

Density Functional Descriptions of Classical Inhomogeneous Fluids*

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Abstract

Microscopically inhomogeneous states such as crystals and amorphous phases are wide-spread in nature, and it has become relatively common to attempt to describe the thermodynamic functions of such structured systems by utilising the corresponding properties of their homogeneous counterparts. One route is via density functional theory, some aspects of which are reviewed and developed here for single-component systems. In particular the possible applicability of coarse-graining or weighted density approximations to the theory of the liquid-crystal transition are discussed in terms of physical implications stemming from the crucial change in symmetry that occurs. Some insight into the apparent inconsistency of weighted-density approaches can be gained by examination of the role of anharmonic terms in the structured phase, and their relation to the nature of the interactions which also control the range of the weight-functions.

1. Introduction

For the most part, density functional descriptions of dense phases of matter have been developed to deal with inhomogeneous states, in both classical and quantum systems. The classical fluid is perhaps not everyone's cup of tea, and the inhomogeneous classical fluid possibly less so. Nevertheless, quite evident progress has been made of late in accounting for the properties of these non-uniform systems entirely in terms of the properties of their uniform counterparts. The topic has been the subject of extensive and rather recent reviews (Evans 1990, 1992; Baus 1990; Haymet 1992; Löwen 1994; Ashcroft 1995) and in view of this the intent of what follows is limited by but two aims. First, to set down certain aspects of density functional theory, especially in the classical domain, that may now be considered as reasonably well established. Second, to formulate density functional theory for its use in applications to structured systems through coarse graining or weighted density methods. Prominent practical applications of these methods include fluids at interfaces, fluids in confined geometries, wetting, absorption, and to the general problem of liquid–solid phase transition in systems possessing realistic non-singular interactions. The latter problem is distinguished from the others in that the inhomogeneities to be associated with the solid phase can be seen to possess a distributed character.

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In the classical domain, the simplest example of an inhomogeneous system might be considered to be the canonical assembly of N identical particles entirely free of mutual interactions, but each particle experiencing a force wholly derivable from an external one-body potential $\phi^{(1)}(\vec{r})$. Thus, if the coordinates of the particles are $\vec{r}_i (i = 1, \dots, N)$, and they are confined to a volume V , the Hamiltonian is just $\hat{H}_N = \hat{T}_N + \int_V \vec{dr} \hat{\rho}^{(1)}(\vec{r}) \phi^{(1)}(\vec{r})$, where $\hat{T}_N = \sum_{i=1}^N \vec{p}_i^2/2m$, and $\hat{\rho}^{(1)}(\vec{r}) (= \hat{\rho}_N^{(1)}(\vec{r})) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i)$ is the one-particle density operator. In the canonical ensemble, the corresponding average $\langle \rho^{(1)}(\vec{r}) \rangle$ of this quantity follows directly from the definition, i.e. $\rho^{(1)}(\vec{r}) = \text{Tr}_c \hat{\rho}^{(1)}(\vec{r}) \exp(-\beta \hat{H}) / \text{Tr}_c \exp(-\beta \hat{H})$ and is easily seen to be $\rho^{(1)}(\vec{r}) = \rho^{(1)} \exp(-\beta \phi^{(1)}(\vec{r})) / \int_V (\vec{dr}/V) \exp(-\beta \phi^{(1)}(\vec{r}))$ where by $\rho^{(1)}$ we mean the quantity N/V . Using a similar average we may construct a quantity $\mathcal{F}_{ni}$ which is the Helmholtz free energy F_{ni} of the non-interacting system diminished by contributions directly identifiable with the external potential. It is also easily seen to be

$$\mathcal{F}_{ni} = F_{ni} - \int_V \vec{dr} \rho^{(1)}(\vec{r}) \phi^{(1)}(\vec{r}) = k_B T \int_V \vec{dr} \rho^{(1)}(\vec{r}) \{ \ln(\rho^{(1)}(\vec{r}) \Lambda^3) - 1 \}, \quad (1)$$

where $(\hbar^2/2m)(2\pi/\Lambda)^2 = \pi k_B T$ defines the thermal de Broglie wavelength for particles whose masses are taken to be m . If the external potential is removed ($\phi^{(1)}(\vec{r}) \rightarrow 0$) then the free energy per particle is $f_0(\rho^{(1)}) = k_B T \{ \ln(\rho^{(1)} \Lambda^3) - 1 \}$ for the necessarily homogeneous system. From these elementary considerations it follows that with $\phi^{(1)}(\vec{r})$ restored

$$\mathcal{F}_{ni} = \int_V \vec{dr} \rho^{(1)}(r) f_0(\rho^{(1)}(\vec{r})), \quad (2)$$

a form that is obtained entirely from a direct substitution in the *inhomogeneous* state free energy per particle of the inhomogeneous one-particle density $\rho^{(1)}(\vec{r})$. Though the result is not valid for quantum non-interacting systems (which are correlated through symmetry or antisymmetry of the N -particle wave-functions) the form of (2) becomes known as the local-density approximation when applied to a certain fragment (the exchange-correlation energy) of the overall internal energy of a corresponding quantum system. It expresses an appealing and somewhat intuitive notion, namely, that the free energy of a system that is not homogeneous may be developed from a knowledge of the properties of its homogeneous companion and of the one particle density itself.

An examination of this proposition for an arbitrary interacting system requires an initial specification of its fundamental Hamiltonian. For thermodynamic conditions that typify ordinary condensed matter, we can begin by regarding them as neutral canonical assemblies of electrons (e) and nuclei (n). If each assembly is permitted to interact with external fields $\phi_\alpha^{(1)}(\vec{r})$ ($\alpha = e, n$) then, if $\phi^{(2)}(\vec{r} - \vec{r}') = e^2/|\vec{r} - \vec{r}'|$ is the fundamental Coulomb interaction, the Hamiltonian in the absence of further one-body potentials is

$$\begin{aligned} \hat{H} = & \sum_{\alpha} \{ \hat{T}_{\alpha} + \int_V \vec{dr} \hat{\rho}_{\alpha}^{(1)}(\vec{r}) \phi_{\alpha}^{(1)}(\vec{r}) \\ & + \frac{1}{2} \sum_{\alpha'} Z_{\alpha} Z_{\alpha'} \int_V \vec{dr} \int_V \vec{dr}' \hat{\rho}_{\alpha\alpha'}^{(2)}(\vec{r}, \vec{r}') \phi^{(2)}(\vec{r} - \vec{r}') \} . \end{aligned} \quad (3)$$

Here $Z_\alpha = Z_e = -1$ for electrons, and $Z_\alpha = Z_n = Z_a$, the atomic number, for nuclei. In (3)

$$\hat{\rho}_{\alpha\alpha'}^{(2)}(\vec{r}, \vec{r}') = \hat{\rho}_\alpha^{(1)}(\vec{r}')\hat{\rho}_{\alpha'}^{(1)}(\vec{r}) - \delta_{\alpha\alpha'}\delta(\vec{r} - \vec{r}')\hat{\rho}_\alpha^{(1)}(\vec{r}) \quad (4)$$

is the two-particle density operator, and its average

$$\rho_{\alpha\alpha'}^{(2)}(\vec{r}, \vec{r}') = \text{Tr}_q \hat{\rho}_{\alpha\alpha'}^{(2)} \exp(-\beta \hat{H}) / \text{Tr}_q \exp(-\beta \hat{H}) \quad (5)$$

defines the pair distribution function $g_{\alpha\alpha'}^{(2)}(\vec{r}, \vec{r}')$ through the statement

$$\rho_{\alpha\alpha'}^{(2)}(\vec{r}, \vec{r}') = \rho_\alpha^{(1)}(\vec{r})\rho_{\alpha'}^{(1)}(\vec{r}')g_{\alpha\alpha'}^{(2)}(\vec{r}, \vec{r}'). \quad (6)$$

Equation (5) indicates that to begin with the problem must be addressed at the level of quantum mechanics. The quantum trace (Tr_q) usually simplifies, however, because of the vast disparity in time scales ($m_e \ll m_n$); accordingly an effective Hamiltonian controlling the motion of the more massive degrees of freedom can be obtained by invoking the Born-Oppenheimer approximation and for temporarily fixed $\{\vec{r}_n\}$ by tracing out the electronic states according to

$$\text{Tr}_q e^{-\beta \hat{H}} = \text{Tr}_n \{ \text{Tr}_{e(n)} e^{-\beta \hat{H}} \} = \text{Tr}_n e^{-\beta \hat{H}_{\text{eff}}^n}. \quad (7)$$

Here $\hat{H}_{\text{eff}}^n$ is, by definition, dependent on temperature, but it will only be weakly so if the electron system is close to its ground state. Again, this is almost always a good approximation for condensed matter under common thermodynamic conditions. Accordingly for a narrow band insulating $\hat{H}_{\text{eff}}^n$ can be expected to take the general form (Ashcroft 1991)

$$\begin{aligned} \hat{H}_{\text{eff}}^n = & \hat{T}_n + \frac{1}{2} \int_V \vec{dr} \int_V \vec{dr}' \hat{\rho}_{nn}^{(2)} \phi^{(2)}(\vec{r} - \vec{r}') \\ & + \frac{1}{3!} \int_V \vec{dr} \int_V \vec{dr}' \int_V \vec{dr}'' \hat{\rho}^{(3)}(\vec{r}, \vec{r}', \vec{r}'') \phi^{(3)}(\vec{r}, \vec{r}', \vec{r}'') + \dots, \end{aligned} \quad (8)$$

where $\hat{\rho}^{(3)}$ is the three-particle density operator. In writing H_{eff}^n in this manner it is assumed that conditions are placed on the system such that the coupling between electrons and nuclei (i.e. $-Z_a e^2 \int_V \vec{dr} \int_V \vec{dr}' \phi_c^{(2)}(\vec{r} - \vec{r}') \hat{\rho}_e^{(1)}(\vec{r}) \hat{\rho}_n^{(1)}(\vec{r}')$) leads to essentially neutral localised objects through nearly complete condensation of electrons into atoms. A quite different possibility is that electron condensation leads instead to ions and a complementary electron problem admitting extended states sensitive to a volume boundary condition (examples being the metals and wide-band semiconductors). If this is the case, then (8) is replaced by

$$\begin{aligned} \hat{H}_{\text{eff}}^n = & \hat{T}_n + f(V) + \frac{1}{2} \int_V \vec{dr} \int_V \vec{dr}' \hat{\rho}^{(2)}(\vec{r}, \vec{r}') \phi^{(2)}(\vec{r} - \vec{r}'; V) \\ & + \frac{1}{3!} \int_V \vec{dr} \int_V \vec{dr}' \int_V \vec{dr}'' \hat{\rho}^{(3)}(\vec{r}, \vec{r}', \vec{r}'') \phi^{(3)}(\vec{r}, \vec{r}', \vec{r}'') + \dots, \end{aligned} \quad (9)$$

where $f(V)$ is a function of volume and not of structure. In either case, the $\phi^{(2)}, \phi^{(3)} \dots$ are effective two-, three-, ..., body interactions controlling the motions for the composite objects regarded as atoms or ions. They are functions of

state for the wide-band systems. For $Z_a = 2$ (the heliums), and for ordinary pressures, (8) leads to bulk phases that, apparently, are entirely homogeneous ($\rho^{(1)}(\vec{r}) = \text{const}$) to the lowest temperatures. By $\hat{\rho}^{(1)}(\vec{r})$ and $\hat{\rho}^{(2)}(\vec{r}, \vec{r}')$ we shall now mean $\hat{\rho}_n^{(1)}(r)$ and $\hat{\rho}_{nn}^{(1)}(\vec{r}, \vec{r}')$.

A major point to be made is that, although the focus in what follows is the treatment of (8) or (9) in the classical domain (and extended by the restoration of further one-body terms), a quite significant application of density functional theory in the electronic context underlies the determination of the $\phi^{(n)}$ or the $\phi^{(n)}(V)$. This matter is dealt with fully elsewhere in the present volume, but we may note that so far as the electrons are concerned, the fields of the nuclei can be formally included with any putative one-particle potentials truly external to the system, at least at the level of the Born–Oppenheimer approximation.

From this point onwards we shall suppose that thermodynamic conditions are actually such that (8) or (9) can be treated within the framework of the thermodynamic limit of classical statistical mechanics (i.e., $\Lambda \ll |\vec{r}_{nn'}|$, where $|\vec{r}_{nn'}|$ is a near-neighbour separation typical of the condensed state). The consequence is that in (7) we will now carry out a classical trace (Tr_c). In the absence of further external interactions, the common phases of these simple systems are gas, liquid, and solid, the first pair usually being separated by a continuous gas–liquid transition with associated critical phenomena. Liquid and crystal are separated by the freezing or melting transition and accompanied by a fundamental breaking of the symmetry of (8) or (9). As noted, a quite extensive application of density-functional theory has been directed towards this problem starting with a reformulation by Haymet and Oxtoby (1981) of the initiating paper by Ramakrishnan and Youssouff (1979). We shall outline some of the later developments in density functional theory and its primary impact on treatments of the solid–liquid transition, however we will do so with the standard pairwise truncated forms of (8) or (9), but now rewritten to express the presence of external interactions represented by one-body potentials $\phi^{(1)}(\vec{r})$. Thus a limited representation of the original problem is either

$$\hat{H}_{\text{eff}}^n = \hat{T}_n + \int_V \vec{dr} \hat{\rho}^{(1)}(\vec{r}) \phi^{(1)}(\vec{r}) + \frac{1}{2} \int_V \vec{dr} \int_V \vec{dr}' \hat{\rho}^{(2)}(\vec{r}, \vec{r}') \phi^{(2)}(\vec{r} - \vec{r}') \quad (10)$$

for insulating systems, or

$$\begin{aligned} \hat{H}_{\text{eff}}^n = \hat{T}_n + f(V) + \int_V \vec{dr} \hat{\rho}^{(1)}(\vec{r}) \phi^{(1)}(\vec{r}, V) \\ + \frac{1}{2} \int_V \vec{dr} \int_V \vec{dr}' \hat{\rho}^{(2)}(\vec{r}, \vec{r}') \phi^{(2)}(\vec{r} - \vec{r}', V) \end{aligned} \quad (11)$$

for metallic systems. The most serious restriction of (10) or (11) is that they cannot describe systems where three-body interactions are notably important (the elemental semiconductors being prominent examples). Setting $\phi^{(2)}$ to zero in (10) recovers the introductory example whose intrinsic free energy is given by (1).

Though geometric packing considerations have very much guided the development of the statistical physics of the condensed state, and particularly the liquid state, it is important to note that the associated assumption, namely that $\phi^{(2)}$ can be well approximated as a first step by the hard-sphere interaction, is not an entirely

plausible guide to the nature of broken symmetry transitions occurring between dense phases in systems with more physical interactions. Nevertheless it is of some interest that considerable analytic progress can be made on inhomogeneous hard-sphere systems by purely geometric arguments (Rosenfeld 1988), although it must be noted that the collisional character shared by both hard-sphere liquids and solids is not an attribute of realistic systems which in their crystalline phases possess considerable coherence. This matter will be further developed below.

2. Functional Connections

We continue with a canonical ensemble for which $N = \int_V \vec{dr} \rho^{(1)}(\vec{r})$. The Helmholtz free energy F , and the corresponding quantity $\mathcal{F}$ (i.e. F diminished by one-body contributions) are linked by

$$\mathcal{F} = F - \int_V \vec{dr} \rho^{(1)}(\vec{r}) \phi^{(1)}(\vec{r}) = -k_B T \ln \text{Tr}_c e^{-\beta \hat{H}_{\text{eff}}^n} - \int_V \vec{dr} \rho^{(1)}(\vec{r}) \phi^{(1)}(\vec{r})$$

and it is immediately clear from (7) and (10) (or (11)) that $\mathcal{F} = \mathcal{F}[\phi^{(1)}(\vec{r})]$, and $F = F[\phi^{(1)}(\vec{r})]$, i.e. $\mathcal{F}$ and F are both functionals of the one-body potential $\phi^{(1)}(\vec{r})$. From the definitions of $\hat{\rho}^{(1)}(\vec{r})$ and $\hat{\rho}^{(2)}(\vec{r}, \vec{r}')$ it is also clear that for an arbitrary infinitesimal change $\delta\phi^{(1)}\vec{r}$ in $\phi^{(1)}(\vec{r})$

$$\delta F = \int_V \vec{dr} \langle \hat{\rho}^{(1)}(\vec{r}) \rangle \delta\phi^{(1)}(\vec{r})$$

so that

$$\rho^{(1)}(\vec{r}) = \delta F / \delta\phi^{(1)}(\vec{r}), \quad (12)$$

and from the succeeding variation

$$-\beta \{ \langle (\hat{\rho}^{(1)}(\vec{r}) - \rho^{(1)}(\vec{r})) (\hat{\rho}^{(1)}(\vec{r}') - \rho^{(1)}(\vec{r}')) \rangle \} = \delta^2 F / \delta\phi^{(1)}(\vec{r}) \delta\phi^{(1)}(\vec{r}'). \quad (13)$$

The last result can also be written

$$\begin{aligned} \delta\rho^{(1)} / \delta\phi^{(1)}(\vec{r}') &= -\beta \{ \rho^{(1)}(\vec{r}) \rho^{(1)}(\vec{r}') h^{(2)}(\vec{r}, \vec{r}') + \delta(\vec{r} - \vec{r}') \rho^{(1)}(\vec{r}) \} \\ &= \chi^{(2)}(\vec{r}, \vec{r}'), \end{aligned} \quad (14)$$

where $\chi^{(2)}$ is the standard static two-point response function. In (14) $h^{(2)}(\vec{r}, \vec{r}') = g^{(2)}(\vec{r}, \vec{r}') - 1$ is the total correlation function for the inhomogeneous system. For a canonical assembly of particles, it is constrained by the sum rule

$$\int_V \vec{dr}' \rho^{(1)}(\vec{r}') h^{(2)}(\vec{r}, \vec{r}') = -1$$

for any $\vec{r}$. Further functional derivatives with respect to $\phi^{(1)}(\vec{r})$ lead to three-, four-, and higher-particle correlation functions.

It is apparent that a stipulated $\phi^{(1)}(\vec{r})$ will lead to a certain physical density response embodied by $\rho^{(1)}(\vec{r})$. However, a crucial point in the density functional method is that the converse is also true: knowledge of a given $\rho^{(1)}(\vec{r})$ determines uniquely the $\phi^{(1)}(\vec{r})$, at least to within constant terms. This is the content of a theorem by Mermin (1965), which is a generalisation to finite temperatures of the

important ground state theorem of Hohenberg and Kohn (1964). The theorems offer, immediately, the possibility of working with the inhomogeneous one-particle density as the primary physical variable. A direct consequence is that if a coupling constant α ($0 \leq \alpha \leq 1$) is associated with the pair interactions (taken to be non-singular) then for a system subject only to one-body and two-body interactions (see, for example, Ashcroft 1995) which develops a one-particle density $\rho^{(1)}(\vec{r})$

$$\mathcal{F} = \mathcal{F}_{ni}[\rho^{(1)}(\vec{r})] + \frac{1}{2} \int_V \vec{dr} \int_V \vec{dr}' \rho^{(1)}(\vec{r}) \rho^{(1)}(\vec{r}') \bar{g}^{(2)}(\vec{r}, \vec{r}') \phi^{(2)}(\vec{r}, \vec{r}'), \quad (15)$$

where

$$\bar{g}^{(2)}(\vec{r}, \vec{r}') = \int_0^1 d\alpha g_\alpha^{(2)}(\vec{r}, \vec{r}').$$

This result can also be obtained by functional integration (along the linear path $0 \leq \alpha \phi^{(2)}(\vec{r}, \vec{r}') \leq \phi^{(2)}(\vec{r}, \vec{r}')$) of the relation

$$\delta F / \delta \phi^{(2)}(\vec{r}, \vec{r}') = \frac{1}{2} \rho^{(2)}(\vec{r}, \vec{r}').$$

In terms of the total correlation function $\bar{h}^{(2)}(\vec{r}, \vec{r}') = \bar{g}^{(2)}(\vec{r}, \vec{r}') - 1$ we may also write

$$\begin{aligned} \mathcal{F} = & \mathcal{F}_{ni}[\rho^{(1)}(\vec{r})] + \frac{1}{2} \int_V \vec{dr} \int_V \vec{dr}' \rho^{(1)}(\vec{r}) \rho^{(1)}(\vec{r}') \phi^{(2)}(\vec{r}, \vec{r}') \\ & + \mathcal{F}_c[\rho^{(1)}(\vec{r}')], \end{aligned} \quad (16)$$

where

$$\mathcal{F}_c[\rho^{(1)}(\vec{r})] = \frac{1}{2} \int_V \vec{dr} \int_V \vec{dr}' \rho^{(1)}(\vec{r}') \rho^{(1)}(\vec{r}) \phi^{(2)}(\vec{r}, \vec{r}') \bar{h}(\vec{r}, \vec{r}'). \quad (17)$$

In the electron gas context, the second term of (16) would be regarded as part of the ‘Hartree’ energy, and its meaning is equally clear here. Correspondingly, the term $\mathcal{F}_c$ would be called the exchange-correlation energy; here it is the correlation term and for strongly interacting systems it is not adequately represented by a local approximation simply because dense classical fluids are far more correlated than their electronic counterparts.

3. The Direct Correlation Functions

If the particle number is fixed then, as noted, for any realisation of the density $\rho^{(1)}(\vec{r})$ the constraint $\int_V \vec{dr} \rho^{(1)}(\vec{r}) = N$ is immediate. Its consequence in equilibrium conditions is the statement

$$\mu = \phi^{(1)}(\vec{r}) + \delta \mathcal{F} / \delta \rho^{(1)}(\vec{r}), \quad (18)$$

where μ can be identified with the chemical potential. But since kinetic energy terms in the Hamiltonian separate from interaction terms, let us write

$$\mathcal{F} = \mathcal{F}_{ni} + \mathcal{F}_{\text{exc}},$$

where $\mathcal{F}_{ni}$ is just $\mathcal{F}$ in a system free of interactions in which a density $\rho^{(1)}(\vec{r})$ has been established. Then

$$\rho^{(1)}(\vec{r}) = \rho^{(1)} \exp\{-\beta\phi^{(1)}(\vec{r}) + c^{(1)}(\vec{r}) - c_0^{(1)}\}. \quad (19)$$

In (19) we have

$$c^{(1)}(\vec{r}) = -\delta\beta\mathcal{F}_{\text{exc}}/\delta\rho^{(1)}(\vec{r}), \quad c_0^{(1)} = \log(\rho^{(1)}/z), \quad (20)$$

where

$$z = (1/\Lambda^3) \exp\{\beta(\mu - \phi^{(1)}(\vec{r}))\}, \quad z = (1/\Lambda^3) \exp\{\beta\mu\}.$$

Equation (19) is easily seen to be the extension for the interacting system of the earlier result

$$\rho^{(1)}(\vec{r}) = \rho^{(1)} \exp(-\beta\phi^{(1)}(\vec{r})) \bigg/ \int_V (\vec{dr}/V) \exp(-\rho\phi^{(1)}(\vec{r}))$$

for a non-interacting system. With (18) it is also seen as the counterpart of the Kohn-Sham equations for the electron systems and its form is equally suggestive, namely, that for the non-uniform classical interacting system there is an equivalent underlying system which may be taken as non-interacting, but subject to an effective one body external potential

$$\tilde{\phi}^{(1)}(r) = \phi^{(1)}(\vec{r}) - \beta c^{(1)}(\vec{r}) = \phi^{(1)}(\vec{r}) + \beta\delta\mathcal{F}_{\text{exc}}/\delta\rho^{(1)}(\vec{r}).$$

It is an exact statement.

A clear possibility now emerges from (19). If the external potential is taken to be exceedingly small ($\phi^{(1)} \rightarrow 0$) then, in addition to the obvious solution $\rho^{(1)} \rightarrow \text{constant}$ conforming to the symmetry of $\hat{H}$, there is also the possibility of a self-consistently sustained solution

$$\rho^{(1)}(\vec{r}) = \rho_0 \exp\{c^{(1)}(\vec{r}; [\rho^{(1)}(\vec{r})]) - c_0^{(1)}\},$$

but one conforming to an entirely different symmetry. The obvious case is the occurrence of crystalline symmetry, whose existence implies a periodic form for $\rho^{(1)}(\vec{r})$, and hence also for $c^{(1)}(\vec{r})$. This example of bifurcation of the density will be discussed in more detail below.

The quantity $c^{(1)}(\vec{r})$ is the first order direct correlation function, and it plays a central role in classical density functional theory. It is also a functional of the one-particle density $\rho^{(1)}(\vec{r})$, and if this functional dependence were known then at fixed temperature the free energies of two systems, one with inhomogeneous density $\rho_f^{(1)}(\vec{r})$, the other with $\rho_i^{(1)}(\vec{r})$, would be related immediately by

$$\beta\mathcal{F}_{\text{exc}}[\rho_f^{(1)}] = \beta\mathcal{F}_{\text{exc}}[\rho_i^{(1)}] - \int_V \vec{dr} (\rho_f^{(1)}(\vec{r}) - \rho_i^{(1)}(\vec{r})) \int_0^1 d\lambda c^{(1)}(\vec{r})[\rho_\lambda^{(1)}(\vec{r})], \quad (21)$$

where $\rho_\lambda^{(1)}(\vec{r})$ defines a linear path according to

$$\rho_\lambda^{(1)}(\vec{r}) = \rho_i^{(1)}(\vec{r}) + \lambda(\rho_f^{(1)}(\vec{r}) - \rho_i^{(1)}(\vec{r})) \quad (0 < \lambda \leq 1). \quad (22)$$

This result is based on the implicit assumption that $c^{(1)}$ itself exists at all points along the path $\rho_\lambda^{(1)}(\vec{r})$.

Just as a hierarchy of total correlation functions follows from successive functional differentiation of F (or $\mathcal{F}$) with respect to $\phi^{(1)}(\vec{r})$, so a parallel stream of direct correlation functions follows from successive functional differentiation of the excess free energy with respect to $\rho^{(1)}(\vec{r})$. Accordingly the second functional derivative leads to the definition

$$\begin{aligned} c^{(2)}(\vec{r}, \vec{r}'') &= \delta c^{(1)}(\vec{r}) / \delta \rho^{(1)}(\vec{r}'') = (\delta / \delta \rho^{(1)}(\vec{r}'')) \{ \ln \rho^{(1)}(\vec{r}) / \tilde{z}(\vec{r}) \} \\ &= (1 / \rho^{(1)}(\vec{r})) \delta(\vec{r} - \vec{r}'') - \delta \ln \tilde{z}(\vec{r}) / \delta \rho^{(1)}(\vec{r}''), \end{aligned} \quad (23)$$

a two-point function which bears a clear inverse relationship to $h^{(2)}(\vec{r}, \vec{r}')$ through the equation

$$h^{(2)}(\vec{r}, \vec{r}') = c^{(2)}(\vec{r}, \vec{r}') + \int_V \vec{dr}'' \rho^{(1)}(\vec{r}'') c^{(2)}(\vec{r}, \vec{r}'') h^{(2)}(\vec{r}'', \vec{r}') \quad (24)$$

which follows from (23), from (13) recast in the form

$$\frac{\delta \rho^{(1)}(\vec{r})}{\delta \phi^{(1)}(\vec{r}')} = -\beta \{ \rho^{(1)}(\vec{r}) \rho^{(1)}(\vec{r}') h^{(2)}(\vec{r}, \vec{r}') + \delta(\vec{r} - \vec{r}') \rho^{(1)}(\vec{r}) \},$$

and from the functional identity

$$\delta(\vec{r} - \vec{r}') = \delta \ln \tilde{z}(\vec{r}) / \delta \ln \tilde{z}(\vec{r}') = \int_V \vec{dr}'' \frac{\delta \ln \tilde{z}(\vec{r})}{\delta \rho^{(1)}(\vec{r}'')} \frac{\delta \rho^{(1)}(\vec{r}'')}{\delta \ln \tilde{z}(\vec{r}')}.$$

In the limit of a uniform fluid (both $\phi^{(1)} \rightarrow 0$ and $\rho^{(1)}(\vec{r}) = \rho^{(1)}$) equation (24) reduces to the standard Ornstein-Zernike equation. For a system which is both rotationally and translationally invariant, it takes the form

$$h_0^{(2)}(r) = c_0^{(2)}(r) + \rho^{(1)} \int_V \vec{dr}' c_0^{(2)}(\vec{r} - \vec{r}') h_0^{(2)}(r'), \quad (25)$$

where $c_0^{(2)}(r)$ is the equally standard Ornstein-Zernike function. Its Fourier transform satisfies

$$c_0^{(2)}(k) = (1 / \rho^{(1)}) (1 - 1 / S^{(2)}(k)),$$

where $S^{(2)}(k)$, or more commonly $S(k)$, is defined by

$$S^{(2)}(k) - 1 = \int_V \vec{dr} \rho^{(1)} e^{i\vec{k} \cdot \vec{r}} h_0^{(2)}(r)$$

and is generally measurable over a wide range of k , depending on method. Accordingly, from

$$c_0^{(2)}(r) = (1 / 2\pi^2 \rho^{(1)}) \int_0^\infty k^2 dk (\sin kr / kr) (1 - 1 / S^{(2)}(k)),$$

then except for the critical regime the Ornstein-Zernike function can be constructed from a measured quantity, and it is generally seen to reflect the range of interactions

in the system. From successive functional differentiation of $c^{(2)}(\vec{r}, \vec{r}')$ with respect to $\rho^{(1)}(\vec{r})$ a sequence of higher-order direct correlation functions $c^{(3)}, c^{(4)}, \dots$, etc. can be obtained, and their homogeneous counterparts $c_0^{(3)}, c_0^{(4)}, \dots$ then follow from the limit $\rho^{(1)}(\vec{r}) \rightarrow \rho^{(1)}$. As shown in the Appendix, density functional theory is a compact and direct route to the theory of homogeneous fluids; the $c_0^{(n)}$ just introduced enters into the definition of the *bridge-function* of that theory.

The Ornstein–Zernike function plays a very important role in the theory of inhomogeneous classical systems and is part of the primary input for many applications. Because of the inverse relationship between $c^{(2)}$ and $h^{(2)}$, and the direct relation of the latter to the linear response function, we have

$$c_0^{(2)}(k) = \beta\{1/\chi_0^{(2)}(k) - 1/\chi_{ni}^{(2)}(k)\}, \quad (26)$$

where $\chi_{ni}^{(2)}(k) = -\beta\rho^{(1)}$ is the response function for the non-interacting system. If the system is inhomogeneous, we find from the defining relation (23), and from (16) that

$$c^{(2)}(\vec{r}, \vec{r}') = -\beta\phi^{(2)}(\vec{r}, \vec{r}') - \frac{\delta^2}{\delta\rho^{(1)}(\vec{r})\delta\rho^{(1)}(\vec{r}')} \left\{ \frac{\beta}{2} \int_V \vec{dr} \int_V \vec{dr}' \rho^{(1)}(\vec{r}) \rho^{(1)}(\vec{r}') \bar{h}^{(2)}(\vec{r}, \vec{r}') \right\}$$

for non-singular interactions. The second term obviously reflects correlation in the system and if conditions on density or argument are imposed so that this term is small, then for either the inhomogeneous system, or its homogeneous counterpart, the result is $c^{(2)} \rightarrow -\beta\phi^{(2)}$. Finally, given that $c^{(1)}$ in the functional integral (21) can itself now be obtained by a further functional integral over $c^{(2)}$, the excess free energy can also be given as

$$\begin{aligned} \beta\mathcal{F}_{\text{exc}}[\rho^{(1)}(\vec{r})] &= \beta\mathcal{F}_{\text{exc}}(\tilde{\rho}) - \int_V \vec{dr} \rho^{(1)}(\vec{r}) \int_V \vec{dr}' \int_0^1 d\lambda (\lambda \rho^{(1)}(\vec{r}') - \tilde{\rho}) \\ &\quad \times \int_0^1 d\lambda' c^{(2)}(\vec{r}, \vec{r}'; [\tilde{\rho} + \lambda'(\lambda \rho^{(1)}(\vec{r}') - \tilde{\rho})]), \end{aligned} \quad (27)$$

where once more there is an assumption that $c^{(2)}$ exists at all points along a certain path. In the present case it is again a linear path starting from a homogeneous state with density $\tilde{\rho}$, and terminating in an inhomogeneous state with density $\rho^{(1)}(\vec{r})$. Equation (27) is an important initiating point for the exercise that follows below, namely the development of the thermodynamic functions of inhomogeneous systems from a knowledge of the thermodynamic and correlation functions of their homogeneous counterparts.

Before proceeding it may be useful to note that although the development sketched above has been carried out with classical systems in mind, the strategies themselves can be repeated, almost unchanged, in the quantum domain. The application of density functional methods to the freezing of quantum liquids originated with McCoy *et al.* (1989, 1990) who introduced a quantum direct correlation function. If $E_{\text{exc}}[\rho^{(1)}(\vec{r})]$ is the excess internal energy in the ground state of a quantum system (excess to the energy of non-interacting particles

subject to the same imposed density $\rho^{(1)}(r)$, then the parallel of the classical direct correlation function is the quantity

$$\delta^2 E_{\text{exc}}[\rho^{(1)}]/\delta\rho^{(1)}(\vec{r})\delta\rho^{(1)}(\vec{r}')$$

which, in the limit of a homogeneous quantum liquid ($\rho^{(1)}(\vec{r}) \rightarrow \rho^{(1)}$), can be taken as a function $v_0^{(2)}(|\vec{r} - \vec{r}'|; \rho^{(1)})$. It is clearly the analog of the classical Ornstein-Zernike function, and by the arguments leading to (26) just as clearly related to the linear response function for the Bose or Fermi liquid, as the case may be. Therefore, the transcription discussed next for the classical system has a direct parallel for quantum systems, for example, as in the treatment of the freezing of hard-sphere bosons (Denton *et al.* 1990) and fermions (Moroni and Senatore 1991).

4. Transcribing Inhomogeneous Systems onto Homogeneous Systems

For a non-interacting but inhomogeneous system characterised by a one-particle density $\rho^{(1)}(\vec{r})$, the excess free energy (see equation 2) is

$$\mathcal{F}_{ni} = \mathcal{F}_{ni}[\rho^{(1)}(\vec{r})] = \int_V \vec{d}r \rho^{(1)}(\vec{r}) f_{ni}^0(\rho^{(1)}(\vec{r}))$$

which as already stated expresses an intuitive physical idea, namely that the $\rho^{(1)}(\vec{r})\vec{d}r$ particles in the volume element $\vec{d}r$ are each assigned an ideal homogeneous free energy $f_{ni}^0(\rho^{(1)}(\vec{r}))$ as if, in addition to position $\vec{r}$, the system were wholly uniform at a density $\rho^{(1)}(\vec{r})$. For an interacting classical system the equivalent proposition

$$\mathcal{F}_{\text{exc}} = \mathcal{F}_{\text{exc}}[\rho^{(1)}(\vec{r})] = \int_V \vec{d}r \rho^{(1)}(\vec{r}) f_{ni}^0(\rho^{(1)}(\vec{r})) \quad (28)$$

is no longer tenable, as recognised by Van der Waals who observed that in addition to a knowledge of f^0 at a point it was also necessary to know the corresponding gradients. However, some quite general forms of approximate equivalents to (28) can be advanced, in particular

$$\mathcal{F}_{\text{exc}} = N f_{ni}^0(\bar{\rho}^{(1)}), \quad (29)$$

$$\mathcal{F}_{\text{exc}} = \int_V \vec{d}r \rho^{(1)}(\vec{r}) f_{ni}^0(\bar{\rho}^{(1)}(\vec{r})). \quad (30)$$

In both, the excess free energies are given in terms of homogeneous system properties; in (29) a positionally independent effective density is involved, whereas in (30) it is clearly spatially varying. We may observe that an antecedent of this equation is already found in (15) which can be formally rewritten as

$$\mathcal{F}[\rho^{(1)}(\vec{r})] = \mathcal{F}_{ni}[\rho^{(1)}(\vec{r})] + \int_V \vec{d}r \rho^{(1)}(\vec{r}) \tilde{f}(\vec{r}; [\rho^{(1)}(\vec{r})]),$$

where

$$\tilde{f}(\vec{r}; [\rho^{(1)}(\vec{r})]) = \frac{1}{2} \int_V \vec{d}r' \rho^{(1)}(\vec{r}') \bar{g}^{(2)}(\vec{r}, \vec{r}') \phi^{(2)}(\vec{r} - \vec{r}').$$

At this juncture we would be entitled to ask whether, for the selected point $\vec{r}$, this quantity $\tilde{f}$ could be obtained in principle as a *particular* value of the known free energy per particle of the corresponding homogeneous fluid, itself prescribed by a certain density. Thus, at identical temperatures we should seek a certain density $\tilde{\rho}$ such that

$$\tilde{f}(\vec{r}; [\rho^{(1)}(\vec{r})]) = f^0(\tilde{\rho}^{(1)}),$$

and if this is achievable (i.e. the homogeneous fluid is stable at $\tilde{\rho}$) then we move to a point neighbouring $\vec{r}$ and repeat the process, mapping out thereby the function

$$\tilde{\rho}^{(1)}(\vec{r}) = \tilde{\rho}^{(1)}(\vec{r}; [\rho^{(1)}(\vec{r})])$$

whose functional dependence on the physical one-particle density $\rho^{(1)}(\vec{r})$ is quite evident. The simplest functional dependence (i.e. a proposed relation between $\tilde{\rho}$ and $\rho^{(1)}$) was given by Tarazona (1984). In general this dependence must reflect any fundamental differences in phases, as mirrored in physical forms of $\rho^{(1)}(\vec{r})$. An example we shall come to below is the crystal, a solid phase which, like glasses, supports static shear distortions. Depending on the symmetry of such a crystal the definition of shear distortion can require the specification of the coordinates of four or five particles, or of correspondingly high correlation functions when cast in a statistical framework. If a structured phase of this character is to be mapped onto an equivalent homogeneous state, then the nature of the mapping is required to be such as to ensure that information taken from the uniform phase must propagate to correlation functions whose order matches the domain where distinctions between solid and liquid are being made (here via the strain characteristics). Theories of an iterative or self-consistent nature can achieve precisely this goal and this therefore argues that approximations to $\tilde{\rho}^{(1)}(\vec{r}) = \tilde{\rho}^{(1)}(\vec{r}; [\rho^{(1)}(\vec{r})])$ should be both self-consistent and non-local. The reason for the latter is that given the identity of particles, and the fact that on the scale of the nearest neighbour separation the distinctions between configurations of the dynamic crystal and those of the liquid are then considerably blurred, averging of a non-local character will very much preserve this aspect.

To illustrate the origins of (29) within density-functional theory, consider a classical system sustaining an inhomogeneous one-particle density $\rho^{(1)}(\vec{r})$. If we select a path $\lambda\rho^{(1)}(\vec{r})$ ($0 \leq \lambda \leq 1$) then we may write the excess free energy as

$$\beta\mathcal{F}_{\text{exc}}[\rho^{(1)}(\vec{r})] = - \int_V \vec{dr} \rho^{(1)}(\vec{r}) \int_0^1 d\lambda c^{(1)}(\vec{r}; [\lambda\rho^{(1)}(\vec{r})]).$$

But if we also select a (so far unspecified) uniform density $\tilde{\rho}^{(1)}$ and a second path $\lambda\tilde{\rho}^{(1)} + \lambda'[\lambda\rho^{(1)}(\vec{r}) - \lambda\tilde{\rho}^{(1)}]$, for $0 \leq \lambda' \leq 1$, then following the strategy of Kroll and Laird (1990)

$$\begin{aligned} \beta\mathcal{F}_{\text{exc}}[\rho^{(1)}(\vec{r})] &= \beta\mathcal{F}_{\text{exc}}(\tilde{\rho}^{(1)}) - \int_V \vec{dr} \rho^{(1)}(\vec{r}) \int_V \vec{dr}' (\rho^{(1)}(\vec{r}') - \tilde{\rho}^{(1)}) \\ &\times \int_0^1 d\lambda \lambda \int_0^1 d\lambda' c^{(2)}(\vec{r}, \vec{r}'; [\lambda(\tilde{\rho}^{(1)} + \lambda'(\rho^{(1)}(\vec{r}) - \tilde{\rho}^{(1)}))]). \end{aligned} \quad (31)$$

With this form it is apparent that in principle a particular value of $\tilde{\rho}^{(1)}$ can be chosen so that the second term in (31) vanishes, leaving

$$\beta\mathcal{F}_{\text{exc}}[\rho^{(1)}(\vec{r})] = \beta\mathcal{F}_{\text{exc}}(\tilde{\rho}^{(1)})$$

as in (29). The chosen value of $\tilde{\rho}^{(1)}$ then necessarily enters the argument of $c^{(2)}$ in the second term of (31) and this is the formal origin of an important self-consistency condition that we shall soon encounter, but one whose necessity was argued above on physical grounds.

The requisite effective density is given by

$$\tilde{\rho}^{(1)} = \int_V \vec{dr} \rho^{(1)}(\vec{r}) \int_V \vec{dr}' \rho^{(1)}(\vec{r}') \omega(\vec{r}, \vec{r}'; \tilde{\rho}^{(1)}; [\rho^{(1)}(\vec{r})]) \quad (32)$$

and is written in a form that emphasises the double weighting of the physical density by a weight function $\omega(\vec{r}, \vec{r}'; \tilde{\rho}^{(1)}; [\rho^{(1)}(\vec{r})])$. It is here both a functional of the one-particle density itself, and a function of the sought for weighted density. From (31) it is seen that

$$\omega(\vec{r}, \vec{r}'; \tilde{\rho}^{(1)}; [\rho^{(1)}(\vec{r})]) =$$

$$W(\vec{r}, \vec{r}'; \tilde{\rho}^{(1)}; [\rho^{(1)}(\vec{r})]) \Big/ \int_V \vec{dr} \rho^{(1)}(\vec{r}) \int_V \vec{dr}' \rho^{(1)}(\vec{r}') W, \quad (33)$$

with

$$W(\vec{r}, \vec{r}'; \tilde{\rho}^{(1)}; [\rho^{(1)}(\vec{r})]) =$$

$$\int_0^1 d\lambda \lambda \int_0^1 d\lambda' c^{(2)}(\vec{r}, \vec{r}'; [\lambda(\tilde{\rho}^{(1)} + \lambda'(\rho^{(1)}(\vec{r}) - \tilde{\rho}^{(1)}))]). \quad (34)$$

In this form, the importance of the Ornstein–Zernike function in determining the weight function and its range is quite evident. We may note that $c^{(2)}(\vec{r}, \vec{r}')$ can itself be obtained by a further functional integral along yet a third chosen path, say $\tilde{\rho}^{(1)} + \lambda''(\lambda\rho_{\lambda'}^{(1)} - \tilde{\rho}^{(1)})$, where $\rho_{\lambda'}^{(1)}(\vec{r}) = \tilde{\rho}^{(1)} + \lambda'(\rho^{(1)}(\vec{r}) - \tilde{\rho}^{(1)})$. This procedure introduces the third-order direct correlation function into the specification of $\tilde{\rho}^{(1)}$, an extension which is in fact useful for the treatment of inhomogeneous systems with long-range interactions (Likos and Ashcroft 1992).

For the present we will persist with systems with short-range interactions where knowledge of $c^{(2)}$ is mainly required. Then the simplest implementation of (32) which embodies the essential requirement of self-consistency is to invoke a local approximation to $\omega(\vec{r}, \vec{r}')$; i.e.

$$\tilde{\rho}^{(1)} = \int_V \vec{dr} \rho^{(1)}(\vec{r}) \int_V \vec{dr}' \rho^{(1)}(\vec{r}') w(\vec{r} - \vec{r}'; \tilde{\rho}^{(1)}), \quad (35)$$

which is the form given by Denton and Ashcroft (1989). Together with (29), and a condition for determining w , it is known as the modified weighted density approximation (MWDA). The weighted density approximation itself (the WDA, Curtin and Ashcroft 1985) generally refers to the positionally dependent equivalent (equation 30), and the equivalent to (35) can be obtained by arguments similar

to those given above, as also shown by Kroll and Laird (1990) and Meister and Kroll (1985). The various forms of weighted or effective density approximations (for example, Nordholm *et al.* 1980; Tarazona 1984; Baus and Colot 1985) have been critically discussed in the reviews cited above. Both positionally dependent and positionally independent approaches require a strategy for the determination of the weight function w . This follows most readily from the necessity that in the uniform limit the Ornstein-Zernike function for the homogeneous system is given by

$$c_0^{(2)}(\vec{r} - \vec{r}'; \tilde{\rho}^{(1)}) = \lim_{\rho^{(1)}(\vec{r}) \rightarrow \tilde{\rho}^{(1)}} (\delta^2 \beta \mathcal{F}_{\text{exc}} / \delta \rho^{(1)}(\vec{r}) \delta \rho^{(1)}(\vec{r}'))$$

and if $\mathcal{F}_{\text{exc}}$ is now given by the *approximate* form (29) and with $\tilde{\rho}^{(1)}$ determined by equations (32)–(34). This leads to a condition on the Fourier transform of w , namely

$$\omega(k; \tilde{\rho}^{(1)}) = (-1/2f'_0(\tilde{\rho})) \{k_B T c_0^{(2)}(k; \tilde{\rho}^{(1)}) + \delta_{k,0} f''_0(\tilde{\rho}^{(1)})\}, \quad (36)$$

where the presence of the $k = 0$ term guarantees that the compressibility sum rule is satisfied, i.e.

$$-k_B T c_0^{(2)}(k \rightarrow 0; \tilde{\rho}^{(1)}) = 2f'_0(\tilde{\rho}^{(1)}) + \hat{\rho}^{(1)} f''_0(\tilde{\rho}^{(1)}). \quad (37)$$

Here f_0 is the excess free energy per particle of the homogeneous phase.

The MWDA is now completely specified [equations (29), (35) and (36)]; it is an approximation that transcribes the thermodynamic properties of a classical inhomogeneous system specified by a one-particle density $\rho^{(1)}(\vec{r})$, onto those of an equivalent homogeneous system with effective density $\tilde{\rho}^{(1)}$. It does so in a way that preserves the exact hierarchy relation

$$d/d\rho^{(1)} \{c^{(n)}(\vec{r}_1, \dots, \vec{r}_n)\} = \int_V d\vec{r}_{n+1} c^{(n+1)}(\vec{r}_1, \dots, \vec{r}_{n+1})$$

and it also does so in a way that includes terms to all orders. The steps leading to this approximation have assumed that the inhomogeneities are of a non-localised or distributed nature (an example is the crystalline phase, to be discussed below). Evans (1992) has emphasised that this type of approximation is not necessarily well suited to physical situations where the inhomogeneities are localised (or in the terminology here, non-distributed), as in wetting transitions or in the growth of films. It appears to be more promising in its treatment of true bulk properties, such as the transitions between equilibrium phases, though its ability to discriminate between such phases is evidently dependent on the nature of $\phi^{(2)}(\vec{r})$.

5. Density Functional Approaches for Periodic Systems

It was noted earlier that if the external potential was systematically reduced to near vanishing values, there is nevertheless the possibility of an emergent self-consistently sustained inhomogeneous state with a density given by

$$\rho^{(1)}(\vec{r}) = \rho_0 \exp\{c^{(1)}(\vec{r}; [\rho^{(1)}(\vec{r})]) - c_0^{(1)}\}. \quad (38)$$

Familiar practical examples might now include equilibrium glassy structures, quasicrystals (in multi-component systems) and, for the case that is of most interest here, periodic crystalline phases. For the simplest of these, monatomic systems in Bravais lattices, the one-particle density $\rho^{(1)}(\vec{r})$ and first-order direct correlation function $c^{(1)}(\vec{r})$ of such dynamic structures satisfy simple discrete translation symmetries, namely

$$\rho^{(1)}(\vec{r} + \vec{R}) = \rho^{(1)}(\vec{r}), \quad c^{(1)}(\vec{r} + \vec{R}) = c^{(1)}(\vec{r})$$

for all vectors $\{\vec{R}\}$ in the lattice. Their Fourier transforms $\rho^{(1)}(\vec{k})$ and $c^{(1)}(\vec{k})$ therefore vanish unless $\vec{k}$ is a vector belonging to the reciprocal lattice $\{\vec{K} : \exp(i \vec{K} \cdot \vec{R}) = 1, \forall \vec{R}\}$.

Under common thermodynamic conditions where the crystal is the stable phase, it is a matter of observation that for the standard bonding types (metals, molecular crystals, etc.) the root-mean square displacements of atoms are generally a quite small fraction of nearest-neighbour separations. For this reason the harmonic expansion of the crystalline renditions of (10) or (11) generates an acceptable alternative Hamiltonian for describing the dynamic crystalline state. The corresponding collective excitations are then phonons, and for these a suitable approximation to $\rho^{(1)}(\vec{r})$ is a sum of Gaussians, i.e.

$$\rho^{(1)}(\vec{r}) = (\alpha/\pi)^{\frac{3}{2}} \sum_{\vec{R}} \exp\{-\alpha(\vec{r} - \vec{R})^2\}. \quad (39)$$

Comparison with (38) shows that, near the sites $\{\vec{R}\}$, $c^{(1)}(\vec{r})$ is quadratic in displacement, something which we now expect from its earlier interpretation as an effective one-body potential. Notice that α^{-1} is a measure of the mean-square displacement, and directly related to derivatives of the pair interaction $\phi^{(2)}$. More generally the exponents in (39) can be cast in quadratic forms which reflect point-group symmetries lower than those assumed here.

In applications of density functional theory to first order phase transitions involving crystals, the principal assumption is that the general transcriptions described in Section 4 apply even if there is a non-trivial change in the symmetry when proceeding from one phase to another. For most physical forms of $\phi^{(2)}(\vec{r})$ that lead to *self-stabilised* matter, a crystalline phase can appear under appropriate conditions of density and temperature. The characteristics required of $\phi^{(2)}(\vec{r})$ are normally the presence of a strongly repulsive region at short range, and a longer range attractive region of sufficient strength. If the interactions fall in this class, the Hamiltonian can be reformulated for the anticipated broken symmetry, as noted, and it is usually carried out at the level of a harmonic approximation established about equilibrium sites that very much reflect the minimum in $\phi^{(2)}(\vec{r})$. However, it is also well established that crystalline phases exist for forms of $\phi^{(2)}(\vec{r})$ that are wholly repulsive, providing only that the system is stabilised externally, by application of appropriate pressure. Familiar examples are the Yukawa interaction and the inverse power potentials, $a(\sigma/r)^n$. For the latter it is also well known that the static structure factors of such systems placed under comparably dense conditions differ surprisingly little. Fig. 1 shows the limiting cases $n = \infty$, the hard spheres, and $n = 1$, the one-component plasma, both near their respective freezing points. However, the details of the underlying dynamics can be quite another matter.

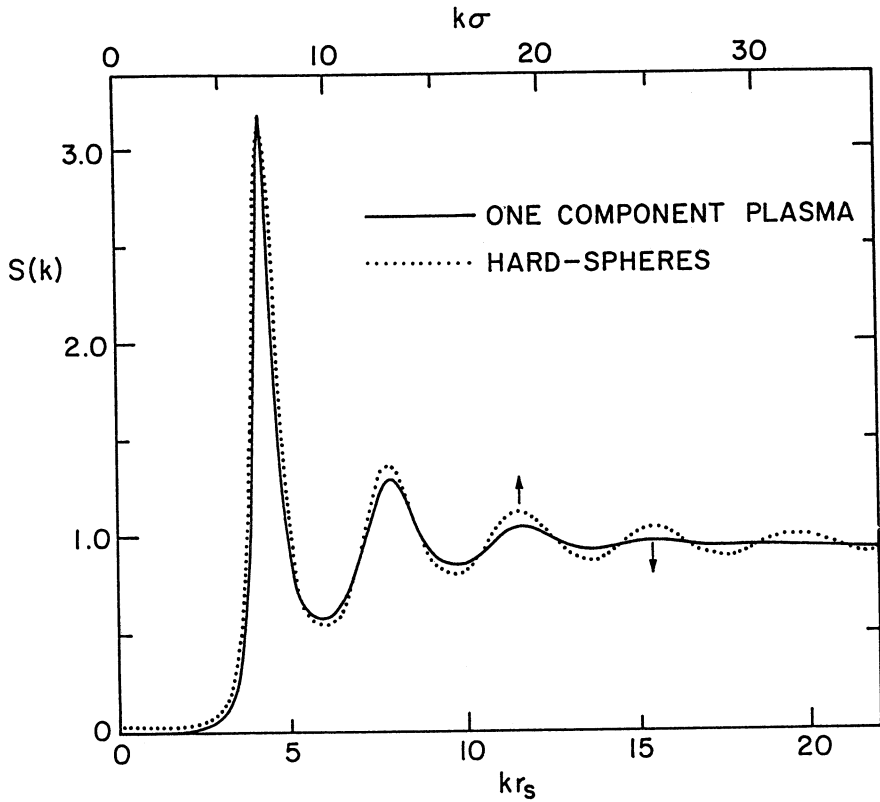


Fig. 1. Static structure factor for the one-component plasma close to melting conditions (Young *et al.* 1991): solid curve. Here r_s is the radius of the ion sphere. The dotted curve is the static structure factor, also determined near melting (packing fraction ≈ 0.49) and given by the solution to the Percus-Yevick equation. Here σ is the hard-sphere diameter. Note that the upper and lower abscissa scales are different.

In its relation to real systems, and particularly from the standpoint of the accepted descriptions of lattice dynamics, the hard-sphere crystal must be seen as anomalous, even though simulation studies reveal that its one-particle density can be quite accurately described by a sum of Gaussians, as in equation (39). No expansion of its Hamiltonian in orders of displacement from time-average equilibrium sites exists; it is completely anharmonic, and the system is perhaps better regarded as a collisional crystal. Because of this, it is expected that between collisions the motions of the particles in this crystal should exhibit a rapidly diminishing coherence, from one cell to another. This stands in considerable contrast to the motion expected in the familiar harmonic limit of lattice dynamics where coherence of this motion, via the phonons, is established over long distances. Van Hove (1954) was evidently the first to note that within the harmonic model $\rho^{(1)}(\vec{r})\rho^{(1)}(\vec{r}')h^{(2)}(\vec{r},\vec{r}')$ falls at long distances as approximately $|\vec{r} - \vec{r}'|^{-1}$.

This important difference in the mechanics of the hard-sphere system can be pursued a little further: between collisions, the ballistic motion of freely moving atoms is actually no different from the corresponding motions in the fluid. What is different is that in the solid the average domain of motion of a given atom is constrained. It is a domain that has dimensions which for hard-sphere interactions

are also shared by the range of the direct correlation function $c^{(2)}$, a quantity which, as we have noted, enters the weight function in the construction of effective densities. Evidently within this range of averaging (a near neighbour distance or so) the *character* of the dynamics of the collisional hard-sphere crystal cannot differ markedly from what is found in the liquid.

This similarity does not necessarily persist for other systems and the importance of the role played in density functional theory by the attractive components of realistic interactions has been emphasised by Sokolowski and Fischer (1992). But, if for example we continue with the inverse power potentials, it is clear that as n in $a(\sigma/r)^n$ falls towards values more typical of short-range interactions in real matter (say $n \sim 10$) then providing a is also reasonable the anharmonic content of the motion is expected to fall (i.e. coherence of motion is expected to rise). By this argument the local mechanics typical of the liquid are then no longer characteristic of the solid, as they are in a limited sense for the completely anharmonic case. However, the character of the interaction enters in another important way: as n falls to even lower values, say to the dimensionality, or below, then the range of $c^{(2)}$ also grows accordingly, and the averaging domain encountered in the construction of weighted densities is then expected to encompass ever increasing volumes. A physical consequence of this is that the implications (relative to the homogeneous state) of starting with densities $\rho^{(1)}(\vec{r})$ originating with a highly structured phase must begin to diminish, a line of reasoning that suggests that the practical implimentation of coarse-graining or weighted density approaches to the construction of thermodynamic functions is likely to face difficulties if limited strictly to the lowest order of approach.

And so it proves; the applications of weighted density and related methods to the melting problem has seen only limited success for ‘softer’ interactions (Evans 1992). In the case of the plasma ($n = 1$, together with necessary background terms) some additional discrimination between phases can be achieved by inclusion of $c^{(3)}$ in the construction of the weighted density (see below). As will be argued later, it may well be that in the full treatment of realistic systems, the inclusion of at least $c^{(3)}$ will be a necessary pursuit. For these reasons the hard-sphere system, though a useful qualitative paradigm (as it has been for fluids) is not a reliable predictor of a realistic theory of melting. We need only consider the fact that for hard spheres under isochoric conditions entropy decreases on passing from solid to liquid phases, whereas for simple systems in nature it generally increases.

In the approach to the melting problem, the theory is used in a straightforward way to obtain thermodynamic functions of the crystalline phase using complete knowledge for the thermodynamic functions, and as noted, certain low-order correlation functions for the continuous phase. Liquids and crystals represent nearly isochoric phases of *identical* particles in which average coordination numbers are also often extremely close. Thus from the local point of view, and on appropriate timescales of re-arrangement, the dense liquid and solid bear certain physical similarities though, as noted, not necessarily in their local dynamics. An elementary rewriting of the internal energy of an inhomogeneous system with pairwise interactions emphasises this point. Thus

$$E = N \left\{ \frac{3}{2} k_B T + \frac{1}{2N} \int_V \vec{dr} \int_V \vec{dr}' \rho^{(2)}(\vec{r}, \vec{r}') \phi^{(2)}(\vec{r} - \vec{r}') \right\} \quad (40)$$

can be written as

$$E = N \left\{ \frac{3}{2} k_B T + \frac{1}{2} \int_V \vec{d}r \rho^{(1)} \tilde{g}^{(2)}(\vec{r}) \phi^{(2)}(r) \right\}, \quad (41)$$

where $\tilde{g}^{(2)}(r)$ is given by

$$\tilde{g}^{(2)}(r) = \int (d\Omega/4\pi) \int_V (\vec{d}r' / V) \rho^{(2)}(\vec{r} + \vec{r}', \vec{r}') / (\rho^{(1)})^2 \quad (42)$$

with solid angle being measured from the pole $\hat{r}$. Though the entropy is quite different, equation (41) emphasises the fact that the internal energy can be formally rewritten in a manner entirely equivalent to that expected for a dense homogeneous fluid. Starting with known forms of $\rho^{(2)}(\vec{r}, \vec{r})$, the *major* structure of the corresponding $\tilde{g}^{(2)}$ in, for example, crystalline systems, is quite comparable to that found in the dense fluid state.

Guided by the harmonic approximation the one particle density for an otherwise perfect crystalline phase is given by (39) and is also taken to have this form for the hard-sphere limiting case (reflecting what is known from simulation studies). We may note that the stipulation of $\rho^{(1)}(\vec{r})$ involves the structure of the emerging lattice (which is not presaged by the theory). In recognition of the fact that (39) can at best be approximate, and that the theory itself is limited, the quantity α is taken as a variational parameter, the intent being to obtain a bound on the free energy of the structured phase. To illustrate the practical implementation of the manner in which a crystal is transcribed onto an equivalent homogeneous liquid, we first note that the periodic solid conforms to the requirements of distributed inhomogeneity. Accordingly, starting with (35) and (39) we may seek an equivalent uniform phase, with density $\tilde{\rho}^{(1)}$ where

$$\tilde{\rho}^{(1)} = \rho^{(1)}(N\omega(0)) + \frac{1}{V} \sum_{\vec{K} \neq 0} \omega(\vec{K}; \tilde{\rho}^{(1)}) \rho^{(1)}(\vec{K})^2.$$

Since the weight function is fixed by utilising properties of the transcription in the uniform limit (see 36) we therefore have the self-consistent equation

$$\tilde{\rho} = \rho^{(1)} \left[1 - (k_B T / 2 f'_0(\tilde{\rho}^{(1)}, \alpha)) \sum_{\vec{K} \neq 0} e^{-K^2/2\alpha} c_0^{(2)}(\vec{K}; \tilde{\rho}^{(1)}(\rho^{(1)}, \alpha)) \right]. \quad (43)$$

The free energy (and hence all thermodynamic functions) of the structured phase now follows from (29) when augmented by the contribution from non-interacting particles; it can be minimised with respect to α . It is important that the liquid state properties be accurate. For a detailed discussion on the somewhat variable performance of the second-order weighted density approximation to the melting problem, the reader is directed to the reviews cited earlier. As shown by Likos and Ashcroft (1992) the modified weighted density approximation can be extended to include the effects of the three-particle direct correlation function (see equation 33 and succeeding comments). The equivalent of (43) is then

$$\begin{aligned}
\tilde{\rho}^{(1)} = \rho^{(1)} & \left[1 - k_B T / 2 f'_0(\tilde{\rho}^{(1)}) \sum_{\vec{K} \neq 0} e^{-K^2/2\alpha} c^{(2)}(\vec{K}; \tilde{\rho}^{(1)}) \right. \\
& - k_B T / 6 f'_0(\tilde{\rho}^{(1)}) \sum_{\vec{K} \neq 0} \sum_{\vec{K}' \neq 0, -\vec{K}} e^{-K^2/4\alpha} e^{-K'^2/4\alpha} e^{-(\vec{K} + \vec{K}')^2/4\alpha} \\
& \left. \times c^{(3)}(\vec{K}, \vec{K}'; \tilde{\rho}^{(1)}) \right]. \tag{44}
\end{aligned}$$

A particularly important point concerning the application of (44) is that while for hard spheres ($n = \infty$) (43) already gives satisfactory results for the freezing problem, the third-order extension nevertheless leads to additional improvements. In the opposite extreme ($n = 1$) it is (44) that leads to freezing (for the one-component plasma) within the context of the modified weighted density approximation; (43) does not. This suggests that while the intent of density functional theory as applied generally to inhomogeneous systems has been to utilise correlation information from the homogeneous phase of low order (and particularly $c^{(2)}$) in applications to highly structured systems such as in the melting problem, inclusion of at least the third-order direct correlation function may be important as discussed above. Some relatively simple arguments can be brought to bear on this point, as follows:

6. Commentary

In applications of classical density functional theory to the melting problem, the major physical doubts must centre on the fundamental differences in symmetry that occur in passing from the liquid to the crystalline solid, or vice versa. Yet the theories appear to do quite well in describing this transition in the hard-sphere system. It has been suggested above that this may be linked to the degree of anharmonicity of the system under consideration, and to the associated range of the functions entering the construction of the weighted density, both aspects being tied to the fundamental nature of the pair interaction. Some substance can be given to this by noting that a traditional measure of anharmonic effects in dynamic crystals is provided by the Grüneisen parameter γ , which records the assignment of anharmonic terms to an effective volume dependence of otherwise harmonic frequencies. Within a Debye picture it is related to the logarithmic derivative of the normal mode frequencies with respect to volume. For the inverse power potentials simple scaling arguments (Hoover *et al.* 1971) show that $\gamma = (n + 2)/6$ so that as noted above, anharmonic contributions indeed rise with the ‘steepness’ of the potential. The connection that can now be made with density functional theory is this: in the crystalline phase, it is $c^{(1)}$ that is playing the role of an effective potential at each site being constructed, however, from a summation over all sites of a function bearing a close relation to the actual pair potential $\phi^{(2)}(\vec{r})$. Now it can be shown (McCarley and Ashcroft 1996) that a dynamic crystalline phase can be described within precisely the same statistical framework used for fluid (but non-uniform) phases. For a crystal there is an equation which parallels exactly the Ornstein–Zernike equation, but given in a

site oriented picture that simply exploits the fact that excursions of particles from sites are small in the crystalline phase. Moreover, an equivalent of the Percus identity (see the Appendix) can also be established in the crystalline phase and its consequence is that the resulting hypernetted-chain equation that it predicts is closely linked to the harmonic model of the crystal. The main point is that in this site oriented representation the direct-correlation function then possesses a close inverse relationship to the elements of the dynamic matrix, these being related to second derivatives of $\phi^{(2)}(\vec{r})$. The connection to $c^{(1)}(\vec{r})$ (expected from the functional route) is simply through the diagonal components summed over sites.

With this connection we may return to the role of anharmonicity, as embodied in the Grüneisen parameter. Changes in frequency with density are now seen to be related to equivalent changes in $c^{(2)}$ with density, but cast again in a site oriented picture. This introduces $c^{(3)}$, the third-order direct correlation function in the solid which should be directly related to anharmonicities. In arguing its connection to corresponding properties in the fluid, the role of the form of $\phi^{(2)}$ in controlling the range of weighting is also of considerable importance. Finally, we may note that if the emphasis now shifts to the triplet structure in representing structured systems in terms of the properties of the corresponding homogeneous phases then by the techniques outlined in the Appendix, the three-particle distribution is given by an extension of the Percus argument by

$$\begin{aligned} \vec{\nabla} \log\{g^{(3)}(0, \vec{r}, \vec{r}') \exp[-\beta(\phi^{(2)}(0, r) + \phi^{(2)}(0, r'))]\} \\ = - \int_V d\vec{r}'' \rho^{(1)} \nabla \beta \phi^{(2)}(|\vec{r} - \vec{r}''|) g^{(2)}(0, r'') g_{\phi}^{(3)}(\vec{r}, \vec{r}', \vec{r}'') / g_{\phi}^{(2)}(\vec{r}, \vec{r}'), \end{aligned} \quad (45)$$

where $g_{\phi}^{(3)}$ and $g_{\phi}^{(2)}$ are the triplet and pair functions respectively in the presence of a triplet-external potential whose form is precisely $\phi^{(2)}$.

Compared with the almost universal interest in continuous transitions and associated critical phenomena, first order transitions (the paradigm being melting) have evoked relatively modest theoretical effort. It may be noted that the weighted density approximations take a system with a given microscopic scale of inhomogeneity and produce one with a different spatially varying scale (in the WDA, for example) or even a constant density (as in the MWDA). In either case the starting system suffers a certain ‘thinning’ of its degrees of freedom, particularly those associated with the shortest wavelengths of inhomogeneity. However, the mapped system is still characterised by the same starting interactions (as we have seen, the solid is to be described in terms of the properties of the associated continuous phase). Apart from this latter point there is a certain similarity in viewpoint to the ideas underlying the renormalisation group, whose success with systems undergoing transitions between phases of continuous symmetry needs no further emphasis. Nevertheless, it can be asked whether as a more general possibility the renormalisation group framework is capable of describing both continuous and broken symmetry phase transitions. The possibility of applying renormalisation group techniques to first order-transitions in problems lacking obvious small parameters dates back almost to the beginning of the theory itself (Nienhuis and Nauenberg 1975), the implication being that the associated transformation might

develop additional singular structure near the phase instability points. It appears that this question is not completely resolved (Gawędzki *et al.* 1987), but we can see that if the formal basis of the positionally dependent weighted density mapping is rigorously established, then the emerging effective liquid (generally possessing a longer scale of inhomogeneity) could be mapped once again, and then the process repeated. Whether this will lead to a fixed point structure has yet to be seen.

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Appendix: Density Functional Theory and Uniform Fluids

If we take $\phi^{(1)}(\vec{r}) \rightarrow 0$, and choose thermodynamic conditions appropriately, uniform phases of systems governed by (10) or (11) develop. For temperatures less than the critical temperature, it is the dense fluid phase. Though homogeneous,

the density functional method for inhomogeneous systems has much to say about it. This follows from an observation of Percus (1962, 1964) that the one-particle density in response to an external potential whose form is taken as $\phi^{(2)}(0, r)$ (i.e. the pair interaction) is precisely $\rho^{(1)}g^{(2)}(0, r)$. From equation (19) this leads immediately to the conclusion that

$$g^{(2)}(r) = \exp\{-\beta\phi^{(2)}(r) + c^{(1)}(\vec{r}; [\rho^{(1)}(\vec{r})]) - c_0^{(1)}\},$$

where in $c^{(1)}(\vec{r}; [\rho^{(1)}(\vec{r})])$ the appropriate inhomogeneous density is now $\rho^{(1)}g^{(2)}(r)$. This strategy can be taken a step further; for example, let the 'external potential' $\phi^{(2)}(0, r)$ be located at the origin, and consider two points in the fluid at $\vec{r}$ and $\vec{r}'$. Then we may ask for the pair density at $\vec{r}$ and $\vec{r}'$, which by our earlier definition is

$$\rho^{(2)}(\vec{r}, \vec{r}') = \rho^{(1)}(\vec{r})\rho^{(1)}(\vec{r}')g_\phi^{(2)}(\vec{r}, \vec{r}'),$$

and since the particle supplying the 'external potential' $\phi^{(2)}(0, r)$ could be any of the N , then by the Percus (1964) argument we are actually asking for the probability of finding three particles at $(0, \vec{r}, \vec{r}')$ in the homogeneous fluid. Thus we get

$$g^{(3)}(0, \vec{r}, \vec{r}') = g^{(2)}(0, r)g^{(2)}(0, \vec{r}')g_\phi^{(2)}(\vec{r}, \vec{r}'),$$

a result also obtained independently by Attard in 1989. The familiar superposition approximation of Kirkwood is recovered by the statement $g_\phi^{(2)}(\vec{r}, \vec{r}') = g^{(2)}(|\vec{r} - \vec{r}'|)$. Notice that in terms of $g_\phi^{(2)}(\vec{r}, \vec{r}')$ the first of the Yvon-Born-Green hierarchy of equations becomes

$$\begin{aligned} \vec{\nabla} \log\{g^{(2)}(0, r)e^{\beta\phi^{(2)}(0, r)}\} &= - \int_V \vec{dr}' \rho^{(1)}g^{(2)}(0, r')g_\phi^{(2)}(\vec{r}, \vec{r}') \\ &\times \vec{\nabla}\beta\phi^{(2)}(|\vec{r} - \vec{r}'|), \end{aligned}$$

which offers additional routes to closure via propositions for $g_\phi^{(2)}(\vec{r}, \vec{r}')$ going beyond $g^{(2)}(|\vec{r} - \vec{r}'|)$. The next member of the hierarchy is obtained by similar reasoning and is given as equation (45).

Since the higher-order direct correlation functions can be obtained from $c^{(1)}(\vec{r})$ by repetitive functional differentiation, then the result of a functional Taylor expansion of $c^{(1)}(\vec{r})$ about the uniform density $\rho^{(1)}$ gives

$$\begin{aligned} c^{(1)}(\vec{r}; [\rho^{(1)}g^{(2)}(r)]) - c_0^{(1)} &= \sum_{n=1}^{\infty} (\rho^{(1)})^n / n! \int_V \vec{dr}_1 \cdots \int_V \vec{dr}_n \\ &\times c_0^{n+1}(\vec{r}; \vec{r}_1 \cdots \vec{r}_n; \rho^{(1)}) h_0^{(2)}(r_1) \cdots h_0^{(2)}(r_n). \end{aligned}$$

Alternatively, if we excerpt the first term in this sum, and for it use the Ornstein-Zernike equation appropriate to the uniform fluid (equation 25), then for $g^{(2)}(r)$ we have the relation

$$g^{(2)}(r) = \exp\{-\beta\phi^{(2)}(r) + c_0^{(2)}(r) - h_0^{(2)}(r) + b_0^{(2)}(r)\},$$

where

$$b_0^{(2)}(r) = \sum_{n=2}^{\infty} (\rho^{(1)})^n / n! \int_V \bar{d}\vec{r}_1 \cdots \int_V \bar{d}\vec{r}_n c_0^{n+1}(\vec{r}; \vec{r}_1 \cdots \vec{r}_n) h_0^{(2)}(r_1) \cdots h_0^{(2)}(r_n).$$

This new two point function $b_0^{(2)}(r) = b_0^{(2)}(0, r)$ is the *bridge function* of diagrammatic perturbation theory (Van Leeuwen *et al.* 1959). Since $c^{(2)}$ has an obvious functional relationship to $h^{(2)}$, and the $c^{(n)}$ are obtained by further functional differentiation of $c^{(2)}$ with respect to $\rho^{(1)}(\vec{r})$, it follows that

$$b_0^{(2)}(r) = b_0^{(2)}(\vec{r}; [h_0^{(2)}(r)]),$$

a result also established by Van Leeuwen *et al.* (1959). The result for $g^{(2)}$ may also be written

$$g^{(2)}(r) = \exp\{-\beta\tilde{\phi}^{(2)}(r) + h_0^{(2)}(r) - c_0^{(2)}\},$$

where $\tilde{\phi}^{(2)}(r) = \phi^{(2)}(r) - k_B T b_0^{(2)}(r)$ can be seen as an ‘effective’ interaction in an approximation that together with

$$h_0^{(2)}(r) - c^{(2)} = \int_V \bar{d}\vec{r}' \rho^{(1)} c_0^{(2)}(|\vec{r} - \vec{r}'|) h_0^{(2)}(r')$$

attempts closure. If the distinction between $\phi^{(2)}$ and $\tilde{\phi}^{(2)}$ is neglected, the resulting theory is the hypernetted-chain approximation. More generally it is possible to exploit the fact that for *dense* fluids $h^{(2)}(r)$ is relatively insensitive to the form of $\phi^{(2)}(r)$ under isochoric conditions. Closure can then be effected by assuming $b^{(2)}$ to be known for a chosen system, for instance for a system of hard spheres with diameters σ . Thus, for example, a theory of thermodynamics and structure follows from

$$g_0^{(2)}(r) = \exp\{-\beta\phi^{(2)}(r) + h_0^{(2)}(r) - c_0^{(2)}(r) + b_{\text{HS}}^{(2)}(r, \sigma)\},$$

$$h_0^{(2)}(r) - c_0^{(2)}(r) = \int_V \bar{d}\vec{r}' \rho^{(1)} c_0^{(2)}(|\vec{r} - \vec{r}'|) h_0^{(2)}(r'),$$

where $b_{\text{HS}}^{(2)}$ is the bridge function for a hard-sphere system with σ being determined variationally. This is the modified hypernetted-chain procedure and it appears satisfactory to the point of reproducing, with considerable accuracy (Young *et al.* 1991), even the one-component plasma structure factor as shown in Fig. 1. Given that near the critical point hierarchical models of liquid structure are now capable of reproducing non-classical critical exponents (Meroni *et al.* 1990) it would appear that for relatively simple systems the entire fluid range is presently within range of reasonable theoretical description.