A Two Dimensional Molecular Dynamic Model For Thermal Lens Oscillation

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Abstract

A molecular dynamics simulation is designed to explain the thermal lens oscillation. Two type of Boundary condition were imposed to simulate the wall as a heat bath: 1) Redistributing the velocity of the particle hitting the wall and 2) Simulating the wall by layers of particles with the heating as the redistribution of lowermost the wall's velocity. Both of the boundary condition are checked to be sufficient to establish a canonical ensemble when the temperature gradient is set to zero. The surface tension of the system is calculated as the function of pressure, and the fluid velocity field are studied. However, the results were fluctuating due to the small size of the system.

Keywords: Molecular Dynamic, Thermal Lens Oscillation, Fluid Dynamics

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1. Introduction

Thermal lens oscillation is a phenomena that occurs as the horizontal laser is propagating through a fluid in a container. With low laser intensity, the laser induced density change in the fluid, leading to the gradient of refractive index. The fluid, acts as a lens, refracts the laser beam and creates the light ring in the projection. As the intensity of the laser beam increases, the natural convection occurs as a steady flow. Increase the intensity further, the flow increases and couples with the surface of the fluid in the chamber, creating an oscillatory or chaotic flow of the fluid which can be observed via the projection of the laser [1].

In addition, the system also has a real-world application on the precise method for measuring the organic solutions concentrations [2]. This make laser-induced thermal lens became the system of interest both in the theoretical and practical aspect.

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However, most of the investigation of the problem available is either a dimensional analysis, numerically solved with the complicated differential equations, or an analytic model with oversimplification of the phenomena (e.g. neglecting convection.) In the paper, we present a simple molecular dynamics model for the liquid heating that takes into account both the effect of convection and the effect of fluid surface with the hope to understand more on the phenomena and how it emerge from the microscopic perspective.

This paper will be organized as followed. Section 2 will be devoted to the background knowledge and theory that will be used throughout the paper. Section 3 explains how the model is formulated and show the consistency check of the model to justified the use if the model in later section. Section 4 studies the system from the prospect of the fluid property e.g. Surface Tension, Convection current. Section 4.2 and 5 discusses the result and conclusion respectively.

2. Background and theory

2.1. Molecular Dynamic

Molecular dynamic is a method in simulating the physical system by the microscopic description of the system e.g. molecule and its interaction. In classical system, this can be applied to the system by integrating newton's law for each particle in the system. Suppose there is a system composed of n particle in two dimensional space. The state of each particle can be described by its position and velocity. Therefore, the system can be represented by

$$s = [x_1^1, x_2^1, ..., x_1^n, x_2^n]$$

where x_1^i and x_2^i is x and y coordinate respectively.By applying the Newton law to the system one can find the acceleration of each particle by

$$\frac{d^2 x_j^i}{dt^2} = \frac{f_j^i(s)}{m_i}$$

where $j = 1, 2$ and where $f_1^i(s)$ and $f_2^i(s)$ is the force act upon the particle i in x and y axis respectively.

Then we can numerically solve the system with the Verlet algorithm [3]

$$v_j^i(t+\frac{1}{2}\delta t) = v_j^i(t) + \frac{1}{2}\delta t \frac{f_j^i(t)}{m_i} \tag{1}$$

$$x_j^i(t+\delta t) = x_j^i(t) + \delta t(v_j^i) \tag{2}$$

$$v_j^i(t+\delta t) = v_j^i(t+\frac{1}{2}\delta t) + \frac{1}{2}\delta t \frac{f_j^i(t+\delta t)}{m_i} \tag{3}$$

2.2. Lennard-Jones Potential

In molecular dynamic, one of the most common potential between between molecule is the Lennard-Jones potential and is defined by

$$U_{ij}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} \right] \tag{4}$$

Where $U_{ij}(r_{ij})$ is the potential of the particle pair i, j when the particle is r_{ij} apart However, with the long range potential, the computation of the potential energy and force could be computationally expensive. In order to reduce the computation, one can instead truncates and shifts the potential in such a way that the potential is continuous and smooth[4].

$$U_{ij}^{truncated-shifted}(r_{ij}) = \begin{cases} U_{ij}(r_{ij}) - U_{ij}(r_c) & r_{ij} < r_c \\ 0 & else \end{cases} \tag{5}$$

For the purpose of this simulation, the value $r_c = 2.5\sigma$ is used. This would also five the force of

$$F_{ij}^{truncated-shifted}(r_{ij}) = \begin{cases} F_{ij}(r_{ij}) & r_{ij} < r_c \\ 0 & else \end{cases} \tag{6}$$

Where the Force $F_{ij}(r)ij)$ can be calculated by

$$F_{ij}(r_{ij}) = -\nabla U_{ij}(r_{ij}) \tag{7}$$

quantity	unit	unit for Argon
Length	σ	$3.4x10^{10}$ m
Mass	m	$6.69x10^{-26}$ kg
Time	$\sqrt{\frac{m\sigma}{\epsilon}}$	$1.17x10^{-212}$ kg
Energy	ϵ	$1.659x10^{-21}$ J
Force	$\frac{\epsilon}{\sigma}$	$4.85x10^{-12}$ m
Temperature	$\frac{\epsilon}{k_B}$	120 K

Figure 1: The Natural unit in molecular dynamic

2.3. Dimensionless Quantity in Molecular Dynamic

For the complicated system with have the scale of phenomena so different from the standard unit, it is easier to redefined the dimensionless unit to describe the system. For the system of molecular dynamic, σ,ϵ, and $m_{molecule}$ would be the natural unit for the length, energy, and mass of the system. As a result, one can deduced other fundamental unit as followed for Argon Atom. From now on, we will use the natural unit for in every calculation and convert it back when we were analyzing the data unless state otherwise.

2.4. Periodic Boundary Condition

With the limitation of computational power, the molecular dynamic simulation can only describe the system up to 600 millions atom [5] and even less with the more complicated system. With the small size system, the effect of the boundary condition would be much stronger than the effect in the large system, and could potentially affect the system evolution. Therefore, periodic boundary condition is imposed so that the effect of the boundary can be minimized [3]. In this particular research, the left and right edge of the system will be imposed with the periodic boundary condition.

2.5. Virial Expression For Surface Tension

With the system described in section 3 one can find the surface tension of the system from a statistical ensemble [6]

$$\gamma L = \left\langle \sum_{i<j} (r_{ij}^2 - 2z_{ij}^2) \frac{u'_{ij}}{r_{ij}}) \right\rangle \tag{8}$$

where L is the circumference of the system. r_{ij} is the distance between particles, z_{ij} is the vertical distance between particle. u'_{ij} is the derivative of the potential between particle. The angle bracket indicate the average over all the possible ensemble of the system. In molecular dynamic, this is equivalent to finding the average of the value inside the bracket for a state and average it over time.

2.6. Pair Correlation Function

In order for us to determine the phase of the matter whether it is solid, liquid, or gas, we need a systematic way of calculated a related quantity. A simple way to distinguish those phase is to see how the particle "clump" together. For solid, the particle should have a regular spacing. For liquid, the particle should be somewhat more mixed. For gas, particle distance should be mostly independent from one another. To quantify the "clumpness" of the system, the pair correlation function is defined.

Pair correlation can be defined as an normalized average over reference particle density of the particle at distance r from the reference particle which can be calculated in two dimension by

$$g(r) = \frac{1}{2\pi r\rho} \langle \delta(r - r_i) \rangle$$

where ρ is the average number density of the particle, δ is Dirac delta function, and r_i is the distance between particle pair. The average is taken over all the existing particle. The factor of $2\pi r$ is corresponding to the fact that the area enclose by radius r to $r + dr$ is growing as r increase; thus, there are more chance of having particle at large distance even though the particle is distributed randomly. Computationally, this is done using using histogram of the radial distribution, then normalized each bins by the number of particle and the infinitesimal area $2\pi r dr$.

3. Computational Model and Justification of The System

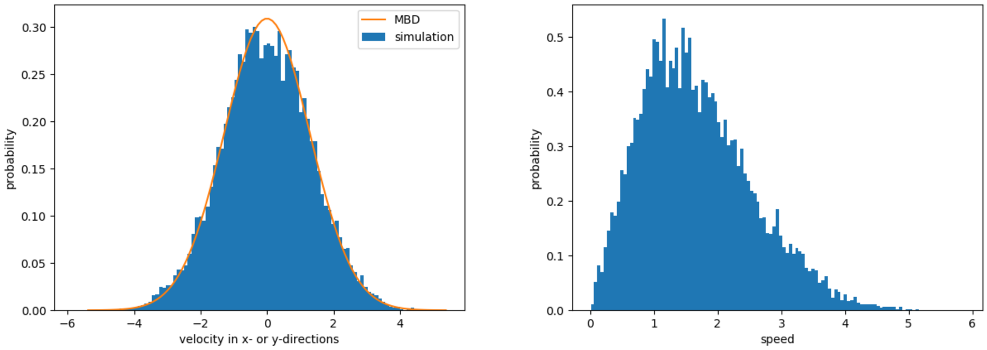
3.1. Heat Bath

Firstly, we need to create a computational model which simulated the system of particle while being able to control the temperature of the system. For this part, we imposed the boundary condition between the upper and lower wall of the system to mimic with the connection of thermal bath by redistributing the vertical velocity of the particle that exceed the wall limit accordingly to Maxwell-Boltzmann distribution.

```
0: procedure THERMAL WALL REFLECTION
  for particle ← System do
    if location(particle) within Box then
      Do nothing
    else
      redistribute velocity by $V_y(particle) \sim \mathcal{N}(0, T_{wall})$
    end if
  end for
```

Figure 2: Wall Reflection Algorithm

With the algorithm described in Figure 2, one can simulate the system to check the velocity histogram of the particle and comparing it with the Maxwell-Boltzmann distribution to check the consistency of the particle distribution. Note that this is not trivial since we only redistribute the velocity on the edge, not the whole particle system. According to Figure 3, one can see the consistency between the particle velocity distribution and the expected distribution according to the Maxwell-Boltzmann distribution. This validate our simulated heat bath.



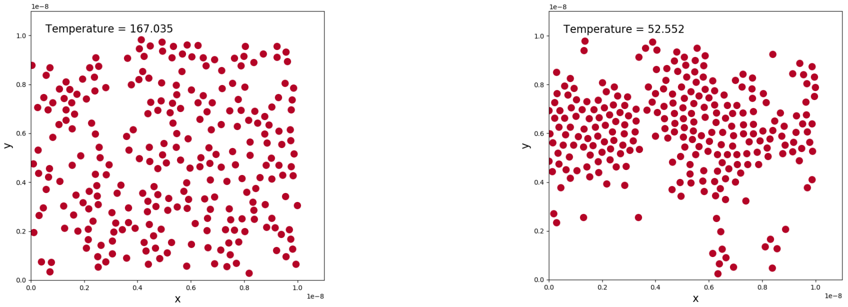
(a) (b)

Figure 3: Histogram of the particles' velocity in natural unit in the system of 1024 particles at 200K after leaving the system for 10000 steps. Figure 3a shows the distribution the velocity in natural unit of the system in horizontal /vertical axis in a blue line and the Maxwell-Boltzmann distribution in orange line. Figure 3b shows the distribution the magnitude of the velocity of the particle

3.2. Phase of the System

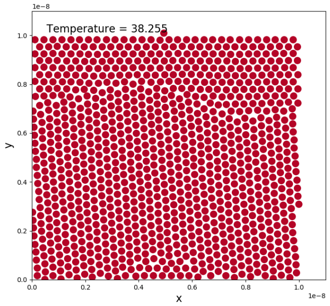
With the simulation of heat bath, one can adjust the temperature of the system and observe the state of the system at a different temperature. The Figure 4 shows a snapshot of the system at different phases. One can see that for a high temperature system in 4a, the particle scatter over the box and there is no qualitative phase boundary. However, as the temperature is lowered in 4b, most of the particles cluster together with a few of them which can escape the cluster and moving freely. This will be our system of interest because it exhibits the clear phase boundary between the clustered particles(liquid) and free particles(gas).

To justify that the real phase of the Lennard-Jone particle is consistence with our qualitative explanation in the paragraph before, the pair correlation of the state is calculated in Figure 6. One can see that for gas in Figure 6a, the system have only one small peak which corresponds to the effective radius of the gas particle. As the distance increases, the correlation function converge to the true density just like what we expect from a random distribution. For liquid in Figure 6b, there exist couple peaks before the pair correlation converge to true density, this mean that the particle is more clump than gas but still not regularly space as in solid. For solid in Figure 6c,one can clearly see the periodic peak which can be interpreted as the particle which is regularly space in the lattice. With the consistency between our intuition about phase of the system and the pair correlation function, we can justify that our system of interest resembles the real fluid system.



(a) N = 256, T = 167K

(b) N = 256, T = 53K



(c) N = 1024, T = 38K

Figure 4: The 2D Lennard-Jones system in a 10nm box with temperature 167K For 4a, 50 K for 4b, and 39K for 4c

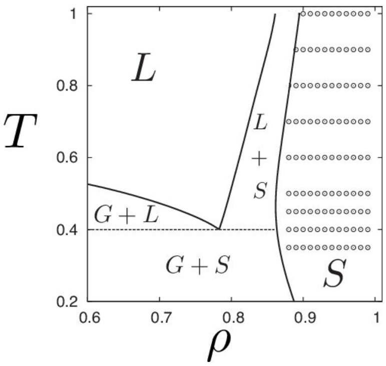
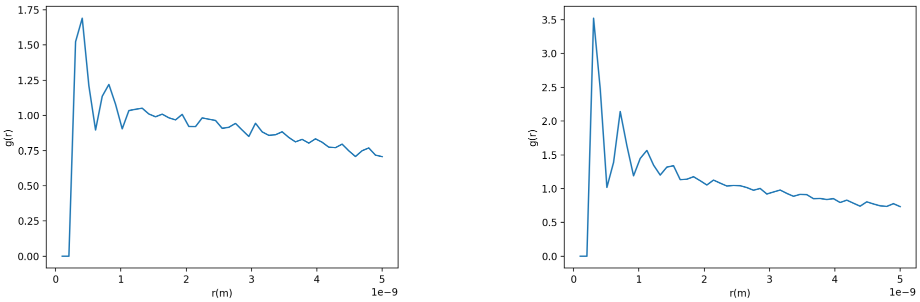
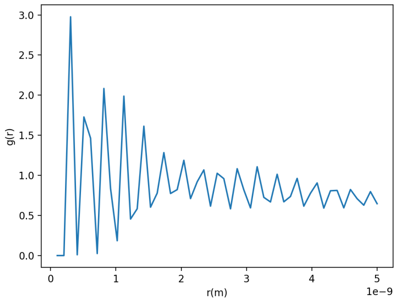


Figure 5: Phase diagram of 2D Lennard-Jones. Reprinted from "Nonaffine heterogeneities and droplet fluctuations in an equilibrium crystalline solid" by T. Das, S. Sengupta, M. Rao, 2010, Physical review. E, Statistical,nonlinear, and soft matter physics 82



(a) N = 256, T = 167K (gas)

(b) N = 256, T = 53K (liquid)



(c) N = 1024, T = 38K (solid)

Figure 6: The figure show pair correlation function for the system in different phase of matter.

3.3. Surface Tension Between The Wall and The System

Even though we impose the heat bath, and the boundary condition on the system, we found that after we include the gravity in the model, there exists a problem in the simulated heat transfer in the system. For the gravity pull the liquid particles toward the lower edge of the box, the reflection from the wall create the gap layer between the wall and the fluid as in Figure 7, disrupting its heat transfer from the heat bath. This occurs because the wall and the liquid have no interaction e.g. surface tension , mimicking the wall with super-hydrophobic property.

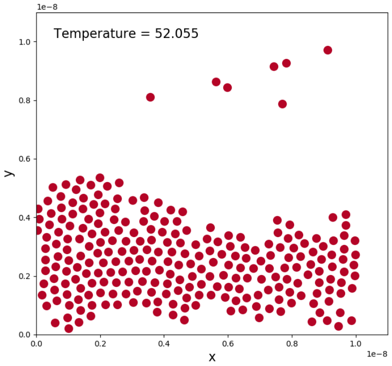


Figure 7: A snapshot of the system at 50K (The Temperature shown in graph is the instantaneous temperature) when impose with the gravitational field of 5g

In order to resolve the problem, we model the lower edge of the box as a solid particle with the same σ as the fluid but with higher binding energy($\epsilon = 20\epsilon_{fluid}$.) Also, the coupling parameter between the wall and the fluid, σ and ϵ, is chosen to be the same as the parameters of the fluid to keep the wall to be neither extremely hydrophilic or hydrophobic. For the heat transfer of the system, we impose the velocity of the lowermost layer of the wall. With enough layer of the particle, the upper layer of the wall should exchange the energy with the lowermost layer and become in thermal equilibrium with the heat bath. Then, the uppermost layer of the wall will act as a heat bath itself during the process of heat transfer between the wall in the fluid.

Note that the Lennard-Jones parameter for the wall shouldn't affect our system as long as the wall stays solid.Even if the stronger binding force would decrease the oscillation amplitude of the wall, it would also increase a natural frequency of the wall too. The two effects cancel each other and resulting in the same velocity distribution, which is the principal part of the heat transfer (Naively, one can think of it as an elastic collision of the particle against the wall where the velocity change of the particle only depends on the wall's velocity.) Also, to make sure that the wall have zero net momentum, the average velocity of all the particle in the wall is subtracted. For this paper, we decided to use 5 layers of particle for the wall since it is the smallest number of layer having the Maxwell-Boltzmann distribution as shown in Figure 9.

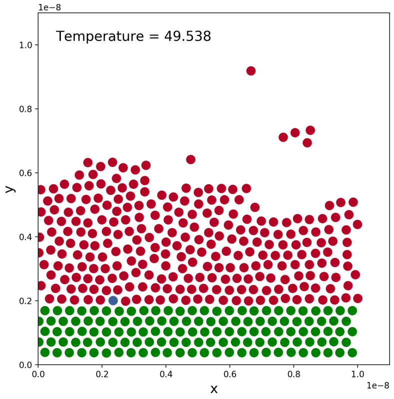
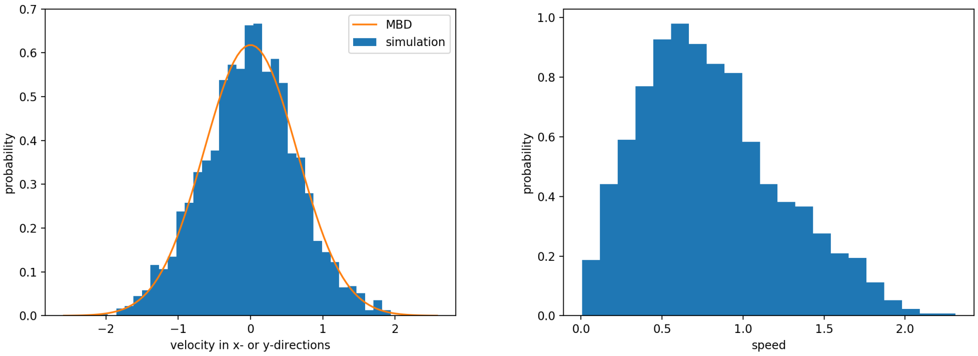


Figure 8: The system of 260 particles in a box of size 10nm at 50K with 50g (The Temperature shown in graph is the instantaneous temperature). The red and blue particle is the fluid(blue is only for tracking purpose.) The green particle is the solid imitating the wall



(a) (b)

Figure 9: Histogram of the wall's velocity(not including the lowermost layer) in natural unit in the system with 5 layers of wall particles at 50K after leaving the system for 20000 steps. Figure 9a shows the distribution the velocity in natural unit of the system in horizontal /vertical axis in a blue line and the Maxwell-Boltzmann distribution in orange line. Figure 9b shows the distribution the magnitude of the velocity of the particle

4. Results and Discussion

4.1. Surface tension as a function of temperature

The time-averaged surface tension of the system is shown in Figure 10. One can see the convergence of the surface tension in figure 10a, 10b, and 10d. However, Figure 10c seems to keep increasing even after 1.6 Million iteration. The possible explanation is that the system at the parameter is quasi-periodic with the low Lyapunov exponent. This mean that the system filled up the phase space slowly and mostly it stuck in the similar phase region. Thus, the time average of the surface tension will not reflects the true canonical ensemble of the system. However, as one plot the surface tension as a function of temperature, one can still see the pattern that as the temperature increase, the surface tension decreases consistently. This agrees with our intuition of the surface tension since the increase of temperature will make the molecule less bounded to one another.

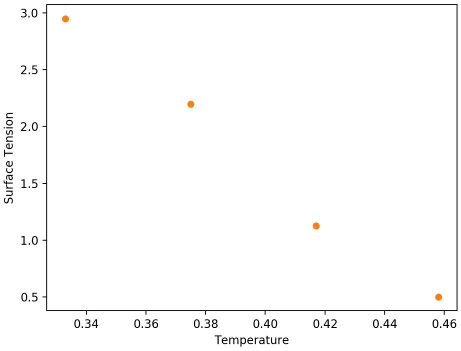
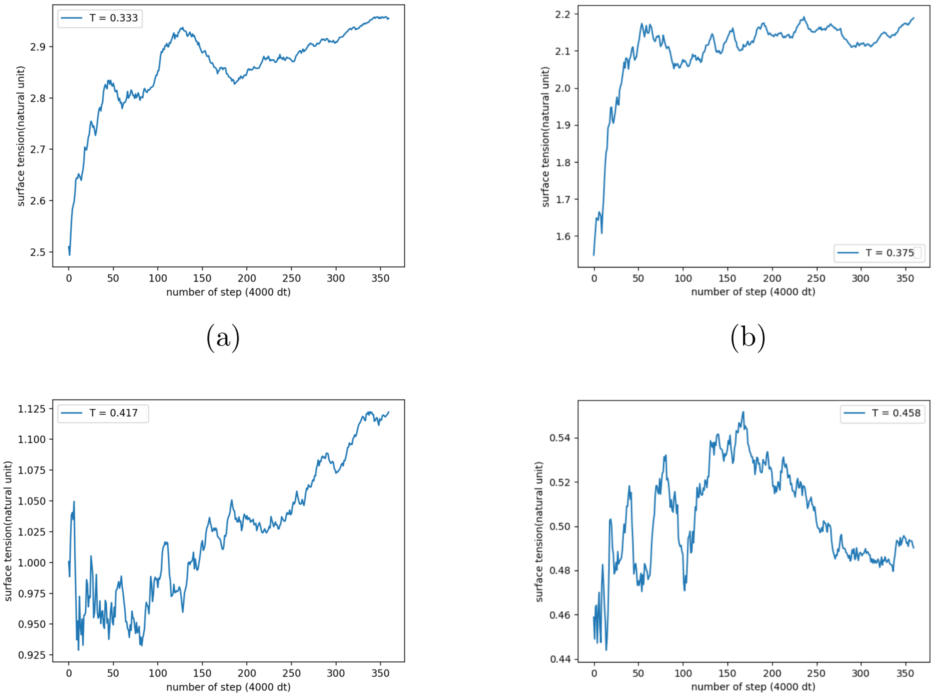


Figure 11: A Graph between temperature and the surface tension of the system in natural unit



(a)

(b)

(c)

(d)

Figure 10: Cumulative average of the surface tension over time of the system with Temperature 0.333(40K), 0.375(45K), 0.417(50K), 0.458(55K) respectively

4.2. Convection current

Figure 12 has shown the trace of the fluid in the heating system. One can see that the motion of each particle have the same feature with the random walk and exhibit no cycle. When we calculate the average velocity of the fluid at each portion in Figure 13, there is no pattern in velocity field that indicate the existence of convection current. We suspect it is due to the fact the number of particles in the system is too small. Therefore, the fluctuation of the fluid pressure exceeds the buoyancy pressure needs for RayleighBnard convection. For the convection current to occurs, the system need as much as 5000 particles, which could be achieve by increasing the computing power[8].

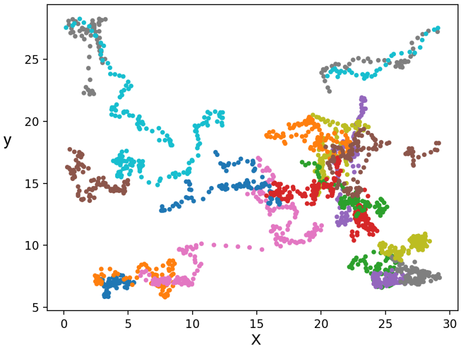


Figure 12: Sample of the particle movement in the system with the lower wall of temperature 55 K and upper wall of temperature 50 K

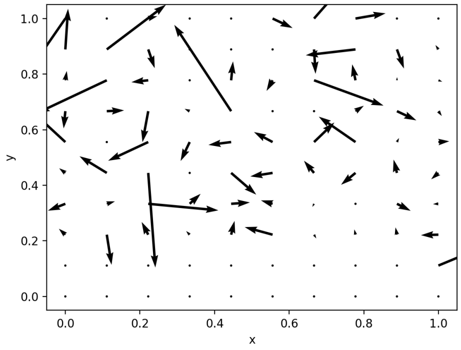


Figure 13: Velocity field of fluid particle

5. Conclusion

We have created a simulation of NVT ensemble of Lennard-Jones particle and justified that the particle's velocity in the model converge to the Maxwell-Boltzmann distribution. Furthermore, we demonstrate that our system can exhibit the liquid-gas interface according to pair correlation function. We also study the liquid surface tension of the system as a function of temperature which gives a good agreement with the property of real liquid. However, it is worth pointing that the limitation of computing power led us to the system that is not completely ergodic and rich. To make the simulation of thermal lens oscillation possible, one needs to create a larger model which exhibit the convection and the surface wave.

6. Appendix

The source code can be found here `https://github.com/PHYS1600Spring2019/phys1600-final-project-GeneSiriviboon`

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