7.2: Fluids, Magnets, and the Ising Model

Lattice Gas Description of a Fluid

The usual description of a fluid follows from a continuum Hamiltonian of the form

$$\hat{H}(\mathbf{p},\mathbf{x}) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \sum_{i<j} u(\mathbf{x}_i - \mathbf{x}_j)\ . \tag{7.2.1}$$

The potential $u(\mathbf{r})$ is typically central, depending only on the magnitude $|\mathbf{r}|$, and short-ranged. Now consider a discretized version of the fluid, in which we divide up space into cells (cubes, say), each of which can accommodate at most one fluid particle (due to excluded volume effects). That is, each cube has a volume on the order of a^3, where a is the diameter of the fluid particles. In a given cube i we set the occupancy $n_i = 1$ if a fluid particle is present and $n_i = 0$ if there is no fluid particle present. We then have that the potential energy is

$$U = \sum_{i<j} u(\mathbf{x}_i - \mathbf{x}_j) = \frac{1}{2} \sum_{\mathbf{R}\neq\mathbf{R}'} V_{\mathbf{R}\mathbf{R}'}\, n_{\mathbf{R}}\, n_{\mathbf{R}'}\ , \tag{7.2.2}$$

where $V_{\mathbf{R}\mathbf{R}'} \approx v(\mathbf{R}-\mathbf{R}')$, where R_k is the position at the center of cube k. The grand partition function is then approximated as

$$\Xi(T,V,\mu) \approx \sum_{\{n_{\mathbf{R}}\}} \left(\prod_{\mathbf{R}} \xi^{n_{\mathbf{R}}} \right) \exp\left(-\frac{1}{2}\beta \sum_{\mathbf{R}\neq\mathbf{R}'} V_{\mathbf{R}\mathbf{R}'}\, n_{\mathbf{R}}\, n_{\mathbf{R}'} \right)\ , \tag{7.2.3}$$

where

$$\xi = e^{\beta\mu}\, \lambda_T^{-d}\, a^d\ , \tag{7.2.4}$$

where a is the side length of each cube (chosen to be on the order of the hard sphere diameter). The λ_T^{-d} factor arises from the integration over the momenta. Note $\sum_{\mathbf{R}} n_{\mathbf{R}} = N$ is the total number of fluid particles, so

$$\prod_{\mathbf{R}} \xi^{\,n_{\mathbf{R}}} = \xi^N = e^{\beta\mu N}\, \lambda_T^{-Nd}\, a^{Nd}\ . \tag{7.2.5}$$

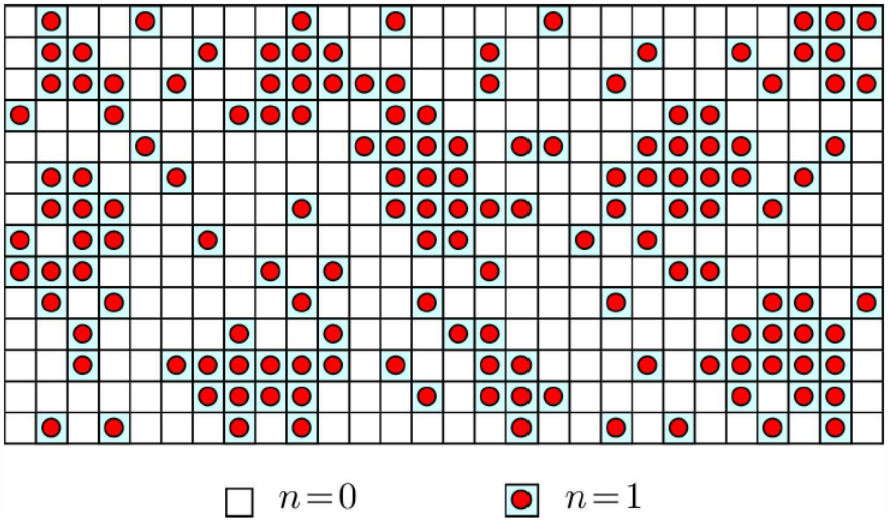

Figure 7.2.1: The lattice gas model. An occupied cell corresponds to $n = 1$ ($\sigma = +1$), and a vacant cell to $n = 0$ ($\sigma = -1$).

Thus, we can write a lattice Hamiltonian,

$$\hat{H} = \frac{1}{2} \sum_{\mathbf{R}\neq\mathbf{R}'} V_{\mathbf{R}\mathbf{R}'}\, n_{\mathbf{R}}\, n_{\mathbf{R}'} - k_B T \ln\xi \sum_{\mathbf{R}} n_{\mathbf{R}} \tag{7.2.6}$$

$$= -\frac{1}{2} \sum_{\mathbf{R}\neq\mathbf{R}'} J_{\mathbf{R}\mathbf{R}'}\, \sigma_{\mathbf{R}}\, \sigma_{\mathbf{R}'} - H \sum_{\mathbf{R}} \sigma_{\mathbf{R}} + E_0\ , \tag{7.2.7}$$

where $\sigma_{\mathbf{R}} \equiv 2n_{\mathbf{R}} - 1$ is a spin variable taking the possible values $\{-1, +1\}$, and

$$J_{\mathbf{R}\mathbf{R}'} = -\frac{1}{4} V_{\mathbf{R}\mathbf{R}'} \tag{7.2.8}$$

$$H = \frac{1}{2} k_B T \ln \xi - \frac{1}{4} {\sum_{\mathbf{R}'}}' V_{\mathbf{R}\mathbf{R}'} \ , \tag{7.2.9}$$

where the prime on the sum indicates that $\mathbf{R}' = \mathbf{R}$ is to be excluded. For the Lennard-Jones system, $V_{\mathbf{R}\mathbf{R}'} = v(\mathbf{R} - \mathbf{R}') < 0$ is due to the attractive tail of the potential, hence $J_{\mathbf{R}\mathbf{R}'}$ is positive, which prefers alignment of the spins $\sigma_{\mathbf{R}}$ and $\sigma_{\mathbf{R}'}$. This interaction is therefore *ferromagnetic*. The spin Hamiltonian in Equation 7.2.7 is known as the Ising model.

Phase diagrams and critical exponents

The physics of the liquid-gas transition in fact has a great deal in common with that of the transition between a magnetized and unmagnetized state of a magnetic system. The correspondences are[5]

$$p \longleftrightarrow H \qquad , \qquad v \longleftrightarrow m \ , \tag{7.2.10}$$

where m is the magnetization density, defined here to be the total magnetization M divided by the number of lattice sites N_S:[6]

$$m = \frac{M}{N_S} = \frac{1}{N_S} \sum_{\mathbf{R}} \langle \sigma_{\mathbf{R}} \rangle \ . \tag{7.2.11}$$

Sketches of the phase diagrams are reproduced in Figure 7.2.2. Of particular interest is the *critical point*, which occurs at (T_c, p_c) in the fluid system and (T_c, H_c) in the magnetic system, with $H_c = 0$ by symmetry.

In the fluid, the coexistence curve in the (p, T) plane separates high density (liquid) and low density (vapor) phases. The specific volume v (or the density $n = v^{-1}$) jumps discontinuously across the coexistence curve. In the magnet, the coexistence curve in the (H, T) plane separates positive magnetization and negative magnetization phases. The magnetization density m jumps discontinuously across the coexistence curve. For $T > T_c$, the latter system is a *paramagnet*, in which the magnetization varies smoothly as a function of H. This behavior is most apparent in the bottom panel of the figure, where $v(p)$ and $m(H)$ curves are shown.

For $T < T_c$, the fluid exists in a *two phase region*, which is spatially inhomogeneous, supporting local regions of high and low density. There is no stable homogeneous thermodynamic phase for (T, v) within the two phase region shown in the middle left panel. Similarly, for the magnet, there is no stable homogeneous thermodynamic phase at fixed temperature T and magnetization m if (T, m) lies within the coexistence region. Rather, the system consists of blobs where the spin is predominantly up, and blobs where the spin is predominantly down.

Note also the analogy between the isothermal compressibility κ_T and the isothermal susceptibility χ_T:

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \quad , \quad \kappa_T(T_c, p_c) = \infty$$

$$\chi_T = \left(\frac{\partial m}{\partial H}\right)_T \quad , \quad \chi_T(T_c, H_c) = \infty$$

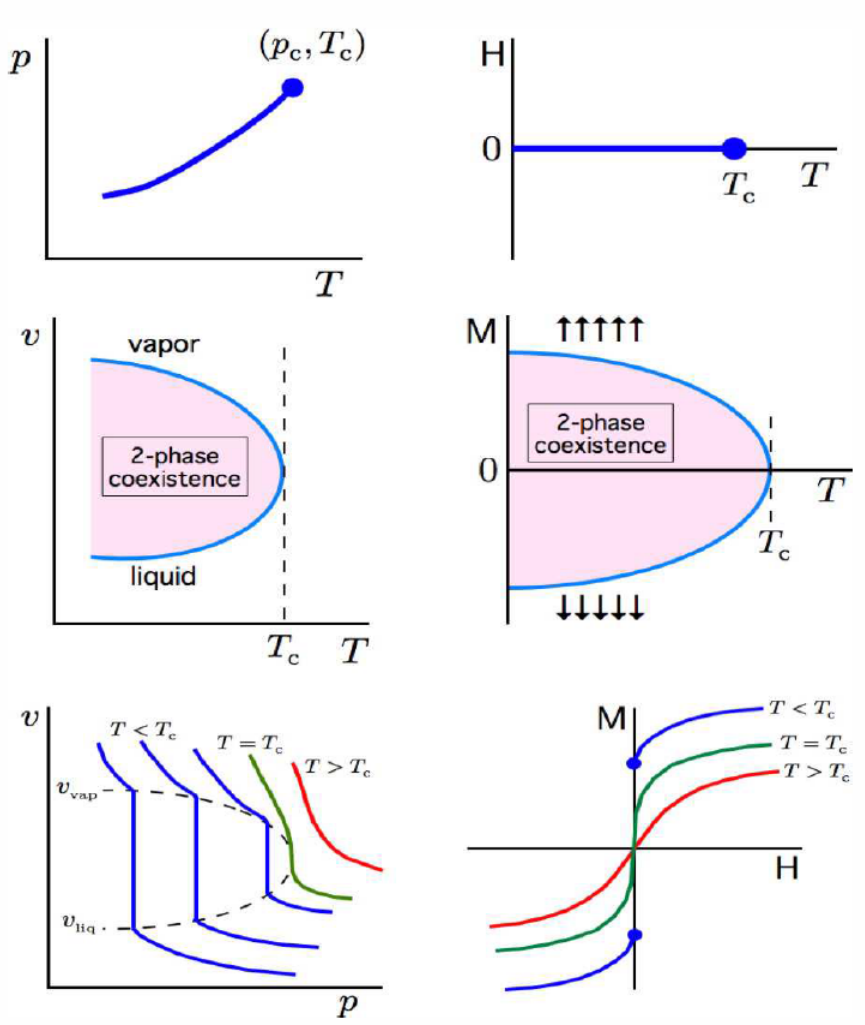

Figure 7.2.2: Comparison of the liquid-gas phase diagram with that of the Ising ferromagnet.

The 'order parameter' for a second order phase transition is a quantity which vanishes in the disordered phase and is finite in the ordered phase. For the fluid, the order parameter can be chosen to be $\Psi \propto (v_{vap} - v_{liq})$, the difference in the specific volumes of the vapor and liquid phases. In the vicinity of the critical point, the system exhibits power law behavior in many physical quantities, *viz.*

$$m(T, H_c) \sim (T_c - T)_+^{\beta}$$

$$\chi(T, H_c) \sim |T - T_c|^{-\gamma}$$

$$C_M(T, H_c) \sim |T - T_c|^{-\alpha}$$

$$m(T_c, H) \sim \pm |H|^{1/\delta} .$$

The quantities α, β, γ, and δ are the *critical exponents* associated with the transition. These exponents satisfy certain equalities, such as the Rushbrooke and Griffiths relations and hyperscaling,[7]

$$\begin{aligned} \alpha + 2\beta + \gamma &= 2 \qquad \text{(Rushbrooke)} \\ \beta + \gamma &= \beta\delta \qquad \text{(Griffiths)} \\ 2 - \alpha &= d\,\nu \qquad \text{(hyperscaling)} . \end{aligned}$$

Originally such relations were derived as inequalities, and only after the advent of scaling and renormalization group theories it was realized that they held as equalities. We shall have much more to say about critical behavior later on, when we discuss scaling and

renormalization.

Gibbs-Duhem relation for magnetic systems

Homogeneity of $E(S, M, N_S)$ means $E = TS + HM + \mu N_S$, and, after invoking the First Law $dE = T\,dS + H\,dM + \mu\,dN_S$, we have

$$S\,dT + M\,dH + N_S d\mu = 0\ . \tag{7.2.12}$$

Now consider two magnetic phases in coexistence. We must have $d\mu_1 = d\mu_2$, hence

$$d\mu_1 = -s_1\,dT - m_1\,dH = -s_2\,dT - m_2\,dH = d\mu_2\ , \tag{7.2.13}$$

where $m = M/N_S$ is the magnetization per site and $s = S/N_S$ is the specific entropy. Thus, we obtain the Clapeyron equation for magnetic systems,

$$\left(\frac{dH}{dT}\right)_{coex} = -\frac{s_1 - s_2}{m_1 - m_2}\ . \tag{7.2.14}$$

Thus, if $m_1 \neq m_2$ and $\left(\frac{dH}{dT}\right)_{coex} = 0$, then we must have $s_1 = s_2$, which says that there is *no latent heat associated with the transition*. This absence of latent heat is a consequence of the *symmetry* which guarantees that $F(T, H, N_S) = F(T, -H, N_S)$.

Order-disorder transitions

Another application of the Ising model lies in the theory of order-disorder transitions in alloys. Examples include Cu_3Au, CuZn, and other compounds. In CuZn, the Cu and Zn atoms occupy sites of a body centered cubic (BCC) lattice, forming an alloy known as β-brass. Below $T_c \simeq 740\ K$, the atoms are ordered, with the Cu preferentially occupying one simple cubic sublattice and the Zn preferentially occupying the other.

The energy is a sum of pairwise interactions, with a given link contributing ε_{AA}, ε_{BB}, or ε_{AB}, depending on whether it is an A-A, B-B, or A-B/B-A link. Here A and B represent Cu and Zn, respectively. Thus, we can write the energy of the link $\langle ij \rangle$ as

$$E_{ij} = \varepsilon_{AA}\,P_i^A\,P_j^A + \varepsilon_{BB}\,P_i^B\,P_j^B + \varepsilon_{AB}\left(P_i^A\,P_j^B + P_i^B\,P_j^A\right)\ , \tag{7.2.15}$$

where

$$P_i^A = \frac{1}{2}(1+\sigma_i) = \begin{cases} 1 & \text{if site } i \text{ contains Cu} \\ 0 & \text{if site } i \text{ contains Zn} \end{cases}$$

$$P_i^B = \frac{1}{2}(1-\sigma_i) = \begin{cases} 1 & \text{if site } i \text{ contains Zn} \\ 0 & \text{if site } i \text{ contains Cu} \backslash \end{cases}\ .$$

The Hamiltonian is then

$$\begin{aligned} \hat{H} &= \sum_{\langle ij \rangle} E_{ij} \\ &= \sum_{\langle ij \rangle} \left\{ \frac{1}{4}\left(\varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB}\right)\sigma_i\,\sigma_j + \frac{1}{4}\left(\varepsilon_{AA} - \varepsilon_{BB}\right)(\sigma_i + \sigma_j) + \frac{1}{4}\left(\varepsilon_{AA} + \varepsilon_{BB} + 2\varepsilon_{AB}\right) \right\} \\ &= -J\sum_{\langle ij \rangle} \sigma_i\,\sigma_j - H\sum_i \sigma_i + E_0\ , \end{aligned}$$

where the exchange constant J and the magnetic field H are given by

$$\begin{aligned} J &= \frac{1}{4}\left(2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}\right) \\ H &= \frac{1}{4}\left(\varepsilon_{BB} - \varepsilon_{AA}\right)\ , \end{aligned}$$

and $E_0 = \frac{1}{8}Nz\left(\varepsilon_{AA} + \varepsilon_{BB} + 2\varepsilon_{AB}\right)$, where N is the total number of lattice sites and $z = 8$ is the *lattice coordination number*, which is the number of nearest neighbors of any given site.

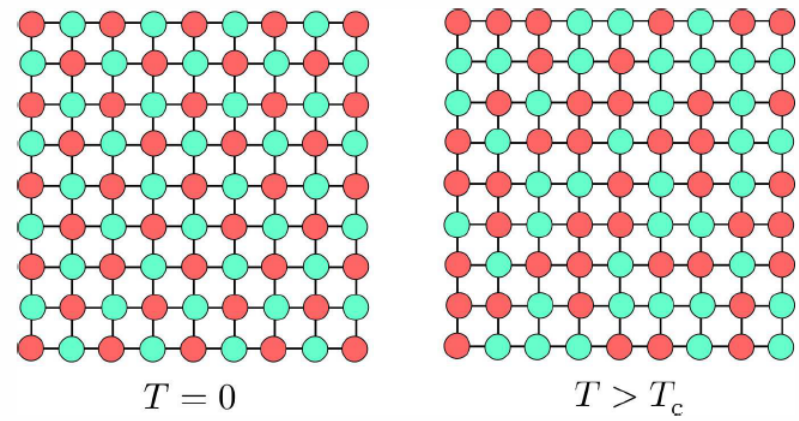

Figure 7.2.3: Order-disorder transition on the square lattice. Below $T = T_c$, order develops spontaneously on the two $\sqrt{2} \times \sqrt{2}$ sublattices. There is perfect sublattice order at $T = 0$ (left panel).

Note that

$$\begin{aligned} 2\varepsilon_{AB} > \varepsilon_{AA} + \varepsilon_{BB} \quad &\Longrightarrow \quad J > 0 \quad \text{(ferromagnetic)} \\ 2\varepsilon_{AB} < \varepsilon_{AA} + \varepsilon_{BB} \quad &\Longrightarrow \quad J < 0 \quad \text{(antiferromagnetic)} \, . \end{aligned}$$

The antiferromagnetic case is depicted in Figure 7.2.3.