

PHY 831: Statistical Mechanics

Homework 4

Due Friday Oct 15, 2021

1. **Summation over exponential quantities.** The purpose of this exercise is to tie up some mathematical loose ends from our class discussion (see Lecture 10 notes) showing that for $N \rightarrow \infty$, the canonical and microcanonical ensembles become identical. Consider a sum of the form

$$\mathcal{S} = \sum_{i=1}^{\mathcal{N}} \mathcal{E}_i$$

where each term in the sum is the exponential of some extensive (i.e., proportional to N) quantity,

$$0 \leq \mathcal{E}_i \sim e^{N\phi_i},$$

and the number of terms in the sum grows as a power of N , i.e., $\mathcal{N} \sim N^p$. We want to show that $\log \mathcal{S} \sim \log \mathcal{E}_{\max}$ with better and better accuracy as $N \rightarrow \infty$.

Since for each term in the sum $0 \leq \mathcal{E}_i \leq \mathcal{E}_{\max}$, start by bounding the sum as

$$\mathcal{E}_{\max} \leq \mathcal{S} \leq \mathcal{N} \mathcal{E}_{\max}.$$

- (a) From the above bound for \mathcal{S} , develop a bound for the *intensive* quantity $\frac{1}{N} \log \mathcal{S}$.
- (b) Now use that $\mathcal{N} \sim N^p$ to argue that as $N \rightarrow \infty$,

$$\lim_{N \rightarrow \infty} \frac{\log \mathcal{S}}{N} = \frac{\log \mathcal{E}_{\max}}{N} = \phi_{\max}$$

Do you see how this connects with our class discussion that at $N \rightarrow \infty$, the canonical ensemble F becomes equal to the microcanonical (Landau) free energy evaluated at the most probable energy?

2. **Dynamical origin of the 2nd Law.** Consider a system which is disturbed from equilibrium by some external perturbation, so that the probability per unit time of a transition from microstate $i \rightarrow j$ is ω_{ij} . Time reversal implies that $\omega_{ij} = \omega_{ji}$. Write down a differential equation for $\frac{dp_i}{dt}$, and use it to show that $\frac{dS}{dt} \geq 0$.
3. Consider a classical ideal gas treated in the grand canonical ensemble.

- (a) Calculate the partition function, expressing your answer in terms of the so-called fugacity $z = e^{\beta\mu}$ and the thermal de Broglie wavelength l_Q defined in the class lectures.
- (b) Show that you recover the ideal gas law $PV = Nk_B T$.
- (c) Show that the probability $P(N)$ of finding N particles in the system can be written as a Poisson distribution

$$P(N) = \frac{\langle N \rangle^N e^{-\langle N \rangle}}{N!}$$

4. Consider a classical system of N non-interacting diatomic molecules in a box V at temperature T . The Hamiltonian for a *single* molecule is

$$\mathcal{H}(\mathbf{p}_1, \mathbf{p}_2, \mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2m}(p_1^2 + p_2^2) + \frac{K}{2}|\mathbf{r}_1 - \mathbf{r}_2|^2,$$

where the indicated coordinates/momenta are for the 2 atoms in the molecule. Calculate the following quantities:

- (a) The Helmholtz free energy F for the gas.
 - (b) The specific heat C_V for the gas.
 - (c) The mean square molecular diameter $\langle |\mathbf{r}_1 - \mathbf{r}_2|^2 \rangle$.
5. **General motivation for statistical density matrices.** Suppose we want to use QM to calculate the properties of some actual physical system in our lab. In reality, the system is never fully isolated from the rest of the universe. Let $\{|\alpha\rangle\}$ denote some complete set of states that spans the Hilbert space of our system, and let $\{|i\rangle\}$ denote a complete set for the Hilbert space of the rest of the universe. The most general state vector for this situation is then

$$|\Psi\rangle = \sum_{\alpha, i} C_{\alpha i} |\alpha\rangle \otimes |i\rangle.$$

Let A be some hermitian operator corresponding to some observable that only acts on the system. (E.g., A could be the total kinetic energy operator for the N particles in our system.) Note that this means A acts on a tensor product state as

$$A|\alpha\rangle \otimes |i\rangle = \left(A|\alpha\rangle \right) \otimes |i\rangle.$$

In other words, it doesn't touch the states of the rest of the universe.

- (a) Show that the expectation value in the state Ψ can be written as

$$\langle \Psi | A | \Psi \rangle = \sum_{\alpha, \beta} \langle \beta | A | \alpha \rangle \rho_{\alpha\beta} = \text{Tr}_s(A\rho)$$

where we've defined matrix elements of the so-called density operator as

$$\rho_{\alpha\beta} = \sum_j C_{\alpha j} C_{\beta j}^*,$$

and Tr_s means we're taking the trace only a basis that spans the system's Hilbert space.

- (b) Show that ρ is hermitian and write it in its spectral representation.
- (c) Show that the eigenvalues ρ sum up to 1 and are all between 0 and 1. (Hint: Consider $A = 1$ and $A = |\gamma\rangle\langle\gamma|$.) In this way the eigenvalues can be interpreted as probabilities. In the definition of the density matrix, you're basically averaging over the possible states of the rest of the universe. In essence, the density matrix eigenvalues are ensemble probabilities.