

4.11: Ensemble Problems I

4.5 Classical monatomic ideal gas in the canonical ensemble

In section 5.1 we will show that the canonical partition function of a classical monatomic ideal gas is

$$Z(T, V, N) = \frac{1}{N!} \left[\frac{V}{\lambda^3(T)} \right]^N, \quad (4.11.1)$$

where

$$\lambda(T) \equiv \frac{h_0}{\sqrt{2\pi m k_B T}}. \quad (4.11.2)$$

a. Show that in the thermodynamic limit, the Helmholtz free energy per particle is

$$\frac{F(T, V, N)}{N} = -k_B T \left[\ln \left(\frac{V/N}{\lambda^3(T)} \right) + 1 \right]. \quad (4.11.3)$$

b. Differentiate with respect to T to find $S(T, V, N)$.

c. Change variables to $S(E, V, N)$ using $E = \frac{3}{2} N k_B T$, and compare the resulting expression to the entropy derived in class through the microcanonical ensemble.

4.6 Number fluctuations in the grand canonical ensemble

Calculate ΔN , the root mean square fluctuations in the particle number, for a system in the grand canonical ensemble. (Clue: Take derivatives with respect to μ .) Show that this result is related to the isothermal compressibility κ_T through

$$\frac{\Delta N}{N} = \sqrt{\frac{k_B T \kappa_T}{V}}. \quad (4.11.4)$$

(Clue: Use the results of problem 3.33.)

4.7 Classical monatomic ideal gas in the grand canonical ensemble

a. Use the fact that

$$Z(T, V, N) = \frac{1}{N!} \left[\frac{V}{\lambda^3(T)} \right]^N, \quad (4.11.5)$$

to find $\Xi(T, V, \mu)$ for the classical monatomic ideal gas.

b. Use the connection to thermodynamics for the grand canonical ensemble, namely

$$p(T, \mu)V = k_B T \ln \Xi(T, V, \mu), \quad (4.11.6)$$

to show that for any substance

$$N(T, V, \mu) = k_B T \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{T, V}. \quad (4.11.7)$$

c. Derive the ideal gas equation of state in the grand canonical ensemble.

4.8 Isobaric ensemble

This problem encourages you to think about an ensemble with a specified temperature, pressure, and particle number. A physical model to keep in mind is a collection of systems each with the same number of particles and all connected to the same heat bath but enclosed in balloons rather than in rigid boxes. I want you to guess the answers to the following questions rather than produce mathematical or verbal arguments. If you are uncomfortable making guesses in a physics problem assignment then do only the first two parts.

a. Given that T , p , and N are fixed, what quantities fluctuate?

- b. In going from the canonical to the isobaric ensemble, what control parameter (comparable to $\beta = 1/k_B T$ or $\alpha = -\mu/k_B T$) must be introduced, and how is it related to the pressure?
- c. What is the (unnormalized) probability of finding the system in microstate x with energy $H(x)$ and volume $V(x)$?
- d. What is the relevant state sum (comparable to Z or Ξ), and how is it related to the thermodynamic master function $G(T, p, N)$?
- e. The relevant fluctuation-susceptibility relation connects the fluctuations in volume to what susceptibility?
- f. Write out the fluctuation-susceptibility relation, using B to represent a product of several unguessable intensive quantities but writing out the extensive quantities explicitly.
- g. What are the dimensions of B ? Can you use this knowledge to guess at the unguessable?

4.9 Fluctuation-susceptibility relation for a magnetic system

In the Ising model for a magnet, the spins are located at fixed sites (labeled by i), and can point either up or down ($s_i = \pm 1$). The Ising Hamiltonian is

$$\mathcal{H} = \mathcal{H}_0(s_1, \dots, s_N) - mH \sum_{i=1}^N s_i, \quad (4.11.8)$$

where m is the magnetic moment of each spin, H is the applied magnetic field, and \mathcal{H}_0 represents some spin-spin interaction energy, the details of which are not important here except for the fact that it is independent of H . The microscopic magnetization, which varies from configuration to configuration, is

$$\mathcal{M}(s_1, \dots, s_N) = m \sum_i s_i \quad (4.11.9)$$

while the macroscopic (or thermodynamic) magnetization is the canonical average over all such microscopic magnetizations:

$$M(T, H) = \langle \mathcal{M} \rangle. \quad (4.11.10)$$

The magnetic susceptibility—easily measured experimentally—is

$$\chi_T(T, H) = \frac{\partial M}{\partial H}_T. \quad (4.11.11)$$

Show that in the canonical ensemble the fluctuations in magnetization are related to the susceptibility by

$$\Delta M = \sqrt{k_B T \chi_T}. \quad (4.11.12)$$

4.10 Two definitions of magnetization

The previous problem gave a statistical mechanical definition of magnetization:

$$M(T, H) = \langle \mathcal{M} \rangle, \quad (4.11.13)$$

while equation (3.100) gave a thermodynamic definition:

$$M(S, H) = -\left(\frac{\partial E}{\partial H}\right)_S. \quad (4.11.14)$$

Show that these two definitions give equivalent results.

4.11 Values for the approach to the thermodynamic limit

In problem 2.13, “The approach to the thermodynamic limit,” you were given a value of $EV^{2/3}/h_0^2$ and told that it was appropriate “for a gas at room temperature and atmospheric pressure.” Justify this value as

$$EV^{2/3}/h_0^2 = \left[\frac{3}{2} (k_B T)^{5/3} / (p^{2/3} h^2) \right] N^{5/3} \quad (4.11.15)$$

4.12 Integrals by parametric differentiation

To find the mean energy or energy dispersion in the canonical ensemble, we introduced the “slick trick” of differentiating with respect to β . This trick, called parametric differentiation, is in fact useful in a number of circumstances. For example, in a graduate electrodynamics class I was once assigned a problem (Jackson, *Classical Electrodynamics*, problem 14.5(b)) for which I needed to evaluate

$$\int_0^{2\pi} \frac{\cos^2 \theta}{(1 + b \sin \theta)^5} d\theta \quad (4.11.16)$$

where b is a constant with $|b| < 1$. My classmates and I tried everything: substitutions, partial fractions, conversion to a contour integral in the complex plane, and, most popular of all, “look it up in reference books”. I puzzled over it for a dozen hours before giving up. When the solutions were handed out, I expected to find many pages devoted to evaluating the integral. Instead I found a two-line argument that began with the known integral (see Dwight 858.546 or Gradshteyn and Ryzhik 3.644.4)

$$\int_0^{2\pi} \frac{\cos^2 \theta}{a + b \sin \theta} d\theta = \frac{2\pi}{a + \sqrt{a^2 - b^2}} \quad (4.11.17)$$

and then took a fourth derivative. What was the argument, and what is the value of the integral?

4.13 Parametric differentiation in quantum mechanics

The previous problem showed how parametric differentiation could be useful in electrodynamics. This one shows how it can be useful in quantum mechanics. In quantum mechanics, an infinite square well of width π has energy eigenfunctions

$$\eta_n(x) = \sqrt{\frac{2}{\pi}} \sin(nx) \quad n = 1, 2, 3, \dots \quad (4.11.18)$$

One frequently needs to evaluate matrix elements such as

$$\langle n | x^2 | m \rangle = \frac{2}{\pi} \int_0^\pi \sin(nx) x^2 \sin(mx) dx. \quad (4.11.19)$$

Show how this integral—as well as a host of other useful matrix elements—can be obtained easily from the well known result

$$\int_0^\pi \sin(ax) \sin(bx) dx = \frac{1}{2} \left[\frac{\sin(a-b)\pi}{a-b} - \frac{\sin(a+b)\pi}{a+b} \right] \quad a \neq \pm b. \quad (4.11.20)$$

4.14 Polymers

A primitive model for a polymer is a random walk on a simple cubic lattice. A random walk consists of n steps (or “links”) starting at (“anchored to”) the origin. (In this model a polymer unit can step back onto a lattice site already occupied by a different polymer unit. This unrealistic feature is corrected in a more sophisticated model, the so-called “self avoiding walk.”)

- a. Show that the number of distinct walks consisting of n links is $N_n = 6^n$. Does this formula hold when $n = 0$?

For many purposes it is valuable to consider the ensemble of all random walks, regardless of their size. In this ensemble there is a “size control parameter” α such that the probability of finding a walk x consisting of $n(x)$ links is proportional to $e^{-\alpha n(x)}$. (Thus longer walks are less probable in this ensemble, but there are more of them.) The partition function associated with this model is

$$\Xi(\alpha) = \sum_{\text{walks } x} e^{-\alpha n(x)}. \quad (4.11.21)$$

- b. Show that the mean walk size in this ensemble is a function of α given through

$$\langle n \rangle = - \frac{\partial \ln \Xi(\alpha)}{\partial \alpha}. \quad (4.11.22)$$

- c. Show that

$$\Xi(\alpha) = \frac{1}{1 - 6e^{-\alpha}} \quad \text{and that} \quad \langle n \rangle = \frac{6}{e^{\alpha} - 6}. \quad (4.11.23)$$

Clue: the geometric series sums to

$$1 + x + x^2 + x^3 + \dots = \frac{1}{1 - x} \quad \text{when} \quad |x| < 1. \quad (4.11.24)$$

d. What is the smallest possible value of the control parameter α ? Does large α correspond to long polymers or short polymers?

e. Show that the dispersion in n is given through

$$(\Delta n)^2 = \frac{\partial^2 \ln \Xi}{\partial \alpha^2}, \quad (4.11.25)$$

whence

$$\frac{\Delta n}{\langle n \rangle} = \sqrt{\frac{e^{\alpha}}{6}} = \sqrt{\frac{1}{\langle n \rangle} + 1}. \quad (4.11.26)$$

Thus the relative dispersion decreases for longer polymers.

(See also loops: S. Leibler, R.R.P. Singh, and M.E. Fisher, “Thermodynamic behavior of two-dimensional vesicles,” *Phys. Rev. Lett.* **59** (1987) 1989–1992; C. Richard, A.J. Guttmann, and I. Jensen, “Scaling function and universal amplitude combinations for self-avoiding polygons,” *J. Phys. A* **34** (2001) L495–501.)

4.15 A class of new ensembles

Any mechanical parameter in the Hamiltonian can be “traded in” for a control parameter. This problem details the procedure if the mechanical parameter is intensive and an intrinsically positive quantity. Examples to keep in mind are 1) the particle mass, 2) the spacing between planes of a high temperature superconductor, or 3) the natural frequency of vibration for a diatomic molecule modeled as a simple harmonic oscillator. In honor of this last example I will call the parameter ω . In the “micro- ω ” ensemble, all of the systems in the ensemble have a particular value of the parameter. In the “grand- ω ” ensemble, the systems in the ensemble have a variety of values for the parameter, but larger values are less probable. In fact, the probability is proportional to $e^{-\gamma N \omega}$, where γ is a “control parameter” which can be adjusted to set the mean value of ω to any desired positive value. We suspect that, in the thermodynamic limit, the results of the two ensembles will be identical when the mean value of ω in the grand- ω ensemble is the same as the fixed value of ω in the micro- ω ensemble.

a. The thermodynamic assembly corresponding to the micro- ω ensemble has as master function the Helmholtz free energy $F(T, V, N, \omega)$. Using the definition

$$B(T, V, N, \omega) = -\left(\frac{\partial F}{\partial \omega}\right)_{T, V, N}, \quad (4.11.27)$$

write out the differential equation for dF . b. Execute a Legendre transformation to an assembly with master function

$$K(T, V, N, B) = F + B\omega, \quad (4.11.28)$$

and show that in this assembly, the function (not variable!) ω is

$$\omega(T, V, N, B) = \left(\frac{\partial K}{\partial B}\right)_{T, V, N}. \quad (4.11.29)$$

In the grand- ω ensemble, the probability that a system has a parameter falling within $d\omega$ about ω is

$$\frac{e^{-\gamma N \omega} Z(T, V, N, \omega) d\omega}{\int_0^{\infty} e^{-\gamma N \omega'} Z(T, V, N, \omega') d\omega'}. \quad (4.11.30)$$

Define the partition function

$$Y(T, V, N, \gamma) = \frac{1}{\omega_0} \int_0^{\infty} e^{-\gamma N \omega} Z(T, V, N, \omega) d\omega, \quad (4.11.31)$$

where ω_0 is an arbitrary constant with the dimensions of ω whose only purpose is to make Y dimensionless. Presumably, the relationship between thermodynamics and statistical mechanics in the grand- ω ensemble is

$$K = -k_B T \ln Y, \quad (4.11.32)$$

by analogy to the similar relation in the canonical ensemble. We will assume this relationship and use it, first to find the relationship between the statistical mechanical γ and the thermodynamic B and second to show that the statistical mechanical equation (4.96) is consistent with the thermodynamic equation (4.93).

c. Show that, in the grand- ω ensemble,

$$\langle \omega \rangle = -\frac{1}{N} \frac{\partial \ln Y}{\partial \gamma} \quad (4.11.33)$$

and

$$\Delta \omega^2 = \frac{1}{N^2} \frac{\partial^2 Y}{\partial \gamma^2}. \quad (4.11.34)$$

Note that $\langle \omega \rangle$ and $\Delta \omega$ are functions of T, V, N , and γ .

d. Compare equations (4.94) and (4.98) and conclude that, if (4.97) is to hold, then

$$B = N k_B T' \gamma. \quad (4.11.35)$$

e. Show that

$$\Delta \omega = \sqrt{k_B T \frac{\partial \omega}{\partial B}}_{T,V,N}. \quad (4.11.36)$$

f. We suspect that, in the thermodynamic limit $N, V \rightarrow \infty$, $\ln Y \sim N$. If true, show that $\langle \omega \rangle$ is intensive (independent of N) whereas $\Delta \omega$ falls like $1/\sqrt{N}$.

g. To evaluate $Y(\gamma)$ in the thermodynamic limit, write

$$Y(T, V, N, \gamma) = \frac{1}{\omega_0} \int_0^\infty e^{-\gamma N \omega} Z(T, V, N, \omega) d\omega \approx e^{-\gamma N \langle \omega \rangle} Z(T, V, N, \langle \omega \rangle) \frac{\Delta \omega}{\omega_0}. \quad (4.11.37)$$

Take logarithms to show that

$$\ln Y \approx -\gamma N \langle \omega \rangle + \ln Z + \ln(\Delta \omega / \omega_0), \quad (4.11.38)$$

and argue that in the thermodynamic limit the last term becomes negligible. Finally conclude that

$$K = k_B T \gamma N \langle \omega \rangle + F \quad (4.11.39)$$

or, in light of relationship (4.100),

$$K = F + B \langle \omega \rangle \quad (4.11.40)$$

which should be compared to equation (4.93).

We have shown only that this ensemble scheme is “not inconsistent”. It is not obviously wrong, but of course this does not prove that it is right. A flawless general proof would require detailed mathematical reasoning, but proofs for particular situations are outlined in the next problem and in problem 4.18.

4.16 The grand- ω ensemble for the classical monatomic ideal gas

Apply the concepts of the previous problem to the classical monatomic ideal gas where the mechanical parameter ω is the particle mass. In particular, find expressions

- for $B(T, V, N, m)$,
- for $m(T, V, N, B)$,
- and for $\langle m \rangle$ and Δm as functions of T, V, N , and γ .

4.17 An ensemble of your own

Any mechanical parameter in the Hamiltonian can be traded in for a control parameter. Can you think up a good problem *using* this fact where the parameter is, say, an applied magnetic field? Or the spring constant (or relaxed length) between two atoms in a diatomic molecule (or in the Einstein model)? Or the moment of inertia of a diatomic molecule modeled as a dumbbell? Or a parameter in the Lennard-Jones potential? Or the size of hard-sphere atoms? Or the spacing between atoms in a crystal?

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