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On the connections and differences among three mean-field approximations: a stringent test†

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This letter attempts to clarify the meaning of three closely related mean-field approximations: random phase approximation (RPA), local molecular field (LMF) approximation, and symmetry-preserving mean-field (SPMF) approximation, and their use of reliability and validity in the field of theory and simulation of liquids when the long-ranged component of the intermolecular interaction plays an important role in determining density fluctuations and correlations. The RPA in the framework of classical density functional theory (DFT) neglects the higher order correlations in the bulk and directly applies the long-ranged part of the potential to correct the pair direct correlation function of the short-ranged system while the LMF approach introduces a nonuniform mimic system under a reconstructed static external potential that accounts for the average effect arising from the long-ranged component of the interaction. Furthermore, the SPMF approximation takes the viewpoint of LMF but instead instantaneously averages the long-ranged component of the potential over the degrees of freedom in the direction with preserved symmetry. The formal connections and the particular differences of the viewpoint among the three approximations are explained and their performances in producing structural properties of liquids are stringently tested using an exactly solvable model. We demonstrate that the RPA treatment often yields uncontrolled poor results for pair distribution functions of the bulk system. On the other hand, the LMF theory produces quite reasonably structural correlations when the pair distribution in the bulk is converted to the singlet particle distribution in the nonuniform system. It turns out that the SPMF approach outperforms the other two at all densities and under extreme conditions where the long-ranged component significantly contributes to the structural correlations.

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A molecular description of realistic liquids often involves long-ranged potentials that fall off much more slowly than the harshly repulsive short-ranged interaction in a simple hard sphere model. An accurate analytic approach for the structure and thermodynamics of liquids must therefore account for both the excluded volume effect and the effect arising from the long-ranged slowly varying forces.[1,2] On the other hand, numerical molecular dynamics (MD) or Monte-Carlo (MC) simulations of nonuniform complex liquids often require an efficient and accurate algorithm to handle the long-ranged Coulomb forces.[3–5] Mean-field ideas suggesting that a certain long-ranged component of the intermolecular interaction can be replaced by either a static or a dynamic effective field have proven to be successful in producing accurate structural, thermodynamic and even dynamical properties both analytically and numerically.[2,6–12] Certainly, these mean-field treatments of short- and long-ranged forces in terms of the local molecular

field (LMF) theory developed by the Weeks group using a static effective field and the follow-up symmetry-preserving mean field (SPMF) approach[11] using a dynamic effective field make necessary connections to other well-established theoretical approaches such as perturbation theory of liquids[12–16] and classical density functional theory (DFT).[1,17–20] Indeed, Archer and Evans (AE) have recently recast the LMF theory in the framework of classical DFT for nonuniform fluids and the DFT-based applications of LMF are able to capture the subtle features in a drying transition.[19] In particular, they have asserted that the physics of the mean-field treatment in DFT can be alternatively understood by the standard random phase approximation (RPA) which fails for a one-dimensional (1D) model system that constitutes a very stringent test of any mean-field approximation. On the other hand, Weeks and coworkers argued that the LMF approximation does not make use of any mean-field approximation in the framework of DFT and emphasized that the LMF theory "is not a blind assertion of mean-field behaviour but rather a controlled and accurate approximation, provided that we choose our mimic system carefully".[8,12] Stimulated by these fruitful discussions, this letter attempts to clarify the connections and differences among the three

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approximations: RPA, LMF and SPMF and to address whether the LMF- and SPMF-based mean-field treatments can go beyond the crude RPA for the same model system investigated by AE when we properly choose its mimic system as a non-uniform system under the external potential due to a particle fixed at the origin.

Considering the DFT perspective for a classical mechanics system under an arbitrary external field $\phi(\mathbf{r})$ at a given chemical potential μ and temperature T, the grand (Landau) potential is written as a density functional

$$\Omega[\tilde{\rho}] = F^{\text{in}}[\tilde{\rho}] - \int d\mathbf{r}[\mu - \phi(\mathbf{r})]\tilde{\rho}(\mathbf{r}) \tag{1}$$

where F^{in} is the intrinsic (bulk) Helmholtz free energy independent of ϕ. The minimization of $\Omega[\tilde{\rho}]$ yields the Euler–Lagrange equation for the equilibrium nonuniform singlet particle density $\rho(\mathbf{r})$

$$\left.\frac{\delta F^{\text{in}}[\tilde{\rho}]}{\delta \tilde{\rho}(\mathbf{r})}\right|_{\tilde{\rho}=\rho} = \mu - \phi(\mathbf{r}), \tag{2}$$

where $\rho(\mathbf{r})$ is defined as an average over the instantaneous density of a given configuration $(\bar{\mathbf{R}})$ of the system

$$\rho(\mathbf{r}) = \langle \rho(\mathbf{r}, \bar{\mathbf{R}}) \rangle = \left\langle \sum_j \delta(\mathbf{r} - \mathbf{R}_j) \right\rangle. \tag{3}$$

Using the Euler–Lagrange equation to determine $\rho(\mathbf{r})$ requires an accurate expression for the external-field-independent density functional $F^{\text{in}}[\tilde{\rho}]$, which is always difficult to obtain when the intermolecular interaction of the system $w(r) = u_0(r) + u_1(r)$ includes both short- and long-ranged components: u_0 and u_1 respectively. In the past, good progress has been made in relating the density functional of the full system $F^{\text{in}}[\tilde{\rho};[w]]$ to that of the short-ranged system $F^{\text{in}}[\tilde{\rho};[u_0]]$.[1,17,18] One mean-field approximation suggesting such a general relation between the two density functionals irrespective of any external field reads (see *e.g.* ref. 1 and page 54 of ref. 18)

$$F^{\text{in}}[\tilde{\rho};[w]] - F^{\text{in}}[\tilde{\rho};[u_0]] \simeq \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\tilde{\rho}(\mathbf{r})\tilde{\rho}(\mathbf{r}')u_1(|\mathbf{r}-\mathbf{r}'|). \tag{4}$$

Once an accurate density functional $F^{\text{in}}[\tilde{\rho};[u_0]]$ is known, the Euler–Lagrange equation for the system interacting through w is readily solved for the equilibrium nonuniform density $\rho(\mathbf{r};[w])$. Indeed, AE have used the Rosenfeld functional for the hard sphere system[21,22] and have shown that the mean-field treatment to hard-core Yukawa liquids absorbed at the planar hard wall produces exceptional details of the density response that are hardly obtained using numerical MD or MC simulations.[19]

From the perspective of the LMF theory, this mean-field process can be exactly split into two coupled equations that determine self-consistently the reconstructed external field $\phi_R(\mathbf{r})$ for a mimic reference system interacting through u_0 and its nonuniform singlet density $\rho_R(\mathbf{r};[u_0])$. The Euler–Lagrange equation for the reference system is used to determine $\rho_R(\mathbf{r};[u_0])$ for any given $\phi_R(\mathbf{r})$

$$\left.\frac{\delta F^{\text{in}}[\tilde{\rho}, [u_0]]}{\delta \tilde{\rho}(\mathbf{r})}\right|_{\tilde{\rho}(\mathbf{r})=\rho_R(\mathbf{r};[u_0])} = \mu_R - \phi_R(\mathbf{r}). \tag{5}$$

and $\phi_R(\mathbf{r})$ depends on $\rho_R(\mathbf{r};[u_0])$ *via* the LMF equation eventually[2,8,10]

$$\phi_R(\mathbf{r}) = \phi(\mathbf{r}) + \int d\mathbf{r}'\rho_R(\mathbf{r}';[u_0])u_1(|\mathbf{r}-\mathbf{r}'|) + C, \tag{6}$$

where both constants μ_R and C can be chosen such that ϕ_R vanishes in the bulk.

The above discussion closely follows the detailed derivation of LMF in the framework of DFT presented by AE.[19] To the best of our knowledge, the insight from the LMF viewpoint relies on the following three implications. First, even if an accurate analytic $F^{\text{in}}[\tilde{\rho};[u_0]]$ is not available, which is often the case for a complicated reference system, well-developed simulation techniques or other approximated analytical theories for short-ranged systems can be alternatively employed to accurately determine $\rho_R(\mathbf{r};[u_0])$.[23] Applicability of the LMF theory for a variety of simple and complex systems has been well demonstrated by studying dewetting, nonuniform electrostatics and solvation. Secondly, although the DFT-based LMF approach in eqn (5) and (6) is identical to the usual mean-field approximation (4) for the Euler–Lagrange equation,[19] it is by no means necessary to acquire any "top-down" knowledge of DFT before understanding the LMF approximation that relates $\rho(\mathbf{r};[w])$ of the full system to $\rho_R(\mathbf{r};[u_0])$ of the reference system under a specific ϕ_R. To see this more clearly, one takes the second derivative of both sides of eqn (4) giving the standard RPA for the bulk system

$$c(\mathbf{r},\mathbf{r}';[w]) \simeq c(\mathbf{r},\mathbf{r}';[u_0]) - \beta u_1(\mathbf{r},\mathbf{r}') \tag{7}$$

where $\beta = 1/(k_b T)$ and the pair direct correlation function is generally defined as

$$\frac{\delta^2 \beta F^{\text{in}}[\rho]}{\delta \rho(\mathbf{r}')\rho(\mathbf{r})} \equiv \frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho(\mathbf{r})} - c(\mathbf{r},\mathbf{r}') \tag{8}$$

with the term $\delta(\mathbf{r}-\mathbf{r}')/\rho(\mathbf{r})$ contributed by the ideal gas.[24] The RPA for the bulk does not address the external field and the induced nonuniform density any more and it is not necessarily accurate for other structural properties such as the pair correlation function. In contrast, when the pair correlation function is converted to the nonuniform singlet density arising from a fixed particle at the origin, the LMF theory might still work for an appropriately chosen reference system.

Finally, while the derivation of LMF from the DFT perspective from eqn (1)–(6) provides no information about how u_0 and u_1 can be chosen, the original derivation of the LMF equation emphasizes a "bottom-up" understanding by safely neglecting high order correlations in the difference between the YBG hierarchy of the full system and that of the short-ranged system provided that u_1 remains slowly varying over a characteristic distance of the structure correlation.[2,8] Very recently, Weeks and coworkers further state the importance of the "bottom-up" understanding by deriving the correction to the free energy changes when applying the LMF approach to study solvation systems.[12] Perhaps, it is easier to understand and even improve the mean-field approximation using physical insight into correlations and fluctuations rather than to develop a more accurate

expression for the general free energy density functional. Following this implication, an alternative understanding of the LMF equation becomes clear when the equilibrium singlet density in the LMF equation defined as eqn (3) is replaced by the instantaneous density $\rho_R(\mathbf{r}, \bar{\mathbf{R}})$

$$\phi_R(\mathbf{r}, \bar{\mathbf{R}}) = \phi(\mathbf{r}) + \int d\mathbf{r}' \sum_j \delta(\mathbf{r}' - \mathbf{R}_j) u_1(\mathbf{r} - \mathbf{r}'). \quad (9)$$

This equation rewrites the long-ranged part of the intermolecular interaction into a formally exact configuration-dependent effective field, which captures the density fluctuations of instantaneous configurations in all directions. When the external field $\phi(\mathbf{r}) = \phi(\mathbf{r}^p, \mathbf{r}^b) = \phi(\mathbf{r}^b)$ depends only on the $\mathbf{r}^b$ direction with broken symmetry (*e.g.* $\mathbf{r}^p = (\theta, \phi)$ and $\mathbf{r}^b = r$ for a spherical external field and $\mathbf{r}^p = (x, y)$ and $\mathbf{r}^b = z$ for a planar external field), density fluctuations along the $\mathbf{r}^p$ directions with preserved symmetry would average out to 0 exactly in the ensemble average. An improved mean-field approximation called SPMF treatment thus suggests a dynamical effective field that accounts for the remaining long-ranged contribution in the $\mathbf{r}^b$ direction configuration by configuration[11]

$$\phi_R(\mathbf{r}^b, \bar{\mathbf{R}}^b) = \langle \phi_R(\mathbf{r}, \bar{\mathbf{R}}) \rangle_{sp} \equiv \phi(\mathbf{r}^b)$$
$$+ \int d\mathbf{r}' \sum_j \langle \delta(\mathbf{r}' - \mathbf{R}_j) \rangle_{sp} u_1(\mathbf{r} - \mathbf{r}'), \quad (10)$$

where $\langle \rangle_{sp}$ is the symmetry-preserving operator defined as the normalized integration over the degrees of freedom in the directions with no broken symmetry (*e.g.* integration over collective variables $(\bar{\Theta}, \bar{\Phi})$ for a spherical external field and $(\bar{X}, \bar{Y})$ for a planar external field). The application of the SPMF approach to a nonuniform electrostatic problem has shown that it follows the essential idea of introducing an effective field to account for the long-ranged contribution and therefore it inherits advantages from the LMF theory when the external field has a symmetry.[11,25] In addition, it permits an efficient and accurate determination of dynamical properties in excellent agreement with results from the complex Ewald-type algorithms.[5,26–28] This letter will investigate the importance of instantaneous density fluctuations by applying both SPMF and LMF approaches to study the 1D system with a left–right symmetry.

To see the clear difference among the three approximations, we now study the exactly solvable nearest-neighbor 1D model which was used by AE to check the validity of the RPA treatment. The intermolecular interaction $w(x)$ contains a hard-core repulsive interaction defining an excluded region $|x| < \sigma$ and a soft tail not exceeding the distance of 2σ

$$\beta w(x) = \begin{cases} \infty & |x| < \sigma \\ z_p(|x| - \sigma - \sigma_p) & \sigma \leq |x| \leq \sigma + \sigma_p \\ 0 & |x| > \sigma + \sigma_p \end{cases} \quad (11)$$

where $z_p > 0$ and $\sigma_p < \sigma$. This 1D model is particularly interesting because the mean-field approximations may gradually break down when the tail part becomes not slowly varying by adjusting z_p.

The equation of state is exactly given by[29]

$$\rho^B = -\frac{L(s)}{L'(s)}\bigg|_{s = \beta P}, \quad (12)$$

where P is the pressure with the unit of force in 1D and $L(s)$ is the Laplace transform of the Boltzmann factor $\exp(-\beta w)$ defined as:

$$L(s) = \int_0^\infty dx e^{-\beta w(x)} e^{-sx} = \frac{e^{-s\sigma + z_p \sigma_p}}{s + z_p} + \frac{z_p e^{-s(\sigma + \sigma_p)}}{s(s + z_p)}. \quad (13)$$

The Fourier transform of the pair direct correlation function has an ordinary closed form[24]

$$\rho^B \hat{c}(k) = \frac{J(k,s) + J(-k,s) - 2J(k,s)J(-k,s)}{1 - J(k,s)J(-k,s)}, \quad (14)$$

with $J(k,s)$ defined as the ratio between the two Laplace transforms

$$J(k,s) = \frac{L(s + ik)}{L(s)}. \quad (15)$$

However, it is difficult to analytically work out $c(x)$ for arbitrary values of z_p and σ_p. Instead, one performs numerical inverse Fourier transform of $\hat{c}(k)$ to obtain accurate $c(x)$ shown as the solid lines in Fig. 1 for $\sigma_p = 0.9\sigma$ at several values of the bulk density ρ^B and the depth of the attractive well z_p.

When $z_p = 0$ or $\sigma_p = 0$, the model reduces to the hard sphere model with only the repulsive u_0 interaction. The corresponding pair direct correlation function vanishes outside the hard core region and has a simple explicit expression inside
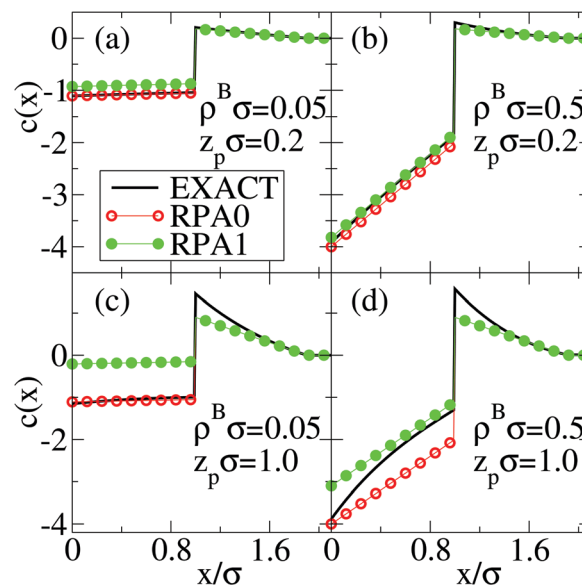

Fig. 1 Exact pair direct correlation functions $c(x)$ (black lines, numerically inverted from eqn (14)) and their approximations using the RPA treatments (open circles for u_1 in eqn (17) and filled circles for u_1 in eqn (18)) for the system with $z_p\sigma = 0.2$ (a and b) or $z_p\sigma = 1.0$ (c and d) at the bulk density $\rho^B\sigma = 0.05$ (a and c) or $\rho^B\sigma = 0.5$ (b and d). $\sigma_p/\sigma = 0.9$. Note that the open circles overlap the filled circles for $x > \sigma$.

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the region

$$c(x; [u_0]) = -\frac{1 - \rho^B |x|}{(1 - \rho^B \sigma)^2} \quad \text{for } 0 \leq x \leq \sigma. \quad (16)$$

The remaining u_1 in this model is not well-defined inside the hard core region. It could be the pure attractive part of $w(x)$ outside the hard core region

$$\beta u_1(x) = z_p(|x| - \sigma - \sigma_p)\varepsilon(|x| - \sigma)\varepsilon(\sigma + \sigma_p - |x|), \quad (17)$$

where $\varepsilon(x)$ is the step function. Alternatively, u_1 can be taken as a continuous function by including an extra constant part that penetrates inside the hard core

$$\beta u_1(x) = z_p(|x| - \sigma - \sigma_p)\varepsilon(|x| - \sigma)\varepsilon(\sigma + \sigma_p - |x|) - z_p\sigma_p\varepsilon(\sigma - |x|). \quad (18)$$

The standard RPA to $c(x)$ thus suggests that

$$c(x) \simeq c_{RPA}(x) = c(x; [u_0]) - \beta u_1(x) \quad (19)$$

For the two choices of $u_1(x)$ in eqn (17) and (18), the corresponding $c_{RPA}(x)$ values for the given set of parameters are shown in Fig. 1. Clearly, the RPA approximation remains accurate only for the small value $z_p\sigma = 0.2$ where the attractive part contributes little. Significant deviations appear at the moderately large value $z_p\sigma = 1.0$. Indeed, AE have shown that the RPA treatment for structural factors in Fourier space is very poor as well for moderately large values of $z_p\sigma$. Note that while the direct correlation function is useful for RPA, both LMF and SPMF do not use $c(x)$ either in their formulation or in the numerical determination of their results.

For the bulk system, the usual pair correlation function $g(x)$ for which $\rho^B g(x)dx$ gives the conditional probability of finding any other particle in the vicinity of x is related to $c(x)$ via the exact Ornstein–Zernike (OZ) equation[30]

$$g(x) - 1 = c(x) + \rho^B \int dy c(y - x)(g(y) - 1) \quad (20)$$

which shows that the discontinuity of $c(x)$ at $x = \sigma$ is fully reflected in $g(x)$. An alternative way to derive $g(x)$ and its connection to $\hat{c}(k)$ is shown in the ESI.†

When an approximated c_{RPA} is used in the OZ equation, its solution gives an unphysical pair correlation function that does not vanish inside the hard core. To overcome this difficulty, the constraint $g(x) = 0$ for $|x| \leq \sigma$ is imposed when solving the OZ equation self-consistently in the RPA treatment. This implementation of RPA resembles the Optimized RPA[31] under the exact condition that the intermolecular separations smaller than σ are physically inaccessible. On the other hand, the pair correlation function in the bulk can be exactly converted to the relative singlet density in a nonuniform system under the external field due to a fixed particle, $g(x) = \rho(x)/\rho^B \equiv \rho(x; [w])/\rho^B$. Therefore, one may choose the reference system of the LMF theory as the nonuniform 1D hard sphere system under a reconstructed external field ϕ_R analogous to eqn (6) for $\phi(x) = w(x)$ and u_1 expressed in eqn (18).

Using the exact Euler–Lagrange equation for the 1D hard sphere system[24]

$$\mu_R - \phi_R(x) = \ln \frac{\rho_R(x; [\phi_R])\sigma}{1 - \int_{x-\sigma}^x dy \rho_R(y; [\phi_R])} + \int_x^{x+\sigma} dz \frac{\rho_R(z; [\phi_R])}{1 - \int_{z-\sigma}^z dy \rho_R(y; [\phi_R])}, \quad (21)$$

the LMF equation can be solved self-consistently to yield $\rho(x; [w]) \simeq \rho_R(x; [\phi_R])$. As pointed out by AE, implementation of LMF using the above density functional for the reference system is identical to the mean-field treatment of DFT in eqn (2) and (4).

Furthermore, the symmetry involved in the system with the fixed particle is a left–right symmetry and therefore the SPMF treatment employs a dynamical effective potential

$$\phi_R(x, \bar{X}) = w(x) + \sum_j \frac{u_1(x, X_j) + u_1(-x, X_j)}{2} \quad (22)$$

corresponding to a mean-field intermolecular interaction with the long-ranged u_1 interaction averaged over the left and right directions. The corresponding nonuniform singlet density can thus be computed using a Monte-Carlo simulation. Results for the exact and approximated pair correlation functions are shown in Fig. 2 and 3 for moderately to very large values of z_p at different densities. Clearly, deviations of the RPA results from the exact values are severe when u_1 plays an important role in determining the structure correlations. Although u_1 by itself is not sufficiently slowly varying, results from the LMF
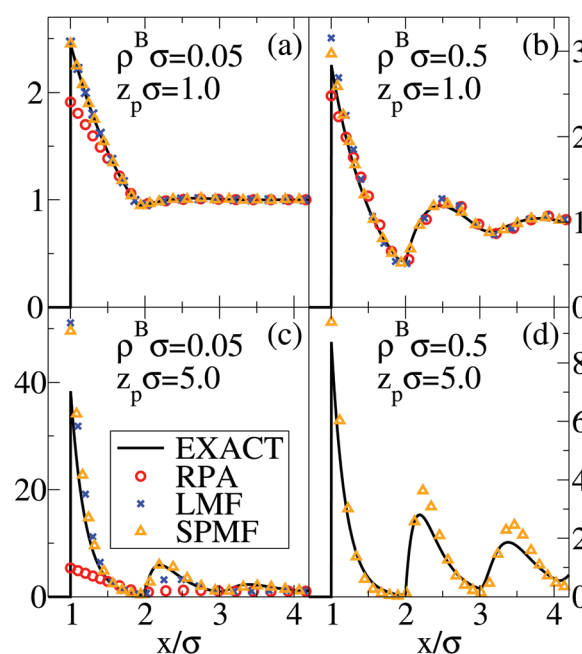

Fig. 2 Exact pair correlation functions $g(x)$ (black lines) and the corresponding approximations using RPA (circles), LMF (crosses), or SPMF treatment (triangles) for $\rho^B\sigma = 0.05$ (a and c), $\rho^B\sigma = 0.5$ (b and d), $z_p\sigma = 1.0$ (a and b), and $z_p\sigma = 5.0$ (c and d). u_1 in eqn (17) is used for RPA and u_1 in eqn (18) is used for LMF and SPMF. Eqn (18) for RPA produces worse structural results. Solutions for RPA and LMF at $z_p\sigma = 5.0$ and $\rho^B\sigma = 0.5$ do not converge.
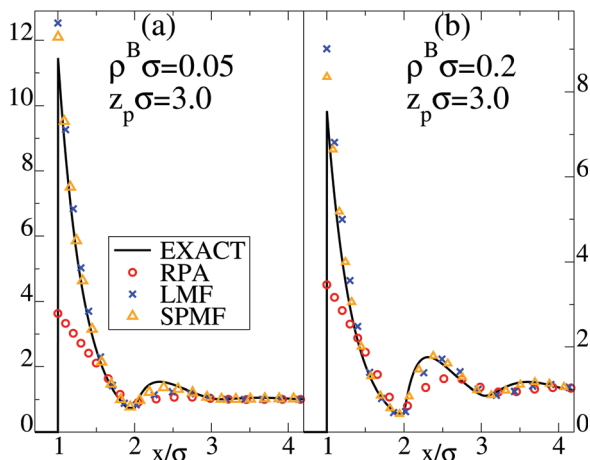
Fig. 3 Same as the previous figure but for the moderately large well depth $z_p\sigma = 3.0$ at the reduced bulk density $\rho^B\sigma = 0.05$ (a) and $\rho^B\sigma = 0.2$ (b).

theory are generally acceptable unless under the extreme condition of very large z_p. The SPMF results are slightly better than, but in general resemble, the LMF results in most of the cases examined. In principle, SPMF uses a dynamical configuration-dependent effective field while LMF, being considered as the static limit of SPMF, uses a configuration-independent effective field (see the difference between eqn (6) and (10)). When z_p is sufficiently large and the bulk density is high, the instantaneous density varies significantly configuration by configuration and may play a crucial role in determining the overall singlet density distribution. Therefore, in the extreme case of Fig. 2(d), the LMF result does not converge because the solution strongly oscillates while the SPMF result is still quite reasonable.

The LMF theory argues that the singlet density of a full system can be accurately determined by studying the short-ranged reference system under a reconstructed single particle external field ϕ_R given by the LMF equation provided that u_1 is a slowly varying function. In practice, both LMF and SPMF work well for structures and thermodynamics when they are applied to complex systems involving Lennard-Jones and Coulomb potentials because the long-ranged components of these potentials remain quite slowly varying. However, this 1D model by itself is helpful in emphasizing the importance of the viewpoint by providing a challenging test for any mean-field approximation. We hope that realizing the particular differences among related mean-field approximations might stimulate the applications and the development of mean-field approaches for both theories and simulations of liquids.

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