Introduction to Molecular Simulation

Carl T. Lira

This supplement complements and extends the textbook discussion in Chapter 7 of *Introductory Chemical Engineering Thermodynamics*, 2^{nd} ed., J.R. Elliott, C.T. Lira.
Comment on notation: vectors in this handout are denoted by bold typeface.

The importance of configuration

A major objective of the engineering community is to represent the macroscopic PVT fluid properties with sufficient accuracy to provide representations of the departure functions. For a real fluid, the density dependence of energy and entropy are equally important; the Gibbs energies are used in phase equilibria, $G = U + PV - TS$. However, consider that relatively little molecular information is used in the development of the cubic equations such as the Peng-Robinson equation of state discussed in Chapter 7. The equation is an extension of the van der Waals approach that uses a parameter to represent the hard cores of molecules, b, and a parameter to represent the attractive potential, a. The objective of EOS modeling is to fit the critical point and the dependence of macroscopic properties on the acentric factor, which is also an empirical property.

Significant improvements in equations of state have occurred over the past thirty years, and some of the major advances are introduced in Chapters 15 and 19 where fluid structure and hydrogen bonding are represented more fundamentally. However, equally important are insights gained by molecular simulations that permit study of microscopic phenomena that challenge engineering models. Sometimes the behavior can be explored only marginally with experimentation. Often spectroscopic measurements can be used to infer certain molecular ordering, but modeling fluids with molecular simulation enhances such studies. Many of the systems of significant interest in the chemical and biological engineering communities are too complex to model accurately with conventional engineering models. For example, emulsions, proteins, RNA, DNA and biological membranes are composed of large molecules with complicated structures and are highly ordered due to hydrogen bonding.

Atoms, sites and molecules

For simulations of thermodynamics properties molecules are represented by models of atoms connected by bonds. Atoms are typically the smallest particles modeled. Commonly even this level of detail is not necessary, and a functional group such as CH_3 may be a modeled as a sphere with an equivalent volume and a mass calculated by summing the atoms in the site. Such a functional group is called a *united atom site*. Within simulation literature, a *site* refers to either an atom or a functional group, depending on the level of detail in the simulation. The united atom characteristic is implied when discussing sites composed of multiple atoms.

The Boltzmann Distribution

A principle important to understanding some of the equations in this handout is the Boltzmann distribution. Briefly, the distribution gives the relative weights for probability of events. Consider that the probability $p(\underline{E}_i)$ of a particular energy state must be some function of the energy $p(\underline{E}_i) \propto f(\underline{E}_i)$. Likewise, in some other system, the probability should follow the same equation $p(\underline{E}_j) \propto f(\underline{E}_j)$. The probabilities should be independent, and the probability of a joint probability is the product, $p(\underline{E}_i + \underline{E}_j) = p(\underline{E}_i)p(\underline{E}_j) \propto f(\underline{E}_i)f(\underline{E}_i)$. However, the composite system should follow the same statistics and $p(\underline{E}_i + \underline{E}_j) \propto f(\underline{E}_i + \underline{E}_j)$. The only way these last two expressions can be consistent is if $f(\underline{E}_i + \underline{E}_j) = f(\underline{E}_i)f(\underline{E}_j)$. We have such a mathematical function – the exponential function, $\exp(\underline{E}_i + \underline{E}_j) = \exp(\underline{E}_i)\exp(\underline{E}_j)$. By further analysis by connecting the systems thermally, introductory statistical mechanics shows[1] that the correct weighting function including the temperature is $p(\underline{E}_i) \propto \exp(-\underline{E}_i / kT)$. This is known as the Boltzmann distribution.

Maxwell-Boltzman Velocity Distribution

Consider kinetic energy. The velocity distribution is given by the Boltzman probability in each principle direction. Since the probability function is $\exp(-\underline{E}_k / kT)$ and since for a single particle, $\underline{E}_k = (1/2)mv^2$, the velocity probability weighting function is a Gaussian curve, $p(\vec{v}_x) \propto \exp(-mv_x{}^2/(2kT))$. Normalizing gives $p(\vec{v}_x) = (m/(2\pi kT)^{1/2}\exp(-mv_x{}^2/(2kT))$. Converting to molecular weight, M_w and velocities in Å/ps, T in K, $p(\vec{v}_x) = (5M_w/(\pi 8.314T)^{1/2}\exp(-5M_w v_x{}^2/(8.314T))$. The most probable velocity (expectation value) is zero because velocity is a vector and the probabilities are equally likely in opposite directions. Note that determination of expectation values are often ‘unsigned’ so often involve integrating from zero to infinity and doubling the integral value.

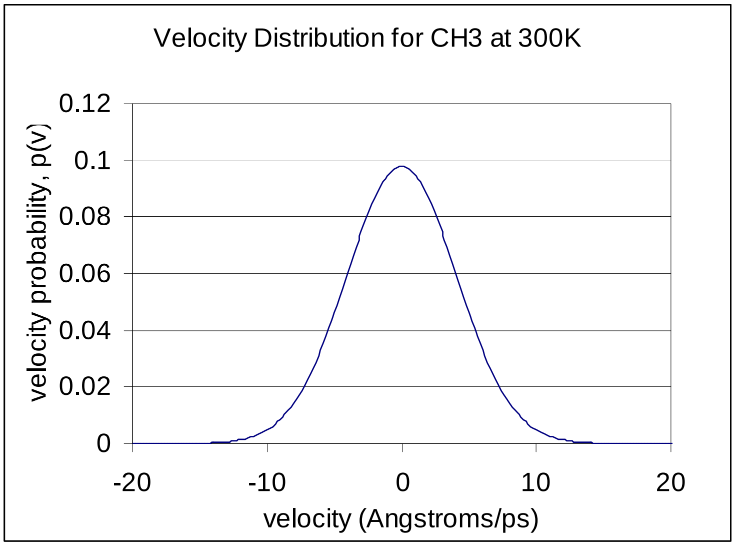


Figure 1. Velocity distribution for united atom CH3 site at 300K.

Since the probability of velocity in each principle direction is an independent probability, so the simultaneous probability is $p(\vec{v}_x)p(\vec{v}_y)p(\vec{v}_z)$. The probability of simultaneous velocities in an element of ‘velocity space’ is

$$dF(\vec{v}_x,\vec{v}_y,\vec{v}_z) = p(\vec{v}_x)p(\vec{v}_y)p(\vec{v}_z)d\vec{v}_x d\vec{v}_y d\vec{v}_z = (M_w/(2\pi 8.314T)^{3/2}\exp(-5M_w v^2/(8.314T))d\vec{v}_x d\vec{v}_y d\vec{v}_z.$$

where note that when the exponent terms are multiplied the arguments in the exponents add, and $v^2 = v_x{}^2 + v_y{}^2 + v_z{}^2$. We wish to discuss the speed distribution. To discuss this, we convert the velocity distribution to an integral over speed. The conversion results in $d\vec{v}_x d\vec{v}_y d\vec{v}_z = 4\pi v^2 dv$, where v is the scalar speed. If you have trouble seeing this conversion, recall that the conversion of the volume differential conversion from Cartesian to radial coordinates is $dxdydz = 4\pi r^2 dr$. The resulting speed distribution is discussed next. (For more details on this manipulation, see also http://galileo.phys.virginia.edu/classes/252/kinetic_theory.html). A Gaussian distribution in velocities results in the Maxwell-Boltzman distribution for speeds.

Maxwell-Boltzmann Speed Distribution

The Maxwell-Boltzmann speed distribution for the probability of a particular speed $P(v)$ is typically written in terms of the differential probability, $dF(v)$. It is convenient to work with velocities in Å/ps. Expressed in ps/ Å the differential is

$$dF(v) = P(v)dv = \frac{100}{\sqrt{5\pi}}\left(\frac{M_w}{8.314T}\right)^{3/2} v^2 \exp\left(\frac{-5M_w v^2}{8.314T}\right)dv$$

Where M_w is molecular weight, v is velocity in Å/ps, T is temperature in Kelvin. The probability is normalized so that $1 = \int_0^\infty P(v)dv$. The cumulative speed distribution is $F(v) = \int_0^v P(v)dv$ which gives the percentage under a certain speed. The Maxwell-Boltzmann velocity and speed distributions can be confirmed by sampling during molecular simulations. Also, the Maxwell-Boltzmann distribution can be used to select initial velocities for a simulation.

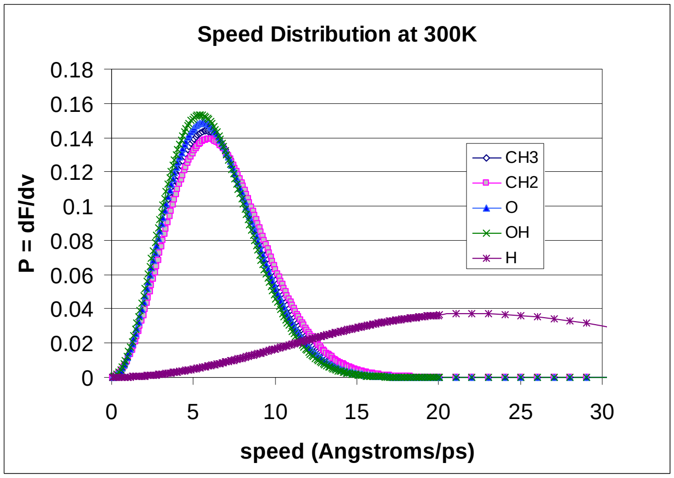


Figure 2. Maxwell-Boltzmann speed distribution for several united atom sites at 300K. Note that the speed of H is much higher than other atoms or sites. Simulations including H atoms must use small time steps because the velocities are so high.

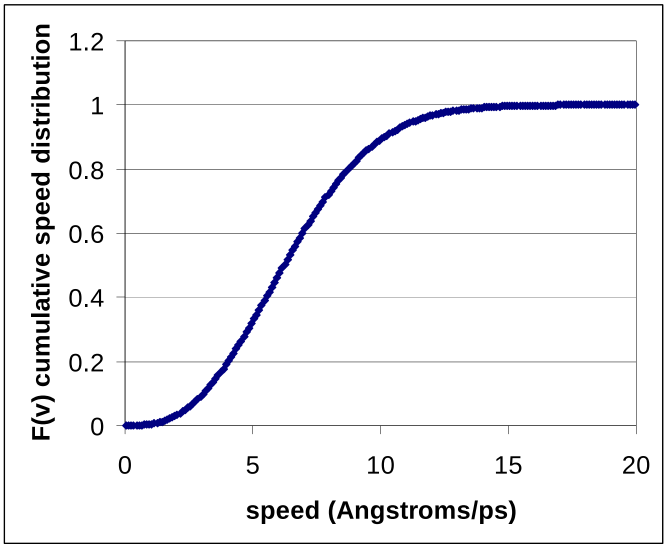


Figure 3. Cumulative speed distribution for united atom CH3 site at 300K.

Calculating Energy in Simulated Systems

Recall from Chapter 1 that the internal energy is the sum of the kinetic and potential energies of the particles that comprise a fluid, $U = \underline{E}_{KE} + \underline{E}_{PE}$. The kinetic energy contribution is determined by temperature, independent of whether the fluid is an ideal gas. When a molecule contains multiple atoms, we can consider each atom or a group of atoms (e.g. CH3) as a *united atom* site. When we consider a united atom site, we typically ignore vibrations and rotations of the site. A site has a translational degree of freedom in each dimension of $(1/2)kT$, which results in $(1/2)mv^2 = (3/2)kT$. On a molecular basis, the kinetic energy for an N molecule system is given by

$$\underline{E}_{KE} = \frac{1}{2}\sum_{sites} m_i v_i^2 = \frac{3}{2} N_m NkT \tag{S7.1}$$

where N_m is the number of sites per molecule and m_i is the mass of the corresponding sites[1]. It is more convenient to use the site molecular weight instead of the site molecular mass. On this basis, multiplying both sides by Avagadro's number, and since $N_A m_i = M_{w,i}$ is the molecular weight,

$$\frac{1}{2}\sum_{sites} M_{w,i} v_i^2 = \frac{3}{2} N_m NRT \tag{S7.2}$$

The kinetic energy of a multisite molecule may be calculated from the kinetic energies of the sites that make up the molecule. For a molecule composed of more than one site, the total translational kinetic energy of the *sites* in the molecule is equal to the sum of the vibrational, rotational, and center of mass translational kinetic energies of the *molecule*. Monatomic molecules have only translational kinetic energy.

Vibrational and rotational kinetic energies are important for understanding spectroscopy, but are not necessary for relating the total kinetic energy to temperature. While the kinetic energy of a molecule can be computed by summing the vibrational and rotational energies relative to the center of mass and the translational energy of the center of mass, it is easier to sum the kinetic energy of all the atoms. The equivalence of the two summations can be established through a reference frame argument.

To understand this subtlety more completely, consider the translational kinetic energy of the center of mass. The center of mass kinetic energy is calculated by squaring the net momentum of the molecule, and then dividing by the molecular mass,

$$\frac{\left(\sum_{\text{sites k in one molecule}} M_{w,k}\mathbf{v}_k\right)^2}{2\sum_{\text{sites k in one molecule}} M_{w,k}} \tag{S7.3}$$

---

[1] One degree of freedom must be removed in each dimension if the system's center of mass is fixed. For a large system, this correction is negligible. For a small system, the right side becomes $(3/2)(N_m N-1)kT$; for formulas using M_w, use $(3/2)(N_m N-1)RT$.

the summation of momentum in the numerator is a vector sum over the sites in the molecule.[2] The translational kinetic energy for the center of mass is not equal to the sum of the kinetic energies of the sites that make up the molecule; some of the sites have velocities in opposing directions (vibrational) or around the center of mass (rotational), thus the translational center of mass kinetic energy will always be less that the kinetic energy calculated by summing the site kinetic energies. The average kinetic energy per molecule will be

$$\frac{1}{2N}\sum_{sites} M_{w,i} v_i^2 = \frac{3}{2} N_m RT \qquad \text{(S7.4)}$$

Because the kinetic energy of a system depends on temperature only, a liquid phase molecule at temperature T has the same kinetic energy as a vapor phase molecule of the same species at T. Therefore, differences in the internal energies of the vapor and liquid phases are determined by the potential energies only. This is a significant finding because it permits decoupling of the kinetic and potential energies in property models.

Modeling of the potential energies is determined fundamentally by adding up the pair potentials of atomic sites and including potential energies of bonds (often modeled as springs with Hooke's law), and bending and torsional potentials due to twisting of molecules. The summed potential energy is called the *configurational energy.*

The configurational energy is determined by summing all the intramolecular energies and by separately summing all the intermolecular energies due to pair potentials. In multi-atom molecules, the pair potentials are often represented by the sums of the pairs of interactions for all sites in the molecules as illustrated in Figure 4.

(b)

Figure 4. (a) Arrows representing the four pair interactions for two diatomic molecules. (b) Arrows representing a wagging motion that changes the potential energy by pulling the atoms from their equilibrium positions.

Rigorous representation of all potential energy effects in complex molecules is an advanced topic with details sufficient for an entire academic course. The objective of this brief section is to provide an overview of the major concepts of simulation with the expectation that all chemical engineers benefit from understanding the basic principles.

The Ergodic Theorem

Fluid molecules undergo constant motion. Collisions of fluid molecules with the container walls result in abrupt changes in momentum. The changes in momentum create forces on the container walls that are measured as fluid pressure. The collisions are fundamentally discrete events that result in minute fluctuations in pressure. A pressure gauge displays a steady pressure at equilibrium because the readout responds to the average effect of collisions on the instrument. Local density undergoes constant fluctuations also due to changes in the number of

---

[2] A convenient method to calculate the square of momentum is to use the dot product discussed later in this document.

particles in a given region of the container as the particles move about. Since intermolecular potentials are dependent on constantly changing intermolecular distances, the configurational energy fluctuates about a mean value. Particles accelerate when falling into a potential energy well, and they decelerate when leaving a potential energy well. Considering the kinetic theory and the coupling between velocity and temperature, this means that the temperature fluctuates. Similar consideration leads to the conclusion that all state properties fluctuate about mean values.

Molecular simulations sample fluid fluctuations using two fundamentally equivalent methods. The Ergodic theorem states that the average of samples (snapshots) of molecular configurations taken at a given time from a large system is equivalent to following a small system as it fluctuates over time. These two approaches form the basis for two major simulation methods; the Monte Carlo method and the Molecular Dynamics method. The two simulation methods confirm the theorem because simulations from the two methods result in the same equilibrium properties.

Both simulation methods involve starting with a set of molecules packed into a simulation box. In some cases, the molecules are initially packed in lattice structures; in other cases the molecules are placed randomly, by choice of the programmer. Then the average value that would be determined from experiment, known as the *expectation value*, is determined by sampling configurations of the molecules.

Limitations of Simulation System Size and Time

Despite continuing advances in computational speed and continuing decreases in costs of computer technology, simulations are currently used to study very small systems for very short times. Consider the complexity of pair interactions together with bond vibrations and torsions. For two tetra-atomic molecules, there are sixteen pair interactions (N^2). Add to this the bond vibrations that depend on the symmetry of the molecule, and the effects of bond torsions if they are present. Now consider a portion of a single protein molecule with a molecular weight of 10,000 g/mol. Then add sufficient solvent to solvate the protein. Usually the pair potentials are truncated after about three molecular diameters, so that it is not necessary to sum the intermolecular potentials for a given atom with all pairs in the system, but the task is still significant because of the bookkeeping to track the neighbors and the neighbor changes as the system evolves during the simulation. This means that atomistic simulations of systems as large as living cells are not yet possible. Simulations are usually limited to portions of proteins for example, or portions of cell membranes. Consider that one cubic centimeter of water contains one gram, 1g/(18g/mol)*(6.022E23molecules/mol) = 3.3E22 molecules. Simulation of a system of this size is daunting and not done atomistically.

For homogeneous, single component systems, most simulations are performed with less than 100,000 atoms, closer to 1000 atoms if possible. For homogeneous systems, a simulation box with an equivalent length on 10 atoms on a side results in 1000 molecules (10x10x10). For a potential that with a cutoff of 2.5σ, the number of neighbors in that range, N_n, goes as $N_n \sim (N/\underline{V})\,\pi\,(2.5\sigma)^3/6 - 1$. Consider a simulation of 1000 methane molecules represented as spheres with diameters of 0.36nm at a liquid density near the normal boiling point of 0.42 g/cm^3. The number density is $N/\underline{V}$ = (0.42g/cm^3)(1E-21 cm^3/nm^3)(6.022E23/mol)/(16g/mol) = 15 molec/nm^3. The size of the sphere with nearest neighbors is $\underline{V} = \pi(2.5*0.36)^3/6 = 0.4$ nm^3. Thus the number of nearest neighbors for calculations of the pair potentials is approximately N_n = 15*0.4 – 1 = 5. Each time step requires an update of 5*1000 = 5,000 calculations of the pair potential. Considering that a normal time step in an atomistic simulation is 1-2 fs, the number of intermolecular pair potential evaluations needed is approximately 5,000,000,000 per nanosceond of simulation time.

Simulation time is limited for full atom simulations. If the objective is to obtain equilibrium properties for a homogeneous fluid, properties can often be obtained by simulating the system for a few nanoseconds. However, events that occur on time scales of microseconds are still a challenge reach for an atomistic simulation, especially for atomistic molecular dynamics. Sometimes the systems are simplified to retain only the most crucial elements of the atomistic details. Such a procedure is called *coarse graining*, and results in a *course grain model*. United atom sites are used commonly in coarse grain simulations.

Periodic Boundary Conditions, Cutoff distances, and the Minimum Image Convention

Limitations on system size are addressed in homogeneous systems using *periodic boundary conditions*. As illustrated in Figure 5 below, the simulation system is represented as 2D simulation of disks in a gray box. For simplicity of discussion, the system has only six monatomic molecules. The particle number 1 of interest for this discussion is shown with a continuous boundary, and the other equivalent molecules are sketched with a dotted line. Note that eight unshaded periodic replicas of the system have been placed around the simulation box. Suppose a trajectory moves particle 1 as indicated with the arrow. When particle 1 moves out of the box, a replacement particle is moved into the cell from the appropriate replica box. In this case a replica particle 1' moves from the box above. Instead of simulating all the boxes around the boundary, the periodic boundary can be implemented in a very simple way. The movement of the particle places it at $y_{trial} < 0$, the y coordinate is replaced by $y_{accepted} = y_{trial} + L$, where L is the length of the box side. Similar corrections are made for the other dimensions. Multi-atom molecules near the boundary will often lie partly across the boundary. However, the 'cut' atoms lying outside the boundary are still bonded, but are 'wrapped' to the other side of the box. The software code is written to track bonds to assure that molecules are intact as they are wrapped. A good illustration of periodic boundary conditions is available at http://etomica.org/app/modules/sites/swmd/pbcCubic.html.

Note that particle 4 is near the right edge of the box and thus does not have cell neighbors on the right edge of the box. To calculate the intermolecular potential and forces, the *images* of particles are used as neighbors for particles near the edge of the box. In this case, when the neighbors for particle 4 are evaluated, the images 2', 5' are used as the *minimum image* of the atoms in the box. The image of 2 is quickly calculated using $(x_{2'},y_{2'}) = (x_2 + L, y_2)$. The box must be large enough so that when long chain molecules are simulated, the distances are large enough that the molecular chain running out of one side of the simulation box and back in the other side by periodic boundary conditions does not 'sense' its own image by the minimum image convention.

Note that the configurational energy may be stated simply as the 'intramolecular energies plus sum of (each pair)*(potential energy of the pair)'. When the minimum image condition is applied, each pair potential must be counted once only. Thus if the pair potential 4+2' of Figure 5 is calculated, the pair 4+2 must be omitted. Such double-counting is assured by using a *cutoff* distance after which the atomistic potentials are no longer summed. The box size is chosen with dimensions such that the box length is at least twice the cutoff distance, which eliminates any double-counting (relative to particle 4, particle 2' is less than half the box length, but particle 2 is more than half the box length). The long range configurational energies thus omitted atomistically due to the cutoff are summed by integrating the pair potential using the mean density to determine the number of pairs in a particular volume element, and thus comprise a *long-range correction*.

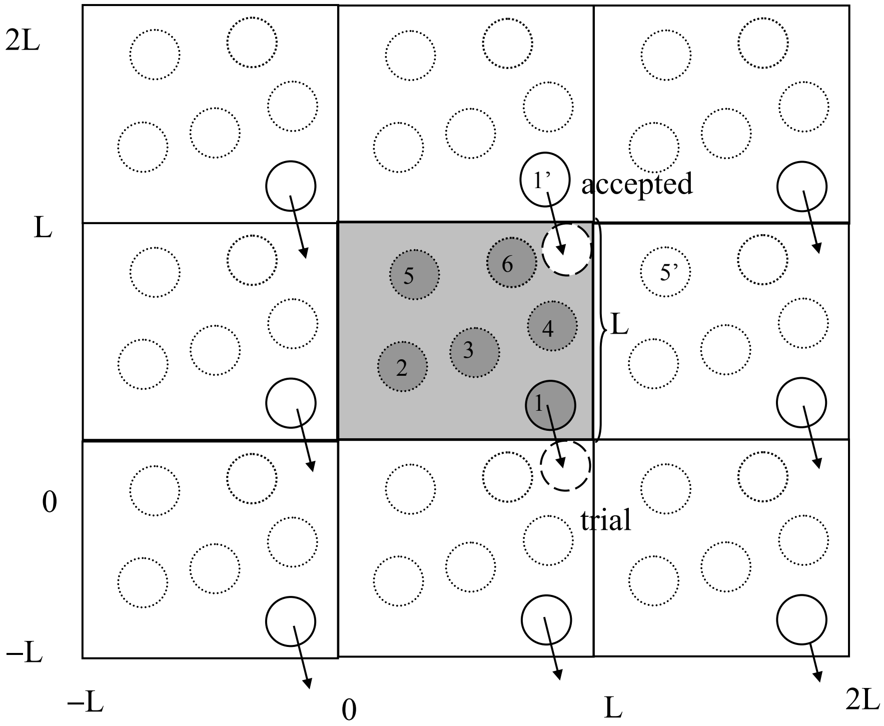


Figure 5. Illustration of the periodic boundary conditions (PBC) for a particle. When a particle 1 moves out of a box, the particle is replaced with the periodic image that moves back into the box. Also for pair potentials, interactions the minimum images are illustrated for particles 2, 5 relative to particle 4. A good illustration is at http://etomica.org/app/modules/sites/swmd/pbcCubic.html

The Principles of Monte Carlo

The Monte Carlo method simulates only the configurational energy of a molecular system. This is acceptable because kinetic energy is fixed with temperature (independent of density), and it can be added to the simulated configurational energy; the rate of molecular motion is not important in determining equilibrium properties. Monte Carlo simulates molecular motion by generating configurations solely for sampling the potential energy terms at all probable locations/arrangements. Monte Carlo methods can be very fast, however a limitation of the method is that motions are difficult to simulate for dense systems or molecular structures that are highly complex or large.

In principle, atoms are moved random distances (within some maximum displacement) in random directions, and the potential energy of each sampled configuration is recorded. A technique known as 'biased' sampling constrains the configurations that are to be sampled to be configurations most likely to be in the equilibrium structure, while not preventing sampling of fluctuations near the equilibrium structure. In molecular simulations, all atom motions that lead to a decrease in potential energy are accepted. If a step goes to a higher energy state, $\Delta \underline{E} > 0$, the move is not immediately discarded. For example, a system will always have fluctuations in state properties, and there is a probability that such a transition may occur in a real system. The correct weighting for this probability is given by the Boltzmann factor, $\exp(-\Delta \underline{E}/kT)$. A random number is generated between zero and one. If the random number is less than $\exp(-\Delta \underline{E}/kT)$, then the move is accepted. If the random number is greater than $\exp(-\Delta \underline{E}/kT)$, then the move is rejected. Due to the functional form of the Boltzmann factor, small positive energy fluctuations are accepted frequently. At higher temperatures, the probability increased for accepting higher positive energy changes. Configurations that result in very high energies are rejected, so no time is wasted sampling configurations that occur with only miniscule probability. The net result of this biased is an efficient evaluation for the representation of the energy states sampled by a real system.

The Principles of Molecular Dynamics (MD)

Molecular dynamics has some advantages over Monte Carlo. A principle advantage is that complicated systems and dense systems can be studied without developing complex algorithms to simulate displacements. Time-dependent events such as diffusion can also be studied quantitatively. Molecular dynamics implements Newton's equations of motion on the site scale, so individual sites move as dictated by the net forces acting upon them. For a pair of sites, the force of interaction is calculated from the gradient of the potential energy, u,

$$\mathbf{F} = -\, d\mathbf{u}/d\mathbf{r} \qquad \text{(S7.5)}$$

For an ensemble of molecules, the pair-wise forces are summed to determine the net force on each molecule. The acceleration vector is then determined. The technique appears simple, but requires careful implementation because the actual motions are continuous but the simulation is implemented with finite time steps. The Verlet leapfrog algorithm will be described here. For an atom at position **r**, the new position can be determined by writing a Taylor expansion, noting that $\dot{\mathbf{r}} = \mathbf{v}$, and $\ddot{\mathbf{r}} = \mathbf{a}$, using h to denote the small time step,

$$\mathbf{r}(t+h) = \mathbf{r}(t) + h\dot{\mathbf{r}}(t) + (h^2/2)\ddot{\mathbf{r}}(t) + \mathrm{O}(h^3) = \mathbf{r}(t) + h\mathbf{v}(t) + (h^2/2)\mathbf{a}(t) + \mathrm{O}(h^3) \qquad \text{(S7.6)}$$

The acceleration at any time is a known quantity, calculated from summing the relevant pair potentials.

$$\mathbf{F}(t) = m_i\mathbf{a}(t) = -\sum_{neighbors} d\mathbf{u}/d\mathbf{r}(\mathrm{t}) \quad \Rightarrow \quad \mathbf{a}(t) = (-\sum_{neighbors} d\mathbf{u}/d\mathbf{r}(t))/m_i \qquad \text{(S7.7)}$$

Rigorously, the velocities and accelerations change instantaneously with position, however the computer needs to calculate new positions using quantities that are considered 'average' over a small time interval. We know that **v** and **a** will be different at $t + h$ because of the new positions. The velocity at a half time step should be more accurate than a full time step,

$$\mathbf{v}(t+h/2) = \mathbf{v}(t) + (h/2)\mathbf{a}(t) \quad \Rightarrow \quad \mathbf{v}(t) = \mathbf{v}(t+h/2) - (h/2)\mathbf{a}(t) \qquad \text{(S7.8)}$$

Inserting this second argument into eq S7.6 results in

$$\mathbf{r}(t+h) = \mathbf{r}(t) + h\mathbf{v}(t+h/2) \qquad \text{(S7.9)}$$

For a time step to the next half interval for velocity,

$$\mathbf{v}(t+h/2) = \mathbf{v}(t-h/2) + (h)\mathbf{a}(t) \qquad \text{(S7.10)}$$

From an initial state, to start a simulation, eq. S7.7 is used to determine **a**(t), eq. S7.8 is used once to give $\mathbf{v}(t+h/2) = \mathbf{v}(t) + (h/2)\mathbf{a}(t)$. Then eqs. S7.9, S7.7 and S7.10 are looped successively to constitute the leapfrog routine. The velocities and positions 'leapfrog' over each other as estimated by different half time-steps. The routine is repeated to follow the movements. Each initial state results in a set of motions known as the *trajectory*.

Discontinuous Molecular Dynamics (DMD)

A special case of molecular dynamics uses the hard sphere potential for the atoms. Since no forces are exerted except at collision, the velocity of the particles is constant between collisions. Collision events are considered elastic, so the post-collision velocities are known for the incoming trajectories and velocities. The collisions events are calculated using the conservation of momentum and the conservation of energy. Therefore, the trajectory of a particle can be simulated discontinuously between collision events. The simulation code for DMD is significantly different than that for traditional molecular dynamics because the particles are moved discontinuously from one collision event to the next with known velocities.

Vector Mathematics for DMD

Consider the trajectories of two particles i and j, each with diameter σ as shown in Figure 6(a). The coordinates of the particles are the vectors $\mathbf{r}_i = [x_i, y_i, z_i]$ and $\mathbf{r}_j = [x_j, y_j, z_j]$ and they have velocity vectors $\mathbf{v}_i$ and $\mathbf{v}_j$. The position at any time, in the absence of acceleration is

$$\boxed{\mathbf{r}_j = \mathbf{r}_j^{\mathrm{o}} + \mathbf{v}_j^{\mathrm{o}}(t - t^{\mathrm{o}})} \qquad \text{(S7.11)}$$

The collision event and collision time are most easily determined by using the relative position and relative velocities, (note the subscript conventions used here)

$$\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j = [r_{ix} - r_{jx}, r_{iy} - r_{jy}, r_{iz} - r_{jz}] \qquad \text{(S7.12)}$$

$$\mathbf{v}_{ij} \equiv \mathbf{v}_i - \mathbf{v}_j = [v_{ix} - v_{jx}, v_{iy} - v_{jy}, v_{iz} - v_{jz}] \qquad \text{(S7.13)}$$

Figure 6(a) shows how the relative position can be expressed as a vector difference. Figure 6(b) shows a relative position vector, and a relative velocity vector. If particle '2' is stationary as a special case, then the particles will collide when '1' reaches the position shown with the dotted outline. When $\mathbf{r}_{ij}$ and $\mathbf{v}_{ij}$ have opposite sense, the particles will be approaching and a collision is possible. The principle can be quantified using the dot product $\mathbf{r}_{12} \bullet \mathbf{v}_{12}$. The dot product of two vectors is a scalar that may be calculated by two equivalent methods. The dot product can be determined using summed term-by-term multiplication of the vector components, or it can be found using the angle between the two vectors as shown in Figure 6(c). The vectors from Figure 6(b) have been rearranged to show the dot product and cosine in Figure 6(c). The dot product is usually easier to implement.

$$\mathbf{r}_{12} \bullet \mathbf{v}_{12} = (r_{12x}, r_{12y}, r_{12z}) \bullet (v_{12x}, v_{12y}, v_{12z}) = r_{12x}\, v_{12x}, + r_{12y}\, v_{12y} + r_{12z}\, v_{12z} = |r_{12}||v_{12}|\cos\beta \qquad \text{(S7.14)}$$

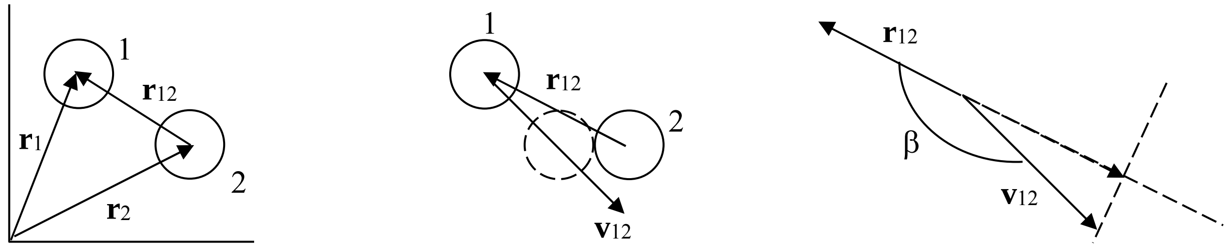
The dot product has a negative value when the relative position and relative velocity have an opposite sense as shown in Figures 6(b) and (c). When the vectors have an opposite sense, r_{12} will be decreasing with time (particles approaching). We define the variable b as the dot product.

$$\boxed{b_{ij} \equiv \mathbf{r}_{ij} \bullet \mathbf{v}_{ij}} \qquad \text{(S7.15)}$$

If $b_{ij} > 0$, the relative position $|r_{12}|$ is increasing with time. If $b_{ij} = 0$, the relative velocity and relative position vectors are perpendicular. If $b_{ij} < 0$, the relative position $|r_{12}|$ is decreasing and there may be a collision. Two cases are illustrated in Figure 7(*a*) and (*b*). Another application of the dot product is useful. The dot product of a vector with itself is the magnitude squared. Thus

$$\boxed{r_{ij}^2 = \mathbf{r}_{ij} \bullet \mathbf{r}_{ij}, \quad v_{ij}^2 = \mathbf{v}_{ij} \bullet \mathbf{v}_{ij}} \tag{S7.16}$$

and the kinetic energy of a particle can be calculated quickly using $m_i(\mathbf{v}_i \bullet \mathbf{v}_i) / 2$.



(a) (b) (c)

Figure 6. (*a*) Illustration of the relative position expressed as a vector difference, $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$. Each particle has diameter σ. (*b*) Coordinate system for study of a 2D collision of disks as discussed in the text. (c) Dot product, $\mathbf{r}_{12} \cdot \mathbf{v}_{12}$ as the projection of $\mathbf{v}_{12}$ onto $\mathbf{r}_{12}$, with magnitude $r_{12} v_{12} \cos\beta$.

A collision event is dependent on whether the intermolecular separation becomes equal to the average molecular diameter $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ sometime in the future. Using superscript o to represent an initial conditions, the relative position vector at any time in the future is found by a generalization of eq S7.11

$$\mathbf{r}_{ij} = \mathbf{r}_{ij}^{o} + \mathbf{v}_{ij}^{o}(t - t^{o}) \tag{S7.17}$$

We may check to see if the dot product $\mathbf{r}_{ij} \bullet \mathbf{r}_{ij}$ becomes equal to σ_{ij}^2 in the future at some time increment $(t - t^{o})$,

$$\begin{aligned}\sigma_{ij}^2 = \mathbf{r}_{ij} \bullet \mathbf{r}_{ij} &= (\mathbf{r}_{ij}^{o} + \mathbf{v}_{ij}^{o}(t - t^{o})) \bullet (\mathbf{r}_{ij}^{o} + \mathbf{v}_{ij}^{o}(t - t^{o})) \\ &= \mathbf{r}_{ij}^{o} \bullet \mathbf{r}_{ij}^{o} + 2\, \mathbf{r}_{ij}^{o} \bullet \mathbf{v}_{ij}^{o}(t - t^{o}) + \mathbf{v}_{ij}^{o} \bullet \mathbf{v}_{ij}^{o}(t - t^{o})^2 \\ &= r_{ij}^2 + 2b_{ij}\,(t - t^{o}) + v_{ij}^2(t - t^{o})^2\end{aligned}$$

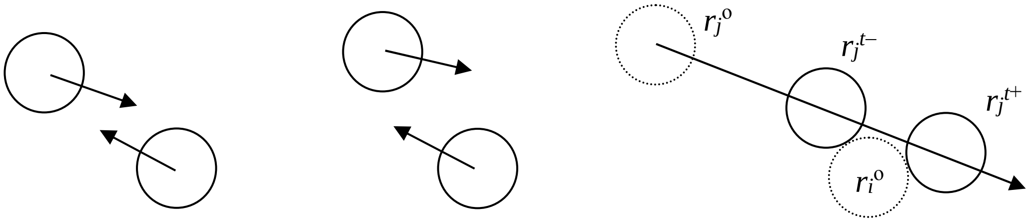
or

$$v_{ij}^2(t - t^{o})^2 + 2b_{ij}(t - t^{o}) + (r_{ij}^2 - \sigma_{ij}^2) = 0 \tag{S7.18}$$

Solving for time using the quadratic formula, the time of collision is:

$$\boxed{t^c = (t - t^{o}) = \frac{-b_{ij} + s_{time}\sqrt{b_{ij}^2 - v_{ij}^2(r_{ij}^2 - \sigma_{ij}^2)}}{v_{ij}^2}} \quad \text{sphere collisions} \tag{S7.19}$$

where $s_{time} = \pm 1$. The argument in the square root, $b_{ij}^2 - v_{ij}^2(r_{ij}^2 - \sigma_{ij}^2)$, is called the discriminant, and must be non-negative for a collision to occur. If it is negative, then the particles miss each other. The smaller real root $s_{time} = -1$ is used for the solution to the quadratic as shown in Figure 7(*c*). For purposes of illustration, particle *i* is considered stationary, and particle *j* is moved with velocity v_{ij}. The smaller real root ($s_{time} = -1$) occurs when the particles collide at r_j^{t-}. The location labeled r_j^{t+} is the root that will not occur physically.



(*a*) (*b*) (*c*)

Figure 7. (*a*) illustration of two particles with positions and relative velocities that will result in a collision. For this case $b < 0$ and the discriminant > 0. (*b*) A case where particles are approaching at t^o but will not collide; $b < 0$, but the discriminant < 0. (*c*) Illustration of why the smaller real root is used, $s = -1$.

Velocity changes

Calculation of velocity changes upon collision is more complex. A 2-D case of colliding disks will illustrate the results. Consider the situation illustrated in Figure 8. Particle '1' is moving towards '2' with relative velocity $\mathbf{v}_{12}$. To keep the derivation brief, particle '2' is initially stationary and identical masses will be used. The collision location of 1 is shown with a dotted sphere. The collision will create a force on particle '2' that will instataneously accelerate it to a fixed velocity. *The force will act in the direction of the vector between the point of contact and the center of mass.* By application of this principle, particle 2' will move after collision in the *x*-direction only, without a *y*-component of velocity. By Newton's third law, an equal and opposite force acts on particle '1'. The direction of the collision force is most easy found using the relative position at contact $\mathbf{r}_{12}^c$ as shown in Figure 8, where the superscript c denotes a property calculated at collision. Creating a unit vector by dividing by the magnitude of the relative force, σ, the force acts on particle 1 in the direction $\mathbf{r}_{12}^c/\sigma$ and acts on particle 2 in the direction $-\mathbf{r}_{12}^c/\sigma$,

Upon an elastic collision, the momentum and kinetic energy are conserved. Conservation of momentum is written using primes to denote post-collision properties,

$$m\mathbf{v}_1' + m_2\mathbf{v}_2' = m\mathbf{v}_1 + m\mathbf{v}_2 \text{, which becomes } m(\mathbf{v}_1' - \mathbf{v}_1) = -m(\mathbf{v}_2' - \mathbf{v}_2) \qquad \text{(S7.20)}$$

For the case of discussion, $\mathbf{v}_2 = 0$, $\mathbf{v}_1 = \mathbf{v}_{12}$. The momentum must be conserved in each direction. Equating the momentum before and after collision,

x-momentum conservation, before = after: $m\,|v_{12}|\cos\gamma + 0 = m\,|v_1'|\cos(\alpha) + m\,|v_2'|$ (S7.21)

y-momentum conservation, before = after: $-m\,|v_{12}|\sin\gamma + 0 = -m\,|v_1'|\sin(\alpha) + 0$ (S7.22)

Equating kinetic energy before and after collision,

$$mv_{12}^2 + 0 = m(v_1')^2 + m(v_2')^2 \qquad \text{(S7.23)}$$

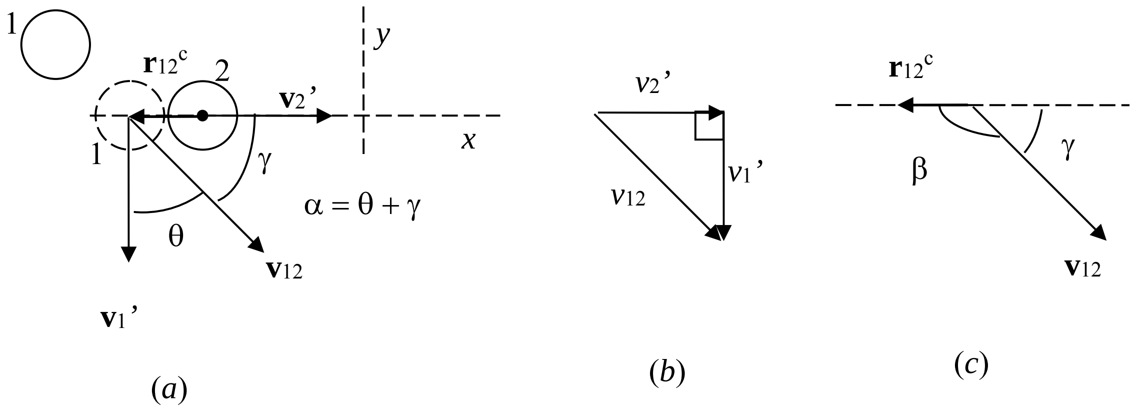


Figure 8. (*a*) Illustration of a collision of two disks to derive the 2D result for collision of objects with the same mass and same diameter. (*b*) Pythagorean theorem applied to the velocity vectors (*c*) relation of the dot product to angle γ as described in the text.

which for equal masses becomes

$$v_{12}^2 = (v_1')^2 + (v_2')^2 \tag{S7.24}$$

Eq. S7.24 is also the result of the Pythagorean theorem for a triangle with hypotenuse v_{12} and sides v_1' and v_2' at 90° (see Figure 8(*b*)). This result means that the angle $\alpha = \gamma + \theta = 90^{\circ}$.

The angle γ may be related to the dot product of relative position at collision with the incoming relative velocity as shown in Figure 8(*c*).

$$b_{12}^c = \mathbf{r}_{12}^c \bullet v_{12} = \sigma \,|\, v_{12} \,|\cos\beta = -\sigma \,|\, v_{12} \,|\cos(180-\beta) = -\sigma \,|\, v_{12} \,|\cos\gamma \tag{S7.25}$$

which can be written

$$\frac{-\mathbf{r}_{12}^c \bullet v_{12}}{\sigma} = |\, v_{12} \,|\cos\gamma \tag{S7.26}$$

Inserting eq. S7.26 and $\alpha = 90^{\circ}$ into eq S7.21-22, gives the scalar magnitude of the velocity change. Including the unit vector $-\mathbf{r}_{12}^c/\sigma$ to specify the direction of the impulse force on particle 2 results in

$$\frac{\mathbf{r}_{12}^c \bullet v_{12}}{m\sigma^2}\mathbf{r}_{12}^c = \frac{b_{12}^c}{m\sigma^2}\mathbf{r}_{12}^c = \frac{\Delta\mathbf{v}_2}{m} = \frac{-\Delta\mathbf{v}_1}{m} \text{ for equal masses, equal size} \tag{S7.27}$$

where for the last equality, eq. S7.20 has been used to relate to $\mathbf{v}_1$. It should be noted that the result $\alpha = 90^{\circ}$ is a consequence that when one of the particles is initially stationary; the pythagorean theorom results as in eq. S7.24, which permitted a simple analysis to be applied. However the other aspects of the collision are general results. A general derivation relaxing the constraints of equal mass and equal size is available as an appendix. The general result is

$$\boxed{\frac{\Delta\mathbf{v}_i}{m_j} = -\frac{\Delta\mathbf{v}_j}{m_i} = \frac{-2b_{ij}^c}{(m_i + m_j)\sigma_{ij}^2}\mathbf{r}_{ij}^c} \text{ sphere collisions} \tag{S7.28}$$

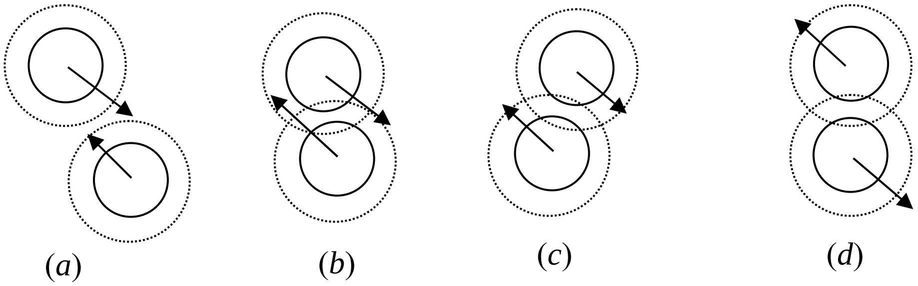


Figure 9. (*a*) Approaching spheres that will enter the square well; (*b*) Spheres in the well that will collide; (*c*) Spheres in the well that will miss, but will experience a well event after they pass; (*d*) Spheres moving away that will experience a well event at the well limit.

Event Tracking

Since collision events can be forecast from existing positions and velocities, there is little reason to advance the simulation by discrete time steps. Instead the simulation can be advanced by from one collision event time to the next event time. To start the simulation, the particles are given initial velocities and the neighborhood surrounding a particle is scanned for collision events that are scheduled on a calendar. As each event is predicted, it is sorted with respect to time as it is entered in the calendar. Then the earliest event is executed. Whenever a collision occurs, all events for the two colliding particles are discarded and new events for only the colliding particles are predicted. Only the area in the vicinity of the event need be scanned for new events. These are then added to the calendar, and then the earliest event is executed.

DMD and the Square-Well Potential

A square-well potential can be added to the DMD simulation with relatively few changes. The square well creates an edge at $R\sigma$ around the hard sphere, as shown in Figure 9. Since the gradient of the potential is zero except at the discontinuous well edge, velocities will be constant for distances inside or outside the well, and change only for collision or events at the well edge. If particles enter a well, velocities will increase. Whether particles escape from a well or bounce back depends on kinetic energy as explained below. This well edge is treated like a penetrable boundary; the velocities change discontinuously at position $\lambda\sigma$. Thus, the times that the well edges are encountered need to be added as events.

The equations for these and subsequently discussed events are most briefly summarized using generalized notation. The general equation for the well or collision event time is a modification of eq. S7.19

$$\boxed{t^c = (t - t^o) = \frac{-b_{ij} + s_{time}\sqrt{b_{ij}^2 - v_{ij}^2(r_{ij}^2 - d_{ij}^2)}}{v_{ij}^2}} \text{ collision or well event} \qquad \text{(S7.29)}$$

where d_{ij} is the generic variable to represent the distance of centers for the event (well edge or core collision) and $s_{time} = \pm 1$ specifies which root is valid. The velocity changes due to either type of event will be

$$\boxed{\frac{\Delta \mathbf{v}_i}{m_j} = -\frac{\Delta \mathbf{v}_j}{m_i} = \phi \mathbf{r}_{ij}^c \text{ where } \phi = \frac{-b_{ij}^c + s_{vel}\sqrt{(b_{ij}^c)^2 - 2d_{ij}^2 \Delta\varepsilon / m_r}}{d_{ij}^2 (m_i + m_j)}} \text{collision or well event} \quad \text{(S7.30)}$$

and $\Delta\varepsilon$ is the relevant energy change due to the event ($\Delta\varepsilon = 0$ for a core collision or if there is insufficient energy to escape the well) and the reduced mass is defined $m_r \equiv m_i m_j/(m_i + m_j)$. The well distance is calculated using combining rules, typically $(\lambda\sigma)_{ij} = (\lambda_i\sigma_i + \lambda_j\sigma_j)/2$ which becomes d_{ij} in eq. S7.29 and S7.30. Note that eq. S7.30 reduces to eq. S7.28 when $s_{vel} = -1$, $\Delta\varepsilon = 0$, and d_{ij} is the core collision distance. Before discussing the particulars of collisions and well crossings, we introduce bonds that can be represented by infinite wells. A general flow sheet for tracking events is shown in Figure 10. The appendix shows the general derivations.

DMD and Bonded Sites

Bonded sites can be modeled using infinite wells to constrain the sites to realistic distances. As shown in Figures 11 and 12 the sites can be constrained at distances by creating a well with zero potential within some tolerance of equilibrium position, but an infinite potential at the limits of the bond stretch and bond compression. The detail of such a bond is shown in Figure 12. Bond angles can be constrained using pseudobonds with the same type of bond potentials illustrated in Figure 13. While these are not real bonds, they provide the same general constraints and movements as more complex continuous bond bending potentials.

Evaluation of bonded site dynamics is very similar to the free particle dynamics discussed above for the square well potential, except: (1) sites can never escape from the wells; (2) bond distances are less than the site diameters so the bond wells are 'inside' the site spheres. The collisions with wells can be implemented using the flow sheet in Figure 10.

Applications of DMD

Recently, DMD has been utilized in two applications that will be highlighted here. Hall and coworkers[2] have simulated the formation of fibrils from protein molecules. These fibrils are associated with the plaques that form in Alzheimer's disease. The proteins are quite large, and fibrils are formed by many protein strands. In the work of Hall et. al, the protein strands were simplified by coarse graining to create the amino acids of the protein chain as a set of spherical sites. The bond angles were constrained using pseudobonds. Simulations were conducted with up to 96 protein strands. To represent the potential energies, square well potentials were used at selected sites. In the simulations, the solvent was omitted, creating a fast simulation. Thus the protein parameters are considered to be parameters that represent energies 'relative to the solvent'. Also, the simulations run faster in the presence of simulated solvent because the proteins are devoid of collisions with solvent. The workers have studied the phase transitions that occur in the system and the events leading to fibril formation.

In another application, Elliott and coworkers[3] have used DMD together with perturbation theory to develop a powerful method to calculate real fluid vapor pressure. The goal of this work is also to use coarse grained simulations to represent large molecules. The work has been recognized with a prize for simulation of vapor pressure.[4] A major objective of the work is to develop *transferable site potentials.* A transferable potential for methyl group for instance could

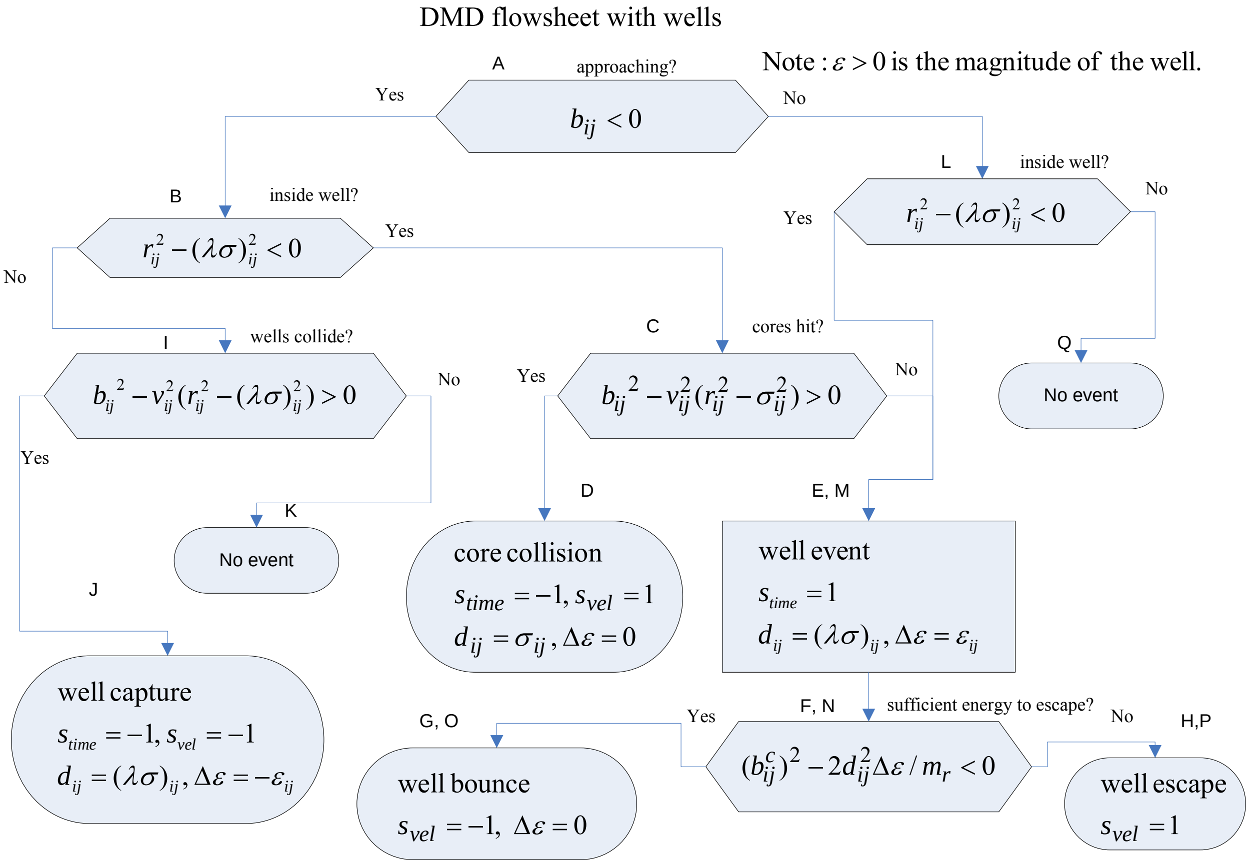


Figure 10. Flowsheet for DMD with wells. The alphabet labels are used in supplementary computer code to indicate the relation of code to the flowsheet. Bonded sites use $\varepsilon_{ij} = \infty$ at E,M and cannot escape from the bond wells.

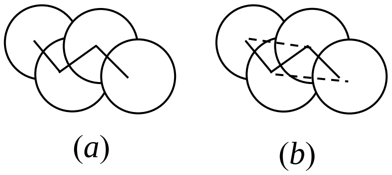


Figure 11. (*a*) Creation of a molecule by bonding sites. The solid lines represent equilibrium distances. (*b*) Addition of pseudobonds (dotted lines) to constrain the bond angles.

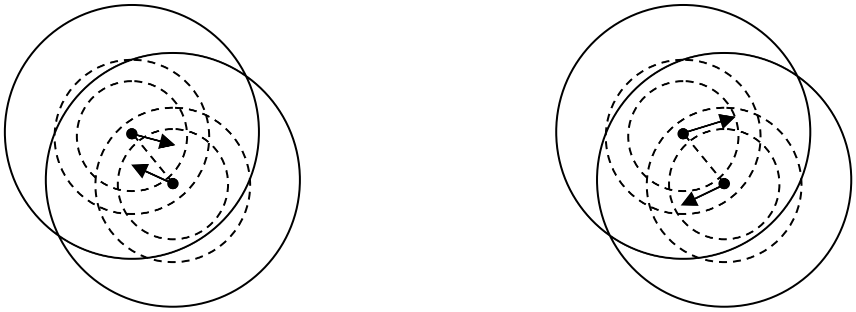


Figure 12. (*a*) Illustration of sites bonded with wells with velocities that will result in a collision with the compression limit. (*b*) Bonded sites moving with velocities that result in a event at the stretch limit.

be used for any molecule with a methyl group in a similar location within a molecule. This is similar to the UNIFAC approach in concept, but substantially more fundamental because it involves fewer assumptions, and the representation of the effect of shape on mixing is very accurate. The method involves using a DMD simulation of the hard molecule. Then the attractive potential is 'added' on top of the simulation using perturbation theory. Since the simulation provides information about the nearest neighbor identity and distance, the potential energy can be 'added' after the hard molecule simulation. For this perturbation calculation, the attractive potential is a step potential approximation to a continuous potential, such as that shown in Figure 13 below. The parameters for the attractive wells are adjusted to fit the vapor pressure or other fundamental fluid properties. Though the step wells could be incorporated into the simulation, it is faster to add them to the simulation as a perturbation.

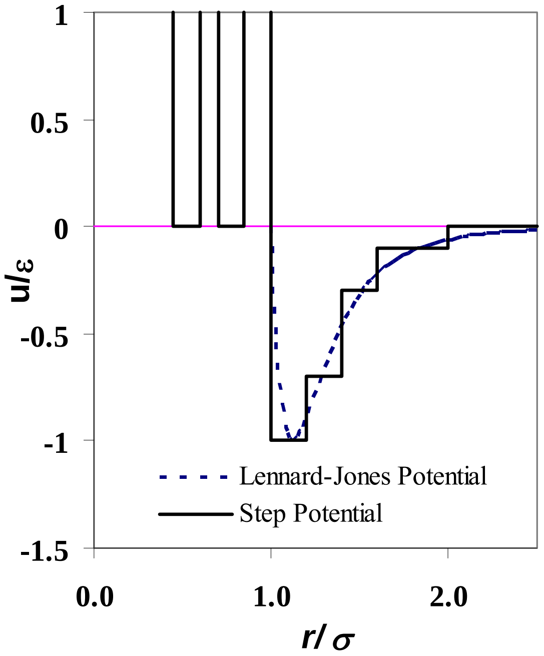


Figure 13. Representation of the intermolecular potential as a series of discontinuous wells. The infinite wells at diameters less than σ represent bonds as shown in Figure 12.

1. Denbigh, K.G, (1981). *The principles of Chemical Equilibrium*, 4th ed. Cambridge University Press, London.
2. Nguyen, H. D.; Hall, C. K. (2006). "Spontaneous fibril formation by polyalanines; Discontinuous molecular dynamics simulations." *JACS* **128**(6): 1890-1901.
3. Unlu, O.; Gray, N. H.; Gerek, Z. N.; Elliott, J. R. (2004). "Transferable step potentials for the straight-chain alkanes, alkenes, alkynes, ethers, and alcohols." *Ind. Eng. Chem. Res.* **43**(7): 1788-1793.
4. Case, F.; Chaka, A.; Friend, D. G.; Frurip, D.; Golab, J.; Gordon, P.; Johnson, R.; Kolar, P.; Jonathan Moored; Mountain, R. D.; Olson, J.; Ross, R.; Schiller, M. (2005). "The second industrial fluid properties simulation challenge." *Fluid Phase Equil.* **236**: 1-14.

This supplemental example is an alternative to the textbook example. This example uses vector mathematics.

Example S7.1 Computing molecular collisions in 2D

Let the diameters of two disks, σ, be 4 Å, the masses be 16 g/mole, and the length of the square box, L, be 50 Å. Start the disks at [16.7 16.7], [33.3 33.3] Å and initial velocities (Å/ps): [1.67 2.22], [–1.67 –2.22] where 1 Å $= 10^{-10}$ m and 1ps $= 10^{-12}$ s. Note that Å and ps are convenient units to use, and that the gas constant 8.314 J/mol-K = 8.314 kg-m^2/(s^2-mol-K) = 0.8314 g-(Å)^2/(ps^2-mol-K).

(a) Compute the temperature (K).
(b) Compute the collision times with the walls.
(c) Compute the collision times with the disks. Which event occurs first?
(d) Compute the velocity vectors (Å/ps) after the first collision event.

Solution:

(a) $T_{2D} = M_w\langle v^2\rangle/(2R)$; $\langle v^2\rangle = (1.67^2 + 2.22^2 + 1.67^2 + 2.22^2)/2 = 7.717$ (Å/ps)^2
T_{2D} = (16g/mol)(7.717 (Å/ps)^2)/(2·0.8314 g-Å^2/(ps^2-mol-K)) = 74.3K.

(b) The collision time with the walls depends on the wall being approached. Note that the molecular coordinate will be within $0.5\sigma = 2$ Å 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 found by Eqn. S7.11 are
$t_1^N = (48 - y_1^o)/v_{1,y} = (48 - 16.7)/2.22 = 14.10$ps,
$t_1^E = (48 - x_1^o)/v_{1,x} = (48 - 16.7)/1.67 = 18.74$ps.
Similarly,
$t_2^S = (2 - y_2^o)/v_{2,y} = (2 - 33.3)/(-2.22) = 14.10$ps;
$t_2^W = (2 - x_2^o)/v_{2,x} = (2 - 33.3)/(-1.67) = 18.74$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.

(c) For disk1 and disk2, the relative velocity and position are:
$\vec{v}_{12}$ = [(1.67 + 1.67) (2.22 + 2.22)] = [3.34 4.44];
$\vec{r}_{12}$ = [(16.7 – 33.3) (16.7 – 33.3)] = [–16.6 –16.6];
by Eqn. S7.15, $b_{12} = (-16.6)(3.34) + (-16.6)(4.44) = -129.148$.
Because $b_{21} < 0$, the particles are approaching.
$v_{12}^2 = (3.34^2 + 4.44^2) = 30.869$; $r_{21}^2 = (16.6^2 + 16.6^2) = 551.12$;
the discriminant of S7.19 is $D = (-129.148)^2 - (30.869)(551.12-16) = 160.6$
Then by Eqn. S7.19,
$t^c = \Delta t_{12} = (-(-129.148) - 160.6^{1/2})/(30.869) = 3.773$ps
The intermolecular collision occurs before the wall collisions calculated in part (b).

(d) Computing the direction after collision requires knowing relative positions and b at collision,
$\vec{r}_{12}^{\,c}$ = [–16.6 –16.6] + [3.34 4.44]Δt_{12}. So $\vec{r}_{12}^{\,c}$ = [–16.6+3.34•3.773 –16.6+4.44•3.773] = [–3.998 0.1521].
Then by Eqn. S7.15,
$b_{12}^c = -3.998(3.34) - 0.1521(-4.44) = -12.678$
and by Eqn. S7.28 (note the signs)
$\Delta\vec{v}_1 = -b_{12}^c\vec{r}_{12}^{\,c}/\sigma^2 = -\Delta\vec{v}_2$ = –(–12.678)[–3.998 0.1521]/16 = [–3.1679 0.1205]
$\vec{v}_1$ = [1.67 2.22] + [–3.1679 0.1205] = [–1.498 2.34],
$\vec{v}_2$ = [–1.67 –2.22] + [–3.1679 0.1205] = [1.498 2.34]. From this point, the procedure for the next collision is exactly the same.

Example S7.1 Computing molecular collisions in 2D (Continued)

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 of speeds 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.

Let us perform another example with three particles and relax the constraint of net velocity. The interchange of subscripts for relative vectors is acceptable when applied consistently.

Example S7.2 Computing molecular collisions in 2D

Let the diameters of three disks, σ, be 4 Å, masses be 16 g/mole, and the length of the square box, L, be 50 Å. Start the disks at [0.33L 0.33L], [0.67L 0.33L], [0.67L 0.67L] and initial velocities (Å/ps) of [2.22 3.33], [−1.11 –2.22], [−1.11 −1.11]. Note that Å and ps are convenient units to use, and that the gas constant 8.314 J/mol-K = 8.314 kg-m^2/(s^2-mol-K) = 0.8314 g-(Å)^2/(ps^2-mol-K).
(a) Compute the temperature (K).
(b) Compute the collision times with the walls and disks. Which event occurs first?
(c) Compute the velocities vectors (m/s) after the first collision event.

Solution:

(a) From textbook Eqn. 1.22, $T_{2D} = MW\langle v^2\rangle/(2R)$; $\langle v^2\rangle = (2.22^2+3.33^2+1.11^2+2.22^2+1.11^2+1.11^2)/3 =$ 8.214 Å^2/ps^2, T = (16g/mol)(8.214 Å^2/ps^2)/(2•0.8314 g-(Å)^2/(ps^2-mol-K)) = 79K.

(b) The collision time with the walls depends on the wall being approached. Recall that the particle coordinate will be within 0.5σ = 2Å of the wall coordinate when a wall collision occurs. Using cardinal directions to indicate walls, disk1 is approaching the north wall and west wall, The times of collision are found by rearranging Eqn. S7.11 using the impact coordinate for each wall,
$t_1^N = (48 - y_1^o)/v_{1,y} = (48 - 16.5)/3.33 = 9.46$ps,
$t_1^E = (48 - x_1^o)/v_{1,x} = (48 - 16.5)/2.22 = 14.2$ps.
Similarly disk2 and disk3 are approaching the south and west wall,
$t_2^S = (2 - y_1^o)/v_{1,y} = (2 - 16.5)/(-2.22) = 6.53$ps;
$t_2^W = (2 - x_1^o)/v_{1,x} = (2 - 33.5)/(-1.11) = 28.4$ps;
$t_3^W = (2 - x_1^o)/v_{1,x} = (2 - 33.5)/(-1.11) = 28.4$ps;
$t_3^S = (2 - y_1^o)/v_{1,y} = (2 - 33.5)/(-1.11) = 28.4$ps.

For disk1 and disk2, the relative velocity and position are:
$\vec{v}_{21}$ = [(−1.11–2.22) (–2.22–3.33)] = [–3.33 –5.55]; $\vec{r}_{12}$ = [(33.5–16.5) (16.5–16.5)] = [17 0];
by Eqn. S7.15, $b_{21} = 17(-3.33)+0 = -56.61$; Because $b_{21} < 0$, the particles are approaching.
$v_{21}^2 = (3.33^2 + 5.55^2) = 41.8914$; $r_{21}^2 = (17^2 + 0^2) = 289$;
the discriminant of S7.16 is $D = (-56.61)^2 - (41.8914)(289-16) = -8231.7$; Thus the particles will miss.

For disk1 and disk3,
$\vec{v}_{31}$ = [(−1.11–2.22) (−1.11–3.33)] = [−3.33 –4.44]; $\vec{r}_{31}$ = [(33.5–16.5) (33.5–16.5)] = [17 17];
$v_{31}^2 = (3.33)^2 + (4.44)^2 = 30.8025$; $r_{31}^2 = 2(33.5-16.5)^2 = 578$; $b_{31}^c = -3.33(17) - 4.44(17) = -132.09$;
$D = (-132.09)^2 - (30.8025)(578-16) = 136.76$.
Then by Eqn. S7.19, $\Delta t_{31} = (-(-132.0.9) - 136.76^{1/2})/(30.8025) = 3.909$ps.

A similar calculation gives $b_{32} = 18.87 > 0$, so particles are not approaching. Since Δt_{31} is the smallest positive value for particle or wall collisions, it occurs first.

Example S7.2 Computing molecular collisions in 2D

(c) Computing the direction after collision requires knowing relative positions and *b* at collision,
$\vec{r}^{\,c}_{31} = (17,17) + (-3.33,-4.44)t^c$. So $\vec{r}_{31} = [17-3.33\bullet 3.909\ \ 17-4.44\bullet 3.909] = [3.98303\ \ -0.35596]$.
Then by Eqn. S7.15,
$b_{31}{}^c = -3.33(3.98303)-4.44(-0.35596) = -11.683$, and by Eqn. S7.28 (note the signs and subscripts)
$\Delta\vec{v}_3 = -\vec{r}_{31}b^c_{31}/\sigma^2 = -\Delta\vec{v}_1 = -[3.98303(-11.683)/16\ \ -0.35596(-11.683)/16] = [2.91\ \ -0.260]$

$\vec{v}_3 = [-1.11\ \ -1.11] + [2.91\ \ -0.26] = [1.80\ \ -1.37]$, $\vec{v}_1 = \begin{bmatrix}2.22 & 3.33\end{bmatrix} + \begin{bmatrix}-2.91 & 0.26\end{bmatrix} = \begin{bmatrix}-0.69 & 3.59\end{bmatrix}$.

Appendix - Generalized Derivation of Hard Molecule Collision Events

This document will present results for velocity changes following a collision event or well crossing. The prime ' will be used to denote the state after the collision. In this document, vectors are denoted by the overbar arrow.

The change in potential energy for an event is indicated by $\Delta\varepsilon = \varepsilon' - \varepsilon$, which may be positive or negative depending on whether the particles enter or escape from the well. Lower energy is a larger negative value.

Total energy is conserved upon an event between particles *i* and *j*:

$$\frac{1}{2}m_i\vec{v}_i\cdot\vec{v}_i + \frac{1}{2}m_j\vec{v}_j\cdot\vec{v}_j + \varepsilon = \frac{1}{2}m_i\vec{v}_i{}'\cdot\vec{v}_i{}' + \frac{1}{2}m_j\vec{v}_j{}'\cdot\vec{v}_j{}' + \varepsilon' \tag{S7.31}$$

which may be written

$$\frac{1}{2}m_i(\vec{v}_i - \vec{v}_i{}')\cdot(\vec{v}_i + \vec{v}_i{}') = -\frac{1}{2}m_j(\vec{v}_j - \vec{v}_j{}')\cdot(\vec{v}_j + \vec{v}_j{}') + \Delta\varepsilon \tag{S7.32}$$

Defining the contact value for relative position

$$\vec{r}_{ij}{}^c \equiv \vec{r}_i{}^c - \vec{r}_j{}^c \tag{S7.33}$$

The change in momentum for an event is proportional to the collision vector $\vec{r}_{ij}{}^c$,

$$m_i(\vec{v}_i{}' - \vec{v}_i) = -m_j(\vec{v}_j{}' - \vec{v}_j) \propto \vec{r}_{ij}{}^c \tag{S7.34}$$

or

$$\boxed{\frac{(\vec{v}_i{}' - \vec{v}_i)}{m_j} = -\frac{(\vec{v}_j{}' - \vec{v}_j)}{m_i} = \phi\vec{r}_{ij}{}^c} \tag{S7.35}$$

Plugging Eqn. S7.35 into Eqn. S7.32,

$$\phi\vec{r}_{ij}{}^c\cdot(\vec{v}_i + \vec{v}_i{}') = \phi\vec{r}_{ij}{}^c\cdot(\vec{v}_j + \vec{v}_j{}') - 2\Delta\varepsilon/(m_im_j) \tag{S7.36}$$

Rearranging S7.35, also leads to

$$\vec{v}_i{}' = \vec{v}_i + m_j\phi\vec{r}_{ij}{}^c \tag{S7.37}$$

and

$$\vec{v}_j{}' = \vec{v}_j - m_i\phi\vec{r}_{ij}{}^c \tag{S7.38}$$

plugging Eqn. S7.37 and Eqn. S7.38 into Eqn. S7.35 to eliminate the primed variables in Eqn. S7.32,

$$\phi\vec{r}_{ij}^{\,c}\cdot(2\vec{v}_i + m_j\phi\vec{r}_{ij}^{\,c}) = \phi\vec{r}_{ij}^{\,c}\cdot(2\vec{v}_j - m_i\phi\vec{r}_{ij}^{\,c}) - 2\Delta\varepsilon/(m_i m_j) \tag{S7.39}$$

Recognizing $\vec{r}_{ij}^{\,c}\cdot\vec{r}_{ij}^{\,c} = d_{ij}^2$, which is the distance when the event occurs.

$$(m_j + m_i)d_{ij}^2\phi^2 + 2(\vec{r}_{ij}^{\,c}\cdot(\vec{v}_i - \vec{v}_j))\phi + 2\Delta\varepsilon/(m_i m_j) = 0 \tag{S7.40}$$

Defining $\vec{v}_{ij} \equiv (\vec{v}_i - \vec{v}_j)$, and $b_{ij}^c \equiv \vec{r}_{ij}^{\,c}\cdot\vec{v}_{ij}$,

$$(m_j + m_i)d_{ij}^2\phi^2 + 2b_{ij}^c\phi + 2\Delta\varepsilon/(m_i m_j) = 0 \tag{S7.41}$$

Applying the quadratic formula,

$$\phi = \frac{-2b_{ij}^c \pm \sqrt{4(b_{ij}^c)^2 - 8(m_j + m_i)d_{ij}^2\Delta\varepsilon/(m_i m_j)}}{2(m_j + m_i)d_{ij}^2} \tag{S7.42}$$

recognizing the reduced mass, $m_r = (m_i m_j)/(m_i + m_j)$, and factoring constants,

$$\boxed{\phi = \frac{-b_{ij}^c + s\sqrt{(b_{ij}^c)^2 - 2d_{ij}^2\Delta\varepsilon/m_r}}{(m_j + m_i)d_{ij}^2}} \tag{S7.43}$$

where the sign of s depends on the context of the event. The discriminant must be non-negative for physical events, $D = (b_{ij}^c)^2 - 2d_{ij}^2\Delta\varepsilon/m_r \geq 0$. For an event where $\Delta\varepsilon = 0$, then $s = -1$ is the only reasonable solution. For collision of repulsive cores, the event distance is the interparticle radius, $d_{ij} = \sigma_{ij}$ and the relation becomes

$$\boxed{\phi = \frac{-2b_{ij}^c}{(m_j + m_i)\sigma_{ij}^2}} \tag{S7.44}$$

Other cases are discussed elsewhere. In all cases the velocity changes are calculating using the either Eqn. S7.43 or S7.44 along with S7.35.

Compressibility Factor

The compressibility factor for a hard molecule system is calucalated using the virial theorem.

$$\langle E_k\rangle = \frac{3}{2}P\underline{V} + \frac{\sum\limits_{\text{samples over time } t_s} \vec{F}_i\cdot\vec{r}_{ij}^{\,c}}{2t_s} = \frac{3}{2}N_m NkT \tag{S7.45}$$

where t_s is a long sample time. Because the forces are impulses, the magnitude of the forces can be obtained from the change in momentum at each event. The change in momentum for particle *i* will be

$$\vec{F}_i = \Delta\vec{p}_i = m_i m_j\phi\vec{r}_{ij}^{\,c} \tag{S7.46}$$

When the simulation involves only core collisions without wells, the resulting formula is

$$Z = N_m - \frac{2}{3t_sNkT} \sum_{\text{samples over time } t_s} b_{ij}^c m_r \tag{S7.47}$$

When wells are present in the simulation, Eqn. S7.45-6 must be used.