

32.1 Landau theory

We have ‘derived’ the Ginzburg-Landau Hamiltonian in Lecture 18. If we apply the mean field theory, that is, if we ignore fluctuations, then

$$H = \frac{1}{2}\tau\psi^2 + \frac{1}{4}g\psi^4, \tag{0.0.1}$$

should be interpreted as the free energy density, and is called the *Landau free energy* (Landau free energy (density)). ψ could be a n -dimensional vector. Minimizing this with respect to ψ , the order parameter, various phases are predicted. Certainly, we know that the above free energy correctly describes the phase diagram of a ferromagnet.

How can we justify the use of such a simple free energy model to understand the phase diagram? A possible justification is that the phase diagram may be studied through the study of the codimension 0 fixed point of the renormalization group flow, so the mean field approach starting with the ϕ^4 -model is enough. However, this justification is not quite satisfactory, because the ϕ^4 -model is introduced only to understand universal features of the system close to the critical point.

Today I outline a global (top-down) justification of the Landau approach. I use *Thom’s ‘main theorem’*: Thom’s theorem roughly speaking the theorem tells us the following.

Classification of elementary catastrophes: Suppose the minimum of a C^∞ ¹ potential V corresponds to a bulk phase, and the bifurcations in the system are at most codimension 4 (i.e., the phase diagram is described in a coordinate space with less than or equal to 4 dimensions). If the potential is structurally stable,² then V is C^∞ -homeomorphic to one of the following potentials, where Q is the quadratic form of the rest of variables:

# of control parameters	potential function	name
1	$x^3 + ax + Q$	fold
2	$x^4 + ax^2 + bx + Q$	cuspl
3	$x^5 + ax^3 + bx^2 + cx + Q$	swallow’s tail
4	$x^6 + ax^4 + bx^3 + cx^2 + dx + Q$	butterfly
3	$x^3 + y^3 + axy + bx + cy + Q$	hyperbolic umbilic
3	$x^3 - xy^2 + a(x^2 + y^2) + bx + cy + Q$	elliptic umbilic
4	$x^2y + y^4 + ax^2 + by^2 + cx + dy + Q$	parabolic umblic

Here, $a, b, \dots d$ are the control parameters governing the shape of the potential.

In the above, ‘structural stability’ is equivalent to that the nature of the phase diagram structure does not change qualitatively by a small change in the potential. For example, four phase coexistence in 2 dimensional phase diagram (‘the four corner’) must not appear. You might object to imposing this condition, saying there may be hidden symmetry or hidden conservation laws that may stabilize otherwise structurally fragile structures by restricting possible perturbations. Therefore, to be precise, we *assume* that the phase diagram structure

¹infinite times differentiable

²i.e., any small perturbation added to the potential may be ‘gauged away,’ or there is a C^∞ homeomorphism (= one-to-one map) that maps the perturbed result to the original one.

is structurally stable: the mutual relation of the phases cannot be altered by small deformation of the phase boundaries. For this phase diagram we wish to make a ‘potential function’ whose minima describe the bulk phases. We wish to avoid pathological potentials that are extremely sensitive to the choice of parameters. Therefore, we may impose the structural stability condition on the potential we seek.

Remark. Generally speaking, if the phase diagram is in 7 or higher dimensional space, there can be continuously many different types of free energy functions. If the number of control parameters is less than or equal to 6, there are three types for each (Mather and Siersma 1973). The potential cannot be bounded from below if the number of the control parameters is odd.

Now, the thermodynamic system must be stable, so V must be $+\infty$ for large variables. Therefore, in the above table, only the cusp and butterfly are meaningful in statistical thermodynamics. That is, if we wish to describe the bulk phases in the phase space that have at most four coordinates (T, p, H and impurity concentration, for example) through minimization of the ‘Landau free energy,’ then it must be a function of a single scalar ψ with the following form

$$\mathcal{F} = \frac{1}{2}\tau\psi^2 + \frac{1}{4}\psi^4 - h\psi, \quad (0.0.2)$$

or

$$\mathcal{F} = \frac{1}{2}\tau\psi^2 + \frac{1}{4}g\psi^4 + \frac{1}{6}\psi^6 - h\psi + \frac{1}{3}b\psi^3. \quad (0.0.3)$$

There is *no* other case.

What is the implication? For example, if the phase space is 2 dimensional, then the order parameter *must* be scalar, and the Landau Hamiltonian that describes the bulk phases in the neighborhood of the phase transition point³ can always be written as (0.0.2). τ and h specify the location in the phase diagram. However, by construction, the obtained free energy offers only the arrangements of bulk phases around the highest codimension singular point on the phase diagram, and it is not designed to understand the nature of the phase transition. For example, as we know well, its predictions at the critical point are generally wrong.

You might ask: it is claimed that the TH -phase diagram requires only a scalar order parameter, but most magnetic systems have spin dimensions larger than 1. How come? Let us consider the Heisenberg model in 3-space. We know that its phase diagram is just like that of the Ising model. Is this a correct statement? It is, only when we ignore the direction of the magnetization vector. As we will clearly recognize later, the symmetry broken phases with different magnetization vector directions are distinct phases (like liquid and gas phases).

³Its precise meaning is as follows. It is a domain that contains only one singular point (phase boundary or critical point) whose codimension is the same as the dimension of the phase diagram (that is a point in the phase diagram like the triple point on the pT -diagram of a simple fluid). Furthermore, the domain must not contain any phase boundaries that cannot be reached along the phase boundaries from the unique singular point just mentioned without going through any other highest codimension singular points on the phase diagram.

Therefore, the true phase diagram of the Heisenberg model in 3-space *cannot* be written as a two dimensional phase diagram.

However, we know that if we identify all the phases with the same magnitude of the magnetization, that is, if we identify the phases that can be superposed by a three dimensional rotation, then the phase diagram is two dimensional. This implies that if we respect the full symmetry of the phase diagram, then we may use the fully symmetric potential when there is no symmetry breaking external field. Then, the Landau potential must be a function of a scalar constructed from the order parameter. Thus, Thom's theorem still applies; That is, except for the odd order terms, x may be understood as the length of the vector order parameter. The odd order terms may be considered through projecting the order parameter to the direction of the symmetry breaking field.

Another criticism you might wish to extend is: the Heisenberg model in 2D does not have any phase transition, so clearly the prediction of the Landau free energy is wrong. Isn't it a counterexample for the above argument? Do not forget the rule of our game. We *assume* that there is a phase transition when we construct the potential. Consider the phase diagram of the 2D Heisenberg model. Since there is no phase transition, the phase diagram is structureless for all T and H . That is, we do not need any phase diagram; actually the phase diagram is zero dimensional (no parameter is needed to describe its singular behavior). Therefore, the potential is just homeomorphic to Q in the above table, a positive definite quadratic potential.

To summarize the rule to construct the Landau free energy \mathcal{F} that can explain the phase diagram may be summarized as follows:

- (0) \mathcal{F} is a polynomial without the constant term.
- (1) \mathcal{F} must have the highest order monomial term that have the same symmetry as the unique high temperature phase. This term can be chosen to have a positive constant coefficient.
- (2) The lower order terms can be anything, but you can discard any term that may be eliminated by shifting the variable $\psi \rightarrow \psi + c$.
- (3) The number of parameters must be identical to the dimension of the phase diagram.

Remark When there was catastrophe theory fever, many people tried to describe the phase transition and in particular the critical phenomenon with the aid of the 'universal framework' of catastrophe theory. As you have already realized well, these attempts are in principle futile. I believe that the proper use of the theory is to map the global structure of the phase diagram away from the critical point. The structure determined by this universal forms characterizes the phase boundary structure (topologically with the aid of continuity of the phases until they hit the phase boundary). Landau correctly recognized this general feature well before Thom.

It should be clear that (0.0.2) is obtained according to (0)-(3). The potential function changes its shape as illustrated in Fig 21.1.

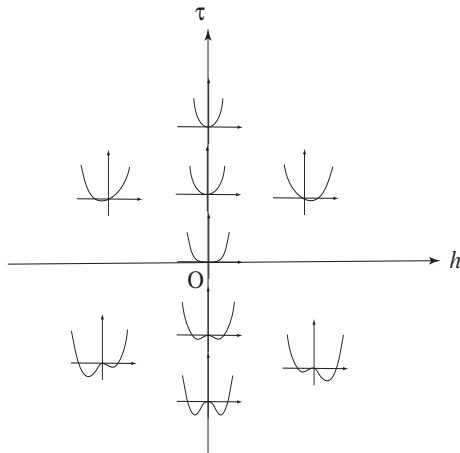


Fig. 21.1 Landau free energy (0.0.2).

Depending on the nature of the order parameter there are two interpretations.

(a) If the order parameter is *nonconserved* (NCOP = non-conserved order parameter), the phase is completely determined by the global minimum of the Landau function. For magnetic spins, the order parameter is not conserved, so this rule applies.

(b) If the order parameter is conserved (COP = conserved order parameter), the sum of the order parameter is conserved. Consequently, the phase point cannot simply jump from the old minimum position to a new minimum when the parameters (say, T or p) change. In this case the so-called *lever rule* applies. The system wishes to minimize the total free energy keeping the total sum of the order parameter constant.⁴ The rule is illustrated in Fig 21.2 with the aid of the binary liquid mixture as an example. In this case the concentration difference of one component is the order parameter, and is conserved.

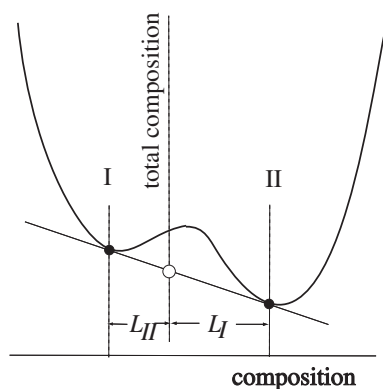


Fig. 21.2 The lever rule. Suppose the total composition of the mixture is given by the vertical broken line. The uniform state of this composition is unstable, so it separates into phase I and phase II to minimize the total free energy. The lowest total free energy realized is indicated by the open circle. The ratio of the phase I and II is given by the ratio of L_I and L_{II} .

Let α be the fraction of phase I, and the compositions of phase I and II be c_I and c_{II} , respectively. Then, $\alpha c_I + (1 - \alpha)c_{II} = c$ must be kept constant. Under this condition we

⁴This conservation is usually required spatially locally, because atoms cannot jump a long distance at once.

must choose α , c_I and c_{II} to minimize

$$F = \alpha F(c_I) + (1 - \alpha)F(c_{II}). \quad (0.0.4)$$

The answer is geometrically given as the *lever rule*. The locations of c_I and c_{II} give the *phase coexistence curve* (cf. Fig. 21.5).

If the Landau free energy is locally convex around a phase, it is stable against small perturbations. However, there may be a way to realize lower free energy by phase decomposition. In this case the phase is called *metastable*. If the free energy is not locally convex, then spontaneously the phase decomposes into other phases. Such a state is called an *unstable phase* (see Fig 21.3).

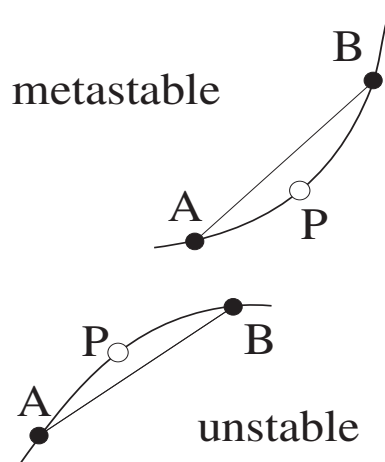


Fig. 21.3 If the free energy is locally convex around P, no decomposition of this state into A and B can occur, because this would increase the free energy. Therefore, P is a metastable state. However, if the free energy is not locally convex around P, a small spontaneous fluctuation can drive the system from the state P into A and B, where the free energy can be lowered. P is an unstable state in this case.

If the phase is neither metastable nor unstable, it is stable. See Fig 21.4.

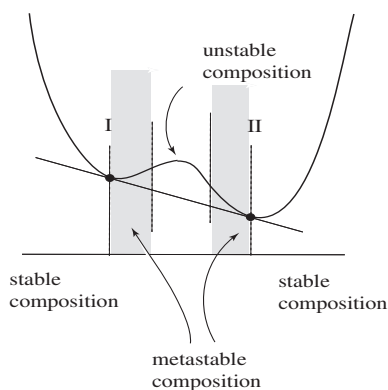


Fig. 21.4 Stable, metastable and unstable phase for conserved order parameter phases.

The corresponding phase diagram is given in Fig 21.5. The boundary between the metastable and the unstable phases is called the *spinodal line*. This line is well defined only when we may ignore fluctuations. Thus, closer to the critical point this line becomes vague.

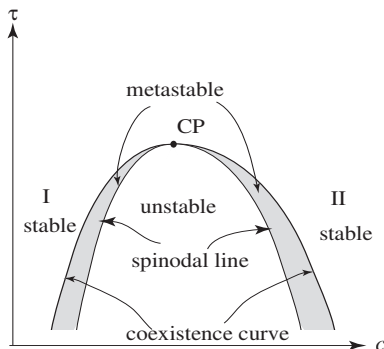


Fig. 21.5 The phase diagram of binary liquid mixture corresponding to Fig. 21.4.

In the NCOP case the phases are determined by the minimum point of the Landau free energy. Therefore, states corresponding to the global minimum is the stable phase, and other local minima correspond to metastable states.

I have introduced the Landau free energy \mathcal{F} to describe the phase diagram. It was introduced from the bifurcation (or singularity) theoretical point of view; it is a potential function that reproduces the phase diagram from its minimization. Although it is called ‘free energy,’ and looks similar to the Ginzburg-Landau Hamiltonian we already used, up to this point its statistical thermodynamic meaning is not clear.

Since \mathcal{F} is not convex upward, it is not a thermodynamically respectable free energy. However, it is expected to describe the fluctuation in a volume element. Therefore, we expect the following $\tilde{\mathcal{F}}$ is ‘homeomorphic’ to the Landau free energy:

$$Z_V = \sum_{V,\psi} e^{-H} = e^{-V\tilde{\mathcal{F}}}, \quad (0.0.5)$$

where V is the volume of the chunk we are considering, and $\sum_{V,\psi}$ implies the state sum over all the microscopic state compatible with the order parameter value ψ . If we take $V \rightarrow \infty$, then $\tilde{\mathcal{F}}$ becomes the true free energy (density). It is a *large deviation function* and $-\tilde{\mathcal{F}}$ must be convex.⁵

Since the Landau free energy is the potential function for the local average (mesoscale average) of the order parameter, the free energy can be used to describe spatially inhomogeneous phases. To this end we must connect the order parameters at different places. The simplest way is to add the gradient term just as we did in the heuristic derivation of the Ginzburg-Landau Hamiltonian:

$$F = \int d^d \mathbf{r} \left[\frac{1}{2} (\nabla \psi)^2 + \mathcal{F}(\psi) \right]. \quad (0.0.6)$$

⁵For a quick introduction to large deviation theory, see Appendix of Prog. Theor. Phys. **99**, 165-205 (1989).

A more phenomenological approach is to use the observed form factor $S(\mathbf{k})$:

$$\langle \psi_{\mathbf{k}} \psi_0 \rangle = S(\mathbf{k}). \quad (0.0.7)$$

This implies that the reciprocal of $S(\mathbf{k})$ may be used to model the spatial inhomogeneous part of the free energy:

$$F = \int d^d \mathbf{k} \frac{1}{2} \psi_{\mathbf{k}}^* S(\mathbf{k})^{-1} \psi_{\mathbf{k}} + \dots, \quad (0.0.8)$$

where \dots denotes the nonlinear terms.⁶

⁶The roton theory due to Feynman has this structure; notice that his derivation is not at all microscopic, although it is pretended so. For me it seems to be the rule that there is absolutely no honest microscopic derivation of any free energy functional in physics. Perhaps it could even be said that there is no reliable microscopic theory at all except for trivial universal cases.