

# Multiscale dissipative particle dynamics

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We present a simplified kinetic derivation of the multiscale Voronoi based dissipative particle dynamics (DPD) method (Flekkøy & Coveney 1999; Flekkøy, Coveney & De Fabritiis 2000). The Voronoi tessellation is used to coarse-grain the molecular level of a fluid resulting in mesoscopic equations of motion for local mass, momentum and energy. The dissipative particles follow the dynamics of extended objects subject to forces including pressure and stresses. The stresses and heat fluxes are computed through constitutive relations which lead to fluctuating Navier-Stokes hydrodynamics for the solvent. The present formulation is based on the use of statistical mechanical distribution functions and the connection with the underlying molecular description of the fluid is maintained through the pair distribution function and the intermolecular potential. The main features of this DPD method are the adaptivity of the dissipative particles to the important length scales of the problem and the explicit role played by the molecular pair distribution function.

**Keywords:** mesoscopic fluids; Voronoi tessellation; dissipative particle dynamics; kinetic theory

## 1. Introduction

There is currently considerable interest in the study of so-called ‘mesoscale’ modeling and simulation methods, which are being used to describe many kinds of soft condensed matter. Examples of such fluids include multi-phase flows, particulate and colloidal suspensions, polymers and emulsions, where there may be several co-existing length and time scales. Fluctuations and Brownian motion frequently play a central role in determining their behaviour.

The dissipative particle dynamics (DPD) method introduced by Hoogerbrugge & Koelman (1992) is one such mesoscopic model. It has given rise to a whole family of subsequent improvements and variations. Although in their original formulation time was discrete and space continuous, a more recent re-interpretation 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 (Español 1995).

The DPD technique has been successfully applied to colloidal suspensions (Boek *et al.* 1997), polymer solutions (Schlijper *et al.* 1995) and binary immiscible fluids (Coveney & Novik 1996). The particles within the DPD scheme are ill-defined ‘mesoscopic’ quantities of the underlying fluid which evolve in a similar way to

MD particles, but with different inter-particle forces: since the DPD particles are envisaged to have internal degrees of freedom, the forces between them have both fluctuating and dissipative components in addition to the conservative forces. Newton's third law is still satisfied, however, and consequently momentum conservation together with mass conservation produce hydrodynamic behaviour at the macroscopic level.

The DPD model we derived is formally similar to conventional DPD, the interactions conserve mass and momentum, as well as energy (Avalos & Mackie 1997; Español 1997). 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 (1998) which links DPD to smoothed particle hydrodynamics (Monaghan 1992) and defines the DPD forces by hydrodynamic considerations in a way analogous to earlier DPD models. Recently, Serrano & Español (2001) have introduced a model very much like ours using the so-called "GENERIC" scheme to include fluctuations.

The purpose of the present paper is to present a kinetic derivation of our multiscale DPD model. The kinetic approach has the benefit of explicitly maintaining the connection to the microscopic level through the two-particle or pair distribution function appropriate to pairwise inter-molecular interactions. Compared to our previous papers (Flekkøy & Coveney 1999; Flekkøy *et al.* 2000) the present work also presents a number of theoretical simplifications and some important practical improvements. The theoretical simplifications include a more direct and simple derivation of the fluctuations.

## 2. The coarse-grained sampling procedure

The dynamics of our model involves the central idea of fluid volumes on which thermodynamic quantities such as density, pressure and temperature are defined. A partition of space is given in terms of the Voronoi tessellation. Given a set of points  $\{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ , a partition of the space assigning every point to its nearest site is called a Voronoi tessellation. The Voronoi partition  $k$  consists of all points  $\mathbf{x}$  at least as close to  $\mathbf{r}_k$  as to any other point, i.e.  $\{\mathbf{x} : |\mathbf{r}_k - \mathbf{x}| \leq |\mathbf{r}_l - \mathbf{x}|, \forall k \neq l\}$ . If we partition a fluid region in terms of a Voronoi tessellation, then to each partition is associated a mass  $M_k$ , a momentum  $\mathbf{P}_k$  and an internal energy  $E_k$  for the fluid contained in the volume  $k$ . If we coarse-grain the information inside the volumes we obtain a mesoscopic model of our fluid.

A partition of a domain  $D$  into space-filling sub-volumes describing mesoscopic dissipative particles (DPs) represented by their centres  $\{\mathbf{r}_1(t), \dots, \mathbf{r}_{N_{DP}}(t)\}$ , is defined through the sampling function  $H_k : D \times \mathbf{R} \rightarrow \{0, 1\}$  for the partition (DP) named  $k$ :

$$H_k(\mathbf{x}, t) = \prod_{l=1}^{N_{DP}} H_{kl}(\mathbf{x}, t) \quad (2.1)$$

$$H_{kl}(\mathbf{x}, t) = H\left(\left(\mathbf{x} - \frac{\mathbf{r}_k(t) + \mathbf{r}_l(t)}{2}\right) \cdot \mathbf{e}_{kl}\right) \quad (2.2)$$

where  $H$  is the one-dimensional Heaviside function with derivative  $\delta(x)$ ,  $\mathbf{e}_{kl} = \mathbf{r}_{kl}/r_{kl}$ ,  $\mathbf{r}_{kl} = \mathbf{r}_k(t) - \mathbf{r}_l(t)$  and  $N_{DP}$  is the total number of dissipative particles. The function  $H_{kl}$  is the characteristic function of the half-plane with Cartesian equation  $(\mathbf{x} - \frac{\mathbf{r}_l + \mathbf{r}_k}{2}) \cdot \mathbf{e}_{kl} = 0$  containing  $\mathbf{r}_k$ . The function  $H_k$  is 1 for all  $\mathbf{x}$  that are closer to  $\mathbf{r}_k$  than any other  $\mathbf{r}_l$ . As this is the exact definition of the Voronoi tessellation,  $H_k$  is the characteristic function of the Voronoi partition  $k$  and  $l_{kl}$  is the length (area in three dimensions) of the Voronoi edge between  $k$  and  $l$ . Several different characteristic functions for the Voronoi tessellation can be written down. For instance in our previous paper (Flekkøy *et al.* 2000), a smooth characteristic function  $f_k^a$  was used to develop the model (note that in the present paper the letter  $f$  is used to denote the single-particle distribution function). Mathematically, the function  $f_k^a$  is a partition of unity of  $D$  (Gel'fand & Shilov 1964) and a regularisation of the function  $H_k$ , which is then a discontinuous partition function.

The function  $H_k(\mathbf{x}, t)$  is literally used to count the number of molecules  $N_k$  which fall inside the Voronoi partition  $k$  using the formula

$$N_k(t) = \sum_{i=1}^N H_k(\mathbf{x}_i(t), t) \quad (2.3)$$

where  $N$  is the total number of molecules contained in the space  $D$ . Using the properties of delta functions and noting that Eq. (2.3) does not depend on the velocity it is possible to write

$$N_k(t) = \int \sum_{i=1}^N \delta(\mathbf{x} - \mathbf{x}_i(t)) \delta(\mathbf{v} - \mathbf{v}_i(t)) H_k(\mathbf{x}, t) d\mathbf{x} d\mathbf{v}, \quad (2.4)$$

where the integral is intended to be over the single-particle phase space of the system  $D \times \mathbf{R}^d$  (the spatial dimensionality  $d$  will be taken to be 2 or 3 here). The number of particles inside the partition  $k$  can be written in terms of the functional

$$f(\mathbf{x}, \mathbf{v}, t) = \sum_{i=1}^N \delta(\mathbf{x} - \mathbf{x}_i(t)) \delta(\mathbf{v} - \mathbf{v}_i(t)), \quad (2.5)$$

which is the microscopic single-particle distribution functional which, once ensemble-averaged over initial conditions, gives the statistical mechanical single-particle distribution function. Note the drastic change that the use of  $f$  introduces by ensemble-averaging which changes the deterministic description based on an operator containing all the information of the dynamics to a simple function containing only probabilistic information. Using this notation it is possible to write

$$N_k(t) = \int f(\mathbf{x}, \mathbf{v}, t) H_k(\mathbf{x}, t) d\mathbf{x} d\mathbf{v}. \quad (2.6)$$

The mass and momentum of the  $k$ th DP are defined as

$$M_k(t) = \sum_{i=1}^N H_k(\mathbf{x}_i(t), t) m = \int f_k(\mathbf{x}, \mathbf{v}, t) m d\mathbf{x} d\mathbf{v} \quad (2.7)$$

$$\mathbf{P}_k(t) = \sum_{i=1}^N H_k(\mathbf{x}_i(t), t) m \mathbf{v}_i = \int f_k(\mathbf{x}, \mathbf{v}, t) m \mathbf{v} d\mathbf{x} d\mathbf{v} \quad (2.8)$$

where  $f_k(\mathbf{x}, \mathbf{v}, t) = H_k(\mathbf{x}, t)f(\mathbf{x}, \mathbf{v}, t)$  is the single-particle distribution functional localised on the partition  $k$ .

The energy of a single particle is given by  $\varepsilon_i(t) = \frac{1}{2}mv_i^2 + \Phi_i$  where  $\Phi_i$  is the interaction potential which is given, in the pair interaction approximation we shall henceforth assume, by  $\Phi_i = \frac{1}{2} \sum_{j \neq i}^N \Phi(\mathbf{r}_i - \mathbf{r}_j)$ . The total energy of the partition  $k$  is given by the sum of the kinetic and potential energies

$$E_k^{tot}(t) = \frac{1}{2} \sum_{i=1}^N H_k(\mathbf{x}_i(t), t)mv_i^2 + \frac{1}{2} \sum_{i=1}^N H_k(\mathbf{x}_i(t), t) \sum_{j \neq i}^N \Phi_2(\mathbf{x}_i - \mathbf{x}_j). \quad (2.9)$$

The contribution given by the second (potential) term on the right hand side of (2.9) can be expressed with the same technique used for momentum and mass equations as  $\frac{1}{2} \int H_k(\mathbf{x}, t)\Phi_2(\mathbf{x} - \mathbf{y})n^{(2)}(\mathbf{x}, \mathbf{y}, t)d\mathbf{x}d\mathbf{y}$ , where  $n^{(2)}(\mathbf{x}, \mathbf{y}, t) = \sum_{i=1}^N \sum_{j \neq i}^N \delta(\mathbf{x} - \mathbf{x}_i(t))\delta(\mathbf{y} - \mathbf{x}_j(t))$  is the expression for the microscopic two-particle number density functional. This can be re-written in the energy Eq. (2.9) as

$$E_k^{tot}(t) = \frac{1}{2} \int_{D \times R^2} f_k(\mathbf{x}, \mathbf{v}, t)mv^2 d\mathbf{x}d\mathbf{v} + \frac{1}{2} \int_{D \times D} n_k^{(2)}(\mathbf{x}, \mathbf{y}, t)\Phi_2(\mathbf{x} - \mathbf{y})d\mathbf{x}d\mathbf{y}, \quad (2.10)$$

where  $n_k^{(2)}(\mathbf{x}, \mathbf{y}, t) = n^{(2)}(\mathbf{x}, \mathbf{y}, t)H_k(\mathbf{x}, t)$  is the localisation on the partition  $k$  of the two-particle density functional.

It must be stressed that it is not generally possible to define multiplication of a generalised function by another generalised function in a manner consistent with the normal product between functions unless one of the two functions is the derivative of a characteristic function. Here, we will take the time derivative of a characteristic function for the Voronoi partition, hence ending up with the product of two generalised functions.

The time dependence of  $f_k$  is contained in the characteristic function  $H_k$  through the positions  $\mathbf{r}_k$  and  $\mathbf{r}_l$  and the positions and velocities of the particles  $\mathbf{x}_i, \mathbf{v}_i$ , whereas the variables  $\mathbf{x}, \mathbf{v}$  are integration variables. The time derivatives of these quantities are calculated via the total derivatives of  $f_k$  and  $n_k^{(2)}$ :

$$\frac{df_k}{dt} = \frac{dH_k}{dt}f + H_k \frac{df}{dt} \quad (2.11)$$

$$\frac{dn_k^{(2)}}{dt} = \frac{dH_k}{dt}n^{(2)} + H_k \frac{dn^{(2)}}{dt} \quad (2.12)$$

$$\frac{df}{dt} = \sum_{i=1}^N \left[ -\mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{x}} \delta(\mathbf{x} - \mathbf{x}_i) \delta(\mathbf{v} - \mathbf{v}_i) - \mathbf{a}_i \cdot \frac{\partial}{\partial \mathbf{v}} \delta(\mathbf{v} - \mathbf{v}_i) \delta(\mathbf{x} - \mathbf{x}_i) \right] \quad (2.13)$$

$$\frac{dn^{(2)}}{dt} = \sum_{i=1}^N \sum_{j \neq i}^N \left[ -\mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{x}} \delta(\mathbf{x} - \mathbf{x}_i) \delta(\mathbf{y} - \mathbf{x}_j) - \mathbf{v}_j \cdot \frac{\partial}{\partial \mathbf{y}} \delta(\mathbf{y} - \mathbf{x}_j) \delta(\mathbf{x} - \mathbf{x}_i) \right] \quad (2.14)$$

$$\frac{dH_k}{dt} = \sum_{l=1}^{NDP} \prod_{h \neq l} H_{kh} \delta(\mathbf{x}' \cdot \mathbf{e}_{kl}) \left( -\frac{\dot{\mathbf{r}}_k + \dot{\mathbf{r}}_l}{2} \cdot \mathbf{e}_{kl} + \mathbf{x}' \cdot \frac{d\mathbf{e}_{kl}}{dt} \right) \quad (2.15)$$

where  $\mathbf{x}' = \mathbf{x} - \frac{\mathbf{r}_k + \mathbf{r}_l}{2}$  and  $\delta(\mathbf{x}' \cdot \mathbf{e}_{kl})$  is a delta function over the surface of the Voronoi partition or dissipative particle  $k$ . It is worth pointing out that Eq. (2.13) has the same structure as the Liouville equation.

### 3. Microscopic description

At this stage, only coarse-graining of the observables mass, momentum and energy within the Voronoi cells has been introduced, but the entire dynamics of the Voronoi volumes is still governed by the microscopic dynamics of the molecules contained in the functional  $f(\mathbf{x}, \mathbf{v}, t)$ . This evolution can be computed from the time derivative of the coarse-grained values of the observables. The evolution equations will still be given in term of the operator  $f$  which involves knowledge of the positions and velocities of all the molecules.

A kinematic assumption is that the centre of the Voronoi cell  $\mathbf{r}_k$  moves with average velocity  $\mathbf{U}_k$

$$\dot{\mathbf{r}}_k = \mathbf{U}_k \quad (3.1)$$

for any  $k = 1, \dots, N_{DP}$ . This assumption is an approximation because the centre of the Voronoi cell is not generally the centre of mass of the cell.

The average velocity  $\mathbf{U}(\mathbf{x}, t) = \int f \mathbf{v} d\mathbf{v}$  on the surface between two DPs  $k, l$  is approximated by  $\mathbf{U} = \frac{\mathbf{U}_k + \mathbf{U}_l}{2}$  and therefore the relative velocity on the surface between Voronoi  $k$  and  $l$  is  $\mathbf{v}' = \mathbf{v} - \mathbf{U}(\mathbf{x}, t) = \mathbf{v} - \frac{\mathbf{U}_k + \mathbf{U}_l}{2}$ .

#### (a) Mass equation

The exchange of mass for the DP  $k$  is given by

$$\frac{dM_k}{dt} = \int \frac{df_k}{dt} m d\mathbf{x} d\mathbf{v}. \quad (3.2)$$

The derivative of the delta function (2.13) in  $\frac{df}{dt}$  can be expressed as a derivative of the other integrands using the definition of derivatives of generalised functions:

$$\frac{\partial}{\partial \mathbf{x}} H_k(\mathbf{x}, t) = \sum_{l=1}^{N_{DP}} \delta(\mathbf{x}' \cdot \mathbf{e}_{kl}) \mathbf{e}_{kl} \prod_{h \neq l} H_{kh} \quad (3.3)$$

$$H_k \frac{df}{dt} m = m \mathbf{v} f \frac{\partial}{\partial \mathbf{x}} H_k = \sum_{l=1}^{N_{DP}} m f \prod_{h \neq l} H_{kh} \delta(\mathbf{x}' \cdot \mathbf{e}_{kl}) \mathbf{v} \cdot \mathbf{e}_{kl}. \quad (3.4)$$

It is now possible to write the exact mass variation for the fluid particle  $k$  in the form

$$\frac{dM_k}{dt} = \sum_{l \in \mathcal{N}_k} \dot{M}_{kl}, \quad (3.5)$$

where

$$\dot{M}_{kl} = \int m f(\mathbf{x}, \mathbf{v}, t) \delta(\mathbf{x}' \cdot \mathbf{e}_{kl}) (\mathbf{v}' \cdot \mathbf{e}_{kl} + \mathbf{x}' \cdot \frac{d\mathbf{e}_{kl}}{dt}) d\mathbf{x} d\mathbf{v}, \quad (3.6)$$

$\mathcal{N}_k$  is the set of particle indices in the nearest neighbourhood of particle  $k$ , and the integral with the delta function is intended to be over the surface of the adjacent DPs or Voronoi partitions  $k$  and  $l$ . The integral on the right hand side of (3.6) means that the exchange of mass depends only on the mass exchange along the surface of the Voronoi partition between DP  $k$  and  $l$  for all the surfaces of the Voronoi partition  $k$ .

## (b) Momentum equation

The exchange of momentum for the volume  $k$  is given by

$$\frac{d\mathbf{P}_k}{dt} = \int \frac{df_k}{dt} m \mathbf{v} d\mathbf{x} d\mathbf{v}. \quad (3.7)$$

Expanding this equation using the result  $H_k \frac{df}{dt} m \mathbf{v} = m \left( \frac{\partial}{\partial \mathbf{x}} H_k \cdot \mathbf{v} \right) \mathbf{v} f + \sum_{i=1}^{N_{DP}} H_k(\mathbf{x}_i, t) \mathbf{F}_i$  we obtain the total momentum exchange as

$$\frac{d\mathbf{P}_k}{dt} = \sum_{l \in \mathcal{N}_k} \dot{\mathbf{P}}_{kl} + \sum_{i=1}^N H_k(\mathbf{x}_i, t) \mathbf{F}_i \quad (3.8)$$

where

$$\dot{\mathbf{P}}_{kl} = \int m f(\mathbf{x}, \mathbf{v}, t) \prod_{h \neq l} H_{kh} \delta(\mathbf{x}' \cdot \mathbf{e}_{kl}) \times \left( \mathbf{v}' \cdot \mathbf{e}_{kl} + \mathbf{x}' \cdot \frac{d\mathbf{e}_{kl}}{dt} \right) \mathbf{v} d\mathbf{x} d\mathbf{v}. \quad (3.9)$$

The kinetic and potential components of the momentum Eq. (3.8) are now analysed in turn.

The first term in the integral on the right hand side of Eq. (3.9) can be re-written using the vectorial identity  $(\mathbf{a} \cdot \mathbf{b})\mathbf{c} = \mathbf{c}\mathbf{a} \cdot \mathbf{b}$ , while the factor  $\prod_{h \neq l} H_{kh}$  confines the domain of integration of the delta function to the Voronoi surface  $kl$

$$\dot{\mathbf{P}}_{kl} = \dot{M}_{kl} \frac{\mathbf{U}_k + \mathbf{U}_l}{2} + \int m f(\mathbf{x}, \mathbf{v}, t) \delta(\mathbf{x}' \cdot \mathbf{e}_{kl}) \left( \mathbf{v}' \mathbf{v}' \cdot \mathbf{e}_{kl} + (\mathbf{x}' \cdot \frac{d\mathbf{e}_{kl}}{dt}) \mathbf{v}' \right) d\mathbf{x} d\mathbf{v}. \quad (3.10)$$

The last term within the momentum conservation equation (3.10) averages to zero because the positions and velocities of the particles are assumed to be uncorrelated and the relative velocity  $\mathbf{v}'$  is averaged to zero. From kinetic theory, we can interpret the term  $\int m f(\mathbf{x}, \mathbf{v}, t) \mathbf{v}' \mathbf{v}' d\mathbf{v}$  as being identical to  $\Pi(\mathbf{x}, t)$  where  $\Pi(\mathbf{x}, t)$  is exactly the kinetic contribution to the pressure tensor (Cercignani 1969).

The second term on the right hand side of the momentum Eq. (3.8) is given by the potential contributions responsible for the hydrostatic pressure between DPs and can be rewritten in the pair approximation using the assumed pair-interaction approximation for the inter-molecular force  $\mathbf{F}_i = \sum_{j \neq i} \mathbf{F}(\mathbf{x}_i - \mathbf{x}_j)$ . Thus the second summation in Eq. (3.8) becomes

$$\sum_{i=1}^N H_k(\mathbf{x}_i, t) \mathbf{F}_i = \int H_k(\mathbf{x}, t) \mathbf{F}(\mathbf{x} - \mathbf{y}) \sum_{i=1}^N \sum_{j \neq i} \delta(\mathbf{y} - \mathbf{x}_j) \delta(\mathbf{x} - \mathbf{x}_i) d\mathbf{x} d\mathbf{y}. \quad (3.11)$$

The ensemble average of  $n^{(2)}(\mathbf{x}, \mathbf{y}) = \sum_{i=1}^N \sum_{j \neq i} \delta(\mathbf{y} - \mathbf{x}_j) \delta(\mathbf{x} - \mathbf{x}_i) = n^{(1)}(\mathbf{x}) n^{(1)}(\mathbf{y}) g(\mathbf{x}, \mathbf{y})$  is the two-particle number density function and the second equality follows from the definition of  $g$  as the pair distribution function. Thus, considering that inside the partition  $V_k$  the summation of the forces over the molecules is zero because of Newton's third law, the integral can be written in terms of the variable  $\mathbf{x} = \mathbf{y} + \mathbf{r}$

$$\sum_{i=1}^N H_k(\mathbf{x}_i, t) \mathbf{F}_i = \int_{V_k} d\mathbf{x} \int_{D \setminus V_k} n^{(1)}(\mathbf{x}) n^{(1)}(\mathbf{x} + \mathbf{r}) g(\mathbf{x}, \mathbf{x} + \mathbf{r}) \mathbf{F}(\mathbf{r}) d\mathbf{r}. \quad (3.12)$$

The dependence on the pair distribution function is one particularly interesting feature of our model compared with more conventional DPD (P. Español & P. Warren 1995). In applications, this function can either be inserted explicitly or handled implicitly by using an equation of state for the specific fluid of interest. The pair distribution function  $g$  depends on the position  $\mathbf{x}$  only through the thermodynamic quantities of mass density  $\rho(\mathbf{x}, t)$  and temperature  $T(\mathbf{x}, t)$  at the interface between DP  $k$  and  $l$ . A proper description of multicomponent fluids would depend critically on the presence of this function.

(c) *Energy equation*

The total interaction energy for the  $k$ th DP is given in terms of the kinetic and potential energy contributions via the equation

$$\frac{dE_k^{tot}}{dt} = \frac{1}{2} \int \frac{df_k}{dt} m v^2 d\mathbf{x}d\mathbf{v} + \frac{1}{2} \int \frac{dn_k^{(2)}}{dt} \Phi_2(\mathbf{x} - \mathbf{y}) d\mathbf{x}d\mathbf{y}. \quad (3.13)$$

The first integral on the right hand side of Eq. (3.13) corresponds to the time variation of the kinetic part of the energy and the second to the time derivative of the potential, so that Eq. (3.13) may be written

$$\frac{dE_k^{tot}}{dt} = \sum_{l \in \mathcal{N}_k} \dot{K}_{kl} + \dot{E}_k^\Phi \quad (3.14)$$

where the kinetic component is

$$\dot{K}_{kl} = \int m f(\mathbf{x}, \mathbf{v}, t) \prod_{h \neq l} H_{kh} \delta(\mathbf{x}' \cdot \mathbf{e}_{kl}) (\mathbf{v}' \cdot \mathbf{e}_{kl} + \mathbf{x}' \cdot \frac{d\mathbf{e}_{kl}}{dt}) \frac{1}{2} m v^2 d\mathbf{x}d\mathbf{v} \quad (3.15)$$

and the potential component is

$$\dot{E}_k^\Phi = \sum_{i=1}^N H_k(\mathbf{x}_i, t) \mathbf{F}_i \cdot \mathbf{v}_i + \frac{1}{2} \int \frac{dn_k^{(2)}}{dt} \Phi_2(\mathbf{x} - \mathbf{y}) d\mathbf{x}d\mathbf{y}. \quad (3.16)$$

We now analyse each of these contributions in turn.

The term  $\dot{K}_{kl}$  in Eq. (3.15) is re-written using the vectorial identity  $(\mathbf{a} \cdot \mathbf{b})(\mathbf{c} \cdot \mathbf{d}) = (\mathbf{c}\mathbf{a} \cdot \mathbf{b}) \cdot \mathbf{d}$  and the identity  $\frac{1}{2} m v^2 = \frac{1}{2} m (v')^2 + m \mathbf{v}' \cdot \frac{\mathbf{U}_k + \mathbf{U}_l}{2} + \frac{1}{2} m \left( \frac{\mathbf{U}_k + \mathbf{U}_l}{2} \right)^2$  in order to express the kinetic energy in terms of the relative velocity  $\mathbf{v}'$ . Then, using the definition of the thermal energy  $E_k(t) = E_k^{tot}(t) - \frac{1}{2} \frac{P_k^2}{M_k}$  together with  $\frac{d}{dt} \frac{P_k^2}{2M_k} = \mathbf{U}_k \cdot \dot{\mathbf{P}}_k - \frac{1}{2} \dot{M}_k U_k^2$ , the kinetic part of the internal interaction energy is given by

$$\dot{E}_k = \sum_l \int f(\mathbf{x}, \mathbf{v}, t) \delta(\mathbf{x}' \cdot \mathbf{e}_{kl}) \left[ \mathbf{v}' \cdot \mathbf{e}_{kl} \frac{1}{2} m (v')^2 + \mathbf{x}' \cdot \dot{\mathbf{e}}_{kl} \frac{1}{2} m (v')^2 - m (\mathbf{v}' \cdot \mathbf{v}' \cdot \mathbf{e}_{kl}) \cdot \frac{\mathbf{U}_{kl}}{2} \right] d\mathbf{x}d\mathbf{v}. \quad (3.17)$$

where terms of order  $U_{kl}^2$  are discarded, as well as terms depending on the relative velocity  $\mathbf{v}'$  only, which average to zero. We can interpret the term  $\mathbf{J}^q(\mathbf{x}, t) = \int f(\mathbf{x}, \mathbf{v}, t) \frac{1}{2} m (v')^2 d\mathbf{v}$  as the kinetic expression for the heat flux. As for the pressure

tensor, at this level of coarse-graining, this is still the exact operator corresponding to the heat flux.

The second term contributing to the energy Eq. (3.14), corresponding to Eq. (3.16), is given by the contributions arising from the non-locality of the inter-molecular potential. The quantity  $\frac{dn_k^{(2)}}{dt} = \frac{dH_k}{dt}n^{(2)} + H_k\frac{dn^{(2)}}{dt}$  is computed using Eq. (2.14) leading to the following expression

$$\begin{aligned} \dot{n}^{(2)}H_k(\mathbf{x})\Phi_2(\mathbf{x}-\mathbf{y}) &= \frac{1}{2}f^{(2)}(\mathbf{x}, \mathbf{y}, \xi, \eta, t) \left[ \xi \cdot \frac{\partial}{\partial \mathbf{x}} (H_k(\mathbf{x}, t)\Phi_2(\mathbf{x}-\mathbf{y})) \right. \\ &\quad \left. + \eta \cdot \frac{\partial}{\partial \mathbf{y}} \Phi_2(\mathbf{x}-\mathbf{y})H_k(\mathbf{x}, t) \right], \end{aligned} \quad (3.18)$$

where  $f^{(2)}(\mathbf{x}, \mathbf{y}, \xi, \eta, t) = \sum_i \sum_{j \neq i} \delta(\mathbf{x} - \mathbf{x}_i(\tau))\delta(\mathbf{y} - \mathbf{x}_j(\tau))\delta(\xi - \mathbf{v}_i(\tau))\delta(\eta - \mathbf{v}_j(\tau))$  is the microscopic two-particle distribution functional. The final expression for the potential energy of interaction considering the additional potential term arising from the transformation from total to internal energy is thus

$$\begin{aligned} \dot{K}_k^\Phi &= \frac{1}{2} \sum_{l \in \mathcal{N}_k} \int m f^{(2)}(\mathbf{x}, \mathbf{y}, \xi, \eta, t) \delta(\mathbf{x}' \cdot \mathbf{e}_{kl}) \left( \xi' \cdot \mathbf{e}_{kl} + \mathbf{x}' \cdot \frac{d\mathbf{e}_{kl}}{dt} \right) \Phi_2(\mathbf{x}-\mathbf{y}) dx dy d\xi d\eta \\ &\quad + \frac{1}{2} \int f^{(2)}(\mathbf{x}, \mathbf{y}, \xi, \eta, t) H_k(\mathbf{x}, t) \mathbf{F}(\mathbf{x}-\mathbf{y}) \cdot (\xi + \eta - 2\mathbf{U}_k) dx dy d\xi d\eta. \end{aligned} \quad (3.19)$$

The first integral is added to the kinetic term in Eq. (3.17) to produce the internal energy  $E_k$ , while the second term is added to the work terms in the same Eq. (3.17); it can be thought of as an additional contribution due to the work performed by the intermolecular forces (de Groot & Mazur 1962).

#### 4. Temporal and ensemble averaging

The foregoing equations of mass, momentum and energy conservation were derived without any loss of information from the microscopic description of the fluid. At this point, we reduce the operator  $f$  to a function containing only statistical mechanical information about the dynamics of the system. To do this, we define a characteristic timescale  $\delta t_n$  and we discretise the time evolution as  $t_{n+1} = t_n + \delta t_n$ , where  $\delta t_n$  is the size of the time step at time  $t_n$ . From this, we can compute the average of the function  $f$  over the time interval  $\delta t_n$ . An integration over time is carried out yielding

$$\bar{f}_{t_n}(\mathbf{x}, \mathbf{v})\delta t_k + \tilde{f}_{t_n}(\mathbf{x}, \mathbf{v}) = \int_{t_n}^{t_{n+1}} \langle \sum_{i=1}^N \delta(\mathbf{x} - \mathbf{x}_i(\tau))\delta(\mathbf{v} - \mathbf{v}_i(\tau)) \rangle d\tau, \quad (4.1)$$

where  $\langle \dots \rangle$  denotes an ensemble average and time averages are taken to split the information contained in the rapidly varying function  $f$  into averaged and fluctuating parts denoted by bars ( $\bar{f}$ ) and tildes ( $\tilde{f}$ ) respectively. In the mass, momentum and energy equations time enters only through the function  $f$ , therefore the time integral can always be computed as in Eq. (4.1). To indicate these dynamical averages we use the notation

$$\langle F(\mathbf{x}, \mathbf{v}) \rangle_{kl} := \int \bar{f}(\mathbf{x}, \mathbf{v}, t) \delta(\mathbf{x}' \cdot \mathbf{e}_{kl}) F(\mathbf{x}, \mathbf{v}) d\mathbf{x} d\mathbf{v} \quad (4.2)$$



to define the time average of any dynamical function  $F(\mathbf{x}, \mathbf{v})$  on the DP surface  $kl$ .

In the momentum Eq. (3.10) the one-particle distribution functional can be averaged to the local Maxwell-Boltzmann distribution and the integral carried out to obtain the inviscid pressure tensor. Considering as well the first non-equilibrium contribution to the Maxwell-Boltzmann equilibrium we would obtain the Navier-Stokes pressure tensor, which is therefore the first approximation to the non-equilibrium pressure tensor (Huang 1987). The transport coefficients in the stress tensor, i.e. the first and second viscosity coefficients, and consequently the form of the pressure tensor itself are indirectly related to the inter-molecular potential, via the dynamics of the one-particle distribution function. In fact, the averaged one-particle distribution function  $f$  depends on the two-particle distribution function via the BBGKY hierarchy. Thus, for an interacting multicomponent fluid, say, its description in these terms, while not producing the correct kinetic pressure tensor, would enable the potential contribution to be explicitly and correctly computed. This first non-equilibrium approximation produces a macroscopic term

$$\langle \mathbf{v}' \mathbf{v}' \cdot \mathbf{e}_{kl} \rangle_{kl} = l_{kl} \Pi_{kl} \cdot \mathbf{e}_{kl}, \quad (4.3)$$

where  $\Pi_{kl}$  is the kinetic pressure tensor evaluated on the Voronoi surface  $kl$  given by the expression  $\Pi^{(\alpha\beta)} = p\delta_{\alpha\beta} - \eta \left( \frac{\partial U_\alpha}{\partial x_\beta} + \frac{\partial U_\beta}{\partial x_\alpha} \right)$ , where the Einstein notation has been used for the tensorial indices and the second viscosity coefficient  $\zeta = (2/d)\eta$  has been assumed with  $d$  the spatial dimension.

The kinetic heat flux  $\mathbf{J}_q(\mathbf{x}, t) = \int \tilde{f}(\mathbf{x}, \mathbf{v}, t) \mathbf{v}' v'^2 d\mathbf{v}$  of Eq. (3.17) is given by the constitutive relation  $\mathbf{J}_q = -\lambda \nabla T$  where  $T$  is the temperature.

The fluctuating components of the pressure tensor and heat flux are given according to Landau and Lifshitz (1989) by the  $\tilde{f}$  function as two additional stochastic terms in the pressure tensor and the heat flux

$$\sigma^{\alpha\beta} = \eta \left( \frac{\partial U_\alpha}{\partial x_\beta} + \frac{\partial U_\beta}{\partial x_\alpha} \right) + s^{\alpha\beta}, \quad (4.4)$$

$$\mathbf{J}_q = -\lambda \nabla T + \mathbf{q}, \quad (4.5)$$

where  $s^{\alpha\beta}(\mathbf{x}, t) = \int \tilde{f}(\mathbf{x}, \mathbf{v}, t) \mathbf{v}' \mathbf{v}' d\mathbf{v}$  and  $\mathbf{q}(\mathbf{x}, t) = \int \tilde{f}(\mathbf{x}, \mathbf{v}, t) \mathbf{v}' \frac{1}{2} v'^2 d\mathbf{v}$ . The fluctuations are not present in the mass equation because the continuity equation is supposed to be an *exact* equation on the velocity field. The use of these constitutive relations assures Navier-Stokes fluctuating hydrodynamics for the solvent represented as a DPD fluid. Applications of the DPD formalism to simulate complex fluids in this way then consists of using such a DPD fluid for the solvent and the use of flexible boundary conditions to describe complex fluid behaviour involving colloids, polymers, multiphase fluids, and so on.

## 5. Mesoscopic description

The differential equations for mass, momentum and energy become stochastic differential equations (SDEs) when the averaged and the fluctuating components are inserted. The formalism of SDEs is better understood by interpreting the fluctuations as Wiener processes (van Kampen 1992; Kloeden & Platen 1992), simultaneously specifying which interpretation (Stratonovich or Itô) we choose for the

stochastic terms (Flekkøy *et al.* 2000). Given the coarse-grained nature of the random force and fluctuating heat flux, the stochastic terms must be understood as internal noise and the Stratonovich interpretation used for stochastic integrals.

(a) *Mass equation*

The coarse-grained mass exchange can be interpreted on the basis of the previous assumptions. In order to calculate the integral on the right hand side of Eq. (3.6) a change of variable must be made for the  $\mathbf{x}$  variable. In two dimensions, considering the change of frame of reference  $q_1 = \mathbf{x}' \cdot \mathbf{e}_{kl}$ ;  $q_2 = \mathbf{x}' \cdot \mathbf{i}_{kl}$  the right hand side of Eq. (3.6) becomes

$$\dot{M}_k = \int mf(\mathbf{q}, \mathbf{v}, t) \delta(q_1) \left( \mathbf{v}' \cdot \mathbf{e}_{kl} + q_2 \frac{d\mathbf{e}_{kl}}{dt} \right) dq_1 dq_2 d\mathbf{v}. \quad (5.1)$$

The first integrand on the right hand side of (5.1) is zero because, assuming linear interpolation of the macroscopic velocity field, the averaged velocity on the Voronoi edge  $kl$  is  $(\mathbf{U}_k + \mathbf{U}_l)/2$ . This is consistent with the fact that the DPs move by following the hydrodynamic flux. The second term in the integral in Eq. (5.1) can be easily computed assuming linear interpolation of the mass density as

$$dM_k = \sum_l \frac{\rho_k + \rho_l}{2} \Omega_{kl} dt, \quad (5.2)$$

where  $\Omega_{kl} = l_{kl} \frac{\mathbf{U}_{kl} \cdot \mathbf{L}_{kl}}{r_{kl}}$  is a factor accounting for the twisting of the Voronoi edge  $kl$ ,  $\mathbf{L}_{kl} = (\mathbf{l}_{cm} - \frac{\mathbf{r}_k + \mathbf{r}_l}{2})$  and  $\mathbf{l}_{cm}$  is the position of the center of mass of the Voronoi edge between  $k$  and  $l$  (note that  $L_{kl}$  is defined in a slightly different way to that given by Flekkøy *et al.* 2000). As noted earlier, the mass equation does not contain any stochastic term.

It is important to stress that the right hand side of Eq. (5.2) is entirely due to the motion of the Voronoi partition, in particular to the rotation of the edge between two DPs due to the component of the relative velocity in the  $\mathbf{i}_{kl}$  direction; it is zero if the centre of mass of the edge  $kl$  corresponds to the point  $\mathbf{x}' = 0$ . We can interpret it as a consequence of the discretisation in terms of the Voronoi tessellation.

(b) *Momentum equation*

The velocity field must be discretised in order to obtain a closed scheme for the pressure tensor. Any change in the discretisation of the velocity produces a change in the sizes and structure of the fluctuations. In fact, the force fluctuations are designed to re-introduce into the system the energy dissipated by the stress tensor and are derived from the stress tensor via the fluctuation-dissipation theorem.

Our discretisation of the stress tensor keeps the interaction between DPs pairwise. The velocity gradients are computed via finite differences between the Voronoi *centres of mass*  $\mathbf{r}_k^{cm}$  and  $\mathbf{r}_l^{cm}$ . Given the pairwise nature of the stresses, the velocity gradient matrix is composed only of one single component corresponding to the derivative along  $\mathbf{e}_{kl}^{cm} = \mathbf{r}_{kl}^{cm}/r_{kl}^{cm}$  given by  $\frac{\partial \mathbf{U}}{\partial \mathbf{e}_{kl}^{cm}} = \frac{\mathbf{U}_{kl}}{r_{kl}^{cm}}$ , where  $\mathbf{r}_k^{cm}$  is the

centre of mass of DP  $k$  and  $\mathbf{r}_{kl}^{cm} = \mathbf{r}_k^{cm} - \mathbf{r}_l^{cm}$ . The resulting stress tensor is  $\sigma = \frac{\eta}{r_{kl}^{cm}}(\mathbf{e}_{kl}^{cm} \mathbf{U}_{kl} + \mathbf{U}_{kl} \mathbf{e}_{kl}^{cm})$ , giving the following pressure forces

$$\sum_l l_{kl} \mathbf{\Pi}_{kl} \cdot \mathbf{e}_{kl} = \sum_l l_{kl} \left[ \frac{p_k + p_l}{2} \mathbf{e}_{kl} - \frac{\eta}{r_{kl}^{cm}} (\mathbf{e}_{kl} \cdot \mathbf{e}_{kl}^{cm} \mathbf{U}_{kl} + \mathbf{U}_{kl} \cdot \mathbf{e}_{kl} \mathbf{e}_{kl}^{cm}) \right]. \quad (5.3)$$

Other discretisations of the stress tensor could be used (Serrano & Espaol 2001; Serrano *et al.* 2001). In particular, when the Voronoi centre is used, instead of the Voronoi centre of mass, the pressure tensor (5.3) reduces to the discretisation of Flekkoy *et al.* (2000).

### (c) Energy equation

In this subsection, we develop the energy conservation Eq. (3.17) making similar assumptions to those used in the derivation of the mass and momentum equations. The new terms we have to deal with in the energy equation are the average heat flux  $\mathbf{J}_q$ , which is approximated using finite differences as

$$\mathbf{J}_q = -\lambda \frac{T_{kl}}{r_{kl}^{cm}} \mathbf{e}_{kl}, \quad (5.4)$$

and the average of the term  $\langle m(\mathbf{v}' \mathbf{v}' \cdot \mathbf{e}_{kl}) \cdot \frac{\mathbf{U}_{kl}}{2} \rangle_{kl}$  in Eq. (3.17) representing the increase of internal energy due to the work done by the stress forces. The final average energy equation is

$$dE_k = \sum_l \left( -\lambda l_{kl} \frac{T_{kl}}{r_{kl}^{cm}} + \frac{1}{2} \left( \frac{E_k}{V_k} + \frac{E_l}{V_l} \right) \Omega_{kl} - l_{kl} (\mathbf{\Pi}_{kl} \cdot \mathbf{e}_{kl}) \cdot \frac{\mathbf{U}_{kl}}{2} \right) dt. \quad (5.5)$$

### (d) Fluctuations from fluctuating hydrodynamics

To derive the fluctuations in *fluctuating hydrodynamics* (FH) the correct entropy production is needed (Landau & Lifshitz 1989). In the Landau and Lifshitz theory of FH this entropy production  $\dot{S}$  is derived on the basis of continuum fields. In our case there is already a fundamental discretisation present, and we need to re-derive  $\dot{S}$  on the basis of the forces acting between these discrete elements, i.e. the DP's.

As in FH we start out by assuming a local thermodynamic equilibrium on the scale of the DP's. This implies that we can write the second law of thermodynamics for each DP in the form

$$T_k \Delta S_k = \Delta E_k + p_{kl} \Delta V_k - \mu_{kl} \Delta M_k \quad (5.6)$$

where  $T_k$  is the temperature of DP $_k$  while the pressure  $p_{kl}$  and the chemical potential  $\mu_{kl}$  are associated with the overlap region where the volume and mass exchange take place. Eq. (5.6) is to be interpreted as a fluctuationless equation. The average of the energy Eq. (5.5) may be written in the form

$$\begin{aligned} \frac{\Delta E_k}{\Delta t} &= \sum_l -p_{kl} \Delta V_k + \frac{1}{2} \mathbf{F}_{kl}^{DIS} \cdot \mathbf{U}_{kl} - \lambda l_{kl} \frac{T_{kl}}{r_{kl}^{cm}} \\ &+ \text{boundary twisting terms} \end{aligned} \quad (5.7)$$

where  $\mathbf{F}_{kl}^{DIS}$  is the dissipative or viscous force acting between  $DP_k$  and  $DP_l$ . Using the velocity-gradient discretisation with the distance  $r_{kl}^{cm}$  between centres of mass, the dissipative force takes the form

$$\mathbf{F}_{kl}^{DIS} = \frac{\eta^{lkl}}{r_{kl}^{cm}} (\mathbf{e}_{kl} \cdot \mathbf{e}_{kl}^{cm} \mathbf{U}_{kl} + (\mathbf{U}_{kl} \cdot \mathbf{e}_{kl}) \mathbf{e}_{kl}^{cm}), \quad (5.8)$$

where  $\mathbf{e}_{kl}^{cm}$  is the unit vector pointing between the DP centres of mass.

The boundary twisting terms in Eq. (5.7) are the advective terms that are caused by the motion of the Voronoi boundaries. But only the overall entropy production  $S_{TOT}$  is of interest for the determination of the fluctuations, and boundary motion cannot affect  $S_{TOT}$ . This is so because, when boundaries move, the entropy transported out of one cell must equal the entropy transported into the neighbouring cell. This follows from the extensive nature of entropy (which we assume applies here). Substituting Eq. (5.7) in Eq. (5.6) and summing over  $k$  we may write

$$\Delta S_{TOT} = \sum_k \Delta S_k = \Delta t \sum_{kl} \frac{1}{T_k} \left( \frac{1}{2} \mathbf{F}_{kl}^{DIS} \cdot \mathbf{U}_{kl} - \lambda_{kl} \frac{T_{kl}}{r_{kl}^{cm}} \right). \quad (5.9)$$

This result implies that the mass and volume exchange do *not* affect the fluctuations in the energy and momentum currents. These fluctuations only depend on the heat conduction and the work done by the dissipative force.

We would like to write Eq. (5.9) in the form of a sum over contributions that correspond to the overlap regions  $l_{kl}$ , i.e.  $\Delta S_{TOT} = \sum \Delta S_{kl}$ , where the sum runs over all segments  $l_{kl}$ . Since the sum in Eq. (5.9) runs over all  $k$  and  $l$  we order it in pairs  $(\Delta S_{kl})$  that consist of the entropy contribution from  $k$  to  $l$  plus the contribution from  $l$  to  $k$ . This way of making Eq. (5.9) symmetric yields

$$\Delta S_{kl} = \left( -\frac{\lambda_{kl}}{r_{kl}^{cm}} \left( \frac{T_{kl}}{T_k} - \frac{T_{lk}}{T_l} \right) + \mathbf{F}_{kl}^{DIS} \cdot \frac{\mathbf{U}_{kl}}{\Theta_{kl}} \right) \Delta t, \quad (5.10)$$

where  $\Theta_{kl} = \frac{2T_k T_l}{T_k + T_l}$ . Using  $T_{kl} = T_k - T_l = -T_{lk}$ , a simple Taylor expansion to lowest order in  $T_{kl}$  and  $\dot{S}_{kl} = \Delta S_{kl} / \Delta t$  gives

$$\dot{S}_{kl} = \lambda \frac{T_{kl} l_{kl}}{r_{kl}^{cm}} \left( \frac{T_{kl}}{\Theta_{kl}} \right) + \mathbf{F}_{kl}^{DIS} \cdot \frac{\mathbf{U}_{kl}}{\Theta_{kl}}, \quad (5.11)$$

where we have used the fact that to lowest order in  $T_{kl}$  we may interchange  $\Theta_{kl}$  and  $T_k$ . The Landau formalism of fluctuating hydrodynamics is based on the general fluctuation-dissipation relation for Langevin equations. We shall apply the same formalism here as well, and so we first briefly summarise it (Landau & Lifshitz 1989; de Groot & Mazur 1962) If some flux variable  $\dot{x}$  is linearly related to the corresponding force  $X = \partial S / \partial x$ , where  $S$  is the total entropy of the system, then the magnitude of the fluctuations in that relation is given by the linear coefficient relating  $\dot{x}$  and  $X$ . Mathematically, if

$$\dot{x}_a = \Gamma_{ab} X_b + \tilde{y}_a(t) \quad (5.12)$$

then

$$\langle \tilde{y}_a(t) \tilde{y}_b(0) \rangle = (\Gamma_{ab} + \Gamma_{ba}) \delta(t), \quad (5.13)$$

where as before summation over repeated indices is implied. If  $\dot{x}_a$  is known (or chosen) and  $\dot{S}$  is determined,  $X_a$  may be identified. Then the fluctuations follow directly from the coefficient  $\Gamma$  in Eq. (5.12). This Langevin dynamics will produce the Gibbs distribution  $e^{S(x)/k_B}$  for the variables  $x$  (Landau & Lifshitz 1989).

We choose  $\dot{x}_a \rightarrow \mathbf{F}_{kl}^{DIS}$ , and  $\lambda \frac{l_{kl} T_{kl}}{r_{kl}^{cm}}$  and thus obtain  $X_a \rightarrow \frac{\mathbf{U}_{kl}}{\Theta_{kl}}$ , and  $\frac{T_{kl}}{\Theta_{kl}^2}$ . Using the above identifications and replacing the index  $a$  with the index for the link  $kl$  and correspondingly  $b \rightarrow (kl)'$  we may write

$$\dot{x}_{kl} = \frac{\Theta_{kl} \eta_{kl}}{r_{kl}^{cm}} \delta_{(kl)(kl)'} (\mathbf{e}_{kl} \cdot \mathbf{e}_{kl}^{cm} \mathbf{1} + \mathbf{e}_{kl} \mathbf{e}_{kl}^{cm}) \cdot X_{(kl)'} \quad (5.14)$$

where  $\delta_{(kl)(kl)'} = \delta_{kk'} \delta_{ll'} + \delta_{kl'} \delta_{lk'}$  is nonzero (with the value one) only if the pair  $(kl)$  coincides with  $(kl)'$ . Likewise, for the heat flow terms we may write

$$\dot{x}_{kl} = \frac{\Theta_{kl}^2 \lambda_{kl}}{r_{kl}^{cm}} \delta_{(kl)(kl)'} X_{(kl)'} \quad (5.15)$$

for the components of  $\dot{x}$  containing the heat conduction terms. This determines  $\Gamma$  and hence we have that

$$\begin{aligned} \langle \tilde{\mathbf{F}}_{kl}(t) \tilde{\mathbf{F}}_{kl}(0) \rangle &= \frac{2k_B \Theta_{kl} \eta_{kl}}{r_{kl}^{cm}} (\mathbf{e}_{kl} \cdot \mathbf{e}_{kl}^{cm} \mathbf{1} + \mathbf{e}_{kl}^{cm} \mathbf{e}_{kl}), \\ \langle \tilde{q}_{kl}(t) \tilde{q}_{kl}(0) \rangle &= \frac{2k_B \Theta_{kl}^2 \lambda_{kl}}{r_{kl}^{cm}} \end{aligned} \quad (5.16)$$

where we have re-inserted Boltzmann's constant at the appropriate places. These are exactly the relations we could have established alternatively by means of a Fokker-Planck analysis. Finally, we may multiply the force equation through by  $\mathbf{e}_{kl}$  or its normal to obtain

$$\langle \tilde{F}_{kl}^{\parallel}(t) \tilde{F}_{kl}^{\parallel}(0) \rangle = 2 \langle \tilde{F}_{kl}^{\perp}(t) \tilde{F}_{kl}^{\perp}(0) \rangle = \frac{4k_B \Theta_{kl} \eta_{kl}}{r_{kl}^{cm}} \mathbf{e}_{kl} \cdot \mathbf{e}_{kl}^{cm}. \quad (5.17)$$

## 6. Conclusions

Our model is derived from a microscopic description as in standard kinetic theory. The kinetic derivation is coarse-grained on Lagrangian finite volumes given by the Voronoi tessellation. One of the advantages of using the Voronoi tessellation is the immediately derivable form of the dissipative part of the evolution equations, although this comes at the price of a more complicated geometry and requires knowledge of the volume associated with each DP. The Voronoi tessellation is used because it provides a local volume for the DPs which represents well the local properties of the fluid, in terms of mass, momentum and energy. The fluctuations in the model have been derived via the entropy from fluctuating hydrodynamics, without the need to compute the Fokker-Planck equation as in previous DPD models. The kinetic derivation shows where and how the contributions of the intermolecular potential appear. This new DPD model can be used *inter alia* as a starting point for simulations of complex fluids where more sophisticated physical relationships need to be inserted via the pair-distribution function and on which work is currently in progress. An important feature of this multiscale DPD model is that there is no  $a$

*priori* fixed scale for the dissipative particles. They can represent, for example, the correct physical scales for polymer molecules inserted within a fluid described by other DPs, including full hydrodynamic interactions. By contrast, the fixed scale of the earlier DPD models leads to both fundamental and practical difficulties in problems involving more than one length scale.

Extended numerical validation of this Voronoi based model is in progress, at equilibrium (Serrano *et al.* 2001) to check the thermodynamic consistency and in three spatial dimensions (De Fabritiis & Coveney 2001).

The Ph.D. studentship of GDF is funded by Queen Mary, University of London, and Schlumberger Cambridge Research. EGF thanks the Centre for Computational Science for funding his visits to London during 1999 and 2000. We are grateful to CGAL (Computational Geometry Algorithmic Library), [www.cgal.org](http://www.cgal.org), for help and support in the implementation of the Voronoi tessellation, and to P. Español and M. Serrano for several valuable discussions.

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