Theoretische Physik IV: Statistische Mechanik und Thermodynamik

Problem Set No. 5

Due on: Friday, 23.5.08 in the practice groups

Exercise 5.1 *(Ideal Gas in the great canonical ensemble)* **(10 points)**

We consider an ideal monoatomic gas of indistinguishable particles of mass m.

(a) Calculate the canonical N-particle partition sum Z_N. Write Z_N as a function of V, N and λ. Here $\lambda := h\sqrt{\beta/(2\pi m)}$ is the thermal de-Broglie wavelength and $\beta = (k_B T)^{-1}$ (3 points).

(b) Calculate the great canonical partition sum Z_{grk} and write it as a function of V, λ and the fugacity $z := e^{\beta\mu}$. Determine the great canonical potential $J = -k_B T \ln Z_{grk}$. (2 points)

(c) Show that the following relation generally holds in the great canonical ensemble:

$$\langle N \rangle = \beta^{-1} \frac{\partial}{\partial \mu} \ln Z_{grk}$$

(3 points)

(d) Calculate the average particle number $\langle N \rangle$ for the ideal gas. (2 points)

Exercise 5.2 *(Extensive Variables)* **(10 points)**

(a) The Gibbs free energy G (free enthalpy) for a one-component system with variable number of particles N is given by $G = G(T, p, N)$ as a function of temperature, pressure and the particle number. Using the fact that N is the only extensive variable of G, show that the chemical potential is given for this system by $\mu = G/N$. (5 points)

(b) In contrast to the Gibbs free energy, the entropy $S = S(E, V, N)$ depends on *three* extensive variables. Use the property of extensitivity to proof the following relation:

$$E = TS + \mu N - pV$$

(5 points)

Exercise 5.3 *(Thermodynamic Relations)* **(10 points)**

Show for fixed particle number N:

(a) $\frac{\partial T}{\partial V}\big|_E = \frac{1}{C_V}\left(p - T\,\frac{\partial p}{\partial T}\Big|_V\right)$ (3 points)

(b) $\frac{\partial E}{\partial p}\Big|_T = V\kappa_T\left(p - T\,\frac{\partial p}{\partial T}\Big|_V\right)$ (2 points)

(c) $\frac{\partial p}{\partial T}\Big|_S = \frac{C_p}{\alpha V T}\Big|_p$ (3 points)

(d) $\frac{\partial p}{\partial T}\Big|_S = \frac{\partial S}{\partial V}\big|_p$ (2 points)

Here $C_V = \frac{\partial E}{\partial T}\big|_V = T\,\frac{\partial S}{\partial T}\big|_V$ is the specific heat capacity at constant volume, $C_p = \frac{\partial E}{\partial T}\big|_p$ the specific heat capacity at constant pressure, $\alpha = \frac{1}{V}\,\frac{\partial V}{\partial T}\big|_p$ the thermal expansion coefficient and $\kappa_T = -\frac{1}{V}\,\frac{\partial V}{\partial p}\Big|_T$ the isothermal compressibility.

Bonus Exercise 5.4 *(Energy fluctuations in the canonical ensemble)* **(10 extra points)**
Note: This exercise is optional. You may want to solve it to improve your score.

We want to consider the probability distribution of the energy fluctuations in the great canonical ensemble. The moments of the fluctuations are defined by

$$\sigma_n = \frac{1}{Z} \sum_j (E_j - \epsilon)^n \, e^{-\beta E_j}$$

where $\beta = 1/k_B T$, ϵ is an arbitrary energy and Z the canonical partition sum.

(a) Show that

$$Z\sigma_n = (-1)^n e^{-\beta\epsilon} \frac{\partial^n}{\partial \beta^n} \left[Z e^{\beta\epsilon} \right]$$

(3 points)

(b) Use this result to show that the fluctuations in an ideal gas follow a normal distribution around $\epsilon := \sigma_1$ (in the thermodynamic limit) by studying the convergence behaviour of the moments σ_0 up to σ_8 (We do not want to consider higher-order moments for reasons of simplicity).
Hint: Use a computer algebra program to solve this exercise! (7 points)