Supporting Information for “Hyperscaling relation between the interfacial tension of liquids and their correlation length near the critical point”

E. Mayoral\textsuperscript{a1}\textsuperscript{*} and A. Gama Goicochea\textsuperscript{b2}\textsuperscript{*}

\textsuperscript{a} Instituto Nacional de Investigaciones Nucleares, Carretera México-Toluca s/n, La Marquesa Ocoyoacac, 52750 Estado de México, Mexico

\textsuperscript{b} Instituto de Física, Universidad Autónoma de San Luis Potosí, Av. Álvaro Obregón 64, 78000 San Luis Potosí, Mexico.

1. The DPD forces

The dissipative particle dynamics (DPD) algorithm [S1] is in essence the same as that of traditional, microscopic molecular dynamics: Newton’s second law of motion is solved for the total force acting on each particle using finite time steps to calculate the momenta and positions of each particle at each time step. The main distinction between DPD and atomistic simulations is that the force acting between any two particles \( i \) and \( j \) in DPD is given not only by a conservative force \( F_{ij}^C \), but also by dissipative \( F_{ij}^D \), and random \( F_{ij}^R \) forces. The total force acting on any given pair of particles is the sum of these three forces. The conservative force is modeled as a soft, short range linearly decaying repulsion:

\[
F_{ij} = \sum_{i \neq j}^N \left[ F_{ij}^C + F_{ij}^D + F_{ij}^R \right].
\]

(S1)

The conservative force is given by a soft, linearly decaying repulsion:

\[
F_{ij}^C = \begin{cases} 
  a_{ij}(1 - r_{ij}) \hat{r}_{ij} & r_{ij} \leq r_c \\
  0 & r_{ij} > r_c 
\end{cases}
\]

(S2)

\textsuperscript{1} Electronic mail: emayoral@inin.gob.mx

\textsuperscript{2} Electronic mail: agama@alumni.stanford.edu
where \( \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j \), \( |\mathbf{r}_{ij}| \) is the magnitude of the relative position between particles \( i \) and \( j \), and \( \alpha_{ij} \) is the intensity of the repulsion between a pair of particles. The dissipative and the random forces are, respectively:

\[
F_{ij}^D = -\gamma \omega^D (r_{ij}) \hat{r}_{ij} \cdot \mathbf{v}_{ij} \hat{r}_{ij} \quad \text{(S3)}
\]

\[
F_{ij}^R = \sigma \omega^R (r_{ij}) \xi_{ij} \hat{r}_{ij} \quad \text{(S4)}
\]

where \( \sigma \) is the noise amplitude and \( \gamma \) is the friction coefficient and they are related in a way as follows: \( k_B T = \sigma^2 / 2\gamma \); \( k_B \) is the Boltzmann’s constant and \( T \) the absolute temperature, \( \mathbf{v}_i = \mathbf{v}_i - \mathbf{v}_j \) is the relative velocity between the particles, and \( \xi_{ij} = \xi_{ji} \) is a random number uniformly distributed between 0 and 1 with Gaussian distribution and unit variance. The weight functions \( \omega^D \) and \( \omega^R \) depend on distance and vanishing for \( r > r_c \), usually they are chosen for computational convenience to be (see [S1]):

\[
\omega^D (r_{ij}) = [\omega^R (r_{ij})]^2 = \max \left\{ \left( 1 - \frac{r_{ij}}{r_c} \right)^2, 0 \right\}. \quad \text{(S5)}
\]

All forces between particles \( i \) and \( j \) vanish further than a finite cutoff radius \( r_c \), which represents the inherent length scale of the DPD model and it is regularly chosen as the reduced unit of length, \( r_c = 1 \). We chose \( \sigma = 3 \) and \( \gamma = 4.5 \) so that \( k_B T = 1 \), and use the canonical ensemble, where the number of particles \( (N) \), temperature and volume \( (V) \) are kept constant [S2].

2. Temperature dependence of the DPD model

The standard procedure to choose the conservative force parameter for particles of the same type, \( a_{ii} \) in equation (S2), is given by

\[
a(T)_{ii} = \left[ \frac{\kappa^{-1}(T)N_m - 1}{2\alpha \rho} \right] k_B T \quad \text{(S6)}
\]
where $\rho$ is the DPD number density, $N_m$ is the coarse-graining degree (number or water molecules grouped into a single DPD bead), and $\alpha$ is a numerical constant equal to 0.101 [S2]. The symbol $\kappa^{-1}$ is the inverse of the compressibility of the system. If we use a coarse-graining degree equal to 3 and take the compressibility of water at standard conditions, $\kappa^{-1} \approx 16$, the parameter in eq. (S6) is $a_{ii} = 78.3$ [S3]. The DPD conservative interaction parameter $a_{ij}$ at different temperatures is obtained from the following expression [S4]:

$$a(T)_{ij} = a(T)_{ii} + 3.27 \chi_{ij}(T),$$  \hspace{1cm} (S7)

with $\chi_{ij}(T)$ being the temperature dependent Flory–Huggins parameter:

$$\chi(T)_{ij} = \frac{v_{ij}}{RT} (\delta_i(T) - \delta_j(T))^2.$$  \hspace{1cm} (S8)

In eq. (S8) $\delta_i(T)$ is the solubility parameter of the $i$–component at the temperature $T$. Here $v_{ij}$ is the partial molar volume, and $\delta_i(T)$ is given by the square root of the cohesive energy density which in turn is given by the enthalpy of vaporization, $\Delta H^{VAP}$, and the molar volume, $V^0_i$ as follows ($R$ is the gas constant) [S4]:

$$\delta_i = \sqrt{\frac{\Delta E_{coh}}{V^0_i}} = \sqrt{\frac{\Delta H^{VAP} - RT}{V^0_i}}.$$  \hspace{1cm} (S9)

Substituting (S9) into (S8) we arrive at the following expression for the temperature dependent $a(T)_{ij}$ parameters [S4]:

$$a(T)_{ij} = a(T)_{ii} + 3.27 \frac{v_{ij}}{RT} (\delta_i(T) - \delta_j(T))^2.$$  \hspace{1cm} (S10)

Equation (S10) represents the only successfully tested procedure to obtain the temperature dependence of the interfacial tension between immiscible liquids within the DPD model, and therefore it is the route we have adopted here.

Solubility parameters as a function of several temperatures $\delta(T)$ for dodecane, dodecanol, hexanol, benzene and water were calculated using atomistic molecular dynamics...
simulations. The cohesive energy density $E_{coh}(T)$ and the $\delta(T)$ values were obtained from periodic cells of amorphous fluid structures constructed using the Amorphous Cell module of the Materials Studio suite [S5]. First, $NpT$ (constant particle number, pressure and temperature) dynamics simulations were performed to equilibrate the density of the system at the temperature of interest and then the Discover Molecular Dynamics engine [S5] was used to evolve the systems, generating statistically independent structures. The lateral dimension of the cubic simulation box was in all cases equal to 25 Å and the COMPASS force field [S6] was used to model the interatomic interactions. In the present work we follow the formulation of Groot and Warren [S2] and have taken like – like interaction parameters to be equal: $a(T)_{ii}= a(T)_{jj}$. The dimensionless number density $\rho^* = \rho r_c^3$ and interaction parameters $a^{\ast}_{ij} = a_{ij} r_c/k_B T$ were used. The total average density $\rho^* = 3.0$, the values of the dissipative and random force constants $\gamma = 4.5$ and $\sigma = 3$ were used to keep the temperature fixed, $k_B T^* = 1$. We used a reduced time step $\Delta t^* = \Delta t (k_B T/m r_c^2)^{1/2} = 0.03$ and the standard velocity - Verlet algorithm adapted for the velocity – dependent dissipative force of the DPD model [S7]. Periodic boundary conditions in all directions were imposed; the total number of DPD particles was 4500 in a cubic box with $L^* = 11.4$. We performed simulations of 25 blocks with $10^4$ time steps each and the properties of interest were calculated by averaging over the last 10 blocks. The systems studied are 50:50 binary mixtures of DPD particles of water/dodecane, water/dodecanol, water/benzene and water/hexanol, at temperatures in the range from $T = 298$ K up to $433$ K.

### 3. Coarse – graining procedure

The coarse graining of the molecules we modeled is as follows. Three water molecules are grouped into one DPD bead; dodecane and dodecanol are both grouped into linear chains of four DPD beads, while benzene and hexanol are both modeled by two DPD beads. In all cases DPD beads are joined by a harmonic spring with constant $k = 100.0$, and equilibrium distance $r_{eq}=0.1$ [S8], except water, which is monomeric. With these structures each DPD bead has a volume equal to 90 Å$^3$. Water is modeled as a DPD monomer. Dodecane and dodecanol are both modeled as four – DPD bead linear molecules, with each bead joined with the others using harmonic springs with constants $k_0 = 100.0$ and $r_0 = 0.7$. Benzene and hexanol are modeled as dimers joined also by the same type of springs. The interaction
parameters for beads of the same type are all set equal to $a_{ii} = 78.3$, regardless of the chemical nature of the bead. The values of the cross interaction parameters ($a_{ij}$ with $i \neq j$) can be found in the last column in Tables S1 – S4.

4. Interfacial tension

The interfacial tension is calculated using the following method. If the interface between the liquids is found to be on the $xy$–plane, then one can calculate it from time averages over the simulations using the expression:

$$
\sigma(T) = \frac{1}{2} \int_{-L_z/2}^{L_z/2} \left[ \langle P_{zz}(T) \rangle - \frac{1}{2}\left( \langle P_{xx}(T) \rangle + \langle P_{yy}(T) \rangle \right) \right] dz,
$$

where $L_z$ is the length of the simulation box in the $z$–direction, the brackets indicate time average over the production phase of the simulation, and $P_{ii}(T)$ are the temperature dependent $ii$–components of the pressure tensor. The latter are calculated using the virial theorem route [S9], which provides kinetic and “potential” contributions to the pressure tensor. The components of the pressure tensor were calculated following the model of Irving and Kirkwood [S10], given as follows:

$$
P_{xx} = \sum_i m_i \vec{v}_i \cdot \vec{v}_i + \sum_i \sum_{j > i} F_{ijx} x_{ij}
$$

where the first sum is the kinetic contribution. The second term is the product of the $x$–component of the conservative DPD force acting between particles $i$ and $j$, and the $x$–component of the $r_{ij}$ vector (see eq. (S2)). The pressure tensor components $P_{yy}$ and $P_{zz}$ are obtained by replacing $y$ and $z$ by $x$ in eq. (S12), respectively. The temperature dependence is incorporated in the second term through the variation of the conservative force constant, as detailed in the previous section. There are periodic boundary conditions in all space directions, which leads to the formation of two interfaces perpendicularly to the $z$–axis,
hence the $\frac{1}{2}$ factor in front of the integral in eq. (S11). For a comparison of the performance of the Irving – Kirkwood method as compared with others, see for example [S11].

It is also important to point out that our simulations are relatively insensitive to finite size effects (FSE). In the past we have carried out extensive studies of the influence of finite size in the prediction of thermodynamic properties [S12] and non-equilibrium properties [S13], which demonstrate that the short range nature of the DPD interactions is responsible for this feature, which is another appealing aspect of the DPD model. As is shown in those references, the size of the simulation box we used is large enough to assure us that our calculations are relatively free of finite size effects. In fact, a detailed study of these FSE in the calculation of the components of the pressure tensor and interfacial tension showed [S12] that the interfacial tension calculated via the integration of the components pressure tensor is very insensitive to the size of the simulation box. In Fig.S1, which was prepared with data taken [S12], we show precisely how the interfacial tension between two simple, immiscible monomeric fluids behaves as a function of the size of the simulation box. In fact, the difference between the interfacial tension of the smallest and the largest boxes amounts to 0.8%, which would be undetectable experimentally. The reasons why the calculation of $\sigma^*$ is relatively free from FSE in DPD are the short range of the interactions and the symmetry of the box; cubic boxes are found to reduce FSE. Therefore we believe that the size of our systems is adequate to capture the essential thermodynamic behavior of the binary mixtures. By contrast, the calculation of $\sigma^*$ as a function of the size of the simulation box using the capillary wave method [S14] requires of much larger boxes to reach the thermodynamic limit value than those in Fig.S1.
5. Results

(a) Interfacial tension data for all binary mixtures at various temperatures

Here we provide additional detailed information such as the tables we used to generate all the figures in the main manuscript [S15], where we report the results for the solubility parameter $\delta (J/cm^3)$ for each component and the Flory-Huggins $\chi_{ij}$ and $a_{ij}$ DPD parameter calculation for benzene/water, hexanol/water, dodecanol/water, and dodecane/water systems at different $T$ (Tables S1 – S4), and the interfacial tension as at each temperature predicted from our simulations both in reduced DPD units and in dyn/cm (Table S5 – S8).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\delta_{\text{benzene}}$ (J/cm$^3$)</th>
<th>$\delta_{\text{water}}$ (J/cm$^3$)</th>
<th>$\chi_{ij}$</th>
<th>$a_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>19.2369</td>
<td>46.8461</td>
<td>5.5580</td>
<td>96.9936</td>
</tr>
</tbody>
</table>
Table S1. Solubility parameters for benzene/water at different $T$ calculated by atomistic simulations.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\delta_{\text{hexanol}}$ (J/cm$^3$)</th>
<th>$\delta_{\text{water}}$ (J/cm$^3$)</th>
<th>$\chi_{ij}$</th>
<th>$a_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>21.7408</td>
<td>48.259</td>
<td>5.5970</td>
<td>97.1298</td>
</tr>
<tr>
<td>283</td>
<td>21.598</td>
<td>47.7002</td>
<td>5.2311</td>
<td>95.8506</td>
</tr>
<tr>
<td>293</td>
<td>21.603</td>
<td>47.0798</td>
<td>4.8134</td>
<td>94.3900</td>
</tr>
<tr>
<td>298</td>
<td>21.5838</td>
<td>46.8461</td>
<td>4.6533</td>
<td>93.8301</td>
</tr>
<tr>
<td>303</td>
<td>21.0638</td>
<td>46.6109</td>
<td>4.6802</td>
<td>93.9245</td>
</tr>
<tr>
<td>313</td>
<td>21.0258</td>
<td>46.0648</td>
<td>4.3523</td>
<td>92.7778</td>
</tr>
<tr>
<td>323</td>
<td>20.8672</td>
<td>45.3419</td>
<td>4.0296</td>
<td>91.6494</td>
</tr>
<tr>
<td>333</td>
<td>20.5783</td>
<td>44.8825</td>
<td>3.8543</td>
<td>91.0366</td>
</tr>
<tr>
<td>343</td>
<td>20.4469</td>
<td>44.2196</td>
<td>3.5801</td>
<td>90.0777</td>
</tr>
</tbody>
</table>
Table S2. Solubility parameters for hexanol/water at different $T$ calculated by atomistic simulations.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\delta_{\text{dodecanol-head}}$ (J/cm$^3$)</th>
<th>$\delta_{\text{water}}$ (J/cm$^3$)</th>
<th>$\chi_{ij}$</th>
<th>$a_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>18.9763</td>
<td>46.8461</td>
<td>5.6634</td>
<td>97.3622</td>
</tr>
<tr>
<td>303</td>
<td>18.9547</td>
<td>46.6109</td>
<td>5.4849</td>
<td>96.7380</td>
</tr>
<tr>
<td>313</td>
<td>18.7722</td>
<td>46.0648</td>
<td>5.1710</td>
<td>95.6403</td>
</tr>
<tr>
<td>323</td>
<td>18.5153</td>
<td>45.3419</td>
<td>4.8412</td>
<td>94.4874</td>
</tr>
<tr>
<td>333</td>
<td>18.3676</td>
<td>44.8825</td>
<td>4.5874</td>
<td>93.5997</td>
</tr>
<tr>
<td>343</td>
<td>18.082</td>
<td>44.2196</td>
<td>4.3278</td>
<td>92.6921</td>
</tr>
<tr>
<td>373</td>
<td>17.4318</td>
<td>42.3669</td>
<td>3.6219</td>
<td>90.2241</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\delta_{\text{dodecanol-tail}}$ (J/cm$^3$)</th>
<th>$\delta_{\text{water}}$ (J/cm$^3$)</th>
<th>$\chi_{ij}$</th>
<th>$a_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>16.392</td>
<td>46.8461</td>
<td>6.7624</td>
<td>101.2049</td>
</tr>
<tr>
<td>303</td>
<td>16.2256</td>
<td>46.6109</td>
<td>6.6208</td>
<td>100.7097</td>
</tr>
<tr>
<td>313</td>
<td>16.0878</td>
<td>46.0648</td>
<td>6.2382</td>
<td>99.37189</td>
</tr>
<tr>
<td>323</td>
<td>15.9394</td>
<td>45.3419</td>
<td>5.8156</td>
<td>97.8942</td>
</tr>
<tr>
<td>333</td>
<td>15.5427</td>
<td>44.8825</td>
<td>5.6169</td>
<td>97.1995</td>
</tr>
<tr>
<td>343</td>
<td>15.4618</td>
<td>44.2196</td>
<td>5.2389</td>
<td>95.8780</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>$\delta_{\text{dodecanol-tail}}$ (J/cm$^3$)</td>
<td>$\delta_{\text{dodecanol-head}}$ (J/cm$^3$)</td>
<td>$\chi_{ij}$</td>
<td>$a_{ij}$</td>
</tr>
<tr>
<td>----------------</td>
<td>---------------------------------</td>
<td>---------------------------------</td>
<td>-------------</td>
<td>--------</td>
</tr>
<tr>
<td>298</td>
<td>16.392</td>
<td>18.9763</td>
<td>0.1965</td>
<td>78.2471</td>
</tr>
<tr>
<td>303</td>
<td>16.2256</td>
<td>18.9547</td>
<td>0.1679</td>
<td>78.1470</td>
</tr>
<tr>
<td>313</td>
<td>16.0878</td>
<td>18.7722</td>
<td>0.1693</td>
<td>78.1519</td>
</tr>
<tr>
<td>323</td>
<td>15.9394</td>
<td>18.5153</td>
<td>0.1634</td>
<td>78.1312</td>
</tr>
<tr>
<td>333</td>
<td>15.5427</td>
<td>18.3676</td>
<td>0.1655</td>
<td>78.1385</td>
</tr>
<tr>
<td>343</td>
<td>15.4618</td>
<td>18.082</td>
<td>0.1574</td>
<td>78.1104</td>
</tr>
<tr>
<td>373</td>
<td>14.8552</td>
<td>17.4318</td>
<td>0.1085</td>
<td>77.9393</td>
</tr>
</tbody>
</table>

**Table S3.** Solubility parameters for dodecanol-head/water, dodecanol-tail/water and dodecanol-head/dodecanol-tail at different $T$ calculated by atomistic simulations.
Table S4. Solubility parameters for dodecane/water at different $T$ calculated by atomistic simulations.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>298</th>
<th>303</th>
<th>313</th>
<th>323</th>
<th>333</th>
<th>343</th>
<th>373</th>
<th>383</th>
<th>393</th>
<th>413</th>
<th>453</th>
<th>466</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{DPD}$ (Units)</td>
<td>3.0725</td>
<td>3.0107</td>
<td>2.8174</td>
<td>2.6343</td>
<td>2.5758</td>
<td>2.3684</td>
<td>1.9244</td>
<td>1.7592</td>
<td>1.6389</td>
<td>1.3886</td>
<td>0.8249</td>
<td>0.6621</td>
</tr>
</tbody>
</table>

Table S5. Interfacial tension for dodecane/water system at different temperatures obtained by DPD simulations.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>298</th>
<th>303</th>
<th>313</th>
<th>323</th>
<th>333</th>
<th>373</th>
<th>393</th>
<th>433</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{DPD}$</td>
<td>2.3249</td>
<td>2.2730</td>
<td>2.0891</td>
<td>1.9133</td>
<td>1.8340</td>
<td>1.2752</td>
<td>1.0142</td>
<td>0.5179</td>
</tr>
<tr>
<td>$\gamma$ (dyn/cm)</td>
<td>23.0629</td>
<td>22.5478</td>
<td>20.7237</td>
<td>18.9802</td>
<td>18.1933</td>
<td>12.6499</td>
<td>10.0605</td>
<td>5.1374</td>
</tr>
</tbody>
</table>
Table S6. Interfacial tension for benzene/water system at different temperatures obtained by DPD simulations.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>273</th>
<th>283</th>
<th>293</th>
<th>298</th>
<th>303</th>
<th>313</th>
<th>323</th>
<th>333</th>
<th>343</th>
<th>373</th>
<th>383</th>
<th>393</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{\text{DPD}}$</td>
<td>1.9043</td>
<td>1.7121</td>
<td>1.4854</td>
<td>1.3890</td>
<td>1.3938</td>
<td>1.2052</td>
<td>0.9997</td>
<td>0.9215</td>
<td>0.7026</td>
<td>0.2944</td>
<td>0.2678</td>
<td>0.00765</td>
</tr>
</tbody>
</table>

Table S7. Interfacial tension for hexanol/water system at different temperatures obtained by DPD simulations.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>273</th>
<th>283</th>
<th>293</th>
<th>298</th>
<th>303</th>
<th>313</th>
<th>323</th>
<th>333</th>
<th>343</th>
<th>373</th>
<th>383</th>
<th>393</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{\text{DPD}}$</td>
<td>2.7492</td>
<td>2.2130</td>
<td>2.0229</td>
<td>1.9483</td>
<td>1.8218</td>
<td>1.6807</td>
<td>1.4940</td>
<td>1.3472</td>
<td>1.1815</td>
<td>0.7434</td>
<td>0.5106</td>
<td></td>
</tr>
</tbody>
</table>

Table S8. Interfacial tension for dodecanol/water system at different temperatures obtained by DPD simulations.
Figure S2. Solubility parameters for benzene, dodecanol, hexanol, and dodecane at different temperatures obtained by atomistic simulations. The inset shows the temperature dependence of the water solubility parameter obtained from atomistic simulations also.
Figure S3. Flory-Huggins parameter as a function of temperature for benzene/water, hexanol/water, dodecanol/water and dodecane/water.
\[ \sigma = 71.91 \left(1 - \frac{T}{489}\right)^{1.2} \]

\[ \sigma = 57.32 \left(1 - \frac{T}{486}\right)^{1.2} \]

\( \sigma \) vs \( T \)

(b) benzene/water

(c) hexanol/water
Figure S4. Interfacial tension for all the binary mixtures simulated, as a function of temperature, obtained from DPD simulations. (a) Dodecane/water interfacial tension. The exponent $\mu$ obtained from the best fit is $\mu = 1.20 \pm 0.07$; $T_c = 531 \pm 9$; $\sigma_0 = 81.79 \pm 0.02$; $R^2 = 0.99887$. (b) Benzene/water system. The best fit for the exponent yields $\mu = 1.2 \pm 0.1$; $T_c = 489 \pm 11$; $\sigma_0 = 71.91 \pm 0.03$. $R^2 = 0.99845$. (c) Hexanol/water interfacial tension. The best fit yields $\mu = 1.2 \pm 0.1$; $T_c = 468 \pm 9$; $\sigma_0 = 57.32 \pm 0.03$; $R^2 = 0.99719$. (d) Dodecanol/water interfacial tension. The exponent obtained from the best fit is $\mu = 1.3 \pm 0.3$; and $T_c = 543 \pm 38$; $\sigma_0 = 81.61 \pm 0.04$; $R^2 = 0.99934$. The data obtained from the simulations are shown in red circles; the lines represent the best fits.

(b) Density profiles and interfacial thickness of the binary mixtures at various temperatures

The correlation length $\xi$ is defined as the thickness of the interface, which in turn was obtained from the density profiles of the various mixtures, which were averaged over 10 blocks of $10^4$ time steps each. We chose this simple procedure because it includes the fluctuations induced by capillary waves. We remind the reader that all our simulations were carried out for cubic boxes of the same size, with lateral length $L^* = 11.4$ units. Now, although one expects $\xi$ to depend on $L^*$, as do most thermodynamic properties in any simulation including the interfacial tension, we do not expect Widom’s relation $\mu = \nu(d - 1)$ to depend strongly on $L^*$. However, such study goes beyond the scope of the present work.
- Density profiles for benzene/water at temperatures $T = 303, 373$ and $433$ K

![Graph](image-url)
Figure S5. Evolution of the density profiles for the mixture benzene/water at the indicated temperatures. The axes are shown in reduced DPD units.

In critical phenomena one there is no unique way to define the correlation length [S16]. The natural order parameter in our case is the density of the liquids, therefore it seems reasonable to define the correlation length as the thickness to the interface formed between the immiscible fluids. To calculate it we determine the point where the density of the liquid has achieved its bulk value, as shown in Fig. 3 of [S15]. We have also estimated that the uncertainty using the procedure amount to no more than 5%. Since the simulation box has the same size for all binary mixtures no size dependent artifacts are introduced by this method of calculating the correlation length.
- Interfacial thickness $\delta$ vs $T$ ($\delta$ = interface width) for benzene/water

![Graph showing the evolution of the thickness of the interface between benzene and water at different temperatures. The y-axis is expressed in reduced DPD units.](image)

**Figure S6.** Evolution of the thickness of the interface between benzene and water at different temperatures. The $y$-axis is expressed in reduced DPD units.

- $\ln \delta$ vs $\ln (1-T/T_c)$ for benzene/water
Figure S7. Scaling law of the thickness of the interface between benzene and water at different temperatures. The line represents the best fit, with the parameters given in the legend.

- Density profiles for dodecane/water at temperature $T = 303, 373$ and $466$ K
\[ \rho(T) = 373 \text{ K} \]

\[ \rho(x) = 303 \text{ K} \]

**Diagram:**

- Water (solid line)
- Dodecane (dotted line)

**Legend:**

- Water
- Dodecane

**Temperature:**

- $T = 373 \text{ K}$
- $T = 303 \text{ K}$
**Figure S8.** Evolution of the density profiles for the mixture dodecane/water at the indicated temperatures. The axes are shown in reduced DPD units.

- $\delta$ vs $T$ ($\delta$ = interface width) for dodecane/water

**Figure S9.** Evolution of the thickness of the interface between dodecane and water at different temperatures. The $y$ – axis is expressed in reduced DPD units.
- $\ln \delta$ vs $\ln (1-T/T_c)$ for dodecane/water

**Figure S10.** Scaling law of the thickness of the interface between dodecane and water at different temperatures. The line represents the best fit, with the parameters given in the legend.
Density profiles for dodecanol/water at temperatures $T = 303$ and $373$K

**Figure S11.** Evolution of the density profiles for the mixture dodecanol/water at the indicated temperatures. The axes are shown in reduced DPD units.

$\delta$ vs $T$ ($\delta$ = interface width) for dodecanol/water
Figure S12. Evolution of the thickness of the interface between dodecanol and water at different temperatures. The y-axis is expressed in reduced DPD units.

\[-\ln \delta \text{ vs } \ln (1-T/T_c)\] for dodecanol/water

Figure S13. Scaling law of the thickness of the interface between dodecanol and water at different temperatures. The line represents the best fit, with the parameters given in the legend.
- Density profiles for hexanol/water at temperatures $T = 323, 373$ and $433$ K.
Figure S14. Evolution of the density profiles for the mixture hexanol/water at the indicated temperatures. The axes are shown in reduced DPD units.

– \( \delta \) vs. \( T \) (\( \delta \) = interface width) for hexanol/water

Figure S15. Evolution of the thickness of the interface between hexanol and water at different temperatures. The y-axis is expressed in reduced DPD units.
- \( \ln \delta \) vs \( \ln (1-T/T_c) \) for hexanol/water

**Figure S16.** Scaling law of the thickness of the interface between hexanol and water at different temperatures. The line represents the best fit, with the parameters given in the legend.

**References**


[S5] See the web site [www.accelrys.com](http://www.accelrys.com) for full information.


[S15] E. Mayoral and A. Gama Goicochea, “Hyperscaling relation between the interfacial tension of liquids and their correlation length near the critical point”, manuscript submitted.