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Statistical Mechanics of Dissipative Particle Dynamics.

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Abstract. – The stochastic differential equations corresponding to the updating algorithm of Dissipative Particle Dynamics (DPD), and the corresponding Fokker-Planck equation are derived. It is shown that a slight modification to the algorithm is required before the Gibbs distribution is recovered as the stationary solution to the Fokker-Planck equation. The temperature of the system is then directly related to the noise amplitude by means of a fluctuation-dissipation theorem. However, the correspondingly modified, discrete DPD algorithm is only found to obey these predictions if the length of the time step is sufficiently reduced. This indicates the importance of time discretisation in DPD.

Recently, Hoogerbrugge and Koelman have introduced a new method for simulating hydrodynamic behaviour which has been coined Dissipative Particle Dynamics (DPD) [1,2]. This technique was conceived as an improvement over conventional molecular dynamics (MD) in order to describe complex hydrodynamic behaviour with computational efficiency. Although there have been attempts to study hydrodynamic phenomena with MD [3-6], the number of particles needed to obtain collective behaviour is extremely large. The reason is that hydrodynamic collective behaviour only appears for typical distances L much larger than the interparticle distance and for typical times T much larger than a collision time τ. Other techniques have also been introduced to deal with the computation burden of hydrodynamic flow. Lattice-Gas (LG) dynamics, which constitute a discrete caricature of MD [7] and the more efficient Lattice-Boltzmann dynamics (LB), which is essentially a discretisation of Boltzmann equation [8], both capture hydrodynamic behaviour. The main problem of LG/LB is that the lattice may induce spurious dynamics (due to the absence of perfect isotropy and, in LG, Galilean invariance). Although some of the problems can be eliminated with convenient lattices and rescaling of velocities, the problems show up in more severe forms when dealing with complex flows in complex boundaries as in immiscible mixtures or colloidal

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suspension. Also the lattice makes it difficult to deal with the forcing boundary conditions required for sheared or extensional flows. Therefore, an off-lattice method of simulation as in conventional MD is very desirable in order to deal with these complex boundary conditions.

The point of view taken by Hoogerbrugge and Koelman is that conventional MD provides too much detail of the actual motion of the molecules of the fluid. If one is interested in hydrodynamic behaviour one can look at a more coarse-grained level. The particles in DPD are not regarded as molecules in a simple fluid but lumps of molecules grouped to form a «fluid particle» in much the same spirit as the renormalisation group has been applied in polymer physics where lumps of monomers are grouped to form a «bead». The fluid particles no longer interact conserving the energy in each «collision» and this is modelled by means of Brownian dashpots. By introducing dissipation into a molecular-dynamics simulation, one expects that the system is described in a coarse-grained level and therefore there is more chance to observe hydrodynamic behaviour with a considerably smaller number of particles, thus reducing the computational effort.

There exists an obvious way to introduce dissipation into a conventional molecular dynamics. One simply adds to the force felt by any particle a random force and a viscous frictional force. The result is conventional Brownian dynamics, intended to model colloidal particles in suspension in a fluid. However, in Brownian dynamics the only conserved quantity in the system is the number of particles, and, therefore, the only macroscopic behaviour will be diffusive. The crucial point in DPD is that not only the number of particles is a conserved quantity, but also the total momentum of the system is conserved. This implies that the macroscopic behaviour will not be diffusive, but hydrodynamic, that is, there will be a transport equation for the momentum density field, coupled to the transport of mass. On the other hand, energy is not conserved and there is no transport equation for energy in DPD. It is assumed that the model thus describes isothermal situations. However, there are no expressions relating the temperature of the system and the model parameters, *i.e.* the friction coefficient and the noise amplitude of the Brownian dashpots.

The purpose of this note is to give a theoretical foundation to DPD by formulating the continuous stochastic differential equation that corresponds to the original algorithm. This allows to derive the associated Fokker-Planck equation and study its equilibrium solution. In doing this, a clear definition of temperature emerges. It should be noted that without the basic equation for the microscopic dynamics, such as the Fokker-Planck equation obtained below, it is not possible to derive in a rigorous way the hydrodynamic equations for DPD. In addition, the relevance of the time step length in DPD becomes clear, because only for sufficiently small time steps the correct equilibrium results are recovered.

Hoogerbrugge and Koelman present the simplest model that contains dissipation and conserve the total momentum. We rephrase a continuous version of the model in a notation that will be convenient for our purposes. The total force on a given particle is written in the form

$$\dot{\boldsymbol{p}}_i = \sum_{j \neq i} \boldsymbol{F}_{ij}^{\mathrm{C}} + \sum_{j \neq i} \boldsymbol{F}_{ij}^{\mathrm{D}} + \sum_{j \neq i} \boldsymbol{F}_{ij}^{\mathrm{R}} , \tag{1}$$

where $\boldsymbol{F}_{ij}^{\mathrm{C}}$ is a conservative force deriving from a potential exerted on particle i by the j-th particle, $\boldsymbol{F}_{ij}^{\mathrm{D}}$ is a dissipative force and $\boldsymbol{F}_{ij}^{\mathrm{R}}$ is a random force. Note that pair additivity has been assumed. In addition, Galilean invariance requires that the forces $\boldsymbol{F}_{ij}^{\mathrm{D}}$ and $\boldsymbol{F}_{ij}^{\mathrm{R}}$ depend only on the combinations $\boldsymbol{r}_{ij} \equiv \boldsymbol{r}_i - \boldsymbol{r}_j$ and $\boldsymbol{v}_{ij} \equiv \boldsymbol{v}_i - \boldsymbol{v}_j$, where $\boldsymbol{r}_i$, $\boldsymbol{v}_i$ are the position and velocity vectors of particle i. The further requirement of isotropy demands that the forces should transform under rotations as vectors. Finally, it is required that the dissipative forces $\boldsymbol{F}^{\mathrm{D}}$ are linear on the momentum and the random forces $\boldsymbol{F}^{\mathrm{R}}$ are independent of the momentum. This requirement will imply that the Fokker-Planck equation has a drift term linear in the

variable and a diffusion term independent of the variable. As a result, the Fokker-Planck equation has the very appealing property of having a Gaussian equilibrium solution [9].

A simple form of the forces that satisfy these hypotheses is

$$\begin{cases} \boldsymbol{F}_{ij}^{\mathrm{D}} = -\gamma\omega_{\mathrm{D}}(r_{ij})(\boldsymbol{e}_{ij}\cdot\boldsymbol{v}_{ij})\boldsymbol{e}_{ij}\,, \\ \boldsymbol{F}_{ij}^{\mathrm{R}} = \sigma\omega_{\mathrm{R}}(r_{ij})\boldsymbol{e}_{ij}\zeta_{ij}\,, \end{cases} \tag{2}$$

where $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$, and $\boldsymbol{e}_{ij} = (\boldsymbol{r}_i - \boldsymbol{r}_j)/r_{ij}$ is the unit vector from the j-th particle to the i-th particle. The term ζ_{ij} is a Gaussian white-noise term such that $\zeta_{ij} = \zeta_{ji}$ and with stochastic properties

$$\begin{cases} \langle\zeta_{ij}(t)\rangle = 0\,, \\ \langle\zeta_{ij}(t)\,\zeta_{i'j'}(t')\rangle = (\delta_{ii'}\delta_{jj'} + \delta_{ij'}\delta_{ji'})\,\delta(t-t')\,. \end{cases} \tag{3}$$

The symmetry property $\zeta_{ij} = \zeta_{ji}$ ensures that the total momentum is conserved, $\mathrm{d}\left(\sum_i \boldsymbol{p}_i\right)\Big/\mathrm{d}t = 0$. Finally, the weight functions ω_{D}, ω_{R} provide the range of interaction for the dissipative and random forces and γ and σ are interpreted as the friction coefficient and the amplitude of the noise. The physical interpretation of the dissipative force is as follows. If $(\boldsymbol{v}_{ij}\cdot\boldsymbol{e}_{ij}) > 0$, it means that particle i is moving apart from j and, therefore, it feels a viscous force towards j. If it moves towards j the viscous force is in the opposite direction. If only $\boldsymbol{F}^{\mathrm{C}}$ and $\boldsymbol{F}^{\mathrm{D}}$ were present, the particles would eventually stop in their relative motions. The random forces $\boldsymbol{F}_{ij}^{\mathrm{R}}$ which are also radially directed provide the continuous kicks that keep the system in thermal motion. These kicks do satisfy Newton's third law and then conserve the total momentum.

By substituting the form (2) for the forces into Newton's second law (1) we obtain a set of Langevin equations. We write the resulting Langevin equations in the mathematically well-defined form of stochastic differential equations [10]

$$\begin{cases} \mathrm{d}\boldsymbol{r}_i = \dfrac{\boldsymbol{p}_i}{m_i}\,\mathrm{d}t\,, \\ \mathrm{d}\boldsymbol{p}_i = \left[\displaystyle\sum_{j\neq i}\boldsymbol{F}_{ij}^{\mathrm{C}}(\boldsymbol{r}_{ij}) + \sum_{j\neq i} -\gamma\omega_{\mathrm{D}}(r_{ij})(\boldsymbol{e}_{ij}\cdot\boldsymbol{v}_{ij})\boldsymbol{e}_{ij}\right]\mathrm{d}t + \displaystyle\sum_{j\neq i}\sigma\omega_{\mathrm{R}}(r_{ij})\boldsymbol{e}_{ij}\,\mathrm{d}W_{ij}\,, \end{cases} \tag{4}$$

where m_i is the mass of particle i and $\mathrm{d}W_{ij} = \mathrm{d}W_{ji}$ are independent increments of the Wiener process. We will assume Itô interpretation which implies the Itô calculus rule

$$\mathrm{d}W_{ij}\,\mathrm{d}W_{i'j'} = (\delta_{ii'}\delta_{jj'} + \delta_{ij'}\delta_{ji'})\,\mathrm{d}t\,, \tag{5}$$

i.e. $\mathrm{d}W_{ij}(t)$ is an infinitesimal of order 1/2 [10].

The above SDE are very similar to the ones that correspond to the updating algorithm proposed by Hoogerbrugge and Koelman under slightly different notation. However, note that we have in principle different weight functions $\omega_{\mathrm{D}}(r)$, $\omega_{\mathrm{R}}(r)$ for the dissipative and fluctuating terms whereas $\omega_{\mathrm{D}}(r) = \omega_{\mathrm{R}}(r)$ in ref. [1].

Our next aim is to derive the Fokker-Planck equation that corresponds to the above SDE. Following standard procedures [10], one considers the differential $\mathrm{d}f$ of an arbitrary function f to second order and substitutes the SDE (4). By using (5) and the fact that $\mathrm{d}W$ is an infinitesimal of order 1/2 one can obtain $\langle\mathrm{d}f/\mathrm{d}t\rangle$ and extract the Fokker-Planck equation governing the temporal evolution of the distribution function $\varrho(r, p; t)$ of the positions and

momenta of all the particles [10]. The resulting Fokker-Planck equation takes the form

$$\partial_t \rho(r, p; t) = L_C \rho(r, p; t) + L_D \rho(r, p; t), \tag{6}$$

where we have defined the operators

$$\begin{cases} L_C \rho(r, p; t) \equiv -\left[\sum_i \frac{\boldsymbol{p}_i}{m} \frac{\partial}{\partial \boldsymbol{r}_i} + \sum_{i,j \neq i} \boldsymbol{F}_{ij}^C \frac{\partial}{\partial \boldsymbol{p}_i}\right] \rho(r, p; t), \\ L_D \rho(r, p; t) \equiv \sum_{i,j \neq i} \boldsymbol{e}_{ij} \frac{\partial}{\partial \boldsymbol{p}_i}\left[\gamma \omega_D(r_{ij})(\boldsymbol{e}_{ij} \cdot \boldsymbol{v}_{ij}) + \frac{\sigma^2}{2} \omega_R^2(r_{ij}) \boldsymbol{e}_{ij}\left(\frac{\partial}{\partial \boldsymbol{p}_i} - \frac{\partial}{\partial \boldsymbol{p}_j}\right)\right] \rho(r, p; t). \end{cases} \tag{7}$$

The operator L_C is the usual Liouville operator of a Hamiltonian system interacting with conservative forces $\boldsymbol{F}^C$. The operator L_D contains second derivatives and takes into account the effects of the dissipative and random forces. Note that the diffusion tensors accompanying the second derivatives with respect to the momentum do not depend on the momenta of the particles. This implies that the Itô and Stratonovich interpretations provide exactly the same answers [10].

The steady-state solution of eqs. (6) and (7), $\partial_t \rho = 0$, gives the equilibrium distribution ρ^{eq}. In statistical mechanics of Hamiltonian systems any function of the dynamical invariants (energy, momentum, etc.) can be an equilibrium distribution to which the system evolves provided it is ergodic or mixing. The question of which equilibrium ensemble is selected is a matter of initial conditions [11]. In contrast, the equilibrium distribution of (6) is unique, and no ergodic hypothesis is required since any initial distributions will relax towards the steady-state distribution [9]. We now consider the conditions under which the steady-state solution is the Gibbs canonical ensemble:

$$\rho^{eq}(r, p) = \frac{1}{Z} \exp[-H(r, p)/k_B T] = \frac{1}{Z} \exp\left[-\left(\sum_i \frac{p_i^2}{2m_i} + V(r)\right) \Big/ k_B T\right], \tag{8}$$

where H is the Hamiltonian of the system, V is the potential function that gives rise to the conservative forces $\boldsymbol{F}^C$, k_B is Boltzmann's constant, T is the equilibrium temperature and Z is the normalising partition function. The canonical ensemble is the equilibrium solution for the conservative system, *i.e.* $L_C \rho^{eq} = 0$. In addition, we can satisfy $L_D \rho^{eq} = 0$ by requiring

$$\omega_R(r) = \omega_D^{1/2}(r), \tag{9}$$

$$\sigma = (2k_B T \gamma)^{1/2}. \tag{10}$$

This is the fluctuation-dissipation theorem for the DPD method, which has exactly the same structure as the fluctuation-dissipation theorem as in conventional Brownian motion.

The requirement (9) suggests a simple modification to the original DPD algorithm of Hoogerbrugge and Koelman [1]: insert an extra factor in the dissipative term in their algorithm so that (9) is functionally satisfied. In order to remain close to the original algorithm we used $2(1 - r/r_c)$ in the notation in their paper. Comparison with a discrete algorithm obtained by integrating (4) over a time step Δt, keeping terms only of $O(\Delta t)$, and setting $\Delta t = 1$, allows identification of σ, γ and $\omega_R = \omega_D^{1/2}$ in terms of the parameters in the Hoogerbrugge and Koelman algorithm.

We have implemented both the original and modified algorithms, and tested (10) and the Gibbs distribution (8) by looking for equipartition in a mixture of particles of different masses. We find that, with the parameters suggested by Hoogerbrugge and Koelman,

neither the original *nor* the modified algorithms obey (10) or equipartition. The measured temperature is nearly 25% greater than the predicted value from (10).

We argue that this is an effect due to time discretisation as follows. One of the natural time scales in DPD is set by the range of the interaction r_c and the r.m.s. particle velocity $v_{\text{r.m.s.}}$: $t_c = r_c/v_{\text{r.m.s.}}$. In a model with a well-defined temperature $v^2_{\text{r.m.s.}} = 3k_B T/m$, and may be determined from the model parameters (if temperature is not well defined, $v_{\text{r.m.s.}}$ has to be measured by simulation). The dimensionless quantity $\Delta t/t_c$ has a physical interpretation: as $\Delta t/t_c$ approaches unity, the distance the particles jump in one time step approaches the range of the interaction. Thus we would only expect the continuous DPD results to be recovered in the limit where $\Delta t/t_c \ll 1$.

For the parameters suggested by Hoogerbrugge and Koelman we calculate $\Delta t/t_c \approx \approx 0.05$–$0.08$ for the range of densities used in the modified algorithm (the density dependence of t_c is a consequence of our choice of $2(1 - r/r_c)$: it could be removed if desired). Whilst this is small, the simulation results suggest that it may not be small enough to follow the continuous DPD model. To test this hypothesis we use the discrete algorithm obtained by integrating (4) over a *variable* time step Δt. Other parameters are such that the algorithm coincides with the (modified) Hoogerbrugge and Koelman algorithm at $\Delta t = 1$ [1]. We find that equipartition is much improved in both algorithms as $\Delta t/t_c$ is reduced, the improvement being more marked in the modified algorithm. Thus at $\Delta t/t_c \approx 0.005$–$0.008$ equipartition is recovered within statistical errors for the modified algorithm. There is still a statistically significant violation in the original algorithm. At this value of $\Delta t/t_c$ the temperature of the system with the modified algorithm is found to agree with (10) to within 5%.

In summary, we have presented stochastic differential equations which correspond to Hoogerbrugge and Koelman's dissipative particle dynamics algorithm (4). After a minor modification the system has as equilibrium solution the same equilibrium solution as the conservative system (*i.e.* (4) with $\gamma = \sigma = 0$), at a temperature $k_B T = \sigma^2/2\gamma$. The Fokker-Planck equation obtained in this note is the starting point for a formal derivation (for example, by means of projection operators [12]) of the hydrodynamic equations that govern the mass and momentum density fields, in the same way as the Liouville equation is the starting point in classical statistical mechanics [13].

We have also found that the time step in the original algorithm of Hoogerbrugge and Koelman is large enough that the behaviour no longer follows that predicted by the stochastic differential equations (4). This is not to say that the algorithm with the large time step should be abandoned, merely that the effect of time discretisation should be acknowledged. It would be very interesting to derive a discrete Fokker-Planck equation analogous to (7), and use it to analyse the equilibrium and hydrodynamic behaviour of discrete DPD.

An interesting point is to prove that the introduction of noise and dissipation, together with the large time step, produces hydrodynamic behaviour at smaller time and distance scales, *i.e.* times not much longer than one time step and distances not much larger than the separation between particles. This is what is actually observed in simulation. It is an extremely useful feature, and it should be adequately explained.

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[1] There is a degree of arbitrariness here since factors of Δt may be inserted in any of the terms without affecting the result at $\Delta t = 1$. We have made the simplest choice.

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