

Thermal Expansion

1. Review

So far we have considered each atom to be connected to other atoms by "springs" since the potential energy due to the binding in the crystal was similar to that of a spring: $PE(x) \approx \frac{1}{2}C(x-a)^2$ where a is the equilibrium distance from the adjacent lattice point, and C is the spring constant. This was the result of expanding $PE(x)$ in a **Taylor series** about the equilibrium point, a :

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

where we have **neglected the higher order terms** (we call this assumption the **harmonic approximation**); where $[dPE(x)/dx]_{x=a} = 0$ since the slope of the PE vs x curve is zero at the equilibrium point; and where the $PE(a)$ is just a constant [what is really important is ΔPE , so any constant cancels out - just like $PE = mgh$ for gravity: h is measured from any "nice" place]. This leaves $PE(x) \approx \frac{1}{2}[d^2PE(x)/dx^2]_{x=a}(x-a)^2$, and so we identify the spring constant as $C = [d^2PE(x)/dx^2]_{x=a}$. Note the notation: C here is NOT the heat capacity as it was in the last section, here it is the "spring constant".

2. Idea of thermal expansion

The basic explanation of thermal expansion is that as energy (heat) is added, the atoms oscillate with bigger amplitudes about their equilibrium position. The average distance between atoms may then be different than the constant, a , we have assumed for the equilibrium position. We need to determine that average distance and see how it depends on temperature.

We start with the idea of average:

$$x_{\text{avg}} = \frac{\sum \{x P(x)\}}{\sum \{P(x)\}}$$

where $P(x)$ is the probability of the atom being at position x , where here x is the distance from equilibrium, $x = (x-a)$ in the terminology of part 1 above. Since the potential energy depends on x , and since the Boltzmann distribution says that the probability of having any energy decreases exponentially with that energy, then

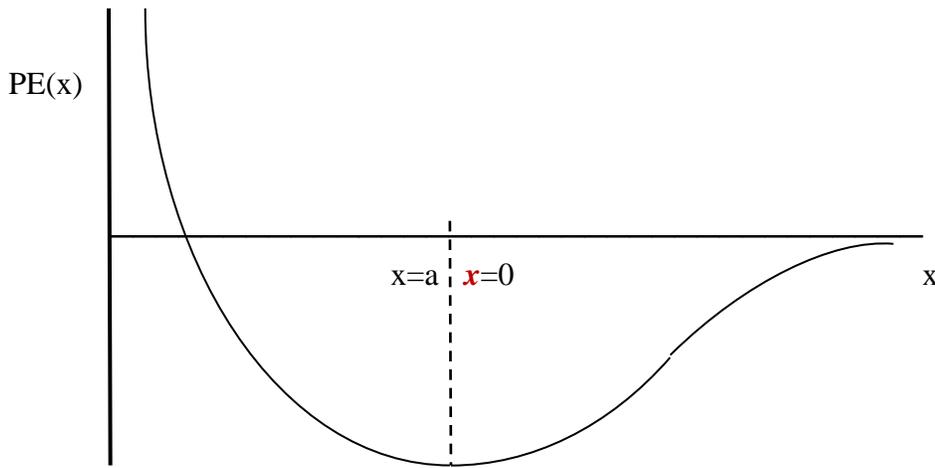
$$P(x) = A e^{-PE(x)/kT}. \quad (\text{The } kT \text{ in the exponent is } k_B T.)$$

Putting the above two ideas together allows us to calculate x_{avg} :

$$x_{\text{avg}} = \frac{\int x A e^{-PE(x)/kT} dx}{\int A e^{-PE(x)/kT} dx}.$$

3. Thermal expansion under the harmonic approximation

As a homework problem, you are to show that the average distance from equilibrium is zero under the harmonic approximation ([homework problem 20](#)). The more complete problem of thermal expansion is done on the next page, so to do problem 20 simply follow the steps on the next page but take out the higher order terms in the expansion of $PE(x)$.



4. Thermal expansion including non-harmonic terms

See excel spreadsheet [SlopeOfSlopeOfSlope](#) linked here and from the course web page

Consider the shape of the $PE(x)$ vs x curve (same as in the Introduction for Part 2). For $x < 0$ (that is, one atom closer to the previous atom than the normal distance, $x < a$), we expect that $PE(x)$ will go up steeper than the parabola $\frac{1}{2}Cx^2$, while for $x > 0$ (farther from the previous atom, $x > a$) we expect that $PE(x)$ will go up slower than the parabola. This means that we expect the third order term in the expansion of $PE(x)$ to be negative. For a parabola, the slope of the slope (2nd derivative) is a positive constant, so the 3rd derivative is zero. In our case, the slope of the slope is not constant but is decreasing (not rising as fast for $x > a$). We will use the coefficient $-g$ (where g itself is positive). Let's also carry along a fourth order term and specify its coefficient as f . Thus, we have:

$$PE(x) \approx PE(a) + \frac{1}{2}Cx^2 - gx^3 + fx^4.$$

Therefore, our expression for x_{avg} becomes:

$$x_{\text{avg}} = \frac{\int x A \exp\{-PE(a) - \frac{1}{2}Cx^2 + gx^3 - fx^4\}/k_B T\} dx}{\int A \exp\{-PE(a) - \frac{1}{2}Cx^2 + gx^3 - fx^4\}/k_B T\} dx}$$

or, since $e^{a+b} = e^a e^b$, we can write:

$$x_{\text{avg}} = \frac{\int x A \exp[-PE(a)/k_B T] \exp[-\frac{1}{2}Cx^2/k_B T] \exp[+gx^3/k_B T] \exp[-fx^4/k_B T] dx}{\int A \exp[-PE(a)/k_B T] \exp[-\frac{1}{2}Cx^2/k_B T] \exp[+gx^3/k_B T] \exp[-fx^4/k_B T] dx}$$

We can cancel out the A 's and the $\exp[-PE(a)/k_B T]$'s (since they do not depend on x and can be taken outside the integral):

$$x_{\text{avg}} = \frac{\int x \exp[-\frac{1}{2}Cx^2/k_B T] \exp[+gx^3/k_B T] \exp[-fx^4/k_B T] dx}{\int \exp[-\frac{1}{2}Cx^2/k_B T] \exp[+gx^3/k_B T] \exp[-fx^4/k_B T] dx}$$

This is a hard integral to do as is, so we will use an approximation [in addition to the one that keeps only terms to fourth order in PE(x)]. Since $\exp[-\frac{1}{2}Cx^2/k_B T]$ will give only very small values for large x 's, we will **approximate the $\exp[+gx^3/k_B T]$ and the $\exp[-fx^4/k_B T]$ in Taylor series expansions:**

$$\exp[+gx^3/k_B T] \approx 1 + gx^3/k_B T \quad \text{and} \quad \exp[-fx^4/k_B T] \approx 1 - fx^4/k_B T.$$

[If we keep only the zero order terms in the numerator (that is, $\exp[+gx^3/k_B T] \approx 1$ and $\exp[-fx^4/k_B T] \approx 1$), we get the harmonic approximation which you are going to show in problem 20 gives $x_{\text{avg}} \approx 0$.] However, if we keep only zero order terms in the denominator, the denominator does not equal zero; therefore we can reasonably keep only zero order terms in the denominator (to make it simpler without wiping out our result):

$$x_{\text{avg}} = \frac{\int x \exp[-\frac{1}{2}Cx^2/k_B T] [1 + gx^3/k_B T] [1 - fx^4/k_B T] dx}{\int \exp[-\frac{1}{2}Cx^2/k_B T] [1] [1] dx};$$

and multiplying out the expression and keeping only fourth order terms:

$$x_{\text{avg}} = \frac{\int \exp[-\frac{1}{2}Cx^2/k_B T] [x + (gx^4/k_B T) - (fx^5/k_B T)] dx}{\int \exp[-\frac{1}{2}Cx^2/k_B T] dx}.$$

Now we can look in a table of integrals to find: $\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = [\pi/\alpha]^{1/2}$.

[Trick: let $I = \int \exp[-\alpha x^2] dx$; let $I^2 = \int \exp[-\alpha x^2] dx \cdot \int \exp[-\alpha y^2] dy$
 $= \iint \exp[-\alpha(x^2+y^2)] dx dy = \iint \exp[-\alpha r^2] r dr d\theta$; but $r dr = \frac{1}{2} d(r^2)$; $I^2 = \frac{1}{2}(2\pi)(1/\alpha)$]

From this we can integrate $\int_{-\infty}^{+\infty} x^n e^{-\alpha x^2} dx$ by parts. But first note that if the power (n) is odd, the integral gives zero since we are integrating an even function, the $\exp[-\alpha x^2]$, times an odd function, the x^n , over symmetric limits. Therefore we are left with one even power term:

$$x_{\text{avg}} = \frac{\int \exp[-\frac{1}{2}Cx^2/k_B T] (gx^4/k_B T) dx}{\int \exp[-\frac{1}{2}Cx^2/k_B T] dx};$$

and now integrating:

$$x_{\text{avg}} = \frac{(g/k_B T) [3/\{4(\frac{1}{2}C/k_B T)^2\}] [\pi/(\frac{1}{2}C/k_B T)]^{1/2}}{[\pi/(\frac{1}{2}C/k_B T)]^{1/2}} = 3gk_B T/C^2.$$

Our final result says that x_{avg} is proportional T, which predicts thermal expansion! But since this is a **third order effect**, it should be very small - as thermal expansion is for solids. (The fourth order term [the one with f in it] will show up not in the numerator [since it will give an odd power], but in the denominator [where it will give an even power], and will provide an even smaller effect.)

We can "see" that we should expect thermal expansion from the PE(x) vs x plot. Since the sides of the potential well are steep on the $x < 0$ side and are less steep and flatten out on the $x > 0$ side, as the energy goes up (the temperature goes up), we would expect the atom to go further and spend more time on the $x > 0$ side than on the $x < 0$ side - which on average will give thermal expansion.

The above holds for large T; for small T we must be more concerned with the quantum effects involved. Here we have integrated which assumes that energy is continuous. This assumption works well for large T's, but not for small T's.