PHYSICAL REVIEW E VOLUME 62, NUMBER 2 AUGUST 2000

Foundations of dissipative particle dynamics

Eirik G. Flekkøy,[1] Peter V. Coveney,[2] and Gianni De Fabritiis[2]
[1]*Department of Physics, University of Oslo, P.O. Box 1048 Blindern, 0316 Oslo 3, Norway*
[2]*Centre for Computational Science, Queen Mary and Westfield College, University of London, London E1 4NS, United Kingdom*

(Received 7 February 2000)

We derive a mesoscopic modeling and simulation technique that is very close to the technique known as dissipative particle dynamics. The model is derived from molecular dynamics by means of a systematic coarse-graining procedure. This procedure links the forces between the dissipative particles to a hydrodynamic description of the underlying molecular dynamics (MD) particles. In particular, the dissipative particle forces are given directly in terms of the viscosity emergent from MD, while the interparticle energy transfer is similarly given by the heat conductivity derived from MD. In linking the microscopic and mesoscopic descriptions we thus rely on the macroscopic or phenomenological description emergent from MD. Thus the rules governing this form of dissipative particle dynamics reflect the underlying molecular dynamics; in particular, all the underlying conservation laws carry over from the microscopic to the mesoscopic description. We obtain the forces experienced by the dissipative particles together with an approximate form of the associated equilibrium distribution. Whereas previously the dissipative particles were spheres of fixed size and mass, now they are defined as cells on a Voronoi lattice with variable masses and sizes. This Voronoi lattice arises naturally from the coarse-graining procedure, which may be applied iteratively and thus represents a form of renormalization-group mapping. It enables us to select any desired local scale for the mesoscopic description of a given problem. Indeed, the method may be used to deal with situations in which several different length scales are simultaneously present. We compare and contrast this particulate model with existing continuum fluid dynamics techniques, which rely on a purely macroscopic and phenomenological approach. Simulations carried out with the present scheme show good agreement with theoretical predictions for the equilibrium behavior.

PACS number(s): 47.11.+j, 47.10.+g, 05.40.−a

I. INTRODUCTION

The nonequilibrium behavior of fluids continues to present a major challenge for both theory and numerical simulation. In recent times, there has been growing interest in the study of so-called mesoscale modeling and simulation methods, particularly for the description of the complex dynamical behavior of many kinds of soft condensed matter, whose properties have thwarted more conventional approaches. As an example, consider the case of complex fluids with many coexisting length and time scales, for which hydrodynamic descriptions are unknown and may not even exist. These kinds of fluids include multiphase flows, particulate and colloidal suspensions, polymers, and amphiphilic fluids, including emulsions and microemulsions. Fluctuations and Brownian motion are often key features controlling their behavior.

From the standpoint of traditional fluid dynamics, a general problem in describing such fluids is the lack of adequate continuum models. Such descriptions, which are usually based on simple conservation laws, approach the physical description from the macroscopic side, that is, in a ‘‘top down’’ manner, and have certainly proved successful for simple Newtonian fluids [1]. For complex fluids, however, equivalent phenomenological representations are usually unavailable and instead it is necessary to base the modeling approach on a microscopic (that is, particulate) description of the system, thus working from the bottom upward, along the general lines of the program for statistical mechanics pioneered by Boltzmann [2]. Molecular dynamics (MD) presents itself as the most accurate and fundamental method [3] but it is far too computationally intensive to provide a practical option for most hydrodynamic problems involving complex fluids. Over the last decade several alternative ‘‘bottom up’’ strategies have therefore been introduced. Hydrodynamic lattice gases [4], which model the fluid as a discrete set of particles, represent a computationally efficient spatial and temporal discretization of the more conventional molecular dynamics. The lattice-Boltzmann method [5], originally derived from the lattice-gas paradigm by invoking Boltzmann's *Stosszahlansatz*, represents an intermediate (fluctuationless) approach between the top-down (continuum) and bottom-up (particulate) strategies, insofar as the basic entity in such models is a single particle distribution function; but for interacting systems even these lattice-Boltzmann methods can be subdivided into bottom-up [6] and top-down models [7].

A recent contribution to the family of bottom-up approaches is the dissipative particle dynamics (DPD) method introduced by Hoogerbrugge and Koelman in 1992 [8]. Although in the original formulation of DPD time was discrete and space continuous, a more recent reinterpretation asserts that this model is in fact a finite-difference approximation to the ‘‘true’’ DPD, which is defined by a set of continuous time Langevin equations with momentum conservation between the dissipative particles [9]. Successful applications of the technique have been made to colloidal suspensions [10], polymer solutions [11], and binary immiscible fluids [12]. For specific applications where comparison is possible, this algorithm is orders of magnitude faster than MD [13]. The basic elements of the DPD scheme are particles that represent rather ill-defined ''mesoscopic'' quantities of the underlying molecular fluid. These dissipative particles are stipulated to evolve in the same way that MD particles do, but with different interparticle forces: since the DPD particles are pictured to have internal degrees of freedom, the forces between them have both a fluctuating and a dissipative component in addition to the conservative forces that are present at the MD level. Newton's third law is still satisfied, however, and consequently momentum conservation together with mass conservation produce hydrodynamic behavior at the macroscopic level.

Dissipative particle dynamics has been shown to produce the correct macroscopic (continuum) theory; that is, for a one-component DPD fluid, the Navier-Stokes equations emerge in the large scale limit, and the fluid viscosity can be computed [14,15]. However, even though dissipative particles have generally been viewed as clusters of molecules, no attempt has been made to link DPD to the underlying microscopic dynamics, and DPD thus remains a foundationless algorithm, as is that of the hydrodynamic lattice gas and *a fortiori* the lattice-Boltzmann method. It is the principal purpose of the present paper to provide an atomistic foundation for dissipative particle dynamics. Among the numerous benefits gained by achieving this, we are then able to provide a precise definition of the term ''mesoscale,'' to relate the hitherto purely phenomenological parameters in the algorithm directly to the average of microscopic fluxes of the conserved quantities. These averages may be given by a local hydrodynamic description of the underlying molecular system, as in the present work, or they may be derived from the specific microscopic interactions at hand. The general scheme thus lays down the structure of DPD algorithms for *specific* physicochemical systems, defined in terms of their molecular constituents. The DPD that we derive is a representation of the underlying MD given by the hydrodynamic values of the fluxes. Consequently, to the extent that the approximations made are valid, the DPD and MD will have the same hydrodynamic descriptions, and no separate kinetic theory for, say, the DPD viscosity will be needed once it is known for the MD system. Since the MD degrees of freedom will be integrated out in our approach the MD viscosity will appear in the DPD model as a parameter that may be tuned freely.

In our approach, the ''dissipative particles'' (DP's) are defined in terms of appropriate weight functions that sample portions of the underlying conservative MD particles, and the forces between the dissipative particles are obtained from the hydrodynamic description of the MD system: the microscopic conservation laws carry over directly to the DPD, and the hydrodynamic behavior of MD is thus reproduced by the DPD, albeit at a coarser scale. The mesoscopic (coarse-grained) scale of the DPD can be precisely specified in terms of the MD interactions. The size of the dissipative particles, as specified by the number of MD particles within them, furnishes the meaning of the term ''mesoscopic'' in the present context. Since this size is a freely tunable parameter of the model, the resulting DPD introduces a general procedure for simulating microscopic systems at any convenient scale of coarse graining, provided that the forces between the dissipative particles are known. When a hydrodynamic description of the underlying particles can be found, these forces follow directly; in cases where this is not possible, the forces between dissipative particles must be supplemented with the additional components of the physical description that enter on the mesoscopic level.

The DPD model that we derive from molecular dynamics is formally similar to conventional, albeit foundationless, DPD [14]. The interactions are pairwise and conserve mass and momentum, as well as energy [16,17]. Just as the forces conventionally used to define DPD have conservative, dissipative, and fluctuating components, so too do the forces in the present case. In the present model, the role of the conservative force is played by the pressure forces. However, while conventional dissipative particles possess spherical symmetry and experience interactions mediated by purely central forces, our dissipative particles are defined as space-filling cells on a Voronoi lattice whose forces have both central and tangential components. These features are shared with a model studied by Español [18]. This model links DPD to smoothed particle hydrodynamics [19] and defines the DPD forces by hydrodynamic considerations in a way analogous to earlier DPD models. Español *et al.* [20] have also carried out MD simulations with a superposed Voronoi mesh in order to measure the coarse grained inter-DP forces.

While conventional DPD defines dissipative particle masses to be constant, this feature is not preserved in our model. In our first publication on this theory [21], we stated that, while the dissipative particle masses fluctuate due to the motion of MD particles across their boundaries, the average masses should be constant. In fact, the DP masses vary due to distortions of the Voronoi cells, and this feature is now properly incorporated in the model.

To obtain the fluctuation-dissipation relations that give the magnitude of the thermal forces, we make use of a Fokker-Planck equation [9]. We show that the DPD system is described in an approximate sense by the isothermal-isobaric ensemble. Simulations confirm that, with the use of these forces, the measured DP temperature is equal to the MD temperature that is provided as input. This is an important finding in the present context as the most significant approximations we have made underlie the derivation of the thermal forces.

In a recent publication Español *et al.* have advocated a general strategy to obtain a Langevin description of various physical systems [22]. Using this methodology together with our coarse-graining scheme [21], Serrano and Español [23] have recently developed a model complementary to ours by working systematically from a ''top-down'' continuum description to a mesoscopic representation, the result being very close to ours.

II. COARSE-GRAINING MOLECULAR DYNAMICS: FROM MICRO- TO MESOSCALE

The essential idea motivating our definition of mesoscopic dissipative particles is to specify them as clusters of MD particles in such a way that the MD particles themselves remain unaffected while *all* being represented by the dissipative particles. The independence of the molecular dynamics from the superimposed coarse-grained dissipative particle dynamics implies that the MD particles are able to move between the dissipative particles. The stipulation that all MD particles must be fully represented by the DP's implies that, while the mass, momentum, and energy of a single MD particle may be shared between DP's, the sum of the shared components must always equal the mass and momentum of the MD particle.

A. Definitions

Full representation of all the MD particles can be achieved in a general way by introducing a sampling function

$$f_k(\mathbf{x})=\frac{s(\mathbf{x}-\mathbf{r}_k)}{\sum_l s(\mathbf{x}-\mathbf{r}_l)}, \tag{1}$$

where the positions $\mathbf{r}_k$ and $\mathbf{r}_l$ define the DP centers, $\mathbf{x}$ is an arbitrary position, and $s(\mathbf{x})$ is some localized function. It will prove convenient to choose it as a Gaussian,

$$s(\mathbf{x})=\exp(-x^2/a^2), \tag{2}$$

where the distance a sets the scale of the sampling function, although this choice is not necessary. The mass, momentum, and internal energy E of the kth DP are then defined as

$$\begin{aligned} M_k&=\sum_i f_k(\mathbf{x}_i)m,\\ \mathbf{P}_k&=\sum_i f_k(\mathbf{x}_i)m\mathbf{v}_i,\\ \frac{1}{2}M_kU_k^2+E_k&=\sum_i f_k(\mathbf{x}_i)\left(\frac{1}{2}mv_i^2+\frac{1}{2}\sum_{j\neq i}V_{MD}(r_{ij})\right)\\ &\equiv\sum_i f_k(\mathbf{x}_i)\epsilon_i, \end{aligned} \tag{3}$$

where $\mathbf{x}_i$ and $\mathbf{v}_i$ are the position and velocity of the ith MD particle, which are all assumed to have identical masses m, $\mathbf{P}_k$ is the momentum of the kth DP, and $V_{MD}(r_{ij})$ is the potential energy of the MD particle pair ij, separated a distance r_{ij}. The particle energy ϵ_i thus contains both the kinetic and a potential term. The kinematic condition

$$\dot{\mathbf{r}}_k=\mathbf{U}_k\equiv\mathbf{P}_k/M_k \tag{4}$$

completes the definition of our dissipative particle dynamics.

It is generally true that mass and momentum conservation suffice to produce hydrodynamic behavior. However, the equations expressing these conservation laws contain the fluid pressure. In order to get the fluid pressure a thermodynamic description of the system is needed. This produces an equation of state, which closes the system of hydrodynamic equations. Any thermodynamic potential may be used to obtain the equation of state. In the present case we shall take this potential to be the internal energy E_k of the dissipative particles, and we shall obtain the equations of motion for the DP mass, momentum, and energy. Note that the internal energy would also have to be computed if a free energy had been chosen for the thermodynamic description. For this reason it is not possible to complete the hydrodynamic description without taking the energy flow into account. As a by-product of this the present DPD also contains a description of the heat flow and corresponds to the recently introduced DPD with energy conservation [16,17]. Español previously introduced an angular momentum variable describing the dynamics of extended particles [18]: this is needed when forces are noncentral in order to avoid dissipation of energy in a rigid rotation of the fluid. Angular momentum could be included on the same footing as momentum in the following developments. However, for reasons of both space and conceptual economy we shall omit it in the present context, even though it is probably important in applications where hydrodynamic precision is important. In the following sections, we shall use the notation $\mathbf{r}$, M, $\mathbf{P}$, and E with the indices k, l, m, and n to denote DP's, while we shall use $\mathbf{x}$, m, $\mathbf{v}$, and ϵ with the indices i and j to denote MD particles.

B. Equations of motion for the dissipative particles based on a microscopic description

The fact that all the MD particles are represented at all instants in the coarse-grained scheme is guaranteed by the normalization condition $\Sigma_k f_k(\mathbf{x})=1$. This implies directly that

$$\begin{aligned} \sum_k M_k&=\sum_i m,\\ \sum_k \mathbf{P}_k&=\sum_i m\mathbf{v}_i,\\ \sum_k E_k^{\text{tot}}=\sum_k\left(\frac{1}{2}M_k\mathbf{U}_k^2+E_k\right)&=\sum_i \epsilon_i; \end{aligned} \tag{5}$$

thus, with mass, momentum, and energy conserved at the MD level, these quantities are also conserved at the DP level. In order to derive the equations of motion for dissipative particle dynamics we now take the time derivatives of Eqs. (3). This gives

$$\frac{dM_k}{dt}=\sum_i \dot{f}_k(\mathbf{x}_i)m, \tag{6}$$

$$\frac{d\mathbf{P}_k}{dt}=\sum_i[\dot{f}_k(\mathbf{x}_i)m\mathbf{v}_i+f_k(\mathbf{x}_i)\mathbf{F}_i], \tag{7}$$

$$\frac{dE_k^{\text{tot}}}{dt}=\sum_i[\dot{f}_k(\mathbf{x}_i)\epsilon_i+f_k(\mathbf{x}_i)\dot{\epsilon}_i], \tag{8}$$

where d/dt is the substantial derivative and $\mathbf{F}_i=m\dot{\mathbf{v}}_i$ is the force on particle i.

The Gaussian form of s implies that $\dot{s}(\mathbf{x})=-(2/a^2)\dot{\mathbf{x}}\cdot\mathbf{x}s(\mathbf{x})$. This makes it possible to write

$$\dot{f}_k(\mathbf{x}_i)=f_{kl}(\mathbf{x}_i)(\mathbf{v}_i'\cdot\mathbf{r}_{kl}+\mathbf{x}_i'\cdot\mathbf{U}_{kl}), \tag{9}$$

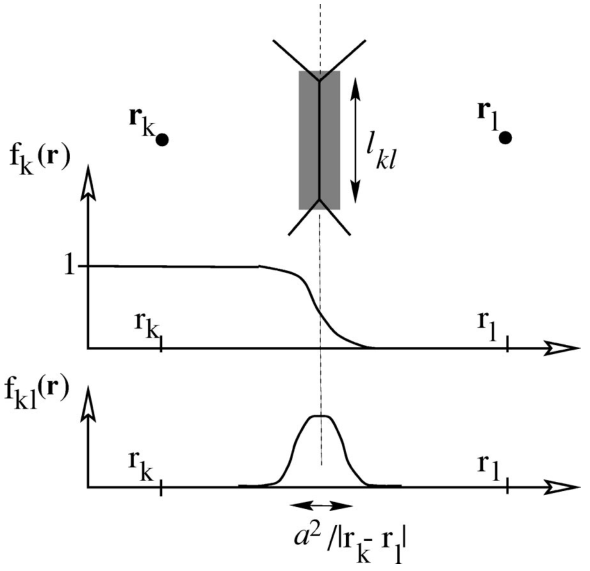

FIG. 1. The overlap region between two Voronoi cells is shown in gray. The sampling function $f_k(\mathbf{r})$ is shown in the top graph and the overlap function $f_{kl}(\mathbf{r}) = (2/a^2) f_k(\mathbf{r}) f_l(\mathbf{r})$ in the bottom graph. The width of the overlap region is $a^2/|\mathbf{r}_k - \mathbf{r}_l|$ and its length is denoted by l.

where the overlap function f_{kl} is defined as $f_{kl}(\mathbf{x}) \equiv (2/a^2) f_k(\mathbf{x}) f_l(\mathbf{x})$, $\mathbf{r}_{kl} \equiv (\mathbf{r}_k - \mathbf{r}_l)$, and $\mathbf{U}_{kl} \equiv (\mathbf{U}_k - \mathbf{U}_l)$, and we have rearranged terms so as to get them in terms of the centered variables

$$\mathbf{v}_i' = \mathbf{v}_i - \frac{(\mathbf{U}_k + \mathbf{U}_l)}{2}, \qquad \mathbf{x}_i' = \mathbf{x}_i - \frac{(\mathbf{r}_k + \mathbf{r}_l)}{2}. \tag{10}$$

Before we proceed with the derivation of the equations of motion it is instructive to work out the actual forms of $f_k(\mathbf{x})$ and $f_{kl}(\mathbf{x})$ in the case of only two particles k and l. Using the Gaussian choice of s we immediately get

$$f_k(\mathbf{x}) = \frac{1}{1 + (\exp\{2[\mathbf{x} - (\mathbf{r}_k + \mathbf{r}_l)/2] \cdot \mathbf{r}_{kl}/(a^2)\})^2}. \tag{11}$$

The overlap function similarly follows:

$$f_{kl}(\mathbf{x}) = \frac{1}{2a^2} \cosh^{-2}\left[\left(\mathbf{x} - \frac{\mathbf{r}_k + \mathbf{r}_l}{2} \right) \cdot \left(\frac{\mathbf{r}_{kl}}{a^2} \right) \right]. \tag{12}$$

These two functions are shown in Fig. 1. Note that the scale of the overlap region is not a but $a^2/|\mathbf{r}_k - \mathbf{r}_l|$. Dissipative particle interactions take place only where the overlap function is nonzero. This happens along the dividing line which is equally far from the two particles. The contours of nonzero f_{kl} thus define a Voronoi lattice with lattice segments of length l_{kl}. This Voronoi construction is shown in Fig. 2 in which MD particles in the overlap region defined by $f_{kl} > 0.1$ are shown, though presently not actually simulated as dynamic entities. The volume of the Voronoi cells will in general vary under the dynamics. However, even with arbitrary dissipative particle motion the cell volumes will approach zero only exceptionally, and even then the identities of the DP particles will be preserved so that they subsequently reemerge.

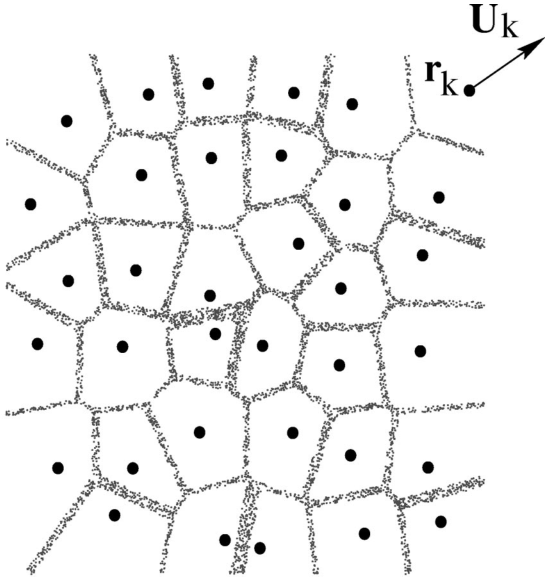

FIG. 2. The Voronoi lattice defined by the dissipative particle positions $\mathbf{r}_k$. The gray dots that represent the underlying MD particles are drawn only in the overlap region.

1. Mass equation

The mass equation (6) takes the form

$$\frac{dM_k}{dt} \equiv \sum_l \dot{M}_{kl}, \tag{13}$$

where

$$\dot{M}_{kl} = \sum_i f_{kl}(\mathbf{x}_i) m (\mathbf{v}_i' \cdot \mathbf{r}_{kl} + \mathbf{x}_i' \cdot \mathbf{U}_{kl}). \tag{14}$$

The $\mathbf{v}_i'$ term will be shown to be negligible within our approximations. The $\mathbf{x}_i' \cdot \mathbf{U}_{kl}$ term, however, describes the geometric effect that the Voronoi cells do not conserve their volume: The relative motion of the DP centers causes the cell boundaries to change their orientation. We will return to give this ‘‘boundary twisting’’ term a quantitative content when the equations of motion are averaged—an effect that was overlooked in our first publication of this theory [21] where it was stated that $\langle \dot{M}_{kl} \rangle = 0$.

2. Momentum equation

The momentum equation (7) takes the form

$$\frac{d\mathbf{P}_k}{dt} = \sum_{li} f_{kl}(\mathbf{x}_i) m \mathbf{v}_i (\mathbf{v}_i' \cdot \mathbf{r}_{kl} + \mathbf{x}_i' \cdot \mathbf{U}_{kl}) + \sum_{li} f_k(\mathbf{x}_i) \mathbf{F}_i. \tag{15}$$

We can write the force as $\mathbf{F}_i = m\mathbf{g} + \Sigma_j \mathbf{F}_{ij}$, where the first term is an external force and the second term is the internal force caused by all the other particles. Newton's third law then takes the form $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$. The last term in Eq. (15) may then be rewritten as

$$\sum_i f_k(\mathbf{x}_i)\mathbf{F}_i = M_k\mathbf{g} + \sum_{ij} f_k(\mathbf{x}_i)\mathbf{F}_{ij}, \tag{16}$$

where

$$\begin{aligned}\sum_{ij} f_k(\mathbf{x}_i)\mathbf{F}_{ij} &= -\sum_{ij} f_k(\mathbf{x}_i)\mathbf{F}_{ji} \\ &= -\sum_{ij} f_k(\mathbf{x}_j + \Delta\mathbf{x}_{ij})\mathbf{F}_{ji} \\ &\approx -\sum_{ij} f_k(\mathbf{x}_j)\mathbf{F}_{ji} - \sum_{ij} [\Delta\mathbf{x}_{ij}\cdot\nabla f_k(\mathbf{x}_i)]\mathbf{F}_{ji} \\ &= -\frac{1}{2}\sum_{ij} [\Delta\mathbf{x}_{ij}\cdot\nabla f_k(\mathbf{x}_i)]\mathbf{F}_{ji} \\ &= \sum_l \left(\sum_{ij} \frac{1}{2} f_{kl}(\mathbf{x}_i)\mathbf{F}_{ij}\Delta\mathbf{x}_{ij}\right)\cdot\mathbf{r}_{kl}, \end{aligned} \tag{17}$$

where $\Delta\mathbf{x}_{ij} = \mathbf{x}_i - \mathbf{x}_j$, we have Taylor expanded $f_k(\mathbf{x})$ around $\mathbf{x}_j$, and used a result similar to Eq. (9) to evaluate $\nabla f_k(\mathbf{x})$. In passing from the third to the fourth equality in the above equations we have moved the first term on the right hand side to the left hand side and divided by 2. Now, if we group the last term above with the $\mathbf{r}_{kl}$ term in Eq. (15), make use of Eq. (10), and do some rearranging of terms we get

$$\begin{aligned}\frac{d\mathbf{P}_k}{dt} &= M_k\mathbf{g} + \sum_l \dot{M}_{kl}\frac{\mathbf{U}_k + \mathbf{U}_l}{2} + \sum_{li} f_{kl}(\mathbf{x}_i)\mathbf{\Pi}'_i\cdot\mathbf{r}_{kl} \\ &\quad + \sum_{li} f_{kl}(\mathbf{x}_i) m\mathbf{v}'_i\mathbf{x}'_i\cdot\mathbf{U}_{kl}, \end{aligned} \tag{18}$$

where we have used the relation $\dot{M}_k = \Sigma_l \dot{M}_{kl}$ and defined the general momentum-flux tensor

$$\mathbf{\Pi}_i = m\mathbf{v}_i\mathbf{v}_i + \frac{1}{2}\sum_j \mathbf{F}_{ij}\Delta\mathbf{x}_{ij}. \tag{19}$$

This tensor is the momentum analog of the mass-flux vector $m\mathbf{v}_i$. The prime indicates that the velocities on the right hand side are those defined in Eq. (10). The tensor $\mathbf{\Pi}_i$ describes both the momentum that the particle carries around through its own motion and the momentum exchanged by interparticle forces. It may be arrived at by considering the momentum transport across imaginary cross sections of the volume in which the particle is located.

3. Energy equation

In order to get the microscopic energy equation of motion we proceed as with the mass and momentum equations and the two terms that appear on the right hand side of Eq. (8).

Taking V_{MD} to be a central potential and using the relations $\nabla V_{MD}(r_{ij}) = V'_{MD}(r_{ij})\mathbf{e}_{ij} = -\mathbf{F}_{ij}$ and $\dot{V}_{MD}(r_{ij}) = V'_{MD}(r_{ij})\mathbf{e}_{ij}\cdot\mathbf{v}_{ij} = -\mathbf{F}_{ij}\cdot\mathbf{v}_{ij}$, where $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, we get the time rate of change of the particle energy

$$\dot{\epsilon}_i = m\mathbf{g}\cdot\mathbf{v}_i + \frac{1}{2}\sum_{j\neq i} \mathbf{F}_{ij}\cdot(\mathbf{v}_i + \mathbf{v}_j). \tag{20}$$

This gives the first term of Eq. (8) in the form

$$\sum_i f_k(\mathbf{x}_i)\dot{\epsilon} = \mathbf{P}_k\cdot\mathbf{g} + \frac{1}{2}\sum_{i\neq j} f_k(\mathbf{x}_i)\mathbf{F}_{ij}\cdot(\mathbf{v}_i + \mathbf{v}_j). \tag{21}$$

The last term of this equation is odd under the exchange $i\leftrightarrow j$ and exactly the same manipulations as in Eq. (17) may be used to give

$$\begin{aligned}\sum_i f_k(\mathbf{x}_i)\dot{\epsilon} &= \mathbf{P}_k\cdot\mathbf{g} + \sum_{l,i\neq j} f_{kl}(\mathbf{x}_i)\frac{1}{4}\mathbf{F}_{ij}\cdot(\mathbf{v}_i + \mathbf{v}_j)\Delta\mathbf{x}_{ij}\cdot\mathbf{r}_{kl} \\ &= \mathbf{P}_k\cdot\mathbf{g} + \sum_{l,i\neq j} f_{kl}(\mathbf{x}_i)\left(\frac{1}{4}\mathbf{F}_{ij}\cdot(\mathbf{v}'_i + \mathbf{v}'_j)\right. \\ &\quad \left. + \frac{1}{2}\mathbf{F}_{ij}\cdot\frac{\mathbf{U}_k + \mathbf{U}_l}{2}\right)\Delta\mathbf{x}_{ij}\cdot\mathbf{r}_{kl}, \end{aligned} \tag{22}$$

where for later purposes we have used Eqs. (10) to get the last equation. The last term of Eq. (8) is easily written down using Eq. (9). This gives

$$\sum_i \dot{f}_k(\mathbf{x}_i)\epsilon_i = \sum_{li} f_{kl}(\mathbf{x}_i)(\mathbf{v}'_i\cdot\mathbf{r}_{kl} + \mathbf{x}'_i\cdot\mathbf{U}_{kl})\epsilon_i. \tag{23}$$

As previously we write the particle velocities in terms of $\mathbf{v}'_i$. The corresponding expression for the particle energy is $\epsilon_i = \epsilon'_i + m\mathbf{v}'_i\cdot(\mathbf{U}_k + \mathbf{U}_l)/2 + (1/2)m[(\mathbf{U}_k + \mathbf{U}_l)/2]^2$, where the prime in ϵ'_i denotes that the particle velocity is $\mathbf{v}'_i$ rather than $\mathbf{v}_i$. Equation (23) may then be written

$$\begin{aligned}\sum_i \dot{f}_k(\mathbf{x}_i)\epsilon_i &= \sum_l \frac{1}{2}\dot{M}_{kl}\left(\frac{\mathbf{U}_k + \mathbf{U}_l}{2}\right)^2 \\ &\quad + \sum_{li} f_{kl}(\mathbf{x}_i)\left(\epsilon'_i\mathbf{v}'_i + m\mathbf{v}'_i\mathbf{v}'_i\cdot\frac{\mathbf{U}_k + \mathbf{U}_l}{2}\right)\cdot\mathbf{r}_{kl} \\ &\quad + \sum_{li} f_{kl}(\mathbf{x}_i)\epsilon_i\mathbf{x}'_i\cdot\mathbf{U}_{kl}. \end{aligned} \tag{24}$$

Combining this equation with Eq. (22) we obtain

$$\begin{aligned}\dot{E}_k^{\mathrm{tot}} &= \sum_{li} f_{kl}(\mathbf{x}_i)\left(\mathbf{J}'_{\epsilon i} + \mathbf{\Pi}'_i\cdot\frac{\mathbf{U}_k + \mathbf{U}_l}{2}\right)\cdot\mathbf{r}_{kl} + M_k\mathbf{U}_k\cdot\mathbf{g} \\ &\quad + \sum_l \frac{1}{2}\dot{M}_{kl}\left(\frac{\mathbf{U}_k + \mathbf{U}_l}{2}\right)^2 + \sum_{li} f_{kl}(\mathbf{x}_i) \\ &\quad \times\left[\epsilon'_i + m\mathbf{v}'_i\cdot\left(\frac{\mathbf{U}_k + \mathbf{U}_l}{2}\right)\right]\mathbf{x}'_i\cdot\mathbf{U}_{kl}, \end{aligned} \tag{25}$$

where the momentum-flux tensor is defined in Eq. (19) and we have identified the energy-flux vector associated with a particle i,

$$\mathbf{J}_{\epsilon i}=\epsilon_i\mathbf{v}_i+\frac{1}{4}\sum_{i\neq j}\mathbf{F}_{ij}\cdot(\mathbf{v}_i+\mathbf{v}_j)\Delta\mathbf{x}_{ij}. \tag{26}$$

Again the prime denotes that the velocities are $\mathbf{v}_i'$ rather than $\mathbf{v}_i$. To get the internal energy $\dot{E}_k$ instead of $\dot{E}_k^{\mathrm{tot}}$ we note that $d(\mathbf{P}_k^2/2M_k)/dt=\mathbf{U}_k\cdot\dot{\mathbf{P}}_k-(1/2)\dot{M}_k\mathbf{U}_k^2$. Using this relation, the momentum equation Eq. (18), as well as the substitution $(\mathbf{U}_k+\mathbf{U}_l)/2=\mathbf{U}_k-\mathbf{U}_{kl}/2$ in Eq. (25), followed by some rearrangement of the $\dot{M}_{kl}$ terms, we find that

$$\begin{aligned}\dot{E}_k^{\mathrm{tot}}=&\frac{d}{dt}\left(\frac{1}{2}M_k\mathbf{U}_k^2\right)+\sum_l\frac{1}{2}\dot{M}_{kl}\left(\frac{\mathbf{U}_{kl}}{2}\right)^2\\&+\sum_{li}f_{kl}(\mathbf{x}_i)\left(\mathbf{J}_{\epsilon i}'-\Pi_i'\cdot\frac{\mathbf{U}_{kl}}{2}\right)\cdot\mathbf{r}_{kl}\\&+\sum_{li}f_{kl}(\mathbf{x}_i)\left(\epsilon_i'-m\mathbf{v}_i'\cdot\frac{\mathbf{U}_{kl}}{2}\right)\mathbf{x}_i'\cdot\mathbf{U}_{kl}.\end{aligned} \tag{27}$$

This equation has a natural physical interpretation. The first term represents the translational kinetic energy of the DP as a whole. The remaining terms represent the internal energy E_k. This is a purely thermodynamic quantity which cannot depend on the overall velocity of the DP, i.e., it must be Galilean invariant. This is easily checked as the relevant terms all depend on velocity differences only.

The $\dot{M}_{kl}$ term represents the kinetic energy received through mass exchange with neighboring DP's. As will become evident when we turn to the averaged description, the term involving the momentum and energy fluxes represents the work done on the DP by its neighbors and the heat conducted from them. The ϵ_i' term represents the energy received by the DP due to the same ''boundary twisting'' effect that was found in the mass equation. Upon averaging, the last term proportional to $\mathbf{v}_i'$ will be shown to be relatively small since $\langle\mathbf{v}_i'\rangle=0$ in our approximations. This is true also in the mass and momentum equations. Equations (14), (18), and (27) have the coarse-grained form that will remain in the final DPD equations. Note, however, that they retain the full microscopic information about the MD system, and for that reason they are time reversible. Equation (18), for instance, contains only terms of even order in the velocity. In the next section terms of odd order will appear when this equation is averaged.

It can be seen that the rate of change of momentum in Eq. (18) is given as a sum of separate pairwise contributions from the other particles, and that these terms are all odd under the exchange $l\leftrightarrow k$. Thus the particles interact in a pairwise fashion and individually fulfill Newton's third law; in other words, momentum conservation is again explicitly upheld. The same symmetries hold for the mass conservation equation (14) and energy equation (25).

III. DERIVATION OF DISSIPATIVE PARTICLE DYNAMICS: AVERAGE AND FLUCTUATING FORCES

We can now investigate the average and fluctuating parts of Eqs. (27), (18), and (14). In so doing we shall need to draw on a hydrodynamic description of the underlying molecular dynamics and construct a statistical mechanical description of our dissipative particle dynamics. For concreteness we shall take the hydrodynamic description of the MD system in question to be that of a simple Newtonian fluid [1]. This is known to be a good description for MD fluids based on Lennard-Jones or hard sphere potentials, particularly in three dimensions [3]. Here we shall carry out the analysis for systems in two spatial dimensions; the generalization to three dimensions is straightforward, the main difference being of a practical nature as the Voronoi construction becomes more involved.

We shall begin by specifying a scale separation between the dissipative particles and the molecular dynamics particles by assuming that

$$|\mathbf{x}_i-\mathbf{x}_j|\ll|\mathbf{r}_k-\mathbf{r}_l|, \tag{28}$$

where $\mathbf{x}_i$ and $\mathbf{x}_j$ denote the positions of neighboring MD particles. Such a scale separation is in general necessary in order for the coarse-graining procedure to be physically meaningful. Although for the most part in this paper we are thinking of the molecular interactions as being mediated by short-range forces such as those of Lennard-Jones type, a local description of the interactions will still be valid for the case of long-range Coulomb interactions in an electrostatically neutral system, provided that the screening length is shorter than the width of the overlap region between the dissipative particles. Indeed, as we shall show here, the result of doing a local averaging is that the original Newtonian equations of motion for the MD system become a set of Langevin equations for the dissipative particle dynamics. These Langevin equations admit an associated Fokker-Planck equation. An associated fluctuation-dissipation relation relates the amplitude of the Langevin force to the temperature and damping in the system.

It is observed that Langevin equations suffer from the ambiguity of the Itô-Stratonovitch dilemma. However, while this dilemma is important in principle, we will return to show that the difference between the Itô and Stratonovitch interpretations is negligible in the present context.

A. Definition of ensemble averages

With the mesoscopic variables now available, we need to define the correct average corresponding to a dynamical state of the system. Many microstates of the MD system are consistent with a given value of the set $\{\mathbf{r}_k,M_k,\mathbf{U}_k,E_k\}$. Assuming detailed balance on the microscopic level of the MD system we may rely on the standard hypothesis in statistical mechanics—that every microstate is equally probable [24]. In the following we shall average over all those microstates that have the same values of the mesocopic variables $\{\mathbf{r}_k,M_k,\mathbf{U}_k,E_k\}$, taking the set $\{\mathbf{r}_k\}$ to be given. Now, while these microstates give rise to the same values $\{\mathbf{r}_k,M_k,\mathbf{U}_k,E_k\}$ upon spatial coarse graining, they will evolve differently in time. Hence, the time derivatives of the set $\{\mathbf{r}_k,M_k,\mathbf{U}_k,E_k\}$, now considered as variables, will be different for different microstates. In other words, the fluxes of mass, momentum, and energy will have fluctuating parts.

Using the averaging described above, it is possible, at least in principle, to compute the average MD particle velocity $\langle\mathbf{v}\rangle$ *between* dissipative particle centers, given $\{\mathbf{r}_k,M_k,\mathbf{U}_k,E_k\}$. This velocity depends in general on all neighboring dissipative particle velocities. However, for simplicity we shall employ only a ''nearest neighbor'' approximation, which consists in assuming that $\langle \mathbf{v} \rangle$ interpolates linearly between the two nearest dissipative particles. This implies that in the overlap region between dissipative particles k and l

$$\langle \mathbf{v}' \rangle = \langle \mathbf{v}' \rangle (\mathbf{x}) = \frac{\mathbf{x}' \cdot \mathbf{r}_{kl}}{r_{kl}^2} \mathbf{U}_{kl}, \tag{29}$$

where the primes are defined in Eqs. (10) and $r_{kl} = |\mathbf{r}_k - \mathbf{r}_l|$. The above approximation is likely to be the most significant one in our entire development as it neglects variations in the velocity field in the direction normal to $\mathbf{e}_{kl}$. [See Sec. IV B where it is shown that the fluctuations linked to the dissipation associated with the velocity gradient of Eq. (29) are smaller than those linked to the full gradient.]

At the end of our development approximate distributions for $\mathbf{U}_k$'s and E_k's will follow from the Fokker-Planck equations. These distributions refer to the larger equilibrium ensemble that contains all fluctuations in $\{\mathbf{r}_k, M_k, \mathbf{U}_k, E_k\}$, and not only in the fluxes of these quantities.

A preliminary mathematical observation is useful in splitting the equations of motion into average and fluctuating parts. Let $r(\mathbf{x})$ be an arbitrary, slowly varying function on the a^2/r_{kl} scale. Then we shall employ the approximation corresponding to a linear interpolation between DP centers that $r(\mathbf{x}) = (1/2)(r_k + r_l)$ where $\mathbf{x}$ is a position in the overlap region between DP's k and l and r_k and r_l are values of the function r associated with the DP centers k and l, respectively. Then

$$\begin{aligned} \sum_i f_{kl}(\mathbf{x}_i) r(\mathbf{x}) &\approx \int dx\, dy \frac{\rho_k + \rho_l}{2} f_{kl}(\mathbf{x}) \frac{r_k + r_l}{2} \\ &\approx \frac{l_{kl}}{2a^2} \frac{\rho_k + \rho_l}{2} \frac{r_k + r_l}{2} \int_{-\infty}^{\infty} dx' \\ &\quad \times \cosh^{-2}(x' r_{kl}/a^2) \\ &= \frac{l_{kl}}{r_{kl}} \frac{\rho_k + \rho_l}{2} \frac{r_k + r_l}{2}, \end{aligned} \tag{30}$$

where $(\rho_k + \rho_l)/2$ is the MD particle number density and we have used the identity $\tanh'(x) = \cosh^{-2}(x)$. We will also need the first moment in $\mathbf{x}'$,

$$\begin{aligned} \sum_i f_{kl}(\mathbf{x}_i) \mathbf{x}_i' r(\mathbf{x}_i) &\approx \int dx dy \frac{\rho_k + \rho_l}{2} f_{kl}(\mathbf{x}) \mathbf{x}' \frac{r_k + r_l}{2} \\ &\approx \frac{1}{2a^2} \frac{\rho_k + \rho_l}{2} \frac{r_k + r_l}{2} \int dx\, dy \\ &\quad \times \cosh^{-2}\left(\frac{x r_{kl}}{a^2} \right) y \mathbf{i}_{kl} \\ &= \frac{l_{kl}}{2 r_{kl}} L_{kl} \frac{\rho_k + \rho_l}{2} \frac{r_k + r_l}{2} \mathbf{i}_{kl}, \end{aligned} \tag{31}$$

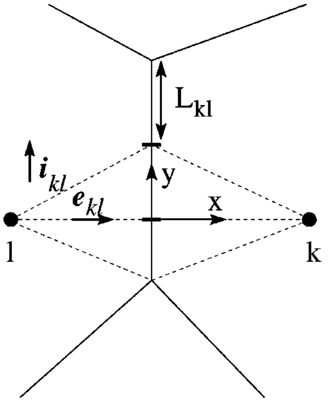

FIG. 3. Two interacting Voronoi cells. The length of the intersection between DP's k and l is l_{kl}, the shift from the center of the intersection between $\mathbf{r}_{kl}$ and l_{kl} is L_{kl} ($L_{kl} = 0$ when $\mathbf{r}_{kl}$ intersects l_{kl} in the middle), and the unit vector $\mathbf{i}_{kl}$ is normal to $\mathbf{e}_{kl}$. The coordinate system x-y used for the integration has its origin on the intersection.

where the unit vectors $\mathbf{e}_{kl} = \mathbf{r}_{kl}/r_{kl}$ and $\mathbf{i}_{kl}$ are shown in Fig. 3, we have used the fact that the integral over $x \mathbf{e}_{kl} \cosh^{-2}(\cdots)$ vanishes since the integrand is odd, and the last equation follows by the substitution $x \rightarrow (a^2/r_{kl}) x$. In contrast to the vector $\mathbf{e}_{kl}$ the vector $\mathbf{i}_{kl}$ is even under the exchange $k \leftrightarrow l$, as is L_{kl}. This is a matter of definition only as it would be equally permissible to let $\mathbf{i}_{kl}$ and L_{kl} be odd under this exchange. However, it is important for the symmetry properties of the fluxes that $\mathbf{i}_{kl}$ and L_{kl} have the same symmetry under $k \leftrightarrow l$.

B. The mass conservation equation

Taking the average of Eq. (14), we observe that the first term vanishes if Eq. (29) is used, and the second term follows directly from Eq. (31). We thus obtain

$$\dot{M}_k = \sum_l (\langle \dot{M}_{kl} \rangle + \tilde{\dot{M}}_{kl}), \tag{32}$$

where

$$\langle \dot{M}_{kl} \rangle = \sum_{li} f_{kl} m(\mathbf{x}_i) \langle \mathbf{x}_i' \rangle \cdot \mathbf{U}_{kl} = \frac{l_{kl}}{2 r_{kl}} L_{kl} \frac{\rho_k + \rho_l}{2} \mathbf{i}_{kl} \cdot \mathbf{U}_{kl}, \tag{33}$$

and $\tilde{\dot{M}}_{kl} = \dot{M}_{kl} - \langle \dot{M}_{kl} \rangle$. The finite value of $\langle \dot{M}_{kl} \rangle$ is caused by the relative DP motion *perpendicular* to $\mathbf{e}_{kl}$. This is a geometric effect intrinsic to the Voronoi lattice. When particles move the Voronoi boundaries change their orientation, and this boundary twisting causes mass to be transferred between DP's. This mass variation will be visible both in the energy flux and in the momentum flux. It will later be shown that the effect of mass fluctuations in the momentum and energy equations may be absorbed in the force and heat-flux fluctuations.

In the following we shall neglect the fluctuations in the updating of the DP masses, while we shall keep the effect of mass fluctuations in the energy and momentum equations. This means that the forces and energy fluxes will still be correctly captured, but that we will rely on the *averaged* variations in the mass only. This is an approximation as the microscopic velocities will cause mass fluctuations. However, since the DP volumes are evolved according to $\{\mathbf{r}_k\}$, which are determined by the $\mathbf{P}_k$'s, the DP volumes fluctuate as they should and we are neglecting only fluctuations in the mass density. Since the variance of these fluctuations corresponds directly to the variance in the local pressure (see Sec. IV A), they are limited and vary as $1/N_k$, where N_k is the number of MD particles inside a given DP_k.

C. The momentum conservation equation

Using Eq. (33) we may split Eq. (18) into average and fluctuating parts to get

$$\frac{d\mathbf{P}_k}{dt}=M_k\mathbf{g}+\sum_l \langle \dot{M}_{kl}\rangle \frac{\mathbf{U}_k+\mathbf{U}_l}{2}+\sum_{li} f_{kl}(\mathbf{x}_i)\langle \mathbf{\Pi}_i\rangle\cdot \mathbf{r}_{kl}$$
$$+\sum_i f_{kl}(\mathbf{x}_i)m\langle \mathbf{v}_i'\mathbf{x}_i'\rangle\cdot\mathbf{U}_{kl}+\sum_l \tilde{\mathbf{F}}_{kl}, \tag{34}$$

where the fluctuating force or, equivalently, the momentum flux is

$$\tilde{\mathbf{F}}_{kl}=\sum_i f_{kl}(\mathbf{x}_i)[(\mathbf{\Pi}_i-\langle\mathbf{\Pi}_i\rangle)\cdot\mathbf{r}_{kl}+m(\mathbf{v}_i'\mathbf{x}_i'-\langle\mathbf{v}_i'\mathbf{x}_i'\rangle)\cdot\mathbf{U}_{kl}]$$
$$+\dot{\tilde{M}}_{kl}\frac{\mathbf{U}_k+\mathbf{U}_l}{2}. \tag{35}$$

Note that by definition $\tilde{\mathbf{F}}_{lk}=-\tilde{\mathbf{F}}_{kl}$. The fact that we have absorbed mass fluctuations with the fluctuations in $\tilde{\mathbf{F}}_{kl}$ deserves a comment. In general, force fluctuations will cause mass fluctuations, which in turn will couple back to cause momentum fluctuations. The time scale over which this will happen is the viscous diffusion time $t_\eta=r_{kl}^2/\eta$, where η is the dynamic viscosity of the MD system. This is the time it takes for a velocity perturbation to decay over a distance of r_{kl}. Perturbations mediated by the pressure, i.e., sound waves, will have a shorter time. In the following we shall need to make the assumption that the forces are Markovian, and it is clear that this assumption may only be valid on time scales larger than t_η. Since the time scale of a hydrodynamic perturbation of size l, say, is also given as a viscous diffusion time, but with the length scale l, l^2/η this restriction implies the scale separation requirement $r_{kl}^2 \ll l^2$, consistent with the scale r_{kl} being mesoscopic.

Since $\langle\mathbf{\Pi}_i\rangle$ is in general dissipative in nature, Eq. (34) and its mass and energy analogs will be referred to as DPD1. It is at the point of taking the average in Eq. (34) that time reversibility is lost. Note, however, that we do not claim to treat the introduction of irreversibility into the problem in a mathematically rigorous way. This is a very difficult problem in general, which so far has been realized by rigorous methods only in the case of some very simple dynamical systems with well-defined ergodic properties [25–27]. We shall instead use the constitutive relation for a Newtonian fluid which, as noted earlier, is an emergent property of Lennard-Jones and hard sphere MD systems, to give Eq. (34) a concrete content. The momentum-flux tensor then has the following simple form:

$$\rho\langle\mathbf{\Pi}_i\rangle=m\rho\mathbf{v}\mathbf{v}+\mathbf{I}p-\eta(\nabla\mathbf{v}+(\nabla\mathbf{v})^T), \tag{36}$$

where p is the pressure and $\mathbf{v}$ the average velocity of the MD fluid, ^{T} denotes the transpose, and $\mathbf{I}$ is the identity tensor [1]. In the above equation we have for simplicity assumed that the bulk viscosity $\zeta=(2/d)\eta$ where d is the space dimension 2. The modifications to include an independent ζ are completely straightforward.

Using the assumption of linear interpolation [Eq. (29)], the advective term $\rho\mathbf{v}\mathbf{v}$ vanishes in the frame of reference of the overlap region since there $\mathbf{v}'\approx\mathbf{0}$. The velocity gradients in Eq. (36) may be evaluated using Eq. (29); the result is

$$\nabla\mathbf{v}+(\nabla\mathbf{v})^T=\frac{1}{r_{kl}}(\mathbf{e}_{kl}\mathbf{U}_{kl}+\mathbf{U}_{kl}\mathbf{e}_{kl}). \tag{37}$$

Note further that $\Sigma_l l_{kl}$ is in fact a surface integral over the DP surface. Consequently,

$$\sum_l l_{kl}\mathbf{e}_{kl}g_k=\mathbf{0} \tag{38}$$

for any function g_k that does not depend on l. In particular, we have $\Sigma_l l_{kl}\mathbf{e}_{kl}(p_k+p_l)/2=-\Sigma_l l_{kl}\mathbf{e}_{kl}p_{kl}/2$, where $p_{kl}=p_k-p_l$. Combining Eqs. (36), (30), and (37), Eq. (34) then takes the form

$$\frac{d\mathbf{P}_k}{dt}=M_k\mathbf{g}+\sum_l\langle\dot{M}_{kl}\rangle\frac{\mathbf{U}_k+\mathbf{U}_l}{2}-\sum_l l_{kl}\bigg(\frac{p_{kl}}{2}\mathbf{e}_{kl}$$
$$+\frac{\eta}{r_{kl}}[\mathbf{U}_{kl}+(\mathbf{U}_{kl}\cdot\mathbf{e}_{kl})\mathbf{e}_{kl}]\bigg)+\sum_l\tilde{\mathbf{F}}_{kl}, \tag{39}$$

where we have assumed that the pressure p, as well as the average velocity, interpolates linearly between DP centers, and we have omitted the $\langle\mathbf{v}_i'\mathbf{x}_i'\rangle\approx 0$ term. Note that all terms except the gravity term on the right hand side of Eq. (39) are odd when $k\leftrightarrow l$. This shows that Newton's third law is unaffected by the approximations made and that momentum conservation holds exactly. The same statements can be made for the mass equation and the energy equation. The pressure will eventually follow from an equation of state of the form $p_k=p(E_k,V_k,M_k)$, where V_k is the volume and M_k is the mass of DP k.

D. The energy conservation equation

Splitting Eq. (27) into an average and a fluctuating part gives

$$\dot{E}_k=\sum_{li} f_{kl}(\mathbf{x}_i)\bigg(\langle\mathbf{J}_{\epsilon i}'\rangle-\langle\mathbf{\Pi}_i'\rangle\cdot\frac{\mathbf{U}_{kl}}{2}\bigg)\cdot\mathbf{r}_{kl}+\sum_{li} f_{kl}(\mathbf{x}_i)$$
$$\times\langle\epsilon_i'\mathbf{x}_i'\rangle\cdot\mathbf{U}_{kl}+\sum_l\frac{1}{2}\langle\dot{M}_{kl}\rangle\bigg(\frac{\mathbf{U}_{kl}}{2}\bigg)^2-\sum_l\tilde{\mathbf{F}}_{kl}\cdot\frac{\mathbf{U}_{kl}}{2}+\tilde{q}_{kl}, \tag{40}$$

where we have defined

$$\tilde{q}_{kl}=\sum_i f_{kl}(\mathbf{x}_i)(\mathbf{J}'_{\epsilon i}-\langle\mathbf{J}'_{\epsilon i}\rangle)\cdot\mathbf{r}_{kl}+\frac{\dot{\tilde{M}}_{kl}}{2}\left(\frac{\mathbf{U}_{kl}}{2}\right)^2+\sum_i f_{kl}(\mathbf{x}_i)\times\left[(\epsilon'_i\mathbf{x}'_i-\langle\epsilon'_i\mathbf{x}'_i\rangle)-m\frac{\mathbf{U}_{kl}}{2}\cdot\mathbf{v}'_i\mathbf{x}'_i\right]\cdot\mathbf{U}_{kl}, \tag{41}$$

i.e., the fluctuations in the heat flux also contains the energy fluctuations caused by mass fluctuations. This is like the momentum case.

Note that in taking the average in Eq. (40) the $\mathbf{\Pi}\cdot\mathbf{U}_{kl}$ product presents no problem as $\mathbf{U}_{kl}$ is kept fixed under this average. If we had averaged over different values of $\mathbf{U}_{kl}$ the product of velocities in $\mathbf{\Pi}\cdot\mathbf{U}_{kl}$ would have caused difficulties. Equation (40) is the third component in the description at the DPD1 level.

The average of the energy flux vector $\mathbf{J}_\epsilon$ is taken to have the general form [1]

$$\rho\langle\mathbf{J}_\epsilon\rangle=\epsilon\mathbf{v}+\sigma\cdot\mathbf{v}-\lambda\boldsymbol{\nabla}T \tag{42}$$

where $\sigma=\mathbf{\Pi}-\rho\mathbf{v}\mathbf{v}$ is the stress tensor, λ the thermal conductivity, and T the local temperature. Note that in Eq. (27) only $\mathbf{J}'_\epsilon$ appears. Since $\mathbf{v}'\approx\mathbf{0}$ we have $\langle\mathbf{J}'_\epsilon\rangle=-\lambda\boldsymbol{\nabla}T$. Averaging of Eq. (40) gives

$$\dot{E}_k=-\sum_l l_{lk}\lambda\frac{T_{kl}}{r_{kl}}-\sum_l l_{lk}\left(\frac{p_k+p_l}{2}\mathbf{e}_{kl}-\frac{\eta}{r_{kl}}\times[\mathbf{U}_{kl}+(\mathbf{U}_{kl}\cdot\mathbf{e}_{kl})\mathbf{e}_{kl}]\right)\cdot\frac{\mathbf{U}_{kl}}{2}+\sum_l\frac{1}{2}\langle\dot{M}_{kl}\rangle\left(\frac{\mathbf{U}_{kl}}{2}\right)^2+\frac{l_{kl}}{4r_{kl}}L_{kl}\mathbf{i}_{kl}\cdot\mathbf{U}_{kl}\left(\frac{E_k}{V_k}+\frac{E_l}{V_l}\right)-\sum_l\tilde{\mathbf{F}}_{kl}\cdot\frac{\mathbf{U}_{kl}}{2}+\tilde{q}_{kl}, \tag{43}$$

where $T_{kl}=T_k-T_l$ is the temperature difference between DP's k and l, and we have used linear interpolation to write $\langle\epsilon'_1\rangle=(1/2)(E_k/V_k+E_l/V_l)$. The first term above describes the heat flux according to Fourier's law. The next nonfluctuating terms, which are multiplied by $\mathbf{U}_{kl}/2$, represent the (rate of) work done by the interparticle forces, and the $\tilde{\mathbf{F}}_{kl}$ term represents the work done by the fluctuating force.

As has been pointed out by Avalos and Mackie and by Español [16,17], the work done by $\tilde{\mathbf{F}}_{kl}$ has the effect that it increases the thermal motion of the DP's at the expense of a reduction in E_k. This is the case here as well since the above $\tilde{\mathbf{F}}_{kl}\cdot\mathbf{U}_{kl}$ term always has a positive average due to the positive correlation between the force and the velocity increments.

Equation (43) is identical in form to the energy equation postulated by Avalos and Mackie [16], save for the fact that here the conservative force $[(p_k+p_l)/2]\mathbf{e}_{kl}\cdot\mathbf{U}_{kl}/2$ (which sums to zero under Σ_k) is present. The pressure forces in the present case correspond to the conservative forces in conventional DPD—it will be observed that they are both derived from a potential. However, while the conservative force in conventional DPD must be thought to be carried by some field external to the particles, the pressure force in our model has its origin within the particles themselves. There is also a small difference between the present form of Fourier's law and the description of thermal conduction employed by Avalos and Mackie. While the heat flux here is taken to be linear in differences in T, Avalos and Mackie use a flux linear in differences in $(1/T)$. As both transport laws are approximations valid to lowest order in differences in T, they should be considered equivalent.

With the internal energy variable at hand it is possible to update the pressure and temperature T of the DP's provided an equation of state for the underlying MD system is assumed, and written in the form $P=P(E,V,N)$ and $T=T(E,V,N)$. For an ideal gas these are the well-known relations $PV=(2/d)E$ and $k_BT=(2/d)(E/N)$.

Note that we need only the average evolution of the pressure and temperature. The fluctuations of p are already contained in $\tilde{\mathbf{F}}_{kl}$ and the effect of temperature fluctuations is contained within $\tilde{q}_{kl}$.

At this point we may compare the forces arising in the present model to those used in conventional DPD. In conventional DPD the forces are pairwise and act in a direction parallel to $\mathbf{e}_{kl}$, with a conservative part that depends only on r_{kl} and a dissipative part proportional to $(\mathbf{U}_{kl}\cdot\mathbf{e}_{kl})\mathbf{e}_{kl}$ [8,9,28]. The forces in our version of DPD are pairwise too. The analog of the conservative force, $l_{kl}(p_{kl}/2)\mathbf{e}_{kl}$, is central and its $\mathbf{r}$ dependence is given by the Voronoi lattice. When there is no overlap l_{kl} between dissipative particles their forces vanish. (A cutoff distance, beyond which no physical interactions are permitted, was also present in the earlier versions of DPD—see, for example, Ref. [8]—where it was introduced to simplify the numerical treatment.) Due to the existence of an overlap region in our model, the dissipative force has both a component parallel to $\mathbf{e}_{kl}$ and a component parallel to the relative velocity $\mathbf{U}_{kl}$. However, due to the linear nature of the stress-strain relation in the Newtonian MD fluid studied here, this force has the same simple linear velocity dependence that has been postulated in the literature.

The friction coefficient is simply the viscosity η of the underlying fluid times the geometric ratio l_{kl}/r_{kl}. As has been pointed out both in the context of DPD [14] and elsewhere, the viscosity is generally *not* proportional to a friction coefficient between the particles. After all, conservative systems like MD are also described by a viscosity. Generally the viscosity will be caused by the combined effect of particle interaction (dissipation, if any) and the momentum transfer caused by particle motion. The latter contribution is proportional to the mean free path. The fact that the MD viscosity η, the DPD viscosity, and the friction coefficient are one and the same therefore implies that the mean free path effectively vanishes. This is consistent with the space-filling nature of the particles. See Sec. VI B for a further discussion of the zero viscosity limit.

Note that constitutive relations like Eqs. (36) and (42) are usually regarded as components of a top-down or macroscopic description of a fluid. However, any bottom-up mesoscopic description necessarily relies on the use of some kind of averaging procedure; in the present context, these relations represent a natural and convenient although by no means a necessary choice of average. The derivation of emergent constitutive relations is itself part of the program of nonequilibrium statistical mechanics (kinetic theory), which provides a link between the microscopic and macroscopic levels. However, as noted above, no general and rigorous procedure for deriving such relations has hitherto been realized; in the present theoretical treatment, such assumed constitutive relations are therefore a necessary input in the linking of the microscopic and mesoscopic levels.

IV. STATISTICAL MECHANICS OF DISSIPATIVE PARTICLE DYNAMICS

In this section we discuss the statistical properties of the DP's with the particular aim of obtaining the magnitudes of $\tilde{\mathbf{F}}_{kl}$ and $\tilde{q}_{kl}$. The discussion is based on the conventional Fokker-Planck description of DPD [16].

It is not straightforward to obtain a general statistical mechanical description of the DP system. The reason is that the DP's, which exchange mass, momentum, energy, and volume, are not captured by any standard statistical ensemble. For the grand canonical ensemble, the system in question is defined as the matter within a fixed volume, and in the case of the isobaric ensemble the particle number is fixed. Neither of these requirements holds for a dissipative particle in general.

A system that exchanges mass, momentum, energy, and volume without any further restrictions will generally be ill defined as it will lose its identity in the course of time. The DP's, of course, remain well defined by virtue of the coupling between the momentum and volume variables: The DP volumes are defined by the positions of the DP centers and the DP momenta govern the motion of the DP centers. Hence the quantities that are exchanged with the surroundings are not independent and the ensemble must be constructed accordingly.

However, for present purposes we shall leave aside the interesting challenge of designing the statistical mechanical properties of such an ensemble, and derive the magnitude of $\tilde{\mathbf{F}}_{kl}$ and $\tilde{q}_{kl}$ from an approximation. This approximation is justifiable from the assumption that $\tilde{\mathbf{F}}_{kl}$ and $\tilde{q}_{kl}$ have a negligible correlation time. It follows that their properties may be obtained from the DP behavior on such short time scales that the DP centers may be assumed fixed in space. As a result, we may take either the DP volume or the system of MD particles as fixed for the relevant duration of time. Hence, for the purpose of obtaining $\tilde{\mathbf{F}}_{kl}$ and $\tilde{q}_{kl}$, we may use either the isobaric ensemble applied to the DP system, or the grand canonical ensemble applied to the MD system. The analysis of the DP system using the isobaric ensemble follows the standard procedure using the Fokker-Planck equation, and the result for the equilibrium distribution is valid only in the short time limit. The analysis of the MD system corresponding to the grand canonical ensemble could be conducted along similar lines.

The Langevin equations that have been discussed in the literature have all been given the Itô interpretation [14,16,17,29]. The present equations are derived on the conceptual basis of molecules, and it is clear that the fluctuating forces cannot be strictly δ correlated. On the contrary, they must have smooth correlation functions, and consequently the Stratonovitch interpretation is the appropriate one [29]. We shall later show that on the level of the Fokker-Planck equations there is no significant contradiction between the two interpretations. For that reason and in order to connect with the existing analyses [14,16,17] we will apply the Itô interpretation in what follows.

A. The thermal forces

We consider the system of $N_k \gg 1$ MD particles inside a given DP$_k$ at a given time, say, all the MD particles with positions that satisfy $f_k(\mathbf{x}_i) > 1/2$ at time t_0. At later times it will be possible to associate a certain volume per particle with these particles, and by definition the system they form will exchange volume and energy but not mass. We consider all the remaining DP's as a thermodynamic bath with which DP$_k$ is in equilibrium. The system defined in this way will be described by the Gibbs free energy and the isobaric ensemble. Due to the diffusive spreading of MD particles, this system will only initially coincide with the DP; during this transient time interval, however, we may treat the DP's as systems of fixed mass and describe them by the approximation $\langle \dot{M}_{kl} \rangle = 0$. In fact, the $\langle \dot{M}_{kl} \rangle = 0$ approximation may represent a practical numerical strategy for which the following analysis will be exact.

The magnitudes of $\tilde{q}$ and $\tilde{\mathbf{F}}$ follow in the form of fluctuation-dissipation relations from the Fokker-Planck equivalent of our Langevin equations. The mathematics involved in obtaining fluctuation-dissipation relations is essentially well known from the literature [9], and our analysis parallels that of Avalos and Mackie [16]. However, the fact that the conservative part of the conventional DP forces is here replaced by the pressure and that the present DP's have a variable volume makes a separate treatment enlightening.

The probability $\rho(V_k, \mathbf{P}_k, E_k)$ of finding DP$_k$ with a volume V_k, momentum $\mathbf{P}_k$, and internal energy E_k is then proportional to $\exp(S_T/k_B)$ where S_T is the entropy of all DP's given that the values $(V_k, \mathbf{P}_k, E_k)$ are known for DP$_k$ [30]. If S' denotes the entropy of the bath we can write S_T as

$$\begin{aligned} S_T &= S'\left(V_T - V_k, \mathbf{P}_T - \mathbf{P}_k, E_T - \frac{P_k^2}{2M_k} - E_k \right) + S_k \\ &\approx S'(V_T, \mathbf{P}_T, E_T) - \frac{\partial S'}{\partial E}\left(E_k + \frac{P_k^2}{2M_k} \right) - \frac{\partial S'}{\partial V} V_k \\ &\quad - \frac{\partial S'}{\partial \mathbf{P}} \mathbf{P}_k + S_k, \end{aligned} \tag{44}$$

where the derivatives are evaluated at $(V_T, \mathbf{P}_T, E_T)$ and thus characterize the bath only. Assuming that $\mathbf{P}_T$ vanishes there is nothing in the system to give the vector $\partial S'/\partial \mathbf{P}$ a direction, and it must therefore vanish as well [24]. The other derivatives give the pressure p_0 and temperature T_0 of the bath, and we obtain

$$S_T = S'(V_T, \mathbf{P}_T, E_T) - \frac{1}{T_0}\left(G_k + \frac{P_k^2}{2M_k} \right), \tag{45}$$

where the Gibbs free energy has the standard form $G_k = E_k + p_0 V_k - T_0 S_k$. Since there is nothing special about DP$_k$ it immediately follows that the the full equilibrium distribution has the form

$$\rho^{\mathrm{eq}}=Z^{-1}(T_0,p_0)\exp\left(-\beta_0\sum_k\frac{P_k^2}{2M_k}+G_k\right), \tag{46}$$

where $\beta_0=1/(k_BT_0)$.

The distribution given in Eq. (46) implies that the total energy and momentum will fluctuate. These quantities are conserved, however, and the system of all DP's thus has three degrees of freedom fewer than Eq. (46) suggests. This is potentially important in the case of only a few DP's. In the thermodynamic limit, i.e., when the difference between the thermodynamic reservoir represented by a finite and infinite number of DP's is negligible, Eq. (46) is a good approximation for the computation of single DP quantities.

The temperature $T_k=(\partial S_k/\partial E_k)^{-1}$ and pressure $p_k=T_k(\partial S_k/\partial V_k)$ will fluctuate around the equilibrium values T_0 and p_0. The above distribution is analyzed by Landau and Lifshitz [24], who show that the fluctuations have the magnitude

$$\langle\Delta P_k^2\rangle=\frac{k_BT_0}{V_k\kappa_S},\quad \langle\Delta T_k^2\rangle=\frac{k_BT_0^2}{Vc_v}, \tag{47}$$

where the isentropic compressibility $\kappa_S=-(1/V)(\partial V/\partial P)_S$ and the specific heat capacity c_v are both intensive quantities. Comparing our expression with the distribution postulated by Avalos and Mackie, we have replaced the Helmholtz by the Gibbs free energy in Eq. (46). This is due to the fact that our DP's exchange volume as well as energy.

We write the fluctuating force as

$$\tilde{\mathbf{F}}_{kl}=\boldsymbol{\omega}_{kl\|}W_{kl\|}+\boldsymbol{\omega}_{kl\perp}W_{kl\perp}, \tag{48}$$

where, for reasons soon to become apparent, we have chosen to decompose $\tilde{\mathbf{F}}_{kl}$ into components parallel and perpendicular to $\mathbf{e}_{kl}$. The W's are defined as Gaussian random variables with the correlation function

$$\langle W_{kl\alpha}(t)W_{nm\beta}(t')\rangle=\delta_{\alpha\beta}\delta(t-t')(\delta_{kn}\delta_{lm}+\delta_{km}\delta_{ln}), \tag{49}$$

where α and β denote either $\perp$ or $\|$. The product of δ factors ensures that only equal vectorial components of the forces between a pair of DP's are correlated, while Newton's third law guarantees that $\boldsymbol{\omega}_{kl}=-\boldsymbol{\omega}_{lk}$. Likewise, the fluctuating heat flux takes the form

$$\tilde{q}_{kl}=\Lambda_{kl}W_{kl} \tag{50}$$

where W_{kl} satisfies Eq. (49) without the $\delta_{\alpha\beta}$ factor and energy conservation implies $\Lambda_{kl}=-\Lambda_{lk}$.

The force correlation function then takes the form

$$\begin{aligned}\langle\tilde{\mathbf{F}}_{kn}(t)\tilde{\mathbf{F}}_{lm}(t')\rangle&=(\boldsymbol{\omega}_{kn\perp}\boldsymbol{\omega}_{lm\perp}+\boldsymbol{\omega}_{kn\|}\boldsymbol{\omega}_{lm\|})\\&\quad\times(\delta_{kl}\delta_{nm}+\delta_{km}\delta_{ln})\delta(t-t')\\&\equiv\boldsymbol{\omega}_{klnm}(\delta_{kl}\delta_{nm}+\delta_{km}\delta_{ln})\delta(t-t'),\end{aligned} \tag{51}$$

where we have introduced the second order tensor $\boldsymbol{\omega}_{knlm}$.

It is a standard result in nonequilibrium statistical mechanics that a Langevin description of a dynamical variable $\mathbf{y}$,

$$\dot{\mathbf{y}}=\mathbf{a}(\mathbf{y})+\tilde{\mathbf{G}}(\mathbf{y}), \tag{52}$$

where $\tilde{\mathbf{G}}(\mathbf{y})=\boldsymbol{\omega}(\mathbf{y})W(t)$, is a δ correlated force so that $\langle W(t)W(0)\rangle=\delta(t)$. Equation (52) has a probabilistic representation in terms of the Fokker-Planck equation

$$\frac{\partial\rho(\mathbf{y},t)}{\partial t}=-\boldsymbol{\nabla}\cdot[\mathbf{a}(\mathbf{y})\rho(\mathbf{y})]+\frac{1}{2}\boldsymbol{\nabla}\boldsymbol{\nabla}:[\mathbf{A}(\mathbf{y})\rho(\mathbf{y})], \tag{53}$$

where $\boldsymbol{\nabla}$ denote derivatives with respect to $\mathbf{y}$ and $\rho(\mathbf{y},t)$ is the probability distribution for the variable $\mathbf{y}$ at time t, $\langle\tilde{\mathbf{G}}(\mathbf{y},t)\tilde{\mathbf{G}}(\mathbf{y},t')\rangle=\mathbf{A}\delta(t-t')$, and $\mathbf{A}$ is a symmetric tensor of rank 2 [31]. Equation (53) corresponds to the Itô interpretation [29] of our Langevin equations. In Sec. IV C and the Appendix we will return to show that the different interpretations are equivalent at the relevant order of approximations.

In the preceding paragraph, $\mathbf{G}$ denotes all the fluctuating terms in Eqs. (39) and (43). Using the above definitions it is a standard matter [9] to obtain the Fokker-Planck equation

$$\frac{\partial\rho}{\partial t}=(L_0+L_{\mathrm{DIS}}+L_{\mathrm{DIF}}),\rho \tag{54}$$

where

$$\begin{aligned}L_0&=-\sum_k\frac{\partial}{\partial\mathbf{r}_k}\cdot\mathbf{U}_k+\sum_{k\neq l}l_{kl}\left(\frac{\partial}{\partial\mathbf{P}_k}\cdot\mathbf{e}_{kl}\frac{p_{kl}}{2}\right.\\&\quad\left.+\frac{\partial}{\partial E_k}\mathbf{e}_{kl}\cdot\mathbf{U}_{kl}\frac{p_k+p_l}{4}\right),\\L_{\mathrm{DIS}}&=\sum_{k\neq l}l_{kl}\left[\frac{\partial}{\partial\mathbf{P}_k}\cdot\mathbf{F}_{kl}^D-\frac{\partial}{\partial E_k}\left(\frac{\mathbf{U}_{kl}}{2}\cdot\mathbf{F}_{kl}^D-\lambda\frac{T_{kl}}{r_{kl}}\right)\right],\\L_{\mathrm{DIF}}&=\frac{1}{2}\sum_{k\neq l}\left\{\boldsymbol{\omega}_{klkl}\cdot\frac{\partial}{\partial\mathbf{P}_k}\cdot\mathcal{L}_{kl}-\frac{\partial}{\partial E_k}\left[\boldsymbol{\omega}_{klkl}\cdot\frac{\mathbf{U}_{kl}}{2}\cdot\mathcal{L}_{kl}\right.\right.\\&\quad\left.\left.-\Lambda_{kl}^2\left(\frac{\partial}{\partial E_k}-\frac{\partial}{\partial E_l}\right)\right]\right\},\end{aligned} \tag{55}$$

$\mathbf{F}_{kl}^D=(\eta/r_{kl})[\mathbf{U}_{kl}+(\mathbf{U}_{kl}\cdot\mathbf{e}_{kl})\mathbf{e}_{kl}]$, and the sum $\Sigma_{k\neq l}$ runs over both k and l. The operator $\mathcal{L}_{kl}$ is defined as in Ref. [16]:

$$\mathcal{L}_{kl}=\left(\frac{\partial}{\partial\mathbf{P}_k}-\frac{\partial}{\partial\mathbf{P}_l}\right)-\frac{\mathbf{U}_{kl}}{2}\left(\frac{\partial}{\partial E_k}-\frac{\partial}{\partial E_l}\right). \tag{56}$$

The steady-state solution of Eq. (54) is already given by Eq. (46); following conventional procedures we can obtain the fluctuation-dissipation relations for $\boldsymbol{\omega}$ and Λ by inserting ρ^{eq} in Eq. (54).

Apart from the tensorial nature of $\boldsymbol{\omega}_{klkl}$ the operators L_{DIS} and L_{DIF} are essentially identical to those published earlier in conventional DPD [16,17]. However, the "Liouville" operator L_0 plays a somewhat different role as it contains the $\partial/\partial E_k$ term, corresponding to the fact that the pressure forces do work on the DP's to change their internal energy.

While $L_0\rho^{\mathrm{eq}}$ conventionally vanishes exactly by construction of the inter-DP forces, here it vanishes only to order $1/N_k$. In order to evaluate $L_0\rho^{\mathrm{eq}}$ we need the relationship

$$\frac{\partial}{\partial \mathbf{r}_k}=\frac{1}{2}\sum_{k\neq l} l_{kl}\mathbf{e}_{kl}\left(\frac{\partial}{\partial V_l}-\frac{\partial}{\partial V_k}\right), \tag{57}$$

which is derived by direct geometrical consideration of the Voronoi construction. By repeated use of Eq. (38) it is then a straightforward algebraic task to obtain

$$L_0\rho^{\mathrm{eq}}=\frac{\rho^{\mathrm{eq}}}{4}\sum_{k\neq l} l_{kl}\mathbf{e}_{kl}\cdot\mathbf{U}_k\left[\frac{\partial p_l}{\partial E_l}-\frac{p_{kl}T_{kl}}{k_BT_kT_l}\right], \tag{58}$$

which does not vanish identically. However, note that if we estimate $E_l\approx N_lk_BT$ we obtain $\partial p_l/\partial E_l\approx(1/N_k)(p_l/k_BT)$. Similarly, we may estimate p_{kl} and T_{kl} from Eq. (47) to obtain

$$\frac{p_{kl}T_{kl}}{k_BT_kT_l}\approx\frac{\sqrt{\Delta P^2\Delta T^2}}{k_BT_kT_l}=\frac{1}{N_k}\sqrt{\frac{N_k/V_k}{\kappa_S c_v T_0^2}}. \tag{59}$$

The last square root term is an intensive quantity of the order $p_0/(k_BT_0)$, as may be easily demonstrated for the case of an ideal gas. Since each separate quantity that is contained in the differences in the square brackets of Eq. (58) is of the order p_0/T_0 we have shown that they cancel up to relative order $1/N_k\ll 1$. In fact, it is not surprising that Langevin equations which approximate local gradients to first order only in the corresponding differences, like T_{kl}, give rise to a Fokker-Planck description that contains higher order correction terms.

Having shown that $L_0\rho^{\mathrm{eq}}$ vanishes to a good approximation we may proceed to obtain the fluctuation-dissipation relations from the equation $(L_{\mathrm{DIS}}+L_{\mathrm{DIF}})\rho^{\mathrm{eq}}=0$. It may be noted from Eq. (55) that this equation is satisfied if

$$\begin{gathered}\left(l_{kl}\mathbf{F}^D_{kl}+\frac{1}{2}\boldsymbol{\omega}_{klkl}\mathcal{L}_{kl}\right)\rho^{\mathrm{eq}}=0,\\ \left[l_{kl}\lambda\frac{T_{kl}}{r_{kl}}+\frac{1}{2}\Lambda^2_{kl}\left(\frac{\partial}{\partial E_k}-\frac{\partial}{\partial E_l}\right)\right]\rho^{\mathrm{eq}}=0.\end{gathered} \tag{60}$$

Using the identity

$$\mathbf{e}_{kl}\mathbf{e}_{kl}+\mathbf{i}_{kl}\mathbf{i}_{kl}=\mathbf{I}, \tag{61}$$

where $\mathbf{i}_{kl}$ is a vector normal to $\mathbf{e}_{kl}$, we may show that Eq. (60) implies that

$$\begin{gathered}\omega^2_{kl\|}=2\,\omega^2_{kl\perp}=4\,\eta k_B\Theta_{kl}\frac{l_{kl}}{r_{kl}},\\ \Lambda^2_{kl}=2k_BT_kT_l\lambda\frac{l_{kl}}{r_{kl}},\end{gathered} \tag{62}$$

where $\Theta^{-1}_{kl}=(1/2)(T_k^{-1}+T_l^{-1})$.

B. The Itô-Stratonovitch dilemma and the final equations of motion

Consider the integration of the momentum equation (39) $\mathbf{P}_k\rightarrow\mathbf{P}_k+\tilde{\mathbf{F}}_k dt$ plus the hydrodynamic terms. Observing from Eq. (62) that $\tilde{\mathbf{F}}_k$ depends on time through the dependence on the position and temperature, we need to decide whether to evaluate $\tilde{\mathbf{F}}_k$ at time t or $t+dt$ or some time in between. This is the well-known Itô-Stratonovitch dilemma. It is possible to show [29] that when the time correlation function of $\tilde{\mathbf{F}}_k$ is not strictly δ correlated, the Stratonovitch interpretation, where $\tilde{\mathbf{F}}_k$ is evaluated at time $(t+dt)/2$, is appropriate. In fact, with nonsingular correlation functions there is no dilemma, and the only reason for using the Itô interpretation is mathematical convenience.

With this convenience in mind we have applied the Itô interpretation in writing the Fokker-Planck equations. In the Appendix we derive the additional terms that enter the Fokker-Planck equation when we switch to the correct Stratonovitch interpretation. There we show that the correction terms are all of order $(1/\sqrt{N_k})$ or smaller. What importance can these terms have? To answer this question we note that Langevin descriptions always include some sort of hydrodynamic or macroscopic description that holds for the average behavior of the system. This necessarily implies that $N_k\gg 1$. A hydrodynamic description would be meaningless if it were sensitive to the removal or addition of single particles. The idea of keeping terms of relative order $1/N_k$ is thus inconsistent with the level of coarse graining used in the description. We have therefore discarded terms of this order throughout. It follows from this that Eqs. (62) remain correct.

In the Appendix it is shown that in passing between the Itô and Stratonovitch interpretations there is no modification of the Fokker-Planck equation due to the $\mathbf{r}_k$ dependence in Eq. (62). Likewise, the modification due to the temperature dependence in $\boldsymbol{\omega}_{kl}$ is of relative order $1/N_k$ only. The corresponding terms in the Langevin equations, the so-called spurious drift terms, are therefore safely negligible as well.

However, the situation is not so clear for the corrections due to the $\tilde{\mathbf{F}}\cdot\mathbf{U}_{kl}/2$ term in the Langevin energy equation, and so we discuss this issue here. In the Fokker-Planck equation only the $\partial/\partial E_k$ part of the L_{DIS} term is modified by the $\tilde{\mathbf{F}}\cdot\mathbf{U}_{kl}/2$ term. Hence, only the magnitude of the heat-flux fluctuations Λ_{kl} is affected, and not the momentum fluctuations. The Fokker-Planck equation decomposes into a momentum part and an energy part, and within the energy part Λ_{kl} receives a correction of relative order $1/\sqrt{N_k}$ which is discarded. In the Langevin equation (43), on the other hand, the $\tilde{\mathbf{F}}\cdot\mathbf{U}_{kl}/2$ term also needs to be compared with terms like ηU^2_{kl}. From the statistical mechanical relation Eq. (47) it may be seen that $T_{kl}\sim 1/\sqrt{N_k}$, while the equipartition principle gives $U^2_{kl}=k_BT/M_k\sim 1/N_k$. This means that the work terms in Eq. (43) are smaller than the heat conduction terms by a factor $1/\sqrt{N_k}$. Consequently, while the $\tilde{\mathbf{F}}\cdot\mathbf{U}_{kl}/2$ term can be discarded in the Fokker-Planck equation it should be kept in the Langevin equation. The result of doing this is the energy equation

$$\dot{E}_k = -\sum_l l_{lk}\lambda \frac{T_{kl}}{r_{kl}} - \sum_l l_{lk}\left(\frac{p_k+p_l}{2}\mathbf{e}_{kl} - \frac{\eta}{r_{kl}}\right.$$
$$\left.\times[\mathbf{U}_{kl} + (\mathbf{U}_{kl}\cdot\mathbf{e}_{kl})\mathbf{e}_{kl}]\right)\cdot\frac{\mathbf{U}_{kl}}{2} + \sum_l \frac{1}{2}\langle\dot{M}_{kl}\rangle\left(\frac{\mathbf{U}_{kl}}{2}\right)^2$$
$$+\frac{l_{kl}}{4r_{kl}}L_{kl}\mathbf{i}_{kl}\cdot\mathbf{U}_{kl}\left(\frac{E_k}{V_k}+\frac{E_l}{V_l}\right) - \sum_l \tilde{\mathbf{F}}'_{kl}\cdot\frac{\mathbf{U}_{kl}}{2}$$
$$-\frac{3}{2}\frac{l_{kl}}{r_{kl}}\eta k_B\Theta_{kl}\left(\frac{1}{M_l}+\frac{1}{M_k}\right) + \tilde{q}_{kl}, \tag{63}$$

where we have written $\tilde{\mathbf{F}}'_{kl}$ with a prime to denote that it is uncorrelated with $\mathbf{U}_{kl}$. In a numerical implementation this implies that $\tilde{\mathbf{F}}'_{kl}$ must be generated from a different random variable than $\tilde{\mathbf{F}}_{kl}$ which is used to update $\mathbf{U}_{kl}$. In other words, while Eq. (43) is to be subjected to the Stratonovitch interpretation the equivalent Eq. (70) is to be interpreted according to Itô, as may Eq. (39).

What is the physical significance of the different magnitude of the terms in the energy equation? If one tries to heat a pot, rubbing it is generally a less efficient means than the conduction from a hotplate. We have observed that the same is true when the heat conduction and work are due to spontaneous fluctuations. In Eq. (70) we could consistently have discarded all work terms, since they are order $1/\sqrt{N}$ compared to the conduction terms. However, we keep them both for comparison with existing work [16,17] and for the (rather unrealistic) event that the thermal conductivity λ vanishes, or becomes very small, while η does not. In this case the order $1/\sqrt{N}$ correction to Λ, which is derived in the Appendix, must be retained.

Equations (32), (39), and (70) together with Eq. (62) complete the derivation of our Voronoi based dissipative particle dynamics.

V. SIMULATIONS

While the present paper primarily deals with theoretical developments, we have carried out simulations to test the equilibrium behavior of the model in the isothermal case. This is a crucial test as the derivation of the fluctuating forces relies on the most significant approximations. The simulations are carried out using a periodic Voronoi tessellation described in detail elsewhere [32].

Figure 4 shows the relaxation process toward equilibrium of an initially motionless system. The DP temperature is measured as $\langle \mathbf{P}_k^2/(2M_k)\rangle$ for a system of DP's with internal energy equal to unity. The simulations were run for 4000 iterations of 4000 dissipative particles with a time step $dt = 0.0005$ using the molecular mass, density, and viscosity of water at 300 K. The Reynolds number (see Sec. VI B) is Re = 0.38. It can be seen that the convergence of the DP system toward the MD temperature is good, a result that provides strong support for the fluctuation-dissipation relations of Eq. (62).

VI. POSSIBLE APPLICATIONS

A. Multiscale phenomena

For most practical applications involving complex fluids, additional interactions and boundary conditions need to be specified. These too must be deduced from the microscopic dynamics, just as we have done for the interparticle forces. This may be achieved by considering a particulate description of the boundary itself and including molecular interactions between the fluid MD particles and other objects, such as particles or walls. Appropriate modifications can then be made on the basis of the momentum-flux tensor of Eq. (19), which is generally valid.

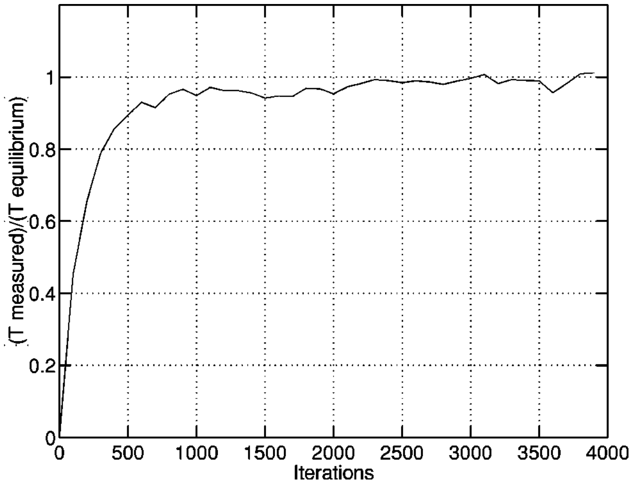

FIG. 4. The DPD temperature, averaged over 4000 dissipative particles, as a function of time (iteration number in the integration scheme), showing good convergence to the underlying equilibrium molecular dynamics temperature, which was fixed at 300 K. This simulation provides strong support for the approximations used to derive the fluctuation-dissipation relations in our DPD model from molecular dynamics.

Consider, for example, the case of a colloidal suspension, which is shown in Fig. 5. Beginning with the hydrodynamic

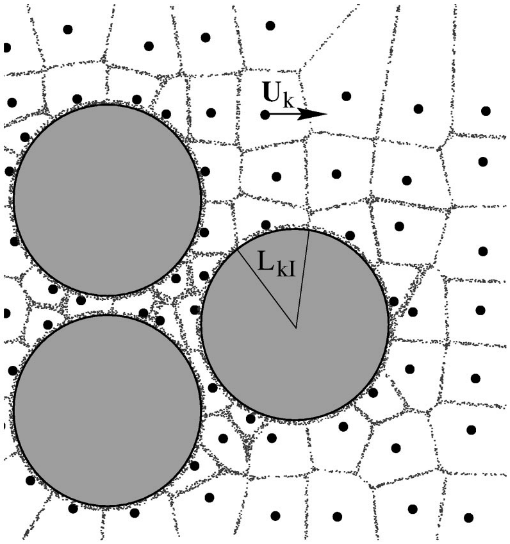

FIG. 5. Multiscale modeling of colloidal fluids. As usual, the dissipative particles are defined as cells in the Voronoi lattice. Note that there are four relevant length scales in this problem: the scale of the large, gray colloid particles, the two distinct scales of the dissipative particles in between and away from the colloids, and finally the molecular scale of the MD particles. These mediate the mesoscopic interactions and are shown as dots on the boundaries between dissipative and colloidal particles.

momentum-flux tensor Eq. (19) and Eq. (39), it is evident that we also need to define an interaction region where the DP-colloid forces act: the DP-colloid interaction may be obtained in the same form as the DP-DP interaction of Eq. (39) by making the replacement $l_{kl} \rightarrow L_{kI}$, where L_{kI} is the length [or area in three dimensions (3D)] of the arc segment where the dissipative particle meets the colloid (see Fig. 6) and the velocity gradient $r_{kl}^{-1}[(\mathbf{U}_{kl} \cdot \mathbf{e}_{kl})\mathbf{e}_{kl} + \mathbf{U}_{kl}]$ is that between the dissipative particle and the colloid surface. The latter may be computed using $\mathbf{U}_k$ and the velocity of the colloid surface together with a no-slip boundary condition on this surface. In Eq. (62) the replacement $l_{kl} \rightarrow L_{kI}$ must also be made.

Although previous DPD simulations of colloidal fluids have proved rather successful [10] at low to intermediate solid volume fractions, they break down for dense systems whose solid volume fraction exceeds a value of about 40%, because the existing method is unable to handle multiple length scale phenomena. However, our version of the algorithm provides the freedom to define dissipative particle sizes according to the local resolution requirements as illustrated in Fig. 6. In order to increase the spatial resolution where colloidal particles are within close proximity, it is necessary and perfectly admissible to introduce a higher density of dissipative particles there; this ensures that fluid lubrication and hydrodynamic effects are properly maintained. After these dissipative particles have moved it may be necessary to retile the DP system; this is easily achieved by distributing the mass and momentum of the old dissipative particles on the new ones according to their area (or volume in 3D). Considerations of space prevent us from discussing this problem further in the present paper, but we plan to report in detail on such dense colloidal particle simulations using our method in future publications. We note in passing that a wide variety of other complex systems exist where modeling and simulation are challenged by the presence of several simultaneous length scales, for example, in polymeric and amphiphilic fluids, particularly in confined geometries such as porous media [33].

B. The low viscosity limit and high Reynolds numbers

In the kinetic theory derived by Marsh, Backx, and Ernst [15] the viscosity is explicitly shown to have a kinetic contribution $\eta_K = \rho D/2$ where D is the DP self-diffusion coefficient and ρ the mass density. The kinetic contribution to the viscosity was measured by Masters and Warren [34] within the context of an improved theory. How then can the viscosity η used in our model be decreased to zero while kinetic theory puts the lower limit η_K to it?

To answer this question we must define a physical way of decreasing the MD viscosity while keeping other quantities fixed, or, alternatively rescale the system in a way that has the equivalent effect. The latter method is preferable as it allows the underlying microscopic system to remain fixed. In order to do this we nondimensionalize the DP momentum equation Eq. (39).

For this purpose we introduce the characteristic equilibrium velocity $U_0 = \sqrt{k_B T/M}$, and the characteristic distance r_0 as the typical DP size. Then the characteristic time $t' = r_0/U_0$ follows.

Neglecting gravity for the time being, Eq. (39) takes the form

$$\frac{d\mathbf{P}_k'}{dt'} = -\sum_l l_{kl}'\left(\frac{p_{kl}'}{2}\mathbf{e}_{kl} + \frac{1}{\text{Re}}[\mathbf{U}_{kl}' + (\mathbf{U}_{kl}' \cdot \mathbf{e}_{kl})\mathbf{e}_{kl}]\right) + \sum_l \frac{l_{kl}' L_{kl}'}{2r_{kl}'} \frac{\rho_k' + \rho_l'}{2} \mathbf{i}_{kl} \cdot \mathbf{U}_{kl}' \frac{\mathbf{U}_k' + \mathbf{U}_l'}{2} + \sum_l \tilde{\mathbf{F}}_{kl}', \tag{64}$$

where $\mathbf{P}_k' = \mathbf{P}_k/(MU_0)$, $p_{kl}' = p_{kl} r_0^2/(MU_0^2)$, $M = \rho r_0^2$ in 2D, the Reynolds number $\text{Re} = U_0 r_0 \rho/\eta$, and $\tilde{\mathbf{F}}_{kl}' = (r_0/MU_0^2)\tilde{\mathbf{F}}_{kl}$ and $\tilde{\mathbf{F}}_{kl}$ given by Eqs. (48) and (62). A small calculation then shows that if $\tilde{\mathbf{F}}_{kl}'$ is related to ω_{kl}' and t' as $\tilde{\mathbf{F}}_{kl}$ is related to ω_{kl} and t, then

$$\omega_{kl}'^2 \approx \frac{1}{\text{Re}} \frac{k_B T}{MU_0^2} \approx \frac{1}{\text{Re}}, \tag{65}$$

where we have neglected dimensionless geometric prefactors like l_{kl}/r_{kl} and used the fact that the ratio of the thermal to kinetic energy by definition of U_0 is 1.

The above results imply that when the DPD system is measured in nondimensionalized units everything is determined by the value of the mesoscopic Reynolds number Re. There is thus no observable difference in this system between increasing r_0 and decreasing η.

Returning to dimensional units again, the DP diffusivity may be obtained from the Stokes-Einstein relation [35] as

$$D = \frac{k_B T}{a r_0 \eta}, \tag{66}$$

where a is some geometric factor ($a = 6\pi$ for a sphere) and all quantities on the right hand side except r_0 refer directly to the underlying MD. As we are keeping the MD system fixed and increasing Re by increasing r_0, it is seen that D and hence η_K vanish in the process.

We note in passing that if D is written in terms of the mean free path λ, $D = \lambda\sqrt{k_B T/(\rho r_0^2)}$, and this result is compared with Eq. (73), we get $\lambda' = \lambda/r_0 \sim 1/r_0$ in 2D, i.e., the mean free path measured in units of the particle size decreases as the inverse particle size. This is consistent with the decay of η_K. The above argument shows that decreasing η is equivalent to keeping the microscopic MD system fixed while increasing the DP size, in which case the mean free path effect on viscosity is decreased to zero as the DP size is increased to infinity. It is in this limit that high Re values may be achieved.

Note that in this limit the thermal forces $\tilde{\mathbf{F}}_{kl} \sim \text{Re}^{-1/2}$ will vanish, and we are effectively left with a macroscopic, fluctuationless description. This is no problem when using the present Voronoi construction. However, the effectively spherical particles of conventional DPD will freeze into a colloidal crystal, i.e., into a lattice configuration [8,9], in this limit. Also, while conventional DPD has usually required calibration simulations to determine the viscosity, due to discrepancies between theory and measurements, the viscosity

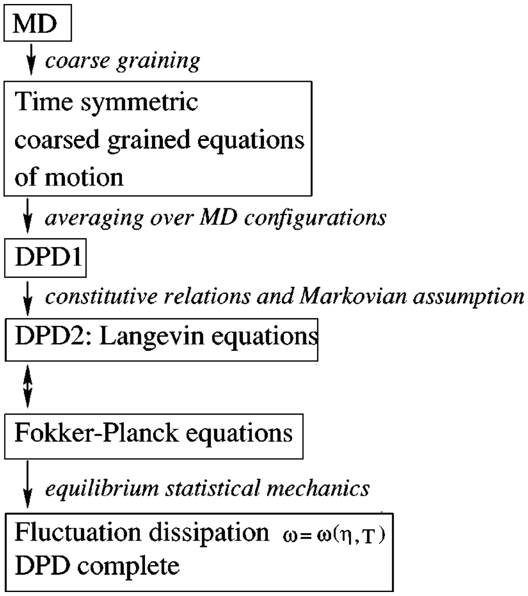

FIG. 6. Outline of the derivation of dissipative particle dynamics from molecular dynamics as presented in the present paper. The MD viscosity is denoted by η and ω is the amplitude of the fluctuating force $\widetilde{\mathbf{F}}$ as defined in Eq. (48).

in our form of DPD is simply an input parameter. However, there may still be discrepancies due to the approximations made in going from MD to DPD. These approximations include the linearization of the inter-DP velocity fields, the Markovian assumption in the force correlations, and the neglect of a DP angular momentum variable.

None of the conclusions from the above arguments would change if we had worked in three dimensions instead of two.

VII. CONCLUSIONS

We have introduced a systematic procedure for deriving the mesoscopic modeling and simulation method known as dissipative particle dynamics from the underlying description in terms of molecular dynamics. Figure 6 illustrates the structure of the theoretical development of DPD equations from MD as presented in this paper. The initial coarse graining leads to equations of essentially the same structure as the final DPD equations. However, they are still invariant under time reversal. The label DPD1 refers to Eqs. (32), (34), and (40), whereas the DPD2 equations have been supplemented with specific constitutive relations for both the nonequilibrium fluxes (momentum and heat) and an equilibrium description of the thermodynamics. These equations are Eqs. (39) and (43) or (70) along with Eqs. (62). The development we have made that is shown in Fig. 6 does not claim to derive the irreversible DPD equations from the reversible ones of molecular dynamics in a rigorous manner, although it does illustrate where the transition takes place with the introduction of molecular averages. The kinetic equations of this DPD satisfy an H theorem, guaranteeing an irreversible approach to the equilibrium state. Note that in passing to the time-asymmetric description by the introduction of the averaged description of Eq. (36), a time-asymmetric nonequilibrium ensemble is required [26].

This is the first time to our knowledge that any of the various existing mesoscale methods have been put on a bottom-up theoretical foundation. To be precise, we have placed the present version of DPD on a molecular basis in the sense that (i) the DP's have a consistent conceptual interpretation as collections of molecules; (ii) the forces between the DP's are averages of explicit microscopic particle fluxes (DPD1); and (iii) the conservation laws of our DPD derive explicitly and directly from the underlying conservation laws of the molecular system. We have applied this particle interpretation to resolve the Itô-Stratonovich dilemma as an $O(1/N)$ effect, where N is the number of molecules in a dissipative particle. We have further used the particle interpretation as a natural basis for the statistical mechanical discussion of the fluctuating fluxes $\widetilde{\mathbf{F}}$ and $\tilde{q}$, for example, to identify the DPD and MD temperatures. On the other hand, the method still relies on some phenomenological input parameters. Thus, neither the equation of state nor the fluid viscosity have been obtained from molecular potentials (or Green-Kubo formulas related explicitly to microscopic properties). Moreover, we have not claimed to introduce time irreversibility in a rigorous way. Finally, no attempt has been made to include any quantum mechanical effects in the present paper.

Our development brings with it some insights as well as practical advantages. One of the main virtues of this procedure is the capability it provides to choose one or more coarse-graining length scales to suit the particular modeling problem at hand. The relative scale between molecular dynamics and the chosen dissipative particle dynamics, which may be defined as the ratio of their number densities $\rho_{\mathrm{DPD}}/\rho_{\mathrm{MD}}$, is a free parameter within the theory. Indeed, this rescaling may be viewed as a renormalization-group procedure under which the fluid viscosity remains constant: since the conservation laws hold exactly at every level of coarse graining, the result of doing two rescalings, say, from MD to DPDα and from DPDα to DPDβ, is the same as doing just one with a larger ratio, i.e., $\rho_{\mathrm{DPD}\beta}/\rho_{\mathrm{MD}}=(\rho_{\mathrm{DPD}\beta}/\rho_{\mathrm{DPD}\alpha})(\rho_{\mathrm{DPD}\alpha}/\rho_{\mathrm{MD}})$.

The present coarse-graining scheme is not limited to hydrodynamics. It could in principle be used to rescale the local description of any quantity of interest. However, only for locally conserved quantities will the DP particle interactions take the form of surface terms as here, and so it is unlikely that the scheme will produce a useful description of nonconserved quantities.

In this context, we note that the bottom-up approach to fluid mechanics presented here may throw light on aspects of the problem of homogeneous and inhomogeneous turbulence. Top-down multiscale methods and, to a more limited extent, ideas taken from renormalization-group theory have been applied quite widely in recent years to provide insight into the nature of turbulence [36,37]; one might expect an alternative perspective to emerge from a fluid dynamical theory originating at the microscopic level, in which the central relationship between conservative and dissipative processes is specified in a more fundamental manner. From a practical point of view it is noted that, since the DPD viscosity is the same as the viscosity emergent from the underlying MD level, it may be treated as a free parameter in the DPD model, and thus high Reynolds numbers may be reached. In the $\eta\rightarrow 0$ limit the model thus represents a potential tool for hydrodynamic simulations of turbulence. However, we have not investigated the potential numerical complications of this limit.

The dissipative particle dynamics that we have derived is formally similar to the conventional version, incorporating as it does conservative, dissipative, and fluctuating forces. The interactions are pairwise, and conserve mass and momentum as well as energy. However, now all these forces have been derived from the underlying molecular dynamics. The conservative and dissipative forces arise directly from the hydrodynamic description of the molecular dynamics and the properties of the fluctuating forces are determined via a fluctuation-dissipation relation. This relation was derived using the approximate isobaric ensemble. An exact ensemble that describes the full interaction between DP's exists, however, and work is in progress to understand it.

The simple hydrodynamic description of the molecules chosen here is not a necessary requirement. Other choices for the average of the general momentum- and energy-flux tensors Eqs. (26) and (19) may be made, and we hope these will be explored in future work. More significant is the fact that our analysis permits the introduction of specific physicochemical interactions at the mesoscopic level, together with a well-defined scale for this mesoscopic description.

While the Gaussian basis we used for the sampling functions is an arbitrary albeit convenient choice, the Voronoi geometry itself emerged naturally from the requirement that all the MD particles be fully accounted for. Well-defined procedures already exist in the literature for the computation of Voronoi tessellations [38] and so algorithms based on our model are not computationally difficult to implement. Nevertheless, it should be appreciated that the Voronoi construction represents a significant computational overhead [32].

Finally, we note the formal similarity of the present particulate description to existing continuum fluid dynamics methods incorporating adaptive meshes, which start out from a top-down or macroscopic description. These top-down approaches include in particular smoothed particle hydrodynamics [19] and finite-element simulations. In these descriptions too the computational method is based on tracing the motion of elements of the fluid on the basis of the forces acting between them [39]. However, while such top-down computational strategies lack macroscopic and purely phenomenological fluid descriptions, the present approach rests on a *molecular* basis.

ACKNOWLEDGMENTS

It is a pleasure to thank Frank Alexander, Bruce Boghosian, and Jens Feder for helpful and stimulating discussions. We have also benefited from the constructive criticism of Pep Español. We are grateful to the Department of Physics at the University of Oslo and Schlumberger Cambridge Research for financial support which enabled P.V.C. to make several visits to Norway; and to NATO and the Center for Computational Science at Queen Mary and Westfield College for funding visits by E.G.F. to London.

APPENDIX: THE ITÔ-STRATONOVITCH DILEMMA

The Fokker-Planck equation (54) corresponds to the Itô interpretation of Eq. (52). This is inconsistent with the observation that our fluctuating forces have smooth correlation functions, and that the corresponding Langevin equations consequently should be treated according to the Stratonovitch interpretation [29].

In this appendix we compute the extra terms in the Fokker-Planck equation (54) that enter with the correct Stratonovitch interpretation. We show that these terms are of relative order $1/\sqrt{N}$ or smaller, and are thus negligible.

Following the discussion in Ref. [29] we note that the extra terms that enter the Fokker-Planck equation with the Stratonovitch interpretation may be obtained by first modifying the drift term in the Langevin equation and then applying the Itô interpretation. This extra term appears directly if one integrates Eq. (52) over an interval Δt, keeping the correct orders of dt:

$$\begin{aligned}\Delta\mathbf{y}(t+\Delta t)&=\int_t^{t+\Delta t} dt'\,\dot{\mathbf{y}}(t')\\ &=\mathbf{a}(\mathbf{y})\Delta t+\int dt'\,\Delta\mathbf{y}(t')\cdot\boldsymbol{\nabla}\tilde{\mathbf{G}}(\mathbf{y}(t)),\end{aligned}\tag{A1}$$

which upon averaging and use of Eq. (52) again takes the form [29]

$$\langle\Delta y\rangle=\left(\mathbf{a}(\mathbf{y})+\int_t^{t'} dt''\langle\tilde{\mathbf{G}}(t'')\cdot\boldsymbol{\nabla}\tilde{\mathbf{G}}(t)\rangle\right)\Delta t,\tag{A2}$$

where the last integral contains a δ function that must be treated as a peaked but regular function so that $\int_0^\infty dt\,\delta(t)=1/2$. The last term in the above equation is the correction term, sometimes referred to as the ''spurious drift term,'' that distinguishes the two interpretations.

Now we apply the above formalism to evaluate the spurious drift term that arises from the $\tilde{\mathbf{F}}_{kl}\cdot\mathbf{U}_{kl}/2$ term in Eq. (43), and then again to estimate the remaining spurious drift terms that arise from the T_k and $\mathbf{r}_k$ dependence in ω and Λ.

In order to compute the spurious drift term corresponding to the work done by $\tilde{\mathbf{F}}_{kl}$, we define $\tilde{E}_k=-\Sigma_l\tilde{\mathbf{F}}_{kl}\cdot\mathbf{U}_{kl}/2$. Now, Eq. (A2) takes the form

$$\begin{aligned}\langle\tilde{E}_k\rangle&=\left\langle\frac{\partial\tilde{E}_k(t)}{\partial\mathbf{P}_{k'}}\cdot\Delta\mathbf{P}_{k'}(t')\right\rangle\\ &=\left\langle\frac{\partial\tilde{E}_k(t)}{\partial\mathbf{P}_{k'}}\cdot\int_t^{t'} dt''\sum_{l'}\tilde{\mathbf{F}}_{kl}(t'')\right\rangle.\end{aligned}\tag{A3}$$

Using the fact that $\partial\tilde{E}_k(t)/\partial\mathbf{P}_{k'}=-\tilde{\mathbf{F}}_{kl}(\delta_{kk'}-\delta_{lk'})/(2M_{k'})$ and then Eqs. (49) and (62), we obtain the correction term

$$\langle\tilde{E}_k\rangle=-\frac{3}{2}\sum_l\frac{l_{kl}}{r_{kl}}\left(\frac{1}{M_k}+\frac{1}{M_k}\right)\eta k_B\Theta_{kl},\tag{A4}$$

which is the term cited in Eq. (70).

This correction term gives rise to the following modification of the Fokker-Planck equation (54):

$$L_{\mathrm{DIS}}\rightarrow L_{\mathrm{DIS}}-\sum_k\frac{\partial}{\partial E_k}\langle\tilde{E}_k\rangle,\tag{A5}$$

which amounts to the replacement

$$-\lambda\frac{T_{kl}}{r_{kl}}\to-\lambda\frac{T_{kl}}{r_{kl}}\left[1-\frac{3}{2\lambda T_{kl}}\left(\frac{1}{M_k}+\frac{1}{M_l}\right)\eta k_B\Theta_{kl}\right]. \tag{A6}$$

We shall estimate the additional term as

$$D_{kl}=\frac{1}{M_k}\frac{\Theta_{kl}}{T_{kl}}k_B\cdot\frac{\eta}{\lambda}. \tag{A7}$$

To do this we introduce the viscous and thermal decay times

$$\begin{aligned} t_\lambda&=\frac{k_B\rho l^2}{m\lambda},\\ t_\eta&=\rho l^2/\eta, \end{aligned} \tag{A8}$$

where m is the molecular mass and l the length over which the temperature and velocity vary. We also recall from Eq. (47) that when T_{kl} is taken to have the value of the equilibrium fluctuation and the heat capacity of a DP is estimated as $Vc_v=N_k k_B$, then $\Theta_{kl}/T_{kl}\approx 1/\sqrt{N_k}$. Combining these results and using $M_k=mN_k$ we get that

$$D_{kl}=\frac{1}{\sqrt{N_k}}\frac{t_\lambda}{t_\eta}. \tag{A9}$$

Now, for most normal fluids $t_\lambda/t_\eta\sim 1$. For water, air, and glycerol at room temperature t_λ/t_η is approximately 0.001, 0.1, and 1.0, respectively. More importantly, t_λ/t_η is an intensive quantity so that D_{kl} depends on N_k through the square root only. Hence the D term that estimates the difference between the Itô and Stratonovitch versions of the Fokker-Planck equations is safely negligible.

The same is true for all other spurious drift terms, as we now proceed to show. In order to simplify the development we suppress both the vectorial and particle indices and write Eq. (39) in the form

$$\dot{\mathbf{P}}=\mathbf{B}(M,\mathbf{P},E)+\tilde{\mathbf{F}}, \tag{A10}$$

where the drift component in the force has been written in shorthand notation as $\mathbf{B}$ and the fluctuations as $\tilde{\mathbf{F}}\sim\boldsymbol{\omega}(\mathbf{r},T)W(t)$ where $W(t)$ is δ correlated and the amplitude depends on position and temperature as shown in Eq. (62).

Equation (A2) now takes the form

$$\langle\Delta\mathbf{P}\rangle=\mathbf{B}\Delta t+\int dt'\langle\Delta\mathbf{r}(t')W(t')\rangle\frac{\partial\boldsymbol{\omega}}{\partial\mathbf{r}}+\frac{\partial\boldsymbol{\omega}}{\partial T}\langle\Delta T(t')W(t')\rangle. \tag{A11}$$

In this equation it is easily observed that since $\Delta\mathbf{r}\sim\int\mathbf{U}dt\sim\int\int dt'dt''\tilde{\mathbf{F}}$ contains a double integral over time, it will only give a contribution of order Δt^2. The temperature term, however, will give an order Δt contribution. Introducing the heat capacity per particle c_v' (which is just k_B for an ideal gas), we may write $\Delta T=\Delta E/(Nc_v')$ and thus

$$\langle\Delta\mathbf{P}\rangle\approx\mathbf{B}\Delta t+\frac{1}{c_v'N}\int dt'\frac{\partial\boldsymbol{\omega}}{\partial T}\langle\Delta E(t')W(t')\rangle. \tag{A12}$$

Now, the only part of E that is correlated with the momentum fluctuation function $W(t)$ is $\tilde{E}$, and by a derivation that is completely similar to that which led to Eq. (A4) we obtain

$$\int\langle\Delta E(t')W(t')\rangle dt'=\boldsymbol{\omega}^2U\sim\eta k_B TU. \tag{A13}$$

Using the fact that $\mathbf{B}\sim\eta\mathbf{U}$ we may combine the above results to get

$$\langle\Delta\mathbf{P}\rangle\sim\eta U\left(1+\frac{k_B}{c_v'N}\right)\sim\left(1+\frac{1}{N}\right). \tag{A14}$$

This completes the demonstration that the terms in the Fokker-Planck equation that distinguish the Itô and Stratanovitch interpretations are negligible. It also shows that the Langevin equations for the momentum evolution may be interpreted in either way without affecting the results.

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