Stochastic and dynamic properties of molecular dynamics systems: Simple liquids, plasma and electrolytes, polymers

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Abstract

The concept of dynamical memory time t_m is discussed. The relation between t_m, fluctuation of energy ΔE and K-entropy (Lyapunov exponent) is treated. The meaning of t_m for real systems is related to the thermal and Langevin noise and quantum uncertainty. Relaxation of kinetic energy to equilibrium state was studied by MDM for non-equilibrium strongly coupled plasmas. Violation of the microscopic reversibility principle in some enzymatic reactions is discussed. © 2002 Elsevier Science B.V. All rights reserved.

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The molecular dynamics method (MDM) is usually called a dynamic method whereas the Monte Carlo method is referred to as a stochastic method of molecular simulation. The objective of the present paper is to show that MDM possesses both dynamic and stochastic features. Moreover, if MDM had no hidden stochastic features MDM would not probably be able to achieve well-known successful results. Another objective is to present examples of MDM simulation of non-equilibrium relaxation when stochastic features influence the dynamics. The topic is related to the occurrence of irreversibility in the case of the classical molecular systems, which has been discussing since the Boltzmann–Zermelo debate [1–3].

1. Divergence of trajectories in MDM

The idea of MDM is very simple: all possible classical systems and media are simulated by a set of N moving atoms and/or molecules, which interact with each other (e.g., see [4–11]). The numerical integration of the corresponding system of Newton equations

$$m_i \frac{\mathrm{d}\mathbf{v}_i(t)}{\mathrm{d}t} = \mathbf{F}_i\big[\mathbf{r(t)}\big], \qquad \frac{\mathrm{d}\mathbf{r}_i(t)}{\mathrm{d}t} = \mathbf{v}_i(t) \qquad (1)$$

results in the determination of the trajectories of all particles $\{\mathbf{r}, \mathbf{v}\}$. Here, m_i, $\mathbf{v}_i$, $\mathbf{r}_i$, and $\mathbf{F}_i$ are the mass, velocity, and coordinate of the ith particle and the force acting on this particle, respectively ($i = 1, \ldots, N$); the $\mathbf{v}_i$ and $\mathbf{r}_i$ values explicitly depend only on time t; $\mathbf{F}_i$ depends only on the coordinates of particles; $\mathbf{r}(t)$ is the set of the coordinates of

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all particles, $\mathbf{r}(t) = \{\mathbf{r}_1(t), \mathbf{r}_2(t), \ldots, \mathbf{r}_N(t)\}$; $\mathbf{v}(t)$ is defined similarly; and

$$\mathbf{F}_i = -\frac{\partial}{\partial \mathbf{r}_i(t)} U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N), \qquad (2)$$

where U is the potential energy. Function U (forces $\mathbf{F}$) is assumed to be given in MDM. The total energy E of the system is the sum of the kinetic E_{kin} and potential U energies,

$$E = E_{kin} + U, \quad E_{kin} = \sum_{i=1}^{N} \frac{m v_i^2}{2}. \qquad (3)$$

Set (1) is exponentially unstable for a system of more than two particles (e.g., see [3–16]). The parameter that determines the degree of instability, that is, the rate of divergence of initially close phase trajectories, is the averaged Lyapunov exponent or K-entropy K. It can be determined in several ways. For a given U function and particles of the same mass m and for identical initial conditions corresponding to the kth point on an equilibrium molecular-dynamical trajectory, solutions $\{\mathbf{r}(t), \mathbf{v}(t)\}$ to system (1) are found in steps Δt and trajectories $\{\mathbf{r}'(t), \mathbf{v}'(t)\}$ are calculated in steps $\Delta t'$. Averaged differences of the coordinates (velocities) of the first and second trajectories are determined at coinciding time moments,

$$\langle \Delta v^2(t) \rangle = \frac{1}{NI} \sum_{j,k}^{N,I} \left(v_{jk}(t) - v'_{jk}(t) \right)^2, \qquad (4)$$

$$\langle \Delta r^2(t) \rangle = \frac{1}{NI} \sum_{j,k}^{N,I} \left(r_{jk}(t) - r'_{jk}(t) \right)^2. \qquad (5)$$

To improve accuracy, averaging over $k = 1, \ldots, I$ is also performed. In some transient time t_l the differences begin to increase exponentially with the same value of K,

$$\langle \Delta v^2(t) \rangle = A \exp(Kt),$$
$$\langle \Delta r^2(t) \rangle = B \exp(Kt) \qquad (6)$$

at $t_l < t < t_m$. The calculated data for Lennard-Jones system is given in Fig. 1. The values of A and B are determined by the difference of Δt and $\Delta t'$. The exponential increase of $\langle \Delta v^2(t) \rangle$ is limited by the finite value of the thermal velocity of particles v_T. Thus after the time t'_m

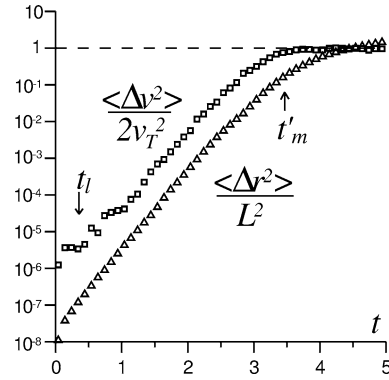$$t'_m \approx K^{-1} \ln(6kT/Am), \qquad (7)$$

Fig. 1. Normalized averaged differences of (squares) velocities and (triangles) coordinates at coinciding time moments along two trajectories calculated for identical initial conditions with time steps $\Delta t = 0.001$ and $\Delta t' = 0.0001$; L is the main cell edge length, $N = 64$, $n = 0.5$, $T/k = 0.44$. Number density n, temperature T/k and time t are given in reduced Lennard–Jones units.

where T is the temperature, saturation is reached

$$\langle \Delta v^2(t) \rangle = 2\langle v_T^2 \rangle = 6kT/m, \qquad (8)$$
$$\langle \Delta r^2(t) \rangle = 6D(t - t'_m) + \langle \Delta r^2(t'_m) \rangle \qquad (9)$$

for $t > t'_m$, where D is the diffusion coefficient. Estimates show that $\langle \Delta r^2(t'_m) \rangle$ is about the mean path of particles between collisions $(\sqrt{2}n\sigma)^{-1}$.

2. Dynamical memory time

Although the calculations [14] showed that the dependence of t'_m on $\Delta t'$ at fixed Δt is rather weak we applied the following procedure to determine *the dynamical memory time t_m*. The values of t'_m are calculated at the same Δt value and different $\Delta t'$ values of $\Delta t/2$, $\Delta t/5$, $\Delta t/10$, etc. The limiting value of t'_m when $\Delta t'/\Delta t \to 0$ is the dynamical memory time t_m for a given system and the selected numerical integration step Δt [14,15].

The physical sense of time t_m consists in the following. During numerical integration after the time t_m the molecular-dynamical trajectory calculated with time step Δt completely "forgets" its initial conditions. This means that the MD-trajectory ceases to correlate with the hypothetical Newtonian trajectory (an exact solution of set (1)). In other words, the value of t_m determines the time interval during which the behavior of the molecular-dynamical system can be pre-
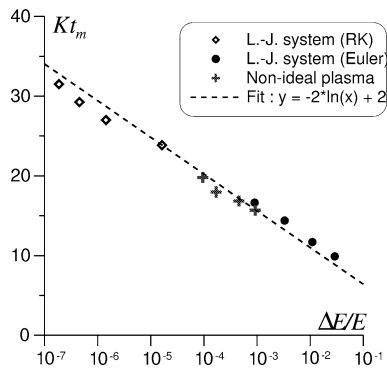
Fig. 2. Calculated dependence of Kt_m value on the relative fluctuations of the system's total energy $\Delta E/E$ for two different many-particle systems and Euler (2nd order) and Runge–Kutta (4th order) numerical schemes.

dicted from initial conditions and deterministic equations of motion at a certain level of accuracy defined by the Δt value and a particular scheme of numerical integration. Such a definition of t_m correlates with that given in [17,18].

The calculated dependencies of Kt_m on the integration step Δt can be presented in the form

$$Kt_m = -p\ln(\Delta t) + \text{const},\qquad(10)$$

where p is determined by the accuracy order of the numerical integration scheme, or, in another form,

$$K(t_{m1} - t_{m2}) = p\ln(\Delta t_2/\Delta t_1),\qquad(11)$$

where t_{m1} and t_{m2} are the dynamical memory times for the steps Δt_1 and Δt_2, respectively. This result does not depend on either temperature, density, or the system under study [14,15].

Because of the approximate character of numerical integration, energy E [Eq. (3)] is constant only on average. The E value fluctuates about the average value from step to step, and the trajectory obtained in molecular dynamics simulations does not lie on the surface $E = \text{const}$, in contrast to exact solutions to Newton equations (1). This trajectory is situated in some layer of thickness $\Delta E > 0$ near the surface $E = \text{const}$ [7,8]. The value $\langle\Delta E^2\rangle \sim \Delta t^p$ depends on the accuracy and the scheme of numerical integration [7, 8,19–22]. Therefore

$$Kt_m = -\ln(\langle\Delta E^2\rangle) + \text{const}.\qquad(12)$$

Eq. (12) relates the K-entropy and the dynamical memory time to the noise level in the dynamical system (Fig. 2).

It follows from (10)–(12) that t_m grows no faster than logarithmically as the accuracy of numerical integration increases. The available computation facilities allow ΔE to be decreased by 5 orders of magnitude even with the use of refined numerical schemes [20–22]. This would only increase t_m two times. It means that t_m is much less than the usual MDM run. So MDM is a method which retains Newtonian dynamics only at times less than t_m and carries out a *statistical averaging* over initial conditions along the trajectory run.

The K-values were calculated by MDM for systems of neutral particles [3,7–12,23,24], two-component [15] and one-component [16] plasmas and the primitive polymer model [25]. Estimates of dynamical memory times showed that, e.g., in Ar fluid [14], t_m lies in the picosecond range. The values of K turn out to be the same for both velocities and coordinates deviations. It is also seen that the K-values for electrons and ions are close to each other at the initial stage of divergence. At $t = t_{me}$ the quantity $\langle\Delta v^2(t)\rangle$ for electrons reaches its saturation value and, therefore, at $t > t_{me}$ only ion trajectories continue to diverge exponentially with another value of K-entropy depending on the electron-ion mass ratio M/m as $K_i \sim (M/m)^{-1/2}$. The dependence of t_{mi} on M/m also fits the same square root law, while t_{me} is independent of M [15].

A system of 10 polymer molecules with atom-atom interaction potential and periodic boundary conditions was studied in [25]. Each model molecule consisted of 6 atoms with constant interatomic distances and variable angles ϕ between links. The divergence of velocities $\Delta v^2(t)$ and coordinates $\Delta r^2(t)$ for both atoms and molecule center-of-masses as well as angles $\Delta\phi^2(t)$ was calculated. All the five dependencies follow the exponential law before saturation. All the five exponents turned out to be equal to each other, as for electrons and ions in plasmas. One can expect that this is a general conclusion for systems with different degrees of freedom.

Kravtsov et al. [17,18] considered the measuring noise, fluctuation forces and uncertainty in knowledge of differential deterministic equations of the system as the reasons why t_m has a finite value. It is a

characteristic of a simulation model in [7,14–16]. The time t_m might be related to the concept of a quasi-classical trajectory, which takes into account small but finite quantum effects in classical systems: broadening of particle wave packets and diffraction effects at scattering [14,15,26,27], to weak inelastic processes [18].

Our premise coincides with Karl Popper's conviction foundation stone that "nontrivial probabilistic conclusions can only be derived (and thus explained) with the help of probabilistic premises" [28]. The probabilistic premise we use consists in the fact that any motion which is used to be considered as a deterministic classical actually has quantum nature. The idea was inspired by an old remark of John von Neumann [29] and Landau [30] that any irreversibility is related to the probabilistic character of measurement procedure in quantum mechanics.

Estimates of dynamical memory times were obtained for molecular dynamics numerical schemes. Since t_m values very weakly (logarithmically) depend on the noise level, it allowed us to extend qualitative conclusions to real systems of atoms.

Though the primary source of the stochastic noise is the probabilistic character of the measurement procedure there are other factors which remarkably increase the noise value and permit us to forget about quantum uncertainty at simulation. For example, it is the water molecule background that creates the stochastic noise in electrolytes. One is able to add Langevin forces into (1) and apply MDM to study their influence on the dynamic properties of Coulomb systems. Calculations [31] showed that collisions of ions with water molecules does not change essentially the value of t_m.

3. Boltzmann and non-Boltzmann relaxation

The molecular chaos hypothesis is a basis of the kinetic theory, i.e. it is implied that molecule motion is stochastized. However, it is apparent that dynamic motion precedes stochastic processes [13, 32,33]. It is implied that dynamic motion governed by intermolecular interactions defines the values of collision cross-sections but does not influence the time dependence of kinetic processes. One can expect that the Boltzmann description of kinetic processes is valid

only for the times greater than t_m. MDM can be a powerful tool for studying non-Boltzmann relaxation phenomena in more or less dense media. Some non-equilibrium processes have already been studied with MDM, for example, in [14,23,34–38].

MDM was applied in [39] to the study of electron and ion kinetic energy relaxation in strongly coupled plasmas. A two-component fully ionized system of $2N$ single-charged particles with masses m (electrons) and M (ions) was considered. It is assumed that the particles of the same charge interact via the Coulomb potential, whereas the interaction between particles with different charges was described by the effective pair potential ("pseudo-potential"). The nonideality was characterized by a parameter $\gamma = e^2 n^{-1/3}/kT$, where $n = n_e + n_i$ is the total density of charged particles. The values of γ were taken in the interval from 0.2 to 3. The details of the plasma model and the numerical integration scheme are presented in [15].

The following procedure was used to prepare the ensemble of non-equilibrium plasma states. An equilibrium trajectory was generated by MD for a given value of γ. Then a set of $I = 50$–200 statistically independent configurations was taken from this run with the velocities of electrons and ions dropped to zero. Thus, the ensemble of initial states of non-equilibrium plasma was obtained. MD simulations were carried out for each of these initial states and the results were averaged over the ensemble.

MD simulations [39] revealed a Boltzmann character for time $t > 5\tau_e$. The difference between the electron and ion kinetic energies follows an exponential decay law. The character of this long time relaxation agrees qualitatively with earlier results [34, 36]. At the times less than $0.1\tau_e$ both the electron and the ion kinetic energies increase according to the quadratic fit. Then the electron kinetic energy passes through the maximum and undergoes several oscillations damping at $t \approx t_m$ while the ion kinetic energy increases monotonously. The relative importance of the non-Boltzmann relaxation stage decreases with the decrease of plasma nonideality. The oscillatory character of non-Boltzmann relaxation vanishes when the nonideality parameter is less than $\gamma = 0.5$. The possibility of two stages of relaxation was noted in [36].

Another example of a particular relaxation process is related to the arising of irreversibility in the case of enzyme catalysis. The microscopic reversibility prin-
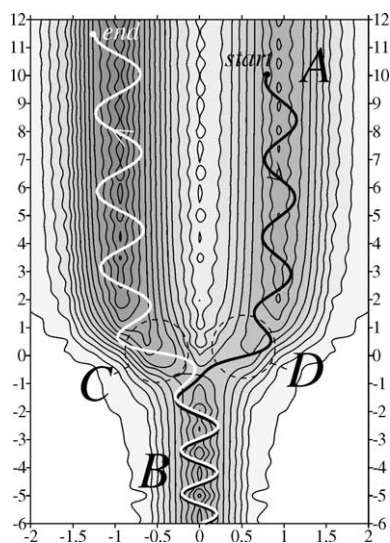
Fig. 3. An example of irreversible behavior in the simple 2D-system that motion is disturbed by random noise (picture of motion on the surface of potential energy).

ciple is a fundamental principle of physical and chemical kinetics. However, Vinogradov [40] obtained experimental evidence for different pathways for direct and reverse enzymatic reactions in the case of hydrolysis and synthesis of ATP and some other mitochondrial molecular machines and supposed that "the one-way traffic" principle was realized at the level of a single enzyme.

If there are two pathways along the hyper-surface of potential energy between initial and final states there should be at least two bifurcation points: in the first of them (during the direct reaction) *nearly always* the system chooses one path and in the second (during the reverse reaction) *nearly always* chooses another. We suppose that this "nearly always" condition can be realized in the case of specific asymmetry of the potential relief in the vicinity of the bifurcation point. It is not a Maxwell demon but Lyapunov instability, stochastic terms and a complicated potential relief with a developed system of relatively hard valence bonds that define the local choice of the reaction pathway in the bifurcation point [41]. In the case of enzymatic reactions the physical sense of the stochastic terms is related to thermal fluctuations of the potential relief and noise produced by collisions with water molecules while the main features of the relief do not depend on time essentially.

The molecular simulation example [42] of a primitive model confirms this conclusion (Fig. 3). The local choice is determined by the local parameters. The situation is equivalent to the statement that there is no thermodynamic equilibrium in the area around the bifurcation point and the transient state theory is not valid here.

Recent results of molecular simulations [43] confirm the introduced thesis that thermal fluctuations are able to result in completely different pathways of particular biochemical processes.

Acknowledgements

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