FREEZING: DENSITY FUNCTIONAL THEORY

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WHY DO LIQUIDS FREEZE?

At fixed pressure, as the temperature is decreased all liquids freeze. [Liquid helium at pressures below about 25 atm appears to be the only exception!] Why do liquids abandoned their random, 'disordered' structure, and form periodic arrays? As surprising as it seems, at present there is no molecular level, 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 (DF) theory, has been developed.[1] The mathematical structure of the theory is simple enough that it provides an attractive starting point for theories of more complex, dynamical phenomena.

Here we will discuss simple liquids, where by 'simple' we mean liquids such as pure methane, sodium or water. The crystallization of huge molecules, such as proteins, is an essential first step in the determination of structure from scattering experiments. Even for the simplest, classical liquids there is no universal (or universally accepted) theory of freezing, or indeed of first order phase transitions in general. Theories for the behavior of glass formers, such as many polymeric systems, are a separate issue not discussed here, but start from ideas developed for materials which crystallise. [Even glass formers have a lower free energy crystalline state, which may be kinetically inaccessible under many conditions.]

The lack of theory might seem puzzling, since the thermodynamic conditions

for phase equilibrium stated by Gibbs are well known. At a given temperature T and pressure p, the laws of Thermodynamics prove that the phase with the lowest free energy 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 μ_j of all components 'j' must be equal:

$$T_L = T_S \qquad p_L = p_S \qquad \mu_L^{(j)} = \mu_S^{(j)} \; . \tag{1}$$

From a microscopic point of view, the prediction of freezing, and phase diagrams in general, is straightforward in principle. One should use the techniques of statistical mechanics to predict the thermodynamic properties of the material under study, and use equation (1) to determine the phase boundaries. In practice, the calculation of reliable values for the free energy has proven extremely difficult, and hence the phenomenon of freezing/melting has attracted the attention of many scientists and generated a huge literature.

TRANSLATIONAL SYMMETRY BREAKING

There are additional, much deeper questions concerning freezing. Why do materials adopt a specific symmetric crystal structure at all? This phenomenon is called 'spontaneous translational symmetry breaking' and occurs in many branches of science, including particle physics. The short answer is: we do not know. Even within classical mechanics, we have no theory which can analyse a given Hamiltonian and predict the symmetry of the crystal to which it will freeze. At present, the symmetry breaking has to be put into the theory 'by hand'. By this we mean that a particular symmetry is assumed and its free energy evaluated relative to other candidate crystal symmetries.

Most substances contract when they freeze, but water and a few other materials (silicon, gallium arsenide, gallium and bismuth, to name a few) expand. The degree of expansion or contraction varies widely, even for simple materials at one atmosphere pressure. Liquid sodium metal contracts 3% when it freezes at 98 °C, molten sodium chloride contracts 39% at 801 °C, and gallium expands by 3% at 30 °C! The fractional density change on freezing, denoted η, may be calculated from the liquid (number) density ρ_L and the average crystal density ρ_S, using the definition

$$\eta = \frac{\rho_S - \rho_L}{\rho_L} \; . \tag{2}$$

This 'non-universal' property of the freezing transition is displayed in Table 2 for a variety of materials. Prediction of this property constitutes a major challenge to any theory.

THE DENSITY WAVE PICTURE

Both qualitative and quantitative predictions for freezing arise from a relatively new, approximate theory of freezing, known from its mathematical structure as the 'density functional' (DF) theory. Although it side-steps the most fundamental mathematical question of crystallization, namely the spontaneous symmetry breaking discussed above, the density functional theory is proving to be a useful, numerically simple tool for treating practical problems of phase coexistence. It has been used to construct approximate theories of the crystal/melt interface, nucleation, glasses, the stability of quasicrystals, the prediction of vacancy concentrations in the crystal at melting, and the freezing of quantum liquids, as well as the standard mathematical models of freezing such as hard spheres, the Lennard-Jones system and mixtures. There are a number of review articles which cover these developments.[2,3,1,4]

Here we focus on the qualitative ideas, which should turn out to be helpful in other areas. At fixed pressure, the determination of the freezing points amounts to finding the temperature of at which the free energy of the random liquid exactly equals the free energy of the spatially ordered crystal. The density wave point of view, which originates with Ramakrishnan, views the crystal as a liquid permeated with standing waves in the density. These waves measure the displacement of the particles from their perfect lattice sites, and have wavelengths corresponding to all possible reciprocal lattice vectors (RLV's) in the crystal. The amplitudes of the waves are related to the (wavevector dependent) Debye-Waller factor in the equilibrium crystal. The freezing temperature is that unique temperature at which the free energy penalty for creating such an infinite network of density waves is exactly zero.

MATHEMATICAL THEORY

The complete mathematical theory has been reviewed in detail very recently.[1] Here we focus on the concepts. The central mathematical quantity in the DF freezing theory is the equilibrium average, single particle 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

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

where η is the fractional density change on freezing defined above, $\{k_n\}$ is the set of reciprocal lattice vectors which defines the lattice, and μ_n are order parameters which measure the degree of periodic order of wavevector k_n in the crystal.

The goal of the freezing theory is simply to predict the temperature dependence of these order parameters. At high temperature all will be zero. At the freezing

point they will assume some non-zero, finite value, which will gradually increase as the temperature is lowered further, until absolute zero temperature is reached, or a second (crystal-crystal) phase transition intervenes. In some more recent work the crystal density is expanded as a sum of Gaussians centered at each lattice site; this additional approximation simply imposes a relation which fixes all the order parameters μ_n given just one of them, say μ_1. Such an approximation is often useful and accurate for close-packed crystals.

The free energy $\mathcal{F}$ of the liquid or crystal, along with the other thermodynamic quantities, can be expressed as a functional $\mathcal{F}[\rho(\mathbf{r})]$ of the density $\rho(\mathbf{r})$. This is the origin of both the name 'density functional theory', and the power of the technique. Since we are seeking the temperature at which phases coexist at the same pressure and chemical potential, it is convenient to express the theory in terms of the grand potential difference between the liquid and crystal, $\Delta\beta\Omega$, where $\beta^{-1} = kT$. The exact expression for this difference, which will vanish exactly at the freezing point, is given, for example, in a paper by Laird, McCoy and Haymet,[5] equation (4.13). Simplifying that equation we obtain the form,

$$\frac{\Delta\beta\Omega}{\rho_L V} = c_0\eta + \tfrac{1}{2} \sum_n c_n\mu_n^2 + \text{ higher order terms },\tag{4}$$

where the sum is over all RLV's of the crystal $\{k_n\}$. The first term is the change in grand potential due to the overall contraction (or expansion) of the liquid on freezing. The sum is nothing but the free energy of setting up standing waves of wavelength $\{k_n\}$.

The theory is completed by specifying the coefficients c_0 and c_n. To first order in thermodynamic perturbation theory, these coefficients are related to the structure factor of the equilibrium liquid, a quantity which is accessible via X-ray or neutron elastic scattering. Specifically, $c_n = c(k_n) = 1 - 1/S(k_n)$. These coefficients c_n of course depend on the temperature and pressure of the liquid. In the years since the original calculations, a host of other methods have been devised for relating the coefficients c_n to known properties, but in each case knowledge of the equilibrium liquid is required. Since we focus only on qualitative concepts here, we will not review the strengths and weaknesses of each method.

The freezing point is then located by lowering the temperature of the liquid. At a certain unique temperature, the terms in equation (4) will exactly balance each other, and the grand potential difference between liquid and crystal will be zero. That is, the temperatures, pressures and chemical potentials of the liquid and crystal will be exactly equal. Although it may not be obvious from the above discussion, this process is simply the Maxwell construction in the grand ensemble.

Note that some density waves lower the free energy of the crystal relative to the liquid, and other raise it (depending on the sign of c_n for the wave vector k_n of the density wave). But the crystal cannot just select a subset of density waves: it has to take them all. The crystal symmetry dictates that if the crystal has one density wave,

it has all the overtones, sums and differences; that is, all the symmetry related density waves consistent with the specified symmetry. Hence the process of crystallization is seen to be an incredibly delicate balance of three contributions, (i) the overall expansion or contraction of the crystal (which may raise or lower the free energy, depending on the crystal), (ii) those standing waves in the singlet density which increase the free energy, and (iii) those standing waves which lower the free energy. Only when all three contributions cancel does the free energy of the periodic crystal exactly equal the free energy of the liquid. Perhaps this density wave point of view can be transferred to other, even more complex problems.

SUMMARY

The radical feature of the DF theory is that the free energy is assumed to be an analytic functional of the singlet density. For a second order transition, such as the gas-liquid critical point, this would be a poor approximation (and lead, among other things, to incorrect 'classical' critical exponents). However, for certain first order phase transitions, the empirical evidence is that the truncation of this expansion at first order is useful. The mathematical approximations mean that the density functional theory is far from a rigorous solution to the freezing problem. Nevertheless, by building upon 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.

References

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