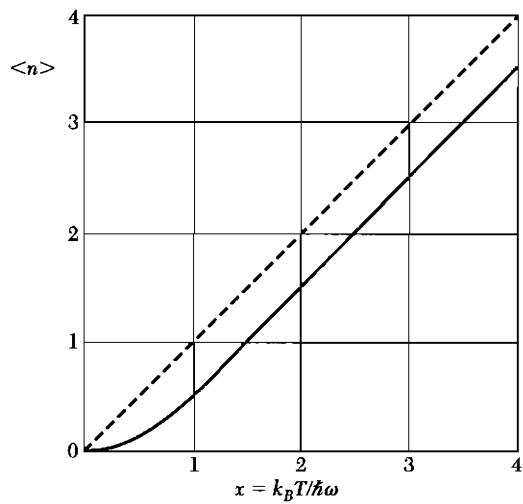


# 5

## *Phonons II. Thermal Properties*

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**Figure 1** Plot of Planck distribution function. At high temperatures the occupancy of a state is approximately linear in the temperature. The function  $\langle n \rangle + \frac{1}{2}$ , which is not plotted, approaches the dashed line as asymptote at high temperatures.

We discuss the heat capacity of a phonon gas and then the effects of anharmonic lattice interactions on the phonons and on the crystal.

### PHONON HEAT CAPACITY

By heat capacity we shall usually mean the heat capacity at constant volume, which is more fundamental than the heat capacity at constant pressure, which is what the experiments determine.<sup>1</sup> The heat capacity at constant volume is defined as  $C_V \equiv (\partial U / \partial T)_V$  where  $U$  is the energy and  $T$  the temperature.

The contribution of the phonons to the heat capacity of a crystal is called the lattice heat capacity and is denoted by  $C_{\text{lat}}$ . The total energy of the phonons at a temperature  $\tau (= k_B T)$  in a crystal may be written as the sum of the energies over all phonon modes, here indexed by the wavevector  $K$  and polarization index  $p$ :

$$U_{\text{lat}} = \sum_K \sum_p U_{Kp} = \sum_K \sum_p \langle n_{Kp} \rangle \hbar \omega_{Kp} , \quad (1)$$

where  $\langle n_{Kp} \rangle$  is the thermal equilibrium occupancy of phonons of wavevector  $K$  and polarization  $p$ . The form of  $\langle n_{Kp} \rangle$  is given by the Planck distribution function:

$$\langle n \rangle = \frac{1}{\exp(\hbar \omega / \tau) - 1} , \quad (2)$$

where the  $\langle \cdots \rangle$  denotes the average in thermal equilibrium. A graph of  $\langle n \rangle$  is given in Fig. 1.

#### Planck Distribution

Consider a set of identical harmonic oscillators in thermal equilibrium. The ratio of the number of oscillators in their  $(n + 1)$ th quantum state of excitation to the number in the  $n$ th quantum state is

$$N_{n+1}/N_n = \exp(-\hbar \omega / \tau) , \quad \tau \equiv k_B T , \quad (3)$$

<sup>1</sup>A thermodynamic relation gives  $C_p - C_V = 9\alpha^2 BVT$ , where  $\alpha$  is the temperature coefficient of linear expansion,  $V$  the volume, and  $B$  the bulk modulus. The fractional difference between  $C_p$  and  $C_V$  is usually small in solids and often may be neglected. As  $T \rightarrow 0$  we see that  $C_p \rightarrow C_V$ , provided  $\alpha$  and  $B$  are constant.

by use of the Boltzmann factor. Thus the fraction of the total number of oscillators in the  $n$ th quantum state is

$$\frac{N_n}{\sum_{s=0}^{\infty} N_s} = \frac{\exp(-n\hbar\omega/\tau)}{\sum_{s=0}^{\infty} \exp(-s\hbar\omega/\tau)} . \quad (4)$$

We see that the average excitation quantum number of an oscillator is

$$\langle n \rangle = \frac{\sum_s s \exp(-s\hbar\omega/\tau)}{\sum_s \exp(-s\hbar\omega/\tau)} . \quad (5)$$

The summations in (5) are

$$\sum_s x^s = \frac{1}{1-x} ; \quad \sum_s s x^s = x \frac{d}{dx} \sum_s x^s = \frac{x}{(1-x)^2} , \quad (6)$$

with  $x = \exp(-\hbar\omega/\tau)$ . Thus we may rewrite (5) as the Planck distribution:

$$\langle n \rangle = \frac{x}{1-x} = \frac{1}{\exp(\hbar\omega/\tau) - 1} . \quad (7)$$

### Normal Mode Enumeration

The energy of a collection of oscillators of frequencies  $\omega_{K,p}$  in thermal equilibrium is found from (1) and (2):

$$U = \sum_K \sum_p \frac{\hbar\omega_{K,p}}{\exp(\hbar\omega_{K,p}/\tau) - 1} . \quad (8)$$

It is usually convenient to replace the summation over  $K$  by an integral. Suppose that the crystal has  $D_p(\omega)d\omega$  modes of a given polarization  $p$  in the frequency range  $\omega$  to  $\omega + d\omega$ . Then the energy is

$$U = \sum_p \int d\omega D_p(\omega) \frac{\hbar\omega}{\exp(\hbar\omega/\tau) - 1} . \quad (9)$$

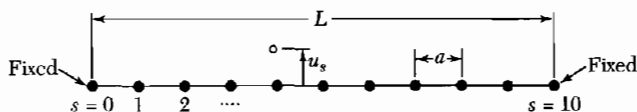
The lattice heat capacity is found by differentiation with respect to temperature. Let  $x = \hbar\omega/\tau = \hbar\omega/k_B T$ ; then  $\partial U/\partial T$  gives

$$C_{\text{lat}} = k_B \sum_p \int d\omega D_p(\omega) \frac{x^2 \exp x}{(\exp x - 1)^2} . \quad (10)$$

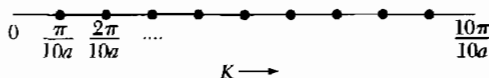
The central problem is to find  $D(\omega)$ , the number of modes per unit frequency range. This function is called the density of modes or, more often, density of states.

### Density of States in One Dimension

Consider the boundary value problem for vibrations of a one-dimensional line (Fig. 2) of length  $L$  carrying  $N + 1$  particles at separation  $a$ . We suppose



**Figure 2** Elastic line of  $N + 1$  atoms, with  $N = 10$ , for boundary conditions that the end atoms  $s = 0$  and  $s = 10$  are fixed. The particle displacements in the normal modes for either longitudinal or transverse displacements are of the form  $u_s \propto \sin sKa$ . This form is automatically zero at the atom at the end  $s = 0$ , and we choose  $K$  to make the displacement zero at the end  $s = 10$ .



**Figure 3** The boundary condition  $\sin sKa = 0$  for  $s = 10$  can be satisfied by choosing  $K = \pi/10a, 2\pi/10a, \dots, 9\pi/10a$ , where  $10a$  is the length  $L$  of the line. The present figure is in  $K$  space. The dots are not atoms but are the allowed values of  $K$ . Of the  $N + 1$  particles on the line, only  $N - 1$  are allowed to move, and their most general motion can be expressed in terms of the  $N - 1$  allowed values of  $K$ . This quantization of  $K$  has nothing to do with quantum mechanics but follows classically from the boundary conditions that the end atoms be fixed.

that the particles  $s = 0$  and  $s = N$  at the ends of the line are held fixed. Each normal vibrational mode of polarization  $p$  has the form of a standing wave, where  $u_s$  is the displacement of the particle  $s$ :

$$u_s = u(0) \exp(-i\omega_{K,p}t) \sin sKa, \quad (11)$$

where  $\omega_{K,p}$  is related to  $K$  by the appropriate dispersion relation.

As in Fig. 3, the wavevector  $K$  is restricted by the fixed-end boundary conditions to the values

$$K = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \dots, \frac{(N-1)\pi}{L}. \quad (12)$$

The solution for  $K = \pi/L$  has

$$u_s \propto \sin (s\pi a/L) \quad (13)$$

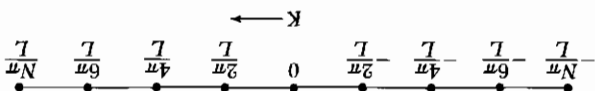
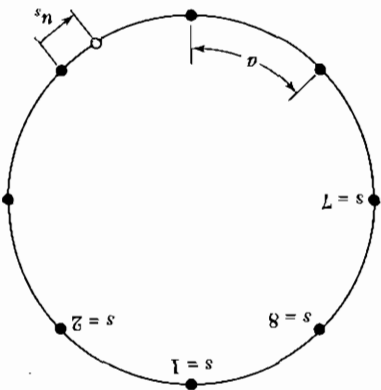
and vanishes for  $s = 0$  and  $s = N$  as required.

The solution for  $K = N\pi/L = \pi/a = K_{\max}$  has  $u_s \propto \sin s\pi$ ; this permits no motion of any atom, because  $\sin s\pi$  vanishes at each atom. Thus there are  $N - 1$  allowed independent values of  $K$  in (12). This number is equal to the number of particles allowed to move. Each allowed value of  $K$  is associated with a standing wave. For the one-dimensional line there is one mode for each interval  $\Delta K = \pi/L$ , so that the number of modes per unit range of  $K$  is  $L/\pi$  for  $K \leq \pi/a$ , and 0 for  $K > \pi/a$ .

There are three polarizations  $p$  for each value of  $K$ : in one dimension two of these are transverse and one longitudinal. In three dimensions the polarizations are this simple only for wavevectors in certain special crystal directions.

Another device for enumerating modes is equally valid. We consider the medium as unbounded, but require that the solutions be periodic over a large

**Figure 4** Consider  $N$  particles constrained to slide on a circular ring. The particles can oscillate if connected by elastic springs. In a normal mode the displacement  $u_s$  of atom  $s$  will be of the form  $\sin sKa$  or  $\cos sKa$ ; these are independent modes. By the geometrical periodicity of the ring the boundary condition is that  $u_{N+s} = u_s$  for all  $s$ , so that  $NKa$  must be an integral multiple of  $2\pi$ . For  $N = 8$  the allowed independent values of  $K$  are  $0, 2\pi/8a, 4\pi/8a, 6\pi/8a$ , and  $8\pi/8a$ . The value  $8\pi/8a$  has a meaning only for  $\sin sKa = 0$ . The value  $8\pi/8a$  has a meaning only for the cosine form, because  $\sin(s8\pi/8a) = \sin s\pi = 0$ . The three other values of  $K$  are allowed for both the sine and cosine modes, giving a total of eight allowed modes for the eight particles. Thus the periodic boundary condition leads to one allowed mode per particle, exactly as for the fixed-end boundary condition of Fig. 3. If we had taken the modes in the complex form  $\exp(isKa)$ , the periodic boundary condition would lead to the eight modes with  $K = 0, \pm 2\pi/Na, \pm 4\pi/Na, \pm 6\pi/Na$ , and  $8\pi/Na$ , as in Eq. (14).



**Figure 5** Allowed values of wavevector  $K$  for periodic boundary conditions applied to a linear lattice of periodicity  $N = 8$  atoms on a line of length  $L$ . The  $K = 0$  solution is the uniform mode. The special points  $\pm N\pi/L$  represent only a single solution because  $\exp(i\pi s) = \exp(-i\pi s)$ ; thus there are eight allowed modes, with displacements of the  $s$ th atom proportional to  $1, \exp(\pm i\pi s/4), \exp(\pm i\pi s/2), \exp(\pm i3\pi s/4), \exp(i\pi s)$ .

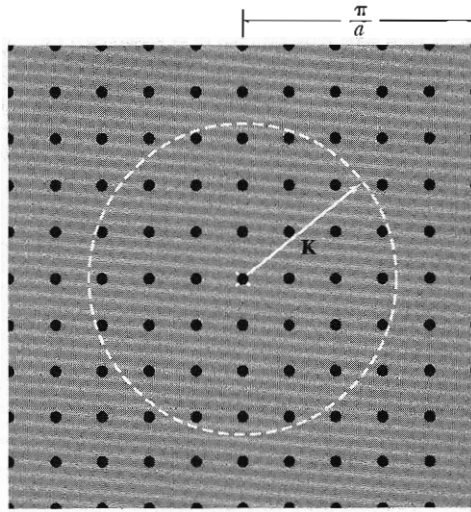
distance  $L$ , so that  $u(sa) = u(sa + L)$ . The method of **periodic boundary conditions** (Figs. 4 and 5) does not change the physics of the problem in any essential respect for a large system. In the running wave solution  $u_s = u(0) \exp[i(sKa - \omega t)]$  the allowed values of  $K$  are

$$K = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \pm \frac{6\pi}{L}, \dots, \pm \frac{N\pi}{L}. \quad (14)$$

This method of enumeration gives the same number of modes (one per mobile atom) as given by (12), but we have now both plus and minus values of  $K$ , with the interval  $\Delta K = 2\pi/L$  between successive values of  $K$ . For periodic boundary conditions, the number of modes per unit range of  $K$  is  $L/2\pi$  for  $-\pi/a \leq K \leq \pi/a$ , and 0 otherwise. The situation in a two-dimensional lattice is portrayed in Fig. 6.

We need to know  $D(\omega)$ , the number of modes per unit frequency range for a given polarization. The number of modes  $D(\omega) d\omega$  in  $d\omega$  at  $\omega$  is given in one dimension by

$$D_1(\omega) d\omega = \frac{L}{2\pi} \frac{dK}{d\omega} d\omega = \frac{\pi}{L} \cdot \frac{d\omega}{dK}. \quad (15)$$



**Figure 6** Allowed values in Fourier space of the phonon wavevector  $\mathbf{K}$  for a square lattice of lattice constant  $a$ , with periodic boundary conditions applied over a square of side  $L = 10a$ . The uniform mode is marked with a cross. There is one allowed value of  $\mathbf{K}$  per area  $(2\pi/10a)^2 = (2\pi/L)^2$ , so that within the circle of area  $\pi K^2$  the smoothed number of allowed points is  $\pi K^2 (L/2\pi)^2$ .

We can obtain the group velocity  $d\omega/dK$  from the dispersion relation  $\omega$  versus  $K$ . There is a singularity in  $D_1(\omega)$  whenever the dispersion relation  $\omega(K)$  is horizontal; that is, whenever the group velocity is zero.

### Density of States in Three Dimensions

We apply periodic boundary conditions over  $N^3$  primitive cells within a cube of side  $L$ , so that  $\mathbf{K}$  is determined by the condition

$$\exp[i(K_x x + K_y y + K_z z)] = \exp[i\{K_x(x + L) + K_y(y + L) + K_z(z + L)\}] , \quad (16)$$

whence

$$K_x, K_y, K_z = 0 ; \quad \pm \frac{2\pi}{L} ; \quad \pm \frac{4\pi}{L} ; \quad \dots ; \quad \frac{N\pi}{L} . \quad (17)$$

Therefore, there is one allowed value of  $\mathbf{K}$  per volume  $(2\pi/L)^3$  in  $\mathbf{K}$  space, or

$$\left( \frac{L}{2\pi} \right)^3 = \frac{V}{8\pi^3} \quad (18)$$

allowed values of  $\mathbf{K}$  per unit volume of  $\mathbf{K}$  space, for each polarization and for each branch. The volume of the specimen is  $V = L^3$ .

The total number of modes with wavevector less than  $K$  is found from (18) to be  $(L/2\pi)^3$  times the volume of a sphere of radius  $K$ . Thus

$$N = (L/2\pi)^3 (4\pi K^3/3) \quad (19)$$

for each polarization type. The density of states for each polarization is

$$D(\omega) = dN/d\omega = \langle VK^2/2\pi^2 \rangle \langle dK/d\omega \rangle . \quad (20)$$

### **Debye Model for Density of States**

In the Debye approximation the velocity of sound is taken as constant for each polarization type, as it would be for a classical elastic continuum. The dispersion relation is written as

$$\omega = vK , \quad (21)$$

with  $v$  the constant velocity of sound.

The density of states (20) becomes

$$D(\omega) = V\omega^2/2\pi^2v^3 . \quad (22)$$

If there are  $N$  primitive cells in the specimen, the total number of acoustic phonon modes is  $N$ . A cutoff frequency  $\omega_D$  is determined by (19) as

$$\omega_D^3 = 6\pi^2v^3N/V . \quad (23)$$

To this frequency there corresponds a cutoff wavevector in  $\mathbf{K}$  space:

$$K_D = \omega_D/v = (6\pi^2N/V)^{1/3} . \quad (24)$$

On the Debye model we do not allow modes of wavevector larger than  $K_D$ . The number of modes with  $K \leq K_D$  exhausts the number of degrees of freedom of a monatomic lattice.

The thermal energy (9) is given by

$$U = \int d\omega D(\omega) \langle n(\omega) \rangle \hbar\omega = \int_0^{\omega_D} d\omega \left( \frac{V\omega^2}{2\pi^2v^3} \right) \left( \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1} \right) , \quad (25)$$

for each polarization type. For brevity we assume that the phonon velocity is independent of the polarization, so that we multiply by the factor 3 to obtain

$$U = \frac{3V\hbar}{2\pi^2v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/\tau} - 1} = \frac{3Vk_B^4T^4}{2\pi^2v^3\hbar^3} \int_0^{x_D} dx \frac{x^3}{e^x - 1} , \quad (26)$$

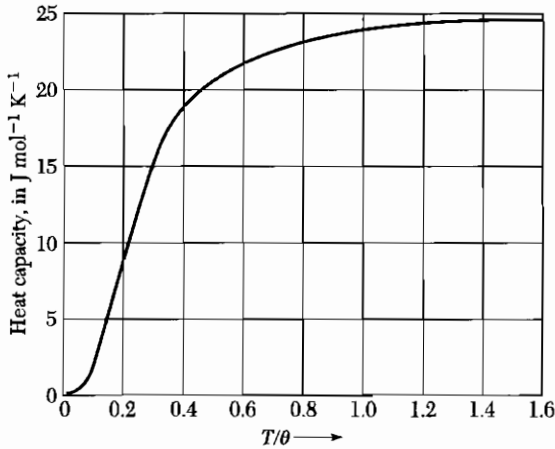
where  $x \equiv \hbar\omega/\tau \equiv \hbar\omega/k_B T$  and

$$x_D \equiv \hbar\omega_D/k_B T \equiv \theta/T . \quad (27)$$

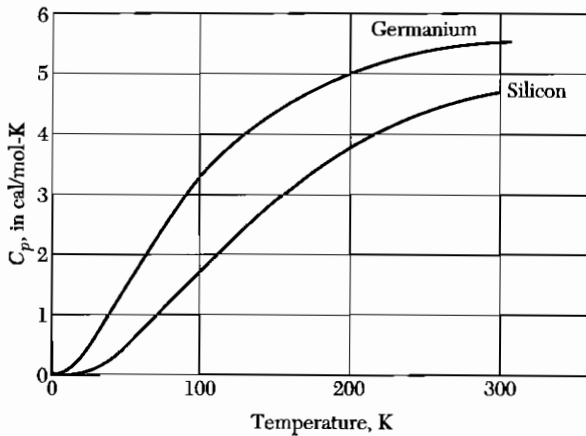
This defines the **Debye temperature**  $\theta$  in terms of  $\omega_D$  defined by (23). We may express  $\theta$  as

$$\theta = \frac{\hbar v}{k_B} \cdot \left( \frac{6\pi^2N}{V} \right)^{1/3} , \quad (28)$$





**Figure 7** Heat capacity  $C_V$  of a solid, according to the Debye approximation. The vertical scale is in  $\text{J mol}^{-1} \text{K}^{-1}$ . The horizontal scale is the temperature normalized to the Debye temperature  $\theta$ . The region of the  $T^3$  law is below  $0.1\theta$ . The asymptotic value at high values of  $T/\theta$  is  $24.943 \text{ J mol}^{-1} \text{deg}^{-1}$ .



**Figure 8** Heat capacity of silicon and germanium. Note the decrease at low temperatures. To convert a value in  $\text{cal/mol-K}$  to  $\text{J/mol-K}$ , multiply by 4.186.

so that the total phonon energy is

$$U = 9Nk_B T \left( \frac{T}{\theta} \right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1}, \quad (29)$$

where  $N$  is the number of atoms in the specimen and  $x_D = \theta/T$ .

The heat capacity is found most easily by differentiating the middle expression of (26) with respect to temperature. Then

$$C_V = \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{w_D} dw \frac{\omega^4 e^{\hbar w/\tau}}{(e^{\hbar w/\tau} - 1)^2} = 9Nk_B \left( \frac{T}{\theta} \right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2}. \quad (30)$$

The Debye heat capacity is plotted in Fig. 7. At  $T \gg \theta$  the heat capacity approaches the classical value of  $3Nk_B$ . Measured values for silicon and germanium are plotted in Fig. 8.

### Debye $T^3$ Law

At very low temperatures we may approximate (29) by letting the upper limit go to infinity. We have

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \int_0^\infty dx x^3 \sum_{s=1}^\infty \exp(-sx) = 6 \sum_{s=1}^\infty \frac{1}{s^4} = \frac{\pi^4}{15}, \quad (31)$$

where the sum over  $s^{-4}$  is found in standard tables. Thus  $U \cong 3\pi^4 N k_B T^4 / 5\theta^3$  for  $T \ll \theta$ , and

$$C_V \cong \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta}\right)^3 \cong 234 N k_B \left(\frac{T}{\theta}\right)^3, \quad (32)$$

which is the Debye  $T^3$  approximation. Experimental results for argon are plotted in Fig. 9.

At sufficiently low temperature the  $T^3$  approximation is quite good; that is, when only long wavelength acoustic modes are thermally excited. These are just the modes that may be treated as an elastic continuum with macroscopic elastic constants. The energy of the short wavelength modes (for which this approximation fails) is too high for them to be populated significantly at low temperatures.

We understand the  $T^3$  result by a simple argument (Fig. 10). Only those lattice modes having  $\hbar\omega < k_B T$  will be excited to any appreciable extent at a low temperature  $T$ . The excitation of these modes will be approximately classical, each with an energy close to  $k_B T$ , according to Fig. 1.

Of the allowed volume in  $\mathbf{K}$  space, the fraction occupied by the excited modes is of the order of  $(\omega_T/\omega_D)^3$  or  $(K_T/K_D)^3$ , where  $K_T$  is a "thermal" wavevector defined such that  $\hbar v K_T = k_B T$  and  $K_D$  is the Debye cutoff wavevector. Thus the fraction occupied is  $(T/\theta)^3$  of the total volume in  $\mathbf{K}$  space. There are of the order of  $3N(T/\theta)^3$  excited modes, each having energy  $k_B T$ . The energy is  $\sim 3Nk_B T(T/\theta)^3$ , and the heat capacity is  $\sim 12Nk_B(T/\theta)^3$ .

For actual crystals the temperatures at which the  $T^3$  approximation holds are quite low. It may be necessary to be below  $T = \theta/50$  to get reasonably pure  $T^3$  behavior.

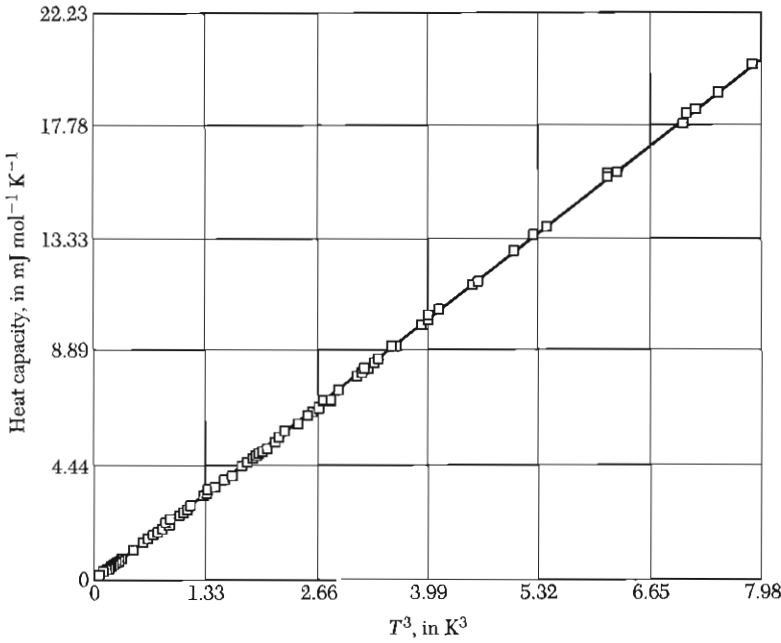
Selected values of  $\theta$  are given in Table 1. Note, for example, in the alkali metals that the heavier atoms have the lowest  $\theta$ 's, because the velocity of sound decreases as the density increases.

### Einstein Model of the Density of States

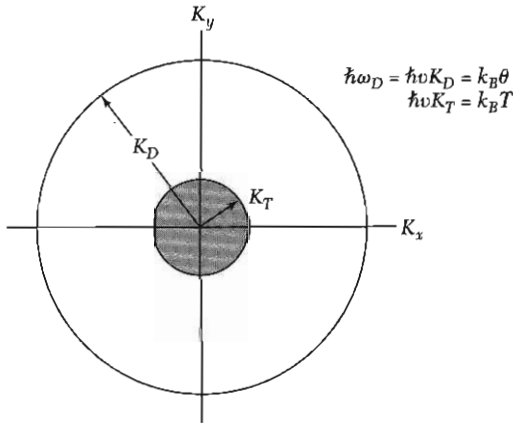
Consider  $N$  oscillators of the same frequency  $\omega_0$  and in one dimension. The Einstein density of states is  $D(\omega) = N\delta(\omega - \omega_0)$ , where the delta function is centered at  $\omega_0$ . The thermal energy of the system is

$$U = N\langle n \rangle \hbar\omega = \frac{N\hbar\omega}{e^{\hbar\omega/\tau} - 1}, \quad (33)$$

with  $\omega$  now written in place of  $\omega_0$ , for convenience.



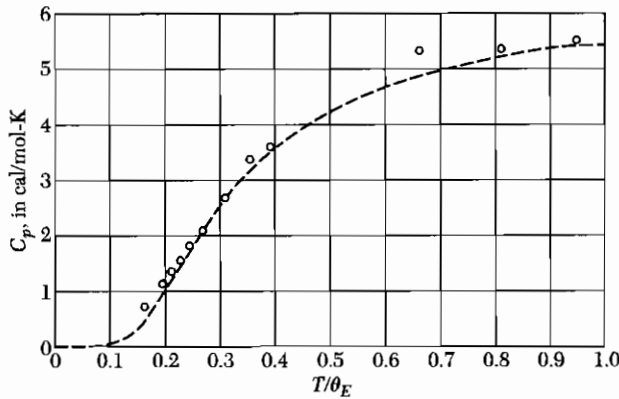
**Figure 9** Low temperature heat capacity of solid argon, plotted against  $T^3$ . In this temperature region the experimental results are in excellent agreement with the Debye  $T^3$  law with  $\theta = 92.0$  K. (Courtesy of L. Finegold and N. E. Phillips.)



**Figure 10** To obtain a qualitative explanation of the Debye  $T^3$  law, we suppose that all phonon modes of wavevector less than  $K_T$  have the classical thermal energy  $k_B T$  and that modes between  $K_T$  and the Debye cutoff  $K_D$  are not excited at all. Of the  $3N$  possible modes, the fraction excited is  $(K_T/K_D)^3 = (T/\theta)^3$ , because this is the ratio of the volume of the inner sphere to the outer sphere. The energy is  $U \approx k_B T \cdot 3N(T/\theta)^3$ , and the heat capacity is  $C_V = \partial U / \partial T = 12Nk_B(T/\theta)^3$ .

Table 1 Debye temperature and thermal conductivity

Table 1 Debye temperature and thermal conductivity																							
Li	Be																	B	C	N	O	F	Ne
344	1440																	2230					75
0.85	2.00																	0.27	1.29				
Na	Mg																	Al	Si	P	S	Cl	Ar
158	400																	428	645				92
1.41	1.56																	2.37	1.48				
Low temperature limit of $\theta$ , in Kelvin																							
Thermal conductivity at 300 K, in $\text{W cm}^{-1}\text{K}^{-1}$																							
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr						
91	230	360	420	380	630	410	470	445	450	343	327	320	374	282	90		72						
1.02		0.16	0.22	0.31	0.94	0.08	0.80	1.00	0.91	4.01	1.16	0.41	0.60	0.50	0.02								
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn <sup>w</sup>	Sb	Te	I	Xe						
56	147	280	291	275	450	500	600	480	274	225	209	108	200	211	153		64						
0.58		0.17	0.23	0.54	1.38	0.51	1.17	1.50	0.72	4.29	0.97	0.82	0.67	0.24	0.02								
Cs	Ba	La $\beta$	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn						
38	110	142	252	240	400	430	500	420	240	165	71.9	78.5	105	119									
0.36		0.14	0.23	0.58	1.74	0.48	0.88	1.47	0.72	3.17		0.46	0.35	0.08									
Fr	Ra	Ac																					
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu							
			0.11	0.12	0.16		0.13		0.11	0.11	0.11	0.16	0.14	0.17	0.35	0.16							
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr							
			163		207																		
			0.54		0.28	0.06	0.07																



**Figure 11** Comparison of experimental values of the heat capacity of diamond with values calculated on the earliest quantum (Einstein) model, using the characteristic temperature  $\theta_E = \hbar\omega/k_B = 1320$  K. To convert to J/mol-deg, multiply by 4.186.

The heat capacity of the oscillators is

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = Nk_B \left( \frac{\hbar\omega}{\tau} \right)^2 \frac{e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau} - 1)^2}, \quad (34)$$

as plotted in Fig. 11. This expresses the Einstein (1907) result for the contribution of  $N$  identical oscillators to the heat capacity of a solid. In three dimensions  $N$  is replaced by  $3N$ , there being three modes per oscillator. The high temperature limit of  $C_V$  becomes  $3Nk_B$ , which is known as the Dulong and Petit value.

At low temperatures (34) decreases as  $\exp(-\hbar\omega/\tau)$ , whereas the experimental form of the phonon contribution is known to be  $T^3$  as accounted for by the Debye model treated above. The Einstein model, however, is often used to approximate the optical phonon part of the phonon spectrum.

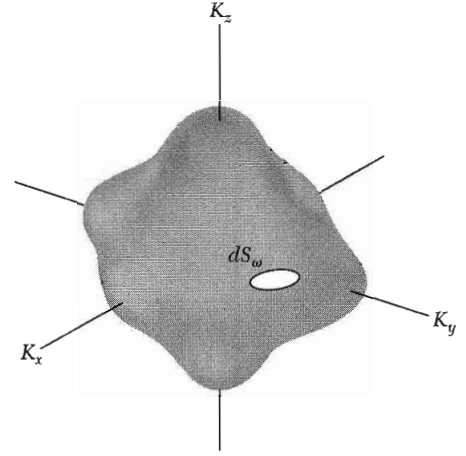
### General Result for $D(\omega)$

We want to find a general expression for  $D(\omega)$ , the number of states per unit frequency range, given the phonon dispersion relation  $\omega(\mathbf{K})$ . The number of allowed values of  $\mathbf{K}$  for which the phonon frequency is between  $\omega$  and  $\omega + d\omega$  is

$$D(\omega) d\omega = \left( \frac{L}{2\pi} \right)^3 \int_{\text{shell}} d^3K, \quad (35)$$

where the integral is extended over the volume of the shell in  $\mathbf{K}$  space bounded by the two surfaces on which the phonon frequency is constant, one surface on which the frequency is  $\omega$  and the other on which the frequency is  $\omega + d\omega$ .

The real problem is to evaluate the volume of this shell. We let  $dS_\omega$  denote an element of area (Fig. 12) on the surface in  $\mathbf{K}$  space of the selected constant



**Figure 12** Element of area  $dS_\omega$  on a constant frequency surface in  $\mathbf{K}$  space. The volume between two surfaces of constant frequency at  $\omega$  and  $\omega + d\omega$  is equal to  $\int dS_\omega d\omega / |\nabla_{\mathbf{K}}\omega|$ .

frequency  $\omega$ . The element of volume between the constant frequency surfaces  $\omega$  and  $\omega + d\omega$  is a right cylinder of base  $dS_\omega$  and altitude  $dK_\perp$ , so that

$$\int_{\text{shell}} d^3K = \int dS_\omega dK_\perp, \quad (36)$$

Here  $dK_\perp$  is the perpendicular distance (Fig. 13) between the surface  $\omega$  constant and the surface  $\omega + d\omega$  constant. The value of  $dK_\perp$  will vary from one point to another on the surface.

The gradient of  $\omega$ , which is  $\nabla_{\mathbf{K}}\omega$ , is also normal to the surface  $\omega$  constant, and the quantity

$$|\nabla_{\mathbf{K}}\omega| dK_\perp = d\omega,$$

is the difference in frequency between the two surfaces connected by  $dK_\perp$ . Thus the element of the volume is

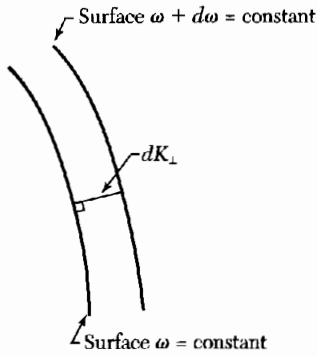
$$dS_\omega dK_\perp = dS_\omega \frac{d\omega}{|\nabla_{\mathbf{K}}\omega|} = dS_\omega \frac{d\omega}{v_g},$$

where  $v_g = |\nabla_{\mathbf{K}}\omega|$  is the magnitude of the group velocity of a phonon. For (35) we have

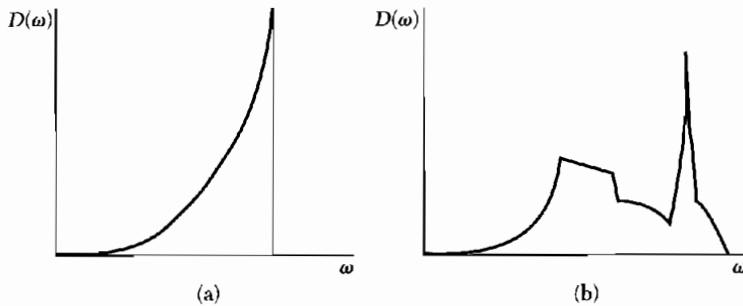
$$D(\omega) d\omega = \left( \frac{L}{2\pi} \right)^3 \int \frac{dS_\omega}{v_g} d\omega.$$

We divide both sides by  $d\omega$  and write  $V = L^3$  for the volume of the crystal: the result for the density of states is

$$D(\omega) = \frac{V}{(2\pi)^3} \int \frac{dS_\omega}{v_g}. \quad (37)$$



**Figure 13** The quantity  $dK_{\perp}$  is the perpendicular distance between two constant frequency surfaces in  $\mathbf{K}$  space, one at frequency  $\omega$  and the other at frequency  $\omega + d\omega$ .



**Figure 14** Density of states as a function of frequency for (a) the Debye solid and (b) an actual crystal structure. The spectrum for the crystal starts as  $\omega^2$  for small  $\omega$ , but discontinuities develop at singular points.

The integral is taken over the area of the surface  $\omega$  constant, in  $\mathbf{K}$  space. The result refers to a single branch of the dispersion relation. We can use this result also in electron band theory.

There is a special interest in the contribution to  $D(\omega)$  from points at which the group velocity is zero. Such critical points produce singularities (known as Van Hove singularities) in the distribution function (Fig. 14).

### ANHARMONIC CRYSTAL INTERACTIONS

The theory of lattice vibrations discussed thus far has been limited in the potential energy to terms quadratic in the interatomic displacements. This is the harmonic theory; among its consequences are:

- Two lattice waves do not interact; a single wave does not decay or change form with time.
- There is no thermal expansion.
- Adiabatic and isothermal elastic constants are equal.
- The elastic constants are independent of pressure and temperature.
- The heat capacity becomes constant at high temperatures  $T > \theta$ .

In real crystals none of these consequences is satisfied accurately. The deviations may be attributed to the neglect of anharmonic (higher than quadratic) terms in the interatomic displacements. We discuss some of the simpler aspects of anharmonic effects.

Beautiful demonstrations of anharmonic effects are the experiments on the interaction of two phonons to produce a third phonon at a frequency  $\omega_3 = \omega_1 + \omega_2$ . Three-phonon processes are caused by third-order terms in the lattice potential energy. The physics of the phonon interaction can be stated simply: the presence of one phonon causes a periodic elastic strain which (through the anharmonic interaction) modulates in space and time the elastic constant of the crystal. A second phonon perceives the modulation of the elastic constant and thereupon is scattered to produce a third phonon, just as from a moving three-dimensional grating.

### Thermal Expansion

We may understand thermal expansion by considering for a classical oscillator the effect of anharmonic terms in the potential energy on the mean separation of a pair of atoms at a temperature  $T$ . We take the potential energy of the atoms at a displacement  $x$  from their equilibrium separation at absolute zero as

$$U(x) = cx^2 - gx^3 - fx^4, \quad (38)$$

with  $c$ ,  $g$ , and  $f$  all positive. The term in  $x^3$  represents the asymmetry of the mutual repulsion of the atoms and the term in  $x^4$  represents the softening of the vibration at large amplitudes. The minimum at  $x = 0$  is not an absolute minimum, but for small oscillations the form is an adequate representation of an interatomic potential.

We calculate the average displacement by using the Boltzmann distribution function, which weights the possible values of  $x$  according to their thermodynamic probability:

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx x \exp[-\beta U(x)]}{\int_{-\infty}^{\infty} dx \exp[-\beta U(x)]},$$

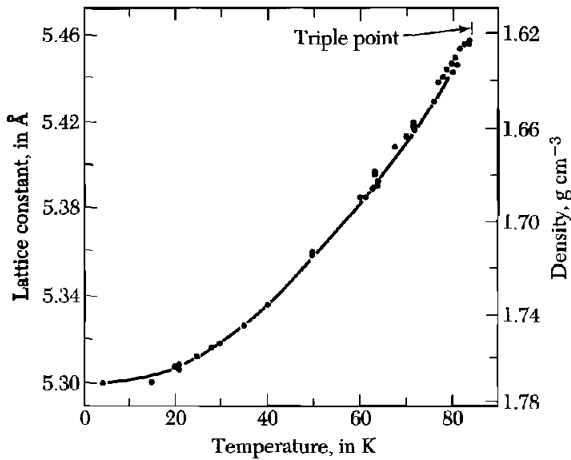
with  $\beta \equiv 1/k_B T$ . For displacements such that the anharmonic terms in the energy are small in comparison with  $k_B T$ , we may expand the integrands as

$$\begin{aligned} \int dx x \exp(-\beta U) &\cong \int dx [\exp(-\beta cx^2)](x + \beta gx^4 + \beta fx^5) = (3\pi^{1/2}/4)(g/c^{5/2})\beta^{-3/2}; \\ \int dx \exp(-\beta U) &\cong \int dx \exp(-\beta cx^2) = (\pi/\beta c)^{1/2}, \end{aligned} \quad (39)$$

whence the thermal expansion is

$$\langle x \rangle = \frac{3g}{4c^{3/2}} k_B T \quad (40)$$





**Figure 15** Lattice constant of solid argon as a function of temperature.

in the classical region. Note that in (39) we have left  $cx^2$  in the exponential, but we have expanded  $\exp(\beta gx^3 + \beta fx^4) \cong 1 + \beta gx^3 + \beta fx^4 + \dots$ .

Measurements of the lattice constant of solid argon are shown in Fig. 15. The slope of the curve is proportional to the thermal expansion coefficient. The expansion coefficient vanishes as  $T \rightarrow 0$ , as we expect from Problem 5. In lowest order the thermal expansion does not involve the symmetric term  $fx^4$  in  $U(x)$ , but only the antisymmetric term  $gx^3$ .

### THERMAL CONDUCTIVITY

The thermal conductivity coefficient  $K$  of a solid is defined with respect to the steady-state flow of heat down a long rod with a temperature gradient  $dT/dx$ :

$$j_U = -K \frac{dT}{dx}, \quad (41)$$

where  $j_U$  is the flux of thermal energy, or the energy transmitted across unit area per unit time.

This form implies that the process of thermal energy transfer is a random process. The energy does not simply enter one end of the specimen and proceed directly (ballistically) in a straight path to the other end, but diffuses through the specimen, suffering frequent collisions. If the energy were propagated directly through the specimen without deflection, then the expression for the thermal flux would not depend on the temperature gradient, but only on the difference in temperature  $\Delta T$  between the ends of the specimen, regardless of the length of the specimen. The random nature of the conductivity process brings the temperature gradient and, as we shall see, a mean free path into the expression for the thermal flux.

**Table 2 Phonon mean free paths**

[Calculated from (44), taking  $v = 5 \times 10^5$  cm/sec as a representative sound velocity. The  $\ell$ 's obtained in this way refer to umklapp processes.]

Crystal	$T, ^\circ\text{C}$	$C, \text{ in } \text{J cm}^{-3}\text{K}^{-1}$	$K, \text{ in } \text{W cm}^{-1}\text{K}^{-1}$	$\ell, \text{ in } \text{\AA}$
Quartz <sup>a</sup>	0	2.00	0.13	40
	-190	0.55	0.50	540
NaCl	0	1.88	0.07	23
	-190	1.00	0.27	100

<sup>a</sup> Parallel to optic axis.

From the kinetic theory of gases we find below the following expression for the thermal conductivity:

$$K = \frac{1}{3}Cv\ell, \quad (42)$$

where  $C$  is the heat capacity per unit volume,  $v$  is the average particle velocity, and  $\ell$  is the mean free path of a particle between collisions. This result was applied first by Debye to describe thermal conductivity in dielectric solids, with  $C$  as the heat capacity of the phonons,  $v$  the phonon velocity, and  $\ell$  the phonon mean free path. Several representative values of the mean free path are given in Table 2.

We give the elementary kinetic theory which leads to (42). The flux of particles in the  $x$  direction is  $\frac{1}{2}n\langle v_x \rangle$ , where  $n$  is the concentration of molecules; in equilibrium there is a flux of equal magnitude in the opposite direction. The  $\langle \cdots \rangle$  denote average value.

If  $c$  is the heat capacity of a particle, then in moving from a region at local temperature  $T + \Delta T$  to a region at local temperature  $T$  a particle will give up energy  $c \Delta T$ . Now  $\Delta T$  between the ends of a free path of the particle is given by

$$\Delta T = \frac{dT}{dx} \ell_x = \frac{dT}{dx} v_x \tau,$$

where  $\tau$  is the average time between collisions.

The net flux of energy (from both senses of the particle flux) is therefore

$$j_U = -n\langle v_x^2 \rangle c \tau \frac{dT}{dx} = -\frac{1}{3}n\langle v^2 \rangle c \tau \frac{dT}{dx}. \quad (43)$$

If, as for phonons,  $v$  is constant, we may write (43) as

$$j_U = -\frac{1}{3}Cv\ell \frac{dT}{dx}, \quad (44)$$

with  $\ell \equiv v\tau$  and  $C \equiv nc$ . Thus  $K = \frac{1}{3}Cv\ell$ .

### Thermal Resistivity of Phonon Gas

The phonon mean free path  $\ell$  is determined principally by two processes, geometrical scattering and scattering by other phonons. If the forces between atoms were purely harmonic, there would be no mechanism for collisions between different phonons, and the mean free path would be limited solely by collisions of a phonon with the crystal boundary, and by lattice imperfections. There are situations where these effects are dominant.

With anharmonic lattice interactions, there is a coupling between different phonons which limits the value of the mean free path. The exact states of the anharmonic system are no longer like pure phonons.

The theory of the effect of anharmonic coupling on thermal resistivity predicts that  $\ell$  is proportional to  $1/T$  at high temperatures, in agreement with many experiments. We can understand this dependence in terms of the number of phonons with which a given phonon can interact: at high temperature the total number of excited phonons is proportional to  $T$ . The collision frequency of a given phonon should be proportional to the number of phonons with which it can collide, whence  $\ell \propto 1/T$ .

To define a thermal conductivity there must exist mechanisms in the crystal whereby the distribution of phonons may be brought locally into thermal equilibrium. Without such mechanisms we may not speak of the phonons at one end of the crystal as being in thermal equilibrium at a temperature  $T_2$  and those at the other end in equilibrium at  $T_1$ .

It is not sufficient to have only a way of limiting the mean free path, but there must also be a way of establishing a local thermal equilibrium distribution of phonons. Phonon collisions with a static imperfection or a crystal boundary will not by themselves establish thermal equilibrium, because such collisions do not change the energy of individual phonons: the frequency  $\omega_2$  of the scattered phonon is equal to the frequency  $\omega_1$  of the incident phonon.

It is rather remarkable also that a three-phonon collision process

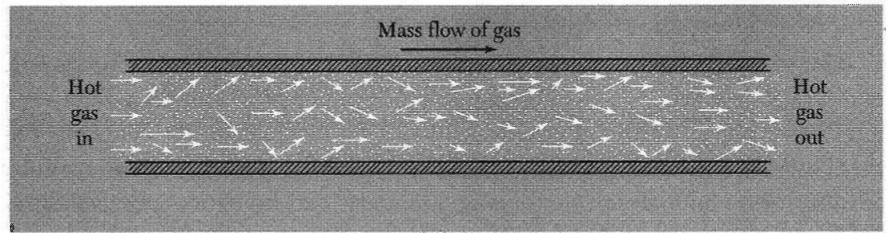
$$\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3 \quad (45)$$

will not establish equilibrium, but for a subtle reason: the total momentum of the phonon gas is not changed by such a collision. An equilibrium distribution of phonons at a temperature  $T$  can move down the crystal with a drift velocity which is not disturbed by three-phonon collisions of the form (45). For such collisions the phonon momentum

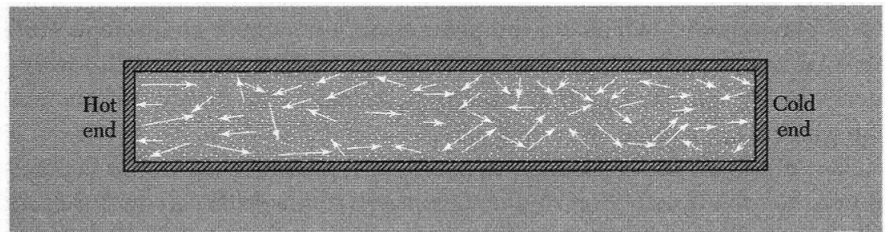
$$\mathbf{J} = \sum_{\mathbf{K}} n_{\mathbf{K}} \hbar \mathbf{K} \quad (46)$$

is conserved, because on collision the change in  $\mathbf{J}$  is  $\mathbf{K}_3 - \mathbf{K}_2 - \mathbf{K}_1 = 0$ . Here  $n_{\mathbf{K}}$  is the number of phonons having wavevector  $\mathbf{K}$ .

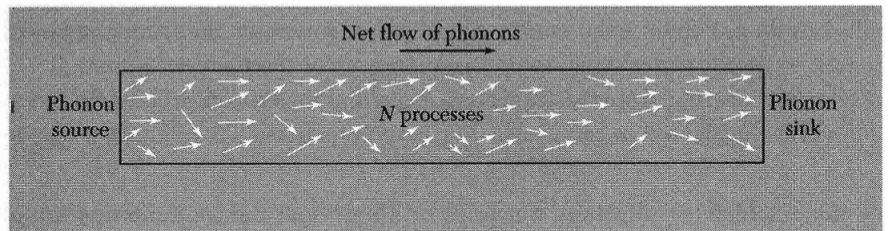
For a distribution with  $\mathbf{J} \neq 0$ , collisions such as (45) are incapable of establishing complete thermal equilibrium because they leave  $\mathbf{J}$  unchanged. If



**Figure 16a** Flow of gas molecules in a state of drifting equilibrium down a long open tube with frictionless walls. Elastic collision processes among the gas molecules do not change the momentum or energy flux of the gas because in each collision the velocity of the center of mass of the colliding particles and their energy remain unchanged. Thus energy is transported from left to right without being driven by a temperature gradient. Therefore the thermal resistivity is zero and the thermal conductivity is infinite.

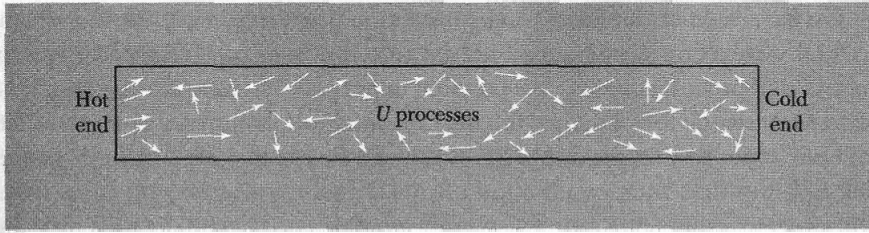


**Figure 16b** The usual definition of thermal conductivity in a gas refers to a situation where no mass flow is permitted. Here the tube is closed at both ends, preventing the escape or entrance of molecules. With a temperature gradient the colliding pairs with above-average center of mass velocities will tend to be directed to the right, those with below-average velocities will tend to be directed to the left. A slight concentration gradient, high on the right, will be set up to enable the net mass transport to be zero while allowing a net energy transport from the hot to the cold end.

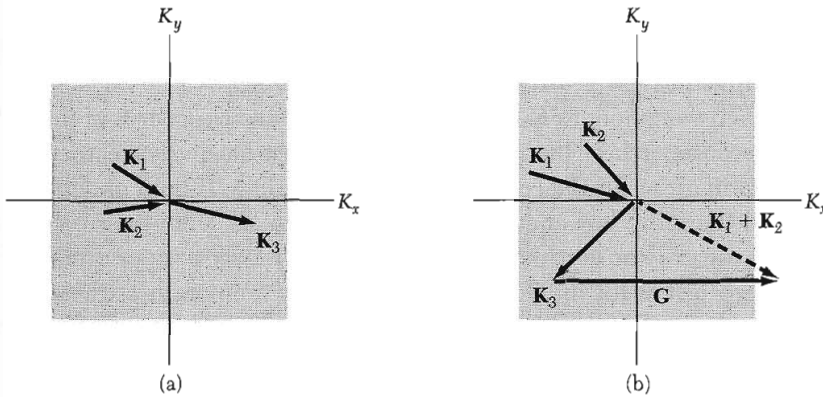


**Figure 16c** In a crystal we may arrange to create phonons chiefly at one end, as by illuminating the left end with a lamp. From that end there will be a net flux of phonons toward the right end of the crystal. If only  $N$  processes ( $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$ ) occur, the phonon flux is unchanged in momentum on collision and some phonon flux will persist down the length of the crystal. On arrival of phonons at the right end we can arrange in principle to convert most of their energy to radiation, thereby creating a sink for the phonons. Just as in (a) the thermal resistivity is zero.

we start a distribution of hot phonons down a rod with  $\mathbf{J} \neq 0$ , the distribution will propagate down the rod with  $\mathbf{J}$  unchanged. Therefore there is no thermal resistance. The problem as illustrated in Fig. 16 is like that of the collisions between molecules of a gas in a straight tube with frictionless walls.



**Figure 16d** In  $U$  processes there is a large net change in phonon momentum in each collision event. An initial net phonon flux will rapidly decay as we move to the right. The ends may act as sources and sinks. Net energy transport under a temperature gradient occurs as in (b).



**Figure 17** (a) Normal  $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$  and (b) umklapp  $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3 + \mathbf{G}$  phonon collision processes in a two-dimensional square lattice. The square in each figure represents the first Brillouin zone in the phonon  $\mathbf{K}$  space; this zone contains all the possible independent values of the phonon wavevector. Vectors  $\mathbf{K}$  with arrowheads at the center of the zone represent phonons absorbed in the collision process; those with arrowheads away from the center of the zone represent phonons emitted in the collision. We see in (b) that in the umklapp process the direction of the  $x$ -component of the phonon flux has been reversed. The reciprocal lattice vector  $\mathbf{G}$  as shown is of length  $2\pi/a$ , where  $a$  is the lattice constant of the crystal lattice, and is parallel to the  $K_x$  axis. For all processes,  $N$  or  $U$ , energy must be conserved, so that  $\omega_1 + \omega_2 = \omega_3$ .

### Umklapp Processes

The important three-phonon processes that cause thermal resistivity are not of the form  $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$  in which  $\mathbf{K}$  is conserved, but are of the form

$$\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3 + \mathbf{G}, \quad (47)$$

where  $\mathbf{G}$  is a reciprocal lattice vector (Fig. 17). These processes, discovered by Peierls, are called **umklapp processes**. We recall that  $\mathbf{G}$  may occur in all momentum conservation laws in crystals. In all allowed processes of the form of (46) and (47), energy is conserved.

We have seen examples of wave interaction processes in crystals for which the total wavevector change need not be zero, but may be a reciprocal lattice vector. Such processes are always possible in periodic lattices. The argument is particularly strong for phonons: the only meaningful phonon  $\mathbf{K}$ 's lie in the first Brillouin zone, so that any longer  $\mathbf{K}$  produced in a collision must be brought back into the first zone by addition of a  $\mathbf{G}$ . A collision of two phonons both with a negative value of  $K_x$  can by an umklapp process ( $G \neq 0$ ), create a phonon with positive  $K_x$ . Umklapp processes are also called  $U$  processes.

Collisions in which  $\mathbf{G} = 0$  are called **normal processes** or  $N$  processes. At high temperatures  $T > \theta$  all phonon modes are excited because  $k_B T > \hbar \omega_{\max}$ . A substantial proportion of all phonon collisions will then be  $U$  processes, with the attendant high momentum change in the collision. In this regime we can estimate the thermal resistivity without particular distinction between  $N$  and  $U$  processes; by the earlier argument about nonlinear effects we expect to find a lattice thermal resistivity  $\propto T$  at high temperatures.

The energy of phonons  $\mathbf{K}_1, \mathbf{K}_2$  suitable for umklapp to occur is of the order of  $\frac{1}{2}k_B\theta$ , because each of the phonons 1 and 2 must have wavevectors of the order of  $\frac{1}{2}\mathbf{G}$  in order for the collision (47) to be possible. If both phonons have low  $K$ , and therefore low energy, there is no way to get from their collision a phonon of wavevector outside the first zone. The umklapp process must conserve energy, just as for the normal process. At low temperatures the number of suitable phonons of the high energy  $\frac{1}{2}k_B\theta$  required may be expected to vary roughly as  $\exp(-\theta/2T)$ , according to the Boltzmann factor. The exponential form is in good agreement with experiment. In summary, the phonon mean free path which enters (42) is the mean free path for umklapp collisions between phonons and not for all collisions between phonons.

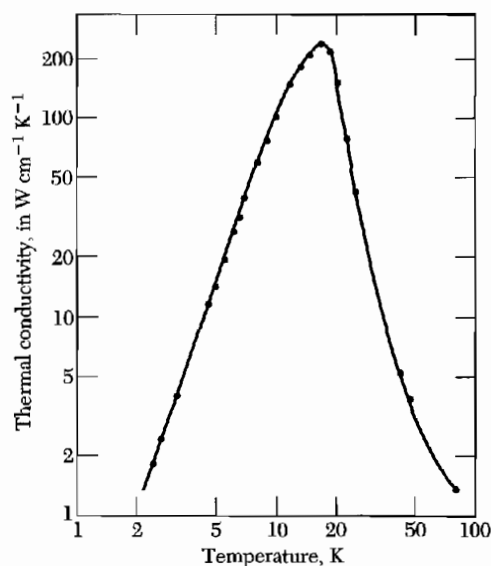
### Imperfections

Geometrical effects may also be important in limiting the mean free path. We must consider scattering by crystal boundaries, the distribution of isotopic masses in natural chemical elements, chemical impurities, lattice imperfections, and amorphous structures.

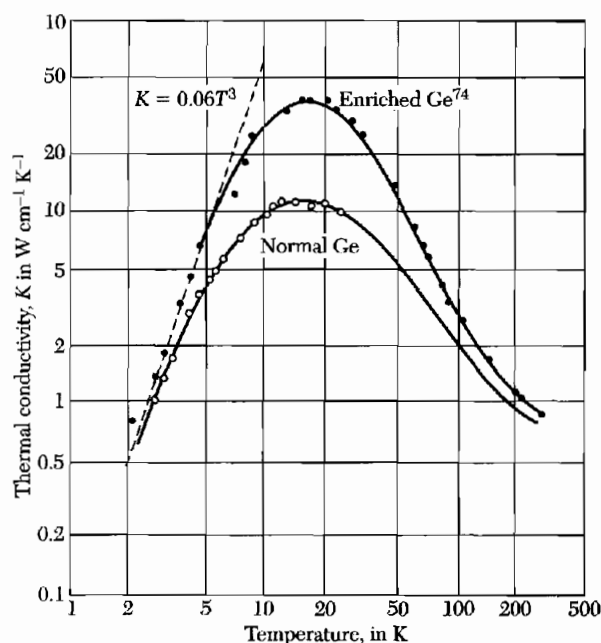
When at low temperatures the mean free path  $\ell$  becomes comparable with the width of the test specimen, the value of  $\ell$  is limited by the width, and the thermal conductivity becomes a function of the dimensions of the specimen. This effect was discovered by de Haas and Biermasz. The abrupt decrease in thermal conductivity of pure crystals at low temperatures is caused by the size effect.

At low temperatures the umklapp process becomes ineffective in limiting the thermal conductivity, and the size effect becomes dominant, as shown in Fig. 18. One would expect then that the phonon mean free path would be constant and of the order of the diameter  $D$  of the specimen, so that

$$K \approx C v D . \quad (48)$$



**Figure 18** Thermal conductivity of a highly purified crystal of sodium fluoride, after H. E. Jackson, C. T. Walker, and T. F. McNelly.



**Figure 19** Isotope effect on thermal conduction in germanium, amounting to a factor of three at the conductivity maximum. The enriched specimen is 96 percent  $\text{Ge}^{74}$ , natural germanium is 20 percent  $\text{Ge}^{70}$ , 27 percent  $\text{Ge}^{72}$ , 8 percent  $\text{Ge}^{73}$ , 37 percent  $\text{Ge}^{74}$ , and 8 percent  $\text{Ge}^{76}$ . Below 5 K the enriched specimen has  $K = 0.06 T^3$ , which agrees well with Casimir's theory for thermal resistance caused by boundary scattering. (After T. H. Geballe and G. W. Hull.)

The only temperature-dependent term on the right is  $C$ , the heat capacity, which varies as  $T^3$  at low temperatures. We expect the thermal conductivity to vary as  $T^3$  at low temperatures. The size effect enters whenever the phonon mean free path becomes comparable with the diameter of the specimen.

Dielectric crystals may have thermal conductivities as high as metals. Synthetic sapphire ( $\text{Al}_2\text{O}_3$ ) has one of the highest values of the conductivity: nearly

$200 \text{ W cm}^{-1} \text{ K}^{-1}$  at 30 K. The maximum of the thermal conductivity in sapphire is greater than the maximum of  $100 \text{ W cm}^{-1} \text{ K}^{-1}$  in copper. Metallic gallium, however, has a conductivity of  $845 \text{ W cm}^{-1} \text{ K}^{-1}$  at 1.8 K. The electronic contribution to the thermal conductivity of metals is treated in Chapter 6.

In an otherwise perfect crystal, the distribution of isotopes of the chemical elements often provides an important mechanism for phonon scattering. The random distribution of isotopic mass disturbs the periodicity of the density as seen by an elastic wave. In some substances scattering of phonons by isotopes is comparable in importance to scattering by other phonons. Results for germanium are shown in Fig. 19. Enhanced thermal conductivity has been observed also in isotopically pure silicon and diamond; the latter has device importance as a heat sink for laser sources.

### Problems

- 1. Singularity in density of states.** (a) From the dispersion relation derived in Chapter 4 for a monatomic linear lattice of  $N$  atoms with nearest-neighbor interactions, show that the density of modes is

$$D(\omega) = \frac{2N}{\pi} \cdot \frac{1}{(\omega_m^2 - \omega^2)^{1/2}}.$$

where  $\omega_m$  is the maximum frequency. (b) Suppose that an optical phonon branch has the form  $\omega(K) = \omega_0 - AK^2$ , near  $K = 0$  in three dimensions. Show that  $D(\omega) = (L/2\pi)^3 (2\pi/A^{3/2})(\omega_0 - \omega)^{1/2}$  for  $\omega < \omega_0$  and  $D(\omega) = 0$  for  $\omega > \omega_0$ . Here the density of modes is discontinuous.

- 2. Rms thermal dilation of crystal cell.** (a) Estimate for 300 K the root mean square thermal dilation  $\Delta V/V$  for a primitive cell of sodium. Take the bulk modulus as  $7 \times 10^{10} \text{ erg cm}^{-3}$ . Note that the Debye temperature 158 K is less than 300 K, so that the thermal energy is of the order of  $k_B T$ . (b) Use this result to estimate the root mean square thermal fluctuation  $\Delta a/a$  of the lattice parameter.
- 3. Zero point lattice displacement and strain.** (a) In the Debye approximation, show that the mean square displacement of an atom at absolute zero is  $\langle R^2 \rangle = 3\hbar\omega_D^2/8\pi^2\rho v^3$ , where  $v$  is the velocity of sound. Start from the result (4.29) summed over the independent lattice modes:  $\langle R^2 \rangle = (\hbar/2\rho V)\Sigma\omega^{-1}$ . We have included a factor of  $\frac{1}{2}$  to go from mean square amplitude to mean square displacement. (b) Show that  $\Sigma\omega^{-1}$  and  $\langle R^2 \rangle$  diverge for a one-dimensional lattice, but that the mean square strain is finite. Consider  $\langle (\partial R/\partial x)^2 \rangle = \frac{1}{2}\Sigma K^2 u_0^2$  as the mean square strain, and show that it is equal to  $\hbar\omega_D^2 L/4MNv^3$  for a line of  $N$  atoms each of mass  $M$ , counting longitudinal modes only. The divergence of  $R^2$  is not significant for any physical measurement.
- 4. Heat capacity of layer lattice.** (a) Consider a dielectric crystal made up of layers of atoms, with rigid coupling between layers so that the motion of the atoms is restricted to the plane of the layer. Show that the phonon heat capacity in the Debye approximation in the low temperature limit is proportional to  $T^2$ .



(b) Suppose instead, as in many layer structures, that adjacent layers are very weakly bound to each other. What form would you expect the phonon heat capacity to approach at extremely low temperatures?

- 5. Grüneisen constant.** (a) Show that the free energy of a phonon mode of frequency  $\omega$  is  $k_B T \ln [2 \sinh (\hbar\omega/2k_B T)]$ . It is necessary to retain the zero-point energy  $\frac{1}{2}\hbar\omega$  to obtain this result. (b) If  $\Delta$  is the fractional volume change, then the free energy of the crystal may be written as

$$F(\Delta, T) = \frac{1}{2}B\Delta^2 + k_B T \sum \ln [2 \sinh (\hbar\omega_{\mathbf{K}}/2k_B T)] ,$$

where  $B$  is the bulk modulus. Assume that the volume dependence of  $\omega_{\mathbf{K}}$  is  $\delta\omega/\omega = -\gamma\Delta$ , where  $\gamma$  is known as the Grüneisen constant. If  $\gamma$  is taken as independent of the mode  $\mathbf{K}$ , show that  $F$  is a minimum with respect to  $\Delta$  when  $B\Delta = \gamma \sum_{\mathbf{K}} \frac{1}{2}\hbar\omega_{\mathbf{K}} \coth (\hbar\omega_{\mathbf{K}}/2k_B T)$ , and show that this may be written in terms of the thermal energy density as  $\Delta = \gamma U(T)/B$ . (c) Show that on the Debye model  $\gamma = -\partial \ln \theta / \partial \ln V$ . Note: Many approximations are involved in this theory: the result (a) is valid only if  $\omega$  is independent of temperature;  $\gamma$  may be quite different for different modes.

\*This problem is somewhat difficult.

