32.1 Order parameters

We have mainly discussed the Ising ferromagnet and related systems (single component fluids, binary liquid mixtures). At least we have reached a reasonable understanding of the order-disorder phase transition in such systems.

The basic framework of our theory utilizes the order parameter and its fluctuation to describe the phase transition. I wish to give a unified theoretical framework to understand phase diagrams and phase transitions.

The first question we must consider is: what is an *order parameter* order parameter? You might say it is a quantity that is nonzero for ordered phases and zero for high temperature disordered phases. Fine, but then any odd function of magnetization would do. Are you happy with this loose characterization?

Why do we need an order parameter at all? We need it to distinguish different bulk phases, or more precisely, to characterize distinct features of equilibrium properties of different bulk phases. Although scattering experiments tell us microscopic distinctions of various phases, it is important to recognize that different phases are distinguishable macroscopically through macroscopic quantities. That is, we have only to have a thermodynamic variable that can distinguish phases. Roughly speaking, an order parameter describing a phase transition between two phases is a thermodynamic quantity that is zero in one phase and non-zero in the other.

There are only two kinds of thermodynamic quantities (the so-called fourth law of thermodynamics), intensive and extensive quantities or rather thermodynamic fields and densities (extensive quantity/volume).

Since we wish to discuss phase coexistence between different phases, the order parameter must be a density (extensive). Indeed, magnetization is an extensive variable.

Let us take a macroscopically small chunk (= volume element) of a bulk phase and describe it mesoscopically. This means we observe a distribution function of mesoscopic observables in an appropriate state space F (the space large enough to describe equilibrium fluctuations). An equilibrium state of the chuck may be described by a distribution function on this space F. We compare the distributions for two phases, and look for a qualitative change of the distributions. Then, a thermodynamic density describing this qualitative change may be chosen as an order parameter to describe the phase transition.

A more microscopic picture is that the order parameter is a thermodynamic density that can represent the characteristic feature of the microscopic arrangement of elements. At least there are two kinds of orders; one is about the spatial arrangement of the elements, and the other is about the orientation of the elements. Let us postpone the combination of these orders, and first discuss the orientational order.

In 3-space the orientational distribution may be described by a density distribution on the unit sphere.

For example, in the case of Ising ferromagnets, the fluctuation of the spin direction is spatial-inversion symmetric at high temperatures, but at sufficiently low temperatures this symmetry is broken.[1] Therefore, magnetization per spin which is a respectable thermodynamic density captures the salient features of the change in the distribution (Fig 20.1).
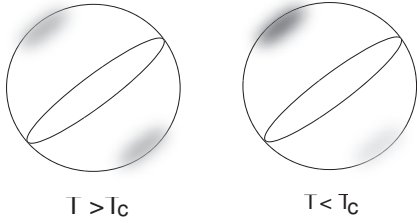

Fig. 20.1 Distribution of spin direction for Ising ferromagnets. The spins need not be confined to one dimension strictly.

For the Heisenberg ferromagnet, the spin can point any direction freely at high temperatures, but this isotropy is broken below T_c (Fig 20.2).
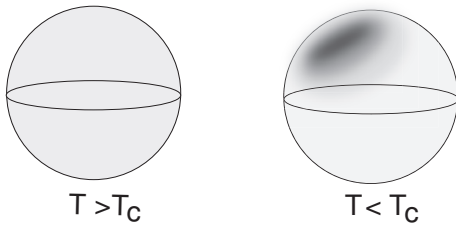

Fig. 20.2 Distribution of spin direction for Heisenberg ferromagnets. Below T_c the spins may point any one direction preferentially.

Any function on a sphere may be expanded in terms of spherical harmonics:

$$f(\theta, \varphi) = \sum_{n=0}^{\infty} \sum_{\ell=-n}^{n} A_{n\ell} Y_{n\ell}(\theta, \varphi). \tag{0.0.1}$$

Therefore, the coefficients $\{A_{n\ell}\}$ can describe the change in the orientational order. That is, these coefficients may be regarded as the order parameter of the system. We do not need all of them; we choose the lowest nontrivial order coefficients reflecting the qualitative change. For example for the Heisenberg ferromagnets, the coefficients of $n = 1$ terms (recall the p wave functions of a hydrogen atom) change from zero to some nonzero values at T_c. Note that if the function f describes the (appropriately smoothed) actual number of spins in the volume element, then these coefficients are thermodynamic densities. Therefore, it is sensible to adopt these coefficients collectively as the order parameter. Thus, we may use a vector as the order parameter for the Heisenberg model.[2]

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[1] The nonzero (spin) angular momentum implies broken time reversal symmetry, so we may understand the transition as a loss of this symmetry, but here I do not stress this point of view.

[2] You may also think that the lowest dimensional irreducible representation of O_3 capturing the symmetry breaking determines the order parameter.

The spins do not have the inversion symmetry, but if the arrow denotes the orientation of a disk (its normal direction) or the longest axis of a symmetric long molecule, then its directional vector $\boldsymbol{n}$ and $-\boldsymbol{n}$ describe the same state (Fig 20.3). Therefore, it is better to express the arrangement with a headless arrow = bar or rod. This 'rod' is called the *director*director instead of spin.
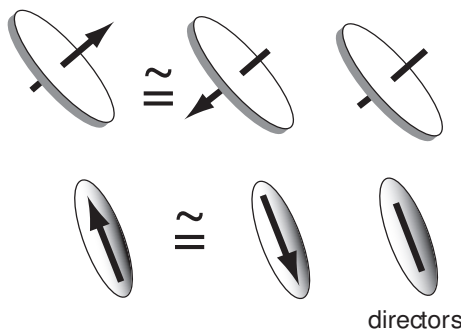

Fig. 20.3 Directors for long or disklike molecules.

directors

In this case if we plot the direction of the arrow at each element, its distribution must always be inversion symmetric on the sphere (Fig 20.4). Therefore, the lowest order terms relevant in (0.0.1) is now $n = 2$ (that is, the configuration on the sphere may be best described by the superposition of d wave functions). Therefore, we need 5 parameters to describe the order. This is equivalent to computing $\langle n_\alpha n_\beta \rangle$ or better

$$Q_{\alpha\beta} = \frac{1}{2}(3 n_\alpha n_\beta - \delta_{\alpha\beta}) \qquad (0.0.2)$$

which is a traceless symmetric tensor (thus it, $= 3 \times 3$ symmetric matrix, has 5 independent elements) the maximum of whose elements is unity. There are two typical orders. One is uniaxial (axially symmetric) (Fig 20.4), and the other not (a *biaxial phase*biaxial phase).
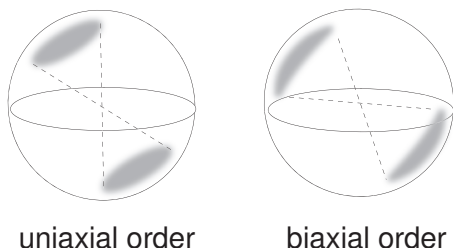

Fig. 20.4 Biaxial and uniaxial order of directors. For the biaxial order the gray zones are not circular but oval.

uniaxial order   biaxial order

Liquid crystals consist of long rod-like molecules, and their directors could order upon cooling. The resultant *nematic phase*nematic phase (see the table below) may be uniaxial or biaxial.

The spatial order could be ordering in 1, 2 or 3 directions. If the system orders in one dimension, the phase is a *lamellar phase*lamellar phase; it is a stack of lamellae in which there is no two dimensional order. If the system orders in 2 dimensions, it is called a *columnar phase*columnar phase; it is a two dimensional crystal of columns in which there is no periodicity. Ordering in all three directions is the *crystalline phase*crystalline phase.

For a pure substance in 3-space is it possible to have all the combinations of spatial and

orientational orders?

orientational\translational	disorder	1D order	2D order	3D order
disorder	fluid			solid
uniaxial order	nematic, discotic nematic	smectic A		solid
biaxial order	biaxial nematic	smectic C		solid
multiple directional order			columnar discotic	solid

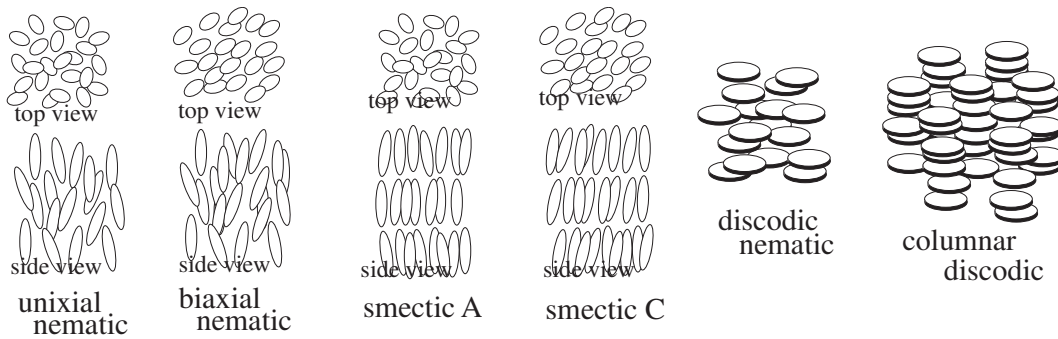I illustrate typical examples in Fig. 20.5.[3]

Fig. 20.5

An important remark on 'ordered phases': We know empirically that with lowering of temperature pure substances usually undergoes phase transitions and lowers its symmetry. Thus, the ground state of a quantum many-body system is expected to be a perfectly ordered phase such as crystals or superfluids. Can we demonstrate this from the first principle? Or, in a more concrete fashion, can we demonstrate that crystalline order or ferromagnetic order appears at sufficiently low temperatures? No one has been able to demonstrate ordering. That is, no one has yet demonstrated that quantum mechanics is consistent with this general observation.

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[3]P M Chaikin and T C Lubensky, *Principles of Condensed Matter Physics* (Cambridge UP, 1995) is an excellent reference.