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 such that they contain at most one gas molecule. The result is a square lattice in two dimensions and a cubic lattice in three dimensions. We neglect the kinetic energy of a molecule and assume that only nearest neighbors interact. 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.

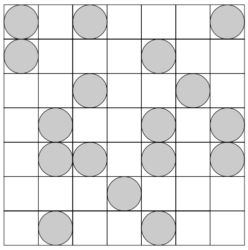

Figure 1: Schematic view of the lattice gas model.

(a) First, 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.

(b) Introduce two mean-field parameters m_{A} and m_{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}?

(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 $\rho_{\mathrm{A}} = \langle n_i \rangle_{i \in \mathrm{A}}$ and $\rho_{\mathrm{B}} = \langle n_i \rangle_{i \in \mathrm{B}}$.

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.

(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:

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

Hint. For the lattice gas, the volume is given by the total number of lattice sites, N_{L}.

(f) Find the phase diagram ($T - p$ diagram). Determine the phase boundary $(T, p_{\mathrm{c}}(T))$ and, in particular, compute the critical point $(T_{\mathrm{c}}, p_{\mathrm{c}}(T_{\mathrm{c}}))$.

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, $\rho_{\mathrm{A}} \neq \rho_{\mathrm{B}}$, below some critical temperature T_{c}.

(g) Discuss the solutions above and below the critical temperature for $\lambda < 0$. Plot the densities ρ_{A} and ρ_{B}, as well as the average, $(\rho_{\mathrm{A}} + \rho_{\mathrm{B}})/2$ for both attractive and repulsive nearest-neighbor interaction at low temperature, $T < T_{\mathrm{c}}$. Interpret the result in terms of compressibility.