

$$t_{12}^c = x_1^{c''}/v_{i,x}'' \quad 7.41$$

Immediately after the collision, the positions become

$$x_i^f = x_i + v_{i,x} \cdot t_{12}^c; y_i^f = y_i + v_{i,y} \cdot t_{12}^c; \quad 7.42$$

The velocities can be reported in the original reference frame by reversing the ϕ_1 rotation,

$$v_{1,x}^f = v_1 \cos(\theta_1 + \phi_1); v_{1,y}^f = v_1 \sin(\theta_1 + \phi_1); \quad 7.43$$

For the second molecule, it is most convenient to apply Eqns. 7.30 and 7.31 in their resolved forms:

$$v_{2,x}^f = v_{2,x}^o + v_{1,x}^o - v_{1,x}^f; v_{2,y}^f = v_{2,y}^o + v_{1,y}^o - v_{1,y}^f \quad 7.44$$

Example 7.10 Computing molecular collisions in 2D

Let the diameters of two disks, σ , be 0.4 nm, the masses be 16 g/mole, and the length of the square box, L , be 5nm. Start the disks at [1.67 1.67], [3.33 3.33] and initial velocities (nm/ps): [0.167 0.222], [-0.167 -0.222] where 1 nm = 10^{-9} m and 1ps = 10^{-12} s. Note that the gas constant $8.314 \text{ J/mol-K} = 8.314 \text{ kg-nm}^2/(\text{ns}^2\text{-mol-K}) = 8.314(10^{-6}) \text{ kg-nm}^2/(\text{ps}^2\text{-mol-K})$.

- Compute the temperature (K).
- Compute the collision times with the walls.
- Compute the collision times with the disks. Which event occurs first?
- Compute the velocity vectors (m/s) after the first collision event.

Solution:

- $T_{2D} = M_w \langle v^2 \rangle / (2R)$; $\langle v^2 \rangle = (0.167^2 + 0.222^2 + 0.167^2 + 0.222^2)/2 = 0.07717$
 $T_{2D} = (0.016\text{kg/mol})(0.07717 \text{ nm}^2/\text{ps}^2)/(2 \cdot 8.314(10^{-6}) \text{ kg-nm}^2/(\text{ps}^2\text{-mol-K})) = 74\text{K}$.
- The collision time with the walls depends on the wall being approached. Note that the molecular coordinate will be within $0.5\sigma = 0.2$ nm of the wall coordinate when a wall collision occurs. Disk1 is approaching the north wall and east wall (using superscripts to denote geographic directions), the collision times are $t_1^N = (4.8 - y_1^o)/v_{1,y} = (4.8 - 1.67)/0.222 = 14.10\text{ps}$, $t_1^E = (4.8 - x_1^o)/v_{1,x} = (4.8 - 1.67)/0.167 = 18.74\text{ps}$. Similarly, $t_2^S = (0.2 - y_2^o)/v_{2,y} = (0.2 - 3.33)/(-0.222) = 14.10\text{ps}$; $t_2^W = (0.2 - x_2^o)/v_{2,x} = (0.2 - 3.33)/(-0.167) = 18.74\text{ps}$. Molecule 1 collides with the north wall, and molecule 2 collides with the south wall at 14.10ps. The wall collisions corresponding to t_1^E and t_2^W will not occur.
- Translating by Eqn.7.36, $x_2' = y_2' = 3.33 - 1.67 = 1.66$. Translating the velocities to make molecule 2 stationary: $v_{1,x}' = 0.167 - (-0.167) = 0.334$, $v_{1,y}' = 0.444$. Using Eqn. 7.37, $\phi_1 = \tan^{-1}(v_{1,y}'/v_{1,x}') = \tan^{-1}(0.444/0.334) = 53.13^\circ$, $\phi_2 = \tan^{-1}(1.66/1.66) = 45^\circ$, $r_2' = 1.66(2)^{1/2} = 2.35\text{nm}$. $x_2'' = 2.35 \cos(45 - 53.13) = 2.33$; $y_2'' = 2.35 \sin(45 - 53.13) = -0.33$. Since $|y_2''| < \sigma$, these molecules do collide. By Eqn. 7.40, $\theta_2 = \sin^{-1}(-0.33/0.4) = -56.10^\circ$. Then, $x_1^{c''} = 2.33 - 0.4 \cos(-56.10) = 2.103$; noting $v_{1,x}'' = (0.334^2 + 0.444^2)^{1/2} = 0.5556$, $t_{12}^c = 2.103/0.5556 = 3.78$ ps. The intermolecular collision occurs before the wall collisions calculated in part (b).

Example 7.10 Computing molecular collisions in 2D (Continued)

(d) Computing the velocities after collision requires Eqn. 7.34, noting by Eqn. 7.33 that $\theta_1 = 90 - 56.10 = 33.9$. $v_2 = v_1 \cos \theta_2 = 0.5556 \cos(-56.10) = 0.3099$, $v_1 = (0.5556^2 - 0.3099^2)^{1/2} = 0.4611$. Also note that Eqn. 7.34 gives only the magnitude of the velocity. $v_{2,x} = v_2 \cos \theta_2 = 0.3099 \cos(-56.10) = 0.173$; $v_{2,y} = -0.257$; $v_{1,x} = 0.257$; $v_{1,y} = 0.173$; Returning to the original reference frame: $v_{1,x}^f = v_1 \cos(\phi_1 + \theta_1) + v_{2,x}^o = 0.4611 \cos(33.9 + 53.13) - 0.167 = -0.143$. $v_{1,y}^f = 0.4611 \sin(33.9 + 53.13) - 0.222 = 0.238$; $v_{2,x}^f = 0.143$. $v_{2,y}^f = -0.238$. Finally, we update all the positions to the time of the collision. $x_1^f = [1.67 + 0.167 \cdot 3.78 \ 1.67 + 0.222 \cdot 3.78] = [2.301 \ 2.514]$; $x_2^f = [3.33 - 0.167 \cdot 3.78 \ 3.33 - 0.222 \cdot 3.78] = [2.695 \ 2.486]$. From this point, the procedure for the next collision is exactly the same.

In retrospect, a major oversimplification of this problem deserves comment. By restricting the system to two particles, it is necessary that the components of velocity be equal and opposite in sign. Otherwise, the system itself would have a net velocity. You should not mistake this equality as a general result. If there were three particles, for example, the velocities would sum to zero, but the individual magnitudes could vary quite substantially.

Analyzing MD Results

For our purposes, we can assume that you have sufficiently grasped the principles of molecular simulation if you can compute a single collision. A second collision is much like the first and computers are made for these kinds of repetitive calculations. At that point, the challenge becomes analyzing the results of the simulations. We can illustrate this kind of analysis with simulations of the hard-sphere fluid to infer the repulsive contribution of the square-well fluid's equation of state. As shown in Fig. 7.9(a), the hard-sphere (HS) potential can be considered as a special case of the square-well potential when the depth of the well approaches zero. Thus, there are two ways that $\beta\epsilon$ can approach zero: the temperature can approach infinity, or the well depth, ϵ , can approach zero. Both results lead to the hard-sphere repulsive term.

The results of hard-sphere simulations by Erpenbeck and Wood¹⁶ are presented in Fig. 7.9(b). Three equations of state are compared to the simulation results: the van der Waals model, the Carnahan-Starling model, and the ESD model. These models are listed below, along with another called the Scott model.

$$Z^{HS} = 1/(1 - \eta_p); \text{ the van der Waals model} \quad 7.45$$

$$Z^{HS} = (1 + 2\eta_p)/(1 - 2\eta_p); \text{ the Scott model} \quad 7.46$$

$$Z^{HS} = 1 + 4\eta_p/(1 - 1.9\eta_p); \text{ the ESD model} \quad 7.47$$

$$Z^{HS} = 1 + 4\eta_p(1 - \eta_p/2)/(1 - \eta_p)^3; \text{ the Carnahan-Starling model} \quad 7.48$$

It is immediately apparent that the van der Waals model is quite inaccurate while the Carnahan-Starling model is practically quantitative. The ESD model is imprecise when the packing fraction exceeds $\eta_p > 0.40$, but it does preserve the prospect of forming the basis for a cubic equation of state. The Scott equation is not shown, but it is slightly less precise than the ESD model and slightly

16. Erpenbeck, J.J., Wood, W.W. 1984. *J. Stat. Phys.* 35:321.