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Freezing

A. D. J. Haymet

There is no first principles theory of freezing or melting, even for the simplest materials. The prediction of phase diagrams is an important first step in understanding the crystal-melt interface, crystallization near equilibrium, and nucleation. Recently, a new approximate theory for the freezing of classical liquids, known as the density functional theory, has been developed. The predictions of the theory are relatively accurate and its mathematical structure is simple enough to provide an attractive starting point for theories of more complex, dynamical phenomena.

ALL SIMPLE LIQUIDS, WITH THE PROBABLE EXCEPTION OF liquid helium at low pressures, crystallize at sufficiently low temperatures. By "simple" we mean liquids such as pure argon, sodium, or nitrogen. In addition, the crystallization of huge molecules, such as proteins, is an essential first step in the determination of structure from scattering experiments. Yet for even the simplest classical liquids there is no accurate, universal (or universally accepted) theory of freezing, or indeed of first-order phase transitions in general.

This might seem puzzling, since the thermodynamic conditions for phase equilibrium are well known and simply stated. At a given temperature T and pressure P, the laws of thermodynamics tell us that the phase with the lowest free energy per mole is the stable phase. For two coexisting phases, denoted here by the subscripts S for solid and L for liquid, the temperatures, pressures, and chemical potentials $\mu^{(j)}$ of all components j must be equal:

$$T_L = T_S,\ P_L = P_S,\ \mu_L{}^{(j)} = \mu_S{}^{(j)} \qquad (1)$$

From a microscopic point of view, the prediction of phase diagrams is straightforward in principle. One may use the techniques of

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statistical mechanics to predict the thermodynamic properties of the material under study and use Eq. 1 to determine the phase boundaries. In practice, the calculation of reliable values for the free energy has proven extremely difficult, and hence the phenomena of freezing and melting have attracted the attention of many scientists and generated a huge literature (*1–8*).

There are additional, more qualitative puzzles concerning freezing. One may ask why materials adopt a specific symmetric crystal structure at all. This phenomenon of "spontaneous translational symmetry breaking" is discussed below. Furthermore, most substances contract when they freeze, but water and a few other materials (silicon, gallium arsenide, and bismuth, to name a few) expand. The degree of expansion or contraction varies widely, even for simple materials at a pressure of 1.0 atm. Liquid sodium metal contracts 2% when it freezes at 98°C, molten sodium chloride contracts 25% at 801°C, and gallium expands by 3% at 30°C. The fractional density change on freezing, denoted η, may be calculated from the number density ρ_L of the liquid and the average crystal density ρ_S, with the expression

$$\eta = (\rho_S - \rho_L)/\rho_L \tag{2}$$

This "nonuniversal" property of the freezing transition is displayed in Table 1 for a variety of materials. Prediction of this property constitutes a major challenge to any theory. In contrast, some other features of melting and freezing, such as those addressed in the Lindemann "law" and the Verlet "rule" discussed below, seem to be common to all simple materials, and a theory should also be able to make sense of these facts.

This article discusses a relatively new, approximate theory of freezing, known from its mathematical structure as the "density functional theory" (*9, 10*). The theory uses the language of correlation functions to calculate the relative stability of liquid and solid phases, and hence has its origins in the work of Kirkwood (*11*). Although it sidesteps the question of symmetry breaking, the most fundamental mathematical question of crystallization, the density functional theory is proving to be a useful, numerically simple tool for treating practical problems of phase coexistence. In the last 3 years it has been used to construct approximate theories of the crystal-melt interface (*12, 13*), nucleation (*14*), glasses (*15*) and the stability of quasicrystals (*16, 17*), as well as the standard mathematical models of freezing such as hard spheres (*18–21*), the Lennard-Jones system (*22*), and mixtures (*23, 24*).

The density functional theory of freezing makes direct contact with a number of much earlier theories of freezing (*25–31*), such as the famous Sutherland-Lindemann (*25, 26*) theory and dislocation theories (*30–35*). Although this article is not intended to be a review of all the old (or new) theories of melting, some connections with the density functional theory are discussed. It should be emphasized that the dynamics of freezing is a separate, equally fascinating and difficult question, the technical details of which have been reviewed at the microscopic level by Oxtoby (*14*).

Approximations in the Theory of Freezing

Crystallization presents perhaps the most easily understood example of a ubiquitous problem in modern physics, known as "spontaneous translational symmetry breaking." In simple terms, the classical Hamiltonian that we believe describes the properties of liquids such as argon is translationally (and rotationally) invariant and hence contains no hint of the periodic crystal type ("broken" symmetry), such as the face-centered cubic structure, which argon adopts in equilibrium at low temperatures. Analogs of this problem pervade modern physics, including particle physics (*27*).

Table 1. Freezing data for a variety of materials.

Substance	Freezing temperature (°C)	Liquid density (g/cm^3)	Solid density (g/cm^3)	Fractional density change on freezing	Latent heat (kJ/mol)
Argon	−189.2	1.40	1.65	0.18	1.2
Sodium	97.81	0.94	0.97	0.03	2.6
Iron	1536	7.0	8.3	0.19	15
Sodium chloride	801	1.55	2.16	0.39	29
Water	0.0	0.99987	0.9168	−0.083	6.0
Silicon	1412	2.52	2.33	−0.075	
Gallium	29.8	6.1	5.9	−0.033	5.59
Bismuth	271.3	10.1	9.81	−0.029	10.7

There is no theory of freezing that can predict the symmetry of the crystalline phase from a knowledge only of the forces between the molecules. In the density functional theory one tests, in principle, all 230 possible lattice symmetries and determines the most stable phase at given thermodynamic conditions. In practical calculations (*22*), only a small number of likely crystal symmetries are tested. The assumption of a particular lattice symmetry is one of only two assumptions in the density functional theory. Although the symmetry is assumed, it should be emphasized that the lattice constant (and equivalently the density of the solid phase) is predicted by the theory.

The second and final assumption of the theory makes powerful use of the recent advances in predicting the structure of equilibrium liquids. Following the original computer simulations of hard spheres (*36*) (which also contained convincing empirical evidence for a freezing transition in hard spheres), a host of methods have been developed for predicting so-called "correlation functions" in liquids. The simplest of these is the pair correlation function, denoted $g(r)$ and shown in Fig. 1, which is the (un-normalized) probability of finding two molecules separated by a certain distance r. For an "ideal" gas this function is unity for all distances. The function $g(r)$ is important for three reasons: (i) it describes the average structure in the liquid; (ii) it is the Fourier transform of the elastic scattering intensity measured in neutron and x-ray experiments; and (iii) the thermodynamic properties of a simple liquid may be calculated by taking simple integrals over $g(r)$. In the last 25 years, the structure and thermodynamics of liquids have been predicted by computer simulations, approximate integral equations, and perturbation theories based on a computer-simulated reference state. For example, the pair correlation functions $g(r)$ for the Lennard-Jones fluid shown in Fig. 1 are obtained from the numerical solution of an integral equation, known as the "mean spherical approximation" (*37*), and agree relatively well with experiments on real argon and ("exact") computer simulations of the same model potential.

The spectacular advances in understanding the structure of liquids are important in the present theory of freezing. The second approximation of the theory is to use thermodynamic perturbation theory to relate the correlation functions in the crystal to correlation functions in the liquid. This idea, due to Kirkwood (*11*), seems quite outrageous: the "hot" crystal which is about to melt can be described from knowledge of the "cool" liquid which is about to freeze. In fact, Kirkwood's original theory was quite unsuccessful from a numerical point of view. The recent advances in this theory have been due to the application of "density functional" ideas, which have been used successfully in other branches of physics and chemistry, particularly in the theory of the inhomogeneous electron gas. In the modern freezing theory, the perturbation expansion is

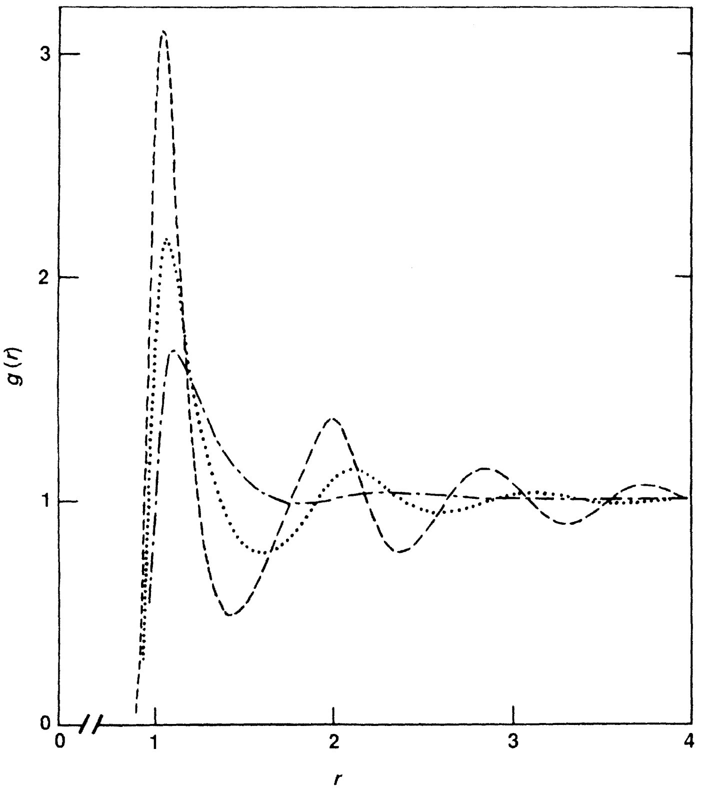

Fig. 1. The pair correlation function $g(r)$ for the Lennard-Jones fluid at the temperature $kT/\epsilon = 1.5$. The critical temperature of this fluid is 1.35 in the same units. The structure of the fluid, which is the input to the freezing theory, is shown for three different densities, $\rho\sigma^3 = 1.0$ (- - -), which is close to the freezing density, 0.7 (. . .), and 0.2 (—— - ——). The parameters ϵ and σ define the energy and length scales in the Lennard-Jones pair potential energy, Eq. 7.

performed at constant temperature and chemical potential, in contrast to Kirkwood's approach. It also makes use of the convenient properties of an alternate representation of liquid structure known as the direct correlation function $c(r)$, which is defined from the pair correlation function $g(r)$ by the Ornstein-Zernike equation.

The central quantity in the freezing theory is equilibrium-averaged, microscopic density $\rho(\mathbf{r})$. In the isotropic liquid phase this quantity is simply a constant, ρ_L, the number density of the material. In the solid phase the density is spatially varying, with a symmetry determined by the crystal type and a period determined by the average (over a unit cell) crystal density ρ_S. It is convenient to write the crystal density as a Fourier sum,

$$\rho(\mathbf{r}) = \rho_L\left[1 + \eta + \sum_n \mu_n e^{i\mathbf{k}_n \cdot \mathbf{r}}\right] \qquad (3)$$

where η is the fractional density change on freezing defined in Eq. 2, $\{\mathbf{k}_n\}$ is the set of reciprocal lattice vectors which defines the lattice symmetry, and μ_n are order parameters which measure the degree of periodic order of wave vector $\mathbf{k}_n$ in the crystal. These order parameters, which in addition to η are to be predicted by the theory, are related to the Debye-Waller factor, which measures the degree of thermal motion of molecules about their lattice sites in the crystal.

The free energy F of the liquid or crystal, along with the other thermodynamic quantities, can be expressed as a functional $F[\rho(\mathbf{r})]$ of the density $\rho(\mathbf{r})$. This is the origin of both the name "density functional theory" and the power of the technique. The radical feature of the second approximation in the theory is that it assumes that the free energy is an analytic functional of the density, and that a perturbation expansion about a reference state, in this case the equilibrium liquid, is valid. For a second-order transition, such as the gas-liquid critical point, this would be a poor approximation (and would lead, among other things, to incorrect "classical" critical exponents). However, for some first-order phase transitions, the empirical evidence suggests that the truncation of this expansion at first order is useful.

The mathematical approximations involved in this second assumption mean that the density functional theory is far from a rigorous solution to the freezing problem. Nevertheless, by building on the advances in liquid theory and using the structure of the liquid as a starting point for perturbation theory, the density functional theory does constitute a complete theory of freezing. It starts from the laws of statistical mechanics and a knowledge of the forces between the molecules, and, by making a series of well-defined (and relatively well-tested) approximations, the theory predicts the phase diagram. The first calculation that used the complete recipe, including correct liquid correlation functions, appeared in 1983 for the model of hard spheres (*20, 21*), even though the two major ingredients, the thermodynamic perturbation theory and the liquid structure of hard spheres (*38*), were already available in 1963.

Mathematical Theory

The density functional theory may be summarized in two equations. We work in the grand ensemble of statistical mechanics, where temperature, volume, and chemical potential (rather than particle number) are the natural variables. To first order in perturbation theory, possible crystal phases are determined by periodic solutions of the implicit equation,

$$\ln[\rho(\mathbf{r}_1)/\rho_L] = \int d\mathbf{r}_2\, c(|\mathbf{r}_1 - \mathbf{r}_2|)\, [\rho(\mathbf{r}_2) - \rho_L] \qquad (4)$$

where $c(r_{12})$ is the direct correlation function of the liquid mentioned above and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between two molecules. At low densities the only solution of Eq. 4 is the constant, liquid solution $\rho(\mathbf{r}) = \rho_L$. At higher densities, additional spatially varying solutions appear, and the densities $\rho(\mathbf{r})$ and ρ_L describe crystal and liquid phases with the same temperature and chemical potential. Owing to the "mean field" approximations in the theory, more than one such pair of densities exists. The equilibrium freezing point is located unambiguously by the condition that the pressures of the two phases also be equal (see Eq. 1). Mathematically, this condition is expressed by means of the grand thermodynamic potential difference $\Delta\beta\Omega$ (the analog of the free energy difference) between the two phases, which to first order in thermodynamic perturbation theory is

$$\begin{aligned}\Delta\beta\Omega = {} & -\int d\mathbf{r}_1[\rho(\mathbf{r}_1) - \rho_L] \\ & + \frac{1}{2}\int d\mathbf{r}_1 \int d\mathbf{r}_2 c(r_{12})[\rho(\mathbf{r}_2) - \rho_L][\rho(\mathbf{r}_1) + \rho_L] \qquad (5)\end{aligned}$$

For a fixed temperature, the liquid freezes at the density for which

$$\Delta\beta\Omega = 0 \qquad (6)$$

This is simply the Maxwell construction in the grand ensemble.

Practical Examples

The utility of the density functional theory may be seen in the predictions of the freezing of the Lennard-Jones liquid by Marshall *et al.* (*22*). This system has been studied intensively as a model for the structure, dynamics, and thermodynamics of simple liquids, such as argon, and even liquids composed of approximately spherical molecules, such as methane. In this model, classical structureless particles interact by means of the pairwise additive potential energy

$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (7)$$

where r is the distance between molecules and σ and ϵ are parameters that determine the length and energy scales. This potential mimics the features of the interaction potentials of rare gas elements: there is an r^{-6} attraction at large distances, an attractive well at intermediate separations, and a steep repulsive wall at short distances, when the molecules begin to overlap. For example, the interaction of two argon molecules is relatively well described if we use the parameters $\sigma = 3.405$ Å and $\epsilon/k_B = 120$ K, where k_B is Boltzmann's constant.

The structure of the Lennard-Jones liquid may be obtained from computer simulations or integral equations. With Eqs. 4 and 5 it is a simple matter to predict the freezing into a close-packed lattice. The predicted phase diagram is shown in Fig. 2, in addition to experimental data for real argon. The agreement is good. Other thermodynamic properties, such as the latent heat, are also predicted by the theory. However, in its present form the theory suffers from the disadvantage (along with even the most elaborate computer simulation experiments) that it cannot predict accurately the relative stability of the two close-packed symmetries, face-centered cubic (fcc) and hexagonally close-packed (hcp). It does predict correctly that these symmetries are more stable than other possible structures, such as body-centered cubic (bcc) or simple cubic (sc).

The complexity of phase diagrams is seen clearly even in binary mixtures, and our second example is the phase diagram of a 1:1 mixture of hard spheres of different diameters (Fig. 3). This model may be viewed as a simplified model of binary mixtures or just as an interesting mathematical example. Smithline and Haymet (*23*) have determined the stable solid that coexists with a liquid of equal concentrations of "big" spheres and "little" spheres, with diameter ratio σ_2/σ_1. For spheres of almost the same size, the stable crystal is a substitutionally disordered fcc solid. More interestingly, in this case phase separation occurs, and as the size ratio decreases the relative concentration of big spheres increases. Below $\sigma_2/\sigma_1 = 0.85$, the stable solid has the cesium chloride symmetry, with the two sizes of sphere ordered on two distinct, interpenetrating simple cubic lattices. For small size ratios, the stable solid has sodium chloride symmetry (two interpenetrating fcc lattices). Metastable (locally stable) solids with two other symmetries have been found. It is interesting that this simple model displays the symmetries commonly found in real materials, indicating that simple geometric factors such as packing, play an important, if not dominant, role in determining phase stability.

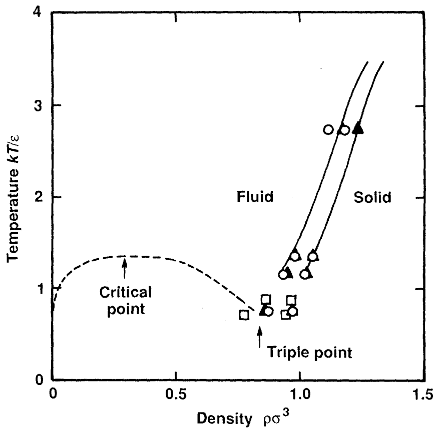

Fig. 2. The phase diagram for the Lennard-Jones system. The solid lines are the densities of the coexisting liquid (or fluid) and fcc crystal, as calculated by Marshall, Laird, and Haymet (*22*). The circles are results from computer simulations, the triangles are experimental data for argon, and the squares are additional theoretical points with the solution of the mean-spherical-approximation integral-equation theory of liquid structure as input. The dashed line is the gas-liquid coexistence curve.

Connection with Other Melting Theories

Perhaps the oldest idea in melting and freezing is that a crystal should melt when the average thermal motion of the molecules exceeds a certain critical amplitude. A measure of thermal motion is the quantity $L = \langle r^2\rangle^{1/2}/d$, where $\langle r^2\rangle$ is the mean square amplitude of the excursions of a molecule from its lattice site, and d is the nearest neighbor spacing. Many materials do in fact melt when L approaches 10%. This idea is usually ascribed to Lindemann (*26*), but was derived 20 years earlier by Sutherland (*25*), a brilliant but little known Australian scientist who also anticipated the Stokes-Einstein equation. It speaks to the rapid progress of science that just 90 years ago Sutherland was trying to understand Mendeleev's periodic table of the elements, searching for a periodically varying mechanical property that would correlate with the periodic arrangements of elements. It turns out that his idea was completely wrong: the amplitude of motion of elements about to melt has nothing to do with the real explanation of the periodic table, namely, electronic structure and quantum mechanics, about which Sutherland knew nothing (or, at least, published nothing).

The Sutherland-Lindemann theory is actually a theory of the absolute instability of the crystal, rather than an equilibrium melting theory. Even modern mean-field theories find that this instability is very close to the freezing transition, a fact that is still not understood. The quantity L in the crystal is actually a wave vector dependent property rather than a constant, and it is one of the predictions of the density functional theory. For certain close-packed materials, the ratio L turns out to be weakly dependent on wave vector and close to 10%, a remarkable tribute to the intuition of Sutherland and Lindemann.

In the course of extensive computer simulations of liquids and crystals, Verlet observed (*39*) that many simple materials freeze when the amplitude of the highest peak in the structure factor $S(k)$, which is the Fourier transform of the pair correlation function $g(r)$ displayed in Fig. 1, exceeds the value $S(k_{\max}) = 2.9 \pm 0.1$. The density functional theory can also be used to rationalize this Verlet "rule." Ramakrishnan noted (*19*) that the free energy cost of setting up periodic density waves of wave vector k is governed, to first order in perturbation theory, by the magnitude of $S(k)$ in the liquid. Hence, the process of freezing may be viewed as a delicate balance between the free energy of expansion (or contraction) of the system

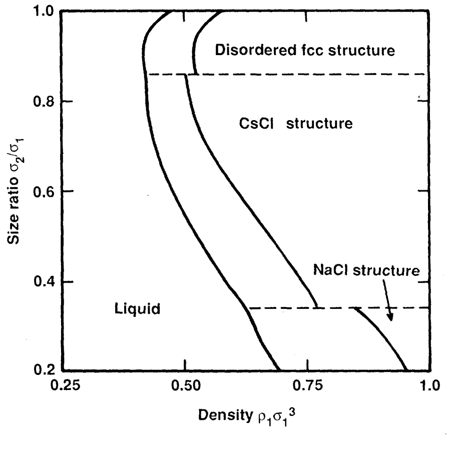

Fig. 3. The phase diagram for a binary mixture of hard spheres (*23*). The "big" spheres have diameter $\sigma_1 = 1$, and the "little" spheres have diameter σ_2, with $0 < \sigma_2 < 1$. Plotted are the coexisting liquid and crystal densities of the big spheres. For all phases except the disordered fcc crystal, the densities of the two components are equal.

and the free energy of setting up an elaborate network of periodic density modulations at every reciprocal vector of the crystal symmetry.

The idea that melting is caused by defects in the perfect crystal was suggested by Frank (*29*). Mott and Gurney formulated their theory of freezing (*30*) in terms of grain boundaries, suggesting that at the melting transition the crystal fragments into crystallites with random orientations. The modern expression of these ideas is due to Shockley (*31*), who described melting as a sudden increase in the density of (closed) dislocation loops, which form a tangled, intertwined "spaghetti" in the crystal. These ideas have been developed and extended by Cotterill *et al.* (*8*), Edwards and Warner (*33*), and many others (*6, 7*).

This dislocation theory is an elegant and popular view of melting, in part because it abandons the molecular description in favor of the "defects" in the crystal, the dislocation loops. To my knowledge, the only version of dislocation theory that allows for a change in density of melting is by Ninomiya (*32*), and this theory has been used recently by Poirier (*35*) to predict the temperature of the iron core at the center of the earth. A limitation of this theory is that there are crucial parameters (which describe the dislocation free energy and density) which are not predicted from first principles. It is also frustrating that dislocations "disappear" in the liquid (owing to the high mobility of the molecules), which is a reason to favor a molecular description. In addition, the dislocation theory, like the Sutherland-Lindemann theory, is essentially a theory of the instability of the crystal, in which the liquid seems to play little role. In contrast, the density functional theory actually tries to calculate the free energy difference between the two phases, and hence it is a true theory of phase coexistence. In fact, the perturbation theory is fully reversible and either phase can be used as the reference system, although our limited knowledge of pair correlations in the hot crystal have restricted density functional calculations to "freezing" rather than "melting."

The freezing both of real systems, such as iron, silicon, and water, and of important mathematical models, such as inverse power potentials, are being studied in laboratories around the world. Applications to liquid crystals, plastic crystals, quasiperiodic materials, nucleation, and dynamical properties are also being explored. There is a multitude of open questions, especially concerning large molecules. Although it falls short of a complete theory of freezing, the density functional theory provides a workable starting point for theories of dynamical phenomena, as well as some information about the mysterious complexity of phase diagrams.

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