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# A Density Functional Theory with a Mean-field Weight Function: Applications to Surface Tension, Adsorption, and Phase Transition of a Lennard-Jones Fluid in a Slit-like Pore

Bo Peng and Yang-Xin Yu\*

Department of Chemical Engineering, Tsinghua University, Beijing 100084, P. R. China, and State Key Laboratory of Chemical Engineering, Tsinghua University, Beijing 100084, P. R. China

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A new density functional theory (DFT) for an inhomogeneous 12–6 Lennard-Jones fluid is proposed based on the modified fundamental measure theory for repulsive interaction and a weighted density functional for attractive interaction. The Helmholtz free energy functional for the attractive part is constructed using the modified Benedict–Webb–Rubin equation of state with a mean-field weight function. Comparisons of the theoretical results with molecular simulation data suggest that the new DFT yields accurate bulk surface tension, density distributions, adsorption–desorption isotherms, pore pressures, and capillary phase transitions for the Lennard-Jones fluid confined in slitlike pores with different widths and solid–fluid interactions. The new DFT reproduces well the vapor–liquid critical temperatures of the confined Lennard-Jones fluid, whereas the mean-field theory always overestimates the critical temperatures. Because the new DFT is computationally as simple and efficient as the mean-field theory, it will provide a good reference for further development of a statistical-thermodynamic theory of complex fluid under both homogeneous and inhomogeneous conditions when disperse force has to be considered.

## I. Introduction

The interplay of intermolecular forces and the external potential makes phase behavior of a confined fluid much richer than that of the corresponding bulk fluid. There are many interesting phenomena of the confined fluid such as adsorption, wetting, capillary condensation, layering transition, etc.<sup>1</sup> The knowledge of the confined fluid is essential for the understanding of a variety of scientific problems such as molecular tribology and adhesion as well as pressure solvation and other geophysical processes.<sup>2</sup> It has been shown that such systems have important applications to chromatography, oil recovery, microphotonic crystal chips, and membrane technologies. However, it is as yet difficult to experimentally measure these properties when the confining geometry approaches molecular dimensions. Therefore, it is desirable to develop new statistical mechanic theories for predicting fluid properties in the confining geometry.

Density functional theory (DFT) has found great utility in theoretical description of the phenomena of the confined fluid.<sup>3</sup> The crucial problem in DFT is to establish the Helmholtz free energy as a functional of density distributions. The simplest approach to approximate Helmholtz free energy functional is the so-called local density functional theory.<sup>4</sup> This approximation is known to predict very poor results for the density profile near a solid surface. Besides local density approximation, there are two ways to obtain the Helmholtz free energy functional: perturbative method and weighted density approximation.<sup>5</sup> The former evaluates the excess Helmholtz free energy functional through a functional Taylor expansion around that for the corresponding bulk fluid.<sup>6</sup> In the latter case, a weight function is chosen to obtain smoothed or “coarse-grained” density at some point  $\mathbf{r}$  so that the theory gives good results for the direct correlation function.<sup>7</sup> Nowadays, both methods are widely

applied to the inhomogeneous fluids at temperatures above the bulk critical point.

Among the DFT approaches, the fundamental measure theory (FMT)<sup>7–9</sup> is the most promising for both its appealing theoretical background and its applicability to mixtures. The recent modifications<sup>10–13</sup> of FMT have improved its accuracy in predicting structures of uniform and nonuniform hard spheres and the solid–fluid transition for a fluid with a purely repulsive force.<sup>14</sup> In particular, the modified FMT (MFMT) proposed by Yu et al.<sup>10,11</sup> predicts very accurate density profiles for hard spheres and polydisperse hard-sphere mixtures inside slit-like pores, around cylinders,<sup>15,16</sup> and around spherical solid surfaces as well as the correlation functions for homogeneous hard spheres and polydisperse hard-sphere mixtures. In contrast to theory for the fluid with the purely repulsive interaction, the DFT for a fluid with a potential containing an attractive interaction, for example, the well-known Lennard-Jones potential, is not so successful. Traditional theories<sup>17–23</sup> for the dispersive interaction are based on the van der Waals or mean field theory (MFT), which is computational efficient and qualitative for the phase diagram and chemical potential calculations.<sup>24</sup> In order to obtain quantitative adsorption isotherms for the Lennard-Jones fluid, an effective hard-sphere diameter is attentively selected to represent the repulsive contribution. This method has been frequently used in predicting the structures of the confined Lennard-Jones fluids<sup>17</sup> and adsorption isotherms of gases on reference MCM-41 and SBA-15 materials in a wide range of pressures.<sup>18,23</sup> The MFT was also modified by adopting the so-called effective reference field or the effective external potential.<sup>25</sup> Even though, the MFT is not only quantitatively unreliable but also qualitatively questionable to represent the depletion near a solid surface at low temperatures. This is due to the neglect of structural correlations in the Helmholtz free energy functional.<sup>6,26</sup> Attempts have been carried out to include the structural correlations using either perturbative method<sup>6,26–31</sup> or weighted density approximation.<sup>32–35</sup>

\* To whom correspondence should be addressed. E-mail: yangxyu@mails.tsinghua.edu.cn.

Most of them use the two-particle direct correlation function (DCF) of the corresponding bulk fluid, in some cases, along with an approximation to the three-particle DCF as an input.<sup>35</sup> The direct correlation functions are generally obtained from either an analytical or a numerical solution to the Ornstein–Zernike equation with a proper closure<sup>36</sup> such as the mean spherical approximation<sup>37</sup> and the Hypernetted-chain (HNC) closure.<sup>33</sup> The theories using DCF as an input predict the density profiles and adsorption isotherms pretty well for the confined Lennard-Jones fluid at temperatures above the critical point. However, when they are used to predict a phase transition in the confining geometry, especially for vapor–liquid phase transition in nanopores, one has a trouble in selecting a DCF in the calculation because there are two corresponding bulk densities and thus two bulk DCFs. We have found that the two bulk DCFs lead to different calculated results of phase transition. Consequently, a weighted density functional theory with a weight function that does not need the DCF as an input is desired to predict the phase transition of the confined Lennard-Jones fluid.

In the weighted DFT proposed by van Swol and Henderson,<sup>32</sup> the weight function is interpolated between the exact low density limit and a mean-field weight function equal to the normalized attractive potential. In their theory, an ad hoc density-dependent switching function was used. From our experience, the fluid structure at low density is insensitive to the choice of weight function even for strongly inhomogeneous fluid. Thus, the purpose of this work is to develop a DFT using the mean-field weight function (MFWDF) and an accurate equation of state for the Lennard-Jones fluid and to show performance of the new DFT in the prediction of density profiles, adsorption isotherms, and phase transition in the slit-like pores. In the proposed DFT, the MFMT<sup>10–12</sup> is used to evaluate the contribution of the repulsive force to the Helmholtz free energy functional, and the mean field weight function is only applied to the attractive part. To reproduce an exact bulk properties, the modified Benedict–Webb–Rubin (MBWR) equation for the Lennard-Jones fluid given by Johnson et al.<sup>38</sup> is adopted in this work. The predicted results from the present MFWDF are compared extensively with those from the molecular simulations.<sup>33,39–41</sup>

## II. Theory

In a standard density functional theory, the grand potential functional  $\Omega[\rho(r)]$  is an appropriate functional of the density distribution  $\rho(r)$  when a fluid is considered in an external field  $V^{\text{ext}}(\mathbf{r})$  at a fixed temperature  $T$  and chemical potential  $\mu$ ,

$$\Omega[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int [V^{\text{ext}}(\mathbf{r}) - \mu]\rho(\mathbf{r}) \, d\mathbf{r} \quad (1)$$

where  $F[\rho(\mathbf{r})]$  denotes the Helmholtz free energy functional.

The 12–6 Lennard-Jones potential can be separated into repulsive and attractive parts according to the method of Weeks, Chandler, and Anderson (CWA).<sup>42</sup>

$$\begin{aligned} u(r) &= 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \\ &= u^{\text{rep}}(r) + u^{\text{att}}(r) \end{aligned} \quad (2)$$

where  $\epsilon$  and  $\sigma$  are, respectively, the well depth and distance parameters of the Lennard-Jones potential. The repulsive and attractive potentials are given by

$$u^{\text{rep}}(r) = \begin{cases} u(r) + \epsilon & (r < 2^{1/6}\sigma) \\ 0 & (r \geq 2^{1/6}\sigma) \end{cases} \quad (3)$$

$$u^{\text{att}}(r) = \begin{cases} -\epsilon & (r < 2^{1/6}\sigma) \\ u(r) & (2^{1/6}\sigma \leq r \leq r_c) \\ 0 & (r > r_c) \end{cases} \quad (4)$$

The repulsive potential is then linked to an equivalent hard-sphere potential with hard-sphere diameter  $d$ . Without loss of generality, we divide the intrinsic Helmholtz energy functional into an ideal gas, with a repulsive and an attractive contribution.

$$F[\rho(\mathbf{r})] = F^{\text{id}}[\rho(\mathbf{r})] + F^{\text{rep}}[\rho(\mathbf{r})] + F^{\text{att}}[\rho(\mathbf{r})] \quad (5)$$

where the ideal-gas contribution to the Helmholtz energy functional is exactly known as

$$F^{\text{id}}[\rho(\mathbf{r})] = k_B T \int d\mathbf{r} \rho(\mathbf{r}) [\ln(\rho(\mathbf{r})\Lambda^3) - 1] \quad (6)$$

here  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\Lambda = h/(2\pi mk_B T)^{1/2}$  represents the thermal wavelength with  $h$  and  $m$  standing for, respectively, the Planck constant and the mass of the particle. In this work, we apply the MFMT<sup>10,11</sup> to the functional  $F^{\text{rep}}[\rho(\mathbf{r})]$  in eq 5 with effective hard-sphere diameter  $d = \sigma$ , that is,

$$F^{\text{rep}}[\rho(\mathbf{r})] = k_B T \int \{ \Phi^{\text{hs(S)}}[n_\alpha(\mathbf{r})] + \Phi^{\text{hs(V)}}[n_\alpha(\mathbf{r})] \} \, d\mathbf{r} \quad (7)$$

here  $\Phi^{\text{hs}}[\rho(\mathbf{r})]$  is the excess Helmholtz free-energy density due to hard-core repulsion, and the superscripts S and V represent the contributions from scalar- and vector-weighted densities, respectively. The scalar repulsive Helmholtz energy density is given by eq 8,<sup>10,11</sup>

$$\begin{aligned} \Phi^{\text{hs(S)}}[n_\alpha(\mathbf{r})] &= -n_0 \ln(1 - n_3) + \frac{n_1 n_2}{1 - n_3} + \\ &\quad \frac{n_2^3 \ln(1 - n_3)}{36\pi n_3^2} + \frac{n_2^3}{36\pi n_3(1 - n_3)^2} \end{aligned} \quad (8)$$

and the vector part is expressed by eq 9.

$$\begin{aligned} \Phi^{\text{hs(V)}}[n_\alpha(\mathbf{r})] &= -\frac{\mathbf{n}_{V1} \cdot \mathbf{n}_{V2}}{1 - n_3} - \frac{n_2 \mathbf{n}_{V2} \cdot \mathbf{n}_{V2} \ln(1 - n_3)}{12\pi n_3^2} - \\ &\quad \frac{n_2 \mathbf{n}_{V2} \cdot \mathbf{n}_{V2}}{12\pi n_3(1 - n_3)^2} \end{aligned} \quad (9)$$

In eq 9,  $\mathbf{n}_{V1}$  and  $\mathbf{n}_{V2}$  are vectors, and  $\mathbf{n}_{V1} \cdot \mathbf{n}_{V2}$  and  $\mathbf{n}_{V2} \cdot \mathbf{n}_{V2}$  are dot products. In the limit of a homogeneous fluid, the two vector-weighted densities  $\mathbf{n}_{V1}$  and  $\mathbf{n}_{V2}$  vanish, and the repulsive excess Helmholtz free-energy density becomes identical to that derived from the Boublik–Mansoori–Carnahan–Starling–Leland equation of state.<sup>43,44</sup> The weighted densities  $n_\alpha(\mathbf{r})$  for the repulsive contribution are defined as

$$n_\alpha(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') w^{(\alpha)}(\mathbf{r} - \mathbf{r}') \quad (10)$$

where  $\alpha = 0, 1, 2, 3, V1$ , and  $V2$ . The weight functions,  $w^{(\alpha)}(r)$ , are given by<sup>7,10,11</sup>

$$w^{(2)}(r) = \pi d^2 w^{(0)}(r) = 2\pi d w^{(1)}(r) = \delta(d/2 - r) \quad (11)$$

$$w^{(3)}(r) = \Theta(d/2 - r) \quad (12)$$

$$\mathbf{w}^{(V2)}(\mathbf{r}) = 2\pi d w^{(V1)}(\mathbf{r}) = (\mathbf{r}/r)\delta(d/2 - r) \quad (13)$$

where  $\Theta(r)$  is the Heaviside step function, and  $\delta(r)$  denotes the Dirac delta function. Integration of the two scalar functions,  $w^{(2)}(r)$  and  $w^{(3)}(r)$ , with respect to the position gives the particle surface area and volume, respectively, and integration of the vector function  $\mathbf{w}^{(V2)}(\mathbf{r})$  is related to the gradient across a sphere in the  $\mathbf{r}$  direction.

It should be pointed out that the tensor weighted density is introduced to describe the structures of the hard sphere crystal by Tarazona,<sup>13</sup> but for a hard sphere fluid, our previous work<sup>11</sup> showed that the repulsive excess Helmholtz free-energy functional without tensor weighted density could also reproduce very accurate density profiles. Therefore, we neglect the tensor-weighted density in this work.

To obtain the contribution of long-range van der Waals interaction to the excess Helmholtz energy functional, the MFT was traditionally used. In the MFT, the attractive contribution is expressed as

$$F^{\text{att}}[\rho(r)] = \frac{1}{2} \int \int \rho(\mathbf{r}) \rho(\mathbf{r}') u^{\text{att}}(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r} d\mathbf{r}' \quad (14)$$

In this work, we use a MFWDFT for the attractive contribution to the excess Helmholtz free energy, which is expressed as

$$F^{\text{att}}[\rho(\mathbf{r})] = \int \bar{\rho}(\mathbf{r}) \psi^{\text{att}}[\bar{\rho}(\mathbf{r})] d\mathbf{r} \quad (15)$$

where  $\psi^{\text{att}}[\bar{\rho}(r)]$  is the attractive contribution to the excess Helmholtz free energy per particle of a bulk fluid with density  $\bar{\rho}(r)$ . The weighted density for attractive part,  $\bar{\rho}(r)$ , is defined by eq 16.

$$\bar{\rho}(\mathbf{r}) = \int \rho(\mathbf{r}') w^{(\text{att})}(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' \quad (16)$$

where  $w^{(\text{att})}(r)$  is a normalized weight function and in the MFWDFT, it can be obtained by eq 17.

$$w^{(\text{att})}(r) = u^{\text{att}}(r) / \int u^{\text{att}}(r) dr \quad (17)$$

To obtain accurate bulk properties for the Lennard-Jones fluid, we adopt the MBWR equation of state with the parameters given by Johnson et al.<sup>38</sup> In the MBWR equation of state the attractive contribution to the excess Helmholtz free energy per particle is taken the form

$$\psi^{\text{att}}(\rho) = \varepsilon \sum_{i=1}^8 \frac{a_i(\rho^*)^i}{i} + \varepsilon \sum_{i=1}^6 b_i G_i - \psi^{\text{CS}} \quad (18)$$

where the coefficients  $a_i$  and  $b_i$  are functions of temperature only, and the coefficients  $G_i$  are functions of density. The functional forms of the  $a_i$ ,  $b_i$  and  $G_i$  as well as the values of the parameters for the MBWR equation of state<sup>38</sup> can be found in ref 38.  $\psi^{\text{CS}}$  is the hard-sphere part of the Helmholtz free energy per particle obtained from the Carnahan–Starling equation of state.<sup>45</sup>

$$\psi^{\text{CS}}(\rho) = k_B T \frac{4\eta - 3\eta^2}{(1 - \eta)^2} \quad (19)$$

where  $\eta = \pi\rho d^3/6$  is the packing fraction.

Once the Helmholtz free energy functional is determined, the density profile is obtained by solving the Euler–Lagrange equation

$$\ln \left[ \frac{\rho(\mathbf{r})}{\rho_b} \right] = \beta \left[ \mu^{\text{ex}} - \frac{\delta \{ F^{\text{rep}}[\rho(\mathbf{r})] + F^{\text{att}}[\rho(\mathbf{r})] \}}{\delta \rho(\mathbf{r})} - V^{\text{ext}}(\mathbf{r}) \right] \quad (20)$$

where  $\rho_b$  and  $\mu^{\text{ex}}$  are, respectively, the density and excess chemical potential of the corresponding bulk fluid. The excess chemical potential is obtained from the MBWR equation of state. In this paper, we refer the calculated density profiles, adsorption isotherms, and phase transitions using eq 14 as the result of the MFT, and that using eqs 15–19 as the result of the MFWDFT. From the comparison of the equations used, one can find that the MFWDFT is almost as simple and computationally efficient as the MFT.

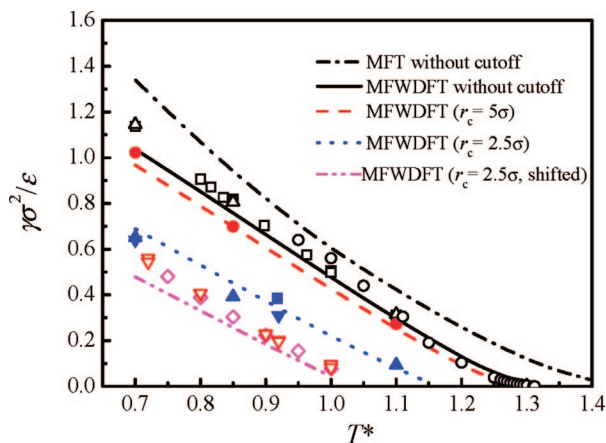
### III. Results and Discussion

In this section, we will demonstrate the applications of the present MFWDFT to Lennard-Jones fluids confined in the slit-like pores with different fluid-wall interactions. We will also provide some MFT results for comparisons. It should be mentioned that in both the MFWDFT and MFT, the attractive potentials are the same as in WCA perturbation theory,<sup>42</sup> and the hard-sphere diameters are taken as  $d = \sigma$  for theoretical reason and simplicity. For the systems with a truncated and shifted potential, a mean-field correction is made to compensate the cutoff effect on the Helmholtz free energy per particle as done by Johnson et al.<sup>38</sup> To test the theories against the molecular simulation data, the fluid–fluid and the solid–fluid interaction parameters in the theories are coordinate to those used in the simulations.<sup>33,39–41</sup>

**A. Surface Tension of Bulk Fluid.** In the bulk limit of our DFT, it reduces to the equation of state of Johnson et al.<sup>38</sup> Because this equation of state predicts the vapor–liquid equilibria for the Lennard-Jones fluid very well, we did not consider the bulk vapor–liquid equilibrium in this paper. Surface tension of bulk Lennard-Jones with different cutoff distances can be predicted from the MFWDFT via

$$\gamma = \{ \Omega[\rho(z)] + p_b V \} / A \quad (21)$$

where  $\gamma$ ,  $p_b$ ,  $V$ , and  $A$  are, respectively, the surface tension, bulk pressure, volume, and surface area of the system.



**Figure 1.** Comparison of theoretical surface tension with those from molecular simulations for Lennard-Jones fluid with different cutoff distances. Without cutoff: dash dot and solid line represent the theoretical results from the MFWDFT and MFT, respectively; opened up-triangles, squares, and circles represent the simulation data of Mecke et al.,<sup>48</sup> Shen et al.,<sup>50</sup> and Potoff and Panagiotopoulos,<sup>51</sup> respectively. Cutoff only ( $r_c = 5.0\sigma$ ): solid circles and dashed line represent the results from the simulation of Mecke et al.<sup>48</sup> and the present MFWDFT, respectively. Cutoff only ( $r_c = 2.5\sigma$ ): solid up-triangles, down-triangles, and squares and dotted line represent the results from the simulation of Mecke et al.,<sup>48</sup> Trokhymchuk et al.,<sup>47</sup> Chapela et al.,<sup>49</sup> and the present MFWDFT, respectively. Cut-and-shifted ( $r_c = 2.5\sigma$ ): opened down-triangles, diamonds, and dash-dot-dot line represent the results from the simulations of Trokhymchuk and Alejandre,<sup>47</sup> Haye and Bruin,<sup>46</sup> and the present MFWDFT, respectively.

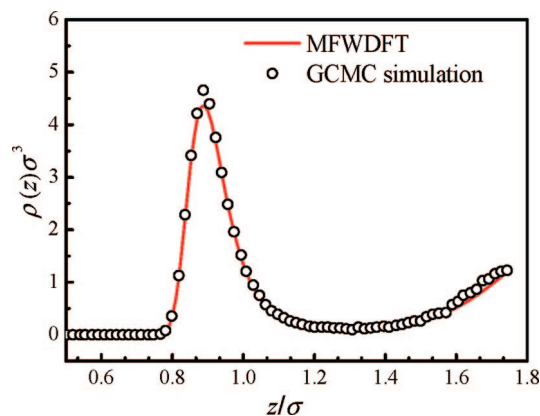
The calculated surface tensions of the Lennard-Jones fluid are compared with the molecular simulation data<sup>46–51</sup> in Figure 1. Because the MFWDFT is established on the basis of full Lennard-Jones potential, it is certainly correct for the true long-ranged potential. For the true Lennard-Jones fluid, the MFWDFT underestimates the surface tension when temperature is lower than  $T^* = 0.9$  and gives good predictions of surface tension at  $T^* > 0.9$ . When a cut-and-shifted Lennard-Jones potential is used as those in many simulation studies, we can use the mean-field method<sup>38</sup> to correct the Helmholtz free energy functional. From Figure 1, one can see that the MFWDFT is accurate for cutoff distance larger than  $r_c = 2.5$  but underestimates the surface tensions of a cut-and-shifted potential with  $r_c = 2.5$ . In general, the present DFT can correctly predict the effect of cutoff distance on the surface tensions if the cutoff distance is not too small. The MFT theory obviously overestimates the surface tensions of Lennard-Jones fluids in all cases.

### B. Density Profiles and Adsorption of Supercritical Fluid.

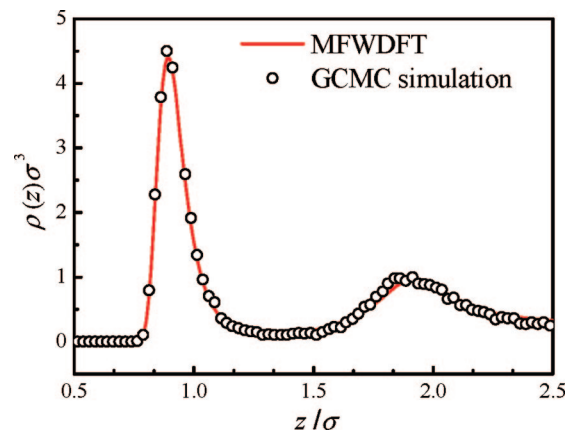
The supercritical adsorption of a Lennard-Jones fluid in a slit-like pore has been used in application to gas adsorption in porous materials.<sup>23,52</sup> In Figures 2–4, the calculated density profiles and adsorption isotherms for supercritical ethane in graphite pores are compared with the corresponding computer simulation data at reduced temperature  $T^* = k_B T/\epsilon = 1.35$ . In the calculation, ethane is modeled by a Lennard-Jones potential which is truncated and shifted at  $r_c = 2.5\sigma$ . The interaction between graphite surface and fluid is represented by a Steele 10–4–3 potential

$$V_s(z) = \epsilon_w \left[ \frac{2}{5} \left( \frac{\sigma_w}{z} \right)^{10} - \left( \frac{\sigma_w}{z} \right)^4 - \frac{\sigma_w^4}{3\Delta(z + 0.61\Delta)^3} \right] \quad (22)$$

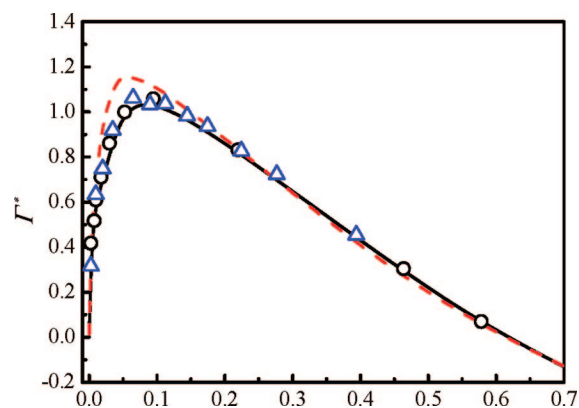
where  $z > 0$  is the coordinate in the direction perpendicular to the surfaces. For the systems shown in Figures 2–4, the values



**Figure 2.** Reduced density profiles of Lennard-Jones fluid in a slit-like pore at reduced temperature  $T^* = 1.35$ , pore width  $H = 3.5\sigma$ , and reduced bulk density  $\rho_b\sigma^3 = 0.0497$ . The opened circles and solid line represent the results from the GCMC simulations of Sweatman<sup>33</sup> and the present MFWDFT, respectively.



**Figure 3.** Reduced density profiles of Lennard-Jones fluid in a slit-like pore at reduced temperature  $T^* = 1.35$ , pore width  $H = 5\sigma$ , and reduced bulk density  $\rho_b\sigma^3 = 0.09334$ . The meaning of the symbols is the same as in Figure 2.



**Figure 4.** Surface excesses for a model of ethane in a graphite slit-like pore with pore width of  $H = 5\sigma$  at reduced temperature  $T^* = 1.35$ . The opened circles, opened triangles, and dashed and solid lines represent the results from the GCMC simulations of Sweatman,<sup>33</sup> those of van Megan and Snook,<sup>39</sup> the MF theory, and the present MFWDFT, respectively.

of the wall parameters are  $\sigma_w = 0.903\sigma$ ,  $\epsilon_w = 12.96\epsilon$  and  $\Delta = 0.8044\sigma$ . For a planar slit pore with width  $H$ , the external potential can be expressed as

$$V^{\text{ext}}(z) = V_s(z) + V_s(H - z) \quad (23)$$

Figures 2 and 3 depict the comparisons of the predicted density profiles with the grand canonical ensemble Monte Carlo (GGEMC) simulation data at reduced bulk densities of  $\rho_b \sigma^3 = 0.0497$  and  $\rho_b \sigma^3 = 0.09334$  with pore width  $H = 3.5\sigma$  and  $H = 5\sigma$ , respectively. It can be seen from both figures that the present MFWDFT predicts accurate density profiles when compared with the GCMC data. The theoretical surface excesses are compared in Figure 4 with the corresponding GCMC data at reduced temperature  $T^* = 1.35$  and pore width  $H = 5\sigma$ . The reduced surface excess  $\Gamma^*$  is calculated from

$$\Gamma^* = \Gamma \sigma^2 = \frac{\sigma^2}{2} \int_0^H [\rho(z) - \rho_b] dz \quad (24)$$

Figure 4 shows that the mean-field weight function applied to attractive functional is better than the MFT. The MFT overestimates surface excess at low bulk densities ( $\rho_b \sigma^3 < 0.2$ ) and slightly underestimates surface excess at high bulk densities ( $\rho_b \sigma^3 > 0.4$ ). The MFWDFT predicts a maximum characteristic of supercritical surface excess as a function of reduced bulk density, which is in good agreement with the simulation results in the literature.<sup>33,39</sup> It should be noted that the adsorption isotherm predicted from the MFT in this work is different from that of Sweatman<sup>33</sup> and that of Tan and Gubbins<sup>53</sup> because they used an effective hard-sphere diameter  $d \neq \sigma$  for the supercritical Lennard-Jones fluid. In contrast, we did not adjust hard-sphere diameter  $d$  in this work to improve the accuracy for the calculation and directly used  $d = \sigma$ .

**C. Average Density and Pressure Inside a Pore below the Bulk Critical Point.** The predicted adsorption isotherms of Lennard-Jones fluids with a cutoff distance  $r_c = 5\sigma$  at temperatures lower than the bulk critical temperature ( $T^* < T_c^*$ ) are examined using the GCMC simulations in this section. Since there are two bulk phases in equilibrium below the bulk critical point, the perturbative density functional theories that use the DCF as an input will face a difficulty in choosing the DCF from bulk liquid or bulk vapor. In contrast, the weighted DFT without the DCF as an input has no such trouble in the calculation. For comparison with the existed computer simulations of Hamada et al.,<sup>40</sup> the following external potential for the slit-like pore is used.

$$V^{\text{ext}}(z) = \begin{cases} \varepsilon_w & (\sigma/2 < z < H - \sigma/2) \\ \infty & \text{otherwise} \end{cases} \quad (25)$$

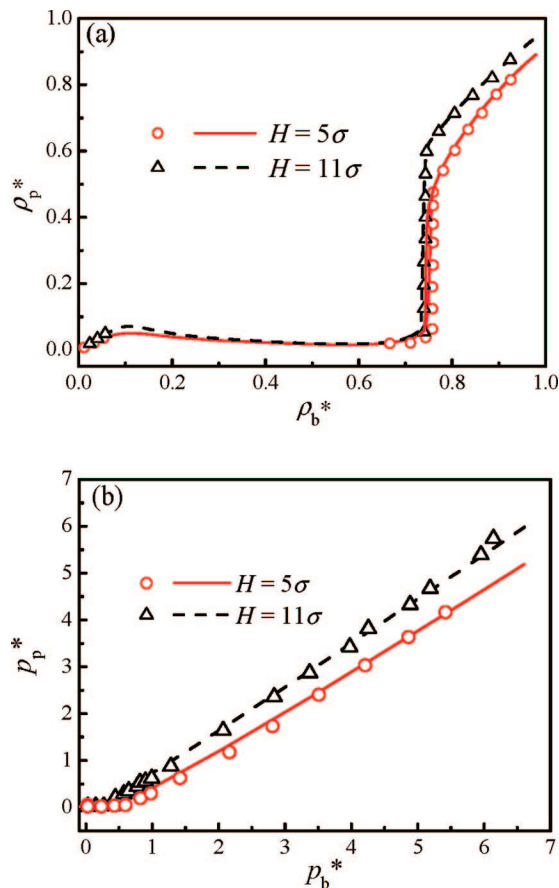
The above external potential indicates that the pore is composed of two parallel hard walls and that there is a uniform field inside the pore.

Figures 5–8 depict the average densities and pressures inside the slit-like pores with pore width  $H = 5\sigma$  and  $11\sigma$  at various temperatures and fluid-solid interactions. Here the reduced average density  $\rho_p^*$  and pressure  $p_p^*$  inside the pore are expressed as

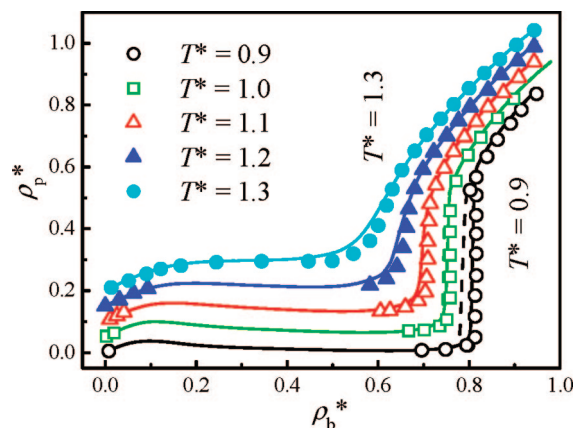
$$\rho_p^* = \rho_p \sigma^3 = \frac{\sigma^3}{H} \int_0^H \rho(z) dz \quad (26)$$

$$p_p^* = p_p \sigma^3 / \varepsilon = \Omega \sigma^3 / (V \varepsilon) \quad (27)$$

where  $\Omega$  and  $V$  are the grand potential and volume inside the pore.

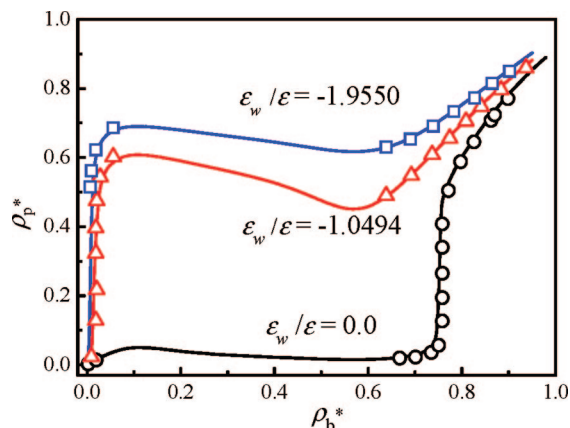


**Figure 5.** (a)  $\rho_p^* - \rho_b^*$  and (b)  $p_p^* - p_b^*$  isotherms of the Lennard-Jones fluids in the hard slit-like pore ( $\varepsilon_w = 0$ ) at reduced temperature  $T^* = 1.0$ . The symbols and lines represent the results from the GCMC simulations<sup>40</sup> and the present MFWDFT, respectively.

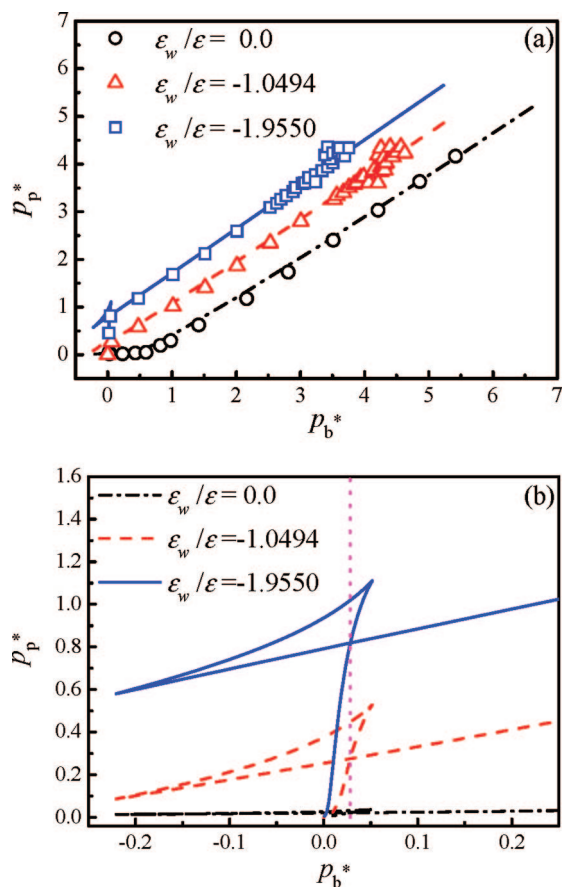


**Figure 6.** Adsorption isotherms of Lennard-Jones fluid in the hard slit-like pore ( $\varepsilon_w = 0$  and  $H = 5\sigma$ ) at different reduced temperatures. The symbols and lines represent the results from the GCMC simulations<sup>40</sup> and the present MFWDFT, respectively. The dashed lines indicate hysteresis. For clarity, the densities in the pore  $\rho_p^*$  at  $T^* = 1.0, 1.1, 1.2,$  and  $1.3$  are shifted upward by 0.05, 0.10, 0.15, and 0.20, respectively.

As shown in Figure 5a, the curves of  $\rho_p^* - \rho_b^*$  plot deviate greatly from the linear relation  $\rho_p^* = \rho_b^*$ . Because the reduced temperature in Figure 5 is  $T^* = 1.0$ , which is lower than the bulk critical temperature ( $T_c^* = 1.316$ ), the vapor–liquid phase transitions may exist for both bulk and confined fluids. The horizontal and vertical parts in each curve verify the existence of such vapor–liquid phase transitions for the bulk and confined fluids, respectively. For the Lennard-Jones fluid



**Figure 7.** Effect of wall-fluid interactions on  $\rho_p^* - \rho_b^*$  isotherms of the Lennard-Jones fluid in the attractive slit-like pores ( $H = 5\sigma$ ) at reduced temperature  $T^* = 1.0$ . The symbols and the solid lines represent the results from the GCMC simulations<sup>40</sup> and the present MFWDFT, respectively.



**Figure 8.** (a) Effect of wall-fluid interactions on  $p_p^* - p_b^*$  isotherms of the Lennard-Jones fluid in the attractive slit-like pores ( $H = 5\sigma$ ) at  $T^* = 1.0$  and (b)  $p_p^* - p_b^*$  isotherms at low pressure region. The symbols and the curves represent the results from the GCMC simulations<sup>40</sup> and present MFWDFT, respectively. The dotted line in (b) represents the bulk saturated pressure, and the crosses in (b) indicate bulk vapor-liquid transitions.

confined in a hard slit pore ( $\epsilon_w = 0$ ) at temperature  $T < T_c$ , the pore width has little influence on the adsorption inside the pore when only vapor-like phase exists inside the pore. When the fluid becomes liquid-like in the pore at higher densities, the average density inside the pore increases as the pore width is increased.

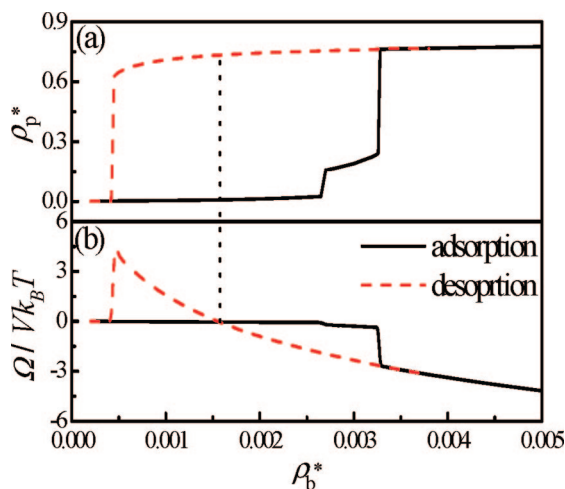
From Figure 5b one can see that the pressure inside the pore keeps almost constant at lower bulk pressure ( $p_b^* = p_b\sigma^3/\epsilon < 0.5$ ). With the increase of bulk pressure, the pore pressure  $p_p^*$  increases as a linear function of the bulk pressure  $p_b^*$ . The larger the pore is, the higher the pressure inside the pore. These qualitative relationships between pore and bulk pressures can be well-understood via  $dp_p/dp_b \approx \rho_p/\rho_b$  with the information from Figure 5a. The comparisons with the GCMC data in Figure 5 show that the present MFWDFT reproduces the  $\rho_p^* - \rho_b^*$  and  $p_p^* - p_b^*$  isotherms very well.

The effect of temperature on the  $\rho_p^* - \rho_b^*$  correlation for the hard slit-like pore with pore width of  $H = 5\sigma$  is plotted in Figure 6. The density difference between vapor-like and liquid-like fluids in equilibrium decreases gradually to zero for both the bulk and confined fluids as the temperature is increased to approach the bulk critical temperature  $T^* = 1.316$ . The average densities in the pore predicted from the present MFWDFT are in good agreement with those from the GCMC simulations at various temperatures studied. Because the  $p_p^* - p_b^*$  correlation for a fixed pore width is almost independent of temperature, the  $p_p^* - p_b^*$  curves are indistinguishable from the one at  $T^* = 1.0$  in Figure 5b.

The effects of pore wall-fluid interaction parameter  $\epsilon_w$  on  $\rho_p^* - \rho_b^*$  and  $p_p^* - p_b^*$  isotherms of the Lennard-Jones fluid confined in the attractive slit-like pores ( $H = 5\sigma$ ) are plotted in Figures 7 and 8, respectively. With the increase of the absolute values of fluid-solid interaction parameter  $\epsilon_w$ , the more fluid molecules are attracted into the pore, resulting in a very large pore density ( $\rho_p \gg \rho_b$ ) when the bulk fluid is a vapor. The pore density is smaller than bulk density for all the cases studied when the bulk fluid is a liquid, although the adsorption in the attractive pore is enhanced as shown in Figure 7. From Figure 8a one can see that the strong attractive force between the fluid and the pore wall also results in an increase of pressure inside the pore.

An interesting change of  $p_p$  as a function of bulk pressure  $p_b$  is found in the region where the bulk pressure is near saturated vapor pressure  $p_b^{\text{sat}}$  for the Lennard-Jones fluid. When the wall parameter  $\epsilon_w = -1.0494\epsilon$  and  $-1.9550\epsilon$ , the  $p_p^* - p_b^*$  curves are nearly vertical at  $p_b^* = 0$ . To illustrate this phenomenon, we have plotted in Figure 8b the  $p_p^* - p_b^*$  curves predicted from the present MFWDFT at low bulk pressure. The crosses of each curve do not indicate the vapor-to-liquid phase transition in the pore but in the corresponding bulk fluid. The bulk pressure  $p_b$  at the cross points is equal to the bulk saturated vapor pressure  $p_b^{\text{sat}}$ . The pore pressure corresponding to the bulk vapor-liquid equilibrium increases as the attractive force between pore wall and fluid is increased. Our MFWDFT captures all the phenomena influenced by the fluid-solid interactions, and its predictions are in good agreement with those from the GCMC simulations. Comparisons in Figures 5–8 show that the present MFWDFT can be successfully applied to the calculation of adsorption and pore pressure of the Lennard-Jones fluid at temperatures below the bulk critical point.

**D. Phase Transition in the Slit-like Pores.** In this section we demonstrate the applicability of the present MFWDFT to the phase behavior of the Lennard-Jones fluid confined in the slit-like pores. The Gibbs ensemble Monte Carlo simulation results of Vishnyakov et al.<sup>41</sup> are used to test the density functional theories. Vishnyakov et al.<sup>41</sup> simulated the vapor liquid equilibria of methane in graphite slit-like pores. In their study, the Lennard-Jones parameters for methane were  $\sigma = 0.373$  nm and  $\epsilon/k_B = 148.1$  K. The expression of the interaction between fluid and the solid surface was the same as eq 22 but

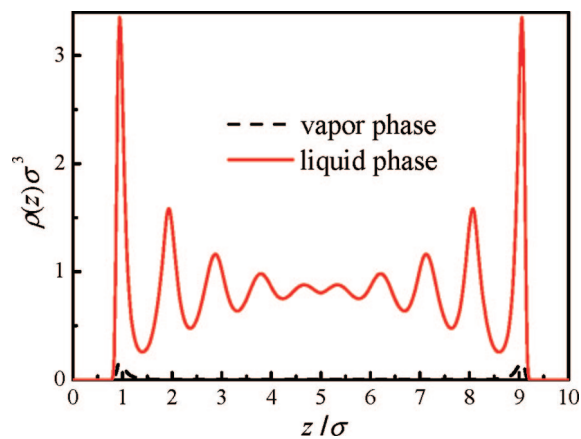


**Figure 9.** (a) Adsorption isotherm and (b) grand potential density as functions of reduced bulk density for the Lennard-Jones fluid in the slit-like pore ( $H = 10\sigma$  and  $\epsilon_{sf}/k_B = 21.5$  K) at  $T^* = 0.7$ . The solid and dashed lines represent the calculated results of adsorption and desorption branches, respectively. The dotted line represents the vapor–liquid phase transition in the pore predicted from the present MFWDFT.

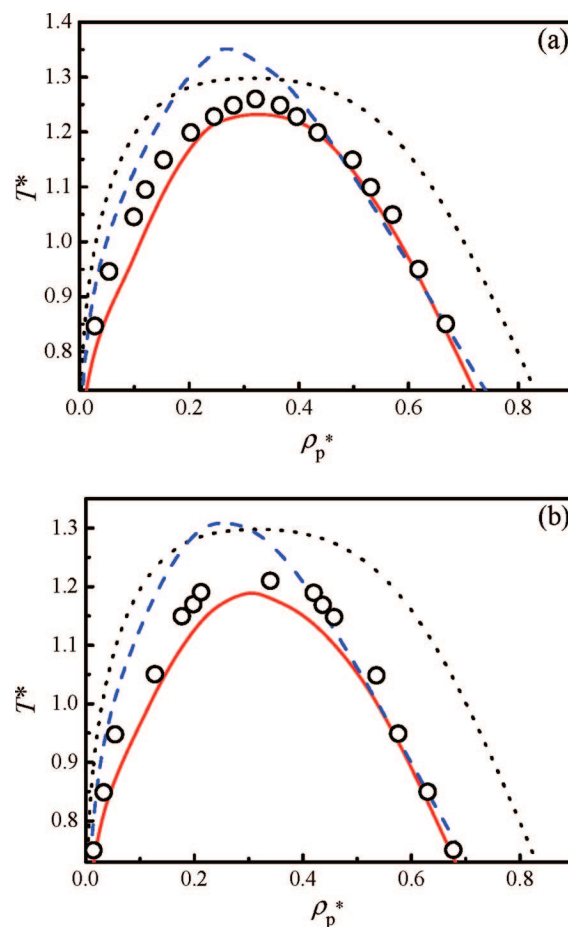
different wall parameters were used. The wall parameters used by Vishnyakov et al.<sup>41</sup> were  $\sigma_w = 0.3565$  nm, and  $\epsilon_w = 2\pi\rho_s\epsilon_{sf}\sigma_w^2\Delta$ , where  $\rho_s = 114$  nm<sup>-3</sup> is the number density of carbon atoms in graphite and  $\Delta = 0.335$  nm is the interlayer spacing parameters. In our density functional theory calculations, the same set of wall parameters are adopted in this section. We also consider a weaker ( $\epsilon_{sf}/k_B = 21.5$  K) and a stronger ( $\epsilon_{sf}/k_B = 64.51$  K) fluid–solid interaction to investigate the effect of fluid–wall interaction on the phase transition in the slit-like pores.

Figure 9 depicts adsorption isotherm and grand potential density as functions of reduced bulk density for methane in the pore with width of  $H = 10\sigma$  and fluid–solid interaction of  $\epsilon_{sf}/k_B = 21.5$  K at reduced temperature  $T^* = 0.7$ . A large hysteresis loop on the  $\rho_p^* - \rho_b^*$  plot indicates that the confined fluid undergoes a vapor–liquid first-order phase transition, and the cross on the curve of grand potential density represents that the vapor- and liquid-like phases are in equilibrium at this bulk density. The density profiles of the two phases in equilibrium are plotted in Figure 10. The density profile of the liquid-like phase oscillates with a period slightly less than  $1\sigma$ . In contrast, molecules of the vapor-like phase only distribute in the first layer near the solid surface, and the densities in other area are very low.

The vapor–liquid phase diagrams in a graphite pore with  $\epsilon_{sf}/k_B = 21.5$  K are plotted in Figure 11. From the figure we can see that the MFT dramatically overestimates the vapor–liquid critical points of the confined fluid, in accordance with the common sense for the MFT in the bulk case. The MFWDFT predicts slightly lower critical temperatures and smaller area of vapor–liquid coexistence than the simulations do. Comparison of Figure 11a with Figure 11b suggests that the narrower the pore is, the lower the critical temperature in the pore. The densities of the liquid-like phase in the pore are smaller than the corresponding bulk ones and decrease as the pore width  $H$  is decreased. However, the densities of the vapor-like phase in the pore are larger than the corresponding bulk ones. All these results are consistent with that obtained in Figure 6. Comparisons with the simulation data indicate that the present MFWDFT



**Figure 10.** Density profiles of vapor- and liquid-like phases of the Lennard-Jones fluid confined in the slit-like pore ( $H = 10\sigma$  and  $\epsilon_{sf}/k_B = 21.5$  K) from the present MFWDFT at reduced temperature  $T^* = 0.7$ .

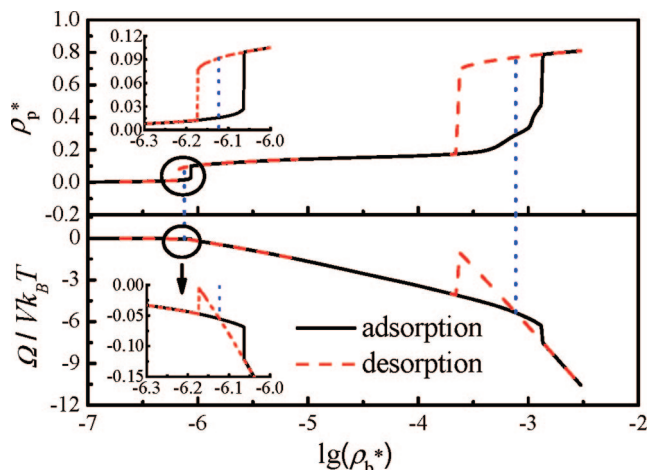


**Figure 11.** Vapor–liquid phase diagrams of methane in a graphite pore with fluid–solid interaction of  $\epsilon_{sf}/k_B = 21.5$  K and pore width of (a)  $H = 10\sigma$  and (b)  $H = 7.5\sigma$ . The opened circles and dashed and solid lines represent the results from the GEMC simulations,<sup>41</sup> MF theory, and present MFWDFT, respectively. The dotted curve represents the bulk vapor–liquid equilibrium.

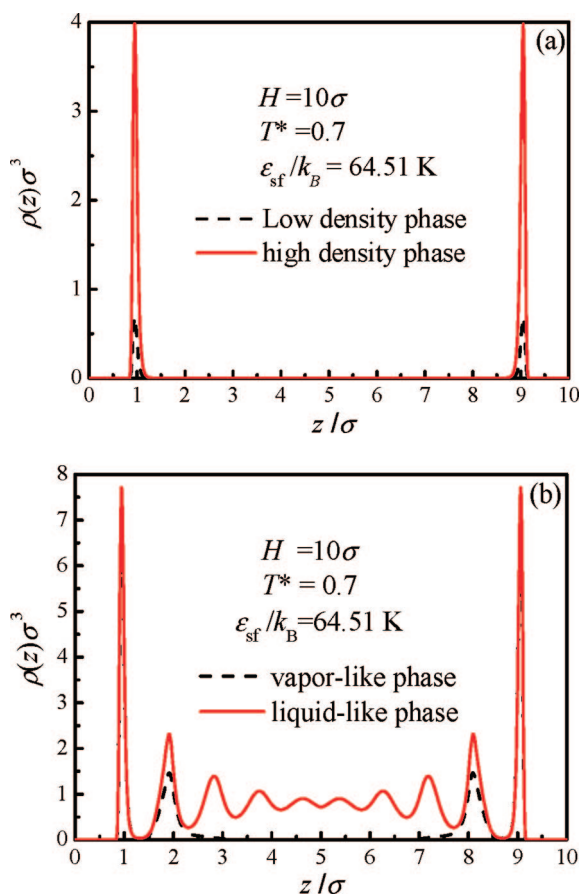
is a good approximation theory for predicting the fluid phase transition for the confined fluid with a weaker fluid–solid interaction.

Now we show some results for methane confined in the slit-like pore with a stronger fluid–solid interaction ( $\epsilon_{sf}/k_B = 64.51$  K). Figure 12 depicts adsorption isotherm and grand potential density as functions of reduced bulk density for methane in the



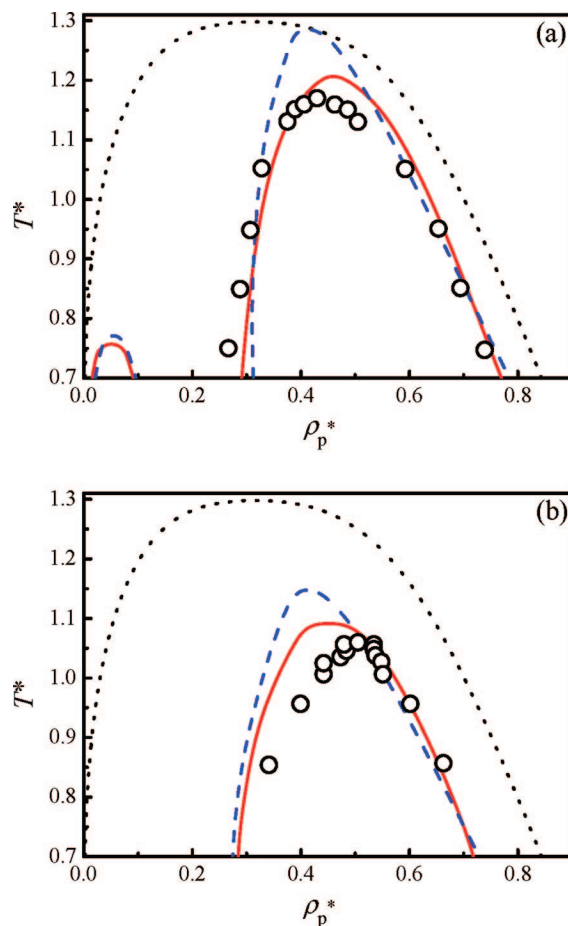


**Figure 12.** (a) Adsorption isotherm and (b) grand potential density as functions of reduced bulk density for the Lennard-Jones fluid in the slit-like pore ( $H = 10\sigma$  and  $\varepsilon_{sf}/k_B = 64.51$  K) at  $T^* = 0.7$ . The solid and dashed lines represent the calculated results of adsorption and desorption branches, respectively. The left and right dotted lines represent, respectively, the layering and vapor–liquid phase transitions in the pore predicted from the present MFWDFT.



**Figure 13.** Density profiles of (a) layering and (b) vapor–liquid transitions of the Lennard-Jones fluid confined in the slit-like pore ( $H = 10\sigma$  and  $\varepsilon_{sf}/k_B = 64.51$  K) at reduced temperature  $T^* = 0.7$ .

slit-like pore with width of  $H = 10\sigma$  and fluid–solid interaction of  $\varepsilon_{sf}/k_B = 64.51$  K at temperature  $T^* = 0.7$ . Different from Figure 9, there is a layer-transition under this condition. The density profiles for the vapor-like and liquid-like phases in equilibrium, and the low density and high density phases in layer transition equilibrium are plotted in Figure 13, panels a and b, respectively. In the pore with the stronger fluid–solid



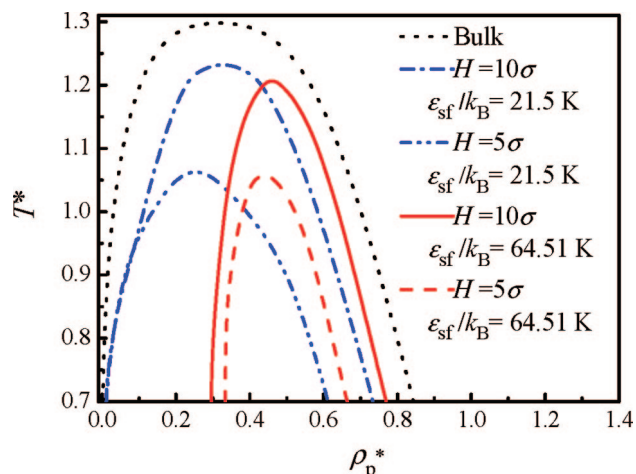
**Figure 14.** Phase diagrams of methane in the graphite pore with fluid–solid interaction of  $\varepsilon_{sf}/k_B = 64.51$  K and pore width of (a)  $H = 10\sigma$  and (b)  $H = 6.5\sigma$ . The opened circles and dashed and solid lines represent the results from the GEMC simulations,<sup>41</sup> MF theory, and present MFWDFT, respectively. The dotted curve represents the bulk vapor–liquid equilibrium.

**TABLE 1: Comparison of Theoretical Critical Temperatures and Densities of Methane Capillary Condensation in the Slit-like Pores with Those from Monte Carlo Simulations**

| $H/\sigma$ | $\varepsilon_{sf}/kT$ | $T_c^*$ |      |                  | $\rho_c^*$ |       |                  |
|------------|-----------------------|---------|------|------------------|------------|-------|------------------|
|            |                       | MFWDFT  | MFT  | MC <sup>41</sup> | MFWDFT     | MFT   | MC <sup>41</sup> |
| $\infty$   |                       | 1.313   | 1.41 | 1.316            | 0.310      | 0.251 | 0.304            |
| 10.0       | 64.51                 | 1.21    | 1.29 | 1.17             | 0.459      | 0.411 | 0.430            |
| 6.5        | 64.51                 | 1.09    | 1.15 | 1.06             | 0.452      | 0.410 | 0.505            |
| 10.0       | 21.50                 | 1.24    | 1.35 | 1.26             | 0.327      | 0.268 | 0.321            |
| 7.5        | 21.50                 | 1.19    | 1.31 | 1.21             | 0.303      | 0.251 | 0.340            |

interaction, the methane molecules of vapor-like phase distribute in the first and second layers near the two solid surfaces. However, for the layer transition the methane molecules only distribute in the first layer near the two solid surfaces. The only difference between the two phases in layer transition equilibrium is that the densities of the high density phase in the pore are at least five times as large as those of the low density phase.

The phase diagrams of methane in the graphite pore with  $\varepsilon_{sf}/k_B = 64.51$  K are plotted in Figure 14. The pore widths of  $H = 10\sigma$  and  $H = 6.5\sigma$  are considered. The MFT again overestimates the vapor–liquid critical points in the pores and the present MFWDFT predicts a satisfactory results. Both the MFT and present MFWDFT predict a layer phase transition in the slit-like pore with the pore width of  $H = 10\sigma$ , which was not given by Vishnyakov et al.,<sup>41</sup> although all the existing DFT



**Figure 15.** Predicted vapor–liquid phase diagrams of the Lennard-Jones fluid confined in the slit-like pores with different pore widths and wall–fluid interactions.

based on the MFT overestimate the onset of the layering transition.<sup>24,54</sup> We have used a more accurate equation of state, therefore our theory gives an improved critical temperature of phase transition. The present DFT slightly overestimates the onset of the layering transition. The layering transition vanishes in the pore with the width of  $H = 6.5\sigma$  when the reduced temperature is  $T^* > 0.7$ . Subsequently, we can conclude that the fluid prefers to behave a layering transition in a wider pore with a stronger fluid–solid interaction.

The critical temperature and density of methane confined in the slit-like pores from the present MFWDFT are summarized in Table 1. For comparison, the results from the Gibbs ensemble Monte Carlo simulations<sup>41</sup> and the MFT are also included in the table. From the table we can see that the MFT always overestimates the critical temperature and underestimates the critical density for the Lennard-Jones fluid in the slit-like pores. The critical property from the present MFWDFT is much closer to those from the simulations than that from the MFT.

From Table 1 and Figure 15, we can see that the phase transitions are strongly dependent on the fluid–solid interaction and the pore width. The increase of the attractive interaction between the fluid and solid surface makes the vapor–liquid coexistence curves narrower and shifted to the higher density region. The stronger fluid–solid surface interaction only causes a small drop in critical temperature for the confined fluid. However, the critical temperature of the confined fluid is greatly influenced by the pore width. It decreases dramatically when the slit-like pore becomes narrow. The critical density slightly decreases when the pore becomes narrow. All these results from the present MFWDFT are verified using the molecular simulations of Vishnyakov et al.<sup>41</sup> In principle, our theory can be extended to the systems with other interaction potentials such as hard-core Yukawa and Sutherland potentials. However, when the pore width becomes very small, the fluid in the pore behaves like a one-dimensional fluid. Because MFWDFT cannot correctly reduce to the one-dimensional case, its performance will be bad in very narrow pores.

#### IV. Conclusions

A DFT is presented to investigate the density profiles, adsorption isotherms, pressures, and fluid phase transitions of a Lennard-Jones fluid confined in slit-like pores with various pore widths and fluid–solid interactions. The Lennard-Jones potential is separated into repulsive and attractive parts in terms

of the spirit of WCA perturbation theory.<sup>42</sup> Accordingly, the proposed excess Helmholtz free energy functional is composed of a repulsive contribution obtained from the MFMT of Yu and Wu,<sup>10,11</sup> and an attractive contribution derived from the modified Benedict–Webb–Rubin equation of state<sup>38</sup> and a mean-field weight function. The obtained theory is as simple and computational efficient as the mean-field theory, but predicts more accurate bulk surface tension, adsorption isotherms, and fluid phase transitions of the Lennard-Jones fluid confined in the slit-like pores. The results predicted from the present weighted density functional theory with the mean-field weight function (MFWDFT) are in good agreement with those from the Monte Carlo simulations. The MFWDFT is applicable to the cut-and-shifted Lennard-Jones fluids with a cutoff distance larger than  $2.5\sigma$ , and in principle to other potentials. Because the theory cannot correctly reduce to the one-dimensional case, it is not suitable for very narrow pores.

When the Lennard-Jones confined in a slit-like pore with a uniform potential inside the pore at a temperature below the bulk critical temperature, the horizontal and vertical parts on each curve of the adsorption isotherm indicate the existence of vapor–liquid phase transition in bulk and confined fluids, respectively. The density difference between vapor-like and liquid-like phases gradually decreases to zero for both bulk and confined fluids as temperature is increased to approach the bulk critical temperature. The  $p_p^* - p_b^*$  curves are nearly vertical when bulk pressure tends to zero for the strongly attractive fluid–solid interactions. There is a cross on the curves of  $p_p^* - p_b^*$  when the bulk pressure is equal to bulk saturated vapor pressure, indicating a phase transition in bulk fluid but not in the confined fluid. The fluid–solid interaction has a great effect on the average density in the pore when the bulk fluid is a vapor, whereas it has almost no effect on the isotherm curves of  $p_p^* - p_b^*$ . Our theory captures all these phenomena very well.

Applications to fluid phase transition in the slit-like pores show that the present theory predicts the capillary and layering transitions in the slit-like pores well when compared with the Monte Carlo simulation data. In contrast, the commonly used mean-field theory substantially overestimates the critical temperature of the confined Lennard-Jones fluid. Both theory and molecular simulation predict that the critical temperature decreases apparently as the pore becomes narrow. The strongly attractive fluid–solid interaction enables the critical density of the vapor–liquid phase transition to become larger and makes a layer transition possible. The calculated results suggest that the present MFWDFT is a satisfactory theory for bulk and confined Lennard-Jones fluids and is a good reference for further developing a new molecular thermodynamic theory of a more complex confined fluid.

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