Chapter 10

Vibrations of Crystal Lattices and Thermodynamic Properties of Solids

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1. Introduction

The heat capacity, C_x, of a system of N interacting particles under an external constraint x is defined by $C_x = (\partial Q/\partial T)_x$, the ratio of the added heat to the corresponding temperature rise of the system. The heat capacities of solids are generally measured at constant pressure, while statistical mechanics leads more naturally to formulas for the constant-volume quantity. The thermodynamic formula

$$C_p - C_v = \frac{9\alpha^2 VT}{\kappa}$$

relates C_p to C_v. The quantities α, V, and κ represent, respectively, the coefficient of thermal expansion, the volume, and the compressibility. The heat capacity at constant magnetic field strength H is of considerable importance in low-temperature physics.

Various types of microscopic degrees of freedom in solids make their characteristic contributions to the heat capacity. The constants associated with these degrees of freedom determine their energy levels and hence the temperature at which their effect on the heat capacity becomes important. Measurements of the temperature variation of the heat capacity have been a rich source of information on the electronic, atomic, and molecular dynamics of crystals.

The constituent atoms and molecules of all solids undergo (either through thermal agitation or quantum-mechanical zero-point energy) small oscillations about their equilibrium positions. At temperatures not too close to the melting point a crystalline solid is essentially a set of a large number of coupled oscillators. Einstein pointed out many years ago that the vibrational contribution to thermodynamic properties of solids can be calculated through the application of the quantum theory of the harmonic oscillator. The free electrons in metals are responsible for most of the heat capacity at very low temperatures. Since they obey Fermi-Dirac statistics, their heat capacity is proportional to T as $T \to 0$, while lattice vibrations have $C_v \alpha T^3$. For discussion of the electron theory of metals, see Part 8. Experimental low-temperature C_v data of metals are frequently fitted to

$$C_v = 464.4\left(\frac{T}{\theta}\right)^3 + aT$$

The appropriate units are calories per mole per degree Kelvin. The θ and a values of a variety of metals are given in Table 10.1. A more complete list can be found in Appendix C of "Phenomena at the Temperature of Liquid Helium" by Burton, Smith, and Wilhelm [1].*

TABLE 10.1. CONSTANTS θ_D AND a FOR LOW-TEMPERATURE HEAT CAPACITIES
[Units are chosen so that $C_v = 464.4(T/\theta_D)^3 + aT$ is in calories per mole per degree Kelvin]

Metal	θ_D	$a \times 10^4$
Al	419	3.48
Ag	229	1.54
Cu	335	1.78
Pt	233	16.07
Pb	90	7.15
Mg	410	42.1
Sn	185	4.0

Anomalies in the form of "λ points" or discontinuities in C_v occur in binary substitution alloys, ferromagnets, ferroelectrics, hydrogen halides, superconductors, various molecular crystals (especially organic ones), etc. These anomalies are generally associated with the disappearance of some kind of long-range order. They are discussed in the chapter on phase transitions. We shall merely point out here that if one wishes to compare the results of a quantitative theory of an anomalous effect with experimental measurements, it is necessary to have an accurate theory of the normal contribution of lattice vibrations to the heat capacities so that the anomalous effect can be obtained by subtraction.

This chapter is a brief survey of the theory of lattice vibrations and their influence on heat capacities of crystals. The equation of state of solids will also be discussed.

The coupled oscillator model of a crystal can be decomposed into its independent normal modes.

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* Numbers in brackets refer to References at end of chapter.

If the normal mode frequencies of a crystal with $3N$ degrees of freedom are $\nu_1, \nu_2, \ldots, \nu_{3N}$, then Eq. (2.77), Chap. 2, implies that the internal energy of the crystal is

$$E = \sum_{j=1}^{3N} h\nu_j \left(\frac{1}{2} + \frac{1}{-1 + \exp \theta_j}\right) \qquad \theta_j = \frac{h\nu_j}{kT} \quad (10.1)$$

while its heat capacity is

$$C_v = k \sum_{j=1}^{3N} \frac{(\frac{1}{2}\theta_j)^2}{\sinh^2 (\frac{1}{2}\theta_j)} \quad (10.2)$$

Generally as the number of degrees of freedom becomes infinite, the normal mode frequencies become so dense that a frequency distribution function $g(\nu)$ exists with the property that

$$\int_0^{\nu} g(\nu)\, d\nu$$

is the number of frequencies less than ν. The heat capacity can be expressed as an integral with respect to ν:

$$C_v = k \int_0^{\nu_L} g(\nu) \frac{(\frac{1}{2}\, h\nu/kT)^2}{\sinh^2 (\frac{1}{2}\, h\nu/kT)}\, d\nu \quad (10.3)$$

where ν_L is the largest normal mode frequency.

The power series expansion of the exponential and hyperbolic functions of (10.1) and (10.2) leads naturally to the following high-temperature formulas [2, 3]:

$$E = 3NkT \left[1 - \sum_{n=0}^{\infty} \frac{(-1)^n B_n}{(2n)!} \left(\frac{h\nu_L}{kT}\right)^{2n} \frac{\mu_{2n}}{\nu_L{}^{2n}}\right] \quad (10.4)$$

$$C_v = 3NkT \left[1 - \sum_{n=1}^{\infty} \frac{(2n-1)(-1)^n B_{2n}}{(2n)!} \left(\frac{h\nu_L}{kT}\right)^{2n} \frac{\mu_{2n}}{\nu_L{}^{2n}}\right] \quad (10.5)$$

The series converge when $h\nu_L/kT < 2\pi$; the B_n's are Bernoulli numbers

$$B_1 = \tfrac{1}{6} \qquad B_2 = \tfrac{1}{30} \qquad B_3 = \tfrac{1}{42} \qquad B_4 = \tfrac{1}{30}$$
$$B_5 = \tfrac{5}{66} \qquad B_6 = \tfrac{691}{2730} \quad \cdots$$

and the μ_n's are the moments of the frequency distribution $g(\nu)$:

$$\mu_n = \sum \nu_j{}^n = \frac{1}{\nu_L} \int_0^{\nu_L} \nu^n g(\nu)\, d\nu \quad (10.6)$$

The calculation of these moments will be discussed in the next sections. It is clear that as $T \to \infty$, (10.5) yields the Dulong-Petit result $C_v \sim 3Nk$.

The low-temperature behavior of C_v depends on the low-frequency form of $g(\nu)$. For example, if there are two constants A and α such that as $\nu \to 0$

$$g(\nu) \sim 3NA\nu^{\alpha} \quad (10.7)$$

Equation (10.3), when written in terms of the variable $x = h\nu/kT$, has the low-temperature form

$$C_v = \frac{3}{4} NAk \left(\frac{kT}{h}\right)^{\alpha+1} \int_0^{\infty} \frac{x^{2+\alpha}}{\sinh^2 \frac{1}{2}x}\, dx$$
$$= 3ANk \left(\frac{kT}{h}\right)^{\alpha+1} (2+\alpha)!\,\zeta(2+\alpha) \quad (10.8)$$

where $\zeta(y)$ is the Riemann zeta function,

$$\zeta(y) = 1 + 2^{-y} + 3^{-y} + \cdots$$

[$\zeta(2) = \pi^2/6$ and $\zeta(4) = \pi^4/90$]. Since low-frequency vibrations in a crystal have wavelengths which are very long compared with lattice spacings, the low-frequency behavior of $g(\nu)$ should have the same form as that of an elastic continuum. Hence in a two-dimensional crystal the appropriate value of α should be 1, while it should be 2 in a three-dimensional crystal. The low-temperature heat capacity of a two-dimensional structure should vary as T^2, while that of a three-dimensional material should vary as T^3.

The asymptotic T^3 law was first observed experimentally by Nernst and his collaborators many years ago and has been verified for most materials. The results of Pitzer [4] and De Sorbo [5] on diamond are typical of a nonmetal.

Several important exceptions to the T^3 law [6–9] exist in graphite, gallium, and BN. Experimental C_v behavior of these materials is better fitted by the form $C_v \propto T^2$; which is, according to (10.8), more appropriate for two-dimensional systems. This is not surprising because the flakiness of pure graphite and BN indicates that the binding forces between crystal layers are very weak.

Thermodynamic properties are then derived by considering these materials as formed of almost independent two-dimensional hexagonal arrays of atoms. Transverse vibrations give the main contribution to thermodynamic quantities. G. F. Newell [10] has made a detailed investigation of weakly interacting layer structures and has reviewed the work of earlier authors. Various other layer structures can be expected to have a T^2 law for the low-temperature heat capacities.

There is also some evidence of a T law in materials such as Se and S which are composed of weakly connected atomic chains [11].

The systematic theory of the variation of thermal properties of polymers and glasses is still in its formative stage. These materials have a network structure of chains with varying length. The work of Dole and his collaborators [12] on the heat capacity of polystyrene is representative of that on polymers. Reversible temperature changes seem to be hard to achieve in polymer systems.

According to Winkelmann [13] the specific heat of glasses can be expressed very well as a linear function of the composition

$$C = \Sigma C_r x_r$$

the x_r's being the weight fraction of oxides occurring in the glasses. The empirical ratio of the thermal factor C_r (so-called Winkelmann factors) to the classical high-temperature specific heat of the particular components has the correct qualitative behavior in that strongly bound atoms in the network contribute low C_r's (reflecting quantum effects)

If the normal mode frequencies of a crystal with $3N$ degrees of freedom are $\nu_1, \nu_2, \ldots, \nu_{3N}$, then Eq. (2.77), Chap. 2, implies that the internal energy of the crystal is

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Dyson [15] has made a first step toward the theory of the heat capacity of networks of particles with varying force constant and masses by studying the normal mode distribution function $g(\nu)$ of a linear chain of coupled springs and mass with random force constants and masses.

At high temperatures anharmonic vibrations yield a contribution above the Dulong-Petit value which is proportional to the temperature (see Born and Brody [16]).

An excellent bibliography of experimental data on heat capacities of solids (as well as other thermal properties) can be found in Partington's treatise on physical chemistry [17].

The complete frequency distribution function $g(\nu)$ is necessary for the description of the behavior of C_v at temperatures out of the range of the two asymptotic formulas (10.5) and (10.8).

2. Debye Theory of Heat Capacities

The first calculation of the distribution of frequencies of normal modes was made by Debye [18]. He postulated a solid to be an elastic continuum. Since a continuum has an infinite number of normal modes, Debye cut the frequency spectrum off at a frequency such that the total number of normal modes was equal to the number of degrees of freedom of the solid. Debye's work was one of the great successes of the early quantum theory. The theoretical heat capacities based on his frequency spectrum are in good agreement with experimental results. The simplicity of the Debye theory combined with this fact has given it a long and fruitful life as the dominant theory of the heat capacity of solids. The classical exposition of the Debye theory was written by Schroedinger [19] (see also Mayer and Mayer [20] and Fowler [21]). Schroedinger collected an enormous amount of heat-capacity data and compared it with the Debye theory.

The equations for wave propagation in an elastic continuum are

$$\frac{1}{c^2}\frac{\partial^2\varphi}{\partial t^2} = \nabla^2\varphi \qquad (10.9)$$

where c is the velocity of propagation and φ is the displacement of a point which at equilibrium is located at (x,y,z). The normal modes of vibration which correspond to stationary crystal boundaries are found as follows. Let our solid have the shape of a rectangular box with sides of length l_1, l_2, and l_3. Solutions of (10.9) of the form

$$\varphi = Ae^{2\pi i\nu t}\sin\frac{x\pi n_1}{l_1}\sin\frac{y\pi n_2}{l_2}\sin\frac{z\pi n_3}{l_3} \qquad (10.10)$$

exist when (n_1,n_2,n_3) range through the integers 0, 1, 2, 3, ... By substituting (10.10) into (10.9), we find that the frequency ν is related to (n_1,n_2,n_3) by

$$\nu^2 = \frac{c^2}{4}\left[\left(\frac{n_1}{l_1}\right)^2 + \left(\frac{n_2}{l_2}\right)^2 + \left(\frac{n_3}{l_3}\right)^2\right]$$
$$n_1,\ n_2,\ n_3 = 0, 1, 2, \ldots \qquad (10.11)$$

The total number of frequencies less than ν, $N(\nu)$, is proportional to the volume of the ellipsoid defined by (10.11) in (n_x,n_y,n_z) space. The volume of the ellipsoid is $(\frac{4}{3})\pi\nu^3 l_1 l_2 l_3/c^3 = (\frac{4}{3})\pi V\nu^3/c^3$, V being the volume of our box. Since all n_i's are positive, only one-eighth of this volume contributes to $N(\nu)$. There is exactly one frequency per unit volume in (n_1,n_2,n_3) space. Hence

$$N(\nu) = \frac{\frac{4}{3}\pi V\nu^3}{c^3} \qquad (10.12)$$

There are two kinds of waves propagated in a continuum model of a solid, transverse and longitudinal, each with its characteristic velocity (which we represent, respectively, by c_t and c_l): indeed there are two transverse waves for every longitudinal one. Hence the total number of normal modes of both types with frequency less than ν are $\frac{4}{3}\pi V\nu^3(2c_t^{-3} + c_l^{-3})$ and the number of normal modes between ν and $\nu + d\nu$ is

$$g(\nu) = 4\pi V\nu^2(2c_t^{-3} + c_l^{-3}) \qquad (10.13)$$

We mentioned above that the frequency spectrum must be cut off at a frequency ν_L such that $N(\nu_L) = 3N$, the number of degrees of freedom of a lattice of N particles. Hence

$$\frac{4\pi}{3}V\nu_L^3(2c_t^{-3} + c_l^{-3}) = 3N$$

so that

$$\nu_L = \left\{\frac{9N}{[4\pi V(2c_t^{-3} + c_l^{-3})]}\right\}^{1/3}$$

and

$$\nu_L g(\nu) = \begin{cases} 9N\left(\dfrac{\nu}{\nu_L}\right)^2 & \text{if } \nu < \nu_L \\ 0 & \text{if } \nu > \nu_L \end{cases} \qquad (10.14)$$

The internal energy of the Debye model is

$$E = \frac{9}{8}Nh\nu_L + 3NkTD\left(\frac{\theta_D}{T}\right) \qquad (10.15a)$$

where θ_D is the so-called Debye temperature

$$\theta_D = \frac{h\nu_L}{k} \qquad (10.15b)$$

and $D(u)$ is the Debye function

$$D(u) = \frac{3}{u^3}\int_0^u \frac{x^3\,dx}{e^x - 1} \qquad (10.15c)$$

The heat capacity at constant volume is

$$C = 3NkD\frac{\theta_D}{T} + 3NkT\frac{\partial}{\partial T}D\frac{\theta_D}{T}$$
$$= 3Nk\left[4D\frac{\theta_D}{T} - \frac{3\theta_D/T}{\exp(\theta_D/T) - 1}\right] \qquad (10.16)$$

and the entropy is

$$S = 3Nk\left\{\frac{4}{3}D\left(\frac{\theta_D}{T}\right) - \log\left[1 - \exp\left(-\frac{\theta_D}{T}\right)\right]\right\}$$

The functions required for calculation of the various thermodynamic quantities have been tabulated by Beattie [22]. An important feature of the Debye theory is that only a single parameter is required to characterize a material. By choosing the temperature scale properly all heat-capacity data can be fitted to a single universal curve. At low temperatures we can apply Eqs. (10.7) and (10.8). The parameters of those equations are $A = 9/\nu_L^3$, $\alpha = 2$, and $\zeta(4) = \pi^4/90$. Hence as $T \rightarrow 0$ we have

$$C_v = 3Nk\left[\frac{4}{5}\pi^4\left(\frac{T}{\theta_D}\right)^3 + \cdots\right] \qquad (10.17)$$

The even moments of $g(\nu)$ are

$$\begin{aligned} u_{2n} &= \sum \nu_j^{2n} = \int_0^{\nu_L} \nu^{2n} g(\nu)\, d\nu \\ &= \frac{9N}{\nu_L^3}\int_0^{\nu_L} \nu^{2n+2}\, d\nu \\ &= \frac{9N\nu_L^{2n}}{2n+3} \end{aligned}$$

Hence the first few terms in the high-temperature expansion of C_v are [Eq. (10.5)]:

$$C_v = 3Nk\left[1 - \frac{1}{20}\left(\frac{\theta_D}{T}\right)^2 + \frac{1}{560}\left(\frac{\theta_D}{T}\right)^4 + \cdots\right]$$

while the entropy goes as

$$S = 3Nk\left[\frac{4}{3} - \log\frac{\theta_D}{T} + \frac{1}{40}\left(\frac{\theta_D}{T}\right)^2 - \cdots\right]$$

The highest frequency ν should correspond to the vibration of shortest wavelength in the lattice. This wavelength would be of the order of the distance between a pair of nearest neighbors and the associated normal mode would involve nearest neighbors oscillating 180° out of phase. This vibration could be excited by an external electric field of the proper frequency in an ionic lattice such as NaCl or KCl in which components of pairs of nearest neighbors have unlike charges. The frequency ν_L therefore corresponds to the highest *reststrahlen* frequency of the crystal.

The largest frequency ν_L, being related to the velocity of elastic waves in the crystal, can also be expressed in terms of its elastic constants. An internal check of the Debye theory has been made by comparing the values of ν_L determined from elastic constants with those which give the best fit of heat-capacity data with the Debye theory (see Blackman [23]). In metals it is assumed that at low temperatures $C_v = aT + bT^3$, the linear term being the electronic contribution to C_v. Some examples of the type of agreement obtained are given in (here we discuss $\theta_D = h\nu_L/k$ rather than ν_L) Table 10.2. The temperatures in the third and fifth columns are those at which the elastic constants have been determined.

If one plots C_v data over a wide temperature range the apparent agreement between experiment and theory is almost unbelievable when he considers the enormous physical differences between various kinds of crystals and the coarseness of the continuum model.

TABLE 10.2. COMPARISON OF θ_D AS DETERMINED BY THERMAL AND ELASTIC DATA [23]

Material	θ_D (thermal)	T, °K	θ_D (elastic)	T, °K
Ag	237	4	216	~290
Zn	308	4	305	~290
NaCl	308	10	320	0
KCl	230	3	246	0

A better appreciation of the lack of agreement is obtained by relating each experiment point to that value of θ_D which is required in Eq. (10.16) to give the measured C_v at the appropriate temperature. If complete agreement were to exist, the set of θ_D's computed would be temperature independent. A typical variation of θ_D with temperature T is plotted in Fig. 10.1. Plots of this type were first proposed by Blackman [23, 24]. The extreme values of θ_D differ by about 15 per cent. In very anisotropic substances such as Li, Zn, and Cd, the deviations are of the order of 30 to 50 per cent, while in gold and tungsten (face-centered crystals which are almost isotropic) the deviations are only 10 per cent.

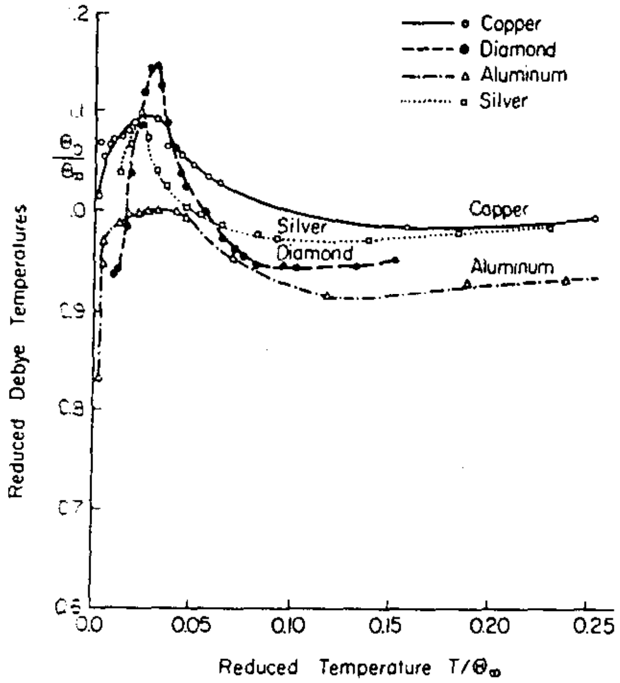

FIG. 10.1. Variation of θ_D/θ_∞ with temperature. Her θ_∞ is the asymptotic Debye temperature at high ten peratures [5]. The face-centered metals Cu, Al, and A and diamond are shown as examples.

It is to be expected that some improvement shoul result from the use of a discrete lattice model rath than a continuum one. Unfortunately the theo becomes much more complicated. No simple un versal formulas for thermodynamic properties see to exist, each example being a special case. T discrete model was first analyzed by Born and v Kármán [25].