Department of Physics - Northern Illinois University
Prof. Andreas Glatz

Homework

HW 5

due *2024-04-09*

Exams final: **Thursday, May 7, 2024**

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

A harmonic oscillator has the energy eigenvalues

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

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 $S = k_B\left(\beta E + \ln Z^{(c)}\right)$, 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 matrix

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

satisfies the Quantum Liouville equation

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

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.,

$$E_\nu = (\nu - 1)\epsilon\,;\ \ \nu = 1, 2, \ldots, f\,;\ \ \epsilon > 0\,.$$

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 $\lambda_\beta = h/\sqrt{2\pi m T}$ 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 $\Delta N^2 = \left\langle (N - \langle N\rangle)^2 \right\rangle$ 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:

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