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

$$H = -\lambda \sum_{(i,j)} n_i n_j$$

where the sum runs over nearest-neighbor pairs and $\lambda$ 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.

(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

$$H - \mu N = -\lambda \sum_{(i,j)} n_i n_j - \mu \sum_i n_i.$$  \hspace{1cm} (S.1)

By introducing Ising spins $s_i$ through the relation

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

we arrive at an Ising model

$$H - \mu N = -J \sum_{(i,j)} s_i s_j - h \sum_i s_i - (h - \frac{\gamma}{2} J) N_L = H_1 - (h - \frac{\gamma}{2} J) N_L$$  \hspace{1cm} (S.3)

with

$$J = \frac{\lambda}{4}, \quad h = \frac{\lambda}{4}\gamma + \frac{\mu}{2}.$$  \hspace{1cm} (S.4)

Here, $\gamma$ denotes the coordination number (number of nearest neighbors) and $N_L$ is the total number of lattice sites. The grand partition function $Z_G = \text{Tr} [\exp[-\beta (H - \mu N)]]$ of the lattice gas is thus related to the canonical partition function $Z_I = \text{Tr} [\exp(-\beta H_1)]$ of the Ising model through

$$Z_G = Z_I e^{(\frac{1}{2} + \frac{\gamma}{2}) N_L}.$$  \hspace{1cm} (S.5)

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

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Figure 1: Schematic view of the lattice gas model.
(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

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

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

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

Now we can write

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

where we assume $\delta_i$ to be small. Now we can expand the Hamiltonian as

$$H_I = -J \sum_{\langle i,j \rangle} (m_A + \delta_i)(m_B + \delta_j) - h \sum_i s_i \approx -J \sum_{\langle i,j \rangle} [m_A m_B + m_B (s_i - m_A) + m_A (s_j - m_B)] - h \sum_i s_i \quad (S.9)$$

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

$$h_{A\text{eff}} = \gamma J m_B + h, \quad h_{B\text{eff}} = \gamma J m_A + h. \quad (S.10)$$

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

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

This immediately leads to the Helmholtz free energy

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

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

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

$$\frac{\partial F_I}{\partial m_B} = 0 \iff m_A = \tanh \left[ \beta h_{B\text{eff}} \right] \quad (S.13b)$$

where $h_{A\text{eff}}$ and $h_{B\text{eff}}$ 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
\[
\Omega(\beta, \mu, N_L) = -\frac{1}{\beta} \log Z_G = F_I(\beta, h, N_L) - \left(\frac{\lambda \gamma}{4} + \mu\right) N_L
\]
\[
= \frac{N_L}{2} \left[-\left(\frac{\lambda \gamma}{4} + \mu\right) + \frac{\lambda \gamma}{4} (2\rho_A - 1)(2\rho_B - 1) \right.
\]
\[
- \frac{1}{\beta} \left\{ \log \left[ 2 \cosh \left(\frac{\beta}{2} (\lambda \gamma \rho_A + \mu)\right) \right] + \log \left[ 2 \cosh \left(\frac{\beta}{2} (\lambda \gamma \rho_B + \mu)\right) \right] \right\},
\]
where we defined \( \rho = \frac{1}{2}(1 + m) \). Here, the effective magnetic fields (S.10) are replaced by
\[
h_{\text{eff}}^{A,B} \rightarrow \frac{1}{2} \left(\lambda \gamma \rho_A \pm \mu\right).
\]
We can now reformulate the self-consistency equations (S.13) for the lattice gas by inserting the relations (S.15). Using \( \text{artanh} x = \frac{1}{2} \log \left[ \frac{1 + x}{1 - x} \right] \) for \( x \in [-1, 1] \), we obtain the two relations
\[
\mu = \frac{1}{\beta} \log \frac{\rho_A}{1 - \rho_A} - \lambda \gamma \rho_B = \frac{1}{\beta} \log \frac{\rho_B}{1 - \rho_B} - \lambda \gamma \rho_A,
\]
which can also be written in the form
\[
\rho_A = \frac{1}{1 + e^{-\beta(\lambda \gamma \rho_B + \mu)}}, \quad (S.17a)
\]
\[
\rho_B = \frac{1}{1 + e^{-\beta(\lambda \gamma \rho_A + \mu)}}. \quad (S.17b)
\]
By inserting Eq. (S.17b) into Eq. (S.17a), we can in principle obtain the single condition
\[
\rho_A = \left[ 1 + \exp \left( -\beta \left(\frac{\gamma \lambda}{1 + \exp \left( -\beta (\gamma \lambda \rho_A + \mu)\right)}\right) \right) \right]^{-1}. \quad (S.18)
\]
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, \( \rho_A = \rho_B = \rho \). 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 \( \rho \) for temperatures above or below \( T_c \). Define also the critical chemical potential \( \mu_0 \) 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
\[
a = \phi(b) \quad b = \phi(a), \quad (S.19)
\]
where the function is given by
\[
\phi(x) = \frac{1}{1 + e^{-\beta (\lambda \gamma x + \mu)}}. \quad (S.20)
\]
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 \( \rho_A = \rho_B \) 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 \( k_B T_c = \gamma \lambda / 4 = -\mu_0 / 2 \) below which there exist two degenerate solutions.
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 \( \Omega \) (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 \( \Omega \). Thus, for \( T < T_c \), the density \( \rho(T, \mu) \) jumps at \( \mu_0 \) 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:

\[
\left( p + \tilde{a} \right) \left( v - \tilde{b} \right) = k_B T.
\]

What is different in our model?

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

**Solution.** The pressure is given by

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

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

\[
p(T, \rho) = -\frac{\lambda \gamma}{2} \rho^2 - \frac{1}{\beta} \log(1 - \rho)
\]

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

\[
p(T, v) = -\frac{\lambda \gamma}{2} \frac{1}{v^2} - k_B T \log(1 - \frac{1}{v}).
\]

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 \( \rho \) as function of the chemical potential \( \mu \) for different temperatures. For \( T < T_c \) there is a jump in \( \rho \) at \( \mu = \mu_0 = -2k_B T_c \).

We can rewrite the van der Waals equation of state as follows:
\[
p(T, v) = -\frac{\tilde{a}}{v^2} + k_B T \frac{1}{v - \tilde{b}}.
\]

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 \( \mu = \mu_0 = -2k_B T_c \) and \( \rho = \rho_{g,l}(T) \)
\[
p_c(T) = -2k_B T_c \rho_{g,l}^2(T) - k_B T \log(1 - \rho_{g,l}(T)), \tag{S.24}
\]
as shown in Fig. 5. In particular, for \( T = T_c \) we have \( \rho_{g,l}(T_c) = 1/2 \) and
\[
p_c(T_c) = \frac{k_B T_c}{2} (\log 4 - 1). \tag{S.25}
\]

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 \( \rho_A \) and \( \rho_B \), 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 $T < T_c$ (equilibrium line). Above $T_c$ there is only one phase (a single density for a given pressure).

**Solution.** Below the same critical temperature $k_B T_c = \gamma |\lambda| / 4$ 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 $\phi(\rho_A)$ and $\phi(\rho_B)$ shown in Fig. 7. There are two degenerate asymmetric solutions $\rho_A \neq \rho_B$, which are related by $\rho_A \leftrightarrow \rho_B$, and one symmetric solution with $\rho_A = \rho_B$.

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

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

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 $\phi$ into Eq. (S.26) and solving for $\mu$, one obtains

$$\mu_0 - \Delta \mu < \mu < \mu_0 + \Delta \mu,$$

with

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

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
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 $T = 0.5 T_c$. The thick lines show the average densities, the dashed and dotted lines the densities of the two sublattices.

Figure 7: Plot of $\phi(\rho_A)$ and $\phi(\rho_B)$, defined in Eq. (S.20), for $\mu \in [\mu_0 - \Delta \mu, \mu_0 + \Delta \mu]$. 