

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

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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:

The functional form of the forces interacting between any two particles i and j in DPD is given by a conservative force (F_{ij}^C), but also dissipative (F_{ij}^D), and random (F_{ij}^R) components [S1]. The total force is constituted by the sum of these three components:

$$F_{ij} = \sum_{i \neq j}^N [F_{ij}^C + F_{ij}^D + F_{ij}^R] \quad (S1)$$

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

$$F_{ij}^C = \begin{cases} a_{ij}(1 - r_{ij})\hat{r}_{ij} & r_{ij} \leq r_c \\ 0 & r_{ij} > r_c, \end{cases} \quad (S2)$$

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where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $r_{ij} = |\mathbf{r}_{ij}|$, $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$, r_{ij} is the magnitude of the relative position between particles i and j , and a_{ij} is the intensity of the repulsion between a pair of particles. The dissipative and the random forces are, respectively:

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

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

where σ is the noise amplitude and γ 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, $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ 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 ω^D and ω^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

$$a(T)_{ii} = [(\kappa^{-1}(T)N_m - 1)/2\alpha\rho]k_B T \quad (\text{S6})$$

where ρ is the DPD number density, N_m is the coarse-graining degree (number of water molecules grouped into a single DPD bead), and α is a numerical constant equal to 0.101 [S2]. The symbol κ^{-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]:

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

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

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

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, ΔH^{VAP} , and the molar volume, V_i^0 as follows (R is the gas constant) [S4]:

$$\delta_i = \sqrt{\frac{\Delta E_{coh}}{V_i^0}} = \sqrt{\frac{\Delta H^{VAP} - RT}{V_i^0}} \quad (S9)$$

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

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

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 $a^*_{ij} = a_{ij}r_c/k_B T$ 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 $\Delta t^* = \Delta t(k_B T/mr_c^2)^{1/2} = 0.03$ 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 \AA^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:

$$\sigma(T) = \frac{1}{2} \int_{-L_z/2}^{L_z/2} \left[\langle P_{zz}(T) \rangle - \frac{1}{2} \{ \langle P_{xx}(T) \rangle + \langle P_{yy}(T) \rangle \} \right] dz, \quad (\text{S11})$$

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:

$$P_{xx} = \sum_i m_i \vec{v}_i \cdot \vec{v}_i + \sum_i \sum_{j>i} F_{ijx}^C x_{ij} \quad (\text{S12})$$

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 σ^* 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 σ^* 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.

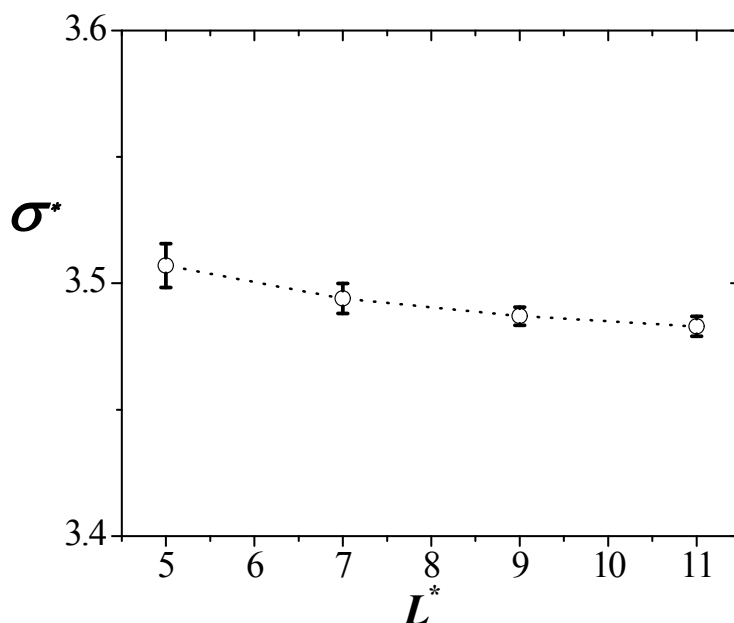


Fig. S1 Interfacial tension (σ^*) between two simple DPD fluids as a function of the size of the simulation box (L^*). Data taken from [S12]. Both axes are shown in reduced units.

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 δ (J/cm³) for each component and the Flory-Huggins χ_{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).

Temperature (K)	δ_{benzene} (J/cm ³)	δ_{water} (J/cm ³)	χ_{ij}	a_{ij}
298	19.2369	46.8461	5.5580	96.9936

303	18.9896	46.6109	5.4711	96.6896
313	18.784	46.0648	5.1665	95.6247
323	18.5978	45.3419	4.81150	94.3834
333	18.1248	44.8825	4.6718	93.8948
343	17.905	44.2196	4.3866	92.8977
373	17.1449	42.3669	3.7058	90.5172
393	16.6494	41.0549	3.2931	89.0745
433	15.6056	38.3861	2.6041	86.6654
453	15.1657	36.8452	2.2544	85.4425
466	14.8222	35.9156	2.0746	84.8138

Table S1. Solubility parameters for benzene/water at different T calculated by atomistic simulations.

Temperature (K)	δ_{hexanol} (J/cm ³)	δ_{water} (J/cm ³)	χ_{ij}	a_{ij}
273	21.7408	48.259	5.5970	97.1298
283	21.598	47.7002	5.2311	95.8506
293	21.603	47.0798	4.8134	94.3900
298	21.5838	46.8461	4.6533	93.8301
303	21.0638	46.6109	4.6802	93.9245
313	21.0258	46.0648	4.3523	92.7778
323	20.8672	45.3419	4.0296	91.6494
333	20.5783	44.8825	3.8543	91.0366
343	20.4469	44.2196	3.5801	90.0777

373	19.1703	42.3669	3.1345	88.5198
383	18.8675	41.7339	2.9664	87.9319
393	18.4683	41.0549	2.8206	87.4221
433	16.8749	38.3861	2.3220	85.6790

Table S2. Solubility parameters for hexanol/water at different T calculated by atomistic simulations.

Temperature (K)	$\delta_{\text{dodecanol-head}}$ (J/cm³)	δ_{water} (J/cm³)	χ_{ij}	a_{ij}
298	18.9763	46.8461	5.6634	97.3622
303	18.9547	46.6109	5.4849	96.7380
313	18.7722	46.0648	5.1710	95.6403
323	18.5153	45.3419	4.8412	94.4874
333	18.3676	44.8825	4.5874	93.5997
343	18.082	44.2196	4.3278	92.6921
373	17.4318	42.3669	3.6219	90.2241

Temperature (K)	$\delta_{\text{dodecanol-tail}}$ (J/cm³)	δ_{water} (J/cm³)	χ_{ij}	a_{ij}
298	16.392	46.8461	6.7624	101.2049
303	16.2256	46.6109	6.6208	100.7097
313	16.0878	46.0648	6.2382	99.37189
323	15.9394	45.3419	5.8156	97.8942
333	15.5427	44.8825	5.6169	97.1995
343	15.4618	44.2196	5.2389	95.8780

373	14.8552	42.3669	4.4091	92.9766
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Temperature (K)	$\delta_{\text{dodecanol-tail}}$ (J/cm ³)	$\delta_{\text{dodecanol-head}}$ (J/cm ³)	χ_{ij}	a_{ij}
298	16.392	18.9763	0.1965	78.2471
303	16.2256	18.9547	0.1679	78.1470
313	16.0878	18.7722	0.1693	78.1519
323	15.9394	18.5153	0.1634	78.1312
333	15.5427	18.3676	0.1655	78.1385
343	15.4618	18.082	0.1574	78.1104
373	14.8552	17.4318	0.1085	77.9393

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

Temperature (K)	δ_{dodecane} (J/cm ³)	δ_{water} (J/cm ³)	χ_{ij}	a_{ij}
298	16.392	46.8461	6.7624	101.2049
303	16.2256	46.6109	6.6208	100.7097
313	16.0878	46.0648	6.2382	99.37189
323	15.9394	45.3419	5.8156	97.8942
333	15.5427	44.8825	5.6169	97.1995
343	15.4618	44.2196	5.2389	95.8780
373	14.8552	42.3669	4.4091	92.9766

383	14.8733	41.7339	4.0932	91.8718
393	14.6147	41.0549	3.8651	91.0744
413	14.2085	39.8495	3.4590	89.6543
433	13.8208	38.3861	3.0282	88.1481
453	13.5009	36.8452	2.6139	86.6995
466	13.3296	35.9156	2.3786	85.8768
533	11.4343	26.2937	0.9001	80.70728909

Table S4. Solubility parameters for dodecane/water at different T calculated by atomistic simulations.

T (K)	298	303	313	323	333	343	373	383	393	413	453	466
γ DPD Units	3.0725	3.01	2.8174	2.6343	2.5758	2.3684	1.9244	1.7592	1.6389	1.3886	0.824 9	0.662 1
γ (dyn/cm)	30.479 2	29.902 8	27.948 2	26.132 3	25.551 8	23.494 1	19.090 5	17.450 8	16.257 9	13.775 3	8.1828	6.5675 6

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

T (K)	298	303	313	323	333	373	393	433
γ_{DPD}	2.3249	2.2730	2.0891	1.9133	1.8340	1.2752	1.0142	0.5179
γ (dyn/cm)	23.0629	22.5478	20.7237	18.9802	18.1933	12.6499	10.0605	5.1374

Table S6. Interfacial tension for benzene/water system at different temperatures obtained by DPD simulations.

T (K)	273	283	293	298	303	313	323	333	343	373	383	393
γ_{DPD}	1.9043	1.7121	1.4854	1.3890	1.3938	1.2052	0.9997	0.9215	0.7026	0.2944	0.2678	0.00765
γ (dyn/cm)	18.8907	16.9842	14.7355	13.7788	13.8264	11.9558	9.9175	9.1413	6.9698	2.9203	2.6564	0.0759

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

T (K)	273	283	293	298	303	313	323	333	343	373	393
γ_{DPD}	2.7492	2.2130	2.0229	1.9483	1.8218	1.6807	1.4940	1.3472	1.1815	0.7434	0.5106
γ (dyn/cm)	27.2717	21.9531	20.0669	19.3271	18.0721	16.6727	14.8206	13.3643	11.7207	7.3744	5.0657

Table S8. Interfacial tension for dodecanol/water system at different temperatures obtained by DPD simulations.

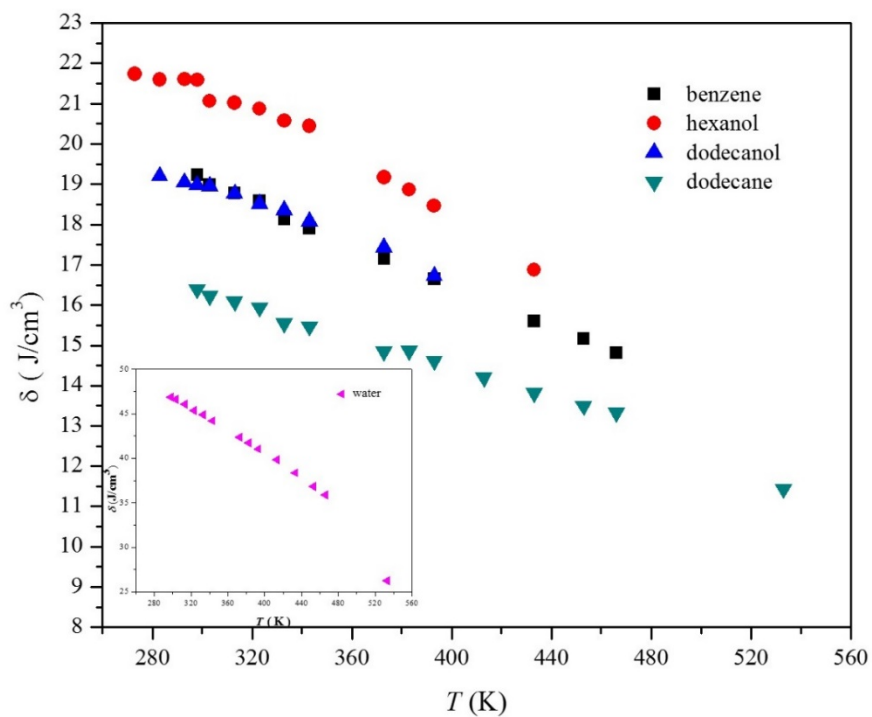


Figure S2. Solubility parameters for benzene, dodecanol, hexanol, and dodecane at different temperatures obtained by atomistic simulations. The inset shows the temperature dependence of the water solubility parameter obtained from atomistic simulations also.

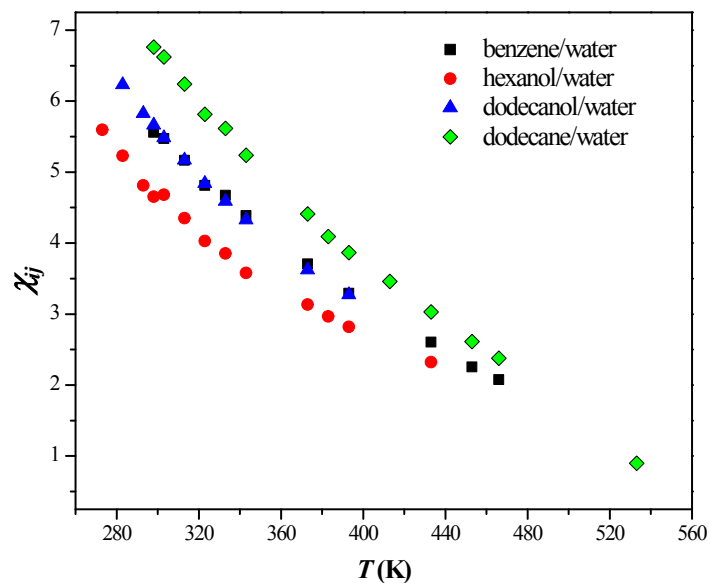
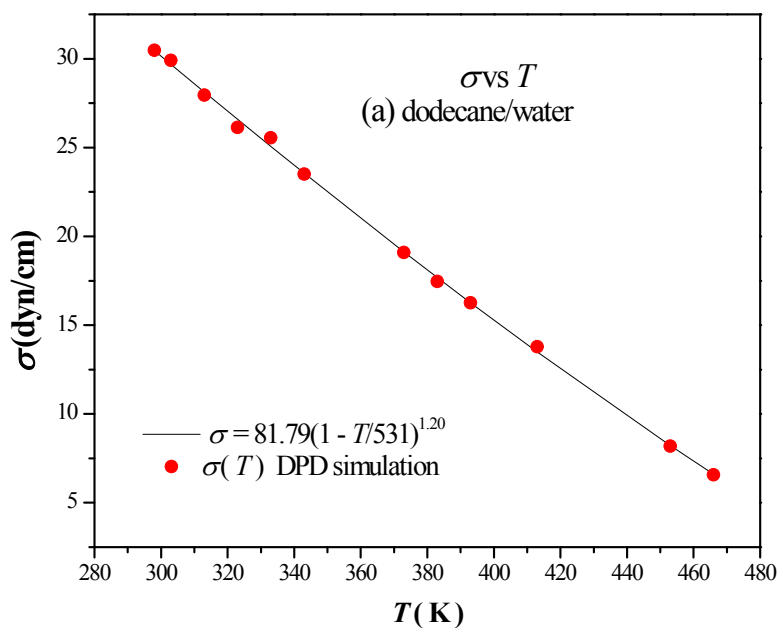
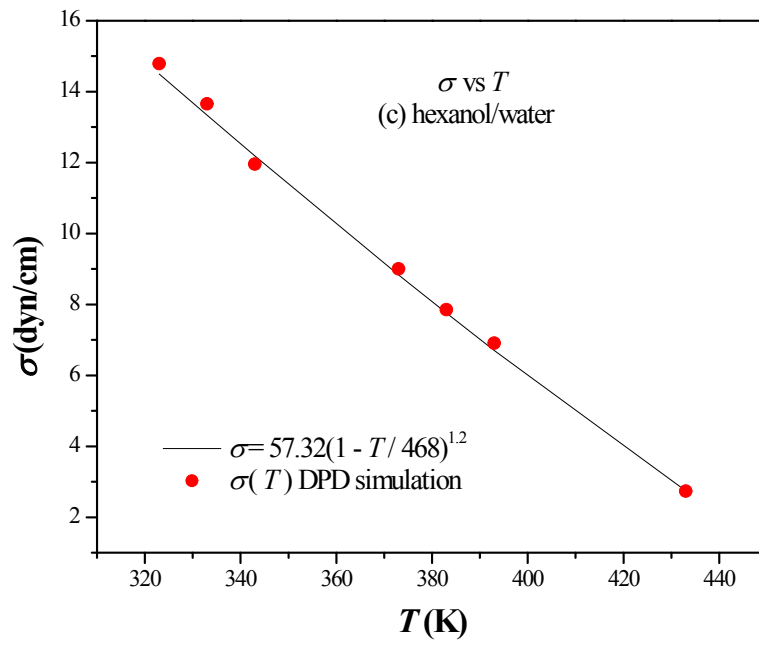
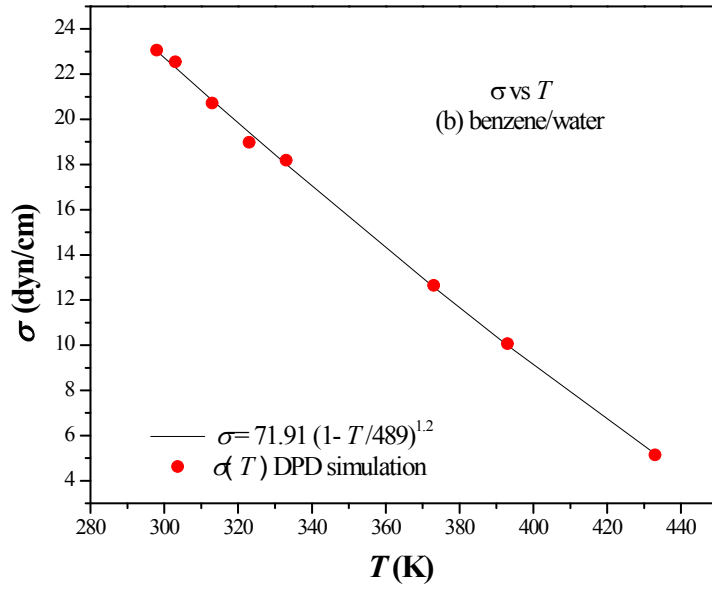


Figure S3. Flory-Huggins parameter as a function of temperature for benzene/water, hexanol/water, dodecanol/water and dodecane/water.





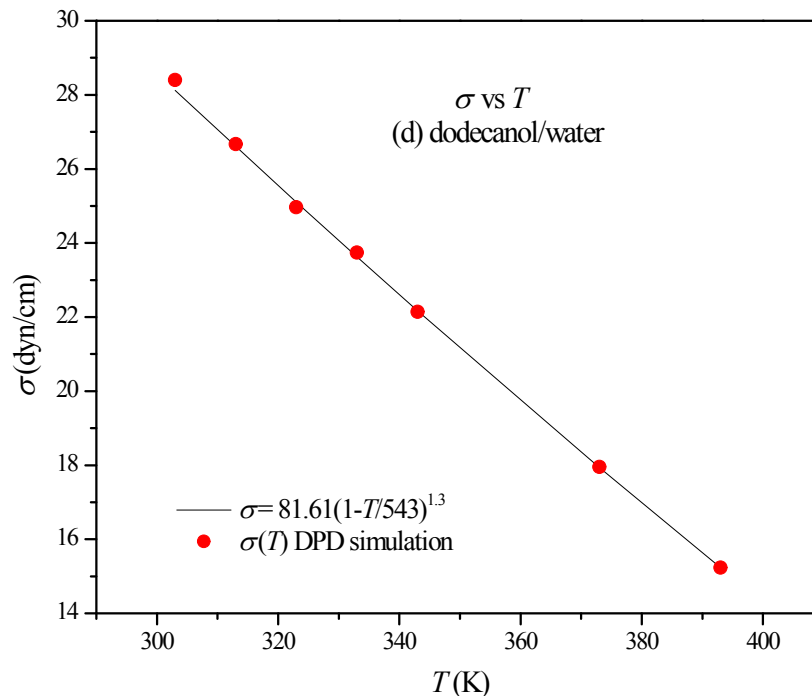
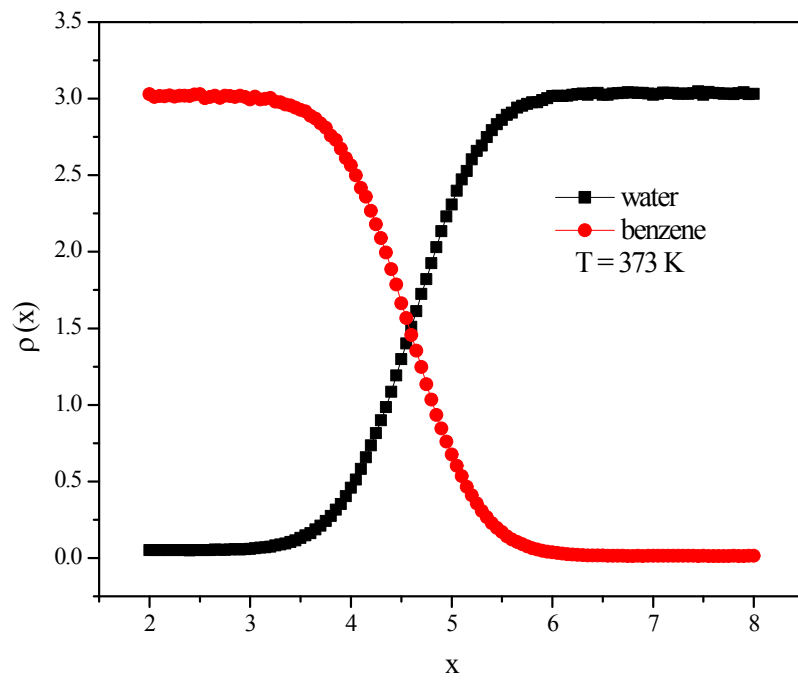
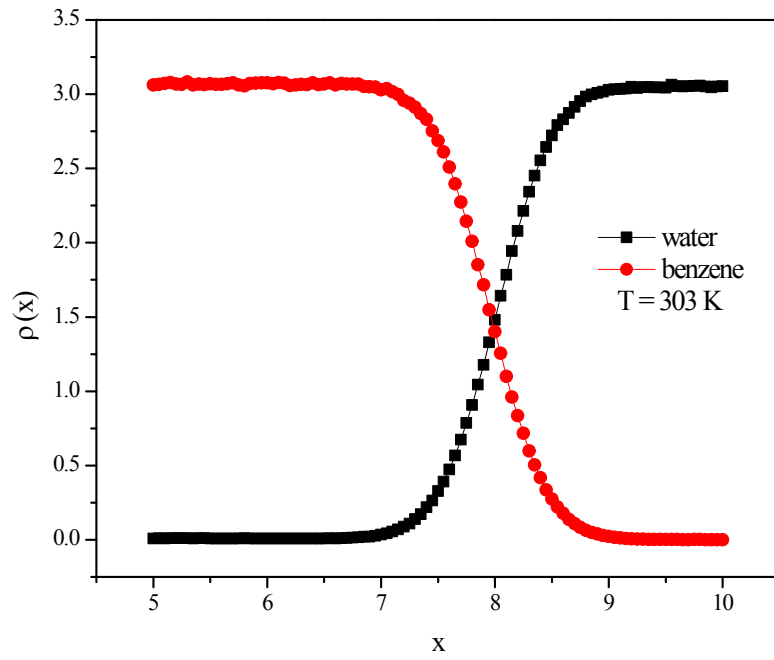


Figure S4. Interfacial tension for all the binary mixtures simulated, as a function of temperature, obtained from DPD simulations. (a) Dodecane/water interfacial tension. The exponent μ obtained from the best fit is $\mu = 1.20 \pm 0.07$; $T_c = 531 \pm 9$; $\sigma_0 = 81.79 \pm 0.02$; $R^2 = 0.99887$. (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 ξ 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 ξ 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



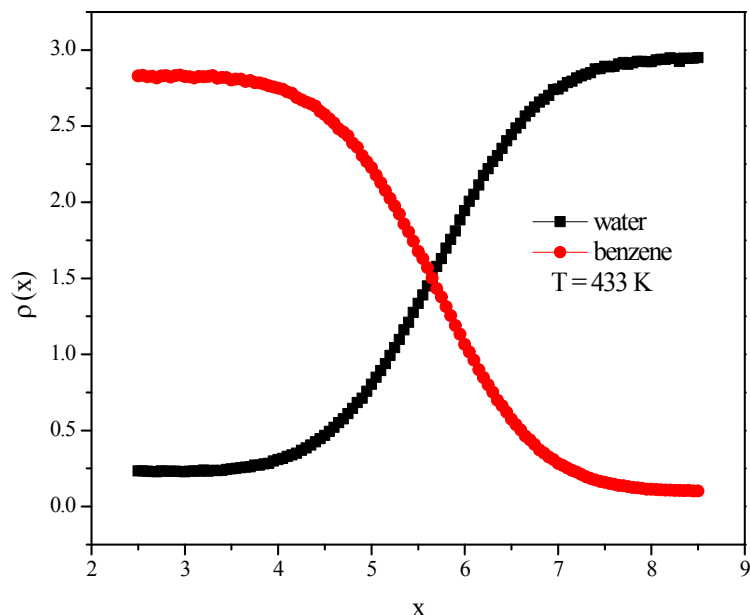


Figure S5. Evolution of the density profiles for the mixture benzene/water at the indicated temperatures. The axes are shown in reduced DPD units.

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 δ vs T (δ = interface width) for benzene/water

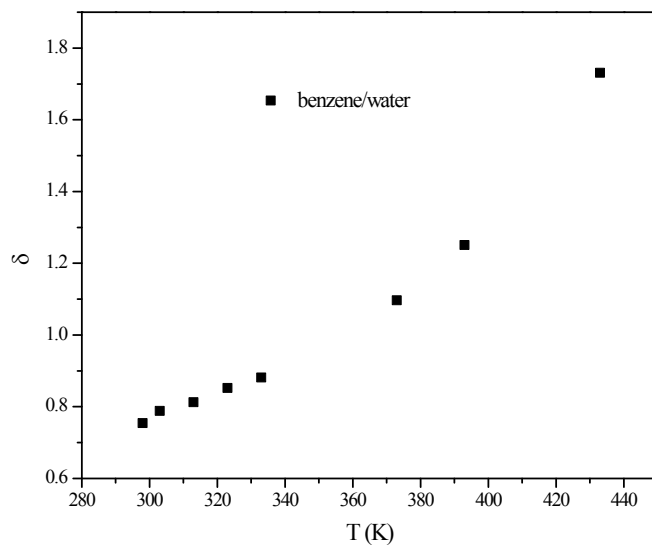


Figure S6. Evolution of the thickness of the interface between benzene and water at different temperatures. The y – axis is expressed in reduced DPD units.

- $\ln \delta$ vs $\ln (1-T/T_c)$ for benzene/water

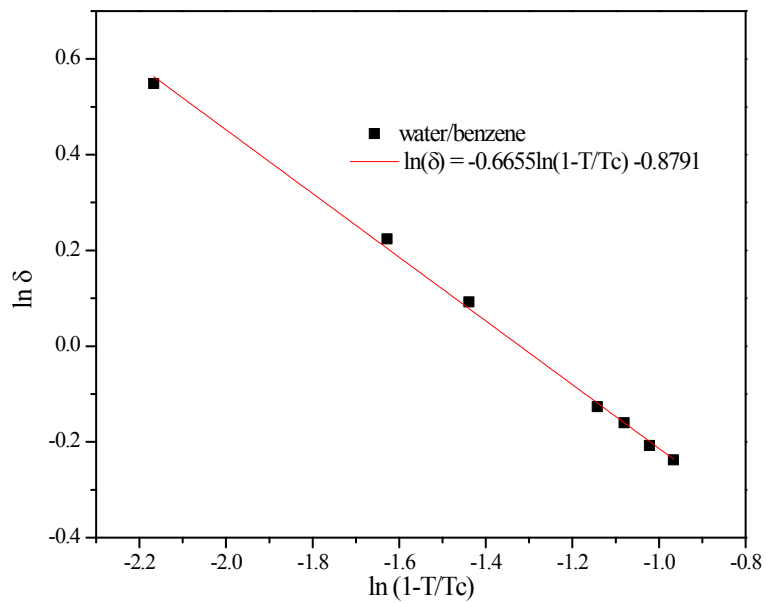
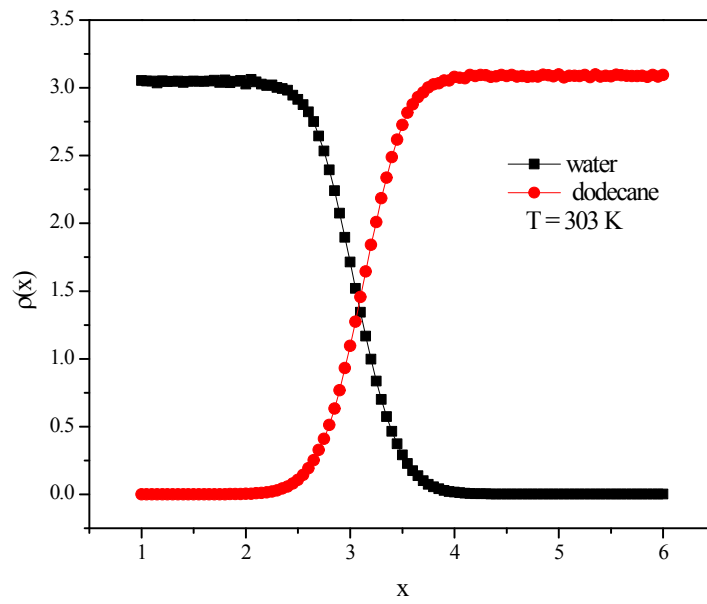
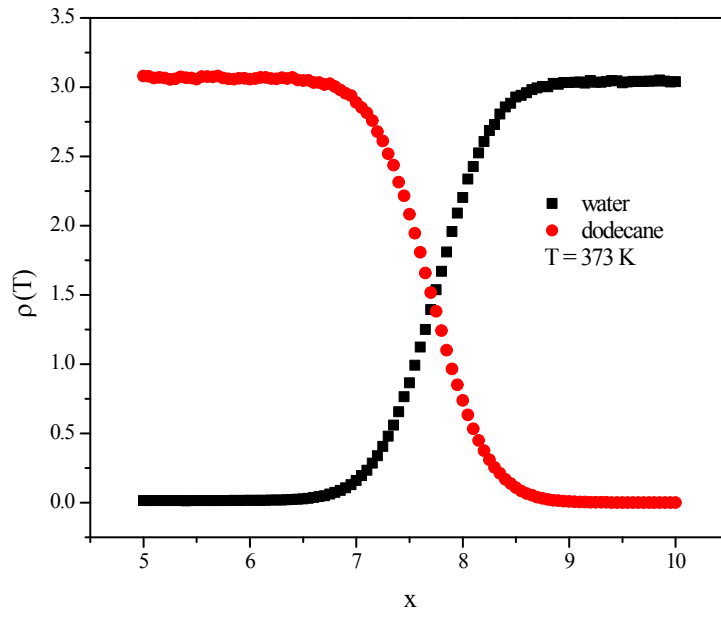


Figure S7. Scaling law of the thickness of the interface between benzene and water at different temperatures. The line represents the best fit, with the parameters given in the legend.

- Density profiles for dodecane/water at temperature $T = 303, 373$ and 466 K



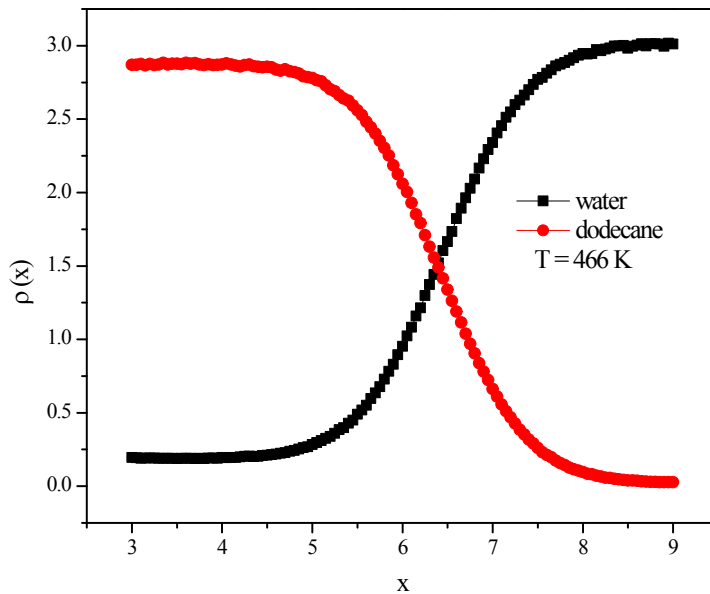


Figure S8. Evolution of the density profiles for the mixture dodecane/water at the indicated temperatures. The axes are shown in reduced DPD units.

– δ vs T (δ = interface width) for dodecane/water

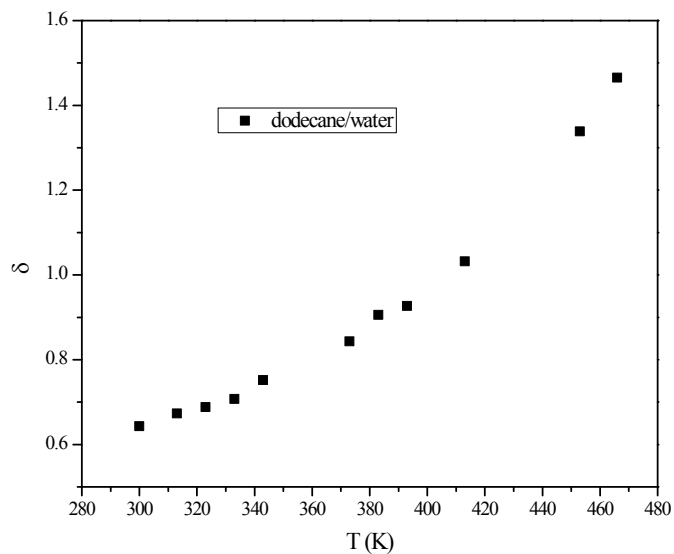


Figure S9. Evolution of the thickness of the interface between dodecane and water at different temperatures. The y – axis is expressed in reduced DPD units.

- $\ln \delta$ vs $\ln (1-T/T_c)$ for dodecane/water

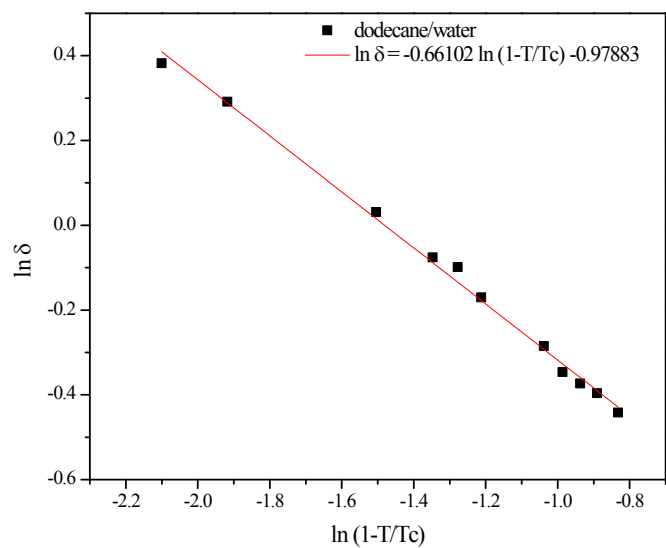


Figure S10. Scaling law of the thickness of the interface between dodecane and water at different temperatures. The line represents the best fit, with the parameters given in the legend.

- Density profiles for dodecanol/water at temperatures $T = 303$ and 373 K

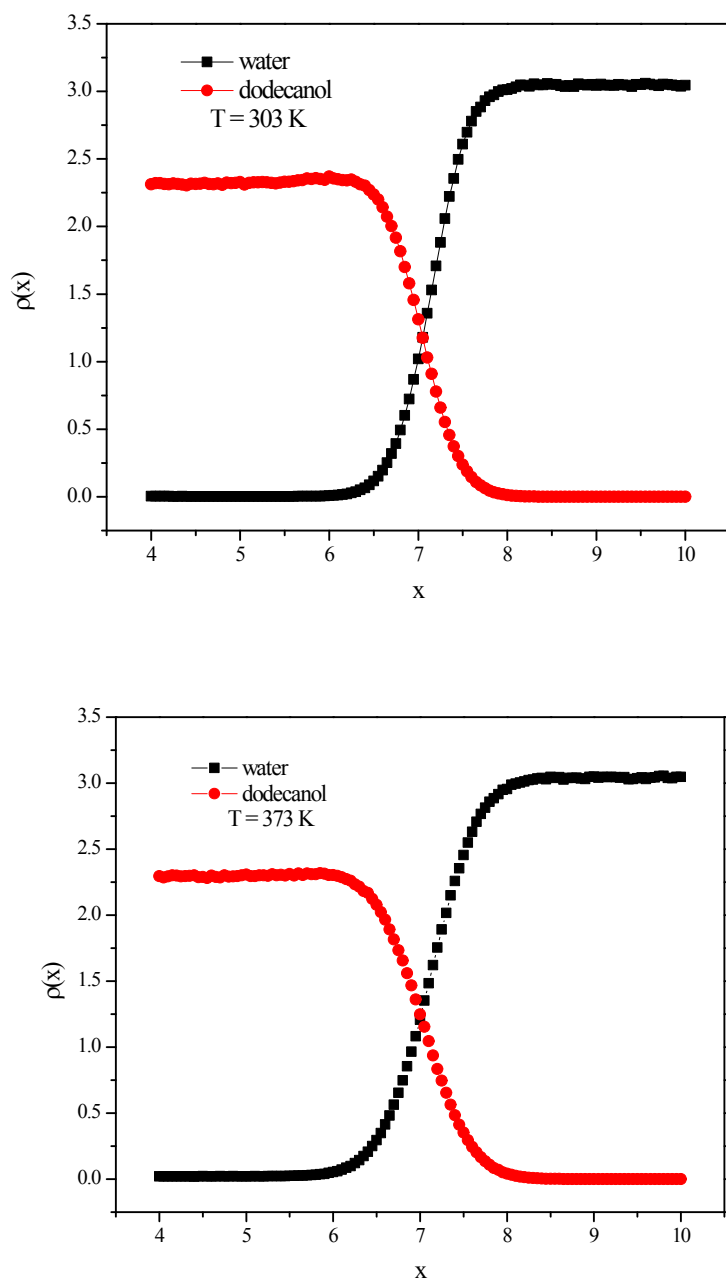


Figure S11. Evolution of the density profiles for the mixture dodecanol/water at the indicated temperatures. The axes are shown in reduced DPD units.

- δ vs T (δ = interface width) for dodecanol/water

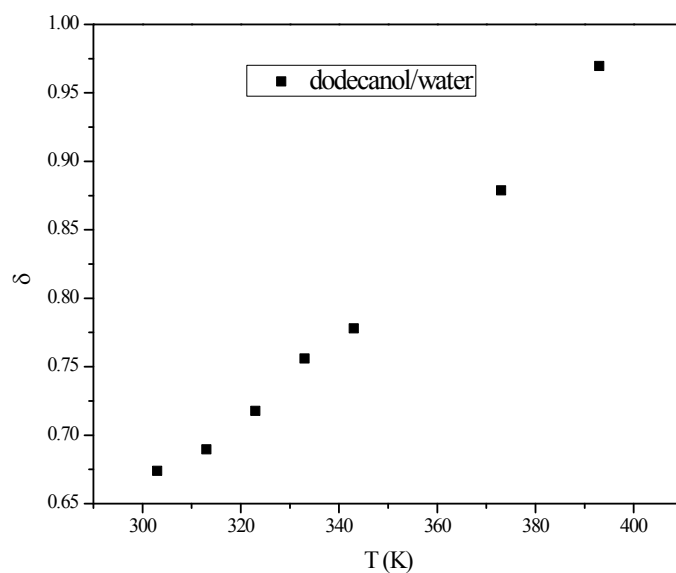


Figure S12. Evolution of the thickness of the interface between dodecanol and water at different temperatures. The y – axis is expressed in reduced DPD units.

- $\ln \delta$ vs $\ln (1-T/T_c)$ for dodecanol/water

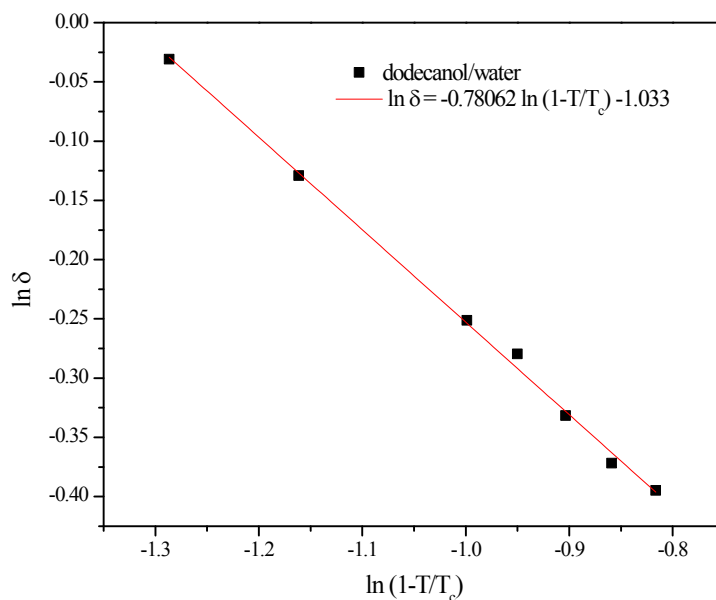
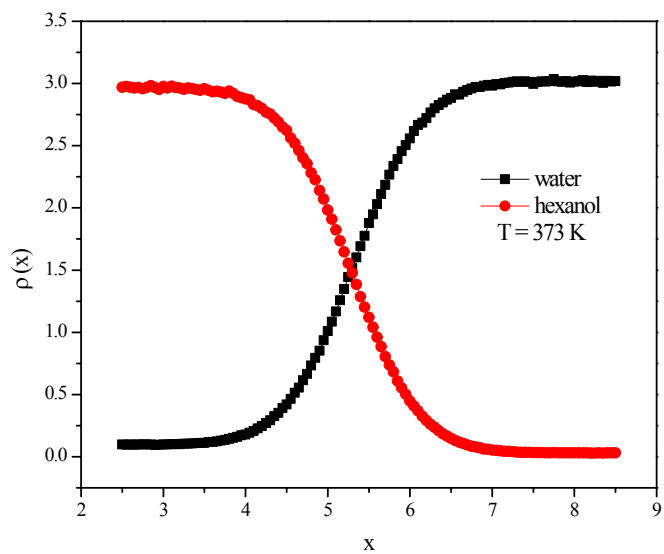
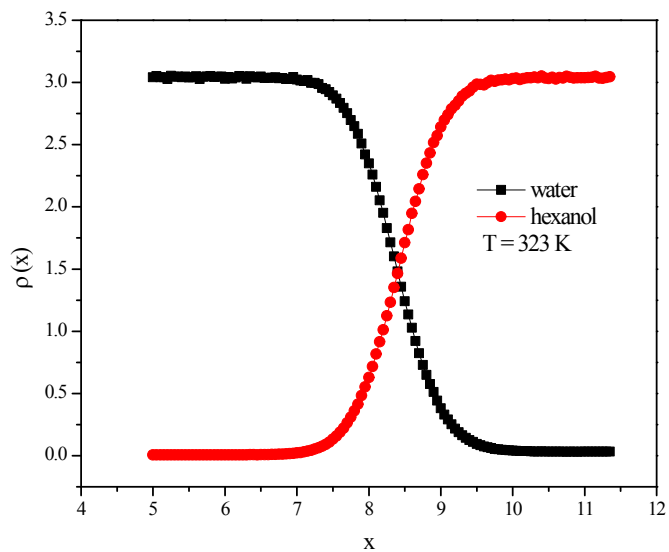


Figure S13. Scaling law of the thickness of the interface between dodecanol and water at different temperatures. The line represents the best fit, with the parameters given in the legend.

- Density profiles for hexanol/water at temperatures $T = 323, 373$ and 433 K.



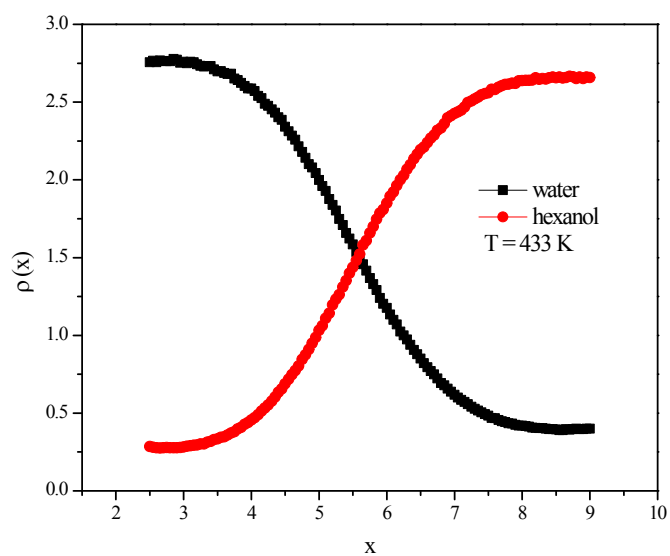


Figure S14. Evolution of the density profiles for the mixture hexanol/water at the indicated temperatures. The axes are shown in reduced DPD units.

– δ vs T (δ = interface width) for hexanol/water

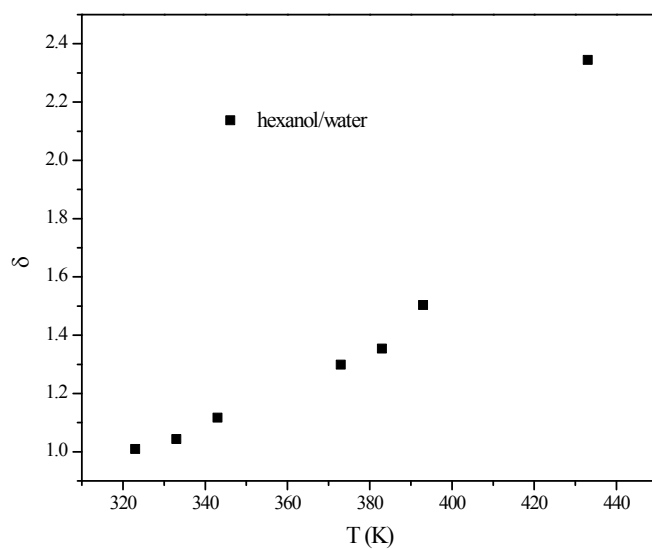


Figure S15. Evolution of the thickness of the interface between hexanol and water at different temperatures. The y – axis is expressed in reduced DPD units.

- $\ln \delta$ vs $\ln (1-T/T_c)$ for hexanol/water

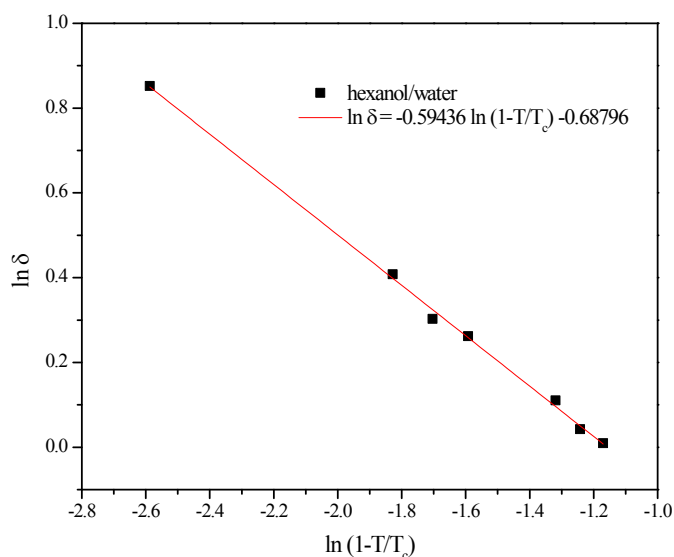


Figure S16. Scaling law of the thickness of the interface between hexanol and water at different temperatures. The line represents the best fit, with the parameters given in the legend.

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