Domain walls and surface tension

An interesting application of the Landau-Ginzburg (LG) theory is found in examining the structure of a domain wall describing coexistence of two phases at the first order transition, such as the liquid-gas interface. As we know from freshman physics, such a domain wall has an energy proportional to its area, defining the surface tension. The LG theory will tell us what happens to the surface tension as the critical point is approached, providing additional support to the emergence of critical fluctuations.

Domain walls in Landau-Ginzburg theory

The simplest example for the coexistence of phases is found within the Landau-Ginzburg theory of an Ising ferromagnet. For $r \lesssim 0$ (i.e. $T \lesssim T_c$) and $j = 0$ the LG equation

$$-\nabla^2 \phi(\mathbf{x}) + r\phi(\mathbf{x}) + u\phi^3(\mathbf{x}) - j(\mathbf{x}) = 0, \tag{1}$$

assumes two uniform symmetry-broken solutions of the form $\phi_o = \pm \left(|r|/u\right)^{1/2}$. In a ferromagnet these correspond to two different orientations of the magnetization; in a liquid gas system they correspond to the liquid and the gas phase. At coexistence (precisely at the first-order transition line corresponding to $j = 0$ in LG theory), these two solutions have precisely the same free energy. Which one does the system choose? Well, an infinitesimal perturbation is then sufficient to tilt the balance, for example an infinitesimal external field. Another way to break the symmetry is provided by **boundary conditions.** For example, if we fix all the spins on the boundary to be "up", then even those in the bulk will all chose this orientation.

But what happens if we have a large sample, and we chose the boundary conditions such that the spins point "up" on the left boundary, but "right" on the right boundary? In this case the domain wall will form separating regions corresponding to the two different phases.

A similar situation is found at the liquid-gas coexistence, where gravity "pushes" the liquid to occupy the lower end of the container, and the gas phase is found on top. At
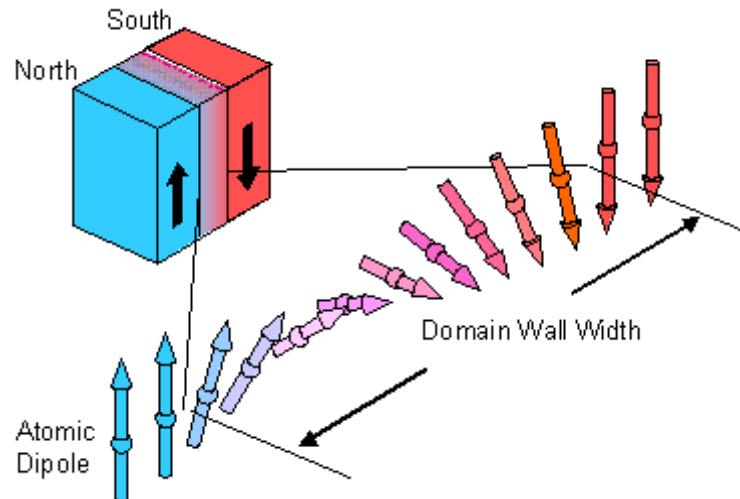
the boundary of the two phases, a thin region forms, where the substance is neither in one nor the other phase, but is somewhere in between. Generally, the order parameter which measures the spontaneous symmetry breaking is reduced in this region, which has the higher free energy then either phase. Therefore, we have to pay a price to introduce such a **domain**

wall, which is proportional to its **area**. The free energy per unit area of a domain wall is called a **surface tension**, since it is energetically favorable to reduce the area of the free surface. This is why the liquid droplets assume a spherical shape in absence of gravity - explaining the formation of planets!

In the following, we use LG theory to compute in detail the shape and form of the domain wall, and calculate the surface tension. We concentrate on a flat domain wall, perpendicular

to the z-axis. To do this, we reexamine the LG equation, but we now allow for a spatially non-uniform solution $\phi = \phi(z)$ assuming the boundary conditions

$$\lim_{x \to \pm\infty} \phi(z) = \pm\phi_o. \tag{2}$$

The LG equation now takes the form

$$\phi"(z) = V'(\phi), \tag{3}$$

where $\phi"(z) = d^2\phi(z)/dz^2$, $V'(\phi) = dV(\phi)/d\phi$, and $V(\phi) = \frac{1}{2}r\phi^2 + \frac{1}{4}u\phi^4$. We note that if we interpret the order parameter ϕ as a coordinate, and x as time, then the LG equation (3) has a form identical to a classical particle moving in a potential energy of the form $-V(\phi)$, i.e. in an **inverted potential** from that of the LG theory.
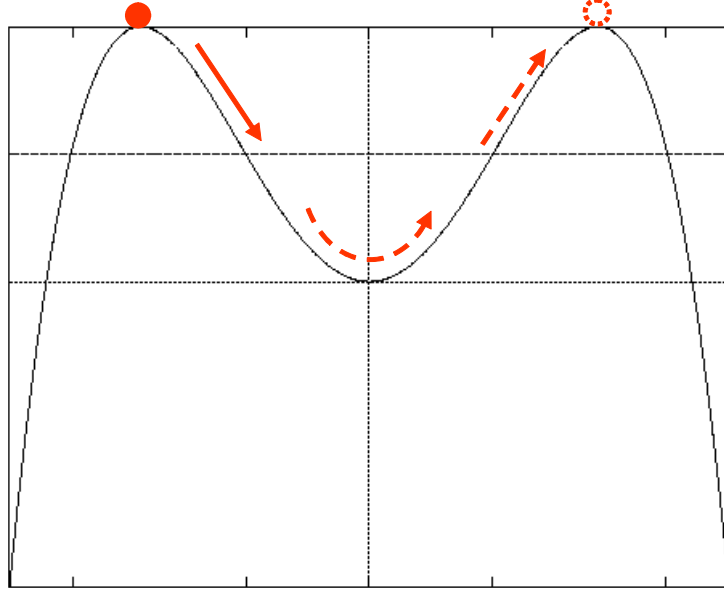
We know how to easily solve such equations of motion. Because the potential is "time"-independent (i.e. z-independent), we can use what corresponds to energy conservation. We can write

$$\phi'(z) = [2(E + V(\phi))]^{1/2},$$

where E is a constant to be determine from boundary conditions. Since at $x \to \pm\infty$ (corresponding to time $t \to \pm\infty$), the "velocity" $\phi'(x)$ vanishes, we conclude

$$E = -V(\phi_o) = \frac{r^2}{4u} = \frac{u}{4}\phi_o^4.$$

Note that $|r| = \phi_o^2/u$, so that we can write (note $r = -|r| < 0$)

$$E + V(\phi) = \frac{u}{4}\phi_o^4 - \frac{u}{2}\phi_o^2\phi^2 + \frac{1}{4}u\phi^4$$
$$= \frac{u}{4}\left[\phi_o^2 - \phi^2\right]^2.$$

We get

$$\phi'(z) = \frac{d\phi}{dz} = \sqrt{\frac{u}{2}}\left[\phi_o^2 - \phi^2\right],$$

or

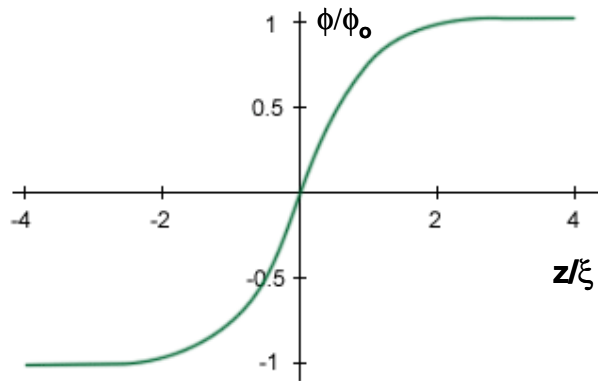$$z = \sqrt{\frac{2}{u}}\int_0^{\phi_o}\frac{d\phi}{\phi_o^2 - \phi^2}.$$

Here we have assumed that the domain wall is located exactly at $z = 0$. The integration is easily done (this is a table integral) and we get

$$z = \sqrt{\frac{2}{u}}\frac{1}{\phi_o}\tanh^{-1}(\phi/\phi_o)$$
$$= \sqrt{2}\xi_o\tanh^{-1}(\phi/\phi_o),$$

or finally

$$\phi = \phi_0\tanh(z/\sqrt{2}\xi_o),$$

with $\xi_o = |r|^{-1/2}$. Here, we used the subscript "o" to indictate that ξ_o is the *mean-field* (LG) correlation length. We conclude that the **domain wall thickness is given by the**

correlation length. The domain walls, while well defined (thin) in the low temperature phase, become "blurred out", i.e. ill-defined as the critical point is approached!

Surface tension

We also have to calculate the free energy of the domain wall, in order to obtain the surface tension.. We recall that within Landau theory, the free energy functional can be written as

$$S[\phi] = \int d\mathbf{x} \left[\frac{1}{2}\phi(\mathbf{x})(-\nabla^2)\phi(\mathbf{x}) + V(\phi) \right],$$

or by partial integration

$$S[\phi] = \int d\mathbf{x} \left[\frac{1}{2}\left(\nabla\phi(\mathbf{x})\right)^2 + V(\phi) \right].$$

In the case we consider, it is assumed that $\phi(\mathbf{x})$ varies only along the z-direction, and the expression simplifies to

$$S[\phi] = A \int_{-\infty}^{+\infty} dz \left[\frac{1}{2}\left(\phi'(z)\right)^2 + V(\phi) \right],$$

where $\phi'(z) = d\phi(x)/dz$, and A is the domain wall area. To compute this integral, note that the term $\frac{1}{2}\left(\phi'(z)\right)^2$ can be regarded as the kinetic energy of a classical particle moving in the "inverted" potential $-V(\phi)$. Using energy conservation as before, we can write that for any z we have

$$\frac{1}{2}\left(\phi'(z)\right)^2 - V(\phi) = E = \frac{u}{4}\phi_o^4,$$

or

$$\frac{1}{2}\left(\phi'(z)\right)^2 = E + V(\phi).$$

Finally, the free energy functional takes the form

$$S[\phi] = A \int_{-\infty}^{+\infty} dz \left[E + 2V(\phi) \right].$$

This expression gives to total free energy of the system with an arbitrary form for $\phi(z)$, which is an **extensive** quantity (proportional to the system volume). We are, on the other hand, interested in calculating not the total free energy, but rather the free energy cost $\delta S[\phi]$ of introducing a domain wall in an otherwise uniform system. The free energy cost of the domain wall per unit area is obtained by subtracting out the free energy of the uniform state

$$\frac{\delta S[\phi]}{A} = \frac{S[\phi] - S[\phi_o]}{A} = \frac{1}{A}S[\phi] - \int_{-\infty}^{+\infty} [V(\phi_o)] \, dz$$

$$= \frac{1}{A}S[\phi] + A\int_{-\infty}^{+\infty} E \, dz = 2\int_{-\infty}^{+\infty} [E+V(\phi)] \, dz$$

$$= \int_{-\phi_o}^{\phi_o} 2\,[E+V(\phi)] \, \frac{dz}{d\phi} d\phi = \sqrt{2}\int_{-\phi_o}^{\phi_o} [E+V(\phi)]^{1/2} d\phi$$

$$= \sqrt{\frac{u}{2}}\int_{-\phi_o}^{\phi_o} [\phi_o^2 - \phi^2] \, d\phi = \frac{2\sqrt{2u}}{3}\phi_o^3 = \frac{|2r|^{3/2}}{3u} \sim |r|^{3/2} \, .$$

The **surface tension** is defined precisely as the domain wall free energy per unit area. We conclude that the surface tension **vanishes at the transition**

$$\sigma \sim \xi_o^{-3} \sim (T_c - T)^{3/2}.$$

This result, together with the fact that the domain walls become "thick" near the critical point, indicates that large order-parameter fluctuations emerge near the critical point. The mean-field approximation, which largely ignores the fluctuations of the order parameter, thus becomes ill suited, and the development of more powerful theoretical tools is in order. The proper theory needs to include fluctuations of the order parameter. To do this we need to sum over all possible spatial fluctuations of the order parameter and the partition function takes the form

$$Z = \int D\phi(\mathbf{x}) \, e^{-S[\phi]}.$$

Such a functional integral expression for the partition function can be formally derived by performing the so-called Hubbard-Stratonovich transformation, as we will discuss in detail shortly. If the functional integral is evaluated in the saddle-point approximation, we are back to LG theory. This is exact in infinite dimensions. But as the dimensions are reduced, the fluctuations around the saddle point become more important, as we will find shortly.