Quantum lattice vibrations

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I. BASICS AND HEAT CAPACITY

We are now going to treat the problem of the harmonic crystal quantum mechanically. For concreteness and simplicity, we will focus throughout on the case of a 3d monatomic Bravais lattice. We have already shown that we can break the problem into $3N$ decoupled harmonic oscillators. Schematically, if the normal mode coordinates are q_i and p_i, then the Hamiltonian is $H = \sum_{i=1}^{3N} H_i$, and

$$H_i = \frac{p_i^2}{2M} + \frac{1}{2} M \omega_i^2 q_i^2 . \tag{1}$$

More specifically, the normal mode coordinates are $u^R_\lambda(\boldsymbol{k}), u^I_\lambda(\boldsymbol{k})$, the normal mode momenta are $p^P_\lambda(\boldsymbol{k}), p^I_\lambda(\boldsymbol{k})$, and the frequencies are $\omega_\lambda(\boldsymbol{k})$. The wavevector $\boldsymbol{k}$ ranges over half of the Brillouin zone, where, say, $k_x \geq 0$. Doing things this way, we should say there are two oscillators for every $(\boldsymbol{k}, \lambda)$ – corresponding to the real and imaginary parts of the coordinates and momenta.

However, since $\omega_\lambda(\boldsymbol{k}) = \omega_\lambda(-\boldsymbol{k})$, it is often more convenient to let $\boldsymbol{k}$ range over the entire Brillouin zone. Then we should say that, for every $(\boldsymbol{k}, \lambda)$, there is a single oscillator with frequency $\omega_\lambda(\boldsymbol{k})$. We will follow this convention.

The energy spectrum of each oscillator is

$$E_{\boldsymbol{k}\lambda} = \hbar \omega_\lambda(\boldsymbol{k})(n_{\boldsymbol{k}\lambda} + 1/2), \tag{2}$$

where $n_{\boldsymbol{k}\lambda} = 0, 1, 2, \ldots$. The integer $n_{\boldsymbol{k}\lambda}$ is the number of quanta (of energy) in the oscillator labeled by $(\boldsymbol{k}, \lambda)$. We adopt the useful convention of thinking about these quanta of energy like particles, called phonons. Then we can equivalently say that $n_{\boldsymbol{k}\lambda}$ is the number of phonons that have crystal momentum $\boldsymbol{k}$ and polarization λ. (Sometimes $n_{\boldsymbol{k}\lambda}$ is referred to as the phonon occupation number, since it tells us how many phonons occupy a given state.)

The total energy is

$$E = \frac{\hbar}{2} \sum_{\boldsymbol{k},\lambda} \omega_\lambda(\boldsymbol{k}) + \sum_{\boldsymbol{k}\lambda} \hbar \omega_\lambda(\boldsymbol{k}) n_{\boldsymbol{k}\lambda} . \tag{3}$$

The first term is the zero point energy.

There are a number of ways to see that the thermal average of the occupation number is

$$\langle n_{\boldsymbol{k}\lambda} \rangle = \frac{1}{e^{\beta \hbar \omega_\lambda(\boldsymbol{k})} - 1} . \tag{4}$$

This is just the Bose distribution with the chemical potential $\mu = 0$. The reason it's the Bose distribution is that the state counting and energy spectrum of the phonon system is exactly the same as a system of bosons with energy $E_{\boldsymbol{k}\lambda} = \hbar \omega_\lambda(\boldsymbol{k})$. The reason $\mu = 0$ is that here, unlike for bosons, the number of phonons is not a conserved quantity. It's also possible to directly calculate $\langle n_{\boldsymbol{k}\lambda} \rangle$ using the partition function of the harmonic oscillator – this is essentially what is done in Ashcroft & Mermin.

We are interested in calculating the specific heat, which is given by

$$c_V = \frac{1}{V} \Big(\frac{\partial \bar{E}}{\partial T} \Big)_V , \tag{5}$$

where $\bar{E} = \langle E \rangle$ is the thermal average of the energy. (Note that this is related to the *heat capacity* C_V by $C_V = V c_V$.) To calculate $\bar{E}$ we can use the above result and drop the zero-point energy, which doesn't give any temperature dependence. We have

$$\bar{E} = \sum_{\boldsymbol{k},\lambda} \frac{\hbar \omega_\lambda(\boldsymbol{k})}{e^{\beta \hbar \omega_\lambda(\boldsymbol{k})} - 1} = V \sum_\lambda \int \frac{d^3 \boldsymbol{k}}{(2\pi)^3} \frac{\hbar \omega_\lambda(\boldsymbol{k})}{e^{\beta \hbar \omega_\lambda(\boldsymbol{k})} - 1} . \tag{6}$$

The integral over $\boldsymbol{k}$ is taken over the Brillouin zone.

Even if we actually knew everything about the frequencies $\omega_\lambda(\boldsymbol{k})$, in general this integral can only be evaluated analytically in certain limits. One simple limit is high temperature, where $\beta\hbar\omega_\lambda(\boldsymbol{k}) \ll 1$ for all frequencies. In this limit,

$$\frac{1}{e^{\beta\hbar\omega_\lambda(\boldsymbol{k})}-1} \approx \frac{1}{\beta\hbar\omega_\lambda(\boldsymbol{k})}, \tag{7}$$

and so

$$\bar{E} \approx V\sum_\lambda \int \frac{d^3\boldsymbol{k}}{(2\pi)^3}\frac{1}{\beta} = 3Nk_BT, \tag{8}$$

where we used the fact that the volume of the Brillouin zone is $(2\pi)^3/a^3$, where a^3 is the volume of a primitive cell of the Bravais lattice. This gives the classical Dulong-Petit result that $C_V = 3Nk_B$, which is exactly what the equipartition theorem gives when we treat the harmonic crystal classically.

We can also evaluate $\bar{E}$ in the low-temperature limit. The integral will be dominated by $\boldsymbol{k}$ where $\omega_\lambda(\boldsymbol{k})$ is *small.* The contributions from other frequencies are exponentially suppressed for low temperature. This means that, in the limit of asymptotically low temperature, we can make two approximations. First, we replace the frequencies by the form near $\boldsymbol{k}=0$: $\omega_\lambda(\boldsymbol{k}) = c_\lambda(\hat{\boldsymbol{k}})|\boldsymbol{k}|$. Here, $c_\lambda(\hat{\boldsymbol{k}})$ is the phonon velocity, which in general depends on the direction of $\boldsymbol{k}$, represented by the unit vector $\hat{\boldsymbol{k}}$. Second, we integrate not just over the Brillouin zone, but over all $\boldsymbol{k}$. This is okay because the contributions from large-$\boldsymbol{k}$ are exponentially suppressed anyway. With these approximations,

$$\bar{E} = V\sum_\lambda \int \frac{d^3\boldsymbol{k}}{(2\pi)^3}\frac{\hbar c_\lambda(\hat{\boldsymbol{k}})|\boldsymbol{k}|}{e^{\beta\hbar c_\lambda(\hat{\boldsymbol{k}})|\boldsymbol{k}|}-1}. \tag{9}$$

To evaluate this integral, we go to spherical coordinates. We introduce the notation $\hat{\boldsymbol{k}} = \hat{\Omega}$, which reminds us that $\hat{\boldsymbol{k}}$ only depends on the angular coordinates of the integration. We have

$$\bar{E} = \frac{V}{(2\pi)^3}\sum_\lambda \int d\Omega \int_0^\infty dk k^2 \frac{\hbar c_\lambda(\hat{\Omega})k}{e^{\beta\hbar c_\lambda(\hat{\Omega})k}-1}. \tag{10}$$

Note how we have chosen the order of integration here. To do the k-integral, we make the change of variables $u = \beta\hbar c_\lambda(\hat{\Omega})k$, obtaining

$$\bar{E} = \frac{V}{(2\pi)^3}\sum_\lambda \int d\Omega \frac{1}{\beta^4\hbar^3 c_\lambda^3(\hat{\Omega})}\int_0^\infty du \frac{u^3}{e^u-1} \tag{11}$$

$$= \frac{V}{(2\pi)^3}\frac{\pi^4(k_BT)^4}{15\hbar^3}\sum_\lambda \int d\Omega \frac{1}{c_\lambda^3(\hat{\Omega})}. \tag{12}$$

In the last line, we used the fact that the u-integral is equal to $\pi^4/15$. Defining

$$\frac{1}{c^3} = \frac{1}{3}\sum_\lambda \int \frac{d\Omega}{4\pi}\frac{1}{c_\lambda^3(\hat{\Omega})}, \tag{13}$$

we have

$$\bar{E} = \frac{\pi^2}{10}\frac{V(k_BT)^4}{(\hbar c)^3}. \tag{14}$$

This gives the T^3 low-temperature specific heat observed in many insulators:

$$c_V = \frac{2\pi^2}{5}k_B\left(\frac{k_BT}{\hbar c}\right)^3 \tag{15}$$

In principle, we can use Eq. (6) to calculate $c_V(T)$ over a wide temperature range, if we know the phonon frequencies. Of course, in general we would have to do such an integral numerically. What we would find by doing this, or by doing a measurement of $c_V(T)$ in an insulator, is that the specific heat crosses over at low temperature from its T^3 behavior, to a roughly constant behavior at high temperature. The temperature scale characterizing this crossover is called the Debye temperature, Θ_D, and can range from 100 K to 1000 K depending on the material in question. For $T \ll \Theta_D$ not very many phonons are thermally excited, and their quantum nature is important. On the other hand, for $T \gg \Theta_D$, many phonons are excited, and it should be legitimate to think about them classically.

Another useful way to think about the Debye temperature is that it roughly is an average phonon energy, $\Theta_D \sim \hbar\bar{\omega}/k_B$, where $\bar{\omega}$ is the average of all the $\omega_\lambda(\boldsymbol{k})$.

A. Density of States

Much of the previous analysis can be redone in terms of a useful quantity called the density of states. It is defined as

$$g(\omega) = \sum_{\lambda} \int \frac{d^3\boldsymbol{k}}{(2\pi)^3} \delta(\omega - \omega_\lambda(\boldsymbol{k})). \tag{16}$$

The meaning of this quantity is that $g(\omega)d\omega$ is the number of phonon modes (per unit volume), with frequencies lying in the range $[\omega, \omega + d\omega]$. It can be shown that

$$\bar{E}/V = \int_{-\infty}^{\infty} d\omega \frac{g(\omega)\hbar\omega}{e^{\beta\hbar\omega} - 1}. \tag{17}$$

This means that, in particular, c_V only depends on the form of the phonon spectrum through $g(\omega)$.