

## Topic 2: Molecular Dynamics of Lennard-Jones System (continued)

An observable which is related to the pressure is the *compressibility factor*

$$Z = \frac{PV}{Nk_{\text{B}}T} = 1 - \frac{1}{3Nk_{\text{B}}T} \left\langle \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle ,$$

which measures the deviation from the ideal gas law  $PV = Nk_{\text{B}}T$  and indicates the nature of the forces between the atoms. At high densities, the forces between the atoms are largely repulsive and  $Z > 1$ . At low densities, the attractive van der Waals forces make  $Z < 1$ .

Many interesting *correlation functions* can also be measured in a simulation. An important example is the *pair correlation function*

$$g(\mathbf{r}) = \frac{V}{N^2} \left\langle \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \delta^3[\mathbf{r} - (\mathbf{r}_i - \mathbf{r}_j)] \right\rangle .$$

This basically measures the probability that two particles are a distance  $\mathbf{r}$  apart relative to a uniform random distribution of non-interacting point particles. The average of this function over angular directions

$$g(r) = \frac{1}{4\pi r^2} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi g(\mathbf{r}) ,$$

is called the *radial distribution function*. It can be measured experimentally by light, light, x-ray or neutron scattering from the system.

## MD Simulation Program: Initialization

Because an MD simulation of a system with a large number  $N$  of argon atoms can only be carried out over a few nanoseconds, it is very important to choose the initial configuration of the system very carefully so that it is as close as possible to equilibrium at the desired temperature  $T$  and density  $\rho$ .

**Volume  $V$ :** The simplest choice is to make this a cube of side  $L$ . Given the total number of particles  $N$ , and the density  $\rho$  particles per unit volume, the size of the system is determined by

$$V = L^3 = \frac{N}{\rho} .$$

**Positions of particles:** If the system very dilute, i.e., a rarefied gas, then the particles should be distributed uniformly and randomly inside the volume  $V$ . However, if the system is dense, i.e., in the liquid or solid phase, then the placement of particles must be done very carefully: the very strong repulsive Lennard-Jones force will blow the system apart if particles are placed too close together! At very low temperatures, the Lennard-Jones system is known to solidify with a *face centered cubic* (fcc) lattice structure. The safest initial configuration is therefore to place the  $N$  particles at the sites of an fcc lattice. Such a lattice contains 4 particles in each cube. To fill the cubical volume  $V$  uniformly with an fcc lattice the number of particles should be chosen as follows:

$$N = 4n^3 = 4, 32, 108, 256, 500, \dots \quad \text{where } n = 1, 2, \dots$$

**Velocities of particles:** If the temperature  $T$  of the system is specified, then the average kinetic energy of a particle in equilibrium is

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{3}{2}k_B T, \quad v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}.$$

In an ideal gas, the velocities of the molecules would obey the Maxwell-Boltzmann distribution

$$P_v dv = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/(2kT)} dv,$$

which could be used to assign random initial velocities to the particles. However, the temperature would not come out right because interactions have not been taken into account. Since the temperature will have to be adjusted, one could choose almost any random distribution of initial velocities with average magnitude  $\sim v_{\text{rms}}$ . It is important in doing this to adjust the total momentum of the system to be zero.