

Validity of Molecular Dynamics for the Simulation of Soft Matter

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Abstract. We examine the validity of molecular dynamics simulations for a simple one-dimensional system having a piecewise continuous linear repulsive potential wall with a constant slope a . The inevitable energy change ΔE that occurs in the collision with the potential wall is shown to be dependent on only two parameters α and $\mu \equiv a\tau/p_0$, where α is a fraction of the time step τ immediately after the contact with the potential wall and p_0 is the momentum just before the collision. The whole space of parameters α and μ can be divided into an infinite number of regions, where each region generates separately a positive or negative energy change ΔE . The envelope of $|\Delta E|$ shows a power law behavior $|\Delta E| \propto \mu^\beta$ with the exponent $\beta \approx 1.08$. The average of $\langle |\Delta E| \rangle_\alpha$ over a uniform distribution of α shows a broken power law behavior $\langle |\Delta E| \rangle_\alpha \propto \mu^\beta$ with $\beta \approx 1.98$ at larger μ values and $\beta \approx 0.99$ at smaller μ values.

Hard core particles only feel repulsive impulses at the time when they collide. To simulate this system, we usually employ event-driven methods [1]-[2] to determine the time at which any two hard-core particles collide. At the time of collision, their longitudinal components of the velocities are exchanged, but their transverse components of the velocities do not change at all. Consequently, their total energy is completely conserved in the molecular dynamics simulations.

However, molecules usually have soft repulsive components in the potential function. This can be modeled by exponential or power functional forms [3]-[5]. For example, noble gases such as argons can be described by the Lennard-Jones potential

$$V_{LJ}(r) = 4\epsilon\left[\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6}\right], \quad (1)$$

where ϵ and σ characterize energy and length scales, respectively. In the simulation of a system with a soft potential [6]-[9], it is practically impossible to keep the energy of the system constant due to the inherent round-off errors involved in the digitization and truncation errors involved in the approximations of mathematical formula.

If the total energy of a system is different from the given initial total energy E , the system may sometimes show somewhat different thermodynamic and dynamic behaviors from what we originally aimed. Molecular dynamics corresponding to the NVE ensemble [10]-[11] generates phase trajectories moving on the constant energy surface $E = \text{const}$. Therefore, it is important to know how the total energy E depends on the control parameters of the system during the process of the molecular dynamics simulations.



To address this problem, we consider a very simple system as an example. The system is composed of a simple particle colliding with the soft potential wall in one-dimension. The soft potential wall is modeled as a piecewise linear potential:

$$V(q) = \begin{cases} 0, & \text{if } q \geq 0, & \text{(Region I),} \\ aq, & \text{otherwise,} & \text{(Region II),} \end{cases} \quad (2)$$

where q is a coordinate of the particle and $a (< 0)$ is a constant that characterizes the slope of the potential. For simplicity, we take the unit mass of the particle. In region I where $q \geq 0$, the particle moves freely with the Hamiltonian $H(p, q) = \frac{p^2}{2}$. In region II where $q < 0$, it moves with the Hamiltonian $H(p, q) = \frac{p^2}{2} + aq$.

In this review, we summarize the previous results [12]-[13] about this problem and examine their implications. We present the analytical expression for energy change ΔE and its average effect over the initial conditions for NVE ensemble.

A velocity Verlet algorithm, one of the symplectic algorithms, is used to solve the Newtonian equation of motion. The equations for the algorithm for a particle moving from region I, with a coordinate q_0 immediately before the contact, to region II, with a coordinate q_1 immediately after the contact, are written as

$$\begin{cases} q_1 & = q_0 + \tau p_0, \\ p_1 & = p_0 - \frac{1}{2}a\tau. \end{cases} \quad (3)$$

For a particle moving in region II, we can write

$$\begin{cases} q_{n+1} & = q_n + \tau p_n - \frac{1}{2}a\tau^2, \\ p_{n+1} & = p_n - a\tau, \end{cases} \quad (4)$$

and thus, the trajectory is a parabola. The number n_c denotes the number of steps immediately after the collision with the potential wall when the particle is leaving region II. Thus, $n_c - 1$ is the number of steps for the particle to stay in the potential wall during the collision. For $(n_c - 1)$ -th step, we have

$$\begin{cases} q_{n_c-1} & = q_1 + (n_c - 2)\tau p_1 - \frac{1}{2}a\tau^2(n_c - 2)^2, \\ p_{n_c-1} & = p_1 - (n_c - 2)a\tau. \end{cases} \quad (5)$$

Furthermore, for a particle moving from region II, with a coordinate q_{n_c-1} immediately before the exit of the potential wall, to region I with a coordinate q_{n_c} immediately after the exit of the potential wall, the equations are written as

$$\begin{cases} q_{n_c} & = q_{n_c-1} + \tau p_{n_c-1} - \frac{1}{2}a\tau^2, \\ p_{n_c} & = p_{n_c-1} - \frac{1}{2}a\tau. \end{cases} \quad (6)$$

Finally, from Eqs. (3)-(6), we get

$$\begin{cases} q_{n_c} & = q_0 + \tau p_0 n_c - \frac{1}{2}a\tau^2 n_c(n_c - 1), \\ p_{n_c} & = p_0 - a\tau(n_c - 1). \end{cases} \quad (7)$$

From Eq. (7), n_c can be calculated to be

$$n_c = \text{ceil}\left(\frac{1 + \frac{1}{2}\mu + \sqrt{(1 + \frac{1}{2}\mu)^2 + 2(\alpha - 1)\mu}}{\mu}\right), \quad (8)$$

where the function $ceil(x)$ denotes the minimum integer larger than x .

If we define ΔE as the relative energy change during the collision,

$$\Delta E \equiv \frac{p_{n_c}^2 - p_0^2}{p_0^2} = \mu(n_c - 1)(\mu(n_c - 1) - 2). \quad (9)$$

We can explicitly derive the analytical expression for an inevitable energy change ΔE due to the discrete process, which is only dependent on two parameters: (1) $\alpha \equiv 1 - \frac{q_0}{\tau p_0}$, which is a fraction of the time step τ immediately after the contact with the potential wall and (2) $\mu \equiv a\tau/p_0$, where q_0 and p_0 are the coordinate and momentum of the particle just before the collision with the wall.

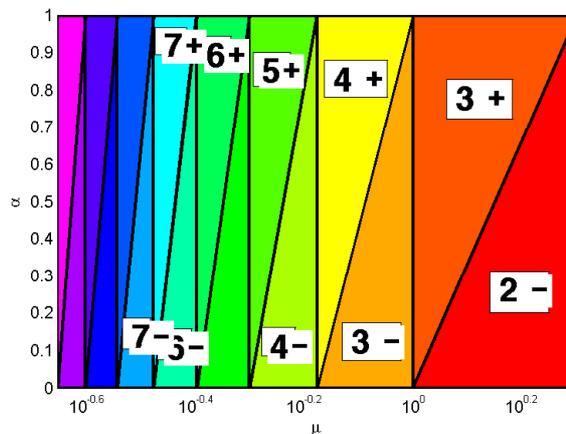


Figure 1. (Color on-line) Divisions of α and μ space up to $n_c = 10$. These divisions can continue up to $n_c \rightarrow \infty$. The cross points with abscissa are given by the formula $\mu = \frac{2}{n_c}, n_c = 2, \dots, \infty$. All points on the vertical lines and diagonal lines, except $\alpha = 0$ show $\Delta E = 0$. Upper right-angled triangles show $\Delta E > 0$, denoted with the '+' symbol shown in the box. Lower right-angled triangles show $\Delta E < 0$, denoted with the '-' symbol shown in the box. The numbers shown in the box are the number n_c .

The whole space by the two parameters α and μ can be divided into an infinite number of regions where each region creates a positive or negative energy change ΔE . Parameter α is in the range of $0 < \alpha \leq 1$, and μ is in the range of $0 < \mu \leq 2$ since n_c is an integer greater than 1. From Eq. (8), for a fixed value of μ , the number of collisions n_c changes by 1 over the whole range of α from 0 to 1, since $n_c(\alpha = 1) - n_c(\alpha = 0) = 1$ for any value of μ . If $\mu(n_c - 1) = 2$, then $\Delta E = 0$ for any value of α . Thus, vertical lines $\mu = \frac{2}{n_c - 1}$ for $n_c = 2, \dots, \infty$ divide the parameter space into an infinite number of subspaces, as shown in Fig. 1. Straight lines $\alpha = (n_c - 1)(\frac{1}{2}n_c\mu - 1)$ for $n_c = 2, \dots, \infty$ divide the subspaces into two regions: upper triangles show a positive change in ΔE , and lower triangles show a negative change in ΔE . At points on the boundaries, $\Delta E = 0$. In Fig. 1, the regions are denoted with different colors and a pair of symbols including a number n_c and a symbol, '+' or '-', up to $n_c = 10$.

Fig. 2 shows the results of ΔE as a function of μ for different values of α . The upper bounds of individual values $|\Delta E|$ show a power law behavior $|\Delta E| \propto \mu^\beta$, with the exponent $\beta \approx 1.08$. This exponent governs the energy fluctuation from the round-off error at a discrete time step τ . This implies that the round-off error in the energy, introduced by the discreteness, is nearly proportional to the time step τ .

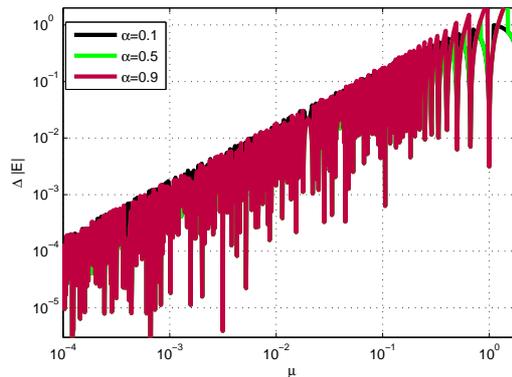


Figure 2. (Color on-line) Energy change $\Delta|E|$ vs. parameter μ along the horizontal lines in Fig. 1 for different values of parameter $\alpha = .1, .5$ and $.9$. The straight line corresponds to the envelope of upper bounds of $\log |\Delta E|$.

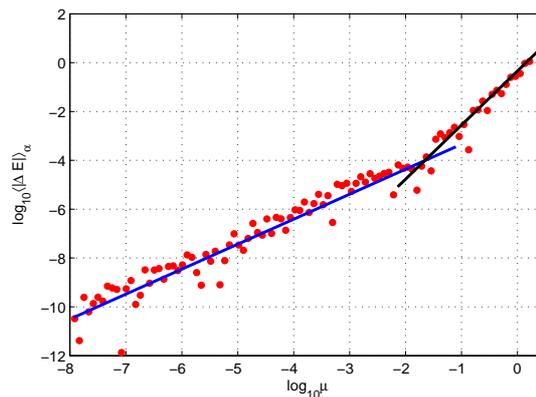


Figure 3. (Color on-line) Log-log plot of energy change $\langle|\Delta E|\rangle_\alpha$ vs. μ . Averages are taken over a uniform distribution of parameter α .

Let us now consider the analytical expression for the averages of energy change ΔE under appropriate distributions of the parameters α and μ . Averages are taken along either the vertical lines (averages over α) or the horizontal lines (averages over μ or p_0). $\langle|\Delta E|\rangle_\alpha$ is defined as the average of $|\Delta E|$ along a horizontal line with $\alpha = \text{constant}$. In the simulations, we actually encounter many different realizations of α ; however, unfortunately, we do not know *a priori* the distribution of α . Thus, we have to assume that the distribution of α is uniform on $(0, 1]$. The calculated results are shown in Fig. 3. To draw on the same side in Fig. 3, we take absolute values. As the value of μ decreases starting from $\mu = 2$ down to $\mu = 10^{-1.5} \approx 0.03$, the average $\langle|\Delta E|\rangle_\alpha$ decreases rather rapidly. Thus, it appears that they show two straight lines having exponents $\beta \approx 1.98$ at larger μ values and $\beta \approx 0.99$ at smaller μ values. The two straight lines intersect around $\mu \approx 0.03$. This implies that choosing a time step of $\tau \approx 0.03p_0/a$ can be thought of as an optimum for the simulations without generating large errors in the energy estimations.

In summary, the validity of molecular dynamics for soft matter has been examined analytically. The envelope of $\log |\Delta E|$ follow a power law with an exponent of 1.08. Furthermore,

the average of $\langle |\Delta E| \rangle_\alpha$ shows a broken power law behavior $\langle |\Delta E| \rangle_\alpha \propto \mu^\beta$ having two exponents $\beta \approx 1.98$ at larger values of μ and $\beta \approx 0.99$ at smaller values of μ . Thus, the error in the energy drift introduced by the discrete process is canceled significantly through the average process. Average over the initial conditions on α and μ can significantly increase the optimum time step up to several times. Although we have demonstrate the validity of molecular dynamics for a very simple system with a linear potential wall, the results can be generalized to a wide range of systems as well.

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