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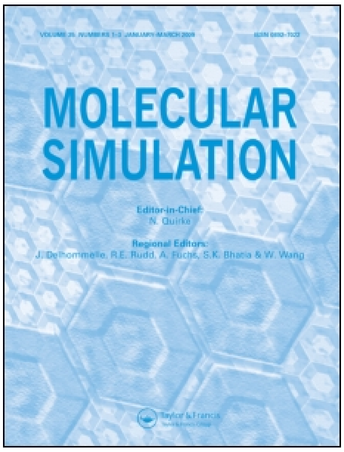

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EQUATIONS OF MOTION AND ENERGY CONSERVATION IN MOLECULAR DYNAMICS

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The differences between the actual equations of molecular dynamics method (MD) and the Newtonian ones due to numerical integration errors are analyzed. Condition of total energy conservation in MD is obtained. The simplest schemes satisfying this condition and the total energy fluctuations in MD are considered. Statistical meaning of MD and possible analogies of the MD equations in real molecular systems are discussed.

KEY WORDS: Molecular dynamics, computational errors, energy conservation

In the molecular dynamics method (MD) the Newtonian equations of motion for an N-particle system with given interparticle potential are solved numerically. The required thermodynamic, transport, structure, correlations and other properties are obtained by averaging the appropriate functions of microvariables along the computed particles trajectories (phase trajectory), see, e.g. the reviews [1–7]. MD has been successfully developed and applied for the last 30 years and the results have proved to be consistent with the general laws of thermodynamics and kinetic theory as well as with diverse experimental data.

Yet, in a number of papers [4–13] attention is paid to an exponential time growth of errors which is a manifestation of the instability of the equations of motion known since Poincaré. Nevertheless, it is necessary [11, 14] that the computed trajectories should remain close to the exact ones where used for statistical averaging. The extreme difficulty of such problem caused Fox [14] to doubt the very validity of MD. His work stimulated Erpenbeck and Wood to perform computations of higher precision [11], and they claim to use in reaching their conclusions sufficiently exact initial segments of the MD trajectories. The averaging in [11], however, was performed over different initial phase points rather than time, so the trajectories were fairly short. The fact that MD can compute trajectories accurately only for short times has been pointed out in [6, 12, 13]. However it was not analyzed in these papers why it works in spite of long time averaging where the computer trajectory is no longer exact. Moreover, ignoring the existence of total energy fluctuations some authors state [1–6] that in the original version of MD the microcanonical ensemble is simulated, i.e. the computed trajectory lies on the hypersurface of the constant total energy. It is also stated [5] that if the equations of motion are solved correctly, the computer-generated trajectories will be time-reversible.

Thus the problem of a correspondence between the MD-system, that is the system which is actually realized in the computer, and the exact Newtonian system requires a more careful analysis. This question is closely connected to the choice of practical numerical schemes. Although "good" schemes have been known empirically for a long time, the absence of a general criterion of "goodness" caused the opinions like ". . . the order of the algorithm . . . should be at least 3" to be stated [2, 6] and the attempts to use complex schemes of higher orders to be made [2, 5, 6].

In the present paper we investigate numerical integration errors arising from a finite-difference approximation of differential equations and derive the expressions for total energy fluctuations. We formulate condition under which the numerical scheme is "good". Finally we give an interpretation of MD as a statistical method providing a true system dynamics for small times.

1. GENERAL FORM OF MOTION EQUATIONS

Phase trajectories of particles $\{x(t), v(t)\}$ obtained by MD for schemes with explicit calculations of the velocities are defined by equations:

$$\dot{x} = v(t) + \xi(t) \tag{1a}$$

$$\dot{v} = F(x) + \eta(t) \tag{1b}$$

where F is a regular force on a particle. The mass of each particle is equal to unity; the equations are written in the x-axis projection; all indexes are omitted. The quantities ξ, η are additional terms resulting from the numerical nature of integration of Newtonian motion equations, for the latter $\xi = \eta = 0$.

For schemes with implicit velocity calculation, for example the Verlet scheme, only one equation remains

$$\ddot{x} = F(x) + z(t) \tag{2a}$$

where z also arises from the numerical integration errors. However, to obtain the phase trajectory it is necessary to supplement Equation (2a) by a procedure for the velocity calculation. The procedure itself is independent of the numerical scheme but it may be also written in the form analogous to (1a),

$$\dot{x} = v(t) + \tilde{\xi}(t) \tag{2b}$$

It is reasonable to choose an accuracy of (2b) to be of the same order as that of (2a).

Equations (1a) and (1b) can be reduced to the form (2a) to yield $\dot{\xi} + \eta = \tilde{z}$. The quantity z as will be seen later is necessary for the analysis of both the cases (2a) and (1). The phase trajectories for (1) and (2) are identical if $z = \tilde{z}$ and $\xi = \tilde{\xi}$.

In general, the MD errors consist of the numerical scheme errors, the round off errors and the erros arising from calculation of forces at large distances. The last source is represented by the errors of the nearest image method, Ewald's method for Coulomb systems, the cut-off distance etc. It may be looked upon as an approximation introduced by the choice of the physical model and not immanent to MD itself. Round off errors as a rule are small compared to the numerical scheme errors. Thus, in the following discussion expressions for ξ, η, z are assumed to result from the computational scheme only.

In practically used numerical methods the ξ, η and z have the typical form

$$\xi = C_\xi \cdot x^{(m+1)} \cdot h^m + 0(h^m)$$

$$\eta = C_\eta \cdot v^{(n+1)} \cdot h^n + 0(h^n)$$

$$z = C_z \cdot x^{(k+2)} \cdot h^k + 0(h^k) \tag{3}$$

where C_ξ, C_η, C_z are coefficients depending on the particular numerical scheme, h is the integration step, m, n and k are the orders of approximation of the schemes for x and v (for case (1)) and x (for case (2)), respectively. Since the motion of nonlinear dynamical systems with a convex interaction potential appears to be mixing [15, 16] and ξ, η, z are expressed in terms of the time derivatives of the dynamics variables x and v, the quantities ξ, η, z can be described probabilistically, that is using the concepts of distribution function, correlation function etc. [7].

Probabilistic properties of ξ, η and z such as correlation and distribution functions can be expressed in terms of a single characteristic, namely, the velocity autocorrelation function. The detailed discussion and numerical verification of this statement are presented elsewhere [7].

It should be mentioned that the instantaneous values of ξ, η and z are not, in general, a small perturbation. These terms take on the maximum values when the force F or its gradient are large at a moment of strong (close) collision of the particles [7]. Meanwhile, according to numerous computations [7, 10, 11], MD results are independent of the magnitude of ξ and η in a wide range of their variation.

2. ENERGY CONSERVATION

The implicit additional forces in the equations of motion depending on higher derivatives of coordinates make the system nonconservative. On the other hand, a reasonable numerical scheme should conserve at least average system energy, therefore the terms ξ, η (or z) should be such that their action would not result in any drift of the average total energy. The total energy can fluctuate near some average value during a motion period, not being the motion integral.

For the energy fluctuations to be stationary in a statistical sense it is necessary that the average work of the force z should be zero

$$\langle z \cdot \dot{x} \rangle = 0 \tag{4}$$

Since $z(t)$ is expressed in terms of the time derivatives of x, condition (4) can be satisfied if $z(t)$ contains only even derivatives of x. Thus, the requirement of conservation of the average total energy results in the time reversibility of the molecular dynamics Equations (2a). Equations (1) can include, however, irreversible terms which cancel when transforming (1) to form (2). In application to finite-difference schemes it means that the truncation error in the approximation of the second time derivative of coordinates should be even with respect to time. This discussion is illustrated below by the example of the simplest eulerian scheme of the first order with respect to both variables

$$v_{k+1} = v_k + F_k \cdot h \qquad x_{k+1} = x_k + v_{k+1} \cdot h \tag{5}$$

The approximation of the second derivative of x corresponds in this case to the second-order finite-difference scheme

$$(x_{k+1} - 2 \cdot x_k + x_{k-1})/h^2 = F_k \tag{6}$$

and the force z is expressed by the series

$$z = \ddot{x} - F = 1/12 \cdot x^{(4)} \cdot h^2 - \ldots - x^{(2n)} h^{(2n-2)}/(2n)!$$

including only even terms with respect to time. Thus, scheme (5) satisfies the necessary condition (4) of the energy conservation.

The first terms in the expansion for ξ and η in equation (1) for scheme (5) are not even functions of time

$$\dot{x} = v + (h/2) \cdot F, \qquad \dot{v} = F - (h/2) \cdot \dot{F} \tag{7}$$

but they cancel when transforming (7) to the form (2a).

Note that the connection between energy conservation and the reversibility of the MD-algorithm has been indicated in [6]. It should be emphasized, however, that this statement is valid only for schemes of type (6) for Equation (2a). The schemes of type (5), on the contrary, are not reversible as is seen from example (7).

It is concluded in [6] that for the energy to be conserved the schemes are necessary which approximate the coordinate to the order at least 3. Example (5) (scheme of the first order with respect to coordinates) indicates that this conclusion is not valid.

The well known Verlet's, Beaman's and "leap-frog" schemes are also based on finite difference (6) and also satisfy condition (4). These schemes in contrast to (5) are two-point ones and require specification of two initial conditions for two, rather than one, different moments of time. If the choice of initial conditions is correct the phase trajectories are computed by these schemes more accurately than by (5), however, the statistical accuracy of the MD-results is not enhanced (see [7, 10] and the concluding section of the present paper).

The discussed schemes as well as (5) can be recommended for MD-computations as the most simple of all known schemes. It should be noted that these schemes have been used in MD for a long time and it is "empirical awareness" of presented consideration that made them the most popular in MD studies.

In the MD studies numerical schemes of higher order of accuracy are often applied. As noted in [7] it does not improve the statistical accuracy of MD-results at all, leading only to an essential growth of the computer time. Sometimes the use of a higher order scheme turns out to be erroneous. As an example consider the scheme

$$v_{k+1} = v_k + F_k \cdot h; \qquad x_{k+1} = x_k + v_k \cdot h + F_k \cdot h^2/2$$

which is of higher order than (5). However, for MD this scheme is not acceptable because it does not satisfy condition (4) and therefore is not "conservative". Other examples can be pointed out when the schemes computing the trajectories at small times much more accurately than (5) turn out to be inadequate for MD since they do not satisfy condition (4).

3. ENERGY FLUCTUATIONS

The estimation of the energy fluctuations for the case when condition (4) is satisfied is based on the fact that the variation of the total energy is contributed by the work of the force z and that the kinetic energy fluctuations are due to the difference between $\dot{x}$ and v:

$$\Delta E = E(t) - E(0) = \int_0^t z\,\mathrm{d}x + (v^2/2 - \dot{x}^2/2)|_0^t \cong \int_0^t z\,\mathrm{d}x - \xi v|_0^t \tag{8}$$

In the case when z is of a higher order of smallness than ξ and η, like for scheme (5), only the last term of the right equation (8) can be retained. Then, squaring (8), averaging the result and using the energy fluctuation decay at long times one can obtain the formula for the total energy fluctuations

$$\sigma_E^2 \equiv \langle \Delta E^2 \rangle = 3 \cdot N \cdot (\langle v_x^2 \cdot \xi_x^2 \rangle - \langle v_x \cdot \xi_x \rangle^2) \tag{9}$$

Here account is taken of the fact that the energy fluctuates independently for each of N particles and for each of the three coordinates (index x refers to the Cartesian component of corresponding value). In particular, $\xi \sim F$ for scheme (5) due to (7). Taking account of the independence of v and F and using the equation $\langle v^2 \rangle = T$, where T is temperature, one obtains:

$$\sigma_E^2 = (h^2/4) \cdot N \cdot T \cdot \langle F^2 \rangle \tag{10}$$

Similarly, it is not difficult to show that for Verlet, Beaman etc. schemes the quantity $\sigma_E^2 \sim h^4$. This result is consistent with the numerical results of [2, 5].

The main dependence of σ_E on N in (9) and (10) has the usual statistical form $\sigma_E/E \sim N^{-1/2}$. Weak dependence of $\langle F \rangle$ on N can be practically neglected at $N > 10$.

The quantity σ_E has purely scheme origin. As for the fluctuations of kinetic and potential energy taken separately, they have the standard thermodynamical form (with an accuracy not less than N^{-1} [17]) and, naturally, are much greater than σ_E.

4. THE NATURE OF MD AVERAGING PROCEDURE

The above analysis allows to compare the nature of averaging over the microcanonical ensemble (implying Hamiltonian dynamics) and in MD. For a Hamiltonian system the phase trajectory always lies on the hypersurface of constant energy $H(p, q) = E$. As was shown above the phase trajectory of the MD-system fills up hyperlayer $H(p, q) = E \pm \sigma_E$ enveloping the constant energy hypersurface. Thus, the domains of averaging for Hamiltonian and corresponding MD systems somewhat differ.

4.1. Thermodynamics Quantities

The statistical distribution function and the statistical properties of a mechanical system are determined by the shape of the phase space domain where the system moves [18]. Therefore the statistical distribution function of MD-system is different from the distribution function of the exact Hamiltonian system. In other words, the ensemble realized in MD is, in general, different from the traditional statistical ensembles since the σ_E value has no analog in statistical physics.

However, according to direct computations the "broadening" σ_E of the hypersurface $H(p, q) = E$ is essentially smaller than canonical ensemble fluctuations even for such a rough scheme as (5). Consequently, differences in statistical properties of a Newtonian and the MD-system would not as well exceed corresponding differences between a closed system and a system in thermostat. In other words, the MD-ensemble occupies an intermediate position between the microcanonical and canonical ensembles.

The validity of average thermodynamical values computed using MD is ensured by conservation of the average energy which is the only quantity determining the system distribution function. To be more exact, the distribution function is determined by the shape of isoenergetic hypersurface $H(p, q) = E$ in the phase space and the validity of statistical characteristics in MD is a consequence of the absence of strong distortion of the hypersurface shape. The present discussion explains the success of MD in application to the computation of the thermodynamical properties in spite of the divergence between MD trajectory and the Newtonian one.

Since it is shown empirically that MD-results are consistent with general laws of statistical physics the phase trajectory might be suggested to pass repeatedly through the main domains of the phase region $H(p, q) = E$ during the computation period. This assertion, except for Sinai billiard, have not yet been proved for any Hamiltonian system of many particles.

4.2. Multi-time Moments for Equilibrium Systems

Such moments are required, for example, when Green–Kubo formulas are used in transport coefficients calculations. The discussion of section 4.1 on a choice of phase space region for averaging remains valid for these quantities as well, but in this case an additional problem arises in connection with the difference between the Hamiltonian and MD-trajectories.

A comparison of the trajectories (see [10, 7]) shows that the MD and Hamiltonian trajectories diverge exponentially. On the other hand, the distance between the trajectories in the phase space becomes close to the interparticle length scale or thermal velocity only at times exceeding correlation time τ_c (time scale of exponential velocity autocorrelation decay). Therefore at times less than several τ_c the trajectories computed by MD do not practically differ from the Newtonian ones. Thus, the MD-results for multi-time moments decaying in times of the order τ_c are equivalent to the results of Newtonian dynamics when averaged over an equilibrium ensemble.

The time scale discussed corresponds to a kinetics stage of relaxation. It was shown in numerical experiments [11], that at large (hydrodynamical) times the MD method gives correct results (e.g. for velocity autocorrelation functions long tails) independently of whether the individual trajectories have just lost accuracy or not. A detailed discussion of this question is beyond the frameworks of the present paper.

4.3. Nonequilibrium Systems

By these are meant the particle systems whose initial conditions correspond to nonequilibrium macrostates. In this case in constrast to the cases of sections 4.1 and 4.2 the averaging over an ensemble cannot be replaced by time-averaging and is performed over the appropriate set of initial microstates. As for time-dependencies of calculated quantities, the considerations presented in section 4.2 refer to this case as well.

Thus, MD constitutes a numerical method permitting a proper representative statistical sampling of the phase points of an N-particle equilibrium system and supporting Newtonian dynamics at times of the order of correlation time.

5. THE POSSIBLE SOURCES OF ξ AND η IN NATURE. CONCLUSION

Since MD has proved its ability for all considered classical systems it is useful to discuss how the MD description relates to real physical systems.

The sources ξ and η (or z and $\tilde{\xi}$) result from numerical integration errors and have no quantitative analogs among real physical systems. However, qualitative analogs can be indicated. First, there always exist external disturbances in any physical system. Quantum effects appear to be another source of the additional terms for any system [4, 19]. These questions deserve a separate discussion.

The above considerations imply some important conclusions. First, as it was mentioned in section 2, the enhancement of the accuracy of individual trajectories does not improve the accuracy of MD averages. Therefore MD should use the simplest numerical schemes satisfying condition (4), thus saving computer time. Secondly, other terms satisfying Equation (4) can be deliberately added to Newtonian equations to simulate various physical situations. It is this fact that provides the success of so-called non-Newtonian MD methods. The canonical ensemble can also be simulated by combination of MD and Monte-Carlo methods [11, 20]. Introduction of Langevin terms, with random sources of appropriate magnitude and spectrum allow to stimulate the system under gradients and other physical cases [21]. All such distortion should not violate condition (4) (if the opposite is not required by the physical situation) and should retain Newtonian dynamics at times $\sim \tau_c$.

As temperature decreases the quantum effects become essential and a dependence of calculated properties on magnitude of the real physical noise may be expected to appear. At the same time, however, the very quantity to be averaged would change their form. After solving these problems the MD would become applicable to quantum system [22].

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