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Structure and effective interactions in multi-component hard-sphere liquids: the fundamental-measure density functional approach*

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Abstract

Non-crystalline solids often emerge from melts with at least three atomic constituents. The study of packing aspects of melts that form glasses or quasi-crystals by investigating effective interactions in *multi-component* hard-sphere liquids is made possible by the geometrically based fundamental-measure density functional theory. It provides analytical approximations for the partial structure factors of the general *m-component* hard-sphere mixture (e.g. the Percus–Yevick approximation), and an accurate solution of the inverse scattering problem for obtaining the effective interactions. The fundamental-measure theory also enables one to extend such studies to more general (soft) interactions.

1. Introduction

Multi-component hard-sphere mixtures [1] serve as important reference systems in condensed matter [2], and are relevant for understanding the behaviour of polydisperse systems of practical interest, colloidal systems for example [3]. Recent studies of local size segregation and size selectivity for adsorption near a wall [4], inside spherical pores [5], and in narrow pores like ionic channels [6] have been carried out by employing the fundamental-measure density functional for multi-component hard-sphere mixtures [7]. The fundamental-measure density functional theory was also widely employed in studies of the depletion interactions in binary mixtures [8, 9], and was used to investigate the depletion interaction between two infinite planes and between two large spheres due to polydisperse mixtures of interacting small hard spheres [10].

* It is a great pleasure to contribute this paper to the issue in honour of Jean-Pierre Hansen. Like many others, I have benefitted from Jean-Pierre's wisdom and his famous 'nose' for research directions. But above all, he is a true friend.

¹ We are saddened by the death of Yasha Rosenfeld on 27 July 2002. Yasha died from lung cancer at the age of 54. He was a leading figure in theories of liquids and his fundamental measure approach to classical density functional theory has been one of the most significant contributions to the subject during the last decade.

Non-crystalline solids often emerge from melts with at least three atomic constituents, and in a recent work [11] (which was limited, however, by its methodology to the study of only the three-component mixture) it was pointed out that the study of packing aspects of melts that form glasses or quasi-crystals can be carried out by investigating effective interactions in *multi-component* hard-sphere liquids. The effective interaction between particles of species i is obtained by reinterpreting the diagonal partial structure factor, $S_{ii}(k)$, as an effective one-component structure factor for this effective (state-dependent) potential $\phi_{eff}(r)$ [11], $S_{ii}(k) = S_{eff}(k)$. This effective interaction represents a special case of the *depletion potentials* which appear in the literature on liquid mixtures and colloidal suspensions [8]. In order to obtain this effective potential $\phi_{eff}(r)$ from the given structure factor $S_{eff}(k)$, one needs to solve the classical inverse scattering problem. Many practical glasses are formed from melts that contain significant numbers of constituent elements (certainly more than three), and the investigations of packing aspects of melts that form glasses or quasi-crystals, as initiated for the three-component mixture [11], should be extended to more general mixtures. In accordance with trends presented in [11] for the ternary case, another depletion interaction study finds [10] that polydispersity has relatively little effect on the depletion attraction, but has considerable effect on the repulsive barrier and on the damping of subsequent oscillations. Indeed, a higher number of components, with variable relative concentrations and relative sizes, can lead to effective potentials with peculiar features (some of which appear already in the ternary case [11]), which inhibit the formation of a crystalline arrangement from the melt. The choice of parameters for study can perhaps be guided by recent experiments such as those on the effects of adding Si to quasi-crystal-forming Al–Cu–Fe alloys [13].

However, these studies require the availability of accurate partial structure factors for the relevant multi-component hard-sphere mixtures, and of an accurate method for solving the inverse scattering problem. The initial study [11] was limited to the ternary case. It was based on the structure factors obtained from the analytic solution of the Percus–Yevick (PY) integral equation for the three-component mixture by the Laplace transform method [1], which was presented as a major undertaking for obtaining a primary result upon which rested the foundation of that entire study. Furthermore, it employed the hypernetted-chain and PY closures for the inversion problem, while a significant improvement of these called [11] for an iterative method [14] involving simulations at each stage, which is impractical for the studies proposed above. On the other hand, it will be shown below how a general investigation for the multi-component hard-sphere mixtures is actually made possible by the geometrically based fundamental-measure density functional theory, which also provides a uniquely effective method for such studies: a brief review is presented here of how it provides analytical approximations for the partial structure factors of the general m -component hard-sphere mixture (e.g. the PY approximation [1, 12]), and how it yields an accurate efficient solution of the inverse scattering problem for obtaining the effective interactions.

Investigations of packing aspects of melts that form glasses or quasi-crystals are readily possible for *arbitrary* mixtures, by using the complete analytical expressions for the PY direct correlation functions of the general m -component hard-sphere mixture as obtained within the fundamental-measure theory [7]. In fact, three different but completely equivalent analytical expressions for the PY direct correlation functions will be presented. It will first be outlined how the PY direct correlation functions for an arbitrary hard-sphere mixture are obtained analytically in a very simple and physically transparent way by using the scaled-field-particle theory [15]. Specifically, it will be shown (section 2) how it becomes possible to obtain the solution of the PY equation for arbitrary mixtures given only the corresponding ‘compressibility’ equation of state given in [1]. This approach then leads (section 3) to the fundamental-measure density functional [7] which provides an even simpler analytic form for

the PY direct correlations, and also yields the so-called ‘bridge functional’ [16]. Furthermore, the same fundamental-measure density functional as yields the analytic solution of the PY equation (as described below) also offers (via the approximation of ‘universality of the bridge functional’ [16]) an accurate solution to the classical inverse scattering problem [17] even for ‘tough’ cases for which the PY and hypernetted-chain closures are considerably less accurate (section 4). All essential expressions are given (corrected for various typographical errors which appeared in previous papers) in order to make this paper self-contained regarding its application to the proposed calculations of the effective interactions, which thus become straightforward. Finally (section 5), it is indicated that due to more recent developments the fundamental-measure theory enables the extension of the proposed studies also to more general soft interactions.

2. Fundamental-measure scaled-field-particle theory: interconnecting the scaled-particle equation of state and the Percus–Yevick direct correlations

The idea for the fundamental-measure theory came from earlier work on integral equation theories for liquid structure. Analysis [18] of all major approximate theories of the structure and thermodynamics of simple liquids [2, 19] revealed that, in effect, they *interpolate* between the standard ‘ideal-gas’, low-density limit, and a high-density, ‘ideal-liquid’, limit [20], which corresponds to an Onsager-type lower bound for the potential energy. The ‘ideal-liquid’ limit is characterized by *single-particle geometries*, and the interpolation to the low-order diagrammatic expansion is achieved by mathematical constructs playing the role of ‘basis functions’ [20]. That limit maps universally [20] onto the corresponding limit for hard spheres, for which it is obtained from the solution of the PY integral equation (i.e. the mean-spherical approximation for hard spheres) [1, 12]. Indeed, the implementation of these general results for the inhomogeneous hard-sphere fluid mixture kept the geometric features to the forefront, with the *fundamental geometric measures* playing the role of *basis functions*: the basic idea was to interpolate between the ‘ideal-liquid’, high-density, limit where the pair direct correlation function is dominated by convolutions of single-particle geometries, i.e. overlap volume and overlap surface area, and the limit of low density where it is given by the pair-excluded volume, and by the overlap volume of pair-excluded volumes.

The two leading low-density terms in the diagrammatic expansion for the direct correlation functions of a general m -component hard-sphere mixture with number density $\rho_{i,0}$ and radius R_i for species i , are

$$c_{ij}(r = |\vec{r}_j - \vec{r}_i|) = f_{ij}(r) \left[1 + \sum_k \rho_{k,0} \text{---} \circ_i \text{---} \bullet_k \text{---} \text{---} \circ_j \right] + \dots \quad (1)$$

In the diagram, a line connecting two particles, say l and k , represents the Mayer function, $f_{lk}(|\vec{r}_l - \vec{r}_k|)$, which is equal to -1 if the particles l and k overlap, and zero otherwise, i.e. representing the pair-excluded volume. A black circle (i.e. ‘field particle’) denotes that one should integrate over all the positions of that particle. The three-particle diagram corresponds to the overlap volume of two pair-excluded volumes, i.e. the overlap volume of two spheres of radii $R_i + R_k$ and $R_j + R_k$ at distance r . Thus, in this notation, the ideal-liquid limit for hard spheres exhibits a behaviour of the type

$$c_{ij}(r = |\vec{r}_j - \vec{r}_i|)_{\text{ideal liquid}} \propto \lim_{R_k \rightarrow 0} [\text{---} \circ_i \text{---} \bullet_k \text{---} \text{---} \circ_j] = \Delta V_{ij}(r) \quad (2)$$

with a zero-radius limit for the field particle, corresponding to the overlap volume $\Delta V_{ij}(r)$ of the two spheres i and j at separation r . The interpolation proposed by the scaled-field-particle (SFP) theory [15] was achieved by *rescaling* the radius of the field particle in the diagram,

$R_k \rightarrow \lambda R_k$, and by approximating the direct correlation function by the four-parameter $\{A_1, A_2, A_3, \lambda\}$ form:

$$c_{ij}^{SFP}(r = |\vec{r}_j - \vec{r}_i|) = f_{ij}(r) \left\{ A_1 + A_2 \sum_k \rho_{k,0} \lim_{R_k \rightarrow \lambda R_k} [\circ \text{---} \text{---} \bullet \text{---} \text{---} \circ] \right. \\ \left. + A_3 \sum_k \rho_{k,0} \lim_{R_k=0} [\circ \text{---} \text{---} \bullet \text{---} \text{---} \circ] \right\}. \quad (3)$$

The corresponding compressibility equation of state as obtained from the standard relation

$$\chi_i \equiv \frac{\partial P}{k_B T \partial \rho_{i,0}} = 1 - \sum_j \rho_{j,0} \int c_{ij}(r) d^3r \quad (4)$$

exhibits the fundamental-measure form, namely [15]

$$\chi_i = \sum_{\alpha=0}^3 \chi^{(\alpha)}(\{n_{\alpha,0}\}) R_i^{(\alpha)} \quad (5)$$

where the coefficients are functions of only the four fundamental-measure reduced densities:

$$n_{\alpha,0} = \sum_j \rho_{j,0} R_j^{(\alpha)}, \quad \text{for } \alpha = 0, 1, 2, 3, \quad (6)$$

with

$$R_i^{(\alpha)} = 1, R_i, S_i, V_i \quad \text{for } \alpha = 0, 1, 2, 3, \text{ respectively}, \quad (7)$$

where $V_i = 4\pi R_i^3/3$, $S_i = 4\pi R_i^2$, R_i denote the volume, surface area, and radius (i.e. the fundamental geometric measures) of the particle i . Note, in particular, that $n_{3,0}$ is the total packing fraction. This type of equation of state can be represented by an excess free-energy density (Ω is the volume of the system)

$$\frac{F_{ex}}{\Omega k_B T} = \Phi(\{n_{\alpha,0}\}) \quad (8)$$

and pressure

$$\frac{P}{k_B T}(\{n_{\alpha,0}\}) = -\Phi + \sum_{\alpha} n_{\alpha,0} \frac{\partial \Phi}{\partial n_{\alpha,0}} + n_{0,0} \quad (9)$$

which are functions of only the four fundamental-measure reduced densities $\{n_{\alpha,0}\}$. The 4-coefficients

$$\chi^{(\alpha)}(\{n_{\alpha,0}\}) = \frac{\partial}{\partial n_{\alpha,0}} \frac{P}{k_B T}(\{n_{\alpha,0}\}) \quad (10)$$

fully determine the four parameters in the SFP direct correlation function (3):

$$\chi^{(0)} = A_1 + A_2 \lambda^3 n_{3,0}, \quad \chi^{(1)} = A_2 \lambda^2 n_{2,0}, \\ \chi^{(2)} = A_2 \lambda n_{1,0}, \quad \chi^{(3)} = (A_2 + A_3) n_{0,0}. \quad (11)$$

Moreover, geometric analysis of the diagrams in (3) reveals [15] that it can be represented by the following alternative simpler form:

$$c_{ij}^{SFP}(r) = f_{ij}(r) \{ \chi^{(3)} [\Delta V_{ij}(r)] + \chi^{(2)} [\Delta S_{ij}(r)] + \chi^{(1)} [\Delta \bar{R}_{ij}(r)] + \chi^{(0)} [\Theta((R_i + R_j) - r)] \} \quad (12)$$

where [15] $\Delta \Omega_{ij}(r)$, $\Delta S_{ij}(r)$, $\Delta \bar{R}_{ij}(r)$ are the overlap volume, overlap surface area, and overlap mean radius for two spheres with separation r .

Thus, the two SFP theory alternative expressions for the direct correlation functions, equations (3) and (12) + (11), provide an interconnection between the fundamental-measure equation of state, given e.g. by the excess free-energy density $\Phi(\{n_{\alpha,0}\})$, and the direct correlation function; but the equation of state is not yet determined and can be determined from further physical considerations. Indeed, the optimal fundamental-measure equation of state is that which corresponds to the scaled-particle theory [21]. The excess chemical potential $\mu_i^{ex} = \frac{\partial F_{ex}}{\partial N_i}$ corresponding to (8) has the form

$$\mu_i^{ex} = k_B T \sum_{\alpha} \left(\frac{\partial \Phi}{\partial n_{\alpha,0}} \right) R_i^{(\alpha)} = \mu_i^{(0)} + \mu_i^{(1)} R_i + \mu_i^{(2)} S_i + \mu_i^{(3)} V_i \quad (13)$$

where $\mu_i^{(\alpha)} = k_B T \frac{\partial \Phi}{\partial n_{\alpha,0}}$. Scaled-particle theory regards this expression as an *interpolation* between the exact limits of *small* ($\mu_i^{(0)} = -\ln(1 - \eta)$) and *large* ($\mu_i^{(3)} = P$) particle size:

$$\mu_i^{ex} = -\ln(1 - \eta) + \mu_i^{(1)} R_i + \mu_i^{(2)} S_i + P V_i; \quad (14)$$

i.e., in view of the expression (9) for the pressure, the excess free-energy density should satisfy the ‘scaled-particle’ differential equation [7]

$$\left(\frac{P}{k_B T} = \right) \frac{\partial \Phi}{\partial n_{3,0}} = -\Phi + \sum_{\alpha} n_{\alpha,0} \frac{\partial \Phi}{\partial n_{\alpha,0}} + n_{0,0} \quad (15)$$

in terms of the weighted densities, and the direct correlation function coefficients (10) take the following form:

$$\chi^{(\alpha)}(\{n_{\alpha,0}\}) = \frac{\partial^2 \Phi}{\partial n_{\alpha,0} \partial n_{3,0}}. \quad (16)$$

Finally, since the PY direct correlation functions maintain the analytic form of the first two diagrams of the exact diagrammatic expansion (1), they must correspond [15] to the SFP expressions (3) and (12) + (11), while a deeper analysis reveals [15] that the PY coefficients $\{\chi^{(\alpha)}\}$ satisfy the fundamental-measure scaled-particle theory (16). Thus, the PY hard-sphere direct correlations are exactly reproduced by the SFP expressions that employ the PY ‘compressibility’ equation of state [1]:

$$\Phi[\{n_{\alpha,0}\}] = -n_{0,0} \ln(1 - n_{3,0}) + \frac{n_{1,0} n_{2,0}}{1 - n_{3,0}} + \frac{\frac{1}{3} n_{2,0}^3}{8\pi(1 - n_{3,0})^2} \quad (17)$$

which is equal the result of scaled-particle theory [21] (see also equation (20) below).

3. The fundamental-measure free-energy functional for hard-sphere mixtures as related to the Percus–Yevick direct correlation functions

The fundamental-measure excess free-energy functional for a general m -component hard-sphere mixture with density $\rho_i(\vec{r})$ and radii R_i for species i has the form [7]

$$\frac{F_{ex}[\{\rho_i(\vec{r})\}]}{k_B T} = \int d\vec{x} \Phi[\{n_{\alpha}(\vec{x})\}] \quad (18)$$

where Φ is a function of only the *weighted densities* $n_{\alpha}(\vec{x})$:

$$n_{\alpha}(\vec{x}) = \sum_{i=1}^m \int \rho_i(\vec{y}) w_i^{(\alpha)}(\vec{x} - \vec{y}) d\vec{y}. \quad (19)$$

The *weight functions* $w_i^{(\alpha)}$ are characteristic functions for the geometry of the spheres. The weighted densities $n_{\alpha}(\vec{x})$ are *dimensional* quantities with dimensions $(n_{\alpha}) = (\text{volume})^{(\alpha-3)/3}$

where $0 \leq \alpha \leq 3$, and provide a functional basis set, $\{v_j\}$, for expanding the function, $\Phi = \sum_i A_i(n_3)v_i$, of dimension (volume) $^{-1}$. The coefficients, $A_i(n_3)$, as functions of the dimensionless n_3 , are determined from the scaled-particle differential equation (15), $-\Phi + \sum_\alpha n_\alpha \frac{\partial \Phi}{\partial n_\alpha} + n_0 = \frac{\partial \Phi}{\partial n_3}$, and the constants of integration can be fixed by known limits or desirable properties. In the bulk fluid limit with $\rho_i(\vec{r}) = \rho_{i,0} =$ the average one-particle density of species i , the corresponding weighted densities were already denoted above by $\{n_{\alpha,0}\}$. The first fundamental-measure free-energy functional [7] was obtained from a basis set which includes only the simplest positive power combinations of the weighted densities, $\{v_j\} = n_0, n_1 n_2, \vec{n}_{V1} \cdot \vec{n}_{V2}, n_2^3, n_2(\vec{n}_{V2} \cdot \vec{n}_{V2})$, and is given by

$$\Phi[\{n_\alpha\}] = -n_0 \ln(1 - n_3) + \frac{n_1 n_2 - \vec{n}_{V1} \cdot \vec{n}_{V2}}{1 - n_3} + \frac{\frac{1}{3}n_2^3 - n_2(\vec{n}_{V2} \cdot \vec{n}_{V2})}{8\pi(1 - n_3)^2} \quad (20)$$

which in the bulk limit corresponds to the PY ‘compressibility’ result (17) given above.

A *unique* minimal weight-function set was found by the following *convolution decomposition* [7] of the Mayer function for two spheres at distance r , $f_{ij}(r) = -\Theta(R_i + R_j - r)$, which represents a special case of the Gauss–Bonnet theorem [22]:

$$\begin{aligned} \Theta(R_i + R_j - r) &= w_i^{(0)} \otimes w_j^{(3)} + w_j^{(0)} \otimes w_i^{(3)} + w_i^{(1)} \otimes w_j^{(2)} - \vec{w}_i^{(V1)} \otimes \vec{w}_j^{(V2)} \\ &\quad + w_j^{(1)} \otimes w_i^{(2)} - \vec{w}_j^{(V1)} \otimes \vec{w}_i^{(V2)} \end{aligned} \quad (21)$$

where \otimes denotes the convolution product:

$$w_i^{(\alpha)} \otimes w_j^{(\gamma)} = \int w_i^{(\alpha)}(\vec{x} - \vec{r}_i) \cdot w_j^{(\gamma)}(\vec{x} - \vec{r}_j) d\vec{x} \quad (22)$$

and $\Theta(x)$ is the standard Heaviside unit step function: $\Theta(x < 0) = 0$, $\Theta(x \geq 0) = 1$. The minimal weight-function space contains three functions: two scalar functions representing the characteristic functions for the volume ($\alpha = 3$) and the surface ($\alpha = 2$) of a sphere, and a surface vector function ($\alpha = V2$):

$$\begin{aligned} w_i^{(3)}(\vec{r}) &= \Theta(R_i - r), & w_i^{(2)}(\vec{r}) &= |\vec{\nabla} w_i^{(3)}(r)| = \delta(R_i - r), \\ \vec{w}_i^{(V2)}(\vec{r}) &= -\vec{\nabla} w_i^{(3)}(r) = \frac{\vec{r}}{r} \delta(R_i - r). \end{aligned} \quad (23)$$

The other weight functions ($\alpha = 0, 1, V1$) are proportional to these three, and given by

$$w_i^{(0)}(\vec{r}) = \frac{w_i^{(2)}(\vec{r})}{4\pi R_i^2}, \quad w_i^{(1)}(\vec{r}) = \frac{w_i^{(2)}(\vec{r})}{4\pi R_i}, \quad \vec{w}_i^{(V1)}(\vec{r}) = \frac{\vec{w}_i^{(V2)}(\vec{r})}{4\pi R_i}. \quad (24)$$

The scalar weights have the property $\tilde{w}_i^{(\alpha)}(k=0) = R_i^{(\alpha)}$ where the $R_i^{(\alpha)}$ are given by (7) for $\alpha = 0, 1, 2, 3$, while the $k=0$ Fourier transforms of the vector-type weights ($\alpha = V1, V2$) vanish. Specifically, the Fourier transforms are given by

$$\frac{\tilde{w}_i^{(\alpha)}(k)}{R_i^{(\alpha)}} = \frac{\sin(kR_i)}{kR_i}, \quad \text{for } \alpha = 0, 1, 2 \quad (25)$$

$$\frac{\tilde{w}_i^{(3)}(k)}{R_i^{(3)}} = 3 \frac{\sin(kR_i) - kR_i \cos(kR_i)}{(kR_i)^3} \quad (26)$$

$$\tilde{\vec{w}}_i^{(V2)}(\vec{k}) = (-1)^{1/2} \vec{k} \tilde{w}_i^{(3)}(k). \quad (27)$$

The bulk weighted densities are given by (6) for $\alpha = 0, 1, 2, 3$, while the vector-type weighted densities vanish in the bulk limit: $n_{\alpha,0} = 0$, for $\alpha = V1, V2$.

The direct correlation functions, which are functional derivatives of $F_{ex}[\{\rho_i(\vec{r})\}]$, are given by convolutions of the geometric characteristic functions. The bulk direct correlation functions are given by

$$-c_{ij}(r) = \sum_{\alpha,\gamma} \Phi_{\alpha\gamma} \int w_i^{(\alpha)}(\vec{x}) w_j^{(\gamma)}(\vec{x} - \vec{r}) d\vec{x} \quad (28)$$

with Fourier transforms

$$-\tilde{c}_{ij}(k) = \sum_{\alpha,\gamma} \Phi_{\alpha\gamma} \tilde{w}_i^{(\alpha)}(\vec{k}) \tilde{w}_j^{(\gamma)}(-\vec{k}) \quad (29)$$

where the coefficients are

$$\Phi_{\alpha\gamma} = \left[\frac{\partial^2 \Phi}{\partial n_\alpha \partial n_\gamma} \right]_{\{n_\alpha\} \rightarrow \{n_{\alpha,0}\}}. \quad (30)$$

Bulk fluid direct correlation functions which are identical to the analytic solution of the PY integral equation for the hard-sphere mixture are obtained with (e.g.) the functional (20) given above. Specifically, the exact analytic solution of the PY equation for an *arbitrary* mixture of hard spheres [1] can be represented in the following geometric simple form [7]:

$$\begin{aligned} -c_{ij}(r = |\vec{r}_j - \vec{r}_i|) = & \chi^{(3)}[\omega_i^{(3)} \otimes \omega_j^{(3)}] + \chi^{(2)}[\omega_i^{(3)} \otimes \omega_j^{(2)} + \omega_j^{(3)} \otimes \omega_i^{(2)}] \\ & + \chi^{(1)} \left[\omega_i^{(3)} \otimes \omega_j^{(1)} + \omega_j^{(3)} \otimes \omega_i^{(1)} + \frac{1}{4\pi} (\omega_i^{(2)} \otimes \omega_j^{(2)} - \vec{\omega}_j^{(V2)} \otimes \vec{\omega}_i^{(V2)}) \right] \\ & + \chi^{(0)}[\omega_i^{(3)} \otimes \omega_j^{(0)} + \omega_j^{(3)} \otimes \omega_i^{(0)} + \omega_i^{(1)} \otimes \omega_j^{(2)} - \vec{\omega}_i^{(V1)} \otimes \vec{\omega}_j^{(V2)} \\ & + \omega_j^{(1)} \otimes \omega_i^{(2)} - \vec{\omega}_j^{(V1)} \otimes \vec{\omega}_i^{(V2)}] \end{aligned} \quad (31)$$

where

$$\chi^{(0)} = \frac{1}{1 - n_{3,0}} \quad (32)$$

$$\chi^{(1)} = \frac{n_{2,0}}{(1 - n_{3,0})^2} \quad (33)$$

$$\chi^{(2)} = \frac{n_{1,0}}{(1 - n_{3,0})^2} + \frac{n_{2,0}^2}{4\pi(1 - n_{3,0})^3} \quad (34)$$

$$\chi^{(3)} = \frac{n_{0,0}}{(1 - n_{3,0})^2} + \frac{2n_{1,0}n_{2,0}}{(1 - n_{3,0})^3} + \frac{n_{2,0}^3}{4\pi(1 - n_{3,0})^4}. \quad (35)$$

The scalar (dot) product between vectors is implied in the convolution product (22), and its Fourier transform

$$\widetilde{\omega_i^{(\alpha)} \otimes \omega_j^{(\gamma)}} = \tilde{w}_i^{(\alpha)}(\vec{k}) \cdot \tilde{w}_j^{(\gamma)}(-\vec{k}). \quad (36)$$

The expression (31) for the PY direct correlations is also identical, for each $\chi^{(q)}$ -term, to the SFP expression [15] given by (12). The fundamental-measure theory provided the first unified derivation of the PY [1, 12] and scaled-particle-theory [21] results for hard spheres, giving a geometric meaning to the PY direct correlation functions, with a particularly simple analytic form for the general *m*-component mixture.

4. The bridge functional in the test-particle limit and the inverse problem for liquid structure

Given the direct correlation functions from the fundamental-measure functional or from the SFP theory, and in particular those corresponding to the PY result, the structure factors are obtained easily. The structure factors

$$S_{ij}(k) = \delta_{ij} + (\rho_{i,0}\rho_{j,0})^{1/2}\tilde{h}_{ij}(k), \quad (37)$$

where

$$h_{ij}(r) = g_{ij}(r) - 1 \quad (38)$$

denote the total pair correlation functions, are related to the Fourier transforms of the direct correlation functions, $\tilde{c}_{ij}(k)$, by the following Ornstein–Zernike matrix equation:

$$\mathbf{S} = (\mathbf{I} - \mathbf{C})^{-1}. \quad (39)$$

The elements of the $m \times m$ matrices (for an m -component system) are: $\mathbf{S}_{ij} = S_{ij}(k)$, $\mathbf{C}_{ij} = (\rho_{i,0}\rho_{j,0})^{1/2}\tilde{c}_{ij}(k)$, and $\mathbf{I}_{ij} = \delta_{ij}$ (\mathbf{I} is the unit matrix).

The ‘effective’ potential $\phi_{eff}(r)$ for the same-species i – i interparticle interaction is obtained by reinterpreting $S_{ii}(k)$ as the structure factor for an ‘effective’ single-component system of particles at number density $\rho_{eff} = \rho_{i,0}$, $S_{eff}(k) = S_{ii}(k)$. From $S_{eff}(k)$ we obtain the ‘effective’ pair correlation function $h_{eff}(r) = g_{eff}(r) - 1$ from

$$S_{eff}(k) = 1 + \rho_{eff}\tilde{h}_{eff}(k). \quad (40)$$

Using the single-component Ornstein–Zernike relation

$$S_{eff}(k) = \frac{1}{1 - \rho_{eff}\tilde{c}_{eff}(k)}, \quad (41)$$

the ‘effective’ pair direct correlation function $c_{eff}(r)$ is obtained. The ‘effective’ potential can then be obtained from the following exact relation [23]:

$$\frac{\phi_{eff}(r)}{k_B T} = g_{eff}(r) - 1 - c_{eff}(r) - \ln g_{eff}(r) - b_{eff}(r), \quad (42)$$

where $b(r)$ is the so-called ‘bridge function’. When the bridge function is ignored, $b(r) = 0$, we have the hypernetted-chain (HNC) approximation. With an approximate bridge function this was termed [23] the ‘modified hypernetted-chain (MHNC) approximation’.

One possibility for obtaining an approximation for the generally unknown exact bridge function is from density functional theory. The starting points for the application of the density functional method for both uniform and non-uniform fluids are the density-profile equations, i.e. the Euler–Lagrange equations for minimizing the grand potential [24]. The equations determining the density profile $\rho(\vec{r})$ for the fluid subject to an external potential $u(\vec{r})$ can be written in the MHNC form [23, 25], involving the *bridge functional* which is related to the sum of all terms beyond second order in the functional Taylor expansion of the excess free energy $F_{ex}[\rho(\vec{r})]$ around some reference density. For a fluid in contact with a reservoir bulk fluid, of average density ρ_0 , the *bridge functional* is given by [16, 25],

$$B[\rho_0; \rho(\vec{r}); \vec{r}] = \frac{\mu_{ex}[\rho(\vec{r}); \vec{r}]}{k_B T} - \frac{\mu_{ex}[\rho_0]}{k_B T} + \rho_0 \int d\vec{r}' c^{(2,FD)}[\rho_0; (|\vec{r} - \vec{r}'|)](\rho(\vec{r}')/\rho_0 - 1). \quad (43)$$

Here $c^{(2,FD)}[\rho_0; (|\vec{r} - \vec{r}'|)]$ is the bulk limit of the direct correlation function given by the second functional derivative $c^{(2,FD)}(\vec{r}_1, \vec{r}_2) = -\frac{\delta^2 F_{ex}[\rho(\vec{r})]}{k_B T \delta\rho(\vec{r}_1) \delta\rho(\vec{r}_2)}$, $\mu_{ex}[\rho(\vec{r}); \vec{r}] = -\frac{\delta F_{ex}[\rho(\vec{r})]}{\delta\rho(\vec{r})}$ is the excess-chemical-potential functional, and $\mu_{ex}(\rho_0)$ is its bulk limit. In the special case where the external potential is generated by a *test particle* at the origin of coordinates [26], $u(\vec{r}) = \phi(r)$. The resulting density profile then corresponds to the bulk pair correlation function, $g(r) = \frac{\rho(r)}{\rho_0}$, and the bridge function, $b(r)$, is derived from the *bridge functional* $B[\rho_0; \rho(\vec{r}); \vec{r}]$ by using $\rho(\vec{r}) = \rho_0 g(r)$:

$$b(r) = B[\rho_0; \rho_0 g(r); r]. \quad (44)$$

This method can be used also for potentials for which the free-energy functional is not available. The assumption that one makes leading to the ‘universality’ hypothesis is that the bridge functional is (approximately) independent of the precise form of the pair interaction; hence it is regarded as being a universal quantity that can be obtained from that for any appropriate *reference* potential. When the potential and the reference potential are different, it is possible to *optimize the reference-system parameters* by a free-energy minimization that leads to an equation of the form [16, 25]

$$\int d\vec{r} [g(\vec{r}) - g^{\text{reference}}(\vec{r})] \delta b(\vec{r}) = 0. \quad (45)$$

The fundamental-measure theory is especially successful for hard spheres, and it can be expected to give a reasonably accurate approximation for the hard-sphere bridge functional. The approximation that the corresponding bridge functional is ‘universal’ makes the above method applicable to any physically reasonable pair potential.

Indeed, with the fundamental-measure functional for hard spheres it was possible to extend the approximation of ‘universality of the bridge functions’ [23] to that of ‘universality of the bridge functional’ [16]:

$$b(r) = B_{FMT}^{HS}[\rho_0; \rho_0 g(r); r; R]. \quad (46)$$

The fundamental-measure bridge functional for the hard spheres, $B_{FMT}^{HS}[\rho_0; \rho_0 g(r); r; R]$, depends parametrically on the hard-sphere radius R . The optimal value, $R = R_{opt}$, is obtained from the following equation [16]:

$$\int d^3 r [g(r) - g_{PY}^{HS}(r)] \frac{\partial B_{FMT}^{HS}[\rho_0; \rho_0 g(r); r; R]}{\partial R} = 0, \quad \text{for } R = R_{opt}, \quad (47)$$

which is similar to (45) and to that obtained [27] for the MHNC approximation with ‘universal’ hard-sphere bridge functions [23]. Note, however, that in accordance with the build-up of the fundamental-measure functional, we must use in (47) the hard-sphere pair function $g_{PY}^{HS}(r)$ corresponding to the result of PY approximation [12].

By considering simulation data for given pair potentials it was found that the resulting bridge function thus obtained from the hard-sphere functional,

$$b(r) = B_{FMT}^{HS}[\rho_0; \rho_0 g(r); r; R_{opt}], \quad (48)$$

is very accurate for both the direct and inverse problems, for both single-component fluids and (with the appropriate corresponding expressions) for mixtures [16, 17, 25, 28]. The penetrable-sphere system is a severe test case, since it is *a priori* unclear whether the universality extends to systems without some sort of effective hard core. It was found, however, that hard-sphere-type bridge functionals are applicable also for bounded potentials with high penetrability [28]. It should be emphasized that:

- (1) The evaluation of $b(r) = B_{FMT}^{HS}[\rho_0; \rho_0 g(r); r; R_{opt}]$ requires only several one-dimensional integrations, so considerable improvements over the methods used in [11] are obtained with a marginal computational cost.

- (2) As discussed in [17], since this bridge function is given by a functional of the input pair correlation function, no iteration procedure is needed.
- (3) The inverted potentials obtained from recent modifications [29, 30] of the fundamental-measure functional are almost identical to those obtained from the original functional [7, 16] using the expressions given in the previous section.

Thus, finally, given the pair correlation function (e.g. $S_{eff}(k)$ or $g_{eff}(r)$) of a one-component bulk fluid of average number density ρ_0 and temperature T , and interacting via an unknown pair potential $\phi_{eff}(r)$, an approximate solution of the inverse problem of obtaining that potential is given by

$$\frac{\phi_{eff}(r)}{k_B T} = g_{eff}(r) - 1 - c_{eff}(r) - \ln g_{eff}(r) - B_{FMT}^{HS}[\rho_0; \rho_0 g_{eff}(r); r; R_{opt}]. \quad (49)$$

In a benchmark test [17] for the Lennard-Jones system near the triple point, it was found comparable to about *ten simulations* in the iterative predictor–corrector scheme [14] for the inverse problem, a significant improvement over the PY or HNC approximations.

5. Conclusions

It appears that the fundamental-measure functional can provide a useful tool for investigating the structure and effective interactions in multi-component hard-sphere liquids. It is particularly well suited for the study of packing aspects of melts that form glasses or quasi-crystals as initiated in [11], yet it enables one to study, in addition to the three-component case, also the more important and physically relevant situations involving more complicated mixtures. Moreover, the fundamental-measure functional can be applied for the same purpose also within the powerful framework of density functional theory, as already demonstrated by studies of the depletion interactions in binary mixtures [8, 9].

Finally, it should be pointed out that the methods offered here for hard-sphere interactions can be extended and applied also to more general soft interactions. Several recent analyses [29, 30] revealed the important role played by the dimensional crossover properties of the fundamental-measure functionals, and in particular their zero-dimensional (0D) limit corresponding to a cavity with at most one particle. It was shown [30] that the correct 0D crossover can be systematically imposed, and the exact 0D limit (of the D -dimensional case) plays the role of a generating functional for D -dimensional hard-sphere fundamental-measure functionals. Using these new insights, fundamental-measure functionals were derived for penetrable spheres [31] and also for general soft interactions [32], with particular extensions to star polymer solutions [33] and to various models for colloid–polymer mixtures [34]. The resulting direct correlation functions when inserted into the Ornstein–Zernike relation feature generally accurate radial pair distribution functions which, however, usually do not satisfy the ‘core condition’ at short distances (the result corresponding to the PY integral equation approximation is very special). However, this can be easily remedied by considering the test-particle method (see, e.g., [33] for a discussion of that point). Thus, the more recent developments of the fundamental-measure theory enable one to extend the studies proposed above for hard spheres also to the more general soft interactions.

References

- [1] Lebowitz J L 1964 *Phys. Rev. A* **133** 895
Lebowitz J L and Rowlinson J S 1964 *J. Chem. Phys.* **41** 133
and see also
Hiroike K 1969 *J. Phys. Soc. Japan* **27** 1415
Leutheusser E 1984 *Physica A* **127** 667

- [2] Hansen J-P and McDonald I R 1986 *Theory of Simple Liquids* 2nd edn (London: Academic)
- [3] Löwen H 2000 Fun with hard spheres *Spatial Statistics and Statistical Physics (Springer Lecture Notes in Physics vol 554)* ed K Mecke and D Stoyan (Berlin: Springer)
- [4] Pagonabarraga I, Cates M E and Ackland G J 2000 *Phys. Rev. Lett.* **84** 911
- [5] Kim S C and Suh S H 2001 *Mol. Phys.* **99** 81
- [6] Goulding D, Hansen J-P and Melchionna S 2000 *Phys. Rev. Lett.* **85** 1132
- [7] Rosenfeld Y 1989 *Phys. Rev. Lett.* **63** 980
Rosenfeld Y 1996 *Chemical Applications of Density-Functional Theory (ACS Symp. Ser. 629)* ed B Laird, T Ziegler and R Ross (Washington, DC: American Chemical Society)
Rosenfeld Y 1996 *J. Phys.: Condens. Matter* **8** 9289
Rosenfeld Y 1999 *New Approaches to Old and New Problems in Liquid State Theory* ed C Caccamo, J-P Hansen and G Stell (Dordrecht: Kluwer) pp 303–20
- [8] See, e.g.,
Roth R, Evans R and Dietrich S 2000 *Phys. Rev. E* **62** 5360 and references therein
- [9] Goulding D and Melchionna S 2001 *Phys. Rev. E* **64** 011403
- [10] Goulding D and Hansen J-P 2001 *Mol. Phys.* **99** 865
- [11] König A and Ashcroft N W 2001 *Phys. Rev. E* **63** 041203
- [12] Percus J K and Yevick G J 1958 *Phys. Rev.* **110** 1
Wertheim M S 1963 *Phys. Rev. Lett.* **10** 321
Thiele E 1963 *J. Chem. Phys.* **39** 474
- [13] Lee S M, Jeon H J, Kim B H, Kim W T and Kim D H 2001 *Mater. Sci. Eng. A* **304** 871
- [14] Levesque D, Weis J-J and Reatto L 1985 *Phys. Rev. Lett.* **54** 451
Dharma-wardana M W C and Aers G C 1986 *Phys. Rev. Lett.* **56** 1211
Levesque D, Weis J-J and Reatto L 1986 *Phys. Rev. Lett.* **56** 1212
Reatto L, Levesque D and Weis J-J 1986 *Phys. Rev. A* **33** 3451
- [15] Rosenfeld Y 1988 *J. Chem. Phys.* **89** 4272
- [16] Rosenfeld Y 1993 *J. Chem. Phys.* **98** 8126
- [17] Kahl G, Bildstein B and Rosenfeld Y 1996 *Phys. Rev. E* **4** 5391
Rosenfeld Y and Kahl G 1997 *J. Phys.: Condens. Matter* **9** L89
- [18] Rosenfeld Y 1982 *Phys. Rev. A* **25** 1206
Rosenfeld Y 1985 *Phys. Rev. A* **32** 1834
Rosenfeld Y 1986 *Phys. Rev. A* **33** 2025
- [19] Barker J A and Henderson D 1976 *Rev. Mod. Phys.* **48** 587
- [20] Rosenfeld Y 1987 *Phys. Rev. A* **35** 938
Rosenfeld Y 1988 *Phys. Rev. A* **37** 3403
Rosenfeld Y 1989 *Phys. Rev. A* **39** 3079
Rosenfeld Y 1991 *High-Pressure Equations of State: Theory and Applications* ed S Eliezer and R Ricci (Amsterdam: North-Holland) pp 285–326
Rosenfeld Y 1994 *The Equation of State in Astrophysics* ed G Chabrier and E Schatzman (Cambridge: Cambridge University Press) pp 78–105
- [21] Riess H, Frisch H and Lebowitz J L 1959 *J. Chem. Phys.* **31** 369
Reiss H 1965 *Adv. Chem. Phys.* **9** 1
Reiss H 1992 *J. Phys. Chem.* **96** 4736
- [22] Rosenfeld Y 1994 *Phys. Rev. E* **50** R3318
Rosenfeld Y 1995 *Mol. Phys.* **86** 637
- [23] Rosenfeld Y and Ashcroft N W 1979 *Phys. Rev. A* **20** 1208
Rosenfeld Y and Ashcroft N W 1979 *Phys. Lett. A* **73** 71
Rosenfeld Y 1980 *J. Physique Coll. Suppl.* **41** C2 77
- [24] Evans R 1992 *Fundamentals of Inhomogeneous Fluids* ed D Henderson (New York: Dekker)
Löwen H 1994 *Phys. Rep.* **237** 249
- [25] Rosenfeld Y 1994 *Phys. Rev. Lett.* **72** 3831
Rosenfeld Y 1995 *J. Phys. Chem.* **99** 2857
Rosenfeld Y 1996 *Phys. Rev. E* **54** 2827
Rosenfeld Y 1996 *Physics of Strongly Coupled Plasmas* ed W Kraeft and M Schlanges (Singapore: World Scientific) pp 27–36
Rosenfeld Y 1998 *Mol. Phys.* **94** 929
- [26] Percus J K 1962 *Phys. Rev. Lett.* **8** 462

- Percus J K 1964 *The Equilibrium Theory of Classical Fluids* ed H L Frisch and J L Lebowitz (New York: Benjamin) II-171
- [27] Lado F 1982 *Phys. Lett. A* **89** 196
Lado F, Foiles S M and Ashcroft N W 1983 *Phys. Rev. A* **28** 2374
- [28] Rosenfeld Y, Watzlawek M, Schmidt M and Löwen H 2000 *Phys. Rev. E* **62** 5006
- [29] Rosenfeld Y, Schmidt M, Löwen H and Tarazona P 1996 *J. Phys.: Condens. Matter* **8** L577
Rosenfeld Y, Schmidt M, Löwen H and Tarazona P 1997 *Phys. Rev. E* **55** 4245
- [30] Tarazona P and Rosenfeld Y 1997 *Phys. Rev. E* **55** R4873
Tarazona P 2000 *Phys. Rev. Lett.* **84** 694
- [31] Schmidt M 1999 *J. Phys.: Condens. Matter* **11** 10 163
- [32] Schmidt M 1999 *Phys. Rev. E* **60** R6291
Schmidt M 2000 *Phys. Rev. E* **62** 3799
- [33] Groh B and Schmidt M 2001 *J. Chem. Phys.* **114** 5450
- [34] Schmidt M, Löwen H, Brader J M and Evans R 2000 *Phys. Rev. Lett.* **85** 1934
Schmidt M 2001 *Phys. Rev. E* **63** 010101(R)
Schmidt M 2001 *Phys. Rev. E* **63** 050201(R)