

## 1 Molecules as Harmonic Oscillators

We're given a Hamiltonian

$$\mathcal{H} = \frac{1}{2m} \sum_{n=1}^N (p_n^2 + p'_n{}^2) + \frac{K}{2} \sum_{n=1}^N |r_n - r'_n|^2 \quad (1)$$

We want to first find the partition function:

$$Q = \int \cdots \int_{4N} d^3\{p_i\} d^3\{p'_i\} d^3\{r_i\} d^3\{r'_i\} e^{-\beta\mathcal{H}} \quad (2)$$

This is  $N$  identical integrals, one for each particle:

$$Q = \left( \iiint d^3p d^3p' d^3r d^3r' e^{-\beta(\frac{1}{2m}(p_n^2 + p'_n{}^2) + \frac{K}{2}|r_n - r'_n|^2)} \right)^N \quad (3)$$

It separates:

$$Q = \left( \left( \int d^3p e^{-\frac{\beta}{2m}p^2} \right)^2 \int d^3r_i d^3r'_i e^{-\beta\frac{K}{2}|r_n - r'_n|^2} \right)^N \quad (4)$$

To evaluate this, let's start with the  $p$  integrals, going right away to spherical coordinates:

$$\int d^3p e^{-\frac{\beta}{2m}p^2} = 4\pi \int_0^\infty dp p^2 e^{-\frac{\beta}{2m}p^2} \quad (5)$$

$$= 4\pi(-2m) \frac{d}{d\beta} \int_0^\infty dp e^{-\frac{\beta}{2m}p^2} \quad (6)$$

This is a Gaussian integral we can do.

$$\int d^3p e^{-\frac{\beta}{2m}p^2} = -8m\pi \frac{d}{d\beta} \sqrt{\frac{m\pi}{2\beta}} \quad (7)$$

$$= 4m\pi \sqrt{\frac{m\pi}{2\beta^3}} \quad (8)$$

Plugging back into (4),

$$Q = \left( \left( 4m\pi \sqrt{\frac{m\pi}{2\beta^3}} \right)^2 \int d^3r_i d^3r'_i e^{-\beta\frac{K}{2}|r_n - r'_n|^2} \right)^N \quad (9)$$

$$= \left( 16m^2\pi^2 \frac{m\pi}{2\beta^3} \int d^3r_i d^3r'_i e^{-\beta\frac{K}{2}|r_n - r'_n|^2} \right)^N \quad (10)$$

$$Q = \left( \frac{8m^3\pi^3}{\beta^3} \int d^3r_i d^3r'_i e^{-\beta\frac{K}{2}|r_n - r'_n|^2} \right)^N \quad (11)$$

I believe the standard trick for the  $r$  integrals is to define a  $\mathbf{q} = \mathbf{r} - \mathbf{r}'$  and integrate over  $q$ :

$$\int d^3r_i d^3r'_i e^{-\beta \frac{K}{2} |r_n - r'_n|^2} = V \int d^3q e^{-\beta \frac{K}{2} q^2} \quad (12)$$

The factor of volume roughly accounts for translation invariance (because each  $q$  integral could take place with  $r$  and  $r'$  shifted by a constant vector, which must be accounted for). I'm not sure how valid that makes this result. If certain molecules could be displaced unrestrictedly far from the solid, I think other things would break. In any case, I'm adding a  $V$ . It makes the units work out too.

$$\int d^3r_i d^3r'_i e^{-\beta \frac{K}{2} |r_n - r'_n|^2} = V \int d^3q e^{-\beta \frac{K}{2} q^2} \quad (13)$$

Spherical coordinates:

$$\int d^3r_i d^3r'_i e^{-\beta \frac{K}{2} |r_n - r'_n|^2} = 4\pi V \int_0^\infty dq q^2 e^{-\beta \frac{K}{2} q^2} \quad (14)$$

$$= 4\pi \left(-\frac{2}{K}\right) V \frac{d}{d\beta} \int_0^\infty dq e^{-\beta \frac{K}{2} q^2} \quad (15)$$

$$= -\frac{8\pi V}{K} \frac{d}{d\beta} \sqrt{\frac{\pi}{2\beta K}} \quad (16)$$

$$= \frac{4\pi V}{K} \sqrt{\frac{\pi}{2\beta^3 K}} \quad (17)$$

$$(18)$$

Plugging this into (11), we get

$$Q = \left( \frac{8m^3\pi^3}{\beta^3} \frac{4\pi V}{K} \sqrt{\frac{\pi}{2\beta^3 K}} \right)^N \quad (19)$$

We can find the Helmholtz free energy from that:

$$A = -\frac{1}{\beta} \ln Q \quad (20)$$

$$= -\frac{N}{\beta} \ln \left( \frac{8m^3\pi^3}{\beta^3} \frac{4\pi V}{K} \sqrt{\frac{\pi}{2\beta^3 K}} \right) \quad (21)$$

**(b) Specific heat**

The specific heat is  $C_V = -T \frac{\partial^2 A}{\partial T^2}$ . Let's write  $A$  in terms of  $T$ :

$$A = -Nk_B T \ln \left( 8m^3 \pi^3 k_B^3 T^3 \frac{4\pi V}{K} \sqrt{\frac{\pi k_B^3 T^3}{2K}} \right) \quad (22)$$

$$= -Nk_B T \ln \left( 8m^3 \pi^3 k_B^3 \frac{4\pi V}{K} \sqrt{\frac{\pi k_B^3}{2K}} T^3 T^{3/2} \right) \quad (23)$$

$$= -Nk_B T \ln \left( \xi T^{9/2} \right) \quad (24)$$

Differentiating twice:

$$\frac{\partial A}{\partial T} = -Nk_B \ln \left( \xi T^{9/2} \right) - Nk_B T \frac{1}{\xi T^{9/2}} \frac{9}{2} T^{7/2} \quad (25)$$

$$\frac{\partial A}{\partial T} = -Nk_B \ln \left( \xi T^{9/2} \right) - Nk_B \frac{1}{\xi} \xi \frac{9}{2} \quad (26)$$

and finally

$$C_V = -T \frac{\partial^2 A}{\partial T^2} \quad (27)$$

$$= -T \frac{\partial}{\partial T} \left( -Nk_B \ln \left( \xi T^{9/2} \right) - Nk_B \frac{1}{\xi} \xi \frac{9}{2} \right) \quad (28)$$

$$= T \frac{\partial}{\partial T} Nk_B \ln \left( \xi T^{9/2} \right) \quad (29)$$

$$= Nk_B T \frac{1}{\xi T^{9/2}} \xi \frac{9}{2} T^{7/2} \quad (30)$$

$$= \frac{9}{2} Nk_B \quad (31)$$