Molecular dynamic simulations of gases using a split-Hamiltonian method

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Abstract

In this paper we present a review of the mathematical formulation of the split-Hamiltonian method and of the mechanics of rigid-body motion. We present the split-Hamiltonian scheme for rigid rotor motion. In addition we present a comparison of the split-Hamiltonian method with DASSL. Finally, we show the results of molecular dynamics simulations of CO 2 and H 2 O.

1. Introduction

Calculation of the thermodynamic properties of real gases and of multicomponent systems is a problem of fundamental interest in applied mathematics, physics, chemistry, and engineering. All thermodynamic quantities can, in principle, be calculated from the thermodynamic potential (Helmholtz free energy):

\[ F = -T \log \left( \Phi \int_{\Gamma} \exp \left( -\frac{E(p,q)}{T} \right) \, dp \, dq \right), \] (1)

where \( T \) is the temperature, \( \Phi \) is a statistical weight, \((p,q)\) represent momentum and position coordinates in configuration space, \( \Gamma \), and \( E \) is the energy of a given configuration. For example, the pressure, \( P = -\partial F/\partial V \), where \( V \) is the volume of the fluid [12, Chapter II].

There are essentially two approaches to the numerical calculations with (1):

1. Monte-Carlo (MC) methods, in which a given phase space configuration is perturbed a large number of times. The method of perturbation is chosen so that a given configuration appears with relative probability \( \exp(-E/T) \). The idea is that an average over the various perturbed states approximates the integral in (1).
2. 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, $\langle \Psi \rangle$, of an observable quantity, $\Psi$, can be calculated in two entirely separate ways:

$$
\langle \Psi \rangle = \frac{\int \Psi(q,p) \exp\left(-\frac{E(p,q)}{T}\right) dp \ dq}{\int \exp\left(-\frac{E(p,q)}{T}\right) dp \ dq},
$$

(2a)

$$
\langle \Psi \rangle = \lim_{t \to \infty} \frac{1}{t} \int_0^t \Psi(q(t'), p(t')) \ dt',
$$

(2b)

where $(q(t), p(t))$ is a trajectory of the system with initial conditions chosen representative of a fixed temperature, $T$. Although Eq. (1) is not used directly, it is required to link time averages to thermodynamic variables. In Appendix A, we present a derivation of various relationships between (1) and averages of observables. This allows us to express thermodynamic quantities as functions of quantities which can be computed via (2b).\(^2\)

We feel that molecular dynamic methods provide a more straightforward approach by which to understand certain systems than do MC methods. This is even more true with the advent of “symplectic integration methods” — methods which explicitly conserve the symplectic structure of phase space. Both MC and MD methods require the implementation of data 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 code to generate acceptable random perturbations, whereas MD methods require the 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, while, with symplectic methods, the code to compute a trajectory of the system is fairly closely related to the physics of the system.

The Verlet algorithm [2, 20] has been a popular algorithm for use in MD simulations of monatomic gases. Generalizations, such as SHAKE [18] and RATTLE [2], have been proposed in which algebraic constraints on the positions of various point particles are used to model systems of polyatomic molecules. Although SHAKE and RATTLE have been used in the majority of molecular dynamics investigations, we have opted to use a type of algorithm referred to as a split-Hamiltonian (SH) integrator. Such algorithms allow the direct approximation of rigid body and rigid rotor motion and have been introduced quite recently [6, 11, 16, 17]. SH algorithms explicitly satisfy the constraints found in molecular dynamics. For example, in the scheme presented in Section 3.1, an orthogonal matrix $Q$ is used to indicate the orientation of a molecule. Throughout the integration, this matrix is only altered by post-multiplication with another orthogonal matrix. Thus, the orthogonality of $Q$ is explicitly conserved.

The organization of this paper is as follows. In Sections 2 and 3, we present an exposition of the mathematics behind SH integration and the mechanics of rigid-body motion as most applicable in MD simulations. In Section 4, we discuss the methodology of our molecular dynamics simulations.

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2 Ergodicity is a physical relation, not a mathematical one. In [12, Chapter I] it is argued, on physical grounds, that the relationship expressed in (2) holds. However to prove that ergodicity is valid for all but the simplest of energy functions is a very difficult problem.
Finally in Section 5, we present the results of our simulations of CO\textsubscript{2} and H\textsubscript{2}O, and a brief comparison of our SH scheme with the Differential Algebraic System Solver (DASSL), a freely available Fortran routine for the integration of certain systems of first order algebraic–differential equations. \footnote{DASSL is available from netlib and http://www.cs.umn.edu/~petzold.}

2. The mechanical modeling of molecules

To a certain degree of approximation, a molecule may be conceived of as a collection of atoms, modeled as classical point particles, bound by forces which cause these atoms to remain close to an equilibrium configuration. 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, those intra-molecular 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 et al. have examined molecular dynamics at multiple time scales in great detail \cite{14}. They have shown that in order to maintain numerical precision, the time step for a computation must be chosen an order 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 and assume that each molecule maintains a fixed internal geometry. \footnote{Certain thermodynamic quantities, such as heat capacities, cannot be calculated if intra-molecular 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.}

There are essentially two ways to describe a molecule with fixed internal geometry:

1. We may consider a collection of point particles (atoms) which evolve in time according to constrained dynamics presented in Section 2.2.

2. We may consider a rigid body which evolves in time according to the equations of rigid body dynamics presented in Section 2.3.

Almost all prior molecular dynamics calculations of which we are aware have proceeded via approach (1) implemented with SHAKE or RATTLE as numerical integration routines. It is only with the advent of split-Hamiltonian schemes that numerical routines for the direct integration of the equations of motion of approach (2) have been available. An overview of the theoretical framework surrounding approaches (1) and (2) is presented in the following sections.

2.1. An overview of classical mechanics

We summarize some results from mechanics. The results and methods are standard, see, for example, Goldstein \cite[Chapters 1, 2, 8 and 9]{7}.

Consider a system of $N$ point particles. Let $m_i \geq 0$ and $r_i \in \mathbb{R}^3$ denote respectively the mass and position of the $i$th particle. Let $T$ denote the kinetic energy, $\sum_{i=1}^{N} \frac{1}{2} m_i \| \dot{r}_i \|^2$. We assume that the potential energy, $V$, is a scalar function of the $r_i$. Define the Lagrangian $L := T - V$, and for each integrable path, $\gamma : [t_0, t] \to \mathbb{R}^{3N}$, define the \textit{action}: $I(\gamma) := \int_{t_0}^{t} L(\dot{\gamma}(t), \gamma(t)) \, dt$. The Lagrangian formulation of
mechanics stems from Hamilton’s principle of least action: along the physical trajectory, \((r_1, \ldots, r_N)\), the action is a extremal. Using standard techniques from the calculus of variations, we find that

\[
0 = \frac{d}{dt} \frac{\partial L}{\partial r_i} - \frac{\partial L}{\partial r_i} = \frac{d}{dt} \frac{\partial T}{\partial \dot{r}_i} + \frac{\partial V}{\partial r_i}, \quad i = 1, \ldots, N.
\]

Upon evaluating the partial derivatives, we see that (3) is identical to Newton’s second law. Hence, Newton’s second law is a consequence of the principle of least action. However, by postulating Hamilton’s principle, we may 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 \(N\) possibly non-Cartesian coordinates \(q_j, j = 1, \ldots, N\). The equations of motion are given by (3) with \((q_1, \ldots, q_N)\) in place of \((r_1, \ldots, r_N)\):

\[
0 = \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i}, \quad i = 1, \ldots, N.
\]

To develop the Hamiltonian formulation of mechanics, we define the momenta “conjugate” to the \(q_i, p_i := \frac{\partial L}{\partial \dot{q}_i}, i = 1, \ldots, M\), and express the Hamiltonian function, \(H := -L + \sum_{i=1}^M p_i \dot{q}_i\), as a function of the coordinates, \(q_i\), and the momenta, \(p_i\). That is, although the Lagrangian is written as a function of \((q_1, \ldots, q_M)\) and \((\dot{q}_1, \ldots, \dot{q}_M)\), we use the definition of the momenta to replace the velocities with \((p_1, \ldots, p_M)\). The equations of motion for the \(q_i\) and \(p_i\) are found to be:

\[
\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad i = 1, \ldots, M.
\]

We refer to the collection \((q_1, \ldots, q_M, p_1, \ldots, p_M)\) 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.

2.2. Mechanics of constrained motion

Suppose that the positions of the \(N\) point particles introduced at the start of Section 2.1 must satisfy \(R\) algebraic constraints, \(f_i(r_1, \ldots, r_N) = 0\), where \(i\) ranges from 1 to \(R\). We introduce \(R\) additional variables, \(\lambda_1, \ldots, \lambda_R\), known as Lagrange multipliers, and seek a trajectory which makes stationary the following action \(I' := \int_{t_0}^t (L + \sum_{i=1}^R \lambda_i f_i) dt\). The equations of motion are easily found to be:

\[
0 = \frac{d}{dt} \frac{\partial L}{\partial r_i} - \frac{\partial L}{\partial r_i} - \sum_{j=1}^R \lambda_j \frac{\partial f_j}{\partial r_i}, \quad i = 1, \ldots, N,
\]

and

\[
0 = f_i(r_1, \ldots, r_N), \quad i = 1, \ldots, R.
\]

The \(R\) algebraic constraints are among the equations of motion, hence a trajectory determined by (6) will lie on the manifold of constrained trajectories.

2.3. Rigid body motion

Traditional approaches to rigid body motion [7, Chapters 4 and 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. In this section, we present an approach to rigid body motion which is at once amenable to numerical solution and conceptually simple. The material herein is due to Reich [17] and can also be found, in a very abbreviated form, in [6,11].

Initially, we consider a molecule to be a collection of point particles. We adopt a preferred orientation of the molecule, a "molecule fixed coordinate system", in which the $n$ point particles have positions, $r_1, \ldots, r_n$, such that $\sum_{i=1}^{n} m_ir_i = 0$, where $m_i$ denotes the mass of the $i$th particle. Representing the center of mass of the molecule by $q$, we note that the position of the point particles in physical space, $[r_i]$, is of the form $[r_i] = q + Qr_i$, where $Q$ is a matrix which describes the orientation of the molecular coordinate system. Since the inter-particle distances and angles must remain constant, $Q$ represents an orthonormal change of basis. That is, $Q$ is orthogonal:

$$QQ^T = 1, \quad (7a)$$

where $Q^T$ indicates the transpose of $Q$ and $1$ is the identity matrix. We may choose the molecular coordinate system and the external coordinate system to be oriented consistently, so that

$$\det(Q) = 1. \quad (7b)$$

The group of all matrices which satisfy (7) is called the Special Orthogonal Group over $\mathbb{R}^3$ and denoted $SO(3)$.

We may express the Lagrangian for the motion of the molecule in terms of $q$ and $Q$ as follows. The velocity of the $i$th point particle is simply the time derivative of its position, $v_i = \dot{q} + \dot{Q}r_i$, so the kinetic energy of the molecule is $\sum_{i=1}^{n} \frac{1}{2}m_i\|\dot{q} + \dot{Q}r_i\|^2$. Because $\sum_{i=1}^{n} m_ir_i = 0$, the kinetic energy splits into two terms, one of which represents the motion of the molecule as a whole, and the other of which represents rotation around the center of mass:

$$T(\dot{q}, \dot{Q}) = \frac{1}{2}M\dot{q} \cdot \dot{q} + \frac{1}{4}tr[\dot{Q}J\dot{Q}^T], \quad (8)$$

where $M$ represents the total mass of the molecule, $tr$ denotes the trace operation, and $J := \sum_{i=1}^{n} m_ir_i^T$. Hence, we can write the Lagrangian:

$$L = \frac{1}{2}M\dot{q} \cdot \dot{q} + \frac{1}{4}tr[\dot{Q}J\dot{Q}^T] - V(q, Q) + \text{tr}[\lambda(Q^TQ - 1)], \quad (9)$$

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

$$0 = M\ddot{q} + \frac{\partial V}{\partial q}, \quad (10a)$$

$$0 = \ddot{Q}J + \frac{\partial V}{\partial Q} - 2Q\lambda, \quad (10b)$$

$$0 = Q^TQ - 1. \quad (10c)$$

The momenta conjugate to $q$ and $Q$ are $p := M\dot{q}$ and $\Pi := \dot{Q}J$. 

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5 We have used the fact that for any two vectors $A, B \in \mathbb{R}^3$, $A \cdot B = A^T B = \text{tr}(AB^T)$.

6 By $\partial f/\partial Q$, the derivative of a quantity with respect to $Q$, we denote the matrix whose $(i, j)$th component is the derivative of $f$ by the $(i, j)$th component of $Q$, $\partial f/\partial Q_{i,j}$. 
2.3.1. Dynamics in \( SO(3) \)

The path followed by \( Q \) is a path in \( SO(3) \). We wish to use certain facts about \( SO(3) \) 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 a lemma which is standard in the theory of Lie groups. Because the proof is brief and elementary, we include it here. Let \( G \subset gl(n, \mathbb{R}) \). Given \( M \in G \), denote the tangent space to \( G \) at \( M \) by \( T_M G \). So \( T_M G \) is the set of all matrices \( A \in gl(n, \mathbb{R}) \) such that \( A = \phi(0) \) for some differentiable path \( \phi : [-1, 1] \rightarrow G \) which satisfies \( \phi(0) = M \).

**Lemma 2.1.** Let \( G \subset gl(n, \mathbb{R}) \) be a group under matrix multiplication. 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 \( \phi(t) = \psi(t) \psi(t) \).

**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, \( \dot{\eta}(s) = \phi(s)^{-1} \dot{\phi}(s) \). 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 \( \dot{\phi}(t) = \phi(t) \psi(t) \). \( \square \)

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:

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

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

\[
\text{sk} \left( \begin{array}{c} v_1 \\ v_2 \\ v_3 \end{array} \right) := \left( \begin{array}{ccc} 0 & v_3 & -v_2 \\ -v_3 & 0 & v_1 \\ v_2 & -v_1 & 0 \end{array} \right).
\]

The map sk is defined so as to have several nice properties, which we summarize in the following lemma:

**Lemma 2.2.** 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 the following are true:

\[
\text{sk}(av + bw) = a \text{sk}(v) + b \text{sk}(w),
\]

\[
\text{sk}(v) = -\text{sk}(v)^T,
\]

\[
\text{sk}(v)w = -v \times w = w \times v = -\text{sk}(w)v.
\]

\footnote{Goldstein [7, 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”.

\footnote{The proper mathematical context for this discussion is the theory of a Lie groups and their associated Lie algebras. The reader familiar with this theory will note that this discussion 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.}

\[\text{(11)}\]
\[ \text{sk}(v)\text{sk}(w) - \text{sk}(w)\text{sk}(v) = -\text{sk}(v \times w) = \text{sk}(w \times v), \]  
\[ M^T \text{sk}(v) + \text{sk}(v)M = \text{sk}(\text{tr}(M)I - M)v, \]  
\[ R^T \text{sk}(v)R = \text{sk}(R^Tv). \]

**Proof.** Verification of (13a)–(13e) requires only straightforward computation. To see that (13f) 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, \( R \in \text{SO}(3) \). Thus, \( -(R^Tv) \times w = -R^T(v \times (Rw)) = R^T\text{sk}(v)Rw \), for any \( w \in \mathbb{R}^3 \). \( \square \)

Returning to rigid body motion, we conclude from Lemma 2.1 and the sk representation of \( \mathfrak{so}(3) \) that, at each time \( t \), there exists a vector \( \omega(t) \) such that

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

The negative sign in (14) has been chosen so that \( \omega \) is the angular velocity defined in the body fixed frame by the usual right handed cross product.

If we suppose \( t \rightarrow \omega(t) \) to be given and take (14) as the equation of motion for \( Q \), then \( Q(t) \in \text{SO}(3) \) for all \( t \), provided \( Q(t_0) \in \text{SO}(3) \) for some \( t_0 \); Lagrange multipliers are not needed to maintain the orthogonality of \( Q \). To use (14) as an equation of motion, we require an equation of motion for \( \omega \).

A crucial observation is that since \( Q \in \text{SO}(3) \), multiplying (10b) on the left by \( Q^T \) and subtracting from the resulting equation its transpose, yields the following equation, which no longer depends on the Lagrange multipliers,

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

Thus,

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

\[ = -\left( Q^T \frac{\partial V}{\partial Q} - \left( \frac{\partial V}{\partial Q} \right)^T \right) - \text{sk}(\omega)^2 J + J \text{sk}(\omega)^2. \]

However, using Lemma 2.2 and (14), we find that

\[ Q^T\dot{Q}J - J\dot{Q}^TQ = -\text{sk}(\text{tr}(J) - J)\omega. \]

Thus, we define the **moment of inertia matrix** \( I := \text{tr}(J)I - J \),\(^9\) and the **angular momentum**, \( L := I\omega \). Inserting these definitions into (16) and applying Lemma 2.2 again yields the equation of motion for \( L \):

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

Note that in order to use (14) and (18) as equations of motion, we must be able to solve for \( \omega \) given \( L \). This is only possible if \( I \) is invertible.

By definition, \( J \) is a symmetric matrix. Thus, there exists an orthonormal basis in which \( J \) is diagonal. We define \( J_1 \), \( J_2 \), and \( J_3 \) to be the diagonal elements of the matrix obtained when \( J \) is expanded in this

\(^9\) Note that, by the definition of \( J \), \( I \) is, in fact, the moment of inertia tensor expressed in the body fixed frame.
basis. Note that \( J_i \geq 0 \) for \( i = 1, 2, 3 \). Clearly, in this basis, \( I \) is also diagonal. Denoting the diagonal elements of \( I \) by \( I_i, i = 1, 2, 3 \), we find that \( I_1 = J_2 + J_3, \ I_2 = J_3 + J_2, \) and \( I_3 = J_1 + J_2, \) and note that \( I_i \geq 0 \) for \( i = 1, 2, 3 \). The possible distributions of the values of the \( I_i \) fall naturally into three cases (see Fig. 1):

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

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

(19)

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 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 atom.

Rigid body and rigid rotor motion are discussed in the following two sections. Atomic motion requires no further discussion, as it is described by the mechanics presented in Section 2.1.

2.3.2. Rigid body motion

For a rigid body, we can obtain a complete set of equations of motion by combining (10a), (14) and (18):

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

(20a)

\[
\dot{p} = -\frac{\partial V}{\partial q},
\]  

(20b)

\[
\dot{Q} = -Q \sk(I^{-1}L),
\]  

(20c)

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

(20d)
where the map rot is defined by
\[ \text{rot}(M) = sk^{-1}(M - M^T). \]  

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

2.3.3. 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. Initially, we 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. On physical grounds, therefore, 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 does not depend on the first two columns of \( \dot{Q} \) (this is precisely what (19) states). Thus, we may express the kinetic energy so that it depends only on \( \dot{q} \) and \( \dot{Q}_3 \):
\[ T = \frac{1}{2} M \dot{q} \cdot \dot{q} + \frac{1}{2} J_3 \dot{Q}_3 \cdot \dot{Q}_3. \]

Henceforth, we shall drop 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 the motion of a rigid rotor in terms of these variables is:
\[ L = \frac{1}{2} M \dot{q} \cdot \dot{q} + \frac{1}{2} I \dot{Q} \cdot \dot{Q} - V(q, Q) + \lambda(Q \cdot Q - 1). \]

We define the angular velocity, \( \omega := Q \times \dot{Q} \), and note that, by the triple product formula \[ A \times (B \times C) = (A \cdot C)B - (A \cdot B)C. \]

As (14) was sufficient to guarantee the orthogonality of the matrix \( Q \), so is (25) sufficient to guarantee the unit-modulus of the vector \( Q \).
As \( I \) is non-zero, we may take the following as the equations of motion for a rigid rotor:

\[
\begin{align*}
\dot{q} &= \frac{p}{M}, \\
\dot{p} &= -\frac{\partial V}{\partial q}, \\
\dot{Q} &= \frac{1}{I} L \times Q, \\
\dot{L} &= -Q \times \frac{\partial V}{\partial Q}.
\end{align*}
\] (28a, 28b, 28c, 28d)

3. Split Hamiltonian integration

We use a superscript to indicate 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 \( \omega \alpha \) to denote the size of an individual time step.

Consider a system described by momentum coordinates, \( p \), and position coordinates, \( q \), where \( p \) and \( q \) are \( N \)-vectors. Suppose that the motion is described by a Hamiltonian, \( H = \frac{1}{2} p \cdot M^{-1} p + V(q) \), where \( M \) is a positive definite matrix, the mass matrix. 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 [6]:

\[
\begin{align*}
p^{i+1/2} &= p^i - \Delta t \frac{\partial V}{\partial q}(q^i), \\
q^{i+1} &= q^i + \Delta t M^{-1} p^{i+1/2}, \\
p^{i+1} &= p^{i+1/2} - \Delta t \frac{\partial V}{\partial q}(q^{i+1}).
\end{align*}
\] (29)

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 \( H \)” [6]. This idea goes back to [22]. In other words, we consider \( H \) to be split into two parts: \( H = T + V \), where \( T = \frac{1}{2} p \cdot M^{-1} p \) and \( V = V(q) \). Note that if we consider \( T \) and \( V \) as Hamiltonians, we can solve for the dynamics of each separately. The exact solutions are:

\[
\begin{align*}
\{ q(t) &= q(0) + t M^{-1} p(0), \\
p(t) &= p(0)
\}
\] (30a)

for \( T \), and

\[
\begin{align*}
\{ q(t) &= q(0), \\
p(t) &= p(0) - t \frac{\partial V}{\partial q}(q(0))
\}
\] (30b)

for \( V \). Using these solutions, the Verlet scheme can be written as follows:

\[
(p^{i+1}, q^{i+1}) = \exp_V(\frac{1}{2} \Delta t) \exp_T(\frac{1}{2} \Delta t) \exp_T(\frac{1}{2} \Delta t) \exp_V(\frac{1}{2} \Delta t) (p^i, q^i),
\] (31)

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 \( G \).
Eq. (31) has an obvious generalization. Consider a Hamiltonian, $H$, and suppose that
\[ H = H_1 + \cdots + H_n, \]
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 (32)) is
\[ (p^{i+1}, q^{i+1}) = \exp_{H_1}(\frac{\Delta t}{2}) \cdots \exp_{H_n}(\frac{\Delta t}{2}) \exp_{H_n}(\frac{\Delta t}{2}) \cdots \exp_{H_1}(\frac{\Delta t}{2}) (p^i, q^i). \] (33)

We refer to $n$ as the size of the splitting. Such schemes have been discussed in [6,15–17,22]. A concise proof that the Verlet algorithm and a specific generalization of the Verlet algorithm with application to rigid body motion are second order is given in [6]. We prefer the following theorem as it states that general split Hamiltonian schemes are second order.

**Theorem 3.1.** 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 $\tilde{x} \in G$:
\[ \phi_i(t) \tilde{x} = \exp_{H_i}(t) \tilde{x} = O(t^3) \]
\[ (i = 1, 2), \]
then, for each $\tilde{x} \in G$:
\[ \phi_2(\frac{t}{2}) \phi_1(\frac{t}{2}) \tilde{x} = \exp_{H}(t) \tilde{x} = O(t^3). \] (35)

The proof of this theorem is elementary and follows from results in [22] and the BCH (Baker–Campbell–Hausdorff) formula for the product of $\exp(X)$ with $\exp(Y)$ where $X$ and $Y$ are non-commuting operators. We do not reproduce this proof here, but simply clarify certain interpretations and consequences of the theorem:

1. Under the appropriate hypotheses of smoothness, it follows from this theorem, via induction on the size of the splitting, that split Hamiltonian integrators have a local truncation error of order 3, and hence a global error of order 2 (see [5] for a discussion of errors).
2. Nearly all potential functions of interest are $C^\infty$ (sometimes with a number of 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 $C^k$ [3], the hypothesis of $C^3$ smoothness will be satisfied for most cases of interest.

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 induced motions. The derivation of these schemes relies on the “Poisson bracket” formalism which allows the statement of the equations of motion ((20) and (28)) in Hamiltonian form. Readers not familiar with this formalism can find a discussion of Poisson brackets in any of the standard mechanics texts, e.g., [7].

---

11 In [15] the scheme
\[ (p^{i+1}, q^{i+1}) = \exp_{H_1}^{-1}(\frac{\Delta t}{2}) \cdots \exp_{H_n}^{-1}(\frac{\Delta t}{2}) \exp_{H_n}(\frac{\Delta t}{2}) \cdots \exp_{H_1}(\frac{\Delta t}{2}) (p^i, q^i) \]
is used, because it explicitly preserves the time reversibility of the dynamics. For the cases we consider $\exp_{H_i}^{-1}(\frac{\Delta t}{2}) = \exp_{H_i}(\frac{\Delta t}{2})$, thus we maintain the notation of (33).

12 We present this scheme in Section 3.1.
3.1. A split Hamiltonian scheme for rigid body motion

In this section, we present a split Hamiltonian scheme for the approximation of the dynamics presented in Section 2.3.2. McLaughlan [15] and Reich [16] independently proposed versions of this scheme valid for free rigid bodies. The scheme presented herein, which allows the potential energy to depend on the orientations, is due to Reich [17]. The scheme has also been used by Dullweber et al. [6].

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 \( V = V(q, Q) \), \( T = (1/(2M))p \cdot p \), and \( S_i = (1/(2I_i))L_i^2 \) for \( i = 1, 2, 3 \). The associated exact solutions with initial condition \( \tilde{x} = (\tilde{q}, \tilde{p}, \tilde{Q}, \tilde{L}) \) are listed below.

1. Motion induced by \( V \):
\[
\exp_V(t)\tilde{x} = \left( \tilde{q}, \tilde{p} - t \frac{\partial V}{\partial \tilde{q}}, \tilde{Q}, \tilde{L} + t \text{rot} \left( \tilde{Q}^T \frac{\partial V}{\partial \tilde{Q}} \right) \right). \tag{36a}
\]

2. Motion induced by \( T \):
\[
\exp_T(t)\tilde{x} = \left( \tilde{q} + \frac{1}{M} \tilde{p}, \tilde{p}, \tilde{Q}, \tilde{L} \right). \tag{36b}
\]

3. Motion induced by \( S_i \), for \( i = 1, 2, 3 \):
\[
\exp_{S_i}(t)\tilde{x} = (\tilde{q}, \tilde{p}, \tilde{Q}R_i(\omega_i t)^T, R_i(\omega_i t)\tilde{L}), \tag{36c}
\]

where \( \omega_i = L_i/I_i \) and \( R_i(\theta) \) is the matrix whose action on \( \mathbb{R}^3 \) is counter-clockwise rotation about the elementary vector \( e_i \) by angle \( \theta \).\(^{13} \) Note that \( R_i(\omega_i t) \in SO(3) \) for all \( t \). Thus \( Q(t) \in SO(3) \) 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:
\[
(q^{i+1}, p^{i+1}, Q^{i+1}, L^{i+1}) = \exp_V(\frac{1}{2}\Delta t) \exp_T(\frac{1}{2}\Delta t) \exp_{S_1}(\frac{1}{2}\Delta t) \exp_{S_2}(\frac{1}{2}\Delta t) \exp_{S_3}(\frac{1}{2}\Delta t) \exp_{S_1}(\frac{1}{2}\Delta t) \exp_{S_2}(\frac{1}{2}\Delta t) \exp_{S_3}(\frac{1}{2}\Delta t)
\times \exp_{S_1}(\frac{1}{2}\Delta t) \exp_T(\frac{1}{2}\Delta t) \exp_V(\frac{1}{2}\Delta t) (q^i, p^i, Q^i, L^i). \tag{37}
\]

3.2. 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 et al. [19] use an explicit algorithm, which they derive geometrically, for molecular dynamics of diatomic fluids. Kol et al. [11] 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 [19] or [11].

As in the Verlet algorithm, we split the Hamiltonian for rigid rotor motion into kinetic and potential parts: \( H = V + T \), where \( V = V(q, Q) \) and \( T = (1/(2M))p \cdot p + (1/(2I))L \cdot L \). The associated exact solutions with initial condition \( \tilde{x} = (\tilde{q}, \tilde{p}, \tilde{Q}, \tilde{L}) \) are presented below:

\(^{13}\) For example,
\[
e_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}
\text{ and } R_1(\theta) = \exp(\theta \text{ sk}(e_1)) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\theta) & \sin(\theta) \\ 0 & -\sin(\theta) & \cos(\theta) \end{pmatrix}.\]
1. Motion induced by $V$:
$$\exp_V(t)\tilde{x} = \left(\tilde{q}, \tilde{p} - t\frac{\partial V}{\partial \tilde{q}} \bigg|_{\tilde{x}}, \tilde{Q} - t\frac{\partial V}{\partial \tilde{Q}} \bigg|_{\tilde{x}} \times \tilde{L} \right).$$  \hfill (38a)

2. Motion induced by $T$:
$$\exp_T(t)\tilde{x} = \left(\tilde{q} + \frac{t}{M}\tilde{p}, \tilde{p}, \cos(\omega t)\tilde{Q} + \frac{\sin(\omega t)}{\|L \times \tilde{Q}\|} \tilde{L} \times \tilde{Q}, \tilde{L} \right),$$  \hfill (38b)

where $\omega = \|\tilde{L}\|/I$.

A split Hamiltonian scheme for the integration of rigid rotor motion is found by composing the solutions found above:
$$\left(q^{i+1}, p^{i+1}, Q^{i+1}, L^{i+1}\right) = \exp_V(\frac{1}{2}\Delta t) \exp_T(\Delta t) \exp_V(\frac{1}{2}\Delta t)(q^i, p^i, Q^i, L^i).$$  \hfill (39)

4. Methodology of simulation

The results presented in Section 5 were obtained with 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.

Each simulation proceeded as follows:

1. The boundary conditions (see Section 4.1) and potential energy model were specified.
2. The initial positions and velocities of the molecules were specified and the system was integrated through the “equilibration phase” (see Section 4.2).
3. The final state of the equilibration phase was used as the initial state for the simulation.
4. The trajectory computed during the simulation was used to calculate time averages which could be interpreted as thermodynamic quantities.

In the following sections, we discuss these steps in more detail.

4.1. 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 involve on the order of 250 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 to correspond to real containers.

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 $L_b$ is a length prescribed at the beginning of the simulation. Since molecules naturally come 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 (see Fig. 2):

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.
2. Reflective boundary conditions: Molecules reflect elastically from the boundaries of the box. This corresponds to a container with walls.

Following an approach suggested by Heermann in [8], 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 their interaction is a sum:

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

where \( U(r) \) represents the energy of the particles separated by a distance \( r \). We wish to avoid such summations, 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 (40) is reduced to at most one term (see Fig. 3).

4.2. Equilibration

The system being simulated must be in thermodynamic equilibrium before we can calculate thermodynamic 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 [8]. 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. 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 (generally, \( n = 6 \)), was placed in an initial configuration:
   (a) The molecules were placed with their centers of mass on a face centered cubic lattice.
   (b) 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 momenta were rescaled so that 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 simulation. 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 equilibration process was that its final state became the initial state for the simulation. See [8] for more details regarding equilibration.

---

Footnote 14: The temperature depends only on the kinetic energy per molecule. Hence it can be adjusted by scaling the molecular momenta.
4.3. The calculation of averages

In Appendix A, we present formulae for thermodynamic quantities as ergodic averages of certain functions. To apply these formulae, 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. 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:

\[
\langle \psi \rangle \approx \frac{1}{n \Delta t} \int_{t_0}^{t_n} \psi(t') \, dt' \approx \frac{1}{n \Delta t} \left( \frac{1}{2} \psi_0 + \sum_{i=1}^{n-1} \psi_i + \frac{1}{2} \psi_n \right).
\]  

(41)

In practice, we consider a sequence of approximations:

\[
\langle \psi \rangle_i = \frac{1}{i \Delta t} \left( \frac{1}{2} \psi_0 + \sum_{j=1}^{i-1} \psi_j + \frac{1}{2} \psi_i \right). \quad (42)
\]

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

5. Simulations

In each simulation, the model of the interaction between molecules was taken to be of the following simple form:

1. A certain number of “Lennard-Jones” centers were specified in each molecule. The centers on distinct molecules interacted via:

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

(43)

where \( \epsilon \) measures the total energy of the interaction, \( \sigma \) the “size” of the Lennard-Jones centers, and \( r \) is the distance between them.

2. A certain number of point charges, \( q \), were assigned to various positions in each molecule. Point charges interacted via the Coulomb potential:

\[
U(r) = \frac{q_1 q_2}{r}.
\]

(44)

The charges and Lennard-Jones parameters were taken from various references in the literature. Of particular use was the book of Kihara [10].

We performed each simulation in dimensionless units by introducing fundamental units of energy, mass and length, denoted, respectively, \( E \), \( l \) and \( M \). We denote a dimensionless quantity with a superscript \( \ast \). Dimensionful quantities can be obtained by multiplying by the appropriate combination of \( E \), \( M \) and \( l \).
In what follows, \( N \) denotes the number of molecules, \( C^* \) the force cutoff length, \( L^*_B \) the bounding box size, \( T^* \) the temperature, \( \Delta t^* \) the step size for the SH-integrator, and \( M \) the number of steps taken during the simulation phase. In addition, \( \rho^* \) indicates the density: \( N/8(L^*_B)^3 \).

### 5.1. Carbon dioxide

Carbon dioxide, being a linear molecule, has a quadrupole moment which can be characterized by a single quantity. If the \( z \) axis is taken as the molecular axis, this quantity is [10, 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.\(^\text{15}\) Kihara provides an experimental value for this quantity [10, Table 3.5]:

\[
\Theta_{zz} = -4.2 \times 10^{-26} \text{ statcoulomb cm}^2 = -0.874416e \text{ Å}^2,
\]

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 Å [10, 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:

\[
\delta_O = -0.331e, \quad \delta_C = 0.661e.
\]

\(^{15}\) The matrix of the quadrupole moment tensor in this coordinate system is:

\[
\Theta = \Theta_{zz} \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}.
\]
Table 1
Simulations of CO$_2$

<table>
<thead>
<tr>
<th>$L_b^*\rho$</th>
<th>$T^*$</th>
<th>Error</th>
<th>$P^*$</th>
<th>Error</th>
<th>$T/P$</th>
<th>$T_{\text{calc}}$</th>
<th>$T_{\text{exp}}$</th>
<th>$\alpha = T_{\text{exp}} / T_{\text{calc}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0</td>
<td>0.1250</td>
<td>0.0474</td>
<td>0.0015</td>
<td>0.0060</td>
<td>1.40</td>
<td>438</td>
<td>578.4</td>
<td>1.32</td>
</tr>
<tr>
<td>6.5</td>
<td>0.0983</td>
<td>0.0496</td>
<td>0.0009</td>
<td>0.0053</td>
<td>1.62</td>
<td>451</td>
<td>781</td>
<td>1.73</td>
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<tr>
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<td>0.0496</td>
<td>0.0019</td>
<td>0.0038</td>
<td>2.28</td>
<td>459</td>
<td>596</td>
<td>1.30</td>
</tr>
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<td>0.0004</td>
<td>0.0118</td>
<td>0.86</td>
<td>812</td>
<td>447</td>
<td>0.55</td>
</tr>
<tr>
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<td>0.0883</td>
<td>0.0004</td>
<td>0.0109</td>
<td>1.44</td>
<td>816</td>
<td>563</td>
<td>0.69</td>
</tr>
<tr>
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<td>0.0870</td>
<td>0.0002</td>
<td>0.0083</td>
<td>1.85</td>
<td>804</td>
<td>570</td>
<td>0.71</td>
</tr>
<tr>
<td>5.0</td>
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<td>0.1277</td>
<td>0.0002</td>
<td>0.0290</td>
<td>0.78</td>
<td>1180</td>
<td>477</td>
<td>0.40</td>
</tr>
<tr>
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<td>0.1291</td>
<td>0.0002</td>
<td>0.0110</td>
<td>2.08</td>
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<td>477</td>
<td>0.40</td>
</tr>
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<td>0.0004</td>
<td>0.0105</td>
<td>2.14</td>
<td>1178</td>
<td>716</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Temperatures ($T^*$) and pressures ($P^*$) were calculated from the formulae of Appendix A via average values computed from the trajectory. The errors were estimated as discussed in Section 4.3 and do not include errors due to the approximation of the trajectory. $T_{\text{calc}}$ and $T_{\text{exp}}$ are given in Kelvin. For an explanation of the experimental temperatures and $\alpha$, see the text.

This information is summarized in Fig. 4. In addition, we place, at each of the oxygen atoms, a Lennard-Jones center with parameters:

$$\varepsilon = 192.5 k_B \text{ Kelvin}, \quad \sigma = 2.90 \text{ Å}.$$ \hfill (48)

These parameters are due to Singer et al. [19]. The value of $\sigma$ is dictated, to a large extent, by the fact that it represents the size of the oxygen charge distribution. Roughly, $\sigma$ must lie between 1 Å and 5 Å. Thus we consider $\sigma$ to be a fixed quantity. However, $\varepsilon$ represents the energy of interaction of two Lennard-Jones centers. We considered the possibility that $\varepsilon$ 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$_2$:

$$I = 16 \text{ amu}(−1.15 \text{ Å})^2 + 16 \text{ amu}(1.15 \text{ Å})^2 = 42.32 \text{ amu Å}^2.$$ \hfill (49)

In Table 1 we have listed the results of simulations of CO$_2$ with the above model. These calculations were performed with the following fundamental units:

$$E = 48\varepsilon = 9240k_B \text{ Kelvin}, \quad M = 44 \text{ amu}, \quad l = \sigma = 2.90 \text{ Å}.$$ \hfill (50)

In each simulation, $N = 216$ molecules were integrated for $M = 2000$ steps of size $\Delta t^* = 0.0064$ with $C^* = 5.0$. The bounding box size $L_b^*$ and the temperature $T^*$ were varied.

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

1. Rescaling $\varepsilon$ is equivalent to rescaling $E = 48\varepsilon$.
2. Neither $\rho$ nor the calculated value of $T/P$ depends on $E$. 

\hfill
Since experimentally determined values of $\rho$ as a function of $T$ and $P$ are available [21], we can exploit these observations to determine $\varepsilon$.

We observed that at constant $\rho$ the experimental value of $T/P$ is a monotonic decreasing function of $P$. Therefore, given calculated values of $\rho$ and $T/P$ for a particular simulation, we were able to determine a unique experimental pressure and temperature. (We used linear interpolation to calculate experimental values of $T/P$ between available data points.) We let $T_{\text{exp}}$ denote this experimental temperature, and calculated the ratio

$$\alpha := \frac{T_{\text{exp}}}{T_{\text{calc}}}.$$  

If we wish to force $T_{\text{calc}}$ to agree with $T_{\text{exp}}$, we must replace $\varepsilon$ with $\alpha\varepsilon$. Values of $T_{\text{exp}}$ and $\alpha$ are shown in Table 1.

It is apparent from Table 1 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 parameters in the model as well.
Table 2
Simulations H$_2$O

<table>
<thead>
<tr>
<th>$L^*_b$</th>
<th>$\rho^*$</th>
<th>$T^*$</th>
<th>Error</th>
<th>$P^*$</th>
<th>Error</th>
<th>$T/P$</th>
<th>$T_{\text{calc}}$</th>
<th>$T_{\text{exp}}$</th>
<th>$\alpha = T_{\text{exp}}/T_{\text{calc}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
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<td>0.3147</td>
<td>0.0015</td>
<td>0.192</td>
<td>0.011</td>
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<td>0.3111</td>
<td>0.0008</td>
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<td>0.007</td>
<td>0.79</td>
<td>1165</td>
<td>1238</td>
<td>1.05</td>
</tr>
<tr>
<td>5.0</td>
<td>0.216</td>
<td>0.3179</td>
<td>0.0005</td>
<td>0.070</td>
<td>0.003</td>
<td>1.03</td>
<td>1190</td>
<td>1441</td>
<td>1.22</td>
</tr>
</tbody>
</table>

Temperatures ($T^*$) and pressures ($P^*$) were calculated from the formulae of Appendix A via average values computed from the trajectory. The errors were estimated as discussed in Section 4.3 and do not include errors due to the approximation of the trajectory. $T_{\text{calc}}$ and $T_{\text{exp}}$ are given in Kelvin. For an explanation of the experimental temperatures and $\alpha$, see the text.

5.2. Water

We began with a well accepted model for water, known as the TIP4P model [9]. The geometry of this model, which makes use of four sites in the water molecule, is illustrated in Fig. 5. The moment of inertia tensor is diagonal in this coordinate system, and the three moments of inertia are:

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

(52)

The model assigns charges to the hydrogen atoms and to the point $M$:

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

(53)

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

$$\begin{align*}
\varepsilon &= 78.02k_B \text{ Kelvin}, \\
\sigma &= 3.154 \text{ Å}.
\end{align*}$$

(54)

In Table 2 we have listed the results of our simulations of water. These calculations were performed with the following fundamental units:

$$\begin{align*}
E &= 48\varepsilon = 3745k_B \text{ Kelvin}, \\
M &= 18 \text{ amu}, \\
l &= \sigma = 3.15 \text{ Å}.
\end{align*}$$

(55)

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

The experimental temperatures and values of $\alpha$ were determined as in Section 5.1. Experimental values were taken from the ASME Steam Tables [1]. Although the spread in the values of $\alpha$ is not as great as in the simulation of CO$_2$, the variation between trials is still substantial.

5.3. Step sizes, the number of molecules, and the length of simulations

We have been rather glib in discussing how we chose the number of molecules, $N$, the step size, $\Delta t$, and the total number of steps taken, $M$. In making 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
Table 3
Dependence of results on step size and number of molecules

<table>
<thead>
<tr>
<th>Section 5.1</th>
<th>N</th>
<th>L_B</th>
<th>Δt*</th>
<th>M</th>
<th>T*</th>
<th>Error</th>
<th>P*</th>
<th>Error</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</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>
<td>0.0004</td>
<td>3:04:10</td>
</tr>
<tr>
<td>2</td>
<td>512</td>
<td>8.0</td>
<td>0.0064</td>
<td>2000</td>
<td>0.0485</td>
<td>0.00078</td>
<td>0.0063</td>
<td>0.0005</td>
<td>7:20:57</td>
</tr>
<tr>
<td></td>
<td>216</td>
<td>6.0</td>
<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>

Temperatures ($T^*$) and pressures ($P^*$) were calculated from the formulae of Appendix A via average values computed from the trajectory. The errors were estimated as discussed in Section 4.3 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.

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 $Δt^*$. However, the time required for computation is an increasing function of $N$ and $M$.

To obtain average quantities, as discussed in Appendix A and Section 4.3, 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 $Δt^*$ 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 $Δt^*$ 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 substantially 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 $Δt^*$ and increased $M$ to maintain a constant length of simulation. The results of these simulations are shown in Table 3 along with the results from the corresponding simulation of CO$_2$ from Section 5.1. Note that the results from all three simulations are comparable, while the results from Section 5.1 were obtained in the least time.

5.4. Comparison of DASSL with the Verlet algorithm

Upon first considering the problem of molecular dynamics, we intended to use constrained dynamics (see Section 2.2) to produce a system of algebraic–differential equations which could be integrated with DASSL. However, we were unable to obtain adequate results for either diatomic or triatomic molecules.

There was, in fact, already a literature describing the pitfalls of using DASSL for molecular dynamics. The pitfalls are two-fold. First, DASSL fails to be symplectic and as such long term approximate conservation of energy cannot be expected [13]. Second, DASSL estimates the solution, $y$, of certain algebraic–differential equations of the form

$$F(t, y, y') = 0,$$  (56)

to within user-specified error tolerances. The user must supply a routine for the calculation of $F$, and $∂F/∂y + c∂F/∂y'$ for arbitrary $c$. DASSL will not solve all systems of the form shown in (56). Specifically, Brenan et al. define the *index* of (56) as the minimum number of times which (56) must
Table 4
Comparison of the Verlet algorithm and DASSL

<table>
<thead>
<tr>
<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>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>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>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>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>

Temperatures (\( T^* \)) and pressures (\( P^* \)) were calculated from the formulae of Appendix A via average values computed from the trajectory. The errors were estimated as discussed in Section 4.3 and do not include errors due to the approximation of the trajectory. Time denotes the time required to perform equilibration and simulation.

be differentiated with respect to \( t \) to uniquely determines \( y' \) as a continuous function of \( y \) and \( t \) [4, Chapter 2]. For DASSL to find an approximate solution to (56), the index must be 0 or 1 [4, Chapter 5]. The difficulties stem, essentially, from the fact that the equations of motion for a constrained mechanical system are most naturally expressed as an index 3 system. To produce an index 1 system, we must replace certain of the equations with their second time derivatives [4, Section 6.2]. Specifically, if there are constraints of the form

\[
\frac{1}{2} (\|r_1 - r_2\|^2 - d^2) = 0, \tag{57}
\]

then we must replace (57) with its second derivative:

\[
\|\dot{r}_1 - \dot{r}_2\|^2 + (r_1 - r_2) \cdot (\ddot{r}_1 - \ddot{r}_2) = 0. \tag{58}
\]

In practice, we substitute into (58) the values of \( \ddot{r}_1 \) and \( \ddot{r}_2 \) obtained from the equations of motion. Since we provide initial conditions which satisfy (57) and its derivative, (57) is satisfied, in principle, along the entire trajectory. However, DASSL uses an iterative scheme to force the numerical solution to satisfy (58). Since this procedure is non-exact, small errors are introduced. However, small errors in the left hand side of (58) produce errors in the left hand side of (57) which grow with time. In fact, the constrained distances are observed to actually change in magnitude. 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 bond lengths changed in magnitude quickly enough that, after approximately 50–200 time steps, the constraints failed to be satisfied within those same error bounds. 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, such tight error bounds force the time required for calculation to become prohibitively large.

However, DASSL uses sophisticated numerical techniques and error checking to guarantee particular bounds on the local truncation error while the SH schemes which we have used are first order. Therefore, it is interesting to ask whether, for those systems to which both integration techniques may be applied, the results so obtained are comparable.

To examine this question, we considered a system of 216 atoms, each of mass 1, interacting via pairwise Lennard-Jones potentials, with the following fundamental units:

\[
E = 48\varepsilon, \quad M = 1, \quad l = \sigma. \tag{59}
\]
In each simulation, we took $C^* = 2.5$, and $M = 2000$ steps of size $\Delta t^* = 0.32$ were taken. Four simulations were performed, two each with DASSL and the Verlet algorithm. Two sets of parameters were considered:\textsuperscript{16}

1. $T^* = 0.05271$, $L_B^* = 3.488745$ and $\rho^* = 0.636$.
2. $T^* = 0.0150417$, $L_C^* = 3.1905216$ and $\rho^* = 0.831$.

In the above, $\rho^* = 216/(8(L_B^*)^3)$ and $T^*$ is the temperature used during equilibration; the actual temperatures computed from the simulated trajectory differed from these values slightly. Table 4 shows the results of these simulations.

Observe that DASSL and the Verlet algorithm provide comparable results and that the Verlet algorithm requires substantially less time. This provides evidence that the Verlet algorithm and other split-Hamiltonian schemes can be used confidently in MD simulations.

6. Conclusions

In this paper we have presented a split-Hamiltonian method for the integration of the equations of motion resulting from molecular simulations. Molecules are considered as rigid body rotators and the formulation explicitly satisfies the constraints of molecular dynamics. The split-Hamiltonian scheme for rigid rotor motion is new. It is a generalization of the Verlet algorithm and is therefore simple to implement.

Simulations were done for CO$_2$ and H$_2$O molecules and average temperature and pressures were obtained by integrating the system long enough. The values obtained were compared with results using the DASSL algorithm and shown to be very close, with the split-Hamiltonian method requiring substantially less time. These results indicate that split-Hamiltonian methods work very well in molecular dynamics calculations, are relatively easy to program and also fairly fast.

Appendix A. The calculation of averages

In a MD simulation, we use ergodicity to calculate the values of macroscopic properties of a system. To do so, we need a relation between these values and statistical mechanical averages. In Appendix A.1 we present a framework for deriving such relations. In Appendix A.2, we present several important relations.

A.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, on physical grounds, effects due to the shape of the volume are negligible. Thus let us consider a system consisting of $N$ molecules at temperature $T$ with volume $V$ which occupy a cube, $B$, of side length $2L$ centered at the origin ($B = \{(x_1, x_2, x_3): |x_i| < L\}$). 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 $\text{SO}(3)$. For our purposes, we must assume a few facts about $S_i$:

\textsuperscript{16}These parameters are those used by Heermann in simulations of Argon [8].
1. We assume that \( S_i \) is a differentiable manifold.

2. We assume that \( S_i \) 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 \( i \)th molecule when it has orientation \( s \) and velocity \( L_i(s) \cdot \omega \) is given by

\[
K(s, L_i(s) \cdot \omega) = (I_i \cdot \omega) \cdot \omega,
\]

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

\[
K(s, L_i(s)\omega) = (I \cdot \omega) \cdot \omega,
\]

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

If, for instance, \( S_i \) is a Lie group, then these assumptions follow.

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

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

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 \( p_i = \partial K / \partial \dot{r}_i = m_i \dot{r}_i \), and \( l_i = \partial K / \partial \omega_i = I_i \cdot \omega_i \), and

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

We assume that the potential energy, \( U \), is independent of \( p_i \) and \( l_i \).

We now introduce some notation. Let \( B_N := \prod_{i=1}^N B \), \( S_N := \prod_{i=1}^N S_i \), \( \mathcal{P}_N := B_N \times S_N \), \( B_N^* := \bigoplus_{i=1}^N \mathbb{R}^{n_i} \), \( S_N^* := \bigoplus_{i=1}^N \mathbb{R}^{n_i} \), and \( \mathcal{P}_N^* := B_N^* \oplus S_N^* \). 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 [12, Chapter 1]:

\[
\rho(p,q) := \frac{e^{-(K(p)+U(q))/T}}{\int_{\mathcal{P}_N^*} \int_{\mathcal{P}_N} e^{-(K(p)+U(q))/T} \, dp \, dq}.
\]

To evaluate the integral with respect to \( p \) in (A.5), we use the following fact: If \( M \) is a positive definite symmetric \( n \times n \) matrix, then \( \int_{\mathbb{R}^n} e^{-x^T M x} \, dx = (\det(2\pi M^{-1}))^{1/2} \). Hence,

\[
\int_{\mathcal{P}_N^*} e^{-(K(p)+U(q))/T} \, dp = \prod_{i=1}^N ((2\pi m_i T)^3 \det(2\pi T I_i))^{1/2}.
\]

Let \( s(N) := 3N + \sum_{i=1}^N n_i \) and \( m(N) := \prod_{i=1}^N ((2\pi)^{3+m_i} m_i^3 \det I_i)^{1/2} \), so that

\[
\rho(p,q) = \frac{e^{-(K(p)+U(q))/T}}{Ts(N)^{1/2}m(N) \int_{\mathcal{P}_N} e^{-(U(q))/T} \, dq}.
\]
The average value, $\langle \psi \rangle$, of a function $\psi(p, q)$ is defined to be $\int_{\mathcal{P}_N} \int_{\mathcal{P}_N^*} \psi \rho \, dp \, dq$. Hence,

$$\langle \psi \rangle = \frac{\int_{\mathcal{P}_N} \int_{\mathcal{P}_N^*} \psi(p, q) e^{-(K(p)+U(q))/T} \, dp \, dq}{T^{n(N)/2} m(N) \int_{\mathcal{P}_N} \rho \, dq}.$$  (A.8)

Throughout the rest of this section, we consider a function, $\psi$, which is independent of $p$. Thus,

$$\langle \psi \rangle = \frac{\int_{\mathcal{P}_N} \psi(q) e^{-(U(q))/T} \, dq}{\int_{\mathcal{P}_N} e^{-(U(q))/T} \, dq}.$$  (A.9)

Differentiating (A.9) with respect to the temperature, $T$, we obtain:

$$\frac{\partial \langle \psi \rangle}{\partial T} = \frac{1}{T^2} ((\psi U) - \langle \psi \rangle \langle U \rangle) + \left\langle \frac{\partial \psi}{\partial T} \right\rangle.$$  (A.10)

In order to differentiate $\langle \psi \rangle$ with respect to the volume, $V$, we must consider how the integrals in (A.9) depend on the side length, $L$, of the box $B$. As written, not only might the integrand depend on $L$, but the limits of integration depend on $L$. Thus we transform the integrals over $B_N$ in (A.9) to integrals over a fixed region. To this end, let $I_N := \prod_{1=1}^{N} I^3$, where $I = (-1, 1)$, and let $R_N := I_N \times S_N$, so that given a function $f(R, S)$, we have the relation $\int_{B_N} f(R, S) \, dR \, dS = \int_{R_N} f(LR, S) L^3 \, dR \, dS$. Hence,

$$\langle \psi \rangle = \frac{\int_{R_N} \psi (LR, S; L) e^{-(U(LR, S; L))/T} \, dR \, dS}{\int_{R_N} e^{-(U(LR, S; L))/T} \, dR \, dS},$$  (A.11)

where we have indicated that $\psi$ and $U$ might depend explicitly on $L$. Using (A.11) we calculate:

$$\frac{\partial \langle \psi \rangle}{\partial L} = \frac{1}{L} \left\langle R \cdot \frac{\partial \psi}{\partial R} + L \frac{\partial \psi}{\partial L} \right\rangle - \frac{1}{L} \left( \left\langle \psi \left( R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right) \right\rangle - \langle \psi \rangle \left\langle R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right\rangle \right).$$  (A.12)

Since $\partial / \partial V = (1/(24L^2)) \partial / \partial L$

$$\frac{\partial \langle \psi \rangle}{\partial V} = \frac{1}{3V} \left\langle R \cdot \frac{\partial \psi}{\partial R} + L \frac{\partial \psi}{\partial L} \right\rangle - \frac{1}{3VT} \left( \left\langle \psi \left( R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right) \right\rangle - \langle \psi \rangle \left\langle R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right\rangle \right).$$  (A.13)

A.2. 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 [12, Chapter 3]:

$$F = -T \log \left( \Phi(N) \int_{\mathcal{P}_N} \int_{\mathcal{P}_N^*} e^{-(1/T)(K+U)} \, d\rho \, dq \right),$$  (A.14)

17 We assume that all integrals are sufficiently convergent to justify bringing the derivative under the integral sign.
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:

$$f := \frac{F}{N} = -T \left[ \frac{1}{N} \log (\Phi(N)m(N)(2\pi h^{-2})^{s(N)}) + \frac{s(N)}{2N} \log T + \log \left( \int_{\mathcal{R}_N} e^{-U(q)/T} dq \right)^{1/N} \right].$$

Letting

$$\Psi(N) := \frac{1}{N} \log (\Phi(N)m(N)(2\pi h^{-2})^{s(N)}) + \log(N),$$

and changing the region of integration to $\mathcal{R}_N$ as above, we find that

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

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 $e^{U/T}$:

$$\langle e^{U/T} \rangle = \frac{A(N)}{\int_{\mathcal{R}_N} e^{-U(L,R,S;L)/T} dS dR},$$

where $A(N)$ denotes $\int_{\mathcal{R}_N} dS dR$. Solving for $\int_{\mathcal{R}_N} e^{-U(L,R,S;L)/T} dS dR$, and substituting into (A.16), we obtain the following formula for $f$:

$$f = -T \left[ \Psi(N) + \frac{1}{N} \log A(N) + \frac{s(N)}{2N} \log T + \log \left( \frac{V}{8N} \right) - \frac{1}{N} \log \langle e^{U/T} \rangle \right],$$

where $V = 8L^3$ is the volume of $B$.

Using equations (A.13) and (A.10), we can now derive expressions for partial derivatives of $f$ of any order. For example,

$$\frac{\partial}{\partial V} f = -T \frac{1}{V} \left( R \cdot \frac{\partial U}{\partial R} + L \frac{\partial U}{\partial L} \right).$$

We introduce the notation $\mathcal{F} = -(R \cdot \partial U/\partial R + L \partial U/\partial L)$, so that

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

Using this notation, we list several important and/or interesting formulae:

1. Temperature [12, Chapter 3]:

$$T := \frac{2}{s(N)} \langle K \rangle.$$

2. Internal energy per particle:

$$\mathcal{E} := \frac{\langle K \rangle + \langle U \rangle}{N} = \frac{s(N)}{2N} T + \frac{\langle U \rangle}{N}.$$
3. Pressure:
\[ P := -N \frac{\partial f}{\partial V} = \frac{NT}{V} + \frac{1}{3V} \langle F \rangle. \]

4. Entropy per particle:
\[ S := -\frac{\partial f}{\partial T} = f + \frac{s(N)}{2N} + \frac{1}{NT} \langle U \rangle. \]

5. Heat capacity per particle at constant volume:
\[ c_V := \frac{\partial E}{\partial T} = \frac{s(N)}{2N} + \frac{1}{NT^2} \left( \langle U^2 \rangle - \langle U \rangle^2 \right). \]

6. The coefficient of thermal expansion:
\[ \alpha_v := \frac{\partial P}{\partial T} = V \left( \frac{\partial P}{\partial V} \right) = -P + \frac{1}{9V} \left( \langle F^2 \rangle - \langle F \rangle^2 \right). \]

7. The isothermal compressibility:
\[ \kappa_T := V \left( \frac{\partial P}{\partial V} \right) = -P + \frac{1}{9V} \left( \langle F^2 \rangle - \langle F \rangle^2 \right). \]

References