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## Dissipative particle dynamics for interacting multicomponent systems

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**Abstract.** We formulate the dissipative particle dynamics technique for multicomponent interacting systems and show that the important property of detailed balance is satisfied.

There is currently growing interest in the development of ‘mesoscale’ modelling and simulation methods for describing the complex dynamical behaviour of many kinds of soft condensed matter, whose properties have defied conventional approaches. One illustration of the challenge faced is provided by complex fluids, which include fluids with many co-existing length and time scales, and those for which a hydrodynamic description is unknown or does not exist at all: examples are ubiquitous and occur in multiphase flows, flow in porous media, colloidal suspensions, microemulsions and polymeric fluids. The traditional continuum-based approach to modelling the behaviour of such fluids, which is centred on the formulation and solution of partial differential equations, has met with only limited success; as a result, new methods are now being developed, which rely on a microscopic description of the fluid.

In principle, the most accurate microscopic approach is based on the use of molecular dynamics (MD), but the computational expense of doing this is so severe that hitherto only a rather restricted number of numerical studies has been performed, mainly limited to two spatial dimensions. (A notable exception is the recent large-scale MD work of Laradji *et al* (1996) on the simulation of spinodal decomposition in three-dimensional binary immiscible fluids.) As a result of these limitations, spatially and temporally discrete lattice-gas automata (LGA) have been developed as an alternative technique since their introduction by Frisch *et al* (1986) and by Wolfram (1986); although originally pitted against computational fluid dynamics in the area of turbulence modelling, more recently it has become apparent that they have particular strengths for modelling non-equilibrium behaviour in complex multicomponent fluids such as microemulsions (see, for example, Rothman and Zaleski (1994) and Boghosian *et al* (1996a)). Simulations using LGA are computationally much faster than MD, particularly since the natural time step—the mean free time between collisions—is several orders of magnitude greater than that required by MD. An important later development of LGA is the lattice-Boltzmann method, in which one studies the dynamical behaviour of single-particle distribution functions (Benzi *et al* 1992, Osborn *et al* 1995).

The LGA method suffers from some disadvantages, however, including the lack of Galilean invariance and the complexity of three-dimensional models (Rothman and Zaleski 1994). While the lattice-Boltzmann approximation method alleviates these difficulties, in virtually every lattice-gas and lattice-Boltzmann model of multicomponent systems the dynamics are microscopically irreversible. Put another way, in such models there is no known detailed balance condition and therefore a Gibbsian equilibrium state is not guaranteed to exist (see, for example, Boghosian and Taylor 1995). On the other hand, certain generalizations of LGA offer the possibility of imposing detailed balance on these models, albeit at increased computational cost (Boghosian *et al* 1996b).

Hoogerbrugge and Koelman (1992) introduced a new mesoscopic technique called dissipative particle dynamics (DPD) with the intention of capturing the best features of MD and LGA in a computationally efficient scheme. Like LGA, DPD should be regarded as being based on a highly simplified microscopic model, which produces correct mesoscopic and macroscopic behaviour. As with LGA, mass and momenta are locally conserved during particle collisions, but while time remains discrete, space is continuous in DPD. The basic properties of the single-component DPD fluid have been studied and its mean-field limit shown to satisfy the Navier–Stokes equations of hydrodynamics (Español 1995). In this paper, we formulate the dissipative particle dynamics of interacting multicomponent systems and prove that, unlike the situation pertaining for LGA, detailed balance is preserved. A multicomponent DPD model has recently been applied to the study of domain growth and phase separation in binary immiscible fluids by Coveney and Novik (1996), with results that can be directly compared to the binary immiscible lattice-gas automaton models of Rothman and Keller (1988) and Emerton *et al* (1997).

Español and Warren (1995) recently wrote down the stochastic differential equations and an equivalent Fokker–Planck equation that correspond, with a minor modification, to the discrete time updating algorithm of Hoogerbrugge and Koelman (1992) for a one-component DPD fluid. In fact, one may regard these stochastic differential equations as furnishing the ‘true’ description of dissipative particle dynamics, and the discrete-time algorithm as an approximation to it, in the same way as the necessarily discrete-time molecular dynamics algorithm is an approximation to Newton’s laws of motion.

For a multicomponent system, the stochastic differential equations (SDE) that govern the position  $\mathbf{r}_{i_\alpha}$  and momentum  $\mathbf{p}_{i_\alpha}$  of the  $i$ th particle of species  $\alpha$  in DPD are given as follows, by a natural extension of the one-component equations (Español and Warren 1995):

$$\begin{aligned} d\mathbf{r}_{i_\alpha} &= \frac{\mathbf{p}_{i_\alpha}}{m_{i_\alpha}} dt \\ d\mathbf{p}_{i_\alpha} &= \left[ \sum_{\beta} \sum_{j_\beta} \mathbf{F}_{i_\alpha j_\beta}^C + \sum_{\beta} \sum_{j_\beta} -\omega_{i_\alpha j_\beta} (\mathbf{e}_{i_\alpha j_\beta} \cdot \mathbf{v}_{i_\alpha j_\beta}) \mathbf{e}_{i_\alpha j_\beta} \right] dt \\ &\quad + \sum_{\beta} \sum_{j_\beta} \sigma \omega^{1/2}(r_{i_\alpha j_\beta}) \mathbf{e}_{i_\alpha j_\beta} dW_{i_\alpha j_\beta} \end{aligned} \quad (1)$$

where  $m_{i_\alpha}$  is the mass of particle  $i_\alpha$ , and we have made the following definitions:

$$\begin{aligned} \mathbf{e}_{i_\alpha j_\beta} &:= \frac{\mathbf{r}_{i_\alpha j_\beta}}{r_{i_\alpha j_\beta}} \\ \mathbf{r}_{i_\alpha j_\beta} &:= \mathbf{r}_{i_\alpha} - \mathbf{r}_{j_\beta} \\ r_{i_\alpha j_\beta} &:= |\mathbf{r}_{i_\alpha} - \mathbf{r}_{j_\beta}| \\ \mathbf{v}_{i_\alpha j_\beta} &:= \mathbf{v}_{i_\alpha} - \mathbf{v}_{j_\beta} \\ \mathbf{v}_{i_\alpha} &:= \mathbf{p}_{i_\alpha} / m_{i_\alpha}. \end{aligned} \quad (2)$$

The conservative force exerted on particle  $i_\alpha$  by particle  $j_\beta$  is

$$\mathbf{F}_{i_\alpha j_\beta}^C := \mathbf{F}_{i_\alpha j_\beta}^C(\mathbf{r}_{i_\alpha j_\beta}) \quad (3)$$

and the friction weight function,

$$\omega_{i_\alpha j_\beta} = \omega_{i_\alpha j_\beta}(\mathbf{r}_{i_\alpha j_\beta}) \quad (4)$$

provides the range of interaction of the dissipative and random forces. Note that we have re-absorbed the friction coefficient of the one-component version into  $\omega$  in order to simplify the notation (since different species might interact with different friction coefficients in general). As a consequence, the normalization  $\int \omega(r) d\mathbf{r} = V/N = n^{-1}$  (with  $V$  the volume,  $N$  the total number of particles and  $n$  the number density), no longer holds and instead  $\omega$  has dimensions of (force/velocity). The noise amplitude  $\sigma$  is given by

$$\sigma = (2k_B T)^{1/2} \quad (5)$$

where  $T$  is the temperature of the equilibrium state towards which the system relaxes (assuming that this is permitted by the boundary conditions) and  $k_B$  is Boltzmann's constant. Finally,  $dW_{i_\alpha j_\beta} = dW_{j_\beta i_\alpha}$  are independent increments of the Wiener process. To be specific, we shall assume the Itô interpretation for these processes, which in turn requires application of the Itô calculus rule

$$dW_{i_\alpha j_\beta} dW_{i'_\alpha j'_\beta} = (\delta_{i_\alpha i'_\alpha} \delta_{j_\beta j'_\beta} + \delta_{i_\alpha j'_\beta} \delta_{j_\beta i'_\alpha}) dt. \quad (6)$$

Equation (6) says that  $dW_{i_\alpha j_\beta}(t)$  is an infinitesimal of order 1/2 (Gardiner 1983).

The SDEs given in equation (1) closely resemble those defining the original DPD updating algorithm proposed by Hoogerbrugge and Koelman (1992), although a slightly different notation is used. Note, however, the occurrence in equation (1) of the square root of the friction weight function in the random force term: this is in contrast to the original algorithm and is required in order to obtain the correct (canonical) equilibrium ensemble (Español and Warren 1995).

The Fokker–Planck equation that is mathematically equivalent to the SDEs in equation (1) is given by

$$\partial_t \rho(\Omega; t) = L\rho(\Omega; t) \quad (7)$$

(Gardiner 1983), where  $\Omega$  denotes the set of all positions and momenta of the particles,  $\rho(\Omega; t)$  is the probability density in phase space and the Fokker–Planck operator is (Español 1995)

$$\begin{aligned} L \equiv & - \left[ \sum_\alpha \sum_{i_\alpha} \frac{\mathbf{p}_{i_\alpha}}{m} \cdot \frac{\partial}{\partial \mathbf{r}_{i_\alpha}} + \sum_{\alpha\beta} \sum_{i_\alpha, j_\beta} \mathbf{F}_{i_\alpha j_\beta}^C \cdot \frac{\partial}{\partial \mathbf{p}_{i_\alpha}} \right] \\ & + \sum_{\alpha\beta} \sum_{i_\alpha, j_\beta} \omega_{i_\alpha j_\beta} \mathbf{e}_{i_\alpha j_\beta} \cdot \frac{\partial}{\partial \mathbf{p}_{i_\alpha}} \left[ (\mathbf{e}_{i_\alpha j_\beta} \cdot \mathbf{v}_{i_\alpha j_\beta}) + k_B T \mathbf{e}_{i_\alpha j_\beta} \cdot \left( \frac{\partial}{\partial \mathbf{p}_{i_\alpha}} - \frac{\partial}{\partial \mathbf{p}_{j_\beta}} \right) \right] \\ = & L^C + L^D. \end{aligned} \quad (8)$$

The first term in square brackets is the Liouville operator  $L^C$ . The second term  $L^D$ , which is proportional to the friction weight function, takes into account the effects of dissipation. In the absence of dissipation, equation (1) reduces to Newton's equations of motion and equation (7) becomes Liouville's equation. Note that the diffusion tensors associated with the second momentum derivatives do not depend on the momenta of the particles, implying that the Itô and Stratonovich interpretations in fact furnish identical descriptions (Gardiner 1983).

It is a matter of substitution to check that the canonical equilibrium ensemble is not only a stationary solution of the Liouville equation but also a stationary solution of the Fokker–Planck equation (7), that is  $L\rho^{\text{eq}} = 0$ , where

$$\rho^{\text{eq}}(\Omega) = \frac{1}{Z} \exp\{-H(\Omega)/k_{\text{B}}T\} = \frac{1}{Z} \exp\left\{-\left(\sum_{\alpha} \sum_{i_{\alpha}} \frac{p_{i_{\alpha}}^2}{2m_{i_{\alpha}}} + V(r)\right)/k_{\text{B}}T\right\} \quad (9)$$

$H(\Omega)$  is the Hamiltonian of the system,  $V$  is the potential function that give rise to the conservative forces  $\mathbf{F}^{\text{C}}$ , and  $Z$  is the canonical partition function.

We shall need several operators related to the Fokker–Planck operator  $L$ . For example, if we use the SDE (1) with the aid of the calculus rule (6) in order to compute the differential  $df$  of an arbitrary function  $f$ , we find

$$\begin{aligned} df &= \sum_{\alpha} \sum_{i_{\alpha}} \frac{\partial f}{\partial \mathbf{r}_{i_{\alpha}}} \cdot d\mathbf{r}_{i_{\alpha}} + \frac{\partial f}{\partial \mathbf{p}_{i_{\alpha}}} \cdot d\mathbf{p}_{i_{\alpha}} \\ &\quad + \sum_{\alpha\beta} \sum_{i_{\alpha}j_{\beta}} \frac{1}{2} \frac{\partial^2 f}{\partial \mathbf{r}_{i_{\alpha}} \partial \mathbf{r}_{j_{\beta}}} d\mathbf{r}_{i_{\alpha}} d\mathbf{r}_{j_{\beta}} + \frac{1}{2} \frac{\partial^2 f}{\partial \mathbf{r}_{i_{\alpha}} \partial \mathbf{p}_{j_{\beta}}} d\mathbf{r}_{i_{\alpha}} d\mathbf{p}_{j_{\beta}} \\ &\quad + \frac{1}{2} \frac{\partial^2 f}{\partial \mathbf{p}_{i_{\alpha}} \partial \mathbf{p}_{j_{\beta}}} d\mathbf{p}_{i_{\alpha}} d\mathbf{p}_{j_{\beta}} + \mathcal{O}(dt^{3/2}) \\ &= L^+ f dt + \sum_{i_{\alpha}j_{\beta}} \sigma \omega^{1/2}(r_{i_{\alpha}j_{\beta}}) \mathbf{e}_{i_{\alpha}j_{\beta}} \frac{\partial f}{\partial \mathbf{p}_{i_{\alpha}}} dW_{i_{\alpha}j_{\beta}} + \mathcal{O}(dt^{3/2}). \end{aligned} \quad (10)$$

The adjoint operator  $L^+$  is given by

$$\begin{aligned} L^+ &:= \left[ \sum_{\alpha} \sum_{i_{\alpha}} \frac{\mathbf{p}_{i_{\alpha}}}{m} \cdot \frac{\partial}{\partial \mathbf{r}_{i_{\alpha}}} + \sum_{\alpha\beta} \sum_{i_{\alpha}j_{\beta}} \mathbf{F}_{i_{\alpha}j_{\beta}}^{\text{C}} \cdot \frac{\partial}{\partial \mathbf{p}_{i_{\alpha}}} \right] \\ &\quad + \sum_{\alpha\beta} \sum_{i_{\alpha}j_{\beta}} \omega_{i_{\alpha}j_{\beta}} \left[ -(\mathbf{e}_{i_{\alpha}j_{\beta}} \cdot \mathbf{v}_{i_{\alpha}j_{\beta}}) \mathbf{e}_{i_{\alpha}j_{\beta}} \cdot \frac{\partial}{\partial \mathbf{p}_{i_{\alpha}}} \right. \\ &\quad \left. + k_{\text{B}}T \mathbf{e}_{i_{\alpha}j_{\beta}} \cdot \frac{\partial}{\partial \mathbf{p}_{i_{\alpha}}} \mathbf{e}_{i_{\alpha}j_{\beta}} \cdot \left( \frac{\partial}{\partial \mathbf{p}_{i_{\alpha}}} - \frac{\partial}{\partial \mathbf{p}_{j_{\beta}}} \right) \right] \\ &= L^{\text{C}+} + L^{\text{D}+}. \end{aligned} \quad (11)$$

This operator is obtained from  $L$  by changing the sign of all partial derivatives. The relevance of  $L^+$  stems from the fact that it allows time derivatives of ensemble averages to be calculated, because of the following property derived from (10)

$$\frac{d}{dt} \langle f \rangle = \langle L^+ f \rangle. \quad (12)$$

A Fokker–Planck equation is said to satisfy detailed balance if the following identity holds (Risken 1989)

$$L\rho^{\text{eq}}\phi = \rho^{\text{eq}}L^{+\epsilon}\phi \quad (13)$$

where  $\phi$  is an arbitrary function of positions and momenta  $\Omega$ . The operator  $L^{+\epsilon}$  is obtained from  $L^+$  by reversing the sign of the momenta. This condition ensures that the joint probability distribution satisfies the reversibility property (Risken 1989)

$$\rho(\Omega, t, \Omega', t') = \rho(\epsilon\Omega', t, \epsilon\Omega, t'). \quad (14)$$

We now show that detailed balance is actually satisfied in DPD. We first note that  $L\rho^{\text{eq}}\phi = L^{\text{C}}\rho^{\text{eq}}\phi + L^{\text{D}}\rho^{\text{eq}}\phi$ . In addition,  $L^{\text{C}}$  contains only first derivatives and, therefore,

$L^C \rho^{\text{eq}} \phi = \phi L^C \rho^{\text{eq}} + \rho^{\text{eq}} L^C \phi = \rho^{\text{eq}} L^{C+\epsilon} \phi$ . In other words, the Liouville operator satisfies detailed balance, as is expected from the reversibility of the conservative part of the dynamics. We now consider the dissipative part

$$\begin{aligned}
L^D \rho^{\text{eq}} \phi &= \sum_{\alpha\beta} \sum_{i_\alpha, j_\beta} \omega_{i_\alpha j_\beta} \mathbf{e}_{i_\alpha j_\beta} \cdot \frac{\partial}{\partial \mathbf{p}_{i_\alpha}} \left[ (\mathbf{e}_{i_\alpha j_\beta} \cdot \mathbf{v}_{i_\alpha j_\beta}) + k_B T \mathbf{e}_{i_\alpha j_\beta} \cdot \left( \frac{\partial}{\partial \mathbf{p}_{i_\alpha}} - \frac{\partial}{\partial \mathbf{p}_{j_\beta}} \right) \right] \rho^{\text{eq}} \phi \\
&= \sum_{\alpha\beta} \sum_{i_\alpha, j_\beta} \omega_{i_\alpha j_\beta} \mathbf{e}_{i_\alpha j_\beta} \cdot \frac{\partial}{\partial \mathbf{p}_{i_\alpha}} \left[ k_B T \rho^{\text{eq}} \mathbf{e}_{i_\alpha j_\beta} \cdot \left( \frac{\partial \phi}{\partial \mathbf{p}_{i_\alpha}} - \frac{\partial \phi}{\partial \mathbf{p}_{j_\beta}} \right) \right] \\
&= -\rho^{\text{eq}} \sum_{\alpha\beta} \sum_{i_\alpha, j_\beta} \omega_{i_\alpha j_\beta} \mathbf{e}_{i_\alpha j_\beta} \cdot \mathbf{v}_{i_\alpha} \left[ \mathbf{e}_{i_\alpha j_\beta} \cdot \left( \frac{\partial \phi}{\partial \mathbf{p}_{i_\alpha}} - \frac{\partial \phi}{\partial \mathbf{p}_{j_\beta}} \right) \right] \\
&\quad + \rho^{\text{eq}} \sum_{\alpha\beta} \sum_{i_\alpha, j_\beta} \omega_{i_\alpha j_\beta} \mathbf{e}_{i_\alpha j_\beta} \cdot \frac{\partial}{\partial \mathbf{p}_{i_\alpha}} \left[ k_B T \mathbf{e}_{i_\alpha j_\beta} \cdot \left( \frac{\partial \phi}{\partial \mathbf{p}_{i_\alpha}} - \frac{\partial \phi}{\partial \mathbf{p}_{j_\beta}} \right) \right] \\
&= -\rho^{\text{eq}} \sum_{\alpha\beta} \sum_{i_\alpha, j_\beta} \omega_{i_\alpha j_\beta} (\mathbf{e}_{i_\alpha j_\beta} \cdot \mathbf{v}_{i_\alpha j_\beta}) \mathbf{e}_{i_\alpha j_\beta} \cdot \frac{\partial \phi}{\partial \mathbf{p}_{i_\alpha}} \\
&\quad + \rho^{\text{eq}} \sum_{\alpha\beta} \sum_{i_\alpha, j_\beta} \omega_{i_\alpha j_\beta} \mathbf{e}_{i_\alpha j_\beta} \cdot \frac{\partial}{\partial \mathbf{p}_{i_\alpha}} \left[ k_B T \mathbf{e}_{i_\alpha j_\beta} \cdot \left( \frac{\partial \phi}{\partial \mathbf{p}_{i_\alpha}} - \frac{\partial \phi}{\partial \mathbf{p}_{j_\beta}} \right) \right] \\
&= \rho^{\text{eq}} L^{D+\epsilon} \phi.
\end{aligned} \tag{15}$$

This proves that detailed balance is satisfied for interacting multicomponent systems in DPD, just as it is for one-component fluids (Español 1995).

Strictly speaking, detailed balance is satisfied for the underlying continuous-time version of dissipative particle dynamics, but is only approximately satisfied by the discrete-time algorithm. The approximation improves as the size of the time-step is reduced. This is analogous to the situation in molecular dynamics. There, Newton's laws ensure that the energy and momentum are rigorously conserved in the absence of external forces, while an MD algorithm only approximately conserves these quantities: small fluctuations and drift in the momentum and energy occur, but these effects diminish as the time-steps become progressively smaller.

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