
Problem Set 4 The liquid-gas phase transition

1 Lattice gas model

In this problem, we are attempting to describe the properties of a classical fluid composed of N molecules at the temperature T . Toward this goal, we will use an extremely simplified model, the lattice gas model. The volume V in which the molecules are enclosed is divided into small cubic boxes of volume v_0 (indexed with the label i). Each box can be either empty (occupation number $n_i = 0$) or occupied by one molecule ($n_i = 1$). Let $N_0 (> N)$ be the number of boxes occupying the whole volume V . The fact that the occupation number of a box is $n_i = 1$ at most models the repulsive part of the interaction between two molecules. In order to describe the attractive short-range interactions between the molecules, we attribute the energy $-\epsilon$ whenever two neighboring sites are both occupied. The Hamiltonian of the lattice gas model then reads

$$\mathcal{H} = -\epsilon \sum_{\langle i,j \rangle} n_i n_j, \quad n_i, n_j = 0 \text{ or } 1, \quad (1)$$

where $\langle i, j \rangle$ corresponds to a pair of nearest-neighbor sites.

1.1 Study of the ideal gas with an excluded volume

In the first part of this Problem, we consider the case of an ideal gas with an excluded volume (i.e., we neglect the attractive interactions among the molecules, $\epsilon = 0$). We describe the system in the canonical ensemble, where the number N of particles is fixed.

- (a) Show that the canonical partition function Z of the system corresponds to the total number of configurations that the system can take, i.e.,

$$Z = \frac{N_0!}{N!(N_0 - N)!}.$$

- (b) At the thermodynamical limit ($N_0 > N \gg 1$), deduce from the question above expressions for the free energy, the average energy, the entropy, and the pressure of the gas. Comment on your results.

1.2 Interacting gas

We now consider the full Hamiltonian (1) of the system and look for an approximate expression of the grand-canonical partition function Ξ . We call μ the chemical potential.

1.2.1 Approximate calculation of the partition function

Let us suppose that we know the average occupation number $\langle n_i \rangle = n$ of a site i , which is assumed to be the same for all sites of the lattice.

- (a) Give an expression for the average number of molecules $\langle N \rangle$ as a function of n .
- (b) Let us define the correlation function $\mathcal{C}_{ij} = \langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle$. By decomposing n_i into its average n and the fluctuations δn_i around it, perform a mean field approximation and show that $\mathcal{C}_{ij} \simeq 0$. Deduce from this result that within the mean field approximation, one can replace the product $n_i n_j$ ($i \neq j$) by $n(n_i + n_j) - n^2$.

- (c) Show that, within the mean field approximation, the Hamiltonian (1) takes the simplified form

$$\mathcal{H} \simeq -6\epsilon n \sum_{i=1}^{N_0} n_i + 3\epsilon N_0 n^2.$$

Deduce from the expression above the grand-canonical partition function Ξ and the grand potential Ω as a function of n .

- (d) Using your results for Ω and question 1.2.1(a), calculate the average number of molecules as a function of n . Deduce from the above calculation a self-consistent equation for n .
- (e) Show that the equation of state of the system reads

$$P = -\frac{k_B T}{v_0} \ln \left(1 - \frac{N}{V} v_0 \right) - 3\epsilon \left(\frac{N}{V} \right)^2 v_0.$$

- (f) Sketch the isothermal curves and comment on the phase diagram. Show that if the temperature is lower than a critical temperature T_c , the system becomes unstable for a certain range of volume. Show that the critical point is located at

$$k_B T_c = \frac{3}{2}\epsilon, \quad V_c = 2Nv_0, \quad P_c = \frac{3}{2} \left(\ln 2 - \frac{1}{2} \right) \frac{\epsilon}{v_0}.$$

Give the values n_c and μ_c of, respectively, n and μ at the critical point.

1.2.2 Study of the critical point

We now consider that the system is close to the critical point. We hence assume that $\mu = \mu_c$ and that n is close to n_c . We therefore set $n = n_c(1 + m)$, with $m \ll 1$.

- (a) Show that the self-consistent equation for n now reads

$$m = \tanh \left(\frac{T_c}{T} m \right). \quad (2)$$

- (b) Solve for Eq. (2) graphically and show that for $T \geq T_c$, there exists one solution $m = 0$, while for $T < T_c$, $m = 0, \pm m_0(T)$.
- (c) Taylor-expand the grand-potential found at question 1.2.1(c) to fourth order in m and show that for T close to T_c , one has

$$\Omega = N_0 k_B T_c \left(\frac{1}{2} - \ln 2 + \frac{1}{2} \frac{T - T_c}{T_c} m^2 + \frac{1}{12} m^4 \right).$$

Discuss then the stability of the solutions found at the preceding question. What is the physical meaning of your results?

- (d) Calculate the isothermal compressibility

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

of the system in the vicinity of the critical point. How does it behave in the limit $T \rightarrow T_c$?

1.2.3 Universality classes

- (a) Compare the mean-field critical exponents of the lattice gas and Ising models (cf. Problem Set 3).
- (b) By introducing $n_i = (1 + s_i)/2$ with $s_i = \pm 1$, show that close to the critical point, $\mathcal{H} - \mu N$ can be mapped into an Ising Hamiltonian with $J = \epsilon/4$ and zero magnetic field.

2 Van der Waals equation of state

Let us consider a fluid of N monatomic molecules with mass m occupying a volume V at the temperature T . Here we shall describe the liquid-gas phase transition with a slightly more realistic model as that in Problem 1. We recall that the canonical partition function of the system is given by

$$Z = \frac{1}{N! \Lambda_T^{3N}} \int d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)},$$

where $\Lambda_T = (2\pi\hbar^2/mk_B T)^{1/2}$ is the thermal de Broglie wavelength, $\beta = 1/k_B T$, and $U(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is the potential energy of the fluid.

2.1 The ideal gas case

Let us first consider the case of an ideal gas, where we assume that $U(\mathbf{r}_1, \dots, \mathbf{r}_N) = 0$.

- Calculate the free energy, and deduce from your result the equation of state of the system.
- In a P - V diagram, sketch the isothermal curves. Does the ideal gas model enable one to describe the liquid-gas phase transition?

2.2 Role of the molecular interactions

- Let us now consider the interactions between pairs of molecules only. Show that the interaction energy reads

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{2} \sum_{\substack{i,j=1 \\ (i \neq j)}}^N u(r_{ij}),$$

where $u(r_{ij})$ is the potential energy between two pairs of molecules separated by the distance r_{ij} . Sketch $u(r)$.

- Consider first the attractive part of $u(r)$ and neglect the correlations between particles.
 - What is the average number of particles in an infinitesimal volume $d^3\mathbf{r}$?
 - Show that the system behaves as an independent-particle one, subject to the potential $U/N \simeq -aN/V$, with $a = -(1/2) \int d^3\mathbf{r} u(r)$ a constant which only depends on the chosen form for $u(r)$. (Determine, e.g., a for $u(r) = -u_0(r_0/r)^s$. What happens if $s \leq 3$?).
 - Determine the partition function of the system, as well as its free energy. What kind of approximation have you performed?
- Close to a given molecule, the approximation above is not valid any longer. Why? In the following, we will assume that one can take care of excluded-volume effects by replacing V by $V - Nb$ in the contribution of the ideal gas to the free energy. Justify such an approximation and give the free energy of the system. Deduce from the above results the van der Waals equation of state

$$\left(P + a \frac{N^2}{V^2} \right) (V - Nb) = Nk_B T. \quad (3)$$

2.3 The liquid-gas phase transition

We now aim at describing the liquid-gas phase transition, using the van der Waals equation of state (3).

2.3.1 Isothermal curves

- Sketch the isothermal curves in a P - V diagram. In particular, show that there exists a critical temperature T_c below which the isothermal curves are no longer monotonic functions. (Denote V_- and V_+ the positions of the two extrema.)
- For the critical isothermal curve, there exists an inflection point (P_c, V_c) called the critical point. Give the expressions of P_c , V_c , and T_c as a function of a and b . For water, one has $a = 9.62 \text{ eV} \cdot \text{\AA}^3$ and $b = 51.1 \text{ \AA}^3$. Give an estimate of T_c and P_c .
- Plot the free energy as function of V for $T > T_c$ and $T < T_c$.
- One can show that a thermodynamical system for which $(\partial P / \partial V)_T > 0$ is unstable. What are the regions in the P - V and F - V diagrams which correspond to thermodynamically unstable states?

2.3.2 Critical instability

We are now aiming at describing the system in the unstable regions of the P - V or F - V diagrams. Let us denote $F(T, V, N)$ the free energy calculated above. We assume that the unstable system (P, V, N) separates into two homogeneous phases and aim at calculating the free energy F_b of the biphasic system. If F_b corresponds to a minimum, the system will choose such a biphasic equilibrium state. Let $F_1 = F(T, V_1, N)$ be the free energy of the homogeneous system of N molecules described by the van der Waals equation of state (3) at the temperature T when its volume is V_1 , and $F_2 = F(T, V_2, N)$ its free energy when its volume is V_2 . (Note that $V \neq V_1 + V_2$!) In what follows, we denote by N_1 and N_2 the number of molecules in the phase 1 and 2, respectively, with $N = N_1 + N_2$.

- Recall what are the equilibrium conditions between the two phases. What is the proportion of molecules in phase 1? In phase 2? Deduce from your results above an expression for the volume V as a function of N_1 , N_2 , V_1 , and V_2 .
- Give an expression of the free energy F_b of the biphasic system as a function of V , V_1 , V_2 , F_1 , and F_2 . Plot F_b in the F - V diagram. Discuss the stability of the system in the different regions of the diagram. What happens for $V \in [V_1, V_-] \cup [V_+, V_2]$?
- How should the van der Waals isothermal curves be transformed? Show that the equilibrium conditions of the two phases translate into a simple geometrical property (i.e., the *Maxwell construction*). Hint: Plot $v = V/N$ as a function of P for $T < T_c$ and use the Gibbs–Duhem equation: $d\mu = -s dT + v dP$, where $s = S/N$.
- Recall how the P - T diagram looks like for an elementary body. What is the region which we have described in this Problem?

2.3.3 Critical fluctuations

We now describe the fluctuations of the density $\rho = N/V$ close to the phase transition. One can show that such fluctuations are related to the isothermal compressibility by the following expression:

$$\frac{\langle (\rho - \langle \rho \rangle)^2 \rangle}{\langle \rho \rangle^2} = \frac{k_B T}{V} \chi_T,$$

where

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T.$$

What can you say about the fluctuations at the critical point? Show that for $\rho = \rho_c$, one has

$$\sqrt{\frac{\langle (\rho - \langle \rho \rangle)^2 \rangle}{\langle \rho \rangle^2}} = \frac{2}{3\sqrt{N}} \frac{1}{\sqrt{T/T_c - 1}}.$$