

Hybrid weighted-density approximation for nonuniform fluid mixtures

Soon-Chul Kim*

Department of Physics, Andong National University, Andong, 760-749 Korea

Chang Hee Lee and Baek Seok Seong

Hanaro Center, Korea Atomic Energy Research Institute, Daejeon, 302-353 Korea

(Received 29 March 1999)

A hybrid weighted-density approximation (HWDA), which is based on both local density and globally averaged density, has been proposed to study the structural properties of nonuniform fluid mixtures. The advantage is that the HWDA is computationally much simpler than the extended weighted-density approximation proposed by Davidchack and Laird. The HWDA has been applied to calculate the density profiles of binary hard-sphere mixtures near a structureless hard wall. Comparison between the theoretical results and simulations for the confined binary hard-sphere mixtures demonstrates the reliable accuracy of the HWDA. [S1063-651X(99)03209-2]

PACS number(s): 61.20.Gy, 61.20.Ja

The physical properties of solid-fluid interfaces are of both fundamental theoretical interest and also considerable practical importance in connection with phenomena such as adsorption, wetting, catalysis, and filtration [1]. Numerous studies have already addressed problems involving simple one-component and two-component fluids near simple walls. The weighted-density approximations for multicomponent systems have been proposed in various forms [2–8]. The approaches of weighted-density approximations have been reasonably successful in describing the structure of binary fluid mixtures. The key to the success of weighted-density approximations appears to lie in the choice of weighting functions. In particular, the advantage of the hybrid weighted-density approximation HWDA proposed by Leidl and Wagner [2] is that it avoids a limitation of the modified weighted-density approximation (MWDA) of Denton and Ashcroft [3], specifically the violation of the wall theorem that generally holds for fluids in contact with a hard wall, without sacrificing the computational convenience of the MWDA. More recently, Davidchack and Laird [8] have proposed an extension to multicomponent systems of the weighted-density approximation (WDA), which can be applied to the multicomponent nonuniform fluid systems with spatially varying compositions. However, the WDA proposed by Davidchack and Laird is computationally more complex in actual applications such as the solid-fluid interfaces. Thus, a version of the weighted-density approximation with the computational convenience of the MWDA is now required to study the structural properties of multicomponent fluid systems.

In this Brief Report, we will propose an extension of the HWDA for the multicomponent fluids that correctly preserves the local nature of the WDA and the advantage of the MWDA. We will apply it to investigate the structural properties of binary hard-sphere fluids near a structureless hard wall and compare the theoretical results with the computer

studies. This paper concludes with a brief discussion of the strengths and weaknesses of the HWDA in actual applications.

As in the case for a one-component system, the free-energy functional for the binary system $F[\rho_1, \rho_2]$ can be divided as the ideal and excess parts as follows [1]:

$$F[\rho_1, \rho_2] = F_{\text{id}}[\rho_1, \rho_2] + F_{\text{ex}}[\rho_1, \rho_2]. \quad (1)$$

The ideal part is simply the sum of the ideal free energies of the individual components,

$$F_{\text{id}}[\rho_1, \rho_2] = \beta^{-1} \sum_{i=1}^2 \int d\vec{r} \rho_i(\vec{r}) \{ \ln[\rho_i(\vec{r}) \Lambda_i^3] - 1 \}, \quad (2)$$

where $\rho_i(\vec{r})$ and $\Lambda_i = h/(2\pi m_i k_B T)^{1/2}$ are the density and thermal de Broglie wavelength of the i th component, respectively.

In order to formulate the HWDA for the binary mixture, we start in the spirit of the WDA of Davidchack and Laird [8] by setting

$$F_{\text{ex}}[\rho_1, \rho_2] = \sum_{i=1}^2 \int d\vec{r} \rho_i(\vec{r}) f[\bar{\rho}_1^{(i)}(\vec{r}), \bar{\rho}_2^{(i)}(\vec{r})] \quad (3)$$

with

$$\bar{\rho}_j^{(i)}(\vec{r}) = \int d\vec{s} \rho_j(\vec{s}) \omega_{ij}(|\vec{r} - \vec{s}|; \hat{\rho}_1^{(i)}, \hat{\rho}_2^{(i)}), \quad i, j = 1, 2 \quad (4)$$

where $\omega_{ij}(r; \hat{\rho}_1^{(i)}, \hat{\rho}_2^{(i)})$ is the weighting function, $\bar{\rho}_j^{(i)}(\vec{r})$ are the weighted densities, and $\hat{\rho}_j^{(i)}$ are the unknown globally averaged densities. This expression differs from those of the WDA proposed by Davidchack and Laird, and the HWDA proposed by Leidl and Wagner [2]; in the HWDA of Leidl and Wagner, the total density $\bar{\rho}^{(i)}(\vec{r})$ and concentration $x = \int d\vec{r} \rho_1(\vec{r}) / [\int d\vec{r} \rho_1(\vec{r}) + \int d\vec{r} \rho_2(\vec{r})]$ have been introduced to specify the weighted densities. Here, we introduce a globally averaged density $\hat{\rho}_j^{(i)}$, which is defined as

*Author to whom correspondence should be addressed. Electronic address: sckim@anu.andong.ac.kr

$$\hat{\rho}_j^{(i)} = \frac{1}{N_j} \int d\vec{r} \int d\vec{s} \rho_i(\vec{r}) \rho_j(\vec{s}) \omega_{ij}(|\vec{r}-\vec{s}|; \hat{\rho}_1^{(i)}, \hat{\rho}_2^{(i)}),$$

$$i, j = 1, 2 \quad (5)$$

where $N = N_1 + N_2$ is the total number of particles in the system and $N_i = \int d\vec{r} \rho_i(r)$. These globally averaged densities have already been tested by Davidchack and Laird to calculate the binary hard-sphere crystal-melt phase diagram [8]. Equation (5) completes the specification of the HWDA; the globally averaged densities $\hat{\rho}_j^{(i)}$ resemble those of the extended MWDA, but the weighting functions differ. The weighting functions $\omega_{ij}(r; \hat{\rho}_1^{(i)}, \hat{\rho}_2^{(i)})$ satisfy the normalization condition

$$\int d\vec{r} \omega_{ij}(r; \hat{\rho}_1^{(i)}, \hat{\rho}_2^{(i)}) = 1, \quad i, j = 1, 2 \quad (6)$$

for all $\hat{\rho}_j^{(i)}$.

For the binary mixture the weighting function $\omega_{ij}(r; \rho_1, \rho_2)$ is related to the two-particle direct correlation functions DCFs $c_{ij}^{(2)}(r; \rho_1, \rho_2)$ of the fluid through the second derivative of the excess free energy with respect to the density,

$$c_{ij}^{(2)}(|\vec{r}-\vec{s}|; \rho_1, \rho_2) = -\beta \lim_{\rho(\vec{r}) \rightarrow \rho} \frac{\delta^2 F_{\text{ex}}[\rho_1, \rho_2]}{\delta \rho_i(\vec{r}) \delta \rho_j(\vec{s})}, \quad i, j = 1, 2 \quad (7)$$

From Eqs. (3)–(7), a system of three coupled equations for $\omega_{11}(r; \rho_1, \rho_2)$, $\omega_{12}(r; \rho_1, \rho_2)$, and $\omega_{22}(r; \rho_1, \rho_2)$ can be led, which reads in the Fourier space

$$-\beta^{-1} c_{11}^{(2)}(k; \rho_1, \rho_2) = 2 \frac{\partial f(\rho_1, \rho_2)}{\partial \rho_1} \omega_{11}(k; \rho_1, \rho_2)$$

$$+ \rho_1 \frac{\partial^2 f(\rho_1, \rho_2)}{\partial \rho_1^2} \omega_{11}^2(k; \rho_1, \rho_2)$$

$$+ \rho_2 \frac{\partial^2 f(\rho_1, \rho_2)}{\partial \rho_1 \partial \rho_2} \omega_{12}^2(k; \rho_1, \rho_2), \quad (8)$$

$$-\beta^{-1} c_{12}^{(2)}(k; \rho_1, \rho_2) = \left(\frac{\partial f(\rho_1, \rho_2)}{\partial \rho_1} + \frac{\partial f(\rho_1, \rho_2)}{\partial \rho_2} \right)$$

$$\times \omega_{12}(k; \rho_1, \rho_2) + \rho_1 \frac{\partial^2 f(\rho_1, \rho_2)}{\partial \rho_1 \partial \rho_2} \omega_{12}^2(k; \rho_1, \rho_2)$$

$$\times \omega_{11}(k; \rho_1, \rho_2) \omega_{12}(k; \rho_1, \rho_2)$$

$$+ \rho_2 \frac{\partial^2 f(\rho_1, \rho_2)}{\partial \rho_1 \partial \rho_2} \omega_{12}(k; \rho_1, \rho_2)$$

$$\times \omega_{22}(k; \rho_1, \rho_2), \quad (9)$$

$$-\beta^{-1} c_{22}^{(2)}(k; \rho_1, \rho_2) = 2 \frac{\partial f(g r_1, \rho_2)}{\partial \rho_2} \omega_{22}(k; \rho_1, \rho_2)$$

$$+ \rho_2 \frac{\partial^2 f(\rho, x)}{\partial \rho_2^2} \omega_{22}^2(k; \rho_1, \rho_2)$$

$$+ \rho_1 \frac{\partial^2 f(\rho_1, \rho_2)}{\partial \rho_2^2} \omega_{12}^2(k; \rho_1, \rho_2), \quad (10)$$

since $\hat{\rho}_j^{(i)} = \rho_j$ and $\bar{\rho}_j^{(i)}(\vec{r}) = \rho_j$ for a uniform binary mixture, $c_{12}^{(2)}(r; \rho_1, \rho_2) = c_{21}^{(2)}(r; \rho_1, \rho_2)$, and $\omega_{12}(r; \rho_1, \rho_2) = \omega_{21}(r; \rho_1, \rho_2)$ due to the symmetrical requirement. It is noted that in the HWDA of Leidl and Wagner $c_{ij}^{(2)}(r; \rho_1, \rho_2)$ contains the terms proportional to $\delta_{k,0}$ that arose from functional derivatives of the concentration x , so that the computed weighting functions are discontinuous in Fourier space at $k=0$ [2]. The above set of equations can generally be solved by a numerical iteration method for known excess free energy $f(\rho_1, \rho_2)$ and two-particle DCFs $c_{ij}^{(2)}(k; \rho_1, \rho_2)$. At $\vec{k}=0$, Eqs. (8)–(10) correctly reduce to the exact compressibility rules for a binary mixture. We can check that the third-order and higher-order direct correlation functions derived from the excess free energy $F_{\text{ex}}[\rho_1, \rho_2]$ satisfy the exact hierarchy relation as well as for the one-component system,

$$\frac{\partial^{n-2} c_{ij}^{(2)}(k)}{\partial \rho_1, \dots, \partial \rho_m} = c_{ij \dots m}^{(n)}(k, 0, \dots, 0), \quad (11)$$

where we have suppressed the arguments of density and concentrations that appeared in $c_{ij \dots m}^{(n)}$. Taken together, Eqs. (1)–(5) and Eq. (7), constitute the generation to a binary mixture of the HWDA. Even if we have not generalized the HWDA to the multicomponent mixture the above procedure for generating to the multicomponent mixture, is straightforward. In this case, the weighted densities and the direct correlation functions are denoted in terms of $n(n+1)/2$ independent weighted densities and direct correlation functions [3].

In the density-functional theory [1], the equilibrium particle density distribution $\rho_i(\vec{r})$ is found by minimizing the grand potential functional $\Omega[\rho_1, \rho_2]$ with respect to variations in $\rho_i(\vec{r})$,

$$\frac{\delta \Omega[\rho_1, \rho_2]}{\delta \rho_i(\vec{r})} = 0, \quad i = 1, 2. \quad (12)$$

Since the grand potential form under an external potential, $u_i^{\text{ext}}(\vec{r})$ can be written as

$$\Omega[\rho_i, \rho_2] = F[\rho_1, \rho_2] - \sum_{i=1}^2 \int d\vec{r} \rho_i(\vec{r}) [\mu_i - u_i^{\text{ext}}(\vec{r})]. \quad (13)$$

Equation (12) yields the Euler-Lagrange relation for the binary mixture

$$\beta \mu_i - \beta u_i^{\text{ext}}(\vec{r}) = \frac{\delta \beta F[\rho_1, \rho_2]}{\delta \rho_i(\vec{r})}, \quad i = 1, 2 \quad (14)$$

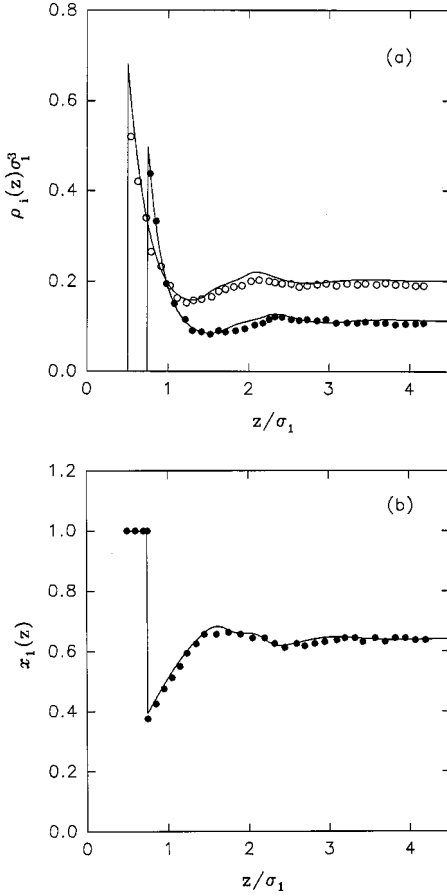


FIG. 1. (a) Density profiles of binary hard-sphere mixture near a hard structure wall ($\alpha = \frac{2}{3}$, $x = 0.642$, and $\eta = 0.2911$). The open [$\rho_1(z)\sigma_1^3$] and solid [$\rho_2(z)\sigma_2^3$] circles are from the computer simulation [5]. (b) Concentration profile of the smaller spheres $x_1(z)$. The solid circles are from the computer simulation [5].

where μ_i is the chemical potential of the component i . From Eqs. (1) and (14), we can obtain the coupled density profile equations for the binary mixture,

$$\rho_i(\vec{r}) = \rho_{ib} \exp\{-\beta u_i^{\text{ext}}(\vec{r}) + c_i^{(1)}(\vec{r}; [\rho_1, \rho_2]) - c_i^{(1)}(\rho_{1b}, \rho_{2b})\}, \quad i = 1, 2 \quad (15)$$

where $c_i^{(1)}(r; [\rho_1, \rho_2])$ and $c_i^{(1)}(\rho_{1b}, \rho_{2b})$ are the one-particle DCFs for the nonuniform and uniform fluid mixture, and ρ_{ib} is the bulk density of the component i ; $c_2^{(1)}(\vec{r}; [\rho_1, \rho_2])$ that appeared in Eq. (15) which can easily be obtained from $c_1^{(1)}(\vec{r}; [\rho_1, \rho_2])$ by interchanging $\bar{\rho}_1^{(i)}(\vec{r}), \rho_1(\vec{r}), \omega_{11}(r; \rho_1, \rho_2)$ with $\bar{\rho}_2^{(i)}(\vec{r}), \rho_2(\vec{r}), \omega_{22}(r; \rho_1, \rho_2)$. The density profiles $\rho_i(\vec{r})$ were obtained by numerical iteration between the old density profiles on the right-hand side and the new one on the left-hand side of Eq. (15).

As an application, we have considered the structural properties of a binary hard-sphere mixture near a structureless hard wall, where the external potentials $u_i^{\text{ext}}(z)$ are given by

$$u_i^{\text{ext}}(z) = \begin{cases} \infty, & z < \sigma_i/2 \\ 0, & z > \sigma_i/2. \end{cases} \quad (16)$$

Because of the planar symmetry of the problem, the spatial dependence of all quantities is only on z ; $\rho_i = \rho_i(z)$, $\bar{\rho}_i = \bar{\rho}_i(z)$, etc. In the case of adsorption at a wall, $\delta\hat{\rho}_j^{(i)}/\delta\rho_j(z)$ is the order of $1/N_j$, where $N = N_1 + N_2$ is the total number of particles in the system. Thus, it is easy to show that for the binary hard-sphere mixture near a structureless hard wall $\delta\hat{\rho}_j^{(i)}/\delta\rho_j(z)$ goes to zero as well as for the uniform state $\delta\hat{\rho}_j^{(i)}/\delta\rho_j(z) = 0$. However, for the binary hard-sphere mixture confined in a spherical cage where N_j is finite, the contribution of $\delta\hat{\rho}_j^{(i)}/\delta\rho_j(r)$ cannot be neglected even if this contribution is relatively small.

We now define the parameters for the binary hard-sphere mixture: the hard-sphere diameter ratio $\alpha = \sigma_1/\sigma_2$ ($\sigma_1 < \sigma_2$) and the total bulk density $\rho_b = \rho_{1b} + \rho_{2b}$. Then, the total packing fraction η is given as $\eta = \pi(\rho_{1b}\sigma_1^3 + \rho_{2b}\sigma_2^3)/6$. To obtain the weighting function $\omega_{ij}(r; \rho_1, \rho_2)$, we have used the expression for $f(\rho_1, \rho_2)$ and $c_{ij}^{(2)} \times (r; \rho_1, \rho_2)$ that follows from Lebowitz's analytic solution of the Percus-Yevick approximation for a hard-sphere mixture [9,10], and which also implies an approximation for the excess free energy $f(\rho_1, \rho_2)$ via the compressibility equation.

In Fig. 1, we show the density profiles $\rho_i(z)$ of a binary hard-sphere mixture against a hard wall at a diameter ratio $\alpha = \frac{2}{3}$, concentration of smaller hard spheres $x = \rho_{1b}/(\rho_{1b} + \rho_{2b}) = 0.642$, and packing fractions $\eta = 0.2911$. In Fig. 2, we present the density profiles for a binary hard-sphere mixture with $\alpha = \frac{1}{2}$ for $x = 0.4902$ and $\eta = 0.30$, and the corre-

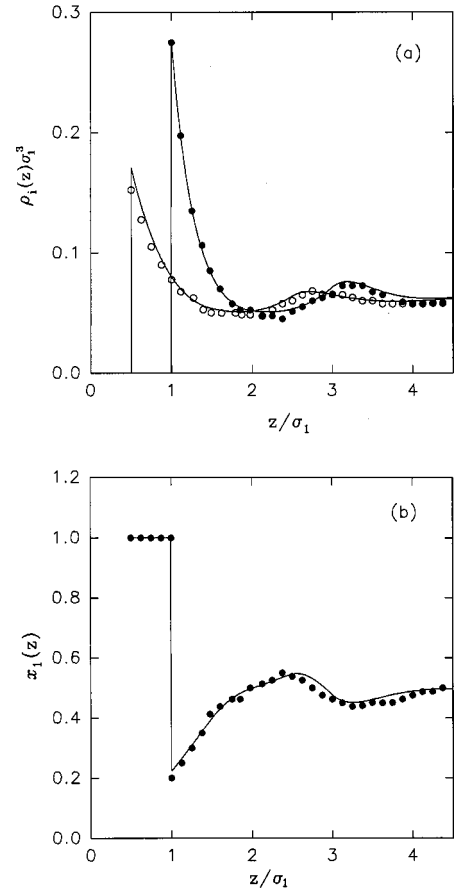


FIG. 2. (a) Same as Fig. 1(a) except that ($\alpha = \frac{1}{2}$, $x = 0.4902$, and $\eta = 0.30$). (b) Same as Fig. 1(b).

sponding concentration profiles $x_1(z)$, where $x_1(z) = \rho_1(z)/[\rho_1(z) + \rho_2(z)]$. The calculated results presented indicate that the present HWDA is in good agreement with the computer simulation data [5], although the density profiles for the smaller sphere $\rho_1(z)$ are slightly overestimated near a hard wall. Even though the HWDA results of Leidl and Wagner have not been displayed in the figures for clarity, the calculated results show that the present HWDA compares well with the HWDA of Leidl and Wagner.

In summary, we have proposed the HWDA to multicomponent systems with the computational convenience of the MWDA. The calculated results show that the present HWDA describes well the structural behaviors of a binary hard-

sphere mixture near a hard wall. Another point to be mentioned is that for the binary hard-sphere mixtures confined in a spherical cage, the structural properties have not been investigated until now. In this case, the minor correction for the HWDA is required, since the contribution of $\delta\rho_j^{(i)}/\delta\rho_j(r)$ cannot be neglected. We will investigate these problems in the near future.

This work was supported by the Korea Research Foundation made in the program year of 1998 (Project No. 1998-015-D00132) and by the Korea Atomic Energy Research Institute (1999).

-
- [1] R. Evans, in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Dekker, New York, 1992); H. Löwen, Phys. Rep. **237**, 249 (1994).
- [2] R. Leidl and H. Wagner, J. Chem. Phys. **98**, 4142 (1993).
- [3] A. R. Denton and N. W. Ashcroft, Phys. Rev. A **42**, 7312 (1990).
- [4] M. Muradi and G. Rickayzen, Mol. Phys. **66**, 143 (1989).
- [5] S. Sokolowski and J. Fischer, Mol. Phys. **70**, 1097 (1990).
- [6] P. Bryk, W. Cyrankiewicz, M. Borowko, and S. Sokolowski, Mol. Phys. **93**, 111 (1998).
- [7] J. P. Noworta, P. Henderson, S. Sokolowski, and K. Y. Chan, Mol. Phys. **95**, 415 (1998).
- [8] R. L. Davidchack and B. B. Laird, Phys. Rev. E **60**, 3417 (1999).
- [9] J. L. Lebowitz, Phys. Rev. **133**, A895 (1964).
- [10] X. C. Zeng and D. W. Oxtoby, J. Chem. Phys. **93**, 4357 (1990).