PHYS455 Statistical Mechanics L5

Phonons and Some Thoughts on Long Range Order in Crystals

1 Introduction to phonons

I was told at the beginning of this semester that many of you are fifth year students. "They have learned too much and many of them are VERY VERY tired", according my colleagues. It is very touching to know that UBC seems to have a tradition to be very considerate to students. And I have certainly intended to be conformal with that spirit from the beginning of this semester.

There are at least two ways to make lives easier for my students. One is to teach something traditional and simple which on the other hand inevitably means boring and tedious to you or to me. Alternatively I can teach something interesting and exciting and yet not too involved. I have taken the later approach for at least two reasons.

The first reason is that most interesting physics in statistics mechanics should be and can be taught at very elementary level, though it is difficult to find a textbook where complicated subjects in statistical mechanics are explained at the level of our current lectures'. I intended to explain to your the concept of renormalization group equation in this way but unfortunately we are running out of time. But still I think we have done well in getting most stuff in the syllabus done, and well done.

It is certainly challenging to even an experienced lecturer, though this probably is NOT a major concern to most of you. And it is possible to do it in a right way because the true beauty of physics lies in its **SIMPLICITY**. That is **The world should be understood with a minimal number of basic assumptions.** This leads me to believe that we can do it. So in this course I try to demonstrate how MUCH you will be able to know about large systems (no matter how complicated they are), with how LITTLE pre-required knowledge about complex systems. It is a good deal, isn't it ?

The second reason is largely "humanistic". Life is short and time is precious, specially to many of you this is probably the last year in UBC. I imagine that there are so many things in your lives you have to take care of: thesis,job fairs, finding out what to do in the future, spending time with friends, go skiing and dating etc. So why should you spend three hours/per week in this class listening to someone who talks about boring stuff? Both you and I deserve something better, something interesting.

As I promised, you will learn one half of the theory for the universe in less than half hour, though the other half you will probably never learn because I even don't know if it exists. The theory of crystals is simple and yet USEFUL, IMPORTANT, SEXY. What else can have all these features at the same time?

I haven't recommended you to spend too much time on reference books because I found the devices involved in most references are too heavy for you to carry. And in most cases you should be able to understand what I talk about in lectures without any heavy artillery. For phonons you can find some nice elementary discussions in Aschroft and Mermin's book. However, this as well as most of other statistic mechanics textbooks fail to mention a very IMPORTANT and well-known aspect of phonons in crystals. I intend to discuss it briefly in this set of notes.

Let me review what we have learned. As discussed in previous lectures, one can introduce the following coordinates for lattice sites in a **cubic** crystal

$$\mathbf{R} = (n_x, n_y, n_z)a, n_\mu = 0, \pm 1, \pm 2, \dots, \mu = x, y, z.$$
(1)

The position of an atom at site \mathbf{R} then is characterized by the following vector

$$\mathbf{r}(\mathbf{R}) = \mathbf{R} + \mathbf{u}(\mathbf{R}). \tag{2}$$

In the Debye-Einstein model, the energy for atoms in a crystal is

$$E = \sum_{\mathbf{R}} \frac{\mathbf{P}^2(\mathbf{R})}{2M} + \frac{1}{2} M \omega^2 \sum_{\langle \mathbf{RR}' \rangle} |\mathbf{U}(\mathbf{R}) - \mathbf{U}(\mathbf{R}')|^2.$$
(3)

The second sum is over all neighboring sites.

In general, by introducing the Fourier transformation of $\mathbf{W}(\mathbf{R})$,

$$\mathbf{W}(\mathbf{R}) = \frac{1}{\sqrt{V_L}} \sum_{\mathbf{Q}} \mathbf{W}(\mathbf{Q}) \exp(i\mathbf{Q} \cdot \mathbf{R}), \tag{4}$$

 V_L is the number of lattice sites in a crystal, one shows that

$$\sum_{\mathbf{R}} \mathbf{W}^2(\mathbf{R}) = \sum_{\mathbf{Q}} \mathbf{W}^2(\mathbf{Q}).$$
(5)

In deriving this we have employed that

$$\sum_{Q} = V_L = N \tag{6}$$

which physically implies that the number of eigen modes be equal to the number of atoms in a crystal.

Introduce

$$\mathbf{U}(\mathbf{R}) = \frac{1}{\sqrt{V_L}} \sum_{\mathbf{Q}} \mathbf{U}(\mathbf{Q}) \exp(-i\mathbf{Q} \cdot \mathbf{R}),$$
$$\mathbf{P}(\mathbf{R}) = \frac{1}{\sqrt{V_L}} \sum_{\mathbf{Q}} \mathbf{P}(\mathbf{Q}) \exp(i\mathbf{Q} \cdot \mathbf{R}).$$
(7)

One then shows that

$$\frac{1}{2}M\omega^2 \sum_{\langle \mathbf{R}\mathbf{R}'\rangle} |\mathbf{U}(\mathbf{R}) - \mathbf{U}(\mathbf{R}')|^2 = \sum_{\mathbf{Q}} \frac{1}{2}M\Omega^2(\mathbf{Q})\mathbf{U}^2(\mathbf{Q}).$$
(8)

 $\Omega(\mathbf{Q})$ is a function of ω , a and \mathbf{Q} . Its asymptotical form at small $|\mathbf{Q}|$ or the linear dispersion is

$$\Omega(\mathbf{Q}) = v_s |\mathbf{Q}|. \tag{9}$$

 v_s is a parameter which defines the speed of sound. We will use this dispersion for the whole Q-space. Below we are going to argue (physicists never prove, remember? we argue!) v_s can be expressed in terms of the Debye frequency.

So far I have shown that the Debye-Einstein Hamiltonian is equivalent to

$$H = \sum_{Q} H_Q, H_Q = \frac{\mathbf{P}^2(\mathbf{Q})}{2M} + \frac{1}{2}M\Omega^2(\mathbf{Q})\mathbf{U}^2(\mathbf{Q})$$
(10)

for a set of decoupled harmonic oscillators. And finally,

$$[\mathbf{P}_{\mu}(\mathbf{Q}), U_{\nu}(\mathbf{Q}')] = i\hbar\delta_{Q,Q'}\delta_{\mu\nu}.$$
(11)

This is the Debye-Einstein model for phonons. This model had been used to explain the phenomenon of superconductivity. It can be also used to study the quantum and thermal fluctuations of atoms or any localized particles in crystals. In the rest of this session I will address the later issue: order in crystals and the influence of zero point or thermal motion of atoms.

2 Thermal Properties of Phonons

Unlike in the case of photons, Q can't be infinity because of periodical structure of a crystal. The total number of modes should be equal to the number of lattice sites ("this is called the conservation of phase volume"). Under this constraint one finds that the upper cut-off of Q, Q_D is

$$\frac{4\pi Q_D^3}{3} \frac{1}{(2\pi)^3} = \frac{N}{V} = \frac{1}{a^3}.$$
(12)

V is the volume of a cubic crystal. Define $\Omega(Q_D)$ as the Debye frequency Ω_D for a crystal. Then,

$$\Omega(Q_D) = Q_D v_s; Q_D = \frac{2\pi}{a} (\frac{3}{4\pi})^{1/3}.$$
(13)

This expresses the speed of sound v_s in terms of the Debye frequency and the lattice constant a.

And I find that the energy of phonons in a crystal is

$$U = \frac{V4\pi}{(2\pi)^3} \int_0^{Q_D} dQ Q^2 \frac{\hbar\Omega(\mathbf{Q})}{\exp(\beta\hbar\Omega(Q)) - 1} = 3NkT(\frac{kT}{\hbar\Omega_D})^3 \int_0^{\beta\hbar\Omega_D} dx \frac{x^3}{\exp(x) - 1}.$$
 (14)

One can easily show that the energy per atom is

$$\frac{U}{N} = 3kT\left(\frac{kT}{\hbar\Omega_D}\right)^3 \int_0^\infty dx \frac{x^3}{\exp(x) - 1} \tag{15}$$

when kT is much less than the Debye energy $\hbar\Omega_D$. At high temperatures, the energy per particle is

$$\frac{U}{N} = kT.$$
(16)

This is all I want to tell about thermal properties of phonons. See more discussions in the textbook.

3 Nature of phonons and long range order: A poor man's approach

NOTE: The notion of "Poor man" was introduced to condensed matter physics by P. W. Anderson when he studied the Kondo problem. I used this notion here to emphasize that the proof I present below is a very very "loose" argument"!!.

3.1 Single Phonon

But what does a phonon mean in terms of atoms? We know that phonons represent *correlated* vibrations of atoms at different lattice sites. Given N phonons with momentum Q, we are able to determine that the Q-th Harmonic oscillator occupies the Nth harmonic oscillator state. Say it differently,

$$\Psi(U(\mathbf{Q})) = \psi_N(U(\mathbf{Q})); \tag{17}$$

 ψ_N is the Nth eigen state of H.O. (We again ignore the issue of polarization.)

Remember that $U(\mathbf{Q})$ is simply the Fourier transformation of $U(\mathbf{R})$. The fact that $U(\mathbf{Q})$ fluctuates around zero implies fluctuations of atoms. And if the H.O. occupies highly excited states, or the number of phonons is high, then we say fluctuations are strong (recall what you learned in QM classes). And if the number of phonons is small, we should expect fluctuations are weak.

However, in a give phonon mode, these fluctuations are correlated and **strongly correlated**. To demonstrate this feature, I consider a phonon with momentum $\hbar Q_0$. In terms of eigen values of harmonic oscillators, I am interested in

$$N_Q = 0, \text{ for } Q \neq Q_0; N_Q = 1, \text{ for } Q = Q_0.$$
 (18)

Furthermore, I am going to sit in a moving frame of an atom at $\mathbf{R} = 0$ and measure the displacement of other atoms at \mathbf{R}_0 . In other words, I am interested in the displacement of other atoms relative to the atom at \mathbf{R} . Obviously

$$< \mathbf{U}(\mathbf{R}_0) - \mathbf{U}(0) >_{N_{Q_0}=1} = 0,$$
 (19)

(Show it by yourselves.)

Next I study the fluctuations. For demonstration I neglect all zero point fluctuations and only consider the contribution of the single phonon. (Argue why one can do this, what if one incudes the zero point fluctuations .) Then I obtain a very intuitive result

$$< (\mathbf{U}(\mathbf{R}_0) - \mathbf{U}(0))^2 >_{N_{Q_0}=1} = \frac{2}{V_L} < U^2(Q_0) >_{N_{Q_0}=1} [1 - \cos(\mathbf{Q}_0 \cdot \mathbf{R}_0)]$$
 (20)

It shows that with respect to the atom at point $\mathbf{R} = 0$, other atoms vibrate orderly, and the amplitude of vibrations is periodical with a period

$$\lambda_0 = \frac{2\pi}{Q_0}.\tag{21}$$

Marvellous!! So the conclusion is that a phonon with momentum $\hbar \mathbf{Q}$ truly represents a propagating wave of atoms with wavelength λ (given above).

3.2 Phonons in equilibrium

In most of cases, we can't control phonons one by one. In generic situations, a crystal is at thermal equilibrium with temperature T. The population of phonons with given momentum $\hbar Q$ is given by Bose-Einstein statistics.

To have more insight into the relation between phonons and fluctuations of atoms, I would like to quantify the statement made in the previous subsection. First let me point out that

$$\langle U^2(\mathbf{Q}) \rangle_N = \frac{\epsilon_N}{M\Omega^2}, \epsilon_N = (N_\Omega + \frac{1}{2})\hbar\Omega(\mathbf{Q}).$$
 (22)

I should emphasize that the fluctuations are nonzero even when N = 0, or when phonons are absent. The fluctuations not associated with phonons are called zero point fluctuations, naturally.

It is clear that the thermal average of fluctuations is

$$\langle \langle U^2(\mathbf{Q}) \rangle \rangle = \frac{\langle \epsilon \rangle}{M\omega^2}, \langle \epsilon \rangle = (\frac{1}{2} + N_\Omega)\hbar\Omega(\mathbf{Q}).$$
 (23)

<<>> means average over all quantum states with proper statistical weight. And

$$N_{\Omega} = \frac{1}{\exp(\beta\hbar\Omega) - 1} \tag{24}$$

is the number of phonons with a given energy $\hbar\Omega$.

Fantastic! We are now ready to crack out solutions to a problem which bothered a few generations of brilliant physicists (1930s-1970s). Before toasting for the victory, let me further remark that

$$<< U^2(\mathbf{R}) >> = \frac{1}{V_L} \sum_{Q} << U^2(\mathbf{Q}) >> .$$
 (25)

Now let me claim that

a) There exist no one dimensional crystals (with usual "long range order") at zero or finite temperatures.

b) There exist no two-dimensional crystals at any finite temperatures.

Proof (again I mean I can argue):

For the first theorem, I only need to prove that at T = 0, one-dimensional crystals don't exist (Why?). Here is my argument.

i) With no phonons, I find the energy for each Q-mode is $1/2\hbar\Omega(\mathbf{Q})$.

ii) So at T = 0

$$\langle \langle U^2(\mathbf{Q}) \rangle \rangle = \frac{\hbar\Omega(\mathbf{Q})}{2M\Omega^2(Q)}.$$
 (26)

iii) Therefore,

$$\langle \langle U^{2}(\mathbf{R}) \rangle \rangle = \frac{1}{V_{L}} \sum_{Q} \langle \langle U^{2}(\mathbf{Q}) \rangle \rangle = \frac{\hbar}{2M\Omega_{D}} \int_{0}^{Q_{D}} \frac{dQ}{Q}.$$
 (27)

I have used that $Q_D a = \pi$.

Note that the integral is divergent!! So we indeed see the fluctuations of atoms are infinity, much larger than the lattice constant a. If we use

$$\langle \langle U^2(\mathbf{R}) \rangle \rangle \langle a^2 \tag{28}$$

as the criteria for the existence of crystals, then the above calculations show that this is always violated in one-dimension at zero temperature. Wonderful!!

So what happens in two-dimensional crystals? If I carry out similar calculations and neglect the zero point fluctuations (show that in two-dimensions at finite T, these contributions are "irrelevant".), I find the following very sexy (I mean very pleasant!!) result

$$<< U^2(\mathbf{R}>> = \frac{kT}{M\Omega_D^2} \int_0^{\hbar\Omega_D\beta} dx \frac{1}{\exp x - 1}.$$
(29)

I have again used the following identity for 2d crystals,

$$\pi Q_D^2 a^2 = (2\pi)^2. \tag{30}$$

The integral again diverges implying at any finite T, there are no two-dimensional crystals because of long wave length soft phonons!!

I have just demonstrated a very important observation made by R. Peierls (1934) in the last century (a very creative figure on the stage of theoretical physics). It is also later known as an example of the "Mermin-Wagner" theorem on spontanuous symmetry breaking in 2d space (1968). The modern theory on two-dimensional crystals, however, involves not only phonons but also topological excitations (vortex-anti vortex pairs). It turns out that 2d crystals only have quasi-long range order because of phonons. This and critical phenomenon were studied by Kosterliz and Thouless (1973) in their very influential paper. The renormalization group equation was introduced for almost the first time to study condensed matter systems. The RG pattern is very similar to Anderson-Yuval's **poor man scaling** for the Kondo problem (1971), another fascinating subject. (P. W. Anderson (Princeton), a pioneer of many things including Anderson localization, Anderson uncertainty relations, Kondo problem, Anderson-Edward theory for spin glasses, and Anderson's RVB theory for High temperature superconductivity, a remarkable man!). Unfortunately both subjects are beyond the scope of this course.

The model of crystals can also be regarded as the simplest version of bosonic "strings" and can be generalized to describe the vacuum structure of our space-time, or other complicated gauge fields. Again this is far beyond what you are required to pass this course. Finally, also remotely the piece of physics we learned here plays an important role in low dimensional physics; just name a few: Luttinger liquid in 1D, conformal field theories and WZW (topological field) theories etc.