Problem Set 7 – Statistical Physics B

Problem 1: Density expansions

(a) Prove that $\int_0^1 d\alpha \int_0^\alpha d\alpha' g(\alpha') = \int_0^1 d\alpha\,(1-\alpha)g(\alpha)$ for arbitrary functions g. Use this result to show that the density expansion approximation Eq. (3.23) follows from Eq. (3.18) (see lecture notes).

(b) Show that one can derive the density expansion also from a functional Taylor expansion of $\mathcal{F}_{\text{ex}}[\rho]$ around the uniform bulk density ρ_{b}.

(c) Suggest ways to improve the density expansion approximation using your answer from (b). Give an explicit form for the next order correction in the density expansion.

Problem 2: Van der Waals theory of the gas-liquid interface

Consider the square-gradient approximation

$$\mathcal{F}[\rho] = \int d\mathbf{r}\ \left[f_0(\rho(\mathbf{r})) + f_2(\rho(\mathbf{r}))|\nabla\rho(\mathbf{r})|^2\right]. \tag{1}$$

First we take the more general case where $f_2(\rho)$ depends on the density ρ.

(a) Show that the Euler-Lagrange equation can be written as

$$f_2(\rho(z))\left[\frac{d}{dz}\rho(z)\right]^2 = \omega(\rho(z)) + p_{\text{co}}, \tag{2}$$

where we can interpret $\omega(\rho_{\text{b}})$ as the grand potential density for bulk systems with constant density ρ_{b} and p_{co} is the coexistence pressure of gas and liquid.

(b) Prove that the surface tension is given by

$$\gamma = 2\int_{\rho_{\text{g}}}^{\rho_{\text{l}}} d\rho\, f_2(\rho)^{1/2}[\omega(\rho) + p_{\text{co}}]^{1/2}. \tag{3}$$

Here, ρ_{l} and ρ_{g} are the densities of the coexisting liquid and gas, respectively. Do we need the explicit profile $\rho(z)$ to compute this quantity?

Within the van der Waals model f_2 is taken to be constant. Furthermore, we make the approximation

$$\omega(\rho) + p_{\text{co}} = K(\rho-\rho_{\text{g}})^2(\rho_{\text{l}}-\rho)^2, \tag{4}$$

with K an phenomenological constant.

(c) Provide arguments why this approximation is reasonable.

(d) Show within this approximation that

$$\rho(z) = \frac{\rho_{\text{l}}+\rho_{\text{g}}}{2} - \frac{\rho_{\text{l}}-\rho_{\text{g}}}{2}\tanh\left(\frac{z}{2\xi}\right), \tag{5}$$

where $\xi = (f_2/K)^{1/2}/(\rho_{\text{l}}-\rho_{\text{g}})$.

(e) Sketch $\rho(z)$ for several values of ξ. Argue that ξ is a measure of the width of the interface.

(f) Close to the critical point $\rho_{\text{l}}-\rho_{\text{g}} \sim (T_{\text{c}}-T)^{1/2}$ within mean-field theory. Show that $\xi \sim (T_{\text{c}}-T)^{-1/2}$. (In reality it diverges as $(T_{\text{c}}-T)^{-\nu}$, with critical exponent $\nu = 0.63$.) What happens at the critical point? Interpret your answer.

(g) Compute the surface tension γ and show that near the critical point $\gamma \sim (T_c - T)^{3/2}$. (In reality $\gamma \sim (T_c - T)^{\tilde{\mu}}$ with $\tilde{\mu} = 2\nu = 1.26$).

Problem 3: Depletion interactions between spherical particles

Consider a binary mixture of two species with N_1 and N_2 particles, respectively. The positional coordinates for species 1 are given by $\mathbf{R}^{N_1} := (\mathbf{R}_1, ..., \mathbf{R}_{N_1})$ and for species 2 by $\mathbf{r}^{N_2} := (\mathbf{r}_1, ..., \mathbf{r}_{N_2})$. The total potential energy can be written as

$$\Phi(\mathbf{R}^{N_1}, \mathbf{r}^{N_2}) = \Phi_{11}(\mathbf{R}^{N_1}) + \Phi_{22}(\mathbf{r}^{N_2}) + \Phi_{12}(\mathbf{R}^{N_1}, \mathbf{r}^{N_2}).$$

(a) Give two examples of a physical system that conform to the above description.

(b) Give expressions for the canonical partition function $Z(N_1, N_2, V, T)$ and the semi-grand partition function $\Xi(N_1, \mu_2, V, T)$. Denote the corresponding thermodynamic potentials as $F(N_1, N_2, V, T)$ and $\Omega(N_1, \mu_2, V, T)$, respectively. How are the thermodynamic potentials related? Furthermore, give expressions in terms of the corresponding partition functions.

(c) Show that we can write for the semi-grand potential

$$\exp[-\beta\Omega(N_1, \mu_2, V, T)] = \frac{1}{N_1!\Lambda^{3N_1}} \int d\mathbf{R}^{N_1} \exp[-\beta\Phi_{\text{eff}}(\mathbf{R}_1^N)].$$

Furthermore, define the induced effective potential Φ_{ind} via $\Phi_{\text{eff}} = \Phi_{11} + \Phi_{\text{ind}}$. What is the difference between Φ_{ind} and Φ_{eff}? Give an expression for both quantities.

(d) Assume that particles of species 2 do not interact amongst each other ($\Phi_{22} = 0$), but do interact with particles of species 1. Furthermore, assume pairwise additivity,

$$\Phi_{12}(\mathbf{R}^{N_1}, \mathbf{r}^{N_2}) = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} \phi_{12}(\mathbf{R}_i - \mathbf{r}_j).$$

What kind of physical system can this be? Prove that

$$\Phi_{\text{ind}}(\mathbf{R}^{N_1}; \mu_2, T) = -z_2 k_B T \int d\mathbf{r} \exp\left[-\beta \sum_{i=1}^{N_1} \phi_{12}(\mathbf{r} - \mathbf{R}_i)\right] =: -z_2 k_B T V_f(\mathbf{R}^{N_1})$$

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(e) Suppose $\phi_{12}(r)$ is a hard-sphere potential with hard-core diameter σ_{12}. How can one interpret $V_f(\mathbf{R}^{N_1})$ in this case?

(f) Consider $N_1 = 2$ and take Φ_{11} to be also a hard-sphere potential with hard-core diameter σ_{11}. Compute $\Phi_{\text{eff}}(\mathbf{R}_1, \mathbf{R}_2)$. Does species 2 generate an attraction or a repulsion between the two spheres? How does the strength of the interaction change when we increase the density of species 2?

(g) Does the entropy of species 2 increase or decrease when we bring the two spheres closer together? Interpret your answer.