Kinetic theory for dissipative particle dynamics: The importance of collisions

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Abstract. – Kinetic theory of dissipative particle dynamics is developed in terms of a Boltzmann pair collision theory. The kinetic transport coefficients are computed from explicit collision integrals and compared favourably with detailed simulations. Previous theory is found to correspond to a weak scattering limit, or Vlasov theory, and previously reported discrepancies with simulations are thereby largely resolved. In the large dissipation limit, we find that qualitatively new scaling behaviour for the transport coefficients is indicated.

Dissipative particle dynamics (DPD) is emerging as an attractive simulation method in such diverse areas as colloidal suspension rheology, explicit multiphase flow problems, polymer solution dynamics, and phase behaviour of block copolymer melts [1]. The basic DPD fluid consists of a large number of identical particles interacting by pairwise soft repulsive, dissipative, and random forces [2]. The soft repulsions typically correspond to an interparticle potential, \( U = A(1 - r/r_c)^2/2 \), where \( r \) is the distance between a pair of particles, \( r_c \) sets the range and \( A \) sets the amplitude. The dissipative forces are similarly specified by \( f = -m\gamma w_D(r)v|| \), where \( m \) is the particle mass, \( \gamma \) (with units of inverse time) sets the overall dissipation rate and \( v|| \) is the relative velocity of the particles projected onto the line joining their centres. A weight function, here taken to be \( w_D(r) = (1 - r/r_c)^2 \), smoothly limits the range of the dissipative interactions. Given the dissipative forces, the random forces are completely determined by a fluctuation-dissipation theorem apart from an overall amplitude which fixes the temperature \( k_BT \); their detailed form need not be further specified [3, 4]. All forces vanish for \( r > r_c \), and are arranged to conserve momentum locally. Thus hydrodynamics is recovered at longer length and time scales just as in a molecular fluid.

For the applications cited above, the basic interactions are typically augmented by extra bond constraints, different types of particles, and so on. In nearly all cases though the properties of the basic DPD fluid are required to calibrate the results against other methods.
and to provide an essential bridge back to the real world. Thus there has been considerable effort in establishing a rigorous theoretical basis for the method [3] and in developing kinetic theories for the transport properties [5-8]. These studies also open up relatively unexplored terrain for kinetic theory. For instance, the “ideal dissipative fluid” (basic DPD fluid with $A = 0$) is probably the simplest example of a completely structureless fluid with non-trivial transport properties. Dimensional analysis indicates that the transport properties of this fluid are completely determined by a dimensionless dissipation rate, $\gamma r_c(k_B T/m)^{1/2}$, and number density, $\rho r_c^3$, where $\rho$ is the number of particles per unit volume. In what follows, we shall use units in which $m = r_c = k_B T = 1$, so that the rms velocity of particles is $v_{\text{rms}} = \sqrt{3}$ for instance. In these units, the general DPD fluid is completely specified by $\gamma$, $\rho$ and $A$.

Our starting point is the kinetic theory developed by Marsh, Backx and Ernst (MBE) [6]. They identify the principal time scales in the ideal dissipative fluid, and provide explicit expressions for the transport coefficients. For instance, the (normalised) MBE velocity auto-correlation function (VACF) is predicted to decay exponentially, $\phi(t) = e^{-t/\tau}$, with a decay rate

$$\tau^{-1} = \frac{1}{3} \int \rho \, d^3 r \, \gamma D(r) = \frac{2\pi \gamma \rho}{45}.$$ \hfill (1)

In simple terms this corresponds to the drag on a DPD particle in a stationary background of other particles at a uniform density $\rho$. For later use we define $\lambda_{\text{MBE}} = \tau v_{\text{rms}} = 45\sqrt{3}/2\pi \gamma \rho$ to be a representative mean free path in the MBE theory. The self-diffusion coefficient in the MBE theory, given our choice of units above, is simply $D = \tau$. The viscosity in the MBE theory has two contributions: a kinetic contribution, $\eta_K = \rho D/2$, and a dissipative contribution arising directly from the dissipative forces, $\eta_D = (\gamma \rho^2/2) \int d^3 r \, r^2 \, w_D(r) = 2\pi \gamma \rho^2/1575$. Again in simple terms these correspond to the internal friction induced by particles diffusing across streamlines, and the drag force that acts between particles on different streamlines.

The MBE theory captures the basic kinetic phenomena in the DPD fluid, and is highly successful in explaining such apparent paradoxes as a decrease in viscosity for certain parameter

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![Fig. 1. – Velocity autocorrelation function for the ideal dissipative fluid: (a) at $\rho = 3$ for $\gamma = 1$ (steepest curve), 2, 4, 8, 16, and (b) at $\gamma = 2$ for $\rho = 1, 2, 3, 4, 5, 6$, showing data collapse (note that a basic scaling prefactor $\rho \gamma$ has been extracted from the time dependence). The dashed line in (b) shows the universal decay predicted by Marsh et al. [6] (MBE). Where single exponential decay occurs over two decades or more, the inset to (b) shows the decay rate normalised by the MBE result, $\tau_{\text{MBE}} = 45/2\pi \rho \gamma$ (points with error bars), as a function of $\gamma$. The open circles in the inset are predictions from the Boltzmann pair collision theory discussed in the text.](image)
ranges, as the dissipation rate $\gamma$ is increased. When compared in detail with simulations though, certain discrepancies were already noted by the original investigators [6], and were explored more recently by Pagonabarraga et al. [9]. Neither set of authors identify the origin of the discrepancies, although correlation effects are an obvious candidate.

To investigate these discrepancies in detail, we carried out a systematic study of the ideal dissipative fluid by simulation [10]. Typical results for the VACF are shown in fig. 1. We find that $\phi(t)$ is remarkably insensitive to $\rho$ but depends significantly on $\gamma$, once a basic scaling prefactor $\rho \gamma$ is removed from the time dependence. For $\gamma < \sim 5$ the VACF decays as a single exponential, to an excellent approximation, over two decades of magnitude (after which the signal becomes swamped by noise). The decay rate is plotted against $\gamma$ in the inset to fig. 1(a); it shows a systematic deviation from the MBE prediction. For $\gamma > \sim 5$ significant deviations from single exponential decay start to appear, indicating the early onset of correlation effects. Of course one would expect correlation effects to be present to some extent for all $\gamma$, since they lead, for instance, to the celebrated long time tail $\phi(t) \sim t^{-3/2}$ [8, 11].

We also studied the two contributions to the viscosity. Typical results are shown in fig. 2. Although $\eta_D$ appears to be well captured by the theory, $\eta_K$ is again systematically wrong, by as much as a factor of three (fig. 2(b)) [12]. It too is remarkably insensitive to density (fig. 2(a)).

When the VACF is well approximated by a single exponential, significant discrepancies with theory cannot be ascribed to the correlation effects hypothesised earlier. Furthermore, the lack of dependence of the kinetic properties on density is startling. For a long time these results puzzled us, until we recalled the basic properties of the classic Boltzmann pair collision theory [13]. Let us introduce an estimate of the number of collisions a particle undergoes before it loses its memory of its initial velocity. To be specific, define $n_{\text{coll}} = \rho \lambda$, where $\lambda$ is the mean free path (note that the collision cross-section $\sim r_c^2 = 1$). In the MBE theory, this gives $n_{\text{coll}} = \rho \lambda_{\text{MBE}} = 45 \sqrt{3}/2 \pi \gamma$; we will use this estimate to analyse the data. The importance of a parameter proportional to $\rho \lambda_{\text{MBE}}$ was recently noted by Evans in a different approach [7].

Our central and perhaps surprising conclusion is that $n_{\text{coll}}$, and pair collisions in general, seem to be the key to rationalising the data. This is supported by three general observations.
Firstly note that in a pair collision theory, the transport coefficients $\rho D$ and $\eta_K$ have no dependence on density. Secondly, when the VACF decay rate (fig. 1) and $\eta_K$ normalised by the MBE prediction (fig. 2(b)) are examined as functions of $n_{\text{coll}} \sim 1/\gamma$, a data collapse is found. Thirdly, both the VACF decay rate and $\eta_K$ systematically asymptote towards the MBE theory in the limit $n_{\text{coll}} \to \infty$. The last observation suggests that MBE theory is actually only a weak deflection theory, valid in the limit where many collisions are required to decorrelate a particle’s velocity.

If pair collisions are the determining factor, one ought to be able to compare the simulation results with the transport properties computed from collision integrals in a Boltzmann theory. It is straightforward to show that the standard expressions hold for the DPD fluid with the minor modification that, for a given impact parameter and pre-collisional set of velocities, the random force leads to a distribution of outgoing velocities rather than a single, unique set as is the case for normal fluids. The collision integrals take the generic form [13]

$$\Omega_{D,\eta} = \int_0^1 \frac{2\pi b db}{d^3 v_{12}} \phi_0(v_{12}) |v_{12}| \langle F_{D,\eta}(v_{12}, v'_{12}) \rangle,$$

where $b$ is the impact parameter in units of $r_c$, $v_{12}$ is the pre-collisional relative velocity, $v'_{12}$ is the post-collisional relative velocity and $\phi_0$ is the Maxwellian distribution function for relative velocities. The functions are $F_D(v, v') = v_x(v'_x - v_x)$ for the self-diffusion coefficient, and $F_\eta(v, v') = v_x v_y(v'_x v'_y - v_x v_y)$ for the kinetic contribution to viscosity. The angle brackets denote an average over the distribution of out-going velocities for a given $b$ and $v_{12}$.

To evaluate these collision integrals, we used a numerical, Monte Carlo approach. A value of $b^2$ was chosen from a uniform distribution in the range [0, 1] and a value of $v_{12}$ was taken from the Maxwellian distribution. We then followed the particle trajectory using the algorithm of Pagonabarraga et al. [9]. We noted the outgoing relative velocity and thus formed the integrand for this particular trajectory. By averaging over many trajectories we obtained the overall integral. Typically we used a time step of 0.005 to compute the trajectory and $10^8$ trajectories to get a precision of better than 1%.

Once the collision integrals were determined, we calculated the diffusion constant and the viscosity using the standard results (in our chosen set of units) $\rho D = -4/\Omega_D$ and $\eta_K = -8/\Omega_\eta$. These results are at a first Sonine polynomial level of approximation. For the hard sphere fluid, for example, this leads to an error of < 2%, compared to the true Boltzmann value [13]. To check whether the first Sonine polynomial approximation was as good for the DPD fluid, we also calculated the second Sonine polynomial correction. Just as in the hard sphere fluid, the correction was of the order of 1% so we believe the results quoted are excellent approximations to the true Boltzmann values.

The predictions of the Boltzmann pair collision theory turn out to be in excellent agreement with the simulation results, thus confirming our premise that the kinetic behaviour is dominated by pair collisions. Results for the decay rate of the VACF (defined by $\tau = D$) are shown as open circles in the inset to fig. 1(b). Similar results for $\eta_K$ in shown in fig. 2(b), and for both $\eta_K$ and $\rho D$ in fig. 3. Moreover, we have been able to prove that the MBE theory is obtained in the Vlasov limit [13], where each collision only weakly perturbs the velocities of the colliding particles.

Now consider the significance of these ideas for the strong deflection limit. Since $n_{\text{coll}} \sim 1/\gamma$ in the MBE theory, it appears that for $\gamma$ sufficiently large, $n_{\text{coll}} < 1$. But in our new picture, at least one collision is needed to decorrelate a particle’s velocity no matter how large $\gamma$ is. Thus for $\gamma$ sufficiently large, one might expect a qualitative change in the scaling behaviour of the kinetic properties, with the crossover occurring at $n_{\text{coll}} \approx 1$ or $\gamma \approx \gamma_c = 45\sqrt{3}/2\pi \approx 12.4$. Turning the argument around, if $n_{\text{coll}} \gtrsim 1$ is enforced for all $\gamma$ there must be a change in the
Fig. 3. – Kinetic transport coefficients for the ideal dissipative fluid: (a) kinetic contribution to viscosity, $\eta_K$, and (b) self-diffusion coefficient, $\rho D$, plotted against $1/\gamma$. The points with error bars are simulation results: in (a), results for $\rho = 0.25–10, \gamma = 2–20$ are included; in (b), we only have results for $\rho = 3$. In both plots, the open circles are predictions from the Boltzmann pair collision theory together with linear regression lines [14]. The apparent intercepts for both the simulation data and the pair collision theory strongly suggest the existence of a plateau in $\eta_K$ and $\rho D$ for large $\gamma$. The dashed line in (a) is $\eta_K = 45/4\pi\gamma$, the prediction of the MBE theory, and in (b) it is $\rho D = 45/2\pi\gamma$, the common prediction of the MBE and Evans’ [7] theories.

scaling of the mean free path from the MBE result, $\lambda_{\text{MBE}} \approx \gamma_c/(\gamma\rho)$ for $\gamma \gtrsim \gamma_c$, to a new behaviour, $\lambda \approx 1/\rho$ for $\gamma \gtrsim \gamma_c$. This argument implies that $\tau, D$ and $\eta_K$ should reach a plateau for $\gamma \gtrsim \gamma_c$. This is in contrast to the predictions of both the MBE [6] and Evans’ [7] theories. Such behaviour is indeed strongly suggested by both the simulation data and the pair collision theory, as shown in fig. 3. The simulation results can be fit by $\eta_K = 0.37(1) + 3.65(5)/\gamma$ and $\rho D = 0.59(4) + 7.6(2)/\gamma$, where the numbers in brackets are estimates of the error in the final digit [14]. These fits define crossovers at $\gamma \approx 3.65(5)/0.37(1) = 9.9(3)$ for $\eta_K$ and $\gamma \approx 7.6(2)/0.59(4) = 13(1)$ for $\rho D$, which are satisfyingly close to $\gamma_c \approx 12.4$.

This discussion on the large-$\gamma$ limit has implications for Schmidt number too, an important dimensionless material parameter defined by $Sc = \eta/\rho D$. In this limit, the viscosity is dominated by $\eta_D \sim \rho^2\gamma$ but the above argument changes the scaling of $D$ from $(\rho\gamma)^{-1}$ to $\rho^{-1}$. This suggests that $Sc$ ultimately grows as $\rho^2\gamma$ and not $(\rho\gamma)^2$ as thought previously [4].

A pair collision theory is strictly valid only when the mean free path is large compared to $r_c$, when effects such as finite collision volumes and correlations are unimportant. The comparison with simulation implies though that the transport coefficients are rather insensitive to these effects so long as $\lambda \gtrsim 1$. There must be a point though where these effects become important, and we now turn to a discussion of this, the large-$\rho$ limit. Firstly, note that from a kinetic theory point of view this limit is rather unusual. For hard spheres, for instance, there is a natural maximum density, but for the ideal dissipative fluid, $\rho$ can be increased indefinitely. In this limit each sphere is in continual interaction with many others simultaneously and a picture in terms of pair collisions is surely invalid. Moreover, one can derive some of the MBE results by assuming a mean field interaction of this type [4,8]. Therefore at very high densities, one would expect the MBE results (for $\tau$ and $D$ at least) to be recovered. A more sophisticated approach would couple the motion of an individual particle to the hydrodynamic modes of the fluid, and recover, for instance, the long time tail in the VACF. An elegant mode-coupling theory along these lines has recently been developed by Español and Serrano [8].
Figure 2(a) shows how $\eta_K$ only starts to drift down from the Boltzmann pair collision theory toward the MBE result for densities $\rho \gtrsim 10$. It is at first sight remarkable that a pair collision theory works at such high densities. We can partially understand this observation though when we consider the fluctuations in $\rho$ in the integral for $\tau^{-1}$ in eq. (1). If we suppose that the number of particles in a volume element $d^3r$ is a Poisson distribution with a mean $\rho d^3r$ and a variance equal to the mean, then $\tau^{-1}$ is a weighted sum of independent random variables whose mean is given by eq. (1) and variance by

$$\text{var} \tau^{-1} = \frac{1}{3} \int \rho d^3r \left[ \gamma w_D(r) \right]^2 = \frac{4\pi\gamma^2 \rho}{315}. \tag{3}$$

Thus the ratio of the standard deviation to the mean for $\tau^{-1}$ is $(\rho/\rho_c)^{-1/2}$, where $\rho_c = 45/7\pi$. For $\rho = 10$, for instance, this ratio is about 45%, and to get the ratio $\lesssim 10\%$ requires $\rho \gtrsim 200$. Thus, unless $\rho \gg 1$, a particle sees large fluctuations in its interaction with other particles (O(1) in essence), and it is perhaps not surprising that a pair collision theory is applicable even though the apparent density becomes rather large.

The above discussions have concerned the ideal dissipative fluid. Let us finish off by briefly discussing the properties of the non-ideal fluid. The main effect of the soft repulsion forces is to provide another collision mechanism which is most significant at low $\gamma$; in fact at $\gamma = 0$ one recovers a regular fluid of soft spheres. The effect is to remove the $1/\gamma$ divergence in the kinetic coefficients as $\gamma \to 0$. Combined with the plateau that is expected for $\gamma \gtrsim \gamma_c$, this makes the transport coefficients very insensitive to parameter variations. The collision integrals can also be evaluated for non-ideal interactions, and again we find a good agreement with simulations. This is so even though the VACF in some instances develops a pronounced non-trivial structure.

Two recent investigations go beyond the MBE theory, and it is worth discussing our results in the light of these. The approach of Evans [7] is to express the true time evolution operator in terms of a truncated basis set and this simplification permits an analytic but approximate solution. The Boltzmann theory discussed here, however, uses exact two-particle dynamics to evaluate the collision integrals and thus yields the true low density limit. In a separate development, Español and Serrano (ES) describe a mode-coupling theory which captures correlation effects beyond the MBE theory [8]. They claim to have successfully compared their theory with simulation results in two dimensions. However, we note that their approach is still underpinned by a Vlasov-like mean field approximation. It is this approximation that our results challenge. Although correlation effects are undoubtedly present in our results too, as indicated by the non-exponential decay of the VACF in fig. 1(a) for example, they are unlikely to be as significant as in two dimensions. This may explain the relative successes of the two approaches [15].

In summary therefore, we argue that for the typical parameters used in applications, the kinetic transport coefficients in DPD are well captured by a Boltzmann pair collision theory, even though the apparent density is rather high. The evidence is the excellent agreement with simulation results, and the fact that the number of collisions a particle experiences in a mean free path appears to be the principal parameter that determines the kinetic properties. The kinetic theory of Marsh et al. [6] is recovered as a weak scattering or Vlasov theory, valid in the low-$\gamma$ limit. Previously reported discrepancies with this theory [6, 9] are thereby largely resolved. We further argue that a qualitative change in the scaling of kinetic transport coefficients occurs at large $\gamma$ since at least one collision per mean free path is required to decorrelate a particle’s initial velocity. This conclusion, too, is supported by our simulation evidence. We understand that very similar conclusions have recently been reached independently by Ernst and co-workers [16].
Finally, the present study is likely to have implications for the analysis of transport behaviour in the various generalisations of DPD [17]. More details of our results and our parallel investigations of the non-ideal fluid will be the subject of a longer paper.

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