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Overview

1.1 Condensed matter physics

Imagine that we knew all of the fundamental laws of nature, understood them completely, and could identify all of the elementary particles. Would we be able to explain all physical phenomena with this knowledge? We could do a good job of predicting how a single particle moves in an applied potential, and we could equally well predict the motion of two interacting particles (by separating center of mass and interparticle coordinates). But there are only a few problems involving three particles that we could solve exactly. The phenomena we commonly observe involve not two or three but of order 10^{27} particles (e.g., in a liter of water); there is little hope of finding an analytical solution for the motion of all of these particles. Moreover, it is not clear that such a solution, even if it existed, would be useful. We cannot possibly observe the motion of each of 10^{27} particles. We can, however, observe macroscopic variables, such as particle density, momentum density, or magnetization, and measure their fluctuations and response to external fields. It is these observables that characterize and distinguish the many different thermodynamically stable phases of matter: liquids flow, solids are rigid; some matter is transparent, other matter is colored; there are insulators, metals and semiconductors, and so on.

Condensed matter physics provides a framework for describing and determining what happens to large groups of particles when they interact via presumably well-known forces. Nature provides us with an almost unlimited variety of many-body systems, from dilute gases and quantum solids to living cells and quark-gluon plasmas. Collections of even the simplest atoms exist in a number of different states. Helium, for example, can be found not only in gaseous, liquid, and solid phases but also as a non-viscous superfluid at low temperatures. Condensed matter physics is the study of all of these many-body states of matter. Its paradigms can and do provide insight into fields as diverse as biology and particle physics.

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Indeed, many of the seminal ideas of modern theories of fundamental interactions, such as broken symmetry, had their origins in condensed matter physics.

Condensed matter physics deals with many-body interacting systems. However, it builds on, and in turn contributes to, other fields. It requires a knowledge of the fundamental force laws between atoms and molecules and the properties of small groups of these particles; it thus builds on atomic and molecular physics as well as on classical and quantum mechanics. Since it focuses on macroscopic properties rather than trajectories of individual particles, condensed matter physics requires an understanding of how things behave under different averaging processes; it builds on statistical mechanics and thermodynamics. Because most of the macroscopic variables of interest vary slowly in space, their statistical mechanics can be described by continuum field theories of the type first introduced in particle physics; modern condensed matter physics thus builds on quantum field theory.

Probably the most important unifying concept to emerge from the study of condensed matter physics is that macroscopic properties are governed by conservation laws and broken symmetries. In a system of particles, particle number, energy, and momentum are conserved. At high temperatures, all such systems are disordered, uncorrelated, uniform and isotropic. The probability of finding a particle at a given point in space is independent of the position of that point in space and independent of whether there is another particle nearby. This high-temperature state has the full rotational and translational symmetry of free space. The low-frequency dynamical properties of this state are controlled entirely by hydrodynamical equations, which in turn are determined by conservation laws. As temperature is lowered, new thermodynamically stable states condense. These states have progressively lower symmetry. For example, a periodic crystal is invariant with respect to only a discrete set of translations rather than to the continuum of translations that leave the high-temperature state unchanged. Associated with each broken symmetry are distortions, defects, and dynamical modes that provide paths to restore the symmetry of the original high-temperature state. The properties of each broken-symmetry phase are largely controlled by these distortions, defects, and modes. A crystalline solid for example can be sheared. The energy of shear distortions is determined by an elastic constant, which is a particular rigidity associated with broken translational symmetry. There are shear sound modes in crystals not found in the high-temperature isotropic phase. Finally, there are various defects that interrupt an otherwise ideal crystal structure.

Conservation laws and broken symmetries are equally important in classical and quantum systems. Their consequences, when expressed in the appropriate language, are to a considerable degree independent of whether the underlying particle dynamics is classical or quantum mechanical. Thus, general truths about all-of nature's phases can be obtained by studying classical rather than quantum systems. This book will explore condensed matter physics in a largely classical context. Many of its ideas, however, apply quite generally.

1.2 An example - H_2O

1 Gaseous and liquid states

To see how some of these ideas work, let us consider our experience with a rather common material – water. Although the water molecule is not the physicist’s ideal (argon would probably be closer to ideal because of its filled atomic shell, spherically symmetric shape, and isotropic interparticle interactions), our experience with the phase transitions and different states of water is more extensive. At high temperature, water is steam or water vapor. Its kinetic energy dominates over its potential energy, and, as a result, it exists in a state that is isotropic and homogeneous and that fills any volume allowed it. This gaseous or fluid phase has complete translational and rotational symmetry. There is equal probability of finding a molecule anywhere in the containing volume. The density is uniform. There are very few correlations between the positions of the molecules. If the gas were ideal, then the pointlike particles would completely ignore the presence of each other.

If we look at this gas, the water vapor in the atmosphere, we do not see it. In order for something that has no direct absorptions at the optical frequency to be seen, it must scatter light. That means there must be a mismatch in the refractive index over some distance. In most cases, the refractive index is directly proportional to the density. Since the density of the gas is uniform, there are no index variations, and there is no scattering. Of course, there will always be fluctuations in the density, but, to be seen, they must have a length scale comparable to the wavelength of light.

Now let us lower the temperature, i.e., the average kinetic energy. As the potential energy becomes more important, specific intermolecular interactions come into play. For neutral water molecules, the dominant interaction is the dipole-dipole interaction, which for particular configurations is attractive. At short distances, comparable to the charge separation in the dipoles, the individual charges attract each other more strongly than the dipole approximation would predict. This stronger, more orientationally-dependent interaction, is called hydrogen bonding. Attraction tends to enhance density fluctuations: each molecule would prefer to spend most of its time in a region where there are other molecules rather than in one where there are none. This clustering leads not only to a lower energy but also to a lower entropy. As temperature is lowered, density fluctuations brought about by clustering grow in amplitude and persist for longer times. The larger fluctuations take longer to develop and longer to decay. Increased size dictates a slower dynamics. Density is still uniform but only when averaged over large regions of space or over long intervals of time. The end result of these attractive interactions is the formation of another fluid phase, a liquid phase (water) whose density is greater than that of the gas phase. The principal physical quantity distinguishing the liquid and gas phases is their density.

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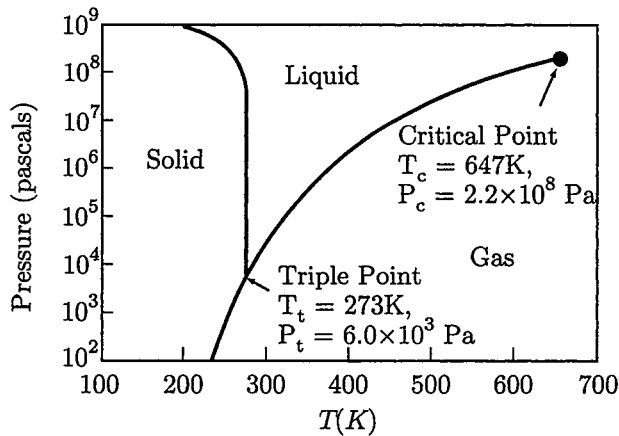


Fig. 1.2.1. The phase diagram for water.

2 The liquid-gas phase transition

Now suppose we have a closed container of water vapor at a density of 0.322 g/cc at high temperature. As the temperature is lowered, density fluctuations continue to grow and live longer. The system now no longer looks homogeneous: there are regions with greater and lesser density. As the size of these regions approaches the wavelength of visible light, scattering increases dramatically – the system looks “milky” (milk has droplets of fat whose diameter is of order one micron (1μ) and comparable to the wavelength of visible light $\sim 0.5\mu$ – that is why it looks “milky”). This is the phenomenon of critical opalescence and critical slowing down (the divergence of length and time scales). Finally, the size and size range of fluctuations become so large that some high- or low-density regions span the container. They also live long enough that the denser regions fall and the lighter ones rise in the gravitational field. The denser regions coalesce on the bottom, and the dense liquid and less-dense gas phases separate. Once again each of the phases is homogeneous and nonscattering. The only evidence we have that the two phases differ is that they are separated by a meniscus, made visible by the difference in the index of refraction of the two phases.

This most common condensation or phase transition from a gas to a liquid is different from most of the other phase transitions we will encounter. The symmetry of the two phases is the same, and there is no loss of symmetry in going to the low-temperature phase (both gas and liquid are fluid phases). This is reflected in the fact that in the phase diagram shown in Fig. 1.2.1, it is possible, by going around the critical point, to go from the gas phase to the liquid phase without traversing any phase boundary.

The scenario in the above paragraph resulted from a special choice of density and does not correspond to our usual experience with water condensation. When

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water is not at the critical density (0.322 g/cc) in a closed container, something else happens. As temperature is lowered (at pressures below the critical pressure), there is a discontinuous change in the thermodynamically stable state as the gas-liquid phase boundary is crossed. Consider now the gas phase at some temperature. Its average density is homogeneous and uniform. There will, however, be rare fluctuations creating droplets of the higher-density liquid phase. As temperature is lowered, the number and size of these droplets will grow, but none will become very large nor persist for a very long time. When the temperature is lowered beyond the gas-liquid phase boundary, the sample does not homogeneously and instantaneously change to the higher-density liquid phase. Rather, droplets of the liquid phase, already present by virtue of fluctuations in the gas phase, will grow larger and persist for longer times. Long before the average size of these droplets diverges, a few droplets will grow to be very large, most often nucleating on a dust particle or a salt molecule. They become large enough that, rather than decaying, they grow with time and absorb surrounding droplets and gas molecules as they grow. Their size is determined by kinetics, by how fast molecules can diffuse to their outer surface and be incorporated into their masses. As the size of these dense droplets becomes comparable to or larger than the wavelength of visible light, they scatter light strongly. This is what is responsible for the milky whiteness of clouds (Fig. 1.2.2), which are suspended droplets of water. This is not critical opalescence, but its effect is similar. The growth of droplets at the discontinuous gas-liquid transition is more rapid than the growth of fluctuations at the critical point. This is one of the characteristic differences between discontinuous, or first-order, transitions and continuous, or second-order, transitions.

If we apply pressure to the gas, its density changes, i.e., it is compressible. At the critical point, the liquid and gas phases with different densities are in equilibrium. Pressure can cause transformation of some volume of gas into the denser liquid phase with no cost in energy: a small pressure change leads to a large density change. There is a divergent rate of change of density with pressure, i.e., a divergent compressibility. Most of the continuous transitions that we will study are signaled by the divergence at a critical temperature of a quantity usually referred to as a susceptibility. The compressibility at the liquid-gas transition is an example of such a susceptibility. The diverging compressibility at the liquid-gas transition can literally be seen via critical opalescence. The diverging size and slowing down of fluctuations are just another manifestation of the same phenomenon that produces a diverging compressibility.

3 Spatial correlations in the liquid state

The liquid state is different from the gaseous state, if not by symmetry then by other properties: density and compressibility, for example. Less obvious is that the particles in the liquid are much more correlated. The distance between particles is now set by the trade-off between the repulsive and attractive parts



Fig. 1.2.2. Clouds are droplets of water or ice with characteristic size $1\text{--}10\mu$. The inhomogeneous density on the scale of the wavelength of visible light ($\sim 0.5\mu$) is responsible for the strong multiple scattering and white or milky appearance. It is similar to the phenomenon of critical opalescence observed in second-order phase transitions.

of the interparticle interactions. Although the density is uniform, the correlation between the positions of neighboring atoms is strong. If there is a particle at one point, there is no chance that another will sit on top of it and a good chance that another will be a particle-diameter away.

We now proceed to cool the system further. The desire of attractive interactions to bring particles close together has largely been satisfied by the formation of the high-density nearly incompressible liquid. The local packing of molecules

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is determined predominantly by the repulsive interaction, which prevents atoms from overlapping. When particles are pushed together, the electronic energy increases very rapidly because particles with the same spin cannot occupy the same point in space (exclusion principle) and because electrons with any spin repel each other via the direct Coulomb interaction. In a simpler liquid, say liquid argon, the repulsive interaction would be well described as a hard-wall potential at twice the atomic radius. Such a hard-sphere model gives us the essence of the liquid and solid physics of many systems. Attraction wants to bring atoms together. Hard-sphere repulsion leads to a discrete set of local configurations that take maximum advantage of attractive interactions. Atoms want to form triangles and then tetrahedra and then fill the triangular faces of the tetrahedra to form larger clusters. Two things prevent this. First, thermal energy keeps atoms from packing too tightly in the liquid phase. Secondly, the local algorithm for packing atoms as densely as possible by making tetrahedra from all exposed triangular faces and so on cannot be continued indefinitely without the introduction of voids that are disfavored by the attractive interaction: it is impossible to fill space by packing tetrahedra or icosahedra. There is a sort of frustration arising from the inability of the system to satisfy simultaneously local packing rules and global packing constraints. This process, however, paints a reasonably good picture of the structure of simple liquids and their atomic correlations. The strong correlations – local order – become increasingly more important as temperature is decreased. In order to see correlations at this intermolecular length scale, we have to probe with X-rays or neutrons which can probe this characteristic distance.

Liquid water behaves in much the same way as liquid argon, but the complex shape of water molecules and the complicated interactions between them lead to interesting differences between argon and water. The oxygen in a water molecule bonds its two hydrogens at an angle of 105° and arranges its four other electrons in two lone-pair bonds. To keep out of each other's way, the four bonds point toward the vertices of a tetrahedron. The liquid gains attractive energy by pointing the negative lone pairs toward the positive hydrogen atoms (this is an alternative description of the hydrogen bonding that is responsible for the structures of water and ice as well as much of biology). The water molecules try to form chains or clumps in which oxygens are tetrahedrally arranged but in which the twisted dumbbell molecules at the same time do not overlap. Liquid water gets its condensation energy from these directional bonds. Correlations again build up in response to these geometrical constraints. An X-ray scattering study of water has been analyzed to show the density of molecules around a molecule located at the origin. In Fig. 1.2.3, we see that the density is depressed near the central molecule, increases in a shell of order a molecular distance away, and then oscillates and decays to the uniform density at fairly short distances. Note also that correlations increase significantly as the water is chilled.

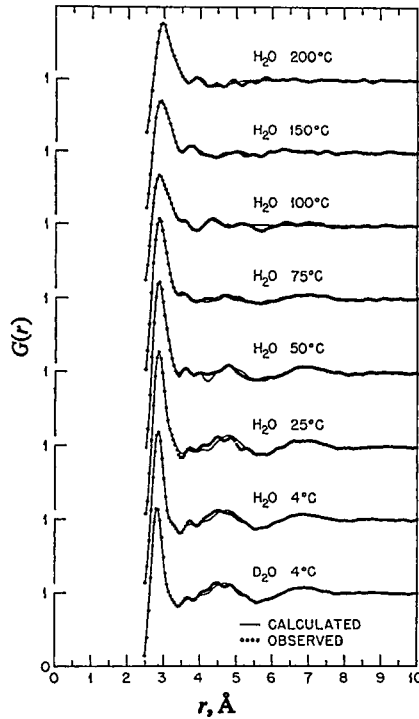


Fig. 1.2.3. The radial distribution function for liquid water is the probability distribution for water molecules surrounding a water molecule. There is an excluded region close to the central molecule, then an increased density for close neighbors, then an oscillating decrease in correlations to the average density at distances of a couple of molecular diameters. [A.H. Narten, W.D. Danford, and H.A. Levy, *Disc. Faraday Soc.*, 43, 97 (1967).]

4 Ice – crystallized water

Our experience tells us that, at some point on cooling, water takes on a different form – ice. Ice is a solid, and the first thing we notice about it is that it does not flow like water. A solid is rigid, it resists shear. But there is a more fundamental difference between ice and water. The molecules in ice are arranged in a uniform repetitive way on a periodic lattice. The crystal structure of ice is illustrated in Fig. 1.2.4. It consists of layers of rippled hexagons in which neighboring atoms do not touch but in which the preferred local tetrahedral arrangement of oxygens is almost maintained. Although we cannot see the periodic lattice directly with our eyes, we can easily see some of its consequences. The hexagonal planar structure is responsible for the faceting planes and six-fold rotation symmetry of the ice crystals we find as snowflakes.

In the far simpler case of argon, the structure of the solid phase is determined

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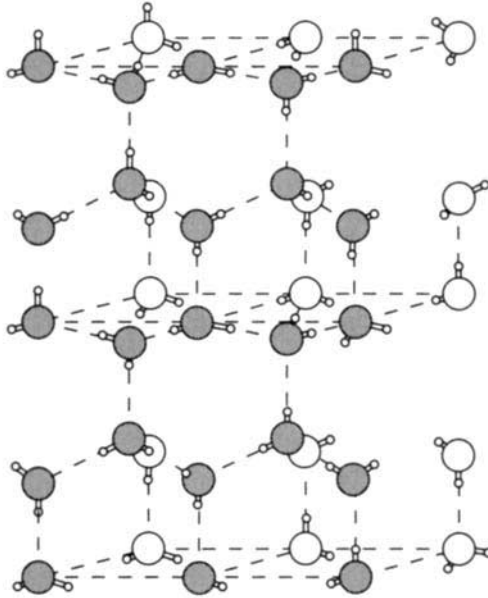


Fig. 1.2.4. Crystal structure of common ice. Note the directionality of the hydrogen bonds and the approximate tetrahedral coordination of each oxygen atom. The structure is a hexagonal “wurzite” form.

by the hard-sphere constraint at short distances and by the attractive interaction at somewhat larger distances. The attraction prefers as many close neighbors as possible and favors the densest periodic packing of spheres consistent with the hard-sphere repulsion. This is the FCC (face-centered cubic) structure with cubic symmetry consisting of hexagonal planes of close-packed spheres stacked on top of each other.

In a liquid, there are substantial local correlations in the positions of particles. Hard-sphere repulsion prevents two molecules from overlapping so that there will be no molecules within a molecular diameter of a given molecule. There will certainly be several molecules about a diameter away and, as a result, a density of molecules greater than the average. By about four to six diameters away, however, the density of particles will differ little from the average (Fig. 1.2.3). Knowledge of the position of one molecule gives essentially no information about the positions of far away molecules. The situation in a crystal is quite different. Molecules occupy, on average, sites on a periodic lattice. The position of one molecule (to specify an origin) and maybe one other (to specify a direction) will determine the positions of all other molecules out to infinity (or at least to the end of the crystallite).

5 Broken symmetry and rigidity

A crystal is not isotropic and homogeneous like a liquid. Rather than being invariant with respect to arbitrary rotations or displacements, it is invariant only under those operations, such as translation by a lattice spacing, that leave the periodic lattice unchanged. Since it is invariant under fewer operations, a crystal has a lower symmetry than a liquid. The transition from the liquid to the crystal *breaks the symmetry* of the liquid state, and the crystal is often referred to as a broken-symmetry phase. The set of rotations and translations leaving the liquid phase unchanged form a continuous group, and the crystal state has a broken continuous symmetry. Translations of a crystal by distances less than a lattice spacing produce a crystal that is not an identical copy of the untranslated lattice. Such uniform translations do not, however, change the energy of the crystal. There is, therefore, a continuous manifold of crystalline ground states with the same energy.

The probability of finding a water molecule at a particular position in space depends on the positions of distant molecules in the crystal. The crystal looks much more ordered than the liquid. How can we characterize the difference between the two states? Average density does not provide a good characterization, although the average density of liquid and crystal phases do differ (ice has a lower density than water at 0°C; most solids have a slightly higher density than the liquids with which they are in equilibrium). There is long-range order in the crystal associated with its periodic density. Molecules in a crystal are situated on the set of periodically arranged mathematical points called a lattice. We can tell whether there is long-range periodic order in the same way we test for periodicity in anything – by taking a Fourier transform and looking for discrete peaks in its spectrum. Scattering waves from a crystal is the experimental way of taking the spatial Fourier transform because the matrix element, $\langle \mathbf{k} | \text{sample} | \mathbf{k}' \rangle$, between incident and scattered plane waves $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle$ is just the Fourier transform of the sample perturbation evaluated at $\mathbf{k} - \mathbf{k}'$. So it is the existence of a discrete spatial Fourier spectrum that distinguishes a crystal from a liquid, i.e. the existence of “Bragg spots” in the scattering spectrum.

The Fourier spectrum or scattering pattern does not change when the sample is displaced as a whole; it is only sensitive to the relative positions of molecules. (It is interferences of waves scattered from the molecules at their various positions that add up to give the Bragg spots.) The molecules are held in their positions by interactions with their neighbors; but even in the solid, individual molecules and groups of molecules are subjected to thermal (or quantum) fluctuations that lead to instantaneous configurations in which molecules are not arranged on an ideal periodic lattice. We can obtain an estimate of the magnitude of molecular displacements at finite temperature by considering the ice to be an elastic medium and using the equipartition theorem. An ideal crystal consists of periodically repeated unit cells with a particular size