

# Perspective: Dissipative particle dynamics F

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## Perspective: Dissipative particle dynamics

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Dissipative particle dynamics (DPD) belongs to a class of models and computational algorithms developed to address mesoscale problems in complex fluids and soft matter in general. It is based on the notion of particles that represent coarse-grained portions of the system under study and allow, therefore, reaching time and length scales that would be otherwise unreachable from microscopic simulations. The method has been conceptually refined since its introduction almost twenty five years ago. This perspective surveys the major conceptual improvements in the original DPD model, along with its microscopic foundation, and discusses outstanding challenges in the field. We summarize some recent advances and suggest avenues for future developments. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4979514>]

### I. INTRODUCTION

The behaviour of complex fluids and soft matter in general is characterized by the presence of a large range of different time and space scales. Any attempt to resolve *simultaneously* several time scales in a *single* simulation scheme is confronted by the problem of taking a prohibitively large number of sufficiently small time steps. Typically one proceeds hierarchically,<sup>1</sup> by devising models and algorithms appropriate to the length and time scales one is interested in. Leaving aside quantum effects negligible for soft matter, at the bottom of the hierarchy we have Hamilton's equations, with accurate albeit approximate potential energy functions, which are solved numerically with molecular dynamics (MD). Nowadays some research teams can simulate billions of particles for hundreds of nanoseconds.<sup>2</sup> This opens up the possibility to study very detailed, highly realistic molecular models that capture essentially all the microscopic details of the system. This is, of course, not enough in many situations encountered in soft matter and life sciences.<sup>3</sup> One can always think of a problem well beyond computational capabilities: from the folding of large proteins, to the replication of DNA, or the simulation of a eukaryotic cell, or the simulation of a mammal, including its brain. While we are still very far from even well-posing some of these problems, it is obvious that science is pushing strongly towards more and more complex systems.

Instead of using atoms moving with Hamilton's equations to describe matter, one can take a continuum approach in which fields take the role of the basic variables. Navier-Stokes-Fourier hydrodynamics, elasticity, and many of the different continuum theories for complex fluid systems are examples of this approach.<sup>4</sup> These continuum theories are, in fact, coarse-grained versions of the atomic system that rely on two key related concepts: (1) the continuum limit, i.e., a "point" of space on which the field is defined is, in fact, a volume element containing a large number of atoms<sup>5</sup> and (2) the local

equilibrium assumption, i.e., these volumes are large enough to reproduce the thermodynamic behaviour of the whole system.<sup>6</sup> The quantities from one volume element to its neighbour are assumed to change little and this allows the powerful machinery of partial differential equations to describe mathematically the system at the largest scales, allowing even to find analytical solutions for many situations. Nevertheless, the continuum equations are usually non-linear and analytical solutions are not always possible. One resorts then to numerical methods to solve the equations. Computational fluid dynamics (CFD) has evolved into a sophisticated field in numerical analysis with a solid mathematical foundation.

The length scales that can be addressed by continuum theories range from microns to parsecs. Remarkably, the same equations (with the same thermodynamics and transport coefficients) can be used at very different scales. Many of the interesting phenomena that occur in complex fluids occur at the *mesoscale*. The mesoscale can be roughly defined as the spatio-temporal scales ranging from  $10-10^4$  nm and  $1-10^6$  ns. These scales require a number of atoms that make the simulation with MD readily unfeasible. On the other hand, it was shown in the early days of computer simulations by Alder and Wainwright<sup>7</sup> that hydrodynamics is valid at surprisingly small scales. Therefore, there is a chance to use continuum theory down to the mesoscale. However, at these short length scales the molecular discreteness of the fluid starts to manifest itself. For example, a colloidal particle of submicron size experiences Brownian motion which is negligible for macroscopic bodies like submarine ships. In order to address these small scales, one needs to equip field theories like hydrodynamics with fluctuating terms, as pioneered by Landau and Lifshitz.<sup>8</sup> The resulting equations of fluctuating hydrodynamics also receive the name of Landau-Lifshitz-Navier-Stokes (LLNS) equation. There is much effort in the physics/mathematical communities to formulate numerical algorithms with the standards of usual CFD for the solution of stochastic partial differential equations modeling complex fluids at mesoscales.<sup>9-17</sup>

While the use of fluctuating hydrodynamics may be appropriate at the mesoscale, there are many systems for which a continuum hydrodynamic description is not applicable (or it is simply unknown). Proteins, membranes, assembled objects, polymer systems, etc., may require inaccessible computational resources to be addressed with full microscopic detail but a continuum theory may not exist. In these mesoscale situations, the strategy to retain some chemical specificity is to use *coarse-grained* descriptions in which groups of atoms are treated as a unit.<sup>18</sup> While the details of how to do this are very system specific, and an area of intense active research (see reviews in Refs. 19–21), it is good to know that there is a well defined and sounded procedure for the construction of coarse-grained descriptions<sup>22,23</sup> that is known under the names of non-equilibrium statistical mechanics, Mori-Zwanzig theory, or the theory of coarse-graining.<sup>4,24–26</sup> Simulating everything, everywhere, with molecular detail can be not only very expensive but also unnecessary. In particular, water is very expensive to simulate and sometimes its effect is just to propagate hydrodynamics. Hence there is an impetus to develop at least coarse-grained *solvent* models but retain enough *solute* molecular detail to render chemical specificity.

At the end of the 20th century, the simulation of the mesoscale was attacked from a computational point of view with a physicist intuitive, quick and dirty, approach. Dissipative particle dynamics (DPD) was one of the products, among others,<sup>27–32</sup> of this approach. DPD is a point particle minimal model constructed to address the simulation of fluid and complex systems at the mesoscale, when hydrodynamics and thermal fluctuations play a role. The popularity of the model stems from its algorithmic simplicity and its enormous versatility. Just by varying at will the conservative forces between the dissipative particles, one can readily model complex fluids like polymers, colloids, amphiphiles and surfactants, membranes, vesicles, and phase separating fluids. Due to its simple formulation in terms of symmetry principles (Galilean, translational, and rotational invariances), it is a very useful tool to explore generic or universal features (scaling laws, for example) of systems that do not depend on molecular specificity but only on these general principles. However, detailed information highly relevant for industrial and technological processes requires the inclusion of chemical detail in order to go beyond qualitative descriptions.

DPD, as originally formulated, does not include this chemical specificity. This is not a drawback of DPD *per se*, as the model is regarded as a coarse-grained version of the system. Any coarse-graining process eliminates details from the description and keeps only the relevant ones associated with the length and time scales of the level of description under scrutiny. However, as it will be apparent, the original DPD model could be regarded as being too simplistic and one can formulate models that capture more accurate information of the system with comparable computational efficiency.

Since its initial introduction, the question “What do the dissipative particles represent?” has lingered in the literature, with intuitively appealing but certainly vague answers like “groups of atoms moving coherently.” In the present

perspective we aim at answering this question by reviewing the efforts that have been taken in this direction. We offer a necessarily brief overview of applications and discuss some open questions and unsolved problems, both of fundamental and applied nature. Since the initial formulation of the DPD model, a number of excellent reviews<sup>26,33–39</sup> and dedicated workshops<sup>40,41</sup> have kept the pace of the developments. We hope that the present perspective complements these reviews with a balanced view about the more recent advances in the field. We also provide a route map through the different DPD variant models and their underlying motivation. In this doing, we hope to highlight a unifying conceptual view for the DPD model and its connection with the microscopic and continuum levels of description.

This perspective is organized as follows. In Sec. II we consider the original DPD model with its virtues and limitations. In Sec. III we review models that have been formulated in order to avoid the limitations of the original DPD model. The smoothed dissipative particle dynamics (SDPD) model, which is the culmination of the previous models that link directly to the macroscopic level of description (Navier-Stokes), is considered in Sec. IV. The microscopic foundation of the DPD model is presented in Sec. V. Finally, we present some selected applications in Sec. VI and conclude in Sec. VII.

## II. THE ORIGINAL DPD MODEL

The original DPD model was introduced by Hoogerbrugge and Koelman<sup>42</sup> and was formulated by the present authors as a proper statistical mechanics model shortly after.<sup>43</sup> The DPD model consists of a set of point particles that move off-lattice interacting with each other with three types of forces: a conservative force deriving from a potential, a dissipative force that tries to reduce radial velocity differences between the particles, and a further stochastic force directed along the line joining the center of the particles. The last two forces can be termed as a “pair-wise Brownian dashpot” (Fig. 1) which, as opposed to ordinary Langevin or Brownian dynamics, is momentum conserving. The Brownian dashpot is a minimal model for representing viscous forces and thermal noise between the “groups of atoms” represented by the dissipative particles. Because of momentum conservation, the behaviour of the system is hydrodynamic at sufficiently large scales.<sup>44–46</sup>

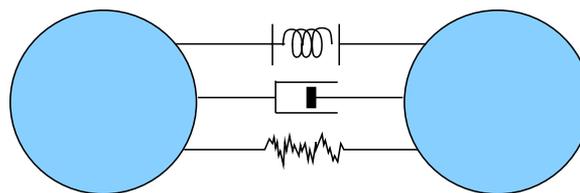


FIG. 1. Dissipative particles interact pair-wise with a conservative linear repulsive force, and a Brownian dashpot made of a friction force that reduces the relative velocity between the particles and a stochastic force that gives kicks of equal size and opposite directions to the particles. These forces vanish beyond a cutoff radius  $r_c$ .

The stochastic differential equations of motion for the dissipative particles are<sup>43</sup>

$$\begin{aligned} \dot{\mathbf{r}}_i &= \mathbf{v}_i, \\ m_i \dot{\mathbf{v}}_i &= -\frac{\partial V}{\partial \mathbf{r}_i} - \sum_j \gamma \omega^D(r_{ij})(\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})\mathbf{e}_{ij} \\ &\quad + \sum_j \sigma \omega^R(r_{ij}) \frac{dW_{ij}}{dt} \mathbf{e}_{ij}, \end{aligned} \quad (1)$$

where  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$  is the distance between particles  $i$  and  $j$ ,  $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$  is the relative velocity, and  $\mathbf{e}_{ij} = \mathbf{r}_{ij}/r_{ij}$  is the unit vector joining particles  $i$  and  $j$ .  $dW_{ij}$  is an independent increment of the Wiener process. In Eq. (1),  $\gamma$  is a friction coefficient and  $\omega^D(r_{ij}), \omega^R(r_{ij})$  are bell-shaped functions with a finite support that render the dissipative interactions local. Validity of the fluctuation-dissipation theorem requires<sup>43</sup>  $\sigma$  and  $\gamma$  to be linked by the relation  $\sigma^2 = 2\gamma k_B T$  and also  $\omega^D(r_{ij}) = [\omega^R(r_{ij})]^2$ . Here  $k_B$  is Boltzmann's constant and  $T$  is the system temperature. As a result, the stationary probability distribution of the DPD model is given by the Gibbs canonical ensemble

$$\rho(\{\mathbf{r}, \mathbf{v}\}) = \frac{1}{Z} \exp \left\{ -\beta \sum_i^N m_i \frac{\mathbf{v}_i^2}{2} - \beta V(\{\mathbf{r}\}) \right\}. \quad (2)$$

The potential energy  $V(\{\mathbf{r}\})$  is a suitable function of the positions of the dissipative particles that is translationally and rotationally invariant in order to ensure linear and angular momentum conservation. In the original formulation, the form of the potential function was taken as the simplest possible form

$$V(\{\mathbf{r}\}) = \frac{1}{2} \sum_{ij} a_{ij} (1 - r_{ij}/r_c)^2, \quad (3)$$

where  $a_{ij}$  is a particle interaction constant and  $r_c$  is a cut-off radius. This potential produces a linear force with the form of a Mexican hat function of finite range. Without any other guidance, the weight function  $\omega^R(r)$  in the dissipative and random forces is given by the same linear functional form. Complex fluids can be modeled through mesostructures constructed by adding additional interactions (springs and/or attractive or repulsive potentials between certain particles) to the particles.<sup>47</sup>

The soft nature of the weight functions in DPD allows for large time steps, as compared with MD that needs to deal with steep repulsive potentials. However, too large time steps lead to numerical errors that depend strongly on the numerical algorithm used. The area of numerical integrators for the stochastic differential equations of DPD has received attention during the years with increasingly sophisticated methods. Starting from the velocity Verlet implementation of Ref. 47 and the self-consistent reversible scheme of Pagonabarraga *et al.*,<sup>48</sup> the field has evolved towards splitting schemes.<sup>49–54</sup> Shardlow's scheme<sup>49</sup> has been recommended after comparison between different integrators,<sup>50</sup> but there are also other recent more efficient proposals.<sup>55–58</sup>

Because of momentum conservation, the original DPD model in Eqs. (1)–(3) can be regarded as a (toy) model for the simulation of fluctuating hydrodynamics of a simple fluid. As a model for a Newtonian fluid at mesoscales,

the DPD model has been used for the simulation of hydrodynamics flows in several situations.<sup>59–65</sup> It should be obvious, though, that the fact that DPD conserves momentum does not make it the preferred method for solving hydrodynamics. MD is also momentum conserving and can be used to solve hydrodynamics as well; for a recent review see the work of Kadau *et al.*<sup>66</sup> However, in terms of computational efficiency hydrodynamic problems are best addressed with CFD methods with, perhaps, inclusion of thermal fluctuations.

In addition, the original DPD model suffers from several limitations that downgrade its utility as a LLNS solver. The first one is the thermodynamic behaviour of the model. Taken as a particle method, the DPD model has an equation of state that is fixed by the conservative interactions. The linear conservative forces of the original DPD model produce an unrealistic equation of state that is quadratic in the density.<sup>47</sup> The quadratic equation of state in DPD seems to be a general property of soft sphere fluids at high overlap density. A well-known exemplar is the Gaussian core model.<sup>67</sup> These systems have been termed as *mean-field* fluids and this includes the linear DPD potential in Eq. (3). Many thermodynamic properties for the linear DPD potential can be obtained by using standard liquid state theory and it has been our experience that the hypernetted chain (HNC) integral equation closure works exceptionally well in describing the behaviour of DPD in the density regime of interest.<sup>68–70</sup> Note that while it is possible to fit the compressibility (related to second derivatives of the free energy) to that of water, for example, the pressure (related to first derivatives) turns out to be unrealistic. The conservative forces of the original model are not flexible enough to specify the thermodynamic behaviour as an input of the simulation code.<sup>71</sup>

A second limitation is due to too simplistic friction forces. The central friction force in Eq. (1) implies that when a dissipative particle passes a second, reference particle, it will not exert any force on the reference particle unless there is a radial component to the velocity.<sup>72,73</sup> Nevertheless, on simple physical grounds one would expect that the passing dissipative particle would drag in some way the reference particle due to shear forces. Of course, if many DPD particles are involved simultaneously in between the two particles, this will result in an effective drag. The same is true for a purely conservative molecular dynamics simulation. It would be nice, though, to have this effect captured directly in terms of modified friction forces in a way that a smaller number of particles need to be used to reproduce large scale hydrodynamics. Note that the viscosity of the DPD model cannot be specified beforehand, and only after a recourse to the methods of kinetic theory can one estimate the friction coefficient to be imposed in order to obtain a given viscosity.<sup>44,45,74–76</sup> As we will see, inclusion of more sophisticated shear forces allows for a more direct connection with Navier-Stokes hydrodynamics.

A third limitation of DPD as a mesoscale hydrodynamic solver is the fact that the DPD model (in an identical manner as MD) is *hardwired to the scale*. What we mean with this is that given a physical problem, with a characteristic length scale, we may always put a given number of dissipative

particles and parametrize the model in order to recover some macroscopic information (typically, compressibilities and viscosity). However, if one uses a different number of particles for exactly the same physical situation, one should start over and reparametrize the system again. This is certainly very different from what one would expect from a Navier-Stokes solver, that specifies the equation of state and viscosity irrespective of the scale, and one simply worries about having a sufficiently large number of points to resolve the characteristic length scales of the flow. In other words, in DPD there is no notion of *resolution*, *grid refinement*, and *convergence* as in CFD. There have been attempts to restore a *scale free* property for DPD,<sup>73,77,78</sup> even for bonded interactions.<sup>79</sup> To get this property, the parameters in the model need to depend on the level of coarse-graining, but this is not specified in the original model. Closely related to this lack of scaling is the fact that there is no mechanism in the model to switch off thermal fluctuations depending on the scale at which the model is operating. On general statistical mechanics grounds, thermal fluctuations should scale as  $1/\sqrt{N}$ , where  $N$  is the number of degrees of freedom coarse-grained into one coarse-grained (CG) particle. As the dissipative particles represent larger and larger volume elements, they should display smaller and smaller fluctuations. But there is no explicit volume or size associated with a dissipative particle. This problem is crucial, for instance, in the case of suspended colloidal particles or in microfluidics applications where flow conditions and the physical dimensions of the suspended objects or physical dimensions of the operating device determine whether and, more importantly, *to what extent* thermal fluctuations come into play.

Finally, another limitation of the DPD model is that it cannot sustain temperature gradients. Energy in the system is dissipated and not conserved, and the Brownian dashpot forces of DPD act as a thermostat.

### III. MANY-BODY (OR MULTI-BODY) DISSIPATIVE PARTICLE DYNAMICS (MDPD), ENERGY-CONSERVING DISSIPATIVE PARTICLE DYNAMICS (EDPD), AND FLUID PARTICLE MODEL (FPM)

During the years, the DPD model has been *enriched* in several directions in order to deal with all the above limitations. In this section, we briefly review these enriched DPD models.

The many-body (or multi-body) dissipative particle dynamics (MDPD) method stands for a modification of the original DPD model in which the purely repulsive conservative forces of the classic DPD model are replaced by forces deriving from a many-body potential; thus the scheme is still covered by Eqs. (1) and (2), but a many-body  $V(\{\mathbf{r}\})$  is substituted for Eq. (3). The MDPD method was originally introduced by Pagonabarraga and Frenkel,<sup>80</sup> Warren,<sup>81</sup> and independently by Groot,<sup>82</sup> and subsequently modified and improved by Trofimov *et al.*,<sup>71</sup> reaching a level of maturity.<sup>38,78,83–87</sup> The key innovation of the MDPD is the introduction of a density variable  $d_i = \sum_{j \neq i} W(r_{ij})$ , as well as a free energy  $\psi(d_i)$  associated with each dissipative particle. Here  $W(r)$  is a normalized bell-shaped weight function that ensures that the density  $d_i$  is

high if many particles are accumulated near the  $i$ th particle. The potential of interaction of these particles is assumed to be of the form  $V = \sum_i \psi(d_i)$ .<sup>88</sup> This is a many-body potential of a form similar to the embedded atom potential in MD simulations.<sup>89,90</sup> For multi-component mixtures, the many-body potential may be generalized to depend on partial local densities.

Despite its many-body character, the resulting forces are still pair-wise, and implementation is straightforward. However, not all pair-wise force laws correspond to a many-body potential. Indeed the existence of such severely constrains the nature of the force laws, and some errors have propagated into the literature (see discussion in Ref. 86). In the Appendix we explore how the force law is constrained by the weight function  $W(r)$ . The message is that if in doubt, always work from  $V(\{\mathbf{r}\})$ .

MDPD escapes the straitjacket of mean-field fluid behaviour by modulating the thermodynamic behaviour of the system directly at the interaction level between the particles. This allows for more general equations of state than in the original DPD model, which is a special case where the one-body terms are linear in local densities. Indeed, one can easily engineer a van der Waals loop in the equation of state to accommodate vapor-liquid coexistence. But this in itself is not enough to stabilize a vapour-liquid interface, since one should additionally ensure that the cohesive contribution is longer-ranged than the repulsive contribution. This can be achieved, for example, by using different ranges for the attractive and repulsive forces<sup>81,83</sup> or modelling the square gradient term in the free energy.<sup>91</sup>

On another front, the energy-conserving dissipative particle dynamics (EDPD) model was introduced simultaneously and independently by Bonet Avalós and Español<sup>92,93</sup> as a way to extend the DPD model to non-isothermal situations. In this case, the key ingredient is an additional internal energy variable associated with the particles. The behaviour of the model was subsequently studied.<sup>94–97</sup> The method has been compared with standard flow simulations,<sup>98,99</sup> and recently a number of interesting applications have emerged,<sup>100,101</sup> including heat transfer in nanocomposites,<sup>102</sup> shock detonations,<sup>103</sup> phase change materials for energy storage,<sup>104</sup> shock loading of a phospholipid bilayer,<sup>105</sup> chemically reacting exothermic fluids,<sup>106,107</sup> thermoresponsive polymers,<sup>108</sup> and water solidification.<sup>109</sup>

Finally, the fluid particle model (FPM) was devised as a way to overcome the limitation of the simplistic friction forces in DPD.<sup>72,73</sup> The method introduced, in addition to radial friction forces, shear forces that depend not only on the approaching velocity but also on the velocity differences directly. Shear forces have been reconsidered recently.<sup>110</sup> The resulting forces are non-central and do not conserve angular momentum. In order to restore angular momentum conservation a spin variable is introduced. Heuristically, the spin variable is understood as the angular momentum relative to the center of mass of the fluid particle. The model has been used successfully by Pryamitsyn and Ganesan<sup>111</sup> in the simulation of colloidal suspensions, where each colloid is represented by just one larger dissipative particle, an approach also used by Pan *et al.*<sup>112</sup>

#### IV. DPD FROM TOP-DOWN: THE SDPD MODEL

While MDPD is still isothermal and EDPD still uses conservative forces too limited to reproduce arbitrary thermodynamics, the two enrichments of a density variable and an internal energy variable introduced by these models suggest a view of the dissipative particles as truly thermodynamic subsystems of the whole system, consistently with the local equilibrium assumption in continuum hydrodynamics. There have been a number of works trying to formalize this view of “moving fluid particles” in terms of Voronoi cells of points moving with the flow field.<sup>113</sup> Flekkøy *et al.* formulated a (semi) bottom-up approach for constructing a model of fluid particles with the Voronoi tessellation.<sup>114,115</sup> A thermodynamically consistent Lagrangian finite volume discretization of LLNS using the Voronoi tessellation was presented by Serrano and Español<sup>116</sup> and compared favourably<sup>117</sup> with the models in Refs. 114 and 115. While this top-down modeling based on the Voronoi tessellation is grounded in a solid theoretical framework, it has not found much application due, perhaps, to the computational complexity of a Lagrangian update of the Voronoi tessellation.<sup>118</sup>

In an attempt to simplify the Lagrangian finite Voronoi volume discretization model, the smoothed dissipative particle dynamics (SDPD) model was introduced shortly after,<sup>119</sup> based on a precursor.<sup>120</sup> SDPD is a thermodynamically consistent particle model based on a particular version of smoothed particle hydrodynamics (SPH) that includes thermal fluctuations. SPH is a mesh-free Lagrangian discretization of the Navier-Stokes equations (NSEs) differing from finite volumes, elements, or differences in that a simple smooth kernel is used for the discretization of space derivatives. This leads to a model of moving interacting point particles whose simulation is very similar to MD. SPH was introduced in an astrophysical context for the simulation of cosmic matter at large scales<sup>121,122</sup> but has been applied since then to viscous and thermal flows,<sup>123,124</sup> including multi-phasic flow.<sup>125</sup> An excellent recent critical review on SPH is given by Violeau and Rogers.<sup>126</sup>

In the particular SPH discretization given by SDPD of the viscous terms in the NSE, the resulting forces have the same structure of the shear friction forces in the FPM. By casting the model within the universal thermodynamically consistent GENERIC framework,<sup>4</sup> thermal fluctuations are introduced consistently in SDPD by respecting an exact fluctuation-dissipation theorem at the discrete level. Therefore, SDPD (as opposed to SPH) can address the mesoscopic realm where thermal fluctuations are important.

The SDPD model consists of  $N$  point particles characterized by their positions and velocities  $\mathbf{r}_i$ ,  $\mathbf{v}_i$  and, in addition, a thermal variable like the entropy  $S_i$  (by a simple change of variables, one can also use alternatively the internal energy  $\epsilon_i$  or the temperature  $T_i$ ). Each particle is understood as a thermodynamic system with a volume  $\mathcal{V}_i$  given by the inverse of the density  $d_i = \sum_i^N W(r_{ij})$ , a fixed constant mass  $m_i$ , and an internal energy  $\epsilon_i = E(S_i, m_i, \mathcal{V}_i)$  which is a function of the entropy of the particle, its mass (i.e., number of moles), and volume. The functional form of  $E(S, M, \mathcal{V})$  is assumed, through the local equilibrium assumption, to be the same function that gives the global thermodynamic behaviour of the fluid system

(but see below). The equations of motion of the independent variables are<sup>119</sup>

$$\begin{aligned} d\mathbf{r}_i &= \mathbf{v}_i dt, \\ md\mathbf{v}_i &= \sum_j \left[ \frac{P_i}{d_i^2} + \frac{P_j}{d_j^2} \right] F_{ij} \mathbf{r}_{ij} dt \\ &\quad - \frac{5\eta}{3} \sum_j \frac{F_{ij}}{d_i d_j} (\mathbf{v}_{ij} + \mathbf{e}_{ij} \mathbf{e}_{ij} \cdot \mathbf{v}_{ij}) dt + md\tilde{\mathbf{v}}_i, \\ T_i dS_i &= \frac{5\eta}{6} \sum_j \frac{F_{ij}}{d_i d_j} (\mathbf{v}_{ij}^2 + (\mathbf{e}_{ij} \cdot \mathbf{v}_{ij})^2) dt \\ &\quad - 2\kappa \sum_j \frac{F_{ij}}{d_i d_j} T_{ij} dt + T_i d\tilde{S}_i. \end{aligned} \quad (4)$$

Here,  $P_i$  and  $T_i$  are the pressure and temperature of the fluid particle  $i$ , which are functions of  $d_i$ ,  $S_i$  through the equilibrium equations of state, derived from  $E(S, M, \mathcal{V})$  through partial differentiation. Because the volume of a particle depends on the positions of the neighbours, the internal energy function plays the role of the potential energy  $V$  in the original DPD model. In addition,  $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$  and  $T_{ij} = T_i - T_j$ . The function  $F(r)$  is defined in terms of the weight function  $W(r)$  as  $\nabla W(r) = -\mathbf{r}F(r)$ . Finally,  $d\tilde{\mathbf{v}}_i, d\tilde{S}_i$  are linear combinations of independent Wiener processes whose amplitude is dictated by the exact fluctuation-dissipation theorem.<sup>127</sup>

It is easily shown that the above model conserves mass, linear momentum, and energy and that the total entropy is a non-decreasing function of time thus respecting the second law of thermodynamics. The equilibrium distribution function is given by the Einstein expression in the presence of dynamic invariants.<sup>128</sup> As the number of particles increases, the resulting flow converges towards the solution of the Navier-Stokes equations, by construction.

SDPD can be considered as the general version of the three models MDPD, EDPD, FPM, discussed in Sec. III, incorporating all their benefits and none of its limitations. For example, the pressure and any other thermodynamic information are introduced as an input, as in the MDPD model. The conservative forces of the original model become physically sounded pressure forces. Energy is conserved and we can study transport of energy in the system as in EDPD. The transport coefficients are the input of the model (though, see below). The range functions of DPD have now very specific forms, and one can use the large body of knowledge generated in the SPH community to improve on the more adequate shape for the weight function  $W(r)$ .<sup>124</sup> The particles have a physical size given by its physical volume and it is possible to specify the physical scale being simulated. One should understand the density number of particles as a way of controlling the *resolution* of the simulation, offering a systematic “grid” refinement strategy. In the SDPD model, the amplitude of thermal fluctuations scales with the size of the fluid particles: *large* fluid particles display smaller thermal fluctuations, in accordance with the usual notions of equilibrium statistical mechanics. While the fluctuations scale with the size of the fluid particles, the resultant stochastic forces on

*suspended* bodies are independent of the size of the fluid particles and only depend on the overall size of the object,<sup>129</sup> as it should.

The SDPD model does not conserve angular momentum because the friction forces are non-central. This may be remedied by including an extra spin variable as in the FPM as has been done by Müller *et al.*<sup>130</sup> This spin variable is expected to relax rapidly, more and more so as the size of the fluid particles decreases. For high enough resolution, the spin variable is slaved by vorticity. The authors of Ref. 130 have shown, though, that the inclusion of the spin variable may be crucial in some problems where ensuring angular momentum conservation is important.<sup>131</sup>

In summary, SDPD can be understood as MDPD for non-isothermal situations, including more realistic friction forces. The SDPD model has a similar simplicity as the original DPD model and its enriched versions MDPD, EDPD, FPM. It has been remarked<sup>132</sup> that SDPD does not suffer from some of the issues encountered in Eulerian methods for the solution of the LLNS equations. The SDPD model is applicable for the simulation of complex fluid simulations for which a *Newtonian solvent* exists. The number of studies using SDPD is now growing steadily and ranges from microfluidics,<sup>133</sup> nanofluidics,<sup>132</sup> colloidal suspensions,<sup>134,135</sup> blood,<sup>136,137</sup> tethered DNA,<sup>138</sup> and dilute polymeric solutions.<sup>55,139,140</sup> Also, it has been used for the simulation of fluid mixtures<sup>141–144</sup> and viscoelastic flows.<sup>145</sup>

Once SDPD is understood as a particle method for the numerical solution of the LLNS equations of fluctuating hydrodynamics, the issue of boundary conditions emerges. While there is an extensive literature in the formulation of boundary conditions in the deterministic SPH,<sup>123</sup> and in DPD,<sup>146–156</sup> the consideration of boundary conditions in SDPD has been addressed only recently.<sup>144,157,158</sup>

In SDPD, what you put is *almost* what you get. The input information is the internal energy of the fluid particle (as a function of density, entropy or temperature), and viscosity. However, only in the high resolution limit, for a large number of particles the convergence towards the continuum equations is ensured. Therefore, for a finite number of particles, there will be always differences between the input viscosity and the actual viscosity of the fluid and, possibly, between the input thermodynamic behaviour of the fluid particle and the bulk system. These differences could be attributed to numerical “artifacts” of the particle model, similar to discretisation errors that arise in CFD. Often the worst effects of these artifacts can be eliminated by using renormalized transport coefficients from calibration simulations. This is similar, for instance, to the way that discretisation errors in lattice Boltzmann are commandeered to represent physics, improving the numerical accuracy of the scheme.<sup>159</sup> In this context, the availability of a systematic grid refinement strategy for SDPD is clearly highly beneficial.

In summary, if one plans to use DPD for the simulation of a simple fluid system (like the solvent in a complex fluid), it seems natural to use SDPD instead, as the latter solves many of the inherent problems of the original DPD model and addresses *the same* time and space scales as those for which DPD was intended for. As we discuss in Sec. V, for the CG objects made

of bonded atoms, the original DPD model may still have its use.

## A. Internal variables

The SDPD model is obtained from the discretization of the continuum Navier-Stokes equations and allows us to simulate Newtonian fluids. Of course, any other continuum equations traditionally used for the description of complex fluids can also be discretized with the same methodology. In general, these continuum models for complex fluids typically involve *additional structural or internal variables*, usually representing mesostructures, that are coupled with the conventional hydrodynamic variables.<sup>4,160</sup> The coupling of hydrodynamics with these additional variables renders the behaviour of the fluid non-Newtonian and complex. For example, polymer melts are characterized by additional conformation tensors, colloidal suspensions can be described by further concentration fields, mixtures are characterized by several density fields (one for each chemical species), and emulsions may be described with the amount and orientation of the interface.

All these continuum models rely on the hypothesis of local equilibrium and, therefore, the fluid particles are regarded as thermodynamic subsystems. Once the continuum equations are discretized in terms of fluid particles (Lagrangian nodes) with associated additional structural or order parameter variables, the resulting fluid particles are “large” portions of the fluid. The scale of these fluid particles is *supra-molecular*. This allows one to study larger length and time scales than the less coarse-grained models where the mesostructures are represented explicitly through additional interactions between particles (i.e., chains for representing polymers, spherical solid particles to represent colloid, different types of particles to represent mixtures). The price, of course, is the need for a deep understanding of the physics at this more coarse-grained level, which should be adequately captured by the continuum equations.

For example, in order to describe polymer solutions, we may take a level of coarse graining in which every fluid particle contains already many polymer molecules. This is a more coarse-grained model than describing viscoelasticity by joining dissipative particles with springs.<sup>161</sup> The state of the polymer molecules within a fluid particle may be described either with the average end-to-end vector of the molecules<sup>162,163</sup> or with a conformation tensor.<sup>145</sup> In this latter case, the continuum limit of the model leads to the Oldroyd-B model of polymer rheology. Another example where the strategy of internal variables is successful is in the simulation of mixtures. Instead of modeling a mixture with two types of dissipative particles as it is usually done in DPD, one may take a thermodynamically consistent view in which each fluid particle contains the concentration of one of the species, for example.<sup>141,142,144,164</sup> Chemical reactions can be implemented by including as an internal degree of freedom an extent of reaction variable.<sup>106</sup>

## V. DPD FROM BOTTOM-UP

The SDPD model<sup>119</sup> and the Voronoi fluid particle model<sup>116</sup> are top-down models which are, essentially,

Lagrangian discretizations of fluctuating hydrodynamics. These models are the *bona fide* connection of the original DPD model with continuum hydrodynamics. However, the connection of the model with the microscopic level of description is less clear. Ideally, one would like to fulfill the program of coarse-graining, in which by starting from Hamilton's equations for the atoms in the system, one derives closed equations for a set of CG variables that represent the system in a fuzzy impressionistic way.

Coarse graining of a molecular system requires a clear definition of the *mapping* between the microscopic and CG degrees of freedom. This mapping is usually well defined when the atoms are bonded, as happens inside complex molecules like proteins and other polymer molecules or in solid systems. In this case, one can choose groups of atoms and look at, for example, the center of mass of each group as CG variables. For unbonded atoms as those occurring in a fluid system, the main problem is that grouping atoms in a system where the atoms may diffuse away from each other is a tricky issue. We discuss separately the strategies that have been followed in order to tackle the coarse-graining of both bonded and unbonded atoms.

### A. DPD for bonded atoms

When the atoms are bonded and belong to definite groups where the atoms do not diffuse away from each other, the CG mapping is well defined, usually through the center of mass variables. In Fig. 2 we show a star polymer melt in which each molecule is coarse-grained by its center of mass, leading to a blob or bead description.<sup>165</sup> The important question is: what are the CG interactions between the blobs. Two CG approaches, static and dynamic, have been pursued, depending on the questions one wishes to answer.

*Static CG* is concerned with approximations to the exact potential of mean force that gives, formally, the equilibrium distribution function of all the CG degrees of freedom. Radial

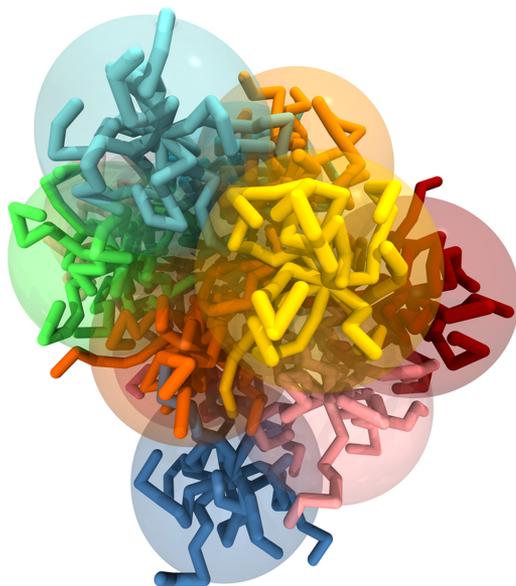


FIG. 2. Star polymer molecules (in different colors) in a melt are coarse-grained at the level of their centers of mass. The resulting model is a blob model of the DPD type.<sup>165</sup>

distributions, equations of state, etc., are the concerns of static coarse graining. There is a vast literature in the construction of the potential of mean force for CG representations of complex fluids<sup>18,166–168</sup> and complex molecules.<sup>19,21,169</sup> Despite these efforts, there is still much room for improvement in the thermodynamic consistency for the modeling of the potentials of mean force.<sup>170</sup> If one uses the CG potential for the motion of the CG degrees of freedom, the resulting dynamics is unrealistically fast, although this may be in some cases convenient computationally.

*Dynamic CG*, on the other hand, focuses on obtaining, in addition to CG potentials, approximations to the friction forces between CG degrees of freedom. Within the theoretical framework of the Mori-Zwanzig approach, it is possible to obtain in general the dynamics of the CG degrees of freedom from the underlying Hamiltonian dynamics. The first attempt to derive the DPD model from the underlying microscopic dynamics was given by Español for the simple case of a one-dimensional harmonic lattice.<sup>171</sup> The centers of mass of groups of atoms were taken as the CG variables and Mori's projection method was used. Because this system is analytically soluble, a flaw in the original derivation could be detected, and an interesting discussion emerged on the issue of non-Markovian effects in solid systems.<sup>172–176</sup>

By following Schweizer,<sup>177</sup> Kinjo and Hyodo<sup>178</sup> obtained a formal equation for the centers of mass of groups of atoms. The momentum equation contains three forces: a conservative force deriving from the exact potential of mean force, a friction force, and a random force. By *modeling* the random forces, the authors of Ref. 178 showed that this equation encompasses both the Brownian Dynamics (BD) and DPD equations. However, to consider the procedure in Ref. 178, a *derivation* of DPD, it is necessary to specify the conditions under which one obtains BD instead of DPD (or vice versa). This was not stated by Kinjo and Hyodo. The crucial insight is that BD appears when “solvent” is eliminated from the description, that is, some (the majority) of the atoms are not grouped and are instead described as a passive thermal bath (or implicit solvent). The friction force in this case is proportional to the velocity of the particles, and the momentum of the CG blobs is not conserved. On the other hand, a DPD description appears when *all* the atoms are partitioned into disjoint groups. In this case, the conservation of momentum induced by Newton's third law at the microscopic level leads to a structure of the friction forces depending on *relative* velocities of the particles. A derivation of the equations of DPD from first principles taking into account linear momentum conservation was presented by Hijón *et al.*<sup>165</sup> The position-dependent friction coefficient was given in terms of a Green-Kubo expression that could be evaluated, under certain simplifying assumptions, directly from MD simulations, within the same spirit of an early derivation of Brownian dynamics for a dimer representation (non-momentum conserving) of a polymer by Akkermans and Briels.<sup>179</sup> The general approach was preliminarily tested for a system of star polymers (as those in Fig. 2). A subsequent thorough study of this star polymer problem by Karniadakis and co-workers<sup>180</sup> has shown that the introduction of an intrinsic spin variable for each polymer molecule seems to be necessary at low concentrations in order to

have an accurate representation of the MD results. The approach in Ref. 165 has been labeled by Li *et al.*<sup>180</sup> as the MZ-DPD approach, standing for Mori-Zwanzig dissipative particle dynamics. Other complex molecules (neopentane, tetrachloromethane, cyclohexane, and n-hexane) have been also considered<sup>181</sup> within the MZ-DPD approach with interesting discussion on the validity of the non-Markovian behaviour (more on this later). A slightly more general approach for the derivation of MZ-DPD equations has been given by Izvekov.<sup>182</sup> Very recently, Español *et al.*<sup>183</sup> have formulated from first principles the dynamic equations for an *energy conserving* CG representation of complex molecules. This work gives the microscopic foundation of the EDPD model for complex molecules (involving bonded atoms only).

## B. DPD for unbonded atoms

The derivation of the equations of hydrodynamics from the underlying Hamiltonian dynamics of the atoms is a well studied problem that dates back to Boltzmann and the origins of kinetic theory.<sup>24,184</sup> It is a problem that still deserves attention for *discrete* versions of hydrodynamics,<sup>185-188</sup> which is what we need in order to simulate hydrodynamics in a computer. These later works show how an *Eulerian* description of hydrodynamics can be derived from the Hamiltonian dynamics of the underlying atoms, by defining mass, momentum, and energy of cells which surround certain points fixed in space. However, *Lagrangian* descriptions, in which the cells “move following the flow,” are much trickier to deal with. Typically, two types of groupings of fluid molecules have been considered based on the Voronoi tessellation or on spherical blobs.

An early attempt to construct a Voronoi fluid particle from the microscopic level was made by Español *et al.*<sup>113</sup> The Voronoi centers were moved according to the forces felt by the molecules inside the cell in the underlying MD simulation. An effective excluded volume potential was obtained from the radial distribution function of the Voronoi centers. The method was revisited by Eriksson *et al.*,<sup>189</sup> who observed “molecular unspecificity” of the Voronoi projection, in the sense that very different microscopic models give rise to essentially the same dynamics of the cells. In an earlier work,<sup>190</sup> a force covariance method, essentially the Einstein-Helfand route to compute the Green-Kubo coefficients,<sup>191</sup> was introduced in order to compute the friction forces under the DPD ansatz. The results are disappointing as these authors showed that the dynamics of the CG particles with the forces of the DPD model measured from MD for a Lennard-Jones system were not consistent with the MD results themselves.

More recently, Hadley and McCabe<sup>192</sup> proposed to group water molecules into beads through the *K*-means algorithm.<sup>193</sup> The algorithm considers a number of beads with initially given positions and constructs their Voronoi tessellation. The water molecules inside each Voronoi cell have a center of mass that does not coincide with the bead position. The bead position is then translated on top of the center of mass and a retessellation is made again, with a possibly different set of water molecules constituting the new bead. The procedure is repeated until convergence. At the end, one has centroidal Voronoi cells in which

the bead position and the center of mass of the water molecules inside the Voronoi cell coincide. The *K*-means algorithm gives for every microstate (coordinates of water molecules) the value of the macrostate (coordinates of the beads) and, therefore, provides a rule-based CG mapping. Unfortunately, there is no analytic function that captures this mapping and, therefore, it is not possible to use the theory of coarse-graining to rigorously derive the evolution of the beads. The strategy by Hadley and McCabe is to construct the radial distribution function and infer from it the pair potential. Recently, Izvekov and Rice<sup>182</sup> have also considered this procedure in order to compute both the conservative force and the friction force between beads by extracting this information from force and velocity correlations between Voronoi cells. They find that very few molecules per cell are sufficient to obtain the Markovian behaviour.

Instead of using Voronoi based fluid particles, Voth and co-workers consider a sphere (termed a *BLOB*) and move the sphere according to the forces experienced by the center of mass of the molecules inside it.<sup>194</sup> The dynamics of the *BLOB* is then modeled in order to reproduce the time correlations of the *BLOB*. Subsequently a system of *N* Brownian *BLOB*s is constructed in order to reproduce the above correlations.

Recently, another attempt to obtain DPD from the underlying MD has been undertaken by Lei *et al.*<sup>195</sup> by using the rigorous approach of the theory of coarse-graining. However, in order to construct the “fluid particles,” these authors constrained a collection of Lennard-Jones atoms to move bonded, by maintaining a specified radius of gyration. The fluid no longer is a simple atomic fluid but rather a fluid made of more complex “molecules” (the atomic clusters constrained to have a radius of gyration) whose rheology is necessarily complex.

Our impression is that we still have not solved satisfactorily the problem of deriving from the microscopic dynamics the dynamics of CG particles that capture the behaviour of a simple fluid made of *unbonded* atoms. Work remains to be done in order to define the proper CG mapping for a fully satisfactory bottom-up model for Lagrangian fluid particles representing a set of few unbonded atoms or molecules “moving coherently.”

At this point, we should introduce a note of caution concerning *non-Markov effects*. The rigorous coarse-graining in which centers of mass of groups of atoms are used as CG variables relies on a basic and fundamental hypothesis, which is the separation of time scales of the evolution of the CG variables and “the rest” of variables in the system. More accurately, the separation of time scales refers to the existence, *in the evolution of the CG variables themselves*, of two well-defined scales, a large amplitude slow component and a small high frequency component that can be modeled in terms of white noise. The dynamics of the CG variables can then be approximately described by a non-linear diffusion equation in the space spanned by the CG variables.<sup>22,23</sup> This separation of time scales does not always exist, either because the groups of atoms are small and the centers of mass momenta evolve in the same time scales as the forces (due to collisions with atoms of other groups)<sup>181</sup> or because of the existence of

coupled slow processes not captured by the selected CG variables. When this happens, one strategy is to tweak the friction and simply fit frictions to recover the time scales. Gao and Fang used this approach in order to coarse grain a water molecule to one site-CG particle.<sup>196</sup> Another strategy is to enlarge the set of CG variables with the hope that the new set will be Markovian. Briels<sup>197</sup> addresses specifically the problem of CG in polymers and introduces transient forces to recover a Markovian description. Davtyan, Voth, and Anderson<sup>198</sup> have considered the introduction of “fictitious particles” in order to recover the CG dynamics observed from MD. The fictitious particles are just a simple and elegant way to model the memory kernel in a particularly intuitive way. If the strategy to increase the dimension of the CG state space does not work yet, it is still possible to formulate from microscopic principles formal non-Markovian models and to extract information about the memory kernel from MD.<sup>199</sup> However, in the absence of the separation of time scales, the computational effort required to get from MD the memory kernel makes the whole strategy of bottom-up coarse graining inefficient. Note that the advantage of a bottom-up strategy for coarse graining is that one needs to run *relatively short* MD simulations to get the information (Green-Kubo coefficients) that is used in the dynamic equations governing much larger time scales. If one needs to run a long MD simulation of the microscopic system to get the CG information, we have already solved the problem by brute force in the first place!

## VI. SYSTEMS STUDIED WITH DPD

The number of systems and problems that have been addressed with DPD or its variants is enormous and we do not pretend to review the extensive literature on the subject. Nevertheless, to illustrate the range and variety of different applications of DPD, we give a necessarily brief survey of the field. A general trend observed in the application side is the shift from the original DPD model, of “balls and springs” models, towards more specific atomistic detail, in the line of MZ-DPD or semi-bottom-up DPD (with structure based CG potentials and fitted friction).

### A. Colloids

A recent review on the simulation of colloidal suspensions with particle methods, including DPD, can be found in Ref. 200. The first application of DPD to a complex fluid was the simulation of colloidal rheology by Koelman and Hoogerbrugge.<sup>201</sup> Since then, a large number of works have addressed the simulation of colloidal suspensions, with a variety of approaches to represent the solute. Typically, a colloidal particle is constructed out of dissipative particles that are moved rigidly<sup>201,202</sup> or connected with springs.<sup>203,204</sup> Arbitrary shapes may be considered in this way,<sup>205</sup> as well as confinement due to walls.<sup>202,206</sup> As a way to bypass the need to update the relatively large number of solid particles, some approaches represent each colloidal particle with a single dissipative particle,<sup>111,112,207</sup> leading to minimal spherical blob models for the colloids. These simplified models for the solute require the introduction of shear forces of the FPM type. Representing a colloidal particle with a point particle is a strategy

also used in minimal blob models in Eulerian CFD methods for fluctuating hydrodynamics.<sup>208</sup> A core can be added in order to represent hard spheres with finite radii, supplemented with a dissipative surface to mimic boundary conditions,<sup>209</sup> and still retain the one-particle-per-colloid scheme. Although general features show semi-quantitative agreement with experimental results,<sup>209</sup> other simulation techniques like Stokesian dynamics, and theoretical work, it is clear that getting more detailed physics of colloid-colloid interactions and colloid-solvent interactions (either through a MZ-DPD approach or by phenomenologically including boundary layers and top-down parametrization) may be beneficial to the field.

### B. Blood

A colloidal system of obvious biological interest is blood. Blood has been simulated with DPD<sup>210</sup> and more recently with SDPD.<sup>136,137,211</sup> Two recent reviews<sup>212,213</sup> discuss the modeling of blood with particle methods. Multi-scale modeling (i.e., MZ-DPD) seems to be crucial to capture platelet activation and thrombogenesis.<sup>214</sup>

### C. Polymers

An excellent recent review on the coarse-graining of polymers is given by Padding and Briels.<sup>215</sup> Below the entanglement threshold, Rouse dynamics holds and this is well satisfied in a DPD polymer melt.<sup>216</sup> Above the threshold, entanglements are a necessary ingredient in polymer melts. Because the structure based CG potential between the blobs is very soft, it is necessary to include a mechanism for entanglement explicitly. This is one example in which the usual simple schemes to treat the many-body potential (through pair-wise interactions) fails dramatically. There are several methods to include entanglements: Padding and Briels<sup>217,218</sup> introduced the elastic band method for coarse-grained simulations of polyethylene. Another alternative to represent entanglements is to use the Kumar and Larson method,<sup>219–221</sup> in which a repulsive potential between bonds linking consecutive blobs is introduced. Finally, entanglements can be enforced in a simpler way by hard excluded volume Lennard-Jones (LJ) interactions<sup>222</sup> or through suitable criterion on the stretching of two bonds and the amount of impenetrability of them.<sup>223</sup>

Beyond scaling properties, effort has been directed towards a chemistry-detailed MZ-DPD methodology, by using structure based CG effective potentials and either fitting the friction coefficient<sup>224–227</sup> or obtaining the dissipative forces from Green-Kubo expressions.<sup>228</sup> In general, one can take advantage of systematic static coarse-graining approaches, like those for heptane and toluene,<sup>229</sup> to be directly incorporated to DPD. Very recently, new Bayesian methods for obtaining the CG potential *and* friction are being considered<sup>230,231</sup> (on pentane). The ultimate goal of all these microscopically informed approaches is to predict rheological properties as a function of the chemical nature of the polymer system with a small computational cost. As mentioned earlier, whatever improvement in the construction of CG potentials will be highly beneficial also for the construction of dynamic CG

models. In this respect, the work on *analytical* integral equation approach of Guenza and co-workers<sup>232</sup> for obtaining the CG potential in polymer systems that ensures both structural properties *and* thermodynamic behaviour seems to be very promising.

We perceive a powerful trend towards more microscopically informed DPD which is able to express faithfully the chemistry of the system. This trend is important when considering hierarchical multi-scale methods in which MD information is transferred to a dynamic CG DPD model, the DPD model is evolved in order to get topology and equilibrium states much faster than MD, and then a back-mapping fine grained procedure recovers microscopic states which is able to be evolved again with MD.<sup>233–235</sup>

Other complex fluid systems involving polymers have been considered. An early work is the study of adsorption of colloidal particles onto a polymer coated surface.<sup>206</sup> Polymer brushes are reviewed by Kreer.<sup>236</sup> Self-assembly of giant amphiphiles made of a nanoparticle with a tethered polymer tail has been considered recently.<sup>237</sup> Polymer membranes for fuel cells have been considered by Dorenbos.<sup>238</sup> Polymer solutions simulated with DPD obey Zimm theory that includes hydrodynamic interactions.<sup>239</sup> Polymer solutions have also been studied with SDPD observing Zimm dynamics.<sup>139</sup>

#### D. Phase separating fluids

In polymer mixtures, the  $\chi$ -parameter mapping introduced by Groot and Madden<sup>240</sup> has been phenomenally popular because it links to long-established polymer physical chemistry (tables of  $\chi$ -parameters exists, for instance, and a large literature is devoted to calculating  $\chi$ -parameters *ab initio*). This has helped incorporate chemical specificity in DPD from solubility parameters.<sup>241,242</sup> It is also known that  $\chi$ -parameters can be composition dependent (PEO in water is the notorious example). This can be accommodated within the MDPD approach. Akkermans<sup>243</sup> presents a first principles coarse-graining method that allows us to calculate the excess free energy of mixing and Flory-Huggins  $\chi$ -parameter. A related effort is given by Goel *et al.*<sup>244</sup>

DPD has been very successful in identifying mechanisms in phase separation: Linear diblock copolymer spontaneously forms a mesoscopically ordered structure (lamellar, perforated lamellar, hexagonal rods, and micelles).<sup>240</sup> DPD is capable to predict the dynamical pathway towards equilibrium structures and it is observed that hydrodynamic interactions play an important role in the evolution of the mesophases.<sup>245</sup> Domain growth and phase separation of binary immiscible fluids of differing viscosity were studied in Ref. 246. New mechanisms via inertial hydrodynamic bubble collapse for late-stage coarsening in off-critical vapor-liquid phase separation have been identified.<sup>81</sup> The effect of nanospheres in the mechanisms for domain growth in a phase separating binary mixture has been considered by Laradji and Hore.<sup>203</sup>

#### E. Drop dynamics

A particular case of phase separating fluids is given by liquid-vapour coexistence giving rise to droplets. Surface-confined drops in a simple shear were studied in an early work.<sup>247</sup> Pendant drops have been studied with MDPD,<sup>83</sup>

while oscillating drops<sup>248</sup> and drops on superhydrophobic substrates<sup>249</sup> have also been considered.

#### F. Amphiphilic systems

An early review of the computer modeling of surfactant systems is by Shelley and Shelley.<sup>250</sup> A more recent review on the modeling of pure membranes and lipid-water membranes with DPD is given by Guigas *et al.*<sup>36</sup> Coarsening dynamics of the smectic mesophase of amphiphilic species for a minimal amphiphile model was studied by Jury *et al.*<sup>251</sup> and mesophase formation in pure surfactants and solvents by Prinsen *et al.*<sup>252</sup> More microscopic details have been included by Ayton and Voth<sup>253</sup> with the DPD model for CG lipid molecules that self-assemble, a problem also considered by Kranenburg and Venturoli.<sup>254</sup> Effort towards more realistic parametrization for lipid bilayers was given by Gao *et al.*<sup>255</sup> Prior to this, Li *et al.*<sup>256</sup> formulated a conservative force derived from a bond-angle dependent potential that allowed considering different types of micellar structures. The microfluidic synthesis of nanovesicles was considered by Zhang *et al.*<sup>257</sup> Simulations of micelle-forming systems have also been reported.<sup>258,259</sup>

#### G. Electrostatics

Charge effects are clearly important for modelling polyelectrolytes, ionic surfactants, and electrokinetic transport phenomena.<sup>260,261</sup> Considerable progress has been made in extending DPD to these application areas,<sup>68,69,262–265</sup> including modelling the dielectric properties of coarse-grained polar solvents.<sup>266,267</sup>

#### H. Oil industry

DPD simulations have also addressed problems in the oil industry, from oil-water-surfactant dynamics,<sup>268</sup> and water-benzene-caprolactam systems,<sup>269</sup> to the aggregate behavior of asphaltenes in heavy crude oil,<sup>270</sup> or the orientation of asphaltene molecules at the oil-water interface.<sup>271</sup>

#### I. Biological membranes

A review of the mesoscopic modeling of biological membranes was given by Venturoli *et al.*<sup>272</sup> Groot and Rabone<sup>273</sup> presented one of the first applications of DPD to the modeling of biological membranes and its disruption due to nonionic surfactants. This work was also notable for its systematic approach to bottom-up coarse graining. In particular in order to fix the length scale, these authors introduced the seminal notion of the “mapping number,”  $N_m$ , being the number of water molecules corresponding to one DPD solvent bead (but see also below). Later, Sevink and Fraaije devised a coarse-graining of a membrane into a DPD model in which the solvent was treated implicitly.<sup>274</sup> Amphiphilic polymer coated nanoparticles for assisted drug delivery through cell membranes have been recently studied.<sup>275,276</sup> The diffusion of membrane proteins has been considered by Guigas and Weiss.<sup>277</sup>

## J. Biomolecular modeling

The CG modeling of complex biomolecules with a focus on static properties has been addressed in the excellent review by Noid.<sup>19</sup> Pivkin *et al.*<sup>267</sup> have modeled proteins with DPD force fields, which compete with the Martini force field.<sup>278</sup>

## K. Inorganic materials

DPD has also been used for the CG modeling of solid inorganic materials. The coarse-grained representation of graphene turns out to be essential for the study of large scale resonator technology.<sup>191,279</sup>

## VII. CONCLUSIONS

The DPD model is a tool for simulating the mesoscale. The model has evolved since its initial formulation towards enriched models that, while retaining the initial simplicity of the original, are now linked strongly to either the microscopic scale or the macroscopic continuum scale. In many respects, the original DPD model of Fig. 1 is a toy model and one can do much better by using these refined models. In this perspective, we wish to convey the message that DPD has a dual role in modeling the mesoscale. It has been used as a way to simulate, on the one hand, coarse-grained (CG) versions of complex molecular *objects* and, on the other hand, *fluctuating fluids*. While the first type of application, involving atoms bonded by their interactions, has a solid ground on the theory of coarse graining, there is no such *microscopic* basis for DPD as a fluid solver. The best we can do today is to descend from the continuum theory and to formulate DPD as a Lagrangian discretization of fluctuating hydrodynamics, leading to the SDPD model.

Therefore as DPD simulators, we are faced with three alternative strategies as follows:

### A. Bottom-up MZ-DPD

When dealing with molecular objects made of bonded atoms, we may formulate an appropriate CG mapping and construct the DPD equations of motion with momentum conserving forces.<sup>165</sup> These equations contain the potential of mean force generating conservative forces and position-dependent friction coefficient, with explicit microscopic formulae: the potential of mean force is given by the configuration dependent free energy function, and the position dependent friction coefficient tensor is given by Green-Kubo expressions. Both quantities are given in terms of expectations *conditional* on the CG variables and are, therefore, many-body functions. These are not, in general, directly computable due to the curse of dimensionality. One needs to formulate simple and approximate models (usually pair-wise with, perhaps, bond-angle and torsion effects) in order to represent the complex functional dependence of these quantities. Together with the initial selection of the CG mapping, finding suitable functional forms is the most delicate part of the problem. Once this simple functional models are selected, constrained MD simulations,<sup>165,179</sup> or optimization methods,<sup>19–21,230</sup> may be used to obtain the CG potential.

The existence of a framework to derive dynamic CG models from bottom-up is a highly rewarding intellectual experience with a high practical value because (1) it provides the *structure* of the dynamic equations and (2) signals at the crucial points where approximations are required. The MZ-DPD approach is, in our view, an important breakthrough in the field, as it connects the well established world of *static coarse-graining* with the DPD world.<sup>19</sup> In this way, it provides a framework for accurately addressing the CG *dynamics*. However, the usefulness to follow the program by the book is not always obvious due to the large effort in obtaining the objects from MD. In this case, one would go to the next strategy.

### B. Parametrization of DPD

We may insist on a particularly simple form of linear repulsive forces and simple friction coefficients (like the ones in the original/cartoon DPD model) and fit the parameters to whatever property of the system one wants to correctly describe (for example, the compressibility). Nowadays, we advise caution with this simple approach because, usually, many other properties of the system go wrong. The simple DPD linear forces are not flexible enough in many situations. However, from what we have already learned from microscopically informed MZ-DPD in the previous strategy, we may give ourselves more freedom in selecting the functional forms (as in MDPD) for conservative and friction forces and have more free parameters to play with. Once it is realized that the potential between beads or blobs in DPD is, in fact, the potential of mean force, one can use semi-bottom-up approaches in which the potential of mean force is obtained from first principles, while the DPD friction forces are fitted to obtain the correct time scales.<sup>224,225,280</sup> Although this strategy is less rigorous, it may be more practical in some cases.

The bottom-up MZ-DPD strategy above has not been yet successful when the interactions of atoms or molecules in the system are *unbonded*, allowing two molecules that are initially close together to diffuse away from each other. These are the kind of interactions present in a fluid system. The main difficulty seems to be in the *Lagrangian* nature of a fluid particle that makes the CG mapping not obvious. Although some attempts have been taken in order to derive DPD for fluid systems with unbonded interactions, we believe that the problem is not yet solved. However, for these systems one may regard the dissipative particles as truly fluid particles (i.e., small thermodynamic systems that move with the flow). We are lead to the third strategy.

### C. Top-down DPD

Assume that we know that a particular field theory describes the complex fluid of interest at a macroscopic scale (Navier-Stokes for a Newtonian fluid, for example). Then one may discretize the theory on moving Lagrangian points according to the SPH mesh-free methodology. The Lagrangian points may be interpreted as fluid particles. If we perform this discretization within a thermodynamically consistent framework like GENERIC,<sup>4</sup> thermal fluctuations are automatically determined correctly,<sup>144</sup> allowing to address the mesoscale. This

strategy leads to enriched DPD models (SDPD is an example corresponding to Navier-Stokes hydrodynamics). The functional forms of conservative and friction forces in this DPD models are dictated by the mesh-free discretization, as well as the input information of the field theory itself. We have the impression that SDPD or its isothermal counterpart MDPD is underappreciated and underused. Although these methods are appropriate for fluid systems, we foresee the use of MDPD many-body potentials of the embedded atom form also for CG potentials for bonded atom systems. While CG potentials depending on the *global* density are potentially a trap,<sup>281,282</sup> the inclusion of many-body functional forms of the embedded atom kind depending on *local* density is a promising route to have more transferable CG potentials,<sup>283</sup> valid for different thermodynamic points. This expectation, though, needs to be substantiated by further research. In particular, liquid state theory for MDPD may need to be further developed.<sup>84,232</sup>

This perspective on DPD also points to several open methodological questions.

We have already mentioned the open problem of deriving from microscopic principles the dynamics of Lagrangian fluid particles made of unbonded atoms. Once this problem is solved, we will need to face the next problem of deriving from first principles the coupling of CG descriptions of bonded and unbonded atoms (a protein in a membrane surrounded by a solvent, for example). A derivation from bottom-up of this kind of coupling in a discrete *Eulerian* setting has been given recently in Ref. 188.

For the simulation of fluids, standard CFD methods equipped with thermal fluctuations are readily catching up with the mesoscale.<sup>9-17</sup> Methods for coupling solvents and suspended structures are being devised,<sup>188,208</sup> and therefore one may well ask what is the advantage of a Lagrangian solver based on the relatively inaccurate SPH discretization over these high quality CFD methods. Note that CFD methods allow for the rigorous treatment of limits (incompressibility, inertia-less, etc.) that may imply large computer savings and which are difficult to consider in SPH based methods. We believe (see the work of Meakin and Xu<sup>284</sup> for a defense of particle methods) that fluid particle models may still compete in situations where biomolecules and other complex molecular structures move in solvent environments because one does not need to change paradigm: only particles for both solvent and beads are used, with the corresponding simplicity in the codes to be used. Nevertheless, a fair comparison between Eulerian and Lagrangian methodologies is still missing.

As SDPD is just SPH plus thermal fluctuations, it inherits the shortcomings of SPH itself. SPH is still facing some challenges in both foundations (boundary conditions) and computational efficiency.<sup>125,126</sup> In this respect, a Voronoi fluid particle model,<sup>116</sup> understood as a Lagrangian finite volume solver, may be an interesting possibility both in terms of computational efficiency and simplicity of implementation of boundary conditions. Serrano compared SDPD and a particular implementation in 2D of Voronoi fluid particles.<sup>285</sup> In terms of computational efficiency, both methods are comparable because the extra cost in computing the tessellation is compensated by the small number of

neighbours required, six on average, while in SDPD one needs 20-30 neighbours.

Another interesting area of research is that of multi-scale modeling. In CFD, one way to reduce the computational burden is to increase the resolution of the mesh only in those places where strong flow variations occur or interesting molecular physics requiring small scale resolution is taking place. An early attempt within DPD was given by Backer *et al.*<sup>286</sup> We envisage that methods for multi-resolution SDPD will be increasingly used in the future.<sup>132,144,157,287</sup> Multi-resolution is a problem of active research also in the SPH community.<sup>126</sup> Eventually, one would like to hand-shake the particle method of SDPD with MD as the resolution is decreased.<sup>288</sup> Note, however, that as the fluid particles become small (say “four atoms per particle”) it is expected that the Markovian property breaks down and one needs to account for viscoelasticity,<sup>289,290</sup> either with additional internal variables<sup>145,162,163</sup> or with “fictitious particles.”<sup>198</sup>

Finally, a very interesting research avenue is given by the thermodynamically consistent (i.e., able to deal with non-isothermal situations) Mori-Zwanzig EDPD introduced theoretically by Español *et al.*<sup>183</sup> Up to now, CG representations of complex molecules have only included the location and velocity of the CG beads or blobs (sometimes its spin<sup>180</sup>), completely forgetting its internal energy content. Given the fundamental importance of the principle of energy conservation, it seems that in order to have thermodynamically consistent and more transferable potentials, we may need to start looking at these slightly more complex CG representations.

To close, let us revisit the question: “What do the dissipative particles represent?” It should be clear there is no single answer to this, since it depends on the model and the application. However there is a clear dichotomy between a top-down model like SDPD and the bottom-up approaches. In a top-down model, the role of the dissipative particles is really just to provide a Lagrangian scaffold on which to hang the continuum physics. In a bottom-up approach though, at least for bonded atom groups, one can definitively point to what the dissipative particle represents. A pragmatic methodology therefore often combines a bottom-up approach to modelling bonded atom groups in *solutes*, such as polymers, with a top-down model for the *solvent*. This works because often the role of the solvent is simply to mediate interactions, such as solvation forces, and to propagate hydrodynamic interactions. Clearly, then, the notion of the *solvent* mapping number  $N_m$  introduced by Groot and Rabone requires a careful interpretation. Its role really derives from the top-down viewpoint:  $N_m$  links the DPD solvent particle number density to the real solvent molecular density. If  $N_m = 3$  for water, for instance, this means that one dissipative particle represents *on average* three water molecules. The qualifier “on average” is essential here and is all too often omitted. From this point of view, it is also clear there is no necessity for  $N_m$  to be an integer.

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## APPENDIX: MDPD CONSISTENCY

In MDPD the potential takes the form described in the main text where  $V(\{\mathbf{r}\}) = \sum_i \psi(d_i)$  and  $d_i = \sum_{j \neq i} W(r_{ij})$ . From this it is easy to show that the forces remain pairwise, with

$$\mathbf{F}_{ij} = -[\psi'(d_i) + \psi'(d_j)] W'(r_{ij}) \mathbf{e}_{ij}. \quad (\text{A1})$$

Note that the weight function here is  $W'(r)$ . However, to our knowledge, there does not exist in the literature a proof of the *converse*, namely, that this relationship between the weight functions is a *necessary* condition to ensure the existence of  $V(\{\mathbf{r}\})$ . We present here such a proof, following the line of argument in Ref. 86.

We start with a generalised MDPD pairwise force law, with an (as yet) arbitrary weight function  $\omega^c(r)$ ,

$$\mathbf{F}_{ij} = A(d_i, d_j) \omega^c(r_{ij}) \hat{\mathbf{r}}_{ij}. \quad (\text{A2})$$

We assume that the amplitude function  $A(d_i, d_j)$  is symmetric since otherwise  $\mathbf{F}_{ij} \neq -\mathbf{F}_{ji}$ . Let us denote partial derivatives with respect to the first and second density arguments by  $A_{[1,0]}$  and  $A_{[0,1]}$ . The symmetry of  $A(d_i, d_j)$  then implies  $A_{[1,0]}(d_i, d_j) = A_{[0,1]}(d_j, d_i)$ .

A generic radial force law can always be integrated, so we cannot deduce anything useful just by considering pairs of particles. Instead, following Ref. 86, let us consider three isolated, collinear particles, at positions  $x_i$  ( $i = 1 \dots 3$ ) such that  $x_1 \leq x_2 \leq x_3$ . For this configuration, the densities are  $d_1 = W(x_{12}) + W(x_{13})$ ,  $d_2 = W(x_{12}) + W(x_{23})$ , and  $d_3 = W(x_{13}) + W(x_{23})$ . The pairwise forces are  $F_{12} = A(d_1, d_2) \omega^c(x_{12})$ ,  $F_{23} = A(d_2, d_3) \omega^c(x_{23})$ , and  $F_{13} = A(d_1, d_3) \omega^c(x_{13})$ . Finally, the summed forces on the particles are  $F_1 = F_{12} + F_{13}$ ,  $F_2 = -F_{12} + F_{23}$ , and  $F_3 = -F_{13} - F_{23}$ .

The existence of a potential implies integrability constraints like  $\partial F_1 / \partial x_2 - \partial F_2 / \partial x_1 = 0$ . Imposing these gives rise to an expression which can be simplified (by consideration of special cases) to a set of requirements for which the representative case is

$$\begin{aligned} &\omega^c(x_{12}) W'(x_{23}) A_{[1,0]}(d_1 + d_3, d_1) \\ &- \omega^c(x_{23}) W'(x_{12}) A_{[1,0]}(d_1 + d_3, d_3) = 0. \end{aligned} \quad (\text{A3})$$

The symmetry relation between  $A_{[0,1]}$  and  $A_{[1,0]}$  has been used. If we are allowed to cancel the  $A_{[1,0]}$  functions, we are home and dry, since this implies  $\omega^c(x) W'(y) = \omega^c(y) W'(x)$  (for arbitrary arguments  $x$  and  $y$ ), and this can only be true if  $\omega^c(x) \propto W'(x)$ . However, the  $A_{[1,0]}$  functions only cancel if  $A_{[1,0]}(x + y, x) = A_{[1,0]}(x + y, y)$  (for arbitrary arguments  $x, y$ ). A little thought shows that a sufficient condition for this to be true is that  $A(d_i, d_j) = f(d_i) + f(d_j)$ . This is precisely the form the force-law takes in Eq. (A1). The conclusion is that in this case  $\omega^c(x) \propto W'(x)$  is a *necessary* condition for the existence of the many-body potential  $V(\{\mathbf{r}\})$ . It is also sufficient, since we can absorb the proportionality constant into the definitions of  $d_i$  and  $\psi(d)$ , and then explicitly  $V(\{\mathbf{r}\}) = \sum_i \psi(d_i)$ . This proves the claimed result above.

For another example, we might be tempted to consider  $A(d_i, d_j) = f(d_i + d_j)$ , but retaining the weight function  $\omega^c(x) \propto W'(x)$ . For this choice  $A_{[1,0]}(x, y) = f'(x + y)$  and Eq. (A3) reduces to  $f'(2x + y) = f'(x + 2y)$ . This is true for arbitrary  $x$

and  $y$  if and only if  $f(x)$  is linear, and therefore the force law is *de facto* of the form shown in Eq. (A1). Thus, a non-linear function  $f(x)$  would be a bad choice. For a further case study, see Ref. 86.

If we fail to satisfy Eq. (A3) then the potential *does not exist*. If the potential does not exist, we lose the underpinning theory that the stationary probability distribution is given by Eq. (2). Without this foundation we are in uncharted waters, and there is no link to established statistical mechanics and thermodynamics.

In our opinion, in MDPD the burden rests on the user to display  $V(\{\mathbf{r}\})$  which gives rise to the chosen force law. The absence of an explicitly displayed potential leads only to unwarranted complications.

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