REVIEW ARTICLE

The present status of the density-functional theory of the liquid–solid transition

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Abstract. Recent attempts at a microscopic description of the liquid–solid transition, within the density-functional theory of non-uniform fluids, are put into a critical perspective by comparing the different methods proposed and the results obtained for the freezing of hard-core systems.

1. Introduction

Notwithstanding the fact that, during the past decade, the density-functional (DF) theory has demonstrated its ability to predict bulk-phase coexistence properties or phase diagrams of a variety of systems with considerable success, it is fair to state from the outset that there still does not exist, as yet, a general first-principles theory of first-order phase transitions. This may not be very surprising since, after all, the phase transition problem is, without doubt, the most difficult problem of equilibrium statistical mechanics (not to mention the unavoidable non-equilibrium aspects of the nucleation kinetics). In the particular case of the liquid–solid transition (to which we limit our discussion), the DF theory has gained wide recognition and it may therefore be useful to put into perspective those items of the DF theory that still prevent us from bridging the gap separating it from a fully first-principles theory. This is what will be attempted here (for earlier discussions of the DF theory of freezing, see Haymet (1987) and Baus (1987)).

The basic idea behind the DF theory of freezing is that good *thermodynamic* properties of the solid can be obtained by using only the *structural* properties of the liquid as input. Since the advent of modern liquid-state theory (see e.g. Hansen and McDonald 1976), the structural properties of liquids are fairly well known, and this then has paved the way to accurate determinations of the free energies of the coexisting liquid and solid phases within one and the same DF theory. Knowledge of the free energies constitutes indeed the basic prerequisite for solving the coexistence aspect (to which we restrict our discussion) of the phase transition problem. Many earlier attempts at a molecular description of phase transitions have already played with the same basic idea, but poor results have generally been obtained because of the use of poor liquid-state data within a more complex theoretical framework such as the Yvon–Born–Green hierarchy or the

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partition function approach (see Baus (1983) for some of the historical background references). The DF theory can bypass most of the difficulties of these more traditional approaches because it directly expresses the thermodynamic potentials of any system (say, liquid or solid) in terms only of its one-body density $\rho(r)$, which exhibits all of the system's observable symmetries, and of its two-body direct correlation function (DCF) $c(r, r'; [\rho])$, which plays the role of an effective pair potential self-consistently determined by $\rho(r)$ through its functional dependence (indicated here by the square brackets) on the latter. All the underlying details concerning the Hamiltonian (such as pair or multiparticle interactions, form of the potential, etc) or the higher-order correlation functions, which usually form the stumbling block of earlier approaches (see e.g. Baus 1984b), remain implicit here. It is thus not surprising that the approximations to DF expressions for the thermodynamic potentials are also easier to keep under control. All present-day limitations of the DF theory of freezing result therefore solely from the absence of a systematic procedure to introduce its basic assumption, enunciated at the beginning of this paragraph, into the exact DF expressions.

The remainder of this paper will be organised as follows. We first critically review the different DF routes to freezing (section 2), then we consider the results obtained for a number of specific (mostly hard-core) systems (section 3) and, finally, conclude (section 4) with some general remarks.

2. Methods

The liquid–solid or freezing transition can be considered as the prototype of a first-order phase transition (for background information on freezing see Stishov (1975) and Frenkel and McTague (1980)). The modern theory of freezing is usually traced back to the pioneering work of Ramakrishnan and Yussouff (1979), although several precursors can be clearly designated (for a discussion of this point see e.g. Baus (1983)). Their paper does not use the DF theory as such, but it can be easily reformulated within the general DF theory of non-uniform fluids (Yang *et al* 1976), as was shown by Haymet and Oxtoby (1981). The DF theory by itself is merely a reformulation of equilibrium statistical mechanics within the direct correlation function language and, hence, is not restricted to freezing. It has already been used to study both uniform and non-uniform fluids, in particular fluid interfaces (see Evans 1979, 1989) and also a variety of other phase coexistence problems (see Haymet 1987). It can also be used to formulate (but not necessarily solve) some of the more fundamental problems of the statistical mechanics of phase transitions in general (see e.g. Baus 1984b, 1987). In the particular context of freezing, the DF theory provides us with a convenient framework in which all the modern theories can be easily reformulated. In retrospect, the most important role of the paper by Ramakrishnan and Yussouff (1979) may well have been to draw the attention of the liquid physics community to the fact that, with the information presently available, a liquid-state-based theory is able to produce good thermodynamic data for the solid· phase. This observation has provoked an avalanche of theories, which we will now try to put into a physical perspective.

2.1. Thermodynamic perturbation expansion

In the original RY (Ramakrishnan and Yussouff 1979) theory, the density of the solid, $\rho_S(r)$, is computed as the response of a uniform liquid of density ρ_L to the introduction of a density change $\Delta\rho(r) = \rho_S(r) - \rho_L$ as ($\beta = 1/k_B T$)

$$\rho_S(r) = \rho_L \exp[-\beta v(r)] \tag{1a}$$

$$\beta v(r) = \beta \varphi(r) - \int dr'\, c_L(|r - r'|; \rho_L) \Delta \rho(r') + O((\Delta \rho)^2) \qquad (1b)$$

where the DCF of the liquid $c_L(|r|; \rho_L)$, plays the role of the linear response function of the mean-field potential $v(r)$ with respect to the local density change $\Delta \rho(r)$. Owing to the highly non-linear character of equation (1a), it may happen, even at linear response order for equation (1b), that periodic solutions with a prescribed crystalline symmetry, viz.

$$\rho_S(r) = \sum_k \rho_k \exp(ik \cdot r) \qquad (2)$$

appear suddenly, above some bifurcation point, even when the external field $\varphi(r)$ is put equal to zero. (In equation (2), the summation is over all reciprocal-lattice vectors (RLV) k.) This bifurcation point was later extensively studied by Bagchi *et al* (1983), who assimilated it to the phase transition point, which is misleading for a first-order phase transition since this point defines only the metastable solid. In the RY theory the phase coexistence was located by equating the grand potentials of the solid, $\Omega[\rho_S]$, and the liquid, $\Omega(\rho_L)$, which was again computed perturbatively as

$$\frac{\beta}{V} \Delta\Omega = -\ln\left[\int \frac{dr}{V} \exp\left(\sum_k c_k \rho_k \exp(ik \cdot r)\right)\right] + \tfrac{1}{2}\sum_k c_k \rho_k^2 + \ldots \qquad (3a)$$

where $\Delta\Omega = \Omega[\rho_S] - \Omega(\rho_L)$, V is the volume and c_k are the RLV Fourier components of $c_L(|r|; \rho_L)$. In equation (3a) the liquid was considered to be incompressible, whereas equation (1) was assumed to realise the extremum of $\Omega[\rho_S]$, which in turn implies that the liquid and the solid have the same chemical potential. The physical interpretation given to equation (1) is that the solid can be viewed as a non-uniform perturbation of the liquid, this non-uniformity being described by equation (2) in terms of 'density waves', while equation (3a) is used to estimate the cost in free energy for setting up such density waves until, at coexistence, it can support such waves self-consistently ($\Delta\Omega = 0$). In practice, equation (1) is solved numerically for $\{\rho_k\}$ for given ρ_L, c_k and $\rho_S \equiv \rho_{k=0}$ (the average density of the solid). The result is substituted into equation (3) until $\Delta\Omega = 0$ is realised, which then determines a first relation between ρ_L and ρ_S. A second relation is obtained by equating the amplitude c_k, for k equal to the smallest RLV, to the maximum with respect to k of the function $c_k(\rho_L)$, taken from liquid-state theory or directly from experiment. In practice, only the density wave corresponding to this smallest RLV was retained in the Fourier series of equations (2) and (3). Occasionally, a second density wave with a RLV close to the secondary maximum of $c_k(\rho_L)$ was also retained. The good results obtained from this one- or two-density-wave theory did surprise many. Indeed, the thermodynamic perturbation expansion of the solid around the liquid in equation (3a) (not to speak of equation (1b)) is difficult to justify, as is the replacement of the infinite Fourier series in equation (3a) by just one or two of its dominant terms. To make things worse, it recently became clear (Lovett 1988) that equation (1) is unstable with respect to small changes in the approximation used for $c_L(r; \rho_L)$. The RY results can thus be understood only if strong compensations are present in, or between, the perturbation expansion and the Fourier expansion, with the RY theory corresponding to some kind of optimal choice of terms. The need for more systematic investigations was clearly felt and these were soon to come.

Equations (1)–(3) were first rederived within the more rigorously based DF theory of non-uniform fluids by Haymet and Oxtoby (1981) (with minor changes in equation (3a) related to the finite compressibility of the liquid):

$$\beta\Delta\Omega|_\mu = -\int d\boldsymbol{r}\,\Delta\rho(\boldsymbol{r}) + \int d\boldsymbol{r}\,\rho_S(\boldsymbol{r})\,\ln[\rho_S(\boldsymbol{r})/\rho_L]$$

$$-\tfrac{1}{2}\int d\boldsymbol{r}\int d\boldsymbol{r}'\,c_L(|\boldsymbol{r}-\boldsymbol{r}'|;\rho_L)\Delta\rho(\boldsymbol{r})\Delta\rho(\boldsymbol{r}') + \ldots \tag{3b}$$

where $\Delta\Omega|_\mu$ indicates that $\Delta\Omega$ is computed at fixed chemical potential μ. The problems related to the Fourier series were considered next by Haymet (1983), who systematically retained all the terms of the Fourier expansion up to the first 15 shells of RLV (each 'shell' containing all the RLV of the same length) or 'density waves' (each density wave corresponding to the terms of equation (2) belonging to a given shell of RLV). This corresponds to describing the phase transition in terms of 15 independent order parameters $\{\rho_k\}$ (one for each density wave). Later, Iglói and Hafner (1986) showed that the slow convergence of the Fourier series (up to 40 shells were retained here) leads to an oscillatory behaviour of the results, with the possibility for the transition to disappear and reappear. These oscillations only disappear when at least 60 shells are retained (Barrat *et al* 1987c). Such a large amount of order parameters could be considered in the last two works only by assuming some relation between them, viz.

$$\rho_k = \exp(-k^2/4\alpha) \tag{4}$$

which corresponds to an isotropic Gaussian density profile for the solid. The results of RY (based on retaining only the first and fourth shells corresponding to the first two maxima of the liquid structure factor) and of Haymet (1983) (based on all the first 15 shells) correspond in some sense to an 'optimum' choice for which the results obtained are comparable to those corresponding to the fully converged series. It is not clear yet whether in the case of the RY choice the resulting 'optimisation' could have some symmetry-related explanation. In any case, the lesson drawn from these results by most authors is that, because of their slow convergence, the use of Fourier series should be avoided. It is relatively easy to bypass this technical problem by using the density profiles of equation (4) in real space, viz.

$$\rho(\boldsymbol{r}) = A\left(\frac{\alpha}{\pi}\right)^{3/2}\sum_{\boldsymbol{R}}\exp[-\alpha(\boldsymbol{r}-\boldsymbol{R})^2] \tag{5}$$

where the $\{\boldsymbol{R}\}$ now denote the Bravais lattice vectors. This allows the solid to be described by a single order parameter α, the inverse width of the Gaussian density peaks in equation (5). As seen from equation (4), all the RLV order parameters are then 'slaved' one to another. The approximation embodied in equation (5) is quite realistic in practice, at least for cubic lattices (see e.g. Young and Alder 1974). Systematic improvements over equation (5) can be introduced, at the expense of adding more order parameters, but these have usually only a marginal effect on the results (see Colot *et al* 1986). Equation (5) also has the advantage of guaranteeing *a priori* the positive character of $\rho(\boldsymbol{r})$, a property that is always lost when equation (2) is used with a finite number of RLV. The slow convergence of the Fourier series (2) can also be easily understood from equation (5) since for the well localised particles of the stable solid the α-values in equation (5) have to be large, whereas equation (4) tells us then that the order parameters ρ_k will become negligible only for correspondingly large k-values. For all these reasons

most authors have now switched from the Fourier representation (2) to the Gaussian approximation (5), although this took some time.

A less technical problem is concerned with the thermodynamic perturbation expansion at the basis of equation (3). The RY theory corresponds to an expansion of the thermodynamic properties of the solid around those of the coexisting liquid, with the expansion being truncated at second order. Because of the lack of a smallness parameter, it is difficult to assess *a priori* the nature of this expansion, except by explicit calculation of the higher-order terms. This, however, would involve DCF of higher order, which are unknown. Several authors (Ramakrishnan and Yussouff 1979, Haymet 1983) have observed that part of the third-order contributions omitted in equation (3) can in fact be obtained from the density derivative of $c_L(r; \rho_L)$, which is known. Adding this contribution to the second-order theory seems to improve the results (Haymet 1983). However, when more of the third-order terms are included (these can only be calculated approximately; see Barrat *et al* (1987b), Curtin and Ashcroft (1987) and Denton and Ashcroft (1989a)), the results worsen (Curtin 1988), again indicating some sort of oscillatory convergence of the expansion, with the second-order RY theory corresponding to some optimum choice of terms. Things get even worse when one slightly changes the liquid around which the properties of the solid are expanded. Indeed, if one starts the thermodynamic perturbation expansion around the liquid with a density equal to that of the solid (i.e. typically 10% above the density of the coexisting liquid), then no transition can be obtained from the second-order theory (Baus and Colot 1985) nor from the third-order theory (Curtin 1988). Because of the instability of the results, one has now clearly also to question the convergence of this expansion *a posteriori*. It thus remains somewhat puzzling why the RY theory should correspond to an optimum selection of terms in a poorly converging series. It would clearly be more comfortable to consider non-perturbative approaches to freezing. Before we consider these, let us also mention a few variants of the RY theory. Jones and Mohanty (1985) have considered the second-order theory (equation (3b)) together with the Gaussian approximation (5), with α determined variationally instead of solving the Euler–Lagrange equation (1). These authors have used equation (5) with A, which gives the ratio of the number of particles N to the number of lattice sites N_s, $A = N/N_s$, considered as an additional variational parameter. When $A < 1$, equation (5) may be considered as describing a solid with vacancies (whereas for $A > 1$ the solid described by equation (5) is presumably unphysical). In this way they found a solid with more than 10% vacancies, which is very unphysical and two orders of magnitude above the generally accepted value. This very loose solid was then found (Jones 1987) also to have unusual elastic properties. It should be observed, however, that the free energy considered here (see equation (3b)) does not contain any of the mechanisms associated with vacancy formation, since this would require an explicit consideration of the solid surface. It does not seem to make sense therefore to use equation (5) with $A \neq 1$ in conjunction with equation (3b). Most authors have therefore considered only the perfect crystal ($A \equiv 1$). In an alternative approach, Iglói and Hafner (1986) have performed the second-order perturbation expansion (3b) of the solid around a reference liquid (different from the coexisting liquid) and minimised the corresponding equation (3b) with respect to the density of this reference liquid. This is a simplified version of an idea put forward by Meister and Kroll (1985) to expand the solid density around a smooth but non-uniform reference density (see also Groot 1987). For freezing, such theories quickly tend to become fairly complicated, but they could be better suited for treating non-uniform fluids by perturbation theory. In any case, for freezing, these theories cannot bypass the intrinsic problems of the thermodynamic perturbation expansion at the very basis of the RY theory.

2.2. Weighted-density approximation

In view of the fundamental difficulties with the perturbation approach, a new non-perturbative line of research was initiated by Tarazona (1984) and later extended by Curtin and Ashcroft (1985) under the name of the weighted-density approximation (WDA). It is based on a refined version of the so-called local-density approximation, whereby a thermodynamic property of a non-uniform phase (here the solid) is approximated by evaluating the thermodynamic property of the uniform phase (here the liquid) at a density equal to the local density of the non-uniform phase. In the present case, this would imply the use of liquid-phase data extrapolated to such high density (for the peak values of $\rho_S(r)$) that the liquid becomes ill-defined even as a metastable phase. In the WDA this difficulty is bypassed by first weighting the density of the solid, and it is the liquid-phase data evaluated at this weighted density that are used to describe the solid. This theory is usually formulated in terms of the canonical or Helmholtz free energy $F[\rho_S]$:

$$F[\rho_S] = F_{id}[\rho_S] + F_{ext}[\rho_S] + F_{ex}[\rho_S]. \tag{6}$$

Here the ideal-gas term

$$\beta F_{id}[\rho_S] = \int d\boldsymbol{r}\, \rho_S(\boldsymbol{r})\{\ln[\Lambda^3 \rho_S(\boldsymbol{r})] - 1\} \tag{7}$$

and the contribution from the external field $\varphi(\boldsymbol{r})$

$$F_{ext}[\rho_S] = \int d\boldsymbol{r}\, \rho_S(\boldsymbol{r})\varphi(\boldsymbol{r}) \tag{8}$$

are known exactly, as functionals of the density of the solid $\rho_S(\boldsymbol{r})$, whereas the excess term $F_{ex}[\rho_S]$ originating from the particle interactions has to be approximated. In the WDA this contribution is written as

$$F_{ex}^{WDA}[\rho_S] = \int d\boldsymbol{r}\, \rho_S(\boldsymbol{r})\psi_L(\bar{\rho}(\boldsymbol{r})) \tag{9}$$

where $\psi_L(\rho)$ is the excess free energy per particle of a uniform liquid of density ρ, while $\bar{\rho}(\boldsymbol{r})$ in equation (9) is the 'weighted' solid density

$$\bar{\rho}(\boldsymbol{r}) = \int d\boldsymbol{r}'\, \rho_S(\boldsymbol{r}')w(\boldsymbol{r} - \boldsymbol{r}'; \bar{\rho}(\boldsymbol{r})) \tag{10}$$

with $w(r; \rho)$ being the weighting function. The difficulty now lies in the appropriate physical definition of $w(r; \rho)$ and the technical problem of solving equation (10), which is an implicit equation for $\bar{\rho}(\boldsymbol{r})$. It is at this stage that appeal is made to the DF theory. The exact DF relation between the DCF of the solid and its excess free energy

$$c(\boldsymbol{r}, \boldsymbol{r}'; [\rho_S]) = -\frac{\delta^2 \beta F_{ex}[\rho_S]}{\delta \rho_S(\boldsymbol{r})\delta \rho_S(\boldsymbol{r}')} \tag{11}$$

is used to determine $w(r; \rho)$. This is done by requiring that, in the limit of a uniform

liquid, $\rho_S(r) \rightarrow \rho$: (i) equations (6)–(10) restore the free energy of the liquid, which implies that $w(r; \rho)$ be normalised for any ρ

$$\int dr\, w(r; \rho) = 1 \tag{12}$$

and (ii) equation (11) restores the DCF of the liquid, $c_L(|r - r'|; \rho)$

$$-\left(\frac{\delta^2 \beta F_{ex}^{WDA}[\rho_S]}{\delta\rho_S(r)\delta\rho_S(r')}\right)_{\rho_S(r) \rightarrow \rho} = c_L(|r - r'|; \rho). \tag{13}$$

This problem was first solved by Tarazona (1984, 1985) using the additional assumption that $w(r; \rho)$, and hence $c_L(|r|; \rho)$, can be expanded in a virial series as

$$w(r; \rho) = w_0(r) + w_1(r)\rho + w_2(r)\rho^2 + \dots \tag{14a}$$

$$c_L(r; \rho) = c_0(r) + c_1(r)\rho + c_2(r)\rho^2 + \dots \tag{14b}$$

which was truncated, first at zeroth order (Tarazona 1984) and later at second order (Tarazona 1985). Although good results were obtained in this manner, this poses the question of the convergence of the freezing results with respect to the truncation of the virial expansion (14), a problem somewhat similar to that of the perturbation expansion in the RY theory. To bypass this difficulty, Curtin and Ashcroft (1985) considered directly the non-linear differential equation for $w(k; \rho)$, the spatial Fourier transform of $w(r; \rho)$, which follows from (13):

$$-\beta^{-1}c_L(k; \rho) = 2\psi'_L(\rho)w(k; \rho) + \rho\frac{\partial}{\partial\rho}\{\psi'_L(\rho)[w(k; \rho)]^2\} \tag{15}$$

where $\psi'_L(\rho) = \partial\psi_L(\rho)/\partial\rho$. This approach yields good results but is quite elaborate because one has to: (i) solve equation (15) numerically for $w(k; \rho)$; (ii) compute $w(r; \rho)$ and solve equation (10) for $\bar\rho(r)$; (iii) perform the volume integral in equation (9); and (iv) finally, minimise the total $F[\rho_S]$ with respect to any variational parameters appearing in $\rho_S(r)$ (see e.g equation (5)). In view of this, a modified WDA (or MWDA) has recently been proposed by Denton and Ashcroft (1989b), for which most of the technical difficulties of the WDA can be avoided. It amounts to replacing equations (9) and (10) by

$$(1/\rho_S V)F_{ex}^{MWDA}[\rho_S] = \psi_L(\bar\rho) \tag{16}$$

where $\bar\rho$ is now a uniform weighted density defined in terms of a new weighting function $\tilde w(r; \rho)$

$$\bar\rho = \frac{\int dr \int dr'\, \rho(r)\rho(r')\tilde w(r - r'; \bar\rho)}{\int dr''\, \rho(r'')} \tag{17}$$

which replaces equation (10). The requirement (13) now no longer leads to equation (15) but to the much simpler linear equation

$$-\beta^{-1}c_L(k; \rho) = 2\psi'_L(\rho)\tilde w(k; \rho) + \rho\psi''_L(\rho)\delta_{k,0} \tag{18}$$

with

$$\psi''_L(\rho) = \frac{\partial^2}{\partial\rho^2}\psi_L(\rho)$$

which is readily solved. The results obtained from this MWDA compare well with those

of the much more involved WDA. Equation (17) is physically less obvious than the original equation (10). The idea behind equation (17) goes back to the theory of Stoessel (1988) in which equation (16) was used with $\bar{\rho}$ determined in such a manner that the liquid of density $\bar{\rho}$ will have the same second virial coefficient as the solid; this then leads to equation (17) with $\tilde{w}(r; \bar{\rho})$ replaced by $\tilde{w}_0(r)$, its lowest-order contribution in a virial expansion similar to equation (14a). Whereas the full $\tilde{w}(r; \bar{\rho})$ leads to good results, the theory of Stoessel (1988), based only on $\tilde{w}_0(r)$, leads to no liquid–solid phase transition (the free-energy curves do not cross). This clearly shows that virial expansions such as those of equation (14) have to be handled with care in the freezing context, which always involves fairly dense phases for which equation (14) is not applicable.

2.3. Effective-liquid approximation

A third line of approach was developed by Baus and Colot (1985). It was based on the desire to use the DF theory in a non-perturbative fashion. This can be achieved by starting from the exact equations (6)–(8) and computing the excess free energy of the solid, $F_{ex}[\rho_S]$, from equation (11). The resulting exact expression can be written

$$F_{ex}[\rho_S] = F_{ex}[\rho_R] + \int dr\, \Delta\rho(r) \frac{\delta F_{ex}[\rho_R]}{\delta \rho_R(r)}$$

$$- k_B T \int dr \int dr' \int_0^1 d\lambda \int_0^\lambda d\lambda'\, c(r, r'; [\rho_R + \lambda'\Delta\rho])\Delta\rho(r)\Delta\rho(r') \quad (19)$$

where the solid is reached by starting from a reference state ($\lambda = 0$) of density $\rho_R(r)$ and 'charging' its density gradually along the path $\rho_R(r) + \lambda\Delta\rho(r)$ up to the solid density $\rho_S(r)$ ($\lambda = 1$), i.e. $\Delta\rho(r) = \rho_S(r) - \rho_R(r)$. Notice that the double charging integral in equation (19) can always be simplified by using the identity

$$\int_0^1 d\lambda \int_0^\lambda d\lambda'\, h(\lambda') = \int_0^1 d\lambda\, (1 - \lambda)h(\lambda)$$

valid for any function $h(\lambda)$. Choosing now a uniform liquid as reference state, $\rho_R(r) \equiv \rho_R$, the first term on the RHS of equation (19) is known, $F_{ex}[\rho_R] \equiv F_{ex,L}(\rho_R)$, while the second can be dropped by taking ρ_R equal to the average density of the solid, i.e. $\int dr\, \Delta\rho(r) = 0$. So, everything boils down to evaluating the DCF of a solid of density $\rho_R + \lambda\Delta\rho(r)$, with $0 \le \lambda \le 1$ and $\Delta\rho(r) = \rho_S(r) - \rho_R$. Since this is as yet not possible, this DCF was approximated by that of an effective liquid of density $\bar{\rho}$, say $c_L(|r - r'|; \bar{\rho})$; hence the name effective-liquid approximation (ELA) given to this approach. If the effective-liquid density $\bar{\rho}$ corresponding to the solid of density $\rho_S(r)$ depends only on the average density of the solid ρ_S,

$$\rho_S = \int \frac{dr}{V} \rho_S(r)$$

then the effective liquids corresponding to $\rho_S(r)$ and $\rho_R + \lambda\Delta\rho(r)$ are the same (because here $\rho_R = \rho_S$) and the ELA of equation (19) reduces to

$$\beta F_{ex}^{ELA}[\rho_S] = \beta F_{ex,L}(\rho_R) - \tfrac{1}{2} \int dr \int dr'\, c_L(|r - r'|; \bar{\rho}(\rho_R))\Delta\rho(r)\Delta\rho(r'). \quad (20)$$

Here $\bar{\rho} = \bar{\rho}(\rho)$ is the density of the effective liquid corresponding to a solid of average

density ρ. Finally, to fix $\bar\rho(\rho)$, the effective liquid can be chosen in such a way that its DCF will mimic that of the solid. The choice of $\bar\rho(\rho)$ advocated by Baus and Colot (1985) is obtained when imposing the condition that the position of the main peak of the static structure factor of the effective liquid of density $\bar\rho$ coincides with the smallest RLV of the solid of average density ρ. This choice is motivated by the fact that: (i) the angular-averaged pair correlations of the solid and the liquid are similar, justifying the use of the ELA for the DCF in equation (19); and (ii) the strong localisation of the particles in the solid leads to weaker correlations in the solid than in the liquid of the same average density, and hence one should have $\bar\rho(\rho) < \rho$, which is also borne out by the above criterion. The resulting theory is simple to implement because equation (20) is similar to the RY expression (cf equation (3b)), which can easily be recovered from equation (20) by expanding $\bar\rho$ around the coexisting liquid density. The results obtained from the ELA are qualitatively and quantitatively sound. The major drawback of this theory, however, is that it is not obvious how to extend the definition of the effective liquid to other non-uniform systems besides the solid. Recently a modified ELA (or MELA), which bypasses this difficulty, was proposed by Baus (1989). It is based on using the exact equation (19) with $\rho_R \equiv 0$, viz.

$$\beta F_{\text{ex}}[\rho_S] = - \int \mathrm{d}r \int \mathrm{d}r' \int_0^1 \mathrm{d}\lambda \int_0^\lambda \mathrm{d}\lambda'\, c(r, r'; [\lambda'\rho_S])\rho_S(r)\rho_S(r') \tag{21}$$

and introducing now the ELA into equation (21)

$$\beta F_{\text{ex}}^{\text{MELA}}[\rho_S] = - \int \mathrm{d}r \int \mathrm{d}r' \int_0^1 \mathrm{d}\lambda \int_0^\lambda \mathrm{d}\lambda'\, c_L(|r - r'|; \lambda'\bar\rho)\rho_S(r)\rho_S(r'). \tag{22}$$

One obtains finally the MELA by requiring that the effective-liquid density $\bar\rho$ of equation (22) be determined self-consistently from equating the excess free energy per particle of the solid to that of the effective liquid itself:

$$\frac{1}{\rho_S V} F_{\text{ex}}^{\text{MELA}}[\rho_S] = \psi_L(\bar\rho) \equiv -k_B T \bar\rho \int \mathrm{d}r \int_0^1 \mathrm{d}\lambda \int_0^\lambda \mathrm{d}\lambda'\, c_L(|r|; \lambda'\bar\rho) \tag{23}$$

which is seen to determine $\bar\rho$ in terms of $\rho_S(r)$ for any given $c_L(|r|; \rho)$. This MELA is very simple to implement and has, in fact, been shown to yield results that are superior to those of the ELA (see Lutsko and Baus 1989). As a bonus one also finds an unexpected relation between the MELA and the MWDA. Indeed, from equations (22) and (23) it is apparent that $\bar\rho$ can be written in the form of equation (17) with

$$\bar w(r; \rho) = \frac{\int_0^1 \mathrm{d}\lambda \int_0^\lambda \mathrm{d}\lambda'\, c_L(|r|; \lambda'\rho)}{\int_0^1 \mathrm{d}\lambda \int_0^\lambda \mathrm{d}\lambda' \int \mathrm{d}r'\, c_L(|r'|; \lambda'\rho)} \tag{24}$$

i.e. an explicit expression for the weighting function in terms of $c_L(|r|; \rho)$. If, moreover, we rewrite equations (21) and (22) as

$$F_{\text{ex}}[\rho] = \int \mathrm{d}r\, \rho(r)\psi(r; [\rho])$$

and now determine $\bar\rho$ of equation (22) not from equation (23) but from the new self-consistency relation

$$\psi^{\text{MELA}}(r; [\rho_S]) = \psi_L(\bar\rho(r)) \tag{25}$$

then we recover equations (9) and (10) with $w(r; \rho)$ still given by equation (24), i.e. $w =$

$\bar{w}$. Therefore, according to which self-consistency relation is used (equation (23) or (25)), the MELA will have the same structure as (respectively) the WDA or the MWDA, but with weighting functions that are no longer given by (respectively) equation (15) or (18) but by equation (24). These weighting functions are different because in the (M)WDA the 'weighted' density is introduced into the thermodynamics of the solid and required to reproduce the structure of the liquid, whereas in the (M)ELA the 'effective' density is introduced into the structure of the solid and required to reproduce the thermodynamics of the liquid. Such a close relationship between the structure of the effective-liquid and the weighted-density theories, although somewhat unexpected, is of interest since these are also the theories that give the most reliable results. The only remaining difficulty now appears to be the fact that there is still no way to *improve* systematically on a given result. This problem should nevertheless be solved before one can really speak of a fully first-principles theory of phase coexistence.

3. Results

3.1. Hard-sphere freezing

Most of the above DF theories of freezing have been tested for the hard-sphere (HS) fluid–solid transition. The HS transition captures the essence of the freezing transition by focusing attention solely on the hard-core packing aspects of it. HS freezing was first studied in computer simulations and later observed for colloidal HS by Pusey and Van Megen (1986). The pioneering simulations are due to Alder and Wainwright (1957) and Wood and Jacobson (1957), but the two-phase coexistence could be located with precision only much later (Hoover and Ree 1968). It is generally accepted now (see Hansen and McDonald 1976) that the coexisting densities for the fluid (F) and FCC (perfect crystal) solid (S) are $\rho_F^* = 0.943$ and $\rho_S^* = 1.041$, with $\rho^* = \rho\sigma^3$ for HS of diameter σ. This corresponds to a fractional density change $\Delta\rho/\rho_F = 0.104$ and an entropy change per particle $\Delta s = 1.16k_B$, for a melting pressure $\beta p\sigma^3 = 11.8$. The Lindemann ratio L (RMS deviation divided by the nearest-neighbour distance) for the solid at coexistence is $L = 0.126$, while the main peak of the static structure factor of the coexisting fluid, max $S(k) = 2.85$, occurs at $k\sigma = 7.15$. These data are the milestones against which to test the DF theories.

All DF theories of HS freezing have used the PY (Percus–Yevick) DCF except for the original RY theory (Ramakrishnan and Yussouff 1979) where the liquid-state data were taken as input from simulations or experiments. The predictions of the RY theory concern the fractional density change and the Fourier components of the density of the coexisting solid (for which the corresponding 'experimental' values are still unknown). The underlying convergence problems discussed above in section 2 can be seen from the fact that $\Delta\rho/\rho_F$ (for HS) changes from 0.029 to 0.113 when going from the one-order-parameter (or density-wave) to the two-order-parameter theory. This quantity ($\Delta\rho/\rho_F$) appears to be very sensitive to the approximations. This is further illustrated by the fact that the improved second-order theory of Haymet (1983), including part of the third-order contributions and 15 order parameters, instead of improving the RY result further reduces it again to $\Delta\rho/\rho_F = 0.06$. The strictly second-order theory of Iglói and Hafner (1986), using a Gaussian density profile and introducing an additional variational parameter (the density of the reference liquid used in the perturbation theory), brings this quantity back to its 'experimental' value of 0.104, but the solid disappears at higher

Table 1. Coexistence data for the freezing of HS into a perfect FCC crystal as obtained from the non-perturbative DF theories and compared to the Monte Carlo (MC) results. Here, η_F and η_S denote the packing fractions of the coexisting fluid and solid, $\Delta\rho/\rho_F$ is the fractional density change, Δs the change in entropy per particle, P_{coex} the pressure at coexistence and $L = \langle(\Delta r)^2\rangle^{1/2}/d$ the Lindemann ratio. All theories use the PY DCF for the solid phase and also for the fluid phase in the (M)ELA theory, whereas the (M)WDA results are based on the Carnahan–Starling equation for the fluid phase. The latter description of the fluid is better but the theory is less consistent since both phases are described within slightly different approximations.

	η_F	η_S	$\Delta\rho/\rho_F$	$\Delta s/k_B$	$\beta\sigma^3 P_{coex}$	L
MC[a]	0.494	0.545	0.103	1.16	11.7	0.126
WDA[b,c]	0.479	0.547	0.141	1.41	10.4	0.093
MWDA[c]	0.476	0.542	0.139	1.35	10.1	0.097
MELA[d]	0.484	0.538	0.112	1.21	11.2	0.098
ELA[e]	0.520	0.567	0.090	1.36	16.1	0.074

[a] See Hoover and Ree (1968).
[b] See Curtin and Ashcroft (1985).
[c] See Denton and Ashcroft (1989b).
[d] See Lutsko and Baus (1989).
[e] See Baus and Colot (1985).

densities (this is reminiscent of the remelting found by Haymet (1985)). A much more consistent description of the HS transition is found in the theories based on the WDA or the ELA. For these theories, not only the coexistence region but the full HS phase diagram come out to be quite reasonably accurate. A minor exception should be made though for Tarazona's virial expansion of the weighting function, for which $\Delta\rho/\rho_F$ changes from 0.084 (zeroth virial order; Tarazona 1984) to 0.125 (second order; Tarazona 1985), which may signal a slow convergence. In our opinion, the most reliable (expansion-free) DF theories of HS freezing are compared, in the coexistence region, in table 1. Notice that these theories also show no unphysical features outside the coexistence region.

A somewhat more delicate point concerns freezing into other crystal lattices besides the FCC structure. This is important for those cases where the most stable lattice structure is not known *a priori*. In most DF theories the correct lattice structure is taken as input data, although this should in fact be sorted out by the theory itself. Very little attention has been paid to this problem in the DF literature (Popović and Jarić 1988). An interesting, but rather extreme, case concerns the freezing of HS into compact lattices (FCC, HCP, . . .) for which both simulations (Frenkel and Ladd 1984) and DF theory (Colot and Baus 1985, Laird *et al* 1988) have come to the conclusion that, with the present accuracy, it is not possible to distinguish the different compact lattices. Thus, any compact structure (e.g. a random compact stacking of dense lattice planes) yields a stable HS solid. In the simulations this is because the free-energy differences are comparable to the finite-size effects (Frenkel and Ladd 1984). In the theory this results from the fact that the range of the PY DCF is too short to probe the influence of the third-neighbour shells (Colot and Baus 1985), which distinguishes the compact lattices. A different problem concerns the BCC HS solid. Although this phase is usually thought to be unstable with respect to shear (not explicitly considered in the DF theories) of the pure HS system (Hoover *et al* 1972), it could be used as a reference state for a perturbation expansion with respect to the

attractive forces that stabilise the shear motions. In the ELA the BCC HS solid is found to be metastable relative to the fluid phase (Colot and Baus 1985), whereas the MELA (Lutsko and Baus 1989) and the WDA (Curtin and Runge 1987) predict a BCC solid that is stable relative to the fluid phase and metastable relative to the FCC phase. When the same analysis is carried out for the SC HS solid, this phase is found to be unstable in the ELA (Colot and Baus 1985) but stable relative to the fluid phase in the MELA (Lutsko and Baus 1989). The MELA thus appears to be superior to the ELA for the description of such (shear-)constrained HS solids. The related attempts to improve on the PY DCF have revealed only minor changes (Haymet and Oxtoby 1986, Colot *et al* 1986, Curtin and Runge 1987).

3.2. The hard-sphere solid

An interesting application of the DF theories of freezing concerns the theoretical study of the intrinsic properties of the solid phase, such as its elastic constants. In the case of the FCC solid where these predictions could be compared with the simulation results (Frenkel and Ladd 1987, Runge and Chester 1987), these studies have exhibited once more the superiority of the non-perturbative theories (Velasco and Tarazona 1987, Xu and Baus 1988) over the (RY-like) perturbation expansions (Jones 1987, Jarić and Mohanty 1987), which did predict a negative elastic constant not seen in the simulation results. It should be of interest to repeat these calculations for the unconstrained BCC HS solid in order to probe its shear instability. All these studies concern the perfect, defect-free, solid. A first attempt to describe a solid with topological defects (dislocations) was performed by Raj Lakshmi *et al* (1988) within the original RY theory. A simple model for the HS glass was similarly studied and found to be stable within the RY theory (Singh *et al* 1985) but unstable (relative to the perfect FCC solid) in the ELA (Baus and Colot 1986). A simple attempt to study the externally driven or forced freezing of (colloidal) HS systems was considered by Xu and Baus (1986) but these authors could not reproduce the crossover from first- to second-order freezing seen in a recent (two-dimensional) experiment by Chowdhury *et al* (1985).

3.3. The crystal–melt interface

One of the most difficult problems within the equilibrium theory of liquid–solid coexistence concerns the full-scale description of the two-phase system (including its interface). Interesting results have been obtained from a simplified version of the DF theory where one minimises the excess of the free energy over its bulk value with respect to a parametrised density profile that interpolates smoothly between the bulk crystal and the bulk liquid, the previously computed results for the (infinite) bulk system being used as input bulk values. A very early attempt was the one performed by Haymet and Oxtoby (1981) on the basis of the RY theory using just one order parameter whose spatial dependence was treated within the square gradient approximation. In this way they found a rather broad fluid–solid interface, 10–15 layers thick. Using a Gaussian profile for the HS solid and a 'tanh' interpolation for the interface region, Moore and Raveché (1986) found the interface to be 5–8 layers thick from the same second-order RY theory with a square gradient approximation in the interfacial region. Using the WDA and a two-parameter interpolation function for the interfacial density profile, Curtin (1987) was able to avoid all the expansion problems for the free energy and also the doubtful gradient expansion. He found the interface to be only 4–5 layers thick. Recently,

McMullen and Oxtoby (1988) reconsidered the earlier theory of Haymet and Oxtoby (1981) with a parametrised interfacial density profile and no square gradient approximation and found the interfacial thickness to be reduced to only three layers. Both HS and Lennard–Jones systems have been considered, but the differences are relatively small. The results of Curtin (1987) appear to lead to the best agreement with the computer simulations of Broughton and Gilmer (1986), Cape and Woodcock (1980) and Tallon (1986).

3.4. Dimensional effects

Another hard-core system that exhibits a fluid–solid transition, although the solid has only quasi-long-range order, is the hard-disc model of monolayers adsorbed on smooth substrates. The hard-disc transition has been studied by computer simulations (Alder and Wainwright 1962, Hoover and Alder 1967, Wood 1968) and also within DF theory (Ramakrishnan and Yussouff 1979, Tarazona 1984, Colot and Baus 1986, Laird *et al* 1988). The behaviour of the results is similar to that of the HS case. A problem specific to hard discs is that the DCF of the fluid phase, which is required as input for the DF theories, is not readily available. This difficulty can be overcome with the analytic expression for the DCF of D-dimensional HS proposed by Baus and Colot (1987). On this basis it was shown (Colot and Baus 1986) that the hard-rod solid ($D = 1$) is unstable while from $D = 2$ on the first-order character of the freezing transition increases with D, the transition being pushed towards the close-packing density, which itself decreases with increasing D-values. It is possible, but this remains to be shown, that the situation would become trivial (as claimed by Wyler *et al* 1987) when D tends to infinity, although this may be of little practical use.

3.5. The freezing of hard-sphere mixtures

An experimentally interesting situation concerns the freezing of mixtures. Very little has been done as yet in this direction, although some simulation results for HS mixtures may soon become available (Frenkel 1989). A straightforward extension of the ELA for the freezing of a binary HS mixture into a substitutionally disordered alloy was proposed by Barrat *et al* (1986). The very rich behaviour of the phase diagram (in terms of the diameter ratio) found there was later shown to persist also when attractive forces are introduced (Barrat *et al* 1987a). The same DF theory has also been extended to a binary mixture of hard discs (Barrat *et al* 1988b, Xu and Baus 1989) and to the case of the partial freezing of large spheres into a host fluid of small spheres (Ermak *et al* 1981, Jackson *et al* 1987) as appropriate for the study of colloidal crystals (Xu and Baus 1986). The case of a strongly dissimilar, but equimolar, HS binary mixture was also studied by Smithline and Haymet (1987) on the basis of the RY theory.

3.6. Related studies

Besides the hard-core systems to which our discussion has been mainly restricted, the DF theory of freezing has also been applied to a vast amount of other systems, such as the following: adhesive HS (Smithline and Haymet 1985), Lennard–Jones systems (Tarazona 1984, Marshall *et al* 1985, Curtin and Ashcroft 1986), soft spheres (Barrat *et al* 1987c), Yukawa potentials (Kloczkowski and Samborski 1988), polydisperse HS (Barrat and Hansen 1986, McRae and Haymet 1988), water (Ding *et al* 1987), helium

(McCoy *et al* 1989), liquid metals (Inglói *et al* 1987), dipolar HS (McMullen and Oxtoby 1987, Smithline *et al* 1988), charged HS (Wu and Baus 1987, Brami *et al* 1988), molten salts (Rovere *et al* 1982, Barrat 1987a), one-component plasma (Haymet 1984, Rovere and Tosi 1985, Barrat 1987b, Iyetomi and Ichimaru 1988), ionic mixtures (Ichimaru *et al* 1988, Barrat *et al* 1988a), etc, not to mention recent related studies of orientational freezing (see e.g. Colot *et al* 1988) and of fluid interfaces and wetting phenomena (see e.g. Evans 1989).

4. Conclusions

The density-functional approach to equilibrium statistical mechanics of non-uniform systems has been widely recognised as an efficient framework for the theoretical study of a large variety of problems involving spatial non-uniformities. In the extreme case of liquid–solid coexistence it has already become a popular means to produce phase diagrams for a large variety of systems. In this review we have discussed the different methods by which such freezing data are usually produced. We have come to the conclusion, which may be subjective, that all theories based on the truncation of infinite series are subject to caution and that the nature of the convergence (if present) of the expansions they generate is not understood. Those theories which are non-perturbative appear instead to be quite reliable and also physically comparable. The latter theories are, however, still far from yielding a complete first-principles theory of first-order phase transitions such as freezing because some of the fundamental problems (such as symmetry breaking) remain unanswered by them whereas there also appears to be no systematic way to improve their predictions. Apart from these limitations, the progress realised during the past decade is considerable. To illustrate these points we have considered a number of explicit results. Because of the already fairly large literature on the subject we have limited ourselves here to the hard-core (mainly hard-sphere) systems. It was shown then that, with the help of computer simulations and present-day liquid-state theory, fairly accurate solid-state and freezing data can be obtained from the DF theories by, after all, fairly simple means. Future research in this area should concentrate now on the freezing of those systems for which the equilibrium state is not a compact lattice structure (e.g. the one component plasma and some of the soft-sphere systems).

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