

Density wave theory of freezing and the solid

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Abstract. The theory of the liquid to solid transition, in three as well as in two dimensions, is reviewed. The transition can be viewed either as the melting of the solid due to phonon or defect proliferation instabilities or alternatively as freezing of the liquid into a density wave state with crystalline symmetry. A theory due to Yussouff and the author, based on the latter idea, is discussed and its predictions are compared with experiment. It is shown that the theory leads to a new approach to the properties of a deformed (*e.g.*, sheared) solid and of defects such as grain boundaries and dislocations in a solid. The approach brings out explicitly the structural nature of these properties, and is not restricted to small deviations from perfect periodicity (harmonic approximation) since the solid, the liquid and anything in between can be handled theoretically.

Keywords. Density wave theory; liquid to solid transition; freezing.

1. Introduction

The liquid to solid transition has not received sufficient attention, despite its inevitability and central importance. The main reason is perhaps that the transition is strongly first order in three dimensions, marked by large discontinuities in the entropy, density and order parameter. It does not seem therefore that properties of one phase determine in any simple, general way those of the other phase or the transition to it. Further, since correlations do not diverge near the transition point and have a short range, one might conclude that there are no universal features to freezing; the transition depends on the details of interatomic forces. The facts however are more interesting. The melting transition is first order, but is characterized by a kind of quasi-universality. This is summarized below in §2.

We discuss in §3 earlier attempts at a theory of the transition. Most of these start from the solid, and examine its stability against vibrations of the lattice, or against proliferation of dislocations or of point defects. Despite much effort and the possibility that they can provide a detailed mechanism for melting, these theories have not been successful; the reasons for this are analyzed. We also summarize briefly a theory of melting due to dislocation pair unbinding in two dimensions, based on the work of Kosterlitz and Thouless (1973), and due to Halperin and Nelson (1979) (and also Young 1979). The theory predicts that the two-dimensional solid transforms to the isotropic liquid in two stages, the transitions being continuous. There is a new intervening fluid phase (called hexatic) with hexagonal angular correlations. The theory has stimulated many experiments. In particular, melting on well-characterized substrates, *e.g.*, graphite has been intensively investigated. The rich variety of results obtained, due partly to the competing periodicity imposed by the substrate, is not fully understood.

The density wave theory of freezing, developed by Ramakrishnan and Yussouff

(1977, 1979) is outlined in § 3. The solid is regarded here as a calculable perturbation on the fluid, and the liquid solid transition is shown to occur when fluid phase correlations attain a particular size. This approach emphasizes the structural nature of the transition, and leads to quasiuniversal predictions in good agreement with experiment, without adjustable parameters. In two dimensions this mean field theory predicts a first order transition; the experimental and computer experimental evidence is discussed.

Shear deformation corresponds to a particular kind of change in the phase of the density wave. The free energy cost of this is determined (§ 5) and the shear elastic constants are obtained in terms of fluid phase correlations. This approach illuminates the observed systematics of shear anisotropy in bcc and fcc crystals. Another application of the density wave theory to a solid state property concerns dislocations. Dislocations are topological singularities in the phase of the density wave. We show how this description can lead to a new theory for dislocation structure, energetics, mobility etc. Other applications are briefly pointed out.

2. Systematics of the liquid solid transition

There are several kinds of relationships, mostly phenomenological, involving melting of monatomic solids, ionic crystals, etc. (see for example Ubbehode (1965) for an extensive early survey). In one class of them, a melting parameter and some other property of the system are related. For example, the melting temperature T_m is roughly proportional to the shear elastic constant for monatomic solids. The ratio of vacancy formation energy to T_m is the same for metals. In alkali halide crystals, the volume change on melting depends systematically on the anion/cation radius ratio. However, as we shall see now, deeper quasi-universal features have been noted (most clearly in simple fluids).

The oldest of these is the Lindemann melting criterion, based on the idea that a solid melts when thermal vibrations exceed a certain critical amplitude. The quantity $L = \langle r^2 \rangle^{1/2}/a$, i.e., the ratio of the mean squared thermal vibration amplitude to the interatomic spacing is considered to have a fixed value at T_m . While this is a criterion for the *absolute* instability of the solid, the instability relative to the fluid phase seems to be close by. From computer experiments and indirectly, from experiment, this ratio is indeed seen to be nearly constant, and to be close to about 0.1. For example, computer simulations over a wide range of pressures (e.g., up to a megabar or so) show that L does not change along the melting curve. There are indications that L is larger for the more open bcc structure than it is for the tight-packed fcc, the values being 0.12 and 0.09, respectively. The Lindemann ratio is not directly measured experimentally, but can be inferred either from the phonon spectrum or from the Debye-Waller factor, using a quasi-harmonic phonon approximation. From the former (actually from elastic constants) L is seen for eight metals to be in the range 0.12 (Pines 1964).

There are surprisingly few direct measurements of $\langle \rho_G \rangle$, the order parameter of the liquid solid transition; the Debye-Waller factor is $\langle \rho_G \rangle^2$. A Mössbauer measurement of $\langle \rho_G \rangle^2$ in Al and Cu near T_m gives $\langle \rho_{G_s} \rangle \simeq 0.8$ where G_s is the smallest reciprocal lattice vector. The dependence of $\langle \rho_G \rangle$ on G seems to be approximately Gaussian. The constancy of the Lindemann ratio implies (in the harmonic approximation) that $\langle \rho_{G_s} \rangle \simeq \text{constant}$ and that $\langle \rho_G \rangle$ is a Gaussian. Again, there is a difference in $\langle \rho_{G_s} \rangle$ for the two cubic structures, the values being $\langle \rho_{G_s} \rangle \simeq 0.75$ (bcc) and $\langle \rho_{G_s} \rangle \simeq 0.9$ (fcc). These

results mean that irrespective of interatomic forces, the order parameter discontinuity jumps to nearly the *same* value on freezing into the crystalline phase, the value depending somewhat on structure.

An even more suggestive correlation was discovered by Verlet (1969) who found, during the course of extensive computer simulation of simple fluids that the peak $S(q_m)$ of the structure factor has the value 2.85 near freezing. The structure factor $S(q)$ is the Fourier transform of the two body correlation function $g(r)$ in the fluid phase. There is direct experimental evidence that simple fluids as different as sodium and argon, in addition to model systems such as hard sphere fluids, Lennard-Jonesium, and the one-component plasma, all freeze when $S(q_m) = 2.9 \pm 0.1$. Since it requires an energy $|A_q|^2 \{k_B T / S(q)\}$ to excite density fluctuations with wavevector q and small amplitude A_q , the mode q_m is easiest to excite, and indeed the smallest reciprocal lattice vector G_s of the solid lies very close to q_m (if not coincident with it). Thus the Verlet criterion means that for all simple fluids the staggered or order parameter susceptibility has the *same* finite value (to within 3%) at the freezing point. In two dimensions, computer simulation results on r^{-n} fluids with $n = 12, 6, 3$ and 1 indicate an $S(q_m) \simeq 5.25$ for all these systems.

Of the thermodynamic parameters associated with melting, the volume change depends on the compressibility which varies considerably. However, the entropy change ΔS , after correction for compressibility effects, is nearly $0.9 k_B$ per unit cell. Since compressibility decreases with increasing pressure, from a measurement of ΔS as a function of pressure the limiting, purely structural entropy change on melting can be obtained. This has been done by Stishov (1975) and coworkers who find $\Delta S \simeq 0.9$ and 0.77 for Ar and Na, respectively. Grimvall (1977) has collected the measured values of ΔS for liquid metals and finds that they are in the range 0.8 to $1.0 k_B$ per cell.

Simple perturbation theories of melting have been quite successful. In these, melting of a hard sphere assembly (not characterized by a free parameter since it occurs at a fixed fractional density) is used as the starting point. For example, Longuet-Higgins and Widom (1964) showed that all the melting parameters of argon could be obtained from those of a hard sphere solid by adding to the (computer simulation generated) free energy of the latter a van der Waals like attractive term.

All the above strongly indicates that simple fluids freeze similarly, even though suddenly. In many cases, the apparent differences are superficial. We now review ideas proposed to describe the transition.

3. Earlier approaches to the liquid solid transition

As mentioned earlier, the liquid solid transition can be viewed either as freezing or as melting. In most cases of phase change, one considers how the symmetry of the high temperature phase is broken leading to an ordered low temperature phase, this corresponding in our case to freezing from the fluid into a crystalline solid. However, since the crystalline solid and its excitations are well characterized, most theoretical approaches discuss the transition as melting of the solid. We now briefly review theories of melting.

The basic excitations of the solid are small amplitude harmonic vibrations of the lattice (phonons), point defects or vacancies, line defects or dislocations and planar defects or grain boundaries. The earliest characterization of melting identifies it with a

vibrational instability of the solid (Lindemann 1910). Platzman and Fukuyama (1974) among others have developed a self-consistent harmonic phonon theory of such an instability. The effective restoring force on an atom depends on the extent of thermal motion. The latter itself depends on the effective restoring force, being larger if the former is smaller. This nonlinear self-consistency requirement is not satisfied beyond a certain amplitude of oscillation about the mean position. This is the Lindemann criterion for which Platzman and Fukuyama find a reasonable number for simple metals. However, this is not a theory of melting *i.e.*, of the solid to liquid transition which occurs when the two phases have the same free energy. It is clearly a theory for the absolute instability of the solid. It is interesting that, empirically, this tracks rather closely the actual melting point. However, by its nature this one phase theory cannot address itself to the systematics of the transition discussed earlier, *e.g.*, constancy of the melting entropy.

Various defect theories of melting have been attempted. Gorecki has collected empirical information suggesting that at the melting point the vacancy concentration jumps from about 0.4% to nearly 10%. While in a frozen crystalline solid a vacancy is an identifiable defect, it is not so in a liquid so that such an approach has obvious problems. Mott and Gurney (1939) proposed that melting occurs when the crystalline solid spontaneously splits up into small crystalline grains with differing orientations. The extra free energy due to grain boundaries is compensated at the melting point by entropy gain due to the large number of configurations possible. This is really a rather primitive quasicrystalline model for the liquid. The most extensively discussed approach to melting involves the proliferation of dislocations.

A dislocation moving through a solid can relax stress, and leads to plastic behaviour. Thus a system with a finite density of mobile dislocations is a fluid since an applied stress can be relaxed by the former. In fact, Shockley (1952) discussed the viscosity of liquids from this point of view. However, since the elastic energy of a dislocation line diverges logarithmically with the size of the crystal, isolated, free dislocations do not exist in thermal equilibrium. Considering a concentration c of dislocations with a distribution of Burgers' vectors, one can expect that the strain field due to a particular dislocation will be screened out in a distance $\sim c^{-1/3}$ atom spacings from its core. This leads in to an elastic energy cost $E(c) \simeq -(Eb^3/\delta\pi)c \ln c\delta^2$ where E is the shear modulus, and b is a typical Burgers' vector of the dislocation and δ a constant less than unity. The configurational and vibrational entropy is proportional to dislocation density, *i.e.*, $S = \alpha c$. It is then clear that above a certain temperature, the free energy of the system decreases for sizable dislocation densities c ($\lesssim 1.0$). Estimates (see *e.g.* Cotterill 1980) suggest $c \simeq 0.3$ at T_m . Computer simulation shows that a strongly dislocated solid with $c \simeq 0.3$ has a two-body correlation function close to that of a liquid near freezing. Such a density is two or more orders of magnitude higher than that in a severely cold worked metal, where already the frozen in, nonequilibrium dislocation configurations are very strongly entangled. The variety of dislocation reactions, entanglement constraints, etc. makes the statistical mechanics of such dense configurations very difficult. Finally, at these densities, there is overlap of dislocation cores, which are the strongly deformed or liquid like regions not described by dislocation theory. Using the theory in such a regime amounts to saying that a liquid is nearly full of liquid. Because of the inevitably high density of dislocations, the thermally relevant configurations of the fluid are not well described in this approach, and the prospects for a real theory of dislocation melting in three dimensions are not bright.

In two dimensions, a detailed and beautiful defect theory of melting has been developed by Halperin and Nelson (1979a), and by Young (1979), following the ideas of Kosterlitz and Thouless (1973) (also Berezinskii 1970). In two dimensions, dislocations interact with a logarithmic long range potential. Those with opposite charges attract. Halperin and Nelson (1979 a, b) showed that the effective large distance dielectric constant of the medium is such that the pairs bind below a certain temperature. In that case, the system is rigid against a shear deformation, and is a solid, even though for an infinite system the Debye Waller factor $|\langle \rho_G \rangle|^2 = 0$. A universal relation exists between the melting temperature and the shear elastic constants at that temperature. Since melting involves unbinding of exponentially distant pairs, thermodynamically the transition is smooth. Above the melting point there is a new phase with hexagonal angular stiffness due to bound disclination pairs. This is the hexatic phase which transforms into an isotropic fluid in a thermodynamically continuous way on heating. The detailed predictions have stimulated a great deal of experimental activity.

The experimental systems studied include rare gases adsorbed on graphite (which is a relatively smooth substrate) and a crystal of electrons trapped on a helium surface in their own image. The experimental results indicate a possible variety in melting behaviour. For example, submonolayer Xe on graphite clearly exhibits first order melting which occurs at a reduced temperature *very* close to that found for Lennard-Jonesium in a computer simulation. Physical changes near melting in electrons on helium suggest a continuous transition. Simulation of various r^{-n} systems and of Lennard-Jonesium suggests a first order melting transition with quasi-universal parameters, but these are short time studies. A numerical study of the melting transition as a function of core energy, due to Saitoh (1982) concludes that the transition changes character, being at best weakly first order for large core energy (low density of dislocations) and strongly first order for small core energy. Thus the situation for two-dimensional melting remains unclear.

In many substrate systems, the underlying periodicity is comparable in wavelength to that of the adatom crystal. This leads to an interesting competition between the tendency to be commensurate (C) with the substrate and the natural incommensurate (I) stability. One possible consequence is formation of commensurate domains bounded by discommensurations. The C-I transition is interesting and not fully understood. Is the transition continuous, discontinuous, or interrupted by a disordered domain wall liquid phase (as seen in some experiments)? This is an area of much current research.

4. Density wave theory of freezing

Yussouff and the present author (Ramakrishnan and Yussouff 1977, 1979; Yussouff 1981; Ramakrishnan 1982) have developed a theory of freezing in which the free energy cost of a density wave state is expressed in terms of its amplitudes and the fluid phase correlation functions. The relation is obtained as follows. In a classical system, the density $\rho(\mathbf{r})$ of the system relative to the fluid density ρ_0 is given by $(\rho(\mathbf{r})/\rho_0) = \exp(-\beta v_{\text{tot}}(\mathbf{r}))$ where $v_{\text{tot}}(\mathbf{r})$ is the total potential at the point \mathbf{r} . The total potential is the sum of any external potential $v(\mathbf{r})$ and the potential set up as a result of forces between the particles in the now inhomogeneous system. The latter, a response potential $v_{\text{resp}}(\mathbf{r})$, depends on the density change $\rho(\mathbf{r})$, and can be expressed as a functional Taylor series in

it, the derivatives being fluid phase direct correlation functions. Keeping only the first term in such an expansion,

$$\{\rho(\mathbf{r})/\rho_0\} = \exp \left[-\beta v(\mathbf{r}) + \int c(\mathbf{r}-\mathbf{r}') (\rho(\mathbf{r}') - \rho_0) d\mathbf{r}' \right]. \quad (1)$$

For a spontaneous density wave state, *i.e.* one with

$$\rho(\mathbf{r}) = \rho_0 \left\{ 1 + \eta + \sum_{\mathbf{G}} \mu_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \right\}$$

where \mathbf{G} 's are reciprocal lattice vectors the above equation must be satisfied with $v(\mathbf{r}) = 0$, *i.e.* the correlations in the fluid self-consistently generate a density wave of crystalline periodicity and symmetry. The equation is highly nonlinear, so solutions can appear suddenly. The liquid solid transition occurs when in addition the thermodynamic potentials Ω of the two phases are equal. Since by definition $(\delta\Omega/\delta\rho(\mathbf{r})) = v(\mathbf{r})$, the change in Ω is obtained by integrating equation (1) regarded as a functional equation for $v(\mathbf{r})$ in terms of $\rho(\mathbf{r})$. The result (omitting minor corrections due to the small compressibility) is:

$$\beta(\Omega - \Omega_0) = -\ln \left\{ V^{-1} \int d\mathbf{r} \exp \left(\sum_{\mathbf{G}} c_{\mathbf{G}} \mu_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \right) \right\} + \frac{1}{2} \sum_{\mathbf{G}} c_{\mathbf{G}} \mu_{\mathbf{G}}^2, \quad (2)$$

where V is the volume of the system. We notice that not interatomic forces, but directly measurable two-body correlation functions $c_{\mathbf{G}}$ (related to the structure factor through the condition $(1 - c_{\mathbf{G}}) = S_{\mathbf{G}}^{-1}$) determine freezing.

In principle, there is an infinite number of order parameters $\mu_{\mathbf{G}}$, so that solving equations (1) and (2) (with $\beta(\Omega - \Omega_0)$ set equal to zero) could be very difficult. However, in simple fluids, $c_{\mathbf{q}}$ has a sharp peak at $\mathbf{q} = |\mathbf{q}_m|$ say. We identify this with the smallest reciprocal lattice vector \mathbf{G}_s of the solid. This mode produces the largest response potential and most strongly affects the free energy balance. In many cases (*e.g.* bcc, and 2d hcp) one can get a good zero order solution by retaining only one order parameter mode, that corresponding to the smallest reciprocal lattice vector set $\{\mathbf{G}_s\}$.

We discuss this case now. The theory involves two quantities $c_{\mathbf{G}_s}$ and $\mu_{\mathbf{G}_s}$ (same for all members of the set). There are two conditions, namely local stability (equation (1)) and free energy balance (equation (2)). Thus both the fluid phase correlation or staggered susceptibility $c_{\mathbf{G}_s}$ and order parameter discontinuity $\mu_{\mathbf{G}_s}$ are determined without *any* adjustable parameters, and are fixed 'universal' numbers for a particular structure *e.g.* bcc. The actual values obtained are given in table 1 (row A) and show good agreement

Table 1. Freezing parameters for the bcc structure (Na).

	Structure factors		Fractional density change	Lattice periodic density		Entropy change [†]
	$c_{\mathbf{G}_s}$	$c_{\mathbf{G}_l}$	η	$\mu_{\mathbf{G}_l}$	$\mu_{\mathbf{G}_s}$	$\Delta S/k_B$
Theory A	0.69	0.00	0.048	0.70	0.31	0.7
Theory B	0.65	0.12*	0.045	0.72	0.41	0.81
Experiment	0.66	0.12	0.027	?	?	0.77

* input from experiment.

† both theory and experiment in the incompressible limit.

with experiment. Thus when fluid phase short range correlations attain a certain size, the system crystallizes.

The effect of other modes on freezing parameters can be calculated in perturbation theory, since $c_{G \neq G_s} \lesssim 0.2$ is much smaller than $c_{G_s} \simeq 0.65$ (the value in three dimensions). The free energy difference, order parameter discontinuity etc. are expressible as a power series in $c_{G \neq G_s}$ and the expansion is convergent. These other correlations then have a small but calculable effect on the freezing parameters, making them vary a little from system to system. Another small parameter is the compressibility, i.e. $S_0 = (1 - c_0)^{-1}$. Perturbation theory in these parameters has been carried out (Ramakrishnan 1982).

For the fcc structure, it is necessary to include two-order parameter modes to start with, namely $G_s = (2\pi/a)(\pm 1, \pm 1, \pm 1)$ and $G_l = (2\pi/a)(\pm 3, \pm 1, \pm 1)$. The effect of other modes on the strongly first-order transition obtained with these is small. The reason that two sets of modes are needed for fcc while one set suffices for bcc is that the latter is denser in reciprocal space (the smallest reciprocal lattice vector set $(2\pi/a)(\pm 1, \pm 1, 0)$ has twelve members) while the latter is more open (the set $(2\pi/a)(\pm 1, \pm 1, \pm 1)$ has only eight members). Thus the nonlinear interference effect involving the G_s 's is stronger for the bcc solid than for the fcc.

Detailed calculations for fcc, bcc and hcp as well for 2d hcp structure have been carried out. Some of the results are presented in tables 1 to 3. When an order parameter mode other than μ_{G_s} is used, the value of the corresponding $c_{G \neq G_s}$ is taken from experiment. This is a noncritical parameter lying in a rather narrow range for most simple fluids. The theory then predicts values for c_{G_s} , and all the order parameter

Table 2. Freezing parameters for the fcc structure (Argon).

	Structure factors		Fractional density change	Lattice periodic density		Entropy change [†] $\Delta S/k_B$
	c_{G_s}	c_{G_l}		μ_{G_s}	μ_{G_l}	
Theory	0.65	0.23*	0.166	0.91	0.74	1.0
Experiment	0.65	0.23	0.148	?	?	0.9

* input from experiment.

† both theory and experiment in the incompressible limit.

Table 3. Freezing parameters for the 2d hcp structure (r^{-12} system; computer simulation).

	Structure factors		Fractional density charge	Lattice periodic density	Entropy change [†] $\Delta S/k_B$
	c_{G_s}	c_{G_l}			
Theory	0.826	0.33*	0.015	0.54	0.32
Computer simulation	0.81	0.33	0.020	?	0.33

* input from experiment.

† both theory and experiment in the incompressible limit.

discontinuities μ_G . These therefore also lie in a limited range. The fractional density change η on freezing can be calculated if the compressibility S_0 is known, and the theory predicts that $\eta = AS_0$ where A depends essentially on structure. This new general result valid for small η is also well verified experimentally (for large η as in, say, argon, known nonlinear corrections are necessary).

The entropy change per unit cell on freezing is

$$\Delta S/k_B = \frac{T}{2} \sum_G \mu_G^2 (dc_G/dT)$$

and can be calculated if the temperature dependence of c_G is known from the fluid state. However, this can be determined as follows. We have above a theory of the hot solid also, so that μ_G 's are determined below T_m in terms of c_G 's. Now in the solid, the temperature dependence of μ_G is quite accurately given by harmonic phonon theory, so that using the theory of the hot solid, (dc_G/dT) can be determined. The result, for an incompressible system, is that ΔS depends only on c_G and μ_G at the freezing point so that it also lies with rather narrow limits. The numerical values are shown in tables 1–3. We see from them that the agreement with available experimental data is good. There are no free parameters in the theory.

The main approximations made in the theory are (i) neglect of order parameters other than μ_G , and generally one more say μ_{G_i} , (ii) neglect of three body correlations. We have discussed the first approximation above. It does *not* mean that in the density wave phase μ_{G_i} (with $i \neq s, l$) is zero. These are non-zero (see below). The assumption is that the corresponding effective potentials c_{G_i} are zero. Since these *are* small, and the G_i 's couple rather weakly to the principal modes, the error involved is small as can be shown by a complete numerical calculations or by perturbation theory. The second approximation is more difficult to assess, since very little is known about three-body correlations except the ones which can be written as density derivatives of two body correlations *e.g.* $(dc_G/d\rho)$. It has been shown that the effect of these is small, except that in argon the rapid decrease of compressibility with density reduces the density change, bringing it in agreement with experiment. However, there is a crucially important three body correlation, namely that involving three wavevectors G_i ($i \sim 1, 2, 3$), all members of the smallest reciprocal lattice vector set such that they add to zero. Such an angular correlation term contributes to free energy in the bcc structure but is not possible for the fcc. It thus plays an important role in deciding the relative stability of the bcc and fcc phases even if the corresponding correlation function $c_{G_1 G_2 G_3}^{(3)}$ is small. One can make a map of the relative stability of fcc and bcc structures in the space of $c^{(3)}$ and c_{G_i} as generalized coordinates measuring the extent of three body or angular and spatial short range correlations. Unfortunately, very little is known about the sign or size of $c^{(3)}$, though the latter is expected to be small. It is possible that $c^{(3)}$ will be measured for model systems using light scattering techniques (Clark *et al* 1983).

The theory predicts a strongly first order transition, with large discontinuities in the order parameter. At the same time, since the transition is largely structural, the freezing parameters lie within narrow limits for simple fluids. One might wonder why such a simple looking theory works. The major physical idea as well as the approximations concern the effective potential equation (1). In the theory of liquids, an analogous theory for the density of particles around a particle fixed at the origin, is called the hypernetted chain (HNC) approximation. This density is obviously the two-particle correlation function $g(r)$, and the HNC is known to be very accurate for dense systems

e.g. the dense one component plasma in which the potential $v_{\text{tot}}(r)$ can be very large ($\beta v_{\text{tot}}(r) \gg 1$) but varies relatively smoothly. In our case, $v_{\text{tot}}(r)$ is a sum of sine waves, and βv_{tot} is moderate, of order unity or so. Thus the approximation used is expected to be quite accurate. What is the physical meaning of the condition $c_G \simeq 0.65$? The sharp peak in $S(q)$ implies damped oscillations in real space. The damping or correlation length depends on $S(q)|_{\text{max}}$ as well as its width. Thus, crudely, the fluid freezes when the correlation length attains a certain size.

A question not addressed yet is the size of fluctuation effects. While a mean field theory is generally accurate for a first order transition, the solid has low lying shear modes while in the liquid the corresponding excitations are relaxational. Do these fluctuation effects balance each other out for the free energy?

The density distribution in a unit cell can be calculated also. It turns out that $\mu_G \propto \exp\{-\lambda^2 G^2\}$ fits the results well. In a phonon theory description this implies harmonic phonons. Further, since $\lambda^2 G_s^2$ is a fixed number at the melting point, a Lindemann-like relation is also satisfied to a first approximation.

In two dimensions, this mean field theory predicts a first order change, with parameters close to those observed in computer simulation experiments on systems with strong short range forces, *e.g.* hard disks, r^{-12} , Lennard-Jonesium etc. It is possible that the transition changes character with say the dislocation core energy as implied by some computer simulation results. For small energy, there is a high density of dislocations, short range correlations are important, and there is a strong first order transition. In this regime, the above type of theory which stresses the role of short range correlations, is a good first approximation. In the real two dimensional system $\mu_G = 0$ but this loss of order occurs over exponentially large length scales so that the free energy balance considered in the mean field is not strongly affected. In the low dislocation density limit, the dislocation unbinding transition could pre-empt first order melting if it occurs at a lower temperature. There is no theory yet which considers both long and short range correlation effects, though Chui's work (1982) on a grain boundary model for 2d melting is an attempt in this direction.

5. Applications and prospects

The density wave approach developed above seems to describe well the freezing transition in three dimensions. Since the perfect crystalline solid and the liquid are both covered by the theory, density configurations representing intermediate states can also be explored usefully. We discuss a few examples here.

A homogeneous shear deformation $\bar{\epsilon}$ can be described as changing the reciprocal lattice vectors \mathbf{G} to $\mathbf{G}(1 + \bar{\epsilon})^{-1}$. This costs energy, since originally c_G had the maximum possible value. For small strains, the energy cost depends on the curvature c_G'' of c_G at its maximum, and is proportional to $\bar{\epsilon}^2$. The elastic constant e_{ij} is roughly of the form

$$e_{ij} = k_B T_m \sum_n A_{ij}^n G_n^2 c_{G_n}'' |\mu_{G_n}|^2. \quad (3)$$

where n 's are the order parameter modes necessary to describe the freezing transition well, and A_{ij}^n are geometrical coefficients. For the bcc structure there is an additional term from the three-body correlation function $c^{(3)}$. The result, equation (3) expresses the shear elastic constants entirely in terms of directly measurable fluid state properties.

It is similar in spirit to the result that the spin wave stiffness in a Heisenberg ferromagnets depends on $J''(q)|_{q=0}$. It represents an alternative to the standard approaches from the low temperature side, involving interatomic forces etc. The numbers for say Ar are within 30% of the experimental values; only the experimentally known values of c_G'' are used. More importantly, however, several systematic features can be seen. For example, since quantities like c_{G_m}'' , G_m^2 and μ_{G_m} do not vary much from system to system, the ratio of the elastic constants $\{(e_{11} - e_{12})/e_{44}\}$ in the fcc phase ought not to vary very much. This is indeed the case. For the bcc structure, the three body term $c^{(3)}$ which can change sign influences elastic constants, so that the above ratio has a considerable range. In fact it varies by about a factor of ten for bcc solids but within a factor of two for fcc solids. Another general conclusion is that near a bcc-fcc transition $(e_{11} - e_{12})$ softens rather than e_{44} . Thirdly, the absolute size of elastic constants is set by the melting temperature T_m .

The solid is strongly deformed locally near point, line or areal defects. These deformations are notoriously difficult to treat within the ambit of models using either interatomic forces, or the harmonic spring (or elastic continuum) approximation. The first approach uses poorly known inputs, a separate interatomic potential for each system, is too detailed, and is very hard to implement at non-zero temperatures. The latter approach is easier to work with but is unrealistic and fails where the deformation is large, *e.g.*, for dislocation cores. Both, the former especially, miss out the fact that much strong deformation behaviour depends only on structure and on reduced temperature (T/T_m) . Indeed, maps with (T/T_m) and stress, (or stress rate or . . .) as coordinate axes have been extremely successful in categorizing deformation behaviour. The kind of approach developed above is structural, parametrizes short range correlations in terms of a few dimensionless numbers, and there is only one basic energy scale, namely the melting temperature. We briefly mention below three specific applications which are being worked out.

A dislocation is characterized by the fact that on going round it the phase of the order parameter changes by $2n\pi$. For example, in case of a crystal with a screw dislocation with core along the z axis, we have

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \mu_{\mathbf{G}}(x, y) \exp(i\mathbf{G} \cdot \hat{e}_z b/2\pi) \exp(i\mathbf{G} \cdot \mathbf{r}) + \rho_0(1 + \eta(\mathbf{r})),$$

where $b\hat{e}_z$ is the Burgers vector of the dislocation and $\mu_{\mathbf{G}}(x, y)$ is a smooth function of x and y , going to zero at the origin (the order parameter has to vanish there for a topological defect) and has the crystalline solid value for $(x^2 + y^2) \rightarrow \infty$. Using an energy functional similar to (2), and minimizing as a functional of $\rho(\mathbf{r})$ a differential equation for the vortex structure ($\mu_{\mathbf{G}}(x, y)$) is found. Questions like the nature of the core, core energy, and variation of core energy with location in the unit cell are being investigated. The latter, known as the Peierls-Nabarro barrier, is directly relevant for plastic behaviour under stress. This approach is the only structural one; it incorporates thermal effects and can handle large deformations. It is similar to the theory of vortex core structure in superconductors using a Ginzburg-Landau functional.

A theory of the liquid-solid interface, based on a free energy functional similar to (2) has been developed by Haymet and Oxtoby (1981). Calculations carried out for the bcc structure (Oxtoby and Haymet 1982) show an interface about five atomic distances wide, and a surface energy hardly dependent on orientation. There are as yet no measurement as interfacial profile, and computer simulations are so far for the fcc

systems. There are some additional density smoothing approximations in the theory whose validity is not known.

The rate at which the liquid to crystalline solid transition takes place depends at least initially on the formation of crystalline nuclei. Little is known about the size, shape and rate of formation of these nuclei as a function of the degree of supercooling. Especially if the solid liquid interface is as broad as suggested by Oxtoby and Haymet (1982) the popular descriptions based on a simple volume to surface energy competition are unrealistic. This problem is being investigated.

We have summarized above a new and fairly successful density wave theory of the liquid to solid transition. We have indicated that some properties of the deformed solid and hot solid can be calculated and their essential structural features brought out. It seems possible that this approach will form a necessary complement to the low temperature theories based on interatomic potentials, harmonic lattice vibrations or elastic continuum models.

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