

The freezing of hard spheres The density functional theory revisited

by M. BAUS† and J. L. COLOT

Faculté des Sciences‡, C.P. 231, Université Libre de Bruxelles,
B-1050 Brussels, Belgium

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We have analysed the recent theories of freezing and found that all results obtained hitherto are biased numerically by the early truncation of slowly converging series. As a result the local density of the solid is shown to become very *negative* in the interstitial regions. Therefore we have reconsidered the theory of freezing starting from formally *exact* equations, making three *physical* approximations and testing all numerical methods for the case of the freezing of hard spheres. A fluid-solid transition is found which is in fair agreement with the known computer experiments.

1. INTRODUCTION

The first-principles description of the freezing-melting transition is one of the most difficult problems of statistical mechanics. In theoretical studies one can conveniently avoid the difficulties related to the possible appearance of metastable glass phases by neglecting all kinetic (nonequilibrium) aspects of the phase transition. Within such an equilibrium context there still remains the problem that, as in any first-order phase transition, the two bulk phases are separated by a thin but complicated interfacial region. Here we will, as usual, simplify the problem of freezing further by considering only the transition between *bulk* phases, i.e. by establishing the conditions under which a uniform bulk liquid can coexist in equilibrium with a periodic bulk solid. Even so this problem of 'bulk phase transitions' has been challenging statistical mechanics for several decades.

Kirkwood and Monroe [1] were the first to think that phase transitions could be studied from the BBGKY hierarchy. Since, many similar ideas have been tried out but, mostly, unsuccessfully. Recently, Ramakrishnan and Yussouff [2] and Ryzhov and Tareyeva [3], have proposed a new theory which is, essentially, a reformulation of the original theory of [1] in terms of the direct correlation function instead of the pair potential and the pair correlation function. This then allows one to take better advantage of the progress made by the theory of liquids during the last decades. This modern version of the theory has been applied by Tosi *et al.* [4], Haymet *et al.* [5] and Rice *et al.* [6] to the freezing of a large variety of systems ranging from the hard sphere fluid, the one component plasma,

† Chercheur Qualifié du F.N.R.S.

‡ Association Euratom-Etat Belge

the Lennard-Jones liquid, molten salts, superionic conductors to various two-dimensional systems of charged and neutral particles. In each case good agreement with the available experimental or simulation data has been announced.

Recently, one of us started a series of theoretical investigations [7] directed towards a better understanding of this impressive series of results. We have now completed this study with a number of numerical investigations. In §2 we reconsider the theoretical background. Using the density functional theory [8] and the results of Saam and Ebner [9] we present a set of *exact* equations for the phase transition problem. This improves the earlier presentations [2-7] which introduce approximations at an early stage. In §3 we question two of these approximations. The expansion of the solid around the liquid phase, which was suspected in [7(c)] to be at the basis of the failure [10] of the Kirkwood-Monroe theory [1], is shown to remain a bad approximation also within the present theory. Most dramatic however, is the use of a truncated Fourier series representation of the crystal density. This is shown to lead to strongly negative densities. Notwithstanding the announced experimental agreement, all previous results [1-7] appear to be biased by severe convergence problems. In order to resolve these difficulties a new proposal is formulated and worked out in §4 for the case of the freezing of hard spheres. Our conclusions are contained in the final §5.

2. EXACT DENSITY FUNCTIONAL THEORY OF FREEZING

The theory of non-uniform systems can be most easily formulated in terms of the density functional language [8]. Throughout we consider a system of particles of constant volume V and constant temperature T . The system is put into an external field, $\phi_{\text{ext}}(\mathbf{r})$, which couples to the local number density. According to the problem at hand this external field may play several roles. It may simulate the walls of the container or any substrates present allowing hereby a proper confinement of the system in the given volume. It may also segregate the different phases leading to the appearance of a well localized interfacial region. In the following we will be interested in the phase transition between two bulk phases, neglecting hereby the influence of the phase boundaries and of the container boundaries. In this case the external field plays the role of a symmetry breaking field, i.e. a tool to select the proper solution of the nonlinear equations. It will be understood moreover that, at least in the thermodynamic limit of a large system, the contribution of this external field to the thermodynamics may be allowed to vanish at the end of the calculations.

2.1. Thermodynamics

The total Helmholtz free energy, $A = F + F_{\text{ext}}$, is the sum of the intrinsic free energy F and a contribution due to the external field, $F_{\text{ext}} = \int d\mathbf{r} \rho(\mathbf{r}) \phi_{\text{ext}}(\mathbf{r})$, both of which are functionals of the average local number density, $\rho(\mathbf{r})$, a fact which we denote by a square bracket, e.g. $A = A[\rho]$. For given V , T and $\phi_{\text{ext}}(\mathbf{r})$ the equilibrium density $\rho(\mathbf{r})$ can then be found by extremizing A

$$\delta A \equiv \int_V d\mathbf{r} \frac{\delta A[\rho]}{\delta \rho(\mathbf{r})} \delta \rho(\mathbf{r}) = 0. \quad (2.1)$$

The solution of (2.1) requires

$$\frac{\delta A[\rho]}{\delta \rho(\mathbf{r})} \equiv \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} + \phi_{\text{ext}}(\mathbf{r}) = \mu \quad (2.2)$$

to be a constant μ which, as will soon become clear, can be identified with the chemical potential. Equation (2.2) will provide a solution of (2.1) whenever

$$\int_V d\mathbf{r} \delta \rho(\mathbf{r}) = 0, \quad (2.3)$$

i.e. at constant average density ρ

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

Splitting the free energy, $F = F_{\text{id}} + F_{\text{ex}}$, into an ideal and an excess contribution

$$\beta F_{\text{id}}[\rho] = \int_V d\mathbf{r} \rho(\mathbf{r}) \{ \ln (\Lambda^3 \rho(\mathbf{r})) - 1 \}, \quad (2.5)$$

$$\frac{\beta \delta F_{\text{ex}}[\rho]}{\delta \rho(\mathbf{r})} = -c_1(\mathbf{r}; [\rho]), \quad (2.6)$$

where $\beta = 1/k_B T$, $\Lambda = h/(2\pi m k_B T)^{1/2}$, for particles of mass m , equation (2.2) can be integrated as

$$\rho(\mathbf{r}) = \frac{\exp [\beta(\mu - \phi_{\text{ext}}(\mathbf{r})) + c_1(\mathbf{r}; [\rho])]}{\Lambda^3} \quad (2.7)$$

in terms of the one-particle direct correlation function, $c_1(\mathbf{r}; [\rho])$, defined by (2.6). Equation (2.7) clearly identifies μ with the chemical potential while any arbitrariness in $\phi_{\text{ext}}(\mathbf{r})$ can be lifted through the normalization condition (2.4)

$$\rho = \frac{\exp(\beta\mu)}{\Lambda^3} \int_V d\mathbf{r} \exp [c_1(\mathbf{r}) - \beta\phi_{\text{ext}}(\mathbf{r})]. \quad (2.8)$$

The restriction (2.3) can also be lifted when using μ as a Lagrange multiplier and switching from the Helmholtz free energy A to the grand potential Ω

$$\Omega = A - \mu \int_V d\mathbf{r} \rho(\mathbf{r}). \quad (2.9)$$

When equation (2.2) is used to eliminate $\phi_{\text{ext}}(\mathbf{r})$ in favour of $\rho(\mathbf{r})$, Ω becomes a functional of the local density alone which is usually designed then as the 'density functional', $\Omega = \Omega[\rho]$. At fixed T , V , and $\phi_{\text{ext}}(\mathbf{r})$ it has a local extremum at the local equilibrium density

$$\frac{\delta \Omega[\rho]}{\delta \rho(\mathbf{r})} = 0 \quad (2.10)$$

as follows from (2.2) and (2.9). The Gibbs–Duhem relation, $\Omega = -pV$, relating Ω to the pressure p , allows then easy access to the thermodynamics. To this end we introduce the densities $f = F/V$, $f_{\text{ext}} = F_{\text{ext}}/V$, $\omega = \Omega/V$ etc., and rewrite $p = -\omega$ using (2.4) and (2.9) as

$$p = \mu\rho - f_{\text{id}} - f_{\text{ex}} - f_{\text{ext}} \quad (2.11)$$

eliminating $\mu\rho - f_{\text{ext}}$ with the aid of (2.7) and using (2.5) we obtain the final relations

$$\beta p = -\frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) \{c_1(\mathbf{r}; [\rho]) - 1\} - \beta f_{\text{ex}}[\rho], \quad (2.12)$$

$$\beta \rho \mu = \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) \{\ln(\Lambda^3 \rho(\mathbf{r})) - c_1(\mathbf{r}; [\rho])\} + \beta f_{\text{ext}}[\rho], \quad (2.13)$$

which express the pressure p and the chemical potential μ as functionals of the local density $\rho(\mathbf{r})$. It will be assumed that the right-hand sides of (2.12) and (2.13) are well behaved in the thermodynamic limit and that at the end of the calculations we can drop f_{ext} from (2.13). This is a much more realistic assumption than simply dropping $\phi_{\text{ext}}(\mathbf{r})$ in, say equation (2.2), since it allows $\phi_{\text{ext}}(\mathbf{r})$ to remain present as a trace which can germinate the proper (say crystal) phase while its contribution to the thermodynamics (2.13) becomes negligible provided

$$f_{\text{ext}} = \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) \phi_{\text{ext}}(\mathbf{r}) \quad (2.14)$$

vanishes when V becomes large.

2.2. Functional integration

We now re-express the right-hand side of equations (2.12) and (2.13) in terms of $\rho(\mathbf{r})$ and the (two-body) direct correlation function:

$$c_2(\mathbf{r}, \mathbf{r}'; [\rho]) = \frac{\delta c_1(\mathbf{r}; [\rho])}{\delta \rho(\mathbf{r}')}, \quad (2.15)$$

which, because of its weak sensitivity to the interaction potential, is known to yield a convenient starting point for approximation schemes. To this end we will functionally integrate equation (2.6) and (2.15). As first observed by Saam and Ebner [9], the uniqueness of $F_{\text{ex}}[\rho]$ guarantees that the result of this integration will depend only on the end-point phases and not on the path going from the initial to the final phase. We label the path in density function space by the parameter λ , $\rho = \rho(\mathbf{r}; \lambda)$, and for simplicity denote the value of say $F[\rho]$ at $\rho = \rho(\mathbf{r}; \lambda)$ simply as $F[\lambda]$. Functionally integrating equations (2.6) and (2.15) between an initial phase $\rho_0(\mathbf{r}) \equiv \rho(\mathbf{r}; \lambda = 0)$ and a final phase $\rho(\mathbf{r}) \equiv \rho(\mathbf{r}; \lambda = 1)$ we obtain

$$-\beta \{F_{\text{ex}}[\rho] - F_{\text{ex}}[\rho_0]\} = \int_V d\mathbf{r} \int_0^1 d\lambda c_1(\mathbf{r}; [\lambda]) \rho'(\mathbf{r}; \lambda), \quad (2.16)$$

$$c_1(\mathbf{r}; [\rho]) - c_1(\mathbf{r}; [\rho_0]) = \int_V d\mathbf{r}' \int_0^1 d\lambda c_2(\mathbf{r}, \mathbf{r}'; [\lambda]) \rho'(\mathbf{r}'; \lambda), \quad (2.17)$$

where $\rho'(\mathbf{r}; \lambda) \equiv [d\rho(\mathbf{r}; \lambda)/d\lambda]$. The basic equations can now be re-expressed entirely in terms of $c_2(\mathbf{r}, \mathbf{r}'; [\lambda])$ and $\rho(\mathbf{r})$. Taking $\rho_0(\mathbf{r}) = 0$, in which case the excess properties $F_{\text{ex}}[\rho_0]$ and $c_1(\mathbf{r}; [\rho_0])$ vanish, we obtain, using (2.16) and (2.17)

$$\beta f[\rho] = \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) \{\ln(\Lambda^3 \rho(\mathbf{r})) - 1\} - \frac{1}{V} \int_V d\mathbf{r} \int_V d\mathbf{r}' \int_0^1 d\lambda \int_0^\lambda d\lambda' \times c_2(\mathbf{r}, \mathbf{r}'; [\lambda']) \rho'(\mathbf{r}'; \lambda') \rho'(\mathbf{r}; \lambda), \quad (2.18)$$

$$\beta p[\rho] = \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) - \frac{1}{V} \int_V d\mathbf{r} \int_V d\mathbf{r}' \int_0^1 d\lambda \times c_2(\mathbf{r}, \mathbf{r}'; [\lambda]) \rho'(\mathbf{r}'; \lambda) \rho(\mathbf{r}; \lambda), \quad (2.19)$$

$$\beta \rho \mu[\rho] = \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) \ln (\Lambda^3 \rho(\mathbf{r})) - \frac{1}{V} \int_V d\mathbf{r} \int_V d\mathbf{r}' \int_0^1 d\lambda c_2(\mathbf{r}, \mathbf{r}'; [\lambda]) \times \rho'(\mathbf{r}'; \lambda) \rho(\mathbf{r}) + \frac{\beta}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) \phi_{\text{ext}}(\mathbf{r}) \quad (2.20)$$

for the thermodynamics (free energy density f , pressure p and chemical potential μ) and

$$\rho(\mathbf{r}) = \frac{1}{\Lambda^3} \exp \left\{ \beta(\mu - \phi_{\text{ext}}(\mathbf{r})) + \int_V d\mathbf{r}' \int_0^1 d\lambda c_2(\mathbf{r}, \mathbf{r}'; [\lambda]) \rho'(\mathbf{r}'; \lambda) \right\} \quad (2.21)$$

for the structure. Equations (2.18)–(2.20) generalize some wellknown relations to non-uniform systems. Indeed for a uniform system, $\rho(\mathbf{r}) \equiv \rho$, $c_2(\mathbf{r}, \mathbf{r}'; [\rho]) \equiv c_2(|\mathbf{r} - \mathbf{r}'|; \rho)$, $\phi_{\text{ext}}(\mathbf{r}) \equiv 0$, and taking a linear path, $\rho(\mathbf{r}; \lambda) = \lambda\rho$, equations (2.18)–(2.20) become

$$\beta f = \rho(\ln (\Lambda^3 \rho) - 1) - \int d\mathbf{r} \int_0^\rho d\rho' \int_0^{\rho'} d\rho'' c_2(|\mathbf{r}|; \rho''), \quad (2.18')$$

$$\beta p = \rho - \int d\mathbf{r} \int_0^\rho d\rho' \rho' c_2(|\mathbf{r}|; \rho'), \quad (2.19')$$

$$\beta \mu = \ln (\Lambda^3 \rho) - \int d\mathbf{r} \int_0^\rho d\rho' c_2(|\mathbf{r}|; \rho'), \quad (2.20')$$

which follow from the well-known relations

$$\beta \rho \frac{\partial \mu}{\partial \rho} = \beta \frac{\partial p}{\partial \rho} = 1 - \rho \int d\mathbf{r} \cdot c_2(|\mathbf{r}|; \rho)$$

and $f = -p + \rho\mu$.

2.3. Two-phase coexistence

The equations governing the bulk phase transition problem can now be easily formulated. Consider the conditions under which a bulk solid of density $\rho(\mathbf{r}) \equiv \rho(\mathbf{r}; \lambda = 1)$ can coexist in equilibrium with a uniform bulk liquid of density $\rho_0 \equiv \rho(\mathbf{r}; \lambda = 0) \neq 0$. In order to simplify the equations we take $\phi_0(\mathbf{r}) = 0$ and use a linear path

$$\rho(\mathbf{r}; \lambda) = \rho_0 + \lambda(\rho(\mathbf{r}) - \rho_0); \quad 0 \leq \lambda \leq 1, \quad (2.22)$$

$$\rho'(\mathbf{r}; \lambda) = \rho(\mathbf{r}) - \rho_0 \equiv \Delta\rho(\mathbf{r}), \quad (2.23)$$

going from the initial liquid ($\lambda = 0$) to the final solid ($\lambda = 1$) phase. The first coexistence condition requires the two phases to be in *thermal* equilibrium, i.e. $\Delta T \equiv T - T_0 = 0$. This condition is automatically satisfied since in the above the temperature T has been kept constant. Next, the two phases have to be in *mechanical* equilibrium, i.e. $\Delta p \equiv p[\rho] - p[\rho_0] = 0$. From (2.19), we have, using (2.22)

and (2.23)

$$\beta \Delta p = \frac{1}{V} \int_V d\mathbf{r} \left(1 - \rho_0 \int d\mathbf{r}' \bar{c}(\mathbf{r}', \mathbf{r}) \right) \Delta \rho(\mathbf{r}) - \frac{1}{2V} \int_V d\mathbf{r} \int_V d\mathbf{r}' \{ 2\bar{c}(\mathbf{r}, \mathbf{r}') - \bar{c}(\mathbf{r}, \mathbf{r}') \} \Delta \rho(\mathbf{r}) \Delta \rho(\mathbf{r}'), \quad (2.24)$$

where we have introduced the shorthand notations

$$\bar{c}(\mathbf{r}, \mathbf{r}') = \int_0^1 d\lambda c_2(\mathbf{r}, \mathbf{r}'; [\lambda]), \quad (2.25)$$

$$\begin{aligned} \bar{c}(\mathbf{r}, \mathbf{r}') &= 2 \int_0^1 d\lambda \int_0^\lambda d\lambda' c_2(\mathbf{r}, \mathbf{r}'; [\lambda']) \\ &= 2 \int_0^1 d\lambda (1 - \lambda) c_2(\mathbf{r}, \mathbf{r}'; [\lambda]), \end{aligned} \quad (2.26)$$

which can be interpreted as 'averages' of the direct correlation function c_2 over the path (2.22). Finally, the two phases have to be in *compositional* equilibrium, i.e. $\Delta\mu \equiv \mu[\rho] - \mu[\rho_0] = 0$. From (2.20)–(2.23) we have

$$\beta \rho \Delta\mu = \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) \ln(\rho(\mathbf{r})/\rho_0) - \frac{1}{V} \int_V d\mathbf{r} \int_V d\mathbf{r}' \rho(\mathbf{r}) \bar{c}(\mathbf{r}, \mathbf{r}') \Delta \rho(\mathbf{r}') + \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) \beta \phi_{\text{ext}}(\mathbf{r}). \quad (2.27)$$

At phase-coexistence, $\Delta T = \Delta p = \Delta\mu = 0$, we have eliminating for simplicity $\bar{c}(\mathbf{r}, \mathbf{r}')$ from (2.24) with the aid of (2.27)

$$\begin{aligned} 0 = \beta \Delta p - \beta \rho \Delta\mu &= \frac{1}{V} \int_V d\mathbf{r} \Delta \rho(\mathbf{r}) - \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) \ln(\rho(\mathbf{r})/\rho_0) \\ &+ \frac{1}{2V} \int_V d\mathbf{r} \int_V d\mathbf{r}' \bar{c}(\mathbf{r}, \mathbf{r}') \Delta \rho(\mathbf{r}) \Delta \rho(\mathbf{r}') - \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) \beta \phi_{\text{ext}}(\mathbf{r}), \end{aligned} \quad (2.28)$$

$$\begin{aligned} 0 = \beta \rho \Delta\mu &= \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) \ln(\rho(\mathbf{r})/\rho_0) - \frac{1}{V} \int_V d\mathbf{r} \int_V d\mathbf{r}' \bar{c}(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}) \Delta \rho(\mathbf{r}') \\ &+ \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) \beta \phi_{\text{ext}}(\mathbf{r}), \end{aligned} \quad (2.29)$$

which are our two basic equations governing the bulk phase coexistence problem ($\Delta p = 0 = \Delta\mu$). For later reference we also quote the structural equation

$$\rho(\mathbf{r}) = \rho_0 \exp \left\{ \beta(\Delta\mu - \phi_{\text{ext}}(\mathbf{r})) + \int_V d\mathbf{r}' \bar{c}(\mathbf{r}, \mathbf{r}') \Delta \rho(\mathbf{r}') \right\}, \quad (2.30)$$

which results from eliminating Λ between the equation (2.21) for the liquid and the solid. Finally we have to stress that all the above equations, e.g. (2.18)–(2.21) and (2.28)–(2.30), are formally *exact* but involve the generally unknown quantities $\bar{c}(\mathbf{r}, \mathbf{r}')$ and $\bar{c}(\mathbf{r}, \mathbf{r}')$.

3. CRITIQUE OF PREVIOUS THEORIES

We have investigated the relation between the existing approximate theories of freezing and the exact results presented above. We have found many difficulties, mainly with respect to the numerical accuracy of the approximations used. Some of these are sufficiently severe as to bias completely the announced results. Below we sketch those points which are of general value and hence are not addressed to any author in particular.

From now on we will drop the contribution of the external field, $\phi_{\text{ext}}(\mathbf{r})$. As stated already above, it appears to us much more realistic to do this at the level of the thermodynamics by dropping f_{ext} (2.14) in (2.27) than by putting abruptly $\phi_{\text{ext}}(\mathbf{r})$ equal to zero in the structural equation (2.30) as done in the literature. Indeed, according to [7(b)] the latter procedure will immediately lead to so-called Wertheim singularities which may then lead to further numerical difficulties.

3.1. Expansion around the liquid phase

All modern theories of freezing [2-7] are based on expansions of the d.c.f. (direct correlation function) of the non-uniform solid phase around the coexisting uniform liquid phase. To show this we consider the Taylor expansion of $c_2(\mathbf{r}, \mathbf{r}'; \lambda)$ around $\lambda = 0$. Using (2.22) and (2.33), we obtain then for (2.25) and (2.26)

$$\begin{aligned}\bar{c}(\mathbf{r}, \mathbf{r}') &= \sum_{n=0}^{\infty} \frac{1}{(1+n)!} \int d\mathbf{r}_1 \dots d\mathbf{r}_n c_{2+n}(\mathbf{r}, \mathbf{r}', \mathbf{r}_1, \dots, \mathbf{r}_n; \rho_0) \Delta\rho(\mathbf{r}_1) \dots \Delta\rho(\mathbf{r}_n), \\ \bar{c}(\mathbf{r}, \mathbf{r}') &= \sum_{n=0}^{\infty} \frac{2}{(2+n)!} \int d\mathbf{r}_1 \dots d\mathbf{r}_n c_{2+n}(\mathbf{r}, \mathbf{r}', \mathbf{r}_1, \dots, \mathbf{r}_n; \rho_0) \Delta\rho(\mathbf{r}_1) \dots \Delta\rho(\mathbf{r}_n),\end{aligned}\tag{3.2}$$

where the $c_n(\mathbf{r}_1 \dots)$ denote the n -body d.c.f. defined as usual [7(a)] by successive functional differentiation of $F_{\text{ex}}[\rho]$. Substituting (3.1) and (3.2) into (2.24), (2.30) and truncating the expansion after a few terms we recover the equations used in all previous investigations (compare, e.g., [5(c), 7(a)]).

The idea of a liquid-based theory of freezing goes back to the classic theory of Kirkwood and Monroe [1]. As shown elsewhere [7(c)], their equation is a particular approximation equivalent to retaining only the first term in the right-hand side of (3.1) and (3.2) and neglecting *moreover* the density derivatives of the pair correlation function. As a result of the latter their approximation violates linear response theory, a fact which, it is argued in [7(c)], may well explain the bad results [10] obtained from the Kirkwood-Monroe theory. In the recent theories [2-7] one or two terms are retained in the right-hand side of (3.1) and (3.2). This certainly improves things with respect to linear response theory but is still very much open to criticism. Indeed, close to freezing density derivatives are usually extremely large. An idea of this can be obtained by studying the expansion (3.1) and (3.2) in the case of uniform fluids. If, for instance, we expand the inverse compressibility of a hard-sphere fluid evaluated at the density of the solid in a Taylor series around its value at the density of the coexisting fluid we obtain a series similar to (3.1) and (3.2) but which can be evaluated term by term from the Carnahan-Starling equation of state (see (4.6) below). One finds then that retaining one term in the Taylor expansion amounts roughly to retaining only 50

per cent of the sum (this corresponds to the fact that the compressibility nearly halves when going from the liquid to the solid) while the next term also represents only 50 per cent of the remainder pointing to a slow convergence of the expansion. Truncating the formal expansion of (3.1) and (3.2) at an early stage is thus bound to introduce large errors†.

In order to avoid this difficulty we return to the original expressions (2.25) and (2.26) and observe that what is needed are not the higher order d.c.f. of the liquid appearing in (3.1)–(3.2) but instead an approximate expression for the ordinary d.c.f., $c_2(\mathbf{r}, \mathbf{r}'; [\lambda])$, of a *solid* (of density $\rho(\mathbf{r}; \lambda) = \rho_0 + \lambda(\rho(\mathbf{r}) - \rho_0)$). We propose therefore to approximate the latter by some 'effective' *liquid* d.c.f., say $c_2(|\mathbf{r} - \mathbf{r}'|; \bar{\rho})$, since this is the only object about which sufficient information is available at present. This approximation is made explicit by considering an effective liquid which *scales* with the *solid*, i.e. such that the smallest r.l.v. (reciprocal lattice vector) of the solid coincides with the position of the main peak of the static structure factor of the effective liquid. The density of the effective liquid, $\bar{\rho}$, will then depend on the average density of the solid, $\rho(\lambda) = \rho_0 + \lambda(\rho - \rho_0)$, but also on the lattice structure

$$c_2(\mathbf{r}, \mathbf{r}'; [\rho(\mathbf{r}; \lambda)]) \simeq c_2^{(L)}(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}(\rho(\lambda))), \quad (3.3 a)$$

$$\rho(\lambda) = \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}; \lambda) \equiv \rho_0 + \lambda(\rho - \rho_0), \quad (3.3 b)$$

$$k_{\min}(\rho(\lambda)) = k^*(\bar{\rho}); \quad \bar{\rho} = \bar{\rho}(\rho(\lambda)), \quad (3.3 c)$$

where $k_{\min}(\rho)$ denotes the smallest r.l.v. of the solid of density ρ and $k^*(\bar{\rho})$ the position of the main peak of the structure factor of the effective liquid of density $\bar{\rho}$. Given $\rho(\lambda)$ and a lattice, equation (3.3 c) provides an implicit equation for $\bar{\rho}$, the density of the effective liquid. Combining (3.3) with (2.25) and (2.26) we see that all that we need to know is the density dependence of the d.c.f. of the effective liquid

$$\bar{c}(\mathbf{r}, \mathbf{r}') = \frac{1}{(\rho - \rho_0)} \int_{\rho_0}^{\rho} d\rho' c_2^{(L)}(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}(\rho')), \quad (3.4)$$

$$\bar{\bar{c}}(\mathbf{r}, \mathbf{r}') = \frac{2}{(\rho - \rho_0)^2} \int_{\rho_0}^{\rho} d\rho' (\rho - \rho') c_2^{(L)}(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}(\rho')), \quad (3.5)$$

which is easier than knowing the higher order d.c.f. of the coexisting liquid. Notice that the effective liquid which describes the solid need not be the same as the coexisting liquid although this may be the most realistic choice. The property by which the effective liquid models (at least in some average sense) the solid is the structural scaling property (3.3 c). The choice of this property is clearly not unique and instead of scaling the structure, $\bar{\rho} = \bar{\rho}(\rho)$ (3.3 c), one could simply scale the density $\bar{\rho} \equiv \rho$. Both choices will be considered below and designed as the effective liquid with scaled density or scaled structure. Scaling the density is clearly only a poor characterization of the solid but both choices retain nevertheless the major effects related to the rapid density changes incorporated in the density-averaged d.c.f., \bar{c} , $\bar{\bar{c}}$ of (3.4) and (3.5). Notice moreover that when the final

† Very recently it was shown (HENDERSON, J. R., 1984, *Molec. Phys.*, **52**, 1467) that for uniform systems a one-term approximation to (3.1) precludes the appearance of a liquid-vapour coexistence region.

phase is a fluid phase (only the density scaling survives in this case) the above approximation (3.4) and (3.5) becomes exact. This is never the case when the expansions (3.1) and (3.2) are truncated as done in the literature (notice also that the widely used one-term truncation of (3.1) and (3.2) corresponds to approximating $c_2^{(L)}(|\mathbf{r}|; \bar{\rho})$ in (3.4) and (3.5) by $c_2^{(L)}(|\mathbf{r}|; \rho_0)$).

3.2. Truncated Fourier expansion

Once $\bar{c}(\mathbf{r}, \mathbf{r}')$ and $\bar{z}(\mathbf{r}, \mathbf{r}')$ have been prescribed in terms of ρ_0 , $\rho(\mathbf{r})$ and say the liquid phase data embodied in $c_2(|\mathbf{r} - \mathbf{r}'|; \bar{\rho})$, the phase transition problem is reduced effectively to solving the non-linear integral equations (2.27)–(2.30) for $\rho(\mathbf{r})$ and ρ_0 . In the case of bulk freezing one has to look for lattice periodic solutions, $\rho(\mathbf{r}) \equiv \rho(\mathbf{r} + \mathbf{a})$, \mathbf{a} being any of the direct lattice vectors. This periodicity has been taken into account previously [1–7] by Fourier expanding $\rho(\mathbf{r})$ into plane waves. Making use of the restricted translational–rotational symmetry of the lattice one obtains then an infinite expansion of the type [7 (a)]

$$\rho(\mathbf{r}) = \rho \left(\sum_n \bar{a}_n \xi_n(\mathbf{r}) \right), \quad (3.6a)$$

$$= \rho_0 \left(1 + \sum_n a_n \xi_n(\mathbf{r}) \right), \quad (3.6b)$$

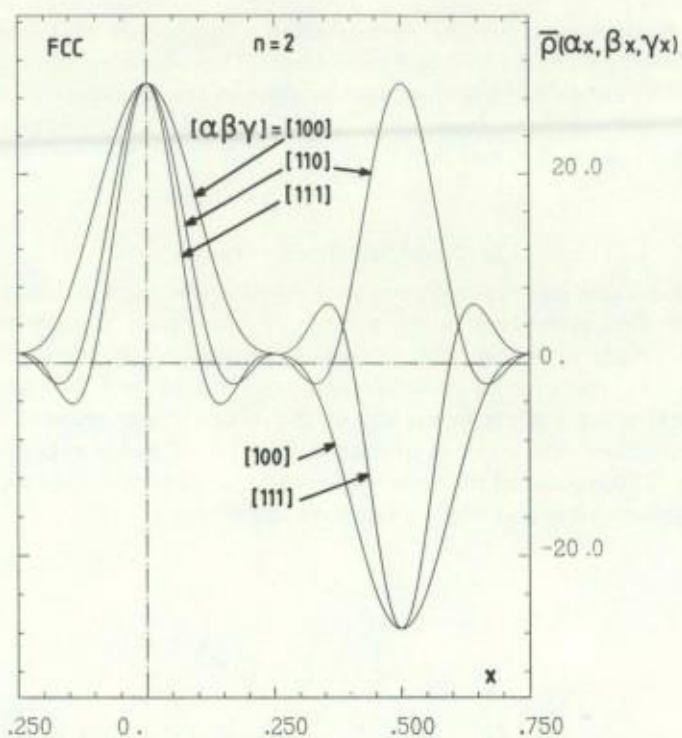
according to whether one expands the local density of the solid around its average density (ρ) or around the density of the liquid (ρ_0). Each term in the reciprocal lattice expansion (3.6) is usually referred to as a 'density wave' or an 'order parameter'. Such a density wave, say $\xi_n(\mathbf{r})$, is obtained by summing the plane waves, $\exp i \mathbf{k}_j \cdot \mathbf{r}$, over all r.l.v. \mathbf{k}_j of a given length, i.e. belonging to the same 'shell' in group theoretic language, the lengths being labelled by the index n (see [7 (a)] for details). The expansion amplitudes in (3.6) are simply related by $\bar{a}_n = a_n / (1 + a_0)$ for $n \neq 0$ and $\bar{a}_0 = 1$, a_0 being the fractional density change on freezing, $\rho = \rho_0(1 + a_0)$, where $n = 0$ corresponds to the trivial r.l.v. $\mathbf{k}_j = 0$, $\xi_0(\mathbf{r}) \equiv 1$.

The strategy followed in all previous investigations [1–7] consists in solving equation (2.30) (with $\Delta\mu = 0$, $\phi_{\text{ext}}(\mathbf{r}) = 0$ and the expansion of $\bar{c}(\mathbf{r}, \mathbf{r}')$ around its liquid phase value as discussed in §3.1) with the aid of (3.6). Since the $\xi_n(\mathbf{r})$ are orthogonal over the unit cell, equation (2.30) can be transformed into

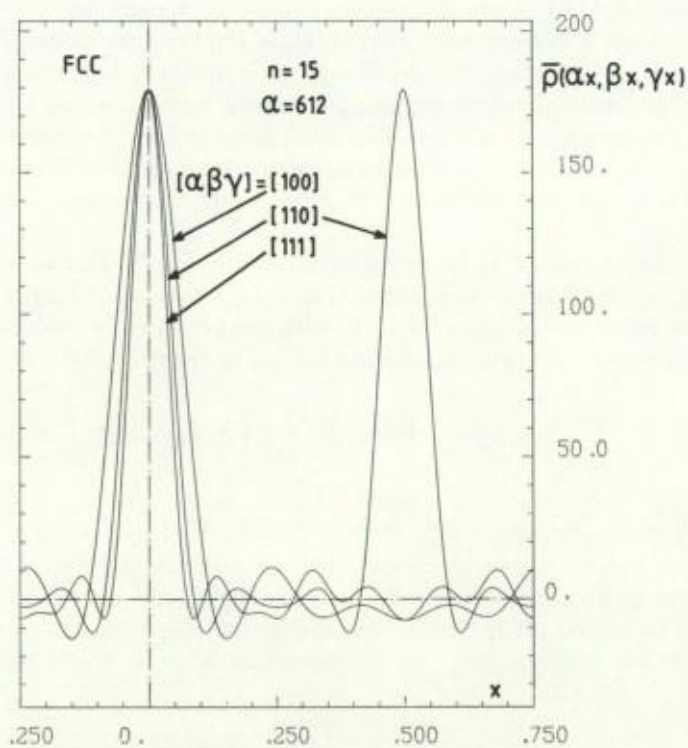
$$\delta_{n,0} + s_n a_n = \frac{1}{\Delta} \int_{\Delta} d\mathbf{r} \xi_n(\mathbf{r}) \exp \left(\sum_m a_m \bar{c}_m \xi_m(\mathbf{r}) \right), \quad (3.7)$$

where $s_n \equiv \xi_n(\mathbf{r} = 0)$ equals the number of r.l.v. in the n th star, Δ the volume of the unit cell and \bar{c}_n the value of the Fourier transform of $\rho_0 \bar{c}(|\mathbf{r} - \mathbf{r}'|)$ evaluated at a wave vector equal to any of the equivalent r.l.v. of the n th star. The integral in (3.7) can then be handled numerically for any given \bar{c}_n and equation (3.7) can then in principle be solved for the unknown amplitudes a_n for any given solid density ρ . The latter can then be fixed by the condition $\Delta p = 0$, which becomes, using (2.24),

$$0 = a_0(1 - \bar{c}_0) - \frac{1}{2} \sum_n s_n a_n^2 (2\bar{c}_n - \bar{c}_n) \quad (3.8)$$



(a)



(b)

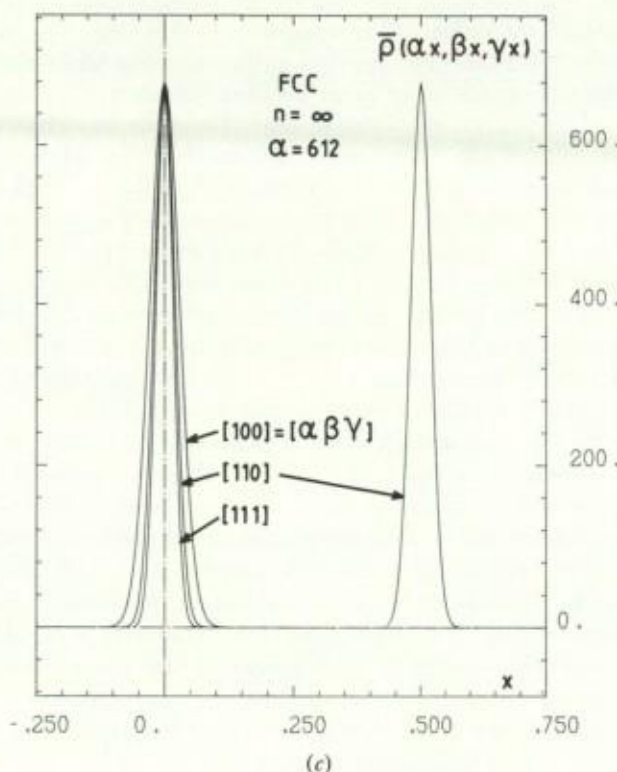


Figure 1. To illustrate the slow convergence of the Fourier series used in the literature [1-7] we have represented the normalized density, $\bar{\rho}(\mathbf{r}) \equiv \rho(\mathbf{r})/\rho$, in the direction of the three crystallographic axes ([100], [110], [111]) of a f.c.c. lattice as a function of the distance to the origin x . Case (a) corresponds to the two order parameter theory of [3 (d)] but similar results hold for [2 (b)] and [6 (a)]. The density is seen to become very negative. Case (b) corresponds to the fifteen order parameter theory of [5 (c)]. Practically the same results can be obtained by truncating equation (3.11 b) instead of (3.6 a) and using $\alpha = 612$. The density peaks become narrower, their height increases by an order of magnitude but there are still regions of negative density ($\bar{\rho} = -10$). Case (c) corresponds to the infinite series (3.11) for the same value of α as used in case (b). The negative values have disappeared but the height and width of the peaks have changed considerably indicating that even case (b) is still far from convergence. (Similar results hold also for the published b.c.c. data.)

or any form equivalent to (3.8). In practice one has however to truncate the infinite Fourier series in (3.6-8). In most investigations a 'two order parameter theory' has been used which corresponds to retaining three terms in the expansion (3.6) since the first term of (3.6) is essentially trivial ($n = 0$). The first order parameter corresponds always to the density wave generated by the smallest nonzero r.l.v. of the given lattice. This contribution is essential for giving the crystal its proper macroscopic periodicity. The second order parameter was then 'selected' on a fairly arbitrary basis omitting for instance r.l.v. of intermediate length. In [7 (a)] an attempt was made to justify this selection on the basis of a symmetry argument. The proof there was based on a moment expansion of the r.h.s. of (3.7). We have checked now this moment expansion by numerical integration and found that its convergence is too slow to make the results of [7 (a)]

reliable for values of the density corresponding to freezing. The reasons behind this order parameter selection remain thus rather obscure while the lack of sufficient convergence has, in the mean time, become the leitmotiv of our conclusions about all previous investigations. Very recently [4(c)] it was observed that some of the published results are not numerically stable since adding or deleting a particular term in the truncated series (3.6) made the solution of (3.7) and (3.8) to appear or disappear altogether. In order to illustrate the lack of convergence resulting from an early truncation of the Fourier series (3.6) we have plotted in figure 1 the density obtained from (3.6) by using the amplitudes \bar{a}_n taken from the literature. It is seen that in some of the interstitial regions the density takes on very large *negative* values (e.g. up to ten times the average density in the best cases!). This is clearly inconsistent with the original equation (2.30) which, as required by the physics, predicts a non-negative density. This difficulty can easily be traced back to the fact that in a solid phase $\rho(\mathbf{r})$ is highly structured and sharply peaked around the lattice sites. To reproduce this behaviour the number of terms which has to be retained in the Fourier series (3.6) is much larger than those retained in the literature. As a consequence the good agreement (which we have checked) of the remaining published freezing data with the experimental data should also be considered as spurious and is presumably due to a compensation of errors between the rough approximation of $\bar{c}(\mathbf{r}, \mathbf{r}')$ (expanded around the liquid) and of $\rho(\mathbf{r})$ (truncated Fourier series). A hint for the existence of these compensations can be found in the fact that when increasing the number of terms in (3.6) it became necessary to increase also the number of terms in (3.1) in order to recover the transition [5(c)].

3.3. Truncated direct lattice expansion

The periodicity of $\rho(\mathbf{r})$ in a solid phase can equally well be taken into account through a direct lattice expansion of the type

$$\rho(\mathbf{r}) = \rho \left(\frac{1}{N_1} \sum_j \varphi(\mathbf{r} - \mathbf{r}_j) \right), \quad (3.9)$$

where ρ is again the average density of the solid, N_1 the number of particles per unit cell while j labels the lattice sites located at $\{\mathbf{r}_j\}$. In (3.9) $\varphi(\mathbf{r} - \mathbf{r}_j)$ describes the density *peak* around the site \mathbf{r}_j . The periodicity is now taken care of by the sum over sites in (3.9) and the fact that for any direct lattice vector \mathbf{a} , $\mathbf{r}_j + \mathbf{a} = \mathbf{r}_{j'}$. The difficulty with the density peak representation (3.9) is that, contrary to the density waves $\xi_n(\mathbf{r})$, the various peak contributions are not orthogonal but instead may show considerable overlap. The advantage of (3.9) however is that, since $\varphi(\mathbf{r} - \mathbf{r}_j)$ is sharply peaked around $\mathbf{r} = \mathbf{r}_j$, the series (3.9) is term by term positive and rapidly converging. In a series of recent related studies [10-12] the use of (3.9) with a *Gaussian* peak function

$$\varphi(\mathbf{r} - \mathbf{r}_j) = \left(\frac{\alpha}{\pi} \right)^{3/2} \exp(-\alpha(\mathbf{x} - \mathbf{x}_j)^2) \quad (3.10)$$

has been advocated. Here α measures the width of the peaks and \mathbf{x}, \mathbf{x}_j are dimensionless coordinates $\mathbf{r} = a\mathbf{x}$, $\mathbf{r}_j = a\mathbf{x}_j$, a being the lattice spacing. The connection between the Gaussian density peak expansion (3.9) and (3.10) and the density

wave expansion (3.6) can easily be obtained from the following Poisson sum formula [13]

$$\rho(\mathbf{r})/\rho = \frac{1}{N_1} \sum_j \left(\frac{\alpha}{\pi}\right)^{3/2} \exp(-\alpha(\mathbf{x} - \mathbf{x}_j)^2), \quad (3.11 a)$$

$$= \sum_n \exp\left(-\frac{\pi^2}{\alpha} q_n^2\right) \xi_n(\mathbf{x}), \quad (3.11 b)$$

where q_n denotes the dimensionless wavenumber ($k_n = (2\pi/a)q_n$) of the n th star.

Comparing (3.11 b) and (3.6 a) we see that in the gaussian peak approximation we have

$$\bar{a}_n = \exp\left(-\frac{\pi^2}{\alpha} q_n^2\right) \quad (3.12)$$

a well-known result from harmonic lattice theory (see e.g. [2 (b)]). As observed previously [2 (b), 5 (c)] equation (3.12) appears to be very well obeyed by the numerical solutions of (3.7) and (3.8). For instance, the values of \bar{a}_n obtained in [5 (c)] correspond to (3.12) with $490 < \alpha < 630$ and the series (3.6 a) cannot be distinguished from the series (3.11 b) with $\alpha \simeq 612$ when both are truncated at a maximum value of $q_n \leq 6$ as used in [5 (c)]. As we show in figure 1, the full series (3.11 b) is however very different from this truncated series displaying once more the lack of convergence of the reciprocal lattice expansion as used in [5 (c)] and *a fortiori* in [1-7].

Finally we notice that the direct lattice expansion (3.9) and (3.10) is a very rapidly converging series. To illustrate this we consider the ideal part of the free energy density (2.18)

$$\beta f_{id} = \rho(\ln(\Lambda^3 \rho) - 1) + \rho G, \quad (3.13)$$

where, writing the normalized local density as $\bar{\rho}(\mathbf{r}) = \rho(\mathbf{r})/\rho$, we have separated f_{id} into a fluid term and a structural contribution G

$$G = \frac{1}{V} \int_V d\mathbf{r} \bar{\rho}(\mathbf{r}) \ln \bar{\rho}(\mathbf{r}), \quad (3.14)$$

which can be further evaluated with the aid of (3.11 a). The integral in (3.14) can be reduced to the unit cell and the result will depend on the lattice type and the degree of localisation as measured for instance by the width of the Gaussian peaks or the corresponding Lindemann ratio L

$$\langle(\Delta \mathbf{x})^2\rangle = \frac{3}{2\alpha}; \quad L = \frac{a}{d} \left(\frac{3}{2\alpha}\right)^{1/2}, \quad (3.15)$$

where a is the lattice spacing and d the nearest neighbour distance. As observed in [11-12], for well localized density distributions $\bar{\rho}(\mathbf{r})$, i.e. for large α values, there is little overlap between the different peaks of (3.11 a) and only the peaks inside the unit cell need to be taken into account in the \ln -term of (3.14). This immediately leads to the following approximate analytic expression for G :

$$G(\alpha) \simeq \frac{3}{2} \ln\left(\frac{\alpha}{\pi}\right) - \frac{3}{2} - \ln N_1. \quad (3.16)$$

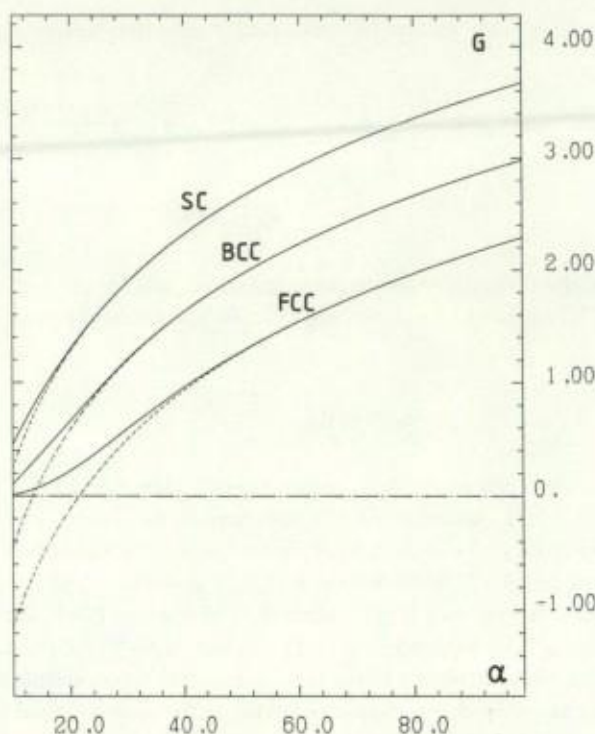


Figure 2. The structural contribution to the free energy density, $G(\alpha)$, as obtained by numerical evaluation of (3.14) (—) and from the analytic approximation (3.16) (---).

We have checked by direct numerical integration of (3.14) (using a 16-point gaussian-quadrature along each coordinate axes and testing the numerical stability with a 24-point method, this large amount of points being necessary because of the highly structured integrand of (3.14)) that the approximation (3.16) is very accurate for large α . In figure 2 we show the results for the cubic lattices (s.c., b.c.c., f.c.c.). The relative error involved in using the approximation (3.16) is less than 10^{-5} for $\alpha > 90$. On the other end, a similar evaluation of (3.14) with the aid of the reciprocal lattice expansion (3.11b) is almost impossible because of the inevitable negative values obtained for $\bar{\rho}(\mathbf{r})$ when the Fourier series (3.11b) is truncated.

4. THE FREEZING OF (PERCUS-YEVICK) HARD SPHERES INTO (GAUSSIAN) CUBIC LATTICES

As discussed in detail in §3, a large number of convergence problems are encountered in the existing theoretical studies of freezing. This makes it necessary to reconsider the question of what is precisely predicted by the theory of freezing when these convergence problems are avoided. Below we study this problem for the case of the freezing of hard spheres (HS). This system is chosen here not because the theory is in any way restricted to this system but because the hard sphere system provides the simplest possible testing ground for the freezing theories.

4.1. The experimental freezing of hard spheres

The fluid–solid transition of the hard sphere system has been thoroughly studied by computer simulations [14]. If we measure the density ρ of the hard spheres of diameter σ in terms of the packing fraction, $\eta = (\pi/6)\sigma^3\rho$, the system is known to freeze at $\eta_0 = 0.494$ into the f.c.c. lattice of density $\eta = 0.545$. This corresponds to a fractional density change $a_0 = 0.103$. At freezing the compressibility factor ($z = \beta p/\rho$) of the fluid is $z_0 = 12.4$ while the change in entropy per particle $\Delta s \equiv s_0 - s$ amounts to $\Delta s = 1.16k_B$. (Notice the agreement with the exact HS relation $\Delta s/k_B = a_0 z_0/(1 + a_0)$ [15] which is at variance with the relations proposed in [2 (b), 3 (d)].) At freezing the main peak of the structure factor of the fluid reaches a value of $S(k^*, \eta_0) = 2.90$ at a wavenumber $k^*\sigma = 7.00$. The mean square deviation in the solid at melting is $\langle(\Delta r)^2\rangle^{1/2} = 0.126d$ where d is the nearest neighbour distance ($d = a/\sqrt{2}$ for a f.c.c. lattice of lattice spacing a).

4.2. The (Percus–Yevick) hard sphere fluid

As stated above (see (3.3)) we will approximate the d.c.f. of the solid phase by the d.c.f. of the fluid phase taken at some effective density $\bar{\eta}$. The HS fluid phase will be described here by the Wertheim–Thiele solution of the Percus–Yevick (PY) equations ($\hat{c}(r > \sigma) = 0 = g(r < \sigma)$) [14]

$$\hat{c}(r/\sigma; \eta) = \sum_{j=0,1,3} \theta(\sigma - r) \left(\frac{r}{\sigma}\right)^j I_j(\eta), \quad (4.1)$$

$$c(k\sigma; \eta) = 24\eta \sum_{j=0,1,3} J_j(k\sigma) I_j(\eta), \quad (4.2)$$

where the dimensionless quantity $c(k\sigma; \eta)$ is the Fourier transform of $\rho\hat{c}(r/\sigma; \eta)$ and

$$I_0(\eta) = -(1 + 2\eta)^2/(1 - \eta)^4, \quad (4.3 a)$$

$$I_1(\eta) = 6\eta(1 + \frac{1}{2}\eta)^2/(1 - \eta)^4, \quad (4.3 b)$$

$$I_3(\eta) = \frac{\eta}{2} I_0(\eta), \quad (4.3 c)$$

while ($\bar{k} = k\sigma$)

$$J_0(\bar{k}) = \bar{k}^{-3}(\sin \bar{k} - \bar{k} \cos \bar{k}), \quad (4.4 a)$$

$$J_1(\bar{k}) = \bar{k}^{-4}\{(2 - \bar{k}^2) \cos \bar{k} + 2\bar{k} \sin \bar{k} - 2\} \quad (4.4 b)$$

$$J_3(\bar{k}) = \bar{k}^{-6}\{(12\bar{k}^2 - \bar{k}^4 - 24) \cos \bar{k} + (4\bar{k}^3 - 24\bar{k}) \sin \bar{k} + 24\}, \quad (4.4 c)$$

are the Fourier transforms of $\theta(\sigma - r)(r/\sigma)^j$, $\theta(x)$ being the Heaviside step function. From (4.2)–(4.4) we obtain the isothermal compressibility

$$K_T = \frac{1}{\rho} \frac{\partial \rho}{\partial p} \Big|_T \text{ via } K_T/K_T^0 = (1 - c(0; \eta))^{-1}$$

and equation (4.2) with $J_j(0) = 1/(3 + j)$, $K_T^0 = \beta/\rho$ being the ideal gas compressibility. The equation of state can then be obtained from

$$\beta p/\rho = (1 + \eta + \eta^2 - \gamma\eta^3)/(1 - \eta)^3, \quad (4.5)$$

$$c(0; \eta) = \{(1 - \gamma)\eta^4 - 4(1 - \gamma)\eta^3 + 2\eta^2 - 8\eta\}/(1 - \eta)^4, \quad (4.6)$$

where $\gamma = 0$ when the compressibility equation, and $\gamma = 3$ when the virial equation is used to obtain the thermodynamics. The γ -dependence of (4.5) and (4.6) displays the thermodynamic inconsistency of the PY approximation. Better, consistent, results can be obtained from the Verlet-Weis expression for the HS p.c.f. [14] since the latter embodies the almost exact Carnahan-Starling thermodynamics (corresponding to equations (4.5) and (4.6) with $\gamma = 1$) [14]. Here we will continue to use the PY approximation so as to allow easy comparison with the earlier investigations [2(b), 3(d), 5(c), 6(a), 12] all of which have used the PY d.c.f. This does however not imply that the results obtained below are insensitive to this approximation.

4.3. The (gaussian) hard sphere solid

In order to be able to tackle the numerical convergence problems more easily we assume, *a priori*, that the HS solid consists of a set of gaussian peaks as described by (3.11) and restrict ourselves to the cubic lattices (s.c., b.c.c., f.c.c.). In (3.11a) we then have $\mathbf{x}_j = (n_1, n_2, n_3)$, n_i ($i = 1, 2, 3$) being a positive or negative integer or zero, for the s.c. lattice ($N_1 = 1$) to which we have to add the sub-lattice generated by $\mathbf{x}_j = (n_1 + \frac{1}{2}, n_2 + \frac{1}{2}, n_3 + \frac{1}{2})$ to form the b.c.c. lattice ($N_1 = 2$) or the three sub-lattices generated by $\mathbf{x}_j = (n_1, n_2 + \frac{1}{2}, n_3 + \frac{1}{2})$ + permutations to form the f.c.c. lattice ($N_1 = 4$). The average density of a defect-free solid is then given by $\rho = N_1/a^3$, where a is the lattice spacing ($\mathbf{r} = a\mathbf{x}$). For a given solid density, ρ , and lattice structure, $\{\mathbf{x}_{jj}\}$, the only remaining parameter in (3.11) is the width parameter α . Because of the *a priori* functional assumption about $\rho(\mathbf{r})$ contained in (3.11) the equilibrium condition (2.10) degenerates here into

$$\frac{\partial \Omega[\rho]}{\partial \alpha} = 0, \quad (4.7)$$

whose solution fixes α for each ρ and lattice structure. It is convenient to subtract from $\Omega[\rho]$ its value (independent of α) for a uniform fluid phase of the same density, $\rho_0 = \rho$, as the average solid density. Using the results of §2 we obtain then

$$\beta \Delta \omega = \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}) \ln (\rho(\mathbf{r})/\rho) - \frac{1}{2V} \int_V d\mathbf{r} \int_V d\mathbf{r}' \Delta \rho(\mathbf{r}) \bar{c}(\mathbf{r}, \mathbf{r}') \Delta \rho(\mathbf{r}'), \quad (4.8)$$

where now $\Delta \rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho$. Using (3.14), (3.11) and (3.3) we approximate the exact result (4.8) as

$$\frac{\beta}{\rho} \Delta \omega = G(\alpha) - \frac{1}{2} \sum_{klm} 2^{3-\delta_k-\delta_l-\delta_m} \times \exp \left[-\frac{2\pi^2}{\alpha} (k^2 + l^2 + m^2) \right] \frac{\eta}{\bar{\eta}(\eta)} c(\bar{k}_{klm}(\eta); \bar{\eta}(\eta)) \quad (4.9)$$

where we have used a constant density path ($\rho(\lambda) \equiv \rho$) in (3.3b) in going from the fluid to the solid phase. In (4.9) the first term of (4.8) has been treated in the direct lattice and the second term in the reciprocal lattice. In the HS case it would be easier to treat also the second term in the direct lattice but this would make our treatment rather specific since in general the r -space d.c.f. is much less easily

accessible than its Fourier transform related to the structure factor. The dash on the sum over r.l.v., $\mathbf{q} = (k, l, m)$, in (4.9) indicates that $\mathbf{q} = 0$ is excluded from the sum while δ_k is a Kronecker delta. Here $\mathbf{k} = (2\pi/a)\mathbf{q}$, $\bar{\mathbf{k}} = \mathbf{k}\sigma$ and

$$\bar{k}_{klm}(\eta) = 2\pi(k^2 + l^2 + m^2)^{1/2} \left(\frac{6\eta}{\pi N_1} \right)^{1/3} \quad (4.10)$$

where k, l, m are non-negative integers (s.c.), all odd or all even for a f.c.c. lattice, and one or all being even for a b.c.c. lattice.

For each lattice, the first quantity to be determined is the effective density $\bar{\eta}$ of the fluid which models the solid of average density η . To this end we first consider the structural scaling condition (3.3 c), $\bar{k}_{\min}(\eta) = \bar{k}^*(\bar{\eta})$, with $S(\bar{k}^*(\eta); \eta) \equiv \max S(\bar{k}, \eta)$, $S(\bar{k}; \eta) = (1 - c(\bar{k}; \eta))^{-1}$, as obtained from (4.2) for $c(\bar{k}; \eta)$, and $\bar{k}_{\min} = \bar{k}_{100}$ (s.c.), \bar{k}_{110} (b.c.c.), \bar{k}_{111} (f.c.c.) as given by (4.10). The resulting relation $\bar{\eta} = \bar{\eta}(\eta)$ is shown in figure 3 for the η values of interest to freezing. In all three cases we have $\eta > \bar{\eta}$ which allows the solid to be described in terms of a stable fluid. The unfavourable situation of the loosely packed s.c. lattice is already apparent from figure 3 since it is described in terms of a very low density fluid.

Next we perform the sum in (4.9) by summing over all r.l.v. within a sphere of radius q_{\max} , $0 < q \leq q_{\max}$. We find that for the α and η values relevant to freezing a radius of $q_{\max} \geq 18$ is required to obtain results which are stable to one within

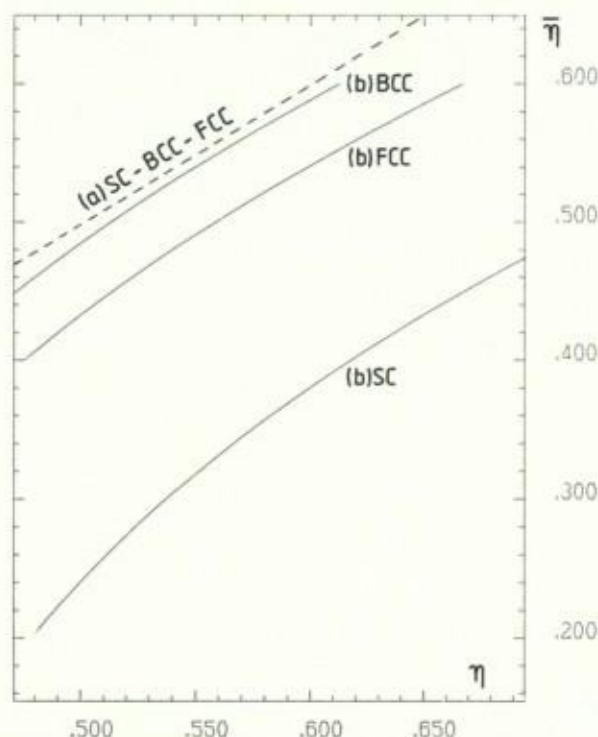
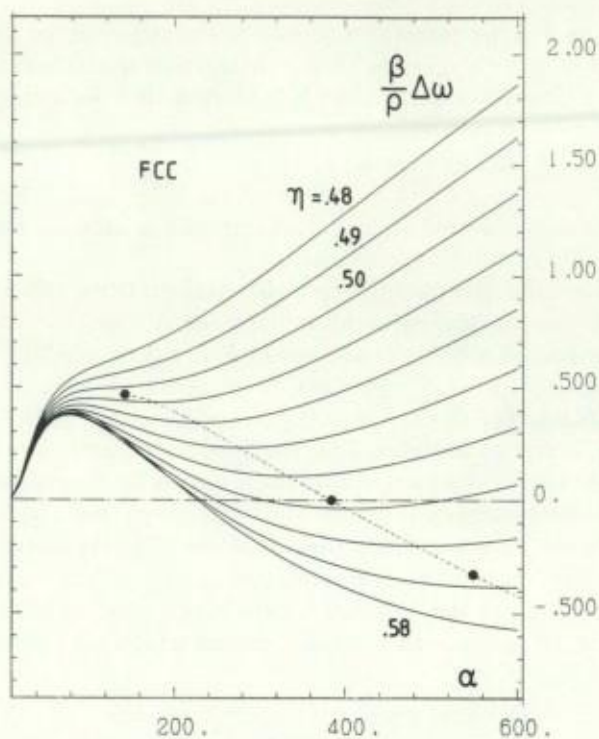
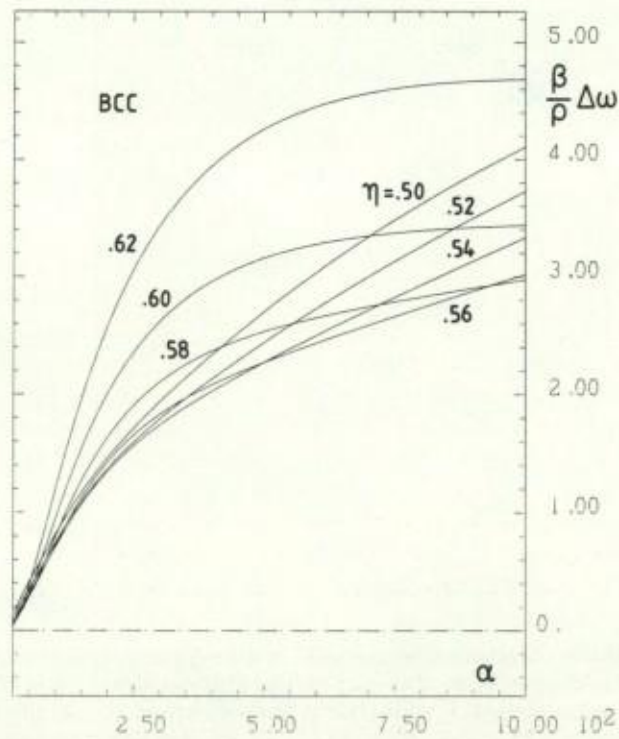


Figure 3. The direct correlations of the solid of average density η are approximated by those of an effective fluid of density $\bar{\eta}$. The effective density $\bar{\eta}$ is chosen such that the two systems are scaled with respect to their density ($\bar{\eta} = \eta$) (a), or with respect to their structure ($\bar{\eta} = \bar{\eta}(\eta)$; equation (3.3 c)) (b). The unfavourable position of the s.c. lattice in case (b) is clearly displayed.



(a)



(b)

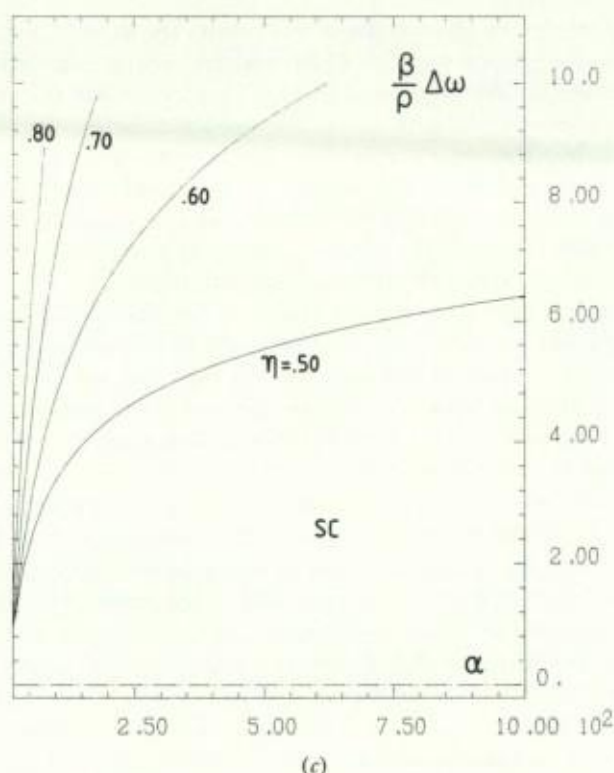


Figure 4. The reduced difference in free energy between a solid and a fluid of the same density as a function of this density η and the width parameter α as obtained from (4.9) and the structural scaling relation $\bar{\eta}(\eta)$ of figure 3. Case (a): the double-minimum structure is obvious for the f.c.c.-lattice although the minimum which corresponds to the fluid phase ($\alpha = 0$) is hardly visible on this scale. The trajectory of the minimum corresponding to the solid phase ($\alpha \neq 0$) is indicated by the dotted line together with the three points (large dots) considered in the table. Case (b): b.c.c. lattice with enlarged α -scale in order to display the plateau structure. Case (c): s.c. lattice showing no second minimum.

10^5 . Since the number of r.l.v. increases as q_{\max}^3 this represents a much larger set of r.l.v. than those used before ($q_{\max} = 6$ for [5(c)] and $q_{\max} < 3.4$ for the remaining studies of [2-7]). The results for (4.9) using (3.16) is shown in figure 4(a) for the f.c.c. lattice. It is seen that for $\eta > 0.504$ there appears a *double-minimum structure* indicating that besides the fluid phase (corresponding to the minimum at $\alpha = 0$) equation (4.7) admits also a solid phase (corresponding to the minimum at $\alpha \neq 0$) as equilibrium solution. For $0.504 < \eta < 0.548$ the solid is less stable than the fluid phase ($\Delta\omega > 0$) while at $\eta = 0.548$ there occurs an exchange of stability ($\Delta\omega = 0$). For each η , the position of the second minimum, say $\alpha_0(\eta)$, determines the value of $\alpha = \alpha_0(\eta)$ to be used in (3.11). It is seen from figure 4(a) that as the average density of the solid, η , increases so does α , leading to an increased localization (3.15) as expected physically. At the absolute lower stability limit of the solid $\eta = 0.504$ we find $\alpha_0 \approx 136$ corresponding to a minimum localization $\langle(\Delta\mathbf{r})^2\rangle^{1/2} \lesssim 0.149d$ ($d = a/\sqrt{2}$ for a f.c.c. lattice) in fair agreement with the Lindemann rule ($L = 0.126$) if the latter is interpreted as a stability limit (instead of a melting rule) which appears to be the most reasonable choice for a one-phase

rule. In figure 4(b)–(c) we show some of the results for the s.c. and b.c.c. lattices. In the s.c. case the lattice sum of (4.9) has the wrong sign and the solid is absolutely unstable (i.e. no solution of (4.7) is found even for the very wide range of α and η values shown in figure 4(c)). For the b.c.c. lattice we find a mechanically stable solid but the second minimum looks more like a plateau than a true minimum and disappears before the solid becomes stable relative to the fluid. It remains an open question whether the presence of this b.c.c. phase is an artefact of the approximations or whether instead better approximations might reveal a b.c.c. phase which is, at least, stable with respect to the fluid.

The above calculations have been repeated for the case of density scaling $\bar{\eta} = \eta$. There is again a stable f.c.c. phase (figure 5) but the second minimum is seen to saturate at a positive value of $\Delta\omega$ so that the solid remains unstable relative to the fluid. The behaviour of the s.c. and b.c.c. lattices (not shown) is similar to that of figure 4(b)–(c) except that no stable b.c.c. phase is found here.

In the present theory the stabilization of the solid is seen to rest on a fairly subtle competition between the structural (or entropy) contribution to the free energy (as given by the first term in the right-hand sides of (4.8) and (4.9) and the correlational (or internal energy) contribution (the second term in the right-hand sides of (4.8) and (4.9)). Even when the solid is mechanically stable its further stabilization relative to the fluid remains sensitive to the way in which the correlations in the solid are being modelled. Density scaling ($\bar{\eta} = \eta$) is seen to yield only a poor characterization of the solid phase correlations and no stable solid while structural scaling ($\bar{\eta}(\eta)$) yields both a thermodynamically stable solid ($\Delta\omega = 0$) and the proper selection mechanism between the three cubic lattices.

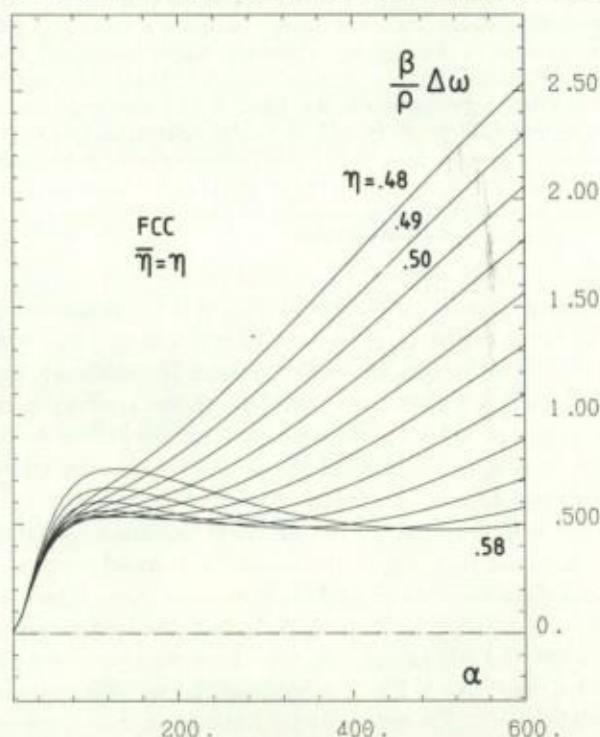


Figure 5. The same as figure 4(a) but using an effective fluid with density scaling ($\bar{\eta} = \eta$) instead of structural scaling ($\bar{\eta}(\eta)$). The second minimum saturates before the solid becomes stable with respect to the fluid.

4.4. The hard-sphere fluid-solid coexistence

We now relax the condition of constant density ($\eta_0 = \eta$) and look for the possibility of a two-phase, fluid-solid, coexistence by allowing the density of the solid, η , and the liquid, η_0 , to adjust themselves to the two-phase equilibrium conditions $\Delta\mu = 0$ and $\Delta p = 0$ ($\Delta T = 0$ being satisfied *a priori* within the present theory). We consider henceforth only f.c.c. solids since this is the only lattice to admit a stable solid phase relative to the fluid. The two-phase coexistence conditions (2.28) and (2.29) become now

$$\beta\Delta\mu = 0 = \ln(1 + a_0) + G(\alpha_0(\eta)) - a_0 \bar{c}_{000} - (1 + a_0) \sum_{klm} 2^{3-\delta_k-\delta_l-\delta_m} \exp\left[-\frac{2\pi^2}{\alpha_0(\eta)}(k^2 + l^2 + m^2)\right] \bar{c}_{klm} \quad (4.11)$$

$$\frac{1}{\rho_0} (-\beta\Delta p + \beta\rho\Delta\mu) = 0 = (1 + a_0) \ln(1 + a_0) - a_0 + (1 + a_0)G(\alpha_0(\eta)) - \frac{a_0^2}{2} \bar{c}_{000} - \frac{(1 + a_0)^2}{2} \sum_{klm} 2^{3-\delta_k-\delta_l-\delta_m} \exp\left[-\frac{2\pi^2}{\alpha_0(\eta)}(k^2 + l^2 + m^2)\right] \bar{c}_{klm}, \quad (4.12)$$

where $\eta = \eta_0(1 + a_0)$, whereas $\alpha = \alpha_0(\eta)$ denotes the solution of (4.7) discussed above and

$$\left\{ \begin{array}{l} \bar{c}_{klm} \\ \bar{c}_{klm} \end{array} \right\} = \int_0^1 d\lambda \left\{ \begin{array}{l} 1 \\ 2(1 - \lambda) \end{array} \right\} \frac{\eta_0}{\bar{\eta}(\eta(\lambda))} c(\bar{k}_{klm}(\eta); \bar{\eta}(\eta(\lambda))), \quad (4.13)$$

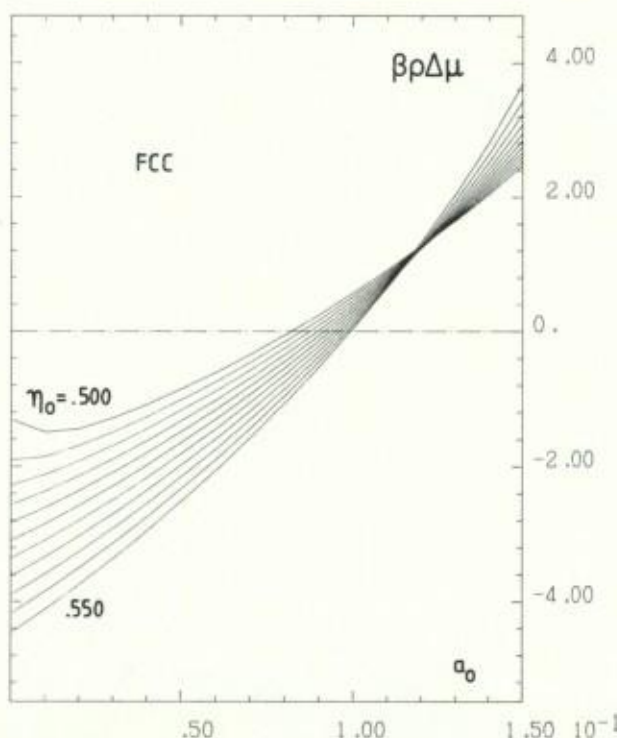


Figure 6. The values of $\beta\rho\Delta\mu$ obtained from (4.11) and $\bar{\eta}(\eta)$ for the f.c.c. lattice as a function of the fluid density η_0 (by steps of 0.005) and the fractional density change $a_0 = (\eta - \eta_0)/\eta_0$. The equilibrium condition $\Delta\mu = 0$ is seen to restrict very strongly the possible a_0 values.

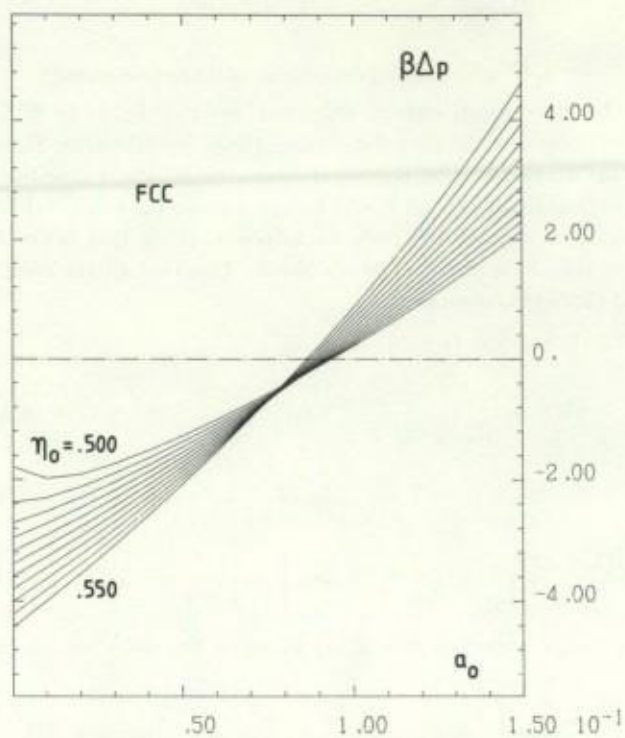


Figure 7. The values of $\beta \Delta \rho$ (as in figure 6).

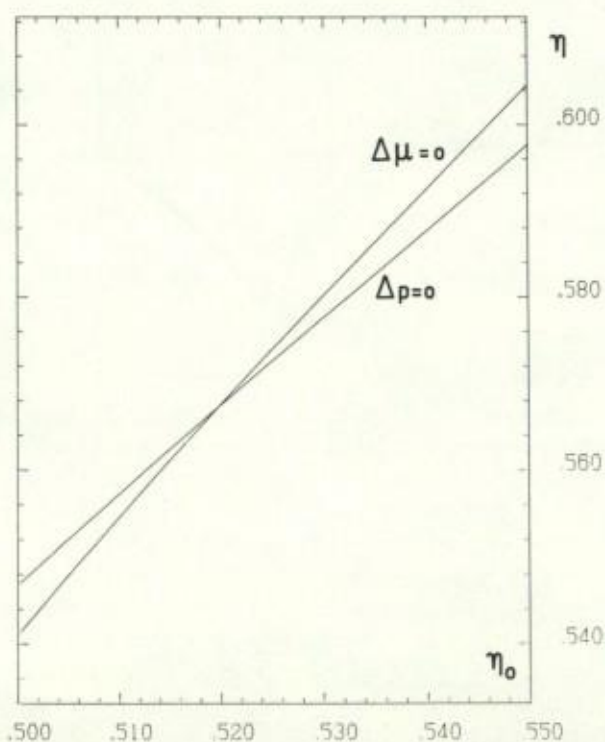


Figure 8. Graphical representation of the f.c.c. phase transition point in the η_0, η plane as the intersection of the solution curves of the two coexistence conditions $\Delta \mu = 0$ and $\Delta \rho = 0$.

with $\eta(\lambda) = \eta_0(1 + \lambda a_0)$ and $\bar{\eta}(\eta)$ determined by the structural scaling condition (3.3 c). The integral in (4.13) has been evaluated by a 4-point gaussian quadrature (accurate to one within 10^5 when tested with a 8-point method) and the lattice sums in (4.11) and (4.12) have been performed up to $q_{\max} = 18$ as discussed above. In figures 6-7 we show the values of $\Delta\mu$ and Δp obtained from (4.11) and (4.12) as a function of η_0 and a_0 . It is seen that the equilibrium conditions are very stringent conditions for the fractional density change a_0 . The solution of the joint coexistence conditions $\Delta p = 0 = \Delta\mu$ is shown graphically in figure 8. The intersection point corresponds to the freezing point, i.e. to a situation where the mechanically stable solid reaches for the first time complete thermodynamic stability with respect to the mechanically stable fluid. No other solutions have been found for lower densities while at higher densities ($\eta_0 > 0.60$) we run into convergence problems with the lattice sums of (4.11) and (4.12). The investigation of the freezing theory along the metastable fluid branch (i.e. for densities close to random close packing $\eta_0 = 0.636$) as performed in [6 (b)] is certainly of interest in relation to the limit of compression of the HS fluid but we doubt that it is consistent to do this with the PY approximation which ignores the existence of such a limit. Such high densities require moreover very precise numerical evaluations which are outside the scope of the present study.

4.5. Results

Our numerical results are gathered in the table where they are compared with the experimental (MC, MD) values [14]. We do not compare them to the other theoretical values [1-6, 12] since the latter have been obtained, as discussed in detail in §3, by early truncation of slowly convergent series and are hence numerically unreliable. The quantitative agreement between theory and experiment obtained here may be considered as fairly good. The modelling of the d.c.f. of the solid by (3.3) is certainly our crudest approximation. Next to this we consider the use of a PY d.c.f. for the effective HS fluid to be somewhat doubtful, at least in the two-phase coexistence region. Finally, the influence of the gaussian density peak representation (3.11) for the solid (although presumably worst for hard spheres) is thought to be only marginal.

5. CONCLUSIONS

The density functional theory has been used to obtain formally exact equations describing the equilibrium two-phase coexistence between a uniform liquid and a periodic solid. This represents an important improvement of the earlier freezing theories which introduced approximations at an early stage such as the truncated Taylor expansion of the free energy of the solid around the free energy of the liquid ignoring the pronounced density variations which are known to exist in the coexistence region. We have also shown that the Fourier expansions of the solid density introduced previously cannot be truncated as done in the literature because the Fourier series converge very slowly for reasonably well localized solids. Early truncation leads to solid densities which become very negative in the interstitial regions. The results obtained previously by these methods are thus numerically biased and the theory has to be reconsidered. We have analysed the theoretical predictions for the freezing of hard spheres using three physical

HS freezing data obtained from the present theory and compared to the computer experiments (between brackets whenever available) [14].

Solid phase data (f.c.c.)

- (1) Point of marginal mechanical stability

$$\eta = 0.504 \quad L = 0.149 \text{ (0.126)}$$

- (2) Point of marginal thermodynamic stability relative to the fluid of the same density ($\Delta f = 0$)

$$\eta = 0.548 \quad L = 0.088$$

- (3) Point of phase coexistence ($\Delta\mu = 0 = \Delta p$)

$$\eta = 0.567 \text{ (0.545)} \quad L = 0.074$$

Fluid phase data

- (1) Freezing point $\eta_0 = 0.520 \text{ (0.494)}$

- (2) Compressibility factor at freezing†

$$z_0 = \begin{cases} 12.4 \text{ (v)} \\ 16.2 \text{ (c)} \end{cases} (12.4)$$

- (3) Height and position of the main peak of the (PY) structure factor at freezing

$$\max S(k\sigma; \eta_0) = 3.65 \text{ (2.90)}$$

$$\text{at } k\sigma = 7.09 \text{ (7.00)}$$

Phase transition data

- (1) Fractional density change $a_0 = 0.091 \text{ (0.103)}$

- (2) Entropy change†

$$\Delta s/k_B = \begin{cases} 1.03 \text{ (v)} \\ 1.36 \text{ (c)} \end{cases} (1.16)$$

† c(v) refers to the use of the compressibility (virial) PY equation of state.

approximations and testing thoroughly the convergence of all the numerical methods employed. As a first approximation we have represented the density of the solid as a sum of gaussian peaks whose width is determined by minimizing the free energy of the solid. Next we have approximated the d.c.f. of the solid by the d.c.f. of a HS fluid of (a) the same average density or (b) the same average structure as the HS solid. Finally, the d.c.f. of the HS fluid has been approximated by the PY d.c.f. The resulting theory predicts a fluid-f.c.c. solid transition in fair agreement with the simulation results justifying hereby the earlier expectations. A thorough investigation of the above physical approximations has not yet been undertaken but there remains little doubt that a quantitative theoretical description of first order phase transitions is possible along the present lines.

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