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Stochastic Hard-Sphere Dynamics Algorithm for Hydrodynamics of Polymers in Flow

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ABSTRACT

With the increased interest in nano- and micro-fluidics, it has become necessary to develop tools for hydrodynamic calculations at the atomistic and mesoscopic scales [1]. Of particular interest is the modeling of flexible polymers in a flowing good solvent for both biological (e.g., cell membranes) and engineering (e.g., micro-channel DNA arrays) applications. Typically the polymer chains are modeled using Molecular Dynamics (MD). Earlier we introduced the Stochastic Event-Driven MD (SEDMD) algorithm that uses Direct Simulation Monte Carlo (DSMC) for the solvent coupled to deterministic EDMD for the polymer chain [3]. However, classical DSMC is limited to perfect gases, and hence does not describe the structure and equation of state (EOS) of the solvent. Efforts have been undertaken to make several mesoscopic solvents have more realistic *non-ideal* EOS, but with considerably greater computational efficiency over brute-force molecular dynamics. Examples include the Lattice-Boltzmann (LB) method [4], Dissipative Particle Dynamics (DPD) [5], and Multi-Particle Collision Dynamics (MPCD) [6], each of which has its own advantages and disadvantages [1]. The *Stochastic Hard Sphere Dynamics* (SHSD) algorithm described here is based on successive stochastic collisions of variable hard-sphere diameters and has thermodynamically-consistent fluctuations. SHSD modifies previous algorithms for solving the Enskog kinetic equation [7] to achieve thermodynamic consistency while maintaining hydrodynamic consistency and good efficiency.

The SHSD algorithm is not as efficient as classical (ideal gas) DSMC when high compressibility is desired, however, it is still several times faster than EDMD for hard spheres, the fastest available MD algorithm. Furthermore, SHSD has several important advantages over EDMD, in addition to its notable simplicity. Firstly, SHSD has several controllable parameters that can be used to change the transport coefficients and compressibility, while EDMD only has density. More importantly, SHSD is time-driven rather than event-driven thus allowing for easy parallelization. Finally, SHSD can be more easily coupled to continuum hydrodynamic solvers, just like ideal-gas DSMC [9].

Fluctuations drive the polymer motion and must be accurately represented in any model. Considerable effort has been invested in recent years in including fluctuations directly into the Navier-Stokes (NS) equations and the associated CFD solvers [2, 9]. Such fluctuating hydrodynamics has been coupled

to molecular dynamics simulations of polymer chains [2], but without proper atomistic coupling between the polymer chain and the solvent. In this work we embed the atomistic SHSD simulation of the region around the polymer chain in a fluctuating hydrodynamics region. The bidirectional coupling between the continuum and particle regions has to be constructed with great care so that both fluxes and fluctuations are preserved [9].

For sufficiently small time steps, the dynamics of the SHSD fluid can be considered as a simple modification of the standard hard-sphere dynamics. Particles move balistically in-between collisions. When two particles i and j are less than a diameter apart, $r_{ij} \leq D$, there is a probability rate $(3\chi/D)v_r\Theta(v_r)$ for them to collide as if they were elastic hard spheres with a variable diameter $D_S = r_{ij}$. Here Θ is the Heaviside function, and χ is a dimensionless parameter determining the collision frequency. The prefactor $3\chi/D$ has been scaled so that if $\chi = 1$ and the structure of the fluid is that of an ideal gas, $g_2 \equiv 1$, the average collisional rate would be that of a low-density hard-sphere gas with density (volume fraction) $\phi = \pi N D^3/(6V)$. The SHSD algorithm is essentially a Kinetic Monte Carlo algorithm to simulate the stochastic hard-sphere fluid defined by the above Markovian stochastic dynamics. Note that the dynamics strictly conserves momentum and energy locally, necessary for hydrodynamic consistency.

We derive a low-density approximation to the equilibrium pair-correlation function $g_2(x) \sim \exp(3\chi x)$ for $x \leq 1$ and $g_2(x) = 1$ for $x > 1$, where $x = r/D$. This is consistent with $g_2^U \approx \exp[-U(r)/kT]$, where $U(r)/kT = 3\chi(1 - r/D)\Theta(1 - r/D)$ is an effective *linear core* pair potential similar to the quadratic core potential used in DPD. Remarkably, it was found *numerically* that this soft sphere potential can predict exactly $g_2(x)$ at *all* liquid densities.

The meso-hydrodynamics of this model is described by a modified (stochastic) Enskog kinetic equation for the single-particle probability distribution $f(t, \mathbf{r}, \mathbf{v})$ as studied in Ref. [11]. The Chapman-Enskog expansion carried out in Ref. [11] produces approximations to the equation of state $p = PV/NkT$, the self-diffusion coefficient ζ, the shear η and bulk η_B viscosities, and thermal conductivity κ of the SHSD fluid, in terms of various moments of $g_2(x)$. Numerical results utilizing the hyper-netted chain (HNC) approximation to $g_2(x)$ are in very good agreement with these predictions for all ϕ and χ of interest. We compare the compressibility calculated from the EOS and the structure factor at the origin $S_0 = S(\omega = 0, k = 0)$ and find that SHSD fluid has thermodynamically consistent density fluctuations, $S_0 = (p + \phi dp/d\phi)^{-1}$.

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