

Simulation of Surface Excess Concentrations for a Binary Hydrocarbon Mixture on Graphite[§]

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Abstract

We perform Molecular Dynamics simulations of thin hydrocarbon films adsorbed on the basal plane of graphite to determine structural and thermodynamic properties. Specifically we study the behaviour of liquid benzene/n-heptane mixtures. The intra adsorbate and the adsorbate-substrate interactions are described using a phenomenological force field whose careful parameterization will be reported in a following paper. The foremost quantity we calculate is the adsorption isotherm, i.e. the surface excess concentration as a function of the benzene bulk mole fraction at $T = 283$ K, which is in quite reasonable agreement with the experiment. Along with the isotherm we compare the surface induced ordering of the two components in terms of order parameter profiles.

Keywords: Molecular Dynamics simulation, Adsorption, Isotherm, Hydrocarbon, Graphite

Introduction

Over the past fifteen years computer simulations have become a useful tool in the study of adsorption phenomena, especially the formation and organization of molecular films. Here we study the interaction of a binary hydrocarbon mixture, i.e. ~ 4 nm thin liquid films containing benzene and n-heptane, with the graphite basal plane. We are interested in the feasibility of modeling the adsorption isotherm, i.e., the surface excess of one species as function of its bulk concentration, by describing the molecular interactions in terms of a common phenomenological force field. The parameterization procedure used here - a complete and de-

tailed description will be presented in a following paper [1] - relies on adjusting the parameters via the temperature dependence of the density and the diffusion behavior of the corresponding bulk systems. Adsorbate-surface interactions are parameterized based on isosteric heats of adsorption in the limit of low coverage and selected points along the isotherm. Our aim is to quantify the competitive adsorption between benzene and n-heptane which experimentally was investigated by Ash, Brown, and Everett [2]. A previous study of the benzene/heptane system [3], where molecular structure and mobility in the vicinity of the surface was analyzed, could not reproduce the quantitative adsorption behavior found in the experiment. In this communication we present the results of the new parameterization, which yields quite reasonable agreement with the above experiment. To the best of our knowledge this is the first time that an attempt has been made to quantitatively model the adsorption isotherm of a real molecular mixture. We also discuss the composition

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and surface induced structural differences of the simulated benzene/heptane films - using the bulk mole fraction $x_{Benzene}^l = 0.5203$ as an example - based on density and order parameter profiles.

Simulation methodology

We employ conventional Molecular Dynamics numerically solving Newton's equations of motion, $m_i \frac{d^2 \vec{r}_i}{dt^2} = -\vec{\nabla}_i U(\vec{r}_1, \dots, \vec{r}_N)$, for all atoms $i=1, \dots, N$ with masses m_i in the adsorbed liquid film. The potential energy U is given by

$$\begin{aligned}
 U(\vec{r}_1, \dots, \vec{r}_N) = & \sum_{\text{bonds } i} k_b^{(i)} (b_i - b_0^{(i)})^2 \\
 & + \sum_{\text{angles } i} k_\alpha^{(i)} (\alpha_i - \alpha_0^{(i)})^2 \\
 & + \sum_{\text{dihed. } i} \sum_l k_{d,l}^{(i)} \left[1 + \cos(n_l^{(i)} \phi_i - \gamma_l^{(i)}) \right] \\
 & + \sum_{\text{atom pairs } ij} \left(\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} \right) \\
 & + \sum_{\text{atom pairs } ij} \frac{q_i q_j}{r_{ij}} \\
 & + \sum_{i=1}^N u_{surf}(\vec{r}_i)
 \end{aligned} \tag{1}$$

The first five terms comprise the AMBER (Assisted Model Building with Energy Refinement) description of the potential energy for a large molecular system [4] (and references therein). The first three sums encompass the valence potential energy contributions due to bond (b_i) and bond angle (α_i) deformations as well as bond rotations (ϕ_i). The next two sums describe the inter-atomic overlap repulsion and dispersion attraction in terms of Lennard-Jones potentials and Coulomb interactions between partial charge sites located on the nuclei. These summations include all atom pairs ij . If i and j belong to the same molecule, then they are separated by at least three covalent bonds. In addition, the non-bonded (1-4)-interaction terms, i.e., there are exactly three bonds separating i and j , are scaled by a factor 1/1.2 in the case of the Coulomb potential. There is no such scaling in the Lennard-Jones case. The non-bonded interactions are calculated using a residue based cutoff of 9 Å, where each molecule constitutes a residue.

The presence of the adsorbing surface is modeled via the last term in equation (1). u_{surf} is the potential energy of an

adsorbate atom i ($i=1, \dots, N$) at the position \vec{r}_i above the surface in terms of Lennard-Jones pair interactions with all atoms in the substrate, neglecting the dynamics of the latter. A discussion of u_{surf} including Lennard-Jones together with other surface interactions can be found in [5]. A detailed description of the present force field along with simulation details is given in [1]. However, the numerical values of the force field parameters used here are compiled in table 1.

In the present study we employ the united-atom approximation for the methyl and methylene units in the alkane, neglecting the charges. Benzene was modeled in the all-atom representation with partial charges centered on the carbons and the hydrogens. The atomic equations of motion are integrated via the half-step leap-frog Verlet algorithm [6] with a time step of 1.5 fs. In addition, the bond lengths are constrained via the SHAKE algorithm (e.g. [7]), and the temperature is kept constant via Berendsen's weak coupling thermostat [8]. The simulations of the benzene/heptane mixtures on graphite are performed using a rectangular cell with periodic boundary conditions parallel to the surface and dimensions commensurate with the substrate surface lattice. Here the number of molecules varies between 286 and 400 depending on the mixture's composition. A typical run for a given mole fraction consisted of 3×10^6 production steps. Note that in these simulations we ignore the particle exchange between the adsorbed films and the gas phase based on the assumption that this does not influence the structure and dynamics of the films. To avoid the loss of molecules at the vacuum-to-liquid interface a reflecting wall reverses the z-component of the molecular center of mass velocity at approximately 50 Å above the interface.

Results

Here we analyze simulation trajectories of thin liquid benzene/heptane films at the interface between the graphite basal plane and vacuum. The average thickness of the films is ≈ 4 nm. We keep the temperature constant at $T=283$ K, but vary the mixing ratio.

An important quantity in this context, i.e., a mixture of two liquid components i and j in equilibrium with a solid interface, is the surface excess concentration of component i , Γ_i . Γ_i is proportional to the difference between the amount of i in the bulk liquid which contains the surface and the amount of i in a corresponding reference liquid without the surface. More precisely

$$\Gamma_i = \frac{n^0}{A} (x_i^0 - x_i^l) = n^0 \frac{\Delta x_i^l}{A} \tag{2}$$

Here A is the surface area of the solid (the specific surface area of graphite measured with N_2 (B.E.T. method) is $86 \text{ m}^2 \text{g}^{-1}$ [2]), and n^0 is the total amount of material, which is the same in both systems. x_i^0 is the mole fraction of i in the

Table 1. Force field parameters used in this simulation. CA and HA indicate the two atom types representing the benzene carbons and hydrogens and C3 und C2 correspond to the methyl and methylene units in the heptane. Note that

$$A_{ij} = \sqrt{\epsilon_i \epsilon_j} \left(\frac{\sigma_i + \sigma_j}{2} \right)^{12} \quad \text{and} \quad B_{ij} = 2 \sqrt{\epsilon_i \epsilon_j} \left(\frac{\sigma_i + \sigma_j}{2} \right)^6.$$

bond	b_0 [Å]	k_b			
CA-CA	1.40	SHAKE			
CA-HA	1.08				
C2-C3	1.53				
C2-C2	1.53				
angle	k_α [kJ·mol ⁻¹ ·rad ⁻²]	α_0 [°]			
CA-CA-CA	335.64	120.0			
CA-CA-HA	146.44	120.0			
X-C2-X	259.83	114.0			
dihedral	l	$k_{d,l}$ [kJ·mol ⁻¹]	n_l	γ_l [°]	
X-CA-CA-X	1	22.175	2	180	
H-CA-CA-X	1	8.368	2	180	
X-C2-C2-X	1	1.473	1	0	
	2	- 0.276	2	180	
	3	3.284	3	0	
atom type	mass [amu]	σ [Å]	ϵ [kJ·mol ⁻¹]	q [el. charges]	
CA	12.010	3.640	0.5021	-0.115	
HA	13.018	3.080	0.0544	+0.115	
C2	14.030	4.404	0.4602	-	
C3	15.030	4.404	0.9540	-	
surface	σ [Å]	ϵ [kJ·mol ⁻¹]			
CA-G	3.8204	0.2414			
HA-G	3.3702	0.1653			
C2-G	4.110	0.2966			
C3-G	4.110	0.2966			

liquid without the surface, and x_i^l the bulk mole fraction of i in the liquid which is in contact with the surface. To obtain the two quantities $x_{Benzene}^l$ and $x_{Benzene}^o$ (defining the surface excess concentration of benzene) from the simulation requires care. Notice that the bulk mole fraction $x_{Benzene}^l$ is affected by the presence of the second surface, the liquid-to-vacuum interface, as a consequence of the small system size. Nevertheless, we calculate $x_{Benzene}^l$ in the usual fashion via

$$x_{Benzene}^l = \frac{\langle n_{Benzene}^{bulk} \rangle}{\langle n_{Benzene}^{bulk} \rangle + \langle n_{Heptane}^{bulk} \rangle} \quad (3)$$

where $\langle n_i^{bulk} \rangle$ refers to the average number density of i -molecules in the bulk portion of the film, i.e., the z -range where no interface induced structure is observed. However, now we cannot just identify x_i^o with $N_i / (N_{Benzene} + N_{Heptane})$,

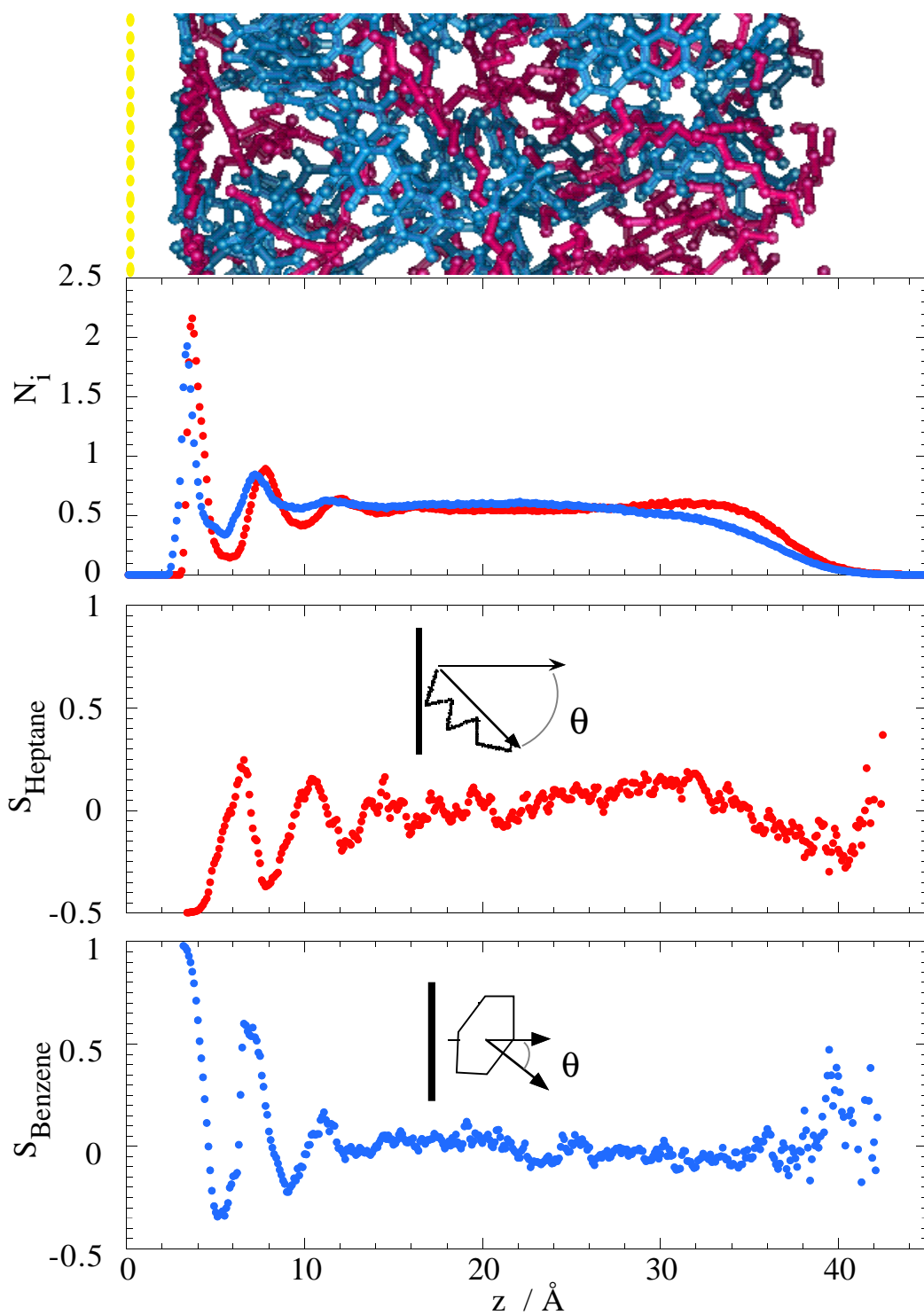


Figure 1. Top: simulation snapshot showing a narrow section of the adsorbed film consisting of benzene (blue) and heptane (red). The graphite basal plane is schematically indicated by the yellow dots on the left. Bottom: center of mass distribution

$N_i(z)$ and orientation order parameter profiles $S_i(z)$ for benzene (blue) and heptane (red) at $x_{\text{Benzene}}^1 = 0.5203$ vs. the distance z from the graphite surface.

where N_i refers to the total number of i -molecules in the simulation. Instead, x_i^0 is calculated as follows. First we determine the excess number of i -molecules, ΔN_i at the solid interface via

$$\Delta N_i \approx \frac{1}{b} \int_{z_{\min(i)}}^{z_{\max}} \left(N_i(z) - \langle N_i^{bulk} \rangle \right) dz \quad (4)$$

Here b is the width of a thin slab parallel to the surface, and $N_i(z)$ is the number of i -molecules in this slab at a distance z from the surface. $\langle N_i^{bulk} \rangle$ again refers to the corresponding average in the bulk-portion of the film. The lower boundary, $z_{\min(i)}$, marks the onset of the distribution $N_i(z)$, whereas the upper boundary, z_{\max} , is an arbitrary z -position in the bulk-portion of the film. Note that z_{\max} is arbitrary as long as $0 \approx N_i(z_{\max}) - \langle N_i^{bulk} \rangle$. Subsequently the excess molecules ΔN_i are distributed evenly over $z_{\min(i)} < z < z_i^{vac}$, where z_i^{vac} is the position of the film-to-vacuum interface for component i . The latter is determined via the relation

$$\frac{1}{b} \int_{z_{\max}}^{\infty} N_i(z) dz = \langle N_i^{bulk} \rangle (z_i^{vac} - z_{\max}) \quad (5)$$

Finally, with these additional molecules we can again apply equation (3), i.e.

$$x_{Benzene}^0 = \frac{\langle n_{Benzene}'^{bulk} \rangle}{\langle n_{Benzene}'^{bulk} \rangle + \langle n_{Heptane}'^{bulk} \rangle} \quad (6)$$

where the primes indicate the new densities

$$n_i'^{bulk} = n_i^{bulk} + \Delta n_i \quad \text{with} \quad \Delta n_i = \Delta N_i / \left(A (z_i^{vac} - z_{\min(i)}) \right).$$

Figure 1 shows a partial snapshot of the simulation box together with the component profiles, $N_i(z)$, for the benzene mole fraction $x_{Benzene}^0 = 0.5203$. $N_i(z)$ is obtained by averaging the molecular center of mass densities within a thin slab (here $b = 0.1 \text{ \AA}$) parallel to the surface. The profiles show the surface induced structure extending over $\sim 15 \text{ \AA}$ into the film followed by a bulk-like region and the film-to-vacuum interface (a detailed analysis of the surface induced structure in pure benzene is given in reference [9]). In the case of benzene the maxima induced by the solid surface correspond to molecules with their planes preferentially parallel to the surface. This can be seen in the last panel of the above figure, where we plot the orientation order parameter profile $S_i(z)$ defined via

$$S_i(z) = \frac{1}{N_i(z)} \left\langle \sum_l N_i(z, \theta_l) \frac{1}{2} (3 \cos^2 \theta_l - 1) \right\rangle \quad (7)$$

$N_i(z, \theta_l)$ is the number of molecules of type i at distance z and with orientation θ_l relative to the surface. Note that $\theta_l = 0$ corresponds to $S = 1$, whereas $\theta_l = \pi/2$ corresponds to $S = -0.5$. Random orientation results in $S = 0$. The exact definition of θ_l is given in the insets in the two bottom panels of Figure 1. In the case of heptane the maxima induced by the solid surface correspond to layers of molecules with their long axis preferentially parallel to the surface. In the bulk portion of the film neither species shows any preferred orientation with respect to the interface. Near the liquid-to-vacuum interface $S_i(z)$ exhibits considerable scatter. Nevertheless, $S_{Heptane}(z)$ shows a weak maximum, perhaps indicating an initial tendency towards perpendicular orientation, which, however, is weak because the molecules are short, i.e. their length is on the order of the width of the interface. Experimental studies indeed show that longer n-alkanes exhibit hexagonal ordering at the melt-to-vacuum interface with their long axis oriented perpendicular to the interface [10].

By analyzing the film profiles for different benzene concentrations as explained above, we obtain $\Gamma_{Benzene}$ at four different mole fractions $x_{Benzene}^0$. Figure 2 shows these values in comparison to the experimental isotherm of Ash, Brown, and Everett [2]. The overall agreement with the experiment is quite reasonable, even though the error bars of the simulated values are considerable. The latter are calculated based on the statistical inefficiency-method as explained in [6]. Note in this context that along the simulation trajectory the values for $\Gamma_{Benzene}$ are correlated over roughly 200 ps so that the production runs need to be several nanosecond long (cf. above). The quantitative simulation of Γ_i is also made difficult by the fact that this quantity is extremely sensitive to the molecule-surface interaction parameters. Our initial attempts were based on Lennard-Jones parameters obtained via experimental isosteric heats of adsorption. However, this results in values for $\Gamma_{Benzene}$ which deviate from the experimental results by up to 500 %. Thus we adjust the parameter ϵ of the heptane-graphite interaction slightly to obtain satisfactory agreement with the experimental isotherm at one particular mole fraction. All other mole fractions are then simulated with the same parameters (see Table 1).

The competitive adsorption between benzene and heptane giving rise to the adsorption behavior shown in Figure 2, can be understood on the basis of a thermodynamic analysis of the adsorption process [11]. From his results Everett concludes that the competitive adsorption from a solution is not just determined by the size of the component-graphite interaction but is also a function of the entropy change accompanying the adsorption. In the benzene-heptane-graphite-system, the entropy ($T\Delta S$) and the enthalpy (ΔH) term are of similar magnitude (at $T = 283 \text{ K}$). Whereas the enthalpy change would lead to a preferential adsorption of heptane (consistent with this we find isosteric heats of adsorption at vanishing coverage of $51.04 \text{ kJ}\cdot\text{mol}^{-1}$ for heptane and $42.68 \text{ kJ}\cdot\text{mol}^{-1}$ for benzene), the entropy term opposes this behavior. The larger decrease in entropy for the alkane is reasonable - considering that the reduction of accessible conformational

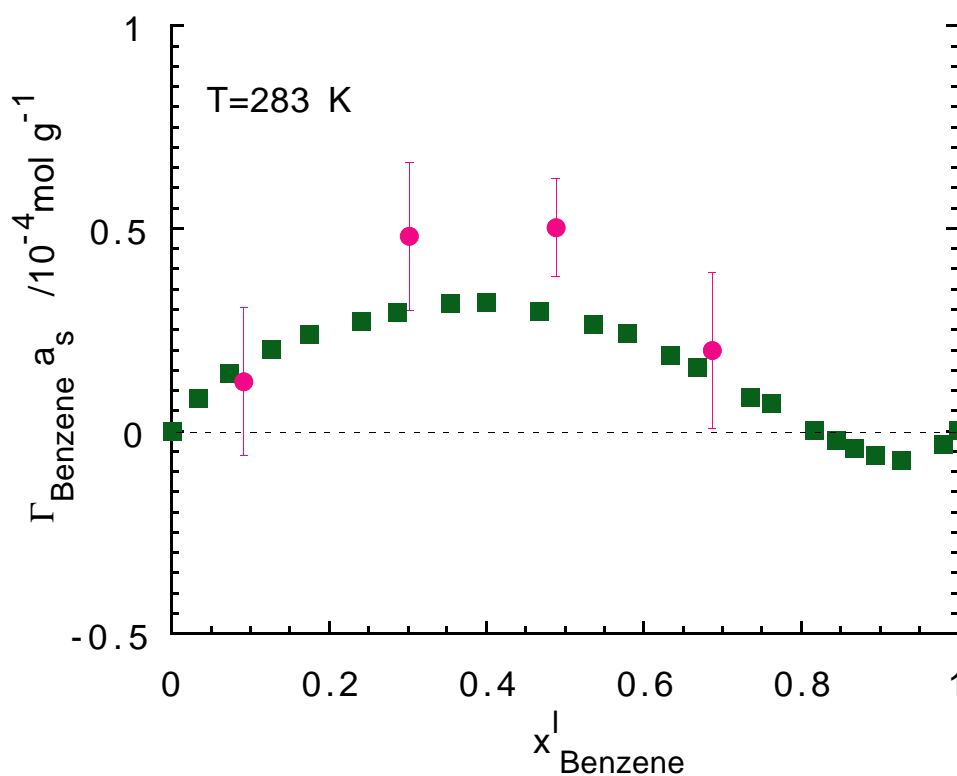


Figure 2. The surface excess concentration Γ_{Benzene} of benzene (multiplied by $a_s = 86 \text{ m}^2 \text{ g}^{-1}$, the specific surface area of graphite) vs. x_{Benzene}^l , the benzene bulk mole fraction in the liquid in contact with the graphite basal plane at $T = 283 \text{ K}$. Green squares: experiment; pink circles: simulation.

space is larger than in the case of the benzene molecule. At high benzene concentrations, however, the dominance of the enthalpy term results in the preferential adsorption of heptane. Work aimed at the calculation of these different contributions of the free enthalpy is currently under way.

Conclusion

We perform molecular dynamics simulation studies of binary hydrocarbon films consisting of liquid benzene and n-heptane interacting with the graphite basal plane. To the best of our knowledge this is the first time that an attempt has been made to quantitatively model the adsorption isotherm of a real molecular mixture on the molecular level. Quantitative or even semi-quantitative agreement with experimental isotherms appears to be extremely sensitive to the interaction parameters, so that the standard parameterization of any 'out-of-the-box' force field would probably fail in such calculations. Our final parameter set results in quite reasonable agreement with the measured isotherm. In addition, we have

analyzed the structure of the simulated thin films as a function of composition.

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