Quantumlike short-time behavior of a classical crystal

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We have performed a molecular-dynamics simulation of a face-centered-cubic Lennard-Jones crystal, and studied its relaxation toward equilibrium and its microcanonical equilibrium dynamics through the computation of the normal modes. At low temperature, the weak interaction among normal modes yields a very slow relaxation of the fluctuation of the kinetic energy; this requires a new formulation of the measure of the microcanonical specific heat at constant volume. This specific heat turns out to depend on the time of observation; for times of the order of 20 ps, its values are much nearer to the quantum ones than to the value $3R$ predicted by the classical Dulong and Petit law. For longer observation times, the classical specific heat progressively approaches $3R$ over most of the temperature range of the solid crystal, with the exception of the lowest temperature range, where it still drops to values close to zero. The time dependence of the specific heat of the crystal is similar to the behavior found in a supercooled liquid near the glass transition.

I. INTRODUCTION

In computer experiments performed by molecular-dynamics (MD) simulation, equilibrium quantities and functions are evaluated by means of time averages on the trajectory of the system in the phase space. Experience has shown that the relaxation times of the computed quantities may vary over a wide range. It has been found, for example, that in a Lennard-Jones crystal at low temperature the kinetic energy relaxes in a time of a few ps, while its fluctuation relaxes in a time that is at least three orders of magnitude larger [1]. Such a slow relaxation prevents the computation of the specific heat at constant volume in a MD experiment at constant energy, as the relevant formula is based on the fluctuation of the kinetic energy [2]. The slowing down of the fluctuation is due to the decoupling at low temperature of the normal modes; this yields an onset of ordered motions and a loss of ergodicity of the system.

A method to measure the specific heat which circumvents this shortcoming has been proposed [3]. In this work, it turns out that the specific heat of a simple lattice goes to zero at very low temperature. This shows that quantumlike features may appear if modern developments of nonlinear classical dynamics are taken into consideration. In a recent paper, Carati and Galgani give a review of theoretical and computer simulation results showing that classical physics—when properly formulated in the sense just mentioned—entails indeed some relevant quantumlike features [4]. While many of the results they review have been derived in the past decade, their starting point is the famous computer experiment performed by Fermi, Pasta, and Ulam (FPU) 50 years ago [5]. As is well known, the FPU computer experiment showed an

unexpected feature in a chain of nonlinear oscillators, i.e., that at low energy there is no equipartition among normal modes, notwithstanding the anharmonicity of the system. With reference to that experiment, Carati and Galgani contrast their own point of view with that of Izrailev and Chirikov [6], who were the first to provide a clue to interpret the new evidence, namely the existence of an *energy threshold* $E^c(\omega)$, depending on the frequency of the initially excited mode. In the view of [6], when the energy is below the threshold, the motion of the system is almost ordered (as when the phase space is foliated in KAM tori), while the motion becomes chaotic when the energy is above the threshold. One relevant feature of this interpretation is that the energy threshold should go to zero when the number of degrees of freedom (DOF's) is increased; that is, in the thermodynamic limit the classical theory would hold in its traditional form, including equipartition among modes.

Carati and Galgani propose a different point of view. They stress the relevance of the *rate of thermalization*, which depends on the characteristic frequency of the DOF's involved in the energy exchange. The relaxation time toward equilibrium increases almost exponentially with the frequency of the DOF [7,8], and at low temperature the system may not have the time to thermalize within the observation period. Moreover, this feature of the "revisited" classical framework should persist in the thermodynamic limit.

Because of the lack of thermalization of the high-frequency degrees, which is equivalent to their freezing over very long times (that depend on their frequency and on the temperature), "one should observe that the temperature at which freezing occurs (namely essentially the Debye temperature, where the specific heat exhibits a rather abrupt decay) depends on the observation time, moving towards the low temperatures as the observation time is increased" [4].

We have performed a classical molecular-dynamics computer experiment on a realistic microcrystal, measuring the

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specific heat at constant volume in the whole temperature range below the fusion point. This specific heat turns out to depend on the duration of the trajectory of the system in the phase space—that is, on the observation time—just in the way anticipated in [4]; moreover, when the temperature approaches zero the dynamics of the system undergoes a transition with features similar to those of a glass transition.

In Sec. II, we present the model on which we perform the computer simulation. Section III is dedicated to the normal modes representation of the system, and in Sec. IV we compare its thermodynamic properties to that of the real system. In Sec. V, we deal with the short-time dynamical behavior, showing that it requires a redefinition of the classical specific heat, which is given in Sec. VI. In Sec. VII, we give the results of our computer experiments, and in Sec. VIII we draw an analogy between our findings and those of a liquid near a glass transition. In Sec. IX, we discuss our results.

II. fcc LENNARD-JONES LATTICE

The system we chose to simulate the behavior of a classical crystal is a face-centered-cubic (fcc) lattice—with periodic boundary conditions—of $N=512$ particles interacting through a Lennard-Jones (LJ) potential,

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

the cutoff of the potential is set at $r_c = 2.746\sigma$, so that each particle interacts with six shells of neighbors. This is known to be a fairly realistic model for a rare-gas solid. In the following, we will use the LJ parameters appropriate to argon in order to compare the results of our simulation to experimental data; these parameters are $\sigma = 3.405$ Å and $\epsilon = 119.8 k_B$, where k_B is Boltzmann's constant.

We have given our system the shape of a nonorthogonal parallelepiped, in order to ease the computation of the normal modes. Let $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ be the unit vectors of the Cartesian axes. When an atom is put at the origin of the axes, the primitive cell of the fcc lattice is composed by that atom and three others, whose equilibrium positions are given by

$$\mathbf{a}_1 = a(\hat{\mathbf{y}}+\hat{\mathbf{z}})/2; \quad \mathbf{a}_2 = a(\hat{\mathbf{z}}+\hat{\mathbf{x}})/2; \quad \mathbf{a}_3 = a(\hat{\mathbf{x}}+\hat{\mathbf{y}})/2,$$

where a is the lattice parameter; the angle between any two of these vectors is $\pi/3$. The equilibrium positions of the 512 atoms are then given by $\mathbf{R}_0 = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, with $n_1, n_2, n_3 = 0,1...,7 = L-1$; they form a parallelepiped with faces having Miller indices $\{-1,1,1\}$, $\{1,-1,1\}$, and $\{1,1,-1\}$. At low temperature, $a = 5.274$ Å $= 1.549\sigma$ for argon. The width of the system is $4a$, larger than $2r_c$: this abides by the minimum image convention of MD systems with periodic boundary conditions. We write the position of each atom as

$$\mathbf{R}(\mathbf{n}) = \mathbf{R}_0(\mathbf{n}) + \mathbf{u}(\mathbf{n}),$$

where $\mathbf{n} \equiv (n_1,n_2,n_3)$ is an integer vector identifying the atom at equilibrium in $\mathbf{R}_0(\mathbf{n})$; $\mathbf{u}(\mathbf{n})$ is the displacement of that atom from its equilibrium position. The Hamiltonian of the system can then be written as

$$H = \sum_{\mathbf{n}} \frac{m}{2}|\dot{\mathbf{u}}(\mathbf{n})|^2 + \frac{1}{2}\sum_{\mathbf{n}\neq\mathbf{l}} V[\mathbf{R}(\mathbf{n})-\mathbf{R}(\mathbf{l})]; \quad (1)$$

in both sums $\mathbf{n}$ runs over all atoms in the system, while in the second sum $\mathbf{l} \equiv (l_1,l_2,l_3)$ runs over the first six shells of neighbors (in the system or in its images produced by the periodic boundary conditions) of the atoms labeled by $\mathbf{n}$.

The equations of motion derived from the Hamiltonian (1) have been integrated by means of the well-known Verlet algorithm [9], with a time step of 0.93×10^{-14} s. The total energy was initially distributed at random among all particles, that is, among all normal modes. The system was initially allowed to evolve for 10^4 time steps, before starting to compute the time averages; this time was sufficient for the system to relax from the initial state, even at the lowest simulated temperatures. The longest simulation runs lasted 10^5 time steps, corresponding to about 1 ns.

III. NORMAL MODES

We introduce the normal modes expanding the potential energy in a Taylor series around the equilibrium positions of the atoms. We may then write $H = H_0 + H'$, where the integrable part is

$$H_0 = \sum_{\mathbf{n}} \frac{m}{2}|\dot{\mathbf{u}}(\mathbf{n})|^2 + \frac{1}{2}\sum_{\mathbf{n}\neq\mathbf{l}} V[\mathbf{R}_0(\mathbf{n})-\mathbf{R}_0(\mathbf{l})]$$

$$+ \sum_{\mathbf{n},\mathbf{l}} \sum_{\alpha,\beta} u_\alpha(\mathbf{n}) A_{\alpha\beta}(\mathbf{n},\mathbf{l}) u_\beta(\mathbf{l}),$$

with $\alpha,\beta = x,y,z$; here

$$A_{\alpha\beta}(\mathbf{n},\mathbf{l}) = \frac{\partial^2 V[\mathbf{R}(\mathbf{n})-\mathbf{R}(\mathbf{l})]}{\partial u_\alpha(\mathbf{n})\partial u_\beta(\mathbf{l})}\bigg|_{\mathbf{R}_0}$$

when $\mathbf{n}\neq\mathbf{l}$, and

$$A_{\alpha\beta}(\mathbf{n},\mathbf{n}) = \sum_{\mathbf{m}(\neq\mathbf{n})} \frac{\partial^2 V[\mathbf{R}(\mathbf{n})-\mathbf{R}(\mathbf{m})]}{\partial u_\alpha(\mathbf{n})\partial u_\beta(\mathbf{n})}\bigg|_{\mathbf{R}_0}$$

when $\mathbf{n}=\mathbf{l}$; the range for $\mathbf{m} \equiv (m_1,m_2,m_3)$ is the same as for $\mathbf{l}$. H' is the perturbative part of the Hamiltonian, entailing derivatives of the potential of order higher than 2. The normal modes are then defined by

$$q_s(\mathbf{k}) = \frac{1}{L^{3/2}}\sum_{\mathbf{n}} \mathbf{u}(\mathbf{n})\cdot\mathbf{e}_s(\mathbf{k})\exp(-i2\pi\mathbf{k}\cdot\mathbf{n}/L),$$

where $\mathbf{e}_s(\mathbf{k})$ are the orthonormal eigenvectors of 3×3 matrices, $s = 1,2,3$ are the polarization directions, and $k_1, k_2, k_3 = 0,1,\ldots,L-1$ define the components of a vector in the reciprocal space: $\mathbf{K} = (2\pi/L)\mathbf{k}$ [10,11]. The integrable part of the Hamiltonian can now be expressed as

$$H_0 = \frac{m}{2} \sum_{\mathbf{k}} \sum_{s} [\dot{q}_s^*(\mathbf{k})\dot{q}_s(\mathbf{k}) + \omega_s^2(\mathbf{k})q_s^*(\mathbf{k})q_s(\mathbf{k})]$$

$$\equiv \sum_{\mathbf{k}} \sum_{s} H_s(\mathbf{k}),$$

where the frequencies $\omega_s(\mathbf{k})$ are the eigenvalues corresponding to the eigenvectors $\mathbf{e}_s(\mathbf{k})$ [10,11]: $D(\mathbf{k})\mathbf{e}(\mathbf{k}) = m\omega^2(\mathbf{k})\mathbf{e}(\mathbf{k})$, where

$$D_{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{l}} A_{\alpha\beta}(\mathbf{n},\mathbf{l})\exp\left\{i\frac{2\pi}{L}[k_1(l_1-n_1)+k_2(l_2-n_2) + k_3(l_3-n_3)]\right\}.$$

At low energy, the relative contribution of the perturbative part H' to the total Hamiltonian becomes negligible, and the total Hamiltonian can be reduced approximatively to its harmonic part H_0.

In this approximation, $H_s(\mathbf{k})$ is the total energy of the mode characterized by $\omega_s(\mathbf{k})$. As the normal modes' amplitudes and their time derivatives are complex variables, they span a $12N$-dimensional space, instead of the $6N$-dimensional space spanned by the atomic displacements and their time derivatives, that are real quantities. It turns out that, because of the periodic boundary conditions of the system, each normal mode $q_s(\mathbf{k})$ has a twin mode $q_s(\mathbf{k}')$ such that $q_s(\mathbf{k})=q_s^*(\mathbf{k}')$. The twin modes have the same polarization and the same frequency and, therefore, the same energy $H_s(\mathbf{k})=H_s(\mathbf{k}')$. The relation between the components of the wave vectors of the twin modes is $0\rightarrow0$, $1\rightarrow7$, $2\rightarrow6$, $3\rightarrow5$, $4\rightarrow4$. Thus, for example, normal modes corresponding to the same polarization s and, respectively, to components $(4,0,7)$ and $(4,0,1)$, are twins. Some modes have no twin, e.g., the mode $(4,0,4)$; but the imaginary component of these modes is zero. The symmetry among modes reduces the dimension of their phase space from $12N$ to $6N$ [11].

The computation of the frequencies of the normal modes of a fcc lattice found in the literature usually includes first and second neighbors [12,13]. We have extended it up to the sixth neighbors. Our computation shows that the 1533 normal modes [512×3, minus the three translational modes $(\mathbf{0})_s$] are divided in 75 groups; each group is characterized by a different frequency, and entails a number of normal modes ranging between 3 and 48, with an average of about 20 modes.

IV. QUANTUM SPECIFIC HEAT

Our model has 512 atoms, and the interaction among atoms is extended to the sixth shell of neighbors. In order to check how well this system approximates the real one, we have computed the specific heat per particle of argon, at constant volume, using the quantum formula valid in the harmonic approximation,
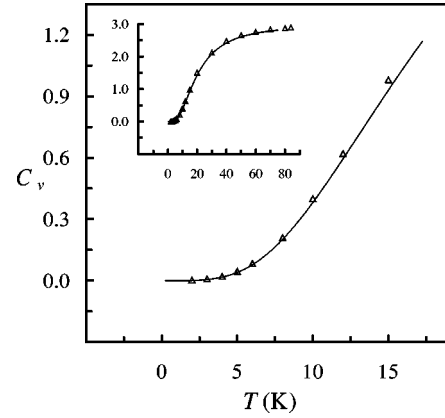

FIG. 1. Quantum specific heat per particle at constant volume (in k_B), for the 512-particle fcc system; LJ parameters appropriate to argon. $\triangle$ experimental data for solid argon [14].

$$C_v = \frac{1}{N}\sum_{\mathbf{k},s}\frac{1}{k_B T^2}\frac{\hbar^2\omega_s^2(\mathbf{k})}{(e^{\beta\hbar\omega_s(\mathbf{k})}-1)^2}e^{\beta\hbar\omega_s(\mathbf{k})}, \qquad (2)$$

where $\beta=(k_B T)^{-1}$ and k_B is Boltzmann's constant. In Fig. 1, we report the low-temperature specific heat given by formula (2) for our system, using the frequencies $\omega_s(\mathbf{k})$ computed as explained in the previous section. The computed specific heat is in fairly good agreement with the experimental data [14]; this shows that our system, albeit small, is already a good representation of the thermodynamic limit. As a matter of fact, we have increased the size of our system up to $N\simeq10^4$, and the results of Fig. 1 do not change in any appreciable way. In the same figure we report a similar comparison between formula (2) and the experimental data in the range 0–80 K. These results show that the harmonic approximation is quite good up to temperatures just below the melting point of argon; they also confirm that our system is a good model for the real system.

V. SHORT-TIME BEHAVIOR

Our simulation of the LJ crystal is performed at constant total energy and total volume; therefore, the time trajectory samples a microcanonical ensemble in the phase space. For such an ensemble, the appropriate formula to compute the specific heat per particle at constant volume is [2]

$$C_v = \frac{3k_B}{2}\left[1-\frac{3N}{2}\frac{\langle K^2\rangle_{\mathrm{mc}}-\langle K\rangle_{\mathrm{mc}}^2}{\langle K\rangle_{\mathrm{mc}}^2}\right]^{-1}, \qquad (3)$$

where K is the kinetic energy of the system and $\langle\ \rangle_{\mathrm{mc}}$ is the average in the microcanonical ensemble. Unfortunately, it turns out that in systems such as the one at hand, the kinetic energy has anomalous fluctuations at low energy, so that formula (3) can be used—with microcanonical averages replaced by time averages—only if the latter are of extraordinary length [1]. The reason for this anomalous behavior is that at low energy the coupling among normal modes of different frequency (the H' term of the Hamiltonian) is very weak; the slow energy exchange yields a slow diffusion in the phase space, so that, in order to reproduce the microca-
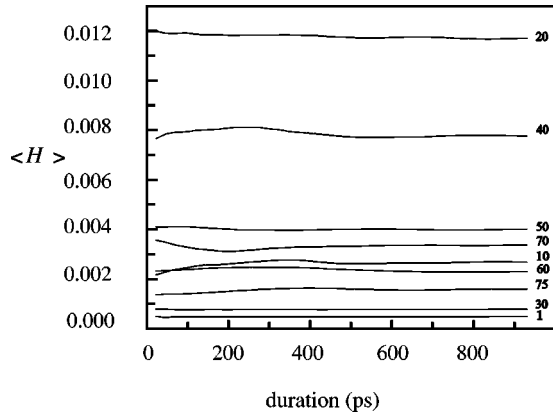
FIG. 2. Average energy per mode $\langle H \rangle$ (in ϵ) of various groups of normal modes, as a function of the duration of the average. The label on each line is the index of the group of modes. Higher indexes correspond to higher frequencies. $T = 0.1$ K.

FIG. 4. As in Fig. 2, with $T = 57$ K.

nonical ensamble averages, the trajectories must be extremely long as compared to the duration of a standard computer experiment.

This phenomenon is evident if one computes the time average of the energy entailed in each group of modes characterized by the same frequency. In Fig. 2 we report the average energy per mode $\langle H \rangle$ of several groups at $T = 0.1$ K, as a function of the simulation time. The results show clearly that there is no trend toward equipartition; when the temperature is raised, a trend toward equipartition appears, as shown in Fig. 3 and Fig. 4. A similar behavior was found before in other lattices [15], and is related to the transition from an Arnold diffusion to an Anosov diffusion in the phase space.

It should be noticed that the lack of equipartition among normal modes at low temperature does not prevent quantities like the kinetic energy or the potential energy from reaching their ensemble average within times that are much shorter than the range of Figs. 2, 3, or 4. These quantities can be expressed as sums of homologous single-particle quantities, and are therefore statistically "well behaved" [16]. On the
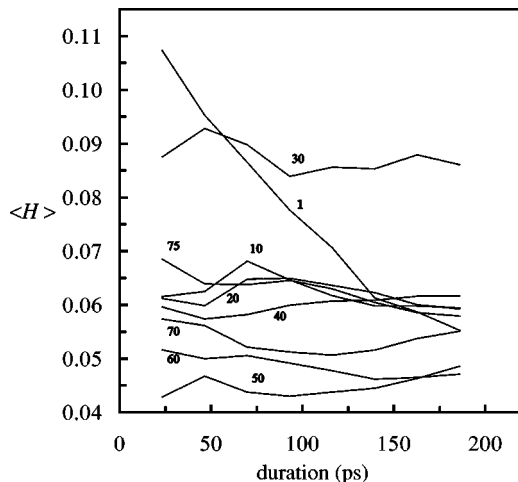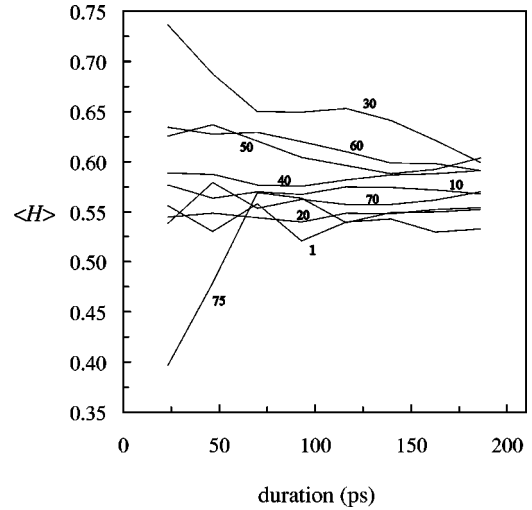
other hand, a quantity like the fluctuation of the kinetic energy in formula (3) cannot be expressed as the sum of single-particle quantities, and is therefore more affected by the lack of ergodicity of a finite-time trajectory in the phase space.

We want to emphasize that because the time average of the total kinetic energy reaches rapidly its equilibrium value, even at low total energy, the temperature of the system can be defined in the usual way through this average of the kinetic energy: $T = 2\langle K \rangle / 3Nk_B$, where $\langle \ \rangle$ is the time average. We will discuss later how to interpret this parameter in the low-temperature range, where there is no equipartition of energy among normal modes.

VI. CLASSICAL SPECIFIC HEAT

There is an alternate way of computing the specific heat at low temperature, which exploits just the weak coupling among modes that hinders the use of formula (3) [3]. As the modes exchange weakly when the total energy of the system is low, the whole system can be approximately decomposed in the sum of many small, weakly interacting subsystems, each subsystem being composed of a few normal modes of equal frequency. If M is the number of subsystems, $H(\mathbf{x}) \simeq \Sigma_{j=1}^{M} H_j(\mathbf{x}_j)$, where $\mathbf{x}$ is a point of the phase space Γ, and H_j is a harmonic Hamiltonian depending only on the subset of coordinates and momenta $\mathbf{x}_j$.

The probability distribution of the energy of the small subsystems is not effectively bound by the condition that the total energy of the system be constant, and is almost identical in the microcanonical and in the canonical ensemble [17]. The probability distribution law for small subsystems in the microcanonical case being practically identical to the canonical one, we can assume in the present case that every small subsystem of normal modes behaves canonically. The distribution law of the whole system can then be written as

$$P(\mathbf{x}) \simeq \prod_{j=1}^{M} \frac{e^{-\beta H_j(\mathbf{x}_j)}}{\int_{\Gamma} e^{-\beta H_j(\mathbf{x}_j)} d\mathbf{x}_j}.$$

FIG. 3. As in Fig. 2, with $T = 5$ K.

In this way, the probability of a state of the system at temperature T is expressed as a product of independent canonical probabilities—at the same temperature—of the M subsystems; it is as if each subsystem were in contact with a thermal bath characterized by the temperature of the system (we will discuss this point further in the last section). In this approach, the thermal bath is composed of all other subsystems, and the thermal contact is realized by the anharmonic part H' of the Hamiltonian, which entails the interaction terms among normal modes, and which becomes negligible at low temperature.

Adopting this point of view, the heat capacity of the system is given by the sum of the canonical contributions of the small subsystems in which it is divided. In the canonical ensemble, the specific heat per DOF is given, in units of k_B, by

$$c_v = \frac{1}{3N} \frac{\langle H^2 \rangle_c - \langle H \rangle_c^2}{k_B^2 T^2}, \tag{4}$$

where H is the total energy and $\langle \rangle_c$ is the average in the canonical ensemble. Considering a group of m_i modes as a weakly coupled subsystem of energy H_i, its contribution to the specific heat per DOF will be, replacing ensemble averages by time averages in Eq. (4),

$$c_v(i) = \frac{\langle H_i^2 \rangle - \langle H_i \rangle^2}{m_i k_B^2 T^2}. \tag{5}$$

The specific heat per DOF for the whole system will then be

$$c_v = \frac{1}{3N-3} \sum_i c_v(i) m_i. \tag{6}$$

Then $C_v = 3c_v$, which we dub multicanonical specific heat. The term -3 in the denominator is needed because the three translational modes $(0,0,0)_s$ do not contribute to the specific heat, and are therefore not included in the sum.

Figure 1 shows that, when computing the specific heat, the harmonic approximation is quite good up to temperatures just below the melting point of argon; therefore, the point of view adopted in this section, which neglects the anharmonic terms of the Hamiltonian in computing the classical specific heat, should be valid in the whole temperature range of existence of an fcc LJ crystal.

VII. RESULTS OF THE COMPUTER EXPERIMENT

In Fig. 5, we show the main results of the present computer experiment, in the temperature range between 0 and 60 K. Together with the experimental data for the specific heat per particle at constant volume [14], we report the values of C_v computed through formulas (5) and (6), in which each group of modes of the same frequency is considered to be a subsystem; there are 75 such groups in our system. The values of C_v at short time (2.5×10^3 time steps, equivalent to about 23 ps) are shown with error bars given by the standard deviations of the kinetic energy and of the energy fluctuation
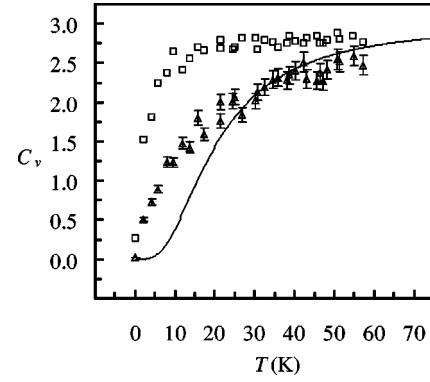

FIG. 5. Multicanonical specific heat per particle (in k_B) computed through formulas (5) and (6): $\triangle$, average over 2.5×10^3 time steps; $\square$, average over 2×10^4 time steps; _, experimental values [14]. The error bars on the values measured after 2×10^4 time steps are smaller than the symbols used in the figure.

that enter formula (5). For the long-time values (2×10^4 time steps, equivalent to about 186 ps), the error bars are smaller than the size of the symbol.

In Fig. 5 we report for comparison the quantum specific heat computed in Sec. IV; as mentioned there, this specific heat is practically not distinguishable from the experimental one. For the shortest average time (2.5×10^3 time steps), the specific-heat values found in the simulation lie quite near to the experimental curve, and definitely far from the classically expected value of $3k_B$. We stress that after 2.5×10^3 time steps, the average total kinetic energy, and therefore the temperature, have already reached the equilibrium value.

On the other hand, after 2×10^4 time steps, the pattern of the values computed in the simulation has changed markedly. With the exception of the temperature range belove 10 K, the multicanonical values are approaching the expected value of $3k_B$, and are clearly swerving from the experimental curve. Nevertheless, the lowest temperature range seems to keep a pattern that, even though different from the quantum one, is also very different from the classical Dulong-Petit law. This can be seen in Fig. 6, where we report the multicanonical specific heat computed through formulas (5) and (6) at $T = 0.1$ K, the lowest simulated temperature, for average times up to 10^5 time steps. At this very low temperature, the aver-
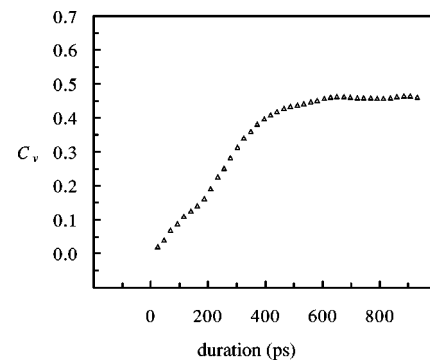

FIG. 6. Multicanonical specific heat (in k_B) computed as in Fig. 5, as a function of the duration of the average. $T = 0.1$ K.
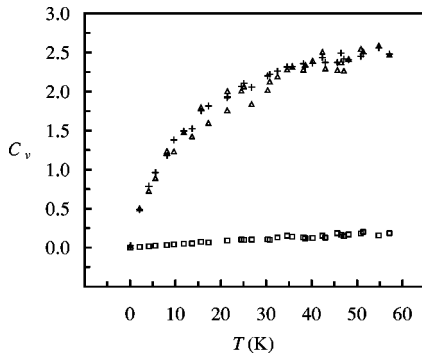
FIG. 7. Multicanonical specific heat (in k_B) for groups of modes of equal frequency ($\triangle$) and for pairs of conjugated modes ($+$). Also shown is the contribution to the specific heat of the anharmonic part of the Hamiltonian ($\square$).

FIG. 8. Multicanonical specific heat (in k_B) for pairs of conjugated modes, computed using the temperature of the system ($+$) or the temperatures of the subsystems ($\square$).

aged specific heat converges to a value of about $0.45k_B$; this value is higher than the corresponding quantum value, but also much lower than the classically expected value of $3k_B$.

We have checked the robustness of our definition of multicanonical specific heat with regard to the composition of the subsystems described in the previous section. We have implemented the same procedure used to derive the results of Fig. 5, but the normal modes entailed in each of the 75 groups were chosen at random, paying no attention to their frequency. The only exception were the conjugate modes, each pair being assigned to the same group. The number of modes entailed in each group was the same as in Fig. 5, where the groups were collected following their frequency. The values of the multicanonical specific heat computed in this way were practically indistinguishable from those of Fig. 5 over the whole temperature range, and are not shown here.

In order to check how far the multicanonical approach could be pushed, we have applied the same procedure yet another time, taking each pair of conjugate modes as a subsystem weakly coupled to the others. The values of C_v found in this case are reported in Fig. 7, together with the data of Fig. 5, those computed breaking down the system in groups of modes of equal frequency. Figure 7 shows that the two sets of values of C_v do not differ significantly. In the same figure we have reported values of C_v computed with formula (5) applied to a group entailing all normal modes; as the energy of the total system is constant, the variance of the energy of this group is equal to the variance of H', the anharmonic part of the Hamiltonian. These results will be discussed in the last section.

Finally, we have verified that in the multicanonical approach the definition of the temperature is not critical. In all data reported so far, the temperature used in formula (5) has been computed through the average kinetic energy of the whole system. One may wonder whether this is correct at low energy, where the normal modes are weakly coupled, and the average kinetic energy per mode of a pair of conjugated modes may differ significantly from the average kinetic energy per mode of the whole system. We have computed a second set of C_v values for the subsystems, each composed of a pair of conjugated modes, using in formula (5), for each subsystem, a temperature defined through the
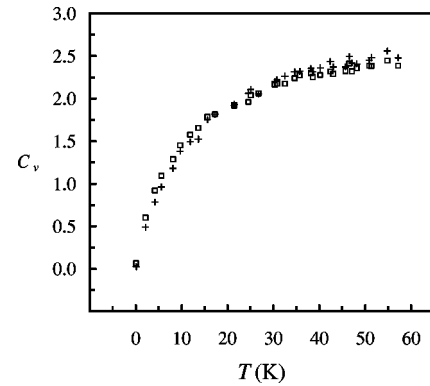
average kinetic energy of that pair of conjugated modes. In Fig. 8, we compare this new set of values with the one reported in Fig. 7, where the average temperature of the whole system was used. Here again the two sets of values do not differ by any appreciable amount, showing that the definition of temperature is not critical in the multicanonical approach.

VIII. GLASSY BEHAVIOR

A time-dependent specific heat, as we find in Figs. 5 and 6, is a common feature in supercooled liquids approaching the glass transition [18,19]. It has been argued that, depending on the cooling rate and on the method of the measure, there may be different ways to define a time-dependent (nonequilibrium) specific heat [20]. The latter depends on the ratio between the time of relaxation of the system and the time of observation. This ratio is called the Deborah number (De), and is used in rheology; the glass transition temperature T_g for a given observation time is defined as the temperature at which De$=1$.

The time dependence of the specific heat of supercooled liquids was detected through an experimental method based on oscillating thermal perturbations of given frequency [18,19]; those results were later interpreted through the hydrodynamic equations and shown to be related to a frequency-dependent viscosity [20]. In a computer simulation of a LJ liquid undergoing the glass transition, a frequency-dependent specific heat was measured, which exhibited relaxation phenomena similar to those found in the real experiment [21]. This specific heat was measured through the fluctuations of the kinetic energy of the system. Zwanzig [20] has observed that because the kinetic energy is not a conserved quantity, the frequency dependence found in that simulation reflected a property of the interconversion of kinetic and potential energy, more than a hydrodynamic process (hydrodynamics dealing with conserved quantities such as mass, momentum, and energy).

In the case of our LJ crystal, the hydrodynamic picture is of little use, but the time dependence of the specific heat found in the paper at hand, and described in Sec. VII, hints at a similarity between the behavior of a liquid at the glass transition and the behavior of our system at low temperature.

TABLE I. Temperature T^* (K) corresponding to the divergence of the specific heat computed through the equilibrium formula (3). N is the number of particles in the system, t^* is the observation time in ps.

N / t^*	256	2048	4096	32 768
20	2.87	2.28	2.80	2.83
200	1.63	1.82	1.50	1.43
1000	0.53	0.81	0.55	0.48
3000	0.27	0.42	0.20	0.19

How far can this similarity be taken? We have used a quantitative frame of reference appropriate for the glass transition to fit specific-heat data computed for the LJ fcc crystal studied in the present work.

In the experiments aimed at measuring the frequency dependence of the specific heat, the data reflect an entanglement of the latter with the thermal conductivity [18,19]. In order to control a possible effect of the thermal conductivity through a size factor due to the periodic boundary conditions imposed on our system, we have used specific-heat data taken from a previous computer experiment [1]. In that work a LJ fcc crystal was simulated with the same density and the same interaction potential as in the present case, but with sizes ranging from 256 to 32 768 particles.

In the supercooled liquid, the center of the glass transition, corresponding to De=1, is located at the peak frequency f of the imaginary part of the product $C_p K$, where C_p is the specific heat at constant pressure and K is the thermal conductivity. The temperature dependence of this peak frequency is fitted with the Vogel-Fulcher-Tamman (VFT) equation $f = f_0 \exp[-A/(T-T_0)]$, where T_0 is the temperature at which the relaxation time diverges [18]. In the LJ crystal, we choose observation times t^*, and for each such time we measure the temperature T^* at which the equilibrium specific heat at constant volume, when computed through formula (3), diverges because the fluctuation of the kinetic energy becomes twice as large as the expected equilibrium value (see Fig. 4 of Ref. [1]). Conversely, for each T^* the corresponding time t^* is the inverse of a frequency characteristic of the relaxation process involved in the transition. It turns out that in our case $T_0 = 0$ (see Fig. 2 of Ref. [3]). Therefore, the VFT equation in our case is $t^* = t_0^* \exp(A/T^*)$. We report in Table I the values of T^* as a function of t^*, for four distinct system sizes: $N = 256$, 2048, 4096, and 32 768. The data do not exhibit any size effect; a plot of T^* versus t^* shows that, besides the sistem with $N = 2048$, the points corresponding to the three other systems are very near to each other (see Fig. 4 of Ref. [1]). Fitting the data of Table I with the VFT equation yields values of t_0^* ranging between 28 and 61 ps, while the values of A range between 2.14 and 0.84 K, depending on the size of the system. The fit is not very good; nevertheless, it shows a definite trend, analogous to that found in a glass transition. It should be noted, however, that the frequencies corresponding to the observation times of Table I are in the range 10^8–10^{10} Hz, much higher than in the case of the supercooled liquid.

IX. DISCUSSION AND CONCLUSION

In our computer experiment, the shortest time averages have been performed over 2500 time steps, corresponding to 23 ps. Even though this is not a long time for computing equilibrium averages, it is long enough for the dynamic quantities that are ''well behaved''—such as the kinetic and potential energy, or the structure factor—to converge to their ensemble average. The specific heat behaves differently. This quantity is computed through the fluctuation of the kinetic energy in the microcanonical ensemble, and through the fluctuation of the total energy in the canonical ensemble. The energies are summable functions, but their fluctuations do not have this property. Therefore, one can expect the microcanonical specific heat to be ill-behaved, that is, to converge to the equilibrium value in a time much longer than the one needed by the kinetic energy [16]; indeed, this turns out to be the case, with a singularity in C_v still present around $T = 1.5$ K after 10^4 time steps. This result is similar to previous computer-simulation results found at low temperature in LJ microcrystals [1,3].

As explained in Sec. VII, this difficulty can be circumvented by computing the specific heat through a scheme that exploits just the weak energy exchange among normal modes that makes the computation of a microcanonical specific heat so difficult. Measuring the classical specific heat in the multicanonical approach yields values that are remarkably close to the experimental ones in the short-time range, that is, for times of the order of 25 ps. This new point of view narrows the gap that has traditionally existed between the classical and the quantum framework, showing that the short-time behavior of a classical system may look similar to the quantum behavior. In the quantum framework, the normal modes are quantized oscillators. When the temperature tends to zero, the thermal energy is not sufficient to excite in a significant way the modes of higher frequency, which leads to a drop of the specific-heat values. In the present, revisited classical framework, when the temperature tends to zero the anharmonic terms in the Hamiltonian become so small that the exchange of energy among normal modes (i.e., their excitation) becomes negligible and, again, the specific-heat values drop.

We have shown in Sec. VII that the multicanonical approach yields quite equivalent results when the composition of the weakly coupled groups is changed, from modes of equal frequency to modes of any frequency. Moreover, the approach is robust also when the size of those groups is reduced, down to the limit of a pair of conjugate modes, the classical equivalent of a quantized oscillator.

On the other hand, in order to apply the canonical computation of the specific heat to a weakly coupled group of modes, this group must be significantly smaller than the rest of system; the latter acts as the thermal reservoir, interacting with the group of modes through the anharmonic terms of the Hamiltonian. In Fig. 7, we have reported also the specific

heat given by formula (5) when one applies it to one group entailing all normal modes. As this group is almost as large as the whole system, it is not astonishing that the use of the canonical formula gives a different result from the multicanonical approach. In our simulation the total energy of the system is kept constant; therefore, the fluctuation of the energy of this group of modes equals the fluctuation of the anharmonic term H' in the Hamiltonian. Thus the value for the canonical specific heat computed for the largest group of modes is in fact equal to the contribution of H' to the total multicanonical specific heat of the system. In other words, the anharmonic part may be considered as yet another subsystem, weakly interacting with the rest of the system, that is, with all harmonic groups of normal modes. Figure 7 shows that this further contribution does not alter the total specific heat in the low-energy range. On the other hand, when this contribution is accounted for in the range above 50 K, it raises the total specific heat to values significantly nearer to the value of $3k_B$ anticipated by the Dulong-Petit law. Therefore, a consistent classical multicanonical computation of the specific heat, taking into account harmonic as well as anharmonic contributions, reproduces the Dulong-Petit law at high temperature, but yields values that drop to zero at low temperature. The temperature range where the change between these two regimes takes place shifts to lower values as the time over which the system is observed increases.

This behavior is reminiscent of what is observed in liquids near the glass transition, where a freezing of modes takes place when the temperature is lowered. The decoupling among normal modes found in our simulation of a LJ crystal yields an effect on the thermodynamics similar to the one produced by that freezing in a glassy transition, as foreseen in [4]. However, further analysis is needed to clarify whether this similarity can be put on firm ground.

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