Diffusion-Entropy Scaling in a Deterministic Hamiltonian System

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Abstract

We present a microscopic derivation of an exponential scaling relation between diffusion and entropy. To test its validity, we study three deterministic systems, (a) the motion of a single point particle with constant energy in two-dimensional periodic potential energy landscape, (b) the same in regular Lorentz gas and (c) motion among the boxes with small apertures. We compute the self-diffusion coefficient of the particle by computer simulations and entropy by quadrature using Boltzmann’s formula. While diffusion is found to exhibit an exponential entropic dependence over a wide range, we find a crossover at energies just above the saddle, due to correlated motions. We explore the relation between the Sinai entropy obtained via Lyapunov exponent and the diffusion coefficient.
I. Introduction

In nature, we often find a one-to-one relation between diffusion coefficient (D) and noise, the latter quantified by a friction term, $\zeta$, via the fluctuation-dissipation theorem. The relationship between them is embodied in the well-known Einstein's relation $D = \frac{k_B T}{\zeta}$.\[1\] This is an exact relation and has found wide use in the liquid state dynamics,\[2\] where the friction is often found to be proportional to the viscosity of the medium. Apart from these stochastic or noisy systems, there has also been keen interest on diffusion in simple deterministic Hamiltonian systems that can exhibit random motions and can become chaotic even in the absence of noise.\[3–5\] In these systems, transport coefficients, particularly diffusion, can be controlled by the characteristics of the potential energy surface. Several works have been dedicated in search for the origin of the transport coefficients like diffusion in these deterministic systems.\[6–8\] We refer to the seminal works by Buminovich-Sinai \[3\] and Machta and Zwanzig.\[4\]

A related, highly discussed and debated issue is the relationship between diffusion (D) and entropy (S). The latter is often invoked to explain temperature dependence of diffusion in strongly correlated systems, like dense liquids and glassy systems.\[2\] At a fundamental level, such a relation is intriguing because while entropy is a logarithmic measure of phase space, diffusion gives the rate of exploration of the configuration space. Thus, the presence of diffusion is regarded as the signature of ergodicity of the system. Two well-known universal relations between D and S are found in the literature. First one is the well-known Adam-Gibbs relation \[9,10\] given by $D = Ae^{\frac{S_c}{T S_c}}$ where $S_c$ represents configurational entropy per particle of the system at a temperature $T$; A and B are two arbitrary scaling constants. Configurational entropy can be determined by subtracting vibrational entropy per particle from the total entropy per particle of the system i.e., $S_c(T) = S(T) - S_{\text{vib}}(T)$. While
this famous relation is found to hold well at a low temperature near the glass transition, its validity at higher temperatures has been questioned.[11–13] The other relationship between entropy and diffusion was proposed by Rosenfeld based on the previous simulation works for the transport coefficients of a wide variety of systems [14] and is given by [Eq.1].

\[ D^* = a \exp\left(bS_{ex}\right) \]  \hspace{1cm} (1)

Here, excess entropy is given by \( S_{ex} = \frac{S - S_{id}}{Nk_B} \) where, \( S \) and \( S_{id} \) represent total entropy of the system and ideal gas respectively. \( D^* \) denotes the reduced diffusion coefficient and \( N \) represents total number of atoms/molecules present in the system. \( a \) and \( b \) are two constants that depend on the nature of the system. While Adam–Gibbs relation was first derived in order to explain the relaxation phenomenon in glassy systems [10,15], Rosenfeld scaling [16–18] is mainly valid at temperatures, higher than the melting temperature where the system is expected to be fully ergodic. But still, there is no precise explanation of the origin of scaling relation between diffusion and entropy.

In this work, we introduce a first principles derivation of the scaling relation and find that it essentially has the same form of Rosenfeld scaling (Eq.1). We then explore the existence of such a relationship in three fully deterministic two-dimensional systems. We inquire several interesting questions. First, what are the conditions for which the motion is diffusive (or, ergodic)? It is of course unclear whether diffusion at all could exist for such a simple system, without any noise term. Second, since the entropy of the system can be calculated exactly, what, if any, is the relation between \( D \) and \( S \)?

II. Theory: Microscopic Derivation
Despite of several studies [16,17] on the origin of diffusion-entropy scaling relation, a precise derivation of the scaling relation is not available. In the earlier derivation of scaling relation by Banerjee et al. [17] the double integral expression of mean first time was employed, with certain approximations. We note that there must be an underlying random walk behind the existence of diffusion in any system. In some cases, random walk nature is easy to decipher, like for Lorentz gas at small value of separation parameter, [4] but can be hard for some others. The regular random walk model allows us to use the relation between the rate constant \(k\) of crossing from one cell to the other, to the diffusion coefficient \(D\) through the relation like, \(D = \frac{1}{2d} k(E) a^2\) where, \(a\) is lattice constant, distance between two adjacent cells, and \(d\) represents dimension of the system. [19]

Again, according to celebrated transition state theory of Wigner and Eyring [20], the rate constant is a property of phase space trajectories. We use this connection to relate diffusion with entropy. In the transition state theory formalism [22], the general expression of total energy \(E\) dependent rate constant in microcanonical ensemble is given by [23–25]

\[
k(E) = \frac{1}{2} \frac{\int dq^N dp^N \delta(H_N - E) \delta(q_1 - q_c) |\dot{q}_1|}{\int dq^N dp^N \delta(H_N - E)}
\]

The above expression (Eq. 2) is derived with an assumption that the critical surface dividing reactant and product states is a function of coordinates only. We also assume that one of the coordinates (say, \(q_1\)) is perpendicular to dividing surface \(\sigma(q_1 = q_c) = 0\) where, \(q_c\) represents critical value of \(q_1\) at the transition point. In Eq. 2 \(H_N\) is the total Hamiltonian of the system with \(N\) degrees of freedom and \(\dot{q}_1\) represents velocity along the reaction coordinate only.
Denominator of the Eq.2 represents classical density of states per units energy and it is denoted by [26]

$$\rho_c(E) = \frac{1}{h^N} \int dq^N dp^N \delta(H_N - E).$$

We simplify $\rho_c(E)$ further as follows,

$$\rho_c(E) = \frac{d}{dE} \int dq^N dp^N \Theta(H_N - E) \frac{d\Omega(E)}{dE}. \text{Here, } \Omega(E) \text{ represents total number of states with energy less than or equal to } E \text{ and } \Theta \text{ is step function. Before proceeding further, we need to take assumption that at critical point one coordinate } (q_1) \text{ becomes separable from the others. So, we can expand potential energy function around } q_1 \text{ as follows, } V_N(q_1, q_2, \ldots, q_N) = E_0 + V_{N-1}(q_2, \ldots, q_N). \text{ Here, } E_0 \text{ denotes bond dissociation energy along } q_1 \text{ coordinate and } V_{N-1} \text{ indicates potential energy for } N-1 \text{ degrees of freedom. We simplify the numerator of Eq.2 in the similar way to obtain } \frac{1}{2\pi h} \Omega^{\text{trans}}(E),$$

where $\Omega^{\text{trans}}(E) = \frac{1}{(2\pi h)^N} \int dq_1 dp_1 \ldots \int dE' \frac{d}{dT} \left( \sum_{i=2}^{N-1} \frac{p_i^2}{2m} + E_0 + V_{N-1} - E + E' \right)$. Here, $m$ represents the mass of the molecules present in the system. Use of this expression in Eq.2 gives, $k(E) = \frac{k_B}{2\pi h} \frac{\Omega^{\text{trans}}(E)}{\Omega(E)}$. This form of equation is analogous to Wigner [20] and Eyring [27] equation [28] obtained from transition state theory approximation if we use the definition of temperature in microcanonical ensemble i.e.

$$\left( \frac{\partial S}{\partial E} \right)_{N,T} = \frac{1}{T}. \text{ Using the relation between } D \text{ and } k(E) \text{ mentioned above and introducing } S^* = k_B \ln \Omega^{\text{trans}} \text{ (i.e. Boltzmann’s formula of entropy [29]) we recover the following interesting expression for the diffusion constant}$$


\[ D = \frac{a^2}{2d} \frac{k_B}{2\pi \hbar} \exp \left( -\frac{S - S^*}{k_B} \right) \]

Eq. 3 is new. It is similar to the form of Rosenfeld, but not identical. *Here \( S^* \) is a scaling constant that serves the same role of \( S_{id} \) involved in Rosenfeld scaling relation (Eq. 1). In the latter, not only the ideal gas entropy term, but also the entire form was adopted phenomenologically.*

### III. System and Simulation Details

We now turn to verifications and justification. We study three systems, (a) the motion of a single point particle with constant energy in a two-dimensional periodic potential energy landscape defined by sum of cosine potentials, (b) the same in a regular Lorentz gas and (c) the same among the boxes with small apertures. Study of diffusion in periodic cosine potential and Lorentz gas is otherwise also important due to the existence of a variety of applications like super-ionic conductors, motion of adsorbates on crystal surfaces, polymers diffusing at the interfaces, molecular graphene, etc.[30–35]

Buminovich and Sinai [3] rigorously proved that a dynamical system of a point particle moving in two-dimensions becomes ergodic in the high-density regime of dispersed hard billiard balls in long time limit. Later, Machta-Zwanzig (MZ) [4] *showed that the system of Lorentz gas becomes diffusive for small value of separation parameter(\( W \)) since, at this limit, the scattering of the particle with the circular disk is dispersive due to the convexity of the scattering surface (Figure 1a).* A related but different model studied by Bagchi *et al.* was a periodic analog of regular Lorentz gas but with continuous potential where the energy surface in two dimensions is given by [5]

\[ V(x, y) = \cos \left( x + \frac{y}{\sqrt{3}} \right) + \cos \left( x - \frac{y}{\sqrt{3}} \right) + \cos \left( \frac{2y}{\sqrt{3}} \right) \]
Figure 1: (a) The location of fixed hard-scatterers in a periodic Lorentz model. The blue shaded region denotes a trapping region of triangular symmetry. W is the separation parameter between hard disks. (b) A schematic representation of potential energy function defined in Eq.4. The range and color codes are given on the right side of the plot. (c) A schematic diagram where the particle moves among the boxes with small holes of width $W_1$ allowing long distance motion only in one direction.

In this case, dynamics of the point particle is complex due to refocusing caused by a concave curvature in the potential energy surface (as shown in Figure 1b). This cause the trajectories of the particle to be trapped during different back-and-forth journeys between the same two cells (Figure 6c). Neither the study of MZ nor the work by Bagchi et al studied the entropy of the system, especially the diffusion-entropy scaling and also did not relate Lyapunov exponent to diffusion and entropy.

Projecting potential function (Eq.4) into the $x$-$y$ plane we note that each cell contains a minimum at the center of the triangle, maxima at the three corners of the triangle and saddle points at the midpoints of the edges. Energies of the maxima, minimum and saddle points of each cell are given by 3.0, -1.5 and -1.0 respectively. The point particle can sample the whole phase space if its energy is more than the saddle point energy. Otherwise, it can get trapped inside a cell forever. We start our simulation in constant NE ensemble placing the particle near the minima of a cell. Velocities of the particle are randomly assigned in such a way that total energy is constant. We use Gear’s fifth order predictor-corrector algorithm for integrating equation of motion of the particle with timestep 0.001. [6] We perform computer simulation for a set of different values of total energy of the system for
10^6 steps. Each calculation is performed for 100 times starting from 100 different initial configurations in order to obtain an estimate of reproducibility.

IV. Result & Discussions

The self-diffusion coefficient (D) of the point particle in the triangular periodic potential (Eq. 4) is calculated using mean square displacement (MSD) and velocity auto-correlation function (VACF). In two-dimension self-diffusion coefficient is defined by

\[
D = \lim_{t \to \infty} \frac{\langle (r(t) - r(0))^2 \rangle}{4t}
\]

Where, \( r(t) \) is the position of the particle at time \( t \) and angular brackets indicate the ensemble average.

Here, we compute the MSD \( \langle (r(t) - r(0))^2 \rangle \) by taking an average over 100 trajectories with completely different initial configurations. Alternatively, the self-diffusion coefficient can be calculated by integrating the un-normalized velocity autocorrelation. According to the Green-Kubo formalism, D is defined as,

\[
D = \frac{1}{d} \int_{0}^{\infty} \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle dt
\]

Where, \( d \) indicates the dimension of the system and \( \mathbf{v}(t) \) is the velocity vector of the particle at time \( t \).

The variations of MSD and un-normalized VACF with time for different values of energy are shown in Figure 2(a) and Figure 2(b).
Both methods give similar values of D. VACF exhibits negative region because of trapping but decays at a faster rate with increasing energy up to a certain critical energy. We discover the critical value of energy (to be calculated -0.4) beyond which the relaxation of VACF becomes more oscillatory in the long-time limit. Hence, above the critical energy, VACF could not provide a well-defined self-diffusion coefficient for this system. In Figure 3a, we plot D obtained from MSD against energy.

We use Boltzmann’s formula, $S = k_B \ln \Omega$ to calculate the entropy, where $\Omega$ represents partition function in the micro-canonical ensemble. For our system, we solve the following integration numerically in order to get an estimation of $\Omega$ for a particular cell using conventional quadrature methods,[Eq.7]

$$
\Omega = \frac{1}{c} \int dx \int dy \int dp_x \int dp_y \delta(H - E)
$$

(7)
Here, $E$ represents the total energy, $c$ denotes normalization constant and $H$ corresponds to the total Hamiltonian of the continuous potential (Eq.4) that is given by

$$H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + V(x, y).$$

As discussed before, $p_x$ and $p_y$ represent the x and y-components of the momentum of the particle respectively and $m$ is the mass of the particle which is taken as unity in this case. Similarly, we compute the entropy of the ideal system by considering constant flat potential energy surface by carrying out the integration as follows,

$$\Omega'' = \frac{A}{c} \int dp_x \int dp_y \delta\left(\frac{p_x^2}{2m} + \frac{p_y^2}{2m} - E'\right) A \text{ is the area of the triangle and } E' \text{ indicates the constant energy of the system because the collisions are elastic and } c \text{ is normalization constant as usual. We define scaled entropy (S_1) of the form } S_1 = k_B \ln \int dx \int dy \int dp_x \int dp_y \delta(H - E) \text{ and variation of } S_1 \text{ against energy is plotted in Figure 3b. In Figure 3c we plot D against the excess entropy for different values of energy (i.e. } E \geq -0.9 \text{ ) of the system. From Figure 3c it is noted that exponential scaling [16] relation holds remarkably well. Hence, regular random walk model (also confirmed by looking into trajectories) is valid at this energy regime but starts to breakdown near saddle energy (i.e. -1.0) as discussed later.}

For Machta-Zwanzig model, [4] D can be estimated analytically as a function of the width of exit($W$) and is given as,

$$D(W) = \left(\frac{W}{\pi}\right)(2 + W)^2 \left[\sqrt{3} (2 + W)^2 - 2\pi\right]^{-1} \quad (8)$$

In Eq.8, $W$, the separation parameter, alone determines the behavior of the system as the speed is constant. We derive an exact expression of Boltzmann entropy for the system which is given as
\[ S(W) = k_B \ln \left( \frac{2\pi}{c} \left[ \frac{\sqrt{3}}{4} \left( 2 + W \right)^2 - \frac{\pi}{2} \right] \right) \]  (9)

Where, \( c \) represents normalization constant. While deriving Eq.9 we assume radii of the scatter to be unity. In order to get an ideal limit of \( S(W) \) we neglect interaction effect by assuming scatterers as point particles. We calculate D and S for a set of values of \( W \) (Figure 3d&3e). In Figure 3f, we plot D against excess entropy for a particular triangular trap and we find that exponential scaling relation holds remarkably for this system also.

Figure 3: For the continuous triangular potential (a) plot of D against energy(E), (b) plot of scaled entropy \( S_1 \) against energy and (c) plot of D against excess entropy. In (c) we use \( D = a \exp(b S_{ex}) \) for fitting the data points (black trace).
This plot (c) resembles well-known Rosenfeld scaling (Eq. 3) with $a=25.91$ and $b=5.32$. For periodic Lorentz model (d) plot of $D$ against separation parameter ($W$), (e) plot of scaled Boltzmann entropy against $W$ and (f) plot of $D$ against excess entropy. Here in (e), we use $D = a \exp(bS_{ex}) + c_1$ for fitting the data sets (black trace). This plot agrees with Rosenfeld scaling with $a=-0.14$ and $b=-0.44$. (g) Plot of relative area ($\mu$) occupied by the chaotic component against $E$. (h) variation of $h_{KS}$ against energy (i) plot of $D$ obtained from MSD against $h_{KS}$. In (i) we use exponential function $D = a \exp(bh_{KS})$ for fitting (black trace) with $a=0.003$ and $b=62.56$. Figure (g), (h) and (i) are for the continuous triangular potential system. In (a), (b), (d), (e), (g) and (h) the lines joining the data points are provided as a guide to the eyes.

We study box-hole model system apart from continuous periodic potential and periodic Lorentz model. In Figure 1c we show the schematic diagram of the model. Initially, the point particle starts from any arbitrary box of length ‘L’ and suffers elastic collision with the wall of the box.

Figure 4: (a) plot of self-diffusion coefficient against $W_1$. Here, the line joining the data points is provided as a guide to the eyes. (b) plot of $D$ against excess entropy. In (b) we use $D = a \exp(hS_{ex})$ for fitting the data points (black trace). This plot (b) resembles well-known Rosenfeld scaling with $a=0.03$ and $b=-12.03$.

The Motion of the point particle is bounded by the wall of the box in the vertical direction. But, each box contains the hole of width $W_1$ in each side in the horizontal direction. As long as $W_1$ is comparably smaller compared to the length of the box (L) diffusion exists for the system since the particle spends long time before leaving the box in each box in order to forget the memory through a large number of elastic collision with the wall of the box. We plot $D$ against $W_1$ in Figure 4a. Like
periodic Lorentz model we use following relation in order to calculate excess entropy for this system for different values of $W_1$,

$$S_{ex} = S - S_{id} = k_B \ln \left(1 - \frac{W}{L}\right)$$

(10).

In Figure 4b we show the variation of D against excess entropy for different values of $W_1$. From Figure 4b, it is noted that Rosenfeld scaling relation holds for this system remarkably.

Formin et al [36] showed the scaling relation is valid only at high temperature, for the system with bounded potential. So, the validation of scaling relation is important. We also find that dependence undergoes a crossover at low energy.

In the subsequent section we only explore the different aspects of the system with continuous periodic potential (Eq.4).

For a deterministic system, dynamical randomness is generally characterized by a positive value of Kolmogrov-Sinai entropy ($h_{KS}$). [37–39] A measure of the onset of chaos or dynamical randomness [40] can be obtained from the sensitivity to the initial conditions in a closed dynamical system which is again characterized by Lyapunov exponent. [41,42] In a two-dimensional Hamiltonian system, the dynamical entropy can be determined by the following formula $h_{KS} = L_n \mu$, where $L_n$ is the maximal average, [43] LCE as discussed later. $\mu$, an important characteristic of the chaotic motion, is defined as $\mu = \frac{n_{ch}}{n}$, where $n$ indicates the total number of grid points accessible to our point particle and $n_{ch}$ denotes the number of grid points responsible for the chaotic motion for a particular triangular cell. In Figure 3g we plot $\mu$ against energy. From the figure we note that $\mu$ increases with the increase in energy as expected. In Figure 3h we show the variation of $h_{KS}$ with energy and plot of D against
$h_{KS}$ is shown in Figure 3i. Interestingly, we find that $D$ exhibits exponential dependence on $h_{KS}$ like Boltzmann entropy since a linear relation holds between Boltzmann entropy and $h_{KS}$ in our system as shown in Figure 5.

![Figure 5: plot of Sinai entropy against $S_1/k_B$ for different values of energy. We use linear function of the form $h_{KS} = a_0 + a_1 S_1/k_B$ for fitting the data points (black trace) with $a_0 = 0.07, a_1 = 0.08$.](image)

In order to understand the spread of the trajectories, Lyapunov exponents are calculated.[44] Chaotic behavior can be generated within a dynamical system even in the absence of external random forces. Quantitatively this chaotic motion can be determined by computing Lyapunov characteristic exponent (LCE).[45] It is found that computing maximum LCE ($L_n$) is sufficient in order to characterize the motion of the system. We use ‘shadow trajectory’ method [43] in order to compute $L_n$ and it is defined as follows,[Eq.11]

$$L_n = \frac{1}{n\Delta t} \sum_{i=1}^{N} \ln \left( \frac{d_i}{d_{i-1}} \right)$$  \hspace{1cm} (11)
In Figure 6a dependence of $L_n$ on different values of energy is shown. Clearly, $L_n$ increases with energy as motion of the particle becomes chaotic at a faster rate. Several studies [46] have been performed to get an estimation of LCE for periodic Lorentz model. So we omit the recalculation of LCE for the well-studied Lorentz model.

![Figure 6: (a) Plot of $L_n$ against energy. We observe a clear crossover near $E=-0.9$ that indicates the presence of distinctly different dynamics in the two regimes. Here, line joining the data points (black and green trace) are provided as a guide to the eyes. (b) Replot of $D$ against excess entropy along with the presence of values just above the saddle point energy. Clearly, two exponential functions (black and green trace) are needed to fit whole regime of the energy landscape. (c) Plot of phase space trajectory of the point particle moving with constant energy. Central black triangle represents the initial cell of the particle. We observe multiple crossing (green circled region) through the saddle surface indicating the signature of correlated motions. Figure 6(a), (b) and (c) are for periodic potential (Eq.4).](image)

Figure 6(a) shows the signature of a crossover at $E=-0.9$ from low energy, quasi-ergodic to ergodic at higher energy. The physical mechanism behind the crossover is the onset of correlated motions at low energy (slightly above the saddle energy) that make the random walk trace the same path repeatedly, by recrossing among the triangular cells (Figure 6c). This makes the expression of rate constant (Eq.2) used to derive the exponential scaling relation invalid.

In the presence of correlated random walk, Eq.2 can be modified [5,47] as

$$k(E) = \langle J_x(S) \rangle_e + \int_0^{\tau_d} dt \langle J_x(S) J_x(S, t) \rangle_e$$

(12)
where, $J_c(S)$ and $J_h(S,t)$ denote the outgoing flux crossing the saddle surface $S$ at time $t=0$ and intrinsically negative flux coming back to the initial surface at later $t$. The second term is negative, thus lowering the value of the rate constant, and hence of the diffusion coefficient. Here, the subscript ‘e’ indicates the equilibrium average in the microcanonical ensemble and $T_M$ is the upper limit of integration in order to avoid the contribution coming from the long time ‘thermalized’ returns. The transition state theory rate constant (Eq. 2) becomes equal to $\langle J_c(S) \rangle_e$ in the absence of correlated returns. The probability of correlated returns becomes more pronounced while the energy of the point particle approaches to the saddle point energy (i.e, -1.0). We also observe the crossover in the exponential scaling plot (Figure 6b) between diffusion and entropy with two distinct exponents near $E=-0.9$. The presence of crossover in Figure 6(a)&(b) is clearly an indication of two distinct dynamical regimes present in the system.[48,49] The appearance of correlated motions purely originates from the characteristics nature of potential energy surface. The identification of complex dynamics through ‘caging’ (Figure 6c) has made a deep connection with slow glassy liquids in the context of inherent structure analyses of liquids.[50,51]

An important dynamical quantity is the exit time dynamics from (or, the residence time of) the starting cell. We define two correlation functions $C_s(t)$ and $C(t)$ for the original cell which are defined as follows,[Eq.13]

$$C_s(t) = \frac{\langle H'(0)H'(t) \rangle}{\langle H'(0) \rangle} \quad \text{and} \quad C(t) = \frac{\langle h'(0)h'(t) \rangle}{\langle h'(0) \rangle}$$

(13)

In the definition of $C_s(t)$, $H'(t)$ is a Heaviside function such that, $H'(t)$ is unity as long as the particle resides inside the original cell. But after leaving the original cell for the first time $H'(t)$ becomes 0 for all later $t$. $H'(0)$ is taken as unity since particle always resides inside the starting cell at
At $t=0$, however, in the definition of $C(t), h'(t)$, another Heaviside function, is always one as long as the particle is inside the original cell even after coming back to the original cell and becomes zero whenever the particle escapes outside the initial cell. As before, $h'(0)$ is unity in this case also.

Variations of $C_S(t)$ and $C(t)$ with time for different values of energy are shown in Figure 7(a) and (b).

![Figure 7](image)

Figure 7: (a) plot of time-correlation function [$C_S(t)$] for different values of energy. (b) plot of another time correlation function [$C(t)$] defined by Eq.13 in the main manuscript for different values of energy. Plot corresponding to $E=-0.9$, is highly oscillating due to trapping near minima, is not shown in (b). We note that $C(t)$ decays slowly compared to $C_S(t)$ for a particular value of energy.

These two functions are mainly introduced in order to capture the short to intermediate dynamics associated with the motion of the point particle moving in continuous potential. We find that for the particular value of energy, $C_S(t)$ exhibits faster decay compared to $C(t)$ since the particle requires longer time to escape from the original cell permanently. We also note that the plots corresponding to higher energy decay at a faster rate for both the cases since escaping probability from the original cell becomes more pronounced with increasing energy.
Time correlation function $C_s(t)$ gives an estimate of the exit time of the point particle from the initial cell for the first time. The time decay of correlation function $C_s(t)$ involves two important time scales namely, (i) the time taken to reach the saddle point boundary starting in the vicinity of the minima of the original cell, and (ii) the time required to return to the original cell through the saddle point from the neighboring cell. Hence, we fit the time correlation function $C_s(t)$ using bi-exponential function of the form $a_1 \exp\left(-\frac{t}{\tau_1}\right) + a_2 \exp\left(-\frac{t}{\tau_2}\right)$. We report fitting parameters in Table 1.

**Table 1**: Below, we report bi-exponential fitting parameters of $[C_s(t)]$

| Energy | $a_1$ | $\tau_1$ | $a_2$ | $\tau_2$ | $\langle \tau \rangle$ |
|--------|-------|---------|-------|---------|----------------|
| -0.5   | 0.52  | 4.46    | 0.48  | 4.55    | 4.50          |
| -0.6   | 0.52  | 5.01    | 0.48  | 4.85    | 4.93          |
| -0.7   | 0.40  | 5.46    | 0.60  | 5.43    | 5.44          |
| -0.8   | 0.05  | 3.83    | 0.95  | 9.35    | 9.07          |
| -0.9   | 0.70  | 38.46   | 0.30  | 33.33   | 36.92         |

Clearly, crossing the barrier near saddle point becomes more feasible with the increase in energy of the particle. When the energy of the particle is close to saddle point energy (i.e, -1.0) particle takes much longer time to escape outside the original cell for the first time because of trapping near the minima of the cell.

V. **Summary & Conclusions**

Finally, the existence of diffusion in a deterministic system by itself is non-trivial in nature and a subject of great interest. According to hydrodynamic mode-coupling theory, [52]diffusion does not
exist in two-dimensions because of its logarithmic diverging nature in the long time limit. But, the origin of the existence of diffusion in our system is something different and discussed below. The most important result is that all the studied systems obey diffusion-entropy exponential scaling relation. Several concluding comments are in order.

(i) We present a general derivation of diffusion-entropy scaling for the first time. In the present derivation we avoid all pitfalls and it is exact. We believe the present derivation will go long way to explain ‘universality’ of the scaling relation.

(ii) Diffusion can never exist in any system without the presence of chaos. On the other hand, chaos is sensitive not only to the initial conditions but also to the characteristics of the potential energy landscape. The energy landscape must be dispersive. This is satisfied for the periodic Lorentz gas, at the high density of the scatterers. In this case the convexity of the surface of disk scatterers disperses two neighboring trajectories in the phase space.

(iii) However, the motion of the point particle on the triangular cosine potential energy surface is more complex. There are three concave regions in each site that focus trajectories back to the configuration line between the two minima of the adjoining cells. However, existence of sufficient configuration space with dispersive character leads to the existence of diffusive motion.

(iv) The long time rate of dispersion of initially close trajectories in the phase space can be quantified by calculating LCE. The latter provides the rate of exponential growth of separation in the phase space of two initially close trajectories. LCE is supposed to provide a measure of the time of the system to be chaotic. We find that system takes less time to be chaotic with the increase in energy, which is of course expected.

(v) We find an energy dependent crossover in the motion of the particle at low energy when the particle exhibit repeated correlated crossings and re-crossings in the energy landscape. This gives rise
to a deviation from exponential diffusion-entropy scaling, and seem to provide an explanation of the breakdown of this scaling at low energies.

(vi) We also estimate the degree of randomness of a time process by evaluating entropy per unit time which is well-known as Kolmogrov-Sinai entropy, or dynamical entropy, of the system for different values of energy.

(vii) Several recent studies have revealed curvature dependent diffusion coefficient for regular Lorentz model motivated by the study of MZ. In case of periodic Lorentz gas because of defocusing character of collisions of the point particle with the hard disks the system exhibits Lyapunov instability. With this analogy we can conclude that trajectories of the particle moving on continuous triangular potential are strongly mixed in the phase space because of the predominantly convex nature of the potential energy surface which itself acts potentially as a trap for the trajectory. As a result the system becomes ergodic in the longtime limit.

(viii) We introduce two timescales namely, permanent and mean first exit time of the particle from the starting cell from $C(t)$ and $C_S(t)$ functions that capture the short-to-intermediate dynamical features of the motion of the particle.

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