11. The Gibbs Free Energy:
There is another “free energy,” which I did not discuss in class. The Gibbs free energy and is defined as $G \equiv E - TS + PV = G(T,P,N)$ and has T,P,N as its natural variables.
Note: For a system in contact with both a thermal reservoir and a pressure reservoir (i.e., one kept at constant T and P) the Gibbs free energy tends to a minimum.
(a) (2 points) Starting from the basic properties of the entropy, S(E,V,N), $dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$, show that $dG = -SdT + VdP + \mu dN$.

(a) Calculate: $dG = dE - TdS - SdT + PdV + VdP$; but, $dE - TdS + PdV = \mu dN$ (from the microcanonical relation above)
Substitute: $dG = (dE - TdS + PdV) - SdT + VdP = -SdT + VdP + \mu dN$. QED

(b) (2 points) Using the Euler relation and the Gibbs-Duhem relation (Lect. 14.2), show that $G(T,P,N) = N\mu(T,P)$.

(b) The Euler relation (Lect. 14.2) tells us $TS = E + PV - \mu N$, so $G = E - TS + PV = N\mu$. It remains only to show that μ may be regarded as a function of T and P (only). This follows from extensivity. As an intensive variable, μ can only depend on (i) other intensive variables and (ii) intensive ratios of extensive variables. But, in the “Gibbs” representation, the only extensive variable is N, so no intensive ratios can be constructed. All this is encapsulated in the Gibbs-Duhem relation (Lect. 14.2), which states $VdP = SdT + Nd\mu$, i.e., $d\mu = \frac{V}{N}dP - \frac{S}{N}dT$, showing that μ depends only on P and T.

(c) (2 points) Now, suppose that there are several types of particles in the system, $N_1, N_2, \ldots$. Show that these results generalize to
$dG(T,P,\{N_k\}) = -SdT + VdP + \sum_k \mu_k dN_k$ and $G(T,P,\{N_k\}) = \sum_k N_k \mu_k(T,P,\{N_k\})$.
Note that the chemical potential μ_k for the kth type of particle can now depend on the numbers $\{N_k\}$ (in addition to T and P) but only on ratios like N_1/N_2, etc., since chemical potential is intensive.

(c) The definition of G remain $G \equiv E - TS + PV$, so
$dG = dE - TdS - SdT + PdV + VdP$, as above.
Identification of the first derivatives of $S(E,V,\{N_k\})$ give the first law relation,
$dS = \frac{1}{T}dE + \frac{P}{T}dV - \sum_k \frac{\mu_k}{T}dN_k$, so $dE - TdS + PdV = \sum_k \mu_k dN_k$.
Substituting this into the above leads to $dG = -SdT + VdP + \sum_k \mu_k dN_k$. QED

To proceed from here you need the extended Euler and Gibbs-Duhem relations (Lect. 14.2):

Extensivity requires $\lambda S(E,V,\{N_k\}) = S(\lambda E,\lambda V,\{\lambda N_k\})$.

Differentiating wrt to λ and setting λ=1 gives, $S = \frac{\partial S}{\partial E}E + \frac{\partial S}{\partial V}V + \sum_k \frac{\partial S}{\partial N_k}N_k$.

Identifying the derivatives: $S = \frac{1}{T}E + \frac{P}{T}V - \sum_k \frac{\mu_k}{T}N_k$, so $TS = E + PV - \sum_k \mu_k N_k$.

To get the Gibbs-Duhem, take differentials of the Euler relation:

$TdS + SdT = dE + PdV + VdP - \sum_k (N_k d\mu_k + \mu_k dN_k)$ and subtract our the fist law to give $VdP = SdT + \sum_k N_k d\mu_k$, which shows that P is a function of the intensive (field) variables.

Now, the generalized Euler relation gives, $G(T,P,\{N_k\}) = E - TS + PV = \sum_k N_k \mu_k$.

Note that, unlike what happened in part (b) we CANNOT conclude that $\mu_k(T,P)$. Generally, $\mu_k(T,P,\{N_\ell\})$. With only one species of particle, intensivity prevents dependence on N; however, with M>1 species the chemical potentials can depend on M-1 independent (intensive) ratios of the form $\frac{N_i}{N_j}$ (for $i \neq j$).

(d) (4 points) Using class results, find the formula for the Gibbs free energy for the ideal classical monatomic gas and verify that it has the derivatives implied by (a).

(d) This can be done in many different ways. One simple way is to use $G = (E - TS) + PV = F(T,V,N) + Nk_BT$, from the ideal-gas equation of state, and then substitute for F(T,V,N) from Lect. 14.4:

$$F(T,V,N) = -k_BT\ln Z = -Nk_BT\left[\ln\left(\frac{T^{3/2}V}{N}\right) + \frac{3}{2}\ln\left(\frac{mk_B}{2\pi\hbar^2}\right) + 1\right].$$

Thus,

$$G = F + Nk_BT = -Nk_BT\left[\ln\left(\frac{T^{3/2}V}{N}\right) + \frac{3}{2}\ln\left(\frac{mk_B}{2\pi\hbar^2}\right)\right]$$

and then substitute $\frac{V}{N} = \frac{k_BT}{P}$ to express the result in terms of the “natural” variables, T,P,N:

$$G = F + Nk_BT = -Nk_BT\left[\ln\left(\frac{T^{5/2}k_B}{P}\right) + \frac{3}{2}\ln\left(\frac{mk_B}{2\pi\hbar^2}\right)\right]$$

Note that G is linear in N, as expected from part (b).

Thus, we can check derivatives:

$$S \overset{?}{=} -\frac{\partial G}{\partial T} = Nk_B\left[\ln\frac{T^{5/2}k_B}{P} + \frac{3}{2}\ln\left(\frac{mk_B}{2\pi\hbar^2}\right) + \frac{5}{2}\right] = Nk_B\left[\ln\frac{T^{3/2}V}{N} + \frac{3}{2}\ln\left(\frac{mk_B}{2\pi\hbar^2}\right) + \frac{5}{2}\right]$$

$$V \overset{?}{=} \frac{\partial G}{\partial P} = \frac{Nk_BT}{P}$$

$$\mu \overset{?}{=} \frac{\partial G}{\partial N} = \frac{G}{N} = -k_BT\left[\ln\left(\frac{T^{5/2}k_B}{P}\right) + \frac{3}{2}\ln\left(\frac{mk_B}{2\pi\hbar^2}\right)\right] = k_BT\ln\left[\frac{N}{V}\lambda_{th}^3\right],$$

all of which agree with earlier results derived in class.

12. Ligand-Receptor binding for the ideal gas.

Note: I did not grade this problem, since the problem was apparently unclear and no one did the problem I had in mind. Please do look at this problem and its solution.

In class (Lect. 12), I solved for you the problem of ligand-receptor binding in a simplified lattice model. The result (at low densities) was that the probability of binding could be written $P_B = \dfrac{[L]}{\frac{1}{v_0}e^{\beta\Delta\varepsilon} + [L]}$ where $[L] \equiv \dfrac{N_L}{V}$ is the ligand density and v_0 is the volume per cell.

In this problem, I want you to treat the N_L ligand molecules as an ideal monatomic classical gas in which there are two classes of states, those with all ligands moving freely in the volume V and those with only N_L-1 free and one bound to the receptor with a binding energy $\Delta\varepsilon = -\varepsilon_B \quad (\varepsilon_B > 0)$. Show for this situation that

$P_B = \dfrac{[L]}{\frac{1}{\lambda_t^3}e^{\beta\Delta\varepsilon} + [L]}$, where instead of the cell volume v_0 there appears the cube of the "thermal wavelength" defined by $\lambda_t = \left(\dfrac{2\pi\hbar^2}{mk_BT}\right)^{1/2}$ (see Lect. 14.4).

The energies of the two classes of states are:

Free ligands only: $E_n = \sum_{k=1}^{N}\frac{\vec{p}_k^{\,2}}{2m}$; one bound ligand: $E_n = -\varepsilon_B + \sum_{k=1}^{N-1}\frac{\vec{p}_k^{\,2}}{2m}$.

The partition functions for these two classes are:

Free ligands only: $Z_{free} = \dfrac{1}{N!}\displaystyle\int\prod_{k=1}^{N}\left[\frac{\left(d^3r_k\right)\left(d^3p_k\right)}{(2\pi\hbar)^3}e^{-\frac{\vec{p}_k^{\,2}}{2mk_BT}}\right] = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N$

One bound ligand: $Z_{bound} = \dfrac{e^{\frac{\varepsilon_B}{k_BT}}}{(N-1)!}\int \prod_{k=1}^{N-1}\left[\dfrac{\left(d^3r_k\right)\left(d^3p_k\right)}{(2\pi\hbar)^3} e^{-\frac{\vec{p}_k^{\,2}}{2mk_BT}}\right] = \dfrac{Ne^{\frac{\varepsilon_B}{k_BT}}}{N!}\left(\dfrac{V}{\lambda_{th}^3}\right)^{N-1}$

But, $P_B = \dfrac{Z_{bound}}{Z_{free} + Z_{bound}} = \dfrac{Ne^{\frac{\varepsilon_B}{k_BT}}}{\dfrac{V}{\lambda_{th}^3} + Ne^{\frac{\varepsilon_B}{k_BT}}} = \dfrac{[L]}{\dfrac{e^{\beta\Delta\varepsilon}}{\lambda_{th}^3} + [L]}$. QED

13. Maxwell Distribution for an ideal gas in an external potential.
Consider an ideal gas of N particles in a box of volume V whose molecules are subject to a spatially non-uniform potential $U(\vec{r})$. Assume that the whole system is in contact with a thermal reservoir at temperature T, so it can be described by the canonical distribution. Because of the potential, the particles will no longer be distributed uniformly over V.
(a) (4 points) Starting from the full N-particle canonical distribution, show that the probability distribution for observing a particular particle (say, particle "1") in the volume (d^3r) and with momentum in (d^3p) is $P(\vec{r},\vec{p})\left(d^3r\right)\left(d^3p\right)$ with $P(\vec{r},\vec{p}) \sim e^{-\frac{1}{k_BT}\left(\frac{p^2}{2m}+U(\vec{r})\right)}$. What is the normalization factor?
Note: Most people did not get started on this problem. The important distinction is between the probability of the N-particle microstate and the probability of what ONE particle (out of N) is doing. That's important.

(a) The energy of each microstate $\{\vec{r}_k,\vec{p}_k\}_{k=1}^{N}$ is $E_n = \sum_{k=1}^{N}\left(\dfrac{\vec{p}_k^{\,2}}{2m} + U(\vec{r}_k)\right)$.

The probability of observing a microstate with $\vec{r}_k$ in $\left(d^3r_k\right)$ and $\vec{p}_k$ in $\left(d^3p_k\right)$ for k=1,2,…,N is $\dfrac{1}{N!}\prod_{k=1}^{N}\dfrac{\left(d^3r_k\right)\left(d^3p_k\right)}{(2\pi\hbar)^3}P\left(\{\vec{r}_k,\vec{p}_k\}_{k=1}^{N}\right)$ with

$P\left(\{\vec{r}_k,\vec{p}_k\}_{k=1}^{N}\right) = \dfrac{1}{Z}e^{-\frac{E_n}{k_BT}} = \dfrac{1}{Z}\prod_{k=1}^{N} e^{-\frac{1}{k_BT}\left(\frac{\vec{p}_k^{\,2}}{2m}+U(\vec{r}_k)\right)}$, where Z, the "partition function," is the normalization,

$$Z=\frac{1}{N!}\int\prod_{k=1}^{N}\left[\frac{\left(d^3r_k\right)\left(d^3p_k\right)}{(2\pi\hbar)^3}e^{-\frac{1}{k_BT}\left(\frac{\vec{p}_k^2}{2m}+U(\vec{r}_k)\right)}\right]=\frac{1}{N!}\left[\left(\int_V\left(d^3r\right)e^{-\frac{U(\vec{r})}{k_BT}}\right)\left(\int_{-\infty}^{\infty}\frac{\left(d^3p\right)}{(2\pi\hbar)^3}e^{-\frac{\vec{p}^2}{2mk_BT}}\right)\right]^N$$

$$=\frac{1}{N!}\left[\frac{1}{\lambda_{th}^3}\int_V\left(d^3r\right)e^{-\frac{U(\vec{r})}{k_BT}}\right]^N.$$

Comment:
There are a couple of subtle points here.

1. I have chosen to put in the N factors $\frac{1}{(2\pi\hbar)^3}$, so that the factors $\prod_{k=1}^{N}\left[\frac{\left(d^3r_k\right)\left(d^3p_k\right)}{(2\pi\hbar)^3}\right]$ are actually counting the number of quantum-mechanical microstates in each region and the factor $\prod_{k=1}^{N}e^{-\frac{1}{k_BT}\left(\frac{\vec{p}_k^2}{2m}+U(\vec{r}_k)\right)}$ represents the canonical weighting of each state. Since these factors also appear in the normalization Z, they cancel in the overall result.

2. The factors $\frac{1}{N!}$ reflect the particle-permutation symmetry of quantum mechanics. Again, these factors cancel between the numerator and the denominator.

Thus, in this calculation, both these factors are irrelevant, and could be omitted. Nevertheless, they are not unphysical: If you don't put the 1/N! into Z, then the free energy $-k_BT\ln Z$ is not extensive.

At this point, we have a representation for the N-particle probability distribution. To find the distribution for particle "1", we simply integrate out the coordinates r_k, p_k for the other N-1 particles. Thus,

$$P(\vec{r}_1,\vec{p}_1)=\frac{1}{(2\pi\hbar)^3N!}\int\prod_{k=2}^{N}\frac{(d^3r_k)(d^3p_k)}{(2\pi\hbar)^3}P\left(\{\vec{r}_k,\vec{p}_k\}_{k=1}^{N}\right)$$

$$=\frac{1}{(2\pi\hbar)^3N!}\frac{1}{Z}e^{-\frac{1}{k_BT}\left(\frac{\vec{p}_1^2}{2m}+U(\vec{r}_1)\right)}\int\prod_{k=2}^{N}\left[\frac{(d^3r_k)(d^3p_k)}{(2\pi\hbar)^3}e^{-\frac{1}{k_BT}\left(\frac{\vec{p}_k^2}{2m}+U(\vec{r}_k)\right)}\right]$$

$$=\frac{1}{(2\pi\hbar)^3N!}\frac{1}{Z}e^{-\frac{1}{k_BT}\left(\frac{\vec{p}_1^2}{2m}+U(\vec{r}_1)\right)}\left[\frac{1}{\lambda_{th}^3}\int_V(d^3r)e^{-\frac{U(\vec{r})}{kT}}\right]^{N-1}$$

$$=\frac{1}{(2\pi\hbar)^3}\frac{1}{\left[\frac{1}{\lambda_{th}^3}\int_V(d^3r)e^{-\frac{U(\vec{r})}{kT}}\right]}e^{-\frac{1}{k_BT}\left(\frac{\vec{p}_1^2}{2m}+U(\vec{r}_1)\right)}$$

$$\boxed{P(\vec{r}_1,\vec{p}_1)=\frac{1}{(2\pi mk_BT)^{3/2}}\frac{e^{-\frac{1}{k_BT}\left(\frac{\vec{p}_1^2}{2m}+U(\vec{r}_1)\right)}}{\left[\int_V(d^3r)e^{-\frac{U(\vec{r})}{kT}}\right]},}$$

a final result which is evidently normalized.

(b) (4 points) Specialize this result to particles in a box of volume V=AH (H is the height and A is the base area) which sits in a gravitational potential $U(\vec{r})=mgz$ so that z=0 is the bottom of the box and z=H is the top. Show that the density of particles inside the box as a function of the height is

$$n(z)=\frac{N}{V}\cdot\frac{H}{H_0}\cdot\frac{e^{-z/H_0}}{1-e^{-H/H_0}},\quad \text{where } H_0=H_0(T)\equiv\frac{k_BT}{mg} \text{ is called the scale height.}$$

Note: This is called the "gravitational distribution." You can see that the gas is denser at the bottom of the box than at the top. When T is large and/or m is small so H_0 becomes >>H, n(z) approaches the uniform distribution N/V.

Note: People did not do well on this. There are two issues:

(i) If you have the probability distribution for $(\vec{r},\vec{p})$, then to get the probability distribution for $\vec{r}$ alone, you need to integrate out the (irrelevant) $\vec{p}$ variable. that makes the factor involving the thermal wavelength disappear.

(ii) Even if you start with $n(\vec{r})\sim e^{-\beta U(\vec{r})}$, you still need to normalize this distribution so that the total number of particles in the box is N. I don't think anyone got this right, and I still don't understand the difficulty.

(b) To get the probability P(z) such that P(z)dz is the probability that the particle "1" be found between z and z+dz, we need only integrate out the momentum in the result (a). Thus,

$$P(z)=\int_{-\infty}^{\infty}\left(d^3p\right)P(z,\vec{p})=\frac{e^{-\frac{mgz}{k_BT}}}{\left[\int_V\left(d^3r\right)e^{-\frac{mgz}{kT}}\right]}=\frac{e^{-\frac{z}{H_0}}}{A\int_0^H dze^{-\frac{z}{H_0}}}=\frac{e^{-\frac{z}{H_0}}}{AH_0\left(1-e^{-\frac{H}{H_0}}\right)}.$$

Since all N particles have the same distribution, the spatial density n(z) of particles is

$$n(z)=NP(z)=N\cdot\frac{H}{H}\cdot\frac{e^{-\frac{z}{H_0}}}{AH_0\left(1-e^{-\frac{H}{H_0}}\right)}=\frac{N}{V}\cdot\frac{H}{H_0}\cdot\frac{e^{-\frac{z}{H_0}}}{\left(1-e^{-\frac{H}{H_0}}\right)}.$$

Note: The limits of this result for H large or small with respect to H_0 are instructive:
For $H<<H_0$: The bracketed factor in the denominator becomes small and approaches H/H_0, thus canceling the H/H_0 factor in front. Thus, $n(z)\to\frac{N}{V}$. This is the "normal" situation for the air in a room, for example. The gravitational density gradient between the floor and the ceiling is negligible.

For $H>>H_0$: In this case, $e^{-\frac{H}{H_0}}\to 0$, so $n(z)\to\frac{N}{V}\cdot\frac{H}{H_0}\cdot e^{-\frac{z}{H_0}}=\frac{N}{AH_0}e^{-\frac{z}{H_0}}$, and the "atmospheric" density falls off exponentially with height.

(c) (2 points) Calculate the scale height for the atmosphere at 0° C (take m to be the mass of an N_2 molecule).

(c) $H_0=\frac{k_BT}{mg}=\frac{1.38\times10^{-23}(273)}{(2\times14)1.66\times10^{-27}(9.8)}=\boxed{8271\text{ m or about }8.3\text{ km.}}$

This is a reasonable approximation for the earth's atmosphere. There are two important correction. First, the atmosphere contains other gases (principally oxygen). Each molecule has its own mass and, hence, its own scale height. Since oxygen is heavier than nitrogen, its scale height is smaller than what we calculated. Second, we have assumed an atmosphere at constant temperature. In reality, the earth's atmosphere cools significantly as you go up. This also decreases the effective scale height. An approximate figure for the lower atmosphere is said to be (Wikipedia) $H_0\sim 7.6\text{ km}$. However, really to understand things better, you need to consider more carefully, the changing composition of the atmosphere with altitude and the reasons for the non-uniform temperature profile.

14. PKT Problems.

(a) (5 points) PKT Problem 5.5(a) (p. 212)

(a) When liquid water vaporizes at 100 C, heat flow into the water to produce steam. The heat flow is $\Delta Q = T\left(S_{gas} - S_{liquid}\right) = k_B T \ln \frac{W_{gas}}{W_{liquid}}$. Hence,

$$\frac{W_{gas}}{W_{liquid}} = e^{\frac{\Delta Q}{k_B T}} = \exp\left(\frac{2.26\times10^{3}}{1.38\times10^{-23}(373)}\right) = \exp\left(4.39\times10^{23}\right) \boxed{= 10^{1.91\times10^{23}},}$$

where I have used T=373 K and

$$\Delta Q = (1\ g)\cdot\left(\frac{1}{18}\ \frac{mol}{g}\right)\cdot\left(40.66\times10^{3}\ \frac{J}{mol}\right) = 2.26\times10^{3}\ J.$$

At constant T and N, the entropy of a GAS varies as $Nk_B\ln V$ (see Lect. 14.4), so we might guess—as suggested in the problem—that $\frac{W_{gas}}{W_{liquid}} \approx \left(\frac{V_{gas}}{V_{liquid}}\right)^{N}$ (except, of course, that liquid water is not a gas).

In order that this ratio should give the multiplicity ratio in the red box above we would need $\left(\frac{V_{gas}}{V_{liquid}}\right) = \left(10^{1.91\times10^{23}}\right)^{1/N} = \left(10^{1.91\times10^{23}}\right)^{1/3.34\times10^{22}} \boxed{= 5.23\times10^{5}}$, since the number of molecules in 1 cm^3 of water is $N = \frac{N_A}{18} = \frac{6.02\times10^{23}}{18} = 3.34\times10^{22}$.

Is this reasonable?

We can calculate the gas volume occupied by this number of gas molecules using the ideal gas law: $V_{gas} = \frac{NkT}{P} = \frac{3.34\times10^{22}\left(1.38\times10^{-23}\right)373}{1.01\times10^{5}} = 1.70\times10^{-3}\ m^3$, compared to the original liquid volume $V_{water} = 10^{-6}\ m^3$, so actual volume ratio is

$$\frac{V_{gas}}{V_{liquid}} = \frac{1.70\times10^{-3}}{10^{-6}} \boxed{= 1.70\times10^{3}.}$$

The agreement between these figures is not very good, from which I conclude that treating the entropy of liquid water like the entropy of a gas is a poor approximation.

(b) (5 points) PKT Problem 5.7 (p. 213)

5.7 (a) $\text{No. arrangements} = \frac{8!}{4!\cdot4!} = 70$, since it makes no difference how we order the four particles on each side.

5.7 (b) Since each particle's position left or right of the membrane is independently random:

4 blacks to the left: only one configuration of this type, so $P_4 = \frac{1}{70}$.

3 blacks to the left: 16 configurations, since one black (out of four) is not there and one white (out of four) is, so $P_3 = \frac{16}{70} = \frac{8}{35}$.

Note that $P_0 = P_4 = \frac{1}{70}$ and $P_1 = P_3 = \frac{16}{70}$. It follows that

$$P_2 = \frac{70-1-1-16-16}{70} = \frac{36}{70} = \frac{18}{35}.$$

An equal number of blacks and whites on the two sides is the most likely.

5.7 (c)

To get four black particles on the left after one time step, you would need to choose the one white on the left to move right (prob.=1/4) and the one black on the right to move left (prob=1/4), so the overall probability of such an outcome is $\boxed{1/16.}$

Conversely, to end up with 2 blacks on each side, the particle selected on the left can be any black (prob.=3/4) and likewise for the probability of selecting a white on the left, so the overall probability of going to two and two at the next step is $\boxed{9/16.}$

Of course, the remaining outcomes are to stay with the 3+1 arrangement. It is easy to show that the probability of this is 6/16.

The lesson here is that, when you are NOT in an "equilibrium" configuration, you are more likely to go towards equilibrium than away in the next step. That, after all, is why you reach equilibrium.

15. An atom has three possible states which we label $n = 0,1,2$ with corresponding energies $\varepsilon_n = n\Delta$. Consider a set of N (distinguishable) atoms of this type. Such a set of atoms can have a total energy between $E = 0$ (all atoms in the n=0 state) and $E = 2N\Delta$ (all atoms in the n=2 state).

(a) (3 points) To get a feeling for what is going on, suppose N=4 and consider a microcanonical ensemble with a known total energy $E = 4\Delta$. What is the average number of atoms $\langle N_n \rangle$ in each of the three states $n = 0,1,2$?

(a) A table showing the possible values of N_0, N_1, and N_2 is shown below along with the number of distinct configurations of each type:

N_0	N_1	N_2	configs
2	0	2	6
1	2	1	12
0	4	0	1

We read off: $$\boxed{\begin{aligned}\langle N_0\rangle &= \frac{1}{19}(2\cdot 6+1\cdot 12+0\cdot 1)=\frac{24}{19}\\ \langle N_1\rangle &= \frac{1}{10}(0\cdot 6+2\cdot 12+4\cdot 1)=\frac{28}{19}\\ \langle N_2\rangle &= \frac{1}{10}(2\cdot 6+1\cdot 12+0\cdot 1)=\frac{24}{19}\end{aligned}}$$

(b) (4 points) Now, suppose that N>>1. What are the averages $\langle N_n\rangle$, if it is known that $E = N\Delta$? Again, assume a microcanonical ensemble.
Note: Assume that N is divisible by 4 for simplicity.
Hint: Just as in part (a), you will need to figure out the combinatorial expression for the number of different "microstates" with N_1,N_2,N_3 and then use the Stirling formula to simplify for large N.

(b) Note that the possible values of N_0, N_1, and N_2 are of the form $$\begin{cases} N_0 = \frac{N}{2} - M \\ N_1 = 2M \\ N_2 = \frac{N}{2} - M \end{cases}$$

with $0 \le M \le N/2$.

The number G of such configurations is $G(M) = \dfrac{N!}{(N_0!)(N_1!)(N_2!)} \equiv e^{F(M)}$, with

$$F(M) = [N\ln N - N] - [N_0 \ln N_0 - N_0] - [N_1 \ln N_1 - N_1] - [N_2 \ln N_2 - N_2] + O(\ln N)$$

$$= N_0 \ln\frac{N}{N_0} + N_1 \ln\frac{N}{N_1} + N_2 \ln\frac{N}{N_2}$$

$$= -N\left[\left(\frac{1}{2}-\frac{M}{N}\right)\ln\left(\frac{1}{2}-\frac{M}{N}\right) + \left(\frac{2M}{N}\right)\ln\left(\frac{2M}{N}\right) + \left(\frac{1}{2}-\frac{M}{N}\right)\ln\left(\frac{1}{2}-\frac{M}{N}\right)\right]$$

We look for the maximum at $\dfrac{dF}{dM} = \ln\left(\dfrac{1}{2}-\dfrac{M}{N}\right) - 2\ln\left(\dfrac{2M}{N}\right) + \ln\left(\dfrac{1}{2}-\dfrac{M}{N}\right)$=0,

i.e., (with $m \equiv M/N$) $\left(\dfrac{1}{2}-m\right)^2 = (2m)^2$, so $m = -\dfrac{1}{2}$, $m = \dfrac{1}{6}$.

The negative root is spurious and we conclude: $$\begin{aligned}\langle N_0\rangle = \langle N_2\rangle &= N\left(\frac{1}{2}-m\right) = \frac{N}{3}\\ \langle N_1\rangle = 2M &= 2\left(\frac{N}{6}\right) = \frac{N}{3}\end{aligned}$$

(note that this is different from the N=4 result)

Note that $\left.\dfrac{d^2F}{dM^2}\right|_{\max} = -\dfrac{2}{N}\left[\dfrac{1}{\left(\frac{1}{2}-m\right)} + \dfrac{1}{m}\right] = -\dfrac{18}{N}$, which is negative in the allowed range of m (showing that this is, indeed, a maximum) and of order 1/N (showing that M deviates from its average only at order $\sqrt{N}$).

(c) (3 points) Redo part (b) using the “equivalent” canonical ensemble.
Hint: This is much simpler than (b).
Note: As long as N is large, the two ensembles are equivalent, so you will get the same answer as in (b) provided, of course, that you choose the right temperature to match the microcanonical energy.

(c) Using the canonical ensemble, we calculate $\begin{cases} \langle N_0 \rangle = \dfrac{N}{1+e^{-\beta\Delta}+e^{-2\beta\Delta}} \\ \langle N_1 \rangle = \dfrac{Ne^{-\beta\Delta}}{1+e^{-\beta\Delta}+e^{-2\beta\Delta}} \\ \langle N_2 \rangle = \dfrac{Ne^{-2\beta\Delta}}{1+e^{-\beta\Delta}+e^{-2\beta\Delta}} \end{cases}$, with a value of β to b chosen such that $E = \langle H \rangle_{can}^{\beta}$, i.e.,

$$E = N\Delta = 0 \cdot \langle N_0 \rangle + \Delta \cdot \langle N_1 \rangle + 2\Delta \cdot \langle N_2 \rangle = \frac{N\Delta\left(e^{-\beta\Delta}+2e^{-2\beta\Delta}\right)}{1+e^{-\beta\Delta}+e^{-2\beta\Delta}}.$$

Equating the two parts of this expression gives $1 = \dfrac{\left(e^{-\beta\Delta}+2e^{-2\beta\Delta}\right)}{1+e^{-\beta\Delta}+e^{-2\beta\Delta}}$ or $e^{-\beta\Delta}=1$, and the previous results reemerge.

Comment: $e^{-\beta\Delta}=1$ means that $\beta = 0,\text{i.e.}, T = \pm\infty$. This may seem peculiar; however, for the n-state system and others for which the energy spectrum is bounded above it is possible to access negative temperature at high energy by passing through $T = \pm\infty$.