Problem Set 9: SOLUTIONS

(1) Osmotic Pressure. $PV = Nk_BT$, i.e. $P = nk_BT$. The simplest treatment is, as indicated, to think of the solute as an ideal gas. (A more thorough approach is to worry about the solvent concentration as well, but this isn't necessary if the density of solute is much smaller than the density of solvent. You can verify that this is indeed the case for the situation described.) The concentration $n = 0.15$ M $= 0.15 \times 6.02 \times 10^{23}$ particles per liter $= 0.15 \times 6.02 \times 10^{23} \times 10^3$ particles per m^3. (I remember the conversion from liters to cubic meters by recalling that 1 cm^3 = 1ml.) The corresponding pressure is $P = nk_BT = 0.15 \times 6.02 \times 10^{23} \times 10^3 \times 310 \times 1.38 \times 10^{-23}$, so $\boxed{P = 386000\,Pa = 3.8atm}$.

(2) A 2-state system, revisited. Two states, with energies 0 and ε.
(a) Helmholtz Free Energy $F \equiv U - \tau\sigma$. What is σ? I don't know. Given the energy levels, it's easy to calculate the partition function: $Z = \sum_i \exp\left(-\frac{E_i}{\tau}\right) = \exp\left(-\frac{0}{\tau}\right) + \exp\left(-\frac{\varepsilon}{\tau}\right) = 1 + e^{-\varepsilon/\tau}$.

We've proven that $F = -\tau \ln(Z)$, so $F = -\tau \ln\left(1 + e^{-\varepsilon/\tau}\right)$.

(b) Two equally good solutions -- just to show yet again that there are many possible approaches

(if we are curious about the energy)

(c) As $\varepsilon/\tau \to 0$ (i.e. high temperature) we would expect both states to be populated – so there are two states available, and hence entropy $\sigma \to \ln 2$.

As $\varepsilon/\tau \to \infty$, (i.e. low temperature) we would expect only the low energy state to be populated, and hence entropy $\sigma \to \ln 1 = 0$.

Note that it is **not correct** to state that since there are two states, the entropy is always $\ln 2$.
    Entropy is the logarithm of the number of **accessible** states, and accessibility depends on τ

(d) As $\varepsilon/\tau \to 0$, $\dfrac{\varepsilon}{\tau}\dfrac{1}{\left(\exp(\varepsilon/\tau)+1\right)} \to 0$ and $1+\exp(-\varepsilon/\tau) \to 2$, so $\sigma \to \ln 2$, as expected from (c).

As $\varepsilon/\tau \to \infty$, $\dfrac{\varepsilon}{\tau}\dfrac{1}{\left(\exp(\varepsilon/\tau)+1\right)} \to \dfrac{\infty}{\infty}$, but the denominator goes to infinity faster.

$1+\exp(-\varepsilon/\tau) \to 1$, so $\sigma \to \ln 1 = 0$, as expected from (c).

(3) Relating F and Z.

We showed in class $\quad \dfrac{F}{\tau} = -\ln Z + B \overset{\text{const. of integration}}{}$.

Also: $\quad \sigma = -\left.\dfrac{\partial F}{\partial \tau}\right|_V \quad$ (which follows simply from considering dF)

In general, $\quad \sigma = \ln \Omega$, the number of available states.

As $\tau \to 0$, only the ground state energy levels are occupied. Use this fact to evaluate σ as $\tau \to 0$.

From $\sigma = \ln \Omega$, $\quad \boxed{\sigma_{\tau \to 0} = \ln \Omega_0}$, where Ω_0 is the degeneracy of the ground state energy level.

From $\sigma = -\left.\dfrac{\partial F}{\partial \tau}\right|_V$, $\quad \sigma_{\tau \to 0} = \left[-\dfrac{\partial}{\partial \tau}\left(-\tau \ln Z + B\tau\right)\right]_{\tau \to 0}$

$= \sigma_{\tau \to 0} = \left[\tau \dfrac{\partial}{\partial \tau}\ln Z + \ln Z - B\right]_{\tau \to 0}$

As $\tau \to 0$, $Z \to \Omega_0 e^{-E_0/\tau}$, since only the lowest energy level is occupied. (See the last problem set).

$\Rightarrow \ln Z \to \ln \Omega_0 - E_0/\tau \quad ; \quad \dfrac{\partial}{\partial \tau}\ln Z \Rightarrow E_0/\tau^2$

So $\sigma_{\tau \to 0} = \dfrac{E_0}{\tau} + \ln \Omega_0 - \dfrac{E_0}{\tau} - B = \boxed{\ln \Omega_0 - B = \sigma_{\tau \to 0}}$

Comparing the two boxed equations, we see that

$\underline{B \text{ must be zero}}$.

(4, 7 pts.**) A one-dimensional gas.**

$$E = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \qquad \text{For a single particle}$$

$$n = 1, 2, 3, \ldots$$

$$Z_1 = \sum_i e^{-E_i/\tau}$$

$$= \sum_{n=1}^{\infty} \exp\left(-\frac{\hbar^2 \pi^2}{2mL^2} \frac{n^2}{\tau}\right)$$

"classical limit"

$$\frac{\hbar^2 \pi^2}{2mL^2} \ll \tau$$

$$Z_1 \to \int_0^{\infty} e^{-\frac{\hbar^2 \pi^2}{2mL^2 \tau} n^2} \, dn \qquad , \text{ the same Gaussian}$$

Integral as in PS8

$$\Rightarrow \quad Z_1 = \sqrt{\frac{2m\tau L^2}{\hbar^2 \pi^2}} \frac{\sqrt{\pi}}{2} = \sqrt{\frac{m\tau}{2\pi}} \frac{1}{\hbar} L$$

The energy of a single particle U_1
is in general: $U_1 = \tau^2 \frac{\partial}{\partial \tau} \ln Z_1$

$$= U_1 = \tau^2 \frac{\partial}{\partial \tau} (\ln \tau^{1/2} + \ldots)$$

$$= \frac{1}{2} \tau^2 \frac{1}{\tau} \qquad = U_1 = \frac{\tau}{2}.$$

The energy of N non-interacting particles
is $U = NU_1 \qquad = \boxed{U = \frac{1}{2} N\tau}$

(b) The heat capacity at constant volume $c_V = \left.\frac{\partial U}{\partial \tau}\right|_V = \frac{1}{2}N$.

(5) A one-dimensional polymer.
(a) A 1D random walk. We showed that $\langle x^2 \rangle \propto N$, where N is the number of steps. Here, each link is a step, and the length L is like x. Therefore $\langle L^2 \rangle \propto N$, or $L \propto N^{1/2}$. So $p = 1/2$.

(b) $L \propto N^{1/2}$. Incorporating our step size, $L \propto N^{1/2} \ell$. $\frac{L}{N\ell} \propto \frac{N^{1/2}\ell}{N\ell} = \frac{1}{N^{1/2}}$. For large N, $\sqrt{N} \gg 1$, so $L \ll N\ell$.

(c) The polymer (or random walk) looks just like the binary spins with the following mapping:

polymer	↔	binary spins
number of links N		number of spins N
$N_{right} - N_{right} = L/\ell$		spin excess $s = N_{up} - N_{down}$

(think about this: $L = N_{right}\ell - N_{left}\ell$)		

For the binary spins, the entropy $\sigma = N \ln 2 - s^2/2N$ (for large N). So the polymer entropy is $\sigma = N \ln 2 - L^2/2\ell^2 N$.

(d) The thermodynamic identity $đQ = dU + đW$, where $đW$ is the work done **by** the system. If the force is defined to be positive when the polymer is pulling inwards, $đW = -fdL$, so increasing length is positive work. Therefore $\tau \, d\sigma = dU - fdL$.

(e) From the above expression, $f = \dfrac{\partial U}{\partial L} - \tau \dfrac{\partial \sigma}{\partial L}$. The first term $\dfrac{\partial U}{\partial L} = 0$ -- we haven't introduced **any** length dependence of the internal energy. Therefore the force $f = -\tau \dfrac{\partial \sigma}{\partial L}$. Using our entropy expression, $f = \dfrac{\tau}{\ell^2 N} L$. A linear restoring force!

(f) At fixed L, the force increases linearly with temperature. Therefore, if we increase τ the force increases (i.e. pulls inward – see (d)) and the polymer contracts.

(6.) Diffusion. We showed in class that for a one-dimensional random walk, the mean-squared distance traveled, $\langle x^2 \rangle$, is proportional to the travel time: $\langle x^2 \rangle = 2Dt$. In two dimensions, if the walk is random, its components in the x- and y-directions are random and unrelated. (If they weren't, it wouldn't be a random walk!) Therefore $\langle y^2 \rangle = 2Dt$ also. The mean-squared distance from the origin is $\langle r^2 \rangle = \sqrt{\langle x^2 \rangle + \langle y^2 \rangle} = 4Dt$.

(7) Hypersphere volumes.

See the following pages.