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## The consistent Boltzmann algorithm for the van der Waals equation of state

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### Abstract

The direct-simulation Monte Carlo method is generalized by introducing an advection displacement that models a hard-core exclusion with a weak and constant interparticle attraction. Simulation results demonstrate that both the van der Waals equation of state and its Maxwell tie-line construction can be obtained.

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Direct-simulation Monte Carlo (DSMC) is a particle-based computational model for gas dynamics [1,2]. DSMC can be viewed as a simplified (and more efficient) form of molecular dynamics (MD) at low densities or as a stochastic method for solving the time-dependent nonlinear Boltzmann equation. In its original formulation, the method was restricted to dilute gases since it gives the equation of state (EOS) for a gas to lowest order in the density, that is, for point particles (perfect gas) and the transport properties correctly to first order in density. Note, however, that both DSMC and the Boltzmann equation are inconsistent since the collision rate and transport properties are functions of the particles' cross-section while the EOS is not.

Recently an extension of DSMC was introduced, called the Consistent Boltzmann Algorithm (CBA), for which the hard-sphere (HS) equation of state is also correctly obtained to first order in density [3,4]. Furthermore, replacing the low-density collision rate by the true HS collision rate, the method yields the correct HS equation of state at all densities. While transport properties are not exact (due to the molecular chaos approximation), they are in good agreement with HS MD data even at high density, comparable to the results given by the Enskog approximation [5,6].

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The present paper is concerned with a further extension to a more general potential with attractive forces so that one can, for example, model systems in the two-phase gas–liquid region. The simplest way to achieve this is to add a weak and constant potential to the hard core since this is known to lead to the van der Waals equation of state [7]. The manner in which the advection process in CBA is modified to give the van der Waals EOS is described below.

The pressure in a fluid of van der Waals particles (hard-spheres with a weak, long-range attraction) of mass  $m$  at temperature  $T$  and density  $n$  is given by the virial theorem as

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

where  $\Theta \equiv \langle \Delta\mathbf{v}_{ij} \cdot \mathbf{r}_{ij} \rangle$  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  $\Gamma$  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.

For a gas of hard-spheres with diameter  $\sigma$ , CBA introduces a correlation in  $\Theta$  by displacing the particles in the advection step by  $\mathbf{d}_{\text{HS}} = \sigma\hat{\mathbf{d}}$ , where the unit vector  $\hat{\mathbf{d}}$  is,

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

where  $\mathbf{v}_r$  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

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}'_i(t)\Delta t + \mathbf{d}_{\text{HS}}, \tag{3}$$

$$\mathbf{r}_j(t + \Delta t) = \mathbf{r}_j(t) + \mathbf{v}'_j(t)\Delta t - \mathbf{d}_{\text{HS}}. \tag{4}$$

As an illustration, to make the above formula physically transparent, in a one-dimensional system, when two hard rods of length  $\sigma$  collide, after the collision the distance between centers will be larger by  $2\sigma$  than the separation between similarly colliding point particles. Moving to contact *each* point particle travels an extra distance  $\sigma/2$  (as compared with hard rods). Moving apart after the collision, each point particle must again travel an additional distance  $\sigma/2$ . Note that  $\hat{\mathbf{d}}$  points in the direction of the apse-line (line passing through the centers of molecules at the moment of closest approach in a collision).

Eq. (2) leads to an average virial  $\Theta = \sigma\sqrt{\pi kT/m}$ , so that using the Boltzmann (dilute gas) collision rate,  $\Gamma_{\text{B}} = 2\sigma^2 n^2 \sqrt{\pi kT/m}$ , the consistent pressure is now  $P = nkT(1 + b_2 n)$ , where  $b_2 = \frac{2}{3}\pi\sigma^3$  is the HS second virial coefficient. Introducing the Enskog Y-factor [5,9], which corrects the low-density collision rate to the correct hard-sphere collision rate at any density ( $\Gamma_{\text{HS}} = Y(n)\Gamma_{\text{B}}$ ), into CBA gives the correct HS EOS at all densities and transport coefficients at high-densities corresponding to an uncorrelated collision (Markov) approximation [3,8].

CBA is generalized to yield the van der Waals EOS by changing the advection displacement to account for the attractive force. The direction,  $\hat{d}$ , cannot be modified without violating detailed balance, however, the magnitude, which is constant for HS, can be made a function of density and temperature. Specifically, one obtains the van der Waals EOS [5],

$$\frac{P_{vdw}}{nkT} = 1 + b_2 n Y - \frac{an}{kT}, \tag{5}$$

when the magnitude of the displacement is

$$d_{vdw} = \sigma - \frac{a\sigma}{b_2 Y k T} = d_{HS} - d_a. \tag{6}$$

In the van der Waals model the collision probability, the collision rate and the transport properties should remain those of hard-spheres. As the strength of the attraction term vanishes ( $a \rightarrow 0$ ), the advection displacement due to the attractive force,  $d_a$ , vanishes and the HS CBA displacement is recovered. Fig. 1 illustrates how  $d_{vdw}$  varies with density; all the numerical results presented in this paper take  $m = k = \sigma = a = 1$ .

To represent the liquid–gas coexistence region correctly, the van der Waals EOS needs to be modified using the Maxwell tie-line construction [10]. Below the critical temperature,  $T_c$ , the Maxwell tie-line EOS is defined as

$$P_M(n, T) = \begin{cases} P_{vdw}(n_g, T) = P_{vdw}(n_l, T) & \text{if } n_g < n < n_l, \\ P_{vdw}(n, T) & \text{otherwise,} \end{cases} \tag{7}$$

where  $n_g$  and  $n_l$  are the gas and liquid densities at the endpoints of the Maxwell coexistence tie-line. The displacement for the Maxwell tie-line EOS can be obtained using

$$d_M = \frac{\sigma}{b_2 n Y} \left( \frac{P_M}{nkT} - 1 \right). \tag{8}$$

Fig. 1 shows how  $d_M$  will vary with density under these conditions.

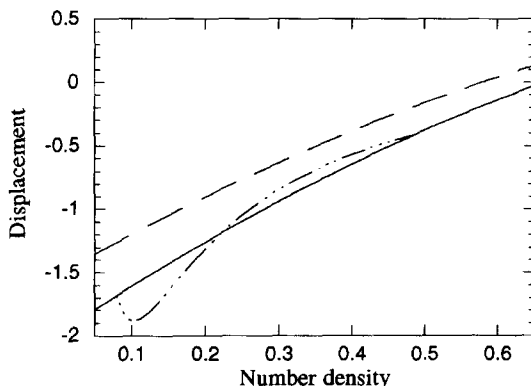


Fig. 1. Net CBA displacement,  $d_{vdw}$  and  $d_M$ , as a function of number density for: van der Waals EOS,  $T = 0.19$  (dashed line) and  $T = 0.16$  (solid line); Maxwell tie-line EOS  $T = 0.16$  (dot-dashed line). The critical temperature is  $T_c \approx 0.18$ .

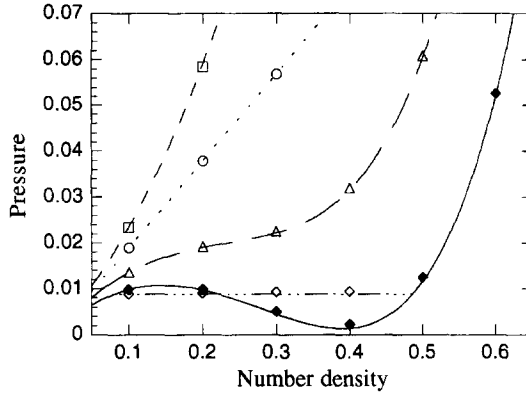


Fig. 2. Pressure as a function of density for: ideal gas law,  $T = 0.19$  (dotted line and circles); hard-sphere EOS,  $T = 0.19$  (short-dashed line and squares); van der Waals EOS,  $T = 0.19$  (dashed line and triangles); van der Waals EOS,  $T = 0.16$  (solid line and filled diamonds); Maxwell tie-line EOS,  $T = 0.16$  (dot-dashed line and open diamonds). Lines are given by theory and points are data from CBA simulations with error bars approximately the size of the symbols. The critical temperature is  $T_c \approx 0.18$ .

The results from the CBA simulations for the pressure, as measured by normal momentum transfer across a plane, are shown in Fig. 2. In these equilibrium simulations, the displacement is held fixed at its global average value and the collision rate in a cell is linearized about the global average density,  $\bar{n}$ . In other words, the mean-field expression for the collision rate,

$$\Gamma_{mf} = 2\sigma^2 n \bar{n} \bar{Y} \sqrt{\frac{\pi k \bar{T}}{m}} \tag{9}$$

is used, where  $\bar{Y} \equiv Y(\bar{n})$ . Working with local values for the relevant variables is a delicate issue since  $\Gamma$  and  $d$  are both nonlinear in  $n$  and coupled through the dynamics. Simulations using local, running averages give poor results for some densities and temperatures, specifically when  $d_{HS}$  and  $d_a$  are approximately equal. In these cases where the net displacement is small, the probability distribution for the local value of  $n$  was found to deviate unphysically from Poissonian. Adding a small random displacement to the displacement  $d$  breaks up this unphysical coupling of the fluctuations and restores the Poissonian distribution and the correct pressure. Details regarding the use of this random displacement and its effect on the transport coefficients will be presented elsewhere [11].

As a demonstration problem involving an inhomogeneous system, a van der Waals gas in the two-phase region was considered. The system is closed, held at fixed temperature, and subjected to a constant external acceleration  $\mathbf{g}$  (e.g., gravity). From an initially homogeneous density, the simulation evolves until the system reaches a steady-state with separate regions of gas and liquid. This steady-state density profile may be obtained from the hydrostatic condition,  $\nabla P = m\mathbf{g}$ , with the constraint that the total number density is conserved. The results from a CBA simulation of this system, along

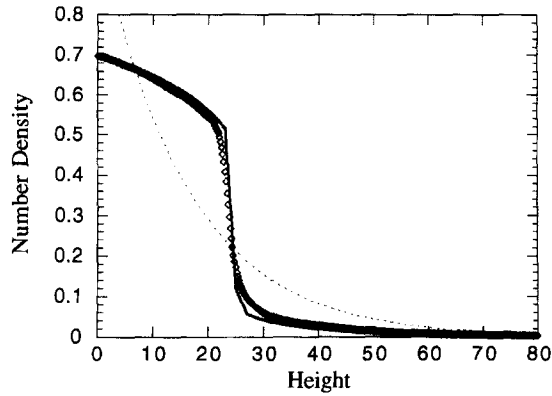


Fig. 3. Density as a function of height for a closed equilibrium system at  $T=0.16$  ( $T_c \approx 0.18$ ) with an acceleration of  $g=0.01$  and a random displacement of  $\sigma/2$ . Points are from a CBA simulation using the Maxwell tie-line EOS; solid line is found by numerically solving the hydrostatic condition. Dotted line is the hydrostatic density profile for an ideal gas under the same conditions.

with the hydrostatic solution, are shown in Fig. 3. Local running average values must be used to calculate  $d$  and  $\Gamma$  because the system is inhomogeneous, requiring a random displacement of  $\sigma/2$  to be employed.

In conclusion, this paper presents a generalization of CBA that yields the van der Waals EOS and its Maxwell tie-line construction. One is tempted to use Eq. (8) to obtain an arbitrary EOS, however only the van der Waals EOS has the consistent collision probability, the collision rate, and the transport coefficients of HS [7]. For other equations of state the CBA advection displacement should scale with the corresponding density dependent kinetic properties of the microscopic potential used in the collision integral if the method is to retain its theoretical foundation.

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