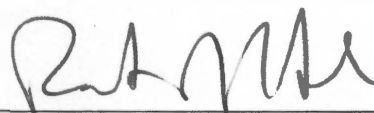


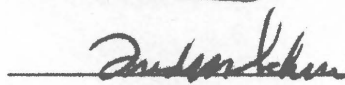
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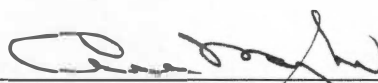


Robert J. Hinde, Major Professor

We have read this dissertation
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Vice Chancellor and Dean of
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Atomistic Investigation of Anomalous Diffusion on Surfaces: A Deterministic Approach

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

James Wesley Mancillas
May 2005

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Dedication

This dissertation is dedicated to Ann Mancillas. She has been a supporting wife and loving mother to our four children; James, Christopher, Andrew and Timothy.

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I would like to thank my advisor, Dr. RJ Hinde. He has provided a work environment that is supportive of free investigative thought. Through his guidance I have developed the skills of a scientist. These skills are: critical thinking, perserverance in the completion of seemingly impossible tasks, and the ability to identify and pursue questions of interest.

I would also like to give a special acknowledgement to Dr. JZ Larese for access to his computational faculties, without which I would not have been able to complete this research in such a timely manner.

Abstract

The observation of anomalous diffusion rates on surfaces by recent experiments has renewed interest in diffusion mechanics. In order to provide a better understanding of the atomistic motions resulting in anomalous diffusion, we have investigated the diffusion dynamics of sodium on a copper surface using conservative molecular dynamics. The properties of diffusing adatoms transitioning between normal diffusive motion and anomalous motion have then been examined. Utilizing short time approximation Lyapunov exponents, stable cantori within chaotic manifolds are identified. At the periphery of these stable cantori from which anomalous diffusion originates, we have examined the transition properties of diffusive motions with abnormally long jump properties. We have verified statistically their Levy distributions, and have examined the transition life cycle of these Levy flights using Poincare section analysis.

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Chapter 1

Introduction

1.1 Surface Diffusion

The transport of matter on surfaces proceeds by the diffusion of atoms and molecules in the two-dimensional regime of the surface. This elementary diffusive process is the first step in many complicated surface phenomena, such as heterogeneous catalysis and thin film formation, and can significantly control their overall efficiency. Potential uses of these processes in industrial applications results in continued interest in the fundamental study of surface diffusion. Advancements in experimental methods have revealed a new and unprecedented view of surface diffusion. The use of scanning electron microscopy¹⁸, field ion microscopy²³ and quasielastic helium atom scattering¹² in surface diffusion experiments have given scientists the ability to observe diffusion on an atomistic scale. The motions of single atoms and molecules can now be readily followed and this ability has broadened the study of surface diffusion immensely.

However the theoretical and computational treatment of diffusion on surfaces remains a challenging problem. The simulation of diffusive systems requires the analysis of a system with a large number of degrees of freedom. Evaluating the dynamics of adatom interactions with surface atoms and the underlying dynamics of the surface substrate atoms is a nearly intractable problem. These challenges necessitate the use of a simplified treatment of diffusion mechanics. An often chosen method of computational modeling for diffusive processes is the use of Langevin mechanics^{17,20,25}. Langevin mechanics is used to evaluate the dynamic motions of diffusing particles using simplified interaction potentials and dynamics. The major simplification in this method is treatment of the surface atoms which are held in fixed positions. The fluctuating effects of the previously mobile surface are replaced by a single stochastic force. The effect of the stochastic force is to randomly jostle the diffusing adatom to simulate the effects of thermal fluctuation in a real system. This method has in general proved to be reliable over a wide energy range for many systems at predicting

accurate diffusion rates, but because of the consolidation of the intractable dynamics of the surface mechanics into a single stochastic force, this method acquires a *black box* nature. While this method provides good agreement with experimental data, it does not provide insight about how specific interaction dynamics affect net diffusion rates.

Several recent experimental studies^{12,17,18,20,23,25} have observed that surface diffusion in some systems does not occur according to classic diffusion mechanics⁴ and that significant diffusive motion occurs through the occurrence of long jumps or flights. Diffusion exhibiting this type of behavior has been labeled *anomalous diffusion*. The occurrence of these long jumps are not predicted by Langevin calculations. Since the black box nature of Langevin mechanics precludes further development (within the Langevin treatment) to account for the occurrence of anomalous diffusion another route needs to be found to explain the occurrence of anomalous diffusion.

In order to better understand the occurrence of anomalous diffusion we have chosen to pursue a further idealized diffusive system. Using a Hamiltonian evaluation of the diffusive motions of adatoms on fixed surfaces, we hope to readdress the occurrence of anomalous diffusion from a different perspective. Our goal is to investigate the underlying phase space without the distorting effects of stochastic forces. The structure of the underlying phase space dictates the fundamental motions of the diffusion process. Identifying and examining phase space structures may provide insight into the fundamental characteristics of diffusion on surfaces.

1.2 Anomalous Diffusion on Surfaces

Anomalous diffusion is generally characterized by systems exhibiting superlinear diffusive rates, which have been attributed to the occurrence of *Levy flights* during the diffusion process. Levy flights are a type of diffusive motion characterized by long periods of non-stochastic motion in which the movement of a particle is highly correlated along a single spatial vector²⁴. This motion differs significantly from the classic *random walk* which is the foundation of classic diffusion theory⁴. The conditions which result in the manifestation of Levy flights and control their behaviors are not well understood.

In an effort to better understand anomalous diffusion, research has recently been refocused on the investigation of simple diffusive systems. These systems which are prototypical in nature and lend themselves readily to theoretical analysis can be used during the evaluation of improved diffusion theories. One such system is the diffusion of Na adatoms on a Cu(001) surface. The importance of this system lies in its fundamental simplicity. The copper surface is symmetric in the *xy*-planes of the surface and can be constructed with a very clean and regular surface face; additionally the adsorbed particle is a single spherical atom. These conditions make it an ideal system to study.

Analysis of recent experimental measurements of the diffusion of sodium on a copper surface has shown promising results^{6,11}. At low energies, anomalous diffusion rates have been observed, thus providing a simple system with appropriate behaviors to use in an investigation of anomalous diffusion.

The results of these experimental observations have been used to create a interaction potential of Na adatoms on a Cu(001) surface¹⁴, which has been used to accurately reproduce diffusion rates over a wide energy range. Molecular dynamics simulations using conservative Hamiltonian mechanics have revealed several interesting behaviors in this system¹⁴. A major feature of the Na-Cu(001) system simulations is the separation of phase space into two distinct types. One type of phase space is *regular*, motion within these pockets of phase space are periodic or quasiperiodic. The other type of phase space is *chaotic* in nature, motion within these regions of the phase space exhibit a strong sensitivity to initial conditions, exhibiting exponential divergences between trajectories which are initially separated by only a small difference. Motion in these regions seems to explore the available phase space stochastically with very little intuitive predictability about the modest or distant future of the system. The occurrence of this type of behavior in deterministic calculations is generally referred to as deterministic chaos. The display of irregular and unpredictable time evolution behaviors is an intrinsic property of the system and is not the result of calculational errors nor does it result from unknown stochastic influences. Additionally, because of the deterministic nature of these calculations, trajectories cannot transition between regular and chaotic regions of space; these regions are completely exclusive to each other.

The result of the co-existence of regular and chaotic phase space is a system behavior which is rich in complexity. Motions within the regular regions of phase are predictable, while motions within the chaotic regions can be described as generally stochastic. However these motions are deterministically evaluated and as such, they must, at least to some minor degree, display some predictable behaviors. One such behavior is the occurrence of Levy flights. These occur when chaotic trajectories approach the periphery of a regular region of phase space. As a trajectory approaches a regular region of phase space, the chaotic trajectory will briefly acquire stability which parallels that of the nearby regular region. This results in a behavior that is briefly *non-stochastic*. The occurrence of Levy flights upsets the typical statistical distribution of the diffusive motions.

Clarifying our definition of anomalous diffusion, we state that the occurrence of *super-linear* diffusive rates is the result of Levy flights which produce an enhanced net diffusion rate. The mean square displacement (MSD) of diffusing particles is used to further illustrate this point. The MSD is mathematically defined as

$$MSD = \langle (\vec{x}(t) - \vec{x}(0))^2 \rangle, \quad (1.1)$$

where the MSD is the ensemble average of the squared displacement of particles through an elapsed time t . Particles which move randomly will, according to classic Brownian motion, have a MSD which increases linearly with respect to time, see figure 1.1. Particles moving along a constant vector will, however, have a MSD that increase quadratically with respect to time. This type of motion is referred to as ballistic motion. Levy flights, which by definition have a high degree of correlated motion, will then tend to increase in a nearly quadratic manner. Thus a diffusion process involving a combination of both normal diffusive motion and Levy flights will have a MSD which is a weighted proportion of both types of behaviors, see figure 1.1.

The complete relevance of these Levy flights, and how they affect the net diffusion rate is not clearly understood. More to the point, there is a fundamental lack of understanding concerning the occurrence of the Levy flights in simple diffusive systems. There is no clear understanding about how normal diffusive motion transitions to and from ballistic motion. Nor are the influences of a substrates' spatial arrangements and energy barriers on ballistic motion well understood. There are numerous questions to be answered before a complete theoretical model can be proposed which can adequately describe fully the nature of anomalous diffusion.

This study of anomalous diffusion will principally be concerned with an evaluation of numerical methods which might be useful in the evaluation of anomalous diffusion. Using molecular dynamics to simulate diffusion on a surface, we will explore the use of Lyapunov exponents as a means to identify specific regions of phase space: chaotic, stable, and that responsible for Levy flights. Throughout the rest of this chapter we will present a brief introduction of several key concepts as they apply to this study. These topics will include the specific nature of the computational model we will employ to simulate a diffusive system, and a description of Lyapunov exponents and Poincare sections.

1.3 Diffusion Model

An algorithm simulating the diffusion of an adatom on a surface requires two fundamental components. The first component is a reliable potential energy surface (PES) describing the interaction between the adatom and the surface on which it resides. The second component is a numerical method for computing the motion of the adatom on the surface. In this work Newton's equation of motion,

$$F(r) = m \cdot a, \quad (1.2)$$

is used to evaluate the motion of a particle, where $F(r)$ is the force exerted on an object, m is the mass of the object, and $a = \frac{\delta^2 r(t)}{\delta t^2}$ is the acceleration of the particle. The gradient of the PES evaluated at a position on the surface determines the force exerted on the particle

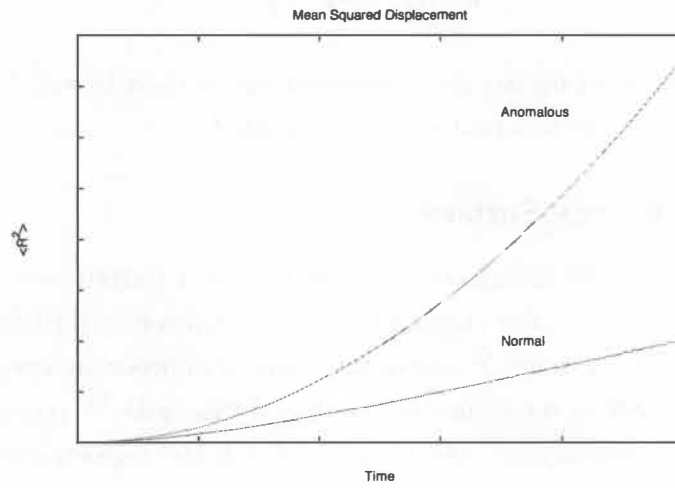


Figure 1.1: Plot of normal and anomalous MSD. The linear function labeled as normal is a MSD calculated from a diffusion simulation at 105 meV for the sodium copper adatom system. This is well behaved MSD that increases linearly with respect to time as predicted by classic diffusion theories. The anomalous MSD was calculated from the same system at 85 meV. This MSD which increases faster than linearly is indicative of anomalous diffusion.

by the surface, expressed mathematically as

$$F(r) = -\nabla U(r). \quad (1.3)$$

Solving eqns. 1.2 and 1.3 gives the following equation and allows the determination of the acceleration of a particle under the influence of the potential,

$$a = \frac{-1}{m} \nabla U(r). \quad (1.4)$$

The trajectory of the adatom can then be evaluated using the following second order differential equation

$$\frac{\delta^2 r(t)}{\delta t^2} = \frac{-1}{m} \nabla U(r). \quad (1.5)$$

The specific PES employed during this study and the method by which this second order differential equation for $r(t)$ is solved are now presented.

1.3.1 Potential Energy Surface

Recently, the diffusion of Na adatoms at low coverage on a Cu(001) surface has been studied experimentally with the quasi-elastic helium-atom scattering (QHAS) method¹¹. This method has proven to be a valuable tool in the study of diffusion dynamics by allowing the measurement of diffusion on an atomistic length and time scale¹², providing the ability to discriminate diffusion mechanisms and better establish the importance of Levy flights in the diffusion process.

Guantes et al.¹⁴ have used the results of these experiments to produce a two dimensional semiempirical PES for studying Na adatom diffusion on a Cu(001) surface. The adjustable parameters of this PES have been fit to produce calculated diffusion rates which agree well with experimental observations when employing molecular dynamics simulations (using both Hamiltonian and Langevin mechanics)^{14,15}. This PES is depicted in figure 1.2 and a corresponding contour surface is shown in figure 1.3.

A fundamental simplification of this PES is the treatment of diffusion in a strict two dimensional plane. In reality, as a particle diffuses along a surface, there are simultaneous motions both across the plane of the surface and perpendicular to it. The vibration of the Na adatom normal to the surface however, has a significantly higher vibrational frequency (~ 4 GHz) than that parallel to the surface (translational modes). Thus the potential with respect to z can be approximated as an average of the potential experienced during normal mode vibrations. The normal coordinate z can be considered fixed and the potential energy interaction can be described as a two dimensional function, $U(x, y)$, of position parallel to the surface. An additional assumption of this PES is that there are no adatom adatom

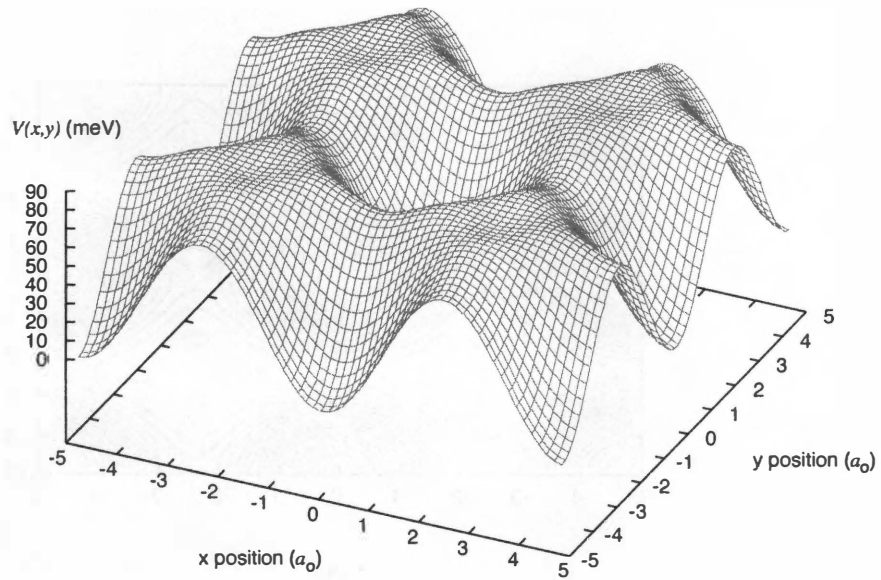


Figure 1.2: Two dimensional potential of the Na Cu(001) interaction for a single unit cell. The center of the each major peak, with a energy height of 82.76 meV, corresponds to the location of a copper atom site. The barrier minimum between the major peaks has a height of 74.58 meV. At the top of each peak is a crown of four minor peaks with peak heights of 85.40 meV with a saddle barrier for diagonal motion at 84.45 meV.

Contour Surface of GVM PES

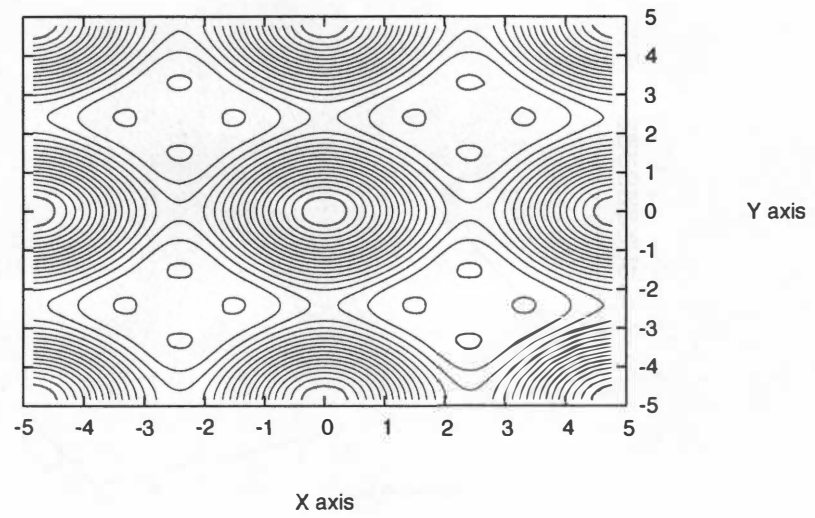


Figure 1.3: Contour surface of the NA Cu(001) PES. Centered at the origin (0,0) is a global minimum, 0.0 meV. Surrounding the minimum are four copper sites. On this surface the four prongs of the crown atop each copper site are clearly identifiable. The x and y axes are in atomic units and the contour spacing is 4.25 meV.

interactions. This is a minor assumption which is valid for the low coverage scenario from which the experimental data was derived.

The PES of Guantes et al. is composed of three separate terms;

$$V(x, y) = V_o[V_1(x, y) + V_2(x, y) + V_3(x, y)] \quad (1.6)$$

The first term is a separable cosine function

$$V_1(x, y) = [2 - \cos(2\pi x/a) - \cos(2\pi y/a)] \quad (1.7)$$

where a is the lattice constant of the Cu(100) surface ($a=4.832 a_0$) and $V_o = 41.4$ meV. The second term is a sum of Gaussians, used to reduce the potential barrier height in the diagonal direction:

$$V_2(x, y) = -2 \sum_{m,n} \exp(-b[(x/a - [m + 1/2])^2 + (y/a - [n + 1/2])^2]) \quad (1.8)$$

with $b = 11.8$. The third term which changes the curvature near the minima is given by

$$V_3(x, y) = C\pi^2 \sum_{m,n} [(x/a - m)^2 + (y/a - n)^2] \times \exp[-(x/a - m)^2 - (y/a - n)^2] \quad (1.9)$$

with $C = -0.2$. The adjustable parameters V_o, A, b and C were fit¹⁴ to give the best agreement between theoretical (Langevin simulations) and experimental values. The x and y directions correspond to the $[1\bar{1}0]$ and $[110]$ azimuths, respectively. The summation indices m and n in equations 1.8 and 1.9 must be run through the entire set of integer pairs (m, n) . The infinite summation of m and n ensure that the PES is converged in both the x and y directions on the surface. In practice only a small region of the surface, near the system origin (0,0) and extending out only two or three cell lengths is evaluated to high precision. This region is then employed in a periodic fashion to evaluate adatom behaviors along an entire copper surface.

The potential minima for the Na adatom on the Cu(001) surface are in the interstitial lattice positions. These global minima have an interaction potential of 0.0 meV. Copper site positions correspond to high energy local minima. The potential at each copper site is 82.76 meV. Atop each copper site is a four pronged crown, whose tips are aligned along the x and y axes. The prongs have peak heights of 85.40 meV and the crown saddle points aligned along the bisecting angle between the x and y axes have a height of 84.45 meV. Starting from the origin, saddle point barriers for diffusion along the x or y axes occur between copper atom sites at $(x, y) = (\pm a/2, 0)$ and $(x, y) = (0, \pm a/2)$. These barriers have a height of 74.58 meV. Again starting from the origin, motion along the 45 degree angles

with respect to the x and y axes encounter the bulk potential of the copper sites and pass through the copper crown saddle point minima.

I note that the saddle point and maxima values that I have calculated differ slightly (< 0.1 meV) from the values presented by R Guantes *et al.*¹⁵. The causes for these differences are not clear but the essence of the potential is still maintained.

During the initial testing of this potential, energy values within a single unit cell centered at the origin (0,0) were found to be well converged when the indices (m,n) had been summed from -10 to 10. These large summations result in a PES which is computationally expensive. This expense compelled us to investigate alternate methods to calculate this PES. The periodic nature of the PES suggests that the use of a truncated Fourier transform of the PES would be an ideal method to gain an improvement in computational efficiency. Comparing the potential energy surface computed by direct summation over m and n with that reconstructed from a truncated Fourier transform showed that a faithful reconstruction of the original potential requires as few as 36 Fourier coefficients.

An analysis of the differences in energy, first derivatives and second derivatives between the original PES and the reconstructed PES show differences on the order of double precision accuracy (error $\approx 1.0 \times 10^{-14}$ hartrees). This method of calculation significantly reduces calculational costs (by a factor of about 40), while maintaining the integrity of the initial PES. Unless stated otherwise, calculations performed throughout the rest of this study have been completed using the reconstructed PES which will be referred to as the Fourier Guantes Vega Miret-Artes (FGVM) potential, and is described in more detail in Appendix A.

1.3.2 Molecular Dynamics : Velocity Verlet Algorithm

The term molecular dynamics (MD) refers to a broad spectrum of numerical methods which are used to numerically evaluate the atomistic motions of a system by solving Newton's equations of motion¹. Given a particle position, $\vec{x}(t)$, and velocity, $\vec{v}(t) = \delta\vec{x}(t)/\delta t$, at time t , MD is used to evaluate the position and velocity at a later time ($t + \delta t$). Molecular dynamics is a deterministic method in that once the initial conditions $\vec{x}(t)$ and $\vec{v}(t)$ are specified the particle's trajectory at any subsequent time is completely determined.

In MD calculations there are several key issues of concern dealing with the conservation of energy and momentum. Evaluating system parameters (energy, position, and velocity) in finite steps introduces the possibility for integration errors to occur. The magnitude of these errors can be minimized by selecting an integration method which is appropriate for the system being studied and by choosing a integration step size which minimizes error propagations while affording acceptable computational speed and performance.

One frequently chosen integration method for MD calculations is the *velocity Verlet*

algorithm^{1,26}. This method is often selected because of its ease of implementation and proven reliability. It provides good short term conservation of total energy and linear momentum. Additionally, this is a symplectic method²⁶ which provides good preservation of phase space structures and is therefore ideally suited for an investigation studying phase space structures. Using the velocity Verlet algorithm, the time evolution of a particle is expressed as a Taylor series expansion of the position of the particle, truncating at the second term.

$$x(t + \delta t) = x(t) + \frac{1}{m}p(t) \cdot \delta t + \frac{1}{2}a(t) \cdot \delta t^2, \quad (1.10)$$

where δt is the time step for the simulation, $x(t)$, $p(t)$ and $a(t)$ are respectively, the position, momentum ($m \cdot dx/dt$) and acceleration (also written as $-\frac{1}{m}dU(x)/dx$, where $U(x)$ is the potential energy at position x) at the previous time step. The momentum of the particle for the next time step is then,

$$p(t + \delta t) = p(t) + \frac{m^2}{2}[a(t) + a(t + \delta t)]\delta t, \quad (1.11)$$

Given the initial conditions $x(0)$ and $p(0)$, the values $x(t)$ and $p(t)$ can be calculated by successively applying equations 1.10 and 1.11, with time steps $\delta t = t/n$ for n iterations.

A principal concern during the implementation of the velocity Verlet algorithm, as with any method for solving Newton's equations of motion is the conservation of energy during the course of a simulation. The accuracy of this method is a function of the time step (δt) with a short time error in position of $\mathcal{O}(\delta t^4)$ ²⁶ and momentum of $\mathcal{O}(\delta t^2)$ ²⁶. These short time errors generally are stochastic in nature and do not accumulate to produce long term drifts in values²⁶.

Trajectories of chaotic systems are especially sensitive to initial conditions, so in addition to the typical concerns for the conservation of energy and linear momentum, we have given special attention to the divergence between trajectories with the same initial conditions that are computed using differing time steps for the MD integration. Ideally one would like to use the largest time step possible, which if reduced would produce a trajectory that is identical to one calculated using a longer time step. However, because of the chaotic nature of this system this is not possible. As the time step for MD integration changes, small differences in location between initially identical systems will result. Regardless of the size of these minute differences, divergence between the two systems will rapidly occur.

Instead we must select a time step which, in addition to providing conservation of energy and momentum, provides reasonable short term similarity between initially identical systems that have been integrated with differing time steps. Weighting these concerns we have chosen a time step length of 1 atomic time unit.

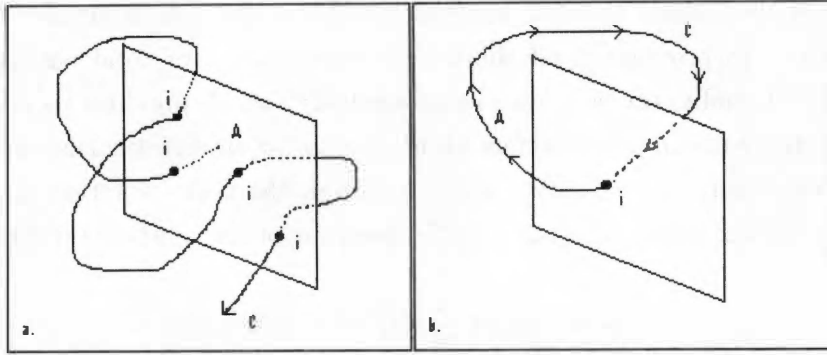


Figure 1.4: Graphical representation of a trajectory intersecting with a Poincare hyperplane. 1.4.a. The trajectory begins and ends at points A and C and intersect the Poincare surface at the points labeled i . 1.4.b. A regular trajectory which repeatedly intersects a fixed point i on the Poincare surface.

1.4 Poincare Sections

In any system containing significant degrees of freedom, isolating conditions which result in a particular or distinct behavior can be difficult to identify. Often the first step in the determination of these properties is the construction of a *Poincare section*^{2,8}. The fundamental idea behind this method is to reduce the amount of information that an interpreter needs to analyze in order to identify regions of phase space responsible for an interesting behavior. In this two dimensional system ($N=2$), the phase space of the system is composed of four coordinates, two position and two momentum coordinates. A full description of the system conditions at constant energy generally requires three coordinates ($2N-1$). This subspace manifold is described as a constant energy shell upon which the particle trajectory resides. Further constraining the system to a single section of the constant energy shell reduces the dimensionality of the subspace by an additional dimension. The Poincare section is then a two dimensional representation of a trajectory as it passes through phase space hyperplane.

Conceptually Poincare sections can be explained by considering a dynamical system's trajectory as it makes repeated intersections with a hyperplane defined by an algebraic relationship among the system's degrees of freedom. Thus when the trajectory intersects the hyperplane, the information of the system (on the hyperplane) has been reduced by the dimensionality of the hyperplane, see figure 1.4. By recording the successive intersections of the system with the hyperplane, one can produce a *picture* of the system behavior. Throughout the rest of this discussion this hyperplane will be referred to as a *Poincare surface* and the *picture* of the intersections with the hyperplane will be referred to as the *Poincare section*. The Poincare section presents succinctly long term system behaviors, thereby providing an easy means to qualitative identify and interpret regions of phase space

exhibiting distinct behaviors. It is important to point out that a single point on the Poincare section contains sufficient information to fully reconstruct the system's complete trajectory at all past and future times. In figure 1.4, a graphical representation of an orbit as it intersects the Poincare surface is shown. A trajectory can intersect with the Poincare surface multiple times. If these intersections are regular (producing recognizable geometric patterns) one is inclined to believe that the trajectory is regular or quasiperiodic. While on the other hand if the intersections occur in a seemingly random manner one must suspect that the trajectory behavior is qualitatively chaotic.

Trajectories may also intersect with the Poincare surface at the same points repeatedly. This occurrence is mathematically expressed as,

$$X(T^*) = X(0) \quad (1.12)$$

where $X = (q_1, p_1, \dots, q_n, p_n)$ describes a point in phase space and T^* is the period of the orbit. These types of intersections are called fixed points and the corresponding trajectories are called principal orbits^{2,8,13}. The fundamental motions of the principal orbits dictate the types of motions that the system will exhibit in neighboring phase space. Because of their importance, locating these fixed points is often a first step in the analysis of a system's dynamical behavior and its relationship to the Poincare section.

One other feature of a Poincare surface is that a Poincare section can be observed as having two sides, which we might call positive and negative. The passage of a trajectory through the Poincare surface from the positive side to the negative side can be labeled as a positive intersection and conversely a passage from the negative to the positive side as a negative intersection.

In our study of the Na-Cu(001) system we have constructed the Poincare surface of section in a very straightforward manner. Since the PES that we have employed is two dimensional, the phase space variables are simply x , y , p_x , and p_y . The x and y are the coordinates and p_x and p_y are the corresponding momenta, all in the plane of the surface. The Poincare surface is defined as the phase plane which lies along the y axis at $x = a \cdot m$ where m is integer ($\dots, -1, 0, 1, \dots$). Thus when a trajectory passes through a unit cell and intersects points on the phase plane, the y momenta and y position are recorded to produce a Poincare section. Throughout this study the Poincare section will be a composite of both the positive and negative intersections with the Poincare surface.

The construction of a Poincare section typically involves one of two methods. A Poincare section can be constructed by recording the intersections of a single long trajectory with the Poincare surface. A single trajectory if initially within a regular region of phase space will, if run long enough, complete a regular orbit. This type of trajectory will not reveal any significant information about the system beyond its own existence. However, a

single trajectory which is started within region chaotic phase space will begin to interrogate the entire chaotic phase space. This chaotic type of trajectory can be viewed as an orbit with a nearly infinite recursion time. As the trajectory explores the phase space it will, in general, produce a map of the regular and chaotic phase space. The regular regions will, because they are exclusive to a chaotic orbit, remain unpenetrated by the trajectory, while the chaotic regions will be identifiable by the many irregular intersections with the Poincare surface.

A second method of constructing a Poincare section involves the calculation of many short trajectories. Many trajectories calculated which have initial starting conditions that are selected to sample the entire available phase phase in either a regular or random fashion. The cumulative intersections with the Poincare surface, by all the trajectories, are then used to create a single Poincare section. This method provides a more complete Poincare section, but is limited to observation of modest time scale behaviors.

Figure 1.5 is an example of a Poincare section generated using many short trajectories which were calculated using the FGVM potential. Clearly visible in this Poincare section are several distinct regions displaying characteristic behaviors. Regions of phase space corresponding to regular or quasiperiodic dynamics are marked with an 'A' in figure 1.5, and show regular patterns as trajectories progress through this type of phase space and repeatedly intersect the Poincare surface. These areas of the Poincare section contain a high density of periodic orbits (only a few of which are shown). Trajectories residing in chaotic regions of phase space will repeatedly intersect the Poincare surface in an irregular manner creating a *stochastic sea* of intersections, see figure 1.5. The co-existence of both regular and chaotic regions on a Poincare section is of immense interest because when it occurs a third type of behavior may be observed (which is not evident on this Poincare section). This third type of behavior occurs when a chaotic trajectory nears the edge of a regular region of phase space. As a trajectory approaches the outer boundary of a regular region it can acquire stability from the regular region and tends to cling to its outer edge. This stabilization is a transitory effect and the orbit eventually returns to the bulk stochastic sea. The behavior of these *sticky* (Levy) trajectories is extremely interesting. The duration of *stickiness* and how trajectories enter and exit from their *sticky* Levy behavior is the subject of much study^{5,6,24}. However, the stabilization of dynamic behaviors in the regions of phase space surrounding the quasiperiodic region does not always occur. Only special types of regular regions exhibit this stabilizing property. Those that do are generally referred to as stable attractors, and those which do not are referred to as strange attractors^{2,8}

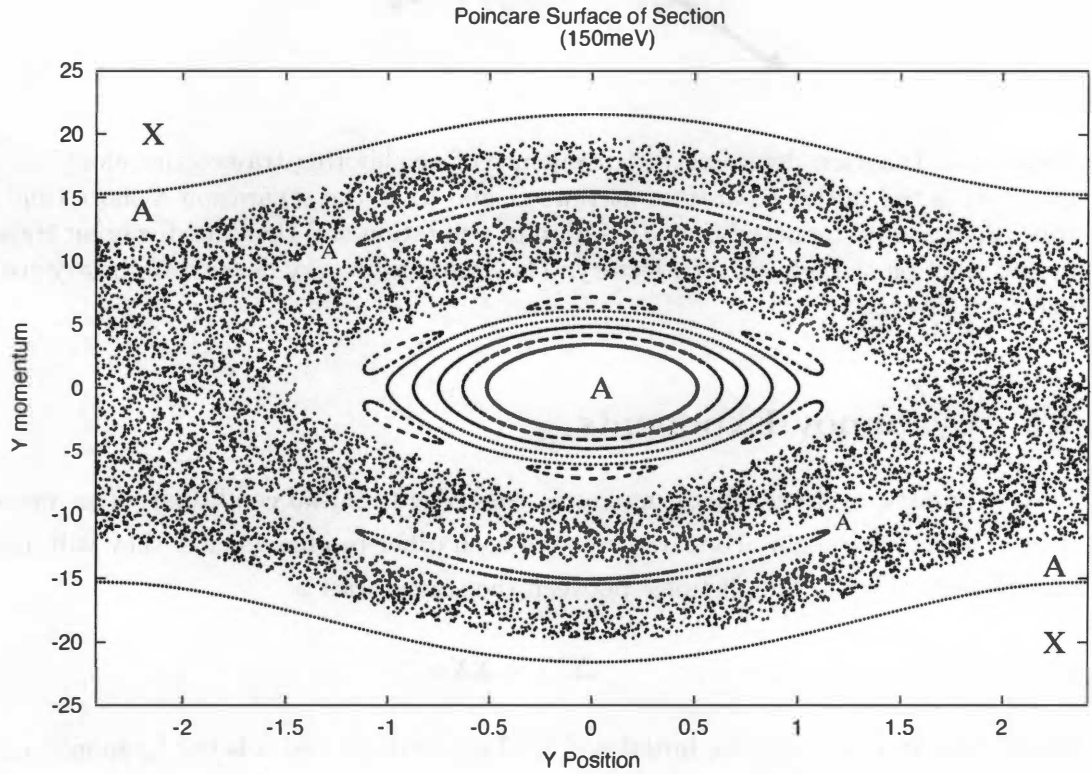


Figure 1.5: Explanation of the regions of a Poincare section. Regions (A) are regions of regularity; Regions (X) are energetically unavailable regions; Speckled area is the chaotic region or *stochastic sea*. The boundary between A and X regions is the energetic limit of the system. The geometric features contained within the regions of regular phase space are the Poincare intersections of regular periodic orbits.

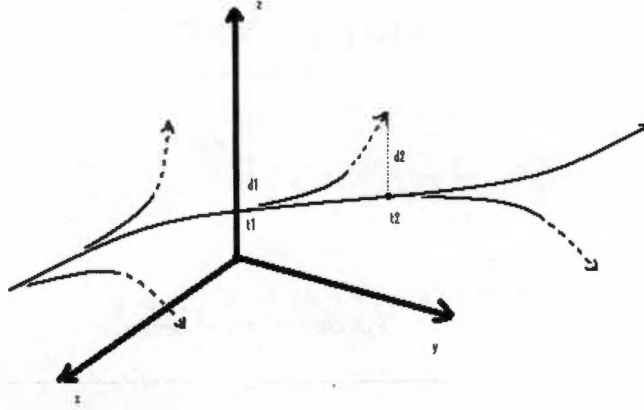


Figure 1.6: Diagram depicting the divergence of neighboring trajectories along a fiduciary path. $d1$ is the initial separation at time $t1$ and $d2$ is the separation a short time later at time $t2$. It should be noted that $d1$ is a finite separation and that the diverging trajectories do not start on the fiduciary trajectory. They only begin very near the fiduciary trajectory and then diverge.

1.5 Lyapunov Exponents

In deterministic systems, chaos implies a sensitivity to initial conditions. This means that if two trajectories begin arbitrarily close to each other in phase space, they will diverge at an exponential rate. The distance between the trajectories is

$$\Delta X_t = \Delta X_o e^{\lambda t}, \quad (1.13)$$

where ΔX_o and ΔX_t are the initial and final separations, and λ is the Lyapunov exponent which gives the rate of exponential divergence between states. A graphical example of the divergence of nearby trajectories is shown in figure 1.6. Solving for the Lyapunov exponent, equation 1.13 becomes

$$\lambda = \lim_{t \rightarrow \infty} \frac{1}{t} \ln \left[\frac{\Delta X_t}{\Delta X_o} \right]. \quad (1.14)$$

This formal definition of the Lyapunov exponent is more rigorously defined as a converging value as time approaches to infinity. It is important to observe that this definition is based on the asymptotic behavior of a system. Any information about short time dynamics is lost in this formal definition.

To illustrate this definition of the Lyapunov exponents, consider two trajectories which separate at a rate which is less than exponential. Under these conditions, in the limit of infinite time the Lyapunov exponent will converge to a value of zero. Again using this equation, consider two trajectories residing on a unstable or chaotic manifold. They diverge

at an exponential rate (chaotic manifold) and the Lyapunov exponent should converge a finite value. Thus, one can define a criterion which can be used to discriminate between chaotic and regular behaviors, where

$$\begin{aligned}\lambda &> 0 && \text{chaotic motion} \\ \lambda &= 0 && \text{regular motion.}\end{aligned}\tag{1.15}$$

In multidimensional systems we can further refine our definition of the Lyapunov exponents. We can define an initial trajectory separation as a unit vector $\vec{X}_o$ which resides on a hypersphere surrounding a fiducial trajectory. The principal axes of the hypersphere correspond to phase space coordinate separations (Δx , Δy , Δp_x , and Δp_y). In conservative systems as the hypersphere evolves in time it deforms into a hyperellipsoid whose volume is guaranteed by Liouville's theorem³ to remain constant. This constraint requires that expansions or contractions along some axes must be compensated by contractions or expansions along the other axes. The Lyapunov exponents in a multidimensional system are then defined as

$$\lambda_i = \lim_{t \rightarrow \infty} \frac{1}{t} \ln \left[\frac{\Delta \vec{X}_t}{\Delta \vec{X}_o} \right], \tag{1.16}$$

where each phase space coordinate separation has a corresponding Lyapunov exponent (λ_i), which measures the rates of expansion or contraction along that phase space coordinate. Oseledec's theorem of ergodicity²² dictates that for a four coordinate system with a singular constraint (constant energy) the Lyapunov exponents should occur in two pairs. One pair will have two Lyapunov exponents whose values are both zero. The second pair will have a two Lyapunov exponents whose sum is equal to zero. The result of this pairing is a zero change in volume for the hyperellipsoid. A consequence of this relationship is that the divergence of trajectories is controlled by the expansion along a single principal axis, whose corresponding Lyapunov exponent is referred to as the *largest Lyapunov exponent*. During further discussions, unless otherwise stated, when referring to either Lyapunov exponents or Lyapunov values, the largest Lyapunov exponent will be the implied meaning.

The calculation of the Lyapunov exponent is not quite as simple as it might at first seem. One might simply assume that to calculate the Lyapunov exponent, one could calculate a fiducial trajectory. Then one could calculate a few trajectories within an arbitrarily small hyperellipsoid surrounding the fiducial trajectory and then follow the divergence of these trajectories in time. One could then determine which trajectory diverged the most and calculate its Lyapunov exponent. However because of the fundamental nature of chaotic systems and their sensitivity to initial conditions, when trajectories are started infinitesimally close to each other, possibly with $\Delta \vec{X}_o$ equal to the minimum of machine precision, the divergence between the trajectories will grow at an exponential rate. This results in Lyapunov

exponents which may rapidly grow at computationally unmanageable sizes. Additionally, this method may completely miss or only crudely identify the vector along which the largest Lyapunov exponent lies, thus to reliably determine Lyapunov exponents a different method must be devised.

1.5.1 Tangent Space Method

Wolf et al.²⁷ developed a robust method for numerically determining the Lyapunov exponent. This method uses linearized equations of motion to approximate the time evolution growth of the hyperellipsoid, developed by Wolf et al.²⁷. Eckmann et al. concisely presents this algorithm in several articles^{7,9,10}. This method commonly referred to as the *tangent space method* was employed in the determination of Lyapunov exponents in this study.

Examining the foundation for this method, one can represent the time evolution of a system with the function F , which in this instance represents the trajectory of the system obtained by using the velocity Verlet algorithm to solve the Newtonian equations of motion.

$$\vec{x}_t = F(\vec{x}_0) \quad (1.17)$$

$$\vec{x}_t + \delta\vec{x}_t = F(\vec{x}_0 + \delta\vec{x}_0), \quad (1.18)$$

where $\vec{x}_t$ in equation 1.17 is the new state at time t of the system which was initially located at the phase point $\vec{x}_0$. The vector $\delta\vec{x}_0$ in equation 1.18 is an infinitesimal hyperellipsoid surrounding the fiduciary trajectory and $\delta\vec{x}_t$ is the evolution hyperellipsoid after time t . The purpose of this method is to provide a means to estimate the divergence ($\delta\vec{x}_t$) between trajectories without requiring the calculation of the secondary trajectories ($F(\vec{x}_0 + \delta\vec{x}_0)$).

Constructing a Taylor series expansion of F at $\vec{x}_0$ (equation 1.18) and keeping only the first order term produces the equation,

$$F(\vec{x}_0 + \delta\vec{x}_0) = F(\vec{x}_0) + \frac{\delta F(\vec{x}_0)}{\delta\vec{x}} \cdot \delta\vec{x}_0, \quad (1.19)$$

where $\frac{\delta F}{\delta\vec{x}}$ is the Jacobian matrix (J) of F with respect to the components of the state vector $\vec{x}$. Subtracting the function $F(\vec{x}_0)$ from $F(\vec{x}_0 + \delta\vec{x}_0)$ to estimate the divergence at time t between the trajectories started at $\vec{x}_0$ and $\vec{x}_0 + \delta\vec{x}_0$ gives

$$\delta\vec{x}_t = F(\vec{x}_0 + \delta\vec{x}_0) - F(\vec{x}_0) = \frac{\delta F(\vec{x}_0)}{\delta\vec{x}} \cdot \delta\vec{x}_0 \quad (1.20)$$

Evaluating the divergence of trajectories for longer periods of time can be determined

by the iterative application of this method.

$$F^N(\vec{x}_o + \delta\vec{x}_o) - F^N(\vec{x}_o) = \frac{\delta^N F(\vec{x}_{N-1})}{\delta\vec{x}} \cdot \delta\vec{x}_o, \quad (1.21)$$

where N is the number of iterative steps taken and the superscript notation is defined as follows,

$$F^N(\vec{x}_o) = F(F(\dots(F(\vec{x}_o))\dots)) \quad (1.22)$$

and

$$\frac{\delta^N F(\vec{x}_{N-1})}{\delta\vec{x}} = \frac{\delta F(\vec{x}_{N-1})}{\delta\vec{x}} \cdot \frac{\delta F(\vec{x}_{N-2})}{\delta\vec{x}} \cdot \dots \cdot \frac{\delta F(\vec{x}_o)}{\delta\vec{x}} \quad (1.23)$$

The long term behavior of the hyperellipsoid surrounding the principal trajectory is then determined by multiplying the successive Jacobian matrices evaluated as the trajectory evolves in time,

$$\delta\vec{x}_n = \frac{\delta^N F(\vec{x}_{N-1})}{\delta\vec{x}} \cdot \delta\vec{x}_o. \quad (1.24)$$

This equation is relatively simple to evaluate allowing us to determine the vector along which the greatest growth has occurred. Using these vectors, $\delta\vec{x}_o$ and $\delta\vec{x}_t$, the largest Lyapunov exponent can be calculated,

$$[\mathcal{J}] \times [\vec{x}_o] = [\vec{x}_t], \quad (1.25)$$

by evaluating the eigenvectors and eigenvalues using standard linear algebra techniques.

Implementing this method in our 2 dimensional system, the Jacobian is defined as

$$J = \begin{bmatrix} df(x)/dx & df(x)/dy & df(x)/dp_x & df(x)/dp_y \\ df(y)/dx & df(y)/dy & df(y)/dp_x & df(y)/dp_y \\ dp(x)/dx & dp(x)/dy & dp(x)/dp_x & dp(x)/dp_y \\ dp(y)/dx & dp(y)/dy & dp(y)/dp_x & dp(y)/dp_y \end{bmatrix}, \quad (1.26)$$

where $f(x)$ and $p(x)$ are the functions of position and momentum, respectfully. Using the velocity Verlet definitions of motion (equations 1.10 and 1.11) the individual Jacobian components become;

$$df(x)/dx = 1 - \frac{1}{2m} \left(\frac{d^2 U(x_o, y_o)}{dx^2} \right) \Delta t^2, \quad (1.27)$$

$$df(x)/dy = df(y)/dx = -\frac{1}{2m} \left(\frac{d^2 U(x_o, y_o)}{dydx} \right) \Delta t^2, \quad (1.28)$$

$$df(y)/dy = 1 - \frac{1}{2m} \left(\frac{d^2 U(x_o, y_o)}{dy^2} \right) \Delta t^2, \quad (1.29)$$

and

$$dp(x)/dx = -\frac{1}{2} \left(\frac{d^2U(x_o, y_o)}{dx^2} + \frac{d^2U(x_1, y_1)}{dx^2} \right) \Delta t^2, \quad (1.30)$$

$$dp(x)/dy = dp(y)/dx = -\frac{1}{2} \left(\frac{d^2U(x_o, y_o)}{dxdy} + \frac{d^2U(x_1, y_1)}{dxdy} \right) \Delta t^2, \quad (1.31)$$

$$dp(y)/dy = -\frac{1}{2} \left(\frac{d^2U(x_o, y_o)}{dy^2} + \frac{d^2U(x_1, y_1)}{dy^2} \right) \Delta t^2, \quad (1.32)$$

where the subscripts 0 and 1 refer to the last and current time step positions, respectively. The terms in the last two columns reduce to the following

$$\begin{bmatrix} df(x)/dp_x & df(x)/dp_y \\ df(y)/dp_x & df(y)/dp_y \end{bmatrix} = \begin{bmatrix} \Delta t/m & 0 \\ 0 & \Delta t/m \end{bmatrix} \quad (1.33)$$

and

$$\begin{bmatrix} dp(x)/dp_x & dp(x)/dp_y \\ dp(y)/dp_x & dp(y)/dp_y \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad (1.34)$$

The product of multiplying together the Jacobian for each step is

$$\mathcal{J} = J^N \times J^{N-1} \times \dots J^1 \times J^0, \quad (1.35)$$

which gives the net Jacobian $\mathcal{J}$ for the trajectory, as in equation 1.24,

$$\delta \vec{x}_t = \mathcal{J} \vec{x}_0. \quad (1.36)$$

Neither the initial separation $\vec{x}_0$ nor the final separation $\vec{x}_t$ need to be explicitly specified to employ this method. Once the net Jacobian $\mathcal{J}$ has been calculated its eigenvectors and eigenvalues can be determined. These can then be used to determine the initial vector along which the maximum divergence occurs. Using typical linear algebra notation this method is expressed as

$$M \vec{A} = \Lambda \vec{A} \quad (1.37)$$

where M is a matrix, Λ is the largest eigenvalue of M and $\vec{A}$ is the corresponding eigenvector.

The eigenvalue Λ is then a direct measure of the largest divergence which occurs for the fiduciary trajectory. The Lyapunov exponent is simply calculated as

$$\lambda = \lim_{t \rightarrow \infty} \frac{1}{t} \ln [\Lambda]. \quad (1.38)$$

The principal approximations involved in this method are first, the use of linear approximations to evaluate the divergence of the tangent phase space. The error of this approximation is, for a system which has well behaved derivatives, controlled by time step

size (Δt). We have treated this in the same manner as we did for the velocity Verlet integration step size, using the same step size for both the MD and the Lyapunov exponent calculations. A second possible approximation is the evaluation of the derivatives contained within the Jacobian matrices. However during the evaluation of each Jacobian, analytical derivatives of the PES have been employed. These derivatives were taken directly from analytical derivatives of the FGVM potential and therefore have no contribution to the overall error of this method.

This method then provides a means to calculate Lyapunov exponents in a reliable manner, and does not suffer from the limitations which occur during the direct method of calculating Lyapunov exponents. The tangent space method does have some significant drawbacks. The evaluation of the Jacobian matrix for each time step is computationally expensive, as is the multiplication of the individual matrices to obtain the net Jacobian. The computational expense of this method is sufficient enough to prevent it from being liberally applied to every trajectory calculation, limiting its use to prudently chosen trajectories which might provide insight for specific questions.

Chapter 2

Initial Investigation

We began studying the diffusion properties of this system by running MD simulations at several different energies. These simulations were calculated using the FGVM potential and the velocity Verlet MD integrator. The behaviors of this system will be studied at energies between 85 and 155 meV. Below 85 meV the barrier heights of the FGVM potential are sufficiently high to prevent nearly all diffusive motions and above 155 meV diffusive motions become predominately ballistic in nature. It is within this energy range that we hope to observe a mixture of normal and anomalous diffusive motions.

In the lower energy regime, 85-95 meV, trajectories exhibit a mixture of ballistic and normal diffusive motion. Figure 2.1 is a plot of a typical trajectory at 85 meV. In this figure, there two distinct motions. First, there are stretches of time during which the diffusing particle rambles around in a meandering fashion. This type of motion is well modeled by random walk formalisms, with an MSD that increases linearly with time, and thus represents normal diffusive motion. There are also stretches of time during which the adatom undergoes long unimpeded flights which correspond to a nearly quadratic time dependence of the MSD. Additionally, there appears to be two differing types of ballistic motions. First, there are ballistic flights which occur parallel to the x and y axes. The other type of ballistic flights occur at diagonal angles of 45 degrees.

The trend in occurrences for ballistic flights appears to be energy dependent. At 85 meV the relative rate of occurrence for ballistic flights is high, but as the system energy increases the frequency of occurrence rapidly diminishes, between 85 and 95 meV. The occurrence of ballistic flights at 95 meV is very low.

At energies between 95-110 meV, there are no occurrences of ballistic flights. Figure 2.2 is a typical trajectory calculated at 105 meV. Throughout the entire trajectory are no observable flights of extended length, with respect to scale of general motion. The particle's trajectory is seemingly random and uncoordinated. In this energy region, diffusive motion is almost exclusively characterizable as normal, with a MSD that is expected to increase

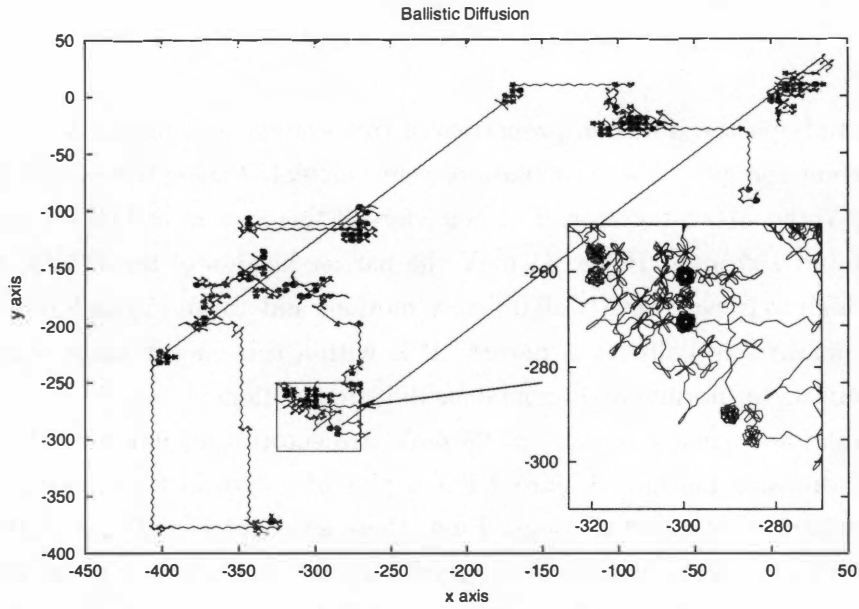


Figure 2.1: Diffusion trajectory simulation ($0.012\mu\text{sec}$) at 85 meV. The long unperturbed periods of motion are ballistic motions or Levy-like flights. Notice there are two *types* of ballistic motion, horizontal flights and diagonal flights. Inset box shows an expanded view of a period of normal diffusive motion, which is characterizable by short meandering motion (*drunkard walk*).

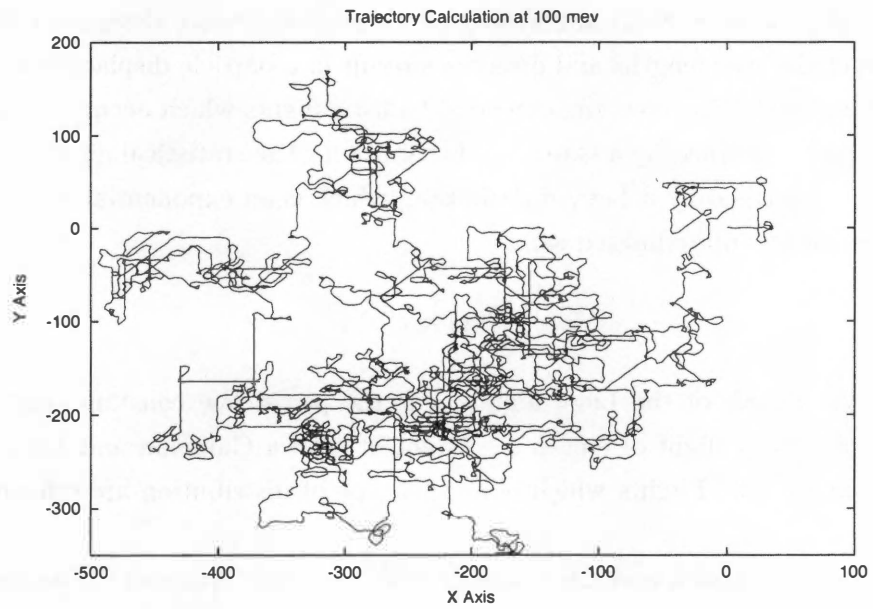


Figure 2.2: Diffusion trajectory simulation ($0.012\mu\text{sec}$) at 105 meV. This trajectory exhibits typical diffusive motion ($0.012\mu\text{sec}$). This trajectory may at first appear to contain ballistic flights, but these straight flights are within the normal Gaussian distribution for this system.

linearly with time.

The trajectory depicted in figure 2.2 may at first appear to contain ballistic (Levy-like) flights. The trajectory contains short segments which are straight. But the lengths and frequencies of these *straight* flights are well described by the standard Gaussian statistical distribution for normal diffusive motions.

It is in the lower energy range, 85 to 95 meV, where we have observed straight flights which differ significantly in length scale when compared to the rest of the trajectory's diffusive motions. Using this observation we must clarify our definition of what are Levy flights.

During the analysis of diffusion, diffusive motion can be described as a series of steps. Each step is the distance a diffusing particle travels before changing directions. The distribution of the step lengths and directions result in a particle displacement distribution which is Gaussian²¹. However, the extended ballistic flights which occur during anomalous diffusion are not described by a Gaussian distribution. The statistical distribution of ballistic flights are described by a Levy distribution, which is an exponential distribution. This distribution can be approximated as,

$$P(x) \approx e^{m|x|}, \quad (2.1)$$

where x is the length of the Levy flight, m is the power law constant, and $P(x)$ is the probability of a Levy flight of length x . A plot of both a Gaussian and Levy distribution is shown in figure 2.3. Flights which obey this type of distribution are referred to as Levy flights²⁴.

Both the Gaussian and Levy distributions are scale invariant¹⁹. As an example of scale invariance, we can imagine a diffusion system which exhibits only normal diffusive motion. We can expect that at some arbitrarily low energy the motion of a particle is slow and the distance it travels is short. In addition, we can expect that at significantly higher energy the motion of a particle is very fast and the distance it travels is very long. In both cases, the particle's displacement fluctuations are described by a Gaussian distribution, but length scale of the two Gaussian distributions differ. Likewise, we can imagine then a diffusion system which exhibits anomalous diffusion and at differing energies the length scales of the ballistic flights changes, but the distribution of the ballistic flights in both instances obeys a Levy distribution.

The scale invariance of these distributions implies that the length of a single flight can not be used to identify it as either Gaussian or Levy. Only an analysis of an ensemble of flights can be used to identify whether an ensemble is either Gaussian or Levy.

As the system energy is increased further, between 110-155 meV, ballistic flights begin to occur again and increase in frequency as the system energy increases. A trajectory

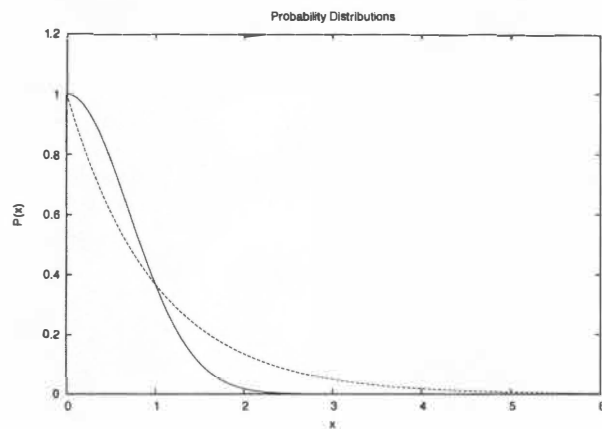


Figure 2.3: Probability distributions; Gaussian distribution, solid line. Levy distribution, dotted line

calculated at 155 meV shown in figure 2.4 is representative of the behavior exhibited in this energy region. These ballistic flights do not occur as frequently as they did in the low energy regime, but their reappearance in this regime is interesting. This reoccurrence suggests that a unique combination of parameters are necessary for the ballistic flights to exist.

The occurrence of both normal and ballistic diffusive motions results in an overall diffusion distribution which is then a superposition of both Gaussian and Levy distributions.

The occurrence of these Levy-like flights is an interesting behavior which is not explained by classic diffusion models. In order to better understand their origins and how they relate to the overall diffusion motions, we will attempt to characterize the phase space from which they originate.

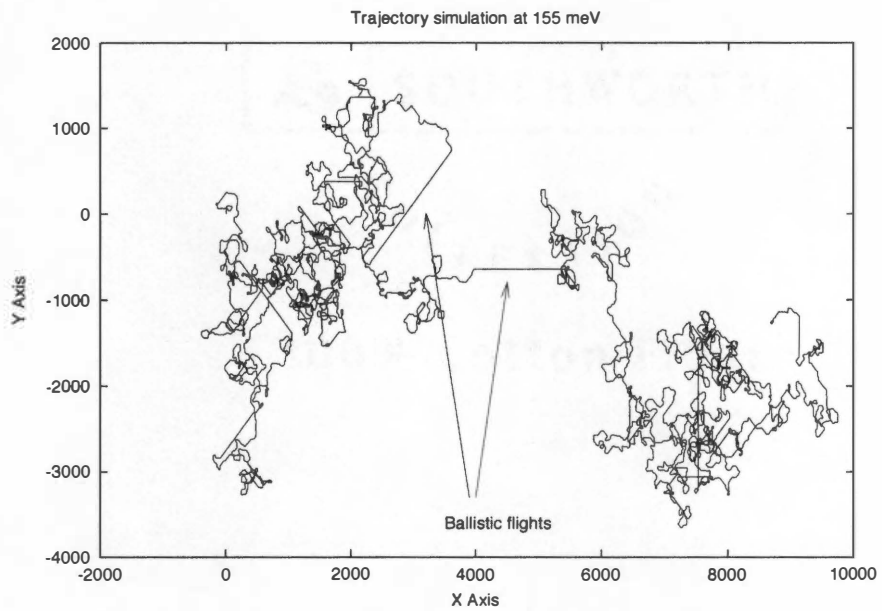


Figure 2.4: Diffusion trajectory simulation ($0.012\mu\text{sec}$) at 155 meV. This trajectory exhibits typical diffusive motion inter-mixed with occasional Levy-like flights. Arrows depict periods of ballistic motion.

Chapter 3

Poincare Surfaces

3.1 Calculation of Poincare Sections

During our initial investigation of the Na-Cu(001) system, we have created Poincare sections at several several evenly spaced energies between 85 and 155 meV. The hyperplane for these Poincare surfaces were set at $x = a \cdot m$, where a is the lattice constant and m is an integer. The Poincare sections were created by first determining the energetic boundary of the available phase space, then performing a grid sampling of the allowed phase space. On the Poincare surface the grid sampling started at the origin ($y = 0, p_y = 0$) and extended to the energetic boundary of the system with a grid spacing which divided the positive y space and positive p_y space into 20 evenly spaced sample points, producing a little over 200 sample points per Poincare surface.

Beginning at each sample point a MD diffusion trajectory was calculated for 20 million time steps, with each time step equal to one atomic time unit. The y and p_y values values for intersections of these trajectories with the Poincare surface were then recorded. These individual trajectory Poincare sections were then combined to produce a single compound Poincare section which was a thorough map of the available phase space. The result of this method was a compound Poincare section in which almost every energetically allowed point on the section was filled. This excessive amount of data prevented any direct interpretation of the Poincare sections. To reduce the density of data points, only a select few data sets were combined to produce a compound Poincare section which could provide fruitful insight into system behaviors. Individual trajectories and their corresponding Poincare section were visually inspected. Then only trajectories or corresponding Poincare sections which displayed unique features were combined to form the compound Poincare section. During this selection process regular trajectories were excluded from the Poincare section, leaving empty phase space to represent areas of regular phase space. This simplified Poincare section maintains the essence of the original compound Poincare section while

presenting data with more interpretability.

3.2 Poincare Figures

The following Poincare sections in figures 3.1-3.15 have been constructed as previously discussed. Thick solid lines representing the energetic boundary of the system have been added to each Poincare section. All the intersections made by regular trajectories have been removed and as such their locations are demarked by an absence of points on the Poincare section. Chaotic regions of phase space are denoted by the stochastic peppering of trajectory intersections with the Poincare surface. Both the y coordinate and p_y momentum are plotted in atomic units.

3.3 Trends

Examining these Poincare sections sequentially, it becomes apparent that the contraction and dilation of regular regions of phase space occur in a predictable and well behaved manner. Starting at 80 meV we observe large regions of regular phase space throughout the entire Poincare section. Then as the system energy increases from 85 to 100 meV, the regular regions progressively contract. Between 100 and 115 meV the Poincare sections contain no apparent regions of stability. Then as the system energy increases further, from 115 to 155 meV, the regular regions return, growing progressively larger as the energy increases.

Comparing these trends in the contraction and expansion of the regular regions of phase space with some initial trajectory calculations, a strong relationship can be observed. Figure 2.1 is a trajectory calculated at 85 meV. During this trajectory there are periods of long ballistic motion which greatly enhances the diffusion of the particle. The corresponding Poincare section (calculated at 85 meV) in figure 3.1 shows large regions of regular dynamics within the available phase space. Examining figure 2.4, which is a diffusion trajectory at 155 meV again shows the presence of long ballistic flights which have again enhanced the diffusion of the particle. Its corresponding Poincare section in figure 3.15 also contains a large regular region. However at energies near 105 meV as shown in figure 2.2 these trajectories do not contain long ballistic flights. The corresponding Poincare section in figure 3.5 does not contain any visible regular regions.

A relationship between ballistic flights and regular regions of phase space clearly exists. As the regular regions expand and contract the occurrence of ballistic flights rises and falls. However, it can be concluded that quasiperiodic orbits contained within the regular regions do not participate directly in the diffusive process. This is because trajectories which sample the chaotic region of phase space cannot enter the regular regions. The occurrence

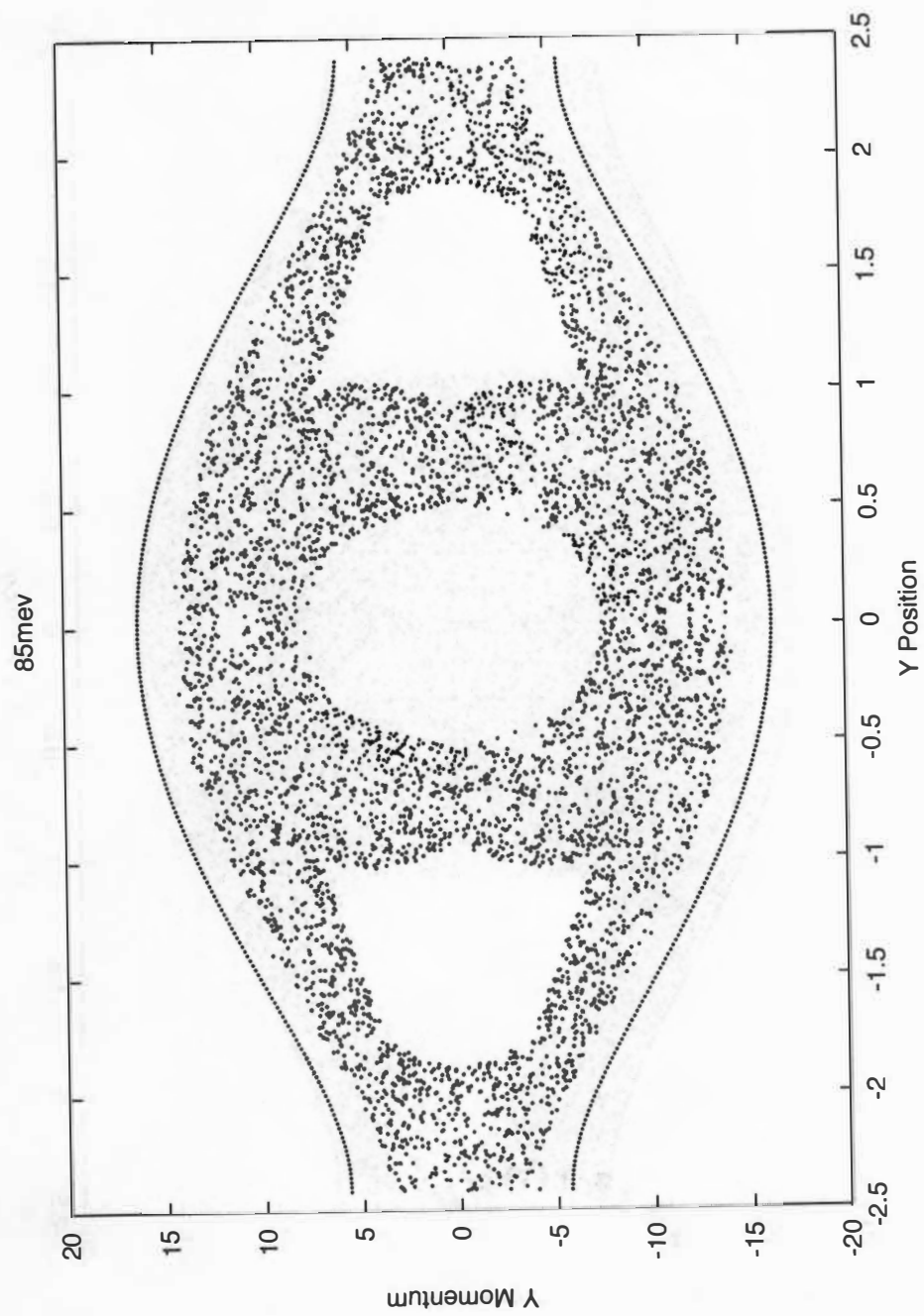


Figure 3.1: Poincare section (85 meV)

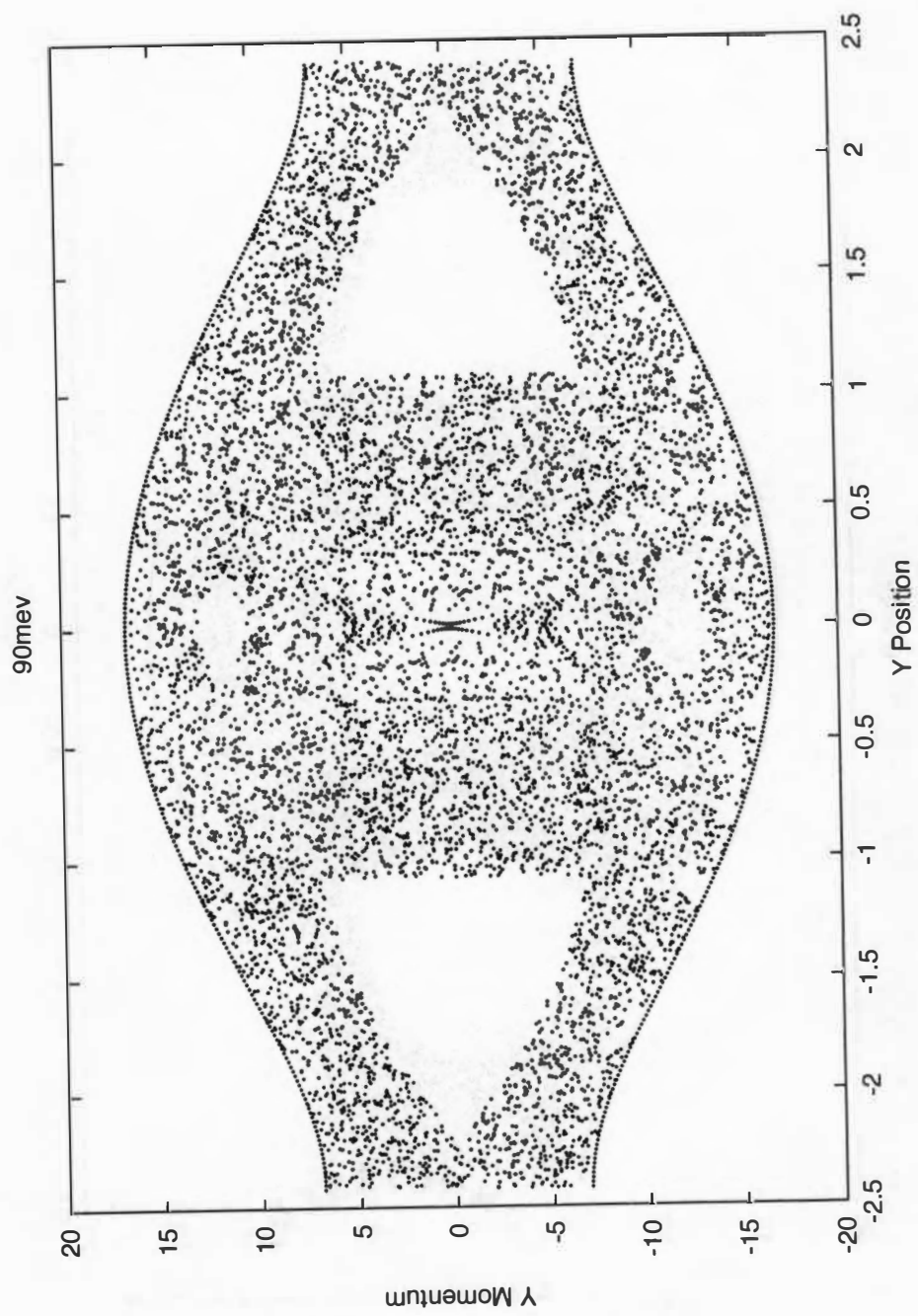


Figure 3.2: Poincare section (90 meV)

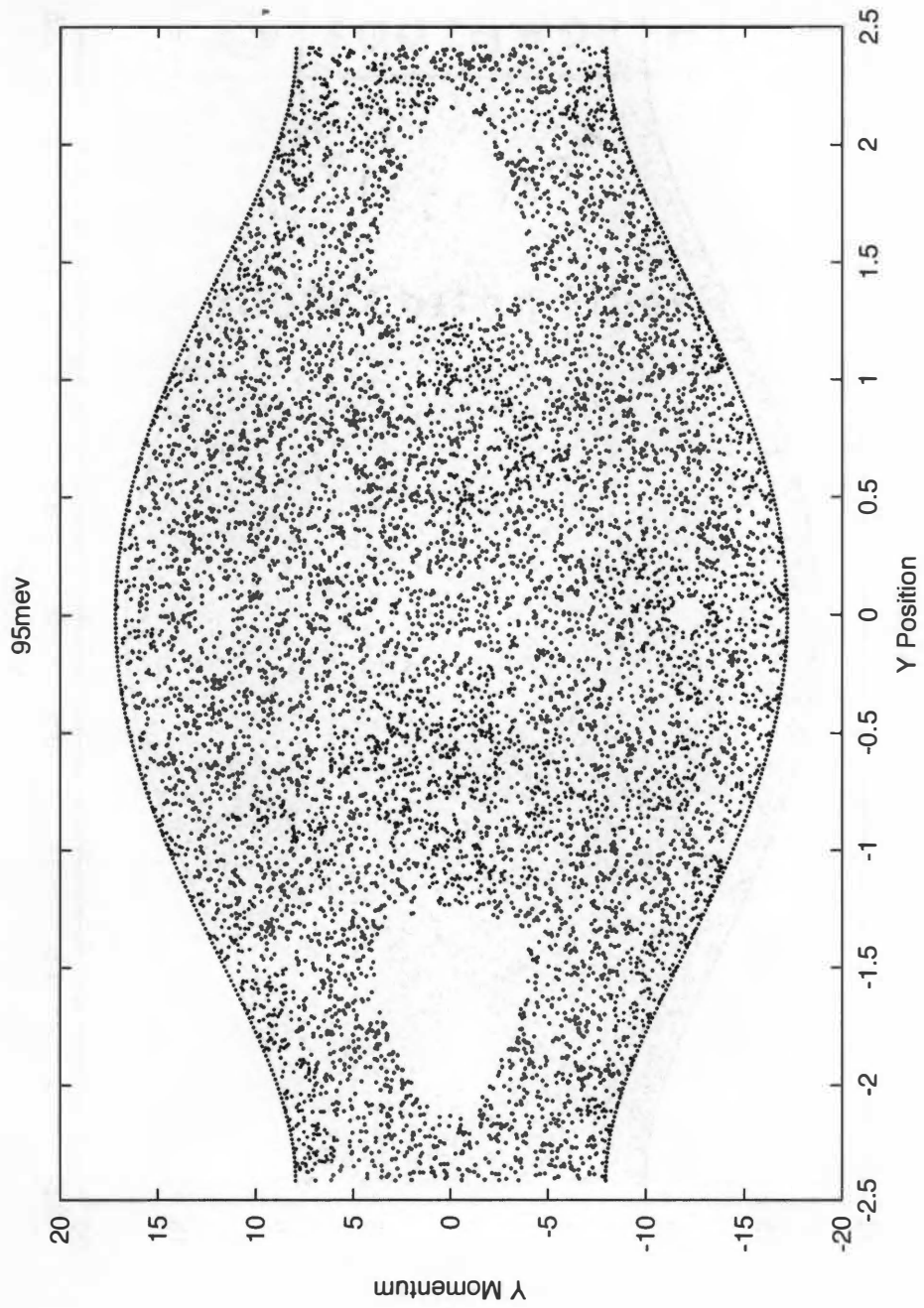


Figure 3.3: Poincare section (95 meV)

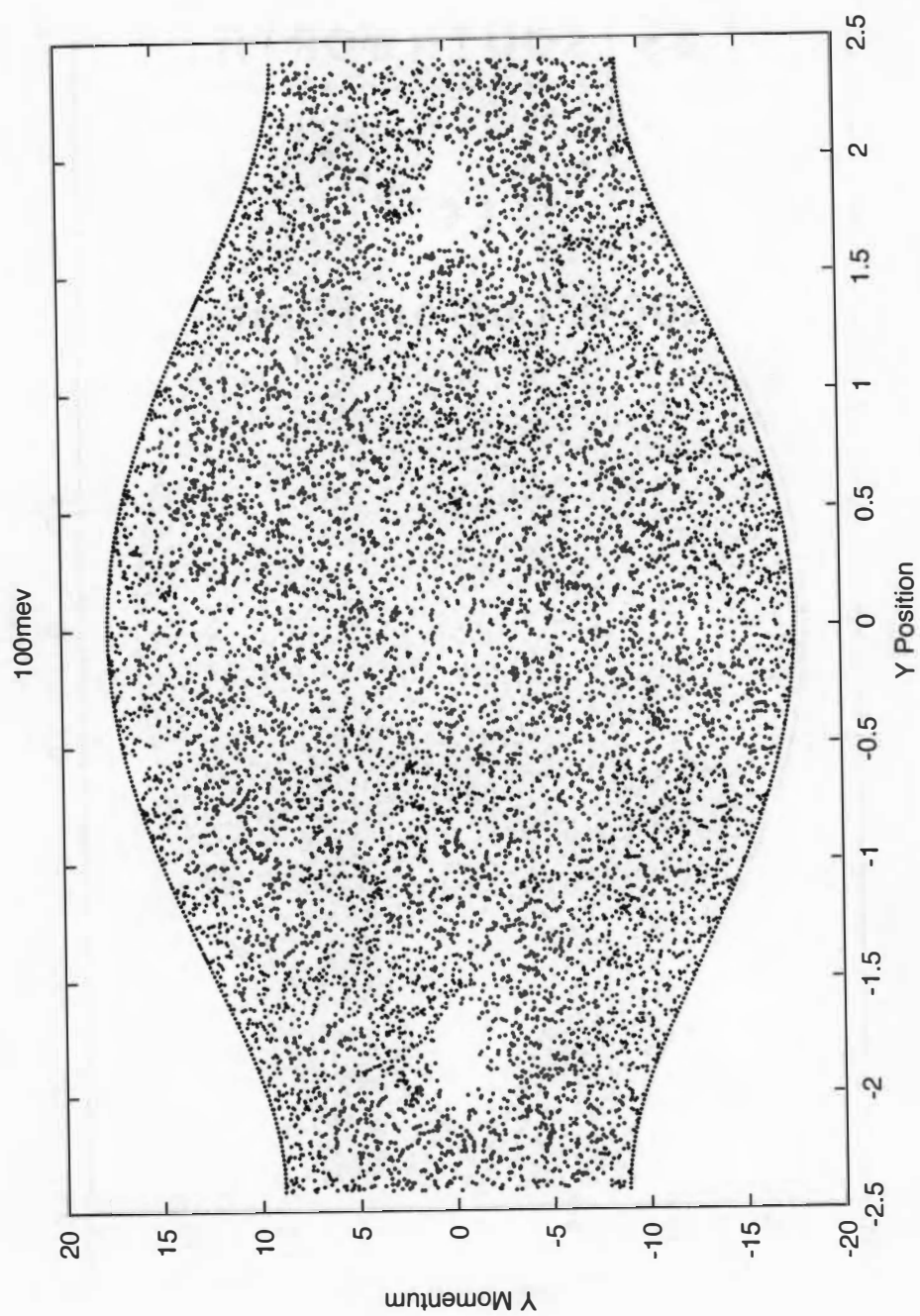


Figure 3.4: Poincare section (100 meV)

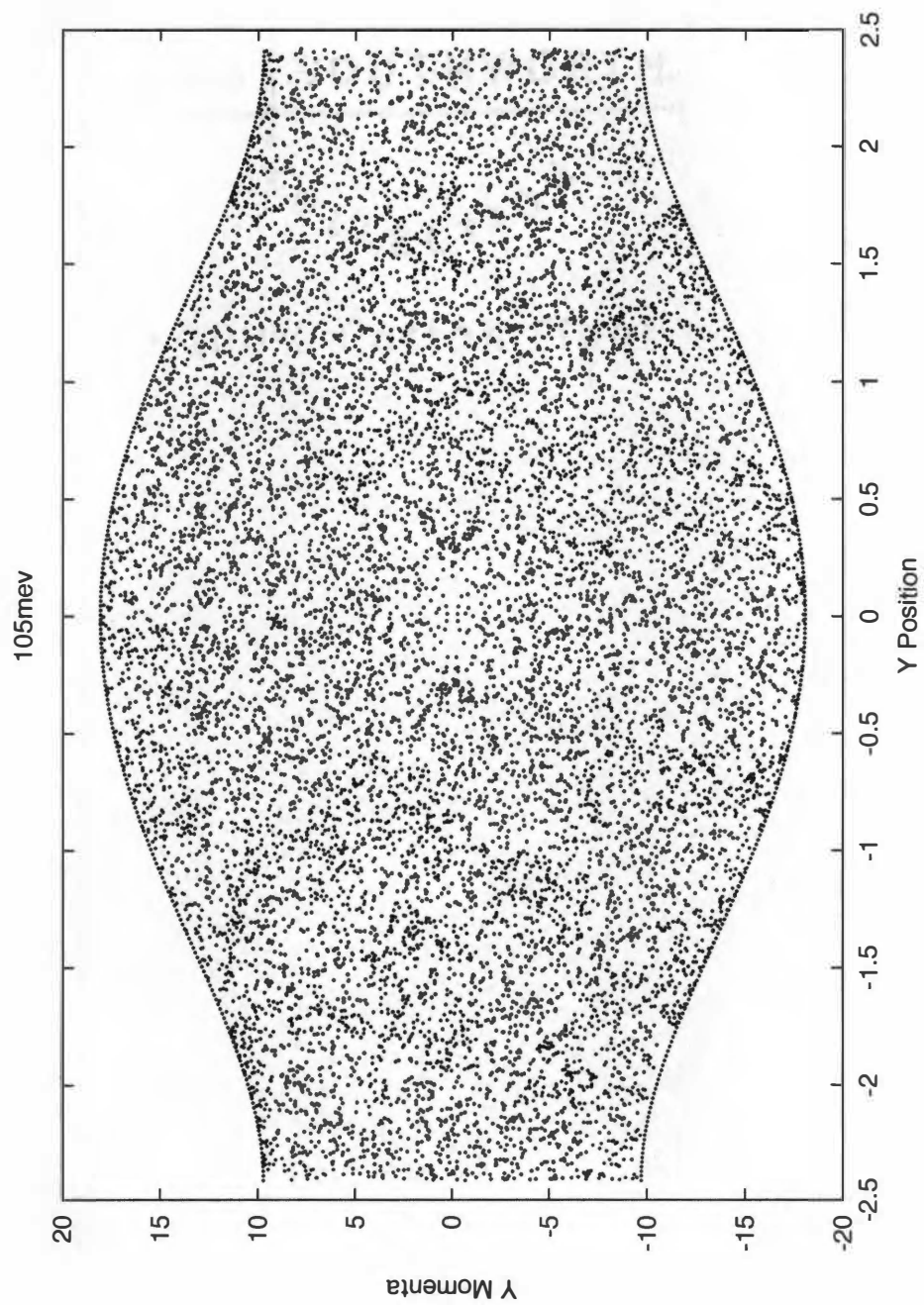


Figure 3.5: Poincare section (105 meV)

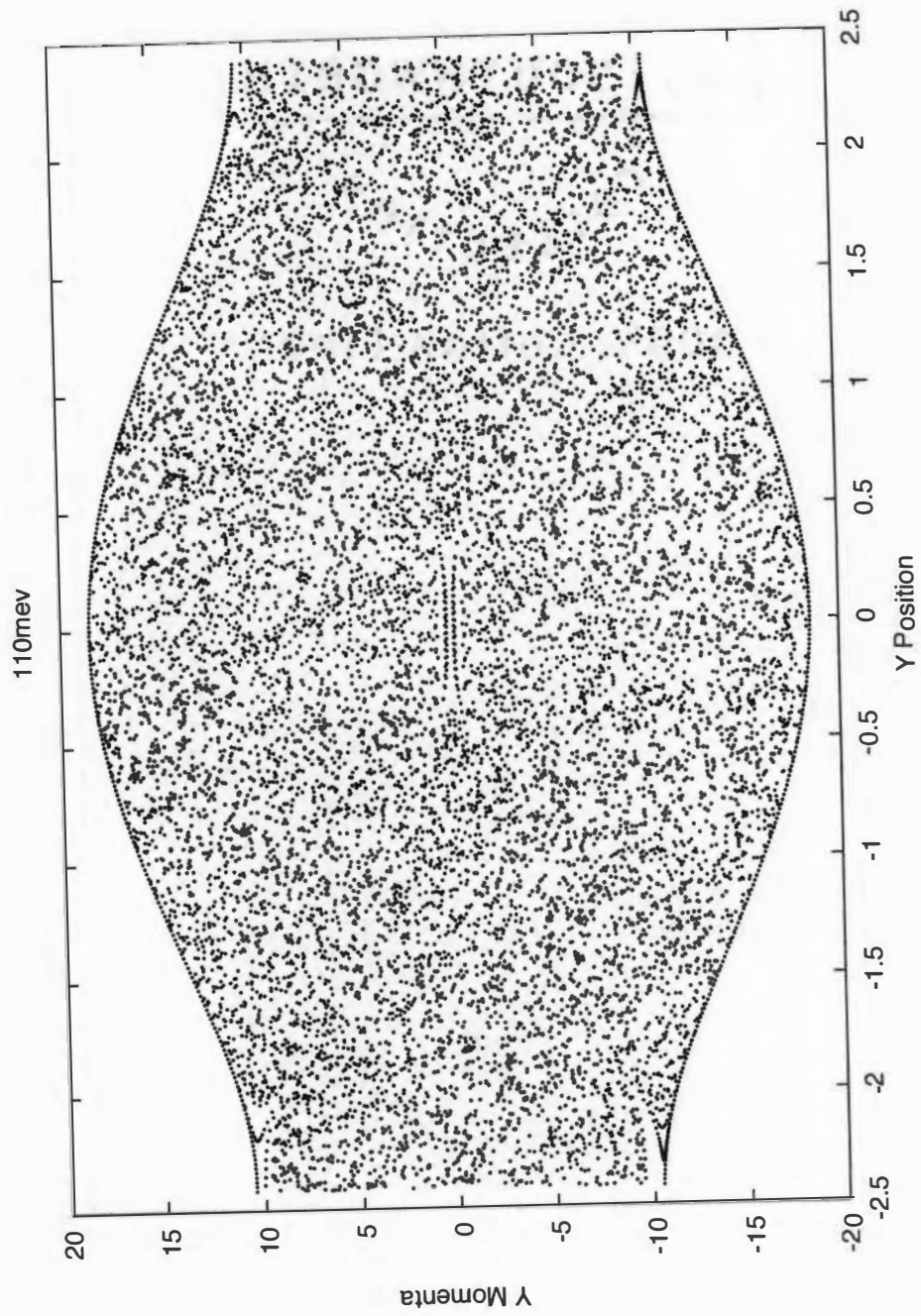


Figure 3.6: Poincare section (110 meV)

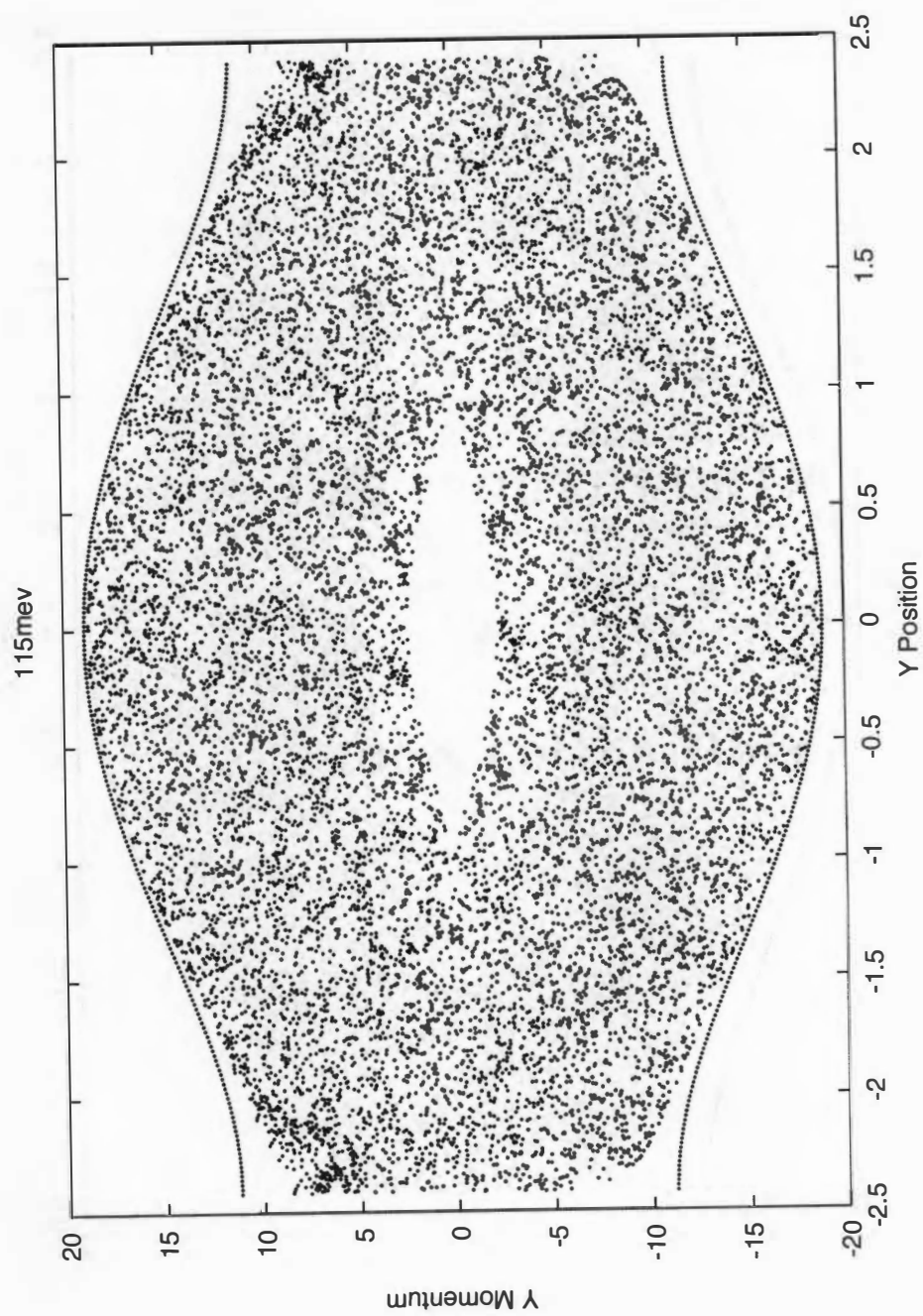


Figure 3.7: Poincare section (115 meV)

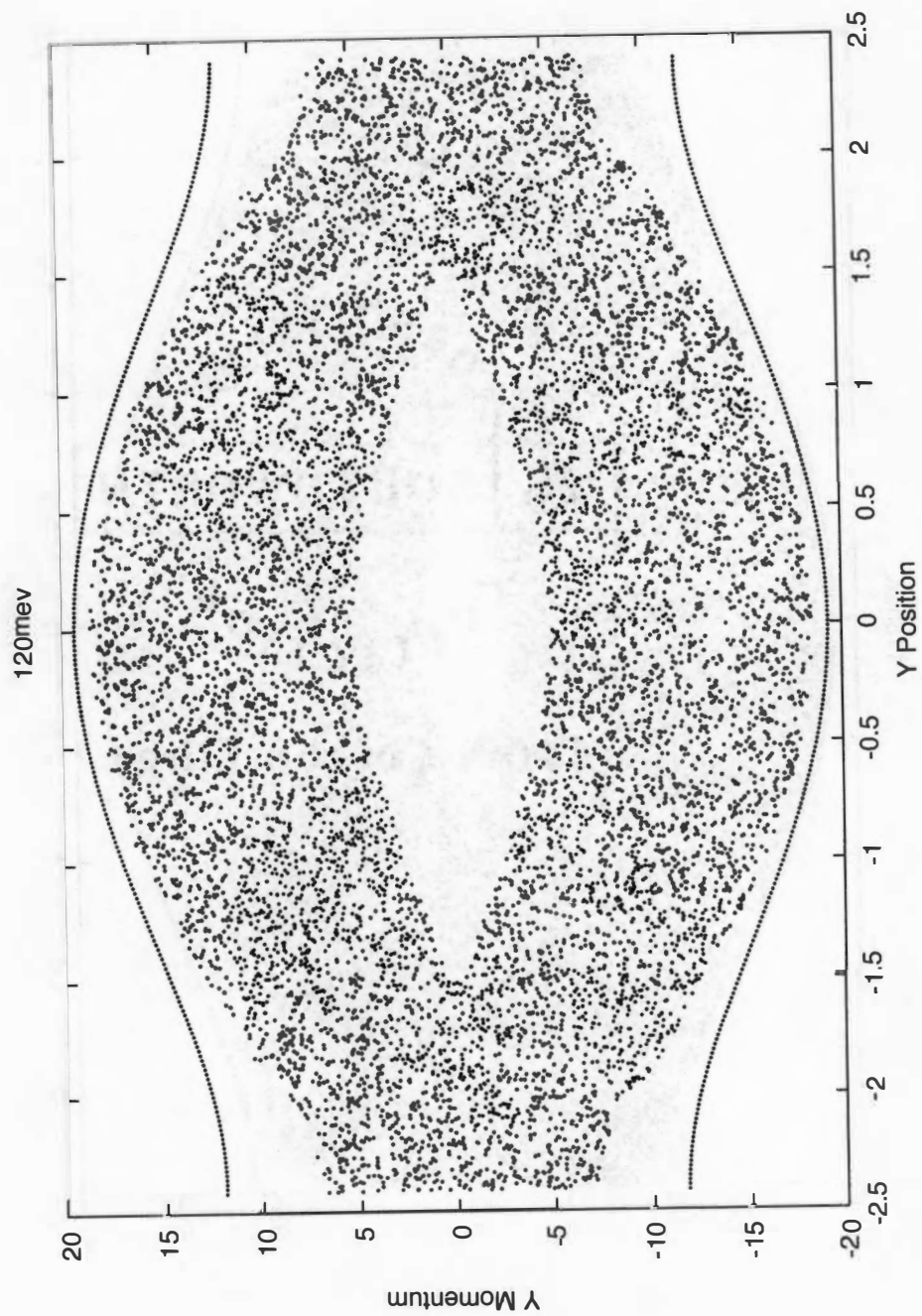


Figure 3.8: Poincare section (120 meV)

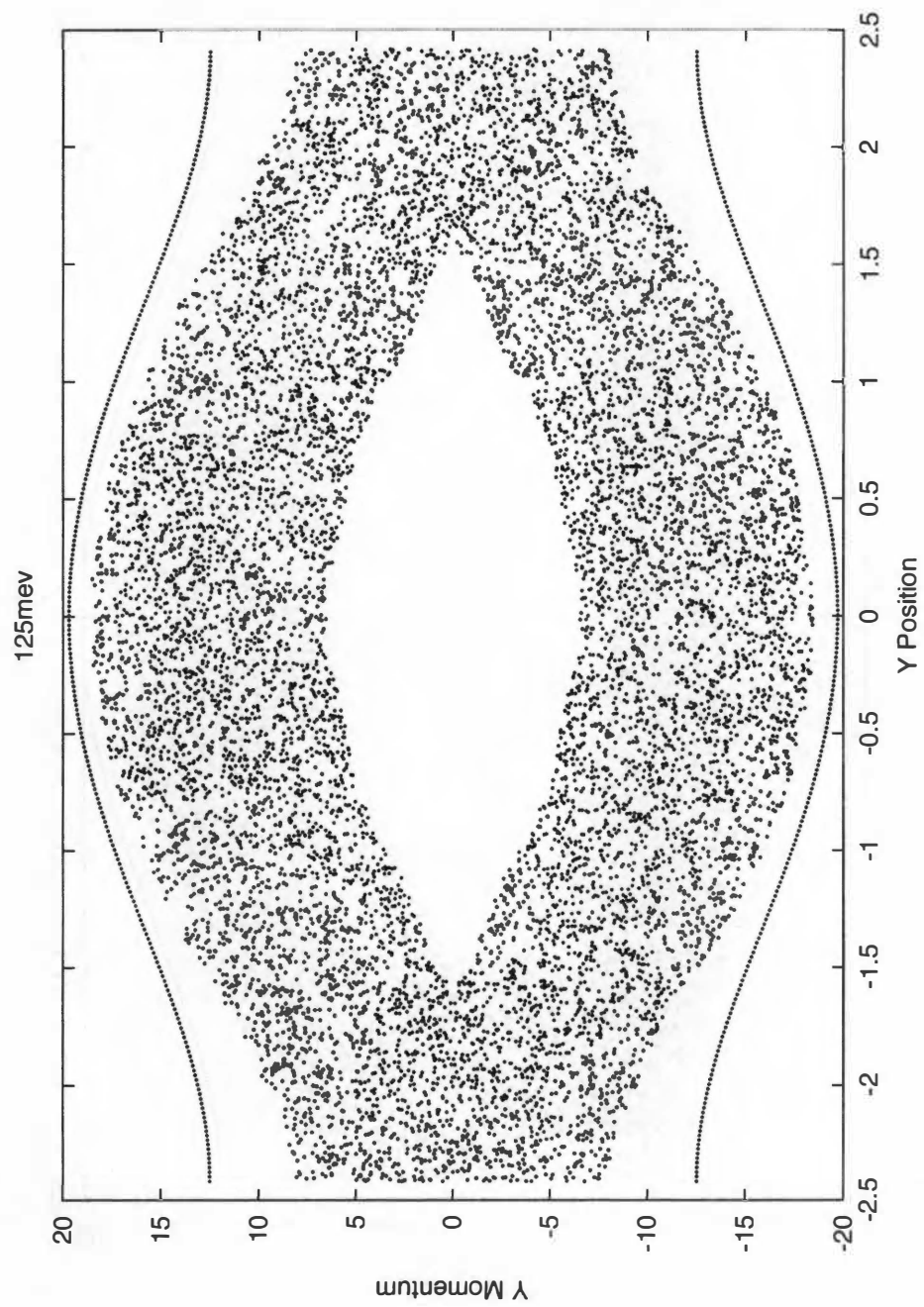


Figure 3.9: Poincare section (125 meV)

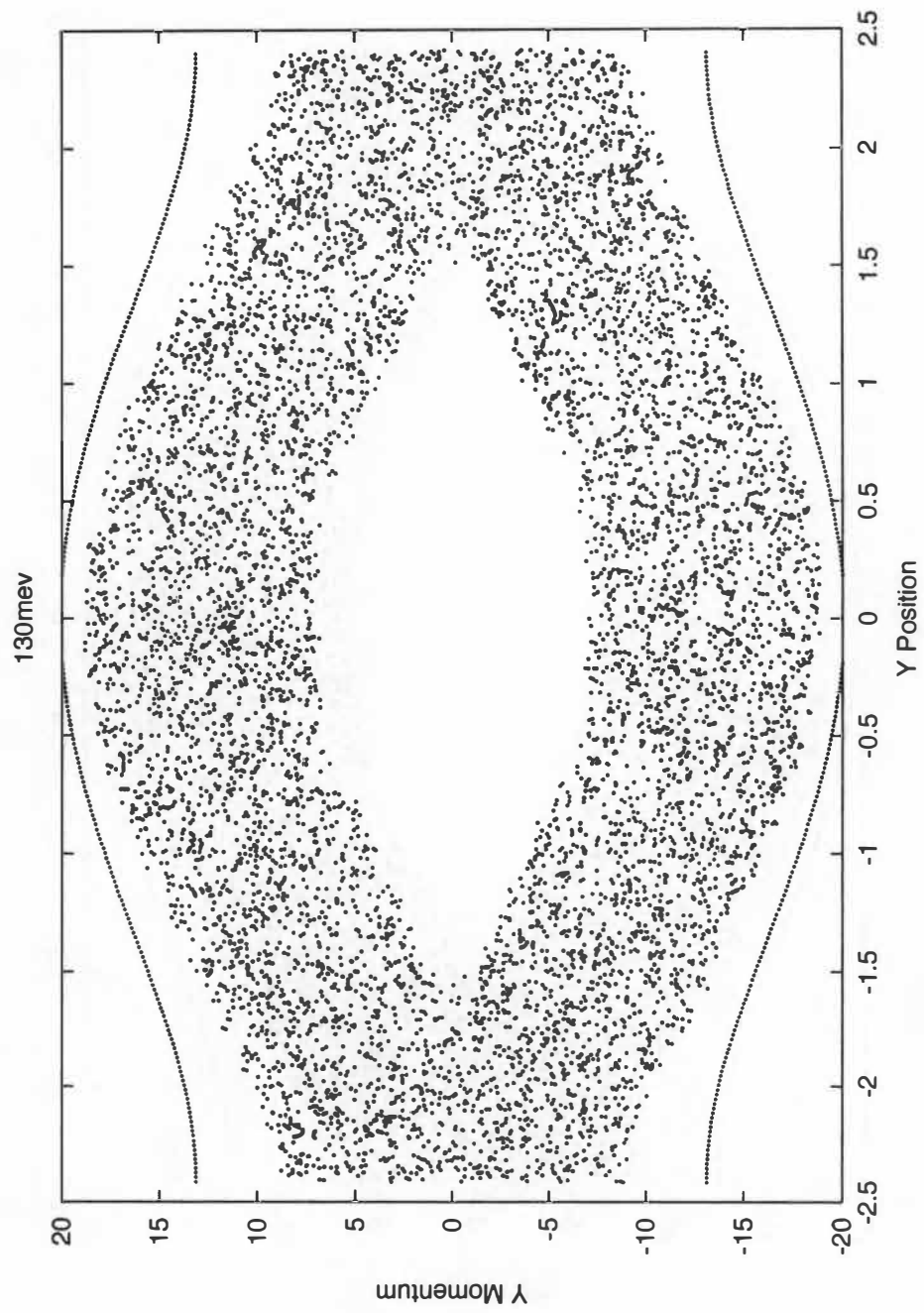


Figure 3.10: Poincare section (130 meV)

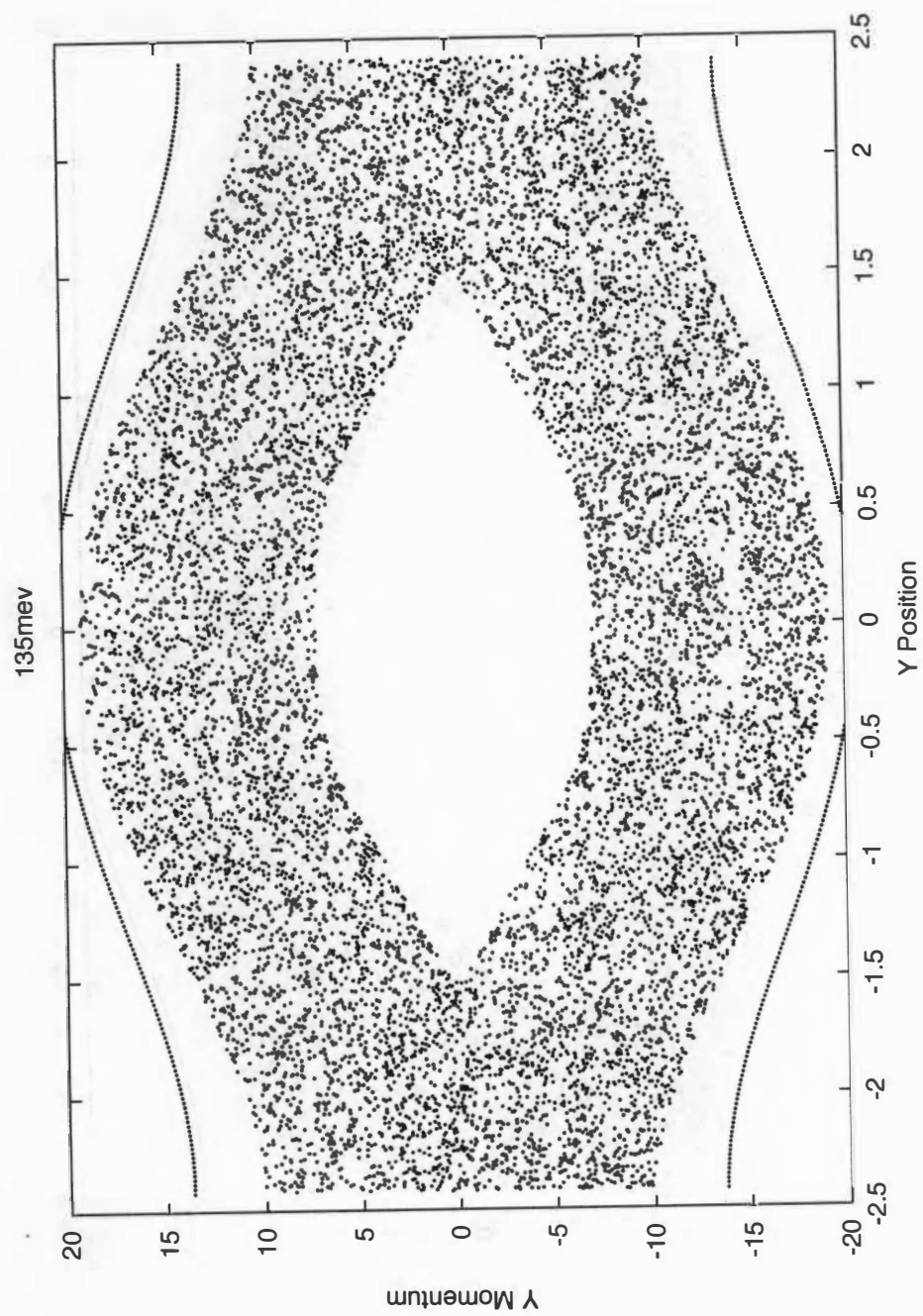


Figure 3.11: Poincare section (135 meV)

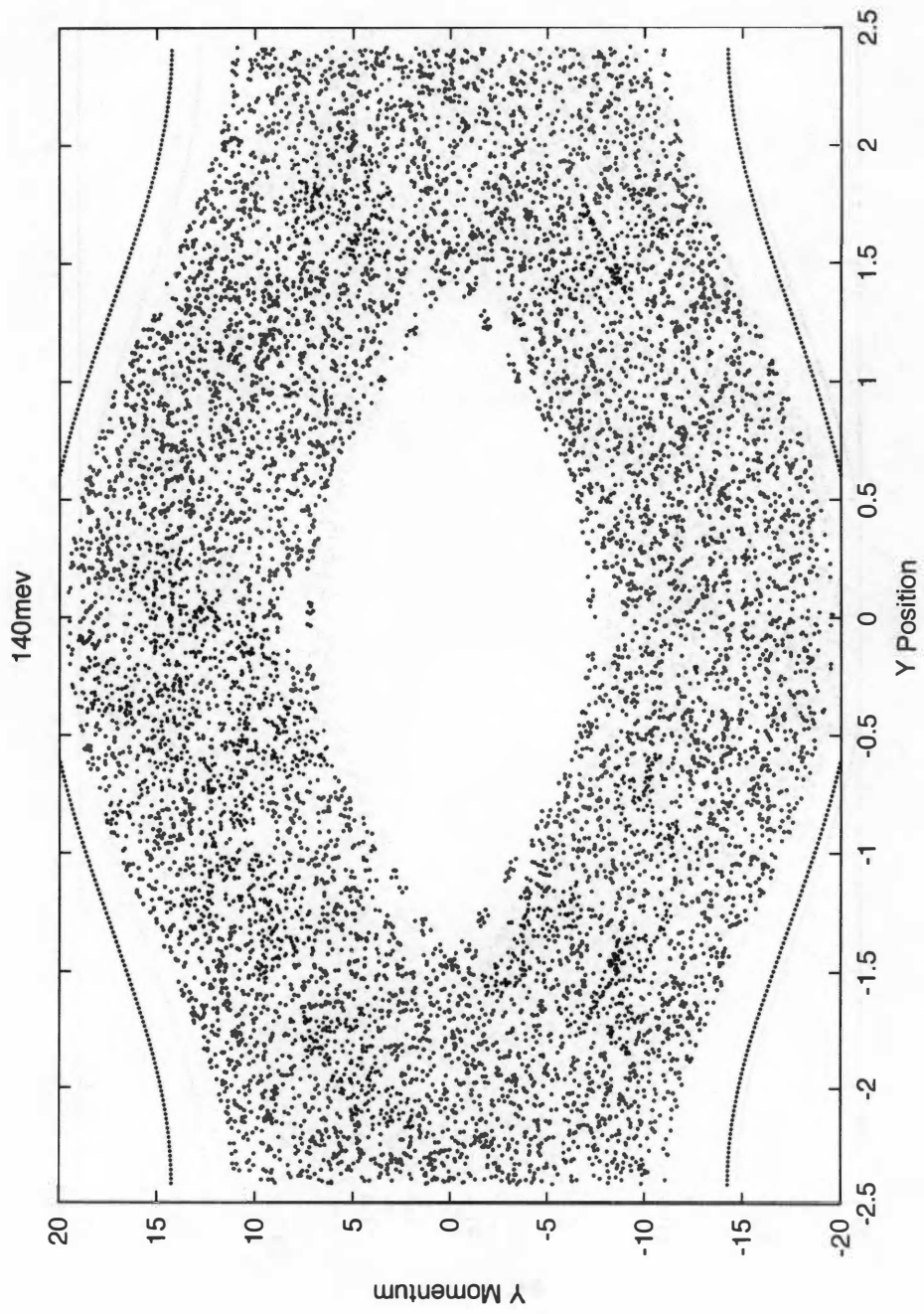


Figure 3.12: Poincare section (140 meV)

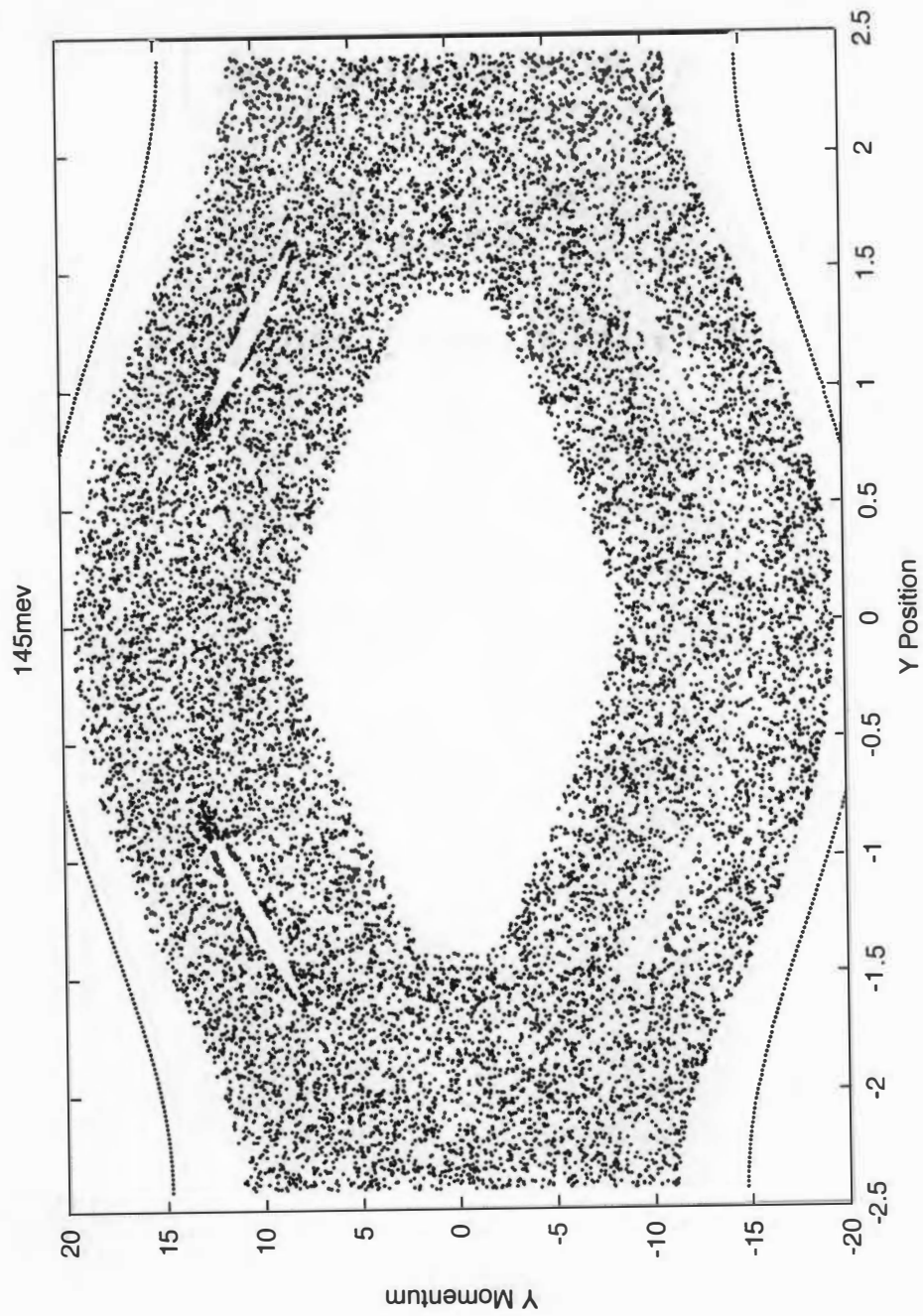


Figure 3.13: Poincare section (145 meV)

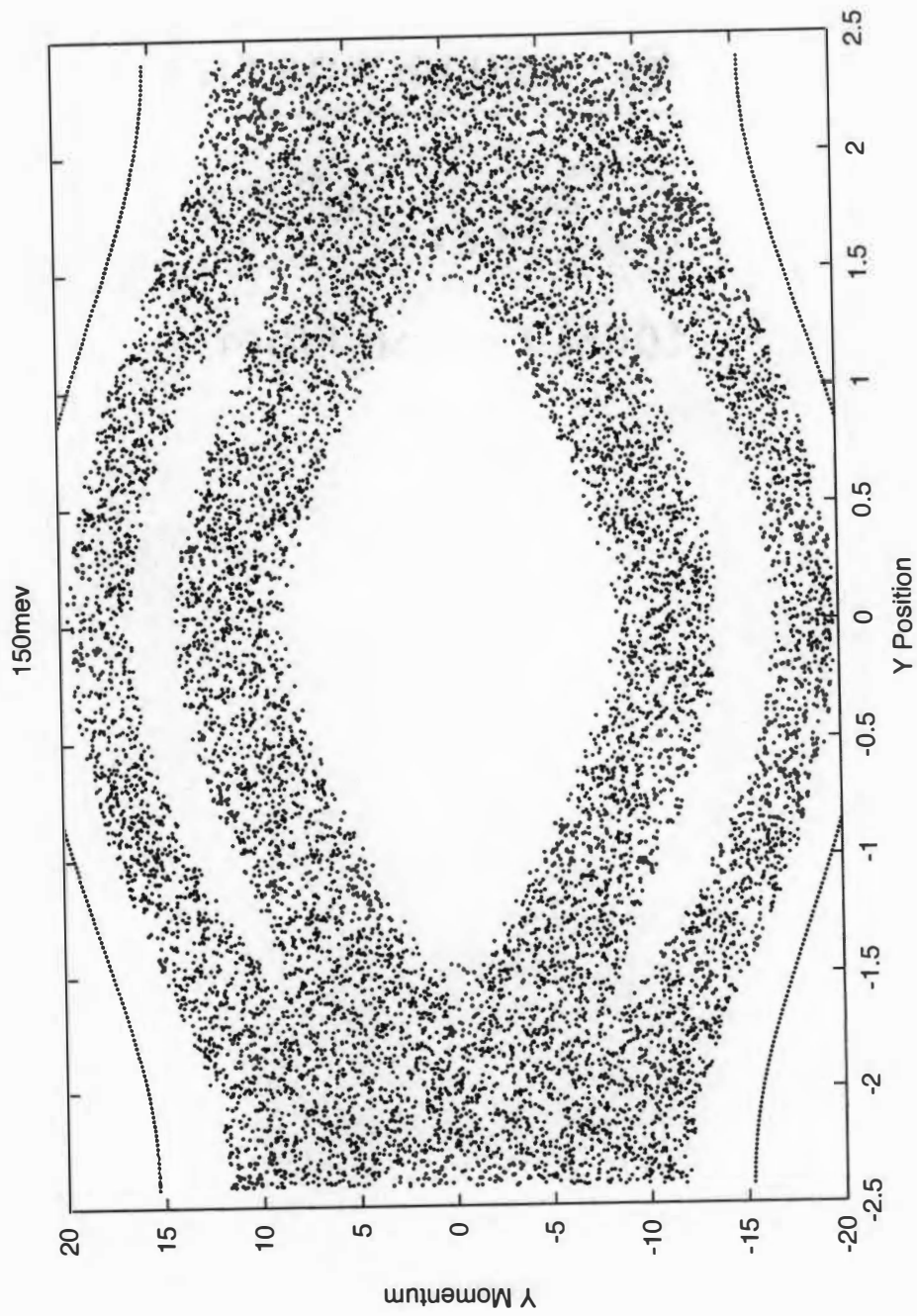


Figure 3.14: Poincare section (150 meV)

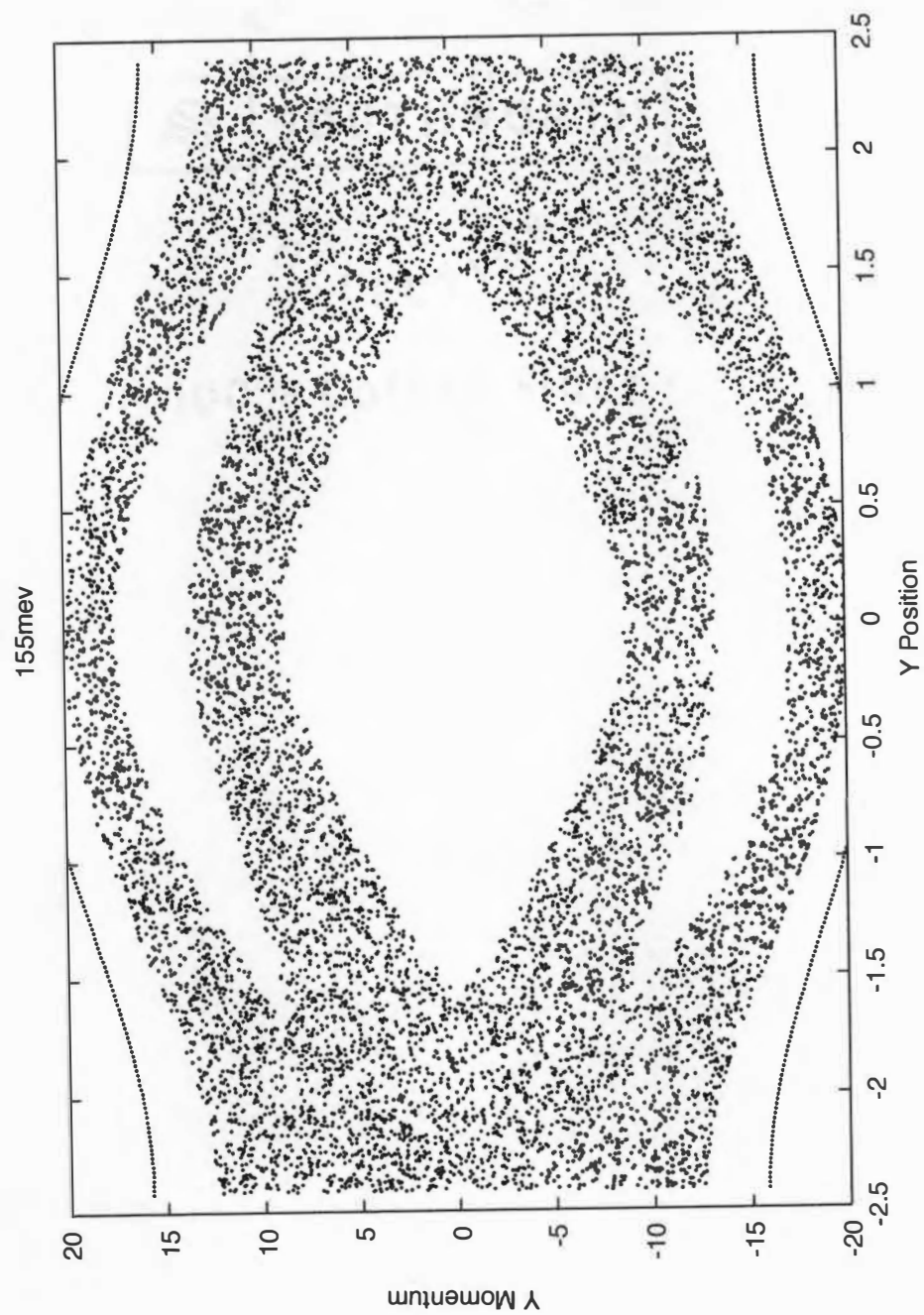


Figure 3.15: Poincare section (155 meV)

of ballistic flights must then be the result of a stabilizing influence on the phase space neighboring the regular phase space regions.

Chapter 4

Lyapunov Values

Previously we have calculated several Poincare sections between 85 and 155 meV. We have visually observed the simultaneous existence of chaotic and regular phase space regions within single Poincare sections. We have also identified a correlation between the occurrence of ballistic flights and the existence of regular regions of phase space. To better understand how these regular regions affect the overall rate of diffusion, we would like to be able to mathematically identify whether a calculated trajectory is chaotic or regular. This ability to numerically identify trajectories could then be used to quickly evaluate and then ignore trajectories which do not contribute to diffusive motions. Additionally, we would like to evaluate the relative size of regular or chaotic regions within the energetically allowable phase space.

We have chosen to use Lyapunov exponents as a method to numerically distinguish between chaotic and regular trajectories. Our specific goal is to determine the Lyapunov exponent of a trajectory and use it to classify the trajectory as either regular or chaotic. Using the definition of the Lyapunov exponent it seems that this determination should be relatively easy. Regular trajectories should have a Lyapunov exponent of zero and chaotic trajectories should have a Lyapunov exponent which is finite. However these values are guaranteed only in the limit of infinite time. There is an uncertainty in how the Lyapunov exponents approach their asymptotic (infinite time) values. An evaluation of short time approximations for Lyapunov exponents must therefore be performed before the Lyapunov exponents can be used to uniquely identify regions of phase space.

4.1 Roots

A first step in the evaluation of Lyapunov exponent behaviors is the identification of principal orbits. The principal orbits, which give rise to fixed points on the Poincare section, were previously discussed in section 1.3. The principal orbits are a category of motion in

which a trajectory repeatedly intersects the Poincare surface at the same point. Identifying the location of the fixed points provides several key pieces of information. Knowing their locations allows one to identify and examine the motions of the principal orbits. These are the fundamental motions, of which all regular motions are derivatives. Another importance of the principal roots then comes from the simplicity in their motions. Since the behavior of the short time approximations for the Lyapunov exponent calculations are not known, the evaluation of Lyapunov exponents for these simple motions will provide a benchmark to evaluate the behavior of Lyapunov exponents as they converge.

Identifying the location of the fixed points on the Poincare section was performed using a standard two-dimensional Newton-Raphson algorithm¹⁶. This is a well known algorithm which uses a Taylor series expansion to locate the roots of a system and is both stable and robust¹⁶. However this algorithm is only guaranteed to converge on *a root* contained within the system. In order to converge to specific roots one must start with an initial estimate which is very close to the desired root thus requiring *a priori* knowledge of the approximate location of roots within the system. A casual inspection of a trajectory simulation at 85 meV (figure 2.1) and its corresponding Poincare section (figure 4.1) aids us in the deduction of possible root locations and their typical motions. Inspecting the trajectory for motions which are clearly identifiable, one will observe four distinct types of nearly regular motion. The first is a horizontal type motion, another is a vertical type motion and the remaining two are diagonal motions with either positive or negative slopes.

We can expect that the principal orbits corresponding to horizontal (along the x -axis) and vertical (along the y -axis) motion exist at points in phase space where $p_x \times p_y = 0$. We can further expect that these regular flights transverse a unit cell through its origin at $(x = 0, y = 0)$, passing from cell to cell through the saddle point which separates the unit cells. Examining the equations of energy for this Hamiltonian system,

$$E_{total} - U(x, y) = \frac{1}{2m}p_y^2 + \frac{1}{2m}p_x^2, \quad (4.1)$$

we can determine likely locations for the horizontal and vertical roots.

For $p_x = 0$, the y momentum is at its maximum value as the adatom passes over the origin and can be calculated as

$$p_{y_{max}} = \pm(2mE_{total})^{\frac{1}{2}}, \quad (4.2)$$

when $U(0, 0) = 0$. We should then expect to find the roots responsible for vertical motion at $(y = 0, p_y = \pm p_{y_{max}})$ on the Poincare section. In the case $p_x = \pm p_{x_{max}}$, the y momentum

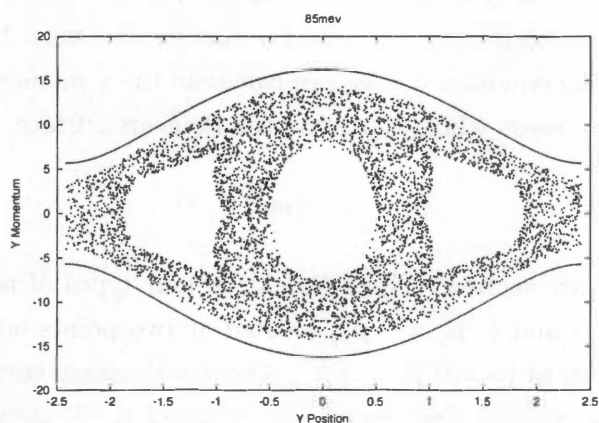


Figure 4.1: Poincare section at 85 meV. Contained within each regular region is a principal orbit (fixed point), whose motion is the fundamental motion in that region of phase space. A careful examination of this Poincare section reveals seven regular regions; The obvious center region, two outer regions, two regions left and right of the center region, and two small but distinct areas above and below the center region.

is zero,

$$p_y = 0. \quad (4.3)$$

Thus the roots corresponding to vertical motion should be found at $(y = 0, p_y = 0)$ on the Poincare section.

To determine the location of the principal roots responsible for diagonal motions, we can again inspect the same Poincare section and corresponding trajectory, to provide clues to their locations. Because of the symmetry of the PES, we might imagine that stable diagonal motions occur by passing through the unit cells at a 45° angle, crossing through the center of the cell, through the potential minima. The trajectory then passes directly across a copper site, bisecting it also at a 45° angle. This reasoning directs our search for roots to locations on the y -axis at $y = 0$ on the Poincare section. If a diagonal root does exist under these assumptions, the x and y momentums must be equal in magnitude, $|p_y| = |p_x|$. Again using equation 4.1 we can calculate the y momentum which a diagonal principal orbit should possess when it crosses the Poincare surface,

$$p_{ydia} = \pm(mE_{total})^{\frac{1}{2}}, \quad (4.4)$$

at $y = 0$ on the Poincare section. There should be four types of motion with $(p_y = p_x)$, $(p_y = -p_x)$, $(-p_y = p_x)$ and $(-p_y = -p_x)$ located at two points on the Poincare section. These two points located at $(y = 0, p_y = \pm p_{ydia})$ on the Poincare surface encompass all four motions because of the positive and negative crossings of the Poincare section.

Using these predictions as starting points, we have employed the Newton-Raphson algorithm to evaluate the root locations. The predicted root locations and the Newton-Raphson derived root locations are presented in table 4.1. We found that the predicted values for the vertical roots did not converge properly. We have reasoned that since the orbits for this motion lies within the Poincare surface (*ie* does not pass through the Poincare surface), that the root does not explicitly exist on the Poincare section. The root and its motion does occur, but it is not contained on the Poincare section as it is currently defined. This occurrence is non-detrimental to our investigation and analysis of root properties.

Additionally, slight differences between some predicted and calculated values were observed for the horizontal and diagonal root locations. These differences are most likely caused by the convergence of the Newton-Raphson algorithm on close neighboring regular orbits in the vicinity of the principal root orbit. Inspecting the Poincare surface, we find that the space surrounding the predicted root locations are densely packed with trajectories whose motions are periodic or quasiperiodic, and very similar in nature to the principal orbit. The Newton-Raphson algorithm may then converge onto one of these neighboring periodic or quasiperiodic orbit. It is then a reasonable assumption that in the instances

Table 4.1: Table of predicted and calculated principal root locations

Energy (meV)	Predicted Momenta (p_y) for Horizontal roots, Vertical roots, Diagonal roots (<i>atomic units</i>)	Calculated Momenta (p_y) for Horizontal roots, Vertical roots, Diagonal roots (<i>atomic units</i>)
85	0, ± 16.295 , ± 11.483	0, **, ± 11.483
95	0, ± 17.168 , ± 12.139	0, **, ± 12.139
105	0, ± 18.049 , ± 12.762	0, **, ± 12.762
115	0, ± 18.889 , ± 13.357	0, **, ± 13.357
125	0, ± 19.693 , ± 13.925	0, **, ± 13.925
135	0, ± 20.466 , ± 14.472	0, **, ± 14.472
145	0, ± 21.210 , ± 14.998	0, **, ± 15.001
155	0, ± 21.929 , ± 15.507	0, **, ± 15.508
		** Did not converge properly

where the calculated root locations slightly differ from the predicted locations, that the Newton-Raphson algorithm converged to a neighboring periodic or quasiperiodic orbit. In these instances it is most likely that our predicted root locations are correct.

In addition to regular trajectories associated with ballistic motion, we found one other type of regular motion. These trajectories exist only at the lower energies (system energy < 105 meV) and can be categorized as *trapped* trajectories, in which the trajectory exhibits a frustrated translational motion. In figures 3.1 through 3.4 the regular regions associated with these frustrated motions are the regular regions located left and right of the Poincare section origin ($y = 0, p_y = 0$).

4.2 Lyapunov Exponent Calculations

The use of the Lyapunov exponent as an analytic tool will require the analysis of regular and chaotic trajectory Lyapunov exponents. A comparison of their short time behaviors may then allow us to establish a method which can be used to mathematically differentiate the two types of trajectories.

4.2.1 Principal Orbit Lyapunov Exponents

Knowing the location of the principal orbits, we then investigated the convergence behavior of their finite time Lyapunov exponents with respect to time and energy. Calculations of Lyapunov exponents were performed using the previously discussed tangent space method. The time step used for these calculations is the same as for our general MD simulations, 1 atomic time unit.

To provide a robust estimation of how the Lyapunov exponents converge for principal orbits, we have chosen to evaluate their convergence behaviors at several different energies between 85 and 155 meV. For each root we have evaluated its Lyapunov exponent for varying lengths of time, at intervals of 25,000 time steps, with simulation lengths lasting between 0 and 600,000 time steps.

Figure 4.2 is a plot of Lyapunov exponents calculated at central roots ($y = 0, p_y = 0$) on the Poincare surface at several energies. At short time intervals, the Lyapunov exponents are generally high and oscillate rapidly. The oscillations are a result of the regular expansion and contraction of the local phase space. However, as time progresses, the local phase space expansions and contractions become less significant (equation 1.14), and the overall stability of the orbits become evident. After approximately 300,000 time steps, the Lyapunov exponents have settled down and have begun to slowly converge (ultimately to zero).

The convergence behavior of the finite time Lyapunov exponents for these regular

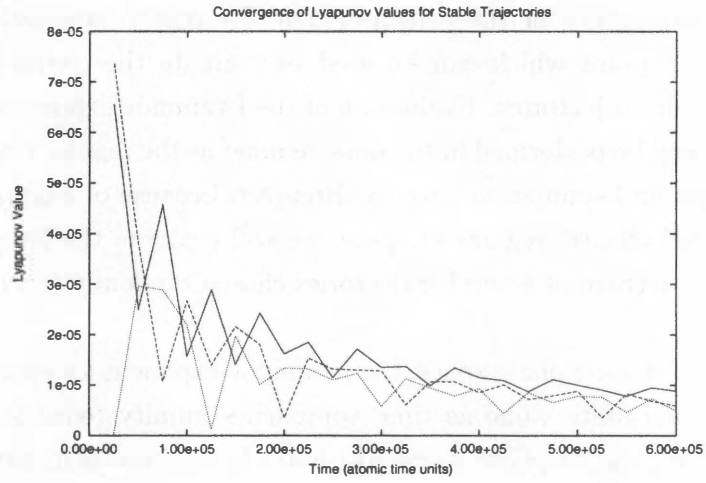


Figure 4.2: Lyapunov convergence behavior for central roots. The Lyapunov exponents at central root locations ($y = 0, p_y = 0$) should converge to zero as time approaches infinity. Solid line; 85 meV. Dashed line; 115 meV. Dotted line; 155 meV

trajectories is exactly as one might expect. At short time lengths the Lyapunov exponents oscillate because of local phase space effects. Then as time increases, the $1/t$ factor damps out these short time effects. Finally at long time lengths only the average divergence behavior is evident. In the case of principal orbits, this is a non exponential divergence, which results in a Lyapunov exponent that should converge to zero. Additionally, all trajectories contained within a regular region containing a principal orbit should converge in a similar manner. These trajectories are simply minor variants of the principal orbit and should be grouped together as a single class of regular trajectories all of which will have the same general behavior.

4.2.2 Chaotic Orbit Lyapunov Exponents

The near ideal convergence of the principal orbit Lyapunov exponent is promising and provides a reference point which can be used to evaluate the convergence of Lyapunov exponents for chaotic trajectories. Evaluation of the Lyapunov exponents for chaotic phase space trajectories will be performed in the same manner as the regular trajectories, using the same time intervals and simulation lengths. However, because of characteristic differences between regular and chaotic regions of space, we will evaluate the Lyapunov convergence behaviors using an average of several trajectories chosen randomly from within the chaotic space.

In regions of chaotic phase space, the Lyapunov exponent for every trajectory should converge to the same finite value as time approaches infinity (equation 1.14). However, unlike the regular regions of phase space which are homogeneous in nature, the behaviors contained within the stochastic sea are extremely inhomogeneous, especially during short time periods ($\sim 100,000$ time steps). It is therefore expected that trajectories within chaotic regions of space will converge to the true Lyapunov exponent irregularly. Some may converge very quickly while others may require a protracted amount of time to converge. In order to provide a reliable estimate of how chaotic Lyapunov exponents converge and what the true Lyapunov exponent is, an ensemble of several (~ 10) trajectories will be used.

As an example we show the results of several trajectories calculated at 155 meV, plotting their Lyapunov exponents as a function of time in figure 4.3.

Averaging these values together we intend to obtain an estimate of the Lyapunov exponent, and its convergence rate, and then use the converged Lyapunov exponents to establish a selection criteria in order to discriminate between chaotic and regular phase space. But we must be cautious when selecting which values to include into our average. The computational expense for these Lyapunov calculations is substantial, which limits us to sample sets of modest time lengths and minimal sample points. Additionally, the selection of random points within the stochastic sea must be performed manually. Compli-

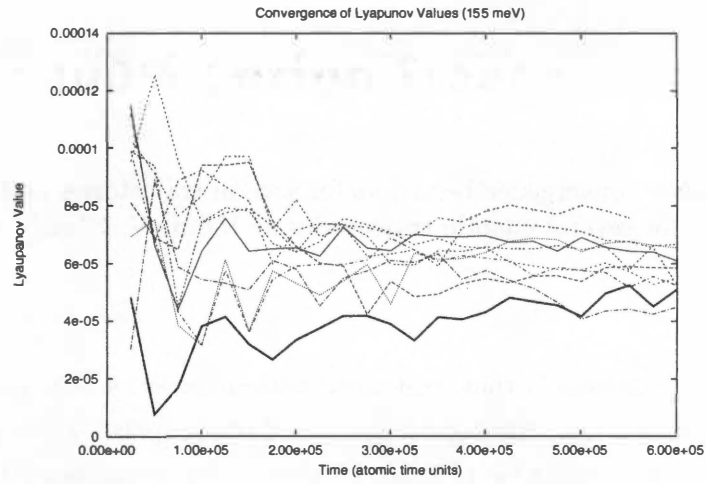


Figure 4.3: Lyapunov convergence behavior for several chaotic trajectories at 155 meV. These trajectories were chosen randomly within the stochastic sea at 155 meV. Data set denoted with a heavy line is suspiciously different from the other data sets. Additionally a few Lyapunov exponent calculations produced non-sensible results. These non-sensible results typically occurred after 500,000 time steps and are most likely the result of finite mathematical errors.

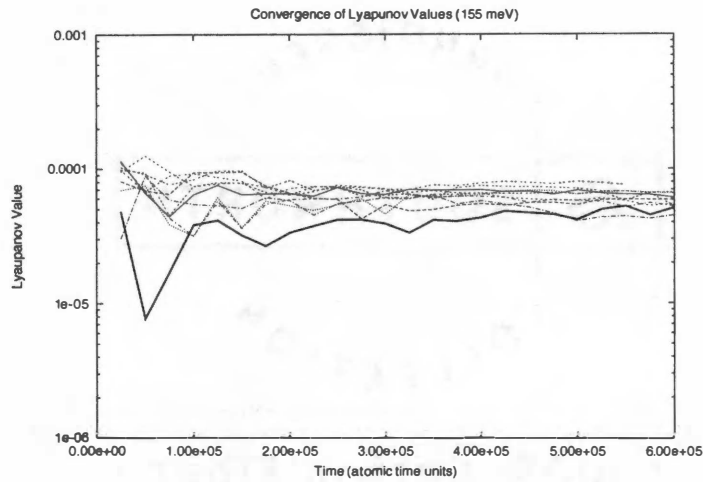


Figure 4.4: Lyapunov convergence behaviors for several trajectories at 155 meV plotted on a log scale. values for several chaotic trajectories at 155 meV. Clearly visible is an outlier data set (heavy line).

cating the averaging process is that, contained within the stochastic sea are small regions of high stability, located near the regular regions of phase space. These partially stabilized trajectories will possess, for a short time, Lyapunov exponents similar to regular trajectories. However, if we were to evaluate their Lyapunov exponents for very long periods of time we would find they would ultimately converge to a value consistent with all other trajectories within the stochastic sea. If we include these partially stabilized trajectories into our average, before their Lyapunov values have completely converged our estimate of the system Lyapunov exponent would be artificially low. The convergence rate would be equally affected resulting in an artificially shortened convergence time. So when averaging values together we have been careful to include only well behaved data sets for converging Lyapunov exponents. In figure 4.3 one of the convergence plots (heavy line) is suspiciously different. Replotting the same data on a semi-log plot, it becomes clear that this trajectory significantly differs from the rest of the data sets, figure 4.4. The behavior of this data set is indicative of a trajectory that has extensive (initial) stability which is transitory. The Lyapunov exponent at time=50,000 time steps is a full magnitude lower than corresponding values in the other trajectories. The data set is consistently lower than the other data sets, with its Lyapunov exponent still converging to the mean value well after the other data set values have plateaued. A reasonable estimate of the average Lyapunov exponent behavior and value should not include the outlier set.

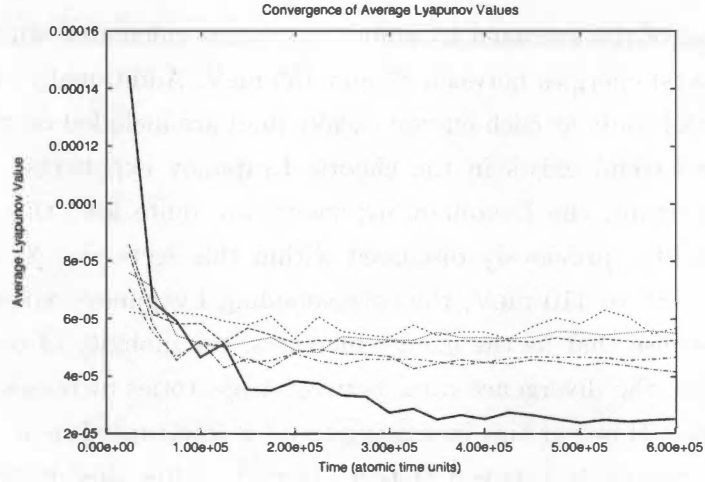


Figure 4.5: Average Lyapunov exponents for chaotic trajectories at several system energies between 85 and 155 meV. The heavy line is the convergence data at 85 meV. This data set significantly differs from the rest of the data sets.

Using this selection criteria the average chaotic Lyapunov exponent convergence behaviors were determined at several system energies. Plotting a few of the resulting averages in figure 4.5, we observed that most Lyapunov exponents were well converged by 400,000 time steps. The light lines in figure 4.5 are the average values calculated at several energies between 95 and 155 meV. The heavy line in this figure is the averaged data calculated at 85 meV. The convergence time for this data set is longer than at any other energy and its converged Lyapunov exponent ($\approx 2.5 \times 10^{-5}$) is significantly lower than all other converged values. These differences are most likely the result of reduced mobility at 85 meV. These trajectories tend to remain trapped for extended periods of time within a single unit cell (minimum energy barrier between unit cells is 74.58 meV and the maximum energy barrier is 84.45 meV).

Using the results of these and other data sets, we have set the Lyapunov convergence time to 400,000 time steps. This length of time is consistently long enough to ensure that the Lyapunov exponents are sufficiently converged. Additionally, during Lyapunov exponent calculations run longer than 500,000 time steps we have observed a few calculations which have produced non-sensible results ($< 5\%$ occurrence). We have attributed these erroneous results to progressively growing roundoff errors incurred during the multiplication of the Jacobian matrices.

4.3 Trends in Lyapunov Exponents

Figure 4.6 is a plot of the averaged Lyapunov exponents calculated with a time of 400,000 time steps for several energies between 85 and 155 meV. Additionally the Lyapunov exponents for the central roots at each energy (heavy line) are included on the same plot.

An obvious trend exists in the chaotic Lyapunov exponents. At the lower end of the energy spectrum, the Lyapunov exponents are quite low, this is most likely the result of low mobility (previously discussed within this section). As the system energy begins to increase, 85 to 110 meV, the corresponding Lyapunov exponents increase. We might initially surmise that as the energy increases, the mobility of our system increases and because of this, the divergence rates between trajectories increases (ie. the Lyapunov exponents increase). However this increasing trend is interrupted by a significant decrease in the Lyapunov exponents between 100 to 145 meV. After this decrease, the Lyapunov exponents begin to progressively increase. A similar trend also occurs for the principal root Lyapunov exponents. An examination of the Poincare sections for these energies can provide insight into the causes of these trends. In figure 4.7 there are three select Poincare sections which depict the overall trend in their throughout this energy range. At 85 meV there are large regions of stability. These regions rapidly contract as the energy increases from 85 to 105 meV and become no longer observable near 105 meV. Then as the energy of the system increases, regions of stability return and progressively expand. These expansions and contractions coincide with the trends in the Lyapunov exponents.

The trends for the principal orbits and Poincare sections are as follows: As the regular regions contract, the principal orbit Lyapunov exponents increase. This trend in increasing Lyapunov exponents indicates a loss of stability, which is consistent with the contraction of the regular phase space. As the regular regions begin to expand, the principal orbit Lyapunov exponents begin to decrease. This signifies an increase in stability, which is again consistent with the expansion of the regular phase space.

For the chaotic Lyapunov exponents a similar trend is observed. As the regular regions contract, the chaotic Lyapunov exponents increase. Likewise, as the regular regions expand, the chaotic Lyapunov exponents decrease. However the exact nature of this correlation is not as easily explained as in the regular phase space case. The increase and decrease in the chaotic Lyapunov exponents could have several contributing factors. The trends in the chaotic Lyapunov exponents could be a result of the expansion and contraction of the chaotic space. This correlation could be supported by the observation that as the chaotic space expands or contracts the chaotic space becomes more or less chaotic, respectively. However it is already suspected that regular regions partially stabilize the chaotic phase space surrounding it. If there is a large contact surface between the two regions, it is possible that this local stabilizing effect can have large impact on the chaotic nature of the

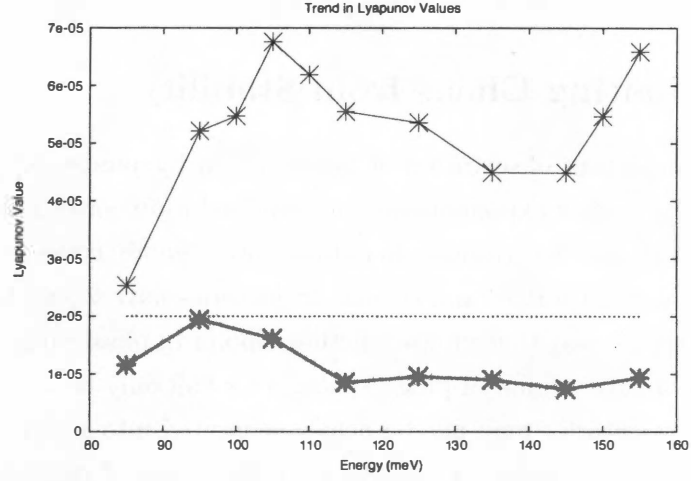


Figure 4.6: Plot of averaged Lyapunov exponents ($t = 400,000$) with respect to system energies. The light line is the averaged value for chaotic trajectories. The heavy line is central principal root (un-averaged). The dotted line at 2.0×10^{-5} segregates the chaotic trajectories from the regular trajectories.

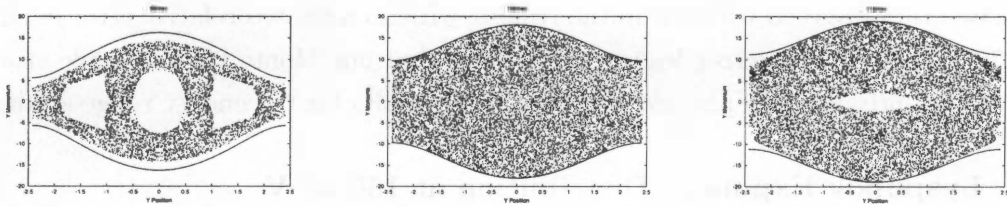


Figure 4.7: Three Poincare sections: 85 meV (left), 105 meV (center), and 115 meV (left). The regular region of phase space surrounding the central root shrinks rapidly from 85 meV to 105 meV. Then they begin to expand as the system energy begins to increase further.

chaotic phase space. Then as the regular regions contract the amount of contact surface with the chaotic phase space decreases. Additionally the magnitude of the stabilization at the periphery of the regular regions may also be changing. The result is that a combination of effects may control the Lyapunov exponent within the chaotic phase space.

4.4 Discriminating Chaos from Stability

Perhaps the most important observation of the trends in Lyapunov exponents in figure 4.6 is that the highest Lyapunov exponents for the principal roots and the lowest average Lyapunov exponents for chaotic trajectories do not overlap. Chaotic trajectories have Lyapunov exponents greater than 2.0×10^{-5} and regular trajectories have values less than that. This provides us with a simple way to evaluate whether a point in phase space is either contained within a regular or chaotic region of phase space. This will only be a crude discrimination, because Levy-like trajectories may not be neatly separated into either category. However, we can use this general descriptor to evaluate bulk properties of phase space regions.

Using a Lyapunov exponent cutoff value of 2.0×10^{-5} after 400,000 au of propagation in time, we can estimate whether a point exists within a regular or chaotic region of phase space. The proportion of phase space that is either regular or chaotic can be determined by using a Monte Carlo sampling of the available phase space to estimate the areas of regular and chaotic phase space.

Implementing this method, we evaluated 3000 points on a Poincare surface to evaluate the spatial fractions of chaotic and regular space. At each point we evaluated the Lyapunov exponent at 400,000 time steps and then categorized the trajectory as regular or chaotic depending on whether the value is below or above the cutoff value 2.0×10^{-5} .

At several energies (150, 100, and 85 meV) we have calculated an additional 3000 points and using the combined larger data sets we recalculated the phase space ratios. The recalculated ratios agreed with our initial results, with an unbiased relative error of no more than 0.3%. This minimal error leads us to believe that our Monte Carlo sample size is, in general sufficiently large to provide well converged results for the energy range studied.

4.4.1 Lyapunov Exponent Distribution at 150 meV

An example of this method is now presented with a system energy of 150 meV. Figure 4.8 is a plot of the Monte Carlo sampling of phase space points. Comparing the figure 4.8 to its corresponding Poincare section at 150 meV (figure 3.14), the phase space appears to have been sampled completely and uniformly with no obvious bias in any particular region of phase space.

Plotting the resulting Lyapunov exponents as a function of the initial y coordinate

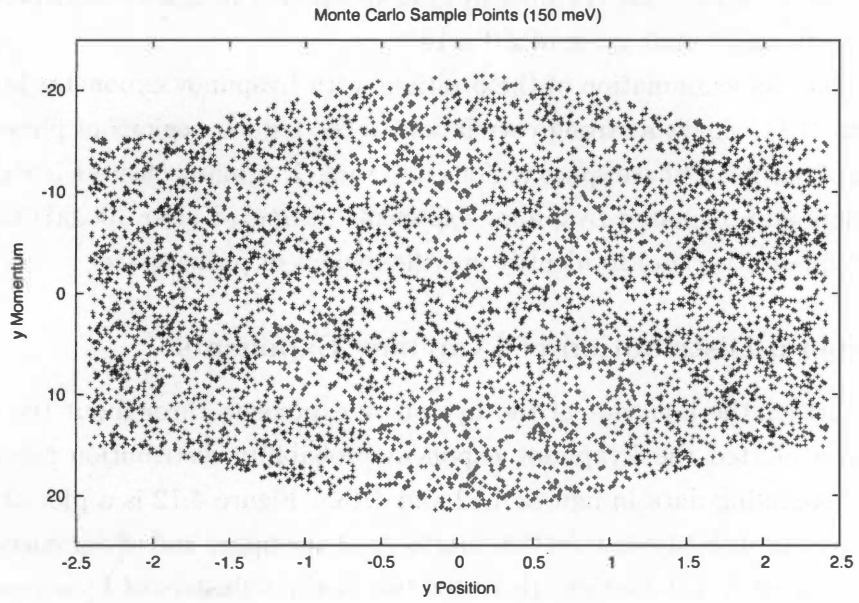


Figure 4.8: Sample points for Lyapunov exponent calculations, selected randomly from within energetically available space space at 150 meV.

on the Poincare surface in figure 4.9, it is evident that there exist two distinct groups of Lyapunov exponents separated by a region which is only sparsely populated. The higher values are clustered near 6×10^{-5} and the lower values are clustered near 1×10^{-5} . Both of these values agree well with the average Lyapunov exponents we had previously calculated to represent the regular and chaotic phase space regions at this energy (figure 4.6).

Plotting the positions (y, p_y) of Lyapunov exponents greater than 2.0×10^{-5} in figure 4.10 reveals a strong correlation between Lyapunov exponents and phase space positions. A comparison between these positions and the corresponding Poincare section at 150 meV show a strong similarity. The Lyapunov exponents with values higher than 2.0×10^{-5} have positions which match neatly with the locations of the stochastic sea of the Poincare section at 150 meV, figure 3.14. This corroborates our estimation of chaotic trajectories by using a Lyapunov exponent cutoff value of 2.0×10^{-5} .

Likewise, an examination of the positions with Lyapunov exponents less than 2.0×10^{-5} in figure 4.11, shows a strong correlation to the regular regions of phase space. The partitioning of occupied phase space regions into these Lyapunov clusters is strong evidence that short time approximated Lyapunov exponents computed after 400,000 time steps can be used as a qualitative tool to identify specific regions of phase space.

4.4.2 General Distribution of Lyapunov Exponents

Examining further the behavior of the Lyapunov exponents throughout the energy spectrum, we have plotted the Lyapunov exponent probability distribution functions for the Monte Carlo sampling data in figures 4.12 and 4.13. Figure 4.12 is a plot of several Lyapunov exponent probability distribution functions at the upper end of our energy range, 150 to 100 meV. For each distribution, there are two distinct clusters of Lyapunov exponents: a sharp distribution centered at 1.0×10^{-5} which corresponds to regular trajectories and a broader distribution centered at 6.0×10^{-5} , which corresponds to the chaotic trajectories. As the system energy decreases, the intensity of the distribution centered at 1.0×10^{-5} decreases, while the upper distribution centered near 6.0×10^{-5} sharpens. The chaotic peak increases in relative intensity and its width slightly narrows. This trend demarks an increase in system chaos and an increase in uniformity within the chaotic space, as the system energy decreases from 150 to 100 meV. Additionally, the location of the regular phase space Lyapunov distribution remains fixed, while the chaotic distribution shifts slightly towards lower values. This behavior is consistent with our previously predicted trend in figure 4.6. This provides a small clue about how the homogeneity of chaotic space is affected by the expansion and contraction of regular regions of phase space.

Unfortunately as the system energy decreases further, the clear distinction between the regular Lyapunov exponents and the chaotic Lyapunov exponents is lost. Figure 4.13 is

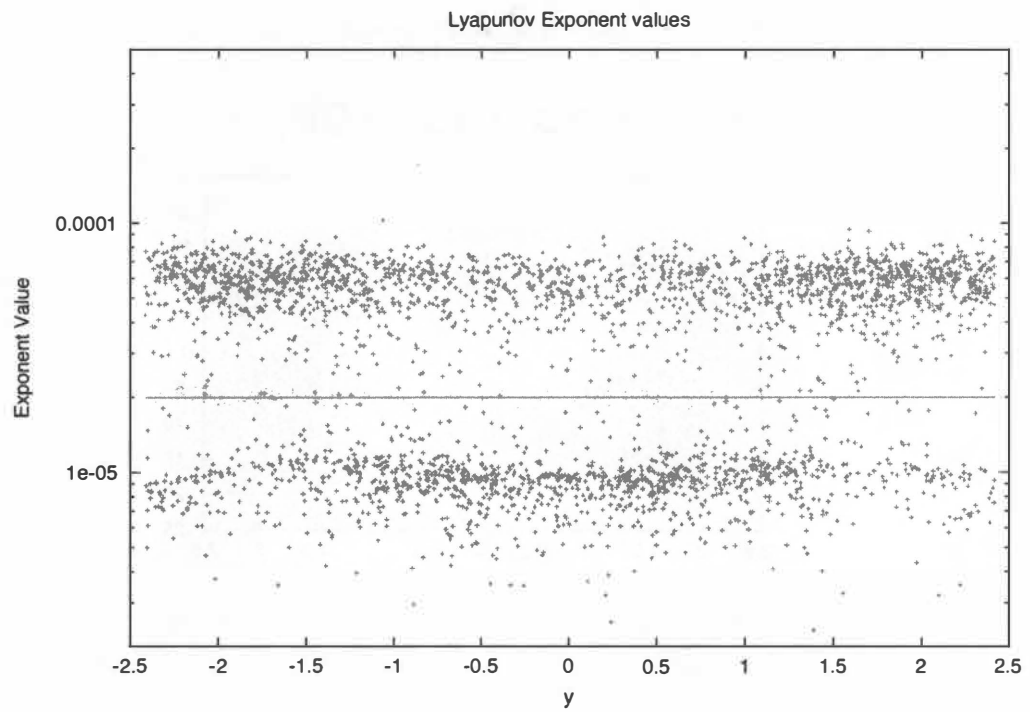


Figure 4.9: 3000 Lyapunov exponents of Monte Carlo sampled points, calculated for 400,000 time steps at 150 meV. The results are clustered into two distinct regions above and below 2.0×10^{-5} (light line).

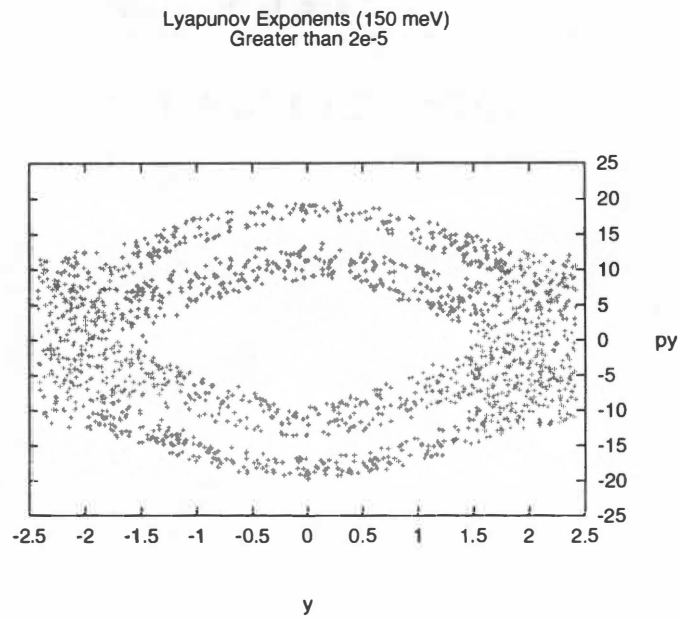


Figure 4.10: Distribution of Lyapunov exponents greater than 2.0×10^{-5} at 150 meV. The location of these points correlate to the regions of the stochastic sea within the Poincare section at 150 meV.

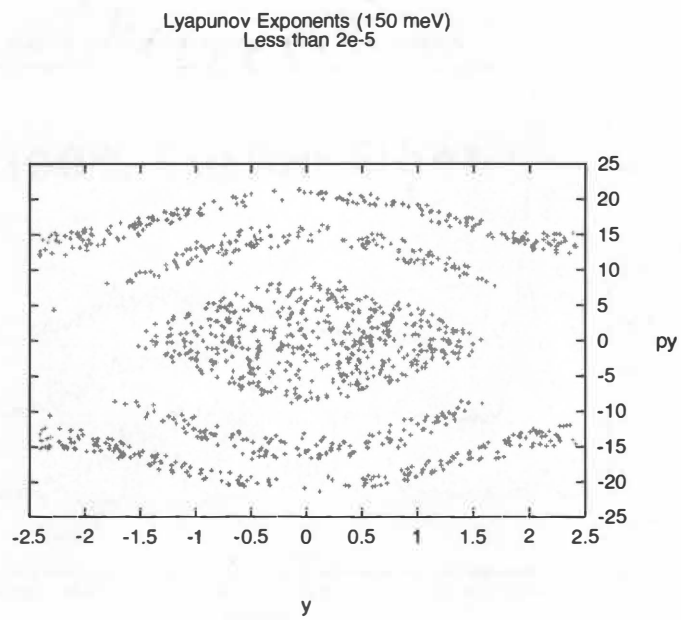


Figure 4.11: Distribution of Lyapunov exponents less than 2.0×10^{-5} at 150 meV. The location of these points correlate to regular regions of phase space within the Poincare section at 150 meV.

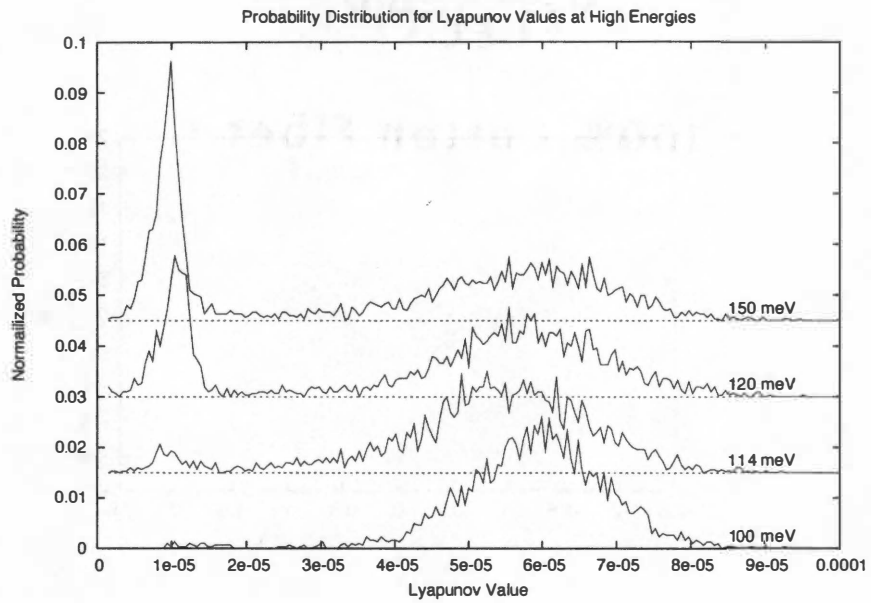


Figure 4.12: Lyapunov exponent distributions for several energies between 150 and 100 meV. Notable are the clear separations of the two distributions peaks at each energy, and that as the system energy decreases the positions of the peaks are well preserved. Values are offset by increasing steps of 0.015.

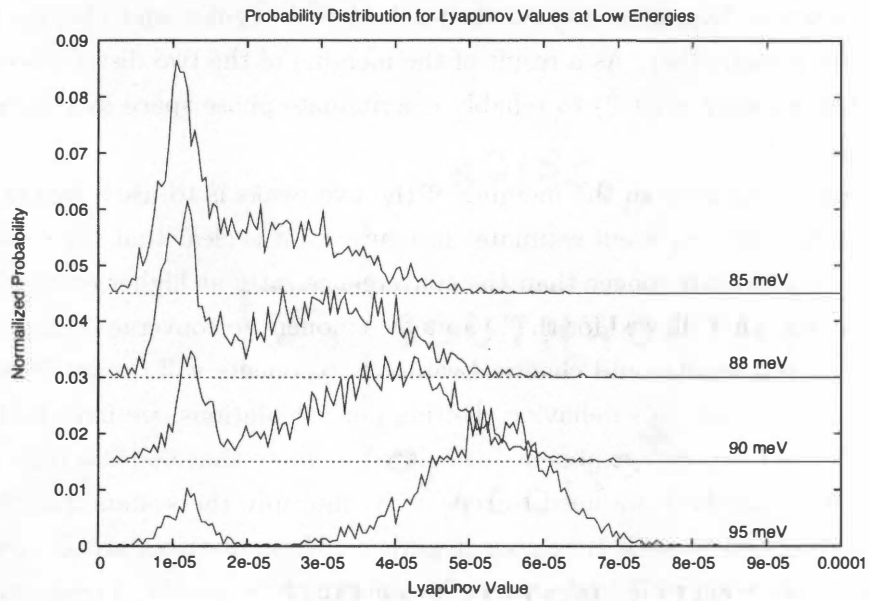


Figure 4.13: Lyapunov exponent distributions for several energies between 95 and 85 meV. Most notable is the merging of the two distributions peaks at each energy as the system energy decreases. Values for each distribution are offset by increasing steps of 0.015.

a plot of the Lyapunov distribution functions at the lower end of our energy range, 95 to 85 meV. At 95 meV, the regular space distribution centered at 1.0×10^{-5} , which had decayed away at 100 meV, returns centered slightly above 1×10^{-5} . The chaotic space distribution, which has continued its downward drift, is now centered near 5×10^{-5} .

As the system energy continues to decrease, the regular space distribution begins to grow in intensity, and the chaotic space distribution quickly drifts to lower values. The boundary between the two peaks is well distinguishable at 95 and 90 meV, but as the system energy decreases further the two peaks begin to rapidly merge. This merging of Lyapunov exponent distributions does not signify loss of chaotic phase space in the low energy regime. An inspection the Poincare sections at these energies rules out this possibility. The short time approximation Lyapunov exponents for both the regular and chaotic regions have begun to overlap each other. As a result of the merging of the two distributions, the use of a simple cutoff value (2×10^{-5}) to reliably discriminate phase space as regular or chaotic, becomes impossible.

A possible solution to the merging of the two peaks is to use a longer convergence time for the Lyapunov exponent estimate. In figure 4.5 it is clear that the convergence rate at 85 meV is significantly longer than the convergence rates at higher energies. We should expect that as the time allowed for the Lyapunov exponent to converge is increased a clearer distinction between regular and chaotic Lyapunov exponents will occur. However, at this time we can not explore this behavior. During our calculations, we have had difficulty in obtaining reliable Lyapunov exponents calculated at more that 600,000 time steps. Using the tangent space method, we need to repeatedly multiply the system Jacobian matrices, which are determined at each time step, together. These matrices are *ill conditioned*, resulting in multiplication round off errors which accumulate quickly. These round off errors are the result of computational limitations and are not a result of the underlying theories involving the Lyapunov exponent calculations. The use of a longer time step (we have used a time step of 1 atomic time unit) may provide a method to investigate the convergence behavior of Lyapunov exponents for longer periods of time. Future investigations of the convergence behaviors of the Lyapunov exponents using differing step sizes might provide useful information, which could be used to evaluate optimum time step sizes when calculating Lyapunov exponents, for this system.

In figure 4.14 there is a good correlation between the average Lyapunov exponents calculated from the larger data set containing 3000 points and our original data set which contained ~ 10 points. However in the lower energy regime this agreement is poor and we have already discussed the factors which have contributed poor Lyapunov exponent estimates in this energy range.

The generally good correlation between the two data sets provides us an assurance that the two regions of phase space are reasonably well behaved. We can conclude then

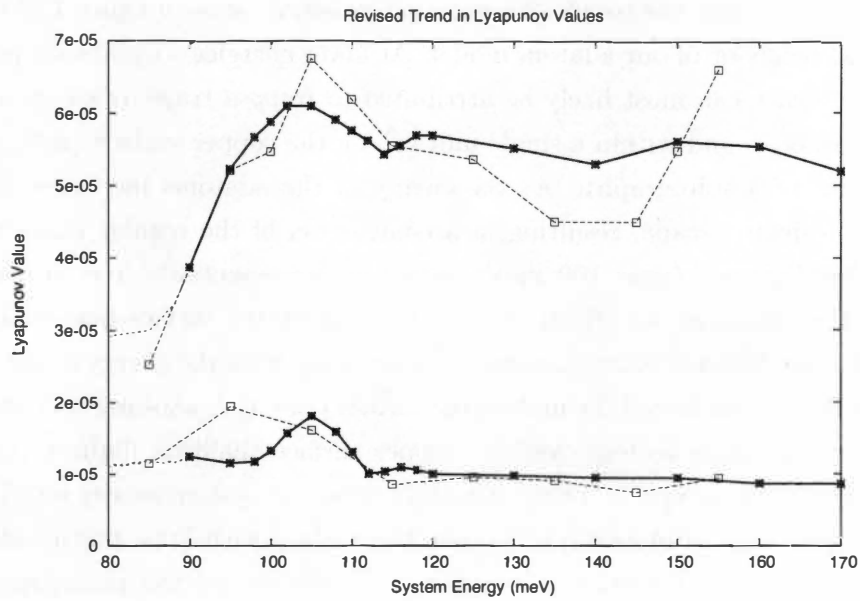


Figure 4.14: Recalculated average Lyapunov exponents for regular and chaotic regions of phase space using 3000 trajectories (heavy lines). The trends initially predicted using only ten points averages (fig. 4.6) are shown (dashed lines) for comparison. Values below 90 meV (dotted line) are not well determined due to overlapping distributions (see fig. 4.13), and should be considered extremely unreliable.

that small samplings can be reliably used during trial investigations to evaluate possible analytic methods.

Plotting the proportion of regular phase space within the total available phase space, through the energy range 85 to 170 meV, in figure 4.15, a clear trend appears. At low energies, the fraction of regular phase space is large. And as the system energy increases the area of regular space contracts, with a minimum occurring near 100 meV. As the system energy increases from 100 to 120 meV, the fraction of regular phase space rapidly increases. Following this, as the system energy continues to increase, the fraction of regular space generally increases at a modest rate.

We can interpret the trends of regular phase space ratios in figure 4.15 by examining the suspected behavior of our adatom model. At lower energies a significant portion of this regular phase space can most likely be attributed to *trapped* trajectories, in which the adatom stably rolls around within a single unit cell on the copper surface (with an trajectory much like that of a spirograph). As the energy of the adatoms increases, some trapped trajectories begin to escape, resulting in a contraction of the regular phase space. Then at some critical energy (near 100 meV), adatoms are essentially free to roam from cell to cell, but their motions are still tightly constrained by the surface potential, resulting in motion that is random and uncoordinated. Further increasing the energy of the adatoms, the adatoms begin to break free of the underlying surface potential, allowing trajectories to move more freely along single vectors over the copper surface (ballistic flights), resulting in an increase in regular phase space. Then ultimately, when the system energy is sufficiently high, adatoms become able to move rapidly along the surface with little perturbation resulting from the adatom copper surface interactions; at this energy the phase space is almost entirely regular.

Comparisons between the Lyapunov averages and the regular phase space ratio trends can also be made. In general as the fraction of regular space increases the Lyapunov exponent decreases and vice versa. At 105 meV we find in both, trends of complementary behavior, Lyapunov exponents have reached their highest values and the fraction of regular space is at its lowest. Classifying this as a cause and effect phenomena is a tempting response. We can imagine that as the regions of regular space decay away, a chaotic trajectory is less inhibited by the boundaries of the system and becomes more divergent and chaotic (higher Lyapunov exponents). Then as the regions of regular space return, a chaotic trajectory is increasingly constrained by the growing boundaries of the regular phase space resulting in less divergent trajectories (lower Lyapunov exponents). However, at this time, we cannot definitively explain the mechanism controlling the dilation or contraction of the regular phase space regions or its effect on the Lyapunov exponent of the chaotic space.

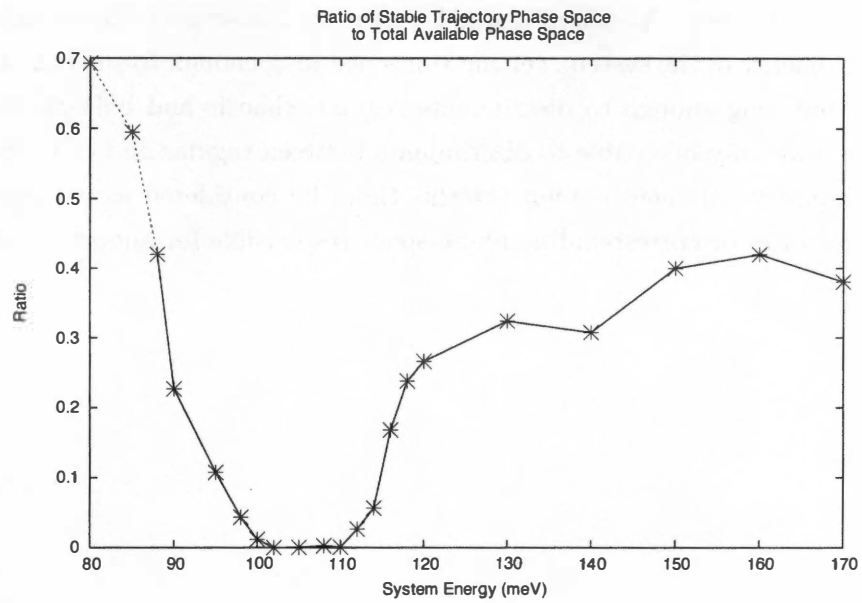


Figure 4.15: Ratio of regular phase space to total phase space using a Lyapunov threshold value of 2.0×10^{-5} . The ratio values below 88 meV (dotted line) are expressed with some uncertainty. At these energies there did not exist a clear distinction between chaotic and regular Lyapunov exponents when evaluated for 400,000 time steps.

4.5 Conclusions

We had begun the investigation of the Lyapunov exponents to determine if they could be used to discriminate between the different types of trajectories; regular and chaotic. Our initial investigation has shown that there are indeed clear distinctions between regular and chaotic trajectories when using Lyapunov convergence times on the order of several hundred thousand time steps. However, because the stability of Levy-type trajectories tends to be short lived, their behavior has been blurred out with our long convergence time, preventing a clear identification of them or their locations in phase space. It is possible that a larger sampling of phase ($\approx 10^5$ sample points vs. 3000) space may reveal regions which are clearly neither regular or chaotic. Another possibility is the use convergence times which are tuned to the specific energy of the system, setting times just long enough to smooth out short time fluctuations, but long enough to discriminate regular, chaotic and ballistic behaviors. At this time, we have only been able to discriminate between regular and chaotic trajectories. Thus the Lyapunov exponent cannot (at this time) be considered as a viable method to evaluate trajectories or corresponding phase space responsible for anomalous diffusion.

Chapter 5

Levy Flight Analysis

Previously we had stated that the occurrence of ballistic flights, which are most likely Levy flights, are the principal cause of anomalous diffusion. We have tried to use Lyapunov exponents to numerically identify these types of trajectories and their locations on the Poincare surface. But because Lyapunov exponents are technically defined as a measure of long term behaviors, we have not (at this time) been able to construct a reliable method employing Lyapunov exponents to identify the relatively short lived behaviors of Levy flights. We can however still pursue a analysis of Levy flights by using other properties to identify them.

Most obviously, Levy flights can be identified directly by the characteristic property of their motion. Their principal identifying characteristic is correlated motion lasting for statistically significant lengths of time. One method to identify and study Levy flights would be to analyze the motions of an entire trajectory and extract only those portions of the trajectory which match these criteria. These candidates could then be studied as an ensemble to identify other features which are not readily observable during sparse observations.

5.1 Simplification of Trajectory Flights

A straightforward method to identify Levy flights is to simplify a trajectory by representing it as a series of short linear segments, as shown in figure 5.1. The angles between individual segments could then be used to identify long straight flights from normal diffusive motion.

Levy flights, because of their near ballistic linear motion, will be composed of a series of segments whose segment-segment angle θ will be nearly 180° as shown in figure 5.2. In contrast, normal diffusive motions will have segment angles which will tend to be acute and vary sporadically.

Implementing this method, we have selected segment lengths which correspond to Poincare surface intersections (a segment's end points are Poincare surface intersections). Candidates for Levy flight analysis will be selected from straight flights which maintain

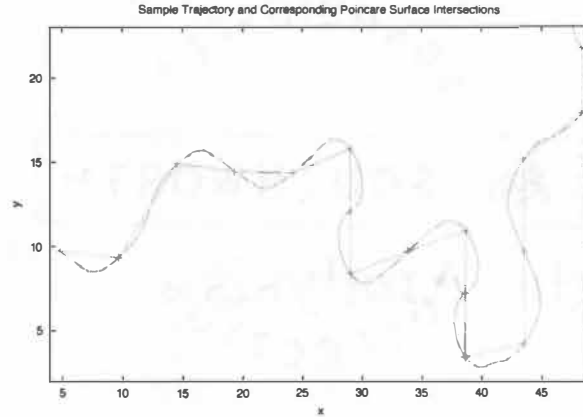


Figure 5.1: Plot of continuous and segmented diffusion trajectory. The smooth function is a portion of a typical diffusion trajectory. The simplified trajectory is constructed from the segments created as the trajectory passes repeatedly through the Poincare surface ($x=0$ within a unit cell). It is apparent in this diagram that each segment is not of equal length, but the essence of the original trajectory is maintained.

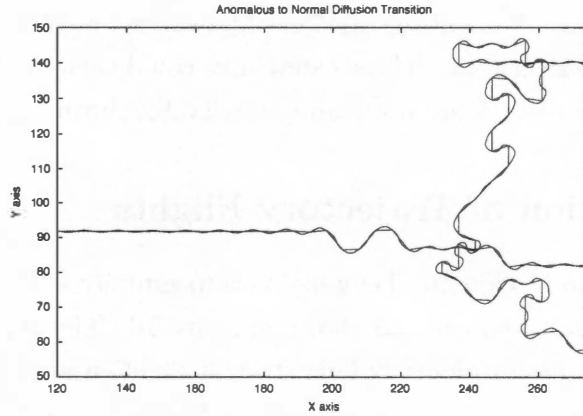


Figure 5.2: Plot of segments displaying both normal and ballistic motions. During periods of anomalous diffusion ($120 < x < 190$) the segment angles tend to be large, $\theta \approx 180^\circ$, while during periods of normal diffusion ($x > 190$) the segment angle θ fluctuates with typically acute values.

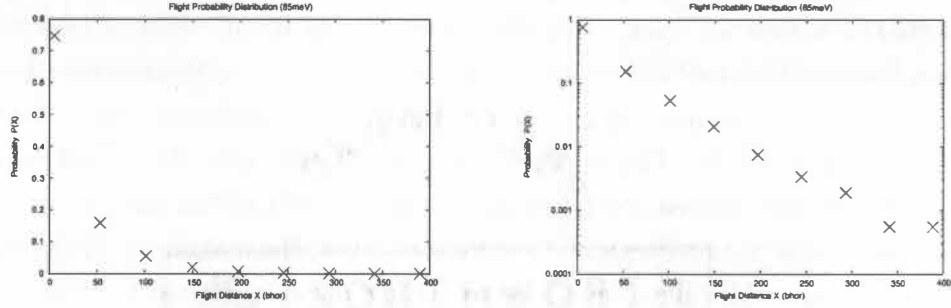


Figure 5.3: Plots of distribution functions for straight flights isolated at 85 meV ($.96\mu\text{sec}$ trajectory). The left figure shows an exponential decay in the probability of flights as flight distances increase. This is indicative of a Levy distribution. The right figure shows the same data plotted on a log scale.

segment angles greater than 165° for four or more consecutive segments. Using Poincare surface intersections as the method of determining segment lengths means that the duration (time) and actual path distance will vary between segments. This will result in the loss of a significant amount of information about the actual trajectory. However the trade off for this information is the ability to readily use the segment terminus to create Poincare sections. These Poincare sections can be used to examine the isolated behavior of Levy flights. As each segment and its angle is evaluated, its Poincare surface intersection is recorded. The generation of a Poincare section is then a natural byproduct of this analytic method, reducing the need for further calculations.

5.2 Levy Flight Statistics at 85 meV

Several long trajectory simulations ($.96\mu\text{sec}$) were run at several evenly spaced energies between 85 and 155 meV. Using the selection method previously mentioned, the distribution properties of the recorded flights were then analyzed. Selecting only flights which maintained large segment angles for four consecutive segments should have removed any random diffusive flights, leaving only Levy flights in our selected data set. Ensuring that only the Levy flights had been retained into our selected data set, we examined the statistical distributions of the stored flights. If these are indeed Levy flights then they should have an exponential distribution (Levy distribution).

Examining the flight distribution properties at 85 meV, there is an apparently exponential decay in the probability of flight occurrences as flight lengths increase. In figure 5.3 we have generated two graphs. The left graph is the normalized probability distribution of

the selected flights ($P(x)$) on a linear scale. The right graph is the same probability distribution plotted on a semi log scale. There is a clearly linear trend, which indicates that the distribution function is indeed exponential, and that this is a Levy distribution. The inverse power law coefficient m in equation 2.1 can be obtained directly from the distribution data plotted on the semi log scale. The coefficient m is simply the slope of the data on the right hand graph and can be derived using a common least squares fitting method.

The coefficient m provides a method for estimating the magnitude of the stabilizing effect that principal orbits have on the surrounding regions of chaotic phase space. If there exists a large amount of stabilization near the regular regions of phase space, the Levy flights will have longer flights occurring with a higher statistical probability. Thus the probability decay rate should be lower and the coefficient m should be less negative. If there is little stabilization near the regular regions, the Levy flights will tend to be short, with long flights occurring with significantly lower probability, resulting in a quickly decaying probability distribution of flight lengths. The coefficient m under these conditions should have a large negative value.

In addition to a basic Levy distribution analysis, we are from our studies aware of potentially two distinct types of Levy flights. One type is composed of horizontal and vertical (HV) motions which are, because of system symmetry, fundamentally the same motion. A second type is composed of diagonal motions (DD). There are also two types of DD motion, those with relative positive slopes and those with relative negative slopes. Both of these diagonal motions are also the same fundamental motion.

An examination of the independent distribution characteristics of these two types of Levy flights can provide pertinent information about the construction of the phase space. The relative degree of stabilization that results from the different types of principal orbits (HV and DD) is readily determinable. This can be used to evaluate the how the different types of principal orbits affect their surrounding chaotic space. An estimate can then be made of the relative contribution that each type of Levy flight provides to the net anomalous diffusion rate.

5.3 Levy Distribution Analysis

We have evaluated the statistical distribution of the selected ballistic flights derived from long trajectory calculations and have insured that the ballistic flight distributions at each energy are indeed Levy distributions. The power law coefficients m , which we will now refer to as the Levy coefficient, were then determined at each energy for both the HV and DD motions individually as well as the combined set of motions. The Levy coefficients were then plotted as a function of energy in figure 5.4.

The heavy solid line in this figure is a plot of the Levy coefficients for the combined

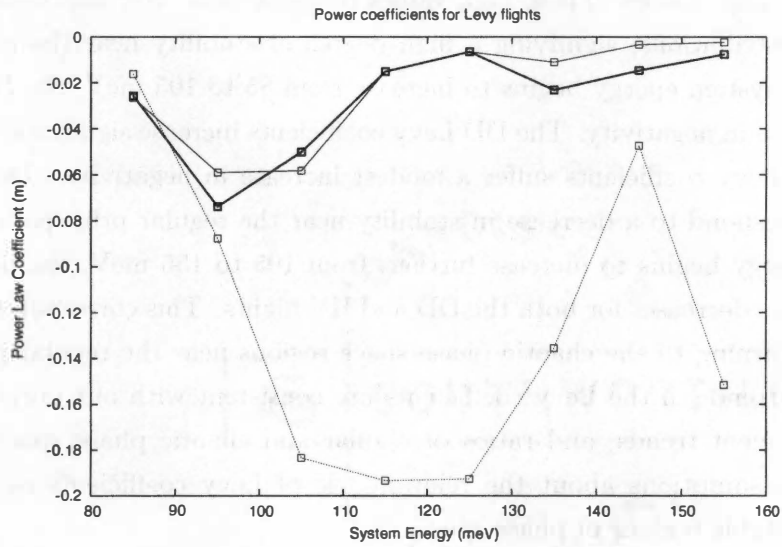


Figure 5.4: Plot of Levy coefficient values as a function of energy. Values are presented at several energies between 85 and 155 meV. The heavy line is a plot of the Levy coefficients for the net Levy flights (both HV and DD). The light solid is a plot of the Levy coefficients for the HV Levy flights. The dotted line is a plot of the Levy coefficients values for DD Levy flights. The last point at 155 meV in the DD data set is suspicious and is inconsistent with previous trends and Poincare comparisons.

HV and DD Levy distributions. The light solid line is a plot of the Levy coefficients for the HV Levy distributions and the dotted line is a plot of the Levy coefficients for DD Levy distributions. Examining this data we draw several conclusions. The first is that while the independent HV and DD Levy coefficients differ dramatically at several energies, the combined HV-DD Levy coefficients very closely parallel the HV Levy coefficients. The Levy coefficients for the combined HV-DD Levy distributions are significantly influenced by the HV Levy distributions. This observation implies that at most energies the majority of anomalous diffusion occurs along the horizontal and vertical directions.

It is also observed that at the lower energy of 85 meV all the Levy coefficients have relatively high values. These high values correspond to slow exponential decay rates in the Levy distributions, signifying a high degree of stability near the regular principal orbits. As the system energy begins to increase from 85 to 105 meV, the Levy coefficients begin to increase in negativity. The DD Levy coefficients increase significantly in negativity, while the HV Levy coefficients suffer a modest increase in negativity. These increases in negativity correspond to a decrease in stability near the regular principal orbits. Then as the system energy begins to increase further, from 105 to 155 meV, the negativity of the Levy coefficients decreases for both the DD and HV flights. This corresponds to an increase in stability returning to the chaotic phase space regions near the regular principal orbits. These general trends in the Levy coefficients are consistent with our previous determined Lyapunov exponent trends, and ratios of regular and chaotic phase space regions. This confirms our assumptions about the relevant use of Levy coefficients as an estimate of stability near stable regions of phase space.

A comparison between the trends in the Levy coefficients and the behavior in corresponding Poincare sections can also be made. A strong increase in negativity for the HV Levy coefficients corresponds to the loss of the phase space structure (on the Poincare sections) responsible for the HV motions. Additionally, the DD Levy coefficients suffer a similar but much more significant increase in negativity which also corresponds to a loss of the phase space structure responsible for the DD motions. The large differences between relative values of the HV and DD Levy coefficients cannot be just a result of the loss of phase space structure. If that were the case we should have observed similar Levy coefficients for both the HV and DD loss of phase space structure. This suggests that as the regular phase space structures dissipate residual stability persists at their previous locations and that the dissipation of the DD regular region is more complete and prolonged than that of the HV regions. A close examination of the Poincare sections at these energies supports this assertion. This correlation also clarifies another important issue, that as regular regions of phase space contract or dilate the magnitude of their stabilization of the neighboring chaotic space decreases or increases respectively.

5.4 Transition Poincare Sections at 85 meV

After examining the distribution characteristics of the selected flights and confirming that they are Levy flights, we have begun to examine Poincare sections constructed from the Levy flights. Specifically, these *transition* Poincare sections will be constructed using only the Poincare intersections bounding the transition to and from Levy motion. This transition period can be decomposed into three periods; immediately prior to the transition, the transition moment, and immediately after the transition. The Poincare sections immediately prior to and immediately after the transition will be constructed from the three intersections each trajectory makes with the Poincare surface immediately before and after the transition. The transition moment Poincare section will contain only a single Poincare surface intersection point from each trajectory. These transition Poincare sections can then be used identify the gateways which control the transition from normal diffusion to anomalous diffusion. The location and relative sizes of these gateways may then provide information which can be used to determine how system parameters affect anomalous diffusion.

A general Poincare surface calculated at 85 meV (figure 5.5) shows no coherent structure within the stochastic sea. There exist several identifiable several regions of stability: The first is a central region containing periodic orbits which correspond to ballistic motion along the y axis, Another is the outer region of stability containing periodic orbits corresponds to ballistic motion along the x axis. A set of left-right flanking regions containing stable orbits corresponding to stationary cyclic motion (stable frustrated motion) is another region of regular phase space. A last set of regular regions are two small regions of stability centered near $(y = 0, P_y \approx \pm 11)$, which contain periodic orbits corresponding to ballistic motion along the diagonal vectors. The transition Poincare surface in figure 5.6 stands in stark contrast to its corresponding Poincare surface figure 5.5.

This transition Poincare surface was constructed from a single trajectory calculation, initially started within the stochastic sea. The trajectory was simulated for 0.96 microseconds. The transition Poincare section records all three periods for the Levy to normal diffusion transitions. Overlaying the transition Poincare surface on to the general Poincare surface in figure 5.7, the differences between the two can be more closely examined.

A first observation in this overlay is that all of the recorded intersections for the transition Poincare section occur within the stochastic sea (as we should expect). A second observation is that these intersections occur with a clearly distinct pattern. The structure visible in the transition Poincare section suggests that the transition to and from Levy motion occurs in specific regions of phase space. The striations near the boundaries of regular regions further imply that a general proximity to regular regions of phase space is insufficient to guarantee a transition and that transitions must occur along specific vectors. Another obvious feature of the transition Poincare surface is its two-fold rotational symme-

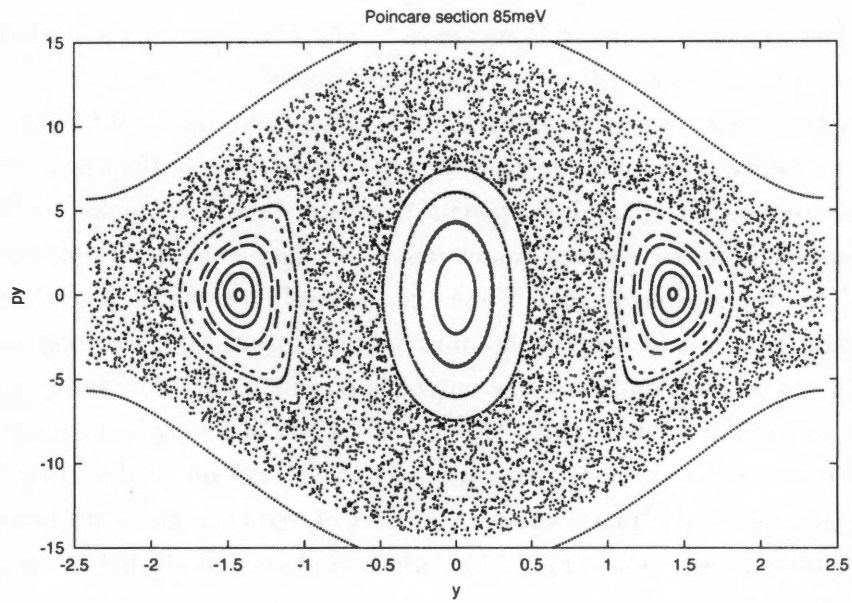


Figure 5.5: Examination of the Poincare section at 85 meV. There are several regions of stability located: center, flanking the center left and right, small regions above and below the central region of stability and the region between the stochastic sea and the energetic boundary of the system. Notice there are no discernible structures within the stochastic sea.

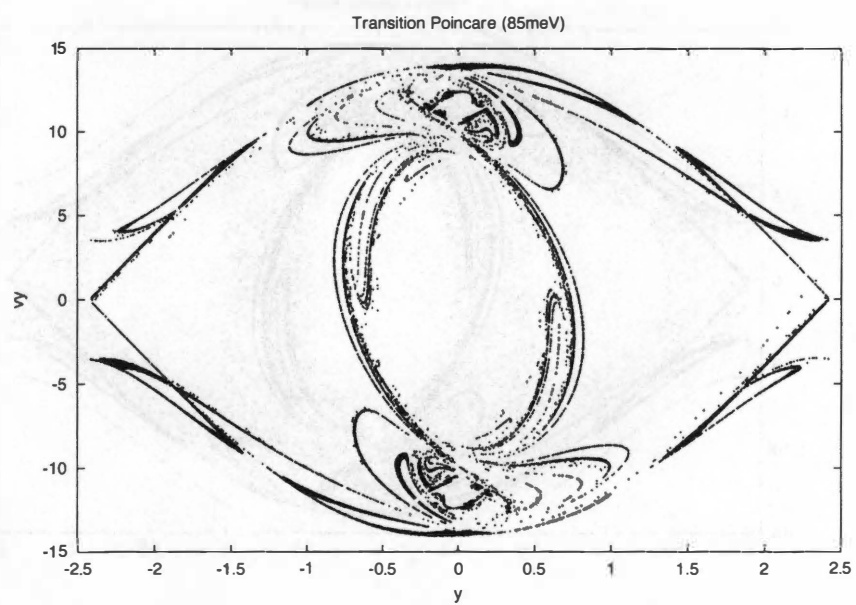


Figure 5.6: Transition Poincare section for Levy to normal diffusive motion transitions at 85 meV.

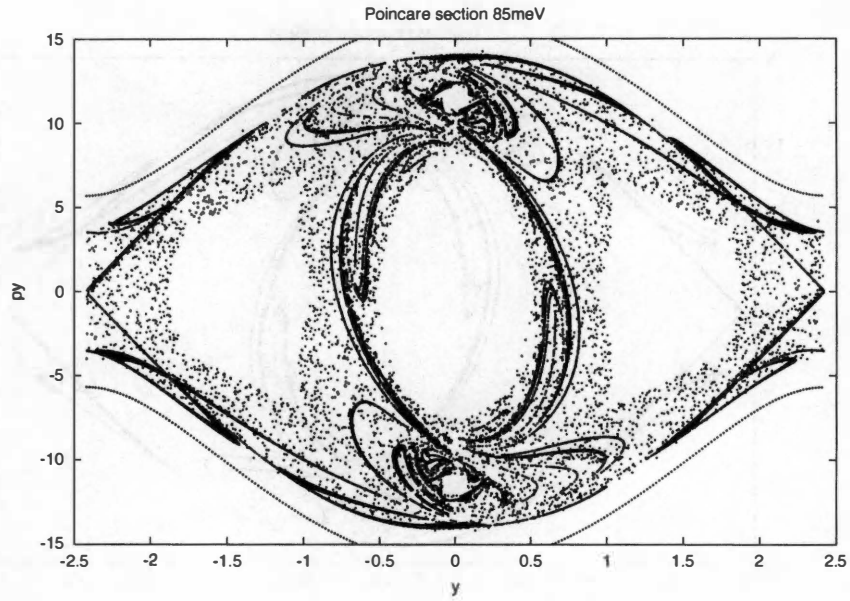


Figure 5.7: Overlay of a general Poincare section and a transition Poincare section at 85 meV. This figure shows the transition Poincare section for the transition from Levy motion to normal diffusive motion superimposed onto the general Poincare section at 85 meV.

try. Additionally a transition Poincare section recording both the transition to and from Levy motion is presented in figure 5.8. This figure clearly depicts the symmetric nature of the Levy flight transitions.

The clustering of transition intersections on the Poincare surface near the edges of the regular phase space for HV and DD motions in figure 5.7 further supports previous assumptions about the stabilization effect that principal orbits have on their neighboring phase space.

The stabilization of the space near the regular regions of phase space does indeed result in trajectories which are *sticky* and tend to cling to the edge of the regular regions. We have also shown that these *sticky* portions of the trajectory are Levy flights.

The lack of points near the edge of the regular regions responsible for trapped cyclic motions in figure 5.7 (left and right of the central regular region) indicates that these regular regions are non-stabilizing. We can now assert that there exist two types of regular regions for this system, stabilizing and non-stabilizing. These types of behaviors are referred to typically as *chaos attractors* and *strange attractors*^{2,8}, respectively.

These different types of regular regions could provides us with additional interpretive powers for the analysis of Poincare sections by providing an additional avenue in which to pursue a better understanding of this system. One could more closely examine the Lyapunov exponents within different types of regular regions to see if there are observable differences in Lyapunov exponents between the two different types of regular regions, stabilizing and non-stabilizing. If there are discernible differences between the two, this could provide a more detailed method to evaluate how the types and sizes of the regular regions affect the chaotic space. To more fully analyze the transition process we have decomposed the transition Poincare section into the three time regimes; immediately prior to the transition, the exact transition, and immediately after the transition.

Immediately prior to the transition from Levy to normal diffusive motion, we observe in figure 5.9 that all the intersections are located on the periphery of regular regions. This is consistent with the notion that Levy flights occur near the edge of a regular region and display a transient stability characteristics similar to that regular region. We have further decomposed the pre-transition behavior into unique HV and DD Poincare sections. In figure 5.10 we have plotted the separated HV and DD Poincare sections. In this figure it is evident that the HV and DD Levy flights occur in distinct non-overlapping regions of phase space as is expected. These Levy flights occur within a tight proximity to their respective regular regions.

Following the transition process we have then plotted a transition Poincare section of the position of the Levy flights at the moment when the Levy flights end and diffusive motion begins to return. This transition point was determined by evaluating the segment-segment angles. The transition for each flight was selected as the first segment terminus which had

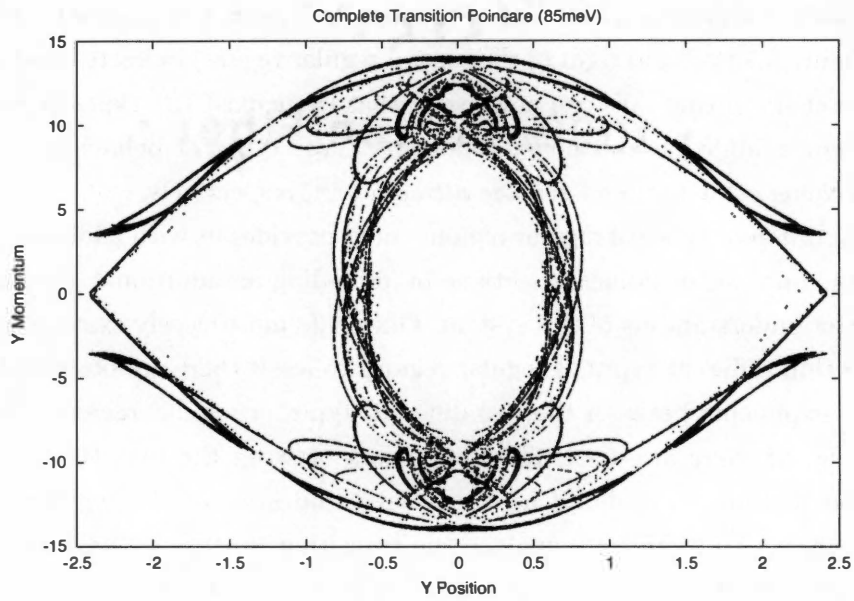


Figure 5.8: Transition Poincare section of transitions to and from Levy motions at 85 meV. The symmetric nature of this Poincare section can be compared to the transition Poincare section in figure 5.6 to confirm that the transition process is symmetric.

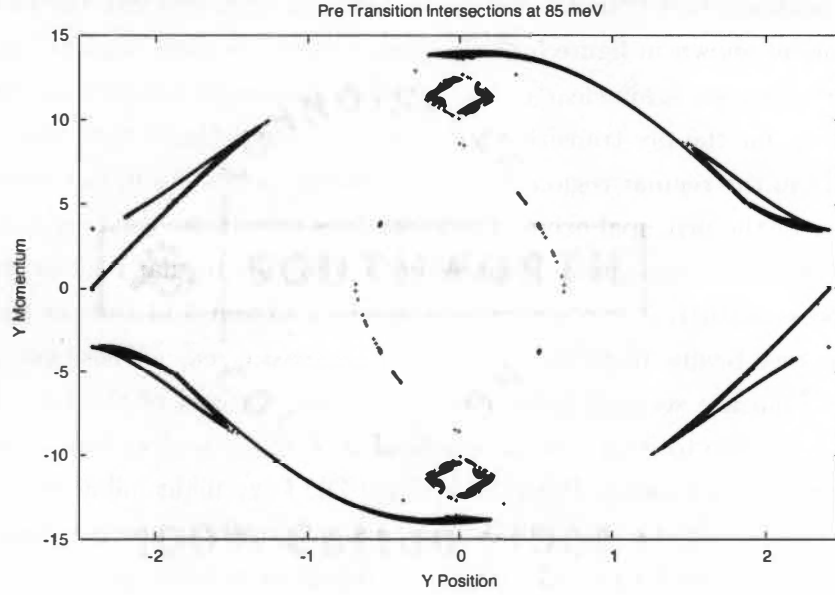


Figure 5.9: Poincare surface intersections immediately prior to the transition from Levy motion to normal diffusive motion at 85 meV. All intersections lie within immediate proximity to regular regions of phase space which should be expected for Levy motions.

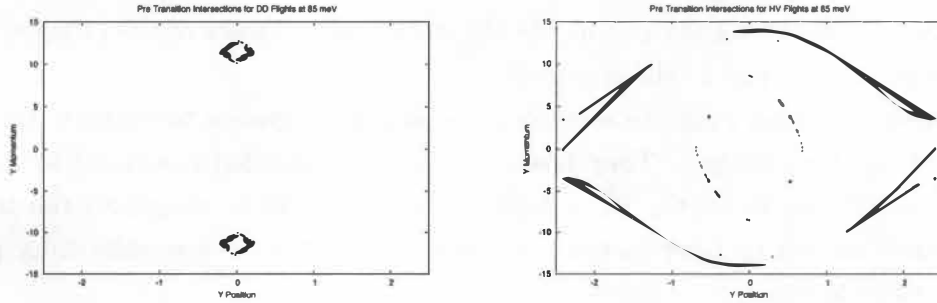


Figure 5.10: Two transition Poincare sections of the pre-transition Levy intersections; Right: DD Levy flights, Left: HV Levy flights. The left Poincare section shows the intersections for the DD type Levy flights and right Poincare section shows the intersections for the HV type Levy flights. In these two Poincare sections it is observable that the two types of Levy flights are indeed unique and occupy different regions of phase space.

a segment angle less than 165° after a series of at least four consecutive angles of greater than 165° . The transition Poincare section containing these intersections is presented in figure 5.11. This transition Poincare section was then decomposed into the unique HV and DD components as shown in figure 5.12. In these figures, the clear separation between the two types of motions are again clearly observable. Additionally, comparisons between these figures and those for the pre-transition show that the Levy flights have begun to migrate further away from the regular regions. These transition points are in fact at the very edge of the influence of the principal orbit. Their locations provide a visual estimate of the size and shape of the stabilized regions of space surrounding the regular regions. Following the transition process farther, it is observable in figures 5.13 and 5.14 that as the Levy flight ends the trajectory begins to return to the bulk stochastic sea. These two figures show the trajectory Poincare sections immediately following the end of the Levy flights. The trajectories have begun to return to the stochastic sea, but it is clear that these transitions occur along very distinct paths. Both the HV and DD Levy flight follow differing paths as they return to the stochastic sea. However as time progresses it becomes more difficult to determine the history (or future) of a trajectory based on its location.

The observed behavior of the Levy flight transitions agree with our intuitive expectation of these transitions. Furthermore, examinations of the transition Poincare sections for the reverse process, the transition from normal motion to Levy motion, show that it occurs in a similar fashion, but in the reverse order. The life cycle of a Levy flight is then relatively straight forward. A trajectory begins within the stochastic sea, where its motions are essentially random (on the Poincare section). Eventually the trajectory acquires the appropriate vector on the Poincare surface (y and p_y) and is funnelled towards a regular region. Once the trajectory reaches the limit of its approach to the regular region, it begins to move away from the regular region. As the stabilizing influence of the principal orbit is lost the trajectory returns to the stochastic sea.

These transition Poincare sections have provided a means to evaluate the general behavior of the Levy flights. They however, have not provided a method to determine dynamic information about the Levy flights. We would like to determine the transition rates between normal to Levy motion. However this method is not sufficiently powerful enough to provide this type of information.

5.5 Conclusions

We have verified that the ballistic motions resulting in anomalous diffusion in our sodium adatom diffusion simulations are indeed Levy flights. We have also shown that the Levy flights are the result of stabilizing effects near regular regions of phase space. We have evaluated the life cycle of these Levy flights using analysis of transition Poincare sections

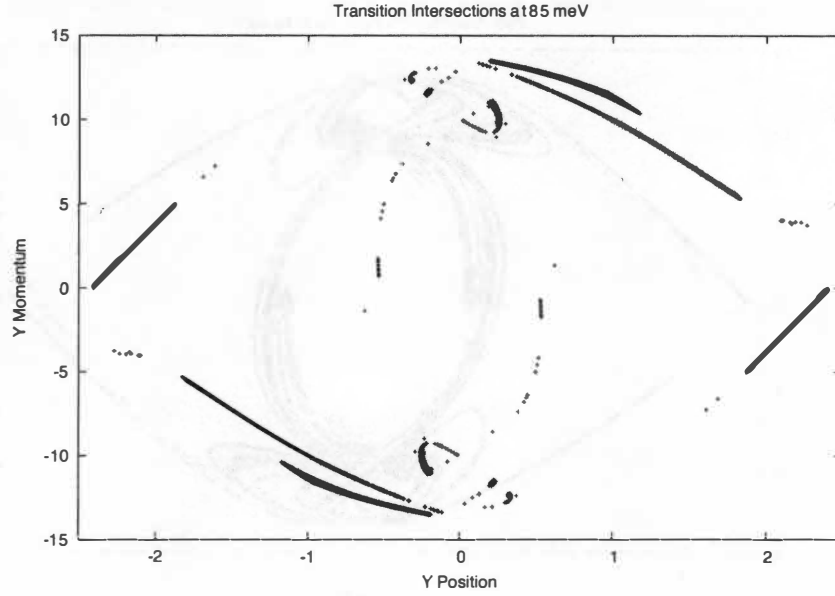


Figure 5.11: Transition Poincare section at the moment of the Levy to normal motion transition at 85 meV. It is observable that these intersection have moved farther away from the regular regions, and that these flights are beginning to lose their stability. But the intersections are occurring within very confined positions. This suggests that the transition between anomalous and normal diffusion occurs under very stringent conditions.

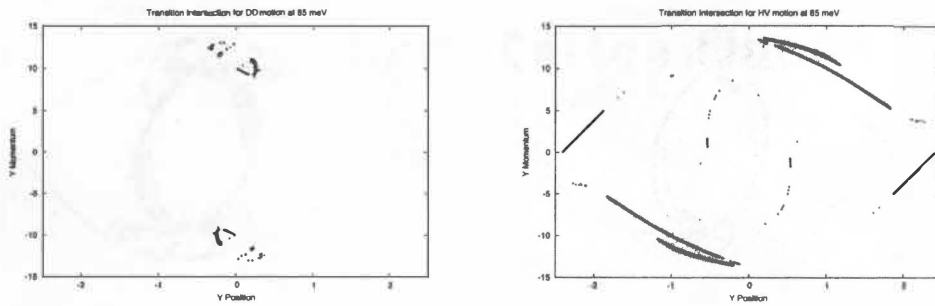


Figure 5.12: The two diagrams in this figure again show the intersections for both types of Levy flights, DD on the left and HV on the right. There is a clear distinction between HV and DD locations on these Poincare sections, signifying that each type of Levy flight has its own transition gateway.

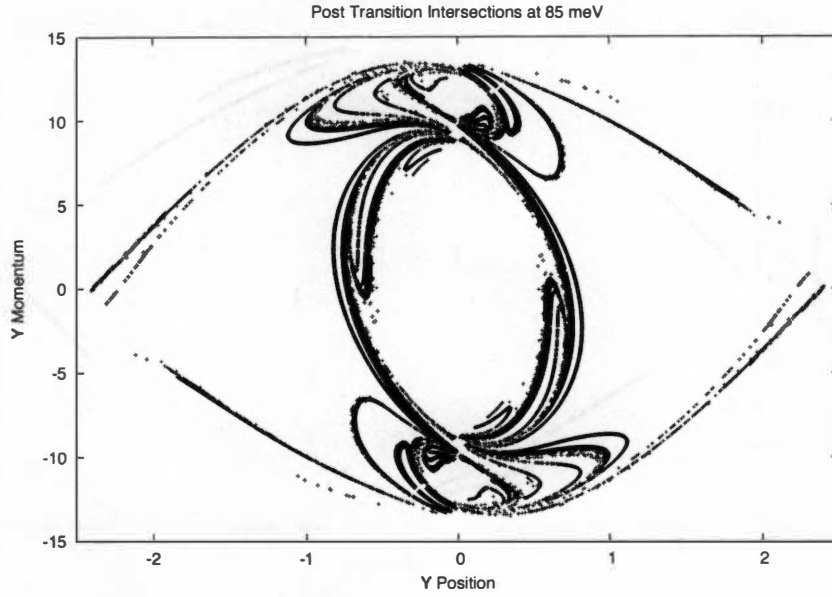


Figure 5.13: Transition Poincaré surface intersections immediately after the transition from Levy motion to normal diffusive motion. The intersections have moved away from the regular regions of phase space and into the general stochastic sea. The patterns and striations of the post-transition intersections indicate a very ordered transition.

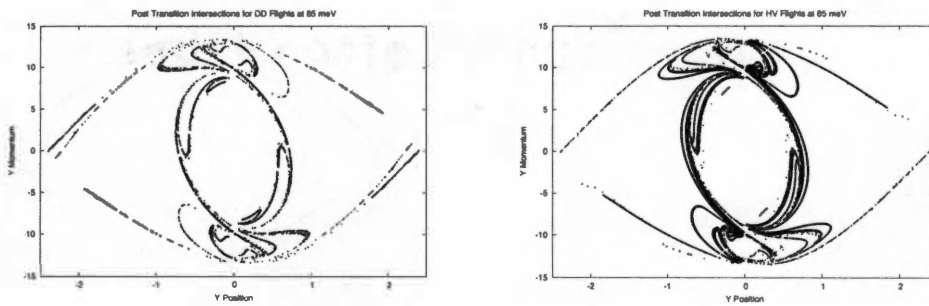


Figure 5.14: Two transition Poincaré sections of the post-transition behaviors for Levy to normal motion transitions; Right: DD Levy flights, Left: HV Levy flights. The distinction between HV and DD locations is beginning to fade as the trajectories return to the stochastic sea.

and have shown that transitions to and from Levy motion occur in a ordered manner. Additionally we have shown that small gateways exist in phase space which control the occurrence of Levy flights and consequently anomalous diffusion. However, the method of analysis we have followed has not revealed any dynamical information about the transition process. Similar transition analysis using Poincare sections which are defined in different coordinate systems (eg. (P_y, P_x) rather than (y, P_y)) may provide a more direct method to evaluate dynamical properties.

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Appendix

Appendix A

Fourier Transform

The direct calculation of the GVM potential requires the summation of three inseparable functions (eqns. 1.7, 1.8, 1.9). The first equation is a simple cosine function, but the remaining two functions require the double summation of exponential functions. In practice, these functions require the summation of M and N to span from -10 to 10, thus requiring approximately 800 exponential calculations (plus general overhead calculations) every time the GVM potential is calculated. This potential is computationally expensive and prohibitively costly when evaluating long simulations.

Examining the GVM potential (figure 1.2), it is apparent that this function is smooth, symmetric and periodic, on a regular interval L (L = cell length, 4.832 bhor) in the xy -space. These properties make the GVM potential an excellent candidate for a Fourier transform.

The general form for a 2D Fourier transform is

$$\mathcal{F}(u, v) = \int \int f(x, y) \exp(2\pi i(ux + vy)) \delta x \delta y \quad (\text{A.1})$$

with the reverse transform being

$$f(u, v) = \int \int \mathcal{F}(u, v) \exp(2\pi i(ux + vy)) \delta u \delta v, \quad (\text{A.2})$$

where $\mathcal{F}(u, v)$ is the Fourier transform of $f(x, y)$ at the frequencies u and v .

The regular periodicity and even nature of the GVM potential allow the use of a simplified form of the Fourier transform,

$$\mathcal{F}(u, v) = \int_0^L \int_0^L f(x, y) \cos(2\pi ux/L) \cos(2\pi vy/L) \delta x \delta y, \quad (\text{A.3})$$

where the integrals in xy -space are continuous. But frequencies u and v are now restricted to a principal frequency, with a period of length L , and integer multiples of that frequency.

The reverse transform for the discrete frequencies is then

$$f(x, y) = \frac{1}{MN} \sum_{u=0,1,2,..}^M \sum_{v=0,1,2,..}^N \mathcal{F}(u, v) \cos(2\pi ux/L) \cos(2\pi vy/L). \quad (\text{A.4})$$

Implementing the Fourier transform (eqn. A.3), the GVM potential was calculated with N, M spanning from -12 to 12. And the integration was performed numerically, using the simple trapezoid method with a dx, dy equal to $\frac{L}{500}$. These parameters provided Fourier transform coefficients ($\mathcal{F}(u, v)$) which are robust and well converged.

When constructing a potential using the reverse Fourier transform (eqn. A.4), no more than 5 discrete frequencies (in u and v) are necessary to provide double precision agreement with the original GVM potential. This greatly reduces the computational expense of calculating the GVM potential, requiring only 40 trigonometric calculations instead of 800 exponential calculations.

Additionally, calculations of the first and second derivatives of the GVM potential maintain similar precision and efficiency when derived from the Fourier transform coefficients. The convolution theorem allows us to evaluate the derivative of a function by using the derivative of the reverse transform, simply

$$\frac{df(x, y)}{\delta x} = \frac{1}{MN} \sum_{u=0,1,2,..}^M \sum_{v=0,1,2,..}^N \mathcal{F}(u, v) \frac{d(\cos(2\pi ux/L) \cos(2\pi vy/L))}{\delta x}. \quad (\text{A.5})$$

This provides a means to calculate analytic derivatives of the GVM potential very simply, using the Fourier transform coefficients already obtained.

The use of a Fourier transform of the GVM potential has greatly increased the efficiency of our calculations, while maintaining a high degree of integrity with respect to the GVM potential, allowing for longer simulations with smaller integration errors. Thus providing more reliable data to evaluate statistical distributions and system behaviors which might otherwise have gone unnoticed or been unobservable.

The Fourier coefficients we employed during the calculation of the FGVM are listed in table A. The GVM potential is symmetric in the x and y directions resulting in transposable values for u and v (ie. $\mathcal{F}(1, 2) = \mathcal{F}(2, 1)$). Therefore only unique Fourier coefficient values have been presented in table A.

Table A.1: Table of Fourier coefficients ($F(u, v)$)

u	v	$F(u, v)$ (hartrees)
0	0	-7.201996034498E-03
0	1	-8.107756710399E-04
0	2	-5.709384998901E-05
0	3	8.716743649175E-07
0	4	-2.498189530704E-09
0	5	1.342940051812E-12
1	1	-6.082918482886E-04
1	2	4.947346339481E-05
1	3	-7.553309131960E-07
1	4	2.164751978353E-09
1	5	-1.164805292327E-12
2	2	-4.023752700984E-06
2	3	6.143222230167E-08
2	4	-1.760626167916E-10
2	5	9.471929637210E-14
3	3	-9.379100100403E-10
3	4	2.688017509187E-12
3	5	-1.446094926439E-15
4	4	-7.703661125173E-15
4	5	4.071281003134E-18
5	5	2.338875978660E-20

Vita

James Wesley Mancillas born in Norfolk, Virginia on October 13, 1970, the oldest of three boys of Robert Ruiz Mancillas and Lorna Lum Mancillas. After graduating in 1988 from Pheobus High School, Hampton Virginia, he joined the United States Navy and successfully completed the Naval Nuclear Power Program, and served in the military until 1994, at which time he was given an Honorable Discharge. He then moved to Panama City Florida and married Ann Mancillas and began attending Gulf Coast Community College, Panama City Florida. In 1996 he received an Associate of Science from Gulf Coast Community College, Panama City Florida and began attendance at the University of West Florida, Pensacola Florida. In 1999 he received a Bachelor of Science degree *magna cum laude* In 2000, after a one year academic hiatus, he enrolled in the University of Tennessee, Knoxville. During the next five years, under the tutelage of Robert J. Hinde he studied methods of numerical evaluation of quantum mechanical and thermodynamic systems. Then in 2005 he received a Doctorate of Philosophy from the University on Tennessee, Knoxville, in the field of Chemistry. James Mancillas has now gone to find his fortune in places unknown.

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