

# Collective behavior, from particles to fields

## 1.1 Introduction

One of the most successful aspects of physics in the twentieth century was revealing the atomistic nature of matter, characterizing its elementary constituents, and describing the laws governing the interactions and dynamics of these particles. A continuing challenge is to find out how these underlying elements lead to the myriad of different forms of matter observed in the real world. The emergence of new collective properties in the *macroscopic* realm from the dynamics of the *microscopic* particles is the topic of statistical mechanics.

*The microscopic description* of matter is in terms of the many degrees of freedom: the set of positions and momenta  $\{\vec{p}_i, \vec{q}_i\}$ , of particles in a gas, configurations of spins  $\{\vec{s}_i\}$ , in a magnet, or occupation numbers  $\{n_i\}$ , in a grand canonical ensemble. The evolution of these degrees of freedom is governed by classical or quantum equations of motion derived from an underlying Hamiltonian  $\mathcal{H}$ .

*The macroscopic description* usually involves only a few phenomenological variables. For example, the equilibrium properties of a gas are specified by its pressure  $P$ , volume  $V$ , temperature  $T$ , internal energy  $E$ , entropy  $S$ . The laws of thermodynamics constrain these equilibrium state functions.

A step-by-step derivation of the macroscopic properties from the microscopic equations of motion is generally impossible, and largely unnecessary. Instead, statistical mechanics provides a *probabilistic connection* between the two regimes. For example, in a canonical ensemble of temperature  $T$ , each microstate,  $\mu$ , of the system occurs with a probability  $p(\mu) = \exp(-\beta\mathcal{H}(\mu))/Z$ , where  $\beta = (k_B T)^{-1}$ . To insure that the total probability is normalized to unity, the *partition function*  $Z(T)$  must equal  $\sum_{\mu} \exp(-\beta\mathcal{H}(\mu))$ . Thermodynamic information about the *macroscopic* state of the system is then extracted from the *free energy*  $F = -k_B T \ln Z$ .

While circumventing the dynamics of particles, the recipes of statistical mechanics can be fully carried out only for a small number of simple systems; mostly describing non-interacting collections of particles where the partition function can be calculated exactly. Some effects of interactions can be included by perturbative treatments around such exact solutions. However, even for the

relatively simple case of an imperfect gas, the perturbative approach breaks down close to the condensation point. On the other hand, it is precisely the multitude of new phases and properties resulting from interactions that renders macroscopic physics interesting. In particular, we would like to address the following questions:

- (1) In the thermodynamic limit ( $N \rightarrow \infty$ ), strong interactions lead to new phases of matter such as solids, liquid crystals, magnets, superconductors, etc. How can we describe the emergence of such distinct macroscopic behavior from the interactions of the underlying particles? What are the thermodynamic variables that describe the macroscopic state of these phases; and what are their identifying signatures in measurements of bulk response functions (heat capacity, susceptibility, etc.)?
- (2) What are the characteristic low energy excitations of the system? As in the case of phonons in solids or in superfluid helium, low energy excitations are typically *collective modes*, which involve the coordinated motions of many microscopic degrees of freedom (particles). These modes are easily excited by thermal fluctuations, and probed by scattering experiments.

The underlying microscopic Hamiltonian for the interactions of particles is usually quite complicated, making an *ab initio* particulate approach to the problem intractable. However, there are many common features in the macroscopic behavior of many such systems that can still be fruitfully studied by the methods of statistical mechanics. Although the interactions between constituents are quite specific at the microscopic scale, one may hope that averaging over sufficiently many particles leads to a simpler description. (In the same sense that the central limit theorem ensures that the sum over many random variables has a simple Gaussian probability distribution function.) This expectation is indeed justified in many cases where the collective behavior of the interacting system becomes more simple at long wavelengths and long times. (This is sometimes called the *hydrodynamic limit* by analogy to the Navier–Stokes equations for a fluid of particles.) The averaged variables appropriate to these length and time scales are no longer the discrete set of particle degrees of freedom, but slowly varying continuous *fields*. For example, the velocity field that appears in the Navier–Stokes equations is quite distinct from the velocities of the individual particles in the fluid. Hence the appropriate method for the study of collective behavior in interacting systems is the statistical mechanics of fields. Accordingly, the aims of this book are as follows:

- **Goal:** To learn to describe and classify states of matter, their collective properties, and the mechanisms for transforming from one phase to another.
- **Tools:** Methods of classical field theories; use of symmetries, treatment of nonlinearities by perturbation theory, and the renormalization group (RG) method.
- **Scope:** To provide sufficient familiarity with the material to follow the current literature on such subjects as phase transitions, growth phenomena, polymers, superconductors, etc.

## 1.2 Phonons and elasticity

The theory of elasticity represents one of the simplest examples of a field theory. We shall demonstrate how certain properties of an elastic medium can be obtained, either by the complicated method of starting from first principles, or by the much simpler means of appealing to symmetries of the problem. As such, it represents a prototype of how much can be learned from a phenomenological approach. The actual example has little to do with the topics that will be covered later on, but it fully illustrates the methodology that will be employed. The task of computing the low temperature heat capacity of a solid can be approached by either *ab initio* or *phenomenological* methods.

### Particulate approach

Calculating the heat capacity of a solid material from first principles is rather complicated. We briefly sketch some of the steps:

- The *ab initio* starting point is the Schrödinger equation for electrons and ions which can only be treated approximately, say by a density functional formalism. Instead, we start with a many-body potential energy for the *ionic* coordinates  $\mathcal{V}(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N)$ , which may itself be the outcome of such a quantum mechanical treatment.
- Ideal lattice positions at zero temperature are obtained by minimizing  $\mathcal{V}$ , typically forming a lattice  $\vec{q}^*(\ell, m, n) = [\ell\hat{a} + m\hat{b} + n\hat{c}] \equiv \vec{q}_{\vec{r}}^*$ , where  $\vec{r} = \{\ell, m, n\}$  is a triplet of integers, and  $\hat{a}$ ,  $\hat{b}$ , and  $\hat{c}$  are unit vectors.
- Small fluctuations about the ideal positions (due to finite temperature or quantum effects) are included by setting  $\vec{q}_{\vec{r}} = \vec{q}_{\vec{r}}^* + \vec{u}(\vec{r})$ . The cost of deformations in the potential energy is given by

$$\mathcal{V} = \mathcal{V}^* + \frac{1}{2} \sum_{\vec{r}, \vec{r}'} \sum_{\alpha, \beta} \frac{\partial^2 \mathcal{V}}{\partial q_{\vec{r}, \alpha} \partial q_{\vec{r}', \beta}} u_{\alpha}(\vec{r}) u_{\beta}(\vec{r}') + O(u^3), \quad (1.1)$$

where the indices  $\alpha$  and  $\beta$  denote spatial components. (Note that the first derivative of  $\mathcal{V}$  vanishes at the equilibrium position.) The full Hamiltonian for small deformations is obtained by adding the kinetic energy  $\sum_{\vec{r}, \alpha} p_{\alpha}(\vec{r})^2/2m$  to Eq. (1.1), where  $p_{\alpha}(\vec{r})$  is the momentum conjugate to  $u_{\alpha}(\vec{r})$ .

- The next step is to find the normal modes of vibration (phonons) by diagonalizing the matrix of derivatives. Since the ground state configuration is a regular lattice, the elements of this matrix must satisfy various translation and rotation symmetries. For example, they can only depend on the difference between the position vectors of ions  $\vec{r}$  and  $\vec{r}'$ , i.e.

$$\frac{\partial^2 \mathcal{V}}{\partial q_{\vec{r}, \alpha} \partial q_{\vec{r}', \beta}} = K_{\alpha\beta}(\vec{r} - \vec{r}'). \quad (1.2)$$

This translational symmetry allows us to at least partially diagonalize the Hamiltonian by using the Fourier modes,

$$u_{\alpha}(\vec{r}) = \sum_{\vec{k}} \frac{e^{i\vec{k} \cdot \vec{r}}}{\sqrt{N}} u_{\alpha}(\vec{k}). \quad (1.3)$$

(The above sum is restricted, in that only wavevectors  $\vec{k}$  inside the first Brillouin zone contribute to the sum.) The Hamiltonian then reads

$$\mathcal{H} = \mathcal{V}^* + \frac{1}{2} \sum_{\vec{k}, \alpha, \beta} \left[ \frac{|p_\alpha(\vec{k})|^2}{m} + K_{\alpha\beta}(\vec{k}) u_\alpha(\vec{k}) u_\beta(\vec{k})^* \right], \quad (1.4)$$

where  $u_\beta(\vec{k})^*$  is the complex conjugate of  $u_\beta(\vec{k})$ . While the precise form of the Fourier transformed matrix  $K_{\alpha\beta}(\vec{k})$  is determined by the microscopic interactions, it has to respect the underlying symmetries of the crystallographic point group. Let us assume that diagonalizing this  $3 \times 3$  matrix yields eigenvalues  $\{\kappa_\alpha(\vec{k})\}$ . The quadratic part of the Hamiltonian is now decomposed into a set of independent (non-interacting) harmonic oscillators.

- The final step is to quantize each oscillator, leading to

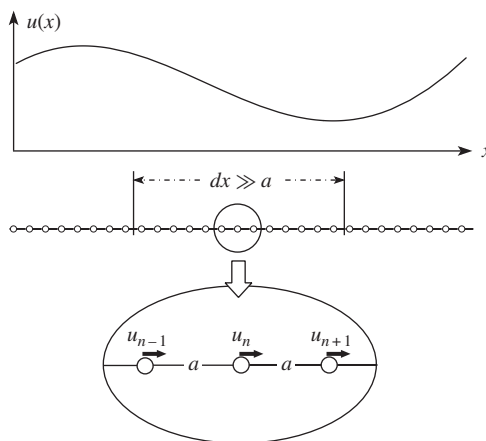
$$\mathcal{H} = \mathcal{V}^* + \sum_{\vec{k}, \alpha} \hbar \omega_\alpha(\vec{k}) \left( n_\alpha(\vec{k}) + \frac{1}{2} \right), \quad (1.5)$$

where  $\omega_\alpha(\vec{k}) = \sqrt{\kappa_\alpha(\vec{k})/m}$ , and  $\{n_\alpha(\vec{k})\}$  are the set of occupation numbers. The average energy at a temperature  $T$  is given by

$$E(T) = \mathcal{V}^* + \sum_{\vec{k}, \alpha} \hbar \omega_\alpha(\vec{k}) \left( \langle n_\alpha(\vec{k}) \rangle + \frac{1}{2} \right), \quad (1.6)$$

where we know from elementary statistical mechanics that the average occupation numbers are given by  $\langle n_\alpha(\vec{k}) \rangle = 1/(\exp(\frac{\hbar \omega_\alpha}{k_B T}) - 1)$ . Clearly  $E(T)$ , and other macroscopic functions, have a complex behavior, dependent upon microscopic details through  $\{\kappa_\alpha(\vec{k})\}$ . Are there any features of these functions (e.g. the functional dependence as  $T \rightarrow 0$ ) that are independent of microscopic features? The answer is positive, and illustrated with a one-dimensional example.

**Fig. 1.1** Displacements  $\{u_n\}$  of a one-dimensional chain of particles, and the coarse-grained field  $u(x)$  of the continuous string.



Consider a chain of particles, constrained to move in one dimension. A most general quadratic potential energy for deformations  $\{u_n\}$ , around an average separation of  $a$ , is

$$\mathcal{V} = \mathcal{V}^* + \frac{K_1}{2} \sum_n (u_{n+1} - u_n)^2 + \frac{K_2}{2} \sum_n (u_{n+2} - u_n)^2 + \dots, \quad (1.7)$$

where  $\{K_i\}$  can be regarded as the Hookian constants of springs connecting particles that are  $i$ -th neighbors. The decomposition to normal modes is achieved via

$$u_n = \int_{-\pi/a}^{\pi/a} \frac{dk}{2\pi} e^{-ikna} u(k), \quad \text{where} \quad u(k) = a \sum_n e^{ikna} u_n. \quad (1.8)$$

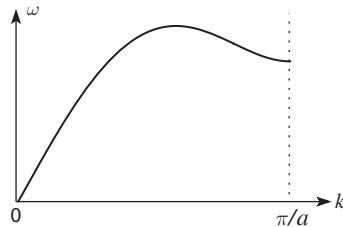
(Note the difference in normalizations from Eq. 1.3.) The potential energy,

$$\mathcal{V} = \mathcal{V}^* + \frac{K_1}{2} \sum_n \int_{-\pi/a}^{\pi/a} \frac{dk}{2\pi} \frac{dk'}{2\pi} (e^{ika} - 1)(e^{ik'a} - 1) e^{-i(k+k')na} u(k) u(k') + \dots, \quad (1.9)$$

can be simplified by using the identity  $\sum_n e^{-i(k+k')na} = \delta(k+k')2\pi/a$ , and noting that  $u(-k) = u^*(k)$ , to

$$\mathcal{V} = \mathcal{V}^* + \frac{1}{2a} \int_{-\pi/a}^{\pi/a} \frac{dk}{2\pi} [K_1(2 - 2\cos ka) + K_2(2 - 2\cos 2ka) + \dots] |u(k)|^2. \quad (1.10)$$

A typical frequency spectrum of normal modes, given by  $\omega(k) = \sqrt{[2K_1(1 - \cos ka) + \dots]/m}$ , is depicted in Fig. 1.2. In the limit  $k \rightarrow 0$ , the dispersion relation becomes linear,  $\omega(k) \rightarrow v|k|$ , and from its slope we can identify a ‘sound velocity’  $v = a\sqrt{\bar{K}/m}$ , where  $\bar{K} = K_1 + 4K_2 + \dots$ .



**Fig. 1.2** Typical dispersion relation for phonons along a chain.

The internal energy of these excitations, for a chain of  $N$  particles, is

$$E(T) = \mathcal{V}^* + Na \int_{-\pi/a}^{\pi/a} \frac{dk}{2\pi} \frac{\hbar\omega(k)}{\exp(\hbar\omega(k)/k_B T) - 1}. \quad (1.11)$$

As  $T \rightarrow 0$ , only modes with  $\hbar\omega(k) < k_B T$  are excited. Hence only the  $k \rightarrow 0$  part of the excitation spectrum is important and  $E(T)$  simplifies to

$$E(T) \approx \mathcal{V}^* + Na \int_{-\infty}^{\infty} \frac{dk}{2\pi} \frac{\hbar v|k|}{\exp(\hbar v|k|/k_B T) - 1} = \mathcal{V}^* + Na \frac{\pi^2}{6\hbar v} (k_B T)^2. \quad (1.12)$$

## Note

- (1) While the full spectrum of excitation energies can be quite complicated, as  $k \rightarrow 0$ ,

$$\frac{K(k)}{2} = K_1(1 - \cos ka) + K_2(1 - \cos 2ka) + \dots \rightarrow \frac{\bar{K}}{2}k^2 \quad \text{where,} \quad (1.13)$$

$$\bar{K} = K_1 + 4K_2 + \dots$$

Thus, further neighbor interactions change the speed of sound, but not the form of the dispersion relation as  $k \rightarrow 0$ .

- (2) The heat capacity  $C(T) = dE/dT$  is proportional to  $T$ . This dependence is a *universal* property, i.e. not material specific, and independent of the choice of the interatomic interactions.
- (3) The  $T^2$  dependence of energy comes from excitations with  $k \rightarrow 0$  (or  $\lambda \rightarrow \infty$ ), i.e. from collective modes involving many particles. These are precisely the modes for which statistical considerations may be meaningful.

## Phenomenological (field) approach

We now outline a mesoscopic approach to the same problem, and show how it provides additional insights and is easily generalized to higher dimensions. Typical excitations at low temperatures have wavelengths  $\lambda > \lambda(T) \approx (\hbar v/k_B T) \gg a$ , where  $a$  is the lattice spacing. We can eliminate the unimportant short wavelength modes by an averaging process known as **coarse graining**. The idea is to consider a point  $x$ , and an interval of size  $dx$  around it (Fig. 1.1). We shall choose  $a \ll dx \ll \lambda(T)$ , i.e. the interval is large enough to contain many lattice points, but much shorter than the characteristic wavelength of typical phonons. In this interval all the displacements  $u$  are approximately the same; and we can define an average deformation field  $u(x)$ . By construction, the function  $u(x)$  varies slowly over  $dx$ , and despite the fact that this interval contains many lattice points, from the perspective of the function it is infinitesimal in size. We should always keep in mind that while  $u(x)$  is treated as a continuous function, it does not have any variations over distances comparable to the lattice spacing  $a$ .

- By examining the displacements as a function of time, we can define a velocity field  $\dot{u}(x) \equiv \partial u / \partial t$ . The kinetic energy is then related to the mass density  $\rho = m/a$  via  $\rho \int dx \dot{u}(x)^2 / 2$ .
- What is the most general potential energy functional  $\mathcal{V}[u]$ , for the chain? A priori, we don't know much about the form of  $\mathcal{V}[u]$ , but we can construct it by using the following general principles:

**Locality:** In most situations, the interactions between particles are short range, allowing us to define a potential energy *density*  $\Phi$  at each point  $x$ , with  $\mathcal{V}[u] = \int dx \Phi(u(x), \partial u / \partial x, \dots)$ . Naturally, by including all derivatives we can also describe long-range interactions. In this context, the term *locality* implies that the higher derivative terms are less significant.

**Translational symmetry:** A uniform translation of the chain does not change its internal energy, and hence the energy density must satisfy the constraint  $\Phi[u(x) + c] = \Phi[u(x)]$ . This implies that  $\Phi$  cannot depend directly on  $u(x)$ , but only on its derivatives  $\partial u/\partial x$ ,  $\partial^2 u/\partial x^2$ ,  $\dots$ .

**Stability:** Since the fluctuations are around an *equilibrium* solution, there can be no linear terms in  $u$  or its derivatives. (Stability further requires that the quadratic part of  $\mathcal{V}[u]$  must be positive definite.)

The most general potential consistent with these constraints can be expanded as a power series

$$\mathcal{V}[u] = \int dx \left[ \frac{K}{2} \left( \frac{\partial u}{\partial x} \right)^2 + \frac{L}{2} \left( \frac{\partial^2 u}{\partial x^2} \right)^2 + \dots + M \left( \frac{\partial u}{\partial x} \right)^2 \left( \frac{\partial^2 u}{\partial x^2} \right) + \dots \right], \quad (1.14)$$

which after Fourier transformation gives

$$\begin{aligned} \mathcal{V}[u] = & \int \frac{dk}{2\pi} \left[ \frac{K}{2} k^2 + \frac{L}{2} k^4 + \dots \right] |u(k)|^2 \\ & - iM \int \frac{dk_1}{2\pi} \frac{dk_2}{2\pi} k_1 k_2 (k_1 + k_2)^2 u(k_1) u(k_2) u(-k_1 - k_2) + \dots \end{aligned} \quad (1.15)$$

As  $k \rightarrow 0$ , higher order gradient terms (such as the term proportional to  $L$ ) become unimportant. Also, for small deformations we may neglect terms beyond second order in  $u$  (such as the cubic term with coefficient  $M$ ). Another assumption employed in constructing Eq. (1.14) is that the mirror image deformations  $u(x)$  and  $u(-x)$  have the same energy. This may not be valid in more complicated lattices without inversion symmetry.

Adding the kinetic energy, we get a simple one-dimensional field theory, with a Hamiltonian

$$\mathcal{H} = \frac{\rho}{2} \int dx \left[ \left( \frac{\partial u}{\partial t} \right)^2 + v^2 \left( \frac{\partial u}{\partial x} \right)^2 \right].$$

This is a one-dimensional elastic (string) theory with material dependent constants  $\rho$  and  $v = \sqrt{K/\rho}$ . While the phenomenological approach cannot tell us the value of these parameters, it does show that the low energy excitations satisfy the dispersion relation  $\omega = v|k|$  (obtained by examining the Fourier modes).

We can now generalize the elastic theory of the string to arbitrary dimensions  $d$ : The discrete particle deformations  $\{\vec{u}_n\}$  are coarse grained into a continuous deformation field  $\vec{u}(\vec{x})$ . For an *isotropic* material, the potential energy  $\mathcal{V}[\vec{u}]$  must be invariant under both rotations and translations (described by  $u_\alpha(\vec{x}) \mapsto R_{\alpha\beta} u_\beta(\vec{x}) + c_\alpha$ , where  $R_{\alpha\beta}$  is a rotation matrix). A useful local quantity is the symmetric *strain field*,

$$u_{\alpha\beta}(\vec{x}) = \frac{1}{2} \left( \frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right), \quad (1.16)$$

in terms of which the most general quadratic deformation Hamiltonian is

$$\mathcal{H} = \frac{1}{2} \int d^d \vec{x} \left[ \sum_{\alpha} \left( \rho \frac{\partial u_{\alpha}}{\partial t} \frac{\partial u_{\alpha}}{\partial t} \right) + \sum_{\alpha, \beta} (2\mu u_{\alpha\beta} u_{\alpha\beta} + \lambda u_{\alpha\alpha} u_{\beta\beta}) \right]. \quad (1.17)$$

The elastic moduli  $\mu$  and  $\lambda$  are known as *Lamé coefficients*. Summing over the repeated indices ensures that the result is rotationally invariant. This rotational invariance is more transparent in the Fourier basis,  $\vec{u}(\vec{k}) = \int d^d \vec{x} e^{i\vec{k} \cdot \vec{x}} \vec{u}(\vec{x})$ , since the Hamiltonian

$$\mathcal{H} = \int \frac{d^d \mathbf{k}}{(2\pi)^d} \left[ \frac{\rho}{2} |\dot{\vec{u}}(\vec{k})|^2 + \frac{\mu}{2} k^2 |\vec{u}(\vec{k})|^2 + \frac{\mu + \lambda}{2} (\vec{k} \cdot \vec{u}(\vec{k}))^2 \right], \quad (1.18)$$

manifestly includes only rotationally invariant quantities  $\vec{k} \cdot \vec{k}$ ,  $\vec{u} \cdot \vec{u}$ , and  $\vec{k} \cdot \vec{u}$ . We can further decompose the Hamiltonian into two types of sound modes: *longitudinal modes* where  $\vec{k} \parallel \vec{u}$ , with  $v_{\ell} = \sqrt{(2\mu + \lambda)/\rho}$ , and *transverse modes* with  $\vec{k} \perp \vec{u}$ , where  $v_t = \sqrt{\mu/\rho}$ . The internal energy in a volume  $L^d$  is then given by

$$E(t) = L^d \int \frac{d^d \mathbf{k}}{(2\pi)^d} \left[ \frac{\hbar v_{\ell} k}{\exp(\hbar v_{\ell} k / k_B T) - 1} + \frac{(d-1)\hbar v_t k}{\exp(\hbar v_t k / k_B T) - 1} \right] \quad (1.19)$$

$$\approx \mathcal{A}(v_{\ell}, v_t) L^d (k_B T)^{d+1}.$$

The specific heat now vanishes as  $C \propto T^d$ , as  $T \rightarrow 0$ .

## Note

- (1) All material dependent parameters end up in the coefficient  $\mathcal{A}$ , while the scaling with  $T$  is *universal*.
- (2) The universal exponent originates from the (hydrodynamic) modes with  $\vec{k} \rightarrow 0$ . The high frequency (short wavelength) modes come into play only at high temperatures.
- (3) The scaling exponent depends on dimensionality and the range of interactions. (Long-range Coulomb interactions lead to a different result.)
- (4) Experimental observation of a power law alerts us to the physics. For example, in superfluid helium, the observation of  $C \propto T^3$  (as opposed to  $C \propto T^{3/2}$  expected for an ideal Bose gas), immediately implies phonon-like excitations as noted by Landau.

There are many other well known examples demonstrating the universality and importance of power laws. For example, consider a cloud of tracers moving in some unspecified medium. The scaling of some characteristic dimension  $x$  with time  $t$  can alert us to the possible dynamics that governs the motion of the particles. Three simple possibilities are:

- (1) *Diffusion*, in which case  $x \propto \sqrt{Dt}$ .
- (2) *Dissipate transport*, where  $x \propto vt$ .
- (3) *Free forced motion*, where  $x \propto gt^2/2$ , as in a gravitational field.



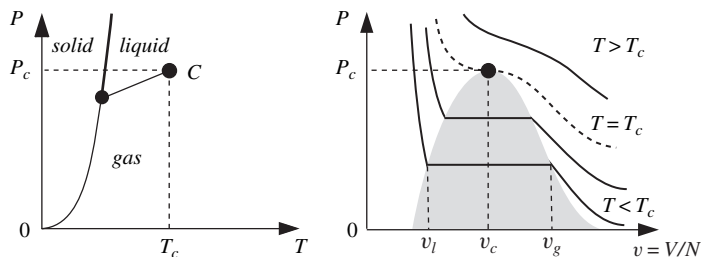
The Navier–Stokes equation for fluid flow is yet another example. We can use these examples to construct general guidelines for setting up and analyzing phenomenological field theories. Some of the steps in the procedure are:

- (1) **Input** for construction of the coarse grained Hamiltonian comes from considerations of symmetry, range of interactions, and dimensionality.
- (2) Unlike the above example, in general nonlinearities cannot be ignored in the resulting effective field theory. We shall learn how to treat such nonlinearities by the methods of perturbation theory and the renormalization group.
- (3) **Output** of the analysis is expressed in terms of universal exponents, and other functional dependencies that can then be compared with observations.

### 1.3 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*,  $N \rightarrow \infty$ . 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. Two perspectives of the phase diagram for a typical system of particles is given in Fig. 1.3. Some important features of the liquid–gas condensation transition are:



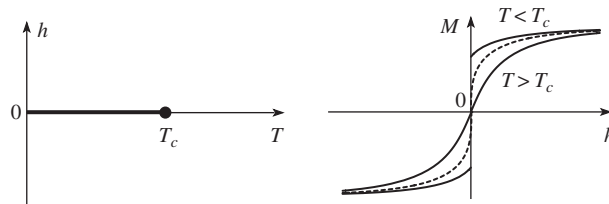
**Fig. 1.3** Schematic phase diagrams of a typical system in the pressure, temperature coordinates (*left*). The isotherms in the pressure, specific volume coordinates (*right*) are flat in the coexistence region below the critical point.

- (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  $\rho_\ell = 1/v_\ell$ , 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 a 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.  $\rho_{\text{liquid}} \rightarrow \rho_{\text{gas}}$ , as  $T \rightarrow T_c^-$ .
- (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,  $\kappa_T = -\partial V/\partial P|_T/V$ , diverges as  $T \rightarrow T_c^+$ .
- (6) The fluid appears “milky” close to criticality. This phenomenon, known as *critical opalescence*, suggests that collective fluctuations occur 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.

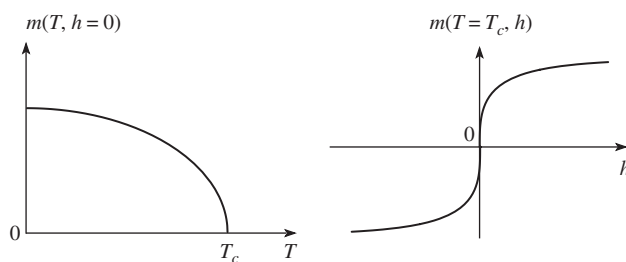
**Fig. 1.4** *Left:* Phase diagram for a typical magnet in the magnetic-field, temperature coordinates. *Right:* Magnetization versus field isotherms.



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  $h_c = M_c = 0$ .

## 1.4 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:



**Fig. 1.5** Singular behavior for the magnetization of a magnet.

- **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

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

serves as the order parameter. In zero field,  $m$  vanishes for a paramagnet and is non-zero in a ferromagnet, and close to the transition behaves as

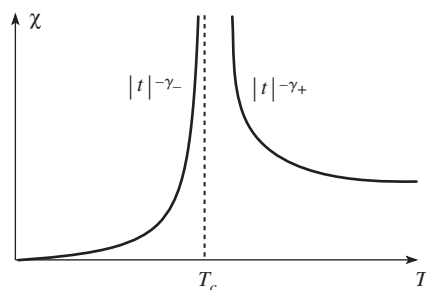
$$m(T, h=0) \propto \begin{cases} 0 & \text{for } T > T_c, \\ |t|^\beta & \text{for } T < T_c, \end{cases} \quad (1.20)$$

where  $t = (T_c - T)/T_c$  is the *reduced temperature*. The singular behavior of the order parameter along the coexistence line is traditionally indicated by the critical exponent  $\beta$ . The phase transition disappears in a finite magnetic field, i.e. the magnetization varies continuously with  $T$  at a finite  $h$ . This non-analyticity is thus reminiscent of a *branch cut* in a complex plane. The magnetization is non-analytic for any trajectory in the  $(T, h)$  plane that passes through the critical point at  $T = T_c$  and  $h = 0$ . In particular, it vanishes along the critical isotherm, with another exponent denoted by  $\delta$ , defined through

$$m(T = T_c, h) \propto h^{1/\delta}. \quad (1.21)$$

The two phases along the liquid–gas coexistence line can be differentiated by their densities  $\rho_g$  and  $\rho_\ell$ . Their differences from the critical point density,  $\rho_\ell - \rho_c$  and  $\rho_c - \rho_g$  can serve as the order parameter. In the vicinity of the critical point, both

**Fig. 1.6** Divergence of the susceptibility is described by the critical exponents  $\gamma_{\pm}$ .



these quantities, as well as  $\rho_\ell - \rho_g$  vanish with the exponent  $\beta$ . The exponent  $\delta$  now describes the singular form of the critical isotherm in Fig. 1.3.

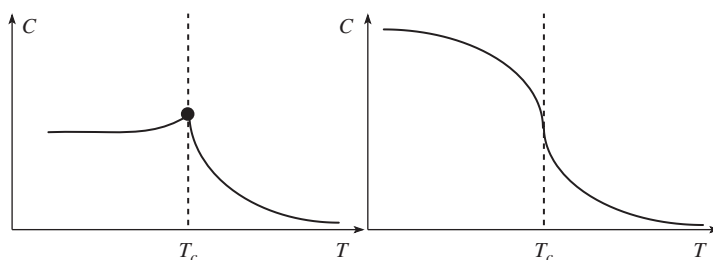
- **Response functions:** The critical system is quite sensitive to external perturbations, as typified by the infinite compressibility at the liquid–gas critical point.

The divergence in the response of the order parameter to a field conjugate to it is indicated by an exponent  $\gamma$ . For example, in a magnet,

$$\chi_{\pm}(T, h = 0) \propto |t|^{-\gamma_{\pm}}, \quad (1.22)$$

where in principle two exponents  $\gamma_+$  and  $\gamma_-$  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  $\gamma_+ = \gamma_- = \gamma$ .

**Fig. 1.7** A negative heat capacity exponent  $\alpha$  may (left) or may not (right) describe a cusp singularity depending on the relative signs of amplitudes.



The heat capacity is the thermal response function, and its singularities at zero field are described by the exponent  $\alpha$ , i.e.

$$C_{\pm}(T, h = 0) \propto |t|^{-\alpha_{\pm}}. \quad (1.23)$$

A positive  $\alpha$  corresponds to a divergence as in Fig. 1.6, while a negative  $\alpha$  describes a finite heat capacity, possibly with a cusp, as in Fig. 1.7. We shall also encounter cases where  $\alpha$  is zero.

- **Long-range correlations:** There is an intimate connection between the macroscopic response functions, and fluctuations of microscopic constituents of a material. In fact divergences of the response functions at a critical point imply, and are a consequence of, correlated fluctuations over large distances. Let us explore this connection in the

context of the susceptibility of a magnet. A convenient starting point is the (Gibbs) partition function in a magnetic field  $h$ , given by

$$Z(h) = \text{tr}\{\exp[-\beta\mathcal{H}_0 + \beta hM]\}, \quad (1.24)$$

where  $\mathcal{H}_0$  describes the internal energy of the magnet, while  $-hM$  is the work done against the magnetic field to produce a magnetization  $M$ . The symbol  $\text{tr}$  is used to indicate the sum over all microscopic degrees of freedom. The equilibrium magnetization is computed from

$$\langle M \rangle = \frac{\partial \ln Z}{\partial (\beta h)} = \frac{1}{Z} \text{tr}\{M \exp[-\beta\mathcal{H}_0 + \beta hM]\}, \quad (1.25)$$

and the susceptibility is then related to the variance of magnetization by

$$\begin{aligned} \chi = \frac{\partial M}{\partial h} &= \beta \left\{ \frac{1}{Z} \text{tr}[M^2 \exp(-\beta\mathcal{H}_0 + \beta hM)] - \frac{1}{Z^2} \text{tr}[M \exp(-\beta\mathcal{H}_0 + \beta hM)]^2 \right\} \\ &= \frac{1}{k_B T} (\langle M^2 \rangle - \langle M \rangle^2). \end{aligned} \quad (1.26)$$

The overall magnetization is obtained by adding contributions from different parts of the system as

$$M = \int d^3\vec{r} m(\vec{r}), \quad (1.27)$$

where  $m(\vec{r})$  is the local magnetization at position  $\vec{r}$ . (For the time being we treat the magnetization as a scalar quantity.) Substituting the above into Eq. (1.26) gives

$$k_B T \chi = \int d^3\vec{r} d^3\vec{r}' (\langle m(\vec{r})m(\vec{r}') \rangle - \langle m(\vec{r}) \rangle \langle m(\vec{r}') \rangle). \quad (1.28)$$

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

$$\langle m(\vec{r})m(\vec{r}') \rangle_c \equiv (\langle m(\vec{r}) - \langle m(\vec{r}) \rangle \rangle (\langle m(\vec{r}') - \langle m(\vec{r}') \rangle \rangle)) = G(\vec{r} - \vec{r}') - m^2. \quad (1.29)$$

Integrating over the center of mass coordinates in Eq. (1.28) results in a factor of volume  $V$ , and the susceptibility is given by

$$\chi = \beta V \int d^3\vec{r} \langle m(\vec{r})m(0) \rangle_c. \quad (1.30)$$

The left-hand side of the above expression is the bulk response function, which is related to the integral of the connected correlation functions of the microscopic degrees of freedom. 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  $\xi$ , 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  $|\vec{r}| > \xi$ .) The microscopic correlations can be probed by scattering experiments. For example, the milky appearance (critical opalescence) of a near critical liquid–gas mixture is due to the scattering of light by density fluctuations. Since the wavelength of light is

much larger than typical atomic distances, the density fluctuations must be correlated over long distances to scatter visible light.

Let  $g$  denote a typical value of the correlation function for  $|\vec{r}| < \xi$ . It then follows from Eq. (1.30) that  $k_B T \chi / V < g \xi^3$ ; and  $\chi \rightarrow \infty$ , necessarily implies  $\xi \rightarrow \infty$ . This divergence of the correlation length explains the observation of critical opalescence. On approaching the critical point, the correlation length diverges as

$$\xi_{\pm}(T, h = 0) \propto |t|^{-\nu_{\pm}}, \quad (1.31)$$

characterized by exponents  $\nu_+ = \nu_- = \nu$ .

## Problems for chapter 1

1. *The binary alloy:* A binary alloy (as in  $\beta$  brass) consists of  $N_A$  atoms of type  $A$ , and  $N_B$  atoms of type  $B$ . The atoms form a simple cubic lattice, each interacting only with its six nearest neighbors. Assume an attractive energy of  $-J$  ( $J > 0$ ) between like neighbors  $A-A$  and  $B-B$ , but a repulsive energy of  $+J$  for an  $A-B$  pair.
  - (a) What is the minimum energy configuration, or the state of the system at zero temperature?
  - (b) Estimate the total interaction energy assuming that the atoms are randomly distributed among the  $N$  sites; i.e. each site is occupied independently with probabilities  $p_A = N_A/N$  and  $p_B = N_B/N$ .
  - (c) Estimate the mixing entropy of the alloy with the same approximation. Assume  $N_A, N_B \gg 1$ .
  - (d) Using the above, obtain a free energy function  $F(x)$ , where  $x = (N_A - N_B)/N$ . Expand  $F(x)$  to the fourth order in  $x$ , and show that the requirement of convexity of  $F$  breaks down below a critical temperature  $T_c$ . For the remainder of this problem use the expansion obtained in (d) in place of the full function  $F(x)$ .
  - (e) Sketch  $F(x)$  for  $T > T_c$ ,  $T = T_c$ , and  $T < T_c$ . For  $T < T_c$  there is a range of compositions  $x < |x_{sp}(T)|$  where  $F(x)$  is not convex and hence the composition is locally unstable. Find  $x_{sp}(T)$ .
  - (f) The alloy globally minimizes its free energy by separating into  $A$  rich and  $B$  rich phases of compositions  $\pm x_{eq}(T)$ , where  $x_{eq}(T)$  minimizes the function  $F(x)$ . Find  $x_{eq}(T)$ .
  - (g) In the  $(T, x)$  plane sketch the phase separation boundary  $\pm x_{eq}(T)$ ; and the so called spinodal line  $\pm x_{sp}(T)$ . (The spinodal line indicates onset of metastability and hysteresis effects.)
2. *The Ising model of magnetism:* The local environment of an electron in a crystal sometimes forces its spin to stay parallel or anti-parallel to a given lattice direction. As a model of magnetism in such materials we denote the direction of the spin by a

single variable  $\sigma_i = \pm 1$  (an Ising spin). The energy of a configuration  $\{\sigma_i\}$  of spins is then given by

$$\mathcal{H} = \frac{1}{2} \sum_{i,j=1}^N J_{ij} \sigma_i \sigma_j - h \sum_i \sigma_i;$$

where  $h$  is an external magnetic field, and  $J_{ij}$  is the interaction energy between spins at sites  $i$  and  $j$ .

- For  $N$  spins we make the drastic *approximation* that the interaction between all spins is the same, and  $J_{ij} = -J/N$  (the equivalent neighbor model). Show that the energy can now be written as  $E(M, h) = -N[Jm^2/2 + hm]$ , with a magnetization  $m = \sum_{i=1}^N \sigma_i / N = M/N$ .
- Show that the partition function  $Z(h, T) = \sum_{\{\sigma_i\}} \exp(-\beta \mathcal{H})$  can be rewritten as  $Z = \sum_M \exp[-\beta F(m, h)]$ ; with  $F(m, h)$  easily calculated by analogy to problem (1). For the remainder of the problem work only with  $F(m, h)$  expanded to fourth order in  $m$ .
- By saddle point integration show that the actual free energy  $F(h, T) = -k_B T \ln Z(h, T)$  is given by  $F(h, T) = \min[F(m, h)]_m$ . When is the saddle point method valid? Note that  $F(m, h)$  is an analytic function but not convex for  $T < T_c$ , while the true free energy  $F(h, T)$  is convex but becomes non-analytic due to the minimization.
- For  $h = 0$  find the critical temperature  $T_c$  below which spontaneous magnetization appears; and calculate the magnetization  $\bar{m}(T)$  in the low temperature phase.
- Calculate the singular (non-analytic) behavior of the response functions

$$C = \left. \frac{\partial E}{\partial T} \right|_{h=0}, \quad \text{and} \quad \chi = \left. \frac{\partial \bar{m}}{\partial h} \right|_{h=0}.$$

**3. The lattice-gas model:** Consider a gas of particles subject to a Hamiltonian

$$\mathcal{H} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \frac{1}{2} \sum_{i,j} \mathcal{V}(\vec{r}_i - \vec{r}_j), \quad \text{in a volume } V.$$

- Show that the grand partition function  $\Xi$  can be written as

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \left( \frac{e^{\beta\mu}}{\lambda^3} \right)^N \int \prod_{i=1}^N d^3 \vec{r}_i \exp \left[ -\frac{\beta}{2} \sum_{i,j} \mathcal{V}(\vec{r}_i - \vec{r}_j) \right].$$

- The volume  $V$  is now subdivided into  $\mathcal{N} = V/a^3$  cells of volume  $a^3$ , with the spacing  $a$  chosen small enough so that each cell  $\alpha$  is either empty or occupied by one particle; i.e. the cell occupation number  $n_\alpha$  is restricted to 0 or 1 ( $\alpha = 1, 2, \dots, \mathcal{N}$ ). After approximating the integrals  $\int d^3 \vec{r}$  by sums  $a^3 \sum_{\alpha=1}^{\mathcal{N}}$ , show that

$$\Xi \approx \sum_{\{n_\alpha=0,1\}} \left( \frac{e^{\beta\mu} a^3}{\lambda^3} \right)^{\sum_\alpha n_\alpha} \exp \left[ -\frac{\beta}{2} \sum_{\alpha,\beta=1}^{\mathcal{N}} n_\alpha n_\beta \mathcal{V}(\vec{r}_\alpha - \vec{r}_\beta) \right].$$

- (c) By setting  $n_\alpha = (1 + \sigma_\alpha)/2$  and approximating the potential by  $\mathcal{V}(\vec{r}_\alpha - \vec{r}_\beta) = -J/\mathcal{N}$ , show that this model is identical to the one studied in problem (2). What does this imply about the behavior of this imperfect gas?

4. *Surfactant condensation:*  $N$  surfactant molecules are added to the surface of water over an area  $A$ . They are subject to a Hamiltonian

$$\mathcal{H} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \frac{1}{2} \sum_{i,j} \mathcal{V}(\vec{r}_i - \vec{r}_j),$$

where  $\vec{r}_i$  and  $\vec{p}_i$  are two dimensional vectors indicating the position and momentum of particle  $i$ .

- (a) Write down the expression for the partition function  $Z(N, T, A)$  in terms of integrals over  $\vec{r}_i$  and  $\vec{p}_i$ , and perform the integrals over the momenta.

The interparticle potential  $\mathcal{V}(\vec{r})$  is infinite for separations  $|\vec{r}| < a$ , and attractive for  $|\vec{r}| > a$  such that  $\int_a^\infty 2\pi r dr \mathcal{V}(r) = -u_0$ .

- (b) Estimate the total non-excluded area available in the positional phase space of the system of  $N$  particles.
- (c) Estimate the total *potential* energy of the system, *assuming a uniform density*  $n = N/A$ . Using this potential energy for all configurations allowed in the previous part, write down an approximation for  $Z$ .
- (d) The surface tension of water without surfactants is  $\sigma_0$ , approximately independent of temperature. Calculate the surface tension  $\sigma(n, T)$  in the presence of surfactants.
- (e) Show that below a certain temperature,  $T_c$ , the expression for  $\sigma$  is manifestly incorrect. What do you think happens at low temperatures?
- (f) Compute the heat capacities,  $C_A$ , and write down an expression for  $C_\sigma$  without explicit evaluation, due to the surfactants.
5. *Critical behavior of a gas:* The pressure  $P$  of a gas is related to its density  $n = N/V$ , and temperature  $T$  by the truncated expansion

$$P = k_B T n - \frac{b}{2} n^2 + \frac{c}{6} n^3,$$

where  $b$  and  $c$  are assumed to be positive, temperature independent constants.

- (a) Locate the critical temperature  $T_c$  below which this equation must be invalid, and the corresponding density  $n_c$  and pressure  $P_c$  of the critical point. Hence find the ratio  $k_B T_c n_c / P_c$ .
- (b) Calculate the isothermal compressibility  $\kappa_T = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T$ , and sketch its behavior as a function of  $T$  for  $n = n_c$ .
- (c) On the critical isotherm give an expression for  $(P - P_c)$  as a function of  $(n - n_c)$ .



- (d) The instability in the isotherms for  $T < T_c$  is avoided by phase separation into a liquid of density  $n_+$  and gas of density  $n_-$ . For temperatures close to  $T_c$ , these densities behave as  $n_{\pm} \approx n_c (1 \pm \delta)$ . Using a Maxwell construction, or otherwise, find an implicit equation for  $\delta(T)$ , and indicate its behavior for  $(T_c - T) \rightarrow 0$ . (Hint: Along an isotherm, variations of chemical potential obey  $d\mu = dP/n$ .)
- (e) Now consider a gas obeying Dieterici's equation of state:

$$P(v-b) = k_B T \exp\left(-\frac{a}{k_B T v}\right),$$

where  $v = V/N$ . Find the ratio  $Pv/k_B T$  at its critical point.

- (f) Calculate the isothermal compressibility  $\kappa_T$  for  $v = v_c$  as a function of  $T - T_c$  for the Dieterici gas.
- (g) On the Dieterici critical isotherm expand the pressure to the lowest non-zero order in  $(v - v_c)$ .
6. *Magnetic thin films*: A crystalline film (simple cubic) is obtained by depositing a finite number of layers  $n$ . Each atom has a three component (Heisenberg) spin, and they interact through the Hamiltonian

$$-\beta\mathcal{H} = \sum_{\alpha=1}^n \sum_{\langle i,j \rangle} J_H \vec{s}_i^\alpha \cdot \vec{s}_j^\alpha + \sum_{\alpha=1}^{n-1} \sum_i J_V \vec{s}_i^\alpha \cdot \vec{s}_i^{\alpha+1}.$$

(The unit vector  $\vec{s}_i^\alpha$  indicates the spin at site  $i$  in the  $\alpha$ th layer.) A mean-field approximation is obtained from the variational density  $\rho_0 \propto \exp(-\beta\mathcal{H}_0)$ , with the trial Hamiltonian

$$-\beta\mathcal{H}_0 = \sum_{\alpha=1}^n \sum_i \vec{h}^\alpha \cdot \vec{s}_i^\alpha.$$

(Note that the most general single-site density matrix may include the higher order terms  $L_{c_1, \dots, c_p}^\alpha s_{c_1}^\alpha \cdots s_{c_p}^\alpha$ , where  $s_c$  indicates component  $c$  of the vector  $\vec{s}$ .)

- (a) Calculate the partition function  $Z_0(\{\vec{h}^\alpha\})$ , and  $\beta F_0 = -\ln Z_0$ .
- (b) Obtain the magnetizations  $m_\alpha = |\langle \vec{s}_i^\alpha \rangle_0|$ , and  $\langle \beta\mathcal{H}_0 \rangle_0$ , in terms of the *Langevin function*  $\mathcal{L}(h) = \coth(h) - 1/h$ .
- (c) Calculate  $\langle \beta\mathcal{H} \rangle_0$ , with the (reasonable) assumption that all the variational fields  $(\{\vec{h}^\alpha\})$  are parallel.
- (d) The exact free energy,  $\beta F = -\ln Z$ , satisfies the Gibbs inequality,  $\beta F \leq \beta F_0 + \langle \beta\mathcal{H} - \beta\mathcal{H}_0 \rangle_0$ . Give the self-consistent equations for the magnetizations  $\{m_\alpha\}$  that optimize  $\beta\mathcal{H}_0$ . How would you solve these equations numerically?
- (e) Find the critical temperature, and the behavior of the magnetization *in the bulk* by considering the limit  $n \rightarrow \infty$ . (Note that  $\lim_{m \rightarrow 0} \mathcal{L}^{-1}(m) = 3m + 9m^3/5 + \mathcal{O}(m^5)$ .)
- (f) By linearizing the self-consistent equations, show that the critical temperature of film depends on the number of layers  $n$ , as  $kT_c(n \gg 1) \approx kT_c(\infty) - J_V \pi^2 / (3n^2)$ .

- (g) Derive a continuum form of the self-consistent equations, and keep terms to cubic order in  $m$ . Show that the resulting nonlinear differential equation has a solution of the form  $m(x) = m_{\text{bulk}} \tanh(kx)$ . What circumstances are described by this solution?
- (h) How can the above solution be modified to describe a *semi-infinite* system? Obtain the critical behaviors of the healing length  $\lambda \sim 1/k$ .
- (i) Show that the magnetization of the surface layer vanishes as  $|T - T_c|$ .

The result in (f) illustrates a quite general result that the transition temperature of a finite system of size  $L$ , approaches its asymptotic (infinite-size) limit from below, as  $T_c(L) = T_c(\infty) - A/L^{1/\nu}$ , where  $\nu$  is the exponent controlling the divergence of the correlation length. However, some liquid crystal films appeared to violate this behavior. In fact, in these films the couplings are stronger on the surface layers, which thus order before the bulk. For a discussion of the dependence of  $T_c$  on the number of layers in this case, see H. Li, M. Paczuski, M. Kardar, and K. Huang, Phys. Rev. B **44**, 8274 (1991).