

Self-diffusion coefficient in smoothed dissipative particle dynamics

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Smoothed dissipative particle dynamics (SDPD) is a novel coarse grained method for the numerical simulation of complex fluids. It has considerable advantages over more traditional particle-based methods. In this paper we analyze the self-diffusion coefficient D of a SDPD solvent by using the strategy proposed by Groot and Warren [J. Chem. Phys. **107**, 4423 (1997)]. An analytical expression for D in terms of the model parameters is developed and verified by numerical simulations. © 2009 American Institute of Physics. [DOI: [10.1063/1.3058437](https://doi.org/10.1063/1.3058437)]

Soft matter systems, such as polymer suspensions, polymer melts, colloids, or emulsions, are an extremely active area of research for both academic and industrial purposes. The interest in dealing with increasingly complex problems in the micro- and macroscale has provided a strong stimulus for the development of a wide class of numerical methods specifically designed to model complex mesoscopic flow physics. A straightforward computational tool to study the transport properties of liquids is molecular dynamics (MD).¹ The obvious disadvantage of an atomistic representation of the liquid is the overwhelming computational cost for practically relevant length and time scales of macroscopic experiments. For simple configurations extensive studies by MD of transport properties have been performed, e.g., a self-diffusion coefficient has been extracted with high accuracy.² The large scale separation between atomistic and typical lengths occurring in soft matter systems has triggered the development of a new class of so-called mesoscopic methods allowing for simulations on much larger length and time scales than MD. Lattice gas automata,³ lattice Boltzmann methods,^{4,5} and multiparticle collision dynamics⁶ represent some popular examples. Among them, dissipative particle dynamics (DPD) (Ref. 7) is receiving considerable attention. A DPD fluid is represented as a collection of particles, which interact through conservative, dissipative, and stochastic forces. Stochastic forces take into account the thermal fluctuations, which describe diffusive processes at the mesoscopic scales. The correct hydrodynamics is recovered at larger scales due to the fact that linear and angular momenta are locally conserved by the particle interactions. Equilibrium and transport properties of DPD systems have been extensively studied in literature.^{8–10} Following the introduction of the method in Ref. 7, the basis of its statistical mechanics was established in Ref. 11.

A critical issue in DPD is the determination of the transport coefficients of the simulated liquid. In Refs. 12 and 13 explicit predictions for the viscosity and the self-diffusion coefficient in terms of the model parameters were given. However, the validity of these analytical expressions is re-

stricted to the ideal-gas equation of state and to the limit of small time step. Furthermore, as found in Ref. 14, the prediction failed to reproduce correctly the diffusion coefficient for the widely used velocity-Verlet integration scheme. In a recent work Noguchi and Gompper¹⁵ studied the time step dependence of the viscosity and diffusion coefficient. However, how to predict self-diffusion accurately in DPD is still an open question.

A few years ago a generalization of the smoothed particle hydrodynamics methods (SPH) (Ref. 16) for flow problems occurring at mesoscopic scales was introduced as smoothed dissipative particle dynamics (SDPD).¹⁷ Despite a resemblance with DPD, it has been shown that the new method possesses several improved features: (i) SDPD is based on a second-order discretization of the Navier–Stokes equations such that the transport coefficients (i.e., viscosity, thermal conductivity, etc.) are input parameters; (ii) hydrodynamic behavior is obtained at length scales of the same order of particle dimension and no coarse-graining assumption is needed; (iii) arbitrary expressions for the equation of state can be adopted and they are not restricted to the specific form used in DPD;¹³ and (iv) the fluid particles have a specified physical length and the thermal fluctuations scale correctly with this size.¹⁸

Concerning the transport properties of SDPD, viscosity is an input parameter; therefore no kinetic theory or preliminary computations are necessary to evaluate viscosity. However, the self-diffusion coefficient D of a fluid particle cannot be specified *a priori* and therefore needs to be estimated. It should be noted that an accurate expression for D in terms of the model parameters is crucial for the determination of the Schmidt number Sc of the model liquid. For instance, the value of Sc affects strongly the nonequilibrium properties of suspended polymer molecules.¹⁴

The objective of this Communication is the following: first, we will develop an analytical expression for the self-diffusion coefficient D in a SDPD liquid and, second, we will check numerically the accuracy and the robustness of this prediction over a wide range of the model parameters. The result allows for a systematic control of the self-diffusion coefficient and the Schmidt number of the simu-

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lated liquid without the need to perform preliminary computations.

In the following we briefly review the main SDPD equations. The discretized isothermal Navier–Stokes equations (continuity and momentum) for a set of Lagrangian particles have been given, for example, in Refs. 16 and 19 and they read

$$\rho_i = m_i \sum_j W_{ij}, \quad (1)$$

$$\begin{aligned} \frac{d\mathbf{v}_i}{dt} = & -\frac{1}{m_i} \sum_j \left(\frac{p_i}{\sigma_i^2} + \frac{p_j}{\sigma_j^2} \right) \frac{\partial W_{ij}}{\partial r_{ij}} \mathbf{e}_{ij} \\ & + \frac{\mu}{m_i} \sum_j \left(\frac{1}{\sigma_i^2} + \frac{1}{\sigma_j^2} \right) \frac{\mathbf{v}_{ij}}{r_{ij}} \frac{\partial W_{ij}}{\partial r_{ij}}, \end{aligned} \quad (2)$$

where μ is the dynamic viscosity, m_i is the mass of a particle, W_{ij} is a kernel function, $\sigma_i = \sum_j W_{ij}$ is the inverse of the particle volume, and \mathbf{e}_{ij} and r_{ij} are the normalized vector and distance from particle i to particle j , respectively. ρ and p are related by the equation of state: In this work $p = p_0(\rho/\rho_0)^\gamma + b$ is adopted, where p_0 , ρ_0 , b , and γ are model parameters, which may be chosen such that the local mass density variation is smaller than a given magnitude. Equations (1) and (2) represent the deterministic part of the particle dynamics. By using the general equation for non-equilibrium reversible-irreversible coupling formalism,^{20,21} thermal fluctuations can be directly introduced in Eqs. (1) and (2) by adding the following terms:¹⁷ $d\tilde{m}_i = 0$ and $d\tilde{\mathbf{P}}_i = \sum_j B_{ij} d\tilde{W}_{ij} \mathbf{e}_{ij}$, where $d\tilde{W}_{ij}$ is the traceless symmetric part of an independent increment of a Wiener process and B_{ij} is defined as

$$B_{ij} = \left[-4k_B T \mu \left(\frac{1}{\sigma_i^2} + \frac{1}{\sigma_j^2} \right) \frac{1}{r_{ij}} \frac{\partial W}{\partial r_{ij}} \right]^{1/2}. \quad (3)$$

This expression represents the SDPD fluctuation-dissipation theorem and guarantees that all the energy introduced by the stochastic kicks on the particles is entirely dissipated by the viscous terms in Eq. (2).¹⁷ Unlike DPD, the tensorial generalization of the Wiener process in $d\tilde{\mathbf{P}}_i$ allows for a rigorous identification of the irreversible part of the dynamics as a second-order accurate SPH discretization of the Navier–Stokes equations.

Let us present now a derivation of the self-diffusion coefficient for the SDPD fluid particles. The following notation for the particle accelerations will be used:

$$\frac{d\mathbf{v}_i}{dt} = \frac{1}{m_i} (\mathbf{F}_i^C + \mathbf{F}_i^D + \mathbf{F}_i^R), \quad d\mathbf{r}_i = \mathbf{v}_i dt, \quad (4)$$

where $\mathbf{F}_i^{\{C,D,R\}} = \sum_j \mathbf{F}_{ij}^{\{C,D,R\}}$ are the total conservative, dissipative, and random force acting on particle i expressed as a sum of contributions of interactions with all the particles.

According to the derivation given by Groot and Warren in Ref. 13, we neglect the conservative forces and assume that all the particles except particle i are at rest. Additionally, by assuming that the density is uniformly distributed, one can write the following:

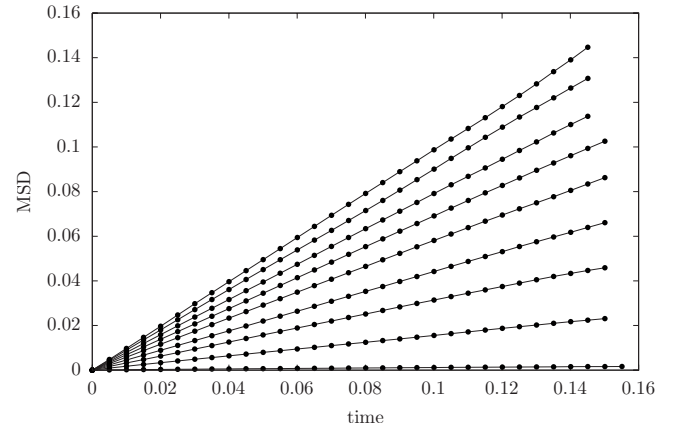


FIG. 1. Mean square displacement for different values of the viscosity: $\mu = 2200.2, 48.9, 24.7, 16.5, 12.4, 10.0, 8.3, 7.1$, and 6.2 (from top to bottom).

$$\frac{d\mathbf{v}_i}{dt} = \frac{1}{m_i} \sum_{j \neq i} \mathbf{F}_{ij}^D + \frac{1}{m_i} \sum_{j \neq i} \mathbf{F}_{ij}^R. \quad (5)$$

Using the fact that the dissipative part is linear in the velocity differences, one can rewrite the equation in a Langevin form as follows:

$$\frac{d\mathbf{v}_i}{dt} + \frac{\mathbf{v}_i}{\tau} = \frac{\mathbf{F}^R}{m_i}, \quad \frac{1}{\tau} = -\frac{2m\mu}{\rho^2} \sum_{i \neq j} \frac{1}{r_{ij}} \frac{\partial W_{ij}}{\partial r_{ij}}. \quad (6)$$

In SPH/SDPD the kernel typically takes the form¹⁶

$$W(\mathbf{r}_{ij}, h) = \frac{1}{h^3} f\left(\frac{|\mathbf{r}_{ij}|}{h}\right). \quad (7)$$

By replacing the summation in the viscous and random forces with an integration, we obtain

$$\frac{1}{\tau} = \frac{8\pi\mu}{\rho h^2} \int_0^{+\infty} f(s) ds. \quad (8)$$

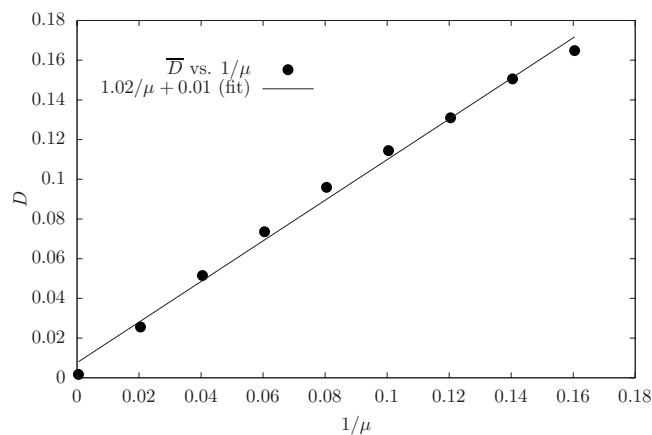
The solution of the Langevin equation (6) leads therefore to the following expression for the diffusion coefficient:

$$D = \frac{\tau k_B T}{3m} = \frac{\rho h^2 k_B T}{24\pi m \mu} \left(\int_0^{+\infty} f(s) ds \right)^{-1}. \quad (9)$$

Finally, for the quintic spline kernel²² used in this work, we obtain the following Stokes–Einstein-type relation:

$$D = \frac{\rho h^2 k_B T}{12m\mu}. \quad (10)$$

This represents the main result of this Communication. In order to verify numerically this expression, the following simulations are performed: A three-dimensional periodic box domain is considered. We take $k_B T = 1$, box size $L = 1.25$, mass density $\rho = 1$, number of particles $N = 15 \times 15 \times 15 = 3375$, and dynamic viscosity μ varying between 6 and 2200. As an initial condition a uniform distribution with the particles placed on a cubic lattice is taken. Particle mass is $m = \rho L^3 / N$, where $h = L/15$ is the kernel cutoff radius. With this choice of input parameters, Eq. (10) simplifies to $D\mu = 1$.

FIG. 2. Diffusion coefficient D plotted against the inverse viscosity $1/\mu$.

The system is advanced in time and the mean square particle displacement $\text{MSD} = \langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle$ is calculated for different viscosities. The results are plotted in Fig. 1. We found that the domain size effects are negligible and do not affect the results.

The values of the diffusion coefficient for the different simulations performed are computed by fitting the MSD in the limiting linear regime and are plotted against the inverse viscosity in Fig. 2. The best linear approximation to the data is $\mu D = 1.02 \pm 0.03$, which is in good agreement with the prediction of Eq. (10) and confirms the validity of the approximation made by neglecting the conservative terms in Eq. (5). Simulations were repeated for temperatures $k_B T = 0.5, 2$ with the same results.

As mentioned above, an accurate analytical expression of D provides an easy way to control the Schmidt number. This is defined as $\text{Sc} = \nu/D$, where $\nu = \mu/\rho$ is the kinematic viscosity and gives an estimate of the time scale of momentum diffusion with respect to mass diffusion. In a liquid such as water Sc should be on the order of 10^3 or larger. With DPD, Sc does not always agree with the theoretical predictions¹⁴ so that for an unambiguous characterization of the diffusional properties of the solvent, extensive preliminary computations are needed. In the results reported here, very good agreement has been found between the diffusion coefficient evaluated from the simulations and the theoretical

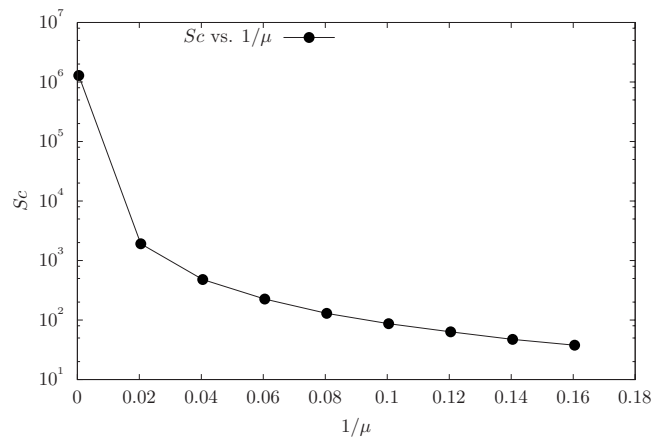
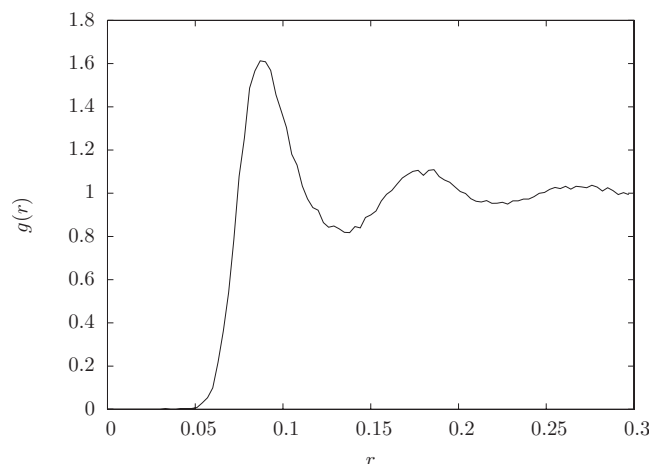


FIG. 3. Schmidt number plotted against inverse viscosity.

FIG. 4. Radial distribution function for $\mu = 2200.2$.

predictions over a wide range of viscosities. Therefore one can specify *a priori* the simulated Schmidt number. Its values for the different viscosities considered are shown in Fig. 3 and indicate that, for the largest values of μ , $\text{Sc} \approx 10^6$ as encountered in real experiments. It should be pointed out that the Schmidt number defined in terms of Eq. (10) depends on the fluid particle size h , which is consistent with the physical view that large patches of fluid display less fluctuations than small ones and, consequently, different diffusion properties.¹⁸

As a last remark, we noticed that in Ref. 23 the authors were concerned about the existence of a solidlike structure in DPD simulations at high coarse-graining levels. When a solid structure develops the MSD, after an initial increase, it remains approximately constant, which could produce a misleading result of a very small self-diffusion coefficient and, consequently, large Sc . We have explicitly checked that this situation does not occur in our simulations: first, by looking at the MSD (always linearly increasing with time) and, second, by inspecting the radial distribution function $g(r)$. No indications of secondary peaks (typically indicating partially crystallized structures) were found, as can be seen from the plot in Fig. 4.

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