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Stochastic transition in two-dimensional Lennard-Jones systems

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We study by computer simulation the behavior at low energy of two-dimensional Lennard-Jones systems, with square or triangular cells and a number of degrees of freedom N up to 128. These systems exhibit a transition from ordered to stochastic motions, passing through a region of intermediate behavior. We thus find two stochasticity borders, which separate in the phase space the ordered, intermediate, and stochastic regions. The corresponding energy thresholds have been determined as functions of the frequency ω of the initially excited normal modes; they generally increase with ω and appear to be independent of N. Their values agree with those found by other authors for one-dimensional LJ systems. We computed also the maximal Lyapunov characteristic exponent χ^* of our systems, which is a typical measure of stochasticity; this analysis shows that even in the ordered region certain stochastic features may persist. At higher energies, χ^* increases linearly with the energy per degree of freedom e. The law $\chi^*(e)$ has been determined in the thermodynamic limit by extrapolation. The values found for the stochasticity thresholds fall in a physically significant energy range. The behavior of the thresholds as a function of ω and N is compatible with the hypothesis on the existence of a classical zero-point energy, advanced by Cercignani, Galgani, and Scotti.

I. INTRODUCTION

It is well known that in general the phase space Γ of a classical system of coupled oscillators is decomposed, at least roughly, into regions characterized by very different dynamical properties.[1]

On one hand, around the point of Γ which represents the minimum of energy and close enough to it, one finds the so-called ordered region, characterized by the presence of quasiperiodic motions. These motions were first observed by Fermi, Pasta, and Ulam in their celebrated model,[2] and were subsequently found in other systems with many degrees of freedom, in one[3-8] or two dimensions.[9,10] Such dynamical behavior is in evident contrast with the ergodic hypothesis on which classical statistical mechanics is usually based.

On the other hand, far enough in Γ from the point of lowest energy, in any direction, one finds a "good" statistical behavior: the system loses rapidly the memory of its initial state, the energy is well distributed among all normal modes, etc. The region where this happens is called stochastic; it is separated from the ordered region by the so-called stochasticity threshold. In fact, stochasticity is not a very precise and defined concept, so that neither is its threshold well defined. A more realistic description of Γ can be the following: three regions (ordered, intermediate, and stochastic) exist in Γ, separated by two borders. In the intermediate region the behavior of the system looks ordered or stochastic depending on the point of view; this fact is evident when using different criteria of stochasticity to analyze the same orbit. Moving in Γ from the equilibrium point in a given direction (that is, raising the energy of the system) one thus expects to find two thresholds corresponding to the crossing of the two borders. Such structure of Γ will play a relevant role in the present work.

In order to preserve the assumptions of classical statistical mechanics, some authors suggest that only the stochastic region should persist when the number of degrees of freedom is sufficiently increased.[4,11] However, some numerical experiments with one-dimensional models, and a number of degrees of freedom up to several hundreds, have given a different indication, i.e., that also ordered motions persist.[5,6,8]

In the paper at hand we analyze in detail the dynamical behavior of a two-dimensional system of identical particles, in order to get a better insight into this open problem. The particles are supposed to interact via a Lennard-Jones potential; this has been chosen both for its physical relevance and to allow direct comparison with other numerical experiments. A two-dimensional system exhibits a qualitative behavior which is more similar to that of a real physical system than a one-dimensional chain. Furthermore, in particu-

lar conditions it has the peculiarity that its normal modes are naturally divided into groups of equal frequency, thus making our stochasticity tests easier and clearer.

An impressive interpretation of the persistence of the stochasticity threshold has also been proposed,[12] according to which ordered motions are nothing but motions at zero temperature; i.e., there exists a classical zero-point energy. Following this line of thought, it has been conjectured that if only a group of normal modes of close frequencies is initially excited, one should find a stochasticity threshold at an energy which is an increasing function of that frequency, possibly a linear function. Such hypothesis has been tested on a one-dimensional model of particles interacting via a Lennard-Jones potential.[8] The results are not conclusive, but appear to support that conjecture. This question is also studied in the present work.

We describe in Sec. II the model and in Sec. III the kind of numerical experiments we performed on it. Sections IV and V are devoted to the presentation of the results of our computer experiments; these results are discussed in Sec. VI. In Sec. VII we give some concluding remarks together with an indication for further developments of this research.

II. THE MODEL

The particles of our system interact through a Lennard-Jones potential

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

$V(r)$ has a minimum at $r_0=2^{1/6}\sigma$, where it takes the value zero; ϵ is the depth of the potential well. For such a short-range potential the triangular lattice, that is, the most compact one, is the most stable. We used it for a few numerical experiments, as described in Sec. V. However, in order to perform a simple normal-modes analysis of the dynamics of the system, we used in most computations a square cell lattice with only nearest-neighbor interaction, and fixed boundary conditions (such a lattice is also stable).

To be more definite, consider a square lattice of $(L+2)^2$ sites, with a square cell of side d. Each site can be labeled by a couple of indices (l,m) with $0\leq l,\ m\leq L+1$. The boundary sites are occupied by fixed particles; the other L^2 particles oscillate around their equilibrium positions (for sufficiently low energy), each being coupled with four neighboring particles. We denote by $x^0_{lm}=ld$ and $y^0_{lm}=md$ the coordinates of site (l,m), and by x_{lm}, y_{lm} the coordinates of the corresponding particle.

Let

$$r_{lml'm'}=[(x_{lm}-x_{l'm'})^2+(y_{lm}-y_{l'm'})^2]^{1/2} .$$

The model is fully described by the Lagrangian

$$\mathcal{L}=\frac{M}{2}\sum_{l,m=1}^{L}(\dot{x}^2_{lm}+\dot{y}^2_{lm})-\sum_{l,m,l',m'}{}' V(r_{lml'm'}),$$

where $\sum'_{lml'm'}$ is extended over all pairs of interacting particles. From this Lagrangian we obtain the equations of motion

$$\ddot{x}_{lm}=\frac{48\epsilon}{M\sigma^2}\sum_{l'm'}{}''(x_{lm}-x_{l'm'})\left[\left(\frac{\sigma}{r_{lml'm'}}\right)^{14}-\frac{1}{2}\left(\frac{\sigma}{r_{lml'm'}}\right)^{8}\right],$$

$$\ddot{y}_{lm}=\frac{48\epsilon}{M\sigma^2}\sum_{l'm'}{}''(y_{lm}-y_{l'm'})\left[\left(\frac{\sigma}{r_{lml'm'}}\right)^{14}-\frac{1}{2}\left(\frac{\sigma}{r_{lml'm'}}\right)^{8}\right], \tag{1}$$

where the sums $\sum''_{l'm'}$ are extended over all particles $(l'm')$ which interact with particle (l,m).

The normal-mode coordinates are defined by

$$q^x_{hk}=\sum_{l,m=1}^{L}(x_{lm}-x^0_{lm})U_{hklm},$$

$$q^y_{hk}=\sum_{l,m=1}^{L}(y_{lm}-y^0_{lm})U_{hklm},\quad h,k=1,\ldots,L,$$

and

$$U_{hklm}=\frac{2}{L+1}\sin\frac{hl\pi}{L+1}\sin\frac{km\pi}{L+1} .$$

In these coordinates, the equations of motion become

$$\ddot{q}^x_{hk}=-(\omega^x_{hk})^2q^x_{hk}+\cdots,$$
$$\ddot{q}^y_{hk}=-(\omega^y_{hk})^2q^y_{hk}+\cdots, \tag{2}$$

where the ellipses represent higher-order terms. The terms of higher order in the coordinates in Eqs. (2) are small at low energies. Our system is then equivalent to a set of weakly coupled harmonic oscillators. The energy E of the system can be written as

$$E=\sum_{h,k=1}^{L}(E^x_{hk}+E^y_{hk})+E',$$

where

$$E^x_{hk}=\tfrac{1}{2}M[(\dot{q}^x_{hk})^2+(\omega^x_{hk}q^x_{hk})^2]$$

and

$$E^y_{hk}=\tfrac{1}{2}M[(\dot{q}^y_{hk})^2+(\omega^y_{hk}q^y_{hk})^2]$$

are the energies of x and y oscillators, respectively, and E' is the energy of the coupling. E' is negligible when E is small. The angular frequencies are given by

TABLE I. Frequencies ω_n of the groups of normal modes, for two square cell lattices.

$\omega_n\left(\frac{\text{radian}}{\text{time}}\right)$	$L=6$	$L=8$
ω_1	0.4856	0.3789
ω_2	0.9468	0.7464
ω_3	1.3606	1.0911
ω_4	1.7061	1.4027
ω_5	1.9661	1.6717
ω_6	2.1275	1.8899
ω_7		2.0506
ω_8		2.1491

$$\omega^x_{hk}=2\left[\frac{K_L}{M}\left(\sin\frac{h\pi}{2(L+1)}\right)^2+\frac{K_T}{M}\left(\sin\frac{k\pi}{2(L+1)}\right)^2\right]^{1/2},$$

$$\omega^y_{hk}=2\left[\frac{K_T}{M}\left(\sin\frac{h\pi}{2(L+1)}\right)^2+\frac{K_L}{M}\left(\sin\frac{k\pi}{2(L+1)}\right)^2\right]^{1/2}.$$

K_L and K_T are the elastic constants for longitudinal and transversal waves, respectively, and are given by

$$K_L=\left.\frac{\partial^2 V}{\partial r^2}\right|_{r=d};\quad K_T=\left.\frac{1}{r}\frac{\partial V}{\partial r}\right|_{r=d}.$$

K_T vanishes for $d=r_0$. As a consequence, in this case there are only L distinct frequencies, and the normal modes are naturally divided into L groups, each including $2L$ modes of equal frequency (L x modes and L y modes). Actually we set $d=r_0$. Concerning the various constants characterizing the model, we set $\sigma=1$, $\epsilon=1$, $M=48$; this corresponds to the choice (standard in molecular dynamics) of σ as a unit of length, ϵ as a unit of energy, and $(M\sigma^2/48\epsilon)^{1/2}$ as a unit of time. With these choices the angular frequencies turn out to be

$$\omega^x_{hk}=\omega^y_{hn}\equiv\omega_n=3^{1/2}2^{1/3}\sin[n\pi/2(L+1)]$$

for $h,k,n=1,\ldots,L$. The frequencies for the lattices with $L=6$ and 8 are reported in Table I.

III. NUMERICAL EXPERIMENTS

Most of the computations have been performed on a square cell lattice with $L=6$ or 8, that is, with $N=72$ or 128 degrees of freedom. The numerical integration of the equations of motion (1) has been carried on by means of a standard numerical algorithm (the so-called central-differences method), shortly resumed in the Appendix.

Typically, we chose the initial conditions by giving all the energy (as kinetic energy) to a few modes belonging to the same group. Following the orbit in Γ, we computed several quantities:

(i) The time averages $\bar{E}^x_{hk}$ and $\bar{E}^y_{hk}$ of the energy of each mode;

(ii) the time averages $\bar{E}_n$ ($n=1,\ldots,L$) of the energy E_n of each group:

$$E_n=\sum_{k=1}^{L}E^x_{nk}+\sum_{h=1}^{L}E^y_{hn};$$

(iii) a parameter λ, measuring the oscillation of the energy of the initially excited group of modes: precisely, we set $\lambda=(E^{\max}-E^{\min})/E^{\max}$ where $E^{\max}$ and $E^{\min}$ denote the maximal and minimal energies attained by the initially excited group of modes during the evolution of the system. $\lambda=0$ means that this group does not share its energy with any other group. $\lambda=1$ means that there is at least a time where this group has given all its energy to some other groups. Our criterion to determine the boundary of the region of highly ordered motions is based on the measure of λ. In the spirit of the already cited Refs. 8 and 12, if a sharp change in λ is observed at a given energy, the latter could be interpreted as the zero-point energy of the initially excited modes.

(iv) A parameter μ, measuring the distance from complete energy sharing among modes: more precisely, if n' and n'' are the indices for which $\bar{E}_n$ attains its maximum and its minimum, respectively, then we set $\mu=(\bar{E}_{n'}-\bar{E}_{n''})/\bar{E}_{n'}$. $\mu=1$ means that at least one group of modes has not received any energy; $\mu=0$ means that all groups shared energy equally. Thus, lower values of μ indicate an approach to ergodicity. Our criterion to determine the boundary of the stochastic region is therefore based on the measure of μ. Of course a small λ implies a large μ, but there can be a region where they are both close to 1: in such a case the initially excited group already shares its energy with other groups, but not with all of them. This is what we call the intermediate region.

All the above quantities concern the behavior of the normal modes. They are meaningful only if the total energy is sufficiently small, so that the anharmonic energy E' (see Sec. II) can be neglected. In addition to these quantities, we computed another parameter which does not depend on the normal modes analysis, precisely:

(v) The maximal Lyapunov characteristic exponent (LCE) χ^*. Its definition and significance will be now shortly resumed, but only for our model; for a more general description see Refs. 13 and 14.

Already in the first study of the stochastic transition, on the Hénon-Heiles model,[15] it clearly appeared that a property characterizing the stochastic region is the exponential divergence of nearby orbits. The LCE's permit giving a neat quantita-

tive definition of such divergence. They are a useful tool in the numerical study of stochasticity, being numerically computable.

Let z denote the position of the system in the phase space:

$$z=(z_1,\ldots,z_K)$$
$$\equiv(x_{11},\ldots,x_{LL},y_{11},\ldots,y_{LL},\dot{x}_{11},\ldots,\dot{y}_{LL})$$

with $K=4L^2$. It is well known that the system of $2L^2$ equations of second order (1) can be rewritten as a system of K equations of first order, of the form

$$\dot{z}_i=f_i(z),\quad i=1,\ldots,K \tag{3}$$

with suitable f_i's.

Let us denote by $F_i(z^0,t)$ the solution of the system (3) with initial point z^0, and by $d(z,z')$ the distance in the phase space between the points z and z'. As our phase space is Euclidean, it is $d(z,z')=\|z'-z\|$, where $\|\ \|$ denotes the ordinary Euclidean norm. Properly speaking, the definition of the norm depends on the units of length and velocity that are chosen, and is not independent of a change of coordinates. However, the relevant quantities we are going to define will be independent of such changes.

Let us now consider in the phase space two initial points z^0 and $z^0+\alpha\zeta^0$, where α is a real number and ζ^0 any given vector of norm one. For any $t>0$ we are interested in the quantity

$$\gamma(z^0,\zeta^0,t)=\lim_{\alpha\to 0}\frac{d[F(z^0,t),F(z^0+\alpha\zeta^0,t)]}{d[z^0,z^0+\alpha\zeta^0]},$$

where $F(z^0,t)\equiv[F_1(z^0,t),\ldots,F_K(z^0,t)]$. Denoting by $A(z^0,t)$ the matrix $[\partial F_i(z,t)/\partial z_j]_{z=z^0}$, it clearly follows that

$$\gamma(z^0,\zeta^0,t)=\|A(z^0,t)\zeta^0\|.$$

One says that the orbit originating at z^0 is exponentially unstable, in the direction of ζ^0, if the limit

$$\chi(z^0,\zeta^0)=\lim_{t\to\infty}(1/t)\ln\|A(z^0,t)\zeta^0\| \tag{4}$$

exists and is positive. Actually, this limit is known to exist[13] for almost all z^0 (in the sense of Lebesgue measure) and for all ζ^0. By varying ζ^0, χ can assume up to K different values, called Lyapunov characteristic exponents. However, a relevant fact is that almost all ζ^0 give the maximal one that will be denoted by χ^*.

A vanishing χ^* indicates that nearby orbits do not diverge exponentially, that is, no stochasticity. It follows from the definition (4) of the LCE's that χ^* is a constant of motion. As a consequence, for an ergodic system, χ^* depends only on the total energy; however, if a given energy surface is divided into invariant components, then χ^* can assume different positive values on them. An example of such behavior, which is stochastic but not ergodic, will be given in Sec. V.

As already remarked, the normal-modes analysis does not enter into the definition of the LCE's, It could be easily seen that they are also independent of the choice of coordinates and units of measure, that is, the LCE's are parameters characterizing intrinsic properties of a given dynamical system.

The numerical computation of χ^* is based on the property that almost all ζ^0 give the maximal LCE. As a consequence, given z^0 and having chosen ζ^0 at random, one has to compute for any t the vector $\zeta(t)=A(z^0,t)\zeta^0$, in order to apply the definition (4). Now, it is very easy to obtain for ζ the differential equation

$$\dot{\zeta}=a(F(z^0,t))\zeta, \tag{5}$$

where $a(z)$ is the matrix $[\partial f_i(z)/\partial z_j]$; such an equation, which is called the variational equation, can be easily handled with a computer, provided a certain care is taken to overcome some technical difficulties. For a short discussion see the Appendix.

Let us finally make a comment about all the parameters (i)–(v) we have here introduced. It is clear from their definitions that one should in principle compute them over an infinite time. We have carried on the computations typically up to the time $T=10^4$ in our units; at this time the above quantities seemed rather well stabilized around a limit value. This stabilization, however, is poorer in the transition region: indeed, it is typical that, in the neighborhood of a border separating regions of different dynamical behavior, the time an orbit requires to exhibit its asymptotic behavior diverges. This could be the main source of errors in determining our thresholds. We recall that, in our units, the shortest and longest periods of the harmonic normal modes are 3.0 and 12.9, respectively, for the lattice with $L=6$, to be compared with T.

IV. STOCHASTICITY THRESHOLDS

A. Stochastic parameter λ

The dynamical behavior of the system has been studied by exciting, in each experiment, a couple of x modes and a couple of y modes of equal frequency, that is, of the same group. We observed that the energy initially given (E) is rapidly shared among all modes of this group, so that indeed one has excited them all, roughly to the same degree. The relevant energy to be considered in the analysis of the behavior of our system is therefore the

energy initially given to the group of frequency ω_n, divided by the number $(2L)$ of the modes in that group, that is, the energy per mode: $\tilde{e}=E/2L$.

We want to stress that even when the energy is low and practically not transferred to other groups, we observe a good energy partition among all modes in the initially excited group. This phenomenon suggests that also ordered orbits may exhibit a certain degree of stochasticity: this fact will be emphasized by studying the maximal LCE, χ^* (Sec. V).

When the energy $\tilde{e}$ of the modes of the nth group is raised, we observe that a significant transfer initiates, typically to the modes of the groups contiguous in frequency. Raising further the energy, the transfer process extends to the other groups. As a consequence, the value of the parameter λ increases from a value close to 0 to a value close to 1. When λ is at its lower values, the group initially excited has lost typically a few percent of its initial energy. This fraction of energy is shared, although in very different amounts, by all other groups, both with even and odd indices.[16]

The results of the computation of λ, executed on the lattice with $L=6$ and for different initially excited groups of modes, are reported in Fig. 1. We see that the variation of λ takes place in an energy range which is narrow and clearly depends on the index n of the excited group. To fix quantitatively the energy thresholds $\tilde{e}_t$, we have considered the intersection of the curves of Fig. 1 with the horizontal line $\lambda=\frac{1}{2}$. The profiles $\lambda(\tilde{e})$ are similar for the different initially excited groups, but are shifted toward higher energies for higher frequencies. Group 6 is an exception: the corresponding curve is on the left of the curve of group 5, near the one of group 4. This is certainly related to the fact that ω_4 and ω_6 are resonant frequencies, with ratio $\frac{4}{5}$ (within 0.2%). In such conditions, the energy initially given to group 6 is transferred to a great extent to the modes of group 4, thus lowering the threshold of the former group. (The transfer of energy from group 4 also takes place preferentially towards group 6, but the threshold of group 4 does not seem to be affected.)

Also groups 1 and 2 give very similar thresholds for λ. Looking at their frequencies, one observes that they are resonant with ratio $\frac{1}{2}$ (within 2.5%).[17]

The parameter λ has been computed also on the lattice with $L=8$, exciting subsequently, as for $L=6$, the different groups of modes, the frequencies of which are reported in Table I. The behavior of λ is similar to that found for the lattice with $L=6$. The threshold energies are well defined also in this case, due to the narrowness of the energy interval in which λ grows from low to high values. For three groups (2, 7, and 8) λ was always greater than $\frac{1}{2}$, even at the lowest energy which was considered ($\tilde{e}=4\times10^{-3}$). Therefore, for these groups we set $\tilde{e}_t=0$.

The threshold energies $\tilde{e}_t$ for λ in the cases $L=6$ and 8 are reported in Fig. 2, as a function of the frequency of the initially excited modes (lower curves). In the case $L=6$ the threshold increases definitively with ω, with the exclusion of the last group, as mentioned before. The curve found in the case $L=8$ is nicely superimposed for most values of ω; however, there is an anomalous lowering of the threshold for those groups which exhibit resonances. The resonances of this system are reported in Table II. The connection between the presence of resonances and the lowering of the threshold is evident but not transparent. Furthermore, it must be noticed that the above resonance ratios are calculated only in the harmonic approximation. In any case, we want to stress that reso-

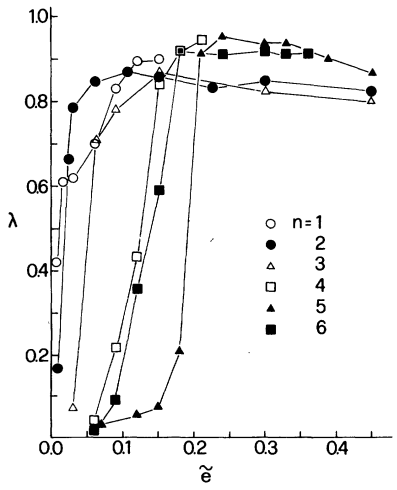

FIG. 1. Stochastic parameter λ for a square lattice with $L=6$, as a function of the energy per mode $\tilde{e}$. n is the index of the initially excited group of normal modes.

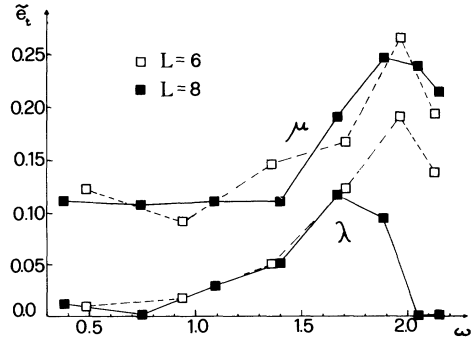

FIG. 2. Energy threshold $\tilde{e}_t$ for λ and μ, as a function of the frequency ω of the initially excited modes, for the square cell lattices with $L=6$ and 8.

TABLE II. Resonances between groups of normal modes for the square cell lattice with $L=8$. Δ is the relative deviation of the actual frequency ratio from the resonance.

Frequencies	Resonance	Δ
ω_2/ω_1	2/1	0.015
ω_3/ω_2	3/1	0.040
ω_3/ω_4	3/2	0.020
ω_7/ω_5	5/4	0.020
ω_8/ω_6	8/7	0.005
ω_6/ω_5	8/7	0.010

nances give rise to energy transfer through well defined "channels." They do not produce energy sharing among all modes, that is, completely disordered motion. On the other hand, the onset of such a motion cannot be properly studied by the parameter λ. This analysis has been performed by means of the stochastic parameter μ.

B. Stochastic parameter μ

The results of the computation of μ in the case $L=6$ are reported in Fig. 3. The profile of μ, for different initially excited groups, is sigmoidal, as in the case of λ. In this case, also, the transition from the value 1 to values close to 0 takes place in a narrow range of energy. Thus, we can define an energy threshold $\bar{e}_t$ for μ as the value $\bar{e}_t$ such that $\mu(\bar{e}_t)=\frac{1}{2}$. The threshold energies for μ are reported in Fig. 2 as a function of the frequency of the initially excited group. One sees that also for μ the threshold generally increases with ω. Because of the resonance between ω_6 and ω_4, in this case the threshold for group 6 is also lowered.

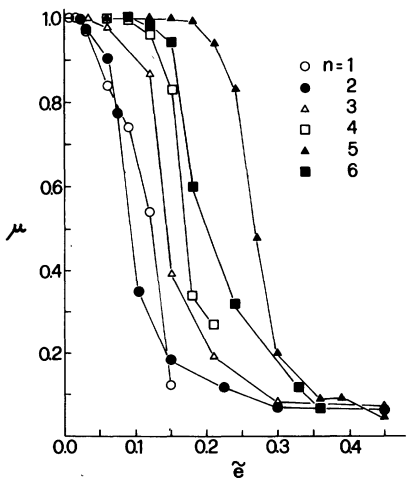

FIG. 3. Stochastic parameter μ as a function of the energy per mode $\bar{e}$, for the square cell lattice with $L=6$. n is the index of the initially excited group of normal modes.

The parameter μ has been computed also on the lattice with $L=8$, and the threshold energies for the different excited groups have been determined. As for λ, μ also behaves rather similarly to the case $L=6$. The threshold energies for μ, $L=8$, are reported in Fig. 2. Two features can be noticed: the threshold is quite constant for the low frequency modes and, although lowered, does not go to zero for those frequencies which were shown to be in resonance with others (groups 2, 7, 8). The curve drawn through these threshold points, found in the case $L=8$, is interlaced with the analogous curve drawn for the case $L=6$.

The relative stability of the curves drawn for λ and μ thresholds, when the number of degrees of freedom is increased from 72 to 128, suggests that this pattern should persist in the thermodynamic limit.[18]

V. MAXIMAL LCE χ^*

A. Square cell lattice

Beside the parameters λ and μ, and along the same orbits in Γ, we have computed the maximal LCE χ^*, as described in Sec. IV. We have already seen that for a sufficiently high energy, and independently of the initial excitation, all normal modes equally share energy. Correspondingly, we found for χ^* values which also do not depend on the particular initial excitation, but only on the energy. This is in agreement with the idea that at high energy the system has good ergodic properties. On the contrary, at lower energies the system is very far from ergodicity, and different values are found for χ^* at the same energy, depending on the initially excited group of modes. Exactly the same behavior was found in Ref. 7 for a one-dimensional Lennard-Jones system. This situation is illustrated in Fig. 4(a), which refers to $L=6$: by lowering the energy one observes a branching, each branch corresponding to a given group of initially excited modes. In Fig. 4(a) the values of χ^* are reported as functions of the energy per degree of freedom $e=E/2L^2$. In fact, for a given L, the choice of $\bar{e}$ or e as energy variable is irrelevant. The results for $L=6$ will be compared with those for $L=8$ in the higher energy region, where all the $2L^2$ modes share energy. Therefore, we use in this section e as the appropriate variable.

Figure 4(a) allows one to draw two relevant conclusions: First, χ^* is positive even below the λ thresholds. This means that the energy sharing, which takes place among modes of the same group,

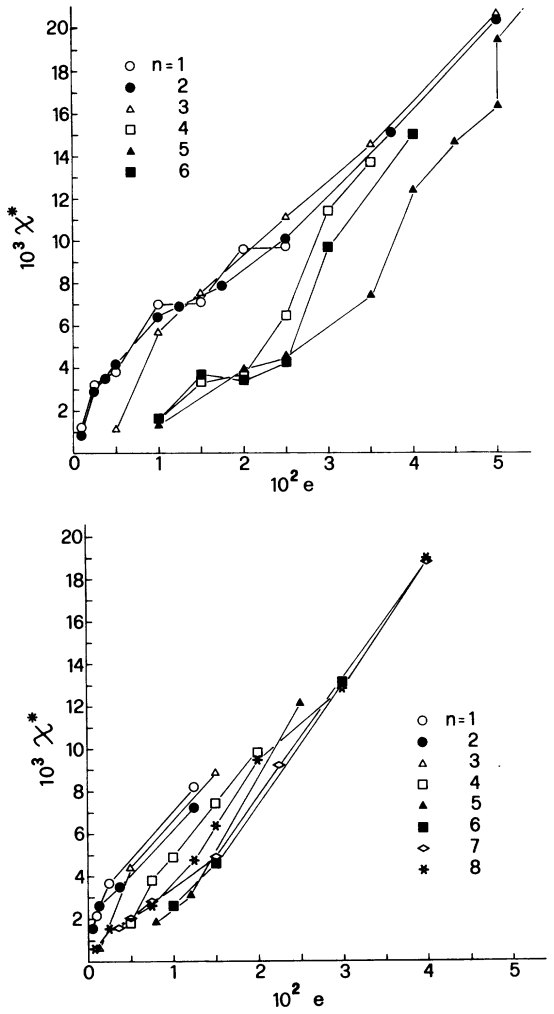

FIG. 4. The maximal LCE χ^* as a function of the energy per degree of freedom e, for the square cell lattices with (a) 72 and (b) 128 degrees of freedom. n is the index of the initially excited group of normal modes.

is always of stochastic nature, even in the absence of any energy sharing among groups. Second, by comparison with Fig. 3 one notices that at a given energy those modes which have a higher threshold behave more stochastically. In other words, in order to reach a given stochasticity of the system, that is a given value of χ^*, a higher energy must be given to groups with higher threshold. Thus, for example, the value 0.005 of χ^* is reached, in order, by groups 1-2, 3, 4, 6, 5; this is just the order of increasing stochasticity thresholds, both for λ and μ.

The values of χ^* at low energies for the lattice with $L=8$ are reported in Fig. 4(b). The branching phenomenon is evident in this case as well. Again, we find nonvanishing stochasticity below the λ thresholds. Furthermore, the order in which the groups ramify (1-3-2, 4, 8, 5-7-6 at $\chi^* = 0.005$) corresponds roughly to the order of increasing thresholds for μ (1-2-3-4, 5, 8, 7, 6, see Fig. 2) and differs substantially from the order of increasing thresholds for λ. This difference cannot be observed in the case $L=6$, as mentioned before. χ^*, as a measure of the stochasticity of the system as a whole, seems thus closely related to the stochasticity threshold μ, which is a measure of the degree of energy partition in the system, or ergodic-like behavior. One can also notice that the values of χ^* corresponding to the μ thresholds $\tilde{e}_t$ fall in the same range 7×10^{-3}–14×10^{-3} for both lattices.

Outside the branching region, χ^* is a function only of e. It increases with e, and its behavior is markedly linear in the energy range considered here (for both $L=6$ and 8). These two lines are shown in Fig. 5 (dotted lines); their extrapolation to $\chi^*=0$ leads to a "pseudothreshold" e^* which is similar in the two cases: precisely, $e^*=0.024$ for $L=6$, and $e^*=0.018$ for $L=8$. e^* is the stochasticity threshold one would find if the branching phenomenon would not occur. The problem naturally arises whether the threshold e^* approaches zero when the number of degrees of freedom N goes to infinity. To have an insight into this problem, we performed some experiments on a two-dimensional lattice with triangular cells. As remarked in Sec. II, the triangular cell lattice

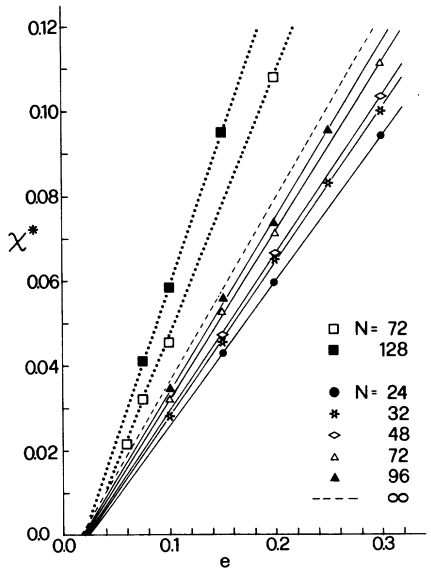

FIG. 5. Maximal LCE χ^* for various square cell and triangular cell lattices, as a function of the energy per degree of freedom e. N is the number of degrees of freedom. ····· square cell lattices; ——— triangular cell lattices; ----- triangular cell lattice, extrapolation for $N\to\infty$.

is a natural one for a two dimensional Lennard-Jones system. On the other hand, as we have seen in Sec. IV, the computation of the maximal LCE χ^* does not require a normal-modes analysis, and can thus be performed on any lattice.

B. Triangular cell lattice

Several two-dimensional lattices with triangular cells and periodic boundary conditions have been considered, with N equal to 24, 32, 48, 72, and 96 (see Fig. 6). As for the square lattice, only nearest-neighbor interactions have been taken into account, so that each particle interacts with six other particles. Periodic boundary conditions are of common use in molecular dynamics: the system is supposed to lie on a two-dimensional torus. The cell side has been put equal to r_0, in order to have zero pressure as for the square cell lattices.

We computed the maximal LCE χ^* for different values of e, by distributing randomly the energy among all particles (thus exciting randomly all modes). For small energies, where one expects to find the branching phenomenon, we actually obtained different values for different random excitations. An extended study, however, has been made only in the higher energy region, where χ^* turns out to depend only on e. The values of χ^* we have found for the different lattices are reported in Fig. 5. The linear behavior of χ^* in this energy range is evident and is stressed by the straight lines drawn through the computed points. For each N we have then a law of the form

$$\chi^* = \alpha_N (e - e_N^*), \tag{6}$$

where e_N^* is a pseudothreshold, as for the square cell lattices. The N dependence of α_N and e_N^* turns out to be rather well fitted (see Fig. 7) by the relations

$$\begin{aligned} \alpha_N &= 0.42 - 2.1 N^{-1}, \\ e_N^* &= 0.016 - 0.19 N^{-1}. \end{aligned} \tag{7}$$

On the base of relations (6) and (7) one expects the relation

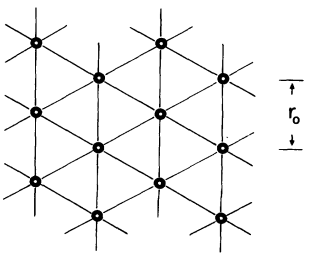

FIG. 6. Triangular cell lattice with periodic boundary conditions; 24 degrees of freedom.

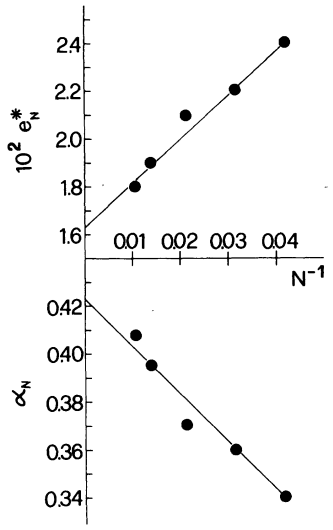

FIG. 7. Fit of the parameters of Eq. (6) for the triangular cell lattices. N is the number of degrees of freedom.

$$\chi^* = \alpha_\infty (e - e_\infty^*)$$

to hold in the thermodynamic limit. Here $\alpha_\infty = 0.42$ and $\epsilon_\infty^* = 0.016$. This limit line is also drawn in Fig. 5 (dashed line). Of course, the numerical values just produced are indicative, being affected by the numerical error entailed in our computation of χ^*. However, we think that the essential features of the phenomenon have been correctly described, and that a more precise estimate of the errors would not change substantially relations (6) and (7).

Let us compare the behavior of χ^* for the triangular cell lattice with that for the square cell lattice. One notices that the pseudothresholds are very close. The slope of the straight lines on the contrary is sensibly lower for the triangular cell lattice; that is, at a given energy this lattice is less stochastic. This may be explained in the following way: each particle in the triangular lattice interacts with six neighbors, and consequently is in a steeper potential well. This in turn produces a change in the spectrum of frequencies: in fact, we checked numerically that frequencies in the triangular case are sensibly higher than in the square case. But, as we have seen in the preceding sections, higher frequencies give rise to higher thresholds, and higher thresholds to lower stochasticity. So these experimental results are coherent with the preceding ones.[19]

VI. DISCUSSION

In this section we add some remarks on our results and make a comparison with other related papers.

We have determined the different stochasticity thresholds by exciting in each experiment a given group of modes. One could wonder whether these thresholds hold their meaning and their values when more groups are excited at the same time. To answer this question, we performed an experiment by exciting two groups of modes (4 and 6) in the square cell lattice with $L=6$. The energy given to each of the two groups was lower than the corresponding λ threshold, while the total energy was higher than the λ thresholds of both groups. With this initial condition, both excited groups exhibited a behavior typical for the ordered region. The values of λ found for the two groups, although higher than the values found by exciting separately each group, were significantly below the value $\frac{1}{2}$. We therefore argued that the stochasticity thresholds for the different modes persist for more general initial conditions, although their values may change slightly.

A second point we want to discuss is our choice of the energy per initially excited mode $\bar{e}=E/2L$ as the physically significant energy in determining the λ and μ thresholds (see Sec. IV). As already seen, with this choice the curves for these thresholds, in the cases $L=6$ and 8, overlap significantly (see Fig. 2). This would not happen if one would consider either the total energy (E) or the energy per degree of freedom ($e=E/2L^2$). In other words, the total energy E must be scaled with the factor $1/L$ if one wants to put in evidence the characteristic properties of the system which are independent of N (i.e., the thermodynamic limit). However, in the square cell lattice L not only is proportional to the number of modes in each group ($2L$) but is also the number of different groups of the system. Thus, the question may be raised if the degree of stochasticity of the system, at a given total energy, is related to the number of modes in the excited group or to the number of groups of modes. A way to answer this question could be the following: one can perform an experiment analogous to ours on a suitable lattice, the normal modes of which are divided into groups of different multiplicities; in this case the scale factor we would use would be different for different groups. If our choice of the scaling factor is the correct one, the stochasticity thresholds should be regular functions of the frequency, as in the paper at hand. An example of such a lattice is simply a rectangular square cell lattice at zero pressure.

Finally, we compare our results for the stochasticity thresholds with those of two related papers.[8,10] In Ref. 8 a stochasticity threshold was computed for one-dimensional Lennard-Jones systems with 20 and 100 particles. This threshold is very similar in definition to our λ threshold, and has been found to be practically independent of the number of particles. Moreover, the numerical values of the threshold, transformed to our units, are very close to our values at corresponding frequencies. This agreement between the results in one and two dimensions seems to us very relevant, and suggests the existence of an analogous phenomenon also in three dimensions. We want also to stress that the numerical values of this stochasticity threshold fall in an energy region (around 0.1ϵ) which is physically significant.

In Ref. 10 the low-energy behavior of a two-dimensional Lennard-Jones square cell lattice, with next-nearest-neighbor interaction, has been studied. They considered systems up to 50 degrees of freedom; their results are in qualitative agreement with ours. A quantitative comparison is not possible because of the difference in the computed quantities. Anyhow, we want to comment on one conclusion there drawn, namely that the stochasticity threshold diminishes when passing from one to two dimensions. A possible explanation of this fact is the following. The inclusion, in two dimensions, of the interaction with the next-nearest neighbors (when $d=r_0$) makes the lattice "softer," i.e., lowers the frequency spectrum. We have checked this by numerically computing the frequencies in lattices of different sizes.[20] Now, as shown in the present work, a lower frequency corresponds to a lower stochasticity threshold. We believe that their conclusion is due to the comparison between lattices with different frequency spectra.

VII. CONCLUSIONS

The main conclusions of the present work are the following.

(i) A two-dimensional Lennard-Jones system, when its energy is raised above the minimum, exhibits a stochastic transition. Two criteria of stochasticity lead to two different thresholds, λ and μ, which bound a region of intermediate behavior.

(ii) The two energy thresholds increase, in general, with the frequency of the initially excited normal modes. Anomalies in this behavior are due to the presence of resonances between modes.

(iii) The values of λ and μ thresholds seem to be roughly constant when the number of degrees of freedom increases, with possible exceptions corresponding to the anomalies just mentioned; i.e., these thresholds seem not to vanish in the thermodynamic limit, in agreement with the behavior of one-dimensional LJ systems. This

agreement is also quantitative, at least for the λ threshold.

(iv) Even a system below the lower threshold exhibits a certain amount of stochasticity, due to the energy exchange among modes of close frequencies.

(v) The estimated values of the threshold energies are in a physically significant region; therefore, a relevance of the stochastic transition to the behavior of real systems can be expected. In particular, the existence of the lower stochasticity threshold λ, which increases generally with the frequency of the excited modes and does not vanish in the thermodynamic limit, is compatible with the hypothesis, quoted in the Introduction, about a relation between this phenomenon and the zero-point energy.

ACKNOWLEDGMENT

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APPENDIX

We give here a short description of the algorithm we have used to integrate numerically the equations of motion and to compute the LCE χ^*. We restrict ourselves to the case of a single variable x, with equation of motion of the form

$$\ddot{x}=f(x). \tag{A1}$$

The generalization to a system of equations for many variables is straightforward.

Let τ be a small interval of time. By means of a Taylor expansion, we can write

$$\begin{aligned} x(t+\tau)&=x(t)+\tau\dot{x}(t)+\tfrac{1}{2}\tau^2\ddot{x}(t)+\tfrac{1}{6}\tau^3\dddot{x}(t)+O(\tau^4),\\ x(t-\tau)&=x(t)-\tau\dot{x}(t)+\tfrac{1}{2}\tau^2\ddot{x}(t)-\tfrac{1}{6}\tau^3\dddot{x}(t)+O(\tau^4). \end{aligned} \tag{A2}$$

Using Eq. (A1) in the sum of Eqs. (A2) one obtains

$$x(t+\tau)+x(t-\tau)=2x(t)+\tau^2 f(x(t))+O(\tau^4);$$

the $O(\tau^4)$ term is neglected. By introducing the notations

$$x_n=x(n\tau),$$

$$D_n=x_{n+1}-x_n,$$

one finally obtains the very simple recursive relations

$$x_{n+1}=x_n+D_n,$$

$$D_{n+1}=D_n+\tau^2 f(x_{n+1}),\quad n=0,1,\ldots.$$

x_0 is the initial point, D_0 is found by an ordinary Taylor expansion. Velocities do not enter in the algorithm, except for the first Taylor expansion, necessary to compute D_0. When needed, they can be obtained by means of the relation $v(n\tau)=(D_n+D_{n-1})/2\tau+O(\tau^2)$, as is immediately obtained by taking the difference between Eqs. (A2). The velocity is therefore less accurate than the position, but this does not influence the dynamics which are computed correctly up to the third order in τ. (We do not enter here into the problem of the accuracy for long time calculations. For a discussion, see Ref. 21.) This integration scheme is in common use in the field of molecular dynamics. Practically the same method can be used for the integration of the variational equation (5), which can be easily rewritten as a second-order equation for the position components of $\zeta(t)$. There is, however, one technical problem: when $\chi^*>0$, then $\|\zeta(t)\|$ diverges exponentially with time, and a computer overflow is rapidly found. This difficulty is easily overcome: at arbitrary instants of time t_i, one can divide each component of $\zeta(t)$ by a coefficient C_i, for example, the one necessary to reset $\|\zeta(t)\|$ equal to 1. The computation goes on after each reduction with the scaled $\zeta(t)$. Due to the linearity of the variational equation one has after the kth reduction to unity,

$$\ln\|\zeta(t)\|=\sum_{i=1}^{k}\ln C_i,$$

where, of course, $\zeta(t)$ is the unscaled vector. This is sufficient to compute χ^*. For more details about the computation of LCE's in the general case, see Ref. 22.

Most of our computations were performed with the time step $\tau=0.05$. The integration of a typical orbit up to time 10^4, with the $L=6$ lattice, requires about 500 sec on the CDC-CY76 computer. About 30% of this time is spent in the integration of the variational equation.

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[16]In principle, certain energy exchanges among modes of opposite parity should be forbidden, because of the symmetry of the initial conditions. As a matter of fact, such limitation does not exist in the present case because of the errors involved in the numerical calculations, which break this symmetry.
[17]In general, if the excited group is resonant with another group, the transfer of energy to the latter is competitive with the transfer to the contiguous groups. For example, this is the case of groups 1 and 5, which are resonant with ratio $\frac{1}{4}$ (within 1%).
[18]It is evident that this conclusion is not affected by the particular criterion ($\lambda=\frac{1}{2}$ or $\mu=\frac{1}{2}$) chosen to determine the threshold energies, although a different choice would slightly shift the curves in Fig. 2.
[19]By comparing the lines $\chi^*(e)$ for the two lattices with $N=72$ in Fig. 5, one observes that the ratio of the slopes is equal to 1.5. As each particle in a triangular cell lattice interacts with six neighbors, while each particle in a square cell lattice interacts with four neighbors, 1.5 is also the ratio of the depths of the potential wells in the two cases. We think that this point should be further analyzed.
[20]When the system considered in Ref. 10 reaches the size of 7×7 particles, some frequencies become even imaginary, that is, the configuration with all particles at rest at the lattice sites becomes unstable.
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