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Molecular Simulation

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713644482>

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Online publication date: 13 May 2010

To cite this Article Lu, Jiu-Fang , Fu, Dong , Liu, Jin-Chen and Li, Yi-Gui(2003) 'Study on Surface Tension for Non-polar and Associating Fluids Based on Density Functional Theory', *Molecular Simulation*, 29: 12, 809 — 815

To link to this Article: DOI: 10.1080/0892702031000121897

URL: <http://dx.doi.org/10.1080/0892702031000121897>

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Study on Surface Tension for Non-polar and Associating Fluids Based on Density Functional Theory

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(Received September 2002; In final form December 2003)

A method for the prediction of surface tension of non-polar and associating fluids has been developed based on the density functional theory (DFT). The WCA perturbation theory and the SAFT are used to establish the equation of state (EOS). The adjustable parameters are correlated by simultaneously fitting the saturated vapor pressure and the liquid density data with the EOS. The local density approximation (LDA) is applied to the reference term and the mean field approximation (MFA) is used for perturbation term. The density profile is obtained by minimizing the grand potential functional. The surface thickness is calculated by "10%-to-90%-width" method. By use of the regressed parameters in EOS and the obtained density profile, the surface tensions for 13 non-polar fluids and 10 associating fluids are predicted satisfactorily.

Keywords: Surface tension; Density functional theory; Density profile; Equation of state; Surface thickness

INTRODUCTION

The understanding of surface tension is of great significance for both fundamental research and engineering applications. In recent years, interest in surface tension and interfacial tension has rapidly increased.

Many empirical and semi-empirical equations which can result in good accuracy of surface tension are established based on the traditional Gibbs method [1–3]. Many theoretical equations have also been built to calculate or predict the surface tension based on the perturbation theory [4–6]. In most of these equations, the surface region is considered as a so called "two dimensional surface"

and the fluid in the surface is treated as homogeneous fluid.

However, both the experiments and computer simulations have proved the surface has thickness and the fluid in the surface region is inhomogeneous. In the last two decades, many thermodynamic methods such as the integral equation theory, the density gradient theory and the density functional theory (DFT) have been applied to the surface tension of inhomogeneous fluids. Among these theories, the DFT is the most popular approach to the statistical mechanics of inhomogeneous fluids, because the density gradient, the surface thickness and the heterogeneity are taken into account in this theory.

The DFT is widely used to solve the interfacial phenomena [7]. Winkelmann *et al.* [8–10] did the research on DFT to model the surface tension of fluids. They used the mean field approximation (MFA), Week-Chandler-Anderson (WCA) perturbation theory and local density approximation (LDA) to correlate both the saturated liquid density and surface tension for spherical fluids and used the hard convex body EOS for chainlike molecules and their mixtures. Telo da Gama *et al.* [11,12] and Abbas and Nordholm [13] applied the DFT to dipolar fluids.

In this paper, a theoretical method based on the DFT is established to predict the surface tensions for pure non-polar and associating fluids. An EOS based on WCA perturbation theory and the statistical associating fluid theory (SAFT) [14,15] is built to regress the parameters. The density and the surface thickness are calculated, and the surface tensions are predicted.

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THEORIES

Density Functional Theory

The DFT is based on the grand potential functional $\Omega[\rho(\mathbf{r})]$, which can be expressed as:

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

where $E_{\text{ext}}(\mathbf{r})$ is the external potential, μ is the chemical potential; $d\mathbf{r}$ is the infinitesimal, $\rho(\mathbf{r})$ is the local number density of molecules in $d\mathbf{r}$. $F[\rho(\mathbf{r})]$ is the Helmholtz free energy functional, which can be expressed as:

$$F[\rho(\mathbf{r})] = F^{\text{ref}}[\rho(\mathbf{r})] + F^{\text{per}}[\rho(\mathbf{r})] \quad (2)$$

where the perturbation term $F^{\text{per}}[\rho(\mathbf{r})]$ stands for the contribution to the free energy of attractive interaction and the reference term $F^{\text{ref}}[\rho(\mathbf{r})]$ stands for the relevant contributions of the intermolecular interactions, which can be expressed as:

$$F^{\text{ref}}[\rho(\mathbf{r})] = F^{\text{id}}[\rho(\mathbf{r})] + F^{\text{hs}}[\rho(\mathbf{r})] + F^{\text{chain}}[\rho(\mathbf{r})] + F^{\text{assoc}}[\rho(\mathbf{r})] \quad (3)$$

where F^{id} is the Helmholtz free energy of an ideal gas with the same density and temperature as the system, F^{hs} is the free energy of a hard-sphere fluid relative to the ideal gas, F^{chain} is the free energy change when chains are formed from hard spheres and F^{assoc} is the free energy change due to association.

The LDA is applied for the reference term as follows:

$$\begin{aligned} F^{\text{ref}}[\rho(\mathbf{r})] &= \int f^{\text{ref}}[\rho(\mathbf{r})] d\mathbf{r} \\ &= \int [f^{\text{id}}[\rho(\mathbf{r})] + f^{\text{hs}}[\rho(\mathbf{r})] + f^{\text{chain}}[\rho(\mathbf{r})] \\ &\quad + f^{\text{assoc}}[\rho(\mathbf{r})]] d\mathbf{r} \end{aligned} \quad (4)$$

where $f^{\text{ref}}[\rho(\mathbf{r})]$ stands for the Helmholtz free energy density of the reference term:

$$f^{\text{ref}}[\rho(\mathbf{r})] = \frac{F^{\text{ref}}[\rho(\mathbf{r})]}{V} = \rho(\mathbf{r})F^{\text{ref}}[\rho(\mathbf{r})] \quad (5)$$

Since the perturbation term $F^{\text{per}}[\rho(\mathbf{r})]$ includes only the contribution to the free energy of attractive interaction, we substitute $F^{\text{att}}[\rho(\mathbf{r})]$ for it. $F^{\text{att}}[\rho(\mathbf{r})]$ is expressed as:

$$\begin{aligned} F^{\text{att}}[\rho(\mathbf{r})] &= \frac{m^2}{2} \iint d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') g^{\text{ref}}(\mathbf{r}, \mathbf{r}') \\ &\quad \times \phi^{\text{att}}(|\mathbf{r} - \mathbf{r}'|) \end{aligned} \quad (6)$$

where m is the number of segments for a molecule, $g^{\text{ref}}(\mathbf{r}, \mathbf{r}')$ is the radial distribution function and

$\phi^{\text{att}}(|\mathbf{r} - \mathbf{r}'|)$ is the attractive part of the intermolecular potential. Here we use the following form:

$$\begin{aligned} \phi^{\text{att}}(|\mathbf{r} - \mathbf{r}'|) &= \begin{cases} -\varepsilon, & |\mathbf{r} - \mathbf{r}'| \leq r_{\text{min}} \\ 4\varepsilon \left(\frac{\sigma^{12}}{|\mathbf{r} - \mathbf{r}'|^{12}} - \frac{\sigma^6}{|\mathbf{r} - \mathbf{r}'|^6} \right), & r_{\text{cut}} \geq |\mathbf{r} - \mathbf{r}'| > r_{\text{min}} \end{cases} \end{aligned} \quad (7)$$

with WCA perturbation theory as reference potential. Here r_{cut} stands for the cut-off radial and r_{min} is the distance when the LJ potential has the minimum of $-\varepsilon$, $r_{\text{min}} = \sqrt[6]{2}\sigma$.

When the MFA is used, $g^{\text{ref}}(\mathbf{r}, \mathbf{r}') = 1$, we have:

$$F^{\text{att}}[\rho(\mathbf{r})] = \frac{m^2}{2} \iint d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \phi^{\text{att}}(|\mathbf{r} - \mathbf{r}'|) \quad (8)$$

For a free surface, no external potential exists, hence $E_{\text{ext}}(\mathbf{r}) = 0$. Equation (1) then can be expressed as:

$$\Omega[\rho(\mathbf{r})] = \int f^{\text{ref}}[\rho(\mathbf{r})] d\mathbf{r} - \mu \int \rho(\mathbf{r}) d\mathbf{r} + F^{\text{att}}[\rho(\mathbf{r})] \quad (9)$$

At equilibrium, the grand potential functional $\Omega[\rho(\mathbf{r})]$ has a minimum. The density profile $\rho_0(\mathbf{r})$ can be obtained by minimizing Eq. (9). The surface tension is calculated by use of the density profile $\rho_0(\mathbf{r})$.

To calculate the density profile and the surface tension, we divided the surface into many extreme thin layers.

At a constant temperature, the grand potential functional $d\Omega$ can be expressed as:

$$d\Omega = \gamma dA - p dV$$

where p is the normal pressure tensor, which is equal to the vapor pressure of the bulk phase.

The surface tension in the surface region is summed as:

$$\begin{aligned} \gamma &= \sum_i^n \gamma_i = \int_{-\infty}^{\infty} \left[\frac{d\Omega[\rho_0(z)]}{dV} + p \right] dz \\ &\approx \sum_{i=1}^n [p - p[\rho_0(z)]] \Delta z \end{aligned} \quad (10)$$

where A stands for the surface area, Δz is the thickness of every layer in the surface, $\rho_0(z)$, $p[\rho_0(z)]$ and γ_i are the equilibrium local number density, the tangential pressure tensor and the surface tension of layer i , respectively.

Equation of State

The WCA perturbation theory and the SAFT are used to build the EOS for pure non-polar and chainlike associating molecules, respectively.

The $F^{\text{id}}[\rho(\mathbf{r})]$ is as follows:

$$F^{\text{id}}[\rho(\mathbf{r})] = kT [\ln(\Lambda^3 \rho(\mathbf{r})) - 1] \quad (11)$$

where Λ is the thermal de Broglie wavelength.

The hard-sphere term $F^{\text{hs}}[\rho(\mathbf{r})]$ can be expressed by the Carnahan-Starling equation [16]:

$$\frac{F^{\text{hs}}[\rho(\mathbf{r})]}{kT} = m \frac{4\eta(\mathbf{r}) - 3\eta^2(\mathbf{r})}{[1 - \eta(\mathbf{r})]^2}, \quad (12)$$

where $\eta(\mathbf{r})$ is the local packing fraction, which can be expressed as:

$$\eta(\mathbf{r}) = \frac{\pi}{6} m \rho(\mathbf{r}) d^3 \quad (13)$$

where d is the hard-sphere diameter for each segment. The relationship between d and σ , the soft-sphere diameter, is as follows [17]:

$$\frac{d}{\sigma} = \frac{0.3837 + 1.068/T^*}{0.4293 + 1/T^*} \quad (14)$$

The term of $F^{\text{chain}}[\rho(\mathbf{r})]$ is as follows [14]:

$$\frac{F^{\text{chain}}[\rho(\mathbf{r})]}{kT} = (1 - m) \ln[g^{\text{hs}}(d)] \quad (15)$$

where $g^{\text{hs}}(d)$ is the radial distribution function of hard sphere system, which can be expressed as:

$$g^{\text{hs}}(d) = \frac{1 - 0.5\eta(\mathbf{r})}{[1 - \eta(\mathbf{r})]^2} \quad (16)$$

For associating fluids, $F^{\text{assoc}}[\rho(\mathbf{r})]$ can be expressed as [14]:

$$\frac{F^{\text{assoc}}[\rho(\mathbf{r})]}{kT} = \sum_A \left[\ln X^A[\rho(\mathbf{r})] - \frac{X^A[\rho(\mathbf{r})]}{2} \right] + \frac{1}{2} M \quad (17)$$

where M is the number of association sites on each molecule. The M values for water and alcohol are three and two, respectively. \sum_A represents a sum over all associating sites on the molecule and $X^A[\rho(\mathbf{r})]$ is the mole fraction of molecules not bonded at site A , which can be expressed as:

$$X^A[\rho(\mathbf{r})] = \left[1 + N_0 \sum_B \rho(\mathbf{r}) X^B[\rho(\mathbf{r})] \Delta^{AB} \right]^{-1} \quad (18)$$

where N_0 is the Avogadro constant and Δ^{AB} stands for the association strength which can be expressed as:

$$\Delta^{AB} = g(d)^{\text{seg}} [\exp(\varepsilon^{AB}/kT) - 1] (d^3 \kappa^{AB}) \quad (19)$$

where κ^{AB} and ε^{AB}/k stand for the volume and the energy of association, respectively. $g(d)^{\text{seg}}$ is

the segment radial distribution function, it is approximated as:

$$g(d)^{\text{seg}} \approx g^{\text{hs}}(d) = \frac{1 - 0.5\eta(\mathbf{r})}{[1 - \eta(\mathbf{r})]^2} \quad (20)$$

The chemical potential and pressure of the reference term are expressed as:

$$\mu^{\text{ref}}[\rho(\mathbf{r})]/NkT = F^{\text{ref}}[\rho(\mathbf{r})]/NkT + Z^{\text{ref}}[\rho(\mathbf{r})] \quad (21)$$

$$p^{\text{ref}}[\rho(\mathbf{r})] = Z^{\text{ref}}[\rho(\mathbf{r})] \rho(\mathbf{r}) kT \quad (22)$$

where $Z^{\text{ref}}[\rho(\mathbf{r})]$ is the compressibility factor of the reference term, which can be expressed as:

$$Z^{\text{ref}}[\rho(\mathbf{r})] - Z^{\text{id}}[\rho(\mathbf{r})] = Z^{\text{hs}}[\rho(\mathbf{r})] + Z^{\text{chain}}[\rho(\mathbf{r})] + Z^{\text{assoc}}[\rho(\mathbf{r})] \quad (23)$$

where

$$Z^{\text{id}}[\rho(\mathbf{r})] = 1 \quad (24)$$

$$Z^{\text{hs}}[\rho(\mathbf{r})] = m \frac{4\eta(\mathbf{r}) - 2\eta^2(\mathbf{r})}{[1 - \eta(\mathbf{r})]^3} \quad (25)$$

$$Z^{\text{chain}}[\rho(\mathbf{r})] = (1 - m) \frac{2.5\eta(\mathbf{r}) - \eta^2(\mathbf{r})}{[1 - \eta(\mathbf{r})][1 - 0.5\eta(\mathbf{r})]} \quad (26)$$

$$Z^{\text{assoc}}[\rho(\mathbf{r})] = \rho(\mathbf{r}) \sum_A \left[\frac{1}{X^A[\rho(\mathbf{r})]} - \frac{1}{2} \right] \frac{\partial X^A[\rho(\mathbf{r})]}{\partial \rho[\rho(\mathbf{r})]} \quad (27)$$

The term of $F^{\text{att}}[\rho(\mathbf{r})]$ is shown in Eq. (6). $f^{\text{att}}[\rho(\mathbf{r})]$, the density of $F^{\text{att}}[\rho(\mathbf{r})]$, can be expressed as:

$$f^{\text{att}}[\rho(\mathbf{r})] = \frac{F^{\text{att}}[\rho(\mathbf{r})]}{V} = \frac{m^2}{2} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \phi^{\text{att}}(|\mathbf{r} - \mathbf{r}'|) \quad (28)$$

The contribution of attractive interaction to the chemical potential and pressure can be expressed as follows:

$$\mu^{\text{att}}[\rho(\mathbf{r})] = \frac{\partial f^{\text{att}}[\rho(\mathbf{r})]}{\partial \rho(\mathbf{r})} \quad (29)$$

$$p^{\text{att}}[\rho(\mathbf{r})] = - \frac{\partial F^{\text{att}}[\rho(\mathbf{r})]}{\partial V} \quad (30)$$

The chemical potential and the pressure of the system are expressed as:

$$p[\rho(\mathbf{r})] = p^{\text{ref}}[\rho(\mathbf{r})] + p^{\text{att}}[\rho(\mathbf{r})] \quad (31)$$

$$\mu[\rho(\mathbf{r})] = \mu^{\text{ref}}[\rho(\mathbf{r})] + \mu^{\text{att}}[\rho(\mathbf{r})] \quad (32)$$

TABLE I Regressed parameters and the average relative deviations (ARD%) of p^v and p^l for pure non-polar and associating fluids

Compound	Temp range (K)	Segment parameters					ARD % of p^v	ARD % of p^l
		m	σ (10^{-10} m)	ε/k (K)	ε^{AB}/k (K)	κ^{AB}		
Ar	85–125	3.26	115.75	1.00			4.8	0.6
Xe	160–260	3.79	226.47	1.00			7.5	0.8
O ₂	65–120	3.14	125.44	1.00			8.2	0.9
N ₂	70–106	3.46	97.54	1.00			8.7	0.8
CH ₄	100–150	3.61	150.80	1.00			4.8	0.7
C ₂ H ₆	140–210	3.20	163.55	1.81			7.4	1.1
C ₃ H ₈	210–350	3.07	149.24	2.64			9.2	0.8
C ₄ H ₁₀	230–370	3.16	160.41	3.14			9.4	1.0
C ₅ H ₁₂	313–413	2.99	148.91	4.07			7.8	1.2
C ₆ H ₁₄	283–383	3.11	158.98	4.45			8.3	0.8
C ₇ H ₁₆	313–413	3.10	158.69	5.05			8.1	0.9
C ₈ H ₁₈	310–430	3.08	158.41	5.69			13.9	1.2
C ₉ H ₂₀	400–550	3.11	158.97	5.81			12.5	1.0
NH ₃	210–370	3.12	270.1	1098.2	0.064	1.0	6.27	0.58
H ₂ S	212–340	3.50	250.1	808.2	0.060	1.0	1.87	0.91
H ₂ O	283–493	2.75	300.3	2951.1	0.055	1.0	3.81	4.54
CH ₃ OH	290–493	3.28	210.9	2700.9	0.059	1.1	5.42	4.70
C ₂ H ₅ OH	273–463	3.09	185.8	2890.9	0.026	2.0	7.11	2.50
C ₃ H ₈ OH	293–493	3.27	199.8	2899.2	0.013	2.3	6.28	2.22
C ₄ H ₁₀ OH	390–530	3.27	195.6	3050.2	0.006	3.0	5.59	3.84
C ₅ H ₁₂ OH	327–508	3.20	192.8	3134.4	0.004	3.7	5.59	2.03
C ₈ H ₁₈ OH	338–532	3.36	188.8	3470.4	0.005	4.6	4.66	2.43
C ₉ H ₂₀ OH	360–457	3.50	178.8	3620.4	0.003	5.3	3.52	4.51
Total average deviation %							6.6	1.4

Experimental data are taken from Beaton and Hewitt [18].

CALCULATION AND DISCUSSION

Correlation of Segment Parameters

Calculation of surface properties such as the density profile, surface tension and surface thickness needs accurate values of bulk densities, bulk chemical potential and bulk pressure. In the two bulk phases, the fluid is considered as homogenous fluid. The liquid-vapor phase equilibrium requires:

$$\begin{cases} p(\rho^v) = p(\rho^l) \\ \mu(\rho^v) = \mu(\rho^l) \end{cases} \quad (33)$$

The segment parameters m , σ , ε/k , ε^{AB}/k and κ^{AB} for associating fluids and m , σ and ε/k for non-polar fluids can be obtained by simultaneously fitting the experimental saturated vapor pressures p^v and liquid densities ρ^l .

The regressed segment parameters with their correlated deviations for 11 pure non-polar and 8 pure associating fluids are listed in Table I.

Calculation of Density Profile $\rho(z)$ and Surface Thickness

The density profile can be obtained by solving the Euler–Lagrange equations. Minimizing Eq. (9), we can get the form of Euler–Lagrange equations as:

$$\frac{\delta \Omega[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = 0 \quad (34)$$

The fluid in the surface region is considered as an inhomogeneous one. In the horizontal directions of the surface, it is assumed that no density gradient exists. However, in the vertical direction of the surface, there exists the density gradient, that is, $d\rho(z)/dz \neq 0$. Since we treat the vapor–liquid surface as a planar surface, the density profile in the surface region can be expressed as a function of z .

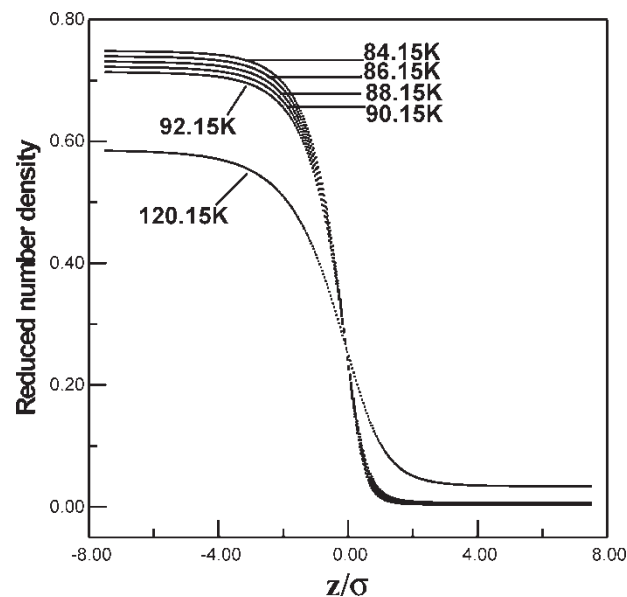


FIGURE 1 The density profiles of argon from 84.15 to 120.15 K.

TABLE II Calculated surface thickness of argon liquid

Temperature (K)	Winkelmann's work [9] t/σ	MC values [20] t/σ	MD values [21] t/σ	This work t/σ
84.0	2.18	1.54	1.71	1.91
85.0		1.74		1.99
88.0				2.08
90.0	2.39		3.21	2.34
120.0	3.99			3.85

Consequently, the Euler–Lagrange equations can be rewritten as:

$$\frac{\delta\Omega[\rho(z)]}{\delta\rho(z)} = \left(\frac{\partial f^{\text{id}}[\rho(z)]}{\partial\rho(z)} + \frac{\partial f^{\text{hs}}[\rho(z)]}{\partial\rho(z)} + \frac{\partial f^{\text{chain}}[\rho(z)]}{\partial\rho(z)} + \frac{\partial f^{\text{assoc}}[\rho(z)]}{\partial\rho(z)} \right) + m^2 \int_{-\infty}^{+\infty} \rho(z') \overline{\phi^{\text{att}}(|z-z'|)} dz' - \mu^{\text{bulk}} = 0 \quad (35)$$

where $\overline{\phi^{\text{att}}(|z-z'|)} = ((\int \int \phi^{\text{att}}(r, \theta, z) dr d\theta dz) / (dz))$ and the boundary conditions of $\rho(z)$ are:

$$\rho(z) = \begin{cases} \rho^v, & z \rightarrow z_{\min} \\ \rho^l, & z \rightarrow z_{\max} \end{cases} \quad (36)$$

Figure 1 shows the density profiles of argon from 84.15 to 120.15 K. The density values are expressed as the reduced number density $\rho^* = \rho\sigma^3$.

From this figure, we can see that the equilibrium density profile in the liquid–vapor surface region shows a typical hyperbolic tangent shape and as expected, the surface broadens when the temperature increases.

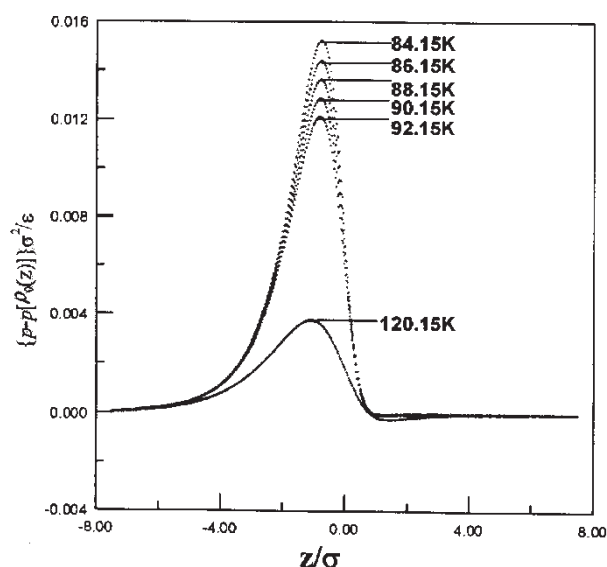


FIGURE 2 The difference between normal and tangential pressure tensors of argon from 84.15 to 120.15 K.

Once the density profile is obtained, the surface thickness is calculated by the so called “10%-to-90%–width” method, where the width of the surface is defined as the distance over which the density changes from $\rho^v + 0.1(\rho^l - \rho^v)$ to $\rho^v + 0.9(\rho^l - \rho^v)$ [19]. Table II shows the calculated surface thickness of argon and the comparison with those from literatures.

Prediction of Surface Tension

By using Eq. (10), the surface tensions of 11 pure non-polar liquids and 8 associating fluids are predicted. The pressure differences $[p - p[\rho_0(z_i)]]$ for argon from 84.15 to 120.15 K are shown in Fig. 2. This figure shows that the values $[p - p[\rho_0(z_i)]]$ have a maximum in the surface region and the absolute value of $[p - p[\rho_0(z_i)]]$ decreases when the temperature increases.

The predicted surface tensions have been shown in Table III and Figs. 3–5. The total average relative

TABLE III Prediction of the surface tension for pure non-polar and associating fluids

Compound	Data points of γ	ARD % of γ
Ar	6	4.34
Xe	8	3.50
O ₂	7	3.51
N ₂	9	3.66
CH ₄	6	3.25
C ₂ H ₆	6	7.68
C ₃ H ₈	6	6.29
C ₄ H ₁₀	5	4.07
C ₅ H ₁₂	3	7.31
C ₆ H ₁₄	6	4.93
C ₇ H ₁₆	7	4.05
C ₈ H ₁₈	8	5.39
C ₉ H ₂₀	5	4.27
NH ₃	7	4.23
H ₂ S	7	4.06
H ₂ O	10	6.96
CH ₃ OH	6	3.86
C ₂ H ₅ OH	4	6.12
C ₃ H ₇ OH	7	7.77
C ₄ H ₉ OH	9	6.61
C ₅ H ₁₁ OH	10	2.69
C ₈ H ₁₇ OH	7	4.66
C ₉ H ₁₉ OH	10	4.98
Total average deviation %		4.96

Experimental data are taken from Beaton and Hewitt [18] and Jasper [22].

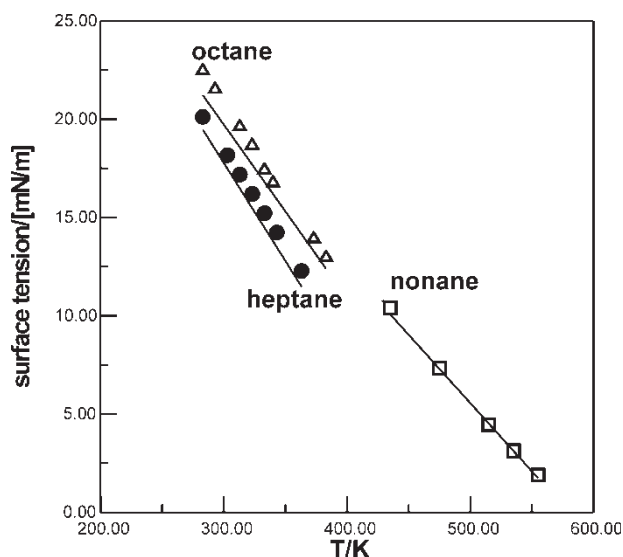


FIGURE 3 Prediction of surface tension for heptane, octane and nonane (symbol: experimental data; —: predicted data).

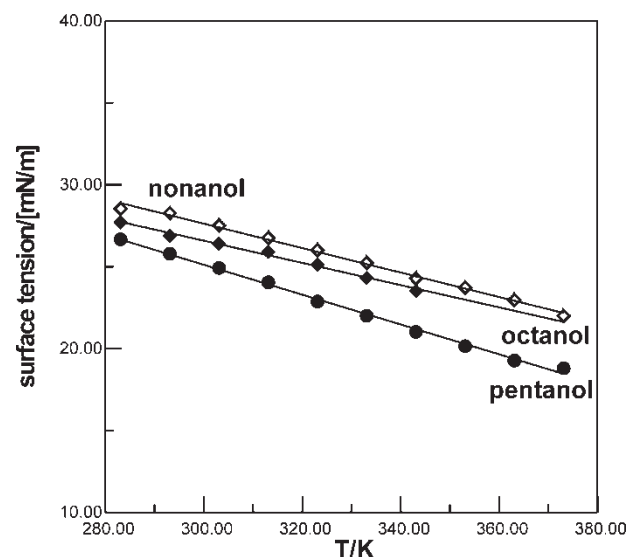


FIGURE 5 Prediction of surface tension for pentanol, octanol and nonanol (symbol: experimental data; —: predicted data).

deviation of prediction is 5.20%. From Figs. 3–5 and Table III, it can be seen that the predicted surface tensions agree well with the experimental data.

CONCLUSION

1. The WCA perturbation theory and SAFT are applied to build the equation of state (EOS) for pure non-polar fluids and associating fluids, respectively. The segment parameters m , ε/k and σ for pure non-polar fluids and m , σ , ε/k ,

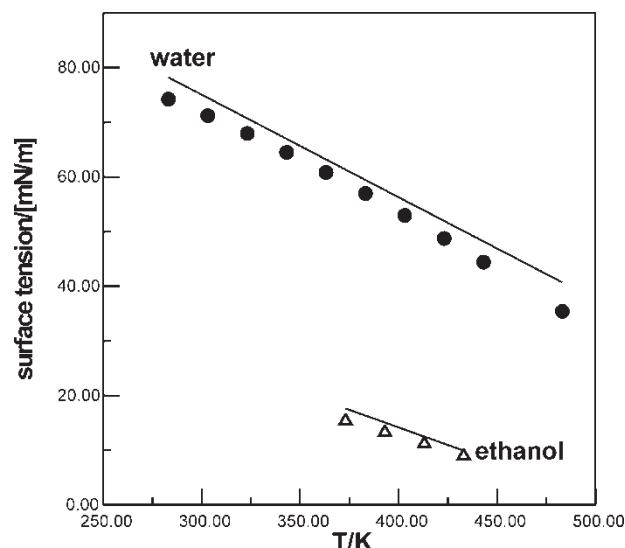


FIGURE 4 Prediction of surface tension for water and ethanol (symbol: experimental data; —: predicted data).

ε^{AB}/k and κ^{AB} for associating fluids are obtained by simultaneously fitting the experimental saturated vapor pressures and liquid densities. The correlation deviations of the vapor pressure and liquid density are 6.6 and 1.4%, respectively.

2. The DFT is applied in this work. The density profiles are obtained by minimizing the grand potential functional $\Omega[\rho(r)]$ and solving the Euler–Lagrange equations. The surface thickness is calculated by the “10%-to-90% -width” method. The results show the equilibrium density profile in the liquid–vapor surface region is a typical hyperbolic tangent curve and the surface thickness increases with the temperature.
3. The surface tensions of 23 non-polar or associating fluids are predicted by use of the obtained density profiles and the same set of parameters from EOS. The average deviation of prediction is 4.96%.
4. Our method has good correlation capabilities of pVT and density profile in VLE for pure fluids. It shows a good prediction of surface tension for pure non-polar fluids and associating fluids.

Acknowledgements

The financial supports of this work by the National Natural Science Foundation of China (No. 20106007) and the Fundamental Research Fund of Tsinghua University in China (No. JC1999038) are gratefully appreciated.

NOMENCLATURE

A	surface area, nm ²
d	hard-sphere diameter, nm
E_{ext}	external potential, J
F	Helmholtz free energy, J
f	Helmholtz free energy density, J·m ⁻³
k	Boltzmann constant, J·K ⁻¹
M	the number of association sites on each associating molecule
m	number of segments for one molecule
N_0	Avogadro constant, mol ⁻¹
p	pressure, Pa
dr	infinitesimal, m ³
T	absolute temperature, K
T^*	reduced temperature
V	volume, m ³
X^A	mole fraction of molecules not bonded at site A
Z	compressibility factor
z	distance, nm
Δ	association strength, m ³
ε	dispersion energy parameter, J
γ	surface tension, mN·m ⁻¹
η	packing factor
κ	association volume
Λ	de Broglie wavelength, m
μ	chemical potential, J·mol ⁻¹
ρ	number density, m ⁻³
ρ^*	reduced number density
ρ_0	equilibrium number density, m ⁻³
σ	soft-sphere diameter, nm
Ω	grand potential, J
assoc	associating
att	attractive
chain	hard-sphere chain
hs	hard sphere
id	ideal
l	liquid
per	perturbation term
ref	reference terms
v	vapor
ext	external
i	layers
n	number of layers

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