Problem Set 11 – Statistical Physics B

Problem 1: The hard-rod fluid in one spatial dimension

For a one-dimensional hard-rod fluid the intrinsic Helmholtz free energy functional $\mathcal{F}[\rho]$ functional is analytically known. It is given by

$$\beta\mathcal{F}[\rho] = \int_{-\infty}^{\infty} dz\, \rho(z) \left\{ \ln\left[\frac{\rho(z)\Lambda}{1-t(z)}\right] - 1 \right\}, \quad t(z) = \int_{z-\sigma}^{z} dz'\, \rho(z').$$

Here $\rho(z)$ is the one-body density profile and Λ is the thermal wavelength.

(a) Derive from $\mathcal{F}[\rho]$ the Helmholtz free energy density and pressure for the homogeneous hard-rod fluid. Express your result in terms of the one-dimensional packing fraction $\eta = \rho\sigma$, with ρ the number density and σ the length of the rods. Interpret the result for the pressure in terms of the free volume available to the centres of the rods.

(b) Derive an expression for the isothermal compressibility $\kappa_\mathrm{T} = -L^{-1}(\partial L/\partial p)_{N,T}$ for the homogeneous hard-rod fluid. What happens to κ_T when $\eta \to 1$? Give a physical interpretation of your results.

The excess functional can be expressed in terms of weighted densities $\{n_\alpha | \alpha = 0, 1\}$,

$$\beta\mathcal{F}_\mathrm{ex}[\rho] = \int_{-\infty}^{\infty} dz\, \Phi(\{n_\alpha(z)\}), \quad \Phi(\{n_\alpha\}) = -n_0(z)\ln[1 - n_1(z)].$$

This relation is exact. The weighted densities are defined by

$$n_\alpha(z) = \int_{-\infty}^{\infty} dz'\, \rho(z') w^{(\alpha)}(z - z'), \quad \alpha \in \{0, 1\},$$

with weight functions

$$w^{(0)}(z) = \frac{1}{2}[\delta(z - R) + \delta(z + R)], \quad w^{(1)}(z) = \Theta(R - |z|),$$

with Θ the Heaviside step function and $R = \sigma/2$.

(c) Consider $V_\mathrm{ext}(z) = 0$. In this case, show that $\Phi(\{n_\alpha\})$ is the excess Helmholtz free energy density (per $k_\mathrm{B}T$) for a homogeneous fluid.

(d) Derive explicit expressions for the one-body direct correlation functions for inhomogeneous hard-rod fluids. It might be beneficial to first show that

$$c^{(1)}(z) = -\int dz' \sum_\alpha \frac{\partial\Phi}{\partial n_\alpha(z')} \omega^{(\alpha)}(z' - z), \tag{1}$$

with $\omega^{(\alpha)}$ ($\alpha = 0, 1$) the weight functions of the one-component fluid. Evaluate your answer in terms of the equilibrium density profile and simplify it to an expression that does contain any of the weight functions.

(e) Prove for general $V_\mathrm{ext}(z)$ that

$$c^{(2)}(z_1, z_2) = -\int_{-\infty}^{\infty} dz \sum_{\alpha,\beta=0,1} \frac{\partial^2\Phi}{\partial n_\alpha(z) n_\beta(z)} \omega^{(\alpha)}(z - z_1)\omega^{(\beta)}(z - z_2),$$

Evaluate this expression explicitly in terms of $n_0(z)$ and $n_1(z)$ and the weight functions.

(f) Prove that

$$\int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' \, w^{(\alpha)}(z') w^{(\beta)}(z'-z) e^{-ikz} = \tilde{w}^{(\alpha)}(k)\tilde{w}^{(\beta)}(k), \quad \alpha, \beta \in \{0,1\}.$$

where we defined the Fourier transform of a function f as $\tilde{f}(k) = \int_{-\infty}^{\infty} dz \, f(z) e^{-ikz}$.

(g) Compute $c^{(2)}(z)$ when $V_{\text{ext}}(z) = 0$. Sketch this function for various values of η including the case $\eta = 0$ and $\eta = 1$.

(h) Consider the case where $V_{\text{ext}}(z) = 0$. Show that the structure factor is given by

$$S(k) = \left[1 + \frac{2\eta}{1-\eta}\left(\frac{\sin q}{q} + \frac{\eta}{1-\eta}\frac{1-\cos q}{q^2}\right)\right]^{-1}, \quad q = k\sigma.$$

(i) Show that this expression for $S(k)$ reproduces the result in (b). Give representative sketches of $S(k)$ for some values of η. Do you observe crystallisation? Explain.