Statistical Physics

Oxford
Physics

Second year physics course

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

Problem Sets 1 & 2

Introductory Note (from A. Schekochihin)

Lectures

I will teach the first 12 lectures of the 22 in Michaelmas Term. My lectures will cover Kinetic Theory and Foundations of Statistical Mechanics. Professor Andrew Boothroyd will take over in Week 5 and teach Thermodynamics (based on Statistical Mechanics) and further Statistical Mechanics of simple systems. In Hilary Term, we will cover Statistical Mechanics of Quantum Gases (AS, 6 lectures) and Thermodynamics of Real Gases and Phase Transitions (AB, 8 lectures).

I will not be following any single book, so I advise you to attend lectures and **take notes** *(a very useful skill!). I will make my hand-written notes available, but they come with no guarantee of legibility and are not intended as the sole source for you to learn from.*

Of the books on the Reading List, I particularly like Blundell & Blundell, Pauli, and Landau & Lifshitz (Vols. 5 and 10 of the Course of Theoretical Physics — these are quite advanced, you may find them a hard read). This said, I urge you to explore the literature on the Reading List and beyond — how to find things out independently is the most important skill one learns at a university.

The course will be quite mathematical, probably more so than you have so far experienced. But physics is a mathematical subject and there is no point pretending otherwise. Our ability to describe Nature mathematically and predict things on this basis is one of the most impressive achievements of human civilisation. So become civilised!

Please ask questions during the lectures or by email (to `a.schekochihin1@physics.ox.ac.uk`*) if anything is unclear. This is the first time this course is taught by me and Andrew and the first time (at Oxford, as far as I know) it is taught this way, with 20th-century Statistical Mechanics coming before 19th-century Thermodynamics. So I will appreciate real-time feedback.*

Problem Sets

There will be 5 problem sets in Michaelmas, the 5th of which is vacation work.

Problem Set 1 covers the material of Lectures 1-2. Start it at the end of Week 1.

Problem Set 2 covers the material of Lectures 3-6. Start working on it in Week 3 (note that this problem set is, in my estimation, harder than Problem Set 2, so give yourself more time!).

Problem Set 3 will be circulated soon. It covers the material of Lectures 7-12. Start working on it in Week 5.

Problem Sets 4 and 5 will be circulated by Professor Boothroyd.

Questions that may prove quite difficult — probably more so than anything you are likely to face in the exam — are marked with a star (*). Try them if you like a challange. Skip them if you are not feeling enthusiastic or are running out of time.

Some Useful Constants

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

PROBLEM SET 1: Particle Distributions

1.1 *This question illustrates the sensivity of many-body systems to small perturbations of initial conditions.*

Imagine we are observing the motion of frictionless, elastically colliding billiard balls. Using sensible assumptions about the size of things, show that, if someone enters the room, small deflections of the balls due this visitor's gravitational pull will completely alter their trajectories after just ~ 10 collisions. The value of the gravitational constant is $G = 6.6726 \times 10^{-11}$ m^{3}s^{-2}kg^{-1}.

Hint: For simplicity, consider all balls but one fixed in place and then analyse the motion of one ball. Don't attempt a precise calculation — this question is about quick back-of-the-envelope estimates.

1.2 (*) *This question illustrates how probabilities are calculated and how well averages describe reality for large numbers of events.*

If I flip a coin N times, demonstrate that the number of ways, W, that I can get exactly half of them heads and half of them tails is:

$$\frac{N!}{(\frac{N}{2}!)^2}. \tag{1}$$

Let us now work out the probability of getting nearly, but not quite, $N/2$ heads. Write down the number of ways in which I can get $(\frac{N}{2} - m)$ heads and $(\frac{N}{2} + m)$ tails. Show that the number of ways of doing this gets to be half of the value of getting exactly 0.5 heads and 0.5 tails when

$$(\frac{N}{2} - m)!\,(\frac{N}{2} + m)! = 2(\frac{N}{2}!)^2, \tag{2}$$

and hence, assuming $N \gg m \gg 1$:

$$\left(\frac{N}{2}\right)^m + [1 + 2 + \cdots + m]\left(\frac{N}{2}\right)^{m-1} \approx 2\left[\left(\frac{N}{2}\right)^m - [1 + 2 + \cdots + m]\left(\frac{N}{2}\right)^{m-1}\right]. \tag{3}$$

Noting that $1 + 2 + \cdots m \approx m^2/2$, show this leads to

$$m \propto N^{1/2}, \tag{4}$$

and the fractional width therefore goes as $N^{-1/2}$. Comment on this result for $N \approx 10^{23}$.

Calculating Averages

1.3 a) If θ is a continuous random variable which is uniformly distributed between 0 and π, write down an expression for $p(\theta)$. Hence find the value of the following averages:

(i) $\langle\theta\rangle$

(ii) $\langle\theta - \frac{\pi}{2}\rangle$

(iii) $\langle\theta^2\rangle$

(iv) $\langle\theta^n\rangle$ (for the case $n \geq 0$)

(v) $\langle\cos\theta\rangle$

(vi) $\langle\sin\theta\rangle$

(vii) $\langle|\cos\theta|\rangle$

(viii) $\langle\cos^2\theta\rangle$

(ix) $\langle\sin^2\theta\rangle$

(x) $\langle\cos^2\theta + \sin^2\theta\rangle$

Check that your answers are what you expect.

b) If particle velocities are distributed isotropically, how are their angles distributed? Is the angle between the velocity vector and a fixed axis distributed uniformly? Why? Answer these questions for the case of 2 and 3 dimensional world.

1.4 a) Consider an isotropic distribution of particle velocities: $f(\mathbf{v}) = g(v)$, where $v = |\mathbf{v}|$ is the particle speed and g some function. In 3D, what is the distribution of the speeds, $\tilde{f}(v)$?

b) Calculate the following averages of velocity components in terms of averages of speed ($\langle v\rangle$, $\langle v^2\rangle$, etc.)

(i) $\langle v_i\rangle$, where $i = x, y, z$

(ii) $\langle|v_i|\rangle$, where $i = x, y, z$

(iii) $\langle v_i^2\rangle$, where $i = x, y, z$

(iv) $\langle v_i v_j\rangle$, where $i, j = x, y, z$ (any index can designate any of the components)

(v) $\langle v_i v_j v_k\rangle$, where $i, j = x, y, z$

You can do them all by direct integration with respect to angles, but think carefully whether this is necessary in all cases. You may be able to obtain the answers in a quicker way by symmetry considerations (being lazy often spurs creative thinking).

Hint for (iv). Here is a smart way of doing this. $\langle v_i v_j\rangle$ is a symmetric rank-2 tensor (i.e., a tensor, or matrix, with two indices). It can only depend on some averages of v because the velocity distribution is isotropic and on constant rank-2 tensors. The only symmetric rank-2 tensor idependent of anything that we can construct is δ_{ij} (Kronecker delta). So it must be that $\langle v_i v_j\rangle = C\delta_{ij}$, where C is some average of speed v, with some numerical coefficient. Can you figure out what C is? Is it the same in a 2D and in a 3D world? This is a much simpler derivation than doing velocity integrals directly, but please feel free to check the result by direct integration.

c*) Calculate $\langle v_i v_j v_k v_l\rangle$, where $i, j, k, l = x, y, z$ (any index can designate any of the components) — in terms of averages of v.

Hint. Doing this by direct integration is *a lot* of work. Generalise the symmetry argument given above: see what rank-4 tensors (i.e., tensors with 4 indices) you can cook up. It turns out that they have to be products of Kronecker deltas, e.g., $\delta_{ij}\delta_{kl}$ (what other combinations are there?). Then $\langle v_i v_j v_k v_l\rangle$ must be a linear combination of these tensors, with coefficients that are some averages of v. By examining the symmetry properties of $\langle v_i v_j v_k v_l\rangle$, work out what these coefficients are (if you have done question b(iv) above, you'll know what to do). How does the answer depend on the dimensionality of the world (2D, 3D)?

1.5 The probability distribution of molecular speeds in a gas in thermal equilibrium is described the Maxwellian distribution (also known as a Maxwell-Boltzmann distribution). It says that a given molecule (mass m) will have a velocity in a 3-dimensional interval $[v_x, v_x + dv_x] \times [v_y, v_y + dv_y] \times [v_z, v_z + dv_z]$ (denoted $d^3\mathbf{v}$) with probability

$$f(\mathbf{v})d^3\mathbf{v} \propto e^{-v^2/v_{\rm th}^2} d^3\mathbf{v},$$

where $v_{\rm th} = \sqrt{2k_BT/m}$ is the "thermal speed," T temperature, k_B Boltzmann's constant, and I have used a proportional sign ($\propto$) because a normalisation constant has been omitted (you can correct for this by dividing any averages you work out by $\int d^3\mathbf{v} f(\mathbf{v})$ — calculate it!).

a) Given the Maxwellian distribution, what is the distribution of particle speeds, $\tilde{f}(v)$? Calculate the mean speed $\langle v \rangle$ and the mean inverse speed $\langle 1/v \rangle$. Show that

$$\langle v \rangle \langle 1/v \rangle = \frac{4}{\pi}.$$

b) Calculate $\langle v^2 \rangle$, $\langle v^3 \rangle$, $\langle v^4 \rangle$, $\langle v^5 \rangle$.

c*) Work out a general formula for $\langle v^n \rangle$. What do you think is larger, $\langle v^{27} \rangle^{1/27}$ or $\langle v^{56} \rangle^{1/56}$? Do you understand why that is?

Hint. Consider separately odd and even n. Use $\int_{-\infty}^{\infty} dx e^{-x^2} = \sqrt{\pi}$. [These things are worked out in Blundell & Blundell, but do try to figure them out yourself!]

Pressure

1.6 Remind yourself how one calculates pressure from a particle distribution function. Let us consider an *anisotropic* system, where there exists one (and only one) special direction in space (call it z), which affects the distribution of particle velocities (an example of such a situation is a gas of charged particles in a straight magnetic field).

a) How many variables does the distribution function now depend on? (Recall that in the isotropic case, it depended only on one, v.) Write down the most general form of the distribution under these symmetries — what is the appropriate transformation of variables from (v_x, v_y, v_z)?

b) What is the expression for pressure $p_\parallel$ (in terms of averages of those new velocity variables) that the gas will exert on a wall perpendicular to the z axis? (It is called $p_\parallel$ because it is due to particles whose velocities have non-zero projections onto the special direction z.) What is $p_\perp$, pressure on a wall parallel to z?

c) Now consider a wall with a normal $\hat{\mathbf{n}}$ at an angle θ to z. What is the pressure on this wall in terms of $p_\parallel$ and $p_\perp$?

Effusion

1.7 a) Show that the number of molecules hitting unit area of a surface per unit time with speeds between v and $v + dv$ and angles between θ and $\theta + d\theta$ to the normal is

$$\frac{1}{2}\, nv\tilde{f}(v)dv\, \sin\theta\cos\theta\, d\theta,$$

where $\tilde{f}(v)$ is the distribution of particle speeds.

b) Show that the average value of $\cos\theta$ for these molecules is $\frac{2}{3}$.

c) Using the results above, show that for a gas obeying the Maxwellian distribution (i.e., the speed distribution $\tilde{f}(v) \propto v^2 e^{-mv^2/2k_\mathrm{B}T}$) the average energy of all the molecules is $\frac{3}{2}k_\mathrm{B}T$, but the average energy of those which hit the surface is $2k_\mathrm{B}T$.

1.8 a) A Maxwellian gas effuses through a small hole to form a beam. After a certain distance from the hole, the beam hits a screen. Let v_1 be the most probable speed of atoms that, during a fixed interval of time, hit the screen. Let v_2 be the most probable speed of atoms situated, at any instant, between the small hole and the screen. Find expressions for v_1 and v_2. Why are these two speeds different?

b) You have calculated the most probable speed (v_1) for molecules of mass m which have effused out of an enclosure at temperature T. Now calculate their mean speed $\langle v\rangle$. Which is the larger and why?

1.9 A vessel contains a monatomic gas at temperature T. Use Maxwell's distribution of speeds to calculate the mean kinetic energy of the molecules.

Molecules of the gas stream through a small hole into a vacuum. A box is opened for a short time and catches some of the molecules. Assuming the box is thermally insulated, calculate the final temperature of the gas trapped in the box.

1.10 *This question requires you to think geometrically.*

a) A gas effuses into a vacuum through a small hole of area A. The particles are then collimated by passing through a very small circular hole of radius a, in a screen a distance d from the first hole. Show that the rate at which particles emerge from the circular hole is $\frac{1}{4}nA\langle v\rangle(a^2/d^2)$, where n is the particle density and $\langle v\rangle$ is the average speed. (Assume no collisions take place after the gas effuses and that $d \gg a$.)

b) Show that if a gas were allowed to leak into an evacuate sphere and the particles condensed where they first hit the surface they would form a uniform coating.

1.11 A closed vessel is partially filled with liquid mercury; there is a hole of area 10^{-7} m^2 above the liquid level. The vessel is placed in a region of high vacuum at 273 K and after 30 days is found to be lighter by 2.4×10^{-5} kg. Estimate the vapour pressure of mercury at 273 K. (The relative molecular mass of mercury is 200.59.)

1.12 A gas is a mixture of H_2 and HD in the proportion 7000:1. As the gas effuses through a small hole from a vessel at constant temperature into a vacuum the composition of the remaining mixture changes. By what factor will the pressure in the vessel have fallen when the remaining mixture consists of H_2 and HD in the proportion 700:1.

(H=hydrogen, D=deuterium)

1.13 (*) In the previous question, you worked out a differential equation for the time evolution of the number density of the gas in the container and then solved it (if that is not what you did, go back and think again). The container was assumed to have constant temperature. Now consider instead a thermally insulated container of volume V with a small hole of area A, containing a gas with molecular mass m. At time $t = 0$, the density in it is n_0 and temperature is T_0. As gas effuses out through a small hole, both density and temperature inside the container will drop. Work out their time dependence, $n(t)$ and $T(t)$ in terms of the quantities given above.

Hint. Teperature is related to the total energy of the particles in the container. Same way you calculated the flux of particles through the hole (leading to density decreasing), you can now also calculate the flux of energy, leading to temperature decreasing. As a result, you will get two differential (with respect to time) equations for two unknowns, n and T. Derive and then integrate these equations (you may find it hard, but it is doable!).

PROBLEM SET 2: Collisions and Transport

Mean Free Path

2.1 Recall the example of billiard balls sensitive to the gravitational pull of a passerby. Consider now a room filled with air. Work out how long it will take for the trajectories of the molecules to be completely altered by the gravitational interaction with a stray electron at the edge of the Universe (ignore all non-A-level physics involved).

2.2 Consider a gas that is a mixture of two species of molecules: type-1 with diameter d_1, mass m_1 and mean number density n_1 and type-2 with diameter d_2, mass m_2 and mean number density n_2. If we let them collide with each other for a while (for how long? answer this after you have solved the rest of the problem), they will eventually settle into a Maxwellian equilibrium and the temperatures of the two species will be the same.

a) What will be the rms speeds of the two species?

b) Show that the combined pressure of the mixture will be $p = p_1 + p_2$ (Dalton's law).

c) What is the cross-section for the collisions between type-1 and type-2 molecules?

d) What is the mean collision rate of type-1 molecules with type-2 molecules?

Hint. You will find the answer in Pauli's book, but do try to figure it out on your own.

2.3 Consider particles in a gas of mean number density n and collisional cross-section σ, moving with speed v (let us pretend they all have the same speed).

a) What is the probability $P(t)$ for a particle to experience *no* collisions up to time t? Therefore, what is the mean time between collisions?

Hint. Work out the probability for a particle not to have a collision between t and $t+dt$. Hence work out $P(t+dt)$ in terms of $P(t)$ and the relevant parameters of the gas. You should end up with a differential equation for $P(t)$, which you can then solve. [You will find this derivation in Blundell & Blundell, but do try to figure it out yourself!]

b) What is the the probability $P(l)$ for a particle to travel a distance l between two collisions? Show that the root mean square free path is given by $\sqrt{2}\lambda$ where λ is the mean free path.

c) What is the most probable free path length?

d) What percentage of molecules travel a distance greater than (i) λ, (ii) 2λ, (iii) 5λ?

2.4 Given that the mean free path in a gas at standard temperature and pressure (S.T.P.) is about 10^3 atomic radii, *estimate* the highest allowable pressure in the chamber of an atomic beam apparatus 10^{-1} m long (if one does not want to lose an appreciable fraction of atoms through collisions).

2.5 A beam of silver atoms passing through air at a temperature of 0°C and a pressure of 1 Nm^{-2} is attenuated by a factor 2.72 in a distance of 10^{-2} m. Find the mean free path of the silver atoms and estimate the effective collision radius.

2.6 Show that particles hitting a plane boundary have travelled a distance $2\lambda/3$ perpendicular to the plane since their last collision, on average.

Conductivity, Viscosity, Diffusion

2.7 Obtain an expression for the thermal conductivity of a gas at ordinary pressures (bookwork). The thermal conductivity of argon (atomic weight 40) at S.T.P. is 1.6×10^{-2} $\mathrm{Wm^{-1}K^{-1}}$. Use this to calculate the mean free path in argon at S.T.P. Express the mean free path in terms of an effective atomic radius for collisions and find the value of this radius. Solid argon has a close packed cubic structure, in which, if the atoms are regarded as hard spheres, 0.74 of the volume of the structure is filled. The density of solid argon is 1.6 g $\mathrm{cm^{-3}}$. Compare the effective atomic radius obtained from this information with the effective collision radius. Comment on the result.

2.8 Define the coefficient of viscosity. Use kinetic theory to show that the coefficient of viscosity of a gas is given, with suitable approximations, by

$$\eta = K\rho\langle v\rangle\lambda$$

where ρ is the density of the gas, λ is the mean free path of the gas molecules, $\langle v\rangle$ is their mean speed, and K is a number which depends on the approximations you make.

In 1660 Boyle set up a pendulum inside a vessel which was attached to a pump which could remove air from the vessel. He was surprised to find that there was no observable change in the rate of damping of the swings of the pendulum when the pump was set going. Explain the observation in terms of the above formula.

Make a rough order of magnitude estimate of the lower limit to the pressure which Boyle obtained; use reasonable assumptions concerning the apparatus which Boyle might have used. [The viscosity of air at atmospheric pressure and at 293 K is 18.2 μN s $\mathrm{m^{-2}}$.]

Explain why the damping is nearly independent of pressure despite the fact that fewer molecules collide with the pendulum as the pressure is reduced.

2.9 Two plane disks, each of radius 5 cm, are mounted coaxially with their adjacent surfaces 1 mm apart. They are in a chamber containing Ar gas at S.T.P. (viscosity 2.1×10^{-5} $\mathrm{N\,s\,m^{-2}}$) and are free to rotate about their common axis. One of them rotates with an angular velocity of 10 rad $\mathrm{s^{-1}}$. Find the couple which must be applied to the other to keep it stationary.

2.10 Measurements of the viscosity, η, of argon gas (^{40}Ar) over a range of pressures yield the following results at two temperatures:

$$\begin{array}{ll} \text{at 500 K} & \eta \approx 3.5\times10^{-5}\ \mathrm{kg\ m^{-1}\ s^{-1}} \\ \text{at 2000 K} & \eta \approx 8.0\times10^{-5}\ \mathrm{kg\ m^{-1}\ s^{-1}} \end{array}$$

The viscosity is found to be approximately independent of pressure. Discuss the extent to which these data are consistent with (i) simple kinetic theory, and (ii) the diameter of the argon atom (0.34 nm) deduced from the density of solid argon at low temperatures.

2.11 a) Argue qualitatively or show from elementary kinetic theory that the coefficient of self-diffusion D, the thermal conductivity κ and the viscosity η of a gas are related via

$$D \sim \frac{\kappa}{c_V} \sim \frac{\eta}{\rho},$$

where c_V is the heat capacity per unit volume ($3nk_B/2$ for ideal monatomic gas) and ρ is the density of the gas.

b*) *This question is an opportunity to check whether you have understood the principle of the derivation of fluid equations (which, however, is non-examinable).*

Starting from the kinetic equation for the distribution function $F^*(t, \mathbf{r}, \mathbf{v})$ of some labelled particle admixture in a gas, derive the self-diffusion equation

$$\frac{\partial n^*}{\partial t} = D\nabla^2 n^*$$

for the number density $n^*(t, \mathbf{r}) = \int d^3\mathbf{v} F^*(t, \mathbf{r}, \mathbf{v})$ of the labelled particles and the expression for the self-diffusion coefficient D. The molecular mass of the labelled particles is m^*. You may assume that the temperature of the unlabelled gas T is uniform, that this ambient gas is static (no mean flows), that the density of the labelled particles is so low that they only collide with the unlabelled particles and that the frequency of these collisions is much larger than the rate of change of any mean quantities. Use the Krook collision operator, assuming that collisions act to relax the distribution of the labelled particles to a Maxwellian F_M^* with density n^* and the same velocity (zero) and temperature T as the ambient unlabelled gas.

Hint. Is the momentum of the labelled particles conserved? You should discover that self-diffusion is related to the mean velocity $\mathbf{u}^*$ of the labelled particles. You can calculate this velocity either directly from $\delta F^* = F^* - F_M^*$ or from the momentum equation for the labelled particles. If you take the second option, you will, in the course of your derivation, also find the result you have known since school: friction force (collisional drag exerted on labelled particles by the ambient population) is proportional to velocity — what is the proportionality coefficient? This, by the way, is the "Aristotelian equation of motion" — Aristotle thought force was proportional to velocity. It took a while for someone to figure out the more general formula.

Heat Diffusion Equation

2.12 a) A cylindrical wire of thermal conductivity κ, radius a and resistivity ρ uniformly carries a current I. The temperature of its surface is fixed at T_0 using water cooling. Show that the temperature $T(r)$ inside the wire at radius r is given by

$$T(r) = T_0 + \frac{\rho I^2}{4\pi^2 a^4 \kappa}(a^2 - r^2).$$

b) The wire is now placed in air at temperature $T_{\rm air}$ and the wire loses heat from its surface according to Newton's law of cooling (so that the heat flux from the surface of the wire is given by $\alpha(T(a) - T_{\rm air})$ where α is a constant. Find the temperature $T(r)$.

2.13 A microprocessor has an array of metal fins attached to it, whose purpose is to remove heat generated within the processor. Each fin may be represented by a long thin cylindrical copper rod with one end attached to the processor; heat received by the rod through this end is lost to the surroundings through its sides.

The internal energy density ε of the rod is related to its temperature T via $\varepsilon = \rho c_m T$, where ρ is mass density, c_m the specific (i.e., per unit mass) heat capacity of the metal (not $3k_B/2m$; you will learn what it is later in the course). Show that the temperature $T(x,t)$ at location x along the rod at time t obeys the equation

$$\rho c_m \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} - \frac{2}{a} R(T),$$

where a is the radius of the rod, and $R(T)$ is the rate of heat loss per unit area of surface at temperature T.

The surroundings of the rod are at temperature T_0. Assume that $R(T)$ has the form (Newton's law of cooling)

$$R(T) = A(T - T_0).$$

In the steady state:

(a) obtain an expression for T as a function of x for the case of an infinitely long rod whose hot end has temperature $T_{\rm m}$;

(b) show that the heat that can be transported away by a long rod of radius a is proportional to $a^{3/2}$, provided that A is independent of a.

In practice the rod is not infinitely long. What length does it need to have for the results above to be approximately valid? The radius of the rod is 1.5 mm.

[The thermal conductivity of copper is $380\,\mathrm{W\,m^{-1}\,K^{-1}}$. The cooling constant $A = 250\,\mathrm{W\,m^{-2}\,K^{-1}}$.]