

Statistical Physics



Second year physics course

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Problem Set 5: Statistical Mechanics

PROBLEM SET 5: Foundations of Statistical Mechanics

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_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.

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, 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 γ and so let the energy of each segment be 0 when it is horizontal and γa 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 γ 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. 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! Determine under what conditions this happens. Why is this possible in this system and not, say, for the ideal gas? Why does the stability argument from Lecture Notes 10 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).

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 α of the chain as functions of their energies E_α and corresponding chain lengths ℓ_α . 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) 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) 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 that in the formula for an adiabat, $PV^\gamma = \text{const}$, the exponent γ 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 such a gas, pressure $p = \varepsilon/3$, where ε 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?

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.

Some Useful Constants

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