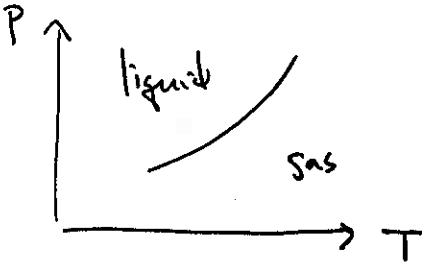
May 18

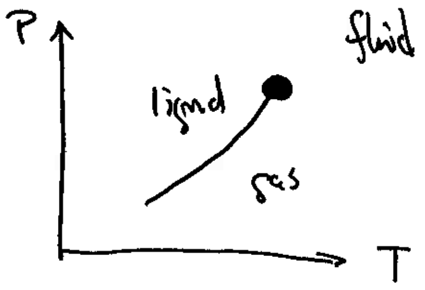
The Liquid-Gas Transition

Our analysis of thermodynamic phases and critical points has used symmetry as an organizing principle. The phenomenological Landau theory of critical phenomena that we have been using is based on the idea that the order parameter that characterizes spontaneous symmetry breaking is the crucial thermodynamic variable. However, there are systems with coexisting phases and long-range order in which the phases are not distinguished by symmetry. The most important example is that of the liquid-gas phase transition. In this lecture, I will discuss the liquid-gas transition and show how it connects to our earlier discussion.

The liquid and gas phases are distinct phases that are distinguished by their density. These phases are separated by a line of transitions in which the density changes discontinuously. In the pressure vs. temperature plane, this line of transitions is called the *coexistence curve*



As T and P increase along the coexistence curve, the density of the gas increases while the density of the liquid decreases. Eventually, one comes to a point where the two densities become equal. This point is called the *critical point.* Since the liquid and gas phases are distinguished only by density, the coexistence curve does not continue beyond the critical point. The distinction of phases disappears and we have only a single *fluid* phase.



A simple model of the liquid and gas phases was written down in the 19th century by *van der Waals.* This model had a huge influence on the development of thermodynamics and statistical mechanics. Maxwell learned Dutch to study van der Waals' thesis. The model is instructive qualitatively, as we will see in a moment. It is also useful quantitatively, in the sense that, by adjusting the parameters of the model, it is possible to fit the equations of state for liquids made of simple molecules.

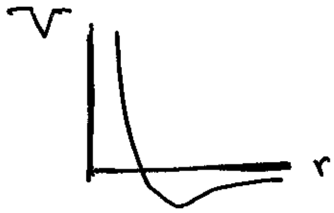
Starting from the ideal gas law

$$PV = NT$$

van der Waals generalized this formula to the equation of state

$$\left[P + \left(\frac{N}{V}\right)^2 a\right]\left[V - Nb\right] = NT$$

This equation adds two parameters to the ideal gas law. The term Nb gives the molecules of the fluid a hard-core repulsive interaction. The term $(N/V)^2 a$ decreases the pressure at high density and so models a attractive interaction. We have discussed already that interatomic potentials are typically of the form

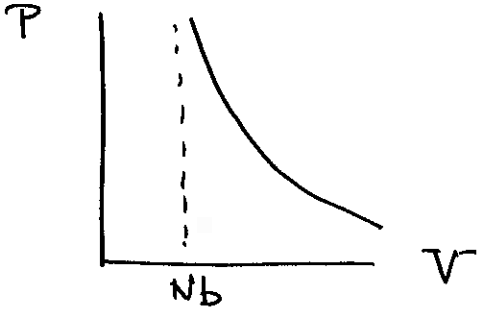


with short-range repulsive and long-ranged attractive interactions. The van der Waals model is a simple equation of state that captures both effects.

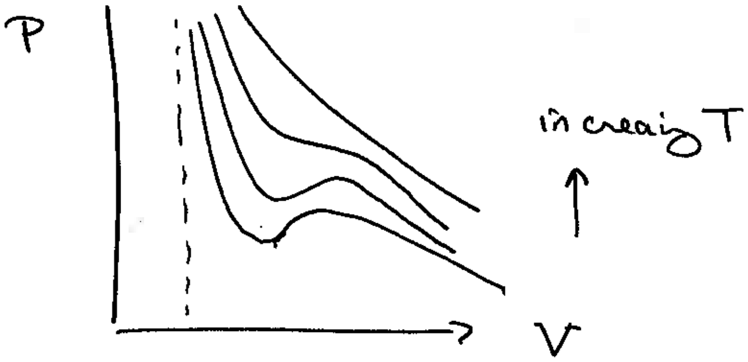
To study the behavior of a van der Waals fluid, solve for P,

$$P = \frac{NT}{V - Nb} - \left(\frac{N}{V}\right)^2 a$$

At high T, the attractive a term is unimportant. The pressure P diverges at $V = Nb$ and is roughly a hyperbola at higher values of V.



Also, at large values of V, the first term in the equation for P is the dominant one at all temperatures. At low temperatures and intermediate values of V, the a term can significantly lower P; this effect, however, must go away at large V. For fixed V, P increases monotonically as T increases. Then the curves of P vs. V for a range of temperatures have the form



This is quite an interesting diagram. For sufficiently low temperature, there is a range of P that is compatible with *three* distinct values of V.

I claim, and I will demonstrate in a moment, that there is a pressure for which two of these values of V—the largest and the smallest—correspond to states of equal thermodynamic stability. Then that pressure gives a point of liquid-gas coexistence, with the largest value of V giving the density N/V of the gas and the smallest value giving the density N/V of the liquid.

To find the most stable state at fixed pressure, we must minimize the (original) Gibbs free energy

$$G = F + PV$$

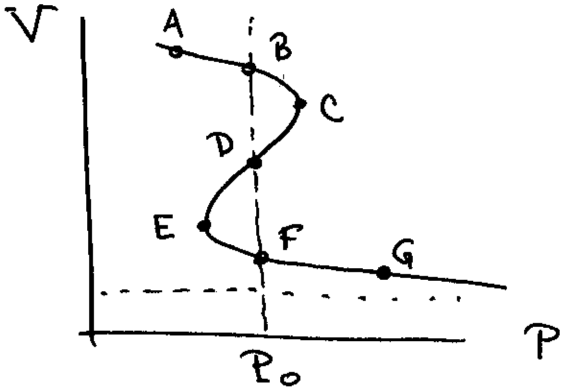
This quantity includes F but also takes into account the work that must be done in changing the volume of the sample from one state to another. We saw earlier in the course that G satisfies

$$\left.\frac{\partial G}{\partial T}\right|_{P,N} = -S \qquad \left.\frac{\partial G}{\partial P}\right|_{N,T} = V$$

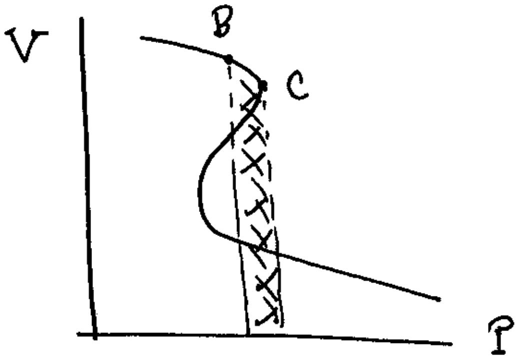
It is useful to rewrite the second of these relations as

$$\Delta G = \int dP \quad V(P)$$

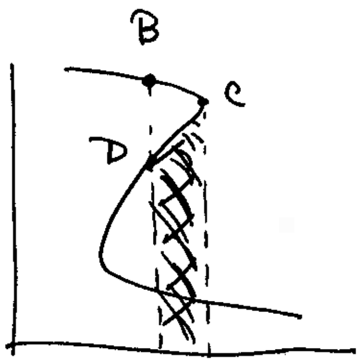
at fixed T. To apply this equation, turn one of the van der Waals curves on its side



The points B, D, and F are the three solutions for V at the fixed pressure P_0. The expression for ΔG allows us to graphically compute the free energy relation of these points. If we move from B to C, the free energy increases by the area of the shaded region



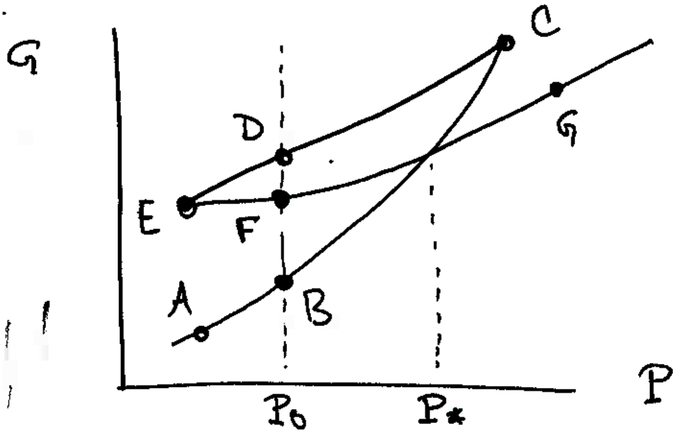
The free energy G then rises to a maximum at C. From C to D, the area



gives a *negative*, but smaller, contribution to G. Then

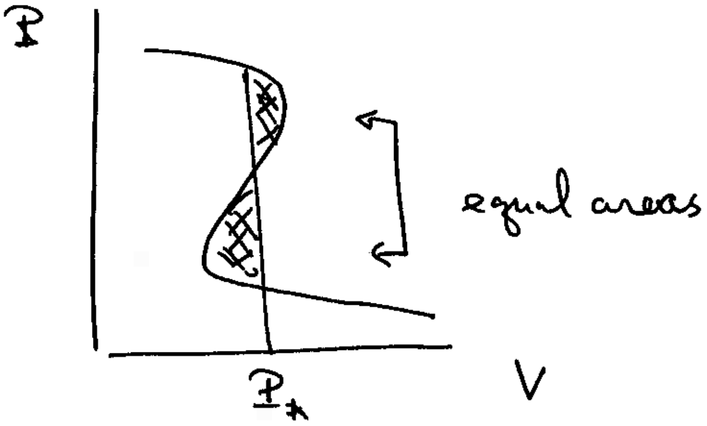
$$G(B) < G(D)$$

Working in this way, we can trace the value of G along the whole curve. There is a local minimum at E, then a rise in G as the curve continues to the point F and beyond.



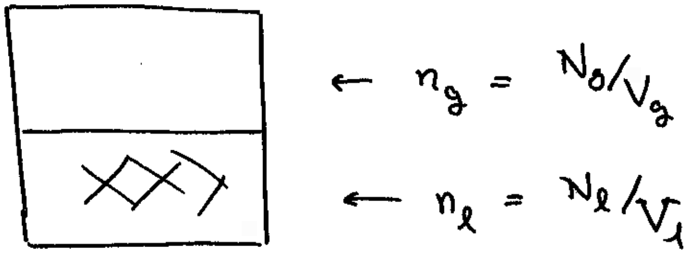
Notice that there is a pressure P_* at which the Gibbs free energy of the point on the curve between B and C, in the gas phase, equals the Gibbs free energy of a point on the curve between F and G, in the liquid phase. This pressure $P_*(T)$ is the coexistence pressure for the given temperature T. For $P < P_*$, the gas phase is the more stable. For $P > P_*$, the liquid state is the more stable.

The condition that determines P_* is that the *net area* swept out from the point in the gas phase to the point in the liquid phase should be zero. This is the condition that the two areas shaded in this figure should be equal:



This condition is called the *Maxwell construction.* For any T at which there is a region of pressure with three solutions for P, we can always find the coexistence pressure P_* by drawing the curve $P(V)$ and adjusting the position of a vertical line to balance these areas.

Imagine now that we start from a system at a pressure $P < P_*(T)$ and systematically increase the pressure. As long as P remains below $P_*(T)$, the equilibrium state is a uniform medium in the gas phase. Eventually, we reach a $P > P_*(T)$; then the equilibrium state is a uniform medium in the liquid phase. If V_g and V_ℓ are the gas and liquid volumes at coexistence, when the pressure crosses P_*, the volume changes *discontinuously* from V_g to V_ℓ. Values of V between these two values are possible only in a system with *phase separation*



The part of thermodynamic space with $V_g < V < V_\ell$ is then similar to the *excluded region* of the thermodynamic space of a magnet, the region with $|M| < M_0(T)$.

In general, the *entropy* of the system also changes discontinuously across the phase boundary. Entropy is not so easy to measure directly. However, entropy is related to the *heat* required for a change of state,

$$\Delta Q = T \Delta S$$

Thus, converting the liquid to a gas at the coexistence pressure requires the addition of heat

$$\Delta Q = T\,(S_{gas} - S_{liquid})$$

Usually, this is given as the *specific heat of vaporization*

$$\Delta q = \frac{S_{gas} - S_{liquid}}{N}$$

It is useful to define also the *specific entropy* and *specific volume*,

$$s = \frac{S}{N} \qquad\qquad v = \frac{V}{N} = \frac{1}{n}$$

To relate these quatities, recall that the identities

$$\left.\frac{\partial F}{\partial T}\right|_{V,N} = -S \qquad\qquad \left.\frac{\partial F}{\partial V}\right|_{T,N} = -P$$

yield the Maxwell relation

$$\left.\frac{\partial S}{\partial V}\right|_{T} = \left.\frac{\partial P}{\partial T}\right|_{V}$$

We can apply this relation in the region of 2-phase coexistence. Here

$$\left.\frac{\partial S}{\partial V}\right|_{T} = \frac{\Delta S}{\Delta V}$$

if we convert a macroscopic amount of liquid to gas or vice versa. This in turn equals

$$\frac{s_g - s_\ell}{v_g - v_\ell} = \frac{1}{T} \frac{\Delta q}{\Delta v}$$

and, by the Maxwell relation, this equals

$$\frac{dP}{dT}$$

along the coexistence curve. The full set of equalities gives the shape of the coexistence curve as

$$\frac{dP}{dT} = \frac{1}{T} \frac{\Delta q}{\Delta v} = \frac{\Delta s}{\Delta v}$$

This relation is called the *Clausius-Clapeyron equation.* It is a general relation that applies to any situation of 2-phase coexistence.

In the case of liquid-gas coexistence, both the volume and the entropy increase in passing from the liquid to the gas. Thus,

$$\frac{dP}{dT} > 0$$

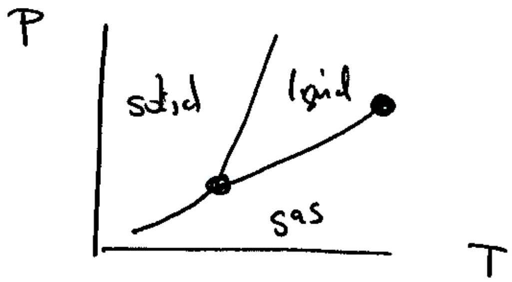
justifying the shape of the phase diagram shown at the beginning of this lecture. For *liquid-solid* coexistence, there are more possibilities. The most typical situation is

$$s_{liq} > s_{solid} \qquad v_{liq.} > v_{solid}$$

This gives

$$\frac{dP}{dT} > 0$$

so that the phase diagram has the form,



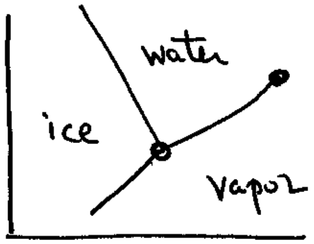
There are two special points in this diagram, a *critical endpoint* marking the end of the line of liquid-gas coexistence, and a *triple point*, a point of 3-phase coexistence with discontinuous transitions between each pair of phases.

In the diagram above, the liquid-solid coexistence curve has *positive* slope. However, this is not always the case. In *water*, the entropy of the liquid is greater than that of the solid, but

$$v_{\text{solid}} > v_{\text{liquid}}$$

since *ice* has an open crystal structure. (We know this because ice floats.) Then

$$\frac{dP}{dT} < 0$$



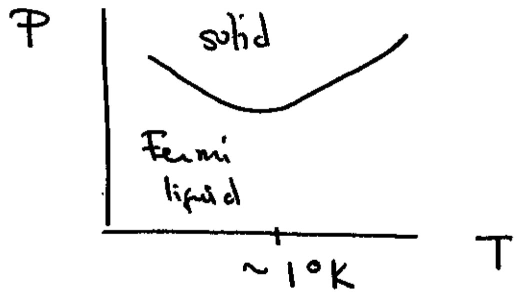
In He^3, the reverse situation occurs. The liquid is less dense than the solid. However, the liquid is a dense quantum fluid of fermions. Like the ideal fermion gas, the entropy of this system goes to zero as T goes to zero. On the other hand, the solid is a crystal of nuclei, each of which has an unpaired neutron and therefore a spin-$\frac{1}{2}$ which is free to flip even at temperatures below 1° K. Then

$$s_{liq.} \sim \frac{T}{T_F} \to 0 \,, \qquad s_{solid} \sim \log 2 \quad \underset{T\to 0}{\text{as}}$$

This implies that

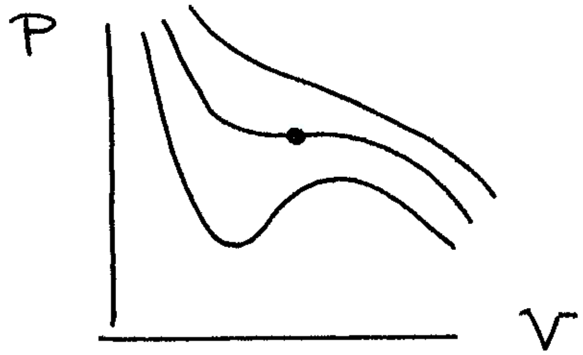
$$\frac{dP}{dT} < 0$$

The liquid-solid coexistence curve then has the form



Pomeranchuk pointed out that it should be possible to cool He^3 by squeezing samples with liquid-solid coexistence. In a Nobel-prize winning experiment, *Osheroff, Lee, and Richardson* used this method to cool He^3 to a temperature of a few mK. In the process, they discovered that liquid He^3 makes a transition at very low temperatures to a superfluid phase characterized by pairing of He^3 atoms near the Fermi surface.

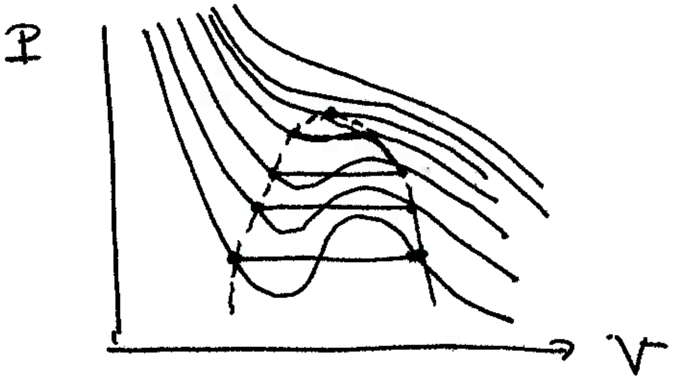
We return now to our discussion of the van der Waals equation of state. At low temperatures, this equation gives three solutions for V for a given value of P. However, for sufficiently high temperature, the curve $P(V)$ decreases monotonically with V. The behavior changes at a particular temperature at which the curve $P(V)$ begins to develop a local maximum and a local minimum.



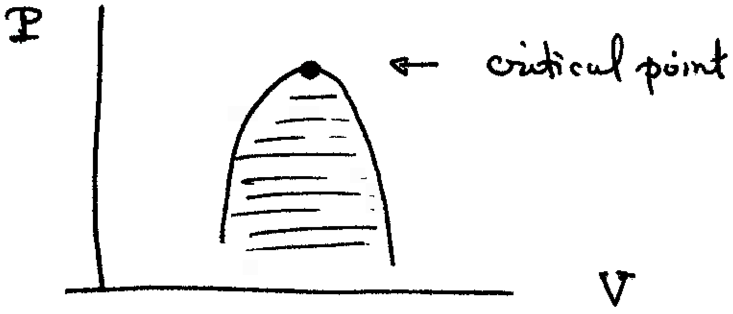
These arise from a point in the (V, P) plane where

$$\frac{dP}{dV} = 0 \qquad \frac{d^2P}{dV^2} = 0$$

The temperature T_C and pressure P_C of this point give the location of the critical endpoint. If we draw the van der Waals curves at lower temperatures and make the Maxwell constructions, we find



The locus of the solutions for V at each coexistence pressure is



The interior of this figure is an excluded region realized as phase coexistence.

As $T \to T_C$ at the pressure P_C, the compressibility dV/dP behaves as

$$\frac{dV}{dP} \sim \frac{1}{(T-T_c)^1}$$

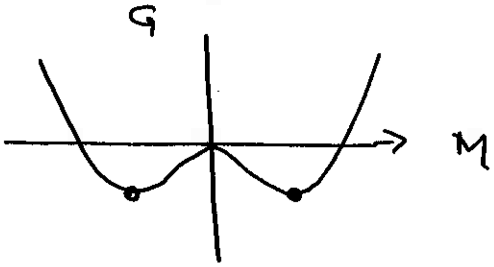
This is similar to the behavior of the *magnetic susceptibility* in the mean field theory analysis of the Ising model. The behavior of the coexisting volumes is

$$V_g - V_\ell \sim (T_c - T)^{\frac{1}{2}} \quad \text{as} \quad T \to T_c^-$$

In a similar way, the other non-analytic behaviors seen in the van der Waals theory near T_C can be mapped to those in the Ising model, with the same power laws as in mean field theory.

In the rest of this lecture, I will describe the behavior of systems with a discontinuous phase transition just in the vicinity of the phase transition point. The phenomenon that I will describe is most familiar in the case of a liquid-gas transition. In that case, if one lowers or raises the temperature quickly through the coexistence temperature at a given pressure, one temporarily obtains a state of gas or liquid on the wrong side of the coexistence curve. This is a *supercooled* gas or a *superheated* liquid. At a certain point, the system converts itself to the thermodynamically more stable phase. I will discuss the mechanism and rate of this transition. I will give the analysis in the analogous case of an Ising magnet prepared with the wrong sign of the magnetization, for which the Landau theory with Z_2 symmetry gives simpler equations.

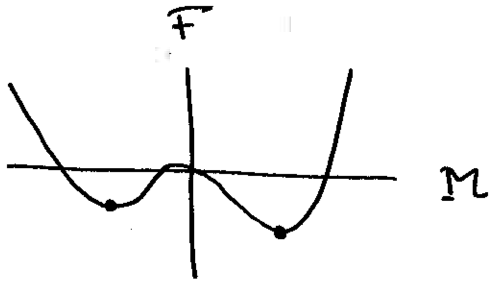
At coexistence, the free energy of a Ising model with $T < T_C$ has the form



with two degenerate minima. If we turn on a small positive magnetic field, the free energy

$$F = G - Mh$$

has the form



stabilizing the minimum with $M > 0$ and destabilizing the minimum with $M < 0$. However, by preparing the magnet with $h < 0$ and then smoothly changing the direction of the external field, we can prepare the magnet in a state with $M < 0$. There is a local minimum of F that is *locally stable.* If we start with the magnet in this state, what happens?

For small values of h, the state with the wrong sign of M should be extremely stable. A fluctuation of finite size would sample the lower free energy available by flipping the sign of M. However, I claim that the size of the region that must be flipped becomes larger and larger, and therefore more and more unlikely, as $h \to 0$.

To demonstrate this, I will construct the localized configuration build on the state with $M \approx -M_0$ that can evolve into the more stable state with $M \approx +M_0$ and has *minimal free energy.* Let ΔF be the free energy above that of the local minimum that is required to build this configuration. This configuration will then arise in the canonical ensemble with probability

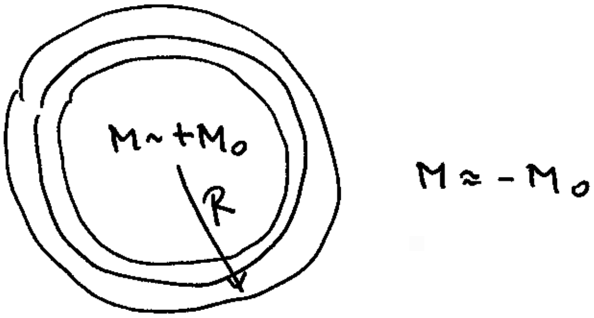
$$e^{-\Delta F/T}$$

Then the transition rate for a transition from the local minimum to the global minimum will behave as

$$\Gamma \sim e^{-\Delta F/T}$$

as $h \to 0$.

The general form of this configuration will be one in which, for $r = |\vec{x}|$ outside of a sphere of radius R, $M(r) \approx -M_0$. Inside this circle, $M(r)$ will cross over to the other side, so that at $r = 0$, $M(r) > 0$. Roughly at $r \approx R$, this solution contains a shape in $M(r)$ similar to a domain wall.



The excess free energy ΔF of this configuration is determined by a balance of two effects:

1. ΔF contains a negative term of the order of

$$-\Delta \cdot \text{Volume} = -\Delta \frac{4\pi}{3} R^3$$

   where Δ is the free energy difference $2hM_0$ between the local minimum and the global minimum of $F(M,h)$.

2. ΔF constains a positive term of the order of

$$+\sigma \cdot 4\pi R^2$$

   where σ is the surface tension of the domain wall.

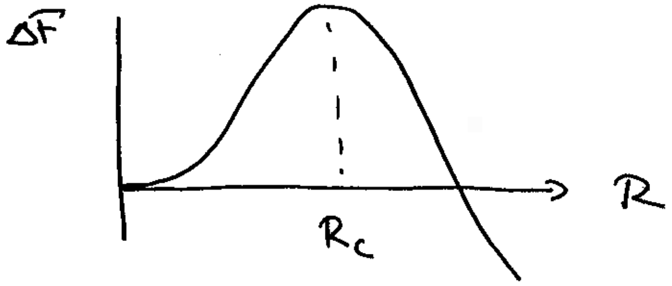
As a function of R, ΔF must behave as

$$\Delta F \sim +R^2$$

for small R and as

$$\Delta F \sim - R^3$$

for large R. Then



The *maximum* of this curve gives a value R_C, the *critical bubble size.* Bubbles larger than R_C can lower their free energy by becoming larger. Eventually, they expand and convert the whole system from the state with $M < 0$ to the true minimum with $M > 0$.

The critical bubble size is given, in the approximations above, by

$$\frac{\partial \Delta F}{\partial R} = 0 = 8\pi \sigma R - 4\pi \Delta R^2$$

which gives

$$R_c = \frac{2\sigma}{\Delta} = \frac{2\sigma}{2M_0 h}$$

As $h \to 0$ and we approach the phase coexistence line, $\Delta \to 0$ while σ tends to a constant. Then

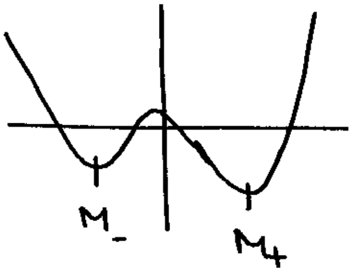
$$\Gamma \sim e^{-\frac{A\sigma^3}{TM_0^2} \cdot \frac{1}{h^2}}$$

This is an *essential singularity* in h as $h \to 0$. A singularity of this type appears in the free energy at any line of discontinuous transitions.

Using the Landau effective free energy, we can build a more precise theory of the critical bubble. The free energy is computed from the functional

$$F[M] = \int d^3x \left\{ \frac{1}{2} \rho (\vec{\nabla} M)^2 + \frac{a}{2} (T - T_c) M^2 + \frac{b}{4} M^4 - M h \right\}$$

For $h > 0$, the integrand has the form



The critical bubble should be a spherically symmetric configuration for which $M(r) \to M_-$ as $r \to \infty$. The critical bubble is a *maximum* of $F[M]$ with respect to changes in the radius of the bubble and a *minimum* of $F[M]$ with respect to all other variations. Thus, it is a *stationary point* of $F[M]$. Therefore, it is a solution to the variational equation derived from $F[M]$,

$$\rho \nabla^2 M = - a (T_c - T) M + b M^3 - h$$

For a spherically symmetric solution, this equation becomes

$$\frac{d^2}{dr^2} M + \frac{2}{r} \frac{dM}{dr} = - \frac{a (T_c - T)}{\rho} M + \frac{b}{\rho} M^3 - \frac{h}{\rho}$$

To solve this equation, I will first analyze the equation without the term with dM/dr. We can solve the resulting equation by a mechanical analogy. Replace M by x and r by t. Then the equation becomes that of a mechanics problem

$$\frac{d^2x}{dt^2} = -\frac{d}{dx}V(x) \quad a \quad \frac{d^2M}{dr^2} = -\frac{d}{dM}V(M)$$

with

$$V(M) = \frac{a(T_c - T)}{2\rho}M^2 - \frac{b}{4\rho}M^4 + \frac{h}{\rho}M$$

Going back from t to r, the conserved energy of this problem is .

$$\mathcal{E} = \frac{1}{2}\left(\frac{dM}{dr}\right)^2 + V(M)$$

Conservation of energy is the statement that

$$\frac{d\mathcal{E}}{dr} = 0 = \frac{dM}{dr} \cdot \left(\frac{d^2M}{dr^2} + \frac{d}{dM}V(M)\right)$$

Now add back the dM/dr term; then we can rewrite the original equation as

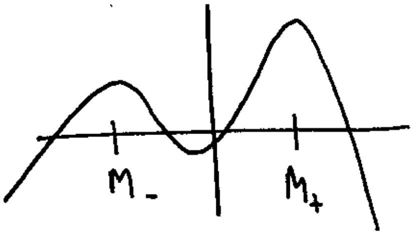
$$\frac{d^2M}{dr^2} = -\frac{d}{dM}V(M) - \frac{2}{r}\frac{dM}{dr}$$

The added term is analogous to a term

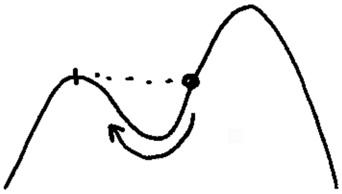
$$-\gamma(t)\frac{dx}{dt}$$

that would represent a friction force in the particle mechanics.

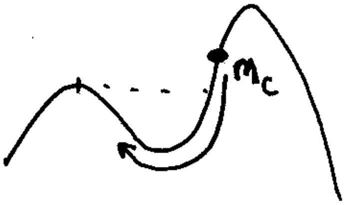
For $h > 0$, the potential $V(M)$ has the form



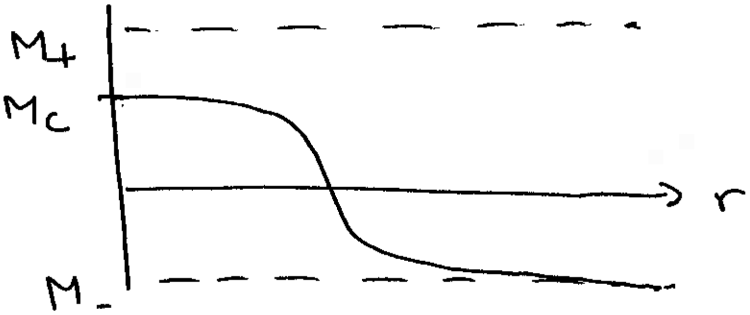
The solution for which $M(r) \to M_-$ as $r \to \infty$ is the solution that just reaches the top of the lower hill in infinite time. Without friction, this would be a solution that starts from an energy equal to $V(M_-)$ on the higher hill.



In the presence of friction, we need to start higher on the hill to reach M_- at the end of the motion. However, if we started near the top of the higher hill, the particle would take a very long time to roll away from the point where $M = M_+$. Then r would be large, the friction would be negligible, and the particle would overshoot the other maximum. Thus, there must be a solution to the original equation corresponding to a particle motion of the form



As a function of r, this solution looks like



Note that, at the center of the bubble, $M_c < M_+$. Nevertheless, any bubble with a *larger* radius has a central value *closer* to M_+ and *lower* free energy. Any such bubble expands to fill the whole volume with a state $M = M_+$.