

# Statistical Physics



## Second year physics course

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(with thanks to S. J. Blundell)

## Problem Sets 5–8: Statistical Mechanics *Hilary Term 2015*

### Some Useful Constants

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Boltzmann's constant	$k_B$	$1.3807 \times 10^{-23} \text{ J K}^{-1}$
Proton rest mass	$m_p$	$1.6726 \times 10^{-27} \text{ kg}$
Avogadro's number	$N_A$	$6.022 \times 10^{23} \text{ mol}^{-1}$
Standard molar volume		$22.414 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$
Molar gas constant	$R$	$8.315 \text{ J mol}^{-1} \text{ K}^{-1}$
1 pascal (Pa)		$1 \text{ N m}^{-2}$
1 standard atmosphere		$1.0132 \times 10^5 \text{ Pa (N m}^{-2}\text{)}$
1 bar (= 1000 mbar)		$10^5 \text{ N m}^{-2}$
Stefan–Boltzmann constant	$\sigma$	$5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$

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## PROBLEM SET 5: Foundations of Statistical Mechanics

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If you want to try your hand at some practical calculations first, start with the Ideal Gas questions

### Maximum Entropy Inference

5.1 *Factorials.* a) Use your calculator to work out  $\ln 15!$ . Compare your answer with the simple version of Stirling's formula ( $\ln N! \approx N \ln N - N$ ). How big must  $N$  be for the simple version of Stirling's formula to be correct to within 2%?

b\*) Derive Stirling's formula (you can look this up in a book). If you figure out this derivation, you will know how to calculate the next term in the approximation (after  $N \ln N - N$ ) and therefore how to estimate the precision of  $\ln N! \approx N \ln N - N$  for any given  $N$  without calculating the factorials on a calculator. Check the result of (a) using this method.

5.2 *Tossing coins and assigning probabilities.* This example illustrates the scheme for assignment of *a priori* probabilities to microstates, discussed in the lectures.

Suppose we have a system that only has two states,  $\alpha = 1, 2$ , and no further information about it is available. We will assign probabilities to these states in a fair and balanced way: by flipping a coin  $\mathcal{N} \gg 1$  times, recording the number of heads  $\mathcal{N}_1$  and tails  $\mathcal{N}_2$  and declaring that the probabilities of the two states are  $p_1 = \mathcal{N}_1/\mathcal{N}$  and  $p_2 = \mathcal{N}_2/\mathcal{N}$ .

a) Calculate the number of ways,  $W$ , in which a given outcome  $\{\mathcal{N}_1, \mathcal{N}_2\}$  can happen, find its maximum and prove therefore that the most likely assignment of probabilities will be  $p_1 = p_2 = 1/2$ . What is the Gibbs entropy of this system?

b) Show that for a large number of coin tosses, this maximum is sharp. Namely, show that the number of ways  $W(m)$  in which you can get an outcome with  $\mathcal{N}/2 - m$  heads (where  $\mathcal{N} \gg m \gg 1$ ) is

$$\frac{W(m)}{W(0)} \approx \exp(-2m^2/\mathcal{N}),$$

where  $W(0)$  corresponds to the most likely situation found in (a) and so the relative width of this maximum is  $\delta p = m/\mathcal{N} \sim 1/\sqrt{\mathcal{N}}$ .

*Hint.* Take logs and use Stirling formula.

5.3 *Loaded die.* Imagine throwing a die and attempting to determine the probability distribution of the outcomes. There are 6 possible outcomes:  $\alpha = 1, 2, 3, 4, 5, 6$ ; their probabilities are  $p_\alpha$ .

a) If we know absolutely nothing and believe in maximising entropy as a guiding principle, what should be our *a priori* expectation for  $p_\alpha$ ? What then do we expect the average outcome  $\langle \alpha \rangle$  to be?

b) Suppose someone has performed very many throws and informs us that the average is in fact  $\langle \alpha \rangle = 3.667$ . Use the principle of maximum entropy to determine all  $p_\alpha$ .

*Hint.* You will find the answer (not the solution) in J. Binney's lecture notes. This is a good opportunity to verify your solution. To find the actual probabilities, you may have to find the root of a transcendental equation — this is easily done on the computer or even on an advanced calculator.

## Canonical Ensemble

### 5.4 Heat Capacity, Thermal Stability and Fluctuations.

- a) Derive the general expression for heat capacity at constant volume,  $C_V$ , in terms of derivatives of the partition function  $Z(\beta)$  with respect to  $\beta = 1/k_B T$ .
- b) Use the partition function of the monatomic ideal gas to check that this leads to the correct expression for its heat capacity.
- c) From the result of (a), show that  $C_V \geq 0$  (so thermal stability, derived in Lecture Notes §10.5.1, is not in peril).
- d) In (c), you should have obtained an expression that relates  $C_V$  to mean square deviation (or variance, or fluctuation) of the exact energy of the system from its mean value,  $\langle \Delta E^2 \rangle = \langle (E_\alpha - U)^2 \rangle$ . Show that  $\langle \Delta E^2 \rangle / U^2 \rightarrow 0$  as the size of the system  $\rightarrow \infty$ .



5.5 *Elastic chain.* A very simplistic model of an elastic chain is illustrated above. This is a 1D chain consisting of  $N$  segments, each of which can be in one of two (non-degenerate) states: horizontal (along the chain) or vertical. Let the length of the segment be  $a$  when it is horizontal and 0 when it is vertical. Let the chain be under fixed tension  $\gamma$  and so let the energy of each segment be 0 when it is horizontal and  $\gamma a$  when it is vertical. The temperature of the chain is  $T$ .

- a) What are the microstates of the chain? Treating the chain using the canonical ensemble, work out the single-segment partition function and hence the partition function of the entire chain.
- b) Work out the relationship between mean energy  $U$  and mean length  $L$  of the chain and hence calculate the mean length as a function of  $\gamma$  and  $T$ . Under what approximation do we obtain Hooke's law:  $L = L_0 + A\gamma/T$ , where  $L_0$  and  $A$  are constants?
- c) Calculate the heat capacity for this chain and sketch it as a function of temperature (pay attention to what quantity is held constant for the calculation of the heat capacity). Why physically does the heat capacity vanish both at small and large temperatures?
- d) *Negative temperature.* If you treat the mean energy  $U$  of the chain as given and temperature as the quantity to be found, you will find that temperature can be negative! Sketch  $T$  as a function of  $U$  and determine under what conditions  $T < 0$ . Why is this possible in this system and not, say, for the ideal gas? Why does the stability argument

from Lecture Notes §10.5.2 not apply here? Where else in this problem set have you encountered negative temperature and why was it OK there?

e\*) *Superfluous constraints.* This example illustrates that if you have more measurements and so more constraints, you do not necessarily get a different statistical mechanics (so the maximum entropy principle is less subjective than it might seem; this is discussed in Lecture Notes §12.5).

So far we have treated our chain as a canonical ensemble, i.e., we assumed that the only constraint on probabilities would be the mean energy  $U$ . Suppose now that we have both a thermometer and a ruler and so wish to maximise entropy subject to two constraints: the mean energy is  $U$  and also the mean length of the chain is  $L$ . Do this and find the probabilities of the microstates  $\alpha$  of the chain as functions of their energies  $E_\alpha$  and corresponding chain lengths  $\ell_\alpha$ . Show that the maximisation problem only has a solution when  $U$  and  $L$  are in a specific relationship with each other — so the new constraint is not independent and does not bring in any new physics. Show that in this case one of the Lagrange multipliers is arbitrary (and so can be set to 0 — e.g., the one corresponding to the constraint of fixed  $L$ ; this constraint is superfluous so we are back to the canonical ensemble).

### Classical Monatomic Ideal Gas

5.6 Consider a classical ideal monatomic gas of  $N$  spinless particles of mass  $m$  in a volume  $V$  at a temperature  $T$ .

a) Derive the formula for its partition function. Show that if particles in the gas were distinguishable, the entropy would be a non-extensive (non-additive) function. Why is this a problem? Show that if indistinguishability is properly accounted for, this problem disappears. Under what assumption is it OK to use a simple  $1/N!$  compensating factor to account for indistinguishability?

b) Consider two equal volumes containing two classical ideal gases at the same temperature and pressure. Using the Sackur-Tetrode equation, find the entropy change on mixing the two gases (i) when the gases are identical, and (ii) when they are different. If the answers for these two cases are different (or otherwise), explain why that makes physical sense.

c) Using the explicit expression for the entropy of the classical ideal monatomic gas in equilibrium, show that for such a gas undergoing an adiabatic process,  $PV^{5/3} = \text{const}$ .

5.7 *Relativistic Ideal Gas.*

a) Show that the equation of state of an ideal gas is still  $PV = Nk_B T$  even when the gas is heated to such a high temperature that the particles are moving at relativistic speeds. Why is it unchanged?

b) Although the equation of state does not change when the particles in a monatomic ideal gas start to move at relativistic speeds, show, by explicit calculation of the expression for the entropy, that in the formula for an adiabat,  $PV^\gamma = \text{const}$ , the exponent  $\gamma$  in the relativistic limit is  $\frac{4}{3}$ , rather than  $\frac{5}{3}$  as in the non-relativistic case. You can assume

that the particles are ultrarelativistic, i.e., their rest energy is negligible compared to their kinetic energy.

c) Show that for an ultra-relativistic gas, pressure  $p = \varepsilon/3$ , where  $\varepsilon$  is the internal energy density. Is it different than for a non-relativistic gas? Why?

### 5.8 *Density of States.*

a) Consider a particle living in a 2D box. What is the density of states  $g(k)$  for it? What is  $g(k)$  for a particle in a 1D box? (The 3D case was done in the Lectures.)

b\*) Calculate the density of states in a  $d$ -dimensional box.

*Hint.* You will need to calculate the area of a unit sphere in  $d$  dimensions (the full solid angle in  $d$  dimensions). You have done it before (Q3.3d, last term). You can look it up somewhere (e.g., in Kardar's book) or figure it out yourself.

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## PROBLEM SET 6: Statistical Mechanics of Simple Systems

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*This Problem Set can be attempted during Weeks 4 and 5 of Hilary Term, with the tutorial or class on this material held at the end of Week 5 or later.*

### Calculation of thermodynamic quantities from the partition function

6.1 Consider an array of  $N$  localised spin- $\frac{1}{2}$  paramagnetic atoms. In the presence of a magnetic field of flux density  $B$ , the two degenerate spin states split by  $\pm\mu_B B$ , where  $\mu_B$  is the Bohr magneton.

- (i) Derive the single-particle partition function for the system.
- (ii) Show that the heat capacity  $C_B$  can be written as

$$C_B = \left( \frac{\partial Q_{\text{rev}}}{\partial T} \right)_B = Nk_B \left( \frac{\theta}{T} \right)^2 \frac{e^{\theta/T}}{(e^{\theta/T} + 1)^2}. \quad (1)$$

Show that  $C_B$  has a maximum at a temperature  $T_{\text{max}} = A\mu_B B/k_B$  where  $A$  is a numerical constant. Determine  $A$ , and sketch  $C_B$  as a function of  $\theta/T$ .

(iii) Given that the largest static magnetic field that can easily be produced in the laboratory is of order 10 Tesla, estimate the temperature at which the magnetic heat capacity of such a system will be largest.

6.2 An array of  $N$  1D simple harmonic oscillators is set up with an average energy per oscillator of  $(m + \frac{1}{2})\hbar\omega$ . Show that the entropy per oscillator is given by

$$\frac{S}{Nk_B} = (1 + m) \ln(1 + m) - m \ln m. \quad (2)$$

Comment on the value of the entropy when  $m = 0$ .

6.3 An assembly of  $N$  particles per unit volume, each having angular momentum  $J$ , is placed in a magnetic field. The field splits the level into  $2J + 1$  different energies, given by  $m_J g_J \mu_B B$ , where  $m_J$  runs from  $-J$  to  $+J$ .  $g_J$  is known as the Landé g-factor, which you will presently meet in atomic physics.

(i) Show that the single-particle partition function  $Z_{\text{mag}}$  of the magnetic system can be written as

$$Z_{\text{mag}} = \frac{\sinh[(J + \frac{1}{2})y]}{\sinh(y/2)}. \quad (3)$$

where  $y = g_J \mu_B B/k_B T$ .

(ii) Show that the susceptibility,  $\chi$ , (defined as  $\mu_0 M/B$  as  $B \rightarrow 0$ ) is given by

$$\chi = \frac{\mu_0 N g_J^2 \mu_B^2 J(J + 1)}{3k_B T}. \quad (4)$$

Prove that this is consistent with the result derived in lectures for a spin- $\frac{1}{2}$  paramagnet. [N.B. In the limit of small  $x$ ,  $\coth x \approx 1/x + x/3$ ]

## Diatomic gases and the equipartition theorem

6.4 Comment on the following values of molar heat capacity at constant pressure  $C_p$  in  $\text{JK}^{-1}\text{mol}^{-1}$ , all measured at 298 K.

Al	24.35	Pb	26.44
Ar	20.79	Ne	20.79
Au	25.42	N <sub>2</sub>	29.13
Cu	24.44	O <sub>2</sub>	29.36
He	20.79	Ag	25.53
H <sub>2</sub>	28.82	Xe	20.79
Fe	25.10	Zn	25.40

[Hint: express the values in terms of  $R$ , and compare them with the predictions of the equipartition theorem. Which substance is a solid and which is gaseous?]

6.5 Experimental data for the molar heat capacity of N<sub>2</sub> as a function of temperature are shown in the table below.

$T$ (Kelvin)	170	500	770	1170	1600	2000	2440
$C_V/R$	2.5	2.57	2.76	3.01	3.22	3.31	3.4

(i) Estimate the frequency of vibration of the N<sub>2</sub> molecule.

(ii) By making a rough estimate of the moment of inertia of the molecule, comment on the possibility of quenching the rotational degrees of freedom and hence reducing the heat capacity of nitrogen to  $3R/2$  per mole.

6.6 Show that for a diatomic molecule at a temperature,  $T$ , such that  $\theta_{\text{rot}} \ll T \ll \theta_{\text{vib}}$ , where  $\theta_{\text{rot}}$  and  $\theta_{\text{vib}}$  are its characteristic temperatures of rotation and vibration respectively, the partition function satisfies  $Z \propto VT^{5/2}$ . Hence show that  $pV^{7/5}$  is a constant along an adiabat.

## Grand canonical ensemble and chemical potential

6.7 *Classical Ideal Gas.*

a) Starting from the grand canonical distribution, prove that the equation of state for a classical ideal gas is  $P = nk_B T$ , where  $n = \bar{N}/V$  is the mean number density.

b) Find the chemical potential  $\mu$  as a function of pressure  $P$  and temperature  $T$  for a diatomic classical ideal gas whose rotational levels are excited but vibrational ones are not. The mass of each of the two atoms in the molecule is  $m$ , the separation between them is  $r$ .

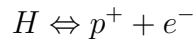
6.8 *Rotating Gas.* A cylindrical container of radius  $R$  is filled with ideal gas at temperature  $T$  and rotating around the axis with angular velocity  $\Omega$ . The molecular mass is  $m$ . The mean density of the gas without rotation is  $\bar{n}$ . Assuming the gas is in isothermal equilibrium, what is the gas density at the edge of the cylinder,  $n(R)$ ? Discuss the high and low temperature limits of your result.

*Hint.* You should be able to write the centrifugal force in terms of a potential, which then tells you what the energy levels of molecular motion in a rotating gas are.

6.9 *Particle Number Distribution.* Consider a volume  $V$  of classical ideal gas with mean number density  $n = \bar{N}/V$ , where  $\bar{N}$  is the mean number of particles in this volume. Starting from the grand canonical distribution, show that the probability to find exactly  $N$  particles in this volume is a Poisson distribution (thus, you will have recovered the result you proved in PS-3 by a different method).

### Multispecies systems

6.10 *Ionisation-Recombination Equilibrium.* Consider hydrogen gas at high enough temperature that ionisation and recombination are occurring (i.e., we are dealing with a partially ionised hydrogen plasma). The reaction is



(hydrogen atom becomes a proton + an electron or vice versa). Our goal is to find, as a function of density and temperature (or pressure and temperature), the degree of ionisation  $\chi = n_p/n$ , where  $n_p$  is proton number density,  $n = n_H + n_p$  is total number density of hydrogen, ionised or not, and  $n_H$  is the number density of the un-ionised  $H$  atoms. Note that  $n$  is fixed (conservation of nucleons). Assume overall charge neutrality of the system.

a) What is the relation between chemical potentials of the  $H$ ,  $p$  and  $e$  gases if the system is in chemical equilibrium?

b) Treating all three species as classical ideal gases, show that in equilibrium

$$\frac{n_e n_p}{n_H} = \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-R/k_B T},$$

where  $R = 13.6$  eV (1 Rydberg) is the ionisation energy of hydrogen. This formula is known as the Saha Equation.

*Hint.* Remember that you have to include the internal energy levels into the partition function for the hydrogen atom. You may assume that only the ground state energy level  $-R$  matters (i.e., neglect all excited states).

c) Hence find the degree of ionisation  $\chi = n_p/n$  as function of  $n$  and  $T$ . Does  $\chi$  go up or down as density is decreased? Why? Consider a cloud of hydrogen with  $n \sim 1 \text{ cm}^{-3}$ . Roughly at what temperature would it be mostly ionised? These are roughly the conditions in the so called “warm” phase of the interstellar medium — the stuff that much of the Galaxy is filled with (although the law of mass action is not



thought to be a very good approximation for interstellar medium, because it is not exactly in equilibrium).

d) Now find an expression for  $\chi$  as a function of total gas pressure  $p$  and temperature  $T$ . Sketch  $\chi$  as a function of  $T$  at several constant values of  $p$ .

### Other Ensembles

6.11 *Microcanonical Ensemble Revisited.* Derive the grand canonical distribution starting from the microcanonical distribution (i.e., by considering a small subsystem exchanging particles and energy with a large, otherwise isolated system).

*Hint.* This is a generalisation of the derivation in Lecture Notes §12.3. If you can't figure it out on your own, you will find the solution in Blundell & Blundell's or Kittel's books.

6.12 (\*) *Pressure Ensemble.* Throughout this course, we have repeatedly discussed systems whose volume is not fixed, but allowed to come to some equilibrium value under pressure. Yet, in both canonical and grand canonical ensembles, we treated volume as an external parameter, not as a quantity only measurable in the mean. In this question, your objective is to construct an ensemble in which the volume is not fixed.

a) Consider a system with (discrete) microstates  $\alpha$  to each of which corresponds some energy  $E_\alpha$  and some volume  $V_\alpha$ . Maximise Gibbs entropy subject to measured mean energy being  $U$  and the mean volume  $\bar{V}$ , whereas the number of particles  $N$  is exactly fixed and find the probabilities  $p_\alpha$ . Show that the (grand) partition function for this ensemble can be defined as

$$\mathcal{Z} = \sum_{\alpha} e^{-\beta E_{\alpha} - \sigma V_{\alpha}},$$

where  $\beta$  and  $\sigma$  are Lagrange multipliers. How are  $\beta$  and  $\sigma$  determined?

b) Show that if we demand that the Gibbs entropy  $S_G$  for those probabilities be equal to  $S/k_B$ , where  $S$  is the thermodynamic entropy, then the Lagrange multiplier arising from the mean-volume constraint is  $\sigma = \beta P = P/k_B T$ , where  $P$  is pressure. Thus, this ensemble describes a system under pressure set by the environment.

c) Prove that  $dU = TdS - Pd\bar{V}$ .

d) Show that  $-k_B T \ln \mathcal{Z} = G$ , where  $G$  is the Gibbs free energy defined in the usual way. How does one calculate the equation of state for this ensemble?

e) Calculate the partition function  $\mathcal{Z}$  for classical monatomic ideal gas in a container of changeable volume but impermeable to particles (e.g., a balloon made of inelastic material). You will find it useful to consider microstates of an ideal gas at fixed volume  $V$  and then sum up over all possible values of  $V$ . This sum (assumed discrete) can be converted to an integral via  $\sum_V = \int_0^\infty dV/\Delta V$ , where  $\Delta V$  is the "quantum of volume." You will also need to use the formula  $\int_0^\infty dx x^N e^{-x} = N!$

f) Calculate  $G$  and find what conditions  $\Delta V$  must satisfy in order for the resulting expression to coincide with the standard formula for the ideal gas (derived in the lectures and Q6.7) and be independent of  $\Delta V$  (assume  $N \gg 1$ ).

g) Show that the equation of state is  $P = nk_B T$ , where  $n = N/\bar{V}$ .

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## PROBLEM SET 7: Quantum Gases

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*This Problem Set can be attempted during Weeks 6 and 7 of Hilary Term, with the tutorial or class on this material held in Week 7 or later. Some of the questions (1, 2, 5-7, 8, 9) require quite long calculations, so start working on this Problem Set early! Note that gaining good command of these techniques is crucial both for your understanding of this course and for several 3rd-year papers.*

### Basic Calculations for Quantum Gases

7.1 *Ultrarelativistic Quantum Gas.* Consider an ideal quantum gas (Bose or Fermi) in the ultrarelativistic limit.

(a) Find the equation that determines its chemical potential (implicitly) as a function of density  $n$  and temperature  $T$ .

(b) Calculate the energy  $U$  and grand potential  $\Phi$  and hence prove that the equation of state can be written as

$$PV = \frac{1}{3}U,$$

regardless of whether the gas is in the classical limit, degenerate limit or in between.

(c) Consider an adiabatic process with the number of particles held fixed and show that

$$PV^{4/3} = \text{const}$$

for any temperature and density (not just in the classical limit).

(d) Show that in the hot, dilute limit (large  $T$ , small  $n$ ),  $e^{\mu/k_B T} \ll 1$ . Find the specific condition on  $n$  and  $T$  that must hold in order for the classical limit to be applicable. Hence derive the condition for the gas to cease to be classical and become degenerate. Estimate the minimum density for which an electron gas can be simultaneously degenerate and ultrarelativistic.

(e) Find the Fermi energy  $\varepsilon_F$  of an ultrarelativistic electron gas and show that when  $k_B T \ll \varepsilon_F$ , its energy density is  $3n\varepsilon_F/4$  and its heat capacity is

$$C_V = Nk_B\pi^2 \frac{k_B T}{\varepsilon_F}$$

(it is not terribly essential that you can calculate the  $\pi^2$  numerical factor in this formula, so if you prefer qualitative calculations to quantitative ones, simply give a qualitative argument showing that  $C_V \sim Nk_B^2 T/\varepsilon_F$ ).

Sketch the heat capacity of an ultrarelativistic electron gas as a function of temperature, from  $T \ll \varepsilon_F/k_B$  to  $T \gg \varepsilon_F/k_B$ .

*Note:* The calculations you are asked to do here are precisely analogous to the calculations in the Lectures, which were done for the non-relativistic limit and so used a different relationship  $\varepsilon(k)$  between energy and wave number. This relationship is the only difference for the ultra-relativistic case — you will have to track down through the standard calculation how things are modified as a result.

## 7.2 Degenerate Bose Gas in 2D.

(a) Show that Bose condensation does not occur in 2D.

*Hint.* The integral you will get when you write the formula for  $N$  is doable in elementary functions. You should find that that  $N \propto \ln(1 - e^{\beta\mu})$ .

(b) Calculate the chemical potential as a function of  $n$  and  $T$  in the limit of small  $T$ . Sketch  $\mu(T)$  from small to large  $T$ .

(c) Show that the heat capacity (at constant area) is  $C \propto T$  at low temperatures and sketch  $C(T)$  from small to large  $T$ .

*Note:* The 2D calculations you are asked to do here are again precisely analogous to the 3D calculations in the lectures. The challenge is to track down how the switch from 3D to 2D affects things and so figure out why the condensation phenomenon does not occur (to do this, it will be useful also to work through the 3D calculation to see why it does occur in 3D).

## Non-relativistic Fermi Gases at Zero Temperature

7.3 Calculate the Fermi energies  $\varepsilon_F$  (in units of eV) and the corresponding Fermi temperatures  $T_F$  for:

(a) Liquid  $^3\text{He}$  (density  $0.0823 \text{ g cm}^{-3}$ ).

(b) Electrons in aluminium (valence 3, density  $2.7 \text{ g cm}^{-3}$ ).

(c) Neutrons in the nucleus of  $^{16}\text{O}$ . The radius  $r$  of a nucleus scales roughly as  $r \approx 1.2A^{1/3} \times 10^{-15} \text{ m}$ , where  $A$  is the atomic mass number.

7.4 (i) Consider a system where  $N$  electrons are constrained to move in two dimensions in a region of area  $A$ . What is the density of states for such a system? Obtain an expression for the Fermi energy of such a system as a function of the surface density  $n = N/A$ .

(ii) The electrons in a GaAs/AlGaAs heterostructure (this just means they act as though they are in 2D!) have a density of  $4 \times 10^{11} \text{ cm}^{-2}$ . The electrons act as free particles, but their interaction with the lattice means that they “appear” to have a mass of only 15% of their normal mass (don’t worry about this — this property is something you will come across in the Solid State course). What is the Fermi energy of the electrons?

(iii) Derive an expression for the density of states and Fermi energy for electrons confined in 1D.

(iv) There are certain long-chain molecules which contain mobile electrons. The electrons can move freely along the chain, and the system is a 1D organic conductor, with  $n$  electrons per unit length. A typical molecule of this type has a spacing of  $2.5 \text{ \AA}$  between the atoms that donate electrons, and “on average” each atom donates 0.5 electrons. What is the Fermi energy of this system?

## Stability of Stars

7.5 A solar-mass star ( $M_\odot = 2 \times 10^{30}$  kg) will eventually run out of nuclear fuel (all the fusion processes stop). At this point it will collapse into a white dwarf, and comprise a degenerate electron gas (i.e. one that obeys quantum statistics) with the nuclei neutralizing the charge and providing the gravitational attraction. The radius of the star can be found by balancing the gravitational energy with the energy of the electrons. The electrons can, to a good approximation, be treated as though  $T = 0$  (because, as we shall find, the Fermi energy is very large). The real calculation of this problem is quite sophisticated, and we are only going to use a very crude method to illustrate the basic physics.

(i) Assume a star of mass  $M$  and radius  $R$  is of uniform density (clearly this will not be the case in reality — and the next best method uses a pressure balance equation — but we are going to do the easiest calculation that gets answers in the right ball park). Show that the gravitational potential energy of the star is

$$U_{\text{grav}} = -\frac{3GM^2}{5R}, \quad (5)$$

where  $G$  is the gravitational constant. [Hint: “build” the star up out of spherical shells].

(ii) Assume that the star contains equal numbers of electrons, protons, and neutrons. If the electrons can be treated as being non-relativistic, show that the total energy of the degenerate electrons is given by

$$U_{\text{electrons}} = 0.0088 \frac{h^2 M^{5/3}}{m_e m_p^{5/3} R^2}, \quad (6)$$

where the mass of a neutron or proton is  $m_p$ .

(iii) The white dwarf will have a radius,  $R$ , that minimizes the total energy. Sketch  $U_{\text{total}}$  as a function of  $R$ , and derive an expression for the equilibrium radius  $R(M)$ .

(iv) Show that the equilibrium radius for a solar-mass white dwarf is of order the radius of the earth.

(v) Evaluate the Fermi energy. Do you think we were correct in treating the electrons as being non-relativistic?

7.6 (i) If the electrons in the white dwarf considered in the previous question were relativistic, show that the total energy of the electrons in the star would scale as  $R^{-1}$  rather than  $R^{-2}$  as in the non-relativistic case.

(ii) If the electrons are relativistic, the star is no longer stable and will collapse further. This will happen when the average energy of an electron is of order its rest mass. Above what mass would you expect a white dwarf to be unstable? (This limit is called the Chandrasekhar limit, and was first derived by him when he was aged 19, during his voyage from India to England — it was published in 1931).

7.7 A white dwarf with a mass above the Chandrasekhar limit collapses to such a high density that the electrons and protons react to form neutrons (+neutrinos): the star comprises neutrons only, and is called a *neutron star*.

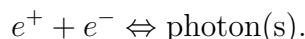
(i) Using the same methods as in the two previous questions, find the mass-radius relationship of a neutron star, assuming the neutrons are non-relativistic.

(ii) What is the radius of a neutron star of 1 solar mass?

(iii) Again, if the average energy of the neutrons becomes relativistic, the star will be unstable. When a neutron star collapse occurs, a black hole is formed. Make an *estimate* of the critical mass of a neutron star.

### Further Applications of Quantum Statistics

7.8 *Pair Production*. At relativistic temperatures, the number of particles can stop being a fixed number, with production and annihilation of electron-positron pairs providing the number of particles required for thermal equilibrium. The reaction is



(a) What is the condition of “chemical” equilibrium for this system?

(b) Assume that the numbers of electrons and positrons are the same (i.e., ignore the fact that there is ordinary matter and, therefore, a surplus of electrons). This allows you to assume that the situation is fully symmetric and the chemical potentials of electrons and positrons are the same. What are they equal to? Hence calculate the density of electrons and positrons  $n^\pm$  as a function of temperature, assuming  $k_B T \gg m_e c^2$ . You will need to know that

$$\int_0^\infty \frac{dx x^2}{e^x + 1} = \frac{3}{2} \zeta(3), \quad \zeta(3) \approx 1.202$$

(see, e.g., Landau & Lifshitz §58 for the derivation of this formula).

(c) To confirm an *a priori* assumption you made in (b), show that at ultrarelativistic temperatures, the density of electrons and positrons you have obtained will always be larger than the density of electrons in ordinary matter. This will require you to come up with a simple way of estimating the upper bound for the latter.

(d\*) Now consider the non-relativistic case,  $k_B T \ll m_e c^2$ , and assume that temperature is also low enough for the classical (non-degenerate) limit to apply. Let the density of electrons in matter, without the pair production, be  $n_0$ . Show that the density of positrons due to spontaneous pair production, in equilibrium, is exponentially small:

$$n^+ \approx \frac{4}{n_0} \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^3 e^{-2m_e c^2 / k_B T}.$$

*Hint.* Use the law of mass action. Note that you can no longer assume that pairs are more numerous than ordinary electrons. Don't forget to reflect in your calculation the fact that the energy cost of producing an electron or a positron is  $m_e c^2$ .

7.9 (\*) *Paramagnetism of a Degenerate Electron Gas (Pauli Magnetism)*. Consider a fully degenerate non-relativistic electron gas in a weak magnetic field. Since the electrons have two spin states (up and down), take the energy levels to be

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} \pm \mu_B B,$$

where  $\mu_B = e\hbar/2m_e c$  is the Bohr magneton (in cgs-Gauss units). Assume the field to be sufficiently weak so that  $\mu_B B \ll \varepsilon_F$ .

(a) Show that the magnetic susceptibility of this system is

$$\chi = \left( \frac{\partial M}{\partial B} \right)_{B=0} = \frac{3^{1/3}}{4\pi^{4/3}} \frac{e^2}{m_e c^2} n^{1/3},$$

where  $M$  is the magnetisation (total magnetic moment per unit volume) and  $n$  density (the first equality above is the definition of  $\chi$ , the second is the answer you should get).

*Hint.* Express  $M$  in terms of the grand potential  $\Phi$ . Then use the fact that energy enters the Fermi statistics in combination  $\varepsilon - \mu$  with the chemical potential  $\mu$ . Therefore, in order to calculate the individual contributions from the spin-up and spin-down states to the integrals over single-particle states, we can use the unmagnetised formulae with  $\mu$  replaced by  $\mu \pm \mu_B B$ , viz., the grand potential, for example, is

$$\Phi(\mu, B) = \frac{1}{2} \Phi_0(\mu + \mu_B B) + \frac{1}{2} \Phi_0(\mu - \mu_B B),$$

where  $\Phi_0(\mu) = \Phi(\mu, B = 0)$  is the grand potential in the unmagnetised case. Make sure to take full advantage of the fact that  $\mu_B B \ll \varepsilon_F$ .

(b) Show that in the classical (non-degenerate) limit, the above method recovers Curie's law. Sketch  $\chi$  as a function of  $T$ , from very low to very high temperature.

(c\*) Show that at  $T \ll \varepsilon/k_B$ , the finite-temperature correction to  $\chi$  is quadratic in  $T$  and negative (i.e.,  $\chi$  goes down as  $T$  increases).

### Thermal radiation

7.10 Thermal radiation can be treated thermodynamically as a gas with internal energy  $U = u(T)V$ , pressure  $p = u/3$  and chemical potential  $\mu = 0$ . Starting from the fundamental equation  $dU = TdS - pdV + \mu dN$ , show that

(i) the energy density  $u \propto T^4$ ,

(ii) the temperature  $T \propto V^{-1/3}$  in an adiabatic expansion.

The Universe is filled uniformly with radiation called the cosmic microwave background (CMB) which is left over from an early stage of development when the Universe contained a hot dense plasma of electrons and baryons. The CMB became thermally *decoupled* from the plasma when the Universe was very young, and since then has expanded adiabatically. The temperature of the CMB is currently 2.73 K, and the *cosmic scale factor* which describes the relative expansion of the Universe is approximately 1,100 times larger today than it was at the time of decoupling. Determine the temperature of the Universe at the time of decoupling.

- 7.11 Outline the steps leading to the formula for the number of photons with angular frequencies between  $\omega$  and  $\omega + d\omega$  in blackbody radiation at a temperature  $T$ :

$$n(\omega)d\omega = 2 \times \frac{V}{2\pi^2 c^3} \frac{\omega^2 d\omega}{e^{\hbar\omega/k_B T} - 1}.$$

Show that  $n(\omega)$  has a peak at a frequency given by  $\omega = 1.59k_B T/\hbar$ . Show further that the spectral energy densities  $u_\lambda$  and  $u_\omega$  peak at  $\lambda_{\max} = hc/(4.97k_B T)$  and  $\omega_{\max} = 2.82k_B T/\hbar$ , respectively.

- 7.12 (i) The gas pressure at the centre of the Sun is  $4 \times 10^{11}$  atmospheres, and the temperature is  $2 \times 10^7$  K. Estimate the radiation pressure and show that it is very small compared with the gas pressure.
- (ii) The surface temperature of the Sun is 5,700 K, and the spectrum of radiation it emits has a maximum at a wavelength of 510 nm. Estimate the surface temperature of the North Star, for which the corresponding maximum is 350 nm.
- (iii) Assuming the Sun (radius  $6.955 \times 10^8$  m) emits radiation as a black body, calculate the solar power incident on a thin black plate of area  $1 \text{ m}^2$  facing the Sun and at a distance of 1 Astronomical Unit ( $= 1.496 \times 10^{11}$  m) from it. Find the temperature of the plate given that it emits radiation from both surfaces. Neglect any radiation incident on the surface of the plate facing away from the Sun.

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## PROBLEM SET 8: Real Gases, Expansions and Phase Equilibria

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Problem set 8 can be covered in 1 tutorial. The relevant material will be done in lectures by the end of week 8 of Hilary Term. Starred questions (\*) are harder. Revision questions are designed to build on the understanding of Statistical Mechanics developed in the two previous problem sets.

### Real gases

8.1 A gas obeys the equation  $p(V - b) = RT$  and has  $C_V$  independent of temperature. Show that (a) the internal energy is a function of temperature only, (b) the ratio  $\gamma = C_p/C_V$  is independent of temperature and pressure, (c) the equation of an adiabatic change has the form  $p(V - b)^\gamma = \text{constant}$ .

8.2 Dieterici's equation of state for 1 mole is

$$p(V - b) = RTe^{-a/RTV}. \quad (7)$$

(a) Show that the critical point is specified by

$$T_c = a/4Rb; \quad V_c = 2b; \quad p_c = a/4e^2b^2.$$

(b) Show that equation (7) obeys a *law of corresponding states*, i.e. show that it can be written in reduced units as

$$\tilde{p}(2\tilde{V} - 1) = \tilde{T} \exp \left[ 2 \left( 1 - \frac{1}{\tilde{T}\tilde{V}} \right) \right],$$

where  $\tilde{p} = p/p_c$ ,  $\tilde{T} = T/T_c$ ,  $\tilde{V} = V/V_c$ .

### Real gas expansions

8.3 Explain why enthalpy is conserved in a Joule–Kelvin process. Show that the Joule–Kelvin coefficient may be written

$$\mu_{\text{JK}} = \left( \frac{\partial T}{\partial p} \right)_H = \frac{1}{C_p} \left[ T \left( \frac{\partial V}{\partial T} \right)_p - V \right].$$

The equation of state for helium gas may be expressed as a virial expansion

$$pV = RT \left( 1 + \frac{B}{V} + \dots \right)$$

in which  $B$  is a function of temperature only. The table below gives some values of  $B$  for 1 mole of helium. Determine the Boyle temperature and the inversion temperature.



Temperature (K)	10	20	30	40	50	60	70
B (cm <sup>3</sup> mol <sup>-1</sup> )	-23.3	-4.0	2.4	5.6	7.6	8.9	9.8

8.4 For a van der Waals gas, show that

$$\lim_{p \rightarrow 0} \mu_{\text{JK}} = \frac{1}{C_p} \left( \frac{2a}{RT} - b \right) \quad \text{and} \quad T_i^{\text{max}} = \frac{2a}{Rb},$$

where  $T_i^{\text{max}}$  is the maximum inversion temperature.

8.5\* Prove that the equation of the inversion curve of a Dieterici gas is, in reduced units,

$$\tilde{p} = (8 - \tilde{T}) \exp \left( \frac{5}{2} - \frac{4}{\tilde{T}} \right),$$

and sketch it in the  $\tilde{p}$ - $\tilde{T}$  plane. Hence, show that the maximum inversion temperature is  $T_i^{\text{max}} = 2a/(Rb)$ .

### Phase equilibria

8.6 When lead is melted at atmospheric pressure the melting point is 327.0°C, the density decreases from  $11.01 \times 10^3$  to  $10.65 \times 10^3$  kg m<sup>-3</sup> and the latent heat is 24.5 kJ kg<sup>-1</sup>. Estimate the melting point of lead at a pressure of 100 atm.

8.7 Some tea connoisseurs claim that a good cup of tea cannot be brewed with water at a temperature less than 97°C. Assuming this to be the case, is it possible for an astronomer, working on the summit of Mauna Kea in Hawaii (elevation 4194 m) where the air pressure is 615 mbar, to make a good cup of tea without the aid of a pressure vessel?

[Latent heat of vaporisation of water = 40.7 kJ mol<sup>-1</sup>.]

8.8 (a) Show that the temperature dependence of the latent heat of vapourisation  $L$  of an incompressible liquid is given by the following expression:

$$\frac{dL}{dT} = \frac{L}{T} + \Delta C_p - \frac{L}{V_{\text{vap}}} \left( \frac{\partial V_{\text{vap}}}{\partial T} \right)_p,$$

where  $\Delta C_p = C_{p,\text{vap}} - C_{p,\text{liq}}$ .

(b) Treating the vapour as an ideal gas, and assuming  $\Delta C_p$  is independent of temperature, show that  $L = \Delta C_p T + L_0$ .

(c) Show further that when the saturated vapour is expanded adiabatically, some liquid condenses out if

$$C_{p,\text{liq}} + T \frac{d}{dT} \left( \frac{L}{T} \right) < 0.$$

[Hint: For condensation, what is the condition on  $\left( \frac{\partial p}{\partial T} \right)_S$  in relation to the gradient of the liquid–vapour phase boundary in the  $p$ - $T$  plane?]

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## REVISION QUESTIONS on Statistical Mechanics

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*The purpose of these questions is not to provide an exam- or collection-style experience (for which you can use past exam papers) but to give you an opportunity to try your hand at some new calculations and thus find out whether you have a working understanding of the physics and the techniques that we have learned.*

R.1 *Heat Capacity of Metals.* The objective of this question is to find at what temperature the heat capacity of the electron gas in a metal dominates over the heat capacity associated with the vibrations of the crystal lattice.

(a) Calculate the heat capacity of electrons in aluminium as a function of temperature for  $T \ll T_F$ .

(b) To estimate the heat capacity due to the vibrations of the lattice, you will need to use the so-called Debye model. Derive it from the results you obtained in PS-7 via the following assumptions.

The vibrations of the lattice can be modelled as sound waves propagating through the metal. These in turn can be thought of as massless particles (“phonons”) with energies  $\varepsilon = \hbar\omega$  and frequencies  $\omega = c_s k$ , where  $c_s$  is the speed of sound in a given metal and  $k$  is the wave number (allowed wave numbers are set by the size of the system, as usual). Thus, the statistical mechanics for the phonons is the same as for photons, with two exceptions: (i) they have 3 possible polarisations in 3D (1 longitudinal, 2 transverse) and (ii) the wave number cannot be larger, roughly, than the inverse spacing of the atoms in the lattice (do you see why this makes sense?).

Given these assumptions,

- derive an expression for the density of states  $g(\varepsilon)$  (or  $g(\omega)$ );
- derive an expression for the mean energy of a slab of metal of volume  $V$ ;
- figure out the condition on temperature  $T$  that has to be satisfied in order for it to be possible to consider the maximum wave number effectively infinite;
- calculate the heat capacity in this limit as a function of  $T$  (you may need to use the fact that  $\int_0^\infty dx x^3/(e^x - 1) = \pi^4/15$ )

*Hint.* You already did all the required maths in Q7.1, so all you need is to figure out how to modify it to describe the phonon gas.

(c) Roughly at what temperature does the heat capacity of the electrons in aluminium become comparable to that of the lattice?

[You may need the density of atoms and electrons in Al — see Q7.3(b). The speed of sound in Al is  $c_s \approx 6000$  m/s. You may find it convenient to define the Debye temperature  $\Theta_D = \hbar c_s (6\pi^2 n)^{1/3} / k_B$ , where  $n$  is the number density of the metal. This is the temperature associated with the maximal wave number in the lattice, which Debye defined by stipulating that the total number of possible phonon modes was equal to 3 times the number of atoms:  $\int_0^{k_{\max}} dk g(k) = 3N$ . For Al,  $\Theta_D = 394$  K.]

- R.2 *Low Energy Levels in Degenerate Bose Gas.* In a degenerate Bose gas, the lowest energy level (particle energy  $\varepsilon_0 = 0$ ) is macroscopically occupied, in the sense that its occupation number  $\bar{n}_0$  is comparable with the total number of particles  $N$ . Is the first energy level (particle energy  $\varepsilon_1$ , the next one above the lowest) also macroscopically occupied? In order to answer this question, estimate the occupation number of the first level and show that  $\bar{n}_1 \propto N^{2/3}$ . Comment on the significance of this result: do the particles in the first level require special consideration as a condensate the same way the zeroth-level ones did?
- R.3 *Paramagnetism of Degenerate Bose Gas.* Consider bosons with spin 1 in a weak magnetic field, with energy levels

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} - 2\mu_B s_z B, \quad s_z = -1, 0, 1,$$

where  $\mu_B = e\hbar/2m_e c$  is the Bohr magneton (in cgs-Gauss units).

- (a) Derive an expression for the magnetic susceptibility of this system. Show that Curie's law ( $\chi \propto 1/T$ ) is recovered in the classical limit.
- (b) What happens to  $\chi(T)$  as the temperature tends to the critical Bose-Einstein condensation temperature from above ( $T \rightarrow T_c + 0$ )? Sketch  $\chi(T)$ .
- (c) At  $T < T_c$  and for a given  $B$ , which quantum state will be macroscopically occupied? Taking  $B \rightarrow +0$  (i.e., infinitesimally small), calculate the spontaneous magnetisation of the system,  $M_0(n, T) = \lim_{B \rightarrow 0} M(n, T, B)$ , as a function of  $n$  and  $T$ . Explain why the magnetisation is non-zero even though  $B$  is vanishingly small. Does the result of (b) make sense in view of what you have found?

- R.4 *Creation/Annihilation of Matter.* When the number of particles  $N$  in an ideal gas is fixed, its chemical potential  $\mu$  is determined implicitly from an equation that relates  $N$  to  $\mu$ , the gas volume  $V$ , its temperature  $T$ , and the spin  $s$  and mass  $m$  of the particles. Now, instead of fixing the number of particles, let us include them into the energy budget of our system (energy cost of making a particle is  $mc^2$ ). How must the formula for  $N$  be modified?

Using the equation you have obtained, calculate the number density of an ideal gas in equilibrium, at room temperature. Does this result adequately describe the room you are sitting in? If not, why do you think that is?

- R.5 (\*) *Entropy of Fermi and Bose Gases out of Equilibrium.* In this question, we will learn how to construct the statistical mechanics for quantum ideal gases directly in terms of occupation numbers. In the spirit of Gibbs, consider an ensemble of  $\mathcal{N}$  copies of our system (gas in a box). Let  $N_i$  be the number of particles that are in the single-particle microstate  $i$  across this entire set of copies. Then the average occupation number of  $i$  per copy is  $\bar{n}_i = N_i/\mathcal{N}$ . The (Boltzmann) entropy of the whole ensemble of copies associated with a given assignment  $(N_1, N_2, \dots, N_i, \dots)$  of particles to microstates is  $S_B = \ln \Omega_{\mathcal{N}}(N_1, N_2, \dots)$ , where  $\Omega_{\mathcal{N}}$  is the number of ways in which such an assignment can be achieved. Then the Gibbs entropy of the set of occupation numbers  $(\bar{n}_1, \bar{n}_2, \dots, \bar{n}_i, \dots)$  will be  $S_G(\bar{n}_1, \bar{n}_2, \dots) = S_B/\mathcal{N}$  in the limit  $\mathcal{N} \rightarrow \infty$  and all

$N_i \rightarrow \infty$  while keeping  $\bar{n}_i$  constant. This is very similar to the construction in the Lectures (§8.1.3) of the Gibbs entropy of a set of probabilities of microstates, except we now have different rules about how many particles can be in any given microstate  $i$ :

— for fermions, each copy of the system in the ensemble can have only one or none of the  $N_i$  particles available for each state  $i$ ;

— for bosons, the  $N_i$  particles in each state  $i$  can be distributed completely arbitrarily between the  $\mathcal{N}$  copies.

(a) Prove that the Gibbs entropy, as defined above, will be

$$S_G = - \sum_i [\bar{n}_i \ln \bar{n}_i \pm (1 \mp \bar{n}_i) \ln(1 \mp \bar{n}_i)],$$

where the upper sign is for fermions and the lower for bosons.

*Hint.* Observe that  $\Omega_{\mathcal{N}}(N_1, N_2, \dots) = \prod_i \Omega_i$ , where  $\Omega_i$  is the number of ways to assign the  $N_i$  particles available for the microstate  $i$  to the  $\mathcal{N}$  copies in the ensemble.

Note that this formula certainly holds for Fermi and Bose gases *in equilibrium* as derived in the Lectures (convince yourself that this is the case), but you have shown now is that it also holds *out of equilibrium*, i.e., for arbitrary occupation numbers.

(b) Considering a system with fixed average energy and number of particles and maximising  $S_G$ , derive from the above the Fermi-Dirac and Bose-Einstein formulae for the mean occupation numbers in equilibrium.

(c) Devise a way to treat a classical gas by the same method.