Part VII: Lattice vibrations – phonons

So far, we pretended that the nuclei are frozen at their equilibrium positions, i.e. that they are at rest at well specified positions. As we know only too well, this is wrong because the nuclei are quantum objects and therefore must satisfy Heisenberg's uncertainty principle. In this section we will try to understand the consequences of relaxing this approximation. We will start with a brief review of the simple harmonic oscillator, which provides us with a simple example of how to go from a classical to a quantum model, as well as a simple way to understand how one uses quantum excitations (particles) to describe the excited states.

1 The simple harmonic oscillator

The simplest system that comes to mind described by this problem is a body of mass m attached to a spring with an elastic constant k, but the equations I will discuss next appear in a multitude of examples from various areas of physics – for example, an RC circuit is described by an identical differential equation. For simplicity, though, let's keep our oscillating mass in mind as our example, and let's assume that the motion is along 1 axis, i.e. one-dimensional. Generalization to 3 dimensions is trivial and I'll briefly discuss it at the end.

The classical Hamiltonian for this system is:

$$\mathcal{H} = \frac{p^2}{2m} + \frac{m\omega^2(x - x_{eq})^2}{2}$$

where p is the momentum in the x direction, x_{eq} is the equilibrium value (when the spring is uncompressed) and $\omega = \sqrt{k/m}$ is, as we will see soon, the frequency of oscillations. As usual, the Hamiltonian contains the kinetic energy (first term) and the potential energy (second term), which here is the elastic energy stored in the deformed spring.

Classically, from the Hamiltonian we derive Hamilton's equations of motion:

$$\frac{dx}{dt} = \dot{x} = \frac{\partial \mathcal{H}}{\partial p} = \frac{p}{m}$$

and

$$\frac{dp}{dt} = \dot{p} = -\frac{\partial \mathcal{H}}{\partial x} = -m\omega^2(x - x_{eq})$$

which, taken together, lead to

$$m\frac{d^2x}{dt^2} = -m\omega^2(x - x_{eq}) = -k(x - x_{eq}).$$

Of course, this is just Newton's second law $ma = F$, where the force is the elastic force. (Do not worry if you have not studied Lagrangian and Hamiltonian mechanics, it's just a formal and powerful way to derive Newton's second law. It helps to use it for very complicated systems, but for what we need Newton's 2nd law will suffice).

This differential equation has the general solution:

$$x(t) = x_{eq} + a_1 \sin(\omega t) + a_2 \cos(\omega t) = x_{eq} + b_1 e^{i\omega t} + b_2 e^{-i\omega t} = x_{eq} + A\cos(\omega t + \phi).$$

All those forms are equivalent. Each depends on two unknown constants, a_1, a_2 or b_1, b_2 or A, ϕ which are found from the initial conditions that specify the initial location x_0 and the initial momentum p_0

of the object. The last form is the one you are probably most familiar with from first year physics – in those terms, A is the amplitude of the oscillations and ϕ is the relative phase.

In any event, substituting this general solution in the Hamiltonian, one finds that

$$\frac{p^2}{2m} + \frac{m\omega^2(x - x_{eq})^2}{2} = \frac{p_0^2}{2m} + \frac{m\omega^2(x_0 - x_{eq})^2}{2} = E$$

i.e. the total energy is conserved to a value determined by its initial value. Note that classically, this energy E could have absolutely any non-negative value we wish, by simply adjusting x_0 and p_0. In particular, $E = 0$ is possible if $x_0 = x_{eq}$ and $p_0 = 0$, in other words if the object was initially at rest at the equilibrium position, then it will remain forever at rest.

Before going on, let me point out that it would have been slightly easier to define $u = x - x_{eq}$ as the **displacement out of equilibrium**, and use this as the variable. It doesn't make a huge difference for this simple problem, but for more complicated problems it will help if we use as variables the displacements from equilibrium, as we will see soon enough.

Let me now quickly remind you how we go from this classical problem to its quantum counterpart. Roughly speaking, the rules are:

(i) get the quantum Hamiltonian from the classical one by making x and p into operators, so that:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2(\hat{x} - x_{eq})^2}{2},$$

where from now I will use a hat to denote an operator, so we don't confuse them with simple numbers.

(ii) because position and momentum are conjugate variables, their operators must satisfy the quantum version of the Poisson brackets:

$$[\hat{x}, \hat{p}] = i\hbar$$

where $[\hat{a}, \hat{b}] = \hat{a}\hat{b} - \hat{b}\hat{a}$ is called the commutator of the two operators.

This is why if we use wavefunctions $\phi(x) = \langle x|\phi\rangle$ on which the action of the position operator is trivial, $\hat{x}\phi(x) = x\phi(x)$, we must choose $\hat{p} = -i\hbar\frac{d}{dx}$. With this choice, you can see that:

$$[\hat{x}, \hat{p}]\,\phi(x) = x(-i\hbar\frac{d\phi}{dx}) - (-i\hbar\frac{d(x\phi)}{dx}) = i\hbar\phi(x)$$

for any $\phi(x)$, so indeed the commutator is equal to $i\hbar$.

This requirement for the commutator, however, allows us to figure out other possible representations. For example, we might want to work with wavefunctions in the momentum space $\phi(p) = \langle p|\phi\rangle$, which are defined so that $|\phi(p)|^2 dp$ is the probability to find the particle to have momentum between $p, p + dp$. In this case, $\hat{p}$ has trivial action $\hat{p}\phi(p) = p\phi(p)$, and the commutation relation requires that now we choose $\hat{x} = i\hbar\frac{d}{dp}$.

(iii) evolution of the state is describe by Schrödinger's equation $i\hbar\frac{\partial}{\partial t}|\Phi\rangle = \hat{H}|\Phi\rangle$. This translates into

$$i\hbar\frac{\partial}{\partial t}\phi(x,t) = \left[-\frac{\hbar^2}{2m} + \frac{m\omega^2(x - x_{eq})^2}{2}\right]\phi(x,t)$$

if we use the usual wavefunctions and the corresponding meaning of the operators in this representation, but we don't necessarily have to do that, as we'll see in a minute.

In any event, if these rules are news to you (meaning, you haven't yet taken an advanced QM course), this is how one can go from any classical problem to its quantum version, so long as we know the classical Hamiltonian. What are the conjugate variables and what the commutation relation for their operators leads to, can vary quite a bit and sometime look quite strange. But these rules work in all cases where we have tried them over the last 70-80 years since QM was discovered.

When I reviewed the needed notions of QM, at the beginning of the course, I already told you what are the eigenvalues and eigenfunctions of the time-independent Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}+\frac{m\omega^2(x-x_{eq})^2}{2}\right]\phi(x)=E\phi(x).$$

They are characterized by a single quantum number $n=0,1,2,....$:

$$E_n=\hbar\omega\left(n+\frac{1}{2}\right)$$

and :

$$\phi_n(x)=\frac{1}{\sqrt{2^n n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}e^{-\frac{m\omega(x-x_{eq})^2}{2\hbar}}H_n\left(\sqrt{\frac{m\omega}{\hbar}}(x-x_{eq})\right)$$

where $H_n(x)=(-1)^n e^{x^2}\frac{d^n}{dx^n}\left(e^{-x^2}\right)$ are the Hermite polynomials.

So the ground-state has energy $E_0=\frac{\hbar\omega}{2}$ (this is also known as the **zero point energy** because it would be the energy at $T=0$), and this is the minimum possible for a quantum harmonic oscillator. Zero is no longer an option, like it was for the classical oscillator, because a quantum oscillator obeys the uncertainty principle which forbids it to be at rest at a known location.

It turns out that there is a much nicer way to find the eigenstates and eigenvalues of this Hamiltonian, than brute force solving of the Schrodinger equation for wavefunctions. This will also show us the power of working with abstract operators and states, as opposed to insisting on working with wavefunctions.

The idea is that instead of working with the abstract $\hat{x}$ and $\hat{p}$ operators, we define two other operators (known as **ladder operators**) $\hat{a},\hat{a}^\dagger$:

$$\hat{a}=\sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x}-x_{eq}+\frac{i}{m\omega}\hat{p}\right)$$

$$\hat{a}^\dagger=\sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x}-x_{eq}-\frac{i}{m\omega}\hat{p}\right)$$

in terms of which:

$$\hat{x}=x_{eq}+\sqrt{\frac{\hbar}{2m\omega}}(\hat{a}+\hat{a}^\dagger)$$

$$\hat{p}=i\sqrt{\frac{m\omega\hbar}{2}}(\hat{a}^\dagger-\hat{a})$$

Using these last equations in the commutation relation for $\hat{x}$ and $\hat{p}$ leads immediately to

$$[\hat{a},\hat{a}^\dagger]=1;[\hat{a},\hat{a}]=[\hat{a}^\dagger,\hat{a}^\dagger]=0$$

(the last two are obvious from the definition of the commutator); while putting them into the Hamiltonian leads to:

$$\hat{H}=\hbar\omega\left(\hat{a}^\dagger a+\frac{1}{2}\right).$$

Of course, in reality things worked the other way around, namely people noticed that the Hamiltonian is the sum of two terms which are perfect squares, and wondered if they could rewrite it as one perfect "square" plus a constant, which is what is achieved by expressing it in terms of the $a, a^\dagger$ operators.

To find the eigenstates, let me define the new operator (known as the **number operator**, for reasons that will soon be clear) $\hat{N} = \hat{a}^\dagger \hat{a}$ and note that if we can find its eigenstates and eigenvalues: $\hat{N}\,|n\rangle = n\,|n\rangle$, then we automatically know the eigenstates and eigenvalues of the Hamiltonian $\hat{H}|n\rangle = \hbar\omega(n+\frac{1}{2})|n\rangle \to E_n = \hbar\omega(n+\frac{1}{2})$.

Suppose that we know an eigenstate $|n\rangle$, and we'd like to figure out what is the meaning of the states $\hat{a}^\dagger|n\rangle$ and $\hat{a}|n\rangle$, in particular if they are also eigenstates of $\hat{N}$. Let me do the first one:

$$\hat{N}\left[\hat{a}^\dagger|n\rangle\right] = \hat{a}^\dagger\hat{a}\hat{a}^\dagger|n\rangle$$

However, we know that $[\hat{a}, \hat{a}^\dagger] = 1 \to \hat{a}\hat{a}^\dagger = 1 + \hat{a}^\dagger\hat{a} = 1 + \hat{N}$, which we can be used above to give:

$$\hat{N}\left[\hat{a}^\dagger|n\rangle\right] = \hat{a}^\dagger\left[1+\hat{N}\right]|n\rangle = (n+1)\left[\hat{a}^\dagger|n\rangle\right]$$

In other words, the state $\hat{a}^\dagger|n\rangle \sim |n+1\rangle$. Similarly, you can show that $\hat{a}|n\rangle \sim |n-1\rangle$. This explains why these are also known as raising and lowering operators – by applying them one increases or decreases the index of the state. In particular, this also tells us that n must be an integer, because we can argue that any eigenvalue n of the operator $\hat{N}$ must be positive or at most zero (this has to do with the fact that $\hat{a}^\dagger\hat{a}$ is like a perfect square, in operator notation. If n was not an integer, for example if $n = 0.3$ was an acceptable eigenstate of $\hat{N}$, then I could use the lowering operator repeatedly to find that $n-1, n-2, n-3, ...$ are also acceptable eigenstates of $\hat{N}$, as we showed above. But this leads to negative eigenstates unless n is an integer). Thus, the lowest eigenvalue it can have is $n = 0$, in which case $\hat{N}|0\rangle = 0 \to \hat{a}|0\rangle = 0$, and there is no way to generate negative eigenvalues.

These arguments show that $n = 0, 1, 2, ...$ are non-negative integers, so indeed we found the same spectrum as expected, but without solving that complicated differential equation. How about finding the wavefunctions? For example, in the ground-state $\phi_0(x) = \langle x|0\rangle$ is, as discussed, the amplitude of probability to find the object at location x while it is in its ground-state $|n = 0\rangle$. To find this, we use:

$$0 = \langle x|\hat{a}|0\rangle = \langle x|\sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - x_{eq} + \frac{i}{m\omega}\hat{p}\right)|0\rangle = \sqrt{\frac{m\omega}{2\hbar}}\left(x - x_{eq} + \frac{i}{m\omega}(-i\hbar\frac{d}{dx})\right)\phi_0(x).$$

Using separation of variables, this ODE is re-written as:

$$\frac{d\phi_0}{\phi_0} = -\frac{m\omega}{\hbar}(x - x_{eq}) \to \phi_0(x) = Ce^{-\frac{m\omega}{2\hbar}(x-x_{eq})^2}$$

where C is the normalization constant. Since $H_0(x) = 1$, this agrees perfectly with the solution we found by solving directly Schrödinger's equation, but I hope you agree that doing this was a lot easier than solving that 2nd order ODE. The excited states can be found by similar means, for instance once we know $\phi_0(x) = \langle x|0\rangle$, we can then use the fact that $|1\rangle \propto \hat{a}^\dagger|0\rangle$ to find that $\phi_1(x) = \langle x|1\rangle \propto \langle x|\sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - x_{eq} - \frac{i}{m\omega}\hat{p}\right)|0\rangle = \sqrt{\frac{m\omega}{2\hbar}}\left(x - x_{eq} - \frac{i}{m\omega}(-i\hbar\frac{d}{dx})\right)\phi_0(x)$. After taking the derivative and doing some simple algebra, you can check that this agrees with $\phi_1(x)$ obtained in terms of Hermite polynomials. And so on and so forth, we can generate all $\phi_n(x)$ just by calculating derivatives of $\phi_{n-1}(x)$. Hopefully, this gives you a taste why working in abstract spaces is sometimes preferable to using wavefunctions.

One more thing: so far I only showed that $\hat{a}^\dagger|n\rangle \sim |n+1\rangle$, but not what is the proportionality constant. It turns out that if we normalize these states, $\langle n|m\rangle = \delta_{n,m}$, then the normalization coefficients are:

$$|n\rangle = \frac{\hat{a}^{\dagger,n}}{\sqrt{n!}}|0\rangle$$

(it is a straightforward calculation to check this using the commutation relations. Ask me if you'd like more details). As a result, the exact relations are:

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle; \qquad \hat{a}|n\rangle = \sqrt{n}|n-1\rangle.$$

Hopefully you found this discussion useful, but now let me discuss something important for the rest of this chapter. The results we've got for the quantum harmonic oscillator can be viewed in two different ways. The way I suspect you are used to is to say: this system has quantized levels with equidistant energies, characterized by an integer n. The higher the n of the eigenstate, the larger is the energy of the object because its oscillations are "bigger" (or something to that effect). Finally, in this view $\hat{a}, \hat{a}^\dagger$ are ladder operators, in the sense that they take you up or down by one between the excited states.

In modern physics, we rephrase this in a way that may seem at first a bit strange, but it turns out to be extremely useful. We prefer to think of the ground-state as a "vacuum", in the sense of being the state without any excitations. The excited states $|n\rangle$, $n \geq 1$, we view as states which contain n quanta of excitations, each of which costs $\hbar\omega$. We like to give names to things, so for instance we would call these excitations "vibrons". In this language, the state $|n\rangle$ has energy $E_n = \hbar\omega(n+\frac{1}{2})$ because it has n vibrons, each with energy $\hbar\omega$, on top of the vacuum which has $\hbar\omega/2$ energy. In this view, $\hat{a}^\dagger$ is a vibron creation operator, and $\hat{a}$ is a vibron annihilation operator. As a result, $|n\rangle \sim \left(a^\dagger\right)^n|0\rangle$ because I get to it by creating n vibrons in the vacuum. Or $\hat{a}|n\rangle \sim |n-1\rangle$ because if I remove (annihilate) one of the n vibrons from the original $|n\rangle$ state, I am left with a state with $n-1$ vibrons, hence the answer must be the $|n-1\rangle$ state (of course, one always has to normalize properly). I hope you see that the two formulations agree in terms of final results, such as the spectrum and eigenstates, they are just different ways of thinking of the underlying reasons for them.

While this might seem rather strange, you have actually used precisely such language for photons. The way this works is quite similar to what I just did. Classically, an electromagnetic wave is described by Maxwell's equations instead of Newton's second law – that is the main difference. We can also derive Maxwell's equations as being the Hamilton equations for a classical Hamiltonian for the EM field, in direct analogy with how Newton's 2nd law comes out of Hamilton's equations for the classical Hamiltonian of the harmonic oscillator. As I said above, once we know the classical Hamiltonian for any system (in particular, an EM field in vacuum) we use those 3 rules to quantize it, and find its quantum counterpart. For EM field it is much less intuitive what the conjugate variables are, and their commutation relations can look rather peculiar, but we know how to do this. Once we have the quantum Hamiltonian, it turns out that we can put it in a very similar form to the one for the harmonic oscillator, namely:

$$\hat{H}_{EM} = \sum_{\vec{k},\lambda} \hbar\omega_{\vec{k}} \left(\hat{a}^\dagger_{\vec{k},\lambda}\hat{a}_{\vec{k},\lambda} + \frac{1}{2}\right)$$

where the new operators satisfy commutation relations $[\hat{a}_{\vec{k},\lambda}, \hat{a}^\dagger_{\vec{k}',\lambda'}] = \delta_{\lambda,\lambda'}\delta_{\vec{k},\vec{k}'}, [\hat{a}_{\vec{k},\lambda}, \hat{a}_{\vec{k}',\lambda'}] = 0$. In other words, operators with the same indexes satisfy $[a, a^\dagger] = 1$ like for the harmonic oscillator, while operators with different labels commute with each other.

The fact that we can put the Hamiltonian in this form should not come as a huge shock, because we know that EM fields are collections of oscillating electric and magnetic fields; the equation above shows that the quantum Hamiltonian is a sum of Hamiltonians for quantum oscillators.

Before going on, let me just mention that $\vec{k}$ is a momentum and $\lambda = \pm$ is a polarization (associated with the fact that EM waves can be polarized circularly left or right, there are two possible "flavors"). Also, going through the calculations one finds that $\omega_{\vec{k}} = ck$, where c is the speed of light and $k = |\vec{k}|$. You'll have to take a quantum electrodynamics course to do this derivation and get this Hamiltonian, but now that we have it we can easily figure out its spectrum based on what we know for a single harmonic oscillator. Its eigenenergies must be

$$E_{\{n_{\vec{k},\lambda}\}} = \sum_{\vec{k},\lambda} \hbar\omega_{\vec{k}} \left(n_{\vec{k},\lambda} + \frac{1}{2} \right)$$

and the eigenfunctions must be:

$$|\{n_{\vec{k},\lambda}\}\rangle = \prod_{\vec{k},\lambda} \frac{\left(\hat{a}^{\dagger}_{\vec{k},\lambda}\right)^{n_{\vec{k},\lambda}}}{\sqrt{n_{\vec{k},\lambda}!}} |0\rangle.$$

In other words, for each mode $(\vec{k}, \lambda)$ I must specify an integer $n_{\vec{k},\lambda}$ which tells me the excitation state for that quantum harmonic oscillator. I used $\{n_{\vec{k},\lambda}\}$ to denote the collection of all these integers. This is where the photons come in. We say that $\hat{a}^{\dagger}_{\vec{k},\lambda}$ is the creation operator of a photon with momentum $\vec{k}$ and polarization λ; the Hamiltonian shows us that each such photon has energy $\hbar\omega_k = \hbar ck$. As a result, the energy of a state is obtained by summing the energy of each kind of photon, times how many such photons there are. Finally, eigenstates are labelled in terms of how many photons of which type are present in that state. I hope you see the analogy with the vibrons discussed above.

For completeness, let me say one more thing. Both the vibrons discussed above, and the photons, are bosons – we have already seen that we can have an arbitrarily large number n of vibrons, or an arbitrarily large number of phonons of the same kind, i.e. with the same $(\vec{k}, \lambda)$. The reason for this can be tracked back to the fact that they satisfy the commutation relations of the type $[a, a^{\dagger}] = 1$.

We can also introduce similar notation, in terms of creation and annihilation operators, for fermionic objects – in fact, I already told you in class that we need better notation to keep track of our many-electrons eigenstates. This is precisely what this notation gives us. We still have a pair of $a, a^{\dagger}$ operators for each allowed state for the fermion – for example, for a 1D lattice with sites indexed by i, we would have $a^{\dagger}_{i,\sigma}, a_{i,\sigma}$ to create or annihilate an electron with spin σ in the valence orbital of the atom i. For fermions, these operators satisfy anti-commutation relations of the type $\{a, a^{\dagger}\} = aa^{\dagger} + a^{\dagger}a = 1$ while $\{a, a\} = \{a^{\dagger}, a^{\dagger}\} = 0$. It's this tiny difference, of a plus instead of a minus, that makes all the difference in their behaviour. In particular, we now find that while we again need an integer n to specify how many electrons are in a given state, the anticommutation relations insure that we can only have $n = 0, 1$ (look at the last one, which gives $a^{\dagger}a^{\dagger} = 0$, i.e. we cannot create 2 fermions in the same state, we get zero probability for that). In other words, Pauli's principle is enforced automatically. In this language, instead of using $|i, \sigma\rangle$ to signify that there is an electron at site i with spin σ, we use $a^{\dagger}_{i,\sigma}|0\rangle$ – i.e., the state obtained by creating an electron with spin σ at site i, starting from vacuum. With this notation, the hopping Hamiltonian is written as:

$$\mathcal{H} = -t \sum_{i,\sigma} \left(a^{\dagger}_{i,\sigma} a_{i+1,\sigma} + a^{\dagger}_{i+1,\sigma} a_{i,\sigma} \right).$$

The first term literally says that this operator removes a spin-σ electron from site $i+1$ and adds it to site i, which is precisely what hopping does – this notation is quite easy to read. For single electron eigenstates there isn't much of an advantage in using this language, but it makes all the difference for many-electron states; for example the Hamiltonian I just wrote is correct irrespective of how many electrons are in the system since this notation doesn't depend on that. To see more about why or how this notation helps, you will have to take more advanced cond-mat or QED courses.

Back to our problem: what has this all got to do with lattice vibrations? Well, as we'll see next, the situation there is very similar. If we can (and we will) be able to solve the classical problem for the oscillations of the atoms around their equilibrium positions, then we can find its quantum counterpart which will look like a collection of quantum harmonic oscillators. Its excitations are called **phonons**, in direct analogy with the photons we use for EM oscillations. Let's see how this works in practice: as always, I will start with the simplest possible model.

2 Longitudinal phonons in a one-dimensional crystal

Let us consider the following problem: we have a one-dimensional crystal, which we can think of as a linear chain of equally-spaced identical atoms of mass m. Let a be the equilibrium distance between consecutive atoms. Then, at equilibrium, the position of the nth atom of the chain will be

$$x_n^{(0)} = na$$

Let us assume that there are N atoms in the chain, so that $n = 1, 2, ..., N$.

We would like to answer the following question: if the atoms are constrained to move along the x-axis, what are the normal frequencies of oscillations of this system? These are called longitudinal vibrations, where longitudinal (as opposed to transverse) shows that we are only looking for oscillations along the x-axis. We could also look at transverse oscillations, when the atoms move along the y or z axes.

The Hamiltonian of this system is

$$\mathcal{H} = \sum_{n=1}^{N} \frac{p_n^2}{2m} + U(x_1, ..., x_N)$$

Let us use a simple model for the interaction energy (the second term). First, we assume that each atom interacts only with its two neigh boring atoms, which implies

$$U(x_1, ..., x_N) = \sum_{n=1}^{N-1} U_{\text{pair}}(x_{n+1} - x_n)$$

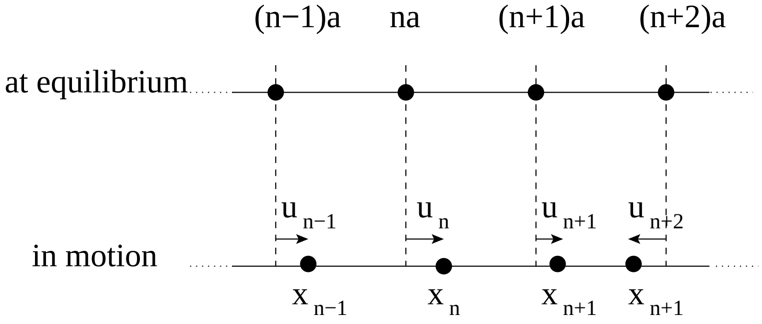
where $U_{\text{pair}}(x_{n+1} - x_n)$ describes the interaction between atoms n and $n+1$. Of course, we can add longer range interactions, but we know that the further apart atoms are, the smaller their interactions. If we are interested in small oscillations, we can Taylor expand this to obtain

$$U_{\text{pair}}(x) = U_{\text{pair}}(a) + \frac{K}{2}(x-a)^2 + ...$$

where we ignore the higher order terms. Then we have a simplified version of the Hamiltonian, valid near the equilibrium positions:

$$\mathcal{H} = \sum_{n=1}^{N} \frac{p_n^2}{2m} + \sum_{n=1}^{N} \frac{K}{2}(x_{n+1} - x_n - a)^2$$

Like always, we will assume periodic boundary conditions, i.e. atoms 1 and N are neighbours to one another and so $x_{N+1} \equiv x_1$, and in general $x_{n+N} = x_n$ for any n.



We can make things easier if instead of x_n, we use the coordinates to be $u_n = x_n - x_n^{(0)} = x_n - na$, i.e. the displacement of each atom from its equilibrium position (see the figure above for an illustration). With these new variables, we have

$$\mathcal{H} = \sum_{n=1}^{N} \frac{p_n^2}{2m} + \sum_{n=1}^{N} \frac{K}{2}(u_{n+1} - u_n)^2$$

where $u_{n+N} = u_n$. The resulting Hamilton's equations lead, after a bit of work, to:

$$m\frac{d^2 u_n}{dt^2} = -K(2u_n - u_{n-1} - u_{n+1})$$

or, if we define $\omega_0 = \sqrt{K/m}$, we have:

$$\frac{d^2 u_n}{dt^2} = -\omega_0^2(2u_n - u_{n-1} - u_{n+1})$$

and we have one such equation for each value of $n = 1, 2, ..., N$. This is nothing but Newton's 2nd law for each of these atoms, since atom n feels "elastic" forces from its two neighbours $m\frac{d^2 u_n}{dt^2} = F_{n+1,n} + F_{n-1,n}$, where for example the "elastic" force from its neighbour to the left is $F_{n-1,n} = +K(u_{n-1} - u_n)$. Why? Because if $u_{n-1} - u_n > 0$ that means the distance between these two atoms is smaller than at equilibrium, therefore the elastic force is pushing them apart, meaning that atom n is pushed towards right with a positive force; and viceversa.

Now we have to solve these coupled equations. I hope you already know what am I going to say: all the atoms are identical therefore we expect plane-wave like solutions (no a-priori reason for one atom to oscillate a lot more or a lot less than its neighbours). So we try solutions of the form:

$$u_n(t) = A(t)e^{ikna}$$

where $A(t)$ is the amplitude. Right away, we know that the periodic boundary conditions will restrict the allowed values for k to be of the form $k = \frac{2\pi}{Na}m$, where m is an integer. A bit of further thought will show that only N consecutive values of m give distinct solutions, for precisely the same reasons this happened for electron wavefunctions – all answers will be periodic in ka with a period of 2π, so we should restrict ourselves to the solutions falling inside one such period; we usually choose it symmetrical, $-\pi < ka \leq \pi$. So the allowed values of k are restricted to the Brillouin zone, $-\frac{\pi}{a} < k \leq \frac{\pi}{a}$ (this should all be very familiar by now).

Putting the plane-wave guess into the differential equation leads to:

$$m\frac{d^2A}{dt^2} = -m\omega_0^2\left(2 - e^{-ika} - e^{ika}\right)A(t) = -m\omega_0^2 2(1-\cos(ka))A(t) = -m\omega_k^2 A(t)$$

where $\omega_k = \omega_0\sqrt{2(1-\cos(ka))} = 2\omega_0|\sin\frac{ka}{2}|$, if you happen to remember that $1-\cos(x) = 2\sin^2\frac{x}{2}$. This is a very simple ODE, with the general solution:

$$A(t) = A\cos(\omega_k t + \phi)$$

This shows that each of these N distinct solutions corresponding to the N allowed k values oscillates with a frequency:

$$\omega_k = 2\omega_0|\sin\frac{ka}{2}|$$

that depends on the momentum of the wave. This frequency and its associated energy $\hbar\omega_k$ is also periodic, with the Brillouin zone covering one period. This is yet another proof (or check) that it suffices to restrict ourselves to the Brillouin zone when dealing with k-dependent quantities.

These simple oscillating plane-wave solutions are called "normal modes". One can show that any general solution of Newton's second law can be written as a sum of such modes, each with its own relative amplitude and phase:

$$u_n(t) = \sum_k \alpha_k e^{ikna}\cos(\omega_k t + \phi_k)$$

where the $2N$ parameters α_k and ϕ_k are determined from the $2N$ initial conditions that specify where each atom is at the initial time, and what is its momentum.

Of course, we will not go down this road because our atoms are quantum so we'd like to know the solution to the quantum version of this classical Hamiltonian. To do this, one follows steps similar to what we did for the single harmonic oscillator: one declares u_n and p_n to be operators satisfying the proper commutation relations $[u_n, p_m] = i\hbar\delta_{n,m}$, and then tries to solve the corresponding Schrödinger equation. Instead of brute force solution of the corresponding ODEs, it is again smarter to define judiciously chosen operators $\hat{a}_k, \hat{a}_k^\dagger$ which simplify the Hamiltonian (these are related to the normal modes discussed above, which is why it is always useful to first solve the classical problem. You'll learn in a more advanced course precisely how this works). The end result is:

$$\hat{H} = \sum_k \hbar\omega_k\left(\hat{a}_k^\dagger\hat{a}_k + \frac{1}{2}\right)$$

where ω_k are the frequencies discussed above. We already know the general eigenstates and eigenenergies of this Hamiltonian: we need N quantum numbers n_k, each telling us how many excitations (called **phonons**) with momentum k there are. For a given set of such quantum numbers $\{n_k\}$, the energy of the eigenstate is:

$$E_{\{n_k\}} = \sum_k \hbar\omega_k\left(n_k + \frac{1}{2}\right)$$

while the eigenstate is

$$|\{n_k\}\rangle = \prod_k \frac{\left(a_k^\dagger\right)^{n_k}}{\sqrt{n_k!}}|0\rangle$$

where $|0\rangle$ is the state without any phonons, i.e. the ground-state. Phonons turn out to be bosons as well, so there are no restrictions on how large the integers n_k can be. Just like for the simple harmonic oscillator, a larger n_k (i.e., having more phonons of that type) lead to "stronger" oscillations with that frequency. If one calculates the expectation value of $\hat{u}_n$, to see the position of the nth atom in this state, one finds something very reminiscent of the classical normal mode with that momentum and frequency. In the general state with many phonons of many modes, the expectation value of $\hat{u}_n$ will be a linear superposition of normal modes, just like in the classical solution written above.

Here are a few more interesting facts:

(i) we now see that even in the GS, i.e. the state with no phonons, there is a finite energy due to the zero-point motion of the atoms. This energy is:

$$E_{GS} = \frac{1}{2}\sum_k \hbar\omega_k.$$

As we discussed in class, in the limit when $N \to \infty$ the sum evolves into an integral, and:

$$E_{GS} = \frac{Na}{4\pi}\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} dk\hbar\omega_k = N\frac{2\hbar\omega_0}{\pi}$$

This scales with the chain length, as expected, and is an additional contribution to the GS energy of the lattice which should be included in the total energy. For example, remember that when we discussed the van der Waals bonding, we pretended that the atoms are frozen in place; this E_{GS} is the contribution from their small oscillations about the equilibrium positions and should be added to $U_{tot}(R)$. This correction becomes more significant for lighter atoms, because $\omega_0 = \sqrt{\frac{K}{m}}$ increases as the atomic mass decreases. Including this energy contribution in the total energy allows us to find the corrections in the predictions for the lattice constant, due to lattice oscillations (see discussion at the end of van der Waals bonding, if you don't recall what I'm talking about).

(ii) This type of phonon mode, with the property that $\omega_k \to 0$ when $k \to 0$, is known as an **acoustic phonon**. The reason is that at small $ka \ll 1$, we can approximate $\omega_k \approx \omega_0 ak = v_s k$. This looks just like the relationship between energy and momentum for a photon, but with a different speed $v_s = \omega_0 a$ instead of the speed of light. It turns out that this is the **speed of sound**, i.e. the speed at which longitudinal oscillations propagate through this material. For example, if you have a long bar of metal and you tap it at one end, it takes awhile for the vibrations to propagate to the other end. The speed at which this happens is precisely v_s. As you see, we can relate this value (that can be measured experimentally) to microscopic quantities such as the mass of the atoms and how they interact with on another – in other words, we can check that our microscopic model for where the atoms are and how they interact with one another is accurate, by checking that the resulting speed of sound that we calculate from it agrees with what is measured experimentally.

(iii) As I mentioned above, beside this longitudinal mode, there are two transverse phonon modes. Their energies can be calculated very similarly – the only difference is the value of the constant K in the Taylor expansion, and therefore the value of ω_0 and the corresponding speed of sound – the remaining calculation is similar. As a result, their energies will be $\omega_k^{(t)} = 2\omega_0^{(t)}|\sin\frac{ka}{2}| \to v_s^{(t)}a$ when $k \to 0$. As a result we have one longitudinal and two transverse acoustic phonon modes (by the way, we should also include the zero-point contribution from the transverse modes in the total energy, see discussion at (i)).

This turns out to be generally true: any crystal has one longitudinal and two transverse acoustic phonon modes. They are defined with respect to the momentum $\vec{k}$: in the longitudinal mode the atoms oscillate parallel to $\vec{k}$, while in the transverse modes they oscillate perpendicular to $\vec{k}$ (strictly speaking this is only true in the limit $|\vec{k}| \to 0$; at larger values the oscillations are not precisely parallel or orthogonal to $\vec{k}$, but close enough).

As we will see next, if the crystal has a more complicated basis of more than one atom, there are also so-called **optical phonon** modes. These are also characterized by their energy ω_k, but in this case $\omega_{k=0}$ is finite, not zero like for the acoustic modes. How many optical modes there are depends on how many additional atoms are in the basis. These modes also come in both longitudinal and transverse flavors.

(iv) Finally, for the acoustic phonons, we see that something rather peculiar happens when $k = 0$. If you look back at the classical equation of motion, in this case $d^2A/dt^2 = 0 \to A(t) = \alpha + \beta t$, i.e. this is not an oscillation. In fact, this describes an overall translation of the crystal, since the classical solution here is $u_n(t) = \alpha + \beta t$ for all n (the planewave goes to 1 at $k = 0$) so all sites move by the same amount. This explains why this excitation costs zero energy: simply moving the crystal towards left or right, as a whole, doesn't change its state and therefore it doesn't change its total energy. This gives you one way to see that such acoustic phonons (which cost zero energy when $k = 0$) must exist in any crystal, since any crystal can be moved as a whole at no cost. This also explains why there should always be 3 kinds of such acoustic phonons, namely one longitudinal and 2 transverse, since we can move a crystal in three independent directions. The existence of these excitations which cost zero energy, (also called Goldstone modes, also called gapless) is, thus, linked directly to the symmetry of space, namely its homogeneity.

3 Phonons in a chain with a more complicated basis

Let us quickly consider what happens if we have a chain with a two-site basis, for instance in equilibrium atoms A are located at even sites, i.e. at $2na$, and have mass m, while atoms B are located at odd sites, i.e. at $(2n + 1)a$, and have mass M. For simplicity, let u_{2n} and u_{2n+1} be the displacements out of equilibrium of these atoms along the chain direction – in other words, we consider again only longitudinal vibrations.

The classical equations of motion change from what we had before to:

$$m\frac{d^2u_{2n}}{dt^2} = -K(2u_{2n} - u_{2n-1} - u_{2n+1})$$

and

$$M\frac{d^2u_{2n+1}}{dt^2} = -K(2u_{2n+1} - u_{2n} - u_{2n+2})$$

In other words, the forces acting on these atoms are the same as before, but their masses differ so we need to write different equations for even and odd sites.

Again we will guess plane wave solutions, but now with different amplitudes at the A and B sites, since there is no reason to expect them to vibrate equally. So we try the guess:

$$u_{2n}(t) = A(t)e^{ik2na}$$

while

$$u_{2n+1}(t) = B(t)e^{ik(2n+1)a}$$

Plugging these into the equations of motion we find:

$$m\frac{d^2A}{dt^2} = -2K[A(t) - \cos(ka)B(t)]$$

while

$$M\frac{d^2B}{dt^2} = -2K[B(t) - \cos(ka)A(t)]$$

Since we expect oscillatory solutions with the same frequency, we try the guess $A(t) = ae^{-i\omega_k t}, B(t) = be^{-i\omega_k t}$ where ω_k is the (as yet unknown) frequency of oscillations. Plugging this guess in the equations above allows us to find two possible solutions for ω_k – one acoustic, i.e such that $\omega_{k=0} = 0$, and one optical, i.e. such that $\omega_{k=0} > 0$. I will let you work out the details (or hand this as a homework). The end results are that if I defined $\omega_0 = \sqrt{\frac{K}{\mu}}$, where $\mu = \frac{mM}{m+M}$ is the reduced mass, then the two solutions are:

$$\omega_k^{\pm} = \omega_0 \sqrt{1 \pm \sqrt{1 - 4\frac{\mu}{m+M}\sin^2(ka)}}$$

Plotting these in the Brillouin zone (which, in this case, extends from $-\frac{\pi}{2a}$ to $\frac{\pi}{2a}$ because the lattice constant for this crystal is $2a$) we find something as shown below:

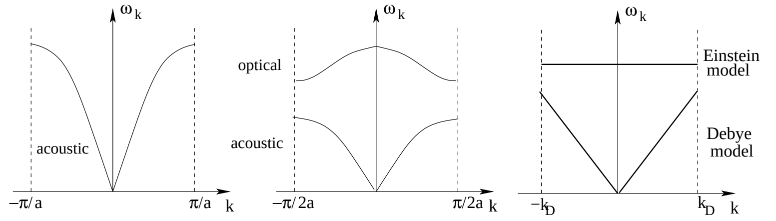


Figure 1: Left: energy $\omega_k = 2\omega_0|sin\frac{ka}{2}|$ of the longitudinal acoustic phonon for a chain with one atom in the basis. Center: energy of the acoustic and optical longitudinal phonons, $\omega_k^{\pm}$, for a chain with two atoms in the unit cell. Right: simplified Debye model for the acoustic phonons, assuming linear dispersion at all k but in a spherical Brillouin zone; and Einstein model for the optical phonons, assuming the same energy for all k.

Note that if $m = M$, this should agree with the previous solution – you might want to check this.

One final comment: once we know $\omega_k^{\pm}$, we could go back to calculate the amplitudes a and b of these modes (again, the reason why this classical calculation is meaningful is because when we do the quantum one, the expectation values of the displacement operators, in states with phonons with a given k, look similar to the classical solution corresponding to that k). In the limit $k \to 0$, for the acoustic phonon we find $a \sim b$, which is just the translation we already discussed. For the optical mode, we find that $\frac{a}{b} < 0$, i.e. the atoms move in anti-phase: if the A atoms move towards right then the B atoms move towards left, and viceversa. In an ionic crystal, A and B would have opposite charges and if we subjected them to an oscillating electric field (for instance, by illuminating the crystal with light) then we would expect precisely this kind of oscillating pattern, where A and B move in anti-phase because the electric forces have opposite signs. This suggests that optical phonons can be easily excited by light, which turns out to be true and is the reason why we call them "optical".

For more complicated bases we have more phonons modes, as you can see from counting, basically. If we have N units cells we expect N allowed k values (periodic boundary conditions plus restriction to the Brillouin zone). If the basis has p atoms, then the crystal has a total of Np atoms and we expect Np normal modes. Since they are characterized by k, for each allowed k we must have p solutions, i.e. there will be p phonon bands, of each one is always acoustic, and the remaining $p - 1$ are optical. What I just said is true for the longitudinal vibrations, and there are twice as many more transverse ones.

4 Contribution of phonons to various crystal properties

Let me start with thermal properties, first. Since the lattice vibrations (the phonons) contribute to the total energy of the crystal, they will contribute to its specific heat $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$. We already discussed the electronic contribution to it, and found it to be linear with T for metals, and exponentially small $\propto e^{-\beta\Delta/2}$ for semiconductors. We would like now to know what is the additional contribution from the phonons.

At $T = 0$ there are no phonons, so the lattice energy at finite T must be:

$$U_{lat}(T) = U_{lat}(0) + \sum_k \hbar\omega_k \langle n_k \rangle$$

where $\langle n_k \rangle$ is the average number of phonons with momentum k, since each of them adds an $\hbar\omega_k$ to the energy. Note: in all these equalities we have to sum over both longitudinal and transverse modes, and if there are also optical phonons we should add their contributions, too. Formally, we should add another index to tell us which phonon mode we're talking about, like in $\omega_{k,\lambda}$ where, for example $\lambda = 1$ would be acoustic longitudinal, $\lambda = 2, 3$ would be acoustic transverse, etc. The formula above would become $U_{lat}(T) = U_{lat}(0) + \sum_{k,\lambda} \hbar\omega_{k,\lambda}\langle n_{k,\lambda}\rangle$, where the sum over λ would run over however many kinds of phonons there are in that crystal.

I already told you that the average occupation number of a free bosonic mode is given by the Bose-Einstein distribution, and since our phonons are bosons and they do not interact with one another, it follows that:

$$\langle n_{k,\lambda} \rangle = \frac{1}{e^{\beta\hbar\omega_{k,\lambda}} - 1}.$$

Note that the chemical potential is set to zero: $\mu = 0$. This is true for bosons such as phonons and photons, which are not true particles but just a way to describe excitations.

For a phonon with a certain energy $\hbar\omega_{k,\lambda}$, this average number has simpler to understand expressions in the asymptotic limits. First, at "low" temperature, by which we mean such that $k_B T \ll \hbar\omega_{k,\lambda}$ (so, what is low and what is high depends on what phonon you're considering!), we have $\beta\hbar\omega_k \gg 1$, so the exponential is very large and we can ignore the -1 to find:

$$\langle n_{k,\lambda} \rangle \approx e^{-\beta\hbar\omega_{k,\lambda}}$$

In other words, at low temperatures the number of such bosons is exponentially small, just because there is not enough thermal energy to excite them. On the other hand, at high T where $k_B T \gg \hbar\omega_{k,\lambda}$ we now have $\beta\hbar\omega_k \ll 1 \rightarrow e^{\beta\hbar\omega_{k,\lambda}} \approx 1 + \beta\hbar\omega_{k,\lambda} + ...$, which leads to:

$$\langle n_{k,\lambda} \rangle \approx \frac{k_B T}{\hbar\omega_{k,\lambda}} \gg 1$$

i.e., at high temperatures we have a large number of phonons. This is also easy to understand, since we expect $k_B T$ energy per normal mode from the equipartition theorem (classical prediction for oscillators, which must be accurate at high T), and if this must be divided between the phonons of that mode, each of which costs $\hbar\omega_{k,\lambda}$. Their ratio is how many such phonons there must be.

Back to our specific heat. The calculation is now clear: we should plug the Bose-Einstein distribution in that formula, turn sums into integrals since we have big crystals with $N \rightarrow \infty$, do them numerically, and then estimate $\partial U_{lat}/\partial T$ to find the lattice contribution to C_V. This can be done and you'll likely see examples in a stat mech course.

For our purposes, let's simplify things just to get a feeling for what we expect. For acoustic phonons, it is convenient to use the so-called Debye model, where we pretend that their energy is $\hbar\omega_k = v_s k$ for all k, not just near the origin (see figure above). There is also a second approximation, which is to assume that the Brillouin zone is spherical and has a radius k_D, instead of being a cube or whatever true shape it has (the logic is that since we're not describing too well the energy of the phonons near the Brillouin zone edge, we can give up on trying to describe very accurately what its precise shape is, too. Especially since for something like an FCC lattice, we saw that the BZ can be quite complicated. However, the volume of the BZ is meaningful because it's linked to how many modes N can fit in, so that has to be preserved).

Suppose we only consider the longitudinal acoustic phonon. Then, we take $\omega_k = v_s k$, where v_s is the speed of sounds found from the true dispersion in the limit $k \approx 0$; and if our lattice is cubic, then we ask:

$$\left(\frac{2\pi}{a}\right)^3 = \frac{4\pi k_D^3}{3}$$

i.e. the spherical BZ has the same volume as the true BZ. From this, it follows that the highest possible energy of these phonons, known as the Debye frequency, is:

$$\hbar\omega_D = v_s k_D = v_s \frac{2\pi}{a}\left(\frac{3}{4\pi}\right)^{\frac{1}{3}}.$$

It is also customary to define a Debye temperature:

$$k_B T_D = \hbar\omega_D$$

so that if $T \gg T_D$, we are at "high temperatures" for all these acoustic phonons.

With this approximation, the energy becomes:

$$U_{lat}(T) = U_{lat}(0) + N\left(\frac{a}{2\pi}\right)^3 \int d\vec{k} \frac{\hbar\omega_k}{e^{\beta\omega_k} - 1}$$

where the integral is over the (now spherical) Brillouin zone. Using spherical coordinates, the integral over angles is 4π and we get:

$$U_{lat}(T) = U_{lat}(0) + N\left(\frac{a}{2\pi}\right)^3 4\pi \int_0^{k_D} dk k^2 \frac{\hbar\omega_k}{e^{\beta\omega_k} - 1}$$

where $\omega_k = v_s k$. Let me introduce a new variable $x = \hbar v_s k/(k_B T)$, in terms of which:

$$U_{lat}(T) = U_{lat}(0) + N\left(\frac{a}{2\pi}\right)^3 4\frac{(k_B T)^4}{(\hbar v_s)^3}\pi \int_0^{\frac{T_D}{T}} dx x^2 \frac{x}{e^x - 1}$$

This may look scary, but we are basically done. At small temperatures $T \ll T_D$, the upper limit of the integral goes to infinity. It turns out that that integral then equals $4\pi^4/15$, but what really matters is that it's a number, it doesn't depend on T. So, at small T we find $U_{lat} \sim aNT^4$, where a collects all those other constants, and so $C_V^{(lat)} \sim T^3$. As a result, for a metal at low T we expect $C_V = \alpha T + \beta T^3$, where the first part is from the electrons and the second from the phonons. Because the dependence on T is through different powers, we can easily disentangle how much each contribution is, and compare it to our individual predictions. For example, if one plots C_V/T vs T^2, one should get a straight line with slope β and y-axis intercept of α.

At high temperatures $T \gg T_D$ the upper limit goes towards zero, so we're only interested in the integrand for small x. As a result, we can approximate $e^x - 1 \sim x$, and the integral becomes trivial, i.e. $\int_0^{\frac{T_D}{T}} dx x^2 = \frac{1}{3}\left(\frac{T_D}{T}\right)^3$. As a result, we find that U_{lat} increases linearly with T so that $C_V^{(lat)} = 3Nk_B = const$. This (the fact that the lattice contribution to C_V is constant at high T) is known as the law of Dulong and Petit and can be onbtained much faster from the equipartition theorem.

So far, we've only considered the contribution from acoustic phonons, which exist in any crystal. If there are also optical phonons, then we need to add their contributions. To deal with them, it is also customary to make a simplification, and assume that their energy is a constant, $\omega_k = \Omega$ (their energy usually changes rather little with momentum). This is known as **Einstein's model**. With this approximation, their contribution to the energy is very simple, namely $N(p-1)\frac{\hbar\Omega}{e^{\beta\hbar\Omega}-1}$, where the first term is the total number of optical phonons modes. High and low temperatures (now defined with respect to Ω) can be easily considered, just like we did for the average phonon number.

For completeness, let me quickly mention something about contributions of phonons to optical and transport properties. For transport properties, I already said that phonons provide one of the scattering mechanisms which are responsible for increasing the resistivity. To properly calculate their contribution to the scattering rate $\frac{1}{\tau}$ one needs to do a QM calculation, but at high T it turns out to be proportional to the average number of phonons present. The number of phonons increases proportionally with T at high T, explaining why resistivity increases linearly with temperature at high temperatures.

In terms of optical properties, light couples strongly to optical phonons in all ionic materials, but also those based on covalent bonds which have partially ionic character (i.e., so long as the constituent ions in the basis have different charges). In practice, what this means is that if we shine photons with energy equal to the energy of optical phonons on a crystal, they are absorbed and optical phonons are excited. This gives us one of the ways to figure out their energies, by seeing what photon frequencies are absorbed from a continuous spectrum.