Dissipative particle dynamics: The equilibrium for finite time steps

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Abstract. – Dissipative particle dynamics (DPD) is a relatively new technique which has proved successful in the simulation of complex fluids. We caution that for the equilibrium achieved by the DPD simulation of a simple fluid the temperature depends strongly on the time step. An analytic expression for the dependence is obtained and shown to agree well with simulation results.

Modelling the rheological behaviour of complex fluids using standard numerical techniques is very difficult and often impossible. Molecular-dynamics simulations which can faithfully represent the microscopic nature of the fluid require intensive computational power to reach time scales over which hydrodynamic effects are operative. Macroscopic approaches, based on the Navier-Stokes equations, must include phenomenological constitutive relations which are difficult to verify.

In recent years a new class of techniques for hydrodynamic simulation have been developed. These include lattice-gas cellular automata [1], lattice Boltzmann simulations [2], and dissipative particle dynamics [3]. In some sense these methods may be termed mesoscopic because the fluid is modelled on a length scale that allows input of the relevant physics but not the details of the interatomic interactions. For example, a long polymer may be represented by a few particles connected by springs in the spirit of the Rouse-Zimm model [4]. Hydrodynamics then follows from the constraints of conservation of local mass and momentum. Although application of these techniques to complex fluids is in its infancy promising, results have been obtained for several systems including microemulsions [5], colloidal suspensions [6], and multiphase flow in porous media [7].

One of the most flexible but least explored of the approaches is dissipative particle dynamics (DPD) [3]. A set of particles, each of which may be interpreted as representing a mesoscopic region of fluid, move in continuous space and discrete time. Each particle is subjected to Brownian noise, and a friction force acts between them in such a way that mass and momentum are conserved. As pointed out by Español and Warren [8], DPD is an extension of the Langevin
equation of Brownian motion to a system which conserves momentum as well as mass and hence obeys hydrodynamics.

DPD has been used to simulate phase separation in a binary fluid by designating the particles to be of two different types and adding a conservative repulsive force between unlike particles [9]. It has been applied to dilute solutions of polymers by choosing a few of the particles to represent sections of the polymer chain and adding springs between them [4]. A third application is to the observance of shear thinning in particulate suspensions [10]. In each case the simulations have been very successful in reproducing the expected behaviour.

The success of the method is surprising given its seemingly ad hoc nature. Much remains to be understood about the theoretical justification for the approach. In an important first step Espa˜nol and Warren [8] showed that, given the correct relation between the forms of the random and dissipative forces, the system relaxes to a Gibbs distribution characterised by a temperature related to the noise amplitude via a fluctuation-dissipation theorem. However their results hold only in the limit that the time step becomes infinitesimal. This is a severe limitation because the power of DPD relies on its ability to take large time steps in order to probe long time scales.

Therefore our aim in this letter is to study the equilibrium of the system for a general time step. Away from the limit, $\Delta t \to 0$, it is not obvious that the equilibrium distribution is the Gibbs distribution. However, it is expected that, close to this limit, it will be a good approximation. Numerical simulations verify this. We demonstrate that, under this assumption, the distribution would remain unchanged under the full finite $\Delta t$ evolution and derive the dependence of the corresponding temperature $T$ on the time step $\Delta t$ and, it transpires, the density $n$. The dependence is large. For example, for $n = 2$, $T(\Delta t = 0.25) \sim 2 \times T(\Delta t = 0)$.

We first describe the DPD algorithm in more detail. Then we derive an expression for the temperature in terms of the parameters involved in the updating step. The formula is compared to simulation results.

Consider a set of particles $i$ of equal mass $m$ at positions $r_i$ with momentum $p_i$. The system is updated according to the algorithm [3]

$$r_i^\alpha(t + \Delta t) - r_i^\alpha(t) \equiv \Delta r_i^\alpha = \frac{p_i^\alpha}{m} \Delta t,$$

$$p_i^\alpha(t + \Delta t) - p_i^\alpha(t) \equiv \Delta p_i^\alpha = \sum_{j \neq i} \left\{ -\gamma w_D(r_{ij})(e_{ij}^\beta v_{ij}^\beta) \Delta t + \sigma w_R(r_{ij}) \xi_{ij}(\Delta t)^{\frac{1}{2}} \right\} e_{ij}^\alpha,$$

where superscripts $\alpha, \beta, \ldots$ are used to represent Cartesian components of a vector and the usual summation convention is assumed for the Cartesian labels. Subscripts $i, j, \ldots$ distinguish different particles. $e_{ij}$ is the unit vector between the $i$-th and $j$-th particles, $r_{ij}$ their separation and $v_{ij} \equiv v_i - v_j$ their relative velocity. $\gamma$ is the strength of the dissipative force and $\sigma$ the strength of the random force and $w_D(r_{ij})$ and $w_R(r_{ij})$ are radial weighting functions for each. The random variables $\xi_{ij}$ obey

$$\xi_{ij} = \bar{\xi}_{ij}, \quad \bar{\xi}_{ij}(t) = 0, \quad \bar{\xi}_{ij}(t)\bar{\xi}_{kl}(t') = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta_{tt'},$$

where a bar represents an average over the ensemble of all $\xi_{ij}$. The evolution algorithm can be written more conveniently as

$$\Delta p_i^\alpha(t) = \sum_{j, \beta} L_{ij}^{\alpha\beta} p_j^\beta + \sum_{j} M_{ij}^\alpha \xi_{ij},$$
where

\[ L_{ij}^{\alpha} = -\delta_{ij} \frac{\gamma}{m} \sum_t w_D(r_{ij}) c_i^\alpha c_j^\beta \Delta t + \left[ 1 - \delta_{ij} \right] \frac{\gamma}{m} w_D(r_{ij}) c_i^{\alpha} c_j^{\beta} \Delta t, \]

\[ M_{ij}^{\alpha} = \sigma w_R(r_{ij}) c_i^{\alpha} (\Delta t)^{\frac{3}{2}} \left[ 1 - \delta_{ij} \right]. \]

Let the \( N \)-particle distribution function of the system be \( f^{(N)}(\Gamma_{p,r}) \), where \( \Gamma_{p,r} \) represents all the momenta and position variables of \( N \) particles. The one-particle distribution function can then be defined as [11]

\[ f(1)(r,p,t) = \sum_i \int d\Gamma_{p,r} \delta(r - r_i(t)) \delta(p - p_i(t)) f^{(N)}(\Gamma). \]

For \( \Delta t \to 0 \), it has been demonstrated [8] that the equilibrium distribution function in the absence of a conservative force is the Gibbs distribution

\[ f_{eq}^{(N)} = \frac{1}{Z} \exp \left[ -\frac{1}{k_B T} \sum_i \frac{p_i^2}{2m} \right]. \]

We shall assume that this distribution function also provides an equilibrium solution for \( \Delta t \) finite and derive the constraints on the system for this to be consistent.

The change in the one-particle distribution function between times \( t \) and \( t + \Delta t \) is given by

\[ \Delta f^{(1)} = \sum_i \int d\Gamma_{p,r} \{ \delta(r - r_i - \Delta r_i) \delta(p - p_i - \Delta p_i) - \delta(r - r_i) \delta(p - p_i) \} f_{eq}^{(N)}. \]

Expanding the integrand

\[ \Delta f^{(1)} = \sum_i \int d\Gamma_{p,r} \left\{ -\frac{p_i^\alpha (\Delta t) \partial}{m} - \Delta p_i^\alpha \frac{\partial}{\partial p^\alpha} + \frac{p_i^\alpha p_i^\beta (\Delta t)^2}{2m^2} \frac{\partial^2}{\partial r^\alpha \partial r^\beta} + \frac{\Delta p_i^\alpha \Delta p_i^\beta}{2} \frac{\partial^2}{\partial p^\alpha \partial p^\beta} + \frac{p_i^\alpha (\Delta t)}{m} \Delta p_i^\beta \frac{\partial}{\partial r^\alpha \partial p^\beta} + \ldots \right\} f_{eq}^{(N)} \delta(r - r_i) \delta(p - p_i). \]

Defining the averages

\[ \langle A \rangle_{p,r} = \sum_i \int d\Gamma_{p,r} f_{eq}^{(N)} \delta(r - r_i) \delta(p - p_i) A(\Gamma_{p,r}), \]

\[ \langle A \rangle_r = \sum_i \int d\Gamma_r f_{eq}^{(N)} \delta(r - r_i) A(\Gamma_r) \]

gives

\[ \Delta f^{(1)} = -\frac{\Delta t}{m} \frac{\partial}{\partial r^\alpha} (p_i^\alpha)_{p,r} - \frac{\partial}{\partial p^\alpha} (\Delta p_i^\alpha)_{p,r} + \frac{(\Delta t)^2}{2m^2} \frac{\partial^2}{\partial r^\alpha \partial r^\beta} (p_i^\alpha p_i^\beta)_{p,r} + \]

\[ + \frac{\Delta t}{m} \frac{\partial}{\partial p^\alpha \partial p^\beta} (\Delta p_i^\alpha \Delta p_i^\beta)_{p,r} + \frac{\partial^2}{\partial r^\alpha \partial p^\beta} (p_i^\alpha \Delta p_i^\beta)_{p,r} + \ldots \]

We shall follow the evolution of \( f^{(1)} \) under the finite time step algorithm. The easiest way to do this is to calculate the changes in the moments of this distribution function. Firstly consider

\[ \Delta \int dp \int dr f^{(1)} p = \int dp \int dr \Delta f^{(1)} p. \]
Upon substitution of eq. (13), integration by parts removes all terms except for that involving only one momentum derivative. This gives

$$\Delta \int dp \int dr f^{(1)}(p) = \int dp \int dr \langle \Delta p \rangle_{p,r} = 0 ,$$  \hspace{1cm} (15)

where the last equality follows from the fact that the collisions conserve total momentum. Similarly consider the change in the second moment of the distribution function

$$\Delta \int dp \int dr f^{(1)}(p)^2 = \int dp \int dr \Delta f^{(1)}(p)^2 .$$  \hspace{1cm} (16)

In this case two terms remain after integration by parts giving

$$\Delta \int dp \int dr f^{(1)}(p)^2 = \int dp \int dr \langle (2p_i + \Delta p_i) \cdot \Delta p_i \rangle_{p,r} .$$  \hspace{1cm} (17)

Substituting in the momentum evolution equation (4) and neglecting all terms that are first order in momenta or $\xi$ because they will be zero inside the $\langle \rangle_{p,r}$ average

$$\Delta \int dp \int dr f^{(1)}(p)^2 = \int dp \int dr \left( \sum_{\gamma} L_{\gamma ij}^\gamma p_j^\gamma + \sum_{\gamma j} (L_{\gamma ij}^\gamma)^2 + \sum_{\gamma j r} (M_{\gamma ij}^\gamma)^2 \right)_{p,r} .$$  \hspace{1cm} (18)

Using the expressions (5), (6) this integral can be evaluated recalling that the distribution function (8) is trivial in position space:

$$\Delta \int dp \int dr f^{(1)}(p)^2 = -2\gamma \Delta t k_B T \left[ w_D^2 \right] + \sigma^2 \Delta t \left[ w_R^2 \right] + \frac{k_B T \gamma^2 (\Delta t)^2}{m} \left\{ 2n \left[ w_D^2 \right] + \frac{n^2 [w_D]^2}{d} \right\} ,$$  \hspace{1cm} (20)

where $d$ is the number of space dimensions and the square brackets denote the integral

$$[f(r)] = \int dr f(r) .$$  \hspace{1cm} (21)

The expression (20) must be zero for the one-particle distribution function to remain unchanged:

$$mk_B T_{eq} = \frac{A_3}{A_1 (2 - A_1 n \Delta t) - A_2 \Delta t} ,$$  \hspace{1cm} (22)

where

$$A_1 = \frac{\gamma}{md} \left[ w_D \right] , \hspace{0.5cm} A_2 = \frac{2\gamma^2}{m^2 d} \left[ w_D^2 \right] , \hspace{0.5cm} A_3 = \frac{\sigma^2}{d} \left[ w_R^2 \right] .$$  \hspace{1cm} (23)

We also note that, for the distribution function (8), higher moments are related by

$$\int dp f^{(1)}(p)^{n+2} \propto \int dp f^{(1)}(p)^n .$$  \hspace{1cm} (24)

Therefore, if the constraint (22) is satisfied and momentum is conserved (15), all moments of $f^{(1)}$, and therefore $f^{(1)}$ itself, will remain constant.

We make the following comments on the result (22):
Fig. 1. – Dependence of the inverse temperature, $1/T_0$, on the time step $\Delta t$ for different values of the density $n$ for DPD simulations of an ideal fluid. The system parameters were $\gamma = 1$, $\sigma = 1$. The lines correspond to the predictions of eq. (22).

1) For $\Delta t \to 0$ and $w_D = w_R^2$ the formula obtained by Españañol and Warren [8] is recovered.

2) For a given ($\gamma, \sigma, w_D, w_R, n$) the measured temperature of the system will increase as the time step becomes larger.

3) For a given set of input parameters, the system will become unstable for time steps $\Delta t > \Delta t_c$ where

$$\Delta t_c = \frac{2A_1}{(nA_1^2 + A_2)}.$$  \hspace{1cm} (25)

4) Similarly, once a value of $\Delta t$ is chosen, the density must not be allowed to exceed a critical density

$$n_c = \frac{(2A_1 - A_2\Delta t)}{(A_1^2\Delta t)}$$ \hspace{1cm} (26)

for a stable simulation.

5) The choice of a small value of $\gamma$ will decrease the effect of a finite $\Delta t$.

Simulation results, shown in fig. 1, show that eq. (22) gives a good prediction of the dependence of the temperature on the time step for several densities and time steps. The simulations were run in two dimensions with periodic boundary conditions. The system size was 100 units and the interaction range was 4 units. Averages were taken over 9 runs each of duration 1000. Error bars are of the order of the size of the points in fig. 1. The small deviations between the analytic and numerical results arise because correlations between particles modify the Gibbs distribution (8) for finite $\Delta t$. However, the result (22) is a good prediction of the temperature of the system over a wide range of system parameters relevant to numerical simulations.

To conclude, we have demonstrated that, for a DPD simulation of an ideal fluid, the equilibrium temperature of the system depends strongly on the time step. This implies that caution is necessary if DPD is used to probe equilibrium thermodynamic properties.
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