Problem Set 5 – Statistical Physics B

Problem 1: The random-phase approximation

(a) Consider the direct correlation function $c(r)$. What is the asymptotic behaviour of $c(r)$? Write down an expression for $S(k)$ in the RPA for a general pair potential $v(r)$. When is the expression for $S(k)$ well defined? What physical systems can we model within the RPA?

(b) Consider the Gaussian-core model, which models polymer blobs that are allowed to overlap

$$v(r) = \epsilon \exp(-r^2/R^2). \tag{1}$$

Here $\epsilon > 0$ is an energy scale and R is roughly the radius of gyration of a polymer coil. Within the random-phase approximation, compute the structure factor of such a fluid. Plot a few examples of $S(k)$ in the range of $1 < \eta < 5$, with η the volume fraction. Why are we allowed to take such high values of η?

(c) Compute $g(r)$ numerically. Comment on the qualitative features of $g(r)$ and $S(k)$ for various parameter values and give a physical interpretation. Do you see oscillations?

(d) Use the compressibility route to find the Helmholtz free energy of the Gaussian-core model within the RPA.

Problem 2: Law of corresponding states

Within the van der Waals approximation the free energy density $f = F/V$ of a homogeneous bulk system with density ρ is

$$\beta f = \rho \left(\log \frac{\rho \Lambda^3}{1 - b\rho} - 1 \right) - \beta a \rho^2, \tag{2}$$

with a and b positive constants.

(a) What are the physical meaning and dimension of the parameters a and b? Argue how one can derive microscopic expressions for these quantities from the partition function of, for example, Lennard-Jones particles.

(b) Calculate the pressure p and chemical potential μ from f.

(c) Determine the critical point (ρ_c, T_c). Is it crucial that a and b are positive?

(d) Show that the equation of state can be written as

$$h\left(\frac{p}{p_c}, \frac{\rho}{\rho_c}, \frac{T}{T_c} \right) = 0. \tag{3}$$

This is called the law of corresponding states. What is the interpretation of this equation?

(e) Sketch $p(\rho)$ and $\mu(\rho)$ for $T < T_c$, $T = T_c$, and $T > T_c$. Describe in words how one can obtain the phase diagram from these two quantities in theory and in practice. Make a sketch of a typical phase diagram, and indicate spinodal, binodal, and critical point. Furthermore, explain what these lines represent.

Problem 3: Phase behaviour of a binary mixture

It is straightforward to extend the virial expansion of a one-component system to a mixture. For a (bulk) binary mixture, the Helmholtz free energy $F(N_1, N_2, V, T)$ is given within the second virial approximation by

$$\frac{\beta F(N_1, N_2, V, T)}{V} = \sum_{i=1}^{2} \rho_i[\log(\rho_i \Lambda_i^3) - 1] + \sum_{i,j}^{2} B_{ij}(T)\rho_i\rho_j,$$

with $B_{ij}(T) = (1/2)\int d\mathbf{r}\,\{\exp[-\beta v_{ij}(r)] - 1\}$ and $v_{ij}(r)$ is the pair potential between particles of species i and j. Furthermore, $\rho_i = N_i/V$ for $i = 1, 2$.

(a) Consider two identical canonical subsystems characterized in equilibrium by (N_1, N_2, V, T) that are allowed to exchange both species of particles. Via an internal constraint we redistribute particles by transferring ΔN_1 and ΔN_2 particles from one subsystem to another. Show that

$$2F(N_1, N_2, V, T) < F(N_1 + \Delta N_1, N_2 + \Delta N_2, V, T) + F(N_1 - \Delta N_1, N_2 - \Delta N_2, V, T).$$

(b) Show for an infinitesimal redistribution of particles, the condition you derived in (b) translates to the Hessian matrix $H_{ij} := (\partial^2 F/\partial N_i \partial N_j)_{V,T}$ being positive definite. In other words, show that the thermodynamic stability criteria are $\mathrm{Tr}\,\mathbf{H} > 0$ and $\det \mathbf{H} > 0$. What are the conditions that determine the spinodal?

(c) An additive mixture of hard spheres is characterized by the pair potential,

$$v_{ij}(r) = \begin{cases} \infty, & (r < \sigma_{ij}), \\ 0, & (r > \sigma_{ij}), \end{cases}$$

with $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ where σ_i is the diameter of a particle of type i. Can a binary additive mixture of hard spheres phase separate? Support your answer with calculations.

(d) Show that for the special case $B_{11} = B_{22} =: B$, the spinodal is given by

$$B\rho(x) = \frac{1 + \sqrt{1 + 4x(1-x)\Delta}}{4x(1-x)\Delta}.$$

Here, $x = N_1/N$ is the mole fraction of species 1, and $\rho = \rho_1 + \rho_2$. Derive an explicit expression for Δ.

(e) Suppose now that both species of particles occupy the same volume a^3, and we define the volume fraction as $\phi_i = a^3\rho_i$ for $i = 1, 2$. Furthermore, we assume the system to be incompressible such that $\phi_1 + \phi_2 = 1$. Set $\phi = \phi_1$. Show from the virial expansion that the free energy can be written as

$$\frac{\beta F_{\mathrm{LG}} a^3}{V} = \phi \ln \phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi).$$

Give an expression for χ. Note that the expression for F_{LG} can also be obtained from a lattice-gas model.

(f) Derive the spinodal for the free energy derived in (f). Explain why χ^{-1} plays the role of temperature and plot the spinodal as function of ϕ and χ^{-1}. Mark important points in your plot.