Problem 6.32. Consider a classical particle moving in a one-dimensional potential well $u(x)$, as shown in Figure 6.10. The particle is in thermal equilibrium with a reservoir at temperature T, so the probabilities of its various states are determined by Boltzmann statistics.

(a) Show that the average position of the particle is given by

$$\overline{x} = \frac{\int x e^{-\beta u(x)}\, dx}{\int e^{-\beta u(x)}\, dx},$$

where each integral is over the entire x axis.

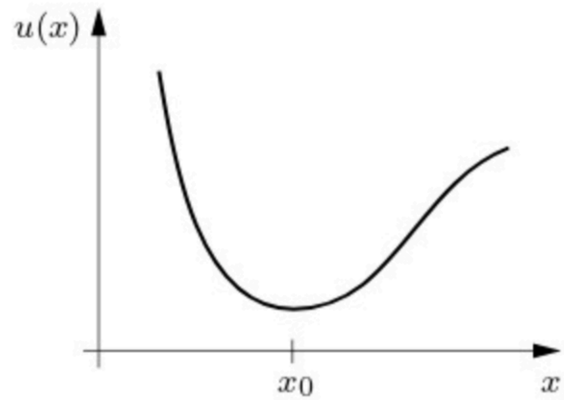


Figure 6.10. A one-dimensional potential well. The higher the temperature, the farther the particle will stray from the equilibrium point.

(b) If the temperature is reasonably low (but still high enough for classical mechanics to apply), the particle will spend most of its time near the bottom of the potential well. In that case we can expand $u(x)$ in a Taylor series about the equilibrium point x_0:

$$u(x) = u(x_0) + (x - x_0)\left.\frac{du}{dx}\right|_{x_0} + \frac{1}{2}(x - x_0)^2 \left.\frac{d^2u}{dx^2}\right|_{x_0} + \frac{1}{3!}(x - x_0)^3 \left.\frac{d^3u}{dx^3}\right|_{x_0} + \cdots.$$

Show that the linear term must be zero, and that truncating the series after the quadratic term results in the trivial prediction $\overline{x} = x_0$.

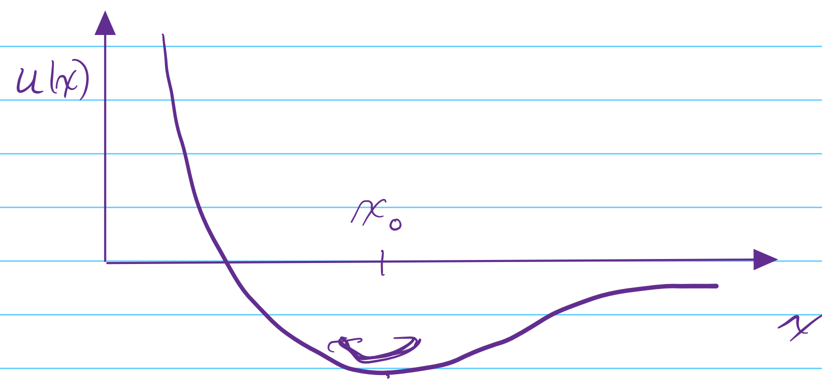
Phys 335: Problem 6.32: Thermal Expansion

How can we relate the partition function to measurable quantities, such as thermal expansion?

(a) Average position: Motion in a potential well $u(x)$

$$\bar{x} = \frac{\int_{-\infty}^{\infty} x\, e^{-\beta u(x)}\, dx}{\int_{-\infty}^{\infty} e^{-\beta u(x)}\, dx}$$

(b) Sample $u(x)$



Why does increasing T increase x? Why doesn't $\bar{x}$ Stay the same, even if oscillations get bigger? The well is a-symmetric.

Taylor Series

$$u(x) \simeq u(x_0) + \left(\frac{du}{dx}\right)_{x_0} (x - x_0) + \frac{1}{2!} \underbrace{\left.\frac{d^2u}{dx^2}\right|_{x_0}}_{\text{spring constant}} (x - x_0)^2 + \frac{1}{3!} \left.\frac{d^3u}{dx^3}\right|_{x_0} (x - x_0)^3 + \cdots$$

At the minimum, $\left.\frac{du}{dx}\right|_{x_0} = 0$.

$$u(x) = u(x_0) + a(x - x_0)^2 + b(x - x_0)^3$$

what is $\bar{x}$?

First, suppose we only take the first 2 terms

$$\bar{x} = \frac{\int x e^{-\beta u(x)} dx}{\int e^{-\beta u(x)} dx}$$

Numerator

$$\int_{-\infty}^{\infty} x e^{-\beta u_0} e^{-\beta a(x-x_0)^2} dx$$

Let $z = x - x_0 \Rightarrow x = z + x_0, \; dx = dz$

$$N = \int_{-\infty}^{\infty} (z + x_0) e^{-\beta u_0} e^{-\beta a z^2} dz$$

$$= \underbrace{\int_{-\infty}^{\infty} z e^{-\beta u_0} e^{-\beta a z^2} dz}_{0 \text{ (odd func. over even limits)}} + x_0 e^{-\beta u_0} \int_{-\infty}^{\infty} e^{-\beta a z^2} dz$$

Denominator:

$$D = \int_{-\infty}^{\infty} e^{-\beta u(x)} dx = \int_{-\infty}^{\infty} e^{-\beta u_0} e^{-\beta a(x-x_0)^2} dx$$

$$= \int_{-\infty}^{\infty} e^{-\beta u_0} e^{-\beta a z^2} dz$$

$\therefore$

$$\bar{x} = \frac{N}{D} = x_0 .$$ unsurprising.

(c) If we keep the cubic term in the Taylor series as well, the integrals in the formula for $\overline{x}$ become difficult. To simplify them, assume that the cubic term is small, so its exponential can be expanded in a Taylor series (leaving the quadratic term in the exponent). Keeping only the largest temperature-dependent term, show that in this limit $\overline{x}$ differs from x_0 by a term proportional to kT. Express the coefficient of this term in terms of the coefficients of the Taylor series for $u(x)$.

(d) The interaction of noble gas atoms can be modeled using the **Lennard-Jones potential**,

$$u(x) = u_0\left[\left(\frac{x_0}{x}\right)^{12} - 2\left(\frac{x_0}{x}\right)^{6}\right].$$

Sketch this function, and show that the minimum of the potential well is at $x = x_0$, with depth u_0. For argon, $x_0 = 3.9$ Å and $u_0 = 0.010$ eV. Expand the Lennard-Jones potential in a Taylor series about the equilibrium point, and use the result of part (c) to predict the linear thermal expansion coefficient (see Problem 1.8) of a noble gas crystal in terms of u_0. Evaluate the result numerically for argon, and compare to the measured value $\alpha = 0.0007\ \mathrm{K}^{-1}$ (at 80 K).

(c) What if you include the cubic?

$$D = \int_{-\infty}^{\infty} (z + x_0)\, e^{-\beta u_0}\, e^{-\beta a z^2}\, e^{-\beta b z^3}\, dz$$

What to do here? No closed solution.

Approximate! Assume $\beta b z^3 << 1$

(i.e. extra energy $b z^3 << kT$)

Then $e^{-\beta b z^3} \approx 1 - \beta b z^3$

$$N = \int_{-\infty}^{\infty} (z + x_0)\, e^{-\beta u_0} e^{-\beta a z^2} (1 - \beta b z^3)\, dz$$

4 terms. Look at symmetries to see what is 0.

$$N = \int_{-\infty}^{\infty} z \cdot 1\, e^{-\beta u_0} e^{-\beta a z^2}\, dz \leftarrow 0 \quad +$$

$$\int_{-\infty}^{\infty} x_0 \cdot 1\, e^{-\beta u_0} e^{-\beta a z^2}\, dz \quad +$$

$$\int_{-\infty}^{\infty} -\beta b z^4\, e^{-\beta u_0} e^{-\beta a z^2}\, dz \quad +$$

$$\int_{-\infty}^{\infty} -x_0 (\beta b z^3)\, e^{-\beta u_0} e^{-\beta a z^2}\, dz \leftarrow 0$$

$$N = x_0 \int_{-\infty}^{\infty} e^{-\beta u_0} e^{-\beta a z^2}\, dz - \beta b \int_{-\infty}^{\infty} z^4 e^{-\beta u_0} e^{-\beta a z^2}\, dz$$

Denominator: Make the same approximation

$$D = \int_{-\infty}^{\infty} e^{-\beta u_0} e^{-\beta a z^2} (1 - \underbrace{\beta b z^3}_{\text{integrates to } 0})\, dz$$

$\therefore$

$$\bar{x} = x_0 - \frac{\beta b\, e^{-\beta u_0} \int_{-\infty}^{\infty} z^4 e^{-\beta a z^2}\, dz}{e^{-\beta u_0} \int_{-\infty}^{\infty} e^{-\beta a z^2}\, dz}$$

How to evaluate such integrals?

Step 1: Make dimensionless

e.g. $y \equiv \sqrt{\beta a}\, z$

$$dy = \sqrt{\beta a}\, dz \Rightarrow dz = \frac{1}{\sqrt{\beta a}}\, dy$$

$$\int_{-\infty}^{\infty} e^{-\beta a z^2} dz = \frac{1}{\sqrt{\beta a}} \underbrace{\boxed{\int_{-\infty}^{\infty} e^{-y^2} dy}}_{\sqrt{\pi}}.$$

See Appendix B.1.

Numerator: See Appendix B-1, esp. problem B.2

$$\int_{-\infty}^{\infty} z^4 e^{-\beta a z^2} dz = \frac{1}{(\beta a)^2} \cdot \frac{1}{\sqrt{\beta a}} \boxed{\int_{-\infty}^{\infty} y^4 e^{-y^2} dy}$$

This is $\frac{3}{4}\sqrt{\pi}$

$\therefore$

$$\bar{x} = x_0 - \frac{\beta b \cdot \frac{1}{(\beta a)^2} \cdot \frac{1}{\sqrt{\beta a}} \cdot \frac{3}{4}\sqrt{\pi}}{\frac{1}{\sqrt{\beta a}}\sqrt{\pi}}$$

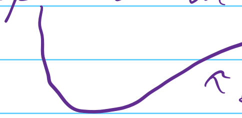
$$\bar{x} = x_0 - \frac{3}{4} \cdot \frac{b}{\beta a^2} = x_0 - \frac{3}{4}\frac{b}{a^2} kT$$

Units check: Recall $u(x) = u_0 + a(x-x_0)^2 + b(x-x_0)^3$

$$\left[\frac{b}{\beta a^2}\right] = \frac{J/m^3}{\frac{1}{J} \cdot (J/m^2)^2} = m \quad \checkmark$$

What is the sign for b? Depends on shape of potential.

$$b = \frac{1}{3!}\frac{d^3u}{dx^3}$$



$\nwarrow$ b is negative if it gets less steep

$\therefore$

$x > x_0$ due to thermal expansion.

Example: Lennard-Jones Potential

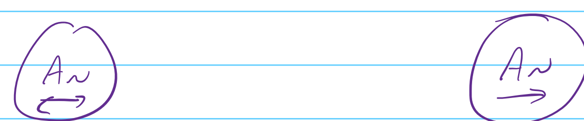
$$u(x) = u_0\left[\left(\frac{x_0}{x}\right)^{12} - 2\left(\frac{x_0}{x}\right)^{6}\right]$$

Is this familiar?
where does it come from?

Argon: $x_0 = 0.39\,nm$
$u_0 = 0.010\,eV$

Expt. $\alpha = 0.0007/K$ at $80\,K$.

$\frac{1}{x^6}$ term: Dipole/Dipole interaction



fluctuating dipole

field $\sim \frac{1}{x^3}$

induced dipole, proportional to field,

interaction energy $\sim \frac{p^2}{x^3}$

Short range repulsion
complex/exclusion principle as orbitals overlap.
Hard to calculate.
Easy numerical approximation: You already have $1/x^6$, Square it to get $\frac{1}{x^{12}}$.

More on the dipole interaction

$\vec{p}_1$ is (instantaneous) dipole moment in atom 1.

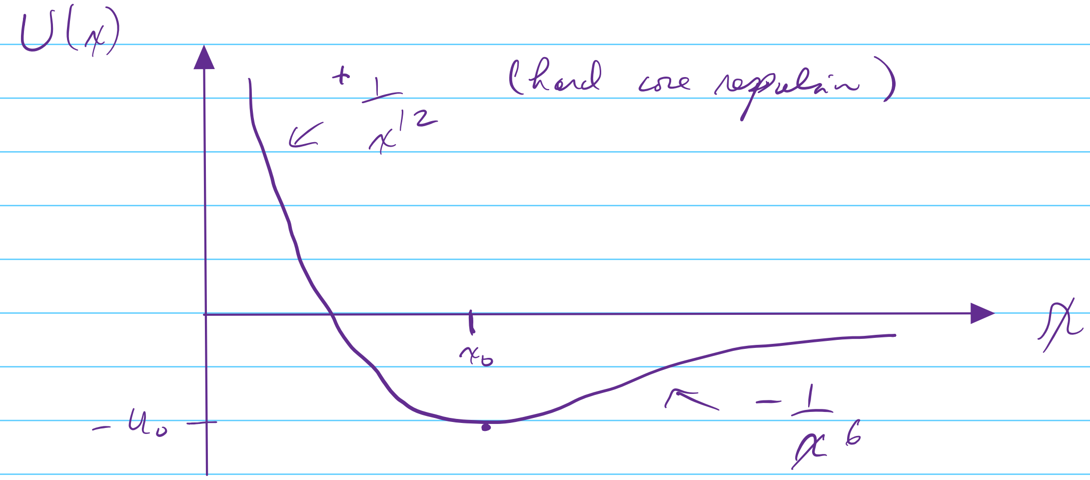
$\vec{E}_1$ due to $\vec{p}_1 \propto \frac{1}{r^3}$.

$\vec{E}_1$ due to $\vec{p}_1$ induces dipole $\vec{p}_2 \propto \vec{E}_1$.

Interaction energy is (Eq. 4-26 in Jackson)
(for 2 parallel dipole moments)

$$U_{12} = \frac{-2 p_1 p_2}{4\pi\epsilon_0 r^3}, \text{ and since } p_2 \propto \frac{1}{r^3})$$

$$U_{12} \propto -\frac{1}{r^6}$$



$$u(x) = u_0\left[\left(\frac{x_0}{x}\right)^{12} - 2\left(\frac{x_0}{x}\right)^6\right]$$

$$\frac{du}{dx} = u_0\left[-12\frac{x_0^{12}}{x^{13}} + 12\frac{x_0^6}{x^7}\right]$$

This is 0 at x_0.

$$\left.\frac{d^2u}{dx^2}\right|_{x_0} = u_0\left[156\frac{x_0^{12}}{x^{14}} - 84\frac{x_0^6}{x^8}\right]_{x_0} = 72\,u_0/x_0^2$$

Then $a = \frac{1}{2!}\left.\frac{d^2u}{dx^2}\right|_{x_0} = \frac{36\,u_0}{x_0^2} = a$

$$\left.\frac{d^3u}{dx^2}\right|_{u_0} = u_0\left[-14\cdot156\frac{x_0^{12}}{x^{15}} + 8\cdot84\frac{x_0^6}{x^9}\right]_{x_0} = -1512\,u_0/x_0^3$$

Then $b = \frac{1}{3!}\left.\frac{d^3u}{dx^3}\right|_{x_0} = -252\,u_0/x_0^3$

Plugging in numbers

$x_0 = 0.39\,nm$

$u_0 = 0.010\,eV$

$a = 2.367\,eV/nm^2$

$b = 42.48\,eV/nm^3$

Then

$$\bar{x} = x_0 - \frac{3}{4}\frac{b}{a^2} kT$$

$$\bar{x} = x_0 - \frac{3}{4}\left(\frac{-252\, u_0/x_0^3}{(36\, u_0/x_0^2)^2}\right) kT$$

$$= x_0 \left[1 + \frac{3}{4} \cdot \frac{252}{(36)^2} \frac{kT}{u_0}\right]$$

$$= x_0 [1 + \alpha T]$$

$$\alpha = \frac{3}{4} \frac{252}{(36)^2} \cdot \frac{8.617 \times 10^{-5} eV/K}{0.01 eV} = 0.00126/K$$

$$\alpha_{exp} = 0,0007 /K$$

So we get to within a power of 2.

Take-away)

1. Boltzmann factor can lead to real physical measureable quantities
2. Handling integrals + calculations
   - scaling
   - approximations