Adsorption of Lennard−Jones Molecules on a Hard Wall: A Case Study in the Star-Function Based Density Functional Theory[†]

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For conventional density functional theories (DFTs), the mean-field perturbation theory was commonly invoked to evaluate the excess free energy due to attractions in the bulk fluid of an inhomogeneous system. This simplification caused inaccuracies in the predictions. We develop here a version of the DFT based on the functional Taylor expansions of the intrinsic free energy functional $F[\rho]$ and the singlet density $\rho^{(1)}(\mathbf{r})$ to arrive at closed-form expressions for these quantities without truncations. This is made possible by incorporating the bridge functional and a "star function" proposed earlier in *J. Chem. Phys.* **1992**, *97*, 8606. The results are generally applicable to both repulsive and attractive potentials. The new formulation is applied to the Lennard−Jones molecules adsorbed on a planar hard wall. It is demonstrated that without using the mean-field approximation, we can obtain accurate density profiles for this system. A "two-way street" formulation between the uniform fluids and the nonuniform fluids is established via Percus's concept of the "source particle" (or the test particle) approach that enables the transference of successful homogeneous liquid-theory quantities and procedures to the nonuniform systems, such as the zero-separation closure for the bridge functions. The proposed DFT is formally exact (without approximations), general (applicable to repulsive as well as attractive pair potentials), and complete (without truncations). A pair of mutually consistent equations for the free energy $F[\rho]$ and the singlet density $\rho^{(1)}(\mathbf{r})$ result from this marriage. Prospects of application to Yukawa potentials in colloidal chemistry and Coulomb potentials in electrical double layers of electrochemistry are envisioned.

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1. Introduction

Modern density functional theories are based primarily on the hard sphere fluid adsorbed on hard walls. The most prominent among these is the fundamental measure theory (FMT) pioneered by Rosenfeld[1] which is based on hard-sphere geometric measures within a scaled-particle theory[2] (SPT) framework. It is closely linked to the Percus−Yevick (PY) approximation[3] in liquid theory. As for bulk fluids other than the hard spheres, especially those with attractive potentials, such as the Lennard−Jones (LJ) potential (ε is the energy parameter and σ the size parameter)

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1.1}$$

the FMT is not directly applicable. The common practice is to divide the pair potential into a repulsive part u_R (which is treated perturbatively with the hard sphere fluid as a reference) and an attractive part u_A:

$$u(r) = u_R(r) + u_A(r) \tag{1.2}$$

The contribution to the free energy F_R from u_R can be dealt within the FMT framework (or with the weighted density approximation, WDA, theories) in the normal fashion. The contribution F_A from the attractive potential u_A is approximated by a mean-field theory (MFT) expression

$$\beta F_A \cong \frac{1}{2}\int d1d2\ \rho_w^{(1)}(1)\ u_A(12)\ \rho_w^{(1)}(2) \tag{1.3}$$

It is this expression that is problematic and is the source of many inaccuracies for potentials with attraction.[4−6] To fix this problem, different remedies have been proposed.[4−6] In this work, we aim at removing this difficulty by reformulating the density functional theory (DFT) from an entirely different while thorough way that naturally extends the applicability to most classes of simple fluids, attractive or otherwise. To demonstrate its use, we make a test on the case of LJ fluid adsorbed on a hard wall.

DFT has been applied to the freezing transition, wetting phenomena, adsorption at fluid−solid interfaces, and recently to electric double layers in electrochemistry.[4] Historically, more than a century ago, van der Waals proposed the first gradient theory[7,8] for the nonuniform density distributions. The modern origin is usually attributed to Hohenberg and Kohn[9] for quantum electron gas from the early 1960s. Many approaches[10] have been developed in the interim. Since the nonuniformities, in general, are extremely complex, and nonuniform distributions (such as high-order direct correlation functions, DCFs) are difficult to evaluate, a majority of DFT theories undertook the task of simplification (thus introducing approximations) by "mapping" via various means the nonuniform distributions onto their uniform counterparts, the latter being more accessible and easier to handle numerically. These attempts have generated many WDAs.[11,12] (1) For example, there are formulations based on the weighted density $\bar{\rho}(\mathbf{r})$ through various postulations on the weighting functions, $\omega(\mathbf{r},\mathbf{r}')$, so that the nonuniform DCF is made equal (in a plausible way) to the uniform DCF, namely, instead of using the physical density value $\rho^{(1)}(\mathbf{r})$ at $\mathbf{r}$ in the argument to the nonuniform DCF $C^{(n)}(\mathbf{r};[\rho^{(1)}(\mathbf{r})])$, one replaces the nonuniform DCF by a uniform fluid DCF evaluated at a (nonexistent or nonphysical) weighted density $\bar{\rho}(\mathbf{r})$, then equating

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$C^{(n)}(\mathbf{r};[\rho^{(1)}(\mathbf{r})]) = C_0^{(n)}(\mathbf{r};\bar{\rho})$ (where subscript 0 denotes uniformity). $\bar{\rho}(\mathbf{r})$ is generated through the weighting function $\omega(\mathbf{r},\mathbf{r}')$ via convolution: $\bar{\rho}(\mathbf{r})' \equiv \int \mathrm{d}\mathbf{r}'\ \rho^{(1)}(\mathbf{r}')\ \omega(\mathbf{r},\mathbf{r}')$. For each and every position $\mathbf{r}$, a $C_0^{(n)}(\mathbf{r};\bar{\rho})$ is generated and put in place of $C^{(n)}(\mathbf{r};[\rho^{(1)}(\mathbf{r})])$. This approach is the gist of the WDAs. The advantage is that one does not have to deal directly with the inhomogeneous quantities. Only the uniform correlations need be evaluated. Many different formulations of the weighting functions have been proposed (e.g., WDA,[11] modified weighted density approximation (MWDA),[12] simplified weighted density approximation (SWDA), etc.[13]). These theories are also called the nonlocal density approximations (NLDAs). (2) On the other hand, there are formulations that treat the local density at the spot (at coordinates $\mathbf{r}$) without averaging, such as the van der Waals square-gradient theory.[7,8] These are called the local density approximations (LDAs). There are other variants of the theme, such as those based on the nonuniform Ornstein–Zernike (OZ) equation.[14] We propose here instead a functional Taylor expansion theory that is local (using local densities), complete (including all high-order correlations), and formally exact (without weighted densities). The resulting formulation will be tested on a bulk fluid with attractive potential, the LJ molecules.

Earlier, Denton and Ashcroft[15] noticed a connection between the nonuniform system and a uniform system based on the Percus's intuition.[16] When the source of the spatial inhomogeneity in density is not generated by a planar wall, but instead by a "test particle", the external potential $w(\mathbf{r})$ will metamorphose into the bulk pair potential $u_0(|\mathbf{r}_0 - \mathbf{r}|)$. The nonuniform system now mimics the bulk uniform system, and the singlet (one-body) density $\rho^{(1)}(\mathbf{r}_1,[w])$ becomes the uniform pair correlation function $\rho_0 g_0(|\mathbf{r}_1 - \mathbf{r}_0|)$. As a consequence, all of the theories that are applicable to the nonuniform case (e.g., the WDAs) can now be transferred en masse to the uniform case for the benefit of the uniform fluid theory. In particular, the singlet direct correlation function (s-DCF) $C^{(1)}(\mathbf{r}_1;[w])$ can be expanded in functional series around the uniform s-DCF $C_0^{(1)}(\mathbf{r}_1;[w = 0])$, and the closure relation necessary for the solution of the uniform OZ equation can be obtained gratis from the WDA vantage point.

On the other hand, this procedure can be reversed by rebrousser chemin, that is, we go the reverse path: from uniformity to nonuniformity. If we know a good closure or an accurate bridge function $B_0(|\mathbf{r}_1 - \mathbf{r}_0|)$ for the uniform fluids, we can start from the uniform $\rho_0 g_0(|\mathbf{r}_1 - \mathbf{r}_0|)$ and identify it as the nonuniform singlet density $\rho^{(1)}(\mathbf{r}_1,[w])$ when all of the while the test particle is going through "contortions" from a test sphere into a wall, to parallel slit planes, or to a spherical cavity, as the external potential changes. Meanwhile, the uniform bridge function $B_0(|\mathbf{r}_1 - \mathbf{r}_0|)$ can transmute into its nonuniform counterpart $B(\mathbf{r}_1;[w])$. This two-way street has been recognized and has been actually traversed in a number of studies applied to nonuniform systems (see, e.g., Zhou and Ruckenstein,[17] Kim et al.,[18] and Lu et al.[19]). This method is known as the bridge DFT (i.e., DFT based on the bridge functions: such as the PY closure, the Verlet modified (VM) closure, and the hypernetted chain (HNC) closure). Reasonably accurate $\rho^{(1)}(\mathbf{r}_1,[w])$ were obtained.

This bilateral (two-way) relation has been established[17−19] for the quantity of the singlet density $\rho^{(1)}(\mathbf{r}_1,[w])$. In DFT, however, there is one other major quantity: the intrinsic free energy functional (IFEF), $F[\rho]$. Can the same theoretical reversal be applied to $F[\rho]$? An inkling of this possibility was given in 1992 in a paper[20] on the so-called star function $S(\mathbf{r})$ and the star series S^*. These functions have well-defined cluster diagrams for the uniform systems. S^* was constructed as the "primitive" (in the sense of the calculus of functional differentiation) of the bridge function. In the present work, we shall further generalize these quantities to the nonuniform systems and shall give closed form expressions for both the density profile $\rho^{(1)}(\mathbf{r}_1,[w])$ and the free energy functional $F[\rho]$. The resulting theory will be called the star-function based density functional theory.

In Section 2, we shall review the DFT. In Section 3, we make Taylor's functional expansion of the singlet density $\rho^{(1)}(\mathbf{r}_1,[w])$. In Section 4, we expand the free energy functional $F[\rho]$ into Taylor series and make resummations of the infinite high-order terms into a single function: the star series. We delineate the functional relations between the singlet density and the free energy functional. In Section 5, we perform numerical calculations on the LJ fluid adsorbed on a hard wall (LJ/HW). We shall show that the new formulation here correctly treats the attractive forces in the LJ potential and corrects the inadequacies of the mean field results.

2. Fundamental Relations

To establish the theoretical framework without ambiguity, we recapitulate some of the essential tenets of the DFT. The grand potential Ω is defined for a nonuniform system in general (not necessarily at equilibrium), subject to an external potential $w(\mathbf{r})$

$$\Omega \equiv F[\rho^{(1)}(\vec{r},[w])] + \int \mathrm{d}\vec{r}\ \rho^{(1)}(\vec{r},[w])\ \{w(\vec{r}) - \mu\} \tag{2.1}$$

The notation $F[.]$ indicates that F is a functional. Ω thus defined is a functional of the singlet density $\rho^{(1)}(\mathbf{r},[w])$. The singlet density $\rho^{(1)}(\mathbf{r},[w])$ is a function of the distance $\mathbf{r}$ from the origin and at the same time also a functional of the external potential $w(\mathbf{r})$. To simplify the notation, we shall write $\rho_w(\mathbf{r})$ for $\rho^{(1)}(\mathbf{r},[w])$ (subscript w denotes nonuniform quantities). μ is the chemical potential of the bulk fluid. F is the IFEF as mentioned before, being a functional of $\rho_w(\mathbf{r})$. When the system attains equilibrium, the grand potential is minimized with respect to the singlet density and can thus be equated to the grand canonical partition function $\ln \Xi$

$$\beta\Omega = -\beta PV = -\ln \Xi \text{ (at equilibrium)} \tag{2.2}$$

with the extremum condition

$$\frac{\delta\Omega}{\delta\rho_w(\mathbf{r})} = 0 \text{ (at equilibrium)} \tag{2.3}$$

From eqs 2.1 and 2.3, the Euler–Lagrange condition is

$$-\frac{\delta\beta F[\rho]}{\delta\rho_w(\vec{r})} = \beta w(\vec{r}) - \beta\mu = C^{(1)}(\vec{r};[w]) - \ln[\rho_w(\vec{r})\Lambda^3] \tag{2.4}$$

where we have applied the definition of the singlet direct correlation, namely,

$$C^{(1)}(\vec{r};[w]) \equiv \ln[\rho_w(\vec{r})\Lambda^3] + \beta w(\vec{r}) - \beta\mu \tag{2.5}$$

The s-DCF is a very useful quantity in liquid physics (see, e.g., Lee[21]). The symbol β is the reciprocal temperature $1/(kT)$, where k = Boltzmann constant, T = absolute temperature; Λ = de Broglie wavelength. To simplify, we shall write $C_w^{(1)}(\mathbf{r})$ for $C^{(1)}(\mathbf{r};[w])$. In the limit that the external potential vanishes, $w(\mathbf{r})$

= 0, $C_0^{(1)}(\mathbf{r}) = C^{(1)}(\mathbf{r};[w = 0])$ becomes the (negative) excess chemical potential of the uniform fluid:

$$C^{(1)}(\vec{r};[w] = 0) = C_0^{(1)}(\vec{r}) = \ln[\rho\Lambda^3] + 0 - \beta\mu = -\beta\mu^{\mathrm{ex}} \tag{2.6}$$

In view of the potential distribution theorem[22] (PDT) (or the SPT), $C^{(1)}(\mathbf{r};[w])$ is (the negative of) the work needed to insert a new particle into a fluid of existing molecules, uniform or otherwise. Rearrangement gives

$$\rho_w(\vec{r}) = \rho_0 \exp[-\beta w(\vec{r}) + \beta\mu^{\mathrm{ex}} + C_w^{(1)}(\vec{r})] \tag{2.7}$$

Thus, knowledge of the s-DCF will straightforwardly give the singlet density profile.

3. Functional Expansion of the Singlet Direct Correlation

Lebowitz and Percus[23] have shown earlier that high-order DCFs can be derived in terms of the s-DCF via functional differentiation

$$C^{(n)}(1, 2, 3, \ldots n) \equiv \frac{\delta^{n-1} C^{(1)}(1)}{\delta\rho(2)\ldots\delta\rho(n)} \tag{3.1}$$

for all $n > 1$. If we consider two states of the same fluid: at the beginning at state 0 the fluid is uniform ($w = 0$), and $C_0^{(1)} = C^{(1)}(\mathbf{r};[w = 0]) = -\beta\mu^{\mathrm{ex}}$. Upon turning on the external potential $w(\mathbf{r})$, the fluid reaches a final state w, with the singlet DCF $C_w^{(1)} = C^{(1)}(\mathbf{r};[w])$. The s-DCF at state $w \neq 0$ can be related to itself at $w = 0$ by a functional Taylor expansion

$$\begin{aligned} C^{(1)}(1;[w]) &= C^{(1)}(1;[w = 0]) + \\ &\frac{1}{1!}\int d2 \frac{\delta C^{(1)}(1;[w = 0])}{\delta\rho_w(2)} \delta\rho_w(2) + \\ &\frac{1}{2!}\int d2d3 \frac{\delta^2 C^{(1)}(1;[w = 0])}{\delta\rho_w(2)\, \delta\rho_w(3)} \delta\rho_w(2)\, \delta\rho_w(3) + \\ &\frac{1}{3!}\int d2d3d4 \frac{\delta^3 C^{(1)}(1;[w = 0])}{\delta\rho_w(2)\, \delta\rho_w(3)\, \delta\rho_w(4)} \delta\rho_w(2)\, \delta\rho_w(3)\, \delta\rho_w(4) + \\ &\frac{1}{4!}\int d2d3d4d5 \frac{\delta^4 C^{(1)}(1;[w = 0])}{\delta\rho_w(2)\, \delta\rho_w(3)\, \delta\rho_w(4)\, \delta\rho_w(5)} \times \\ &\delta\rho_w(2)\, \delta\rho_w(3)\, \delta\rho_w(4)\, \delta\rho_w(5) + \frac{1}{5!}\ldots + \frac{1}{6!} + \ldots \end{aligned} \tag{3.2}$$

Note that the functional derivatives $\delta^n C^{(1)}/(\delta\rho\ldots\delta\rho)$ are evaluated at the initial state 0 where $w(\mathbf{r}) = 0$ (the uniform bulk fluid). Thus the functional derivatives of the DCF are uniform fluid properties. The density difference $\delta\rho_w(\mathbf{r})$ is defined as

$$\delta\rho_w(\vec{r}) \equiv \rho_w(\vec{r}) - \rho_0 \equiv \rho_0 h_w(\vec{r}) \tag{3.3}$$

namely, it is the difference between the nonuniform density (ρ_w) and the uniform density (ρ_0). To simplify the notation, we shall use subscript w (wall) to denote nonuniform quantities, and subscript 0 ($w = 0$) for uniform quantities (no walls). For example, $C_0^{(2)}(|\mathbf{r}_1 - \mathbf{r}_2|) = C^{(2)}(\mathbf{r}_1, r_2;[w = 0])$. We have also defined a nonuniform total correlation function (tcf) $h_w(\mathbf{r})$ in 3.3.

For the uniform fluid, the counterpart of the expansion is (this happens when we use the test particle at $\mathbf{r}_0$ as the source of the external potential, that is, $w(\mathbf{r}_1) = u(|\mathbf{r}_1 - \mathbf{r}_0|)$, see Percus[16])

$$\begin{aligned} &C^{(1)}(1;[w = u(|\vec{r}_1 - \vec{r}_0|)]) - C_0^{(1)}(1;[w = 0]) = \\ &\ln y_0(|\vec{r}_1 - \vec{r}_0|) = \frac{1}{1!}\int d\vec{r}_2\, C_0^{(2)}(|\vec{r}_1 - \vec{r}_2|) \times \\ &\rho h_0(|\vec{r}_2 - \vec{r}_0|) + \frac{1}{2!}\int d\vec{r}_2 d\vec{r}_3\, C_0^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \times \\ &\rho h_0(|\vec{r}_2 - \vec{r}_0|)\, \rho h_0(|\vec{r}_3 - \vec{r}_0|) + \\ &\frac{1}{3!}\int d\vec{r}_2 d\vec{r}_3 d\vec{r}_4\, C_0^{(4)}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4) \times \\ &\rho h_0(|\vec{r}_2 - \vec{r}_0|)\, \rho h_0(|\vec{r}_3 - \vec{r}_0|) \rho h_0\, (|\vec{r}_4 - \vec{r}_0|) + \\ &\frac{1}{4!}\ldots + \frac{1}{5!}\ldots = \gamma_0(|\vec{r}_1 - \vec{r}_0|) + B_0(|\vec{r}_1 - \vec{r}_0|) \end{aligned} \tag{3.4}$$

where we have identified a uniform bridge function $B_0(|\mathbf{r}_1 - \mathbf{r}_0|)$ as the sum of the higher-order terms in the series ($n > 2$).

$$\begin{aligned} B_0(|\vec{r}_1 - \vec{r}_0|) \equiv &\frac{1}{2!}\int d\vec{r}_2 d\vec{r}_3\, C^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \times \\ &\rho h(|\vec{r}_2 - \vec{r}_0|)\, \rho h(|\vec{r}_3 - \vec{r}_0|) + \\ &\frac{1}{3!}\int d\vec{r}_2 d\vec{r}_3 d\vec{r}_4\, C^{(4)}(\vec{r}_1, r_2, \vec{r}_3, \vec{r}_4)\, \rho h(|\vec{r}_2 - \vec{r}_0|) \times \\ &\rho h(|\vec{r}_3 - \vec{r}_0|)\, \rho h(|\vec{r}_4 - \vec{r}_0|) + \frac{1}{4!}\ldots \end{aligned} \tag{3.5}$$

It is noted that in liquid theory, the derivation through functional derivatives has a similar counterpart in cluster series. Comparison of 3.2, 3.4, and 3.5 says, in the language of clusters, that we can also identify a nonuniform bridge functional $B_w(\mathbf{r})$ with similar cluster diagrams as the uniform bridge $B_0(|\mathbf{r}_1 - \mathbf{r}_0|)$ in eq 3.5. We thus define it as the following.

Nonuniform Bridge Functional $B_w(\mathbf{r})$.

$$\begin{aligned} B_w(1) \equiv &\frac{1}{2!}\int d2d3\, C_0^{(3)}(1, 2, 3)\, \delta\rho_w(2)\, \delta\rho_w(3) + \\ &\frac{1}{3!}\int d2d3d4\, C_0^{(4)}(1, 2, 3, 4)\, \delta\rho_w(2)\, \delta\rho_w(3)\, \delta\rho_w(4) + \\ &\frac{1}{4!}\int d2d3d4d5\, C_0^{(5)}(1, 2, 3, 4, 5)\, \delta\rho_w(2)\, \delta\rho_w(3) \times \\ &\delta\rho_w(4)\, \delta\rho_w(5) + \frac{1}{5!}\ldots + \frac{1}{6!} + \ldots \end{aligned} \tag{3.6}$$

Equation 3.2 can now be written as the following.

Closed Exact Expression for the s-DCF.

$$\begin{aligned} C_w^{(1)}(1) &= C_0^{(1)} + \int d2\, C_0^{(2)}(1, 2)\, \delta\rho_w(2) + B_w(1) \\ &\equiv C_0^{(1)} + \gamma_w(1) + B_w(1) \end{aligned} \tag{3.7}$$

This expression has been derived and used earlier.[18,19] Since the exact $B_w(\mathbf{r})$ is not readily amenable to numerical calculation, some conventional DFT theories chose to truncate the series (eq 3.4) at the second order, by setting $B_w(\mathbf{r}) = 0$ (see e.g. Ramakrishnan and Yussouff[24]). We instead choose to deal directly with the bridge function as it stands without truncation, and retain all orders in the Taylor expansion.

We have defined a nonuniform indirect correlation function (icf) $\gamma_w(\mathbf{r})$ in eq 3.7 by analogy with the uniform case, namely

$$\gamma_w(1) \equiv \int d2\, C_0^{(2)}(1, 2)\, \delta\rho_w(2) \tag{3.8}$$

Next, from the definition of the nonuniform singlet DCF

$$C_w^{(1)}(\vec{r}) = C_0^{(1)} + \gamma_w(\vec{r}) + B_w(\vec{r}) = -\beta\mu^{\text{ex}} + \gamma_w(\vec{r}) + B_w(\vec{r})$$

or

$$C_w^{(1)}(\vec{r}) = \ln[\rho_w(\vec{r})\Lambda^3] + \beta w(\vec{r}) - \beta\mu = \ln[\rho_0(\vec{r})\Lambda^3] - \beta\mu + \ln[\rho_w(\vec{r})/\rho_0] + \beta w(\vec{r}) \tag{3.9}$$

Nonuniform Singlet Density Formula.

$$\rho_w(\vec{r}) = \rho_0 \exp[-\beta w(\vec{r}) + \int d\vec{r}\,' C_0^{(2)}(\vec{r}, \vec{r}\,')\,\delta\rho_w(\vec{r}\,') + B_w(\vec{r})]$$

$$= \rho_0 \exp[-\beta w(\vec{r}) + \gamma_w(\vec{r}) + B_w(\vec{r})] \tag{3.10}$$

This expression has been used previously in the bridge DFT.[17−19] Note that in the hypernetted-chain (HNC) approximation, $B_w = 0$ and eq 3.10 simplifies to the Ramakrishnan−Yussouff[24] expression.

In this section, we have defined a nonuniform bridge functional, mirroring the uniform case. We are thus able to give a complete expression for the singlet direct correlation without truncation. This bridge functional formally contains all orders of DCF's ($n > 2$). The formulation is theoretically complete. In contrast, previous approaches (e.g., WDA, MWDA, SWDA) did not include, as a matter of principle, all higher-order DCF's in the Taylor expansion. (They may have included a subset ($k = 0$) of the higher order terms, see WDA.[11,12]) There is no possibility of amelioration in these latter formulations, since the correct higher-order terms are missing in their formulations.

4. Functional Expansion of the Free Energy Functional

In this section we shall carry out a similar expansion for the IFEF, $F[\rho]$. The development shall parallel the s-DCF expansion above. Given the definition of $F[\rho]$ in eq 2.1, we functionally differentiate the IFEF with respect to ρ_w, the equilibrium singlet density

$$\frac{\delta\beta\Omega}{\delta\rho_w(\vec{r})} = 0 = \frac{\delta\beta F_{[\rho]}}{\delta\rho_w(\vec{r})} + [\beta w(\vec{r}) - \beta\mu]$$

or

$$\frac{\delta\beta F_{[\rho]}}{\delta\rho_w(\vec{r})} = -[\beta w(\vec{r}) - \beta\mu] = \ln(\rho_w\Lambda^3] - C_w^{(1)}(\vec{r}) \tag{4.1}$$

Note that the grand potential is stationary with respect to $\rho_w^{(1)}$ at the equilibrium density ($\delta\Omega/\delta\rho = 0$). In the second equality we have applied the definition of s-DCF from eq 2.5. The IFEF can be split into two parts: one being the ideal gas part, $F^{\text{id}}[\rho] = \int d\mathbf{r}\ \rho_w(\mathbf{r})[\ln \rho_w(\mathbf{r})\Lambda^3 - 1]$, and the other the excess part, $F^{\text{ex}}[\rho]$

$$\beta F_{[\rho]} = \beta F_{[\rho]}^{\text{id}} + \beta F_{[\rho]}^{\text{ex}} = \int d\vec{r}\ \rho_w(\vec{r})[\ln \rho_w(\vec{r})\Lambda^3 - 1] + \beta F_{[\rho]}^{\text{ex}} \tag{4.2}$$

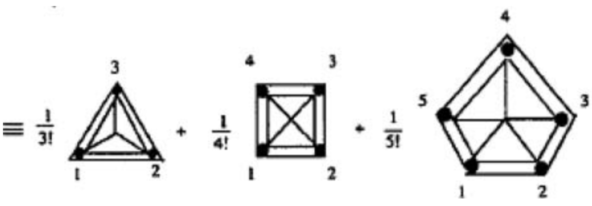
Combining 4.1 and 4.2 results in the following:

$$\frac{\delta\beta F_{[\rho]}^{\text{ex}}}{\delta\rho_w(1)} = -C_w^{(1)}(1) \tag{4.3}$$

In other words, the excess IFEF $-\beta F^{\text{ex}}[\rho]$ is the primitive of the singlet DCF, $C_w^{(1)}(\mathbf{r})$. Utilizing the Lebowitz−Percus[23] definition of the nth order DCF's from eq 3.1, we can expand the excess IFEF in the Taylor series

$$\begin{aligned}-\beta F_{[\rho]}^{\text{ex}} = -\beta F_0^{\text{ex}} &+ \frac{1}{1!}\int d1\ C_0^{(1)}(1)\,\delta\rho_w(1) + \frac{1}{2!}\int d1d2\ C_0^{(2)}(1,2)\,\delta\rho_w(1)\,\delta\rho_w(2) + \\ &\frac{1}{3!}\int d1d2d3\ C_0^{(3)}(1,2,3)\,\delta\rho_w(1)\,\delta\rho_w(2)\,\delta\rho_w(3) + \\ &\frac{1}{4!}\int d1d2d3d4\ C_0^{(4)}(1,2,3,4)\,\delta\rho_w(1) \times \delta\rho_w(2)\,\delta\rho_w(3)\,\delta\rho_w(4) + \frac{1}{5!}... + \frac{1}{6!}... + ...\end{aligned} \tag{4.4}$$

In a previous study,[20] we have defined a star series, S^*, for uniform fluids which has the cluster diagrams



(4.5)

These diagrams express exactly the same terms in eq 4.4 up to the fifth order. Note that the single-line bonds are defined as the ρh_0 (tcf) bonds; the double-lined polygons forming the outer frames were the nth-order DCFs, or the $C^{(n)}$ bonds, namely, the triangle is the $C^{(3)}(1,2,3)$ DCF, and the pentagon is the $C^{(5)}(1,2,3,4,5)$ DCF, and so forth. The black circles represent integrals over the indexed position vector: $\int d\mathbf{r}_i.(.)$. Now if we replace each and every ρh_0 bonds by the nonuniform $\delta\rho_w$

$$\rho h_0 \rightarrow \delta\rho_{\text{w}}$$

we shall have defined a new function, say S_w*, with exactly the same topological clusters as in the uniform case. Since $\delta\rho_w(\mathbf{r}) = \rho_w(\mathbf{r}) - \rho_0 = \rho_0 h_w(\mathbf{r})$ (where $h_w(\mathbf{r})$ is the nonuniform total correlation), the nonuniform star series S_w* is defined as

$$\begin{aligned}S_w^* \equiv &\frac{1}{3!}\int d1d2d3\ C_0^{(3)}(1,2,3)\,\delta\rho_w(1)\,\delta\rho_w(2)\,\delta\rho_w(3) + \\ &\frac{1}{4!}\int d1d2d3d4\ C_0^{(4)}(1,2,3,4)\,\delta\rho_w(1)\,\delta\rho_w(2)\,\delta\rho_w(3)\,\delta\rho_w(4) + \\ &\frac{1}{5!}\int d1d2d3d4d5\ C_0^{(5)}(1,2,3,4,5)\delta\rho_w(1)\,\delta\rho_w(2)\,\delta\rho_w(3) \times \\ &\delta\rho_w(4)\,\delta\rho_w^{(1)}(5) + \frac{1}{6!}... + ...\end{aligned} \tag{4.6}$$

Thus, eq 4.4 becomes the following.

Closed Form Expression for the IFEF.

$$-\beta F_{[\rho]}^{\text{ex}} = -\beta F_0^{\text{ex}} + \int d1\ C_0^{(1)}(1)\,\delta\rho_w(1) + \frac{1}{2}\int d1d2\ C_0^{(2)}(1,2)\,\delta\rho_w(1)\,\delta\rho_w(2) + S_w^* \tag{4.7}$$

We have given a closed form expression for the IFEF in terms of a star series that has been defined in eq 4.6.

Comparing the IFEF expansion here with the s-DCF expansion in Section 3 and functionally differentiating eq 4.7 (with respect to the singlet density $\rho_w(\mathbf{r})$)

$$C_w^{(1)}(\vec{r}) = C_0^{(1)}(\vec{r}) + \int d2\ C_0^{(2)}(2,\vec{r})\,\delta\rho_w(2) + \frac{\delta S_w^*}{\delta\rho_w(\vec{r})} \tag{4.8}$$

We have shown earlier[20] that the star series S_w* is the primitive of the bridge function $B_w(\mathbf{r})$, that is,

$$\frac{\delta S_w^*}{\delta \rho_w(\vec{r})} = B_w(\vec{r}) \tag{4.9}$$

Thus, eq 4.8 is identical to eq 3.7

$$C_w^{(1)}(\vec{r}) = C_0^{(1)}(\vec{r}) + \int d2\, C_0^{(2)}(\vec{r}, 2)\, \delta\rho_w(2) + B_w(\vec{r}) \tag{4.10}$$

The development shows that the formula 4.7 for the excess IFEF is consistent with the s-DCF given earlier in eq 3.7. They are all complete expressions without truncation. If we know the bridge functional, we can calculate consistently the free energy. But, these formal equations would amount to very little if we did not have means of obtaining the quantities involved, that is, the star function or the bridge functional. We shall examine these quantities further.

Reflections on the Star Series and the Bridge Functional. If a homotopy can be established in the Kirkwood charging formula for the chemical potentials and the bridge function satisfies unique functionality conditions, we have shown[20] that the bridge function and the star function are related by (hereby generalized to the nonuniform case)

$$S_w^* = \int \mathrm{d}\vec{r}\, \frac{\delta\rho_w(\vec{r})}{\gamma_w(\vec{r})} \int_{x=\gamma_0}^{x=\gamma_1} \mathrm{d}x\, \hat{B}(x) \tag{4.11}$$

This transcription (from the uniform system to the nonuniform system) is possible on the basis of their cluster expansions. A similar expression[28] has been derived recently.

$B(\mathbf{r};[w])$ as a bridge functional is dependent, in liquid theory, on the function $w(\mathbf{r}')$ through the partition function and its subsequent expansion into cluster series. Other types of correlation functions also admit cluster expansions. Thus, we can swap the arguments $[w]$ to other surrogate functions (such as the icf $\gamma_w(r)$ or the cavity function $y_w(r)$) where a one-to-one correspondence can be established

$$B_1(\vec{r};[w]) = B_2(\vec{r};[\gamma_w]) = B_3(\vec{r};[\ln y_w]) \tag{4.12}$$

The notation $B(\mathbf{r};[w])$ indicates that B, while itself a function of $\mathbf{r}$, is further dependent on all values of $w(\mathbf{r}')$ on the entire domain of $\mathbf{r}'$, that is, a functional of $w(\mathbf{r}')$.

Note that $\hat{B}(x)$ in 4.11 (with a caret) defines B as a function of x. In general $B(\mathbf{r};[w])$ should be a functional of $w(\mathbf{r}')$: physics says that $B(\mathbf{r})$ depends on the function $w(\mathbf{r}')$ through the cluster integrals. To use 4.11, we need somehow alter the nature of the function's dependence.

Renormalization of the Bridge Functional. We call the procedure of changing the dependence of $B(\mathbf{r};[w])$ on $w(\mathbf{r}')$ from a functional to a function $\hat{B}(x(\mathbf{r}))$ (so as to depend on some target variable x) the renormalization operation. The trick is to alter the argument $w(\mathbf{r}')$, by mathematical manipulations such as adding and/or multiplying, integration, or differentiation, with factors in such a way as to "extract" out all the $\mathbf{r}'$-dependences that are subversive (misbehaving) toward functionality. The renormalizing factor will be denoted by $\gamma_0(\mathbf{r})$.

In liquid-state theories, a number of relations called the "closures" are in common use which are de facto (approximate) renormalizations. The well-known ones (see ref 27) are the PY closure and the HNC closure and later the Verlet closure, the hybrid MSA (HMSA) closure, the Ballone−Pastore−Galli−Gazillo (BBPG) closure, and the Martynov−Sarkisov (MS) closure. These closures are all functions where $B = \hat{B}(x)$. We list a few of them below.

$$\hat{B}(\gamma) = \ln(1 + \gamma) - \gamma \quad \text{(PY)} \tag{4.13a}$$

$$\hat{B}(\gamma) = -\frac{1}{2}\left(\frac{\gamma^2}{1 + a\gamma}\right) \quad \text{(Verlet)} \tag{4.13b}$$

where a is a parameter and is equal to 0.8. These closure relations have so far been used for both uniform[21] and nonuniform[17−19] fluids. For the majority of these closures, the target x is chosen to be the icf γ, namely, the bridge B is assumed to be a function of γ, that is, $\hat{B}(\gamma)$. These closures were derived mostly from truncations of cluster series or from the consideration of collective coordinates. Thus, the above closures are more or less different approximations. The few closures that have made an attempt to address the issue of renormalization are the HMSA closure of Hansen and Zerah[29] and the RY closure of Rogers−Young. These approaches modify γ to γ^* and use the latter as the argument of $\hat{B}(\gamma^*)$

$$\gamma^* = \gamma - \beta u_{\mathrm{att}} \tag{4.14}$$

where u_{att} is the attractive part of the uniform pair potential. Other schemes[25] are also available. Duh and Haymet[26] have proposed a $B-\gamma^*$ plot (the Duh−Haymet plot) that traces the variations of the bridge function $B(\mathbf{r})$ versus the original (or the renormalized) icf $\gamma^*(\mathbf{r})$ at the same $\mathbf{r}$. If the $B-\gamma^*$ curve is well-behaved, we consider the closure a success. If $B-\gamma^*$ plot is multivalued, we consider the closure failed to achieve unique functionality[27] (it remains a functional).

One closure that we found quite effective in uniform fluids for a variety of pair potentials is the zero-separation (ZSEP) based closure[27]

$$\hat{B}(\gamma^*) = -\frac{\zeta}{2}\gamma^{*2}\left((1 - \phi) + \frac{\phi}{1 + \alpha\gamma^*}\right) \quad \text{(ZSEP)} \tag{4.15}$$

where γ^* is the renormalized target function. The parameters α, ϕ, and ζ are adjustable, in such a fashion as to enforce thermodynamic consistencies (e.g., the pressure consistency, Gibbs−Duhem relation, etc.) and structural consistencies (the contact value theorem, zero-separation theorem, etc.). For modification of the icf γ, we have in the past used several choices:[25,27] the attractive pair interaction βu_{att}, the WCA Mayer factor, f_{WCA}, and a number of other formulations. Tests on hard spheres, hard sphere mixtures, hard diatomics, LJ molecules, soft spheres (Gaussian potential), Coulomb interaction, for bulk systems, and for fluids included in random pores all demonstrated satisfactory accuracy.[27]

For nonuniform fluids in the external field $w(\mathbf{r})$, we shall write the ZSEP closure for $B_w(\mathbf{r})$ as

$$\hat{B}_w(\gamma_w^*) = -\frac{\zeta}{2}\gamma_w^{*2}\left[(1 - \phi) + \frac{\phi}{1 + \alpha\gamma_w^*}\right] \quad \text{(ZSEP, nonuniform)} \tag{4.16}$$

with

$$\gamma_w^* = \gamma_w - \beta u_{\mathrm{att}} \tag{4.17}$$

and γ_w being the nonuniform indirect function from eq 3.8. For this bridge function 4.16, we have derived its primitive, the S^* series,[27] where the necessary integration has been preformed. In the following section we shall apply these formulas to the system of LJ fluid at a hard wall.

5. LJ Fluid on a Planar Hard Wall

We shall test on an adsorptive system with which the MFT has been applied to in the past.[5] We want to verify if the present methodology can improve upon the MFT approach.

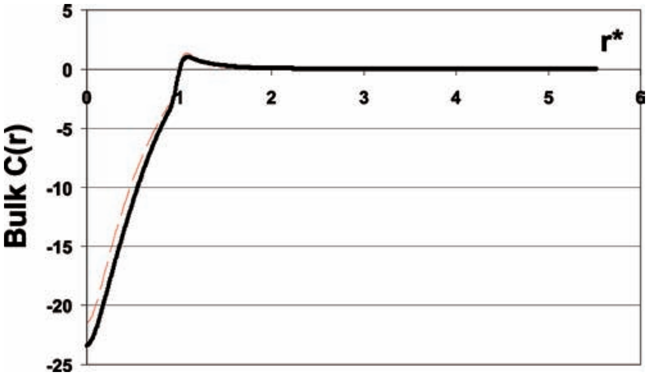


Figure 1. Bulk DCF $C_0^{(2)}(\mathbf{r})$ of LJ fluid at $T^* = 1.35$ and $\rho^* = 0.82$ as obtained from the ZSEP closure eq 4.15 (thick line) and the PY closure (thin line). The parameters of the ZSEP closure in eq 4.15 that give thermodynamically consistent properties are $\alpha = 0.6$, $\varphi = 0.997$, and $\zeta = 0.7$. The PY results are less accurate at this high density.

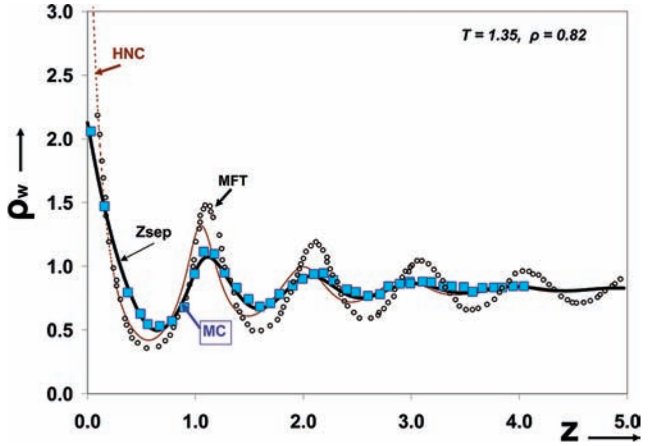


Figure 2. Comparison of the density profiles $\rho_w(z)$ derived from theories and from the Monte Carlo (MC) simulation[30] for the (LJ fluid/hard wall) system. ■, MC; ○, MFT; dotted line indicates HNC; solid line indicates ZSEP, the present theory. State conditions: $T^* = 1.35$, $\rho^* = 0.82$. Both the MFT and the HNC produce inaccurate predictions. The ZSEP theory in eq 4.16 gives a correct contact value and close agreement with MC data. The parameters of ZSEP are $\alpha = 0.6$, $\varphi = 1$, and $\zeta = 1$. The hard wall sum rule, eq 5.1, has been enforced.

Numerical Procedure. The state condition chosen is T^* $(= kT/\varepsilon) = 1.35$, and ρ^* $(= \rho\sigma^3) = 0.82$. ε and σ are parameters of the LJ potential. We calculate the density profile in eq 3.10. The steps are the following.

(i) The uniform pair DCF $C_0^{(2)}(\mathbf{r})$ is generated in a separate calculation for the bulk LJ fluid by using the ZSEP method.[27] The pair DCF thus obtained is of high accuracy. It is shown in Figure 1 together with that obtained from the PY closure. We can detect some tangible differences between the two closures. At this high density, the PY is less accurate.

(ii) The indirect correlation is evaluated according to its definition in eq 3.8.

(iii) For the bridge function, we use the ZSEP closure in eq 4.16 with renormalization as in eq 4.17.

(iv) The parameters in ZSEP are determined by satisfying the consistency conditions. We shall use the hard wall sum rule (which expresses the contact density as the result of the linear momentum transfer from the molecules to the flat wall, i.e., the bulk pressure)

$$\rho_w(z = 0) = \frac{P_0}{kT} \qquad (5.1)$$

where P_0 is the bulk pressure. The parameters in the ZSEP closure α, φ, and ζ, are adjusted so that the sum rule 5.1 is satisfied. As we have three parameters and only one condition, we choose to adjust α only and leave φ and ζ to their default values ($\varphi = 1$ and $\zeta = 1$). The value of α thus determined is 0.6.

Table 1. Calculations for the Excess Free Energy βF^{ex} of the LJ Fluid/Hard Wall System[a]

term	$\beta F_i^{\text{ex}}/a$
$\beta F_0^{\text{ex}}/a$	–1.4106
$\beta\mu_0^{\text{ex}}\int d2\ \rho_0 h_w(2)$	–0.5817
$-(\rho_0^2/2)\int d2d3\ c_0^{(2)}(2,3)\ h_w(2)\ h_w(3)$	2.4018
$-S_w{}^*/a$	–0.2227
sum	0.1868

[a] Individual contributions from the terms in eq 5.2 are listed. The units are specific energy per area a divided by kT, that is, $\beta F^{\text{ex}}/a$ (conditions: $T^* = 1.35$, $\rho^* = 0.82$).

The density profile $\rho_w(z)$ obtained is shown in Figure 2. We have also used the HNC closure (namely $B_w = 0$) in our calculations. Its results are plotted together in Figure 2 for comparison. The squares are the Monte Carlo (MC) data from Balabanic et al.[30] The small empty circles are the MFT results. We see that the MFT theory is inadequate here. It has exaggerated oscillations and also the wrong contact value. The HNC data, being close to MFT, gives a worse comparison, being too large at contact and oscillating out of phase with respect to MC. The full line is the present results (ZSEP). It matches the MC data closely. The oscillations are in-phase with the MC curve; the contact value $\rho_w(0) = 2.1$ (from ZSEP) compared well with $\rho_w(0) = 2.06$ (MC) (to within < 2 %). Of course, this is largely due to the fact that we have fitted the parameters to satisfy this condition.

Evaluation of the Free Energy Properties. We use eq 4.7 to evaluate the excess free energy βF^{ex}

$$\beta F_{[\rho]}^{\text{ex}} = \beta F_0^{\text{ex}} + \beta\mu_0^{\text{ex}} \int d1\ \rho_0\ h_w(1) - \frac{\rho_0^2}{2} \int d1d2\ C_0^{(2)}(1,2)\ h_w(1)\ h_w(2) - S_w^* \qquad (5.2)$$

We need input from the uniform LJ fluid for the quantities βF_0^{ex} and $\beta\mu_0^{\text{ex}}$. This was done in a separate calculation with the uniform OZ equation. The rest of terms can be evaluated from the output obtained from the DFT calculations. The results are listed in Table 1.

We observe that the star function contributes substantially to the total excess free energy (−0.2227 versus 0.1868: over 120 %). We can ill-afford to ignore the $S_w{}^*$ term. Traditional DFT discarded the star series and made up with the altered direct correlations through the WDAs. In our approach, this detour is not needed.

6. Conclusions

In this work, the IFEF $F[\rho]$ acts as a generating functional in the sense of Lebowitz−Percus.[23] Its functional Taylor expansion leads to an infinite series in the nonuniform density. By invoking the star series $S_w{}^*$ from an earlier development,[20] we are able to terminate the Taylor series without approximation. The resulting IFEF is formally exact and complete in terms of all orders of the DCFs. Functionally differentiating this free energy functional gives the singlet direct correlation in terms of the familiar bridge functional $B_w(\mathbf{r})$. The two formulations are mathematically mutually consistent. Since the star series can be obtained from the bridge function with the aid of an explicit formula in eq 4.11, we can easily calculate both quantities once any one of them is known. To obtain the bridge functional, parallelism between the uniform and the nonuniform systems as established by Denton and Ashcroft[15] via the Percus test particle intuition enables us to employ and deploy the liquid theory closures to the calculation of the density profiles of the LJ fluid on a hard wall. Use of the ZSEP closure shows that we can obtain accurate singlet density without the MFT. In fact, the new approach cures the inaccuracies of the MFT. This opens the door of applications to other simple attractive-force potentials, such as attractive Yukawa potential (for colloidal systems) and Coulomb interactions (on electrodes and in electrochemistry). We anticipate future work in these directions.

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