A MOLECULAR DYNAMIC INVESTIGATION INTO THE COMPETITIVE ADSORPTION OF GAS SPECIES ON COAL

by

Jeffrey H. Schenker

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Chapter 1

Introduction

At the interface between a solid and a fluid there is frequently found a thin layer of fluid which is bound to the surface. This phenomenon is known as adsorption. Adsorption has been the focus of much theoretical and experimental research in chemistry and chemical engineering, with applications as disparate as spectroscopy and catalysis.

Professor Pradeep Agarwal, at the University of Wyoming, has suggested that adsorption could be used to improve the efficiency of coal transportation. Dry coal, when stacked in open topped rail cars, may heat sufficiently that spontaneous combustion occurs. However, raw coal contains up to 30% $H_2O$, and is usually not dried prior to transport. Clearly, a certain amount of energy is wasted in the transportation of water from the mining site to the destination site, where the coal must be dried prior to use. Dr. Agarwal has suggested that water could be removed from the coal and $CO_2$ adsorbed on its surface at or near the mining site, thus preventing combustion while lowering the cost of transport. [2]

In this report we consider such a scenario at the molecular level. We have used molecular scale computer simulations to consider whether a layer of $CO_2$ adsorbed on a coal like surface prevents $O_2$ and $H_2O$ from reaching the surface. The question we seek to answer herein is: Can computer simulations provide useful information regarding the efficacy of Dr. Agarwal’s scheme for coal transport?

We first attempt to describe the conceptual framework of molecular simulations. Fortunately, there is a substantial literature on this subject. Unfortunately, the subject suffers from conceptual complexity, requiring tools and ideas from several areas of mathematics, physics, and chemistry. Most of the material contained in chapters one through five is standard, although certain of the results are original. Specifically, we have seen in the literature neither the formulae derived in chapter 3 nor the proof, in §4.1, that split Hamiltonian integrators have second order accuracy. Second, we present the results of preliminary simulations to predict adsorption of $CO_2$ on a coal like surface and the subsequent interactions with $O_2$ and $H_2O$. These simulations were performed on a Silicon Graphics Challenge work station.
Before proceeding to specifics, let us introduce the topic of molecular simulation by taking up a few broad questions regarding calculations and adsorption.

1.1 Why use calculation to study adsorption?

Most adsorption studies of which we are aware have focused on two species systems: those consisting of adsorbate and substrate. In these systems, the surface density of adsorbate can be determined from the weight gained by the substrate during adsorption. In fact, a qualitative discussion of adsorption appears in most Physical Chemistry texts (see, for example, [5, Chapter 29] and [22, Chapter 13]). Such discussions tend to focus consideration on the shapes of isotherms.

Regarding more complicated systems, the experimental picture is much less clear. Even a system consisting of only substrate and two types of adsorbate presents remarkable difficulties. In this case, weight gained during adsorption no longer provides information about the relative adsorption of each species. Due to the small number of molecules present in the adsorbed layer it is usually difficult to isolate these molecules and subject them to traditional analytical techniques.

Calculation provides us with a method of gaining information about more complicated systems. Experimental data from one and two component systems provide vital information about the nature of molecular interactions. When coupled with appropriate calculations, these data allow us to predict the behavior of multi-component systems.

1.2 What methods are available for calculation?

Many of the parameters with which we usually characterize fluid systems, such as temperature and pressure, are thermodynamic quantities. Hence, in theory, these parameters are derived from statistical mechanics. To calculate these quantities from specific molecular properties, we must consider their statistical definitions.

All thermodynamic quantities can be calculated from the **thermodynamic potential** (Helmholtz free energy):

\[
F = -T \log \left( \Phi \int_{\Gamma} \exp \left( -E(p, q)/T \right) dp dq \right),
\]

where \(T\) is the temperature, \(\Phi\) is a statistical weight, \((p, q)\) represents momentum and position coordinates in configuration space, \(\Gamma\), and \(E\) is the energy of a given configuration. For example, the pressure is

\[\text{curves, set in a plane parameterized by fluid pressure and adsorbate surface density, which represent states at one temperature}\]
where $V$ is the volume of the fluid. [20, Chapter II]

There are essentially three approaches to (1.1):

1. The analytic approach, in which various methods from real and complex analysis are used to evaluate (1.1) (or related equations) using power series in the thermodynamics variables of interest. This approach has been used to study systems of fundamental significance (low temperature Bose gases, hard sphere systems, etc.), and leads to certain important formal expressions, such as the virial equation of state for a real gas [20, Chapter VII]:

\[
P = \frac{NT}{V} \left(1 + \frac{NB_1(T)}{V} + \frac{N^2 B_2(T)}{V^2} + \ldots\right),
\]

where the virial coefficients, $B_i(T)$, are functions of temperature expressible as integrals of the potential energy over configuration space. Unfortunately, for most gases of interest, realistic expressions for the potential energy produce intractable integrals.

2. Monte-Carlo (MC) methods, in which a given phase space configuration is randomly perturbed a large number of times. The method of perturbation is chosen such that a given configuration should appear with probability $\exp\left(-\frac{E}{T}\right)$, so that an average over the various perturbed states approximates the integral in (1.1).

3. Molecular dynamic (MD) methods, in which a precise initial configuration is specified and the trajectory of the system is calculated from the equations of motion via a numerical integration technique. A relation between the trajectory and statistical mechanics is exploited to calculate thermodynamic variables. This relation, known as ergodicity, asserts that the average value of an observable quantity can be calculated in two entirely separate ways:

\[
< \Psi > = \frac{\int \Psi(q,p) \exp\left(-E(p,q)/T\right)dpdq}{\int \exp\left(-E(p,q)/T\right)dpdq}, \tag{1.2a}
\]

and

\[
< \Psi > = \lim_{t \to \infty} \frac{1}{t} \int_{0}^{t} \Psi(q(t'), p(t')) dt', \tag{1.2b}
\]

3
where \((q(t), p(t))\) is a trajectory of the system with initial conditions chosen representative of a fixed temperature, \(T\). In chapter 3, we derive a relationship between (1.1) and averages of observables. This will allow us to express thermodynamic quantities as functions of quantities which can be computed with (1.2b).\(^2\)

We feel that molecular dynamic methods provide a better approach by which to understand adsorption than MC methods or the analytic approach \(^3\). First, and perhaps foremost, among our reasons is the ease of implementing molecular dynamics simulations. Both MC and MD methods require the implementation of structures to store a specific phase space configuration and code to calculate the potential energy of the system. In addition, MC methods require the implementation of computer code to generate acceptable random perturbations, whereas MD methods require the relatively simple addition of code to compute a trajectory of the system. The problem of deciding which perturbations are acceptable is essentially extraneous to the problem under consideration. On the surface this objection does not suggest that we should favor MD methods over MC methods, since, if we consider (1.1) as the basis of statistical mechanics, knowledge of a trajectory, as computed in an MD simulation, seems extraneous as well. However, a trajectory of the system is what actually occurs in nature. Statistical mechanics is a method by which we seek to paint a picture, in quite broad strokes, of an incomprehensibly complicated system. Thus ergodicity can be seen as more fundamental than the calculation of the thermodynamic potential. So considered, MD methods are seen to be more fundamental.\(^4\)

Our final consideration is that MD methods allow us, in principle, to consider non-equilibrium states. The use of (1.1) is well defined only for certain states in which the system has reached thermodynamic equilibrium [20, Chapter I]. Thermodynamic equilibrium is a somewhat nebulous term. Like ergodicity, it is a physical concept which is somewhat difficult to phrase precisely in mathematical terms. Essentially the requirement is that the system has a well defined temperature. Regarding the coal/\(CO_2/H_2O/O_2\) system, it is possible that \(CO_2\) adsorbed on a coal surface in the presence of atmospheric \(H_2O\) and \(O_2\) might constitute a system not in equilibrium but in a meta-stable non-equilibrium state. That is the system might be able to persist in this state for extremely long periods of time, despite the

\(^2\)Ergodicity is a physical relation, not a mathematical one. In [20, Chapter I] it is argued, on physical grounds, that the relationship expressed in (1.2) holds. However to prove that ergodicity is valid for all but the simplest of energy functions is a very difficult problem.

\(^3\)If the analytic method provided a series solution of (1.1) in terms of a small number of macroscopic variables, it would be an excellent approach to the problem. However, searching for such a solution is essentially a quest for a thermodynamic grail.

\(^4\)We can view MD methods from a perspective directly opposed to that just proposed and use an MD simulation to study ergodicity. Computing a trajectory and observing that actual approximations to an average value, calculated via (1.2b) at finite time, appear to approach a well defined limit is a reaffirming experience for those, like the author, of little faith.
The system tends to move in the direction of decreasing free energy, however if there is not enough thermal energy to overcome the barrier, the system cannot escape from the meta-stable state.

Figure 1.1: A Representation of a Meta-Stable Non-Equilibrium State

fact that a transition to another state is thermodynamically favored (see figure 1.1). MD simulations will allow us to see this behavior when MC simulations might only find the equilibrium configuration.\textsuperscript{5}

\begin{figure}[h]
\centering
\includegraphics[scale=0.5]{meta-stable-state.png}
\caption{A Representation of a Meta-Stable Non-Equilibrium State}
\end{figure}

\textsuperscript{5}The phenomenon of meta-stable states is relatively common. Many chemical reactions, although thermodynamically favored, require a certain \textbf{activation energy} in order to take place. A famous example is that of the fusion of deuterium at room temperature. A back of the envelope calculation indicates that fusion is thermodynamically favored at room temperature–thus there is \textit{hope of cold fusion}. However, no one seems to be able to provide the necessary activation energy.
Chapter 2

Mechanics

Molecular dynamics simulations require the solution of the classical equations of motion for an $N$-molecule system. This chapter consists of a provide a brief overview of classical mechanics followed by a discussion of specific methods for modeling molecules mechanically.

2.1 An Overview of Classical Mechanics

In this section we summarize some results from mechanics. The results and methods are standard, see, for example, Goldstein [14, Chapters 1,2,8,9].

The equations of motion for $N$ point particles are most easily stated in terms of Newton’s second law:

$$m_i \ddot{r}_i = F_i,$$ (2.1)

where $m_i$ is the mass of the $i$th particle, $r_i$ is its position, and $F_i$ is the force on it. For our purposes, $F_i$ is always derivable from a potential:

$$F_i = -\frac{\partial V}{\partial r_i}.$$ (2.2)

Since the forces are derivable from a potential, we can reformulate the equations of motion in terms of a Lagrangian:

$$L := T - V,$$ (2.3)

Note that $r_i$ and hence $F_i$ are vector quantities. Thus a more standard notation might be

$$F_i = -\nabla r_i V.$$

We prefer the notation

$$F_i = \frac{\partial V}{\partial r_i},$$

although it obscures the vector nature of the equation, because it avoids subscriptsing the symbol $\nabla$ to indicate with respect to which variable we wish to differentiate.
where $T$ is the Kinetic energy:

$$T := \sum_{i=1}^{N} \frac{1}{2} m_i \| \dot{r}_i \|^2.$$  \hfill (2.4)

For each integrable path, $\gamma : [t_0, t] \rightarrow \mathbb{R}^{3N}$, we define the action:

$$I(\gamma) := \int_{t_0}^{t} L(\dot{\gamma}(t), \gamma(t)) dt.$$  \hfill (2.5)

The equations of motion are obtained by postulating Hamilton’s principle of least action: along the physical trajectory, $(r_1, ..., r_N)$, the action is a minimum. Using standard techniques from the calculus of variations, we find that

$$0 = \frac{d}{dt} \frac{\partial L}{\partial \dot{r}_i} - \frac{\partial L}{\partial r_i} + \frac{\partial V}{\partial r_i}, \quad i = 1, ..., N.$$  \hfill (2.6)

Writing out the terms in (2.6), we reproduce Newton’s second law:

$$0 = \frac{d}{dt} (m_i \dot{r}_i) + F_i.$$  

Hence, Newton’s’ second law is seen to be a consequence of the principle of least action. By postulating Hamilton’s principle, we will use the Lagrangian approach to consider dynamics in which the coordinates are non-Cartesian or in which the trajectory must satisfy certain algebraic constraints. Suppose that, in place of the $r_i$, we parameterize the system by $M$ possibly non-Cartesian coordinates $q_j$, $j = 1, ..., M$. The equations of motion are now given by (2.6) with $(q_1, ..., q_M)$ in place of $(r_1, ..., r_N)$:

$$0 = \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i}, \quad i = 1, ..., M.$$  \hfill (2.7)

From (2.7) we proceed to the Hamiltonian formulation of mechanics. We define the momenta “conjugate” to the $q_i$:

$$p_i := \frac{\partial L}{\partial \dot{q}_i} \quad i = 1, ..., M.$$  \hfill (2.8)

We then express the Hamiltonian function:

$$H := -L + \sum_{i=1}^{M} p_i \dot{q}_i.$$  \hfill (2.9)

---

2Of course, (2.6) is only a necessary condition for a minimum. That the trajectory obtained from (2.6) is a true minimum will usually follow from the specific form of $L$. 

7
as a function of the coordinates, \( q_i \), and the momenta, \( p_i \). That is, although the Lagrangian is written as a function of \((q_1, ..., q_M)\) and \((\dot{q}_1, ..., \dot{q}_M)\), we use (2.8) to replace the velocities with \((p_1, ..., p_M)\). The equations of motion are then:

\[
\dot{q}_i = \frac{\partial H}{\partial p_i},
\]

(2.10a)

and

\[
\dot{p}_i = -\frac{\partial H}{\partial q_i},
\]

(2.10b)

where \( i \) ranges from 1 to \( M \). We refer to the collection \((q_1, ..., q_M, p_1, ..., p_M)\) as a point in **phase space**. If the Hamiltonian does not depend explicitly on the time, it will be constant along every physical trajectory. Thus it is a conserved quantity. In fact, when conserved, it represents the total energy.

We present one additional formulation of mechanics; one which is, perhaps, less well known. Consider the Hamiltonian formalism of the previous paragraph and define the **Poisson bracket** of \( F \) and \( G \), two arbitrary differentiable functions of \((q_1, ..., q_M)\) and \((p_1, ..., p_M)\):

\[
\{F, G\} := \sum_{i=1}^{M} \left( \frac{\partial F}{\partial q_i} \frac{\partial G}{\partial p_i} - \frac{\partial G}{\partial q_i} \frac{\partial F}{\partial p_i} \right).
\]

(2.11)

A short calculation, using the chain rule and (2.10), demonstrates that:

\[
\dot{F} := \{F, H\} + \frac{\partial F}{\partial t}
\]

(2.12)

for any differentiable function, \( F \), of the phase variables and time. In addition, it is easily verified that the Poisson bracket satisfies the following algebraic relations. Let \( a \in \mathbb{R} \) and let \( F, G, \) and \( H \) be any differentiable functions defined on the phase space, then

\[
\{F, G\} = -\{G, F\},
\]

(2.13a)

\[
\{a, F\} = 0,
\]

(2.13b)

\[
\{FG, H\} = \{F, H\}G + F\{G, H\},
\]

(2.13c)

and

\[
\{F, \{G, H\}\} + \{G, \{H, F\}\} + \{H, \{F, G\}\} = 0.
\]

(2.13d)

By allowing the Poisson bracket to be the basis of mechanical calculation, we reformulate mechanics once again. Consider a given phase space, \( \Gamma \), and let \( C^k(\Gamma) \)
denote the space of continuous functions on $\Gamma$ which are $k$-times differentiable.\(^3\) Suppose that we are given a “bracket” $\{\cdot, \cdot\} : C^1(\Gamma) \times C^1(\Gamma) \rightarrow C^0(\Gamma)$ which satisfies the relations of (2.13). We choose a function $H \in C^1(\Gamma)$ which we wish to play the part of a Hamiltonian, and construct the dynamics via (2.12). The coordinates with which we parameterize phase space can, of course, be regarded as functions defined on the phase space.\(^4\) Hence, (2.12) is sufficient to determine the trajectory of the system completely.

What the Poisson bracket formalism allows us is the opportunity to define phase space coordinates which are not canonical. In the Hamiltonian formalism, the phase space must split neatly into coordinates and momenta, and the momenta must be derivable from (2.8). Such coordinates are called canonical. With the Poisson bracket formalism, we may introduce variables which are not canonical, provided that we can produce a physically reasonable Hamiltonian and Poisson bracket.

### 2.2 Mechanical Modelling of Molecules

Molecules are not classical point particles, but are collections of subatomic particles bound by electro-magnetic forces. Precise modeling of molecules, even of intermolecular interactions, requires quantum mechanics. However, to a certain degree of approximation, a molecule can be thought of as a collection of atoms, modeled as classical point particles, bound by forces which tend to cause the molecule to remain close to a certain fixed equilibrium configuration. By definition, these forces are semi-empirical. That is, the form of the forces can be determined from theory, but there are usually undetermined constants which must be determined from experiment. Near equilibrium, these intra-molecular forces are generally modelled as strong harmonic forces.\(^5\) The force constants may be determined from spectrometry or by quantum mechanical calculation.

For our purposes, we need only know that the force constants associated with intra-molecular forces are generally much larger than those associated with inter-molecular forces. Thus a molecule tends, rather strongly, to maintain its equilibrium configuration. Further, the vibrations which do occur take place on a time scale much shorter than that associated with the motion of the molecule as a whole. Leimkuhler,
Reich and Skeel have examined molecular dynamics at multiple time scales in great detail [21]. In order to maintain numerical precision, the time step for a computation must be chosen several orders of magnitude smaller when intra-molecular motion is considered. In view of the almost total separation of intra-molecular and extra-molecular motion, we choose to neglect intra-molecular motion; we assume that each molecule maintains a fixed internal geometry.\footnote{Certain thermodynamic quantities, such as heat capacities, can not be calculated if intra-motion is neglected. Due to the \textit{equipartition of energy}, kinetic energy is distributed such that, on average, there is $\frac{1}{2}k_B T$ energy of motion for each degree of freedom ($T$ is the temperature, and $k_B$ is Boltzmann’s constant). In particular, we must estimate the contribution from intra-molecular degrees of freedom in calculating heat capacities and the internal energy.}

In considering molecules with a fixed geometry, we have two options:

1. We may consider each molecule to be a collection of point particles (atoms) which are maintained in a fixed geometry by constraints imposed on the solution of the equations of motion.

2. We may consider each molecule to be a rigid body, and derive equations of motion for the position and orientation of the molecule.

Approaches to each of these problems are considered in the following two sections.

\subsection{2.3 Mechanics of Constrained Motion}

The Lagrangian formulation was developed, in part, to consider constrained motion. The advantage of the Lagrangian approach is that it allows us to \textit{derive} the equations of motion for a constrained system; we simply assume that the principal of least action continues to hold. Thus we solve a constrained minimization problem: \textit{we demand that the trajectory is a minimum of the action on the manifold of trajectories which satisfy the constraints.}

Suppose that the point particles satisfy $R$ algebraic constraints:

$$f_i(r_1, ..., r_N) = 0, \quad (2.14)$$

where $i$ ranges from 1 to $R$. We introduce $R$ additional variables, $\lambda_1, ..., \lambda_R$, known as \textbf{Lagrange multipliers}, and seek a trajectory which minimizes

$$I' := \int_{t_0}^{t} (L + \sum_{i=1}^{R} \lambda_i f_i) dt. \quad (2.15)$$

The equations of motion derived from (2.15) are:

$$0 = \frac{d}{dt} \frac{\partial L}{\partial \dot{r}_i} - \frac{\partial L}{\partial r_i} - \sum_{j=1}^{R} \lambda_j \frac{\partial f_j}{\partial r_i}, \quad (2.16a)$$
where $i$ ranges from 1 to $N$, and

$$0 = f_i(r_1, ..., r_N),$$

(2.16b)

where $i$ ranges from 1 to $R$. The $R$ algebraic constraints are among the equations of motion, hence a trajectory determined from (2.16) will lie on the manifold of constrained trajectories. Further $I' = I$ on this manifold, so in minimizing $I'$ we have found the minimum of $I$ on this manifold, i.e. we have found the trajectories sought.

### 2.3.1 Diatomic Molecules

Let us derive the constrained equations satisfied by a diatomic molecule. Let $r_1$ and $r_2$ denote the positions of the two atoms which comprise the molecule. There is a single constraint satisfied (see figure 2.1):

$$\frac{1}{2}(||r_1 - r_2||^2 - d^2) = 0,$$

(2.17)

where $d$ is the fixed distance between the two atoms$^7$. Letting $\lambda$ represent the Lagrange multiplier, we use (2.16) to find the equations of motion:

$$m_1\ddot{r}_1 + \frac{\partial V}{\partial r_1} - \lambda(r_1 - r_2) = 0,$$

(2.18a)

$$m_2\ddot{r}_2 + \frac{\partial V}{\partial r_2} - \lambda(r_2 - r_1) = 0,$$

(2.18b)

---

$^7$Such distances are typically of the order of 1 or 2 Angstroms.
and

\[ \frac{1}{2}(\|r_1 - r_2\|^2 - d_3^2) = 0. \] \hspace{1cm} (2.18c)

### 2.3.2 Triatomic Molecules

To derive the equations for a triatomic molecule, we must consider how to express the constraints algebraically. Let \( r_1, r_2, \) and \( r_3 \) denote the positions of the three atoms. Since the geometry is that of a triangle (see figure 2.2), we have two choices for expressing the constraints:

1. Two distances and an angle:

\[
\begin{align*}
\|r_1 - r_2\|^2 - d_3^2 &= 0 \quad \text{(2.19a)} \\
\|r_1 - r_3\|^2 - d_2^2 &= 0 \quad \text{(2.19b)} \\
(r_2 - r_1) \cdot (r_3 - r_1) - d_2d_3\cos(\theta_1) &= 0 \quad \text{(2.19c)}
\end{align*}
\]

2. Three distances:

\[
\begin{align*}
\|r_1 - r_2\|^2 - d_3^2 &= 0 \quad \text{(2.20a)} \\
\|r_1 - r_3\|^2 - d_2^2 &= 0 \quad \text{(2.20b)} \\
\|r_2 - r_3\|^2 - d_1^2 &= 0 \quad \text{(2.20c)}
\end{align*}
\]
Using the law of cosines, these two formulations are equivalent. We prefer the second, since it does not break the symmetry between the atoms. Letting $\lambda_i \, i = 1, 2, 3$ represent the Lagrange multipliers, we find the equations of motion:

\begin{align*}
    m_1 \ddot{r}_1 + \frac{\partial V}{\partial r_1} - \lambda_3 (r_1 - r_2) - \lambda_2 (r_1 - r_3) &= 0, \\
    m_2 \ddot{r}_2 + \frac{\partial V}{\partial r_2} - \lambda_1 (r_2 - r_3) - \lambda_3 (r_2 - r_1) &= 0, \\
    m_3 \ddot{r}_3 + \frac{\partial V}{\partial r_3} - \lambda_2 (r_3 - r_1) - \lambda_1 (r_3 - r_2) &= 0,
\end{align*}

(2.21a, 2.21b, 2.21c)

\begin{align*}
    \frac{1}{2} (\|r_1 - r_2\|^2 - d_3^2) &= 0, \\
    \frac{1}{2} (\|r_2 - r_3\|^2 - d_2^2) &= 0,
\end{align*}

(2.21d, 2.21e)

and

\begin{align*}
    \frac{1}{2} (\|r_3 - r_1\|^2 - d_1^2) &= 0.
\end{align*}

(2.21f)

### 2.3.3 Polyatomic Molecules

For a molecule consisting of $n$ atoms constrained to maintain a particular geometry there are, generally, 6 degrees of freedom (provided $n > 2$) (see Goldstein, [14, Chapter 4]). Hence, there must be $3n - 6$ independent constraints. The pairwise distances between atoms produce $n(n - 1)/2$ possible constraints. However, $n(n - 1)/2 > 3n - 6$ for $n \geq 5$, so it is not possible to use each pairwise distance for general polyatomic molecules. In formulating the equations of motion, we must choose a particular subset of the available constraints. The best method for making this choice appears to depend strongly on the geometry of the individual molecule. Since we will not consider molecules with more than 3 atoms, this need not concern us.

### 2.4 Rigid Body Motion

Traditional approaches to rigid body motion [14, Chapters 4,5] suffer from various difficulties. Euler angles, although conceptually the simplest approach, produce equations of motion which, due to singularities, are not amenable to numerical solution. Quaternions suffer from a great deal of conceptual complexity. Thus most molecular dynamics simulations have proceeded via constrained mechanical motion. However, recent research reports by Kol, Laird, and Leimkuhler [19] and by Dullweber, Leimkuhler, and McLachlan [11] use an approach to rigid body motion which is at once amenable to numerical solution and conceptually simple.
We begin by, formally, considering a molecule to be a collection of point particles. Then, we adopt a preferred orientation of the molecule, a “molecule fixed coordinate system,” in which the \( n \) point particles have positions, \( r_1,...,r_n \), such that:

\[
\sum_{i=1}^{n} m_i r_i = 0.
\] (2.22)

Denoting the center of mass of the molecule by \( q \), we note that the position of the point particles in physical space, \([r_i]_s\), is given by:

\[
[r_i]_s = q + Qr_i,
\] (2.23)

where \( Q \) is a matrix which describes the orientation of the molecular coordinate system. Clearly, the position and orientation of the molecule are described completely by \( q \) and \( Q \).

The matrix, \( Q \), is subject to certain constraints which stem from the requirement that the molecular geometry remains fixed. Since the lengths of all of the \( r_i \) and the angles between them must remain constant, \( Q \) represents an orthonormal change of basis. Thus, the columns of \( Q \) form an orthonormal set. That is \( Q \) is orthogonal:

\[
QQ^T = 1,
\] (2.24a)

where \( Q^T \) indicates the transpose of \( Q \) and \( 1 \) is the identity matrix. We also assume that the molecular coordinate system and the external coordinate system are oriented consistently, so

\[
\det(Q) = 1.
\] (2.24b)

The set of all matrices which satisfy (2.24) is called the Special Orthogonal Group over \( \mathbb{R}^3 \), denoted \( SO(3) \). In fact, \( SO(3) \) is a group under matrix multiplication.\(^8\)

We wish to express the Lagrangian for the motion of the molecule in terms of \( q \) and \( Q \). We assume, therefore, that the potential energy, \( V \), is a given function of these variables. Using (2.23), this is equivalent to \( V \) being a given function of the position of each particle in the molecule. Note that the kinetic energy of the

\(^8\)This discussion could be summarized by noting that the motion of an individual molecule takes place on the manifold \( M = \mathbb{R}^3 \times SO(3) \). One approach to molecular motion would be to consider \( M \) as a Riemannian manifold. Lagrangian mechanics can be formulated in this setting, so we could derive equations of motion. However, since we are interested in numerical calculation, we would eventually have to return to a more concrete description of the motion.
molecule is:

\[ T(\dot{q}, \dot{Q}) = \sum_{i=1}^{n} \frac{1}{2} m_i \| \dot{q} + \dot{Q} r_i \|^2 \]

\[ = \frac{1}{2} \sum_{i=1}^{n} m_i (\| \dot{q} \|^2 + 2 \dot{q} \cdot \dot{Q} r_i + \| Q r_i \|^2) \]

\[ = \frac{1}{2} \left( \sum_{i=1}^{n} m_i \right) \| \dot{q} \|^2 + \dot{q} \cdot \dot{Q} \left( \sum_{i=1}^{n} m_i r_i \right) + \frac{1}{2} \sum_{i=1}^{n} m_i \| Q r_i \|^2 \]

\[ = \frac{1}{2} \left( \sum_{i=1}^{n} m_i \right) \| \dot{q} \|^2 + \frac{1}{2} \text{tr} \left[ \dot{Q} \left( \sum_{i=1}^{n} m_i r_i^T r_i \right) \dot{Q}^T \right], \tag{2.25} \]

where \( \text{tr} \) denotes the trace operation, and we have used the fact that for any two vectors \( A, B \in \mathbb{R}^3 \), \( A \cdot B = A^T B = \text{tr}(A^T B) = \text{tr}(B^T A) \). We define the following matrix:

\[ J := \sum_{i=1}^{n} m_i r_i^T r_i, \tag{2.26} \]

and let \( M \) denote the total mass of the molecule, so that

\[ T(\dot{q}, \dot{Q}) = \frac{1}{2} M \dot{q} \cdot \dot{q} + \frac{1}{2} \text{tr} \left[ \dot{Q} J \dot{Q}^T \right]. \tag{2.27} \]

Hence, we can write the Lagrangian:

\[ L = T(\dot{q}, \dot{Q}) - V(q, Q) + \text{tr} \left[ \lambda (Q^T Q - I) \right] \]

\[ = \frac{1}{2} M \dot{q} \cdot \dot{q} + \frac{1}{2} \text{tr} \left[ \dot{Q} J \dot{Q}^T \right] - V(q, Q) + \text{tr} \left[ \lambda (Q^T Q - I) \right], \tag{2.28} \]

where \( \lambda \) is a symmetric matrix of Lagrange multipliers introduced to enforce the constraint of orthogonality on \( Q \). The equations of motion derived from this Lagrangian are:

\[ M \ddot{q} + \frac{\partial V}{\partial q} = 0, \tag{2.29a} \]

\[ \ddot{Q} J + \frac{\partial V}{\partial Q} - 2Q \lambda = 0, \tag{2.29b} \]

and

\[ Q^T Q - I = 0. \tag{2.29c} \]

\[ ^9 \text{By } \frac{\partial f}{\partial Q}, \text{ the derivative of a quantity with respect to } Q, \text{ we denote the matrix whose } (i, j)^{th} \text{ component is the derivative of } f \text{ by the } (i, j)^{th} \text{ component of } Q, \frac{\partial f}{\partial Q_{ij}}. \]
The momenta conjugate to \( q \) and \( Q \) are:

\[
p := M \dot{q},
\]

and

\[
\Pi := \dot{Q} J.
\]

2.4.1 Dynamics in \( SO(3) \)

The path followed by \( Q \) is a path in \( SO(3) \). We wish to use certain facts about matrix groups in general, and \( SO(3) \) in particular, to simplify the equations of motion for \( Q \). Our ultimate goal is a set of variables, which will include the angular momentum, with which we can formulate the equations without Lagrange multipliers.

We begin by stating and proving a lemma regarding groups of matrices. Let \( \mathfrak{gl}(n, \mathbb{R}) \) denote the vector space of all \( n \times n \) matrices. Let \( G \subset \mathfrak{gl}(n, \mathbb{R}) \). Consider the set of all matrices \( A \in \mathfrak{gl}(n, \mathbb{R}) \), where \( A = \dot{\phi}(0) \) for some differentiable path \( \phi : [-1, 1] \rightarrow G \) such that \( \phi(0) = M \) for some fixed \( M \in G \). This set is called the tangent space to \( G \) at \( M \) and is denoted \( T_M G \).

**Lemma 2.4.1.** Let \( G \subset \mathfrak{gl}(n, \mathbb{R}) \) be a group under matrix multiplication.\(^{10}\) Let \( T = T_1 G \) be the tangent space to \( G \) at the identity. If \( \phi : [t_0, t_1] \rightarrow G \) is a differentiable path in \( G \) then there exists a path \( \psi : [t_0, t_1] \rightarrow T \) such that \( \dot{\phi}(t) = \phi(t) \psi(t) \).

**Proof.** Fix \( s \in [t_0, t_1] \). Consider the path \( \eta = \phi(s)^{-1} \phi \). Clearly, \( \eta(s) = 1 \), so \( \dot{\eta}(s) \in T \). However \( \dot{\eta}(s) = \dot{\phi}(s)^{-1} \dot{\phi}(s) \). Hence, we define \( \psi(t) := \phi(t)^{-1} \dot{\phi}(t) \) and note that by the above argument \( \psi(t) \in T \) for each \( t \in [t_0, t_1] \). Clearly \( \dot{\phi}(t) = \phi(t) \psi(t) \).

To apply the previous lemma, we make use of the well known fact that the tangent space to \( SO(3) \) at the identity is the space of skew-symmetric matrices.\(^{11}\)

\[
T_1 SO(3) = \mathfrak{so}(3) := \{ A \in \mathfrak{gl}(3, \mathbb{R}) : A^T = -A \}.
\]

Note \( \mathfrak{so}(3) \) can be put into one to one correspondence with \( \mathbb{R}^3 \) by the following map, which we denote \( \text{sk} \):\(^{12}\)

\[
\text{sk} \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix} := \begin{pmatrix} 0 & v_3 & -v_2 \\ -v_3 & 0 & v_1 \\ v_2 & -v_1 & 0 \end{pmatrix}.
\]

\(^{10}\)So, the identity matrix, \( 1 \), is in \( G \). Further, if \( S \) and \( T \) are in \( G \), then \( ST \in G \) and \( S^{-1} \) exists and is in \( G \).

\(^{11}\)Goldstein \[14, Section 4.8\] discusses this fact in an intuitive fashion. In his terminology, which is standard in physics, \( SO(3) \) is the set of “finite rotations” and \( T_1 SO(3) \) is the set of “infinitesimal rotations.”

\(^{12}\)pronounced: skew
The map \( sk \) is defined so as to have several nice properties, which we summarize in the following lemma.\(^{13}\)

**Lemma 2.4.2.** Let \( a, b \in \mathbb{R} \), \( v, w \in \mathbb{R}^3 \), \( M \in \text{gl}(3, \mathbb{R}) \), and \( R \in SO(3) \). Let \( v \times w \) denote the usual (right handed) cross product. Then:

\[
\begin{align*}
\text{sk}(av + bw) &= a \text{ sk}(v) + b \text{ sk}(w), \\
\text{sk}(v) &= -\text{ sk}(v)^T, \\
\text{sk}(v)w &= -v \times w = w \times v = -\text{ sk}(w)v, \\
\text{sk}(v) \text{ sk}(w) - \text{ sk}(w) \text{ sk}(v) &= -\text{ sk}(v \times w) = \text{ sk}(w \times v), \\
M^T \text{ sk}(v) + \text{ sk}(v)M &= \text{ sk}(\text{tr}(M)1 - M)v,
\end{align*}
\]

and

\[
R^T \text{ sk}(v)R = \text{ sk}(R^Tv). \tag{2.33f}
\]

**Proof.** Verification of (2.33a) through (2.33e) requires only straightforward computation. To see that (2.33f) holds, note that \( \text{sk}(R^Tv) \) is uniquely determined by its action as a linear transformation on \( \mathbb{R}^3 \):

\[
\text{sk}(R^Tv)w = (R^Tv) \times w,
\]

for any \( w \in \mathbb{R}^3 \). However, since \( R \in SO(3) \),

\[
(R^Tv) \times w = R^T(v \times (Rw)) = R^T \text{ sk}(v)Rw,
\]

for any \( w \in \mathbb{R}^3 \). Equation (2.33f) follows. \( \square \)

Returning to rigid body motion, we conclude from Lemma 2.4.1 that, at each time \( t \), there exists a vector \( \omega(t) \) such that:

\[
\dot{Q}(t) = Q(t) \text{ sk}(\omega(t)). \tag{2.34}
\]

The negative sign in (2.34) has been chose so that \( \omega \) is the angular velocity defined in the body fixed frame by the usual right handed cross product. Note that (2.34)

\(^{13}\)A connoisseur of algebra will note that the previous discussion and Lemma 2.4.2 can be summarized as follows:

1. The Lie algebra associated to the Lie group \( SO(3) \) is isomorphic to the Lie algebra of skew symmetric matrices with the commutator as its Lie bracket.

2. The Lie algebra of skew symmetric matrices is isomorphic to the Lie algebra \( \mathbb{R}^3 \) with the cross product as its Lie bracket.

For more details on Lie groups and Lie algebras, see [33].
is sufficient to guarantee that \( Q(t) \in SO(3) \) for all \( t \) provided \( Q(t_0) \in SO(3) \) for some \( t_0 \). To see this, suppose that \( \omega: [t_0, \infty) \to \mathbb{R}^3 \) is a given, sufficiently smooth function. Then, by the uniqueness theorem for ODE's[4]:

\[
Q(t) = Q(t_0) \exp \left( - \int_{t_0}^{t} \mathbf{s}k(\omega(t')) dt' \right)
= Q(t_0) \exp \left( - \mathbf{s}k \left( \int_{t_0}^{t} \omega(t') dt' \right) \right),
\]

where \( \exp \) is the matrix exponential:

\[
\exp(A) := 1 + \sum_{n=1}^{\infty} \frac{1}{n!} A^n.
\]

Hence,

\[
Q(t)^T Q(t) = \exp \left( - \mathbf{s}k \left( \int_{t_0}^{t} \omega(t') dt' \right) \right) Q(t_0)^T Q(t_0) \left( - \mathbf{s}k \left( \int_{t_0}^{t} \omega(t') dt' \right) \right)
= \exp \left( \mathbf{s}k \left( \int_{t_0}^{t} \omega(t') dt' \right) \right) 1 \left( - \mathbf{s}k \left( \int_{t_0}^{t} \omega(t') dt' \right) \right) = 1.
\]

In view of the calculation which led to (2.35), it would be advantageous to use (2.34) as an equation of motion, for in so doing we would no longer need Lagrange multipliers to maintain the orthogonality of \( Q \). However, in order to use (2.34) as an equation of motion, we must derive an equation of motion for \( \omega \). A crucial observation is that it is possible to eliminate the Lagrange multipliers, \( \lambda \), from (2.29):

\[
Q^T \ddot{Q} J - J \dot{Q}^T Q = - \left( Q^T \frac{\partial V}{\partial Q} - \left( \frac{\partial V}{\partial Q} \right)^T Q \right),
\]

where we have used the fact that \( J \) and \( \lambda \) are symmetric and have assumed that \( Q \in SO(3) \). Now,

\[
\frac{d}{dt} (Q^T \dot{Q} J - J \dot{Q}^T Q) = Q^T \ddot{Q} J - J \ddot{Q}^T Q + \dot{Q}^T \dot{Q} J - J \dot{Q}^T \dot{Q}.
\]

Replacing \( \dot{Q} \) with \( - \mathbf{s}k(\omega) \), and using the identities in Lemma 2.4.2, we find that

\[
Q^T \dot{Q} J - J \dot{Q}^T Q = - Q^T Q \mathbf{s}k(\omega) J - J \mathbf{s}k(\omega) Q^T Q
= - (\mathbf{s}k(\omega) J + J \mathbf{s}k(\omega))
= - \mathbf{s}k ((\text{tr}(J)) \mathbf{1} - J) \omega.
\]
We define the **moment of inertia matrix**

\[
I := \text{tr}(J)\mathbf{1} - J, 
\]

and note that, by the definition of \(J\), this is, in fact, the moment of inertia tensor expressed in the body fixed frame. Hence, we define the **angular momentum**:

\[
L := I\omega = (\text{tr}(J)\mathbf{1} - J)\omega. 
\]

Setting this into (2.37) and applying (2.36), we find that

\[
\sk(\dot{L}) = Q^T \frac{\partial V}{\partial Q} - \left( \frac{\partial V}{\partial Q} \right)^T Q - Q^T \dot{Q} J + J \dot{Q}^T \dot{Q} \\
= Q^T \frac{\partial V}{\partial Q} - \left( \frac{\partial V}{\partial Q} \right)^T Q \\
\quad + \sk(\omega) Q^T Q \sk(\omega) J - J \sk(\omega) Q^T Q \sk(\omega) \\
= Q^T \frac{\partial V}{\partial Q} - \left( \frac{\partial V}{\partial Q} \right)^T Q \\
\quad + \sk(\omega)^2 J + \sk(\omega) J \sk(\omega) - \sk(\omega) J \sk(\omega) - J \sk(\omega)^2 \\
= Q^T \frac{\partial V}{\partial Q} - \left( \frac{\partial V}{\partial Q} \right)^T Q \\
\quad + \sk(\omega) \sk(I\omega) - \sk(I\omega) \sk(\omega) \\
= Q^T \frac{\partial V}{\partial Q} - \left( \frac{\partial V}{\partial Q} \right)^T Q + \sk(L \times \omega). 
\]

Note that, given \(L\), we can only solve for \(\omega\) if \(I\) is invertible. Thus we must consider the invertibility of the moment of inertia matrix. Note that, by (2.26), \(J\) is a symmetric matrix. Thus, there exists an orthonormal basis in which \(J\) is diagonal. We assume that this basis is used for the molecular fixed frame, and define \(J_1\), \(J_2\), and \(J_3\) to be the diagonal elements of \(J\), so that:

\[
J = \begin{pmatrix} J_1 & 0 & 0 \\ 0 & J_2 & 0 \\ 0 & 0 & J_3 \end{pmatrix}. 
\]

Note that the diagonal elements of \(J\) are necessarily positive (see (2.26)), so \(J_i \geq 0\) for \(i = 1, 2, 3\). Clearly, in this basis,

\[
I = \begin{pmatrix} J_2 + J_3 & 0 & 0 \\ 0 & J_3 + J_1 & 0 \\ 0 & 0 & J_1 + J_2 \end{pmatrix}. 
\]
We make the obvious definitions:

\[ I_1 := J_2 + J_3, \]
\[ I_2 := J_3 + J_2, \]
\[ I_3 := J_1 + J_2. \]  

(2.44)

Note that \( I_i \geq 0 \) for \( i = 1, 2, 3 \). We now distinguish three possibilities (see figure 2.3):

1. The moment of inertia matrix is invertible. Then, \( I_i > 0 \) for \( i = 1, 2, 3 \). In this case, we refer to the molecule as a \textbf{rigid body}.

2. The moment of inertia matrix is singular, but non-zero. We may assume, without loss of generality, that \( I_3 = 0 \). Thus, \( J_1 + J_2 = 0 \). By the positivity of the \( J_i \), \( J_1 = J_2 = 0 \). Therefore

\[ I = \begin{pmatrix} J_3 & 0 & 0 \\ 0 & J_3 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \]

and \( J_3 > 0 \). In this case, all of the particles making up the molecule are located along the molecular z axis. We refer to this type of molecule as a \textbf{rigid rotor}.

3. The moment of inertia matrix is identically zero. This is only possible if all of the particles making up the molecule are located at a single point. In this case, we refer to the molecule as an \textbf{atom}.

Rigid body and rigid rotor motion are discussed in the following two sections. Atomic motion requires no further discussion, as it was analyzed in §2.1.
2.4.2 Rigid Body Motion

For a rigid body, \( I \) is invertible. Hence we can solve for \( \omega \), given \( L \). Thus, we can obtain a complete set of equations of motion by combining (2.29), (2.30), (2.34), and (2.41):

\[
\begin{align*}
\dot{q} &= \frac{p}{M}, \\
\dot{p} &= -\frac{\partial V}{\partial q}, \\
\dot{Q} &= -Q \sk{I^{-1}L},
\end{align*}
\]

and

\[
\dot{L} = \text{rot} \left( Q^T \frac{\partial V}{\partial Q} \right) + L \times (I^{-1}L),
\]

where the map \( \text{rot} \) is defined by:

\[
\text{rot}(M) = \sk^{-1}(M - M^T). \tag{2.47}
\]

We have stated (2.46) in a form reminiscent of Hamilton’s equations. In fact, these equations are derivable from a Hamiltonian:

\[
H = \frac{1}{2M}p \cdot p + \frac{1}{2}L \cdot I^{-1}L + V(q, Q) \tag{2.48}
\]

via a Poisson bracket [11]:

\[
\{F, G\} = \frac{\partial F}{\partial q} \cdot \frac{\partial G}{\partial p} - \frac{\partial F}{\partial q} \cdot \frac{\partial G}{\partial p} + \text{tr} \left[ Q^T \left( \frac{\partial F}{\partial Q} \sk \left( \frac{\partial G}{\partial L} \right) - \frac{\partial G}{\partial Q} \sk \left( \frac{\partial F}{\partial L} \right) \right) \right] - L \cdot \left( \frac{\partial F}{\partial L} \times \frac{\partial G}{\partial L} \right). \tag{2.49}
\]

2.4.3 Rigid Rotor Motion

Since a rigid rotor is a linear molecule, the position and the orientation of the molecule are completely specified by a vector to the center of mass, \( q \), and a unit vector which points along the molecular axis. We will denote this unit vector by \( Q_3 \), as it can be thought of as the third column of \( Q \). The other two columns of \( Q \) are not needed to specify the orientation of the rotor, and hence the potential energy must not depend on them. That is, the dynamics of rotation take place in the unit sphere, \( S^2 \), rather than in \( SO(3) \).
Similarly, the kinetic energy cannot depend on the first two columns of $\hat{Q}$. In fact, this is precisely what (2.45) implies. Thus, we may express the kinetic energy so that it depends only on $q$ and $\hat{Q}_3$:

$$T = \frac{1}{2} M \ddot{q} \cdot \dot{q} + \frac{1}{2} J_3 \dot{\hat{Q}}_3 \cdot \dot{\hat{Q}}_3,$$

(2.50)

In the following discussion, we no longer need the orthogonal matrix, $Q$, with which previously described the molecular orientation. Hence, we shall drop the subscripts, and refer to the unit vector $Q_3$ and the moment of inertia $J_3$ simply as $Q$ and $I$ respectively. The Lagrangian for this motion is:

$$L = \frac{1}{2} M \ddot{q} \cdot \dot{q} + \frac{1}{2} I \dot{Q} \cdot \dot{Q} - V(q, Q) + \lambda (Q \cdot Q - 1),$$

(2.51)

where $\lambda$ is a Lagrange multiplier introduced to preserve the modulus of $Q$. From this Lagrangian, we derive equations of motion:

$$M \ddot{q} + \frac{\partial V}{\partial q} = 0,$$

(2.52a)

$$I \ddot{Q} + \frac{\partial V}{\partial Q} - 2\lambda Q = 0,$$

(2.52b)

and momenta:

$$p = M \dot{q},$$

(2.53a)

$$\Pi = I \dot{Q}.$$  

(2.53b)

We define the angular velocity:

$$\omega := Q \times \dot{Q},$$

(2.54)

and note that\footnote{We use the triple product formula:}

$$\omega \times Q = (Q \times \dot{Q}) \times Q = -(Q \cdot \dot{Q})Q + (Q \cdot Q)\dot{Q}. $$

(2.55)

However, $Q$ is a unit vector, so

$$Q \cdot Q = 1,$$

(2.56)

and

$$0 = \frac{d}{dt} Q \cdot Q = 2Q \cdot \dot{Q}.$$  

(2.57)
Thus,
\[ \omega \times Q = \dot{Q}. \] (2.58)

As (2.34) was sufficient to guarantee the orthogonality of the matrix \( Q \), so is (2.58) sufficient to guarantee the unit-modulus of the vector \( Q \), since, so long as (2.58) holds:
\[ \frac{d}{dt} Q \cdot Q = 2Q \cdot \dot{Q} = Q \cdot (\omega \times Q) = 0. \] (2.59)

Paralleling our derivation of the rigid body equations of motion, we wish to use (2.58) as one of the equations of motion and thereby eliminate \( \lambda \). To this end, we note that:
\[ Q \times I \ddot{Q} = -Q \times \frac{\partial V}{\partial Q}. \] (2.60)

Thus, if we let \( L = I \omega \) denote the angular momentum,
\[ \dot{L} = I \left( \dot{Q} \times \dot{Q} + Q \times \ddot{Q} \right) \]
\[ = -Q \times \frac{\partial V}{\partial Q}. \] (2.61)

As \( I \) is nonzero, solving for \( L \) is sufficient to solve for \( \omega \). Hence we may take the following as a complete set of equations of motion for a rigid rotor:
\[ \dot{q} = \frac{p}{M}, \] (2.62a)
\[ \dot{p} = -\frac{\partial V}{\partial q}, \] (2.62b)
\[ \dot{Q} = \frac{1}{I} L \times Q, \] (2.62c)

and
\[ \dot{L} = -Q \times \frac{\partial V}{\partial Q}. \] (2.62d)

As in the rigid body case, these equations are derivable from a Hamiltonian:
\[ H = \frac{1}{2M} p \cdot p + \frac{1}{2I} L \cdot L + V(q, Q), \] (2.63)
via a Poisson bracket [11]:
\[ \{F, G\} = \frac{\partial F}{\partial q} \cdot \frac{\partial G}{\partial p} - \frac{\partial G}{\partial q} \cdot \frac{\partial F}{\partial p} - Q \cdot \left( \frac{\partial F}{\partial Q} \times \frac{\partial G}{\partial L} - \frac{\partial G}{\partial Q} \times \frac{\partial F}{\partial L} \right) - L \cdot \left( \frac{\partial F}{\partial L} \times \frac{\partial G}{\partial L} \right). \] (2.64)
Chapter 3

Statistical Mechanics

To use ergodicity to calculate the values of macroscopic properties of a system, we
must obtain a relationship between these values and statistical mechanical averages.
We begin this chapter by developing a mathematical framework in which we can
discuss appropriate systems. Then we derive expressions for the derivatives of statis-
tical mechanical averages with respect to volume and temperature. Finally, we show
how to derive formulae for various thermodynamic quantities in terms of averages.
Although the use of time averages is crucial to MD simulations, we have not seen in
the literature a general approach, such as that presented herein, to deriving formulae
involving these averages.

3.1 The Mathematical Framework

The systems which we consider have several macroscopic parameters which must
be specified at the outset: temperature, volume, and the number of molecules. We
consider fluid systems; hence, the shape of the volume is unimportant. Thus, let us
consider $N$ molecules at temperature $T$ with volume $V$ which occupy a cube, $B$, of
side length $2L$ centered at the origin:

$$B = \{(x_1, x_2, x_3) : |x_i| < L\}. \quad (3.1)$$

Let $r_i$ denote the center of mass of the $i$th molecule. Let the “orientation” of this
molecule be described by “internal” coordinates, $s_i$, where $s_i$ takes values in some
space $S_i$. If the molecule is rigid, this space is one of: $\{0\}$, $S^2$, or $SO(3)$. For our
purposes, we must assume a few facts about $S_i$. It is not necessary to understand the
following assumptions in detail in order to understand this chapter; we discuss them
largely to point out that the following derivation depends only in a very general way
on the structures of $\{0\}$, $S^2$ and $SO(3)$.

1. We assume that it is possible to differentiate paths in $S_i$. That is, $S_i$ is a
differentiable manifold.
2. We assume that it is possible to integrate over the whole of \( S_i \). That is, \( S_i \) is endowed with a choice of a volume form. We assume, further, that the total volume of \( S_i \) is finite.

3. Let \( n_i \) denote the dimension of \( S_i \), as a manifold. We assume that to each point \( s \in S_i \) is associated a vector space isomorphism \( L_i(s) : \mathbb{R}^{n_i} \to T_s S_i \) such that the kinetic energy of the molecule when it has orientation \( s \) and velocity \( L_i(s) \cdot \omega \) is given by:

\[
K(s, L_i(s) \cdot \omega) = (I_i \cdot \omega) \cdot \omega, \tag{3.2}
\]

where \( I_i \) is a positive definite linear operator on \( \mathbb{R}^{n_i} \). For example, in the case of rigid body motion, \( S_i = SO(3) \), \( L_i(Q) \cdot \omega = Q \mathbf{sk}(\omega) \) for \( \omega \in \mathbb{R}^3 \), and

\[
K(s, L_i(s)\omega) = (I \cdot \omega) \cdot \omega, \tag{3.3}
\]

where \( I \) is the moment of inertia matrix.

If, for instance, \( S_i \) is a Lie group,\(^1\) then these assumptions follow. This is a standard, but fairly deep, result.\(^2\)

The total kinetic energy is seen to be of the form:

\[
K = \sum_{i=1}^{N} \left( \frac{1}{2} m_i \| \dot{r}_i \|^2 + \frac{1}{2} (I_i \cdot \omega_i) \cdot \omega_i \right) \tag{3.4}
\]

where \( m_i \) is the mass of the \( i \)th molecule, and \( \omega_i \in \mathbb{R}^{n_i} \). As in Hamiltonian mechanics, we re-express \( K \) in terms of momenta:

\[
p_i = \frac{\partial K}{\partial \dot{r}_i} = m_i \dot{r}_i, \tag{3.5a}
\]

and

\[
l_i = \frac{\partial K}{\partial \dot{\omega}_i} = I_i \cdot \omega_i. \tag{3.5b}
\]

Thus

\[
K = \sum_{i=1}^{N} \left( \frac{1}{2m_i} p_i \cdot p_i + \frac{1}{2} (I_i^{-1} \cdot l_i) \cdot l_i \right). \tag{3.6}
\]

---

\(^1\)A differentiable manifold which is imbued with a group structure in such a fashion that the group operations are smooth.

\(^2\)For completeness, we mention why this is true. It is certainly not necessary for the reader to understand the content of this note in detail. Assumption one follows from the definition of a Lie group. Requirement two follows from the existence of a Haar measure on \( S_i \) [12, Chapter 10]. Requirement three follows from the canonical association of the Lie algebra of \( S_i \) with the tangent space to \( S_i \) at the identity [33].
We assume that the potential energy, $U$, is independent of $p_i$ and $l_i$.

We now introduce some notation. Let

$$B_N := \prod_{i=1}^{N} B,$$  \hspace{1cm} (3.7a)

$$S_N := \prod_{i=1}^{N} S_i,$$  \hspace{1cm} (3.7b)

$$\mathcal{P}_N := B_N \times S_N,$$  \hspace{1cm} (3.7c)

$$B^*_N := \bigoplus_{i=1}^{N} \mathbb{R}^3,$$  \hspace{1cm} (3.7d)

$$S^*_N := \bigoplus_{i=1}^{N} \mathbb{R}^{n_i},$$  \hspace{1cm} (3.7e)

and

$$\mathcal{P}^*_N := B^*_N \oplus S^*_N.$$  \hspace{1cm} (3.7f)

Thus, given a configuration of the $N$ molecules, there is a point in $\mathcal{P}_N$ which denotes their positions and orientations, and a point in $\mathcal{P}^*_N$ which denotes their momenta. We shall, at our convenience, denote elements of $\mathcal{P}_N$ by $q$ or by $(R, S)$ where $R \in B_N$ and $S \in S_N$. Similarly, we shall denote elements of $\mathcal{P}^*_N$ by $p$ or by $(P, \Omega)$ where $P \in B^*_N$ and $\Omega \in S^*_N$.

Note that the potential energy, $U$, is a function of $q \in \mathcal{P}_N$ and that the kinetic energy, $K$, is a function of $p \in \mathcal{P}^*_N$, so the statistical density for the system at temperature $T$ is [20, Chapter 1]:

$$\rho(p, q) := \frac{e^{-(K(p)+U(q))/T}}{\int_{\mathcal{P}_N} \int_{\mathcal{P}^*_N} e^{-(K(p)+U(q))/T} dpdq}$$  \hspace{1cm} (3.8)

To evaluate the integral with respect to $p$ in (3.8), we use the following fact. If $M$ is a positive definite symmetric $n \times n$ matrix, then

$$\int_{\mathbb{R}^n} e^{-x^T M x} dx = (\det(2\pi M^{-1}))^{\frac{1}{2}}.$$  \hspace{1cm} (3.9)

Equation (3.9) follows easily from the standard fact that for $a > 0$:

$$\int_{\mathbb{R}} e^{-ax^2} dx = \left(\frac{2\pi}{a}\right)^{\frac{1}{2}},$$  \hspace{1cm} (3.10)
and the fact that any positive definite symmetric matrix can be brought into a 
diagonal form by an orthonormal change of basis. Hence, we can evaluate the integral 
with respect to $p$ in (3.8):

$$\int_{\mathcal{P}_N^*} e^{-K(p)/T} dp = \prod_{i=1}^{N} \left( (2\pi m_i T)^3 \text{det}(2\pi T I_i) \right)^{\frac{1}{2}}. \quad (3.11)$$

Let

$$s(N) := 3N + \sum_{i=1}^{N} n_i, \quad (3.12)$$

and

$$m(N) := \prod_{i=1}^{N} \left( (2\pi)^{3+n_i} m_i^3 \text{det} I_i \right)^{\frac{1}{2}}. \quad (3.13)$$

Then,

$$\int_{\mathcal{P}_N^*} e^{-K(p)/T} dp = Ts(N)/2m(N), \quad (3.14)$$

and

$$\rho(p, q) = \frac{e^{-(K(p)+U(q))/T}}{Ts(N)/2m(N) \int_{\mathcal{P}_N} e^{-U(q)/T} dq}. \quad (3.15)$$

The average value of a function $\psi(p, q)$ is defined to be:

$$< \psi > := \int_{\mathcal{P}_N} \int_{\mathcal{P}_N} \psi(p, q)\rho(p, q)dpdq$$

$$= \frac{\int_{\mathcal{P}_N} \int_{\mathcal{P}_N} \psi(p, q)e^{-(K(p)+U(q))/T}dpdq}{Ts(N)/2m(N) \int_{\mathcal{P}_N} e^{-U(q)/T} dq}. \quad (3.16)$$

If the function is independent of $p$, then:

$$< \psi > = \frac{\int_{\mathcal{P}_N} \psi(q)e^{-U(q)/T} dq}{\int_{\mathcal{P}_N} e^{-U(q)/T} dq}. \quad (3.17)$$

### 3.2 The Derivatives of Average Quantities

How does a statistical average, such as that expressed in (3.17), depend on the 
macroscopic variables, $T$ and $V$? To answer this question, we must consider how 
the integrals in (3.17) depend on the length, $L$, of a side of the box $B$. As they 
are written, not only might the integrand depend on $L$, but the limits of integration 
depend on $L$. Thus we begin by transforming the region of integration to a standard region.
Throughout this section, $\psi$ will denote a function which is independent of $p$.

We shall transform the integration over $B_N$ in (3.17) to an integration over a fixed region. To this end, let

$$\mathcal{I}_N := \prod_{i=1}^N I^3,$$

(3.18a)

where $I = (-1, 1)$, and let

$$\mathcal{R}_N := \mathcal{I}_N \times S_N.$$  

(3.18b)

Then, given a function $f(R, S)$,

$$\int_{P_N} f(R, S) dRdS = \int_{\mathcal{R}_N} f(LR, S) L^{3N} dRdS. \quad (3.19)$$

Thus

$$\langle \psi \rangle = \int_{\mathcal{R}_N} \psi(LR, S; L) e^{-U(LR, S; L)/T} dRdS \int_{\mathcal{R}_N} e^{-U(LR, S; L)/T} dRdS,$$

(3.20)

where we have indicated that $\psi$ and $U$ might depend explicitly on $L$. Using (3.20) we calculate:

$$\frac{\partial < \psi >}{\partial L} = \frac{\int_{\mathcal{R}_N} (R \cdot \left[ \frac{\partial \psi}{\partial R} + \frac{\psi}{T} \frac{\partial U}{\partial R} \right] + \left[ \frac{\partial \psi}{\partial L} - \frac{\psi}{T} \frac{\partial U}{\partial L} \right]) \left[ e^{-U/T} \right] dRdS}{\int_{\mathcal{R}_N} [e^{-U/T}] dRdS} + \frac{1}{T} \left( \int_{\mathcal{R}_N} \left[ \psi e^{-U/T} \right] dRdS \right) \left( \int_{\mathcal{R}_N} \left( R \cdot \left[ \frac{\partial U}{\partial R} + \frac{\partial U}{\partial L} \right] \right) \left[ e^{-U/T} \right] dRdS \right)^2$$

$$= \frac{1}{L} \left( \langle R \cdot \frac{\partial \psi}{\partial R} + L \frac{\partial \psi}{\partial L} \rangle \right) - \frac{1}{TL} \left( \langle \psi \left( R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right) \rangle - \langle \psi \rangle \langle \psi \left( R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right) \rangle \right),$$

(3.21)

where terms in square brackets are evaluated at $q = (LR, S)$. Since $V = 8L^3$, $\frac{\partial}{\partial V} = \frac{1}{3VT} \frac{\partial}{\partial L}$. Thus,

$$\frac{\partial < \psi >}{\partial V} = \frac{1}{3V} \left( \langle R \cdot \frac{\partial \psi}{\partial R} + L \frac{\partial \psi}{\partial L} \rangle \right) - \frac{1}{3VT} \left( \langle \psi \left( R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right) \rangle - \langle \psi \rangle \langle \psi \left( R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right) \rangle \right).$$

(3.22)

$^3$We assume that all functions are smooth enough to justify bringing the derivative under the integral sign.
A similar calculation yields:

$$\frac{\partial < \psi >}{\partial T} = \frac{1}{T^2} \left( < \psi U > - < \psi >< U > \right) + \left\langle \frac{\partial \psi}{\partial T} \right\rangle.$$  \hfill (3.23)

### 3.3 Formulae for Thermodynamic Quantities

We are now in a position to derive expressions for thermodynamic quantities. We begin with the following expression for the thermodynamic potential:[20, Chapter 3]

$$F = -T \log \left( \Phi(N) \int_{\mathcal{P}_N} \int_{\mathcal{P}_N} e^{-\frac{1}{T} (K+U)} \frac{dpdq}{h^{s(N)}} \right)$$  \hfill (3.24)

where $\Phi(N)$ is a statistical weight depending on the number of identical particles of each type, and $h$ is Planck’s constant. Performing the integration with respect to $p$ and dividing by $N$, we obtain an expression for the free energy per particle:

$$f := \frac{F}{N}$$

$$= -T \log \left( \Phi(N) \left( \frac{2\pi m_i T}{h^2} \right)^{s(N)/2} m(N) \int_{\mathcal{P}_N} e^{-U(q)/T} dq \right)$$

$$= -T \left[ \frac{1}{N} \log \left( \Phi(N) m(N) (2\pi h^{-2})^{s(N)} \right) + \frac{s(N)}{2N} \log T \right.$$  \hfill (3.25)

$$+ \log \left( \int_{\mathcal{P}_N} e^{-U(q)/T} dq \right)^{1/N} \right]$$

Let $\Psi(N) := \frac{1}{N} \log \left( \Phi(N) m(N) (2\pi h^{-2})^{s(N)} \right) + \log(N)$. By changing the region of integration to $\mathcal{R}_N$ as above:

$$f = -T \left[ \Psi(N) + \frac{s(N)}{2N} \log T + \log \left( \frac{L^3}{N} \left( \int_{\mathcal{R}_N} e^{-U(LR,S;L)/T} dSdR \right)^{1/N} \right) \right]. \hfill (3.26)$$

We wish to express $f$ in terms of average values of functions of the phase variables. With this in mind, consider the average value of $e^{U/T}$:

$$< e^{U/T} > = \frac{\int_{\mathcal{R}_N} dSdR}{\int_{\mathcal{R}_N} e^{-U(LR,S;L)/T} dSdR}.$$  \hfill (3.27)

We let $A(N)$ denote $\int_{\mathcal{R}_N} dSdR$. Then

$$\int_{\mathcal{R}_N} e^{-U(LR,S;L)/T} dSdR = \frac{A(N)}{< e^{U/T} >}. \hfill (3.28)$$
Noting that the volume of $B$ is $V = 8L^3$, we obtain the following formula for $f$:

$$f = -T \left[ \Psi(N) + \frac{1}{N} \log A(N) + \frac{s(N)}{2N} \log T + \log \left( \frac{V}{8N} \right) - \frac{1}{N} \log < e^{U/T} > \right]. \quad (3.29)$$

Using equations 3.22 and 3.23, we can now derive expressions for partial derivatives of $f$ of any order. For example

$$\frac{\partial f}{\partial V} = -\frac{T}{V} + \frac{T}{N} \frac{1}{< e^{U/T} >} \frac{\partial}{\partial V} < e^{U/T} >$$

$$= -\frac{T}{V} + \frac{T}{N} \frac{1}{< e^{U/T} >} \left[ \frac{1}{3V} \left\langle \frac{1}{T} \left( R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right) e^{U/T} \right\rangle \right]$$

$$- \frac{1}{3VT} \left( \left\langle e^{U/T} \left( R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right) \right\rangle \right)$$

$$- < e^{U/T} > \left( R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right) \right) \right]$$

$$= -\frac{T}{V} + \frac{1}{3NV} \left\langle R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right\rangle.$$ 

(3.30)

It follows that the pressure is:

$$P := -N \frac{\partial f}{\partial V} =$$

$$= \frac{NT}{V} - \frac{1}{3V} \left\langle R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right\rangle.$$ 

(3.31)

Similarly, the entropy per particle is:

$$S := -\frac{\partial f}{\partial T} = -\frac{f}{T} + \frac{s(N)}{2N} + \frac{1}{NT} < U > .$$

(3.32)

Finally, we list several important and/or interesting formulae, first introducing the notation:

$$\mathcal{F} = - \left( R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right),$$

so that

$$\frac{\partial < \psi >}{\partial V} = \frac{1}{3V} \left\langle R \cdot \frac{\partial \psi}{\partial R} + L \frac{\partial \psi}{\partial L} \right\rangle + \frac{1}{3VT} \left( < \psi \mathcal{F} > - < \psi > < \mathcal{F} > \right).$$

(3.34)

1. Temperature [20, Chapter 3]:

$$T = \frac{2}{s(N)} < K > .$$

(3.35a)
2. Internal energy per particle:
\[ E = \frac{s(N)}{2N} + \frac{< U >}{N}. \] (3.35b)

3. Pressure:
\[ P = \frac{NT}{V} + \frac{1}{3V} < \mathcal{F} >. \] (3.35c)

4. Heat capacity per particle at constant volume:
\[ c_V = \frac{\partial E}{\partial T} = \frac{s(N)}{2N} + \frac{1}{N} \frac{1}{T^2} ( < U^2 > - < U >^2 ) \] (3.35d)

5. The coefficient of thermal expansion:
\[ \alpha_V = \frac{\partial P}{\partial T} = \frac{N}{V} + \frac{1}{3VT^2} ( < \mathcal{F} > - < U > < \mathcal{F} > ) \] (3.35e)

6. The isothermal compressibility:
\[ \kappa_T = V \left( \frac{\partial P}{\partial V} \right) = - P \left( \mathcal{F} + R \frac{\partial \mathcal{F}}{\partial R} + L \frac{\partial \mathcal{F}}{\partial L} \right) \frac{1}{9VT} \left( < \mathcal{F}^2 > - < \mathcal{F} >^2 \right) \] (3.35f)
Chapter 4

Numerical Approximation of the Trajectory

The heart of a molecular dynamics simulation is the numerical method used to produce an approximate trajectory. In this chapter we considered two types of numerical methods: a family of schemes known as split Hamiltonian integrators, and DASSL, a packaged Fortran routine for solving algebraic differential equations.

4.1 Split Hamiltonian Integrators

One of the most popular algorithms for atomic dynamics is the Verlet algorithm [31], [3]. Generalizations, such as SHAKE and RATTLE [3], in which algebraic constraints are allowed have been proposed. These generalizations have been used heretofore in the majority of molecular dynamics investigations. We are not concerned with SHAKE or RATTLE, but with another family of generalizations, known as split Hamiltonian integrators, which allow us to consider rigid body and rigid rotor motion. We were made aware of such schemes by B. Leimkuhler. In a University of Cambridge Numerical Analysis Report issued in May of 1997, Leimkuhler, with Dullweber and McLachlan, develop a scheme for rigid body molecular dynamics [11]. In this section, following the notation of [11], we define split Hamiltonian integrators and present a theorem which justifies their use.

Throughout this section, we use a superscript notation for calculated values of variables at different time steps, thus $q^0$ is the initial value of $q$ and $q^n$ is the value calculated for $q$ after $n$ time steps. We use $\Delta t$ to denote the size of an individual time step.

By way of an introduction, we present the Verlet algorithm. Consider a system described by momentum coordinates, $p$, and position coordinates, $q$, where $p$ and $q$ are $N$ vectors. Suppose that $M$ is a positive definite matrix, the mass matrix, and
that the Hamiltonian is given by:

\[ H = \frac{1}{2} p \cdot M^{-1} p + V(q). \]  \quad (4.1)

An example of such a system, with \( N \) a multiple of three, is \( N/3 \) interacting point particles. The Verlet algorithm for the propagation of the calculated solution from step \( i \) to step \( i + 1 \) is [11]:

\[
\begin{align*}
    p^{i+\frac{1}{2}} &= p^i - \Delta t \frac{\partial V}{\partial q}(q^i) \\
    q^{i+1} &= q^i + \Delta t M^{-1} p^{i+\frac{1}{2}} \\
    p^{i+1} &= p^{i+\frac{1}{2}} - \Delta t \frac{\partial V}{\partial q}(q^{i+1})
\end{align*}
\]  \quad (4.2)

The idea at the heart of split Hamiltonian integration is to note that: “The Verlet method can be viewed as constructing an approximate solution by pasting together the exact solutions of the kinetic and potential parts of \( H \).” [11] In other words, we consider \( H \) to be split into two parts:

\[ H = T + V, \]  \quad (4.3a)

where

\[ T = \frac{1}{2} p \cdot M^{-1} p, \]  \quad (4.3b)

and

\[ V = V(q). \]  \quad (4.3c)

Note that if we consider \( T \) and \( V \) as Hamiltonians, we can solve for the dynamics of each separately. The exact solutions are:

\[
\begin{align*}
    q(t) &= q(0) + tM^{-1}p(0) \\
    p(t) &= p(0)
\end{align*}
\]  \quad (4.4a)

for \( T \), and

\[
\begin{align*}
    q(t) &= q(0) \\
    p(t) &= p(0) - t \frac{\partial V}{\partial q}(q(0))
\end{align*}
\]  \quad (4.4b)

for \( V \). The Verlet scheme can be written as follows:

\[ (p^{i+1}, q^{i+1}) = \exp_T\left(\frac{1}{2} \Delta t\right) \exp_V\left(\frac{1}{2} \Delta t\right) \exp_V\left(\frac{1}{2} \Delta t\right) \exp_T\left(\frac{1}{2} \Delta t\right)(p^i, q^i), \]  \quad (4.5)
where \( \exp_G(t)(\tilde{p}, \tilde{q}) \) represents the solution, at time \( t \), of the motion of the initial conditions \((\tilde{p}, \tilde{q})\) induced by Hamiltonian \( G \).

Equation (4.5) has an obvious generalization. Consider a Hamiltonian, \( H \), and suppose that:

\[
H = H_1 + \ldots + H_n, \tag{4.6}
\]

where the exact solution to \( H_i, i = 1, \ldots, n \), is known. The split Hamiltonian scheme for \( H \) with step size \( \Delta t \) (relative to the splitting shown in (4.6)) is

\[
(p^{i+1}, q^{i+1}) = \exp_{H_1}(\frac{1}{2}\Delta t) \ldots \exp_{H_n}(\frac{1}{2}\Delta t) \exp_{H_n}(\frac{1}{2}\Delta t) \ldots \exp_{H_1}(\frac{1}{2}\Delta t)(p^i, q^i). \tag{4.7}
\]

We refer to \( n \) as the size of the splitting. Such schemes have been discussed in [23], [25], [26] and [11]. A concise proof that the Verlet algorithm and a specific generalization of the Verlet algorithm with application to rigid body motion\(^2\) are second order is given in [11]. We prefer the following theorem and proof which make use of the Poisson bracket formalism, as they allow us to show that general split Hamiltonian schemes are second order. To our knowledge, the theorem and proof do not appear elsewhere in the literature.

**Theorem 4.1.1.** Let \( H_1, H_2, \) and \( H = H_1 + H_2 \) be real-valued \( C^3 \) functions defined on an open set \( G \subset \mathbb{R}^n \). Consider these functions as Hamiltonians which generate dynamics on \( G \) via a Poisson bracket, \( \{\cdot, \cdot\} \). Suppose that, for each \( \tilde{x} \in G \), \( \exp_{H_1}(t)\tilde{x}, \exp_{H_2}(t)\tilde{x} \), and \( \exp_H(t)\tilde{x} \) are \( C^3 \) at \( t = 0 \). Let \( \phi_1(t)\tilde{x} \) and \( \phi_2(t)\tilde{x} \) be approximations to \( \exp_{H_1}(t)\tilde{x} \) and \( \exp_{H_2}(t)\tilde{x} \) respectively. If for each \( \tilde{x} \in G \):

\[
\phi_i(t)\tilde{x} - \exp_{H_i}(t)\tilde{x} = \mathcal{O}(t^3) \quad (i = 1, 2), \tag{4.8}
\]

then, for each \( \tilde{x} \in G \):

\[
\phi_2(\frac{1}{2}t)\phi_1(t)\phi_2(\frac{1}{2}t)\tilde{x} - \exp_{H}(t)\tilde{x} = \mathcal{O}(t^3). \tag{4.9}
\]

Before proceeding to the proof, let us discuss the notation, and clarify certain interpretations and consequences of the theorem:

1. The notation \( f(t) = \mathcal{O}(g(t)) \) indicates that:
   
   (a) \( f(t) \) and \( g(t) \) are defined for \( t \) in some neighborhood of 0.

---

\(^1\)In [23] the scheme

\[
(p^{i+1}, q^{i+1}) = \exp_{H_1}^{-1}(-\frac{1}{2}\Delta t) \ldots \exp_{H_n}^{-1}(-\frac{1}{2}\Delta t) \exp_{H_n}(\frac{1}{2}\Delta t) \ldots \exp_{H_1}(\frac{1}{2}\Delta t)(p^i, q^i)
\]

is used, because it explicitly preserves the time reversibility of the dynamics. For the cases we consider \( \exp_{H_i}^{-1}(-t) = \exp_{H_i}(t) \), thus we maintain the notation of (4.7).

\(^2\)We present this scheme in section 4.1.1.
(b) For \( t \) in some neighborhood of zero (possibly smaller than the domain of definition), there exists a constant \( C > 0 \) such that \( \| f(t) \| < C \| g(t) \| \).

The notation \( f_1(t) = f_2(t) + O(g(t)) \) indicates, of course, that \( f_1(t) - f_2(t) = O(g(t)) \).

2. Under the appropriate hypotheses of smoothness, it follows from this theorem, via induction on the size of the splitting, that split Hamiltonian integrators for Poisson bracket systems have a local truncation error of order 3, and hence a global error of order 2 (see [9] for a discussion of errors).

3. It is not necessary for a successful scheme that the solutions which are pasted together be exact. However, the schemes which we will consider will all consist of exact solutions pasted together.

4. Nearly all potential functions of interest are \( C^\infty \) (sometimes with a few poles or discontinuities). Kinetic energy functions are almost always homogeneous polynomials of degree 2, also \( C^\infty \). Since the solutions of a first order ODE with \( C^k \) forcing functions are \( C^k \) [4], the hypothesis of \( C^3 \) smoothness will be satisfied for most cases of interest. Hence, the hypotheses guaranteeing smoothness simply prevent pathological cases.

**Proof.** In what follows, if \( F \) is a function and \( V \) is a vector field, with components \( V_i \), then \( \{ F, V \} \) denotes the vector field whose components are \( \{ F, V_i \} \), and \( \{ V, F \} \) denotes the vector field whose components are \( \{ V_i, F \} \). We also use the notation \( \{ F, G \}_x \) to indicate that the Poisson bracket of \( F \) and \( G \) is to be evaluated at the point \( x \).

Consider the solution, \( \exp \tilde{H}(t) \tilde{x} \), to a Hamiltonian \( \tilde{H} \). If the solution is \( C^3 \), then the following equation, in which we write the first and second derivatives with respect to time in terms of the Poisson bracket, follows from Taylor’s theorem with remainder:

\[
\exp \tilde{H}(t) \tilde{x} = \tilde{x} + t \{ \tilde{H}, x \}_\tilde{x} + \frac{1}{2} t^2 \{ \tilde{H}, \{ \tilde{H}, x \}_\tilde{x} \} + O(t^3),
\]

(4.10)

Fix \( \tilde{x} \in G \). Since \( H = H_1 + H_2 \),

\[
\exp H(t) \tilde{x} = \tilde{x} + t \left( \{ H_1, x \}_\tilde{x} + \{ H_2, x \}_\tilde{x} \right) \\
+ \frac{1}{2} t^2 \left( \{ H_1, \{ H_1, x \}_\tilde{x} \} + \{ H_1, \{ H_2, x \}_\tilde{x} \} \\
+ \{ H_2, \{ H_1, x \}_\tilde{x} \} + \{ H_2, \{ H_2, x \}_\tilde{x} \} \right) + O(t^3).
\]

(4.11)
We show that (4.11) holds with $\phi_2\left(\frac{1}{2}t\right)\phi_1(t)\phi_2\left(\frac{1}{2}t\right)\tilde{x}$ in place of $\exp_H(t)\tilde{x}$, thus demonstrating the theorem.

Since $\phi_2(t)\tilde{x} - \exp_{H_2}(t)\tilde{x} = O(t^3)$, the Taylor series for $\phi_2\left(\frac{1}{2}t\right)$ agrees with that for $\exp_{H_2}(\frac{1}{2}t)\tilde{x}$ up to terms of order $t^2$:

$$\phi_2\left(\frac{1}{2}t\right)\tilde{x} = \tilde{x} + \frac{1}{2}t\{H_2, x\}|_{\tilde{x}}t + \frac{1}{8}t^2\{H_2, \{H_2, x\}\}|_{\tilde{x}} + O(t^3). \quad (4.12)$$

Similarly, since $\phi_1(t)\tilde{x} - \exp_{H_1}(t) = O(t^3)$,

$$\phi_1(t)\phi_2\left(\frac{1}{2}t\right)\tilde{x} = \phi_2\left(\frac{1}{2}t\right)\tilde{x} + t\{H_1, x\}|_{\phi_2\left(\frac{1}{2}t\right)\tilde{x}} + \frac{1}{2}t^2\{H_1, \{H_1, x\}\}|_{\phi_2\left(\frac{1}{2}t\right)\tilde{x}} + O(t^3). \quad (4.13)$$

In (4.11), each Poisson bracket is evaluated at $\tilde{x}$. Thus, we expand each term of (4.13) in a Taylor series about $\tilde{x}$, keeping terms up to order $t^2$:

$$\phi_1(t)\phi_2\left(\frac{1}{2}t\right)\tilde{x} = \tilde{x} + t\left(\{H_1, x\}|_{\tilde{x}} + \frac{1}{2}\{H_2, x\}|_{\tilde{x}}\right)$$

$$+ t^2\left(\frac{1}{2} \frac{\partial\{H_1, x\}}{\partial x} \right|_{\tilde{x}} \{H_2, x\}|_{\tilde{x}} + \frac{1}{2}\{H_1, \{H_1, x\}\}|_{\tilde{x}}$$

$$+ \frac{1}{8}\{H_2, \{H_2, x\}\}|_{\tilde{x}} + O(t^3). \quad (4.14)$$

In (4.14), $\frac{\partial\{H_1, x\}}{\partial x}$ denotes the Jacobian matrix of $\{H_1, x\}$.

We must digress to derive a formula for the terms of (4.14) which involve Jacobian matrices. To this end we note that:

$$\{F, G\} = \left(\frac{\partial F}{\partial x}\right)^T M(x) \frac{\partial G}{\partial x}, \quad (4.15)$$
for some antisymmetric matrix function, $M$. Thus,

$$\{H_2, \{H_1, x\}\} = -\{\{H_1, x\}, H_2\}$$

$$= -\frac{\partial \{H_1, x\}}{\partial x} M(x) \frac{\partial H_2}{\partial x} = \frac{\partial \{H_1, x\}}{\partial x} \left( -1 M(x) \frac{\partial H_2}{\partial x} \right)$$

$$= \frac{\partial \{H_1, x\}}{\partial x} \left( -\{x, H_2\} \right) = \frac{\partial \{H_1, x\}}{\partial x} \{H_2, x\}.$$  \hfill (4.16)

Using (4.16), we may rewrite (4.14) as follows:

$$\phi_1(t) \phi_2 \left( \frac{1}{2} t \ddot{x} \right) = \ddot{x} + t \left( \{H_1, x\}_{\ddot{x}} + \frac{1}{2} \{H_2, x\}_{\ddot{x}} \right)$$

$$+ \frac{1}{2} t^2 \left( \{H_1, \{H_1, x\}\}_{\ddot{x}} + \{H_2, \{H_1, x\}\}_{\ddot{x}} \right.$$

$$+ \frac{1}{4} \{H_2, \{H_2, x\}\}_{\ddot{x}} + \mathcal{O}(t^3).$$  \hfill (4.17)

---

3Equation (4.15) follows from the three identities:

1. $\{F, G\} = -\{G, F\}$,

2. $aF + bG, H = a\{F, H\} + b\{G, H\}$,


From equations 2 and 3, we conclude that, for fixed $G$, the map $F \rightarrow \{F, G\}$ is a linear derivation \cite[Chapter 1]{33}. Thus, $\{F, G\} = \frac{\partial F}{\partial x} \cdot Y_G$ for some vector field $Y_G$ \cite[Chapter 1]{33}. By the first equation, for fixed $F$, the map $G \rightarrow \{F, G\}$ is also a linear derivation. Thus, the vector field $Y_G$ is a linear function of $\frac{\partial G}{\partial x}$. Hence, $Y_G = M(x) \frac{\partial G}{\partial x}$ for some matrix function $M$. That $M$ is antisymmetric follows from the first identity.

4We suggest considering (4.16) component-wise if the identities are not clear.
We complete the proof by applying $\phi_1(\frac{1}{2}t)$ to both sides of (4.17):

$$
\phi_2(\frac{1}{2}t)\phi_1(t)\phi_2(\frac{1}{2}t)\ddot{x} = \phi_1(t)\phi_2(\frac{1}{2}t)\dddot{x} + \frac{1}{2}t\{H_2, x\}|_{\phi_1(t)\phi_2(\frac{1}{2}t)\ddot{x}} \\
+ \frac{1}{8}\{H_2, \{H_2, x\}\}|_{\phi_1(t)\phi_2(\frac{1}{2}t)\ddot{x}} + \mathcal{O}(t^3) \\
= \dddot{x} + t\left(\{H_1, x\}|_{\ddot{x}} + \{H_2, x\}|_{\ddot{x}}\right) \\
+ \frac{1}{2}t^2\left(\{H_1, \{H_1, x\}\}|_{\dddot{x}} + \{H_2, \{H_1, x\}\}|_{\dddot{x}}\right) \\
+ \frac{1}{4}\{H_2, \{H_2, x\}\}|_{\dddot{x}} \\
+ \frac{\partial\{H_2, x\}}{\partial x}\left|_{\ddot{x}} \left(\{H_1, x\}|_{\ddot{x}} + \frac{1}{2}\{H_2, x\}|_{\ddot{x}}\right) + \frac{1}{4}\{H_2, \{H_2, x\}\}|_{\ddot{x}}\right) + \mathcal{O}(t^3) \\
= \dddot{x} + t\left(\{H_1, x\}|_{\ddot{x}} + \{H_2, x\}|_{\ddot{x}}\right) \\
+ \frac{1}{2}t^2\left(\{H_1, \{H_1, x\}\}|_{\dddot{x}} + \{H_2, \{H_1, x\}\}|_{\dddot{x}}\right) \\
+ \{H_1, \{H_2, x\}\}|_{\dddot{x}} + \{H_2, \{H_2, x\}\}|_{\dddot{x}} \right) \\
+ \mathcal{O}(t^3).
$$

The Verlet algorithm is a split Hamiltonian scheme for atomic dynamics. In the next two sections we consider the Hamiltonians for rigid body and rigid rotor dynamics. We present split Hamiltonian schemes for the integration of their motion.

### 4.1.1 A Split Hamiltonian Scheme for Rigid Body Motion

The Hamiltonian for rigid body motion, and the associated Poisson brackets, were presented in (2.48) and (2.49). In this section, we present a split Hamiltonian scheme for the approximation of the associated dynamics. McLachlan [23] and Reich [25] independently proposed versions of this scheme for the case of free rigid bodies, i.e. when the potential energy does not depend on their orientations. The scheme herein, which allows the potential energy to depend on the orientations, is due to Reich [26]. The scheme has also been used by Dullweber, Leimkuhler, and McLachlan [11].
To obtain a split Hamiltonian scheme for rigid body dynamics, we split the Hamiltonian for an individual rigid body into five pieces:

\[ H = V + T + S_1 + S_2 + S_3, \]  

where

\[ V = V(q, Q), \]  

\[ T = \frac{1}{2M} p \cdot p, \]  

and

\[ S_i = \frac{1}{2I_i} L_i^2, \]  

for \( i = 1, 2, 3 \). The associated equations of motion and exact solutions with initial condition \( \tilde{x} = (\tilde{q}, \tilde{p}, \tilde{Q}, \tilde{L}) \) are listed below. Only those equations of motion corresponding to variables which are non-constant are shown:

1. Equations derived from \( V \):

\[ \begin{align*}
\dot{p} &= -\frac{\partial V}{\partial q} \\
\dot{L} &= \text{rot} \left( Q^T \frac{\partial V}{\partial Q} \right).
\end{align*} \]  

Solution of these equations:

\[ \exp_V(t)\tilde{x} = \left( \tilde{q}, \tilde{p} - t \left. \frac{\partial V}{\partial q} \right|_{\tilde{x}}, \tilde{Q}, \tilde{L} + t \text{rot} \left( \left. \frac{\partial V}{\partial Q} \right|_{\tilde{x}} \right) \right). \]  

2. Equations derived from \( T \):

\[ \dot{q} = \frac{p}{M}.\]  

Solution of these equations:

\[ \exp_T(t)\tilde{x} = \left( \tilde{q} + t \frac{\tilde{p}}{M}, \tilde{p}, \tilde{Q}, \tilde{L} \right). \]  

3. Equations derived from \( S_i, \ i = 1, 2, 3 \):

\[ \begin{align*}
\dot{L} &= \frac{L_i}{I_i} L \times e_i \\
\dot{Q} &= \frac{L_i}{I_i} Q \text{sk}(e_i)
\end{align*} \]  

(4.20e)
where $e_i$ are the elementary vectors.$^5$ Solution of these equations:

$$\exp_{S_i}(t)\tilde{x} = \left(\tilde{q}, \tilde{p}, \tilde{Q}_i(\omega_i t)^T, R_i(\omega_i t)^T \tilde{L}\right),$$  

(4.20f)

where $\omega_i = \frac{\tilde{L}_i}{I_i}$ and $bfR_i(\theta)$ is the matrix whose action on $\mathbb{R}^3$ is counterclockwise rotation about $e_i$ by angle $\theta$.$^6$ Note that $R_i(\omega_i t) \in SO(3)$ for all times, $t$. Thus $\tilde{Q}(t) \in SO(3)$ provided that $\tilde{Q} \in SO(3)$.

A split Hamiltonian scheme for the integration of rigid body motion is found by composing the solutions found above:

$$(q^{i+1}, p^{i+1}, Q^{i+1}, L^{i+1})$$

$$= \exp_V(\frac{1}{2}\Delta t) \exp_T(\frac{1}{2}\Delta t) \exp_{S_1}(\frac{1}{2}\Delta t) \exp_{S_2}(\frac{1}{2}\Delta t) \exp_{S_3}(\Delta t)$$

$$\exp_{S_2}(\frac{1}{2}\Delta t) \exp_{S_1}(\frac{1}{2}\Delta t) \exp_T(\frac{1}{2}\Delta t) \exp_V(\frac{1}{2}\Delta t)(q^i, p^i, Q^i, L^i).$$  

(4.21)

### 4.1.2 A Split Hamiltonian Scheme for Rigid Rotor Motion

There does not seem to have been a split Hamiltonian scheme for rigid rotor motion presented in the literature. Singer, Taylor, and Singer [29] use an explicit algorithm, which they derive geometrically, for molecular dynamics of diatomic fluids. Kol, Laird, and Leimkuhler [19] present a scheme, RSHAKE, a version of which can be used for linear molecules. The scheme which we present herein is a simple generalization of the Verlet algorithm and, as such, is simpler to implement than those in [29] or [19].

The Hamiltonian for rigid rotor motion, and the associated Poisson brackets, were presented in (2.63) and (2.64). As in the Verlet algorithm, we split the Hamiltonian into kinetic and potential parts:

$$H = V + T,$$  

(4.22a)

where

$$V = V(q, Q),$$  

(4.22b)

For example,

$$e_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}.$$

For example,

$$R_1(\theta) = \exp(\theta sk(e_1)) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\theta) & \sin(\theta) \\ 0 & -\sin(\theta) & \cos(\theta) \end{pmatrix}.$$
\[ T = \frac{1}{2M} p \cdot p + \frac{1}{2I} L \cdot L. \]  \hspace{1cm} (4.22c)

The resulting equations of motion and solutions with initial condition \( \tilde{x} = (\tilde{q}, \tilde{p}, \tilde{Q}, \tilde{L}) \) follow. As before, only those equations of motion corresponding to variables which are non-constant are shown:

1. Equations of motion derived from \( V \):
\[
\begin{align*}
\dot{\tilde{p}} &= -\frac{\partial V}{\partial \tilde{q}}, \\
\dot{\tilde{L}} &= -\tilde{Q} \times \frac{\partial V}{\partial \tilde{Q}}.
\end{align*}
\]  \hspace{1cm} (4.23a)

Solution of these equations:
\[
\exp_V(t)\tilde{x} = \left( \tilde{q}, \tilde{p} - t \frac{\partial V}{\partial \tilde{q}} \bigg|_{\tilde{x}}, \tilde{Q}, \tilde{L} - t \tilde{Q} \times \frac{\partial V}{\partial \tilde{Q}} \bigg|_{\tilde{x}} \right). \]  \hspace{1cm} (4.23b)

2. Equations derived from \( T \):
\[
\begin{align*}
\dot{\tilde{q}} &= \frac{\tilde{p}}{M}, \\
\dot{\tilde{Q}} &= \frac{\tilde{Q} \times L}{I}.
\end{align*}
\]  \hspace{1cm} (4.23c)

Solution of these equations:
\[
\exp_T(t)\tilde{x} = \left( \tilde{q} + \frac{t}{M} \tilde{p}, \tilde{p}, \cos(\omega t)\tilde{Q} + \frac{\sin(\omega t)}{\|L \times Q\|} \tilde{L} \times \tilde{Q}, \tilde{L} \right), \]  \hspace{1cm} (4.23d)

where \( \omega = \frac{\|L\|}{I} \).

A split Hamiltonian scheme for the integration of rigid rotor motion is found by composing the solutions found above:
\[
(q^{i+1}, p^{i+1}, Q^{i+1}, L^{i+1}) = \exp_V(\frac{1}{2}\Delta t) \exp_T(\Delta t) \exp_V(\frac{1}{2}\Delta t)(q^i, p^i, Q^i, L^i). \]  \hspace{1cm} (4.24)

### 4.1.3 Properties of Split Hamiltonian Integrators

The Poisson bracket can be seen, loosely, as inducing a certain geometric structure on the phase space. This perspective can be made somewhat precise by defining the gradient of a function to be \( \nabla F := \{x, F\} \). We do not intend to make this geometric approach any more precise; we simply wish to note that the motion induced by a Hamiltonian \( H \) follows the flow lines of \( \nabla H \). Split Hamiltonian integrators respect this geometric structure, since locally the motion they induce follows flow lines of pieces of \( H \). This naturality with respect to the geometry of phase space gives split Hamiltonian integrators several nice properties:
1. Split Hamiltonian methods are **symplectic** (see [19] and [11] for a definition of symplectic and further discussion). This allows us to conclude that the scheme conserves an energy function $\tilde{H}$ which is "close" to $H$ [11]. Thus, in certain cases, we can expect the scheme to approximately conserve the energy of the system over long periods of time.

2. When other integrals of the motion are present, such as the total momentum and the total angular momentum, they are often conserved *exactly*.

In short, split Hamiltonian integrators are, in a certain sense, the natural schemes with which to approximate mechanical systems. To quote from Dullweber, Leimkuhler and McLachlan:

> Compared to standard methods, the symplectic approach is more stable, enabling the use of larger time steps. Compared to the semi-explicit SHAKE-based scheme, the splitting method is more efficient (since it is explicit). For multiple rigid bodies not coupled by constraints, the splitting method thus appears to offer a substantial improvement over existing schemes. [11]

### 4.2 DASSL

DASSL is a freely available Fortran routine for the integration of certain systems of first order algebraic-differential equations. It is well documented in a book by Brenan, Campbell, and Petzold [8, Chapter 5]. In this section, we consider DASSL as a possible method for the consideration of constrained dynamics.

DASSL estimates the solution, $y$, of certain algebraic-differential equations of the form

$$F(t, y, y') = 0, \quad (4.25)$$

to within user-specified error tolerances. The user must supply a routine for the calculation of $F$, and $\frac{\partial F}{\partial y} + c \frac{\partial F}{\partial y'}$ for arbitrary $c$. DASSL will not solve all systems of the form shown in (4.25). Specifically, Brenan, *et. al.* define the **index** of (4.25). For DASSL to find an approximate solution to (4.25), the index must be 0 or 1 [8, Chapter 5].

Upon first considering the problem of molecular dynamics, we intended to use the mechanics of section 2.3 to produce a system of algebraic-differential equations which could be integrated with DASSL. However, we were unable to obtain adequate

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7Dullweber, Leimkuhler and McLachlan provide two references here: [19] and [6].
8Available from netlib and [http://www.cs.umn.edu/~petzold](http://www.cs.umn.edu/~petzold)
9The index is the minimum number of times which (4.25) must be differentiated with respect to $t$ to uniquely determine $y'$ as a continuous function of $y$ and $t$ [8, Chapter 2].
results for either diatomic or triatomic molecules. We include discussion of DASSL largely for completeness and comparison.

There is, in fact, already a literature describing the pitfalls of using DASSL for molecular dynamics [8, Section 6.2], [13]. The difficulties stem, essentially, from the fact that the constraints, when implemented as in section 2.3, cause the system to be index 3. To produce an index 1 system, we must replace each constraint with its second time derivative [8, Section 6.2]. That is, if the constraints are stated as in section 2.3:

\[
\frac{1}{2} (\|r_1 - r_2\|^2 - d^2) = 0, \quad (4.26)
\]

then we must differentiate this equation once:

\[
(r_1 - r_2) \cdot (\dot{r}_1 - \dot{r}_2) = 0, \quad (4.27)
\]

and then a second time:

\[
\|\dot{r}_1 - \dot{r}_2\|^2 + (r_1 - r_2) \cdot (\ddot{r}_1 - \ddot{r}_2) = 0. \quad (4.28)
\]

In practice, we substitute into (4.28) the values of \(\ddot{r}_1\) and \(\ddot{r}_2\) obtained from (2.16). Equation (4.28) is then used in place of (2.3). Since we provide initial conditions which satisfy (4.26) and (4.27), (4.26) is satisfied, in principle, along the entire trajectory.

However, DASSL uses an iterative scheme to attempt to force the numerical solution to satisfy (4.28). Since this procedure is non-exact, small errors are introduced. All of this would be fine, if we were able to approximately satisfy (4.26) at each step. However, small errors in the left hand side of (4.28) produce errors in the left hand side of (4.26) which grow with time. In fact, the constrained distances are observed to actually change in magnitude.\(^{10}\) Systems consisting of a small number of molecules may be integrated with DASSL by setting very tight error bounds. However, for systems with larger numbers of molecules, this is impossible as such tight error bounds force the time required for calculations to become prohibitively large.

Schemes which stabilize the constraints have been proposed by Führer and Leimkuhler [13] and by Baumgarte [7]. However these schemes involve the addition of at least one extra Lagrange multiplier per constraint. Thus, extraneous variables are introduced, complicating the expression of the equations and increasing computation time.

The split Hamiltonian schemes presented in §4.1 are superior to DASSL with regard to the type of constraints present in molecular dynamics. The split Hamiltonian

\(^{10}\)Although we did not do an extensive study of the rate of change of the constrained distances, we performed a number of simulations with 216 diatomic and triatomic molecules. We observed that, with error bounds that allowed for reasonable computation time, the constrained distances changed in magnitude quickly enough that after approximately 50 to 200 time steps the constraints failed to be satisfied within those same error bounds.
schemes are explicit schemes which require no iteration at each time step. Nonetheless, because the constraints are explicitly satisfied at each step, there is very little drift in the constrained quantities. For example, in the scheme presented in §4.1.1, the orientation matrix $Q$ is altered at each step by post-multiplication with an orthogonal matrix. Thus, the orthogonality of $Q$ is explicitly conserved. Similarly, the orientation vector of rigid rotor motion is explicitly conserved by the scheme presented in §4.1.2. We show, in section 6.2, that DASSL and the Verlet algorithm give comparable results for atomic dynamics.
Chapter 5

Intermolecular Interactions

The mechanical and numerical methods discussed previously allow us to approximate
the motion of an N-molecule system, once the potential energy function of the system
is specified. Choosing a potential function is a non-trivial problem. We wish to model
the system as accurately as possible, hence we would like to use a great many terms
in the potential energy. However, when an explicit numerical scheme (such as the
split-Hamiltonian techniques) is used, nearly all of the computation time is spent
evaluating the forcing terms. Thus, we would like to use the simplest potential
energy function available. Clearly, a compromise must be found.

Owing to the great importance of inter-molecular interactions in understanding
of material properties, a substantial literature exists on the subject. We recommend,
in particular, a survey by Tajo Kihara of the University of Tokyo [18].

All of the forces observable at the molecular scale stem from electro-magnetic
interactions. Molecules are, in general, found to be moving at speeds well below
the speed of light. Hence, the effects of magnetism are negligible when considering
molecular interactions.\(^1\) Thus the most important forces in molecular dynamics stem
from the Coulomb potential:
\[ U = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{r}, \]  
(5.1)

where \( U \) represents the energy of interaction between point charges \( q_1 \) and \( q_2 \) separate\(\)d by a distance \( r \).\(^2\) However, the point charges of concern for the production of
molecular potentials are electrons and nuclei. Since we do not possess the time, will,
nor resources to consider so many degrees of freedom,\(^3\) we must use (5.1) to derive

---

\(^1\)This statement is true only as long as we consider molecules with zero spin.

\(^2\)The constant of proportionality \( \frac{1}{4\pi\varepsilon_0} \) is approximately \( 8.9874 \times 10^9 \text{ Joules meters/Coulomb} \)\(^2\) [27, Page 29].

\(^3\)For example, a water molecule is made up of three nuclei and eighteen electrons. Thus, even if
we constrain the nuclei to a particular geometry, \( 6 + 3 \times 18 = 60 \) degrees of freedom are needed. In
addition, the dynamics of the electrons must be considered via quantum mechanics if any agreement
between experiment and calculation is to be expected.
expressions that model inter-molecular interactions without introducing any further degrees of freedom.

5.1 Multi-pole Moments of Molecules

We do not wish, herein, to introduce the unwieldy machinery and notation\(^4\) necessary for a thorough discussion of the multi-pole expansion of an electric field, preferring to leave this well documented subject to the textbooks on electricity and magnetism [24, Section 9], [16, Section 25.2]. Let us note, however, that if a, continuous or discrete, charge distribution, \(\rho\), is specified in some region, \(V\), the potential energy of its interaction with a point charge \(q\) at position \(r\) (see figure 5.1) is, \(q\phi(r)\), where \(\phi\) is the electric potential produced by the charge distribution, which, by Coulomb’s law and the linearity of the electric field, is:

\[
\phi(r) = \frac{1}{4\pi\epsilon_0} \int_V \frac{\rho(\tilde{r})}{\|r - \tilde{r}\|} d^3\tilde{r}.
\]  

(5.2)

The multi-pole expansion is obtained by expanding the expression \(\frac{1}{\|r - \tilde{r}\|}\) in (5.2) as a series in \(\frac{1}{\|r\|}\) using the binomial theorem. Thus, the first few terms of the expansion are:

\[
\phi(r) = \frac{1}{4\pi\epsilon_0} \left( \frac{Q}{\|r\|} + \frac{p \cdot \hat{r}}{\|r\|^2} + \frac{\hat{r} \cdot \Theta \cdot \hat{r}}{\|r\|^3} + O\left(\frac{1}{\|r\|^4}\right) \right),
\]  

(5.3a)

\(^4\)n-rank tensors and the associated notation
where \( \hat{r} \) is a unit vector in the direction of \( r \), \( Q \) is the \textbf{total charge} of the distribution:

\[
Q = \int_V \rho(\hat{r}) d^3\hat{r},
\]

(5.3b)

\( p \) is the \textbf{dipole moment vector}:

\[
p = \int_V \rho(\hat{r}) \hat{r} d^3\hat{r},
\]

(5.3c)

and \( \Theta \) is the \textbf{quadrapole moment tensor}:

\[
\Theta = \frac{1}{2} \int_V \rho(\hat{r}) \left( 3(\hat{r} \cdot \hat{r}) \mathbf{1} - \hat{r}\hat{r}^T \right) d^3\hat{r}.
\]

(5.3d)

It is possible to obtain expressions for the interaction energy of two disjoint charge distributions in terms of their various multi-pole moments [24, Section 9]. For example two point dipoles,\(^5\) \( p_1 \) and \( p_2 \), separated by a vector \( r \), have an interaction energy:

\[
U(r, p_1, p_2) = \frac{1}{4 \pi \epsilon_0} \frac{1}{||r||^3} \left( p_1 \cdot p_2 - 3(p_1 \cdot r)(p_2 \cdot r) \right).
\]

(5.4)

It is tempting to model the charge distributions of molecules as point dipoles. Not all molecules have non-zero dipole moments, however. For example, \( CO_2 \) and \( O_2 \) each possess a non-zero quadrapole as the first moment of their charge distributions (see sections 6.3 and 6.5). Of course, equations analogous to (5.4), for the dipole-quadrapole and quadrapole-quadrapole contributions to the energy, exist, however they are rather unwieldy to express. In addition, the size of molecules is, in general, not small enough to warrant their consideration as point dipoles. For example, \( H_2O \) has a diameter of, roughly, 1 Å,\(^6\) while a typical simulation takes place in a box of side length 15 Å. Hence, we prefer to use experimental values of dipole and quadrapole moments to assign point charges to various positions in the molecule, using (5.1) to calculate the electrostatic contribution to the energy.

5.2 London Forces

A rare gas atom, such as \( He \) or \( Ar \), in its equilibrium state possesses a charge distribution which is neutrally charged and spherically symmetric. Hence each of its

\(^5\)A point dipole is an hypothetical charge distribution for which the only non-zero multi-pole moment is the dipole. In the language of Schwartz’s distribution theory, a point dipole at the origin can be represented by the charge distribution \( \rho(r) = p \cdot \nabla \delta(r) \), where \( p \) is the vector of the dipole and \( \delta \) is the Dirac distribution. As such, a point dipole is no more hypothetical than a point charge, for which \( \rho(r) = q \delta(r) \).

\(^6\)The length of the \( H - O \) bond is 0.96 Å[22, Section 20.7].
Figure 5.2: Lennard-Jones 6-12 Potential with $\sigma = 1$ and $\epsilon = 1$

<table>
<thead>
<tr>
<th>$\epsilon/k_B$ (K)</th>
<th>$\sigma$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2.575</td>
</tr>
<tr>
<td>Ne</td>
<td>8.95</td>
</tr>
<tr>
<td>Ar</td>
<td>29.75</td>
</tr>
</tbody>
</table>

The values are taken from [18, Table 6.1].

Table 5.1: Lennard-Jones Parameters for Rare Gas Atoms

multi-poles is identically zero.\(^7\) However, distant rare gas atoms are observed to exert on each other a slight attractive force,\(^8\) known as the London force[22, Section 22.10]. This force is understood to arise from a correlation in the motion of the electrons in the two gas atoms. Two oppositely oriented induced dipoles tend to form in the atoms, thus causing them to attract one another. Using quantum mechanical perturbation theory, London in 1930 was able to calculate the first term in the energy of interaction (known as the London or dispersion energy) [22, Section 22.10]:

$$U \approx -C \frac{1}{r^6},$$  \hspace{1cm} (5.5)

where $C$ is a proportionality constant, and $r$ is the separation between the two atoms. Kihara includes this calculation in his book [18, Chapter 4]. It is possible to calculate $C$ from quantum mechanics, however it is generally determined from experiment. In addition, the dispersion energy of three interacting atoms is not, in general, the sum of three pairwise interactions. Kihara’s book includes a brief discussion of this effect [18, Section 4.4].
5.3 The Lennard Jones Potential

At close distances, all molecules must repel each other. The London forces of section 5.2 are always attractive, while the nature of the electrostatic interactions of section 5.1 depends on the relative orientations of the molecules. Hence, an additional repelling force must exist between all molecules. This force is purely quantum mechanical in origin, stemming ultimately from the Pauli exclusion principal. However, it is absolutely crucial that such a force be present, for otherwise all matter would collapse to a point. This repulsive force is typically modelled by adding a term to (5.5). The most widely used such potential, the one which we adopt, is the Lennard-Jones 6-12 potential:

\[ U(r) = 4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right). \]  

(5.6)

Figure 5.2 shows a graph of the Lennard-Jones potential as a function of \( r \). Observe that the equilibrium value of \( r \), i.e. the value of \( r \) which minimizes \( U \), is \( 2^{\frac{1}{6}} \sigma \), and that \( U(2^{\frac{1}{6}} \sigma) = -\epsilon \). Also, note that the choice of 12 as the exponent for the repulsive part of the potential is essentially arbitrary–any large exponent would produce a similar potential. Table 5.1 lists some values of \( \epsilon \) and \( \sigma \) for rare gas atoms.

5.4 Point Charges and Lennard-Jones Centers

As mentioned in Section 5.1, it is computationally easier to assign point charges to various locations in the molecule. We would like to extend this notion to the Lennard-Jones potential. Thus, we will assume that in any molecule there are a certain number of “Lennard-Jones” centers. However, the Lennard-Jones potential requires parameters which depend on the pair of centers under consideration. To estimate the interaction between dissimilar atoms, we make use of the following approximation [18, Section 6.5]. Consider two Lennard Jones centers \( A \) and \( B \) with parameters \((\epsilon_A, \sigma_A)\) and \((\epsilon_B, \sigma_B)\) respectively. The potential energy of the interaction between \( A \) and \( B \) is taken to be:

\[ U_{AB}(r) = 4(\sqrt{\epsilon_A \epsilon_B}) \left( \left( \frac{1}{2}(\sigma_A + \sigma_B) \right)^{12} - \left( \frac{1}{2}(\sigma_A + \sigma_B) \right)^6 \right). \]  

(5.7)

We will consider models in which the interactions are exclusively due to point charges and Lennard-Jones centers assigned to various points in the molecules.

---

7 An homogeneous spherical shell of charge produces a field which, outside of the sphere, is identical to that of a point charge at the center of the sphere.

8 If this were not the case, \( He \) could not condense into a liquid. The very low temperatures needed to condense \( He \) are indicative of the weak nature of this force.
Chapter 6

Simulating Pure Gases

6.1 The Computer Simulation

We implemented a computer program for the approximation, via split Hamiltonian integration, of the trajectory of $n$ body systems consisting of atoms, rigid rotors, and rigid bodies. The code, written in the C++ programming language, was such that the potential energy model could be altered without necessitating the alteration of the rest of the program. In addition, we implemented C++ code to work with DASSL and integrate systems of atoms, diatomic molecules, and triatomic molecules. As mentioned previously, the integration of diatomic and triatomic molecules via DASSL suffers from drift in the constraints.

There are certain procedures and practical requirements of the computer simulations which we must describe prior to discussing actual results. Following is a comparison of DASSL with the Verlet Algorithm.

6.1.1 Boundary conditions and Force Cutoffs

We can simulate only a finite number of molecules. Further, the number which we are able to consider in practice is small in comparison to the number present in macroscopic volumes. Each of our simulations has involved no more than 300 molecules, while 1 liter of air at STP contains roughly $10^{22}$ molecules. Thus, in order to model systems with a fixed density, we must constrain the molecules in our simulation to remain in a bounded region. However, we do not wish to introduce terms to the potential energy that correspond to “walls,” since the regions we consider are not large enough.

The procedure which we adopt is to constrain the molecules to remain in a box $B = \{(x, y, z) : |x|, |y|, |z| < L_b\}$, where $L_b$ was a length prescribed at the beginning of the simulation. Since molecules naturally came to the boundary of the box during motion, we adopt rules, “boundary conditions,” which tell us what happens to these molecules. The most natural choices for boundary conditions are:
1. **Periodic boundary conditions**: When a molecule crosses a boundary of the box, it re-enters on opposite side of the box with its momentum unchanged. (see figure 6.1).

2. **Reflective boundary conditions**: Molecules reflect from the boundaries of the box. That is, when a molecule reaches a boundary, the component of its linear momentum perpendicular to the boundary changes sign (see figure 6.1).

Following an approach suggested by Dieter W. Heermann in [15], we adopt periodic boundary conditions with the following interpretation. We consider the system to be infinite in extent, but periodic. Thus, a particle with position $q_A$ represents an infinity of particles with positions $q_A + 2L_b \hat{n}$, where $\hat{n} \in \mathbb{Z}^3$. Since a second particle, at $q_B$, interacts with all of these images, the potential energy of the interaction will be a sum:

$$U_{AB} = \sum_{\hat{n}, \hat{m} \in \mathbb{Z}^3} U(\|q_A + 2L_b \hat{n} - q_B + 2L_b \hat{m}\|),$$

(6.1)

where $U(r)$ represents the energy of the particles separated by a distance $r$. We wish to avoid such summations, and so we introduce a cut-off radius $C > 0$ and assume that $C < L_b$. The potential energy of interaction is assumed to be zero if the inter-particle distance is greater than $C$. Hence the sum in (6.1) is reduced to at most one term (see figure 6.2).
Particle $A$, whose images are shown in black, and particle $B$, whose images are shown in grey, interact. The large circles are drawn at the cutoff radius around each particle. Note that each particle feels the influence of only one image of the other.

Figure 6.2: Inter-Molecular Interactions and the Cutoff Radius

6.1.2 Equilibration

As mentioned in chapter 1, a system must be in thermodynamic equilibrium before we can define certain quantities. Since systems in nature are presumably found in states which approximate thermodynamic equilibrium, some attempt must be made to produce initial conditions which bring the system rapidly into equilibrium. Heermann suggests introducing an equilibration phase of the simulation [15]. During this phase, the system is integrated for a short period of time, after which the momenta are scaled so as to force the temperature to a desired value.$^{1}$ This process is repeated a number of times before the simulation is begun in earnest.

Our simulations made use of the following procedure:

1. The system, consisting of $n^3$ molecules (in most cases, $n = 6$), was placed in the initial configuration:

   (a) The molecules were placed with their centers of mass on a face centered cubic lattice.

   (b) The orientations were chosen randomly so as to be uniformly distributed among all possible orientations.

---

$^{1}$Observe that the temperature, via (3.35a), depends only on the kinetic energy per molecule. Hence it can be adjusted by scaling the molecular momenta.
(c) The momenta were chosen so as to approximate a Maxwell-Boltzmann
distribution corresponding to the desired temperature.

2. The system was subjected to the equilibration process:

(a) The system was integrated for 50 time steps, following which the linear
momentum and angular momentum were separately rescaled so that the
contribution of each to the temperature was as desired.

(b) This process of integration and rescaling was repeated 20 times.

3. The system was integrated without interference for the desired length of simula-
tion. The trajectory thus obtained was used to calculate quantities of interest.

It is important to note that the only use of the trajectory obtained during the equi-
libration process was that its final state became the initial state for the simulation.
See [15] for more details regarding equilibration.

6.1.3 Dimensionless Units

It is convenient to parameterize the system with quantities measured in dimensionless
units. Thus, we introduce into each model fundamental units of energy, length and
mass, denoted $E$, $l$, and $M$ respectively. We denote a dimensionless quantity with a
superscript $\ast$. Un-superscripted symbols indicate quantities measured in mks units
unless specific units are give. See table 6.1.

6.1.4 The Calculation of Averages

To use the results of chapter 3, we must, from an approximate trajectory, estimate the
average values of certain quantities. Suppose that we are interested in some quantity,
$\psi$, which is a function of the coordinates and momenta of the various molecules. To
find the average, we use the following procedure:

1. The calculated trajectory is used to estimate the value of $\psi$ at each time step.
   As in chapter 4, we let $\psi^i$ denote the calculated value of $\psi$ at the $i^{th}$ time step.

2. The average value of $\psi$ is estimated by assuming that $\psi$ is piecewise linear, i.e.
   $\psi$ proceeds linearly from $\psi^i$ to $\psi^{i+1}$. Thus, if $n$ steps of size $\Delta t$ are taken:

   $\langle \psi \rangle \approx \frac{1}{n\Delta t} \int_{t^0}^{t^0+n\Delta t} \psi(t') dt' \approx \frac{1}{n\Delta t} \left( \frac{1}{2} \psi^0 + \sum_{i=1}^{i=n-1} \psi^i + \frac{1}{2} \psi^n \right). \quad (6.2)$

   In practice, we consider a sequence of approximations:

   $\langle \psi \rangle^i = \frac{1}{i\Delta t} \left( \frac{1}{2} \psi^0 + \sum_{j=1}^{j=i-1} \psi^j + \frac{1}{2} \psi^i \right). \quad (6.3)$
We will have occasion to use several other units of measure for certain quantities:

- Mass: 1 amu = 1.6605 × 10^{-27} kg.
- Pressure: 1 atmosphere = 101325 Pa, 1 bar = 100000 Pa.

Note that the scaling of charge is chosen so that, in dimensionless units, Coulomb's law is:

\[ U^*(r^*) = \delta_1^* \delta_2^* \frac{1}{r^*} \]

Table 6.1: Dimensionless Expressions for Quantities Used in Simulations

We plot the sequence \(< \psi >^i\) versus \(i\) for \(i = 1, ... n\). If, graphically, the sequence appears to approach a limit, then \(< \psi >^n\) is accepted as an approximation for \(< \psi >\). The error in this approximation can be estimated from the oscillation of \(< \psi >^i\) for values of \(i\) near to \(n\).

### 6.2 Comparison of DASSL with the Verlet Algorithm

We consider a system of 216 atoms, each of mass 1, interacting via pairwise Lennard-Jones potentials. The scaling factors are taken to be:

\[ E = 48 \epsilon \]
\[ M = 1 \]
\[ \ell = \sigma \]

where \(\epsilon\) and \(\sigma\) are the parameters of the potential.

Four simulations of this system were performed to test the differences between DASSL and the split Hamiltonian scheme. In each simulation, the cutoff length was...
Temperatures \((T^*)\) and pressures \((P^*)\) were calculated from (3.35a) and (3.35c) via average values computed from the trajectory. The errors were estimated as discussed in section 6.1.4 and do not include errors due to the approximation of the trajectory. Time denotes the time required to perform equilibration and simulation.

<table>
<thead>
<tr>
<th>Date</th>
<th>Method</th>
<th>(\rho^*)</th>
<th>(T^*)</th>
<th>error</th>
<th>(P^*)</th>
<th>error</th>
<th>Time (H:M:S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/26/97</td>
<td>Verlet</td>
<td>0.636</td>
<td>0.0513</td>
<td>0.0002</td>
<td>0.0324</td>
<td>0.0006</td>
<td>24:41</td>
</tr>
<tr>
<td>4/30/97</td>
<td>DASSL</td>
<td>0.636</td>
<td>0.0529</td>
<td>0.0002</td>
<td>0.0348</td>
<td>0.0006</td>
<td>1:31:34</td>
</tr>
<tr>
<td>6/26/97</td>
<td>Verlet</td>
<td>0.831</td>
<td>0.01495</td>
<td>0.00006</td>
<td>0.0123</td>
<td>0.0002</td>
<td>24:51</td>
</tr>
<tr>
<td>5/05/97</td>
<td>DASSL</td>
<td>0.831</td>
<td>0.01574</td>
<td>0.00002</td>
<td>0.0129</td>
<td>0.0007</td>
<td>1:41:47</td>
</tr>
</tbody>
</table>

Table 6.2: Comparison of the Verlet Algorithm and DASSL

\(C = 2.5\), and 2000 time steps of size \(\Delta t^* = 0.32\) were taken. Two sets of parameters were considered:

1. \(T^* = 0.05271, L_b^* = 3.488745\), and \(\rho^* = 0.636\).

2. \(T^* = 0.0150417, L_b^* = 3.1905216\), and \(\rho^* = 0.831\).

In the above, \(\rho^* = \frac{216}{8(L_b^*)^3}\) and \(T^*\) is the temperature used during equilibration; the actual temperatures computed from the simulated trajectory via (3.35a) differed from these values slightly. Table 6.2 shows the results of these simulation.

Observe that DASSL and the Verlet algorithm provide comparable results and that the Verlet algorithm requires substantially less time.

### 6.3 Carbon Dioxide

Carbon Dioxide, being a linear molecule, has a quadrapole moment which can be characterized by a single quantity. If the \(z\) axis is taken as the molecular axis, this quantity is [18, Section 3.3]:

\[
\Theta_{zz} = \frac{1}{2} \int (2z^2 - x^2 - y^2)\rho d\tau,
\]

where \(\rho\) represents the charge distribution and the integral is taken over the extent of the molecule.\(^2\) Kihara provides an experimental value for this quantity [18, Table

\[^2\]The matrix of the quadrapole moment tensor in this coordinate system is:

\[
\Theta = \Theta_{zz} \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}.
\]
3.5][3]

$$\Theta_{zz} = -4.2 \times 10^{-26} \text{ statcoulomb cm}^2 = -0.874416 \text{ eÅ}^2,$$

(6.6)

where $e = 1.6022 \times 10^{-19}$ coulomb is the absolute value of the electron charge. According to Kihara, the length of the $C-O$ bond is $1.15 \text{ Å}$ [18, Table 2.1].

We propose a model for $CO_2$ in which point charges are assigned to each of the atoms. The given value of $\Theta_{zz}$, combined with the fact that the total charge is zero, allows us to calculate the charges on each atom:

$$\delta_O = -0.331e,$$

$$\delta_C = 0.661e.$$

(6.7)

This information is summarized in figure 6.3. In addition, we place, at each of the Oxygen atoms, a Lennard Jones center with parameters:

$$\begin{align*}
\epsilon &= 192.5k_B\text{Kelvin} \\
\sigma &= 2.90\text{Å}
\end{align*}$$

(6.8)

These parameters are due to Singer, et. al. [29]. The value of $\sigma$ is dictated, to a large extent, by the fact that it represents the size of the oxygen charge distribution.

---

3 A statcoulomb is the cgs electrostatic unit of electric charge.

1 coulomb = 10$^8$ statcoulomb,

where $c = 2.9979 \times 10^8$ m/s is the speed of light.
Temperatures \((T^*)\) and pressures \((P^*)\) were calculated from (3.35a) and (3.35c) via average values computed from the trajectory. The errors were estimated as discussed in section 6.1.4 and do not include errors due to the approximation of the trajectory. For an explanation of the experimental temperatures and \(\alpha\), see the text.

Table 6.3: Simulations of Gaseous \(CO_2\)

Roughly, \(\sigma\) must lie between 1 Å and 5 Å. Thus we consider \(\sigma\) to be a fixed quantity. However, \(\epsilon\) represents the energy of interaction of two Lennard Jones centers. We considered the possibility that \(\epsilon\) must be scaled in order to obtain agreement with the available experimental data.

Assuming the mass of each atom to be concentrated at its center of mass, we calculate the moment of inertia of \(CO_2\):

\[
I = 16 \text{amu}(-1.15 \text{Å})^2 + 16 \text{amu}(1.15 \text{Å})^2 = 42.32 \text{amu \ Å}^2. \tag{6.9}
\]

In Table 6.3 we have listed the results of simulations of \(CO_2\) with the above model. These calculations were performed in dimensionless units with the following fundamental units:

\[
E = 48\epsilon = 9240k_B \text{ Kelvin,}
\]

\[
M = 44 \text{ amu,} \tag{6.10}
\]

\[
l = \sigma = 2.90 \text{ Å.}
\]

In each simulation, 216 molecules were integrated for 2000 steps of size \(\Delta t^* = 0.0064\) with \(C^* = 5.0\).

Recall that we wish to vary \(\epsilon\) so as to obtain the best possible agreement with experiment. To do so, we make the following observations:

1. Rescaling \(\epsilon\) is equivalent to rescaling \(E = 48\epsilon\).

2. Neither \(\rho\) nor the calculated value of \(T/P\) depends on \(E\).
Since experimentally determined values of ρ as a function of T and P are available [32], we can exploit these observations to determine ϵ. It was observed that as ρ is held constant the experimental value of T/P is a monotonically decreasing function of P. Therefore, given calculated values of ρ and T/P for a particular simulation, we were able to determine a unique experimental pressure and temperature.\(^4\) We let \(T_{\text{exp}}\) denote this experimental temperature, and calculated the ratio

\[
\alpha = \frac{T_{\text{exp}}}{T_{\text{calc}}}.
\]

(6.11)

If we wish to force \(T_{\text{calc}}\) to agree with \(T_{\text{exp}}\), we must replace ϵ with \(\alpha \epsilon\). Values of \(T_{\text{exp}}\) and \(\alpha\) are shown in table 6.3.

It is apparent from table 6.3 that there is not a single value of \(\alpha\) which works to scale the model at all temperatures and pressures. This indicates that it is necessary to scale other the other parameters in the model as well. We discuss this need in more detail in §8.1.

For our purposes, we chose not to consider the three simulations with \(\alpha > 1\) and to accept an average value \(\alpha = 0.58\). Note that, in addition to altering \(\epsilon\), we must alter the atomic charges as well. The new values of these three quantities are:

\[
\epsilon = 111.7 k_B \text{ Kelvin},
\]

\[
\delta_O = -0.252 e,
\]

\[
\delta_C = 0.504 e.
\]

(6.12)

We will refer to this model for CO\(_2\) as the 3c2lj CO\(_2\) model.

### 6.4 Water

We began with a well accepted model for water, known as the TIP4P model[17]. The geometry of this model, which makes use of four sites in the water molecule, is illustrated in Figure 6.4. The moment of inertia tensor is diagonal in this coordinate system, and the three moments of inertia are:

\[
\begin{align*}
I_1 &= 1.7555 \text{ amu} \, \text{Å}^2 \\
I_2 &= 0.6103 \text{ amu} \, \text{Å}^2 \\
I_3 &= 1.1452 \text{ amu} \, \text{Å}^2
\end{align*}
\]

(6.13)

The model assigns charges to the hydrogen atoms and to the point \(M\):

\[
\begin{align*}
\delta_H &= 0.52 e, \\
\delta_M &= -1.04 e.
\end{align*}
\]

(6.14)

\(^4\)We used linear interpolation to calculate experimental values of T/P between available data points.
The origin of the figure is the center of mass. The four points have the following coordinates (all distances are in Å):

- Left H: \((0, -0.7567, 0.5208)\)
- Right H: \((0, 0.7567, 0.5208)\)
- M: \((0, 0, 0.085)\)
- O: \((0, 0, -0.0651)\)

The angle \(\theta = 104.52^\circ\).

Figure 6.4: The Geometry of TIP4P Water

The oxygen atom is a Lennard-Jones center with parameters:

\[
\begin{align*}
\epsilon &= 78.02 k_B \text{ Kelvin} \\
\sigma &= 3.154 \text{ Å}
\end{align*}
\]

In Table 6.4 we have listed the results of our simulations of water. These calculations were performed in dimensionless units with the following fundamental units:

\[
\begin{align*}
E &= 48\epsilon = 3745 k_B \text{ Kelvin,} \\
M &= 18 \text{ amu,} \\
l &= \sigma = 3.15 \text{ Å}
\end{align*}
\]

In each simulation, 216 molecules were integrated for 2000 steps of size \(\Delta t^* = 0.0064\) with \(C^* = 3.0\).

The experimental temperatures and values of \(\alpha\) were determined as in §6.3. Experimental values were taken from the ASME Steam Tables [1]. The average value
\[ L_b^* \quad \rho^* \quad T^* \quad \text{error} \quad P^* \quad \text{error} \quad \frac{T}{P} \quad T_{\text{calc}} \quad T_{\text{exp}} \quad \alpha = \frac{T_{\text{exp}}}{T_{\text{calc}}} \]

\begin{array}{ccccccccc}
3.5 & 0.630 & 0.3147 & 0.0015 & 0.192 & 0.011 & 0.37 & 1179 & 930 & 0.79 \\
4.0 & 0.422 & 0.3160 & 0.0008 & 0.133 & 0.007 & 0.54 & 1183 & 1159 & 0.98 \\
4.5 & 0.296 & 0.3111 & 0.0008 & 0.090 & 0.007 & 0.79 & 1165 & 1238 & 1.05 \\
5.0 & 0.216 & 0.3179 & 0.0005 & 0.070 & 0.003 & 1.03 & 1190 & 1441 & 1.22 \\
\end{array}

Temperatures \((T^*)\) and pressures \((P^*)\) were calculated from (3.35a) and (3.35c) via average values computed from the trajectory. The errors were estimated as discussed in section 6.1.4 and do not include errors due to the approximation of the trajectory. For an explanation of the experimental temperatures and \(\alpha\), see the text.

Table 6.4: Simulations of Gaseous Water

of \(\alpha\) was 1.1, so we decided not to alter the parameters of the well accepted TIP4P model.

6.5 Oxygen

According to Kihara, in molecular oxygen \((O_2)\) the \(O-O\) bond length is 1.10 Å and \(\Theta_{zz} = -0.4 \times 10^{-26}\) statcoulomb cm\(^2\) = \(-0.08328\) e Å\(^2\). We propose a model for \(O_2\) in which charges are assigned to the Oxygen atoms and to a point \(M\) located at the center of mass of the molecule:

\[
\delta_O = -0.13765e, \\
\delta_M = 0.2753e.
\] (6.17)

The geometry and charges are shown in Figure 6.5. We place, at each of the Oxygen atoms, a Lennard Jones center with parameters identical to those originally proposed for \(CO_2\):

\[
\epsilon = 192.5k_B\text{Kelvin}, \\
\sigma = 2.90\text{Å}.
\] (6.18)

The moment of inertia of \(O_2\) is:

\[ I = 9.68\text{ amu Å}^2. \] (6.19)

In Table 6.5 we have listed the results of our simulations of \(O_2\). These calculations were performed in dimensionless units with the following fundamental units:

\[
E = 48e = 9240k_B\text{ Kelvin}, \\
M = 36\text{ amu}, \\
l = \sigma = 2.90\text{Å}.
\] (6.20)

60
Figure 6.5: The Geometry and Atomic Charges of $O_2$

<table>
<thead>
<tr>
<th>$L_b^*$</th>
<th>$ρ^* \times 10^4$</th>
<th>$T^* \times 10^2$</th>
<th>error$\times 10^6$</th>
<th>$P^* \times 10^5$</th>
<th>error$\times 10^9$</th>
<th>$T(°C)$</th>
<th>$P(\text{atm})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.4</td>
<td>6.09</td>
<td>3.1730</td>
<td>84</td>
<td>1.93</td>
<td>60</td>
<td>20.04</td>
<td>0.996</td>
</tr>
<tr>
<td>35.8</td>
<td>5.88</td>
<td>3.2809</td>
<td>13</td>
<td>1.93</td>
<td>9</td>
<td>30.01</td>
<td>0.996</td>
</tr>
<tr>
<td>36.2</td>
<td>5.69</td>
<td>3.3893</td>
<td>2</td>
<td>1.93</td>
<td>5</td>
<td>40.02</td>
<td>0.996</td>
</tr>
</tbody>
</table>

Temperatures ($T^*$) and pressures ($P^*$) were calculated from (3.35a) and (3.35c) via average values computed from the trajectory. The errors were estimated as discussed in section 6.1.4 and do not include errors due to the approximation of the trajectory.

Table 6.5: Simulation of Gaseous $O_2$

In each simulation, 216 molecules were integrated for 2000 steps of size $\Delta t^* = 0.0064$ with $C^* = 20$.

We used the experimental densities of $O_2$ under one atmosphere of pressure at 20°C, 30°C, and 40°C [30] to determine $L_B$ for 216 molecules. As can be seen from table 6.5, the pressure and temperatures were reproduced almost exactly. Hence, we did not scale $\epsilon$.

### 6.6 Step Sizes, the Number of Molecules, and the Length of Simulations

We have been rather glib in discussing certain aspects of the simulations. In particular, we have not indicated how we chose several parameters: the number of molecules, $N$, the step size, $\Delta t$, and the total number of steps taken, $M$. In making
Temperatures ($T^*$) and pressures ($P^*$) were calculated from (3.35a) and (3.35c) via average values computed from the trajectory. The errors were estimated as discussed in section 6.1.4 and do not include errors due to the approximation of the trajectory. Time indicates the total length of time, in hours:minutes:seconds, required for the equilibration and simulation to complete.

Table 6.6: Dependence of Results on Step Size and Number of Molecules

<table>
<thead>
<tr>
<th></th>
<th>$N$</th>
<th>$L_B$</th>
<th>$\Delta t^*$</th>
<th>$M$</th>
<th>$T^*$</th>
<th>error</th>
<th>$P^*$</th>
<th>error</th>
<th>time</th>
</tr>
</thead>
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<td>§6.3</td>
<td>216</td>
<td>6.0</td>
<td>0.0064</td>
<td>2000</td>
<td>0.0474</td>
<td>0.00015</td>
<td>0.0060</td>
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</tr>
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<td>8.0</td>
<td>0.0064</td>
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<td>0.0485</td>
<td>0.00078</td>
<td>0.0063</td>
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</tr>
<tr>
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<td>216</td>
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<td>0.00064</td>
<td>20000</td>
<td>0.0477</td>
<td>0.00046</td>
<td>0.0061</td>
<td>0.0004</td>
<td>23:28:03</td>
</tr>
</tbody>
</table>

these choices, we were motivated by two conflicting concerns: a desire, on the one hand, to produce accurate simulations, and a need, on the other hand, to perform all of the simulations in the time available. The accuracy of any simulation is certainly increased by an increase in $N$ and $M$ coupled with a decrease of $\Delta t^*$. However, the time required for computation is an increasing function of $N$ and $M$.

To obtain average quantities, as discussed in chapter 3 and §6.1.4, it is necessary to integrate the system for long enough that the quantities of interest are observed to approach an average value. Hence, once $N$ and $\Delta t^*$ are specified, $M$ is, in effect, specified.

In practice, we chose values which allowed complete equilibration and simulation to complete within three to four hours. Because we started each simulation with a cubic lattice of initial conditions, we were restricted to perfect cubes for values of $N$. We found that 216 was the largest perfect cube which produced results in this time frame. For each of the models, we chose $\Delta t^*$ small enough that the energy was observed to be conserved over the length of the simulation.

It is our assertion that these choices do not affect the accuracy of our results. To provide support for this assertion, we computed the results for two additional simulations of $CO_2$. In the first, we increased $N$ and $L_B$ to maintain a constant density. In the second, we decreased $\Delta t^*$ and increased $M$ to maintain a constant length of simulation. The results of these simulations are shown in table 6.6 along with the results from the corresponding simulation of $CO_2$ from §6.3. Note that the results from all three simulations are comparable, while the results from §6.3 were obtained in the least time.
Chapter 7

Adsorption Studies

7.1 Developing a Surface Model

The geometry of a coal surface is quite complicated. As these simulations are of a preliminary nature, we propose a surface modeled on graphite. Graphite is composed of pure carbon, the major atomic constituent of coal.

We use a method, proposed by Crowell and Steele [10], in which the position of the carbon atoms in each graphite plain is averaged over the plain. Each carbon atom is considered as a Lennard-Jones site with parameters:

\[
\begin{align*}
\epsilon &= 15.9k_B \text{ Kelvin} \\
\sigma &= 3.39 \text{ Å}
\end{align*}
\]

(7.1)

The surface density of these sites is \( \rho = \frac{2.4}{2\pi} \text{ Å}^{-2} \), which is the approximate density of carbon atoms in graphite [28]. Suppose that a Lennard-Jones site with parameters \( \hat{\epsilon} \) and \( \hat{\sigma} \) is located a distance \( z \) from the surface. We express the energy of interaction with the surface as an average value of (5.7):

\[
U = \rho 2\pi \int_0^\infty 4(\hat{\epsilon})^{\frac{1}{2}} \left( \left( \frac{\sigma + \hat{\sigma}}{2} \right)^{\frac{12}{2}} - \left( \frac{\sigma + \hat{\sigma}}{2} \right)^{\frac{6}{2}} \right) R dR
\]

\[
= 4 \rho 2\pi (\hat{\epsilon})^{\frac{1}{2}} \left[ \frac{1}{10} \left( \frac{\sigma + \hat{\sigma}}{2} \right)^{\frac{12}{2}} - \frac{1}{4} \left( \frac{\sigma + \hat{\sigma}}{2} \right)^{\frac{6}{2}} \right]
\]

(7.2)

We refer to a surface whose energy of interaction is given by (7.2) as a uniform LJ-surface.
We define adsorption as follows. If a molecule’s energy of motion is such that, in the absence of all other molecules, it is in a bound orbit of the surface, then it is adsorbed. Let us consider the motion of a molecule with several Lennard-Jones centers under the influence of a surface in the $x$, $y$ plane. This molecule will have energy given by a sum of terms as in (7.2). The energy will not depend, however, on the $x$ and $y$ components of the position of the center of mass. Hence, the conjugate momenta, the $x$ and $y$ components of the linear momentum, are conserved. In general, however, the orientation of the molecule will affect the energy. The molecule is, therefore, in a bound orbit, if and only if:
\[
U + K - \frac{1}{2M} (p_x^2 + p_y^2) < 0,
\]
where $U$ is the energy of interaction with the surface, $K$ is the total kinetic energy of the molecule, $M$ is the mass of the molecule, and $p_x$ and $p_y$ are the $x$ and $y$ components of the molecule’s linear momentum.

### 7.2 Atmospheric Pressure $H_2O$

Table 7.1 shows the results of modelling water vapor at atmospheric temperatures and pressures. The trajectories in these simulations will be used in the following section.

### 7.3 Adsorption Studies

In studying adsorption, we consider a system of gas phase molecules in a box as in chapter 6. In addition, there is assumed to be a uniform LJ-surface located at the upper and lower edges of the box bounding the simulation. It was necessary to consider two surfaces because of the periodicity induced by the boundary conditions.

For each simulation and each type of molecule, we calculated the following two quantities at each time step:

1. The number of molecules of that type adsorbed.
2. The number of molecules within 4 Å of either surface. These molecules are said to have been located in the boundary layer.
Note that a molecule may be present in the boundary layer without being adsorbed, and a molecule may be adsorbed outside the boundary layer.

The following procedure was used:

1. Uniform LJ-surfaces were introduced at the upper and lower edges of a box of side length, $L_B$, containing the final configuration of a simulation of pure $CO_2$. This system was simulated to create an adsorbed layer on the uniform LJ-surface.

2. After the simulation in step 1 was completed, we recorded the position and momenta of the molecules of $CO_2$ in the boundary layer.

3. We now considered a box of side length $2L_B$. To obtain an adsorbed layer, we tiled the upper and lower edges with the boundary layer from step 2. Increasing the size of our bounding box allowed us to introduce a significant number of water and oxygen molecules into the box at atmospheric temperatures and pressures.

4. With the configuration of adsorbed $CO_2$ from step 3, we performed several simulations, monitoring, in each case, the number of molecules of each type adsorbed and present in the boundary layer:
   
   (a) $O_2$ at 20°, 30°, and 40°.
   
   (b) $H_2O$ at 20°, 30°, and 40°.
   
   (c) A mixture of $O_2$ and $H_2O$ at 20°, 30°, and 40°.

Tables 7.2, 7.3, and 7.4 show the peak values of adsorption and boundary layer occupation during these simulations. In certain of the simulations, a molecule fell too close to another molecule, forcing the system to a very high energy. The results of these simulations are not reported.
Table 7.2: Adsorption Studies at 20° Celsius

<table>
<thead>
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<th>$H_2O$ Total</th>
<th>Boundary Layer</th>
<th>Steps</th>
<th>$L_B$</th>
<th>$O_2$ Peak Adsorp.</th>
<th>$O_2$ Peak Bound.</th>
<th>$H_2O$ Peak Adsorp.</th>
<th>$H_2O$ Peak Bound.</th>
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Table 7.3: Adsorption Studies at 30° Celsius

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<th>$H_2O$ Peak Adsorp.</th>
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Table 7.4: Adsorption Studies at 40° Celsius
Chapter 8

Conclusions

We have developed a simple model of surface interactions and used this model to examine the phenomenon of competitive adsorption. In so doing, we have learned that it is possible to observe adsorption in molecular dynamics simulations. Hence we may answer affirmatively the question posed in the introduction:

Can computer simulations provide useful information regarding the efficacy of Dr. Agarwal’s scheme for coal transport?

Specifically, we note that, according to the adsorption data presented in chapter 7, the presence of $CO_2$ adsorbed on a uniform LJ-surface and in the boundary layer does not seem to have a consistent effect on the adsorption of either $O_2$ or $H_2O$ or the entry of these species into the boundary layer. Thus, we are forced to suggest, in the case of a uniform LJ-surface, that Dr. Agarwal’s scheme will not work. However, with regards to real coal surfaces, we do not take this conclusion seriously for a couple of reasons:

1. The models for $CO_2$, $O_2$ and $H_2O$ have not been tested thoroughly.

2. The surface model lacks complexity and realism.

3. The simulations do not include a sufficiently large number of molecules.

Because of the time available for the project, we have not been able to consider these issues as thoroughly as should be done. We suggest, therefore, that the information in this report be viewed as a starting point for further research into the competitive adsorption of atmospheric gases on coal. In this spirit, we close with certain observations regarding the solution of the above problems.
8.1 Developing Appropriate Models for the Constituent Gases

As mentioned in §6.3, we were unable to obtain a model for $CO_2$ which agrees with the experimental data at all temperatures and pressures. This difficulty arose because we scaled only a single parameter, the Lennard-Jones interaction strength, $\epsilon$. We suggest that it would be possible to improve on our model by more carefully trying to fit the experimental data.

The parameters which may be adjusted in the $3c2lj CO_2$ model are the Lennard Jones parameters, $\epsilon$ and $\sigma$. The charges were assigned so as to produce the correct quadrapole moment, and hence should not be altered. Since calculations are performed in dimensionless units, it is possible to choose values for $\epsilon$ and $\sigma$ after the calculations are finished. However, in so doing (see §6.3) we change the values of the atomic charges. We suggest the following procedure to overcome this difficulty:

1. Start with a guess for $\epsilon$ and $\sigma$, and calculate the corresponding dimensionless values of the atomic charges from the MKS values given in (6.7).
2. Simulate the pure gas at a wide range of dimensionless temperatures and pressures.
3. Use non-linear curve fitting techniques, and the available experimental data to choose new values of $\epsilon$ and $\sigma$.
4. Recalculate the dimensionless atomic charges, using the new Lennard-Jones parameters.
5. Repeat steps two, three, and four several times. After a number of iterations, the values of $\epsilon$ and $\sigma$ may not change significantly. In this case, the final values of $\epsilon$ and $\sigma$ can be accepted as those best fitting the experimental data. If no such, “self consistent,” values are obtained, the charge distribution may be assumed to be incorrect, and greater care must be taken in choosing sites at which to assign charges.

Clearly, the implementation and execution of such a scheme would be a substantial project. In addition to implementing an appropriate non-linear curve fitting scheme to obtain optimal values of $\epsilon$ and $\sigma$, it would be necessary to obtain a computerized data-base consisting of the available experimental data. To our knowledge, the only freely available versions of the experimental data are in text form, hence many hours would need to be spent manually converting this data to a computerized format. However, we suggest that no model of the gases discussed herein can be trusted until it has been optimized by the above or a similar procedure. Future
researchers will need to face the task of optimizing each of the models proposed in chapter 6.\(^1\)

### 8.2 Developing a More Realistic Surface Model

Clearly, a uniform LJ-surface is not an accurate model of coal. Any study which involves this type of surface alone isolates a particular type of adsorption. Adsorption phenomena that arise from inhomogeneity, periodicity, and impurities in the surface structure are clearly ignored. As these phenomena are certainly present in adsorption on coal surfaces, future research will need to focus attention on modeling such structures. We suggest that the uniform LJ-surface represents a type of “background” model to which other structures may be added. Assuming that Dr. Agarwal’s scheme is found to be effective at real coal surfaces, it will be interesting to ask whether this effect can be attributed to adsorption at a uniform LJ-surface or whether the pore structure and impurities in coal are the crucial factors. The adsorption data presented in chapter 7 suggest that Dr. Agarwal’s scheme is not effective for uniform LJ-surfaces.

We mention that adsorption at a uniform LJ-surface suffers from a peculiar, non-physical, pathology: adsorbed molecules may have arbitrary mobility parallel to the surface. Because there are no periodicities or heterogeneities to bind molecules to particular sites, they may be adsorbed and still be quite mobile (note the definition of adsorption in §7.1).

### 8.3 Pressure and the Size of The Simulations

Although, as we demonstrated in §6.6, simulations with 216 molecules are sufficient to consistently calculate thermodynamic quantities, there is a difficulty with simulations involving so few molecules with regards to adsorption. Because we wish to model a dense layer of \(CO_2\) adsorbed at the surface, we use high pressure simulations of gaseous \(CO_2\) to create the adsorbed layer. In the simulations presented in chapter 7, there were generally around 150 \(CO_2\) molecules included, while there were 30 or 40 \(O_2\) and/or \(H_2O\) molecules present. The number of \(O_2\) and \(H_2O\) molecules present are chosen to obtain the density of these gases at atmospheric pressure and the chosen temperatures. However, as the simulation progresses, certain \(CO_2\) molecules leave the boundary layer and enter into the regions of the simulation which correspond to the gaseous molecules. Physically, this increase of molecules in the gas phase must correspond to an increase of pressure. In the cases we have considered, because the number of \(CO_2\) molecules is so large, the pressure may have increased by two

---

\(^1\)The TIP4P model for \(H_2O\) is well accepted, however we did have some difficulty with it as well. We attempted a few simulations of liquid water at room temperature with little success.
or three times.\textsuperscript{2} Note that all $CO_2$ molecules start the simulation in the boundary layer. Hence, the number of $CO_2$ molecules needed is proportional to the square of the length, $L_B$. However, at constant density, the number of $O_2$ and $H_2O$ molecules needed is proportional to $L_B^3$. In order to obtain realistic results, we must increase the $L_B$ until the number of $CO_2$ molecules is negligible. Unfortunately, the size of $L_B$ will then be quite large, and the time required by each simulation substantial as well.

\section{The Future of this Research}

The difficulties discussed in the previous three sections are not the only obstacles to further computational research into the efficacy of Dr. Agarwal’s scheme. However, it is our opinion that they represent the biggest problems facing future researchers in this field. Certainly it is true that a computational test of the efficacy of Dr. Agarwal’s scheme requires the resolution of each of these difficulties. In turn, the resolution of any of these problems will require a long term, systematic program of research and computation. In particular, future research is dependent on the development and testing of realistic models for each of the three atmospheric gases considered. There is interesting and useful information to be obtained from this research, however the processes will be long, involved, and computationally expensive.

\footnote{We write, “may have,” because it is not feasible to calculate this increase. Note that the number of $CO_2$ molecules in the gas phase is changing, hence the system is not in equilibrium. We are arguing, in this paragraph, heuristically and on physical grounds.}
Bibliography


