

## Introduction to Part 2: Thermal Properties

We now have **lattice structure** as confirmed by Bragg diffraction.

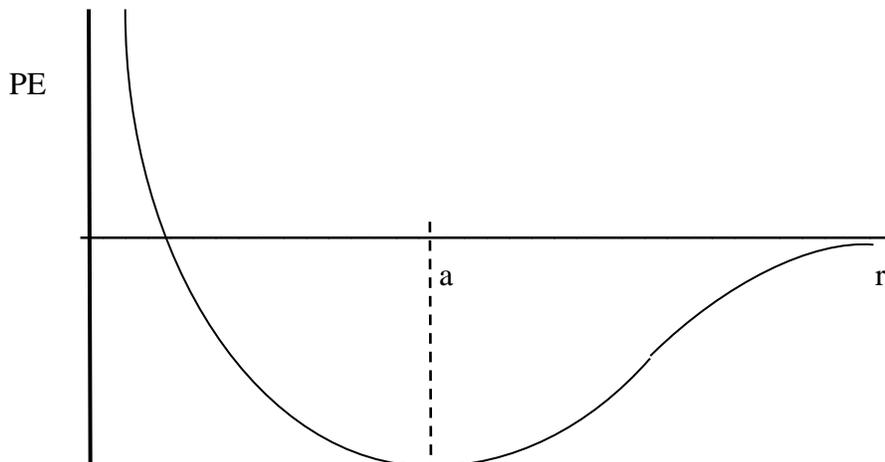
- As temperature goes up, Bragg diffraction lines do NOT broaden as would happen in a gas, but we do get more diffuse scattering.
- As temperature goes up, where does heat energy go (heat capacity)?
- As temperature goes up, what causes crystals to expand?
- For a temperature difference between ends, how does the heat energy travel from the hot end to the cold end?

### 1. What is temperature?

We'll be referring a lot to temperature in this and the following sections, so it would be a good idea to talk about what temperature is. From thermodynamics, we get that  **$k_B T = \text{average energy per available mode}$**  that anything has. Actually, average energy per degree of freedom =  $\frac{1}{2}k_B T$ , but in the case of oscillations we have both kinetic and potential energies and with light we have both electric and magnetic energies so the average energy per oscillation/wave mode =  $k_B T$  as above. This relation effectively **defines temperature**. The constant,  $k_B$ , is called Boltzmann's constant, and  $k_B = 1.38 \times 10^{-23}$  J/K. The  $T$  is the temperature in Kelvin. This is based on the simplest case of a monatomic gas, one that only has 3 degrees of freedom due to the velocity going in a 3-D space since a monatomic gas can't vibrate or rotate – see the [Appendix on Definition of Temperature](#). More complicated systems have more degrees of freedom, but quantum mechanics imposes limitations on some of these degrees of freedom so the situation can be somewhat complicated. [Case in point: a monatomic atom can't vibrate, but it can spin; however, since its moment of inertia,  $I$ , is so tiny, its frequency of spin,  $\omega$ , would be so high for its angular momentum,  $L=I\omega$ , to reach  $\hbar$  that its energy of spin ( $\frac{1}{2}I\omega^2$ ) would be much greater than the available energy needed to activate its lowest non-zero quantum level.] This definition of temperature also leads to the idea of **equipartition of energy** – that is, on average energy is equally distributed among the different available modes.

### 2. Why is the lattice stable?

- If atoms get too close, there is a repulsion (basically between the positive ion cores).
- If the atoms get too far away, there is an attraction (basically due to the negative electrons attracting the positive ion cores).
- Therefore, there is some equilibrium distance between the atoms which is what we call the lattice spacing,  $a$ . (This is actually for a monatomic lattice [one atom per basis].)
- Using the idea that objects bound to something have negative total energy [and hence negative potential energy since kinetic energy can't be negative - like earth bound to the sun and electrons bound to nuclei], and objects able to escape have positive total energy, the potential energy should look something like the following:



- e) Also, recall that  $F = -d(PE)/dx$  [this follows from the definition of  $\Delta PE = -\int F \cdot dx$ ]. Thus, a negative slope of the PE vs x curve indicates a force in the positive direction, and a positive slope indicates a force in the negative direction.

### 3. Harmonic approximation

We can expand any function in a Taylor series expansion, so we will expand the PE(x) in a Taylor series expansion about the equilibrium position, a:

$$PE(x-a) = PE(a) + [d(PE)/dx]_a (x-a) + \frac{1}{2}[d^2(PE)/dx^2]_a (x-a)^2 + \text{higher order terms}$$

The zero order term, PE(a), is merely some constant; and since PE is defined relative to some arbitrary standard [like PE of gravity = mgh where h is measured relative to whatever is convenient], the first term is relatively unimportant.

The first order term,  $[d(PE)/dx]_a (x-a)$ , is zero since the potential energy curve is flat at  $x=a$ , that is,  $[d(PE)/dx]_{x=a} = 0$ .

The second order term is the one of interest because it is of the form of  $\frac{1}{2}kx^2$  (spring potential energy) where the spring constant, k, is  $[d^2(PE)/dx^2]_a$  and the distance x in  $\frac{1}{2}kx^2$  is really the distance from equilibrium, (x-a). Since we are using k as a wavevector, we will use C for the spring constant instead. Hence our second order term will look like  $\frac{1}{2}C(x-a)^2$ , where  $C = [d^2(PE)/dx^2]_{x=a}$ .

The higher order terms will be very small (negligible) as long as (x-a) is small since they involve (x-a) to higher powers than the harmonic (second order) term. In the **harmonic approximation** we neglect these higher order terms. Note: the higher order terms will be needed when we consider thermal expansion which is small but not negligible in solids and thermal conduction.

Thus we can approximate the atoms in the lattice as being bound to one another by springs! When we hit one atom in a lattice, such as by a photon, by a high speed (hot) atom from the surrounding gas or liquid, or from another solid touching our solid, then the atom will move; and this movement will cause its neighboring atom to move, etc. This leads to the idea that the heat energy is in the form of oscillations, i.e., waves!

### 4. Waves

How fast will these oscillations/waves travel? What properties of the solid will that speed depend on? We'll start with looking at how waves travel and get an expression for the phase velocity and for the group velocity if we have a combination of waves. We'll then use Newton's 2<sup>nd</sup> Law to get a relation between the frequency and the wavelength (or wavevector) to see what properties of the solid that wave velocity depends on.

Do these waves have energy, and is this how the solid stores heat energy and so has a heat capacity? We'll look at both the kinetic and potential energies of the oscillations to see how much energy a wave has. We'll also see what kind of waves can exist in the solid and relate this to heat capacity.

Do the waves carry energy with them, and is this involved in heat transfer?

Is there a wave/particle duality with these waves as there is with electromagnetic waves? Does Quantum Theory enter into our analysis/predictions? The last parts of this section will attempt to answer these questions.