Statistical Physics

Second year physics course

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(with thanks to Prof. S. J. Blundell)

Problem Set 3: Kinetic Theory

Introductory Note from A. Schekochihin

Lectures

In Michaelmas, I will teach Kinetic Theory, after Professor Andrew Boothroyd has covered Basic Thermodyanmics.

I will not be following any single book, so I advise you to attend lectures and **take notes** *(a very useful skill to learn as early as possible!). I will make my hand-written notes available via the course webpage,* `http://www-thphys.physics.ox.ac.uk/people/AlexanderSchekochihin/A1/`*, but they are just that — my hand-written notes for the lectures — and so come with* **no guarantee of legibility or book-level transparency of structure***. I do of course hope that you might find them helpful, but whether you do or not, you must not regard them as the sole source to learn from.*

Oxford has 99 libraries and you are missing out if you have not yet become an avid explorer of the world of books. Learning a subject and making sense of it from a variety of sources is an essential part of high education — and indeed it is part of the thrill of one's intellectual formation to find that you are free to decide whom you believe and what does and doesn't make sense. I will give you reading suggestions, both specific ones based on the Reading List, and others, designed for you to explore the subject laterally or in more depth — but don't stop there, you do not want to be intellectual clones of me, so make your own decisions what to read!

Of the books on the Reading List, I particularly like Blundell & Blundell, Pauli, Schrödinger, and Landau & Lifshitz. The first two are on the undergraduate level, the third does not deal with Kinetic Theory and will become relevant in HT, and "Landaushitz"—Vol. 10 does everything on a very high level of analytical sophistication, so reading it would be a challenge and you should not despair if you find it too hard. If you prefer a much more ponderous and meticulously precise mathematical treatment in the old Cambridge style, Chapman & Cowling can be your bible of Kinetic Theory. This said, I'll do it all largely my way.

The course will be quite mathematical, possibly more so than you have so far experienced. But physics has been a mathematical subject since Newton and Leibniz and we would be moving backwards if we did it A-level style. Learning to describe and predict Nature mathematically is one of the most impressive achievements of our civilisation. So become civilised!

Please ask questions during the lectures or by email (to `a.schekochihin1@physics.ox.ac.uk`*). This is only the second time I am teaching this material and will appreciate real-time feedback.*

Problem Sets

Problem Set 3 covers the material of Lectures 1-2. Start working on it at the end of Week 6.

Problem Set 4 will cover the rest of Kinetic Theory and is intended as vacation work.

Questions that may prove difficult — probably more so than anything you are likely to face in an exam — or that deal with lateral issues are marked with (*). Skip them if you must, although I do hope you will relish the challenge rather than seek the minimum-energy state.

PROBLEM SET 3: Particle Distributions

Calculating Averages

3.1 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 (chosen by you) distributed uniformly? Why? Answer these questions for the case of a 2- and 3-dimensional world.

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

Please note that the notation I use is different from Blundell & Blundell: $f(\mathbf{v})d^3\mathbf{v}$ is velocity distribution in 3D, normalised to 1; when it is isotropic, $f(\mathbf{v}) = f(v)$ (same letter used, f, although if I had been more mathematically fastidious, I would have used a different letter); the speed distribution is $\tilde{f}(v)dv$. In contrast, Blundell & Blundell use $f(v)$ for the speed distribution and $g(\mathbf{v})$ for velocity distribution.

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). Since the velocity distribution is isotropic, this tensor must be rotationally invariant (i.e., not change under rotations of the coordinate frame). The only symmetric rank-2 tensor that has this property is a constant times Kronecker delta δ_{ij}. So it must be that $\langle v_i v_j \rangle = C\delta_{ij}$, where C can only depend on the distribution of *speeds* v (not vectors $\mathbf{v}$). Can you figure out what C is? Is it the same in 2D and in 3D? This is a much simpler derivation than doing velocity integrals directly, but it is worth checking the result by direct integration to convince yourself that the symmetry magic works.

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 powers of v.

Hint. Doing this by direct integration is *a lot* of work. Generalise the symmetry argument given above: see what symmetric rotationally invariant 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 depend on some moments (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)?

3.3 The probability distribution of molecular speeds in a gas in thermal equilibrium is a Maxwellian: a molecule of 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 $v_{\rm th} = \sqrt{2k_B T/m}$ is the "thermal speed," T temperature, k_B Boltzmann's constant, and I have used the proportionality sign ($\propto$) because the normalisation constant has been omitted (work it out by integrating $f(\mathbf{v})$ over all velocities).

a) Given the Maxwellian distribution, what is the distribution of speeds, $\tilde{f}(v)$? Calculate the mean speed $\langle v \rangle$ and the mean inverse speed $\langle 1/v \rangle$. Show that $\langle v \rangle \langle 1/v \rangle = 4/\pi$.

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 is larger, $\langle v^{27} \rangle^{1/27}$ or $\langle v^{56} \rangle^{1/56}$? Do you understand why that is, qualitatively?

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!]

d*) What is the distribution of speeds $\tilde{f}(v)$ in an n-dimensional world (for general n)?

Pressure

3.4 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 function under these symmetries — what is the appropriate transformation of variables from (v_x, v_y, v_z)?

b) What is the expression for pressure $p_{\|}$ (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 $p_{\|}$ 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 $p_{\|}$ and $p_{\perp}$?

Effusion

3.5 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

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

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, the average energy of all the molecules is $(3/2)k_{\mathrm{B}}T$, but the average energy of those hiting the surface is $2k_{\mathrm{B}}T$.

3.6 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?

3.7 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.

3.8 *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 $\frac{1}{4} n A \langle v \rangle (a^2/d^2)$, 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.

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

3.10 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)

3.11 (*) 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 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 (here you will have to brush up on what learned in your 1-st year maths course).

Thermodynamic Limit

3.12 (*) 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: $\mathcal{N}/\mathcal{V} \to n = \text{const}$.

a) Show that in this limit, the probability p_N 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 $\langle N \rangle = nV$.

Hint. This involves proving Poisson's limit theorem. 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).

b) Prove that

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

(so fluctuations around the average are very small as $\langle N \rangle \gg 1$).

c) Show that, if $\langle N \rangle \gg 1$, p_N has its maximum at $N \approx \langle N \rangle = nV$; then show that in the vicinity of this maximum,

$$p_N \approx \frac{1}{\sqrt{2\pi nV}}\, e^{-(N-nV)^2/2nV}.$$

Hint. Use Stirling's formula for $N!$ (look it up if you don't know what that is). Taylor-expand $\ln p_N$ around $N = nV$.

The result of (a) 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 (b) — another demonstration that the world is constructed in a sensible way.

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)		$10^5\,\mathrm{N\,m^{-2}}$