UIC Physics Ph.D. Preliminary Exam
Friday January 9 2004, 9-11 AM
Thermodynamics and Statistical Mechanics

Solve four out of five problems. If you present solutions to more than four problems, your four highest scoring problem solutions will be counted.

1. Spin-1/2 Paramagnetism

Consider N independent spin-1/2 particles in an external magnetic field. Each spin has a magnetic moment μ.

(a) Find the magnetization of the spins as a function of external magnetic field and temperature.

(b) Find the entropy of the spins as a function of external magnetic field and temperature.

(c) At fixed temperature, calculate the low-field limiting behaviors of (a) and (b).

2. Entropy of an Ideal Gas

(a) For an ideal gas with constant heat capacities C_P and C_V, calculate the entropy as a function of pressure and volume, up to a constant.

(b) Find the entropy change when an ideal gas is expanded from initial volume V_0 to final volume V_1, at fixed temperature. Explain your result (1 sentence).

3. Gas of Massless Fermions

Consider N **massless** noninteracting spin-S fermions, in a three-dimensional box of volume V.

(a) Find the Fermi energy as a function of N, V and S.

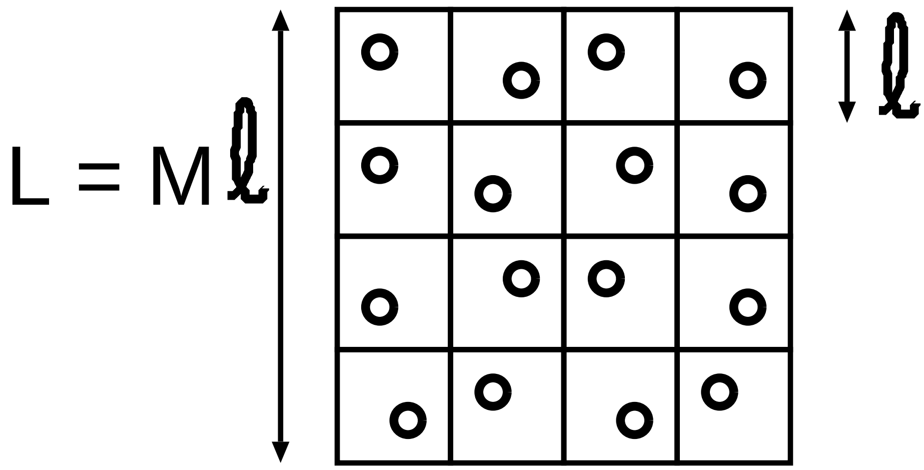
(b) For zero temperature, find the pressure.

(c) Draw a graph of the occupation of states as a function of energy, at a temperature of $(0.1)\epsilon_F/k_B$, showing the effect of temperature clearly.

(d) Suppose that you start with a gas of these particles in a box of volume V, near to $T = 0$. Now, suppose that we open a valve, allowing the gas to undergo a free expansion, allowing it to come to equilibrium in a new, larger volume $2V$. Assuming no work or heat transfer occurs during the expansion, does the *gas temperature* go up, down or stay the same? Explain!

4. Atoms in Small Boxes

A new material is developed, consisting of a bunch of carbon atoms arranged so as to produce an array of small cubic boxes, with each box of size $\ell \times \ell \times \ell$ in size; one helium atom is placed inside each small box. Each helium atom moves freely around inside its little carbon box, and the whole system is in thermal equilibrium at temperature T.



(a) For a cubic array of M boxes on a side (total number of boxes $N = M^3$ and $N >> 1$), find the Helmholtz free energy for the motion of the helium atoms (your result should be expressed in terms of a *sum*). You need consider only the translational motion of the atoms.

(b) Find the low-temperature limiting behavior of the specific heat of the helium atoms, keeping only the terms in the sum which are necessary to obtain the low-temperature behavior. Find the characteristic temperature below which your limiting result is accurate.

(c) Would you expect to be able to observe the result (b) in the extreme low-temperature behavior of the *total* specific heat of the boxes plus helium atom?

(d) Find the *high-temperature* limit of the entropy of the helium atoms.

(e) Explain the difference between your result, and the result for the entropy of the N helium atoms in one large cubic box of edge size $L = M\ell$ (i.e of the same volume as the total volume of all the little boxes), ignoring any effects of interactions between helium atoms.

5. Velocity Distribution of an Ideal Gas:

Consider an ideal gas in a box, in equilibrium at temperature T. The particles each have kinetic energy $m\mathbf{v}^2/2$ and are spinless point particles. They are at sufficiently low density that their quantum statistics are unimportant.

The box is made of a thin but impermeable material, and is surrounded by vacuum.

(a) Find the normalized velocity distribution for the particles inside the sealed box, $P(v_x, v_y, v_z)$.

Now, suppose that a small hole of area a is made in the box, but where the hole diameter is much larger than the thickness of the material that the box is made of. Particles will start to escape from the box.

(b) What is the velocity distribution for the particles that escape from the box, just after the hole is made? (suppose that the direction coming out of the hole is the +z direction)

(c) What is the average (vector) velocity and the average energy per particle that escapes?

(d) What is the rate that particles escape from the box, just after the hole is made?

Constants

$k_B = 1.38 \times 10^{-23}$ J/K $\qquad$ $h = 6.6 \times 10^{-34}$ J·sec $\qquad$ $c = 3.0 \times 10^{8}$ m/sec

Room temperature = 300 K

Integrals

$$\int_{-\infty}^{\infty} dx e^{-x^2/(2\sigma^2)} = \sqrt{2\pi\sigma^2}$$

$$\frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} dx x^n e^{-x^2/(2\sigma^2)} = 1 \cdot 3 \cdot 5 \cdots (n-1)\sigma^n$$

for $n = 2, 4, 6 \cdots$

Series

$$1 + x + x^2 + \cdots x^P = \frac{1 - x^{P+1}}{1 - x}$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \cdots$$

$$\sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\pi^2}{6}$$

$$\ln N! = N \ln N - N + \cdots$$

Solutions

Spin-1/2 Paramagnetism

(a) Consider magnetic field along the $+z$ direction. For one spin, use Boltzmann weights of orientations in the $\pm z$ direction of $\exp[\pm\beta\mu B]$. Average magnetic moment of one spin is

$$\frac{\mu e^{+\beta\mu B} - \mu e^{-\beta\mu B}}{e^{+\beta\mu B} + e^{-\beta\mu B}} = \mu \tanh[\beta\mu B]$$

Total magnetization of N spins, since they are independent, is just N times this, or

$$M = N\mu \tanh\left[\frac{\mu B}{k_B T}\right]$$

(b) Partition function of one spin is

$$e^{+\beta\mu B} + e^{-\beta\mu B} = 2\cosh[\beta\mu B]$$

For all the spins we have just this to the Nth power

$$Z = 2^N (\cosh[\beta\mu B])^N$$

Helmholtz free energy from log of this

$$\ln Z = -\beta F = S/k_B - \beta E = N\ln 2 + N\ln\cosh[\beta\mu B]$$

Energy is

$$E = -\frac{\partial}{\partial\beta}\ln Z = -N\mu B\tanh[\beta\mu B]$$

So entropy is

$$\frac{S}{Nk_B} = \ln 2 + \ln\cosh\left[\frac{\mu B}{k_B T}\right] - \frac{\mu B}{k_B T}\tanh\left[\frac{\mu B}{k_B T}\right]$$

(c) For low fields, we have $\beta\mu B << 1$, so we can approximate $\tanh x \approx x$, $\cosh x \approx 1+x^2/2$, and $\ln\cosh x \approx x^2/2$, to obtain

$$M \approx \frac{N\mu^2 B}{k_B T}$$

and

$$\frac{S}{Nk_B} \approx \ln 2 - \left(\frac{\mu B}{k_B T}\right)^2$$

Entropy of an Ideal Gas

(a) Definitions $C_{\substack{P\\V}} \equiv \left(\frac{dQ}{dT}\right)_{\substack{P\\V}}$ let us write

$$dS = \frac{C_P}{T}dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$dS = \frac{C_V}{T}dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Now we eliminate dT from these equations to give

$$dS = \frac{C_P}{C_P - C_V}\left(\frac{\partial S}{\partial P}\right)_T dP - \frac{C_V}{C_P - C_V}\left(\frac{\partial S}{\partial V}\right)_T dP$$

Now use Maxwell relations $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ to obtain

$$dS = \frac{C_P}{C_P - C_V}\left(\frac{\partial P}{\partial T}\right)_V dV + \frac{C_V}{C_P - C_V}\left(\frac{\partial V}{\partial T}\right)_P dp$$

The derivatives can be evaluated using the ideal gas law $PV = Nk_BT$ giving

$$\frac{dS}{Nk_B} = \frac{C_P}{C_P - C_V}\frac{dV}{V} + \frac{C_V}{C_P - C_V}\frac{dP}{P}$$

Now integrate this from reference values V_0, P_0 to obtain

$$S(P,V) - S(P_0,V_0) = \frac{Nk_B}{C_P - C_V}\left(C_P \ln(V/V_0) + C_V \ln(P/P_0)\right)$$

or

$$S(P,V) = \frac{Nk_B}{C_P - C_V}\left(C_P \ln V + C_V \ln P\right) + \text{const.}$$

Note that $C_P - C_V = Nk_B$ for the ideal gas, so that we finally have

$$S(P,V) = C_P \ln V + C_V \ln P + \text{const.}$$

(b) At fixed T we have $P = Nk_BT/V$, giving us

$$\Delta S = C_P \ln(V_1/V_0) + C_V \ln(V_0/V_1) = (C_P - C_V)\ln(V_1/V_0) = Nk_B \ln(V_1/V_0)$$

The expansion allows the particles of the gas to access more states. Each particle has V_1/V_0 times the positions and thus $k_B \ln V_1/V_0$ times the entropy after the expansion. Note that the momentum state occupation does not change since the expansion is done at fixed temperature.

Gas of Massless Fermions

(a) Fermi energy is the top occupied energy level. Each momentum state can have $2S+1$ spin polarizations, so the number of particles

$$N = \frac{(2S+1)V}{h^3} \int_{|\mathbf{p}|<p_F} d^3p = \frac{(2S+1)V}{h^3} \frac{4\pi p_F^3}{3}$$

where $cp_F = \epsilon_F$, or since

$$p_F = \left(\frac{3Nh^3}{4\pi(2S+1)V} \right)^{1/3}$$

therefore

$$\epsilon_F = cp_F == c \left(\frac{3}{4\pi(2S+1)} \frac{N}{V} \right)^{1/3}$$

(b) At zero temperature, the total energy is

$$E = \frac{(2S+1)V}{h^3} \int_{|\mathbf{p}|<p_F} d^3p cp = \frac{(2S+1)V}{h^3} \frac{4\pi c p_F^4}{4}$$

$$= \frac{3}{4} N \epsilon_F$$

Since $\epsilon_F \propto V^{-1/3}$, $\partial \epsilon_F / \partial V == -1/3 \epsilon_F / V$ From $P = -(\partial F/\partial V)_N$ applied to $T=0$ where $E = F$ we have

$$P(T=0) = \frac{1}{4} \frac{N\epsilon_F}{V}$$

(c) Plot of fermi function at $T = 0.1\epsilon_F/k_B$. The width of the transition from filled to occupied states should be about $0.1\epsilon_F$; states a few times this amount above or below ϵ_F should be almost empty or fully occupied, respectively.

(d) After the expansion, the fermi energy will be lower, but the internal energy per particle will remain the same. Thus the energy per particle will now be well above the zero-temperature limit calculated in (b); states well above the Fermi level will now be populated. Thus, the expansion will be accompanied by an increase in the temperature of the gas.

Atoms in Small Boxes

(a) The quantum states for each helium atom are those of a particle in a cubic box:

$$E_{abc} = \frac{\pi^2\hbar^2}{2m\ell^2}(a^2+b^2+c^2)$$

where a, b and c are positive integers. So, the canonical partition function for one helium atom is

$$Z_1 = \sum_{a,b,c} \exp\left[-\beta E_{abc}\right] = \sum_{n=1,2,3\cdots}\left(\exp\left[-\frac{\beta\pi^2\hbar^2}{2m\ell^2}n^2\right]\right)^3$$

For N boxes, the partition function is just $Z = (Z_1)^N$, and $F = -k_B T \ln Z$ so

$$F = -3k_B TN \ln\left\{\sum_{n=1,2,3\cdots} \exp\left[-\frac{\beta\pi^2\hbar^2}{2m\ell^2}n^2\right]\right\}$$

(b) At low temperatures, the sum will be dominated by the the ground state $(a,b,c) = (0,0,0)$ and the three degenerate first excited states $(1,0,0)$, $(0,1,0)$ and $(0,0,1)$. Using $\epsilon \equiv \frac{\pi^2\hbar^2}{2m\ell^2}$ we have

$$\sum_{n=1,2,3\cdots} \exp\left[-\beta\epsilon n^2\right] \approx \exp\left[-\beta\epsilon\right] + 3\exp\left[-4\beta\epsilon\right]$$

giving an approximate partition function

$$\ln Z \approx 3N\ln\left[e^{-\beta\epsilon}+3e^{-4\beta\epsilon}\right] = -3N\beta\epsilon + 3N\ln\left[1+3e^{-3\beta\epsilon}\right] \approx -3N\beta\epsilon + 9Ne^{-3\beta\epsilon}$$

where we have used $\ln(1+x)\approx x$.

The characteristic temperature below which this approximation is reasonable is

$$T \approx \frac{\epsilon}{k_B} \approx \frac{\pi^2\hbar^2}{mk_B\ell^2}$$

The average energy is $\langle E\rangle = -\partial_\beta \ln Z$, and the specific heat is

$$C = \frac{\partial\langle E\rangle}{\partial T} = -\frac{1}{k_BT^2}\frac{\partial\langle E\rangle}{\partial\beta} = \frac{1}{k_BT^2}\frac{\partial^2\ln Z}{\partial\beta}$$

plugging in the above gives

$$C = 81N\frac{\epsilon^2}{k_BT^2}e^{-3\beta\epsilon}$$

(c) If the box lattice is an electrical insulator, we would expect $\propto T^3$ specific heat at low temperature. If the box lattice conducts electricity, we would expect $\propto T$ specific heat at low temperature. In either case, at low temperature this is much larger than the exponentially small specific heat associated with the helium atoms, so you would not be able to detect the contribution (b) at very low temperature.

(d) At high temperature $\beta\epsilon >> 1$ the sum in (a) may be approximated as an integral:

$$\sum_{n=1,2,3,\cdots} e^{-\beta\epsilon n^2} \approx \int_0^\infty dn e^{-\beta\epsilon n^2} = \frac{1}{2\sqrt{\beta\epsilon}} \int_{-\infty}^{+\infty} dx e^{-x^2} = \sqrt{\frac{\pi}{4\beta\epsilon}}$$

The free energy is therefore

$$F = \frac{3Nk_BT}{2} \ln \frac{4\beta\epsilon}{\pi}$$

and the entropy of the atoms is

$$S = -\left(\frac{\partial F}{\partial T}\right)_N = \frac{3Nk_B}{2}\left[1 + \ln \frac{\pi k_B T}{4\epsilon}\right] = \frac{3Nk_B}{2}\left[1 + \ln \frac{2\pi m k_B T \ell^2}{h^2}\right]$$

We can compare with N atoms in box of volume $N\ell^3$ easily, by just noting that at high temp the momentum distribution is the same in the two cases. The difference in entropy comes solely from the difference in volume, and the fact that we must take into account indistinguishability of particles once they are all in the same box:

$$S_{\text{bigbox}} = \frac{3Nk_B}{2}\left[1 + \ln \frac{2\pi m k_B T L^2}{h^2}\right] - k_B \ln N!$$

Use Stirling approx $\ln N! \approx N \ln N - N$ valid for large N, and also $L^3/\ell^3 = N$ to get

$$S_{\text{bigbox}} = \frac{3Nk_B}{2}\left[1 + \ln \frac{2\pi m k_B T \ell^2}{\pi h^2}\right] + 2Nk_B$$

The ideal gas in the big box of the same volume as the sum of the little boxes, has $2k_B$ more entropy per particle.

Velocity Distribution of an Ideal Gas

(a) Velocity distribution follows directly from Boltzmann distribution,

$$P(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left[-\frac{m\mathbf{v}^2}{2k_B T}\right]$$

Normalization is given by $\int d^3vP = 1$.

(b) The particles come through the hole with the +z half of the distribution of (a),

$$P_{\rm exit}(\mathbf{v}) = 2\left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left[-\frac{m\mathbf{v}^2}{2k_B T}\right]\Theta(v_z)$$

The normalization is as in (a).

(c) The average velocity of the particles coming out of the hole must be in the +z direction, by symmetry. This component averaged is

$$\begin{aligned}\langle v_z \rangle &= 2\left(\frac{m}{2\pi k_B T}\right)^{1/2} \int_0^\infty dv_z v_z \exp\left[-\frac{mv_z^2}{2k_B T}\right] \\ &= \left(\frac{2}{\pi}\right)^{1/2}\left(\frac{k_B T}{m}\right)^{1/2}\end{aligned}$$

The average energy per particle that escapes from the box is just $3k_BT/2$, the average energy of particles in the box.

(d) The number of collisions with the hole over time interval Δt is computed by integrating over all possible v_z's. For each value of v_z, particles from a z-distance up to $v_z\Delta t$ will come out in Δt. The total number of particles coming out in time Δt is therefore

$$a\frac{N}{V}\int_0^\infty dv_z \cdot v_z \cdot \Delta t \cdot 2\left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left[-\frac{mv_z^2}{2k_B T}\right] = a\frac{N}{V}\langle v_z \rangle \Delta t$$

So, the rate that particles come out at is

$$\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{k_B T}{m}\right)^{1/2}\frac{aN}{V}$$