Hand-in sheet 2 – Statistical Physics B

- *Please hand in your solution before Thursday 7 November 2024, 16:15.*
- *You can hand in your solutions in digital format as a pdf-file. Make sure to provide a file name which contains the hand-in number, your name, and your student number. You can send your solution to jeffrey.everts AT fuw.edu.pl. Also include your name and student number in the pdf file.*
- *In case of paper format, please do not forget to write your name and student number.*
- *Make sure to answer every question as completely as possible. When you do calculations, provide sufficient explanation for all steps.*
- *In total 100 points can be earned.*

Hard spheres within the Percus-Yevick approximation

In this exercise we will explore the properties of hard-sphere systems within the Percus-Yevick approximation. In this case the direct correlation function $c(r)$ is analytically known, see the lecture notes.

(a) (*15 points*) The hard-sphere potential is not continuous nor differentiable. However, we can introduce the so-called cavity function $y(r)$, which is continuous even if $v(r)$ is not. One can prove that we can always write $g(r) = \exp[-\beta v(r)]y(r)$. Prove using the properties of $y(r)$ that

$$\frac{\beta p}{\rho} = 1 + 4\eta g(\sigma^+), \tag{1}$$

with η the volume fraction and $\sigma^+ = \lim_{\epsilon \downarrow 0}(\sigma + \epsilon)$. This is the contact theorem for hard spheres.

(b) (*20 points*) Recall the virial expansion of the radial distribution function (problem 3.1c). Compute $g^{(0)}$ and $g^{(1)}$ for hard spheres and sketch $g(r)$ to $\mathcal{O}(\rho^2)$. How does your result compare to $g^{(0)}(r)$ of a Lennard-Jones fluid? What do you conclude?

(c) (*10 points*) Compute $p(\rho, T)$ using these results in conjuction with the contact theorem. Is it consistent with the virial expansion?

(d) (*15 points*) Use the contact theorem and the direct correlation function within the PY approximation, to show that

$$\frac{p_{\mathrm{v}}}{\rho k_{\mathrm{B}} T} = \frac{1 + 2\eta + 3\eta^2}{(1-\eta)^2}. \tag{2}$$

Expand the right-hand side to $\mathcal{O}(\eta^4)$. The subscript v denotes the virial route.

(e) (*15 points*) Show from integration of the compressibility route to thermodynamics that

$$\frac{p_{\mathrm{c}}}{\rho k_{\mathrm{B}} T} = \frac{1 + \eta + \eta^2}{(1-\eta)^3}, \tag{3}$$

with subscript denoting compressibility. Expand the right-hand side to $\mathcal{O}(\eta^4)$ and compare your result with p_{v}.

(f) (*10 points*) What is the source of the inconsistency between the virial and compressibility route?

(g) (*15 points*) Compute the expression for the Carnahan-Starling pressure, defines as $p_{\mathrm{CS}} = (2p_{\mathrm{c}} + p_{\mathrm{v}})/3$. Integrate the resulting equation of state *explicitly* (i.e., give all details) to find the free energy per particle

$$\frac{F_{\mathrm{CS}}}{Nk_{\mathrm{B}}T} = \log(\rho\Lambda^3) - 1 + \frac{4\eta - 3\eta^2}{(1-\eta)^2}. \tag{4}$$

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