Physics 35200 R. Wald
Statistical Mechanics Spring, 2002

Problem Set VII Solutions v1.0

Dear Class: Due to the length of the assignment and shortness of the remainder of the quarter, these solutions will necessarily be rather brief. I hope that nonetheless they will be useful to you. Please feel free to email me or call me if you have any questions.

1) a) Calculate the chemical potential, μ, of a classical, monatomic ideal gas of particles of mass, m, as a function of m, its temperature, T, number of particles, N, and volume V. How is the formula for μ modified if the single particle energy is "offset" from zero by ϵ_0, i.e. if

$$H = \sum_i^N \left\{ \frac{|\vec{p}_i|^2}{2m} + \epsilon_0 \right\}$$

Solution: The first law of thermodynamics tells us that

$$dE = TdS - pdV + \mu dN \quad \Rightarrow \quad \mu = -\left(\frac{\partial S}{\partial N}\right)_{V,E}$$

Since the Sackur-Tetrode equation for the entropy of a classical ideal gas is in terms of E, V, and N, we can just differentiate it to yield

$$\mu_{\text{ideal gas}} = -kT\left[\ln\frac{V}{N} + \frac{3}{2}\ln(2\pi mkT)\right].$$

If we shift the Hamiltonian by ϵ_0, then the phase space volume (and hence the entropy) in the new system at energy E will be the same as the entropy in the classical ideal gas at energy $E - N\epsilon_0$ since all we've done is relabel the points in phase space. Hence

$$\mu(N,T,V) = \mu(N,E,V) = T\frac{\partial S(N,E,V)}{\partial N} = T\frac{\partial S_{\text{ideal gas}}(N,E-N\epsilon_0,V)}{\partial N} =$$

$$\mu_{\text{ideal gas}}(N,E-N\epsilon_0,V) + T\frac{\partial S_{\text{ideal gas}}}{\partial(E-N\epsilon_0)}\frac{\partial(E-N\epsilon_0)}{\partial N} = \mu_{\text{ideal gas}}(N,T,V)+\epsilon_0. \blacksquare$$

b) Suppose a dynamical system contains 3 species of particles, labeled A,B,C. Suppose that the chemical reaction $A + B \rightleftharpoons C$ can occur. Show that a necessary condition for thermal equilibrium of the system is $\mu_A + \mu_B = \mu_C$.

Solution: In thermal equilibrium, all three species are at the same temperature and the entropy is extremized. Hence

$$0 = dS = \frac{\partial S}{\partial N_A}dN_A + \frac{\partial S}{\partial N_B}dN_B + \frac{\partial S}{\partial N_C}dN_C.$$

Imposing the equality of temperature and the number conservation relation $dN_A = dN_B = -dN_C$ yields

$$0 = TdN_A(\mu_A + \mu_B - \mu_C) \quad \Rightarrow \mu_A + \mu_B = \mu_C. \blacksquare$$

c) Suppose each of the particle species A, B, C of part (b) can be treated as a monatomic, ideal gas. (For example, A could represent free electrons, B could represent free protons, and C could represent neutral hydrogen atoms.) Suppose further, that the total energy is $E = E_A + E_B + E_C - \epsilon N_C$. Here, E_A, E_B, and E_C are the usual kinetic energies of the three gases, whereas ϵ is the binding energy of the C-particle (so the energy of the C-particle is "offset" from zero). Assume, for simplicity, that $N_A = N_B$. The system is in thermal equilibrium at temperature T. Calculate the ratio N_A^2/N_C as a function of T, ϵ, and the masses of the particles.

Solution: Unfortunately, this problem is not well-posed in classical mechanics. Since the particles are interacting, we need to write down the interaction Hamiltonian, and the answer will depend on the details of the Hamiltonian. This shows up as a dimensionful answer to this dimensionless problem. These dimensions come from the having dropped the cell size in the expression for entropy (incidentitally, this shows that cell size also appears in the chemical potential, since if it is included in the entropy there is an addtional factor of $kTN \ln v$ which survives the differentiation with respect to N. However, since this offset is the same for all species it can be ignored in classical mechanics). If we know from either experiment or our quantum mechanics classes that the cell size is h, then we could simply set $\mu_A + \mu_B = \mu_C$ and solve for the ratio, yielding

$$\frac{N_A^2}{N_C} = V \left(\frac{m_A m_B kT}{m_C h^2} \right)^{\frac{3}{2}} e^{-\frac{\epsilon}{kT}}. \quad \blacksquare$$

2) Suppose we have a dynamical system in contact with a "heat bath" but now, in addition to being able to exchange energy with the heat bath, suppose the system can "exchange volume" with the bath, i.e. the wall separating the systems is mobile. (Physically, this corresponds to "holding our system at fixed pressure".) Show that the probability that our system is in a given macroscopic state (with respect to a coarse-grained observable $\mathcal{O}$) is proportional to $\exp(-\mathcal{G}/kT)$, with $\mathcal{G} \equiv E - T_0 \mathcal{S}_\mathcal{O} + P_0 V$, where T_0 and P_0 are the temperature and pressure of the heat bath, E and V are the energy and volume of our system, and $\mathcal{S}_\mathcal{O}$ is its observable entropy with respect to $\mathcal{O}$ for the given value of E and V.

Solution: The entropy of the total system is $S_T = S_B + S_\mathcal{O}$. Then

$$S_B(E_T - E_0, V_T - V_0, N) \approx S(E_T, V_T, N) - \frac{\partial S_B}{\partial E_B} E_0 - \frac{\partial S_B}{\partial V_T} V_0 = S_B(E_T, V_T, N) - \frac{E}{T_0} - \frac{P_0 V}{T_0},$$

where we have assumed $E_T >> E_0$, $V_T >> V_0$. Since the probability is proportional to the phase space, i.e., the exponential of entropy, we get

$$p \propto e^{S_T} = e^{S_B(E_T,V_T,N)-\frac{E}{T_0}-\frac{P_0 V}{T_0}+S_{\mathcal{O}}} \propto e^{-\beta\mathcal{G}}$$

as $S_B(E_T, V_T, N)$ is constant. ■

3) A cubic box of side L containing a classical gas of N particles of mass m is placed in a uniform gravitational field of strength (i.e., acceleration) g. (The box is oriented so that the gravitational field is normal to a pair of faces.) The gas is in thermal equilibrium at temperature T.

a) Calculate the number density distribution, $n(\vec{x})$, of the gas.

Solution: The number density will clearly only be a function of z, so

$$n(x, y, z) = \frac{N}{L^2} f(z).$$

If we think of each z=constant plane as an allowed state, the relative occupation (in the microcanonical ensemble) will equal to $e^{-\beta E} = e^{-\beta mgz}$. Now all we need to is normalize, so we get

$$f(z) = e^{-\beta mgz} \left[\int_0^L e^{-\beta mgz} dz\right]^{-1} = \frac{\beta mg e^{-\beta mgz}}{1 - e^{-\beta mgL}}.$$

Thus

$$n(x, y, z) = \frac{N}{L^2} \frac{\beta mg e^{-\beta mgz}}{1 - e^{-\beta mgL}}. \quad ■$$

b) Calculate the heat capacity (at constant volume) of the gas.

Solution: Again, we approach this problem via the microcanonical ensemble, using each z=constant plane as a state. At each level, we have an ideal gas whose zero energy has been shifted by mgz. Thus, the energy contained in that plane is

$$n(z) E_{\text{single particle}}(z) = \frac{N}{L^2} \frac{\beta mg e^{-\beta mgz}}{1 - e^{-\beta mgL}} \left[\frac{3}{2\beta} + mgz\right] L^2 dz.$$

Integrating yields

$$E = \frac{5N}{2\beta} - \frac{mgLN}{e^{\beta mgL} - 1}.$$

Hence,

$$C_V = \frac{\partial E}{\partial T} = kN\left[\frac{5}{2} - \left(\frac{\beta mgL}{2\sinh\left(\frac{\beta mgL}{2}\right)}\right)\right]. \quad ■$$

Note: Most or all, of the class did this problem using the partition function. That is perfectly acceptable; it is simply not the quickest way to the answer.

4) One wishes to measure the mass, m, of a classical body by weighing it. The body is hung on a vertical spring of spring constant K in a uniform gravitational field, g, and the mass of the body is then determined from the formula $m = -Kz/g$, where z denotes the displacement of the spring from its equilibrium position. Suppose K and g are known exactly and that z can be measured with perfect accuracy, so that the only source of error is the buffeting of the mass by air molecules at temperature T. Suppose that only one reading of z is taken. What uncertainty, Δm, should be assigned to the measurement of m?

Solution: The key to this problem is that *any* macroscopic parameter has well-defined expectation value and variance. Hence, the we want to compute $\langle z^2\rangle - \langle z\rangle^2$, which is the standard deviation of actual value of z, i.e., z changes in time due to buffeting and is measured perfectly at a single instant, and we need to know the distribution of those measurements. Since the only degree of freedom we're interested in is z, we may consider the momentum of the particle and any other degrees of freedom as part of the "thermal bath." Choosing choosing the zero of gravitational potential and the coordinate z so that $z = 0$ is zero energy, we find that the Hamiltonian for our "system" is

$$H(z) = mgz + \frac{1}{2}Kz^2.$$

In the microcanonical ensemble, the probability is then

$$P(z) = e^{-\beta(\frac{1}{2}kz^2+mgz)}\left[\int_{\infty}^{\infty} e^{-\beta(\frac{1}{2}kz^2+mgz)}dz\right]^{-1} = \sqrt{\frac{\beta K}{2\pi}}e^{-\frac{\beta g^2m^2}{2K}}e^{-\beta(\frac{1}{2}Kz^2+mgz)}$$

This leads to the expectation values

$$\langle z\rangle = -\frac{mg}{K} \qquad \langle z^2\rangle = \frac{kT}{K} + \left(\frac{mg}{K}\right)^2 \qquad \Delta z = \sqrt{\langle z^2\rangle - \langle z\rangle^2} = \sqrt{\frac{kT}{K}}$$

so that the uncertainty is

$$\Delta M = \frac{K}{g}\Delta z = \frac{\sqrt{kKT}}{g}. \quad \blacksquare$$

5) a) Consider a classical spinning particle with magnetic moment $\vec{\mu} = \mu_0\vec{S}$. A magnetic field $\vec{B}$ is applied, resulting in an interaction energy $E = -\vec{\mu}\cdot\vec{B}$. The particle is now placed in contact with a heat bath at temperature T. Find the probability distribution $p(\theta)d\theta$ for finding the angle between $\vec{S}$ and $\vec{B}$ to be within $d\theta$ of θ. If N such particles are present, what is the expected magnetization?

Solution: The relative probability of being within a certain solid angle $d\Omega$ is $e^{\beta\mu_0 SB\cos\theta}d\Omega$. Normalizing and integrate out the trivial ϕ dependence yields

$$p(\theta)d\theta = \frac{\beta\mu_0 SB}{2}\frac{e^{\beta\mu SB\cos\theta}\sin\theta d\theta}{\sinh(\beta\mu_0 SB)}.$$

The magnetization will $N\langle\vec{\mu}\rangle$. Clearly $\mu_x = \mu_y = 0$. Since $\mu_z = \mu_0 S\cos\theta$, we have

$$M = \mu_0 SN\left[\coth\left(\beta\mu_0 SB\right) - \frac{1}{\beta\mu_0 SB}\right]\hat{z} \quad \blacksquare$$

b) Now consider a quantum mechanical particle of spin s, with $\vec{\mu}_0 = \mu_0\vec{S}$. Then S_z can take any of the $(2s+1)$ values, $-s, -s+1, \ldots, s-1, s$. Again a magnetic field $\vec{B}$ (in the z-direction) is applied and the particle is placed in contact with a heat bath at temperature T. Calculate the probability $p(S_z)$ of each of the allowed values of S_z. If N such (distinguishable) particles are present, what is the expected magnetization? Compare your answers to these questions to the classical case in the limit of large s.

Solution: The density matrix is

$$\hat{\rho} = \frac{e^{-\beta\hat{H}}}{\mathrm{Tr}e^{-\beta\hat{H}}} = \frac{\sum_{S_z=-s}^{s} e^{-\beta\mu_0 B\hbar S_z}\left|S_z\right\rangle\left\langle S_z\right|}{\sum_{S_z=-s}^{S_z=s} e^{-\beta\mu_0 B\hbar S_z}}.$$

So the probability of being in a particular eigenstate is

$$p(S_z) = \frac{\sinh\left(\frac{\beta\mu_0 B\hbar}{2}\right)e^{\beta\mu_0 B\hbar S_z}}{\sinh\left(\beta\mu_0 B\hbar\left(s+\frac{1}{2}\right)\right)}.$$

The magnetization is then

$$\begin{aligned} M_z = N\mathrm{Tr}\hat{\mu}_z\hat{\rho} = N\mathrm{Tr}\left[(\mu_0\hat{S}_z)\hat{\rho}\right] &= \frac{\sum_{S_z=-s}^{s} e^{-\beta\mu_0 B\hbar S_z}\mu_0\hbar S_z}{\sum_{S_z=-s}^{s} e^{-\beta\mu_0 B\hbar S_z}} \\ &= N\mu_0\hbar\left[\left(s+\frac{1}{2}\right)\coth\left(\beta\mu_0 B\hbar\left(s+\frac{1}{2}\right)\right) - \frac{1}{2}\coth\left(\frac{\beta\mu_0 B\hbar}{2}\right)\right]. \end{aligned}$$

In the $s\to\infty$ limit the second term in the brackets becomes negligible and $(s+\frac{1}{2})\hbar \to S$ so the quantum mechanical and classical calculations agree (since the 2nd term in the classical result also becomes negligible as S gets large). To compare the probabilities, we use the fact that $S_z\hbar \to S\cos\theta$ for large s, so $\Delta S_z \approx \frac{S}{\hbar}\sin\theta d\theta$. Thus,

$$p_{\mathrm{QM}}(S_z)\Delta S_z \to p_{\mathrm{QM}}(\theta)d\theta = \frac{S}{\hbar}\sinh\left(\frac{\beta\mu_0 B\hbar}{2}\right)\frac{e^{\beta\mu SB\cos\theta}\sin\theta d\theta}{\sinh(\beta\mu_0 SB)},$$

where we have again made the substitution $(s+\frac{1}{2})\hbar \to S$. This has almost the same function form as the classical probability, but differs have an additional $\sinh\beta$ instead of being linear in β. In order to make the two identical, we must further use the smallness of $\hbar$, which allows us to expand the $\sinh(\beta\mu_0 B\hbar/2) \approx \beta\mu_0\hbar B/2$, and so the two are identical. $\blacksquare$