Contents

List of Tables

List of Figures

Chapter 7

Mean Field Theory of Phase Transitions

7.1 References

– M. Kardar, *Statistical Physics of Particles* (Cambridge, 2007)
A superb modern text, with many insightful presentations of key concepts.

– M. Plischke and B. Bergersen, *Equilibrium Statistical Physics* (3^{rd} edition, World Scientific, 2006)
An excellent graduate level text. Less insightful than Kardar but still a good modern treatment of the subject. Good discussion of mean field theory.

– G. Parisi, *Statistical Field Theory* (Addison-Wesley, 1988)
An advanced text focusing on field theoretic approaches, covering mean field and Landau-Ginzburg theories before moving on to renormalization group and beyond.

– J. P. Sethna, *Entropy, Order Parameters, and Complexity* (Oxford, 2006)
An excellent introductory text with a very modern set of topics and exercises. Available online at http://www.physics.cornell.edu/sethna/StatMech

7.2 The van der Waals system

7.2.1 Equation of state

Recall the van der Waals equation of state,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \ , \tag{7.1}$$

where $v = N_{\mathrm{A}} V/N$ is the molar volume. Solving for $p(v,T)$, we have

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \ . \tag{7.2}$$

Let us fix the temperature T and examine the function $p(v)$. Clearly $p(v)$ is a decreasing function of volume for v just above the minimum allowed value $v = b$, as well as for $v \to \infty$. But is $p(v)$ a monotonic function for all $v \in [b, \infty]$?

We can answer this by computing the derivative,

$$\left(\frac{\partial p}{\partial v}\right)_T = \frac{2a}{v^3} - \frac{RT}{(v-b)^2} \ . \tag{7.3}$$

Setting this expression to zero for finite v, we obtain the equation[1]

$$\frac{2a}{bRT} = \frac{u^3}{(u-1)^2} \ , \tag{7.4}$$

where $u \equiv v/b$ is dimensionless. It is easy to see that the function $f(u) = u^3/(u-1)^2$ has a unique minimum for $u > 1$. Setting $f'(u^*) = 0$ yields $u^* = 3$, and so $f_{\mathrm{min}} = f(3) = \frac{27}{4}$. Thus, for $T > T_{\mathrm{c}} = 8a/27bR$, the LHS of eqn. 7.4 lies below the minimum value of the RHS, and there is no solution. This means that $p(v, T > T_{\mathrm{c}})$ is a monotonically decreasing function of v.

At $T = T_{\mathrm{c}}$ there is a saddle-node bifurcation. Setting $v_{\mathrm{c}} = bu^* = 3b$ and evaluating $p_{\mathrm{c}} = p(v_{\mathrm{c}}, T_{\mathrm{c}})$, we have that the location of the *critical point* for the van der Waals system is

$$p_{\mathrm{c}} = \frac{a}{27\,b^2} \qquad , \qquad v_{\mathrm{c}} = 3b \qquad , \qquad T_{\mathrm{c}} = \frac{8a}{27\,bR} \ . \tag{7.5}$$

For $T < T_{\mathrm{c}}$, there are two solutions to eqn. 7.4, corresponding to a local minimum and a local maximum of the function $p(v)$. The locus of points in the (v,p) plane for which $(\partial p/\partial v)_T = 0$ is obtained by setting eqn. 7.3 to zero and solving for T, then substituting this into eqn. 7.2. The result is

$$p^*(v) = \frac{a}{v^2} - \frac{2ab}{v^3} \ . \tag{7.6}$$

Expressed in terms of dimensionless quantities $\bar{p} = p/p_{\mathrm{c}}$ and $\bar{v} = v/v_{\mathrm{c}}$, this equation becomes

$$\bar{p}^*(\bar{v}) = \frac{3}{\bar{v}^2} - \frac{2}{\bar{v}^3} \ . \tag{7.7}$$

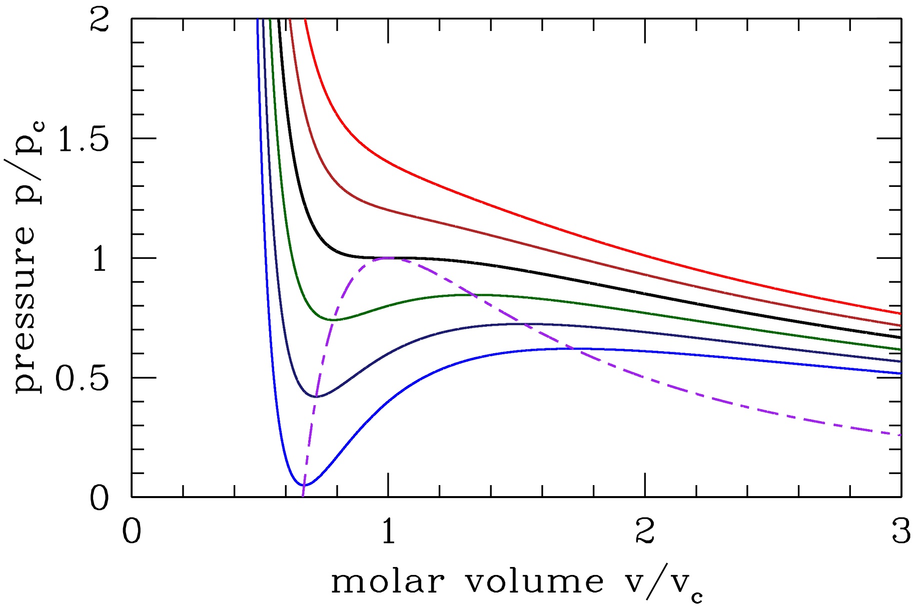

Figure 7.1: Pressure *versus* molar volume for the van der Waals gas at temperatures in equal intervals from $T = 1.10\,T_{\rm c}$ (red) to $T = 0.85\,T_{\rm c}$ (blue). The purple curve is $\bar{p}^*(\bar{v})$.

Along the curve $p = p^*(v)$, the isothermal compressibility, $\kappa_T = -\frac{1}{v}\big(\frac{\partial v}{\partial p}\big)_T$ diverges, heralding a *thermodynamic instability*. To understand better, let us compute the free energy of the van der Waals system, $F = E - TS$. Regarding the energy E, we showed back in chapter 2 that

$$\left(\frac{\partial\varepsilon}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{a}{v^2}\ , \tag{7.8}$$

which entails

$$\varepsilon(T,v) = \tfrac{1}{2} f R T - \frac{a}{v}\ , \tag{7.9}$$

where $\varepsilon = E/\nu$ is the molar internal energy. The first term is the molar energy of an ideal gas, where f is the number of molecular freedoms, which is the appropriate low density limit. The molar specific heat is then $c_V = \big(\frac{\partial\varepsilon}{\partial T}\big)_v = \frac{f}{2}R$, which means that the molar entropy is

$$s(T,v) = \int^T \! dT'\,\frac{c_V}{T'} = \tfrac{f}{2} R \ln(T/T_{\rm c}) + s_1(v)\ . \tag{7.10}$$

We then write $f = \varepsilon - Ts$, and we fix the function $s_1(v)$ by demanding that $p = -\big(\frac{\partial f}{\partial v}\big)_T$. This yields $s_1(v) = R\ln(v-b) + s_0$, where s_0 is a constant. Thus[2],

$$f(T,v) = \tfrac{f}{2} R T \Big(1 - \ln\big(T/T_{\rm c}\big)\Big) - \frac{a}{v} - RT\ln(v-b) - Ts_0\ . \tag{7.11}$$

[1]There is always a solution to $(\partial p/\partial v)_T = 0$ at $v = \infty$.

[2]Don't confuse the molar free energy (f) with the number of molecular degrees of freedom (f)!

gas	a $\left(\frac{\text{L}^2\cdot\text{bar}}{\text{mol}^2}\right)$	b $\left(\frac{\text{L}}{\text{mol}}\right)$	p_{c} (bar)	T_{c} (K)	v_{c} (L/mol)
Acetone	14.09	0.0994	52.82	505.1	0.2982
Argon	1.363	0.03219	48.72	150.9	0.0966
Carbon dioxide	3.640	0.04267	7404	304.0	0.1280
Ethanol	12.18	0.08407	63.83	516.3	0.2522
Freon	10.78	0.0998	40.09	384.9	0.2994
Helium	0.03457	0.0237	2.279	5.198	0.0711
Hydrogen	0.2476	0.02661	12.95	33.16	0.0798
Mercury	8.200	0.01696	1055	1723	0.0509
Methane	2.283	0.04278	46.20	190.2	0.1283
Nitrogen	1.408	0.03913	34.06	128.2	0.1174
Oxygen	1.378	0.03183	50.37	154.3	0.0955
Water	5.536	0.03049	220.6	647.0	0.0915

Table 7.1: van der Waals parameters for some common gases. (Source: *Wikipedia*)

We know that under equilibrium conditions, f is driven to a minimum by spontaneous processes. Now suppose that $\frac{\partial^2 f}{\partial v^2}\big|_T < 0$ over some range of v at a given temperature T. This would mean that one mole of the system at volume v and temperature T could lower its energy by rearranging into two half-moles, with respective molar volumes $v \pm \delta v$, each at temperature T. The total volume and temperature thus remain fixed, but the free energy changes by an amount $\Delta f = \frac{1}{2}\frac{\partial^2 f}{\partial v^2}\big|_T (\delta v)^2 < 0$. This means that the system is unstable – it can lower its energy by dividing up into two subsystems each with different densities (*i.e.* molar volumes). Note that the onset of stability occurs when

$$\frac{\partial^2 f}{\partial v^2}\bigg|_T = -\frac{\partial p}{\partial v}\bigg|_T = \frac{1}{v\kappa_p} = 0 \,, \tag{7.12}$$

which is to say when $\kappa_p = \infty$. As we saw, this occurs at $p = p^*(v)$, given in eqn. 7.6.

However, this condition, $\frac{\partial^2 f}{\partial v^2}\big|_T < 0$, is in fact too strong. That is, the system can be unstable even at molar volumes where $\frac{\partial^2 f}{\partial v^2}\big|_T > 0$. The reason is shown graphically in fig. 7.2. At the fixed temperature T, for any molar volume v between $v_{\text{liquid}} \equiv v_1$ and $v_{\text{gas}} \equiv v_2$, the system can lower its free energy by *phase separating* into regions of different molar volumes. In general we can write

$$v = (1-x)\, v_1 + x\, v_2 \,, \tag{7.13}$$

so $v = v_1$ when $x = 0$ and $v = v_2$ when $x = 1$. The free energy upon phase separation is simply

$$f = (1-x)\, f_1 + x\, f_2 \,, \tag{7.14}$$

where $f_j = f(v_j, T)$. This function is given by the straight black line connecting the points at volumes v_1 and v_2 in fig. 7.2.

The two equations which give us v_1 and v_2 are

$$\frac{\partial f}{\partial v}\bigg|_{v_1,T} = \frac{\partial f}{\partial v}\bigg|_{v_2,T} \tag{7.15}$$

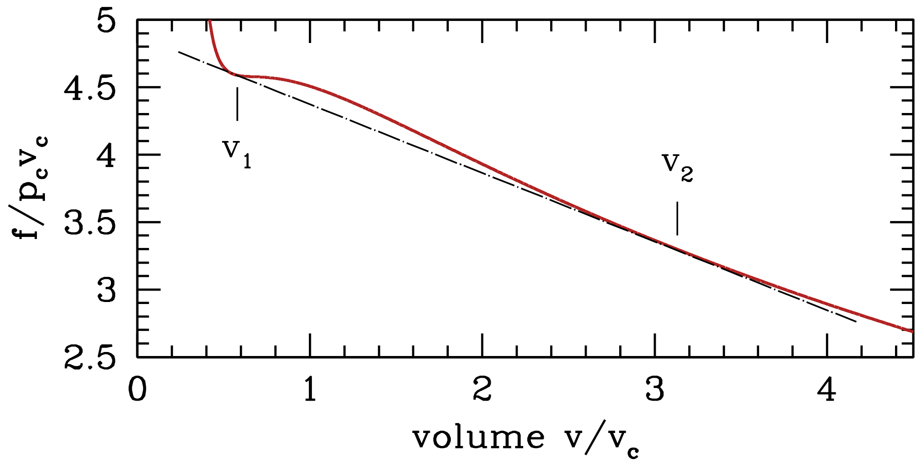

Figure 7.2: Molar free energy $f(T,v)$ of the van der Waals system $T = 0.85\,T_c$, with dot-dashed black line showing Maxwell construction connecting molar volumes $v_{1,2}$ on opposite sides of the coexistence curve.

and

$$f(T,v_1) - f(T,v_2) = (v_2 - v_1)\,\frac{\partial f}{\partial v}\bigg|_{v_1,T} \ . \tag{7.16}$$

In terms of the pressure, $p = -\frac{\partial f}{\partial v}\big|_T$, these equations are equivalent to

$$p(T,v_1) = p(T,v_2) \tag{7.17}$$

$$\int\limits_{v_1}^{v_2} dv\, p(T,v) = \big(v_2 - v_1\big)\, p(T,v_1) \ . \tag{7.18}$$

This procedure is known as the *Maxwell construction*, and is depicted graphically in Fig. 7.3. When the Maxwell construction is enforced, the isotherms resemble the curves in Fig. 7.4. In this figure, all points within the purple shaded region have $\frac{\partial^2 f}{\partial v^2} < 0$, hence this region is unstable to infinitesimal fluctuations. The boundary of this region is called the *spinodal*, and the spontaneous phase separation into two phases is a process known as *spinodal decomposition*. The dot-dashed orange curve, called the *coexistence curve*, marks the instability boundary for *nucleation*. In a nucleation process, an energy barrier must be overcome in order to achieve the lower free energy state. There is no energy barrier for spinodal decomposition – it is a spontaneous process.

7.2.2 Analytic form of the coexistence curve near the critical point

We write $v_{\mathsf{L}} = v_{\mathsf{c}} + w_{\mathsf{L}}$ and $v_{\mathsf{G}} = v_{\mathsf{c}} + w_{\mathsf{G}}$. One of our equations is $p(v_{\mathsf{c}} + w_{\mathsf{L}}, T) = p(v_{\mathsf{c}} + w_{\mathsf{G}}, T)$. Taylor expanding in powers of w_{L} and w_{G}, we have

$$0 = p_v(v_{\mathsf{c}},T)\,(w_{\mathsf{G}} - w_{\mathsf{L}}) + \tfrac{1}{2}\,p_{vv}(v_{\mathsf{c}},T)\,\big(w_{\mathsf{G}}^2 - w_{\mathsf{L}}^2\big) + \tfrac{1}{6}\,p_{vvv}(v_{\mathsf{c}},T)\,\big(w_{\mathsf{G}}^3 - w_{\mathsf{L}}^3\big) + \ldots \ , \tag{7.19}$$

where

$$p_v \equiv \frac{\partial p}{\partial v} \quad , \quad p_{vv} \equiv \frac{\partial^2 p}{\partial v^2} \quad , \quad p_{vvv} \equiv \frac{\partial^3 p}{\partial v^3} \quad , \quad p_{vT} \equiv \frac{\partial^2 p}{\partial v\,\partial T} \quad , \quad \text{etc.} \tag{7.20}$$

The second equation we write as

$$\int\limits_{w_\mathsf{L}}^{w_\mathsf{G}} dw\, p(v_\mathsf{c}+w,T) = \tfrac{1}{2}(w_\mathsf{G}-w_\mathsf{L})\Big(p(v_\mathsf{c}+w_\mathsf{L},T)+p(v_\mathsf{c}+w_\mathsf{G},T)\Big)\ . \tag{7.21}$$

Expanding in powers of w_L and w_G, this becomes

$$\begin{aligned} p(v_\mathsf{c},T)\,(w_\mathsf{G}-w_\mathsf{L}) &+ \tfrac{1}{2}\,p_v(v_\mathsf{c},T)\,\big(w_\mathsf{G}^2-w_\mathsf{L}^2\big)+\tfrac{1}{6}\,p_{vv}(v_\mathsf{c},T)\,\big(w_\mathsf{G}^3-w_\mathsf{L}^3\big)\\ &\qquad + \tfrac{1}{24}\,p_{vvv}(v_\mathsf{c},T)\,\big(w_\mathsf{G}^4-w_\mathsf{L}^4\big)+\tfrac{1}{120}\,p_{vvvv}(v_\mathsf{c},T)\,\big(w_\mathsf{G}^5-w_\mathsf{L}^5\big)+\ldots\\ &= \tfrac{1}{2}(w_\mathsf{G}-w_\mathsf{L})\Big\{2\,p(v_\mathsf{c},T)+p_v(v_\mathsf{c},T)\,(w_\mathsf{G}+w_\mathsf{L})+\tfrac{1}{2}\,p_{vv}(v_\mathsf{c},T)\,\big(w_\mathsf{G}^2+w_\mathsf{L}^2\big)\\ &\qquad + \tfrac{1}{6}\,p_{vvv}(v_\mathsf{c},T)\,\big(w_\mathsf{G}^3+w_\mathsf{L}^3\big)+\tfrac{1}{24}\,p_{vvvv}(v_\mathsf{c},T)\,\big(w_\mathsf{G}^4+w_\mathsf{L}^4\big)+\ldots\Big\} \end{aligned} \tag{7.22}$$

Subtracting the LHS from the RHS, we find that we can then divide by $\frac{1}{6}\big(w_\mathsf{G}^2-w_\mathsf{L}^2\big)$, resulting in

$$0 = p_{vv}(v_\mathsf{c},T)+\tfrac{1}{2}\,p_{vvv}(v_\mathsf{c},T)\,(w_\mathsf{G}+w_\mathsf{L})+\tfrac{1}{20}\,p_{vvvv}(v_\mathsf{c},T)\,\big(3w_\mathsf{G}^2+4w_\mathsf{G}w_\mathsf{L}+3w_\mathsf{L}^2\big)+\mathcal{O}\big(w_{\mathsf{G,L}}^3\big)\ . \tag{7.23}$$

We now define $w_\pm \equiv w_\mathsf{G} \pm w_\mathsf{L}$. In terms of these variables, eqns. 7.19 and 7.23 become

$$\begin{aligned} 0 &= p_v(v_\mathsf{c},T)+\tfrac{1}{2}\,p_{vv}(v_\mathsf{c},T)\,w_+ +\tfrac{1}{8}\,p_{vvv}(v_\mathsf{c},T)\,\big(w_+^2+\tfrac{1}{3}\,w_-^2\big)+\mathcal{O}\big(w_\pm^3\big)\\ 0 &= p_{vv}(v_\mathsf{c},T)+\tfrac{1}{2}\,p_{vvv}(v_\mathsf{c},T)\,w_+ +\tfrac{1}{8}\,p_{vvvv}(v_\mathsf{c},T)\,\big(w_+^2+\tfrac{1}{5}\,w_-^2\big)+\mathcal{O}\big(w_\pm^3\big)\ . \end{aligned} \tag{7.24}$$

We now evaluate $w_\pm$ to order T. Note that $p_v(v_\mathsf{c},T_\mathsf{c}) = p_{vv}(v_\mathsf{c},T_\mathsf{c}) = 0$, since the critical point is an inflection point in the (v,p) plane. Thus, we have $p_v(v_\mathsf{c},T) = p_{vT}\,\Theta + \mathcal{O}(\Theta^2)$, where $T = T_\mathsf{c}+\Theta$ and $p_{vT} = p_{vT}(v_\mathsf{c},T_\mathsf{c})$. We can then see that w_- is of leading order $\sqrt{-\Theta}$, while w_+ is of leading order Θ. This allows us to write

$$\begin{aligned} 0 &= p_{vT}\,\Theta+\tfrac{1}{24}\,p_{vvv}\,w_-^2+\mathcal{O}(\Theta^2)\\ 0 &= p_{vvT}\,\Theta+\tfrac{1}{2}\,p_{vvv}\,w_+ +\tfrac{1}{40}\,p_{vvvv}\,w_-^2+\mathcal{O}(\Theta^2)\ . \end{aligned} \tag{7.25}$$

Thus,

$$\begin{aligned} w_- &= \bigg(\frac{24\,p_{vT}}{p_{vvv}}\bigg)^{1/2}\sqrt{-\Theta}+\ldots\\ w_+ &= \bigg(\frac{6\,p_{vT}\,p_{vvvv}-10\,p_{vvv}\,p_{vvT}}{5\,p_{vvv}^2}\bigg)\,\Theta+\ldots\ . \end{aligned} \tag{7.26}$$

We then have

$$\begin{aligned} w_\mathsf{L} &= -\bigg(\frac{6\,p_{vT}}{p_{vvv}}\bigg)^{1/2}\sqrt{-\Theta}+\bigg(\frac{3\,p_{vT}\,p_{vvvv}-5\,p_{vvv}\,p_{vvT}}{5\,p_{vvv}^2}\bigg)\Theta+\mathcal{O}\big(\Theta^{3/2}\big)\\ w_\mathsf{G} &= \bigg(\frac{6\,p_{vT}}{p_{vvv}}\bigg)^{1/2}\sqrt{-\Theta}+\bigg(\frac{3\,p_{vT}\,p_{vvvv}-5\,p_{vvv}\,p_{vvT}}{5\,p_{vvv}^2}\bigg)\Theta+\mathcal{O}\big(\Theta^{3/2}\big)\ . \end{aligned} \tag{7.27}$$

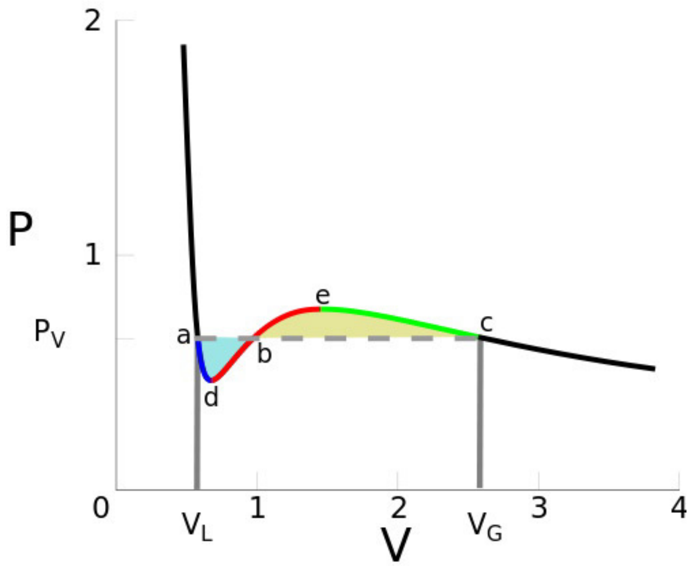

Figure 7.3: Maxwell construction in the (v, p) plane. The system is absolutely unstable between volumes v_{d} and v_{e}. For $v \in [v_{\mathrm{a}}, v_{\mathrm{d}}]$ of $v \in [v_{\mathrm{e}}, v_{\mathrm{c}}]$, the solution is unstable with respect to phase separation. Source: *Wikipedia*.

Suppose we follow along an isotherm starting from the high molar volume (gas) phase. If $T > T_{\mathsf{c}}$, the volume v decreases continuously as the pressure p increases. If $T < T_{\mathsf{c}}$, then at the instant the isotherm first intersects the orange boundary curve in Fig. 7.4, there is a discontinuous change in the molar volume from high (gas) to low (liquid). This discontinuous change is the hallmark of a *first order phase transition*. Note that the volume discontinuity, $\Delta v = w_{-} \propto (T_{\mathsf{c}} - T)^{1/2}$. This is an example of a *critical behavior* in which the *order parameter* ϕ, which in this case may be taken to be the difference $\phi = v_{\mathsf{G}} - v_{\mathsf{L}}$, behaves as a power law in $\big|T - T_{\mathrm{c}}\big|$, where T_{c} is the *critical temperature*. In this case, we have $\phi(T) \propto (T_{\mathsf{c}} - T)_{+}^{\beta}$, where $\beta = \frac{1}{2}$ is the exponent, and where $(T_{\mathsf{c}} - T)_{+}$ is defined to be $T_{\mathsf{c}} - T$ if $T < T_{\mathsf{c}}$ and 0 otherwise. The isothermal compressibility is $\kappa_T = -v/p_v(v, T)$. This is finite along the coexistence curve – it diverges only along the spinodal. It therefore diverges at the critical point, which lies at the intersection of the spinodal and the coexistence curve.

It is convenient to express the equation of state and the coexistence curve in terms of dimensionless variables. Write

$$\bar{p} = \frac{p}{p_{\mathrm{c}}} \quad , \quad \bar{v} = \frac{v}{v_{\mathrm{c}}} \quad , \quad \bar{T} = \frac{T}{T_{\mathrm{c}}} \,. \tag{7.28}$$

The van der Waals equation of state then becomes

$$\bar{p} = \frac{8\bar{T}}{3\bar{v} - 1} - \frac{3}{\bar{v}^2} \,. \tag{7.29}$$

Further expressing these dimensionless quantities in terms of distance from the critical point, we write

$$\bar{p} = 1 + \pi \quad , \quad \bar{v} = 1 + \epsilon \quad , \quad \bar{T} = 1 + t \,. \tag{7.30}$$

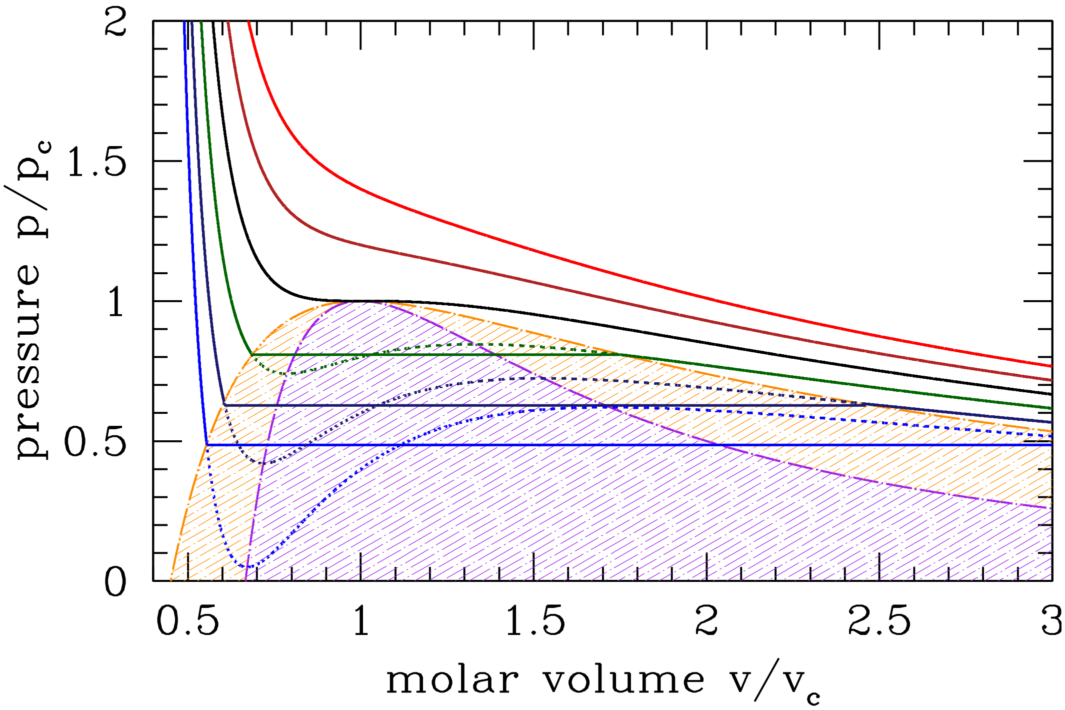

Figure 7.4: Pressure-volume isotherms for the van der Waals system, as in Fig. 7.1, but corrected to account for the Maxwell construction. The boundary of the purple shaded region is the spinodal line $\bar{p}^*(\bar{v})$. The boundary of the orange shaded region is the stability boundary with respect to phase separation.

Thus,

$$\pi(\epsilon,t) = \frac{8(1+t)}{2+3\epsilon} - \frac{3}{(1+\epsilon)^2} - 1 \, . \tag{7.31}$$

Note that the LHS and the RHS of this equation vanish identically for $(\pi,\epsilon,t) = (0,0,0)$. We can then write

$$\epsilon_{\mathsf{L,G}} = \mp\bigg(\frac{6\,\pi_{\epsilon t}}{\pi_{\epsilon\epsilon\epsilon}}\bigg)^{1/2}(-t)^{1/2} + \bigg(\frac{3\,\pi_{\epsilon t}\,\pi_{\epsilon\epsilon\epsilon\epsilon} - 5\,\pi_{\epsilon\epsilon\epsilon}\,\pi_{\epsilon\epsilon t}}{5\,\pi^2_{\epsilon\epsilon\epsilon}}\bigg)t + \mathcal{O}\big((-t)^{3/2}\big) \, . \tag{7.32}$$

7.2.3 History of the van der Waals equation

The van der Waals equation of state first appears in van der Waals' 1873 PhD thesis[3], *"Over de Continuïteit van den Gas - en Vloeistoftoestand"* ("On the continuity of the gas and liquid state"). In his Nobel lecture[4], van der Waals writes of how he was inspired by Rudolf Clausius' 1857 treatise on the nature of heat, where it is posited that a gas in fact consists of microscopic particles whizzing around at high velocities. van der Waals reasoned that liquids, which result when gases are compressed, also consist of 'small

[3]Johannes Diderik van der Waals, the eldest of ten children, was the son of a carpenter. As a child he received only a primary school education. He worked for a living until age 25, and was able to enroll in a three-year industrial evening school for working class youth. Afterward he continued his studies independently, in his spare time, working as a teacher. By the time he obtained his PhD, he was 36 years old. He received the Nobel Prize for Physics in 1910.

[4]See http://www.nobelprize.org/nobel_prizes/physics/laureates/1910/waals-lecture.pdf

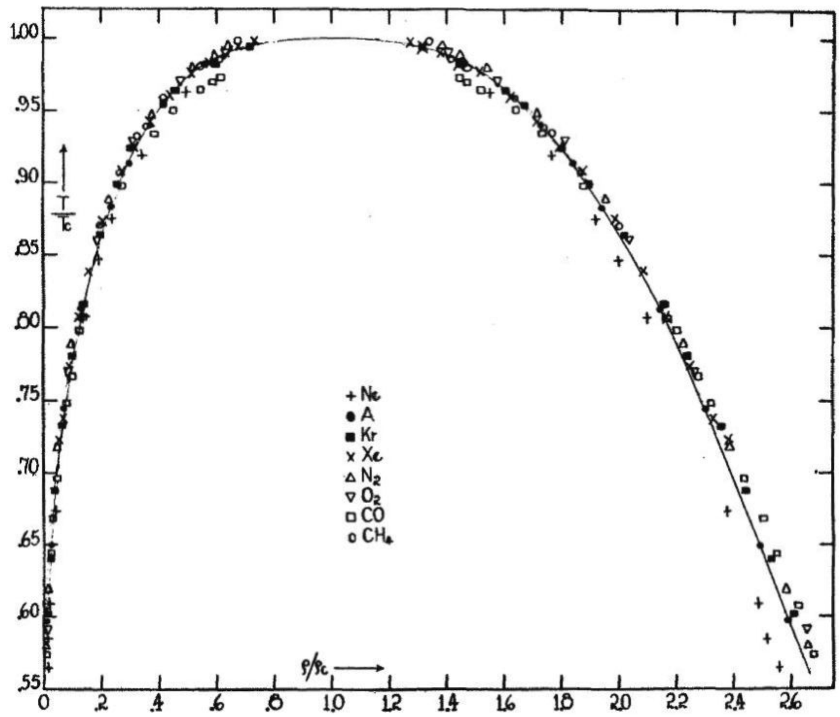

Figure 7.5: 'Universality' of the liquid-gas transition for eight different atomic and molecular fluids, from E. A. Guggenheim, *J. Chem. Phys.* **13**, 253 (1945). Dimensionless temperature T/T_c *versus* dimensionless density $\rho/\rho_c = v_c/v$ is shown. The van der Waals / mean field theory gives $\Delta v = v_{gas} - v_{liquid} \propto (-t)^{1/2}$, while experiments show a result closer to $\Delta v \propto (-t)^{1/3}$. Here $t \equiv \bar{T} - 1 = (T - T_c)/T_c$ is the dimensionless temperature deviation with respect to the critical point.

moving particles': *"Thus I conceived the idea that there is no essential difference between the gaseous and the liquid state of matter…"*

Clausius' treatise showed how his kinetic theory of heat was consistent with Boyle's law for gases ($pV = \text{constant}$ at fixed temperature). van der Waals pondered why this might fail for the non-dilute liquid phase, and he reasoned that there were two principal differences: inter-particle attraction and excluded volume. These considerations prompted him to posit his famous equation,

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \ . \tag{7.33}$$

The first term on the RHS accounts for excluded volume effects, and the second for mutual attractions.

In the limiting case of $p \to \infty$, the molar volume approaches $v = b$. On physical grounds, one might expect $b = v_0/\zeta$, where $v_0 = N_A\,\omega_0$ is N_A times the volume ω_0 of a single molecule, and the *packing fraction* is $\zeta = N\omega_0/V = v_0/v$, which is the ratio of the total molecular volume to the total system volume. In three dimensions, the maximum possible packing fraction is for fcc and hcp lattices, each of which have coordination number 12, with $\zeta_{max} = \frac{\pi}{3\sqrt{2}} = 0.74078$. Dense random packing results in $\zeta_{drp} = 0.634$.

Expanding the vdW equation of state in inverse powers of v yields

$$p = \frac{RT}{v} + \left(b - \frac{a}{RT}\right) \cdot \frac{RT}{v^2} + \mathcal{O}\big(v^{-3}\big) \ , \tag{7.34}$$

and we read of the second virial coefficient $B_2 = \big(b - \frac{a}{RT}\big)/N_{\mathrm{A}}$. For hard spheres, $a = 0$, and the result $B_2 = 4\omega_0$ from the Mayer cluster expansion corresponds to $b_{\mathrm{Mayer}} = 4v_0$, which is larger than the result from even the loosest regular sphere packing, *i.e.* that for a cubic lattice, with $\zeta_{\textsf{cub}} = \frac{\pi}{6}$.

Another of van der Waals' great achievements was his articulation of the *law of corresponding states*. Recall that the van der Waals equation of state, when written in terms of dimensionless quantities $\bar{p} = p/p_{\mathrm{c}}$, $\bar{v} = v/v_{\mathrm{c}}$, and $\bar{T} = T/T_{\mathrm{c}}$, takes the form of eqn. 7.29. Thus, while the a and b parameters are specific to each fluid – see Tab. 7.1 – when written in terms of these scaled dimensionless variables, the equation of state and all its consequent properties (*i.e.* the liquid-gas phase transition) are *universal*.

The van der Waals equation is best viewed as semi-phenomenological. Interaction and excluded volume effects surely are present, but the van der Waals equation itself only captures them in a very approximate way. It is applicable to gases, where it successfully predicts features that are not present in ideal systems (*e.g.* throttling). It is of only qualitative and pedagogical use in the study of fluids, the essential physics of which lies in the behavior of quantities like the pair distribution function $g(r)$. As we saw in chapter 6, any adequate first principles derivation of $g(r)$ - a function which can be measured in scattering experiments - involves rather complicated approximation schemes to close the BBGKY hierarchy. Else one must resort to numerical simulations such as the Monte Carlo method. Nevertheless, the lessons learned from the van der Waals system are invaluable and they provide us with a first glimpse of what is going on in the vicinity of a phase transition, and how nonanalytic behavior, such as $v_{\textsf{G}} - v_{\textsf{L}} \propto (T_{\mathrm{c}} - T)^{\beta}$ with noninteger exponent β may result due to singularities in the free energy at the critical point.

7.3 Fluids, Magnets, and the Ising Model

7.3.1 Lattice gas description of a fluid

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

$$\hat{H}(\boldsymbol{p}, \boldsymbol{x}) = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \sum_{i<j} u(\boldsymbol{x}_i - \boldsymbol{x}_j) \ . \tag{7.35}$$

The potential $u(\boldsymbol{r})$ is typically central, depending only on the magnitude $|\boldsymbol{r}|$, 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

$$U = \sum_{i<j} u(\boldsymbol{x}_i - \boldsymbol{x}_j) = \tfrac{1}{2} \sum_{\boldsymbol{R} \neq \boldsymbol{R}'} V_{\boldsymbol{R}\boldsymbol{R}'} \, n_{\boldsymbol{R}} \, n_{\boldsymbol{R}'} \ , \tag{7.36}$$

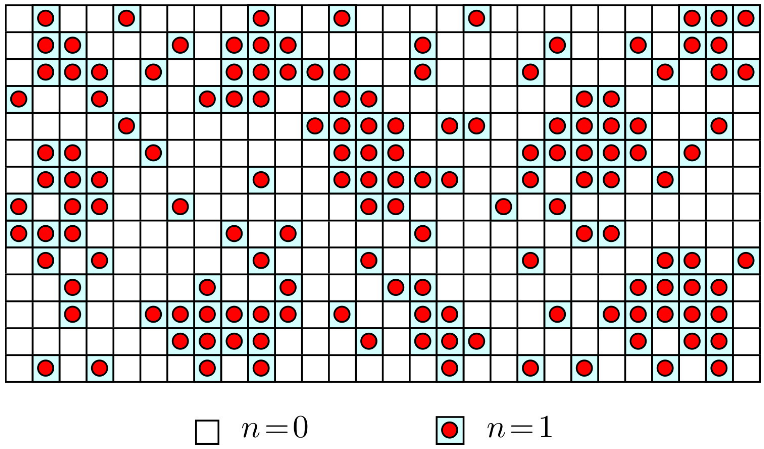

Figure 7.6: The lattice gas model. An occupied cell corresponds to $n = 1$ ($\sigma = +1$), and a vacant cell to $n = 0$ ($\sigma = -1$).

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

$$\Xi(T, V, \mu) \approx \sum_{\{n_{\boldsymbol{R}}\}} \bigg(\prod_{\boldsymbol{R}} \xi^{n_{\boldsymbol{R}}}\bigg) \exp\bigg(-\tfrac{1}{2}\beta \sum_{\boldsymbol{R}\neq\boldsymbol{R}'} V_{\boldsymbol{R}\boldsymbol{R}'}\, n_{\boldsymbol{R}}\, n_{\boldsymbol{R}'}\bigg) , \tag{7.37}$$

where

$$\xi = e^{\beta\mu}\, \lambda_T^{-d}\, a^d , \tag{7.38}$$

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 $\sum_{\boldsymbol{R}} n_{\boldsymbol{R}} = N$ is the total number of fluid particles, so

$$\prod_{\boldsymbol{R}} \xi^{\,n_{\boldsymbol{R}}} = \xi^N = e^{\beta\mu N}\, \lambda_T^{-Nd}\, a^{Nd} . \tag{7.39}$$

Thus, we can write a lattice Hamiltonian,

$$\begin{aligned} \hat{H} &= \tfrac{1}{2} \sum_{\boldsymbol{R}\neq\boldsymbol{R}'} V_{\boldsymbol{R}\boldsymbol{R}'}\, n_{\boldsymbol{R}}\, n_{\boldsymbol{R}'} - k_{\rm B}T \ln\xi \sum_{\boldsymbol{R}} n_{\boldsymbol{R}} \\ &= -\tfrac{1}{2} \sum_{\boldsymbol{R}\neq\boldsymbol{R}'} J_{\boldsymbol{R}\boldsymbol{R}'}\, \sigma_{\boldsymbol{R}}\, \sigma_{\boldsymbol{R}'} - H \sum_{\boldsymbol{R}} \sigma_{\boldsymbol{R}} + E_0 , \end{aligned} \tag{7.40}$$

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

$$\begin{aligned} J_{\boldsymbol{R}\boldsymbol{R}'} &= -\tfrac{1}{4} V_{\boldsymbol{R}\boldsymbol{R}'} \\ H &= \tfrac{1}{2} k_{\rm B}T \ln\xi - \tfrac{1}{4} {\sum_{\boldsymbol{R}'}}' V_{\boldsymbol{R}\boldsymbol{R}'} , \end{aligned} \tag{7.41}$$

where the prime on the sum indicates that $\boldsymbol{R}' = \boldsymbol{R}$ is to be excluded. For the Lennard-Jones system, $V_{\boldsymbol{R}\boldsymbol{R}'} = v(\boldsymbol{R} - \boldsymbol{R}') < 0$ is due to the attractive tail of the potential, hence $J_{\boldsymbol{R}\boldsymbol{R}'}$ is positive, which prefers alignment of the spins $\sigma_{\boldsymbol{R}}$ and $\sigma_{\boldsymbol{R}'}$. This interaction is therefore *ferromagnetic*. The spin Hamiltonian in eqn. 7.40 is known as the Ising model.

7.3.2 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]

$$p \longleftrightarrow H \qquad , \qquad v \longleftrightarrow m \ ,$$

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

$$m = \frac{M}{N_{\mathsf{S}}} = \frac{1}{N_{\mathsf{S}}} \sum_{\boldsymbol{R}} \langle \sigma_{\boldsymbol{R}} \rangle \ . \tag{7.42}$$

Sketches of the phase diagrams are reproduced in fig. 7.7. Of particular interest is the *critical point*, which occurs at $(T_{\mathrm{c}}, p_{\mathrm{c}})$ in the fluid system and $(T_{\mathrm{c}}, H_{\mathrm{c}})$ in the magnetic system, with $H_{\mathrm{c}} = 0$ 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 $T > T_{\mathrm{c}}$, 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 $T < T_{\mathrm{c}}$, 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:

$$\kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T \qquad , \qquad \kappa_T(T_{\mathrm{c}}, p_{\mathrm{c}}) = \infty$$

$$\chi_T = \left(\frac{\partial m}{\partial H} \right)_T \qquad , \qquad \chi_T(T_{\mathrm{c}}, H_{\mathrm{c}}) = \infty$$

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 $\Psi \propto (v_{\mathrm{vap}} - v_{\mathrm{liq}})$, the difference in the specific volumes of the vapor and liquid phases. In the vicinity of the

[5]One could equally well identify the second correspondence as $n \longleftrightarrow m$ between density (rather than specific volume) and magnetization. One might object that H is more properly analogous to μ. However, since $\mu = \mu(p, T)$ it can equally be regarded as analogous to p. Note also that $\beta p = z\lambda_T^{-d}$ for the ideal gas, in which case $\xi = z(a/\lambda_T)^d$ is proportional to p.

[6]Note the distinction between the number of lattice sites N_{S} and the number of occupied cells N. According to our definitions, $N = \frac{1}{2}(M + N_{\mathsf{S}})$.

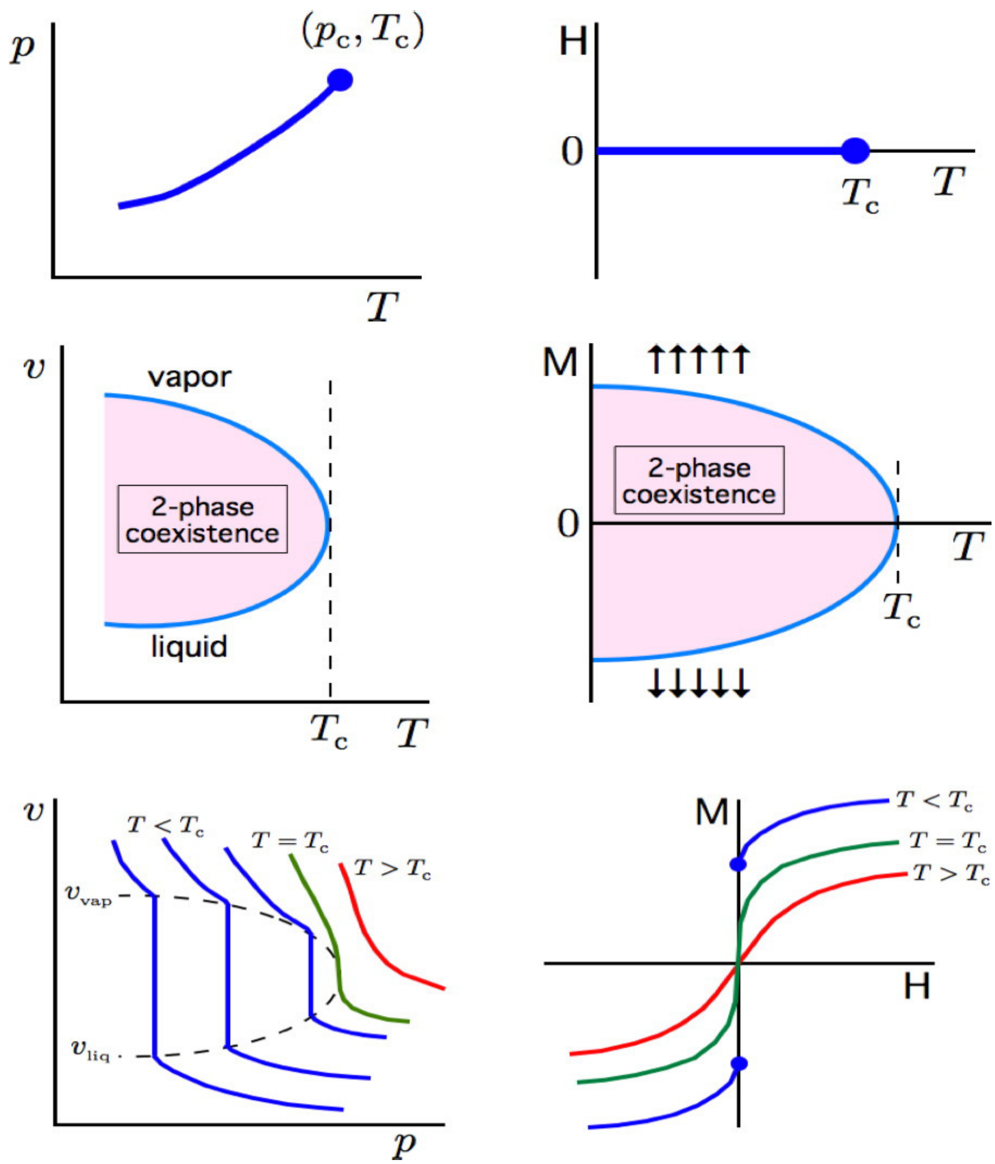

Figure 7.7: Comparison of the liquid-gas phase diagram with that of the Ising ferromagnet.

critical point, the system exhibits power law behavior in many physical quantities, *viz.*

$$\begin{aligned} m(T,H_c) &\sim \big(T_c-T\big)_+^{\beta} \\ \chi(T,H_c) &\sim |T-T_c|^{-\gamma} \\ C_M(T,H_c) &\sim |T-T_c|^{-\alpha} \\ m(T_c,H) &\sim \pm|H|^{1/\delta}\ . \end{aligned} \tag{7.43}$$

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]

$$\begin{aligned} \alpha + 2\beta + \gamma = 2 &\qquad \text{(Rushbrooke)} \\ \beta + \gamma = \beta\delta &\qquad \text{(Griffiths)} \\ 2 - \alpha = d\,\nu &\qquad \text{(hyperscaling)}\ . \end{aligned} \tag{7.44}$$

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.

7.3.3 Gibbs-Duhem relation for magnetic systems

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

$$S\,dT + M\,dH + N_\mathsf{S} d\mu = 0\ . \tag{7.45}$$

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

$$d\mu_1 = -s_1\,dT - m_1\,dH = -s_2\,dT - m_2\,dH = d\mu_2\ , \tag{7.46}$$

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

$$\left(\frac{dH}{dT}\right)_{\text{coex}} = -\frac{s_1 - s_2}{m_1 - m_2}\ . \tag{7.47}$$

Thus, if $m_1 \neq m_2$ and $\left(\frac{dH}{dT}\right)_{\text{coex}} = 0$, 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 $F(T, H, N_\mathsf{S}) = F(T, -H, N_\mathsf{S})$.

7.3.4 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 $T_\mathrm{c} \simeq 740\,\mathrm{K}$, 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 $\varepsilon_{\mathrm{AA}}$, $\varepsilon_{\mathrm{BB}}$, or $\varepsilon_{\mathrm{AB}}$, 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

$$E_{ij} = \varepsilon_{\mathrm{AA}}\,P_i^{\mathrm{A}}\,P_j^{\mathrm{A}} + \varepsilon_{\mathrm{BB}}\,P_i^{\mathrm{B}}\,P_j^{\mathrm{B}} + \varepsilon_{\mathrm{AB}}\left(P_i^{\mathrm{A}}\,P_j^{\mathrm{B}} + P_i^{\mathrm{B}}\,P_j^{\mathrm{A}}\right)\ , \tag{7.48}$$

[7] In the third of the following exponent equalities, d is the dimension of space and ν is the correlation length exponent.

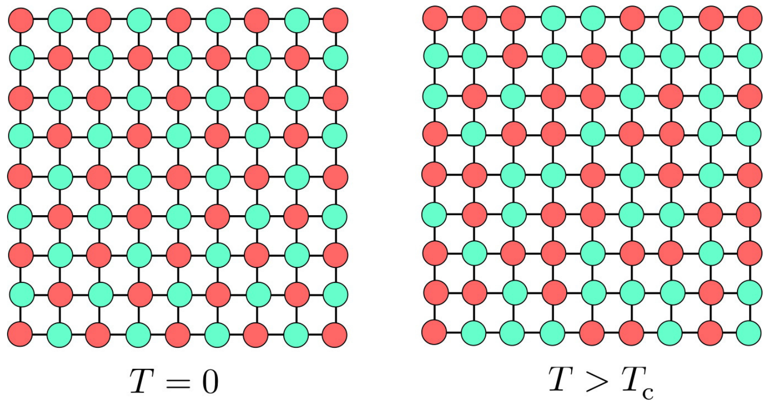

Figure 7.8: Order-disorder transition on the square lattice. Below $T = T_c$, order develops spontaneously on the two $\sqrt{2} \times \sqrt{2}$ sublattices. There is perfect sublattice order at $T = 0$ (left panel).

where

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

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

The Hamiltonian is then

$$\begin{aligned} \hat{H} &= \sum_{\langle ij \rangle} E_{ij} \\ &= \sum_{\langle ij \rangle} \Big\{ \tfrac{1}{4}\big(\varepsilon_{\mathrm{AA}} + \varepsilon_{\mathrm{BB}} - 2\varepsilon_{\mathrm{AB}}\big)\,\sigma_i\,\sigma_j + \tfrac{1}{4}\big(\varepsilon_{\mathrm{AA}} - \varepsilon_{\mathrm{BB}}\big)\,(\sigma_i + \sigma_j) + \tfrac{1}{4}\big(\varepsilon_{\mathrm{AA}} + \varepsilon_{\mathrm{BB}} + 2\varepsilon_{\mathrm{AB}}\big) \Big\} \\ &= -J \sum_{\langle ij \rangle} \sigma_i\,\sigma_j - H \sum_i \sigma_i + E_0\ , \end{aligned} \tag{7.49}$$

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

$$\begin{aligned} J &= \tfrac{1}{4}\big(2\varepsilon_{\mathrm{AB}} - \varepsilon_{\mathrm{AA}} - \varepsilon_{\mathrm{BB}}\big) \\ H &= \tfrac{1}{4}\big(\varepsilon_{\mathrm{BB}} - \varepsilon_{\mathrm{AA}}\big)\ , \end{aligned} \tag{7.50}$$

and $E_0 = \frac{1}{8}Nz\big(\varepsilon_{\mathrm{AA}} + \varepsilon_{\mathrm{BB}} + 2\varepsilon_{\mathrm{AB}}\big)$, 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.

Note that

$$\begin{aligned} 2\varepsilon_{\mathrm{AB}} &> \varepsilon_{\mathrm{AA}} + \varepsilon_{\mathrm{BB}} \quad \Longrightarrow \quad J > 0 \quad \text{(ferromagnetic)} \\ 2\varepsilon_{\mathrm{AB}} &< \varepsilon_{\mathrm{AA}} + \varepsilon_{\mathrm{BB}} \quad \Longrightarrow \quad J < 0 \quad \text{(antiferromagnetic)}\ . \end{aligned} \tag{7.51}$$

The antiferromagnetic case is depicted in fig. 7.8.

7.4 Mean Field Theory

Consider the Ising model Hamiltonian,

$$\hat{H} = -J \sum_{\langle ij \rangle} \sigma_i \, \sigma_j - H \sum_i \sigma_i \, , \tag{7.52}$$

where the first sum on the RHS is over all links of the lattice. Each spin can be either 'up' ($\sigma = +1$) or 'down' ($\sigma = -1$). We further assume that the spins are located on a Bravais lattice[8] and that the coupling $J_{ij} = J\big(|\boldsymbol{R}_i - \boldsymbol{R}_j|\big)$, where $\boldsymbol{R}_i$ is the position of the i^{th} spin.

On each site i we decompose σ_i into a contribution from its thermodynamic average and a fluctuation term, *i.e.*

$$\sigma_i = \langle \sigma_i \rangle + \delta\sigma_i \, . \tag{7.53}$$

We will write $\langle \sigma_i \rangle \equiv m$, the local magnetization (dimensionless), and assume that m is independent of position i. Then

$$\begin{aligned} \sigma_i \, \sigma_j &= (m + \delta\sigma_i)\,(m + \delta\sigma_j) \\ &= m^2 + m\,(\delta\sigma_i + \delta\sigma_j) + \delta\sigma_i \, \delta\sigma_j \\ &= -m^2 + m\,(\sigma_i + \sigma_j) + \delta\sigma_i \, \delta\sigma_j \, . \end{aligned} \tag{7.54}$$

The last term on the RHS of the second equation above is quadratic in the fluctuations, and we assume this to be negligibly small. Thus, we obtain the *mean field Hamiltonian*

$$\hat{H}_{\text{MF}} = \tfrac{1}{2} N z J \, m^2 - \big(H + zJm\big) \sum_i \sigma_i \, , \tag{7.55}$$

where N is the total number of lattice sites. The first term is a constant, although the value of m is yet to be determined. The Boltzmann weights are then completely determined by the second term, which is just what we would write down for a Hamiltonian of *noninteracting* spins in an effective 'mean field'

$$H_{\text{eff}} = H + zJm \, . \tag{7.56}$$

In other words, $H_{\text{eff}} = H_{\text{ext}} + H_{\text{int}}$, where the external field is applied field $H_{\text{ext}} = H$, and the 'internal field' is $H_{\text{int}} = zJm$. The internal field accounts for the interaction with the *average* values of all other spins coupled to a spin at a given site, hence it is often called the 'mean field'. Since the spins are noninteracting, we have

$$m = \frac{e^{\beta H_{\text{eff}}} - e^{-\beta H_{\text{eff}}}}{e^{\beta H_{\text{eff}}} + e^{-\beta H_{\text{eff}}}} = \tanh\!\left(\frac{H + zJm}{k_{\text{B}} T}\right) . \tag{7.57}$$

It is a simple matter to solve for the free energy, given the noninteracting Hamiltonian $\hat{H}_{\text{MF}}$. The partition function is

$$Z = \mathsf{Tr}\; e^{-\beta \hat{H}_{\text{MF}}} = e^{-\frac{1}{2}\beta N z J \, m^2} \bigg(\sum_\sigma e^{\beta (H + zJm)\sigma} \bigg)^{\!N} = e^{-\beta F} \, . \tag{7.58}$$

[8]A Bravais lattice is one in which any site is equivalent to any other site through an appropriate discrete translation. Examples of Bravais lattices include the linear chain, square, triangular, simple cubic, face-centered cubic, *etc.* lattices. The honeycomb lattice is not a Bravais lattice, because there are two sets of inequivalent sites – those in the center of a Y and those in the center of an upside down Y.

We now define dimensionless variables:

$$f \equiv \frac{F}{NzJ} \quad , \quad \theta \equiv \frac{k_{\mathrm{B}}T}{zJ} \quad , \quad h \equiv \frac{H}{zJ} \, , \tag{7.59}$$

and obtain the dimensionless free energy

$$f(m,h,\theta) = \tfrac{1}{2}m^2 - \theta \, \ln\left(e^{(m+h)/\theta} + e^{-(m+h)/\theta}\right) . \tag{7.60}$$

Differentiating with respect to m gives the mean field equation,

$$m = \tanh\left(\frac{m+h}{\theta}\right) , \tag{7.61}$$

which is equivalent to the self-consistency requirement, $m = \langle \sigma_i \rangle$.

7.4.1 $h = 0$

When $h = 0$ the mean field equation becomes

$$m = \tanh\left(\frac{m}{\theta}\right) . \tag{7.62}$$

This nonlinear equation can be solved graphically, as in the top panel of fig. 7.9. The RHS in a tanh function which gets steeper with decreasing t. If, at $m = 0$, the slope of $\tanh(m/\theta)$ is smaller than unity, then the curve $y = \tanh(m/h)$ will intersect $y = m$ only at $m = 0$. However, if the slope is larger than unity, there will be three such intersections. Since the slope is $1/\theta$, we identify $\theta_{\mathrm{c}} = 1$ as the *mean field transition temperature*.

In the low temperature phase $\theta < 1$, there are three solutions to the mean field equations. One solution is always at $m = 0$. The other two solutions must be related by the $m \leftrightarrow -m$ symmetry of the free energy (when $h = 0$). The exact free energies are plotted in the bottom panel of fig. 7.9, but it is possible to make analytical progress by assuming m is small and Taylor expanding the free energy $f(m, \theta)$ in powers of m:

$$\begin{aligned} f(m,\theta) &= \tfrac{1}{2}m^2 - \theta \ln 2 - \theta \, \ln\cosh\left(\frac{m}{\theta}\right) \\ &= -\theta \, \ln 2 + \tfrac{1}{2}\left(1-\theta^{-1}\right) m^2 + \frac{m^4}{12\,\theta^3} - \frac{m^6}{45\,\theta^5} + \ldots \, . \end{aligned} \tag{7.63}$$

Note that the sign of the quadratic term is positive for $\theta > 1$ and negative for $\theta < 1$. Thus, the shape of the free energy $f(m, \theta)$ as a function of m qualitatively changes at this point, $\theta_{\mathrm{c}} = 1$, the mean field transition temperature, also known as the *critical temperature*.

For $\theta > \theta_{\mathrm{c}}$, the free energy $f(m, \theta)$ has a single minimum at $m = 0$. Below θ_{c}, the curvature at $m = 0$ reverses, and $m = 0$ becomes a local maximum. There are then two equivalent minima symmetrically displaced on either side of $m = 0$. Differentiating with respect to m, we find these local minima. For $\theta < \theta_{\mathrm{c}}$, the local minima are found at

$$m^2 = 3\theta^2(1-\theta) = 3(1-\theta) + \mathcal{O}\big((1-\theta)^2\big) \, . \tag{7.64}$$

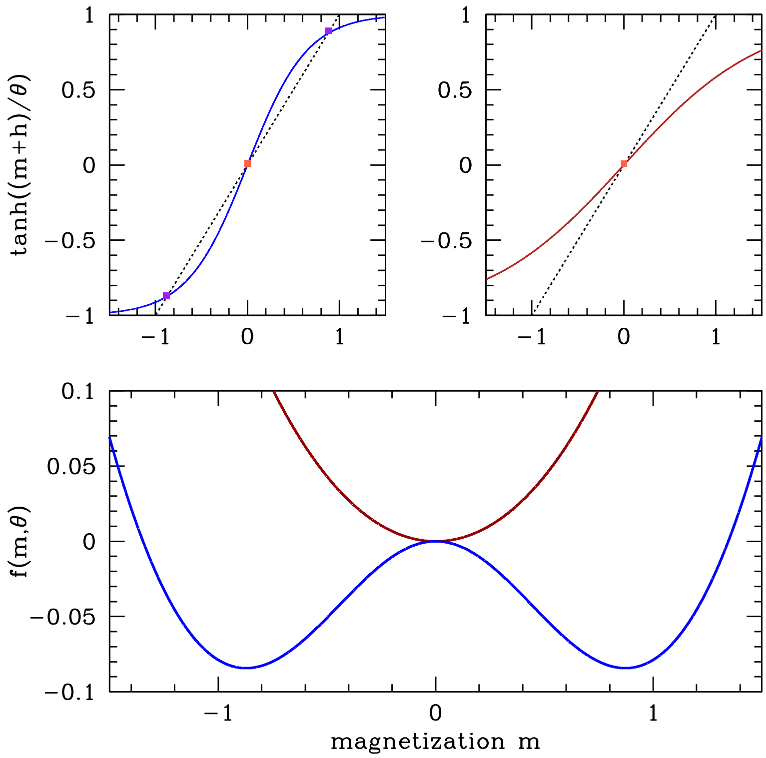

Figure 7.9: .
Results for $h = 0$. Upper panels: graphical solution to self-consistency equation $m = \tanh(m/\theta)$ at temperatures $\theta = 0.65$ (blue) and $\theta = 1.5$ (dark red). Lower panel: mean field free energy, with energy shifted by $\theta \ln 2$ so that $f(m = 0, \theta) = 0$.

Thus, we find for $|\theta - 1| \ll 1$,

$$m(\theta, h = 0) = \pm\sqrt{3}\,\big(1 - \theta\big)_{+}^{1/2}\ , \tag{7.65}$$

where the $+$ subscript indicates that this solution is only for $1 - \theta > 0$. For $\theta > 1$ the only solution is $m = 0$. The exponent with which $m(\theta)$ vanishes as $\theta \to \theta_c^-$ is denoted β. *I.e.* $m(\theta, h = 0) \propto (\theta_c - \theta)_{+}^{\beta}$.

7.4.2 Specific heat

We can now expand the free energy $f(\theta, h = 0)$. We find

$$f(\theta, h = 0) = \begin{cases} -\theta \ln 2 & \text{if } \theta > \theta_c \\ -\theta \ln 2 - \frac{3}{4}(1 - \theta)^2 + \mathcal{O}\big((1 - \theta)^4\big) & \text{if } \theta < \theta_c\ . \end{cases} \tag{7.66}$$

Thus, if we compute the heat capacity, we find in the vicinity of $\theta = \theta_c$

$$c_V = -\theta\,\frac{\partial^2 f}{\partial \theta^2} = \begin{cases} 0 & \text{if } \theta > \theta_c \\ \frac{3}{2} & \text{if } \theta < \theta_c\ . \end{cases} \tag{7.67}$$

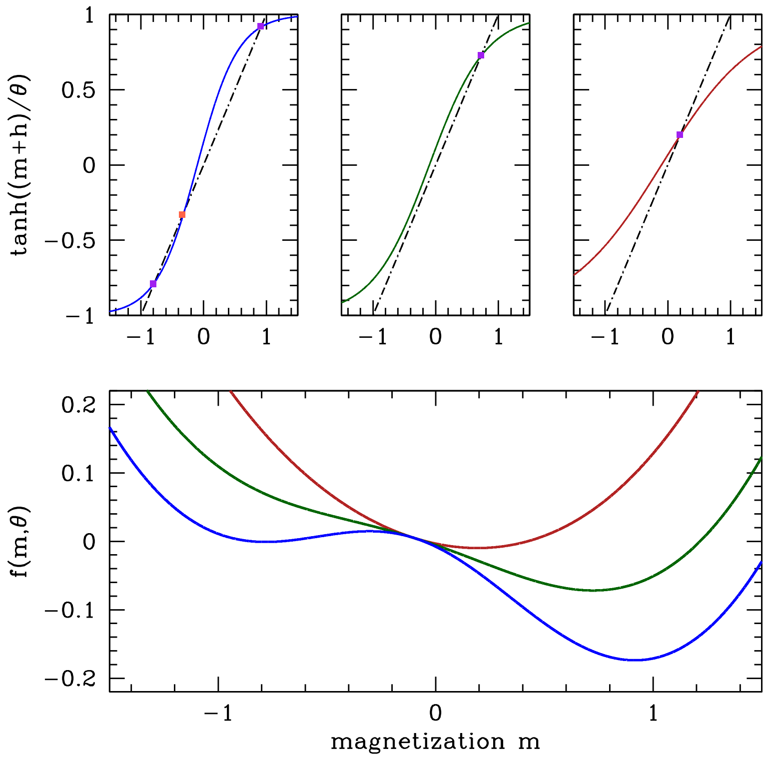

Figure 7.10: .
Results for $h = 0.1$. Upper panels: graphical solution to self-consistency equation $m = \tanh\big((m+h)/\theta\big)$ at temperatures $\theta = 0.65$ (blue), $\theta = 0.9$ (dark green), and $\theta = 1.5$ (dark red). Lower panel: mean field free energy, with energy shifted by $\theta \ln 2$ so that $f(m = 0, \theta) = 0$.

Thus, the specific heat is *discontinuous* at $\theta = \theta_c$. We emphasize that this is only valid near $\theta = \theta_c = 1$. The general result valid for all θ is[9]

$$c_V(\theta) = \frac{1}{\theta} \cdot \frac{m^2(\theta) - m^4(\theta)}{\theta - 1 + m^2(\theta)} \ , \tag{7.68}$$

With this expression one can check both limits $\theta \to 0$ and $\theta \to \theta_c$. As $\theta \to 0$ the magnetization saturates and one has $m^2(\theta) \simeq 1 - 4\, e^{-2/\theta}$. The numerator then vanishes as $e^{-2/\theta}$, which overwhelms the denominator that itself vanishes as θ^2. As a result, $c_V(\theta \to 0) = 0$, as expected. As $\theta \to 1$, invoking $m^2 \simeq 3(1-\theta)$ we recover $c_V(\theta_c^-) = \frac{3}{2}$.

In the theory of critical phenomena, $c_V(\theta) \propto |\theta - \theta_c|^{-\alpha}$ as $\theta \to \theta_c$. We see that mean field theory yields $\alpha = 0$.

[9]To obtain this result, one writes $f = f\big(\theta, m(\theta)\big)$ and then differentiates twice with respect to θ, using the chain rule. Along the way, any naked (*i.e.* undifferentiated) term proportional to $\frac{\partial f}{\partial m}$ may be dropped, since this vanishes at any θ by the mean field equation.

7.4.3 $h \neq 0$

Consider without loss of generality the case $h > 0$. The minimum of the free energy $f(m, h, \theta)$ now lies at $m > 0$ for any θ. At low temperatures, the double well structure we found in the $h = 0$ case is tilted so that the right well lies lower in energy than the left well. This is depicted in fig. 7.10. As the temperature is raised, the local minimum at $m < 0$ vanishes, annihilating with the local maximum in a saddle-node bifurcation. To find where this happens, one sets $\frac{\partial f}{\partial m} = 0$ and $\frac{\partial^2 f}{\partial m^2} = 0$ simultaneously, resulting in

$$h^*(\theta) = \sqrt{1-\theta} - \frac{\theta}{2} \ln\left(\frac{1+\sqrt{1-\theta}}{1-\sqrt{1-\theta}}\right). \tag{7.69}$$

The solutions lie at $h = \pm h^*(\theta)$. For $\theta < \theta_c = 1$ and $h \in \left[-h^*(\theta)\,,\, +h^*(\theta)\right]$, there are three solutions to the mean field equation. Equivalently we could in principle invert the above expression to obtain $\theta^*(h)$. For $\theta > \theta^*(h)$, there is only a single global minimum in the free energy $f(m)$ and there is no local minimum. Note $\theta^*(h = 0) = 1$.

Assuming $h \ll |\theta - 1| \ll 1$, the mean field solution for $m(\theta, h)$ will also be small, and we expand the free energy in m, and to linear order in h:

$$\begin{aligned} f(m, h, \theta) &= -\theta \ln 2 + \tfrac{1}{2}(1 - \theta^{-1})\, m^2 + \frac{m^4}{12\,\theta^3} - \frac{hm}{\theta} \\ &= f_0 + \tfrac{1}{2}\,(\theta - 1)\, m^2 + \tfrac{1}{12} m^4 - hm + \ldots\,. \end{aligned} \tag{7.70}$$

Setting $\frac{\partial f}{\partial m} = 0$, we obtain

$$\tfrac{1}{3} m^3 + (\theta - 1) \cdot m - h = 0\,. \tag{7.71}$$

If $\theta > 1$ then we have a solution $m = h/(\theta - 1)$. The m^3 term can be ignored because it is higher order in h, and we have assumed $h \ll |\theta - 1| \ll 1$. This is known as the *Curie-Weiss law*[10]. The magnetic susceptibility behaves as

$$\chi(\theta) = \frac{\partial m}{\partial h} = \frac{1}{\theta - 1} \propto |\theta - 1|^{-\gamma}\,, \tag{7.72}$$

where the magnetization critical exponent γ is $\gamma = 1$. If $\theta < 1$ then while there is still a solution at $m = h/(\theta - 1)$, it lies at a local maximum of the free energy, as shown in fig. 7.10. The minimum of the free energy occurs close to the $h = 0$ solution $m = m_0(\theta) \equiv \sqrt{3}\,(1 - \theta)$, and writing $m = m_0 + \delta m$ we find δm to linear order in h as $\delta m(\theta, h) = h/2(1 - \theta)$. Thus,

$$m(\theta, h) = \sqrt{3}\,(1 - \theta) + \frac{h}{2(1 - \theta)}\,. \tag{7.73}$$

[10]Pierre Curie was a pioneer in the fields of crystallography, magnetism, and radiation physics. In 1880, Pierre and his older brother Jacques discovered piezoelectricity. He was 21 years old at the time. It was in 1895 that Pierre made the first systematic studies of the effects of temperature on magnetic materials, and he formulated what is known as *Curie's Law*, $\chi = C/T$, where C is a constant. Curie married Marie Sklodowska in the same year. Their research turned toward radiation, recently discovered by Becquerel and Röntgen. In 1898, Pierre and Marie Curie discovered radium. They shared the 1903 Nobel Prize in Physics with Becquerel. Marie went on to win the 1911 Nobel Prize in Chemistry and was the first person ever awarded two Nobel Prizes. Their daughter Irène Joliot Curie shared the 1935 Prize in Chemistry (with her husband), also for work on radioactivity. Pierre Curie met an untimely and unfortunate end in the Spring of 1906. Walking across the Place Dauphine, he slipped and fell under a heavy horse-drawn wagon carrying military uniforms. His skull was crushed by one of the wagon wheels, killing him instantly. Later on that year, Pierre-Ernest Weiss proposed a modification of Curie's Law to account for ferromagnetism. This became known as the Curie-Weiss law, $\chi = C/(T - T_c)$.

Exponent	MFT	2D Ising (exact)	3D Ising (numerical)	CO_2 (expt.)
α	0	0	0.125	$\lesssim 0.1$
β	$1/2$	$1/8$	0.313	0.35
γ	1	$7/4$	1.25	1.26
δ	3	15	5	4.2

Table 7.2: Critical exponents from mean field theory as compared with exact results for the two-dimensional Ising model, numerical results for the three-dimensional Ising model, and experiments on the liquid-gas transition in CO_2. *Source*: H. E. Stanley, *Phase Transitions and Critical Phenomena*.

Once again, we find that $\chi(\theta)$ diverges as $|\theta - 1|^{-\gamma}$ with $\gamma = 1$. The exponent γ on either side of the transition is the same.

Finally, we can set $\theta = \theta_c$ and examine $m(h)$. We find, from eqn. 7.72,

$$m(\theta = \theta_c, h) = (3h)^{1/3} \propto h^{1/\delta} \,, \tag{7.74}$$

where δ is a new critical exponent. Mean field theory gives $\delta = 3$. Note that at $\theta = \theta_c = 1$ we have $m = \tanh(m + h)$, and inverting we find

$$h(m, \theta = \theta_c) = \tfrac{1}{2} \ln\left(\frac{1+m}{1-m}\right) - m = \frac{m^3}{3} + \frac{m^5}{5} + \ldots \,, \tag{7.75}$$

which is consistent with what we just found for $m(h, \theta = \theta_c)$.

How well does mean field theory do in describing the phase transition of the Ising model? In table 7.2 we compare our mean field results for the exponents α, β, γ, and δ with exact values for the two-dimensional Ising model, numerical work on the three-dimensional Ising model, and experiments on the liquid-gas transition in CO_2. The first thing to note is that the exponents are dependent on the dimension of space, and this is something that mean field theory completely misses. In fact, it turns out that the mean field exponents are exact provided $d > d_u$, where d_u is the *upper critical dimension* of the theory. For the Ising model, $d_u = 4$, and above four dimensions (which is of course unphysical) the mean field exponents are in fact exact. We see that all in all the MFT results compare better with the three dimensional exponent values than with the two-dimensional ones – this makes sense since MFT does better in higher dimensions. The reason for this is that higher dimensions means more nearest neighbors, which has the effect of reducing the relative importance of the fluctuations we neglected to include.

7.4.4 Magnetization dynamics

Dissipative processes drive physical systems to minimum energy states. We can crudely model the dissipative dynamics of a magnet by writing the phenomenological equation

$$\frac{dm}{ds} = -\frac{\partial f}{\partial m} \,, \tag{7.76}$$

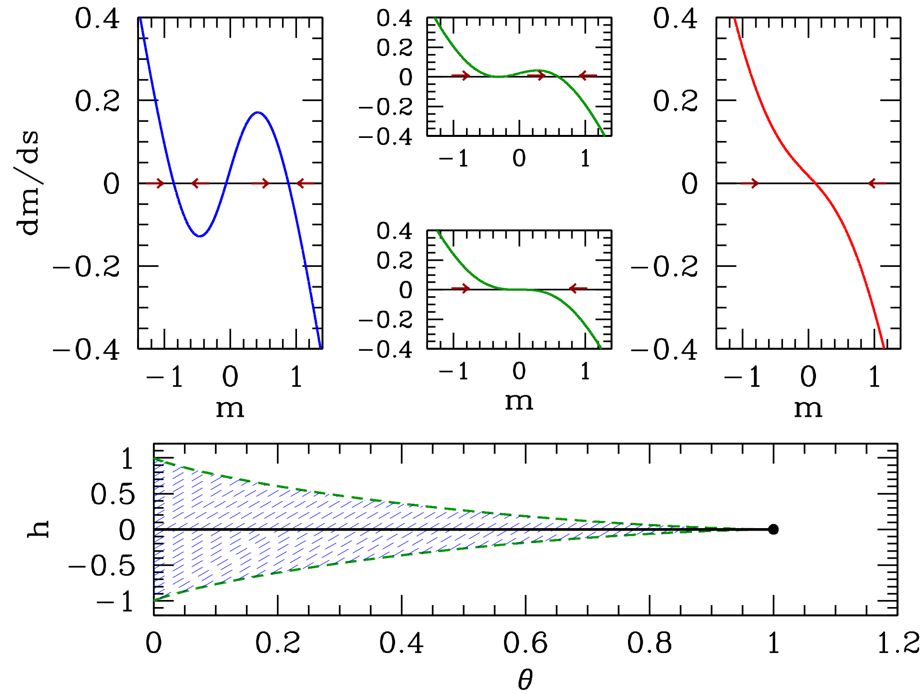

Figure 7.11: Dissipative magnetization dynamics $\dot{m} = -f'(m)$. Bottom panel shows $h^*(\theta)$ from eqn. 7.69. For (θ, h) within the blue shaded region, the free energy $f(m)$ has a global minimum plus a local minimum and a local maximum. Otherwise $f(m)$ has only a single global minimum. Top panels show an imperfect bifurcation in the magnetization dynamics at $h = 0.0215$, for which $\theta^* = 0.90$. Temperatures shown: $\theta = 0.65$ (blue), $\theta = \theta^*(h) = 0.90$ (green), and $\theta = 1.2$. The rightmost stable fixed point corresponds to the global minimum of the free energy. The bottom of the middle two upper panels shows $h = 0$, where both of the attractive fixed points and the repulsive fixed point coalesce into a single attractive fixed point (supercritical pitchfork bifurcation).

where s is a dimensionless time variable. Under these dynamics, the free energy is never increasing:

$$\frac{df}{ds} = \frac{\partial f}{\partial m}\,\frac{\partial m}{\partial s} = -\bigg(\frac{\partial f}{\partial m}\bigg)^2 \le 0\,. \tag{7.77}$$

Clearly the *fixed point* of these dynamics, where $\dot{m} = 0$, is a solution to the mean field equation $\frac{\partial f}{\partial m} = 0$.

The phase flow for the equation $\dot{m} = -f'(m)$ is shown in fig. 7.11. As we have seen, for any value of h there is a temperature θ^* below which the free energy $f(m)$ has two local minima and one local maximum. When $h = 0$ the minima are degenerate, but at finite h one of the minima is a global minimum. Thus, for $\theta < \theta^*(h)$ there are three solutions to the mean field equations. In the language of dynamical systems, under the dynamics of eqn. 7.76, minima of $f(m)$ correspond to attractive fixed points and maxima to repulsive fixed points. If $h > 0$, the rightmost of these fixed points corresponds to the global minimum of the free energy. As θ is increased, this fixed point evolves smoothly. At $\theta = \theta^*$, the (metastable) local minimum and the local maximum coalesce and annihilate in a saddle-note bifurcation. However at $h = 0$ all three fixed points coalesce at $\theta = \theta_c$ and the bifurcation is a supercritical pitchfork. As a function of t at finite h, the dynamics are said to exhibit an *imperfect bifurcation*, which is

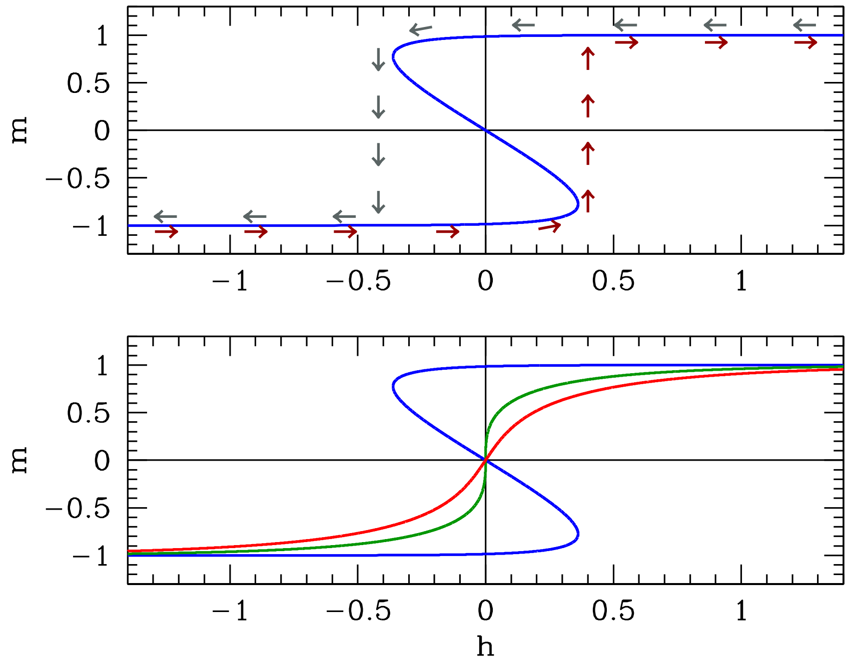

Figure 7.12: Top panel : hysteresis as a function of ramping the dimensionless magnetic field h at $\theta = 0.40$. Dark red arrows below the curve follow evolution of the magnetization on slow increase of h. Dark grey arrows above the curve follow evolution of the magnetization on slow decrease of h. Bottom panel : solution set for $m(\theta, h)$ as a function of h at temperatures $\theta = 0.40$ (blue), $\theta = \theta_c = 1.0$ (dark green), and $t = 1.25$ (red).

a deformed supercritical pitchfork.

The solution set for the mean field equation is simply expressed by inverting the $\tanh$ function to obtain $h(\theta, m)$. One readily finds

$$h(\theta, m) = \frac{\theta}{2} \ln\!\left(\frac{1+m}{1-m}\right) - m \; . \tag{7.78}$$

As we see in the bottom panel of fig. 7.12, $m(h)$ becomes multivalued for $h \in \big[-h^*(\theta) \, , \, +h^*(\theta) \big]$, where $h^*(\theta)$ is given in eqn. 7.69. Now imagine that $\theta < \theta_c$ and we slowly ramp the field h from a large negative value to a large positive value, and then slowly back down to its original value. On the time scale of the magnetization dynamics, we can regard $h(s)$ as a constant. (Remember the time variable is s here.) Thus, $m(s)$ will flow to the nearest stable fixed point. Initially the system starts with $m = -1$ and h large and negative, and there is only one fixed point, at $m^* \approx -1$. As h slowly increases, the fixed point value m^* also slowly increases. As h exceeds $-h^*(\theta)$, a saddle-node bifurcation occurs, and two new fixed points are created at positive m, one stable and one unstable. The global minimum of the free energy still lies at the fixed point with $m^* < 0$. However, when h crosses $h = 0$, the global minimum of the free energy lies at the most positive fixed point m^*. The dynamics, however, keep the system stuck in what is a metastable phase. This persists until $h = +h^*(\theta)$, at which point another saddle-note bifurcation occurs, and the attractive fixed point at $m^* < 0$ annihilates with the repulsive fixed point. The dynamics then act quickly to drive m to the only remaining fixed point. This process is depicted in the top panel of fig. 7.12. As one can see from the figure, the the system follows a stable fixed point until the fixed point disappears, even though that fixed point may not always correspond to a global minimum of the free energy. The resulting $m(h)$ curve is then not reversible as a function of time, and it possesses a characteristic shape known as a *hysteresis loop*. Etymologically, the word *hysteresis* derives from the Greek $\upsilon\sigma\tau\varepsilon\rho\eta\sigma\iota\varsigma$, which means 'lagging behind'. Systems which are hysteretic exhibit a *history-dependence* to their status, which is not uniquely determined by external conditions. Hysteresis may be exhibited with respect to changes in applied magnetic field, changes in temperature, or changes in other externally determined parameters.

7.4.5 Beyond nearest neighbors

Suppose we had started with the more general model,

$$\begin{aligned} \hat{H} &= -\sum_{i<j} J_{ij}\,\sigma_i\,\sigma_j - H\sum_i \sigma_i \\ &= -\tfrac{1}{2}\sum_{i\neq j} J_{ij}\,\sigma_i\,\sigma_j - H\sum_i \sigma_i \ , \end{aligned} \tag{7.79}$$

where J_{ij} is the coupling between spins on sites i and j. In the top equation above, each pair (ij) is counted once in the interaction term; this may be replaced by a sum over all i and j if we include a factor of $\frac{1}{2}$.[11] The resulting mean field Hamiltonian is then

$$\hat{H}_{\rm MF} = \tfrac{1}{2} N \hat{J}(0)\, m^2 - \big(H + \hat{J}(0)\, m\big)\sum_i \sigma_i \ . \tag{7.80}$$

Here, $\hat{J}(\boldsymbol{q})$ is the Fourier transform of the interaction matrix J_{ij}:[12]

$$\hat{J}(\boldsymbol{q}) = \sum_{\boldsymbol{R}} J(\boldsymbol{R})\, e^{-i\boldsymbol{q}\cdot\boldsymbol{R}} \ . \tag{7.81}$$

For nearest neighbor interactions only, one has $\hat{J}(0) = zJ$, where z is the *lattice coordination number*, *i.e.* the number of nearest neighbors of any given site. The scaled free energy is as in eqn. 7.60, with $f = F/N\hat{J}(0)$, $\theta = k_{\rm B}T/\hat{J}(0)$, and $h = H/\hat{J}(0)$. The analysis proceeds precisely as before, and we conclude $\theta_{\rm c} = 1$, *i.e.* $k_{\rm B}T_{\rm c}^{\rm MF} = \hat{J}(0)$.

7.4.6 Ising model with long-ranged forces

Consider an Ising model where $J_{ij} = J/N$ for all i and j, so that there is a very weak interaction between every pair of spins. The Hamiltonian is then

$$\hat{H} = -\frac{J}{2N}\bigg(\sum_i \sigma_i\bigg)^2 - H\sum_k \sigma_k \ . \tag{7.82}$$

[11] The self-interaction terms with $i = j$ contribute a constant to $\hat{H}$ and may be either included or excluded. However, this property only pertains to the $\sigma_i = \pm 1$ model. For higher spin versions of the Ising model, say where $S_i \in \{-1, 0, +1\}$, then S_i^2 is not constant and we should explicitly exclude the self-interaction terms.

[12] The sum in the discrete Fourier transform is over all 'direct Bravais lattice vectors' and the wavevector $\boldsymbol{q}$ may be restricted to the 'first Brillouin zone'. These terms are familiar from elementary solid state physics.

The partition function is

$$Z = \mathsf{Tr}_{\{\sigma_i\}} \exp\left[\frac{\beta J}{2N}\bigg(\sum_i \sigma_i\bigg)^2 + \beta H \sum_i \sigma_i\right] . \tag{7.83}$$

We now invoke the Gaussian integral,

$$\int\limits_{-\infty}^{\infty} \!dx\, e^{-\alpha x^2 - \beta x} = \sqrt{\frac{\pi}{\alpha}}\, e^{\beta^2/4\alpha} . \tag{7.84}$$

Thus,

$$\exp\left[\frac{\beta J}{2N}\bigg(\sum_i \sigma_i\bigg)^2\right] = \left(\frac{N\beta J}{2\pi}\right)^{1/2} \int\limits_{-\infty}^{\infty}\! dm\, e^{-\frac{1}{2}N\beta J m^2 + \beta J m \sum_i \sigma_i} , \tag{7.85}$$

and we can write the partition function as

$$\begin{aligned} Z &= \left(\frac{N\beta J}{2\pi}\right)^{1/2} \int\limits_{-\infty}^{\infty}\! dm\, e^{-\frac{1}{2}N\beta J m^2} \bigg(\sum_\sigma e^{\beta(H+Jm)\sigma}\bigg)^N \\ &= \left(\frac{N}{2\pi\theta}\right)^{1/2} \int\limits_{-\infty}^{\infty}\! dm\, e^{-NA(m)/\theta} , \end{aligned} \tag{7.86}$$

where $\theta = k_{\mathrm{B}}T/J$, $h = H/J$, and

$$A(m) = \tfrac{1}{2}m^2 - \theta \ln\left[2\cosh\left(\frac{h+m}{\theta}\right)\right] . \tag{7.87}$$

Since $N \to \infty$, we can perform the integral using the method of steepest descents. Thus, we must set

$$\frac{dA}{dm}\bigg|_{m^*} = 0 \qquad \Longrightarrow \qquad m^* = \tanh\left(\frac{m^*+h}{\theta}\right) . \tag{7.88}$$

Expanding about $m = m^*$, we write

$$A(m) = A(m^*) + \tfrac{1}{2}A''(m^*)\,(m-m^*)^2 + \tfrac{1}{6}\,A'''(m^*)\,(m-m^*)^3 + \ldots . \tag{7.89}$$

Performing the integrations, we obtain

$$\begin{aligned} Z &= \left(\frac{N}{2\pi\theta}\right)^{1/2} e^{-NA(m^*)/\theta} \int\limits_{-\infty}^{\infty}\! d\nu\, \exp\left[-\frac{NA''(m^*)}{2\theta}\, m^2 - \frac{NA'''(m^*)}{6\theta}\, m^3 + \ldots\right] \\ &= \frac{1}{\sqrt{A''(m^*)}}\, e^{-NA(m^*)/\theta} \cdot \Big\{1 + \mathcal{O}(N^{-1})\Big\} . \end{aligned} \tag{7.90}$$

The corresponding free energy per site

$$f = \frac{F}{NJ} = A(m^*) + \frac{\theta}{2N}\, \ln A''(m^*) + \mathcal{O}(N^{-2}) , \tag{7.91}$$

where m^* is the solution to the mean field equation which minimizes $A(m)$. Mean field theory is *exact* for this model!

7.5 Variational Density Matrix Method

7.5.1 The variational principle

Suppose we are given a Hamiltonian $\hat{H}$. From this we construct the free energy, F:

$$\begin{aligned} F &= E - TS \\ &= \mathrm{Tr}\,(\varrho\,\hat{H}) + k_{\mathrm{B}}T\,\mathrm{Tr}\,(\varrho\,\ln\varrho)\ . \end{aligned} \tag{7.92}$$

Here, ϱ is the *density matrix*[13]. A physical density matrix must be (i) normalized (*i.e.* $\mathrm{Tr}\,\varrho = 1$), (ii) Hermitian, and (iii) non-negative definite (*i.e.* all the eigenvalues of ϱ must be non-negative).

Our goal is to extremize the free energy subject to the various constraints on ϱ. Let us assume that ϱ is diagonal in the basis of eigenstates of $\hat{H}$, *i.e.*

$$\varrho = \sum_\gamma P_\gamma\,\big|\,\gamma\,\big\rangle\big\langle\,\gamma\,\big|\ , \tag{7.93}$$

where P_γ is the probability that the system is in state $\big|\,\gamma\,\big\rangle$. Then

$$F = \sum_\gamma E_\gamma\,P_\gamma + k_{\mathrm{B}}T\sum_\gamma P_\gamma \ln P_\gamma\ . \tag{7.94}$$

Thus, the free energy is a function of the set $\{P_\gamma\}$. We now extremize F subject to the normalization constraint. This means we form the extended function

$$F^*\big(\{P_\gamma\},\lambda\big) = F\big(\{P_\gamma\}\big) + \lambda\Big(\sum_\gamma P_\gamma - 1\Big)\ , \tag{7.95}$$

and then freely extremize over both the probabilities $\{P_\gamma\}$ as well as the Lagrange multiplier λ. This yields the Boltzmann distribution,

$$P^{\mathrm{eq}}_\gamma = \frac{1}{Z}\,\exp(-E_\gamma/k_{\mathrm{B}}T)\ , \tag{7.96}$$

where $Z = \sum_\gamma e^{-E_\gamma/k_{\mathrm{B}}T} = \mathrm{Tr}\,e^{-\hat{H}/k_{\mathrm{B}}T}$ is the canonical partition function, which is related to λ through

$$\lambda = k_{\mathrm{B}}T\,(\ln Z - 1)\ . \tag{7.97}$$

Note that the Boltzmann weights are, appropriately, all positive.

If the spectrum of $\hat{H}$ is bounded from below, our extremum should in fact yield a minimum for the free energy F. Furthermore, since we have freely minimized over all the probabilities, subject to the single normalization constraint, *any distribution* $\{P_\gamma\}$ *other than the equilibrium one must yield a greater value of* F.

Alas, the Boltzmann distribution, while exact, is often intractable to evaluate. For one-dimensional systems, there are general methods such as the transfer matrix approach which do permit an exact

[13] How do we take the logarithm of a matrix? The rule is this: $A = \ln B$ if $B = \exp(A)$. The exponential of a matrix may be evaluated via its Taylor expansion.

evaluation of the free energy. However, beyond one dimension the situation is in general hopeless. A family of solvable ("integrable") models exists in two dimensions, but their solutions require specialized techniques and are extremely difficult. The idea behind the variational density matrix approximation is to construct a tractable *trial* density matrix ϱ which depends on a set of variational parameters $\{x_\alpha\}$, and to minimize with respect to this (finite) set.

7.5.2 Variational density matrix for the Ising model

Consider once again the Ising model Hamiltonian,

$$\hat{H} = -\sum_{i<j} J_{ij}\,\sigma_i\,\sigma_j - H\sum_i \sigma_i\ . \tag{7.98}$$

The states of the system $\big|\,\gamma\,\big\rangle$ may be labeled by the values of the spin variables: $\big|\,\gamma\,\big\rangle \longleftrightarrow \big|\,\sigma_1,\sigma_2,\ldots\,\big\rangle$. We assume the density matrix is diagonal in this basis, *i.e.*

$$\varrho_N\big(\gamma\big|\gamma'\big) \equiv \varrho(\gamma)\,\delta_{\gamma,\gamma'}\ , \tag{7.99}$$

where

$$\delta_{\gamma,\gamma'} = \prod_i \delta_{\sigma_i,\sigma_i'}\ . \tag{7.100}$$

Indeed, this is the case for the exact density matrix, which is to say the Boltzmann weight,

$$\varrho_N(\sigma_1,\sigma_2,\ldots) = \frac{1}{Z}\,e^{-\beta \hat{H}(\sigma_1,\ldots,\sigma_N)}\ . \tag{7.101}$$

We now write a *trial density matrix* which is a product over contributions from independent single sites:

$$\varrho_N(\sigma_1,\sigma_2,\ldots) = \prod_i \varrho(\sigma_i)\ , \tag{7.102}$$

where

$$\varrho(\sigma) = \bigg(\frac{1+m}{2}\bigg)\,\delta_{\sigma,1} + \bigg(\frac{1-m}{2}\bigg)\,\delta_{\sigma,-1}\ . \tag{7.103}$$

Note that we've changed our notation slightly. We are denoting by $\varrho(\sigma)$ the corresponding diagonal element of the matrix

$$\varrho = \begin{pmatrix} \frac{1+m}{2} & 0 \\ 0 & \frac{1-m}{2} \end{pmatrix}\ , \tag{7.104}$$

and the full density matrix is a tensor product over the single site matrices:

$$\varrho_N = \varrho \otimes \varrho \otimes \cdots \otimes \varrho\ . \tag{7.105}$$

Note that ϱ and hence ϱ_N are appropriately normalized. The variational parameter here is m, which, if ρ is to be non-negative definite, must satisfy $-1 \le m \le 1$. The quantity m has the physical interpretation of the average spin on any given site, since

$$\langle \sigma_i \rangle = \sum_\sigma \varrho(\sigma)\,\sigma = m. \tag{7.106}$$

We may now evaluate the average energy:

$$\begin{aligned} E = \mathsf{Tr}\,(\varrho_N \hat{H}) &= -\sum_{i<j} J_{ij}\, m^2 - H \sum_i m \\ &= -\tfrac{1}{2} N \hat{J}(0)\, m^2 - NHm\,, \end{aligned} \tag{7.107}$$

where once again $\hat{J}(0)$ is the discrete Fourier transform of $J(\boldsymbol{R})$ at wavevector $\boldsymbol{q} = 0$. The entropy is given by

$$\begin{aligned} S &= -k_{\rm B}\, \mathsf{Tr}\,(\varrho_N \ln \varrho_N) = -N k_{\rm B}\, \mathsf{Tr}\,(\varrho \ln \varrho) \\ &= -N k_{\rm B} \bigg\{ \Big(\frac{1+m}{2}\Big) \ln \Big(\frac{1+m}{2}\Big) + \Big(\frac{1-m}{2}\Big) \ln \Big(\frac{1-m}{2}\Big) \bigg\}\,. \end{aligned} \tag{7.108}$$

We now define the dimensionless free energy per site: $f \equiv F/N\hat{J}(0)$. We have

$$f(m,h,\theta) = -\tfrac{1}{2}\, m^2 - hm + \theta \left\{ \Big(\frac{1+m}{2}\Big) \ln \Big(\frac{1+m}{2}\Big) + \Big(\frac{1-m}{2}\Big) \ln \Big(\frac{1-m}{2}\Big) \right\}, \tag{7.109}$$

where $\theta \equiv k_{\rm B} T/\hat{J}(0)$ is the dimensionless temperature, and $h \equiv H/\hat{J}(0)$ the dimensionless magnetic field, as before. We extremize $f(m)$ by setting

$$\frac{\partial f}{\partial m} = 0 = -m - h + \frac{\theta}{2} \ln \Big(\frac{1+m}{1-m}\Big)\,. \tag{7.110}$$

Solving for m, we obtain

$$m = \tanh\left(\frac{m+h}{\theta}\right), \tag{7.111}$$

which is precisely what we found in eqn. 7.61.

Note that the optimal value of m indeed satisfies the requirement $|m| \le 1$ of non-negative probability. This nonlinear equation may be solved graphically. For $h = 0$, the unmagnetized solution $m = 0$ always applies. However, for $\theta < 1$ there are two additional solutions at $m = \pm m_{\rm A}(\theta)$, with $m_{\rm A}(\theta) = \sqrt{3(1-\theta)} + \mathcal{O}\big((1-\theta)^{3/2}\big)$ for t close to (but less than) one. These solutions, which are related by the $\mathbb{Z}_2$ symmetry of the $h = 0$ model, are in fact the low energy solutions. This is shown clearly in figure 7.13, where the variational free energy $f(m,t)$ is plotted as a function of m for a range of temperatures interpolating between 'high' and 'low' values. At the *critical temperature* $\theta_{\rm c} = 1$, the lowest energy state changes from being unmagnetized (high temperature) to magnetized (low temperature).

For $h > 0$, there is no longer a $\mathbb{Z}_2$ symmetry (*i.e.* $\sigma_i \to -\sigma_i \ \forall\ i$). The high temperature solution now has $m > 0$ (or $m < 0$ if $h < 0$), and this smoothly varies as t is lowered, approaching the completely polarized limit $m = 1$ as $\theta \to 0$. At very high temperatures, the argument of the $\tanh$ function is small, and we may approximate $\tanh(x) \simeq x$, in which case

$$m(h,\theta) = \frac{h}{\theta - \theta_{\rm c}}\,. \tag{7.112}$$

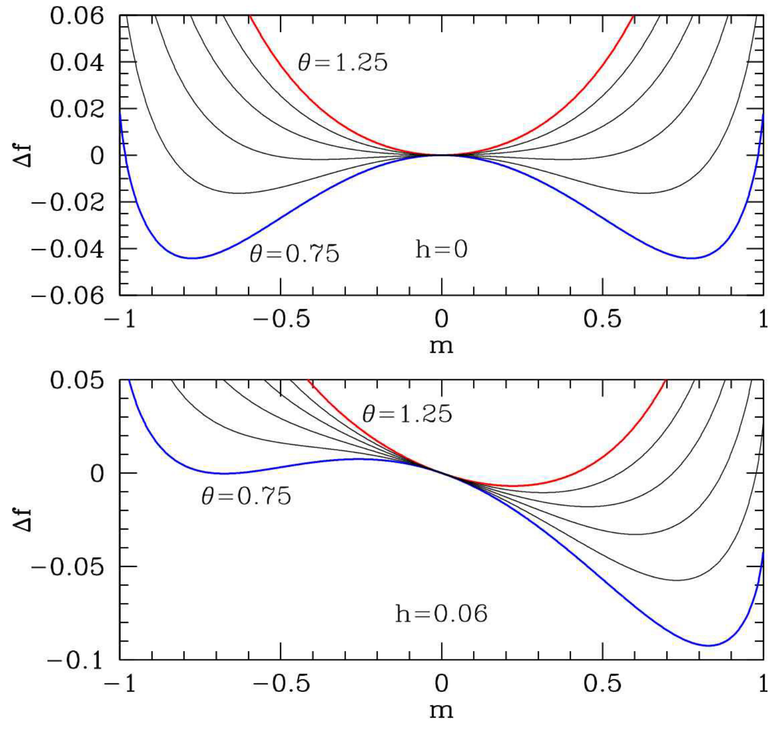

Figure 7.13: Variational field free energy $\Delta f = f(m,h,\theta) + \theta \, \ln 2$ *versus* magnetization m at six equally spaced temperatures interpolating between 'high' ($\theta = 1.25$, red) and 'low' ($\theta = 0.75$, blue) values. Top panel: $h = 0$. Bottom panel: $h = 0.06$.

This is called the *Curie-Weiss law.* One can infer $\theta_{\rm c}$ from the high temperature susceptibility $\chi(\theta) = (\partial m/\partial h)_{h=0}$ by plotting χ^{-1} *versus* θ and extrapolating to obtain the θ-intercept. In our case, $\chi(\theta) = (\theta - \theta_{\rm c})^{-1}$. For low θ and weak h, there are two inequivalent minima in the free energy.

When m is small, it is appropriate to expand $f(m,h,\theta)$, obtaining

$$f(m,h,\theta) = -\theta \, \ln 2 - hm + \tfrac{1}{2}\,(\theta - 1)\, m^2 + \tfrac{\theta}{12}\, m^4 + \tfrac{\theta}{30}\, m^6 + \tfrac{\theta}{56}\, m^8 + \ldots \, . \tag{7.113}$$

This is known as the *Landau expansion* of the free energy in terms of the *order parameter* m. An order parameter is a thermodynamic variable ϕ which distinguishes ordered and disordered phases. Typically $\phi = 0$ in the disordered (high temperature) phase, and $\phi \neq 0$ in the ordered (low temperature) phase. When the order sets in continuously, *i.e.* when ϕ is continuous across $\theta_{\rm c}$, the phase transition is said to be *second order.* When ϕ changes abruptly, the transition is *first order.* It is also quite commonplace to observe phase transitions between two ordered states. For example, a crystal, which is an ordered state, may change its lattice structure, say from a high temperature tetragonal phase to a low temperature orthorhombic phase. When the high T phase possesses the same symmetries as the low T phase, as in the tetragonal-to-orthorhombic example, the transition may be second order. When the two symmetries are completely unrelated, for example in a hexagonal-to-tetragonal transition, or in a transition between a ferromagnet and an antiferromagnet, the transition is in general first order.

Throughout this discussion, we have assumed that the interactions J_{ij} are predominantly *ferromagnetic*, *i.e.* $J_{ij} > 0$, so that all the spins prefer to align. When $J_{ij} < 0$, the interaction is said to be *antiferro-*

magnetic and prefers anti-alignment of the spins (*i.e.* $\sigma_i\,\sigma_j = -1$). Clearly not every pair of spins can be anti-aligned – there are two possible spin states and a thermodynamically extensive number of spins. But on the square lattice, for example, if the only interactions J_{ij} are between nearest neighbors and the interactions are antiferromagnetic, then the lowest energy configuration ($T = 0$ ground state) will be one in which spins on opposite sublattices are anti-aligned. The square lattice is *bipartite* – it breaks up into two interpenetrating sublattices A and B (which are themselves square lattices, rotated by 45° with respect to the original, and with a larger lattice constant by a factor of $\sqrt{2}$), such that any site in A has nearest neighbors in B, and *vice versa*. The honeycomb lattice is another example of a bipartite lattice. So is the simple cubic lattice. The triangular lattice, however, is not bipartite (it is *tripartite*). Consequently, with nearest neighbor antiferromagnetic interactions, the triangular lattice Ising model is highly *frustrated*. The moral of the story is this: antiferromagnetic interactions can give rise to complicated magnetic ordering, and, when frustrated by the lattice geometry, may have finite specific entropy even at $T = 0$.

7.5.3 Mean Field Theory of the Potts Model

The Hamiltonian for the Potts model is

$$\hat{H} = -\sum_{i<j} J_{ij}\,\delta_{\sigma_i,\sigma_j} - H\sum_i \delta_{\sigma_i,1}\ . \tag{7.114}$$

Here, $\sigma_i \in \{1,\ldots,q\}$, with integer q. This is the so-called 'q-state Potts model'. The quantity H is analogous to an external magnetic field, and preferentially aligns (for $H > 0$) the local spins in the $\sigma = 1$ direction. We will assume $H \geq 0$.

The q-component set is conveniently taken to be the integers from 1 to q, but it could be anything, such as

$$\sigma_i \in \{\text{tomato, penny, ostrich, Grateful Dead ticket from 1987},\ \ldots\}\ . \tag{7.115}$$

The interaction energy is $-J_{ij}$ if sites i and j contain the same object (q possibilities), and 0 if i and j contain different objects ($q^2 - q$ possibilities).

The two-state Potts model is equivalent to the Ising model. Let the allowed values of σ be ± 1. Then the quantity

$$\delta_{\sigma,\sigma'} = \tfrac{1}{2} + \tfrac{1}{2}\,\sigma\sigma' \tag{7.116}$$

equals 1 if $\sigma = \sigma'$, and is zero otherwise. The three-state Potts model cannot be written as a simple three-state Ising model, *i.e.* one with a bilinear interaction $\sigma\,\sigma'$ where $\sigma \in \{-1, 0, +1\}$. However, it is straightforward to verify the identity

$$\delta_{\sigma,\sigma'} = 1 + \tfrac{1}{2}\,\sigma\sigma' + \tfrac{3}{2}\,\sigma^2\sigma'^2 - (\sigma^2 + \sigma'^2)\ . \tag{7.117}$$

Thus, the $q = 3$-state Potts model is equivalent to a $S = 1$ (three-state) Ising model which includes both bilinear ($\sigma\sigma'$) and biquadratic ($\sigma^2\sigma'^2$) interactions, as well as a local field term which couples to the square of the spin, σ^2. In general one can find such correspondences for higher q Potts models, but, as should be expected, the interactions become increasingly complex, with bi-cubic, bi-quartic, bi-quintic, *etc.* terms. Such a formulation, however, obscures the beautiful S_q symmetry inherent in the model, where S_q is the permutation group on q symbols, which has $q!$ elements.

Getting back to the mean field theory, we write the single site variational density matrix ϱ as a diagonal matrix with entries

$$\varrho(\sigma) = x\,\delta_{\sigma,1} + \left(\frac{1-x}{q-1}\right)\left(1-\delta_{\sigma,1}\right) , \tag{7.118}$$

with $\varrho_N(\sigma_1,\ldots,\sigma_N) = \varrho(\sigma_1)\cdots\varrho(\sigma_N)$. Note that $\mathsf{Tr}\,(\varrho) = 1$. The variational parameter is x. When $x = q^{-1}$, all states are equally probable. But for $x > q^{-1}$, the state $\sigma = 1$ is preferred, and the other $(q-1)$ states have identical but smaller probabilities. It is a simple matter to compute the energy and entropy:

$$\begin{aligned} E &= \mathsf{Tr}\,(\varrho_N \hat{H}) = -\tfrac{1}{2} N \hat{J}(0) \left\{ x^2 + \frac{(1-x)^2}{q-1} \right\} - NHx \\ S &= -k_{\rm B}\,\mathsf{Tr}\,(\varrho_N \ln \varrho_N) = -Nk_{\rm B} \left\{ x\ln x + (1-x)\ln\left(\frac{1-x}{q-1}\right) \right\} . \end{aligned} \tag{7.119}$$

The dimensionless free energy per site is then

$$f(x,\theta,h) = -\tfrac{1}{2}\left\{ x^2 + \frac{(1-x)^2}{q-1} \right\} + \theta\left\{ x\ln x + (1-x)\ln\left(\frac{1-x}{q-1}\right) \right\} - hx , \tag{7.120}$$

where $h = H/\hat{J}(0)$. We now extremize with respect to x to obtain the mean field equation,

$$\frac{\partial f}{\partial x} = 0 = -x + \frac{1-x}{q-1} + \theta\,\ln x - \theta\,\ln\left(\frac{1-x}{q-1}\right) - h . \tag{7.121}$$

Note that for $h = 0$, $x = q^{-1}$ is a solution, corresponding to a disordered state in which all states are equally probable. At high temperatures, for small h, we expect $x - q^{-1} \propto h$. Indeed, using `Mathematica` one can set

$$x \equiv q^{-1} + s , \tag{7.122}$$

and expand the mean field equation in powers of s. One obtains

$$h = \frac{q\,(q\theta-1)}{q-1}\,s + \frac{q^3\,(q-2)\,\theta}{2\,(q-1)^2}\,s^2 + \mathcal{O}(s^3) . \tag{7.123}$$

For weak fields, $|h| \ll 1$, and we have

$$s(\theta) = \frac{(q-1)\,h}{q\,(q\theta-1)} + \mathcal{O}(h^2) , \tag{7.124}$$

which again is of the Curie-Weiss form. The difference $s = x - q^{-1}$ is the order parameter for the transition.

Finally, one can expand the free energy in powers of s, obtaining the Landau expansion,

$$\begin{aligned} f(s,\theta,h) = -\frac{2h+1}{2q} - \theta\ln q - hs + \frac{q\,(q\theta-1)}{2\,(q-1)}\,s^2 - \frac{(q-2)\,q^3\,\theta}{6\,(q-1)^2}\,s^3 \\ + \frac{q^3\theta}{12}\Big[1 + (q-1)^{-3}\Big]s^4 - \frac{q^4\theta}{20}\Big[1-(q-1)^{-4}\Big]s^5 \\ + \frac{q^5\theta}{30}\Big[1+(q-1)^{-5}\Big]s^6 + \ldots \end{aligned} \tag{7.125}$$

Note that, for $q = 2$, the coefficients of s^3, s^5, and higher order odd powers of s vanish in the Landau expansion. This is consistent with what we found for the Ising model, and is related to the $\mathbb{Z}_2$ symmetry of that model. For $q > 3$, there is a cubic term in the mean field free energy, and thus we generically expect a first order transition, as we shall see below when we discuss Landau theory.

7.5.4 Mean Field Theory of the XY Model

Consider the so-called XY model, in which each site contains a continuous planar spin, represented by an angular variable $\phi_i \in [-\pi, \pi]$:

$$\hat{H} = -\frac{1}{2}\sum_{i\neq j} J_{ij}\cos\big(\phi_i - \phi_j\big) - H\sum_i \cos\phi_i \ . \tag{7.126}$$

We write the (diagonal elements of the) full density matrix once again as a product:

$$\varrho_N(\phi_1, \phi_2, \ldots) = \prod_i \varrho(\phi_i) \ . \tag{7.127}$$

Our goal will be to extremize the free energy with respect to the *function* $\varrho(\phi)$. To this end, we compute

$$E = \mathsf{Tr}\,(\varrho_N\,\hat{H}) = -\tfrac{1}{2}N\hat{J}(0)\,\Big|\mathsf{Tr}\,\big(\varrho\,e^{i\phi}\big)\Big|^2 - NH\,\mathsf{Tr}\,\big(\varrho\,\cos\phi\big) \ . \tag{7.128}$$

The entropy is

$$S = -Nk_{\mathrm{B}}\,\mathsf{Tr}\,(\varrho\,\ln\varrho) \ . \tag{7.129}$$

Note that for any function $A(\phi)$, we have[14]

$$\mathsf{Tr}\ \big(\varrho\,A\big) \equiv \int\limits_{-\pi}^{\pi}\frac{d\phi}{2\pi}\,\varrho(\phi)\,A(\phi) \ . \tag{7.130}$$

We now extremize the *functional* $F\big[\varrho(\phi)\big] = E - TS$ with respect to $\varrho(\phi)$, under the condition that $\mathsf{Tr}\ \varrho = 1$. We therefore use Lagrange's method of undetermined multipliers, writing

$$F^* = F - Nk_{\mathrm{B}}T\,\lambda\,\Big(\,\mathsf{Tr}\,\varrho - 1\Big) \ . \tag{7.131}$$

Note that F^* is a *function* of the Lagrange multiplier λ and a *functional* of the density matrix $\varrho(\phi)$. The prefactor $Nk_{\mathrm{B}}T$ which multiplies λ is of no mathematical consequence – we could always redefine the multiplier to be $\lambda' \equiv Nk_{\mathrm{B}}T\lambda$. It is present only to maintain homogeneity and proper dimensionality of F^* with λ itself dimensionless and of order N^0. We now have

$$\begin{aligned}\frac{\delta F^*}{\delta\varrho(\phi)} = \frac{\delta}{\delta\varrho(\phi)}\bigg\{ &-\tfrac{1}{2}N\hat{J}(0)\,\Big|\mathsf{Tr}\big(\varrho\,e^{i\phi}\big)\Big|^2 - NH\,\mathsf{Tr}\big(\varrho\,\cos\phi\big)\\ &+ Nk_{\mathrm{B}}T\ \mathsf{Tr}\,\big(\varrho\,\ln\varrho\big) - Nk_{\mathrm{B}}T\,\lambda\,\Big(\,\mathsf{Tr}\,\varrho - 1\Big)\bigg\} \ .\end{aligned} \tag{7.132}$$

[14] The denominator of 2π in the measure is not necessary, and in fact it is even slightly cumbersome. It divides out whenever we take a ratio to compute a thermodynamic average. I introduce this factor to preserve the relation $\mathsf{Tr}\ 1 = 1$. I personally find unnormalized traces to be profoundly unsettling on purely aesthetic grounds.

To this end, we note that

$$\frac{\delta}{\delta\varrho(\phi)}\,\mathsf{Tr}\,(\varrho\,A)=\frac{\delta}{\delta\varrho(\phi)}\int\limits_{-\pi}^{\pi}\frac{d\phi}{2\pi}\,\varrho(\phi)\,A(\phi)=\frac{1}{2\pi}\,A(\phi)\ . \tag{7.133}$$

Thus, we have

$$\begin{aligned}\frac{\delta\tilde{F}}{\delta\varrho(\phi)}=-\tfrac{1}{2}N\hat{J}(0)\cdot\frac{1}{2\pi}\bigg[\mathop{\mathsf{Tr}}_{\phi'}\big(\varrho\,e^{i\phi'}\big)\,e^{-i\phi}+\mathop{\mathsf{Tr}}_{\phi'}\big(\varrho\,e^{-i\phi'}\big)\,e^{i\phi}\bigg]-NH\cdot\frac{\cos\phi}{2\pi}\\ +Nk_{\mathrm{B}}T\cdot\frac{1}{2\pi}\Big[\ln\varrho(\phi)+1\Big]-Nk_{\mathrm{B}}T\cdot\frac{\lambda}{2\pi}\ .\end{aligned} \tag{7.134}$$

Now let us define

$$\mathop{\mathsf{Tr}}_{\phi}\big(\varrho\,e^{i\phi}\big)=\int\limits_{-\pi}^{\pi}\frac{d\phi}{2\pi}\,\varrho(\phi)\,e^{i\phi}\equiv m\,e^{i\phi_0}\ . \tag{7.135}$$

We then have

$$\ln\varrho(\phi)=\frac{\hat{J}(0)}{k_{\mathrm{B}}T}\,m\,\cos(\phi-\phi_0)+\frac{H}{k_{\mathrm{B}}T}\,\cos\phi+\lambda-1. \tag{7.136}$$

Clearly the free energy will be reduced if $\phi_0=0$ so that the mean field is maximal and aligns with the external field, which prefers $\phi=0$. Thus, we conclude

$$\varrho(\phi)=\mathcal{C}\,\exp\!\bigg(\frac{H_{\mathrm{eff}}}{k_{\mathrm{B}}T}\,\cos\phi\bigg)\ , \tag{7.137}$$

where

$$H_{\mathrm{eff}}=\hat{J}(0)\,m+H \tag{7.138}$$

and $\mathcal{C}=e^{\lambda-1}$. The value of λ is then determined by invoking the constraint,

$$\mathsf{Tr}\,\varrho=1=\mathcal{C}\int\limits_{-\pi}^{\pi}\frac{d\phi}{2\pi}\,\exp\!\bigg(\frac{H_{\mathrm{eff}}}{k_{\mathrm{B}}T}\,\cos\phi\bigg)=\mathcal{C}\,I_0(H_{\mathrm{eff}}/k_{\mathrm{B}}T)\ , \tag{7.139}$$

where $I_0(z)$ is the Bessel function. We are free to define $\varepsilon\equiv H_{\mathrm{eff}}/k_{\mathrm{B}}T$, and treat ε as our single variational parameter. We then have the normalized single site density matrix

$$\varrho(\phi)=\frac{\exp(\varepsilon\cos\phi)}{\int_{-\pi}^{\pi}\frac{d\phi'}{2\pi}\,\exp(\varepsilon\cos\phi')}=\frac{\exp(\varepsilon\cos\phi)}{I_0(\varepsilon)}\ . \tag{7.140}$$

We next compute the following averages:

$$\big\langle\,e^{\pm i\phi}\,\big\rangle=\int\limits_{-\pi}^{\pi}\frac{d\phi}{2\pi}\,\varrho(\phi)\,e^{\pm i\phi}=\frac{I_1(\varepsilon)}{I_0(\varepsilon)} \tag{7.141}$$

$$\big\langle\cos(\phi-\phi')\big\rangle=\mathsf{Re}\,\big\langle e^{i\phi}\,e^{-i\phi'}\big\rangle=\bigg(\frac{I_1(\varepsilon)}{I_0(\varepsilon)}\bigg)^2\ , \tag{7.142}$$

as well as

$$\mathsf{Tr}\,(\varrho\,\ln\varrho) = \int\limits_{-\pi}^{\pi} \frac{d\phi}{2\pi}\,\frac{e^{\varepsilon\cos\phi}}{I_0(\varepsilon)}\,\Big\{\varepsilon\cos\phi - \ln I_0(\varepsilon)\Big\} = \varepsilon\,\frac{I_1(\varepsilon)}{I_0(\varepsilon)} - \ln I_0(\varepsilon)\ . \tag{7.143}$$

The dimensionless free energy per site is therefore

$$f(\varepsilon,h,\theta) = -\frac{1}{2}\bigg(\frac{I_1(\varepsilon)}{I_0(\varepsilon)}\bigg)^2 + (\theta\varepsilon - h)\,\frac{I_1(\varepsilon)}{I_0(\varepsilon)} - \theta\,\ln I_0(\varepsilon)\ , \tag{7.144}$$

with $\theta = k_{\rm B}T/\hat{J}(0)$ and $h = H/\hat{J}(0)$ and $f = F/N\hat{J}(0)$ as before. Note that the mean field equation is $m = \theta\varepsilon - h = \big\langle\, e^{i\phi}\,\big\rangle$, *i.e.*

$$\theta\varepsilon - h = \frac{I_1(\varepsilon)}{I_0(\varepsilon)} \quad . \tag{7.145}$$

For small ε, we may expand the Bessel functions, using

$$I_\nu(z) = (\tfrac{1}{2}z)^\nu \sum_{k=0}^\infty \frac{(\frac{1}{4}z^2)^k}{k!\,\Gamma(k+\nu+1)}\ , \tag{7.146}$$

to obtain

$$f(\varepsilon,h,\theta) = \tfrac{1}{4}\left(\theta-\tfrac{1}{2}\right)\varepsilon^2 + \tfrac{1}{64}\left(2-3\theta\right)\varepsilon^4 - \tfrac{1}{2}\,h\varepsilon + \tfrac{1}{16}\,h\varepsilon^3 + \ldots\ . \tag{7.147}$$

This predicts a second order phase transition at $\theta_{\rm c} = \frac{1}{2}$.[15] Note also the Curie-Weiss form of the susceptibility at high θ:

$$\frac{\partial f}{\partial\varepsilon} = 0 \quad\Longrightarrow\quad \varepsilon = \frac{h}{\theta - \theta_{\rm c}} + \ldots\ . \tag{7.148}$$

7.5.5 XY model via neglect of fluctuations method

Consider again the Hamiltonian of eqn. 7.126. Define $z_i \equiv \exp(i\phi_i)$ and write

$$z_i = w + \delta z_i \quad , \tag{7.149}$$

where $w \equiv \langle z_i \rangle$ and $\delta z_i \equiv z_i - w$. Of course we also have the complex conjugate relations $z_i^* = w^* + \delta z_i^*$ and $w^* = \langle z_i^* \rangle$. Writing $\cos(\phi_i - \phi_j) = \mathsf{Re}\,(z_i^* z_j)$, by neglecting the terms proportional to $\delta z_i^*\,\delta z_j$ in $\hat{H}$ we arrive at the mean field Hamiltonian,

$$\hat{H}^{\rm MF} = \tfrac{1}{2}N\hat{J}(0)\,|w|^2 - \tfrac{1}{2}\hat{J}(0)\,|w|\sum_i\left(w^* z_i + w z_i^*\right) - \tfrac{1}{2}H\sum_i\left(z_i^* + z_i\right) \tag{7.150}$$

It is clear that the free energy will be minimized if the mean field w breaks the $\mathsf{O}(2)$ symmetry in the same direction as the external field H, which means $w \in \mathbb{R}$ and

$$\hat{H}^{\rm MF} = \tfrac{1}{2}N\hat{J}(0)\,|w|^2 - \left(H + \hat{J}(0)\,|w|\right)\sum_i \cos\phi_i \quad . \tag{7.151}$$

[15] Note that the coefficient of the quartic term in ε is negative for $\theta > \frac{2}{3}$. At $\theta = \theta_{\rm c} = \frac{1}{2}$, the coefficient is positive, but for larger θ one must include higher order terms in the Landau expansion.

The dimensionless free energy per site is then

$$f = \tfrac{1}{2}|w|^2 - \theta \ln I_0\bigg(\frac{h+|w|}{\theta}\bigg) \quad . \tag{7.152}$$

Differentiating with respect to $|w|$, one obtains

$$|w| \equiv m = \frac{I_1\big(\frac{h+m}{\theta}\big)}{I_0\big(\frac{h+m}{\theta}\big)} \quad , \tag{7.153}$$

which is the same equation as eqn. 7.145. The two mean field theories yield the same results in every detail (see §7.10).

7.6 Landau Theory of Phase Transitions

Landau's theory of phase transitions is based on an expansion of the free energy of a thermodynamic system in terms of an *order parameter*, which is nonzero in an ordered phase and zero in a disordered phase. For example, the magnetization M of a ferromagnet in zero external field but at finite temperature typically vanishes for temperatures $T > T_c$, where T_c is the *critical temperature*, also called the *Curie temperature* in a ferromagnet. A low order expansion in powers of the order parameter is appropriate sufficiently close to the phase transition, *i.e.* at temperatures such that the order parameter, if nonzero, is still small.

The simplest example is the quartic free energy,

$$f(m, h=0, \theta) = f_0 + \tfrac{1}{2}am^2 + \tfrac{1}{4}bm^4 \ , \tag{7.154}$$

where $f_0 = f_0(\theta)$, $a = a(\theta)$, and $b = b(\theta)$. Here, θ is a dimensionless measure of the temperature. If for example the local exchange energy in the ferromagnet is J, then we might define $\theta = k_B T/zJ$, as before. Let us assume $b > 0$, which is necessary if the free energy is to be bounded from below[16]. The equation of state ,

$$\frac{\partial f}{\partial m} = 0 = am + bm^3 \ , \tag{7.155}$$

has three solutions in the complex m plane: (i) $m = 0$, (ii) $m = \sqrt{-a/b}$, and (iii) $m = -\sqrt{-a/b}$. The latter two solutions lie along the (physical) real axis if $a < 0$. We assume that there exists a unique temperature θ_c where $a(\theta_c) = 0$. Minimizing f, we find

$$\begin{aligned} \theta < \theta_c \quad &: \quad f(\theta) = f_0 - \frac{a^2}{4b} \\ \theta > \theta_c \quad &: \quad f(\theta) = f_0 \ . \end{aligned} \tag{7.156}$$

The free energy is continuous at θ_c since $a(\theta_c) = 0$. The specific heat, however, is discontinuous across the transition, with

$$c\big(\theta_c^+\big) - c\big(\theta_c^-\big) = -\theta_c \, \frac{\partial^2}{\partial\theta^2}\bigg|_{\theta=\theta_c} \bigg(\frac{a^2}{4b}\bigg) = -\frac{\theta_c \, \big[a'(\theta_c)\big]^2}{2b(\theta_c)} \ . \tag{7.157}$$

[16]It is always the case that f is bounded from below, on physical grounds. Were b negative, we'd have to consider higher order terms in the Landau expansion.

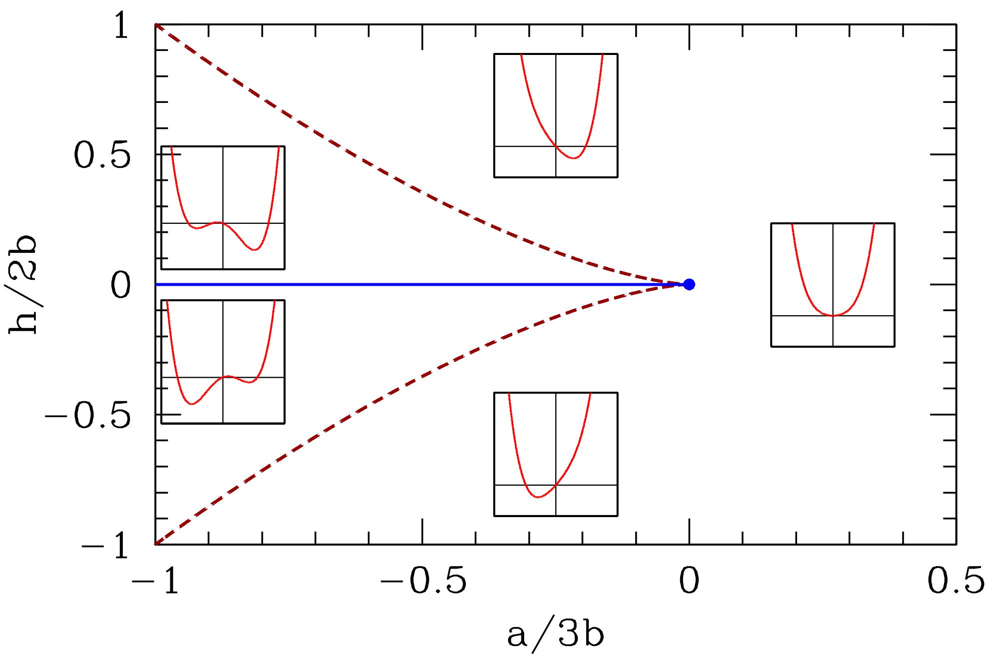

Figure 7.14: Phase diagram for the quartic Landau free energy $f = f_0 + \frac{1}{2}am^2 + \frac{1}{4}bm^4 - hm$, with $b > 0$. There is a first order line at $h = 0$ extending from $a = -\infty$ and terminating in a critical point at $a = 0$. For $|h| < h^*(a)$ (dashed red line) there are three solutions to the mean field equation, corresponding to one global minimum, one local minimum, and one local maximum. Insets show behavior of the free energy $f(m)$.

The presence of a magnetic field h breaks the $\mathbb{Z}_2$ symmetry of $m \to -m$. The free energy becomes

$$f(m, h, \theta) = f_0 + \tfrac{1}{2}am^2 + \tfrac{1}{4}bm^4 - hm \;, \tag{7.158}$$

and the mean field equation is

$$bm^3 + am - h = 0 \;. \tag{7.159}$$

This is a cubic equation for m with real coefficients, and as such it can either have three real solutions or one real solution and two complex solutions related by complex conjugation. Clearly we must have $a < 0$ in order to have three real roots, since $bm^3 + am$ is monotonically increasing otherwise. The boundary between these two classes of solution sets occurs when two roots coincide, which means $f''(m) = 0$ as well as $f'(m) = 0$. Simultaneously solving these two equations, we find

$$h^*(a) = \pm \frac{2}{3^{3/2}} \, \frac{(-a)^{3/2}}{b^{1/2}} \;, \tag{7.160}$$

or, equivalently,

$$a^*(h) = -\frac{3}{2^{2/3}} \, b^{1/3} \, |h|^{2/3}. \tag{7.161}$$

If, for fixed h, we have $a < a^*(h)$, then there will be three real solutions to the mean field equation $f'(m) = 0$, one of which is a global minimum (the one for which $m \cdot h > 0$). For $a > a^*(h)$ there is only a single global minimum, at which m also has the same sign as h. If we solve the mean field equation perturbatively in h/a, we find

$$
\begin{aligned}
m(a,h) &= \frac{h}{a} - \frac{b}{a^4}\,h^3 + \mathcal{O}(h^5) && (a>0) \\
&= \pm\frac{|a|^{1/2}}{b^{1/2}} + \frac{h}{2\,|a|} \pm \frac{3\,b^{1/2}}{8\,|a|^{5/2}}\,h^2 + \mathcal{O}(h^3) && (a<0)\ .
\end{aligned}
\tag{7.162}
$$

7.6.1 Cubic terms in Landau theory : first order transitions

Next, consider a free energy with a cubic term,

$$
f = f_0 + \tfrac{1}{2}am^2 - \tfrac{1}{3}ym^3 + \tfrac{1}{4}bm^4\ , \tag{7.163}
$$

with $b>0$ for stability. Without loss of generality, we may assume $y>0$ (else send $m \to -m$). Note that we no longer have $m \to -m$ (*i.e.* $\mathbb{Z}_2$) symmetry. The cubic term favors positive m. What is the phase diagram in the (a,y) plane?

Extremizing the free energy with respect to m, we obtain

$$
\frac{\partial f}{\partial m} = 0 = am - ym^2 + bm^3\ . \tag{7.164}
$$

This cubic equation factorizes into a linear and quadratic piece, and hence may be solved simply. The three solutions are $m=0$ and

$$
m = m_\pm \equiv \frac{y}{2b} \pm \sqrt{\left(\frac{y}{2b}\right)^2 - \frac{a}{b}}\ . \tag{7.165}
$$

We now see that for $y^2 < 4ab$ there is only one real solution, at $m=0$, while for $y^2 > 4ab$ there are three real solutions. Which solution has lowest free energy? To find out, we compare the energy $f(0)$ with $f(m_+)$[17]. Thus, we set

$$
f(m) = f(0) \quad \Longrightarrow \quad \tfrac{1}{2}am^2 - \tfrac{1}{3}ym^3 + \tfrac{1}{4}bm^4 = 0\ , \tag{7.166}
$$

and we now have two quadratic equations to solve simultaneously:

$$
\begin{aligned}
0 &= a - ym + bm^2 \\
0 &= \tfrac{1}{2}a - \tfrac{1}{3}ym + \tfrac{1}{4}bm^2 = 0\ .
\end{aligned}
\tag{7.167}
$$

Eliminating the quadratic term gives $m = 3a/y$. Finally, substituting $m = m_+$ gives us a relation between a, b, and y:

$$
y^2 = \tfrac{9}{2}\,ab\ . \tag{7.168}
$$

[17] We needn't waste our time considering the $m = m_-$ solution, since the cubic term prefers positive m.

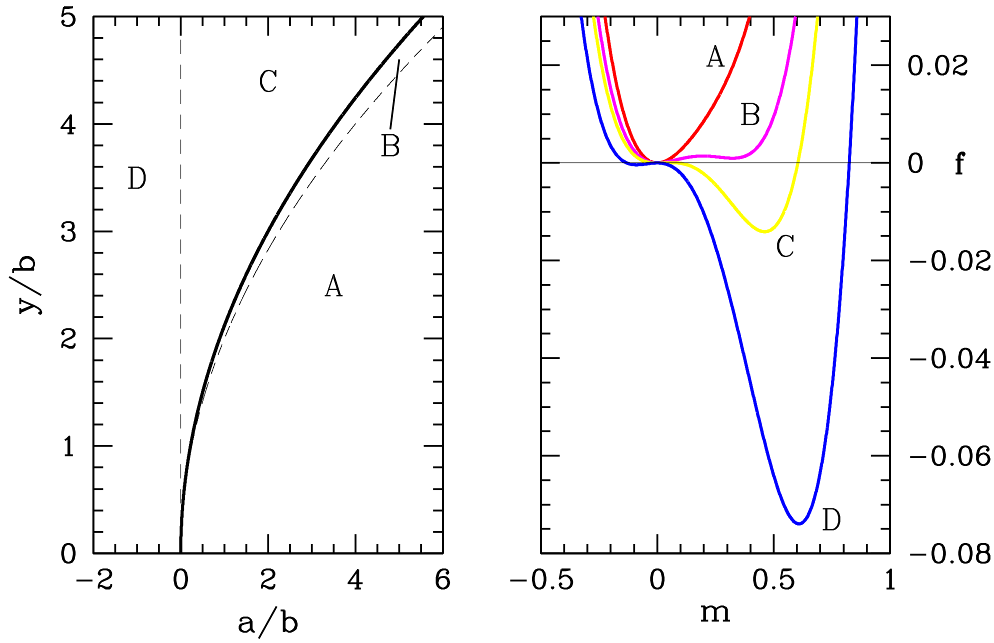

Figure 7.15: Behavior of the quartic free energy $f(m) = \frac{1}{2}am^2 - \frac{1}{3}ym^3 + \frac{1}{4}bm^4$. A: $y^2 < 4ab$; B: $4ab < y^2 < \frac{9}{2}ab$; C and D: $y^2 > \frac{9}{2}ab$. The thick black line denotes a line of first order transitions, where the order parameter is discontinuous across the transition.

Thus, we have the following:

$$\begin{aligned} a > \frac{y^2}{4b} \quad &: \quad \text{1 real root } m = 0 \\ \frac{y^2}{4b} > a > \frac{2y^2}{9b} \quad &: \quad \text{3 real roots; minimum at } m = 0 \\ \frac{2y^2}{9b} > a \quad &: \quad \text{3 real roots; minimum at } m = \frac{y}{2b} + \sqrt{\left(\frac{y}{2b}\right)^2 - \frac{a}{b}} \end{aligned} \tag{7.169}$$

The solution $m = 0$ lies at a local minimum of the free energy for $a > 0$ and at a local maximum for $a < 0$. Over the range $\frac{y^2}{4b} > a > \frac{2y^2}{9b}$, then, there is a global minimum at $m = 0$, a local minimum at $m = m_+$, and a local maximum at $m = m_-$, with $m_+ > m_- > 0$. For $\frac{2y^2}{9b} > a > 0$, there is a local minimum at $a = 0$, a global minimum at $m = m_+$, and a local maximum at $m = m_-$, again with $m_+ > m_- > 0$. For $a < 0$, there is a local maximum at $m = 0$, a local minimum at $m = m_-$, and a global minimum at $m = m_+$, with $m_+ > 0 > m_-$. See fig. 7.15.

With $y = 0$, we have a second order transition at $a = 0$. With $y \neq 0$, there is a discontinuous (first order) transition at $a = 2y^2/9b > 0$. This occurs before a reaches the value $a = 0$ where the curvature at $m = 0$ turns negative. If we write $a = \alpha(T - T_0)$, then the expected second order transition at $T = T_0$ is *preempted* by a first order transition at $T_c = T_0 + 2y^2/9\alpha b$.

7.6.2 Magnetization dynamics

Suppose we now impose some dynamics on the system, of the simple relaxational type

$$\frac{\partial m}{\partial t} = -\Gamma\,\frac{\partial f}{\partial m}\ , \tag{7.170}$$

where Γ is a phenomenological kinetic coefficient. Assuming $y > 0$ and $b > 0$, it is convenient to adimensionalize by writing

$$m \equiv \frac{y}{b}\cdot u \qquad , \qquad a \equiv \frac{y^2}{b}\cdot r \qquad , \qquad t \equiv \frac{b}{\Gamma y^2}\cdot s\ . \tag{7.171}$$

Then we obtain

$$\frac{\partial u}{\partial s} = -\frac{\partial \varphi}{\partial u}\ , \tag{7.172}$$

where the dimensionless free energy function is

$$\varphi(u) = \tfrac{1}{2} r u^2 - \tfrac{1}{3} u^3 + \tfrac{1}{4} u^4\ . \tag{7.173}$$

We see that there is a single control parameter, r. The fixed points of the dynamics are then the stationary points of $\varphi(u)$, where $\varphi'(u) = 0$, with

$$\varphi'(u) = u\,(r - u + u^2)\ . \tag{7.174}$$

The solutions to $\varphi'(u) = 0$ are then given by

$$u^* = 0 \qquad , \qquad u^* = \tfrac{1}{2} \pm \sqrt{\tfrac{1}{4} - r}\ . \tag{7.175}$$

For $r > \frac{1}{4}$ there is one fixed point at $u = 0$, which is attractive under the dynamics $\dot{u} = -\varphi'(u)$ since $\varphi''(0) = r$. At $r = \frac{1}{4}$ there occurs a saddle-node bifurcation and a pair of fixed points is generated, one stable and one unstable. As we see from fig. 7.14, the interior fixed point is always unstable and the two exterior fixed points are always stable. At $r = 0$ there is a transcritical bifurcation where two fixed points of opposite stability collide and bounce off one another (metaphorically speaking).

At the saddle-node bifurcation, $r = \frac{1}{4}$ and $u = \frac{1}{2}$, and we find $\varphi(u = \frac{1}{2}; r = \frac{1}{4}) = \frac{1}{192}$, which is positive. Thus, the thermodynamic state of the system remains at $u = 0$ until the value of $\varphi(u_+)$ crosses zero. This occurs when $\varphi(u) = 0$ and $\varphi'(u) = 0$, the simultaneous solution of which yields $r = \frac{2}{9}$ and $u = \frac{2}{3}$.

Suppose we slowly ramp the control parameter r up and down as a function of the dimensionless time s. Under the dynamics of eqn. 7.172, $u(s)$ flows to the first stable fixed point encountered – this is always the case for a dynamical system with a one-dimensional phase space. Then as r is further varied, u follows the position of whatever locally stable fixed point it initially encountered. Thus, $u\big(r(s)\big)$ evolves smoothly until a bifurcation is encountered. The situation is depicted by the arrows in fig. 7.16. The equilibrium thermodynamic value for $u(r)$ is discontinuous; there is a first order phase transition at $r = \frac{2}{9}$, as we've already seen. As r is increased, $u(r)$ follows a trajectory indicated by the magenta arrows. For an negative initial value of u, the evolution as a function of r will be *reversible*. However, if $u(0)$ is initially positive, then the system exhibits *hysteresis*, as shown. Starting with a large positive

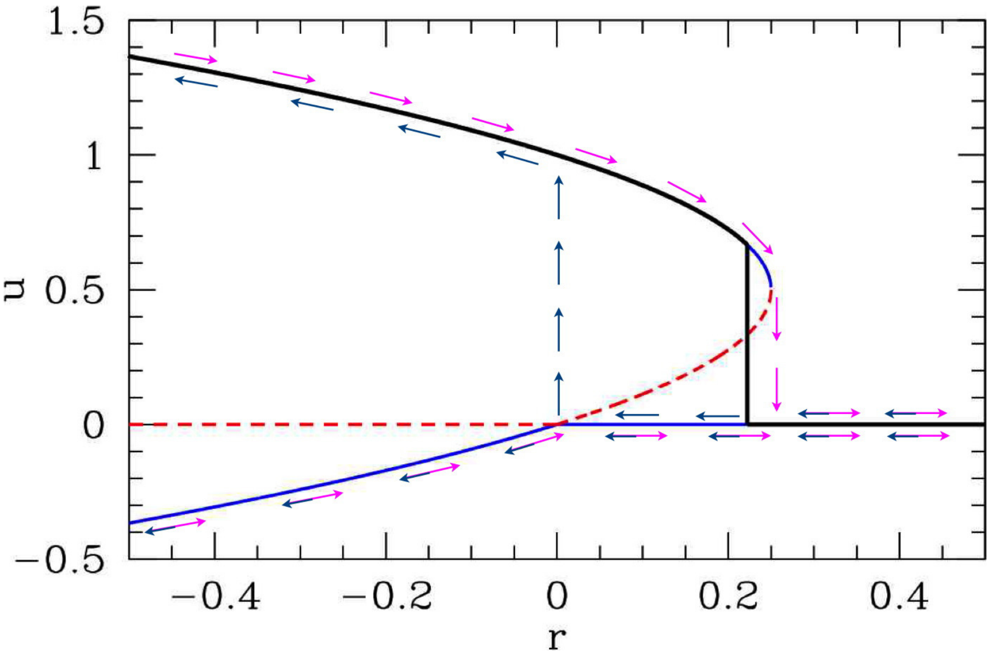

Figure 7.16: Fixed points for $\varphi(u) = \frac{1}{2}ru^2 - \frac{1}{3}u^3 + \frac{1}{4}u^4$ and flow under the dynamics $\dot{u} = -\varphi'(u)$. Solid curves represent stable fixed points and dashed curves unstable fixed points. Magenta arrows show behavior under slowly increasing control parameter r and dark blue arrows show behavior under slowly decreasing r. For $u > 0$ there is a hysteresis loop. The thick black curve shows the equilibrium thermodynamic value of $u(r)$, *i.e.* that value which minimizes the free energy $\varphi(u)$. There is a first order phase transition at $r = \frac{2}{9}$, where the thermodynamic value of u jumps from $u = 0$ to $u = \frac{2}{3}$.

value of r, $u(s)$ quickly evolves to $u = 0^+$, which means a positive infinitesimal value. Then as r is decreased, the system remains at $u = 0^+$ even through the first order transition, because $u = 0$ is an attractive fixed point. However, once r begins to go negative, the $u = 0$ fixed point becomes repulsive, and $u(s)$ quickly flows to the stable fixed point $u_+ = \frac{1}{2} + \sqrt{\frac{1}{4} - r}$. Further decreasing r, the system remains on this branch. If r is later increased, then $u(s)$ remains on the upper branch past $r = 0$, until the u_+ fixed point annihilates with the unstable fixed point at $u_- = \frac{1}{2} - \sqrt{\frac{1}{4} - r}$, at which time $u(s)$ quickly flows down to $u = 0^+$ again.

7.6.3 Sixth order Landau theory : tricritical point

Finally, consider a model with $\mathbb{Z}_2$ symmetry, with the Landau free energy

$$f = f_0 + \tfrac{1}{2}am^2 + \tfrac{1}{4}bm^4 + \tfrac{1}{6}cm^6 \,, \tag{7.176}$$

with $c > 0$ for stability. We seek the phase diagram in the (a, b) plane. Extremizing f with respect to m, we obtain

$$\frac{\partial f}{\partial m} = 0 = m\,(a + bm^2 + cm^4) \,, \tag{7.177}$$

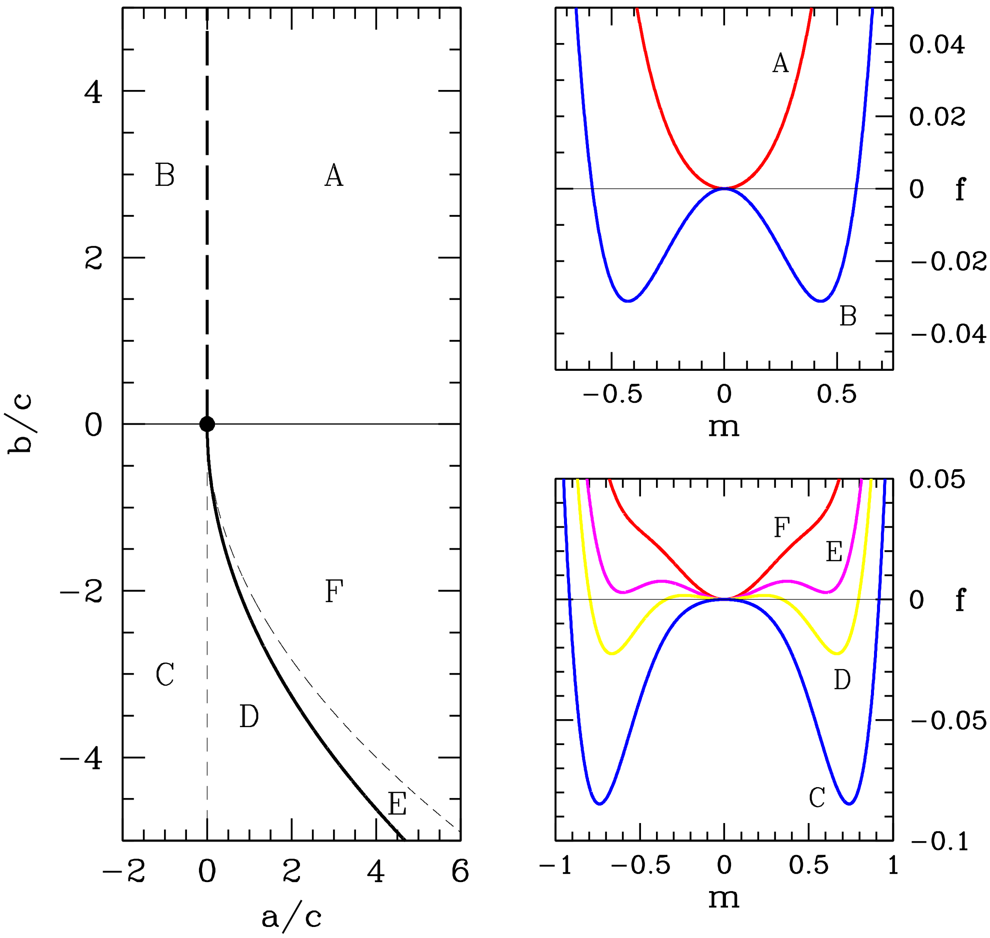

Figure 7.17: Behavior of the sextic free energy $f(m) = \frac{1}{2}am^2 + \frac{1}{4}bm^4 + \frac{1}{6}cm^6$. A: $a > 0$ and $b > 0$; B: $a < 0$ and $b > 0$; C: $a < 0$ and $b < 0$; D: $a > 0$ and $b < -\frac{4}{\sqrt{3}}\sqrt{ac}$; E: $a > 0$ and $-\frac{4}{\sqrt{3}}\sqrt{ac} < b < -2\sqrt{ac}$; F: $a > 0$ and $-2\sqrt{ac} < b < 0$. The thick dashed line is a line of second order transitions, which meets the thick solid line of first order transitions at the tricritical point, $(a, b) = (0, 0)$.

which is a quintic with five solutions over the complex m plane. One solution is obviously $m = 0$. The other four are

$$m = \pm\sqrt{-\frac{b}{2c} \pm \sqrt{\left(\frac{b}{2c}\right)^2 - \frac{a}{c}}} \,. \tag{7.178}$$

For each $\pm$ symbol in the above equation, there are two options, hence four roots in all.

If $a > 0$ and $b > 0$, then four of the roots are imaginary and there is a unique minimum at $m = 0$.

For $a < 0$, there are only three solutions to $f'(m) = 0$ for real m, since the $-$ choice for the $\pm$ sign under the radical leads to imaginary roots. One of the solutions is $m = 0$. The other two are

$$m = \pm\sqrt{-\frac{b}{2c} + \sqrt{\left(\frac{b}{2c}\right)^2 - \frac{a}{c}}} \,. \tag{7.179}$$

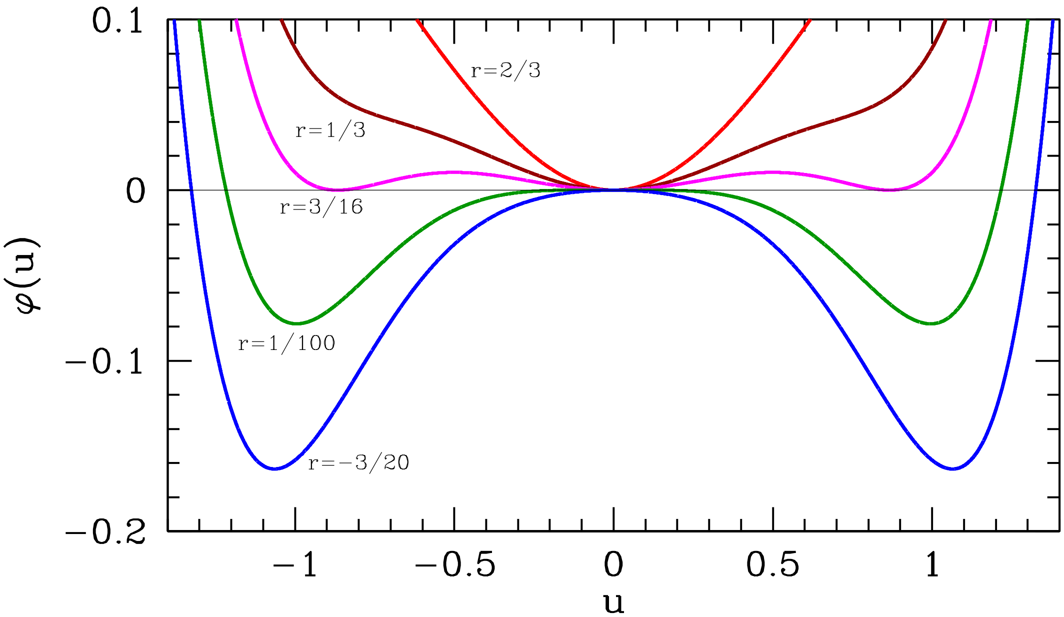

Figure 7.18: Free energy $\varphi(u) = \frac{1}{2}ru^2 - \frac{1}{4}u^4 + \frac{1}{6}u^6$ for several different values of the control parameter r.

The most interesting situation is $a > 0$ and $b < 0$. If $a > 0$ and $b < -2\sqrt{ac}$, all five roots are real. There must be three minima, separated by two local maxima. Clearly if m^* is a solution, then so is $-m^*$. Thus, the only question is whether the outer minima are of lower energy than the minimum at $m = 0$. We assess this by demanding $f(m^*) = f(0)$, where m^* is the position of the largest root (*i.e.* the rightmost minimum). This gives a second quadratic equation,

$$0 = \tfrac{1}{2}a + \tfrac{1}{4}bm^2 + \tfrac{1}{6}cm^4 \,, \tag{7.180}$$

which together with equation 7.177 gives

$$b = -\tfrac{4}{\sqrt{3}}\,\sqrt{ac} \,. \tag{7.181}$$

Thus, we have the following, for fixed $a > 0$:

$$\begin{aligned} b > -2\sqrt{ac} \quad &: \quad \text{1 real root } m = 0 \\ -2\sqrt{ac} > b > -\tfrac{4}{\sqrt{3}}\,\sqrt{ac} \quad &: \quad \text{5 real roots; minimum at } m = 0 \\ -\tfrac{4}{\sqrt{3}}\,\sqrt{ac} > b \quad &: \quad \text{5 real roots; minima at } m = \pm\sqrt{-\frac{b}{2c} + \sqrt{\left(\frac{b}{2c}\right)^2 - \frac{a}{c}}} \end{aligned} \tag{7.182}$$

The point $(a, b) = (0, 0)$, which lies at the confluence of a first order line and a second order line, is known as a *tricritical point*.

7.6.4 Hysteresis for the sextic potential

Once again, we consider the dissipative dynamics $\dot{m} = -\Gamma\, f'(m)$. We adimensionalize by writing

$$m \equiv \sqrt{\frac{|b|}{c}} \cdot u \qquad , \qquad a \equiv \frac{b^2}{c} \cdot r \qquad , \qquad t \equiv \frac{c}{\Gamma\, b^2} \cdot s\,. \tag{7.183}$$

Then we obtain once again the dimensionless equation

$$\frac{\partial u}{\partial s} = -\frac{\partial \varphi}{\partial u}\,, \tag{7.184}$$

where

$$\varphi(u) = \tfrac{1}{2} r u^2 \pm \tfrac{1}{4} u^4 + \tfrac{1}{6} u^6\,. \tag{7.185}$$

In the above equation, the coefficient of the quartic term is positive if $b > 0$ and negative if $b < 0$. That is, the coefficient is $\mathrm{sgn}(b)$. When $b > 0$ we can ignore the sextic term for sufficiently small u, and we recover the quartic free energy studied earlier. There is then a second order transition at $r = 0$. .

New and interesting behavior occurs for $b > 0$. The fixed points of the dynamics are obtained by setting $\varphi'(u) = 0$. We have

$$\begin{aligned} \varphi(u) &= \tfrac{1}{2} r u^2 - \tfrac{1}{4} u^4 + \tfrac{1}{6} u^6 \\ \varphi'(u) &= u\,(r - u^2 + u^4)\,. \end{aligned} \tag{7.186}$$

Thus, the equation $\varphi'(u) = 0$ factorizes into a linear factor u and a quartic factor $u^4 - u^2 + r$ which is quadratic in u^2. Thus, we can easily obtain the roots:

$$\begin{aligned} r < 0 \quad &: \quad u^* = 0\,,\ u^* = \pm\sqrt{\tfrac{1}{2} + \sqrt{\tfrac{1}{4} - r}} \\ 0 < r < \tfrac{1}{4} \quad &: \quad u^* = 0\,,\ u^* = \pm\sqrt{\tfrac{1}{2} + \sqrt{\tfrac{1}{4} - r}}\ ,\ u^* = \pm\sqrt{\tfrac{1}{2} - \sqrt{\tfrac{1}{4} - r}} \\ r > \tfrac{1}{4} \quad &: \quad u^* = 0\,. \end{aligned} \tag{7.187}$$

In fig. 7.19, we plot the fixed points and the hysteresis loops for this system. At $r = \frac{1}{4}$, there are two symmetrically located saddle-node bifurcations at $u = \pm\frac{1}{\sqrt{2}}$. We find $\varphi(u = \pm\frac{1}{\sqrt{2}}, r = \frac{1}{4}) = \frac{1}{48}$, which is positive, indicating that the stable fixed point $u^* = 0$ remains the thermodynamic minimum for the free energy $\varphi(u)$ as r is decreased through $r = \frac{1}{4}$. Setting $\varphi(u) = 0$ and $\varphi'(u) = 0$ simultaneously, we obtain $r = \frac{3}{16}$ and $u = \pm\frac{\sqrt{3}}{2}$. The thermodynamic value for u therefore jumps discontinuously from $u = 0$ to $u = \pm\frac{\sqrt{3}}{2}$ (either branch) at $r = \frac{3}{16}$; this is a first order transition.

Under the dissipative dynamics considered here, the system exhibits hysteresis, as indicated in the figure, where the arrows show the evolution of $u(s)$ for very slowly varying $r(s)$. When the control parameter r is large and positive, the flow is toward the sole fixed point at $u^* = 0$. At $r = \frac{1}{4}$, two simultaneous saddle-node bifurcations take place at $u^* = \pm\frac{1}{\sqrt{2}}$; the outer branch is stable and the inner branch unstable in both cases. At $r = 0$ there is a subcritical pitchfork bifurcation, and the fixed point at $u^* = 0$ becomes unstable.

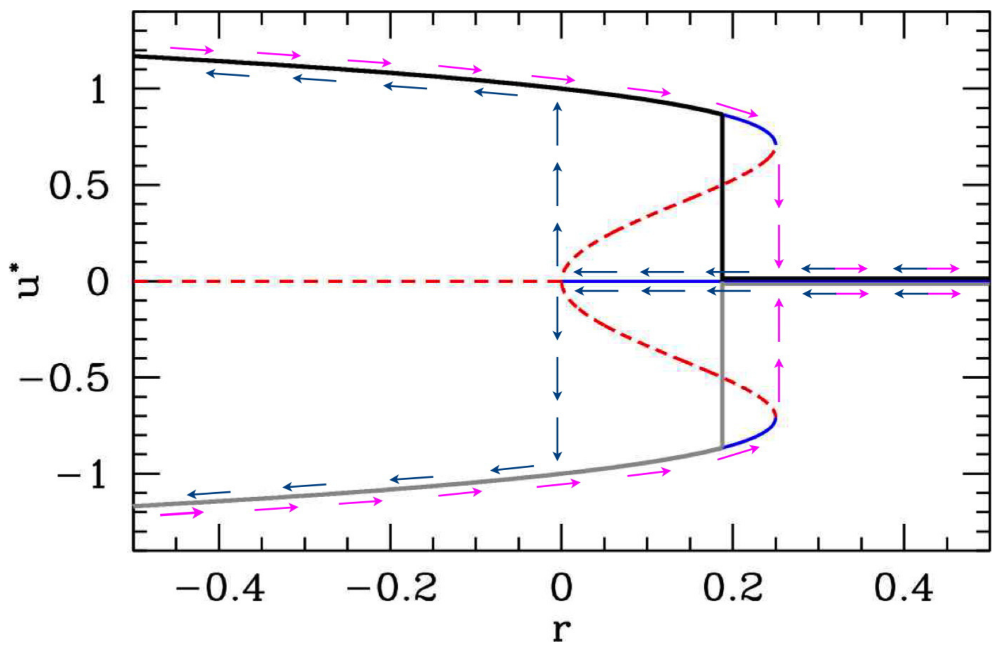

Figure 7.19: Fixed points $\varphi'(u^*) = 0$ for the sextic potential $\varphi(u) = \frac{1}{2}ru^2 - \frac{1}{4}u^4 + \frac{1}{6}u^6$, and corresponding dynamical flow (arrows) under $\dot{u} = -\varphi'(u)$. Solid curves show stable fixed points and dashed curves show unstable fixed points. The thick solid black and solid grey curves indicate the equilibrium thermodynamic values for u; note the overall $u \to -u$ symmetry. Within the region $r \in [0, \frac{1}{4}]$ the dynamics are irreversible and the system exhibits the phenomenon of hysteresis. There is a first order phase transition at $r = \frac{3}{16}$.

Suppose one starts off with $r \gg \frac{1}{4}$ with some value $u > 0$. The flow $\dot{u} = -\varphi'(u)$ then rapidly results in $u \to 0^+$. This is the 'high temperature phase' in which there is no magnetization. Now let r increase slowly, using s as the dimensionless time variable. The scaled magnetization $u(s) = u^*\big(r(s)\big)$ will remain pinned at the fixed point $u^* = 0^+$. As r passes through $r = \frac{1}{4}$, two new stable values of u^* appear, but our system remains at $u = 0^+$, since $u^* = 0$ is a stable fixed point. But after the subcritical pitchfork, $u^* = 0$ becomes unstable. The magnetization $u(s)$ then flows rapidly to the stable fixed point at $u^* = \frac{1}{\sqrt{2}}$, and follows the curve $u^*(r) = \big(\frac{1}{2} + (\frac{1}{4} - r)^{1/2}\big)^{1/2}$ for all $r < 0$.

Now suppose we start increasing r (*i.e.* increasing temperature). The magnetization follows the stable fixed point $u^*(r) = \big(\frac{1}{2} + (\frac{1}{4} - r)^{1/2}\big)^{1/2}$ past $r = 0$, beyond the first order phase transition point at $r = \frac{3}{16}$, and all the way up to $r = \frac{1}{4}$, at which point this fixed point is annihilated at a saddle-node bifurcation. The flow then rapidly takes $u \to u^* = 0^+$, where it remains as r continues to be increased further.

Within the region $r \in \big[0, \frac{1}{4}\big]$ of control parameter space, the dynamics are said to be *irreversible* and the behavior of $u(s)$ is said to be *hysteretic*.

7.7 Mean Field Theory of Fluctuations

7.7.1 Correlation and response in mean field theory

Consider the Ising model,

$$\hat{H} = -\tfrac{1}{2}\sum_{i,j} J_{ij}\,\sigma_i\,\sigma_j - \sum_k H_k\,\sigma_k\ , \tag{7.188}$$

where the local magnetic field on site k is now H_k. We assume without loss of generality that the diagonal terms vanish: $J_{ii} = 0$. Now consider the partition function $Z = \mathsf{Tr}\ e^{-\beta\hat{H}}$ as a function of the temperature T and the local field values $\{H_i\}$. We have

$$\begin{aligned}\frac{\partial Z}{\partial H_i} &= \beta\,\mathsf{Tr}\,\Big[\sigma_i\,e^{-\beta\hat{H}}\Big] = \beta Z\cdot\langle\sigma_i\rangle\\ \frac{\partial^2 Z}{\partial H_i\,\partial H_j} &= \beta^2\,\mathsf{Tr}\,\Big[\sigma_i\,\sigma_j\,e^{-\beta\hat{H}}\Big] = \beta^2 Z\cdot\langle\sigma_i\,\sigma_j\rangle\ .\end{aligned} \tag{7.189}$$

Thus,

$$\begin{aligned}m_i &= -\frac{\partial F}{\partial H_i} = \langle\sigma_i\rangle\\ \chi_{ij} &= \frac{\partial m_i}{\partial H_j} = -\frac{\partial^2 F}{\partial H_i\partial H_j} = \frac{1}{k_B T}\cdot\Big\{\langle\sigma_i\,\sigma_j\rangle - \langle\sigma_i\rangle\,\langle\sigma_j\rangle\Big\}\ .\end{aligned} \tag{7.190}$$

Expressions such as $\langle\sigma_i\rangle$, $\langle\sigma_i\,\sigma_j\rangle$, *etc.* are in general called *correlation functions*. For example, we define the *spin-spin correlation function* C_{ij} as

$$C_{ij} \equiv \langle\sigma_i\,\sigma_j\rangle - \langle\sigma_i\rangle\,\langle\sigma_j\rangle\ . \tag{7.191}$$

Expressions such as $\frac{\partial F}{\partial H_i}$ and $\frac{\partial^2 F}{\partial H_i\,\partial H_j}$ are called *response functions*. The above relation between correlation functions and response functions, $C_{ij} = k_B T\,\chi_{ij}$, is valid *only for the equilibrium distribution*. In particular, this relationship is *invalid* if one uses an approximate distribution, such as the variational density matrix formalism of mean field theory.

The question then arises: within mean field theory, which is more accurate: correlation functions or response functions? A simple argument suggests that the *response functions* are more accurate representations of the real physics. To see this, let's write the variational density matrix ϱ^{var} as the sum of the exact equilibrium (Boltzmann) distribution $\varrho^{eq} = Z^{-1}\exp(-\beta\hat{H})$ plus a deviation $\delta\varrho$:

$$\varrho^{var} = \varrho^{eq} + \delta\varrho\ . \tag{7.192}$$

Then if we calculate a correlator using the variational distribution, we have

$$\begin{aligned}\langle\sigma_i\,\sigma_j\rangle_{var} &= \mathsf{Tr}\,\Big[\varrho^{var}\,\sigma_i\,\sigma_j\Big]\\ &= \mathsf{Tr}\,\Big[\varrho^{eq}\,\sigma_i\,\sigma_j\Big] + \mathsf{Tr}\,\Big[\delta\varrho\,\sigma_i\,\sigma_j\Big]\ .\end{aligned} \tag{7.193}$$

Thus, the variational density matrix gets the correlator right to first order in $\delta\varrho$. On the other hand, the free energy is given by

$$F^{\rm var} = F^{\rm eq} + \sum_{\boldsymbol{\sigma}} \frac{\partial F}{\partial \varrho_{\boldsymbol{\sigma}}}\bigg|_{\varrho^{\rm eq}} \delta\varrho_{\boldsymbol{\sigma}} + \frac{1}{2} \sum_{\boldsymbol{\sigma},\boldsymbol{\sigma}'} \frac{\partial^2 F}{\partial \varrho_{\boldsymbol{\sigma}}\, \partial \varrho_{\boldsymbol{\sigma}'}}\bigg|_{\varrho^{\rm eq}} \delta\varrho_{\boldsymbol{\sigma}}\, \delta\varrho_{\boldsymbol{\sigma}'} + \ldots \ . \tag{7.194}$$

Here $\boldsymbol{\sigma}$ denotes a state of the system, *i.e.* $|\,\boldsymbol{\sigma}\,\rangle = |\,\sigma_1,\ldots,\sigma_N\,\rangle$, where every spin polarization is specified. Since the free energy is an extremum (and in fact an absolute minimum) with respect to the distribution, the second term on the RHS vanishes. This means that the free energy is accurate to second order in the deviation $\delta\varrho$.

7.7.2 Calculation of the response functions

Consider the variational density matrix

$$\varrho(\boldsymbol{\sigma}) = \prod_i \varrho_i(\sigma_i) \ , \tag{7.195}$$

where

$$\varrho_i(\sigma_i) = \left(\frac{1+m_i}{2}\right) \delta_{\sigma_i,1} + \left(\frac{1-m_i}{2}\right) \delta_{\sigma_i,-1} \ . \tag{7.196}$$

The variational energy $E = \mathsf{Tr}\,(\varrho\,\hat{H})$ is

$$E = -\tfrac{1}{2} \sum_{ij} J_{i,j}\, m_i\, m_j - \sum_i H_i\, m_i \tag{7.197}$$

and the entropy $S = -k_{\rm B} T\, \mathsf{Tr}\,(\varrho \ln \varrho)$ is

$$S = -k_{\rm B} \sum_i \left\{ \left(\frac{1+m_i}{2}\right) \ln\!\left(\frac{1+m_i}{2}\right) + \left(\frac{1-m_i}{2}\right) \ln\!\left(\frac{1-m_i}{2}\right) \right\} . \tag{7.198}$$

Setting the variation $\frac{\partial F}{\partial m_i} = 0$, with $F = E - TS$, we obtain the mean field equations,

$$m_i = \tanh\big(\beta J_{ij}\, m_j + \beta H_i\big) \ , \tag{7.199}$$

where we use the summation convention: $J_{ij}\, m_j \equiv \sum_j J_{ij}\, m_j$. Suppose $T > T_{\rm c}$ and m_i is small. Then we can expand the RHS of the above mean field equations, obtaining

$$\big(\delta_{ij} - \beta J_{ij}\big)\, m_j = \beta H_i \ . \tag{7.200}$$

Thus, the susceptibility tensor χ is the inverse of the matrix $(k_{\rm B} T \cdot \mathbb{I} - \mathbb{J})$:

$$\chi_{ij} = \frac{\partial m_i}{\partial H_j} = \big(k_{\rm B} T \cdot \mathbb{I} - \mathbb{J}\big)^{-1}_{ij} \ , \tag{7.201}$$

where $\mathbb{I}$ is the identity. Note also that so-called *connected averages* of the kind in eqn. 7.191 vanish identically if we compute them using our variational density matrix, since all the sites are independent, hence

$$\langle \sigma_i \, \sigma_j \rangle = \mathsf{Tr}\,\big(\varrho^{\text{var}} \, \sigma_i \, \sigma_j\big) = \mathsf{Tr}\,\big(\varrho_i \, \sigma_i\big) \cdot \mathsf{Tr}\,\big(\varrho_j \, \sigma_j\big) = \langle \sigma_i \rangle \cdot \langle \sigma_j \rangle \ , \tag{7.202}$$

and therefore $\chi_{ij} = 0$ if we compute the correlation functions themselves from the variational density matrix, rather than from the free energy F. As we have argued above, the latter approximation is more accurate.

Assuming $J_{ij} = J(\boldsymbol{R}_i - \boldsymbol{R}_j)$, where $\boldsymbol{R}_i$ is a Bravais lattice site, we can Fourier transform the above equation, resulting in

$$\hat{m}(\boldsymbol{q}) = \frac{\hat{H}(\boldsymbol{q})}{k_{\text{B}}T - \hat{J}(\boldsymbol{q})} \equiv \hat{\chi}(\boldsymbol{q}) \, \hat{H}(\boldsymbol{q}) \ . \tag{7.203}$$

Once again, our definition of lattice Fourier transform of a function $\phi(\boldsymbol{R})$ is

$$\begin{aligned} \hat{\phi}(\boldsymbol{q}) &\equiv \sum_{\boldsymbol{R}} \phi(\boldsymbol{R}) \, e^{-i\boldsymbol{q}\cdot\boldsymbol{R}} \\ \phi(\boldsymbol{R}) &= \Omega \int\limits_{\hat{\Omega}} \frac{d^d q}{(2\pi)^d} \, \hat{\phi}(\boldsymbol{q}) \, e^{i\boldsymbol{q}\cdot\boldsymbol{R}} \ , \end{aligned} \tag{7.204}$$

where Ω is the unit cell in real space, called the *Wigner-Seitz cell*, and $\hat{\Omega}$ is the first Brillouin zone, which is the unit cell in *reciprocal space*. Similarly, we have

$$\begin{aligned} \hat{J}(\boldsymbol{q}) &= \sum_{\boldsymbol{R}} J(\boldsymbol{R}) \Big(1 - i\boldsymbol{q}\cdot\boldsymbol{R} - \tfrac{1}{2} (\boldsymbol{q}\cdot\boldsymbol{R})^2 + \ldots \Big) \\ &= \hat{J}(0) \cdot \Big\{ 1 - q^2 R_*^2 + \mathcal{O}(q^4) \Big\} \ , \end{aligned} \tag{7.205}$$

where

$$R_*^2 = \frac{\sum_{\boldsymbol{R}} \boldsymbol{R}^2 J(\boldsymbol{R})}{2d \sum_{\boldsymbol{R}} J(\boldsymbol{R})} \ . \tag{7.206}$$

Here we have assumed inversion symmetry for the lattice, in which case

$$\sum_{\boldsymbol{R}} R^\mu R^\nu J(\boldsymbol{R}) = \frac{1}{d} \cdot \delta^{\mu\nu} \sum_{\boldsymbol{R}} \boldsymbol{R}^2 J(\boldsymbol{R}) \ . \tag{7.207}$$

On cubic lattices with nearest neighbor interactions only, one has $R_* = a/\sqrt{2d}$, where a is the lattice constant and d is the dimension of space.

Thus, with the identification $k_{\text{B}} T_{\text{c}} = \hat{J}(0)$, we have

$$\begin{aligned} \hat{\chi}(\boldsymbol{q}) &= \frac{1}{k_{\text{B}}(T - T_{\text{c}}) + k_{\text{B}} T_{\text{c}} \, R_*^2 \, \boldsymbol{q}^2 + \mathcal{O}(q^4)} \\ &= \frac{1}{k_{\text{B}} T_{\text{c}} \, R_*^2} \cdot \frac{1}{\xi^{-2} + q^2 + \mathcal{O}(q^4)} \ , \end{aligned} \tag{7.208}$$

where

$$\xi = R_* \cdot \left(\frac{T - T_c}{T_c}\right)^{-1/2} \tag{7.209}$$

is the *correlation length*. With the definition

$$\xi(T) \propto |T - T_c|^{-\nu} \tag{7.210}$$

as $T \to T_c$, we obtain the mean field correlation length exponent $\nu = \frac{1}{2}$. The exact result for the two-dimensional Ising model is $\nu = 1$, whereas $\nu \approx 0.6$ for the $d = 3$ Ising model. Note that $\hat{\chi}(\boldsymbol{q} = 0, T)$ diverges as $(T - T_c)^{-1}$ for $T > T_c$.

In real space, we have

$$m_i = \sum_j \chi_{ij} \, H_j \ , \tag{7.211}$$

where

$$\chi_{ij} = \Omega \int \frac{d^d q}{(2\pi)^d} \, \hat{\chi}(\boldsymbol{q}) \, e^{i\boldsymbol{q}\cdot(\boldsymbol{R}_i - \boldsymbol{R}_j)} \ . \tag{7.212}$$

Note that $\hat{\chi}(\boldsymbol{q})$ is properly periodic under $\boldsymbol{q} \to \boldsymbol{q} + \boldsymbol{G}$, where $\boldsymbol{G}$ is a reciprocal lattice vector, which satisfies $e^{i\boldsymbol{G}\cdot\boldsymbol{R}} = 1$ for any direct Bravais lattice vector $\boldsymbol{R}$. Indeed, we have

$$\begin{aligned} \hat{\chi}^{-1}(\boldsymbol{q}) &= k_B T - \hat{J}(\boldsymbol{q}) \\ &= k_B T - J \sum_{\boldsymbol{\delta}} e^{i\boldsymbol{q}\cdot\boldsymbol{\delta}} \ , \end{aligned} \tag{7.213}$$

where $\boldsymbol{\delta}$ is a nearest neighbor separation vector, and where in the second line we have assumed nearest neighbor interactions only. On cubic lattices in d dimensions, there are $2d$ nearest neighbor separation vectors, $\boldsymbol{\delta} = \pm a \, \hat{\boldsymbol{e}}_\mu$, where $\mu \in \{1, \ldots, d\}$. The real space susceptibility is then

$$\chi(\boldsymbol{R}) = \int\limits_{-\pi}^{\pi} \frac{d\theta_1}{2\pi} \cdots \int\limits_{-\pi}^{\pi} \frac{d\theta_d}{2\pi} \, \frac{e^{in_1\theta_1} \cdots e^{in_d\theta_d}}{k_B T - (2J\cos\theta_1 + \ldots + 2J\cos\theta_d)} \ , \tag{7.214}$$

where $\boldsymbol{R} = a \sum_{\mu=1}^{d} n_\mu \, \hat{\boldsymbol{e}}_\mu$ is a general direct lattice vector for the cubic Bravais lattice in d dimensions, and the $\{n_\mu\}$ are integers.

The long distance behavior was discussed in chapter 6 (see §6.5.9 on Ornstein-Zernike theory[18]). For convenience we reiterate those results:

- In $d = 1$,

$$\chi_{d=1}(x) = \left(\frac{\xi}{2k_B T_c R_*^2}\right) e^{-|x|/\xi} \ . \tag{7.215}$$

[18]There is a sign difference between the particle susceptibility defined in chapter 6 and the spin susceptibility defined here. The origin of the difference is that the single particle potential v as defined was repulsive for $v > 0$, meaning the local density response δn should be negative, while in the current discussion a positive magnetic field H prefers $m > 0$.

- In $d > 1$, with $r \to \infty$ and ξ fixed,

$$\chi^{\rm OZ}_d(\boldsymbol{r}) \simeq C_d \cdot \frac{\xi^{(3-d)/2}}{k_{\rm B}T\, R_*^2} \cdot \frac{e^{-r/\xi}}{r^{(d-1)/2}} \cdot \bigg\{ 1 + \mathcal{O}\bigg(\frac{d-3}{r/\xi}\bigg)\bigg\} \quad , \tag{7.216}$$

where the C_d are dimensionless constants.

- In $d > 2$, with $\xi \to \infty$ and r fixed (*i.e.* $T \to T_{\rm c}$ at fixed separation $\boldsymbol{r}$),

$$\chi_d(\boldsymbol{r}) \simeq \frac{C'_d}{k_{\rm B}TR_*^2} \cdot \frac{e^{-r/\xi}}{r^{d-2}} \cdot \bigg\{ 1 + \mathcal{O}\bigg(\frac{d-3}{r/\xi}\bigg)\bigg\} \quad . \tag{7.217}$$

In $d = 2$ dimensions we obtain

$$\chi_{d=2}(\boldsymbol{r}) \simeq \frac{C'_2}{k_{\rm B}TR_*^2} \cdot \ln\bigg(\frac{r}{\xi}\bigg)\, e^{-r/\xi} \cdot \bigg\{ 1 + \mathcal{O}\bigg(\frac{1}{\ln(r/\xi)}\bigg)\bigg\} \quad , \tag{7.218}$$

where the C'_d are dimensionless constants.

7.7.3 Beyond the Ising model

Consider a general spin model, and a variational density matrix $\varrho_{\rm var}$ which is a product of single site density matrices:

$$\varrho_{\rm var}\big[\{\boldsymbol{S}_i\}\big] = \prod_i \varrho_1^{(i)}(\boldsymbol{S}_i) \quad , \tag{7.219}$$

where $\mathsf{Tr}\,\big(\varrho_{\rm var}\,\boldsymbol{S}\big) = \boldsymbol{m}_i$ is the local magnetization and $\boldsymbol{S}_i$, which may be a scalar (*e.g.*, σ_i in the Ising model previously discussed), is the local spin operator. Note that $\varrho_1^{(i)}(\boldsymbol{S}_i)$ depends parametrically on the variational parameter(s) $\boldsymbol{m}_i$. Let the Hamiltonian be

$$\hat{H} = -\tfrac{1}{2} \sum_{i,j} J^{\mu\nu}_{ij}\, S^\mu_i\, S^\nu_j + \sum_i h(\boldsymbol{S}_i) - \sum_i \boldsymbol{H}_i \cdot \boldsymbol{S}_i \quad . \tag{7.220}$$

The variational free energy is then

$$F_{\rm var} = -\tfrac{1}{2} \sum_{i,j} J^{\mu\nu}_{ij}\, m^\mu_i\, m^\nu_j + \sum_i \varphi(\boldsymbol{m}_i, T) - \sum_i H^\mu_i\, m^\mu_i \quad , \tag{7.221}$$

where the single site free energy $\varphi(\boldsymbol{m}_i, T)$ in the absence of an external field is given by

$$\varphi(\boldsymbol{m}_i, T) = \mathsf{Tr}\Big[\varrho_1^{(i)}(\boldsymbol{S})\, h(\boldsymbol{S})\Big] + k_{\rm B}T\, \mathsf{Tr}\Big[\varrho_1^{(i)}(\boldsymbol{S}) \ln \varrho_1^{(i)}(\boldsymbol{S})\Big] \tag{7.222}$$

We then have

$$\frac{\partial F_{\rm var}}{\partial m^\mu_i} = -\sum_j J^{\mu\nu}_{ij}\, m^\nu_j - H^\mu_i + \frac{\partial \varphi(\boldsymbol{m}_i, T)}{\partial m^\mu_i} \quad . \tag{7.223}$$

For the noninteracting system, we have $J^{\mu\nu}_{ij} = 0$, and the weak field response must be linear. In this limit we may write $m^\mu_i = \chi^0_{\mu\nu}(T)\, H^\nu_i + \mathcal{O}(H_i^3)$, and we conclude

$$\frac{\partial \varphi(\boldsymbol{m}_i, T)}{\partial m^\mu_i} = \big[\chi^0(T)\big]^{-1}_{\mu\nu}\, m^\nu_i + \mathcal{O}\big(m_i^3\big) \quad . \tag{7.224}$$

Note that this entails the following expansion for the single site free energy in zero field:

$$\varphi(\boldsymbol{m}_i, T) = \tfrac{1}{2}\left[\chi^0(T)\right]^{-1}_{\mu\nu} m_i^\nu\, m_i^\nu + \mathcal{O}(m^4) \quad . \tag{7.225}$$

Finally, we restore the interaction term and extremize F_{var} by setting $\partial F_{\text{var}}/\partial m_i^\mu = 0$. To linear order, then,

$$m_i^\mu = \chi^0_{\mu\nu}(T)\left(H_i^\nu + \sum_j J_{ij}^{\nu\lambda}\, m_j^\lambda\right) \quad . \tag{7.226}$$

Typically the local susceptibility is a scalar in the internal spin space, *i.e.* $\chi^0_{\mu\nu}(T) = \chi^0(T)\,\delta_{\mu\nu}$, in which case we obtain

$$\big(\delta^{\mu\nu}\,\delta_{ij} - \chi^0(T)\, J_{ij}^{\mu\nu}\big)\, m_i^\nu = \chi^0(T)\, H_i^\mu \quad . \tag{7.227}$$

In Fourier space, then,

$$\hat\chi_{\mu\nu}(\boldsymbol{q}, T) = \chi^0(T)\left(1 - \chi^0(T)\,\hat{\mathbb{J}}(\boldsymbol{q})\right)^{-1}_{\mu\nu} \quad , \tag{7.228}$$

where $\hat{\mathbb{J}}(\boldsymbol{q})$ is the matrix whose elements are $\hat J^{\mu\nu}(\boldsymbol{q})$. If $\hat J^{\mu\nu}(\boldsymbol{q}) = \hat J(\boldsymbol{q})\,\delta^{\mu\nu}$, then the susceptibility is isotropic in spin space, with

$$\hat\chi(\boldsymbol{q}, T) = \frac{1}{\big[\chi^0(T)\big]^{-1} - \hat J(\boldsymbol{q})} \quad . \tag{7.229}$$

Consider now the following illustrative examples:

(i) Quantum spin S with $h(\boldsymbol{S}) = 0$: We take the $\hat{\boldsymbol{z}}$ axis to be that of the local external magnetic field, *i.e.* $\hat{\boldsymbol{H}}_i$. Write $\varrho_1(\boldsymbol{S}) = z^{-1}\,\exp(uS^z/k_\text{B}T)$, where $u = u(m,T)$ is obtained implicitly from the relation $m(u,T) = \mathsf{Tr}(\varrho_1\, S^z)$. The normalization constant is

$$z = \mathsf{Tr}\, e^{uS^z/k_\text{B}T} = \sum_{j=-S}^{S} e^{ju/k_\text{B}T} = \frac{\sinh\big[(S+\frac{1}{2})\,u/k_\text{B}T\big]}{\sinh\big[u/2k_\text{B}T\big]} \tag{7.230}$$

The relation between m, u, and T is then given by

$$\begin{aligned} m = \langle S^z\rangle &= k_\text{B}T\,\frac{\partial \ln z}{\partial u} = (S+\tfrac{1}{2})\,\text{ctnh}\big[(S+\tfrac{1}{2})\,u/k_\text{B}T\big] - \tfrac{1}{2}\,\text{ctnh}\big[u/2k_\text{B}T\big] \\ &= \frac{S(S+1)}{3k_\text{B}T}\,u + \mathcal{O}(u^3) \quad . \end{aligned} \tag{7.231}$$

The free-field single-site free energy is then

$$\varphi(\boldsymbol{m}, T) = k_\text{B}T\,\mathsf{Tr}\,\big(\varrho_1 \ln \varrho_1\big) = um - k_\text{B}T\ln z \quad , \tag{7.232}$$

whence

$$\frac{\partial\varphi}{\partial m} = u + m\,\frac{\partial u}{\partial m} - k_\text{B}T\,\frac{\partial \ln z}{\partial u}\,\frac{\partial u}{\partial m} = u \equiv \chi_0^{-1}(T)\, m + \mathcal{O}(m^3) \quad , \tag{7.233}$$

and we thereby obtain the result

$$\chi_0(T) = \frac{S(S+1)}{3k_\text{B}T} \quad , \tag{7.234}$$

which is the Curie susceptibility.

(ii) Classical spin $\boldsymbol{S} = S\,\hat{\boldsymbol{n}}$ with $h = 0$ and $\hat{\boldsymbol{n}}$ an N-component unit vector : We take the single site density matrix to be $\varrho_1(\boldsymbol{S}) = z^{-1}\exp(\boldsymbol{u}\cdot\boldsymbol{S}/k_{\rm B}T)$. The single site field-free partition function is then

$$z = \int \frac{d\hat{\boldsymbol{n}}}{\Omega_N}\,\exp(\boldsymbol{u}\cdot\boldsymbol{S}/k_{\rm B}T) = 1 + \frac{S^2\,\boldsymbol{u}^2}{N(k_{\rm B}T)^2} + \mathcal{O}(u^4) \tag{7.235}$$

and therefore

$$\boldsymbol{m} = k_{\rm B}T\,\frac{\partial \ln z}{\partial \boldsymbol{u}} = \frac{S^2\,\boldsymbol{u}}{N k_{\rm B}T} + \mathcal{O}(u^3) \quad , \tag{7.236}$$

from which we read off $\chi_0(T) = S^2/Nk_{\rm B}T$. Note that this agrees in the classical ($S \to \infty$) limit, for $N = 3$, with our previous result.

(iii) Quantum spin S with $h(\boldsymbol{S}) = \Delta(S^z)^2$: This corresponds to so-called *easy plane anisotropy*, meaning that the single site energy $h(\boldsymbol{S})$ is minimized when the local spin vector $\boldsymbol{S}$ lies in the (x, y) plane. As in example (i), we write $\varrho_1(\boldsymbol{S}) = z^{-1}\,\exp(uS^z/k_{\rm B}T)$, yielding the same expression for z and the same relation between z and u. What is different is that we must evaluate the local energy,

$$\begin{aligned} \mathrm{e}\,(u,T) &= \mathsf{Tr}\,\big(\varrho_1\,h(\boldsymbol{S})\big) = \Delta\,(k_{\rm B}T)^2\,\frac{\partial^2 \ln z}{\partial u^2} \\ &= \frac{\Delta}{4}\left[\frac{1}{\sinh^2\!\big[u/2k_{\rm B}T\big]} - \frac{(2S+1)^2}{\sinh^2\!\big[(2S+1)u/2k_{\rm B}T\big]}\right] = \frac{S(S+1)\Delta\,u^2}{6(k_{\rm B}T)^2} + \mathcal{O}(u^4) \quad . \end{aligned} \tag{7.237}$$

We now have $\varphi = \mathrm{e} + um - k_{\rm B}T\ln z$, from which we obtain the susceptibility

$$\chi^0(T) = \frac{S(S+1)}{3(k_{\rm B}T + \Delta)} \quad . \tag{7.238}$$

Note that the local susceptibility no longer diverges as $T \to 0$, because there is always a gap in the spectrum of $h(\boldsymbol{S})$.

7.8 Global Symmetries

7.8.1 Symmetries and symmetry groups

Interacting systems can be broadly classified according to their *global symmetry group*. Consider the following five examples:

$$\begin{aligned}
\hat{H}_{\rm Ising} &= -\sum_{i<j} J_{ij}\,\sigma_i\,\sigma_j & \sigma_i &\in \{-1,+1\} \\
\hat{H}_{p-{\rm clock}} &= -\sum_{i<j} J_{ij}\,\cos\bigg(\frac{2\pi(n_i-n_j)}{p}\bigg) & n_i &\in \{1,2,\ldots,p\} \\
\hat{H}_{q-{\rm Potts}} &= -\sum_{i<j} J_{ij}\,\delta_{\sigma_i,\sigma_j} & \sigma_i &\in \{1,2,\ldots,q\} \\
\hat{H}_{XY} &= -\sum_{i<j} J_{ij}\,\cos(\phi_i-\phi_j) & \phi_i &\in \big[0,2\pi\big] \\
\hat{H}_{{\sf O}(n)} &= -\sum_{i<j} J_{ij}\,\hat{\boldsymbol{\Omega}}_i\cdot\hat{\boldsymbol{\Omega}}_j & \hat{\boldsymbol{\Omega}}_i &\in S^{n-1}\ .
\end{aligned} \tag{7.239}$$

The Ising Hamiltonian is left invariant by the global symmetry group $\mathbb{Z}_2$, which has two elements, $\mathbb{I}$ and η, with

$$\eta\,\sigma_i = -\sigma_i\ . \tag{7.240}$$

$\mathbb{I}$ is the identity, and $\eta^2=\mathbb{I}$. By simultaneously reversing *all* the spins $\sigma_i\to-\sigma_i$, the interactions remain invariant.

The degrees of freedom of the *p-state clock model* are integer variables n_i each of which ranges from 1 to p. The Hamiltonian is invariant under the discrete group $\mathbb{Z}_p$, whose p elements are generated by the single operation η, where

$$\eta\,n_i = \begin{cases} n_i+1 & \text{if} \quad n_i\in\{1,2,\ldots,p-1\} \\ 1 & \text{if} \quad n_i=p\ . \end{cases} \tag{7.241}$$

Think of a clock with one hand and p 'hour' markings consecutively spaced by an angle $2\pi/p$. In each site i, a hand points to one of the p hour marks; this determines n_i. The operation η simply advances *all* the hours by one tick, with hour p advancing to hour 1, just as 23:00 military time is followed one hour later by 00:00. The interaction $\cos\big(2\pi(n_i-n_j)/p\big)$ is invariant under such an operation. The p elements of the group $\mathbb{Z}_p$ are then

$$\mathbb{I}\,,\,\eta\,,\,\eta^2\,,\,\ldots\,,\,\eta^{p-1}\ . \tag{7.242}$$

We've already met up with the q-state Potts model, where each site supports a 'spin' σ_i which can be in any of q possible states, which we may label by integers $\{1\,,\,\ldots\,,\,q\}$. The energy of two interacting sites i and j is $-J_{ij}$ if $\sigma_i=\sigma_j$ and zero otherwise. This energy function is invariant under global operations of the *symmetric group on q characters*, S_q, which is the group of permutations of the sequence $\{1\,,\,2\,,\,3\,,\,\ldots\,,\,q\}$. The group S_q has $q!$ elements. Note the difference between a $\mathbb{Z}_q$ symmetry and an S_q

Figure 7.20: A domain wall in a one-dimensional Ising model.

symmetry. In the former case, the Hamiltonian is invariant only under the q-element cyclic permutations, *e.g.*

$$\eta \equiv \begin{pmatrix} 1 \; 2 \cdots q-1 \; q \\ 2 \; 3 \cdots \quad q \quad 1 \end{pmatrix}$$

and its powers η^l with $l = 0, \ldots, q-1$.

All these models – the Ising, p-state clock, and q-state Potts models – possess a global symmetry group which is *discrete*. That is, each of the symmetry groups $\mathbb{Z}_2$, $\mathbb{Z}_p$, S_q is a discrete group, with a finite number of elements. The XY Hamiltonian $\hat{H}_{XY}$ on the other hand is invariant under a *continuous* group of transformations $\phi_i \to \phi_i + \alpha$, where ϕ_i is the angle variable on site i. More to the point, we could write the interaction term $\cos(\phi_i - \phi_j)$ as $\frac{1}{2}\big(z_i^* z_j + z_i z_j^*\big)$, where $z_i = e^{i\phi_i}$ is a phase which lives on the unit circle, and z_i^* is the complex conjugate of z_i. The model is then invariant under the global transformation $z_i \to e^{i\alpha} z_i$. The phases $e^{i\alpha}$ form a group under multiplication, called $\mathsf{U}(1)$, which is the same as $\mathsf{O}(2)$. Equivalently, we could write the interaction as $\hat{\boldsymbol{\Omega}}_i \cdot \hat{\boldsymbol{\Omega}}_j$, where $\hat{\boldsymbol{\Omega}}_i = (\cos\phi_i \, , \, \sin\phi_i)$, which explains the $\mathsf{O}(2)$, symmetry, since the symmetry operations are global rotations in the plane, which is to say the two-dimensional orthogonal group. This last representation generalizes nicely to unit vectors in n dimensions, where

$$\hat{\boldsymbol{\Omega}} = (\Omega^1 \, , \, \Omega^2 \, , \, \ldots \, , \, \Omega^n) \tag{7.243}$$

with $\hat{\boldsymbol{\Omega}}^2 = 1$. The dot product $\hat{\boldsymbol{\Omega}}_i \cdot \hat{\boldsymbol{\Omega}}_j$ is then invariant under global rotations in this n-dimensional space, which is the group $\mathsf{O}(n)$.

7.8.2 Lower critical dimension

Depending on whether the global symmetry group of a model is discrete or continuous, there exists a *lower critical dimension* d_ℓ at or below which no phase transition may take place at finite temperature. That is, for $d \le d_\ell$, the critical temperature is $T_{\rm c} = 0$. Owing to its neglect of fluctuations, mean field theory generally *overestimates* the value of $T_{\rm c}$ because it overestimates the stability of the ordered phase. Indeed, there are many examples where mean field theory predicts a finite $T_{\rm c}$ when the actual critical temperature is $T_{\rm c} = 0$. This happens whenever $d \le d_\ell$.

Let's test the stability of the ordered (ferromagnetic) state of the one-dimensional Ising model at low temperatures. We consider order-destroying *domain wall* excitations which interpolate between regions of degenerate, symmetry-related ordered phase, *i.e.* $\uparrow\uparrow\uparrow\uparrow\uparrow$ and $\downarrow\downarrow\downarrow\downarrow\downarrow$. For a system with a discrete symmetry at low temperatures, the domain wall is abrupt, on the scale of a single lattice spacing. If the exchange energy is J, then the energy of a single domain wall is $2J$, since a link of energy $-J$ is replaced with one of energy $+J$. However, there are N possible locations for the domain wall, hence its entropy

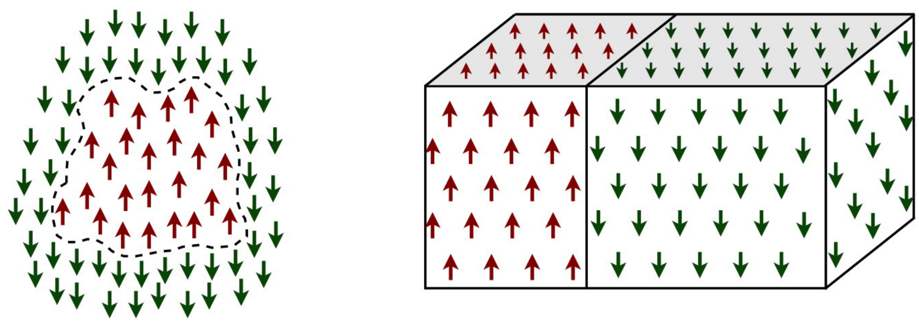

Figure 7.21: Domain walls in the two-dimensional (left) and three-dimensional (right) Ising model.

is $k_{\rm B} \ln N$. For a system with M domain walls, the free energy is

$$\begin{aligned} F &= 2MJ - k_{\rm B}T \ln \binom{N}{M} \\ &= N \cdot \bigg\{ 2Jx + k_{\rm B}T \Big[x \ln x + (1-x) \ln(1-x) \Big] \bigg\} \ , \end{aligned} \tag{7.244}$$

where $x = M/N$ is the density of domain walls, and where we have used Stirling's approximation for $k!$ when k is large. Extremizing with respect to x, we find

$$\frac{x}{1-x} = e^{-2J/k_{\rm B}T} \qquad \Longrightarrow \qquad x = \frac{1}{e^{2J/k_{\rm B}T} + 1} \ . \tag{7.245}$$

The average distance between domain walls is x^{-1}, which is finite for finite T. Thus, the thermodynamic state of the system is *disordered*, with no net average magnetization.

Consider next an Ising domain wall in d dimensions. Let the linear dimension of the system be $L \cdot a$, where L is a real number and a is the lattice constant. Then the energy of a single domain wall which partitions the entire system is $2J \cdot L^{d-1}$. The domain wall entropy is difficult to compute, because the wall can fluctuate significantly, but for a single domain wall we have $S \gtrsim k_{\rm B} \ln L$. Thus, the free energy $F = 2JL^{d-1} - k_{\rm B}T \ln L$ is dominated by the energy term if $d > 1$, suggesting that the system *may* be ordered. We can do a slightly better job in $d = 2$ by writing

$$Z \approx \exp\left(L^d \sum_P N_P \, e^{-2PJ/k_{\rm B}T} \right) \ , \tag{7.246}$$

where the sum is over all closd loops of perimeter P, and N_P is the number of such loops. An example of such a loop circumscribing a domain is depicted in the left panel of fig. 7.21. It turns out that

$$N_P \simeq \kappa^P P^{-\theta} \cdot \Big\{ 1 + \mathcal{O}(P^{-1}) \Big\} \ , \tag{7.247}$$

where $\kappa = z - 1$ with z the lattice coordination number, and θ is some exponent. We can understand the κ^P factor in the following way. At each step along the perimeter of the loop, there are $\kappa = z-1$ possible directions to go (since one doesn't backtrack). The fact that the loop must avoid overlapping itself and must return to its original position to be closed leads to the power law term $P^{-\theta}$, which is subleading since $\kappa^P P^{-\theta} = \exp(P \ln\kappa - \theta \ln P)$ and $P \gg \ln P$ for $P \gg 1$. Thus,

$$F \approx -\frac{1}{\beta}\, L^d \sum_P P^{-\theta}\, e^{(\ln\kappa - 2\beta J)P} \ , \tag{7.248}$$

which diverges if $\ln\kappa > 2\beta J$, *i.e.* if $T > 2J/k_{\mathrm{B}} \ln(z-1)$. We identify this singularity with the phase transition. The high temperature phase involves a proliferation of such loops. The excluded volume effects between the loops, which we have not taken into account, then enter in an essential way so that the sum converges. Thus, we have the following picture:

$$\begin{aligned} \ln\kappa < 2\beta J \ &: \ \text{large loops suppressed ; ordered phase} \\ \ln\kappa > 2\beta J \ &: \ \text{large loops proliferate ; disordered phase} \ . \end{aligned}$$

On the square lattice, we obtain

$$\begin{aligned} k_{\mathrm{B}} T_{\mathrm{c}}^{\mathrm{approx}} &= \frac{2J}{\ln 3} = 1.82\, J \\ k_{\mathrm{B}} T_{\mathrm{c}}^{\mathrm{exact}} &= \frac{2J}{\sinh^{-1}(1)} = 2.27\, J \ . \end{aligned}$$

The agreement is better than we should reasonably expect from such a crude argument.

Nota bene : Beware of arguments which allegedly prove the existence of an ordered phase. Generally speaking, any approximation will *underestimate* the entropy, and thus will overestimate the stability of the putative ordered phase.

7.8.3 Continuous symmetries

When the global symmetry group is continuous, the domain walls interpolate smoothly between ordered phases. The energy generally involves a stiffness term,

$$E = \tfrac{1}{2}\rho_{\mathrm{s}} \int d^d\!r\ (\boldsymbol{\nabla}\theta)^2 \ , \tag{7.249}$$

where $\theta(\boldsymbol{r})$ is the angle of a local rotation about a single axis and where ρ_{s} is the *spin stiffness*. Of course, in $\mathsf{O}(n)$ models, the rotations can be with respect to several different axes simultaneously.

In the ordered phase, we have $\theta(\boldsymbol{r}) = \theta_0$, a constant. Now imagine a domain wall in which $\theta(\boldsymbol{r})$ rotates by 2π across the width of the sample. We write $\theta(\boldsymbol{r}) = 2\pi n x/L$, where L is the linear size of the sample (here with dimensions of length) and n is an integer telling us how many complete twists the order parameter field makes. The domain wall then resembles that in fig. 7.22. The gradient energy is

$$E = \tfrac{1}{2}\rho_{\mathrm{s}}\, L^{d-1} \int_0^L \! dx \left(\frac{2\pi n}{L}\right)^2 = 2\pi^2 n^2 \rho_{\mathrm{s}}\, L^{d-2} \ . \tag{7.250}$$

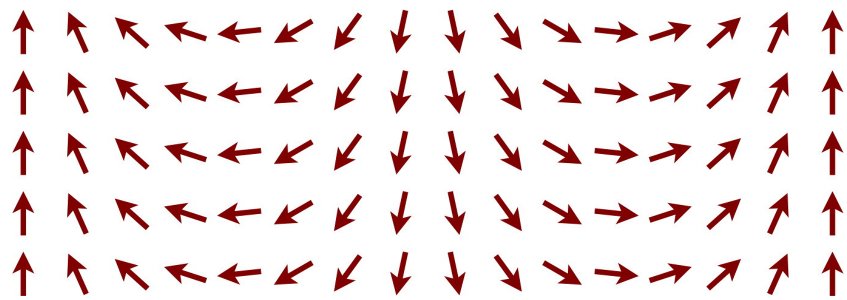

Figure 7.22: A domain wall in an XY ferromagnet.

Recall that in the case of discrete symmetry, the domain wall energy scaled as $E \propto L^{d-1}$. Thus, with $S \gtrsim k_{\rm B} \ln L$ for a single wall, we see that the entropy term dominates if $d \leq 2$, in which case there is no finite temperature phase transition. Thus, the lower critical dimension d_ℓ depends on whether the global symmetry is discrete or continuous, with

$$\begin{aligned} \text{discrete global symmetry} \quad &\Longrightarrow \quad d_\ell = 1 \\ \text{continuous global symmetry} \quad &\Longrightarrow \quad d_\ell = 2 \ . \end{aligned}$$

Note that all along we have assumed local, *short-ranged* interactions. Long-ranged interactions can enhance order and thereby suppress d_ℓ.

Thus, we expect that for models with discrete symmetries, $d_\ell = 1$ and there is no finite temperature phase transition for $d \leq 1$. For models with continuous symmetries, $d_\ell = 2$, and we expect $T_{\rm c} = 0$ for $d \leq 2$. In this context we should emphasize that the two-dimensional XY model *does* exhibit a phase transition at finite temperature, called the *Kosterlitz-Thouless* transition. However, this phase transition is *not* associated with the breaking of the continuous global $\mathsf{O}(2)$ symmetry and rather has to do with the unbinding of vortices and antivortices. So there is still no true long-ranged order below the critical temperature $T_{\rm KT}$, even though there is a phase transition!

7.8.4 Random systems : Imry-Ma argument

Oftentimes, particularly in condensed matter systems, intrinsic randomness exists due to quenched impurities, grain boundaries, immobile vacancies, *etc.* How does this quenched randomness affect a system's attempt to order at $T = 0$? This question was taken up in a beautiful and brief paper by J. Imry and S.-K. Ma, *Phys. Rev. Lett.* **35**, 1399 (1975). Imry and Ma considered models in which there are short-ranged interactions and a random local field coupling to the local order parameter:

$$\hat{H}_{\rm RFI} = -J \sum_{\langle ij \rangle} \sigma_i \, \sigma_j - \sum_i H_i \, \sigma_i \tag{7.251}$$

$$\hat{H}_{{\rm RF}\mathsf{O}(n)} = -J \sum_{\langle ij \rangle} \hat{\boldsymbol{\Omega}}_i \cdot \hat{\boldsymbol{\Omega}}_j - \sum_i H_i^\alpha \, \Omega_i^\alpha \ , \tag{7.252}$$

where

$$\langle\!\langle \, H_i^\alpha \, \rangle\!\rangle = 0 \qquad , \qquad \langle\!\langle \, H_i^\alpha \, H_j^\beta \, \rangle\!\rangle = \varGamma \, \delta^{\alpha\beta} \, \delta_{ij} \ , \tag{7.253}$$

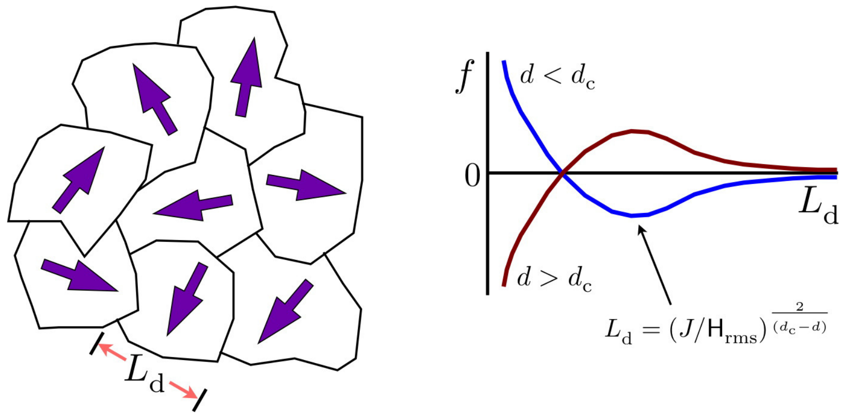

Figure 7.23: Left panel : Imry-Ma domains for an $\mathsf{O}(2)$ model. The arrows point in the direction of the local order parameter field $\langle\hat{\boldsymbol{\Omega}}(\boldsymbol{r})\rangle$. Right panel : free energy density as a function of domain size L_d. Keep in mind that the minimum possible value for L_d is the lattice spacing a.

where $\langle\!\langle \cdot \rangle\!\rangle$ denotes a configurational average over the disorder. Imry and Ma reasoned that a system could try to lower its free energy by forming *domains* in which the order parameter takes advantage of local fluctuations in the random field. The size of these domains is assumed to be L_d, a length scale to be determined. See the sketch in the left panel of fig. 7.23.

There are two contributions to the energy of a given domain: bulk and surface terms. The bulk energy is

$$E_\mathrm{bulk} = -H_\mathrm{rms}\,(L_\mathrm{d}/a)^{d/2}\ , \tag{7.254}$$

where a is the lattice spacing. This is because when we add together $(L_\mathrm{d}/a)^d$ random fields, the magnitude of the result is proportional to the square root of the number of terms, *i.e.* to $(L_\mathrm{d}/a)^{d/2}$. The quantity $H_\mathrm{rms} = \sqrt{\Gamma}$ is the root-mean-square fluctuation in the random field at a given site. The surface energy is

$$E_\mathrm{surface} \propto \begin{cases} J\,(L_\mathrm{d}/a)^{d-1} & \text{(discrete symmetry)} \\ J\,(L_\mathrm{d}/a)^{d-2} & \text{(continuous symmetry)}\ . \end{cases} \tag{7.255}$$

We compute the critical dimension d_c by balancing the bulk and surface energies,

$$\begin{aligned} d-1 &= \tfrac{1}{2}d \qquad \Longrightarrow \qquad d_\mathrm{c} = 2 \qquad \text{(discrete)} \\ d-2 &= \tfrac{1}{2}d \qquad \Longrightarrow \qquad d_\mathrm{c} = 4 \qquad \text{(continuous)}\ . \end{aligned}$$

The total free energy is $F = (V/L_\mathrm{d}^d)\cdot\Delta E$, where $\Delta E = E_\mathrm{bulk} + E_\mathrm{surf}$. Thus, the free energy per unit cell is

$$f = \frac{F}{V/a^d} \approx J\left(\frac{a}{L_\mathrm{d}}\right)^{\frac{1}{2}d_\mathrm{c}} - H_\mathrm{rms}\left(\frac{a}{L_\mathrm{d}}\right)^{\frac{1}{2}d}\ . \tag{7.256}$$

If $d < d_\mathrm{c}$, the surface term dominates for small L_d and the bulk term dominates for large L_d There is global minimum at

$$\frac{L_\mathrm{d}}{a} = \left(\frac{d_\mathrm{c}}{d}\cdot\frac{J}{H_\mathrm{rms}}\right)^{\frac{2}{d_\mathrm{c}-d}}\ . \tag{7.257}$$

For $d > d_c$, the relative dominance of the bulk and surface terms is reversed, and there is a global maximum at this value of L_d.

Sketches of the free energy $f(L_d)$ in both cases are provided in the right panel of fig. 7.23. We must keep in mind that the domain size L_d cannot become smaller than the lattice spacing a. Hence we should draw a vertical line on the graph at $L_d = a$ and discard the portion $L_d < a$ as unphysical. For $d < d_c$, we see that the state with $L_d = \infty$, *i.e.* the ordered state, is never the state of lowest free energy. *In dimensions* $d < d_c$, *the ordered state is always unstable to domain formation in the presence of a random field.*

For $d > d_c$, there are two possibilities, depending on the relative size of J and H_{rms}. We can see this by evaluating $f(L_d = a) = J - H_{rms}$ and $f(L_d = \infty) = 0$. Thus, if $J > H_{rms}$, the minimum energy state occurs for $L_d = \infty$. In this case, the system has an ordered ground state, and we expect a finite temperature transition to a disordered state at some critical temperature $T_c > 0$. If, on the other hand, $J < H_{rms}$, then the fluctuations in H overwhelm the exchange energy at $T = 0$, and the ground state is disordered down to the very smallest length scale (*i.e.* the lattice spacing a).

Please read the essay, "Memories of Shang-Keng Ma," at http://sip.clarku.edu/skma.html.

7.9 Ginzburg-Landau Theory

7.9.1 Ginzburg-Landau free energy

Including gradient terms in the free energy, we write

$$F\big[m(\boldsymbol{x})\,,\,h(\boldsymbol{x})\big] = \int\! d^d\!x\,\Big\{ f_0 + \tfrac{1}{2}a\,m^2 + \tfrac{1}{4}b\,m^4 + \tfrac{1}{6}c\,m^6\, - h\,m + \tfrac{1}{2}\kappa\,(\boldsymbol{\nabla} m)^2 + \ldots \Big\} . \tag{7.258}$$

In principle, any term which does not violate the appropriate global symmetry will turn up in such an expansion of the free energy, with some coefficient. Examples include hm^3 (both m and h are odd under time reversal), $m^2(\boldsymbol{\nabla} m)^2$, *etc.* We now ask: what function $m(\boldsymbol{x})$ extremizes the free energy functional $F\big[m(\boldsymbol{x})\,,\,h(\boldsymbol{x})\big]$? The answer is that $m(\boldsymbol{x})$ must satisfy the corresponding Euler-Lagrange equation, which for the above functional is

$$a\,m + b\,m^3 + c\,m^5 - h - \kappa\,\nabla^2 m = 0\ . \tag{7.259}$$

If $a > 0$ and h is small (we assume $b > 0$ and $c > 0$), we may neglect the m^3 and m^5 terms and write

$$\big(a - \kappa\,\nabla^2\big)\,m = h\ , \tag{7.260}$$

whose solution is obtained by Fourier transform as

$$\hat m(\boldsymbol{q}) = \frac{\hat h(\boldsymbol{q})}{a + \kappa \boldsymbol{q}^2}\ , \tag{7.261}$$

which, with $h(\boldsymbol{x})$ appropriately defined, recapitulates the result in eqn. 7.203. Thus, we conclude that

$$\hat\chi(\boldsymbol{q}) = \frac{1}{a + \kappa \boldsymbol{q}^2}\ , \tag{7.262}$$

which should be compared with eqn. 7.208. For continuous functions, we have

$$\begin{aligned}\hat{m}(\boldsymbol{q}) &= \int\! d^dx\, m(\boldsymbol{x})\, e^{-i\boldsymbol{q}\cdot\boldsymbol{x}} \\ m(\boldsymbol{x}) &= \int\!\frac{d^dq}{(2\pi)^d}\, \hat{m}(\boldsymbol{q})\, e^{i\boldsymbol{q}\cdot\boldsymbol{x}} \ .\end{aligned} \tag{7.263}$$

We can then derive the result

$$m(\boldsymbol{x}) = \int\! d^dx'\, \chi(\boldsymbol{x}-\boldsymbol{x}')\, h(\boldsymbol{x}') \ , \tag{7.264}$$

where

$$\chi(\boldsymbol{x}-\boldsymbol{x}') = \frac{1}{\kappa}\int\!\frac{d^dq}{(2\pi)^d}\, \frac{e^{i\boldsymbol{q}\cdot(\boldsymbol{x}-\boldsymbol{x}')}}{\boldsymbol{q}^2+\xi^{-2}} \ , \tag{7.265}$$

where the correlation length is $\xi = \sqrt{\kappa/a} \propto (T-T_{\mathrm{c}})^{-1/2}$, as before.

If $a<0$ then there is a spontaneous magnetization and we write $m(\boldsymbol{x}) = m_0 + \delta m(\boldsymbol{x})$. Assuming h is weak, we then have two equations

$$\begin{aligned} a + b\, m_0^2 + c\, m_0^4 &= 0 \\ (a + 3b\, m_0^2 + 5c\, m_0^4 - \kappa\, \nabla^2)\, \delta m &= h \ . \end{aligned} \tag{7.266}$$

If $-a>0$ is small, we have $m_0^2 = -a/3b$ and

$$\delta\hat{m}(\boldsymbol{q}) = \frac{\hat{h}(\boldsymbol{q})}{-2a+\kappa\boldsymbol{q}^2} \ , \tag{7.267}$$

7.9.2 Domain wall profile

A particularly interesting application of Ginzburg-Landau theory is its application toward modeling the spatial profile of defects such as vortices and domain walls. Consider, for example, the case of Ising ($\mathbb{Z}_2$) symmetry with $h=0$. We expand the free energy density to order m^4:

$$F\big[m(\boldsymbol{x})\big] = \int\! d^dx\, \Big\{ f_0 + \tfrac{1}{2}am^2 + \tfrac{1}{4}bm^4 + \tfrac{1}{2}\kappa\,(\boldsymbol{\nabla} m)^2 \Big\} \ . \tag{7.268}$$

We assume $a<0$, corresponding to $T<T_{\mathrm{c}}$. Consider now a domain wall, where $m(x\to-\infty) = -m_0$ and $m(x\to+\infty) = +m_0$, where m_0 is the equilibrium magnetization, which we obtain from the Euler-Lagrange equation,

$$a\, m + b\, m^3 - \kappa\, \nabla^2 m = 0 \ , \tag{7.269}$$

assuming a uniform solution where $\boldsymbol{\nabla} m = 0$. This gives $m_0 = \sqrt{|a|/b}$. It is useful to scale $m(\boldsymbol{x})$ by m_0, writing $m(\boldsymbol{x}) = m_0\, \phi(\boldsymbol{x})$. The scaled order parameter function $\phi(\boldsymbol{x})$ interpolates between $\phi(-\infty) = -1$ and $\phi(+\infty) = 1$.

It also proves useful to rescale position, writing $\boldsymbol{x} = \big(2\kappa/|a|\big)^{1/2}\boldsymbol{\zeta}$. Then we obtain

$$\tfrac{1}{2}\boldsymbol{\nabla}^2\phi = -\phi + \phi^3 \ . \tag{7.270}$$

We assume $\phi(\boldsymbol{\zeta}) = \phi(\zeta)$ is only a function of one coordinate, $\zeta \equiv \zeta^1$. Then the Euler-Lagrange equation becomes

$$\frac{d^2\phi}{d\zeta^2} = -2\phi + 2\phi^3 \equiv -\frac{\partial U}{\partial \phi} \,, \tag{7.271}$$

where

$$U(\phi) = -\tfrac{1}{2}\big(\phi^2 - 1\big)^2 \,. \tag{7.272}$$

The 'potential' $U(\phi)$ is an inverted double well, with maxima at $\phi = \pm 1$. The equation $\ddot{\phi} = -U'(\phi)$, where dot denotes differentiation with respect to ζ, is simply Newton's second law with time replaced by space. In order to have a stationary solution at $\zeta \to \pm\infty$ where $\phi = \pm 1$, the total energy must be $E = U(\phi = \pm 1) = 0$, where $E = \frac{1}{2}\dot{\phi}^2 + U(\phi)$. This leads to the first order differential equation

$$\frac{d\phi}{d\zeta} = 1 - \phi^2 \,, \tag{7.273}$$

with solution

$$\phi(\zeta) = \tanh(\zeta) \,. \tag{7.274}$$

Restoring the dimensionful constants,

$$m(x) = m_0 \, \tanh\!\left(\frac{x}{\sqrt{2}\,\xi}\right) , \tag{7.275}$$

where the coherence length $\xi \equiv \big(\kappa/|a|\big)^{1/2}$ diverges at the Ising transition $a = 0$.

7.9.3 Derivation of Ginzburg-Landau free energy

We can make some progress in systematically deriving the Ginzburg-Landau free energy. Consider the Ising model,

$$\frac{\hat{H}}{k_{\rm B}T} = -\tfrac{1}{2}\sum_{i,j} K_{ij}\,\sigma_i\,\sigma_j - \sum_i h_i\,\sigma_i + \tfrac{1}{2}\sum_i K_{ii} \,, \tag{7.276}$$

where now $K_{ij} = J_{ij}/k_{\rm B}T$ and $h_i = H_i/k_{\rm B}T$ are the interaction energies and local magnetic fields in units of $k_{\rm B}T$. The last term on the RHS above cancels out any contribution from diagonal elements of K_{ij}. Our derivation makes use of a generalization of the Gaussian integral,

$$\int\limits_{-\infty}^{\infty}\!dx\; e^{-\frac{1}{2}ax^2 - bx} = \left(\frac{2\pi}{a}\right)^{1/2} e^{b^2/2a} \,. \tag{7.277}$$

The generalization is

$$\int\limits_{-\infty}^{\infty}\!dx_1 \cdots \int\limits_{-\infty}^{\infty}\!dx_N \; e^{-\frac{1}{2}A_{ij}x_i x_j - b_i x_i} = \frac{(2\pi)^{N/2}}{\sqrt{\det A}} \; e^{\frac{1}{2}A^{-1}_{ij}\,b_i b_j} \,, \tag{7.278}$$

where we use the Einstein convention of summing over repeated indices, and where we assume that the matrix A is positive definite (else the integral diverges). This allows us to write

$$\begin{aligned} Z &= e^{-\frac{1}{2}K_{ii}}\,\mathsf{Tr}\left[e^{\frac{1}{2}K_{ij}\sigma_i\,\sigma_j}\,e^{h_i\,\sigma_i}\right] \\ &= \det{}^{-1/2}(2\pi K)\,e^{-\frac{1}{2}K_{ii}}\int\limits_{-\infty}^{\infty}\!d\phi_1\cdots\!\int\limits_{-\infty}^{\infty}\!d\phi_N\;e^{-\frac{1}{2}K^{-1}_{ij}\phi_i\phi_j}\;\mathsf{Tr}\;e^{(\phi_i+h_i)\sigma_i} \\ &= \det{}^{-1/2}(2\pi K)\,e^{-\frac{1}{2}K_{ii}}\int\limits_{-\infty}^{\infty}\!d\phi_1\cdots\!\int\limits_{-\infty}^{\infty}\!d\phi_N\;e^{-\frac{1}{2}K^{-1}_{ij}\phi_i\phi_j}\;e^{\sum_i\ln\left[2\cosh(\phi_i+h_i)\right]} \\ &\equiv \int\limits_{-\infty}^{\infty}\!d\phi_1\cdots\!\int\limits_{-\infty}^{\infty}\!d\phi_N\;e^{-\Phi(\phi_1,\ldots,\phi_N)}\ , \end{aligned} \tag{7.279}$$

where

$$\Phi = \tfrac{1}{2}\sum_{i,j}K^{-1}_{ij}\,\phi_i\,\phi_j - \sum_i \ln\cosh(\phi_i+h_i) + \tfrac{1}{2}\ln\mathsf{det}\,(2\pi K) + \tfrac{1}{2}\,\mathsf{Tr}\;K - N\ln 2\ . \tag{7.280}$$

We assume the model is defined on a Bravais lattice, in which case we can write $\phi_i = \phi_{\boldsymbol{R}_i}$. We can then define the Fourier transforms,

$$\begin{aligned} \phi_{\boldsymbol{R}} &= \frac{1}{\sqrt{N}}\sum_{\boldsymbol{q}}\hat{\phi}_{\boldsymbol{q}}\,e^{i\boldsymbol{q}\cdot\boldsymbol{R}} \\ \hat{\phi}_{\boldsymbol{q}} &= \frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}}\phi_{\boldsymbol{R}}\,e^{-i\boldsymbol{q}\cdot\boldsymbol{R}} \end{aligned} \tag{7.281}$$

and

$$\hat{K}(\boldsymbol{q}) = \sum_{\boldsymbol{R}} K(\boldsymbol{R})\,e^{-i\boldsymbol{q}\cdot\boldsymbol{R}}\ . \tag{7.282}$$

A few remarks about the lattice structure and periodic boundary conditions are in order. For a Bravais lattice, we can write each direct lattice vector $\boldsymbol{R}$ as a sum over d basis vectors with integer coefficients, *viz.*

$$\boldsymbol{R} = \sum_{\mu=1}^{d} n_\mu\,\boldsymbol{a}_\mu\ , \tag{7.283}$$

where d is the dimension of space. The reciprocal lattice vectors $\boldsymbol{b}_\mu$ satisfy

$$\boldsymbol{a}_\mu\cdot\boldsymbol{b}_\nu = 2\pi\,\delta_{\mu\nu}\ , \tag{7.284}$$

and any wavevector $\boldsymbol{q}$ may be expressed as

$$\boldsymbol{q} = \frac{1}{2\pi}\sum_{\mu=1}^{d}\theta_\mu\,\boldsymbol{b}_\mu\ . \tag{7.285}$$

We can impose periodic boundary conditions on a system of size $M_1 \times M_2 \times \cdots \times M_d$ by requiring

$$\phi_{\boldsymbol{R}+\sum_{\mu=1}^{d} l_\mu M_\mu \boldsymbol{a}_\mu} = \phi_{\boldsymbol{R}} \ . \tag{7.286}$$

This leads to the *quantization* of the wavevectors, which must then satisfy

$$e^{iM_\mu \, \boldsymbol{q}\cdot\boldsymbol{a}_\mu} = e^{iM_\mu \theta_\mu} = 1 \ , \tag{7.287}$$

and therefore $\theta_\mu = 2\pi m_\mu / M_\mu$, where m_μ is an integer. There are then $M_1 M_2 \cdots M_d = N$ independent values of $\boldsymbol{q}$, which can be taken to be those corresponding to $m_\mu \in \{1, \ldots, M_\mu\}$.

Let's now expand the function $\Phi(\vec{\phi})$ in powers of the ϕ_i, and to first order in the external fields h_i. We obtain

$$\begin{aligned}\Phi = \tfrac{1}{2} \sum_{\boldsymbol{q}} \Big(\hat{K}^{-1}(\boldsymbol{q}) - 1\Big)\, |\hat{\phi}_{\boldsymbol{q}}|^2 + \tfrac{1}{12} \sum_{\boldsymbol{R}} \phi_{\boldsymbol{R}}^4 - \sum_{\boldsymbol{R}} h_{\boldsymbol{R}}\, \phi_{\boldsymbol{R}} + \mathcal{O}\big(\phi^6, h^2\big) \\ + \tfrac{1}{2}\, \mathsf{Tr}\, K + \tfrac{1}{2}\, \mathsf{Tr}\, \ln(2\pi K) - N \ln 2\end{aligned} \tag{7.288}$$

On a d-dimensional lattice, for a model with nearest neighbor interactions K_1 only, we have $\hat{K}(\boldsymbol{q}) = K_1 \sum_{\boldsymbol{\delta}} e^{i\boldsymbol{q}\cdot\boldsymbol{\delta}}$, where $\boldsymbol{\delta}$ is a nearest neighbor separation vector. These are the eigenvalues of the matrix K_{ij}. We note that K_{ij} is then not positive definite, since there are negative eigenvalues[19]. To fix this, we can add a term K_0 everywhere along the diagonal. We then have

$$\hat{K}(\boldsymbol{q}) = K_0 + K_1 \sum_{\boldsymbol{\delta}} \cos(\boldsymbol{q}\cdot\boldsymbol{\delta}) \ . \tag{7.289}$$

Here we have used the inversion symmetry of the Bravais lattice to eliminate the imaginary term. The eigenvalues are all positive so long as $K_0 > zK_1$, where z is the lattice coordination number. We can therefore write $\hat{K}(\boldsymbol{q}) = \hat{K}(0) - \alpha\, \boldsymbol{q}^2$ for small $\boldsymbol{q}$, with $\alpha > 0$. Thus, we can write

$$\hat{K}^{-1}(\boldsymbol{q}) - 1 = a + \kappa\, \boldsymbol{q}^2 + \ldots \ . \tag{7.290}$$

To lowest order in $\boldsymbol{q}$ the RHS is isotropic if the lattice has cubic symmetry, but anisotropy will enter in higher order terms. We'll assume isotropy at this level. This is not necessary but it makes the discussion somewhat less involved. We can now write down our Ginzburg-Landau free energy density:

$$\mathcal{F} = a\, \phi^2 + \tfrac{1}{2}\kappa\, |\boldsymbol{\nabla}\phi|^2 + \tfrac{1}{12}\, \phi^4 - h\, \phi \ , \tag{7.291}$$

valid to lowest nontrivial order in derivatives, and to sixth order in ϕ.

One might wonder what we have gained over the inhomogeneous variational density matrix treatment, where we found

$$\begin{aligned}F = -\tfrac{1}{2} \sum_{\boldsymbol{q}} \hat{J}(\boldsymbol{q})\, |\hat{m}(\boldsymbol{q})|^2 - \sum_{\boldsymbol{q}} \hat{H}(-\boldsymbol{q})\, \hat{m}(\boldsymbol{q}) \\ + k_{\rm B}T \sum_i \left\{ \left(\frac{1+m_i}{2}\right) \ln\!\left(\frac{1+m_i}{2}\right) + \left(\frac{1-m_i}{2}\right) \ln\!\left(\frac{1-m_i}{2}\right) \right\} .\end{aligned} \tag{7.292}$$

[19] To evoke a negative eigenvalue on a d-dimensional cubic lattice, set $q_\mu = \frac{\pi}{a}$ for all μ. The eigenvalue is then $-2dK_1$.

Surely we could expand $\hat{J}(\boldsymbol{q}) = \hat{J}(0) - \frac{1}{2}a\boldsymbol{q}^2 + \ldots$ and obtain a similar expression for $\mathcal{F}$. However, such a derivation using the variational density matrix is only approximate. The method outlined in this section is exact.

Let's return to our complete expression for Φ:

$$\Phi(\vec{\phi}) = \Phi_0(\vec{\phi}) + \sum_{\boldsymbol{R}} v(\phi_{\boldsymbol{R}}) \; , \tag{7.293}$$

where

$$\Phi_0(\vec{\phi}) = \tfrac{1}{2} \sum_{\boldsymbol{q}} G^{-1}(\boldsymbol{q}) \, \big|\hat{\phi}(\boldsymbol{q})\big|^2 + \tfrac{1}{2} \, \mathsf{Tr} \left(\frac{1}{1+G^{-1}} \right) + \tfrac{1}{2} \, \mathsf{Tr} \, \ln \left(\frac{2\pi}{1+G^{-1}} \right) - N \ln 2 \; . \tag{7.294}$$

Here we have defined

$$\begin{aligned} v(\phi) &= \tfrac{1}{2}\phi^2 - \ln\cosh\phi \\ &= \tfrac{1}{12}\,\phi^4 - \tfrac{1}{45}\,\phi^6 + \tfrac{17}{2520}\,\phi^8 + \ldots \end{aligned} \tag{7.295}$$

and

$$G(\boldsymbol{q}) = \frac{\hat{K}(\boldsymbol{q})}{1 - \hat{K}(\boldsymbol{q})} \; . \tag{7.296}$$

We now want to compute

$$Z = \int \! D\vec{\phi} \; e^{-\Phi_0(\vec{\phi})} \; e^{-\sum_{\boldsymbol{R}} v(\phi_{\boldsymbol{R}})} \tag{7.297}$$

where

$$D\vec{\phi} \equiv d\phi_1 \, d\phi_2 \cdots d\phi_N \; . \tag{7.298}$$

We expand the second exponential factor in a Taylor series, allowing us to write

$$Z = Z_0 \left(1 - \sum_{\boldsymbol{R}} \big\langle v(\phi_{\boldsymbol{R}}) \big\rangle + \tfrac{1}{2} \sum_{\boldsymbol{R}} \sum_{\boldsymbol{R}'} \big\langle v(\phi_{\boldsymbol{R}}) \, v(\phi_{\boldsymbol{R}'}) \big\rangle + \ldots \right) , \tag{7.299}$$

where

$$\begin{aligned} Z_0 &= \int \! D\vec{\phi} \; e^{-\Phi_0(\vec{\phi})} \\ \ln Z_0 &= \tfrac{1}{2} \, \mathsf{Tr} \left[\ln(1+G) - \frac{G}{1+G} \right] + N \ln 2 \end{aligned} \tag{7.300}$$

and

$$\big\langle F(\vec{\phi}) \big\rangle = \frac{\int \! D\vec{\phi} \; F \, e^{-\Phi_0}}{\int \! D\vec{\phi} \; e^{-\Phi_0}} \; . \tag{7.301}$$

To evaluate the various terms in the expansion of eqn. 7.299, we invoke Wick's theorem, which says

$$\begin{aligned} \big\langle x_{i_1} \, x_{i_2} \cdots x_{i_{2L}} \big\rangle &= \int\limits_{-\infty}^{\infty} \! dx_1 \cdots \! \int\limits_{-\infty}^{\infty} \! dx_N \; e^{-\frac{1}{2} \mathcal{G}^{-1}_{ij} x_i x_j} \, x_{i_1} \, x_{i_2} \cdots x_{i_{2L}} \Bigg/ \int\limits_{-\infty}^{\infty} \! dx_1 \cdots \! \int\limits_{-\infty}^{\infty} \! dx_N \; e^{-\frac{1}{2} \mathcal{G}^{-1}_{ij} x_i x_j} \\ &= \sum_{\substack{\text{all distinct} \\ \text{pairings}}} \mathcal{G}_{j_1 j_2} \, \mathcal{G}_{j_3 j_4} \cdots \mathcal{G}_{j_{2L-1} j_{2L}} \; , \end{aligned} \tag{7.302}$$

where the sets $\{j_1,\ldots,j_{2L}\}$ are all permutations of the set $\{i_1,\ldots,i_{2L}\}$. In particular, we have

$$\langle x_i^4\rangle = 3\big(\mathcal{G}_{ii}\big)^2 \ . \tag{7.303}$$

In our case, we have

$$\langle \phi_{\boldsymbol{R}}^4\rangle = 3\left(\frac{1}{N}\sum_{\boldsymbol{q}} G(\boldsymbol{q})\right)^2 \ . \tag{7.304}$$

Thus, if we write $v(\phi)\approx \frac{1}{12}\,\phi^4$ and retain only the quartic term in $v(\phi)$, we obtain

$$\begin{aligned}\frac{F}{k_{\rm B}T} &= -\ln Z_0 = \tfrac{1}{2}\,\mathsf{Tr}\left[\frac{G}{1+G}-\ln(1+G)\right]+\frac{1}{4N}\big(\,\mathsf{Tr}\;G\big)^2 - N\ln 2\\ &= -N\ln 2 + \frac{1}{4N}\big(\,\mathsf{Tr}\;G\big)^2 - \frac{1}{4}\,\mathsf{Tr}\;\big(G^2\big)+\mathcal{O}\big(G^3\big)\ .\end{aligned} \tag{7.305}$$

Note that if we set K_{ij} to be diagonal, then $\hat K(\boldsymbol{q})$ and hence $G(\boldsymbol{q})$ are constant functions of $\boldsymbol{q}$. The $\mathcal{O}\big(G^2\big)$ term then vanishes, which is required since the free energy cannot depend on the diagonal elements of K_{ij}.

7.9.4 Ginzburg criterion

Let us define $A(T,H,V,N)$ to be the usual (*i.e.* thermodynamic) Helmholtz free energy. Then

$$e^{-\beta A} = \int\! Dm\; e^{-\beta F[m(\boldsymbol{x})]} \ , \tag{7.306}$$

where the functional $F[m(\boldsymbol{x})]$ is of the Ginzburg-Landau form, given in eqn. 7.268. The integral above is a *functional integral*. We can give it a more precise meaning by defining its measure in the case of periodic functions $m(\boldsymbol{x})$ confined to a rectangular box. Then we can expand

$$m(\boldsymbol{x}) = \frac{1}{\sqrt{V}}\sum_{\boldsymbol{q}} \hat m_{\boldsymbol{q}}\, e^{i\boldsymbol{q}\cdot\boldsymbol{x}} \ , \tag{7.307}$$

and we define the measure

$$Dm \equiv dm_0 \prod_{\substack{\boldsymbol{q}\\ q_x>0}} d\,\mathsf{Re}\;\hat m_{\boldsymbol{q}}\; d\,\mathsf{Im}\;\hat m_{\boldsymbol{q}} \ . \tag{7.308}$$

Note that the fact that $m(\boldsymbol{x})\in\mathbb{R}$ means that $\hat m_{-\boldsymbol{q}} = \hat m^*_{\boldsymbol{q}}$. We'll assume $T>T_{\rm c}$ and $H=0$ and we'll explore limit $T\to T_{\rm c}^+$ from above to analyze the properties of the critical region close to $T_{\rm c}$. In this limit we can ignore all but the quadratic terms in m, and we have

$$\begin{aligned}e^{-\beta A} &= \int\! Dm\;\exp\bigg(-\tfrac{1}{2}\beta\sum_{\boldsymbol{q}}(a+\kappa\,\boldsymbol{q}^2)\,|\hat m_{\boldsymbol{q}}|^2\bigg)\\ &= \prod_{\boldsymbol{q}}\left(\frac{\pi k_{\rm B}T}{a+\kappa\,\boldsymbol{q}^2}\right)^{1/2} \ .\end{aligned} \tag{7.309}$$

Thus,

$$A = \tfrac{1}{2} k_B T \sum_{\boldsymbol{q}} \ln\!\left(\frac{a + \kappa\, \boldsymbol{q}^2}{\pi k_B T} \right) . \tag{7.310}$$

We now assume that $a(T) = \alpha t$, where t is the dimensionless quantity

$$t = \frac{T - T_c}{T_c} , \tag{7.311}$$

known as the *reduced temperature*.

We now compute the heat capacity $C_V = -T\, \frac{\partial^2 A}{\partial T^2}$. We are really only interested in the singular contributions to C_V, which means that we're only interested in differentiating with respect to T as it appears in $a(T)$. We divide by $N_{\mathsf{S}} k_B$ where N_{S} is the number of unit cells of our system, which we presume is a lattice-based model. Note $N_{\mathsf{S}} \sim V/\mathsf{a}^d$ where V is the volume and a the lattice constant. The dimensionless heat capacity per lattice site is then

$$c \equiv \frac{C_V}{N_{\mathsf{S}}} = \frac{\alpha^2 \mathsf{a}^d}{2\kappa^2} \int^{\Lambda} \frac{d^d q}{(2\pi)^d}\, \frac{1}{(\xi^{-2} + \boldsymbol{q}^2)^2} , \tag{7.312}$$

where $\xi = (\kappa/\alpha t)^{1/2} \propto |t|^{-1/2}$ is the correlation length, and where $\Lambda \sim \mathsf{a}^{-1}$ is an ultraviolet cutoff. We define $R_* \equiv (\kappa/\alpha)^{1/2}$, in which case

$$c = R_*^{-4}\, \mathsf{a}^d\, \xi^{4-d} \cdot \tfrac{1}{2} \int^{\Lambda\xi} \frac{d^d \bar{q}}{(2\pi)^d}\, \frac{1}{(1 + \bar{q}^2)^2} , \tag{7.313}$$

where $\bar{\boldsymbol{q}} \equiv \boldsymbol{q}\xi$. Thus,

$$c(t) \sim \begin{cases} \text{const.} & \text{if } d > 4 \\ -\ln t & \text{if } d = 4 \\ t^{\frac{d}{2}-2} & \text{if } d < 4 . \end{cases} \tag{7.314}$$

For $d > 4$, mean field theory is qualitatively accurate, with finite corrections. In dimensions $d \le 4$, the mean field result is overwhelmed by fluctuation contributions as $t \to 0^+$ (*i.e.* as $T \to T_c^+$). We see that MFT is sensible provided the fluctuation contributions are small, *i.e.* provided

$$R_*^{-4}\, \mathsf{a}^d\, \xi^{4-d} \ll 1 , \tag{7.315}$$

which entails $t \gg t_G$, where

$$t_G = \left(\frac{\mathsf{a}}{R_*} \right)^{\frac{2d}{4-d}} \tag{7.316}$$

is the *Ginzburg reduced temperature*. The criterion for the sufficiency of mean field theory, namely $t \gg t_G$, is known as the *Ginzburg criterion*. The region $|t| < t_G$ is known as the *critical region*.

In a lattice ferromagnet, as we have seen, $R_* \sim \mathsf{a}$ is on the scale of the lattice spacing itself, hence $t_G \sim 1$ and the critical regime is very large. Mean field theory then fails quickly as $T \to T_c$. In a (conventional) three-dimensional superconductor, R_* is on the order of the Cooper pair size, and $R_*/\mathsf{a} \sim 10^2 - 10^3$, hence $t_G = (a/R_*)^6 \sim 10^{-18} - 10^{-12}$ is negligibly narrow. The mean field theory of the superconducting transition – BCS theory – is then valid essentially all the way to $T = T_c$.

7.10 Appendix I : Equivalence of the Mean Field Descriptions

In both the variational density matrix and mean field Hamiltonian methods as applied to the Ising model, we obtained the same result $m = \tanh\big((m+h)/\theta\big)$. What is perhaps not obvious is whether these theories are in fact the same, *i.e.* if their respective free energies agree. Indeed, the two free energy functions,

$$\begin{aligned}
f_{\rm A}(m,h,\theta) &= -\tfrac{1}{2}\,m^2 - hm + \theta\left\{\left(\frac{1+m}{2}\right)\ln\left(\frac{1+m}{2}\right) + \left(\frac{1-m}{2}\right)\ln\left(\frac{1-m}{2}\right)\right\} \\
f_{\rm B}(m,h,\theta) &= +\tfrac{1}{2}\,m^2 - \theta\,\ln\left(e^{+(m+h)/\theta} + e^{-(m+h)/\theta}\right) ,
\end{aligned} \tag{7.317}$$

where $f_{\rm A}$ is the variational density matrix result and $f_{\rm B}$ is the mean field Hamiltonian result, clearly are different functions of their arguments. However, it turns out that upon minimizing with respect to m in each cast, the resulting free energies obey $f_{\rm A}(h,\theta) = f_{\rm B}(h,\theta)$. This agreement may seem surprising. The first method utilizes an approximate (variational) density matrix applied to the exact Hamiltonian $\hat{H}$. The second method approximates the Hamiltonian as $\hat{H}_{\rm MF}$, but otherwise treats it exactly. The two Landau expansions seem hopelessly different:

$$\begin{aligned}
f_{\rm A}(m,h,\theta) &= -\theta\,\ln 2 - hm + \tfrac{1}{2}\,(\theta-1)\,m^2 + \tfrac{\theta}{12}\,m^4 + \tfrac{\theta}{30}\,m^6 + \ldots \\
f_{\rm B}(m,h,\theta) &= -\theta\,\ln 2 + \tfrac{1}{2}m^2 - \frac{(m+h)^2}{2\,\theta} + \frac{(m+h)^4}{12\,\theta^3} - \frac{(m+h)^6}{45\,\theta^5} + \ldots\,.
\end{aligned} \tag{7.318}$$

We shall now prove that these two methods, the variational density matrix and the mean field approach, are in fact equivalent, and yield the *same* free energy $f(h,\theta)$.

Let us generalize the Ising model and write

$$\hat{H} = -\sum_{i<j} J_{ij}\,\varepsilon(\sigma_i,\sigma_j) - \sum_i \Phi(\sigma_i)\ . \tag{7.319}$$

Here, each 'spin' σ_i may take on any of K possible values, $\{s_1,\ldots,s_K\}$. For the $S=1$ Ising model, we would have $K=3$ possibilities, with $s_1=-1$, $s_2=0$, and $s_3=+1$. But the set $\{s_\alpha\}$, with $\alpha\in\{1,\ldots,K\}$, is completely arbitrary[20]. The 'local field' term $\Phi(\sigma)$ is also a completely arbitrary function. It may be linear, with $\Phi(\sigma)=H\sigma$, for example, but it could also contain terms quadratic in σ, or whatever one desires.

The symmetric, dimensionless interaction function $\varepsilon(\sigma,\sigma')=\varepsilon(\sigma',\sigma)$ is a real symmetric $K\times K$ matrix. According to the singular value decomposition theorem, any such matrix may be written in the form

$$\varepsilon(\sigma,\sigma') = \sum_{p=1}^{N_{\rm s}} A_p\,\lambda_p(\sigma)\,\lambda_p(\sigma')\ , \tag{7.320}$$

where the $\{A_p\}$ are coefficients (the singular values), and the $\big\{\lambda_p(\sigma)\big\}$ are the singular vectors. The number of terms $N_{\rm s}$ in this decomposition is such that $N_{\rm s}\le K$. This treatment can be generalized to account for continuous σ.

[20]It needn't be an equally spaced sequence, for example.

7.10.1 Variational Density Matrix

The most general single-site variational density matrix is written

$$\varrho(\sigma) = \sum_{\alpha=1}^{K} x_\alpha \, \delta_{\sigma,s_\alpha} \ . \tag{7.321}$$

Thus, x_α is the probability for a given site to be in state α, with $\sigma = s_\alpha$. *The* $\{x_\alpha\}$ *are the* K *variational parameters, subject to the single normalization constraint,* $\sum_\alpha x_\alpha = 1$. We now have

$$\begin{aligned} f &= \frac{1}{N\hat{J}(0)} \Big\{ \mathsf{Tr}\,(\varrho \hat{H}) + k_{\rm B}T \ \mathsf{Tr}\,(\varrho \ln \varrho) \Big\} \\ &= -\tfrac{1}{2} \sum_p \sum_{\alpha,\alpha'} A_p \, \lambda_p(s_\alpha) \, \lambda_p(s_{\alpha'}) \, x_\alpha \, x_{\alpha'} - \sum_\alpha \varphi(s_\alpha) \, x_\alpha + \theta \sum_\alpha x_\alpha \ln x_\alpha \ , \end{aligned} \tag{7.322}$$

where $\varphi(\sigma) = \Phi(\sigma)/\hat{J}(0)$. We extremize in the usual way, introducing a Lagrange undetermined multiplier ζ to enforce the constraint. This means we extend the function $f\big(\{x_\alpha\}\big)$, writing

$$f^*(x_1, \ldots, x_K, \zeta) = f(x_1, \ldots, x_K) + \zeta \left(\sum_{\alpha=1}^{K} x_\alpha - 1 \right) , \tag{7.323}$$

and freely extremizing with respect to the $(K+1)$ parameters $\{x_1, \ldots, x_K, \zeta\}$. This yields K nonlinear equations,

$$0 = \frac{\partial f^*}{\partial x_\alpha} = -\sum_p \sum_{\alpha'} A_p \, \lambda_p(s_\alpha) \, \lambda_p(s_{\alpha'}) \, x_{\alpha'} - \varphi(s_\alpha) + \theta \, \ln x_\alpha + \zeta + \theta \ , \tag{7.324}$$

for each α, and one linear equation, which is the normalization condition,

$$0 = \frac{\partial f^*}{\partial \zeta} = \sum_\alpha x_\alpha - 1 \ . \tag{7.325}$$

We cannot solve these nonlinear equations analytically, but they may be recast, by exponentiating them, as

$$x_\alpha = \frac{1}{Z} \, \exp\left\{ \frac{1}{\theta} \left[\sum_p \sum_{\alpha'} A_p \, \lambda_p(s_\alpha) \, \lambda_p(s_{\alpha'}) \, x_{\alpha'} + \varphi(s_\alpha) \right] \right\} , \tag{7.326}$$

with

$$Z = e^{(\zeta/\theta)+1} = \sum_\alpha \exp\left\{ \frac{1}{\theta} \left[\sum_p \sum_{\alpha'} A_p \, \lambda_p(s_\alpha) \, \lambda_p(s_{\alpha'}) \, x_{\alpha'} + \varphi(s_\alpha) \right] \right\} . \tag{7.327}$$

From the logarithm of x_α, we may compute the entropy, and, finally, the free energy:

$$f(\theta) = \tfrac{1}{2} \sum_p \sum_{\alpha,\alpha'} A_p \, \lambda_p(s_\alpha) \, \lambda_p(s_{\alpha'}) \, x_\alpha \, x_{\alpha'} - \theta \ln Z \ , \tag{7.328}$$

which is to be evaluated at the solution of 7.324, $\big\{x^*_\alpha(h, \theta)\big\}$

7.10.2 Mean Field Approximation

We now derive a mean field approximation in the spirit of that used in the Ising model above. We write

$$\lambda_p(\sigma) = \big\langle \lambda_p(\sigma) \big\rangle + \delta\lambda_p(\sigma) \ , \tag{7.329}$$

and abbreviate $\bar{\lambda}_p = \big\langle \lambda_p(\sigma) \big\rangle$, the thermodynamic average of $\lambda_p(\sigma)$ on any given site. We then have

$$\begin{aligned} \lambda_p(\sigma)\, \lambda_p(\sigma') &= \bar{\lambda}_p^2 + \bar{\lambda}_p\, \delta\lambda_p(\sigma) + \bar{\lambda}_p\, \delta\lambda_p(\sigma') + \delta\lambda_p(\sigma)\, \delta\lambda_p(\sigma') \\ &= -\bar{\lambda}_p^2 + \bar{\lambda}_p \big(\lambda_p(\sigma) + \lambda_p(\sigma')\big) + \delta\lambda_p(\sigma)\, \delta\lambda_p(\sigma') \ . \end{aligned} \tag{7.330}$$

The product $\delta\lambda_p(\sigma)\, \delta\lambda_p(\sigma')$ is of second order in fluctuations, and we neglect it. This leads us to the mean field Hamiltonian,

$$\hat{H}_{\rm MF} = +\tfrac{1}{2} N \hat{J}(0) \sum_p A_p\, \bar{\lambda}_p^2 - \sum_i \Big[\hat{J}(0) \sum_p A_p\, \bar{\lambda}_p\, \lambda_p(\sigma_i) + \Phi(\sigma_i) \Big] \ . \tag{7.331}$$

The free energy is then

$$f\big(\{\bar{\lambda}_p\}, \theta\big) = \tfrac{1}{2} \sum_p A_p\, \bar{\lambda}_p^2 - \theta\, \ln \sum_\alpha \exp \Bigg\{ \frac{1}{\theta} \Big[\sum_p A_p\, \bar{\lambda}_p\, \lambda_p(s_\alpha) + \varphi(s_\alpha) \Big] \Bigg\} \ . \tag{7.332}$$

The variational parameters are the mean field values $\{\bar{\lambda}_p\}$.

The single site probabilities $\{x_\alpha\}$ are then

$$x_\alpha = \frac{1}{Z}\, \exp \Bigg\{ \frac{1}{\theta} \Big[\sum_p A_p\, \bar{\lambda}_p\, \lambda_p(s_\alpha) + \varphi(s_\alpha) \Big] \Bigg\} \ , \tag{7.333}$$

with Z implied by the normalization $\sum_\alpha x_\alpha = 1$. These results reproduce exactly what we found in eqn. 7.324, since the mean field equation here, $\partial f / \partial \bar{\lambda}_p = 0$, yields

$$\bar{\lambda}_p = \sum_{\alpha=1}^{K} \lambda_p(s_\alpha)\, x_\alpha \ . \tag{7.334}$$

The free energy is immediately found to be

$$f(\theta) = \tfrac{1}{2} \sum_p A_p\, \bar{\lambda}_p^2 - \theta\, \ln Z \ , \tag{7.335}$$

which again agrees with what we found using the variational density matrix.

Thus, whether one extremizes with respect to the set $\{x_1, \ldots, x_K, \zeta\}$, or with respect to the set $\{\bar{\lambda}_p\}$, the results are the same, in terms of all these parameters, as well as the free energy $f(\theta)$. Generically, both approaches may be termed 'mean field theory' since the variational density matrix corresponds to a mean field which acts on each site independently[21].

[21]The function $\Phi(\sigma)$ may involve one or more adjustable parameters which could correspond, for example, to an external magnetic field h. We suppress these parameters when we write the free energy as $f(\theta)$.

7.11 Appendix II : Additional Examples

7.11.1 Blume-Capel model

The Blume-Capel model provides a simple and convenient way to model systems with vacancies. The simplest version of the model is written

$$\hat{H} = -\tfrac{1}{2}\sum_{i,j} J_{ij}\, S_i\, S_j + \Delta \sum_i S_i^2 \; . \tag{7.336}$$

The spin variables S_i range over the values $\{-1\,,\,0\,,\,+1\}$, so this is an extension of the $S=1$ Ising model. We explicitly separate out the diagonal terms, writing $J_{ii} \equiv 0$, and placing them in the second term on the RHS above. We say that site i is occupied if $S_i = \pm 1$ and vacant if $S_i = 0$, and we identify $-\Delta$ as the vacancy creation energy, which may be positive or negative, depending on whether vacancies are disfavored or favored in our system.

We make the mean field *Ansatz*, writing $S_i = m + \delta S_i$. This results in the mean field Hamiltonian,

$$\hat{H}_{\text{MF}} = \tfrac{1}{2} N \hat{J}(0)\, m^2 - \hat{J}(0)\, m \sum_i S_i + \Delta \sum_i S_i^2 \; . \tag{7.337}$$

Once again, we adimensionalize, writing $f \equiv F/N\hat{J}(0)$, $\theta = k_{\text{B}}T/\hat{J}(0)$, and $\delta = \Delta/\hat{J}(0)$. We assume $\hat{J}(0) > 0$. The free energy per site is then

$$f(\theta,\delta,m) = \tfrac{1}{2} m^2 - \theta \ln\Big(1 + 2e^{-\delta/\theta}\, \cosh(m/\theta)\Big) \; . \tag{7.338}$$

Extremizing with respect to m, we obtain the mean field equation,

$$m = \frac{2\sinh(m/\theta)}{\exp(\delta/\theta) + 2\cosh(m/\theta)} \; . \tag{7.339}$$

Note that $m=0$ is always a solution. Finding the slope of the RHS at $m=0$ and setting it to unity gives us the critical temperature:

$$\theta_{\text{c}} = \frac{2}{\exp(\delta/\theta_{\text{c}}) + 2} \; . \tag{7.340}$$

This is an implicit equation for θ_{c} in terms of the vacancy energy δ.

Let's now expand the free energy in terms of the magnetization m. We find, to fourth order,

$$\begin{aligned} f = -\theta \ln\big(1 + 2e^{-\delta/\theta}\big) &+ \frac{1}{2\theta}\bigg(\theta - \frac{2}{2+\exp(\delta/\theta)}\bigg) m^2 \\ &+ \frac{1}{12\,\big(2+\exp(\delta/\theta)\big)\theta^3}\,\bigg(\frac{6}{2+\exp(\delta/\theta)} - 1\bigg) m^4 + \ldots \; . \end{aligned} \tag{7.341}$$

Note that setting the coefficient of the m^2 term to zero yields the equation for θ_{c}. However, upon further examination, we see that the coefficient of the m^4 term can also vanish. As we have seen, when both the

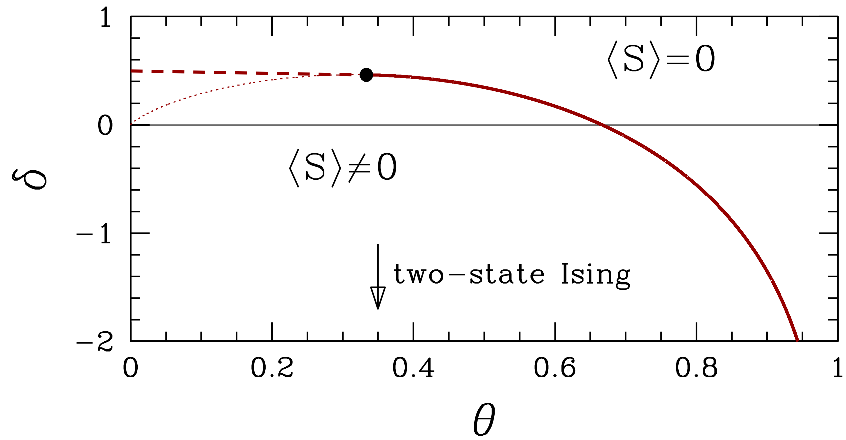

Figure 7.24: Mean field phase diagram for the Blume-Capel model. The black dot signifies a tricritical point, where the coefficients of m^2 and m^4 in the Landau free energy expansion both vanish. The dashed curve denotes a first order transition, and the solid curve a second order transition. The thin dotted line is the continuation of the $\theta_c(\delta)$ relation to zero temperature.

coefficients of the m^2 and the m^4 terms vanish, we have a tricritical point[22]. Setting both coefficients to zero, we obtain

$$\theta_t = \tfrac{1}{3} \quad , \quad \delta_t = \tfrac{2}{3} \ln 2 \,. \tag{7.342}$$

At $\theta = 0$, it is easy to see we have a first order transition, simply by comparing the energies of the paramagnetic ($S_i = 0$) and ferromagnetic ($S_i = +1$ or $S_i = -1$) states. We have

$$\frac{E_{\rm MF}}{N\hat{J}(0)} = \begin{cases} 0 & \text{if } m = 0 \\ \frac{1}{2} - \Delta & \text{if } m = \pm 1 \,. \end{cases} \tag{7.343}$$

These results are in fact exact, and not only valid for the mean field theory. Mean field theory is approximate because it neglects fluctuations, but at zero temperature, there are no fluctuations to neglect!

The phase diagram is shown in fig. 7.24. Note that for δ large and negative, vacancies are strongly disfavored, hence the only allowed states on each site have $S_i = \pm 1$, which is our old friend the two-state Ising model. Accordingly, the phase boundary there approaches the vertical line $\theta_c = 1$, which is the mean field transition temperature for the two-state Ising model.

7.11.2 Ising antiferromagnet in an external field

Consider the following model:

$$\hat{H} = J \sum_{\langle ij \rangle} \sigma_i \, \sigma_j - H \sum_i \sigma_i \,, \tag{7.344}$$

[22]We should really check that the coefficient of the sixth order term is positive, but that is left as an exercise to the eager student.

with $J > 0$ and $\sigma_i = \pm 1$. We've solved for the mean field phase diagram of the Ising ferromagnet; what happens if the interactions are antiferromagnetic?

It turns out that under certain circumstances, the ferromagnet and the antiferromagnet behave exactly the same in terms of their phase diagram, response functions, *etc.* This occurs when $H = 0$, and when the interactions are between nearest neighbors on a *bipartite lattice*. A bipartite lattice is one which can be divided into two sublattices, which we call A and B, such that an A site has only B neighbors, and a B site has only A neighbors. The square, honeycomb, and body centered cubic (BCC) lattices are bipartite. The triangular and face centered cubic lattices are non-bipartite. Now if the lattice is bipartite and the interaction matrix J_{ij} is nonzero only when i and j are from different sublattices (they needn't be nearest neighbors only), then we can simply redefine the spin variables such that

$$\sigma'_j = \begin{cases} +\sigma_j & \text{if } j \in \text{A} \\ -\sigma_j & \text{if } j \in \text{B} \,. \end{cases} \tag{7.345}$$

Then $\sigma'_i \sigma'_j = -\sigma_i\, \sigma_j$, and in terms of the new spin variables the exchange constant has reversed. The thermodynamic properties are invariant under such a redefinition of the spin variables.

We can see why this trick doesn't work in the presence of a magnetic field, because the field H would have to be reversed on the B sublattice. In other words, the thermodynamics of an Ising ferromagnet on a bipartite lattice in a uniform applied field is identical to that of the Ising antiferromagnet, with the same exchange constant (in magnitude), in the presence of a *staggered field* $H_\text{A} = +H$ and $H_\text{B} = -H$.

We treat this problem using the variational density matrix method, using two independent variational parameters m_A and m_B for the two sublattices:

$$\begin{aligned} \varrho_\text{A}(\sigma) &= \frac{1+m_\text{A}}{2}\, \delta_{\sigma,1} + \frac{1-m_\text{A}}{2}\, \delta_{\sigma,-1} \\ \varrho_\text{B}(\sigma) &= \frac{1+m_\text{B}}{2}\, \delta_{\sigma,1} + \frac{1-m_\text{B}}{2}\, \delta_{\sigma,-1} \,. \end{aligned} \tag{7.346}$$

With the usual adimensionalization, $f = F/NzJ$, $\theta = k_\text{B}T/zJ$, and $h = H/zJ$, we have the free energy

$$f(m_\text{A}, m_\text{B}) = \tfrac{1}{2} m_\text{A} m_\text{B} - \tfrac{1}{2}\, h\,(m_\text{A} + m_\text{B}) - \tfrac{1}{2}\, \theta\, s(m_\text{A}) - \tfrac{1}{2}\, \theta\, s(m_\text{B}) \,, \tag{7.347}$$

where the entropy function is

$$s(m) = -\left[\frac{1+m}{2}\, \ln\!\left(\frac{1+m}{2}\right) + \frac{1-m}{2}\, \ln\!\left(\frac{1-m}{2}\right) \right] . \tag{7.348}$$

Note that

$$\frac{ds}{dm} = -\tfrac{1}{2}\, \ln\!\left(\frac{1+m}{1-m}\right) \quad , \quad \frac{d^2 s}{dm^2} = -\frac{1}{1-m^2} \,. \tag{7.349}$$

Differentiating $f(m_\text{A}, m_\text{B})$ with respect to the variational parameters, we obtain two coupled mean field equations:

$$\begin{aligned} \frac{\partial f}{\partial m_\text{A}} = 0 \quad &\Longrightarrow \quad m_\text{B} = h - \frac{\theta}{2} \ln\!\left(\frac{1+m_\text{A}}{1-m_\text{A}}\right) \\ \frac{\partial f}{\partial m_\text{B}} = 0 \quad &\Longrightarrow \quad m_\text{A} = h - \frac{\theta}{2} \ln\!\left(\frac{1+m_\text{B}}{1-m_\text{B}}\right) . \end{aligned} \tag{7.350}$$

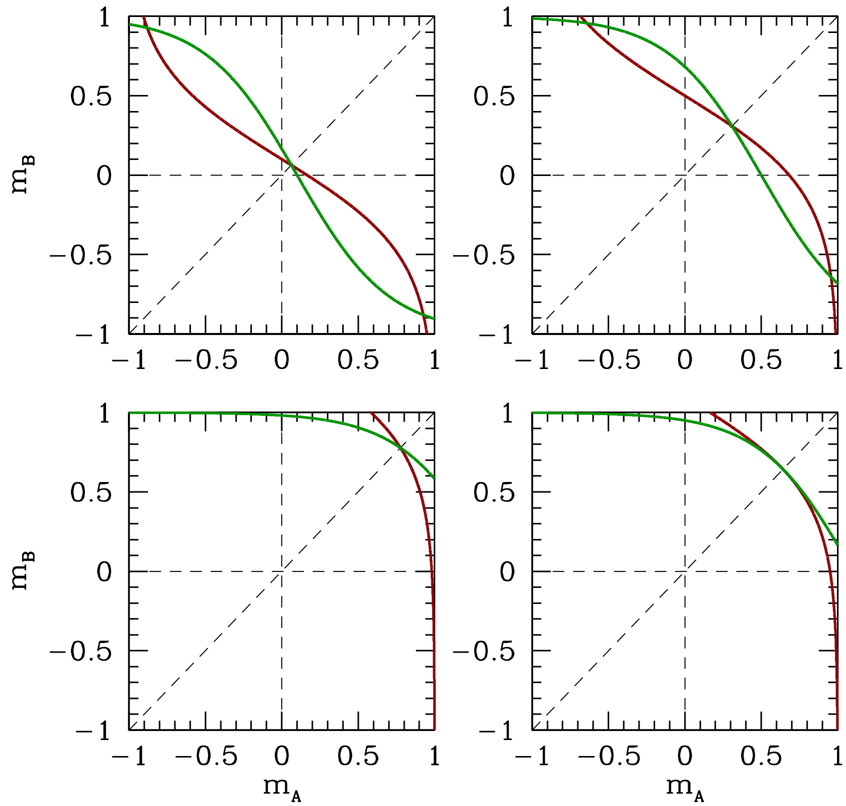

Figure 7.25: Graphical solution to the mean field equations for the Ising antiferromagnet in an external field, here for $\theta = 0.6$. Clockwise from upper left: (a) $h = 0.1$, (b) $h = 0.5$, (c) $h = 1.1$, (d) $h = 1.4$.

Recognizing $\tanh^{-1}(x) = \frac{1}{2}\ln\Big[(1+x)/(1-x)\Big]$, we may write these equations in an equivalent but perhaps more suggestive form:

$$m_{\rm A} = \tanh\left(\frac{h - m_{\rm B}}{\theta}\right) \qquad , \qquad m_{\rm B} = \tanh\left(\frac{h - m_{\rm A}}{\theta}\right) . \tag{7.351}$$

In other words, the A sublattice sites see an internal field $H_{\rm A,int} = -zJm_{\rm B}$ from their B neighbors, and the B sublattice sites see an internal field $H_{\rm B,int} = -zJm_{\rm A}$ from their A neighbors.

We can solve these equations graphically, as in fig. 7.25. Note that there is always a paramagnetic solution with $m_{\rm A} = m_{\rm B} = m$, where

$$m = h - \frac{\theta}{2}\,\ln\!\left(\frac{1+m}{1-m}\right) \qquad \Longleftrightarrow \qquad m = \tanh\left(\frac{h-m}{\theta}\right) . \tag{7.352}$$

However, we can see from the figure that there will be *three* solutions to the mean field equations provided that $\frac{\partial m_{\rm A}}{\partial m_{\rm B}} < -1$ at the point of the solution where $m_{\rm A} = m_{\rm B} = m$. This gives us two equations with which to eliminate $m_{\rm A}$ and $m_{\rm B}$, resulting in the curve

$$h^*(\theta) = m + \frac{\theta}{2}\,\ln\!\left(\frac{1+m}{1-m}\right) \qquad \text{with } \ m = \sqrt{1-\theta}\ . \tag{7.353}$$

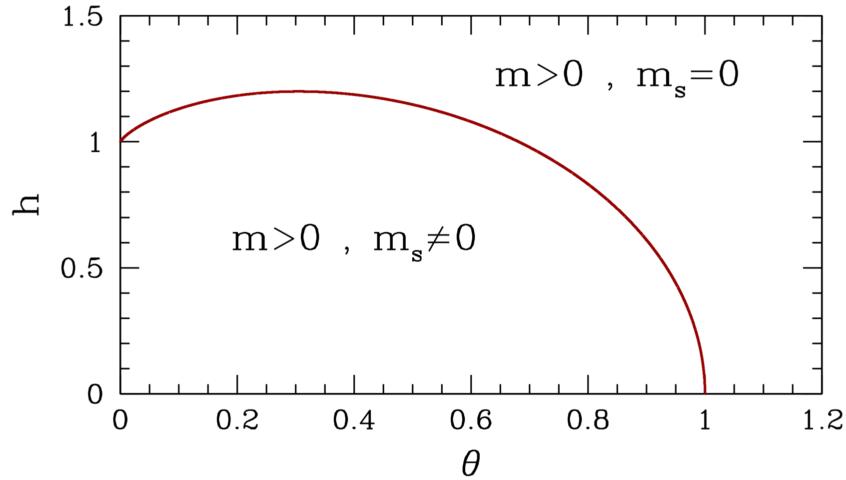

Figure 7.26: Mean field phase diagram for the Ising antiferromagnet in an external field. The phase diagram is symmetric under reflection in the $h = 0$ axis.

Thus, for $\theta < 1$ and $|h| < h^*(\theta)$ there are three solutions to the mean field equations. It is *usually* the case, the broken symmetry solutions, which mean those for which $m_{\rm A} \neq m_{\rm B}$ in our case, are of lower energy than the symmetric solution(s). We show the curve $h^*(\theta)$ in fig. 7.26.

We can make additional progress by defining the average and staggered magnetizations m and $m_{\rm s}$,

$$m \equiv \tfrac{1}{2}(m_{\rm A} + m_{\rm B}) \qquad , \qquad m_{\rm s} \equiv \tfrac{1}{2}(m_{\rm A} - m_{\rm B}) \ . \tag{7.354}$$

We expand the free energy in terms of $m_{\rm s}$:

$$\begin{aligned} f(m, m_{\rm s}) &= \tfrac{1}{2}m^2 - \tfrac{1}{2}m_{\rm s}^2 - h\,m - \tfrac{1}{2}\,\theta\, s(m + m_{\rm s}) - \tfrac{1}{2}\,\theta\, s(m - m_{\rm s}) \\ &= \tfrac{1}{2}m^2 - h\,m - \theta\, s(m) - \tfrac{1}{2}\Big(1 + \theta\, s''(m)\Big)\, m_{\rm s}^2 - \tfrac{1}{24}\,\theta\, s''''(m)\, m_{\rm s}^4 + \ldots \ . \end{aligned} \tag{7.355}$$

The term quadratic in $m_{\rm s}$ vanishes when $\theta\, s''(m) = -1$, *i.e.* when $m = \sqrt{1-\theta}$. It is easy to obtain

$$\frac{d^3 s}{dm^3} = -\frac{2m}{(1-m^2)^2} \qquad , \qquad \frac{d^4 s}{dm^4} = -\frac{2\,(1+3m^2)}{(1-m^2)^3} \ , \tag{7.356}$$

from which we learn that the coefficient of the quartic term, $-\frac{1}{24}\,\theta\, s''''(m)$, never vanishes. Therefore the transition remains second order down to $\theta = 0$, where it finally becomes first order.

We can confirm the $\theta \to 0$ limit directly. The two competing states are the ferromagnet, with $m_{\rm A} = m_{\rm B} = \pm 1$, and the antiferromagnet, with $m_{\rm A} = -m_{\rm B} = \pm 1$. The free energies of these states are

$$f^{\rm FM} = \tfrac{1}{2} - h \qquad , \qquad f^{\rm AFM} = -\tfrac{1}{2} \ . \tag{7.357}$$

There is a first order transition when $f^{\rm FM} = f^{\rm AFM}$, which yields $h = 1$.

7.11.3 Canted quantum antiferromagnet

Consider the following model for *quantum* $S = \frac{1}{2}$ spins:

$$\hat{H} = \sum_{\langle ij \rangle} \Big[-J\big(\sigma_i^x \sigma_j^x + \sigma_i^y \sigma_j^y\big) + \Delta\, \sigma_i^z \sigma_j^z \Big] + \tfrac{1}{4} K \sum_{\langle ijkl \rangle} \sigma_i^z \sigma_j^z \sigma_k^z \sigma_l^z \ , \tag{7.358}$$

where $\boldsymbol{\sigma}_i$ is the vector of Pauli matrices on site i. The spins live on a square lattice. The second sum is over all square plaquettes. All the constants J, Δ, and K are positive.

Let's take a look at the Hamiltonian for a moment. The J term clearly wants the spins to align ferromagnetically in the (x, y) plane (in internal spin space). The Δ term prefers antiferromagnetic alignment along the $\hat{\boldsymbol{z}}$ axis. The K term discourages any kind of moment along $\hat{\boldsymbol{z}}$ and works against the Δ term. We'd like our mean field theory to capture the physics behind this competition.

Accordingly, we break up the square lattice into two interpenetrating $\sqrt{2} \times \sqrt{2}$ square sublattices (each rotated by $45°$ with respect to the original), in order to be able to describe an antiferromagnetic state. In addition, we include a parameter α which describes the *canting angle* that the spins on these sublattices make with respect to the $\hat{\boldsymbol{x}}$-axis. That is, we write

$$\begin{aligned} \varrho_{\text{A}} &= \tfrac{1}{2} + \tfrac{1}{2} m \left(\sin\alpha\, \sigma^x + \cos\alpha\, \sigma^z \right) \\ \varrho_{\text{B}} &= \tfrac{1}{2} + \tfrac{1}{2} m \left(\sin\alpha\, \sigma^x - \cos\alpha\, \sigma^z \right) . \end{aligned} \tag{7.359}$$

Note that $\mathsf{Tr}\ \varrho_{\text{A}} = \mathsf{Tr}\ \varrho_{\text{B}} = 1$ so these density matrices are normalized. Note also that the mean direction for a spin on the A and B sublattices is given by

$$\boldsymbol{m}_{\text{A,B}} = \mathsf{Tr}\,(\varrho_{\text{A,B}}\, \boldsymbol{\sigma}) = \pm\, m \cos\alpha\, \hat{\boldsymbol{z}} + m \sin\alpha\, \hat{\boldsymbol{x}} \ . \tag{7.360}$$

Thus, when $\alpha = 0$, the system is an antiferromagnet with its staggered moment lying along the $\hat{\boldsymbol{z}}$ axis. When $\alpha = \frac{1}{2}\pi$, the system is a ferromagnet with its moment lying along the $\hat{\boldsymbol{x}}$ axis.

Finally, the eigenvalues of $\varrho_{\text{A,B}}$ are still $\lambda_\pm = \frac{1}{2}(1 \pm m)$, hence

$$\begin{aligned} s(m) &\equiv -\,\mathsf{Tr}\,(\varrho_{\text{A}} \ln \varrho_{\text{A}}) = -\,\mathsf{Tr}\,(\varrho_{\text{B}} \ln \varrho_{\text{B}}) \\ &= -\left[\frac{1+m}{2}\, \ln\!\left(\frac{1+m}{2}\right) + \frac{1-m}{2}\, \ln\!\left(\frac{1-m}{2}\right) \right] . \end{aligned} \tag{7.361}$$

Note that we have taken $m_{\text{A}} = m_{\text{B}} = m$, unlike the case of the antiferromagnet in a uniform field. The reason is that there remains in our model a symmetry between A and B sublattices.

The free energy is now easily calculated:

$$\begin{aligned} F &= \mathsf{Tr}\,(\varrho \hat{H}) + k_{\text{B}} T\, \mathsf{Tr}\,(\varrho \ln \varrho) \\ &= -2N \Big(J \sin^2\!\alpha + \Delta \cos^2\!\alpha \Big)\, m^2 + \tfrac{1}{4} N K m^4 \cos^4\!\alpha - N k_{\text{B}} T\, s(m) \end{aligned} \tag{7.362}$$

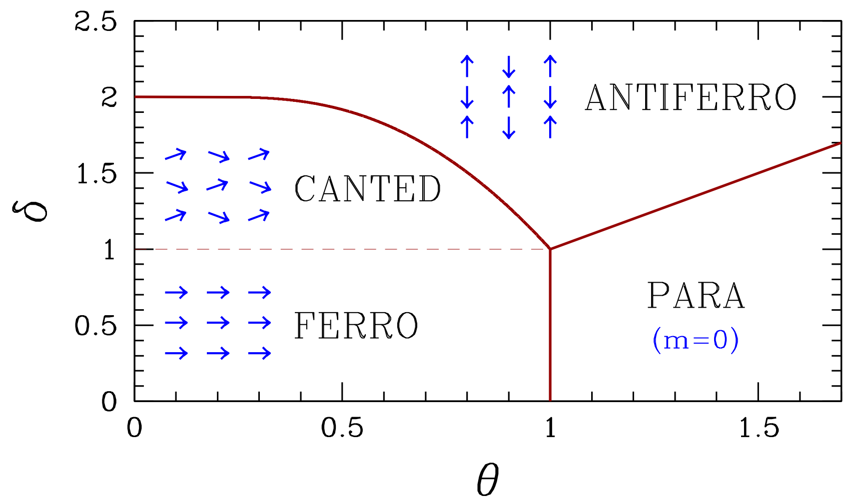

Figure 7.27: Mean field phase diagram for the model of eqn. 7.358 for the case $\kappa = 1$.

We can adimensionalize by defining $\delta \equiv \Delta/J$, $\kappa \equiv K/4J$, and $\theta \equiv k_{\mathrm{B}}T/4J$. Then the free energy per site is $f \equiv F/4NJ$ is

$$f(m,\alpha) = -\tfrac{1}{2}m^2 + \tfrac{1}{2}\big(1-\delta\big)\,m^2\cos^2\!\alpha + \tfrac{1}{4}\kappa\,m^4\cos^4\!\alpha - \theta\,s(m)\ . \tag{7.363}$$

There are two variational parameters: m and θ. We thus obtain two coupled mean field equations,

$$\begin{aligned}\frac{\partial f}{\partial m} &= 0 = -m + \big(1-\delta\big)\,m\,\cos^2\!\alpha + \kappa\,m^3\cos^4\!\alpha + \tfrac{1}{2}\theta\,\ln\!\bigg(\frac{1+m}{1-m}\bigg)\\ \frac{\partial f}{\partial \alpha} &= 0 = \Big(1-\delta+\kappa\,m^2\cos^2\!\alpha\Big)\,m^2\sin\alpha\,\cos\alpha\ .\end{aligned} \tag{7.364}$$

Let's start with the second of the mean field equations. Assuming $m \neq 0$, it is clear from eqn. 7.363 that

$$\cos^2\!\alpha = \begin{cases} 0 & \text{if }\ \delta < 1 \\ (\delta-1)/\kappa m^2 & \text{if }\ 1 \le \delta \le 1+\kappa\,m^2 \\ 1 & \text{if }\ \delta \ge 1+\kappa\,m^2\ . \end{cases} \tag{7.365}$$

Suppose $\delta < 1$. Then we have $\cos\alpha = 0$ and the first mean field equation yields the familiar result

$$m = \tanh\big(m/\theta\big)\ . \tag{7.366}$$

Along the θ axis, then, we have the usual ferromagnet-paramagnet transition at $\theta_{\mathrm{c}} = 1$.

For $1 < \delta < 1 + \kappa m^2$ we have canting with an angle

$$\alpha = \alpha^*(m) = \cos^{-1}\sqrt{\frac{\delta-1}{\kappa\,m^2}}\ . \tag{7.367}$$

Substituting this into the first mean field equation, we once again obtain the relation $m = \tanh\big(m/\theta\big)$. However, eventually, as θ is increased, the magnetization will dip below the value $m_0 \equiv \sqrt{(\delta-1)/\kappa}$. This occurs at a dimensionless temperature

$$\theta_0 = \frac{m_0}{\tanh^{-1}(m_0)} < 1 \qquad ; \qquad m_0 = \sqrt{\frac{\delta-1}{\kappa}} \,. \tag{7.368}$$

For $\theta > \theta_0$, we have $\delta > 1 + \kappa m^2$, and we must take $\cos^2\!\alpha = 1$. The first mean field equation then becomes

$$\delta m - \kappa m^3 = \frac{\theta}{2}\,\ln\!\bigg(\frac{1+m}{1-m}\bigg)\,, \tag{7.369}$$

or, equivalently, $m = \tanh\big((\delta m - \kappa m^3)/\theta\big)$. A simple graphical analysis shows that a nontrivial solution exists provided $\theta < \delta$. Since $\cos\alpha = \pm 1$, this solution describes an antiferromagnet, with $\boldsymbol{m}_{\rm A} = \pm m\hat{\boldsymbol{z}}$ and $\boldsymbol{m}_{\rm B} = \mp m\hat{\boldsymbol{z}}$. The resulting mean field phase diagram is then as depicted in fig. 7.27.

7.11.4 Coupled order parameters

Consider the Landau free energy

$$f(m,\phi) = \tfrac{1}{2}\,a_m\,m^2 + \tfrac{1}{4}\,b_m\,m^4 + \tfrac{1}{2}\,a_\phi\,\phi^2 + \tfrac{1}{4}\,b_\phi\,\phi^4 + \tfrac{1}{2}\varLambda\,m^2\,\phi^2\,. \tag{7.370}$$

We write

$$a_m \equiv \alpha_m\,\theta_m \qquad , \qquad a_\phi = \alpha_\phi\,\theta_\phi\,, \tag{7.371}$$

where

$$\theta_m = \frac{T - T_{{\rm c},m}}{T_0} \qquad , \qquad \theta_\phi = \frac{T - T_{{\rm c},\phi}}{T_0}\,, \tag{7.372}$$

where T_0 is some temperature scale. We assume without loss of generality that $T_{{\rm c},m} > T_{{\rm c},\phi}$. We begin by rescaling:

$$m \equiv \bigg(\frac{\alpha_m}{b_m}\bigg)^{\!1/2}\,\widetilde{m} \qquad , \qquad \phi \equiv \bigg(\frac{\alpha_m}{b_m}\bigg)^{\!1/2}\,\widetilde{\phi}\,. \tag{7.373}$$

We then have

$$f = \varepsilon_0\,\Big\{ r\,\big(\tfrac{1}{2}\theta_m\,\widetilde{m}^2 + \tfrac{1}{4}\,\widetilde{m}^4\big) + r^{-1}\,\big(\tfrac{1}{2}\,\theta_\phi\,\widetilde{\phi}^2 + \tfrac{1}{4}\,\widetilde{\phi}^4\big) + \tfrac{1}{2}\,\lambda\,\widetilde{m}^2\widetilde{\phi}^2 \Big\}\,, \tag{7.374}$$

where

$$\varepsilon_0 = \frac{\alpha_m\,\alpha_\phi}{(b_m\,b_\phi)^{1/2}} \qquad , \qquad r = \frac{\alpha_m}{\alpha_\phi}\,\bigg(\frac{b_\phi}{b_m}\bigg)^{\!1/2} \qquad , \qquad \lambda = \frac{\varLambda}{(b_m\,b_\phi)^{1/2}}\,. \tag{7.375}$$

It proves convenient to perform one last rescaling, writing

$$\tilde{m} \equiv r^{-1/4}\,\mathsf{m} \quad , \quad \tilde{\phi} \equiv r^{1/4}\,\varphi\,. \tag{7.376}$$

Then

$$f = \varepsilon_0 \Big\{ \tfrac{1}{2} q\,\theta_m\,\mathsf{m}^2 + \tfrac{1}{4}\,\mathsf{m}^4 + \tfrac{1}{2} q^{-1}\,\theta_\phi\,\varphi^2 + \tfrac{1}{4}\,\varphi^4 + \tfrac{1}{2}\,\lambda\,\mathsf{m}^2\,\varphi^2 \Big\}\,, \tag{7.377}$$

where
$$q = \sqrt{r} = \left(\frac{\alpha_m}{\alpha_\phi}\right)^{1/2} \left(\frac{b_\phi}{b_m}\right)^{1/4} . \tag{7.378}$$

Note that we may write
$$f(\mathsf{m},\varphi) = \frac{\varepsilon_0}{4} \begin{pmatrix} \mathsf{m}^2 & \varphi^2 \end{pmatrix} \begin{pmatrix} 1 & \lambda \\ \lambda & 1 \end{pmatrix} \begin{pmatrix} \mathsf{m}^2 \\ \varphi^2 \end{pmatrix} + \frac{\varepsilon_0}{2} \begin{pmatrix} \mathsf{m}^2 & \varphi^2 \end{pmatrix} \begin{pmatrix} q\,\theta_m \\ q^{-1}\,\theta_\phi \end{pmatrix} . \tag{7.379}$$

The eigenvalues of the above 2×2 matrix are $1 \pm \lambda$, with corresponding eigenvectors $\binom{1}{\pm 1}$. Since $\varphi^2 > 0$, we are only interested in the first eigenvector $\binom{1}{1}$, corresponding to the eigenvalue $1 + \lambda$. Clearly when $\lambda < 1$ the free energy is unbounded from below, which is unphysical.

We now set
$$\frac{\partial f}{\partial \mathsf{m}} = 0 \qquad , \qquad \frac{\partial f}{\partial \varphi} = 0 \, , \tag{7.380}$$
and identify four possible phases:

- Phase I : $\mathsf{m} = 0$, $\varphi = 0$. The free energy is $f_{\mathrm{I}} = 0$.
- Phase II : $\mathsf{m} \neq 0$ with $\varphi = 0$. The free energy is
$$f = \frac{\varepsilon_0}{2} \left(q\,\theta_m\,\mathsf{m}^2 + \tfrac{1}{2}\,\mathsf{m}^4\right) , \tag{7.381}$$
hence we require $\theta_m < 0$ in this phase, in which case
$$\mathsf{m}_{\mathrm{II}} = \sqrt{-q\,\theta_m} \qquad , \qquad f_{\mathrm{II}} = -\frac{\varepsilon_0}{4}\,q^2\,\theta_m^2 \, . \tag{7.382}$$
- Phase III : $m = 0$ with $\varphi \neq 0$. The free energy is
$$f = \frac{\varepsilon_0}{2} \left(q^{-1}\,\theta_\phi\,\varphi^2 + \tfrac{1}{2}\,\varphi^4\right) , \tag{7.383}$$
hence we require $\theta_\phi < 0$ in this phase, in which case
$$\varphi_{\mathrm{III}} = \sqrt{-q^{-1}\,\theta_\phi} \qquad , \qquad f_{\mathrm{III}} = -\frac{\varepsilon_0}{4}\,q^{-2}\,\theta_\phi^2 \, . \tag{7.384}$$
- Phase IV : $\mathsf{m} \neq 0$ and $\varphi \neq 0$. Varying f yields
$$\begin{pmatrix} 1 & \lambda \\ \lambda & 1 \end{pmatrix} \begin{pmatrix} \mathsf{m}^2 \\ \varphi^2 \end{pmatrix} = -\begin{pmatrix} q\,\theta_m \\ q^{-1}\,\theta_\phi \end{pmatrix} , \tag{7.385}$$
with solution
$$\begin{aligned} \mathsf{m}^2 &= \frac{q\,\theta_m - q^{-1}\,\theta_\phi\,\lambda}{\lambda^2 - 1} \\ \varphi^2 &= \frac{q^{-1}\,\theta_\phi - q\,\theta_m\,\lambda}{\lambda^2 - 1} \, . \end{aligned} \tag{7.386}$$

Since m^2 and φ^2 must each be nonnegative, phase IV exists only over a yet-to-be-determined subset of the entire parameter space. The free energy is

$$f_{\mathrm{IV}} = \frac{q^2\,\theta_m^2 + q^{-2}\,\theta_\phi^2 - 2\lambda\,\theta_m\,\theta_\phi}{4(\lambda^2-1)} \ . \tag{7.387}$$

We now define $\theta \equiv \theta_m$ and $\tau \equiv \theta_\phi - \theta_m = (T_{\mathrm{c},m} - T_{\mathrm{c},\phi)})/T_0$. Note that $\tau > 0$. There are three possible temperature ranges to consider.

(1) $\theta_\phi > \theta_m > 0$. The only possible phases are I and IV. For phase IV, we must impose the conditions $m^2 > 0$ and $\phi^2 > 0$. If $\lambda^2 > 1$, then the numerators in eqns. 7.386 must each be positive:

$$\lambda < \frac{q^2\,\theta_m}{\theta_\phi} \quad , \quad \lambda < \frac{\theta_\phi}{q^2\,\theta_m} \quad \Rightarrow \quad \lambda < \min\!\left(\frac{q^2\,\theta_m}{\theta_\phi}\, , \, \frac{\theta_\phi}{q^2\theta_m}\right) . \tag{7.388}$$

But since either $q^2\theta_m/\theta_\phi$ or its inverse must be less than or equal to unity, this requires $\lambda < -1$, which is unphysical.

If on the other hand we assume $\lambda^2 < 1$, the non-negativeness of m^2 and φ^2 requires

$$\lambda > \frac{q^2\,\theta_m}{\theta_\phi} \quad , \quad \lambda > \frac{\theta_\phi}{q^2\,\theta_m} \quad \Rightarrow \quad \lambda > \max\!\left(\frac{q^2\,\theta_m}{\theta_\phi}\, , \, \frac{\theta_\phi}{q^2\theta_m}\right) > 1 \ . \tag{7.389}$$

Thus, $\lambda > 1$ and we have a contradiction.

Therefore, the only allowed phase for $\theta > 0$ is phase I.

(2) $\theta_\phi > 0 > \theta_m$. Now the possible phases are I, II, and IV. We can immediately rule out phase I because $f_{\mathrm{II}} < f_{\mathrm{I}}$. To compare phases II and IV, we compute

$$\Delta f = f_{\mathrm{IV}} - f_{\mathrm{II}} = \frac{(q\,\lambda\,\theta_m - q^{-1}\,\theta_\phi)^2}{4(\lambda^2-1)} \ . \tag{7.390}$$

Thus, phase II has the lower energy if $\lambda^2 > 1$. For $\lambda^2 < 1$, phase IV has the lower energy, but the conditions $\mathsf{m}^2 > 0$ and $\varphi^2 > 0$ then entail

$$\frac{q^2\theta_m}{\theta_\phi} < \lambda < \frac{\theta_\phi}{q^2\theta_m} \quad \Rightarrow \quad q^2|\theta_m| > \theta_\phi > 0 \ . \tag{7.391}$$

Thus, λ is restricted to the range

$$\lambda \in \left[-1 \, , \, -\frac{\theta_\phi}{q^2|\theta_m|}\right] . \tag{7.392}$$

With $\theta_m \equiv \theta < 0$ and $\theta_\phi \equiv \theta + \tau > 0$, the condition $q^2|\theta_m| > \theta_\phi$ is found to be

$$-\tau < \theta < -\frac{\tau}{q^2+1} \ . \tag{7.393}$$

Thus, phase IV exists and has lower energy when

$$-\tau < \theta < -\frac{\tau}{r+1} \quad \text{and} \quad -1 < \lambda < -\frac{\theta+\tau}{r\theta} \ , \tag{7.394}$$

where $r = q^2$.

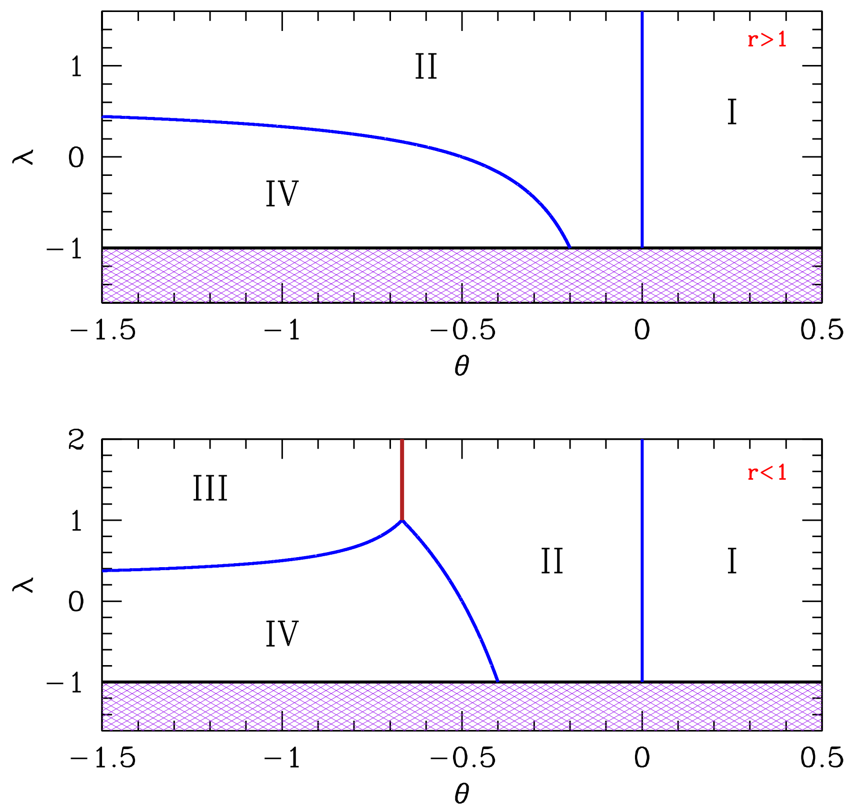

Figure 7.28: Phase diagram for $\tau = 0.5$, $r = 1.5$ (top) and $\tau = 0.5$, $r = 0.25$ (bottom). The hatched purple region is unphysical, with a free energy unbounded from below. The blue lines denote second order transitions. The thick red line separating phases II and III is a first order line.

(3) $0 > \theta_\phi > \theta_m$. In this regime, any phase is possible, however once again phase I can be ruled out since phases II and III are of lower free energy. The condition that phase II have lower free energy than phase III is

$$f_{\text{II}} - f_{\text{III}} = \frac{\varepsilon_0}{4}\big(q^{-2}\theta_\phi^2 - q^2\theta_m^2\big) < 0 \,, \tag{7.395}$$

i.e. $|\theta_\phi| < r|\theta_m|$, which means $r|\theta| > |\theta| - \tau$. If $r > 1$ this is true for all $\theta < 0$, while if $r < 1$ phase II is lower in energy only for $|\theta| < \tau/(1-r)$.

We next need to test whether phase IV has an even lower energy than the lower of phases II and III. We have

$$\begin{aligned} f_{\text{IV}} - f_{\text{II}} &= \frac{(q\,\lambda\,\theta_m - q^{-1}\,\theta_\phi)^2}{4(\lambda^2-1)} \\ f_{\text{IV}} - f_{\text{III}} &= \frac{(q\,\theta_m - q^{-1}\,\lambda\,\theta_\phi)^2}{4(\lambda^2-1)} \,. \end{aligned} \tag{7.396}$$

In both cases, phase IV can only be the true thermodynamic phase if $\lambda^2 < 1$. We then require

$\mathsf{m}^2 > 0$ and $\varphi^2 > 0$, which fixes

$$\lambda \in \Bigg[-1 \, , \, \min\!\bigg(\frac{q^2\,\theta_m}{\theta_\phi} \, , \, \frac{\theta_\phi}{q^2\theta_m} \bigg) \Bigg] \, . \tag{7.397}$$

The upper limit will be the first term inside the rounded brackets if $q^2|\theta_m| < \theta_\phi$, *i.e.* if $r|\theta| < |\theta| - \tau$. This is impossible if $r > 1$, hence the upper limit is given by the second term in the rounded brackets:

$$r > 1 \ : \ \lambda \in \Bigg[-1 \, , \, \frac{\theta+\tau}{r\,\theta} \Bigg] \qquad \text{(condition for phase IV)} \, . \tag{7.398}$$

If $r < 1$, then the upper limit will be $q^2\theta_m/\theta_\phi = r\theta/(\theta+\tau)$ if $|\theta| > \tau/(1-r)$, and will be $\theta_\phi/q^2\theta_m = (\theta+\tau)/r\theta$ if $|\theta| < \tau/(1-r)$.

$$\begin{aligned} r < 1 \, , \, -\frac{\tau}{1-r} < \theta < -\tau \ &: \ \lambda \in \Bigg[-1 \, , \, \frac{\theta+\tau}{r\theta} \Bigg] \qquad \text{(phase IV)} \\ r < 1 \, , \, \theta < -\frac{\tau}{1-r} \ &: \ \lambda \in \Bigg[-1 \, , \, \frac{r\theta}{\theta+\tau} \Bigg] \qquad \text{(phase IV)} \, . \end{aligned} \tag{7.399}$$

Representative phase diagrams for the cases $r > 1$ and $r < 1$ are shown in fig. 7.28.