

Density functional approach to the structure of homogeneous colloidal dispersion

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(Received 17 October 1995)

We employ a simple density functional approach to predict the radial distribution and other structure related functions for a model homogeneous colloidal dispersion. The scheme is based on an interconnection, first pointed out by Percus, between the density of an inhomogeneous fluid in the field of an external potential and the radial distribution function of the corresponding uniform fluid, if the external potential is chosen as the pair potential itself. The two-particle direct correlation function of the homogeneous colloidal dispersion which is required as input is taken from the rescaled mean spherical approximation for particles interacting via screened Coulomb potential. Both perturbative and nonperturbative weighted density approaches are employed and the calculated quantities are shown to agree well with results from other sources.

PACS number(s): 82.70.Dd, 61.20.Gy, 61.25.-f

I. INTRODUCTION

Density functional theory [1] (DFT) has been a highly successful and versatile tool for the study of not only many-electron quantum systems [2] but many-particle classical systems [3] as well. In recent years, DFT has become increasingly popular, particularly for the description of the equilibrium structure and thermodynamics of nonuniform fluids [4]. With this approach, the free energy or the grand potential of a many-particle system is treated as a functional of its single-particle density [5], and the crux of the problem lies in the fact that the exact form of this functional for a general inhomogeneous density distribution $\rho(\mathbf{r})$ is still unknown. A major area of research in this field therefore involves attempts to find a suitable approximate form for this energy density functional.

Although DFT was originally devised for the study of inhomogeneous systems, its applicability is easily extended to uniform systems as well. The connection between the structure of a nonuniform fluid with that of the corresponding uniform fluid was first pointed out by Percus [6]. In a homogeneous fluid of density ρ_0 , the probability of locating one particle at the origin and another at position \mathbf{r} is $\rho_0 g(\mathbf{r})$, where $g(\mathbf{r})$ is the pair distribution function. The same can also be viewed as an inhomogeneous density distribution $\rho(\mathbf{r})$ around the particle fixed at the origin, which provides the external potential to the remaining particles of the fluid. Since a density functional approach as applied to the structure of an inhomogeneous fluid can be used to determine $\rho(\mathbf{r})$ in the presence of the external potential arising from fixing a particle at the origin, which is equal to the pair potential of the system, one can obtain $g(\mathbf{r})$ simply by calculating $\rho(\mathbf{r})/\rho_0$.

This method also provides a means to assess the validity and accuracy of an approximate free energy density functional used for the study of a nonuniform fluid. Re-

cently, this approach has been followed for hard sphere fluids [7–9] involving only short range correlations. It would however be of interest to investigate the suitability of such approaches to systems involving long range interaction potentials as well. Complex fluids such as colloidal suspensions [10] have attracted a great deal of attention in recent times because of their applications in many studies of basic, as well as applied, nature. The structure of homogeneous colloidal suspension is of immense importance and has been studied earlier by using integral equation methods [11], mean spherical approximation [12,13] (MSA), etc. In the present work, it is our intention to investigate the suitability of the density functional approach to the study of structure of the homogeneous colloidal suspension. For this, we employ the currently available approximations [14] to the density functionals as applied to inhomogeneous simple model fluids. Applicability of these procedures, as well as their extension to the case of ionic fluids, has already been shown to be quite successful [15]. The phase diagram of a colloidal dispersion consisting of ordered and liquid phases as a function of the bulk density and the dissolved salt concentration has also been successfully predicted [16] through the use of approximate density functionals.

The interaction between the macro particles of a charge-stabilized colloidal suspension is assumed to be well represented by the Derjaguin-Landau-Verwey-Overbeek (DLVO) expression, which corresponds to the screened Coulomb potential obtained from linearization of the Poisson-Boltzmann equation and is given by

$$\phi(r) = (Z^2 e^2 / \epsilon) (1 + \kappa d / 2)^{-2} \exp[-\kappa(r - d)] / r, \quad (1)$$

for an interparticle distance r higher than the hard sphere diameter d and infinity otherwise (i.e., for $r < d$). Here the inverse screening length κ is given by

$$\kappa^2 = (4\pi\beta/\epsilon) \left[\rho_0 Z e^2 + \sum_{\alpha} n_{\alpha} Z_{\alpha}^2 e^2 \right], \quad (2)$$

where ρ_0 is the number density of the colloidal particles of charge Ze with e as the electronic charge, n_{α} is the number density of the ions of type α with charge $Z_{\alpha}e$, ϵ is the dielectric constant of the medium, and $\beta (=1/k_B T)$ represents the inverse temperature, k_B being the Boltzmann constant.

The purpose of the present work is to obtain the homogeneous phase structure-related functions [$g(r)$ and related quantities] for the colloidal suspension using DFT and to compare the results with other theoretical and simulation results, wherever available. In Sec. II, we discuss the general density functional formalism as applied to the structure of nonuniform (and also uniform) fluids with different approximate routes to the density functionals discussed in Sec. III. The results of calculation of the radial distribution function and related quantities are compared with the MSA and simulation results in Sec. IV. Finally in Sec. V, we present a few concluding remarks.

II. THEORY

In DFT, the grand potential $\Omega[\rho]$ of a many-particle system under the influence of an external potential $v(r)$ is treated as a unique functional of the density distribution $\rho(\mathbf{r})$ and is expressed as

$$\Omega[\rho] = F[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) [v(r) - \mu], \quad (3)$$

where μ is the chemical potential and $F[\rho]$ is the intrinsic Helmholtz free energy consisting of two contributions, viz.,

$$F[\rho] = F_{\text{id}}[\rho] + F_{\text{ex}}[\rho]. \quad (4)$$

Here, the ideal gas contribution $F_{\text{id}}[\rho]$ is the free energy of the system with the same density but having no internal interactions among the particles, and $F_{\text{ex}}[\rho]$ is the excess free energy contribution arising from the interparticle interactions.

The equilibrium density profile of the inhomogeneous fluid corresponds to the minimum of the grand potential satisfying $\delta\Omega[\rho]/\delta\rho(\mathbf{r})=0$, which leads to the Euler-Lagrange equation

$$\begin{aligned} \mu &= v(\mathbf{r}) + \delta F[\rho]/\delta\rho(\mathbf{r}) \\ &= v(\mathbf{r}) + \delta F_{\text{id}}[\rho]/\delta\rho(\mathbf{r}) + \delta F_{\text{ex}}[\rho]/\delta\rho(\mathbf{r}). \end{aligned} \quad (5)$$

Using the functional form of $F_{\text{id}}[\rho]$, which is exactly known and is given by

$$F_{\text{id}}[\rho] = \beta^{-1} \int d\mathbf{r} \rho(\mathbf{r}) \{ \ln[\rho(\mathbf{r})\lambda^3] - 1 \}, \quad (6)$$

where λ is the thermal de Broglie wavelength, one obtains from Eq. (5) the equilibrium density distribution given by

$$\rho(\mathbf{r}) = [\exp(\beta\mu)/\lambda^3] \exp\{-\beta v(\mathbf{r}) + c^{(1)}([\rho]; \mathbf{r})\}, \quad (7)$$

where

$$c^{(1)}([\rho]; \mathbf{r}) = -\beta \delta F_{\text{ex}}[\rho]/\delta\rho(\mathbf{r}) \quad (8)$$

is the one-body direct correlation function (DCF) of the inhomogeneous fluid. If the inhomogeneous fluid is in contact with the bulk fluid, its chemical potential μ is equal to that of the bulk fluid [where $v(r)$ is zero and $\rho(\mathbf{r})=\rho_0$], and this leads to an equation for the density profile, given by

$$\rho(\mathbf{r}) = \rho_0 \exp\{-\beta v(\mathbf{r}) + c^{(1)}([\rho]; \mathbf{r}) - c_0^{(1)}(\rho_0)\}, \quad (9)$$

where c_0 refers to the uniform fluid.

In Eq. (9), if one chooses the external potential $v(\mathbf{r})$ to be equal to $\phi(r)$, the pair potential between one particle at point \mathbf{r} and another singled out and located at the origin, the resulting density function $\rho_{\phi}(\mathbf{r})$ signifies the distribution of the remaining particles around the "tagged" particle at the origin, thus providing a measure of the pair distribution function through the relation

$$\rho_{\phi}(\mathbf{r}) = \rho_0 g(\mathbf{r}). \quad (10)$$

This result, together with Eq. (9), leads to an expression for $g(r)$ of the homogeneous fluid, given by

$$g(r) = \exp\{-\beta\phi(r) + c^{(1)}([\rho_0 g]; \mathbf{r}) - c_0^{(1)}(\rho_0)\}. \quad (11)$$

It is also of interest to calculate other structure related functions, such as the cavity function [11] $y(r) \equiv g(r) \exp[\beta\phi(r)]$ and the bridge function $b(r)$ defined by the relation $g(r) = \exp\{-\beta\phi(r) + h(r) - c_0^{(2)}(r) - b(r)\}$, where $c_0^{(2)}(r)$ is the two-particle direct correlation function defined as

$$c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -\beta \delta^2 F_{\text{ex}}[\rho]/\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2). \quad (12)$$

Using Eq. (11), we can express these two functions as

$$\ln y(r) = c^{(1)}([\rho_0 g]; \mathbf{r}) - c_0^{(1)}(\rho_0) \quad (13)$$

and

$$b(r) = h(r) - c_0^{(2)}(r) - c^{(1)}([\rho_0 g]; \mathbf{r}) + c_0^{(1)}(\rho_0), \quad (14)$$

where $h(r) = g(r) - 1$ denotes the pair correlation function.

Equations (11), (13), and (14) provide in principle an exact route to the calculation of the uniform fluid structure related quantities $g(r)$, $y(r)$, and $b(r)$ if the functional $c^{(1)}([\rho(\mathbf{r}); \mathbf{r})]$ or $F_{\text{ex}}[\rho(\mathbf{r})]$ is known. But, unfortunately, neither of them is known exactly for a general inhomogeneous density profile $\rho(\mathbf{r})$, and hence suitable approximations are essential. In the following section, we discuss the approximate procedures for obtaining $c^{(1)}([\rho_0 g]; \mathbf{r})$ based on experiences for uniform fluids.

III. APPROXIMATION SCHEMES FOR THE DENSITY FUNCTIONALS

The excess free energy functional $F_{\text{ex}}[\rho(\mathbf{r})]$ is a universal (but unknown) functional of the single-particle density $\rho(\mathbf{r})$ for a given interparticle potential $\phi(r)$ and is independent of the external potential $v(\mathbf{r})$. We discuss here three approximation schemes, one of which is a perturbative method and the two others are nonperturbative weighted density based methods. All the schemes are based on the knowledge of $F_{\text{ex}}[\rho]$ or its functional derivatives, viz., the direct correlation functions for the uniform

counterpart of the system concerned, i.e., when the density is uniform.

A. Functional Taylor expansion approach

Although the functional Taylor expansion of $c^{(1)}([\rho(\mathbf{r})]; \mathbf{r})$ about ρ_0 in powers of the density deviation $[\rho(\mathbf{r}) - \rho_0]$ is in principle exact, lack of knowledge about the higher order functional derivatives or the DCF's even for the uniform system forces one to restrict to only a truncated expression. By neglecting higher order terms, the simplest expression that can be written for $c^{(1)}$ is given by

$$c^{(1)}([\rho_0 g]; \mathbf{r}) = c_0^{(1)}(\rho_0) + \int d\mathbf{r}_2 c_0^{(2)}(\mathbf{r}, \mathbf{r}_2; \rho_0) [\rho(\mathbf{r}_2) - \rho_0], \quad (15)$$

where $c_0^{(n)}$ denotes the n -particle DCF of the uniform fluid.

B. Nonperturbative weighted density approach of Denton and Ashcroft

In this weighted density approximation (WDA), originally due to Denton and Ashcroft [17], the quantity $c^{(1)}([\rho(\mathbf{r})]; \mathbf{r})$ for a nonuniform density distribution $\rho(\mathbf{r})$ is assumed to be the same as that obtainable from its uniform fluid counterpart $c_0^{(1)}$, evaluated at an effective density $\bar{\rho}$, which is obtained by the suitable weighted average of the actual inhomogeneous physical density distribution. Although $c_0^{(1)}$ does not depend on \mathbf{r} , the quantity $c^{(1)}([\rho(\mathbf{r})]; \mathbf{r})$ is position dependent because of the r -dependence of $\bar{\rho}(\mathbf{r})$. Thus one has

$$c^{(1)}([\rho_0 g]; \mathbf{r}) \equiv c_0^{(1)}(\bar{\rho}(\mathbf{r})) \quad (16)$$

with the weighted density $\bar{\rho}(\mathbf{r})$, defined as the average

$$\bar{\rho}(\mathbf{r}) \equiv \int d\mathbf{r}' \rho(\mathbf{r}') w(\mathbf{r} - \mathbf{r}'; \bar{\rho}(\mathbf{r})) \quad (17)$$

with respect to a weight function w , which should integrate to unity but is otherwise arbitrary. The normali-

zation of w ensures that Eqs. (16) and (17) yield the correct $c^{(1)}$ in the limit of uniform density, i.e., $\rho(\mathbf{r}) \rightarrow \rho_0$. Further demanding that in the same limit the functional derivative of $c^{(1)}$, given by the WDA expression of Eq. (16), should also correctly reproduce the second order correlation function $c_0^{(2)}$, Denton and Ashcroft [17] have arrived at a simple and unique specification of the weight function given by

$$w(\mathbf{r} - \mathbf{r}'; \rho_0) = c_0^{(2)}(\mathbf{r} - \mathbf{r}'; \rho_0) / [\partial c_0^{(1)}(\rho_0) / \partial \rho_0]. \quad (18)$$

C. Nonperturbative weighted density approach of Tarazona

In the Tarazona [18] version of WDA, it is the excess free energy density (per particle) $\psi_{\text{ex}}(\rho)$ of the inhomogeneous fluid defined as

$$F_{\text{ex}}[\rho(r)] = \int d\mathbf{r} \rho(\mathbf{r}) \psi_{\text{ex}}(\rho(r)) \quad (19)$$

that is evaluated using a weighted density. Here, $\psi_{\text{ex}}(\rho(r))$ is obtained by evaluating the corresponding expression for the uniform fluid, i.e., $\psi_{\text{ex}}^0(\rho_0)$, using an effective density $\bar{\rho}$ in place of ρ_0 , which is again a weighted average of the physical density as given by Eq. (17). The weight function here is different but satisfies the same normalization condition; it is also specified by requiring that the two-particle DCF obtained from the second order functional derivative of the WDA expression for $F_{\text{ex}}[\rho]$, given by

$$F_{\text{ex}}[\rho(r)] = \int d\mathbf{r} \rho(\mathbf{r}) \psi_{\text{ex}}^0(\bar{\rho}(r)), \quad (20)$$

should reproduce the exact result for $c_0^{(2)}$ [see Eq. (12)] in the limit of uniform density. One also employs here a simple expansion for the weight function, viz., $w(r; \rho) = w_0(r) + w_1(r)\rho + w_2(r)\rho^2$, and a suitable expression for the free energy quantity ψ_{ex}^0 . The final expression for the one-body DCF corresponding to the first derivative of the WDA expression for free energy, entering in Eq. (9) and hence Eq. (11) through Eqs. (8) and (20), is given by

$$c^{(1)}(\mathbf{r}; [\rho_0 g]) = -\beta [\psi_{\text{ex}}^0(\bar{\rho}(r)) + \int d\mathbf{r}' \rho(\mathbf{r}') \psi_{\text{ex}}^0(\bar{\rho}(r')) w(\mathbf{r} - \mathbf{r}'; \bar{\rho}(r')) / \{1 - \bar{\rho}_1(r') - 2\rho(r') \bar{\rho}_2(r')\}], \quad (21)$$

where $\bar{\rho}_i$'s are the weighted densities corresponding to the weight functions w_i 's in the expansion of $w(r; \rho)$.

D. Application to colloidal systems

For a fluid of colloidal particles interacting through the DLVO potential, the external potential $v(r)$ that appears in Eq. (11) is just the pair potential $\phi(r)$ given by

Eq. (1). In the perturbative approach, $c^{(1)}(r; \rho_0 g)$ in the inhomogeneous phase is obtained through the perturbation expansion [Eq. (15)] truncated at first order in the density deviation for which the two-particle DCF of the uniform fluid is to be used as input. Analytical expression for this DCF for colloidal suspension interacting through DLVO potential has been obtained using the rescaled mean spherical approximation [12,13] (RMSA) and is given by

$$c_0^{(2)}(x) = A + Bx + (\frac{1}{2})\eta Ax^3 + C \sinh(kx)/x \\ + F[\cosh(kx) - 1]/x, \quad \text{for } x < 1 \quad (22a)$$

$$= -\gamma \exp(-kx)/x, \quad \text{for } x > 1, \quad (22b)$$

where $x = r/d$; $\gamma = \beta(Z^2 e^2 / \epsilon) \exp(\kappa d) / (1 + \kappa d / 2)^2$; and A , B , C , and F can be expressed [12,13] explicitly in terms of the packing fraction $\eta = (\pi/6)\rho_0 d^3$, $k = \kappa d$, and γ . This expression is, however, not directly applicable to systems with very low densities as it leads to unphysical contact values for $g(r)$. Since for the charged colloidal systems, the Coulomb coupling is generally very strong (large value of γ), the distance of closest approach is usually larger than the actual hard sphere diameter. A suitable rescaling of the actual hard sphere diameter to a larger value leading to a fictitious higher value of η has been shown [13] to be essential for the MSA result of Eq. (22) to be applicable for very low densities. Although approximate, the RMSA result for DCF is reasonably accurate and close to other approximations [13,19], and it has also been found to be successful in a number of predictions and studies involving colloidal suspension [see, for example, Refs. [16] and [19]].

While for the perturbative approach (which we call scheme A), the DCF $c_0^{(2)}$ given by Eq. (22) is sufficient, for the nonperturbative weighted density approaches one requires the one-particle correlation function $c_0^{(1)}$ or the free energy density ψ_{ex}^0 , explicit expressions for which are not available. The expression for $c_0^{(2)}$, however, consists of a short range part and a long range part, and this prompts us to propose to obtain $c_0^{(1)}$ by choosing a suitable short range reference system. Thus, in the spirit of the work of Curtin and Ashcroft [20] for Lennard-Jones fluid (see also Refs. [16(b)] and [16(c)]), we obtain only a

reference (short range) part $c_{\text{Ref}}^{(1)}(r; \rho(r))$ of the total correlation through WDA, while the remaining (primarily long range) contribution $\Delta c^{(1)} [= c^{(1)}(r; \rho(r)) - c_{\text{Ref}}^{(1)}(r; \rho(r))]$ is obtained by the perturbative approach.

One possible choice of the reference system is the simple hard sphere fluid, since for this system correlation is of short range and analytical expressions of the required quantities are known. The expression for $c_0^{(2)}$ for hard sphere fluid within the Percus-Yevick approximation is given by

$$(c_0^{(2)})_{\text{HS}}(x) = a + bx + (1/2)\eta ax^3, \quad \text{for } x < 1 \quad (23)$$

and zero otherwise, where $a = -(1 + 2\eta)/(1 - \eta)^4$ and $b = 6\eta(1 + \eta/2)^2/(1 - \eta)^4$. The corresponding results for $(c_0^{(1)})_{\text{HS}}$ and $(\psi_{\text{ex}}^0)_{\text{HS}}$ are given by

$$(c_0^{(1)})_{\text{HS}} = -(7\eta - 13\eta^2/2 + 15\eta^3/2)/(1 - \eta)^3 \\ + \ln(1 - \eta), \quad (24a)$$

$$(\psi_{\text{ex}}^0)_{\text{HS}} = \beta^{-1}\eta(4 - 3\eta)/(1 - \eta)^2, \quad (24b)$$

where $(\psi_{\text{ex}}^0)_{\text{HS}}$ is the accurate Carnahan-Starling result.

In view of the availability of these analytical expressions for $c_0^{(1)}$ and ψ_{ex}^0 for the hard sphere fluid, we consider it to be the reference system and obtain (scheme B) $c_{\text{Ref}}^{(1)}$ by evaluating $(c_0^{(1)})_{\text{HS}}(\bar{\rho}(r))$ with $\bar{\rho}(r)$ obtained from the Denton-Ashcroft procedure given by Eqs. (17) and (18). Alternatively, $c_{\text{Ref}}^{(1)}$ can be obtained (scheme C) from Eq. (21) by evaluating $\psi_{\text{ex}}^0(\bar{\rho}(r))$ with $\bar{\rho}(r)$ obtained from Eqs. (17) and the Tarazona prescription for the weight function. In both schemes B and C, one obtains $\Delta c^{(1)}$ perturbatively through an equation similar to Eq. (15), and hence the quantity involving $c^{(1)}$ appearing in Eqs. (9), (11), (13), and (14) is expressed as

$$\{c^{(1)}([\rho_0 g]; \mathbf{r}) - c_0^{(1)}(\rho_0)\} = (c_0^{(1)})_{\text{HS}}(\bar{\rho}(r)) - (c_0^{(1)})_{\text{HS}}(\rho_0) + \rho_0 \int d\mathbf{r}_2 [c_0^{(2)}(|\mathbf{r}_1 - \mathbf{r}_2|; \rho_0) - (c_0^{(2)})_{\text{HS}}(|\mathbf{r}_1 - \mathbf{r}_2|; \rho_0)] [g(\mathbf{r}_2) - 1]. \quad (25)$$

IV. RESULTS AND DISCUSSION

The nonlinear integral equation [Eq. (11)] for the pair distribution function $g(r)$ [and hence also Eqs. (13) and (14) for the functions $\ln y(r)$ and $b(r)$] have been solved numerically using an iterative self consistent procedure using $g(r) = 1$ as the initial chosen input. Due to spherical symmetry of the problem, all the three-dimensional (3D) integrals are simplified by analytically integrating over the angular variables, requiring only 1D integrals involving the radial coordinate to be evaluated numerically. We have employed a uniform mesh for discretization and trapezoidal rule for numerical integration. The convergence criterion chosen in the iterative procedure corresponds to a small value ($< 10^{-10}$) for the average mean square deviation of $g(r)$, expressed as $\sum_i [g^{(n)}(r_i)$

$-g^{(n-1)}(r_i)]^2$ divided by the number of mesh points, after the n th iteration.

All the calculations presented here correspond to temperature $T = 298$ K and the hard sphere diameter for the colloidal particles $d = 823$ Å. These values have been chosen so that some of the results can be compared with available computer simulation results. The distances are measured in units of d , the bulk density ρ_0 is indicated in terms of the packing fraction $\eta = (\pi/6)\rho_0 d^3$, and the screening parameter κ is measured in terms of the dimensionless quantity (κd) . The quantity $c_0^{(2)}$ for the uniform colloidal suspension has been obtained from Eq. (22), corresponding to the RMSA results of Hansen and Hayter [12,13]; for the hard sphere contributions $(c_0^{(2)})_{\text{HS}}$, $(c_0^{(1)})_{\text{HS}}$, and $(\psi_{\text{ex}}^0)_{\text{HS}}$, used for the WDA of the short

range contribution, we have employed the analytical results given by Eqs. (23) and (24), corresponding to the Percus-Yevick approximation.

The calculations have been performed for a low density suspension ($\eta=0.00042$), as well as a moderately concentrated suspension ($\eta=0.2579$). The effects of higher charges of the colloidal particles and higher values of the screening parameters are also studied.

For the low density colloidal suspension ($\eta=0.00042$) with the parameters $Z=258$, $\kappa d=0.15$, and $\gamma=580$, the scaling parameter ($s=d/d'$) for the diameter is found to be 0.11765. This corresponds to the minimum value of the scaled diameter d' , for which the resulting $g(r)$ from a direct Fourier transform of the correlation function (and use of Ornstein-Zernike equation) becomes nonnegative at short distances. The profiles of the radial distribution function $g(r)$ calculated through the schemes A to C for $c^{(1)}(\rho(r))$, discussed in Sec. III, are shown in Fig. 1 together with the RMSA results obtained from direct numerical Fourier transform of the structure factor corresponding to the RMSA correlation function and also the computer simulation results (taken from Ref. [19]). On average our results are close to the RMSA result, but the peaks (especially near contact) are under predicted as compared to the computer simulation result. The weighted density schemes B and C yield a slightly larger peak height for the first peak as compared to the perturbative approach (scheme A). This deviation of our results from that of simulation near contact (i.e., at $r=d$) may be due to the fact that in the perturbative approach (scheme A) terms beyond $c^{(2)}$ are neglected; and in the nonperturbative approaches (schemes B and C), although higher order correlations are partially taken into account in an averaged manner, for the present case of colloidal dispersion only hard sphere or short range correlations

are treated through WDA because of the constraints mentioned. Other issues, related to the fact that some of these approximate theories do not exactly satisfy the virial equation relating the bulk pressure to the contact density $g(r=d)$, are also to be considered. In this case of very low density, the scaling of the diameter of the particle has been essential according to RMSA, and this is reflected in the peak positions of $g(r)$. The first peak has thus appeared at a distance slightly larger than the scaled diameter (d'), and the separations between the successive peaks are also integral multiples of the scaled diameter (d'). At higher values of η corresponding to higher physical densities, which involve no scaling of the diameter, the first peak position, however, appears near $r/d=1.0$, as shown in Fig. 2, where we have plotted $g(r)$ for $\eta=0.2579$ and other parameters as $\kappa d=1.276$ and $\gamma=68.28$. The values chosen for calculation correspond to the quantities obtained after scaling the corresponding parameters for the low density situation. But here they are taken as physical parameters instead of as fictitious ones arising from scaling, and hence the scaling factor is unity. The plots of $g(r)$ in Figs. 1 and 2 provide insight into the effect of scaling.

The effect of increasing the charge on the colloidal particles is evident from the buildup of more structure in $g(r)$, as shown in Figs. 3(a) and 3(b), where we have plotted the results for $Z=600$ and $Z=1000$, respectively; η is the same as in Fig. 1. The other parameters, however, are modified through their dependence on the charge Z and their values are indicated in the figures. In Fig. 4, we have plotted $g(r)$ obtained for a different value of the screening length, but other parameters are the same as in Fig. 1. All these results are observed to agree quite well with the corresponding RMSA results (shown only for Figs. 1 and 2) obtained by Fourier transforming the

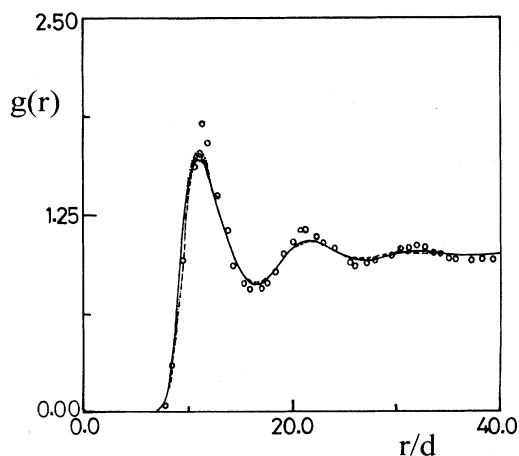


FIG. 1. Plot of radial distribution function $g(r)$ vs r/d for a model colloidal suspension ($\eta=0.00042$, $k=0.15$, $\gamma=580.0$, $Z=258$). Calculated results correspond to different schemes mentioned in the text. Simulation results are from Ref. [19]. \cdots scheme A; $-\cdot-\cdot-$ scheme B; $---$ scheme C; $---$ RMSA; \circ , simulation.

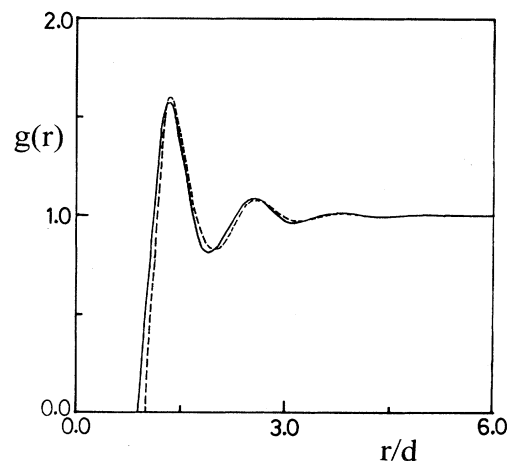


FIG. 2. Plot of radial distribution function $g(r)$ vs r/d for a model colloidal suspension ($\eta=0.25787$, $k=1.2764$, $\gamma=68.28511$, $Z=258$, $s=1.0$). $---$ scheme A (schemes B and C are not distinguishable from scheme A in the present scale); $---$, RMSA.

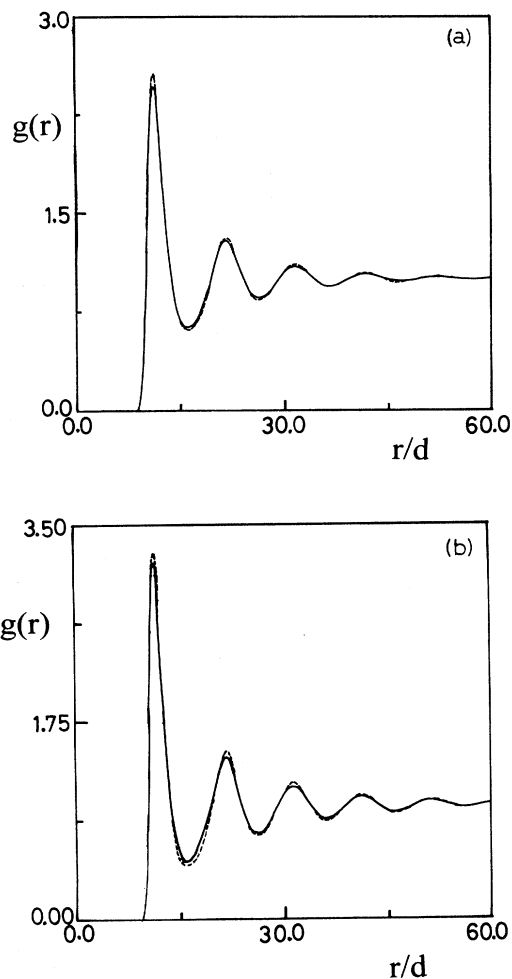


FIG. 3. (a) Plot of radial distribution function $g(r)$ vs r/d for a model colloidal suspension ($\eta=0.00042$, $k=0.2288$, $\gamma=3163.14$, $Z=600$, $s=0.1047$). —, scheme A; - - - scheme B (scheme C is indistinguishable from scheme B in the present scale). (b) ($\eta=0.00042$, $k=0.2954$, $\gamma=8854.52$, $Z=1000$, $s=0.1008$). —, scheme A; - - -, scheme B (scheme C is indistinguishable from scheme B in the present scale).

structure factor $S(Q)$ from Hansen and Hayter's RMSA [13]. The structure related functions $\ln y(r)$ and $b(r)$ calculated through Eqs. (13) and (14) are also plotted in Figs. 5 and 6, respectively, for the same parameters as in Fig. 1. It may be noted that $b(r)=0$ for scheme A, and hence only results of schemes B and C are plotted in Fig. 6. Since computer simulation or other theoretical results are not available for $\ln y(r)$ and $b(r)$, any test of our results has not been possible at this time. However, as is evident from Figs. 5 and 6, the results obtained here from the different approximate schemes are close to each other. It may also be noted that in the WDA based schemes, $c^{(2)}(\rho_0; r)$ of the uniform fluid has been used and the

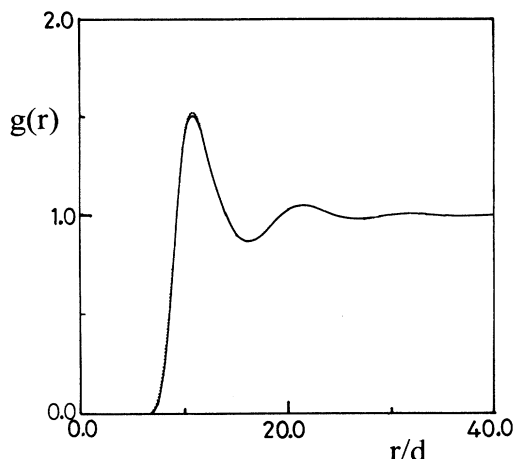


FIG. 4. Plot of radial distribution function $g(r)$ vs r/d for a model colloidal suspension ($\eta=0.00042$, $k=0.25$, $\gamma=586.19$, $Z=258$, $s=0.12204$). —, scheme A; ···, scheme B (scheme C is indistinguishable from scheme B in the present scale).

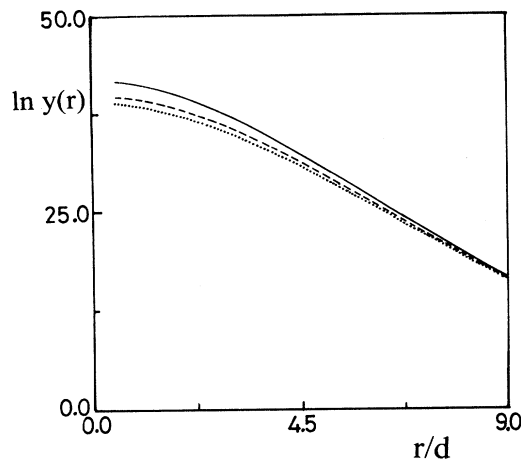


FIG. 5. Plot of $\ln y(r)$ vs r/d for a model colloidal suspension ($\eta=0.00042$, $k=0.15$, $\gamma=580.0$, $Z=258$, $s=0.1175$). —, scheme A; ···, scheme B; - - -, scheme C.

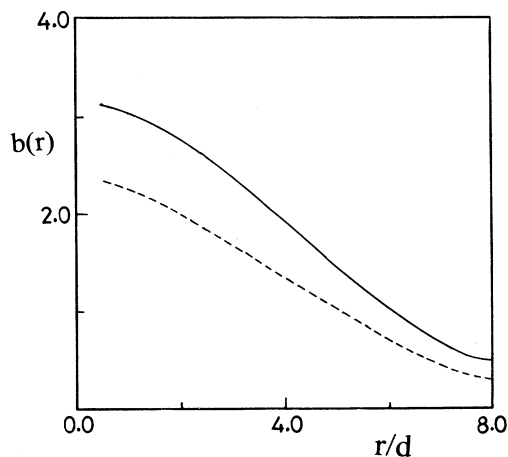


FIG. 6. Plot of $b(r)$ vs r/d for a model colloidal suspension ($\eta=0.00042$, $k=0.15$, $\gamma=580.0$, $Z=258$, $s=0.1175$). - - -, scheme B; —, scheme C.

present scheme of obtaining $g(r)$ can be considered as only the first level of iteration. One can also recalculate it from calculated $g(r)$ through the Ornstein-Zernike equation and use the same through WDA again to obtain new $g(r)$. This second level of iteration, however, requires tremendous computational effort, and moreover, improved accuracy is also not always guaranteed.

V. CONCLUDING REMARKS

In this work, we have presented a simple density functional procedure for the study of properties of model colloidal suspensions. A combined procedure consisting of WDA for the short range (hard sphere here) and a simple perturbative scheme for the remaining long range correlation, even with a first level of iteration, is found to provide quite good prediction of the radial distribution func-

tion of bulk colloidal suspensions. This approach is an attempt to employ WDA in the study of the structure of colloidal systems (see Ref. [16] for studies of freezing), and the present success has provided support for its accuracy and applicability. In view of the recent interest in the study of the structure of inhomogeneous colloidal suspensions [19], it is important to have reasonably accurate simple theories for its prediction. Using the formalism discussed here, we are presently investigating the structure of colloidal suspension confined between planar slits or cylindrical pores, which are of immense importance in various physicochemical phenomena.

ACKNOWLEDGMENTS

It is a pleasure to thank T. G. Varadarajan and H. K. Sadhukhan for their kind interest and encouragement.

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- [1] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); N. D. Mermin, *ibid.* **137**, A1441 (1965); see also W. F. Saam and C. Ebner, *Phys. Rev. A* **15**, 2566 (1977).
 - [2] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
 - [3] R. Evans, *Adv. Phys.* **28**, 143 (1979).
 - [4] *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Dekker, New York, 1992).
 - [5] For a review, see S. K. Ghosh and B. M. Deb, *Phys. Rep.* **92**, 1 (1982); *Single Particle Density in Physics and Chemistry*, edited by N. H. March and B. M. Deb (Academic, New York, 1987).
 - [6] J. K. Percus, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964), Vol. 2, p. 33.
 - [7] A. R. Denton and N. W. Ashcroft, *Phys. Rev. A* **44**, 1219 (1991).
 - [8] G. P. Brenan and R. Evans, *Mol. Phys.* **73**, 789 (1991).
 - [9] G. Richayzen, P. Kalpaxis, and E. Chacon, *J. Chem. Phys.* **101**, 7963 (1994).
 - [10] P. N. Pusey, in *Liquids, Freezing and Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier, New York, 1991).
 - [11] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, New York, 1986).
 - [12] J. B. Hayter and J. Penfold, *Mol. Phys.* **42**, 109 (1981).
 - [13] J. P. Hansen and J. B. Hayter, *Mol. Phys.* **46**, 651 (1982).
 - [14] R. Evans, in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Dekker, New York, 1992).
 - [15] See, for example, L. Mier-y-Teran, S. h. Suh, H. S. White, and H. T. Davis, *J. Chem. Phys.* **92**, 5057 (1990); see also C. N. Patra and S. K. Ghosh, *Phys. Rev. E* **47**, 4088 (1993); **48**, 1154 (1993).
 - [16] (a) S. Sengupta and A. K. Sood, *Phys. Rev. A* **44**, 1233 (1991); (b) P. Salgi and R. Rajagopalan, *Langmuir* **7**, 1383 (1991); (c) N. Choudhury and S. K. Ghosh, *Phys. Rev. E* **51**, 4503 (1995).
 - [17] A. R. Denton and N. W. Ashcroft, *Phys. Rev. A* **39**, 426 (1989). For a different WDA based on local excess free energy, see W. A. Curtin and N. W. Ashcroft, *ibid.* **32**, 2909 (1985).
 - [18] P. Tarazona, *Mol. Phys.* **52**, 81 (1984); *Phys. Rev. A* **31**, 2672 (1985).
 - [19] P. Gonzalez-Mozuelos, J. Alejandro, and M. Medina-Noyola, *J. Chem. Phys.* **95**, 8337 (1991).
 - [20] W. A. Curtin and N. W. Ashcroft, *Phys. Rev. Lett.* **56**, 2775 (1986).