

Homework

5 HW

due 2023-04-13

Exams

final: **Thursday, May 4, 2023, 11:00-12:15**

XVII. HARMONIC OSCILLATOR [(9+9) PTS]

A harmonic oscillator has the energy eigenvalues

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots$$

- a) Calculate the partition function $Z^{(c)} = \sum_n e^{-\beta E_n}$, the internal energy $E = \langle \mathcal{H} \rangle = -\frac{\partial}{\partial \beta} \ln Z^{(c)}$, the entropy $S = k_B (\beta E + \ln Z^{(c)})$, and the heat capacity $C = \frac{\partial E}{\partial T}$ depending on temperature. Use the dimensionless variable $x \equiv \frac{1}{2} \beta \hbar \omega > 0$.
- b) Write the entropy as a function of the dimensionless energy $\eta \equiv 2E/(\hbar\omega)$. Recalculate the entropy using the definition of the Boltzmann entropy. To this end consider $N \gg 1$ equal (indistinguishable) oscillators and their possible distributions on the microstates given a total energy E , which defines the macrostate.

XVIII. QUANTUM LIOUVILLE EQUATION [6 PTS]

Show that the microscopic density

$$\hat{\rho} = \frac{1}{N} \sum_{\nu} n_{\nu} |x_{\nu}\rangle \langle x_{\nu}|$$

satisfies the Quantum Liouville equation

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}].$$

XIX. N-LEVEL SYSTEM, NEGATIVE TEMPERATURES [(2+3+4+4+5) PTS]

The eigen-energies of the system we consider here are equidistant and their number is finite, f , i.e.,

$$E_{\nu} = (\nu - 1)\epsilon; \quad \nu = 1, 2, \dots, f; \quad \epsilon > 0.$$

- a) Calculate the canonical partition function $Z^{(c)} = \sum_{\nu} e^{-\beta E_{\nu}}$.
Remark: Since the spectrum is limited from above, $Z^{(c)}$ exists for all real values of β - in particular also for negative temperatures. It is useful to introduce the dimensionless variable $x \equiv e^{-\beta\epsilon}$ with $0 < x < \infty$.
- b) Using $Z^{(c)}$, calculate the internal energy $E = -\frac{\partial}{\partial \beta} \ln Z^{(c)} = \epsilon x \frac{d}{dx} \ln Z^{(c)}$. At which temperature does E take its minimum, maximum, or value exactly between those?

- c) What are the 'occupation numbers' n_ν , which allow to write the internal energy as $E = \sum_{\nu=1}^f n_\nu E_\nu$? Show and interpret that $n_\nu(x^{-1}) = n_{f-\nu+1}(x)$ ("inversion of the occupation numbers"). Justify why $\beta = -\infty$ (or $T = 0^-$) should be the highest accessible temperature. What is the occupation number of the highest or lowest level at high or low temperatures, respectively?
- d) Calculate the entropy, $S = k_B(\ln Z^{(c)} + \beta E)$ as function of x and find an expression for S , which only depends on the occupation numbers. Calculate the heat capacity $C = \frac{\partial E}{\partial T}$.
- e) Simplify the expressions for $Z^{(c)}$, E , S , and C for the case of a two-level system, $f = 2$, which already shows all the relevant properties of the more general case. Sketch and discuss the qualitative graph of $S(E)$.

XX. GRAND CANONICAL ENSEMBLE [(3+5) PTS]

The canonical partition function of a Boltzmann gas is given by (see lecture)

$$Z^{(c)}(\beta, V, N) = \frac{1}{N!} \left(\frac{V}{\lambda_\beta^3} \right)^N,$$

where $\lambda_\beta = h/\sqrt{2\pi mT}$ is the thermal de Broglie wave length.

- a) Calculate the grand canonical partition function using $Z^{(c)}$ from above.
- b) Calculate the squared deviations of the particle number $\Delta N^2 = \langle (N - \langle N \rangle)^2 \rangle$ in the grand canonical ensemble and show that the relative deviation $\Delta N / \langle N \rangle$ vanishes in the thermodynamic limit.

XXI. THERMODYNAMIC RELATIONS [(3+6) PTS]

Here we consider a system of N identical particles. E , T , V , and μ are the energy, the temperature, the volume, and the chemical potential, respectively.

- a) Prove the following relations:

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

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

- b) Prove the following relation for a system with fixed number of particles:

$$K_T - K_S = V \frac{T \alpha_p^2}{C_p}, \quad \frac{C_p}{C_V} = \frac{K_T}{K_S},$$

where

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V, \quad C_p = \left(\frac{\partial H}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p,$$

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p, \quad K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T, \quad K_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S.$$

Hint: Use the relation derived in the lecture:

$$C_p - C_V = VT \frac{\alpha_p^2}{K_T}.$$