Problem Set 10 – Statistical Physics B

Problem 1: 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

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

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

(b) Prove that the surface tension is given by

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

Here, $\rho_{\rm l}$ and $\rho_{\rm g}$ 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

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

with K an phenomenological constant.

(c) Provide arguments why this approximation is reasonable.

(d) Show within this approximation that

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

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

(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 $\rho_{\rm l}-\rho_{\rm g} \sim (T_{\rm c}-T)^{1/2}$ within mean-field theory. Show that $\xi \sim (T_{\rm c}-T)^{-1/2}$. (In reality it diverges as $(T_{\rm c}-T)^{-\nu}$, 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 $\gamma \sim (T_{\rm c}-T)^{3/2}$. (In reality $\gamma \sim (T_{\rm c}-T)^{\tilde{\mu}}$ with $\tilde{\mu} = 2\nu = 1.26$).

Problem 2: Microscopic interpretation of the square-gradient approximation. Consider the square-gradient approximation Eq. (1).

(a) Argue why terms proportional to $\nabla^2\rho(\mathbf{r})$ and $\nabla\rho(\mathbf{r})$ do not occur.

(b) Consider the functional Taylor expansion of $\mathcal{F}_{\mathrm{ex}}[\rho]$ around the bulk density ρ_{b} to second order in the density deviations to the uniform fluid. Assume slowly varying density profiles which allows us to approximate the direct correlation function in Fourier space as $\tilde{c}^{(2)}(\rho_{\mathrm{b}};k) = a(\rho_{\mathrm{b}}) + b(\rho_{\mathrm{b}})k^2 + ...$ By expanding also Eq. (1) around ρ_{b} and imposing consistency with the result from the functional Taylor expansion, show that one can make the identification

$$\mu_{\mathrm{ex}}(\rho_{\mathrm{b}}) = f'_{\mathrm{ex}}(\rho_{\mathrm{b}}), \quad a(\rho_{\mathrm{b}}) = -\beta f''_{\mathrm{ex}}(\rho_{\mathrm{b}}), \quad b(\rho_{\mathrm{b}}) = -2\beta f_2(\rho_{\mathrm{b}}). \tag{6}$$

Physically interpret these identifications.

(c) Show that

$$\beta f_2(\rho) = \frac{1}{12}\int d\mathbf{r}\, r^2 c^{(2)}(\rho; r). \tag{7}$$

(d) Consider now a Lennard-Jones fluid. Argue that to a very good approximation,

$$f_2(\rho) = -\frac{\pi}{3}\int_\sigma^\infty dr\, r^4 v_{\mathrm{att}}(r) > 0, \tag{8}$$

where $v_{\mathrm{att}}(r)$ is the attractive part of the pair potential. Note that here f_2 does not depend on ρ.

(e) What is $f_2(\rho)$ for a hard-sphere fluid? You can use the Percus-Yevick approximation. What is the physical consequence of your result?