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THE NATIONAL UNIVERSITY OF IRELAND MAYNOOTH

MATHEMATICAL PHYSICS

Year 4

SEMESTER 2

2009-2010

Statistical Mechanics  
MP461

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Time allowed: 1  $\frac{1}{2}$  hours

Answer 2 questions

All questions carry equal marks

*Tip: Take 5 minutes to read through all questions before you begin  
and select the ones which most suit you.*

1. **50 points**

(a) **20 points**

For a system in thermal equilibrium with a heat reservoir at constant temperature  $T$ , show that the variance of the energy  $E$  of the system is related to the heat capacity  $C_V$  by the following equation,

$$C_V = \frac{\langle (E - \langle E \rangle)^2 \rangle}{kT^2}$$

You may assume that the system does not exchange particles with the reservoir.

We have

$$C_V = \left( \frac{\partial \langle E \rangle}{\partial T} \right)_V = \left( \frac{\partial \langle E \rangle}{\partial \beta} \right)_V \frac{\partial \beta}{\partial T} = \frac{-1}{kT^2} \left( \frac{\partial \langle E \rangle}{\partial \beta} \right)_V.$$

We now use the canonical ensemble to calculate  $\langle E \rangle$ , since we have a system in contact with a heat bath but with a constant number of particles. This gives

$$\langle E \rangle = \frac{\sum_s E_s e^{-\beta E_s}}{Z} = -\frac{\partial_\beta Z}{Z},$$

where the sum is over all microstates of the system and  $Z = \sum_s e^{-\beta E_s}$  is the partition function. Hence,

$$\begin{aligned} \partial_\beta \langle E \rangle &= -\frac{\sum_s (E_s)^2 e^{-\beta E_s}}{Z} - \frac{(\sum_s (E_s) e^{-\beta E_s}) \partial_\beta Z}{Z^2} \\ &= -\langle E^2 \rangle + \langle E \rangle^2 = -\langle (E - \langle E \rangle)^2 \rangle. \end{aligned}$$

putting this together, the desired result follows.

(b) **20 points**

State the equipartition theorem for the internal energy of a system with  $N$  degrees of freedom. Then use it to derive Dulong and Petit's law, which states that, at sufficiently high temperatures, the specific heat of a monatomic crystalline solid, per unit mass, will be given by

$$c_V = \frac{3k}{m_p},$$

where  $m_p$  is the mass of one of the atoms of which the solid consists.

The equipartition theorem says that for any classical degree of freedom whose energy is quadratic in the coordinate that describes it, the average energy stored in that degree of freedom will be  $\frac{kT}{2}$ . For quantum systems, this is still true to good approximation for such degrees of freedom for which

the separation between energy levels is much smaller than  $kT$ . A monatomic crystalline solid at high temperature can be modeled as a collection of harmonic oscillators, 3 oscillators for each particle, corresponding to the three directions in which the particle can deviate from its equilibrium position in the crystal lattice. This yields 6 degrees of freedom per particle, the 3 momentum components and the 3 components of the displacement. Hence we find  $E = 3NkT$ , so  $C_V = 3Nk$  and  $c_V = \frac{C_V}{M_{solid}} = \frac{3Nk}{Nm_p} = \frac{3k}{m_p}$ .

(c) **10 points**

Use the results of parts **b.** and **c.** to argue that for a solid consisting of  $N$  atoms, at high temperatures, we have, approximately

$$\frac{\sqrt{\langle (E - \langle E \rangle)^2 \rangle}}{\langle E \rangle} = \sqrt{\frac{1}{3N}}$$

From the results of the previous parts, we find that  $C_V = c_V M_{solid} = \frac{3k}{m_p} Nm_p = 3Nk$  and so  $E = 3NkT$  and  $\langle (E - \langle E \rangle)^2 \rangle = 3Nk^2T^2$ . so the quotient we need equals  $\frac{\sqrt{3Nk^2T^2}}{3NkT} = \sqrt{\frac{1}{3N}}$ .

## 2. 50 points

### (a) 15 points

For a system of  $N$  particles with energy  $E$  volume  $V$ , give expressions for the pressure  $p$ , temperature  $T$ , and chemical potential  $\mu$  in terms of partial derivatives of the entropy with respect to  $E$ ,  $V$  and  $N$ .

Either by definition (following Schroeder's book), or by the thermodynamic relation

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

we have

$$\begin{aligned} T &= 1 / \left( \frac{\partial S}{\partial E} \right)_{V,N} \\ p &= T \left( \frac{\partial S}{\partial V} \right)_{E,N} = \left( \frac{\partial S}{\partial V} \right)_{E,N} / \left( \frac{\partial S}{\partial E} \right)_{V,N} \\ \mu &= -T \left( \frac{\partial S}{\partial N} \right)_{E,V} = - \left( \frac{\partial S}{\partial N} \right)_{E,V} / \left( \frac{\partial S}{\partial E} \right)_{V,N} \end{aligned}$$

### (b) 15 points

Two systems at equal positive temperature  $T$  and pressure  $p$  but with different values  $\mu_1$  and  $\mu_2$  of the chemical potential are brought into contact. Argue that particles will flow from the system at higher chemical potential to the system at lower chemical potential as equilibrium is approached. You may assume that the two systems taken together are isolated from the environment and that no particles are created or destroyed.

In the approach to equilibrium, the entropy  $S$  will increase until it reaches the maximal attainable value. Here we have  $S = S_1 + S_2$  and  $dS = dS_1 + dS_2$ . The entropy will not change through an infinitesimal change in the energies or volumes of the subsystems; since they have equal pressures and temperatures, the infinitesimal variations in the entropies of the subsystems cancel out. However, let us assume that  $\mu_1 > \mu_2$  (obviously this choice does not matter). If we make a small change in  $N_1$  and  $N_2$ , we must have  $N_1 \rightarrow N_1 + dN$  and  $N_2 \rightarrow N_2 - dN$  since the system is isolated and does not exchange particles with the environment. This has the following effect:

$$dS = -\frac{\mu_1}{T}dN + \frac{\mu_2}{T}dN = \frac{\mu_2 - \mu_1}{T}dN$$

Here  $\mu_2 - \mu_1 < 0$  so order for  $dS$  to be positive, we must have  $dN < 0$  in other words the particles must flow from system 1 (which is at higher chemical potential) to system 2 (which is at lower chemical potential).

(c) **20 points**

Now consider a system at fixed volume  $V$  and in contact with a heat and particle bath which remains at constant temperature  $T$  and chemical potential  $\mu$ . Derive the Boltzmann distribution, that is, show that the probability  $P(E, N)$  of a microstate of the system with energy  $E$  and  $N$  particles is given by

$$P(E, N) = \frac{e^{-\beta(E-\mu N)}}{Z}$$

where  $\beta = \frac{1}{kT}$  and  $Z$  does not depend on  $E$  and  $N$ . Also give an expression for  $Z$ .

The probability  $P(E, N)$  of a microstate of the system is proportional to the number of microstates  $\Omega_b(E, N)$  of the bath at these values of  $E$  and  $N$ . Hence we have for the ratio between the probabilities of microstates at  $(E_1, N_1)$  and at  $(E_2, N_2)$  that

$$\frac{P(E_1, N_1)}{P(E_2, N_2)} = \frac{\Omega_b(E_1, N_1)}{\Omega_b(E_2, N_2)}.$$

As a result,

$$\begin{aligned} \log\left(\frac{P(E_1, N_1)}{P(E_2, N_2)}\right) &= \log(\Omega_b(E_1, N_1)) - \log(\Omega_b(E_2, N_2)) \\ &= \frac{1}{k} (S_b(E_1, N_1) - S_b(E_2, N_2)) \end{aligned}$$

The differences in the energy and particle number *of the bath* at system energies and particle numbers  $(E_1, N_1)$  and at  $(E_2, N_2)$  are  $\Delta E_b = E_1 - E_2$  and  $\Delta N_b = N_1 - N_2$ . Since the temperature and chemical potential of the bath are constant, we have

$$\Delta S_b = S_b(E_2, N_2) - S_b(E_1, N_1) = \frac{\Delta E_b}{T} - \frac{\mu \Delta N_b}{T} = \frac{E_1 - \mu N_1}{T} - \frac{E_2 - \mu N_2}{T}$$

Substituting this above, we find (with  $\beta = \frac{1}{kT}$ )

$$\frac{P(E_1, N_1)}{P(E_2, N_2)} = \frac{e^{-\beta(E_1 - \mu N_1)}}{e^{-\beta(E_2 - \mu N_2)}}$$

This also yields

$$\frac{P(E_1, N_1)}{e^{-\beta(E_1 - \mu N_1)}} = \frac{P(E_2, N_2)}{e^{-\beta(E_2 - \mu N_2)}}$$

showing that both sides are in fact independent of the variables  $E_1, E_2$  and  $N_1, N_2$ , and hence equal to some constant  $Z$  (which may still depend on other variables such as  $V$ ). Hence we have  $P(E, N) = \frac{e^{-\beta(E-\mu N)}}{Z}$ . The value

of  $Z$  follows from the fact that the probabilities must sum to 1. We have  $\sum_s P(E_s, N_s) = \frac{1}{Z} \sum_s e^{-\beta(E_s - \mu N_s)} = 1$  and hence

$$Z = \sum_s e^{-\beta(E_s - \mu N_s)},$$

where the sum is over all microstates accessible to the system.

### 3. 50 points

(a) **15 points**

Describe the ground state of a system of  $N$  non-interacting bosons in terms of the occupation numbers of single particle states.

Do the same for a system of  $N$  non-interacting fermions.

In the fermionic case, give an argument that, at  $T = 0$ , we must have  $\mu = \epsilon_F$ , where  $\epsilon_F$  is the energy of the highest occupied state.

For bosons, the ground state has all  $N$  bosons in the single particle ground state, so this state has occupation number  $N$  and all the others have occupation number 0. For fermions, the ground state has occupation number equal to 1 for the lowest  $N$  single particle states and occupation number 0 for all other states. To see that  $\mu = \epsilon_F$  at  $T = 0$ , consider the Fermi-Dirac distribution. We have  $n_{FD}(\beta, \epsilon, \mu) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}$ . As  $T$  approaches 0,  $\beta = \frac{1}{kT}$  goes to infinity and so  $n_{FD} \downarrow 0$  if  $\epsilon > \mu$  and  $n_{FD} \uparrow 1$  if  $\epsilon < \mu$ . Since we know that the system will be in the ground state at  $T = 0$  (third law) and we have defined  $\epsilon_F$  so that all occupation numbers  $n(\epsilon)$  are equal to 1 for  $\epsilon \leq \epsilon_F$  and equal to 0 for  $\epsilon > \epsilon_F$ , we see that we must have  $\mu = \epsilon_F$ .

(b) **15 points**

A particle in two dimensions is confined to a square box of side  $L$ . Its energy levels are given by  $E(\vec{n}) = \frac{\hbar^2 n^2}{8mL^2}$ , where  $\vec{n} = (n_1, n_2)$  and  $n_1$  and  $n_2$  are positive integers. Show that the density of states  $g(E)$  for this system is independent of  $E$  and given by

$$g(E) = \frac{2\pi mL^2}{h^2}.$$

$g(E)$  is defined so that the number of states with energies between  $E$  and  $E + dE$  is equal to  $g(E)dE$ . Here, we have  $E(\vec{n}) = \frac{\hbar^2 n^2}{8mL^2}$  and hence

$$dE = \frac{\hbar^2 n}{4mL^2} dn.$$

The number of states for which  $\vec{n}$  has length between  $n$  and  $n + dn$  is equal to a quarter of the surface area of a ring of radius  $n$  and thickness  $dn$  in  $\vec{n}$ -space. In other words,  $g(E)dE = \frac{\pi}{2} n dn$ . For this, we use that  $dn$  is infinitesimal. We only get a quarter of the surface of the ring because  $n_1$  and  $n_2$  must be nonnegative. We ignored fluctuations due to the fact that the  $\vec{n}$ -vectors lie on a lattice (these effects should mostly average out when integrating over  $\vec{n}$ -space to calculate averages). Now writing  $dn = \frac{4mL^2}{\hbar^2 n} dE$ , we find immediately that  $g(E)dE = \frac{\pi}{2} n \frac{4mL^2}{\hbar^2 n} dE$  and hence  $g(E) = \frac{2\pi mL^2}{h^2}$ .

(c) **10 points**

Calculate or argue that, for a two dimensional gas of identical non-interacting fermions confined to a square box, the average energy per particle in the ground state,  $E_0$  is equal to  $\frac{1}{2}\epsilon_F$ .

In the ground state, the lowest  $N$  single particle states are filled. Since the density of single particle states for this system is constant, the average energy  $E_0$  per particle is just half of the energy of the highest occupied level, which is  $\epsilon_F$ . Alternatively, we may calculate  $E_0$  as follows.

$$E_0 = \frac{1}{N} \int_0^\infty g(E)n_{FD}(E)E dE = \frac{1}{N} \int_0^{\epsilon_F} \frac{2\pi mL^2}{h^2} E dE = \frac{2\pi mL^2}{Nh^2} \frac{1}{2} \epsilon_F^2$$

where we used that, at  $T = 0$ ,  $n_{FD} = 0$  for  $E > \epsilon_F$  and  $n_{FD} = 1$  for  $E < \epsilon_F$ . We can also express  $N$  in terms of  $\epsilon_F$ ,

$$N = \int_0^\infty g(E)n_{FD}(E) dE = \int_0^{\epsilon_F} \frac{2\pi mL^2}{h^2} dE = \frac{2\pi mL^2}{h^2} \epsilon_F,$$

again, using that  $T = 0$ . Substituting this in the expression for  $E_0$ , we immediately obtain that  $E_0 = \frac{1}{2} \epsilon_F$ .

(d) **10 points**

Show that the chemical potential for this two dimensional gas of identical non-interacting fermions confined to a square box, at arbitrary temperature  $T$ , is given by

$$\mu = \frac{1}{\beta} \log(e^{\frac{h^2 \beta N}{2\pi mL^2}} - 1)$$

with  $\beta = \frac{1}{kT}$

The chemical potential  $\mu$  is determined by the requirement that

$$\int_0^\infty g(E)n_{FD}(E) dE = N.$$

In this two dimensional case, we can calculate the integral exactly at any temperature

$$\begin{aligned} N = \int_0^\infty g(E)n_{FD}(E) dE &= \frac{2\pi mL^2}{h^2} \int_0^\infty \frac{1}{e^{\beta(\epsilon-\mu)} + 1} dE \\ &= \frac{2\pi mL^2}{h^2} \int_0^\infty \frac{e^{-\beta(\epsilon-\mu)}}{1 + e^{-\beta(\epsilon-\mu)}} dE \\ &= \frac{2\pi mL^2}{h^2} \left[ \frac{-1}{\beta} \log(1 + e^{-\beta(\epsilon-\mu)}) \right]_0^\infty \\ &= \frac{2\pi mL^2}{h^2 \beta} \log(1 + e^{\beta\mu}). \end{aligned}$$

This yields  $1 + e^{\beta\mu} = e^{\frac{h^2 \beta N}{2\pi mL^2}}$  and  $\mu = \frac{1}{\beta} \log(e^{\frac{h^2 \beta N}{2\pi mL^2}} - 1) = \frac{1}{\beta} \log(e^{\beta\epsilon_F} - 1)$ , with  $\beta = \frac{1}{kT}$ .

4. **50 points**

Consider a paramagnet consisting of  $N$  spin  $\frac{1}{2}$  particles at fixed positions, subject to a magnetic field of magnitude  $B$  pointing in the  $z$ -direction. The system has energy  $U = -\mu B(N_{\uparrow} - N_{\downarrow})$ , where  $N_{\uparrow}$  and  $N_{\downarrow}$  are the number of particles with positive and negative spin in the  $z$ -direction and  $\mu$  is the magnitude of the magnetic moment of the particles.

(a) **15 points**

Show that the number of microstates  $\Omega(U)$  corresponding to a macrostate of energy  $U$  is

$$\Omega(U) = \frac{N!}{\left(\frac{\mu BN + U}{2\mu B}\right)! \left(\frac{\mu BN - U}{2\mu B}\right)!}$$

The number of microstates which has a given number of particles  $N_{\uparrow}$  with spin in the positive  $z$ -direction is clearly equal to the number of ways we can choose  $N_{\uparrow}$  particles from a total of  $N$  particles. In other words, it is  $\frac{N!}{N_{\uparrow}!(N - N_{\uparrow})!}$ . Now we have  $U = -\mu B(N_{\uparrow} - N_{\downarrow}) = -\mu B(2N_{\uparrow} - N)$ , since  $N_{\uparrow} + N_{\downarrow} = N$ . It follows that  $N_{\uparrow} = \frac{1}{2}\left(N - \frac{U}{\mu B}\right) = \frac{\mu BN - U}{2\mu B}$ . Similarly  $N - N_{\uparrow} = \frac{\mu BN + U}{2\mu B}$  and the desired result follows.

(b) **20 points**

Show that, at large  $N$ , the temperature of the system is given, to good approximation, by

$$T = \frac{2\mu B}{k \log\left(\frac{\mu BN - U}{\mu BN + U}\right)}$$

We have

$$T = 1/\frac{\partial S}{\partial U}$$

and

$$S = k \log(\Omega(U))$$

At large  $N$ , we have, using Stirling's formula to approximate the factorials,

$$S/k \approx N \log(N) - \frac{\mu BN + U}{2\mu B} \log\left(\frac{\mu BN + U}{2\mu B}\right) - \frac{\mu BN - U}{2\mu B} \log\left(\frac{\mu BN - U}{2\mu B}\right)$$

we can calculate the derivative with respect to  $U$  straightforwardly, giving

$$\begin{aligned} \frac{1}{k} \partial_U S &= -\frac{1}{2\mu B} \log\left(\frac{\mu BN + U}{2\mu B}\right) - \frac{1}{2\mu B} + \left(\frac{1}{2\mu B}\right) \log\left(\frac{\mu BN - U}{2\mu B}\right) + \frac{1}{2\mu B} \\ &= \left(\frac{1}{2\mu B}\right) \log\left(\frac{\mu BN - U}{\mu BN + U}\right) \end{aligned}$$

(c) **15 points**

This system can have a negative temperature. Indicate for which range of values of  $U$  this happens. Argue that macrostates with negative temperatures must occur in all thermodynamic systems with a finite number of microstates and a continuous density of states.

In this system,  $T$  will be negative if and only if  $\log\left(\frac{\mu BN - U}{\mu BN + U}\right) < 0$ , hence if and only if  $\mu BN - U < \mu BN + U$ , or  $U > 0$ . In general, if a system has a finite number of states, the energy of these states will be bounded from above. In other words, there is some energy  $E_{max}$  above which the density of states is zero. If the density of states is continuous, there must be some region of energy below  $E = E_{max}$  where it is decreasing. In this region,  $\Omega(E)$  and hence  $S(E)$ , is a decreasing function of  $E$ , which means that  $\frac{1}{T} = \partial_E S < 0$  and as a result  $T < 0$ .