Discovery based approach to real gas properties using molecular dynamics simulation

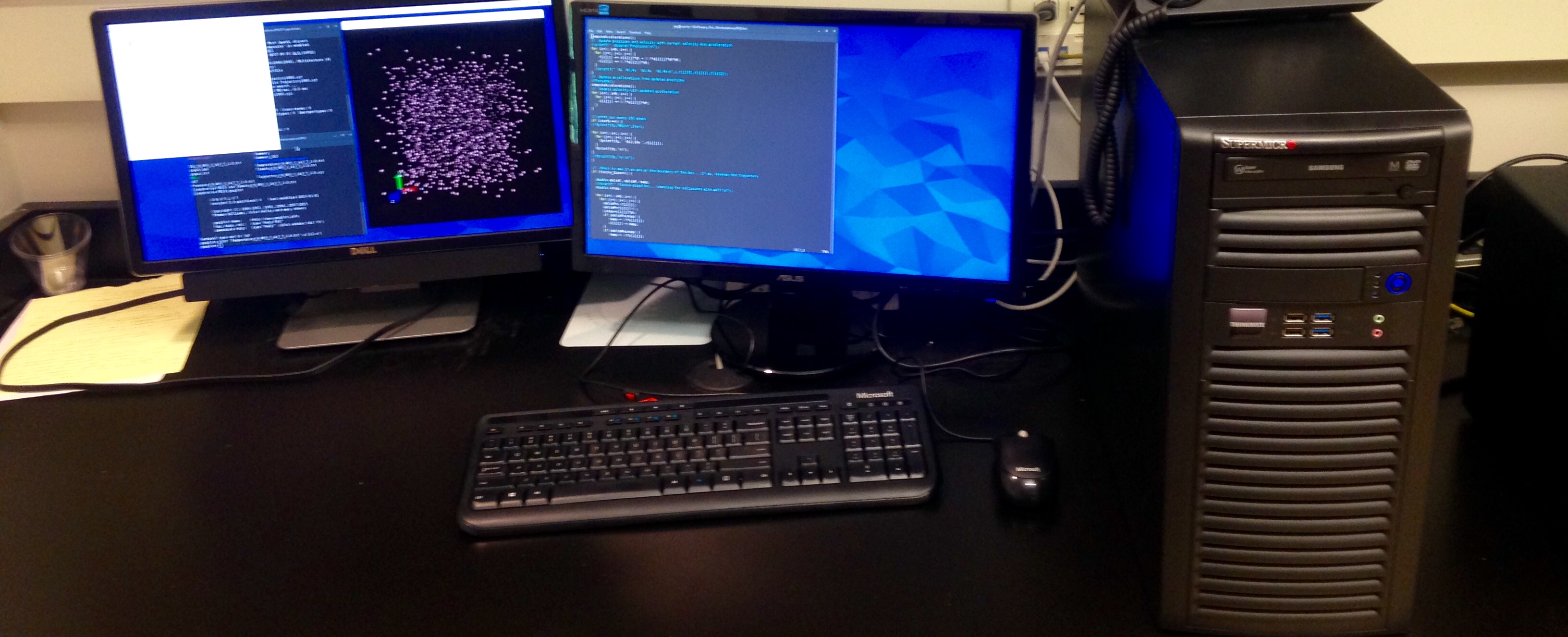
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Abstract

We present an interactive discovery-based approach to studying the properties of real gasses using simple, yet realistic, molecular dynamics software. Use of this approach opens up a variety of opportunities for students to interact with the behaviors and underlying theories of real gasses. Students can visualize gas behavior under a variety of conditions, they can implement kinetic theory expressions as computer code to compute macroscopic quantities from microscopic/kinematic behaviors of the simulated gasses, and they can explore strategies to quantitatively and qualitatively evaluate deviations from ideal gas behavior. A simple and fully-functional molecular dynamics program written in the C programming language that has been tested on Windows, Mac, and Linux platform accompanies this article, and detailed suggestions are provided for implementing this exercise with or without programming activities

Graphical Abstract



Keywords

[First-year undergraduate, Upper-Division Undergraduate, Physical Chemistry, General Chemistry, Computer-based Learning, Inquiry-Based / Discovery Learning, Gasses, Kimetic-Molecular Theory](http://pubs.acs.org/page/jceda8/topics.html)

Gasses are introduced in the elementary science curriculum as one of the fundamental states of matter, providing perhaps the first notion to students that matter is all around us all the time.1 Chemists in particular encounter the ideal gas law in a variety of contexts throughout their training. The ideal gas law is an important part of the particle theory of matter, and is useful in illustrating and quantifying the relationships between different measurable quantities that characterize a gas system.1,2 The ideal gas law is also used extensively to motivate thermodynamic processes and to analyze the changes in energy and entropy associated with them.2,3 Gasses also provide arguably the simplest regime for studying inter-molecular interactions.3,4 The fact that the ideal gas law has such remarkable predictive power in a variety of circumstances despite its neglect of inter-molecular interactions illustrates important concepts about the distance dependence of these forces. That is, the average inter-molecular distance is large in low-density gasses, therefore the average inter-molecular force is negligible. Despite repeated exposure, undergraduate chemistry students struggle to develop both a functional understanding of the ideal gas law and a solid conceptual understanding of the assumptions that define the ideal gas model (non-interacting point masses that undergo elastic collisions with the walls of their container).1-5 We have observed in our own Physical Chemistry curriculum that students also struggle to develop a functional understanding of “real gas” equations of state (e.g. Van der Waals equation) and sound physical intuition about the microscopic inter-molecular forces in gasses. We conjecture that exercises that enable students to develop mental models of realistic gas behavior and discover connections between microscopic and macroscopic properties of gasses will foster a deeper understanding of the phenomenology associated with gaseous matter.

In this article, we present a molecular dynamics simulation module that can aid discovery-driven study of monatomic gasses across the continuum of regimes between ideal and non-ideal behavior. We have utilized this program for physical chemistry laboratories where students discover the conditions under which deviations from ideality are observed in terms of qualitative behaviors observed in 3-D animations derived from the simulations, and in terms of quantitative observables such as the macroscopic compressibility () that can be computed from the simulation.3,6,7 Students may also use the simulation to explore connections between macroscopic indicators of non-ideality and microscopic quantities like the potential energy and kinetic energy. The full commented source code of this simulation, as well as directions for compiling and running the code on Windows, Mac, and Linux platforms, are distributed as a supplement to this paper. The simulation is based upon classical molecular dynamics simulation of particles that interact through the Lennard-Jones potential.6-9 In this technique, Newton's equations of motion are solved for all particles to render their motion in 3-dimensional space. Our code outputs the coordinates of each particle at each step in time in a format that can be readily rendered as an animation by the open-source program VMD10; instructions on obtaining and using VMD are also provided as a supplement. Kinetic theory is used to compute macroscopic quantities including the temperature and pressure from the time-average of the molecular dynamics trajectories.3,6 Microscopic quantities like the kinetic and potential energy of individual particles are also readily computed.

In the remainder of the paper, we will provide an overview of the salient details of molecular dynamics simulations, including a discussion of how macroscopic quantities are connected to the underlying microscopic information that molecular dynamics simulations directly provide. We also provide several suggestions for how to leverage these simulations for discovery-based exercises that can empower students to explore connections between microscopic and macroscopic properties of gasses, and also to develop an intuitive mental model of the behavior of gasses in ideal and non-ideal regimes.

Overview of molecular dynamics simulations

Our simulation module draws inspiration from the pioneering work of Aneesur Rahman, who reported the first molecular dynamics simulation that utilized a physically meaningful potential in 1964.8 Rahman’s seminal paper described a simulation of 864 Argon atoms interacting through a Lennard-Jones potential, and showed that many known experimental properties could be reproduced by such simulations with surprising fidelty.8 A tremendous amount of progress has been made in the development and application of molecular dynamics methods in the decades since its invention so that now [it’s such a great tool, here are some examples.]

The underlying concept behind MD simulations is remarkably simple: atoms and molecules exert forces on one another that affect their motion, and the changes in motion due to these forces can be predicted to high accuracy by solving classical equations of motion, i.e., Newton's 2nd Law. This is concept is similar in spirit to the types of kinematics problems undergraduate students encounter in their general physics course: identify the forces acting on a particle of known mass (e.g. a baseball), then find its position and velocity at some time in the future given its current position and velocity. The two challenges in the case of MD simulations are (i) the calculation of the appropriate forces on the particles and (ii) the solution of the equations of Newton's 2nd Law for the very large number of particles that arise in typical simulations. A variety of computer algorithms are available that permit Newton's Law to be solved for many thousands of atoms even with modest computational resources. In this work, we utilize the Velocity Verlet algorithm to update the positions and velocities of the particles once the forces have been computed.6 Using the Velocity Verlet algorithm, the position of the particle is updated from time to time according to

where represents the position vector of the particle at time , represents the velocity vector of the particle at time , and, represents the acceleration vector of the particle at time . In our MD program, we use a Cartesian coordinate system so has ancomponent: + and similarly for and . In the previous expression, is the unit vector along the *x*-axis. The velocity of the particle is updated is updated from time to time according to

and the acceleration comes from Newton's 2nd law, Practical application of the Velocity Verlet algorithm requires the specification of an initial position and initial velocity for each particle. In this work, the initial positions are specified by arranging the atoms in a simple cubic lattice, and the initial velocities are assigned based on the Maxwell-Boltzmann distribution corresponding

to a user-supplied initial temperature.

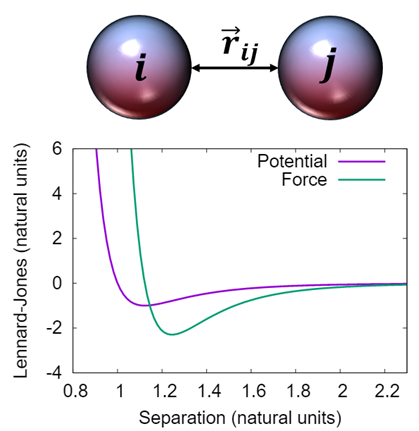
A key ingredient in a molecular dynamics simulation is the potential energy function, also called the force field. This is the mathematical model that describes the potential energy of the simulated system as a function of the coordinates of its atoms. The potential energy function should be capable of faithfully describing the attractive and repulsive interparticle interactions relevant to the system of interest. For simulations of complex molecular or biomolecular systems with many different atom types, the potential energy function may be quite complicated, and it’s determination may itself be a subject of intense research (see, for example, Refs. [11-13] and references therein). Because we are interested in simulating monotomic gasses, we use a particularly simple potential energy function in our simulation known as the Lennard-Jones potential, which was also used in Rahman’s original work,

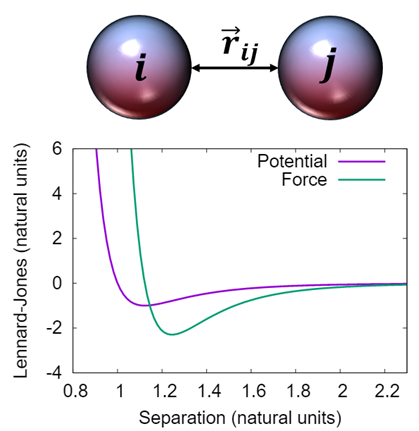
The Lennard-Jones potential is defined by two parameters, and , which may be determined by fitting simulations to experimental data, through *ab initio* calculations, or by a combination of experiment and calculation. The parameter is related to the strength of the interparticle interactions and has dimensions of energy. The value of manifests itself as the minimum value of the potential energy between a pair of particles, , as shown in the plot of the Lennard-Jones potential in Figure 1. The parameter is related to the effective size of the particles and has dimensions of length. In effect, the value of determines at which separations attractive forces dominate and at which separations repulsions dominate. For example, the value of determines the interparticle separation that minimizes the Lennard-Jones potential by the relation where , as shown in Figure 1. Importantly, only the scalar separation between a pair of particles is needed to determine the potential energy of the pair within the Lennard-Jones model. The total potential energy of the system of *N* particles is simply the sum over the potential energy of all unique pairs. This potential neglects orientation effects which may be important for describing molecules that lack spherical symmetry, and also neglects polarization effects which may arise in many chemically relevant situation, water for example.11

Once the potential energy function has been specified, the forces on the particles may be calculated from the derivative on the potential energy function with respect to interparticle separation *vectors:*

That is, each particle experiences a unique force from each of the remaining particles in the system. Each unique force is related to the derivative of the potential energy with respect to the separation vector of the particle pair,

Note that unlike the potential energy, the pair force is fundamentally a vector quantity and has a direction associated with it. We note that the two terms in the force can be equivalently evaluated in terms of the scalar separation, , because they contain even powers of the separation vector, and even powers of the separation vector are equivalent to the same even power of the scalar separation. Once all the unique pair force vectors are determined from evaluation of Equation (5) based on the coordinates of the system, the total force vector acting on the particle is computed as the sum over all the unique pair forces. Hence, the potential energy function is a key ingredient in determining the dynamics through its impact on the forces through Equation (4), and therefore, the instantaneous position and velocity through Equations (1) and (2), respectively. The instantaneous positions and velocities of the particles constitutes the raw data generated by a molecular dynamics simulation. These trajectories may be directly visualized using animation software (e.g. VMD), and a variety of physical quantities can be derived from information contained in these trajectories.

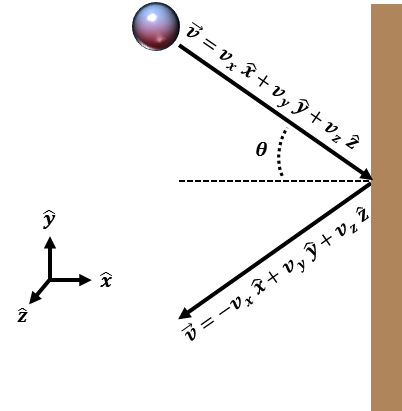




**Figure 1** Illustration of Lennard-Jones potential (purple) and Lennard-Jones force (green) as a function of separation between atoms i and j. All quantities are plotted in a natural unit system where and A table of L-J parameters in SI units for various noble gasses is provided in Table S1 in the Supporting Information.

Two relevant macroscopic quantities that can be derived from molecular dynamics trajectories are the pressure and temperature of the system. As in kinetic theory, the pressure in our program is taken to arise from the changes in particle momentum associated with elastic collisions with their “container walls”, i.e., the boundaries that constrain the particles being simulated. We take the gas system to be constrained by a cubic box with a user-supplied volume. All gas particles in the simulation are given initial positions within the boundaries of this box, and if a gas particle’s position reaches the boundary along a particular axis (say the *x-*axis), the corresponding (*x-)* component of velocity is simply reversed, simulating an elastic collision (see Figure 2). An instantaneous pressure can be defined by accounting for all such momentum changes that occur in a particular time interval,

In this expression, the index runs only over the particles that suffer collisions with the walls, and the index runs over only the components of the velocity that change upon collision with the walls. Figure 2 illustrates a particle colliding elastically with a wall and experiencing a change in the *x*-component of its velocity vector; this collision results in a change in the *x*-component of the particles momentum vector with magnitude



**Figure 2** Schematic of an elastic collision of a particle with its container wall. The particle reaches the container boundary along the x-axis, and so experiences a change in its x-component of velocity. This change in velocity is associated with a change in the x-component of momentum, as well. The sum over all such momentum changes in a given time interval can be interpreted as the instantaneous pressure within the kinetic theory of gasses.

Similarly, within kinetic theory, the instantaneous temperature can be related to the mean squared velocity at a given instant in time by

where the mean squared velocity is defined as

is the particle mass and is Boltzmann’s constant. The thermodynamic pressure and temperature can be approximated time average of the instantaneous and over the duration of the simulation,

and similarly, for the pressure.

molecular dynamics simulation for discovery-driven study of gasses

Realistic computer simulation offers many opportunities to study gas properties and behavior that would not be feasible in the undergraduate experimental laboratory. In particular, it offers access to microscopic insight and yields high precision information about macroscopic quantities provided the simulations are suitably performed. Here we describe several exercises that can be implemented in chemistry courses at the introductory to advanced undergraduate level that can be performed without modification to the software. We provide additional exercises that require programming that can be used for advanced courses that cover computational chemistry content. All of the following exercises assume students have become familiar with the process of changing simulation parameters, running the simulation, and collecting/analyzing/animating the resulting output data. Details on executing these steps on a PC, Mac, and Linux systems are provided in the Supplemental Information. We recommend that all simulations limit the number of particles to roughly 1000 so that simulations can be performed in a reasonable amount of time. Hence, reference to varying the density of particles as a parameter may be viewed as varying the volume of the simulation box while holding the number of particles fixed at ~1000.

Qualitative Assessment of ideal and non-ideal behavior

An extremely powerful aspect of molecular dynamics simulations is that they yield physically meaningful trajectories of chemical systems that can be rendered as movies, and these movies enable investigators to visualize the behavior of complex systems in ways that are extremely difficult, or even impossible, using experimental means. The accompanying MD program can be leveraged for a simple discovery-driven exercise that serves to enhance students intuition and qualitative understanding of ideal and non-ideal behavior of gasses.

Instruct students to use animations of MD trajectories to identify the density and temperature conditions that give rise to the three distinct types of gas behavior: (1) ideal behavior, (2) non-ideal behavior where attractive forces dominate, and (3) non-ideal behavior where repulsive forces dominate. Students may be guided to observe features of the gas behavior including (a) the average separation of the gas particles, (b) the frequency of wall collisions relative to the frequency of inter-particle collisions, (c) the apparent speed of the gas particles, (d) the persistence of particle clusters resulting from attractive interactions, (e) the frequency of collisions that lead to apparent acceleration due to repulsive interactions. Furthermore, students may be asked to hypothesize about the origin of these qualitative behaviors and devise further experiments with the simulation parameters to test their hypotheses. For example, a student may hypothesize that the frequency of ‘repulsive collisions’ may increase with increasing average velocity of the particles, and could test this hypothesis by running a series of simulations with progressively larger initial temperatures.



**Figure 3** Screenshots from animations of molecular dynamics simulation of 1000 Ar atoms. Panel (a) shows Ar simulated under low density conditions where nearly ideal behavior is observed (. Panel (b) shows Ar simulated under higher density and low pressure where deviations from ideality are observed due to attractive forces

Quantitative Assessment of ideal and non-ideal behavior

The previously-described activity can be augmented by asking students to report the macroscopic compressibility associated with each simulation that they run. The macroscopic compressibility, defined as , can be seen as a quantitative measure of ideal and non-ideal behavior.3 For ideal gasses, for non-ideal gasses where repulsive forces dominate and when attractive forces dominate. This quantity can serve as an anchor for students in their qualitative assessment of gas behavior, as well. For example, students may be asked to describe the differences between a non-ideal gas system where and a system where rather than attempting to identify attractive behavior, broadly speaking.

While the compressibility serves as a macroscopic indicator of deviations from ideality, the relative magnitude of the gas systems potential and kinetic energy can be readily computed and provides a measure of ideality that is microscopic in origin. Tracking these quantities along with the compressibility will reinforce valuable concepts about the dominance of the kinetic energy in gas systems that are nearly ideal, which is why the ideal gas model works so well.

Testing the limits of the ideal gas law

A remarkable feature of molecular dynamics simulations is that they can reproduce macroscopic properties with surprising accuracy even with a modest number of particles in the simulation. For example, the universal gas constant can emerge from the quotient even for , provided the conditions of the simulation are such that ideal behavior is approximately observed.

Students may be asked to report the value of the quotient for various simulation conditions and to comment on its agreement with the universal gas constant when ideal behavior is expected. Note that the agreement of this quotient with the universal gas constant will be limited in precision by the number of significant figures to which the gas properties (mass and Lennard-Jones parameters) are specified; this could be used to prompt discussion of propagation of error. For simulation conditions that result in deviations from ideal behavior, students may be asked to evaluate the accuracy of equations of state that account for interparticle interactions, such as the Van der Waals equation of state: .

Programming Kinetic Theory Equations

Developing computer code the computes the temperature and pressure from molecular dynamics trajectories can provide students a unique opportunity to interact with kinetic theory equations. The act of translating the equations into computer instructions requires students to break down the mathematics into elementary steps, which can aid their comprehension of the underlying equations. Furthermore, the process will require students to manipulate the microscopic quantities that give rise to the trajectories they see rendered as animations; this connection can also help students build conceptual bridges between the microscopic forces that lead to gas behavior and the macroscopically observable properties of the gas. Further suggestions for executing this programming exercise can be found in the Supporting Information.

Simulating different Noble Gasses

The identify of the particles being simulated can enter directly into the MD program through the particle mass and the Lennard-Jones parameters if standard unit systems are used, or indirectly through conversion factors for derived quantities (e.g. Temperature, Pressure, and Volume) if natural units are used.6,7 In this program, we use a natural unit system where the particle mass , the Lennard-Jones parameters and , and Boltzmann’s constant are all equal to 1 in natural units. The identity of the particles can therefore be changed by modifying the conversion factors for converting the volume, temperature, and pressure from natural units to SI units. Therefore, changing the identity of the particles serves as an additional programming exercises appropriate for physical chemistry students. Further instructions for executing this programming exercise can be found in the Supporting Information.

Associated content

Supporting Information

A well-commented and fully-functional version of our molecular dynamics code written in the C programming language is provided as associated content for this manuscript. We provide a Supporting Information document that contains detailed instructions for compiling and running the code, and rendering animations of the molecular dynamics trajectories using the open-source software VMD. In these instructions, we also provide instructions for obtaining the associated software through our github account. Further suggestions are provided that will aid programming of the kinetic theory equations and modifying the particle type for those wishing to perform the programming exercises suggested in this manuscript. Instructions are provided for Windows, Mac, and Linux platforms as appropriate.

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