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Application of a multiscale approach for modelling the rheology of complex fluids
 in industrial mixing equipment

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8 (Dated: 15 January 2024)

Many industrial sectors, like the personal care one, make wide use of mixing processes that 9 involve complex fluids. However, modelling the rheology of these fluids is still challeng-10 ing due to their non-Newtonian behaviour, which depends also on the local composition. 11 Computational tools such as Dissipative Particle Dynamics (DPD) have been already used 12 to calculate the equilibrium properties of these systems. Moreover, different works have 13 been focused on the calculation of transport properties from these mesoscale DPD simula-14 tions. Multiscale approaches have been proposed to couple rheological information from 15 DPD with Computational Fluid Dynamics (CFD) simulations. The CFD technique repro-16 duces the macroscale piece of equipment, implementing a rheology model built using the 17 Gaussian Process Regression (GPR), a mathematical tool related to machine learning. In 18 this work, such framework is tested on an industrial process, to asses its performance on 19 a realistic application. The investigated system is a solution at a high concentration of 20 Sodium Lauryl Ether Sulfate (SLES) in water under laminar fluid dynamics regime. The 21 results show that the mixture correctly exhibits a shear-thinning behaviour and presents 22 viscosity values in good agreement with rheology experiments. While the feasibility of the 23 coupling approach is shown, further studies on DPD are needed to improve the accuracy 24 and the predictability of the methodology. 25

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# 26 I. INTRODUCTION

The personal care industry makes extensive use of ionic and non-ionic surfactants mixed with 27 water for the production of everyday items, such as shampoos and soaps. Usually, the final prod-28 ucts for the consumer market have low to moderate concentrations of surfactants ( $\sim 12 - 25\%$ )<sup>1,2</sup>. 29 On the other hand, the semi-finished products present considerably higher concentrations of sur-30 factants. Consequently, during the production step, a great variety of composition conditions are 31 explored. In these blends, the concentration of surfactants plays a crucial role, due to their capabil-32 ity of undergoing self-assembly at the microscopic scale<sup>3</sup>. This process leads to the formation of 33 different microstructures depending on composition, ranging from the micellar one to the hexag-34 onal, cubic, and lamellar ones<sup>4,5</sup>. For this reason, these fluids are often referred to as structured 35 fluids or complex fluids. The self-assembly occurs also in solutions of water and Sodium Lauryl 36 Ether Sulfate  $(SLES)^{3-5}$ , one of the most commonly used surfactants for personal care products. 37 The presence of microstructures influences greatly the rheology of complex fluids, whose appar-38 ent viscosity depends on the composition and on the shear rate $^{3,4}$ . As a result, building a model 39 for this rheological behaviour is considerably challenging and requires a significant amount of 40 experimental data. 41

The continuous advances in the field of computational methods can be a great aid to the mod-42 elling process. Various simulation techniques allow the reproduction of the features of the fluids, 43 from the microstructures at the mesoscale to the macroscopic fluid dynamics in the industrial 44 equipment. In particular, Dissipative Particle Dynamics (DPD) is a computational technique that 45 employs coarse-graining (CG) to describe the molecules in a fluid. The CG description leads to a 46 reduction of the required computational resources when compared to other atomistic techniques, 47 such as Molecular Dynamics (MD). This is due to the reduction of the degrees of freedom, which 48 allows to explore higher spatial and temporal scales while retaining a certain degree of chemical 49 specificity. The DPD technique has already been proven to be able to reproduce a variety of mi-50 crostructures for complex fluids<sup>6,7</sup>. The parameterization of a DPD fluid is a vibrant field of study 51 and various approaches were proposed over the years. Since the initial developments of the tech-52 nique, Groot and Warren<sup>8</sup> built the parameter set for a simple fluid to match the compressibility 53 of water. Moreover, they proposed a method based on Flory-Huggins theory of polymer solutions 54 to derive the interaction parameters for systems with large molecules<sup>8</sup>. This approach found wide 55 usage in the literature in numerous different applications, like surfactants in oil/water systems<sup>9</sup>, 56

phase diagrams for ternary mixtures<sup>6</sup> or polymer solutions<sup>10</sup>. An automated approach to build the 57 coarse-grained model and identify the parameters was developed by Fraaije et al.<sup>11</sup> and recently 58 tested on interfacial systems<sup>12,13</sup>. A parameterization method for small molecules based on fitting 59 the partition coefficients in water-octanol was proposed by Anderson et al.<sup>14</sup>. The method pro-60 duces a set of parameters that can be used for different molecules and has been already used to 61 simulate alkyl surfactants. Among these, there was an interest in investigating the phase diagram 62 for solutions of surfactants in water<sup>15</sup>, in calculating equilibrium properties<sup>16,17</sup> and the effect of 63 cosurfactants<sup>18</sup>. These studies, though, analyzed low concentrations of alkyl surfactants in water, 64 exploring only the typical final formulations for the consumer market. Moreover, they focused on 65 equilibrium properties, leaving aside the calculation of transport properties, such as diffusion coef-66 ficients and viscosity. Nonetheless, since its development, DPD has been considered a promising 67 tool for the evaluation of transport properties for colloidal systems<sup>19,20</sup> and polymer solutions<sup>21</sup>. 68 Various methods have been employed to calculate the viscosity of a DPD fluid<sup>22</sup>. Simple fluids 69 exhibit Newtonian behaviour, and their viscosity can be evaluated both with equilibrium<sup>23,24</sup> and 70 non-equilibrium<sup>22</sup> techniques. On the other hand, non-equilibrium simulations are necessary to in-71 vestigate shear-dependent rheology, typical of complex fluids<sup>7,25–27</sup>. These methods exhibit high 72 uncertainty in viscosity values for low shear rate values<sup>25,28</sup> and bring to a rise in temperature and 73 viscosity for high shear<sup>22</sup>, which is unphysical in many cases<sup>7</sup>. To have a better description of 74 transport properties Junghans, Praprotnik, and Kremer<sup>29</sup> proposed a modification to the standard 75 DPD thermostat, to include the effect of velocity components other than the radial one. For the 76 same reason, increment of the dissipative coefficient  $\gamma$  was investigated<sup>22</sup> and *ad hoc* thermostats 77 have been developed 30,31. 78

While atomistic methods are helpful in calculating the properties of fluids, other techniques are instead suited to obtain useful information for design and optimization at the process scale. Among these, Computational Fluid Dynamics (CFD) has been used to simulate a great variety of applications, including mixing ones<sup>32,33</sup>. Hence, studies were already conducted on static mixers<sup>34–36</sup>, a piece of equipment often used to produce non-Newtonian solutions of surfactants in water.

<sup>84</sup> Using the just described techniques, Zhao *et al.* <sup>37</sup> proposed a multiscale approach to simulate <sup>85</sup> the behaviour of non-Newtonian fluids. The method uses DPD simulations to compute the vis-<sup>86</sup> cosity of the fluid at different shear rates, generating a dataset used to build the rheology model. <sup>87</sup> This latter step is performed using the Gaussian Process Regression (GPR), a mathematical and <sup>88</sup> statistical tool that belongs to the family of machine learning techniques. The GPR is then directly coupled with the CFD simulation, with the model that takes the shear rate values from the latter as input and gives the corresponding apparent viscosity in output. This multiscale approach was tested on a polymer melt<sup>37</sup> and on a diluted polymer solution<sup>38</sup> with promising results, but it was never applied directly to a realistic industrial process.

In this work, the rheological behavior of an industrial blend, made of a highly concentrated 93 solution of SLES in water, is reproduced using an automated multiscale approach. The rheological 94 information is extracted by means of a mesoscale DPD simulation and is used to build a rheology 95 model. This is implemented through the GPR in a CFD simulation of the mixing equipment used 96 for the blend production, i.e. an SMX static mixer. The DPD model of the fluid is successfully 97 tested by a qualitative reproduction of the SLES/water phase diagram. The CFD is used to evaluate 98 useful fluid dynamics details of the flow inside the static mixer together with the pressure drop 99 across the device. The final values are plausible when compared with results obtained for similar 100 blends in the same piece of equipment. 101

The next three sections are structured as follows: Section II illustrates thoroughly the methods and techniques used in this work, adding also information about the computational details. Section III reports and comments on the results, focusing on every step of the multiscale approach in different subsections. At last, the conclusions will be presented in Section IV.

## **106 II. METHODS AND COMPUTATIONAL DETAILS**

#### 107 A. The DPD technique

The first part of the multiscale approach consists in simulating the fluid at the mesoscale, to ob-108 tain information about its rheological behaviour. The technique used to perform these mesoscale 109 simulations is the Dissipative Particle Dynamics (DPD), initially developed by Hoogerbrugge 110 and Koelman<sup>39</sup> and later improved and formalized in detail by Español, Groot and Warren<sup>8,40</sup>. 111 The DPD technique employs a coarse-grained description of the molecules, for which atoms are 112 grouped together in particles called beads. These represent the fundamental elements in DPD 113 simulations and can contain a number of atoms, or a number of molecules, depending on the de-114 sired level of coarse-graining (CG). As a consequence, DPD has the possibility to explore bigger 115 scales in comparison to the full-atom Molecular Dynamics (MD) while keeping low the required 116 computational resources. 117

<sup>118</sup> The dynamics of the DPD particles can be described through Newton's equations of motion:

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i \;, \tag{1a}$$

119

$$\frac{d\boldsymbol{v}_i}{dt} = \frac{\boldsymbol{f}_i}{m_i},\tag{1b}$$

where  $\mathbf{r}_i$  is the position of the bead *i* with mass  $m_i$ , and  $\mathbf{v}_i$  is its velocity. In the standard DPD model of a simple fluid, the beads interact with each other through three pairwise forces, that are summed in the term  $f_i$  of Eq. (1b):

$$\boldsymbol{f}_{i} = \sum_{i \neq j} (\boldsymbol{F}_{ij}^{C} + \boldsymbol{F}_{ij}^{D} + \boldsymbol{F}_{ij}^{R}) .$$
<sup>(2)</sup>

These three forces regulate the interactions of two DPD beads up to a distance equal to the cut-off radius  $r_c$ . More in detail,  $\mathbf{F}^C$  is the conservative force:

$$\boldsymbol{F}_{ij}^{C} = \begin{cases} a_{ij} \left( 1 - \frac{r_{ij}}{r_c} \right) \hat{\boldsymbol{r}}_{ij} & r_{ij} \le r_c \\ 0 & r_{ij} > r_c \end{cases}$$
(3)

which defines a soft repulsive potential, that allows beads to interpenetrate each other and even overlap. In this latter case, the conservative force reaches its maximum, which is equal to the repulsive parameter  $a_{ij}$ , whose value depends on the type of beads *i* and *j*. The distance between a pair of particles is identified with  $r_{ij} = |\mathbf{r}_{ij}| = |\mathbf{r}_i - \mathbf{r}_j|$  and  $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$  is the unit vector representing the direction that connects the centers of the two beads. The dissipative force  $\mathbf{F}_{ij}^D$  and the random force  $\mathbf{F}_{ij}^R$  have the following structure:

$$\boldsymbol{F}_{ij}^{D} = -\gamma w^{D}(r_{ij})(\boldsymbol{r}_{ij} \cdot \boldsymbol{v}_{ij})\hat{\boldsymbol{r}}_{ij} , \qquad (4)$$

$$\boldsymbol{F}_{ij}^{R} = \boldsymbol{\sigma} \boldsymbol{w}^{R}(r_{ij}) \frac{\boldsymbol{\xi}_{ij}}{\sqrt{\Delta t}} \hat{\boldsymbol{r}}_{ij} , \qquad (5)$$

where  $w^D(r_{ij})$  and  $w^R(r_{ij})$  are the weight functions,  $v_{ij} = v_i - v_j$  is the relative velocity between two beads *i* and *j* and  $\xi_{ij}$  is a Gaussian white-noise variable with zero mean value and unit variance. These two forces act like a thermostat, in which  $F^D$  is used to model viscous phenomena and  $F^R$  is used to model the thermal agitation of the molecules. Español and Warren<sup>40</sup> showed that to respect the fluctuation-dissipation theorem the dissipative and random forces must be related, through the values of the parameters  $\gamma$  and  $\sigma$  and through their weight functions:

$$\sigma^2 = 2\gamma k_{\rm B}T , \qquad (6)$$

138

$$w^{D}(r_{ij}) = [w^{R}(r_{ij})]^{2} = \begin{cases} \left(1 - \frac{r_{ij}}{r_{c}}\right)^{2} & r_{ij} \le r_{c} \\ 0 & r_{ij} > r_{c} \end{cases}$$
(7)

These equations ensure the conservation of the energy in the system, in which the two forces act properly as a thermostat. Moreover, the relation between  $F^D$  and  $F^R$  results in momentum conservation and correct hydrodynamic behavior of the DPD fluids for sufficiently large scales<sup>37,41</sup>.

Due to its coarse-grained nature, the DPD model is based on reduced units. It is possible to 142 retrieve the values in physical units from the DPD reduced units through the use of conversion 143 factors. The values of these factors depend on the coarse-graining level of the model, but their 144 identification for a given system is not trivial<sup>27</sup>. While some procedures were developed for equi-145 librium simulations and simple fluids, in the case of non-equilibrium simulations it does not exist 146 a well-established methodology. The approach chosen for the work here presented is based on 147 matching the properties of interest for the systems studied. Hence, the conversion factors are 148 identified in order to match the viscosity of the system at a given shear rate: 149

$$\mu_{\rm cf} = \frac{\mu}{\mu_{\rm DPD}} \,, \tag{8a}$$

150

151

 $\dot{\gamma}_{\rm cf} = \frac{\dot{\gamma}}{\dot{\gamma}_{DPD}} \,, \tag{8b}$ 

$$\mathcal{E}_{\rm cf} = \frac{\mathcal{E}}{\mathcal{E}_{\rm DPD}} = \frac{k_{\rm B}T}{k_{\rm B, DPD}T_{\rm DPD}}.$$
(8c)

In Eq. (8) the subscript "cf" indicates the conversion factor, while the values in DPD units are marked with the subscript DPD, and the remaining quantities are expressed in physical units. Defining also the conversion factor for a third quantity, in this case the energy in Eq. (8c), it is possible to derive the conversion factor for any physical quantity. Considering that the standard model of the DPD is isothermal, it was possible to establish the energy of the system starting from a reference temperature.

6

#### **B.** Non-equilibrium simulations

To simulate a fluid under shear it is possible to apply the Lees-Edwards boundary conditions  $(\text{LEBC})^{42}$ , which is used to obtain the velocity profile corresponding to the desired shear rate

<sup>161</sup> inside a periodic box. The LEBC method was originally developed and widely used in the context <sup>162</sup> of MD simulation, but its implementation has been already studied and used in conjunction with <sup>163</sup> DPD in the past<sup>7,22,27</sup>. From such kind of simulation it is possible to obtain the pressure tensor P, <sup>164</sup> computed according to the following equation, in which *i* and *j* identify different beads:

$$\boldsymbol{P} = \frac{1}{V} \sum_{i=1}^{N} m_i \boldsymbol{v}_i \boldsymbol{v}_i + \frac{1}{V} \sum_{j>i}^{N} \sum_{i=1}^{N-1} \boldsymbol{r}_{ij} \boldsymbol{F}_{ij}^T .$$
(9)

<sup>165</sup> The apparent viscosity of the DPD fluid can be calculated from the elements of the pressure tensor:

$$\mu = -\frac{P_{xy}}{\dot{\gamma}},\tag{10}$$

where  $P_{xy}$  is the non-diagonal component of the pressure tensor relative to the plane in which the shear  $\dot{\gamma}$  is applied.

The DPD simulations were performed using the open-source software LAMMPS<sup>43</sup> (Large-168 scale Atomic/Molecular Massively Parallel Simulator). For non-equilibrium simulations, Lagrangian-169 Rhomboid boundary conditions (LRBC) are implemented in LAMMPS. The LRBC are equivalent 170 to the LEBC as representation for a simple shear flow<sup>44,45</sup> and the main difference consists in how 171 the shear is imposed. For  $\dot{\gamma} = \partial v_x / \partial y \neq 0$  using the LEBC, the shear is imposed using a "sliding 172 brick" approach: the periodic images below and above the simulation box are displaced at  $\pm L\dot{\gamma}\Delta t$ 173 in respect to the box itself. The position and velocity of the particles that cross the y boundaries 174 are set in order to take into account the different values of  $v_x$  in the periodic images. Moreover, the 175 interaction between two particles separated by a boundary is corrected to consider the displace-176 ment of the periodic boxes. To obtain the desired velocity profile using the LRBC instead, the 177 box itself is deformed, as illustrated in Fig. 1, with a rate corresponding to the desired shear. The 178 deformation induces a perturbation in the velocity of the DPD beads and under the condition of 179 linear profile for the velocity within the simulation box, the Eq. (10) can be used to calculate the 180 apparent viscosity. 181

In the approach here described an initial equilibrium simulation is conducted, in order to save the state of the DPD fluid that reached a dynamic equilibrium condition. This state can be used as a starting point since it allows to skip the repetition of the equilibration step for every nonequilibrium simulation. Consequently, the LRBC are directly applied to the equilibrated fluid in the box, imposing the desired shear rate. Due to the rise in temperature resulting from the imposition of the shear rate on the box, the SLLOD equations of motion were used, which in LAMMPS



FIG. 1. Illustration of the deformation resulting from the imposition of the LRBC on a DPD box.

implement a Nose-Hoover thermostat. This approach is widely used in Molecular Dynamics<sup>44,45</sup>,
 and has been lately adopted in some works to perform non-equilibrium DPD simulation with
 shear<sup>46</sup>.

This paragraph reports the parameters that are common to all the DPD simulations of the present work. In particular, the value of numerical density for the beads is  $\rho_{\text{DPD}} = 3$  and all the bead types have unitary mass in DPD units. The simulation domain is a cubic box, with a side of length L = 40 (DPD units) used to test the parameters (as described in Section III A) and one of length L = 20 (DPD units) used to carry out the non-equilibrium simulations. The velocity-Verlet algorithm was used to integrate the equations of motion in all the DPD simulations with a timestep  $\Delta t = 0.01$  (DPD units).

## <sup>198</sup> C. Miraspec UB75 model

The modeled fluid is the Miraspec UB75, a three-component mixture with composition reported in Table I.

<sup>201</sup> Besides water, the table reports the use of other two main components:

- The Inter ESA-70 is a mixture of SLES (Sodium Lauryl Ether Sulfate) at 70% in water, whose main function is cleansing.
- CME/A2 is cocamide monoethanolamine (CMEA), used to control foaming, viscosity, and

| Mass fraction |
|---------------|
| 0.72          |
| 0.08          |
| 0.20          |
|               |

TABLE I. Composition of the blend Miraspec UB75 used for the DPD simulations.

<sup>205</sup> mildness of the product.

As depicted in Fig. 2 and Fig. 3, both SLES and CMEA have an alkyl tail, which can be formed by a different number of carbon atoms. In particular in Table II and Table III are reported the percentages of the molecules for every length of the alkyl chain. These characterize the components of the blend and they are used to calculate the numerical concentrations of the beads in the DPD simulations of the Miraspec UB75.

TABLE II. Percentage of SLES molecules with a specific length of the alkyl chain, expressed in number of carbon atoms, in the Inter ESA-70 component.

| Number of Carbon atoms | Percentage in Inter ESA-70 |
|------------------------|----------------------------|
| 12                     | 70%                        |
| 14                     | 30%                        |

TABLE III. Percentage of CMEA molecules with a specific length of the alkyl chain, expressed in number of carbon atoms, in the CME/A2 component.

| Number of Carbon atoms | Percentage in CME/A2 |
|------------------------|----------------------|
| 8                      | 6%                   |
| 10                     | 6%                   |
| 12                     | 50%                  |
| 14                     | 18%                  |
| 16                     | 9%                   |
| 18                     | 11%                  |

Again in Fig. 2, it is shown that the SLES molecule can have a different number of ethoxyl (EO)

groups  $(CH_2CH_2O)_n$ . While the Miraspec UB75 contains only molecules of SLES with a single EO group, the phase diagram reported in the work of Li *et al.*<sup>3</sup> refers to SLES molecules with three EO groups. Consequently, the molecule used for the validation in Section III A contained two more  $[CH_2OCH_2]$  beads than the one depicted in Fig. 2.

The process of developing the final model went through different steps. Initially, a DPD model 216 for SLES and water is tested, using the set of parameters to reproduce the phase diagram of the 217 mixture. Then a coarse-grained model for CMEA is developed with the same parametrization 218 method, and the correct reproduction of the microstructure of the blend is used as a test. In the 219 end, the non-equilibrium simulations are performed with the developed DPD model, to obtain the 220 information on the rheology of the fluid. It must be remarked that it does not exist a unique stan-221 dardized process to develop the parameters of a DPD model. Hence, depending on the system 222 features and the level of coarse-graining, different methods can be used. Anderson et al.<sup>14</sup> devel-223 oped a parametrization scheme based on the water-octanol partition coefficients. The parameters 224 obtained with this technique have been used to simulate micellar blends of alkyl sulfate, alkyl 225 ethoxylate and alkyl ethoxy sulfate surfactants<sup>14–18</sup>. In this work we used the latter approach to 226 model the SLES molecules, adopting the same CG level depicted in Fig. 2. 227



FIG. 2. Coarse graining model adopted for water and SLES molecules<sup>15</sup>. Changing the length of the alkyl tail results in the addition or the subtraction of  $[CH_2CH_2]$  beads.

The full list of conservative parameters  $a_{ij}$  and cutoff radii  $r_{c,ij}$ , reported in Table IV, was obtained from previous works<sup>14,15</sup>, while in Table V are reported the dissipative parameters  $\gamma$  and the stochastic one  $\sigma$ , common to all the beads.

| TABLE IV: List of conservative repulsive parameter $a_{ij}$ and cut | off |
|---|-----|
|---|-----|

|  |  | radius $r_{c,ij}$ for each pair of beads. |  |
|--|--|---|--|
|--|--|---|--|

| Bead <i>i</i>                                    | Bead j   | conservative coefficient $a_{ij}$ | cutoff radius $r_{c,ij}$ |
|--|--|-----------------------------------|--------------------------|
| [H <sub>2</sub> O]                               | [H <sub>2</sub> O]                               | 25.0                              | 1.000                    |
| [CH <sub>3</sub> ]                               | [CH <sub>3</sub> ]                               | 24.0                              | 0.955                    |
| [CH <sub>2</sub> CH <sub>2</sub> ]               | [CH <sub>2</sub> CH <sub>2</sub> ]               | 22.0                              | 1.074                    |
| [CH <sub>2</sub> OCH <sub>2</sub> ]              | [CH <sub>2</sub> OCH <sub>2</sub> ]              | 25.5                              | 1.116                    |
| [CH <sub>2</sub> OSO <sub>3</sub> <sup>-</sup> ] | [CH <sub>2</sub> OSO <sub>3</sub> <sup>-</sup> ] | 13.30                             | 1.234                    |
| [Na]   | [Na]   | 25.00                             | 1.000                    |
| [CH <sub>3</sub> CH <sub>2</sub> ]               | [CH <sub>3</sub> CH <sub>2</sub> ]               | 22.00                             | 1.098                    |
| [CH <sub>2</sub> CONHCH <sub>2</sub> ]           | [CH <sub>2</sub> CONHCH <sub>2</sub> ]           | 22.00                             | 1.218                    |
| [CH <sub>2</sub> OH]                             | [CH <sub>2</sub> OH]                             | 14.00                             | 0.980                    |
| [H <sub>2</sub> O]                               | [CH <sub>3</sub> ]                               | 45.00                             | 0.977                    |
| [H <sub>2</sub> O]                               | [CH <sub>2</sub> CH <sub>2</sub> ]               | 45.00                             | 1.037                    |
| [H <sub>2</sub> O]                               | [CH <sub>3</sub> ]                               | 24.00                             | 1.058                    |
| [H <sub>2</sub> O]                               | [CH <sub>2</sub> OCH <sub>2</sub> ]              | 17.90                             | 1.117                    |
| [H <sub>2</sub> O]                               | [CH <sub>2</sub> OSO <sub>3</sub> <sup>-</sup> ] | 25.00                             | 1.000                    |
| [H <sub>2</sub> O]                               | [Na]   | 45.00                             | 1.049                    |
| [H <sub>2</sub> O]                               | [CH <sub>3</sub> CH <sub>2</sub> ]               | 19.00                             | 1.109                    |
| [H <sub>2</sub> O]                               | [CH <sub>2</sub> OH]                             | 14.50                             | 0.990                    |
| [CH <sub>3</sub> ]                               | [CH <sub>2</sub> CH <sub>2</sub> ]               | 23.00                             | 1.014                    |
| [CH <sub>3</sub> ]                               | [CH <sub>2</sub> OCH <sub>2</sub> ]              | 28.50                             | 1.020                    |
| [CH <sub>3</sub> ]                               | [CH <sub>2</sub> OSO <sub>3</sub> <sup>-</sup> ] | 28.50                             | 1.071                    |
| [CH <sub>3</sub> ]                               | [Na]   | 45.00                             | 0.962                    |
| [CH <sub>3</sub> ]                               | [CH <sub>3</sub> CH <sub>2</sub> ]               | 23.00                             | 1.026                    |
| [CH <sub>3</sub> ]                               | [CH <sub>2</sub> CONHCH <sub>2</sub> ]           | 32.00                             | 1.086                    |
| [CH <sub>3</sub> ]                               | [CH <sub>2</sub> OH]                             | 26.00                             | 0.967                    |
| [CH <sub>2</sub> CH <sub>2</sub> ]               | [CH <sub>2</sub> OCH <sub>2</sub> ]              | 28.50                             | 1.095                    |
| [CH <sub>2</sub> CH <sub>2</sub> ]               | $[CH_2OSO_3^-]$                                  | 28.50                             | 1.154                    |
| [CH <sub>2</sub> CH <sub>2</sub> ]               | [Na]   | 45.50                             | 1.037                    |

| Bead <i>i</i>                                    | Bead j   | conservative coefficient $a_{ij}$ | cut-off radius $r_{c,ij}$ |
|--|--|-----------------------------------|---------------------------|
| [CH <sub>2</sub> CH <sub>2</sub> ]               | [CH <sub>3</sub> CH <sub>2</sub> ]               | 22.00                             | 1.086                     |
| [CH <sub>2</sub> CH <sub>2</sub> ]               | [CH <sub>2</sub> CONHCH <sub>2</sub> ]           | 32.00                             | 1.146                     |
| [CH <sub>2</sub> CH <sub>2</sub> ]               | [CH <sub>2</sub> OH]                             | 26.00                             | 1.027                     |
| [CH <sub>2</sub> OCH <sub>2</sub> ]              | [CH <sub>2</sub> OSO <sub>3</sub> <sup>-</sup> ] | 15.50                             | 1.175                     |
| [CH <sub>2</sub> OCH <sub>2</sub> ]              | [Na]   | 24.00                             | 1.058                     |
| [CH <sub>2</sub> OCH <sub>2</sub> ]              | [CH <sub>3</sub> CH <sub>2</sub> ]               | 28.50                             | 1.107                     |
| [CH <sub>2</sub> OCH <sub>2</sub> ]              | [CH <sub>2</sub> CONHCH <sub>2</sub> ]           | 15.73                             | 1.167                     |
| [CH <sub>2</sub> OCH <sub>2</sub> ]              | [CH <sub>2</sub> OH]                             | 25.00                             | 1.059                     |
| [CH <sub>2</sub> OSO <sub>3</sub> <sup>-</sup> ] | [Na]   | 17.90                             | 1.117                     |
| $[CH_2OSO_3^-]$                                  | [CH <sub>3</sub> CH <sub>2</sub> ]               | 28.50                             | 1.166                     |
| $[CH_2OSO_3^-]$                                  | [CH <sub>2</sub> CONHCH <sub>2</sub> ]           | 13.57                             | 1.226                     |
| $[CH_2OSO_3^-]$                                  | [CH <sub>2</sub> OH]                             | 21.70                             | 1.048                     |
| [Na]   | [CH <sub>3</sub> CH <sub>2</sub> ]               | 45.00                             | 1.049                     |
| [Na]   | [CH <sub>2</sub> CONHCH <sub>2</sub> ]           | 18.33                             | 1.109                     |
| [Na]   | [CH <sub>2</sub> OH]                             | 25.80                             | 0.990                     |
| [CH <sub>3</sub> CH <sub>2</sub> ]               | [CH <sub>2</sub> CONHCH <sub>2</sub> ]           | 32.00                             | 1.158                     |
| [CH <sub>3</sub> CH <sub>2</sub> ]               | [CH <sub>2</sub> OH]                             | 26.00                             | 1.038                     |
| [CH <sub>2</sub> CONHCH <sub>2</sub> ]           | [CH <sub>2</sub> OH]                             | 26.00                             | 1.099                     |

Table IV (continued): List of conservative repulsive parameter  $a_{ij}$  and cutoff radius  $r_{c,ij}$  for each pair of beads.

TABLE V. DPD parameter in common to every bead of the Miraspec UB75 blend.

| Parameter | Value (DPD units) |
|-----------|-------------------|
| γ         | 10.125            |
| σ         | 4.5               |

The bonded interactions between two consecutive beads are modeled using the harmonic potential in Eq. (11),

$$E_{\text{bond}} = \frac{1}{2} k_{\text{bond}} (r - r_0)^2, \qquad (11)$$

with  $k_{\text{bond}} = 150 \text{ (DPD units)}$  for all the bonds and an equilibrium distance calculated according to the following equation<sup>16</sup>:

$$r_0 = 0.1(n_i + n_j) - 0.01 , \qquad (12)$$

where  $n_i$  and  $n_j$  are the number of heavy atoms linearly bonded in the *i* and *j* bead respectively. According to this rule,  $n_i = 4$  for the sulfate bead, with two oxygen atoms that are considered "branched" from the linear chain. The model also includes an angle harmonic potential, that involves three beads interacting according to the formula:

$$E_{\text{angle}} = \frac{1}{2} k_{\text{angle}} (\theta - \theta_0)^2 , \qquad (13)$$

where  $\theta$  is the angle between two adjacent bonds,  $k_{angle} = 5$  (DPD units) and  $\theta_0 = 180^\circ$  for all the the interactions.

Within the model, it is particularly interesting the treatment of the charged beads, *i.e.* sodium ion and sulfate group. The standard DPD model allows overlapping of the beads, but in the case of  $r_{ij} = 0$  the Coulombic potential diverges, leading to the creation of artificial ionic pairs<sup>47,48</sup>. Previous works on analogous systems adopted a smeared charge approach to overcome this issue<sup>15–18</sup>. The same approach was kept in this work, using a Slater-type charge smearing formulated by González-Melchor *et al.*<sup>48</sup>:

$$E_{\rm el} = \frac{Cq_i q_j}{\varepsilon_r} \left( 1 - \left( 1 + \frac{r_{ij}}{\lambda} \exp\left(-2r_{ij}/\lambda\right) \right) \right) \quad r_{ij} \le r_{c,\rm el} , \qquad (14)$$

where, following the implementation of Anderson *et al.*<sup>16</sup>, the decay length is  $\lambda =$ 247 1/0.929 (DPD units) and  $r_{c,el} = 3$  (DPD units). The latter parameter,  $r_{c,el}$ , acts like a cutoff for 248 the treatment of the electrostatic forces. When  $r_{ij} \leq r_{c,el}$  the interaction between two beads is eval-249 uated through Eq. (14), while for  $r_{ij} > r_{c,el}$  the PPPM (particle-particle particle-mesh) solver, in its 250 LAMMPS implementation, is used to evaluate the electric field. The previous literature focused 251 on the study of solutions of SLES in water in micellar phases, a microstructure formed for low 252 concentrations of the surfactant. Consequently, in these previous studies, the value of the dielec-253 tric permittivity constant was set equal to the one of water,  $\varepsilon_r = 78.3$ . In the case of the Miraspec 254 UB75, the concentration of the SLES is substantially higher, hence the value  $\varepsilon_r = 25$  was used. 255 This latter value was chosen because it allowed to reproduce qualitatively the microstructures for 256 different compositions of the mixture of water and SLES, as reported in Section III A. 257

To simulate the CMEA molecules, a new CG representation was developed, as illustrated in Fig. 3.



FIG. 3. Coarse graining model developed for CMEA molecules. Changing the length of the alkyl tail results in the addition or the subtraction of [CH<sub>2</sub>CH<sub>2</sub>] beads.

The DPD interaction parameters for the beads constituting the CMEA are only in part already present in the literature, in the work of Wand *et al.*<sup>18</sup>; the rest were obtained using the same approach, the water/octanol partition method<sup>14</sup>, and they were kindly provided by Dr. Richard Anderson. These parameters are relative to the interactions of the [CH<sub>2</sub>OH] bead present in the CMEA molecule and are also listed in Table IV.

The set of conversion factors in Table VI was used for the UB75 blend and it comes from 265 matching one experimental value of viscosity. This approach was chosen due to the current im-266 possibility of matching all the properties of a fluid with a single set of conversion factors in DPD. 267 This becomes particularly true for transport properties and when performing non-equilibrium sim-268 ulations. In this case, a linear velocity profile must be obtained in a small box, so the stream 269 velocity must overcome the thermal velocity of the beads. Together with the nature of the DPD 270 forces, this leads to very high shear rates at the macroscale and may result in a shift of the rheol-271 ogy model. Hence, the identification of conversion factors focused on matching the properties of 272 interest, *i.e.* viscosity and shear rate, also intending to compensate for the described shift to higher 273 shear rates. From the available experiments, the viscosity at the lowest shear rate was matched 274 with the lowest meaningful value of the DPD shear rate. This corresponds to the lowest  $\dot{\gamma}_{\text{DPD}}$  that 275 still results in a linear velocity profile from the imposition of the LRBC. For what concerns the en-270 ergy conversion factor, it was obtained considering the temperature T = 298.15 K, the Boltzmann 278 constant  $k_{\rm B} = 1.38 \times 10^{-23} \,\text{J} \cdot \text{K}^{-1}$ ,  $T_{\rm DPD} = 1$ ,  $k_{\rm B} = 1$  with the application of Eq. (8). 279

The equilibration stage lasted  $1.2 \times 10^6$  timesteps, while the deformation of the non-equilibrium

TABLE VI. Set of conversion factors used for the Miraspec UB75 DPD model.

| $\mu_{cf}\left(\mathrm{Pa}\cdot\mathrm{s} ight)$ | $\dot{\gamma}_{\rm cf}({\rm s}^{-1})$ | $\mathscr{E}_{\mathrm{cf}}\left(\mathrm{J} ight)$ |
|--|---------------------------------------|---|
| 2.59   | 10                                    | $4.11 \times 10^{-21}$                            |

stage was set to 10<sup>6</sup> timesteps. The cumulative average of the DPD viscosity is computed, and its
value at the end of the simulation is extracted.

#### 283 D. Gaussian Process Regression

Although the information derived from Dissipative Particle Dynamic simulations is needed to 284 reproduce the behavior of the fluid at the macroscale, a tight coupling between DPD and CFD is 285 unfeasible. In such a coupling, the main hindrance would be the computational effort required to 286 run microscale simulations. For this reason, the development of a kriging strategy to provide an 287 unbiased rheological relationship is devised. A similar approach was proposed by Zhao et al.<sup>37</sup>, 288 who used Gaussian Process Regression (GPR)<sup>49</sup> to link the viscosity values extracted from DPD 289 with the imposed local shear rate. GPR is a mathematical and statistical tool akin to machine 290 learning and to grasp the concept behind it, it is possible to think of a distribution over functions. 291 When there are no training data points, the *prior distribution* is usually a distribution of functions 292 whose mean is equal to zero and whose standard deviation is unitary. Indeed, for every value of the 293 independent variable x, the value of y is normally distributed around a mean, with an associated 294 standard deviation. Hence, it is important to stress that the GPR does not output a functional form 295 of the target function, and it is instead a statistical model that outputs the predicted y values for 296 any tested x in input. The shape of the functions sampled from this distribution derives from the 297 Kernel, which defines the properties, such as derivability, of the mentioned functions. In this work 298 a Radial Basis Function (RBF), or squared exponential, Kernel was used: 290

$$K(x_i, x_j) = \sigma_f^2 \exp\left(-\frac{d(x_i, x_j)^2}{2l^2}\right), \qquad (15)$$

where  $\sigma_f$  is the *signal variance*, a pre-factor related to how much the functions vary vertically,  $d(\cdot, \cdot)$  is the Euclidian distance between the two points  $x_i$  and  $x_j$ , and l is the *characteristic length* $scale^{49}$ . The latter parameter expresses how the functions can vary: a high value of l will output smoother functions, that do not show rapid variations. Often  $\sigma_f$  and l are referred to as *hyper-* *parameters* since they are free parameters, whose value can be varied and it is usually optimized
 through different techniques.



FIG. 4. Result of the GPR on an example function y = sin(x) with RBF kernel. Different steps are illustrated: a) prior distribution, b) posterior distribution obtained with six training data points. The functions in blue are samples from the distributions of functions.

The addition of training points  $(x_{\text{train}}, y_{\text{train}})$  to the training data set changes the distribution of functions, which results in the *posterior distribution*. The effect of adding training data points can be noticed by comparing Fig. 4.a and Fig. 4.b, whose plots illustrate the use of the GPR on a test function  $y = \sin(x)$ . Considering the distribution of functions of a GPR model, it is possible to take samples from this distribution, analogously to what can be done by sampling a distribution of numbers. However, in this case, the samples correspond to functions that respect the constraints imposed by the used kernel and the training data set. Starting from the prior distribution in Fig. 4.a, in which sample functions from the distribution are plotted in blue, the addition of training points forces said functions to pass through them, as in Fig. 4.b. The prediction values, plotted in black, are the result of the regression and they are generated by calculating the mean of the normally distributed functions.

<sup>317</sup> Due to the width of the shear rate intervals, the GPR for the simulated systems was performed <sup>318</sup> on the log-space, *i.e.* using the values of  $\log(\dot{\gamma})$  vs  $\log(\mu)$ , with an approach comparable to the <sup>319</sup> one of Zhao *et al.*<sup>37</sup>.

In this work, the Python module *scikit-learn*<sup>50</sup> was used to perform the GPR step, and in par-320 ticular to optimize the values of the hyperparameters  $\sigma_{f}$  and l. After the evaluation of the quality 321 of the regression, the training data set and the values of the hyperparameter are passed to a GPR 322 viscosity model implemented in the CFD code OpenFOAM. This viscosity model works as a func-323 tion: after reading the GPR hyperparameters, it requires the local value of the strain rate, which 324 is evaluated through the solution of the momentum balance equation, and it provides the viscosity 325 value as output for each cell of the computational domain. The implementation of the GPR in 326 OpenFOAM is written in C<sup>++</sup> and it is inspired by freely available implementations on Github<sup>51</sup>. 327

#### 328 E. The CFD model

The last step of the multiscale approach is the Computational Fluid Dynamics (CFD) simula-329 tion, which makes use of the GPR viscosity model derived from the DPD non-equilibrium sim-330 ulations. As previously mentioned, the CFD simulation can provide information about the fluid 331 dynamics of mixing devices<sup>36,52</sup>. In this work, this simulation is carried out in isothermal condi-332 tions, under laminar regimen, and the fluid is considered incompressible. In this attempt to apply 333 the multiscale approach to a complex fluid to test the feasibility, the concentration of the species 334 in the system was considered uniform. As a consequence, the viscosity of the fluid depends only 335 on the strain rate  $\dot{\gamma}$ , and the system is investigated at the steady state. 336

The CFD simulations were carried out using the software OpenFOAM (version 8)<sup>53</sup> and in particular the steady-state solver simpleFoam. The pressure-velocity coupling algorithm adopted is the SIMPLEC (consistent SIMPLE).

# 340 F. Multiscale coupling

A linking step between the techniques described in the previous sections was developed, to build a functional and automated multiscale approach. The coupling is based on an iterative flow scheme, implemented in Python, reported in Fig. 5, with an approach similar to the one described in Zhao *et al.* <sup>37</sup>.

The starting point, as in Fig. 5, is a CFD simulation that implements a Newtonian model. The 345 viscosity value for this Newtonian model can be obtained from an initial DPD simulation, per-346 formed with a low value of the shear rate  $\dot{\gamma}_{DPD}$ . With the completion of this first CFD simulation, 347 the loop indicated with the blue arrows in Fig. 5 is initiated. This will be called outer loop, and 348 it starts with the extraction of the interval of the strain rate values from the CFD simulation. The 349 strain rate interval is then passed to the GPR, which builds the model from the training data set, 350 *i.e.* the couples of points  $(\dot{\gamma}, \mu(\dot{\gamma}))$  obtained from the DPD simulations. Once the model is built, 351 it takes the strain rate values in input and outputs the corresponding viscosity values (predictions) 352 together with an associated standard deviation  $\sigma$ . This latter variable is then used to test the quality 353 of the model in the whole interval. If the  $\sigma$  associated with any viscosity prediction is higher than 354 a user-set limit  $\sigma_{\text{lim}}$ , the quality of the model is deemed not sufficient. In this case, the *inner loop*, 355 indicated with the orange arrows in Fig. 5, starts and a new DPD simulation is issued. The value of 356  $\dot{\gamma}_{\text{DPD}}$  to impose for this simulation is the one corresponding to the maximum value of  $\sigma$  obtained 357 in the tested interval. This iterative process is repeated until the regression is satisfactory, and a 358 new training data point is added for every cycle of the loop. This makes the algorithm automated, 359 since a certain number of DPD simulations are launched until the desired accuracy on the shape 360 of the constitutive relationship is met. When the exit condition for the *inner loop* is respected, the 361 GPR is implemented in OpenFOAM as a viscosity model, and a new CFD simulation is launched. 362 The updated strain rate interval, extracted from the last simulation, is compared with the one pre-363 viously fed to the GPR. If the new interval is wider than a tolerance set by the user, the GPR model 364 is tested on the updated interval and the *inner loop* may start again, depending on the values of  $\sigma$ . 365 The difference between the extremes of the shear rate intervals is calculated as a relative difference 366 according to the following equations: 367

$$\varepsilon_{\min, rel} = \frac{\dot{\gamma}_{\min}^{(n-1)} - \dot{\gamma}_{\min}^{(n)}}{\dot{\gamma}_{\min}^{(n-1)}},$$
 (16a)



FIG. 5. Flowscheme used in the multiscale coupled approach. The following symbols are used:  $\dot{\gamma}_{\text{DPD}}$  is the shear rate used for a DPD simulation,  $\mu_0$  is the viscosity obtained from the first DPD simulation, and used to perform the Newtonian CFD simulation,  $\dot{\gamma}^{(i)}$  identifies the i-th rate interval from CFD simulations,  $\sigma$  is the standard deviation associated with the regression,  $\sigma_{\text{lim}}$  is the user-set limit for said standard deviation,  $\varepsilon_{.,\text{rel}}$  is the relative difference between the extremes of two shear rate intervals as in Eq. (16), and  $\varepsilon_{\text{lim}}$  is the user-set limit for said relative differences.

368

$$\varepsilon_{\max, rel} = \frac{\dot{\gamma}_{\max}^{(n)} - \dot{\gamma}_{\max}^{(n-1)}}{\dot{\gamma}_{\max}^{(n-1)}},$$
 (16b)

where  $\varepsilon_{\max, rel}$  and  $\varepsilon_{\min, rel}$  must be smaller than a set limit value  $\varepsilon_{\lim}$  to exit the loop. It must be 369 stressed that the absolute value is not used in Eq. (16) because the convergence criterion should 370 discriminate between a wider and a narrower interval. The use of the absolute value will not lead 371 to convergence in case of a much narrower  $\dot{\gamma}^{(n)}$  interval, since it would not take into account the 372 sign of  $\varepsilon_{max,rel}$  and  $\varepsilon_{min,rel}$ . For this reason, the order of the terms at the numerator of Eq. (16) is 373 of paramount importance. Conversely, if the interval is not significantly wider or the quality of the 374 regression is sufficient, the process exits from the *outer loop*. At this point, the CFD simulation 375 that was performed last is considered to be the one that reproduces the studied system. 376

# 377 G. Sulzer SMX static mixer model

The application example selected in this work to test the multiscale coupling procedure is one 378 step of the production process of the Miraspec UB75, namely the post-mixing section of a blend 379 reported in Table I. This phase is carried in a static mixer, like the Sulzer SMX, that consists of a 380 tube filled with mixing elements. Depending on the kind of application, these internal elements 381 can have different shapes. In the studied equipment there are six identical mixing elements, each 382 one rotated by 90° axis with respect to the previous, having the z axis as the axis of rotation. Every 383 element is constituted by inclined bars, as it is possible to notice from Fig. 6. The inclination 384 of each bar, with respect to both the main flux direction and the adjacent bars, is responsible 385 for the mixing itself. The main flow gets broken down following smaller flow paths which are 386 subsequently recombined due to the peculiar geometry of the mixer internals. Still in Fig. 6 is also 387 displayed an initial empty region of the tube, used to obtain a developed flow at the beginning of 388 the mixing section. The details of the static mixer geometry are reported in Table VII. 389

The boundary conditions applied to the system are summarised in Table VIII, where the pressure outlet value was kept at zero. The mesh is completely tetrahedral and contains 5118292 cells, and it has been selected after a grid convergence study. Based on the typical densities of these blends,  $\rho = 1160 \text{ kg m}^{-3}$  was imposed for the CFD simulations.



FIG. 6. Geometry of the SMX Sulzer static mixer used in the simulations. The color scheme identifies different regions of the geometry: green for the inlet, red for the outlet, blue for the wall of the tube, and orange for the mixing elements. This color coding is adopted for clarity, but in the actual computational domain used for the simulations the tube (blue) and the internals (orange) are part of the same wall patch, as in Table VIII.

|                            |      | Symbol            | Value |
|----------------------------|------|-------------------|-------|
| Diameter                   | (mm) | D                 | 16    |
| Tube length                | (mm) | $L_{\mathrm{t}}$  | 160   |
| Internals length           | (mm) | $L_{ m i}$        | 122   |
| Number of elements         |      | Ne                | 6     |
| Number of bars per element |      | $N_{\mathrm{b}}$  | 4     |
| Initial free zone length   | (mm) | $L_{\mathrm{fz}}$ | 30    |

TABLE VII. Geometrical details of the computational domain.

# 394 III. RESULTS AND DISCUSSION

## A. Solvay's UB75 blend: testing the DPD model

<sup>396</sup> Before showing the results obtained by the multiscale approach, it is worth to discuss specif-<sup>397</sup> ically the DPD model and in particular the CG approach reliability. As previously mentioned, <sup>398</sup> among many available approaches to build a DPD model for a large molecule, in this work we <sup>399</sup> used the approach of Anderson *et al.*<sup>14</sup> to build the DPD model of the molecules in the Miraspec <sup>400</sup> UB75 blend<sup>14,16</sup>. The starting point is the Inter ESA-70, a mixture of Sodium Lauryl Ether Sulfate <sup>401</sup> (SLES) molecules with different lengths of the alkyl tail. The coarse-grained model of a SLES

|          | Wall          | Inlet  | Outlet        |
|----------|---------------|--|---------------|
|          |               | Fixed value                                  |               |
| Velocity | No slip       | $U_x, \ U_y=0$                               | Zero gradient |
|          |               | $U_z = 1.38 \times 10^{-2} \text{ m s}^{-1}$ |               |
| D        | 7             | 7 march 1 march                              | Fixed value   |
| Pressure | Zero gradient | Zero gradient                                | p = 0 Pa      |

TABLE VIII. Boundary conditions used for the CFD simulations with the SMX Sulzer.

molecule and the DPD parameters reported in Ref. 15 were tested. The DPD model assessment 402 is carried out through a qualitative comparison between simulation results and the experimental 403 phase diagram of a SLES/water mixture<sup>3</sup>. It is important to notice that the mixture reproduced 404 to test the parameters does not exactly represent the Inter ESA-70. More precisely, the SLES 405 molecules simulated in this step present a higher number of ethoxyl groups and a different length 406 of the alkyl chain<sup>3</sup>. Nonetheless, the ability to reproduce a water/SLES phase diagram can provide 407 a measure of the quality of the DPD model for these kinds of molecules. The lower side of the 408 ternary phase diagram in Ref. 3 represents a binary mixture of SLES and water, from which three 409 regions are identified to conduct the assessment. While for low SLES concentrations (0.00236 -410 28% w/w) a micellar phase is found, intermediate SLES concentrations (31.5 - 56% w/w) lead 411 to the formation of the hexagonal phase and for high SLES concentrations (63 - 70% w/w) a 412 transition to lamellar phase occurs<sup>4</sup>. 413

One equilibrium DPD simulation in each of these regions is performed, and the resulting microstructure is qualitatively analyzed. The three DPD simulations performed are summed up in Table IX, and they resulted in agreement with the phase diagram, as it is possible to see in Fig. 7.

TABLE IX. Values of SLES mass fraction used in the DPD simulation and corresponding expected microstructure according to Refs. 3 and 4.

| Expected structure | Simulated SLES mass fraction |
|--------------------|------------------------------|
| Micellar           | 0.03                         |
| Hexagonal          | 0.45                         |
| Lamellar           | 0.67                         |

In particular, to obtain a qualitative confirmation of the hexagonal structure, it was necessary to conduct a non-equilibrium simulation with an imposed shear rate  $\dot{\gamma} = 0.1$  (DPD units) on the velocity component  $v_x$  along the *y* axis. This kind of behavior was already reported in the literature for a DPD model that simulates a mixture of water and a tri-block co-polymer<sup>7</sup>. When there is no shear applied the fluids form a network of worm-like micelles, as in Fig. 7.c. From Fig. 7.d it is clear how the application of a shear brings to the formation of rodlike micelles, typical of hexagonal structures.



FIG. 7. Resulting microstructures of the DPD simulation performed. SLES mass fraction equal to a) 0.03, b) 0.67, c) and d) 0.45. In c) there is no shear applied, the water and the sulfate groups beads are not shown to highlight the network formed by the wormlike micelles, while in d) the system is shown after the application of a shear of  $\dot{\gamma} = 0.1$  (DPD units) along the *y* axis to the velocity component  $v_x$ . To allow the micelles visualization, the water beads are not shown in a). To facilitate the visualization of the rodlike micelles in d) the box is sliced at 3/4 of its length in the *x* direction. The color coding of the beads is shown in Fig. 2.

Having assessed the qualitative capability of the model to predict the microstructure selfassembly for the binary system made of SLES and water, the addition of the third component was tested. The CME/A2 component is Cocamide Monoethanolamine (CMEA), whose coarsegrained model was developed and as described in Section II C with parameters for the DPD forces retrieved from the literature<sup>14–16</sup>. In Fig. 8 it is shown that, for the composition in Table I, it is <sup>429</sup> obtained a lamellar microstructure, which is indeed expected for the Miraspec UB75.



FIG. 8. Lamellar microstructure obtained from a simulation of the blend Miraspec UB75 with composition reported in Table I. The color coding of the beads is shown in Fig. 2 and Fig. 3.

#### 430 B. Miraspec UB75 blend: pressure drops in Sulzer SMX

#### 431 1. Multiscale approach and GPR

Once the performance of the DPD model for Miraspec UB75, described in detail in Section II C, 432 was assessed, it was then used to simulate a more realistic macroscopic application. The produc-433 tion of this blend requires the usage of a static mixer, in which the components are mixed in 434 multiple steps at various temperatures. The multiscale approach is here applied to a simplified 435 version of the production process, isothermal and with uniform composition. The latter is a strong 436 assumption, equal to having the blend already mixed at the entrance of the equipment. Besides 437 the general performances of the multiscale approach, the macroscopic variable of interest is the 438 pressure drop across the mixer. 439

Table X summarize the CFD simulations performed, using an incremental Roman number every time that an updated GPR model is used. As it is possible to see from this table, three CFD simulations were issued before the whole approach could reach convergence. The criterion here described refers to what, in the multiscale approach, is called *outer loop*, as expressed in Section II F. To evaluate the convergence of the iterative process, the strain rate interval extracted from a CFD simulation was compared with the one extracted from the previous simulation. The

TABLE X. Maximum and minimum value of the strain rate  $\dot{\gamma}$  inside the CFD domain with the different viscosity models. The variable  $\varepsilon$  is the difference, calculated as relative difference, between the values of one CFD run and the previous.

| CFD run   | $\dot{\gamma}_{min}\times 10^{-2}(s^{-1})$ | $\mathcal{E}_{\min, rel}$ | $\dot{\gamma}_{ m max}\left( {{ m s}^{-1}}  ight)$ | $\epsilon_{ m max, rel}$ |
|-----------|--|---------------------------|--|--------------------------|
| Newtonian | 3.606                                      |                           | 324.98   |                          |
| GPR I     | 2.513                                      | 0.303                     | 432.30   | 0.330                    |
| GPR II    | 2.488                                      | 0.010                     | 361.05   | -0.165                   |

convergence criterion is set on the maximum  $(\dot{\gamma}_{max})$  and on the minimum  $(\dot{\gamma}_{min})$  values of the strain rate intervals, as follows:

$$\varepsilon_{\min, rel} = \frac{\dot{\gamma}_{\min}^{(n-1)} - \dot{\gamma}_{\min}^{(n)}}{\dot{\gamma}_{\min}^{(n-1)}} \le 0.01 , \qquad (17a)$$

448

$$\varepsilon_{\max, rel} = \frac{\dot{\gamma}_{\max}^{(n)} - \dot{\gamma}_{\max}^{(n-1)}}{\dot{\gamma}_{\max}^{(n-1)}} \le 0.01 , \qquad (17b)$$

where the superscript (n) refers to the latest CFD simulation and the superscript (n - 1) refers to the previous CFD simulation. If the strain rate interval of the last CFD simulation is wider than 1% with respect to the one from the previous simulation, the GPR should test the training data on the newly extracted interval. One should notice that the condition is tested separately for the upper limit and the lower limit, and both need to be satisfied for convergence.

Fig. 9 shows the regression process applied to the first shear rate interval, which is extracted from the CFD simulation with the Newtonian viscosity model. Besides the rheograms, Fig. 9 depicts also information about the quality of the regression for the GPR loop, called *inner loop* in the multiscale approach (Section II F). As it is possible to see from Fig. 9.a2 and Fig. 9.b2, to reach the convergence of the GPR, the following equation must be satisfied in the whole strain rate interval:

$$\sigma \le \sigma_{\rm lim} = 10^{-2} \tag{18}$$

with  $\sigma_{\text{lim}}$  corresponding to the dotted orange line in the plots. Fig. 9.a1 and Fig. 9.a2 report the results of an incomplete GPR viscosity model, obtained with a partial training data set of two  $(\dot{\gamma}, \mu(\dot{\gamma}))$  couple of points. Fig. 9.b1 and Fig. 9.b2, instead, illustrate the viscosity model GPR I (Table X), obtained after the convergence of the GPR on the interval extracted from the Newtonian CFD simulation. Comparing Fig. 9.a1 and Fig. 9.b1 it is possible to illustrate how the addition of



FIG. 9. Illustration of the regression process to build the viscosity model GPR I, using the shear rate interval extracted from the Newtonian CFD simulation. The different plots show: a1) rheogram of the incomplete GPR I model before convergence, a2) standard deviation associated to the regression of the incomplete GPR I model before convergence, b1) rheogram of the converged GPR I model, b2) standard deviation associated to regression of the converged GPR I model. The inset in b1) contains the magnification of a portion of the regression, to allow the visualization of the narrow 95% confidence interval.

the third data point to the data set substantially improves the regression. This is confirmed by the low values of  $\sigma$  shown in Fig. 9.b2, which correspond to a very narrow 95% confidence interval in Fig. 9.a2, as visible only in the magnified inset.



FIG. 10. Comparison between GPR I and GPR II viscosity model. The plots show: a1) rheogram of the converged GPR I model, a2) standard deviation associated to the regression of the converged GPR I model, b1) converged GPR II model, b2) standard deviation associated to the regression of the converged GPR II model. The 95% confidence intervals in a1) and b1) are slightly visible only close the the extremes of the curves, due to their narrowness. The dotted grey vertical lines highlight the different width between the intervals used for the regression in the two models.

The GPR I and GPR II viscosity models (Table X) are depicted in figure Fig. 10.a and Fig. 10.b respectively. As previously stated, the GPR I model is built on the shear rate interval extracted from the first CFD simulation, which employed a Newtonian viscosity model. The GPR II model

is instead built on the shear rate interval extracted from the second CFD simulation, which imple-471 mented the GPR I model. Moreover, the training data set used is the same for the two viscosity 472 models, indicating that no additional DPD simulations were necessary to reach the convergence 473 of the regression step. Consequently, the two viscosity models are very similar and the only 474 difference resides in the shear rate interval. Indeed, the GPR II is built on a wider interval, as 475 emphasized by the dotted vertical grey lines in Fig. 10. The 95% confidence intervals in Fig. 10.a1 476 and Fig. 10.b1 are very narrow and slightly visible only close to the extremes of the intervals. 477 Hence,  $\sigma$  reaches its maxima in correspondence to the interval extremes in both Fig. 10.a2 and 478 Fig. 10.b2, since the GPR technique performs worse in extrapolating than in interpolating. A third 479 GPR viscosity model was not built since, as reported in Table X, the difference between the last 480  $\dot{\gamma}$  interval and the previous one respected the convergence criteria in Eq. (17). The difference 481 between the limits of the strain rate intervals is also noticeable in Fig. 11, where the cumulative 482 distribution functions of  $\dot{\gamma}$  are plotted. The same figure also shows that the  $\dot{\gamma}$  distributions for the 483 two GPR models are basically superimposed, and the differences with the Newtonian one are not 484 so relevant. The reason for such small differences is probably due to the viscosity value v used for 485 the Newtonian simulation. The initial guess for the value of v resulted to be intermediate when 486 compared with the extreme values of the final viscosity interval (Fig. 14.a). This could explain 487 both the slight shift to higher  $\dot{\gamma}$  values of the Newtonian distribution and the different shape for 488 intermediate values of strain rate. 489

A total of three DPD simulations were necessary during the whole process, to have the Eq. (18) respected, as illustrated by the series labeled as "Training data" in Fig. 9 and Fig. 10. The final viscosity model obtained with the multiscale approach is of a shear-thinning fluid. This is consistent with the experimental measures available, that usually lead to a power-law viscosity model for simulation purposes.

#### 495 2. CFD simulations

The results of the CFD simulations are analyzed qualitatively through contour plots on the slice shown in Fig. 12. In this figure, it is reported the Slice  $\mathscr{A}$ , that cuts the domain with the plane x = 0 m from the inlet section to the outlet one. In Fig. 13 the just described slice is used to compare the strain rate  $\dot{\gamma}$  inside the domain from different simulations. In these contour plots, it is shown that the strain rate trend in the domain is similar regardless of the viscosity model used.



FIG. 11. Volume cumulative distribution function for the shear rate values in the different CFD simulations. The "[" and "]" markers correspond to the  $\dot{\gamma}_{min}$  and  $\dot{\gamma}_{max}$  respectively, for every interval.



FIG. 12. Visual representation of the slice  $\mathscr{A}$  used for contour plots. This cuts the CFD domain with the plane x = 0 m. All the lengths in the figure are expressed in meters.

The strain rate values are higher close to the walls of the tube and close to the mixing elements, while regions of low strain rates are found mostly at the inlet and outlet. Hence, the contour for the  $\dot{\gamma}$  is in a qualitative agreement with the theory since a steeper variation of the velocity of the fluid is expected in correspondence with the walls. The only visible differences in the contour plots are confined to the inlet region in the simulation with the Newtonian model. This is due to the viscosity value of the fluid in that region, lower than the one in the non-Newtonian simulations, which consequently influences the distribution of  $\dot{\gamma}$ 



FIG. 13. Contour plot for the strain rate  $\dot{\gamma}$  in correspondence of the slice  $\mathscr{A}$ . The values are plotted using a logarithmic scale for the colorbar. Different CFD runs are shown: a) Newtonian model, b) GPR I viscosity model, c) GPR II viscosity model.

In general, contour plots with similar trends were already obtained as a result of simulations of different blends with this computational domain. Fig. 14 illustrates the contour plot for viscosity in the same plane. Since the Newtonian model was employed, Fig. 14.a reports a constant value, and the viscosity corresponds to an intermediate value when compared to the whole interval of  $\mu$ 



FIG. 14. Contour plot for the viscosity  $\mu$  in correspondence of the slice  $\mathscr{A}$ . The values are plotted using a logarithmic scale for the colorbar. Different CFD runs are shown: a) Newtonian model, b) GPR I viscosity model, c) GPR II viscosity model.

explored by the GPR models. As already noticeable from the rheogram in Fig. 10, the model of a
shear-thinning fluid resulted from the DPD simulations. This shear-thinning behavior is visible in
Fig. 14.b, where the viscosity is lower in correspondence with the high strain rate regions of the
mixing elements (Fig. 13.b).

<sup>516</sup> When compared with the viscosity of the GPR model, the value of  $\mu$  for the Newtonian sim-<sup>517</sup> ulation resulted lower in the inlet and outlet regions, but higher in the mixing section. Since the <sup>518</sup> latter brings a substantially higher contribution to the pressure drop, the Newtonian model pre-<sup>519</sup> sented a value of  $\Delta p$  higher by one order of magnitude than the GPR models, as in Table XI. <sup>520</sup> The difference between GPR I and GPR II can be ascribed to the different  $\dot{\gamma}$  explored: the GPR

| CFD run   | $\Delta p$ (Pa)      |
|-----------|----------------------|
| Newtonian | $2.90 	imes 10^5$    |
| GPR I     | $2.41 \times 10^{4}$ |
| GPR II    | $2.50 	imes 10^4$    |

TABLE XI. Pressure drop across the static mixer system for the different CFD simulations.

I simulation reached higher values of strain rate (Table X), resulting in a lower viscosity in the 521 mixing section and slightly lower  $\Delta p$ . As the final result, the pressure drop obtained from the 522 last CFD simulation was  $\Delta p = 2.50 \times 10^4$  Pa. Though it is not possible to carry a validation of 523 this result, its order of magnitude can be considered reasonable given the investigations done by 524 Solvay in static mixers. In particular, a comparison can be done with a mixture at 65% of SLES in 525 water, flowing in an SMX static mixer with a smaller diameter of  $4.95 \times 10^{-3}$  m. This system has 526 been studied through CFD simulations and with the correlations proposed by Liu, Hrymak, and 527 Wood<sup>34</sup>, using a power law to model its rheology. For a generalized Metzner – Reed Reynolds 528 number<sup>34,54</sup> of  $Re_{MR} = 6.54 \times 10^{-2}$  it was obtained  $\Delta p = 1.66 \times 10^4$  Pa · s from the CFD simu-529 lations, and  $\Delta p = 1.70 \times 10^4$  Pa · s using the correlation of Liu, Hrymak, and Wood <sup>34</sup>. By fitting 530 the experimental measures available on Miraspec UB75 (see Section III B 3 with a power law, 531 it was possible to calculate  $Re_{MR} = 6.38 \times 10^{-2}$  for the simulation of this work. The compar-532 isons between these results show an agreement on the order of magnitude, though they cannot be 533 considered as a validation process. 534

# 535 3. Viscosity model from DPD simulations

The application of a shear to a DPD fluid still presents some unsolved issues. In particular, 536 an unphysical shear-thickening behaviour was found even for Newtonian fluids in high shear rate 537 conditions<sup>22</sup>. Moreover, for very low shear rate values the thermal noise prevails on the streaming 538 velocity imposed by the box deformation. As a consequence, it becomes impossible to obtain a 539 linear velocity profile, *i. e.* a constant imposed shear rate, and apply Eq. (10). The use of DPD 540 simulations in large shear rate intervals should be tested, to avoid the occurrence of the described 541 computational artifacts. In this work, partial mitigation of these effects was obtained through 542 the use of a higher dissipative DPD constant  $\gamma$  combined with the SLLOD equation of motion. 543

Therefore, the results used to build the rheology model were obtained from simulations performed
in a safe DPD shear rate interval.

The viscosity results obtained from the DPD simulations were compared with the results of 546 two sets of experiments, previously performed at Solvay with the blend Miraspec UB75. The 547 measurements were carried out with the Brookfield DV-II+ viscometer, using the LV3 spindle at 548 25 °C. The results are shown in Fig. 15, where it is important to remember that the first DPD point 549 corresponds perfectly because this point was used to identify the conversion factor in Table VI. The 550 agreement between the simulations and the experiments is remarkably good, but more simulations 551 and experiments are needed to increase the robustness of the model. In particular, the effect of the 552 temperature and composition should be taken into account since they can have a great impact on 553 the value of viscosity of these kinds of mixtures. 554



FIG. 15. Comparison between the viscosity model obtained from experimental results and DPD simulations. The blue hollow circles represent the experiments performed at Solvay, and the red hollow stars are the results of the DPD simulations. The black dashed line is the power law resulting from the fitting of the experimental data, while the green dashed and dotted line is the power law resulting from the fitting of one thousand GPR predictions logarithmically spaced on the interval from GPR I in Table X.

<sup>555</sup> To further assess the quality of the viscosity model built on the DPD simulations, a power law, <sup>556</sup> as in Eq. (19), was used to fit both the experimental data and the prediction from the GPR.

$$\mu = m \cdot \dot{\gamma}^{n-1} \tag{19}$$

The power law is one of the most commonly used functions in rheology to approximate the be-557 haviour of shear-thinning fluids for intermediate shear rates. It must be reminded that the GPR 558 does not output a functional form, but a value of apparent viscosity for every value shear rate 559 value in input. Hence, to obtain a power law model for comparison, the GPR was performed to 560 produce one thousand of  $(\dot{\gamma}, \mu)$  couple of points in the final interval (GPR I in Table X). These 561 points are fitted with a power law and the comparison with the power law generated from the 562 experimental data is illustrated in Fig. 15, while the parameters of the power law are reported in 563 Table XII. As it is possible to see from Fig. 15 and Table XII, the two fitted functions are close to 564 each other, indicating that the GPR model provides a physically reasonable description. 565

TABLE XII. Parameters obtained from the fitting process of the experimental and GPR data using the power law in Eq. (19).

| Data set     | $m, (\operatorname{Pa} \cdot \operatorname{s}^n)$ | n-1                             |
|--------------|---|---------------------------------|
| Experimental | $8.11 \pm 3.0 \times 10^{-1}$                     | $-0.432\pm2.0\times10^{-2}$     |
| GPR          | $8.81 \pm 3.0 	imes 10^{-3}$                      | $-0.383 \pm 1.4 \times 10^{-4}$ |

#### 566 4. Multiscale approach computational performance

The idea behind the approach described in this work is the automatic selection of which DPD 567 simulation to perform. This should lead to a reduction of the computational resources needed, 568 through the minimization of the number of DPD simulations. The simulations were performed 569 on a workstation with a CPU "Intel<sup>®</sup> Xeon<sup>®</sup> Gold 6248 CPU @ 3.00GHz" using 24 cores. The 570 time requested by each simulation is reported in Table XIII. Here the CFD simulations are identi-571 fied through the viscosity model used to perform them, while the DPD simulations are numbered 572 following the order of execution. It is possible to discriminate between these DPD simulations 573 through the applied shear rate, as reported in Table XIV. In Table XIII is, instead, evident that the 574 DPD simulations are the bottleneck of the automated approach, requesting from six to ten times 575 the time of a CFD simulation. 576

For what concerns the variability of the time needed to complete a simulation, it looks that a simulation with the GPR model can take up to four times more time than a Newtonian one. Actually, the Newtonian simulation stopped after 588 iterations, while the GPR model continued until

|                 | Simulation    | Computational time (h:m) |  |
|-----------------|---------------|--------------------------|--|
|                 | CFD Newtonian | 0:14                     |  |
|                 | DPD 1°        | 6:08                     |  |
| 1° GPR–DPD loop | DPD 2°        | 11:24                    |  |
|                 | DPD 3°        | 8:02                     |  |
|                 | CFD GPR I     | 1:09                     |  |
|                 | CFD GPR II    | 1:10                     |  |

TABLE XIII. List of simulations in the order in which they were performed, with the corresponding computational time. The performed *inner loops* are also indicated.

<sup>580</sup> 2000 iterations. This can be the sign of too strict convergence criteria for the CFD simulation, <sup>581</sup> which can be affected not only by the viscosity model but also by the quality of the mesh. Conse-<sup>582</sup> quently, a different mesh or a better choice of the convergence parameter could lead to a reduction <sup>583</sup> of the computational time.

TABLE XIV. List of DPD simulations with the corresponding time to completion and the imposed shear rate  $\dot{\gamma}$ . The simulations are ordered with increasing  $\dot{\gamma}$ , to highlight the dependence of the requested time on the imposed shear rate.

| Simulation | $\dot{\gamma}(\text{DPD units})$ | Computational time (h:m) |
|------------|----------------------------------|--------------------------|
| DPD 1°     | 0.01                             | 6:08                     |
| DPD 3°     | 0.317                            | 8:02                     |
| DPD 2°     | 10                               | 11:24                    |

<sup>584</sup> Conversely, for the DPD simulation, there is a strong dependence of the computational time <sup>585</sup> on the value of  $\dot{\gamma}$ . Higher values of the shear rate imposed on the simulation box lead to longer <sup>586</sup> computational times to complete the simulation, according to Table XIII.

<sup>587</sup> Using an automated approach for choosing the best shear rate value to add a point to the training <sup>588</sup> data set led to satisfactory results in terms of computational time. Nonetheless, it must be noted <sup>589</sup> that the rheogram resulted simple enough to obtain a good quality regression with only three <sup>590</sup> training points. Consequently, to assess the computational advantages of this approach with more <sup>591</sup> accuracy, it should be tested on a more complex rheology model, *e.g.* including the effect of <sup>592</sup> composition. Instead, for what concerns the CFD and DPD techniques, the computational time
 <sup>593</sup> depends strongly on the models implemented in these kinds of simulations, so it is not possible to
 <sup>594</sup> make a generalization.

# 595 IV. CONCLUSIONS

The main purpose of the work was to develop a multiscale automated approach that could allow 596 the simulation of fluids in a typical mixing piece of equipment. The macroscale Computational 597 Fluid Dynamics (CFD) simulations are used to get information on macroscopic variables, such 598 as the pressure drops across a static mixer. The mesoscale Dissipative Particle Dynamics (DPD) 599 simulations are instead used to build a rheology model for the non-Newtonian fluid of interest. 600 In order to reduce the computational resources needed for the simulations, the Gaussian Process 601 Regression (GPR) was used to build the rheological model from the DPD non-equilibrium simu-602 lations. 603

The fluid of interest, the blend Miraspec UB75, was modelled using a parametrization devel-604 oped for similar surfactants. Using this parametrization, a part of the phase diagram of a mixture 605 of SLES and water was successfully reproduced from a qualitative point of view. This confirmed 606 the capabilities of the DPD technique to obtain qualitative information about the microstructure 607 of the simulated fluids. Non-equilibrium simulations were used to reproduce the rheological be-608 haviour of the fluid under the application of shear stress. The application of the shear condition on 609 the simulation box showed some limitations of the DPD method, regarding the explorable shear 610 rates. It was noticed that for too high or too low values of  $\dot{\gamma}$ , the results of the non-equilibrium 611 simulations are less reliable. This is common to all atomistic methods, but it would be beneficial 612 to study how to mitigate the effects of extreme strain rate conditions on the quality of the pre-613 dictions. Despite this issue, it was possible to reproduce the rheological behaviour of the studied 614 fluid. The obtained  $\Delta p$  were realistic when compared to the behavior of similar blends in the same 615 mixing devices. Moreover, the value of viscosity obtained with the DPD simulation resulted in 616 remarkably good agreement with two sets of experiments conducted at different shear rates. This 617 is noteworthy in light of the approach used for the identification of the conversion factors, which 618 is often a weak point in non-equilibrium DPD simulations. Indeed, deriving the conversion factor 619 by matching the value of viscosity for the lowest applicable shear rate led to promising results. 620

To conclude, this work shows the feasibility of an automated multiscale approach to describe a

real system that is relatively simple in terms of chemical composition, but further studies should be conducted to explore the limits of the DPD technique. Among these, the more critical are the parametrization of the molecules and the description of local charges, the width of the explorable shear rate interval in non-equilibrium simulations, and the possibility of simulation for non-isothermal systems. Furthermore, an experimental campaign could allow a more robust validation of the developed model.

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