Statistical Physics

Φxford
Physics

Second year physics course
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Problem Set 3

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		$1.0132 \times 10^5 \, \mathrm{Pa \, (N\,m^{-2})}$
1 bar (= 1000 mbar)		$10^5 \, \mathrm{N\,m^{-2}}$

PROBLEM SET 3: Foundations of Statistical Mechanics

Maximising Entropy

3.1 *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_α.

a) If we know absolutely nothing and believe in maximising entropy as a guiding principle, what should be our a priori expectation for p_α? 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_α.

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.

c*) What (according to Shannon) is the information content of the distribution you have obtained?

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

b) We needed Stirling's formula to find the free energy of the classical ideal gas. What did we need it for and how good was the assumption justifying its use?

c*) Stirling's formula was also useful when we established the connection between Shannon's information content function and Gibbs entropy. What was it needed for and what were the key assumptions that justified its use?

3.3 *Gibbs Distribution.*

a) Maximise the entropy of a generic system subject to its mean energy being U and derive the Gibbs distribution and the expression for the partition function. How is temperature determined in this procedure?

b) Now suppose the energies of all microstates are the same, $E_\alpha = E$. What is the distribution then? (*) What is the information content of this distribution?

3.4 A hypothetical system contains 16 particles which can occupy nondegenerate equally spaced energy levels of spacing ϵ. The system is set up so that it has a total energy of 18ϵ. When measured, it is found in its most probable macrostate, which is shown below:

Energy	0	ϵ	2ϵ	3ϵ	4ϵ	5ϵ	6ϵ $\cdots$
	7	4	2	2	1	0	0

a) Based on this information, make a rough estimate of the temperature of the system in units of ϵ/k_{B}.

b) If the temperature were very low, $k_B T \ll \epsilon$, what distribution would we find? What if the temperature were very high, $k_B T \gg 18\epsilon$? (*) Which of these distributions has higher information content?

3.5 *Macroscopic Motions, Thermal and Mechanical Equilibrium, Stability.* Consider a system isolated from the world and so conserving its total energy, momentum and angular momentum. Let us subdivide it into very many small but macroscopic subsystems, indexed by i, each with total energy E_i, momentum $\mathbf{p}_i$, mass m_i and located at a fixed position $\mathbf{r}_i$ within the big system. Note that the total energy E_i comprises both the internal energy of the subsystem i and the kinetic energy $p_i^2/2m_i$ of its macroscopic motion.

a) The total entropy of the system can be expressed in terms of the entropies of the subsystems as follows:

$$S = \sum_i S_i \left(E_i - \frac{p_i^2}{2m_i} \right).$$

Why is this correct? Why, in particular, is the entropy S_i of each subsystem a function only of its internal energy $E_i - p_i^2/2m_i$ (total energy minus kinetic energy of the macroscopic motion) and not just of the total energy E_i?

b) Using the method of Lagrange multipliers, maximise the entropy subject to the three conservation laws (vary E_i's and $\mathbf{p}_i$'s, but not masses m_i or positions $\mathbf{r}_i$, which are assumed fixed). Hence show that in equilibrium, the temperatures of all subsystems must be the same and that the system can only move as whole, at constant velocity, and/or rotate as a rigid body, with constatnt angular velocity (i.e., there can be no internal macroscopic motions of its parts — this makes sense if you recall that whenever you had velocity gradients in a gas, viscosity acted to iron them out, pushing the system towards global equilibrium).

Hint. You will find the solution in Landau & Lifshitz, but, as usual, I urge you to try and do it yourself.

c) Generalise this argument a little further and allow the subsystems to have different volumes, but the total cumulative volume of the system must be conserved. Show that in equilibrium, all subsystems must be at the same pressure. In this calculation, for simplicity, consider the subsystems to be static (all $\mathbf{p}_i = 0$).

d*) Strictly speaking, in part (b), we only extremised entropy, but did not show that the extremum was indeed a maximum and not a minimum. Show that it is indeed a maximum if temperature and heat capacity are positive: $T > 0$ and $C_V > 0$ (for each subsystem). Note that Landau & Lifshitz give only a hand-wavy argument for $T > 0$, but this can actually be formalised — which is what I am asking you to do here. If you find the calculation involving momenta $\mathbf{p}_i$ difficult, solve a simpler problem: assume all $\mathbf{p}_i = 0$ and just work out the condition for thermal stability ($C_V > 0$).

3.6 *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 $\beta = 1/k_B T$. Hence show that $C_V \geq 0$ (so thermal stability, derived in part (d) of the previous question is not in peril).

b) In the above, 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, $\langle \Delta E^2 \rangle = \langle (E_\alpha - U)^2 \rangle$. Now use it to show that $\langle \Delta E^2 \rangle / U^2 \to 0$ as the size of the system $\to \infty$ (this is called "the thermodynamic limit").

Classical Ideal Gas

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

a) Find a 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. 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) Consider an adiabatic process (entropy $S = $ const). Show that for an ideal monatomic gas undergoing such a process, $PV^{5/3} = $ const.

3.8 *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 alter when the particles in a monatomic ideal gas start to move at relativistic speeds, show that in the formula for an adiabat, $PV^\gamma = $ const, the exponent γ in the relativistic limit is $\frac{4}{3}$, rather than $\frac{5}{3}$ as in the non-relativistic case (see previous question, part (c)). You can assume that the particles are ultrarelativistic, i.e., their rest energy is negligible compared to their kinetic energy.

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

3.9 *Density of States.*

a) Consider a particle living in a two-dimensional "box". What is the density of states $g(k)$ for it? What is $g(k)$ for a particle in a one-dimensional "box"?

b*) Calculate the density of states in d dimensions.

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