Inquiry driven approach to Real Gasses using a DIY Molecular Dyanmics Simulation

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Abstract

What we present - interactive approach to studying the properties of real gasses. Basis of this approach - a DIY molecular dynamics program that enables students to interact with kinetic theory concepts in a variety of ways: (a) visualization of trajectories under a variety of conditions, reinforcing and clarifying fundamental concepts of particulate nature of matter and gas properties (b) programming kinetic theory expressions that connect the microscopic quantities that are directly computed by MD simulations (velocity, change in momentum) to macroscopic quantities T and P (c) Novel opportunities to quantitatively and qualitatively evaluate deviations from ideal gas behavior. A simple and fully-functional molecular dynamics code is provided written in simple C code that can be compiled and run on Windows, Mac, and Linux platforms.

Exercises: (1) Compute R and Z for several scenarios, visualize trajectories, compare Z to VDW equation (2) Determine Boyle temperatures (3) Compare isotherms with VDW equation

Graphical TOC Entry
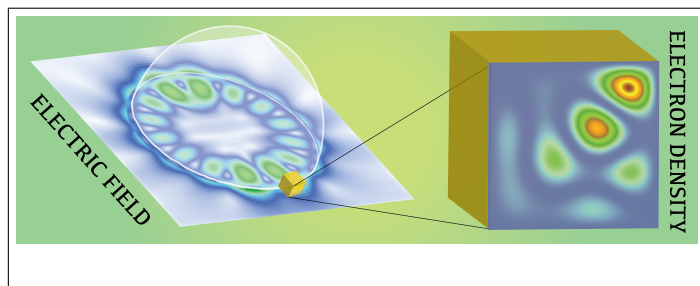
Introduction

The study of gasses has enabled a tremendous number of insights into the nature of chemical structure and reactivity, The study of gasses continues to have substantial pedagogical relevance. Gasses are introduced in the elementary science curriculum as one of the the fundamental states of matter, providing perhaps the first notion to students that matter is all around us all the time. Chemistry students encounter the ideal gas law throughout their education and in a variety of contexts. 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. The ideal gas law is also used extensively to motivate thermodynamic processes and cycles, and the changes in energy and entropy associated with them. Gasses also provide arguably the simplest regime for analyzing inter-molecular interactions. 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 lawand 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). 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 macroscopic equations of state, microscopic models of inter-molecular forces, and mental pictures of gaseous matter tend to lie in different conceptual domains, and that this creates an impediment to a deep understanding of gas properties and behaviors across a variety of chemically relevant contexts.

In this paper, we present a simulation module that can aid inquiry-driven study of gasses

across the continuum of regimes between ideal and non-ideal behavior. 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. In this technique, Newton's equations of motion are solved for all particles to render their motion in 3-dimensional space (i.e., molecular dynamics trajectories). 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 VMD (instructions on obtaining and using VMD are also provided as a supplement). Kinetic theory is used to compute macroscopic quantities including the temperature, pressure, and compressibility (which is a measure of deviation from ideality) from the time-average of the molecular dynamics trajectories. 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 inquiry-driven exercises that can enable students to discover connections between microscopic and macroscopic properties of gasses, and also to develop a intuitive mental model of the behavior of gasses in ideal and non-ideal regimes. We will conclude with suggestions for future advances that can leverage molecular simulation to advance students comprehensive of properties and processes of gasses.

Overview of Molecular Dynamics Simulations

Aneesur Rahman is credited as the pioneer of Molecular Dynamics (MD) simulations, having developed the first computer program to simulate the motion of a system of 864 Argon atoms

in 1964.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 Law). This is concept is similar in spirit to the types of kinematics problems students encounter in first year physics: identify the forces acting on a particle (e.g. a baseball), then find its position and velocity at some time in the future given its current position and velocity along with its mass. The two challenges in the case of MD simulations are the calculation of the appropriate forces on the particles and the solution of the equations of Newton's Law for the very large number N 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. Using the velocity verlet algorithm, the position of the ith particle is updated from time t to time $t + dt$ according to

$$\vec{r}_i(t + dt) = \vec{r}_i(t) + \vec{v}_i(t)\, dt + \frac{1}{2}\vec{a}_i(t)\, dt^2 \tag{1}$$

where $\vec{r}_i(t)$ represents the position vector of the ith particle at time t, $\vec{v}_i(t)$ represents the velocity vector of the ith particle at time t, and $\vec{a}_i(t)$ is the acceleration vector of the ith particle at time t. In our MD program, we use a coordinate system so $\vec{r}$ has an x, y, and z component: $\vec{r} = x\,\hat{i} + y\,\hat{j} + z\,\hat{k}$, and similarly for $\vec{v}$ and $\vec{a}$. The velocity is updated from time t to time $t + dt$ according to

$$\vec{v}_i(t + 1) = \vec{v}_i(t) + \frac{1}{2}\vec{a}_i(t)\, dt, \tag{2}$$

and the acceleration comes from Newton's law,

$$\vec{a}_i = \vec{F}_i/m_i. \tag{3}$$

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. The typical approach to calculating the forces is first to specify a potential energy function for the particles that models the attractive interactions atoms and molecules experience at moderate separations, and the repulsive interactions they experience at small separations. The forces on the particles are then calculated from the derivative of this function;

$$\vec{F}_i = \sum_{j \neq i}^{N} -\frac{dV(\vec{r}_{ij})}{d\vec{r}_{ij}}. \tag{4}$$

In the above expression, $\vec{F}_i$ is the force experienced on the ith particle in a N particle system due to its interaction with all of the remaining $N-1$ particles, and $\vec{r}_{ij}$ is the separation between particles i and j, defined as $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$. This expression assumes pair-wise interactions only contribute to the forces, this assumption can be very poor in some systems (e.g. water), as has been discussed extensively (see, for example, ...). In Rahman's original work, and in the present work, an simple pair potential known as the Lennard-Jones potential is used,

$$V(\vec{r}_{ij}) = 4\epsilon \left(\left(\frac{\sigma}{\vec{r}_{ij}} \right)^{12} - \left(\frac{\sigma}{\vec{r}_{ij}} \right)^{6} \right), \tag{5}$$

where the ϵ parameter defines the interaction strength and the σ parameter defines the effective length-scale of the interactions, which could be analogized to concepts like the Van der Waals radius of the atom or molecule. The specific value of these parameters can be obtained by experimental and theoretical methods. Remarkably, Rahman's early work simulating liquid Argon showed that this simple potential leads to the emergence of a large number of macroscopic properties that tracked experimental measurements with surprising fidelity. Importantly, the derivative of the L-J potential is smooth everywhere, which means

the force is well defined at all separations,

$$\vec{F}_{ij}(\vec{r}_{ij}) = \frac{23\epsilon}{\sigma^2}\vec{r}_{ij}\left(2\left(\frac{\sigma}{r_{ij}}\right)^{14} - \left(\frac{\sigma}{r_{ij}}\right)^8\right).$$ (6)

Boundaries must also be applied to the system of particles. In this program, we define the boundaries to be a cubic box with a user-specified volume with elastic walls. That is, when gas particles collide with the walls, the direction of their velocity changes while the magnitude stays the same. A schematic of a molecular dynamics program is provided in Figure X.

The raw data generated by a molecular dynamics simulation includes the positions and velocities of all particles over a series of discrete time-steps, which are called molecular dynamics trajectories. A tremendous amount of information can be recovered from these trajectories. It is the main purpose of this article to explore the connection between microscopic and macroscopic properties of gasses, so we focus on macroscopic properties including the pressure, temperature, and compressibility of the gas. From kinetic theory of gasses, the pressure can be related to the momentum change the particles experience from collisions with the wall.[?] An instantaneous pressure can be defined at time t_i by

$$P(t_i) = \sum_j^N = \frac{\Delta\vec{p}_j}{\Delta t}.$$ (7)

Also using kinetic theory, the temperature can be related to the mean squared velocity by

$$T(t) = \frac{m\langle v^2(t)\rangle}{3k_B}$$ (8)

where the mean squared velocity is defined as

$$\langle v^2 \rangle = \frac{1}{N}sum_i^N \vec{v}_i(t)$$ (9)

The thermodynamic pressure and temperature can be determined from the time average of the instantaneous T and P.

Associated Content

Additional Figures illustrating hot carrier distributions and dynamics, as well as details of the time-dependent configuration interaction singles method and the finite-difference time domain simulations are provided in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org

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