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Classical specific heat of an atomic lattice at low temperature, revisited

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We present results of a standard (constant energy) molecular dynamics simulation of a Lennard-Jones lattice at low temperature. The kinetic energy fluctuations exhibit an anomalous behavior, due to a dynamics which is only weakly chaotic. Such a dynamics does not allow the use of the usual microcanonical equilibrium formula to compute the specific heat. We devise a different method for computing the specific heat, which exploits just the weak chaos at low temperature. The result is that at low temperature this ''revisited'' specific heat is lower than the classical value, and approaches zero when the temperature goes to zero. Only for exceedingly long trajectories does the specific heat approach the classical value, with the exception of the very low temperature range. These results prompt a reconsideration, in the frame of modern nonlinear dynamics, of early intuitions by Nernst and Jeans. [S1063-651X(98)00101-9]

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I. INTRODUCTION

The failure of classical statistical mechanics in predicting the drop to zero of the specific heat of an atomic lattice, when the temperature goes to zero, is well known. It was one of the major issues, together with the blackbody radiation, which boosted the epochal change in physics from the classical to the quantum paradigm. At that time, several attempts were made by renowned physicists to reconcile the well designed classical scheme with the new experimental data [1]; those attempts were eventually given up. In more recent years the problem of the energy distribution in a radiant cavity was resumed by Benettin and Galgani by means of a computer experiment [2]. Their results showed that modern developments in classical nonlinear dynamics establish a bridge between the classical and the quantum descriptions. In this paper, we show that a similar framework can substantiate, at least qualitatively, some of the attempts mentioned above, providing a hint on how to narrow the gap between the predictions of classical and quantum statistical mechanics for the low temperature specific heat.

In computer experiments performed by molecular dynamics (MD), ensemble averages are replaced by time averages. A practical problem which arises is how long the trajectory must be in order to ensure an equivalence between the two kinds of average. Experience has shown that—despite the fact that practically no realistic condensed matter system has ever been demonstrated to be ergodic—in many cases a trajectory of some thousands of time steps is sufficient to explore the phase space with a good accuracy. There are, however, systems for which this equivalence is not reached even for very long simulation times, which greatly exceed the usual length of a computer experiment. Even if one gives up the requirement of ergodicity and contents oneself with the view that ''... the time averages of phase function ... appear as a natural interpretation of experimental measurements'' [3], one is left with the problem of the reliability of the results computed through time averages. As a matter of fact, in most cases their duration is orders of magnitude shorter than that of a real experiment performed at equilibrium.

A relevant example of this kind of system is given by atomic lattices at low temperature, which do not exhibit equipartition of energy among normal modes up to very long times [4]. In these systems anomalous fluctuations of the kinetic energy indicate that the relaxation toward equilibrium is hindered. More specifically, it has been found, in a Lennard-Jones fcc lattice at a temperature of few degrees K, that the variance of the kinetic energy relaxes to the classical expected value over times which are at least three orders of magnitude larger than the time needed by the kinetic energy itself [5]. This may be related to the fact that the total kinetic energy is a summable function, while its fluctuation is not. Only for summable functions is ergodicity granted if the surface of constant energy is metrically indecomposable in the extended sense, which is assumed to be a generic property of the mechanical systems treated in statistical mechanics [6].

The example just cited shows that quantities depending on one and the same set of microscopic variables (in that case, the particles' momenta) may relax to their asymptotic value over largely different times. This implies that the system may appear to be at equilibrium or out of equilibrium, depending on which quantity is observed in a computer experiment of standard length. In Ref. [5] it was shown that, because of the exceedingly long time needed by the variance of the kinetic energy to reach its equilibrium value, the computation of the specific heat at constant volume, when performed through a formula suitable for the microcanonical ensemble, yields absurd results. In this paper we present a way to circumvent this difficulty. Our method to compute the specific heat is based exactly on the phenomenon which hinders the use of the equilibrium microcanonical formula: the weak interaction among normal modes of the lattice at low temperature.

II. MODEL

We have simulated the dynamics of a two-dimensional system composed of L^2 particles of mass M ($L=8$), ar-

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*Author to whom correspondence should be addressed. Electronic address: tenenbaum@roma1.infn.it ranged on a square lattice with square cells of side a, surrounded by a border of fixed particles. Each particle interacts with the four first neighbors through a Lennard-Jones potential

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

$V(r)$ has its minimum at $r_0=2^{1/6}\sigma$.

In the following, in order to make an approximate comparison with reality, the Lennard-Jones parameters will be given the values appropriate for argon: $\sigma=3.405$ Å, $\epsilon=119.8k_B$ (k_B is Boltzmann's constant); the corresponding reduced time unit is $\tau=(m\sigma^2/48\varepsilon)^{1/2}=3.112\times10^{-13}$ s. Our model is obviously not similar to real argon, which crystallizes in a fcc structure. On the other hand, it has the advantage that its dynamical behavior has already been studied in detail [4,7]. It exhibits a breakdown of ergodicity at low temperature; as a consequence of this breakdown, energy equipartition among normal modes does not hold at low temperature. This fact makes this system a good candidate to study the possible influence of a weakly chaotic dynamics on a thermodynamical quantity like the specific heat, which depends on the energy exchange among degrees of freedom.

The system has been simulated at various temperatures below 17 K. The equations of motion have been integrated with a central difference algorithm, frequently used in MD experiments [8]. We have improved the precision of the standard algorithm for the velocities by one order in the time step; a description of this modified algorithm was given in Ref. [9].

We have used a time step $h=0.032\tau=10^{-14}$ s; each run had a first equilibration stage of 10^3 steps, followed by a stage of up to 10^7 steps, during which equilibrium averages were computed. We have explored the energy range below $e=0.14$, where e is the energy per particle. For argon, this would correspond to temperatures in the range below 17 K, which includes the transition region determined in Refs. [4,7] for our 64-particle system. The total energy was initially distributed at random among all particles; therefore, it was distributed at random among all normal modes. These initial conditions are surely the most generic at high temperature, where the whole system is chaotic. At low temperature, where the dynamics exhibits ordered features, the initial conditions could influence the final result. We have checked that letting the system relax from the initial condition during an equilibration time of 10^4 time steps (instead of the usual 10^3 time steps), the results were not altered in any significant way.

III. MICROCANONICAL SPECIFIC HEAT

The boundary conditions imposed on the simulated system act as a conservative force field; it turns out that the total energy is almost constant within a relative variation of 10^{-5}. Therefore, if the system were ergodic, its trajectory in the phase space would sample a microcanonical ensemble. For this ensemble the specific heat per degree of freedom (DOF) at constant volume is related to the average fluctuation of the kinetic energy through the formula

$$c_v=\frac{k_B/2}{1-\dfrac{Nd}{2}\,\dfrac{\langle K^2\rangle_{\rm mc}-\langle K\rangle_{\rm mc}^2}{\langle K\rangle_{\rm mc}^2}},\tag{1}$$

where N is the number of particles, d the dimensionality of the system, and K its total kinetic energy; $\langle\ \rangle_{\rm mc}$ is a microcanonical ensemble average [10]. As usual in MD experiments, one defines a temperature T through the time average of the kinetic energy:

$$\langle K\rangle=Ndk_BT/2,\tag{2}$$

where $\langle\ \rangle$ is the time average. There is another formula for the specific heat, which coincides with formula (1) in the thermodynamic limit, but should be more precise for finite N [11]:

$$c_v=\frac{k_B}{d}\left[\tfrac{2}{3}\langle K\rangle_{\rm mc}\langle K^{-1}\rangle_{\rm mc}+N(1-\langle K\rangle_{\rm mc}\langle K^{-1}\rangle_{\rm mc})\right]^{-1}.\tag{3}$$

We used formulas (1) and (3) to compute the specific heat per DOF of our system at various temperatures, replacing ensemble averages by time averages. This computation turned out to be a check of the equivalence of time and ensemble averages, and showed that this equivalence does not hold for computer experiments performed at low temperature (with phase space trajectories of standard length).

In order to illustrate this fact, in Fig. 1 we show the result of a simulation performed at $T=0.106$ K. The value given by (1) for c_v at the beginning of the run is about $-0.14k_B$, while the classical value of k_B is reached only after a very long average: about 10^7 time steps (corresponding to 0.1 μs) are needed to reach the expected plateau within an approximation of 1% (curve a). Between these two limits there is a peculiar divergence, due to the denominator of formula (1) going to zero. This in its turn, as already explained in Ref. [5], is related to an anomalous fluctuation of the kinetic energy $\langle(\delta K)^2\rangle=\langle K^2\rangle-\langle K\rangle^2$. Formula (1) shows that the specific heat diverges around a time t^* at which the average fluctuation of the kinetic energy 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 $\langle K\rangle^2/Nd$ [10]. The very long time needed by c_v to reach the value k_B is evidence of the exceedingly slow relaxation of the variance of the kinetic energy, mentioned above. A similar pattern is found when one uses formula (3). In this case, the time needed to reach the asymptotic value of c_v is even longer (curve b).

In Fig. 2, we report the variation of t^* with temperature. Above 0.1 K, t^* decreases exponentially with T, so that for temperatures above 1 K one can expect that the standard simulation time—of the order of some thousands of time steps—is sufficient to find the expected classical value for c_v. On the other hand, when the temperature decreases below 0.1 K, t^* increases very sharply; as a consequence, at very low temperature, time averages of the kinetic energy fluctuations—even over very long times—are not equivalent to ensemble averages. The temperature in the computer experiment is defined in the usual way, through formula (2). This identification deserves some specification. One may

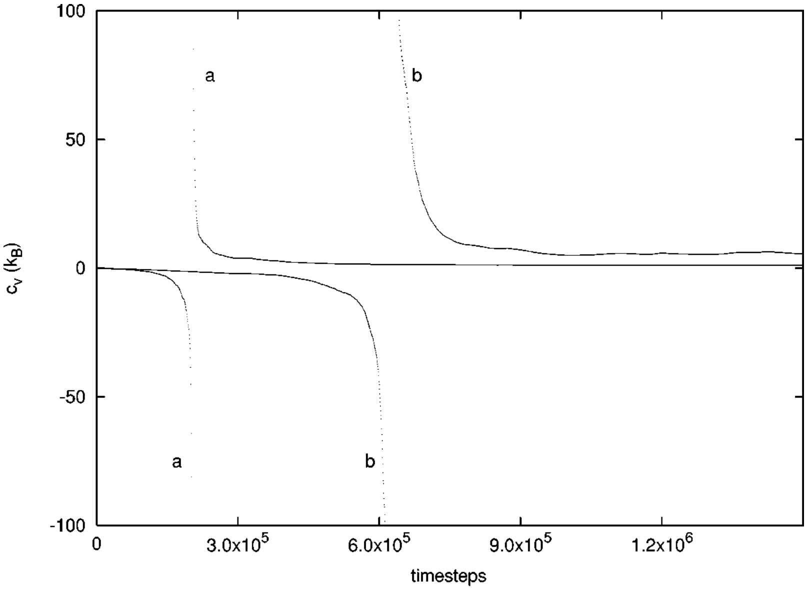

FIG. 1. Specific heat per DOF computed through formula (1), curve a, and formula (3), curve b. The curves diverge, respectively, at $t_a^* \simeq 2\times 10^5$ and $t_b^* \simeq 6.3\times 10^5$ time steps. $T = 0.106$ K.

question the meaning of a (low) thermodynamic temperature, given the apparent lack of ergodicity. On the other hand, in our computer experiments equipartition between the total kinetic and the total 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 particles' kinetic energy, which shows no ''pathology'' in this range.

IV. CANONICAL SPECIFIC HEAT

In order to have a physically significant measure of the specific heat at low temperature, one can try to circumvent the difficulty connected with formula (1) by switching to a canonical ensemble. This could be achevied using a Nosé-Hoover thermostat to sample a canonical ensemble. But an anomalous fluctuation of the kinetic energy has recently been found in computer experiments using Nosé-Hoover dynamics [12]. It turned out that the dynamics of the extended system (particles plus heat-flow variable) was partially ordered; this ''smooth'' integrability was sufficient to hamper the chaotic behavior of the system, and produce unwanted, long-lasting undulations of the kinetic energy. Moreover, the Nosé-Hoover method requires a modification of the equations of motion in the bulk of the system. It can be expected that this would alter substantially the behavior of the system in the low temperature region of the phase space, where the dynamics is known to be partially ordered.

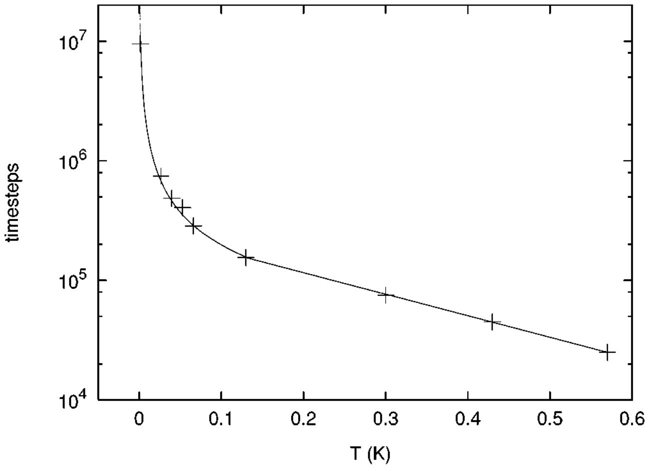

FIG. 2. Divergence time t^* of the microcanonical specific heat, computed through formula (1), in the low temperature range. The curve shows the different behavior of t^* in the temperature ranges below and above 0.1 K.

In order to obtain a physically significant measure of the specific heat at low temperature, we used a method based just on the ''pathological'' dynamics which hinders the use of formula (1). This anomalous behavior can be better represented if one adopts a set of *appropriate* coordinates to describe the dynamics of the system. For a lattice, this set are the normal modes [4], while the particle Cartesian coordinates do not exhibit any appreciable anomaly in their dynamics [13]. It has been shown that in the lattice here described equipartition of energy among normal modes does not hold at low temperature [4]. This lack of ''attrition'' among modes, characteristic of a weakly chaotic dynamical regime, is responsible for the slow relaxation of the kinetic energy fluctuation, and determines the short- and medium-time macroscopic behavior of the system.

We will show below that the normal modes of our system can be divided into groups of equal frequency; within each group the energy exchange among modes is significant and rapid, while the exchange among different groups is usually weak and slow. Exploiting this feature, each group of normal modes can be seen as a small subsystem in weak interaction with a ''thermal bath'' made of all other groups of modes. The interaction takes place through the anharmonic part of the Hamiltonian. While it is evident that the probability distribution of the energy of the whole system, or of a large portion of it, is bound by the condition that the total energy be constant, for small components of the system the energy distribution law is ''almost identical'' in the microcanonical and in the canonical ensemble [14].

In a canonical ensemble the probability of a state of energy E_α is

$$P(E_\alpha) = \frac{e^{-\beta E_\alpha}}{\sum_\alpha e^{-\beta E_\alpha}}, \tag{4}$$

where the sum extends over all possible states and $\beta=(k_BT)^{-1}$. If the system can be decomposed in M small subsystems with negligible interaction, one has $E_\alpha\simeq\Sigma_{j=1}^{M}E_j$, where E_j is the energy of subsystem j (obviously $E_j\leqslant E_\alpha$). One has

$$e^{-\beta E_\alpha}=\prod_{j=1}^{M} e^{-\beta E_j}.$$

On the other hand, one also has

$$\sum_\alpha e^{-\beta E_\alpha}=\sum_\alpha e^{-\beta\Sigma_{j=1}^{M}E_j}=\prod_{j=1}^{M}\sum_\alpha e^{-\beta E_j};$$

therefore,

$$P(E_\alpha)=\prod_{j=1}^{M}\frac{e^{-\beta E_j}}{\sum_\alpha e^{-\beta E_j}}\equiv\prod_{j=1}^{M}P(E_j|E_\alpha),$$

where $P(E_j|E_\alpha)$ is the conditional probability that the jth subsystem has energy E_j when the whole system has energy E_α. If the jth subsystem is small in comparison with the whole system, then the value of total energy is not an effective constraint for the energy of the subsystem; one therefore has $P(E_j|E_\alpha)\simeq P(E_j)$, using definition (4), with E_j taking any value. This means that the canonical probability at temperature T of a state of the system is the product of the independent probabilities of the M subsystems at the same temperature. It is as if each subsystem were individually in contact with the thermal bath which determines the temperature of the system.

Adopting this canonical point of view, we have computed the contribution of each group of modes to the heat capacity of the system through a formula suitable for a canonical ensemble. The anharmonicity of the system has been taken into account by considering the nonlinear terms in the Hamiltonian as a part of the thermal bath; this contribution to the energy of the system becomes negligible at low temperature.

Let u^x_{lm} and u^y_{lm} be the displacements of a particle from its equilibrium position at site (l,m) $(l,m=1{,}8)$. The normal-mode coordinates are defined by

$$q^x_{hk}=\frac{2}{L+1}\sum_{l,m=1}^{L}u^x_{lm}\sin\left(\frac{h\pi l}{L+1}\right)\sin\left(\frac{k\pi m}{L+1}\right),$$

$$q^y_{hk}=\frac{2}{L+1}\sum_{l,m=1}^{L}u^y_{lm}\sin\left(\frac{h\pi l}{L+1}\right)\sin\left(\frac{k\pi m}{L+1}\right),$$

where $h,k=1,L$. In these coordinates the Hamiltonian of the system is

$$H=\frac{M}{2}\sum_{h,k=1}^{L}[(\dot q^x_{hk})^2+(\omega^x_{hk}q^x_{hk})^2+(\dot q^y_{hk})^2+(\omega^y_{hk}q^y_{hk})^2]+H',$$

where H' is the anharmonic part of the Hamiltonian, which entails the coupling among normal modes and is negligible at sufficiently low energies; ω^x_{hk} and ω^y_{hk} are the angular frequencies of the normal modes:

$$(\omega^x_{hk})^2=(\omega^y_{kh})^2=\frac{4}{M}\left[K_l\sin^2\frac{\pi h}{2(L+1)}+K_t\sin^2\frac{\pi k}{2(L+1)}\right],$$

$$K_l\equiv\left.\frac{\partial^2V}{\partial r^2}\right|_d,\quad K_t\equiv\frac{1}{r}\left.\frac{\partial V}{\partial r}\right|_d.$$

We have considered the case in which the lattice parameter $a=r_0$, which gives zero pressure at zero temperature. In this case $K_t=0$. There are only L distinct frequencies ($\omega^x_{hk}=\omega^y_{kh}\equiv\omega_h$) ranging from 0.3789 to 2.1491 in Lennard-Jones reduced units (rad/τ). The normal modes are naturally separated into L groups, each group including $2L$ modes of equal frequency. The total energy of the system may now be found summing the energies E_h of the different groups of modes, plus the energy of the coupling due to the H' term; one has

$$E_h=\frac{M}{2}\sum_{k=1}^{L}[(\dot q^x_{hk})^2+(\omega^x_h q^x_{hk})^2+(\dot q^y_{kh})^2+(\omega^y_h q^y_{kh})^2].$$

In this case, the eight group energies E_h will be the relevant DOF's. In fact, as described in Ref. [4], modes of equal frequency rapidly exchange their energy, always providing a good energy equipartition inside their group. On the other hand, the exchange of energy among groups of modes of different frequency is strongly affected by the breakdown of ergodicity at low temperature. Therefore, the energies of the groups become the relevant DOF's in monitoring the dynamics of the system.

For a system at constant temperature the specific heat per DOF is given, in units of k_B:

$$c_v=\frac{1}{Nd}\frac{\langle H^2\rangle_c-\langle H\rangle_c^2}{k_B^2T^2},\tag{5}$$

where H is the total energy and T the temperature. Here too we replace ensemble averages by time averages. Considering the ith group of Ld normal modes as an independent subsystem of energy H_i, its contribution to the specific heat per DOF will be, using formula (5),

$$c_v(i)=\frac{1}{Ld}\frac{\langle H_i^2\rangle-\langle H_i\rangle^2}{k_B^2T^2},\tag{6}$$

and the specific heat for the total system will be

$$c_v=\frac{\sum_i Ldc_v(i)}{L^2d}.\tag{7}$$

Adopting this point of view, one may wonder whether the temperature used in formula (6) should refer to the whole system or to the subsystem. In the latter case, a *group temperature* T_i could be computed—through formula (2)—from the average kinetic energy of the ith group of normal modes.

Consequently, in formula (6) T should be replaced by T_i. We will show later that the two choices yield almost equivalent results.

In order to make a comparison with quantum statistical mechanics, we have computed also the quantum specific heat of our lattice, in the frame given by the formula of Born and von Karman:

$$U=\int \frac{\hbar\omega D(\omega)}{e^{\hbar\omega/k_BT}-1}d\omega+\int \frac{\hbar\omega}{2}D(\omega)d\omega,$$

where U is the energy of the system and $D(w)$ is the density of states. For our finite lattice, this formula becomes

$$U=2L\sum_{h=1}^{L} \frac{\hbar\omega_h}{e^{\hbar\omega_h/k_BT}-1}+\epsilon_0,$$

which gives for the specific heat per DOF,

$$c_v=k_B\sum_{h=1}^{L} \frac{\left(\dfrac{\hbar\omega_h}{k_BT}\right)^2 e^{\hbar\omega_h/k_BT}}{(e^{\hbar\omega_h/k_BT}-1)^2}. \tag{8}$$

V. RESULTS OF THE COMPUTER EXPERIMENT

We performed simulations in the temperature range below the melting point, which is around 17 K. Due to the instability of the lattice, the higher temperatures were approached from below, first endowing the system with a low kinetic energy and then—after equilibrium was reached—scaling up the velocities; repeating this procedure several times, the final equilibrium temperature was reached, avoiding a melting of the lattice. The results of our simulations are reported in Fig. 3. In the same figure we report the classical specific heat computed through formulas (6) and (7), and also the quantum specific heat computed through formula (8).

Each point on the curve corresponding to 10^3 time steps is the average of five different initial conditions; the error bars show the spread of the five results. The points on the curve corresponding to 10^7 time steps refer to a single initial condition. Using in formula (6) the group temperatures instead of the system temperature, one obtains slightly different values for c_v, not shown in Fig. 3. For the two curves at shorter times the results for c_v differ in some cases by a few percent, and only in one case—after 10^3 time steps—by 20%. For the points obtained after 10^7 time steps, the new results almost coincide with the others. As the use of these two different temperatures does not modify in any significant way the pattern shown in Fig. 3, we have reported for clarity only the data computed with the temperature of the system.

The main feature emerging from Fig. 3 is that at low temperature the specific heat does not have the constant value predicted by the classical law of Dulong-Petit. Indeed, a computation of c_v performed over 10^3 time steps (after 10^3 time steps of equilibration) shows that the classical value for c_v, that is, k_B for degree of freedom, is found at a temperature around 16 K, while close to this point c_v shows the typical increase expected in a lattice when the melting point is approached from below. Below 15 K, the behavior of c_v clearly diverges from the classical prediction, diminishing with a constant slope when 12 K$>T>$2 K, and dropping rapidly to zero below 2 K. The values of c_v below 12 K are closer to the quantum specific heat—computed through formula (8)—than to the classical Dulong-Petit law.

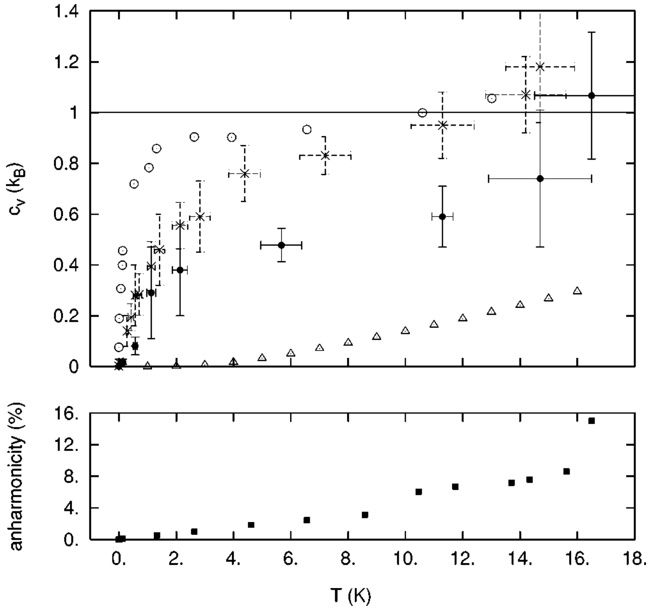

FIG. 3. The upper part shows the specific heat per DOF at various averaging times, computed through formula (6). ●, 10^3 time steps; ×, 10^4 time steps; ⊙, 10^7 time steps. Also shown is the quantum specific heat (△) computed through formula (8). The horizontal line represents the classical value $c_v=k_B$. The lower part shows the anharmonicity of the lattice, computed as $\langle H'\rangle/\langle H\rangle$, in the same temperature range.

Extending the equilibrium simulation over 10^4 time steps, the values of c_v increase, but the general pattern remains similar. If, on one hand, the classical value k_B in now found around 13 K, the fast drop of c_v for $T\rightarrow 0$ is still present, notwithstanding the increase of the simulation time by one order of magnitude.

We have further extended the simulation time up to 10^7 time steps. The curve of c_v is again shifted to higher values, but keeps the main new feature, that is, the drop to zero at low temperatures.

The evolution in time of the curves in Fig. 3 suggests an interpretation based on different dynamical regimes. In the range below 0.1 K the persistent low value of c_v could be ascribed to an ordered dynamics due to the presence of Kolmogorov-Arnold-Moser (KAM) tori in the phase space [15]. Between 1 and 10 K the very slow increase of c_v is reminiscent of a dynamics *à la* Nekhoroshev [16], with a slow Arnold diffusion in the phase space. Above this range the motion becomes chaotic over times which are not very long (10^4 steps), and c_v has a value near to the classical one k_B. The various curves for c_v do not show a plateau at this value. This is due to the strong anharmonicity of the lattice, which is measured by the ratio $\langle H'\rangle/\langle H\rangle$. In the lower part of Fig. 3 we report the value of the anharmonicity; the increase for temperatures above 10 K is indicative of the softness of the lattice, which melts above 16 K, as shown by the sharp rise to 15% of the anharmonicity.

An obvious question raised by these results is what would one find for even longer simulations. The time dependence

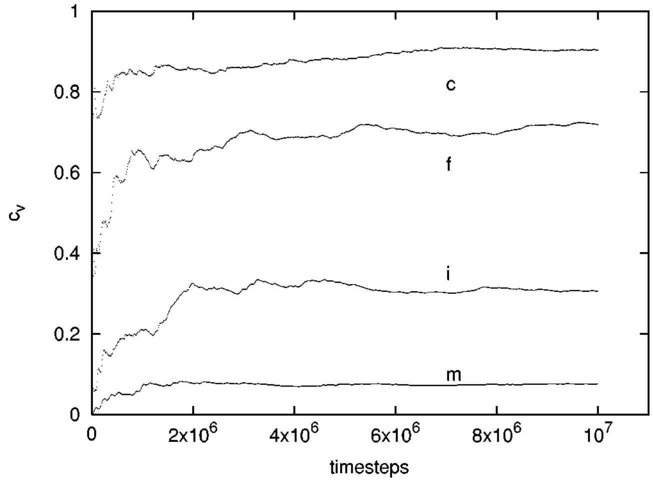

FIG. 4. Specific heat per DOF (in k_B units) as a function of the averaging time. c: $T = 2.63$ K; f: $T = 5.27 \times 10^{-1}$ K; i: $T = 6.59 \times 10^{-2}$ K; m: $T = 1.34 \times 10^{-3}$ K.

of the averaged value of c_v can be seen in Fig. 4, where the results up to 10^7 time steps are given for four temperatures below 3 K. The figure shows clearly that in this temperature range the asymptotic values of c_v are smaller than the classical value k_B. A more detailed analysis of these features is given in Fig. 5, where we plot the function $-\ln(1-c_v)$ for the longest simulation (10^7 time steps), in the temperature range below 7 K. The function shown should diverge if c_v approached from below the classical value k_B. Indeed, for short times the curves exhibit a very steep rise. But as time increases the slope of all curves diminishes progressively, indicating that the value k_B would be reached only in some cases, and over extremely long simulation times. The figure shows that some temperatures give after 10^7 a stabilized value of c_v, while some others do not. Looking more carefully at the various curves, one can distinguish two temperature ranges: below 0.12 K and above 0.12 K. In the first range the values reached by c_v are stable after 10^7 steps; in the second range the behavior is mixed: some values of c_v are still slowly increasing, some are stable. Here again one is induced to assign the first range to a region mainly foliated by KAM tori, while the mixed behavior of the second range seems ascribable to a dynamics *à la* Nekhoroshev. The general pattern which emerges from this figure is that at very low temperature the values found for c_v in our computer experiment are almost asymptotic. For higher temperatures a change of c_v for some temperatures can be expected over exceedingly long runs; however, this shift of values should not qualitatively alter the curve, which would remain significantly below the classical value for temperatures below 10 K.

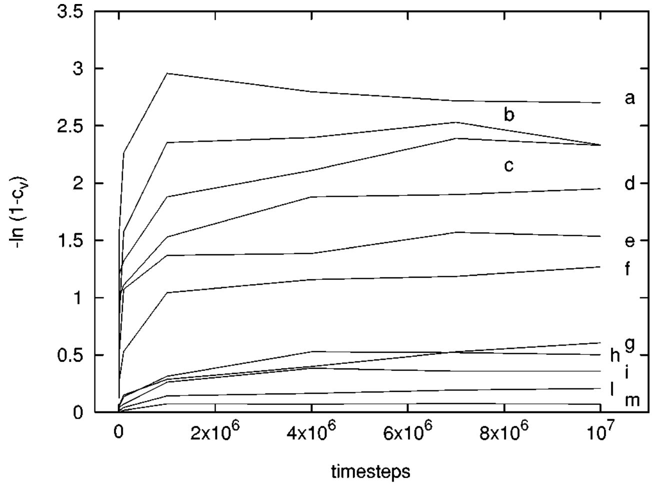

FIG. 5. A function of the specific heat per DOF computed through formula (6), as a function of the averaging time. a: $T = 6.56$ K; b: $T = 3.94$ K; c: $T = 2.63$ K; d: $T = 1.32$ K; e: $T = 1.05$ K; f: $T = 5.27 \times 10^{-1}$ K; g: $T = 1.30 \times 10^{-1}$ K; h: $T = 1.20 \times 10^{-1}$ K; i: $T = 6.59 \times 10^{-2}$ K; l: $T = 1.45 \times 10^{-2}$ K; m: $T = 1.34 \times 10^{-3}$ K.

The results given above show that the low energy region of the phase space is characterized by a core where the dynamics is ordered; here the freezing of the energy exchange among normal modes yields a value of the specific heat which is closer to the quantum value than to the classical one. This should not be surprising, as the quantum behavior at low temperature depends exactly on the fact that the energy exchange among DOF's is heavily hampered. The phase space region near the ordered core is characterized by a weak chaoticity, which manifests itself only over very long times, as predicted by the Nekhoroshev theorem. As a consequence, in the energy (temperature) range corresponding to this region, the specific heat increases slowly towards its classical value. But this can be observed only if the simulation time is increased by orders of magnitude over the typical duration of an equilibrium computer experiment.

VI. RETRIEVAL OF EARLY INTUITIONS

The idea of a freezing of the degrees of freedom was first proposed by Boltzmann in his work on the theory of gases. A rigorous attempt do develop a formal scheme supporting this idea was made by Jeans in his mechanical model of ether. Following Jeans, a system is in a *normal state* if the energy distribution turns out to be independent of the initial conditions: this is clearly a property of ergodic systems.

The time needed to reach this state depends on the rate of energy exchanges, and Jeans improved in this context the original idea of Boltzmann. Jeans said that for some systems the normal state is achieved after a long relaxation which can even be of the order of ''hundred of centuries'' (as roughly computed by him through heuristic considerations) [17]. On the other hand, he admitted that the Planck distribution correctly describes those states of equilibrium (i.e., independent of the initial conditions) which can be reached during the time of a typical experiment. But, he argued, one cannot exclude that during a typical experiment some degrees of freedom are still frozen, and that the distribution will eventually evolve over a very long time, of the order of magnitude mentioned above.

Later, an equilibrium approach to this problem was attempted by Nernst in 1916 [18]. An important character of Planck's quantum zero-point energy is that it is not available: it is only the ground state, that is, a new zero for the energy which can be exchanged. The zero-point energy is neither ordered, nor disordered: it is fixed. Instead, the central idea of Nernst is that the zero-point energy is always free in principle and can be exchanged by continuous amounts (this concept was the basis for a new model of ether). It is not always used by the system; for example, in some cases it is not exchanged during molecular collisions: it is ''ordered.'' Nevertheless, whenever this zero-point energy is used, it is transformed into thermal energy. Nernst thought of a zero-point energy which is physically singled out by peculiar characteristics, but free to pass into degraded (thermal) energy. He asserted that this contribution of the zero-point energy to the thermal energy reduces the energy exchange; therefore, the specific heat decreases.

This work was reviewed by Cercignani, Galgani, and Scotti in 1972 [19], and by Galgani in 1981 [20], introducing the concept of a stochastic threshold. Their treatment of the energy exchanges in a system was in the frame of classical statistical mechanics, without using concepts similar to the zero-point energy. The available energy is always thermal, but they distinguished betweeen states of different order (or disorder).

Following only classical considerations, they found an energy ordering in the system due to the persistence of KAM tori in the region of lower energy. On the other hand, this ordered energy cannot be identified straightaway with the quantum zero-point energy, using the concept developed by Nernst. Indeed, as shown by Boyer [21], if one wants to introduce rigorously a ''real'' zero-point energy *à la* Nernst, one has to admit an infinite energy density (with peculiar characteristics) at $T=0$.

The results of our simulation of c_v are intermediate between the quantum and the (traditionally) classical ones. Extending the simulation time they tend to the latter, but keep the quantum feature that $c_v \rightarrow 0$ when $T \rightarrow 0$.

This suggests that our system reaches a state of equilibrium which is neither the state of quantum equilibrium, nor the classical one (which Jeans called the normal state): it appears to be an intermediate metastable equilibrium state—which Jeans called stationary.

We can thus say that the present simulation retrieves early intuitions of both Jeans and Nernst, but in a different physical context. The exceedingly long relaxation time of c_v toward the classical value emphasizes the existence of the stationary states predicted by Jeans. On the other hand, the low values we found for c_v at low temperatures are related, through the scheme of a stochastic threshold introduced in the work cited above, to the intuition by Nernst of an ordered dynamics.

VII. DISCUSSION

An important question raised by the results of our computer experiment is: how generic is this kind of behavior of a lattice at low temperature? 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 a system of hard spheres, in the second case to that of a system of perturbed harmonic oscillators. Now, the system of hard spheres is assumed to be ergodic [22], while the KAM theorem demonstrates that a system of perturbed harmonic oscillators behaves in an ordered way in a region of positive measure of the phase space [15]. One has therefore to expect that, by lowering the temperature of a generic condensed matter system, its behavior will be driven through a dynamical chaos-to-order transition.

A second question about the genericity of the behavior described above is related to the size of the system. Of course, no computer experiment can definitely answer the question of what would one find in the thermodynamic limit. It has been found very recently that in a Fermi-Pasta-Ulam (FPU) α model there is, at low temperature, an energy threshold which separates ordered and chaotic dynamics, and that this treshold goes to zero in the thermodynamical limit [23]. As the Hamiltonian of the FPU α model is very similar to that of our system at low energy, this implies that the range below 0.1 K, in which we assume the dynamics of our model to be determined by the presence of KAM tori, would further shrink for $N \rightarrow \infty$; in this limit, therefore, the behavior of the system in the whole temperature range below 10 K would show the slow time dependence that we attribute to Arnold diffusion. This can be expected because the energy corresponding to 10 K can be identified with the *strong stochasticity threshold* (SST), a critical value of the energy per DOF which has been shown to exist in nonintegrable systems [24,25]. Above the threshold the motion is strongly chaotic, and all dynamical functions relax rapidly. Below the threshold very long relaxation times appear, as in the case of the specific heat computed in the paper at hand; this is due to the weak chaoticity, which yields an apparently ordered dynamics for short and medium observation times. The SST seems to be independent of the number of DOF's in the system. Therefore, one should also find extremely long relaxation times at low temperature in large systems (our lattice is not suited to study very large systems because, due to the interaction being limited to first neighbors, it is stabilized only by the rigid boundary, and therefore becomes unstable in its core region when N becomes very large). As far as the specific heat is concerned, we expect a quantum-similar behavior at short times, if one computes it using the method introduced in this paper. As a matter of fact, this is what was found in a realistic microcrystal; these results will be reported in a forthcoming paper [26].

In the retrieval of the early intuitions by Jeans and Nernst proposed above a difference remains between the classical revisited approach and the traditional quantum one. Nevertheless, it is interesting to observe a point of contact between the two mechanical frameworks. At low temperature, classical physics, reviewed from the point of view of modern nonlinear mechanics, predicts a weak interaction among oscillators because of the presence of ordered dynamics. On the other hand, at low temperature quantum physics predicts a weak interaction among oscillators because of the difficulty of activating the energy quanta which must be exchanged. So the effect which is responsible for the drop to zero of the specific heat when the temperature goes to zero, can be handled in the two frameworks, yielding qualitatively similar results.

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[1] For a review, see T. S. Kuhn, *Black-Body Theory and the Quantum Discontinuity, 1894-1912* (Oxford University Press, Oxford, 1978).

[2] G. Benettin and L. Galgani, J. Stat. Phys. **27**, 153 (1982).

[3] A. I. Khinchin, *Mathematical Foundations of Statistical Mechanics* (Dover, New York, 1949), p. 46.

[4] G. Benettin and A. Tenenbaum, Phys. Rev. A **28**, 3020 (1983).

[5] R. Simonazzi and A. Tenenbaum, Phys. Rev. E **54**, 964 (1996).

[6] A. I. Khinchin, *Mathematical Foundations of Statistical Mechanics* (Ref. [3]), p. 57.

[7] G. Benettin, G. Lo Vecchio, and A. Tenenbaum, Phys. Rev. A **22**, 1709 (1980).

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

[9] M. D'Alessandro, A. D'Aquino, and A. Tenenbaum (unpublished).

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

[11] E. M. Pearson, T. Halicioglu, and W. A. Tiller, Phys. Rev. A **32**, 3030 (1985).

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

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

[14] A. I. Khinchin, *Mathematical Foundation of Statistical Mechanics* (Ref. [3]), p. 113.

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

[16] N. N. Nekhoroshev, Russ. Math. Surv. **32**, 1 (1977).

[17] J. H. Jeans, Philos. Mag. **6**, 279 (1903).

[18] W. Nernst, Verh. Dtsch. Phys. Ges. **18**, 83 (1916).

[19] B. Cercignani, L. Galgani, and A. Scotti, Phys. Rev. A **12**, 2120 (1972).

[20] L. Galgani, Lett. Nuovo Cimento **31**, 65 (1981).

[21] T. H. Boyer, Phys. Rev. **182**, 1374 (1969).

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

[23] L. Casetti, M. Cerruti-Sola, M. Pettini, and E. G. D. Cohen, Phys. Rev. E **55**, 6566 (1997).

[24] M. Pettini and M. Landolfi, Phys. Rev. A **41**, 768 (1990).

[25] M. Pettini and M. Cerruti-Sola, Phys. Rev. A **44**, 975 (1991).

[26] G. Marcelli and A. Tenenbaum (unpublished).