Hand-in sheet 5 – Statistical Physics B

- *Please hand in your solution before Thursday 15 January 2026, 16:15. This can be done during the lectures or tutorials or in mailbox 50 (J. Everts) located close to the secretariat of the Institute of Theoretical Physics on the 5th floor.*
- *We only accept hand-written or printed solutions. Digital format, such as pdf, will not be accepted.*
- *Please do not forget to write your name and student number.*
- *Make sure to answer every question as completely as possible. When you do calculations, provide sufficient explanation for all steps. Unless stated otherwise, saying that you used Mathematica (or equivalent) does not count as an explanation!*
- *In total 100 points can be earned.*

Spinodal decomposition 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) (*10 points*) 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) (*10 points*) 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) (*20 points*) 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) (*15 points*) 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) (*10 points*) 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) (*10 points*) 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.

(g) (*15 points*) We promote the bulk free energy of the lattice gas to a density functional within the square-gradient approximation. In other words,

$$\beta a^3 \mathcal{F}[\phi] = \int d\mathbf{r}\, \left\{\kappa|\nabla\phi(\mathbf{r})|^2 + \phi(\mathbf{r})\ln\phi(\mathbf{r}) + [1-\phi(\mathbf{r})]\ln[1-\phi(\mathbf{r})] + \chi\phi(\mathbf{r})[1-\phi(\mathbf{r})]\right\},$$

with κ a stiffness parameter. Determine within the lattice-gas model an expression for the growth factor $R(q)$ for spinodal decomposition using linear Cahn-Hilliard theory. Express your answer in the overall volume fraction ϕ_0 for which we perform the quench and the interaction parameter χ.

(h) (*10 points*) Derive an expression for the fastest growing mode q_* in terms of the χ parameter. Sketch q_* as function of χ. How do you interpret this result?