

# Energy equipartition of monatomic molecules in equilibrium

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## 1. Introduction

We are going to observe the phenomenon about energy equipartition of monatomic molecules in equilibrium. Energy equipartition is a physics mechanism in classical. It is state that for a system in thermal equilibrium, the energy is shared equally by each degree of freedom of the motion. The energy is continuous, so it not applicable under quantum state. Monatomic molecules which mean single atoms that we consider them as spherical particles and unbound to each other.

In addition, find out the paradox about the degree of freedom of the spring-like potential. It is predicted that the kinetic energy in thermal equilibrium should be  $k_B T$  for the monatomic ideal gas in two dimensions. We have the system with the external potential that is  $kx^2 + ky^2$  in Cartesian coordinate, and  $kr^2$  in polar coordinate. By the equipartition theorem, there is an average energy  $1/2k_B T$  for each quadratic term. The potential has two degree of freedom in the Cartesian coordinate, so the total average potential is  $k_B T$ . Changing to the polar coordinate, it is one degree of freedom therefore the average potential should be  $1/2k_B T$ . The problem comes out to be that the total average potential is different in two coordinates.

The first is that we create a system which is several particles in two dimensions. We construct the programs according to D. C. Rapaport, *The Art of Molecular Dynamics Simulation*, 2<sup>nd</sup> ed. from the method in this book by chapter 1 to 3. We translate the codes in the book by python to make our work more efficient. Using computer simulation to check the system we made if corresponds to the physics laws. Secondly, we give those particles initial conditions and set the boundaries to simulate at the given temperature. We use energy conservation and the Boltzmann distribution to confirm our programs.

Our purpose is to solve the problem about energy equipartition in equilibrium with the numerical method and the computer simulation.

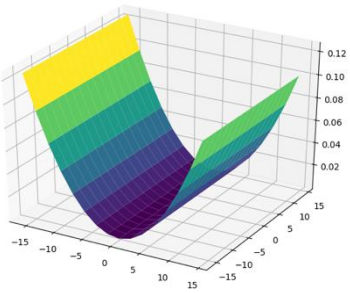
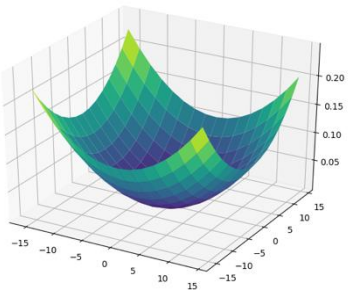
## 2. Method

Our system contains monatomic molecules that we only need to calculate the interaction between particles. The internal potential that we use Lennard-Jones potential (LJ potential) which is a mathematic method to approximate the interaction. It describes the motion by two terms. The former (12-order) is the potential of repulsive. If the molecules are close enough, their electron orbits may overlap. For example, Pauli repulsion. The latter (6-order) which is the attraction such as van der Waals force and dispersion force.

$$\text{Lennard-Jones potential: } U(r_{ij}) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right], & r_{ij} < r_c \\ 0, & r_{ij} > r_c \end{cases}$$

The real physical units are complicated. To simplify the simulation and to correspond to the atomic scale, we change the units based on the LJ potential. The units we convert is the MD units, with length  $\sigma$ , the mass of an argon atom  $m$ , energy  $\epsilon$ , and the time  $t$ . If we model the system as liquid Argon, the MD units correspond to the real physics unit as follows. Length is  $3.4\text{\AA}$  and the mass of an atom is given that  $39.95 \times 1.6747 \times 10^{-24}g$ . Energy is expressed by  $\epsilon/k_B$  equal to 120K that  $\epsilon$  is  $120 \times 1.3806 \times 10^{-16} \text{erg/atom}$ . The physical time is  $2.61 \times 10^{-12}s$ .

We have made several 2D molecular simulations with period boundaries (Appendix A). There are  $20 \times 20$  number of molecules. We give the system some initial conditions (MD unit) that the density is 0.05. The time interval  $dT$  is 0.005. In addition, do the integration in the programs by numerical method which is leapfrog (Appendix B). Calculating the interaction by cell subdivision (Appendix C) with two kind of external potential we add in the programs and LJ potential. The tables below are the simulations with 3D image of the external potential that they are spring like potential, with the direction also along x axis or radial direction.

Simulation	potential	k
No external potential	-	-
x-0.03	 $U = \frac{1}{2}kx^2$	0.03
x-0.01		0.01
r-0.03	 $U = \frac{1}{2}kr^2 = \frac{1}{2}k(x^2 + y^2)$	0.03
r-0.01		0.01

To confirm whether our system is at equilibrium state, we will plot the velocity and position distribution, also fit the data points and check the H-function (Appendix D). At the beginning, we use the region  $89 \times 89$ , and plot the x and y position distribution. If the system has no external force along a direction, then the distribution is evenly. If the systems have an external force, then the distribution will be a certain form based on what type the force we use. To our expectation, it may be the Gaussian distribution, so the probability of the molecules much possible appeared in the middle of the region and decreased outward, and out of the region the probability should be negligible. The probability close to the boundaries needed to approach to zero avoiding the interference of our data. However, we find that the region is not large enough for simulation 1~4, such that the probability distribution is not small enough at the boundaries. Since our boundary is about the order of 2, and the external potential is proportional to distance's square, we require the probability at the boundary need to be smaller than one millionth of the probability at the middle.

As a result, we expand the region and wait for the system to be equilibrium again to check whether the region is large enough. If the region is large enough then we will take the result to analyze.

### 3. Result and discussion

When the systems reach equilibrium, we calculate the average kinetic energy  $\langle K \rangle$  and the average external potential energy  $\langle U \rangle$  per molecular. The total energy including LJ potential, kinetic energy, and external potential remain almost the same correspond to the physical law of energy conservation. Because of the spring-like potential, the kinetic energy and the potential energy convert to each other periodically.

Since our simulations are only in two dimensions, temperature of the system is equal to the kinetic energy per atom. For different simulation we have different initial temperature. And we have set  $k_B = 1$ , so average kinetic energy is equal to  $k_B T$ .

Simulation	$\langle K \rangle = k_B T$	$\langle U \rangle$
x-0.03	7.081	$0.542k_B T$
x-0.01	2.763	$0.556k_B T$

In simulation x-0.03 and x-0.01,  $\langle U \rangle \approx 0.55k_B T$ , which we consider to be roughly  $0.5k_B T$ , so it is one degree of freedom. The result is corresponding to our expectation for systems have external potential energy in the form  $\frac{1}{2}kx^2$ .

For simulation r-0.03 and r-0.01, we do several simulations with different temperature, and fitting  $\langle U \rangle$  verse temperature, the fitting result is great. Although it didn't pass the origin, the slope is close to 1, so we consider the degree of freedom in potential energy of this system should be 2. We can know that it is right if we make prediction using Cartesian coordinate rather than polar coordinate.

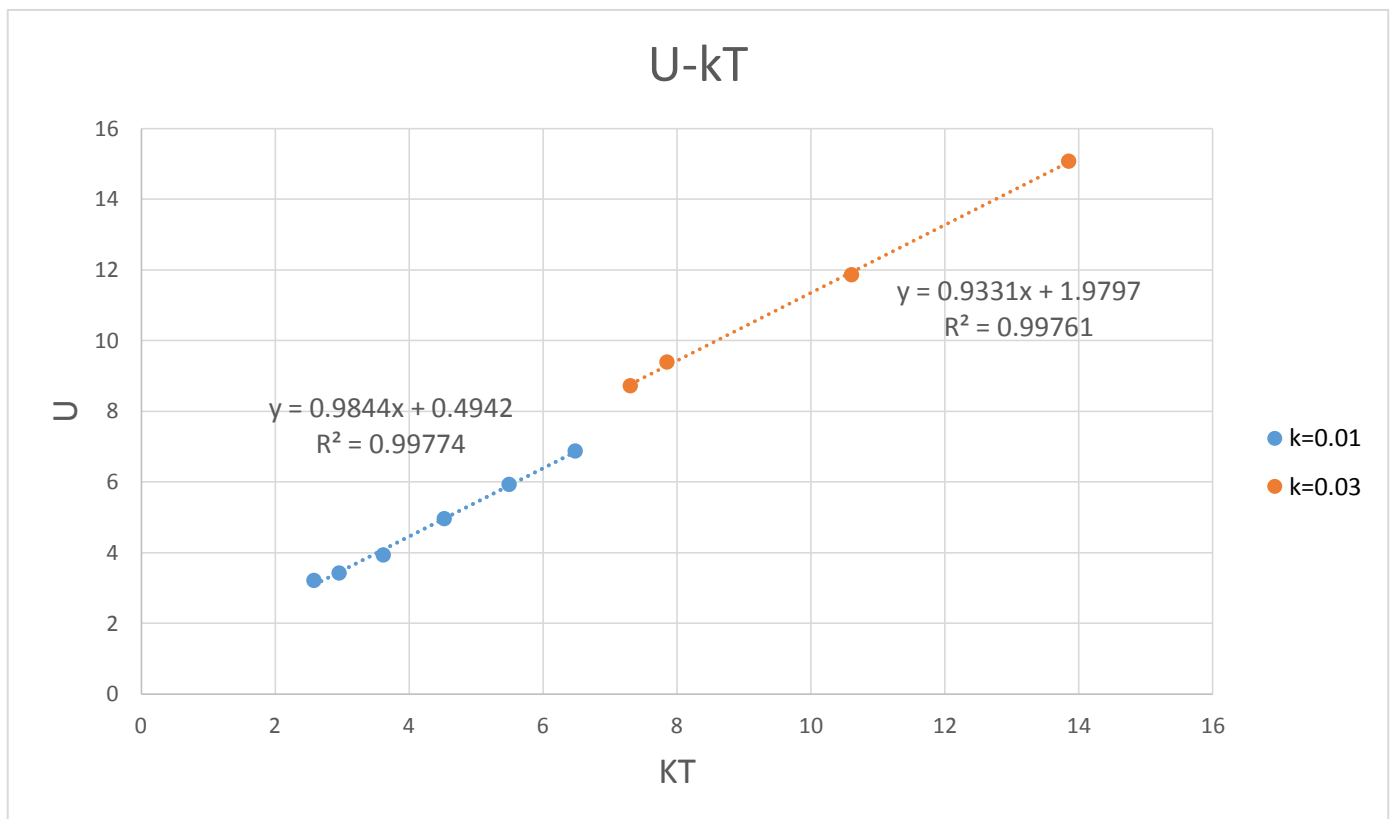
For  $k=0.03$ :

$\langle K \rangle = k_B T$	$\langle U \rangle$
7.303	8.721
7.850	9.392
10.606	11.862

13.849	15.074
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For  $k=0.01$ :

$\langle K \rangle = k_B T$	$\langle U \rangle$
2.578	3.214
2.954	3.424
3.614	3.935
4.525	4.961
5.492	5.930
6.480	6.875



Why it is wrong if we use  $U(r, \theta) = \frac{1}{2}kr^2$  to predict the average potential energy? To explain this, we write Hamiltonian of a particle in the system in both coordinates, and go back to the general form of the equipartition theorem, where it states that  $\langle x_m \frac{\partial H}{\partial x_n} \rangle = \delta_{mn} k_B T$ . Use the theorem to calculate the average value of different energy for our simulation.

Simulation x-0.03 and x-0.01:

	Cartesian coordinate (x, y)
Hamiltonian	$\frac{1}{2m} (p_x^2 + p_y^2) + \frac{k}{2} x^2$
Equipartition	$\langle x \frac{\partial H}{\partial x} \rangle = \langle kx^2 \rangle = k_B T$ $\langle p_x \frac{\partial H}{\partial p_x} \rangle = \langle \frac{p_x^2}{m} \rangle = k_B T$ $\langle p_y \frac{\partial H}{\partial p_y} \rangle = \langle \frac{p_y^2}{m} \rangle = k_B T$
Average energy	$\langle K_x \rangle = \langle \frac{1}{2m} p_x^2 \rangle = \frac{1}{2} k_B T$ $\langle K_y \rangle = \langle \frac{1}{2m} p_y^2 \rangle = \frac{1}{2} k_B T$ $\langle U \rangle = \langle \frac{1}{2} kx^2 \rangle = \frac{1}{2} k_B T$

Simulation r-0.03 and r-0.01:

	Cartesian coordinate (x, y)	Polar coordinate (r, $\theta$ )
Hamiltonian	$\frac{1}{2m} (p_x^2 + p_y^2) + \frac{k}{2} (x^2 + y^2)$	$\frac{1}{2m} p_r^2 + \frac{1}{2mr^2} p_\theta^2 + \frac{k}{2} r^2$
Equipartition	$\langle x \frac{\partial H}{\partial x} \rangle = \langle kx^2 \rangle = k_B T$ $\langle y \frac{\partial H}{\partial y} \rangle = \langle ky^2 \rangle = k_B T$ $\langle p_x \frac{\partial H}{\partial p_x} \rangle = \langle \frac{p_x^2}{m} \rangle = k_B T$ $\langle p_y \frac{\partial H}{\partial p_y} \rangle = \langle \frac{p_y^2}{m} \rangle = k_B T$	$\langle r \frac{\partial H}{\partial r} \rangle = \langle -\frac{p_\theta^2}{mr^2} + kr^2 \rangle = k_B T$ $\langle p_\theta \frac{\partial H}{\partial p_\theta} \rangle = \langle \frac{p_\theta^2}{mr^2} \rangle = k_B T$ $\langle p_r \frac{\partial H}{\partial p_r} \rangle = \langle \frac{p_r^2}{m} \rangle = k_B T$
Average energy	$\langle K_x \rangle = \langle \frac{1}{2m} p_x^2 \rangle = \frac{1}{2} k_B T$ $\langle K_y \rangle = \langle \frac{1}{2m} p_y^2 \rangle = \frac{1}{2} k_B T$ $\langle U \rangle = \langle \frac{1}{2} kx^2 + \frac{1}{2} ky^2 \rangle = k_B T$	$\langle K_r \rangle = \langle \frac{1}{2m} p_r^2 \rangle = \frac{1}{2} k_B T$ $\langle K_\theta \rangle = \langle \frac{1}{2mr^2} p_\theta^2 \rangle = \frac{1}{2} k_B T$ $\langle U \rangle = \langle \frac{1}{2} kr^2 \rangle = \frac{1}{2} (\langle \frac{p_\theta^2}{mr^2} \rangle + k_B T) = k_B T$

In simulation  $r=0.03$  and  $r=0.01$ , we get the same result from both Cartesian coordinate and polar coordinate. And it is agreed with our simulation result, that is the average potential energy in the field  $U = \frac{1}{2}kr^2 = \frac{1}{2}k(x^2 + y^2)$  being  $k_B T$ . In Cartesian coordinate it looks straightforward since it has two degree of freedom, but not the same case in polar coordinate. The reason why we can get the same result is the kinetic energy in polar coordinate depends explicitly on  $r$ . It is important that we need to know the Hamiltonian of a system. When we express Hamiltonian in polar coordinate the degree of freedom  $r$  appears two times, we cannot say that the average potential energy is  $\frac{1}{2}k_B T$ , merely by the form of potential energy.

To calculate the theoretically value of the average potential energy, in addition to use equipartition theorem we can calculate it directly. In a thermal equilibrium system the probability density in the phase space is proportional to  $e^{-\beta H}$ , where  $H$  is the Hamiltonian and  $\beta = \frac{1}{k_B T}$ . So, we can calculate some property's average value, just by using  $e^{-\beta H}$  as weighting factor to do weighted average for the property over the phase space.

With the help of following integral formula

$$\begin{aligned}\int_0^\infty e^{-Ar^2} dr &= \sqrt{\frac{\pi}{A}} \\ \int_0^\infty r e^{-Ar^2} dr &= \frac{1}{2A} \\ \int_0^\infty r^2 e^{-Ar^2} dr &= \frac{\sqrt{\pi}}{4A^{3/2}} \\ \int_0^\infty r^3 e^{-Ar^2} dr &= \frac{1}{2A^2}\end{aligned}$$

We can compute the average energy.

For simulation  $x=0.03$  and  $x=0.01$ :

$$\langle U \rangle = \left\langle \frac{1}{2} kx^2 \right\rangle = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} e^{-\beta H} \times \frac{1}{2} kx^2 \, dP_y dP_x dy dx}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} e^{-\beta H} \, dP_y dP_x dy dx}$$

$$= \frac{\int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} e^{-\beta \frac{1}{2m}(p_x^2 + p_y^2)} dP_y dP_x dy \int_{-\infty}^{\infty} e^{-\beta \frac{k}{2} x^2} \frac{1}{2} k x^2 dx}{\int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} e^{-\beta \frac{1}{2m}(p_x^2 + p_y^2)} dP_y dP_x dy \int_{-\infty}^{\infty} e^{-\beta \frac{k}{2} x^2} dx} = \frac{k}{2} \frac{1}{\beta k}$$

$$= \frac{1}{2} k_B T$$

$$\begin{aligned} \langle K_x \rangle &= \left\langle \frac{1}{2m} p_x^2 \right\rangle = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} e^{-\beta H} \times \frac{1}{2m} p_x^2 dP_y dP_x dy dx}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} e^{-\beta H} dP_y dP_x dy dx} \\ &= \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} e^{-\beta(\frac{1}{2m} p_y^2 + \frac{k}{2} x^2)} dP_y dy dx \int_0^{\infty} e^{-\beta \frac{1}{2m} p_x^2} \times \frac{1}{2m} p_x^2 dP_x}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} e^{-\beta(\frac{1}{2m} p_y^2 + \frac{k}{2} x^2)} dP_y dy dx \int_0^{\infty} e^{-\beta \frac{1}{2m} p_x^2} dP_x} = \frac{1}{2} k_B T \end{aligned}$$

$$\begin{aligned} \langle K_y \rangle &= \left\langle \frac{1}{2m} p_y^2 \right\rangle = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} e^{-\beta H} \times \frac{1}{2m} p_y^2 dP_y dP_x dy dx}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} e^{-\beta H} dP_y dP_x dy dx} \\ &= \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} e^{-\beta(\frac{1}{2m} p_x^2 + \frac{k}{2} x^2)} dP_x dy dx \int_0^{\infty} e^{-\beta \frac{1}{2m} p_y^2} \times \frac{1}{2m} p_y^2 dP_y}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} e^{-\beta(\frac{1}{2m} p_x^2 + \frac{k}{2} x^2)} dP_x dy dx \int_0^{\infty} e^{-\beta \frac{1}{2m} p_y^2} dP_y} = \frac{1}{2} k_B T \end{aligned}$$

For simulation r=0.03 and r=0.01:

$$\begin{aligned} \langle U \rangle &= \left\langle \frac{1}{2} k r^2 \right\rangle = \frac{\int_0^{\infty} \int_0^{2\pi} \int_0^{\infty} \int_0^{\infty} e^{-\beta H} \times \frac{1}{2} k r^2 dP_{\theta} dP_r d\theta dr}{\int_0^{\infty} \int_0^{2\pi} \int_0^{\infty} \int_0^{\infty} e^{-\beta H} dP_{\theta} dP_r d\theta dr} \\ &= \frac{\int_0^{\infty} e^{-\beta \frac{1}{2m} p_r^2} dP_r \int_0^{2\pi} \int_0^{\infty} \left( \int_0^{\infty} e^{-\beta \frac{1}{2m} p_{\theta}^2} dP_{\theta} \right) e^{-\beta \frac{k}{2} r^2} \times \frac{1}{2} k r^2 dr}{\int_0^{\infty} e^{-\beta \frac{1}{2m} p_r^2} dP_r \int_0^{2\pi} \int_0^{\infty} \left( \int_0^{\infty} e^{-\beta \frac{1}{2m} p_{\theta}^2} dP_{\theta} \right) e^{-\beta \frac{k}{2} r^2} dr} = \frac{\frac{1}{2} k \int_0^{\infty} r^3 e^{-\beta \frac{k}{2} r^2} dr}{\int_0^{\infty} r e^{-\beta \frac{k}{2} r^2} dr} = \frac{k}{2} \frac{2}{\beta k} \end{aligned}$$

$$= k_B T$$

$$\begin{aligned} \langle K_r \rangle &= \left\langle \frac{1}{2m} p_r^2 \right\rangle = \frac{\int_0^{\infty} \int_0^{2\pi} \int_0^{\infty} \int_0^{\infty} e^{-\beta H} \times \frac{1}{2m} p_r^2 dP_{\theta} dP_r d\theta dr}{\int_0^{\infty} \int_0^{2\pi} \int_0^{\infty} \int_0^{\infty} e^{-\beta H} dP_{\theta} dP_r d\theta dr} \\ &= \frac{\int_0^{\infty} e^{-\beta \frac{1}{2m} p_r^2} \times \frac{1}{2m} p_r^2 dP_r \int_0^{\infty} \int_0^{\infty} e^{-\beta \frac{1}{2m} p_{\theta}^2} dP_{\theta} e^{-\beta \frac{k}{2} r^2} dr}{\int_0^{\infty} e^{-\beta \frac{1}{2m} p_r^2} dP_r \int_0^{\infty} \int_0^{\infty} e^{-\beta \frac{1}{2m} p_{\theta}^2} dP_{\theta} e^{-\beta \frac{k}{2} r^2} dr} = \frac{1}{2m} \frac{2m}{2\beta} = \frac{1}{2} k_B T \end{aligned}$$



$$\begin{aligned}
\langle K_\theta \rangle &= \left\langle \frac{1}{2mr^2} p_\theta^2 \right\rangle = \frac{\int_0^\infty \int_0^{2\pi} \int_0^\infty \int_0^\infty e^{-\beta H} \times \frac{1}{2mr^2} p_\theta^2 dP_\theta dP_r d\theta dr}{\int_0^\infty \int_0^{2\pi} \int_0^\infty \int_0^\infty e^{-\beta H} dP_\theta dP_r d\theta dr} \\
&= \frac{\int_0^\infty \left( \int_0^\infty e^{-\beta \frac{1}{2mr^2} p_\theta^2} p_\theta^2 dP_\theta \right) e^{-\beta \frac{k}{2} r^2} \times \frac{1}{2mr^2} dr}{\int_0^\infty \left( \int_0^\infty e^{-\beta \frac{1}{2mr^2} p_\theta^2} dP_\theta \right) e^{-\beta \frac{k}{2} r^2} dr} = \frac{m \int_0^\infty r^3 e^{-\beta \frac{k}{2} r^2} \times \frac{1}{2mr^2} dr}{\int_0^\infty r e^{-\beta \frac{k}{2} r^2} dr} = \frac{1}{2} k_B T
\end{aligned}$$

If we use Cartesian coordinate the process will be similar, and we can have the same result. Which is right both with simulation result and equipartition theorem.

Since only in an equilibrium system the probability will be proportional to  $e^{-\beta H}$ , we need to wait for the system to be equilibrium. The equipartition can only apply to those equilibrium systems.

For different simulation the initial kinetic energy and potential energy are different. When the systems reach equilibrium the energy is being rearranged according to the proportion predict by equipartition theorem.

#### 4. Conclusion

We have successfully using computer simulation to examine the equipartition theorem in some easy case. Check the relation between average potential energy and the form of external potential, and solve the paradox. The key point of the paradox is that we need to know each term in the Hamiltonian before we use equipartition. In the Cartesian coordinates an infinitesimal area element is purely  $dx dy$ , hence the kinetic energy term does not depend explicitly on  $x$  or  $y$ . By contrast, in the polar coordinates an infinitesimal area element is  $dA = r dr d\theta$ , so the kinetic energy term depends explicitly on  $r$ .

We also calculate the average potential by theorem, to double check the simulation result is follow our prediction. And we have a better understanding of equipartition theorem.

#### 5. Appendix

##### A. Boundary

This system is bounded but free of physical walls, so we use periodic boundary conditions. There are two conditions. First, if an atom leaves the

boundary, there will make another atom into the region through the opposite face. Second, the space is homogeneous and it is identical copy of the nearby cell.

#### B. Leapfrog

The leapfrog method is a numerical technique to calculate the integration of the equations of motion. It can evaluate the coordinates and velocities at different times. By splitting the computations in to two parts, the coordinates and velocities can be evaluated at the same time.

Part 1:

$$\begin{aligned}v_{ix}(t + h/2) &= v_{ix}(t) + (h/2)a_{ix}(t) \\r_{ix}(t + h) &= r_{ix}(t) + hv_{ix}(t + h/2)\end{aligned}$$

Part 2:

$$v_{ix}(t + h) = v_{ix}(t + h/2) + (h/2)a_{ix}(t + h)$$

#### C. Interaction computations

To make the computation more efficient, we use cell subdivision in our program.

All-pairs: It is the simplest way to construct the programs, however it cost a lot of time to calculate. It chooses any two atoms to compute their interaction, so there are  $C_2^n$  pairs to be examined.

Cell subdivision: This method avoids computing repeatedly and makes the program organize. It divides the MD region into several cells of lattice which is the current positions of atoms. The interaction is only including in the same or nearby cells. In addition, there is the property of symmetry in the system, it may reduce the calculation.

#### D. H-Function

We use the Boltzmann H-function to see whether the distribution of velocity is the Maxwell–Boltzmann distribution. H-function is defined as

$$H(t) = \int f(v, t) \log f(v, t) dv, \text{ when } \frac{dH}{dt} \leq 0, f(v) \text{ is the Maxwell–Boltzmann}$$

distribution. Since the density we use is pretty small, convergence is very fast.

### 6. Reference

D. C. Rapaport, *The Art of Molecular Dynamics Simulation*, 2nd ed.

Equipartition theorem, Wikipedia