Theoretische Physik IV: Statistische Mechanik und Thermodynamik

Problem Set No. 7

Due on: Friday, 13.6.08 in the practice groups

Exercise 7.1 *(Van-der-Waals' equation of state)* **(10 points)**

Here we want to derive the van der Waals equation of state for a model system of interacting particles. The pairwise interaction consists of an attractive and a repulsive part. For the repulsive interaction the particles are modelled as hard spheres, while the attractive interaction is a potential well. The potential is thus given by:

$$V(r) = \begin{cases} +\infty & \text{for } 0 \leq r \leq \delta_1 \\ -\epsilon & \text{for } \delta_1 < r \leq \delta_2 \\ 0 & \text{for } r > \delta_2 \end{cases}$$

Show by means of the virial expansion, that for such a system in the case of weak attraction $\beta\epsilon \ll 1$ one obtains the van der Waals' equation of state. What are the constants a and b in this case?

Exercise 7.2 *(Fluctuations)* **(10 points)**

The fluctuations of the energy and the particle number in the canonical resp. grandcanonical ensemble are tightly connected to the thermodynamic quantities C_V resp. κ_T.

(a) We consider the connection between energy fluctuations and C_V in the canonical ensemble:

(i) Show the following equations for the canonical ensemble:

$$(\Delta E)^2 = \frac{\partial^2}{\partial \beta^2} \ln Z_{kan} = kT^2 C_V$$

(4 points)

(ii) Show that the relative energy fluctuations behave like

$$\frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}}$$

(2 points)

Therefore in the thermodynamic limit the fluctuations vanish (equivalence between micro-canonical and canonical ensemble in the thermodynamic limit!).

(b) Now we consider the connection between particle number fluctuations and κ_T in the grandcanonical ensemble. Show that

$$(\Delta N)^2 = \frac{\partial^2}{\partial (\beta\mu)^2} \ln Z_{gk} = kT \frac{N^2}{V} \kappa_T$$

Hint: Use the following representation of the isothermal compressibility (without proof): $\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial p}\Big|_{T,N} = \frac{V}{N^2} \frac{\partial N}{\partial \mu}\Big|_{T,V}$. (4 points)

Exercise 7.3 *(Pair distribution function and fluctuations)* **(10 points)**

The particle number fluctuations are also connected to the pair distribution function $g(\mathbf{r})$ of a homogeneous fluid system. Consider such a system consisting of N interacting particles. The spatial probability density is given by $F_N(\mathbf{r}_1, \ldots, \mathbf{r}_N)$, which is normalized $\int F_N(\mathbf{r}_1, \ldots, \mathbf{r}_N) d^3r_1 \ldots d^3r_N = 1$. We define the one-particle distribution function

$$F_1(\mathbf{r}_1) = N \int_V F_N(\mathbf{r}_1, \ldots, \mathbf{r}_N) d^3r_2 \ldots d^3r_N = \rho$$

which is the particle density at position $\mathbf{r}_1$. In a homogeneous system it is a constant. The pair distribution function $g(\mathbf{r})$ is defined by

$$F_2(\mathbf{r_1}, \mathbf{r_2}) = N(N-1) \int_V F_N(\mathbf{r}_1, \ldots, \mathbf{r}_N) d^3r_3 \ldots d^3r_N = \rho^2 g(\mathbf{r})$$

ρ is the particle number density of the system. $g(\mathbf{r})$ gives the probability density of having a particle at position $\mathbf{r}$ if there is already a particle at position $\mathbf{r} = \mathbf{0}$.

We now consider a macroscopic region of the total system consisting of N_A particles in a volume V_A and calculate the fluctuations of the particle number in this region.

(a) Express N_A in terms of the function $\mu(\mathbf{r})$ defined by

$$\mu(\mathbf{r}) = \begin{cases} 1 & \mathbf{r} \in V_A \\ 0 & \mathbf{r} \notin V_A \end{cases}$$

(2 points)

(b) Show by means of (a) that

$$\frac{\langle N_A^2 \rangle - \langle N_A \rangle^2}{\langle N_A \rangle} = 1 + \rho \int_{V_A} (g(\mathbf{r}) - 1) d^3r$$

(8 points)