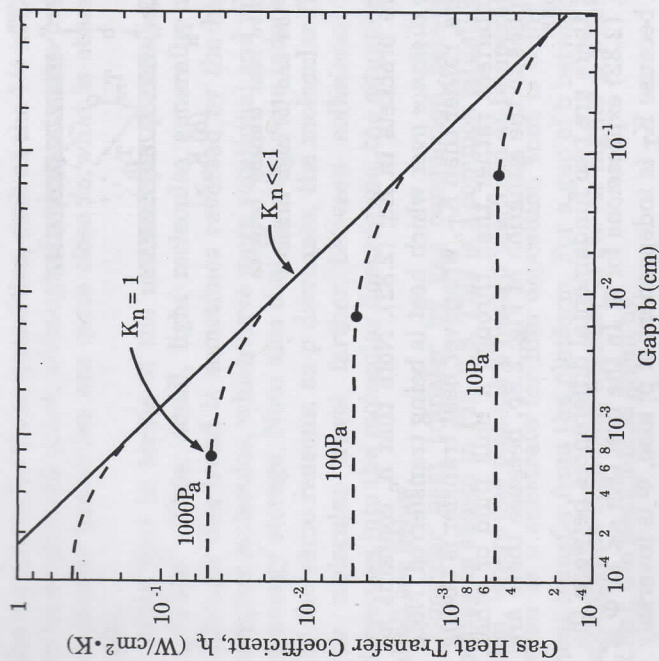


Figure 2.9 Gas-film heat-transfer coefficient,  $h_c$ , vs. plate gap,  $b$ , for various pressures of Ar. For  $Kn \ll 1$ ,  $h_c = K_T/b$ , where  $K_T$  = bulk thermal conductivity of the gas.

is the same at both surfaces, it can be shown (Exercise 2.10) that the overall reduction in heat flux represented by  $\gamma'$  in Eq. (2.32) is given by

$$\gamma' = \frac{\gamma}{2 - \gamma} \quad (2.34)$$

Thus, if  $\gamma = 0.2$ , then  $\gamma' = 0.11$ . From Eq. (2.32), it can be seen that the best choice for a heat-transfer gas is one having low molecular mass to give high  $J_i$ , while also having many rotational modes to give high  $c_v$  per Eq. (2.12). Choices will usually be limited by process chemistry, of course.

## 2.9 Conclusion

We now have all the basic gas-kinetics concepts that we need to examine the interaction of gases and vapors with surfaces in the deposition process. It is useful to keep in mind this motion of individual molecules even though one is controlling the film-deposition process using macroscopic quantities such as  $T$  and  $p$ .

## 2.10 Exercises

- 2.1 List six molecules that are gases (excluding the noble gases) and six that are vapors at room temperature. Distinguish the vapors listed as to whether their vapor pressures are above or below 1 atm at room  $T$ .
- 2.2 (a) Calculate the ratio between the mean molecular speed and the rms speed in the Maxwell-Boltzmann distribution. (b) Calculate the ratio between the mean speed and the most probable speed (the peak of the distribution).
- 2.3 Show that  $1 \text{ sccm} = 4.48 \times 10^{17} \text{ mc/s}$ .
- 2.4 Show that the proportionality factor is indeed  $2.63 \times 10^{20}$  in Eq. (2.19).
- 2.5 An Al film is being deposited at  $5 \mu\text{m/h}$  in a background of  $1 \times 10^{-7}$  torr of  $\text{O}_2$ . What will be the maximum atomic percent oxygen in the deposit?
- 2.6 For a gas of 0.3 nm diameter molecules at 1 bar pressure and  $25^\circ\text{C}$ : (a) What fraction of the total volume is occupied by the molecules? (b) What is the ratio of the mean free path to the molecular diameter?
- 2.7 Show how  $R$  enters into  $c_p = c_v + R$  by differentiating the ideal gas law.
- 2.8 Show that the molecular concentration is  $2.69 \times 10^{19} \text{ mc/cm}^3$  at stp.
- 2.9 Single-crystal Si is being deposited at  $1.0 \mu\text{m/h}$  onto one face of a 4 inch diameter heated substrate in a CVD process by pyrolysis (thermal decomposition) of the reactant dichlorosilane ( $\text{SiH}_2\text{Cl}_2$ ) flowing at 10 sccm. What fraction of the reactant is being utilized in the deposition?
- 2.10 Show that  $\gamma' = \gamma/(2 - \gamma)$  for the geometry of Fig. 2.8, assuming that  $\gamma$  is the same at both surfaces. To simplify the algebra, normalize the temperatures to  $T_h = 1$  and  $T_s = 0$ .

## 2.11 References

1. Perry, R.H., et al. (eds.). 1984. *Chemical Engineers' Handbook*, 6th ed. New York: McGraw-Hill, 3-285.
2. Fowler, R., and E.A. Guggenheim. 1952. *Statistical Thermodynamics*. London: Cambridge University Press, 124.
3. For  $K_T$ ,  $c_v$ , and  $\eta$ , see, for example, *CRC Handbook of Chemistry and Physics*. Boca Raton, Fla.: CRC Press. For more comprehensive listings, see Touloukian, Y.S., et al. (eds.) 1970. *Thermophysical Properties of Matter*. New York: Plenum Press.
4. Ho, C.Y., S.C. Saxena, and R.K. Joshi (eds.). 1989. *Thermal Accommodation and Adsorption Coefficients of Gases*, part A. New York: Hemisphere Publishing.

## 2.12 Recommended Readings

- Glang, R. 1970. Chap. 1, "Vacuum Evaporation." In *Handbook of Thin Film Technology*, L. I. Maissel and R. Glang (eds.). New York: McGraw-Hill.
- Sears, F.W. 1950. *An Introduction to Thermodynamics, the Kinetic Theory of Gases, and Statistical Mechanics*, Chap. 12-13. Cambridge, Mass.: Addison-Wesley.

# Vacuum Technology

Most of the film deposition processes to be discussed in this book operate under some degree of vacuum. Only atmospheric-pressure CVD does not, but the same vacuum techniques of contamination reduction and process control still apply to it. Vacuum technology is a large topic which is well treated in textbooks such as those in the recommended readings list at the end of this chapter. Our purposes here are more specific: first, to become oriented to the general topic and, second, to examine certain aspects of vacuum technology that are particularly relevant to film deposition and deserve special emphasis. As we know, "Nature abhors a vacuum," so good equipment and techniques are needed to create one.

Figure 3.1 is a schematic diagram of a typical vacuum system for thin-film deposition. The purpose and functioning of the components shown will be elaborated upon in the subheadings below. Sometimes not all of these components will be required for a particular process. As shown, the substrate is introduced through a "load-lock" chamber to allow the main process chamber to remain under vacuum, because this reduces contamination and shortens substrate turnaround time. The roughing pump evacuates the load-lock chamber from atmospheric pressure after the substrate has been loaded into it and before the valve is opened into the process chamber. Once the substrate is in the process chamber, it is heated and controlled at the film deposition temperature. Process gases and vapors are metered into the chamber through mass flow-controlled supply lines, which are discussed more in Sec. 7.1.2. Process pressure is measured by a vacuum gauge that can be coupled to a motor-driven throttle valve in the pump throat for pressure control. Sometimes, pressure is controlled instead by cou-