THE STATIC AND DYNAMIC PROPERTIES OF LENNARD-JONES CLUSTERS
AND CHAINS OF LENNARD-JONES PARTICLES

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ABSTRACT

Groups of identical particles interacting through Lennard-Jones (LJ) potentials may serve as a model for atomic clusters at low temperatures. A model for polymer chains is obtained when the LJ particles are connected by harmonic springs. The focus of this work is the comparison of static and dynamic properties of clusters and chains of LJ particles. Small clusters of LJ particles have been studied in detail using molecular dynamics simulations. In agreement with work in the literature, the LJ clusters have been found to exhibit phase properties similar to those of macroscopic systems. In particular, they exhibit solid-like behavior at low energies and liquid-like behavior at higher energies. In addition, the dynamics of LJ clusters has been found to be chaotic at all energies. The methods used to study LJ clusters have been extended in this work to investigate the properties of chains of LJ particles connected by harmonic springs. It has been found that the bonds have an effect on both the static and dynamic properties of the chain. Specifically, it has been discovered that chains of LJ particles exhibit solid-like and liquid-like behavior similar to LJ clusters. For the chains, however, the transition between these two “phases” occurs at higher energy. Additionally, the chains of LJ particles exhibit a lower degree of chaotic behavior than the corresponding LJ clusters.
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CHAPTER I
INTRODUCTION

Small systems of particles may have very complex and interesting physical properties. Small clusters of Lennard-Jones (LJ) particles have been studied in detail using molecular dynamics (MD)\textsuperscript{1-3} and Monte Carlo simulations.\textsuperscript{4, 5} It has been found that LJ clusters exhibit phase properties similar to those found in macroscopic systems. In particular, they exhibit solid-like behavior at low energies and liquid-like behavior at higher energies. These phase properties have also been studied experimentally for small clusters of atoms.\textsuperscript{6, 7} In addition to the static properties, the dynamic properties of LJ clusters have been investigated, and it has been shown that LJ clusters exhibit chaotic behavior at all energies. In general, a dynamical system is considered chaotic if nearby trajectories in phase space diverge exponentially. The rate of exponential divergence in these trajectories may be described in terms of Lyapunov exponents, which provide a means of quantifying chaos.

Chains of LJ particles connected by harmonic springs provide a simple model for polymer chains. It is expected that the presence of these bonds has an effect on both the static and dynamical properties of the chains. The focus of this work is the comparison of static and dynamical properties of clusters and chains of LJ particles. The computational methods used previously in the study of LJ clusters\textsuperscript{1, 2} have been applied
here. Static properties of the chain have been calculated to determine if they exhibit the same “phase” properties exhibited by the LJ clusters, and dynamical properties have been examined through the calculation of Lyapunov exponents. In addition, the effect of modifying the bond constraints on the chain has been investigated by changing the strength of harmonic springs connecting particles.

The Lennard-Jones model for atomic clusters is introduced in Chapter II. This is followed by an explanation of the molecular dynamics simulation method in Chapter III. Chapter IV presents the results of simulations involving the static properties of the LJ clusters. Chapter V details a method for calculating Lyapunov exponents and gives the results obtained from its implementation and execution. In Chapter VI, the static and dynamical properties of a chain of LJ particles are investigated and comparisons are drawn between the properties of the chain and the cluster. Finally, Chapter VII summarizes the results presented in this study.
CHAPTER II

LENNARD-JONES MODEL FOR ATOMIC CLUSTERS

The Lennard-Jones model for atomic clusters is commonly employed in molecular dynamics simulations to approximate the behavior of groups of atoms. Clusters are composed of \( N \) identical particles of mass \( m \), the positions and velocities of which are given by \( \vec{r}_i \) and \( \vec{v}_i \), where \( \vec{r}_i \) and \( \vec{v}_i \) are vectors in three dimensions and \( i \in \{1, 2, \ldots, N\} \) gives the particle number. The particles interact with each other via a Lennard-Jones potential defined as follows:

\[
V_{ij}^{LJ} = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right].
\]  

(1)

Here, \( r_{ij} \) is the magnitude of the distance between the \( i \)th and \( j \)th particles defined by

\[
r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2},
\]

(2)

where \( x, y, \) and \( z \) are the three components of \( \vec{r} \) in Cartesian coordinates. The energy parameter \( \varepsilon \) determines the depth of the potential, and the size parameter \( \sigma \) determines the position of the potential minimum \((2^{1/6} \sigma)\). Figure 1 displays how the potential changes as a function of interparticle distance.
Figure 1. The Lennard-Jones potential as a function of interparticle distance. The figure shows how the parameters $\varepsilon$ and $\sigma$ determine the depth and location of the potential minimum, respectively. In this case, both $\varepsilon$ and $\sigma$ are set to one.

Throughout the simulation several quantities related to the energy and momentum of the system are routinely calculated. The potential energy of the system is calculated by summing over the potential energy of the pairs of particles as follows:

$$E_{pot} = \sum_{i=1, i<j}^{N} V_{ij}^{LJ}.$$  \hfill (3)

Similarly, the kinetic energy of the system is obtained by summing over the kinetic energies of individual particles; i.e.,

$$E_{kin} = \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2,$$  \hfill (4)

where $m_i$ is the mass of the $i$th particle and $v_i$ is the magnitude of the velocity of the $i$th particle given by

$$v_i = \sqrt{v_{x,i}^2 + v_{y,i}^2 + v_{z,i}^2}.$$  \hfill (5)
Here, $v_x$, $v_y$, and $v_z$ are the three components of $\vec{v}$ in Cartesian coordinates. The total energy of the system is determined by adding the kinetic and potential energies:

$$E_{\text{tot}} = E_{\text{pot}} + E_{\text{kin}}.$$  \hfill (6)

The total momentum of the system is calculated by summing over the individual momenta of the particles as follows:

$$\vec{p} = \sum_{i=1}^{N} m_i \vec{v}_i.$$  \hfill (7)

The total angular momentum of the system about the center of mass is given by

$$\vec{L} = \sum_{i}^{N} (\vec{r}_i - \vec{r}_{cm}) \times (m_i \vec{v}_i),$$  \hfill (8)

where $\vec{r}_{cm}$ is the vector from the origin to the center of mass of the cluster determined by

$$\vec{r}_{cm} = \frac{\sum_{i=1}^{N} m_i \vec{r}_i}{\sum_{i=1}^{N} m_i}.$$  \hfill (9)

For the case when $\vec{r}_{cm} = 0$ (which is true for the simulations that follow), the angular momentum in terms of individual components can be calculated using the following:

$$L_j = \sum_{i}^{N} m_i (r_{i,j} v_{i,l} - r_{i,l} v_{i,j}),$$  \hfill (10)

where $j$, $k$, and $l$ are cyclic permutations of the Cartesian components $x$, $y$, and $z$.

With the exception of Lyapunov exponents, whenever error estimates are included in the results, they are calculated using block averages. The error estimate is given by
\[ \sqrt{\frac{1}{n} \sum_{i}^{n} \left( \langle w^2 \rangle_i - \langle w \rangle_i^2 \right)}, \]

(11)

where \( \langle w \rangle_i \) represents the average of any quantity \( w \) over block \( i \) of simulation time, and \( \langle w^2 \rangle_i \) is the corresponding average of the squared velocity. Here, \( n \) is the total number of blocks being used to determine the error estimate. Unless otherwise noted, \( n = 10 \) for all the results that follow.

Throughout this work, unless otherwise noted, use is made of Lennard-Jones reduced units, where dimensionless units are defined by choosing \( \epsilon, \sigma, \) and \( m \) to be units of energy, length, and mass, respectively. This implies that time is measured in units of \( \sqrt{\frac{m\sigma^2}{\epsilon}} \). Using argon as an example, which has LJ parameters \( \epsilon = 1.67 \times 10^{-21} \) J, \( \sigma = 3.4 \times 10^{-10} \) m, and \( m = 6.63 \times 10^{-26} \) kg, one unit of simulation time corresponds to \( 2.14 \times 10^{-12} \) s.
CHAPTER III
SIMULATION METHOD

Molecular Dynamics Simulation

Molecular dynamics simulations are used to produce trajectories for the LJ cluster. In molecular dynamics simulations Newton’s equations of motion are used to advance the positions and velocities of the particles over a series of time steps. For example, the motion of a particle in one dimension can be described by the equations

$$x_{n+1} = x_n + v_n \Delta t + \frac{F_n \Delta t^2}{2m}$$

(12)

and

$$v_{n+1} = v_n + \frac{F_n \Delta t}{m}.$$  

(13)

The positions and velocities of the particle are advanced from the $n$th to $(n+1)$th time step, the size of which is determined by $\Delta t$. $F_n$ represents the net force on the particle at time step $n$. Given a potential $V(x)$, this force can be calculated at any point using

$$F = -\frac{\partial V}{\partial x}.$$  

If the particle is assigned a position and velocity at the beginning of simulation, its subsequent trajectory can then be determined through repeated applications of Equations (12) and (13). Time steps are chosen to be small enough that
error due to discretization is minimal, but not so small as to require impractically long
computing times to generate a useful trajectory.

For the data gathered from the molecular dynamics simulations to be useful, the
trajectory must cover a representative sample of the total phase space of the system. This
means that the results from the simulation must be independent of the initial state of the
system.\(^8\) To ensure that the system retains no “memory” of its initial conditions, the
positions and velocities of the system are advanced over a series of so-called
equilibration steps before any data are taken. After the system has reached an
equilibrium state independent of the initial conditions, the subsequent time steps are
referred to as production steps.

Molecular dynamics simulations can be performed in a variety of statistical
mechanical ensembles. All the molecular dynamics simulations in this work are
performed in the microcanonical ensemble, so the number of particles, volume, and total
energy are held constant. All three of these parameters are fixed at the beginning of
simulation.

Molecular Dynamics Simulation Implementation

The positions and velocities of the particles are advanced using the velocity Verlet
method,\(^9\) where the velocity Verlet equations are defined as

\[
\vec{r}_{i,n+1} = \vec{r}_{i,n} + \vec{v}_{i,n} \Delta t + \frac{\vec{F}_{i,n} \Delta t^2}{2m_i}
\]  

(14)

and
These equations are multiparticle three dimensional equivalents of Equations (12) and (13), except for the fact that the velocity is updated using an average of the net forces at two consecutive positions rather than one. The net force is calculated at each step based on the current spatial configuration of the cluster and the consequent interactions of the particles with each other. For the particles in the cluster, the net force is the sum of the forces due to interactions with each other; i.e.,

\[ \vec{F}_i = \sum_{j=1, j\neq i}^{N} F_{ij}^{LJ}. \]  

The force on an object in a potential field is the negative gradient of the potential, \( F = -\nabla V \). In the Lennard-Jones model, the forces due to interaction between particles \( i \) and \( j \) can then be calculated as follows:

\[ F_{ij}^{LJ} = -\nabla V_{ij}^{LJ} = \frac{24 \varepsilon}{m_i} \left[ 2 \sigma_{ij}^{12} \frac{1}{r_{ij}^{13}} - \sigma_{ij}^{6} \frac{1}{r_{ij}^{7}} \right]. \]  

The direction of this force can be determined by noting that the force is always directed along a straight line connecting the two particles. In addition, a negative value for \( F_{ij}^{LJ} \) indicates that the interaction between the two particles is attractive, so that the forces acting on particles \( i \) and \( j \) are directed towards each other. A positive value for \( F_{ij}^{LJ} \) indicates that the interaction between the two particles is repulsive, so that the forces acting on particles \( i \) and \( j \) are directed away from each other.
Conserved Quantities

In the molecular dynamics simulations performed in this work, there are several conserved quantities that can be used to test the quality of the simulations. Because all the forces acting on the particles are derived from a conservative potential, it is expected that the total energy remain constant. A variable total energy would suggest a flawed method for advancing the state of the system and/or a poor choice for the value of $\Delta t$.\(^8\)

To determine how well the total energy was being conserved, the percent relative deviation in $E_{\text{tot}}$ was calculated using

$$\frac{E_{\text{tot}} - \langle E_{\text{tot}} \rangle}{\langle E_{\text{tot}} \rangle} \times 100\%,$$  

(18)

where $\langle E_{\text{tot}} \rangle$ is the average value of $E_{\text{tot}}$ over the entire run. Figure 2 shows the results of this calculation for a typical simulation of a cluster of three particles.

![Graph showing percent relative deviation in total energy as a function of time steps](image)

Figure 2. The percent relative deviation in the total energy as a function of time steps for a cluster of three identical Lennard-Jones particles. This sample was taken for $E_{\text{tot}} = -2.7$
and $\Delta t = .00467$. The percent relative variation is shown for every ten thousandth time step.

The total energy is conserved to within .01% of the desired value, which is in agreement with previously published research that made use of the Verlet method with an identical time step.$^1$

Because there are no external forces acting on the system, the total linear momentum should also be conserved. Furthermore, since there are no boundaries that would break spherical symmetry, the angular momentum is expected to be conserved. Figures 3 and 4 show how the total linear and angular momentum change with time for a typical simulation of a 3-particle cluster. Initial conditions were defined so that the initial values of both linear and angular momentum were zero.

![Figure 3](image)

Figure 3. The x, y, and z components of linear momentum as a function of time steps for a 3-particle cluster. This sample was taken for $E_{\text{tot}} = -2.7$ and $\Delta t = .00467$. Data are displayed for every ten thousandth time step.
Figure 4. The x, y, and z components of angular momentum as a function of time steps for a 3-particle cluster. This sample was taken for $E_{tot} = -2.7$ and $\Delta t = .00467$. Data are displayed for every ten thousandth time step.

Note that the values for the linear and angular momenta are on the order of $10^{-14}$, which is very close to zero and indicates that linear and angular momenta are conserved to a very high degree.

**Initial Conditions**

To begin the simulation, the particles are arranged so that the cluster is near its ground state configuration. In the case of the 3-particle cluster, particles are placed on the corners of an equilateral triangle, so that they are the same distance from each other and the origin. The 13-particle cluster is arranged in an icosahedral fashion with one particle centered at the origin and the remaining twelve placed on the corners of the icosahedron. The initial configuration of both clusters is shown in Figures 5 and 6.
The spacing between particles is adjusted so that the potential is near its minimum. Both configurations are placed in such a way that the center of mass is located at the origin.

The initial velocity of each particle is generated randomly. The velocity of the center of
mass is then calculated and subtracted from the velocity of each particle, which sets the total linear momentum to zero. Components of the velocity that cause the angular momentum to be nonzero are subtracted to yield zero angular momentum.

The total energy of the system is set to the desired value by increasing or decreasing the kinetic energy by scaling the velocities of each particle by a common factor. When a series of simulations at different total energies are performed in succession, the ending configuration of the previous simulation is used as the starting configuration of the subsequent simulation, with ending velocities of the previous simulation being rescaled to reach the desired energy.
CHAPTER IV
THE SOLID-LIKE AND LIQUID-LIKE BEHAVIOR OF LENNARD-JONES CLUSTERS

Introduction

Molecular dynamics simulations were performed on Lennard-Jones (LJ) clusters of size three and thirteen. Of particular interest was how the behavior of the clusters changed depending on the total energy of the system. At low energy, the clusters exhibited rigid, solid-like behavior; at high energy, the clusters exhibited a less-ordered liquid-like behavior; and between the two distinct regions, the clusters exhibited a transitional “two-phase” behavior.

“Snapshots” of Lennard-Jones Clusters

To illustrate how the behavior of the cluster changes between the low and high energy regions, “snapshots” of a 13-particle cluster were taken at select time intervals at two different energies.
Figure 7. Configuration of a 13-particle cluster at different times for $E_{tot} = -39.0$. $t = 0$ represents the beginning of production time. The cluster was equilibrated over $2 \times 10^5$ time steps for $\Delta t = 5 \times 10^{-4}$.

Figure 7 shows the arrangement of the particles of the cluster at three different times in the low energy region. The configurations at each time do not appear to differ significantly from one another and bear a strong resemblance to the icosahedral starting configuration shown in Figure 6.
Figure 8. Configuration of a 13-particle cluster at different times for $E_{\text{tot}} = -26.0$. $t = 0$ represents the beginning of production time. The cluster was equilibrated over $2 \times 10^5$ time steps for $\Delta t = 5 \times 10^{-4}$.

Figure 8 shows the arrangement of the particles of the cluster at three different times in the high energy region. The time intervals used are the same as those in the low energy case, so the results may be readily compared. In contrast to the low energy cluster, the high energy cluster appears to be decidedly less ordered; the arrangement of particles changes noticeably with time, and the particles do not appear to be bound to any type of rigid structure.

To further illustrate how the behavior of the cluster changes between the low and high energy regions, the trajectory of the particles in the cluster was plotted for each of the energies shown above. The results are shown in Figures 9 and 10.
Figure 9. The trajectory of a 13-particle cluster over $1 \times 10^5$ production steps for $\Delta t = 5 \times 10^{-4}$ and $E_{tot} = -39.0$. The cluster was equilibrated over $2 \times 10^5$ time steps.

Figure 10. The trajectory of a 13-particle cluster over $1 \times 10^5$ production steps for $\Delta t = 5 \times 10^{-4}$ and $E_{tot} = -26.0$. The cluster was equilibrated over $2 \times 10^5$ time steps.

The trajectories displayed in Figures 9 and 10 confirm the conclusions drawn from observation of the “snapshsots.” At low energy, the motion of each particle is bound to a
small volume, and the regions of space where each particle is allowed to travel are distinctly separated. At higher energy, the particles gain more freedom of motion, and their trajectories are shown to fill the regions of space that are inaccessible at lower energy.

Probability Distributions of the Kinetic Energy

A more quantitative approach to analyzing the shift from solid-like to liquid-like behavior is to observe probability distributions of the kinetic energy of the cluster. This was done previously by Jellinek, Beck, and Berry for the 13-particle cluster\(^1\), and their results show good agreement with the results presented in this work. Probability distributions were created by averaging the kinetic energy of the system over sets of 500 time steps and counting the number of times each average kinetic energy value fell within a certain energy interval. Results were accumulated in intervals of size

\[ \Delta E_{\text{kin}} / N = 3 \times 10^{-3}, \]

uniformly distributed over the range of energies shown. Figures 11-15 show the distribution of the average kinetic energy for increasing values of total energy.
Figure 11. Distribution of short time averages of the kinetic energy for $E_{\text{tot}}/N = -2.83$.

Figure 12. Distribution of short time averages of the kinetic energy for $E_{\text{tot}}/N = -2.56$. 
Figure 13. Distribution of short time averages of the kinetic energy for $E_{tot}/N = -2.42$.

Figure 14. Distribution of short time averages of the kinetic energy for $E_{tot}/N = -2.32$. 
In addition to creating probability distributions of short-time averages of the kinetic energy, the kinetic energy averaged over the entire simulation was also calculated and is shown in Figure 16 as a function of total energy.

Figure 16. Kinetic energy per particle as a function of total energy per particle. Open diamonds represent data from this work, while crosses represent Jellinek, Beck, and
Our simulation was performed for $2 \times 10^5$ equilibration steps and $1 \times 10^6$ production steps with $\Delta t = 5 \times 10^{-4}$.

The average kinetic energy presented in Figure 16 is an average over probability distributions of the kind shown in Figures 11-15. The average kinetic energy can be expressed as

$$\langle E_{\text{kin}} \rangle = \int P(E_{\text{kin}}) E_{\text{kin}} dE_{\text{kin}},$$

where

$$P(E_{\text{kin}}) = \frac{\text{frequency}(E_{\text{kin}})}{\Delta E_{\text{kin}} \sum_{E_{\text{kin}}} \text{frequency}(E_{\text{kin}})}.$$

In the solid-like region (Figure 11) and in the liquid-like region (Figure 15) the probability distribution consists of a single peak. The position of the maximum and the width of the distribution increase with increasing total energy, which gives rise to the average kinetic energy shown in Figure 16. In the “coexistence region,” where both solid-like and liquid-like behaviors are observed, the probability distribution is bimodal with the peak at higher kinetic energy belonging to the solid-like state. As total energy increases, the positions of the maxima of both peaks increase, while the probability, indicated by the area under the curve, decreases for the solid-like state and increases for the liquid-like state. Because the liquid-like state has a lower kinetic energy than the solid-like state, the average kinetic energy remains relatively constant until the cluster is in a completely liquid-like state.
The Modified Lennard-Jones Cluster

The behavior of Lennard-Jones clusters in the region of phase transition has been studied previously by Calvo. The model for Lennard-Jones clusters used by Calvo differs from the one presented earlier in that the cluster is enclosed in a repulsive spherical shell potential defined by

\[ V_{i}^{rep} = \begin{cases} \chi (r_i - R)^4 / 4, & r_i \geq R \\ 0, & r_i < R \end{cases}, \]  

(21)

where \( \chi \) determines the strength of the potential, \( R \) is the radius of the spherical shell, and \( r_i \) is the magnitude of the distance of the \( i \)th particle from the center of the shell given by

\[ r_i = \sqrt{x_i^2 + y_i^2 + z_i^2}. \]  

(22)

For all the results that follow \( \chi \) is given a value of 100.0. Figure 17 shows how the potential changes as a function of the distance from the origin.

Figure 17. The repulsive spherical potential as a function of distance from the origin. Shown here for \( \chi = 100.0 \) and \( R = 2.0 \).
If the quantities involving the potential defined previously are modified to include this spherically repulsive potential, the following changes are made. The potential energy of the system is given by

\[
E_{\text{pot}} = \sum_{i=1}^{N} \sum_{i<j} V_{ij}^{LJ} + \sum_{i=1}^{N} V_i^{\text{rep}} .
\]

(23)

The net force exerted on a particle is given by

\[
\vec{F}_i = \sum_{j=1}^{N_p} \vec{F}_{ij}^{LJ} + \vec{F}_{i}^{\text{rep}} ,
\]

(24)

where

\[
F_{i}^{\text{rep}} = -\nabla V_{i}^{\text{rep}} = \begin{cases} 
\frac{X}{m_i} (r_i - R)^3, & r_i \geq R \\
0, & r_i < R 
\end{cases}
\]

(25)

The direction of the force due to the confining potential always points towards the center of the sphere.

The advantage of including such a potential is that it prevents individual particles from escaping the cluster, or “evaporating,” which is a common occurrence for long simulations at high energies. This allows long simulations to be completed without the cluster size being reduced as time progresses. There are some disadvantages related to introducing such a potential, however. Particle interaction with the confining shell causes linear momentum to become nonconserved, and quantities calculated from the behavior of the cluster become dependent on the size of the radius chosen for the confining sphere. For the moment, these disadvantages are accepted for the sake of easily reproducing Calvo’s results.
The Root Mean Square Bond Length Fluctuation

Calvo reports the root mean square (rms) bond length fluctuation as a function of total energy for several different cluster sizes. Measuring the root mean square (rms) bond length fluctuation of a cluster is an excellent means of determining at what energy a cluster undergoes a transition from a solid-like to liquid-like state. The rms bond length fluctuation is calculated as

\[ \delta = \frac{2}{N(N-1)} \sum_{i<j} \left( \frac{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}{\langle r_{ij} \rangle} \right)^{1/2}. \]  

(26)

Figures 18 and 19 show \( \delta \) as a function of total energy for clusters of size three and thirteen, respectively.

Figure 18. The rms bond length fluctuation as a function of total energy per particle for a 3-particle cluster. Open diamonds represent data from this work, while crosses represent Calvo’s results.\(^2\) This simulation was performed for \( 2 \times 10^5 \) equilibration steps and \( 1 \times 10^6 \) production steps with \( \Delta t = 4.67 \times 10^{-3} \) and \( R = 2.0 \). \( \delta \) was averaged over \( 1 \times 10^5 \) steps.
Figure 19. The rms bond length fluctuation as a function of total energy per particle for a 13-particle cluster. Open diamonds represent data from this work, while crosses represent Calvo’s results. This simulation was performed for $2 \times 10^5$ equilibration steps and $1 \times 10^6$ production steps with $\Delta t = 1 \times 10^{-2}$ and $R = 2.7$. $\delta$ was averaged over $1 \times 10^5$ steps.

In Figures 18 and 19, the lower portion of the curve on the left corresponds to the energy region where the cluster behaves in a solid-like manner, while the higher portion on the right corresponds to the energy region where the cluster behaves in a liquid-like manner. The increase in $\delta$ between these two regions indicates a transition from a solid-like to a liquid-like phase.

A close investigation of $\delta$ in the high energy region for the 13-particle cluster reveals some discrepancy between our results and Calvo’s. A possible reason for inconsistency of the data in this region is that Calvo’s results were generated using a different radius for the confining potential. Calvo reports choosing $R$ to be twice the ground state radius of the cluster, which is defined in a previous work as the distance
from the center of mass to the furthest atom when the cluster is in the ground state.\textsuperscript{10} For clusters of size three and thirteen the ground state radii are .6481 and 1.0818, respectively.\textsuperscript{11} When choosing $R$ to be two times either of these values, however, we were unable to reproduce Calvo’s results, as the values for $\delta$ produced were noticeably smaller than Calvo’s in the high energy region, where interaction with the confining potential is to be expected. By increasing the size of $R$ from twice the ground state radius better agreement with Calvo’s values was achieved. The dependence of $\delta$ on $R$ was explored by calculating $\delta$ over the same range of total energy for several values of $R$. The results are shown in Figure 20.

![Figure 20](image)

Figure 20. The rms bond length fluctuation as a function of energy for several different confining potential radii. Open circles correspond to $R = 4.05$, open diamonds correspond to $R = 2.7$, and crosses correspond to $R = 1.35$. All other parameters are identical to those listed for Figure 19.

The middle curve is identical to the one shown in Figure 19. The lower curve corresponds to shrinking the radius by 50%, which leads to a decrease in the values of $\delta$.
in the high energy region. The upper curve corresponds to expanding the radius by 50%, which leads to an increase in the values of $\delta$ in the high energy region. In the low energy region the curves are identical, because the particles remain tightly bound to the cluster and do not interact with the confining potential.

In addition to its dependence on the radius of the confining sphere, it was found that $\delta$ was also dependent on the amount of time over which it was calculated. Simulations were performed in which the averages in Equation (26) for $\delta$ were calculated over several different periods of time. Results are shown in Figure 21.

![Figure 21. The rms bond length fluctuation as a function of total energy calculated over different lengths of time. Open diamonds correspond to calculation over $1 \times 10^5$ production steps, open circles correspond to calculation over $5 \times 10^5$ production steps (the error bars for this simulation were generated using only eight averages of $\delta$), and crosses correspond to calculation over $4 \times 10^6$ production steps. All other parameters are identical to those listed for Figure 19.]

At low energy, when the cluster is in a solid-like state, the length of the simulation does not affect $\delta$. As the energy approaches the transition region, however, an increase in the
length of the simulation is characterized by an increase in $\delta$. It is theorized that the increase in $\delta$ is due to “rare events” (the cluster exhibiting liquid-like behavior at low total energy, for example) which, while unlikely, have a strong impact on the overall value of $\delta$. An increase in production time increases the likelihood that one of these events occurs sometime during the calculation. At high energy, when the cluster is in a liquid-like state, the values for $\delta$ once again coincide, regardless of the length of the simulation.
CHAPTER V
THE CHAOTIC BEHAVIOR OF LENNARD-JONES CLUSTERS

Lyapunov Exponent Theory

In general, a dynamical system is chaotic if nearby trajectories in phase space diverge exponentially. Lyapunov exponents provide a means of quantifying the degree of chaos in a system by measuring the rate of such a divergence. Hence, a system is considered chaotic if it has at least one positive Lyapunov exponent. A mechanical system has an entire spectrum of Lyapunov exponents, where the number of Lyapunov exponents is equal to the dimension of phase space. If two nearby points in phase space are initially separated by an infinitesimal displacement \( \delta q \), and the trajectories are advanced so that at some later time they are separated by the displacement \( \delta q_t \), the largest Lyapunov exponent \( \lambda \) may be calculated from

\[
\lambda = \lim_{t \to \infty} \frac{1}{t} \log_2 \left( \frac{||\delta q_t||}{||\delta q_o||} \right).
\]

An arbitrary choice for \( \delta q_o \) in Equation (27) necessarily produces the largest Lyapunov exponent, because as time progresses any \( \delta q_o \) tends to reorient itself along the direction of greatest divergence in phase space.\(^{12}\) Figure 22 provides a pictorial illustration of this phenomenon for a two dimensional case.
Figure 22. An illustration of the time evolution of initially orthogonal displacement vectors $\delta \hat{p}_o$ and $\delta \hat{q}_o$. As time progresses the vectors tend to reorient themselves in the direction of greatest "stretch."

The circle represents a collection of displacements, equal in magnitude, from an initial trajectory located at the center of the circle. Vectors $\delta \hat{p}_o$ and $\delta \hat{q}_o$ represent an orthogonal pair of these displacements. As time evolves, the circle becomes stretched along the direction of greatest divergence, and the once orthogonal vectors tend to be redirected towards this stretch. Eventually, $\delta \hat{p}_i$ and $\delta \hat{q}_i$ become indistinguishable from one another, which leads to the same Lyapunov exponent value being generated from either of them.

In order calculate the full spectrum of Lyapunov exponents, it becomes necessary to choose a set of initial displacement vectors equal to the dimension of the phase space and periodically orthogonalize them as time progresses. Figure 23 provides an illustration of how the orthogonalization process can be used to help calculate a full spectrum of Lyapunov exponents in two dimensions.
Figure 23. An illustration of how reorthogonalizing the initial displacement vectors can be used to help calculate the entire spectrum of Lyapunov exponents.\textsuperscript{13}

The circle represents a collection of displacements of magnitude $\delta q_o$ from an initial trajectory. To prevent any pair of initially orthogonal vectors from being pulled in the same direction, they are periodically reorthogonalized. One vector is reoriented to lie along the direction of greatest stretch, and the second is directed perpendicularly to it. This allows a Lyapunov exponent to be calculated for each dimension in phase space by monitoring the rate of expansion or contraction of the vector pointing in each orthogonal direction.

In addition to orthogonalizing the vectors, it also commonly becomes necessary to normalize them. For a chaotic system, where the divergence of nearby trajectories is exponential, the size of the vectors can quickly grow to sizes that cannot be stored as a 64-bit double precision number (for example). To prevent a vector from becoming larger than the largest possible number that can be represented on a given computer system, it is
periodically renormalized while keeping track of its magnitude at the time of normalization. By taking the logarithm of these magnitudes and adding them together, it is possible to keep track of the expansion of a vector without numbers increasing to sizes beyond the maximum possible.

For a Hamiltonian system, in which the volume of phase space is constant, all nonzero Lyapunov exponents occur in pairs of positive and negative numbers of equal magnitude. The number of nonzero Lyapunov exponents is equal to the dimension of phase space minus the number of constraints placed on the motion of the system.\textsuperscript{12}

Method for Calculating Lyapunov Exponents

Lyapunov exponents are calculated using the method described by Wolf, Swift, Swinney, and Vastano.\textsuperscript{14} Consider a one dimensional, single particle system with phase space coordinates $q$ and $p$ and Hamiltonian $H(q, p)$, where $q$ is the spatial coordinate and $p$ is the momentum coordinate. If the set of phase space coordinates is perturbed by a small amount, i.e.,

$$\left( \begin{array}{c} q \\ p \end{array} \right) \rightarrow \left( \begin{array}{c} q + \delta q \\ p + \delta p \end{array} \right),$$

we wish to follow the trajectory of $\delta q$ and $\delta p$ as the state of the system is advanced as a means of determining the Lyapunov exponents. The time evolution of the phase space coordinates is determined by Hamilton’s equations of motion, which may be written as

$$\frac{d}{dt} \left( \begin{array}{c} q \\ p \end{array} \right) = \left( \begin{array}{c} F_q(q, p) \\ F_p(q, p) \end{array} \right) = \tilde{F}(q, p),$$

(29)
where $F_q = \frac{\partial H}{\partial p}$ and $F_p = -\frac{\partial H}{\partial q}$. Then, if only $q$ and its perturbation are considered, the time derivative of the perturbed $q$ may be written as

$$\frac{d}{dt}(q + \delta q) = F_q(q + \delta q, p) = F_q(q, p) + \left(\frac{\partial F_q}{\partial q}\right)\delta q + \ldots,$$

where a Taylor expansion has been used to construct the final expression.

If this result is extended to include both $q$ and $p$ the expression becomes

$$\frac{d}{dt}\begin{pmatrix} q + \delta q \\ p + \delta p \end{pmatrix} = \tilde{F}(q + \delta q, p + \delta p) = \tilde{F}(q, p) + dF\begin{pmatrix} \delta q \\ \delta p \end{pmatrix} + \ldots,$$

where

$$dF = \begin{pmatrix} \frac{\partial F_q}{\partial q} & \frac{\partial F_q}{\partial p} \\ \frac{\partial F_p}{\partial q} & \frac{\partial F_p}{\partial p} \end{pmatrix}.$$  

The number of rows and columns in $dF$ is equal to the to the dimension of phase space.

Additionally, $dF$ is a function of time, because it depends on $q(t)$ and $p(t)$. By noting that

$$\frac{d}{dt}\begin{pmatrix} q + \delta q \\ p + \delta p \end{pmatrix} = \frac{d}{dt}\begin{pmatrix} q \\ p \end{pmatrix} + \frac{d}{dt}\begin{pmatrix} \delta q \\ \delta p \end{pmatrix},$$

it can be seen that

$$\frac{d}{dt}\begin{pmatrix} \delta q \\ \delta p \end{pmatrix} = dF\begin{pmatrix} \delta q \\ \delta p \end{pmatrix}.$$  

Thus, the rate of change of in $(\delta q, \delta p)$ is determined through multiplication with $dF$.

Any infinitesimal displacement $(\delta q, \delta p)$ may be expressed in terms of orthonormal basis vectors. In this example, if basis vectors
\[ \tilde{h}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \]  

(35)

and

\[ \tilde{h}_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \]  

(36)

are introduced, then

\[ \begin{pmatrix} \delta q \\ \delta p \end{pmatrix} = \delta q \tilde{h}_1 + \delta p \tilde{h}_2 . \]  

(37)

Lyapunov exponents are determined by advancing the basis vectors in time using Equation (34) and periodically applying a reorthonormalization procedure to the basis vectors.

The approach described above is easily extended to the multiparticle, three dimensional system being used to describe the Lennard-Jones cluster. For the LJ cluster, the phase space has dimension 6N and vectors \( \tilde{h}_i \) are chosen so that

\[ \tilde{h}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad \tilde{h}_2 = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ 1 \end{pmatrix}, \ldots, \tilde{h}_{6N} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix} . \]  

(38)

The matrix \( dF \) is calculated from the Hamiltonian of the system given by

\[ H = \sum_{i=1}^{N} \frac{1}{2m_i} \tilde{p}_i^2 + V(\{\tilde{q}_i\}) , \]  

(39)

where \( \tilde{p}_i \) is the momentum of the particle \( i \), and \( V(\{\tilde{q}_i\}) \) is the total potential energy of the system as a function of the set of position coordinates \( \{\tilde{q}_i\} \). Then
\[
\begin{pmatrix}
F_q(\ddot{q}_i, \ddot{p}_i) = \frac{d}{dt} \ddot{q}_i = \frac{\partial H}{\partial \dot{q}_i} = \left( \frac{1}{m_i} \dot{p}_i \right), \\
F_p(\ddot{q}_i, \ddot{p}_i) = \frac{d}{dt} \ddot{p}_i = \frac{\partial H}{\partial \dot{p}_i} = \left( -\frac{\partial V}{\partial \dot{q}_i} \right)
\end{pmatrix},
\]

and \(dF\) may be written as

\[
dF = \begin{pmatrix}
\frac{\partial F_q}{\partial \dot{q}_i} & \frac{\partial F_q}{\partial \dot{p}_i} \\
\frac{\partial F_p}{\partial \dot{q}_i} & \frac{\partial F_p}{\partial \dot{p}_i}
\end{pmatrix} = \begin{pmatrix}
\frac{1}{m_i} \ddot{p}_i & \frac{1}{m_i} \ddot{p}_i \\
\frac{\partial V}{\partial \dot{q}_i} & \frac{\partial V}{\partial \dot{q}_i} & \frac{\partial V}{\partial \dot{q}_j}
\end{pmatrix}.
\]

For a system of \(N\) particles of unit mass in three Cartesian dimensions \(dF\) may be written more explicitly as

\[
dF = \begin{pmatrix}
0 & 0 & \ldots & 0 & 1 & 0 & \ldots & 0 \\
0 & 0 & \ldots & 0 & 0 & 1 & \ldots & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \ddots & \vdots \\
-\ddot{x}_i & -\ddot{y}_i & -\ddot{z}_i & -\ddot{V}_{xx} & \frac{\partial^2 V}{\partial x_i \partial x_j} & \frac{\partial^2 V}{\partial x_i \partial x_N} & 0 & 0 \\
-\ddot{x}_i & -\ddot{y}_i & -\ddot{z}_i & -\ddot{V}_{xx} & \frac{\partial^2 V}{\partial x_i \partial x_j} & \frac{\partial^2 V}{\partial x_i \partial x_N} & 0 & 0 \\
\ddot{x}_i & \ddot{y}_i & \ddot{z}_i & \ddot{V}_{xx} & \frac{\partial^2 V}{\partial x_i \partial x_j} & \frac{\partial^2 V}{\partial x_i \partial x_N} & \ddots & \ddots \\
\ddot{x}_i & \ddot{y}_i & \ddot{z}_i & \ddot{V}_{xx} & \frac{\partial^2 V}{\partial x_i \partial x_j} & \frac{\partial^2 V}{\partial x_i \partial x_N} & \ddots & \ddots \\
\ddot{x}_i & \ddot{y}_i & \ddot{z}_i & \ddot{V}_{xx} & \frac{\partial^2 V}{\partial x_i \partial x_j} & \frac{\partial^2 V}{\partial x_i \partial x_N} & \ddots & \ddots \\
\ddot{x}_i & \ddot{y}_i & \ddot{z}_i & \ddot{V}_{xx} & \frac{\partial^2 V}{\partial x_i \partial x_j} & \frac{\partial^2 V}{\partial x_i \partial x_N} & \ddots & \ddots \\
\ddot{x}_i & \ddot{y}_i & \ddot{z}_i & \ddot{V}_{xx} & \frac{\partial^2 V}{\partial x_i \partial x_j} & \frac{\partial^2 V}{\partial x_i \partial x_N} & 0 & 0
\end{pmatrix}.
\]

In our simulations, vectors \(\vec{h}_i\) are defined at the beginning of the production period. Lyapunov exponents are then determined by monitoring their time evolution and
applying a reorthonormalization method. In particular, each vector \( \vec{h} \) is advanced in time through application of a fourth order Runge-Kutta method,\(^\text{15}\) whereby

\[
\vec{h}_i(t + \Delta t) = \vec{h}(t) + \frac{\Delta t}{6} \left( \vec{k}_1 + 2\vec{k}_2 + 2\vec{k}_3 + \vec{k}_4 \right),
\]

where

\[
\begin{align*}
\vec{k}_1 &= dF(t)\vec{h}_i(t) \\
\vec{k}_2 &= dF(t)(\vec{h}_i(t) + \frac{1}{2}\vec{k}_1) \\
\vec{k}_3 &= dF(t)(\vec{h}_i(t) + \frac{1}{2}\vec{k}_2) \\
\vec{k}_4 &= dF(t)(\vec{h}_i(t) + \vec{k}_3)
\end{align*}
\]

and \( i \) is an integer less than or equal to the dimension of phase space.

At the conclusion of this step, the vectors \( \vec{h}_i \) are orthonormalized by using a Gram-Schmidt orthonormalization procedure whereby

\[
\vec{h}_i^{\text{ON}} = \left( \vec{h}_i - \sum_{j=1}^{i-1} (\vec{h}_i \cdot \vec{h}_j^{\text{ON}})\vec{h}_j^{\text{ON}} \right) / \beta_j,
\]

where

\[
\beta_j = \left\| \vec{h}_i - \sum_{j=1}^{i-1} (\vec{h}_i \cdot \vec{h}_j^{\text{ON}})\vec{h}_j^{\text{ON}} \right\|.
\]

and \( \| \| \) denotes the magnitude of a vector. \( \vec{h}_i^{\text{ON}} \) is given by

\[
\vec{h}_i^{\text{ON}} = \frac{\vec{h}_i}{\|\vec{h}_i\|}.
\]

Starting at \( i = 1 \) and successively applying the equation for increasing \( i \), an orthonormal set of vectors is created.\(^\text{12}\)
Following the Gram-Schmidt orthonormalization procedure, the \( \log_2(\beta_i) \) is calculated and added to a running sum of all the previous \( \log_2(\beta_j) \). If this sum is defined as
\[
\gamma_i = \sum_{j=1}^{n} \log_2 \beta_j,
\]
where \( n \) corresponds to the current time step. Then an estimate for the Lyapunov exponents at any time can be calculated by
\[
\lambda_i^{\text{est}} = \frac{1}{n \Delta t} \gamma_i.
\]
These values become increasingly accurate estimates of \( \lambda_i \) as time progresses, and generally, \( \lambda_i^{\text{est}} \) approaches a limiting value for times much less than infinity. In Figure 24, \( \lambda_i^{\text{est}} \) is shown as a function of time for a typical simulation of a 3-particle cluster.

![Figure 24. The Lyapunov spectrum for a typical simulation of a 3-particle cluster.](image-url)
Final values for $\lambda$ are generated by averaging $\lambda^{est}$ over the last fifth of the total production steps. Error bars are calculated from the standard deviation,

$$\sqrt{\langle (\lambda^{est})^2 \rangle - \langle \lambda^{est} \rangle^2},$$

where averages are taken over the last fifth of the total production steps.

Lyapunov Exponent Results

Calvo and others have investigated the chaotic behavior of LJ clusters through calculation of Lyapunov exponents.\textsuperscript{2, 16, 17} The largest Lyapunov exponent was calculated over a range of energies near the transition from solid-like to liquid-like states for clusters of size three and thirteen. Unfortunately, a direct comparison with Calvo’s Lyapunov exponent results is not possible, because the published data have been rescaled by an unknown factor. However, in order to draw some comparison between the data presented here and the previously published results, Calvo’s results have been rescaled so that values for the Lyapunov exponents at lowest and highest energy values are in near agreement. The results for the 3-particle and 13-particle clusters are presented in Figures 25 and 26 and show very good agreement with Calvo’s values.
Figure 25. The largest Lyapunov exponent as a function of energy for a 3-particle cluster. Open diamonds represent data from this work, while crosses represent Calvo’s results. Our results were averaged over two simulations performed for $2 \times 10^5$ equilibration steps and $2 \times 10^6$ production steps with $\Delta t = 5 \times 10^{-4}$ and $R = 2.0$.

Figure 26. The largest Lyapunov exponent as a function of energy for a 13-particle cluster. Open diamonds represent data from this work, while crosses represent Calvo’s results. Our simulation was performed for $2 \times 10^5$ equilibration steps and $2 \times 10^6$ production steps with $\Delta t = 5 \times 10^{-4}$ and $R = 2.7$. 
CHAPTER VI

CHAINS OF PARTICLES BONDED BY SPRINGS

The Spring Potential

In an effort to explore the effects of modifying the bond conditions between particles, the Lennard-Jones clusters are modified to become a chain of particles connected by springs. A potential of the form

\[
V_{ij}^c = \begin{cases} 
  c + \frac{1}{2} k (r_{ij} - b)^2, & |i - j| = 1 \\
  0, & |i - j| \neq 1
\end{cases}
\]  

(54)

is introduced to govern the interactions between neighboring particles in the chain. \(c\) sets the reference level of the potential, \(k\) determines the strength of the spring, and \(b\) sets the bond length between particles. The LJ potential is modified to exclude interactions between neighboring particles; i.e.

\[
V_{ij}^{LJ} = \begin{cases} 
  4 \varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right], & |i - j| \neq 1 \\
  0, & |i - j| = 1
\end{cases}
\]  

(55)

If a Taylor expansion is performed on \(V_{ij}^{LJ}(r_{ij})\) about \(r_c\), the following expression is obtained:

\[
V_{ij}^{LJ}(r_{ij}) = V_{ij}^{LJ}(r_c) + \frac{dV_{ij}^{LJ}(r_c)}{dr_{ij}} (r_{ij} - r_c) + \frac{1}{2} \frac{d^2V_{ij}^{LJ}(r_c)}{dr_{ij}^2} (r_{ij} - r_c)^2 + \ldots
\]  

(56)
If the expansion is performed about the minimum value of $V_{ij}^{LJ}(r_{ij})$, i.e., the expansion is performed for $r_c = 2^{1/6}$, the second term becomes zero, as it is the first derivative of a function evaluated at an extremum. Then, ignoring higher order terms, the equation becomes

$$V_{ij}^{LJ}(r_{ij}) \equiv V_{ij}^{LJ}(r_c) + \frac{1}{2} \frac{d^2V_{ij}^{LJ}(r_c)}{dr_{ij}^2}(r_{ij} - r_c)^2,$$

(57)

the form of which shows strong similarity to that of Equation (54), where

$$c = V_{ij}^{LJ}(r_c) = -1, \quad k = \frac{d^2V_{ij}^{LJ}(r_c)}{dr_{ij}^2} \approx 57.146438, \quad \text{and} \quad b = r_c = 2^{1/6}.$$  It can be surmised that the spring potential with these parameters serves as a good approximation of the LJ potential in the region near its minimum. Figure 27 shows both $V_{ij}^{LJ}$ and $V_{ij}^s$ as a function of interparticle distance.

Figure 27. LJ and spring potentials as a function of interparticle distance. The solid line corresponds to the LJ potential, while the dotted line corresponds to the spring potential.
If the quantities involving the potential defined previously are modified to include the spring potential, the following changes are made. The potential of the system is given by

\[ E_{\text{pot}} = \sum_{i=1, i<j}^{N} V_{ij}^{\text{LJ}} + \sum_{i=1, i<j}^{N} V_{ij}^{s}. \]  

(58)

The net force exerted on a particle is given by

\[ \vec{F}_i = \sum_{j=1, j \neq i}^{N} \vec{F}_{ij}^{\text{LJ}} + \sum_{j=1, j \neq i}^{N} \vec{F}_{ij}^{s}, \]  

(59)

where

\[ F_{ij}^{\text{LJ}} = -\nabla V_{ij}^{\text{LJ}} = \begin{cases} \frac{24 \varepsilon}{m_i} \left[ \frac{2 \sigma^{12}}{r_{ij}^{13}} - \frac{\sigma^6}{r_{ij}^{9}} \right], & |i - j| \neq 1 \\ 0, & |i - j| = 1 \end{cases} \]  

(60)

and

\[ F_{ij}^{s} = -\nabla V_{ij}^{s} = \begin{cases} -k(r_{ij} - b), & |i - j| = 1 \\ 0, & |i - j| \neq 1 \end{cases}. \]  

(61)

Comparisons Between Chains and Lennard-Jones Clusters

In order to compare the behavior of a chain to that of a LJ cluster, several of the quantities calculated for the clusters have also been determined for chains. Unless otherwise noted, the initial configuration of the chain at the beginning of a simulation is identical to the initial configuration of the corresponding cluster. For all simulations, the spring constant \( k \) is taken to be 57.146438. In the case of the 13-particle chain, care is
taken in defining the order of the particles, so that only adjacent particles are bonded to each other. This prevents the chain from beginning the simulation in a “tangled” state.

Probability distributions were created for a 3-particle cluster and a 3-particle chain for several different total energies. Kinetic energies were averaged over sets of 500 time steps and then accumulated in energy intervals of size $1 \times 10^{-2} / N$. The results are displayed in order of increasing total energy in Figures 28-30.

![Figure 28. Distribution of short time averages of the kinetic energy for $E_{tot} / N = -.9$. Open diamonds correspond to the 3-particle cluster, while filled circles correspond to the 3-particle chain. Simulations were performed for $2 \times 10^5$ equilibration steps and $1 \times 10^9$ production steps with $\Delta t = 5 \times 10^{-4}$](image-url)
Figure 29. Distribution of short time averages of the kinetic energy for $E_{\text{tot}} / N = -0.7$. Open diamonds correspond to the 3-particle cluster, while filled circles correspond to the 3-particle chain. Simulations were performed for $2 \times 10^5$ equilibration steps and $1 \times 10^9$ production steps with $\Delta t = 5 \times 10^{-4}$.

Figure 30. Distribution of short time averages of the kinetic energy for $E_{\text{tot}} / N = -0.5$. Open diamonds correspond to the 3-particle cluster, while filled circles correspond to the
3-particle chain. Simulations were performed for $2 \times 10^5$ equilibration steps and $1 \times 10^9$ production steps with $\Delta t = 5 \times 10^{-4}$

Note that the distribution in the low energy range is far more narrow than any of the distributions that follow. This is characteristic of the rigid solid-like behavior that is expected at low energies.

Also of note is that the cluster appears to exhibit liquid-like behavior at lower total energy than the chain does. Recall that liquid-like behavior is associated with a lower kinetic energy than solid-like behavior. Figure 29 shows that the cluster is more likely to have lower kinetic energy than the chain at $E_{\text{tot}} / N = -0.7$. At $E_{\text{tot}} / N = -0.5$, the chain displays two well-defined peaks; one of which is located at higher energy than the single well-defined peak of the cluster, suggesting that the chain is exhibiting some solid-like behavior while the cluster is behaving almost entirely in a liquid-like fashion.

It is not entirely unexpected that the cluster transition more quickly from solid-like to liquid-like behavior with increasing total energy. By observing the graphs of the potential energies shown in Figure 27, it can be seen that for increasing energy the motion of the particles under the influence of the spring potential is more restricted than the motion of the particles under the influence of the Lennard-Jones potential. Restricting the motion of the particles to a narrowly defined region naturally leads to more solid-like behavior.

Rms bond length fluctuations were calculated for a cluster and chain of size three. The results are shown in Figure 31.
Figure 31. The rms bond length fluctuation as a function of total energy for a 3-particle system. Open diamonds correspond to the 3-particle cluster, while filled circles correspond to the 3-particle chain. Simulations were performed for $2 \times 10^5$ equilibration steps and $2 \times 10^6$ production steps with $\Delta t = 5 \times 10^{-4}$ and $R = 2.0$. $\delta$ was averaged over $2 \times 10^6$ steps.

The data obtained for the rms bond length fluctuations support the conclusions drawn from the probability distributions of the kinetic energy. The transition from solid-like to liquid-like state occurs at a higher energy for the chain than for the cluster. For the lowest total energies, the values of $\delta$ for the chain and the cluster match very closely, because the spring and LJ potentials are nearly identical near the potential minimum. As total energy increases, the values of $\delta$ grow further apart as the differences between the spring and LJ potentials become more pronounced. The more restrictive nature of the spring potential is evident in that the values of $\delta$ are smaller for the chain than for the cluster.

In addition to calculating $\delta$ for a system of three particles, $\delta$ was calculated for a 13-particle cluster and chain. The results are shown in Figure 32.
Figure 32. The rms bond length fluctuation as a function of total energy for a 13-particle system. Open diamonds correspond to the 13-particle cluster, while open circles correspond to the 13-particle chain. Simulations were performed for $6.10^5 \times$ equilibration steps and $2.10^7 \times$ production steps with $\Delta t = 5 \times 10^{-4}$ and $R = 2.7$. $\delta$ was averaged over $2 \times 10^6$ steps.

As was found with the 3-particle systems, the transition from a solid-like state to a liquid-like state occurs at higher total energy for the 13-particle chain than for the 13-particle cluster. Similarly, the value of $\delta$ is less for the chain than for the cluster at higher total energy.

The largest Lyapunov exponent was calculated as a function of total energy for 3-particle and 13-particle systems. The results are shown in Figures 33 and 34.
Figure 33. The largest Lyapunov exponent as a function of energy for a 3-particle system. Open diamonds correspond to the 3-particle cluster, while open circles correspond to the 3-particle chain. These results were averaged over two simulations performed for $2 \times 10^6$ equilibration steps and $2 \times 10^6$ production steps with $\Delta t = 5 \times 10^{-4}$ and $R = 2.0$.

Figure 34. The largest Lyapunov exponent as a function of energy for a 13-particle system. Open diamonds correspond to the 3-particle cluster, while open circles correspond to the 13-particle chain. These results were averaged over two simulations.
performed for $2 \times 10^5$ equilibration steps and $2 \times 10^6$ production steps with $\Delta t = 5 \times 10^{-4}$ and $R = 2.7$.

In both cases the largest Lyapunov exponent for the chain is less than the largest Lyapunov exponent for the cluster. For the 3-particle cluster $\lambda$ is characterized by a decrease in value after the total energy reaches a certain value. Interestingly, $\lambda$ for the 3-particle chain does not exhibit this behavior.

The Effects of Modifying the Spring Constant

In order to study the effects modifying the spring constant, several quantities were calculated for increasing values of $k$. First, quantities related to the spring bonds of the 3-particle chain are considered. The average bond lengths as well as the rms bond length fluctuations of the spring bonds are calculated as a function of $k$. In order to calculate the rms bond length fluctuations of only the spring bonds, the previous definition of $\delta$ is modified to include only neighboring pairs of particles in the chain as follows:

$$
\delta_s = \frac{2}{N(N-1)} \sum_{i,j=j+1} \left( \frac{r_{ij}^2 - \langle r_{ij} \rangle^2}{\langle r_{ij} \rangle} \right)^{1/2}.
$$

(62)

The results are shown in Figure 35.
Figure 35. Average bond length (left) and rms bond length fluctuation (right) as a function of $k$. Open squares correspond to $\langle r_{12} \rangle$ and open circles correspond to $\langle r_{23} \rangle$. Simulations were performed for $2 \times 10^5$ equilibration steps and averages were taken over $2 \times 10^6$ production steps with $\Delta t = 5 \times 10^{-4}$ and $E_{tot}/N = -.4$. These data represent averages over three separate simulations.

The increase in $k$ results in a decrease in both $\langle r_{ij} \rangle$ and $\delta_s$. For low $k$, the influence of the LJ potential between nonbonded particles causes $\langle r_{ij} \rangle$ to be slightly higher than the natural length of the spring ($b = 2^{1/6} \approx 1.1225$). As $k$ rises and the strength of the bond increases, the influence of the LJ potential is not as great and the average bond length approaches the spring’s natural length. The decrease in $\delta_s$ is caused by an increased restriction in the motion of the particles. As $k$ increases, the spring potential becomes more narrow, and the allowable range of motion of the particles for a given total energy is reduced.

The largest Lyapunov exponent was calculated for a 13-particle chain at select values $E_{tot}$ for increasing values of $k$. $E_{tot}$ was chosen so that one series of Lyapunov
exponents was calculated for a solid-like chain, and one series of Lyapunov exponents was calculated for a liquid-like chain. The results for the solid-like case are displayed in Figure 36.

![Graph showing the largest Lyapunov exponent as a function of k for E_{tot} / N = -3.0.](image)

Simulations were performed for $5 \times 10^2 \times$ equilibration steps and $6 \times 10^2 \times$ production steps with $\Delta t = 5 \times 10^{-4}$.

From these data no correlation between $\lambda$ and $k$ is evident. Figure 37 shows the results for the liquid like case.
Figure 37. The largest Lyapunov exponent as a function of $k$ for $E_{tot}/N = -2.0$. Simulations were performed for $2 \times 10^5$ equilibration steps and $2 \times 10^6$ production steps with $\Delta t = 5 \times 10^{-4}$.

These results show that $\lambda$ increases with increasing $k$ in the liquid-like region.

In general, an increase in a spring constant corresponds to an increase in a natural frequency and faster dynamics. Hence, it seems surprising that the Lyapunov exponent is independent of $k$ for low total energy. To investigate this further, the relationship between the spring constant and the temperature was explored. In Figure 38, we present results for the largest Lyapunov exponent of a 13-particle chain with fixed spring constant $k = 28.57$. The data show that $\lambda$ increases monotonically with temperature at a fixed spring constant. The temperature $T$ may be determined from the average kinetic energy through

$$T = \frac{2}{3N-6} \frac{\langle E_{kin} \rangle}{k_B},$$

where $k_B = 8.268 \times 10^{-3} / K$ is Boltzmann’s constant in LJ reduced units.\(^1\)
Figure 38. The largest Lyapunov exponent of a 13-particle chain as a function of temperature for $k = 28.57$. Simulations were performed for $2 \times 10^5$ equilibration steps and $2 \times 10^6$ production steps with $\Delta t = 5 \times 10^{-4}$.

Figure 39. Temperature as a function of the spring constant for a 13-particle chain with $E_{\text{tot}} = -3.0$. Simulations were performed for $2 \times 10^5$ equilibration steps and $2 \times 10^6$ production steps with $\Delta t = 5 \times 10^{-4}$.
Figure 40. Temperature as a function of the spring constant for a 13-particle chain with \( E_{\text{tot}} = -2.0 \). Simulations were performed for \( 2 \times 10^5 \) equilibration steps and \( 2 \times 10^6 \) production steps with \( \Delta t = 5 \times 10^{-4} \).

In Figures 39 and 40 we present results for the temperature as a function of the spring constant for total energies corresponding to solid-like and liquid-like behavior, respectively. The data show that \( T \) decreases with increasing \( k \) for the solid-like case, and \( T \) appears to have no correlation with \( k \) in the liquid-like case, where \( T \) fluctuates about a median value of 45.9 K. It can be concluded that changes in \( \lambda \) with respect to \( k \) are not simply a consequence of the \( k \)-dependence of the average temperature. In the solid-like case, the expected increase of \( \lambda \) with \( k \) may be offset by a decrease in \( T \) as \( k \) increases.

Approximating Fixed Bond Lengths by Using Large Values of \( k \)

In an attempt to approximate the behavior of a 5-particle chain with fixed bond lengths, simulations were performed on a 5-particle chain bonded by springs with a very large spring constant, \( k = 1 \times 10^6 \). The initial configuration of the chain is generated
randomly within certain constraints: bonded particles are a fixed distance apart

\( b = 2^{1/6} \), the center of mass is located at the origin, the total linear and angular momenta are zero, and the total energy has a desired value.

The entire Lyapunov spectrum was calculated for a 5-particle chain at several different total energies. For a chain with bonds of fixed length, it is expected that the Lyapunov spectrum have no more than four positive Lyapunov exponents. A 5-particle system in three dimensions has a total of 30 Lyapunov exponents, one for each dimension of phase space. Of these 30, fifteen are positive (since energy is conserved), and eleven of those fifteen are zero due to constraints placed on the system: three due to conservation of linear momentum, three due to angular momentum, one due to energy conservation, and four due to fixed bond constraints. For a chain connected by springs, there are no bond length constraints, so there may be up to eight positive Lyapunov exponents. The Lyapunov spectrum for a relatively low energy simulation is shown in Figure 41.
Figure 41. The Lyapunov spectrum of a 5-particle chain for \( k = 1 \times 10^6 \) and \( E_{\text{tot}} / N = -1.2 \). This simulation was performed for \( 2 \times 10^5 \) equilibration steps and \( 2 \times 10^6 \) production steps with \( \Delta t = 5 \times 10^{-4} \).

The graph shows four positive Lyapunov exponents, which is consistent with the prediction made for a fixed bond length system. The spectrum for a higher energy simulation is shown in Figure 42.
Figure 42. The Lyapunov spectrum of a 5-particle chain for $k = 1 \times 10^6$ and $E_{\text{tot}} / N = 0.0$. This simulation was performed for $2 \times 10^5$ equilibration steps and $2 \times 10^6$ production steps with $\Delta t = 5 \times 10^{-4}$.

Unlike the lower energy simulation, the Lyapunov spectrum at higher energies is composed of eight positive Lyapunov exponents, which is consistent with the prediction made for a system without fixed bond lengths. This suggests that when there is a sufficient amount of energy in the system, the spring bonds vibrate significantly, and the fixed bond length approximation fails.

The positive Lyapunov exponents for the 5-particle chain are shown ordered from smallest to largest values for several total energies in Figure 43.
Figure 43. The positive Lyapunov spectrum for a 5-particle chain with $E_{\text{tot}} / N = -1.2$ (open squares), $E_{\text{tot}} / N = -0.24$ (open circles), and $E_{\text{tot}} / N = 0.0$ (open diamonds). All other parameters are identical to those listed in Figure 41.

The exponents for $E_{\text{tot}} / N = 0.0$ are larger than those for $E_{\text{tot}} / N = -0.24$, because of the increase in the total energy of the system. Interestingly, the largest exponents for $E_{\text{tot}} / N = -1.2$ are larger than either of the two higher energy systems. This is most likely due to the fact that less of its kinetic energy is devoted to vibration in the spring bonds, leaving more kinetic energy for use in other types of motion, and thus increasing the associated Lyapunov exponents.
CHAPTER VII
CONCLUSION

Molecular dynamics simulations were performed on small Lennard-Jones clusters and chains of LJ particles connected by harmonic springs. Static properties of the systems, such as the distribution of the kinetic energy and root mean square bond length fluctuations, were determined. In addition, the dynamic properties of the systems were investigated through the calculation of Lyapunov exponents.

For LJ clusters, previously published data were able to be reproduced, thereby validating the simulation method. It was found that LJ clusters behaved in a solid-like manner at low total energy and a liquid-like manner at higher total energy. The transition from a solid-like to liquid-like state was found to have similarities to the solid-liquid transition of macroscopic systems in which there exists a coexistence region characterized by a bimodal probability distribution of the kinetic energy. Calculation of Lyapunov exponents for the LJ clusters revealed that the value of the largest Lyapunov exponent increased with total energy and exhibited no sharp change in the transition region.

Quantities calculated for LJ clusters were also calculated for chains of LJ particles connected by harmonic springs. Like LJ clusters, chains of LJ particles exhibited solid-
like properties at low total energy and liquid-like properties at higher total energy. It was found that the transition from a solid-like to liquid-like state occurred at a higher total energy for the chains than the clusters. Because of the way the spring bonds were defined, the behavior of the chains at low total energy was shown to be very similar to the behavior of the clusters. For higher total energy, however, the spring potential created changes in the static and dynamical properties of the chain when compared to the clusters.

As with the clusters, the largest Lyapunov exponent of the chains increased with total energy, although the value of the largest Lyapunov exponent was found to be less than that of the clusters. In addition, it was shown that the largest Lyapunov exponent increased with the temperature of the system.

Simulations were performed to study the effect modifying the spring constant in a chain. For solid-like chains, it was found that the largest Lyapunov exponent was independent of the spring constant. For liquid-like chains, it was found that the largest Lyapunov exponent increased as the spring constant increased. It was also shown that the temperature of a system decreased with an increasing spring constant for solid-like chains but had no correlation to the spring constant for liquid-like chains.

Chains with very high spring constants were studied in an attempt to approximate the behavior of a chain with fixed bond lengths. It was found that for low energy the chains with stiff bonds served as a good model for chains with fixed bond length. At high energies, however, the vibration modes in the spring bonds became excited and the approximation failed.
REFERENCES


