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Advanced Statistical Physics
Wintersemester 2022/23

Problem sheet 1, handed out: Friday 28th October, 2022
due: **Sunday 6th November, 2022 (via email/ studip)**

1 Microcanonical and canonical ensemble (25 pts.)

Let two subsystems $\mathcal{A}$ and $\mathcal{B}$ be in contact, with the whole system $\mathcal{A}+\mathcal{B}$ being isolated. Suppose that $\mathcal{A}$ and $\mathcal{B}$ can only exchange energy. We also neglect the interaction energy between the subsystems, so that the energy of a microstate mn for the joint system is the sum of the energies of the microstates in $\mathcal{A}$ and $\mathcal{B}$.

In the formal limit of small energy uncertainty ($\Delta \to 0$), the microcanonical distribution for the total system is

$$\rho_{mn} = \frac{\delta(E - E_{mn})}{\Omega_{\mathcal{A}+\mathcal{B}}(E)}$$

with $\Omega_{\mathcal{A}+\mathcal{B}}(E) = \sum_{mn} \delta(E - E_{mn})$ the density of the states for the entire system. Let $\Omega_{\mathcal{A}}(E_{\mathcal{A}})$ and $\Omega_{\mathcal{B}}(E_{\mathcal{B}})$ be the corresponding densities of states for the subsystems and $S_{\mathcal{A}}(E_{\mathcal{A}}) = k_{\mathrm{B}} \ln \Omega_{\mathcal{A}}(E_{\mathcal{A}})$ and $S_{\mathcal{B}}$ the microcanonical entropies.

a) Show that the total probability of finding subsystem $\mathcal{A}$ in any microstate with energy $E_{\mathcal{A}}$ is

$$P(E_{\mathcal{A}}) = \frac{\Omega_{\mathcal{A}}(E_{\mathcal{A}})\Omega_{\mathcal{B}}(E - E_{\mathcal{A}})}{\Omega_{\mathcal{A}+\mathcal{B}}(E)}$$

(4 pts.)

b) Derive a Gaussian approximation to $P(E_{\mathcal{A}})$ by expanding $\ln P(E_{\mathcal{A}})$ around its maximum (call this $E_{\mathcal{A}}^*$) and show that its variance is given by

$$\sigma^2_{E_{\mathcal{A}}} = -\frac{k_{\mathrm{B}}}{\left.\frac{\partial^2 S_{\mathcal{A}+\mathcal{B}}}{\partial {E_{\mathcal{A}}}^2}\right|_{E_{\mathcal{A}}^*}} \tag{1}$$

where

$$S_{\mathcal{A}+\mathcal{B}} = S_{\mathcal{A}}(E_{\mathcal{A}}) + S_{\mathcal{B}}(E - E_{\mathcal{A}}) \tag{2}$$

(4 pts.)

c) Show that the condition determining $E^*_{\mathcal{A}}$ can be expressed as the equality of temperatures defined in the two systems (hint: use the microcanonical definition of T), and rewrite $\sigma^2_{E_{\mathcal{A}}}$ as a function of $\partial^2 S_{\mathcal{A}}/\partial E^2_{\mathcal{A}}$ and $\partial^2 S_{\mathcal{B}}/\partial E^2_{\mathcal{B}}$. (3 pt.)

d) In the Gaussian approximation, $E^*_{\mathcal{A}}$ equals the mean energy $\langle E_{\mathcal{A}}\rangle$. Use this to relate the heat capacity $C_{\mathcal{A}} = \partial\langle E_{\mathcal{A}}\rangle/\partial T$ to $\partial^2 S_{\mathcal{A}}/\partial {E_{\mathcal{A}}}^2$. Deduce an expression for $\sigma^2_{E_{\mathcal{A}}}$ involving $C_{\mathcal{A}}$ and $C_{\mathcal{B}}$, the heat capacities of subsystems $\mathcal{A}$ and $\mathcal{B}$. (4 pts.)

e) Using the fact that average energies are extensive, i.e. scale with particle number, deduce that the relative standard deviation $\sigma_{E_{\mathcal{A}}}/\langle E_{\mathcal{A}}\rangle$ decays at least as fast as $1/\sqrt{N_{\mathcal{A}}}$ with the number of particles $N_{\mathcal{A}}$ in subsystem $\mathcal{A}$. (3 pts.)

We now suppose that system $\mathcal{B}$ is much bigger than system $\mathcal{A}$.

f) From the result of question d), show that the fluctuations in subsystem $\mathcal{A}$ are independent of $C_{\mathcal{B}}$ if $C_{\mathcal{B}}$ is very large, as expected in the canonical ensemble. Also derive the first order correction in $1/C_{\mathcal{B}}$ to this result. (2 pts.)

g) Show that the probability of finding subsystem $\mathcal{A}$ in a specific microstate m with energy $E_m = E_{\mathcal{A}}$ is (contrast part a))

$$\rho_m = \frac{\Omega_{\mathcal{B}}(E - E_{\mathcal{A}})}{\Omega_{\mathcal{A}+\mathcal{B}}(E)}$$

Expand $S_{\mathcal{B}}(E - E_{\mathcal{A}})$ for $E_{\mathcal{A}} \ll E$ to first order in order to obtain the canonical distribution form for ρ_m. Extend the expansion to the next term, and discuss in which case the second-order term can be neglected. Compare this case to the result of part f). (5 pts.)

2 Distribution of particles in a partitioned box (20 pts.)

Consider a box with volume V. The box consists of two sections A and B of volume V_A and $V_B = V - V_A$, and is in contact with a heat bath at temperature T. The box contains N ideal gas particles that can move freely from one section to the other.

a) Starting from the Hamiltonian $H = \sum_i \boldsymbol{p}_i^2/(2m)$ for the ideal gas, show that the partition function of the entire system is $Z = (V/\lambda^3)/N!$ where λ is the thermal de Broglie wavelength. (4 pts.)

b) Show that the constrained partition function $Z(N_A)$ that only counts configurations $\boldsymbol{r} = (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$ with N_A particles in section A is

$$Z(N_A) = \frac{(V_A/\lambda^3)^{N_A}}{N_A!}\frac{(V_B/\lambda^3)^{N_B}}{N_B!}$$

where $N_B = N - N_A$. (Hint: Constrain N_A integration variables $\boldsymbol{r}_i$ to lie in V_A and the others to lie in V_B, and multiply by the number of ways of picking the N_A integration variables in V_A.)

The result factorizes into the partition functions of the two sections. Would this still hold if we had not included the $1/N!$ normalization? (4 pts.)

c) Calculate the probability $P_A(N_A) = Z(N_A)/Z$ to find N_A particles in section A. What is the name of this probability distribution? (2 pts.)

d) Now, take the limit $N \to \infty$ with V_A and $\frac{V}{N} = V_0$ fixed. Here V_0 is the average volume occupied by each particle. What is the name of the resulting probability distribution? (Hint: use Stirling's formula $N! \approx \sqrt{2\pi N}(N/e)^N$.) (4 pts.)

e) In what limit does the distribution approach a Gaussian form? (2 pt.)

f) Confirm that the distribution of d) is equivalent to that of an ideal gas in the grand canonical ensemble in a volume V_A, by starting from the grand canonical partition function:

$$\mathcal{Z}_{\mathrm{G}} = \sum_{N_A=0}^{\infty} \frac{1}{N_A!} \left(\frac{V_A}{\lambda^3}\right)^{N_A} e^{\beta N_A \mu},$$

where μ is the chemical potential. Find an expression for μ by comparison with the result of d). (4 pts.)

3 Extremal properties of Boltzmann distribution (15 pts)

Consider a generic system with microstates n and corresponding energies E_n. The probabilities ρ_n for the microstates are to be chosen to maximize the entropy $S/k_{\mathrm{B}} = -\sum_n \rho_n \ln \rho_n$, subject to the constraint that the average energy $E = \sum_n \rho_n E_n$ has a fixed value

a) Write down the Lagrange function L that needs to be maximized, including two Lagrange multipliers for the constraints on normalization ($\sum_n \rho_n = 1$) and on the average energy, respectively. Show that the distribution that maximizes L has the form of a Boltzmann distribution, and relate your Lagrange multipliers to $\beta = 1/(k_{\mathrm{B}}T)$ and Z. (4 pts.)

b) To show that the Boltzmann distribution really gives the *global* optimum of the entropy, also in the quantum case, let $\rho = Z^{-1}e^{-\beta H}$ be the Boltzmann density operator. Using that $\mathrm{KL}(\rho'||\rho) \geq 0$, show that

$$S \geq S' + \frac{1}{T}(E - E')$$

where S' and E' are the entropy and average energy of the arbitrary density operator ρ'. Deduce that the Boltzmann operator is the global maximizer of the entropy at fixed average energy. (7 pts.)

c) If we define the free energy (sometimes called "variational free energy") at temperature T for arbitrary ρ' as $F' = E' - TS'$, show that

$$F \leq F'$$

and interpret this result physically. (4 pts.)

4 Paramagnet (15 pts.)

Consider a quantum spin-$\frac{1}{2}$ particle with gyromagnetic ratio γ, in thermal equilibrium at temperature T, neglecting its orbital motion. The Hamiltonian of the system in the presence of an external magnetic field $\boldsymbol{B} = B_0\hat{\boldsymbol{e}}_z$ is given by

$$H = -\gamma\boldsymbol{\sigma} \cdot \boldsymbol{B} \tag{3}$$

where $\boldsymbol{\sigma} = \sigma_z\hat{\boldsymbol{e}}_z$ and σ_z can take values $+1$ or -1. (These are the eigenvalues of the Pauli matrix for σ_z; the actual spin is $(\hbar/2)\sigma_z$ and this prefactor has been absorbed into γ.)

a) Calculate the two energy levels and the probability of finding the spin in the $+1$ and -1 states. (2 pts.)

b) Calculate the average z-component of the magnetization $\langle m_z\rangle = \gamma\langle\sigma_z\rangle$ and plot it against $\gamma B_0/T$. (3 pts.)

c) Calculate the magnetic susceptibility χ of the system, which is defined as

$$\chi = \left.\frac{\partial\langle m_z\rangle}{\partial B_0}\right|_{B_0\to 0}. \tag{4}$$

(3 pts.)

d) Carry out the same analysis for a *classical* spin $\boldsymbol{\sigma}$, which is a vector of fixed unit length that can point in any direction, and discuss the differences to the quantum case. (7 pts.)