Problem Set 3 – Statistical Physics B

Problem 1: Derivation of the virial expansion

(a) Derive the virial expansion for the pressure up until $\mathcal{O}(\rho^4)$. You might want to consider the strategy from the lecture notes. Give explicit expressions for $B_2(T)$ and $B_3(T)$ in terms of the Mayer function.

(b) Suppose one would add a three-body potential to the microscopic classical Hamiltonian. Will the second virial coefficient depend on this three-body potential? Prove your answer.

(c) Derive the virial expansion of the radial distribution function for a pair-wise additive interacting classical system,

$$g(r;\rho,T) = g^{(0)}(r;T) + \rho g^{(1)}(r;T) + ... \tag{1}$$

and give an explicit expression for the expansion coefficients in terms of the Mayer function. What is the physical interpretation of these expansion coefficients?

Problem 2: The second virial coefficient for model potentials

We recall the definition of the second virial coefficient, $B_2(T) = -(1/2)\int d\mathbf{r}\, f_{\mathrm{M}}(r)$, with f_{M} the Mayer function.

(a) Compute $B_2(T)$ for a hard-sphere system and for a square-well fluid. Under which conditions does the square-well fluid reduce to the hard-sphere limit? Check that this is also reflected in the expression of $B_2(T)$. What is the Boyle temperature in both cases? Give a physical explanation.

(b) Show that under certain conditions

$$B_2(T) = -\frac{1}{6k_{\mathrm{B}}T}\int_0^\infty dr\, 4\pi r^3 v'(r)\exp[-\beta v(r)]. \tag{2}$$

What are these conditions? Compute $B_2(T)$ for potentials of the form $v(r) = \alpha/r^n$ with $n > 3$ in terms of the Euler Gamma function.

(c) Consider a Lennard-Jones fluid. Explain the terms in this potential. What is the minimum of the potential? Give a physical interpretation. Compute the force acting on a particle. What is the direction of the force? When is the force maximal/minimal?

(d) Give an expression of the ratio $B^* = B_2^{\mathrm{LJ}}/B_2^{\mathrm{HS}}$ in terms of dimensionless temperature $T^* = k_{\mathrm{B}}T/\epsilon$. By a suitable variable substitution, show that

$$B^*(T^*) = \frac{8}{\sqrt{2}T^*}e^{1/T^*}\frac{1}{2}\int_0^\infty du\,\frac{u-1}{\sqrt{u}}e^{-(1/T^*)(u-1)^2}. \tag{3}$$

For which temperature does the LJ fluid reduce to the hard-sphere fluid based on the second virial coefficient?

(e) Compute the integral numerically or analytically. For an analytical calculation, you might consider the following steps:

- Use the coordinate transformations $u = 1 + \cosh(t/2)$ for $u > 2$ and $u = 1 + \cos(t/2)$ for $0 < u < 2$.

- Express your result in terms of modified Bessel functions of the first kind. The following integral representation might be useful:

$$I_\nu(x) = \frac{1}{\pi}\int_0^\pi dt\, e^{x\cos t}\cos(\nu t) - \frac{\sin(\pi\nu)}{\pi}\int_0^\infty dt\, e^{-x\cosh t-\nu t}. \tag{4}$$

- Obtain the final result

$$B^*(T^*) = \frac{\sqrt{2}\pi}{2T^*}e^{1/(2T^*)}\sum_{n=0,1}(-1)^{n+1}\left[I_{(2n+1)/4}\left(\frac{1}{2T^*}\right) + I_{-(2n+1)/4}\left(\frac{1}{2T^*}\right)\right]. \tag{5}$$

(f) Determine numerically the Boyle temperature as a function of ϵ for a Lennard-Jones fluid.

Problem 3: Higher order virial coefficient for hard spheres

The third virial coefficient is given by

$$B_3(T) = -\frac{1}{3V}\int d\mathbf{r}_1\int d\mathbf{r}_2\int d\mathbf{r}_3\, f_{\mathrm{M}}(r_{12})f_{\mathrm{M}}(r_{13})f_{\mathrm{M}}(r_{23}). \tag{6}$$

(a) Give a geometric interpretation of this formula in the case of hard-sphere interactions. Using these geometric arguments, compute B_3 for hard spheres.

(b) Introduce the Fourier transform $\tilde{f}_{\mathrm{M}}(k) = \int d\mathbf{r}\, f_{\mathrm{M}}(r)e^{-i\mathbf{k}\cdot\mathbf{r}}$ of the Mayer function and show that

$$B_3(T) = -\frac{1}{3}\int\frac{d\mathbf{k}}{(2\pi)^3}\,\tilde{f}_{\mathrm{M}}(k)^3. \tag{7}$$

Derive an expression for $\tilde{f}_{\mathrm{M}}(k)$ for hard spheres, and then compute $B_3(T)$ from it. The following integral might be useful,

$$\int_0^\infty dx\, x^{-5/2}J_{3/2}(x)^3 = \frac{5}{48\sqrt{2\pi}}, \tag{8}$$

where $J_\nu(x)$ is ν-th order Bessel function of the first kind.