

Problem Set 2 – Statistical Physics B

Problem 1: Thermodynamic stability

- (a) Let Φ stand for a general thermodynamic potential, which is a natural function of the extensive variables X_1, X_2, \dots, X_r and the intensive variables I_{r+1}, \dots, I_n . The total differential is given by

$$d\Phi = \sum_{i=1}^r I_i dX_i - \sum_{j=r+1}^n X_j dI_j.$$

Note that a pair X_i and I_i are thermodynamically conjugate with each other. Prove the thermodynamic stability criteria

$$0 \leq \left(\frac{\partial I_i}{\partial X_i} \right)_{X_1, \dots, X_{i-1}, X_{i+1}, \dots, X_r, I_{r+1}, \dots, I_n}.$$

- (b) An experimentalist claims to have found that a certain gaseous material obeys the conditions (i) $(\partial p / \partial v)_T < 0$, (ii) $(\partial p / \partial T)_v > 0$, (iii) $(\partial \mu / \partial v)_T < 0$, (iv) $(\partial T / \partial v)_s > 0$. Here $v = V/n$, and $s = S/n$. Which one of these inequalities is determined by thermodynamic stability? Which pairs of inequalities are inconsistent with each other?

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

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

with a and b positive constants.

- (a) Calculate the pressure p and chemical potential μ from f .
 (b) Determine the critical point (ρ_c, T_c) . Is it crucial that a and b are positive?
 (c) Show that the equation of state can be written as

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

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

- (d) 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: Lattice-gas model in the mean-field approximation

The lattice gas model consist of a collection of M cells that can be either empty or filled with a particle. We denote a filled cell i by the occupation number $n_i = 1$ and an empty cell by $n_i = 0$, with $i = 1, \dots, M$. The energy of a configuration $\{n_i\}$ is given by

$$E(\{n_i\}) = -\varepsilon \sum_{\langle i, j \rangle} n_i n_j.$$

Here ε is a positive constant. Furthermore, the canonical partition function is

$$Z(N, V, T) = \sum_{\{n_i\}} \exp[-\beta E(\{n_i\})] \delta_{N, \sum_{i=1}^M n_i}.$$

- (a) What do the various contributions in above expressions represent? How does this model incorporate steric repulsions between particles?
- (b) The lattice gas model in the grand-canonical ensemble is isomorphic to the Ising model in an external magnetic field in the canonical ensemble. Give the precise mapping between the Ising model and the lattice gas model.
- (c) Determine the Helmholtz free energy of the system within the mean-field approximation.
- (d) What are the conditions for the binodal?
- (e) Determine the spinodal and critical point within the mean-field approximation.
- (f) Make a sketch of the phase diagram and indicate all point and lines of relevance in your sketch. How does your phase diagram differ from the one obtained in Problem 2?

Problem 4: Magnetism in a classical system

Consider a system of N classical point charges in an external magnetic field. Can such a system generally exhibit a non-zero magnetisation? Provide a mathematical explanation and discuss the repercussions qualitatively.