Anomalous fluctuations in low-temperature molecular dynamics simulations

Riccardo Simonazzi*
Thera s.r.l., via Pietro l'Eremita 1, 00162 Rome, Italy

Alexander Tenenbaum†
Physics Department, ''La Sapienza'' University, Piazzale Aldo Moro 2, 00185 Rome, Italy
(Received 27 December 1995)

We present results of a standard (constant energy) molecular dynamics simulation of Lennard-Jones microcrystals at low temperature. The kinetic energy fluctuations exhibit an anomalous behavior, being much larger than expected in a microcanonical ensemble; this is due to a dynamics, which is only weakly chaotic. Such a dynamics does not warrant the equivalence of time and ensemble averages, unless one extends the simulation over exceedingly long times. A similar phenomenon has been recently found in the simulation of a canonical ensemble through a Nosé-Hoover dynamics. [S1063-651X(96)03807-X]

PACS number(s): 05.40.+j, 63.70.+h, 65.40.+g

In condensed matter systems, the atoms typically interact through a potential characterized by a strongly repulsive core at short distances and a soft attractive part at large distances; an example of this kind is the well known Lennard-Jones potential, widely used for systems that can be modeled by a pairwise additive interaction. At high temperature the dynamics of the atoms will be determined mainly by the repulsive core. At low temperature, on the other hand, the atoms will oscillate around the bottom of a potential well; they can therefore be described by a harmonic Hamiltonian perturbed by nonlinear terms.

In the first case the dynamics will be similar to that of hard spheres, in the second case to that of perturbed harmonic oscillators. Now, the system of hard spheres is supposed to be ergodic [1], while the Kol'mogorov-Arnol'd-Moser theorem demonstrates that a system of perturbed harmonic oscillators behaves in an ordered way in a region of positive measure of the phase space [2]. One therefore has to expect that when lowering the temperature of a generic condensed matter system, its behavior will be driven through a dynamical chaos-to-order transition.

Great progress has been made in understanding the dynamical properties of nonlinear Hamiltonian systems with many degrees of freedom (DOFs), since the famous numerical work by Fermi, Pasta and Ulam at Los Alamos [3]. However, the transition region from a highly chaotic to a highly ordered dynamics in those systems is still a quite unexplored field. Recently, extensive numerical simulations [4] have clearly shown the generic existence, for nonintegrable systems, of a critical value of the energy per DOF, called *strong stochasticity threshold* (SST). Above the threshold the motion appears strongly chaotic, and fast relaxation and fast mixing are observed. On the other hand, at energies lower than the SST, the motion is *apparently* regular, and very long relaxation times can be found by reducing the energy of the initial excitation; in any event, the largest Lyapunov exponent λ_1 [5] is always found positive, which means that at least weak chaos is always present. The SST seems to be independent of N.

Does this dynamical transition through the SST affect macroscopic (thermodynamical) properties of the system? If the answer were positive, would it be so also in the thermodynamic limit? In this paper we give an example of how the chaos-to-order transition may strongly affect standard properties of standard systems in a molecular dynamics (MD) experiment. We have performed computer experiments on three-dimensional (3D) face centered cubic (fcc) Lennard-Jones microcrystals of different sizes, and measured the kinetic energy fluctuations in the temperature range below 15 K (for argon). We have found that their average can be significantly different from the expected one, for simulation times that are typical in this kind of computer experiment. For very long trajectories in the phase space, this average slowly relaxes to the expected value; this behavior can be explained by the existence of weak chaos, i.e., of a partially ordered dynamics, in the low-temperature region of the phase space.

The systems we study are fcc lattices with periodic boundary conditions, with square or rectangular faces, and a number of atoms varying between 256 ($4\times4\times4$ elementary cells) and 32 768 ($8\times8\times128$ elementary cells). The atoms interact through a Lennard-Jones potential

$$V(r)=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]. \tag{1}$$

The cutoff of the potential is at $r_c=2.746\sigma$, so that the interaction reaches the shell of the sixth neighbours; the lattice parameter is 1.548σ. In the following, the Lennard-Jones parameters will be given the values appropriate for argon: $\sigma=3.405$ Å, $\epsilon=119.8k_B$; the corresponding time unit is $\tau=(m\sigma^2/48\varepsilon)^{1/2}=3.112\times10^{-13}$ s.

The systems have been simulated at various temperatures below 15 K. The equations of motion have been integrated with a central difference algorithm, frequently used in MD experiments [6]. We have used a time step $h=0.032\tau=10^{-14}$ s; each run had a first equilibration stage of 5000

*Electronic address: riccardo@thera.iunet.it
†Author to whom correspondence should be addressed. Electronic address: tenenbaum@roma1.infn.it

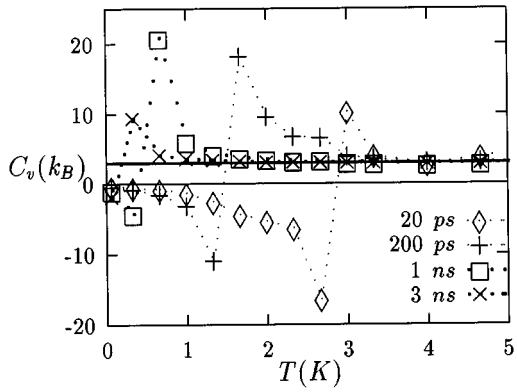

FIG. 1. Specific heat vs temperature, in a 4096 particles system, for increasing averaging times. The horizontal line corresponds to $C_v = 3k_B$.

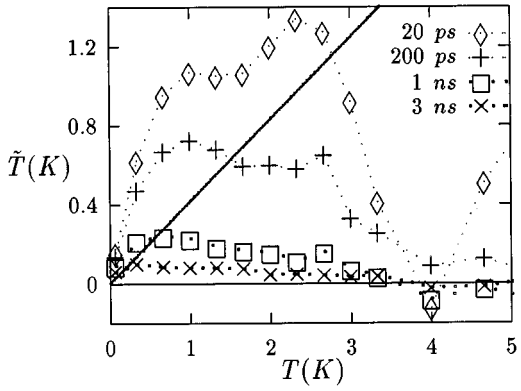

FIG. 2. Excess temperature vs temperature, in a 4096 particle system, for increasing averaging times.

steps, followed by a stage of up to 300 000 steps, during which equilibrium averages were computed.

The computations were performed on APE100, a special purpose parallel computer designed and produced by the Istituto Nazionale di Fisica Nucleare in Italy [7]. For systems up to 2048 atoms we used a *board* with 8 processors, while for the systems with 4096 and 32 768 atoms we used a *crate* with 128 processors. The processors of APE100 are put on a 3D toroidal structure, i.e., on a cubic lattice with first neighbour connection and periodic boundary conditions. We have simulated the Lennard-Jones (LJ) lattice through a ''domain decomposition technique with frames'' [8]. The computation time varied between 4 h on a board for the smallest system and 9 h on a crate for the largest one. The latter computation would have lasted for 140 d on the CPU of an alfa-VAX 3000-400 workstation.

The periodic boundary conditions imposed on the simulated systems keep the total energy constant; therefore, if the system were ergodic, its trajectory in the phase space would sample a microcanonical ensemble. For this ensemble the specific heat per particle at constant volume is related to the average fluctuation of the kinetic energy through the formula:

$$C_v = \frac{dk_B/2}{1-(Nd/2)(\langle K^2\rangle - \langle K\rangle^2)/\langle K\rangle^2}, \qquad (2)$$

where N is the number of particles, d the dimensionality of the system, and K its total kinetic energy; $\langle\ \rangle$ is an ensemble average [9]. The temperature has been defined through $\langle K\rangle = Ndk_BT/2$. We have used formula (2) to check the ergodicity of our systems, that is, the equivalence of time and ensemble averages.

We have performed equilibrium runs for systems of 256, 2048, 4096, and 32 768 atoms, computing the specific heat per particle through formula (2), averaging over 2×10^3, 2×10^4, 10^5, and 3×10^5 time steps. Above 4 K, after 5000 steps of equilibration, an average over 2000 steps (20 ps) is already sufficient to find $C_v = 3k_B$. This is the value expected at low temperature for the harmonic limit of a solid. But below 4 K, the situation changes completely. In Fig. 1 we report the results relative to an intermediate system. The figure shows the following features, which are common also to the other simulated systems of different size: (i) C_v has the expected value of $3k_B$ when $T>4$ K, except for some values computed over 20 ps, which are not yet fully stabilized. (ii) Lowering the temperature below 4 K, one finds a temperature T_a at which the specific heat starts increasing above its expected value. T_a tends to zero for increasing averaging times. (iii) In the temperature range below T_a the specific heat changes abruptly from positive to negative values; there is a temperature T^* where C_v diverges, positively from the right and negatively from the left. Also T^* tends to zero for increasing averaging times. (iv) C_v tends to zero at the lowest temperature. (v) All these features do not seem to depend on N.

The peculiar results for the specific heat are a clear sign that, at low temperature, time averages of the kinetic energy fluctuations—even over very long times—are not equivalent to ensemble averages. Formula (2) shows that the specific heat diverges at the temperature (T^*) at which the average fluctuation of the kinetic energy $\langle(\delta K)^2\rangle = \langle K^2\rangle - \langle K\rangle^2$ equals $2\langle K\rangle^2/Nd$. Such a fluctuation would be expected in a canonical ensemble, while the value expected in a microcanonical ensemble is $\langle K\rangle^2/Nd$ [9]. The fact that C_v tends to zero from negative values when $T\to0$ means that $\langle K\rangle^2 \to 0$ faster than $\langle(\delta K)^2\rangle$, again a sign of an anomalously high fluctuation of the kinetic energy.

In order to give a quantitative description of these anomalous fluctuations, and of their dependence on temperature and system size, we proceed as follows. The results reported above show that—below 4 K—at a given temperature (i.e., at a given average kinetic energy) the fluctuation of the kinetic energy is higher than expected, that is, has the value one would expect at a higher temperature. We call *excess temperature* the difference between the latter (''measured'' through the fluctuation of K) and the former temperature (measured through $\langle K\rangle$). We define an excess kinetic energy as $Z_N = [Nd(\langle K^2\rangle - \langle K\rangle^2)]^{1/2} - \langle K\rangle$; in a microcanonical ensemble one should have $Z_N = 0$. When the fluctuation of the kinetic energy exceeds the expected value, $Z_N > 0$ and an excess temperature, independent of N, can be defined through $\tilde{T} = 2k_BZ_N/Nd$.

In Fig. 2 we report the values of $\tilde{T}$ for a system of 4096 particles; the other systems show similar features. The curves in the figure show that the excess temperature tends to zero, but very slowly: the fluctuation of the kinetic energy tends to

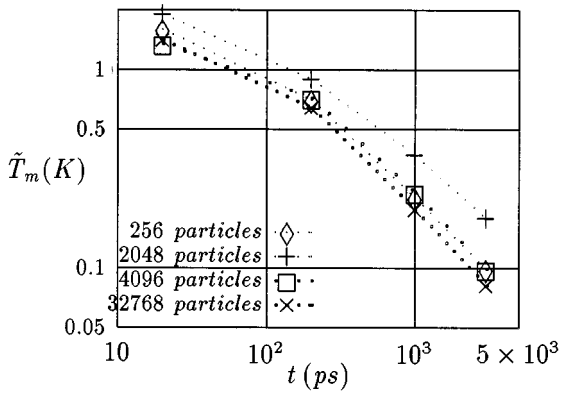

FIG. 3. Maximum excess temperature vs averaging time in the four systems.

become ''normal'' when averaged over times that are much longer than those used in standard MD experiments. To make this statement quantitative, we report in Fig. 3 the maximum value of $\widetilde{T}$ as a function of the averaging time t, for the four simulated systems. For large times the behavior of the maximum excess temperature can be represented by a law $\widetilde{T}_m \simeq A(t/\tau)^{\alpha}$. The parameters A and α have been determined fitting the values of $\widetilde{T}_m$ averaged over three curves (we discarded the curve relative to the system of 2048 atoms, which behaves in a slightly different way than the others) for $t \geqslant 200$ ps. We found $A = 5.33$ K and $\alpha = -0.85$.

The curves in Fig. 2 allow also an easy location of the temperature T^*. The values $Z_N = \sqrt{2}\langle K \rangle - \langle K \rangle$, where the denominator in (2) vanishes and C_v diverges, give in that figure the straight line $\widetilde{T} = 0.414T$. The intercept of this line with the curves $\widetilde{T}(T)$ locates the values $T = T^*$ at different times, more precisely than can be done through the curves of Fig. 1. In Fig. 4 we report the values of T^* at various times, for the four simulated systems. T^* diminishes with t more rapidly than a power law, which would give a straight line in the $\log_{10} T^*/\log_{10} t$ plot. On the other hand, T^* diminishes more slowly than an exponential law, as could be seen in a $\log_{10} T^*/t$ plot.

The results reported so far show that, when sampling a microcanonical ensemble at low energy, the fluctuation of the kinetic energy has an anomalous amplitude over times

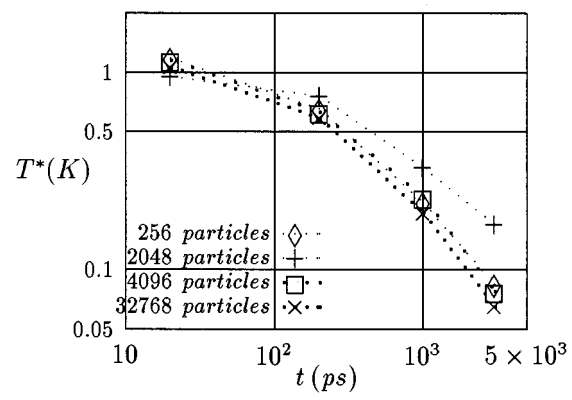

FIG. 4. Temperature at which C_v diverges vs averaging time, in the four systems.

that are more than sufficient to compute thermodynamic averages of other, ''well-behaved'' quantities. The low-energy range corresponds, for argon, to temperatures below 4 K, where the temperature in the computer experiment is defined in the usual way, through the average kinetic energy. This identification deserves some specification. It has been shown through computer experiments, several years ago, that a Lennard-Jones crystal at low temperature exhibits a behavior that is quite different from what is expected in the framework of the traditional classical statistical mechanics: this is due to the presence of a dynamics that is at least partially ordered. In particular, in this temperature range equipartition of energy among normal modes does not hold [10]. One may wonder what meaning should be given in this context to the thermodynamic temperature. On the other hand, in the same computer experiments, one observes that equipartition between kinetic and potential energy holds quite strictly, having taken into account the small anharmonicity left at low energy; therefore, the temperature may be defined as usual through the particle kinetic energy, which shows no ''pathology'' in this range.

The persistence of an average kinetic energy fluctuation larger than expected is evident at very low energy, like the one corresponding to the first points (on the left) in Fig. 2, where the descent of $\widetilde{T}$ with time is nearly frozen. This is not related to the general reduction of all vibrational amplitudes and velocities when the temperature is lowered. In a computer experiment performed on an fcc LJ system similar to ours [11], it was found that at a low temperature, corresponding to 1.8 K for argon, the position and velocity autocorrelations of the particles had an oscillating structure decaying over less than ten vibrational periods, where a typical vibrational period is of the order of 0.7 ps. Therefore, the very long decaying time of the excess temperature, which can be seen in Figs. 3 and 4 to extend over more than 1000 ps, cannot be related to the particles' autocorrelations. On the other hand, as shown in [11], the normal modes do indeed exhibit long-lasting oscillations, when excited individually. It is this lack of ''attrition'' among modes, characteristic of a weakly chaotic dynamical regime, which is responsible for the slow relaxation of the kinetic energy fluctuation, and influences the short- and medium-time macroscopic behavior of the system.

The anomalous behavior of $\langle (\delta K)^2 \rangle$, translated into excess temperature, seems to depend very slightly on N; other computer experiments on 2D systems, not reported here, indicate that it is also independent of the dimensionality and of the connectivity (interaction range). This anomaly is therefore quite generic, and one can expect other thermodynamic quantities to be influenced, in a classical statistical mechanics framework, by an ordered dynamics, which certainly prevents the systems from being quasiergodic [12]. Figure 2 indicates that, at low temperature, a significant systematic error is to be expected in a computation of C_v through formula (2), if ensemble averages are substituted by time averages performed over the usual time of a standard equilibrium MD simulation (~ 100 ps). From the point of view of somebody simulating a real system under realistic conditions, this point should be disquieting, because in the same energy range several quantities behave as expected, so that no warning ensues from their computation. In other words, the

anomalous behavior (if any) can be detected only if one adopts a set of *appropriate* coordinates to describe the dynamics of the system. For a lattice, this set are the normal modes [10], while the particle Cartesian coordinates do not exhibit a visible anomaly in their dynamics [11].

Our results on the computation of C_v shade the belief, current in the community of condensed matter simulators, that the rate of convergence of time averages to ensemble averages of thermodynamic quantities is fast enough in the usual computers experiments. Indeed, it is known that the rate of energy sharing among collective modes may be very slow if the DOFs of the system have very different characteristic frequencies, as may happen in molecules, macromolecules, and molecular crystals [13]. This simulation warns that also in systems endowed with a limited set of characteristic frequencies, such as an fcc crystal, a slow relaxation in the phase space may strongly affect the computation of thermodynamic quantities at low temperature.

When one simulates a real system at equilibrium, how can one check whether the system behaves correctly from a statistical point of view? For a system with many DOFs, the usual indicators of chaos and order (Lyapunov exponents, spectral entropy, fractal dimension) give a global characterization; therefore, they cannot unveil whether a subset of the variables has an ordered dynamics. This problem can be tackled using a diagnostic tool, recently developed for the analysis of the order-to-chaos transition: the *coherence angles*, defined through the dynamics in the tangent space [14]. They allow one to analyse the short and medium time dynamics of single variables in a complex structure, and are suitable for systems with many DOFs. The coherence angle of a DOF is a measure of its degree of chaos; therefore, a coherence spectrum of the whole system tells whether all DOFs are roughly equivalent (which should secure the quasi-ergodic character of the dynamics) or not.

Anomalous fluctuations of the kinetic energy have been found recently in computer experiments using Nosé-Hoover dynamics to sample a canonical ensemble [15]. In that simulation, a fluid or solid LJ system of about 100 particles is coupled to a thermal bath through a heat-flow variable ζ. It turns out that also in this case the dynamics of the extended system (particles + heat-flow variable) is partially ordered, as can be seen through a coarse-grained description of the instantaneous kinetic temperature and of ζ, which gives rise to a Toda oscillator. This ''smooth'' integrability is sufficient to hamper the chaotic behavior of the system, and produces unwanted, long-lasting undulations of the kinetic energy. In order to recover the expected canonical value of the fluctuation of the kinetic energy, one has to simulate the system for as much as 5000 ps. Quoting those authors, ''this behavior violates the Principle of Exhaustion of the Observer.''

[1] Ya. G. Sinai, Russ. Math. Surv. **25**, 137 (1970).

[2] A. N. Kolmogorov, Dokl. Akad. Nauk SSSR **98**, 527 (1954), English translation in *Stochastic Behaviour in Classical and Quantum Hamiltonian Systems*, edited by G. Casati and G. Ford, Lectures Notes in Physics Vol. 93 (Springer-Verlag, Berlin, 1979); V. I. Arnold, Usp. Mat. Nauk **18**, 13 (1963) [Russ. Math. Surv. **18**, 9 (1963)]; **18**, 91 (1963) [**18**, 85 (1963)]; J. Moser, Nachr. Akad. Wiss. Göttingen, Math.-Phys. Kl. **2**, 1 (1962).

[3] E. Fermi, J. Pasta, and S. Ulam, in *Collected Papers of Enrico Fermi*, edited by E. Segré (University of Chicago, Chicago, 1965), Vol. 2, p. 978.

[4] M. Pettini and M. Landolfi, Phys. Rev. A **41**, 768 (1990); M. Pettini and M. Cerruti-Sola, *ibid.* **44**, 975 (1991).

[5] G. Benettin, L. Galgani, and J-M. Strelcyn, Phys. Rev. A **14**, 2338 (1976).

[6] L. Verlet, Phys. Rev. **159**, 98 (1967).

[7] C. Battista *et al.*, Int. J. Mod. Phys. **1**, 56 (1994).

[8] L. M. Barone, R. Simonazzi, and A. Tenenbaum, Comput. Phys. Commun. **90**, 44 (1995).

[9] J. L. Lebowitz, J. K. Percus, and L. Verlet, Phys. Rev. **153**, 250 (1967).

[10] G. Benettin, G. Lo Vecchio, and A. Tenenbaum, Phys. Rev. A **22**, 1709 (1980); G. Benettin and A. Tenenbaum, *ibid.* **28**, 3020 (1983).

[11] J. M. Dickey and A. Paskin, Phys. Rev. **188**, 1407 (1969).

[12] A. I. Khinchin, *Mathematical Foundations of Statistical Mechanics* (Dover, New York, 1949).

[13] L. Casetti, R. Livi, A. Macchi, and M. Pettini, Europhys. Lett. **32**, 549 (1995).

[14] M. D'Alessandro and A. Tenenbaum, Phys. Rev. E **52**, R2141 (1995).

[15] B. L. Holian, A. F. Voter, and R. Ravelo, Phys. Rev. E **52**, 2338 (1995).