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Thin-Thick Film Transitions on a Planar Solid Surface: A Density Functional Study *

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A weighted density functional theory is proposed to predict the surface tension and thin-thick film transition of a Lennard–Jones fluid on a planar solid surface. The underlying density functional theory for the Lennard–Jones fluid at low temperature is based on a modified fundamental measure theory for the hard-core repulsion, a Taylor expansion around zero-bulk-density for attraction, and a correlation term evaluated by the weighted density approximation with a weight function of the Heaviside step function. The predicted surface tension and thin-thick film transition agree well with the results from the Monte Carlo simulations, better than those from alternative approaches. For the Ar/CO_2 system, the prewetting line has been calculated. The predicted reduced surface critical temperature is about 0.97, and the calculated wetting temperature is below the triple-point temperature. This is in agreement with the experimental observation.

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Wetting is a common phenomenon of a liquid adsorbed on a solid substrate surrounded by a vapor phase. It is an area where chemistry, physics and engineering intersect.[1] The theoretical investigations for fluid-solid interfaces indicate that the first-order wetting transition is probably the more frequent case, so that the prewetting (thin-thick film) transition should appear in many of these systems.[2] However, up to date, seldom has the prewetting phase transition been observed in experiment. It is also very difficult to search for the prewetting line with the molecular simulations.[3]

Prewetting phase transition was first investigated independently by Cahn[4] using van der Waals' square-gradient theory and by Ebner and Samm[5] using a gradient expansion of the Helmholtz energy functional. The theoretical understanding of wetting transition has been developed considerably since then. Regrettably, the developed theories are either qualitative[2,6] or most complicated.[7]

In this Letter, we propose a density functional theory that is accurate at low temperature for the Lennard–Jones (LJ) fluid. The theory is tested by the Ar/CO_2 system modeled with the truncated 12-6 LJ potential.[8] The truncated 12-6 LJ potential is expressed as

$$u(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], & r \le r_c, \\ 0, & r > r_c, \end{cases} \quad (1)$$

where σ and ε are, respectively, the size and energy parameters, r is the center-to-center distance of the two interacting molecules, and r_c is the cutoff distance. The grand potential functional Ω is related to the Helmholtz energy functional F via a Legendre transform

$$\Omega[\rho(\boldsymbol{r})] = F[\rho(\boldsymbol{r})] + \int [V^{\rm ext}(\boldsymbol{r}) - \mu]\rho(\boldsymbol{r})d\boldsymbol{r}, \quad (2)$$

where $\rho(\boldsymbol{r})$ is the density distribution, $V^{\rm ext}(\boldsymbol{r})$ is the external potential resulting from the solid surface, and μ is the chemical potential of the fluid. Without loss of generality, we divide the intrinsic Helmholtz energy functional into an ideal gas, a correlation term, a repulsive and an attractive contribution, i.e.,

$$F = F^{\rm id} + F^{\rm rep} + F^{\rm cor} + F^{\rm att}. \quad (3)$$

The ideal gas contribution to the Helmholtz energy functional is exactly known,[9]

$$F^{\rm id}[\rho(\boldsymbol{r})] = k_B T \sum_i \int d\boldsymbol{r}\rho_i(\boldsymbol{r})[\ln\{\rho_i(\boldsymbol{r})\lambda_i^3\} - 1], \quad (4)$$

where λ_i is the de Broglie thermal wavelength, T is the absolute temperature, and k_B is the Boltzmann constant.

The hard-sphere repulsive contribution $F^{\rm rep}$ can be obtained from the modified fundamental measure theory,[10]

$$F^{\rm rep} = k_B T \int \Phi^{\rm hs}\left[\{n_\alpha(\boldsymbol{r})\}\right]d\boldsymbol{r}, \quad (5)$$

where $\Phi^{\rm hs}[\{n_\alpha(\boldsymbol{r})\}]$ is the excess Helmholtz free-energy density due to hard-core repulsion. It consists of scalar (S) and vector (V) parts

$$\Phi^{\rm hs}\left[\{n_\alpha(\boldsymbol{r})\}\right] = \Phi^{\rm hs(S)} + \Phi^{\rm hs(V)}. \quad (6)$$

According to the modified fundamental measure theory of Yu *et al.*,[10] the scalar part is given

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by the Boublik–Mansoori–Carnahan–Starling–Leland equation of state,

$$\Phi^{\mathrm{hs(S)}} = -n_0\ln(1-n_3) + \frac{n_1 n_2}{1-n_3} + \frac{n_2^3\ln(1-n_3)}{36\pi n_3^2} + \frac{n_2^3}{36\pi n_3(1-n_3)^2}, \tag{7}$$

and the vector part is expressed as

$$\Phi^{\mathrm{hs(V)}} = -\frac{\boldsymbol{n}_{V1}\cdot\boldsymbol{n}_{V2}}{1-n_3} - \frac{n_2\boldsymbol{n}_{V2}\cdot\boldsymbol{n}_{V2}\ln(1-n_3)}{12\pi n_3^2} - \frac{n_2\boldsymbol{n}_{V2}\cdot\boldsymbol{n}_{V2}}{12\pi n_3(1-n_3)^2}. \tag{8}$$

The weighted densities in Eqs. (7) and (8) are defined as

$$n_\alpha(\boldsymbol{r}) = \int d\boldsymbol{r}'\rho(\boldsymbol{r}')w^{(\alpha)}(\boldsymbol{r}-\boldsymbol{r}'), \tag{9}$$

where $\alpha = 0$, 1, 2, 3, V1 and V2. The weight functions $w^{(\alpha)}(r)$ are defined by[10]

$$w^{(2)}(r) = \pi d^2 w^{(0)}(r) = 2\pi d w^{(1)}(r) = \delta(d/2-r), \tag{10}$$

$$w^{(3)}(r) = \Theta(d/2-r), \tag{11}$$

$$\boldsymbol{w}^{(V2)}(\boldsymbol{r}) = 2\pi d\boldsymbol{w}^{(V1)}(\boldsymbol{r}) = (\boldsymbol{r}/r)\delta(d/2-r). \tag{12}$$

In Eqs. (10)–(12), $\Theta(r)$ is the Heaviside step function, $\delta(r)$ denotes the Dirac delta function, and d is the hard-core diameter which is a function of temperature. Khedr *et al.*[11] discussed different approaches to calculate the ratio d/σ. Because we use an accurate equation of state which is independent of the ratio d/σ and the results of present theory are insensitive to the ratio d/σ, we select the simple expression of the ratio d/σ given by Cotterman *et al.*[12] When the reduced temperature $T^* = k_BT/\varepsilon = 0$–15, d can be accurately expressed by[12]

$$\frac{d}{\sigma} = \frac{1+0.2977T^*}{1+0.33163T^*+1.0477\times10^{-3}T^{*2}}. \tag{13}$$

The attractive contribution to the Helmholtz energy functional is derived from a truncated second-order functional Taylor expansion around a reference bulk fluid,

$$F^{\mathrm{att}} = F^{\mathrm{att}}(\rho_b^0) + \int\frac{\delta F^{\mathrm{att}}}{\delta\rho(\boldsymbol{r})}\Delta\rho(\boldsymbol{r})d\boldsymbol{r} + \iint\frac{\delta F^{\mathrm{att}}}{\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r}')}\Delta\rho(\boldsymbol{r})\Delta\rho(\boldsymbol{r}')d\boldsymbol{r}d\boldsymbol{r}' + \cdots, \tag{14}$$

where $\Delta\rho(\boldsymbol{r}) = \rho(\boldsymbol{r}) - \rho_b^0$, and ρ_b^0 is the reference bulk density. The direct correlation functions due to the attractive interaction are defined as

$$c^{(1)}(\boldsymbol{r}) = -\beta\delta F^{\mathrm{att}}/\delta\rho(\boldsymbol{r}) = -\beta\mu^{\mathrm{ex}}(\rho_b^0), \tag{15}$$

$$c^{(2)}(|\boldsymbol{r}'-\boldsymbol{r}|) = -\beta\delta^2 F^{\mathrm{att}}/\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r}'), \tag{16}$$

where $\beta = 1/k_BT$. If we neglect all higher-order terms $c^{(n)}$ $(n>2)$ in Eq. (14), and let the reference bulk density $\rho_b^0 \to 0$, F^{att} becomes

$$\beta F^{\mathrm{att}} = -\frac{1}{2}\iint d\boldsymbol{r}d\boldsymbol{r}'c^{(2)}(|\boldsymbol{r}'-\boldsymbol{r}|)\rho(\boldsymbol{r})\rho(\boldsymbol{r}'). \tag{17}$$

For a fluid at bulk density limit $\rho_b \to 0$, the second-order direct correlation function can be exactly expressed as

$$c^{(2)}(r) = \exp\left[-\beta u^{\mathrm{att}}(r)\right] - 1, \tag{18}$$

where $u^{\mathrm{att}}(r)$ is the attractive part of LJ potential, i.e.,

$$u^{\mathrm{att}}(r) = \begin{cases} 0, & r<\sigma, \\ 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], & \sigma\le r\le r_c, \\ 0, & r>r_c. \end{cases} \tag{19}$$

For numerical convenience, we expand $c^{(2)}(r)$ in Taylor series since $|\beta u|$ is a small quantity. Generally the first-order expansion is accurate enough, but because temperature is low at thin-thick film transition and the expansion converges slowly, we truncate the expansion at the second-order term, i.e.,

$$c^{(2)}(r) \approx -\beta u^{\mathrm{att}}(r) + \frac{1}{2}\beta^2[u^{\mathrm{att}}(r)]^2. \tag{20}$$

From Eqs. (17) and (20) we can derive the expression of the attractive contribution to the Helmholtz energy functional, which can be approximated by

$$F^{\mathrm{att}} = \frac{1}{2}\iint d\boldsymbol{r}d\boldsymbol{r}'\left\{u^{\mathrm{att}}(|\boldsymbol{r}'-\boldsymbol{r}|) - \frac{\beta}{2}\left[u^{\mathrm{att}}(|\boldsymbol{r}'-\boldsymbol{r}|)\right]^2\right\}\rho(\boldsymbol{r})\rho(\boldsymbol{r}'). \tag{21}$$

It should be pointed out that if we truncate the Taylor expansion of $c^{(2)}(r)$ at the first-order term, Eq. (21) will reduce to the result of the mean-field theory.[13]

In this work, we use a weighted density approximation to evaluate the correlation contribution to the Helmholtz energy functional, i.e.,

$$F^{\mathrm{cor}} = \int\bar{\rho}(\boldsymbol{r})\psi^{\mathrm{cor}}[\bar{\rho}(\boldsymbol{r})]d\boldsymbol{r}, \tag{22}$$

where $\psi^{\mathrm{cor}}[\bar{\rho}(\boldsymbol{r})]$ is the correlation contribution to the Helmholtz free energy per particle of a bulk fluid with density $\bar{\rho}(\boldsymbol{r})$. The weighted density for the correlation part is defined by

$$\bar{\rho}(\boldsymbol{r}) = \int\rho(\boldsymbol{r}')w^{(\mathrm{cor})}(|\boldsymbol{r}'-\boldsymbol{r}|)d\boldsymbol{r}', \tag{23}$$

where $w^{(\mathrm{cor})}(r)$ is a normalized weight function, and we use the Heaviside step function $\Theta(r)$ to express it, i.e.,

$$w^{(\mathrm{cor})}(r) = \frac{3}{4\pi d^3}\Theta(d-r). \tag{24}$$

The excess Helmholtz free-energy per particle due to correlation effect is obtained from the MBWR equation of state with the parameters given by Johnson *et al.*,[14]

$$\psi^{\rm cor}(\rho) = \varepsilon \sum_{i=1}^{8} \frac{a_i(\rho^*)^i}{i} + \varepsilon \sum_{i=1}^{6} b_i G_i - \psi^{\rm CS} - \psi^{\rm att}, \quad (25)$$

where the coefficients a_i and b_i are functions of temperature only, the coefficient G_i are functions of density, and ρ^* is reduced density defined as $\rho* = \rho\sigma^3$. The functional forms of a_i, b_i and G_i as well as the values of the parameters for the MBWR equation of state can be found in the literature[14] $\psi^{\rm CS}$ is the hard-sphere part of the Helmholtz free-energy per particle obtained from the Carnahan–Starling equation of state,[15]

$$\psi^{\rm CS}(\rho) = k_B T \frac{4\eta - 3\eta^3}{(1-\eta)^2}, \quad (26)$$

where $\eta = \pi\rho d^3/6$ is the packing fraction. $\psi^{\rm att}$ is obtained from Eq. (21), i.e.,

$$\psi^{\rm att}(\rho) = \frac{1}{2}\rho \int_{\sigma}^{r_c} \left\{ u^{\rm att}(r) - \frac{\beta}{2}\left[u^{\rm att}(r)\right]^2 \right\} d\boldsymbol{r}. \quad (27)$$

Density profile is then obtained by solving the Euler–Lagrange equation

$$\ln\left[\frac{\rho(\boldsymbol{r})}{\rho_b}\right] = \beta\left[\mu^{\rm ex} - \frac{\delta(F^{\rm rep}+F^{\rm cor}+F^{\rm att})}{\delta\rho(\boldsymbol{r})} - V^{\rm ext}(\boldsymbol{r})\right], \quad (28)$$

where $\mu^{\rm ex}$ is the excess chemical potential of the fluid.

For the Ar/CO_2 system, following Finn and Monson,[3] we model Ar as an LJ fluid truncated at $r_c = 2.5\sigma$. The fluid-solid potential is modeled with the 9-3 form

$$V^{\rm ext}(z) = \frac{2\pi\rho_w\sigma_w^3\varepsilon_w}{3}\left[\frac{2}{15}\left(\frac{\sigma_w}{z}\right)^9 - \left(\frac{\sigma_w}{z}\right)^3\right], \quad (29)$$

with the parameters $\rho_w\sigma_w^3 = 0.988$, $\varepsilon_w = 1.2771\varepsilon$ and $\sigma_w = 1.0962\sigma$. The surface tension γ can be obtained from the present density functional theory through

$$\gamma = \{\Omega[\rho(z)] + p_b V\}/A, \quad (30)$$

where p_b, V and A are, respectively, the bulk pressure, volume, and surface area of the system. The adsorption is expressed by the surface excess defined as

$$\Gamma^{\rm ex} = \int_0^{\infty} [\rho(z) - \rho_b]\, dz. \quad (31)$$

Figure 1 depicts the adsorption isotherm and surface tension for the Ar/CO_2 system at reduced temperature $T^* = 1.0$. There is no coexistence of the thin and thick films, indicating that the system temperature is above the surface critical point. The surface excess predicted from the proposed density functional theory is in good agreement with the Monte Carlo simulation results.[3]

We compare the various theoretical results with the Monte Carlo simulation data in Fig. 2 at $T^* = 0.88$. The vertical lines in Fig. 2 denote the location of the prewetting phase transition. From the figure one can see that there is no coexistence of the thin and thick films from the mean-field theory. This indicates that the mean-field theory is qualitatively wrong in predicting wetting phase transition. Although both theories of Tarazona[2] and Sweatman[7] predict the prewetting phase transition, the theory of Tarazona underestimates the pressure at the prewetting phase transition while the theory of Sweatman slightly overestimates the pressure at the prewetting phase transition. The result from our density functional theory is much closer to the Monte Carlo simulation data[3,7,16] than the other two theories. It should be pointed out that our density functional theory is much simpler in form than the theory of Sweatman.

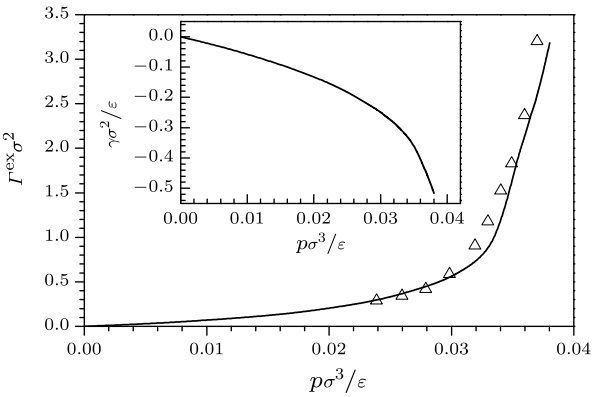

Fig. 1. Adsorption isotherm and fluid-solid interfacial tension (inset) for the Ar/CO_2 system modeled with the truncated 12-6 potential at $T^* = 1.0$. Symbols and solid lines represent the results from the Monte Carlo simulations[3] and our theory, respectively.

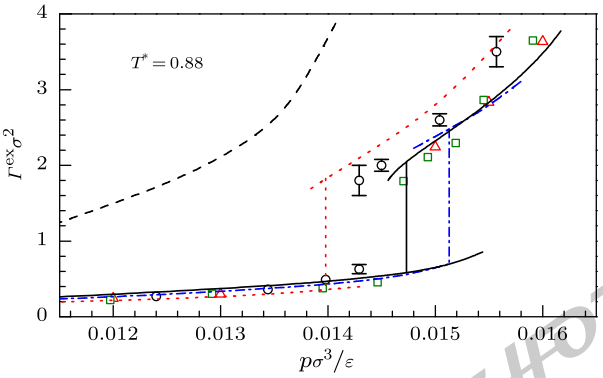

Fig. 2. Adsorption isotherm for the Ar/CO_2 system modeled with the truncated 12-6 potential at $T^* = 0.88$. Circles, triangles and squares represent the molecular simulation results of Sweatman,[7] Finn and Monson,[3] Fan and Monson,[16] respectively. Dashed, dotted, dash-dotted and solid lines represent the theoretical calculated results from mean-field theory, Tarazona,[2] Sweatman[7] and the present theory, respectively.

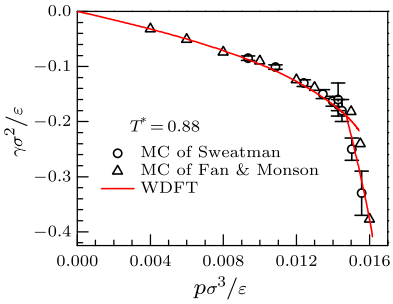

Fig. 3. Fluid-solid interfacial tension isotherm for the Ar/CO_2 system modeled with the truncated 12-6 potential at $T^* = 0.88$. Triangles, circles represent the Monte Carlo results of Fan and Monson[16] and Sweatman,[7] respectively. Solid lines represent the theoretical results from the present theory.

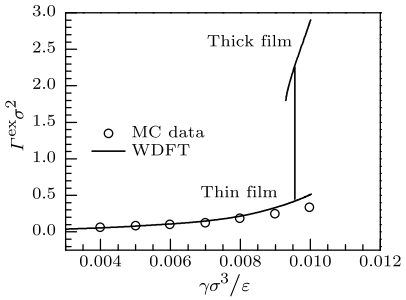

Fig. 4. Adsorption isotherm for the Ar/CO_2 system modeled with the truncated 12-6 potential at $T^* = 0.83$. Symbols and solid lines represent the results from the Monte Carlo simulations[3] and present theory, respectively.

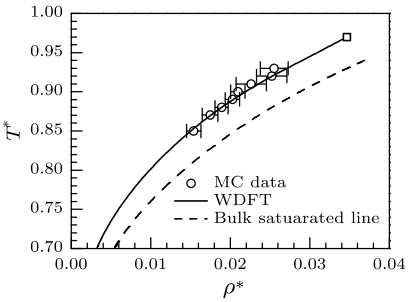

Fig. 5. Thin-thick liquid film transition (prewetting) temperature as a function of reduced bulk density. The circles with the horizontal error bars are the Monte Carlo results of Finn and Monson,[3] the solid line is the prediction of our theory, the large square gives our estimation of the surface critical point, and the dashed line is the bulk coexistence curve predicted from our theory.

Figure 3 depicts the fluid-solid interfacial tension at $T^* = 0.88$. Clearly there are two branches which meet at a cusp, the location of the prewetting phase transition.

Figure 4 depicts the adsorption isotherm for the Ar/CO_2 system at reduced temperature $T^* = 0.83$. The surface excess predicted from our density functional theory is in good agreement with the Monte Carlo result for the thin film branch. Unfortunately, the Monte Carlo simulation of Finn and Monson did not give the surface excess for the thick film branch. Our theory predicts the thin-thick film transition at $T^* = 0.83$.

The prewetting transition temperature as a function of the bulk reduced density is plotted in Fig. 5. Also included in Fig. 5 is the bulk coexistence curve predicted by our density functional theory. We locate the surface critical point at $T^*_{SC} = 0.97 \pm 0.01$ to be compared with the Monte Carlo result of $T^*_{SC} = 0.94 \pm 0.02$. Our theoretical prewetting line is in very good agreement with the Monte Carlo simulation data of Finn and Monson. However, Finn and Monson showed in their work that their prewetting line appears to go into the saturated vapor just below $T^* = 0.85$, so that they locate the wetting transition at $T^*_w = 0.84 \pm 0.1$. In contrast, our theoretical results approach the saturated vapor density much more slowly, as can be seen from Fig. 5. We still find a prewetting transition at reduced temperature $T^* = 0.70$ or below. This suggests that the wetting point is below the triple-point temperature of Ar from our density functional theory. This conclusion is in agreement with the experimental evidence that there is a first-order triple-point wetting transition for Ar/CO_2 system.[17] The reason for the discrepancy of the wetting temperature between our theory and the result of Finn and Monson[3] is probably because Finn and Monson used a less accurate equation of state.

In conclusion, we have proposed a weighted density functional theory for the Lennard–Jones fluid at low temperature phase transition. The proposed density functional theory predicts accurate adsorption isotherms and surface tensions for the Lennard–Jones fluid on the planar solid wall at low temperatures. In comparison with alternative density functional theories, the present theory has the advantage of predicting accurate thin-thick film transition location.

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