

## Statistical Physics and Thermodynamics (SS 2017)

### Problem sheet 11

**Hand in: Friday, July 7 during the lecture**

<http://www.physik.fu-berlin.de/en/einrichtungen/ag/ag-netz/lehre/>

#### Virial expansion (20 points)

In the lecture, we derived the virial expansion for pairwise interacting particles as

$$\frac{P}{k_B T} = c + a_2 c^2 + \mathcal{O}(c^3), \quad (1)$$

where  $c = N/V$  is the particle density and

$$a_2(\beta) = -\frac{1}{2V} \int d^3 \vec{q}_1 \int d^3 \vec{q}_2 [\exp(-\beta w(|\vec{q}_2 - \vec{q}_1|)) - 1], \quad (2)$$

is the second virial coefficient, with  $w$  the interaction potential that depends only on the distance  $|\vec{q}_2 - \vec{q}_1|$  between two particles, and  $\beta^{-1} = k_B T$ .

In this exercise, we will derive some general consequences of the second order virial expansion and illustrate them with the potential

$$w(r) = \begin{cases} \infty & 0 < r < r_0, \\ -\epsilon & r_0 < r < r_1, \\ 0 & r_1 < r, \end{cases} \quad (3)$$

which describes particles of radius  $r_0$  that attract each other via a short range interaction of strength  $\epsilon > 0$  and range  $r_1$ .

a) Calculate the second virial coefficient  $a_2$  for the potential (3). Derive the high and low temperature limits of  $a_2$ . Which part (attractive/repulsive) of the potential dominates in which limit, and is the pressure increased or decreased relative to that of the ideal gas? **(5 points)**

b) Show that eq. (1) leads to the isothermal compressibility

$$\kappa_T \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T,N} = \frac{1}{k_B T c} (1 - 2a_2 c + \mathcal{O}(c^2)). \quad (4)$$

**(2 points)**

c) For high temperatures, one expands the second virial coefficient in powers of  $\beta$  as

$$a_2 = a_2^{(0)} + a_2^{(1)} \beta + \mathcal{O}(\beta^2). \quad (5)$$

Derive the relation between  $a_2^{(0)}$ ,  $a_2^{(1)}$  and the Van der Waals coefficients  $a'$ ,  $b'$ , which appear in the Van der Waals equation of state

$$(P + a' c^2)(V - b' N) = N k_B T. \quad (6)$$

What are the values of  $a'$ ,  $b'$  for the potential (3)? **(5 points)**

*Hint: Remember that the Van der Waals equation of state neglects terms of order  $c^3$ , and that we work in the high temperature limit. This means you should think of eq. (6) as  $\beta(P + a'c^2)(1 - b'c) = c + \mathcal{O}(\beta^2) + \mathcal{O}(c^3)$ .*

d) Derive the Helmholtz free energy  $F$  corresponding to the second order virial expansion. You should get that

$$F(T, V, N) = F_{\text{ideal}}(T, V, N) + a_2 N k_B T \frac{N}{V}, \quad (7)$$

where  $F_{\text{ideal}} = N k_B T [\ln(\lambda^3 \frac{N}{V}) - 1]$  is the Helmholtz free energy of an ideal gas, with  $\lambda = h/\sqrt{2\pi m k_B T}$  the thermal wavelength, where  $h$  is the Planck constant and  $m$  the mass of a gas particle. **(3 points)**

*Hint: Use  $P = -(\partial F/\partial V)_{T,N}$  and the fact that  $F$  is extensive and in the limit  $c \equiv N/V \rightarrow 0$  you should recover the free energy of the ideal gas.*

e) Use your result from d) to derive the deviations of the entropy  $S$  and internal energy  $U$  from the ideal gas results, i.e. calculate

$$\Delta S \equiv S - S_{\text{ideal}}, \quad (8)$$

$$\Delta U \equiv U - U_{\text{ideal}}. \quad (9)$$

Finally, explicitly evaluate these for the potential (3), and show that in the high temperature limit you obtain

$$\Delta S \approx -k_B N_{\text{pairs}} \frac{V_0}{V}, \quad (10)$$

$$\Delta U \approx N_{\text{pairs}} \langle w \rangle, \quad (11)$$

where  $N_{\text{pairs}} = N(N-1)/2 \approx N^2/2$  is the number of pairs of molecules,  $V_0 = 4\pi r_0^3/3$  is the excluded volume due to a particle, and  $\langle w \rangle = 4\pi/V \int_{r_0}^{\infty} dr r^2 w(r)$  is the spatial average over the potential energy. **(5 points)**