Anharmonic Chain with Lennard-Jones Interaction

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The classical equations of motion of a one-dimensional, finite, anharmonic lattice, with nearest-neighbor interaction of the Lennard-Jones type, are investigated numerically. The results indicate that when the vibrational energy per particle is equal to or greater than 2–3% of the depth of the potential well, one has, in time average, equipartition of the energy among the normal modes, thus giving a hint toward ergodicity of the system at sufficiently high energy. For lower energies one finds recurrent motions if initially only one normal mode is excited in analogy with a famous result due to Fermi, Pasta, and Ulam. In this case the numerical results are consistent both with the existence of a long relaxation time and with a lack of ergodicity for low energies.

INTRODUCTION

In recent years the problem originally considered by Fermi, Pasta, and Ulam (FPU),[1] i.e., the solution of the classical equations of motion of a one-dimensional finite chain of particles with forces between neighbors containing nonlinear terms has been extensively studied.[2] The surprising result obtained by FPU is the lack of equipartition of energy in time average among the normal modes of the system. Whether this is due to the relatively short time over which the time averages are computed or to an intrinsic nonergodicity of the system is up to now still an open question, notwithstanding the progress and the new insights made in the problem by many authors.

The most interesting advances are concerned with systems which are not exactly those considered by FPU. In particular, Toda[3] has studied a model, with exponential interaction, for which exact solutions can be given in closed form, representing states for which equipartition of energy among the normal modes is never attained in time average. However, no conclusion can be drawn from this regarding the ergodicity properties of the system. In fact, the measure of the set of the soliton states on the energy surface is zero.[4]

On the other hand, Kruskal and Zabusky,[5] approximating the one-dimensional chain by means of a continuum – in which case one is led, corresponding to the Fermi model, to the well-known Korteweg–De Vries equation – have shown that their model has solitonlike solutions, but the properties of these solutions represent those of the discrete model only for finite and not too long intervals of time. Finally, in a very interesting paper, Northcote and Potts[6] have proved that if the nonlinearity is represented by a hard-core interaction, there is, in time average, equipartition of energy among the normal modes, as predicted by standard statistical mechanics.

In the present paper a one-dimensional chain of particles with nearest-neighbor interaction is studied numerically; the interaction potential is of the Lennard-Jones (LJ) type. The numerical results indicate that there is equipartition of energy in time average among the normal modes only if the energy per particle is of the order of, or higher than, a few percent of the depth of the LJ potential. At energies lower than 1% of the depth of the LJ potential, one obtains again results similar to those of FPU, which was to be expected since in this range of energies the poten-

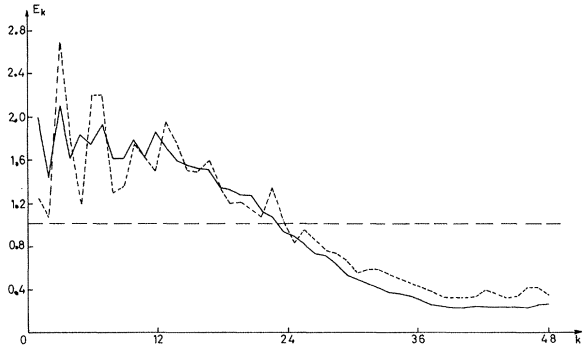

FIG. 1. Particle number $N=48$; total energy $E=50$; initial condition: first normal mode excited; solid line: time average on 116 longest cycles; dotted line: time average on the last 19.4 cycles. From Figs. 1–4 it is evident that, as the total energy increases, there is an increasing tendency towards energy equipartition, in time average, among the normal modes. From Figs. 1 and 2 one sees that the partial average, over the last 19.4 longest cycles, of the energy of the normal modes is nearer the equipartition than the general average.

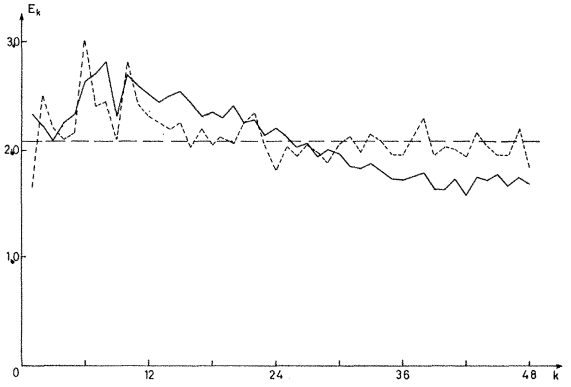

FIG. 2. $N=48$; $E=100$; initial condition, as before; solid line: time average on 116 longest cycles: dotted line: time average on the last 19.4 cycles.

tial can be reasonably approximated by quadratic and cubic terms.

Furthermore, if one *assumes* that the temperature of the system is proportional to the time average of the kinetic energy of one particle, one obtains the well-known results of the classical ensemble theory concerning the specific heats.

DESCRIPTION OF MODEL

We shall study the classical motion of a one-dimensional chain of particles with nearest-neighbor interaction and fixed ends; the interaction potential is the LJ potential:

$$V=4\epsilon[(\sigma/R)^{12}-(\sigma/R)^{6}]\,, \qquad (1)$$

where $\epsilon=120\ ^{\circ}\mathrm{K}$, $\sigma=3.4\times10^{-8}$ cm, and the mass M of the interacting particles is equal to 6.4×10^{-23} g. The model represents a chain of argon atoms.

It is convenient to introduce a new system of units in which the unit mass, the unit time, and the unit length have the following values: 6.4×10^{-23} g, 10^{-11} sec, 3.4×10^{-3} cm. In these new units the Boltzmann constant is equal to 0.23 and,

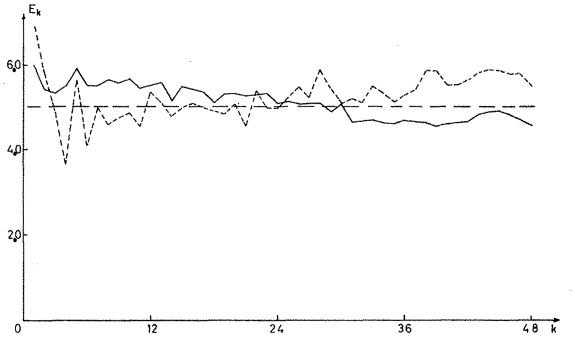

FIG. 3. $N=48$; $E=240$; initial condition: as before; solid line: time average on 116 longest cycles; dotted line: time average on the last 19.4 cycles.

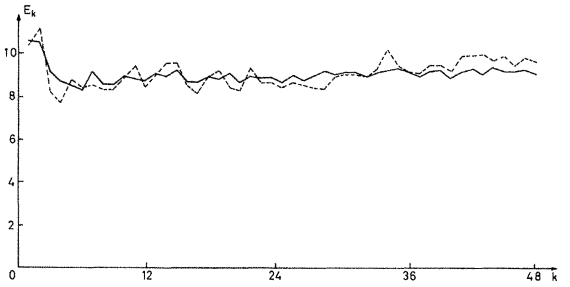

FIG. 4. $N=48$; $E=400$; initial condition: as before; solid line: time average on 116 longest cycles; dotted line: time average on the last 19.4 cycles.

if one normalizes to zero the minimum of the potential energy, the interaction potential between two particles can be written in the following way:

$$V=-110\,(1-1/x^{6})(1/x^{6})+27.5\,, \qquad (2)$$

x being the distance between two particles. The equilibrium distance is $x_{eq}=2^{1/6}$. Now if y_i is the displacement of the ith particle from its equilibrium position, the equations of motion of the N particles of the one-dimensional chain can be written

$$\ddot{y}_i=-660\left(1-\frac{2}{(2^{1/6}+y_i-y_{i-1})^{6}}\right)\frac{1}{(2^{1/6}+y_i-y_{i-1})^{7}}$$

$$+660\left(1-\frac{2}{(2^{1/6}+y_{i+1}-y_i)^{6}}\right)\frac{1}{(2^{1/6}+y_{i+1}-y_i)^{7}}$$

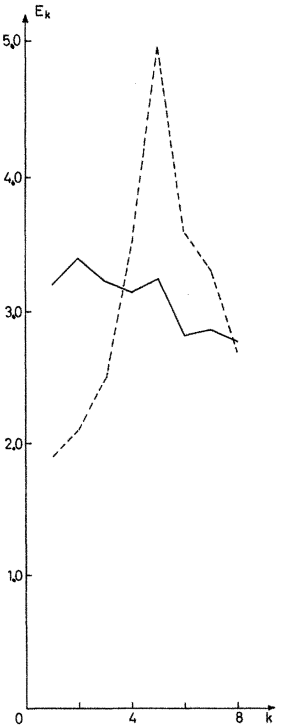

FIG. 5. $N=8$; $E=24$; initial condition: first normal mode excited; solid line: time average on 1917 longest cycles; dotted line: time average on the last 383 cycles. Figures 5–12 show that there is no appreciable increase in the tendency towards equipartition, in time average, when the particle number increases.

FIG. 6. $N=11$; $E=11$; initial condition: first normal mode excited; solid line: time average on 1441 longest cycles; dotted line: time average on the last 288 cycles.

$$(i=1,2,\ldots,N)\,. \qquad (3)$$

In the harmonic approximation the equations of motion are

$$\ddot{y}_i=-(1980/2^{1/3})(2y_i-y_{i-1}-y_{i+1})$$

$$(i=1,2,\ldots,N)\,.$$

It is convenient to introduce the normal modes by means of the relations

$$a_k=\left(\frac{2}{N_1}\right)^{1/2}\sum_{i=1}^{N} y_i \sin\frac{ik\pi}{N_1}$$

$$(N_1=N+1,\quad k=1,2,\ldots,N)\,.$$

FIG. 7. $N=11$; $E=33$; initial condition: first normal mode excited; solid line: time average on 1441 longest cycles; dotted line: time average on the last 288 cycles.

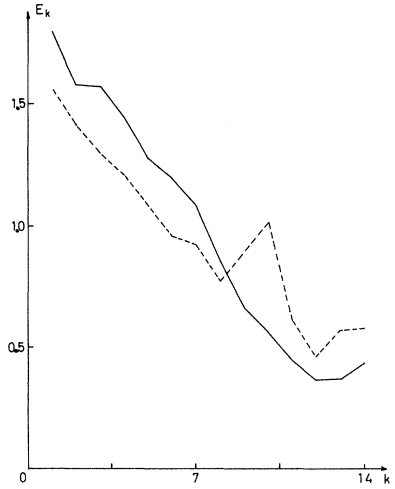

FIG. 8. $N=14$; $E=14$; initial condition: first normal mode excited; solid line: time average on 1154 longest cycles; dotted line: time average on the last 235 cycles.

The total energy of the kth normal mode, in the harmonic approximation, is given by

$$E_k=\tfrac{1}{2}\dot{a}_k^2+1980\times 2^{2/3}a_k^2\sin^2(\pi k/2N_1)\,,$$

from which one easily gets the frequency of the mode. In our units the longest period of the unperturbed normal modes is approximately $\frac{1}{20}N_1$, while in real time units this period is equal to $5\times10^{-13}\,N_1$ sec.

DISCUSSION OF NUMERICAL SOLUTION

Equation (3) has been integrated numerically. In the computational program the time average of the energy of every normal mode was evaluated

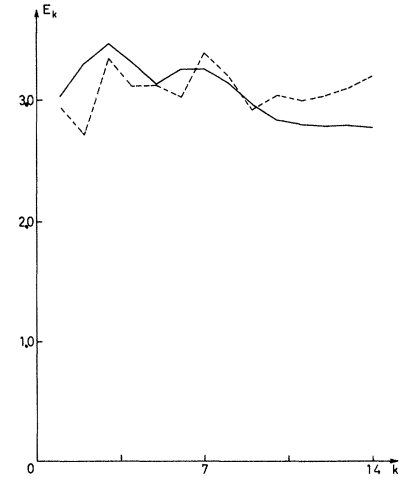

FIG. 9. $N=14$; $E=42$; initial condition: first normal mode excited; solid line: time average on 1154 longest cycles; dotted line: time average on the last 231 cycles.

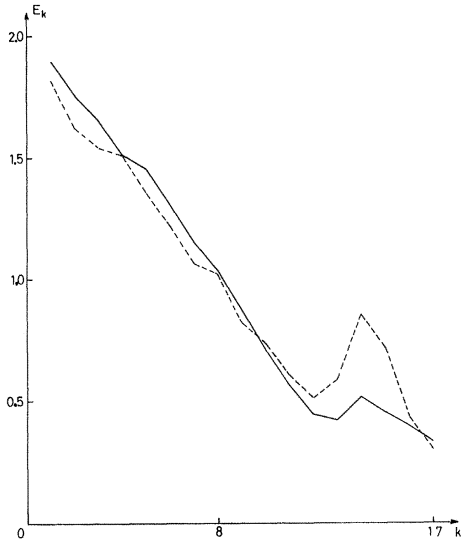

FIG. 10. $N=17$; $E=17$; initial condition: first normal mode excited; solid line: time average on 962 longest cycles; dotted line: time average on the last 192 cycles.

together with the time average of the kinetic energy of each particle and of the potential energy of each normal mode. The time averages were evaluated both on the complete interval of time over which the system evolved and on partial intervals of time in which the complete interval could be divided. The initial conditions of the system were such that one or more normal modes were excited. The energy was equally divided among the excited normal modes, and the positions and velocities of the particles were chosen in a random way, consistently with the initial energy distribution.

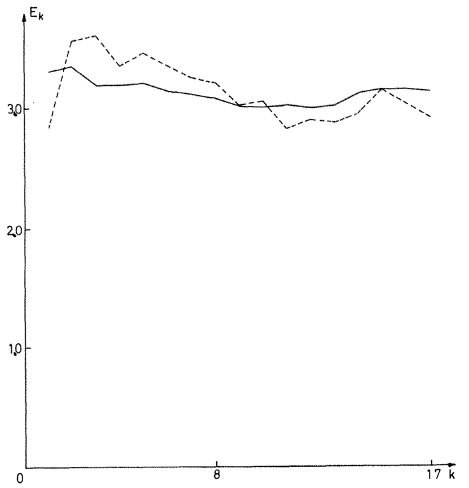

FIG. 11. $N=17$; $E=52$; initial condition: first normal mode excited; solid line: time average on 962 longest cycles; dotted line: time average on 192 cycles.

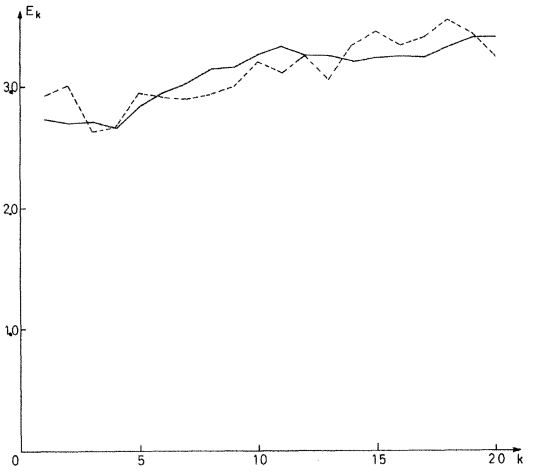

FIG. 12. $N=20$; $E=60$; initial condition: first normal mode excited; solid line: time average on 825 longest cycles; dotted line: time average on the last 165 cycles.

The accuracy of the computation was tested in different ways. The simplest one is based on the conservation of the energy of the system, which was satisfied even in the longest runs within two or three parts in 10^4. Direct control of the accuracy of the positions and velocities of the particles was obtained in two ways: (i) The equations of motion were solved in the case of harmonic forces, and the numerical solutions compared with the exact ones. (ii) The use of time reversibility of the system allowed us to compare the direct motion and its time reversal. In both cases the accuracy, insofar as coordinates and velocities were concerned, has been within several percent on the longest times over which the system was studied. The accuracy was by far greater for the more significant quantities, such as the time averages, both partial and total, of the total energy of the single modes.

Since it is important, in order to study the equilibrium properties of the system, to follow its motion over long times, great effort was spent to make the calculation as fast as possible in order to minimize the computer time. This could be obtained by reading the interaction force from a table calculated in advance, in which the force was evaluated at 25 000 points on the range 0.5–2.5; for distances different from those given by the mesh points, the forces were linearly interpolated.

The computation was performed in such a way that the elementary step of integration was taken to be equal to 1. This avoided all multiplications; therefore only sums were involved in the elementary step. To give an idea of the computer time we mention that a typical calculation concerning a system of 20 particles, whose evolution was followed

for 825 longest periods of the unperturbed system, took 16 min on a 360/65 IBM.

DISCUSSION OF RESULTS

It follows from classical statistical mechanics that the microcanonical averages of the kinetic energy of the particles and of the normal modes are all equal (equipartition theorem of the kinetic energy). One of the aims of our calculations was to verify whether this holds true on a purely dynamical basis. Of course this would not prove the ergodicity (or the nonergodicity) of the model, but in any case it would be a dynamical justification (or a dynamical disproof) of many standard results of statistical mechanics.

From our computations it follows that the time averages of the kinetic energies *of the particles* have the same value (within a few parts in 10^3). Even for not too long time evolutions (of the order of 50 longest periods of the harmonic unperturbed system), they have the same value within a few parts in 10^2.

Since all our results show that the average potential energy, *for the* LJ *potential*, practically coincides with the average kinetic energy, it follows that the total energy of the system is proportional to the average kinetic energy of a particle. This result is more accurate at low energies, while at high energies, of the order of $10N$, it is true within 4–5%. If one assumes that the temperature is proportional to the average kinetic energy of a particle, one obtains the classical result that the specific heats are constants.

Insofar as the normal modes are concerned, the discussion is somewhat more complex and a more detailed discussion is required.

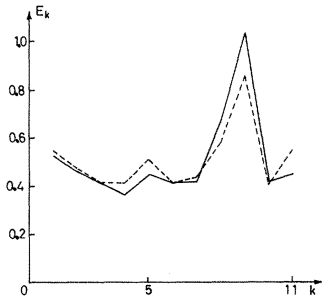

FIG. 13. $N=11$; $E=5.6$; initial condition: equidistribution of the energy among the normal modes; solid line: time average on 1441 longest cycles; dotted line: time average on the last 288 cycles. From Figs. 13–16 one sees that, when the energy is initially equidistributed among the normal modes, there are random fluctuations of the average energies of the normal modes. These fluctuations become less evident when the total energy E increases.

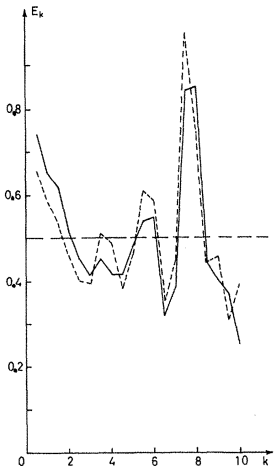

FIG. 14. $N=20$; $E=10$; initial condition: equidistribution of the energy among the normal modes.

TIME BEHAVIOR OF NORMAL MODES

We have found it convenient to study first of all the behavior of systems of very few particles for a very long interval of time. This study was useful for identifying in systems of many particles those properties which are common to systems of any number of particles. In this case the computation was continued until the average values of the energies of the normal modes were constant in time. This was not practically feasible for many particles but the long time properties of the systems of few particles were of great help in interpreting the results obtained in the case of many particles.

The case $N=2$ was studied (as were the other cases) for a wide range of initial energies starting from $E=0.01$ up to $E=24$, i.e., to an energy very near the depth of the potential well, which is, in our units, equal to 27.5. The initial conditions were chosen in such a way that either a single normal mode only was excited, or the energy was equally shared between the two normal modes. In both cases the time averages of the energy of the normal modes reach very soon an asymptotic value which remains unaltered in the time evolution, within the numerical error. The partial averages over sufficiently long time intervals are also independent of the time origin.

The exchanges of energy between the normal modes become strong and fast when the energy of the system approaches the value 1. In this case, if initially only one normal mode is excited, the other can acquire for short times even a large fraction of the energy of the system. Such a fraction grows with the energy and can reach practically the value 1 for energies equal to 24. However, the initially excited mode remains always predominant in time average and tends to keep practically the whole energy of the system for a total energy not far from unity, and a large fraction of it, well

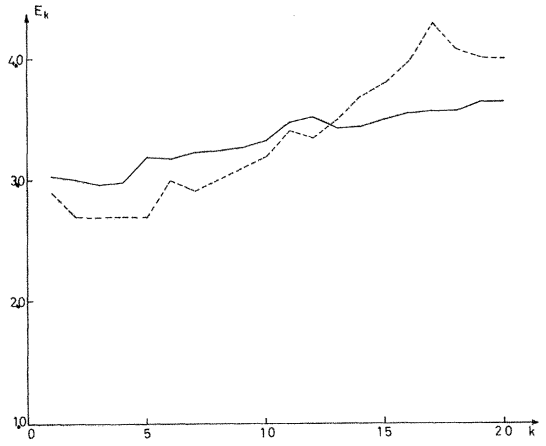

FIG. 15. $N=20$; $E=64$; initial condition: equidistribution of the energy among the normal modes: solid line: time average on 1101 longest cycles; dotted line: time average on the last 220 cycles.

above 50%, when the energy is as large as 24. If one starts instead from an initial state in which the energy is equally shared between the two modes, one gets, from a wide statistics, the following results: Only in a few cases is the equal sharing conserved in time average within several percent; in all the others the distribution of the averages depends on the initial positions and velocities of the particles and in some cases the lower mode prevails in time average, in others the higher. However, averaging over the initial conditions gives equipartition of energy as expected from the microcanonical theory of statistical mechanics.

The numerical calculations show that the system is recurrent within the limits of the numerical error. In one period of recurrence the system does not run through the whole energy surface, as is proved by the fact that the time averages of the energy of the modes are far from the equipartiton. At this point one can make two conjectures that are both consistent with the numerical results. (i) The system is ergodic and its trajectory changes only slightly from one quasiperiod to the other. In such a case the time that the system would require to go through the whole energy surface would be very large. (ii) The system is nonergodic, and it runs only through a part of the energy surface depending on the initial conditions. This second conjecture is supported to a certain extent by the fact

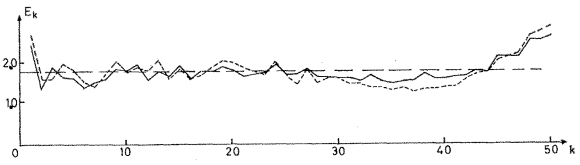

FIG. 16. $N=50$; $E=80$; initial condition: equidistribution of the energy among the normal modes.

that the cases we have studied can be divided into groups such that within each group the time averages of the energies of the normal modes are the same. This conjecture seems to us to be the most probable one and is consistent with the existence of constants of the motion other than the energy.

The case $N=4$ is completely similar to $N=2$. The motion is clearly recurrent within the numerical error. The period of recurrence, when only one normal mode is excited, is shorter than when all the normal modes are excited; such a recurrence remains evident up to $N=20$.

However, when one passes from $N=4$ to $N=8$ one observes an important change in the properties of the system. While for 2 or 4 particles, starting from an initial condition in which only one normal mode is excited, one never reaches a practical equipartition of the energy, for $N=8$ or larger ($N=8, 11, 14, 17, 20, 40, 50, 100$) one reaches, in time average, a practical equipartition of the energy among the normal modes when the energy per particle is near or greater than 1.

When the number of particles becomes greater (e.g., $N=20$), the behavior of the system becomes more complex and the recurrence of the motion is still present only when one normal mode is excited with total energy lower than N. In the other cases (high energy of excitation and only one normal mode excited, or all the normal modes excited), the recurrence of the motion is no longer evident; one has only some indications that it might still be present, but with a period much larger than in the case of few particles. For $N=20, 50, 100$, one has, in time average, equipartition of the energy among the normal modes for total energies of the order of N or higher, when in the initial state either one mode or all the initial modes are excited.

For lower energies (of the order of $\frac{1}{10}N$ or

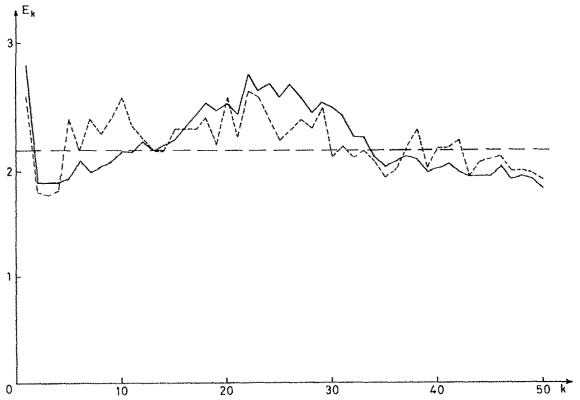

FIG. 17. $N=50$; $E=100$; initial condition: excitation of the 25th and 26th modes; solid line: time average on 77 longest cycles; dotted line: time average on the last 19.4 cycles. The behavior of the system is practically the same when only the first mode is initially excited.

smaller), when in the initial state one normal mode is excited, equipartition of the energy is never achieved. On the contrary, in this case, when in the initial state the energy is equally distributed among the normal modes, one has in general, during the motion, a nonequipartition in time average. However, the modes with greater energy are scattered at random over the whole spectrum of the normal modes, and one has a coarse-grained equipartition. Of the many cases studied we present in Figs. 1–17 a selection which illustrates some typical behaviors discussed above.

CONCLUSIONS

The most important conclusion of this paper is that when the energy of vibration per particle is equal to or greater than 2 or 3% of depth of the potential well and the number of particles is sufficiently large, one has, in time average, equipartition of the energy among the normal modes, in spite of the fact that there is no evidence for the system to be ergodic. For lower energies one has recurrent motions if, in the initial condition, only one normal mode is excited, as found by FPU. In this respect one must remark two facts: The times over which the system is studied, i.e., some thousands of longest periods of the unperturbed system, are in effect rather short. A thousand longest periods of the system amounts to $5\times10^{-10}N$ sec, and that means that for 20–100 atoms, if the energy is sufficiently great, one reaches equipartiton in 10^{-8} sec.

The practical difficulty of keeping the numerical error small over times longer, for some order of magnitudes, than those over which the system has been studied makes it difficult to reach numerical conclusions on the equipartition of the energy for low excitation of the system. However, in such a case if the initial state is one of equal distribution of the energy, such a state is macroscopically conserved in time average, the more excited modes being distributed randomly over the whole frequency spectrum.

We may conclude by saying that, in the case of very low total energies, the relaxation mechanism towards the standard Boltzmann distribution of the normal modes might act so slowly that the coupling of the system with a thermal bath could be very important in determining the approach of the model towards such a distribution.

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[1]E. Fermi, J. Pasta, and S. Ulam, Los Alamos Scientific Laboratory Report No. 1940, 1955 (unpublished).

[2]The literature on the FPU model is very large. We shall mention only the papers which are most relevant to our analysis.

[3]M. Toda, J. Phys. Soc. Japan 23, 501 (1967).

[4]M. Toda (private communication).

[5]M. D. Kruskal, and N. J. Zabusky, Phys. Rev. Letters 15, 240 (1965); N. J. Zabusky, Phys. Rev. 168, 124 (1968).

[6]R. S. Northcote and R. B. Potts, J. Math Phys. 5, 383 (1964).

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Scattering Probability for Fast Test Particles in a Plasma*

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An effective total cross section is calculated for elastic scattering of a monoenergetic beam of test particles in a plasma of arbitrary velocity distribution. Closed-form solutions are obtained for the special case of Maxwellian field particles taking into account small-angle scattering. The result are compared with those obtained using the Debye cutoff technique, and it is shown that such an arbitrary cutoff can lead to erroneous results in the effective cross section and can lead to different conclusions with regard to the relative importance of plasma ions and electrons in test-particle scattering.

I. INTRODUCTION

Recent feasibility studies[1–4] of possible steady-state thermonuclear reactors have shown the need to investigate in detail the behavior of fast charged particles in energetic plasmas. Such studies are important in calculating the thermalization rates of fast test ions,[1,2] the slowing-down time necessary for these ions to transfer a major fraction of their energy to the plasma,[1] secondary fusion reactions,[3]