Water nanodroplet on a graphene surface—a new old system

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Water nanodroplet on a graphene surface—a new old system

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Abstract

The major subject of our study is the accuracy of contact angle calculations. Reporting new simulation data for graphene-water systems, we show that the majority of previously reported data should be treated with caution, since the proper contact angle can be recorded only after a sufficiently long simulation time. It has been proven that—if one wants to gain accuracy greater than 0.1°—long calculations (exceeding 50 ns) are required. Finally, we also show, using both a Groningen Machine for Chemical Simulations (GROMACS) package and our new molecular dynamics (MD) code, that the changes in the contact angle, caused by graphene bottom layer rotation, are within the range of calculation error. We also propose a novel definition of the bottom of the droplet as the height where the density is half the density of liquid water. This new definition is applied in the method of the contact angle calculation from the MD simulation data.

Keywords: graphene, water nanodroplet, contact angle, molecular simulation

(Some figures may appear in colour only in the online journal)

1. Introduction and the aims of the study

The potential application of graphene and graphene-based nanomaterials continues to grow, and this is caused mainly by their high surface area, electron mobility, thermal and mechanical properties. Recent applications in electronic devices (together with procedures of graphene fabrication) have been discussed by Sood et al [1], some potential environmental usage has been reviewed by Perreault et al [2] and the application of theoretical methods for the description of functionalized graphene materials has been discussed by Pykal et al [3]. In this field, a number of authors point out the importance of the water-graphene contact angle (CA) determination, especially in areas where water-graphene interactions play an important role (e.g.: adsorption, lubrication, adhesion, nucleation, etc [4–6] fabrication of antifreeze [7] or self-cleaning surfaces [8], and/or fabrication of graphene-based water treatment membranes or electrodes [2]).

On the other hand, the water-graphene system is widely studied, because of the fundamental questions still pending a final solution. Generally it can be stated that still little is known about the role of the macroscopic factors of a drop shape change with the reduction in scale, as was pointed out by Quere [9]. Thus, some new results continue to appear, revealing the influence of additives on graphite/graphene wetting by water [10–14] along with others showing extraordinary behaviour of water confined between graphene walls [15]. The graphene/graphite-water system has also been widely studied to check the influence of heterogeneity/roughness on the wetting properties [16–31].

The CA is the fundamental value determining the wetting process and reflecting balance between forces on the contact line [32]. However, for water-graphene/graphite systems there are still contradictory reports about the experimental CA value. Hence, Ashraf et al [5] have recently pointed out some problems and difficulties in the determination of this angle, resulting in values for water-graphene systems varying in the
this study we are trying to find the missing answers. Generally, questions arise from the analysis of the literature data, and in CA calculation. Thus, it can be stated that some fundamental doubts related to the application of different ensembles for instead).

et al off applied by Werder the obtained values are somewhat lower (than observed by

Note — Reference [41] — 50 ns.

– ε0 interaction (of C–O) on the CA values, pointed out that

<table>
<thead>
<tr>
<th>Reference</th>
<th>Contact angle (°)</th>
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<tbody>
<tr>
<td>[41]†</td>
<td>θ_R (°)</td>
</tr>
<tr>
<td>0</td>
<td>94.3</td>
</tr>
<tr>
<td>10</td>
<td>95.5</td>
</tr>
<tr>
<td>20</td>
<td>93.0</td>
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<tr>
<td>30</td>
<td>93.7</td>
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<tr>
<td>40</td>
<td>97.8</td>
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<tr>
<td>50</td>
<td>94.6</td>
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†The values assessed from [41].

Table 1. The comparison of CA values reported and analyzed in this study.

(1) The authors discussed possible reasons causing those differences). As a consequence, not only the water-graphene CA value [33, 34] but also the influence of support and time [35] have been the subject of debate. However, until now, the mechanism explaining the influence of support on the water CA on graphene is still unclear [35].

All of the above questions are the reason why a wide range of parameters is still applied during simulations of water nanodroplets on graphene surfaces (for example [36, 37]). It should be pointed out that, in fact, there is a huge parameter mismatch in literature related to the application of different procedures during molecular dynamics (MD) simulations. For example, Jaffe et al [36] tabulated different water—carbon force fields (see table 1 in [36]), pointing out that the application of two of them led to complete wetting of the graphite surface, but, after the application of the remaining force fields, this wetting was not observed. The authors claim that the force field will remain unverified until the matching experimental CA is used. Also, Wu and Aluru [37] presented a summary of different carbon—water force fields (see table 1 in [37]), pointing out differences in water—carbon binding energies. However, the most popular parameters are those reported by Werder et al [38] who calibrated the water-graphene force field. However, one should remember that Werder’s original calibration [38], based on the application of the SPC/E model of Berendsen et al [39], was performed using a smoothly truncated Coulomb potential. It is well documented that the influence of the method applied for electrostatic interactions calculations is crucial for the value of the corresponding CA calculated from the MD [40]. For example Daub et al [18] while checking the influence of well depth in the potential of C–O interaction (εCO) on the CA values, pointed out that the obtained values are somewhat lower (than observed by Werder et al [38]), due to the omission of a pair-potential cut-off applied by Werder et al [38] (Ewald sums were applied instead).

Considering the molecular simulation reports, there are also doubts related to the application of different ensembles for CA calculation. Thus, it can be stated that some fundamental questions arise from the analysis of the literature data, and in this study we are trying to find the missing answers. Generally, we want to stress the following major subjects: the influence of simulation time on CA values, and the proper method of CA calculation from the MD simulation data. Finally, we discuss some doubts that arise from performing the simulations in a microcanonical ensemble (N, V, E) for calculation of the CA value. To our knowledge, the topics mentioned above will be explored in our study for the first time. Subjects mentioned above are illustrated by the new simulation data, checking how the rotation of the graphene bottom layer affects the CA of the water nanodroplet. This subject is not new, however—in our opinion—it has not been sufficiently discussed yet. Namely, Liu and Xu [41] have recently published a study showing the influence of (two-layered) graphene bottom layer rotation (θR) on the CA of water. The MD simulation technique was applied together with a circular fitting to determine the CA value. The value for the initial graphene conformation (θR = 0°) was estimated as equal to 94.30 ± 1.25°. The maximum difference between the CA values recorded after rotation was reported as equal to 4.72°. In fact, the results obtained by the authors mentioned above suggest that CA value is affected by the orientation of the lower layers of graphite/graphene. One can say that such structures are unrealistic ones. But, in fact, they can be obtained just by putting one monolayer graphene on top of another. The real resulting structures can be of a different physical nature to those suggested by Liu and Xu. But such simulations lead to more general questions. Namely, it is known that graphite exists in various forms, differing in their position of the graphene layers (known as ‘stacking”). If the considerations reported by Liu and Xu are correct, different contact angles should be observed for different forms of graphite. Such a question/problem can be applied to other similar systems as well. This is why we decided to verify the results, especially as these authors have drawn their conclusions from the fact that the errors are lower than the deviations in the values of the CA. But how these errors are assessed (calculated) is unclear. In practice, if these errors are larger that means that there is no evidence of the influence from the orientation of the lower layers on the CA. For that purpose we have carried out much longer simulations with particular emphasis on actual errors, which can be drawn from the dependence of values of the CA on the time of the simulations. In this article, we also propose a slightly different method of CA calculation. Since the authors used the parameters provided by Werder et al [38], in our study we rely on similar procedures, applying 2000 SPC/E water molecules topology.

2. Simulation details

Structures studied in this article were created with a view to reflect those described by Liu and Xu [41]. A graphene plane of size approximately 12 × 12 nm was generated with a C–C bond length 0.1421 nm and placed in the simulation box, with periodic conditions preserved in the x and y directions and of height 6 nm. Another plane of excessive size was similarly created, rotated in sequence by (θR =) 10°, 20°, 30°, 40° and 50°, and trimmed to fit a 12 × 12 nm rectangle. Each of the obtained planes were placed 0.34 nm below the initial
one, which is recognized as a typical distance between graphene layers (see figure 1). Note that in our study the central benzene ring (lying in the center of graphene layer) is the rotation center, which is in contrast to the study of Liu and Xu, where the rotation center is unknown (lying somewhere beyond the images presented) [41]. The choice of the center of rotation is crucial, since the topologies of the pairs of structures ($\theta_R = 10^\circ$ and $50^\circ$, $\theta_R = 20$ and $40^\circ$) are symmetrical and should provide the same values of CA. This implies that symmetry in the plot of the CA versus $\theta_R$ is expected. Such symmetry cannot be found in such a plot by Liu and Xu [41].

All interaction parameters were taken from table 2 from [38], namely: $\varepsilon_{\text{CO}} = 0.392$ kJ mol$^{-1}$ and $\sigma_{\text{CO}} = 0.319$ nm (where $\sigma_{\text{CO}}$ is the carbon–oxygen collision diameter). A cube containing 2000 water molecules of SPC/E model [39] was placed in the central position of each system, distanced from the upper graphene layer. Molecular dynamics simulations were carried out using the GROMACS 4.5.7 package [42] and the OPLS/AA force field [43]. A temperature of 300 K was kept by the Nose–Hoover thermostat; interatomic interactions were modeled by a well known Lennard-Jones 9-3 potential (cut-off radius 1.0 nm) and electrostatic interactions by a Coulomb relation with cut-off radius 2.0 nm. Initial pre-runs were held for 250 ps in order to allow water molecules to form a proper drop. Thus, the top of the box was limited by a wall made of nitrogen atoms with a Lennard-Jones 9-3 potential. The resulting coordinates served as the input for actual (production) runs, held for 6 ns (time step 0.002 ps), without a limiting wall, but in xyz periodic conditions. During the production run, each of the 0.5 ps positions of water molecules had been stored for density matrix calculations. It should be pointed out that—in contrast to Liu and Xu [41]—we have not applied the PPPM method for calculation of electrostatics. This is due to two major reasons. First of all, Werder et al [38], during the force field calibration, applied a truncated Coulomb potential. As we pointed out above, the method applied for the calculation of electrostatic interactions strongly influences the shape of a droplet, and consequently the CA value. Moreover, we applied a truncated Coulomb potential since it was used for the SPC/E model calibration by Berendsen et al [39].

Some additional MD simulations were also preformed for the purpose of this study and the appropriate procedures are described below.

3. Calculation of CA from molecular simulation data

Before we compare the methods applied for the calculation of the static CA value from simulation data, we should briefly stress the approach applied in a real experiment. Fundamental
discussion on this subject was provided by Kwok and Neumann [44, 45]. It is well known that the experimentally determined CA value (often called ‘apparent CA’) can more or less approach Young’s contact angle, and the authors stressed the necessary experimental conditions for minimizing this difference. They also discussed the method of an axisymmetric drop shape analysis profile (ADSA-P), leading to the correct surface interfacial tension. From this, the CA can be determined by a numerical integration of the Young–Laplace equation. Similar, but not always the same, approaches are applied during the CA calculation from the MD simulation data. Recently Santiso et al. [46] discussed the major problems associated with the application of the most popular procedures of CA determination from molecular simulation. Among them one can consider: asymmetry of droplets, capillary fluctuations with time, problems with choice of a line separating the phases, etc. In the opinion of the mentioned authors, typically the CA is extracted by superimposing a circle on the droplet profile originated from the simulations. Both values, the center and the radius of the circle, are obtained using a fitting procedure. The authors mentioned above proposed a new method of CA calculation, which does not assume the shape of the droplet. The approach presented by Santiso et al. [46] is relatively new; however, in literature, some alternative and older approaches are also used. Some of them are examined below.

In their study, Hautman and Klein [47] proposed the procedure in which the droplet is assumed to be spherical (the part of the droplet making contact with the surface is ignored), and the microscopic CA is calculated from the angle of intersection between the surface of the sphere and the surface of the plane. Generally, as seen in literature, to compute the CA from a simulation of a droplet, usually the method proposed by de Ruijter et al. is applied [48]. Authors, using radial symmetry, assume that, away from the surface, the drop contour should form a spherical cap and the profile should be a circle. This profile, however, is more or less disturbed by the wall, thus first ca. Ten layers should be excluded from the analysis. The CA is the angle tangent to the profile measured at the surface formed by a solid substrate. Ingebrigtsen and Toxvaerd [49] applied the Stirling criterion of a particle belonging to a cluster to determine the CA. Next, the results of the final 1 million time steps of the MD simulation are averaged to calculate the local density profiles. Cylindrical volume elements are applied and the authors do not assume the spherical shape of the droplet. Next, to determine the location of the surface and the CA, they fit the density-radius function of the droplet using the same equation as used by de Ruijter et al. [48] Werder et al. [39], also applying the cylindrical coordinates and the procedure proposed by de Ruijter et al. [48]. The same and/or a slightly modified procedure has been widely applied by others as well (see for example [23, 29, 50–52]). Yang et al. obtained the CA by fitting the density profile of the droplet to a cylinder [53]. Shi and Dhir [54] determined the CA value by dividing the simulation cell on cubes. Next, by the density calculation, they defined the boundary of the droplet. The CA is calculated by drawing a tangent line near the contact line in such a way that it overlaps the contour in the region \(0 \leq z \leq 3\sigma\) (where \(\sigma\) is the collision diameter). The CA in this approach is calculated as the average value from sampling in the \(xz\) and \(yz\) planes. Sergi et al. [55] calculated the CA from the tangent at the contact line point. The profile of the droplets is approximated by a piecewise linear function, and the average values of \(x\) and \(y\) are calculated. The CA is calculated from the slope of the linear function, applied for the points located above \(21/6\sigma_{\text{CO}}\). Weijis et al. [56] used the method of isodensity plots. The authors simulated two types of droplets, namely cylindrical and spherical ones. Next, they ignored the part of the droplet where layering occurs (close to the surface) and used the circular fit of the upper part of the droplet. To find the CA values they extrapolated the circle to the surface (defined as \(\sigma/2\) above the top row of the surface atoms). In the choice of the proper isodensity surface, the data from the cylindrical droplets simulation were used (the data were not affected by the line tension). Scocchi et al. [57] have compared the CA values obtained for the cylindrical and spherical droplets. In both cases, the water profiles were approximated by a circular fit. What is important, in both cases, is that all points are included in the fitting, i.e. the authors also included the points representing water molecules at the vicinity of the graphite surface. Recently, Chen et al. [58] provided a review of the methods in CA calculation from molecular simulation data. The authors discuss the most popular approaches (pointing out advantages and disadvantages), i.e. the neglecting of droplet molecules at the vicinity of the solid surface and detecting the shape of the droplet from the density profile.

Summing up the mini-review given above, there are generally two major groups of approaches in the determination of the CA value from simulation data. Also two types of density profile fit are used (spherical and cylindrical) and the major difference is the approximation of the CA, since in one group of methods it is assumed that the CA is the angle tangent to the profile measured at the solid substrate (labeled as \(\text{CA}_\text{S}\) in our work), while in the second group that it is measured at the bottom of the droplet (see for example: [54–56] (labeled as \(\text{CA}_\text{G}\)). This way, using different procedures of CA calculation, one can observe more or less proper CA values, and/or larger or smaller differences between them.

In this study the value of the CA is calculated in a typical manner, i.e. from the profile of density, obtained via the mapping of water molecules’ positions of mass centers in the cylindrical coordinate system. The axis of this system is perpendicular to the graphite structure and is running through the droplet mass center. The space around the droplet is evenly divided into slabs and sub-cylinders along and about the cylinder axis. The thickness in both cases is the same, equal to 0.2 Å (see figure 2). From the obtained maps, points of density within the range of 0.5 ± 0.03 are chosen, and points within the distance of 11 Å from the substrate and in the proximity of the axis are excluded. Finally, these points are fitted with the use of a circle. Such an approximation is not trivial, since—if planar Cartesian system is used—the points arrange...
themselves in a non-linear fashion. To avoid this problem, we decided to choose a bit of a different approach. Namely, we use polar coordinates. In this system the fitting curve takes the vector form:

\[ Y = X_0 + R = (0, z_0) + (r \cdot \cos(\alpha), r \cdot \sin(\alpha)) = (0, z_0) + r \cdot \hat{\alpha}. \]  

(1)

where \( X_0 \) is the center of the circular coordinates system and \( R \) is the radius vector of the fitting circle. This equation consists of two adjustable parameters \( z_0 \) and \( r \).

In this coordinates system, the position of the \( i \)th (being fitted) point has the vector representation:

\[ Y_i = X_0 + R_i = (0, z_0) + r_i \cdot \hat{\alpha}_i. \]  

(2)

The approximation can be done with the use of the mean squares method and the target function of the form:

\[ F_T = \sum \left| Y_i - Y_i^F \right|^2. \]  

(3)

where \( Y_i \) and \( Y_i^F \) are coordinates of the fitting curve and fitted points, respectively.

For the accomplishment of the approximation, any optimization method with gradient estimation can be used. The main advantage of this approach is that if a circle is sufficiently adjusted, fitted points run about the straight line in a circular coordinate system. Finally, in order to calculate the values of the CA, the obtained curves are extrapolated to the outer surface of the substrate (CA_S) and to the surface of the bottom part of the droplet (CA_B) (see figure 2). ‘Bottom’ is defined (see figure 2) as the lowest part of droplet with a density no smaller than 0.5 g cm\(^{-3}\). This is a novel definition of the bottom of the droplet, as the height where the density is half the density of liquid water. This new definition is applied in the method of the contact angle calculation from the MD simulation data. As will be shown below (see figure 5), CA_B is more physically meaningful than CA_S.

4. The influence of graphene layers orientation on CA values

Since the effect of the rotation of the bottom graphene layer was studied, with reference to the CA_S [41], figure 3 shows the comparison of the respective values published by Liu and Xu [41] and the CA_S values obtained in this study from the application of the GROMACS package. From the obtained results, it can be seen that there is no clear dependency of the CA_S on the angle of rotation of the bottom graphene layer. The CA_S values are much less scattered than those obtained by Liu and Xu. Additionally, there is not any expected symmetry observed about the angle of 30°. This led us to the conclusion that the scatter of the CA_S values is the result of unsatisfactory averaging, rather than of any dependency on a bottom layer rotation angle.

In order to assess the real values of the calculations error, we decided to perform a series of much longer additional calculations (final results are also shown in figure 3). If a GROMACS package had been used for that purpose, dumping of necessary data would have led to the production of very large files needed. Although that is not necessarily a big problem for modern computers, we calculated relevant density matrices ‘on the fly’ with a self-made MD algorithm, written in OpenCL programming language. For that purpose, the same water SPC/E model is used. These MD simulations are carried out with the computer experiment resembling the real one. No long range interactions or periodic boundary conditions for moving water particles are considered. Only the structure of the substrate is visible for the water molecules in the periodic boundary conditions. In order to prevent the escaping of water molecules forming the droplet to infinity, a simple (reversing the direction of velocity of mass center only) repulsive spherical wall is used. For the mutual interactions of water particles, the parameters of the Coulomb and L-J interactions provided by Berendsen are applied [39], but without a typical

Figure 2. Water droplet density matrix and isodensity profile applied for the fitting procedure, leading to determination of the CA according to the substrate surface (CA_S), and to the bottom of the droplet (CA_B). On the RHS of the figure, the red solid line shows the bottom of the droplet, and black solid line the fit to a circle.
cut-off scenario and with a 8 Å particle–particle cut-off used instead. It allows us to overcome the typical ‘partial charge’ of polar molecules problem if a charge-charge cut-off is used. For the interaction of water molecules with the substrate, the same parameters, provided by Werder et al, are used [38].

For the time integration of the water molecules trajectory, the approach by Smith [59] is applied. In essence, being similar to a velocity Verlet integrator, it is a direct usage of rigid body dynamics. This is very elegant and simple, not requiring any complicated calculations (e.g. quaternions) or vector-tensor arithmetic. It was found in our tests that the deviation of the temperature of a free rotating (not interacting) particle is of the order of 0.01 K per few nanoseconds of simulation. All the simulations were carried out for 50 ns, with time step of 2 fs at 300 K. To keep the temperature constant, many algorithms were available. They have advantages and disadvantages. With the use of GROMACS, we tested all accessible thermostats with various adjustable parameters. We have found no substantial influence of the choice of these thermostats on values of the CA and density profiles. In practice, this means that every thermostat algorithm can be used for CA calculations. Therefore, in our algorithm we decided to use a bit of a different approach. Because we used rigid body dynamics for the trajectory of molecules calculations, it is easy to separate rotational and translational freedoms of movement. On this occasion we used a semi-constraining algorithm. The instantaneous temperature was calculated from the kinetic energies of translation and rotation velocities of water particles. Afterwards, the classical rescaling factor is calculated. This factor is used for the rescaling of velocities, but for translational ones only. Rotational velocities were left unconstrained i.e. no correction is used for them. This algorithm allows the temperature of the system to fluctuate. The main feature of this attempt is that no arbitrary parameters were used. In order to check the behavior of our new MD algorithm, we have tested it on a water droplet freely suspended in space, consisting of the target number (2000) of molecules. It is not necessary to prove that this thermostatic procedure conserves both system linear and angular momenta, if set to zero at the beginning of simulations. During tests, the values of instantaneous temperatures were collected in order to obtain the probability density profile of instantaneous temperature. The test was carried out for 30 ns. The temperature distribution occurred to be a purely Gaussian one, with the maximum lying at 300.03 K. However, it should be pointed out that small drifts of the mass center of the droplet were observed, but that is due to the inaccuracies of the cutoff scheme and/or time integrator, rather than to the thermostatic algorithm. No unphysical behavior of the system (uneven velocity distribution or rotation of the system) was observed. The density profile quantitatively is practically the same (within the uncertainty error) as that which was obtained from the GROMACS calculations. We decided to use this method for the following reason: there is a debate among scientists about what type of thermodynamic ensemble to use: NVT or NVE. Both approaches can be found in the literature. There are ‘pros and cons’ for each of them. However, in our opinion, the NVE ensemble is the least appropriate one. There are a few reasons for that: there is no possibility for calculating most thermodynamic parameters, no real experimental investigation of the wetting phenomenon is carried out under adiabatic conditions, and the energy of the droplet cannot be constant, due to the fact that the droplet is strongly coupled to the bath—namely the substrate itself. In the case of the NVT ensemble, numerous available thermostat algorithms consist of arbitrary adjustable parameters that can lead to a different range and nature of temperature fluctuations.
All of the calculations had been carried out on an nVidia GTX580 Graphic Processing Unit using a SPDP (Single Precision Double Precision) technique, i.e. with the positions of atoms and their two-body interaction forces in Single Precision, but all the cumulative parameters (total forces, torques, momenta) and trajectories in Double Precision. Prior to the main calculations, a testing simulation had been carried out in order to find out if the proper values of CA are obtained and if the systems indicate proper behaviour. Unfortunately, the obtained CA were higher by about 2° than those reported by Werder et al [38]. However—surprisingly (and by accident)—when testing the Jaffe and co-workers model of graphite [36] for 100 ns, we have obtained exactly the same value for the CAs as reported by those authors (94.88°). It was a rather
‘pure’ accident, because after 70 ns it was equal to 94.67°. We think that this discrepancy can be explained by insufficient averaging, due to carrying the simulations for too short a time (a few ns). We hope to present this in a readable manner in light of our findings. To explore this, we have calculated the changes in the CAS values with the simulation time (figure 4).

As mentioned previously, during the main simulations the mapping of water molecules positions took place ‘on the fly’. But, additionally, each 0.5 ns cumulative value of the CA was calculated. In this way the evolution of these angles with time could be observed. Based on the plots obtained that way, errors in the CA calculations could be assessed (figure 3).

As one can observe from figures 3 and 4, there is no influence of the bottom layer rotation on the CAS values. Both data obtained from the GROMACS simulations, as well as those obtained using our MD code, show that the CAS changes caused by rotation are in the range of calculation error. The differences between the CAS calculated using GROMACS and our code are caused by slight distinctions in applied procedures.

5. Suggestions for CA determination from MD simulation data

As mentioned above, two types of CA values are used in the literature (CAS and CAB). Taking into account the data collected in figures 2 and 3, one can conclude that the differences between CAS and CAB are not expected to be large. However, to decide which value is more appropriate, one can analyze the data collected in figure 5 where we present the water droplet to decide which value is more appropriate, one can analyze the evolution of CA with graphene bottom layer rotation. Considering the changes in the CA values during the simulation, it is concluded that the proper CA can be recorded only after a sufficiently long time. If the typical time of a production run (2 ns) is used, the accuracy of the CA calculations is no lower than 2°. After 6 ns, the error is approximately equal to 0.7°. For the error equal to 0.2° simulation time should be longer than 20 ns. If one wants to gain accuracy better than 0.1°, much longer calculations (exceeding 50 ns) are required.

Finally, we recommend the new procedure of CA determination by using the cylindrical and spherical mapping described above. In order to calculate the values of the contact angle, obtained curves should be extrapolated to the bottom part of the droplet, and not to the outer surface of the substrate. This leads to the conclusion that the CAB should be analyzed and discussed while the wetting phenomenon is studied by molecular simulations.

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