

1 — a) True, b) 2 Legendre transforms, c) all of the above

d) 4^{20} , e) i, ii, and iii

2a — Total length:

$$L = aN_a + bN_b, \quad N = N_a + N_b.$$

Fixing L fixes N_a and N_b , but for a given L , there are

$$\Omega = \binom{N}{N_b} = \binom{N}{\frac{L-aN}{b-a}}$$

possible microstates.

The value of N_a that maximizes this is $N/2$, so $L = (a+b)N/2$.

2b — The entropy at a given L is

$$S = k_B \log \Omega(L) = k_B \log \left(\binom{N}{\frac{L-aN}{b-a}} \right).$$

The Helmholtz free energy is just $-TS$, because there is no internal energy in this model, we consider only entropic effects.

$$A = -TS = -k_B T \log \left(\binom{N}{\frac{L-aN}{b-a}} \right).$$

If you want, you can go to the canonical ensemble:

$$Q = \sum_{\nu} \omega_{\nu} e^{-\beta E_{\nu}}.$$

Here, $\omega_{\nu} = \Omega(L)$ and $E_{\nu} = 0$ for all states ν , so there's no sum over ν at all, because all the states have the same energy, and our degeneracy is $\Omega(L)$, so the canonical is the same as the microcanonical ensemble here:

$$A = -k_B T \log Q = -k_B T \log \Omega(L).$$

We use Stirling's approximation on $\binom{N}{N_b}$ and we get:

$$A = -k_B T (N \log N - N_b \log N_b - (N - N_b) \log (N - N_b)).$$

2c — From $dA = -SdT + JdL$, we see that

$$J = \left. \frac{\partial A}{\partial L} \right|_T.$$

and we have

$$\frac{\partial}{\partial L} = \frac{1}{b-a} \frac{\partial}{\partial N_a}.$$

So we get

$$J = -k_B T \frac{\partial}{\partial N_b} (-N_b \log N_b + (N - N_b) \log(N - N_b)).$$

$$J = \frac{k_B T}{b-a} \log \frac{N_b}{N - N_b}.$$

Notice that when $N_b > N/2$, when we have the polymer extended beyond its equilibrium length, $J > 0$, and when $N_b < N/2$, we have $J < 0$. This is the meaning of entropic elasticity.

3a — We're given

$$\left. \frac{\partial S}{\partial L} \right|_T < 0.$$

And from our fundamental relation

$$dE = TdS + JdL \rightarrow dA = dE - d(TS) = -SdT + JdL.$$

From this we can read off a Maxwell relation:

$$-\left. \frac{\partial S}{\partial L} \right|_T = \left. \frac{\partial J}{\partial T} \right|_L > 0.$$

3b — We can use the cyclic derivative rule here

$$\left. \frac{\partial T}{\partial L} \right|_S \left. \frac{\partial L}{\partial S} \right|_T \left. \frac{\partial S}{\partial T} \right|_L = -1.$$

$$\left. \frac{\partial T}{\partial L} \right|_S = - \left. \frac{\partial S}{\partial L} \right|_T \left(\frac{T}{C_L} \right) > 0.$$

4a — If we pin n particles to the surface, there are $\binom{N}{n}$ ways to arrange them on the surface. This also leave $N - n$ particles to roam free in the bulk. The number of ways to arrange *those* particles is $\binom{M}{N-n}$, so we have

$$\Omega = \binom{N}{n} \binom{M}{N-n}.$$

The entropy is

$$S = k_B \log \Omega.$$

4b — Here, it is *really hard* to work in the canonical ensemble. We stay in the microcanonical ensemble here. So we have

$$\begin{aligned} E &= -\varepsilon n, & \frac{1}{T} &= \frac{\partial S}{\partial E}. \\ \frac{1}{T} &= -\frac{1}{\varepsilon} \frac{\partial S}{\partial n}. \\ -\beta\varepsilon &= \frac{\partial \log \Omega}{\partial n}. \end{aligned}$$

So after doing all the Stirling expansion:

$$\frac{\partial \log \Omega}{\partial n} = \frac{\partial}{\partial n} (N \log N - n \log n - 2(N - n) \log(N - n) + M \log M - (M - N + n) \log(M - N + n)).$$

$$\begin{aligned} -\beta\varepsilon &= \log \left(\frac{(N - n)^2}{n(M - N + n)} \right). \\ e^{-\beta\varepsilon} &= \frac{(N - n)^2}{n(M - N + n)}. \end{aligned}$$

It's really hard to invert this, I think, I haven't tried. But it's not very interesting if it is invertible.

4c — If $T \rightarrow 0$, then $\beta \rightarrow \infty$ and $e^{-\beta\varepsilon} \rightarrow 0$, so we have

$$\begin{aligned} (N - n)^2 &= 0. \\ \frac{n}{N} &= 1. \end{aligned}$$

4d — Now we send $T \rightarrow \infty$, $\beta \rightarrow 0$, and $e^{-\beta\varepsilon} \rightarrow 1$,

$$\begin{aligned} (N - n)^2 &= n(M - N + n). \\ \frac{n}{N} &= \frac{N}{M + N}. \end{aligned}$$

5a — The magnetic degree of freedom is just in the dipole, the orientation of the particle. The ideal gas partition function only cared about momentum and position, so this is a degree of freedom that isn't coupled at all to the ideal gas degrees of freedom, so I'll abbreviate those:

$$\begin{aligned} Q &= Q_{\text{ideal}} Q_{\text{magnetic}} = Q_I Q_M. \\ Q_I &= \frac{1}{N!} \left(\frac{V}{\Lambda^3} \right)^N. \end{aligned}$$

The magnetic degree of freedom is quantized, and it only has six states:

$$Q_M = e^{\beta Bm} + 1 + 1 + 1 + 1 + e^{-\beta Bm} = e^{\beta Bm} + e^{-\beta Bm} + 4.$$

5b — Since the partition functions are multiplicatively decoupled, then the free energy separates into two additive terms:

$$A = A_I + A_M.$$

$$A = A_I - Nk_B T \log(e^{\beta Bm} + e^{-\beta Bm} + 4).$$

5c — Since the magnetic free energy doesn't depend on the volume, it won't contribute to the pressure:

$$P = - \left. \frac{\partial A}{\partial V} \right|_T = - \left. \frac{\partial A_I}{\partial V} \right|_T = \frac{Nk_B T}{V}.$$

5d — The internal energy also separates:

$$E = - \frac{\partial \log Q}{\partial \beta} = - \frac{\partial \log Q_I}{\partial \beta} - \frac{\partial \log Q_M}{\partial \beta}.$$

$$E = \frac{3}{2} \frac{N}{\beta} - NBm \frac{e^{\beta Bm} - e^{-\beta Bm}}{e^{\beta Bm} + e^{-\beta Bm} + 4}.$$