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Introduction to Modeling and Simulation (IM/S)
(Spring 2005)

Lecture MD2 (4/13/05) Property Calculations by Molecular Dynamics

MD Property calculations

Let $\langle A \rangle$ denote time average over the trajectory generated by MD, where A is a dynamical variable, A(t). Two kinds of calculations are of interest, equilibrium properties and time correlation functions. The first is a running time average over the MD trajectories,

$$\langle A \rangle = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt' A(t') \quad (1)$$

with t taken to be as long as possible. In terms of discrete timesteps, Eq.(1) becomes

$$\langle A \rangle = \frac{1}{N_t} \sum_{k=1}^{N_t} A(t_k) \quad (2)$$

where N_t is the number of time steps in the trajectory. The second is a time-dependent quantity of the form,

$$\langle A(0)B(t) \rangle = \frac{1}{N} \sum_{i=1}^N \frac{1}{N_i} \sum_{k=1}^{N_i} A_i(t_k) B_i(t_k + t) \quad (3)$$

where B is in general another dynamical variable, and N_i is the number of time origins. (3) is called a correlation function of two dynamical variables; since it is manifestly time-dependent, it is able to represent dynamical information of the system.

We give examples of both types of averages by considering the properties commonly calculated in MD simulation.

$$U = \left\langle \sum_{i < j}^N V(r_{ij}) \right\rangle \quad \text{potential energy} \quad (4)$$

$$T = \frac{1}{3Nk_B} \left\langle \sum_{i=1}^N m_i \underline{v}_i^2 \right\rangle \quad \text{temperature} \quad (5)$$

$$P = \frac{1}{3V} \left\langle \sum_{i=1}^N (m_i \underline{v}_i^2 + \underline{r}_i \cdot \underline{f}_i) \right\rangle \quad \text{pressure} \quad (6)$$

$$g(r) = \frac{1}{n4\pi r^2 dr} \left\langle \sum_{i \neq j}^N \delta(r - |\underline{r}_i - \underline{r}_j|) \right\rangle \quad \text{radial distribution function} \quad (7)$$

$$\langle \Delta r^2 \rangle = \frac{1}{N} \sum_{i=1}^N [\underline{r}_i(t) - \underline{r}_i(0)]^2 \quad \text{mean squared displacement} \quad (8)$$

$$\langle \underline{v}(0) \cdot \underline{v}(t) \rangle = \frac{1}{N} \sum_{i=1}^N \frac{1}{N_i} \sum_{k=1}^{N_i} \underline{v}_i(t_k) \cdot \underline{v}_i(t_k + t) \quad \text{velocity autocorrelation function} \quad (9)$$

We have already discussed the thermodynamic properties of pressure, temperature and potential energy, along with the radial distribution function and the mean squared displacement, in the lecture MD1.basic. The velocity autocorrelation function gives information about the atomic motions of particles in the system. Since it is a correlation of the particle velocity at one time with the velocity of the same particle at another time, the information refers to how a particle moves in the system, such as diffusion. If one correlates instead the velocity of a particle at one time with the velocity of another particle at another time, then different information is obtained, referring to the cooperative (collective) motions of particles in the system, such as sound waves and lattice vibrations. In the study of dynamical properties of simple liquids and solids, the velocity correlation function plays an important role.

There are many other properties which one can calculate using the particle trajectories given by an MD simulation. One can classify properties according to the following grouping:

Structural – crystal structure, $g(r)$, defects such as vacancies and interstitials, dislocations, grain boundaries, precipitates

Thermodynamic -- equation of state, heat capacities, thermal expansion, free energies

Mechanical -- elastic constants, cohesive and shear strength, elastic and plastic deformation, fracture toughness

Vibrational -- phonon dispersion curves, vibrational frequency spectrum, molecular spectroscopy

Transport -- diffusion, viscous flow, thermal conduction,

There are properties which classical MD cannot calculate because electrons are involved. To treat electrons properly one needs quantum mechanics. In addition to electronic properties, optical and magnetic properties also require quantum mechanical (first principles or ab initio) treatments. Such methods will be discussed in the quantum simulation part of the lectures.

Simulation of particle and radiation transport

MC is quite extensively used to track the individual particles as each moves through the medium of interest, streaming and colliding with the atomic constituents of the medium. To give a simple illustration, we consider the trajectory of a neutron as it enters a medium, as depicted in Fig.1. Suppose the first interaction of this neutron is a scattering collision at point 1. After the scattering the neutron moves to point 2 where it is absorbed, causing a fission reaction which emits two neutrons and a photon. One of the neutrons streams to point 3 where it suffers a capture reaction with the emission of a photon, which in turn leaves the medium at point 6. The other neutron and the photon from the fission event both escape from the medium, to points 4 and 7 respectively, without undergoing any further collisions. By sampling a trajectory we mean that process in which one determines the position of point 1 where the scattering occurs, the outgoing neutron direction and its energy, the position of point 2 where fission occurs, the outgoing directions and energies of the two fission neutrons and the photon, etc. After tracking many such trajectories one can estimate the probability of a neutron penetrating the medium and the amount of energy deposited in the medium as a result of the reactions induced along the path of each trajectory. This is the kind of information that one needs in shielding calculations, where one wants to know how much material is needed to prevent the radiation (particles) from getting across the medium (a biological shield), or in dosimetry calculations where one wants to know how much energy is deposited in the medium (human tissue) by the radiation.

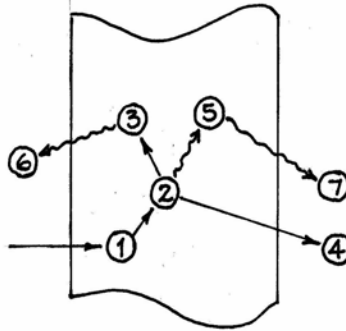


Fig. 1. Schematic of a typical particle trajectory simulated by Monte Carlo. By repeating the simulation many times one obtains sufficient statistics to estimate the probability of radiation penetration in the case of shielding calculations, or the probability of energy deposition in the case of dosimetry problems, etc.

Comparison of Monte Carlo (MC) with Molecular Dynamics (MD)

Recall from Lec MD1 that the purpose of MD is to generate the atomic trajectories of a system of N particles by direct numerical integration of the Newton's equations of motion. In a similar spirit, we can say that the purpose of MC is to generate an ensemble (collection) of atomic configurations by stochastic sampling. In both cases we have a system of N particles interacting through the same interatomic potential. In MD the system evolves in time by following the Newton's equations of motion where particles move in response to forces created by their neighbors. The particles therefore follow the correct dynamics according to classical mechanics. In contrast, in MC the particles move by sampling a distribution such as the canonical distribution (the Boltzmann factor). The dynamics thus generated is *stochastic* or probabilistic rather than *deterministic* which is the case for MD. The difference is dynamics becomes important in problems where we wish to simulate the system over a long period of time. Because MD is constrained to real dynamics, the time scale of the simulation is fixed by such factors as the interatomic potential, and the mass of the particle. This time scale is of the

order of picoseconds (10^{-12}) which is a microscopic time scale. If one wants to observe a phenomenon on a longer scale such as microseconds, it would not be possible to simulate it directly by MD. On the other hand, the time scale of MC is not fixed in the same way. In fact, the time scale depends on the transition probability which one is free to choose. Then MC can be used to study the kinetics of system evolution over arbitrary time scale. This implementation of Monte Carlo is commonly called kinetic Monte Carlo which is quite an active field of simulation.

Another way to characterize the difference between MC and MD is to consider each as a technique to sample the degrees of freedom of the system. Since we follow the particle positions and velocities in MD, we are sampling the evolution of the system of N particles in its phase space, the $6-N$ dimensional space of the positions and velocities of the N particles. In MC we generate a set of particle positions in the system of N particles, thus the sampling is carried out in the $3-N$ configurational space of the system. In both case, the sampling generates a trajectory in the respective spaces, as shown in Fig. 2. Such trajectories then allow properties of the system to be calculated as averages over these trajectories. In MD one performs a time average whereas in MC one performs an ensemble average. Under appropriate conditions MC and MD give the same results for equilibrium properties, a consequence of the so-called *ergodic hypothesis* (which assumes that ensemble average is equal time average). However, dynamical properties calculated using the two methods in general will not be the same.



Fig. 2. Schematic depicting the evolution of the same N -particle system in the $3-N$ dimensional configurational space (μ) as sampled by MC, and in the $6-N$ dimensional phase space (γ) sampled by MD. In each case, the sampling results in a trajectory in the

appropriate space which is the necessary information that allows average system properties to be calculated. For MC the trajectory is that of a random walk (Markov chain) governed by stochastic dynamics, whereas for MD the trajectory is what we believe the correct dynamics as given by the Newton's equations of motion in classical mechanics. The same interatomic potential is used in the two simulations.