Institutt for fysikk, NTNU

Homework 6 TFY4230 Statistical physics. Spring 2017.

Assistance with the homework: Friday 24.03 and 21.04, kl. 09.15-11.00 in R8

Deadline for handing in: Wednesday 03.05.2017, kl. 16.00

Problem 1 Second Virial Coefficient $B_2(T)$

The virial expansion of the equation of state of a gaseous system is derived from the fugacity expansion as follows. On parametric form, the exact equation of state of a real gas may be written on form

$$\begin{aligned} \beta p &= \chi(z) \\ \rho &= z\frac{\partial \chi(x)}{\partial z}. \end{aligned}$$

Here, the fugacity $z = \exp(\beta\mu)/\Lambda^3$, where Λ is the thermal de Broglie wavelength and μ is the chemical potential. Moreover,

$$\begin{aligned} \chi(z) &= \frac{\ln Z_g}{V}, \\ Z_g &= e^{\beta p V} = \sum_{N=0}^{\infty} \frac{z^N}{n!} Q_N \\ Q_N &= \int d\mathbf{r}_1 ... d\mathbf{r}_N \;\; e^{-\beta V(\mathbf{r}_1,..\mathbf{r}_N)}. \end{aligned}$$

Here, Z_g is the grand canonical partition function, and Q_N is the so-called configurational integral for N particles. In the grand canonical ensemble, one sums over all possible values of the number of particles in the system to get the corresponding partition function. The power series for $\chi(z)$ is given by

$$\chi(z) = \sum_{l=1}^{\infty} b_l \;\; z^l$$

with $b_1 = Q_1/V$, $b_2 = (Q_2 - Q_1^2)/2V$, etc. Inverting the series for ρ in terms of z, namely $z = a_1\rho + a_2\rho^2 + ..$, we find $a_1 = 1$, $a_2 = -2b_2$, etc. Inserting this into the fugacity expansion for the pressure finally gives

$$\beta p = \sum_{l=1}^{\infty} B_l(T) \;\rho^l,$$

with $B_1 = 1$ and

$$B_2(T) = -b_2 = \frac{1}{2}\int d\mathbf{r} \left(1 - e^{-\beta\phi(|\mathbf{r}|)}\right),$$

where $\phi(|\mathbf{r}|)$ is the pair-potential of the problem.

a) Consider the pair-potential

$$\phi(r) = \begin{cases} \infty, & \text{if } r \leq R_1 \\ -U_0, & \text{if } R_1 \leq r \leq R_2 \\ 0, & \text{if } r \geq R_2 \end{cases}$$

Compute $B_2(T)$ analytically in three spatial dimensions, and from this find an explicit expression for the Boyle-temperature of the system.

b) NB!! This problem must be solved numerically and is a mandatory part of the HW. Consider the pair-potential

$$\phi(r) = \begin{cases} -U_0 \left(\frac{R}{r}\right)^\alpha, & \text{if } r \geq R \\ \infty, & \text{if } r \leq R \end{cases}$$

Here, $\alpha = 5, 6, 7$. Comment on your results for increasing values og α, comparing to the analytically obtained results in **a)**.

Compute the second virial coefficient $B_2(T)$ numerically as a function of temperature T, for dimensionality $d = 1, 2, 3$. (Hint: Since the integrand is spherically symmetric, one may use spherical coordinates $\int d\mathbf{r} = \Omega_d \int_0^\infty dr r^{d-1}$, with $\Omega_1 = 2, \Omega_2 = 2\pi, \Omega_3 = 4\pi$. Plot your results as a function of the dimensionless parameter $1/\beta U_0$, and normalize $B_2(T)$ to the hard-sphere result $B_{2\text{hs}}(T) = \Omega_d R^d / 2d$. Numpy also has a useful representation of infinity, numpy.inf, which can be used along with the integration routine quad.)

c) Compute the second virial coefficient $B_2(T)$ analytically at high temperatures and compare with your numerical results found in **b)**. Compare also with the hard-sphere result in d dimensions. Explain on physical grounds why $B_2(T)$ approaches the hard-sphere result from *below* in the high-temperature limit $\beta U_0 \to 0$.

Problem 2 Two-level system in the grand canonical ensemble

Consider a system where each particle of the system can be in a state with two possible values of the energy, $\varepsilon_1 = -\varepsilon_0$, and $\varepsilon_2 = \varepsilon_0$. The possible number of particles in the system, N, are assumed to take the values $N = 1, 2, 3, ...$

a) Compute the grand canonical partition function $Z_g = \sum_{N=0}^{\infty} \exp(\beta\mu N) Z(N)$, where $Z(N)$ is the canonical partition function for a system with N particles. (Hint: Compute first $Z(N)$ by exploting that the particles are independent.)

b) Calculate $\langle N \rangle$.

c) Use this to express the chemical potential μ of the system in terms of $\langle N \rangle$, β, ε_0.