1 Molecules as Harmonic Oscillators

We're given a Hamiltonian

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

We want to first find the partition function:

$$Q = \underbrace{\int \cdots \int}_{4N} d^3\{p_i\}\, d^3\{{p'}_i\}\, d^3\{r_i\}\, d^3\{{r'}_i\}\, e^{-\beta\mathcal{H}} \tag{2}$$

This is N identical integrals, one for each particle:

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

It separates:

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

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

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

This is a Gaussian integral we can do.

$$\int d^3p\, e^{-\frac{\beta}{2m}p^2} = 4\pi\sqrt{\frac{m\pi}{2\beta}} \tag{6}$$

Plugging back into (4),

$$Q = \left(\left(4\pi\sqrt{\frac{m\pi}{2\beta}}\right)^2 \int d^3r_i\, d^3{r'}_i\, e^{-\beta\frac{K}{2}|r_n-{r'}_n|^2}\right)^N \tag{7}$$

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

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

$$\int d^3r_i\, d^3{r'}_i\, e^{-\beta\frac{K}{2}|r_n-{r'}_n|^2} = V\int d^3q\, e^{-\beta\frac{K}{2}q^2} \tag{9}$$

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.

$$\int d^3r_i\, d^3{r'}_i\, e^{-\beta\frac{K}{2}|r_n - {r'}_n|^2} = V \int d^3q\, e^{-\beta\frac{K}{2}q^2} \tag{10}$$

Spherical coordinates:

$$\int d^3r_i\, d^3{r'}_i\, e^{-\beta\frac{K}{2}|r_n - {r'}_n|^2} = 4\pi V \int_0^\infty dq\, e^{-\beta\frac{K}{2}q^2} \qquad = 4\pi V\sqrt{\frac{\pi}{2\beta K}} \tag{11}$$

Plugging this into (8), we get

$$Q = \left(\frac{8m\pi^3}{\beta} 4\pi V\sqrt{\frac{\pi}{2\beta K}}\right)^N \tag{12}$$

We can find the Helmholtz free energy from that:

$$A = -\frac{1}{\beta}\ln Q \tag{13}$$

$$= -\frac{N}{\beta}\ln\left(\frac{8m\pi^3}{\beta} 4\pi V\sqrt{\frac{\pi}{2\beta K}}\right) \tag{14}$$