Study on Surface Properties for Non-polar Fluids with Density Functional Theory*

WU Wei(吴畏), **LU Jiufang**(陆九芳)**, **FU Dong**(付东), **LIU Jinchen**(刘金晨) and **LI Yigui**(李以圭)
Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Abstract The density functional theory, simplified by the local density approximation and mean-field approximation, is applied to study the surface properties of pure non-polar fluids. A reasonable long rang correction is adopted to avoid the truncation of the potential. The perturbation theory is applied to establish the equation for the phase equilibrium, in which the hard-core chain fluid is as the reference fluid and the Yukawa potential is used as the perturbation term. Three parameters, ε/k, d and m_s, are regressed from the vapor-liquid equilibria, and the surface properties, including density profile, surface tension and local surface tension profile are predicted with these parameters.

Keywords density functional theory, surface tension, density profile, pure non-polar fluids

1 INTRODUCTION

The density functional theory (DFT)[1,2] and the molecular simulation are the most popular approaches to statistical mechanics of the inhomogeneous fluid. The results from the DFT are not as accurate as that from the simulation methods yet, but the DFT is much more convenient for the investigation of the chain molecules.

The DFT is a systematic method for statistical thermodynamic study. In its frame, the rigorous proofs of the Ornstein-Zernike integral equation and the perturbation theory can be given concisely, which were presented by Evans *et al.*[1] Since some approximations need to be introduced for numerical computation for inhomogeneous systems, the DFT falls mainly into two categories[3]: (1) the weighted (non-perturbative) density functional theories (WDFT), and (2) the perturbative density functional theories (PDFT). In the former, the excess free energy of an inhomogeneous system is approximately treated as a homogeneous system with an effective or weighted density. In the latter case, the excess free energy is functionally expanded about that of the uniform system. The local density approximation (LDA) is one of the PDFT. Because the short-range correlations of molecules in the fluid are neglected in it, the LDA does not befit to investigate the behavior of the fluid in contact with walls[2,4]. Nevertheless, this method is a reasonable approach in the study for the vapor-liquid surface.

Winkelmann *et al.*[5−7] did a systematic investigation on density functional theory of simple liquids and their mixtures. They used the mean field approximation (MFA), WCA perturbation theory and LDA to correlate both the saturated liquid density and surface tension for spherical fluids and used the hard convex body equation of state for chainlike molecules[5]. Using the density profile across the vapor-liquid surface, they made prediction of ellipsometric parameters of pure fluids[6]. Winklemann also made comparisons among different LDA approximations and MD molecular simulation[7]. According to their description, the intermolecular potential in their work is cutoff and shifted, which means the long-range interaction is truncated and a tiny modification is made.

Fu *et al.*[8] established a new method for the study of the Lennard-Jones fluid surface by assuming that the density profile can be described as a hyperbolic tangent curve. In their work, the molecular parameters are regressed from the PVT experimental data, and were used to predict the surface tension.

In the present paper, a DFT method for the hard-core Yukawa potential is established to study the surface properties and microscopic structure for the pure non-polar fluids. The free energy is divided into two parts. One is the contribution from the reference fluid, and the other is from the perturbation term for the Yukawa potential. In our work, the intermolecular potential is not cut-off and a rigorous long range correction is applied. The solution for the vapor-liquid equilibrium is used to obtain the molecular parameters and the unique chemical potential in the inhomogeneous system. In this approach, the macroscopic surface tensions of some real pure fluids are predicted

from the molecular parameters.

2 THEORIES

2.1 Intermolecular potential energy

The intermolecular potential used in this work is a hard sphere potential coupled with an attractive Yukawa potential.

$$\phi(r) = \begin{cases} \infty & r < d \\ -\varepsilon \dfrac{\exp\left[-z_{\mathrm{Yu}}(r-d)/d\right]}{r/d} & r \geqslant d \end{cases} \quad (1)$$

where r is the distance between two molecules, ε is the energy parameter representing the minimum energy between two molecules, d is the hard sphere diameter, and z_{Yu} is the Yukawa range parameter that attributes the rate of potential decay.

The advantage of the hard-core Yukawa potential function is that the range of interaction can be varied easily by changing the parameter z_{Yu}, which can be used to model many different interactions including dispersion and electrostatic repulsion. There is an extra convenience that the exponential form makes the solution of the integral equation more easily with the mean sphere approximation (MSA). Liu $et\ al.$[9] used an explicit EOS with one-Yukawa potential to correlate the PVT data for pure real fluids with success, and Lin $et\ al.$[10] proposed an EOS with two-Yukawa potential to study the osmotic pressure for the charged colloidal systems. Meanwhile, the Yukawa potential is convenient to make a perturbation expansion without any adjustment of the hard sphere diameter.

2.2 Density functional theory

The system considered in our work is a grand canonical ensemble. Based on such a ensemble, the density functional theory begins with the grand potential functional $\Omega[\rho(\boldsymbol{r})]$, which can be expressed as[1]

$$\begin{aligned} \Omega[\rho(\boldsymbol{r})] =& \int_{\Gamma} [K(\boldsymbol{r}) + U_{\mathrm{int}}(\boldsymbol{r}) + U_{\mathrm{ext}}(\boldsymbol{r}) + \\ & TS(\boldsymbol{r}) - \rho(\boldsymbol{r})\mu] \mathrm{d}\boldsymbol{r} \\ =& F_{\mathrm{int}}[\rho(\boldsymbol{r})] + \int_{\Gamma} \rho(\boldsymbol{r})[u_{\mathrm{ext}}(\boldsymbol{r}) - \mu]\mathrm{d}\boldsymbol{r} \end{aligned} \quad (2)$$

where $\boldsymbol{r}$ is a vector that refers to a position in the system, $\mathrm{d}\boldsymbol{r}$ is the integration volume element, Γ is the phase space, $\rho(\boldsymbol{r})$ is the local number density of molecules, $K(\boldsymbol{r})$ is the local kinetic energy, $U_{\mathrm{int}}(\boldsymbol{r})$ is the local "intrinsic" potential energy from the interaction in the system, $U_{\mathrm{ext}}(\boldsymbol{r})$ is the local external potential energy from the steady external potential field, $u_{\mathrm{ext}}(\boldsymbol{r}) = U_{\mathrm{ext}}(\boldsymbol{r})/\rho(\boldsymbol{r})$ is the field strength, $S(\boldsymbol{r})$ is the entropy per volume in the volume element $\mathrm{d}\boldsymbol{r}$, and $F_{\mathrm{int}}[\rho(\boldsymbol{r})]$ is the "intrinsic" Helmholtz free energy function.

The perturbation expansion of $F_{\mathrm{int}}[\rho(\boldsymbol{r})]$ can be expressed as

$$\begin{aligned} F_{\mathrm{int}}[\rho(\boldsymbol{r})] =& F^{\mathrm{ref}}[\rho(\boldsymbol{r})] + \frac{1}{2}\int_0^1 \mathrm{d}\alpha \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 \\ & [\phi(\boldsymbol{r}_1, \boldsymbol{r}_2) - \phi^{\mathrm{ref}}(\boldsymbol{r}_1, \boldsymbol{r}_2)]\rho^{(2)}(\phi_\alpha; \boldsymbol{r}_1, \boldsymbol{r}_2) \\ =& F^{\mathrm{ref}}[\rho(\boldsymbol{r})] + F^{\mathrm{per}}[\rho(\boldsymbol{r})] \end{aligned} \quad (3)$$

where ϕ is the real potential function, $F^{\mathrm{ref}}[\rho(\boldsymbol{r})]$ corresponds to an initial reference system in which the pairwise potential is ϕ^{ref} and the distribution of density is $\rho(\boldsymbol{r})$, $\rho^{(2)}(\phi_\alpha; \boldsymbol{r}_1, \boldsymbol{r}_2)$ is the pairwise distribution function for a system of density $\rho(\boldsymbol{r})$ in which the molecules interact via a pairwise potential $\phi_\alpha = \phi_{\mathrm{ref}} + \alpha(\phi - \phi_{\mathrm{ref}})$, and α is a variable in the region $[0, 1]$. If $\rho^{(2)}(\phi_\alpha; \boldsymbol{r}_1, \boldsymbol{r}_2) = \rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)$, which means that $\rho^{(2)}$ is independent of α, the perturbation term F^{per} in Eq. (3) can be expressed as

$$\begin{aligned} F^{\mathrm{per}}[\rho(\boldsymbol{r})] =& \frac{1}{2}\int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 \big[\phi(\boldsymbol{r}_1, \boldsymbol{r}_2) - \\ & \phi^{\mathrm{ref}}(\boldsymbol{r}_1, \boldsymbol{r}_2)\big] \int_0^1 \mathrm{d}\alpha \rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) \\ =& \frac{1}{2}\iint \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)g(\boldsymbol{r}_1, \boldsymbol{r}_2) \\ & [\phi(\boldsymbol{r}_1, \boldsymbol{r}_2) - \phi^{\mathrm{ref}}(\boldsymbol{r}_1, \boldsymbol{r}_2)] \end{aligned} \quad (4)$$

where $g(\boldsymbol{r}_1, \boldsymbol{r}_2) = \rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)/[\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)]$ is the radial distribution function that is independent of the intermolecular action. Therefore, it equals to the radial distribution function of the reference fluid: $g(\boldsymbol{r}_1, \boldsymbol{r}_2) = g^{\mathrm{ref}}(\boldsymbol{r}_1, \boldsymbol{r}_2)$

Ignoring the short-range correlation contribution to free energy of reference fluid according to the LDA method, the reference term F^{ref} can be expressed with the local density.

$$F^{\mathrm{ref}}[\rho(\boldsymbol{r})] \approx \int \mathrm{d}\boldsymbol{r} f^{ro}[\rho(\boldsymbol{r})] \quad (5)$$

where $f^{ro}[\rho(\boldsymbol{r})]$ is the free energy density of the homogeneous reference liquid whose density is $\rho(\boldsymbol{r})$.

In this work, the reference fluid is hard-core chain fluid, so the Helmholtz free energy density is as follows

$$f^{ro}[\rho(\boldsymbol{r})] = f^{\mathrm{id}}[\rho(\boldsymbol{r})] + f^{\mathrm{hs}}[\rho(\boldsymbol{r})] + f^{\mathrm{chain}}[\rho(\boldsymbol{r})] \quad (6)$$

where f^{id} is the free energy density of the ideal gas with the same density and temperature as the system, f^{hs} is the free energy density of a hard-sphere fluids relative to the ideal gas and is expressed by Carnahan-Starling equation[11], and f^{chain} is the free energy density change when chains are formed from hard spheres[12].

Considering that the intermolecular interaction can be expressed as the sum of the interactions be-

tween segments, from Eq. (4) it follows

$$F^{\text{per}}[\rho(r)] = \frac{1}{2} \iint dr_1 dr_2 m_s^2 \rho(r_1)\rho(r_2) g^{\text{ref}} \cdot$$
$$(r_1, r_2)\phi^{\text{ss}}(r_{12}) \qquad (7)$$

where $r_{12} = |r_1 - r_2|$ is the distance between the two space positions, $\phi^{\text{ss}}(r_{12})$ is the perturbation potential between segments, and equals to the attractive Yukawa potential tail here.

$g^{\text{ref}}(r_{12})$ can be obtained approximately by being treated as a function of radial distribution function in the homogeneous fluid $g^{\text{hs}}(\rho, r_{12})$. This method will cause a great difficulty that a term from the density derivative of $g^{\text{hs}}(\rho, r_{12})$ will be included in the pressure and the chemical potential expression. Tang et $al.$[13] proposed a nonlocal density functional perturbation theory with this method, but they omitted the derivative term without overcoming this problem. The mean field approximation is the simplest method in this case. Similar to Hu et $al.$[14], we adopt a method to modify the mean field approximation, in which the radial distribution function $g(r)$ is as follows, and is illustrated in Fig. 1.
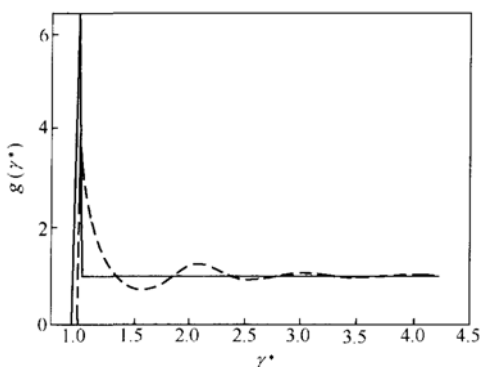

Figure 1   Comparison between the accurate RDF
of the hard sphere fluid and the approximate
RDF in this study
- - - - accurate RDF for hard sphere fluid;
———— approximate RDF for hard sphere fluid

$$g^{\text{hs}}(r) = \begin{cases} 0 & r < d \\ w(r)\delta(r-d) & r = d \\ 1 & r > d \end{cases} \qquad (8)$$

where $\delta(x) = \dfrac{1}{2\pi} \displaystyle\int_{-\infty}^{\infty} e^{-ikx} dk$ is Dirac Delta function, $w(r)$ is a weight function which has a dimension of length and is presumed to be position (r) dependent. The Delta function used here is to describe the maximum peak appeared on the hard sphere surface.

The function $w(r)$ is established from the compressibility equation, which is shown as

$$kT\left(\frac{\partial \rho}{\partial p}\right)_T = 1 + \rho \int [g(r) - 1]dr \qquad (9)$$

As a usual choice, $w(r)$ should make the compressibility coefficient equal to that of the idea gas $kT(\partial \rho/\partial p)_T = 1$. Thus, we obtain

$$\int w(r)\delta(r-d)dr = \int_{r \leqslant d} dr \qquad (10)$$

and then Eq. (7) becomes

$$F^{\text{per}}[\rho(r)]$$
$$= \frac{1}{2} m_s^2 \left[\iint_{r_{12} \leqslant d} \rho(r_1)\rho(r_2)\phi(d)dr_1 dr_2 + \iint_{r_{12} > d} \rho(r_1)\rho(r_2)\phi^{\text{ss}}(r_{12})dr_1 dr_2 \right] \qquad (11)$$

For a plain surface, the liquid density is only dependent on the z direction perpendicular to the surface, which means that $\rho(r) = \rho(z)$. In this case, it is more convenient by use of the cylindrical coordinates. The integral is $\int dr = \iiint r_p d\varphi dr_p dz$, where r_p indicates the distance from a specified point to the z axis. When ϕ^{ss} is substituted by Eq. (1), it follows

$$F^{\text{per}}[\rho(z)]$$
$$= -\frac{1}{2} A\pi\varepsilon^{\text{ss}} m_s^2$$
$$\left\{ \int_{-\infty}^{+\infty} \int_{-d}^{d} \rho(z_1)\rho(z_2) \left[(d^2 - z_{12}^2) + \frac{2d^2}{z_{\text{Yu}}} \right] dz_1 dz_2 + \iint_{|z_{12}| > d} \frac{2e^{(1-z_{12}/d)z_{\text{Yu}}}}{z_{\text{Yu}}} d^2 \rho(z_1)\rho(z_2)dz_1 dz_2 \right\} \qquad (12)$$

where A is the sectional area, and $z_{12} = |z_1 - z_2|$ is the distance between two planes. The external potential field is zero for the free surface, then Eq. (2) becomes

$$\Omega[\rho(z)] = A\left\{ \int f^{\text{r0}}[\rho(z)]dz - \mu \int \rho(z)dz \right\} + F^{\text{per}}[\rho(z)] \qquad (13)$$

At equilibrium in the grand canonical ensemble, the grand potential function $\Omega[\rho(r)]$ has a minimum. The density distribution $\rho_0(r)$ can be obtained by minimizing Eq. (13). The necessary condition for function $\Omega[\rho(r)]$ attaining its minimum value is $\delta\Omega = 0$, which is the so-called Euler-Lagrange equation. Thus the chemical potential expression is

$$\mu = \frac{\delta F_{\text{int}}}{\delta\rho} = \left(\frac{\partial f^{\text{r0}}}{\partial\rho}\right)_T + \frac{\delta F^{\text{per}}}{\delta\rho}$$
$$= \left(\frac{\partial f^{\text{id}}}{\partial\rho}\right)_T + \left(\frac{\partial f^{\text{hs}}}{\partial\rho}\right)_T + \left(\frac{\partial f^{\text{chain}}}{\partial\rho}\right)_T + \frac{\delta F^{\text{per}}}{\delta\rho} \qquad (14)$$

Assuming that g^{ref} is independent of $\rho(\mathbf{r})$, we will have that $\delta g^{\text{ref}}/\delta\rho = 0$. Then the following expression can be obtained after differentiating Eq. (11)

$$\frac{\delta F^{\text{per}}}{\delta\rho} = m_s^2 \int_V g_{12}^{\text{ref}}\rho(\mathbf{r}_{12})\phi^{\text{ss}}(r_{12})\mathrm{d}\mathbf{r}_{12} \qquad (15)$$

Using the cylindrical coordinates as in Eq. (12), Eq. (15) can be converted as

$$\frac{\delta F^{\text{per}}}{\delta\rho}$$
$$= -A\pi\varepsilon^{\text{ss}}m_s^2\Bigg\{ \int_{z_{12}\leqslant d}\rho(z_2)\left[(d^2 - z_{12}^2) + \frac{2d^2}{z_{\text{Yu}}}\right]\mathrm{d}z_2 + \int_{z_{12}>d}\rho(z_2)\frac{2\mathrm{e}^{(1-z_{12}/d)z_{\text{Yu}}}}{z_{\text{Yu}}}d^2\mathrm{d}z_2\Bigg\} \qquad (16)$$

Then the chemical potential μ in the system is obtained. And the density distribution in an equilibrium system can be calculated by solving the equations $\mu[\rho(z_1)] = \mu[\rho(z_2)]$.

For a system with the plain surface, the grand potential functional Ω can be expressed as

$$\Omega = \gamma A - pV \qquad (17)$$

where p is the bulk phase pressure, which equals to the normal part of the pressure tensor in the surface, and V is the total volume of the system. The "local" surface tension $\gamma(z)$ is defined as[15]

$$\gamma(z) = f[\rho(z)] - \mu\rho(z) + p \qquad (18)$$

In this case, Eq. (17) and (18) yield the result

$$\gamma = \int_{-\infty}^{\infty}\gamma(z)\mathrm{d}z \qquad (19)$$

When μ and p are obtained, both the profile of the density and local surface tension can be computed. These two parameters are solved from the vapor-liquid phase equilibrium.

2.3 Equation of state

The expression of Helmholtz free energy F for the uniform phase is obtained with the similar procedure from Eq. (3). It is clear that F^{ref} is the same as Eq. (6). Substituting $\rho(\mathbf{r}) = \rho = \text{const}$ into Eq. (11), F^{per} can be written as

$$F^{\text{per}}(\rho) = \frac{1}{2}V\int_0^{\infty}4\pi r^2 m_s^2\rho^2 g^{\text{ref}}(\rho, r)\phi^{\text{ss}}(r)\mathrm{d}r \qquad (20)$$

When substituting Eqs. (1) and (8) into Eq. (20), we obtain

$$F^{\text{per}}(\rho) = -2\pi V\left[\varepsilon d^3 m_s^2\rho^2\left(\frac{1 + z_{\text{Yu}}}{z_{\text{Yu}}^2} + \frac{1}{3}\right)\right] \qquad (21)$$

The dispersion contribution to chemical potential μ_k^{per} is

$$\mu^{\text{per}} = \frac{1}{V}\left(\frac{\partial F^{\text{per}}}{\partial\rho}\right)_T = -4\pi m_s^2 d^3\varepsilon\rho\left(\frac{1 + z_{\text{Yu}}}{z_{\text{Yu}}^2} + \frac{1}{3}\right) \qquad (22)$$

Similarly, the compressibility factor Z of the fluid can be given by

$$Z = \frac{p}{\rho kT} = \frac{\rho}{V}\left(\frac{\partial F}{\partial p}\right)_{T,x_i}$$
$$= Z^{\text{ref}} + Z^{\text{per}} = Z^{\text{id}} + Z^{\text{hs}} + Z^{\text{chain}} + Z^{\text{per}} \qquad (23)$$

From Eq. (21) the term of Z^{per} is obtained as

$$Z^{\text{per}}(\rho) = 4\pi\varepsilon d^3 m_s^2\rho^2\left(\frac{1 + z_{\text{Yu}}}{z_{\text{Yu}}^2} + \frac{1}{3}\right) \qquad (24)$$

For a plain surface, the pressures in the two bulk phases are the same, so that we have the following equations at vapor-liquid phase equilibrium.

$$\begin{cases} p^{\text{L}} = p^{\text{V}} = p \\ \mu^{\text{L}} = \mu^{\text{V}} = \mu \end{cases} \qquad (25)$$

where the superscripts represent the phases. From these equations, the fluid phase equilibrium can be solved.

3 CALCULATION

3.1 Methodology

The vapor-liquid region with thickness of $60\,d$ along the z direction, in which there is a plain surface, is divided into N layers, where d is the diameter of segment. With this treatment, the Adams-Moulton method is adopted to calculate the numerical integration.

The ranges of integration in Eqs. (12), (16), and (19) are $(-\infty, +\infty)$, and the integration in the region out of the identification must be calculated additionally as a long-range correction (LRC). The thickness of surface region is only several times of molecular diameter at normal temperature. In our calculation, the range of $60\,d$ is enough for holding a complete surface region. In this way, the surface region is located in the middle. Thus, it is reasonable that the density out of the range is invariant.

$$\begin{cases} \rho = \rho^{\text{L}} & z < z_0 \\ \rho = \rho^{\text{V}} & z > z_N \end{cases} \qquad (26)$$

Substituting Eq. (26) into Eq. (16) and dividing the integrating range into three parts, $[-\infty, z_0]$, $[z_0, z_N]$ and $[z_N, +\infty]$, we obtain the long-range correction as the integration out of the range $[z_0, z_N]$.

$$\left(\frac{\delta F^{\mathrm{per}}}{\delta\rho}\right)^{\mathrm{LRC}} = \begin{cases} -\left\{A\pi\varepsilon^{\mathrm{ss}}\rho^{\alpha}m_{\mathrm{s}}^2 d^3\left[\dfrac{z_{\mathrm{b}}^3 + 2d^3 - 3z_{\mathrm{b}}d^2}{3} + \dfrac{2d^2(d - z_{\mathrm{b}})}{z_{\mathrm{Yu}}} + \dfrac{2}{z_{\mathrm{Yu}}^2}\right]\right\} & z_{\mathrm{b}} < d \\ -A\pi\varepsilon^{\mathrm{ss}}\rho^{\alpha}m_{\mathrm{s}}^2 d^3 \dfrac{2e^{(1-z_{\mathrm{b}}/d)z_{\mathrm{Yu}}}}{z_{\mathrm{Yu}}^2} & z_{\mathrm{b}} \geqslant d \end{cases} \qquad (27)$$

where ρ^{α} represents the numerical density in the bulk phase α, and z_{b} is the distance from the specified layer to the boundary.

$$z_{\mathrm{b}} = z - z_0 \quad \text{or} \quad z_{\mathrm{b}} = z_N - z \qquad (28)$$

The density profile, which makes the calculated chemical potential in every layer equal to one another, can be obtained with the above equations. In the computation process the criterion is that the maximum relative deviation of the calculated chemical potentials between two layers are less than 0.001%.

Three molecular parameters, hard sphere diameter d, minimum potential ε and segment number m_{s}, are needed for the pure non-polar fluid in this method. In this work, they are regressed from the vapor-liquid equilibria data during the respective temperature.

For convenience, some reduced thermodynamic quantities are used as $T^* = kT/\varepsilon$, $z^* = z/d$, $\rho^* = \rho d^3$, and $r^* = \gamma d^2/\varepsilon$. It means that the d and ε are treated as the unit of the length and the energy, respectively.

3.2 Results and discussions

The reduced surface tensions for pure non-polar fluids with different segment number are computed, and the results are shown in Fig. 2. From this figure, it can be found that at the same reduced temperature T^*, the larger m_{s} is, the larger γ^* will be. As m_{s} increases, the decreasing rate of γ^* with the increase of T^* will be reduced. It is because the attractive interaction is more affected by m_{s} than the repulsion, and the surface tension is derived from the intermolecular attraction directly. This figure also shows that the surface tension γ^* reaches zero at the critical temperature. The profiles of the reduced density and the
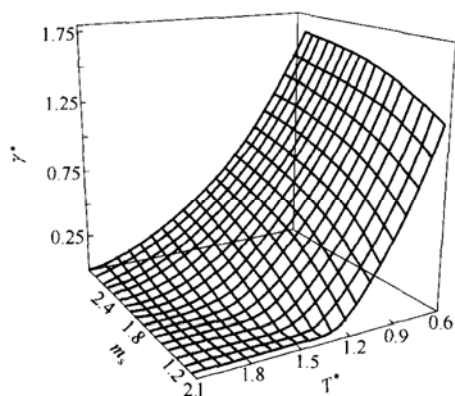
reduced chemical potential of one-segment molecule are given in Fig. 3. The density profile shows that the region of the surface is expanded when the temperature rises, and it will tend to be infinite near the critical temperature. The chemical potential profile represents that the chemical potential does not depend on the space position in a thermodynamic equilibrium, which is the prime criterion for judging whether the iteration has finished successfully.
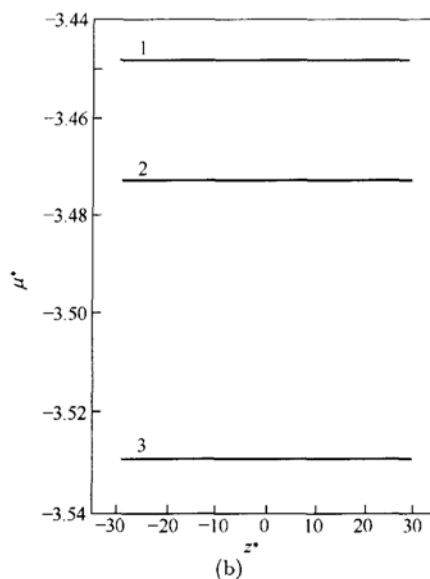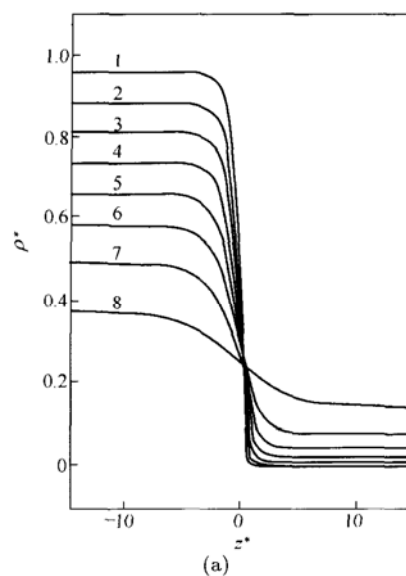

(a)

(b)

Figure 3   Reduced density and chemical potential profile at different temperatures for one segment molecule

T^*: 1—0.5; 2—0.6; 3—0.7; 4—0.8;
5—0.9; 6—1.0; 7—1.1; 8—1.2

Figure 2   Reduced surface tension *vs.* reduced temperature and molecular segment

Table 1 Regressed parameters for pure non-polar fluids

Compound	Temperature K	Segment parameters		
		m_s	d, nm	ε/k, K
methane	91—101	1.000	0.3803	159.38
argon	87—116	1.000	0.3422	125.45
oxygen	90—140	1.185	0.3093	116.67
chlorine	239—283	1.550	0.3323	270.50
tetra-chloromethane	349—495	2.000	0.3827	318.51
ethane	129—183	1.738	0.3420	183.91
propane	167—300	1.884	0.3577	218.80
n-butane	217—288	2.074	0.3768	240.74
n-pentane	269—306	2.332	0.3815	252.02
n-hexane	341—430	2.454	0.3866	264.28
n-heptane	280—402	2.567	0.4081	284.54
n-octane	312—416	2.654	0.4206	297.86
n-nonane	344—424	2.680	0.4360	313.16
cyclohexane	279—347	1.871	0.4218	337.96
benzene	284—355	2.021	0.3833	326.70
toluene	320—442	2.241	0.3889	327.47

Note: Experimental data are taken from the references [16] and [17].

The methane is chosen as the standard one-segment molecule, and then the best range parameter z_{Yu} is obtained from the regression of the methane vapour-liquid equilibrium (VLE), which equals to 1.985. In the regression of methane, the average relative deviation (ARD) for the saturated vapor pressure p^0 is 0.72%, and ARD for the saturated liquid density is 5.21%. For other compounds, only the molecular parameters d, ε and m_s are needed, which are also obtained by regressing the VLE experimental data[16,17]. The regressed parameters are listed in Table 1. In the regression, the average value of ARD is 6.69% for p^0, and 3.29% for ρ. These parameters are used to predict the respective surface property of the same compound with a corresponding method. Using these parameters, the respective surface tensions of the real compounds are predicted as shown in Figs. 4 and 5.
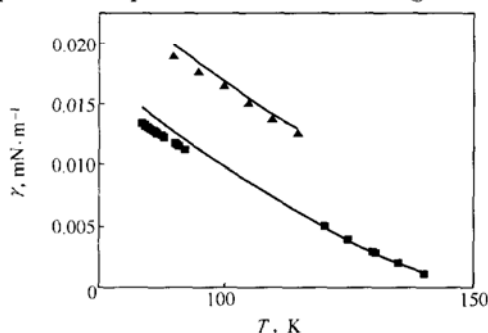

Figure 4 Comparison of calculated surface tension with experimental data at different temperatures for one segment molecules
▲ Methane; ■ Argon

Figure 4 shows the calculating results of the surface tension and the experimental data for the one-segment molecules. In Fig. 5 the surface tension of the multi-segment molecules at different temperatures predicted from this work is compared with the experimental values[18-20]. The predictive results are agreeable with the experimental data for the alkanes and the aromatics etc.

The ARD for all compounds are listed in Table 2, The total average ARD is 3.87%, and the largest ARD is 7.97%. As a predicted result from the molecular parameters, it is satisfactory.
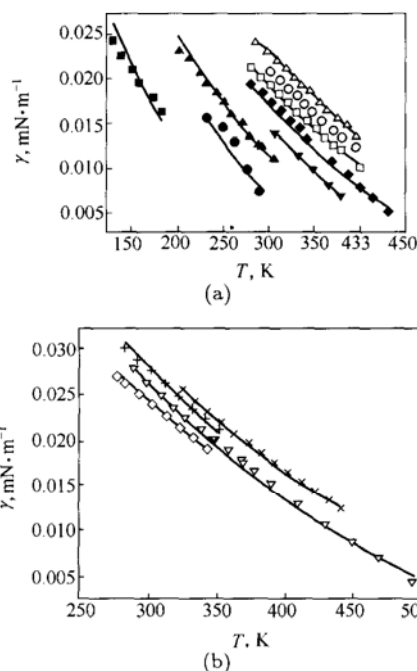

(a)

(b)

Figure 5 Comparison of calculated surface tension with experimental data at different temperatures for multi-segment molecules
(Solid line-calculated results; points-experimental data)
■ ethane; ● propane; ▲ n-butane;
▼ n-pentane; ◆ n-hexane; □ n-heptane;
○ n-octane; △ n-nonane; ▽ tetra-chloromethane;
◇ cyclohexane; + benzene; × toluene

Table 2 Deviations of prediction for surface tension of pure fluids

Compound	Temperature K	ARD of γ, %	Data source
methane	90—115	7.97	[20]
argon	84—141	4.78	[18], [19]
oxygen	90—140	5.75	[18]
chlorine	193—283	9.10	[18]
tetra-chloromethane	288—495	4.54	[18]
ethane	133—184	4.70	[18]
propane	231—292	6.93	[18]
n-butane	203—305	2.86	[18]
n-pentane	309—380	3.74	[18]
n-hexane	283—430	4.67	[18]
n-heptane	283—400	1.08	[18]
n-octane	303—394	1.13	[18]
n-nonane	344—424	1.12	[18]
cyclohexane	283—394	1.12	[18]
benzene	283—354	1.53	[18]
toluene	323—444	0.88	[18]
average		3.87	

4 CONCLUSIONS

The density functional theory, simplified by LDA and MFA, is applied to study the surface properties for 16 pure non-polar fluids. Then the expression of the chemical potential for the inhomogeneous fluid is deduced, which is reasonable because the chemical potential is the function of the molecular interaction and the density distribution only. The intermolecular potential is not truncated with a reasonable long range correction. Base on above, the fluid phase equation is gotten as a special condition of the inhomogeneous fluid. Then the fluid phase equilibrium and the surface properties can be studied in one uniform method. Three parameters are needed at most, which are regressed by the phase equilibrium for the pure fluid. The calculated surface tensions are in good agreement with the experimental data and the total average relation deviation is 4.5%.

NOMENCLATURE

A	surface area, nm^2
d	hard-sphere diameter, nm
F	Helmholtz free energy, J
k	Boltzmann constant, $J \cdot K^{-1}$
m_s	number of segments for one molecule
p	pressure, Pa
r	distance to the center of hard sphere
$d\boldsymbol{r}$	infinitesimal, m^3
T	thermodynamic temperature, K
U	potential, J
V	volume, m^3
Z	compressibility factor
z	coordinate, nm
z_{Yu}	range parameter of Yukawa potential
α	bulk phase
Γ	phase space
γ	surface tension, $mN \cdot m^{-1}$
ε	dispersion energy parameter, J
μ	chemical potential, $J \cdot mol^{-1}$
ρ	number density, m^{-3}
ρ_0	equilibrium number density, m^{-3}
ϕ	pairwise potential
Ω	grand potential, J

Superscripts

*	reduced values, dimensionless
chain	hard-sphere chain
hs	hard sphere
id	ideal
per	perturbation term
ref	reference term
L	liquid
V	vapor

Subscripts

1,2	specified molecule
ext	external
int	intrinsic

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