Notes for Lecture 12

Quantum particles

In the last lecture, we already mentioned phonons and photons. Here we describe them fully.

12.1 Phonons

Phonons refer to quantized lattice vibrations. They are elementary but their applications in practice and in conceptual matters are quite broad. So, it is important to know these things well.

12.1.1 Normal modes

Before we can discuss phonons, we must discuss the *normal modes* of the coupled oscillator problem in classical mechanics. If you are not familiar with this problem, you might want to read up on your old note.[1]

The grand result is the following: for a three dimensional solid that consists of N atoms, there must be $3N$ normal modes, which can be thought of as completely independent simple harmonic oscillators within the *harmonic approximation*. The harmonic approximation means that the inter-atomic potential is approximated to the lowest non-constant order, i.e. to the quadratic order,[2] just as in the usual "Hooke's law" picture. Due to this problem being expressed in terms of real symmetric matrices,

[1]My teaching web site for 105 may be of help.

[2]Since the linear order must vanish at mechanical equilibrium.

within the Lagrangian formalism, it can be proved formally that the problem can always be diagonalized to yield exactly $3N$ completely independent simple harmonic oscillators. These are what we refer to as "normal modes."

So, it means that the Hamiltonian of *any* stable object (be it a molecule or a solid) can be written as

$$H = \sum_{i=1}^{3N} \left(\frac{p_{\eta,i}^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 \eta_i^2 \right) \tag{12.1}$$

where η_i is the normal mode coordinate, $p_{\eta,i}$ is its conjugate momentum, and m_i is the effective mass, and ω_i the frequency, of each normal mode, as long as the displacements of the atoms are not too large.[3]

Quantizing the above equation we get

$$H = \sum_{i=1}^{3N} \left(a_i^\dagger a_i + \frac{1}{2} \right) \hbar\omega_i \tag{12.2}$$

where $a_i, a_i^\dagger$ are the lowering and raising operators that can be formed by "taking the square root of the Hamiltonian," so to speak

$$a_i = \sqrt{\frac{1}{2\hbar\omega_i}} \left(\sqrt{m_i}\omega_i \, \eta_i + i \, \frac{p_{\eta,i}}{\sqrt{m_i}} \right) \tag{12.3}$$

$$a_i^\dagger = \sqrt{\frac{1}{2\hbar\omega_i}} \left(\sqrt{m_i}\omega_i \, \eta_i - i \, \frac{p_{\eta,i}}{\sqrt{m_i}} \right) \tag{12.4}$$

These two operators satisfy the following fundamental relation

$$\left[a_i, a_j^\dagger \right] = \delta_{i,j} \tag{12.5}$$

While elementary quantum mechanics books refer to these operators as simply lowering and raising operators, they are, in fact, the annihilation, or the destruction, operator and the creation operator for a boson. What is this boson? It is a particle in term of which we can describe how vigorously a string vibrates. Quantum mechanically, we describe the high energy state of a vibrating string as the state in which there are lots of lots of particles – lots of vibration quanta. In other words, lots of *phonons*. By the same token, this same mathematical formalism can describe photons as well. Photons are much like phonons, as we shall see, except that they

[3] If the displacements are significant, then the normal modes are independent only in an approximate sense. Many interesting non-linear effects occur, which involve their modification and mixing.

are related to light wave not sound wave. When you are looking at a bright object, you are being hit by lots and lots of photons. So, a bright light corresponds to lots of photons. The precise meaning of "lots of photons," or "lots of phonons" is simply that $n_i = a_i^\dagger a$ is a high number.[4]

What are these indices i, j? They are simply labels for vibrational modes. However, note that each vibrational mode is an eigenstate of a Lagrangian, which could well have certain symmetries. For instance, in a crystal, the Lagrangian will have crystal translation symmetry as well as certain crystal rotational symmetry and others. It then follows that the normal modes can be taken as eigenstates of the corresponding translation, rotation or other operation. Thus, in general, the index i can be taken as a symmetry label. Notably, in a crystal, it can be taken as, among other things, the "crystal momentum," $\vec{k}$. The full explanation of the crystal momentum is out of the scope of this course[5]. Here, a one dimensional crystal example suffices. Consider a one crystal consisting with the lattice constant a. This means that the crystal consists of a unit that is repeated by the translation by a indefinitely. It turns out that this view of a crystal as "something that repeats" is not just applicable in the real space, but applicable just as well in the wave vector space. In the wave vector space, any wave number k is equivalent to $k + 2\pi/a$ in this one dimensional crystal. This defines the notion of the crystal momentum. It ($\hbar\vec{k}$) is just like the momentum, except that its value itself is periodic. In this one dimensional example, $\hbar k$ and $\hbar(k + 2\pi/a)$ are completely equivalent, due to these wave vectors applicable to waves in crystal. In addition to the crystal momentum, the label i can have other symmetry labels, and so i is a collective index. In particular, note that it will in general, in dimensions higher than 1, include the polarization label. A similar consideration applies to photons, as well: i is a collective index for the momentum $\vec{k}$ and the polarization.

12.1.2 Dispersion relation

With i in ω_i being identified as a symmetry label, which include the crystal momentum and the polarization, one can ask what is the relationship between say $\vec{k}$ (crystal momentum) and ω for a given polarization?

Such a relationship is called the *dispersion relation*

$$\omega = \omega(\vec{k}) \tag{12.6}$$

[4]The commutation relation of Eq. 12.5 is the canonical commutation relation for bosons. Fermion creation and destruction operators satisfy $\{a_i, a_j^\dagger\} = \delta_{i,j}$, where $\{a, b\} \equiv ab + ba$ is the *anti-commutator*. The formulation of the many body problem with these creation/destruction operators is referred to as the *second quantization*, which is beyond the scope of this course.

[5]My lecture notes for physics 155 may be of help

As $\hbar\vec{k}$ is the momentum and $\hbar\omega$ is the energy, the dispersion relation can be viewed as defining the relation between the energy and the momentum.

12.1.3 Einstein phonons

This seemingly crude model has survived to this day, while it had not achieved its original goal in full, namely explaining the low temperature heat capacity of the diamond (and other solids).

The Einstein model simply assumes that all normal modes inside a solid is a single frequency mode.

$$\omega(\vec{k}) \;=\; \omega_E \tag{12.7}$$

You might ask how is this possible? Indeed, it may seem quite unlikely. However, for a crystal in which the repeating unit consists of more than one atom, there are phonon modes called "optical phonons." The Einstein model has survived as the simplest model to describe these optical phonons.

Now, given the fact that the Einstein model considers $3N$ independent oscillators of the same frequency, it follows that the thermodynamics of Einstein phonons is exactly the same as what has been described in Section 11.1, except that we have to apply the following transformations: $\omega \to \omega_E$, $Z \to Z^{3N}$, $E \to 3NE$, $C_V \to 3NC_V$ etc.

Therefore, the following qualitative behavior, much like the one oscillator problem, persists. (1) At high temperature ($k_BT \gg \hbar\omega_E$), the system behaves classically, and obeys the equipartition theorem and, thus, the Du-Long Petit law $C_V = 3Nk_B$. (2) At low temperature ($k_BT \ll \hbar\omega_E$), the system behaves quantum mechanically, and shows an activated behavior: e.g. the temperature dependence of C_V is dominated by $\exp\left(-\frac{\hbar\omega_E}{k_BT}\right)$.

While this model was originally suggested for explaining the heat capacity of the diamond, the behavior (2) is unlike what is actually observed. The actually observed behavior is $C_V \propto T^3$, the Debye-T^3 law, which needs to be explained with the help of universal[6] acoustic phonons (sound waves).

[6] In contrast, optical phonons are not universal, as they do not exist in a monatomic crystal.

12.1.4 Debye phonons

In the Debye model, the photon dispersion relation is assumed to be

$$\omega(\vec{k}) \;=\; vk \qquad\qquad k \;\equiv\; |\vec{k}| \tag{12.8}$$

Note that this becomes exactly the dispersion relation for photons in vacuum, if one substitutes c for v.

The phonons that obey the above dispersion relation are called Debye phonons. In solids, sound waves propagate as waves that satisfy the above dispersion relation at long wave length. So, sound waves, or acoustic phonons, are Debye phonons at long wave lengths. For them, v is about 10^{-5} of c.

While the Einstein model failed to explain the heat capacity of the diamond, the Debye model succeeded in explaining it, and as the result Debye received a big prize. Why the difference?

The difference lies in the fact that acoustic phonons are *universal*. The reason is deep. Consider a crystal place in vacuum. Now consider a wave (in other words, a particle) existing inside the crystal. Then, it is clear that from the point of view of that wave, the continuous translation symmetry of the vacuum is broken. By the Goldstone theorem, this situation allows the so-called Goldstone mode to exist. The Goldstone mode is a bosonic wave, whose energy goes to zero as the momentum goes to zero. More intuitively, the Goldstone mode can be thought of as the oscillation of the system that locally exploits the continuous symmetry that used to exist. The acoustic phonon case exemplifies such a mode perfectly. "Exploiting the continuous symmetry that used to exist" means, in this case, all atoms moving in one direction. The translational symmetry of the vacuum means that there is no restoring force for such a motion. Now, consider a sound wave, and make the wave length grow larger and larger. You have a wave whose local atomic displacements are just those of a translation, which does not cause any restoring force. Thus, a sound wave frequency goes to zero as $k \to 0$. This is the precise sense in which the sound wave is a Goldstone mode associated with the broken translational (and rotational) symmetry state of a crystal.

Note that this discussion assumes that the atomic interactions are local. If there is a long-range interaction, then this argument does not hold. Also, it happens that for typical short-ranged atomic interactions, the sound wave frequency goes to zero exactly as the above dispersion, i.e. $\omega \propto k$.

The calculations that lead to the T^3 law, as shown during the class, are not repeated here. Only key steps are now summarized.

Using the periodic boundary condition for wave in a box, we get that each $\vec{k}$ value "owns" a volume element of

$$\Delta k = \frac{8\pi^3}{V} \tag{12.9}$$

By considering a sphere with radius k, dividing the volume of the radius by Δk, we get the number of phonon modes, N_m, in that volume. $N_m = \frac{4\pi k^3}{3}/\Delta k$. Expressing k in terms of ω using the dispersion relation, and then taking the derivative, we get the density of states

$$D(\omega) = \frac{3V\omega^2}{2\pi^2 v^3} \tag{12.10}$$

where the 3 in the numerator takes into account the three polarizations per $\vec{k}$. We have the particle sum rule

$$\int_0^{\omega_D} d\omega D(\omega) = 3N \tag{12.11}$$

with N given by the number of atoms. From this, one gets

$$\omega_D = v(6\pi^2 n)^{1/3} \tag{12.12}$$

and

$$D(\omega) = \frac{9N\omega^2}{\omega_D^3} \tag{12.13}$$

The frequency scale ω_D (Debye frequency) leads to the definition of other scales

$$\theta_D = \frac{\hbar\omega_D}{k_B} \qquad \text{Debye temperaure} \tag{12.14}$$

$$k_D = \frac{\hbar\omega_D}{v} \qquad \text{Debye wave vector} \tag{12.15}$$

By carrying out the integral $E = E_0 + \int_0^{\omega_D} d\omega D(\omega) f_P(\hbar\omega)\hbar\omega$ where f_P is the Planck distribution function (Bose-Einstein function with $\mu = 0$: Eq. 11.11) we get

$$E = E_0 + 9Nk_BT\left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} dx \frac{x^3}{e^x - 1} \tag{12.16}$$

This leads to

$$C_V \approx \begin{cases} 3Nk_B & \text{if } T \gg \theta_D \\ \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta_D}\right)^3 & \text{if } T \ll \theta_D\text{, Debye } T^3 \text{ law} \end{cases} \tag{12.17}$$

Please consult your note and my other note which can be accessed by following link here (my 155 course lecture 09), which should be essentially the same thing that I wrote on the blackboard. In the note, please note that the qualitative part (page 3) is as important as the quantitative part. Since the qualitative argument is so important, it is worth repeating here.

When $T \ll \theta_D$, only phonons with $\omega \lesssim \omega_{max} = k_B T/\hbar$ are excited substantially. These are "classical phonons," which contribute dominantly to the thermodynamics. The maximum wave vector for these classical phonons is $k_{max} = \omega_{max}/v \propto T$. Thus, the number of all classical phonon modes is $\propto k_{max}^3 \propto T^3$. The total energy is obtained by multiplying this by $k_B T$, the equipartition energy per mode. So, $E - E_0 \propto T^4$. By dimensional argument and the extensivity, we must have $E - E_0 = BNk_BT\left(\frac{T}{\theta_D}\right)^3$, where B is a dimensionless constant. Then, $C_V = 4BNk_B\left(\frac{T}{\theta_D}\right)^3$.

12.2 Photons

Photons are just like Debye phonons, except for a few differences. (1) The speed in vacuum is given by the constant c. (2) There are only two polarizations in vacuum. (3) We do not know what medium, if any, corresponds to photon's vibration. (4) There is no fixed number of photon modes.

By re-using the results of the Debye phonon problem, or simply re-doing it with the density of states and so on, one gets

$$E \;=\; E_0 + V\frac{\pi^2}{15}\left(\frac{k_BT}{\hbar c}\right)^3 k_BT \tag{12.18}$$

Now, from the energy, the pressure can be obtained very simply

$$P \;=\; \frac{1}{3}\frac{E}{V} \tag{12.19}$$

The reason is because in the current problem, the only volume dependence in the partition function is through the dispersion relation $\omega(\vec{k}) = ck$ where $k \propto V^{-1/3}$. And, so for a microstate energy E_μ, we have $E_\mu \propto V^{-1/3}$, and thus,

$$\frac{\partial E_\mu}{\partial V} \;=\; -\frac{1}{3}\frac{E_\mu}{V} \tag{12.20}$$

So, it follows that

$$\left(\frac{\partial Z}{\partial V}\right)_T = \sum_{\mu} \frac{\partial \exp(-\beta E_\mu)}{\partial V} \tag{12.21}$$

$$= \frac{\beta}{3} \sum_{\mu} \frac{E_\mu}{V} \exp(-\beta E_\mu) \tag{12.22}$$

$$= \frac{\beta}{3} \frac{E}{V} \tag{12.23}$$

Using this and the fact that $P = -\frac{\partial F}{\partial V} = k_B T \frac{\partial \log Z}{\partial V}$, the above result that $P = \frac{1}{3}\frac{E}{V}$ follows easily. Note that this result applies to the whole E, not just the thermal part $E - E_0$.

Please read the book for the Wien's law and the Stefan's law.