Statistical Physics

Oxford Physics

Second year physics course

Dr A. A. Schekochihin and Prof. A. Boothroyd
(with thanks to Prof. S. J. Blundell)

Problem Set 6

Introductory Note (from A. Schekochihin)

Lectures

Welcome to the second half of the Statistical Physics course. In HT, we will cover some Further Statistical Mechanics (Grand Canonical Ensemble, Multicomponent Systems and — finally! — Quantum Gases; 7 lectures, A. Schekochihin) and Thermodynamics of Real Gases and Phase Transitions (as well as some other fun things, time permitting; 7 lectures, A. Boothroyd).

Again, there is no set text, so do attend lectures and read my lecture notes. This said, the books by Blundell & Blundell, Schrödiger, and Landau & Lifshitz ("Statistical Physics") remain my favorite sources of inspiration, but I urge you to find your own by exploring the Reading List and beyond. One book that was not on the Reading List that I recommend highly is C. Kittel, "Elementary Statistical Physics" (Dover 2004, very cheap on Amazon).

Do please ask questions during the lectures or by email (to `a.schekochihin1@physics.ox.ac.uk`*) if anything is unclear.*

Problem Sets

Problem Set 6 covers grand canonical ensemble, chemical potential and related topics and Fermi gases at zero temperature. This material is in Lectures 1-5. You should be ready to start this Problem Set at the end of Week 2.

Problem Set 7 will cover the rest of the material from my part of the course (Lectures 5-7) plus photon gas and black-body radiation (Lectures 8-9 by Prof. Boothroyd). You should be ready to start working on it at the end of Week 3.

Problem Set 8 will cover the material of Lectures 10-14 by Prof. Boothroyd (real gases, phase transitions, inversion curves etc.) You should be ready to start working on it at the end of Week 5.

Both Prof. Boothroyd and I will be grateful for any feedback from you.

Some Useful Constants

Boltzmann's constant	$k_{\rm B}$	$1.3807 \times 10^{-23}\,{\rm J\,K^{-1}}$
Proton rest mass	$m_{\rm p}$	$1.6726 \times 10^{-27}\,{\rm kg}$
Avogadro's number	$N_{\rm A}$	$6.022 \times 10^{23}\,{\rm mol^{-1}}$
Standard molar volume		$22.414 \times 10^{-3}\,{\rm m^3\,mol^{-1}}$
Molar gas constant	R	$8.315\ {\rm J\,mol^{-1}\,K^{-1}}$
1 pascal (Pa)		$1\,{\rm N\,m^{-2}}$
1 standard atmosphere		$1.0132 \times 10^5\,{\rm Pa}\,({\rm N\,m^{-2}})$
1 bar (= 1000 mbar)		$10^5\,{\rm N\,m^{-2}}$

PROBLEM SET 6: Grand Canonical Ensemble and Fermi Gases at Zero Temperature

Note that Questions 6.3, 6.4 and 6.6 will help you with understanding the conceptual foundations of the general theory covered in lectures (and are mostly bookwork). If you want to solve some practical problems first, leave those questions to the end.

Grand Canonical Distribution and Chemical Potential

6.1 *Grand Canonical Distribution and Chemical Potential for Classical Ideal Gas.*

a) Starting from the grand canonical distribution, show that the chemical potential for classical ideal gas is

$$\mu = -k_B T \ln \frac{Z_1}{\overline{N}},$$

where Z_1 is the single-particle partition function and $\overline{N}$ is the mean number of particles in the system.

b) Using this result, prove that the equation of state is $p = nk_B T$, where the mean number density is $n = \overline{N}/V$.

c) Using the results above, for a monatomic ideal gas (molecular mass m), derive an expression for μ as a function of pressure p and temperature T.

6.2 *Isothermal Atmosphere.* Now consider a classical ideal gas in a uniform gravitational field (acceleration of gravity g in the direction z). Assume this gas is in thermal and particle equilibrium. Use the results of the previous question to show that the number density in such a situation is

$$n(z) = n(0)e^{-mgz/k_B T}.$$

Hint. If you can't solve this question yourself, you will find the solution to it (and to the next one) in the book by C. Kittel, *Elemtary Statistical Physics* (Dover 2004).

6.3 *Particle Number Distribution.*

a) Consider a volume V of classical ideal gas with mean number density $n = \overline{N}/V$. Starting from the grand canonical distribution, show that the probability to find N particles in this volume is a Poisson distribution.

b) Hence show that the mean square fluctuation of particle number around the mean tends to zero as $\overline{N} \to \infty$.

c*) Using your knowledge of probability theory, you can in fact obtain the result of (a) without using statistical mechanics at all. Consider a large system of volume $\mathcal{V}$ containing $\mathcal{N}$ non-interacting particles. Take some fixed subvolume $V \ll \mathcal{V}$. Calculate the probability to find N particles in volume V. Now assume that both $\mathcal{N}$ and $\mathcal{V}$ tend to ∞, but in such a way that the particle number density is fixed: $\mathcal{N}/\mathcal{V} \to n = \text{const}$.

Show that in this limit, the probability to find N particles in volume V (both N and V are fixed, $N \ll \mathcal{N}$) tends to the Poisson distribution whose average is $\langle N \rangle = nV$. This last result is, of course, intuitively obvious, but it is nice to be able to prove it mathematically and even to know with what precision it holds (see part (b) above) — another demonstration that the world is constructed in a sensible way.

Hint. Part (c) involves proving Poisson's limit theorem (not really hard!). You will find inspiration or possibly even the solution in standard probability texts, e.g., Ya. G. Sinai, *Probability Theory: An Introductory Course* (Springer 1992).

6.4 *Microcanonical World 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. If you can't figure it out on your own, you will find the solution in Blundell & Blundell's or Kittel's books.

Multispecies Systems

6.5 *Ionisation-Recombination Equlibrium.* 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

$$H \Leftrightarrow p^+ + e^-$$

(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). We will also assume overall charge neutrality (what does that imply about densities of particles?).

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

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

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

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 χ go up or down as density is decreased? Why? Consider a cloud of hydrogen with $n \sim 1$ cm^{-3}. Roughly at what temperature would it be mostly ionised? This is 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 χ as a function of total gas pressure p and temperature T.

6.6 *Grand Canonical Distribution and Thermodynamics for Multispecies Systems.*

a) Consider a system containing several particle species, indexed by i (for example the H-p-e system from the previous question). Let the system be in contact with the world so its mean energy U and the mean number of particles $\overline{N}_i$ of each species are fixed. Show that the probability of a microstate α for which the energy of the system is E_α and the number of partices of each species contained in it is $N_{i\alpha}$, is

$$p_\alpha = e^{\beta(\Phi - E_\alpha + \sum_i \mu_i N_{i\alpha})},$$

where $\beta = 1/k_B T$, μ_i is the chemical potential of species i, and $\Phi = U - TS - \sum_i \mu_i \overline{N}_i$ is the grand potential.

b) Hence show that energy, Helmholtz free energy and Gibbs free energy satisfy

$$dU = TdS - pdV + \sum_i \mu_i d\overline{N}_i,$$

$$dF = -SdT - pdV + \sum_i \mu_i d\overline{N}_i,$$

$$dG = -SdT + Vdp + \sum_i \mu_i d\overline{N}_i.$$

c) If you knew F as a function of V, T and all $\overline{N}_i$, how would you calculate μ_i? If you then wanted to know μ_i as a function of $p, T, \overline{N}_i$ rather than of $V, T, \overline{N}_i$, what would be the strategy for obtaining such an expression?

d) Prove that $G = \sum_i \mu_i \overline{N}_i$, where μ_i's are functions of p, T and of fractional concentrations $c_i = \overline{N}_i/\overline{N}$, but not of the number of particles $\overline{N} = \sum_i \overline{N}_i$.

Fermi Gases at Zero Temperature

6.7 Calculate the Fermi energies E_F (in units of eV) and the corresponding Fermi temperatures T_F for:

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

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

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

6.8 (i) Show that the mean energy of non-relativistic electrons at absolute zero is $3E_\mathrm{F}/5$, where E_F is the Fermi Energy, and thus the total energy of the system, U, is $3NE_\mathrm{F}/5$.

(ii) Show that the pressure p exerted by this electron gas at absolute zero is given by $p = 2U/3V$.

6.9 (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 2-D!) have a density of $4 \times 10^{11}\,\mathrm{cm}^{-2}$. 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 - again 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 one dimension.

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

6.10 (i) Consider a very, very dense gas of fermions (with n fermions per unit volume). At $T = 0$ the fermions stack up in the quantum states all the way to the Fermi energy. If the gas is extremely dense (as in dense stars – see below), this energy can be so large that the velocity of the vast majority of the fermions becomes relativistic ($E \approx pc$). Show that under these circumstances the Fermi energy of the system is

$$E_{\mathrm{F}} = hc\left(\frac{3n}{8\pi}\right)^{1/3} \tag{1}$$

(ii) Show that the energy density u of this relativistic fermion gas is $3nE_{\mathrm{F}}/4$.

6.11 A solar-mass star ($M_{\odot} = 2 \times 10^{30}\,\mathrm{kg}$) 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

$$U_{\mathrm{grav}} = -\frac{3GM^2}{5R}, \tag{2}$$

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

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

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_{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?

6.12 (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).

6.13 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 questions 4.6 and 4.7, 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.