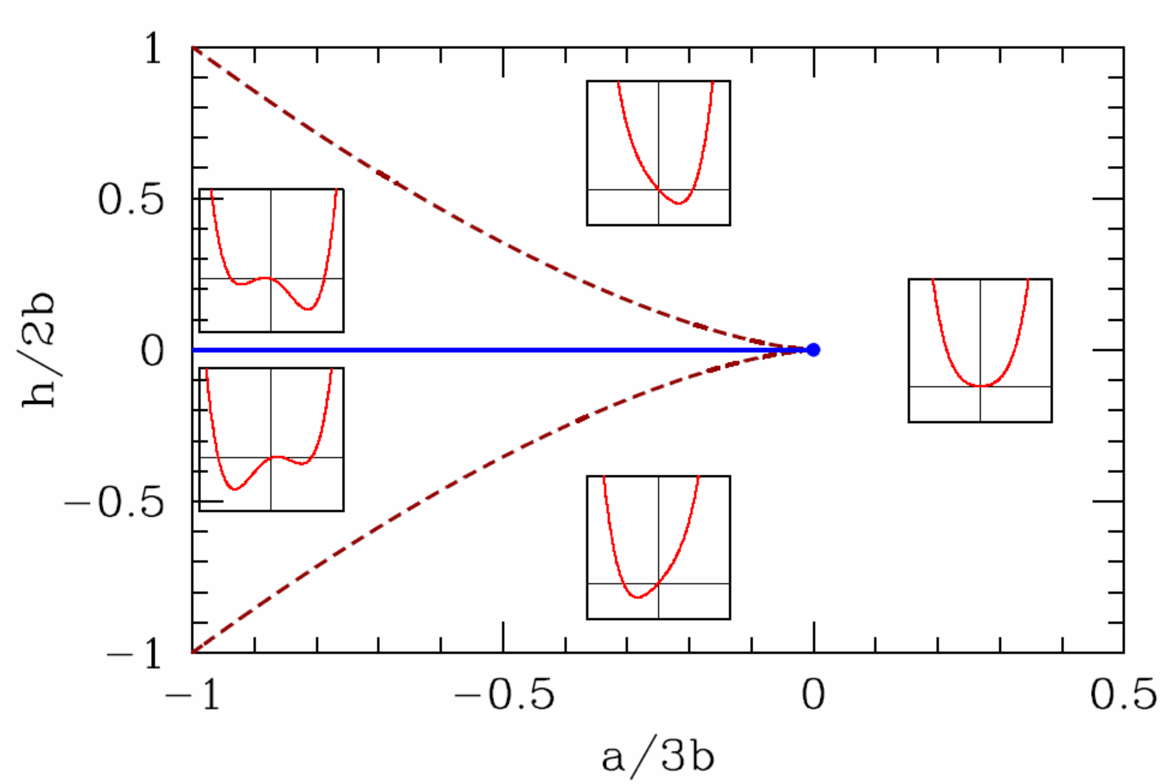
7.5: Landau Theory of Phase Transitions

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, at temperatures such that the order parameter, if nonzero, is still small.



[Landau_a] 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 $f(m)$.

Quartic free energy with Ising symmetry

The simplest example is the quartic free energy,

$$f(m, h=0, \theta) = f_0 + \frac{1}{2}am^2 + \frac{1}{4}bm^4 \ , \tag{7.5.1}$$

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 ,

$$\frac{\partial f}{\partial m} = 0 = am + bm^3 \ , \tag{7.5.2}$$

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

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

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

$$c\big(\theta_c^+\big) - c\big(\theta_c^-\big) = -\theta_c \, \frac{\partial^2}{\partial\theta^2}\bigg|_{\theta=\theta_c} \left(\frac{a^2}{4b}\right) = -\frac{\theta_c \left[a'(\theta_c)\right]^2}{2b(\theta_c)} \ . \tag{7.5.3}$$

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

$$f(m,h,\theta) = f_0 + \frac{1}{2}am^2 + \frac{1}{4}bm^4 - hm \ , \tag{7.5.4}$$

and the mean field equation is

$$bm^3 + am - h = 0 \ . \tag{7.5.5}$$

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

$$h^*(a) = \pm \frac{2}{3^{3/2}} \, \frac{(-a)^{3/2}}{b^{1/2}} \ , \tag{7.5.6}$$

or, equivalently,

$$a^*(h) = -\frac{3}{2^{2/3}} \, b^{1/3} \, |h|^{2/3}. \tag{7.5.7}$$

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

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

Cubic terms in Landau theory : first order transitions

Next, consider a free energy with a cubic term,

$$f = f_0 + \frac{1}{2}am^2 - \frac{1}{3}ym^3 + \frac{1}{4}bm^4 \ , \tag{7.5.8}$$

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 $m \to -m$ ($\mathbb{Z}_2$) 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

$$\frac{\partial f}{\partial m} = 0 = am - ym^2 + bm^3 \ . \tag{7.5.9}$$

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

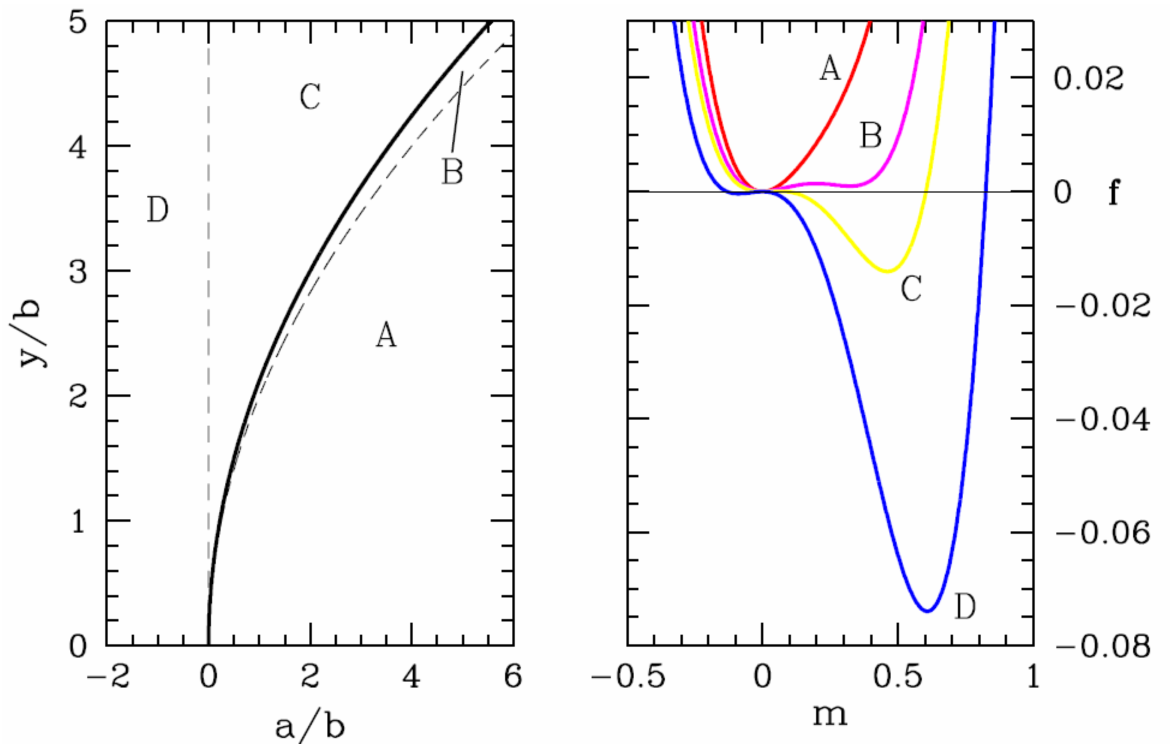
$$m=m_{\pm}\equiv\frac{y}{2b}\pm\sqrt{\left(\frac{y}{2b}\right)^2-\frac{a}{b}}\ . \tag{7.5.10}$$

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

$$f(m)=f(0)\quad\Longrightarrow\quad\frac{1}{2}am^2-\frac{1}{3}ym^3+\frac{1}{4}bm^4=0\ , \tag{7.5.11}$$

and we now have two quadratic equations to solve simultaneously:

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



[quartic] 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.

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

$$y^2=\frac{9}{2}\,ab\ . \tag{7.5.12}$$

Thus, we have the following:

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

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 Figure [quartic].

With $y = 0$, we have a second order transition at $a = 0$. With $y \neq 0$, there is a discontinuous (first order) transition at $a_c = 2y^2/9b > 0$ and $m_c = 2y/3b$. 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 $T_c = T_0 + 2y^2/9\alpha b$.

Magnetization dynamics

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

$$\frac{\partial m}{\partial t} = -\Gamma \, \frac{\partial f}{\partial m} \ , \tag{7.5.13}$$

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

$$m \equiv \frac{y}{b} \cdot u \qquad , \qquad a \equiv \frac{y^2}{b} \cdot r \qquad , \qquad t \equiv \frac{b}{\Gamma y^2} \cdot s \ . \tag{7.5.14}$$

Then we obtain

$$\frac{\partial u}{\partial s} = -\frac{\partial \varphi}{\partial u} \ , \tag{7.5.15}$$

where the dimensionless free energy function is

$$\varphi(u) = \frac{1}{2} r u^2 - \frac{1}{3} u^3 + \frac{1}{4} u^4 \ . \tag{7.5.16}$$

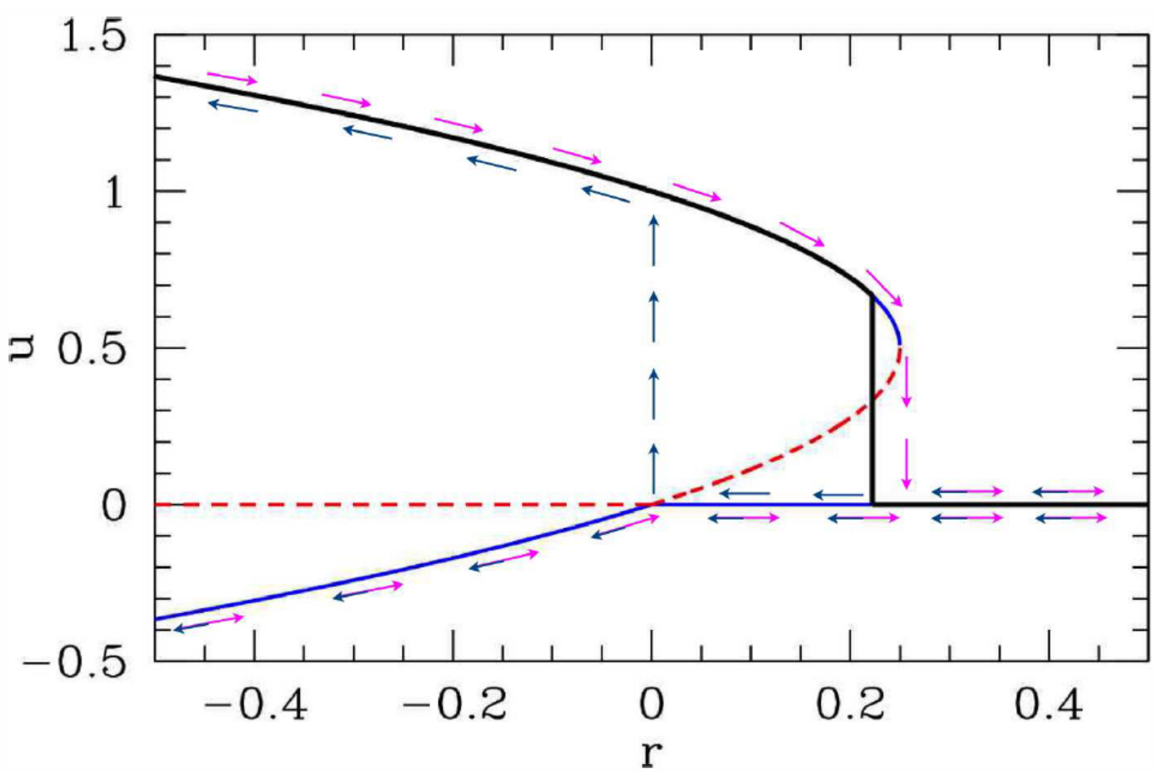
We see that there is a single control parameter, r. The fixed points of the dynamics are then the stationary points of $\varphi(u)$, where $\varphi'(u) = 0$, with

$$\varphi'(u) = u \, (r - u + u^2) \ . \tag{7.5.17}$$

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

$$u^* = 0 \qquad , \qquad u^* = \frac{1}{2} \pm \sqrt{\frac{1}{4} - r} \ . \tag{7.5.18}$$

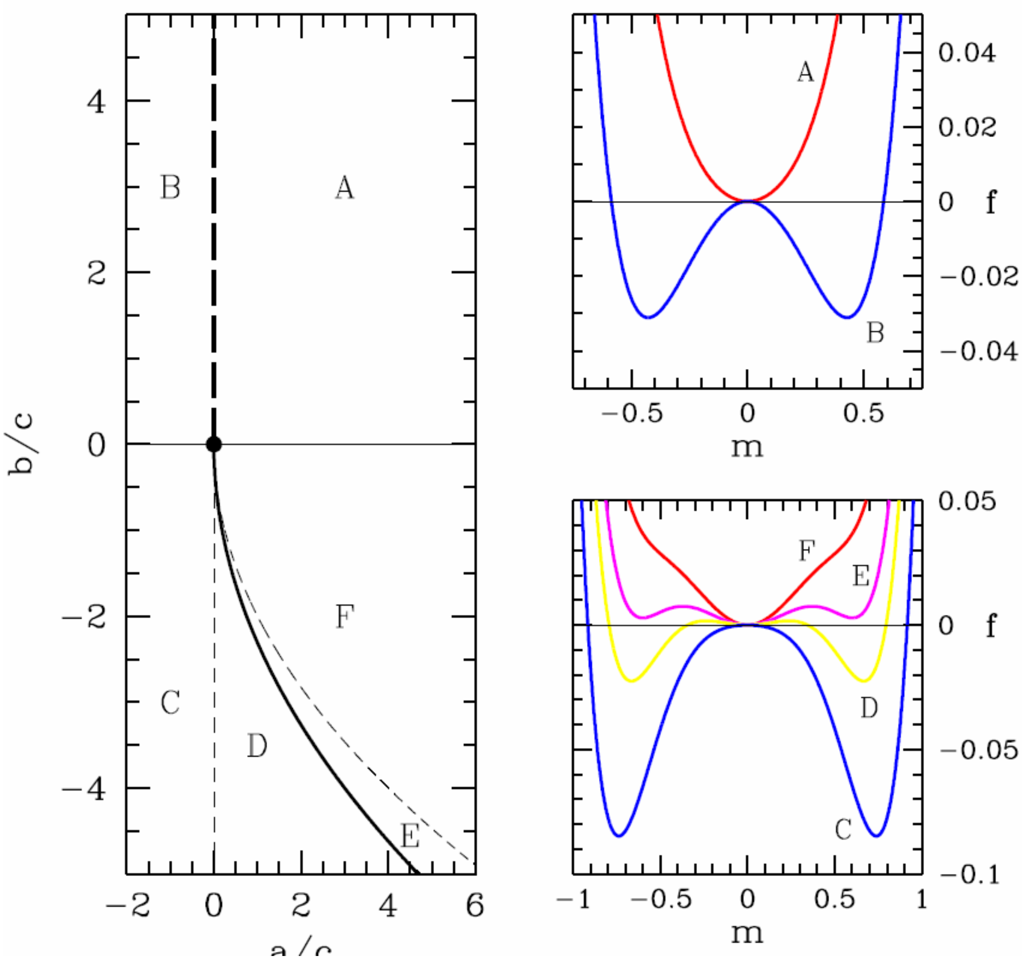
For $r > \frac{1}{4}$ there is one fixed point at $u = 0$, which is attractive under the dynamics $\dot{u} = -\varphi'(u)$ since $\varphi''(0) = r$. At $r = \frac{1}{4}$ there occurs a saddle-node bifurcation and a pair of fixed points is generated, one stable and one unstable. As we see from Figure [Landau_a], 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).



[Landau_b] 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 $u(r)$, 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 $u = \frac{2}{3}$.

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 Equation [LBdyn], $u(s)$ 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 Figure [Landau_b]. 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 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.



[fsextic] 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, $(a,b)=(0,0)$.

Sixth order Landau theory: tricritical point

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

$$f=f_0+\frac{1}{2}am^2+\frac{1}{4}bm^4+\frac{1}{6}cm^6\ , \tag{7.5.19}$$

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

$$\frac{\partial f}{\partial m}=0=m\,(a+bm^2+cm^4)\ , \tag{7.5.20}$$

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

$$m=\pm\sqrt{-\frac{b}{2c}\pm\sqrt{\left(\frac{b}{2c}\right)^2-\frac{a}{c}}}\ . \tag{7.5.21}$$

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

$$m=\pm\sqrt{-\frac{b}{2c}+\sqrt{\left(\frac{b}{2c}\right)^2-\frac{a}{c}}}\ . \tag{7.5.22}$$

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 (the rightmost minimum). This gives a second quadratic equation,

$$0=\frac{1}{2}a+\frac{1}{4}bm^2+\frac{1}{6}cm^4\ , \tag{7.5.23}$$

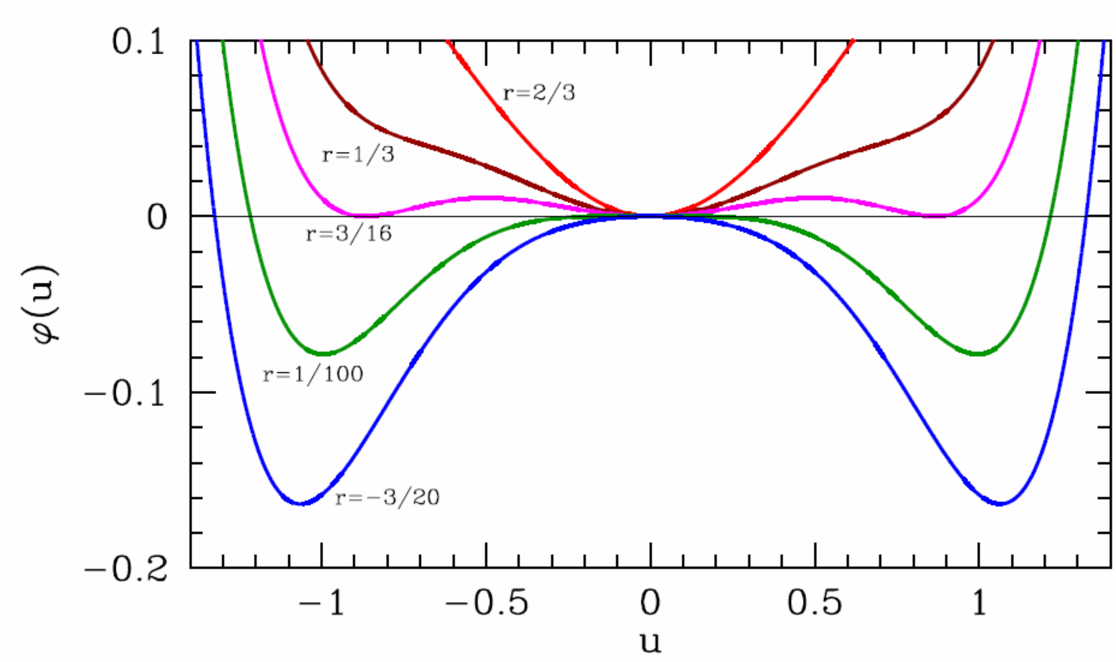
which together with equation [quintic] gives

$$b=-\frac{4}{\sqrt{3}}\,\sqrt{ac}\ . \tag{7.5.24}$$

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

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

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*.



[sexfree] 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.

Hysteresis for the sextic potential

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

$$m\equiv\sqrt{\frac{|b|}{c}}\cdot u \qquad , \qquad a\equiv\frac{b^2}{c}\cdot r \qquad , \qquad t\equiv\frac{c}{\Gamma\, b^2}\cdot s\,. \tag{7.5.25}$$

Then we obtain once again the dimensionless equation

$$\frac{\partial u}{\partial s} = -\frac{\partial \varphi}{\partial u} \, , \tag{7.5.26}$$

where

$$\varphi(u) = \frac{1}{2} r u^2 \pm \frac{1}{4} u^4 + \frac{1}{6} u^6 \, . \tag{7.5.27}$$

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 $sgn(b)$. 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

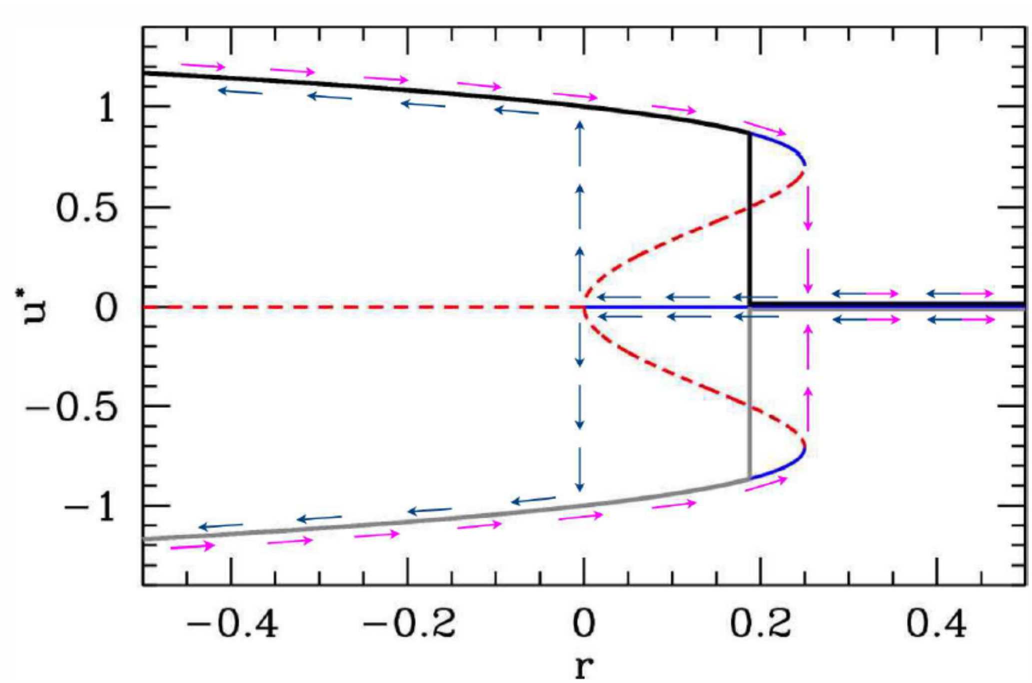
$$\begin{aligned} \varphi(u) &= \frac{1}{2} r u^2 - \frac{1}{4} u^4 + \frac{1}{6} u^6 \\ \varphi'(u) &= u \left(r - u^2 + u^4 \right) . \end{aligned}$$

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:

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

In Figure [Landau_c], 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.



[Landau_c] 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 (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*.
