Computational Nanoscience

NSE C242 & Phys C203

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Lecture 3:

Computing Physical Properties

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Preparing for a Simulation

Today, we'll prepare ourselves to do and analyze a MD simulation of a classical one-component liquid in which particles interact via a Lennard-Jones potential.

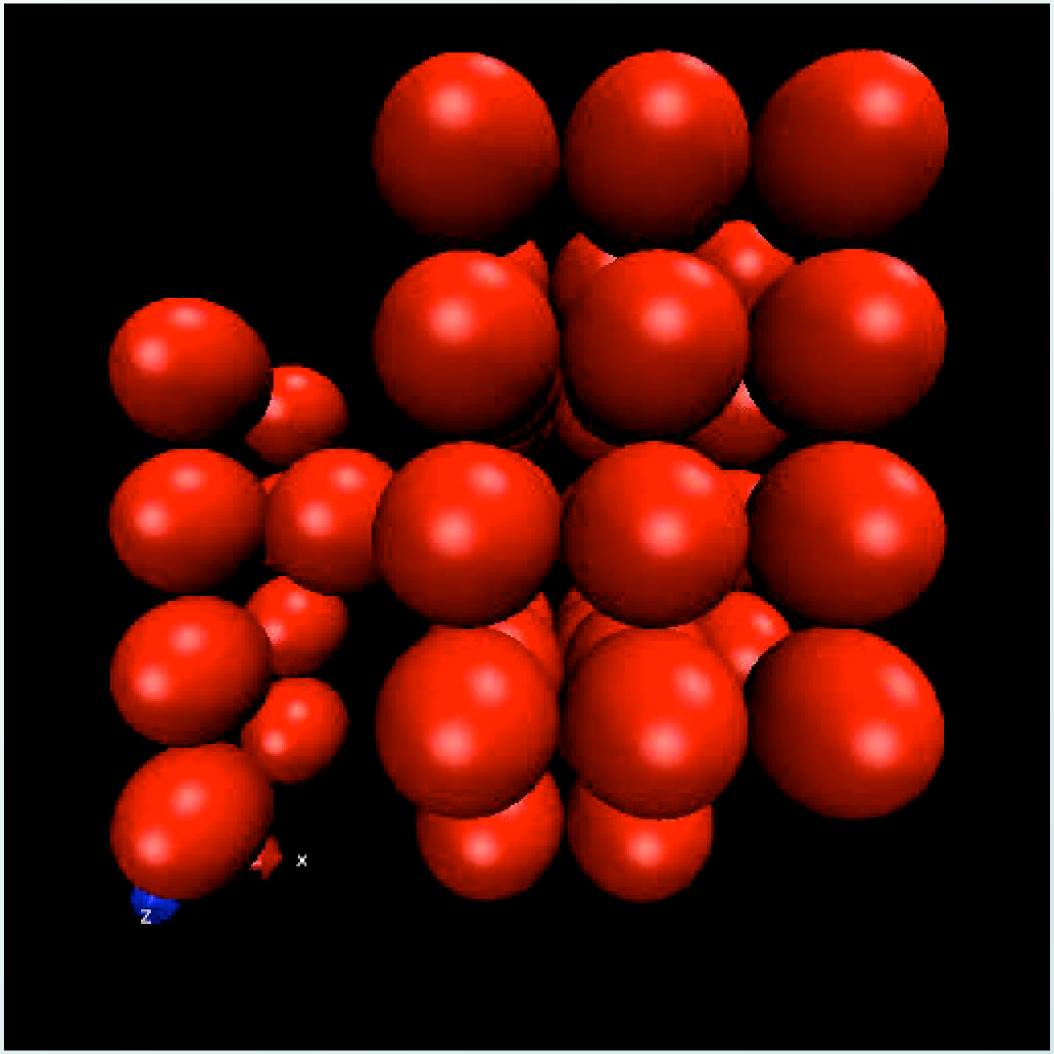
In this simulation temperature appears, as it is appropriate for a physical system with very many particles.

The temperature cannot be strictly held fixed in a MD simulation, at least not without appropriate modifications of the algorithm, but must be given as an input and monitored in the course of the simulation.

The techniques adopted to integrate the Newtonian equations of motion for a classical liquid are the same as for the harmonic oscillator, the only relevant difference being the use of periodic boundary conditions.

And the fact that there's a lot more to analyze…

Preparing for a Simulation

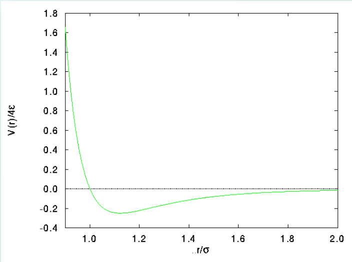


Units

As we have seen, the Lennard-Jones potential describing the interaction of two particles is given by:

$$v(r_{12}) = 4\varepsilon\left\{\left(\frac{\sigma}{r_{12}}\right)^{12} - \left(\frac{\sigma}{r_{12}}\right)^{6}\right\}$$

with the two phenomenological parameters σ and ε



The form of the potential suggests which units should be used. It contains an explicit length, which is σ. Thus, it proves very convenient to express all lengths in terms of σ.

The other unit is the energy unit ε (we will actually take 4ε as the energy unit).

The mass unit is simply the mass of the particles; with only one component in the system, the mass disappears (formally) from the calculation.

All other units are derivable from the above ones. For example: $t = \sqrt{\dfrac{m\sigma^2}{4\varepsilon}}$

Initial Conditions

In principle the choice of initial conditions is irrelevant, as a truly ergodic system should, given enough time, explore all of its accessible portion of phase space.

In practice, ergodicity problems are often highly nontrivial, given the fact that a MD simulation can only last a finite time. It is generally rather important, therefore, to choose the initial conditions appropriately, depending on the type of system that one wants to simulate.

If we are interested in a liquid, we would think that we could put particles pretty much at random; this turns out to be generally a poor choice, though, particularly for small systems.

If particles are initially positioned at random, more than likely at least two of them will be unphysically close to one another, and, as a result, they will acquire a tremendous acceleration due to the hard core of the potential, and this can be sufficient to offset completely the entire simulation, as they exchange momentum with the other particles.

Initial Conditions

More generally, one has to avoid starting the simulation with an *unphysical configuration*. Thus, it is in practice a better choice to put particles at regular lattice positions (such as simple cubic, for instance).

If one is interested in simulating a lattice, on the other hand, one is basically *forced* to put particles at lattice positions, as one has no chance (in a finite amount of time) of recovering the correct crystal structure if the simulation starts from a liquid, or from the wrong structure.

It is usually a safe choice to start from a lattice of some sort; if the system is stable as a liquid, then the initial lattice should melt (hopefully rapidly).

Initial Conditions

The choice of the initial velocities is even trickier: the simulation takes place at a given, desired temperature **T**, and this imposes a precise condition on the mean square velocity of the particles.

From the Maxwell equipartition theorem we know that: $dkT = m\langle \mathbf{v} \cdot \mathbf{v} \rangle$

where **d** is the dimensionality of the problem, **k** is the Boltzmann constant (we will set it to 1 from now on and measure all energies in Kelvin) and <v•v> is the mean square velocity of a particle in the system.

So, we could assign each particle a velocity whose components are, in magnitude, equal to √T.

It is necessary, however, to ensure that the total momentum of the system be zero, as the system is supposed to be at rest. That means that particles cannot be assigned velocities all pointing in the same direction.

Calculation of Physical Quantities

The energy is generally divided by the number of particles **N**, as the total energy clearly grows linearly with **N**.

The temperature is easily evaluated from the kinetic energy, using the equipartition theorem:

$$T(t) = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}m\mathbf{v}_i(t)\cdot\mathbf{v}_i(t)$$

Note that, in general, temperature is not constant in an MD simulation of the type we are now considering, namely at constant volume and energy.

What will typically happen is that the temperature will change in the course of the simulation, to settle asymptotically on a final value, that may or may not be close to the one selected initially. This has to do both with the physics of the system as well as with the particular initial conditions chosen.

If the temperature is to remain constant, then appropriate modifications to the simulation technique are required, namely the introduction of a *thermostat*.

Pressure

The pressure is defined as the average force on the container wall due to the physical system enclosed therein.

Thermodynamically, it is defined as, $P = -\left(\frac{\partial E}{\partial V}\right)$ where E is the energy and V is the volume of the system

It can also be expressed microscopically as, $P = \frac{NT}{V} + \frac{1}{dT}\left\langle \sum_i \sum_{j>i} \mathbf{r}_{ji} \cdot \mathbf{f}_{ji} \right\rangle$

where $\mathbf{r}_{ji}$ is the vector $\mathbf{r}_i$-$\mathbf{r}_j$ and $\mathbf{f}_{ji}$ is the force on the particle **i** due to particle **j**.

The second term on the right-hand side of the above equation is referred to as *virial*, and it represents the correction due to the interparticle interaction to the classical equation of state of a perfect gas, which is just the above equation without the second term on the right-hand side.

Pair Distribution Function

The pair distribution function provides a measure of the probability of finding any two particles at a given physical distance.

Typically, this is defined (in 3 dimensions) as:

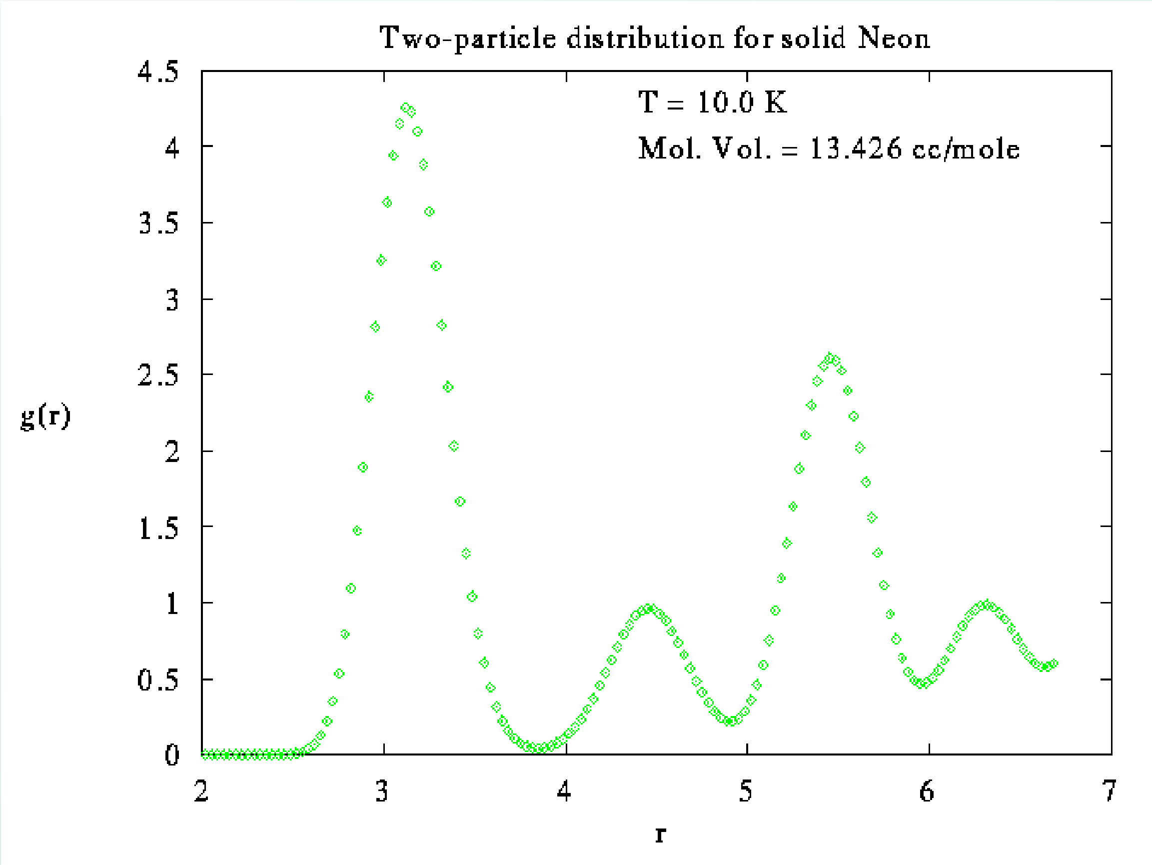
$$g(r) = (N-1)\frac{p(r)}{r^2}$$

The prefactor is defined in such a way so that:

$$\frac{\int r^2 g(r)dr}{\int r^2 dr} = 1 - \frac{1}{N}$$

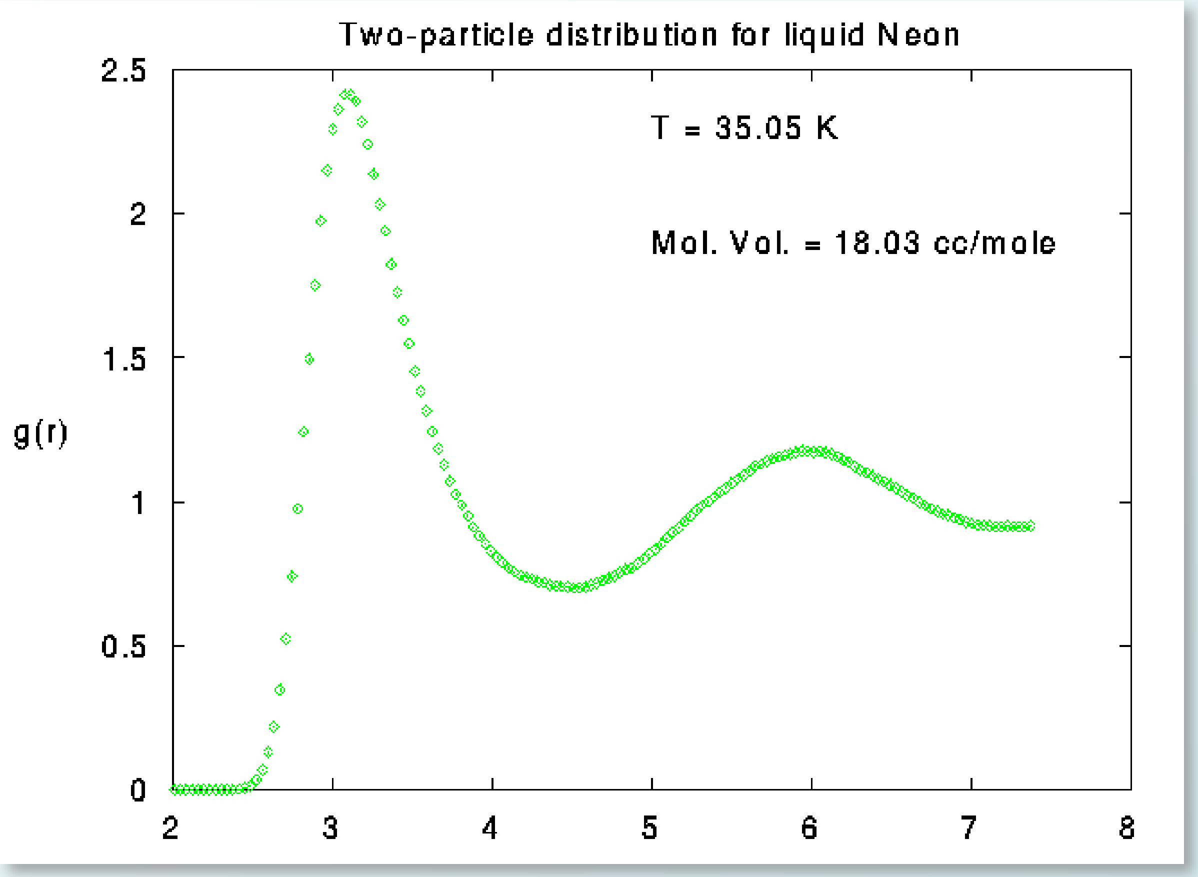
Example Pair Distribution Function

Solid FCC Neon at low temperature. The different peaks show how particles can be found at preferred distances from one another, typical of a solid.



Example Pair Distribution Function

Liquid Neon: peaks are much less pronounced and are at short distances, whereas for larger distances is basically uniform, typical for a liquid.



Diffusion Coefficient

The pair distribution function is an example of *correlation function*, i. e. a measure of the relationship of the value of a physical quantity at a given point in time/space for a system under study and the value of the same quantity (or, possibly, of another one) at a different point.

The pair distribution function is appropriate to characterize a system in thermal equilibrium, and it is a *static*, or time-independent, quantity.

One of the big advantages of MD is that it permits to calculate time-dependent quantities; these are typically *dynamic correlation functions*, of great practical interest as they describe the behavior of a system under the influence of an external probe.

For example, physically relevant quantities such as transport coefficients can be determined by studying the long-time behavior of appropriate dynamic correlations.

Diffusion Coefficient

It is usually of interest to determine the capability of a system to allow *diffusion* of matter throughout itself.

Diffusion can be modeled microscopically; Fick's first law of diffusion associates the *diffusion coefficient D* (or *self-diffusion coefficient*), to the average square displacement of particles from their initial positions as follows:

$$\lim(t \to \infty) \frac{\left\langle \left\{ \mathbf{r}(t) - \mathbf{r}(t=0) \right\}^2 \right\rangle}{2dt} = D$$

commonly known as "Einstein relation"

This relation permits to evaluate the coefficient *D* straightforwardly using MD, by simply averaging the mean square displacement of all particles.

Note that the time-formulation of MD is crucial in permitting to follow the time displacement of all the particles; this is not possible in any other computational scheme, such as Monte Carlo, if not very indirectly, as the time disappears from the formulation.

Boundary Conditions

How many particles should there be for the system we simulate to be "realistic"?

Periodic Boundary Conditions

In principle one could simulate, say, a liquid, by putting a bunch of particles in a box and adjusting its size to obtain the desired density.

Perhaps the box walls are infinite (in the potential), so that when a particle hits the surface it is reflected back in.

What's wrong with this?

It is important to remember that in a real physical sample the fraction of particles lying in the vicinity of the container wall is vanishingly small. Thus, the observed properties of the sample do not depend at all on the particles near the container wall.

Periodic Boundary Conditions

If we perform a simulation with 10000 particles (a respectable number) in a cubic box, a rough calculation tells us that about 3000 of them (almost 30% of the entire system!) will be near the wall.

With 1000 particles, about 60% of the particles will lie in the vicinity of the wall, and even with one million particles nearly 10% of them will be near the wall, a small but not insignificant fraction.

Thus, the physical properties of a typical system that can be studied by computer simulation would be greatly affected by surface effects, given the number of particles that can be handled, if the system were to be considered enclosed in a container with impenetrable walls.

Instead, useful predictions can be obtained using smaller systems, by adopting different boundary conditions, which greatly reduce surface effects. These are known as *periodic boundary conditions* (PBC).

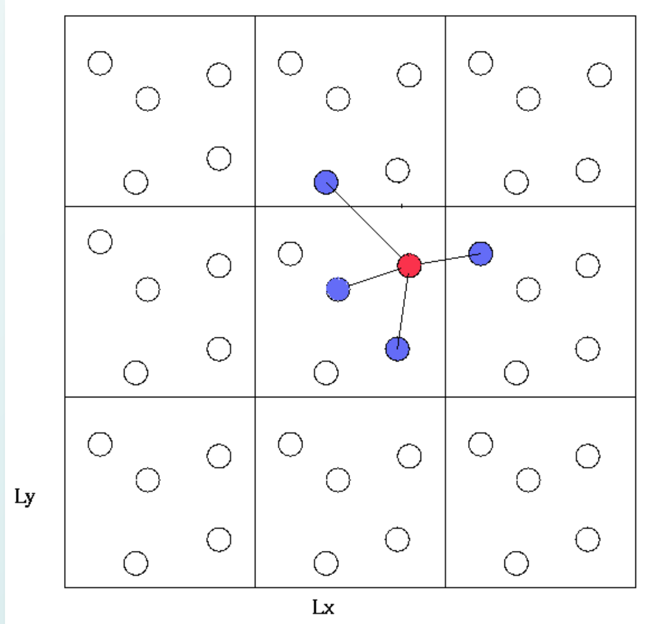
Periodic Boundary Conditions

Cells are tiled to fill all of space, as shown here:

When a particle crosses a boundary, it re-enters the cell from the opposite side.

Cells are not distinguishable from one another.

Interactions are counted only between the closest N particles (or images)



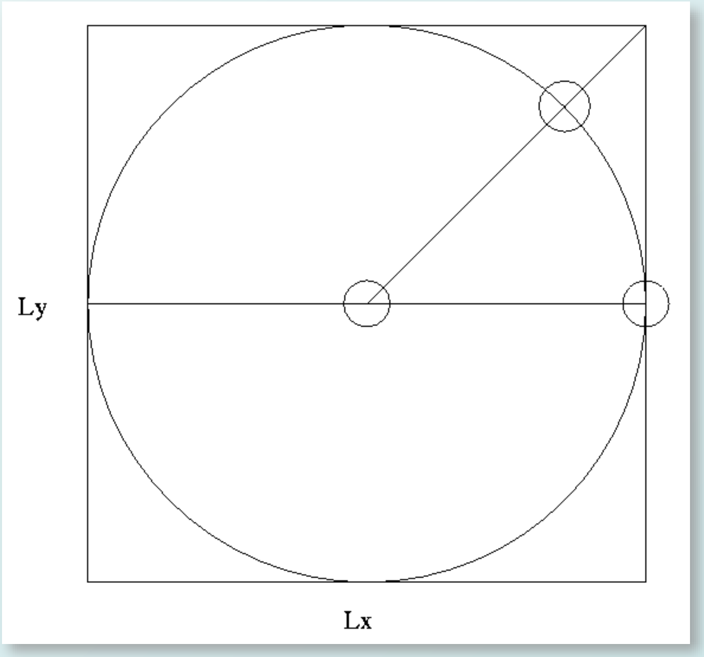
Does this have an impact on the potential?

PBC Impact on Potential

PBC introduces an unphysical effect, namely it alters the spherical symmetry of the potential.

This is easily seen by considering a two-dimensional system with two particles only.

If both particles are moved away from the center by a distance dr, then one particle will become 1-dr away and the other will be 1+dr away from the center.



What can we do about this?

→ One possibility is to truncate the potential at $r=L_x/2$

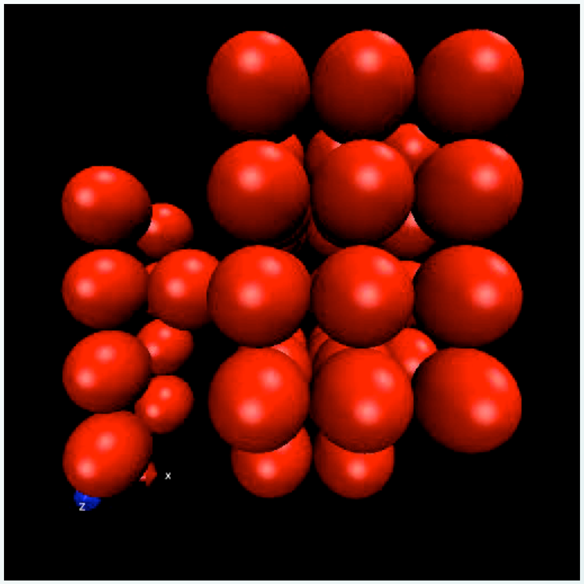
However, if the potential is not short-ranged, alternative strategies may be needed. What is short-ranged?

Lennard-Jones MD

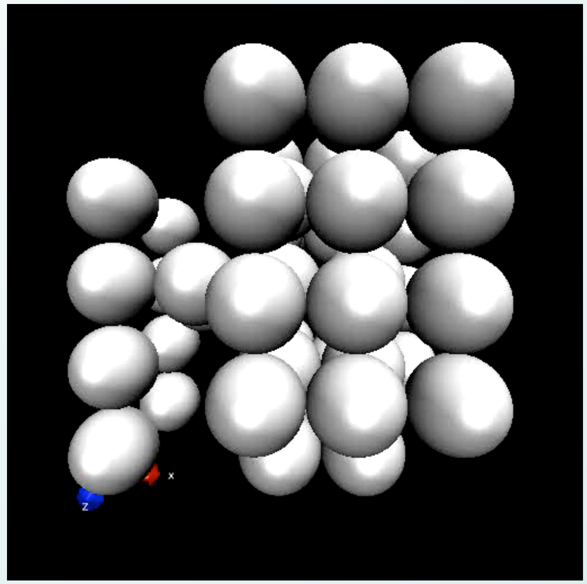
We're ready to do some MD simulations of a LJ liquid.

Nanohub Toolkit: LJMD

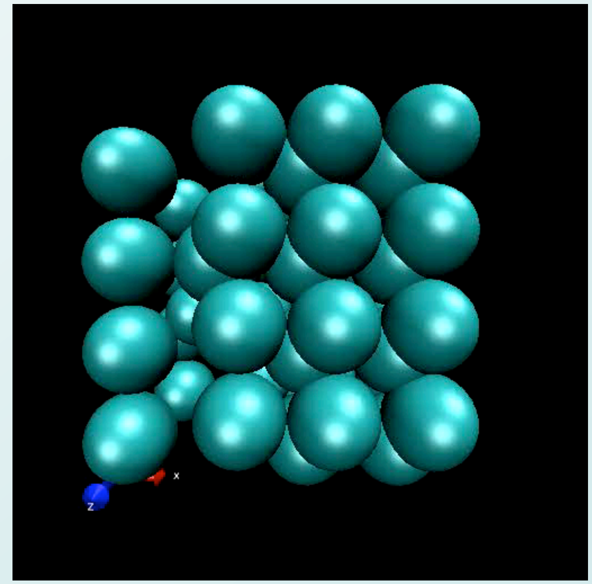
Lennard-Jones MD



T=0.5



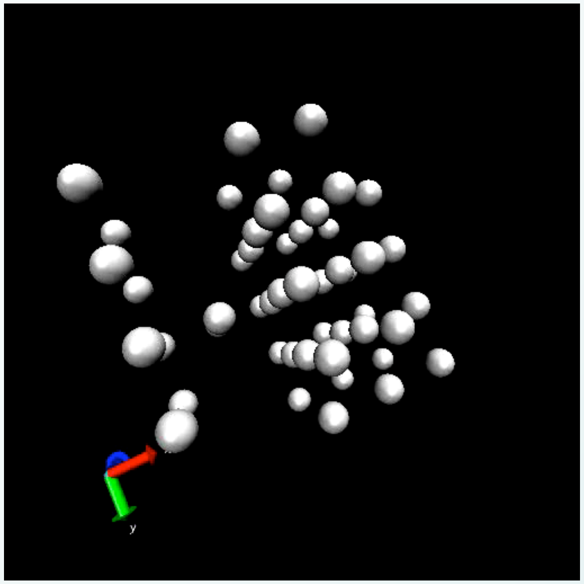
T=5



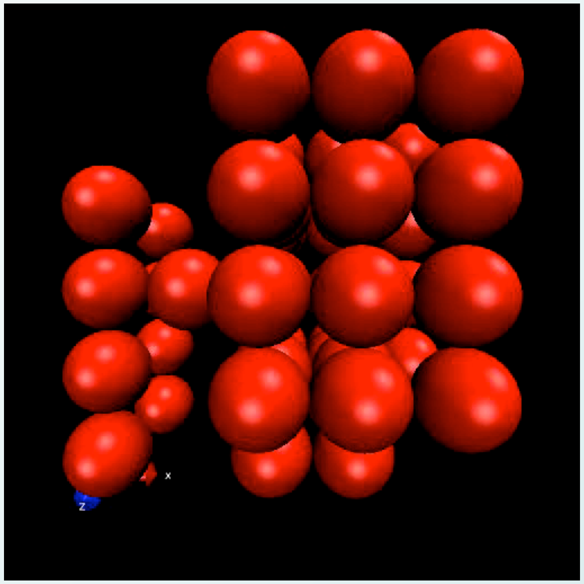
T=50

What kind of behavior should we expect as the temperature is increased?

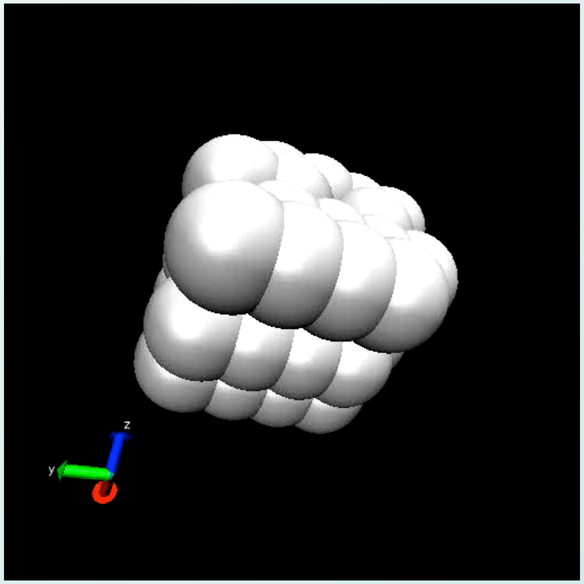
Lennard-Jones MD



Rho=.01



Rho=.1



Rho=1

What kind of behavior should we expect as the density is changed?