Dynamical regimes in the dissipative particle dynamics model

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We discuss theoretically the behavior of the velocity autocorrelation function in the dissipative particle dynamics (DPD) model. Two dynamical regimes are identified depending on the dimensionless model parameters. For low values of the dimensional friction, a mean field behavior is observed in which the kinetic theory for the DPD model provides good predictions. For high values of the friction, collective hydrodynamic effects are dominant. We have performed numerical simulations that validate the theory presented.
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I. INTRODUCTION

The dissipative particle dynamics (DPD) model allows one to simulate hydrodynamics at mesoscopic scales in which thermal fluctuations are important [1,2]. For this reason, it appears as a good simulation technique for the study of complex fluids like polymer or colloidal suspensions where both hydrodynamic interactions and Brownian motion are important [3–7]. Being an off lattice technique, it does not suffer from the restrictions imposed by the lattice as in lattice gas cellular automata or the lattice Boltzmann approach, and it is much more flexible for modeling.

Even though the technique has a very sound theoretical support and many applications have been undertaken, there is at present no systematic study of the region of parameters suitable for a simulation of particular hydrodynamic problems. In addition, recent simulations [8] have shown deviations from the transport coefficients predicted by the kinetic theory developed in Ref. [9]. The two approximations involved in this kinetic theory are the small gradient expansion around local equilibrium, and the molecular chaos hypothesis. However, it is difficult to investigate the origin of the discrepancies between theory and simulations within the kinetic theory context. The theory just produces explicit expressions for the transport coefficients with no hint about its range of validity. It has been suggested that it is precisely in the region of parameters where kinetic theory fails where it is more sensible to conduct simulations that reproduce hydrodynamic behavior [8].

We shed some light on the problem by presenting a theory that allows us to compute the velocity autocorrelation function (VAF) of the dissipative particles. The theory is based on the physical picture in which the DPD particles are regarded as Brownian-like particles moving in an environment created by the rest of the DPD particles. Strictly speaking, however they are not Brownian particles because the total moment of the system is conserved. This approach was introduced by Groot and Warren as a way of computing the diffusion coefficient [6]. We identify the basic dimensionless parameters which allow us to classify and discuss the dynamical regimes displayed by the model. By assuming that the environment of a DPD particle behaves hydrodynamically, it is possible to obtain an explicit analytical expression for the velocity autocorrelation function. Here we follow pioneering works on mode coupling theory [10,11] that allowed one to derive the celebrated long time tails in the velocity autocorrelation. Finally, we present numerical simulations that allow us to validate the hypothesis made in the theory.

II. DPD MODEL

The stochastic differential equations that govern the position $\mathbf{r}_i$ and velocity $\mathbf{v}_i$ of the ith particle of mass m in the DPD model are given by [2]

$$d\mathbf{r}_i=\mathbf{v}_i dt,$$

$$m d\mathbf{v}_i=-\gamma m\sum_j \omega(r_{ij})(\mathbf{e}_{ij}\cdot\mathbf{v}_{ij})\mathbf{e}_{ij}dt + \sigma\sum_j \omega^{1/2}(r_{ij})\mathbf{e}_{ij}dW_{ij}, \tag{1}$$

where the following quantities are defined:

$$\mathbf{e}_{ij}\equiv\frac{\mathbf{r}_{ij}}{r_{ij}},$$

$$\mathbf{r}_{ij}\equiv\mathbf{r}_i-\mathbf{r}_j,$$

$$r_{ij}\equiv|\mathbf{r}_i-\mathbf{r}_j|, \tag{2}$$

$$\mathbf{v}_{ij}\equiv\mathbf{v}_i-\mathbf{v}_j.$$

In order to compare with the kinetic theory in Ref. [9], it is assumed that the usual conservative force is not present. The noise amplitude σ is given by the detailed balance condition

$$\sigma=(2k_BT\gamma m)^{1/2}, \tag{3}$$

where T is the temperature of the equilibrium state toward which the system relaxes (if the boundary conditions allow for it), and k_B is Boltzmann's constant. Finally, $dW_{ij}=dW_{ji}$ are independent increments of the Wiener process that obey the Itô calculus rule

$$dW_{ij}dW_{i'j'}=(\delta_{ii'}\delta_{jj'}+\delta_{ij'}\delta_{ji'})dt, \tag{4}$$

i.e., dW_{ij} is an infinitesimal of order 1/2 [12]. The dimensionless weight function $\omega(r)$ is normalized according to [1]

$$\int d\mathbf{r}\,\omega(r)=\frac{1}{n}, \tag{5}$$

where n is the number density of the system. In this paper we will work in two spatial dimensions, and we select the following weight function with range r_c:

$$\omega(r)=\frac{3}{\pi r_c^2 n}\left(1-\frac{r}{r_c}\right), \tag{6}$$

if $r<r_c$, and zero if $r>r_c$.

We discuss now which are the fundamental parameters for the DPD model. By an appropriate choice of units of mass, time, and space, it is always possible to reduce the number of relevant parameters of the model. It is obvious that the dynamical regimes are independent of the units used, and will depend on *dimensionless* parameters only. There are six parameters in the model: $m,\gamma,r_c,k_BT,\lambda$, and L, where λ is the average distance between particles, related to the number density n of particles by $\lambda=n^{-1/d}$, d is the space dimension, and L is the box size (or any other boundary length scale). From these six parameters we can form three dimensionless parameters. By defining the thermal velocity $v_T=(k_BT/m)^{1/2}$, we select

$$\Omega\equiv\frac{\gamma r_c}{dv_T}=\frac{\tau_T}{d\tau_\gamma},$$

$$s\equiv\frac{r_c}{\lambda}, \tag{7}$$

$$\mu\equiv\frac{L}{r_c}.$$

The physical meaning of these parameters is as follows: τ_T is the time taken by a particle moving at the thermal velocity to move a distance r_c, whereas $\tau_\gamma=\gamma^{-1}$ is the time associated with the friction. Therefore, the *dimensionless friction* Ω is the ratio of these two time scales. On the other hand, s is the *overlapping* between particles which is related to the number of particles that are within the range of interaction (the *action sphere*) of a given one. Finally, μ is the dimensionless box length. These dimensionless parameters Ω,s, and μ fix the dynamical regimes of the model.

III. VELOCITY AUTOCORRELATION FUNCTION

The velocity equation in Eq. (1) can be written in the form

$$\dot{\mathbf{v}}_i=-\gamma\left[\sum_{j\neq i}\omega(r_{ij})\mathbf{e}_{ij}\mathbf{e}_{ij}\right]\cdot\mathbf{v}_i+\frac{\gamma}{d}\mathbf{V}_i(t)+\frac{\tilde{\mathbf{F}}_i}{m}, \tag{8}$$

where the random force is $\tilde{\mathbf{F}}_i dt=\sigma\Sigma_j\omega^{1/2}(r_{ij})\mathbf{e}_{ij}dW_{ij}$. In Eq. (8) we have introduced the *environment* velocity through

$$\mathbf{V}_i(t)=d\sum_{j\neq i}\omega(r_{ij})(\mathbf{e}_{ij}\cdot\mathbf{v}_j)\mathbf{e}_{ij}. \tag{9}$$

This velocity is a weighted average of the velocities of the neighboring particles of particle i. Next, we observe that the factor of $\mathbf{v}_i$ in the right hand side of Eq. (8) can be written as

$$\sum_{j\neq i}\omega(r_{ij})\mathbf{e}_{ij}\mathbf{e}_{ij}=\int d\mathbf{r}\,\omega(\mathbf{r}_i-\mathbf{r})\frac{\mathbf{r}_i-\mathbf{r}}{|\mathbf{r}_i-\mathbf{r}|}\frac{\mathbf{r}_i-\mathbf{r}}{|\mathbf{r}_i-\mathbf{r}|}n(\mathbf{r},t), \tag{10}$$

where we have introduced the microscopic density field $n(\mathbf{r},t)=\Sigma_{j\neq i}\delta(\mathbf{r}_j-\mathbf{r})$. If we assume that the density field is constant with value n (which will be confirmed by the results obtained later) then we may approximate

$$\int d\mathbf{r}\,\omega(\mathbf{r}_i-\mathbf{r})\frac{\mathbf{r}_i-\mathbf{r}}{|\mathbf{r}_i-\mathbf{r}|}\frac{\mathbf{r}_i-\mathbf{r}}{|\mathbf{r}_i-\mathbf{r}|}n(\mathbf{r},t)$$

$$\approx n\int d\mathbf{r}\,\omega(\mathbf{r})\frac{\mathbf{r}}{|\mathbf{r}|}\frac{\mathbf{r}}{|\mathbf{r}|}=\frac{\mathbf{1}}{d}. \tag{11}$$

The last equality is obtained by noting that the integral is an isotropic second order tensor, which must be proportional to the identity [the constant of proportionality can be obtained by taking the trace of the integral and using the normalization equation (5)].

The assumption of constant density is, in fact, an assumption that neglects density fluctuations and correlations. One expects that, for large overlapping, when there are many particles within an action sphere, the importance of density fluctuations will be very small. It is convenient to compute the fluctuations of the environment velocity from the definition of $\mathbf{V}_i$ in Eq. (9):

$$\frac{1}{d}\langle\mathbf{V}_i\cdot\mathbf{V}_i\rangle=d\left\langle\left(\sum_{j\neq i}\omega_{ij}\mathbf{e}_{ij}\mathbf{e}_{ij}\cdot\mathbf{v}_j\right)\left(\sum_{k\neq i}\omega_{ik}\mathbf{e}_{ik}\mathbf{e}_{ik}\cdot\mathbf{v}_k\right)\right\rangle$$

$$\simeq\frac{dk_BTN}{mV}\int d\mathbf{r}\,\omega^2(r)$$

$$=\frac{dk_BT}{m}\frac{3}{2\pi s^2}, \tag{12}$$

for large number N of DPD particles in the system. We observe that the magnitude of this correlation decreases with the overlapping coefficient s. This is physically meaningful because the environment velocity is a weighted average of the velocities of the particles that are within an action sphere. These velocities are distributed at random and, therefore, if there are many particles within an action sphere, the average will be proportionally smaller.

After using Eqs. (10) and (11) in Eq. (8), one obtains

$$d\mathbf{r}_i=\mathbf{v}_i dt,$$

$$d\mathbf{v}_i=-\frac{\gamma}{d}[\mathbf{v}_i-\mathbf{V}_i]dt+\frac{\tilde{\mathbf{F}}_i}{m}dt. \tag{13}$$

We observe that DPD particles behave similarly to Brownian particles, but in a systematic velocity field determined by the rest of its neighboring particles. The stochastic properties of the random force are not exactly those of a Brownian particle

because the total momentum of the system is conserved but for the rest of the development they are irrelevant.

The formal solution of Eq. (13) is

$$\mathbf{v}_i(t)=\exp\{-\gamma t/d\}\mathbf{v}_i(0)+\int_0^t dt'\exp\{-\gamma(t-t')/d\}\times\left[\frac{\gamma}{d}\mathbf{V}_i(t')+\frac{\tilde{\mathbf{F}}_i(t')}{m}\right]. \tag{14}$$

By multiplying this equation by $\mathbf{v}_i(t)$ and averaging, one can show that the average $\langle\mathbf{v}_i(t)\cdot\mathbf{v}_i(t)\rangle$ tends toward the equipartition value on a time scale of order d/γ. On the other hand, by multiplying Eq. (14) by $\mathbf{v}_i(0)$ and $\mathbf{V}_i(0)$ and averaging, one obtains a set of equations for the velocity autocorrelation function at equilibrium:

$$\begin{aligned}\frac{1}{d}\langle\mathbf{v}_i(t)\cdot\mathbf{v}_i(0)\rangle&=\exp\{-\gamma t/d\}\frac{k_BT}{m}+\frac{\gamma}{d}\int_0^t dt'\exp\{-\gamma(t-t')/d\}\times\frac{1}{d}\langle\mathbf{V}_i(t')\cdot\mathbf{v}_i(0)\rangle,\\ \frac{1}{d}\langle\mathbf{v}_i(t)\cdot\mathbf{V}_i(0)\rangle&=\frac{\gamma}{d}\int_0^t dt'\exp\{-\gamma(t-t')/d\}\times\frac{1}{d}\langle\mathbf{V}_i(t')\cdot\mathbf{V}_i(0)\rangle,\end{aligned} \tag{15}$$

where use has been made of the fact that the random force is not correlated with the velocity at present and past times and the property $\langle\mathbf{V}_i(0)\cdot\mathbf{v}_i(0)\rangle=0$ [which can be checked from definition (9)]. Substitution of the second equation in Eq. (15) into the first one leads to an expression that relates the particle VAF with the environment VAF, this is

$$\frac{1}{d}\langle\mathbf{v}_i(t)\cdot\mathbf{v}_i(0)\rangle=\exp\{-\gamma t/d\}\frac{k_BT}{m}+\left(\frac{\gamma}{d}\right)^2\int_0^t dt'(t-t')\times\exp\{-\gamma(t-t')/d\}\frac{1}{d}\langle\mathbf{V}_i(t')\cdot\mathbf{V}_i(0)\rangle. \tag{16}$$

The second term on the right hand side represents *collective effects*. When this term is negligible we say that a *mean field* approximation is valid, in which the velocity autocorrelation function decays exponentially. The reason for the name ''mean field'' comes from the observation that Eq. (13), in which the average value $\langle\mathbf{V}_i\rangle=0$ is used instead of the instantaneous value $\mathbf{V}_i$, produces an exponential decay of the velocity autocorrelation function. In the Appendix of Ref. [6], the velocity autocorrelation function and the diffusion coefficient of the DPD particles were computed by using this mean field approximation.

Solution (16) is still formal because we do not explicitly know the form of the correlation of the environment velocity (which will be given in Sec. IV). Nevertheless, it is possible to extract useful information from this expression. This is most conveniently done by taking dimensionless variables. Let $\bar{t}$ be the dimensionless time tv_T/r_c, that is, the time expressed in units in which $r_c=1$ and $v_T=1$, and $\bar{\mathbf{v}}=\mathbf{v}/v_T$ is a dimensionless velocity. In these units, Eqs. (15) take the forms

$$\begin{aligned}\frac{1}{d}\langle\bar{\mathbf{v}}_i(\bar{t})\cdot\bar{\mathbf{v}}_i(0)\rangle&=\exp\{-\Omega\bar{t}\}+\Omega\int_0^{\bar{t}}d\bar{t}'\exp\{-\Omega(\bar{t}-\bar{t}')\}\times\frac{1}{d}\langle\bar{\mathbf{V}}_i(\bar{t}')\cdot\bar{\mathbf{v}}_i(0)\rangle,\\ \frac{1}{d}\langle\bar{\mathbf{v}}_i(\bar{t})\cdot\bar{\mathbf{V}}_i(0)\rangle&=\Omega\int_0^{\bar{t}}d\bar{t}'\exp\{-\Omega(\bar{t}-\bar{t}')\}\times\frac{1}{d}\langle\bar{\mathbf{V}}_i(\bar{t}')\cdot\bar{\mathbf{V}}_i(0)\rangle,\end{aligned} \tag{17}$$

and Eq. (16) takes the form

$$\frac{1}{d}\langle\bar{\mathbf{v}}_i(\bar{t})\cdot\bar{\mathbf{v}}_i(0)\rangle=\exp\{-\Omega\bar{t}\}+\Omega^2\int_0^{\bar{t}}d\bar{t}'(\bar{t}-\bar{t}')\times\exp\{-\Omega(\bar{t}-\bar{t}')\}\frac{1}{d}\langle\bar{\mathbf{V}}_i(\bar{t}')\cdot\bar{\mathbf{V}}_i(0)\rangle \tag{18}$$

For later notational convenience we introduce

$$\begin{aligned}c(\bar{t})&\equiv\frac{1}{d}\langle\bar{\mathbf{v}}_i(\bar{t})\cdot\bar{\mathbf{v}}_i(0)\rangle,\\ C(\bar{t})&\equiv\frac{1}{d}\langle\bar{\mathbf{V}}_i(\bar{t})\cdot\bar{\mathbf{V}}_i(0)\rangle.\end{aligned} \tag{19}$$

Now several qualitative predictions concerning the different dynamical regimes can be made from expressions (17) or (18). For fixed Ω, the large overlapping s limit produces a small contribution from the collective part, and the velocity correlation function decays in an exponential way. Note that the overall magnitude of the correlation of the environment velocity is determined by the value at the origin [Eq. (12)]. For a fixed overlapping s, when Ω is small (in the limit of small friction or high temperature) the behavior of the VAF is again exponential. In the opposite regime of large Ω, the exponential contribution decays in a very short time and the main contribution for times larger than Ω^{-1} is given by the collective term. Actually, in the limit $\Omega\to\infty$ the exponential memory function acts as a δ function, and for times larger than Ω^{-1} one obtains

$$\begin{aligned}\langle\bar{\mathbf{v}}_i(\bar{t})\cdot\bar{\mathbf{v}}_i(0)\rangle&\approx\langle\bar{\mathbf{V}}_i(\bar{t})\cdot\bar{\mathbf{v}}_i(0)\rangle\\ &\approx\langle\bar{\mathbf{V}}_i(\bar{t})\cdot\bar{\mathbf{V}}_i(0)\rangle.\end{aligned} \tag{20}$$

The physical meaning of expressions (20) is also clear. When the friction is high, in a very short time the velocity of a given particle is slaved by the average velocity of its environment.

IV. HYDRODYNAMIC HYPOTHESIS

In this section we present a hydrodynamic hypothesis similar to the mode coupling approximation introduced in, for example, Ref. [10] (see Ref. [11] for a review on mode coupling theories). The environment velocity $\mathbf{V}_i$ defined in Eq. (9) can be rewritten as an average over the action sphere of the microscopic velocity field, that is,

$$\mathbf{V}_i(t)=d\int d\mathbf{r}\,\omega(\mathbf{r}_i-\mathbf{r})\frac{\mathbf{r}_i-\mathbf{r}}{|\mathbf{r}_i-\mathbf{r}|}\frac{\mathbf{r}_i-\mathbf{r}}{|\mathbf{r}_i-\mathbf{r}|}n(\mathbf{r},t)\mathbf{v}(\mathbf{r},t), \tag{21}$$

where

$$n(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)=\sum_{j\neq i}\mathbf{v}_j\delta(\mathbf{r}_j-\mathbf{r}). \tag{22}$$

The velocity field $\mathbf{v}(\mathbf{r},t)$ obeys the equations of hydrodynamics when its characteristic length scale is much larger than the interparticle distance. We expect that the average involved in $\mathbf{V}_i$ will be dominated by the hydrodynamic modes whenever the range of interaction r_c is much larger than the interparticle distance λ (i.e., large overlapping s). Actually, under the assumption that the hydrodynamic fields vary slowly on the scale r_c, we could substitute the environment velocity with the hydrodynamic velocity field evaluated at the particle position, i.e., $\mathbf{V}_i(t)=\mathbf{v}(\mathbf{r}_i(t),t)$, by convenient use of Eq. (10). This leads to a correct long time behavior but an inaccurate short time behavior.

In what follows we still neglect density fluctuations, $n(\mathbf{r},t)\sim n$, but keep the hydrodynamic velocity inside the integral, weighted with $\omega(|\mathbf{r}-\mathbf{r}_i|)$. From Eq. (21), the environment velocity is conveniently expressed in terms of the Fourier components of the velocity field $\mathbf{v}(\mathbf{k},t)$, that is

$$\mathbf{V}_i(t)=dn\int\frac{d\mathbf{k}}{(2\pi)^2}\boldsymbol{\omega}(\mathbf{k})\cdot\mathbf{v}(\mathbf{k},t)n_s(\mathbf{k},t), \tag{23}$$

where we have introduced the tagged particle density $n_s(\mathbf{k},t)=\exp\{i\mathbf{k}\cdot\mathbf{r}_i(t)\}$ and the second order tensor

$$\boldsymbol{\omega}(\mathbf{k})=\int d\mathbf{r}\,\omega(r)\hat{\mathbf{r}}\hat{\mathbf{r}}\exp\{-i\mathbf{k}\cdot\mathbf{r}\}. \tag{24}$$

The explicit form of this tensor when the weight function is given by Eq. (6) is given in the Appendix. The environment velocity correlation function is given by

$$\langle\mathbf{V}_i(0)\cdot\mathbf{V}_i(t)\rangle=(dn)^2\int\frac{d\mathbf{k}}{(2\pi)^2}\frac{d\mathbf{k}'}{(2\pi)^2}\boldsymbol{\omega}(\mathbf{k})\boldsymbol{\omega}(\mathbf{k}')\langle n_s(\mathbf{k},0)n_s(\mathbf{k}',t)\mathbf{v}(\mathbf{k},0)\mathbf{v}(\mathbf{k}',t)\rangle. \tag{25}$$

We will assume that the position of particle i is weakly correlated with the velocity field $\mathbf{v}(\mathbf{k},t)$ in such a way that we can approximate

$$\langle n_s(\mathbf{k},0)n_s(\mathbf{k}',t)\mathbf{v}(\mathbf{k},0)\mathbf{v}(\mathbf{k}',t)\rangle\approx\langle n_s(\mathbf{k},0)n_s(\mathbf{k}',t)\rangle\langle\mathbf{v}(\mathbf{k},0)\mathbf{v}(\mathbf{k}',t)\rangle. \tag{26}$$

We further assume that the correlation of the velocity field is given by the linear hydrodynamics result [13]

$$\langle\mathbf{v}(\mathbf{k}',0)\mathbf{v}^T(\mathbf{k},t)\rangle=\frac{k_BT}{nm}(2\pi)^2\delta(\mathbf{k}+\mathbf{k}')[\exp\{-\nu k^2t\}(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})+\exp\{-\Gamma k^2t\}\cos kct\hat{\mathbf{k}}\hat{\mathbf{k}}]. \tag{27}$$

Here ν is the kinematic viscosity, Γ is the sound absorption coefficient, and c is the sound speed of the DPD fluid. The correlation function (27) is different from zero only when $\mathbf{k}=-\mathbf{k}'$. The first average in the right hand side of Eq. (26) is, therefore, given by the incoherent intermediate scattering function $F_s(\mathbf{k},t)=\langle n_s(\mathbf{k},0)n_s(-\mathbf{k},t)\rangle$ [13]. By further assuming a hydrodynamic behavior for this function, we obtain [13]

$$F_s(\mathbf{k},t)=\exp\{-Dk^2t\}, \tag{28}$$

where D is the self-diffusion coefficient of the DPD particles.

The final hydrodynamic expression for the environment velocity correlation function is found by substitution of Eqs. (26), (27), (28), into Eq. (25),

$$\frac{1}{d}\langle\mathbf{V}_i(0)\cdot\mathbf{V}_i(t)\rangle=\frac{3dk_BT}{4\pi r_c^2nm}\left[\Phi\left(\frac{(\nu+D)t}{r_c^2}\right)+\Psi\left(\frac{(\Gamma+D)t}{r_c^2},\frac{ct}{r_c}\right)\right], \tag{29}$$

where the following functions are defined:

$$\Phi(x)=\frac{\int d\mathbf{k}a^2(k)\exp\{-xk^2\}}{\int d\mathbf{k}a^2(k)}$$

$$\Psi(y,z)=\frac{\int d\mathbf{k}[a(k)+b(k)]^2\exp\{-yk^2\}\cos kz}{\int d\mathbf{k}[a(k)+b(k)]^2}, \tag{30}$$

which satisfy $\Phi(0)=1,\Psi(0,0)=1$, with the definitions for $a(k),b(k)$ given in the Appendix.

In this way, the environment velocity correlation function is explicitly given in terms of hydrodynamic fluid properties, i.e., the transport coefficients of the DPD fluid. The prediction is not complete until particular values for these transport coefficients are provided. One possibility is to measure these transport coefficients in a simulation. Another possibility,

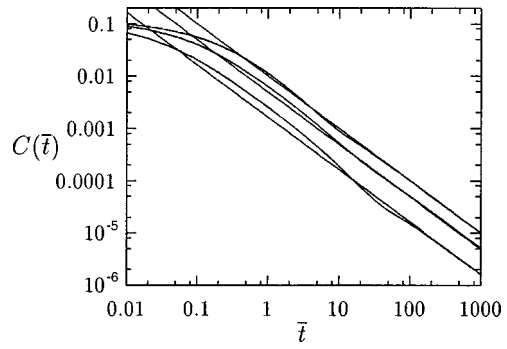

FIG. 1. Theoretical hydrodynamic prediction for the environment velocity correlation function $C(\bar{t})$ for a value of $s=2.82$ and three different values for Ω. The lowest curve is for $\Omega=0.5$, the middle curve is for $\Omega=25$, and the upper curve is for $\Omega=8.3$. The algebraic long time tail behavior appears for very long times, typically when the correlation has decayed three orders of magnitude from its initial value. Straight lines are the asymptotic result in Eq. (33).

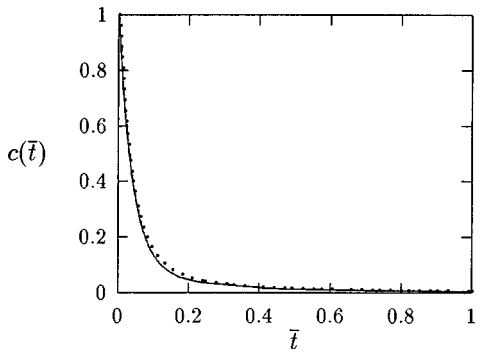

FIG. 2. Comparison between the simulation result for $c(\bar{t})$ (solid line) and the value given by Eq. (18) (dotted line) using the simulation result for the environment velocity correlation function $C(\bar{t})$. Parameters: $s=2.82$, $\Omega=25$, and $\mu=10.0$

which is the one we follow here, is to use the values for ν, D, Γ, and c provided by the kinetic theory in Ref. [9]. This has the advantage that one knows the explicit dependence of the transport coefficients in terms of the dimensionless parameters Ω, and s. Even though for some dynamical regimes the kinetic theory predictions are not in exact quantitative agreement with the measured transport coefficients [8,14], the discrepancies between theoretical and simulation transport coefficients are small.

The kinetic theory results are [9,15]

$$
\begin{aligned}
D &= \frac{d}{\gamma}\frac{k_B T}{m}, \\
\nu &= \frac{1}{2}\left[\gamma n \frac{1}{d(d+2)}\int r^2 \omega(r) d\mathbf{r} + c^2 \frac{d}{\gamma n \int \omega(r) d\mathbf{r}}\right], \\
\nu_b &= \gamma n \frac{1}{2d^2}\int r^2 \omega(r) d\mathbf{r} + c^2 \frac{1}{\gamma n \int \omega(r) d\mathbf{r}}, \\
c &= \sqrt{\frac{k_B T}{m}}.
\end{aligned}
\tag{31}
$$

The sound absorption coefficient is given by $\Gamma = 2\nu + \frac{1}{2}\nu_b$ for the case that the equation of state is that of the ideal gas [13].

We are now in position to write the hydrodynamic prediction (29) in terms of dimensionless variables. Substitution of Eq. (31) with expression (6) into Eq. (29) leads to

$$
C(\bar{t}) = \frac{3d}{4\pi s^2}\left[\Phi\left(\left[\frac{3}{80}\Omega + \frac{3}{2\Omega}\right]\bar{t}\right) + \Psi\left(\left[\frac{9}{80}\Omega + \frac{11}{4\Omega}\right]\overline{t,t}\right)\right]. \tag{32}
$$

We observe that the time scale of the environment velocity correlation function is determined by Ω, while its amplitude is determined by s. In Fig. 1 we show the theoretical prediction (32) for a particular value of s and three different values of Ω. An algebraic dependence like t^{-1} is observed for very long times, which is the celebrated long time tail $t^{-d/2}$ arising from the diffusive character of the shear and tagged particle modes. Actually, it is straightforward to obtain the asymptotic behavior of $C(\bar{t})$ for long times, which is given by

$$
C(\bar{t}) \sim \frac{1}{8\pi s^2}\frac{80\Omega}{3\Omega^2+120}\frac{1}{\bar{t}}. \tag{33}
$$

In dimensional terms, this result reads

$$
\frac{1}{d}\langle \mathbf{V}_i(t)\cdot\mathbf{V}_i(0)\rangle \sim \frac{k_B T}{mn}\frac{1}{8\pi(\nu+D)t}, \tag{34}
$$

which coincides with the result given in Ref. [10] for the particle velocity autocorrelation function [note that, for long times, Eq. (20) applies].

V. SIMULATION RESULTS

We have simulated Eqs. (1) in two spatial dimensions in a system with periodic boundary conditions. The velocity autocorrelation function of the DPD particles and also the environment velocity autocorrelation function have been computed at equilibrium.

In order to derive Eq. (18), we made the approximation that the density field is approximately constant. We check now that this assumption is reasonable by computing in a simulation the environment velocity correlation $C(\bar{t})$, evaluating numerically the integral term in Eq. (18), and adding up the first exponential term in Eq. (18). The result is the dotted line in Fig. 2. Also shown is the result for the velocity correlation function $c(\bar{t})$ obtained directly from the simulation (solid line). We see that both results are in quite good agreement, giving confidence in Eq. (18) as a sounded starting point for theoretical analysis. Similarly good agreement is obtained for all the values of Ω studied ($\Omega=0.5$,8.3, and 25).

For a given value of $\Omega=25$, in Fig. 3 we plot the value of $s^2 C(\bar{t})$ for different values of s. According to the hydrodynamic prediction (32), this curve should be independent of the overlapping coefficient s (dotted curve in Fig. 3). We observe that the simulation results converge toward the theoretical prediction only when the overlapping coefficient is sufficiently large. This is expected from the fact that hydro-

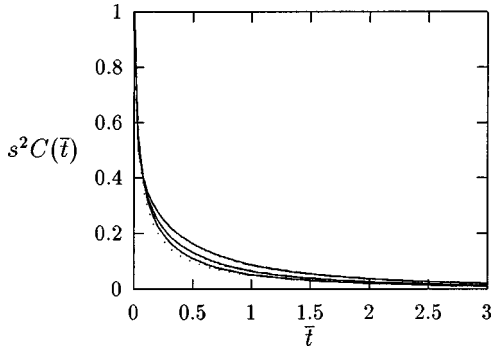

FIG. 3. Simulation results for the velocity correlation function $s^2C(\bar{t})$ for a fixed value of $\Omega=25$, and different values of the overlapping coefficient $s=1.5$, 2.18, and 3.2 (the upper curve corresponds to lower s). The dotted line is the hydrodynamic prediction (32). As the overlapping increases, the simulation results converge toward the theoretical prediction.

dynamic behavior appears only on length scales that involve a relatively large number of particles.

We have also investigated the effect of the finite system size. In Fig. 4 we plot the environment velocity correlation function for different system sizes, while keeping the rest of the parameters constant ($s=2.82$, and $\Omega=25$). We observe a large discrepancy between the hydrodynamic prediction and the simulation results when the box is small. This discrepancy appears at large times, and is reduced when the system size increases. This is a standard finite size effect, which is related to the discreteness of the k spectrum in small systems, where the slowest mode decays as $\exp[-ak_{\min}^2 t]$ with $k_{\min}=2\pi/L$.

Next, we study the effect of Ω on the velocity autocorrelation function of the DPD particles. In Fig. 5 we show the velocity correlation function for given $s=2.82$, and $\mu=10.0$, and three different values of $\Omega=0.5$,8.3, and 25. We also plot the corresponding exponential terms in Eq. (18). For small Ω (small friction or high temperature) the decay of the VAF is very accurately given by the exponential term. As long as Ω increases, discrepancies from the exponential behavior are observed. This discrepancies are due to the effect of the collective term in Eq. (18). In Fig. 6 it is shown that,

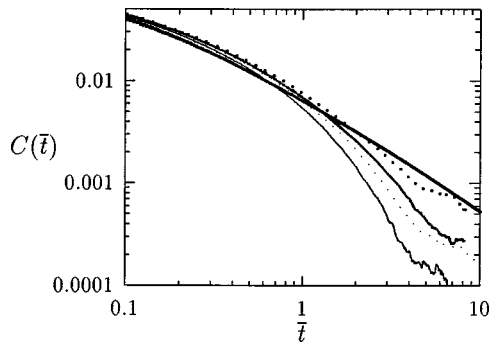

FIG. 4. Simulation results for the velocity correlation function $C(\bar{t})$ for fixed values of $s=2.82$, and $\Omega=25$ and different values of the box size $\mu=7.9$, 11.2, 15.8, and 35.5 (the lower curve correspond to lower μ). The thicker line is the hydrodynamic prediction (32).

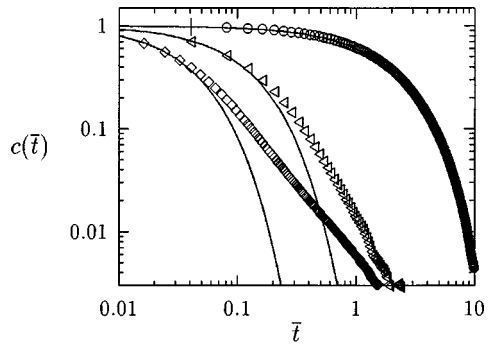

FIG. 5. Simulation results for the velocity correlation function $c(\bar{t})$ for fixed values of $s=2.82$, and $\mu=10.0$, and different values of $\Omega=0.5$ (circles), 8.3 (triangles), and 25 (diamonds). Solid lines are the term $\exp\{-\Omega\bar{t}\}$ in Eq. (18).

for large Ω, at large times the environment and particle velocities coincide according to Eq. (20).

VI. SUMMARY AND DISCUSSION

We have presented a theory for dissipative particle dynamics that allows one to understand the different dynamical regimes displayed by the model. The theory is based on the physical picture that DPD particles behave like Brownian particles in a nonequilibrium environment due to the rest of the DPD particles. An explicit expression for the velocity autocorrelation function is derived in which the Brownian exponential behavior is corrected by the presence of collective effects. By using dimensionless variables it is possible to assess the range of parameters for which the collective effects are important. Three dimensionless parameters appear in the model, — s,Ω, and μ, — and they characterize the different dynamical regimes in the system. The relevance of precisely these dimensionless groups is motivated by the theory presented.

Two dynamical regimes are identified: the mean field regime and the collective behavior regime. The transition between both is governed essentially by the dimensionless friction Ω with important effects of s and μ. A mean field behavior appears for small friction Ω or large overlapping s. This is physically reasonable: For small friction, the dynamics of the environment of a given particle hardly affects the

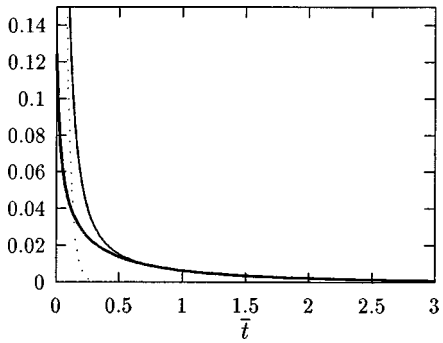

FIG. 6. Simulation results for the velocity correlation function $c(\bar{t})$ (thin line) and the environment velocity correlation function $C(\bar{t})$ (thick line). Also shown is the term $\exp\{-\Omega\bar{t}\}$ in Eq. (18) (dotted line). Here $s=2.82$, $\mu=10.0$, and $\Omega=25$.

behavior of this particle. For a large overlapping the collective effects are smeared out over large regions. The mean field approximation is closely related to the molecular chaos assumption made in kinetic theory. Actually, it is possible to compute the diffusion coefficient of the DPD particles by using the mean field approximation for the VAF into the usual Green-Kubo formula for the diffusion coefficient [6]. The result is precisely the prediction for the diffusion coefficient given by kinetic theory [9] [with due account of the normalization given in Eq. (5)], i.e.,

$$D=\int_0^\infty \frac{1}{d}\langle \mathbf{v}_i(t)\cdot\mathbf{v}_i(0)\rangle=\frac{d}{\gamma}\frac{k_BT}{m}. \tag{35}$$

When the dimensionless friction Ω is high, the VAF does not decay in an exponential way because it is dominated by the collective dynamics. We have presented a theoretical prediction for the collective part of the VAF by assuming that the correlation function of the environment velocity reflects an underlying hydrodynamic behavior. Such a behavior is expected (and observed in the simulations) when the overlapping coefficient s is large enough. In this case, the collective effect is small but well described by hydrodynamics.

The fact that hydrodynamics governs the dynamics of the velocity of the particles implies the appearance of the celebrated long time tails in the VAF. These algebraic tails occur at very long times (for which the VAF has decayed to a factor 10^{-3} from its original value) and are difficult to observe in our simulations due to both the statistical noise and finite size effects. Nevertheless, we have provided sufficient numerical evidence for the hydrodynamic behavior at smaller times, and we expect the presence of long time tails at large times for sufficiently large system sizes. The t^{-1} dependence of the VAF, when introduced into the Green-Kubo formula (35), leads to a logarithmically divergent diffusion coefficient. It is apparent that this ''small'' divergence will be hardly observable in any simulation with a finite box size.

Dissipative particle dynamics is designed to simulate hydrodynamic problems. Actually, one would like to have the DPD particles moving in such a way that they accurately follow the flow field intended to be modeled. We see that this will happen whenever the friction is sufficiently large (in this case, the velocity of a DPD particle is slaved by its environment) and the overlapping is sufficiently large (in such a way that the environment velocity moves hydrodynamically). In this regime, the dynamics of the particles is mainly collective, and kinetic theory gives inaccurate values for the transport coefficients [8].

In regimes for which collective effects are important, we expect that deviations from the predictions of kinetic theory occur not only for the diffusion coefficient, but also for the rest of the transport coefficients of the DPD fluid [8]. It is actually possible to use the theory presented in this paper in order to compute the transport coefficients for the DPD fluid expressed in the form of Green-Kubo formulas [16]. One then obtains a set of recursive equations in which the transport coefficients are expressed in terms of the transport coefficients used in the hydrodynamic assumption. This provides a self-consistent set of mode coupling equations for D,ν, and Γ. This is a celebrated method used by Kawasaki [17] and Kadanoff and Swift [18] to calculate transport properties near critical points [11]. It should provide further insight into interesting regimes where collective effects are important.

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APPENDIX

On simple symmetry grounds, the tensor $\boldsymbol{\omega}(\mathbf{k})$ has the form

$$\boldsymbol{\omega}(\mathbf{k})=\int d\mathbf{r}\ \omega(r)\hat{\mathbf{r}}\hat{\mathbf{r}}\ \exp\{-i\mathbf{k}\mathbf{r}\}=a(kr_c)\mathbf{1}+b(kr_c)\hat{\mathbf{k}}\hat{\mathbf{k}}. \tag{A1}$$

In order to calculate the functions $a(kr_c)$ and $b(kr_c)$, we double contract $\boldsymbol{\omega}(\mathbf{k})$ with the dyadic $\hat{\mathbf{k}}\hat{\mathbf{k}}$ and also take its trace. This leads to

$$\hat{\mathbf{k}}^{\mathbf{T}}\boldsymbol{\omega}(k)\hat{\mathbf{k}}=a(kr_c)+b(kr_c)=2\pi\int_0^\infty dr\,\omega(r)\times\left(\frac{J_1(kr)}{k}-rJ_2(kr)\right), \tag{A2}$$

$$\mathrm{tr}[\boldsymbol{\omega}(k)]=2a(kr_c)+b(kr_c)=2\pi\int_0^\infty r\omega(r)J_o(kr).$$

The integrals are given in terms of generalized hypergeometric functions ${}_pF_q\{\mathbf{a},\mathbf{b},z\}$ [19], and Bessel functions

$${}_pF_q\{\mathbf{a},\mathbf{b},z\}=\sum_{k=0}^{\infty}\frac{(a_1)_k\ldots(a_p)_k}{(b_1)_k\ldots(b_q)_k}\frac{z^k}{k!}, \tag{A3}$$

where $(m)_k=m(m+1)\cdots(m+k-1)$. More precisely,

$$a(kr_c)+b(kr_c)=-\frac{1}{n}{}_1F_2\left\{\left(\frac{3}{2}\right),\left(2,\frac{5}{2}\right),-\frac{(kr_c)^2}{4}\right\}-\frac{6}{n(kr_c)^2}+\frac{6}{n(kr_c)^2}J_0(kr_c)+\frac{6}{nkr_c}J_1(kr_c)$$
$$+\frac{6(kr_c)^2}{n}{}_1F_2\left\{\left(\frac{5}{2}\right),\left(3,\frac{7}{2}\right),-\frac{(kr_c)^2}{4}\right\}, \tag{A4}$$

$$2a(kr_c)+b(kr_c)=\frac{6J_1(kr_c)}{kr_cn}-\frac{2}{n}{}_1F_2\left\{\left(\frac{3}{2}\right),\left(1,\frac{5}{2}\right),-\frac{(kr_c)^2}{4}\right\}.$$

The solution of this system of two equations provides the values for $a(kr_c)$ and $b(kr_c)$.

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