NOTES 8: STATISTICAL MECHANICS OF LATTICE WAVES AND PHONONS

Classical Average Energy Analysis of a Single Atom

So far we have addressed the instantaneous *mechanical behavior* of lattice waves – classical and quantum mechanical. This led to an emphasis on the modal nature of every lattice wave, and the quanta of excitation for each mode – the *phonon*. Now we take the analysis one step further to understand the statistical mechanics, starting as before with the classical analysis and then developing the quantum description.

We start with a monatomic linear lattice of atomic mass m, spacing a, and nearest neighbor (spring constant) C and ask the following question ? What is the energy of a single atom when a lattice wave is propagating. This will lead to a straightforward application of the Boltzmann formalism treating the atom itself as the subsystem. The total energy of the sth atom (chosen arbitrarily) is the kinetic plus *half* the potential with all neighbors (the *half* serving the requirement of counting each potential only once in summing to get the total energy)

$$KE_s \rightarrow \frac{1}{2} M \upsilon_s^{\,2} = \frac{1}{2} M \left(\frac{d\Delta r_s}{dt} \right)^2$$

Accounting for nearest-neighbor interactions only, half the potential energy is

$$PE_s \rightarrow \frac{1}{2} C \left(\Delta r_{s+1} - \Delta r_s \right)^2 = \frac{1}{2} C \left(\Delta r_s - \Delta r_{s+1} \right)^2$$

And thus

$$U(t) = \frac{1}{2} M \left(\frac{d\Delta r_s}{dt} \right)^2 + \frac{1}{2} C \left(\Delta r_s - \Delta r_{s+1} \right)^2 \text{ (instantaneous)} \qquad (1)$$

To apply this we start with a unidirectional lattice wave of the (real) form: $\Delta r_s = A \cos\left(\omega t - ska\right)$. , so that $\frac{d\Delta r_s}{dt} = -\omega A \sin\left(\omega t - ska\right)$ and

$$U_k(t) = \frac{1}{2} M \omega^2 A^2 \sin^2\left(\omega t - ska\right) + \frac{1}{2} C A^2 \left[\cos\left(\omega t - ska\right) - \cos\left(\omega t - ska - ka\right) \right]^2$$

The where the subscript k reminds us that the energy is just for the wave of k. The last term has the form $\left[\cos(\alpha - \beta) - \cos\alpha \right]^2$ *with* $\alpha = \omega t - ska, \quad \beta = ka$. So we can use the trigonometric identity $\cos\left(\alpha - \beta\right) = \cos\alpha \cos\beta + \sin\alpha \sin\beta$ to write

$$U_k(t) = \frac{1}{2}M\omega^2 A^2 \sin^2\alpha + \frac{1}{2}CA^2\left(\cos\alpha\left(\cos\beta - 1\right) + \sin\alpha\sin\beta\right)^2$$

$$= \frac{1}{2}M\omega^2 A^2 \sin^2\alpha + \frac{1}{2}CA^2\left(\cos^2\alpha\left(\cos\beta - 1\right)^2 + 2\cos\alpha\left(\cos\beta - 1\right)\sin\alpha\sin\beta + \sin^2\alpha\sin^2\beta\right)$$

To do the statistical mechanics, we do not need the instantaneous energy but rather the average over time. So we integrate over the period of wave, τ , and define

$$\bar{U}_k \equiv \int_o^\tau U_k(t)dt, \quad \tau = \frac{2\pi}{\omega} = \frac{1}{f}$$

$$\int_o^\tau \sin^2\alpha dt = \frac{\tau}{2}; \quad \int_2^\tau \cos^2\alpha dt = \frac{\tau}{2}; \quad \int_o^\tau 2\sin\alpha\cos\alpha dt = \int_o^\tau \sin 2\alpha dt = 0$$

So,

$$\bar{U}_k = \frac{1}{2}M\omega^2 A^2 \frac{\tau/2}{\tau} + \frac{1}{2}CA^2\left[\frac{\tau/2}{\tau}\left(\cos\beta - 1\right)^2 + \frac{\tau/2}{\tau}\sin^2\beta\right]$$

$$\bar{U}_k = \frac{1}{4}M\omega^2 A^2 + \frac{1}{4}CA^2\left[\cos^2\beta - 2\cos\beta + 1 + \sin^2\beta\right]$$

$$\bar{U}_k = \frac{1}{4}M\omega^2 A^2 + \frac{1}{2}CA^2\left[1 - \cos\beta\right]$$

For a linear monatomic lattice, the lattice waves all have the acoustical form $\omega^2 = \frac{2C}{M}\left(1 - \cos\beta\right)$.

$$\bar{U}_k = \frac{1}{4}M\omega^2 A^2 + \frac{1}{4}M\omega^2 A^2 = \frac{1}{2}M\omega^2 A^2$$

And there are always two k values for the same ω, corresponding to the two different directions of wave flow. If we added two such waves of the same amplitude A, the time-averaged total energy would be

$$\bar{U}_\omega = \mathrm{M}\omega^2\mathrm{A}^2 \tag{2}$$

Statistical Mechanics

We now assume the sth atom is in thermal equilibrium with the bath at temperature *T*. The Boltzmann pdf can be applied if the amplitude *A* is treated as a random variable and each wave from (2) is treated as a statistically independent mode. The mean value of the atomic energy is then given by

$$< U >_{atom} = \frac{\int_0^\infty \bar{U}_\omega exp\left[-\bar{U}_k / k_B T\right] dA}{\int_0^\infty exp\left[-\bar{U}_k / k_B T\right] dA} = \frac{\int_0^\infty M\omega^2 A^2 exp\left[-M\omega^2 A^2 / 2k_B T\right] dA}{\int_0^\infty exp\left[-M\omega^2 A^2 / 2k_B T\right] dA}$$

To account for lattice waves in all possible directions, the amplitude must be considered three-dimensional and can always be decomposed into three Cartesian components, so that A = (A_x, A_y, A_z) and $A^2 = A_x^{\,2} + A_y^{\,2} + A_z^{\,2}$. But we need to keep A confined to one octant since it is an amplitude factor, and thus the above expression becomes

$$< U >_{atom} = \frac{\int_0^\infty M\omega^2 \left(A_x^2 + A_y^2 + A_z^2\right) exp\left[-M\omega^2 (A_x^2 + A_y^2 + A_z^2)/2k_B T\right] dA_x dA_y dA_z}{\int_0^\infty exp\left[-M\omega^2 (A_x^2 + A_y^2 + A_z^2)/2k_B T\right] dA_x dA_y dA_z}$$

Both numerator and denominator can be evaluated using closed-form Gaussian integrals:

$$\int_0^\infty exp\left[-ax^2\right] x^n dx = I_n = \frac{\sqrt{\pi}}{2}\frac{1}{\sqrt{a}} \text{ for n = 0; } = \frac{1}{2a} \text{ for n = 1;} = \frac{\sqrt{\pi}}{4}\frac{1}{a^{3/2}} \text{ for n = 2}$$

so that,

$$\int_0^\infty \exp\left[-M\omega^2\left(A_x^{\,2} + A_y^{\,2} + A_z^{\,2}\right)/2k_B T\right] dA_x dA_y dA_z = \left(\frac{\sqrt{\pi}}{2}\sqrt{\frac{2k_B T}{m\omega^2}}\right)^3 = \left(\frac{\pi k_B T}{2m\omega^2}\right)^{3/2}$$

$$\int m\omega^2 \left(A_x^{\,2} + A_y^{\,2} + A_z^{\,2}\right) \exp\left[-m\omega^2 \left(A_x^{\,2} + A_y^{\,2} + A_z^{\,2}\right)/2k_B T\right] dA_x dA_y dA_z$$

$$= 3\int m\omega^2 A_x^{\,2} \exp\left[-m\omega^2 \left(A_x^{\,2} + A_y^{\,2} + A_z^{\,2}\right)/2k_B T\right] dA_x dA_y dA_z$$

$$= 3 \cdot m\omega^2 \left(\frac{\sqrt{\pi}}{4}\left(\frac{2k_B T}{m\omega^2}\right)^{3/2} \cdot \frac{\pi}{4}\left(\frac{2k_B T}{m\omega^2}\right)\right)$$

Note: the factors containing (2) and (4) inside occur because of the double-sided Gaussian integrals in Δx, Δy, and Δz. So we get the simple result:

$$< U >_{atom} = \frac{3\left(\frac{m\omega^2}{8}\left(\frac{2\pi k_B T}{m\omega^2}\right)^{3/2}\frac{k_B T}{m\omega^2}\right)}{\left(\frac{\pi k_B T}{2m\omega^2}\right)^{3/2}} = 3k_B T$$

And $$<U_{tot}> = N_A<U_{atom}> = 3N_A k_B T \qquad (3)$$

where N_A is the number of atoms in the sample.

The surprising simplicity of Eq (3) is a shining example of the elegance and power of statistical mechanics in solids. The complicated effect of N_A atoms in random motion reduces to an expression that depends on only two parameters N_A and T (that can both be measured accurately) and a fundamental constant. Eqn (3) is also a great example of a fundamental principle of classical statistical mechanics that was discovered for the Maxwell distribution of velocities of "free" particles, but also applies to the atoms in our solid. Namely, the amount of total average energy in any solid will be (1/2) k_BT per *"degree-of-freedom"*. In our model of a monoatomic solid, each primitive unit cell provides 6 "degrees-of-freedom": three positional variables (Δr_x, Δr_y, and Δr_z), and three momentum variables ($md\Delta r_x/dt = p_x$, $md\Delta r_y/dt = p_y$, and $md\Delta r_z/dt = p_z$). Note that in the Maxwellian distribution of N_P "free" particles, the position variables are no longer relevant because they do not contribute to energy (i.e., there is no interaction between neighboring atoms), so there are just 3 "degrees-of-freedom" and the average energy becomes $<U_{tot}> = N_P<U>_{particle} = (3/2)N_P k_B T$.

Eqn (3) is important for another fundamental reason related to the hierarchy of solids in Chapter 1. From the macroscopic perspective of thermodynamics, the time-averaged atomic energy of Eqn (2) is entirely *heat*. This statement may at first appear contradictory since the analysis depended on two separate kinetic and potential energy terms, and we have on occasion defined *heat* as being the collective microscopic kinetic energy (i.e., "atoms in motion"). For a Maxwellian distribution of "free" particles, all of the microscopic energy is kinetic and the *kinetic* description is accurate. But in solids the strong bonding between atoms creates a constant oscillation between atomic kinetic and potential energy. And since both terms are time varying, both contribute to the energy of "atoms in motion" and, therefore, to the *heat*. With this clarification, we can use (3) immediately to calculate the one of the most important macroscopic cross-derivatives in thermodynamics, the heat capacity

$$C_V \equiv \delta Q/\delta T = T(dS/dT)|_V \approx \partial <U_{tot}>/\partial T = 3N_A k_B \qquad (4)$$

This is called the law of Dulong and Petit, named after two 19th century chemists that discovered it in doing careful experiments on solids during the seminal period of Thermodynamics long before the development of statistical mechanics, the atomic picture of matter, or the quantum theory. It is often evaluated as follows in the conventional units of solid-state chemistry:

$$C_V \approx 4.14\times10^{-23}\ J/K\cdot atom = 1.29\times10^{-4}\ eV/K\cdot atom$$

$$C_V \approx 4.14\times10^{-23}\ J/K\cdot atom\cdot\frac{6.023\times10^{23}\ atom}{mole} = \frac{24.94J}{K\cdot mole}$$

$$C_V \approx \frac{24.94J}{K\cdot mole}\cdot\frac{Cal}{4.19J} = \frac{5.95cal}{K\cdot mole}$$

In fact, the Dulong-Petit law is a good example of how science usually works. It is the seminal experiments that drive the development of theory, not vice versa.

Phonons

In the quantum mechanical picture, the amplitude of each lattice wave of wave vector k is quantized according to the rule $U_k = (n_k + ½)\,\hbar\,\omega_k$. This expression already accounts for quantum uncertainty, but not statistical mechanics. To get the latter, we proceed as done earlier assuming that the lattice wave, or "mode" of wave vector k, is now the subsystem in equilibrium with the rest of the solid represented as a bath at temperature T. Interestingly, this approach is highly *delocalized* since any lattice wave is distributed over the entire lattice at any given time. In addition, the statistical ensemble of states formed by all possible configurations of the subsystem is now *just all the possible amplitudes* of the chosen mode. So according to the Boltzmann principle, we can write

$$f_k = \frac{e^{-U_k/k_BT}}{\sum e^{-U_k/k_BT}} = \frac{e^{-(n_k+\frac{1}{2})\frac{\hbar\omega_k}{k_BT}}}{\sum e^{-(n_k+\frac{1}{2})\frac{\hbar\omega_k}{k_BT}}} \equiv f_{nk}\ ,\ \text{n = 0, 1, 2, …}$$

which means the probability of occupancy of mode k having excitation n_k. This is a difficult sum to evaluate. But average quantities are easier, the most important one being the mean "amplitude", or mean number of phonons in mode k:

$$\langle n_k\rangle = \frac{\sum_{n_k=1}^{\infty} n_k e^{-(n_k+\frac{1}{2})\frac{\hbar\omega_k}{k_BT}}}{\sum_{n_k=0}^{\infty} e^{-(n_k+\frac{1}{2})\frac{\hbar\omega_k}{k_BT}}} = \frac{e^{-\frac{\hbar\omega_k}{2k_BT}}\sum_{n_k=0}^{\infty} n_k e^{\frac{-n_k\hbar\omega_k}{k_BT}}}{e^{-\frac{\hbar\omega_k}{2k_BT}}\sum_{n_k=0}^{\infty} e^{\frac{-n_k\hbar\omega_k}{k_BT}}}$$

The sum in the denominator can be written $\sum = (e^{\frac{-0\hbar\omega_k}{k_BT}} + e^{\frac{-1\hbar\omega_k}{k_BT}} + e^{\frac{-2\hbar\omega_k}{k_BT}} +)e^{\frac{-\hbar\omega_k}{2k_BT}}$

$$= e^{\frac{-\hbar\omega_k/2}{k_BT}}(1 + e^{\frac{-\hbar\omega_k}{k_BT}} + e^{\frac{-2\hbar\omega_k}{k_BT}} + ...)$$

which is a geometric series, each term in the parenthesis having magnitude < 1. Thus

$$\sum_{n_k=0}^{\infty} e^{\frac{-n_k\hbar\omega_k}{k_BT}} = \sum_{n_k}^{\infty}\left(e^{\frac{-\hbar\omega_k}{kT}}\right)^{n_k} = \frac{1}{1-e^{\frac{-\hbar\omega_k}{kT}}}$$

To evaluate the numerator we invoke a trick, noting that

$$n_k = (-\frac{kT}{\hbar}\frac{d}{d\omega_k}e^{\frac{-n_k\hbar\omega_k}{k_BT}})(e^{\frac{n_k\hbar\omega_k}{k_BT}})$$

Thus $\sum_{n_K=0}^{\infty} ne^{-(n_k)\hbar\omega/k_BT} = \sum -\frac{k_BT}{\hbar}\frac{d}{d\omega_k}e^{-(n_k)\hbar\omega_k/k_BT} = \frac{-k_BT}{\hbar}\frac{d}{d\omega_k}\sum_{n_k=0}^{\infty} e^{-(n_k)(\hbar\omega_k/k_BT)}$

$$= \frac{-k_BT}{\hbar}\frac{d}{d\omega_k}\left(\frac{1}{1-e^{-\hbar\omega_k/k_BT}}\right) = +\frac{k_BT}{\hbar}\frac{\hbar}{k_BT}\frac{e^{-\hbar\omega/k_BT}}{\left(1-e^{-\hbar\omega/k_BT}\right)^2}$$

So in the end, we get

$$\langle n_k\rangle = \frac{\sum_{n_k=0}^{\infty} n_k e^{-n_k\hbar\omega_k/k_BT}}{\sum_{n_k=0}^{\infty} e^{-n_k\hbar\omega_k/k_BT}} = \frac{\frac{e^{-\hbar\omega_k/k_BT}}{\left(1-e^{-\hbar\omega_k/k_BT}\right)^2}}{\left(\frac{1}{1-e^{-\hbar\omega_k/k_BT}}\right)} = \frac{1}{\left(e^{\hbar\omega_k/k_BT}-1\right)}$$

which is the famous Planck function. It applies to each particular lattice wave, so different wave types, e.g., longitudinal and transverse, will have different $<n_k>$, which we will designate by the "polarization" p. A useful approximation occurs for "low-lying" phonons for which $\hbar\omega << k_BT$ and

$$\langle n_k\rangle = \frac{1}{\left(1+\hbar\omega/k_BT+..-1\right)} \approx \frac{k_BT}{\hbar\omega} .$$

Because of its importance in Planck description of radiation, this is called the classical or Rayleigh-Jeans approximation.

Example 1: Mean number of phonons in acoustical modes

In the previous chapter we saw that the classical amplitude corresponding to a single phonon is an extremely small number typically less than 10^{-20} m. A related quantity is the mean number of phonons which can computed directly from the Planck distribution given a mode. Suppose one has a 1 cm^3 sample

of crystalline aluminum at room temperature (300 K), which has an fcc Bravais lattice with conventional cubic lattice constant a = 4.05 Ang. What is the mean number of phonons in the longitudinal acoustic (LA) mode of minimum k and of maximum k, both along one of the <100> axes ?

Answer: We start with the dispersion curve for LA phonons:

$$\omega = \{(2C/m)[1 - \cos(kd)]\}^{1/2} \tag{11}$$

where d, the interplanar distance, is 2.02 Ang along the [100] direction. The long-wavelength LA wave velocity (i.e., speed of sound) is known from acoustics (or elasticity theory) to be $v_s \approx$ 6290 m/s along the [100] direction. In the long-wavelength limit of (11), we get $\omega = (C/m)^{1/2}$ kd, or $(C/m)^{1/2} = v_s/d = 3.1\text{x}10^{13}$ s^{-1} . The minimum k is dictated by the size of the sample such that $2\pi/L = 628$ m^{-1}, for which $\omega_{min} \approx k_{min}v = 3.95\text{x}10^{6}$ s^{-1}, $\hbar\omega_{min} = 4.16\text{x}10^{-28}$ J = $2.6\text{x}10^{-9}$ eV, $\hbar\omega_{min} / k_BT = 1.0\text{x}10^{-7}$, and $<n_k> \approx k_BT / \hbar\omega_{min} = 1.0\text{x}10^{7}$. The maximum k is $k_{max} = \pi/d =$ $1.55\text{x}10^{10}$ m^{-1}, for which $\omega_{max} = \{(2C/m)[1 + 1]\}^{1/2} = 6.2\text{x}10^{13}$ s^{-1}, , $\hbar\omega_{max} = 6.5\text{x}10^{-21}$ J = 0.041 eV, $\hbar\omega / k_BT = 1.57$, and $<n_k> \approx \{\exp(\hbar\omega / k_BT) - 1\}^{-1} = 0.26$. So now we see how the low-lying phonons are important in solids not because of their large size, but because of their large numbers.

Statistical Mechanics of Phonons

Mean energy and other thermodynamic quantities are averages just over all the possible n_k values, since different k values correspond to different modes and, therefore, different statistical subsystems. Thus the mean energy in mode k can be written

$$\langle U_k \rangle = \frac{\sum_{n_k=0}^{\infty} U_k e^{-n_k\hbar\omega_k/k_BT}}{\sum_{n_k=0}^{\infty} e^{-n_k\hbar\omega_k/k_BT}} = \frac{\sum_{n_k=0}^{\infty} (n_k + 1/2)\hbar\omega_k e^{-n_k\hbar\omega_k/k_BT}}{\sum_{n_k=0}^{\infty} e^{-n_k\hbar\omega_k/k_BT}} = (< n_k > + 1/2)\hbar\omega_k$$

With these considerations, the mean energy from all modes and polarizations is given by

$$\langle U_{tot} \rangle = \sum_{k,p} \cdot \left(\langle n_k \rangle + \frac{1}{2} \right) \cdot \hbar\omega_k = \sum_{k,p} \cdot \left[\frac{1}{e^{\hbar\omega_k/k_BT} - 1} + \frac{1}{2} \right] \cdot \hbar\omega_k \tag{12}$$

And the sum is carried out from k = 0 to $k_{max} = \pi/d$, consistent with the Nyquist criterion for lattice waves.

To evaluate this quantity we first convert it from a sum over k to an integral over k. We seek the quantity N(k)dk that describes the number of modes between k and k + dk. Since **k** is always a vector, k

represents its scalar magnitude. As might be expected, N(k)dk is a function of crystal size and lattice dimensionality, and always starts with the fact that the finest increment, or length-per-state of **k** space is $2\pi/L$ where L is the size of the sample along the direction of **k** specified. Reciprocally, the number of states-per-unit-length in k space is $L/2\pi$. In 1-dim the number of states in the length between k and k + dk is thus $N(k)dk = (L/2\pi)dk$. Similar reasoning applies to 2- and 3-dim where the number of states-per-unit-area and states-per-unit-volume are $(LxLy)/(2\pi)^2 = A/(2\pi)^2$ and $(LxLyLz)/(2\pi)^3 = V/(2\pi)^3$, respectively. Hence, in 2-dim and using circular coordinates with radial variable k, the number of states between k and k + dk is $A/(2\pi)^2$ times the annulus of area $2\pi kdk$, or $N(k)dk = 2\pi Akdk/(2\pi)^2 = Akdk/2\pi$. And in 3-dim and using *spherical* coordinates with radial variable k, the number of states between k and k + dk is $V/(2\pi)^3$ times the *shell* of volume $4\pi k^2 dk$, or $N(k)dk = Vk^2 dk/(2\pi^2)$. These relationships are summarized in Table I and they convert (12) to the integral

$$\left\langle U_{tot} \right\rangle = \sum_p \cdot \int_0^{k_{\max}} \left[\frac{1}{e^{\hbar\omega_k / k_B T} - 1} + \frac{1}{2} \right] \cdot \hbar\omega_k N(k) dk \tag{13}$$

Table I. State densities in k and ω space.

Dimensionality	N(k)dk	D(ω)dω
1	$(L/2\pi)dk$	$(L/2\pi)(dk/d\omega)d\omega$
2	$(Ak/2\pi)dk$	$(Ak/2\pi)(dk/d\omega)d\omega$
3	$(Vk^2)/2\pi^2)dk$	$(Vk^2)/2\pi^2)(dk/d\omega)d\omega$

For analytic evaluation of (12) the next step is to convert from an integral over k to an integral over ω, taking advantage of the fact that all the terms in the integrand of (13) are written explicitly in terms of ω. Now we must compute the number of states between ω and ω + dω, which is defined by D(ω)dω. An expression for D(ω) follows from the conservation of states such that $D(\omega)d\omega = N(k)dk$, leading to the (Jacobian) transformation $D(\omega) = N(k)(dk/d\omega) = N(k)/v_g$, where v_g is the group velocity. Substitution into (13) along with the dispersion relation ω(k) yields the useful expression

$$\left\langle U_{tot} \right\rangle = \sum_p \cdot \int_0^{\omega_{\max}} \left[\frac{1}{e^{\hbar\omega_k / k_B T} - 1} + \frac{1}{2} \right] \cdot \hbar\omega_k D(\omega) d\omega \tag{14}$$

We will analyze this using two famous approximation techniques before evaluating it exactly by modern numerical techniques.

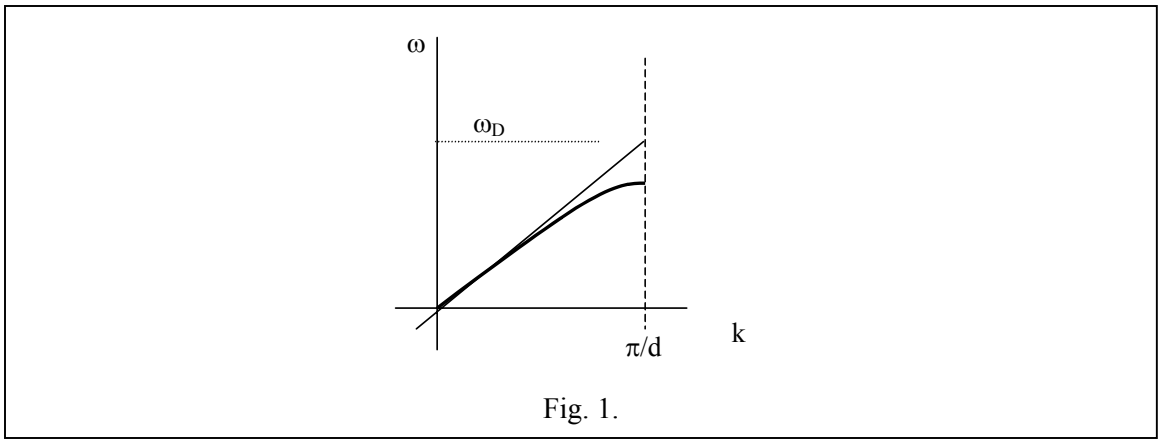

Fig. 1.

Debye Approximation for Acoustical Branch

In one of the greatest derivations in solid-state history, P. Debye analyzed (14) for acoustical lattice waves under the assumption that they always obeyed the long-wavelength limit such that

$$\omega^2 = (2C/m)(1 - \cos ka) = (kv_{s,p})^2 \qquad \text{for all k}$$

where $v_{s,p}$ is the long-wavelength speed-of-sound for the pth polarization, be it compressional or shear. By doing this there is a loss of meaning in k_{max} and ω_{max}, so an additional constraint must be applied to determine the upper limit on the integral in (14). This is found by recalling our rule for phonon types: the number of acoustical phonons is always $3N_C$, where N_C is the number of primitive lattice cells in the solid. Thus, no matter what type of crystal lattice we have (in 3-dim) N_C = #states-per-unit-volume in k space times the volume occupied of significant states, or mathematically,

$$N_C = [V/(2\pi)^3](4/3)\pi(k_{max})^3 \equiv [V/(2\pi)^3](4/3)\pi(\omega_{D,p}/v_{s,p})^3$$

where $\omega_{D,p}$ is the Debye frequency for the pth polarization. Re-arrangement leads to

$$\omega_{D,p}{}^3 = \frac{6\pi^2 v_{s,p}{}^3 N_C}{V} \quad \text{and} \qquad k_D \equiv \frac{\omega_{D,p}}{v_{s,p}}\left(\frac{6\pi^2 N_C}{V}\right)^{\frac{1}{3}}$$

A graphical summary of the Debye approximations is shown in Fig. 1. Substitution of them into (14) yields

$$\langle U_{tot} \rangle = \sum_p^3 \int_0^{\omega_{D,p}} \left[\frac{1}{e^{\hbar\omega/k_B T} - 1} + \frac{1}{2}\right] \hbar\omega \frac{V}{2\pi^2} \frac{\omega^2}{v_{s,p}{}^3} d\omega$$

where the subscript k on ω has been dropped for simplicity. The temperature independent part of this integral is trivial and leads to a term called the "zero-point" lattice energy

$$\left\langle U_{tot,0} \right\rangle = \sum_{p}^{3} \frac{\hbar V \omega_{D,p}^4}{16\pi^2 v_{s,p}^3}$$

As in photon theory, it is an energy term that can not do work, nor receive work from outside forces. However, it is the source of "quantum fluctuations" in temperature and other thermodynamic quantities of particular interest in nanoscience.

To analyze the temperature dependent part, we make the substitutions

$x = \frac{\hbar\omega}{kT}$, $x_D = \frac{\hbar\omega_D}{kT}$, $\omega = \frac{kTx}{\hbar}$, and $d\omega = \frac{kT}{\hbar}dx$. So we get

$$\left\langle U_{tot} \right\rangle = \sum_{p=1}^{3} \frac{\hbar V}{2\pi^2 v_{s,p}^3} \left(\frac{k_B T}{\hbar}\right)^4 \int_0^{x_{D,p}} \frac{x^3 dx}{e^x - 1} \tag{15}$$

Since $(\hbar\omega_D / k_B)^3$ has units of a temperature, it is natural to define $\hbar\omega_D / k_B \equiv T_D$ and $x_D \equiv T_D/T$ where T_D is called the Debye temperature. Hence, the temperature-dependent part becomes

$$\left\langle U_{tot} \right\rangle = \sum_{p=1}^{3} 3N_C k_B T \left(\frac{T}{T_D}\right)^3 \int_0^{x_{D,p}} \frac{x^3 dx}{e^x - 1} \tag{16}$$

This expression leads to some very simple and important forms. For high temperatures $T > T_D$, the e^x factor in the denominator is small so we can Taylor expand $e^x \approx 1 + x$..

$$\left\langle U_{tot} \right\rangle \approx \sum_{p=1}^{3} 3N_C k_B T \left(\frac{T}{T_D}\right)^3 \int_0^{x_{D,p}} x^2 dx \cong \sum_{p=1}^{3} 3N_C k_B T \left(\frac{T}{T_D}\right)^3 \frac{x_{D,p}^{\ 3}}{3} = \sum_{p=1}^{3} N_C k_B T \left(\frac{T}{T_D}\right)^3 \left(\frac{\hbar\omega_D}{k_B}\right)^3 \frac{1}{T^3}$$

$$\text{So } < U_{tot} >= \sum_{p=1}^{3} N_C k_B T = 3N_C k_B T \tag{17}$$

where the last step follows from the fact that the dependence on p has disappeared owing to some fortuitous cancellations. We are back to expression (3)

This impressively simple expression allows us to take an important thermodynamic cross-derivative, the heat capacity. Because we are dealing with the total energy of lattice waves as opposed to the static lattice, all the energy can be considered kinetic and therefore as *heat.* So provided that the volume is assumed to stay nearly constant (a good approximation for most solids), the temperature derivative of $<U_{tot}>$ is a good approximation to the heat capacity,

$$C_v \approx \frac{d < U_{tot} >}{dT} = 3N_C k_B \qquad T > T_D \ldots$$

At low temperatures defined by $T << T_D$, something even more interesting occurs. The e^x factor in denominator causes the integrand to decay very fast over the range $0 < x < x_D$. So with little error we

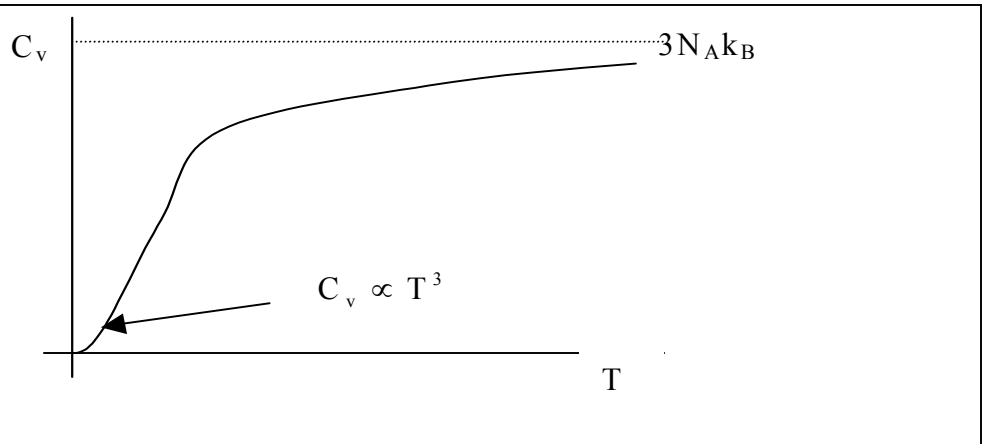

Fig. 2

can let x_D go to ∞ which allows the application of a very useful exact integral formula:

$\int_0^\infty dx\left(\frac{x^3}{e^x-1}\right)=\frac{\pi^4}{15}$. The total energy then becomes

$$\langle U_{tot}\rangle=\sum_{p=1}^{3}\frac{\pi^4 N_C k_B T^4}{5T_D^3}$$

Again, the temperature derivative of $<U_{tot}>$ is a good approximation to the heat capacity,

$$C_v\approx\frac{d<U_{tot}>}{dT}=\sum_{p=1}^{3}\frac{4\pi^4}{5}N_C k_B\left(\frac{T^3}{T_D}\right)\quad\left(T<<T_D\right)\ldots$$

This is the famous Debye "T^3" law observed experimentally during the early 20th century after the advent of cryogenics, and considered by many to be a great triumph in science because it provided the first unequivocal demonstration of the then-revolutionary quantum theory of solids. The overall qualitative behavior of the heat capacity of monatomic crystalline solids then takes on the form in Fig. 2.

Einstein Approximation for Optical Branch

Debye's model works remarkably well for the acoustical branch. However in all lattice consisting of two or more atoms per primitive cell, or in any crystal having two or more atoms that differ elementally, there will be an optical branch as well. In general all optical-lattice-wave dispersion curves $\omega(k)$ decrease vs k in the 1st Brillouin zone, but the change of ω is much less than for the acoustical curves. So a useful starting approximation is to assume that the dispersion curves are flat at frequencies $\omega_{E,P}$, where p denotes the polarizations (longitudinal or transverse) within the optical lattice-wave branch. This makes the density-of-states $D(\omega)$ behave like a Dirac delta function. Furthermore, there are $3N_A - 3$ optical wave polarizations where N_A is the number of atoms per primitive unit cell. So we can write

$$\rightarrow D(\omega) = N_C \delta\left(\omega - \omega_{E,P}\right)$$

from Eqn (14)

$$< U_{tot} > \rightarrow \sum_p \left(\frac{N_C \hbar\omega_{E,P}}{e^{\frac{\hbar\omega_{E,P}}{k_B T}} - 1} + \frac{N_C \hbar\omega_{E,P}}{2} \right)$$

And as for the acoustical modes, the heat capacity is simply

$$C_v \cong \frac{d\left\langle U_{tot} \right\rangle}{dT} = \frac{\sum_p N_C \hbar\omega_{E,P} \left(\frac{\hbar\omega_{E,P}}{k_B T^2} \right) e^{\frac{\hbar\omega_{E,P}}{k_B T}}}{\left(e^{\frac{\hbar\omega_{E,P}}{k_B T}} - 1 \right)^2}$$

In the limit of high temperature, $\hbar\omega_{E,P} < k_B T$, this displays the behavior

$$C_v \rightarrow \sum_p \frac{N_C k_B \left(\frac{\hbar\omega_{E,P}}{k_B T} \right)^2 \left(1 + \frac{\hbar\omega_{E,P}}{k_B T} \right)}{\left(1 + \frac{\hbar\omega_{E,P}}{k_B T} - 1 \right)^2} \cong \sum_p N_C k_B \left(1 + \frac{\hbar\omega_{E,P}}{k_B T} \right) \approx \sum_p N_C k_B$$

As in the acoustical phonon case, the dependence on polarization vanishes in this limit, so that the sum can be carried out over the number of optical lattice-wave polarization (e.g., = 3 for a diatomic basis such as Si or GaAs).

In the opposite limit of low temperature, $\hbar\omega_{E,P} > k_B T$, we find

$$C_v \rightarrow \sum_p N_C k_B \left(\frac{\hbar\omega_{E,P}}{k_B T} \right)^2 e^{\frac{-\hbar\omega_{E,P}}{k_B T}}$$

This becomes exponentially small as the temperature drops, generally making it unimportant at all but the higher temperatures.

Quantum "Freeze-Out"

The Debye T^3 law is a profound consequence of the interplay between quantum mechanics and statistical mechanics that occurs in solids. According to the Planck function, the phonon number, or amplitude, of a given lattice wave (of wave number k) drops monotonically with temperature. This is also predicted classically through the derivation of the mean energy of an atom $<U_{atom}>$ undergoing wave excitation of amplitude Δr. This is the expected result from the Boltzmann probability assumption.

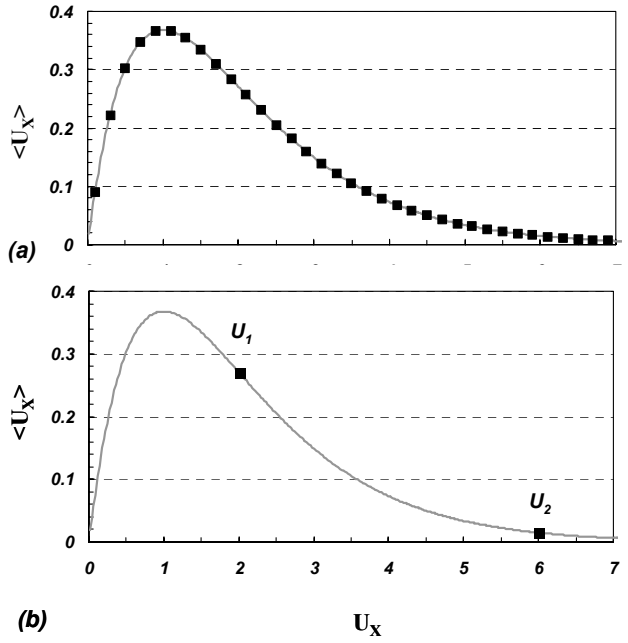

Fig. 3.

But also through the Planck function, there is a second temperature dependence on the lattice wave frequency ω and its associated quantum, $\hbar\omega$. This does not appear in the classical derivation, as evidenced by the fact that there are no lattice-wave parameters in the classical result $<U_{tot}> = 3N_Ak_BT$, or the associated heat capacity $C_V = 3N_Ak_B$. In contrast, according to the quantum theory the lattice-wave modes are *not* excited equally. *Higher frequency modes are always less likely to be excited no matter what the temperature*. This important result is called generically "freeze-out" in modern physics because it represents the tendency for nature to depopulate the higher-lying (i.e., higher frequency) modes in favor of the lower ones as the temperature is decreased. It is always associated with the condition $<n_k> << 1$, where k is the modal "quantum number" – usually the wave vector, but now always. And it is a consequence of the quantization effect itself, not the statistical or thermodynamic behavior !

To capture this last conclusion graphically, Fig. 3 shows the effect of quantum mechanics on the process of taking a statistical average of energy based on the Boltzmann criterion. The energy is represented by values U_X parameterized by mechanical variables represented collectively by X, such that $<U_X> = C\ \Sigma x_i\ U_X \exp(-U_X/k_BT)$, where C is the normalization constant. The energy "spectrum" is assumed to have three forms: (i) classical-mechanical with associated continuous distribution of U_X; (ii) "fine" quantum mechanical having a discrete form $U_X = U_0 + \Delta U_X$, with $U_0 = 0.1\ k_BT$ and $\Delta U = 0.2\ k_BT$; and (3) "course" quantum mechanical having the same discrete form but with $U_0 = 2\ k_BT$ and $\Delta U_X = 4\ k_BT$. The "fine" quantum mechanical is superimposed on the classical spectrum in Fig. 3(a). The continuous spectrum is closely approximated by the discrete one over the entire range of behavior,

including energies below the peak where $U_X << k_BT$ and above the peak where $U_X >> k_BT$. But in Fig. 3(b) where the "course" quantum mechanical is superimposed on the classical spectrum, the first quantum energy level U_1 does not occur until well above the peak. Hence, the discrete spectrum does not sample the portion of the continuus spectrum near the peak and below, and the quantum levels are effectively "frozen-out" of the averaging process. Again, it is the quantum mechanics causing this effect, not the statistical averaging.

An exact mathematical representation of "freeze-out" can usually be derived once one knows the quantization rules for the "modes" of the solid. In the case of the Debye model of acoustic phonons, the freeze-out condition is simply that $T < T_D$, since in this range of temperature, there will be high-lying lattice waves for which hbar $\omega > k_BT$ and, therefore, $<n_k> << 1$ according to the Planck function. We will see similarly simple conditions for "freeze-out" in the behavior of "free" electrons in metals, semimetals, and semiconductors, where T_D gets replaced by T_F - the Fermi temperature.