Problem Set 8 – Statistical Physics B

Problem 1: Reversible work theorem

Consider the radial distribution function $g(r)$ in a system with general potential energy $\Phi(\mathbf{r}^N)$. We define the function w as $g(r) = e^{-\beta w(r)}$. Prove that

$$-\frac{\partial}{\partial \mathbf{r}_1} w(\mathbf{r}_{12}) = \left\langle -\frac{\partial \Phi}{\partial \mathbf{r}_1} \right\rangle_{\mathbf{r}_1, \mathbf{r}_2 \text{ fixed}}.$$

Explain why $w(r)$ is sometimes called the potential of mean force.

Problem 2: 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) 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) Recall the virial expansion of the radial distribution function (problem 7.1c). 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) Compute $p(\rho, T)$ using these results in conjuction with the contact theorem. Is it consistent with the virial expansion?

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

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

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

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

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

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

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

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

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

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Problem 3: Properties of bulk systems

We consider a bulk system for which the particles interact with each via pairwise-additive potentials, i.e. $\Phi(\mathbf{r}^N) = \sum_{i<j} v(|\mathbf{r}_i - \mathbf{r}_j|)$.

(a) The classical density operator is given by $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$. Prove that in this case $\rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle$ equals a constant denoted by ρ_b. Derive an expression for ρ_b in the canonical ensemble and in the grand-canonical ensemble. Comment on how they differ.

(b) Consider the correlation function,

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j) \right\rangle .$$

We define the radial distribution function as $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \rho_\mathrm{b}^2 g(|\mathbf{r} - \mathbf{r}'|)$, which is valid for homogeneous and isotropic systems. Give two physical interpretations of $g(r)$. Motivate these interpretations sufficiently with mathematical equations.

(c) Sketch $g(r)$ for a typical gas, liquid, and solid and comment on the differences. Make sure to mark important features of $g(r)$ in your sketch.

(d) Consider a typical phase diagram of a one-component classical system. Can the liquid-solid melting transition line end in a critical point? Motivate your answer.