Diffusion in a two-dimensional periodic potential

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We report a numerical study of the self-diffusion of a single-point particle in a two-dimensional periodic potential of triangular symmetry. The self-diffusion coefficient is obtained via computer simulations for several values of the particle energy. We find that the self-diffusion process is complicated due to the existence of correlated motions involving two or more cells. A random-walk model which takes into account the effects of correlated motions involving only the nearest-neighbor cells is constructed, and compared with the experimental results.

I. INTRODUCTION

In this paper we present a numerical study of the self-diffusion of a single-point particle in a two-dimensional periodic potential of the following form:

$$V(x,y)=\cos(x+y/\sqrt{3})+\cos(x-y/\sqrt{3}) +\cos(2y/\sqrt{3})\ . \tag{1}$$

The potential $V(x,y)$ defines an infinite lattice of triangular symmetry. The geometry is shown in Fig. 1. Each cell is characterized by a minimum at the center of the cell, maxima at the three corners, and saddle points at the midpoints of the edges. The point particle moves with a constant energy E on this potential surface. If the energy E is less than the saddle-point energy, $V_{\text{saddle}}(=-1.0)$, then the particle is trapped in a single cell. But if the energy E is greater than the saddle-point energy, the particle can make transitions to the adjacent cells and can wander over the entire plane. The dynamical behavior of the system is determined completely by the energy E of the particle. The width W of the saddle boundary available to the particle for exit to another cell is given by

$$W=2\left[\pi-\cos^{-1}\left[\frac{E-1}{2}\right]\right]\ . \tag{2}$$

When the energy E is close to V_{saddle}, W is small compared to the length of an edge of the cell and the particle may spend a long time in each cell before making a transition to the adjacent cell. On the other hand, when E is much larger than V_{saddle}, the particle sees an infinite horizon and may move a long distance without spending much time in any cell. In this paper, we will mainly study the dynamics of the point particle for values of the energy E close to V_{saddle}.

A single-point particle in the periodic potential (1) is a deterministic system. It is of considerable theoretical interest to see if such a simple system can show diffusive behavior. The present dynamical system is a generalization of the periodic Lorentz gas where a single-point particle moves in a triangular array of immobile disc scatterers. For the periodic Lorentz gas, rigorous results of Bunimovich and Sinai[1] show that the self-diffusion coefficient exists in the high-density regime. We are not aware of any such rigorous results for the continuous potential defined by Eq. (1). Since the self-diffusion coefficient D does not exist for the motion of a point particle on a square lattice of potential $\cos(x)+\cos(y)$, the existence of D for the potential (1) is not obvious. When the energy E of the particle is slightly above the saddle-point energy, however, one suspects that the present system will be ergodic and there will be a well-defined diffusion coefficient. Our experimental results support this view. However, there is a threshold energy E_c above which the velocity correlation function undergoes a qualitative change and the diffusion coefficient does not appear to exist. We find that the threshold energy is approximately $E_c\cong-0.4$. The present study is confined to values of the energy E less than E_c.

The motivation for the present study comes partly from the recent work of Machta and Zwanzig[2] (MZ) on the self-diffusion in a periodic Lorentz gas. These authors found that in the high-density regime a simple picture of random walks between triangular trapping regions gives a surprisingly good estimate of the self-diffusion coefficient D. For the present problem, however, the simple random-walk picture breaks down due to correlated re-

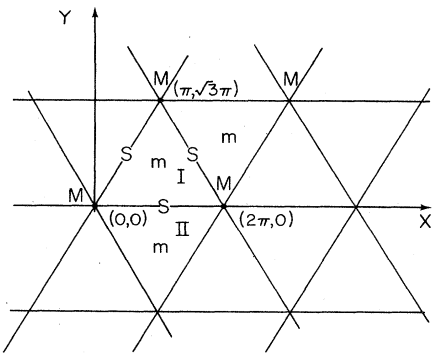

FIG. 1. Geometry of the periodic potential (1). The positions of maxima, minima, and saddle points are denoted by M, m, and S, respectively.

turns of the particle to the initial cell. A heuristic correction of the random-walk model gives reasonable agreement with the simulation results.

The contents of the paper are as follows. In the next section we discuss the computer simulation and present the experimental results. Section III contains a theoretical analysis of the problem. Section IV concludes with a brief discussion.

II. SIMULATION AND RESULTS

The computer simulation of the motion of a point particle on the potential surface given by Eq. (1) was carried out for several values of the energy E of the particle. The classical equations of motion were integrated using Gear's fifth-order predictor-corrector algorithm.[3] The energy of the particle was conserved at least up to five significant digits. The velocity correlation function was calculated as follows. Initially the particle was placed at a random position with random velocities constrained to total energy E. The subsequent motion of the particle was recorded up to a total time of 60 000. The velocity correlation function (VCF) was then computed by taking the standard time average. For lower energies ($E \leq -0.8$), the VCF was computed up to a time of 100, whereas for higher values of E, calculation of the VCF up to a time of 60 was found sufficient. The self-diffusion coefficient was calculated by integrating the velocity correlation function. The whole procedure was repeated three times for each energy to obtain a measure of the reproducibility.

A well-defined self-diffusion coefficient is obtained, within the numerical accuracy, for values of the energy less than a critical value $E_c \cong -0.4$. Above this critical energy, the velocity correlation function undergoes a qualitative change in its long-time behavior, characterized by a much slower decay than the ones observed below E_c. Also, we find that the integral defining the self-diffusion coefficient fails to converge to any well-defined value, in contrast to the situation below E_c. However, we have not carried out a detailed analysis of the crossover behavior. The present study is confined to values of the energy E significantly less than E_c. Figures 2(a)–2(c) show the computed velocity correlation function for three values of the energy. The graphs reveal surprisingly rich structures, similar to the ones observed by MZ in their simulation of the periodic Lorentz gas.

Table I records the values of the self-diffusion coefficient of the point particle for several values of the energy. The error bars in Table I represent the spread in the values obtained in three different runs starting with different initial conditions. We attribute this spread to the finite time averaging of the VCF.

The dynamics underlying the rich structure of the velocity correlation function is best understood by analyzing its Fourier transform. Fourier transform was performed using the IMSL (International Mathematical and Statistical Libraries, Inc.) supplied fast Fourier-transform subroutine FFTRC. A total number of 2048 VCF points was used with a time spacing equal to 0.04. Near a sharp peak in the Fourier spectrum, a direct numerical integration was employed to obtain better resolution in the frequency plane.

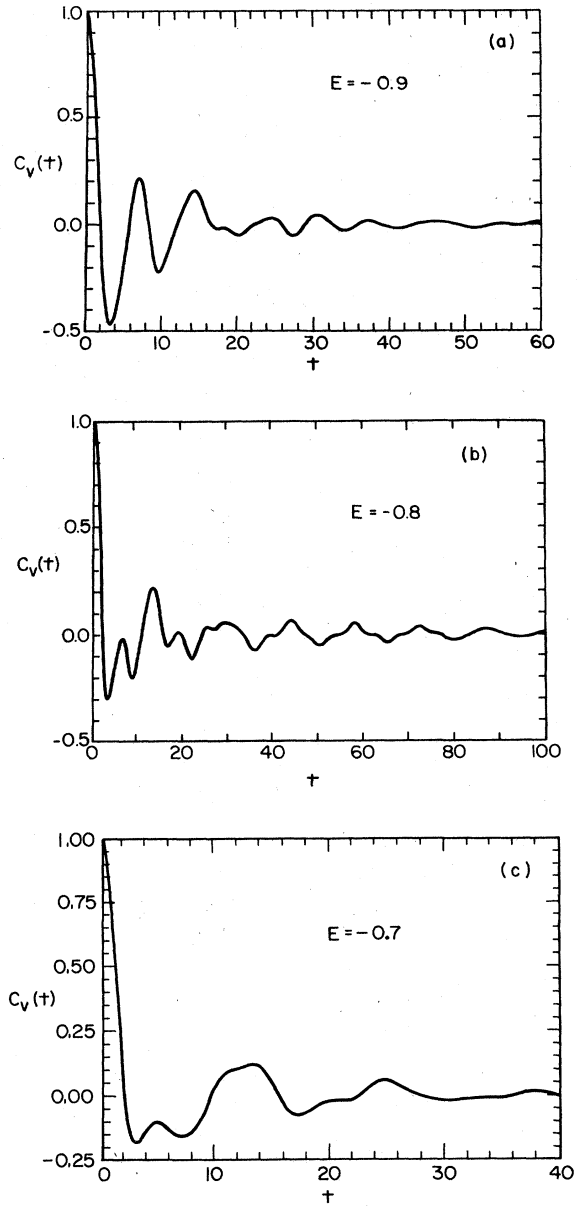

FIG. 2. Velocity correlation function $C_v(t)$ for (a) $E=-0.9$, (b) $E=-0.8$, and (c) $E=-0.7$.

TABLE I. The values of the self-diffusion coefficient D as a function of the energy E as determined from the computer simulation.

E	D^{expt}
−0.95	0.020±0.004
−0.9	0.047±0.006
−0.85	0.10±0.008
−0.8	0.14±0.02
−0.7	0.22±0.01
−0.6	0.31±0.01
−0.5	0.51±0.01

Figures 3(a)—3(c) show the frequency spectrum $C_v(\omega)$ for three values of the particle energy. At low values of E, the spectrum consists of two sharp peaks. The peak at higher frequency occurs always near $\omega=1$. This peak is due to the "trapping" of the particle near the potential minimum at the center of the cell. As expected, this peak becomes weaker as the energy of the particle is increased. The sharp, first peak, however, is somewhat unexpected. The position of this peak, at frequency $\omega_R(E)$, depends weakly on energy. It dominates the dynamics in the intermediate-energy regime ($-0.8 \leq E \leq -0.6$) and has an appreciable effect even at higher energies where the second peak, due to trapping at a cell minimum, disappears.

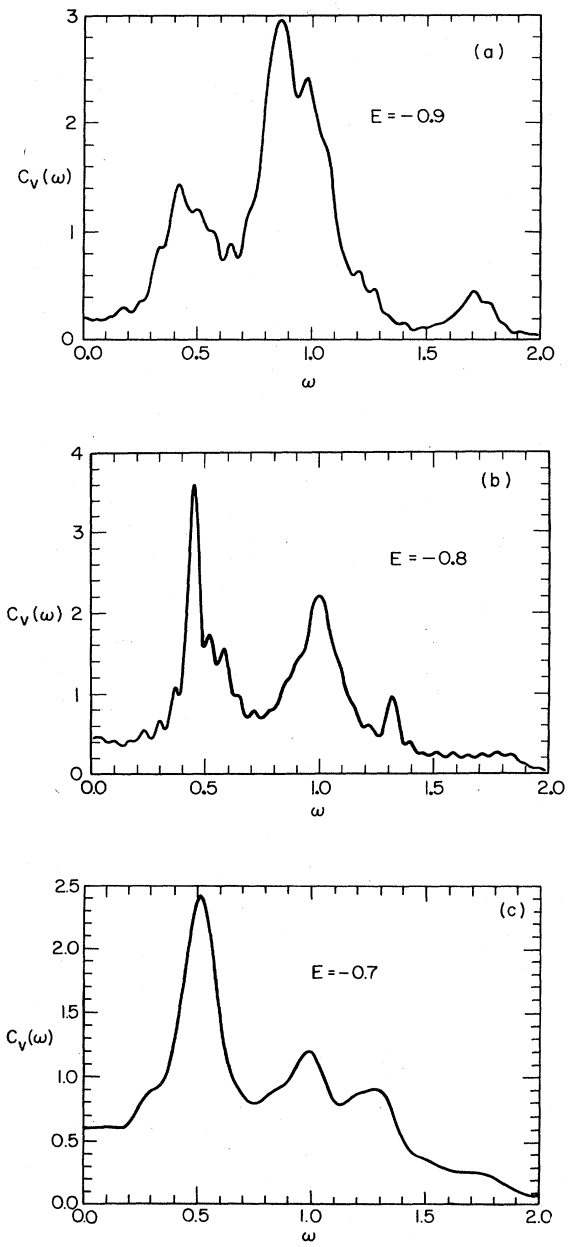

FIG. 3. Fourier spectrum $C_v(\omega)$ of the velocity correlation function for (a) $E=-0.9$, (b) $E=-0.8$, and (c) $E=-0.7$. The smallest ripples may be due to truncation of the Fourier transform.

The origin of the first peak at frequency $\omega_R(E)$ can be traced back to quasiperiodic motions of trajectories moving between any two adjacent cells. A significant number of trajectories, originating in one cell and entering a nearest-neighbor cell at an arbitrary time t_1, return to the original cell during a short-time interval centered around a later time $t_2=t_1+2\pi/\omega_R$. These quasiperiodic trajectories can persist for a rather long time. In the next section, we present a theoretical calculation of ω_R and make the above discussion more quantitative.

III. THEORETICAL ANALYSIS

In the first part of this section we present a theoretical estimate of the characteristic frequency ω_R of correlated returns. In the second part we shall discuss the inadequacy of the simple random-walk model of MZ and construct an *ad hoc* correction to such a model to include the effect of correlated returns.

The frequency $\omega_R(E)$ of the quasiperiodic motion of a point particle between two adjacent cells may be evaluated as follows. Consider a trajectory at $x=\pi$ traveling between the two cells indicated by I and II in Fig. 1. At time $t=0$, the particle enters cell II with an outward velocity normal to the x axis and with a magnitude equal to $\sqrt{2(E+1)}$. We want to calculate the time T_B it takes to return to the original cell. If the correlated return is mainly due to the bouncing back of the particles from the maximum opposite to the exit window between cells I and II, then this time T_B is related to ω_R by

$$\omega_R=\frac{2\pi}{2T_B}=\frac{\pi}{T_B}\ . \tag{3}$$

With the given initial conditions, the classical equations of motion can be integrated to obtain

$$\omega_R=\frac{\pi}{2K(m)}\left[\frac{3}{2\sqrt{1+2\epsilon}}\right]^{1/2}, \tag{4}$$

where $K(m)$ is the standard complete elliptic integral, and

$$\epsilon=E-V_{\text{saddle}}=E+1\ , \tag{5}$$

$$m=\frac{2+\epsilon+2\sqrt{1+2\epsilon}}{4\sqrt{1+2\epsilon}}\ . \tag{6}$$

The return frequency predicted by Eq. (4) is compared in Fig. 4 with the experimental values of the position of the first peak in the frequency spectrum of the VCF. The good agreement confirms that this first peak is mainly due to the quasiperiodic motion between two nearest-neighbor cells.

It is now obvious that the diffusion process in the present system *cannot* be described as an uncorrelated random walk between triangular trapping regions. This is in marked contrast to the situation in the periodic Lorentz gas where the random-walk model works surprisingly well. As pointed out by MZ, the crucial feature of the

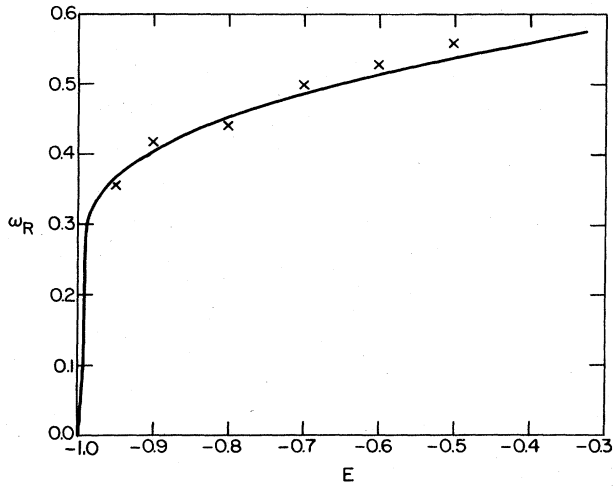

FIG. 4. Theoretical prediction (solid line) for $\omega_R(E)$, given by Eq. (4), is compared with the experimental results (crosses).

periodic Lorentz gas which allows an accurate mapping of the dynamical system into a stochastic model is that the trajectories are strongly mixed within each trapping region in the configuration space. In effect the particle spends sufficient time in each trap to forget its initial conditions. The transitions between traps are, to a good approximation, uncorrelated. The present model does not satisfy the criteria of strong mixing of trajectories in individual trapping regions.

However, we find experimentally well-defined diffusion constants for some values of the particle energy E. Thus, some kind of random-walk description of the diffusion process should hold. The exact formulation of such a description is not simple. We, therefore, choose an approximate procedure to calculate the self-diffusion constant. We assume that the self-diffusion coefficient D is still given by the standard expression for random walks on two-dimensional lattices

$$D=\frac{l^2}{4}k \tag{7}$$

where l is the distance between the traps, given by

$$l=\frac{2\pi}{\sqrt{3}}\ , \tag{8}$$

and k is now interpreted as the rate of "permanent" escape from a trapping region. Thus, the nonreactive trajectories which return to the original cell without getting trapped or "thermalized" in the adjacent cells do not contribute to k. We shall see that there is a clear separation of time scale between the early correlated returns and the later thermalized returns. This separation of time scale will allow us to estimate k unambiguously. In the following we shall consider correlated returns involving two cells only. Higher-order correlations will be neglected.

Following Northrup and Hynes,[4] we write the expression for the rate constant k in the following time correlation form:

$$k=\langle J_e(S)\rangle_c+\int_0^{T_M}dt\langle J_e(S)J_R(S,t)\rangle_c\ , \tag{9}$$

where $J_e(S)$ is the outgoing flux crossing the saddle surface S at time $t=0$. $J_R(S,t)$ is the intrinsically negative flux of particles that return to the original surface at a later time t. The upper limit of integration in the second term is restricted to a maximum time T_M in order to eliminate contribution from long-time "thermalized" returns. The precise value of T_M, as we shall see, is not important due to the separation of time scale mentioned earlier. The brackets $\langle\ \rangle_c$ in Eq. (9) denote a microcanonical averaging over the original cell.

In the absence of correlated returns, the second term on the right-hand side of Eq. (9) is zero and k is equal to $\langle J_e(S)\rangle_c$ which is just the transition-state rate constant. In the case of the periodic Lorentz gas, this term alone was sufficient. But in the present case, the second term plays an important role. It gives a finite negative contribution to the total rate constant k.

Next, we approximate Eq. (9) by

$$k=\langle J_e(S)\rangle_c-\langle J_e(S)\rangle_c\int_0^{T_M}dtP_R(t)\ , \tag{10}$$

where $P_R(t)$ is the conditional probability of return between time t and $t+dt$ given that the particle crossed the saddle surface at $t=0$ to enter the adjacent cell. The integral over $P_R(t)$ is just the fraction of particles that have returned to the original cell within time T_M. So, we rewrite Eq. (10) in the following simple form:

$$k=\langle J_e(S)\rangle_c[1-f(T_M)]\ , \tag{11}$$

where

$$f(T_M)=\int_0^{T_M}dt\,P_R(t) \tag{12}$$

is the fraction returned within T_M. We are still faced with the formidable problem of calculating $P_R(t)$, hence $f(T_M)$. An analytic calculation of $P_R(t)$ appears to be nontrivial. However, it is straightforward to estimate $f(T_M)$ by a computer simulation via microcanonical averaging. We have done this and the behavior of f as a function of the cutoff time T_M for two values of the energy E is shown in Fig. 5. In each case there is a sharp rise

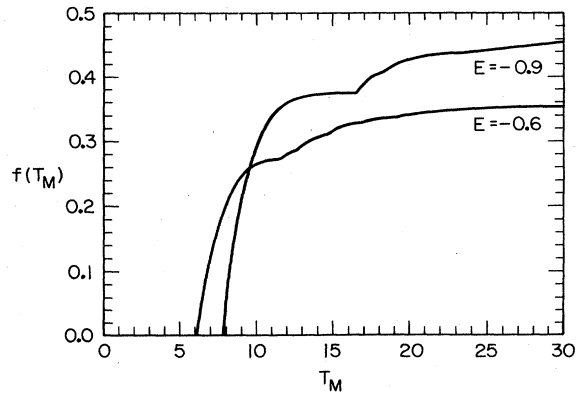

FIG. 5. Numerical values of the function $f(T_M)$, defined by Eq. (12), are plotted against the cutoff time T_M (defined in the text) for two values of the energy E. The values of the energy are labeled on the graph.

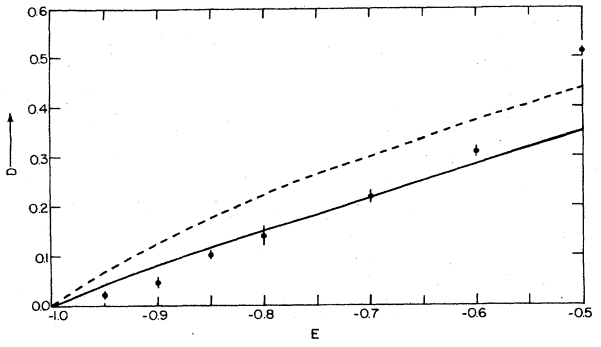

FIG. 6. Theoretical prediction (solid line) for D is compared with the experimental results (solid circles with error bars). We have also plotted the prediction of the uncorrelated random-walk model (dashed line).

in f followed by a well-defined plateau region. The sharp rise is in agreement with our earlier observation that the motion of returning trajectories has an oscillatory character with a well-defined frequency ω_R. The value of f at the plateau is the fraction $f(T_M)$ to be used in Eq. (11). The existence of a plateau, which makes the choice of f unambiguous, is due to the separation of time scales involved between correlated returns and latter "thermalized" returns.

We still have to calculate the transition-state rate $\langle J_e(s)\rangle_c$. This can be done by methods discussed in Refs. 2 and 5. Here we simply quote the final expression

$$\langle J_e(S)\rangle_c = \frac{3\sqrt{2}I}{\pi A} , \tag{13}$$

where

$$I = \int_{\pi - W/2}^{\pi + W/2} dx (E - 2\cos x - 1)^{1/2} , \tag{14a}$$

$$A = \sqrt{3}\pi^2 - 3\int_0^1 dy \cos^{-1}[\alpha(y,E)] + \frac{\sqrt{3}}{2} y_1^2 , \tag{14b}$$

with

$$\alpha(y,E) = \frac{E - \cos(2y/\sqrt{3})}{2\cos(y/\sqrt{3})} , \tag{14c}$$

$$y_1 = \sqrt{3}\cos^{-1}(W/4) . \tag{14d}$$

The self-diffusion coefficient D can be obtained by combining Eqs. (7), (8), (11)—(14).

Figure 6 records the results of this calculation along with the experimental values of D. For comparison, we have also drawn the results of the simple random-walk model without corrections for the correlated returns. As can be seen from the graph, the modified random-walk model provides a good description of the diffusion coefficient in the intermediate-energy regime. However, the agreement for values of E close to V_{saddle} is poor. In this regime, correlated returns which involve more than two cells may be important. The failure of the theoretical prediction for higher values of $E (E > -0.6)$ is due to a breakdown of the random-walk picture; cells no longer act as good traps for the particle.

IV. CONCLUSION

Our motivation for the foregoing study was twofold. Firstly, we wanted to know whether the deterministic motion of a point particle in potential (1) can become diffusive at long times. Since the self-diffusion coefficient does not exist for the motion of a point particle in a square lattice of potential $\cos x + \cos y$, the answer for the present problem was not obvious. Secondly, we wanted to see if the simple picture of diffusion as uncorrelated random walks of the particle between triangular cells works for this system as well.

Our numerical work gives well-defined values of the self-diffusion coefficient for values of the energy below a threshold value E_c. Moreover, we find that the velocity correlation function and the self-diffusion coefficient have some new features that distinguish the present system from the periodic Lorentz gas.

The breakdown of the uncorrelated random-walk model of Machta and Zwanzig is unfortunate but not surprising. In some realistic situations the *details* of the potential play an important role.

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