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Application of dissipative particle dynamics to interfacial systems: parameterization and scaling

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Dissipative Particle Dynamics (DPD) is a stochastic particle model which is able to simulate larger systems over longer time scales than atomistic modeling approaches by including the concept of coarse-graining. Whether standard DPD can cover the whole mesoscale by changing the level of coarse-graining is still an open issue. A scaling scheme originally developed by Füchslin et al. (2009) was here applied to interfacial systems as being one of the most successful uses of the classical DPD method. In particular, equilibrium properties such as the interfacial tension were analyzed at different levels of coarse-graining for planar oil-water interfaces with and without surfactant. A scaling factor for the interfacial tension was found due to the combined effect of the scaling scheme and the coarse-graining parameterization. Although the level of molecular description was largely decreased, promising results showed that it is possible to conserve the interfacial tension trend at increasing surfactant concentration, remarkably reducing modeling complexity. The same approach was also employed to simulate a droplet configuration. Both planar and droplet conformations were maintained, showing that typical domain formations of multi-component systems can be performed in DPD by means of the scaling procedure. Therefore, we explored the possibility to describe oil-water and oil-water-surfactant systems in standard DPD using a scaling scheme with the aim to highlight its advantages and limits.

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¹ I. INTRODUCTION

Computer modeling techniques are widely used to enhance the comprehension of the way 2 the molecules organize themselves in a liquid, 1-3 especially when experimental evidence is 3 ardly available due to the difficulty in isolating individual chemical species.^{4,5} Among molec-4 lar techniques, Dissipative Particle Dynamics (DPD) is a well-established method for simu-5 ating soft matter systems at the mesoscale level of description.^{6–8} DPD is a coarse-graining 6 echnique designed for modeling various fluid systems. For example, this method has been 7 used to simulate particulate suspensions,^{9–11} microfluidic systems,¹² polymer solutions,^{13,14} 8 and interfacial systems.^{5,15–20} Moreover, DPD is well-suited for modeling of multi-component 9 ystems such as emulsions, and it has been used in a number of studies to look at the effect 10 of adsorbing molecules on the stability of oil or water droplets in emulsions.^{21–24} Therefore, 11 interfacial systems have been largely investigated by means of DPD due to its remarkable 12 applications to industrial cases, such as for food engineering research.⁵ Indeed, DPD has 13 een successfully employed to analyze both static (most notably phase diagrams and inter-14 facial tension calculations) 5,14,18,25 and dynamic properties (such as transport processes), 26 15 even with amphiphilic and protein molecules acting as surfactants.^{5,15–19} 16

Initially, DPD was developed to be a truly mesoscopic method, in which both hydrody-17 namics and thermal fluctuations have a role. In fact, it was considered capable to bridge 18 the whole gap between the atomistic scale, which is accessible by Molecular Dynamics (MD) 19 simulations, and the macroscopic scale, investigated by the continuum modeling approach.⁸ 20 Recent works have seen this ambition of DPD being deeply discussed and developed.²⁷ It 21 was shown that by using a top-bottom approach, i.e., starting from continuum description 22 going to the mesoscale, it is possible to obtain a thermo-fluid dynamic consistent method, 23 which includes both hydrodynamics and thermal fluctuations at lower scales. This method 24 is referred to as Smoothed Dissipative Particle Dynamics (SDPD)^{28,29} since it combines 25 Smoothed Particle Hydrodynamics (SPH) and DPD in a way that respects the fluctuation-26 dissipation theorem through the so-called GENERIC formalism.^{28,29} The main features of 27 this method are the prescription of bead volume and transport properties, which are now 28 input parameters of the simulation, rather than undefined or output values as in classi-29 cal DPD. Moreover, a lot of effort has been put into addressing many issues of classical 30 DPD, like the resulting unrealistic Equation of State with Many-Body Dissipative Parti-31

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cle Dynamics (MDPD),³⁰ the influence of temperature with Energy-Conserving Dissipative 32 Particle Dynamics (EDPD)³¹ and the lack of all possible friction forces between beads with 33 Fluid Particle Method.³² Speaking instead of the bottom-up approach to mesoscale, the the-34 oretical framework to link the atomistic description and DPD has been recently established 35 through the Mori-Zwanzig projection theory (MZ-DPD), which works very well for bonded 36 atoms-molecules but not so well for unbonded interactions, which are very important in fluid 37 systems to describe transport phenomena like diffusion.²⁷ Mainly due to this reason, together 38 with the complexity of the newer DPD methods, classical DPD is still used nowadays by 39 the scientific community, as it is a simpler and computationally cheaper method compared 40 to more rigorous ones, with the caveat that all the parameters must be tuned every time a 41 new system and the corresponding properties of interest are investigated. 42

In classical DPD the governing equations are usually expressed in reduced units, which means that the same equations represent a whole family of physical systems.⁸ Füchslin *et al.*³³ and Arienti *et al.*³⁴ showed that physical properties such as the mass density and the compressibility of a system can be invariant with respect to a specific choice for model parameters, that one can associate to the level of coarse-graining. Mai-Duy *et al.*³⁵ applied a similar reasoning also for the viscosity and the Schmidt number.

When applying the appropriate scaling procedure, it was established that a single set 49 of parameters expressed in reduced units represents systems at arbitrary length scales,^{32–34} 50 even for bonded interactions.^{36,37} Such scale independence reported for bulk fluid interactions 51 an hold because the energy associated with an individual particle is made proportional to 52 the number of molecules it represents.³³ On the other hand, surface-dependent interaction 53 parameters may be expected to vary with the level of coarse-graining. In fact, assuming 54 system that exhibits domain formation, it is physically plausible that those interaction а 55 parameters effectively shrink with an increase in the level of coarse-graining. However, if a 56 DPD calculation can be performed at a small scale, then calculations at larger scales will 57 also be feasible, at least with respect to the scaling of parameters.³³ 58

Therefore, in this work applications of the scaling scheme to oil-water interfacial systems are investigated by means of DPD, also including a coarse-graining procedure for a surfactant molecule referring to our previous work.⁵ Instead of transport processes (viscosity), particular attention is paid to equilibrium properties such as the interfacial tension, highlighting the advantages and limits of the proposed scaling scheme for different levels of

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coarse-graining. Hence, the combined coarse-graining and scaling procedure are tested for 64 planar interfaces with and without surfactants and the main findings are, eventually, com-65 pared with the previous work. Finally, an example of simulating a droplet configuration is 66 also illustrated and discussed. Although many improvements have been made to the original 67 model to include the aspects aforementioned, standard DPD is still recognized as a powerful 68 tool to study interfacial systems. Therefore, the main novelty of this work is to study the 69 effects of upscaling the classical DPD model to different coarse-graining levels by conserving 70 the equilibrium properties of interfacial systems. 71

This paper is structured as follows: in section II a general background of the DPD 72 method and of the scaling relations is illustrated; simulation details are provided in section 73 III, together with all assumptions and simplifications of the modeling approach employed; 74 then, the main results are shown and discussed in section IV, and, finally, section V reports 75 conclusions of this work. 76

THEORETICAL BACKGROUND II. 77

An extensive overview of the standard Dissipative Particle Dynamics (DPD) method 78 can be found elsewhere, $6^{-8,27,38}$ therefore, here only the main concepts of this technique are 79 presented, together with the scaling procedure employed in this work. 80

Dissipative Particle Dynamics Α. 81

DPD is a stochastic mesoscale particle model that has been devised to allow the simulation 82 of the dynamics of mesoscopic particles, such as colloidal particles and/or groups of molecules 83 that would require extremely long simulations and very large systems to be studied with 84 atomistic scale molecular modeling technique, such as Molecular Dynamics (MD).^{38,39} Unlike 85 classic MD, each DPD particle *i*, called bead, represents a molecular cluster (a molecule 86 fragment or a group of solvent molecules) rather than an individual atom. The DPD system 87 consists of N point particles of mass m_i , position \mathbf{r}_i and velocity \mathbf{v}_i , whose time evolution 88 is determined by Newton's second law of motion, usually integrated using the modified 89 velocity Verlet algorithm.^{8,40} The major difference between MD and DPD, apart from the 90 coarse-grained nature of the molecules, is the nature of the forces between them. The force 91

$$\mathbf{f}_i = \sum_{j \neq i} (\mathbf{F}_{ij}^{\mathrm{C}} + \mathbf{F}_{ij}^{\mathrm{D}} + \mathbf{F}_{ij}^{\mathrm{R}}) , \qquad (1)$$

where $\mathbf{F}_{ij}^{\text{C}}$, $\mathbf{F}_{ij}^{\text{D}}$, and $\mathbf{F}_{ij}^{\text{R}}$ represent the conservative, dissipative, and stochastic (random) 93 forces, respectively and the sum runs over all other particles within a certain cutoff radius 94 r_c . The dissipative force $\mathbf{F}_{ij}^{\mathrm{D}}$ is a friction term that acts to push particles apart if they 95 are approaching each other and to pull them back together if they are moving apart. It 96 is represented as a pair potential between the particles that conserves both angular and 97 linear momentum. This frictional term leads to a gradual loss of kinetic energy in the 98 system, which is compensated for by the stochastic force $\mathbf{F}_{ij}^{\mathrm{R}}$ to ensure the conservation 99 of energy. The dissipation-fluctuation theorem⁷ leads to a relation between the friction 100 coefficient γ and the DPD-sigma parameter σ , namely the amplitudes of the dissipative 101 and random force, respectively. These two forces effectively act as a thermostat in DPD 102 and their mathematical description is investigated in detail elsewhere,^{6–8,38} since they are 103 mostly responsible for determining dynamic properties (such as transport processes).^{8,26,41} 104 Therefore, here only the definition of the conservative force is given since it is involved in 105 studying static properties of equilibrium systems.^{8,27,41,42} In this work the conservative force 106 $\mathbf{F}_{ij}^{\text{C}}$ felt by bead *i* includes contributions from repulsive interactions with surrounding beads 107 and, possibly, contributions due to the springs connecting bead i to other beads in the same 108 molecule. The repulsive force \mathbf{F}_{ij}^r , which is modeled as a soft repulsion between beads i and 109 j, is defined as follows: 110

$$\mathbf{F}_{ij}^{r} = \begin{cases} a_{ij}(1 - r_{ij}/r_{c})\hat{\mathbf{r}}_{ij} & \text{if } r_{ij} \le r_{c} \\ 0 & \text{if } r_{ij} > r_{c} \end{cases},$$
(2)

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between beads *i* and *j* at positions \mathbf{r}_i and \mathbf{r}_j respectively, and $\hat{\mathbf{r}}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/r_{ij}$ is the direction between the two beads. The parameter a_{ij} is the DPD interaction parameter defined for each bead pair, while r_c stands for the cutoff distance. When dealing with a chain molecule, an additional conservative term is considered to maintain bonds between neighbor beads. In this study, the bonds were modeled using a harmonic spring quadratic potential given as:

$$U_{ij}^{S} = k_{S}(r_{ij} - l_{H})^{2} , \qquad (3)$$

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where l_H is the equilibrium length for beads *i* and *j* and the stiffness of the length bond constraint is defined by the value of k_S .

¹¹⁹ B. Scaling Relations

In this section, the basic concepts of scaling DPD simulations are presented, together with the nomenclature and notation originally used in the work of Füchslin *et al.*³³.

As already stated, the operation of coalescing ν physical particles into one DPD bead is 122 denoted as "coarse-graining".⁴³ Being N the total number of DPD beads in a simulation, 123 it holds that $\nu N = N_{phys}$, with N_{phys} is the number of physical molecules represented in 124 the simulation. In order to compare DPD simulations with different coarse-graining levels 125 and ν' , the scaling ratio $\phi = N/N' = \nu'/\nu$ is introduced. Therefore, functions of ϕ ν 126 are identified to describe the scaling of various quantities at different coarse-graining levels 127 and these scaling expressions refer to relations between the respective parameters of two 128 systems with different coarse-graining levels ν and ν' . When $\phi > 1$, this means that the 129 same physical space (L' = L) is represented by a smaller particle density since each DPD 130 bead in the system denoted by ν' contains a larger number of physical particles. In contrast 131 with the results of Groot and Rabone⁴³ where the bead density ρ is decreased to ρ' while 132 keeping relevant properties (in particular the particles' radius of interaction) constant, here 133 an alternative scaling process is employed. When changing the level of coarse-graining for 134 the DPD particles, their number is accordingly scaled and their size (radius of interaction) 135 is adjusted in order to keep instead the relative overlap of the interacting particles constant. 136 Hence when a system with many DPD beads is mapped onto one with fewer but larger and 137 heavier particles, the interaction parameters have to be changed in order to maintain the 138 overall system properties. The following scaling relations in three dimensions are therefore 139 here employed: 33 140

$$\nu' = \phi \nu , \qquad N' = \phi^{-1} N ,$$

$$m'_{i} = \phi m_{i} , \qquad \rho' = \phi^{-1} \rho ,$$

$$a'_{ij} = \phi^{2/3} a_{ij} , \qquad r'_{c,ij} = \phi^{1/3} r_{c,ij} ,$$

$$\sigma'_{ij} = \phi^{5/6} \sigma_{ij} , \qquad \gamma'_{ij} = \phi^{2/3} \gamma_{ij} ,$$

$$\epsilon' = \phi \epsilon , \qquad \tau' = \phi^{1/3} \tau ,$$
(4)

where $\epsilon = k_b T$ and τ are energy and time scales, respectively, while k_b stands for the Boltz-

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mann constant and T for the temperature. With these scaling relations, the same physical 142 system shares properties, such as mass density, temperature, and compressibility,^{33,35} but it 143 is represented by different coarse-graining levels, using different length and time scales. As 144 it is customary in DPD modeling, energy, mass, time, and length are expressed in reduced 145 units while parameters in Eq. (4) have to be considered as dimensional quantities.³³ Indeed, 146 the mass of a single DPD particle, force cutoff radius, and thermal energy are typically em-147 ployed as basic units in DPD. The length, mass, time, and energy of the system are, thus, 148 not defined explicitly but in terms of these DPD units.⁸ It is also shown that the velocity 149 increments $\Delta \mathbf{v}$ obtained from integrating the forces are unchanged when the scaling is com-150 bined with the according reduction of units, which implies that the relative particle motions 151 are unaffected by scaling in the reduced unit systems (denoted by a tilde).³³ Then when 152 going to the reduced units of the primed system, it gives that for the reduced parameter $\widetilde{a_{ij}}$: 153

$$\widetilde{a_{ij}}' = a_{ij}' \frac{r_{c,ij}'}{\epsilon'} = \frac{\phi^{2/3} \phi^{1/3}}{\phi} a_{ij} \frac{r_{c,ij}}{\epsilon} = \widetilde{a_{ij}} , \qquad (5)$$

since a_{ij} scales like energy over length. Similarly, it follows for the reduced $\widetilde{\gamma_{ij}}$:

$$\widetilde{\gamma_{ij}}' = \gamma_{ij}' \frac{r_{c,ij}'^2}{\epsilon'\tau'} = \frac{\phi^{2/3}\phi^{2/3}}{\phi\phi^{1/3}}\gamma_{ij}\frac{r_{c,ij}^2}{\epsilon\tau} = \widetilde{\gamma_{ij}} , \qquad (6)$$

since γ_{ij} scales like energy over length and velocity. Finally, from the fluctuation-dissipation relation⁸ it gives again that:

$$\widetilde{\sigma_{ij}}' = \widetilde{\sigma_{ij}} \ . \tag{7}$$

These relations indicate that the two coarse-graining systems are stochastically equivalent 157 and, therefore, every system with the same values of the reduced variables $\widetilde{a_{ij}}$, $\widetilde{\gamma_{ij}}$, and 158 $\widetilde{\sigma_{ij}}$ have the same state space.^{33,35} This implies that, in reduced units, a DPD calculation 159 performed for a system with small extensions and over a small time interval is numerically 160 identical to one for a much larger system and covering a longer time range. As a result, it 161 can be shown that DPD is a scale-free (truly mesoscopic) method when dealing with simple 162 bulk fluids.^{33,35} The independence of scale for these systems cannot necessarily be upheld 163 for other types of interactions, namely binary mixtures of liquids A and B where more 164 conservative interaction parameters are employed to describe the relative repulsion, such as 165 a_{AA} , a_{AB} , and a_{BB} . Following the scaling relations in Eq. (4), the scale independence holds 166 for bulk interactions $(a_{AA} \text{ and } a_{BB})$ because the energy associated with an individual DPD 167 particle scale linearly with ϕ , i.e., it is made proportional to the number of molecules a DPD 168

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¹⁶⁹ bead represents. On the other hand, a_{AB} is a surface-dependent interaction parameter that ¹⁷⁰ determines interfacial energy and therefore may be expected to scale differently.^{33,34} However, ¹⁷¹ in this work, the original scaling relations in Eq. (4) are used for any pair interaction ¹⁷² *i*, *j* and the relative effects will be discussed in section IV, in particular as regards the ¹⁷³ interfacial tension. Therefore, the scaling relations derived by Füchslin *et al.*³³ are here ¹⁷⁴ directly employed for studying their effects on interfacial DPD systems (binary and ternary). ¹⁷⁵ Further discussion on their derivation can be found in the original work.³³

When dealing with bonded interactions, the following scaling relations for the parameters k_S and l_H of the harmonic spring quadratic potential (Eq. (3)) are employed:

$$k'_S = \phi^{1/3} k_S , \quad l'_H = \phi^{1/3} l_H , \qquad (8)$$

simply obtained by dimensional analysis of units, instead of a more sophisticated method.³⁷ Indeed, the stiffness parameter k_s scales like energy over squared length, while l_H scales like the length as being the equilibrium length of the bond constraint.

181 III. SIMULATION DETAILS

In this section, the details of DPD simulations performed are presented, together with 182 the appropriate approximations and simplifications adopted. Two case studies are investi-183 gated in this work: first, the interfacial system of a binary mixture modeled via a standard 184 parameterization for the oil and water liquids, and, secondly, the ternary system where a 185 protein surfactant molecule is introduced and modeled accordingly to our previous work.⁵ 186 For the first case, the effects of applying the scaling relations in Eq. (4) even to a standard 187 interfacial system are studied and the resulting outcome is used for the second case to scale 188 up the ternary system by comparing the equilibrium proprieties of the reference model with 189 of the upscaled one. A last example of a droplet configuration is also provided in order to 190 illustrate the capability of the scaling approach to maintain the domain conformation for 191 multi-component systems. 192

The simple oil/water interfacial system was simulated in an orthorhombic box of constant size $2L \times L \times L$ with L = 50 (in absolute units) with periodic boundary conditions, representing the same physical space for different coarse-graining level ratio ϕ where DPD beads have different radii. This can be seen in Figure 1 where an example of the simulating

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boxes of the interfacial oil/water system for $\phi = 1$ (a) and for $\phi = 100$ (b) are reported, 197 highlighting the decrease of the DPD particle number density due to the scaling approach. 198 The initial configuration consisted of a central water phase segregated by two oil phases, 199 thus forming two planar interfaces in equidistant yz-planes. The 50/50 oil-to-water bead 200 ratio was kept constant for all DPD simulations for this case at increasing coarse-graining 201 ratio ϕ . By denoting the oil bead with O and the water bead with W, typical simulation 202 parameters⁸ in absolute units for $\phi = 1$ are $r_{c,OO} = r_{c,WW} = r_{c,WO} = 1$, $m_O = m_W = 1$, 203 = 3, $\gamma_{OO} = \gamma_{WW} = \gamma_{WO} = 4.5$, $\sigma_{OO} = \sigma_{WW} = \sigma_{WO} = 3$, $a_{OO} = a_{WW} = 25$, and $a_{WO} = 3$. ρ 204 ranging from 50 to 100. These parameters have then been scaled according to Eq. (4) for 205 other coarse-graining values of ϕ . Following the energy and time scaling in Eq. (4), DPD 206 simulations were run with a time step $\Delta t = 0.02\tau$ for 10⁴ equilibration steps and for a pro-207 duction period of 5×10^4 steps. Pressure and interfacial tension were then measured from 208 simulations. In particular, here the interfacial tension (IFT) was computed by integrating 209 the difference between normal and tangential stress across the interface separating the seg-210 regated components.⁴⁴ Thus, if the normal to the interface lies along the x-direction, the 211 interfacial tension (in physical unit) is deduced from the local components of the pressure 212 tensor: 213

IFT =
$$\frac{1}{2} \int (p_{\rm N} - p_{\rm T}) dx = \frac{1}{2} \int \left(p_{xx} - \frac{1}{2} \left(p_{yy} + p_{zz} \right) \right) dx$$
, (9)

where $p_{\rm N}$ and $p_{\rm T}$ are the normal and tangential components of the pressure tensor profile. The factor 1/2 before the integral sign is due to the presence of two symmetric interfaces in the DPD simulation box when using periodic boundary conditions.

The second case, where the scaling approach was tested, focused on reproducing a ternary 218 system made by water, oil, and protein surfactant, which was investigated in our previous 219 work,⁵ thus labeled here as the reference model for $\phi = 1$. The general idea is therefore 220 to scale the DPD model up to the protein molecule level by maintaining the appropriate 221 differences between the three phases. In the reference model, the protein surfactant was 222 modeled as a chain molecule with bonded interactions. Here this level of detail will be lost 223 but favoring instead the mutual repulsion with the remaining two phases (oil and water). 224 First of all, the new coarse-graining level ν' (and ϕ) was decided in order to represent the 225 protein molecule as a single DPD particle or as two bonded beads. In line with the volume 226 equivalence of DPD particles employed in previous works,^{5,41,45} the coarse-graining level ratio 227 $= \nu'/\nu$ was chosen by referring to the protein molecule size, namely by comparing the ϕ 228

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FIG. 1. Snapshots of DPD boxes of the planar interfaces between oil (yellow) and water (blue) for $\phi = 1$ (a) and for $\phi = 100$ (b).

²²⁹ bead volume of the primed system with that of the reference model. As it has been shown, ²³⁰ the protein molecule assumed an almost stable mean radius of gyration of about 36.5 Å after ²³¹ a certain surface concentration at the oil/water interface.⁵ As a first guess when the protein ²³² molecule was modeled with a single DPD bead, this value is then assumed as the radius ²³³ of the sphere whose volume is compared with that used in the reference model for defining ²³⁴ the coarse-graining level ν , namely the volume of a cluster of three water molecules.^{5,45} ²³⁵ This leads to preserving bead-size effects when dealing with chain molecules,^{37,45} instead of







FIG. 2. Schematic representation of the coarse-grained protein molecule in the reference DPD model⁵ with $\phi = 1$ (a) and in the upscaled DPD model with $\phi = 3008$ (b) and $\phi = 1504$ (c).

simply comparing the number of beads representing the protein molecule in the reference 236 model. So the coarse-graining ratio ϕ was defined as the ratio of particle volumes: 3008 237 and 1504 for coarse-graining the protein as a single bead (P) and as two bonded beads (H 238 and T), respectively (Figure 2). Therefore, the scaling procedure was applied to the ternary 239 system with these values of ϕ , making the comparison with the reference model. Water (W) 240 and oil (O) beads are then represented by taking into account the coarse-graining ratio ϕ 241 respectively employed. While the water bead in the primed system is made by coalescing ν' 242 number of physical water molecules, oil was also modeled as a chain molecule in the reference 243 system, thus the ratio between the protein and oil molecular volumes gives the number of 244 oil molecules gathered to represent the O bead in the primed system. 245

As it was done for the simple O/W interfacial system, all DPD simulations of the ternary interfacial system were performed in an orthorhombic box of constant size $2L \times L \times L$ with L = 128 (in absolute units) with periodic boundary conditions. This box size was employed in order to simulate a number of total particles N' large enough to gather statistically 251

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adjusted to keep the same overall number density ρ' when the protein beads were also added in the DPD box. Indeed, simulations were performed to study equilibrium proprieties of the interfacial system, such as the interfacial tension, at increasing protein surfactant concentration, where its surface number density was calculated as will explain in Appendix A. The initial configuration again here consisted of a central water phase segregated by two oil phases, thus forming two planar interfaces in equidistant yz-planes. The protein molecule beads were initially located at the oil-water interface to make sure that both interfaces contain the same number of surfactants in order to perform averages on both interfaces. In line with our previous work⁵ for $\phi = 1$, simulation parameters in absolute units are $\rho = 5$ and $\gamma_{ij} = 4.5, \sigma_{ij} = 3$, for any bead pair ij, then scaled according to Eq. (4) for corresponding coarse-graining values of ϕ (3008 or 1504). $m'_P = 2m'_H = 2m'_T$ is determined by the ratio between the molecular mass of the protein and that of three water molecules, while m'_O by the ratio of the oil molecule mass and that of three water molecules multiplied for the number of oil molecules coalesced in the O particle based on the ϕ value used. As regards the repulsion a_{ij} parameters, they are listed in Tables I and II, and, apart from $r_{c,WO} = 1$, $r_{c,ij}$ is equal to 0.7 according to Ferrari *et al.*⁵ for $\phi = 1$. Also, these parameters have been scaled following Eq. 4. It is straightforward to underline here that self-repulsion parameters of oil and water $(a_{WW} \text{ and } a_{OO})$ have been obtained by respective bulk simulations. Since the pressure of bulk fluids is independent of the coarse-graining ratio ϕ by means of Eq. 4, a_{WW} was exactly the same used in the reference work⁵ while a_{OO} was determined by letting the oil bulk phase pressure in the primed system being the same as for $\phi = 1$ (results not shown). The inter-repulsion parameters were obtained in order to give the best matching with the interfacial tension values as it will be shown in section IV. In particular, three parameterization cases have been tested for the P bead when the protein molecule was modeled as a single particle while a clear distinction between the hydrophilic (H) and hydrophobic (T) part was made if the protein was described by two beads. Therefore, when applying such a coarse-graining procedure, the obtained repulsion parameters were still representative of surfactant interactions, however, the level of molecular details was much smaller than the case of $\phi = 1$. Moreover, the harmonic potential parameters used

for the bond between H and T beads are $k_S = 400$ and $l_H = 1$, as a first guess, then scaled

relevant results. For the interfacial system, the 50/50 oil-to-water bead ratio was again

kept constant, and both the number of water and oil beads filling the simulation box was

a _{ij}		W	Ο	Р		
				case 1	case 2	case 3
W		25				
0		16.5	50			
	case 1	60	90	30		
Р	case 2	70	105		35	
	case 3	80	120			40

TABLE I. Repulsion parameters a_{ij} used in this work. Note that these parameters have to be scaled according to Eq. 4 based on the value of $\phi = 3008$.

TABLE II. Repulsion parameters a_{ij} used in this work. Note that these parameters have to be scaled according to Eq. 4 based on the value of $\phi = 1504$.

a_{ij}	W	0	Н	Т
W	25			
Ο	16.5	50		
Η	20	200	15	
Т	90	40	15	15

according to Eq. 8. Following again the time and energy scaling in Eq. 4, these DPD simulations were performed with a time step $\Delta t = 0.001\tau$ for 3×10^4 equilibration steps and a production period of 10^5 steps. Density profiles, pressure, and interfacial tension were then measured from simulations. Here the interfacial tension was calculated again as reported in Eq. 9.

An illustrative test was also conducted by simulating an oil droplet in water bulk in presence of protein surfactants at equilibrium in order to investigate the capability of the parameterization employed and the scaling procedure for an additional interfacial system setup. For both $\phi = 3008$ and $\phi = 1504$, the initial conditions and the physical space simulated are the same. Being R = 65 the initial radius of the sphere containing the oil phase, DPD simulations were performed in a cubic box with L = 4R. As in the previous case, these box dimensions were used to simulate a number of total particles N' large enough

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to gather statistically relevant results. The sphere was then filled with oil beads and the 296 remaining space with 700 protein molecules (single bead or two-bead molecule depending 297 on the value of ϕ adopted) and with a number of water particles in order to have an overall 298 $=\phi \rho'$ equal to 5. The same simulation parameters were employed and, in particular, only 0 299 case 3 of Table I was studied for the P bead type parameterization. Simulations were run for 300 total of 2.5×10^5 steps, out of which 5×10^4 steps are used to equilibrate the system, saving а 301 time frame data for post-processing every 250 steps. Thus, the time-averaged distributions of 302 the radius of gyration of the oil droplet surrounded by protein molecules were then measured 303 for both ϕ cases. 304

All DPD simulation setup, runs, and post-processing analyzes were conducted within the CULGI software package,⁴⁶ together with all other tools and algorithms employed in this work.

308 IV. RESULTS AND DISCUSSION

In this section, the main findings of our work are presented and discussed. First, the analysis of the simple DPD O/W interface is carried out, and, then, applications of the scaling procedure to more complex systems are reported.

Figure 3 shows the pressure (a) and IFT' (b) trends with varying the coarse-graining 312 ratio ϕ for the simple O/W interface, for three values of the a_{WO} parameter. A relatively 313 small non-linear increment is detected as regards pressure values at increasing ϕ . Füchslin 314 et al.³³ already reported that pressure in a DPD simulation of a bulk fluid with periodic 315 boundary conditions for different self-repulsion parameters a and for various ϕ values is 316 independent of the coarse-graining. Therefore applying the scaling relations in Eq. (4) to a 317 binary system leads to the loss of pressure independence of the coarse-graining ratio. This 318 can be related to the use of the same scaling expression also for the surface term a_{WO} .³³ 319 Therefore, a limitation of such a scaling scheme is observed since the pressure of the binary 320 mixture might not be conserved with increasing the level of the coarse-graining ratio. On the 321 other hand, for each a_{WO} value it is clearly evident that the interfacial tension (in physical 322 unit) IFT' computed from DPD simulations (Eq. (9)) scales with ϕ^C , where $C = 1/3 \leq 1$ 323 as suggested by Füchslin *et al.*³³, so that: 324

$$IFT' = \phi^{1/3}IFT . (10)$$

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It is important to highlight here that this result is in line with the works of Arienti *et al.*³⁴, Vanya, Sharman, and Elliott⁴⁷. Such scaling relation for the interfacial tension can be expected by dimensional analysis of units in Eq (4). In fact, following the notation of reduction of units from the work of Füchslin *et al.*³³, it is also possible to show that:

$$\widetilde{\mathrm{IFT}'} = \mathrm{IFT}' \frac{r_c'^2}{\epsilon} = \phi^{1/3} \mathrm{IFT} \frac{\phi^{2/3} r_c^2}{\phi \epsilon} = \widetilde{\mathrm{IFT}} , \qquad (11)$$

since interfacial tension reduces as energy over squared length. Hence, scaling and unit 329 reduction precisely cancel each other. As a result, in the DPD framework, the reduced 330 interfacial tension IFT is scale-free, meaning that the calculation of this equilibrium property 331 with a single set of parameter values represents interfaces at arbitrary length scales. In 332 order to study how the scaling relations affect the interfacial tension calculation, the stress 333 profiles of the simple O/W system along the normalized x-direction normal to the interfaces 334 at increasing coarse-graining ratios ϕ are shown in Figure 4. The mechanical equilibrium of 335 the system is reached in both the oil and water phases since the stress profiles fluctuate with 336 small oscillations around zero in the bulk regions. As a consequence, the local contribution 337 to the interfacial tension is located only at the interfaces, with an increase in the stress in 338 the O/W interface region. Therefore, the accuracy of the interfacial tension calculation is 339 achieved for all ϕ values, and curvature effects are not detected as Eq. (9) is only valid for 340 flat interfaces.⁴⁴ As it can be seen, both pick heights and interface region width increase as 341 the coarse-graining ratio ϕ increases, determining an increment in the IFT' value (see Eq. 342 (9)). This can be referred to as a combined effect of scaling both $r_{c,ij}$ and a_{ij} parameters 343 according to Eq. (4). 345

Let us move now on the discussion of the ternary system made by oil, water, and surfac-346 tant (protein) when applying the scaling relations (Eq. (4)) to a reference system ($\phi = 1$) 347 investigated in our previous work,⁵ for two coarse-graining ratios ϕ . In order to study the 348 equilibrium properties of such a system, the starting configuration of the DPD box consists 349 of two symmetrical interfaces due to the periodic boundary conditions applied in the three 350 directions. Figure 5 shows the equilibrated DPD boxes representing the oil-water planar 351 interfaces covered by surfactant molecules for $\phi = 3008$ (case 3 in Table I) (a) and $\phi = 1504$ 352 (b). Figure 6 reports the number density profiles of oil, water, and surfactant beads along 353 the normalized x-direction for the coarse-graining ratios ϕ investigated in this work at two 354 surfactant molecule number density c_p . By looking at Figures 5 and 6, the symmetry of the 355

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FIG. 3. Pressure (a) and IFT' (b) trends with varying the coarse-graining ratio ϕ for the simple O/W interface. Empty symbols stand for the results of DPD simulations with the repulsion parameter a_{WO} equal to 50 (red squares), 75 (blue circles), and 100 (green triangles), respectively. Black dashed lines represent the scaling relation for the interfacial tension: IFT' = $\phi^{1/3}$ IFT.

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FIG. 4. Stress profiles (difference between normal and tangential pressures, $p_{\rm N} - p_{\rm T}$) along the normalized x-direction normal to the interfaces at increasing coarse-graining ratios ϕ for the simple DPD O/W system with $a_{WO} = 50$.

equilibrated ternary system can be seen. Density profiles define the interfacial region that 356 contains the surfactant layer and the bulk region that lies between the interfaces, highlighting 357 the mutual interpenetration of each component at equilibrium. Therefore, the parameteri-358 zation of the three species combined with the scaling procedure explained in section II are 359 able to maintain the structural properties of the interfacial system, even at a high level 360 of coarse-graining ratio ϕ . In Figure 6, it is straightforward to note that number density 361 values are expressed as $\phi \rho'$ to make profiles comparable between ϕ equal to 3008 and 1504. 362 Although the overall number density ρ is kept constant, the local bulk density of oil and 363 water beads fluctuates around a value different from 5 due to the fact that self-repulsion 364 parameters used in this work for oil and water (a_{OO} and a_{WW} in Tables I and II) are not 365 the same value.⁴⁸ A closer look at the surfactant density profiles reveals that an appreciable 366

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number of surfactant beads are not adsorbed at interfaces since surfactant density values 367 are not zero at the oil and water bulk regions. This effect is more relevant at higher c_p and 368 for the case of $\phi = 3008$. In fact, at the same c_p the surfactant density peaks are higher 369 for $\phi = 1504$ than for $\phi = 3008$, meaning that a higher number of surfactants molecules 370 are adsorbed at the interface in the former case than in the latter. This effect justifies the 371 quantification of the surfactant molecules actually adsorbed at the interface at increasing 372 surfactant concentration. This is obtained from the surfactant density profiles by imple-373 menting an automatic procedure to determine the protein surface density at equilibrium 374 as explained in Appendix A. However, Figure 6 also shows that, when using the upscaled 375 DPD model, a clear distinction between hydrophilic and hydrophobic parts in the surfactant 376 molecule as done for $\phi = 1504$ (see Figure 2 and Table II) provides better results in terms 377 preserving the reference conformation at equilibrium. In particular, for $\phi = 1504$ the 378 surfactant molecules penetrate the water bulk to a much larger extent than the oil bulk, 379 especially at higher c_p values as already reported in our previous work.⁵ 380

Figure 7 represents the most interesting result of this work. It reports the interfacial 382 tension as a function of the surfactant (protein) surface number density by comparing the 383 reference results for $\phi = 1$ from Ferrari *et al.*^{5,49} with those obtained in this work with 384 = 3008 (a) and ϕ = 1504 (b). Three independent DPD runs were carried out and ϕ 385 the averaged values are shown together with the corresponding standard deviations. Error 386 bars are generally smaller than symbols indicating high reproducibility of the current DPD 387 model. As it is shown that the interfacial tension scales following the Eq. (10), it is expressed 388 here as $IFT'/\phi^{1/3}$ in order to make its values comparable at different coarse-graining ratios 389 ϕ . When no surfactant is added to the simulation box, it is important to highlight that, 390 besides the scaling relation, the interfacial tension value between the oil and water phase 391 is accurately reproduced by using the same parameterization of water and oil beads for 392 different ϕ (Tables I and II). As it can be seen, a very good agreement is achieved for both ϕ 393 values investigated here at increasing protein surface number density. Apart from a simple 394 aparameters fine-tuning, then it is possible to preserve the interfacial tension trend in an 395 upscaled DPD model with surfactant (protein) molecules. In both cases, the interfacial 396 tension decreases as the protein surface density increases until it reaches a minimum value 397 at the saturation of the interface. As it is shown, a further increase in protein surface 398 concentration has almost no effect on the interfacial tension, which is a typical behavior 399

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FIG. 5. Snapshots of equilibrated DPD boxes of the planar interfaces between oil (yellow) and water (blue) covered by surfactant molecules (brown beads for $\phi = 3008$ (case 3 in Table I) (a), green and red beads for $\phi = 1504$ (b)), at the surfactant molecule number density c_p equal to 3.05×10^{-4} [numbers per unit volume].

of an interfacial system stabilized by surfactant proteins.^{50,51} However, some differences are identified with respect to the reference system with $\phi = 1$. As regards $\phi = 3008$, all three protein bead parameterization leads to larger deviations from the reference data at lower protein concentrations while smaller ones correspond to the protein parameterization of case 3 in Table I at higher protein concentrations. On the other hand, concerning $\phi = 1504$, an almost perfect match with the reference case is obtained at lower protein concentrations. Nevertheless, the interfacial tension reaches the minimum value at the saturation of the

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FIG. 6. Number density profiles of oil (yellow lines), water (blue lines), and surfactant (red lines) along the normalized x-direction normal to the interfaces with the coarse-graining ratio ϕ equal to 3008 (case 3 in Table I) ((a.i) and (b.i)) and 1504 ((a.ii) and (b.ii)) at two surfactant molecule number densities c_p ((a.i), (a.ii) and (b.i), (b.ii), respectively).

interface at a lower protein concentration than that of $\phi = 1$. The values of protein surface 407 number density are obtained as explained in Appendix A. As already illustrated in Figure 408 6, each symbol corresponds to the same initial protein volume number density c_p in Figure 409 7, thus the effect of the different number of molecules adsorbed at the interface depending 410 on the coarse-graining ratio ϕ is here even more evident. In fact, when ϕ is equal to 3008, 411 increasing oil, water, and self-repulsion parameters of P bead type (from case 1 to case 3 of 412 Table I) leads to a better absorbing capability but a worse surfactant behavior in terms of 413 the interfacial tension reduction. If the protein molecule is modeled as two bonded beads 414 by distinguishing between the hydrophobic and the hydrophilic contribution as done for 415 = 1504, the best adsorbing activity is obtained. In Figure 8 the pressure trends for ϕ 416

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different ϕ values are then reported at increasing protein volume number density. When 417 the oil/water interface is free of protein molecules, the pressure value increases non-linearly 418 going from the case of $\phi = 1$ up to $\phi = 3008$ as expected by looking at Figure 3 (a). Then, 419 clear differences in the pressure trends are observed. Although pressure decreases slight 420 linearly for $\phi = 1$ at increasing protein concentration, it increases non-linearly for $\phi = 3008$. 421 This appears to be related to the protein coarse-grained model used for $\phi = 3008$. In fact, 422 if $\phi = 1504$ and the protein molecule is represented by at least two bead types, the pressure 423 trend is decreasing as well. Nevertheless, its slope is relatively larger in absolute value than 424 that of $\phi = 1$. Therefore, it seems that the pressure profile cannot be precisely reproduced 425 at higher coarse-graining levels when most molecular details are lost. 426

As the last result of this work, Figure 9 shows an illustrative example of using the scaling 428 procedure to simulate an oil droplet in water bulk in presence of surfactants. As explained in 429 section III, the initial conditions and the physical space simulated are the same for $\phi = 3008$ 430 and for $\phi = 1504$. Hence similarities and differences between the two coarse-graining ratio 431 cases are investigated. In both of them, it is important to highlight that the equilibrium 432 configuration as a single droplet is observed due to the parameterization and the scaling 433 procedure employed. This can demonstrate once again that the scaling relations in the DPD 434 framework are able to describe different structural conformations. However, by comparing 435 the $\phi = 3008$ case with the $\phi = 1504$ one it is again shown that the adsorbing capability 436 of protein molecules is better reproduced if they are modeled by two bonded beads than a 437 single bead. This can be seen by looking at the time-frequency distributions of the radius of 438 gyration value of the oil droplet covered by surfactant molecules and at the corresponding 439 snapshots of clipped simulation boxes in Figure 9. In fact, the protein beads appear to be 440 more dispersed in the simulation box for $\phi = 3008$ than for $\phi = 1504$, also represented by 441 a bit smaller mean value of the droplet radius of gyration, meaning fewer protein molecules 442 adsorbed at the oil droplet interface with respect to the case of $\phi = 1504$. Moreover, 443 the smaller standard deviation of the frequency distribution and the better quality of the 444 fitting through the Gaussian distribution indicate more stability of the droplet modeled with 445 $\phi = 1504$ than with $\phi = 3008$. If the same length conversion factor is used from our previous 446 work,⁵ then the corresponding mean values of the droplet radius of gyration are 43.7 and 447 45.4 nm for $\phi = 3008$ and for $\phi = 1504$, respectively. However, it must be stated that 448 these numbers are based on speculative assumptions on spatial and time scales associated 449

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FIG. 7. Interfacial tension as a function of the protein surface number density, comparing between reference results for $\phi = 1$ and for $\phi = 3008$ (a) and $\phi = 1504$ (b). Error bars are estimated from three independent DPD simulations.

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FIG. 8. Pressure trends for different ϕ values at increasing protein volume number density. Similar data are obtained with different parameterizations of P bead type, thus results for $\phi = 3008$ only referring to case 3 of Table I are reported. Error bars related to three independent DPD simulations are much smaller than the symbol size, thus they are not shown.

with DPD units. However, this seems in line with respect to previous works on simulating
a single droplet via DPD.⁵²⁻⁵⁴



FIG. 9. Time-frequency distributions (blue histograms) of the radius of gyration value of an oil droplet covered by surfactant molecules in water bulk for $\phi = 3008$ (case 3 of Table I) (a.i) and for $\phi = 1504$ (b.i) and the relative Gaussian fitting curves (red lines). Corresponding snapshots of clipped simulation boxes are shown in (a.ii) and (b.ii), where oil and water are represented by yellow and blue beads respectively while protein molecules by brown beads for $\phi = 3008$ and green and red beads for $\phi = 1504$.

453 V. CONCLUSIONS

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In this work, we explored the possibility to use classical DPD to describe an oil-water and 454 an oil-water-surfactant system using the concept of level of coarse-graining, with the aim 455 to obtain a simplified model capable of reproducing properly the drop of interfacial tension 456 observed with more detailed mesoscale simulations. We found that the classical DPD model 457 is invariant with respect to the proper definition of the level of coarse-graining, as discussed 458 in the work of Füchslin *et al.*³³. When dealing with interfacial systems which are one of 459 the most successful applications of the DPD method, they tend to exhibit a typical length 460 scale due to the domain formation. This means that the independence of the length scale 461 cannot anymore be achieved. However, in this work, we showed that, if an interfacial system 462 can be simulated with DPD on a small scale, the scaling of interactions does not prevent 463 simulation on a larger scale unless specific issues are dealt with. Indeed, equilibrium а 464 proprieties of planar interfaces with and without a protein surfactant for different ratios of 465 the level of coarse-graining were investigated by applying the scaling scheme. Although the 466 level of description is much smaller, it was shown that the equilibrium interfacial tension 467 trend can be conserved for different coarse-graining ratios besides a scaling factor. This 468 can be achieved by a simple representation of molecules involved, meaning that very few 469 interaction parameters need to be set, thus decreasing the model complexity. The same 470 approach for planar interfaces was also employed for a droplet configuration, showing that 471 in both cases it is possible to maintain the domain conformation by applying an appropriate 472 combined scaling procedure and coarse-graining parameterization. On the other hand, the 473 pressure of interfacial systems appears to be not independent of the coarse-graining ratio, in 474 contrast with the result of bulk fluids. The surface concentration of surfactants also seems to 475 be related to the coarse-graining level and parameterization. Hence, possible applications of 476 such findings will focus on investigating droplet coalescence and breakage events, which occur 477 at a time- and space-scale larger than that of thermal fluctuations of single particles. Future 478 works will pay the way for a better understanding of to what extent DPD can be considered 479 truly mesoscopic in terms of also dynamics proprieties by studying multi-component non-480 equilibrium systems. 481

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490 AUTHORS' CONTRIBUTIONS

All authors contributed to the study conception and design. Software programming, data collection, and analysis were performed by Marco Ferrari. The first draft of the manuscript was written by Marco Ferrari and all the authors iteratively corrected and contributed to the final version of the manuscript.

495 CONFLICT OF INTEREST

⁴⁹⁶ The authors have no conflicts to disclose.

497 DATA AVAILABILITY

The data that support the findings of this study are openly available in Zenodo at http: //doi.org/10.5281/zenodo.6930825, reference number 55.

500 Appendix A

The method used in this work to automatically determine the protein surface number density is here explained as it has been seen that a certain number of surfactants are not adsorbed at the interface. This is similar to the procedure already employed to identify the bulk concentration of solutes in interfacial systems found in the literature.⁴⁸ Figure 10 shows an illustrative example of the method here used. From simulations of the ternary system with

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two symmetrical interfaces the time-averaged number density profiles of protein molecules 506 along the normalized x-direction normal to the interface expressed as $\phi \rho'$ are extracted (a) 507 (see Figures 5 and 6 for reference). The gradient of the number density is then computed 508 with respect to x/L_x (b). The regions where the gradient fluctuates around zero define 509 the bulk phases. The interface region can be identified by looking for spikes (positive and 510 negative) in the gradient that are an order of magnitude greater than the fluctuations seen 511 in the bulk regions. These spikes define the interface region to be included in number density 512 calculations. Hence the standard deviation S_e of the gradient (distance between horizontal 513 grey dashed lines) is used to identify the distinction between bulk and interface regions. 514 The first and last intersections between the gradient curve and horizontal lines in Figure 515 10 (b) define the interval limits $(\hat{x}_{1,a} \text{ and } \hat{x}_{1,b})$ of the interface region labeled as 1 where 516 protein molecules can be considered adsorbed at the interface. The same is done for the 517 interface labeled as 2 (not shown). From the area (in red) subtended by the number density 518 profile, the equilibrated surface density of protein molecules at interface c_i is then obtained 519 as follows: 520

$$c_{i} = \frac{L_{x}}{2n\phi L^{2}} \left(\int_{\hat{x}_{1,a}}^{\hat{x}_{1,b}} \phi \rho'(x/L_{x}) L^{2} d(x/L_{x}) + \int_{\hat{x}_{2,a}}^{\hat{x}_{2,b}} \phi \rho'(x/L_{x}) L^{2} d(x/L_{x}) \right) , \qquad (A1)$$

where *n* corresponds to the number of beads representing the protein molecule, thus equal to 1 or 2 for $\phi = 3008$ or $\phi = 1504$, respectively (see Figure 2). Hence c_i values are used as abscissas in Figure 7. ACCEPTED MANUSCRIPT

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FIG. 10. Illustrative example on how the protein surface number density is determined in this work from the number density profile of surfactants along the normalized x-direction normal to the interface (a) by means of evaluating its gradient curve (b). The portion of the simulation box relative to the interface labeled as 1 is only shown. Further details on the meaning of the symbol notation can be found in the text.

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(a) $\phi = 1$

(b) $\phi = 100$









(a) $\phi = 3008$



(b) $\phi = 1504$







