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Blatt 8 zur Theoretischen Physik IV, WS 2023/2024

(Abgabe bis 05.01.2024, 8:30 Uhr)

Exercise 1: Fluctuations and Response Functions

a) Show that the fluctuation of energy, ΔE, in the canonical ensemble is given by

$$(\Delta E)^2 = k_B T^2 \frac{\partial E(N,V,T)}{\partial T},$$

with $E(N,V,T) = \langle E \rangle$. Use this result to demonstrate that the heat capacity $C_V = \frac{\partial E(T,V,N)}{\partial T}$ is positive (i.e., greater than zero) for $T \neq 0$. Why does $\Delta E/E = \mathcal{O}(N^{-\frac{1}{2}})$ hold?

b) Show that the fluctuation of the particle number, ΔN, in the grand canonical ensemble can be expressed as

$$(\Delta N)^2 = k_B T \left(\frac{\partial N}{\partial \mu}\right)_{T,V}.$$

Then, prove that the isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{N,T}$$

is positive for $T \neq 0$ by expanding $\mathrm{d}P$ (in terms of its partial derivatives) in $N\mathrm{d}\mu = V\mathrm{d}P - S\mathrm{d}T$ and reading off $\left(\frac{\partial N}{\partial \mu}\right)_{T,V}$. Does $\Delta N/N = \mathcal{O}(N^{-\frac{1}{2}})$ hold here as well?
Hint: Consider that pressure is an intensive quantity, i.e., $P(T,V,N) = P(T,V/N)$.

[5+7=12 Points]

Exercise 2: Thermodynamic Relations

For a given particle number N, show that the following general relations are valid:

a)
$$\left(\frac{\partial T}{\partial V}\right)_E = \frac{1}{C_V}\left(p - T\left(\frac{\partial p}{\partial T}\right)_V\right)$$

b)
$$\left(\frac{\partial E}{\partial p}\right)_T = V\kappa_T\left(p - T\left(\frac{\partial p}{\partial T}\right)_V\right)$$

c)
$$\left(\frac{\partial p}{\partial T}\right)_S = \left(\frac{\partial S}{\partial V}\right)_p$$

d)

$$\left(\frac{\partial p}{\partial T}\right)_S = \frac{C_p}{\alpha V T}$$

[2.5+1+1+1.5=6 Points]

Exercise 3: Pressure in Statistical Mechanics and Thermodynamics

Show that the statistical definition of pressure

$$p = -\left\langle \frac{\partial H}{\partial V} \right\rangle,$$

with $H(\mathbf{Q}, \mathbf{P}, V)$ being the Hamiltonian operator of the system, matches the thermodynamic definition

$$p = T\left(\frac{\partial S}{\partial V}\right)_{E,N}$$

for sufficiently large N.
Hint: Use

$$\Omega(E) = \int \delta(E - H(\mathbf{Q}, \mathbf{P}, V))\, \mathrm{d}\mathbf{Q}\, \mathrm{d}\mathbf{P} = \frac{\partial}{\partial E} \int \Theta(E - H(\mathbf{Q}, \mathbf{P}, V))\, \mathrm{d}\mathbf{Q}\, \mathrm{d}\mathbf{P} \quad \text{and} \quad \left.\frac{\partial p}{\partial E}\right|_{V,N} = \mathcal{O}(1/N).$$

[5 Points]

Exercise 4: Density Matrix

a) Is there a real value of α for which the following operator describes a pure state?

$$\hat{\rho} = \alpha \begin{pmatrix} 1 & 2 & 1 \\ 0 & 0 & 3 \\ 1 & 2 & 1 \end{pmatrix}$$

b) The microcanonical density matrix in the energy representation is given by

$$\hat{\rho}(E) = \frac{1}{\Gamma(E)} \sum_m |E_m\rangle\langle E_m|$$

where $\Gamma(E)$ is the phase volume, $E<E_m<E+\Delta$, and $|E_m\rangle$ are the eigenstates of the Hamiltonian operator $\hat{H}$ (Note that in the microcanonical density matrix, the relative weight of all possible states is the same and $\frac{\mathrm{e}^{-\beta E_m}}{Z}$ is replaced by $\frac{1}{\Gamma(E)}$). Determine the form of $\hat{\rho}$ when a different complete orthonormal system is used for representation instead of the eigenstates $|E_m\rangle$. Does the phase volume $\Gamma(E)$ change in this process?

c) Let $\hat{A}$ be an observable that does not commute with $\hat{H}$, and for which the eigenstates $|a_n\rangle$ with eigenvalues a_n are known. Compute the microcanonical average $\langle \hat{A} \rangle$.

[2+6+5=13 Points]

Exercise 5: Computational Task: Two-State System

Consider a system with only two discrete states, one of energy E_1 and the other of higher energy $E_2>E_1$. Assuming that the system is coupled to a heat bath of temperature T, find the contour lines in the $(\Delta E, T)$ plane for arbitrary values of the equilibrium Boltzmann probability ratio ρ_2/ρ_1 between the two states. How the results change if the equilibrium probabilities are proportional to $\exp(-E_i^2/T^2)$ instead? Set k_B=1 and E=E_1+$E_2 = 1$ for simplicity. You can use the given code (Blatt8-TwoStateSystem-Code1.py) as a guide.

[4 Points]