

## UNIT IIID

### THE PROPERTIES OF GASES COMPOSED OF LOW-MASS PARTICLES

#### Free Electrons and Electromagnetic and Acoustical Radiation

Determination of properties for gases composed of particles lighter than a proton require techniques that are different from those studied in Unit IIIC. This unit develops the methods required for the study of electromagnetic and acoustical waves, and free electrons. Since electromagnetic radiation is always present in a physical space it is a necessary part of any system. But its contribution to the properties of matter occupying the space is shown to be negligible. Properties of solids are developed by considering acoustic waves and free electrons.

#### Objectives.

At the conclusion of this unit the student should be able to:

1. Determine the energy, entropy, and particle density of a photon gas at a specified temperature.
2. Evaluate the phonon contribution to internal energy, specific heat, and entropy of an atomic lattice of specified Debye temperature.
3. Determine the Fermi temperature of a metallic solid.
4. Evaluate the free electron contribution to the internal energy or specific heat of a metallic solid.
5. Combine the phonon and free electron contributions to determine the total properties of an atomic lattice solid.
6. Describe the differences between the properties of an atomic and molecular lattice point crystal.

#### Supplementary References

1. Sonntag, R. E., and Van Wylen, G. J., Introduction to Thermodynamics: Classical and Statistical, Wiley (1971). Sect. 19.10 and Chapter 20, with Exers. 19.36 to 19.41, 20.1 to 20.7, 20.11, 20.13 to 20.18. Similar to this unit. A good supplement.
2. Holman, J. P., Thermodynamics, Second Ed., McGraw-Hill (1974). Sects. 8-7, 8-8 and 8-10 with Exmps. 8-3 to 8-7 and Exers. 8-2, 8-4, 8-7, 8-14, 8-18 to 8-23. Very brief treatment, though comprehensive and similar to this unit.
3. Wark, K., Thermodynamics, Second Ed., McGraw-Hill (1971). Sects. 10-17 to 10-19 with Exers. 10-38 to 10-45. Very brief.
4. Incropera, F. P., Molecular Structure and Thermodynamics, Wiley (1974). Sect. 13.3. Uses a different approach to radiation properties in Sect. 2.1, followed by an approach similar to that of this unit in Sect. 13.3. Chapter 12 and Sects. 13.1 and 13.2 complete the topics considered in this unit with examples and exercises. A good supplement.
5. Tien, C. L., and Lienhard, J. H., Statistical Thermodynamics, Holt, Rinehart, and Winston (1971). Chapter 6 develops the statistics of degenerate particles using a different approach from the unit. Photons and free electrons are discussed. The

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### THE PROPERTIES OF GASES COMPOSED OF LOW-MASS PARTICLES

#### Free Electrons and Electromagnetic and Acoustical Radiation

Unit IIIC investigated the properties of indistinguishable independent particles in the Boltzmann limit,  $n_j \ll g_j$ . It was found that satisfaction of the limit is facilitated by small particle density,  $n_v (= N/V)$ , high temperature, and large particle mass.<sup>1</sup>

$$\left. \frac{n_j}{g_j} \right|_{\max} \sim n_v \left( \frac{h^2}{2\pi m^* kT} \right)^{3/2} \ll 1 \quad (\text{IIIC-15})$$

In the consideration of molecular gases we found that only the lightest molecules, helium and hydrogen, ever fail to satisfy the limit, see Exer. 7, Unit IIIC. Thus, in discussing systems that do not normally satisfy the limit we need consider only particles whose mass is less than that of a proton.

Exercise 1. Each atom of crystalline copper contributes a single electron to its free electron gas. Determine the magnitude of  $n_v (h^2/2\pi m^* kT)^{3/2}$  for the free electron gas in solid copper at normal temperatures. Also, determine the hypothetical temperature at which the limit would be satisfied by setting it equal to  $10^{-2}$ .

Exer. 1 shows that the free electron gas within a metallic lattice would never satisfy the Boltzmann limit. Systems of this type are said to be *degenerate*. Since a single electron constitutes an odd number of subatomic components, electricity is conducted by *degenerate Fermions*.<sup>2</sup> The only common particles lighter than an electron are massless. And the wave-particle duality principle allows us to envision electromagnetic radiation either as waves or as a gas of massless particles translating at the speed of light, *photons*. Similarly, we may envision acoustical radiation either as waves or as a gas of massless particles translating at the speed of sound, *phonons*. Since zero is an even number of subatomic components, photons and phonons are Bosons. While we cannot apply the limit test directly to these massless particles, we would not expect them to satisfy the Boltzmann limit. Photons and phonons are *degenerate Bosons*. Thus we must employ the exact distribution function to analyze free electrons and waves.

<sup>1</sup>This expression, which involves volume per particle rather than pressure, is equivalent to eqn. IIIC-15, see Appendix IIIC-A, Exmp. A1.

<sup>2</sup>Pairs of electrons would be Bosons. The phenomenon of superconductivity occurs when electron wave functions are coupled creating stable electron pairs. These free electron pairs undergo a Bose degeneracy to establish the characteristics of the superconductor.

$$n_j^{\text{FD}} = \frac{g_j}{e^{\alpha + \epsilon_j/kT} + 1} \quad n_j^{\text{BE}} = \frac{g_j}{e^{\alpha + \epsilon_j/kT} - 1} \quad (\text{IIIB-14,16})$$

We begin with applications to waves.

### I. PROPERTIES OF WAVES

Before we can apply eqn. IIIB-16 to determine the properties of systems of massless Bosons (waves), we must evaluate the parameter  $\alpha$ . Recall that two unknown multipliers,  $\alpha$  and  $\beta$ , were introduced as a step in Lagrange's method of finding a maximum subject to imposed conditions. The problem was to maximize the entropy, or  $\ln W_1$ , for an isolated system.

$$d\left(\frac{S}{k} - \alpha N - \beta U\right) = d\left[\ln W(n_{j,i}) - \alpha \sum_j \delta n_{j,i} - \beta \sum_j \epsilon_j \delta n_{j,i}\right] = 0$$

The parameter  $\beta$  prescribes conservation of energy. After the three equilibrium distribution functions were derived in terms of the unknown multipliers,  $\alpha$  and  $\beta$ , the concept of thermal equilibration was employed to evaluate  $\beta$  in general,  $\beta \equiv 1/kT$  (see Exmps. 2 and B4 and Exer. B4 of Unit IIIB). The parameter  $\alpha$ , on the other hand, is intended to prescribe conservation of mass. In fact, however, it prescribes conservation of particles. In the case of particles of nonzero mass, the two conservation principles are the same. But for systems of massless particles, mass is conserved independent of the number of particles present. Indeed photons and phonons can be created or destroyed subject only to conservation of energy. Thus, the multiplier  $\alpha$  is unnecessary for systems of massless particles. (That is,  $\alpha = 0$ .)<sup>3</sup> Thus, the distribution function for massless particles becomes

$$n_j^o = \frac{g_j}{e^{\epsilon_j/kT} - 1} \quad (\text{IIID-1a})$$

*Note to the Student.* The following exercise is not an objective of the unit. It provides the interested student an opportunity to verify eqn. IIID-1 through a more formal derivation.

**Exercise 2.** Modify the derivation of eqn. IIIB-16 as completed in Exer. B2, Appendix B of Unit IIIB to exclude the conservation of particles requirement. Verify that eqn. IIID-1 is the result. (No answer to this exercise is presented.)

In the following sections we employ eqn. IIID-1 to develop the properties of electromagnetic and acoustical radiation.

<sup>3</sup>This verifies that massless particles do not satisfy the Boltzmann limit. As  $n_j/g_j|_{\text{max}} \ll 1$  requires that  $e^\alpha \gg 1$ ,  $\alpha = 0$  corresponds to a system which is always degenerate, viz., never satisfies the Boltzmann limit.

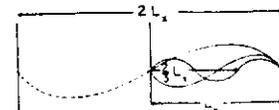
A. The Properties of the Photon Gas

Quantum mechanics was developed by Max Planck as a necessary step to accurately predict the properties of electromagnetic radiation. Planck hypothesized that radiation of frequency  $\nu$  must possess energy in multiples of a minimum quantum,  $h\nu$ . Thus, the distribution of a gas of photons in equilibrium at temperature  $T$ , using eqn. IIID-1, is

$$n_j^o = \frac{g_j}{e^{h\nu_j/kT} - 1}$$

In order to apply this distribution to determine the properties of a photon gas, we require the sequence of allowed frequencies,  $\nu_j$ , and their corresponding degeneracies,  $g_j$ . The allowed frequencies are governed by the geometry of the enclosure, specifically by its *boundary conditions*. The amplitude of waves within an enclosure must vanish at its boundaries. For example, the waves in a one-dimensional enclosure, as shown, are limited to

$$\lambda_\ell = \frac{2L}{\ell} \quad \ell = 1, 2, 3, \dots$$



The relationship between frequency and wavelength is  $\nu \equiv c/\lambda$ .

In a three-dimensional cubic enclosure the combined three-dimensional wavelength limits give the following allowed frequencies

$$\nu_{\ell,m,n} = c \left( \frac{1}{\lambda_x^2} + \frac{1}{\lambda_y^2} + \frac{1}{\lambda_z^2} \right)^{1/2} = \frac{c}{2V^{1/3}} (\ell^2 + m^2 + n^2)^{1/2} \quad n, m, \ell = 1, 2, 3, \dots$$

Note that this expression for the *discrete frequencies* has the form of eqn. IIIC-12. It is expressed as the product of a physical parameter and a dimensionless function of the sequence of integers  $(n, m, \ell)$ . Thus, the characteristic temperature that prescribes the frequency spacing of a photon gas is

$$\theta_{\text{pht}} = \frac{h\Delta\nu}{k} = \frac{hc}{2kV^{1/3}} \quad (\text{IIID-2})$$

Ans. 1. The volume of a free electron is the same as that of an atom. Using the data of Tables IA-1, 2 and ID-2

$$n_{v,el} = \frac{\rho_{Cu} n_e, Cu N_A}{M_{Cu}} = \frac{8.84 \text{ g/cm}^3 \cdot 1 \text{ elect/atom} \cdot 6.023 \cdot 10^{23} \text{ atoms/(g mol)}}{63.43 \text{ g/(g mol)}} = 8.47 \cdot 10^{22} \text{ elect/cm}^3$$

and

$$n_{v,el} \left( \frac{h^2}{2\pi m^* kT} \right)^{3/2} = 8.47 \cdot 10^{22} \text{ elect/cm}^3$$

$$\left[ \frac{(6.625 \cdot 10^{-27} \text{ erg} \cdot \text{s/elect})^2}{2\pi \cdot 9.109 \cdot 10^{-28} \text{ g/elect} \cdot 1.38 \cdot 10^{-16} \text{ erg/(elect K)} \cdot 300 \text{ K}} \right]^{3/2} = 6.75 \cdot 10^3 \text{ elect/state}$$

Obviously the limit is not satisfied at ordinary temperatures. It would theoretically be satisfied ( $n_j/g_j|_{\text{max}} \sim 10^{-2}$ ) if the temperature were increased to  $2.31 \cdot 10^6 \text{ K}$ .

Exercise 3. Determine the magnitude of  $\theta_{\text{pht}}$  for enclosures of volume  $1 \text{ mm}^3$  and  $1 \text{ m}^3$ .

The answer to Exer. 3 shows that, while  $\theta_{\text{pht}}$  is sensitive to the volume of the enclosure, a combination of a very small enclosure at a very low temperature is required for the effect of the discrete spectrum to be noticeable. We will consider only the high temperature limit,  $T \gg \theta_{\text{pht}}$ . In that case the spectrum of eqn. IIID-1a can be approximated as continuous.

$$n_j^0 = n^0(\nu) = \frac{g(\nu)}{e^{h\nu/kT} - 1} \quad (\text{IIID-1b})$$

Thus the distribution of translating photons is similar to that of translating molecules. Both distributions can be approximated as continuous and both sets of allowed energies are prescribed by three distinct sets of positive integers ( $\lambda, m, n$ ) representing three directions of translation.<sup>4</sup> Therefore, the degeneracy of translating photons can be adapted from that developed for translating independent molecules in Appendix IIIC-A

$$g_{\text{tr}}(\epsilon) = \frac{4\pi V m^{*3/2} \epsilon^{1/2}}{h^3} \quad (\text{IIIC-A1})$$

The adaptation consists of eliminating the molecular mass by substituting the energy-mass equivalence,  $\epsilon = m^* c^2$ , and multiplying the result by two to account for the fact that the wave can be polarized in two perpendicular directions. Thus

$$g_{\text{pht}}(\epsilon) = \frac{8\pi V \epsilon^2}{(hc)^3}$$

To express this result in terms of frequency we must employ integral equivalence,  $g(\epsilon)d\epsilon = g(\nu)d\nu$  where  $\epsilon = h\nu$ . Thus

$$g_{\text{pht}}(\nu) = \frac{8\pi V \nu^2}{c^3} \quad (\text{IIID-3a})$$

With this result we have the distribution function of a photon gas in equilibrium in terms of frequency

$$n_{\text{pht}}(\nu) = \frac{8\pi V}{c^3} \frac{\nu^2}{(e^{h\nu/kT} - 1)} \quad (\text{IIID-4a})$$

The principal application of the characteristics of thermal radiation is to the determination of radiant heat transfer, see Unit IIIE. It is much more common in this field to specify the distribution by wavelength rather than frequency. To accommodate this preference we transform eqns. IIID-3 and 4 to a wavelength basis,  $\nu = c/\lambda$ ,  $d\nu = (-c/\lambda^2)d\lambda$ . Then using the condition  $g(\nu)d\nu = -g(\lambda)d\lambda$ , we have

<sup>4</sup>The principal difference is that photons translate at the speed of light with their energies dependent on frequency, whereas molecules translate at various speeds with their energies being dependent on speed squared.

$$g_{\text{pht}}(\lambda) = \frac{8\pi V}{\lambda^4} \quad n_{\text{pht}}(\lambda, T) = \frac{8\pi V}{\lambda^4} \frac{1}{[e^{(hc/\lambda kT)} - 1]} \quad (\text{IIID-3b, 4b})$$

The photon distribution allows us to establish the properties of a photon gas. For example, the energy distribution per unit volume, often called *Planck's Law* is given by<sup>5,6</sup>

$$u_{v\lambda}(T) = \frac{n_{\text{pht}}(\lambda, T)}{V} \frac{hc}{\lambda} = \frac{8\pi ch}{\lambda^5} \frac{1}{[e^{(hc/\lambda kT)} - 1]} \quad (\text{IIID-5})$$

The form of this distribution is represented in Fig. IIID-1. Notice the pronounced maximum that separates the degenerate low energy (long wavelength) photons from the classical high energy (short wavelength) photons.<sup>7</sup> The position of the maximum is an important parameter for the classification of thermal radiation.<sup>8</sup>

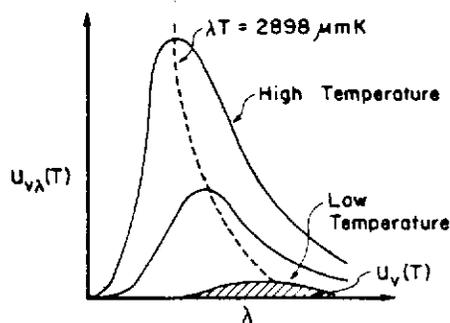


Fig. IIID-1. The Energy Distribution of Thermal Radiation

Example 1. Differentiate  $u_{v\lambda}(T)$  with respect to wavelength and develop a condition for the position of its maximum.

The maximum is defined by

$$0 = \frac{du_{v\lambda}(T)}{d\lambda} = \frac{d}{d\lambda} \left\{ \frac{8\pi hc}{\lambda^5 [e^{(hc/\lambda kT)} - 1]} \right\} = 8\pi hc \cdot \left\{ \frac{-5}{\lambda^6 [e^{(hc/\lambda kT)} - 1]} + \frac{hc e^{(hc/\lambda kT)}}{\lambda^7 kT [e^{(hc/\lambda kT)} - 1]^2} \right\}$$

$$= \frac{8\pi hc}{\lambda^6 [e^{(hc/\lambda kT)} - 1]^2} \left\{ -5 [e^{(hc/\lambda kT)} - 1] + \frac{hc}{\lambda kT} e^{(hc/\lambda kT)} \right\}$$

Thus the condition for the maximum has the form

$$(5 - x_{\text{max}}) e^{x_{\text{max}}} = 5$$

<sup>5</sup>Photon properties cannot be normalized on a per unit mass basis. Photon mass is zero. Molar normalization is possible but inconvenient as the number of photons is a variable.

<sup>6</sup>The wavelength distribution of radiant emission is also called Planck's Law. It differs only from eqn. IIID-5 by a constant, see Unit IIIE.

<sup>7</sup>As discussed above a system of photons never satisfies the Boltzmann limit. But within a system, the high energy (short wavelength) tail of the distribution becomes classical,  $e^{(hc/\lambda kT)} \gg 1$ . This portion of the distribution can be predicted by using classical methods of wave mechanics.

<sup>8</sup>Our development concerns radiation originating due to temperature alone. We exclude radiation that is mechanically generated, e.g., radio, TV, or other communication signals, lasers, etc.

where  $x_{\max} = hc/\lambda_{\max}kT$ . Solving by trial and error we obtain,  $x_{\max} = 4.9651$ . Thus the condition for the wavelength maximum is

$$\lambda_{\max} T = \frac{hc}{x_{\max} k} = \frac{6.625 \cdot 10^{-34} \text{ J s/part} \cdot 2.998 \cdot 10^8 \text{ m/s}}{4.9651 \cdot 1.380 \cdot 10^{-23} \text{ J/(part K)}} = 2.898 \cdot 10^{-3} \text{ m K} = 2898 \text{ } \mu\text{m K}$$

The position of the maximum in Planck's Law is developed in Exmp. 1. The resulting expression is called *Wein's Law*.<sup>9</sup>

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

The maximum shifts to lower wavelength as the temperature level of the radiation is increased.

Exercise 4. Determine the wavelength of maximum emission for objects at 300, 3000, and 30,000 K.

Solar radiation is emitted from the sun's surface at about 5600 K. Thus, the maximum of available "natural" light on earth is at 0.52  $\mu\text{m}$ . It is surely no coincidence that this is the middle of the visible spectrum. The eye is capable of detecting radiation in the wavelength range from about 0.4 to 0.7  $\mu\text{m}$ .

Exercise 5. Alien visitors from a distant solar system have very limited sight on earth. Their eyes are sensitive in the wavelength range 0.2 to 0.3  $\mu\text{m}$ . Estimate the emission temperature of their "sun."

Planck's Law gives the wavelength distribution of thermal radiation. The total energy density is obtained by integrating over all wavelengths.

$$u_v(T) = \int_0^{\infty} u_{v\lambda}(T) d\lambda \quad (\text{IIID-7a})$$

This process is represented graphically as the area under the distribution, see Fig. IIID-1.

Example 2. Substitute Planck's Law into eqn. IIID-7a and express the integral in terms of the dimensionless variable,  $x \equiv (hc/\lambda kT)$ .

Direct substitution gives

$$u_v(T) = \int_0^{\infty} u_{v\lambda}(T) d\lambda = 8\pi hc \int_0^{\infty} \frac{d\lambda}{\lambda^5 [e^{(hc/\lambda kT)} - 1]}$$

Then using

$$x = \frac{hc}{\lambda kT} \quad dx = \frac{-hc}{\lambda^2 kT} d\lambda \quad \lambda = 0, x \Rightarrow \infty; \quad \lambda \Rightarrow \infty, x \Rightarrow 0$$

<sup>9</sup>The normal unit of wavelength is the micrometer,  $\mu\text{m}$ . In this context it is often abbreviated to micron,  $\mu$ .

Ans. 3.

$$\theta_{\text{pht}}|_{V=1\text{mm}}^3 = \frac{6.625 \cdot 10^{-34} \text{ J s/wave} \cdot 2.998 \cdot 10^8 \text{ m/s}}{2 \cdot 1.380 \cdot 10^{-23} \text{ J/wave K} \cdot [10^{-9} \cdot 3^{1/3}]} = 7.196 \text{ K}, \quad \theta_{\text{pht}}|_{1\text{m}}^3 = 7.196 \cdot 10^{-3} \text{ K}$$

We have

$$u_v(T) = 8\pi hc \left(\frac{kT}{hc}\right)^4 \int_0^\infty \frac{\left(\frac{hc}{\lambda^2 kT} d\lambda\right) \left(\frac{hc}{\lambda kT}\right)^3}{[e^{(hc/\lambda kT)} - 1]} = \frac{8\pi (kT)^4}{(hc)^3} \int_0^\infty \frac{-x^3 dx}{(e^x - 1)} = \frac{8\pi k^4}{(hc)^3} \left[ \int_0^\infty \frac{x^3 dx}{(e^x - 1)} \right] T^4$$

Exmp. 2 evaluated eqn. IIID-7a in terms of a definite integral. The general (indefinite limit) form of this function is called the Debye integral; its values are listed in Table IIID-2 at the end of the Unit. Its value for the infinite limit is  $\pi^4/15$  (see Ref. 5, Appendix E). This gives the total energy density as

$$u_{v,pht}(T) = \frac{8\pi^5 k^4}{15 (hc)^3} T^4 \tag{IIID-7b}$$

The number of photons per unit volume, or the *photon density* is developed in a similar manner, see Exer. 6. The result is

$$n_{v,pht}(T) = \frac{N_{pht}}{V} = \frac{1}{V} \int_0^\infty n_{pht,\lambda}(T) d\lambda = 8\pi \cdot 2.404 \left(\frac{k}{hc}\right)^3 T^3 \tag{IIID-8}$$

Exercise 6. Substitute the photon distribution into eqn. IIID-4b and express the required integration in terms of the dimensionless variable,  $x$  ( $\equiv hc/\lambda kT$ ).

Exercise 7. Expressions for photon properties are normalized with volume rather than mass or mole since photons are massless. For purposes of comparison, one can normalize photon energy with Avogadro's number of photons and obtain photon energy in molar units. One should not, however, compare such "molar" photon properties with the molar properties of the matter that occupies the same space, see Exer. 9. The physical bases of these two molar quantities are not the same. Formulate an expression for the internal energy "per mole of photons,"  $u_{pht}$ . Differentiate this expression to derive an expression for  $c_{v,pht}$ .

The energy and particle density of a photon gas were determined by direct application of their defining integrals. The following problems use the same procedures to determine the entropy density and pressure of a photon gas.

*Note to the Student.* The following examples develop expressions for the entropy and pressure of the photon gas. The results are reported as eqns. IIID-9 and 10. The techniques to develop these results are not representative of objectives of the unit.

Example 3. The entropy of a system of independent Bosons is described by eqn. IIIB-17.

$$S^{BE} = \frac{U}{T} + Nk\alpha - k \sum_{j=1}^J g_j \ln \left( 1 - e^{-\alpha - \epsilon_j/kT} \right)$$

Adapt this relationship to the specific case of a photon gas. Incorporate the continuum approximation by replacing the sum by an integral. Express the result as an integral over the dimensionless variable,  $x$  ( $\equiv hc/\lambda kT$ ).

For the photon gas we can substitute:  $\alpha = 0$ ,  $\epsilon_j = h\nu_j$ , and  $U = [8\pi^5 k^4 / 15 (hc)^3] VT^4$ . The continuum approximation allows us to replace the sum over the energy levels by an integral over wavelength. Substituting into eqn. IIIB-17, we obtain

$$S^{BE} = \left[ \frac{8\pi^5 k^4}{15 (hc)^3} \right] VT^4 - k \cdot 8\pi V \int_0^\infty \frac{d\lambda}{\lambda^4} \ln \left[ 1 - e^{-(hc/\lambda kT)} \right]$$

Then substituting the dimensionless function

$$x = \frac{hc}{\lambda kT} \quad dx = \frac{-hc}{\lambda^2 kT} d\lambda \quad \lambda = 0, \quad x \Rightarrow \infty \quad \text{and} \quad \lambda \Rightarrow \infty, \quad x = 0$$

we obtain

$$\begin{aligned} s_{v,\text{pht}} &= \left[ \frac{8\pi^5 k^4}{15 (hc)^3} \right] T^3 - 8\pi k \left( \frac{kT}{hc} \right)^3 \int_0^\infty \left( \frac{hc}{kT} \right)^3 \left( \frac{-hc}{\lambda^2 kT} d\lambda \right) \ln \left[ 1 - e^{-(hc/\lambda kT)} \right] \\ &= \frac{8\pi^5}{15} k \left( \frac{kT}{hc} \right)^3 - 8\pi k \left( \frac{kT}{hc} \right)^3 \int_0^\infty x^2 \ln(1 - e^{-x}) dx \end{aligned}$$

This integral can be transformed to the Debye integral form using "by parts" integration. To that purpose, define

$$W = \ln(1 - e^{-x}) \quad dW = \frac{e^{-x}}{1 - e^{-x}} dx = \frac{dx}{e^x - 1} \quad dV = x^2 dx \quad V = \frac{x^3}{3}$$

Thus

$$\int_0^\infty x^2 \ln(1 - e^{-x}) dx = \frac{x^3}{3} \ln(1 - e^{-x}) \Big|_0^\infty - \frac{1}{3} \int_0^\infty \frac{x^3}{e^x - 1} dx = -\frac{1}{3} \int_0^\infty \frac{x^3 dx}{e^x - 1} = -\frac{1}{3} \left( \frac{\pi^4}{15} \right)$$

Substituting, we obtain

$$s_{v,\text{pht}} = \frac{8\pi^5 k^4}{15 (hc)^3} T^3 \left( 1 + \frac{1}{3} \right) = \frac{32\pi^5 k^4}{45 (hc)^3} T^3$$

Comparing this result to eqn. IIID-7b, we see  $s_{v,\text{pht}} = 4u_{v,\text{pht}}/3T$ .

Example 4. An expression for the entropy of a photon gas was derived in the preceding example. Use this result in conjunction with the Gibbs equation,  $dS = dU/T + (p/T)dV$ , to derive an expression for radiation pressure.

The Gibbs equation is of the form  $S = S(U, V)$ . The definition of the derivative of a function of this form allows us to express pressure in terms of a partial derivative of the entropy

$$dS = \left( \frac{\partial S}{\partial U} \right)_V dU + \left( \frac{\partial S}{\partial V} \right)_U dV = \frac{dU}{T} + \frac{p}{T} dV \quad \text{Hence } p = T \left( \frac{\partial S}{\partial V} \right)_U$$

The total entropy is  $S_{\text{pht}} = V s_{v,\text{pht}} = V \cdot 4u_v / (3T)$ . To facilitate the differentiation, we abbreviate

$$u_v = \left[ \frac{8\pi^5 k^4}{15 (hc)^3} \right] T^4 = aT^4$$

Ans. 4. Wein's Law gives  $\lambda_{\text{max}}$ .

$$T = 300 \text{ K}; \quad \lambda_{\text{max}} = \frac{2898 \mu\text{m K}}{300 \text{ K}} = 9.663 \mu\text{m}$$

Similarly at:  $T = 3000 \text{ K}$ ,  $\lambda_{\text{max}} = 0.9663 \mu\text{m}$ ,  $T = 30,000 \text{ K}$ ,  $\lambda_{\text{max}} = 0.09663 \mu\text{m}$

Ans. 5. Presumably, the alien creatures' eyes have adapted to the maximum emission of their "sun." Thus,

$$T_{\text{star}} = \frac{2898 \mu\text{m K}}{0.25 \mu\text{m}} = 11,600 \text{ K}$$

Thus,

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{\partial}{\partial V} \left(\frac{4}{3} VaT^3\right)_U = \frac{4}{3} aT^3 + \frac{4}{3} Va3T^2 \left(\frac{\partial T}{\partial V}\right)_U$$

The last term can be evaluated using

$$U = VaT^4 \quad V = \frac{U}{aT^4} \quad \left(\frac{\partial V}{\partial T}\right)_U = -\frac{4U}{aT^5} \quad \left(\frac{\partial T}{\partial V}\right)_U = -\frac{aT^4}{4U} = -\frac{T}{4V}$$

Then

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{4}{3} aT^3 + \frac{4}{3} Va3T^2 \left(-\frac{T}{4V}\right) = \frac{aT^3}{3} = \frac{u_v}{3T}$$

Exmps. 3 and 4 derived expressions for the photon entropy density and radiation pressure, respectively. Both results can be written in terms of the photon energy density.

$$s_{v,\text{pht}} = \frac{4}{3} \frac{u_{v,\text{pht}}}{T} \quad p_{\text{pht}} = \frac{u_{v,\text{pht}}}{3} \quad (\text{IIID-9,10})$$

Exercise 8. Determine the number of photons per cubic meter and the photon energy and entropy per cubic meter and the radiation pressure at 300, 3000, and 30,000 K.

The photon gas is always present. Thus, its properties should be added to those of the particles of matter to obtain total properties. In that respect our calculation of perfect gas properties, Unit IIIC, was incomplete. The following problem compares the photon and molecular contributions to perfect gas properties.

Exercise 9. Both photon density and photon energy density are functions of temperature only. Gaseous particle density and therefore gaseous energy density are dependent on both pressure and temperature. To compare the separate property contributions of photons and molecules, determine the pressure level at which molecular density would equal the photon density at 300, 3000, and 30,000 K. In addition, determine the pressure level at which the translational component of molecular energy would equal the photon energy per unit volume. (Use the results of Exer. 8.)

The results of Exer. 9 demonstrate that the property contributions of photons are an appreciable part of the thermodynamic properties of a gas only at extremely high tempera-

Ans. 6. Using  $x = (hc/\lambda kT)$ ,  $dx = -(hc/\lambda^2 kT)d\lambda$  and  $\lambda = 0$ ,  $x = \infty$ ;  $\lambda = \infty$ ,  $x = 0$ , we have

$$n_{v,\text{pht}} = \frac{8\pi V}{V} \int_0^\infty \frac{d\lambda}{\lambda^4 [e^{(hc/\lambda kT)} - 1]} = \pi \left(\frac{kT}{hc}\right)^3 \int_0^\infty \left(\frac{hc}{\lambda kT}\right)^2 \left(\frac{hc}{\lambda^2 kT} d\lambda\right) \frac{1}{[e^{(hc/\lambda kT)} - 1]} = 8\pi \left(\frac{kT}{hc}\right)^3 \left[ \int_0^\infty \frac{x^2 dx}{(e^x - 1)} \right]$$

This integral is evaluated in terms of the Gamma Function and the Riemann Zeta Function, see Ref. 5. The result is expressed as eqn. IIID-8.

Ans. 7. The internal energy per mole of photons is

$$\bar{u}_{\text{pht}}(T) = \frac{u_v(T)N_A}{n_v(T)} = \frac{\frac{4}{c} \left(\frac{2\pi^5 k^4}{15 h^3 c^2}\right) T^4 N_A}{8\pi \cdot (2.404) \cdot \left(\frac{k}{hc}\right)^3 T^3} = \frac{\pi^4 \bar{R} T}{36.06} \quad \text{Thus} \quad \bar{c}_{v,\text{pht}} = \left(\frac{\partial \bar{u}_{\text{pht}}(T)}{\partial T}\right)_v = \frac{\pi^4}{36.06} \bar{R}$$

atures or for an extremely rarefied gas. This result can be extrapolated to the condensed phases as well. Although the photon gas is present within liquid and solid media, its property contributions are negligible in comparison to the contribution of the particles of matter and can be neglected. This does not mean that our study of photon properties was inconsequential. We will find that photons are an important means of transport through evacuated, and frequently, dense gases and certain liquids and solids (see Unit IIIE).

### B. Lattice Vibrations (the Phonon Gas)

Crystalline solids are characterized by relatively strong bonds between the atoms or molecules that occupy their lattice points, see Unit ICS. The principal energy storage mechanism in atomic lattice point crystals is in the form of vibration of each atom about its mean lattice position. Lattice vibrations have been successfully modeled using two fundamentally different approaches. One is based on explicit consideration of the vibration of each atom. The second ignores the details of particle vibration. Instead, it considers the properties of the acoustical waves, or phonons that these vibrations generate. We begin with the vibrating atoms approach, using the *model* first proposed by *Einstein*.

1. The Einstein Model assumes that the  $N$  atoms or molecules that compose the crystal are fixed in position by independent "linear spring" forces in all three directions. That is, the complex lattice is resolved into  $3N$  independent particles all vibrating at a *single (Einstein) frequency*,  $\nu_E$ , see Fig. IIID-2.

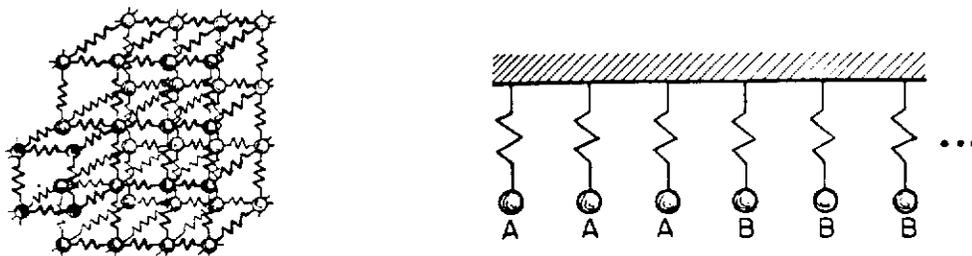


Fig. IIID-2. Schematic of an Actual Lattice and Its Resolved Einstein Form

The energy levels available to a linear oscillator were introduced in Sect. IIIB of Unit IIIC

$$\epsilon_{v,\ell} = \left(\ell + \frac{1}{2}\right) h\nu_E \quad g_\ell = 1 \quad \ell = 0, 1, 2, 3$$

Note that one can distinguish among the  $3N$  linear oscillators by their positions and directions of vibration. The oscillators of the Einstein model are *Boltzons*. Thus the distribution, partition function, and properties under the Einstein model are the same as three modes of intermolecular vibration, see Sect. IIIB of Unit IIIC, with the *Einstein characteristic temperature*

$$\theta_E = \frac{h\nu_E}{k}$$

The property relationships for vibration are listed in Table IIIC-1.<sup>10</sup>

<sup>10</sup>Notice that these expressions for the properties of *solids* are written in terms of the universal *gas* constant. The parameter is a physical constant of nature,  $\bar{R} = N_A k$ . It appears in property relationships for all three phases. In that sense the name gas constant is unfortunate.

Ans. 8. The required values are obtained by substitution into eqns. IIID-7, 8, 9, and 10.

$$[k/hc = 69.49 \text{ m}^{-1} \text{ K}^{-1}, (k/hc)^3 = 3.356 \cdot 10^5 \text{ m}^{-3} \text{ K}^{-3}]$$

$$n_v(300 \text{ K}) = 2.404 \cdot 8\pi \cdot 3.356 \cdot 10^5 \text{ m}^{-3} \text{ K}^{-3} (300)^3 \text{ K}^3 = 5.472 \cdot 10^{14} \text{ photons/m}^3$$

$$u_v(300 \text{ K}) = \frac{8\pi^5 \cdot 1.38 \cdot 10^{-23} \text{ J/(part K)} \cdot 3.356 \cdot 10^5 \text{ m}^{-3} \text{ K}^{-3} \cdot (300)^4 \text{ K}^4}{15} = 6.126 \cdot 10^{-6} \text{ J/m}^3$$

$$s_v(300 \text{ K}) = \frac{4u_v(300 \text{ K})}{3T} = \frac{4 \cdot 6.126 \cdot 10^{-6} \text{ J/m}^3}{3 \cdot 300 \text{ K}} = 2.720 \cdot 10^{-8} \text{ J/(m}^3 \text{ K)}$$

$$p(300 \text{ K}) = \frac{u_v(300 \text{ K})}{3} = \frac{6.126 \cdot 10^{-6} \text{ J/m}^3}{3} = 2.042 \cdot 10^{-11} \text{ bar}$$

Photon properties at other temperatures are found similarly. We summarize.

T(K)	$n_v(\text{ph}/\text{m}^3)$	$u_v(\text{J}/\text{m}^3)$	$s_v[\text{J}/(\text{m}^3 \text{K})]$	p(bar)
300	$5.47 \cdot 10^{14}$	$6.13 \cdot 10^{-6}$	$2.72 \cdot 10^{-8}$	$2.04 \cdot 10^{-11}$
3000	$5.47 \cdot 10^{17}$	$6.13 \cdot 10^{-2}$	$2.72 \cdot 10^{-5}$	$2.04 \cdot 10^{-7}$
30,000	$5.47 \cdot 10^{20}$	$6.13 \cdot 10^2$	$2.72 \cdot 10^{-2}$	$2.04 \cdot 10^{-3}$

Ans. 9. The condition of equal photon and particle densities is specified by

$$n_{v,\text{pht}} = 8\pi \cdot 2.404 \left(\frac{k}{hc}\right)^3 T^3 = n_{v,\text{mol}} = \frac{p}{kT} \quad \text{or} \quad p = 8\pi \cdot 2.404 \frac{(kT)^4}{(hc)^3}$$

Thus at 300 K, using the results of Exer. 8, we find

$$p = kT \cdot n_{v,\text{pht}} = 1.380 \cdot 10^{-23} \text{ J/(part K)} \cdot 300 \text{ K} \cdot 2.03 \cdot 10^7 \text{ pht/m}^3 \cdot 10^{-5} \text{ bar m}^2/\text{N} \\ = 2.26 \cdot 10^{-11} \text{ bar}$$

The translational energy per molecule is (3/2) kT. Thus the equal energy density condition is specified by

$$u_{v,\text{pht}} = \frac{8\pi^5 k^4}{15(hc)^3} T^4 = n_{v,\text{mol}} \frac{3}{2} kT = \frac{3}{2} p$$

Thus at 300 K

$$p = \frac{2}{3} u_{v,\text{pht}} = \frac{2}{3} \cdot 6.13 \cdot 10^{-6} \text{ J/m}^3 \cdot 10^{-5} \text{ bar/p}_a = 4.09 \cdot 10^{-11} \text{ bar}$$

To summarize, the gas pressures needed to have equal molecular and photon densities at 300, 3000, and 30,000 K are  $2.26 \cdot 10^{-11}$ ,  $2.26 \cdot 10^{-7}$ , and  $2.26 \cdot 10^{-3}$  bars. The gas pressures needed to have the translational component of internal energy equal the photon component at 300, 3000, and 30,000 K are  $4.09 \cdot 10^{-11}$ ,  $4.09 \cdot 10^{-7}$ , and  $4.09 \cdot 10^{-3}$  bars.

$$Z_E = \left[ \frac{e^{-\theta_E/2T}}{(1 - e^{-\theta_E/T})} \right]^3 \quad \bar{u}_E = 3\bar{R}\theta_E \left[ \frac{1}{2} + \frac{1}{(e^{\theta_E/T} - 1)} \right] \quad \bar{c}_{v,E} = 3\bar{R} \left( \frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

$$\bar{s}_E = \frac{\bar{u}_E}{T} - \bar{R} \ln Z_E = \frac{3\bar{R}}{T} \frac{\theta_E}{T} - 3\bar{R} \ln (1 - e^{-\theta_E/T})$$

Application of these relationships to perfect gases was facilitated by the availability of spectroscopically measured values of  $\theta_{v,p}$  (Table IIIC-2). These measurements are possible since intramolecular vibration within independent gaseous molecules occurs in the manner of the model, viz., at fixed frequencies. In comparison, the Einstein model bears very little resemblance to an actual vibrating lattice, see Fig. IIIC-2. Vibration of a lattice point along the axis of one of its bonds will obviously induce vibration in both of the other bond directions and the vibration of a single atom will immediately propagate to induce vibration in its nearest neighbors. The  $3N$  oscillators of the lattice are not independent and their vibrations do not occur at a single frequency. Thus the concept of a single Einstein frequency is artificial and one cannot measure  $\theta_E$  directly. It must be interpreted from property data. (Usually it is deduced from specific heat data.) This drawback is sufficient that in practice the Einstein model is used very little for the analysis of lattice vibrations.<sup>11</sup> However, once  $\theta_E$  has been determined, the property predictions of the Einstein model are quite successful.<sup>12,13</sup> The only serious deficiency is its prediction of low temperature properties. For example,  $\bar{c}_{v,E}(T \Rightarrow 0) \propto e^{-\theta_E/T}$ ; but measurements show that  $\bar{c}_{v,phn}(T \Rightarrow 0) \propto T^3$ . The following section shows that both of these deficiencies are overcome by the *Debye Model*.

2. The Debye Model ignores the detailed behavior of individual vibrating lattice points. It deals with the acoustical waves produced by the vibrations. The characteristics of acoustical radiation, or phonons, closely parallel those of electromagnetic radiation, or photons. Photons are generated by electron motions and propagate at the speed of light. Phonons are generated by lattice motions and propagate at the speed of sound. Thus the phonon distribution is governed by eqn. IIID-3 and 4 with the modifications that the average sound speed,  $c_s$ , is

<sup>11</sup>The Einstein model remains accurate for interatomic vibrations in solids whose lattice points are occupied by multiatom molecules rather than atoms, e.g., in solid water ( $H_2O$ ), carbon dioxide ( $CO_2$ ), nitrogen ( $N_2$ ), etc. (See below.)

<sup>12</sup>One frequently finds that transparently superficial microscopic models yield amazingly accurate macroscopic predictions. It seems that the technique of summation or integration to obtain total properties tends to smooth over the detailed inaccuracies of the model.

<sup>13</sup>It is very common for the Einstein model to be compared to data using the measurable characteristic temperature of the Debye model, see below, as the value of the Einstein temperature. This is an unjustified and erroneous assumption,  $\theta_E \neq \theta_D$ . Such reported comparisons are an unfair criticism of the Einstein model.

substituted for the speed of light,  $c$ , and that the multiple two (introduced to account for the two directions of polarization of transverse light waves) becomes three (accounting for both longitudinal waves and the two directions of polarization of the transverse waves).<sup>14</sup> Thus, in terms of frequency the phonon degeneracy is  $g_{\text{phn}}(\nu) = 12\pi V\nu^2/c_s^3$ .

Exercise 10. Is the characteristic temperature that prescribes the frequency spacing of phonons,  $\theta_{\text{phn}}$ , smaller or larger than that for photons, eqn. IIID-2? Draw a conclusion with respect to the significance of the phonon frequency spacing.

In our consideration of electromagnetic waves we focused on the frequency (or wavelength) distribution of photon energy (or emission). In the case of acoustical waves, we are relatively unconcerned about the energy distribution. Instead, we proceed directly to total energy by integrating the energy distribution over the *allowed phonon frequencies*. The fact that there is a limit on phonon, but not photon, frequencies is the principal difference between these otherwise very similar distributions. There is no upper limit on the energy levels accessible to photons. However, the total number of energy states accessible to the phonons is limited by the vibrations of their source. The  $N$  atomic lattice points can each vibrate in three independent directions. Thus, there can be only a total of  $3N$  states accessible to the lattice vibration-generated phonon gas. This limit is imposed by using it to stipulate a *maximum Debye cutoff frequency*,  $\nu_D$

$$3N = \int_0^{\nu_D} g_{\text{phn}}(\nu) d\nu = \frac{12\pi V}{c_s^3} \int_0^{\nu_D} \nu^2 d\nu = \frac{4\pi V}{c_s^3} (\nu_D^3) \quad (\text{IIID-11a})$$

The cutoff frequency is sufficient to determine the contribution of lattice vibrations to crystalline properties. That being the case, eqn. IIID-11a is a particularly important relationship. It defines  $\nu_D$  in terms of the sound speed and particle density of the substance.<sup>14</sup> (Particle density is determinable from the density and molecular weight of the crystal,  $N/V = \rho N_A/M$ ). Following normal practice we express this microscopic energy limit in units of temperature

$$\theta_D \equiv \frac{h\nu_D}{k} = \frac{h c_s}{k} \left( \frac{3N}{4\pi V} \right)^{1/3} = \frac{h c_s}{k} \left( \frac{3\rho N_A}{4\pi M} \right)^{1/3} \quad (\text{IIID-11b})$$

<sup>14</sup>Sound is transmitted through crystals by means of lattice vibrations. Thus sound speed is related to the elastic constants, see Ref. 5, pg. 287. The separate longitudinal and transverse sound speeds are

$$c_l = \left[ \frac{3(1-\mu)}{\rho\kappa(1+\mu)} \right]^{1/2} \quad c_t = \left[ \frac{3(1-2\mu)}{2\rho\kappa(1+\mu)} \right]^{1/2}$$

where  $\kappa$  is the isothermal compressibility and  $\mu$  is Poisson's ratio. Representative values for a few substances are listed in Table ID-2. The average sound speed is defined as

$$\frac{3}{c_s^3} = \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right)$$

Values of the *Debye Temperature*,  $\theta_D$ , of several solids are listed in Table IIID-1 at the conclusion of this unit.

Exercise 11. Use the listed values of  $\theta_D$  to infer the sound speed in iron and lead.

The implication of the cutoff frequency is that no phonons exist at frequencies above  $\nu_D$ . The limit is imposed on the distribution by specifying the degeneracy as

$$g_{\text{phn}}(\nu) = \frac{12\pi V}{c_s^3} \nu^2 \quad 0 \leq \nu \leq \nu_D \quad g_{\text{phn}}(\nu) = 0 \quad \nu > \nu_D \quad (\text{IIID-12a})$$

This gives the phonon distribution as

$$n_{\text{phn}}(\nu) = \frac{g_{\text{phn}}(\nu)}{(e^{h\nu/kT} - 1)} \quad n_{\text{phn}}(\nu) = \frac{12\pi V}{c_s^3} \frac{\nu^2}{(e^{h\nu/kT} - 1)} \quad 0 \leq \nu \leq \nu_D$$

$$n_{\text{phn}}(\nu) = 0 \quad \nu > \nu_D \quad (\text{IIID-12b})$$

With these expressions the energy of a phonon gas is readily formulated.

Example 5. Express the molar internal energy of a phonon gas,  $\bar{u}_{\text{phn}}$ , in terms of an integral over the dimensionless variable  $x \equiv h\nu/kT$  and the dimensionless temperature ratio,  $x_D = \theta_D/T$ .

Phonon internal energy is defined by  $U = \int_0^{\nu_D} (h\nu)n_{\text{phn}}(\nu)d\nu$ . Substituting from eqn. IIID-12 and introducing the dimensionless variable

$$x = \frac{h\nu}{kT} \quad dx = \frac{h d\nu}{kT} \quad \text{when } \nu = 0, \quad x = 0 \quad \text{and when } \nu = \nu_D, \quad x = \frac{\theta_D}{T} = x_D$$

We have

$$U = \frac{12\pi V}{c_s^3} \int_0^{\nu_D} h\nu \left[ \frac{\nu^2}{(e^{h\nu/kT} - 1)} \right] d\nu + \int_{\nu_D}^{\infty} h\nu \cdot (0) \cdot d\nu = \frac{12\pi V}{c_s^3} \int_0^{\nu_D} \left( \frac{h\nu}{kT} \right)^3 \frac{1}{(e^{h\nu/kT} - 1)} \left( \frac{h d\nu}{kT} \right)$$

$$= 12\pi V \frac{(kT)^4}{(hc_s)^3} \int_0^{x_D} \frac{x^3 dx}{(e^x - 1)}$$

Then introducing the relations  $nN_A = N$  and  $\bar{R} = N_A k$ , we obtain the result shown below as eqn. IIID-13a.

Exmp. 5 derived an expression for the internal energy of a phonon gas<sup>15</sup>

$$\bar{u}_{\text{phn}} = 9 \bar{R} T \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1} \quad (\text{IIID-13a})$$

<sup>15</sup>Eqns. IIID-13, 15, and 16 refer to a mole of lattice points in the crystal rather than a mole of phonons.

Ans. 10.  $\theta_{\text{phn}} = h c_s / 2k\nu^{1/3}$ . The only change is that from the speed of light to the speed of sound. Thus,  $\theta_{\text{phn}} \ll \theta_{\text{pht}}$ . It took a combination of a very small enclosure at very low temperatures to achieve conditions under which  $\theta_{\text{pht}} \sim T$ . Thus, we always expect  $\theta_{\text{phn}} \ll T$ .

## PROPERTIES OF WAVES

Evaluation of  $\bar{u}_{\text{phn}}$  requires that the Debye integral be evaluated over a range of arguments.<sup>16</sup> To facilitate its evaluation Table IIID-2, at the conclusion of the unit, lists values of the function

$$D(x_D) \equiv \frac{3}{x_D^3} \int_0^{x_D} \frac{x^3 dx}{(e^x - 1)} \quad \text{where } x_D = \frac{\theta_D}{T} \quad (\text{IIID-14})$$

When it is written in terms of  $D(x_D)$  the phonon energy is

$$\bar{u}_{\text{phn}}(T, \theta_D) = 3 \bar{R} T D(x_D) \quad (\text{IIID-13b})$$

The lattice contribution to the specific heat (see Exmp. 6) and the entropy (see Exer. 12) can be formulated in terms of the same function.<sup>17</sup>

$$\bar{c}_{v, \text{phn}}(x_D) = \left( \frac{\partial \bar{u}_{\text{phn}}}{\partial T} \right)_v = 3 \bar{R} \left[ 4D(x_D) - \frac{3x_D}{e^{x_D} - 1} \right] \quad (\text{IIID-15})$$

$$\bar{s}_{\text{phn}} = \bar{R} \left[ 4D(x_D) - 3 \ln(1 - e^{-x_D}) \right] \quad (\text{IIID-16})$$

*Note to the Student.* The first of these developments requires differentiation of an integral, viz., the use of Leibnitz Rule. The purpose of these developments is to aid the student in understanding eqns IIID-15 and 16. Neither of these developments is representative of student requirements. The use of the relationships to determine properties is a student objective, see Exer. 13.

Example 6. Differentiate eqn. IIID-13a to derive eqn. IIID-15.

The development consists of the following differentiation

$$\begin{aligned} \bar{c}_{v, \text{phn}} &= \left( \frac{\partial \bar{u}_{\text{phn}}}{\partial T} \right)_v = \frac{\partial}{\partial T} \left[ + \frac{9\bar{R}}{\theta_D^3} T^4 \int_0^{\theta_D/T} \frac{x^3 dx}{(e^x - 1)} \right]_v \\ &= 9\bar{R} \left\{ 4 \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3 dx}{(e^x - 1)} + \frac{T^4}{\theta_D^3} \frac{d}{dT} \left[ \int_0^{\theta_D/T} \frac{x^3 dx}{(e^x - 1)} \right] \right\} \end{aligned}$$

In the second term the variable appears in the upper limit of the integral. Its differentiation requires the use of Leibnitz Rule.

$$\frac{d}{dx} \int_a(x) \int_b(x) f(x, \xi) d\xi = f(x, b(x)) \frac{db(x)}{dx} - f(x, a(x)) \frac{da(x)}{dx} + \int_a(x) \frac{\partial}{\partial x} [f(x, \xi)] d\xi$$

<sup>16</sup>Eqn. IIID-12 implies that the minimum lattice energy is zero. But in fact, the minimum energy of each linear oscillator is  $h\nu/2$ . Thus the zero point energy is

$$U_{\text{phn}}^0 = \int_0^{\nu_D} \frac{h\nu}{2} g(\nu) d\nu \quad \text{or} \quad \bar{u}_{\text{phn}}^0 = \frac{9}{8} \bar{R} \theta_D$$

We omit this term for simplicity, since it affects only the level of energy not its change with temperature.

<sup>17</sup>As formulated, the Debye model predicts the specific heat at constant volume,  $c_v$ . Applications to solids require the specific heat at constant pressure,  $c_p$ , almost exclusively. A prediction of the difference between these two functions can be made based on the Debye model, but this requires that we predict the variation of the Debye temperature with volume, see Ref. 5. We omit this development and continue to depend on eqn. ID-6 to account for the difference between specific heats.

$$c_p - c_v = \frac{T\nu\beta^2}{\kappa}$$

Application to the second term gives

$$\bar{c}_{v,\text{phn}} = 9\bar{R} \left[ \frac{T}{x_D^3} \frac{x_D^3}{(e^{x_D} - 1)} \frac{d\left(\frac{\theta_D}{T}\right)}{dT} \right] = 3\bar{R} \left[ 4D(x_D) - \frac{3x_D}{(e^{x_D} - 1)} \right]$$

Exercise 12. Eqn. IIIB-17 was adapted to determine the photon entropy density in Exmp. 3. A similar procedure is needed to derive eqn. IIID-16 for the phonon entropy. Adapt the procedure of Exmp. 3 to the specific case of phonons. Show that the result is eqn. IIID-16.

Exercise 13. Determine the lattice contribution to the internal energy, specific heat, and entropy of aluminum at 100, 300, and 1000 K.

Fig. IIID-3 shows the Debye model for the specific heat of phonons. Notice the similarity of this function to the modes of a molecular gas (see the low- and high-temperature limit summaries, Unit IIIC, Sec. IIIC). In the high-temperature, classical limit,  $T \gg \theta_D$ , the phonon gas is fully excited and  $\bar{c}_{v,\text{phn}} = 6 \cdot (\bar{R}/2)$ . In this low-temperature, quantum limit,  $T \ll \theta_D$ , the phonon gas is unexcited and the specific heat approaches zero. The form of this low temperature asymptote is one of the improvements that the Debye model makes over the Einstein model. Specifically (see Exmp. 7)

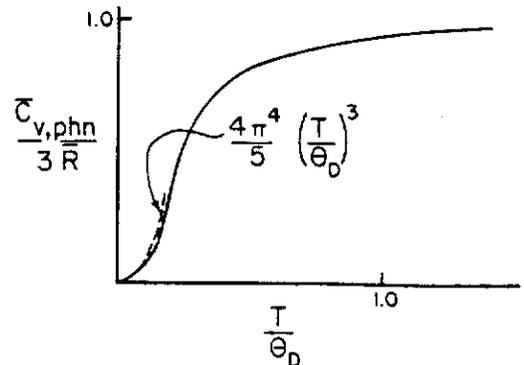


Fig. IIID-3 The Debye Specific Heat

$$\bar{c}_{v,\text{phn}} = \frac{12}{5} \pi^4 \bar{R} \left(\frac{T}{\theta_D}\right)^3 \quad \text{for} \quad \frac{T}{\theta_D} \lesssim \frac{1}{12} \quad (\text{IIID-17})$$

Example 7. Determine the low- and high-temperature asymptotes of the Debye integral, eqn IIID-14. Use these limits to formulate the low- and high-temperature asymptotes of the phonon energy, specific heat, and entropy.

Ans. 11. The necessary densities and molecular weights are found in Tables ID-2 and IA-2, respectively. Thus

$$c_{s,\text{Fe}} = \frac{k\theta_D}{h} \left( \frac{4\pi M}{3\rho N_A} \right)^{1/3} = \frac{1.380 \cdot 10^{-23} \text{ J/(part K)} \cdot 455 \text{ K}}{6.625 \cdot 10^{-34} \text{ Js/part}}$$

$$\cdot \left[ \frac{4\pi \cdot 55.85 \text{ g/(g mol)} \cdot 10^{-6} \text{ m}^3/\text{cm}^3}{3 \cdot 7.88 \text{ g/cm}^3 \cdot 6.023 \cdot 10^{23} \text{ part/(g mol)}} \right]^{1/3} = 3.48 \cdot 10^3 \text{ m/s}$$

Similarly for lead, using  $\theta_D = 86 \text{ K}$ ,  $\rho = 11.34 \text{ g/cm}^3$ ,  $M = 207.2 \text{ g/(g mol)}$ , one obtains,  $c_{s,\text{Pb}} = 901 \text{ m/s}$ .

Low-Temperature Limit,  $T \ll \theta_D$ . At low temperatures the upper limit of the Debye integral approaches infinity. This definite integral can be evaluated in terms of the gamma and Riemann zeta functions, see Ref. 5. Its value is  $\pi^4/15$ . So, limit  $x_D = \infty$ ,  $D(x_D) = (3/x_D^3)(\pi^4/15)$ .

Substituting into eqns. IIID-13, 15, and 16, we have

$$\bar{u}_{\text{phn}} = \frac{3\pi^4}{5} \bar{R} \left( \frac{T}{\theta_D} \right)^3 T \quad \bar{c}_{v,\text{phn}} = \frac{12}{5} \pi^4 \bar{R} \left( \frac{T}{\theta_D} \right)^3 \quad \bar{s}_{\text{phn}} = \frac{4\pi^4}{5} \bar{R} \left( \frac{T}{\theta_D} \right)^3$$

High-Temperature Limit,  $T \gg \theta_D$ . At high temperatures the exponential can be expanded

$$e^x \approx 1 + x \quad x = \frac{h\nu}{kT} < x_D = \frac{h\nu_D}{kT} \gg 1$$

Then the integral becomes

$$D(x_D) \Rightarrow \frac{3}{x_D^3} \int_0^{x_D} \frac{x^3 dx}{(1+x-1)} = \frac{3}{x_D^3} \left( \frac{x_D^3}{3} \right) = 1$$

Substituting into eqns. IIID-15, 17, and 18, we have

$$\bar{u}_{\text{phn}} = 3\bar{R}T \quad \bar{c}_{v,\text{phn}} = 3\bar{R} \left[ 4 - \frac{x_D}{(1+x_D-1)} \right] = 3\bar{R}$$

$$\bar{s}_{\text{phn}} = \bar{R} \left( 4 - 3 \ln[1 - (1 - x_D)] \right) = \bar{R} \left[ 4 - 3 \ln \left( \frac{T}{\theta_D} \right) \right]$$

Exercise 14. A silicon rectifier is to be used at liquid hydrogen temperatures, 22 K. What would be the lattice contribution to  $\bar{c}_v$  at that temperature?

## II. THE PROPERTIES OF FREE ELECTRONS

The valence electrons of a metal are shared among a large number of nearest and next nearest neighbors of the densely packed metallic lattice, see Sect. II of Unit ICS. As a result these electrons can move about within the crystal participating in the conduction of electricity and heat (see Unit IIIE). Thus, free electrons can be realistically modeled as independent particles translating within their crystalline box.<sup>18</sup> Their energy levels and degeneracies are essentially those of the particle in a box, see Table IIIA-1. In Sect. IIIA of Unit IIIC, we treated the translation of molecular gases. The characteristic temperature for translation was found to be

$$\theta_{\text{tr}} = \frac{h^2}{8m^* v^{2/3} k}$$

<sup>18</sup>The potential portion of the internal energy corresponding to the repulsion between the negatively charged electrons and the positively charged lattice points is insignificant in comparison to the kinetic portion of the free electron energy in metallic conductors. Thus, free electrons in a metal can be treated as independent particles. This assumption tends to break down in semiconductors. Free electron-lattice point interactions, or scattering, is important to the determination of the magnitude of free electron transport. This topic is considered in Unit IIIE.

Exercise 15. Determine the volume that would be required to achieve a free electron translational characteristic temperature of 1 K.

Exer. 15 demonstrates that although electrons are far lighter than even the lightest molecules,  $\theta_{tr}$  for free electrons remains low enough that free electron energy can also be considered continuous. Therefore, the free electron distribution can be written in terms of the degeneracy developed for the translation of independent molecules in Appendix

Ans. 12. Phonons are similar to photons in that:  $\alpha = 0$ ,  $\epsilon_j = hv_j$ , and the  $\sum_j \Rightarrow \int dv$ . Thus the general form of eqn. IIIB-17 reduces to

$$S_{phn} = \bar{n} \bar{s}_{phn} = \frac{\bar{n} \bar{u}_{phn}}{T} - k \int_0^{\infty} g_{phn}(v) \ln(1 - e^{-hv/kT}) dv$$

Then substituting from eqns. IIID-12a and 13b

$$S_{phn} = \bar{n} \bar{s}_{phn} = \bar{n} 3\bar{R}D(x_D) - \frac{12\pi V k}{c_s^3} \int_0^{v_D} v^2 \ln(1 - e^{-hv/kT}) dv$$

When the integral term is expressed in dimensionless form and transformed using the same definitions for integration by parts as defined in Exmp. 3, we obtain

$$-\frac{12\pi V k}{c_s^3} \left(\frac{kT}{h}\right)^3 \int_0^{\theta_D/T} x^2 \ln(1 - e^{-x}) dx = -12\pi V k \left(\frac{kT}{hc_s}\right)^3 \left\{ \left[ \frac{x^3}{3} \ln(1 - e^{-x}) \right]_0^{\theta_D/T} - \frac{1}{3} \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx \right\}$$

Then if we introduce the definition of  $\theta_D$  in the form

$$\theta_D^3 = \left(\frac{hc_s}{k}\right)^3 \frac{3N}{4\pi V} = \left(\frac{hc_s}{k}\right)^3 \frac{3nN_A}{4\pi V}$$

we obtain

$$S_{phn} = \bar{n} \bar{s}_{phn} = \bar{n} 3\bar{R}D(x_D) - 9nN_A k \left(\frac{T}{\theta_D}\right)^3 \left[ \frac{x_D^3}{3} \ln(1 - e^{-x_D}) - \frac{1}{3} \int_0^{x_D} \frac{x^3 dx}{e^x - 1} \right]$$

which gives eqn. IIID-16 using  $\bar{R} = \frac{N_A k}{A}$  and the definition of  $D(x_D)$

Ans. 13.  $\theta_D = 396$  K. Thus at 100 K,  $x_D = 396 \text{ K}/100 \text{ K} = 3.96$ . And from Table IIID-2,  $D(3.96) = 0.186$ . Substituting we obtain

$$\bar{u}_{phn} = 3\bar{R}[TD(x_D)] = 3 \cdot 8.314 \text{ J/(g mol K)} \cdot (100 \text{ K} \cdot 0.186) = 464 \text{ J/(g mol)}$$

$$\bar{c}_{v,phn}(x_D) = 3\bar{R} \left[ 4 D(x_D) - \frac{3x_D}{(e^{x_D} - 1)} \right] = 3 \cdot 8.314 \text{ J/(g mol K)} \cdot \left[ 4 \cdot 0.186 - \frac{3 \cdot 3.96}{(e^{3.96} - 1)} \right]$$

$$= 12.8 \text{ J/(g mol K)}$$

$$\bar{s}_{phn} = \bar{R} \left[ 4 D(x_D) - 3 \ln(1 - e^{-x_D}) \right] = 8.314 \text{ J/(g mol K)} \cdot \left[ 4 \cdot 0.186 - 3 \ln(1 - e^{-3.96}) \right]$$

$$= 6.67 \text{ J/(g mol K)}$$

In a similar manner find

T(K)	$x_D$	$D(x_D)$	$\frac{\bar{u}_{phn}(x_D)}{R\theta_D}$	$\frac{\bar{c}_{v,phn}(x_D)}{R}$	$\frac{\bar{s}_{phn}}{R}$
100	1.96	0.186	0.140	1.53	0.802
300	1.32	0.600	1.16	2.87	3.33
1000	0.396	0.860	6.52	2.98	6.79

IIIC-A, eqn IIIC-A1. The only necessary modification is multiplication by a factor of two to account for the fact that free electrons may have either spin up or spin down.<sup>19</sup>

$$g_{el}(\epsilon) = 4\pi V \left( \frac{2 m_e^*}{h^2} \right)^{3/2} \epsilon^{1/2} \quad (\text{IIID-18})$$

The introduction to the unit, specifically Exer. 1, demonstrated that free electrons in a metal do not satisfy the Boltzmann limit. Therefore, before we develop their property contributions, we must evaluate the unknown Lagrange multiplier  $\alpha$  applicable to free electrons. In the preceding section we found that  $\alpha$  equals zero for systems in which the particles are massless. This conclusion was reached by exploiting the fact that massless particles need not be conserved. However, free electrons are not massless; they must be conserved. Thus, we cannot use the same technique with free electrons.

Recall that the Boltzmann limit is prescribed by the condition  $(g_j/n_j)_{\max} \Rightarrow e^\alpha \gg 1$ . The fact that free electrons do not even come close to satisfying the Boltzmann limit restricts the possible values of  $\alpha$  substantially, viz.,  $0 < e^\alpha \sim 1$ . That is,  $\alpha$  is restricted to at most small positive, zero, or negative values. As we noted at the beginning of this unit, approach to the limit is promoted by high temperatures. So we expect  $\alpha$  to be a function of temperature such that it becomes increasingly negative as temperature decreases. With the aid of this perception we introduce the definition<sup>20</sup>

$$\alpha \equiv - \frac{\epsilon_F}{kT} \quad (\text{IIID-19})$$

$\epsilon_F$  has units of energy and is called the *Fermi level* (or *Fermi energy*).<sup>21</sup> With this definition, the Fermi distribution function becomes

$$F(\epsilon) = \frac{n^{FD}(\epsilon)}{g(\epsilon)} = \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1} \quad (\text{IIIB-14})$$

<sup>19</sup>In addition to translation, the electrons undergo rotation about their own axes. Because of their charge, this motion gives rise to a magnetic moment which acts up or down according to the direction of rotation. In the absence of an external field, the energy associated with this motion is constant, so it is neglected. The degeneracy, however, is multiplied by a factor of two due to the up or down orientation of the spin vector.

<sup>20</sup>This definition introduces no new assumptions as long as we do not prescribe that  $\epsilon_F$  is a constant. The significance of the definition is that by separating the anticipated approximate relationship of  $\alpha$  with temperature, we may expect  $\epsilon_F$  to be, at best, only weakly dependent on  $T$ .

<sup>21</sup> $\epsilon_F$  is the chemical potential ( $\mu$ ) or Gibbs function per particle discussed in Unit VID. For a formal identification of  $\alpha$ , see Ref. 7.

Ans. 14. For silicon  $\theta_D = 658$  K. Thus  $x_D = 658 \text{ K} / 22 \text{ K} = 29.9$ . The low-temperature approximation is applicable

$$\bar{c}_{v,phn} = \frac{12}{5} \pi^4 \frac{8.314 \text{ J/(g mol K)}}{(29.9)^3} = 7.27 \cdot 10^{-2} \text{ J/(g mol K)}$$

The Fermi function,  $F(\epsilon)$ , is sketched in Fig. IIID-4 for different temperature ranges.

(Remember that no more than one Fermion can occupy the same state,  $0 \leq F(\epsilon) \leq 1$ .) At absolute zero temperature,  $F(\epsilon)$  is a step function—all of the states up to the Fermi level,  $\epsilon_F^0 = \epsilon_F(0 \text{ K})$ , are full and all of the states above

this level are empty. Notice that the distribution corresponding to  $T \ll \epsilon_F^0/k$ , the degenerate range, departs only slightly from the  $T = 0 \text{ K}$  distribution. It will be seen below that all temperatures below the melting point of metals lie in the range  $T \ll \epsilon_F^0/k$ . Hence the distribution at  $0 \text{ K}$ , or the value of  $\epsilon_F^0$ , is extremely significant in determining the properties of free electrons.

The expression for the degeneracy in conjunction with the simplified distribution function at zero temperature [ $n_{el}(\epsilon) = g_{el}(\epsilon)$  at  $\epsilon \leq \epsilon_F^0$ ;  $n_{el}(\epsilon) = 0$  at  $\epsilon > \epsilon_F^0$ ] and the conservation of particles condition,  $N_{el} = \int_0^{\infty} dn_{el}$ , allows an expression for  $\epsilon_F^0$  to be developed.

**Example 8.** Derive an expression for  $\epsilon_F^0$  in terms of the valence, molecular weight, and density of the crystal by applying the conservation of particles condition at absolute zero.

At zero temperature the distribution function is given as<sup>22</sup>

$$n_{el}|_{T=0} = g_{el}(\epsilon) = 4\pi V \left( \frac{2m_{el}^*}{h^2} \right)^{3/2} \epsilon^{1/2} \quad \epsilon \leq \epsilon_F^0 \quad n_{el}|_{T=0} = 0 \quad \epsilon > \epsilon_F^0$$

Thus we can express the total number of electrons as

$$N_{el} = \int_0^{\infty} g_{el}(\epsilon) d\epsilon = 4\pi V \left( \frac{2m_{el}^*}{h^2} \right)^{3/2} \int_0^{\epsilon_F^0} \epsilon^{1/2} d\epsilon + \int_{\epsilon_F^0}^{\infty} (0) d\epsilon$$

$$N_{el} = 4\pi V \left( \frac{2m_{el}^*}{h^2} \right)^{3/2} \cdot \frac{2}{3} \epsilon_F^0{}^{3/2} \quad \text{or} \quad \epsilon_F^0 = \frac{h^2}{8m_{el}^*} \left( \frac{3 N_{el}}{\pi V} \right)^{2/3}$$

<sup>22</sup>The statement "at zero temperature" should not be taken too literally. At zero temperature, the series cannot be represented as a continuous function and eqn. IIID-18 is invalid.

Ans. 15. Substituting  $m_{el}^* = 9.109 \cdot 10^{-31} \text{ kg}$

$$v = \left( \frac{h^2}{8 m_{el}^* k \theta_{tr}} \right)^{3/2} = \left[ \frac{(6.625 \cdot 10^{-34} \text{ Js/elect})^2}{8 \cdot 9.109 \cdot 10^{-31} \text{ kg} \cdot 1.380 \cdot 10^{-23} \text{ J/(elect K) 1 K}} \right]^{3/2} = 2.88 \cdot 10^{-22} \text{ m}^3$$

or a cube 661 Å on a side.

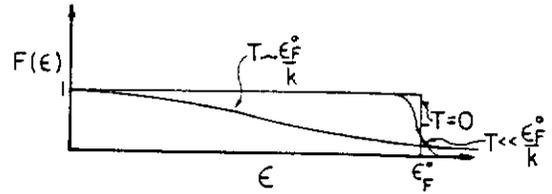


Fig. IIID-4. The Fermi Function

The characteristics of Fermi distribution were delineated in Fig. IIID-4, for the various temperature ranges defined in terms of  $\epsilon_F^\circ/k$ . With the expression for  $\epsilon_F^\circ$  developed in Exmp. 8, we can quantify the comparison of temperatures by defining a characteristic *Fermi temperature*.

$$\theta_F = \frac{\epsilon_F^\circ}{k} = \frac{h^2}{8m_{el}^* k} \left( \frac{3n_e N_A}{\pi \bar{v}} \right)^{2/3} \quad (\text{IIID-20})$$

where  $n_e$  is the valence of the atom and  $\bar{v}$  is the molar crystalline specific volume.

Exercise 16. Determine the magnitude of the Fermi temperature for aluminum, copper, and lead. (The necessary valences, molecular weights, and densities are found in Tables IA-1 and ID-2.)

The answer to Exer. 16 and Table IIID-1 demonstrate that the values of  $\theta_F$  are so large that the free electrons of a metallic crystal are always within the degenerate limit,  $T \ll \theta_F$ . Their distribution is the rounded step of Fig. IIID-4, departing only slightly from the  $T = 0$  K distribution. The average energy of the electrons can be estimated from the absolute zero distribution.

Example 9. Determine the minimum average particle energy for a free electron gas, i.e., at absolute zero temperature. Compare this energy to that which the electrons would have if they were classical translating particles,  $\epsilon_{tr,class} = (3/2) kT$ , by defining the *kinetic temperature* of free electrons:  $T_{kin} \equiv (2/3) \bar{\epsilon}_{tr}/k$ .

The average energy of a system of particles is defined by  $\bar{\epsilon} \equiv \sum_j \rho_j \epsilon_j$ . For a system of free electrons this general relationship becomes

$$\bar{\epsilon}_{el} = \frac{1}{N_{el}} \int_0^\infty \epsilon n_{el} d\epsilon$$

At absolute zero,  $n_{el} = g_{el}$  for  $\epsilon < \epsilon_F^\circ$  and  $n_{el} = 0$ ,  $\epsilon > \epsilon_F^\circ$ .

$$\bar{\epsilon}_{el}^\circ = \frac{1}{N_{el}} \int_0^{\epsilon_F^\circ} \epsilon g_{el}(\epsilon) d\epsilon = \frac{4\pi V}{N_{el}} \left( \frac{2m_{el}^*}{h^2} \right)^{3/2} \int_0^{\epsilon_F^\circ} \epsilon \epsilon^{1/2} d\epsilon = \frac{4\pi V}{N_{el}} \left( \frac{2m_{el}^*}{h^2} \right)^{3/2} \left( \frac{2}{5} \epsilon_F^{\circ 5/2} \right)$$

Then substituting from Exmp. 8 for  $N_{el} = 4\pi V (2m_{el}^*/h^2)^{3/2} (2/3) \cdot \epsilon_F^{\circ 3/2}$ , we obtain  $\bar{\epsilon}_{el}^\circ = \frac{3}{5} \epsilon_F^\circ$ .

Employing the definition of the kinetic temperature, we find

$$T_{kin}^\circ = \frac{2}{3} \frac{\bar{\epsilon}_{el}^\circ}{k} = \frac{2}{3} \cdot \frac{3}{5} \frac{\epsilon_F^\circ}{k} = \frac{2}{5} \theta_F$$

Thus the kinetic temperature of free electrons even in the limit of zero absolute is enormous. The average electron still moves very rapidly.<sup>23</sup>

<sup>23</sup>The concept of kinetic temperature provides a means to compare the energy of degenerate free electrons to a hypothetical classical energy in the more recognizable units of temperature. The thermodynamic temperature of the electrons remains that of the lattice with which they are in equilibrium.

Since free electrons are highly degenerate at ordinary temperatures, only those particles in states within a few  $kT$  of the Fermi level are excited and these only to a few  $kT$  above  $\epsilon_F^0$ .<sup>24</sup> As a result the internal energy of a free electron gas is only slightly more than that at absolute zero. On the basis of the *free electron model* presented in this section the free electron contribution to internal energy and specific heat are found to be (the development of this relationship is rather complicated, see Ref. 7)

$$\bar{u}_{el} = \frac{3}{5} \bar{R} \theta_F \left[ 1 + \frac{5}{12} \pi^2 \left( \frac{T}{\theta_F} \right)^2 \right] \quad \bar{c}_{v,el} = \left( \frac{\partial \bar{u}_{el}}{\partial T} \right)_{\bar{v}} = \frac{\pi^2}{2} \bar{R} \left( \frac{T}{\theta_F} \right) \quad (\text{IIID-21,22})$$

Thus the free electron contribution to the specific heat is predicted to be linearly proportional to temperature and is quite small since  $T \ll \theta_F$ . Both of these general predictions are validated by experiment. However, the simple free electron model is apparently not sufficient to accurately predict the temperature coefficient in all metals. We will nevertheless employ these relationships in the following section to predict the total properties of solids.

### III. THE PROPERTIES OF SOLIDS

We have developed the properties of photon, phonon and free electron gases. All three are present within a conducting solid. Though the photon gas is always present, we saw in Exer. 9 that its property contributions are negligible when compared to, even very low density, matter. Thus the properties of metallic conductors can be approximated as the sum of the phonon and free electron contributions:

$$\bar{u}_{mtl} = \bar{u}_{phn} + \bar{u}_{el} \quad \bar{c}_{v,mtl} = \bar{c}_{v,phn} + \bar{c}_{v,el} \quad (\text{IIID-23a,b})$$

The following problem illustrates the relative magnitudes of these contributions.

Example 10. Determine the phonon and free electron contribution to the zero point energy of copper ( $\bar{u}_{phn}^0 = 9/8 \bar{R} \theta_D$ , see footnote 18). In addition, determine the internal energy ( $\bar{u} - \bar{u}^0$ ) and specific heat contributions of these components at 100, 300, and 1000 K.

The phonon contributions can be determined using  $\theta_D = 315$  K and eqns. IIID-13b and 15.

$$\bar{u}_{phn}^0 = \frac{9}{8} \bar{R} \theta_D = \frac{9}{8} \cdot 8.314 \text{ J/(g mol K)} \cdot 315 \text{ K} = 2947 \text{ J/(g mol)}$$

With  $x_D = \theta_D/T = 315 \text{ K}/100 \text{ K} = 3.15$ , we find  $D(3.15) = 0.268$ . This gives

$$(\bar{u} - \bar{u}^0)(100 \text{ K})_{phn} = 3 \bar{R} T D(x_D) = 3 \cdot 8.314 \text{ J/(g mol K)} \cdot 100 \text{ K} \cdot 0.268 = 669 \text{ J/(g mol)}$$

and

$$\bar{c}_{v,phn}(100 \text{ K}) = 3 \bar{R} \left[ 4D(x_D) - \frac{3x_D}{e^{x_D} - 1} \right] = 3 \cdot 8.314 \text{ J/(g mol K)} \left[ 4 \cdot 0.268 - \frac{3 \cdot 3.15}{(e^{3.15} - 1)} \right] = 16.2 \text{ J/(g mol K)}$$

<sup>24</sup>The Fermi level is depressed very slightly from its value at absolute zero

$$\epsilon_F = \epsilon_F^0 \left[ 1 - \frac{\pi^2}{12} \left( \frac{T}{\theta_F} \right)^2 \right]$$

Free electron properties are determined using eqn. IIID-21 and 22

$$\bar{u}_{el}^{\circ} = \frac{3}{5} \bar{R} \theta_F = \left(\frac{3}{5}\right) \cdot 8.314 \text{ J/(g mol K)} \cdot 8.16 \cdot 10^4 \text{ K} = 4.07 \cdot 10^5 \text{ J/(g mol)}$$

$$\bar{u}_{el}(100 \text{ K}) - \bar{u}_{el}^{\circ} = \bar{u}_{el}^{\circ} \cdot \left(\frac{5}{12}\right) \cdot \pi^2 \left(\frac{T}{\theta_F}\right)^2 = 4.07 \cdot 10^5 \text{ J/(g mol)} \cdot \left(\frac{5}{12}\right) \cdot \pi^2 \left(\frac{100 \text{ K}}{8.16 \cdot 10^4 \text{ K}}\right)^2 = 2.51 \text{ J/(g mol)}$$

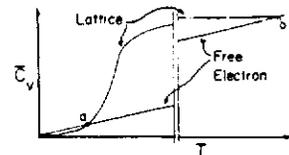
$$\bar{c}_{v,el} = \frac{\pi^2}{2} \bar{R} \left(\frac{T}{\theta_F}\right) = \frac{\pi^2}{2} \cdot 8.314 \text{ J/(g mol K)} \cdot \left(\frac{100 \text{ K}}{8.16 \cdot 10^4 \text{ K}}\right) = 0.0503 \text{ J/(g mol K)}$$

The values at other temperatures are found similarly. The results are shown in tabular form.

T (K)	$\frac{(\bar{u} - \bar{u}^{\circ})_{phn}}{\bar{R}}$ (K)	$\frac{\bar{c}_{v,phn}}{\bar{R}}$	$\frac{(\bar{u} - \bar{u}^{\circ})_{el}}{\bar{R}}$ (K)	$\frac{\bar{c}_{v,el}}{\bar{R}}$	$\frac{\bar{u} - \bar{u}^{\circ}}{\bar{R}}$ (K)	$\frac{\bar{u}_{latl}}{\bar{R}}$ (K)	$\frac{\bar{c}_{v,latl}}{\bar{R}}$
100	80.4	1.95	0.301	$0.605 \cdot 10^{-2}$	80.7	$4.94 \cdot 10^4$	1.96
300	597	2.87	2.72	$1.82 \cdot 10^{-2}$	600	$4.99 \cdot 10^4$	2.89
1000	2660	3.00	30.1	$6.05 \cdot 10^{-2}$	2690	$5.20 \cdot 10^4$	3.06

Although Exmp. 10 treats a specific substance, it allows one to draw general conclusions. The zero point energy of the free electrons is a large component of the total energy of a metallic conductor. So much so that it masks the important effect of the variation of net energy with temperature. At ordinary temperatures,  $\theta_D < T \ll \theta_F$ , phonons make a dominant contribution to energy change or specific heats, although the free electron contribution is not negligible. At low temperatures ( $T \ll \theta_D, \theta_F$ ) the phonon component of specific heat becomes proportional to  $T^3$ , but the free electron contribution remains linear. Thus as temperature is reduced below a certain level the electron contribution becomes more important and it will dominate at sufficiently low temperature levels.

Exercise 17. The linear temperature dependence of  $\bar{c}_{v,el}$  assures that it will dominate  $\bar{c}_{v,phn}$  at both sufficiently low and, in theory, at sufficiently high temperatures. Determine both the low and high temperatures,  $T_a$  and  $T_b$ , where  $\bar{c}_{v,phn} = \bar{c}_{v,el}$  for solid silver.



Ans. 16. The necessary valences and molecular weights can be extracted from Table IA-1 and the densities from Table ID-2.

Al,  $n_e = 3$ ,  $M = 26.98 \text{ g/(g mol)}$ ,  $\rho = 2.70 \text{ g/cm}^3$ ; Cu,  $n_e = 1$ ,  $M = 63.55 \text{ g/(g mol)}$ ,  $\rho = 8.94 \text{ g/cm}^3$ ; Pb,  $n_e = 2$ ,  $M = 207.2 \text{ g/(g mol)}$ ,  $\rho = 11.34 \text{ g/cm}^3$ . Thus using eqn. IIID-20

$$\theta_{F,Al} = \frac{(6.625 \cdot 10^{-34} \text{ Js/elect})^2}{8 \cdot 9.109 \cdot 10^{-31} \text{ kg} \cdot 1.380 \cdot 10^{-23} \text{ J/elect K}} \cdot \left[ \frac{3 \cdot 3 \text{ elect/part} \cdot 2.70 \cdot 10^3 \text{ kg/m}^3 \cdot 6.023 \cdot 10^{26} \text{ part/kg mol}}{\pi \cdot 26.98 \text{ kg/(kg mol)}} \right]^{2/3} = 1.35 \cdot 10^5 \text{ K}$$

Similarly,  $\theta_{F,Cu} = 8.16 \cdot 10^4 \text{ K}$ ,  $\theta_{F,Pb} = 6.91 \cdot 10^4 \text{ K}$ .

Free electrons contribute to the properties of all conductors. Our development of free electron properties, however, has been limited to materials in which the number of free electrons is fixed. This is true for the metallic conductors and of course for non-conductors which have no free electrons. In semiconductors the number of free electrons varies with temperature and eqns. IIID-21 and 22 are inadequate to describe their properties. The manner of this variation is discussed qualitatively in Unit III E in terms of its significance to transport properties. Although free electrons make only marginal contributions to "thermostatic" properties, they are of primary importance to transport and transport properties.

Thus far we have considered only elemental solids that have lattice points occupied by atoms. These elements include the metals, rare gases, and the transition elements (see Unit ICS). In these solids the only vibrational modes are those associated with oscillation of the atoms with respect to the bonds that join them. Since each atom is fixed by the same bonds, the single characteristic temperature of the Debye model is reasonably successful in predicting the vibrational energy of these lattices. This characteristic is shared by the compound crystal formed of ionic molecules—the sodium chloride structure, see Fig. ICS-6. Each atom in this structure is also fixed in position by identical bonds. Thus a single Debye temperature is sufficient to model these crystals as well. It is, however, necessary to account for the fact that there are three modes of vibration per atom or  $2 \cdot 3 = 6$  modes per molecule. The Debye cutoff frequency is determined by the total number of lattice vibration modes. Thus for *ionic molecular solids* formed in the *sodium chloride structure* the *Debye temperature* is related to the sound speed by

$$\theta_D = \frac{hc_s}{k} \left( \frac{6N_A}{4\bar{v}} \right)^{1/3} \quad (\text{IIID-24a})$$

The phonon contribution to the internal energy and specific heat of these insulating crystals becomes

$$\bar{u}_{\text{phn}}(T, \theta_D) = 6\bar{R}T D(x_D) \quad \bar{c}_{v,\text{phn}} = 6\bar{R} \left[ 4D(x_D) - \frac{3x_D}{(e^{x_D}-1)} \right] \quad (\text{IIID-25,26})$$

Exercise 18. What is the specific heat of table salt (NaCl) at STP? What will be the high temperature limit value of  $\bar{c}_v$  and at what temperature will it be achieved?

Exercise 19. The sound speed and density of potassium chloride are reported to be 2430 m/s and 1.99 g/cm<sup>3</sup>. Determine the Debye temperature of this crystal and estimate its specific heat at room temperature.

An examination of eqn. IIID-25 or the answer to Exer. 18 reveals that the classical limit,  $T \gg \theta_D$ , lattice specific heat of a sodium chloride structure solid is  $6\bar{R}$ . (Recall that the limit is  $3\bar{R}$  in atomic lattice point elements.) This result can be generalized to all molecular and atomic solids. Each atom in a solid has three degrees of

vibrational freedom and the classical limit energy of each vibrational degree of freedom is  $2 \cdot (kT/2)$ . Thus the *classical limit vibrational specific heat of all pure substance solids* is  $\bar{c}_v = 3n_a \bar{R}$ , where  $n_a$  is the number of atoms per molecule. However, more detailed consideration of solids whose lattice points are occupied by molecules requires that we differentiate between the intramolecular vibrations that affect the crystal as a whole, *the acoustical modes*, and the vibrations that occur within the molecule, *the optical modes*.<sup>25</sup>

Optical Modes. The molecules that occupy the lattice points of a solid have associated *internal* vibrational modes which number  $3n_a - 5$  in linear molecules and  $3n_a - 6$  in nonlinear molecules (see Unit IIIC, Sect. IIIC). In general these modes are initiated at relatively high temperatures, see Table IIIC-2, and occur at a relatively fixed frequency.<sup>26</sup> The property contributions of these modes can be predicted in the same manner as that for internal vibration of a gas molecule.<sup>27</sup>

Acoustical Modes. Molecular lattice points vibrate both linearly and torsionally with respect to the forces that bind them one to another in the lattice. Vibration of any individual molecule in one of these modes will induce vibration in its other modes and those of its neighbors. Thus the external vibrational modes (five per molecule in linear molecules, six per molecule in nonlinear molecules) are not fixed to any particular lattice point nor do they occur at any single frequency. These modes belong to the lattice as a whole—

<sup>25</sup>Covalent molecules form molecular lattice point crystals. These include the homonuclear diatomic molecule crystals formed by the oxidizing elements, e.g.,  $N_2$ ,  $O_2$ ,  $Cl_2$ .

<sup>26</sup>The internal modes are called the optical modes because their excitation frequencies are sufficiently high that an incident photon is much more likely to be absorbed by excitation of an internal mode vibration than by lattice vibration. The external modes are called the acoustical modes because they are much more likely to absorb an incident phonon, sound wave, than are the high frequency internal modes.

<sup>27</sup>Table IIIC-1 gives a summary of the relationships needed to determine the property contributions of an internal vibrational mode. They were applied to the three modes of vibration of an atomic lattice under the Einstein model for the properties of solids. Application to the internal modes of a molecular lattice is considered in Appendix A.

Ans. 17. If state (a) is within the  $T^3$  region, then  $T_a$  is easily determined from the condition

$$\bar{c}_{v,el} = \frac{\pi^2}{2} \bar{R} \frac{T_a}{\theta_F} = \bar{c}_{v,phn} = \frac{12}{5} \pi^4 \bar{R} \left( \frac{T_a}{\theta_D} \right)^3 \quad \text{or} \quad T_a = \left[ \frac{5(215 \text{ K})^3}{24\pi^2 \cdot 6.35 \cdot 10^4 \text{ K}} \right]^{\frac{1}{3}} = 1.82 \text{ K}$$

Since  $T_a/\theta_D < 1/12$ , our initial assumption is justified.

Similarly if state (b) is at sufficiently high temperatures  $T > \theta_D$ , then  $\bar{c}_{v,phn} = 3\bar{R}$  and  $T_b$  can be determined from the condition.

$$\bar{c}_{v,el} = \frac{\pi^2}{2} \bar{R} \frac{T_b}{\theta_F} = \bar{c}_{v,phn} = 3\bar{R} \quad \text{or} \quad T_b = \frac{6}{\pi^2} \theta_F = \frac{6}{\pi^2} \cdot 6.35 \cdot 10^4 \text{ K} = 3.86 \cdot 10^4 \text{ K}$$

Since  $T_b \gg \theta_D$ , this assumption is also justified.

they generate phonons.<sup>26</sup> Thus like atomic lattices the external vibrational modes of a molecular lattice point crystal can be modeled with satisfactory accuracy using a single Debye cutoff temperature and the Debye continuum model.<sup>28</sup>

From the preceding discussion we conclude that the properties of molecular lattice point crystals can be treated as a linear superposition of an Einstein function for each of the separate internal modes and a Debye continuum for the collective external modes. The procedures required to complete such an evaluation are presented in Appendix A, which includes application to both ice and dry ice. But some general trends can be recognized without detailed study. The internal mode characteristic temperatures,  $\theta_{v,p}$  see Table IIIC-2, are often high enough that the optical modes are unexcited at ordinary temperatures (frequently up to the melting point of the solid). The Debye temperature can be determined from sound speed data. Often it is low enough that the acoustical modes are fully excited at ordinary temperatures. Under these conditions ( $\theta_D < T \ll \theta_{v,p}$ ) the specific heats of linear and nonlinear molecular crystals respectively are  $\bar{c}_{v,l} \approx 5\bar{R}$  and  $\bar{c}_{v,nl} \approx 6\bar{R}$ . A much more quantitative perception of these principles can be gained by studying Appendix A.

<sup>28</sup>The Debye model ignored the detailed motions of the atomic lattice. It accounted for the spring stiffness through the effect of sound speed on the cutoff temperature (or cutoff temperatures, if the longitudinal and transverse waves are treated separately). Improved results can be achieved if a model is used that accounts for the natural frequencies of the spring mass complex constituting the lattice. This can be done in terms of a modified frequency spectrum,  $g_{\text{phn}}(\nu)$ . In most cases the improvement in results is not warranted by the increased difficulty of calculation, see Ref. 6.

Ans. 18. From Table IIID-1,  $\theta_D = 281$  K and  $x_D = \theta_D/T = 281$  K/300 K = 0.937. Thus using Table IIID-2,  $D(x_D) = 0.693$ . So

$$\bar{c}_{v,\text{phn}}(300 \text{ K}) = 6\bar{R} \left[ 4 \cdot 0.693 - \frac{3 \cdot 0.937}{(e^{0.937} - 1)} \right] = 5.76 \bar{R} = 47.9 \text{ J/(g mol K)}$$

The classical limit is established at approximately  $x_D = 0.5$  or  $T = 2 \cdot 281$  K = 562 K. The limiting value is  $\bar{c}_{v,\text{phn}} = 6\bar{R}$ .

Ans. 19.  $M_K = 39.10$  and  $M_{\text{Cl}} = 35.45$ , thus  $M_{\text{KCl}} = 74.55$  kg/(kg mol)

$$\theta_D = \left( \frac{6 N_A \rho}{4\pi M} \right)^{1/3} \frac{hc}{k} = \left[ \frac{6 \cdot 6.023 \cdot 10^{26} / (\text{kg mol}) \cdot 1.99 \cdot 10^3 \text{ kg/m}^3}{4\pi \cdot 74.55 \text{ kg/(kg mol)}} \right]^{1/3} \\ \cdot \frac{6.625 \cdot 10^{-34} \text{ Js/part} \cdot 2430 \text{ m/s}}{1.380 \cdot 10^{-23} \text{ J/(part K)}} = 230 \text{ K}$$

Thus at room temperature,  $x_D = 230$  K/300 K = 0.767 and  $D(x_D) = 0.745$ . Finally

$$\bar{c}_{v,\text{phn}}(300 \text{ K}) = 6\bar{R} \left[ 4 \cdot 0.745 - \frac{3 \cdot 0.767}{(e^{0.767} - 1)} \right] = 5.90 \bar{R} = 49.1 \text{ J/(g mol K)}$$

We have been able to describe the properties of solids rather completely. The properties of liquids are more difficult to predict. At low energy levels, liquids are "solid like." Lattice vibrations predominate over translation of the particles from one region to another within the liquid. Thus the energy and specific heats of atomic and molecular liquids are not too different from those of solids just discussed. A major difference is that we must add an entropy component to account for the fact that liquid particles are nonlocalized indistinguishable particles. One difficulty in analyzing liquid properties is determining just how much of this "communal entropy" to include in evaluating the entropy of liquids. (The full communal entropy is the difference between the Maxwell-Boltzmann and Boltzmann limit entropies,  $s_{\text{comm}} = k \ln N!$ .) As the energy level of the liquid increases, a greater percentage of the particles are able to escape to new positions within the liquid lattice. In these instances a fixed neighbor, simple harmonic vibration model for the lattice energy is increasingly complicated. It may even be necessary to abandon the independent particle assumption. We leave quantitative determination of liquid properties to more advanced treatments.

APPENDIX IIID-A

MOLECULAR LATTICE POINT CRYSTALS

Each molecule in a molecular lattice point crystal contributes  $3n_a$  vibrational modes. In the text we pointed out how and why these modes could be divided between the optical and acoustical branches.

Optical Modes. There are  $P_l = 3n_a - 5$  or  $P_{nl} = 3n_a - 6$  optical modes per lattice point in linear and nonlinear molecule crystals, respectively. These modes are assumed to be *confined within the molecule* and to vibrate at a single fixed frequency. The property contributions of the internal, optical modes are to be predicted using the same relationships and characteristic temperatures as those used for vibration of gaseous molecules, see Table IIIC-1 and 2.

$$\bar{u}_{\text{opt}} = \bar{R} \sum_{p=1}^P \theta_{v,p} \left[ \frac{1}{2} + \frac{1}{(e^{x_{v,p}} - 1)} \right] \quad \bar{c}_{v,\text{opt}} = \bar{R} \sum_{p=1}^P (x_{v,p})^2 \cdot \frac{e^{x_{v,p}}}{(e^{x_{v,p}} - 1)^2} \quad (\text{IIID-A1,A2})$$

$$\bar{s}_{\text{opt}} = \bar{R} \left[ \sum_{p=1}^P \frac{x_{v,p}}{(e^{x_{v,p}} - 1)} - \ln(1 - e^{-x_{v,p}}) \right] \quad \text{where} \quad x_{v,p} = \frac{\theta_{v,p}}{T} \quad (\text{IIID-A3})$$

Acoustical Modes. There are 5 or 6 acoustical modes per lattice point in linear and nonlinear molecules, respectively. These modes are assumed to be distributed throughout the crystal as a whole. Their property contributions are to be predicted using the Debye continuum model. The characteristic temperatures are predicted by eqn. IIID-11b. Their respective property contributions are

$$\bar{u}_{l,l} = 5\bar{R}TD(x_{D,l}) \quad \bar{u}_{l,nl} = 6\bar{R}TD(x_{D,nl}) \quad (\text{IIID-A4a,b})$$

$$\bar{c}_{v(l,l)} = 5\bar{R} \left[ 4D(x_{D,l}) - \frac{3x_{D,l}}{(e^{x_{D,l}} - 1)} \right] \quad \bar{c}_{v(l,nl)} = 6\bar{R} \left[ 4D(x_{D,nl}) - \frac{3x_{D,nl}}{(e^{x_{D,nl}} - 1)} \right] \quad (\text{IIID-A5a,b})$$

$$\bar{s}_{l,l} = \frac{5}{3} \bar{R} \left[ 4D(x_{D,l}) - 3\ln(1 - e^{-x_{D,l}}) \right] \quad \bar{s}_{l,nl} = 2\bar{R} \left[ 4D(x_{D,nl}) - 3\ln(1 - e^{-x_{D,nl}}) \right] \quad (\text{IIID-A6a,b})$$

$$\text{where} \quad x_{D,l} = \frac{\theta_{D,l}}{T} \quad x_{D,nl} = \frac{\theta_{D,nl}}{T}$$

The total properties of the crystal are a linear superposition of optical and lattice properties.

$$\bar{u} = \bar{u}_{\text{opt}} + \bar{u}_l \quad \bar{c}_v = \bar{c}_{v,\text{opt}} + \bar{c}_{v,l} \quad \bar{s} = \bar{s}_{\text{opt}} + \bar{s}_l \quad (\text{IIID-A7a,b,c})$$

We illustrate the use of these relationships in the following problems.

Example A1. The speed of sound in solid water is reported as 3200 m/s. Predict the specific heat at constant volume for ice just below the melting point.

The vibrational characteristic temperatures are listed in Table IIIC-2: 2294 K, 5262 K, 5404 K. The Debye temperature is determined from eqn. IIID-A4b.

The required specific volume can be obtained from Table IC-3:  $v = v_s(0.01^\circ\text{C}) = 1.0908 \text{ cm}^3/\text{g}$ . Thus

$$\theta_D = \left( \frac{3N_A}{4\pi vM} \right)^{1/3} \cdot \frac{hc}{k} = \left[ \frac{3 \cdot 6.023 \cdot 10^{23} / (\text{g mol})}{4\pi \cdot 1.0908 \text{ cm}^3/\text{g} \cdot 18.02 \text{ g}/(\text{g mol})} \right]^{1/3}$$

$$\cdot \frac{6.625 \cdot 10^{-34} \text{ Js/part} \cdot 3.2 \cdot 10^5 \text{ cm/s}}{1.38 \cdot 10^{-23} \text{ J}/(\text{part K})} = 298 \text{ K}$$

Thus, at  $T = 0.01^\circ\text{C} = 273 \text{ K}$ ,  $x_{D,nl} = 298 \text{ K}/273 \text{ K} = 1.09$ .  $D(x_{D,nl}) = 0.653$  and

$$\frac{\bar{c}_{v,nl}}{R} = 6 \left[ 4 \cdot 0.653 - \frac{3 \cdot 1.09}{(e^{1.09} - 1)} \right] = 5.73$$

And  $x_{v,1} = 2294 \text{ K}/273 \text{ K} = 8.40$ ,  $x_{v,2} = 19.3$  and  $x_{v,3} = 19.8$

$$\frac{\bar{c}_{v,1}}{R} = (8.4)^2 \frac{e^{8.4}}{(e^{8.4} - 1)^2} = 0.0159, \quad \frac{\bar{c}_{v,2}}{R} = 1.55 \cdot 10^{-6}, \quad \frac{\bar{c}_{v,3}}{R} = 9.87 \cdot 10^{-7}$$

Finally,  $\bar{c}_{v,nl} = (5.73 + 0.0159 + 0 + 0) \cdot 8.314 \text{ J}/(\text{g mol K}) = 47.8 \text{ J}/(\text{g mol K})$

Exercise A1. The speed of sound in solid carbon dioxide (dry ice) is low enough that the acoustical waves of dry ice are fully excited at the temperature level of its normal sublimation point,  $-78^\circ\text{C}$ . Predict the specific heat at constant volume of dry ice at its normal sublimation point. (Answer on page 30.)

TABLE IIID-1 CHARACTERISTIC TEMPERATURES OF SOLIDS

Substance	Symbol	$\Theta_D$ (K)	$\Theta_F$ (K)
<u>Metals</u>			
Aluminum	Al	396	$13.5 \cdot 10^4$
Copper	Cu	315	$8.16 \cdot 10^4$
Chrome	Cr	402	$12.7 \cdot 10^4$
Gold	Au	165	$6.41 \cdot 10^4$
Indium	In	109	$9.95 \cdot 10^4$
Iron	Fe	455	$13.0 \cdot 10^4$
Lead	Pb	86	$6.91 \cdot 10^4$
Mercury	Hg	90	$5.11 \cdot 10^4$
Nickel	Ni	456	$13.6 \cdot 10^4$
Potassium	K	100	$2.33 \cdot 10^4$
Platinum	Pt	220	$11.0 \cdot 10^4$
Silver	Ag	215	$6.35 \cdot 10^4$
<u>Non Metals</u>			
Diamond	C	1860	
Germanium	Ge	366	
Silicon	Si	658	
Sodium Chloride	NaCl	281	
Tellurium	Te	89	

TABLE IIID-2 THE DEBYE FUNCTION

$x_D$	$D(x_D)$
0.0	1.0000
0.1	0.9630
0.2	0.9270
0.5	0.8250
1	0.6744
2	0.4411
3	0.2836
4	0.1817
5	0.1176
10	0.0193
20	0.0024
$\infty$	0

$$D(x_D) \equiv \frac{1}{x_D^3} \int_0^{x_D} \frac{x^3 dx}{(e^x - 1)}$$

$$\lim_{x_D \rightarrow \infty} x_D^3 D(x_D) = 3 \int_0^{\infty} \frac{x^3 dx}{(e^x - 1)} = 3 \cdot \left(\frac{\pi^4}{15}\right)$$

Ans. A1. The fact that the acoustical modes are fully excited,  $T \gg \Theta_{D,l}$ , implies that  $\bar{c}_{v,2} = 5\bar{R}$ . The characteristic temperatures of the 4 optical modes are: 960.1 K (2), 2932 K, 3380 K. At  $-78^\circ\text{C} = 195\text{ K}$ , their corresponding dimensionless temperatures are:  $x_{v,(1,2)} = 960.1\text{ K}/195\text{ K} = 4.92$ , (2),  $x_{v,3} = 9.91$ ,  $x_{v,4} = 17.3$ . Thus the optical mode specific heats are

$$\frac{\bar{c}_{v,v(1,2)}}{\bar{R}} = (x_{v(1,2)})^2 \frac{e^{x_{v,1,2}}}{e^{x_{v(1,2)}-1} - 1} = (4.92)^2 \frac{e^{4.92}}{(e^{4.92}-1)^2} = 0.179$$

Similarly,  $\bar{c}_{v,3}/\bar{R} = 4.88 \cdot 10^{-3}$ ,  $\bar{c}_{v,4}/\bar{R} = 9.18 \cdot 10^{-6}$ .

Thus the total specific heat is

$$\bar{c}_v = \bar{c}_{v,\ell} + \sum_{p=1}^4 \bar{c}_{v,p} = (5 + 2 \cdot 0.179 + 4.88 \cdot 10^{-3} + 9.18 \cdot 10^{-6})\bar{R} = 5.36 \bar{R} = 44.6 \text{ J/(g mol K)}$$