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:

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

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

This is a Gaussian integral we can do.

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

$$= 4m\pi\sqrt{\frac{m\pi}{2\beta^3}} \tag{8}$$

Plugging back into (4),

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

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

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

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

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

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.

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

Spherical coordinates:

$$\begin{aligned}
\int d^3r_i\, d^3{r'}_i\, e^{-\beta \frac{K}{2}|r_n - {r'}_n|^2} &= 4\pi V \int_0^\infty dq\, q^2 e^{-\beta \frac{K}{2} q^2} && (14)\\
&= 4\pi \left(-\frac{2}{K}\right) V \frac{d}{d\beta} \int_0^\infty dq\, e^{-\beta \frac{K}{2} q^2} && (15)\\
&= -\frac{8\pi V}{K} \frac{d}{d\beta} \sqrt{\frac{\pi}{2\beta K}} && (16)\\
&= \frac{4\pi V}{K} \sqrt{\frac{\pi}{2\beta^3 K}} && (17)\\
& && (18)
\end{aligned}$$

Plugging this into (11), we get

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

We can find the Helmholtz free energy from that:

$$\begin{aligned}
A &= -\frac{1}{\beta} \ln Q && (20)\\
&= -\frac{N}{\beta} \ln\left(\frac{8m^3\pi^3}{\beta^3} \frac{4\pi V}{K} \sqrt{\frac{\pi}{2\beta^3 K}} \right) && (21)
\end{aligned}$$

(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:

$$A = -Nk_\mathrm{B}T\ln\left(8m^3\pi^3k_\mathrm{B}^3T^3\frac{4\pi V}{K}\sqrt{\frac{\pi k_\mathrm{B}^3T^3}{2K}}\right) \tag{22}$$

$$= -Nk_\mathrm{B}T\ln\left(8m^3\pi^3k_\mathrm{B}^3\frac{4\pi V}{K}\sqrt{\frac{\pi k_\mathrm{B}^3}{2K}}T^3T^{3/2}\right) \tag{23}$$

$$= -Nk_\mathrm{B}T\ln\left(\xi T^{9/2}\right) \tag{24}$$

Differentiating twice:

$$\frac{\partial A}{\partial T} = -Nk_\mathrm{B}\ln\left(\xi T^{9/2}\right) - Nk_\mathrm{B}T\frac{1}{\xi T^{9/2}}\frac{9}{2}T^{7/2} \tag{25}$$

$$\frac{\partial A}{\partial T} = -Nk_\mathrm{B}\ln\left(\xi T^{9/2}\right) - Nk_\mathrm{B}\frac{1}{\xi}\xi\frac{9}{2} \tag{26}$$

and finally

$$C_V = -T\frac{\partial^2 A}{\partial T^2} \tag{27}$$

$$= -T\frac{\partial}{\partial T}\left(-Nk_\mathrm{B}\ln\left(\xi T^{9/2}\right) - Nk_\mathrm{B}\frac{1}{\xi}\xi\frac{9}{2}\right) \tag{28}$$

$$= T\frac{\partial}{\partial T}Nk_\mathrm{B}\ln\left(\xi T^{9/2}\right) \tag{29}$$

$$= Nk_\mathrm{B}T\frac{1}{\xi T^{9/2}}\xi\frac{9}{2}T^{7/2} \tag{30}$$

$$C_V = \frac{9}{2}Nk_\mathrm{B} \tag{31}$$

(c) Mean square separation

We want to find the ensemble average for q^2, as defined earlier. We already established that the position and momentum integrals separate, so they'll cancel, and we only need to do the integral over q:

$$\langle q^2 \rangle = \frac{4\pi V \int_0^\infty dq\, q^2 q^2 e^{-\beta \frac{K}{2} q^2}}{4\pi V \int_0^\infty dq\, q^2 e^{-\beta \frac{K}{2} q^2}} \tag{32}$$

$$= \frac{\frac{d^2}{d\beta^2} \frac{4}{K^2} \int_0^\infty dq\, e^{-\beta \frac{K}{2} q^2}}{\frac{d}{d\beta} \frac{-2}{K} \int_0^\infty dq\, e^{-\beta \frac{K}{2} q^2}} \tag{33}$$

$$= -\frac{2}{K} \frac{\frac{d^2}{d\beta^2} \sqrt{\frac{\pi}{2\beta k}}}{\frac{d}{d\beta} \sqrt{\frac{\pi}{2\beta K}}} \tag{34}$$

$$= -\frac{2}{K} \frac{\frac{d^2}{d\beta^2} \sqrt{\frac{1}{\beta}}}{\frac{d}{d\beta} \sqrt{\frac{1}{\beta}}} \tag{35}$$

$$= -\frac{2}{K} \frac{-\frac{d}{d\beta} \frac{1}{2} \beta^{-3/2}}{-\frac{1}{2} \beta^{-3/2}} \tag{36}$$

$$= -\frac{2}{K} \frac{\frac{d}{d\beta} \beta^{-3/2}}{\beta^{-3/2}} \tag{37}$$

$$= -\frac{2}{K} \frac{-\frac{3}{2} \beta^{-5/2}}{\beta^{-3/2}} \tag{38}$$

$$= \frac{3}{\beta K} \tag{39}$$

This gives us our mean square separation. As we'd expect, for higher temperatures, the molecules are further separated.