

Unit 4-6: The Liquid-Gas Phase Transition

The Lattice Gas Model

The Ising model is not just a model for a ferromagnetic phase transition. It is also a model for the liquid-gas phase transition! One way to see this is the *lattice gas* model.

Consider a periodic lattice of N sites i . On each site we define a variable n_i which can take only the values $n_i = 0, 1$.

$$n_i = \begin{cases} 1 & \text{site } i \text{ occupied by a particle} \\ 0 & \text{site } i \text{ unoccupied} \end{cases} \quad (4.6.1)$$

The Hamiltonian for the lattice gas is,

$$\mathcal{H} = -U \sum_{\langle ij \rangle} n_i n_j - \mu \sum_i n_i \quad (4.6.2)$$

The first term is, for $U > 0$, an attractive interaction between particles on nearest neighbor sites. The second term is the chemical potential term $-\mu \sum_i n_i = -\mu N_{\text{part}}$ of the grand canonical ensemble, with N_{part} the number of particles in the system.

We can now map the lattice gas model onto the Ising model. Let

$$s_i = 2n_i - 1 = \pm 1, \quad n_i = \frac{s_i + 1}{2} \quad (4.6.3)$$

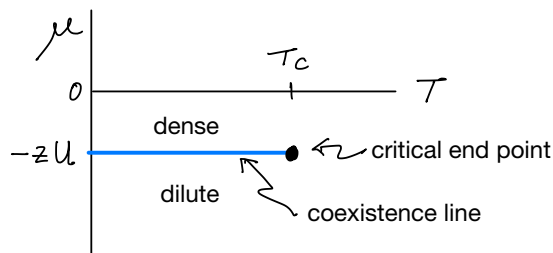
Then

$$\mathcal{H} = -U \sum_{\langle ij \rangle} \left(\frac{s_i + 1}{2} \right) \left(\frac{s_j + 1}{2} \right) - \mu \sum_i \left(\frac{s_i + 1}{2} \right) \quad (4.6.4)$$

$$= -U \sum_{\langle ij \rangle} \left(\frac{s_i s_j}{4} + \frac{s_i}{2} + \frac{s_j}{2} + \frac{1}{4} \right) - \frac{\mu}{2} \sum_i s_i - \frac{\mu N}{2} \quad (4.6.5)$$

$$= -\frac{U}{4} \sum_{\langle ij \rangle} s_i s_j - \left(\frac{Uz}{2} + \frac{\mu}{2} \right) \sum_i s_i - \left(\frac{Uz}{8} + \frac{\mu}{2} \right) N \quad (4.6.6)$$

We thus wind up with an Ising model with coupling $J = U/4$ and magnetic field $h = (zU + \mu)/2$. The last term in the Hamiltonian above is a constant that we can ignore. Note, N is the number of lattice sites, *not* the number of particles $\sum_i n_i$.



We know that the Ising model has a first order coexistence line at $0 \leq T \leq T_c$ for $h = 0$, that ends at the critical end point $T = T_c$, $h = 0$. The lattice gas model thus has a first order coexistence line at $0 \leq T \leq T_c$ for $\mu = -zU$ (so that $h = 0$), that ends at a critical end point at $T = T_c$, $\mu = -zU$. In the mean-field solution for the Ising model we had $k_B T_c = zJ/2$, so in the mean-field solution for the lattice gas model we have $k_B T_c = zU/8$. When one crosses the coexistence line by increasing h in the Ising model there is a jump in the magnetization from $-m_0$ to $+m_0$. Hence, as one crosses

the coexistence line by increasing the chemical potential μ in the lattice gas, there will be a jump in the density of particles $n = \frac{1}{N} \langle \sum_i n_i \rangle = \langle n_i \rangle = (\langle s_i \rangle + 1)/2$, from $n_- = (-m_0 + 1)/2$ to $n_+ = (+m_0 + 1)/2$, i.e. we go from a less dense to a more dense system, with a discontinuous jump in the density $\Delta n = n_+ - n_- = m_0$. As $T \rightarrow T_c$ along the coexistence line, the jump in density vanishes as $\Delta n \sim (T_c - T)^\beta$. Along the coexistence line the average particle density is $\bar{n} = (n_+ + n_-)/2 = 1/2$. In terms of the Landau theory of phase transitions, $n - \bar{n}$ is the “order parameter.”

Thus the lattice gas displays a liquid to gas phase transition, where there is a discontinuous jump in the density of particles as one crosses the coexistence line. The coexistence line ends at a critical point. For $T > T_c$ there is no

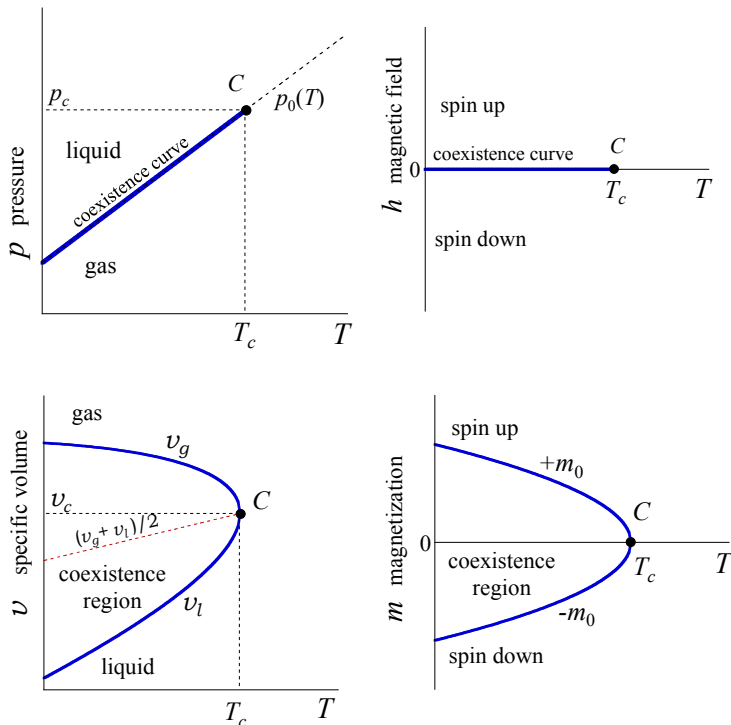
distinction between the liquid and gas phases; the particle density is now continuous as μ varies. The nature of the liquid-gas critical end point is the same as in the Ising model, i.e. the critical exponents, such as β , are all the same. In the usual liquid-gas transition (water to vapor) one usually writes the phase diagram in the pressure – temperature plane. For the lattice gas, where the lattice of sites on which particles may sit is fixed, the total system volume is fixed. There is thus no analog of pressure p . It is therefore the chemical potential μ that plays the role of the “ordering field.”

Landau Theory of the Liquid-Gas Transition

Another way to see that the liquid-gas transition can be described in terms of an Ising model is by using Landau theory.

The liquid-gas transition can be described by a phase diagram in either the $p - T$ or $v - T$ planes, where the specific volume, $v = V/N$, is just the inverse of the particle density $n = N/V$. For the liquid-gas transition, the first order transition or coexistence line, where liquid can coexist in chemical equilibrium with its vapor, is given by a curve in the $p - T$ plane, which we will denote as $p_0(T)$. The curve ends at a critical point C at $T = T_c$ and $p_c = p_0(T_c)$. On the larger pressure side of the coexistence curve, the specific volume of the liquid phase, $v_l(T)$, increases to the critical value v_c as $T \rightarrow T_c$; on the smaller pressure side of the coexistence curve, the specific volume of the gas phase, $v_g(T)$, decreases to the same v_c as $T \rightarrow T_c$. The jump in the specific volume as one crosses the coexistence curve, $\Delta v = v_g - v_l$, vanishes at T_c . In the $v - T$ plane, the coexistence curve becomes the boundary of a coexistence region. If we try to cool down into the coexistence region, the system will phase separate into coexisting domains of gas and liquid – there is no spatially homogeneous equilibrium state within the coexistence region.

The phase diagrams for the liquid-gas transition in the $p - T$ and $v - T$ plane are as shown in the sketches below on the left. The corresponding phase diagrams for the Ising model, in the $h - T$ and $m - T$ planes are shown on the right. We see the qualitative correspondences $h \leftrightarrow p$ and $m \leftrightarrow v$. However, there would seem to be a difference between the two models. The phase diagram for the Ising model has an up-down symmetry, i.e. the magnetization on the lower side of the coexistence curve $-m_0$ is just the negative of the magnetization on the upper side of the coexistence curve $+m_0$, and the coexistence line is given by $h = -0$. In the liquid-gas phase diagram, there is no similar symmetry between v_g and v_l along the coexistence curve, and the coexistence curve is some function $p_0(T)$.



However we can see the equivalence if we transform to new coordinates to describe the liquid-gas transition. We will

analytically extend the curve $p_0(T)$ to temperatures $T > T_c$, and we will define,

$$v_0(T) = \frac{v_l(T) + v_g(T)}{2} \quad \text{for } T < T_c, \text{ and } v_0(T) \equiv v(T, p_0(T)) \quad \text{for } T > T_c. \quad (4.6.7)$$

Below T_c , $v_0(T)$ is the average of the liquid and gas specific volumes on either side of the coexistence curve. Above T_c , $v_0(T)$ is the specific volume of the single phase along the analytically extended curve $p_0(T)$. We have $v_0(T) \rightarrow v_c$ as $T \rightarrow T_c$ from either above or below.

We now define the new coordinates,

$$\delta p \equiv p - p_0(T), \quad \delta v \equiv v - v_0(T) \quad (4.6.8)$$

The coexistence curve is now given by the condition $\delta p = 0$. In terms of δv , the specific volumes of the liquid and gas on either side of the coexistence curve are given by,

$$\delta v_g = v_g - v_0 = v_g - \frac{v_l + v_g}{2} = \frac{v_g - v_l}{2}, \quad \delta v_l = v_l - v_0 = v_l - \frac{v_l + v_g}{2} = \frac{v_l - v_g}{2} \quad (4.6.9)$$

Thus we have $\delta v_g = -\delta v_l$, and so, when expressed in terms of δv , we have recovered the symmetry found in the Ising model.

We thus regard δv as our *order parameter* and δp as our *ordering field*, and the analogy to the Ising model becomes exact. Just like for the Ising model, our order parameter is a scalar quantity.

Near the critical point, we can make a linear expansion and write,

$$p_0(T) \approx p_c + \left(\frac{\partial p_0}{\partial T} \right)_{T=T_c} (T - T_c) = p_c + c_1(T - T_c) \quad (4.6.10)$$

$$v_0(T) \approx v_c + \left(\frac{\partial v_0}{\partial T} \right)_{T=T_c} (T - T_c) = v_c + c_2(T - T_c) \quad (4.6.11)$$

with $c_1, c_2 > 0$.

Following Landau, near the critical point C we can expand the Helmholtz free energy density for small δv and write,

$$f(\delta v, T) = f_0(T) + a\delta v^2 + b\delta v^4 \quad \text{with } a = a_0(T - T_c) \text{ and } b \text{ constant.} \quad (4.6.12)$$

There can be no δv nor δv^3 term because the minima of $f(\delta v, T)$ must be symmetric about $\delta v = 0$. Note, however, that if we expressed f in terms of the original v , substituting into the above $\delta v = v - v_0$, then there would be linear and cubic terms in v , reflecting the lack of symmetry in the original phase diagram.

The equation of state is then given by,

$$\delta p = - \left(\frac{\partial f}{\partial \delta v} \right)_T = -2a\delta v - 4b\delta v^3 \quad (4.6.13)$$

The Gibbs free energy density is determined by minimizing,

$$g(\delta p, T) = \min_{\delta v} [f(\delta v, T) + \delta p \delta v] \quad (4.6.14)$$

with the minimizing value of δv giving the equilibrium value of δv at the given δp .

The above Helmholtz free energy, equation of state, and Gibbs free energy are in complete analogy with the Ising model, with $\delta v \leftrightarrow m$ and $\delta p \leftrightarrow -h$; the minus sign is because for the system of particles $g = f + pv$, while for the spins $g = f - hm$. What is crucial is that the order parameter is a *scalar* quantity and f has inversion symmetry $\delta v \leftrightarrow -\delta v$. The critical exponents of the liquid-gas transition must therefore be the same as those of the Ising model.

We can then immediately write down the corresponding results for the critical behavior of the liquid-gas transition. With $t = (T - T_c)/T_c$, along the coexistence curve, with $p = p_0(T)$ as T varies, we have for $T \leq T_c$,

$$\delta v \sim \pm |t|^\beta \quad \text{along the coexistence curve } p = p_0(T), \text{ with } \beta = 1/2 \text{ in mean-field theory} \quad (4.6.15)$$

In mean-field theory, we have,

$$\delta v = \pm \sqrt{\frac{a_0|T - T_c|}{2b}} \quad \text{and so} \quad v_{g,l} = \pm \sqrt{\frac{a_0|T - T_c|}{2b}} + v_0(T) = \pm \sqrt{\frac{a_0|T - T_c|}{2b}} + v_c + c_2(T - T_c) \quad (4.6.16)$$

On the critical isotherm $T = T_c$ we have

$$\delta p \sim -\delta v^\delta \quad \text{on the critical isotherm } T = T_c, \text{ with } \delta = 3 \text{ in mean-field theory.} \quad (4.6.17)$$

Thus, along the critical isotherm we have $\delta v = -\text{sgn}(\delta p)|\delta p|^{1/\delta}$, where $\text{sgn}(x) = +1$ for $x > 0$ and -1 for $x < 0$.

The isothermal compressibility is,

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T = -\frac{1}{v} \left(\frac{\partial \delta v}{\partial \delta p} \right)_T \quad (4.6.18)$$

Along the critical isotherm $T = T_c$, where $\delta p = p - p_0(T_c) = p - p_c$,

$$\kappa_T = \frac{\text{sgn}(p)}{v} \frac{\partial |\delta p|^{1/\delta}}{\partial \delta p} \sim |\delta p|^{1/\delta - 1} \quad \text{in mean field theory, } 1/\delta - 1 = -2/3, \text{ so } \kappa_T \sim |p - p_c|^{-2/3}. \quad (4.6.19)$$

We see that κ_T diverges as we pass through the critical point C along the critical isotherm.

We can also ask how κ_T behaves as we pass through the critical point C along the critical *isobar* $p = p_c$. We can find this within mean-field theory. Along the critical isobar $p = p_c$ we have $\delta p = p_c - p_0(T) = -c_1(T - T_c)$. The equation of state Eq. (4.6.13) then gives,

$$\delta p = -c_1(T - T_c) = -2a_0(T - T_c)\delta v - 4b\delta v^3 \quad \Rightarrow \quad (T - T_c) = \frac{4b\delta v^3}{c_1 - 2a_0\delta v} \quad (4.6.20)$$

As $T \rightarrow T_c$ along the critical isobar, $\delta v \rightarrow 0$, so close to T_c we can ignore the δv term in the denominator of the above to get,

$$(T - T_c) = \frac{4b}{c_1}\delta v^3 \quad \Rightarrow \quad \delta v = \text{sgn}(T - T_c) \left(\frac{c_1}{4b}|T - T_c| \right)^{1/3} \quad \text{along the critical isobar} \quad (4.6.21)$$

Now, also from the equation of state, we have,

$$\left(\frac{\partial \delta p}{\partial \delta v} \right)_T = -2a_0(T - T_c) - 12b\delta v^2 \quad \Rightarrow \quad \kappa_T = -\frac{1}{v} \frac{1}{(\partial \delta p / \partial \delta v)_T} = \frac{1}{v(2a_0(T - T_c) + 12b\delta v^2)} \quad (4.6.22)$$

So on the critical isobar, using δv from Eq. (4.6.21), we get,

$$\kappa_T = \frac{1}{v(2a_0(T - T_c) + 12b\left(\frac{c_1}{4b}\right)^{2/3}|T - T_c|^{2/3})} = \frac{1}{v|T - T_c|^{2/3} \left[\text{sgn}(T - T_c)2a_0|T - T_c|^{1/3} + 12b\left(\frac{c_1}{4b}\right)^{2/3} \right]} \quad (4.6.23)$$

As $T \rightarrow T_c$ the term $(T - T_c)^{1/3}$, in the square brackets of the denominator, becomes negligible, and so we have,

$$\kappa_T \sim |T - T_c|^{-2/3} \quad \text{along the critical isobar.} \quad (4.6.24)$$

Thus, in mean-field theory, the isothermal compressibility diverges with with the same exponent $-2/3$ whether one approaches the critical point along the critical isotherm $T = T_c$, or along the critical isobar $p = p_c$.

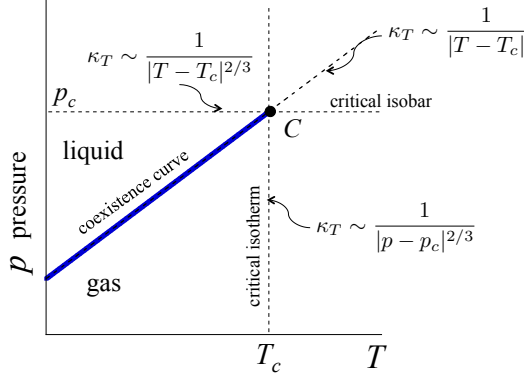
Finally we can ask how κ_T behaves as one passes through the critical point C along the coexistence curve, $p = p_0(T)$. Since we have the identifications, $\delta v \leftrightarrow m$ and $\delta p \leftrightarrow -h$, the isothermal compressibility $\kappa_T = (-1/v)(\partial \delta v / \partial \delta p)$ is analogous to the magnetic susceptibility $\chi = \partial m / \partial h$. Thus, along the coexistence line we have,

$$\kappa_T \sim |T - T_c|^{-\gamma} \quad \text{with } \gamma = 1 \text{ in mean-field theory.} \quad (4.6.25)$$

We also have the amplitude ratio,

$$\lim_{T \rightarrow T_c} \frac{\kappa_T^+}{\kappa_T^-} = 2 \quad (4.6.26)$$

where κ_T^+ is for $T > T_c$, while κ_T^- is for $T < T_c$.



The Clausius-Clapeyron Relation

Along the coexistence line the gas and the liquid phases are in chemical equilibrium and can coexist. The condition for such chemical equilibrium is that the chemical potentials of the two phases must be equal,

$$\mu_l(T, p) = \mu_g(T, p) \quad (4.6.27)$$

This gives one constraint on the two thermodynamic variables T and p , and so determines the location of the coexistence line $p_0(T)$ in the $p - T$ plane.

We now use the Gibbs-Duhem relation to write for the liquid and the gas phases,

$$d\mu_l = -s_l dT + v_l dp, \quad d\mu_g = -s_g dT + v_g dp \quad (4.6.28)$$

where $s = S/N$ is the entropy per particle.

Along the coexistence curve we have $d\mu_l = d\mu_g$, since $\mu_l = \mu_g$. This gives,

$$-s_l dT + v_l dp = -s_g dT + v_g dp \quad \Rightarrow \quad \frac{dp_0}{dT} = \frac{s_g - s_l}{v_g - v_l} = \frac{\Delta s}{\Delta v} \equiv \frac{L}{T\Delta v} \quad (4.6.29)$$

where dp_0/dT is the slope of the coexistence curve, and $L \equiv T\Delta s$ is the *latent heat* of the transition. The latent heat is the energy that must be absorbed to turn one particle of liquid into one particle of gas. We see this as follows. For a system with fixed total V and fixed total N , then the change in total energy is,

$$dE = TdS \quad \Rightarrow \quad \frac{dE}{N} = T \frac{dS}{N} \quad \Rightarrow \quad \Delta E/N = T\Delta s = L \quad (4.6.30)$$

where $\Delta E/N$ is the energy to convert one particle from liquid to gas.

We thus have the *Clausius-Clapeyron relation* which relates the slope of the coexistence curve to the discontinuities in density and entropy upon crossing the coexistence curve,

$$\frac{dp_0}{dT} = \frac{\Delta s}{\Delta v} = \frac{L}{T\Delta v} \quad \text{Clausius-Clapeyron relation} \quad (4.6.31)$$

Since dp_0/dT is in general finite, and we know Δv is finite, but with $\Delta v \rightarrow 0$ as $T \rightarrow T_c$, then similarly it must be that Δs is finite upon crossing the phase boundary, but with $\Delta s \rightarrow 0$ as $T \rightarrow T_c$.

$$\Rightarrow \quad L \text{ is finite along the phase boundary, but with } L \rightarrow 0 \text{ as } T \rightarrow T_c. \quad (4.6.32)$$

A phase transition with finite L is called a *first order phase transition*. A phase transition with $L = 0$ is called a continuous, or second order, phase transition. The transition from liquid to gas along the coexistence curve is therefore a first order phase transition. The critical end point C of the coexistence line is a continuous phase transition.

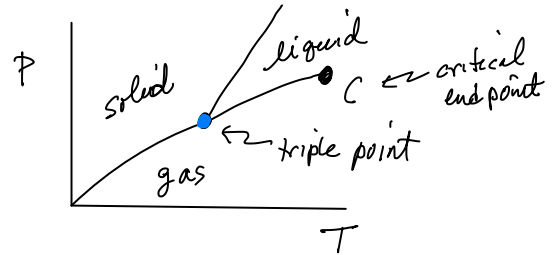
The Gibbs Phase Rule

The coexistence line in the $p - T$ plane, which can also be termed the *phase boundary* between the liquid and gas phases, is the locus of points where the two phases can coexist in equilibrium. We can now ask, can *three* phases coexist together?

For water, such a three phase coexistence occurs at the *triple point* where liquid, gas, and solid phases meet. At such a three phase coexistence we must have,

$$\mu_s(T, p) = \mu_l(T, p) = \mu_g(T, p) \quad (4.6.33)$$

where μ_s is the chemical potential of the solid phase. We therefore have *two* equations of constraint, $\mu_s = \mu_l$ and $\mu_l = \mu_g$, on *two* thermodynamic variables p and T . The locus of solutions is therefore an isolated point, called the *triple point*.



Can *four* phases coexist together? That would require,

$$\mu_1(T, p) = \mu_2(T, p) = \mu_3(T, p) = \mu_4(T, p) \quad (4.6.34)$$

This is three constraints for two thermodynamic variable. The solution is in general over specified and so there is no solution.

One cannot have four (or more) phases coexisting together *unless* there are additional thermodynamic variables besides p and T .

For example, suppose one has a multi-component system of r species of particles, where $c_{i\alpha}, i = 1, 2, \dots, r$ is the fraction of constituent i in the thermodynamic phase α . We have $\sum_{i=1}^r c_{i\alpha} = 1$. Suppose there are s coexisting phases.

Then the thermodynamic degrees of freedom are $p, T, \{c_{i\alpha}\}$, so there are $2 + rs$ degrees of freedom. The constraints are,

$$\sum_{i=1}^r c_{i\alpha} = 1 \quad \text{and} \quad \mu_{i\alpha} = \mu_{i,\alpha+1} \quad \text{for } i = 1 \text{ to } r \text{ and } \alpha = 1 \text{ to } s - 1 \quad (4.6.35)$$

where $\mu_{i\alpha}$ is the chemical potential of species i in phase α . The first condition on the $\{c_{i\alpha}\}$ gives s constraints, one for each phase. The second condition on the $\mu_{i\alpha}$ gives $r(s - 1)$ constraints, for the r different species and the $s - 1$ relations among the chemical potentials for each species. There is thus a total of $s + r(s - 1)$ constraints.

The number of “free” variables is therefore $(2 + rs) - (s + r(s - 1)) = 2 + r - s$. We must have $2 + r - s \geq 0$ for there

to be a solution, or

$$s \leq r + 2$$

The maximum number of coexisting phases for an r -component system is $r + 2$. This is the *Gibbs phase rule*.