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 $X_1, X_2, ..., X_r$ and the intensive variables $I_{r+1}, ..., I_n$. 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

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

(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 $i = 1, ..., M$. 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.