Coarse-graining MARTINI model for molecular-dynamics simulations of the wetting properties of graphitic surfaces with non-ionic, long-chain and T-shaped surfactants

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We report on a molecular dynamics investigation of the wetting properties of graphitic surfaces by various solutions at concentrations 1 – 8 wt% of commercially available non-ionic surfactants with long hydrophilic chains, linear or T-shaped. These are surfactants of length up to 160 [Å]. It turns out that molecular dynamics simulations of such systems ask for a number of solvent particles that can be reached without seriously compromising computational efficiency only by employing a coarse-grained model. The MARTINI force field with polarizable water offers a framework particularly suited for the parameterization of our systems. In general, its advantages over other coarse-grained models are the possibility to explore faster long time scales and the wider range of applicability. Although the accuracy is sometimes put under question, the results for the wetting properties by pure water are in good agreement with those for the corresponding atomistic systems and theoretical predictions. On the other hand, the bulk properties of various aqueous surfactant solutions indicate that the micellar formation process is too strong. For this reason, a typical experimental configuration is better approached by preparing the droplets with the surfactants arranged in the initial state in the vicinity of contact line. Cross-comparisons are possible and illuminating, but equilibrium contact angles as obtained from simulations overestimate the experimental results. Nevertheless, our findings can provide guidelines for the preliminary assessment and screening of surfactants. Most importantly, it is found that the wetting properties mainly depend on the length and apolarity of the hydrophobic tail, for linear surfactants, and the length of the hydrophilic headgroup for T-shaped surfactants. Moreover, the T-shaped topology appears to favor the adsorption of surfactants onto the graphitic surface and faster spreading.

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I. INTRODUCTION

Molecular dynamics (MD) simulations have become an important complement to experimental and theoretical work across a variety of disciplines. Often, one of the encountered obstacles to further advances are the prohibitive computational resources necessary for a description at the molecular level of systems containing a large number of particles. This situation is in general quite common when water is involved as solvent. One way to overcome this limitation is to reduce the degrees of freedom to the essential for the issues under investigation. This procedure is referred to as coarse-graining because the system is suitably organized into units identifying groups of atoms. To achieve this, two schemes are basically available. The differences mainly reside in the decomposition of the system into building blocks and the selected properties according to which inter-particle interactions are calibrated. Our work is based on the MARTINI force field because allowing to build readily and systematically systems of coarse-grained (CG) units in a prescribed way. Within this framework four heavy atoms are generally mapped into one interaction site. The resulting beads are classified into four main categories that separate further into subtypes. Lennard-Jones (LJ) interactions are organized into ten levels of strength and evaluated with a function of type 12-6. In its original formulation, the MARTINI model does not contemplate solid phases. Following empirical arguments, we treat graphitic surfaces and their wetting properties by surfactant solutions. In that respect, the surface tension of water is of course a key property. The polarizable MARTINI model for water still underestimates the experimental value. The expected balance of forces at the interface with the graphitic surface is approximately restored by tuning the interaction strength of the relative LJ potential. In this way, we first reproduce in the macroscopic limit the contact angle for pure water from measurements at present carried out under the most ideal conditions. Interestingly, our results correlate well with those using atomistic models for water consistent with the experimental surface tension. This allows us to conclude that the MARTINI force field can provide an effective framework for investigating the wetting properties of surfaces. Surfactants are molecules exhibiting opposite behavior toward water at their extremes, namely hydrophilic in the headgroup and hydrophobic in the tail group. Importantly, these competing attributes are responsible for the decrease of the surface tension of the resulting solution. In practice, this means that an aqueous solution would wet better a surface with the addition of surfactants. At higher concentrations, another important property related to the amphiphilic nature of surfactants is their ability to self-assemble into micelles. Applications in the industry are innumerable, including printing, detergency, oil recovery, dispersion, emulsification, disinfection, etc. In this work, we concentrate on solutions with non-ionic surfactants. As conveyed by the title, emphasis is put on the wetting properties by measuring the contact angle of droplets. The identity of the surfactants under investigation is confidential for industrial reasons. Specifically, their use as wetting agents is necessary for the optimal dispersion of reinforcement fillers in polymeric matrices (low chemical compatibility to each other). This phase is rather prominent in the manufacturing route of composite materials in order to meet challenging, target properties. Our work aims at providing useful guidance for planning applications.
So, the basic mechanisms governing wetting phenomena by aqueous surfactant solutions are at the center of our attention. The strategy consists in simulating six representative surfactants differing in simple attributes such as the length of the hydrophilic and hydrophobic groups or the topology (linear and T-shaped). Our research develops as follows. In the next Section, the MARTINI representation of all the constituents of the systems is introduced. Section III is concerned with the general MD simulation settings. In Sec IV are presented the results for systems of pure water and with surfactants: first the bulk properties of solutions and then the wetting behavior on graphic surfaces. The last Section is devoted to conclusive remarks.

II. COARSE-GRANING OF THE SYSTEMS

Force field. The MARTINI force field is designed in order to account for a variety of chemical compounds preventing the need to recalculate the various interaction parameters for every application. The idea is to classify atomic functional groups into four main categories: polar, nonpolar, apolar and charged. Every category subdivides further into subtypes so as to represent more finely the underlying structural properties. Ten levels of interaction are possible between the diverse types of CG particles. More precisely, inter-particle LJ forces are derived from the potential energy

\[ U_{LJ}(r_{ij}) = 4\varepsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \],

where \( \varepsilon \) is the inner cutoff distance and \( \sigma \) is the outer cutoff distance. The indices \( i \) and \( j \) label the particles. \( r_{ij} \) is the distance separating pairs of particles. The parameter \( \varepsilon \) adjusts the strength of the force according to the available levels of interaction. The coefficient \( \sigma \) is related to the equilibrium distance between particles via the formula \( 2^{1/6} \sigma \). If \( r_{ij} < 2^{1/6} \sigma \), the force is repulsive, otherwise it is attractive. The parameter \( \sigma \) is also usually referred to as molecular diameter. Electrostatic interactions are computed from the coulombic potential

\[ U_{C}(r_{ij}) = \frac{q_{i}q_{j}}{4\pi\varepsilon_{0}r_{ij}} \]

\( q_{i} \) is the partial charge of the \( i \)-th particle; \( \varepsilon_{0} \) is the permittivity in vacuum and \( \varepsilon \) is the relative dielectric constant. For the standard MARTINI model \( \varepsilon = 15 \), while for the polarizable model used here \( \varepsilon = 2.5 \). Non-bonded interactions are corrected separately to zero using the shift function [13]

\[ S(r_{ij}) = \begin{cases} 0 & r_{ij} \leq r_{\text{shift}} \\ \frac{C}{4}(r_{ij} - r_{\text{shift}})^{3} + \frac{3}{4}(r_{ij} - r_{\text{shift}})^{4} + C & r_{\text{shift}} < r_{ij} < r_{c} \end{cases} \]

where \( r_{\text{shift}} \) is the inner cutoff distance and \( r_{c} \) is the outer cutoff distance. The constants \( A, B, C \) and \( D \) are determined from boundary conditions. Intra-particle interactions take into account bond and angle interactions. Bonded particles interact via the harmonic potential

\[ U_{b}(r_{ij}) = K_{b}(r_{ij} - r_{0})^{2} \]

where \( r_{0} \) is the equilibrium distance and \( K_{b} \) the energy constant. The standard MARTINI values for these parameters are \( r_{0} = 4.7 \, \text{Å} \) and \( K_{b} = 1.5 \, \text{kal/mol/Å}^{2} \). Angle interactions are described by the potential

\[ U(\theta_{ijk}) = K_{\theta}[\cos(\theta_{ijk}) - \cos(\theta_{0})]^{2} \]

\( \theta_{ijk} \) is the angle formed by triplets of bonded particles; \( \theta_{0} \) is the equilibrium angle; \( K_{\theta} \) is the coupling constant, for which the standard MARTINI value is \( K_{\theta} = 3.0 \, \text{kal/mol} \). Water. A CG bead of polarizable MARTINI water [3] consists of three particles \( W_{0}, W_{1}, \) of equal mass 24 [g/mol] and of partial charge \( q_{0} = 0 \) [e] and \( q_{\pm} = \pm 0.46 \) [e], respectively. The charged particles are bonded to the neutral one and the bond length is kept fixed at 1.4 [Å]. The angle degree of freedom is modeled as a harmonic oscillator of elastic constant \( K_{WW} = 0.5019 \, \text{kal/mol} \) and equilibrium angle of 0°. Lennard-Jones forces are considered only among the central particles \( W_{0} \) with interaction parameters \( \varepsilon_{WW} = 0.956 \, \text{kal/mol} \) and \( \sigma_{WW} = 4.7 \, \text{Å} \). With the charged particles \( W_{\pm} \), the polarization is treated explicitly and the relative dielectric constant is thus set to \( \varepsilon_{0} = 2.5 \) (cf. Refs. 2, 3). Furthermore, Coulomb and van der Waals forces among particles belonging to the same water bead are omitted.

Graphene. The graphene is parameterized by placing at the center of every ring of carbon atoms one interaction site. As a consequence, every bead has mass 24 [g/mol] because representing on average two atoms. The interaction parameter \( \varepsilon_{CW} \) between the beads of water (\( W_{0} \)) and graphene is fixed from the wetting properties of pure water. We choose the value of \( \varepsilon_{CW} \) that reproduces the result for the contact angle in the macroscopic limit reported in Ref. 6. The parameter \( \varepsilon_{CW} \) is set equal to \( \varepsilon_{CW} = 6.24 \, \text{Å} \). This value yields approximately the equilibrium distance of 7 [Å]. The solid phase is obtained by two parallel planes of CG graphene. The two planes are separated by 3.4 [Å] with the lower one translated by the vector \( (l/2, \sqrt{3}l/2) \) with respect to the upper one. Here \( l \) is the length of C-C bonds in the all-atom case. This arrangement is intended to reproduce the structure of a graphite crystal.

Surfactants. The atomic structure of the surfactants is reduced according to the guidelines detailed in Ref. 2. In order to compare our work to previous similar studies [14], we also consider solutions containing the non-ionic surfactant C8E4 (tetaethylene glycol octyl ether). We adopt the mappings C1-C1-P2-P3 and C1-C1-Na-Na-P4 proposed in Ref. 14. The first representation will be referenced as C8E4-P3 surfactant while the latter as C8E4-NaNaP4 [14]. Both molecules are linear with every equilibrium bond length equal to \( r_{0} = 4.7 \, \text{Å} \); all equilibrium angles are of course \( \theta_{0} = 180^\circ \). The energy constants are also the standard MARTINI values [2], that is, \( K_{b} = 1.5 \, \text{kal/mol/Å}^{2} \) and \( K_{b} = 3.0 \, \text{kal/mol} \). For the mass of the beads, we use in this case \( m_{W_{0}} = 72 \, \text{[g/mol]} \), \( m_{W_{\pm}} = 56 \, \text{[g/mol]} \) and \( m_{C} = 56 \, \text{[g/mol]} \). The LJ parameters are readily obtained from Ref. 2 with all equilibrium distances set to 4.7 [Å]. The wetting properties of graphitic surfaces are studied in relation to five non-ionic surfactants, long-chain and T-shaped. The first surfactant will be referred to as L1. Its molecule is linear and it is applied the MARTINI representation (C1)3(P4)10. The mass is again \( m_{C} = 56 \, \text{[g/mol]} \) for the
tail beads, while we use \( m_{P_4} = 44 \) [g/mol] for the hydrophilic head. The second surfactant has representation \((C_1)_3(P_4)_{20}\) and will be designated by L2. All topology and interaction parameters are the same as for the surfactant L1. The third linear surfactant L3 is mapped into \((C_1)_4(P_4)_{30}\). All the parameters are the same as for the surfactant L1. Regarding the T-shaped surfactants, we distinguish the T1 and T2 topologies. These surfactants differ by the length of the hydrophilic headgroup. The surfactant T1 has a linear chain made of ten beads \( P_4 \), while the surfactant T2 counts twenty beads \( P_4 \) arranged linearly. In both cases, the hydrophobic tail consists of three aligned beads \( C_1 \) and in the middle is attached the hydrophilic chain. For the angle \( C_1-C_1-P_4 \) (vertex in the central bead), the equilibrium value is set to 90°, and the standard potential and interaction parameter of the MARTINI force field \( [2] \) are used. All the other parameters are the same as for the linear surfactants. The hydrophobic tail of the surfactant T3 is made of five \( C_1 \) beads. At the central bead is attached the linear, hydrophilic head of length twenty \( P_4 \) units. All the other settings for T-shaped surfactants apply also in this case.

### III. SIMULATIONS

All simulations are performed with the molecular dynamics code LAMMPS \([15-17]\). Newton’s equations of motion are integrated with the Verlet algorithm using a Nosé-Hoover scheme in the specified ensemble: the timestep size is of 20 [fs]. Non-bonded interactions are cut off at \( r_e = 12 \) [Å] and computed with the potential lj/gromacs/coul/gromacs \([13]\). The LJ potential is shifted from \( r_{shift} = 9 \) [Å] to \( r_e \), while the electrostatic contribution is shifted from \( r_{shift} = 0 \) [Å] to \( r_e \). Long-range interactions are not taken into account. The bond length between \( W_0 \) and \( W_0 \) particles is maintained rigid with the SHAKE algorithm \([18]\). Three-body interactions of surfactants are computed with the cosine/squared potential. The neighbor list is rebuilt at most every 5 timesteps. It is not necessary to divide the bond and angle coefficients given here by 2. Then, all simulation times must be meant as actual \([3]\). Unless specified otherwise, these parameters remain unchanged in the various simulations. The motivations for these settings can be found in Refs. \([2,3]\).

### IV. RESULTS AND DISCUSSION

**Bulk properties of CG water.** As starting configuration, 1’000 beads of water are arranged with the \( W_0 \) particles on the vertices of a simple cubic lattice. The side of the unit cell is 4.5 [Å]. The system is let evolve for 100 [ns] at NPT conditions. The time of evolution is long in order to verify that we do not incur in freezing. The target temperature and pressure are \( T = 298 \) [K] and \( P = 1 \) [atm]. The system is studied by recording 1’000 evenly-spaced frames over the course of the last 50 [ns]. Table II lists some average bulk properties of the cubic box of CG water. The \( W_0-W_0 \) radial distribution func-

| \( L \) [Å] | \( V \) [Å³] | \( \rho \) [g/Å³] | \( d \) [molecules/Å³] |
|---------|--------|-----------|-------------|
| 48.858  | 116 629 | 1.0255    | 0.0086      |

Table I: Average characteristics of the cubic simulation box during the NPT dynamics, side length \( L \) and volume \( V \), along with the bulk properties of CG water \( \rho \) and \( d \), mass and particle densities respectively.

**Figure 1:** \( W_0-W_0 \) RDF as obtained from the NPT dynamics for the polarizable MARTINI water model.

The radial distribution, \( g(r) \), is computed by means of the formula

\[
\frac{N}{V} g(r) 4\pi r^2 \Delta r = S(r)
\]

\( N \) is the number of water beads and \( V \) the volume of the simulation domain. \( S(r) \) counts the average number of \( W_0 \) particles falling in a shell of width \( \Delta r = 0.05 \) [Å] centered around a given \( W_0 \) particle at distance \( r \). The radial distribution function (RDF) is shown in Fig. 1. In general, our results compare well with those of the original work for the present model of CG water \([3]\). The standard deviation of the volume of the simulation domain is 0.78% of the average value. For this reason, we safely replicate the last configuration of this NPT simulation and extract the asseblies for any subsequent dynamics containing pure CG water.

**Spherical droplets.** As a matter of calibration of the interaction parameter \( \varepsilon_{CW} \), droplets of pure CG water spreading on the CG graphene are first considered. The interaction strength \( \varepsilon_{CW} \) is varied in the range 0.04 – 0.08 [kcal/mol]. Every initial configuration is composed by a hemispherical droplet of 17’927 beads centered above the upper-lying plane of graphene at a distance of 7 [Å]. The radius of the hemisphere is 100 [Å]. The planes of graphene are squared with side length 320 [Å]. The boundary conditions are periodic. Every system is evolved in the canonical ensemble for 60 [ns] at \( T = 298 \) [K]. The systems are studied from 1’000 frames recorded during the last 40 [ns]. These dynamics are shorter because for long times of evolution the droplets systematically exhibit excessive stratification. The onset of this phenomenon
Matching with the experimental result \cite{6} occurs approximately for $\varepsilon_{\text{CW}} = 0.0575$ [kcal/mol].

![Figure 2: Contact angle as a function of the strength parameter.](image)

The profile of the droplet in the $xy$ plane. All other simulation settings are the same except for the droplet size, which is varied. The results of Tab. III suggest that variations in droplet size do not significantly affect the contact angle.

| $r$ [Å] | no. water beads | $\theta$ [°] |
|---------|-----------------|-------------|
| 80      | 25'933          | 128.0°      |
| 90      | 32'742          | 128.7°      |
| 100     | 40'430          | 129.0°      |
| 110     | 48'800          | 129.9°      |
| 120     | 58'173          | 130.4°      |
| 130     | 68'255          | 130.4°      |

Table II: Contact angle as a function of the initial radius of cylinders. The variations of $\theta$ indicate that the macroscopic regime is reached for radii $\sim 130$ [Å].

| $T$ [K] | $d$ [molecules/Å$^3$] | $r_f$ [Å] | $\theta$ [°] |
|---------|----------------------|-----------|-------------|
| 298     | 0.0076               | 100.3     | 130.4°      |
| 305     | 0.0075               | 101.8     | 129.3°      |
| 310     | 0.0075               | 101.1     | 130.6°      |
| 315     | 0.0075               | 101.3     | 130.8°      |
| 320     | 0.0074               | 101.4     | 131.4°      |
| 350     | 0.0071               | 102.0     | 132.9°      |
| 400     | 0.0065               | 104.1     | 136.2°      |

Table III: Variations from temperature rise for the cylinder of initial radius 130 [Å]: particle density $d$, final radius $r_f$ and contact angle $\theta$.

a contact angle of 128.2°. This result reproduces the experimental value reported in Ref. \cite{6}. The profile of the droplet in this case is shown in Fig. \ref{fig:3}. In principle, other coarse-grained force fields are available for such investigations \cite{4,5}. For example, in Ref. \cite{21} the wetting properties of pure water on a flat surface were investigated by using a LJ function of type 6-3 for the interaction between the liquid and solid phases. Using the same CG water, preliminary results indicate that the process of stratification on a molecular graphitic substrate occurs quite fast with the liquid-solid interactions described by a LJ potential of type 12-6. Ultimately, the assessment of other coarse-grained force fields for wetting studies warrants a detailed discussion, which is beyond the scope of the present study.

**Cylindrical droplets.** We now want to investigate the dependence of the contact angle on size and temperature. To achieve this, six hemicylindrical droplets of radii from 80 to 130 [Å] are considered. The $x$ side of the simulation domain is always 300 [Å], corresponding to the height of every hemicylinder. The $y$ side is always 120 [Å] larger than the diameter of the droplets. In the initial configuration, the droplets are centered in the $xy$ plane. All other simulation settings are the same employed for spherical droplets. In Tab. II are listed the contact angles measured from the profiles of cylinders with increasing radii. The contact angles vary only of a few degrees and thus we conclude that size effects are negligible with radii $\sim 130$ [Å]. It is interesting to remark that the contact angle for cylinders is slightly larger than that for the spherical droplet, as observed for atomistic systems approaching the macroscopic regime \cite{8}. For the largest cylinder, different temperatures are considered. The results of Tab. III suggests that variations...
over a range of 100 [K] have no drastic effect. The results reported here for the temperature dependence of contact angle are in line with those for atomistic systems [7]. In the following, cylindrical droplets are preferred to spherical ones because the simulations turn out to be accelerated [22]. More precisely, the CPU timings for the cylindrical droplet of radius 80 [Å] are comparable with those of spherical droplets, of radius 100 [Å]. The former system contains 25'933 water beads while the latter 17'927. The reason for the speed-up is that parallelization based on spatial decomposition [17] is more efficient for cylinders because the projection of the particles on the xy plane of the simulation domain gives a better coverage.

**Bulk properties of surfactant solutions.** Here we consider boxes of CG water containing surfactants. In the initial configuration, the surfactant molecules are arranged regularly between two slabs of water. Every simulation lasted for 300 [ns] at NPT conditions. The target pressure is always 1 [atm] while the temperature is adjusted to different values. Data for analysis are recorded every 5 [ns]. To start, we want to compare the predictions of the MARTINI model with polarizable water [3] to those of the standard version [2]. To this end, we first simulate 175 surfactant molecules of C$_{18}$E$_{4}$-NaNaP$_{4}$ with 18’339 water beads, as done in Ref. [14]. This concentration leads to the formation of micelles [14]. We look at the RDF between C$_{1}$ beads belonging to different surfactant molecules in order to extract the equilibrium distance between tail beads in the same micelle. From Fig. 4, we see that there is a first peak around 5.1 [Å], while the first minimum occurs at about $r_{min} = 7$ [Å]. As a consequence, we shall assume that the surfactants with all of their C$_{1}$ beads separated by more than $r_{min}$ are free with respect to each other. The first pronounced peak, together with the fact that the RDF tends to zero, indicate that the tail beads are confined in relatively small regions of the whole simulation domain. Indeed, for all temperatures it is found that most of the surfactant molecules cluster into micelles, corroborating the results reported in Ref. [14].

Table IV lists basic statistical indicators relative to the size distribution of micelles. As the temperature increases, the average size of micelles increases and there is clearly more dispersion around the mean value (enhanced polydispersity). Furthermore, the size of micelles (aggregation number) tends to increase with temperature, as expected for non-ionic surfactants [23]. In that respect, it is interesting to remark that the removal of molecules leaves the surfactant solution at CMC. After 300 [ns] of dynamics there remain five free surfactant molecules (see Fig. 5 and Tab. IV): it is thus predicted a CMC of $4.4 \times 10^{-3}$ [M]. Now, the CMCs at two different temperatures $T_1$ and $T_2$ are related by $\text{CMC}(T_2) = \text{CMC}(T_1)^{T_1/T_2}$ [14] [24]. From the experimental value $\text{CMC}(T_1 = 298 \text{[K]}) = 8 \times 10^{-3}$ [M] [25] [26] it is obtained a CMC of $16 \times 10^{-3}$ at 350 [K]. It turns out that our result underestimates this value but is closer than the finding within the standard MARTINI model of $35 \times 10^{-3}$ [M] [14]. For the surfactant L2, L3, T1 and T2, we apply the same simulation settings with the exception that the timestep size is reduced to 10 [fs] for stability reasons related to bond interactions of the surfactant molecules. The temperature is always kept fixed at $T = 298$ [K] and the initial state consists of a given number of surfactant molecules, for the concentrations of Tab. IV between two slabs of water beads (50'000 in total). For the typical experimental concentration of 1 wt%, the RDFs of Fig. 5 indicate that the tail beads, for the surfactant L2, are separated by larger distances because the first maximum is lower. From the size distributions of micelles plotted in Fig. 7 it can be seen that the linear surfactants tend to form larger micelles on average. A summary of micelle statistics is given in Tab. V in all cases we used $r_{min} = 7$ [Å] (cf. Fig. 6).

Wetting with surfactants. Also for this train of simulations, the timestep size is reduced to 10 [fs]. In all other respects, the settings used for cylindrical droplets of pure water are maintained. The effect of the presence of surfactants is to lower the contact angle and this is possible if the tail beads, displaying hydrophobic behavior, interact more strongly with the CG graphene than the head beads P$_{4}$. For this reason, it is assumed that the interaction strength is $2 \times \epsilon_{\text{CW}} = 0.115$ [kcal/mol]. This approach is chemically consistent since, in graphene, carbon atoms have no polarity. The parameter $\sigma$ for the LJ interactions with graphene beads is again 6.24 [Å]. The results of Tab. VI indicate that the contact angle is almost insensitive to significant variations of surfactant concentration using equilibrated solutions. Since in general it is observed a stronger micellization process, we repeat the previous simulations with cylindrical droplets of pure water and the surfactants arranged between water and graphene as illustrated in Fig. 8. In this way, the solution is not yet properly equilibrated, but more surfactant molecules are closer to the expected configuration, that is, near the contact line [22] [27] [28]. At 1 wt%, all the systems still do not experience any influence of the presence of surfactants (see Tab. VII). It is worth noting that, in similar studies [29] [30], low surfactant concentrations resulted in a transient increase of the surface tension for the MARTINI model. On the other hand, the concentration around 4 wt% provides a basis of comparison among the different systems. The results for linear surfactants prove that, in first approximation, the dominant factors promoting wetting are the length and apolarity of the hydrophobic tail. Indeed, comparison between surfactants L2 and L3 indicate that one single C$_{1}$ bead is sufficient to counteract the effect of ten P$_{4}$ beads (their contact angles differ by a few degrees). We want to highlight the preferred arrangement of surfactant molecules inside the droplets. To this end, it is useful to look at the spa-
Mapping | $T$ [K] | Volume [Å³] | C [M] | Average | Variance | Size range | no. monomers | CMC [M]
--- | --- | --- | --- | --- | --- | --- | --- | ---
C₈E₄-NaNaP₄ | 298 | 1.845’116 | 0.158 | 17.5 | 81.8 | 5-38 | 0.0 | –
305 | 1.846’956 | 0.158 | 25.0 | 244.9 | 7-53 | 0.0 | –
310 | 1.847’152 | 0.158 | 25.0 | 150.1 | 8-42 | 0.0 | –
315 | 1.847’130 | 0.158 | 25.0 | 305.0 | 11-63 | 0.0 | –
C₈E₄-P₅ | 350 | 1.879’769 | 0.154 | 6.0 | 21.1 | 1-18 | 5.0 | $4.4 \times 10^{-3}$

Table IV: Micelle size statistics over the last 100 [ns] for the simulations of surfactant C₈E₄. With volume we intend the average value of the simulation domain; its standard deviation is always below 0.1%. The symbol C designates the concentration.

Figure 5: Evolution of the number of free surfactants for the C₈E₄-P₅ solution at 350 [K] (see Tab. IV).

Fig. 9 linear surfactant molecules are principally located at the solid-liquid interface. Their organization is not uniform, as indicated by the statistics for micelles of Tab. VII. The weak tendency to form layers, together with the fact that the distribution $P_y$ is strongly peaked around the contact line, give further support to the hypothesis that the number of hydrophobic units is the dominant factor for enhanced wetting. Regarding the T-shaped topology, from Fig. 10 it is seen that less surfactant molecules accumulate along the contact line. The fact that the contact angle remains almost unchanged, as compared to the linear counterparts (see Tab. VII), let us conclude that their action is more effective. In macroscopic systems, they should thus wet better than linear surfactants, since the plateau in Fig. 10 is already almost at the same height of the peaks near the contact line. Interestingly, a longer hydrophobic tail does not lead to a lower contact angle. It thus arises that for T-shaped surfactants a shorter hydrophilic headgroup can enhance wetting more than a longer tail. The plots of Fig. 11 shows that one advantage of the T-shaped topology is...
Figure 6: C\textsubscript{1}-C\textsubscript{1} RDFs for the boxes with linear surfactants at 1 wt%; Left: surfactant L2; Right: surfactant L3. Similar results are obtained for the other equilibrated boxes with higher concentrations of surfactant molecules (cf. Tab. V).

| Surfactant | Mapping | Volume [Å\textsuperscript{3}] | no. surfactants | C [M] - [wt\%] | Average | Variance | Size range | no. monomers | CMC [M] |
|------------|---------|-------------------------------|-----------------|----------------|---------|----------|------------|--------------|---------|
| L2         | (C\textsubscript{1})\textsubscript{3}(P\textsubscript{4})\textsubscript{20} | 5'825'561, 6'503'837 | 34, 288       | 9.7×10\textsuperscript{-3} - 1.0% | 6.2 | 26.0 | 1-14 | 1.7 | 4.8×10\textsuperscript{-4} |
| L3         | (C\textsubscript{1})\textsubscript{4}(P\textsubscript{4})\textsubscript{30} | 5'829'813, 6'386'342 | 24, 194       | 6.8×10\textsuperscript{-3} - 1.0% | 7.4 | 6.9 | 2-11 | 0.0 | – |
| T1         | (C\textsubscript{1})\textsubscript{3}(P\textsubscript{4})\textsubscript{10} | 6'506'929 | 520 | 1.3×10\textsuperscript{-1} - 8.9% | 11.1 | 54.8 | 1-50 | 3.9 | 1.0×10\textsuperscript{-3} |
| T2         | (C\textsubscript{1})\textsubscript{3}(P\textsubscript{4})\textsubscript{20} | 6'487'350 | 288 | 7.4×10\textsuperscript{-2} - 8.4% | 9.3 | 41.7 | 1-39 | 4.2 | 1.1×10\textsuperscript{-3} |

Table V: Basic statistics regarding micelle size for the equilibration of CG water with surfactants at different concentrations. In all cases, the standard deviation of the volume is always around 1\% of the average value. C stands for concentration.

Figure 7: Micelle size distributions as resulting from the simulations of equilibration for two long-chain, linear surfactants and the T-shaped surfactants at 8 wt\% concentration. Top: For the L2 surfactant the distribution is peaked around the size of 10, while for the longer surfactant L3 the more frequent micelle is of size 3. Bottom: T-shaped surfactants have less micelle aggregates composed of fifteen or more surfactants. This occurrence has probability 0.26 for the surfactant T1 and 0.18 for the surfactant T2. The same probabilities in the linear case are 0.33 and 0.37 for the surfactants L2 and L3, respectively.
faster spreading. After 25 [ns] of dynamics, the contact angles for T-shaped surfactants vary at most of 1.7° (surfactant T2 at 4.2 wt%). In the same evolution period, with the exception of the surfactant L2 at 4.2 wt%, the variations of the contact angle for linear surfactants are more marked: at least of 3.9° (surfactant L1 at 5.2 wt%) and at most of 19.2° (surfactant L2 at 8.4 wt%). The influence of the topology for enhanced spreading was already recognized in the literature \[22, 27, 28\].

V. CONCLUSIONS

Small concentrations of surfactants around 1 wt% can cause significant reductions of the contact angle. As an example, for the surfactant Triton® X-100, the surface tension of water of 72.5 [mN/m] decreases linearly with concentration up to 0.03 wt%, when the minimum of 31 [mN/m] is attained; for higher concentrations the surface tension remains of course constant. It turns out that the proper treatment of wetting phenomena by aqueous surfactant solutions requires conditions of difficult realization by the present computational capabilities. Coarse-grained models allowed us to move one step further toward a more realistic representation of such systems in terms of surfactant concentrations. At the typical experimental concentration of 1 wt%, the coarse-grained MARTINI force field \[2, 3\] marks no difference between the surfactants investigated here. For higher concentrations there appears that it is possible to discriminate the wetting behavior of the various surfactants. The main instrumental conclusion of our study is that the length and apolarity of the hydrophobic tail determine to a larger extent the wetting behavior for the linear topology. Instead, the length of the hydrophilic headgroup appears to be more relevant for the T-shaped topology. In the framework of our simulations, the T-shaped topology does not lead to a substantial decrease of contact angle vis-a-vis linear surfactants. Lennard-Jones forces are short range and the reduction of the contact angle is essentially driven by the accumulation of surfactants along the contact line. Micelle statistics demon-

| Surfactant | Mapping | no. surfactants | C [wt%] | \(N_{\text{micelle}}\) | Size range | no. monomers | \(d [\text{molecules/Å}^3]\) | \(\theta [\degree]\) |
|------------|---------|-----------------|---------|--------------------------|-------------|--------------|-----------------|------------------|
| L2         | \((C_1)_3(P_4)_{20}\) | 381 | 0.9% | 10.3 | 1-10 | 6.6 | 0.0074 | 131.1° |
|            | \(68'727\) | 43 | 0.9% | 17.0 | 1-14 | 12.1 | 0.0076 | 131.1° |
|            | \(66'351\) | 359 | 8.7% | 108.3 | 1-52 | 55.5 | 0.0065 | 130.7° |
| L3         | \((C_1)_4(P_4)_{30}\) | 278 | 0.9% | 8.1% | 36.6 | 1-66 | 11.3 | 0.0068 | 131.2° |
|            | \(68'690\) | 28 | 0.9% | 10.3 | 1-10 | 6.6 | 0.0074 | 131.1° |
|            | \(63'555\) | 239 | 8.1% | 36.6 | 1-66 | 11.3 | 0.0068 | 131.2° |

Table VI: Characteristics of the cylindrical droplets of initial radius 130 [Å] containing linear surfactants. C indicates the concentration. The average number of micelles is designated by \(N_{\text{micelle}}\). The cutoff distance for the extraction of micelle clusters is 7 [Å] (see Fig. 6).

| Surfactant | Mapping | no. surfactants | C [wt%] | \(N_{\text{micelle}}\) | Size range | no. monomers | \(d [\text{molecules/Å}^3]\) | \(\theta [\degree]\) |
|------------|---------|-----------------|---------|--------------------------|-------------|--------------|-----------------|------------------|
| L1         | \((C_1)_3(P_4)_{10}\) | 85 | 1.1% | 41.8 | 1-12 | 21.6 | 0.0076 | 129.6° |
|            |         | 424 | 5.2% | 112.4 | 1-37 | 46.3 | 0.0076 | 118.2° |
|            |         | 847 | 10.5% | 112.3 | 1-165 | 40.6 | 0.0076 | 114.5° |
| L2         | \((C_1)_3(P_4)_{20}\) | 39 | 0.8% | 27.4 | 1-9 | 19.4 | 0.0076 | 130.1° |
|            |         | 196 | 4.2% | 75.1 | 1-21 | 35.4 | 0.0075 | 123.5° |
|            |         | 393 | 8.4% | 91.1 | 1-40 | 33.9 | 0.0074 | 111.7° |
| L3         | \((C_1)_4(P_4)_{30}\) | 26 | 0.8% | 15.1 | 1-7 | 8.5 | 0.0076 | 130.5° |
|            |         | 132 | 4.1% | 32.1 | 1-21 | 6.7 | 0.0075 | 125.0° |
|            |         | 265 | 8.3% | 34.3 | 1-43 | 3.7 | 0.0072 | 114.9° |
|            |         | 530 | 16.7% | 65.0 | 1-206 | 28.9 | 0.0065 | 124.7° |
| T1         | \((C_1)_3(P_4)_{10}\) | 85 | 1.1% | 44.4 | 1-13 | 24.1 | 0.0076 | 129.2° |
|            |         | 424 | 5.2% | 119.1 | 1-33 | 45.4 | 0.0076 | 116.0° |
| T2         | \((C_1)_3(P_4)_{20}\) | 39 | 0.8% | 28.3 | 1-7 | 21.0 | 0.0076 | 129.8° |
|            |         | 196 | 4.2% | 66.3 | 1-20 | 23.4 | 0.0075 | 122.1° |
|            |         | 393 | 8.4% | 88.3 | 1-36 | 22.2 | 0.0074 | 108.3° |
| T3         | \((C_1)_3(P_4)_{20}\) | 212 | 5.0% | 43.8 | 1-30 | 9.6 | 0.0075 | 125.1° |

Table VII: Results for the cylindrical droplets of initial radius 130 [Å] with the surfactants arranged in the initial configuration in the proximity of contact line; all droplets contain 68'255 water beads. C stands for concentration; \(N_{\text{micelle}}\) is the average number of micelles, and size range is the aggregation number variation. Micelle clusters are extracted using a cutoff distance of 7 [Å] for all surfactants (see Fig. 6). The simulations for the systems containing linear surfactants with a concentration higher than 1 wt% lasted for 100 [ns] and the analysis is performed on data collected under the same conditions over the last 40 [ns]. This choice is dictated by the fact that longer evolutions are necessary in order to reach a state near the equilibrium in these cases. The contact angle for the surfactant L3 at 16.7 wt% is not in line with the results for the lower concentrations suggesting that the system is not yet well equilibrated. For these longer dynamics, the stratification of water did not occur.
Figure 8: (Color online) From Left to Right: Droplet with surfactant L3 at 8 wt% (see Tab. VII) in the initial configuration, final configuration without water beads and final configuration including water beads. At equilibrium, the surfactant are oriented with their head toward the fluid.

Figure 9: Distributions of C1 beads in space for the cylindrical droplets containing surfactants L2 at concentration 8 wt%. Top: Results for the droplet prepared as shown in Fig. 8 with the surfactants in the proximity of contact line. Many surfactants are near the contact line, i.e. $|y - y_{CM}| \approx 90$ [Å], and at the solid-liquid interface. Bottom: Results obtained from an equilibrated solution (cf. Tab. VI). The position and height of the peaks indicate that a significant number of surfactants is in the bulk of the droplet. Similar conclusions can be inferred from the outcomes for the other case studies.

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Figure 10: Spatial distributions of $C_1$ tail beads for the cylindrical droplet containing surfactant T2 at 8 wt% (see Tab. VII). In this case, the surfactants are no longer neatly localized along the contact line. It also appears that the adsorption layer is more uniform (cf. Fig. 9). The plots for the other T-shaped surfactants lead to the same conclusions.

Figure 11: Contact angle $\theta$ in the course of time for the cylindrical droplets of Tab. VII. In general, T-shaped surfactants spread faster. The analysis uses the data collected in time intervals of 5 [ns].

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