A Particle Method with Adjustable Transport Properties—The Generalized Consistent Boltzmann Algorithm

Alejandro L. Garcia,[1,2] Francis J. Alexander,[3] and Berni J. Alder[4]

The consistent Boltzmann algorithm (CBA) for dense, hard-sphere gases is generalized to obtain the van der Waals equation of state and the corresponding exact viscosity at all densities except at the highest temperatures. A general scheme for adjusting any transport coefficients to higher values is presented.

KEY WORDS: Direct simulation Monte Carlo; van der Waals equation of state; Enskog theory; hard-sphere gas; kinetic theory; molecular dynamics.

The direct simulation Monte Carlo (DSMC) method is a Lagrangian numerical scheme for solving the time-dependent, nonlinear Boltzmann equation for dilute gases.[1,2,3] The method resembles molecular dynamics (MD) since it simulates a system of interacting particles but differs in that DSMC replaces the deterministic evolution by a stochastic dynamics with rates and probabilities obtained from kinetic theory at low densities. In its original formulation, DSMC was thus restricted to dilute gases, yielding only an ideal gas equation of state. A recent extension of the DSMC method, the so-called Consistent Boltzmann Algorithm (CBA), permits the simulation of a hard sphere (HS) gas at all densities.[4,5] The exact equation of state (EOS) is obtained by displacing particles an additional deterministic distance, namely a hard sphere diameter, to yield the correct

[1] Center for Computational Sciences and Engineering, Lawrence Berkeley National Laboratory, Berkeley, California 94720.

[2] Permanent address: Physics Department, San Jose State University, San Jose, California 95192.

[3] Center for Computational Science, Boston University, Boston, Massachusetts 02215.

[4] Lawrence Livermore National Laboratory, Livermore, California 94550.

virial. The resulting transport properties are in good agreement with HS MD simulations, comparable to the results given by the Enskog approximation.[6, 7] CBA has furthermore been generalized to simulate the van der Waals EOS by making a further displacement beyond the hard sphere diameter which is a function of density and temperature, as given by the van der Waals virial.[8] For the van der Waals model, the fluid should retain the transport properties of HS; however, this is not the case using the displacement according to the virial.[8] This paper presents a further modification to the van der Waals displacement that tries to recover the exact MD HS shear viscosity (or other transport coefficient) while preserving the van der Waals EOS.

In DSMC the positions and velocities $\{\vec{r}_i, \vec{v}_i\}$ of the particles (mass m) are evolved in time by two steps: advection and collisions. While advection is deterministic, in the collision step pairs of nearby particles are randomly selected with a HS collision probability. The post collision velocities are also stochastically determined, consistent with the conservation of momentum and energy. The collision is executed with the particles remaining in place. The pressure is given by the virial theorem, at temperature T and number density n, as

$$P = nkT + \tfrac{1}{3}m\Gamma\Theta, \tag{1}$$

where $\Theta \equiv \langle \Delta\vec{v}_{ij} \cdot \vec{r}_{ij} \rangle$ is the projection of the velocity change onto the line connecting centers of particles i and j averaged over collisions (indicated by the brackets) and Γ is the collision rate per unit time and volume. In DSMC the second term on the r.h.s. is zero because the positions of colliding particles are uncorrelated with the change in their velocities.

In a van der Waals fluid the particles have a hard core exclusion and a weak constant attractive potential.[6, 9] For the hard core exclusion a gas of hard spheres with diameter σ is treated as before.[4, 5] CBA introduces a correlation in Θ by displacing the particles in the advection step by $\vec{d}_{HS} = \sigma\hat{d}$, where the unit vector $\hat{d}$ is,

$$\hat{d} = \frac{(\vec{v}'_i - \vec{v}'_j) - (\vec{v}_i - \vec{v}_j)}{|(\vec{v}'_i - \vec{v}'_j) - (\vec{v}_i - \vec{v}_j)|} = \frac{\vec{v}'_r - \vec{v}_r}{|\vec{v}'_r - \vec{v}_r|}, \tag{2}$$

where $\vec{v}_r$ is the relative velocity of the colliding particles, and prime and unprimed indicate post and pre-collision values, respectively. After the collision, the particles are advected as,

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \vec{v}'_i(t)\,\Delta t + \vec{d}_{HS}$$

$$\vec{r}_j(t + \Delta t) = \vec{r}_j(t) + \vec{v}'_j(t)\,\Delta t - \vec{s}_{HS}. \tag{3}$$

The displacement $\vec{d}_{HS}$ leads to an average virial $\Theta = \sigma\sqrt{\pi kT/m}$, so that using the Boltzmann (dilute gas) collision rate, $\Gamma_B = 2\sigma^2 n^2 \sqrt{\pi kT/m}$, the consistent (corresponding to the same order in density as the transport coefficients) pressure is now $P = nkT(1 + b_2 n)$, where $b_2 = 2/3\pi\sigma^3$ is the HS second virial coefficient. Introducing the Enskog Y-factor,[6, 10] which corrects the low density collision rate to the correct hard sphere collision rate at any density ($\Gamma_{HS} = Y\Gamma_B$), into CBA gives the correct HS EOS at all densities and transport coefficients corresponding to an uncorrelated collision (Markov) approximation.[4]

The attractive force in the van der Waals potential is modeled by adding an advection displacement, $\vec{d}_a = d_a \hat{d}$, which is a function of density and temperature. Specifically, one obtains the van der Waals EOS,[6, 9]

$$\frac{P_{vdW}}{nkT} = 1 + b_2 n Y - \frac{an}{kT},\qquad(4)$$

when the net displacement is

$$\vec{d}_{vdW} = \vec{d}_{HS} + \vec{d}_a = \sigma\hat{d} - \frac{a\sigma}{b_2 YkT}\hat{d},\qquad(5)$$

where a is the attraction parameter in the van der Waals EOS. The collision probability and rate remain those of hard spheres since the attraction is long-ranged and weak. Note that the principle of detailed balance requires that the direction of the net displacement is, on average, given by Eq. (2) and that $\hat{d}$ points in the direction of the apse line (line passing through the centers of molecules at the moment of closest approach in a collision). Below the critical temperature, the Maxwell tie-line EOS may be introduced in place of Eq. (4); see ref. 8 for details.

The displacement introduced to model the attractive force spoils the good agreement with the HS transport properties. This can easily be seen at the Boyle point, the density at which the pressure equals that of an ideal gas. At the Boyle point $d_{HS} = -d_a$, so d_{vdW} vanishes and the transport properties are inappropriately those of a dilute gas (with an enhanced collision rate due to the Y-factor) rather than those of a dense HS gas. In general, transport properties for van der Waals CBA are of the Enskog form; that is, there are three separate contributions to the total transport coefficient-a kinetic, a potential, and a kinetic-potential cross term.[11, 12] For an advection displacement of d_{vdW}, kinetic theory gives the three contributions to the shear viscosity, η_{vdW}, as[4]

$$\frac{\eta_{vdW}}{\eta_0} = 1/Y + \frac{4}{5}(b_2 n)\frac{d_{vdW}}{\sigma} + 1.64(b_2 n)^2\left(\frac{d_{vdW}}{\sigma}\right)^2 Y,\qquad(6)$$

to the thermal conductivity, κ_{vdW}, as

$$\frac{\kappa_{vdW}}{\kappa_0} = 1/Y + \frac{6}{5}(b_2 n)\frac{d_{vdW}}{\sigma} + 1.01(b_2 n)^2\left(\frac{d_{vdW}}{\sigma}\right)^2 Y, \qquad (7)$$

and to the self-diffusion coefficient, D_{vdW}, as

$$\frac{D_{vdW}}{D_0} = 1/Y + 0.400\frac{1}{\pi}(b_2 n)^2\left(\frac{d_{vdW}}{\sigma}\right)^2 Y, \qquad (8)$$

where η_0, κ_0 and D_0 are the Chapman–Enskog expressions for viscosity, thermal conductivity, and self-diffusion, respectively.

Table 1 lists the viscosity for selected values of density and temperature and explicitly demonstrates that the CBA van der Waals transport properties differ significantly from relevant MD HS values. For example, at a temperature just below the critical temperature ($T = 0.17$, $T/T_c = 0.94$) and at near liquid densities ($n\sigma^3 = 0.7071$), the CBA van der Waals viscosity, η_{vdW}, is over an order of magnitude smaller than the HS viscosity, η_{HS}. This discrepancy can be turned into great advantage when one wants to study high Reynolds number flows by a numerically stable algorithm which has as low a fluid viscosity as possible. As can be seen from Eq. (6), however, the viscosity cannot be much lower than that

Table 1. Viscosity for Various Densities and Temperatures*

T	$n\sigma^3$	0.0141	0.0707	0.2828	0.4714	0.7071	0.7857	0.8839	0.9428
0.17	η_{HS}	0.075	0.077	0.113	0.211	0.565	0.782	1.558	3.029
	η_{vdW}/η_{HS}	0.915	0.772	0.568	0.219	0.092	0.186	0.286	0.261
	d_{vdW}/σ	−1.757	−1.555	−0.842	−0.365	0.142	0.281	0.435	0.516
	R_η/σ	6.944	2.221	0.791	0.745	0.695	0.638	0.664	0.817
1.00	η_{HS}	0.182	0.187	0.273	0.512	1.371	1.898	3.778	7.346
	η_{vdW}/η_{HS}	0.963	0.930	0.897	1.044	1.274	1.374	1.136	0.789
	d_{vdW}/σ	0.531	0.566	0.682	0.768	0.854	0.878	0.904	0.918
	R_η/σ	4.550	1.227	0.386	0	0	0	0	0.437
∞	η_E/η_{HS}	0.990	1.000	1.010	0.980	0.909	0.909	0.694	0.463
	η_{vdW}/η_{HS}	0.975	1.004	1.292	1.571	1.706	1.758	1.381	0.933
	d_{vdW}/σ	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	R_η/σ	3.746	0	0	0	0	0	0	0.247

*η_{HS} is from MD HS simulations [12]; η_E is from Enskog theory; η_{vdW} is the van der Waals CBA viscosity without a random displacement. With the random displacement, the viscosity equals η_{HS} when $R_\eta > 0$ and η_{vdW} when $R_\eta = 0$. For all tables, $k = m = \sigma = 1$. Critical temperature $T_c \simeq 0.180$; at $T = 0.17$ the Maxwell tie-line extends between $n = 0.1217$ and $n = 0.4089$.

corresponding to the first (the kinetic) term, when d_{vdw} is close to zero, as is the case in a normal liquid.

If one wants to recover the HS transport properties, an additional displacement of the particles needs to be introduced. This new displacement is not deterministic but random so that its contribution to the average virial is zero and hence the EOS is not modified. The random displacement, $\vec{R} = R\hat{u}$, where $\hat{u}$ is a random unit vector uniformly distributed over the unit sphere, leads to a particle being displaced by $\vec{d}_{vdw} + \vec{R}$ and its collision partner by $-\vec{d}_{vdw} - \vec{R}$ so that momentum and energy are exactly conserved. The shear viscosity is then $\eta^*_{vdw} = \eta_{vdw} + \eta_R$ where,

$$\frac{\eta_R}{\eta_0} = \frac{32}{5\pi} (b_2 n)^2 \left(\frac{R}{\sigma}\right)^2 Y, \tag{9}$$

Similarly, the thermal conductivity has the added contribution,

$$\frac{\kappa_R}{\kappa_0} = \frac{64}{25\pi} (b_2 n)^2 \left(\frac{R}{\sigma}\right)^2 Y, \tag{10}$$

and the self-diffusion coefficient,

$$\frac{D_R}{D_0} = \frac{2}{\pi} (b_2 n)^2 \left(\frac{R}{\sigma}\right)^2 Y. \tag{11}$$

The value of R selected at any density and temperature is such that one of the transport coefficients will match that of the corresponding HS value. With only one adjustable parameter, only one transport coefficient can be made to match at a time, so that, to calculate a nonequilibrium flow, for example, the transport property of interest to match would be the viscosity. Table 1 lists the values of R_η, the random displacement that will increase the CBA van der Waals viscosity to match the HS MD viscosity. Note that the random displacement can only increase the transport coefficients and since at high temperatures ($T = 1$) the viscosity at intermediate and high densities is already larger than the HS viscosity, R_η is set to zero so as to get the best agreement possible with HS MD. Similarly, for the hard sphere case ($T = \infty$) a random displacement can be added to improve the agreement with HS MD, however, except at the lowest and highest densities, η_{CBA} is already too large so improvement can only be made at those extreme densities. Nevertheless, at the highest density ($n\sigma^3 = 0.9428$), corresponding to the normal liquid density, the improvement over the Enskog model could be of practical significance.

Table 2 lists the self-diffusion coefficient when the random displacement is selected to match viscosity. In the cases where D_{vdw} is close to D_{HS}

Table 2. Self-Diffusion Coefficient for Various Densities and Temperatures[a]

T	$n\sigma^3$	0.0141	0.0707	0.2828	0.4714	0.7071	0.7857	0.8839	0.9428
0.17	D_{HS}	6.177	1.163	0.247	0.121	0.048	0.032	0.017	0.010
	D_{vdw}/D_{HS}	0.999	0.991	0.908	0.810	0.847	1.260	3.529	8.623
	D^{*}_{vdw}/D_{HS}	1.027	1.071	1.170	1.895	6.522	10.650	31.007	96.610
	R_D/σ	1.181	0.734	0.461	0.308	0.113	0	0	0
1.00	D_{HS}	14.981	2.821	0.599	0.293	0.116	0.079	0.042	0.025
	D_{vdw}/D_{HS}	0.999	0.984	0.888	0.988	2.515	4.454	11.349	23.796
	D^{*}_{vdw}/D_{HS}	1.011	1.099	0.950	0.988	2.515	4.454	11.349	48.897
	R_D/σ	1.398	0.979	0.511	0.062	0	0	0	0
∞	D_E/D_{HS}	0.999	0.983	0.849	0.758	0.800	0.894	1.178	1.605
	D_{vdw}/D_{HS}	0.999	0.986	0.933	1.148	3.150	5.514	13.627	27.796
	D^{*}_{vdw}/D_{HS}	1.007	0.986	0.933	1.148	3.150	5.514	13.627	35.965
	R_D/σ	1.346	0.907	0.393	0	0	0	0	0

[a] D_{HS} is from MD HS simulations [13]; D_E is from Enskog theory; D_{vdw} is the van der Waals CBA self-diffusion without a random displacement; and D^{*}_{vdw} is the van der Waals CBA self-diffusion with a random displacement to best match viscosity, R_η (see Table 1). With random displacement R_D, the self-diffusion equals D_{HS} if $R_D > 0$ and D_{vdw} if $R_D = 0$.

this random displacement generally overcorrects. However, for low to moderate densities, where $D_{vdw} < D_{HS}$, a different random displacement, R_D, can be made that matches the self-diffusion coefficient instead of the viscosity (see Table 2).

An added benefit of using a random displacement in the van der Waals model is that it avoids anomalous correlations which lead to inaccurate results for the pressure when d_{vdw} is small if local (in space and time) average values of density and temperature are used. With the random displacement, the unphysical correlations are eliminated, as demonstrated in the simulation results presented in ref. 8.

In conclusion, the original DSMC algorithm was designed to model a dilute gas. A deterministic CBA displacement allows the simulation to have a non-ideal gas equation of state, and adding a random displacement allows one to adjust the transport properties independently of the EOS. This paper presents results using the van der Waals EOS, the only EOS that can be justifiably modeled at high densities given that hard sphere collision rates and probability distributions are used in selecting and evaluating collisions. The generalization of CBA to arbitrary interaction potentials is possible at low density, but rigorous extensions to high density presents formidable problems.

ACKNOWLEDGMENTS

REFERENCES

1. G. A. Bird, *Molecular Gas Dynamics and the Direct Simulation of Gas Flows* (Clarendon, Oxford, 1994).
2. A. L. Garcia, *Numerical Methods for Physics*, Chapt. 10 (Prentice Hall, Englewood Cliffs NJ, 1994).
3. W. Wagner, *J. Stat. Phys.* 66:1011 (1992).
4. F. J. Alexander, A. L. Garcia, and B. J. Alder, *Phys. Rev. Lett.* 74:5212 (1996).
5. F. J. Alexander, A. L. Garcia, and B. J. Alder, in 25 *Years of Non Equilibrium Statistical Mechanics* edited by J. Brey, J. Marro, M. Rubi, and M. San Miguel (Springer-Verlag, Berlin, 1995).
6. P. Resibois and M. De Leener, *Classical Kinetic Theory of Fluids*, (John Wiley and Sons, New York, 1977).
7. J. M. Montanero and A. Santos, *Phys. Rev. E* 54:438 (1996).
8. F. J. Alexander, A. L. Garcia, and B. J. Alder, submitted to *Physica A*.
9. M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, *J. Math. Phys.* 4:216 (1963); M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, *J. Math. Phys.* 4:229 (1963); J. L. Lebowitz and J. K. Percus, *J. Math. Phys.* 4:248 (1963).
10. J. J. Erpenbeck and W. W. Wood *J. Stat. Phys.* 35:321 (1984); J. J. Erpenbeck and W. W. Wood *J. Stat. Phys.* 40:787 (1985).
11. T. E. Wainwright, *J. Chem. Phys.* 40:2932 (1964).
12. B. J. Alder, D. M. Gass, and T. E. Wainwright, *J. Chem. Phys.* 53:3813 (1970).
13. J. J. Erpenbeck and W. W. Wood, *Phys. Rev. A* 43:4254 (1991).