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Issues on the Choice of a Proper Time Step in Molecular Dynamics

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Abstract

We will discuss herein issues on the proper time step in molecular dynamics simulations. Determination of the proper time step is very important in the simulations, however, still it is determined rather empirically by trial and error and also kept fixed throughout the simulation. These cause severe problems sometimes. We raise these issues and propose a new method, which is quite different from the conventional one.

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Molecular dynamics (MD) [1] is a method to simulate molecular motions governed by classical equations of motion. The first molecular dynamics simulation (MDS) [2] was performed on a simple fluid. With the developments of computing speed and memory/storage capacity, MD for bigger systems have been performed [3]. MD, unlike Monte Carlo, gives biased results due to numerical integrators. In MDS, when we know the configuration of a state at one moment, we can find the state at the next moment using the discrete method to integrate the Newtonian equations of motion. This integration process can be achieved by several different algorithms [4]-[6]. Thus, the most important parameter in MD is the time step τ.

There are so many errors involved in this discrete task. We can classify them into two categories.

a) Systematic Errors

1. Truncation errors.
2. Roundoff errors.
3. The finite size of the simulation sample.
4. The finite simulation time t_S.

b) Statistical Errors

1. The error associated with a distribution function.
2. The variation in temperature during the simulation.

Systematic errors are related with the selection of the time step τ. Ideally, we want to use the largest time step size possible, in order to simulate the longest time. In other words, if a very small value of time step is used, it will not be efficient since it takes a very long calculation time. However, unfortunately, the MD integration algorithm becomes unstable at large time step size. If too large a time step τ is used, the motion of particles becomes unstable due to the

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very big truncation error in the integration process, so the total energy of the system may rapidly increase with time. Therefore, molecules may not have a normal structure any more. This behavior is often called exploding and caused by devastating atomic collisions that occur when a large time step propagates the positions of two atoms to be nearly overlapping; the interaction creates a strong repulsive force repelling these atoms far apart. This can be understood more precisely by considering a single particle in a one dimensional harmonic well. Assume that this particle is to one side of the center and that its initial velocity is zero. This particle would experience a restoring force toward the center of the potential well. The product of the force with the time step size squared would yield the displacement of the particle. A small time step would advance the particle closer to the well center. A too large time step would overshoot the center of the well, and could even place the particle on the opposite side higher than its starting position. This would immediately cause a problem: The total energy of the particle will increase, and subsequent steps at this large time step size will increase the energy more and more. This clearly violates the conservation of energy in NVE ensemble. Truncation errors are related to the accuracy of the finite difference method with respect to the true solution. Finite difference methods are usually based on a Taylor expansion truncated at some term. These errors do not depend on the implementation. They are intrinsic to the selected algorithm.

Roundoff errors come from the finite number of digits employed in digital computing. Any numerical calculation suffers this. In practice, the finiteness of the integration time step and arithmetic rounding errors will eventually cause the computed trajectory to deviate from the true trajectory of the continuous-time equation of motion. The finite step size τ modifies the dynamics in a systematic way, with an effect that can be expressed as an asymptotic expansion in powers of τ. In principle, both truncation error and roundoff error can be reduced by decreasing τ, but the decreasing rate are quite different. For large τ, truncation errors dominate, but they decrease quickly as τ is decreased. For instance, the Verlet algorithm has a truncation error proportional to τ^4 for each integration time step. Round-off errors decrease more slowly with decreasing τ, and thus dominate in the small τ limit. In the absence of round-off error, certain numerical integrators rigorously maintain the phase-space volume conservation property of Hamiltonian dynamics, which are called a symplectic algorithm. In normal MDS for simple fluids, we use about a scale of 1 femto (10^{-15}) second time step. There are some logical explanations about the usage of 1 fs as a proper time step. One of the explanations is that stable dynamics will be executed only if we use the smaller time step compared to the period of the highest vibrational frequency of the molecule. If we can determine the biggest time step for a stable dynamics, it is expected that the efficiency of the MDS will be maximized. It is necessary to investigate the reasons why the dynamics sometimes break down after a maximum limit of time step in the simulation, and to determine the exact point where a chaotic behavior starts in MDS. Even if the model for the molecular system is exact, computational resources limit the simulation length, which introduces statistical error when computing ensemble averages. In MD, it is assumed that time averages of physically meaningful functions do not depend on a detailed description of the initial conditions, which is a consequence of the ergodic hypothesis. Due to this chaotic nature of the underlying equations of motion, it is impossible to construct an exact trajectory over a long time interval. The simulation results for a system should be completely independent on the initialization of the system.

When a symplectic integrator is applied to a Hamiltonian system, the result is a modified Hamiltonian system which is nearly exactly conserved by the symplectic integrator. Hence, it is remarkable that the symplectic integrators can approximately preserve the correct invariant density for very long durations. For example, the Verlet algorithm [4] conserves $H(x,p) = \frac{1}{2}p^T M^{-1} p + V(x)$, to second-order accuracy over long time intervals, where M is a mass matrix and V is the potential energy. However, the modified Hamiltonian $\tilde{H}(x,p) = H(x,p) + \tau^2(\frac{1}{12}p^T M^{-1} V_{xx} M^{-1} p - \frac{1}{24}\nabla V^T M^{-1} \nabla V)$ is preserved to fourth-order accuracy. Estimates of such modified Hamiltonians can be computed at almost no additional cost [8], [9]. However, discrete process for nonsymplectic integrators like Nose-Hoover schemes [7] introduces energy drift.

For numerical stability and accuracy in the conservation of energy, one typically needs to pick a time step that is at least an order of magnitude smaller than the fastest time scale in the system. Practically speaking, the time step limits the length of the MD trajectory. At each time step, the slowest computational operation is the pairwise loop to compute the potential energy and forces, which scales as N^2 in computational expense where N is number of particles in the simulation. The forces and velocities at one step in time are used to calculate the resulting positions at the next step. In practice this violation of energy conservation can be used as a hint in determining the proper time step. One wants to find the largest time step that will maintain the conservation of energy. Physically, this time step size is about 0.0333 to 0.01 of the smallest vibrational period in the simulation. The smallest vibrational period depends most

strongly on the potential adopted, and less strongly on the particular lattice structure and temperature of the system. Actually, the optimum time step is found through trial and error done in a NVE simulation. In practice the total system energy will fluctuate, particularly at the first 10 or so steps of a simulation. The user needs to judge for himself what amount of fluctuation is tolerable. Usually, fluctuations of about 1 part in 5000 of the total system energy per twenty time steps are acceptable. It is useful to plot the value of the total energy versus time step to gauge when the system becomes unstable empirically.

The time step size τ must be specified by the user from the start. It is difficult to determine a proper time step for some cases. If we consider a system which is composed of two quite different temperature regions, then particles in the hot region move very fast, while particles in the cold region move slowly. Thus, in this case, if we choose the time step to match with the fast ones, then it introduces large truncation error in the dynamics of the slow ones and if we choose the time step to match with the slow ones, then it is inefficient for the fast ones. Furthermore, contact of hot particles and cold particles eventually yield an thermal equilibrium with the same temperature. This implies that the time step should be changed accordingly as the system state evolves. Another case is collisions with another object with high impact velocities. There is a heat generation around the collision region. After the collision is finished, the system also returns to the thermal equilibrium. In order to describe this, we need a time step which can changed during the simulations. Thus, we need a new method of choosing the proper time step τ to accommodate the fact that it should be changed adjustably during MDS.

These arguments can be applied to equilibration process. In order to simulate fluid states, we start from the lattice state and assign random initial velocities. As time proceeds, the lattice structure collapses, and eventually attains a fluid state. This process is called an equilibration. To check the equilibration process, we usually calculate Maxwell-Boltzmann distribution of the velocities or Boltzmann's H-value. This implies also that we need an adjustable time step τ. This adjustable time step τ can be used to keep the fluctuations of these quantities as small as possible. Adjustable time step can be used as a check of the equipartition theorem, and they are worth to explore further.

In summary, we examined some issues related with the determination of the proper time step τ. Important point is that the time step should be adjusted and based on the sound ground, not from just trial and error. This needs a new method for the optimal time step τ in MD. This will be accomplished separately in another article [10], which is based on the challengeable assumption that time is intrinsically discrete.

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