

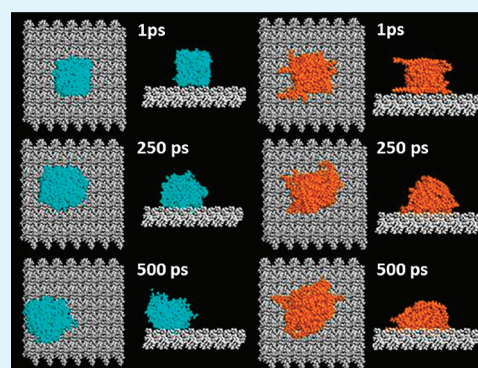
# Simple, Fast, and Accurate In silico Estimations of Contact Angle, Surface Tension, and Work of Adhesion of Water and Oil Nanodroplets on Amorphous Polypropylene Surfaces

Daniel Romero Nieto,<sup>†,‡</sup> Francesca Santese,<sup>†,‡</sup> Radovan Toth,<sup>‡</sup> Paola Posocco,<sup>‡</sup> Sabrina Pricl,<sup>\*,‡,§</sup> and Maurizio Fermeglia<sup>‡</sup>

<sup>‡</sup>Molecular Simulation Engineering (MOSE) Laboratory, Department of Industrial Engineering and Information Technology (DI3), and <sup>§</sup>INSTM, Trieste Unit, University of Trieste, Via Valerio 10, 34127 Trieste, Italy

## S Supporting Information

**ABSTRACT:** In this work, two computational recipes based on atomistic molecular dynamics simulations are developed and compared to quickly and accurately quantify the interactions of amorphous polypropylene surface with water and oil. Fundamental quantities such as contact angle and surface tension are estimated in excellent agreement with the corresponding experimental values, whereas the comparable values of the work of adhesion obtained using both computational recipes confirm the internal consistency in the presented methodologies.



**KEYWORDS:** contact angle, surface tension, work of adhesion, molecular dynamics simulations

## 1. INTRODUCTION

Coatings based on nanostructured materials are receiving progressively increasing attention for potential applications including magnetic storage media, high-surface-area catalysts, selective membranes, photonic band gap materials, etc.<sup>1–10</sup> Generally speaking, coatings are needed to prevent wear, erosion, and corrosion, and to provide thermal insulation of materials. Both for consumer and specialty applications, there is a particular request for coatings with improved durability and performance. In this respect, nanostructured coatings show great promise: indeed, on the basis of extensive laboratory trials, durability improvements of 3 to 5 times can be envisaged for a number of nanocoating applications.<sup>11–14</sup> As a drawback to a large-scale development of such materials, however, the technical and economic viability of these materials on a commercial scale must be carefully evaluated and substantiated. To accomplish these goals in a timely, cost-effective manner, a disciplined concurrent engineering approach is recommended.

The knowledge and control of interfacial wettability of hydrophilic (e.g., water) and hydrophobic (oil) substances on polymeric surfaces is one of the main issues in current practical surface science and interfacial engineering. For example, highly hydrophobic surfaces are designed to avoid the adhesion of snow and raindrops on car windshields, or in order to form self-cleaning surfaces on kitchen furniture tops. On the contrary, hydrophilic surfaces are sought in biomedical applications, e.g., tissue engineering and drug delivery.

Polypropylene is one of the most important plastic materials, because of its good mechanical stability, easy processability, high solvent resistance, and relatively low cost. In particular, amorphous polypropylene (*a*-PP) finds a diversity of applications in different, popular industrial sectors; however, the extremely weak polarity characterizing its chemical structure makes *a*-PP highly hydrophobic and this, in turn, often requires a suitable coating for a given polymer-based manufacture to be employed. For instance, surface dirtying is a concern for this polymer, because *a*-PP is mainly used for housewares.

Manipulating the hydrophobicity/hydrophilicity of a given surface necessarily requires understanding the microscale principles that, in turn, control the macroscale surface wetting behavior. Therefore, understanding the structure and behavior of common fluids such as water and oil at the interface with *a*-PP is of great, practical importance.

In the past few years, substantial progress has been achieved in understanding wetting phenomena from both the experimental and theoretical fronts.<sup>15,16</sup> In particular, as an alternative to experimental campaigns, molecular simulations have been widely applied to the study of solid surfaces/liquid interactions, with especial focus on water spreading on both hydrophobic and hydrophilic material surfaces. Nonetheless,

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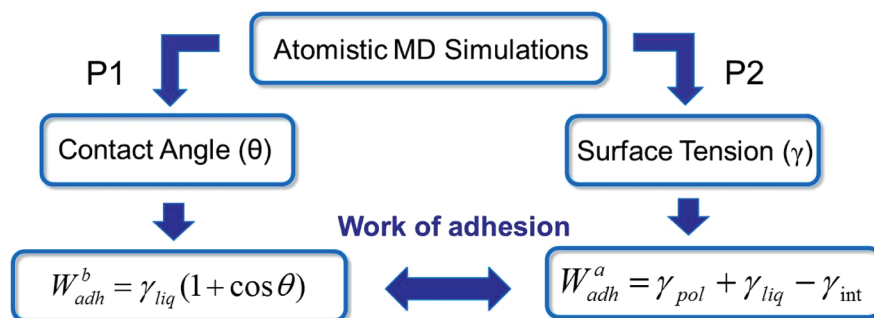


Figure 1. Diagram of the two simulation pathways adopted in this work.

most of the work published so far was based on ideal surfaces, i.e., surfaces with regular, periodic conformation such as crystals and crystalline polymers. On the contrary, computational studies dealing with water spreading onto amorphous polymer surfaces are quite scarce, and this paucity may be ascribed to the fact that constructing a well-defined model for amorphous polymer surfaces and simulating systems having interfacial regions with unconfined roughness requires notable computational time and resources.

The wetting of a surface is essentially determined by molecular interactions between the surface and the liquid, contact angle ( $\theta$ ), surface tension ( $\gamma$ ), and work of adhesion ( $W_{adh}$ ) being the most popular physical parameters used to quantify these phenomena. Thus, approaches based on atomistic molecular simulations should, in principle, yield vital insights on these interactions and constitute ideal tools to estimate the related technological parameter values. Nonetheless, accurate information for these solid/liquid interactions at an atomistic level have been scarcely achieved so far due to many factors, including the lack of well-defined amorphous polymer surface models. Also, the spread of experimental values for both  $\theta$  and  $W_{adh}$  in the current literature highlights the technical difficulties inherent in this research field. For instance, deducing an actual value of the  $W_{adh}$  in a given system is a daunting task as most of the mechanical adhesion tests employed provide largely overestimated values of  $W_{adh}$  due to the large energy dissipation originating in the test samples during measurements.<sup>17</sup>

## 2. METHODOLOGY

In this work, we employed two different computational protocols based on molecular dynamics (MD) simulations to quantify  $\theta$  and  $W_{adh}$  valued for *a*-PP in contact with water and oil (see Figure 1). The results stemming from the accuracy of the force field employed and the computational recipes adopted in the two simulation pathways not only yielded values comparable to each other but, perhaps more importantly, in excellent agreement with the corresponding experimental data.

In the first simulation protocol in Figure 1 (P1, see the Supporting Information for full details), the method of Fan and Cagin<sup>18</sup> was exploited for the calculation of  $\theta$ . Briefly, the  $\theta$  value of a spherical liquid droplet on a given (e.g., polymeric) surface can be obtained as:

$$\cos \theta = 1 - h/R \quad (1)$$

where  $h$  is the height of the liquid droplet relative to the polymer surface and  $R$  is the radius of the spherical droplet.  $R$  in turn can be calculated as:

$$R = h/2 + S/(2\pi h) \quad (2)$$

in which  $S$  is the droplet interfacial area given by:

$$S = \pi R_s^2 \quad (3)$$

$R_s$  being the radius of the droplet interfacial area  $S$ .

In the case of an irregular nanoscopic droplet, the contact angle  $\theta$  value can still be obtained from eqs 1–3 provided the height of the droplet relative to the polymer surface  $h$ , and the radius of the droplet contact surface  $R_s$  are replaced by the corresponding average values obtained from the corresponding radial density distribution (RDD) in the  $z$ -direction (see the Supporting Information for details). Accordingly, in applying P1 extensive atomistic MD simulations of water (oil) onto an *a*-PP surface were performed, the required RDD profiles were obtained from the relevant equilibrated MD trajectories, and the actual values of the contact angle  $\theta$  was estimated using eqs 1–3.

The second simulation protocol (P2 in Figure 1, see the Supporting Information for full details) was based on the adoption of the so-called Dupré equation<sup>19</sup> to estimate the work of adhesion between a liquid droplet and a polymeric surface as follows

$$W_{adh} = \gamma_p + \gamma_l - \gamma_i \quad (4)$$

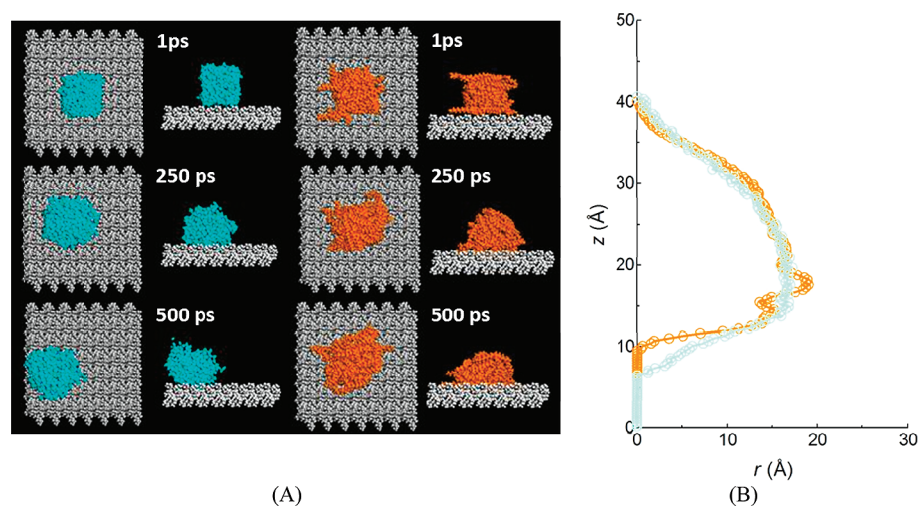
where  $\gamma_p$  and  $\gamma_l$  are the surface tension of the polymeric surface and of the spreading liquid, respectively, while  $\gamma_i$  is the interface tension between the two condensed phases. To this purpose, an alternative MD protocols based on bulk (3D) and thin-film (2D) cell simulations was developed according to which the values of  $\gamma_p$ ,  $\gamma_l$ , and  $\gamma_i$  could be evaluated using eqs 5 and 6

$$\gamma = \frac{\langle U_{2D} \rangle - \langle U_{3D} \rangle}{A} \quad (5)$$

$$\gamma_i = \frac{\langle U_i \rangle - (\langle U_l \rangle + \langle U_p \rangle)}{A_i} \quad (6)$$

In eq 5,  $\langle U_{2D} \rangle$  and  $\langle U_{3D} \rangle$  represent the MD-averaged potential energies of the thin film and bulk phase and simulations, respectively, and  $A$  is the corresponding value of the solvent-accessible surface area (see the Supporting Information for detailed explanations). In eq 6,  $\langle U_i \rangle$  is the average potential energy of the interface,  $\langle U_l \rangle$  and  $\langle U_p \rangle$  are the average potential energy of the liquid and polymer thin film models, and  $A_i$  is the solvent-accessible interface area.

Finally, the liquid surface tension  $\gamma_l$  values for water and for oil obtained via the P2 simulation protocol were exploited in the last step of protocol P1 to obtain the corresponding value



**Figure 2.** (A) Snapshots (top and side views) of the dynamics course of water (light blue, left panels) and oil (orange, right panel) spreading on the *a*-PP surface (gray). (B) Radial density distribution (RDD) profiles for a water (light blue) and oil (orange) droplet spreading on the *a*-PP surface. The corresponding height of the water/oil droplets are 30.2 and 29.6 Å, respectively.

of  $W_{\text{adh}}$  (see Figure 1) by means of the Young–Dupré equation<sup>20</sup>

$$W_{\text{adh}} = \gamma_l(1 + \cos \theta) \quad (7)$$

### 3. RESULTS AND DISCUSSION

**Results from P1.** Figure 2A shows some MD snapshot views from the top and the side of the dynamics course of a typical droplet of pure water (left panels) and oil (right panels) spreading on an *a*-PP surface obtained from the application of protocol P1, whereas the corresponding radial density distribution RDD profiles obtained from the relevant equilibrated MD trajectories are shown in Figure 2B. The relevant values of the contact angle  $\theta$  estimated using eqs 1–3 are listed in the first row of Table 1.

**Table 1. Contact Angle  $\theta$  (deg), Liquid Surface Tension  $\gamma_l$  (mJ/m<sup>2</sup>), Polymer/Liquid Interfacial Tension  $\gamma_i$  (mJ/m<sup>2</sup>), and Work of Adhesion  $W_{\text{adh}}$  (mN/m) for Water and Oil in Contact with an *a*-PP Surface<sup>a</sup>**

	water	oil
$\theta$	109 ± 6 (108) <sup>21</sup>	103 ± 2
$\gamma_l$	62.3 ± 1.4 (71.7) <sup>22</sup>	35.1 ± 3 (31–33) <sup>23,24</sup>
$\gamma_i$	44.4 ± 7.3	40.3 ± 6.6
$W_{\text{adh}}$ P1	43.0 ± 8.4	29.1 ± 4.0
$W_{\text{adh}}$ P2	48.3 ± 8.9	25.3 ± 8.8

<sup>a</sup>Available experimental values are shown in parentheses for comparison.

As can be inferred from these values, the application of the computational protocol P1 yielded a  $\theta$  value for water in contact with *a*-PP in astoundingly good agreement with the corresponding experimental evidence. To our knowledge, a similar comparison for oil is not available so far; however, a lower value of the contact angle is obtained in this case, as expected.

**Results from P2.** Figure 3 shows the 3D and 2D models developed for *a*-PP, and the interface model for the water/*a*-PP system employed in the calculations of the surface and

interfacial tensions according to the second computational protocol adopted (P2).

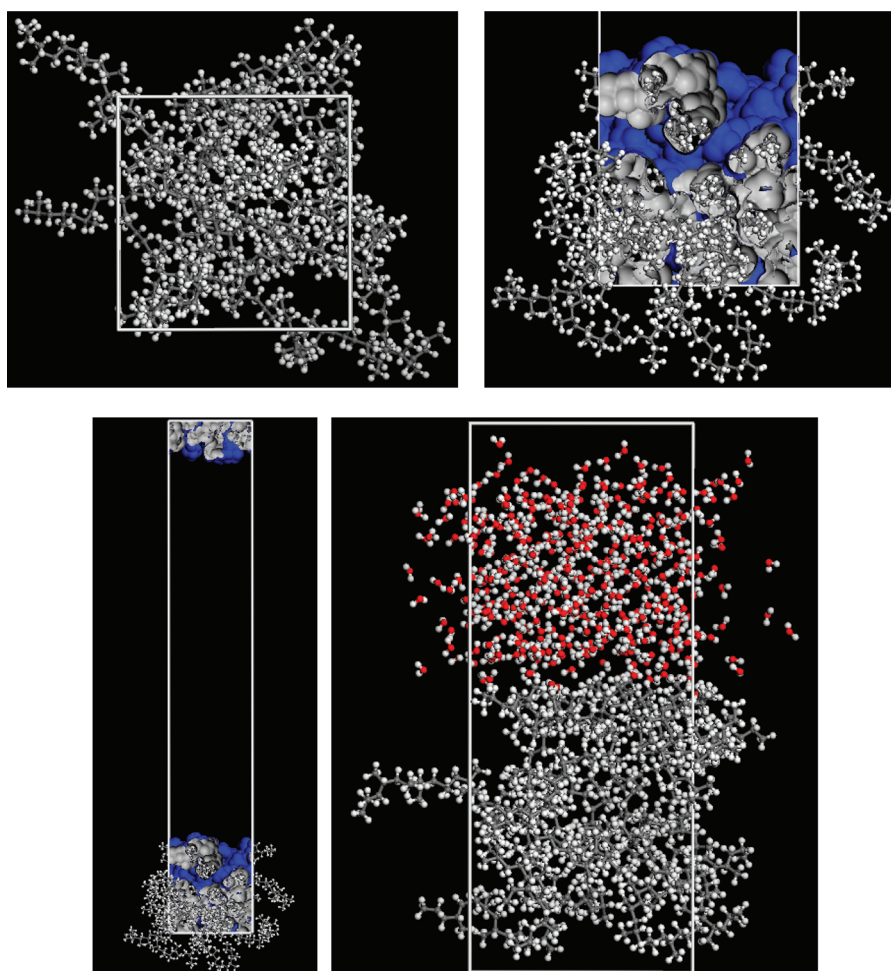
The  $\gamma_l$  values for both water and oil estimated according to P2 are listed in the second row of Table 1, and are found to be in good agreement with the corresponding experimental counterparts. In the case of water, it is important to observe that the simple and relatively fast way proposed in the present work to predict the water  $\gamma_l$  is in excellent agreement with the values obtained from more sophisticated approaches such as the virial method ( $\gamma_l = 63.7$  mJ/m<sup>2</sup>) and the test area method ( $\gamma_l = 63.5$  mJ/m<sup>2</sup>).<sup>25,26</sup> Notably, also the value of  $\gamma_p$  obtained for *a*-PP ( $30.5 \pm 1.2$  mJ/m<sup>2</sup>) matches the most common value reported in literature of 32 mJ/m<sup>2</sup>.<sup>27</sup> The corresponding values of the interfacial tensions  $\gamma_i$  are reported in the third row of Table 1.

The last row of Table 1 show the value of  $W_{\text{adh}}$  estimated for both water and oil via P2 using eq 4. As can be inferred from these data, the  $W_{\text{adh}}$  value obtained in the case of water and *a*-PP is higher than that estimated for oil on the same polymeric surface, as expected. To further verify the reliability of both computational pathways in predicting consistent and reliable values of  $\theta$ ,  $\gamma_l$ , and  $W_{\text{adh}}$  for the systems considered, we finally exploited the  $\theta$  values for water and oil obtained via P1 and the  $\gamma_l$  values obtained by P2 in the alternative  $W_{\text{adh}}$  expression given by eq 7, obtaining the values reported in the fourth row of Table 1. Pleasingly, the two sets of  $W_{\text{adh}}$  values estimated by the two different MD simulation protocols adopted in the present work are in good agreement with each other, thus confirming the reliability of the computational recipes in predicting the values of fundamental quantities characterizing the spreading of water and oil onto an amorphous polymeric surface.

### 4. CONCLUSIONS

In this work, we developed two, alternative atomistic MD simulation-based computational protocols to estimate the contact angle  $\theta$ , the surface and interface tensions  $\gamma$ , and the work of adhesion  $W_{\text{adh}}$  for water and oil in contact with an amorphous polypropylene surface. Both methodologies yielded reliable values of the contact angles and surface tensions, in agreement with available experimental data. Moreover, reasonable and comparable values of  $W_{\text{adh}}$  (a quantity affected





**Figure 3.** 3D model of *a*-PP (top left), zoomed view of the 2D model of *a*-PP (top right) shown in full in the bottom left panel, and interface model (bottom right) for the water/*a*-PP system (see text and the Supporting Information for detailed explanations).

by large errors during experimental determination), were also obtained using both computational recipes, thus confirming the internal consistency in the presented methodologies. Currently, further and highly encouraging work is in progress to expand this computer-based ansatz to the study of liquid spreading onto surfaces of different nature (e.g., crystalline and non-polymeric), to mixture of liquids (e.g., water/soap solutions), and to the inclusion of different effects such as temperature, droplet size, and surface roughness.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Full details of the computational recipes and MD simulations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Phone: (+)39 040 5583750. Fax: (+)39 040 569823. E-mail: [Sabrina.Pricl@di3.units.it](mailto:Sabrina.Pricl@di3.units.it).

### Author Contributions

†These authors equally contributed to this work.

### Notes

The authors declare no competing financial interest.

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