Self-consistent construction of bridge functional based on the weighted density approximation

Cite as: J. Chem. Phys. 154, 124113 (2021); doi: 10.1063/5.0046630 Submitted: 5 February 2021 • Accepted: 9 March 2021 • Published Online: 24 March 2021



Tomoaki Yagi¹ 🕩 and Hirofumi Sato^{1,2,3,a)} 🕩

AFFILIATIONS

¹Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan
 ²Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyoto 615-8520, Japan
 ³Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan

^{a)}Author to whom correspondence should be addressed: hirofumi@moleng.kyoto-u.ac.jp

ABSTRACT

A parameter-free bridge functional is presented using a weighted density approximation (WDA). The key point of this scheme is the utilization of Baxter's relation connecting the second-order direct correlation function (DCF) to the higher-order DCF with the density derivative. The free energy density required for the WDA is determined in a self-consistent manner using Baxter's relation and Percus's test particle method. This self-consistent scheme enables us to employ any type of potential model for simple liquids. The new functional is applied to calculate density distribution functions for the inhomogeneous fluids interacting via the hard-sphere, Lennard-Jones, and hard-core Yukawa potentials under an external field from a planar wall and a slit pore.

Published under license by AIP Publishing. https://doi.org/10.1063/5.0046630

I. INTRODUCTION

Density functional theory (DFT) is a versatile and powerful approach to studying the thermodynamics of inhomogeneous classical fluids.¹ For applications, the main challenge is to construct a functional of the excess free energy that contains all the information about the inter-particle correlation for the system of interest. Among the variety of approximation methods developed so far, the wellknown nonperturbative approaches are based on the weighted density approximation (WDA) techniques.^{2–13} In a WDA approach, the excess free energy is approximated by the spatial integration of the excess free energy density at a smoothed average density, determined from a suitably weighted average of the actual nonuniform density distribution of the system. Other versions of the WDA mainly differ in the procedure for the calculation of the smoothed density by (1) local averaging, 2^{-8} (2) global averaging, 9^{-11} or (3) a hybrid of both local and global averaging.^{12,13} The fundamental measure theory (FMT),¹⁴ which gives the most successful and most accurate free energy functional for hard-sphere mixtures, is categorized into the WDA based on local averaging. The WDA with a mean-field approximation has been quite successful in Lennard-Jones fluids,²

ionic fluids,^{22,23} and dipolar fluids.^{24,25} The drawback of the WDA is that it requires the analytic expression of the free energy density as a function of density. Because the accurate equation of state is only available for the hard-sphere fluids, the application of the WDA is still limited to simple liquids.

The perturbative approach to constructing the excess free energy functional has also been developed. The Taylor expansion of the excess free energy around a uniform bulk density gives the formally exact expression as an infinite series. If the deviation in the density distribution is not so large from the uniform bulk density, the truncation of the higher-order terms gives a good approximation. In particular, the second-order truncation is called the hypernetted-chain (HNC) approximation. The weakness of the HNC approximation has been reported by many authors.² Owing to the quadratic expansion, the free energy as a function of density has a single well instead of a double well. It cannot account for the liquid-gas transition; consequently, it largely overestimates the energy penalty for the depletion of the solvent around a solvophobic surface. This needs to be corrected by including the functional beyond second-order, the so-called bridge functional. Barrat et al. took into account the third-order term by

introducing the factorization ansatz for the triplet DCF.³⁴ However, owing to the infeasible numerical integration of the higher-order terms, the direct implementation of the bridge functional has been limited to less than the fourth-order term. Another attempt is that the bridge functional is approximated as that for the hard-sphere system obtained from the WDA.^{29–32} In this method, the diameter of the hard-sphere is adjusted to reproduce the property of the system of interest. Recently, Borgis *et al.* proposed the ansatz for the bridge part of the free energy density, which is parameterized with thermodynamic properties of the bulk solvent.³⁵ The WDA for the bridge functional with this free energy density gives accurate hydration energies for organic molecules as compared with those from simulation and experiment.

The purpose of this work is to construct a parameter-free bridge functional in a systematic manner. The key point of this method is the utilization of Baxter's relation that connects the second-order DCF to higher-order DCFs with the density derivative.³⁶ Although the full information about the higher-order DCF is inaccessible, its Fourier component at the zero-wave vector is available from Baxter's relation and the density derivative of the Ornstine-Zernike equation. Using the zero-wave vector component of the DCFs, we can construct the free energy density as a finite power series of density. We implement the WDA for the bridge functional with this free energy density. The second-order DCF and its density derivatives are determined in a self-consistent manner by using Percus's test particle method. Because we do not need to preliminarily prepare the free energy density, this scheme is applicable to any type of fluid models. The new functional is applied to calculate density distribution functions for the inhomogeneous fluids interacting via the hard-sphere, Lennard-Jones, and hard-core Yukawa potentials under external fields such as confinement in several geometries.

II. CONSTRUCTION OF BRIDGE FUNCTIONAL

A. Weighted density approximation

In this study, we consider a one-component simple liquid. The generalization of the following to mixture systems is straightforward. We perform the Taylor expansion of the excess Helmholtz free energy around the bulk density,

$$\mathscr{F}^{\mathrm{ex}}[\rho] = \mathscr{F}^{\mathrm{ex}}[\rho_0] + \mu^{\mathrm{ex}}(\rho_0) \int \mathrm{d}\boldsymbol{r}_1 \Delta \rho(\boldsymbol{r}_1) - \frac{1}{2\beta} \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 \mathrm{C}^{(2)} \\ \times (|\boldsymbol{r}_1 - \boldsymbol{r}_2|;\rho_0) \Delta \rho(\boldsymbol{r}_1) \Delta \rho(\boldsymbol{r}_2) + \mathscr{F}^{\mathrm{ex}}_{\mathrm{B}}[\rho], \tag{1}$$

$$\mathscr{F}_{B}^{ex}[\rho] \equiv \sum_{n=3}^{\infty} \frac{1}{n!} \int d\boldsymbol{r}_{1} \cdots \int d\boldsymbol{r}_{n} C^{(n)}(\boldsymbol{r}_{1}, \dots, \boldsymbol{r}_{n}; \rho_{0}) \\ \times \Delta \rho(\boldsymbol{r}_{1}) \cdots \Delta \rho(\boldsymbol{r}_{n}), \qquad (2)$$

where $C^{(n)}$ represents the *n*th order direct correlation function (DCF),

$$C^{(n)}(\mathbf{r}_{1},\ldots,\mathbf{r}_{n};\rho_{0}) \equiv -\beta \frac{\delta^{n} \mathscr{F}^{\mathrm{ex}}[\rho]}{\delta \rho(\mathbf{r}_{1}) \cdots \delta \rho(\mathbf{r}_{n})} \bigg|_{\rho=\rho_{0}}.$$
 (3)

The bridge functional, \mathscr{F}_{B}^{ex} , contains a higher-order correlation beyond the quadratic approximation. The full information of higher-order DCFs is inaccessible, and even if it is accessible, the

numerical integration of the multi-dimensional space is infeasible. Neglecting the bridge functional reduces Eq. (1) to the hypernettedchain (HNC) approximation. To obtain the bridge functional as a tractable form, in this scheme, the excess free energy functional \mathscr{F}^{ex} is assumed to be of the form

$$\mathscr{F}_{\mathrm{B}}^{\mathrm{ex}}[\rho] \approx \frac{1}{\beta} \int \mathrm{d}\boldsymbol{r} f_{\mathrm{B}}^{\mathrm{ex}}(\bar{\rho}[\rho](\boldsymbol{r})), \tag{4}$$

where $f_B^{ex}(\rho)$ denotes the bridge part of the excess free energy density of a uniform liquid of bulk density ρ . The construction of f_B^{ex} is shown in Sec. II B. We perform the first order Taylor expansion of the effective density around the bulk density,

$$\bar{\rho}[\rho](\boldsymbol{r}) \approx \rho_0 + \int \mathrm{d}\boldsymbol{\underline{r}} W(|\boldsymbol{r}-\boldsymbol{\underline{r}}|) \Delta \rho(\boldsymbol{\underline{r}}), \tag{5}$$

where we define the weight function

$$W(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) \equiv \left. \frac{\delta \bar{\rho}[\rho](\boldsymbol{r}_2)}{\delta \rho(\boldsymbol{r}_1)} \right|_{\rho = \rho_0}.$$
 (6)

The self-consistent determination of *W* is shown in Sec. II C.

B. Free energy density

Unfortunately, an accurate expression for the free energy density is available only for hard-sphere systems; a general framework for the system of interest is necessary. From the density expansion of the excess free energy [Eq. (1)], its density is given as

$$f^{\text{ex}}(\rho) = \beta \mathscr{F}^{\text{ex}}(\rho) / V$$

= $f^{\text{ex}}(\rho_0) + \mu^{\text{ex}}(\rho_0) \Delta \rho - \frac{1}{2} \tilde{C}^{(2)}(0;\rho_0) \Delta \rho^2 + f_{\text{B}}^{\text{ex}}(\rho),$ (7)

where \tilde{C} represents the Fourier transform $\tilde{C}(k) \equiv \int d\mathbf{r} e^{i\mathbf{r}\cdot k} C(\mathbf{r})$. The bridge part of the free energy density is written as

$$f_{\rm B}^{\rm ex}(\rho) = -\sum_{n=3}^{\infty} \frac{1}{n!} \tilde{C}^n(0,\ldots,0;\rho_0) \Delta \rho^n.$$
(8)

In contrast to the virial expansion whose reference density is set to zero, the reference density of this method can be set to an arbitrary value. From Baxter's relation,³⁶ the higher-order DCFs are given as the bulk density derivative of the second-order DCF,

$$\partial_{\rho_0}^n \tilde{C}^{(2)}(k;\rho_0) = \tilde{C}^{(n+2)}(k,0,\ldots,0;\rho_0).$$
(9)

The bridge part of the excess free energy density is given by the second-order DCF and its density derivatives,

$$f_{\rm B}^{\rm ex}(\rho) = -\sum_{n=3}^{\infty} \frac{\Delta \rho^n}{n!} \partial_{\rho_0}^{n-2} \tilde{C}^{(2)}(0;\rho_0).$$
(10)

As shown in Sec. II D, the density derivatives of the DCF are determined by using a self-consistent scheme.

C. Weight function

From the definition of the DCF [Eq. (3)], the third-order DCF is written by the convolution of the weight function,

$$C^{(3)}(\boldsymbol{r}_{2} - \boldsymbol{r}_{1}, \boldsymbol{r}_{3} - \boldsymbol{r}_{1}; \rho_{0}) = \tilde{C}^{(3)}(0, 0; \rho_{0}) \int d\underline{\boldsymbol{r}} W(|\boldsymbol{r}_{1} - \underline{\boldsymbol{r}}|) \times W(|\boldsymbol{r}_{2} - \underline{\boldsymbol{r}}|) W(|\boldsymbol{r}_{3} - \underline{\boldsymbol{r}}|).$$
(11)

The Fourier transform of Eq. (11) gives

$$\tilde{C}^{(3)}(\boldsymbol{k}_1, \boldsymbol{k}_2; \rho_0) = \tilde{C}^{(3)}(0, 0; \rho_0) \tilde{W}(|\boldsymbol{k}_1|) \tilde{W}(|\boldsymbol{k}_2|) \tilde{W}(|\boldsymbol{k}_1 + \boldsymbol{k}_2|), \quad (12)$$

where we use the convolution theorem. When $k_1 = 0$ and $k_2 = 0$, Eq. (12) gives

$$\{\tilde{W}(0)\}^3 = 1 \rightarrow \tilde{W}(0) = 1.$$
 (13)

Thus, the weight function is normalized. When $k_1 = k$ and $k_2 = 0$, Eq. (12) gives

$$\tilde{C}^{(3)}(k,0;\rho_0) = \tilde{C}^{(3)}(0,0;\rho_0) \{W(k)\}^2.$$
(14)

Taking the square root of Eq. (14), we obtain the weight function as

$$\tilde{W}(k) = \sqrt{\frac{\tilde{C}^{(3)}(k,0;\rho_0)}{\tilde{C}^{(3)}(0,0;\rho_0)}}.$$
(15)

This expression is problematic. Inside the square root, Eq. (15) has a minus sign at some wave vectors, contradicting the requirement that the weighted density has to be real. To avoid this, we modify the weight function as

$$\tilde{W}(k) = \sqrt{\left|\frac{\tilde{C}^{(3)}(k,0;\rho_0)}{\tilde{C}^{(3)}(0,0;\rho_0)}\right|}.$$
(16)

From Bochner's theorem,³⁷ the non-negativity of the Fourier transform [Eq. (16)] makes the weight function in real space positivedefinite. The positive-definiteness ensures that the spatial average of the weighted density is non-negative. As seen in the expression of Eq. (16), the feature of the weight function is similar to that of the DCF, which almost decays within the core region.

D. Self-consistent determination of bridge functional

The density distribution of the inhomogeneous fluid under the external field $v(\mathbf{r})$ is given as the Boltzmann factor of the effective potential,¹

$$\rho(\mathbf{r}) = \rho_0 \exp\left[-\beta v^{\text{eff}}(\mathbf{r})\right],\tag{17}$$

$$\beta v^{\text{eff}}(\boldsymbol{r}) = \beta v(\boldsymbol{r}) - \int d\boldsymbol{\underline{r}} c(\boldsymbol{r} - \boldsymbol{\underline{r}}) \Delta \rho(\boldsymbol{\underline{r}}) + B(\boldsymbol{r}),$$
 (18)

where the second-order DCF, $C^{(2)}(r)$, is abbreviated as c(r). We define the bridge function as

$$B(\mathbf{r}) \equiv \beta \frac{\delta \mathscr{F}^{\mathrm{B}}[\rho]}{\delta \rho(\mathbf{r})} = \int \mathrm{d}\underline{\mathbf{r}} f_{\mathrm{B}}^{\mathrm{exr}} (\rho^{\mathrm{eff}}(\underline{\mathbf{r}})) W(|\underline{\mathbf{r}} - \mathbf{r}|), \qquad (19)$$

where $f_B^{ext}(\rho)$ is the derivative coefficient of $f_B^{ex}(\rho)$. Percus's relation identifies the pair correlation function (PCF) for the homogeneous bulk system with the density distribution function under the fixed test particle, which is identical to the solvent particle.³⁵ This relation and Ornstein–Zernike equation give self-consistent equations for the PCF and the DCF,

$$h(r) = \exp\left[-u^{\text{eff}}(r)\right] - 1, \qquad (20)$$

$$\beta u^{\text{eff}}(r) = \beta u(r) - h(r) + c(r) + b(r), \qquad (21)$$

$$b(|\mathbf{r}_1 - \mathbf{r}_2|) \equiv \int d\underline{\mathbf{r}} f_{\mathrm{B}}^{\mathrm{ext}}(\rho_0 \tilde{g}(|\mathbf{r}_1 - \underline{\mathbf{r}}|)) W(|\underline{\mathbf{r}} - \mathbf{r}_2|), \qquad (22)$$

$$\tilde{g}(|\mathbf{r}_1 - \mathbf{r}_2|) \equiv \int \mathrm{d}\underline{\mathbf{r}} W(|\mathbf{r}_1 - \underline{\mathbf{r}}|) h(|\underline{\mathbf{r}} - \mathbf{r}_2|) + 1, \qquad (23)$$

where u(r) is the pair potential. The Ornstein–Zernike equation in the Fourier space is written as

$$\tilde{h}(k) = \tilde{c}(k) + \rho_0 \tilde{c}(k)\tilde{h}(k).$$
(24)

Because the expression for the bridge function, b(r), includes the density derivatives of the DCF, these equations are not closed. The *i*th density derivatives of Eqs. (20), (21), and (23) give

$$\partial_{\rho_0}^i h(r) = \partial_{\rho_0}^i \exp\left[-u^{\text{eff}}(r)\right], \qquad (25)$$

$$\partial_{\rho_0}^i u^{\text{eff}}(r) = \partial_{\rho_0}^i [-h(r) + c(r) + b(r)], \qquad (26)$$

$$\partial_{\rho_0}^i \tilde{h}(k) = \partial_{\rho_0}^i \big[\tilde{c}(k) + \rho_0 \tilde{c}(k) \tilde{h}(k) \big].$$
⁽²⁷⁾

To close these equations, we have to truncate the higher-order terms of the free energy density [Eq. (10)]. If we truncate the higher-order terms beyond the *n*th order term, as schematically shown in Fig. 1, Eqs. (20)–(27) give the self-consistent iteration loop to determine the DCF and its density derivatives. First, we set the values of correlation functions as zero. Then, we start the calculation of the self-consistent loop for the PCF, the DCF, and the effective potential. If the iteration is converged, next, we start the calculation of the self-consistent loop for the first derivatives. In the same way, we calculate the *i*th derivatives (i = 1, ..., n) in order. After the calculation of the *n*th derivatives, we return to the first. This procedure is repeated until these become consistent with those obtained in the previous loop.



FIG. 1. The self-consistent loops for (a) the correlation functions of homogeneous systems and (b) the density distribution of the inhomogeneous system.

J. Chem. Phys. **154**, 124113 (2021); doi: 10.1063/5.0046630 Published under license by AIP Publishing The converged DCF and its density derivative give the excess free energy functional. Then, we can obtain the bridge functional and implement the iteration loop to determine the inhomogeneous density distribution. We refer to this functional as the weighted density bridge functional (WDBF).

III. APPLICATION TO HOMOGENEOUS AND INHOMOGENEOUS LIQUID STRUCTURES

A. Computational details

We applied the new method to a hard-sphere (HS) fluid with diameter σ , the Lennard-Jones (LJ) fluid interacting via

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right], \qquad (28)$$

and the hard-core Yukawa fluid interacting via

$$u(r) = \begin{cases} \infty, & r < \sigma \\ -\varepsilon \frac{\sigma}{r} \exp\left[-\lambda \left(\frac{\sigma}{r} - 1\right)\right], & r > \sigma, \end{cases}$$
(29)

where ε , σ , and λ are the depth of the potential well, the diameter of the particle, and the screening length for the Yukawa tail, respectively. In this study, the screening length $\lambda = 1.8$ is used. The reduced temperature, $T^* = k_B T/\varepsilon$, and the reduced density, $\rho^* = \rho \sigma^3$, uniquely specify the thermodynamic state of these fluids.

The self-consistent equations for the homogeneous fluids [Eqs. (20)–(27)] are solved using the fast Fourier transform with 16 384 linear radial grids. To ensure the numerical stability of the iteration loop, we neglect the bulk density dependence of the bridge function included in Eq. (26). The maximum value of the radial distance is set to 50.0σ for the HS and LJ fluids. The obtained solutions for the DFCs are used for the excess Helmholtz free energy [Eq. (1)] and the weight function [Eq. (16)]. The self-consistent equations for the inhomogeneous fluids [Eqs. (17)–(19)] are solved using the fast Fourier transform with 16 384 linear grids. A Picard iteration scheme is employed to solve the equations for both homogeneous and inhomogeneous fluids. The bridge functional truncated to the *n*th order term is denoted by WDBF(*n*). We show the result from WDBF(4) and WDBF(5).

B. Results

1. Homogeneous HS, LJ, and Yukawa fluids

In Fig. 2(a), the DCFs for the hard-sphere fluid are presented for the densities of $\rho^* = 0.6$, 0.8, and 0.9. At the density of $\rho^* = 0.6$, HNC+WDBF(4,5) is quantitatively consistent with the MC result, while the HNC theory slightly overestimates in comparison with the MC result. At densities higher than $\rho^* = 0.6$, the HNC theory largely overestimates. On the other hand, the HNC+WDBF(4) results show a better agreement with these MC results for the densities $\rho^* = 0.8$ and 0.9. However, the iteration loop for the solution of HNC+WDBF(5) was not converged.

The DCFs for the LJ fluid at $T^* = 0.75$ and $\rho^* = 0.84$ are displayed in Fig. 2(b). The thermodynamic state is near the triple point. The agreement of the HNC result with the simulation is somewhat



FIG. 2. The direct correlation functions of homogeneous systems. (a) Hard-sphere fluids. The Monte Carlo (MC) simulation data are taken from Ref. 38. (b) Lennard-Jones fluids. The molecular dynamics (MD) simulation data are taken from Ref. 39.

poor. HNC+WDBF(4,5) shows a better agreement with the simulation result. Although slight overestimation is still observed in HNC+WDBF(4), the result of HNC+WDBF(5) shows a quantitative agreement with the simulation data in the entire range of r.

We calculated the isothermal pressure as a function of density via the virial route. The virial pressure is given by^{26}

$$p(\rho) = k_B T \rho - \frac{2}{3} \pi \rho^2 \int_0^\infty dr r^3 [h(r) + 1] \frac{du(r)}{dr}.$$
 (30)

The extent of the agreement with the simulation data indicates the accuracy of the pair correlation functions h(r) within the range of u(r). In Fig. 3(a), we present the results of $p(\rho)$ for temperatures $T^* = 0.9$ and 1.3. For both high and low temperatures, the HNC largely overestimates the pressure in comparison with the simulation data. For a high temperature, the result of HNC+WDBF(4,5) agrees well with the simulation data. However, for a low temperature, the large overestimation is observed in HNC+WDBF(4) at high density. The result of HNC+WDBF(5) shows a better agreement with simulation data. The iteration loop for the solution of HNC+WDBF(5) at over $\rho^* = 0.85$ was not converged.

We calculated the isothermal excess chemical potential as a function of density. Using the test particle insertion method, the

$$\beta \mu^{\text{ex}} = \rho_0 \int d\mathbf{r} \left[\frac{1}{2} h(r) \{ h(r) - c(r) \} - c(r) \right]$$

- $\rho_0 \int d\mathbf{r} \tilde{g}(r) b(r) + \beta \mathscr{F}_{\text{B}}^{\text{ex}} [\rho = \rho_0 g].$ (31)

In Fig. 3(b), we show the excess chemical potential $\mu^{\text{ex}}(\rho)$ for temperatures $T^* = 0.75$, 1.0, and 1.35. As well as the pressure, for all thermodynamic conditions, the HNC largely overestimates the chemical potential in comparison with the simulation data. HNC+WDBF(4,5) shows a better agreement. More precisely, the results of WDBF(5) are closer to the simulation than those of HNC+WDBF(4), indicating that for the thermodynamic property of the LJ fluid, the WDBF approach provides a great improvement in hightemperature conditions, while the improvement is moderate at low temperatures.

In Fig. 4, we display the structure factors, $S(k) = 1 + \rho_0 \bar{h}(k)$, of the Yukawa fluids for (a) $\rho^* = 0.30$, $T^* = 1.50$ and (b) $\rho^* = 0.60$, $T^* = 1.50$. For both conditions, in comparison with the simulation results, the long-wavelength components, $S(k \rightarrow 0)$, are overestimated by the HNC approximation. HNC+WDBF(4,5) improves



FIG. 3. Thermodynamic quantities of homogeneous Lennard-Jones fluids. (a) Isothermal pressure. The Monte Carlo (MC) simulation data are taken from Ref. 40. (b) Isothermal excess chemical potential. The Monte Carlo (MC) simulation data are taken from Ref. 41.



FIG. 4. The structure factors of the Yukawa fluids: (a) $\rho^* = 0.30$, $T^* = 1.50$ and (b) $\rho^* = 0.60$, $T^* = 1.50$. The Monte Carlo (MC) simulation data are taken from Ref. 42.

the deficiency and provides the quantitative agreement with the simulation results in the entire range of k.

2. HS, LJ, and Yukawa fluids near a planar wall

In Fig. 5, the density profiles of the hard-sphere fluid at a planar hard wall are displayed for the densities (a) $\rho^* = 0.5745$ and (b) $\rho^* = 0.8130$. The surface of the hard wall is located at z = 0. While, at both densities, the HNC and HNC+WDBF(4,5) results agree well with the MC result except at the value of z very close to the wall, these overestimate the contact value of the density distribution. The contact value obtained from HNC+WDBF(4,5) is smaller than that from the HNC, and the density value of HNC+WDBF(4,5) at the vicinity of the wall is closer to the simulation data. HNC+WDBF(5) improves the agreement compared with HNC+WDBF(4).

To get a more comprehensive evaluation of the WDBF, we calculated the excess adsorption of HS fluids near the hard wall. The excess adsorption, defined by

$$\Gamma(\rho_0) = \int_0^\infty \mathrm{d}z [\rho(z) - \rho_0], \qquad (32)$$

provides a systematic check of the overall behavior of density profiles. In Fig. 6, we show the excess adsorption as a function of the reduced density. At low values of ρ^* , the DFT results are almost indistinguishable from each other and agree very well with the MD data.⁴⁴ In the HNC result, the deviation from the simulation



FIG. 5. The density profile of the hard-sphere fluids near the hard wall at (a) $\rho^* = 0.5745$ and (b) $\rho^* = 0.8130$. The Monte Carlo (MC) simulation data are taken from Ref. 43.

data gradually increases for $\rho^* > 0.30$. While the excess adsorption increases toward less negative values for $\rho^* < 0.60$ in the simulation results, the HNC+WDBF(4,5) results display a local minimum and then decrease further for $\rho^* \rightarrow 0.6$. The discrepancy at high densities $\rho^* > 0.7$ is also observed in the FMT.¹⁹



FIG. 6. The excess adsorption of the hard-sphere fluids near the hard wall. The molecular dynamics (MD) simulation data are taken from Ref. 44.

Figure 7 shows the density distributions of the LJ fluids near a hard wall at the bulk densities $\rho^* = 0.50$ and 0.65 and temperature $T^* = 1.30$. As shown in Fig. 7(a), the LJ particles are depleted around the solid-fluid interface, and the density rises monotonously with the separation from the wall until it reaches the bulk density. The depletion is attributed to the attraction from the bulk liquid, which balances the adhesion of particles due to the short-range repulsive interactions. Clearly, all these features are qualitatively captured by WDBF(5). The performance of WDBF(5) is moderately better than that of the HNC theory, which largely overestimates the densities around the hard wall. Figure 6(b) shows the density profile at a higher bulk density. In this case, the density distribution recovers the bulk value in an oscillatory manner, indicating that the repulsion takes more control. As in Fig. 7 (b), HNC+WDBF largely overestimates the densities around the wall. Thus, it suggests that the WDBF is still inappropriate to quantitatively describe LJ fluids near a hard wall. It may be of interest to mention that our WDBF results are very close to those from the modified FMT with the mean-field approximation by Tang and Wu.²¹

Figure 8 displays the density profiles of the Yukawa fluids ($\rho^* = 0.70, T^* = 1.10$) near a planar wall. The interaction potential



FIG. 7. The density profile of the Lennard-Jones fluids near the hard wall at (a) $\rho^* = 0.50$, $T^* = 1.30$ and (b) $\rho^* = 0.65$, $T^* = 1.30$. The Monte Carlo (MC) simulation data are taken from Ref. 45.



FIG. 8. The density profile of the Yukawa fluids ($\rho^* = 0.70$, $T^* = 1.10$, and $\lambda = 1.80$) near (a) the hard wall ($\varepsilon_w/\varepsilon = 0.0$) and (b) the attractive wall ($\varepsilon_w/\varepsilon = 2.5$). The Monte Carlo (MC) simulation data are taken from Ref. 46.

between the Yukawa particles and the wall is expressed as

$$v(z) = \begin{cases} \infty & (z < \frac{\sigma}{2}) \\ -\varepsilon_{w} \exp\left[-\lambda\left(\frac{z}{\sigma} - 1\right)\right] & (z > \frac{\sigma}{2}). \end{cases}$$
(33)

Two potential depths $\varepsilon_w/\varepsilon = 0.0$ and 2.5 are considered. These parameters correspond to the hard wall and the attractive-wall models, respectively. As shown in Fig. 7(a), similar to the LJ fluids, the Yukawa particles are depleted around the hard wall. On the other hand, the depletion does not occur for the attractive wall [Fig. 7(b)]. For both cases, the HNC and WDBF(4,5) largely overestimate the contact densities. Although the contact density obtained from WDBF(4,5) is closer to that from the simulation result, the deviation is still large. As in the case of the LJ fluids, the WDBF underestimates the attraction.

3. LJ fluids in a slit pore

In Fig. 9, we show the density profiles of the LJ fluid at $T^* = 1.2$ and $\rho^* = 0.5925$ in the slit pore with (a) $H/\sigma = 3.0$ and (b) $H/\sigma = 4.0$. The interaction potential between the LJ particles and the



FIG. 9. The density profiles of Lennard-Jones fluids at $\rho^* = 0.5925$ and $T^* = 1.20$ in the slit pore with (a) $H = 3.0\sigma$ and (b) $H = 4.0\sigma$. The Monte Carlo (MC) simulation data are taken from Ref. 47.

planar wall is modeled by Steele's 10-4-3 potential,⁴⁷

$$v_{w}(z) = \varepsilon_{w} \left[\frac{2}{5} \left(\frac{\sigma_{w}}{z} \right)^{10} - \left(\frac{\sigma_{w}}{z} \right)^{4} - \frac{\sigma_{w}^{4}}{3\Delta (z + 0.61\Delta)^{3}} \right], \quad (34)$$

where the parameters are given by $\sigma_w = \sigma$, $\varepsilon_w = 6.283\varepsilon$, and $\Delta = 0.7071\sigma$. In the slit with width *H*, the external field is given by

$$v(z) = v_w(z - H/2) + v_w(H/2 - z).$$
(35)

For both cases (H/σ = 3.0 and 4.0), while the HNC overestimates the absorption density, HNC+WDBF(4,5) underestimates it. The agreement with the simulation result is not much improved by HNC+WDBF(4,5). The accuracy of the HNC+WDBF prediction is less than that of the FMT with the mean-field theory.⁴⁸

IV. CONCLUSION

In this study, we developed a parameter-free bridge functional based on the weighted density approximation. With these developments, we provided the self-consistent integral equations to construct the bridge functional. Unlike the conventional WDA, a benefit of this approach is that we do not need to preliminarily prepare the free energy density. Thus, this scheme is applicable to any type of models for simple liquids.

As an application, we considered the homogeneous and inhomogeneous HS fluids and LJ fluids. In comparison with the simulation results, the self-consistent WDA for the bridge functional provided a good agreement for the equation of state, h(r) and c(r), in the homogeneous fluids and for density profiles of the hard-sphere fluids near the hard wall. However, the attracting fluids such as LJ and Yukawa fluids near the wall are not completely described by the present functional. The deficiency is partly attributed to the slow convergence of the Taylor series expansion of the excess free energy around the reference density. The modification of the reference system^{29,30,32} yields more rapid convergence and may further improve the accuracy of the functional.

ACKNOWLEDGMENTS

This work was supported by the JSPS KAKENHI (Grant Nos. JP17H03009 and JP20J15602). The support from the management of Elements Strategy Initiative for Catalysts and Batteries (ESICB) is also acknowledged. Theoretical computations were partly performed at the Research Center for Computational Science, Okazaki, Japan.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

¹D. Henderson, *Fundamentals of Inhomogeneous Fluids* (Marcel Dekker, New York, 1992).

- ²P. Tarazona, Phys. Rev. A 31, 2672 (1985).
- ³W. A. Curtin and N. W. Ashcroft, Phys. Rev. A 32, 2909 (1985).

⁴A. R. Denton and N. W. Ashcroft, Phys. Rev. A **39**, 426 (1989).

⁵D. M. Kroll and B. B. Laird, Phys. Rev. A **42**, 4806 (1990).

⁶A. R. Denton and N. W. Ashcroft, Phys. Rev. A 44, 1219 (1991).

⁷C. N. Patra and S. K. Ghosh, J. Chem. Phys. **116**, 8509 (2002); **116**, 9845 (2002); **118**, 8326 (2003).

⁸T. Sumi and H. Sekino, J. Phys. Soc. Jpn. 77, 034605 (2008).

⁹A. R. Denton and N. W. Ashcroft, Phys. Rev. A 39, 4701 (1989).

¹⁰J. F. Lutsko and M. Baus, Phys. Rev. A **41**, 6647 (1990).

- ¹¹C. N. Likos and N. W. Ashcroft, Phys. Rev. Lett. 69, 316 (1992).
- ¹²R. Leidl and H. Wagner, J. Chem. Phys. **98**, 4142 (1993).
- ¹³S. C. Kim and S. H. Suh, J. Chem. Phys. **104**, 7233 (1996).

¹⁴Y. Rosenfeld, Phys. Rev. Lett. **63**, 980 (1989); Y. Rosenfeld, D. Levesque, and J. J. Weis, J. Chem. Phys. **92**, 6818 (1990).

- ¹⁶R. Roth, R. Evans, A. Lang, and G. Kahl, J. Phys.: Condens. Matter 14, 12063 (2002).
- ¹⁷Y.-X. Yu and J. Wu, J. Chem. Phys. **117**, 10156 (2002); Y. Tang and J. Wu, Phys. Rev. E **70**, 011201 (2004).
- ¹⁸H. Hansen-Goos and R. Roth, J. Phys.: Condens. Matter 18, 8413 (2006).
- ¹⁹R. Roth, J. Phys.: Condens. Matter **22**, 063102 (2010).
- ²⁰J. F. Lutsko, Phys. Rev. E 102, 062137 (2020).
- ²¹ Y. Tang and J. Wu, J. Chem. Phys. **119**, 7388 (2003).

²² R. Roth and D. Gillespie, J. Phys.: Condens. Matter 28, 244006 (2016).

- ²³ A. Härtel, J. Phys.: Condens. Matter **29**, 423002 (2017).
- ²⁴Z. Tang, L. E. Scriven, and H. T. Davis, J. Chem. Phys. 96, 4639 (1992).
- ²⁵C. N. Patra and S. K. Ghosh, J. Chem. Phys. 106, 2752 (1997).
- ²⁶ J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 3rd ed. (Academic, London, 2006).
- ²⁷ R. Evans, P. Tarazona, and U. M. B. Marconi, Mol. Phys. 50, 993 (1983).
- ²⁸G. Rickayzen and A. Augousti, Mol. Phys. **52**, 1355 (1984).
- ²⁹M. Oettel, J. Phys.: Condens. Matter 17, 429 (2005).
- ³⁰A. Ayadim, M. Oettel, and S. Amokrane, J. Phys.: Condens. Matter **21**, 115103 (2009).
- ³¹ M. Levesque, R. Vuilleumier, and D. Borgis, J. Chem. Phys. **137**, 034115 (2012).
- ³²T. Sumi, Y. Maruyama, A. Mitsutake, and K. Koga, J. Chem. Phys. **144**, 224104 (2016).

³³C. Gageat, L. Belloni, D. Borgis, and M. Levesque, arXiv:1709.10139 (2017);
 D. Borgis, S. Luukkonen, L. Belloni, and G. Jeanmairet, J. Phys. Chem. B 124, 6885 (2020).

³⁴ J.-L. Barrat, J.-P. Hansen, and G. Pastore, Phys. Rev. Lett. **58**, 2075 (1987); Mol. Phys. **63**, 747 (1988).

³⁵J. K. Percus, Phys. Rev. Lett. **8**, 462 (1962).

³⁶R. J. Baxter, J. Chem. Phys. **41**, 553 (1964).

³⁷M. Reed and B. Simon, *Methods of Modern Mathematical Physics II: Fourier Analysis, Self-Adjointness* (Academic Press, New York, London, 1972).

- ³⁸R. D. Groot, J. P. van der Eerden, and N. M. Faber, J. Chem. Phys. **87**, 2263 (1987).
- ³⁹L. Reatto, D. Levesque, and J. J. Weis, Phys. Rev. A 33, 3451 (1986).
- ⁴⁰J. K. Johnson, J. A. Zollweg, and K. E. Gubbins, Mol. Phys. **78**, 591 (1993).
- ⁴¹G. Sarkisov, J. Chem. Phys. 114, 9496 (2001).

⁴² R. Melnyk, F. Moučka, I. Nezbeda, and A. Trokhymchuk, J. Chem. Phys. **127**, 094510 (2007).

- ⁴³R. D. Groot, N. M. Faber, and J. P. van der Eerden, Mol. Phys. 62, 861 (1987).
- ⁴⁴R. L. Davidchack, B. B. Laird, and R. Roth, arXiv:1603.06906 (2016).

⁴⁵C. Balabanic, B. Borstnik, R. Milcic, A. Rubcic, and F. Sokolic, in *Static and Dynamic Properties of Liquids*, Springer Proceedings in Physics Vol. 40, edited by M. Davidoviv and A. K. Soper (Springer, Berlin, 1989), p. 70.

- ⁴⁶F.-Q. You, Y.-X. Yu, and G.-H. Gao, J. Phys. Chem. B **109**, 3512 (2005).
- ⁴⁷J. J. Magda, M. Tirrell, and H. T. Davis, J. Chem. Phys. 83, 1888 (1985).
- ⁴⁸E. Kierlik and M. L. Rosinberg, Phys. Rev. A 44, 5025 (1991).

¹⁵E. Kierlik and M. L. Rosinberg, Phys. Rev. A 42, 3382 (1990).