

Physics 352 – Part 2 – Statistical Mechanics

FINAL EXAMINATION

Format: Closed book. No calculators.

Total Time: 2 hours.

Write clearly!

RELATIONS:

- Binomial Distribution Formula: the number of combinations of k “up” spins out of N

$$\text{spins is } \binom{N}{k} = \frac{N!}{k!(N-k)!}$$

- Stirling’s approximation for factorials: $\ln(N!) \approx N \ln(N) - N$.

- Geometric series: $\sum_{m=0}^{\infty} r^m = \frac{1}{1-r}$

- Pressure is defined by $\frac{P}{\tau} = \left. \frac{\partial \sigma}{\partial V} \right|_{E,N}$.

$$\text{Another relation: } P = - \left. \frac{\partial U}{\partial V} \right|_{\sigma}$$

- $F = -\tau \ln(Z)$

- Energy of a Monatomic Ideal Gas:

$$U = \frac{3}{2} N \tau$$

- Entropy of a Monatomic Ideal Gas:

$$\sigma = N \left(\frac{5}{2} + \ln \left(\frac{n_Q V}{N} \right) \right)$$

- The quantum concentration for a particle of

$$\text{mass } m : n_Q = \left(\frac{m \tau}{2 \pi \hbar^2} \right)^{3/2}$$

- Specific heat capacity at constant volume:

$$c_V \equiv \left. \frac{dQ}{d\tau} \right|_V$$

- Specific heat capacity at constant pressure:

$$c_P \equiv \left. \frac{dQ}{d\tau} \right|_P$$

(1, 3 pts.) **Protons and Neutrons.** Protons (p) and neutrons (n) can convert into each other due to the “weak nuclear interaction,” and readily did so when the universe was small and hot and the particles were in thermal equilibrium with one another. The process is described by chemical equations like: $n + \nu \leftrightarrow p + e^-$, where ν is a neutrino and e^- is an electron. We can think of this as a two-state system, with the “proton state” on the right side of the equation and the “neutron state” on the left. The energy associated with a proton is $m_p c^2$, where m_p is the proton mass and c is the speed of light; similarly, the energy of a neutron is $m_n c^2$. We’ll ignore neutrinos and electrons and other subtleties (not a great idea in “real life,” but it doesn’t change the answer to this problem). Given that neutrons are more massive than protons (i.e. $m_n > m_p$), which would you expect to be more abundant in the universe, protons or neutrons?

$$E_{\text{proton}} = m_p c^2 \quad E_{\text{neutron}} = m_n c^2$$

$$\text{probability } P_i = \frac{1}{Z} e^{-E_i/c} \quad (\text{Boltzmann})$$

$$\rightarrow \frac{P_p}{P_n} = \frac{e^{-m_p c^2}}{e^{-m_n c^2}} = e^{(m_n - m_p) c^2}$$

$m_n - m_p > 0$, so $\frac{P_p}{P_n} > 1$, so we'd expect

protons to be more abundant.

(True, in fact, though another contribution is that neutrons decay.)

(2, 6 pts.) **Magnets.** Consider a collection of spins with “ferromagnetic” interactions, meaning that any pair of spins has a lower energy if the spins are parallel than if they are anti-parallel.

(a, 4 pts.) Suppose at room temperature the collection is non-magnetic, meaning that on average, the spins are randomly oriented. Mr. K. is confused: shouldn't the system lower its energy by making the spins align? What do you say to Mr. K.? If Mr. K wants the spins to align, should he change the temperature? (You do not need to calculate anything; write a few sentences.)

Systems adopt the configuration of lowest free energy ($F \equiv U - T\sigma$), not lowest energy (U).

The spins have a greater entropy in the disordered state — at high T , this configuration provides the lowest F . At low T , the U term is relatively more important, and the system may adopt the ordered (low U , low σ) state.

[2 continued]

(b, 2 pts.) "I see," says Mr. K. "I know that if I apply a magnetic field, I can do work on the system. How can I calculate how much work I would need to do to get from the randomly aligned state to one in which all the spins are aligned?" Answer this. (You needn't do any calculations or prove any relations – just explain what Mr. K. should calculate.)

Work done = change in free energy.
So Mr. K. should calculate U & σ for the ordered & disordered states and thereby calculate $F = U - T\sigma$; the difference in F tells him the work he'll have to do.

(3, 5 pts.) **More Magnets.** We continue with the setup of #2. For a collection of N "binary spins" the entropy $\sigma = N \ln 2 - \frac{s^2}{2N}$, where s is the difference between the number of "up" and "down" spins. The energy $E = s\varepsilon$, where ε describes the energy associated with a single spin – it's proportional, for example, to the strength of any applied magnetic field. For a ferromagnet, ε is proportional to s itself! The spins create a field that aligns other spins. Therefore, we can write $\varepsilon = -C\langle s \rangle$, where C is some constant, and $\langle s \rangle$ is the mean value of s . Consider fixed temperature τ and large N , so that we can simply write $s = \langle s \rangle$ and $E = U$ for any spin value or energy we're considering (i.e. fluctuations from the mean are negligible).

(a, 2 pts.) Write an expression for the Helmholtz Free energy, F , as a function of s and various constants.

$$\sigma = N \ln 2 - \frac{s^2}{2N}$$

$$E = s\varepsilon = -C\langle s \rangle s = -Cs^2 = U$$

$$\Rightarrow F = U - T\sigma = -Cs^2 - T N \ln 2 + T \frac{s^2}{2N}$$

$$\Rightarrow F(s) = -T N \ln 2 + \left(\frac{T}{2N} - C \right) s^2$$

(b, 3 pts.) **Show that** at high temperatures we should expect to find $s=0$, and at low temperatures we should expect to find nonzero s . **Find** the "critical temperature" that separates these regimes.

If $\left(\frac{\tau}{2N} - c\right) > 0$, then $F(s)$ is minimal at $s=0$. I.e. If $\tau > 2cN$, we expect to find $s=0$.

If $\left(\frac{\tau}{2N} - c\right) < 0$, then $F(s)$ is minimal when s is large (i.e. $s=N$). So if $\tau < 2cN$, we expect $s \neq 0$.

The critical temperature $\tau_c = 2cN$.
This is the essence of magnetic phase transitions!

(4, 5 pts.) **Mean Energy.** Derive, from the Boltzmann Distribution and the definition of the partition function (Z), the following relation:

$$U = -\frac{1}{Z} \left(\frac{\partial}{\partial \beta} Z \right), \text{ where } U \text{ is the mean energy and } \beta = 1/\tau.$$

Show also that the above relation can be written as

$$U = \tau^2 \left(\frac{\partial}{\partial \tau} (\ln Z) \right), \text{ where } \tau \text{ is the temperature.}$$

[You **are** allowed to use these results in later problems even if you are not able to derive them here.]

$$u = \langle \epsilon \rangle = \sum_i \epsilon_i p_i = \frac{1}{Z} \sum_i \epsilon_i e^{-\epsilon_i/\tau} = \frac{1}{Z} \sum_i \epsilon_i e^{-\beta \epsilon_i}$$

$$Z = \sum_i e^{-\beta \epsilon_i}, \text{ so } \frac{\partial}{\partial \beta} Z = - \sum_i \epsilon_i e^{-\beta \epsilon_i},$$

$$\text{so } u = - \frac{1}{Z} \left(\frac{\partial}{\partial \beta} Z \right)$$

$$\beta = 1/\tau, \text{ so } \frac{\partial \beta}{\partial \tau} = -\frac{1}{\tau^2}, \text{ so } \frac{\partial}{\partial \beta} = -\tau^2 \frac{\partial}{\partial \tau}$$

$$\rightarrow u = \tau^2 \frac{1}{Z} \frac{\partial}{\partial \tau} Z. \quad \frac{\partial}{\partial \tau} \ln Z = \frac{1}{Z} \frac{\partial}{\partial \tau} Z,$$

$$\text{so } u = \tau^2 \frac{\partial}{\partial \tau} \ln Z$$

(5, 14 pts.) **An ideal diatomic gas.** In class and in the homework, we've examined ideal gases. A single particle of mass m in a three-dimensional cube of volume V has energy levels that depend on three positive integer "quantum numbers," i.e. $E = E_{PB}(n_1, n_2, n_3)$. I'm using the subscript "PB" for "particle in a box." These energy levels describe, for example, the energy of a monatomic molecule – something with no additional "degrees of freedom." You've shown that the partition function $Z_{PB} = n_Q V$. (You do not need to derive this here.)

(a, 1 pt.) What assumptions or approximations did we make in our derivation of the energy of an ideal gas? (A few words are sufficient.) You may make these same assumptions in this problem, except as noted.

We assumed high temperatures, so $\tau \gg$ level spacings, low density ($n \ll n_Q$), equivalent to high temperatures, non-degeneracy (meaning that the number of available states is large and we needn't worry about "quantum effects"), and non-interacting particles. (Any two of these were sufficient for full points on this problem.)

Suppose a molecule **does** have additional degrees of freedom, for example internal rotational and vibrational states, so that its energy is given by $E = E_{PB}(n_1, n_2, n_3) + E_{int}(m_1, m_2)$. The first term is the same as above. The second, internal energy term can depend on other "quantum numbers," for example integers m_1 and m_2 . The internal energy is **independent** of the n_1, n_2, n_3 and also **does not depend** on V .

(b, 2 pts.) Show that the partition function can be written $Z = Z_{PB} Z_{int}$, where Z_{int} is the partition function corresponding solely to the internal energy.

$$\begin{aligned}
 Z &= \sum_i e^{-E_i/\tau} = \sum_{n_1, n_2, n_3} \sum_{m_1, m_2} e^{-[E_{PB}(n_1, n_2, n_3) + E_{int}(m_1, m_2)]/\tau} \\
 &= \sum_{n_1, n_2, n_3} \sum_{m_1, m_2} e^{-E_{PB}(n_1, n_2, n_3)/\tau} e^{-E_{int}(m_1, m_2)/\tau} \\
 &= \left(\sum_{n_1, n_2, n_3} e^{-E_{PB}(n_1, n_2, n_3)/\tau} \right) \left(\sum_{m_1, m_2} e^{-E_{int}(m_1, m_2)/\tau} \right)
 \end{aligned}$$

Since the "n" terms are constant with respect to the "m" sum & vice versa

$$\underline{Z = Z_{PB} Z_{int}}$$

(c, 1 pt.) Using the relations of part (b) and Problem 4, show that the mean energy of one particle, U_1 , can be written as $U_1 = U_{1,PB} + U_{1,int}$ -- i.e. separable terms corresponding to the particle-in-a-box and internal energies. You **do not** need to derive what $U_{1,PB}$ or $U_{1,int}$ are.

$$\begin{aligned}
 U_1 &= \tau^2 \frac{\partial (\ln Z)}{\partial \tau} \text{ from \#4,} \\
 \text{so } U_1 &= \tau^2 \frac{\partial}{\partial \tau} \ln(Z_{PB} Z_{int}) = \tau^2 \frac{\partial}{\partial \tau} [\ln Z_{PB} + \ln Z_{int}] \\
 &= \tau^2 \frac{\partial}{\partial \tau} \ln Z_{PB} + \tau^2 \frac{\partial}{\partial \tau} \ln Z_{int} \\
 &= U_{PB} + U_{int}
 \end{aligned}$$

For a diatomic molecule, (e.g. “dumbbells” like nitrogen, N_2), there are **two** internal degrees of freedom, corresponding to vibration along the dumbbell axis and rotation perpendicular to the axis.

(d, 1 pt.) Using the Equipartition Theorem: What is the energy, U , of the gas of N **diatomic molecules** as a function of the number of particles, N , and the temperature, τ ? Note that you can answer this without answering parts (b) or (c), though part (c) might help you.

[See Phys. 353 Problem Set 1 & Solutions]

(e, 3 pts.) Show that the **equation of state** ($PV = \dots$) for the ideal diatomic gas is the **same** as for the monatomic gas. *Note:* You do not actually have to derive what the equations of state *are*, you just have to show that they are the *same*. (They are, by the way, $PV = N\tau$; you may use this in part (f).) *Hint:* First derive a relation between P and a derivative of the Helmholtz free energy F . Then use $F = -\tau \ln Z$, and the result of part (b).

$F \equiv U - \tau\sigma$, so $dF = dU - \tau d\sigma - \sigma d\tau$. Thermodynamic identity: $\tau d\sigma = dU + PdV$, so $dF = -PdV - \sigma d\tau$, from which $P = -\left. \frac{\partial F}{\partial V} \right|_{\tau}$. Using $F = -\tau \ln(Z)$, we find

$P = \tau \left. \frac{\partial \ln Z}{\partial V} \right|_{\tau}$. From part (b), $Z = Z_{PB} Z_{int}$, so $\ln Z = \ln Z_{PB} + \ln Z_{int}$. The internal

partition function does not depend on V , so

$P = \tau \left. \frac{\partial \ln Z}{\partial V} \right|_{\tau} = \tau \left. \frac{\partial (\ln Z_{PB} + \ln Z_{int})}{\partial V} \right|_{\tau} = \tau \left. \frac{\partial (\ln Z_{PB})}{\partial V} \right|_{\tau}$, which is the same as it would be

for the monatomic case - i.e. with no internal degrees of freedom.

(f, 6 pts.) Defining γ as c_p/c_v , the ratio of the specific heat capacities at constant pressure and constant volume, calculate γ for the ideal diatomic gas. The work done by a change in volume dV is PdV , just as for a monatomic gas (as it must be, since this is just the mechanical work associated with a weight on a piston, for example). Note that definitions of heat capacities are provided on page 1.

Note: If (and only if) you were unable to derive the energy of the diatomic ideal gas, determine γ for a monatomic ideal gas (3 pts.).

[See Phys. 353 Problem Set 1 & Solutions]

(6, 12 pts.) **Grabbing polymers.** Consider a 5-bead polymer chain on a 2D **hexagonal** grid. See the figures, below, which show two possible microstates of the system. Each bead has to sit at a grid vertex, and two beads can't occupy the same site¹. Unlike the system seen earlier in a homework assignment, there is **no** energy (E) difference between the various configurations. **Two beads are glued to particular grid sites**, indicated by “Xs” in the figure; they cannot move.



Mr. K decides to build a “**grabber**.” It consists of an optical trap at the position indicated by the **triangle** in the figures. A free bead, not in the optical trap, has energy 0. A bead at the optical trap site has energy $-\varepsilon$ (negative ε), where $\varepsilon > 0$. Let's call the state of the polymer in which any bead is trapped “grabbed.”

A Suggestion: **Draw** all the microstates of the system – you may find the attached “hexagonal graph paper” useful.

Note: Flipping the drawing left-right **does** create a distinct state, and so should be counted separately. This is because the pinned beads can't move in any way, and no rotations out of the plane are allowed.

[I'll write all the parts of the problem here; indicate clearly which part you're working on in your answer.]

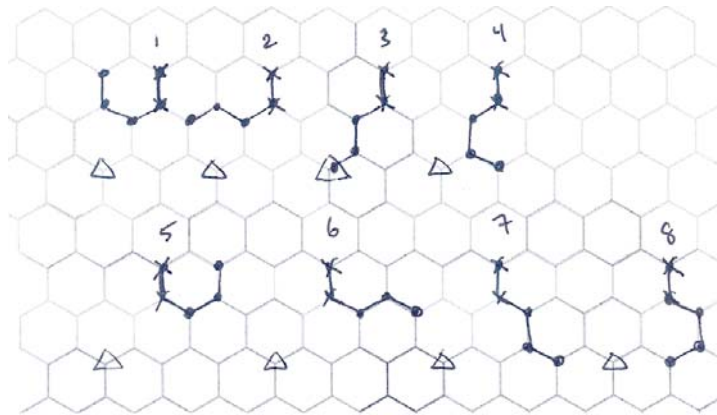
- (a, 2 pts.) Mr. K. thinks, “Clearly, the polymer lowers its energy by being grabbed, so for any positive value of ε , my grabber should effectively hold a polymer.” He finds, however, that the grabber is not very effective – much of the time, the polymer is not trapped. Without doing any calculations, explain what's missing from Mr. K's thinking.
- (b, 2 pts.) What would you expect the **entropy** to be as $\tau \rightarrow 0$? As $\tau \rightarrow \infty$?
- (c, 4 pts.) At temperature, τ , what is the probability of finding the polymer “grabbed”? (*Hint:* One approach is to consider the property “ G ,” for “grabbed,” being 1 for a grabbed state and 0 for an un-grabbed state; calculate $\langle G \rangle$.)
- (d, 2 pts.) How large would ε/τ have to be for a polymer to be “grabbed” at least half the time?
- (e, 2 pts.) If you were to pick a spot to place the trap in order to **maximize** the likelihood of grabbing a polymer **by its end**, where would you put it? Explain.

a

Mr. K is neglecting entropy. There are many more ungrabbed configurations than grabbed ones. Especially at high temperature ($\tau \gg \varepsilon$), entropy dominates the free energy of the system.

¹ If you're worried by a lack of “realism” here, imagine monomer-monomer bonds that prefer 120° angles, equivalent to the hexagonal lattice shown.

b Let's draw all the states:



c The only grabbed state is sketched above.

Its probability $P_g = \frac{1}{Z} e^{-\epsilon/\tau} = \frac{1}{Z} e^{\epsilon/\tau}$.

$$Z = \sum_i e^{-\epsilon_i/\tau} = 7 + e^{\epsilon/\tau}$$

$$\rightarrow P_g = \frac{e^{\epsilon/\tau}}{7 + e^{\epsilon/\tau}} = \frac{1}{7e^{-\epsilon/\tau} + 1} = P_g$$

or: $\langle G \rangle = \sum_i G_i P_i = \frac{1}{Z} [7 \cdot 0 \cdot e^{-0/\tau} + 1 \cdot e^{\epsilon/\tau}]$
 $= \frac{e^{\epsilon/\tau}}{Z}$ as above,

so $\langle G \rangle = \frac{e^{\epsilon/\tau}}{7 + e^{\epsilon/\tau}} = \frac{1}{7e^{-\epsilon/\tau} + 1} = P_g$

d $P_g = \frac{1}{2} \rightarrow \frac{1}{7e^{-\epsilon/\tau} + 1} = \frac{1}{2} \rightarrow 2 = 7e^{-\epsilon/\tau} + 1$

$\rightarrow 7e^{-\epsilon/\tau} = 1 \rightarrow -\frac{\epsilon}{\tau} = \ln \frac{1}{7} \rightarrow \boxed{\frac{\epsilon}{\tau} \geq \ln 7}$

e

Place trap @ circle:



Since two states end there:



Reduces # of "ungrabable" states & hence the entropic cost of grabbing.

