

Technical Memorandum



an HC|ITASCA company

Date: January 6, 2010
To: PFC Development Files and Itasca Website
From: David Potyondy
Re: Internal Technical Memorandum — Molecular Dynamics with PFC

Molecular dynamics (MD) simulation involves solving the classical many-body problem in contexts relevant to the study of matter at the atomistic level. The MD methodology is described in Rapaport (2004), and the methodology for performing MD simulations with the PFC¹ programs that is described in this memo is based on an understanding of MD that is limited to having read Rapaport (2004) and portions of Sutmann (2002).

The introductory section first defines MD simulation, and then situates the PFC programs within the MD framework. The second section presents the Lennard-Jones potential. Then, the PFC implementation of atomic interactions via the Lennard-Jones potential is described in Section 3. The PFC implementation supports any number of atom types with different Lennard-Jones parameters for each combination of atom-atom interaction. Extensions of the PFC implementation to support the TIP4P water molecule are presented in Section 4, and limitations of the PFC implementation are discussed in Section 5.

¹ The term PFC is used to refer to both PFC2D and PFC3D.

1.0 INTRODUCTION

Molecular dynamics (MD) simulation involves solving the classical many-body problem in contexts relevant to the study of matter at the atomistic level. The following excerpts from pages 46–47 of Rapaport (2004) are provided here in an attempt to distill the essence of MD simulation.

Modeling of matter at the microscopic level is based on a comprehensive description of the constituent particles. Although such a description must in principle be based on quantum mechanics, MD generally adopts a classical point of view, typically representing atoms or molecules as point masses interacting through forces that depend on the separation of these objects. More complex applications are likely to require extended molecular structures, in which case the forces will also depend on relative orientation. The quantum picture of interactions arising from overlapping electron clouds has been transformed into a system of masses coupled by exotic ‘springs’. The justification for this antithesis of quantum mechanics is that not only does it work, but it appears to work surprisingly well; on the other hand, the rigorous quantum mechanical description is still hard pressed in dealing with even the smallest systems.

Obviously the structural models and potential functions used in classical MD simulation should not be taken too literally, and the potentials are often referred to as effective potentials in order to clarify their status. The classical approximation to quantum mechanical description of a molecule and its interactions is not derived directly from ‘first principles’, but, rather, is the result of adapting both structure and potential function to a variety of different kinds of information; these include the results of quantum mechanical energy calculations, experimental data obtained by thermodynamic and various kinds of spectroscopic means, the structure of the crystalline state, measurements of transport properties, collision studies using molecular beams, and so on. These models undergo refinement as new comparisons between simulation and experiment become available, and whenever the evidence against a particular model becomes overwhelming, a revised or even an entirely new model must be developed. ...

It is always the simplest models that are tried first. Atoms are modeled as point particles interacting through pair potentials. Molecules are represented by atoms with orientation-dependent forces, or as extended structures, each containing several interaction sites; the molecules may be rigid, flexible, or somewhere in between, and if there are internal degrees of freedom there will be internal forces as well. ... As far as MD is concerned the complexity of the model has little effect on the nature of the computation [Bodies that interact via forces, and whose motion obeys Newton’s laws of motion.], merely on the amount of work involved.

The distinct element method, which is appropriate for the study of granular matter and is the basis of the PFC programs, can be classified as being analogous to MD modeling, although the constituent particles are no longer the atoms and molecules of MD. Rapaport (2004) discusses granular dynamics modeling in Chapter 16, and suggests that

...unlike the molecular scale applications of MD, where the interactions are based on well-founded experimental and theoretical considerations, much remains to be done in order to achieve a detailed understanding of the nature of the interactions between granular particles. In particular, a simplified representation of the salient features of the grain structure and interactions is a prerequisite for simulation, with detailed comparisons between simulation and experiment used to establish how good an approximation has been achieved.

Rapaport characterizes granular dynamics models as being based on inelastically colliding hard or soft spheres (with more complex models utilizing non-spherical particles) that may have rotational motion included in the dynamics and for which normal and tangential velocity-dependent ('viscous') damping forces are used to represent the inelasticity of the interactions. In the terminology of Rapaport, the PFC programs provide a soft-sphere model that includes rotational motion in the dynamics, viscous damping forces at the contacts, and rigid or flexible non-spherical particles that may break.²

² A non-spherical particle can be represented either as a bonded assemblies of spheres or as a rigid clump. The bonded assembly is deformable and may break. The rigid clump is a group of spheres that behaves as a rigid body with a deformable boundary.

2.0 LENNARD-JONES POTENTIAL

The goal of a MD simulation is to compute the atomic trajectories. This requires that the mass and type of each atom be specified, and that a potential function and its associated parameters be specified for each type of pair interaction. The discussion in this section focuses on monatomic systems; extensions to systems with different types of atoms are presented in subsequent sections.

Rapaport (2004) introduces the MD simulation process on pages 11–12 as follows.

The most rudimentary microscopic model for a substance capable of existing in any of the three most familiar states of matter — solid, liquid and gas — is based on spherical particles [more precisely, point masses of zero extent] that interact with one another; in the interest of brevity such particles will be referred to as atoms (albeit without hint of their quantum origins). The interactions, again at the simplest level, occur between pairs of atoms and are responsible for providing the two principal features of an interatomic force. The first is a resistance to compression, hence the interaction repels at close range. The second is to bind the atoms together in the solid and liquid states, and for this the atoms must attract each other over a range of separations. Potential functions exhibiting these characteristics can adopt a variety of forms and, when chosen carefully, actually provide useful models for real substances.

The best known of these potentials, originally proposed for liquid argon, is the Lennard-Jones (LJ) potential; for a pair of atoms i and j located at \mathbf{r}_i and \mathbf{r}_j the potential energy is

$$u(r_{ij}) = u_{ij} = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], & r_{ij} < r_c \\ 0, & r_{ij} \geq r_c \end{cases} \quad (1)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and $r_{ij} = |\mathbf{r}_{ij}|$ is the separation distance³. The parameter ε governs the strength of the interaction and σ defines a length scale; the interaction repels at close range, then attracts, and is eventually cut off at some limiting separation r_c . While the strongly repulsive core arising from (in the language of quantum

³ Atoms are considered to be point masses of zero extent; they are NOT finite-radius spheres. However, it is convenient to visualize them as finite-radius spheres. To do this in PFC, we associate a ‘true’ radius with each particle as described in Section 3.0. The true radius is used only for visualization, and does not affect the behavior of the model.

mechanics) the nonbonded overlap between the electron clouds has a rather arbitrary form, and other powers and functional forms are sometimes used, the attractive tail actually represents the van der Waals interaction due to electron correlations. The interactions involve individual pairs of atoms: each pair is treated independently, with other atoms in the neighborhood having no effect on the force between them.

A system subject to the LJ potential can exist in the solid, liquid, or gaseous states; the attractive part of the potential is used to bind the system when in the solid and liquid states, and the repulsive part prevents collapse. When the particles represented by this potential are repelling one another, they are analogous to soft spheres, although softness is confined to a very narrow range of separations and the spheres rapidly tend to become hard as they are driven together.

The LJ model has parameters ε , σ and r_c : ε is the van der Waal binding energy, σ is the van der Waal diameter and r_c is the cut-off distance. Typical values for the monatomic fluid of liquid argon are $\varepsilon = 1.66 \times 10^{-21}$ J, $\sigma = 3.4 \times 10^{-10}$ m and $r_c = 8.5 \times 10^{-10}$ m, with the atomic mass $m = 6.69 \times 10^{-26}$ kg. If N_m atoms occupy a cubic region of edge length L , then a typical liquid density of 0.942 g/cm^3 implies that $L = 4.142 N_m^{1/3} \times 10^{-10}$ m. One thousand atoms of liquid argon would occupy a cubic region of edge length 41.4×10^{-10} m, and one million atoms of liquid argon would occupy a cubic region of edge length 41.4 nanometers — a small world, indeed!

The force corresponding to the LJ potential that atom j exerts on atom i is

$$\mathbf{f}_{ij} = -\nabla u(r_{ij}) = -\frac{\partial u}{\partial r_{ij}} \hat{\mathbf{r}}_{ij} = \begin{cases} f_{ij} \hat{\mathbf{r}}_{ij}, & r_{ij} < r_c \\ 0, & r_{ij} \geq r_c \end{cases}, \quad f_{ij} = 24\varepsilon [2\sigma^{12} r_{ij}^{-13} - \sigma^6 r_{ij}^{-7}] \quad (2)$$

where the unit vector directed from atom j to atom i is $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$. A positive value of f_{ij} denotes repulsion. The stiffness corresponding to the LJ potential that exists between atom j and atom i is

$$k_{ij} = \left| \frac{\partial f_{ij}}{\partial r_{ij}} \right| = 24\varepsilon \left| -26\sigma^{12} r_{ij}^{-14} + 7\sigma^6 r_{ij}^{-8} \right| \quad (3)$$

The following observations can be made about the form of the LJ potential and its associated force and stiffness by studying the plots of u_{ij} , f_{ij} and k_{ij} for liquid argon in Figures 1–6.

1. The cut-off distance (r_c) is shown in Figure 1, and the van der Waal diameter (σ) and van der Waal binding energy (ε) are shown in Figure 2. σ is the separation distance at

which the potential energy is zero. ε is the minimum potential energy, which occurs at a separation distance of $r_\varepsilon = 2^{1/6}\sigma$, and at which the interatomic force is zero.

2. For separation distances $r_{ij} < r_\varepsilon$, the force is repulsive, and the stiffness becomes extremely large as the atoms are driven together; for separation distances $r_{ij} \geq r_\varepsilon$, the force is attractive, and the stiffness is near zero.

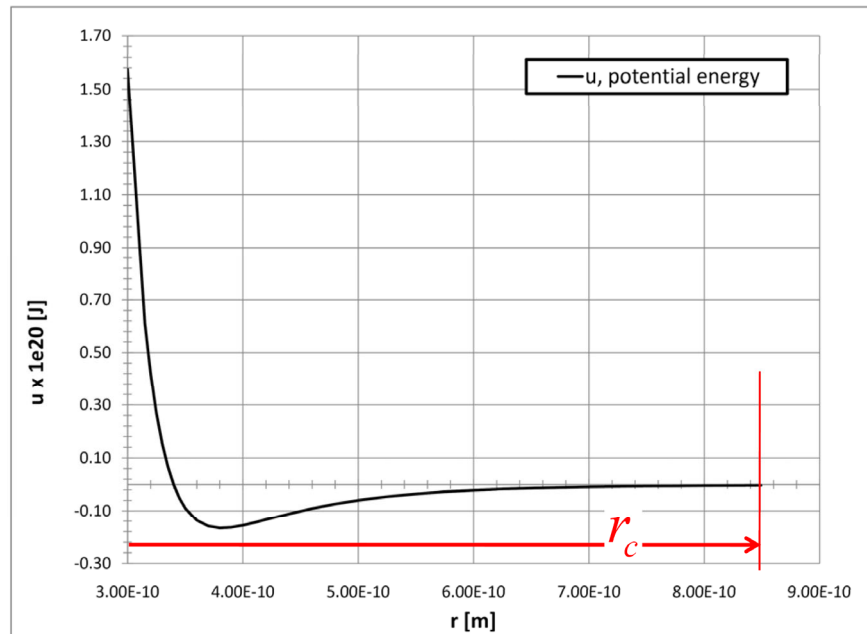


Figure 1 Potential energy versus separation distance (LJ model of liquid argon)

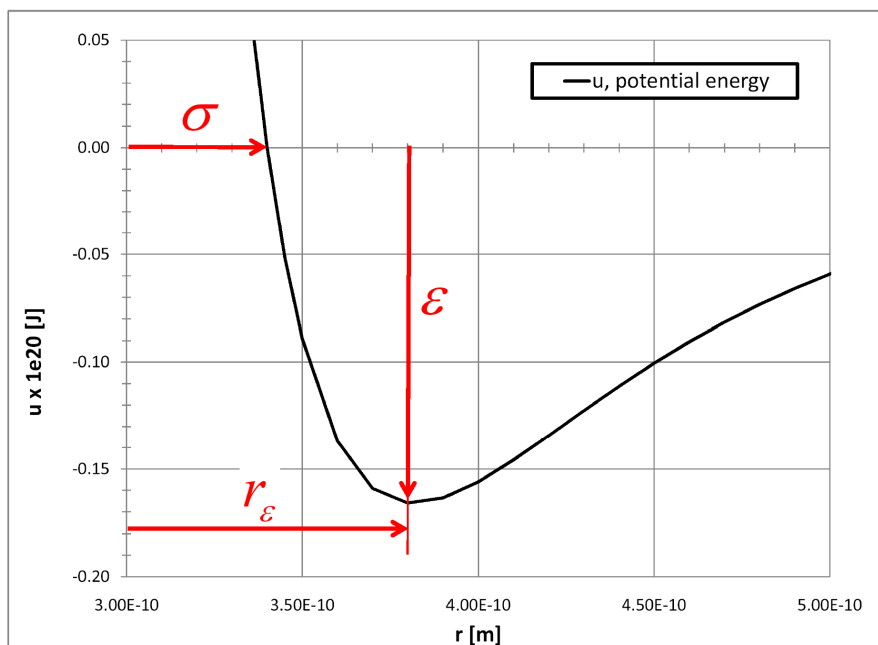


Figure 2 Potential energy versus separation distance, zoom (LJ model of liquid argon)

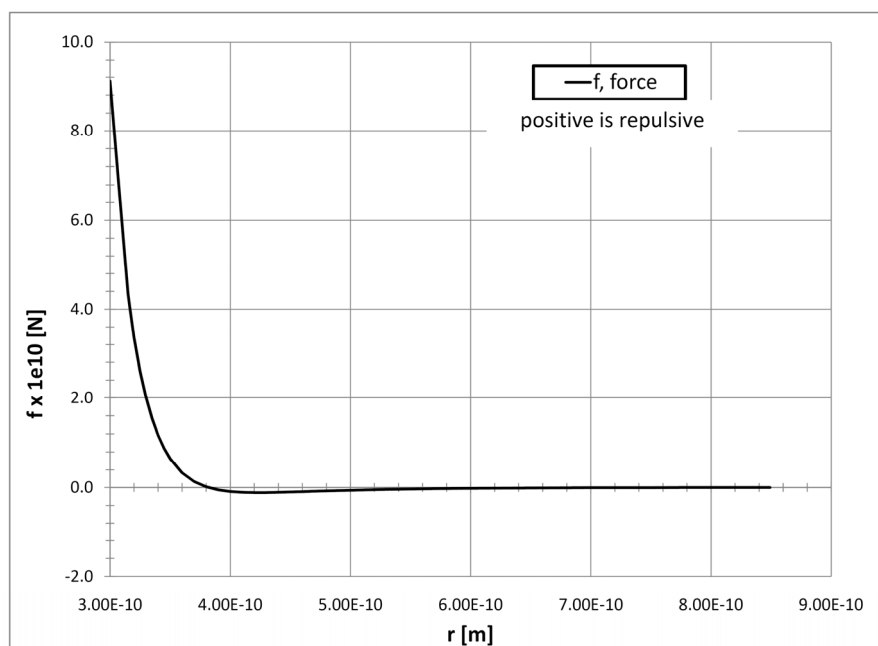


Figure 3 Force versus separation distance (LJ model of liquid argon)

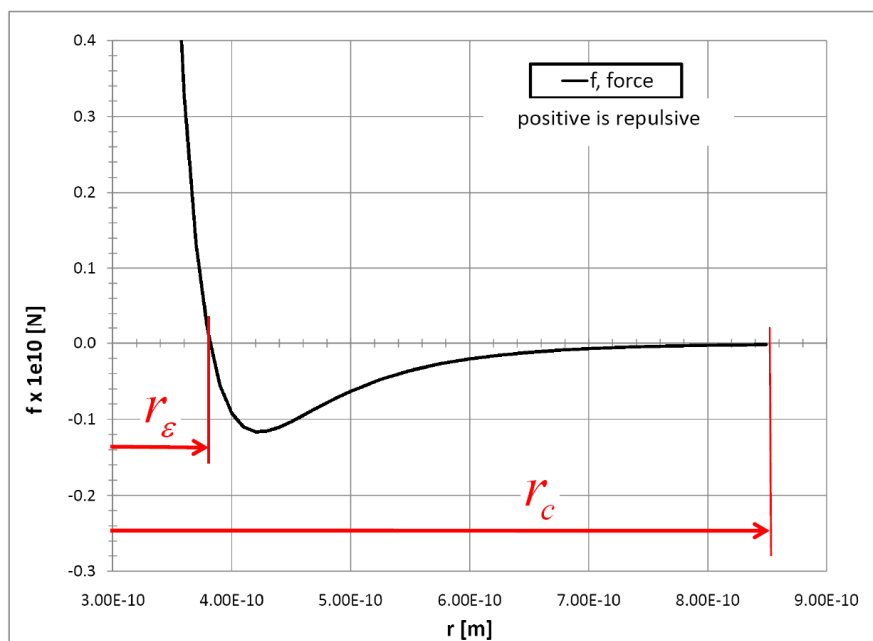


Figure 4 Force versus separation distance, zoomed (LJ model of liquid argon)

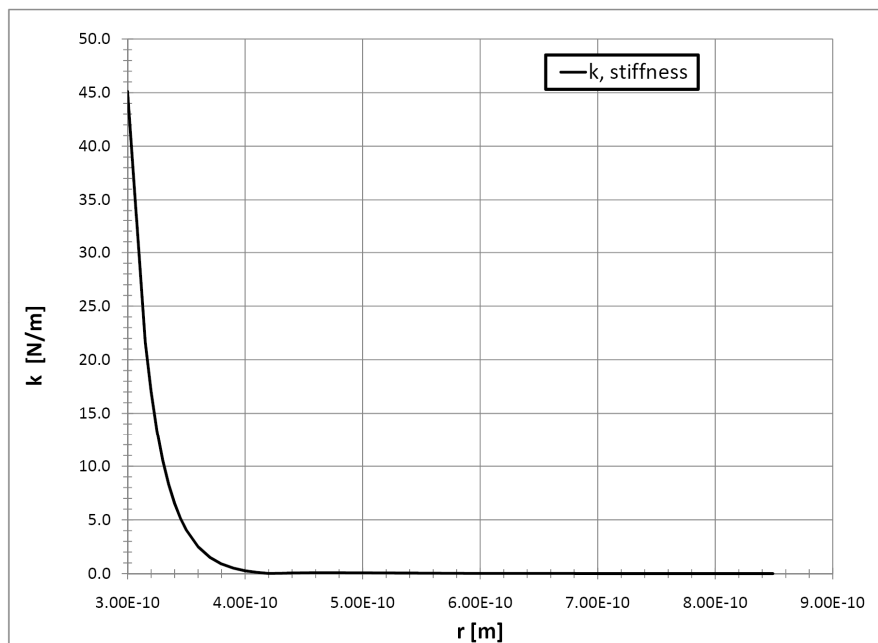


Figure 5 Stiffness versus separation distance (LJ model of liquid argon)

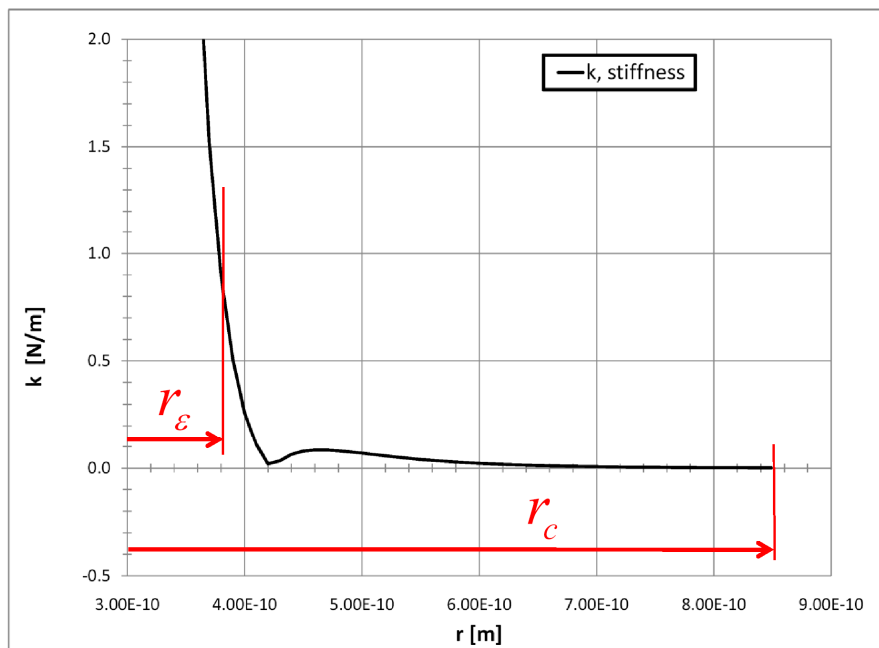


Figure 6 Stiffness versus separation distance, zoomed (LJ model of liquid argon)

3.0 PFC IMPLEMENTATION OF LJ MODEL

In the PFC program, all pair interactions occur at contacts. There is a contact model associated with each contact. The contact model describes the force-displacement response. During each cycle, the PFC program calls each contact model (and makes available relevant information about the two contacting entities such as size, position and velocity), and the contact model updates the force, moment and stiffness. The force and moment then are applied in an equal and opposite sense to the two contacting entities, and the stiffness is used to determine a stable timestep. A cell-space (CS) reduces the computational effort of determining pair interactions. The CS implementation localizes the search for candidate particle pairs, and guarantees that a contact will be created before any two particles overlap. The approach is well-suited for granular systems in which each particle represents a finite-radius sphere, and for which contacts must form when the spheres overlap.⁴ The CS supports contact models with cut-off distances less than or equal to the sum of the radii of the two contacting spheres. In order to support contact models with larger cut-off distances, such as the LJ model, the following steps must be taken.

1. Equate each atom with a particle, and assign a type to each particle to denote the type of atom — e.g., argon, oxygen, etc.

Implementation: Store the particle type in the first slot of the `b_extra` variable associated with each particle.

2. Create a table of all possible atom-atom interactions — e.g., argon-argon, argon-oxygen, etc. For each interaction, specify the contact model and its associated parameters, one of which will be the cut-off distance (r_c).

Implementation: Provide a user-defined contact model for each type of interaction. Create an interaction table to accommodate the N_{cm} possible atom-atom interactions. For each interaction, store the name of the contact model and its parameters. (For the monatomic fluid of liquid argon, $N_{cm} = 1$, the contact model is the LJ model, and the parameters are ϵ , σ and r_c . The LJ contact model computes r_{ij} and then uses equations (2) and (3) to update the force and stiffness at the contact.) Register a FISH function to be called whenever a contact is created. The registered function will determine the atom types of the two contacting particles, and then will use the data in the interaction table to assign the appropriate contact model and its parameter values.

⁴ After a contact is created, it may remain active with a non-zero force even if the particles no longer overlap as the result of subsequent motion. A parallel bond provides such behavior.

3. Assign a ‘true’ radius (R_T) and an interaction radius (R_I) to each particle — see Figure 7. The true radius is used to visualize the particle. (For the monatomic fluid of liquid argon, one can set $R_T = \sigma/2$ such that an interatomic force of zero corresponds with a gap between the two atoms, and a repulsive force exists when the two atoms just begin to overlap.) The interaction radius is used to ensure that a contact between this particle and a potential interacting particle will be created before the separation distance becomes less than the cut-off distance — i.e., a contact between particles i and j will be created before $r_{ij} < r_c$, where r_c is the cut-off distance of the contact model. (For the monatomic fluid of liquid argon, this is achieved by setting $R_I = r_c/2$ for all particles. For a model containing different types of atoms and contact models, each R_I must be chosen such that $(R_I)_i + (R_I)_j \geq (r_c)_{ij}$ where $(r_c)_{ij}$ is the cut-off distance of the contact model at the contact between particles i and j . The cut-off distances for all possible atom-atom interactions must be considered when assigning particle interaction radii.)

Implementation: Store the particle true radius in the second slot of the `b_extra` variable associated with each particle. Provide a FISH plot item that uses these data to draw the particles at their current locations. In the PFC model, set the radius of each particle equal to its interaction radius. By doing this, we utilize the existing CS implementation to ensure that contacts form (Thus, contact models exist.) before the separation distance of interacting particles becomes less than their associated cut-off distances.

4. Assign a mass to each particle.

Implementation: Store the particle mass in the third slot of the `b_extra` variable associated with each particle. Create a FISH function that will be called after all particles are created. The FISH function sets the density of each particle to satisfy $\rho = m/V$, where m is the particle mass and V is the particle volume (which is a function of particle radius). This is an awkward procedure, but it is necessary because particle mass cannot be set directly in PFC, but instead is computed based on particle radius and density.

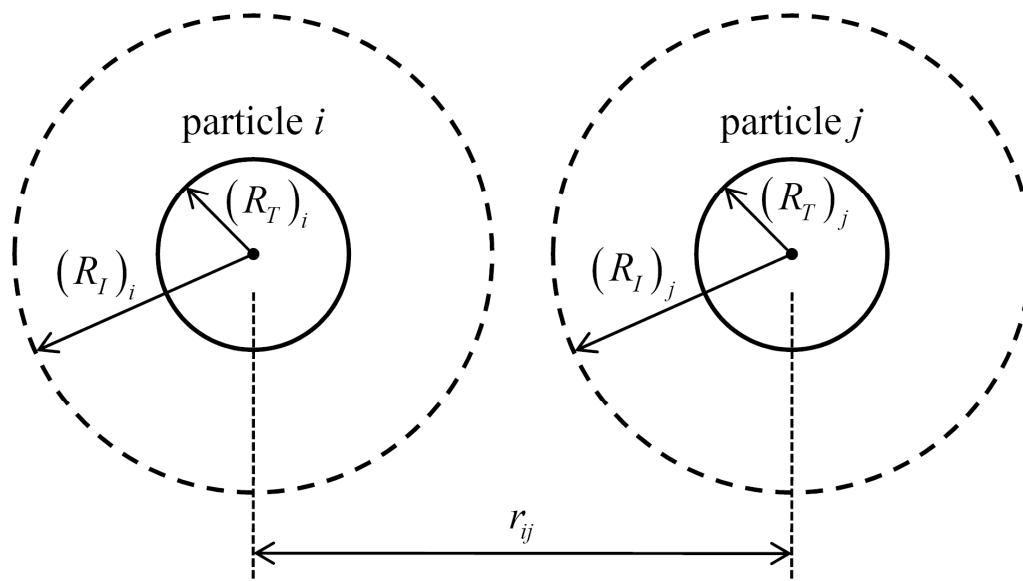


Figure 7 Sketch of separation distance as well as true and interaction radii of particles i and j

3.1 Implementation of LJ model

The steps described above are implemented in PFC2D/3D 4.0-149 and PFC Fishtank 1-92⁵. The implementation consists of a user-defined contact model in the `udm` directory, a set of FISH functions in the file `fist\2d_3d\pmd.fis`, and two- and three-dimensional usage examples in the directories `fist\templates\pmd-{2,3}d`. The Lennard-Jones model described in Section 2.0 is provided in the PFC programs by using the Lennard-Jones and Coulomb (LJC) model and setting the charge product equal to zero. The LJC model adds Coulomb interactions to the LJ model and is described in Section 4.1.1. The implementation supports atom-atom interactions via the LJC model. Any number of atom types can be specified along with a set of LJC parameters for each atom-atom combination.

3.2 Usage Examples of LJ model

The first usage example simulates seven argon atoms initially placed in the xy plane as shown in Figure 8. The PFC2D model results are produced by calling `fist\templates\pmd-2d\pmd-2d.dvr`, and the PFC3D model results are produced by calling `fist\templates\pmd-3d\pmd-3d.dvr`. The PFC2D model uses the **SET DISK OFF**

⁵ The latest PFC3D 4.0 executable can be obtained from <http://www.itascacg.com/software/downloads.php>.

command to treat all particles as spheres; thus, both models produce identical results. The atom interactions use the LJ model for liquid argon described above. If the model is run with high damping, we obtain the final stable configuration with near-zero atom velocities shown in Figure 9. The atoms have rearranged themselves into a single conglomerate with a self-equilibrating internal force system. If the model is run with no damping, then the kinetic energy is not dissipated, and the atoms continue to vibrate. After 1200 steps, two conglomerates have formed, as shown in Figure 10. The kinetic energy of this system corresponds with the temperature of the system.

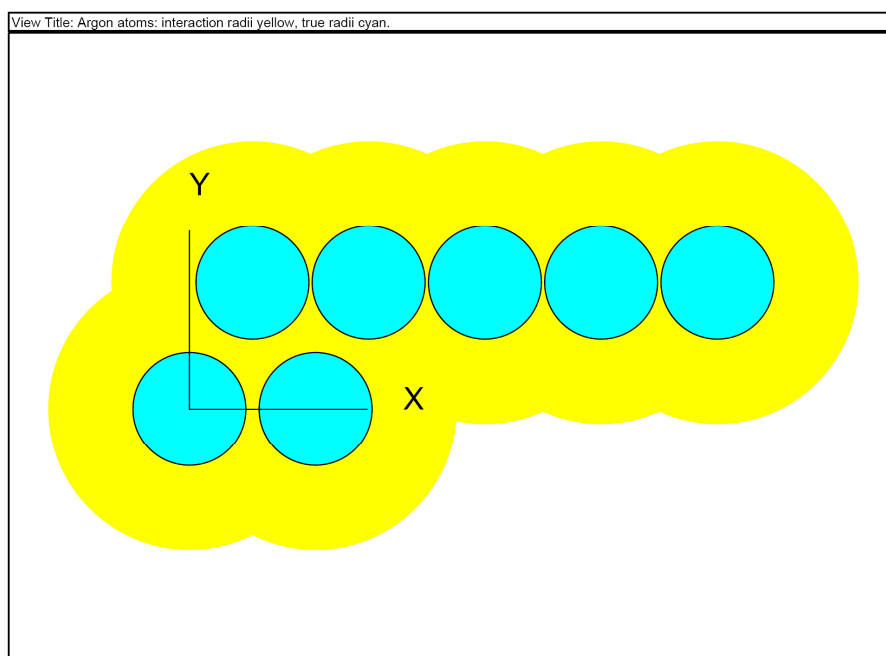


Figure 8 *Initial system consisting of seven argon atoms with zero velocity (interaction radii in yellow, true radii in cyan)*

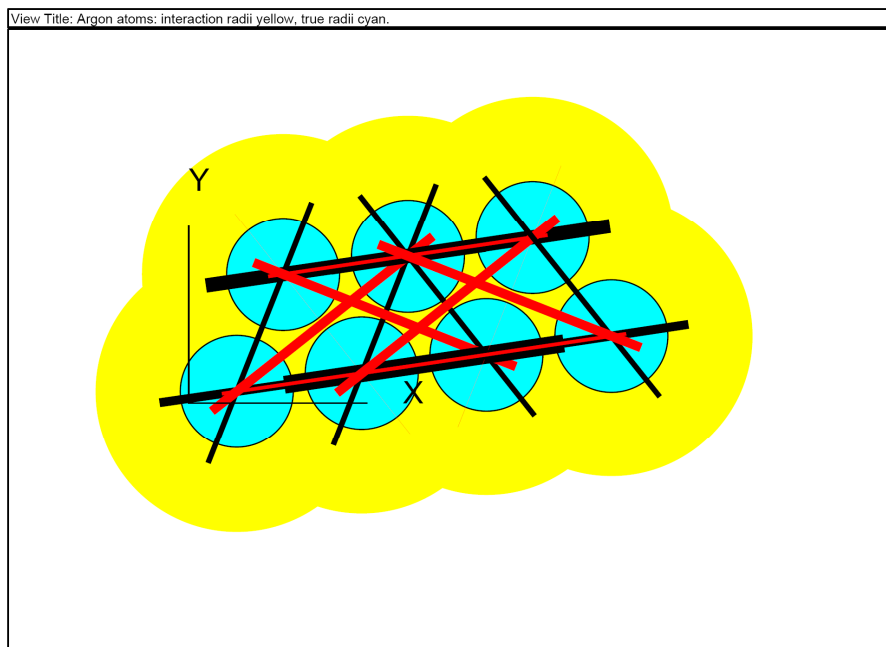


Figure 9 Final stable system configuration when run with high damping (contact forces in black and red to denote compression and tension, respectively)

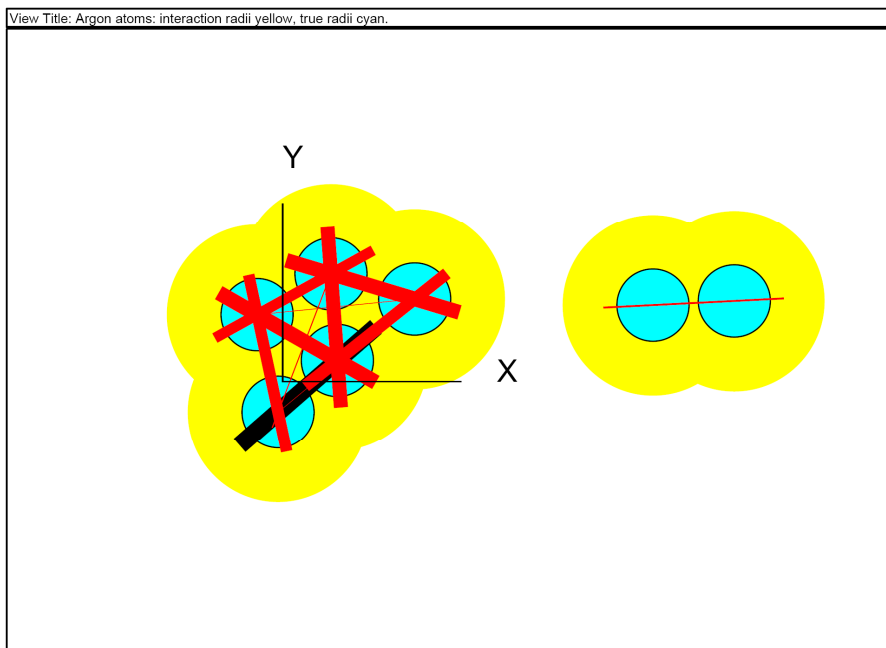


Figure 10 System configuration after 1200 timesteps (constant timestep size of $1e-14$ seconds) when run with no damping

The following comments can be made about the damping and the criterion for selecting the size of the timestep Δt .

1. Kinetic energy can be removed from the PFC model by using local damping (**DAMP LOCAL** command). If we turn off damping, then we obtain the true dynamic response. If we turn on damping, then we may reach a stable configuration.
2. The time integration scheme used in PFC is second-order accurate if Δt remains constant, but degrades to first-order accuracy if Δt changes. The best accuracy is obtained by keeping Δt constant (use the **SET DT MAX** command). If PFC is allowed to modify Δt (**SET DT AUTO** command), the rapidly changing stiffnesses of the LJ model may cause large and rapid changes in Δt , which, in turn, will degrade the accuracy. This effect may be reduced, but not eliminated, by decreasing the computed timestep size (**SET SAFETY_FAC** command).

If the true dynamic response is desired, then Δt should be kept constant. However, if the path that the system traverses is not important, and a well-defined minimum energy state exists and it is only this state that one wishes to obtain, then it may be acceptable to use damping and allow Δt to vary — doing so will decrease the total number of steps required to arrive at the final state.

The second usage example simulates a more complex initial system, consisting of 40 arbitrarily positioned argon atoms, by calling `argon_assembly-{2,3}d.dvr`. The atoms have different initial positions in the PFC2D and PFC3D models. Both models are run with high damping until a stable configuration is reached. In both models, the atoms have rearranged themselves into a small number of conglomerates (see Figures 11 and 12). Two animations (in the form of AVI files) showing the evolution of the atom positions and the internal forces are produced for each model. The dynamics of the conglomeration process are evident in these animations.

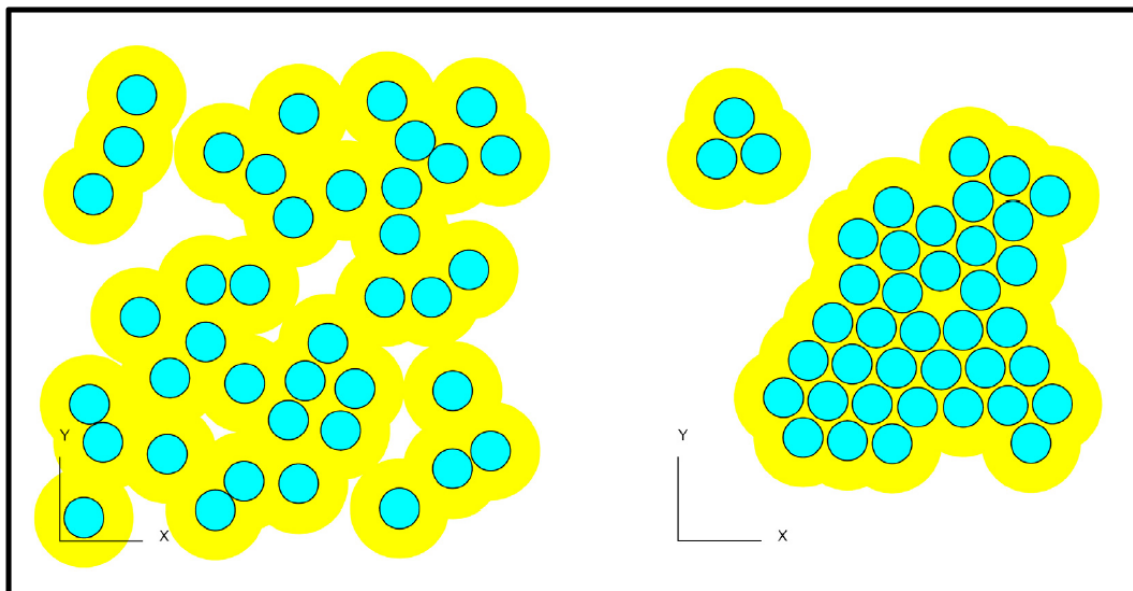


Figure 11 PFC2D initial and final system configurations (interaction radii in yellow, true radii in cyan)

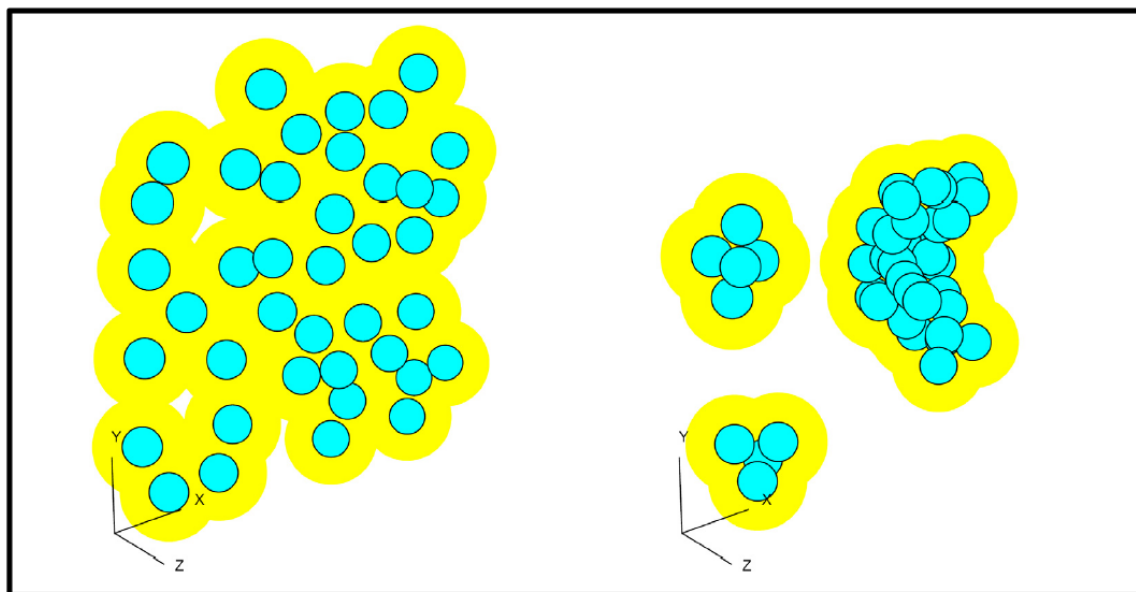


Figure 12 PFC3D initial and final system configurations (interaction radii in yellow, true radii in cyan)

4.0 PFC IMPLEMENTATION OF TIP4P WATER MOLECULE

The implementation that supports atom-atom interactions described in the previous section is here extended to support molecule-molecule interactions for the TIP4P rigid water molecule. The interactions between these rigid molecules are expressed as sums of contributions from pairs of ‘interaction sites’ on different molecules. In the first section, we extend the LJ model to include Coulomb interaction. The new model is called the LJC model, and this model is used for the interactions that occur between interaction sites of the water molecules, which are described in the second section.

4.1 Lennard-Jones and Coulomb Potential

The LJ model is extended to include Coulomb interactions between the electric charges of the atoms by adding a term to (1) that accounts for the charge interaction. The new potential is called the Lennard-Jones and Coulomb (LJC) potential; for a pair of atoms i and j located at \mathbf{r}_i and \mathbf{r}_j the potential energy is

$$u(r_{ij}) = u_{ij} = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \frac{Q}{r_{ij}}, & r_{ij} < r_c \\ 0, & r_{ij} \geq r_c \end{cases} \quad (4)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and $r_{ij} = |\mathbf{r}_{ij}|$ is the separation distance. The LJC model has parameters: ε , σ , Q and r_c . ε is the van der Waal binding energy; σ is the van der Waal diameter; $Q = q_i q_j$ is the charge product, where q_i and q_j are the charges of atoms i and j , respectively⁶; and r_c is the cut-off distance. Typical values for the pair interaction of a negatively charged oxygen ion (O^-) and a positively charged sodium ion (Na^+) are $\varepsilon = 3.47 \times 10^{-21}$ J; $\sigma = 2.45 \times 10^{-10}$ m;

⁶ We store the charge product with the LJC model to increase computational speed by eliminating the need during each force update to obtain the charge values from the two atoms. If the charge of a particular atom is changed during a simulation, then the charge products in all LJC models associated with that atom must also be changed.

$Q = q_{\text{O}^-} q_{\text{Na}^+} = (-1.04e)(+1.00e)$, where e is the elementary charge⁷; and $r_c = \infty$ ⁸. The atomic masses⁹ are $m_{\text{O}} = 15.9994 \text{ u} \cong 2.66 \times 10^{-26} \text{ kg}$ and $m_{\text{Na}} = 22.98977 \text{ u} \cong 3.82 \times 10^{-26} \text{ kg}$.

The force corresponding to the LJC potential that atom j exerts on atom i is

$$\mathbf{f}_{ij} = -\nabla u(r_{ij}) = -\frac{\partial u}{\partial r_{ij}} \hat{\mathbf{r}}_{ij} = \begin{cases} f_{ij} \hat{\mathbf{r}}_{ij}, & r_{ij} < r_c \\ 0, & r_{ij} \geq r_c \end{cases} \quad f_{ij} = 24\epsilon \left[2\sigma^{12} r_{ij}^{-13} - \sigma^6 r_{ij}^{-7} \right] + Q r_{ij}^{-2} \quad (5)$$

where the unit vector directed from atom j to atom i is $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij} / r_{ij}$. A positive value of f_{ij} denotes repulsion. The stiffness corresponding to the LJC potential that exists between atom j and atom i is

$$k_{ij} = \left| \frac{\partial f_{ij}}{\partial r_{ij}} \right| = \left| 24\epsilon \left(-26\sigma^{12} r_{ij}^{-14} + 7\sigma^6 r_{ij}^{-8} \right) - 2Q r_{ij}^{-3} \right| \quad (6)$$

Plots of u_{ij} , f_{ij} and k_{ij} for the $\text{O}^- - \text{Na}^+$ interaction are shown in Figures 13–15.

⁷ The charges are expressed in terms of the mechanical quantities of time, length and mass by dividing the elementary charge by $\sqrt{4\pi\epsilon_0}$, where ϵ_0 is the vacuum permittivity. The charge product is

$$Q = (-1.04)(+1.00) \left(\frac{e^2}{4\pi\epsilon_0} \right) = -2.40 \times 10^{-28} \text{ Jm} \quad (e = 1.602176487 \times 10^{-19} \text{ C and } \epsilon_0 = 8.854187817 \times 10^{-12} \text{ C}^2/\text{Jm}).$$

⁸ The potential energy arising from Coulomb interaction is non-zero for all separation distances; however, to limit the computational burden, one may specify a finite cut-off distance that serves to reduce the number of pair interactions that will be considered. The effect of this choice must be studied for each particular system.

⁹ Atomic and molecular masses are expressed in unified atomic mass units (u), and $1 \text{ u} = 1.66053886 \times 10^{-27} \text{ kg}$.

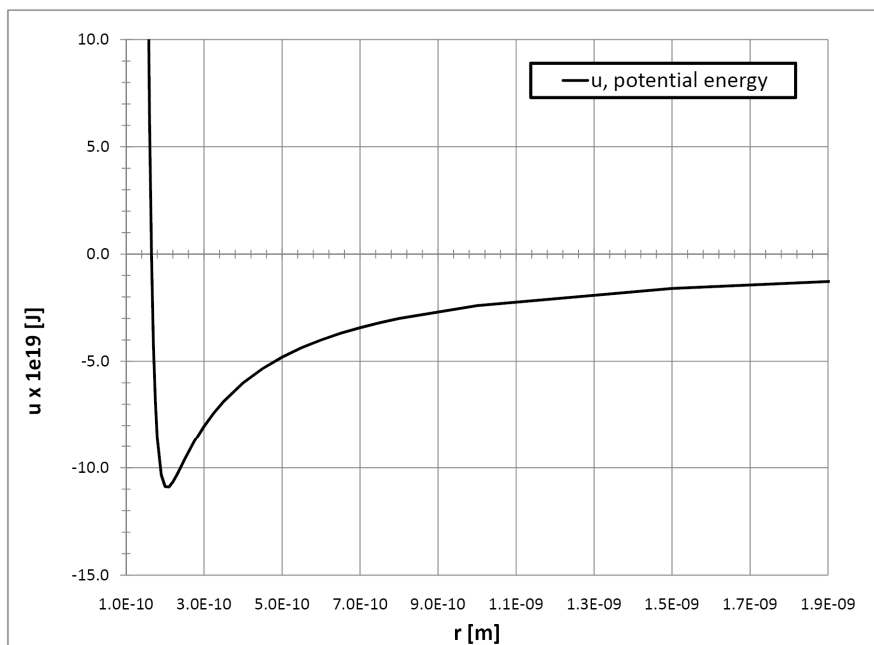


Figure 13 Potential energy versus separation distance (LJC model of oxygen-sodium interaction)

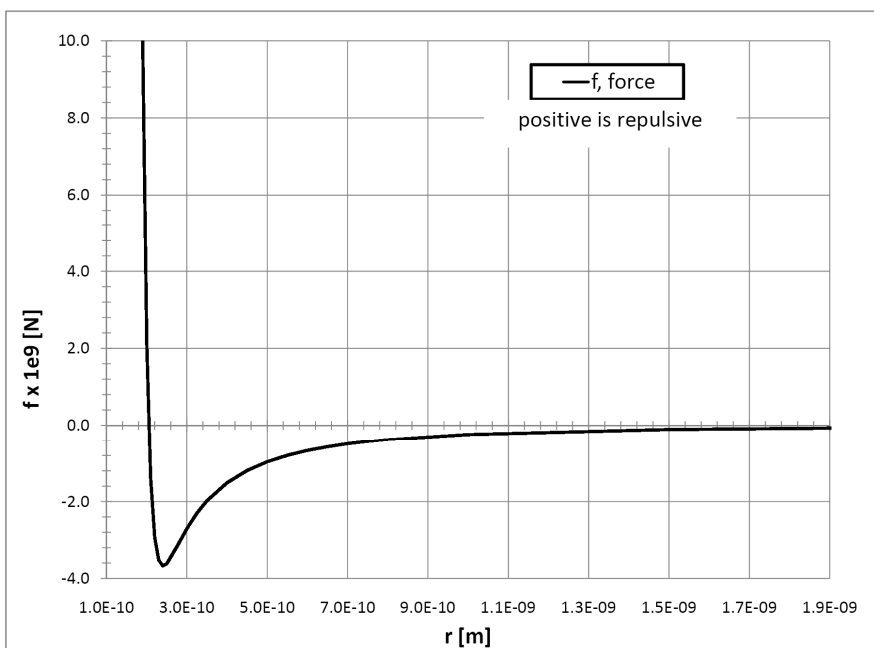


Figure 14 Force versus separation distance (LJC model of oxygen-sodium interaction)

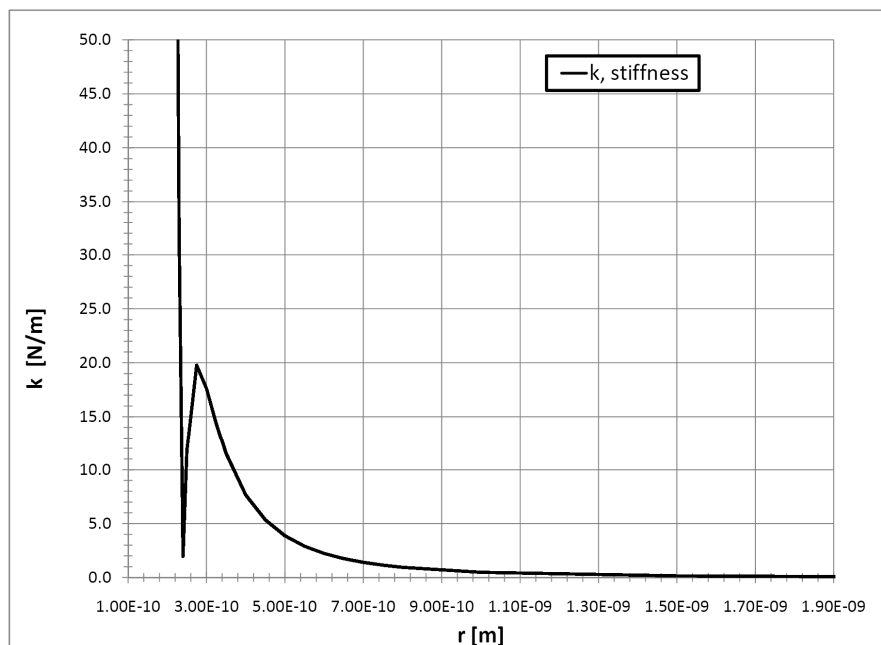


Figure 15 Stiffness versus separation distance (LJC model of oxygen-sodium interaction)

4.1.1 PFC Implementation of LJC Model

The LJC model is implemented in PFC2D/3D 4.0-149 and PFC Fishtank 1-92. The implementation consists of a user-defined contact model in the `udm` directory, a set of FISH functions in the file `fist\2d_3d\pmd.fis`, and two- and three-dimensional usage examples in the directories `fist\templates\pmd-{2,3}d`. The implementation supports atom-atom interactions via the LJC model. Any number of atom types can be specified along with a set of LJC parameters for each atom-atom combination. The user-defined contact model and a usage example are described in the following sections.

4.1.1.1 LJC Contact Model

The Lennard-Jones and Coulomb model is provided in the PFC programs by the LJC contact model. The LJC model is implemented as a user-defined contact model¹⁰ with C++ source files of `ljc.cpp` and `ljc.h`, which are compiled into `udm_LJC_{32,64}.dll`. The 32 and 64 suffixes indicate compatibility with the 32- or 64-bit executable, respectively. The DLL file contains two- and three-dimensional implementations and, thus, can be used with either the

¹⁰ This is an optional model and requires the User-Defined contact Model (UDM) portion of the C++/UDM option.

PFC2D 4.0 or PFC3D 4.0 programs. The model name is **udm_LJC**, and the property names are prefixed by **ljc_**.

The LJC model has the following properties.

- **ljc_type**: interaction type — e.g., oxygen-sodium (The value is an integer denoting the slot in the interaction table that contains the interaction name.)
- **ljc_eps**: van der Waal binding energy (ϵ)
- **ljc_sig**: van der Waal diameter (σ)
- **ljc_Q**: charge product (Q)
- **ljc_rc**: cut-off distance (r_c)

The following internal state variables can also be accessed.

- **ljc_rij**: separation distance (r_{ij})
- **ljc_kij**: stiffness (k_{ij})
- **ljc_uij**: potential energy (u_{ij})

4.1.1.2 LJC Usage Example

The usage example simulates one negatively charged oxygen ion (O^-) and one positively charged sodium ion (Na^+) initially placed in the xy plane with a separation distance of 9.0×10^{-10} m. The PFC2D model results are produced by calling `fist\templates\pmd-2d\pmd_ljc-2d.dvr`, and the PFC3D model results are produced by calling `fist\templates\pmd-3d\pmd_ljc-3d.dvr`. The PFC2D model uses the **SET DISK OFF** command to treat all particles as spheres; thus, both models produce identical results. This oxygen-sodium system contains two atom types. The true radius of each atom type is set equal to one-half of the van der Waal diameter of self interaction: $(R_T)_{O^-} = \frac{1}{2}(\sigma)_{O^-O^-} \cong 1.58 \times 10^{-10}$ m and $(R_T)_{Na^+} = \frac{1}{2}(\sigma)_{Na^+Na^+} \cong 0.95 \times 10^{-10}$ m. The interaction radii are set equal to one-half of the cut-off distance for $O^- - Na^+$ interaction: $(R_I)_{O^-} = (R_I)_{Na^+} = \frac{1}{2}(r_c)_{O^-Na^+} = 9.5 \times 10^{-10}$ m. The LJC parameters and atomic masses are listed after Equation (4).

The model is run with high damping and a fixed timestep size of 1×10^{-15} s. We obtain a final stable configuration with near-zero particle velocities at a separation distance of 2.05×10^{-10} m. This value corresponds with the separation distance at which the contact force is zero, which is the expected and correct result.

4.2 TIP4P Water Molecule

The following excerpts from Chapter 8 of Rapaport (2004) describe MD modeling of rigid molecules and introduce the TIP4P water molecule.

The elementary constituents of most substances are structured molecules, rather than the spherically symmetric atoms described above. Small, relatively compact molecules can be constructed from a rigidly linked atomic framework. There is really no such thing as a rigid molecule, but from the practical point of view it is a very effective simplification of the underlying quantum problem. Interactions between rigid molecules are most readily introduced by specifying the locations of the sites in the molecule at which the forces act. The total force between two molecules is then simply the sum of the forces acting between all pairs of interaction sites. Interaction sites may be associated with the positions of the nuclei, but this is not essential and often just serves as the initial version of a model. There is considerable scope for fine-tuning the structure and interactions in this engineering-like approach, with the simulations themselves being used to refine the models.

The most popular molecular fluid for MD exploration is water. Not only because of its ubiquity and importance, but also for its many unusual features that defy simple explanation, water has long been associated with MD simulation and numerous models have been proposed to help understand the microscopic mechanisms underlying the behavior. The TIP4P water molecule is one of several available rigid models.

A theoretical description of the TIP4P water molecule is provided in the first section. This is followed by a discussion of how the molecule has been implemented in PFC in the second section, which includes a usage example.

4.2.1 Theoretical Description

The model molecule is based on four interaction sites located in a planar configuration (see Figure 16). The sites labeled M and O are associated with the oxygen nucleus, while the sites labeled H are associated with the protons. For a pair of molecules i and j , the potential energy is

$$u^{ij} = \sum_{k \in i} \sum_{l \in j} u(r_{kl}) \quad (7)$$

where $u(r_{kl})$ is the LJC potential of Eqn. (4) with k and l ranging over the four interaction sites of each molecule. The LJ part of the potential acts only between O sites, and the LJ parameters are

$$\begin{aligned}\varepsilon_{O-O} &= 1.08 \times 10^{-21} \text{ J} \\ \varepsilon_{O-M} &= \varepsilon_{O-H} = \varepsilon_{M-M} = \varepsilon_{M-H} = \varepsilon_{H-H} = 0 \\ \sigma_{O-O} &= 3.15 \times 10^{-10} \text{ m} \\ \sigma_{O-M} &= \sigma_{O-H} = \sigma_{M-M} = \sigma_{M-H} = \sigma_{H-H} = 0\end{aligned}\tag{8}$$

The charges in the Coulomb part of the potential are

$$q_H = 0.52e, \quad q_O = 0, \quad q_M = -2q_H\tag{9}$$

which yield charge products:

$$\begin{aligned}Q_{O-O} &= Q_{O-M} = Q_{O-H} = 0 \\ Q_{M-M} &= +2.50 \times 10^{-28} \text{ Jm}, \quad Q_{M-H} = -1.25 \times 10^{-28} \text{ Jm}, \quad Q_{H-H} = +6.24 \times 10^{-29} \text{ Jm}\end{aligned}\tag{10}$$

All cut-off distances of the LJC potential are made effectively infinite by setting them equal to the maximum extent of the modeled region: $r_c = r_E$. If the cut-off distances are made effectively finite, then special coding will be required to ensure that there are no partially interacting molecules (see page 219 of Rapaport (2004)). The interaction radii of all sites are taken as one-half of the single cut-off distance: $R_I = \frac{1}{2}r_E$. The true radii of all sites are chosen to produce good visualization of each molecule; by setting $R_T = 7.5 \times 10^{-12}$ m for all sites, the O and M sites just touch (see Figure 17). The site masses are

$$\begin{aligned}m_O &= 15.9994 \text{ u} \cong 2.66 \times 10^{-26} \text{ kg} \\ m_M &= 0 \\ m_H &= \frac{1}{16} m_O \cong 1.66 \times 10^{-27} \text{ kg}\end{aligned}\tag{11}$$

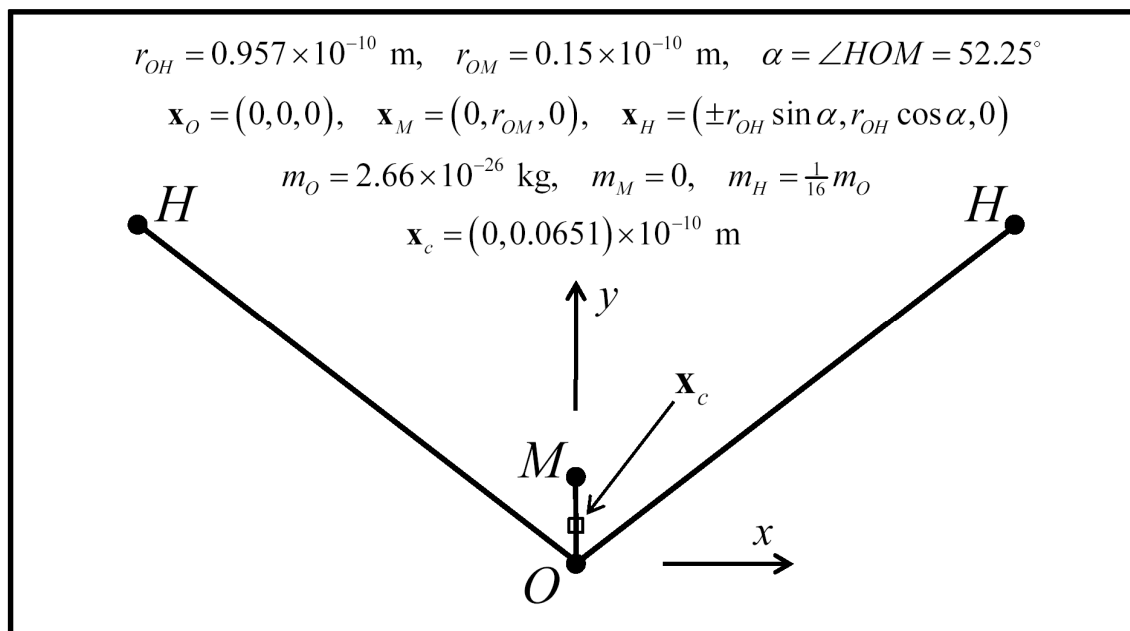


Figure 16 Interaction sites and associated masses of the TIP4P water molecule

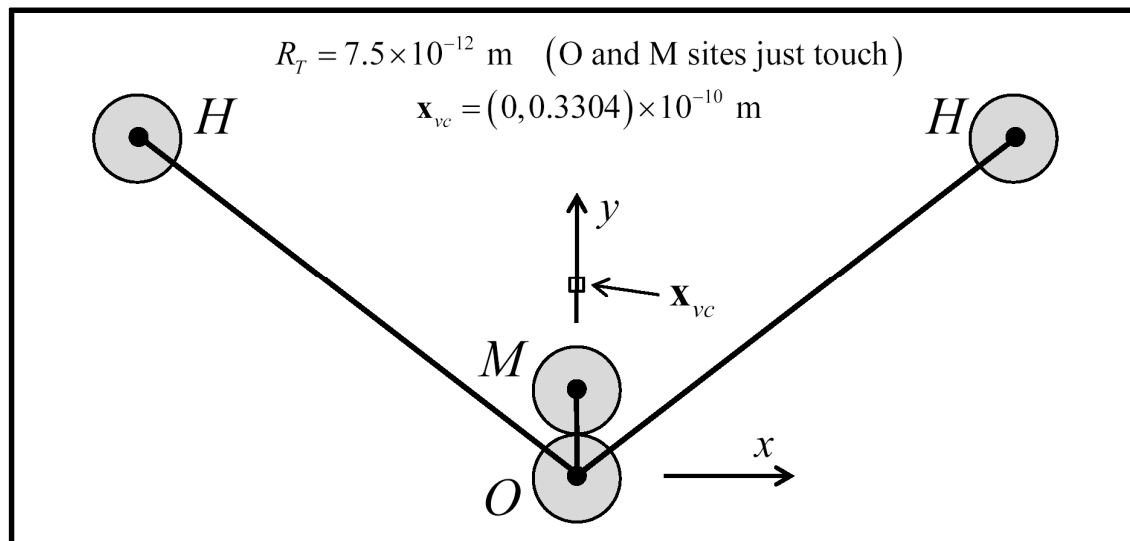


Figure 17 The TIP4P water molecule with true radii chosen to produce good visualization of the molecule

4.2.2 PFC Implementation of TIP4P Water Molecule

The TIP4P water molecule is implemented in PFC2D/3D 4.0-149 and PFC Fishtank 1-92. The implementation utilizes the LJC model (described above), and consists of a set of FISH functions in the file `fist\2d_3d\t4p.fis`, and two- and three-dimensional usage examples in the directories `fist\templates\pmd-{2,3}d`. The implementation supports modeling of isolated atoms and TIP4P water molecules (consisting of four atoms rigidly linked to one another). All interactions are between atoms and use the LJC model. A general description of the implementation and a usage example are provided in the following sections.

4.2.2.1 General Description

The TIP4P water molecule is implemented in PFC by enhancing the scheme (described in Section 3.0) that provides atom-atom interactions via the LJC model. Each molecule is modeled as a permanent¹¹ clump consisting of four particles, one for each interaction site. Each interaction site is equated with an atom, and the atom type (O, M or H) is associated with each particle (see Figure 17). The atom-atom interaction table (containing data for atom-atom interactions O-O, O-M, O-H, M-M, M-H and H-H) is created. The true and interaction radius and the mass of each atom are specified. During subsequent cycling, each clump behaves as a rigid body loaded by forces acting at each of its contacts with other clumps. These contacts form whenever the interaction radii of any two particles in different clumps overlap — by making the cut-off distances effectively infinite and the clumps permanent, contacts will form between the constituent particles of all clumps but not between the constituent particles within the same clump. When contacts form, they are assigned the LJC model with parameter values from the interaction table. The mass properties of each clump are computed automatically based on the position and mass of each of the constituent particles assuming that the particles are point masses (**CLUMP PROPERTY moi_pmass on**).

The following procedure is employed to create models containing isolated atoms and arbitrarily oriented TIP4P water molecules. Each atom is represented by a single PFC particle, and each molecule is represented by the permanent 4-particle PFC clump shown in Figure 17. The positions of the interaction sites relative to one another are absolute, but the value of R_r can be modified to promote better visualization of the molecule. The relative positions of the interaction sites are stored in a TIP4P clump template consisting of 4 balls, each of which has a radius of R_r , positioned as shown in Figure 17. The clump volume assigned to the template is

¹¹ The permanent property ensures that contacts between the constituent particles will be ignored, but new contacts will form with the particles of other clumps.

$$V_c = 4 \begin{cases} \pi R_T^2 t, & \text{PFC2D } (t=1) \\ \frac{4}{3} \pi R_T^3, & \text{PFC3D} \end{cases} \quad (12)$$

The atoms are created and assigned properties as described in Section 3.0. Then the molecules are created first by generating a collection of equal-radius seed particles, each of which will be replaced subsequently by an arbitrarily oriented clump. The seed radius (R_s) is chosen to approximate the size of the molecule. If the seed particles are created using the GENERATE command, then R_s affects the spatial density (because particles created by the GENERATE command cannot overlap one another). We choose $R_s = 0.5 \times 10^{-10}$ m as a reasonable initial value. The seed particles are identified by assigning them to the *t4p_seed* group. Each seed particle then is replaced by an arbitrarily oriented clump derived from the TIP4P clump template as follows.

1. The seed-particle radii are modified so that each seed particle has a volume of V_c . The new seed-particle radius that satisfies this relation is

$$R_s^* = \begin{cases} 2R_T, & \text{PFC2D} \\ 4^{1/3} R_T, & \text{PFC3D} \end{cases} \quad (13)$$

The radii of all seed particles are multiplied by the factor (R_s^*/R_s).

2. All seed particles are replaced by clumps. Each new clump is arbitrarily oriented, with its volume-based centroid¹² located at the center of the particle that it replaces, and has the ball sizes and relative positions shown in Figure 17. The replacement process employs the CLUMP REPLACE command along with the TIP4P clump template.
3. The radii of the balls in each new clump are set equal to the interaction radius R_l by multiplying them by the factor (R_l/R_l). Finally, the balls in each new clump are assigned true radii of R_T and masses of (11).

¹² The volume-based centroid (defined in the CLUMP REPLACE command and shown as \mathbf{x}_{vc} in Figure 17) is computed based on the positions and radii of the balls in the clump template. The volume-based centroid differs from the center of mass shown as \mathbf{x}_c in Figure 16. The center of mass is used in the equations of motion for the clump.

4.2.2.2 TIP4P Usage Examples

The first 2D usage example simulates two TIP4P water molecules initially placed in the xy plane as shown in Figure 18. The PFC2D model results are produced by calling `fist\templates\pmd-2d\t4p-2d_2Mol.dvr`. The PFC2D model uses the SET DISK OFF command to treat all particles as spheres, but these spheres are constrained to remain in the xy plane. If the model is run with high damping, we obtain the final stable configuration with near-zero atom velocities shown in Figure 19. An animation showing the evolution of the molecule positions and orientations is produced for each model. The molecules have rearranged themselves into a single conglomerate with a self-equilibrating internal force system. One of the O-H legs of the left molecule points approximately toward the O site of the right molecule, which has its H sites directed away from the left molecule; this same stable configuration is obtained for different initial positions and orientations of the two molecules.

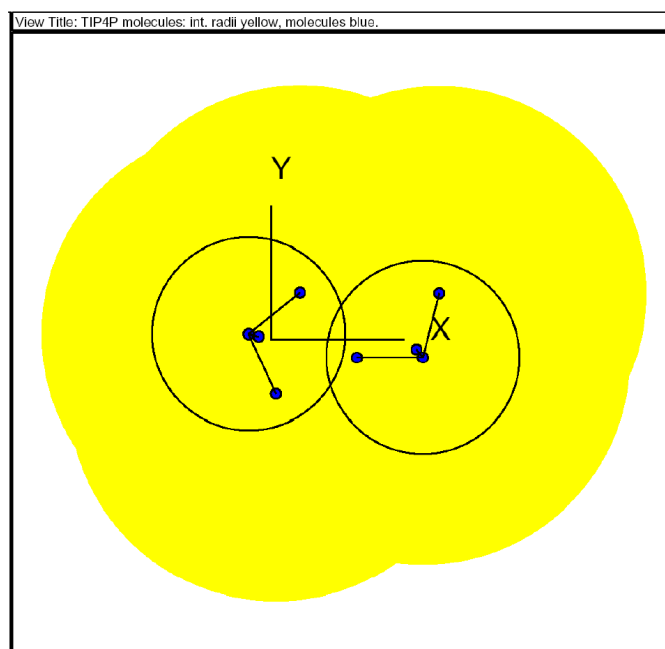


Figure 18 PFC2D initial system consisting of two water molecules with zero velocity (interaction radii in yellow, molecular sites in blue, molecules drawn with sticks joining the O-M and O-H sites and with circle of radius 1.4 angstroms at mass centroid)

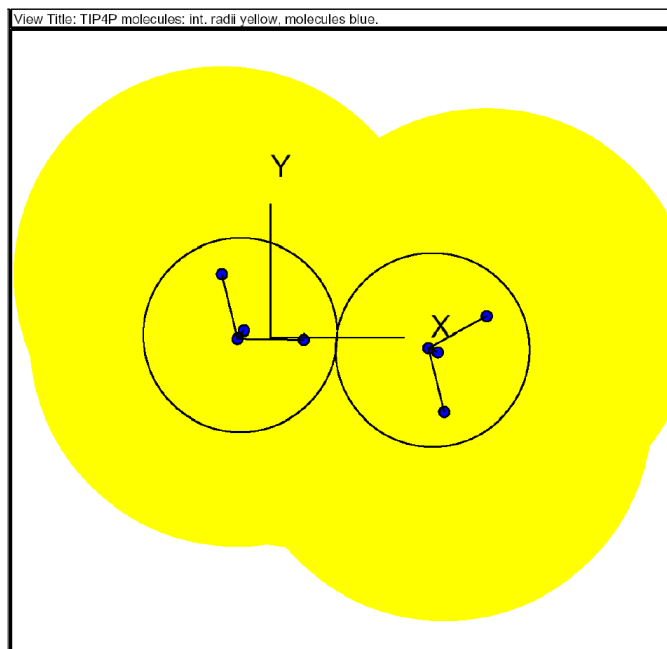


Figure 19 Final stable PFC2D system configuration

The first 3D usage example simulates two TIP4P water molecules initially placed in the xy plane as shown in Figure 20. The PFC3D model results are produced by calling `fist\templates\pmd-3d\t4p-3d_2Mol.dvr`. If the model is run with high damping, we obtain the final stable configuration with near-zero atom velocities shown in Figure 21. An animation showing the evolution of the molecule positions and orientations is produced for each model. The molecules have rearranged themselves into a single conglomerate with a self-equilibrating internal force system. These are planar molecules, and the molecular planes are oriented perpendicular to one another, with one of the O-H legs of the right molecule pointing approximately toward the O site of the left molecule, which has its H sites directed away from the right molecule; this same stable configuration is obtained for different initial positions and orientations of the two molecules.

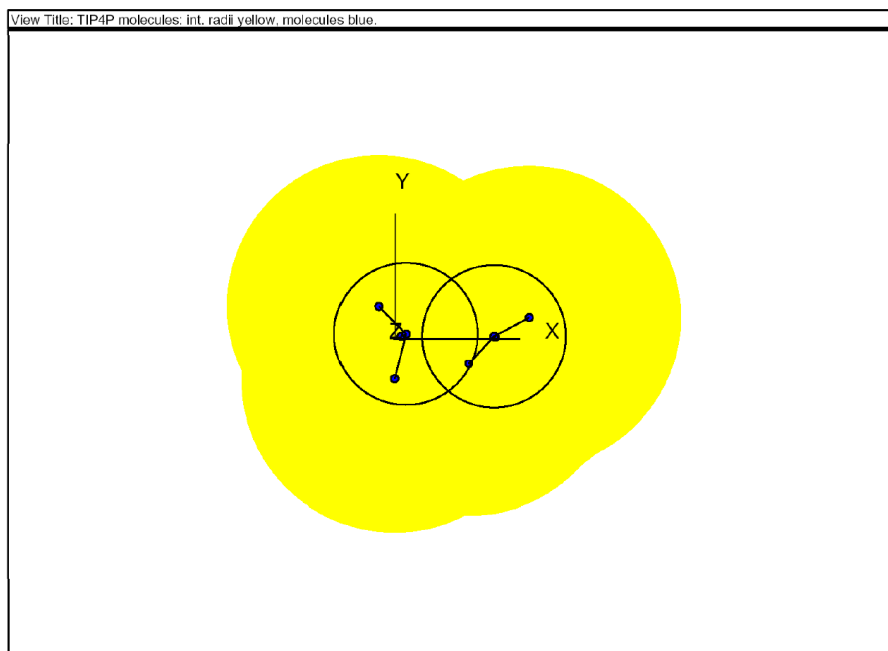


Figure 20 PFC3D initial system consisting of two water molecules with zero velocity (interaction radii in yellow, molecular sites in blue, molecules drawn with sticks joining the O-M and O-H sites and with circle of radius 1.4 angstroms at mass centroid)

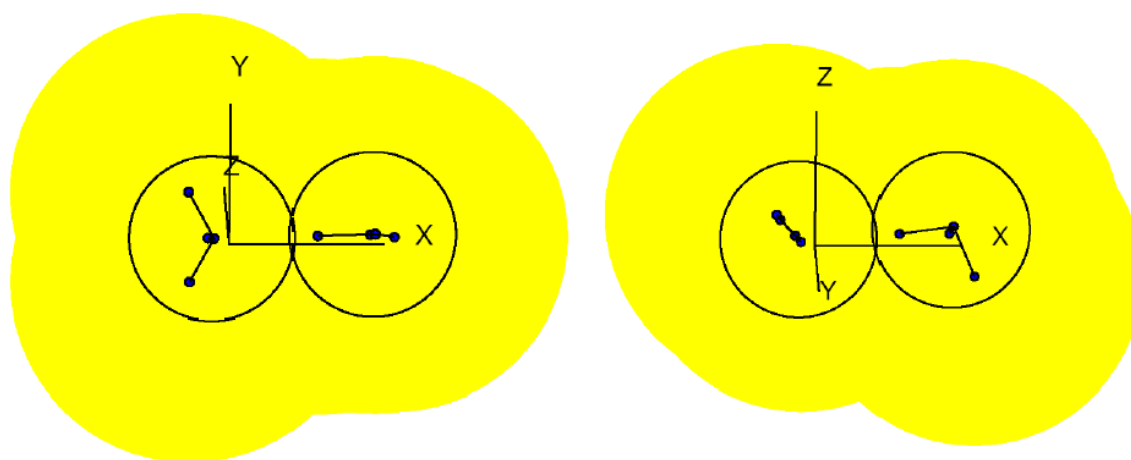


Figure 21 Final stable PFC3D system configuration

The second 2D usage example simulates two TIP4P water molecules and two oxygen atoms initially placed in the xy plane as shown on the left side of Figure 22. The PFC2D model results are produced by calling `fist\templates\pmd-2d\t4p-2d_2Mol2Atom.dvr`. The PFC2D model uses the SET DISK OFF command to treat all particles as spheres, but these spheres are constrained to remain in the xy plane. If the model is run with high damping, we obtain the final stable configuration with near-zero atom velocities shown on the right side of Figure 22. The molecules and atoms have rearranged themselves into a single conglomerate with a self-equilibrating internal force system.

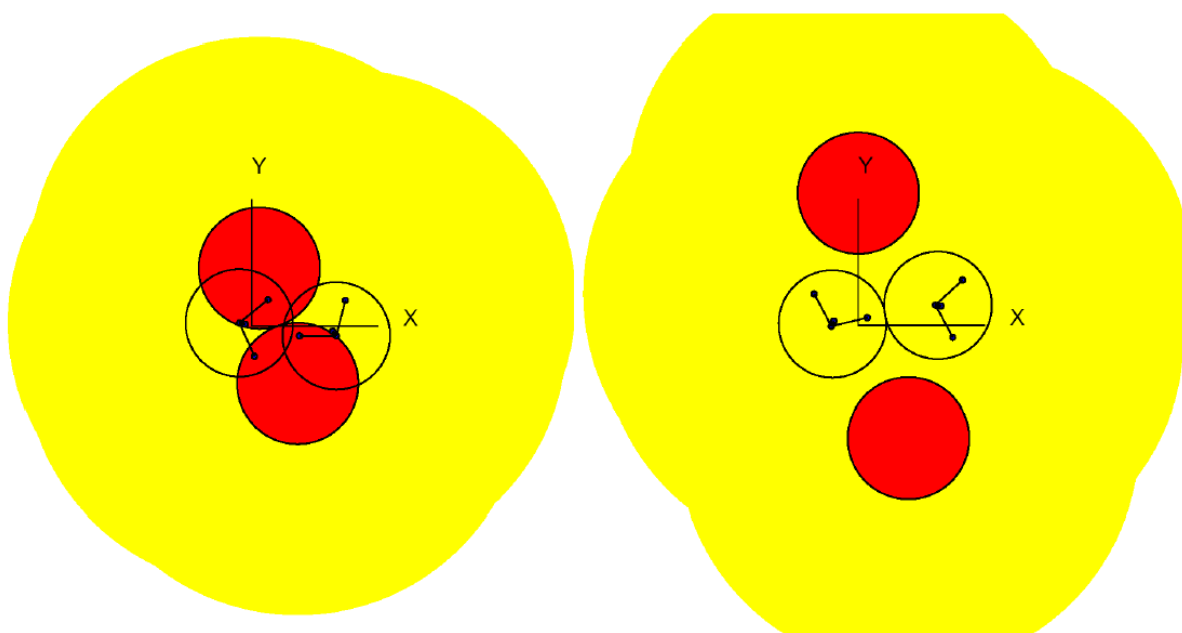


Figure 22 PFC2D initial (left) and final (right) configurations consisting of two water molecules and two oxygen atoms

The second 3D usage example simulates two TIP4P water molecules and two oxygen atoms initially placed in the xy plane as shown on the left side of Figure 23. The PFC3D model results are produced by calling `fist\templates\pmd-3d\t4p-3d_2Mol2Atom.dvr`. If the model is run with high damping, we obtain the final stable configuration with near-zero atom velocities shown on the right side of Figure 23. The molecules and atoms have rearranged themselves into a single planar conglomerate with a self-equilibrating internal force system.

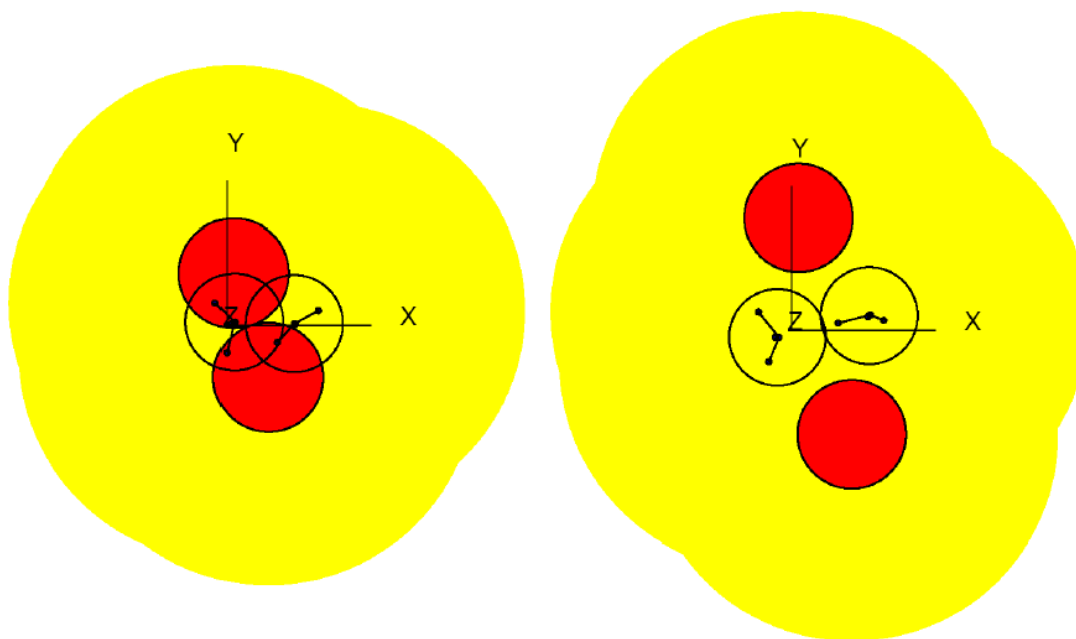


Figure 23 PFC3D initial (left) and final (right) configurations consisting of two water molecules and two oxygen atoms

The third usage example simulates an ensemble of TIP4P water molecules being held together by surface tension. The PFC2D model results are produced by calling `fist\templates\pmd-2d\t4p-2d_25Mol.dvr`, and the PFC3D model results are produced by calling `fist\templates\pmd-3d\t4p-3d_27Mol.dvr`. These models are run with no damping; thus, the dynamic behavior of the system should be similar to that of a real molecular ensemble with a total kinetic energy that corresponds with temperature. It is assumed that the kinetic energies of this example system correspond with water in the liquid state. The behavior of the PFC3D model is summarized here, the behavior of the PFC2D model is similar.

An ensemble of 27 TIP4P water molecules is created such that the initial position of each molecule is that of a perturbed $3 \times 3 \times 3$ lattice (with a uniform spacing of 2.25×10^{-10} m) and the initial velocities (both translational and rotational) are zero. The model is run with no damping at a fixed timestep of 1×10^{-15} s. There is a packing stage followed by a free stage. During the packing stage (first 400 steps), all velocity components are set to zero every 10 steps, thereby eliminating the kinetic energy and allowing the ensemble to expand in a controlled fashion. During the free stage (next 10,000 steps), the ensemble motion is unconstrained, and we simulate 1×10^{-11} seconds of elapsed time. System configurations at the beginning and end of the free stage are shown in Figure 24. The system behavior is seen in the animation file `t4p-3d_27Mol.avi`. The molecules have some mobility within the ensemble, and each molecule is vibrating at a high frequency.

The total potential and kinetic energies of the system are monitored. The sum of these quantities gives the total system energy. During the free stage, the total system energy should be constant; however, it is not (see Figure 25), which indicates that energy is not being conserved. It is hypothesized that energy is not being conserved for the following reasons: (1) the force versus separation distance curves for this system are highly nonlinear, (2) the central-difference time integration scheme is only second-order accurate and (3) a timestep small enough to provide a stable solution may not be small enough to provide low integration error. If this is the case, then reducing the size of the timestep should reduce the integration error. This hypothesis is supported by rerunning the 3D usage example of two TIP4P water molecules described above, but modifying the system to be run with no damping during the free stage (see `fist\templates\pmd-3d\t4p-3d_2MolA.dvr`). The drift in the total energy is reduced as the size of the fixed timestep is reduced from 1×10^{-15} to 1×10^{-18} seconds (see Figure 26). The effect upon model results of this observed non-conservation of energy should be considered when performing fully undamped simulations.

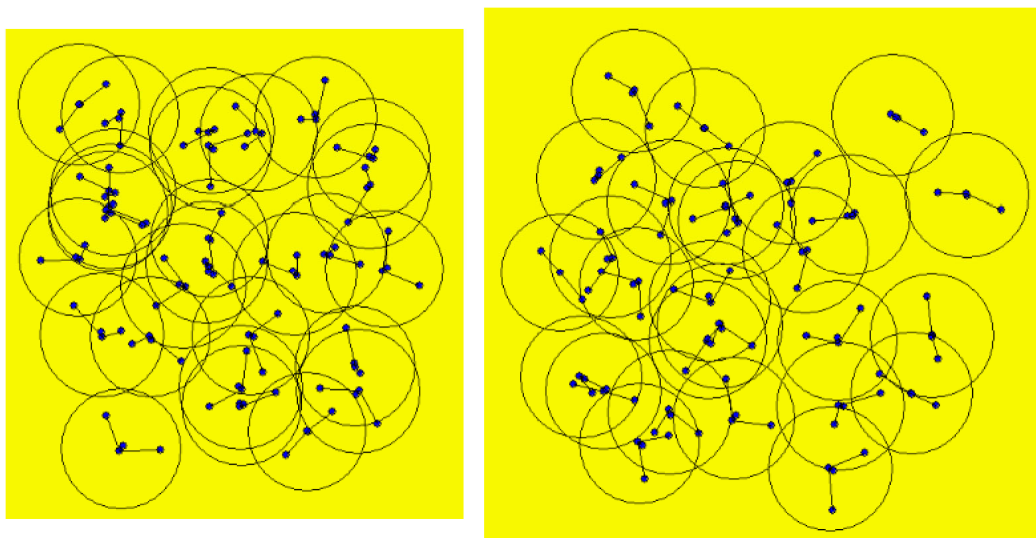


Figure 24 PFC3D initial (left) and final (right) configurations during the free stage (molecular sites in blue, molecules drawn with sticks joining the O-M and O-H sites and with circle of radius 1.4 angstroms at mass centroid — rendered with no hidden-surface algorithm)

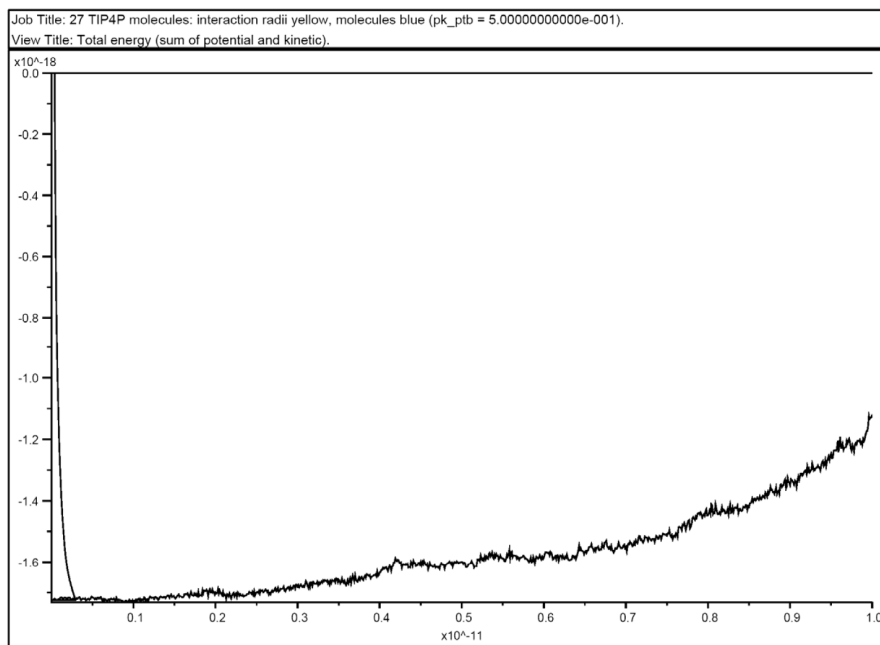


Figure 25 Total energy (sum of potential and kinetic) versus time during the free stage of PFC3D ensemble of 27 TIP4P water molecules

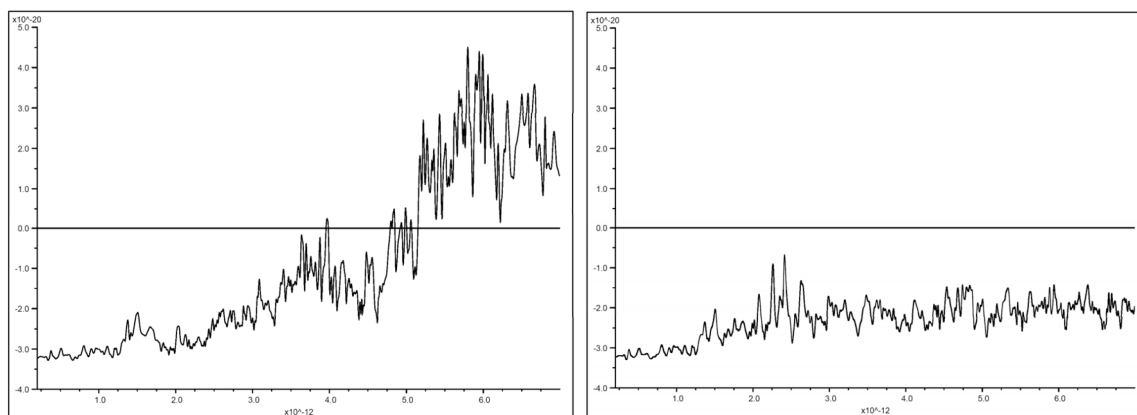


Figure 26 Total energy (sum of potential and kinetic) versus time during the free stage of PFC3D ensemble of 2 TIP4P water molecules with fixed timesteps of 1×10^{-15} (left) and 1×10^{-18} (right) seconds

5.0 LIMITATIONS OF USING PFC FOR MOLECULAR DYNAMICS

PFC was not designed to support molecular dynamics simulations. The general nature of the PFC implementation makes it possible to use PFC to perform such simulations; however, it is awkward to do so. In particular, the inability to specify an interaction radius for each particle, and thereby control when a contact will form, requires one to create particles with radii equal to the interaction radius, assign a true radius to each particle, and use this true radius in user-written contact models and plotting functions.

Most practical MD simulations are performed in a periodic space. Although PFC does provide a periodic space, it does not allow user-written contact models or clumps to migrate across the boundaries of this space. Because any MD simulation requires a user-written contact model and TIP4P molecules are treated as clumps, MD simulations cannot make use of the periodic space; this makes it difficult to model a large enough region to obtain useful information about the molecular system.

The PFC 5.0 code that is now under development will remove these limitations. It will allow specification of an interaction radius for each particle to ensure that a contact forms when these radii overlap, and it will allow particles, clumps and contacts of any type to migrate seamlessly across the periodic boundaries.

6.0 REFERENCES

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Sutmann, G. (2002) Classical Molecular Dynamics. Published in *Quantum Simulations of Complex Many-Body Systems: From Theory to Algorithms*, Lecture Notes, J. Grotendorst, D. Marx, A. Muramatsu (Eds.), John von Neumann Institute for Computing, Julich, NIC Series, Vol. 10, ISBN 3-00-009057-6, pp. 211-254, 2002. Available on 18 February 2009 at <http://www.fz-juelich.de/nic-series/volume10/sutmann.pdf>.