Molecular Dynamics Fluctuation

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(Dated: May 2024)

I. MOTIVATION

Throughout the Physics 140A course, students learn in detail about the physical principles governing quantum systems. To fully comprehend these principles, it is necessary to visualize and understand the statistical framework processes. To process information from these systems in a semi-classical way, we will be using the Molecular Dynamics Simulation. By utilizing the Molecular Dynamics Simulations, we can understand the relationship between each microscopic particle and how they relate to broader state variables, such as temperature and pressure. By using this simulation we can generate a large amount of data quickly, allowing us to implement and prove the statistical methods learned in class. Even though this system calculates forces in accordance with Newton's laws, we observe behaviors reflective of real-life quantum systems such as phase change and crystallization.
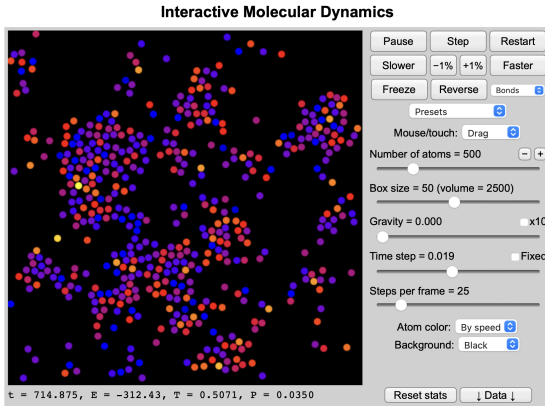

FIG. 1: Interactive Molecular Dynamic Simulation's interface

II. BACKGROUND INFORMATION

The Molecular Dynamics simulate the Brownian motion of particles inside the 2d box. All the particles' motion is governed by Newton's Law of motion $\Sigma F = ma$, when the interaction between each particle is governed by the Lennard-Jones Potential model, giving the potential energy as a function of the distance between the particles. We then solve differential equations using the Velvet Algorithm.
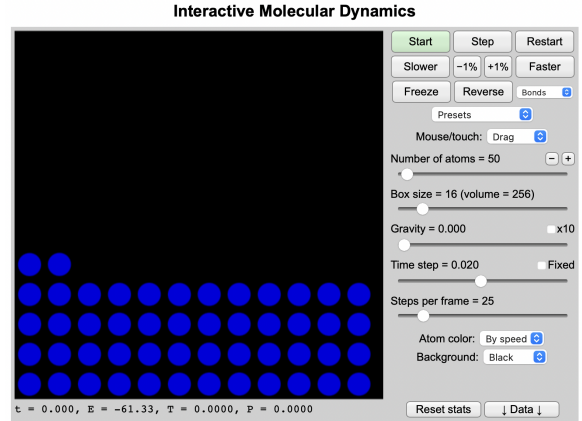

FIG. 2: Initial state when time = 0

A. Lennard-Jones Potential

The Lennard-Jones Potential describes the potential energy of the interaction between two non-bounding molecules based on their distance of separation. The Lennard-Jones Potential is given by,

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \quad (1)$$

When ϵ is the Lennard-Jones potential depth (set to 1) and σ is the van-der-Waals radius or

the distance in which the potential between two molecules is zero.

From the Lennard-Jones Potential, we derive the force on a particle by, $F = -\nabla V(r)$. In 1d, force on a particle is a negative slope of the Lennard-Jones Potential plot. Hence, at the global minima r_m, the force on the molecule is zero. When $r > r_m$ the force is attractive, and repulsive when $r < r_m$
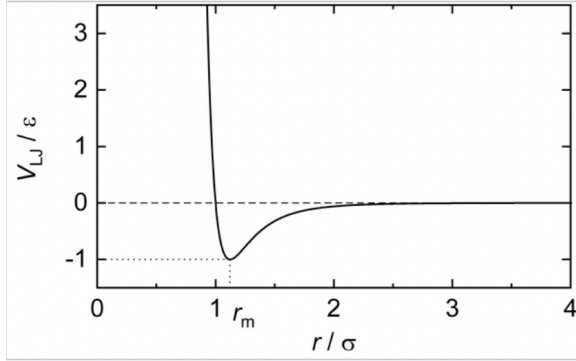

FIG. 3: Graph of Lennard-Jones Potential, when y-axis is the intermolecular potential and x-axis is the distance between a pair of particles

B. Energy of the system

The simulation calculates the total kinetic energy of the system using the formula $KE = \sum \frac{1}{2}mv_i^2$, where m is the mass and v_i is the velocity of each particle. The total potential energy of the system is obtained by summing over the Lennard-Jones Potential, $PE = \sum V_i$. The total energy of the system is the sum of the kinetic energy and potential energy, expressed as $E = KE + PE$.

The temperature is derived from the kinetic energy using the equation $KE = \frac{1}{2}dk_bT$, where d is the degree of freedom and k_b is the Boltzmann constant. The pressure is calculated from the ideal gas law, $PV = Nk_bT$, where P is the pressure, V is the volume, N is the number of particles, and T is the temperature.

When the speed of molecules exceeds the intermolecular forces holding them together, the molecules disperse and move freely within the container, resulting in a gaseous state macroscopically. On the other hand, when the particles move at a slower speed, the intermolecular forces bind all the molecules together, leading to a solid or liquid state macroscopically, depending on the molecular speeds. We can then use the "faster" and "slower" buttons to adjust the temperature of the system, consequently changing its state.
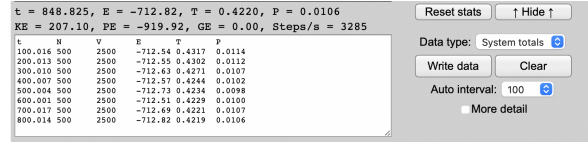

FIG. 4: Collecting data from the simulation

The Molecular Dynamics Simulation automatically computes and records various thermodynamic properties, including pressure P, temperature T, kinetic energy KE, potential energy PE, and total energy E.

C. Central Limit Theorem

The Central Limit Theorem (CLT) is a statistical theory that describes how the distribution of any samples can always be approximated as a Normal Distribution. As the number of samples increases, the standard error decreases, which can be expressed by the following equation:

$$\sigma_{\bar{x}} = \frac{\sigma}{\sqrt{N}} \qquad (2)$$

Where σ is the standard deviation, and N is the number of samples.

D. Maxwell-Boltzmann Distribution

The Maxwell-Boltzmann distribution characterizes how particle speeds are spread out over a range of values at a given temperature for ideal gases. The distribution indicates that most particles have speeds around a most probable value, with fewer particles moving significantly faster or slower. In other words, the particle's speeds follow a normal distribution. Mathematically,
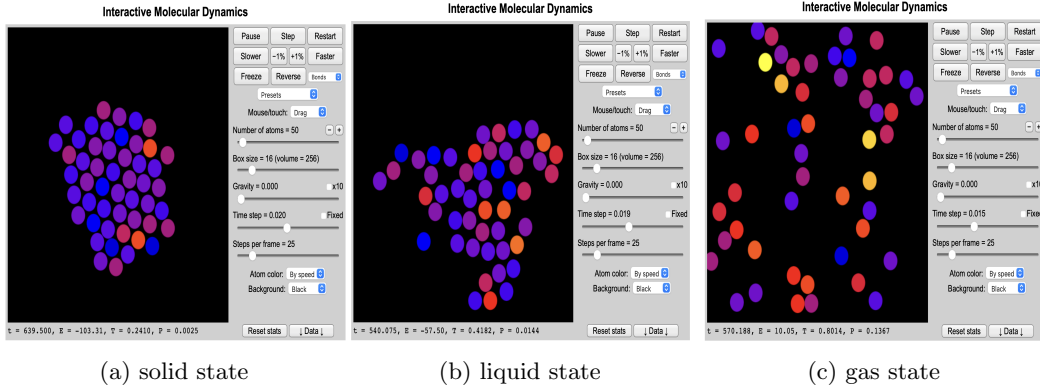
(a) solid state   (b) liquid state   (c) gas state

FIG. 5: The Molecular dynamic simulation of the system consisted of 50 molecules during the solid state at $T = 0.24K$, liquid state at $T = 0.41K$, and gas state at $T = 0.80K$.

the Maxwell-Boltzmann distribution is defined as

$$D(v) = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mv^2}{2kT}\right) \qquad (3)$$

III. PROBLEM: MOLECULAR DYNAMICS EXERCISE 17

The simulation calculates temperature by taking a time average of the average kinetic energy per particle. The time average is needed because the instantaneous average kinetic energy per particle fluctuates significantly for such a small system. To study these fluctuations, start with about 50 atoms in a volume of about 250, at a temperature of about 0.4, so the system consists of a liquid droplet surrounded by gas. While the simulation runs, use the Data panel to measure the total kinetic energy about a hundred times at regular intervals. Copy the kinetic energy values into a spreadsheet and for each, calculate the average kinetic energy per particle; then calculate the standard deviation of these measurements. Repeat this process for systems of about 100, 200, and 500 particles, keeping the density and temperature approximately fixed. How does the standard deviation vary with N? Next, hold N fixed and repeat the process at lower and higher temperatures where the system is entirely solid or entirely gaseous. De-

numbers of molecules	T = 0.21 K	T = 0.4 K	T = 0.69 K
50	0.00087	0.0019	0.0024
100	0.00057	0.00090	0.0014
200	0.00040	0.00088	0.0017
500	0.00062	0.00077	0.00072

TABLE I: Table of the standard deviation of the average energy per particle measured across the 12 trials. Data is used in Figures 6 and 7

scribe and interpret your results as completely as you can.

IV. SOLUTION

To generate our data, we fixed the particle density $= \frac{\#particle}{volume}$ constant at approximately 0.2 particles per unit of volume. Our system does not have gravitational force involved, and, to ensure the stability of our simulation, we fixed the time step at 0.019. For our data analysis, we collected the data at 100 s intervals, while ignoring the first few time steps, that represent the transient state. We, then calculate for the average energy per particle at each time step $\frac{\sum E}{N}$ and calculate for the standard deviation of the average energy per particle. Our recorded data is shown in Table I.

First, it is important to note that temperature affected the state that the particles were in. At 0.21 K the system was a solid, at 0.4 K

(a) solid state, temperature approximately 0.21 K

(b) liquid state, temperature approximately 0.4 K

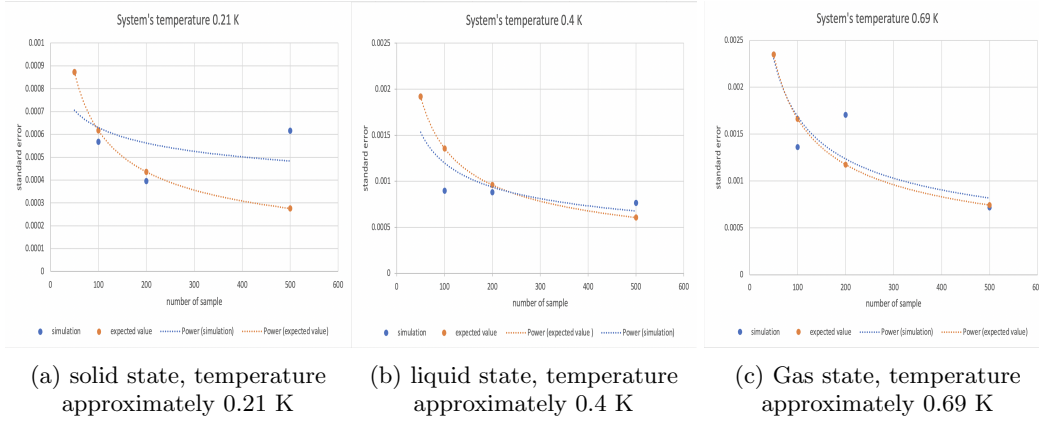(c) Gas state, temperature approximately 0.69 K

FIG. 6: the standard deviation of average energy per particle in the solid, liquid, and gas state. When the blue dot represents the value given by the simulation, the orange dot represents the standard deviation calculated from eq.2
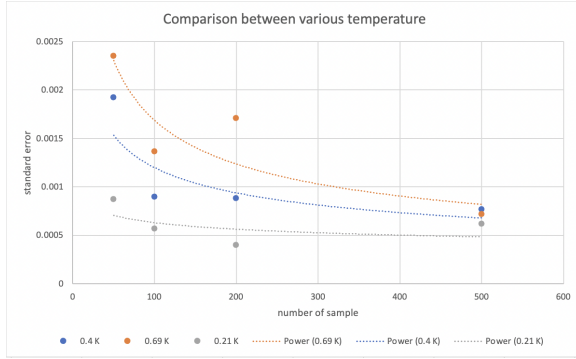

FIG. 7: comparison between the standard deviation of average energy per particle in the solid, liquid, and gas state

the system was a gas, and at 0.69 K the system was a gas. This will be important for our later analysis of Figure 6-7 where our data is shown.

Using the simulation for fixed particle volume and temperature and varying particle amount N resulted in the following trends shown in Figure 6. Here, the energy is proportional to $1/\sqrt{N}$ which means that the probability density function, or PDF, of energy for these systems follows a normal distribution.

Although Figures 6b and 6c's data closely align with our expected curves shown in orange, Figure 6a does not. We can deduce that the state of matter most likely is the contributing factor to this change. In a solid state, the system is more closely packed, meaning particles will have a much greater effect on surrounding particles, creating a distribution less characteristic of a normal distribution. In more fluid states, we see that our expected trend is followed more closely.

When observing our system in a solid state (Figure 6a), our curve is much more flat relative to our expected curve, showing that deviations in particle velocity are much more uniform across different numbers of particles when compared to other states of matter.

When in the gaseous state (Figure 6c), we see that our expected trend is followed almost exactly. And because energy is a function of velocity in this case, the PDF for the particle's velocity will also follow normal distribution since it is related to $1/\sqrt{N}$. This result agrees nicely with our conception of the Central Limit Theorem and more importantly agrees with the result from the Maxwell-Boltzmann Distribution.

Comparing all states of matter in Figure 7, we can deduce that the amount of energy per particle also increases as a function of temperature.