Consistent particle-based algorithm with a non-ideal equation of state

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Abstract. – A thermodynamically consistent particle-based model for fluid dynamics with continuous velocities and a non-ideal equation of state is presented. Excluded-volume interactions are modeled by means of biased stochastic multiparticle collisions which depend on the local velocities and densities. Momentum and energy are conserved locally. The equation of state is derived and compared to independent measurements of the pressure. Results for the kinematic shear viscosity and self-diffusion constants are presented. For fixed density, a caging and order/disorder transition is observed with increasing collision frequency.

Introduction. – The efficient modeling of the long length- and time-scale dynamics of complex liquids such as colloidal and polymeric suspensions requires a simplified, coarse-grained description of the solvent degrees of freedom. There are several particle-based meso-scale simulation algorithms which have been developed for this purpose. They include dissipative particle dynamics (DPD) \cite{1}, smooth particle hydrodynamics (SPH) \cite{2}, and a recently introduced particle-based simulation technique \cite{3} often called stochastic rotation dynamics (SRD) \cite{4–6} or multi-particle collision dynamics \cite{7}. In DPD, the fluid is represented by a collection of particles with prescribed conservative, dissipative, and stochastic interactions that conserve momentum and produce hydrodynamic behavior. SPH is basically a discretization of the Navier-Stokes equations on a Lagrangian grid. The connection between SPH and DPD has been clarified in a recent paper \cite{2}, where it was shown that a thermodynamically consistent SPH model can be constructed from the original DPD model by including two extra state variables, the internal energy and the volume of the particles. This generalization remedied several shortcomings of the original DPD algorithm. However, the resulting algorithms are quite complicated. There is a large computational overhead because of the complexity of the equations and the fact that small time steps are required; thermal noise has yet to be implemented, and the SPH algorithm has only been tested in cases in which the fluid particles are not allowed to move \cite{8}.
SRD has a simple discrete time dynamics consisting of consecutive streaming and collision steps. It shares many features with Bird’s Direct Simulation Monte Carlo (DSMC) algorithm [9] — which is a stochastic, particle-based approach for solving the non-linear Boltzmann equation — but uses more efficient multi-particle instead of binary collisions. SRD enables simulations in the microcanonical ensemble, and fully incorporates both thermal fluctuations and hydrodynamic interactions. Furthermore, its simplicity has made it possible to obtain analytic expressions for the transport coefficients which are valid for both large and small mean free paths. This algorithm is particularly well suited for studying phenomena with Reynolds and Peclet numbers of order one, and it has been used to study the behavior of polymers [7,10], colloids [3,11,12], vesicles in shear flow [13], and complex fluids [14,15].

The original SRD algorithm models a fluid with an ideal-gas equation of state. The fluid is therefore very compressible, and the speed of sound is low. In order to have negligible compressibility effects, as in real liquids, the Mach number has to be kept small, which means that there are limits on the flow velocity in the simulation. It is therefore important to explore ways to extend the algorithm to model dense fluids. Our approach starts from what has been a common theme of most liquid theories, namely the separation of intermolecular forces into short- and long-range parts, which are then treated differently. The short-range component is a strong repulsion when molecules are close together; it leads to excluded-volume effects which cause a decrease in the fluid’s compressibility and eventual crystallization at low temperatures or high density. The long-range component is a weak attraction which can lead to a liquid-gas transition. The generic reference system for the short-range repulsive component of the force is the hard-sphere system.

In this letter we show how the SRD algorithm can be modified to model excluded-volume effects, allowing for a more realistic modeling of dense gases and liquids. This is done in a thermodynamically consistent way by introducing generalized excluded-volume interactions between the fluid particles. The algorithm can be thought of as a coarse-grained multi-particle collision generalization of a hard-sphere fluid, since, just as for hard spheres, there is no internal energy. It is shown that for the chosen set of collision rules (which are not unique), nonideal contributions to the pressure can be an order of magnitude greater than the ideal-gas pressure. Results for the kinematic shear viscosity and self-diffusion constant are presented, and it is shown that there is an order-disorder transition at large collision frequencies for sufficiently large densities. This work is a first step towards developing consistent particle-based algorithms for modeling, in the microcanonical ensemble, more general liquids with additional attractive interactions and a liquid-gas phase transition. Extensions of this approach to model binary mixtures and fluids with internal energy are in progress [16].

Model. — As in the original SRD algorithm, the solvent is modeled by a large number $N$ of point-like particles of mass $m = 1$ which move in continuous space with a continuous distribution of velocities. The system is coarse-grained into $(L/a)^d$ cells of a $d$-dimensional cubic lattice of linear dimension $L$ and lattice constant $a$. The algorithm consists of individual streaming and collision steps. In the free-streaming step, the coordinates, $r_i(t)$, of the solvent particles at time $t$ are updated according to $r_i(t + \tau) = r_i(t) + \tau v_i(t)$, where $v_i(t)$ is the velocity of particle $i$ at time $t$ and $\tau$ is the value of the discretized time step. In order to define the collision, we introduce a second grid with sides of length $2a$ which in $d = 2$ groups four adjacent cells into one “supercell”. As discussed in ref. [4], a random shift of the particle coordinates before the collision step is required to ensure Galilean invariance. All particles are therefore shifted by the same random vector with components in the interval $[-a,a]$ before the collision step. Particles are then shifted back by the same amount after the collision. To initiate a collision, pairs of cells in every supercell are randomly selected. As shown in fig. 1,
We therefore use a collision rule which leads to the maximum transfer of the parallel component of the momentum and kinetic energy. This rule is chosen for its thermodynamic consistency. At each collision, we check if \( \Delta M \) is zero, which indicates that the number of particles in the two cells is the same. If \( \Delta M \neq 0 \), clouds of particles collide and exchange momenta. One three different choices are possible: a) horizontal (with \( \sigma_1 = \hat{x} \)), b) vertical (\( \sigma_2 = \hat{y} \)), and c) diagonal collisions (with \( \sigma_3 = (\hat{x} + \hat{y})/\sqrt{2} \) and \( \sigma_4 = (\hat{x} - \hat{y})/\sqrt{2} \)). Note that diagonal collisions are essential to equilibrate the kinetic energies in the \( x \)- and \( y \)-directions.

In every cell, we define the mean particle velocity, \( \bar{v}_n = (1/M_n) \sum_{i=1}^{M_n} v_i \), where the sum runs over all particles, \( M_n \), in the cell with index \( n \). The projection of the difference of the mean velocities of the selected cell pairs on \( \sigma_j \), \( \Delta u = \sigma_j \cdot (\bar{u}_1 - \bar{u}_2) \), is then used to determine the probability of collision. If \( \Delta u < 0 \), no collision will be performed. For positive \( \Delta u \), a collision will occur with an acceptance probability which depends on \( \Delta u \) and the number of particles in the two cells, \( M_1 \) and \( M_2 \). This rule mimics a hard-sphere collision on a coarse-grained level: For \( \Delta u > 0 \), clouds of particles collide and exchange momenta. One thermodynamically consistent choice for the acceptance probability is [17]

\[
p_A(M_1, M_2, \Delta u) = \Theta(\Delta u) \tanh(\Lambda) \quad \text{with} \quad \Lambda = A \Delta u M_1 M_2
\]

where \( \Theta \) is the unit step function and \( A \) is a parameter which allows us to tune the equation of state. The hyperbolic tangent function was chosen in eq. (1) in order to obtain a probability which varies smoothly between 0 and 1. Once it is decided to perform a collision, an explicit form for the momentum transfer between the two cells is needed. The collision should conserve the total momentum and kinetic energy of the cell pairs participating in the collision, and in analogy to the hard-sphere liquid, the collision should primarily transfer the component of the momentum which is parallel to the connecting vector \( \sigma_j \). In the following, this component will be called the parallel or longitudinal momentum. There are many different rules which fulfill these conditions. Our goal here is to obtain a large speed of sound. We therefore use a collision rule which leads to the maximum transfer of the parallel component of the momentum and
does not change the transverse momentum. The rule is quite simple; it exchanges the parallel component of the mean velocities of the two cells, which is equivalent to a “reflection” of the relative velocities, \( v_{ij}^\parallel (t + \tau) - u_{ij}^\parallel = -(v_{ij}^\parallel (t) - u_{ij}^\parallel) \), where \( u_{ij}^\parallel \) is the parallel component of the mean velocity of the particles of both cells. The perpendicular component remains unchanged. It is easy to verify that these rules conserve momentum and energy in the cell pairs.

Because of \( x\)-\( y \) symmetry, the probabilities for choosing cell pairs in the \( x \)- and \( y \)-directions (with unit vectors \( \sigma_1 \) and \( \sigma_2 \) in fig. 1) are equal, and will be denoted by \( w \). The probability for choosing diagonal pairs (\( \sigma_3 \) and \( \sigma_4 \) in fig. 1) is given by \( w_d = 1 - 2w \). \( w \) and \( w_d \) must be chosen so that the hydrodynamic equations are isotropic and do not depend on the orientation of the underlying grid. This can be done by considering the temporal evolution of the lowest moments of the velocity distribution function.

Assuming molecular chaos, the collision rules can be used to determine the eigenvalues of the relaxation matrix, \( R \), defined by \( \Psi_i(t + \tau) = R\Psi_i(t) \).

Because of the conservation of energy, one of the three eigenvalues of \( R \) is equal to one; the other two are given by \( \lambda_1 = w_d + 2w(2/M - 1) \) and \( \lambda_2 = 2w + w_d(2/M - 1) \), where \( M \) is the average number of particles per cell. Isotropy requires that \( \lambda_1 = \lambda_2 \), a condition that can be fulfilled for arbitrary \( M \) only if \( w_d = 1/2 \) and \( w = 1/4 \). Simulations show that both the speed of sound and the shear viscosity are isotropic for this choice. Note, however, that this does not guarantee that all properties of the model are isotropic. This becomes apparent at high densities or high collision frequency, \( 1/\tau \gg 1 \), where inhomogeneous states with square or rectangular order can be observed.

**Transport coefficients.** – The transport coefficients can be determined using the same Green-Kubo formalism as was used for the original SRD algorithm [4, 5]. In particular, the kinematic shear viscosity is given by

\[
\nu = \frac{\tau}{Nk_BT} \sum_{n=0}^{\infty} \langle S_{xy}(0)S_{xy}(n\tau) \rangle,
\]

where

\[
S_{xy}(n\tau) = \sum_{j=1}^{N} (v_{jx}(n\tau)\Delta \xi_{jy}(n\tau) + \Delta v_{jx}(n\tau)[\Delta \xi_{jy}^s(n\tau) - z_{jy}^s([n+1]\tau)/2])
\]

is the off-diagonal element of the stress tensor \( S \). \( \xi_j(t) \) and \( \xi_j^s(t) \) are the cell coordinates of particle \( j \) in the fixed and shifted frames at time \( t \), respectively, \( \Delta \xi_j(t) = \xi_j(t + \tau) - \xi_j(t) \), \( \Delta \xi_j^s(t) = \xi_j(t + \tau) - \xi_j^s(t + \tau) \), and \( \Delta v_j(t) = v_j(t + \tau) - v_j(t) \). \( z_{jy}^s \) indexes pairs of cells which participate in a collision event; the second subscript, \( l \), is the index of the collision vectors \( \sigma_l \) listed in fig. 1. For example, for collisions characterized by \( \sigma_1 \), \( z_{jy}^{s1} = 1 \) if \( \xi_{jy}^1 \) in eq. (3) is one of the two cells on the left of a supercell and \( z_{jy}^{s1} = -1 \) if \( \xi_{jy}^s \) is on the right-hand side of a supercell; all other components of \( z_{jy}^s \) are zero. In general, the components of \( z_{jy}^s \) are either 0, 1, or -1. Using \( \{z_{jy}^s\} \), the collision invariants of the model can be written as

\[
\sum_j \left( e^{ik\cdot\xi_j^s(t+\tau)/2} + e^{ik\cdot(\xi_j^s(t+\tau)+z_{jy}^s(t+\tau))} \right) [a_{\beta,j}(t + \tau) - a_{\beta,j}(t)] = 0,
\]

where \( a_{1,j} = 1 \) for the density, \( \{a_{\beta,j}\} = \{v_{\beta-1,j}\} \) are components of the particle momentum, and \( a_{d+2,j} = v_{j}^2/2 \) is the kinetic energy of particle \( j \) [4]. The analogous collision invariants
for the standard SRD algorithm are given in eq. (25) of [4]. The vectors $z_i^s$ are constructed so that the sum of the two exponentials in eq. (4) is the same for two particles if and only if they are in partner cells in a collision with index $l$ (see fig. 1).

The self-diffusion constant $D$ is given by a sum over the velocity-autocorrelation function (see, e.g., [4]) and can be evaluated analytically assuming molecular chaos. Ignoring fluctuations in the number of particles per cell (which is justified here since $M \geq 5$), one finds

$$D = k_B T \tau \left( \frac{1}{A} \sqrt{\frac{\pi}{k_B T}} M^{-3/2} - \frac{1}{2} \right),$$

which is in good agreement with simulation data, see fig. 2. The term in brackets cannot become negative, since the appropriate value of $A$ decreases with increasing $M$.

Equation of state. – The collision rules conserve the kinetic energy, so that the internal energy of our system should be the same as that of an ideal gas. Thermodynamic consistency requires that the non-ideal contribution to the pressure is linear in $T$. This is possible if the coefficient $A$ in eq. (1) is sufficiently small (see fig. 3).

We use here the mechanical definition of pressure — the average longitudinal momentum transfer across a fixed interface per unit time and unit surface area — to determine the equation of state. We consider only the momentum transfer due to collisions, since that coming from streaming constitutes the ideal part of the pressure. Take an interface that is parallel to the $y$-axis and consider the component $p_{xx}$ of the pressure tensor. Only collisions with label $l = 1$, 3, and 4 of the collision vector $\sigma_1$ in fig. 1 contribute to the momentum transfer in this case. Consider the contribution to the momentum transfer across the cell boundary from collisions with $l = 1$. For fixed number of particles, $M_1$ and $M_2$, in the two cells, the thermal average of the momentum transfer, $\Delta G_x$, across the dividing line is

$$\langle \Delta G_x \rangle = \frac{w}{2} \int_0^\infty p_G(\Delta u) p_A(M_1, M_2, \Delta u) \Delta G_x \, d(\Delta u).$$

The factor $1/2$ comes from the position average of the dividing line, since the collision occurs in the shifted cells, and the integral is restricted to positive $\Delta u$ because the acceptance rate is zero for $\Delta u < 0$. $p_G(\Delta u)$ is the probability that $u_{1x} - u_{2x}$ for the micro-state of two cells is equal to $\Delta u$. $w = 1/4$ is the probability of selecting this collision. Expanding the acceptance probability, eq. (1), in $\Lambda$ leads to $p_A(M_1, M_2, \Delta u) = \Theta(\Delta u)(\Lambda - \Lambda^3/3 + \ldots)$. Since the resulting contribution to the pressure from the term proportional to $\Lambda^n$ is of order $T^n$, thermodynamic consistency requires that $A$ be chosen sufficiently small that contributions from terms with $n > 1$ are negligible. We therefore only consider the $O(\Lambda)$ term in the following.

The resulting contribution to the pressure is $P(\sigma_1, M_1, M_2) = w A k_B T M_1 M_2/(2a \tau) + O(A^3 T^2)$. A similar calculation can be done for the contributions from the diagonal collisions. Using $w = 1/4$ and $w_d = 1/2$ and averaging over the number of particles per cell, one finds the non-ideal part of the pressure

$$P_n = \left( \frac{1}{2\sqrt{2}} + \frac{1}{4} \right) A M^2 \frac{k_B T}{a \tau} + O(A^3 T^2).$$

Note that the same result is obtained if, instead of averaging over $M_1$ and $M_2$, we simply set $M_1 = M_2 = M$, the average number of particles per cell. $P_n$ is quadratic in the particle density, $\rho = M/a^2$, as one would expect from a virial expansion. We have found that prefactors $A$ leading to acceptance rates of about 20% are sufficiently small to guarantee that the pressure is linear in $T$ (see fig. 3).
Fig. 3 – Non-ideal pressure, $P_n$, as a function of $k_B T/\tau$ averaged over $10^5$ time steps. Both $k_B T$ and $\tau$ ranged from 0.005 to 4. The line represents the theoretical expression, eq. (7). For $\tau = 0.0018$ and $k_B T = 1$, $P_n$ is approximately 12 times larger than $P_{id}$. Parameters: $L = 64a$, $M = 5$, $A = 1/60$.

Fig. 4 – Freezing snapshot after $10^6$ time steps. Parameters: $L_x = L_y = 32a$, $M = 5$, $k_B T = 3.125 \times 10^{-5}$, $\tau = 10^{-3}$, $A = 1/60$.

In order to measure $P_n$, we used the average of the diagonal part of the microscopic stress tensor,

$$ P = P_{id} + P_n = \frac{1}{\tau L_x L_y} \left\langle \sum_j \left\{ \tau v_{jx}^2 - \Delta v_{jx} z_{jlx}^\alpha/2 \right\} \right\rangle. $$

(8)

The first term gives the ideal part of the pressure, $P_{id}$, as discussed in ref. [4]. The average of the second term is the non-ideal part of the pressure, $P_n$. Simulation results for $P_n$ obtained using eq. (8) are in good agreement with the analytical expression, eq. (7) (see fig. 3). In addition, measurements of the static structure factor $S(k \to 0, t = 0) = \rho k_B T \partial \rho / \partial P |_T$ when result (7) is used, and the adiabatic speed of sound obtained from simulations of the dynamic structure factor is also in good agreement with the predictions following from eq. (7). These results provide strong evidence for the thermodynamic consistency of the model. In addition, the structure of $S(k)$ is very similar to that of a simple dense fluid. In particular, for fixed $M$, both the depth of the minimum at small $k$ and the height of the first peak increase with decreasing $\tau$ until there is an order-disorder transition. The scaling behavior of both the self-diffusion constant (fig. 2) as well as the pressure (fig. 3) appears to persist until the transition.

**Caging and order/disorder transition.** – If the non-ideal part of the pressure is large compared to the ideal pressure, ordering effects can be expected. For small $A$, both contributions to the pressure are proportional to the temperature, so that just as in a real hard-sphere fluid, changing the temperature does not lead to an order/disorder transition. On the other hand, the two contributions to the pressure have different dependencies on the density and time step, $\tau$. In fact, $\tau$ can be interpreted as a parameter describing the efficiency of the collisions; lowering $\tau$ results in a higher collision frequency and has a similar effect to making
the spheres larger in a real hard-sphere system. We therefore expect caging and ordering effects if $\tau$ is decreased. This is indeed the case. For $M = 5$ and $k_B T = 1.0$, an ordered cubic phase is observed for $\tau < 0.0016$ (see fig. 4). The cubic symmetry of the ordered state is clearly an artifact of the square cell structure, and it would be interesting to see if this could be removed by using an hexagonal cell structure or incorporating random rotations of the grid. One of the surprising features of this crystalline-like state is that $x$-$y$ symmetry can be broken. Furthermore, there is the possibility of having several metastable crystalline states corresponding to slightly different lattice constants and number of particles per “cloud”. The lattice constant of the ordered phase corresponds to the position $r_p \approx 1.6a$ of the first peak in the pair-correlation function, $g(r)$, in the disordered, fluid phase. The corresponding number of particles in a cloud follows from the system size and the total number of particles. As expected, the lattice constants of these ordered states are slightly smaller than the super-cell spacing, $2a$, which sets the range of the multi-particle interaction. In this state, the diffusion coefficient becomes very small; particles are caged and can barely leave their location.

**Conclusion.** – The model presented in this letter is the first extension of the SRD algorithm to model fluids with a non-ideal equation of state. It was shown that the model is thermodynamically consistent for the correct choice of acceptance probabilities and reproduces the correct isotropic hydrodynamic equations at large length scales. Expressions for the equation of state and the self-diffusion constant were derived and shown to be in good agreement with numerical results. Simulation results for the kinematic viscosity were presented, and it was shown that there is an ordered state for large densities and collision frequencies.

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