I.C Phase Transitions

The most spectacular consequence of interactions among particles is the appearance of new phases of matter whose collective behavior bears little resemblance to that of a few particles. How do the particles then transform from one macroscopic state to a completely different one. From a formal perspective, all macroscopic properties can be deduced from the free energy or the partition function. Since phase transitions typically involve dramatic changes in various response functions they must correspond to singularities in the free energy. The canonical partition function for a finite collection of particles is always an analytical function. Hence phase transitions, and their associated non–analyticities, are only obtained for infinitely many particles, i.e. in the *thermodynamic limit*, $N \to \infty$. The study of phase transitions is thus related to finding the origin of various singularities in the free energy and characterizing them.

The classical example of a phase transition is the condensation of a gas into a liquid. Some important features of the liquid–gas condensation transition are:

(1) In the temperature/pressure plane, (T, P), the phase transition occurs along a line that terminates at a *critical point* (T_c, P_c).

(2) In the volume/pressure plane, $(P, v \equiv V/N)$, the transition appears as a *coexistence interval*, corresponding to a mixture of gas and liquids of densities $\rho_g = 1/v_g$, and $\rho_l = 1/v_l$, at temperatures $T < T_c$.

(3) Due to the termination of the coexistence line, it is possible to go from the gas phase to the liquid phase continuously (without a phase transition) by going around the critical point. Thus there are no fundamental differences between liquid and gas phases.

From a mathematical perspective, the free energy of the system is an analytical function in the (P, T) plane, except for some form of branch cut along the phase boundary. Observations in the vicinity of the critical point further indicate that:

(4) The difference between the densities of coexisting liquid and gas phases vanishes on approaching T_c, i.e. $\rho_{\text{liquid}} \to \rho_{\text{gas}}$, as $T \to T_c^-$.

(5) The pressure versus volume isotherms become progressively more flat on approaching T_C from the high temperature side. This implies that the isothermal compressibility, $\kappa_T = - \left. \partial V / \partial P \right|_T / V$, diverges as $T \to T_c^+$.

(6) The fluid appears "milky" close to criticality. This phenomenon, known as *critical opalescence*, suggests collective fluctuations in the gas at long enough wavelengths to scatter visible light. These fluctuations must necessarily involve many particles, and a coarse graining procedure may thus be appropriate to their description.

A related, but possibly less familiar, phase transition occurs between paramagnetic and ferromagnetic phases of certain substances such as iron or nickel. These materials become spontaneously magnetized below a Curie temperature T_c. There is a discontinuity in magnetization of the substance as the magnetic field h, goes through zero for $T < T_c$. The phase diagram in the (h, T) plane, and the magnetization isotherms $M(h)$, have much in common with their counterparts in the condensation problem. In both cases a line of discontinuous transitions terminates at a critical point, and the isotherms exhibit singular behavior in the vicinity of this point. The phase diagram of the magnet is simpler in appearance, because the symmetry $h \mapsto -h$ ensures that the critical point occurs at $h_c = M_c = 0$.

I.D Critical Behavior

The singular behavior in the vicinity of a critical point is characterized by a set of *critical exponents*. These exponents describe the non–analyticity of various thermodynamic functions. The most commonly encountered exponents are listed below:

● **The Order Parameter:** By definition, there is more than one equilibrium phase on a coexistence line. The order parameter is a thermodynamic function that is different in each phase, and hence can be used to distinguish between them. For a magnet, the magnetization

$$m(T) = \frac{1}{V} \lim_{h \to 0} M(h, T),$$

serves as the order parameter. In zero field, m vanishes for a paramagnet and is non–zero in a ferromagnetic, i.e.

$$m(T, h = 0) \propto \begin{cases} 0 & \text{for} \quad T > T_c, \\ |t|^\beta & \text{for} \quad T < T_c, \end{cases} \tag{I.20}$$

where $t = (T_c - T)/T_c$ is the *reduced temperature*. The singular behavior of the order parameter along the coexistence line is therefore indicated by the exponent β. The singular behavior of m along the critical isotherm is indicated by another exponent δ, defined through

$$m(T = T_c, h) \propto h^{1/\delta}. \tag{I.21}$$

The two phases along the liquid–gas coexistence line are differentiated by their density, and the density difference $\rho - \rho_c$, where ρ_c is the critical density, serves the role of the order parameter.

- **Response Functions:** The critical system is quite sensitive to external perturbations, as typified by the infinite compressibility at the liquid–gas critical point. The divergence in the response of the order parameter to a field conjugate to it is indicated by an exponent γ. For example, in a magnet,

$$\chi_{\pm}(T, h = 0) \propto |t|^{-\gamma_{\pm}}, \tag{I.22}$$

where in principle two exponents γ_+ and γ_- are necessary to describe the divergences on the two sides of the phase transition. Actually in almost all cases, the same singularity governs both sides and $\gamma_+ = \gamma_- = \gamma$. The heat capacity is the thermal response function, and its singularities at zero field are described by the exponent α, i.e.

$$C_{\pm}(T, h = 0) \propto |t|^{-\alpha_{\pm}}. \tag{I.23}$$

- **Long–range Correlations:** Since the response functions are related to equilibrium fluctuations, their divergence in fact implies that fluctuations are correlated over long distances. We shall prove this statement by considering the magnetic susceptibility. Starting from the (Gibbs) partition function in a field h, $Z(h) = \text{tr}\{\exp[-\beta \mathcal{H}_0 + \beta h M]\}$, the magnetization can be computed as $\langle M \rangle = \partial \ln Z / \partial(\beta h) = \text{tr}\{M \exp[-\beta \mathcal{H}_0 + \beta h M]\}/Z$. The susceptibility is then related to the variance of magnetization by

$$\begin{aligned}
\chi = \frac{\partial M}{\partial h} &= \beta \left\{ \frac{1}{Z} \text{tr}\left[M^2 \exp\left(-\beta \mathcal{H}_0 + \beta h M\right)\right] - \frac{1}{Z^2} \text{tr}\left[M \exp\left(-\beta \mathcal{H}_0 + \beta h M\right)\right]^2 \right\} \\
&= \frac{1}{k_B T} \left(\langle M^2 \rangle - \langle M \rangle^2 \right).
\end{aligned} \tag{I.24}$$

The overall magnetization is obtained by adding contributions from different parts of the system, i.e.

$$M = \int d^3 \vec{r} \, m(\vec{r}). \tag{I.25}$$

(For the time being we treat the magnetization as a scalar quantity.) Substituting the above into eq.(I.24) gives

$$k_B T \chi = \int d^3 \vec{r} \, d^3 \vec{r}' \left(\langle m(\vec{r}) m(\vec{r}') \rangle - \langle m(\vec{r}) \rangle \langle m(\vec{r}') \rangle \right). \tag{I.26}$$

Translational symmetry of a homogeneous system implies that $\langle m(\vec{r}) \rangle = m$ is a constant, while $\langle m(\vec{r}) m(\vec{r}') \rangle = G(\vec{r} - \vec{r}')$ depends only on the separation. We can express the result in terms of the *connected* correlation function, defined as

$$\langle m(\vec{r}) m(\vec{r}') \rangle_c \equiv \langle \left(m(\vec{r}) - \langle m(\vec{r}) \rangle \right) \left(m(\vec{r}') - \langle m(\vec{r}') \rangle \right) \rangle = G(\vec{r} - \vec{r}') - m^2. \tag{I.27}$$

Integrating over the center of mass coordinates in eq.((I.26)) results in a factor of volume V, and the susceptibility is given by

$$\chi = \beta V \int d^3 \vec{r} \, \langle m(\vec{r})m(0) \rangle_c \, . \tag{I.28}$$

The connected correlation function is a measure of how the local fluctuations in one part of the system effect those of another part. Typically such influences occur over a characteristic distance ξ, called the *correlation length*. (It can be shown rigorously that this function must decay to zero at large separations; in many cases $G_c(\vec{r}) \equiv \langle m(\vec{r})m(0) \rangle_c$ decays as $\exp(-|\vec{r}|/\xi)$ at separations $|\vec{r}| > \xi$.) Let g denote a typical value of the correlation function for $|\vec{r}| < \xi$. It then follows from eq.(I.28) that $k_B T \chi / V < g\xi^3$; and $\chi \to \infty$, necessarily implies $\xi \to \infty$. This divergence of the correlation length also explains the observation of critical opalescence. The correlation function can be measured by scattering probes and its divergence

$$\xi_{\pm}(T, h = 0) \propto |t|^{-\nu_{\pm}}, \tag{I.29}$$

is controlled by exponents $\nu_+ = \nu_- = \nu$.

II. THE LANDAU–GINZBURG APPROACH

II.A Introduction

We noted in the previous section that the singular behavior of thermodynamic functions at a critical point (the termination of a coexistence line) can be characterized by a set of critical exponents $\{\alpha, \beta, \gamma, \cdots\}$. Experimental observations indicate that these exponents are quite *universal*, i.e. independent of the material under investigation, and to some extent, of the nature of the phase transition. For example, the vanishing of the coexistence boundary in the condensation of CO_2 has the same singular behavior as that of the phase separation of protein solutions into dilute and dense components. This universality of behavior needs to be explained. We also noted that the divergence of the response functions, as well as direct observations of fluctuations via scattering studies, indicate that the correlations become long ranged in the vicinity of the critical point. Such correlated fluctuations involve many particles ($\xi \gg a$, where a is a typical inter-particle spacing), and a coarse graining approach, in the spirit of the theory of elasticity, may be appropriate to their description. Here we shall construct such a *statistical field theory*.

We shall frame the discussion in the language of a magnetic system, whose symmetries are more transparent, although the results are of more general applicability. Consider a metal, say iron, close to its Curie point. The microscopic origin of magnetism is quantum mechanical, involving such elements as itinerant electrons, their spin, and the exclusion principle. Clearly a microscopic approach is rather complicated, and material dependent. Such a theory is necessary to find out which elements are likely to produce ferromagnetism. However, given that there is such behavior, the microscopic theory is not necessarily useful to describe its disappearance as a result of thermal fluctuations. This is because the (quantum) statistical mechanics of the collection of interacting electrons is excessively complicated. The important degrees of freedom close to the Curie point, whose statistical mechanics is responsible for the phase transition, are long wavelength collective excitations of spins (much like the long wavelength phonons that dominate the heat capacity at low temperatures). We can thus coarse grain the magnet to a scale much larger than the lattice spacing, and define a magnetization field $\vec{m}(\mathbf{x})$, which represents the average of the elemental spins in the vicinity of a point $\mathbf{x}$. It is important to emphasize that while $\mathbf{x}$ is treated as a continuous variable, the functions $\vec{m}$ do not exhibit any variations at distances

of the order of the lattice spacing, i.e. their Fourier transforms involve only wave-numbers less than some upper cutoff $\Lambda \sim 1/a$.

In describing other types of phase transitions, the role of $\vec{m}(\mathbf{x})$ is played by the appropriate order parameter density. It is then useful to examine a generalized magnetization for n-component spins, existing in d-dimensional space, i.e.

$$\mathbf{x} \equiv (x_1, x_2, ..., x_d) \in \Re^d \quad \text{(space)} \quad , \quad \vec{m} \equiv (m_1, m_2, ..., m_n) \in \Re^n \quad \text{(spin)}.$$

Some specific problems covered in this framework are:

$n = 1$ describes liquid–gas transitions, binary mixtures, as well as uniaxial magnets;

$n = 2$ applies to superfluidity, superconductivity, and planar magnets;

$n = 3$ corresponds to classical magnets.

While most physical situations occur in three–dimensional space ($d = 3$), there are also important phenomena on surfaces ($d = 2$), and in wires ($d = 1$). Relativistic field theory is described by a similar structure, but in $d = 4$.

As in the case of a deformed solid, we construct a local effective Hamiltonian $\beta \mathcal{H}[\vec{m}] = \int d^d\mathbf{x}\Phi[\vec{m}(\mathbf{x})]$, on the basis of appropriate symmetries. We shall assume that the material is *uniform* and *isotropic*, so that all locations and directions in $\mathbf{x}$ space are equivalent. In the absence of an external magnetic field, all directions for magnetization are equivalent, and hence $\mathcal{H}[R_n\vec{m}(\mathbf{x})] = \mathcal{H}[\vec{m}(\mathbf{x})]$, where R_n is a rotation in the n-dimensional space. Some of the terms consistent with these symmetries that can appear in the expansion of $\Phi[\vec{m}(\mathbf{x})]$ are

$$m^2(\mathbf{x}) \equiv \vec{m}(\mathbf{x}) \cdot \vec{m}(\mathbf{x}) \equiv \sum_{i=1}^{n} m_i(\mathbf{x})m_i(\mathbf{x}) \quad , \quad m^4(\mathbf{x}) \equiv \left(m^2(\mathbf{x})\right)^2 \quad , \quad m^6(\mathbf{x}) \quad , \quad \cdots \quad ,$$

$$(\nabla\vec{m})^2 \equiv \sum_{i=1}^{n}\sum_{\alpha=1}^{d} \partial_\alpha m_i \partial_\alpha m_i \quad , \quad (\nabla^2\vec{m})^2 \quad , \quad m^2(\nabla\vec{m})^2 \quad , \quad \cdots \quad .$$

Including a small magnetic field $\vec{h}$, that breaks the rotational symmetry, the lowest order terms in the expansion of Φ lead to,

$$\beta\mathcal{H} = \int d^d\mathbf{x}\left[\frac{t}{2}m^2(\mathbf{x}) + um^4(\mathbf{x}) + \frac{K}{2}(\nabla m)^2 + \cdots - \vec{h} \cdot \vec{m}(\mathbf{x})\right], \quad \text{(II.1)}$$

which is known as the *Landau–Ginzburg* Hamiltonian. (The magnetic field also generates terms proportional to $m^2\vec{m} \cdot \vec{h}$, which are of higher order, and actually less important than the um^4 term.)

Eq.(II.1) is constructed on the basis of symmetry alone, and depends on a set of *phenomenological* parameters $\{t, u, K, \cdots\}$. These parameters are non-universal functions of microscopic interactions, *as well as external parameters such as temperature and pressure.* It is essential to fully appreciate the latter point, which is usually the source of much confusion. The probability for a particular configuration of the field is given by the Boltzmann weight $\exp\{-\beta\mathcal{H}[\vec{m}(\mathbf{x})]\}$. This *does not imply* that all terms in the exponent are proportional to $(k_B T)^{-1}$. Such dependence holds only for the true microscopic Hamiltonian. The Landau–Ginzburg Hamiltonian is more correctly an effective free energy obtained by integrating over (coarse graining) the microscopic degrees of freedom, while constraining their average to $\vec{m}(\mathbf{x})$. It is precisely because of the difficulty of carrying out such a first principles program that we postulate the form of the resulting effective free energy on the basis of symmetries alone. The price paid is that the phenomenological parameters have an unknown functional dependence on the original microscopic parameters, as well as such on external constraints as temperature (since we have to account for the entropy of the short distance fluctuations lost in the coarse graining process).

II.B Saddle Point Approximation, and Mean–Field Theory

The original problem has been simplified considerably by focusing only on the coarse grained magnetization field described by the Landau–Ginzburg Hamiltonian in eq.(II.1). Various thermodynamic functions (and their singular behavior) can now be obtained from the associated partition function

$$Z = \int \mathcal{D}\vec{m}(\mathbf{x}) \exp\{-\beta\mathcal{H}[\vec{m}(\mathbf{x})]\}. \tag{II.2}$$

Since the degrees of freedom appearing in the Hamiltonian are functions of $\mathbf{x}$, the symbol $\int \mathcal{D}\vec{m}(\mathbf{x})$ refers to a *functional integral*. In actuality, the functional integral should be regarded as a limit of discrete integrals. After discretizing the coordinate x into a lattice of $\mathcal{N}$ points i, at a distance a from each other,

$$\int \mathcal{D}m(x)\mathcal{F}\left[m(x), \frac{\partial m}{\partial x}, \cdots\right] \equiv \lim_{\mathcal{N}\to\infty} \prod_{i=1}^{\mathcal{N}} dm_i \mathcal{F}\left[m_i, \frac{m_{i+1} - m_i}{a}, \cdots\right].$$

(There are some mathematical concerns regarding the existence of functional integrals. The problems are associated with having too many degrees of freedom at short distances, allowing rather badly behaved functions. These issues need not concern us since we know

that the underlying problem has a well defined lattice spacing that restricts the short distance behavior.)

It is still difficult to calculate the Landau–Ginzburg partition function. As a first step, we perform a *saddle point approximation* in which the integral in eq.(II.2) is replaced by the maximum value of the integrand. The natural tendency of interactions in a magnet is to keep the magnetizations vectors parallel, and hence we expect the parameter K in eq.(II.1) to be positive. The configuration of $\vec{m}$ that maximizes the integrand is then uniform, and

$$\beta F = -\ln Z \approx V \min\{\Psi(m)\}_m. \tag{II.3}$$

The uniform magnetization occurs for $\vec{m}(\mathbf{x}) = \bar{m}\hat{h}$, which minimizes

$$\Psi(m) \equiv \frac{t}{2}m^2 + um^4 + \cdots - \vec{h}.\vec{m}. \tag{II.4}$$

In the vicinity of the critical point, m is a small quantity, and it is justified to keep only the lowest powers in the expansion of $\Psi(m)$. (We can later check self consistently that the terms left out are indeed small corrections.) The behavior of $\Psi(m)$ depends strongly on the sign of the parameter t.

(1) For $t > 0$, we can ignore the quartic term, and the minimum occurs for $\vec{m} \approx \vec{h}/t$. The vanishing of magnetization as $\vec{h} \to 0$ signals paramagnetic behavior. The susceptibility $\chi = 1/t$, diverges as $t \to 0$.

(2) For $t < 0$, a quartic term with a positive value of u is required to insure stability (i.e. a finite magnetization). The function $\Psi(m)$ now has degenerate minima, at a non–zero value of $\bar{m}$. There is thus a spontaneous magnetization, even at $\vec{h} = 0$ indicating ferromagnetic behavior. The direction of the $\vec{m}$ is determined by the systems preparation, and can be realigned by an external field $\vec{h}$.

Thus a saddle point evaluation of the Landau–Ginzburg partition function results in paramagnetic behavior for $t > 0$, and ferromagnetic behavior for $t < 0$. Hence we can map the phase diagram of the Landau–Ginzburg Hamiltonian to that of a magnet by setting

$$\begin{aligned} t(T, \cdots) &= a(T - T_c) + \mathcal{O}(T - T_c)^2, \\ u(T, \cdots) &= u + u_1(T - T_c) + \mathcal{O}(T - T_c)^2, \end{aligned} \tag{II.5}$$

where a and u are unknown positive constants, dependent upon material properties. The basic idea is that the phenomenological parameters are functions of temperature that can be expanded in a Taylor series in $T - T_c$. The minimal conditions needed to reproduce the

experimental phase diagram are contained in eqs.(II.5). It is of course possible that some other terms in the expansion, e.g. a or u are also zero. However, these are non-generic situations which can presumably be removed by changing some other system parameter.

We now examine the singular behaviors predicted by eqs.(II.3) and (II.4).

• **Magnetization:** In zero field, from $\partial\Psi/\partial m = t\bar{m} + 4u\bar{m}^3 = \bar{m}(t + 4u\bar{m}^2) = 0$, and we obtain

$$\bar{m} = \begin{cases} 0 & \text{for } t > 0, \\ \sqrt{\frac{-t}{4u}} & \text{for } t < 0. \end{cases} \tag{II.6}$$

We thus find a universal exponent $\beta = 1/2$, while the amplitude is material dependent.

• **Heat Capacity:** The free–energy is given by ($h = 0$)

$$\frac{\beta F}{V} = \min \Psi(m) = \begin{cases} 0 & \text{for } t > 0, \\ -\frac{t^2}{16u} & \text{for } t < 0. \end{cases} \tag{II.7}$$

Since $t = a(T - T_c) + \cdots$; $\partial/\partial T \propto \partial/\partial t$, and

$$C = -T\frac{\partial^2 f}{\partial T^2} \propto -\frac{\partial^2}{\partial t^2}\left(\frac{\beta F}{V}\right) = \begin{cases} 0 & \text{for } t > 0, \\ \frac{1}{8u} & \text{for } t < 0. \end{cases} \tag{II.8}$$

We observe a discontinuity, rather than a divergence, in the heat capacity. If we insist upon describing the singularity by a power law, we have to choose the exponent $\alpha = 0$.

• **Susceptibility:** In the presence of $\vec{h}$, we expect $\vec{m} = \bar{m}(h)\hat{h}$, and from $\partial\Psi/\partial m = 0$, we obtain $t\bar{m} + 4u\bar{m}^3 = h$. Hence

$$\chi_\ell^{-1} = \left.\frac{\partial h}{\partial \bar{m}}\right|_{h=0} = t + 12u\bar{m}^2 = \begin{cases} t & \text{for } t > 0, \\ -2t & \text{for } t < 0. \end{cases} \tag{II.9}$$

Thus the singularity in susceptibility is describable by $\chi_\pm \sim A_\pm|t|^{-\gamma_\pm}$, with $\gamma_+ = \gamma_- = 1$. Although the amplitudes $A_\pm$ are material dependent, their ratio is predicted to be universal, with $A_+/A_- = 2$. (As we shall see later, what we have calculated so far is a *longitudinal susceptibility*. There is also a *transverse susceptibility* that is always infinite below T_c.)

• **Equation of State:** On the critical isotherm $t = 0$, the magnetization behaves as $\bar{m} = (h/4u)^{1/3}$, i.e.

$$\bar{m}(t = 0, h) \sim h^{1/\delta}, \quad \text{with} \quad \delta = 3. \tag{II.10}$$

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