

# Statistical Mechanical Theories of Freezing: An Overview

M. Baus<sup>1</sup>

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Recent progress in the microscopic description of the liquid–solid coexistence is examined critically and put into historical perspective. The emphasis is on the density functional theories, including some of their more controversial aspects. The underlying physical freezing mechanism is discussed in detail.

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**KEY WORDS:** Liquid–solid coexistence; Freezing; Density functional theory; hard spheres; phase transitions.

## 1. INTRODUCTION

Prof. I. Prigogine, to whom this article is dedicated on the occasion of this 70th birthday, may be pleased to hear that in the recent density functional theories the freezing of hard spheres can be described as a competition between two forms of *entropy*: a loss in configurational entropy when the particles go into the ordered state, and a gain in correlational entropy resulting from the particle localization. Before considering this interpretation in more detail, it may be useful to recall briefly some of the main attempts toward a theoretical study of freezing.

In the early days the liquid–solid transition was usually identified with a mechanical instability occurring in one of the coexisting phases. The solid was thought to melt when its shear rigidity vanishes<sup>(1)</sup> or the fluid was considered to freeze when its static structure factor diverges<sup>(2,3)</sup> for a particular lattice periodic density fluctuation. Today it is clear that such one-phase approaches cannot locate the two-phase coexistence accurately, since in a first-order transition, such as freezing, each phase can exist as a thermodynamically metastable but mechanically stable state in a finite region

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<sup>1</sup> Chimie-Physique II, Université Libre de Bruxelles, B-1050 Bruxelles, Belgium.

around the true coexistence point. The phase transition itself can be located unambiguously only by the thermodynamic conditions of equality of the pressure, the temperature, and the chemical potential of the coexisting phases.

This does not imply, however, that a one-phase approach cannot be used as a means to locate *approximately* the phase transition. This is, e.g., the case for the empirical Lindemann melting rule,<sup>(4)</sup> stating that the solid melts when the rms deviation of the atomic positions from their average value exceeds 15% of the nearest neighbor distance. Similarly, the empirical Hansen–Verlet freezing rule<sup>(5)</sup> states that a monoatomic simple liquid will freeze when the maximum of its static structure factor reaches a value of 2.85. These rules, besides being empirical, are only approximate and cannot be used to locate the true thermodynamic coexistence between a liquid and a solid; as already stated, such a study does require the simultaneous consideration of both the liquid and the solid. In principle, one could nevertheless still use different theories to describe the different coexisting phases, but, in practice, this usually leads to uncertainties, e.g., on the location of the melting line,<sup>(6)</sup> almost as large as those of the one-phase theories. A unified description of both phases, based on the integral equations of equilibrium statistical mechanics, was first advocated by Kirkwood and Monroe.<sup>(7)</sup> Unfortunately, at the time of their writing, liquid state theory, and in particular the integral equations, was a recent, almost undeveloped topic. Consequently, these authors bypassed the difficult problem of solving the integral equation for the solid by an undue expansion<sup>(8)</sup> of the solid around the coexisting liquid.

This line of research was then further developed<sup>(9)</sup> in parallel with liquid state theory, but without much success,<sup>(10)</sup> although some more recent attempts should be cited here.<sup>(11)</sup> The final step leading to the modern theory of freezing was taken by Ramakrishnan and Yussouff,<sup>(12)</sup> who, taking advantage of the developments of the theory of liquids during the past decade, reformulated the Kirkwood and Monroe theory into the more flexible language of the direct correlation function. These authors did not solve the problem completely, but showed that one could obtain good freezing data as output by taking experimental liquid state data as input together with some simple approximations of the theoretical expressions.

This agreement between theory and experiment, the first within a statistical theory of freezing, was the basis for a whole series of investigations<sup>(13–35)</sup> aiming mainly at a better understanding of the underlying theory. The common language for all these investigations is the density functional theory of nonuniform systems. The basic feature of the latter theory is that the thermodynamic potentials are viewed as functionals of the local density. Such functionals are not new and have been used for

some time in statistical mechanics.<sup>(36-41)</sup> The density functional language is, however, particularly well suited to the modern freezing theories, since the latter view the solid as a strongly nonuniform liquid, a somewhat antihistorical viewpoint. These theories are hence also strongly liquid-based and therefore usually termed “freezing” theories. Notice that in principle one could take the symmetric viewpoint by considering the liquid as a strongly disordered solid and construct a solid-phase-based theory of melting. The theory of liquids is, however, in a much more advanced stage than the theory of disordered solids and all theories proposed to date are therefore liquid-based freezing theories.

In the next section the main points of the density functional theory of freezing will be presented in a general setup. Details and explicit results can be found in the exhaustive list of original investigations given in the references.<sup>(12-35)</sup> Details about the density functional method itself, whose scope largely exceeds the theory of freezing and has revealed itself recently as a very efficient approach to nonuniform systems in general, can be found in the investigations listed in Ref. 36–41. My main goal here will hence be restricted to a unified presentation of the many differences between the different freezing theories available in the literature together with a number of criticisms and open questions that sooner or later will have to be considered explicitly in order to assess the quality of the results obtained hitherto.

In Section 3 I continue with a detailed explanation of the physical freezing mechanism, already alluded to in the heading, as viewed from the density functional theories, since this topic has not yet been considered in the literature. Section 4 contains a few closing remarks.

## 2. THE DENSITY FUNCTIONAL THEORY OF FREEZING

The original work of Kirkwood and Monroe<sup>(7)</sup> was formulated in the traditional language of the pair correlation function. This leads to difficulties and poor approximations, as already discussed elsewhere.<sup>(8,42)</sup> The seminal work of Ramakrishnan and Yussouff<sup>(12)</sup> instead was formulated in the modern language of the direct correlation function, and its relation to the density functional theory<sup>(39)</sup> was clarified by Haymet and Oxtoby.<sup>(15)</sup> The density functional theory under consideration here is the finite-temperature, classical analog of the zero-temperature, quantal version well known from solid state physics.<sup>(43)</sup>

### 2.1. General Scheme

Although not always clearly stated, the theoretical basis of the density functional theory is a theorem established by Mermin<sup>(37)</sup> and stating that

there is a one-to-one correspondence between the local density  $\rho(\mathbf{r})$  and the external potential  $\phi(\mathbf{r})$ , which uniquely locates the physical system in space (e.g., by fixing the boundaries of the fluid, fixing the crystal axes of the solid, etc.). The thermodynamic potential of a given system (say, the Helmholtz free energy  $F$ , the Gibbs free energy  $G$ , or the grand potential  $\Omega$ ), besides being a function of the appropriate thermodynamic variables, is also a *functional* of  $\phi(\mathbf{r})$ , since the external potential defines uniquely which system is being considered. In what follows I will indicate this functional dependence by square brackets as  $F = F[\phi]$ , and leave the dependence on the remaining thermodynamic variables (such as temperature  $T$  and volume  $V$ ) implicit.

In view of the subsequent variational properties of the thermodynamic potentials, the use of the external potential (as a variational variable) is rather inconvenient and therefore, using Mermin's theorem, we change variable from  $\phi(\mathbf{r})$  to  $\rho(\mathbf{r})$  and consider instead  $F$  (or any other thermodynamic potential) as a functional of the local density,  $F = F[\rho]$ . Henceforth, I consider the Helmholtz free energy  $F$  as the basic thermodynamic potential and  $\rho(\mathbf{r})$  as the basic variational variable. The grand potential  $\Omega = \Omega[\rho]$  is then obtained from  $F[\rho]$  by a Legendre transformation,

$$\Omega[\rho] = F[\rho] - \int_V d\mathbf{r} \rho(\mathbf{r}) \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} \quad (2.1)$$

and using the relation between the potentials  $\Omega = F - G$ , we can also obtain the Gibbs free energy  $G = G[\rho]$ :

$$G[\rho] = \int_V d\mathbf{r} \rho(\mathbf{r}) \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} \quad (2.2)$$

from  $F[\rho]$ . It is also convenient to introduce the intensive quantities

$$\frac{F[\rho]}{V} = f[\rho], \quad \frac{\Omega[\rho]}{V} = -p[\rho], \quad \frac{G[\rho]}{V} = \rho\mu[\rho] \quad (2.3)$$

corresponding to the (Helmholtz) free energy per unit volume  $f = f[\rho]$ , the pressure  $p = p[\rho]$ , and the chemical potential  $\mu = \mu[\rho]$ , where  $\rho$  is the average density:

$$\rho = \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) \quad (2.4)$$

i.e., the spatial average over the volume  $V$  of the local density  $\rho(\mathbf{r})$ . The true equilibrium state, say  $\rho_0(\mathbf{r})$ , and the equilibrium value of the poten-

tials, say  $F_0 = F[\rho_0]$ , can then be obtained from the stationarity properties of the potentials. For instance, at constant average density  $\rho$  the Helmholtz free energy  $F$  has to remain constant,  $\delta F|_\rho = 0$  (it is understood that all remaining implicit arguments are kept constant). The corresponding Euler-Lagrange equation can be written

$$\left. \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} \right|_\rho = \mu \quad (2.5)$$

and ensures that indeed

$$\delta F|_\rho = \int d\mathbf{r} \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} \delta \rho(\mathbf{r}) = 0 \quad (2.6)$$

provided the chemical potential  $\mu$  is (a space-independent) constant. Having located the equilibrium density with the aid of (2.5), we can find the equilibrium thermodynamics from (2.3). The crucial point consists hence in finding the expression of  $F = F[\rho]$ . To this end, write [ $A = h/(2\pi m k_B T)^{1/2}$ ]

$$\begin{aligned} F[\rho] = & k_B T \int_V d\mathbf{r} \rho(\mathbf{r}) \{ \ln[A^3 \rho(\mathbf{r})] - 1 \} \\ & + \int_V d\mathbf{r} \rho(\mathbf{r}) \phi(\mathbf{r}) + F_{\text{ex}}[\rho] \end{aligned} \quad (2.7)$$

where we have separated the purely configurational ideal gas term and the contribution of the external potential from the remaining excess term,  $F_{\text{ex}} = F_{\text{ex}}[\rho]$ . The latter can be related to the direct correlation function  $c(\mathbf{r}, \mathbf{r}'; [\rho])$  through

$$-\beta \frac{\delta^2 F_{\text{ex}}[\rho]}{\delta \rho(\mathbf{r}') \delta \rho(\mathbf{r})} = c(\mathbf{r}, \mathbf{r}'; [\rho]) \quad (2.8)$$

with  $\beta = 1/k_B T$ . Equation (2.8) can be integrated twice between a reference state of density  $\rho_R(\mathbf{r})$ , and the actual state of density  $\rho(\mathbf{r})$ , yielding the following basic expression for the excess free energy:

$$\begin{aligned} F_{\text{ex}}[\rho] = & F_{\text{ex}}[\rho_R] + \int_V d\mathbf{r} \frac{\delta F_{\text{ex}}[\rho_R]}{\delta \rho_R(\mathbf{r})} \Delta \rho(\mathbf{r}) \\ & - k_B T \int_V d\mathbf{r} \int_V d\mathbf{r}' \int_0^1 d\lambda (1 - \lambda) c(\mathbf{r}, \mathbf{r}'; [\rho_R + \lambda \Delta \rho]) \Delta \rho(\mathbf{r}') \Delta \rho(\mathbf{r}) \end{aligned} \quad (2.9)$$

where  $\Delta \rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_R(\mathbf{r})$ . Knowing the rhs of (2.9), i.e., knowing the integration constants  $F_{\text{ex}}[\rho_R]$ ,  $\delta F_{\text{ex}}[\rho_R]/\delta \rho_R(\mathbf{r})$ , and the direct correlation

function  $c(\mathbf{r}, \mathbf{r}'; [\rho])$  as a functional of the local density, one can in principle reconstruct the complete free energy functional  $F[\rho]$  from (2.7). This, however, is usually not the case, and, in practice, it is at this stage that rather drastic approximations [to the rhs of (2.9)] have to be introduced.

## 2.2. Open Questions

To find the local density  $\rho(\mathbf{r})$  of a system of two coexisting (liquid and solid) phases is a largely unsolved problem. This difficulty is bypassed in all the existing freezing theories by approximating the true two-phase coexistence problem by one of bulk-phase coexistence (between a uniform bulk liquid and a periodic bulk solid), neglecting the presence of the difficult interfacial region. The above density functional, say  $F[\rho]$ , is then worked out separately for the liquid and for the solid and the coexistence is found only *a posteriori* by comparing the thermodynamic potentials of the two bulk phases. This procedure has the advantage that each bulk phase can now be formally considered as of infinite extent and in the thermodynamic limit the contribution of the external potential to the thermodynamics can be neglected. The uniform liquid phase is then easily treated according to the above scheme [e.g., taking  $\rho(\mathbf{r}) = \rho_L$  and  $\rho_R(\mathbf{r}) = 0$  in Eq. (2.9), in which case the integration constants vanish] and the real problem amounts to describing the bulk solid [e.g., taking  $\rho(\mathbf{r}) = \rho_S(\mathbf{r})$  lattice periodic and  $\rho_R(\mathbf{r}) = \rho_R$  uniform, so that the integration constants of (2.9) can be borrowed from liquid state theory]. Once this is achieved, the solid of lowest free energy (fcc, bcc,...) is compared to the liquid and the liquid–solid coexistence is determined by finding a liquid and a solid that, at constant temperature, have the same pressure and the same chemical potential.

Although physically quite straightforward, the above procedure raises a number of basic questions to which there are as yet no answers. It is, indeed, clear that treating the thermodynamically metastable and stable phases on the same footing requires a fair amount of analyticity of the basic free energy density functional. Similarly, the formal permutation of the thermodynamic limit with the limit of vanishing (symmetry-breaking) external potential can certainly not be taken for granted. It is, however, my impression that these questions will remain open for some time and that, in view of the almost infinite complexity of a full-scale attack on the phase transition problem, the above procedure represents a quite reasonable starting point. Even so, many controversies have arisen with respect to how the above procedure has to be worked out and each series of authors<sup>(12–35)</sup> has used different (but closely related) approximation schemes. The by far most drastic approximation concerns Eq. (2.9). All authors agree in taking

a uniform reference state,  $\rho_{\mathbf{R}}(\mathbf{r}) = \rho_{\mathbf{R}}$ , in (2.9), but differ in their approximation of the dcf (direct correlation function) of the solid.

### 2.3. The Solid As a Perturbation of the Liquid

In the original work of Ramakrishnan and Yussouff<sup>(12)</sup> the dcf of the solid,  $c(\mathbf{r}, \mathbf{r}'; [\rho_{\mathbf{R}} + \lambda \Delta\rho])$ , appearing in Eq. (2.9) was expanded around  $\lambda = 0$  and only the first term was retained:

$$\begin{aligned} & \int_0^1 d\lambda (1 - \lambda) c(\mathbf{r}, \mathbf{r}'; [\rho_{\mathbf{R}} + \lambda \Delta\rho]) \\ &= \int_0^1 d\lambda (1 - \lambda) \{c(\mathbf{r}, \mathbf{r}'; [\rho_{\mathbf{R}}]) + O(\lambda)\} \\ &= \frac{1}{2} c(\mathbf{r}, \mathbf{r}'; [\rho_{\mathbf{R}}]) + \dots \end{aligned} \quad (2.10)$$

and since the reference state  $\rho_{\mathbf{R}}$  is taken to be the uniform liquid, the rhs of (2.10) [and hence of (2.9)] can be computed from liquid state theory; here  $c(\mathbf{r}, \mathbf{r}'; [\rho_{\mathbf{R}}]) \equiv c(|\mathbf{r} - \mathbf{r}'|; \rho_{\mathbf{R}})$  is the dcf of the liquid at the reference density. This approximation of the dcf of the solid by the dcf of the liquid is a rephrasing of the original Kirkwood–Monroe idea<sup>(7,8)</sup> (of approximating the pair correlations of the solid by those of the liquid) and has been taken over by many authors. In the general sense this idea merely expresses our ignorance of the dcf of the solid and it is difficult to see how this approximation could be bypassed. Physically it is clear that the angle-averaged dcf of the solid should be qualitatively similar to the dcf of the liquid, since the angle average will destroy the long-range order and one is then left with very similar short-range orders. Although Eq. (2.9) is not an angle average but a spatial average [weighted by  $\Delta\rho(\mathbf{r})$ ], one can still argue in favor of this general idea. It is, however, less easy to argue that it will be sufficient to do that only for the first term of the  $\lambda$ -expansion in (2.10). This is nevertheless the way this idea has been implemented in most of the literature.<sup>(12, 14, 22, 30, 32, 34)</sup> Haymet<sup>(17)</sup> has proposed to include also the next term in the series of (2.10):

$$\begin{aligned} & \int_0^1 d\lambda (1 - \lambda) c(\mathbf{r}, \mathbf{r}'; [\rho_{\mathbf{R}} + \lambda \Delta\rho]) \\ &= \int_0^1 d\lambda (1 - \lambda) \left\{ c(\mathbf{r}, \mathbf{r}'; [\rho_{\mathbf{R}}]) \right. \\ & \quad \left. + \lambda \int d\mathbf{r}'' \Delta\rho(\mathbf{r}'') \frac{\delta c(\mathbf{r}, \mathbf{r}'; [\rho])}{\delta \rho(\mathbf{r}'')} \Big|_{\rho = \rho_{\mathbf{R}}} + O(\lambda^2) \right\} \end{aligned} \quad (2.11)$$

but, unfortunately, this term involves the unknown three-point dcf of the liquid:

$$\left. \frac{\delta c(\mathbf{r}, \mathbf{r}'; [\rho])}{\delta \rho(\mathbf{r}'')} \right|_{\rho = \rho_R} = c_3(\mathbf{r}, \mathbf{r}', \mathbf{r}''; [\rho_R]) \quad (2.12)$$

This difficulty was then circumvented by further approximating the new term of (2.11) as

$$\begin{aligned} & \int d\mathbf{r}'' \Delta \rho(\mathbf{r}'') c_3(\mathbf{r}, \mathbf{r}', \mathbf{r}''; [\rho_R]) \\ &= \int d\mathbf{r}'' \Delta \rho(\mathbf{r}'') \int \frac{d\mathbf{x}}{V} c_3(\mathbf{r}, \mathbf{r}', \mathbf{x}; [\rho_R]) + \dots \end{aligned} \quad (2.13)$$

and using the relation (which is exact for the liquid)

$$\int d\mathbf{x} c_3(|\mathbf{r} - \mathbf{x}|, |\mathbf{r}' - \mathbf{x}|; \rho_R) = \frac{\partial}{\partial \rho_R} c(|\mathbf{r} - \mathbf{r}'|; \rho_R) \quad (2.14)$$

so that (2.11) becomes finally

$$\begin{aligned} & \int_0^1 d\lambda (1 - \lambda) c(\mathbf{r}, \mathbf{r}'; [\rho_R + \lambda \Delta \rho]) \\ &= \frac{1}{2} c(|\mathbf{r} - \mathbf{r}'|; \rho_R) + \frac{1}{6} \frac{\partial c(|\mathbf{r} - \mathbf{r}'|; \rho_R)}{\partial \rho_R} \int \frac{d\mathbf{r}''}{V} \Delta \rho(\mathbf{r}'') + \dots \end{aligned} \quad (2.15)$$

where the ellipses denote now not only the terms neglected in (2.11), but also in (2.13). This scheme has, to our knowledge, not been pushed any further and raises the question of the convergence of the underlying expansion of (2.11). This expansion is clearly a density functional analog of Landau's well-known expansion of the free energy in powers of the order parameter [here  $\Delta \rho(\mathbf{r})$ ] of a weakly first-order transition. Freezing, however, is a strongly first-order transition and the expansion of (2.11) remains to be justified. Checking, for instance, the expansion (2.11) in a uniform phase context, such as the liquid-gas transition, one finds<sup>(25)</sup> that (because of the presence of large density derivatives) the convergence is indeed very slow. The adequacy of (2.15) is therefore still poorly understood. In a recent attempt, Igloi and Hafner<sup>(34)</sup> have proposed using the density of the reference fluid  $\rho_R$  appearing in (2.9) as an additional variational parameter by minimizing the free energy also with respect to  $\rho_R$ . This procedure will certainly lower the free energy of the solid, but does not answer the above criticism concerning the convergence of the expansion (2.11) with respect to  $\Delta \rho(\mathbf{r})$ .



## 2.4. The Solid As a Liquid with an Effective Density

In order to avoid the difficulties associated with the above perturbation treatments, a number of authors<sup>(23-29,31,33)</sup> have proposed to describe the solid as a liquid with an effective density  $\bar{\rho}$  determined self-consistently by the actual density of the solid  $\rho(\mathbf{r})$ . This avoids the above expansion problems, but raises instead the delicate question of the choice of the effective liquid density. Various proposals are available. The simplest is presumably the one proposed recently by Stoessel and Wolynes.<sup>(33)</sup> These authors use Eq. (2.7) and approximate the excess free energy of the solid by that of the liquid evaluated at the effective density:

$$F_{\text{ex}}[\rho] = F_{\text{ex,liq}}(\bar{\rho}) \quad (2.16)$$

with  $\bar{\rho}$  determined by the solid density  $\rho(\mathbf{r})$  as a weighted average:

$$\bar{\rho} = \bar{\rho}[\rho] \equiv \int d\mathbf{r}' \rho(\mathbf{r}') w(\mathbf{r}'; [\rho]) \quad (2.17)$$

where the weighting function  $[V(|\mathbf{r}|)]$  is the interaction potential]

$$w(\mathbf{r}; [\rho]) = \int \frac{d\mathbf{r}'}{V} \rho(\mathbf{r}') \{1 - \exp[-\beta V(|\mathbf{r} - \mathbf{r}'|)]\} \\ \times \left( \rho \int d\mathbf{x} \{1 - \exp[-\beta V(|\mathbf{x}|)]\} \right)^{-1} \quad (2.18)$$

has been determined in such a manner that the second virial coefficients of the nonuniform and uniform systems have the same form. In the approach of Tarazona<sup>(23,24)</sup> one uses instead of (2.16)

$$F_{\text{ex}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \psi_{\text{liq}}(\bar{\rho}) \quad (2.19)$$

where  $\psi_{\text{liq}}(\bar{\rho})$  is now the excess free energy per particle of the liquid [i.e.,  $F_{\text{ex,liq}}(\bar{\rho})/V = \bar{\rho}\psi_{\text{liq}}(\bar{\rho})$ ], while  $\bar{\rho}$  is given by a nonlocal weighted average:

$$\bar{\rho} = \bar{\rho}(\mathbf{r}; [\rho]) = \int d\mathbf{r}' \rho(\mathbf{r}') w(\mathbf{r} - \mathbf{r}'; [\rho]) \quad (2.20)$$

defining thus a nonuniform effective density. The weighting function in (2.20) is then determined implicitly by using (2.19) and (2.8) and requiring that, for a *uniform* system, the virial expansion of the weighting function of (2.20) reproduces the virial expansion of the dcf of the uniform liquid system. Tarazona first truncated the virial expansion at zeroth order<sup>(23)</sup> and

next at second order,<sup>(24)</sup> whereas Curtin and Ashcroft<sup>(31)</sup> considered the complete virial series by solving the resulting differential equation for the weighting function numerically. A still different approach was proposed by Baus and Colot<sup>(25-29)</sup> who introduced an effective density  $\bar{\rho}$  in order to approximate not the excess free energy, but instead the dcf of the solid:

$$c(\mathbf{r}, \mathbf{r}'; [\rho]) = c_{\text{liq}}(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}) \quad (2.21)$$

where  $\bar{\rho} = \bar{\rho}[\rho]$ , was determined either by minimizing the free energy of the solid at given average density<sup>(26)</sup> or by looking for a liquid that scales with the given solid.<sup>(25)</sup> To this end, one first considers the oscillations that follow the main peak of the pair correlation function of the liquid. For a dense liquid these oscillations become very persistent (layering) and give rise to the main peak of the static structure factor, the position of which corresponds to the wavelength of the layering in the liquid. The best scaling of the liquid to the solid will then be achieved when the layering in the liquid mimics the layering in the solid, i.e., when the position of the main peak of the static structure factor of the effective liquid (this position being a function of  $\bar{\rho}$ ) coincides with the smallest reciprocal lattice vector of the solid (this lattice vector being a function of the average density of the solid  $\rho$  and of the lattice structure). Both choices yield a relation  $\bar{\rho} = \bar{\rho}(\rho)$  between the average density of the solid  $\rho$  and the effective density  $\bar{\rho}$  of the uniform liquid that is used to describe this solid, which turns out to be quite similar,<sup>(26-28)</sup> especially in the coexistence region.

The main advantage of the effective liquid theories over the perturbation theories discussed in Section 2.3 stems from the fact that the basic idea of the former can be formulated independently of any density expansion<sup>(25, 29, 31)</sup> [although some of the attempts<sup>(23, 24, 33)</sup> have used virial expansions for the determination of the weighting function in (2.20)]. This then allows infinite-order partial resummations of the density series of Section 2.3 to be performed easily. For instance, Eqs. (2.9)–(2.11) become now on using (2.21) and the above effective density  $\bar{\rho} = \bar{\rho}(\rho)$

$$\begin{aligned} & \int_0^1 d\lambda (1 - \lambda) c(\mathbf{r}, \mathbf{r}'; [\rho_{\mathbf{R}} + \lambda \Delta\rho]) \\ &= \frac{1}{\rho - \rho_{\mathbf{R}}} \int_{\rho_{\mathbf{R}}}^{\rho} d\rho' \frac{\rho - \rho'}{\rho - \rho_{\mathbf{R}}} c(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}(\rho')) \end{aligned} \quad (2.22)$$

i.e., the functional integral over the path in density space from the reference state  $\rho_{\mathbf{R}}(\mathbf{r}) = \rho_{\mathbf{R}}$  to the actual state  $\rho(\mathbf{r})$  of the dcf of the nonuniform system as it appears in the rhs of (2.9) is approximated by an ordinary integral of the dcf of the effective liquid over the corresponding average density path

from  $\rho_R$  to  $\rho$ . Moreover, in the case of a uniform system we have  $\bar{\rho} \equiv \rho$  and the theory remains exact, which is not the case for the truncated perturbation theories.

The main drawback of the effective liquid approach, however, is that there appears to be no guiding principle to systematically improve upon the choice of the effective liquid describing a given solid.

## 2.5. The Approximate Euler–Lagrange Equation

Once the approximate free energy density functional  $F[\rho]$  has been set up according to one of the above proposals, it still remains to determine the equilibrium density, say  $\rho(\mathbf{r}) = \rho_0(\mathbf{r})$ , satisfying Eq. (2.6).

(a) A first procedure<sup>(12–22,34)</sup> consists in starting directly from the Euler–Lagrange equation (2.5), which, using (2.7)–(2.9), one can rewrite as

$$\ln[A^3 \rho(\mathbf{r})] = \beta[\mu - \phi(\mathbf{r})] - \beta \frac{\delta F_{\text{ex}}[\rho_R]}{\delta \rho_R(\mathbf{r})} + \int d\mathbf{r}' \int_0^1 d\lambda c(\mathbf{r}, \mathbf{r}'; [\rho_R + \lambda \Delta\rho]) \Delta\rho(\mathbf{r}') \quad (2.23)$$

or, equivalently, eliminating the integration constant (at constant temperature) in favor of the density  $\rho_R$  and chemical potential  $\mu_R$  of some uniform reference state,

$$\frac{\rho(\mathbf{r})}{\rho_R} = \exp \left\{ \beta(\mu - \mu_R) + \int d\mathbf{r}' \int_0^1 d\lambda c(\mathbf{r}, \mathbf{r}'; [\rho_R + \lambda \Delta\rho]) \Delta\rho(\mathbf{r}') \right\} \quad (2.24)$$

Choosing  $\mu_R = \mu$  and treating the rhs in a manner similar to (2.15), one obtains

$$\frac{\rho(\mathbf{r})}{\rho_R} = \exp \int d\mathbf{r}' \left\{ c(|\mathbf{r} - \mathbf{r}'|; \rho_R) + \frac{1}{2} (\rho - \rho_R) \frac{\partial c(|\mathbf{r} - \mathbf{r}'|; \rho_R)}{\partial \rho_R} + \dots \right\} \Delta\rho(\mathbf{r}') \quad (2.25)$$

which, given  $\rho_R$  and the dcf of the liquid, is a nonlinear integral equation for  $\rho(\mathbf{r})$  whose solution defines the equilibrium density  $\rho_0(\mathbf{r})$  corresponding to the approximate free energy function.

(b) A second procedure<sup>(23–33,35)</sup> consists in parametrizing the local density  $\rho(\mathbf{r}) = \rho_\alpha(\mathbf{r})$  in terms of a family of test functions  $\{\rho_\alpha(\mathbf{r})\}$  and deter-

mining the member of the family that minimizes the approximate free energy functional  $F[\rho]$  at constant average density  $\rho_\alpha$  [see Eq. (2.6)]:

$$\left. \frac{\partial F[\rho_\alpha]}{\partial \alpha} \right|_{\rho_\alpha = \rho} = 0; \quad \left. \frac{\partial^2 F[\rho_\alpha]}{\partial \alpha^2} \right|_{\rho_\alpha = \rho} > 0 \quad (2.26)$$

The solution of (2.26), say  $\alpha = \alpha_0$ , defines then the equilibrium density  $\rho_0(\mathbf{r}) = \rho_{\alpha_0}(\mathbf{r})$  corresponding to the approximate free energy functional.

(c) In practice, the approximations specific to the free energy functional and those specific to the Euler–Lagrange minimization [(a) or (b)] have been combined in various ways, making a direct comparison of the different results quite difficult. The main drawback of the minimization based on (b) is that one has to choose *a priori* the family of test functions embedding the equilibrium density. In practice one uses for  $\rho_\alpha(\mathbf{r})$  a sum of identical Gaussians centered on the lattice sites with  $\alpha$  determined by their widths. This choice, which goes back at least to a suggestion of Brout,<sup>(2)</sup> has the advantages that (1) the approximate free energy functional based on (2.21) can be computed analytically, (2) only one number (the equilibrium width  $\alpha_0$ ) has to be determined, (3) a single nonlinear algebraic equation (2.26) has to be solved, and (4) one can explicitly distinguish between the minima and the maxima of the free energy, whereas the Euler–Lagrange equation (2.23) determines only the extrema.

(d) The advantage of the procedure based on (a) is that no *a priori* assumption about  $\rho(\mathbf{r})$  is required. Its drawback, however (besides the lack of convergence of the  $\lambda$ -expansion already discussed in connection with the approximate free energy), is that the nonlinear integral equation (2.25) is difficult to solve. The same type of integral equation also appears in the Kirkwood–Monroe theory,<sup>(2,3,7,9)</sup> and it is usually solved by Fourier expanding the local density as

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}} \rho_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (2.27)$$

where the sum extends over all the reciprocal lattice vectors of the given solid. Substituting (2.27) into (2.25) yields

$$\begin{aligned} \sum_{\mathbf{k}} \rho_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}) = \rho_{\mathbf{R}} \exp \left\{ (\rho - \rho_{\mathbf{R}}) c_{\mathbf{k}=0}(\rho_{\mathbf{R}}) \right. \\ \left. + \sum_{\mathbf{k}' \neq 0} \rho_{\mathbf{k}'} c_{\mathbf{k}'}(\rho_{\mathbf{R}}) \exp(i\mathbf{k}' \cdot \mathbf{r}) \right\} \end{aligned} \quad (2.28)$$

where  $c_{\mathbf{k}}(\rho)$  are the Fourier components of  $c(|\mathbf{r}|; \rho)$ . At first glance the idea is appealing, because the Fourier transform is well suited to treat the con-

volution products appearing in Eq. (2.25). It is clear, however, that in the solid  $\rho(\mathbf{r})$  is strongly peaked around the lattice sites and such a behavior can be reproduced in Fourier space only by retaining a very large number of Fourier components, which is quite impractical. Furthermore, the highly nonlinear character of Eq. (2.25) is such that even after projecting the equation on a given Fourier mode, the resulting equation relates this mode nonlinearly not only to itself, but also to the infinite set of all the remaining Fourier modes [see, e.g., (2.28)]. Therefore, in practice, a truncation procedure of some sort has to be used and, in principle, one should then study the convergence of the solution of the truncated equation toward the solution of the original equation (2.25). This is not an easy problem and has not been considered in the literature. The first authors<sup>(7,13)</sup> simply used a one-term (called density wave) approximation to the series (2.27), retaining only the term with the smallest reciprocal lattice vector. Starting with Ramakrishnan and Yussouff<sup>(12)</sup> several authors<sup>(14,22)</sup> used a two-term approximation to (2.27) with the wavevectors chosen such as to correspond approximately to the first two maxima of the static structure factor of the liquid. Starting with Haymet,<sup>(17)</sup> several dozens of Fourier modes have been retained,<sup>(15-21,34)</sup> but the convergence of the solution (2.27) was not analyzed (only the weaker condition  $\sum_{\mathbf{k}} c_{\mathbf{k}} |\rho_{\mathbf{k}}|^2$  has been considered, but here the convergence is monitored by  $c_{\mathbf{k}}$ ).

As pointed out before,<sup>(25-29)</sup> the convergence is slow and the truncated Fourier series (2.27) exhibit regions with large negative values, whereas both the exact (2.24) and approximate equation (2.25) guarantee that  $\rho(\mathbf{r})$  should remain nonnegative. The important point here (not always correctly appreciated in the literature<sup>(19,20)</sup>) is not so much that these values are negative (and hence nonphysical), but that their very presence indicates that convergence has not been reached yet. The proposal by Haymet and Oxtoby<sup>(15-21)</sup> to add to the truncated Fourier series of  $\rho(\mathbf{r})$  its remainder computed from (2.25) with a truncated Fourier series for the dcf restores the positivity of  $\rho(\mathbf{r})$  [it also modifies the original Eq. (2.25), since the Fourier inverse of the truncated dcf does not restore the original  $c(|\mathbf{r}|)$ ], but it tells us nothing more about the convergence of the underlying truncation scheme. All in all, Eq. (2.25) remains a difficult nonlinear integral equation, which in my opinion deserves a more thorough study than has hitherto been the case.

(e) A final point concerns the fact that several authors<sup>(12-22)</sup> have considered that the reference state  $(\rho_{\mathbf{R}}, \mu_{\mathbf{R}})$  in (2.24) is the liquid  $(\rho_{\mathbf{R}} = \rho_{\mathbf{L}}, \mu_{\mathbf{R}} = \mu_{\mathbf{L}})$  of the same chemical potential as the solid  $(\mu_{\mathbf{L}} = \mu_{\mathbf{S}})$  and have solved (2.25) directly together with the remaining coexistence condition,  $p_{\mathbf{L}} = p_{\mathbf{S}}$ . The chemical potential is thus treated exactly and not on the same approximate level as the free energy (or the pressure) and the Euler-

Langrange equation. The chemical potential is thus no longer given as the density derivative,  $\mu = (\partial/\partial\rho) f[\rho]$ , of the corresponding *approximate* free energy.

### 3. THE PHYSICAL INTERPRETATION OF THE (HARD SPHERE) FREEZING MECHANISM

The density functional theory of freezing, besides yielding quantitative information<sup>(12-35)</sup> about freezing that can be checked against computer simulations and laboratory experiments, also yields physical insight into the mechanism by which the solid is ultimately preferred over the liquid and by which freezing occurs. Since this topic has not been much considered in the literature,<sup>(26)</sup> I will illustrate it here in some detail. The difference  $\Delta f = f[\rho_S] - f[\rho_L]$  in free energy per unit volume between the solid and the liquid at constant average density ( $\rho_S = \rho_L = \rho$ ) can be written, using Eqs. (2.7)–(2.9) and the approximate free energy based on (2.21), as

$$\beta \Delta f = \frac{1}{V} \int d\mathbf{r} \rho(\mathbf{r}) \ln \frac{\rho(\mathbf{r})}{\rho} - \frac{1}{2V} \int d\mathbf{r} \int d\mathbf{r}' c(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}(\rho)) \Delta\rho(\mathbf{r}) \Delta\rho(\mathbf{r}') \quad (3.1)$$

The rhs of (3.1) indicates a competition between the purely configurational contribution originating from the ideal part of the free energy (first term) and a correlational contribution originating from the excess free energy [second term in the rhs of (3.1)]. Recalling that  $\Delta f = \Delta u - T\Delta s$ , where  $u$  and  $s$  are, respectively the internal energy and the entropy per unit volume, one can write the purely configurational term as

$$\Delta s_{\text{conf}} = -k_B \left[ \int \frac{d\mathbf{r}}{V} \rho(\mathbf{r}) \ln \rho(\mathbf{r}) - \rho \ln \rho \right] \quad (3.2)$$

i.e., as the difference in configurational entropy  $s_{\text{conf}}$  between the solid and the liquid. The remainder can then be identified with the change  $\Delta\bar{u}$  in some effective internal energy  $\bar{u} = u - Ts_{\text{corr}}$ :

$$\Delta\bar{u} = \frac{1}{2V} \int d\mathbf{r} \int d\mathbf{r}' [\rho(\mathbf{r}) - \rho] V_{\text{eff}}(|\mathbf{r} - \mathbf{r}'|; \rho) [\rho(\mathbf{r}') - \rho] \quad (3.3)$$

written here in terms of an effective, density-dependent, potential:

$$V_{\text{eff}}(|\mathbf{r}|; \rho) \equiv -k_B T c(|\mathbf{r}|; \bar{\rho}(\rho)) \quad (3.4)$$

so that  $\Delta f = \Delta \bar{u} - T \Delta s_{\text{conf}}$ . The effective internal energy  $\bar{u}$  is a superposition of the true internal energy  $u$  and of the correlational contribution  $s_{\text{corr}}$  to the entropy  $s$ . Both contributions,  $u$  and  $s_{\text{corr}}$ , originate from the interaction part of the free energy and cannot be further separated except in special cases. For instance, in the case of hard spheres there is no internal energy ( $u=0$ ) and  $\bar{u} = -Ts_{\text{corr}}$ . The hard sphere freezing can hence be described as a competition between two forms of entropy, the configurational entropy  $s_{\text{conf}}$  and the correlational entropy  $s_{\text{corr}}$ . The hard sphere freezing can, however, also be described in terms of an effective internal energy  $\bar{u} = -Ts_{\text{corr}}$  resulting from the effective interaction potential defined by (3.4). This clearly indicates that (once rephrased in terms of the effective internal energy  $\bar{u}$ ) there is no fundamental difference between the freezing of hard spheres ( $u=0$ ) and of more general systems ( $u \neq 0$ ).

For the solid to become the thermodynamically stable state, i.e., at constant average density the state of lowest free energy, the free energy difference  $\Delta f$  has to become negative. The configurational entropy of the liquid is always larger than that of the ordered solid,  $\Delta s_{\text{conf}} < 0$ ; this term increases  $\Delta f$  and is opposed to freezing. Hence, the lowering of  $\Delta f$  has to be produced by a lowering of the effective internal energy  $\bar{u}$ . If the solid is the state of lower effective internal energy,  $\Delta \bar{u} < 0$ , it may be possible to reach a situation where  $\Delta f < 0$ . In the hard sphere case the solid can then be interpreted as the state of highest correlational entropy. To understand how this comes about, it is useful to interpret (3.3) as the "electrostatic energy" of a "charge" density  $\rho(\mathbf{r}) - \rho$  interacting via the effective potential (3.4). Around the lattice sites [maxima of  $\rho(\mathbf{r})$ ] the effective charge density is positive [ $\rho(\mathbf{r}) \gg \rho$ ], while it is negative at the interstitials [minima of  $\rho(\mathbf{r})$ ;  $\rho(\mathbf{r}) \ll \rho$ ]. The effective potential of (3.4) is largely repulsive, with a range of the order of the true interaction potential (for instance, within the Percus-Yevick approximation for hard spheres  $V_{\text{eff}}$  is always purely repulsive with a range strictly equal to the hard sphere diameter). Since the distance between the lattice sites (or between the interstitials) is always greater than the range of the (effective) potential, the major contribution to (3.3) comes from the interaction between a lattice site and a nearby interstitial, i.e., between regions of opposite effective charge density. These regions tend to attract each other contracting the solid and facilitating particle localization. The resulting contributions to (3.3) are negative and yield  $\Delta \bar{u} < 0$ . The overall magnitude of this localization effect increases rapidly with the average density  $\rho$  [e.g.,  $-c(r=0; \rho)$  increases with the density roughly as the inverse compressibility] and above a threshold density the decrease of  $\bar{u}$  exceeds the decrease of  $s_{\text{conf}}$  and the solid becomes the stable phase ( $\Delta f < 0$ ). As the density is further increased toward the density of crystal close packing, the positive contributions to (3.3) coming from the

repulsive interaction between two lattice sites (or two interstitials), which at low density was outside the interaction range, returns now within the interaction range (for hard spheres this occurs abruptly at the close-packing density) and at very high density competes with the almost equally large attractive energy, yielding finally an upper density limit above which no solid can exist.

The details of the order-disorder competition between the configurational entropy of the solid and the liquid and of the competition between the repulsive and attractive contributions to the effective internal energy will depend on the details of the solid structure and of the interaction potential, but the overall picture of the resulting freezing mechanism as given above is fairly universal.

#### 4. CONCLUSIONS

I have reviewed the historical background underlying the recent progress toward a statistical mechanical theory of freezing based on the free energy density functional theory of nonuniform systems viewing the solid as a strongly nonuniform liquid. Most of the controversial and open questions have been discussed, while the physical freezing mechanism as viewed from this theory has been described in detail. For the particular case of the hard spheres it has been shown how freezing results from the competition between the configurational entropy favoring disorder and the correlational entropy favoring localization.

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