ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Statistical Physics.
Solutions Sheet 11.

HS 2014
Prof. Manfred Sigrist

Exercise 1. *Condensation and crystallization in the lattice gas model.*

The lattice gas model is obtained by dividing the volume V into microscopic cells which are assumed to be small enough such that they contain at most one gas molecule. In two and three dimensions, the result is a square and a cubic lattice, respectively. We neglect the kinetic energy of a molecule and assume nearest neighbors interactions. The total energy is given by

$$H = -\lambda \sum_{\langle i,j \rangle} n_i n_j \tag{1}$$

where the sum runs over nearest-neighbor pairs and λ is the nearest-neighbor coupling. There is at most one particle in each cell ($n_i = 0$ or 1). This model is a simplification of hard-core potentials, like the Lennard-Jones potential, characterized by an attractive interaction and a very short-range repulsive interaction that prevents particles from overlapping.

In order to study the case of a repulsive interaction, $\lambda < 0$, we divide the lattice into two alternating sublattices A and B. For square or cubic lattices, we find that all lattice sites A only have points in B as their nearest neighbors.
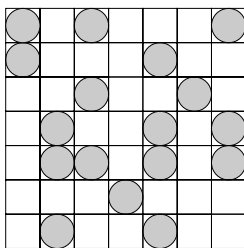

Figure 1: Schematic view of the lattice gas model.

(a) Show the equivalence of the grand canonical ensemble of the lattice gas model with the canonical ensemble of an Ising model in a magnetic field.

Solution. We consider the grand canonical Hamiltonian

$$H - \mu N = -\lambda \sum_{\langle i,j \rangle} n_i n_j - \mu \sum_i n_i \,. \tag{S.1}$$

By introducing Ising spins s_i through the relation

$$n_i = \frac{1}{2}(1 + s_i)\,, \quad s_i = \pm 1\,, \tag{S.2}$$

we arrive at an Ising model

$$H - \mu N = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i - \left(h - \frac{\gamma}{2}J\right)N_{\mathrm{L}} = H_{\mathrm{I}} - \left(h - \frac{\gamma}{2}J\right)N_{\mathrm{L}} \tag{S.3}$$

with

$$J = \frac{\lambda}{4}, \quad h = \frac{\lambda}{4}\gamma + \frac{\mu}{2}\,. \tag{S.4}$$

Here, γ denotes the coordination number (number of nearest neighbors) and N_{L} is the total number of lattice sites. The grand partition function $\mathcal{Z} = \mathrm{Tr}\left[\exp[-\beta(H - \mu N)]\right]$ of the lattice gas is thus related to the canonical partition function $Z_{\mathrm{I}} = \mathrm{Tr}\left[\exp(-\beta H_{\mathrm{I}})\right]$ of the Ising model through

$$\mathcal{Z}_G = Z_{\mathrm{I}}\, \mathrm{e}^{\beta\left(\frac{\lambda}{8}\gamma + \frac{\mu}{2}\right)N_{\mathrm{L}}} \tag{S.5}$$

with the relations (S.4) for the exchange coupling J and the magnetic field h.

(b) Introduce two mean-field parameters m_A and m_B, corresponding to the two sublattices A and B, and adapt the mean-field solution of the Ising model discussed in Sec. 5.2 of the lecture notes for these two parameters. What are the self-consistency conditions for m_A and m_B?

Solution. The Hamiltonian of the Ising model is

$$H_I = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i \,. \tag{S.6}$$

We introduce the mean-field parameters m_A and m_B, which are defined as

$$m_A = \langle s_i \rangle_{i \in A} \,, \qquad m_B = \langle s_j \rangle_{j \in B} \,. \tag{S.7}$$

Now we can write

$$s_i = m_{A,B} + \delta_i := m_{A,B} + (s_i - m_{A,B}) \,, \tag{S.8}$$

where we assume δ_i to be small. Now we can expand the Hamiltonian as

$$
\begin{aligned}
H_I &= -J \sum_{\langle i,j \rangle} (m_A + \delta_i)(m_B + \delta_j) - h \sum_i s_i \\
&= -J \sum_{\langle i,j \rangle} (m_A m_B + m_B \delta_i + m_A \delta_j + \delta_i \delta_j) - h \sum_i s_i \\
&\approx -J \sum_{\langle i,j \rangle} [m_A m_B + m_B(s_i - m_A) + m_A(s_j - m_B)] - h \sum_i s_i \\
&= \frac{\gamma N}{2} J m_A m_B - \gamma J \sum_{i \in A} m_B s_i - \gamma J \sum_{j \in B} m_A s_j - h \sum_i s_i \\
&= \frac{\gamma N}{2} J m_A m_B - \sum_{i \in A} (\gamma J m_B + h) s_i - \sum_{j \in B} (\gamma J m_A + h) s_j \,,
\end{aligned}
\tag{S.9}
$$

where we used that nearest neighbors always belong to different sublattices and neglected the product $\delta_i \delta_j$. We find that the two sublattices A and B behave as paramagnets in the effective fields

$$h_{\text{eff}}^A = \gamma J m_B + h \,, \qquad h_{\text{eff}}^B = \gamma J m_A + h \,. \tag{S.10}$$

The partition function of a paramagnet was already discussed previously, so the partition function of this mean-field Hamiltonian is

$$Z_I = \exp\left[-\tfrac{1}{2} \beta \gamma N J m_A m_B\right] \cdot \left[2 \cosh\left(\beta h_{\text{eff}}^A\right)\right]^{N/2} \cdot \left[2 \cosh\left(\beta h_{\text{eff}}^B\right)\right]^{N/2} \,. \tag{S.11}$$

This immediately leads to the Helmholtz free energy

$$F_I(\beta, h, N) = \frac{N}{2} \left(J \gamma m_A m_B - \frac{1}{\beta} \left\{ \log\left[2 \cosh(\beta h_{\text{eff}}^A)\right] + \log\left[2 \cosh(\beta h_{\text{eff}}^B)\right] \right\} \right) \,. \tag{S.12}$$

The self-consistent solutions are given by the local minima of the free energy. The conditions are therefore

$$\frac{\partial F_I}{\partial m_A} = 0 \quad \Leftrightarrow \quad m_B = \tanh\left[\beta h_{\text{eff}}^A\right] \tag{S.13a}$$

$$\frac{\partial F_I}{\partial m_B} = 0 \quad \Leftrightarrow \quad m_A = \tanh\left[\beta h_{\text{eff}}^B\right] \,, \tag{S.13b}$$

where h_{eff}^A and h_{eff}^A are given by (S.10).

(c) Use your results from parts (a) and (b) to calculate the grand potential for the lattice gas and determine the self-consistency relations for the two mean-field parameters $\rho_A = \langle n_i \rangle_{i \in A}$ and $\rho_B = \langle n_i \rangle_{i \in B}$.

Solution. We use the mean-field approximation (S.12) derived in part (b) and the relations (S.4) in order to write the grand potential

$$\Omega(\beta, \mu, N_{\mathrm{L}}) = -\frac{1}{\beta} \log \mathcal{Z}_G = F_{\mathrm{I}}(\beta, h, N_{\mathrm{L}}) - \left(\frac{\lambda}{8}\gamma + \frac{\mu}{2}\right) N_{\mathrm{L}}$$

$$= \frac{N_{\mathrm{L}}}{2} \left[-\left(\frac{\lambda\gamma}{4} + \mu\right) + \frac{\lambda\gamma}{4}(2\rho_{\mathrm{A}} - 1)(2\rho_{\mathrm{B}} - 1) \right. \tag{S.14}$$

$$\left. -\frac{1}{\beta} \left\{ \log\left[2\cosh\left(\frac{\beta}{2}(\lambda\gamma\rho_{\mathrm{A}} + \mu)\right)\right] + \log\left[2\cosh\left(\frac{\beta}{2}(\lambda\gamma\rho_{\mathrm{B}} + \mu)\right)\right] \right\} \right],$$

where we defined $\rho = \frac{1}{2}(1 + m)$. Here, the effective magnetic fields (S.10) are replaced by

$$h_{\mathrm{eff}}^{A,B} \to \tfrac{1}{2}(\lambda\gamma\rho_{\mathrm{B,A}} + \mu). \tag{S.15}$$

We can now reformulate the self-consistency equations (S.13) for the lattice gas by inserting the relations (S.15). Using $\operatorname{artanh} x = \frac{1}{2}\log[(1 + x)/(1 - x)]$ for $x \in [-1, 1]$, we obtain the two relations

$$\mu = \frac{1}{\beta} \log \frac{\rho_{\mathrm{A}}}{1 - \rho_{\mathrm{A}}} - \lambda\gamma\rho_{\mathrm{B}} = \frac{1}{\beta} \log \frac{\rho_{\mathrm{B}}}{1 - \rho_{\mathrm{B}}} - \lambda\gamma\rho_{\mathrm{A}}, \tag{S.16}$$

which can also be written in the form

$$\rho_{\mathrm{A}} = \frac{1}{1 + \mathrm{e}^{-\beta(\lambda\gamma\rho_{\mathrm{B}} + \mu)}}, \tag{S.17a}$$

$$\rho_{\mathrm{B}} = \frac{1}{1 + \mathrm{e}^{-\beta(\lambda\gamma\rho_{\mathrm{A}} + \mu)}}. \tag{S.17b}$$

By inserting Eq. (S.17b) into Eq. (S.17a), we can in principle obtain the single condition

$$\rho_{\mathrm{A}} = \left[1 + \exp\left(-\beta\left[\frac{\gamma\lambda}{1 + \exp\left(-\beta(\gamma\lambda\rho_{\mathrm{A}} + \mu)\right)} + \mu\right]\right)\right]^{-1}. \tag{S.18}$$

In the following we will use the mean-field solution of the lattice gas model in order to discuss the liquid-gas transition for an attractive interaction $\lambda > 0$.

(d) Argue, why in this case the mean-field results can be simplified as the two densities must be equal, $\rho_{\mathrm{A}} = \rho_{\mathrm{B}} = \rho$. Use your knowledge of the Ising model to define a critical temperature T_{c}, below which there are multiple solutions to the self-consistency equations, and discuss the solutions of ρ for temperatures above or below T_{c}. Define also the critical chemical potential μ_0 corresponding to $h = 0$ in the Ising model and use this for a distinction of cases.

Solution. The two self-consistency equations (S.17) are of the mathematical form

$$a = \phi(b) \qquad b = \phi(a), \tag{S.19}$$

where the function is given by

$$\phi(x) = \frac{1}{1 + \mathrm{e}^{-\beta(\lambda\gamma x + \mu)}}. \tag{S.20}$$

It is easy to see that for $\lambda > 0$ this function is monotonically increasing, while it is decreasing for $\lambda < 0$.

Now if we assume $b > a$, this implies $f(b) > f(a)$. This immediately leads to a contradiction, as $a = f(b) \geq f(a) = b > a$. The same contradiction follows for $b < a$. Therefore, for $\lambda > 0$ there are only symmetric solutions $\rho_{\mathrm{A}} = \rho_{\mathrm{B}}$ for the self-consistency equations and we can simplify the whole treatment by just omitting the second mean-field parameter altogether.

From Eq. (S.4) we see that $h = 0$ corresponds to $\mu = -\lambda\gamma/2 =: \mu_0$. For this case we can use the knowledge about the magnetic transition in the zero-field Ising model. In particular, there is a critical temperature $k_{\mathrm{B}}T_{\mathrm{c}} = \gamma\lambda/4 = -\mu_0/2$ below which there exist two degenerate solutions.
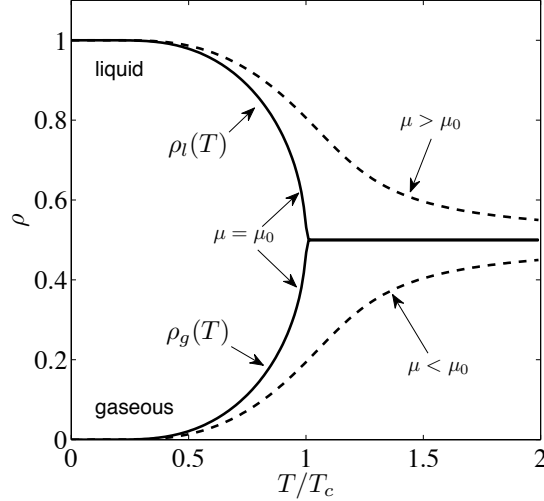
Figure 2: The density ρ as a function of temperature T for different values of the chemical potential μ.

In the lattice gas, these solutions correspond to the liquid and to the gaseous phase and we will denote them by $\rho_l(T)$ and $\rho_g(T)$, respectively (see Fig. 2). The third solution of Eq. (S.17) for $\mu = \mu_0$, namely $\rho = 1/2$, is only stable above T_c.

In the general case, there is a unique solution of Eq. (S.17) for $T > T_c$ while for $T \leq T_c$ there are three solutions in the neighborhood of $\mu = \mu_0 = -2k_B T_c$ but only one minimizes Ω (see Figs. 2 and 3). The solution with $d\rho/d\mu > 0$ is stable or metastable while the solution with $d\rho/d\mu < 0$ is unstable and corresponds to a local maximum of the grand potential Ω. Thus, for $T < T_c$, the density $\rho(T, \mu)$ jumps at μ_0 reflecting the first-order liquid-gas transition (see Fig. 3).

(e) Find the equation of state $p = p(T, \rho)$ or $p = p(T, v)$ and discuss the liquid-gas transition in the $p - v$ diagram. Thereby, $v = 1/\rho$ is the specific volume. Compare with the van der Waals equation of state:

$$\left(p + \frac{\tilde{a}}{v^2} \right) \left(v - \tilde{b} \right) = k_B T \,.$$

What is different in our model?

Hint. For the lattice gas, we have $\tilde{b} = 1$.

Solution. The pressure is given by

$$p(\beta, \mu) = -\frac{\partial}{\partial N_L} \Omega(\beta, \mu, N_L)$$
$$= \frac{\mu}{2} - \left(\frac{\lambda\gamma}{2}(\rho^2 - \rho) - \frac{1}{\beta} \log\left\{ 2\cosh\left[\beta\left(\frac{\lambda\gamma}{2}\rho + \frac{\mu}{2} \right) \right] \right\} \right) \,, \tag{S.21}$$

where we used Eq. (S.14). For $\rho(\beta, \mu) \leq \rho_g(\beta)$ and $\rho(\beta, \mu) \geq \rho_l(\beta)$ we can simply insert Eq. (S.16) into the above equation and obtain

$$p(T, \rho) = -\frac{\lambda\gamma}{2}\rho^2 - \frac{1}{\beta} \log(1 - \rho) \tag{S.22}$$

or in terms of the specific volume $v = 1/\rho$

$$p(T, v) = -\frac{\lambda\gamma}{2}\frac{1}{v^2} - k_B T \log(1 - \frac{1}{v}) \,. \tag{S.23}$$

But for $\rho_g(\beta) \leq \rho(\beta, \mu) \leq \rho_l(\beta)$ there is coexistence of the liquid and the gas. We have to set $\mu = \mu_0$ and $\rho = \rho_{g,l}(T)$ in Eq. (S.21) (this corresponds to the Maxwell construction) leading to a constant pressure! This is shown in the $p - v$ diagram Fig. 4.
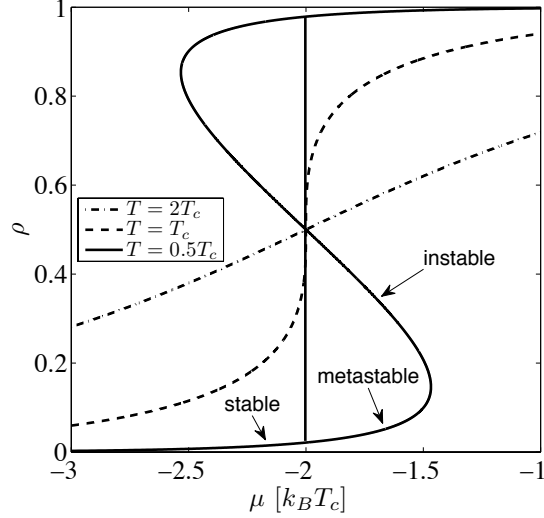
Figure 3: The density ρ as function of the chemical potential μ for different temperatures. For $T < T_c$ there is a jump in ρ at $\mu = \mu_0 = -2k_BT_c$.

We can rewrite the van der Waals equation of state as follows:

$$p(T, v) = -\frac{\tilde{a}}{v^2} + k_BT\frac{1}{v - \tilde{b}} \, .$$

The elementary volume of the gas (hard core volume) $\tilde{b}$ equals 1 in our model, since the volume is given by the total number of lattice sites, N_L. Comparing this with Eq. (S.23), we see that the first term is identical if we set $\tilde{a} = \lambda\gamma/2$, whereas the second term diverges either linearly (van der Walls) or logarithmically (our model) with $v \to 1$. This different behavior is present in the limiting case of high density and can be attributed to the short-range difference of the potential for the discrete lattice gas model and the continuous van der Waals gas.

(f) Find the phase diagram $(T - p$ diagram). Determine the phase boundary $(T, p_c(T))$ and, in particular, compute the critical point $(T_c, p_c(T_c))$.

Solution. The critical pressure is given by Eq. (S.22) for $\mu = \mu_0 = -2k_BT_c$ and $\rho = \rho_{g,l}(T)$

$$p_c(T) = -2k_BT_c\rho_{g,l}^2(T) - k_BT\log(1 - \rho_{g,l}(T)), \tag{S.24}$$

as shown in Fig. 5. In particular, for $T = T_c$ we have $\rho_{g,l}(T_c) = 1/2$ and

$$p_c(T_c) = \frac{k_BT_c}{2}\left(\log 4 - 1\right). \tag{S.25}$$

Instead of the liquid-gas transition, which we have observed for an attractive interaction $\lambda > 0$, a crystallization transition (sublimation) can be observed for nearest-neighbor repulsion, $\lambda < 0$. In this case, we will find that the two mean-field parameters are different, $\rho_A \neq \rho_B$, below some critical temperature T_c.

(g) Discuss the solutions below the critical temperature for $\lambda < 0$. Plot the densities ρ_A and ρ_B, as well as the average, $(\rho_A + \rho_B)/2$ for both attractive and repulsive nearest-neighbor interaction at low temperature, $T < T_c$.

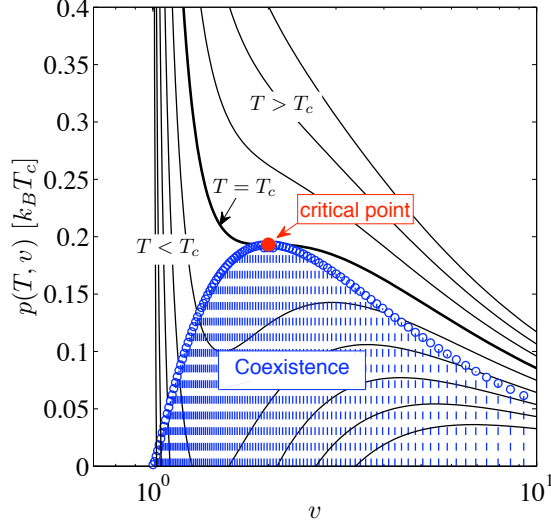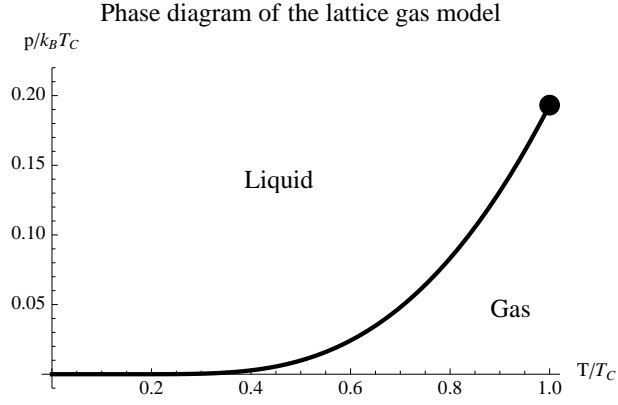Figure 4: The isotherms $p(T, v)$. The shaded region denotes the region of liquid-gas phase coexistence.

Figure 5: p-T phase diagram of the lattice gas model. The two phases coexist when $\mu = \mu_0$ and $T < T_{\mathrm{c}}$ (equilibrium line). Above T_{c} there is only one phase (a single density for a given pressure).

Solution. Below the same critical temperature $k_{\mathrm{B}} T_{\mathrm{c}} = \gamma |\lambda| / 4$ as for an attractive interaction and in a certain range around $\mu_0 = \gamma \lambda / 2$, we find graphically that three different solutions for the self-consistency relations (S.17) exist, corresponding to the crossings of $\phi(\rho_{\mathrm{A}})$ and $\phi(\rho_{\mathrm{B}})$ shown in Fig. 7. There are two degenerate asymmetric solutions $\rho_{\mathrm{A}} \neq \rho_{\mathrm{B}}$, which are related by $\rho_{\mathrm{A}} \leftrightarrow \rho_{\mathrm{B}}$, and one symmetric solution with $\rho_{\mathrm{A}} = \rho_{\mathrm{B}}$.

The exact range $\mu \in [\mu_0 - \Delta\mu, \mu_0 + \Delta\mu]$ for which three solutions exist is given by the condition

$$\phi'(\rho)|_{\phi(\rho)=\rho} < -1 \, . \tag{S.26}$$

This can be understood by looking again at Fig. 7 and by noting that since $\phi(\rho) > 0$, there must exist two asymmetric solutions whenever $\phi'(\rho) < 1$ at the symmetric solution (the middle crossing). By inserting the definition of ϕ into Eq. (S.26) and solving for μ, one obtains

$$\mu_0 - \Delta\mu < \mu < \mu_0 + \Delta\mu, \tag{S.27}$$

with

$$\Delta\mu = \frac{\gamma\lambda}{2}\theta + \frac{1}{\beta}\log\left(\frac{1+\theta}{1-\theta}\right), \qquad \theta = \sqrt{1 + \frac{4}{\beta\gamma\lambda}} \, . \tag{S.28}$$

The asymmetric solutions, which are generally lower in energy, correspond to a crystal structure, where (at $T = 0$) one of the sublattices is occupied while the other one is empty. The densities for attraction and

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repulsion are shown in Fig. 6. While for a nearest-neighbor attraction the densities of the sublattices are identical, there is a symmetry-broken phase for nearest-neighbor repulsion.
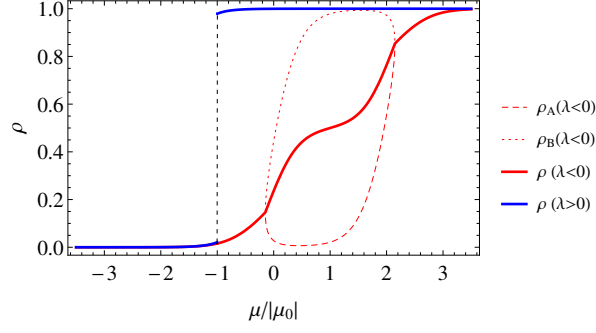

Figure 6: Densities on the two sublattices for attractive ($\lambda > 0$) and repulsive ($\lambda < 0$) nearest-neighbor interaction at $T = 0.5\,T_{\mathrm{c}}$. The thick lines show the average densities, the dashed and dotted lines the densities of the two sublattices.
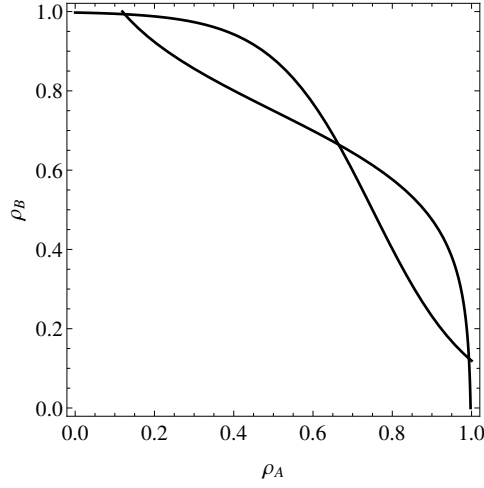

Figure 7: Plot of $\phi(\rho_{\mathrm{A}})$ and $\phi(\rho_{\mathrm{B}})$, defined in Eq. (S.20), for $\mu \in [\mu_0 - \Delta\mu, \mu_0 + \Delta\mu]$.

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