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Analysis of individual molecular dynamics snapshots simulating wetting of surfaces using spheroidal geometric constructions

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Abstract

Accurate characterisation of wettability of minerals is important for efficient oil recovery and carbon geo-sequestration. In studies where molecular dynamics simulations are used to compute the contact angle, emphasis is often placed on results or theoretical details of the simulations themselves, overlooking potentially applicable methodologies for determination of the contact angle. In this manuscript a concept of a method utilizing spheroidal geometric constructions to estimate the contact angle of a water droplet on silica surface in carbon dioxide atmosphere is outlined and applied to the final snapshots of two molecular dynamics simulation runs. Two carbon dioxide pressures and two wettability modes (hydrophilic and hydrophobic) are examined to assess the method's performance. The most stable 6-member ellipse-like rings (001) pristine surface of alpha-quartz is reconstructed using molecular dynamics and its wettability is then investigated for the first time. The outcomes of the calculations are compared with results produced with the iso-density chart method; and good agreement with the latter approach is demonstrated. The proposed method can be used as an alternative, or in conjunction with other techniques, to increase the confidence in contact angle estimations via molecular mechanics calculations. Reliable contact angle estimations on the other hand, can guarantee accurate storage capacity and security of carbon capture and storage projects.

Key words: contact angle, molecular dynamics, simulation snapshot, wettability, spherical droplet

1 Introduction and motivation

2 Carbon capture and storage is a recognized technology that reduces concentration of carbon dioxide
3 in the Earth's atmosphere ¹. Storage capacity and security of formations used to store CO₂ depend on
4 wettability of minerals ²⁻³, specifically quartz in carbon dioxide environment, which was studied
5 experimentally and theoretically ⁴.

6 There are number of works employing molecular dynamics to simulate the wetting behaviour of water
7 on silica surfaces, in particular in the presence of carbon dioxide and often in the context of carbon
8 geo-sequestration ⁵⁻¹⁷. In some studies, formation of the meniscus between two slabs is modelled ⁶, in
9 others a cylindrical droplet is used ¹⁴. While these approaches offer smaller system sizes and less
10 demanding computations, they may miss important wetting features, like preferential wetting
11 directions on some surfaces ¹⁸. With increasing computational power of modern computers these
12 techniques become less popular, thus the majority of researchers directly simulate a water droplet on
13 the solid surface and further analyse the results ^{5, 7-9, 12}.

14 However, the analysis of such simulation results is often limited to two-dimensional structures. From
15 these, the contact angle is determined via second order polynomial fits to the two-dimensional water
16 droplet profile ⁵, or via drawing contours around two-dimensional water density plots ^{6-9, 12}.

17 These approaches are local, thus only a certain part of the droplet's profile cross section is considered.
18 When tangential lines are fitted, the three-dimensional nature of the studied systems is lost, which
19 introduces a bias (when projecting three-dimensional objects into two-dimensional space). The
20 approaches lack appreciation of the physico-chemical aspects of droplet formation in the simulation
21 environment. By the latter we mean that in absence of gravity the system (water droplet) which is
22 destined to minimize its surface energy (and thus the surface area) unavoidably adopts spheroidal
23 shape. In some developments, three-dimensionality of spheroidal droplets was taken into account,
24 with water density profiles constructed in cylindrical coordinates, with further fitting of two-
25 dimensional circles to these profiles ⁷. In a rigorous analysis based on the coarse-grained density of

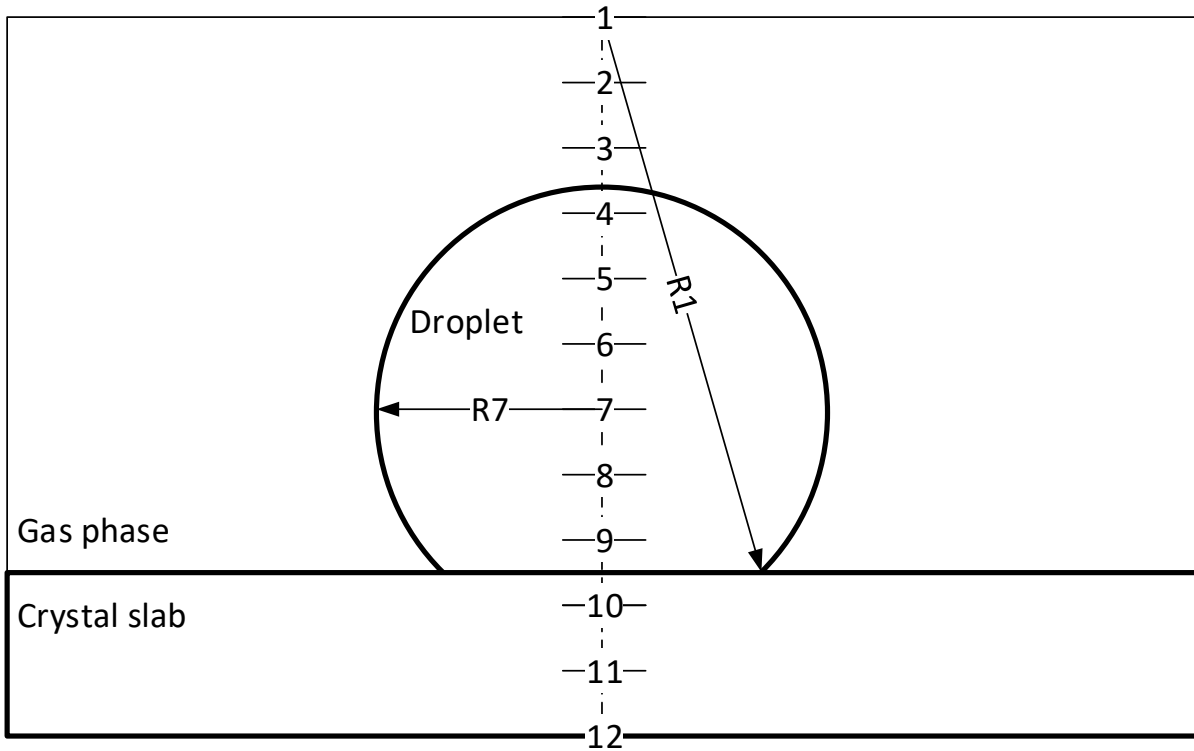
1 fluid molecules¹⁹, the average liquid-vapour interface is set at the half of the bulk liquid density. The
2 contact angle is then calculated using two methods the spherical-cap approximation and the outward
3 unit normal to the interface. In the spirit of this latter study we use the most natural geometrical
4 constructions and a coordinate system for spherically shaped objects, i.e. spheroidal constructions
5 and the spherical coordinate system. Unlike the method outlined in¹⁹, which makes use of position
6 vector dependent coarse-grained fluid density, our approach uses spherical shell averaged fluid
7 density which is a function of the radius vector. This deviation requires different methodological and
8 algorithmic tactics for the method to be simple and work successfully. In this work we thus have a
9 twofold goal. Firstly, we argue that a holistic method to estimate the contact angle can be developed
10 that (i) treats the overall droplet in three dimensions, based on the spherical coordinate system, and
11 (ii) respects intrinsic physics and the resulting geometry of the simulated structures using spheroidal
12 geometric construction. Secondly, we enrich and continue debate on the performance of the
13 approaches used to compute the contact angles and on the rational choice of parameters used in
14 these approaches.

15 To this end we use a water droplet on a pristine (001) α -quartz surface in carbon dioxide environment
16 under 4 and 10 MPa pressure and at 300 K temperature. The pristine quartz surface was previously
17 modelled and reconstructed in²⁰⁻²⁴. According to available information in the literature the pristine
18 surface has two energetically very similar structures the 6-member triangle-like rings and the 6-
19 member ellipse-like rings. To the best of our knowledge the latter and the most stable structure was
20 predicted in²⁰. It was then studied in²²⁻²⁴, with experimental confirmation reported in²². As far as the
21 authors of this paper are concerned, there are no reports where the most stable 6-member ellipse-
22 like rings pristine (001) α -quartz surface is explicitly mentioned in the context of its wettability or
23 reconstructed using classical molecular dynamics.

1 Method development

2 Development of the method that is based on the spherical coordinate system requires identification
3 of the smallest radius of a sphere which encapsulates all water molecules of the droplet. If position of
4 this sphere's centre is known, its radius can be easily calculated as the distance to the furthest water
5 molecule. It is thus necessary to find the location of the smallest circumscribing sphere. As it will be
6 clear from the following discussion this is valid for hydrophobic surfaces; with some minor alterations
7 the approach can then be generalized to also include hydrophilic surfaces.

8 The radius of the circumscribing sphere depends on the position of its centre, and it is reasonable to
9 assume that the centre of the minimal radius sphere lies on a normal of the surface which intersects
10 the centre of mass of the droplet. To find the exact position of the centre we introduce the following
11 scanning algorithm, see Figure 1. Suppose that the vertical line through the centre of mass of the
12 water droplet is found as a locus of points with x and y coordinates of the mass centre. We select a
13 step which divides the line into integer number of segments, e.g. hundredth of the cell height. We
14 loop over every point between segments. For every point we find a distance to every atom of all
15 molecules comprising the water droplet. The largest distance is taken as the encapsulating radius
16 corresponding to the given point. The smallest radius identified is the radius of the sphere we are
17 looking for, and the position of the sphere's centre is the position of the point to which this radius
18 corresponds. We next narrow down the search interval by taking one step backward and one step
19 forward from the point found. We divide this interval by the same number of steps and repeat the
20 search. We keep narrowing down the interval until the step size is below a given accuracy threshold,
21 in this work the threshold 10^{-6} Å is used.



1

2 *Figure 1. Simulation cell with schematic illustration of hydrophobic surface, water droplet and steps of the*
 3 *scanning algorithm.*

4 The described procedure is exemplified for 12 initial steps in Figure 1. The radii of spheres
 5 encapsulating the droplet for steps 1 and 7 are shown as R1 and R7. In the first pass R7 is going to be
 6 identified as the smallest droplet encapsulating radius. In the second pass the search interval is going
 7 to be narrowed down to the interval between points 6 and 8. In this particular example the radius
 8 shown as R7 is going to remain the smallest encapsulating radius until the algorithm reaches the
 9 threshold value for the search interval. In a more general case the smallest encapsulating radius is
 10 refined over the course of algorithm execution. It is worth noting that there is no need to scan the
 11 whole cell. Obviously, the centre of the sphere is inside the droplet, so one only needs to scan from
 12 the top of the droplet to its bottom.

13 For hydrophilic surfaces the above described algorithm finds the wetted radius of the droplet (R_w), see
 14 Figure 2. With known droplet height (H_d) this value can be used to identify the position of the centre
 15 of the circumscribed sphere (Z_c) and its radius (R):

1
$$Z_r = Z_{top} - R,$$

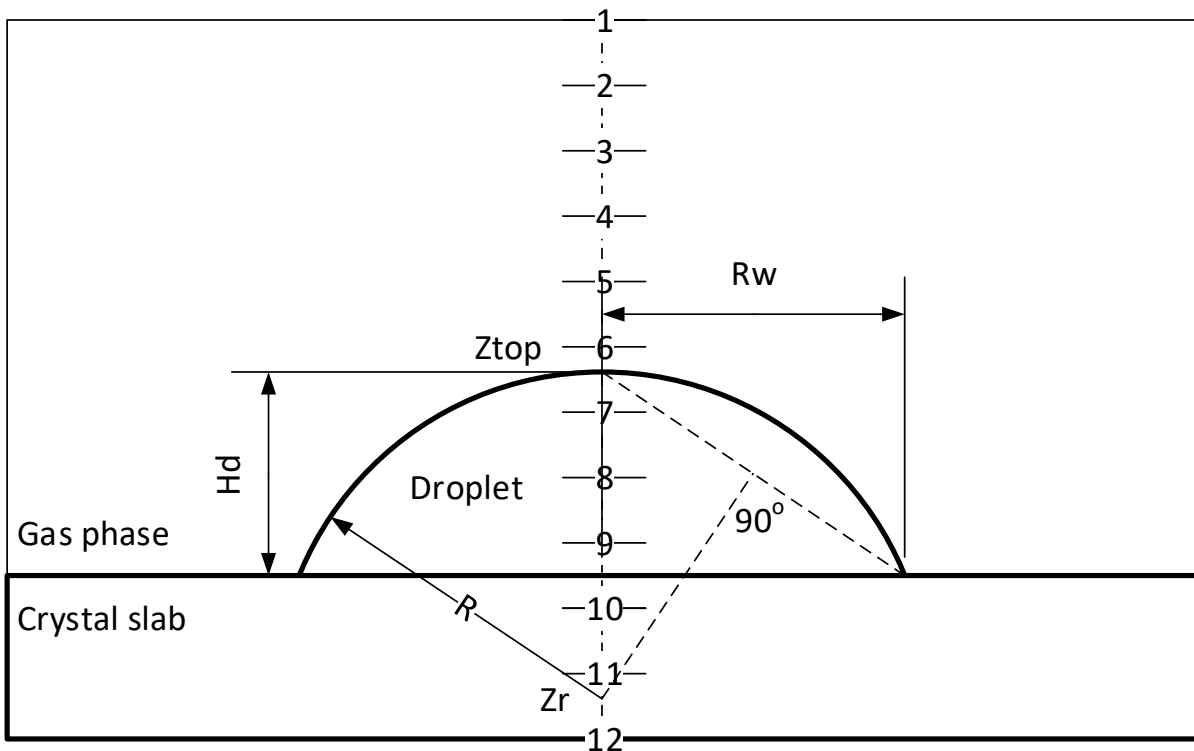
2
$$R = \frac{R_w^2 + H_d^2}{2H_d}.$$

3 To obtain the latter expression note that in the hydrophilic case, see Figure 2:

4
$$R^2 = R_w^2 + (R - H_d)^2.$$

5 For the sake of completeness, it is worth noting that for any two points on circle's contour (R_1, Z_1) and
 6 (R_2, Z_2) within one quadrant, not just $(0, Z_{top})$ and $(R_w, 0)$, a more general expression for the position Z_r
 7 can be derived:

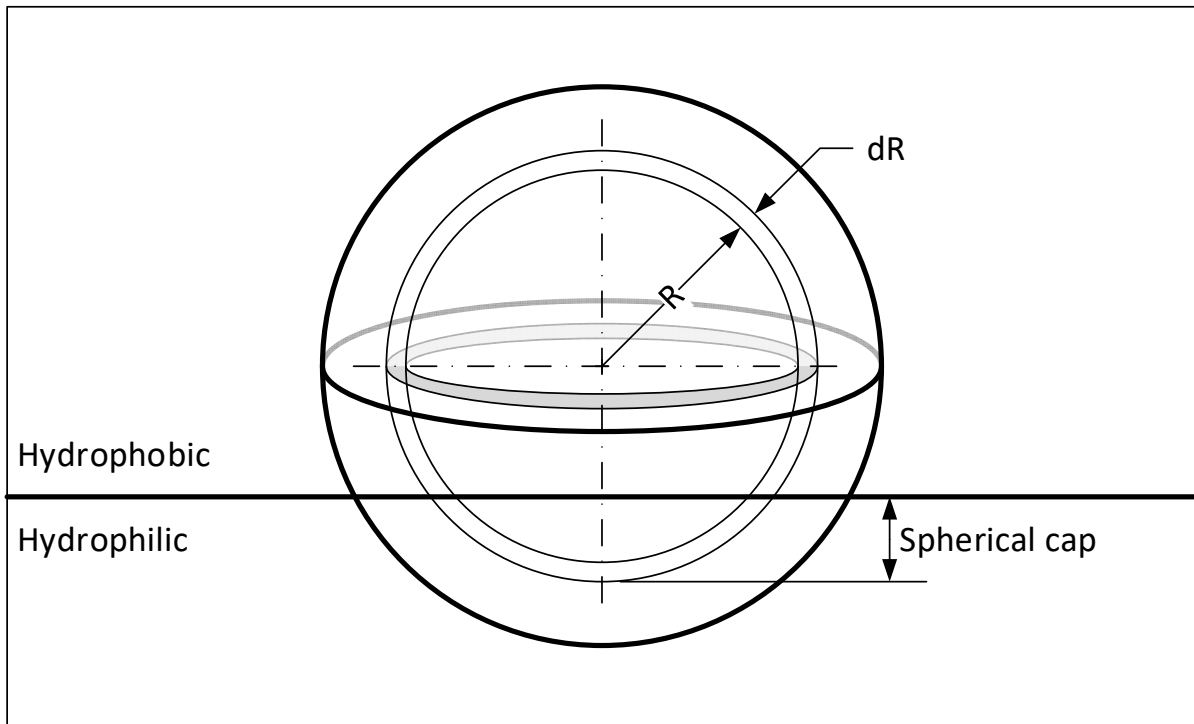
8
$$Z_r = \frac{R_2^2 + Z_2^2 - R_1^2 - Z_1^2}{2(Z_2 - Z_1)}.$$



9
 10 *Figure 2. Simulation cell with schematic illustration of a hydrophilic surface, showing the water droplet, steps*
 11 *and elements of the scanning algorithm.*

12 However, in actual simulations droplets rarely resemble perfect spheres or spherical caps. It is thus
 13 necessary to refine the radii found. This refinement is done for both, the wetted radius (hydrophilic

1 case) and the radius of the circumscribed sphere. For the latter one we construct density plots in
2 spherical coordinates by changing the radius from zero to R in small steps dR and calculating the
3 number of molecules in the spherical shell between R and dR , see Figure 3. For a hydrophobic surface
4 the volume of the spherical shell is equal to the volume of a sphere of radius $R+dR$ minus the volume
5 of the sphere of radius R , and minus volume of the spherical cap. For a hydrophilic surface the volume
6 of the spherical shell is equal to the volume of the spherical cap. The spherical cap, just as the spherical
7 shell, is spatially limited between radii R and $R+dR$. The threshold density, i.e. the density where the
8 water droplet ends (or starts), is assumed to be half the normal water density. The exact figure is taken
9 as $0.033/2$ water molecules per cubic angstrom, which corresponds to half of normal water density
10 1000 kg/m^3 . Example plots of the water density in spherical coordinates are illustrated in Figure 8 and
11 Figure 9. To refine the wetted radius in the hydrophilic case we use an analogous procedure with the
12 only difference being that the cylindrical coordinates are used instead of spherical coordinates. The
13 location of the thin cylinder is at the z coordinate of the radius and its thickness is taken to be 3 \AA ,
14 close to the mean van der Waals diameter of water²⁵. The dR value is taken to be 0.25 \AA for both
15 coordinate systems, the spherical and the cylindrical.



1

2 *Figure 3. Calculation of water density in spherical coordinates for hydrophobic and hydrophilic surfaces.*

3 When the radius of the water molecules encapsulating sphere, and its position relative to the surface
 4 are known calculations of the contact angle become trivial, see Figure 4. With Z_{top} measured from the
 5 surface, for the hydrophobic case the contact angle θ is given by:

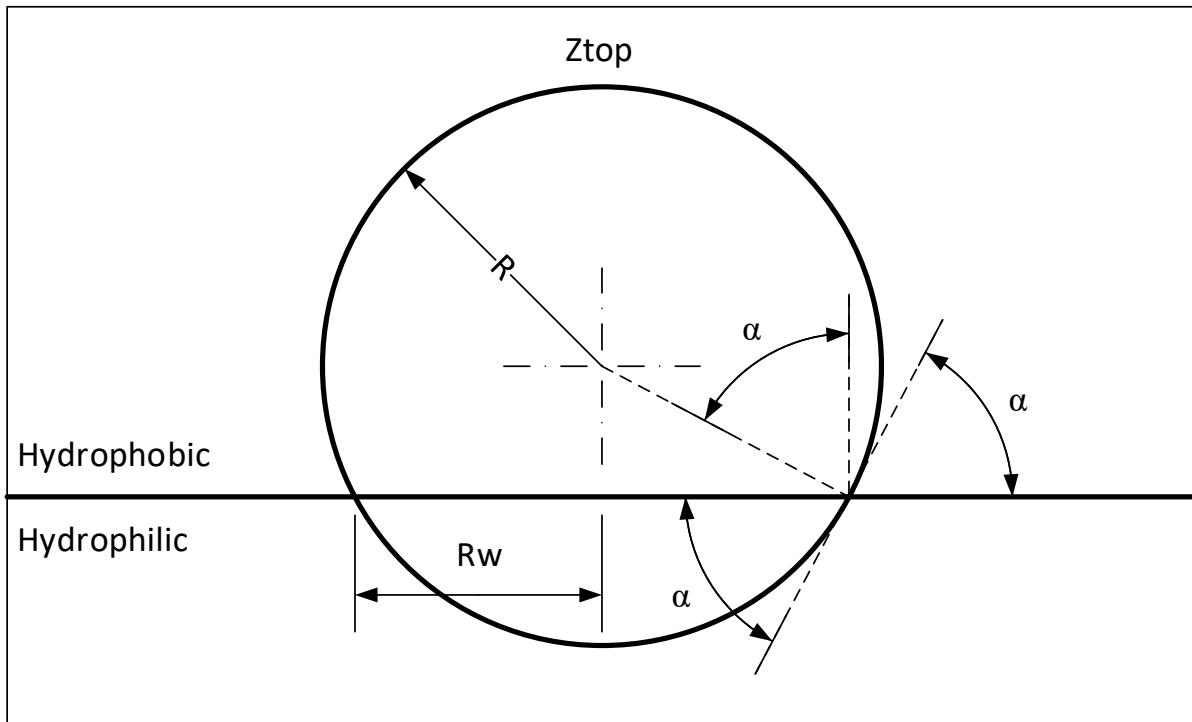
6
$$\theta = 180^\circ - \alpha,$$

7
$$\cos \alpha = \frac{Z_{top} - R}{R}.$$

8 And for the hydrophilic case the contact angle is:

9
$$\theta = \alpha,$$

10
$$\sin \alpha = \frac{R_w}{R}.$$



1

2

Figure 4. Illustration of contact angle calculations.

3 As treatment of hydrophilic and hydrophobic surfaces is different, it is important to distinguish
 4 between them. Thus the following inequality is used to decide if the surface is hydrophilic,

5

$$R > H_d.$$

6 Note that the formulae written in terms of Z_{top} can easily be rewritten in terms of the position of the
 7 centre of the circumscribed sphere once it has been found.

8 Contact angles computed with the circumscribed sphere method are compared with results obtained
 9 from the iso-density chart method. In the latter method the droplet is divided into thin circular layers,
 10 the thickness is taken to be 0.25 Å; in each layer the water density is calculated in the cylindrical
 11 coordinate system starting from well outside of the droplet, i.e. the density is calculated in thin rings
 12 with $dR=0.25$ Å. By proceeding towards the droplet centre the position of iso-density 0.033/2 water
 13 molecules per cubic angstrom is identified in each layer. The resulting line connecting all obtained
 14 data points plotted in coordinates height versus radius contours the extent of the droplet, see Figure
 15 12 and Figure 13 for the example. The average radius of the lowest two points is used to set the

1 intersection of the tangential line with the horizontal axis. The next 5, 7 and 9 data points are used to
2 fit the tangential lines to the iso-density and thus three contact angles are determined. An average
3 (over the three values) contact angle is compared with that obtained with the circumscribed sphere
4 method. Note that in both methods, when calculating water density profiles, the positions of the
5 water molecules are approximated by positions of the oxygen atoms.

6 Computational details

7 A general purpose parallel molecular dynamics simulation package DL_POLY 4.08 was applied to
8 perform computations ²⁶⁻²⁷. Results of the simulations were visualized with VMD ²⁸ and VESTA ²⁹
9 software, the latter one was also used for manipulations with molecular and periodic structures.

10 In all classical molecular dynamics simulations integration of the equations of motion was performed
11 with the velocity Verlet algorithm ³⁰. The time step in all simulations was set to 2 fs. In the NPT
12 simulations the Nose-Hoover thermostat and barostat ³¹⁻³² with the relaxation constants 0.05 and 0.5
13 ps, respectively, were used. In the NVT simulations the Nose-Hoover thermostat with the relaxation
14 constant 0.05 ps was used. Interactions cutoff distance was set to 17 Å in all calculations. Electrostatics
15 were computed with the smoothed particle mesh Ewald summation ³³⁻³⁴.

16 Force fields

17 A set of force fields was employed in this study. The BKS (van Beest, Kramer, Santen) potential ³⁵ was
18 used for the pristine quartz surface. The potential was coupled with the TIP4P/2005 model for water
19 ³⁶ and the EPM2 model for carbon dioxide ³⁷. Only non-bond potential terms were utilized, with all
20 H₂O and CO₂ molecules being treated as rigid bodies. Geometrical details of the rigid bodies are: CO
21 distance (EPM2 CO₂) 1.149 Å; OH distance (TIP4P/2005 H₂O) 0.9572 Å; OM distance (TIP4P/2005 H₂O)
22 0.1546 Å; HOH angle (TIP4P/2005 H₂O) 104.52°.

23 The Buckingham potential ³⁸ was used to model oxygen-oxygen and silicon-oxygen interactions of the
24 pristine quartz surface:

1
$$U(r) = A \exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6},$$

2 where U is the potential energy of interacting atoms separated by the distance r; A, ρ and C are the
 3 parameters of the potential, see Table 1. All silicon-silicon interactions were modelled with
 4 electrostatic forces only.

5 *Table 1. The Buckingham potential parameters used for the pristine quartz surface*³⁵.

Interactions	A, kcal/mol	ρ, Å	C, kcal/mol Å ⁶	q, e	m, amu
O-O	3.20304·10 ⁴	0.3623188	4.03609·10 ³	O=-1.2	O=15.9994
Si-O	4.15225·10 ⁵	0.2052124	3.07983·10 ³	Si=2.4	Si=28.0855

6 The Lennard-Jones potential was used to model dispersion interactions of water, carbon dioxide and
 7 the ions for the pristine quartz surface:

8
$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right].$$

9 Parameters of the potential ε and σ are given in Table 2.

10 *Table 2. The Lennard-Jones potential parameters used to model CO₂-H₂O-SiO₂ systems*^{7, 35-37}.

Atomic sites	ε, kcal/mol	σ, Å	q, e	m, amu
C (CO ₂)	0.05591	2.757	0.6512	12.0107
O (CO ₂)	0.16001	3.033	-0.3256	15.9994
O (H ₂ O)	0.18523	3.1589	0	15.9994
H (H ₂ O)	0	0	0.5564	1.0080
M (H ₂ O)	0	0	-1.1128	0
Si (SiO ₂)	0.12751	3.795	2.4	28.0855
O (SiO ₂)	0.15504	3.154	-1.2	15.9994

11 The interaction parameters between the unlike atoms were obtained as the geometric mean for the
 12 energy parameter and as the arithmetic mean for the distance parameter (the Lorentz-Berthelot
 13 combining rules³⁹⁻⁴⁰):

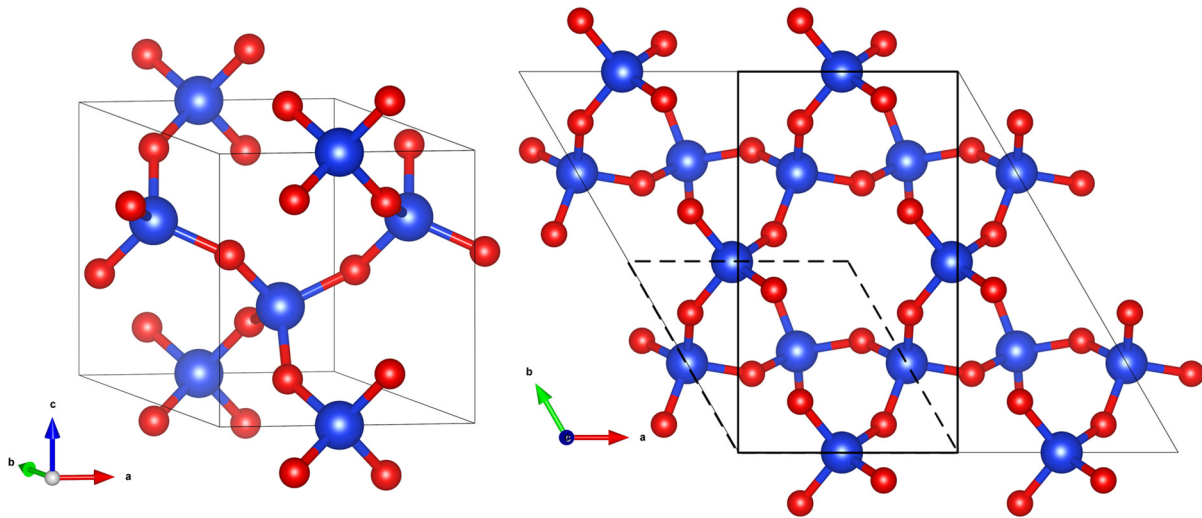
1
$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j},$$

2
$$\sigma_{ij} = (\sigma_i + \sigma_j)/2,$$

3 where i and j are indices of the unlike atoms.

4 **Reconstruction of the pristine quartz surface**

5 From the hexagonal unit cell of α -quartz⁴¹ shown in Figure 5 a super cell 2x2x1 was created. An
6 orthorhombic cell for further preparation of the pristine surface was then extracted from the super
7 cell⁴², see Figure 5. There are 18 atoms in the orthorhombic cell, 6 silicon atoms and 12 oxygen atoms.



8

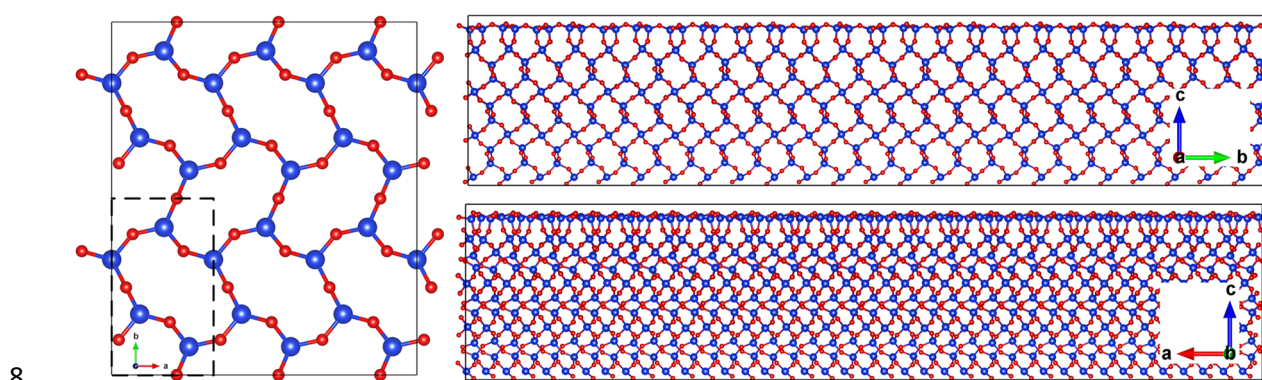
9 *Figure 5. Quartz unit cells used in this work. Left: primitive hexagonal unit cell of α -quartz, isometric view.*
10 *Right: reconstruction of the orthorhombic cell (solid bold rectangle) from 2x2x1 super cell, top view (dashed*
11 *parallelogram shows the primitive cell). Red balls - oxygen atoms, blue balls - silicon atoms.*

12 Crystallographic lattice vectors of the orthorhombic cell amount to: a=4.916 Å, b=8.515 Å, c=5.405 Å.

13 Out of this orthorhombic cell a super cell 12x7x12 was constructed and used to equilibrate the quartz
14 crystal at 1 atm pressure and 300 K temperature for 10⁵ steps. The system was simulated in the NPT
15 ensemble. Lattice vectors of the equilibrated orthorhombic cell were found to be a=4.940 Å,
16 b=8.557 Å, c=5.432 Å, which are only 0.5% larger than the crystallographic values obtained from⁴¹.

17 Using this equilibrated orthorhombic cell a 20x12x4 slab was constructed. Every uncoordinated
18 oxygen atom at the top of the slab was shifted from the host silicon atom towards the neighbouring
19 silicon atom in x and y directions by 0.6 Å to build precursors of the Si-O-Si bridges. After that the slab

1 was relaxed at 10 K for 10^5 steps to form proper Si-O-Si bridges and the initial ordered surface
2 structure. The system was simulated in the NVT ensemble. During the relaxation and in all subsequent
3 simulations described in this work the bottom layer (in terms of the unit cell height) of the four-layer
4 slab was kept frozen to emulate the bulk crystal. The surface was prepared in a simulation box which
5 had the same dimensions as the box used for the fully assembled quartz-water-CO₂ systems.
6 Arrangement of the very top atoms of the surface is the same as in the lowest energy surface obtained
7 in ²³⁻²⁴. The surface consists of 6-member ellipse-like rings, Figure 6.



9 *Figure 6. Four-layer quartz slab used in this work. Left: view of the super cell 3x2x1 along z direction with only*
10 *top atoms shown for clarity (the orthorhombic unit cell is highlighted with dashed rectangle). Right: slab views*
11 *along x (right top) and y (right bottom) directions. Red balls - oxygen atoms, blue balls - silicon atoms.*

12 Simulation setups

13 Utilizing above described force fields and the pristine quartz surface two simulation models were
14 constructed with two different carbon dioxide pressures (4 and 10 MPa). Temperature in all
15 simulations was set to 300K. Preliminary equilibration of carbon dioxide and water with the
16 subsequent construction of the models was performed.

17 Two boxes 120x120x80 Å for carbon dioxide and 50x50x50 Å for water (the TIP4P/2005 ³⁶ were used
18 to pre-equilibrate uniformly distributed molecules at 300K. Density of carbon dioxide at given pressure
19 and temperature were used to determine the volume per every molecule, this density was taken from
20 the NIST data book at 300 K and at the relevant pressures of 4 and 10 MPa ⁴³. Water density was taken
21 to be 1000 kg/m³. Dynamics of these three systems (one for H₂O and two for CO₂) were modelled in
22 the NVT ensembles. Overall $5 \cdot 10^5$ steps were performed for CO₂ and 10^5 for H₂O.

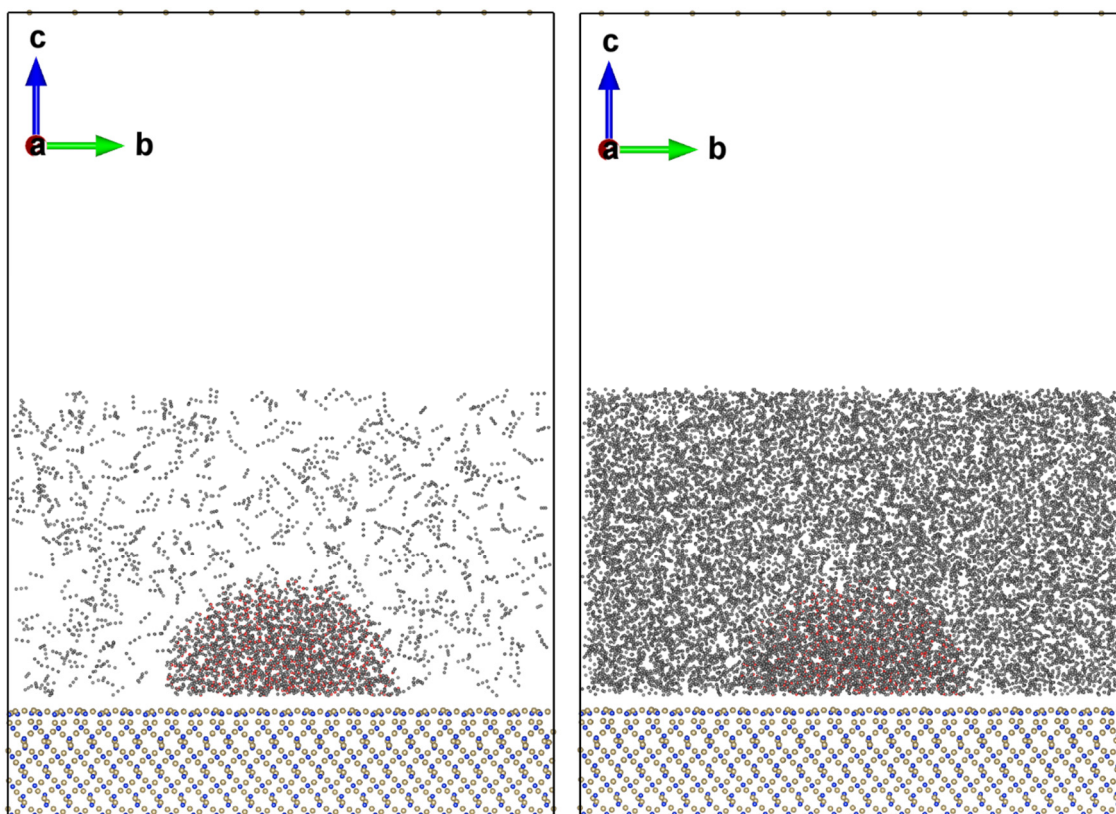
1 On top of the pre-equilibrated quartz slabs a half sphere of radius 24 Å was filled with water molecules
2 from above described box. Overall 772 TIP4P/2005 water molecules fit into the half sphere. These
3 "water droplets" were placed in the centre of the slabs. The rest of the space up to 60 Å above the
4 surface was filled with pre-equilibrated carbon dioxide. There were 642 and 5559 CO₂ molecules
5 above the pristine surface at 4 and 10 MPa, respectively. A gap of 1.5 Å starting from four quartz unit
6 cell heights (the slab's height) was left empty to avoid overlap of atoms and molecules. Note that
7 actual initial distance between top slab atoms and water and gas molecules was slightly larger due to
8 surface construction during relaxation and disposition of molecules in the pre-equilibration boxes,
9 thus molecules located exactly at the border were rejected upon filling the simulation boxes. Vacuum
10 space of 70 Å was provided above the gas phase. All simulations were performed with periodic
11 boundary conditions in x and y directions. In z direction a repulsive force was initially set at 60 Å above
12 from the surface:

$$F = k(z_0 - z), z > z_0,$$

13
14 where $k=0.24$ kcal/mol (1 kJ/mol) - is the force constant, and z_0 is the position of the repulsive
15 potential.

16 The position of this repulsive wall was then corrected in such a way that the density of the pre-
17 equilibrated carbon dioxide filling space above the surface matched its physical density at given
18 pressure and temperature. In all cases the potential was never displaced towards the surface by more
19 than 6 Å, see Table 3. Minimal distance to the repulsive potential of more than 54 Å ensures that the
20 contact angle at the surface is not affected by perturbations in the CO₂ density caused by the wall.

21 Dynamics of two prepared quartz-water-carbon dioxide systems were simulated in the NVT
22 ensembles. Overall 10⁶ steps were performed for every system, 2 ns simulation time, out of which 10⁵
23 were equilibration steps. Dimensions of the simulation boxes were 98.81x102.68x151.73 Å. Figure 7
24 demonstrates the initial simulation setups for two studied systems. Main computational details are
25 summarized in Table 3.



1

2 *Figure 7. Initial simulation setups for systems investigated at two CO₂ pressures - 4 MPa (left) and 10 MPa*
 3 *(right). The hemispherical water droplets above the quartz surfaces surrounded by CO₂ molecules are clearly*
 4 *visible.*

5

Table 3. Summary of computational details.

Parameters	System 1	System 2
CO ₂ pressure, MPa	4	10
Temperature, K	300	
Force fields	BKS, TIP4P/2005, EPM2	
Interactions cutoff, Å	17	
Time step, ps	0.002	
Number of steps (equilibration steps)	10 ⁶ (10 ⁵)	
Ensemble	NVT	
Thermostat	Nose-Hoover	
Thermostat relaxation constant, ps	0.05	

Parameters	System 1	System 2
Repulsive potential z_0 , A	54.64	54.31
Repulsive potential k, kcal/mol	0.24	
Half sphere droplet radius, A	24	
H ₂ O molecules	772	
CO ₂ molecules	642	5559
Slab top layer	240(Si ₆ O ₁₂)	
Slab two middle layers	480(Si ₆ O ₁₂)	
Slab frozen (bottom) layer	240(Si ₆ O ₁₂)	
Slab unit cell dimensions, A	4.94x8.56x5.43	
Slab dimensions in unit cells	20x12x4	
Simulation box dimensions, A	98.81x102.68x151.73	

1 [Method application and discussion](#)

2 For both systems investigated the very last snapshots of the simulations were analysed using above
3 described methodology. Obtained results of the contact angle analysis are summarized in Table 4.

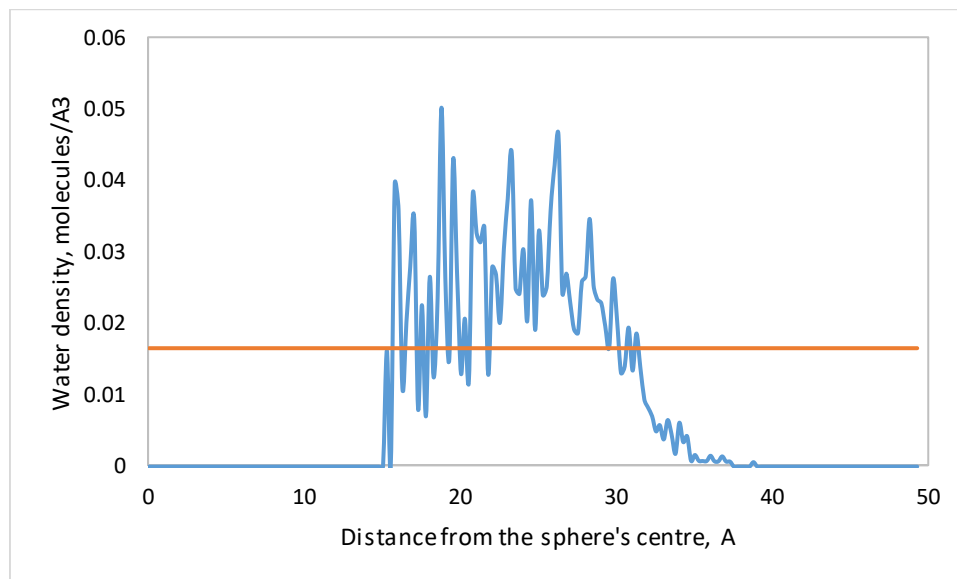
4 *Table 4. Contact angle computational results.*

Initial simulation setup	System 1	System 2
CO ₂ pressure, MPa	4	10
Circumscribed sphere radius, A	31.375	22.125
Position of sphere's centre with respect to the surface, A	-12.82	1.88
Contact angle (circumscribed sphere method), degrees	65.9	94.9
Contact angle (iso-density chart method), degrees	69.0 (+/-4.7)	92.6 (+/-2.6)

5 It is noteworthy to see how the two methods, the circumscribed sphere method and the iso-density
6 chart method, arrived at essentially the same results using different routes. The largest discrepancy in
7 found contact angles is in the range of 5%. Thus, the surface at 4 MPa of CO₂ pressure is hydrophilic

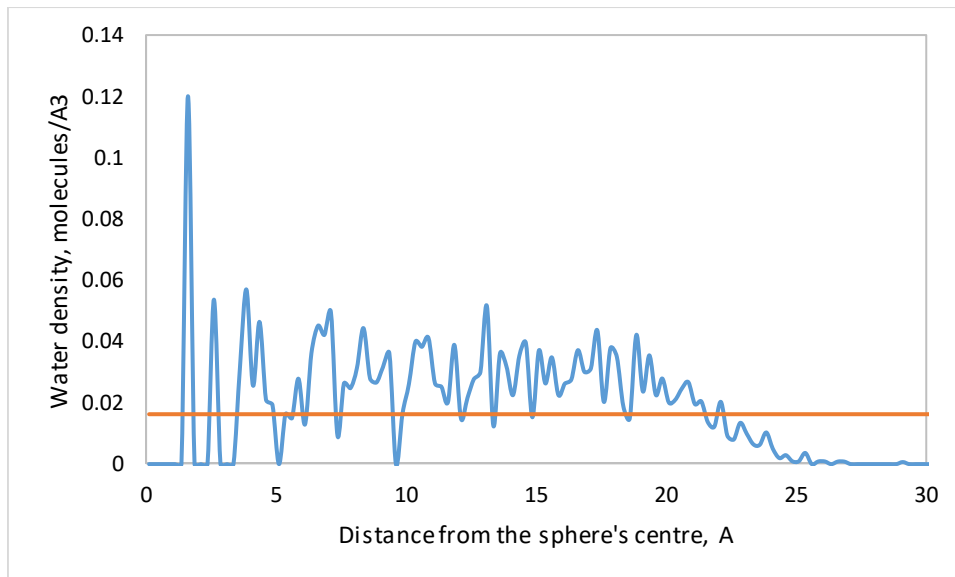
1 (the contact angle is less than 90°), the surface at 10 MPa of CO_2 pressure is slightly hydrophobic (the
2 contact angle is more than 90°). As required by the initial formulation of the problem of this study we
3 are working here with individual molecular dynamics snapshots. Thus comparison between two used
4 here methods is valid and significant. Comparison with previously reported simulation results ⁷, which
5 used the same simulation length (2 ns) on the other hand can be indicative of relative wettability of
6 the most stable 6-member ellipse-like rings (001) pristine surface of α -quartz. Our computed contact
7 angles are in reasonable agreement with previously reported simulation data where the contact
8 angles were found to be 69° and 80° at 300 K and 4 and 10 MPa of CO_2 pressure, respectively ⁷. Higher
9 contact angle at 10 MPa of CO_2 pressure calculated in this work shows that the most stable 6-member
10 ellipse-like rings (001) pristine surface of α -quartz is more hydrophobic than the 6-member triangle-
11 like rings surface used in ⁷. Additional comparison with experimental results can validate used
12 theoretical assumptions and approximations. In an experimental study conducted at 298 K, during
13 repeated exposure to CO_2 , the contact angles of water droplets on quartz substrates were found to
14 be 90° and 80° at 4 and 10 MPa of pressure, respectively ⁴⁴, which are similar to obtained here values.
15 It should be noted here that simulations executed in this work are organized such that the initial
16 atomic configurations are close to the equilibrium (the contact angle of the hemispherical droplet is
17 90° , c.f. to computed above 65.9° and 94.9°). In addition to this, all elements of the initial setups (the
18 slab, CO_2 , water molecules of the droplet) are relaxed and pre-equilibrated. It thus follows that 2 ns
19 simulation time is sufficient for statistically significant results extracted from a single simulation
20 snapshot. Quantitative validation for the latter statement can be produced using tails of generated
21 trajectories. From the last 50 000 steps (0.1 ns simulation time) five simulation snapshots separated
22 by 10 000 steps were extracted and the contact angles were computed using the circumscribed sphere
23 method. For the systems at 4 and 10 MPa CO_2 pressure the contact angles amounted to 62.6° (+/-3.3)
24 and 96.5° (+/-1.7), respectively. Small error bars indicate that the systems are well equilibrated and
25 obtained results used for comparison with works mentioned in the previous paragraph are significant.

1 Water density profiles constructed in spherical coordinates are shown in Figure 8 and Figure 9.
2 Approaching the spheres' centres from the infinity, the threshold water density (0.033/2 water
3 molecules per cubic angstrom) signals where the droplets start. A common feature of both plots is
4 relatively slow increase in the density in the beginning and its abrupt decrease in the end. A slow
5 threshold approach makes refinement of droplets' radii relatively reliable, as the density increases
6 from zero to 0.033/2 water molecules per cubic angstrom over the distance of several angstroms.



7

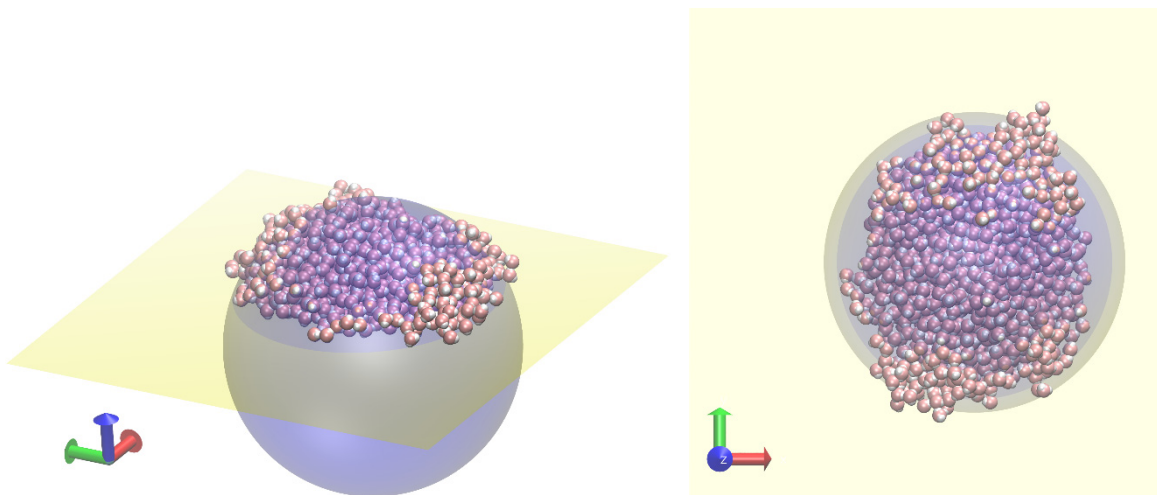
8 *Figure 8. Water density in spherical coordinates for the system at 4 MPa CO₂ pressure. Horizontal line shows*
9 *half of water's normal density.*



1

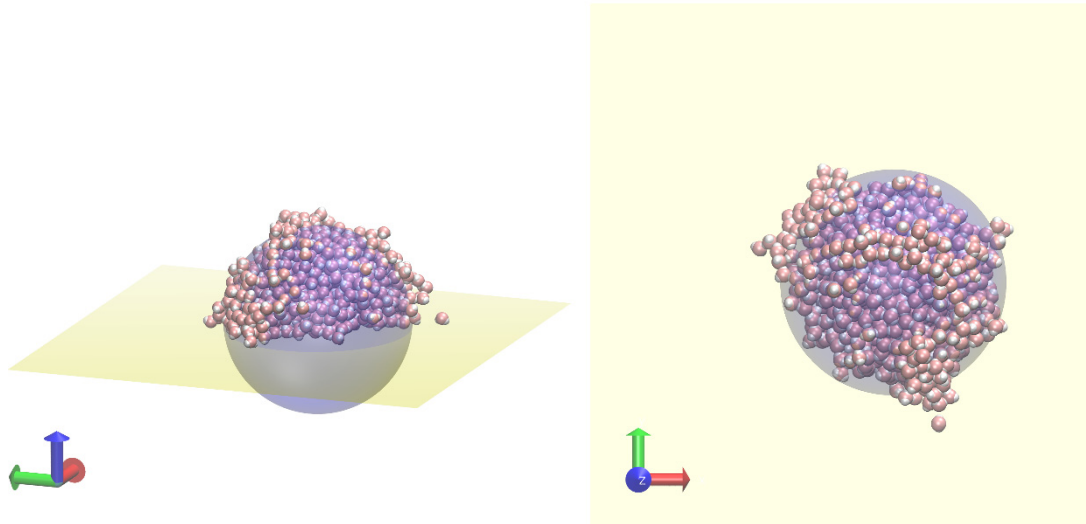
2 *Figure 9. Water density in spherical coordinates for the system at 10 MPa CO₂ pressure. Horizontal line shows*
 3 *half of water's normal density.*

4 Spheres circumscribed around water droplets and their relative positions with respect to the surfaces
 5 are presented in Figure 10 and Figure 11. As expected, circumscribed spheres average fuzzy borders
 6 of the droplets eliminating the directional bias.



7

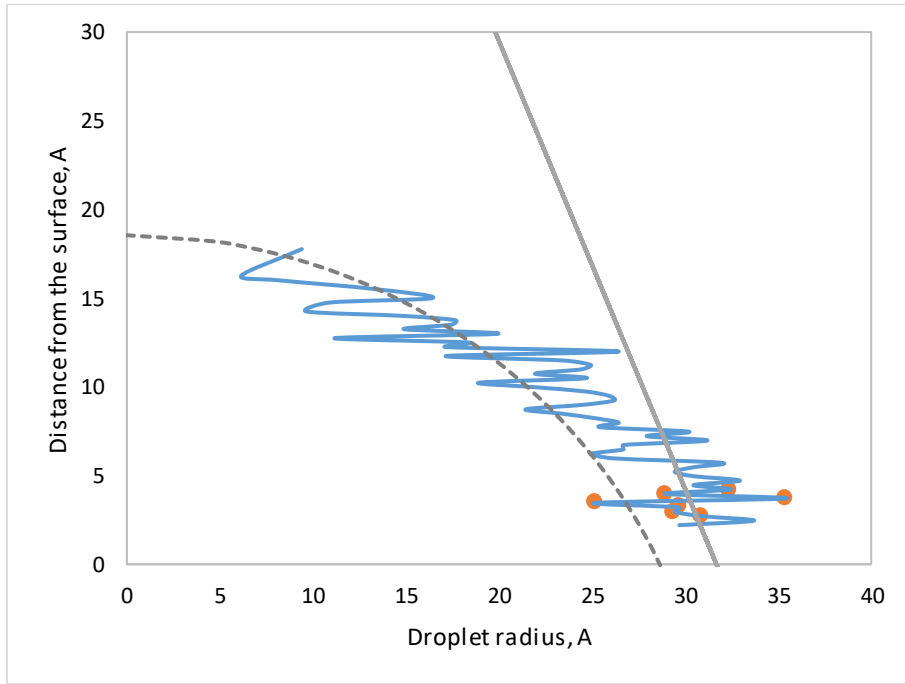
8 *Figure 10. Water droplet and its circumscribed sphere on the quartz surface at 4 MPa CO₂ pressure, isometric*
 9 *view (left) and top view (right). Orange balls are oxygen atoms and white balls are hydrogen atoms of the*
 10 *TIP4P/2005 water.*



1

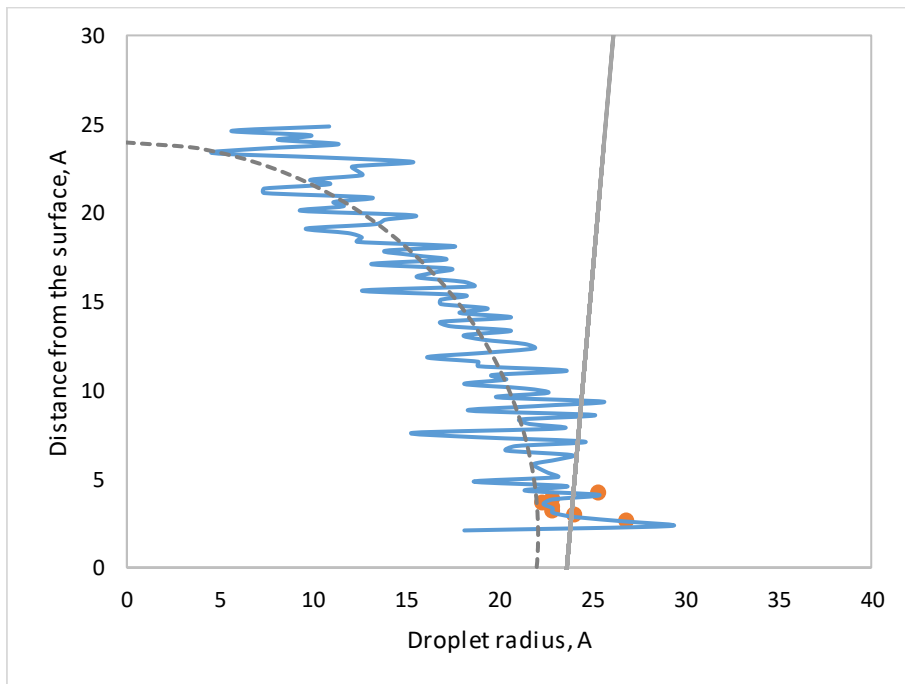
2 *Figure 11. Water droplet and its circumscribed sphere on the quartz surface at 10 MPa CO₂ pressure, isometric*
 3 *view (left) and top view (right). Orange balls are oxygen atoms and white balls are hydrogen atoms of the*
 4 *TIP4P/2005 water.*

5 Iso-density charts used to compare results of the contact angle calculations with the circumscribed
 6 sphere method are shown in Figure 12 and Figure 13. The circumscribed spheres almost average the
 7 iso-density constructed in cylindrical coordinates, especially at 10 MPa CO₂ pressure. The contact
 8 angles calculated using three sets of data points (5, 7 and 9) average the iso-densities close to the
 9 surface and show good agreement between each other (error bars are less than 7%): 69.0° (+/-4.7°)
 10 and 92.6° (+/-2.6°) for systems at 4 and 10 MPa of CO₂ pressure, respectively.



1

2 *Figure 12. Iso-density chart constructed in cylindrical coordinates for a water droplet on a pristine quartz*
 3 *surface at 4 MPa CO₂ pressure. Blue line shows half of water normal density. Red dots depict data points used*
 4 *to fit the tangential line, the straight line (5, 7 and 9 points were used for the averaging, the case for 7 points is*
 5 *shown). The dashed line shows the circumscribed sphere contour found in the spherical coordinates.*



6

7 *Figure 13. Iso-density chart constructed in cylindrical coordinates for a water droplet on a pristine quartz*
 8 *surface at 10 MPa CO₂ pressure. Blue line shows half of water normal density. Red dots depict data points used*
 9 *to fit the tangential line, the straight line (5, 7 and 9 points were used for the averaging, the case for 7 points is*
 10 *shown). The dashed line shows the circumscribed sphere contour found in the spherical coordinates.*

1 Obtained numerical parameters and overall agreement between two methods used to determine the
2 contact angle, as well as visual inspection of the simulation snapshots and the diagrammatic data
3 demonstrate that the spheroidal constructions and the spherical coordinate system have promising
4 potential in the area. The algorithms proposed here are simple and can be intuitively understood, and
5 the required computational effort to analyse a simulation snapshot is minor.

6 Conclusions

7 The concept of how to determine computational contact angles of a liquid droplet resting on a solid
8 surface from individual snapshots of molecular dynamics simulations have been formulated,
9 implemented and analysed in this study. Spherical coordinates to circumscribe a sphere around given
10 configuration of water molecules form the basis of the method, which is thus natural and consistent
11 with the droplet's geometric computational framework. The method also shows good agreement with
12 the iso-density chart method which was applied here.

13 The contact angle of a water droplet on the most stable 6-member ellipse-like rings (001) surface of
14 α -quartz, which was reconstructed here using classical molecular dynamics, was found to be 66 and
15 95° at 4 and 10 MPa of CO₂ pressure, respectively. Comparison with previously done study ⁷ shows
16 that the 6-member ellipse-like rings surface is more hydrophobic than the 6-member triangle-like rings
17 surface of α -quartz (c.f. contact angles at 10 MPa of CO₂ pressure 95° and 80°, respectively).

18 Procedures used to compute the contact angles on basis of molecular dynamics output have
19 deficiencies and limitations when applied on their own. The circumscribed sphere method in its
20 current implementation is best suited for hydrophobic surfaces, but otherwise sensitive to the
21 integrity of the water droplet and may need pre-processing for droplets with poorly defined borders
22 to remove escaped (from the main body of water) molecules. The iso-density chart method is less
23 sensitive to integrity, but local in nature and thus requires caution when fitting the tangential line.
24 Without a universal unbiased method, a combination of several approaches can complement each
25 other in providing a confident estimate of the contact angle from molecular dynamics computations.

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