Maxwellian Distribution in Four Dimensional Classical LJ 6-12 Gas: A Study using Molecular Dynamics Simulation

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Abstract - *The speed distribution function of argon like molecules with LJ 6-12 intermolecular potential in four-dimensional space are investigated at different temperatures through molecular dynamics simulations. It is shown that even in case of argon like molecules in the 4-dimensional space the speed distribution function is Maxwellian.*

Keywords: Maxwell-Boltzmann speed distribution function, molecular dynamics simulation, LJ 6-12 intermolecular potential, four-dimensional classical gas, molecular chaos

1. INTRODUCTION

Using classical theory of ideal gases, the speed distribution function may be derived from the Boltzmann transport equation by considering the assumption of molecular chaos and a dilute enough gas so that only binary collisions are considered and higher collisions are ignored [1]. Maxwell-Boltzmann distribution function describes molecular speed distribution even in non-ideal gases in 1, 2 and 3-dimensional space [2] [3], in the presence of long-range interactions between the particles of the system such as Coulomb potential, as long as the assumption of molecular chaos remains valid [4]. Extremely dense fluid systems with strong interactions between its particles were investigated through molecular dynamics simulations. It was shown that even in these systems the speed distribution of the particles is Maxwellian and the assumption of molecular chaos remains valid [4].

2. MAXWELL BOLTZMANN'S SPEED DISTRIBUTION

If the 4-dimensional space is spanned by the unit vectors $\hat{e}_1$, $\hat{e}_2$, $\hat{e}_3$ and $\hat{e}_4$ and components of velocity along these unit vectors are v_1, v_2, v_3 and v_4 respectively, then velocity in this 4-dimensional space is given by $\mathbf{v} = v_1\hat{e}_1 + v_2\hat{e}_2 + v_3\hat{e}_3 + v_4\hat{e}_4$. Now Maxwell-Boltzmann probability distribution function of velocity for a one-dimensional gas is

$$f(v_1) = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(\frac{-mv_1^2}{2kT}\right) (1)$$

Assuming molecular chaos, the velocity distribution function in four-dimensional space can be written as the product of the one-dimensional distribution functions,

$$f(v_1, v_2, v_3, v_4) = \left(\frac{m}{2\pi kT}\right)^2 \exp\left(\frac{-mv^2}{2kT}\right) (2)$$

where $v^2 = v_1^2 + v_2^2 + v_3^2 + v_4^2$. then probability of finding a particle with velocity in the interval (v_1, v_2, v_3, v_4) to $(v_1 + dv_1, v_2 + dv_2, v_3 + dv_3, v_4 + dv_4)$ is $f(v_1, v_2, v_3, v_4) . dv_1 dv_2 dv_3 dv_4$. Transforming this probability to spherical coordinates in velocity space we get Maxwell-Boltzmann speed distribution in 4-dimensional space as

$$f(v) = \left(\frac{m^2}{2k^2T^2}\right) v^3 \exp\left(\frac{-mv^2}{2kT}\right) (3)$$

3. LENNARD-JONES 6-12 POTENTIAL

The Lennard-Jones 6-12 potential [5] is a simple mathematical model that approximates the interaction between a pair of neutral atoms or molecules. It was first proposed by John Lennard-Jones in 1924. It is given by

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

Where ϵ is the depth of the potential well, σ is that finite distance at which the inter-particle potential is zero and r is the separation between the particles. The r^{-12} term, which is the repulsive term, describes Pauli repulsion at short ranges due to overlapping electron orbitals, and the r^{-6} term, which is the attractive long-range term, describes attraction at long ranges (van der Waals force, or dispersion force). Using L-J 6-12 potential an expression for the net inter-molecular force between two molecules can be calculated just by evaluating the negative of the gradient of the potential with respect to r. This inter-molecular force may be attractive or repulsive, depending on the value of r. When r is very small, the molecules repel each other. The functional form of the attractive term has a clear physical justification, but the repulsive term has no theoretical justification. The repulsive term is due to the Pauli repulsion. r^{-12} term is taken as repulsive term as it is more convenient due to the relative computing efficiency of calculating r^{12} as the square of r^6.

4. MOLECULAR DYNAMICS SIMULATION OF 4-DIMENSIONAL GAS

As the actual atomic parameters are very small in SI units, we use a reduced system of units. In this system the mass m

of the argon gas molecule is the unit of mass and the diameter σ of the argon molecule is the unit of length.

For argon, the molecular mass and the Lennard-Jones potential parameters are [6],

m=6.63 x 10^{-26} Kg, σ=3.43 x 10^{-10} m, ε=6.76 x 10^{-21} J

Therefore, in our system of units, the unit of mass is m=6.63 x 10^{-26} Kg and the unit of length σ=3.43 x 10^{-10} m and unit of time=1.07418117 x 10^{-12} s. Finally, we take ε=6.76 x 10^{-21} J and ε/k=120K to be our units of energy and temperature, respectively, where k= 1.38 x 10^{-23} J/K is the Boltzmann's constant. This completes our system of units. Any other physical quantity in our simulations can be written as a combination of these units. All of the simulations, in 4-dimensions, were carried out using the velocity form of the Verlet algorithm [7] [8],

$$\xi_{n+1}= \xi_n + v_n\Delta t + \frac{1}{2} a_n (\Delta t)^2 \text{ (5)}$$

$$v_{n+1}= v_n + \frac{1}{2} (a_n + a_{n+1}) \Delta t \text{ (6)}$$

With a time step of 0.01 in the reduced unit and ξ stands for the distance along x_1, x_2, x_3 and x_4 axes. In this simulation total 65,536 (=16x16x16x16) argon like molecules were initially taken on 4-dimensional cubic lattice [9] with length of unit cell as 777.959 in the unit of reduced unit of length. Periodic boundary conditions were used to reduce the size effect of the system. Initial velocities of the particles are chosen as uniformly distributed random numbers between 1 and -1 in the unit of 314 m/s in each coordinate direction. after that centre of mass of the system is brought to rest. The temperature of the system was then calculated using the formula [10]
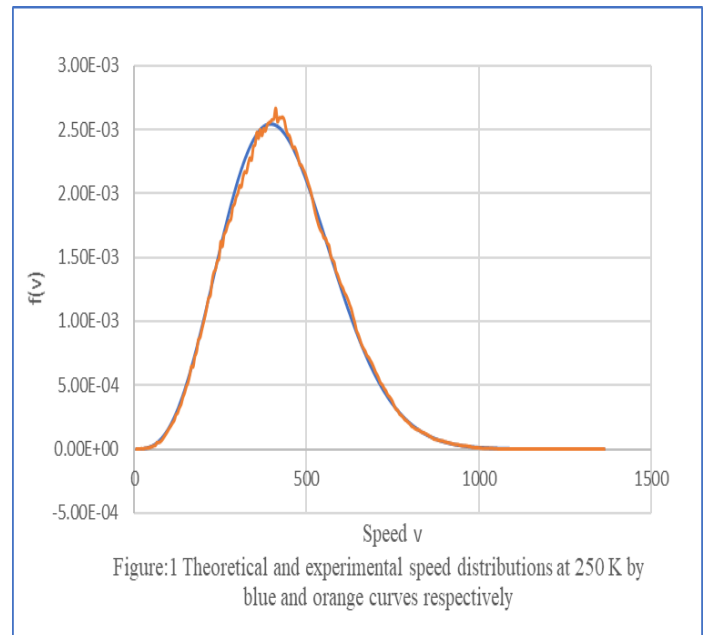
$$T= \frac{(\text{mean kinetic energy of the system})}{2 \times k} \text{ (7)}$$
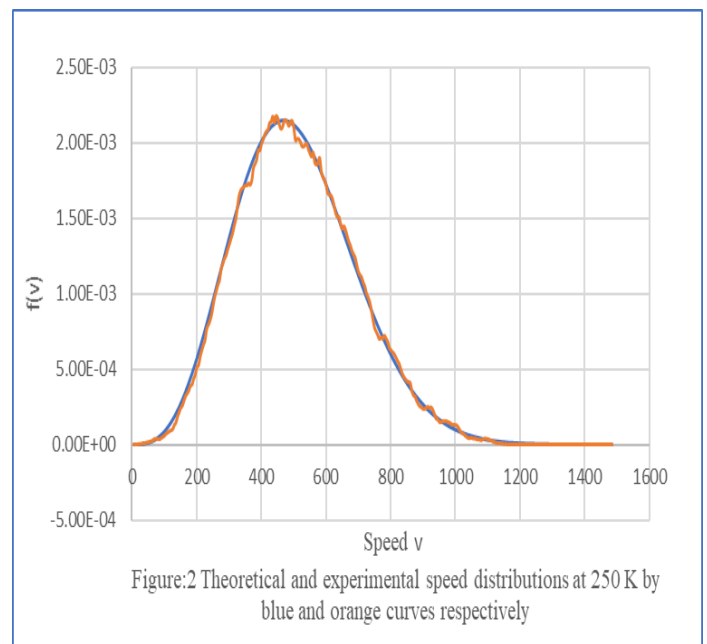
Where k is Boltzmann's constant.

Temperature of the system was brought to any desired value by rescaling the speed of each particle using the relation

$$\text{New speed} = (\text{previous speed}) \sqrt{\frac{\text{desired temperature}}{\text{actual temperature}}} \text{ (8)}$$

For argon like gas in 4-dimensional space at T=250 K, plot of f(v) is shown below-

Figure:1 Theoretical and experimental speed distributions at 250 K by blue and orange curves respectively

For argon like gas in 4-dimensional space at T=350 K, plot of f(v) is shown below-

Figure:2 Theoretical and experimental speed distributions at 250 K by blue and orange curves respectively

After 1000 time steps, system thermalized and then data were collected on the speed distribution of the particles over the next 10^5 time steps. Simulation was done at the temperatures T= 250 K and T=350 K. Temperature remained very steady throughout the simulation.

In figure:1 and figure:2 Speed distributions of argon like molecules in the 4-dimensional space are shown for T=250 K and T=350 K. In each of these figures theoretical curves of the speed distribution are shown by blue colour whereas curves obtained by simulation are shown by orange colour.

5. DISCUSSIONS AND CONCLUSIONS

In this study we have found that Maxwell-Boltzmann speed distribution function for ideal gas in 4-dimensional space is in good agreement with the curve obtained from simulation of the 65536 argon like molecules in 4-dimensional space at both temperatures that is T=250 K and T= 350 K.

As we know for the validity of Maxwell-Boltzmann distribution of speeds the system must be in the classical regime [11]. That is

$$\frac{n}{n_q} << 1 \quad (9)$$

Where n is particle density and n_q is quantum concentration of the system. In case of the system under consideration we have

$$n_q = \left(\frac{2\pi mkT}{h^2}\right)^2 \quad (10)$$

So for T= 250 K, we have

$$\frac{n}{n_q} = 2.45 \times 10^{-18} \quad (11)$$

and for T= 350 K, we have

$$\frac{n}{n_q} = 1.25 \times 10^{-18} \quad (12)$$

Therefore, the system under consideration is in classical regime at both temperatures that is T= 250 K and T= 350 K.

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