Thermodynamic properties of a liquid–vapor interface in a two-component system

I. Inzoli, S. Kjelstrup, D. Bedeaux, J.M. Simon

Abstract

We report a complete set of thermodynamic properties of the interface layer between liquid and vapor two-component mixtures, using molecular dynamics. The mixtures consist of particles which have identical masses and diameters and interact with a long-range Lennard-Jones spline potential. The potential depths in dimensionless units for like interactions is 1 (for component 1) and 0.8 (for component 2). The surface excess entropy decreases when the temperature increases, so the surface has a negative excess heat capacity. This is a consequence of the fact that the surface tension decreases to zero at the critical point, proportional to \( (T_{c,i} - T)^{\beta} \). The surface entropy decreases also as the excess concentration of component 2 increases, at a given temperature. The surface becomes less able to store energy as the more volatile component accumulates. We show that the more volatile component 2 has a maximum in its excess concentration in the interfacial region when the density of component 1 starts to go down. The vapor is described with the Soave–Redlich–Kwong equation of state, and the liquid activity coefficients are described by the three-suffix Margules equation. The observed densities and surface tension variations are fitted with good accuracy, with the critical exponents \( \beta = 0.32 \) and \( 2\nu = 1.26 \), respectively. The results for the critical temperature of mixtures can be fitted to a second order polynomial, with significant deviations from Kay's rule.

1. Introduction

The liquid–vapor phase transition has a crucial role in many mechanical and chemical engineering processes, as well as in nature. Knowledge of phase equilibria of mixtures is thus essential for the design, say of separation and purification apparatuses, or for climate modeling, to take a few examples. The practical concern can be prevention of phase separation, which can cause problems during industrial processes such as cavitation in pumps or precipitation (clathrate formation) in pipelines. But also the rate of absorption or mixing is central, dictating the size of the apparatuses, like distillation columns or adsorption towers. The long-range aim of the present work is to understand and describe the role of the liquid–vapor interface in these contexts. In order to understand the surface resistivities to transport of heat and mass, it is necessary to understand first the nature of the interface itself. In this study, we present for the first time, a complete set of thermodynamic properties of a surface between a two-component non-ideal liquid in contact with its non-ideal vapor.

Molecular dynamics simulations are well suited to obtain information on molecularly thin interfacial layers (Røsjorde et al., 2000, 2001; Lamm and Hall, 2002; Simon et al., 2004; Johannessen and Bedeaux, 2006; Galbraith and Hall, 2006; Ge et al., 2007; Müller and Mejia, 2009). Not only does the technique give a non-invasive way to study the surface, it also allows us to examine the boundaries of the interface, in the presence and absence of global equilibrium. The technique has thus been established in several studies on one-component systems (Røsjorde et al., 2000, 2001; Simon et al., 2004; Johannessen and Bedeaux, 2006; Ge et al., 2007). Some calculations have also been made of two-component systems (Lamm and Hall, 2002; Olivier et al., 2002; Galbraith and Hall, 2006; Müller and Mejia, 2009). The present study shall take advantage of this simulation technique, and contribute to the work on two-component systems.

Many efforts have been made to investigate the liquid–vapor interface of one-component systems, but little is known about interfacial thermodynamic properties of two-component systems. A first study of a binary isotope mixture was made by Hafskjold and Ratkje (1995). Computer simulations have been used to predict phase equilibria and gain insights into the connection between phase change behavior and molecular interactions, but the interface has not been analyzed in terms of Gibbs excess properties. Vapor–liquid phase-diagrams were obtained for binary mixtures of diatomic LJ molecules by Galbraith and Hall...
(2006) using Monte Carlo simulations and the Gibbs–Duhem integration method. They explored the effects of varying the molecular size ratio, intermolecular attraction parameter ratio and binary interaction parameter ratio on the mixture’s phase behavior. Similar investigations were carried out by Lamm and Hall (2002) for binary LJ mixtures of spherical molecules. Also in these cases, no attention was given to the liquid–vapor interface itself. Only Müller and Mejia (2009) have reported such data. They reported subcritical liquid–vapor interfacial properties of three asymmetric binary mixtures composed of long n-alcaines in equilibria with a smaller solvent: hexane + decane, carbon dioxide + decane, and ethane + eicosane. The interfacial region was described by the square gradient theory as well as by molecular dynamics simulations. The surface tension was calculated and compared to experiments and PC-SAFT equations of state. A particularly high excess adsorption in the interface of the smaller solvents was noted. The aim of the present study is therefore more specifically, to add to the understanding of the liquid–vapor interface of two-component systems, by complementing and adding to the studies of Müller and Mejia (2009).

A two-phase fluid can be divided into three separated phases: the liquid, the vapor and, in between, the interface or the surface. We shall use the latter two words interchangeably. Non-equilibrium molecular dynamics simulations were used to prove the validity of local equilibrium in pure fluids subjected to gradients of temperature and concentrations (Rasjord et al., 2000; Xu et al., 2006; Ge et al., 2007). It was shown that local equilibrium holds, not only for the two homogeneous phases, but also for the excess properties of the interface, which could be regarded as a thermodynamic system also when the total system was out of equilibrium. The interface is several molecular layers thick and its extension is defined in the determination of its excess properties. We follow the procedure for determination of such properties, which was prescribed already by Gibbs (1961). By dealing with the surface as a two-dimensional thermodynamic system, we shall take advantage of knowledge on scaling and universal properties near the critical point (Sengers and Jin, 2007; Grigoyev et al., 2006) in the fitting of our computed data, thereby also testing the system for such predicted behavior.

The systems investigated by Hafskjold and Ratkje (1995) and Olivier et al. (2002) consisted of mixtures of two argon-like particles interacting via a Lennard-Jones spline potential, having the same masses and diameters, but different potential depths. The mixture can be said to mimic a mixture of, say hexane and cyclo-hexane, but all calculations are done in reduced units so the results can be applied for any mixture of two species having the same mass, size and the same ratio between the potential depths. We shall continue to use the same system, in order to be able to compare with earlier results (Hafskjold and Ratkje, 1995; Olivier et al., 2002). The calculations are time-consuming, and different overall compositions and temperatures will be considered, before changes are made in say the molecular masses or sizes. The next aim is to obtain transport coefficients at different temperatures and compositions, and to be able to relate these variables to system properties. Equilibrium data are then needed in order to calculate driving forces. This study therefore concentrates on the equilibrium properties of the two bulk phases and its interface. The equation of state of the bulk phases and of the interface shall be obtained, and thermodynamic properties of the interface shall be given.

We shall see that the vapor and liquid can both be described by common thermodynamic functions for non-ideal mixtures (the vapor by the Saven-Reedich–Kwong (SRK) equation and the liquid by the three-suffix Margules equation). The surface can likewise be described well by surface excess properties, as defined by Gibbs, and it behaves according to the predicted universal scaling laws. To predict the surface layer by fitting to hyperbolic tangent functions is no option. In the system that we study, the vapor is always enriched in component 2, the component with the smallest potential depth. Interestingly, the surface has a peak in the concentration of this component 2 right after the density of component 1 starts to go down. As the temperature increases, the specific interface entropy of component 2 decreases. Furthermore, the excess heat capacity at constant area is negative. The surface has thus a small capacity to store heat compared to the liquid and vapor. This is a consequence of the universal variation of the surface tension with temperature as one approaches the critical point. New is that the surface entropy also decreases as component 2 accumulates.

2. System and simulations details

The system considered consisted always of a box containing 4000 particles of two types. The liquid–vapor interfaces were obtained in three steps.

(1) First we considered a rectangular parallelepiped box of dimensions \( L_x L_y L_z \) (\( L_x = 150 \text{ Å}, L_y = L_z = 25 \text{ Å} \)) with \( N = 4000 \) particles placed on a cubic lattice and performed Monte Carlo steps in the NPT ensemble. The relative probabilities for the different types of moves were 0.999 for translation and 0.001 for volume change.

(2) The dimension of the resulting box was then increased in the \( x \)-direction by placing two empty cells on both sides of the bulk liquid box in order to have an elongated box with dimension \( L_x = L_y = L_z / 16 \). Monte Carlo simulations were run in the NVT ensemble for 10 million time steps. Probability attempts for the translational moves were 0.7 and 0.3 for the two molecules, respectively. This procedure gives a system with two liquid–vapor interfaces, with the liquid at the center of the box.

(3) The starting configurations for the equilibrium molecular dynamics simulations in the NVT ensemble were obtained by distributing the two atoms in a random manner. Every EMD simulation run for 20 million time steps, with a time step of \( 5 \times 10^{-15} \text{ s} \). The first 5 million time steps were discarded to avoid transient effects and all the properties were averaged over the last 15 million time steps.

A snapshot of the equilibrium configuration is shown in Fig. 1. We used periodic boundary conditions in the three directions. The size of the box was calculated from \( L_x = \sqrt{4000 / (16^2 N_A p)} \), where \( N_A \) is the Avogadro number, and \( p \) is the overall density. The box was divided in the \( x \)-direction into 128 equal layers of thickness \( l = L_x / 128 \). In previous studies (Rasjorde et al., 2001; Xu et al., 2006) for one-component systems we used temperature gradients to create liquid–vapor interfaces along the \( x \)-direction, but the protocol we choose here is more efficient because it reduces the simulation time required to reach the equilibrium state.

The binary mixture was modeled with the long-range Lennard-Jones spline potential (Ge et al., 2007). The potential \( U_{ij} \) was expressed in terms of the interparticle distance \( r_{ij} \) between any pair of particles \( i \) and \( j \),

\[
U_{ij}(r_{ij}) = \begin{cases} 4\epsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6}, & 0 \leq r_{ij} \leq r_c \\ a(r_{ij}-r_c)^3 + b(r_{ij}-r_c)^2, & r_c \leq r_{ij} \leq r_c \\ 0, & r_{ij} \geq r_c \end{cases}
\]

(1)

where \( \sigma_{ij} \) and \( \epsilon_{ij} \) are the potential parameters, \( r_c = 2.5\sigma_{11} \) is the cut-off distance and \( r_s = (48/67) r_c \) is the switch distance (Ge et al., 2007). The constants \( a \) and \( b \) were chosen so that the potential and its derivative were continuous at the distances \( r_c \) and \( r_s \). In the
of the corresponding two layers in the original system. Ge et al. (2007) gave a wrong sign for $b$.

Table 1

<table>
<thead>
<tr>
<th>Variable</th>
<th>Reduction formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>$m_s = m/m_1$</td>
</tr>
<tr>
<td>Distance</td>
<td>$r^* = r/r_{11}$</td>
</tr>
<tr>
<td>Energy</td>
<td>$U^* = U/U_{11}$</td>
</tr>
<tr>
<td>Time</td>
<td>$t^* = (t/\bar{v}<em>{11}/(\bar{v}</em>{11}/m_{11})$</td>
</tr>
<tr>
<td>Temperature</td>
<td>$T^* = k_B T/\bar{v}_{11}$</td>
</tr>
<tr>
<td>Molar density</td>
<td>$\rho^* = \rho \sigma_{11}^2 N_a$</td>
</tr>
<tr>
<td>Pressure</td>
<td>$p^* = P_{11}/\bar{v}_{11}$</td>
</tr>
<tr>
<td>Velocity</td>
<td>$v^* = \sqrt{(m_{11}/\bar{v}_{11})}$</td>
</tr>
<tr>
<td>Surface tension</td>
<td>$\gamma^* = \gamma \sigma_{11}^2/\bar{v}_{11}$</td>
</tr>
<tr>
<td>Mass flux</td>
<td>$j_s^* = j_m \sigma_{11}^2 N_s \sqrt{(m_{11}/\bar{v}_{11})}$</td>
</tr>
<tr>
<td>Heat flux</td>
<td>$j_s^* = j_m \sigma_{11}^2 N_s \sqrt{(m_{11}/\bar{v}_{11})}$</td>
</tr>
</tbody>
</table>

The MD simulation program made use of reduced (dimensionless) variables which are defined in Table 1. The reduced quantities are denoted with a superscript *.

2.1. Calculations

Fluxes and variables in all 128 layers of the system were found as time averages of instantaneous velocities, kinetic energies, potential energies, and the number of particles. Because the system is symmetric around the central plane in the middle of the box (between layers 64 and 65) and normal to the $x$-direction, the properties in each layer of the box were also averaged with the same properties in the mirror layer. For vectorial properties like velocity, however, the components in the $x$-direction were averaged with the negative value of the symmetric layer. This gives a system with only 64 layers, where each layer is the mean of the corresponding two layers in the original system.

The molar density in each layer $\nu$ was given by

$$c_{i,\nu} = \frac{N_{i,\nu}}{V}$$

where $V = L_x L_y L_z$ being the volume of the box and $N_{i,\nu}$ the average number of particles of type $i$ in layer $\nu$. The temperature of each layer is found from the particles' kinetic energy

$$\frac{3}{2} N \kappa T_{\nu} = \frac{1}{2} \sum_{i=1}^{N_{\nu}} m_i \langle v_i - \bar{v}_{\nu} \rangle^2$$

where $m$ is the particles mass, $v_i$ is the velocity of particle $i$ and $\bar{v}_{\nu}$ the average velocity in the layer. The surface temperature $T_s$ was given by the average kinetic temperature of the surface layers, which were determined as explained below.

The pressure tensor was obtained by time averaging the layer pressure tensor

$$p_{\nu \beta} = \frac{128}{V} \sum_{i=\nu} \left( m_{i} v_{i x} v_{i \beta} + \frac{1}{2} \sum_{j=\nu} F_{x i} \bar{v}_{\beta} \right)$$

where $v_{i x}$ is the component of the velocity of particle $i$ in the direction $x$ and $F_{x i}$ is the component of the force exerted on particle $i$ by particle $j$ in the direction $\alpha$, and $\bar{v}_{\beta}$ is the component of the vector from particle $j$ to particle $i$ in the direction $\beta$. The pressure tensor was found to be diagonal. Away from the surface the diagonal elements in the $x$, $y$, and $z$ directions were the same, while in the neighborhood of the surface the diagonal elements along the surface, $p_{xx} = p_{yy} = p_{zz}$, and normal to the surface, $p_{xx}^\nu = p_{xx}^\nu$, were found to be different, as shown in Fig. 2.

The surface tension was found from this difference using

$$\gamma_s = \frac{L_x}{128} \sum_{i=1}^{128} (p_{XX} - p_{XX}^\nu)$$

As discussed in previous papers (Simon et al., 2004; Evans and MacGowan, 1986) expression (4) is a first order approximation of the pressure assuming the system to be homogeneous. While it is valid in the direction parallel to the surface it is not valid in the direction normal to the surface. Using a higher order expression or alternatively the method of planes proposed by Evans and MacGowan (1986), the shape of the pressure across the surface in the $x$-direction is perfectly flat and its value equals that of the liquid or gas phase. Fig. 2 shows a symmetric tidal shape of $p_{xx}$ around the real pressure value. The average pressure value calculated from the global surface gives exactly the real pressure such that the surface tension obtained from Eq. (5) can be obtained equally well using the real constant $p_{xx}$ or directly the computed values.

![Fig. 1. Equilibrium configuration at $T=87\,K$ for an equimolar mixture.](image1)

![Fig. 2. Reduced diagonal pressures along the box for an equimolar mixture at $T=87\,K$.](image2)
3. The equation of state

The equilibrium pressure of the vapor mixture was calculated as a function of temperature and composition. The Soave–Redlich–Kwong (SRK) equation of state was used to relate the $P$, $v$, $T$—behavior of the system:

$$ P = \frac{RT}{v-B} \frac{A(T)}{v(v+B)} $$

(6)

Here $v$ is the molar volume. For a one-component system one has expressions for $A(T)$ and $B$. Only $A(T)$ depends on the temperature. For a mixture these coefficients are expressed in terms of the coefficients for the separate (pure) components using the so-called one fluid mixing theory. In other words, we assume that the equation of state for the mixture is the same as the equation of state of a hypothetical “pure” fluid whose characteristic constants $A(T)$ and $B$ depend on the vapor composition. This mean-field equation of state does not apply near the critical point so-called one fluid mixing theory. In other words, we assume that the equation of state for the mixture is the same as the equation of state of a hypothetical “pure” fluid whose characteristic constants $A(T)$ and $B$ depend on the vapor composition. This mean-field equation of state does not apply near the critical point for two reasons. First, it incorporates classical power laws for the mean-field equation of state does not apply near the critical point.

4. The equation of state

For a mixture these coefficients are expressed in terms of the

$$ B = \sum_j y_j B_j $$

(7)

with

$$ B_j = \frac{0.08664RT_j/c}{p_j/c} $$

(8)

where $y_j$ is the mole fraction of component $j$ in the mixture and $T_j/c$ and $p_j/c$ are the temperature and pressure of the pure component $j$. The coefficient $B$ does not depend on the temperature.

For the parameter $A(T)$, a quadratic mixing rule is used

$$ A(T) = \sum_{ij} y_i y_j \sqrt{A_i A_j (1-k_j)} $$

(9)

We use $k_j=0$, which according to Reid et al. (1977) is a good approximation for hydrocarbon mixtures. For a binary mixture the coefficients $A_i$ for components 1 and 2 are given by

$$ A_1(T) = 0.42748 \frac{(RT_1/c)^2}{P_{1,c}} \left[ 1 + 0.9349 \left( 1 - \sqrt{\frac{T}{T_{1,c}}} \right) \right] $$

$$ A_2(T) = 0.42748 \frac{(RT_2/c)^2}{P_{2,c}} \left[ 1 + 0.8058 \left( 1 - \sqrt{\frac{T}{T_{2,c}}} \right) \right] $$

(10)

The cubic equation of state, together with the mixing rules, was used to describe the equilibrium behavior of the vapor phase.

4. The equilibrium properties of the mixture

To define the equilibrium properties of the mixture we need a relation between temperature, pressure and compositions. The Gibbs–Duhem equation says that the activity coefficients $\gamma_i$ of individual components $i$ in a binary mixture are related by

$$ x_1 \left( \frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} = x_2 \left( \frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,P} $$

(11)

The mole fraction $x_i$ is simply related to the mole number $n_i$ by

$$ x_i = n_i / (n_1 + n_2). $$

For a binary solution containing $n_1$ moles of component 1 and $n_2$ moles of component 2 we can define the excess Gibbs energy, $G_E$, relative to that of an ideal solution by

$$ G_E = RT(n_1 \ln \gamma_1 + n_2 \ln \gamma_2) $$

(12)

Upon applying the Gibbs–Duhem equation (11) we can relate the individual activity coefficients $\gamma_1$ and $\gamma_2$ by differentiation

$$ RT \ln \gamma_1 = \left( \frac{\partial G_E}{\partial T} \right)_{T,P,n_2} $$

$$ RT \ln \gamma_2 = \left( \frac{\partial G_E}{\partial T} \right)_{T,P,n_1} $$

(13)

Eqs. (12) and (13) are useful because they enable us to interpolate and extrapolate limited data with respect to the composition. To do so, we first have to adopt an expression of $G_E$ as a function of the composition subject to the condition that at fixed composition $G_E$ is proportional to $n_1 + n_2$

$$ G_E = (n_1 + n_2) \delta E $$

(14)

where $\delta E$ is the excess Gibbs energy per mole of mixture. Moreover, if the excess properties are taken with reference to an ideal solution wherein the standard state for each component is pure liquid at the temperature and pressure of the mixture, the molar excess Gibbs energy of the binary solution must obey two boundary conditions:

$$ \delta E = 0 \text{ when } x_1 = 0 $$

$$ \delta E = 0 \text{ when } x_2 = 0 $$

(15)

To represent these conditions, we chose the three-suffix Margules equation (Reid et al., 1977)

$$ \delta E = x_1 x_2 [\alpha + \beta (x_1 - x_2)] $$

(16)

$$ RT \ln \gamma_1 = (\alpha + \beta x_1^2 - 4 \beta x_1) $$

$$ RT \ln \gamma_2 = (\alpha - 3 \beta x_1^2 + 4 \beta x_1) $$

(17)

where $\alpha$ and $\beta$ are adjustable parameters. So for each temperature $T$, we constructed the diagram $P$ versus $x_1$ and $y_1$, where $x_1$ and $y_1$ are, respectively, the mole fractions of component 1 in the liquid and in the vapor. For each simulated point we calculated the activity coefficients as

$$ \gamma_1 = x_1 p / (x_1 p^{lp}) $$

$$ \gamma_2 = x_2 p / (x_2 p^{lp}) $$

(18)

where $p^{lp}$ and $p^{lp}$ are the pure liquid vapor pressures at $T$. Then we obtained the parameters $\alpha$ and $\beta$ by minimizing the deviation between the molar excess Gibbs energy obtained by Eq. (12) to the one calculated through Eq. (16). From Eqs. (17) we were then able to obtain $\gamma_1$ and $\gamma_2$ for any arbitrarily selected values of $x_1$ and to find the corresponding $y_1$ and $p$ by solving Eqs. (18). The composition in the gas phase is more precisely given by the equation of state for the gas, and this must be used to find driving forces with sufficient precision (Røsjorde et al., 2001).

5. Definition of the surface

Away from the critical line, a surface is the thin layer between two homogeneous phases. In our case we consider interfaces between liquid and vapor phases perpendicular to the $x$-direction and indicate these phases with the superscripts $l$ and $g$ respectively. We shall use the two words surface and interface interchangeably.
Fig. 3 shows the variation in concentration of the components of an equimolar mixture at $T=87$ K, as we go from the gas to the liquid phase. A continuous variation in the concentration is seen. Gibbs (1961) defined the closed surface as a transition region with a finite thickness bounded by planes of similarly chosen points. In the figure two such planes are indicated by vertical lines. The position $a$ is the point in the gas left of the closed surface where $c_i(x)$ starts to differ from the concentration of the gas, $c_i^g$, and the position $b$ is the point in the liquid right of the closed surface, where $c_i(x)$ visually starts to differ from the concentration of the liquid, $c_i^l$. The surface thickness is then $\delta = b - a$. Gibbs defined the dividing surface as “a geometrical plane, going through points in the interfacial region, similarly situated with respect to conditions dividing surface as ‘a geometrical plane, going through points in the extension of the interface (Fig. 3).”

Gibbs (1961) defined the closed surface as a transition region with liquid phase. A continuous variation in the concentration is seen. where $c_i(x)$ starts to differ from the concentration of the gas, $c_i^g$, and the position $b$ is the point in the liquid right of the closed surface, where $c_i(x)$ visually starts to differ from the concentration of the liquid, $c_i^l$. The surface thickness is then $\delta = b - a$. Gibbs defined the dividing surface as “a geometrical plane, going through points in the interfacial region, similarly situated with respect to conditions of adjacent matter”. The continuous density, integrated over $\delta$, gives the excess surface concentration of the component $i$ as a function of the position, $(y, z)$, along the surface:

$$\Gamma_i(y,z) = \int_a^b [c_i(x,y,z) - c_i^g(a,y,z)] \theta(y-d-x) - c_i^l(b,y,z) \theta(x-d)] \, dx$$  \quad (19)$$

where $d$ is the position of the dividing surface. The Heaviside function, $\theta$, is by definition, unity when the argument is positive and zero when the argument is negative. Here $a < d < b$. All excess properties of a surface can be given by integrals like Eq. (19).

The equimolar surface of component $i$ is a special choice of the dividing surface. The location is such that the surplus of moles of the component on one side of the surface is equal to the deficiency of moles of the component on the other side of the surface. The vertical line is drawn so that the areas between the curve and the bulk densities are the same, see Fig. 3a. The position, $d$, of the equimolar surface obeys therefore:

$$\int_a^d [c_i(x,y,z) - c_i^g(a,y,z)] \theta(y-d-x) - c_i^l(b,y,z) \theta(x-d)] \, dx = -\int_b^c [c_i(x,y,z) - c_i^g(b,y,z)] \, dx$$  \quad (20)$$

According to Eqs. (19) and (20), $\Gamma_i=0$, when the surface has this position. In a multi-component systems, each component has its “equimolar” surface, but we have to make one choice for the position. We choose the position of the surface as the equimolar surface of the reference component $i$, here component 1. This component has then no excess concentration, while another component $j$ (here component 2), has an excess concentration.

6. Simulations

To obtain the equilibrium properties of the system, the liquid–vapor interface was obtained for seven different temperatures ranging between $T=0.55$ and 0.85. For each temperature, the overall density of the system was kept constant ($\mu=0.2$) while the overall composition of the mixture was varied between $X_1=0.0$ (pure component 2) and $X_1=1.0$ (pure component 1), where $X_1$ is the global mole fraction of component 1. Moreover, in order to increase statistics and avoid dependences on initial conditions, each equilibrium point was computed by averaging results of five simulations starting from five different initial configurations. An overview of the simulated conditions is presented in Table 2.

7. Results and discussion

7.1. Equilibrium properties of the homogeneous phases

Fig. 4a gives the phase diagrams for pure components 1 and 2 in reduced units. For both systems, the molar density difference was fitted to the curve for the coexisting liquid and vapor using the following expression:

$$\rho_i - \rho_v = \rho_0 (\frac{T_c,i- T}{T_c,i})^\beta$$  \quad (21)$$

The universal exponent is $\beta=0.32$ and $\rho_0$ is a system-dependent constant for which we found 1.09 in reduced units. Previously we obtained $\rho_0=1.08 \pm 0.02$ (Ge et al., 2007). The formula applies only close to the critical point (Widom, 1965; Sengers and Jin, 2007). We found here a good fit in a rather wide temperature range; 0.9–0.7 for component 1 and 0.8–0.4 for component 2. The good fit in a wide range may be accidental, and due to the particular system. From the fittings, which are presented in Fig. 5a, we found the critical temperatures for the pure components, $T_{c,1}=1.12$ and $T_{c,2}=0.897$. This corresponds to $T_{c,1}=138.9$ K and $T_{c,2}=111.1$ K in real units. They are rather different from those

<table>
<thead>
<tr>
<th>Sim. no.</th>
<th>$T^*$</th>
<th>$X_1$</th>
</tr>
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<tbody>
<tr>
<td>1–7</td>
<td>0.55</td>
<td>0.0/0.1/0.3/0.5/0.7/0.9/1.0</td>
</tr>
<tr>
<td>8–14</td>
<td>0.6</td>
<td>0.0/0.1/0.3/0.5/0.7/0.9/1.0</td>
</tr>
<tr>
<td>15–21</td>
<td>0.65</td>
<td>0.0/0.1/0.3/0.5/0.7/0.9/1.0</td>
</tr>
<tr>
<td>22–28</td>
<td>0.7</td>
<td>0.0/0.1/0.3/0.5/0.7/0.9/1.0</td>
</tr>
<tr>
<td>29–42</td>
<td>0.75</td>
<td>0.0/0.1/0.3/0.5/0.7/0.9/1.0</td>
</tr>
<tr>
<td>43–49</td>
<td>0.8</td>
<td>0.0/0.1/0.3/0.5/0.7/0.9/1.0</td>
</tr>
<tr>
<td>50–56</td>
<td>0.85</td>
<td>0.0/0.1/0.3/0.5/0.7/0.9/1.0</td>
</tr>
</tbody>
</table>
the system we mentioned for comparison, as n-hexane, for instance, has a critical temperature of 507.43 K (Grigoyev et al., 2006). The system is thus only a model mixture. The phase diagrams for mixtures with global mole fractions \( X_1 \) between 0.1 and 0.9 are shown in Fig. 4b. In our case \( r_{C_1} = r_{C_2} = 11,280 \text{mol/m}^3 \). When the results were plotted with scaled densities, \( r_{CS} = r_{C} \) (not shown), the phase diagrams coincided. This means that the law of corresponding states applies.

The critical temperatures of the mixtures at given overall mole fractions, \( X_i \), were obtained fitting the surface tension of the liquid–vapor interface to the equation of state of the surface (26) (see Section 7.2 for details). The critical temperatures obtained with this procedure were used in Eq. (21) to fit the coexistence curve data (see Fig. 5b) and gave better results than using Kay’s rule to obtain the critical temperatures (Reid et al., 1977), see more details below.

Fig. 6 gives the reduced vapor pressure \( P_i^* \) of pure components 1 and 2 as a function of the reduced temperature \( T^* \). The value of \( P_i^* \) was expressed as a unique function of the temperature using Clausius–Clapeyron’s equation for ideal gas

\[
P_i^*(T) = P_0^i \exp\left( -\frac{A_{\text{vap}}H_i}{RT} \right)
\]

where \( A_{\text{vap}}H_i \) is the enthalpy of vaporization per mole and \( P_{0,1} \) is an integration constant. Fitting this formula to the equilibrium points we found \( P_{0,1} = 27.1 \pm 1 \), \( P_{0,2} = 27.1 \pm 1 \), \( A_{\text{vap}}H_1 = 6490 \pm 50 \) J/mol and \( A_{\text{vap}}H_2 = 5190 \pm 50 \) J/mol. In our previous work for evaporation of one-component system (Ge et al., 2007) we found \( A_{\text{vap}}H = 6490 \pm 80 \) J/mol. We obtained the following values for the critical pressures: \( P_{c,1} = P_1(T_{c,1}) = 42.6 \times 10^5 \text{Pa} \) and \( P_{c,2} = P_2(T_{c,2}) = 34.1 \times 10^5 \text{Pa} \).

Since the two components have a LJ potential with the same cut-off radius, the critical pressure, temperature and the vaporization enthalpy of one component can also be obtained from those of the second component using the following formula:

\[
T_{c,2} = T_{c,1} \left( \frac{\epsilon_2}{\epsilon_1} \right)^{\frac{1}{3}}
\]

\[
P_{c,2} = P_{c,1} \left( \frac{\epsilon_2}{\epsilon_1} \right) \left( \frac{\sigma_1}{\sigma_2} \right)^3
\]

\[
A_{\text{vap}}H_2 = A_{\text{vap}}H_1 \left( \frac{\epsilon_2}{\epsilon_1} \right)^{\frac{3}{2}}
\]

(23)
In our case \( \sigma_2 = \sigma_1 \) and \( \rho_2 = 0.8 \rho_1 \), so we have \( T_C = 0.8 T_{C1} \), \( P_C = 0.8 P_{C1} \) and \( A_{vap} H_2 = 0.8 A_{vap} H_1 \). These relations are indeed confirmed from the results of the simulations performed independently on the two pure fluids.

The SRK equation of state (6) was used to calculate the pressure of the gas bulk phase at different compositions. The parameters \( A \) and \( B \) of the SRK equation of state were calculated using Eqs. (7)–(10). We can notice that \( B_1 = B_2 \), so \( B \) was independent of the composition, while \( A \) depended both on the composition and on the temperature. In Fig. 7 a comparison between the equilibrium pressure obtained from the simulations (cf. Eq. (4) averaged over the gas layers) and the gas pressure calculated with the SRK equation of state is plotted as a function of the vapor composition \( y_1 \) for different temperatures. The agreement is quite good especially at low temperatures. The SRK-equation of state becomes useful for studies of systems away from equilibrium, as it helps us to determine the chemical driving forces (Røsjorde et al., 2001).

The liquid–vapor equilibrium data for different temperatures are reported in Table 3. Fig. 8 shows the pressure of the binary mixture for three given temperatures (\( T^* = 0.6, 0.7 \) and 0.8) as a function of the mole fraction of component 1 in the liquid \( (x_1) \) and in the vapor \( (y_1) \). The points represent the simulation results and the lines are the result of the fitting procedure.

The results shown in Figs. 4–8 document the two homogeneous phases. They define the liquid–vapor phase equilibrium. We can see that a perfectly normal variation is obtained. The results for the homogeneous phases do not give new insight, but the reasonable properties, add credibility to the method used and to the results that we report for the surface properties below. For clarity, a summary of the values of the properties obtained for our system are reported in Table 4. For comparison, the same properties are calculated for the n-hexane (1)–cyclo-hexane (2)-like system.

### 7.2. The equilibrium properties of the surface

The extension of the surface is an issue of discussion. To define it, the density profile was analyzed. On the gas side, the surface was taken to start in the last layer for which the density was given by the SRK equation of state. The next layer registered deviation of 5% of the density from the value given by the SRK equation. On the liquid side, an appropriate equation of state was not found. Since the transition between the liquid and the surface is rather abrupt, the start of the surface was done by visual inspection choosing the layer where the density deviated from the liquid density. This
procedure was first suggested for interfaces by Røsjorde et al. (2001).

Fig. 9 shows the density profiles of components 1 and 2 for simulation nos. 22–28 through the surface. It is common to find the position and the extension of a surface by fitting the density to a symmetric function like the hyperbolic tangent. In other works (Simon et al., 2004) the following empirical function was used:

$$\rho(x) = \frac{1}{2}(\rho^l + \rho^v) + \frac{1}{2}(\rho^l - \rho^v)\tanh\left(\frac{2(x-d)}{\delta}\right)$$

(24)

Here $$\rho^l$$ is the density of the bulk phase ($$l$$) or vapor ($$v$$), $$\delta$$ is a measure of the thickness of the surface, given by the difference $$\delta = a - b$$, corresponding respectively to the position of the boundary between the vapor and the interface and the boundary between the liquid and the interface, and $$d$$ is the position of the equimolar dividing surface, given by

$$\rho(d) = \frac{1}{2}(\rho^l + \rho^v)$$

(25)

While for component 1 the density variation is symmetric, the density variation of component 2 is not (cf. Fig. 3). In Fig. 10 the density profiles of the two components of an equimolar mixture at $$T = 87$$ K are fitted by Eq. (24). We notice that the fitting is quite good for component 1, but cannot be used to represent the density profile of component 2. Moreover, in both cases the thickness of the surface obtained by Eq. (24) is underestimated.

For pure components, the relationship between the surface tension and the surface temperature gives the equation of state of the surface cf. Xu et al. (2006) and Ge et al. (2007). The expression used for representing the surface tension data is derived from current understanding of the critical behavior of fluids. The asymptotic behavior of physical properties approaching the critical point can be represented by scaling laws with universal exponents and substance-dependent parameters (Widom, 1965; Miqueu et al., 2000). Thus, the vanishing of the surface tension on approaching the critical point can be described by

$$\gamma_s = \gamma_0(T_C - T)^{2\nu}$$

(26)

where $$\nu = 0.63$$ is a universal constant.² Fitting the results for pure components to Eq. (26) we obtained $$\gamma_{0,1} = 0.0339$$ N/m² and

$$\gamma_{0,2} = 0.0267$$ N/m². The value of the constant reported in our earlier work on component 1 was $$\gamma_0 = 0.0334$$ N/m² (Ge et al., 2007). Considering Eq. (26) as a two-parameter equation instead of keeping $$\nu = 0.63$$ constant, we obtained $$\nu_1 = 0.63$$, $$\nu_{0,1} = 0.0339$$ N/m² and $$\nu_2 = 0.62$$, $$\nu_{0,2} = 0.0263$$ N/m², which can be taken as a confirmation of the scaling law.

Fig. (26) was therefore used to fit the values of the surface tension versus the surface temperature for the mixtures, and to obtain the critical temperatures of the systems with global mole fraction ranging between 0.1 and 0.9. The values of the critical temperatures are plotted as a function of the composition in Fig. 11. We can observe that the linear relation between the critical temperature of $$T_{C,X_1}$$ of a binary mixture with the overall mole fraction of component 1 equal to $$X_1$$, given by Kay's rule ($$T_{C,X_1} = T_{C,1}X_1 + T_{C,2}(1-X_1)$$), Reid et al., 1977) is too simple to describe the surface tension for our systems. The critical temperatures of the mixtures (in K) were found instead to follow a rule of the type

$$T_{C,X_1} = T_{C,2} - 1.58X_1 + 29.25X_1^2$$

(27)

within less than 1% error in the fit. Sengers and Jin (2007) proposed to fit results for carbon dioxide and ethane to a fifth order polynomial. The fact that we obtain a good fit to a second order polynomial may be due to the simple system that is studied.

### Table 4

Summary of equilibrium properties for our system and for an n-hexane (1)–cyclo-hexane (2) system.

<table>
<thead>
<tr>
<th>Reduced units</th>
<th>Real units</th>
<th>Our system</th>
<th>n-hexane-cyclo-hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>$$\sigma_1$$</td>
<td>3.42 Å</td>
<td>5.909 Å</td>
<td></td>
</tr>
<tr>
<td>$$\sigma_1/\sigma_2$$</td>
<td>1</td>
<td>1.031</td>
<td></td>
</tr>
<tr>
<td>$$\rho_0$$</td>
<td>1.09 g/cm³</td>
<td>45.269 g/cm³</td>
<td>8777 mol/m³</td>
</tr>
<tr>
<td>$$T_C,1$$</td>
<td>1.12 K</td>
<td>138.9 K</td>
<td>462.6 K</td>
</tr>
<tr>
<td>$$T_C,2$$</td>
<td>0.90 K</td>
<td>111.1 K</td>
<td>362.9 K</td>
</tr>
<tr>
<td>$$P_{a,1}$$</td>
<td>27.44 Pa</td>
<td>11.77 × 10³ Pa</td>
<td>7.58 × 10³ Pa</td>
</tr>
<tr>
<td>$$P_{a,2}$$</td>
<td>21.95 Pa</td>
<td>9.40 × 10³ Pa</td>
<td>5.95 × 10³ Pa</td>
</tr>
<tr>
<td>$$P_{c,1}$$</td>
<td>0.10 Pa</td>
<td>42.6 × 10³ Pa</td>
<td>27.5 × 10³ Pa</td>
</tr>
<tr>
<td>$$P_{c,2}$$</td>
<td>0.08 Pa</td>
<td>34.1 × 10³ Pa</td>
<td>19.7 × 10³ Pa</td>
</tr>
<tr>
<td>$$A_{opp}M_1$$</td>
<td>6.29 g/mol</td>
<td>6490 J/mol</td>
<td>21 610 J/mol</td>
</tr>
<tr>
<td>$$A_{opp}M_2$$</td>
<td>5.03 g/mol</td>
<td>5190 J/mol</td>
<td>17 290 J/mol</td>
</tr>
</tbody>
</table>

---

² In our previous works (Røsjorde et al., 2000; Xu et al., 2006; Ge et al., 2007) we accidentally used $$\nu_2 = 1.26$$ as exponent. The present form of Eq. (26) with $$2\nu = 1.26$$ is according to common practice (Rowlinson and Widom, 1982).
The fit was equally good using

$$T_{C,X} = X_1 T_{C,1} + (1-X_1) T_{C,2} + K X_1 (1-X_1) \sqrt{T_{C,1} T_{C,2}}$$  \hspace{1cm} (28)$$

with $K=1.78$, using all data. Fig. 12 shows the surface tension as a function of the surface temperature for different system compositions. The points are the results of our simulations, while the lines come from the fitting to Eq. (26).

Guggenheim (1945) formulated and tested an idea for a generalized principle of corresponding states, which was independent of any specific equation of state. In addition to the pressure as a function of temperature and density, he found other properties, such as the surface tension, to follow a law of corresponding-states, when expressed in suitably reduced units. The law of corresponding-states was shown to hold rigorously for families of fluids for which the interaction potential is spherically symmetric and characterized by only two parameters, one of which sets the energy scale, the other one the characteristic length scale of the fluid model (Hill, 1960). The Lennard-Jones potential is a famous example of such a potential and we expect it to be valid for the pure components in our system.

Following this, we plotted in Fig. 13 the corresponding-state surface tension $\gamma_{CS}=\gamma_s/(\rho_{CS}^2 kT_{CS})$ versus the corresponding-state surface temperature $T_{CS}=T_s/T_{C,1}$ for the pure components 1 and 2. Here $\rho_{CS}$ is the critical density of pure component $i$. In our case $\rho_{C,1}=\rho_{C,2}=11.280$ mol/m$^3$. We observe that although the two components are characterized by different critical temperatures and surface tensions, when the results are plotted in CS units they are aligned, see Fig. 13. This shows again that the principle of corresponding-states for the surface tension holds for the pure components.

The data do not have sufficient accuracy to study properties around the critical point further, even if all fits were made within 8% accuracy, and often within 2 or even 1%.

For a mixture, the equation of state of the surface is given by the relationship between the surface tension, the surface temperature and surface excess concentration. We defined the equimolar surface choosing component 1 as reference component. So we calculated the surface excess concentration of component 2 as well. Fig. 14 shows the surface tension as a function of the surface excess concentration of component 2 for different surface temperatures.

In the present investigation, the surface tension is a decreasing function of the surface temperature and of the excess concentration of component 2 as well.

The decrease in the surface tension with the temperature is normal, also for pure liquids, as one approaches the critical point, where the surface tension vanishes cf. Eq. (26). The surface entropy is given by minus the derivative of the surface tension with respect to the surface temperature and is equal to

$$s_s = s_0 \left( \frac{T_s-T}{T_c} \right)^{2\nu-1}$$  \hspace{1cm} (29)$$
where \( s_0 = 2n_0 / T_C \). We found \( s_{0,1} = s_{0,2} = 3.06 \times 10^{-4} \text{J/K m}^2 \) for the pure component fluids. In our earlier paper we obtained the same value (Ge et al., 2007). In Fig. 15 we plotted the surface entropy as a function of the surface temperature in cases where we have pure fluids. The simulation results were fitted to Eq. (29). The surface entropy variation with temperature is the same, for pure fluids as well as mixtures, see Fig. 16. It is a consequence of the behavior of the surface tension up to the critical point. We can see from the temperature plots already, that the present surface excess entropy is dominated by the presence of excess of component 2. The variation leads to a negative surface excess heat capacity \( C_\Omega \), as we can observe in Fig. 17. Using the formula (29),

\[
C_\Omega = T \frac{d s_0}{dT} = -C_{\Omega,0} \left( \frac{T_C - T}{T_C} \right)^{2n-2}
\]

we find

\[
C_\Omega = T \frac{d s_0}{dT} = -C_{\Omega,0} \left( \frac{T_C - T}{T_C} \right)^{2n-2}
\]

where \( C_{\Omega,0} = (2n-1)s_0 / T_C \). A negative excess heat capacity means that the surface heat capacity (at constant area) is smaller than the heat capacities of the neighboring phases, or that the surface is less able to store energy than the surroundings.

The excess concentration of component 2 is interesting, in particular the observed peaks in the concentration exhibited by
this component. This component is always enriched in the vapor phase compared to the liquid phase. It is more volatile, due to its smaller potential depth. A picture of the mole fraction of component 2 through the surface (not shown) does not have a peak. This implies that both densities first increase proportionally from the vapor to the liquid, until at a certain point the density of the 2nd component starts to lag behind. The integral over the peak in Fig. 9 gives the excess concentration of component 2, see Eq. (19). Component 2, with the smaller potential well, is thus attracted to the side of the surface facing the vapor. The excess of component 2 (the excess density of component 1 is zero) is thus due to a difference in density variations in the two components through the surface. To the best of our knowledge, density functional theory does not seem to find a peak in the concentration of components. The plots of the surface entropy as a function of the surface excess concentration of component 2 at different temperature are shown in Fig. 18. This plot is interesting in this context. The figure shows that the surface entropy is very sensitive to component 2. As soon as component 2 is introduced in the mixture, the surface entropy drops dramatically to lower levels.

The surface entropy drops in this manner as the surface excess concentration of component 2 increases, especially at higher temperatures. This dependency means that the surface becomes less stable as component 2 accumulates in the surface, or as the temperature rises. The surface entropy variation with the excess of component 2 for this particular system must be a consequence of the difference in potential depths, and the surface as a thermodynamic system is highly non-ideal. This is surprising, as there are no structural differences between the particles in our case. They are both spherical. An explanation for the excess enthalpy must therefore also have its origin in the difference in potential depths, and the surface excess properties.

8. Conclusions

We have seen that a particular Lennard-Jones binary mixture is well behaved and have thermodynamic properties that describe the coexisting liquid and vapor in familiar and universal terms. Through molecular dynamics simulations we have been able to find also a complete set of thermodynamic properties for the molecularly thick interface between the liquid and the vapor. The interface can be understood as a two-dimensional thermodynamic system, with excess properties derived according to Gibbs. We have shown that the surface tension varies according to a universal critical exponent and follows the laws of corresponding states with an accuracy between 2% and 8%. From the surface tension, we found the critical temperature of the mixtures, the entropy and the heat capacity at constant area. The procedure may be useful for predicting similar properties of mixtures. In particular for interfaces such information is scarcely known.

It is interesting that the interface has less ability to store energy than the homogeneous phases, as the temperature increases, and that the more volatile component accumulates close to the vapor side of the surface. These properties might well be decisive for transports across the interface, a topic we shall study next.

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References


