

PHYS2020 Assignment 3

Ryan White
44990392

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Question 1

(14 marks)

In this question you will introduce interactions and a cooling process into your Ideal Gas Matlab simulation from Assignment 2, in order to simulate phase changes (e.g. between solid, liquid and gas phase).

- a. Choose or design your own interaction potential V between the particles in the system. You will need a combination of a long range attractive potential and a short range repulsive potential to allow condensation to a condensed phase with non-infinite density, and should assume only position-dependent interactions so that the potential has no dependence on particle velocity. Apart from these constraints, you are free to choose any potential you like, or investigate several. You could, for example, use a Lennard Jones Potential, which is commonly used to model the interactions of neutral atoms or molecules; or an attractive Coulomb-type potential (proportional to $1/r^2$) combined with a repulsive potential that goes as $1/r^k$ where k is some number larger than 2.

The potential chosen was the Lennard-Jones potential, which is described by

$$V = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] = \epsilon \left[\left(\frac{r_m}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^6 \right] \quad (1)$$

where ϵ is the depth of the potential well, r_m is the distance at which the potential reaches its minimum, and r is the separation between two particles.

- b. Calculate the particle separation at the minima of your chosen potential. What does this represent?

Firstly, the force experienced between two particles may be found by the derivative of equation (1) with respect to distance r ,

$$\begin{aligned} F &= -\frac{\partial V}{\partial r} = -\frac{\partial}{\partial r} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \\ &= -\frac{\partial}{\partial r} \left(\frac{4\epsilon\sigma^{12}}{r^{12}} - \frac{8\epsilon\sigma^6}{r^6} \right) \\ &= \frac{48\epsilon\sigma^{12}}{r^{13}} - \frac{24\epsilon\sigma^6}{r^7} \\ &= \frac{24\epsilon\sigma^6 (2\sigma^6 - r^6)}{r^{13}} \end{aligned}$$

The minima of the potential represents the point at which repulsive and attractive forces are equal and cancel out, or when the net force is 0. As the potential minima occurs when $F = 0$ for the two particles, the minima will occur at r_m when $2\sigma^6 - r_m^6 = 0 \Rightarrow r_m = 2^{1/6}\sigma$. Powles et al. quotes the intermolecular potential for Nitrogen to be $\sigma = 3.310 \times 10^{-10}$ meters, and so the minima particle separation is $r_m \approx 3.715 \times 10^{-10}$ meters.

- c. Include interactions in your code by converting your potential to a particle-separation dependent force and applying this between every pair of particles (or between only sufficiently close particles if you need to reduce computational demands) at each step in your simulation. In PHYS2020 we derived the equipartition theorem for situations where the energy of the system depends quadratically on all of the relevant system degrees of freedom (e.g. $K \propto v^2$ or $V \propto x^2$). However, the theorem can in fact be applied more broadly – it can be applied to any variables that the energy has a purely quadratic dependence on, irrespective of other variables. So, since the kinetic energy of our interacting gas is quadratic in velocity and the potential energy is independent of velocity, we should be able to apply equipartition to the particle velocity. Use this fact to calculate the temperature of your interacting gas as a function of time. Explain your observations.

From the equipartition theorem, we have that the temperature of a system of particles is

$$T = \frac{m}{3k} v_{rms}^2 \quad (2)$$

where m is the mass of each particle, k is Boltzmann's constant, and v_{rms} is the root mean square velocity of the particles. The change in temperature over time may be found by taking the derivative of each side of equation (2) with respect to time, resulting in

$$\frac{dT}{dt} = \frac{m}{3k} \frac{d(v_{rms}^2)}{dt} \quad (3)$$

since $\frac{d}{dt}v = a$, equation (3) becomes

$$\begin{aligned} \frac{dT}{dt} &= \frac{m}{3k} 2a \\ &= \frac{2m}{3k} \frac{F}{m} \\ &= \frac{2}{3k} \frac{1}{n} \sum_{\substack{i=1 \\ i \neq j}}^n \frac{24\epsilon\sigma^6 (2\sigma^6 - r_{ij}^6)}{r_{ij}^{13}} \end{aligned} \quad (4)$$

To find the temperature at any time t , the integral of each side of equation (4) may be taken, resulting in

$$\begin{aligned} T(t) &= \int \frac{2}{3k} \frac{1}{n} \sum_{\substack{i=1 \\ i \neq j}}^n \frac{24\epsilon\sigma^6 (2\sigma^6 - r_{ij}^6)}{r_{ij}^{13}} dt \\ &= \frac{2t}{3kn} \left(\sum_{\substack{i=1 \\ i \neq j}}^n \frac{24\epsilon\sigma^6 (2\sigma^6 - r_{ij}^6)}{r_{ij}^{13}} \right) + c \end{aligned} \quad (5)$$

At $t = 0$, the system has a temperature of T_0 , so equation (5) becomes

$$\begin{aligned} T(t) &= T_0 + \frac{2t}{3kn} \left(\sum_{\substack{i=1 \\ i \neq j}}^n \frac{24\epsilon\sigma^6 (2\sigma^6 - r_{ij}^6)}{r_{ij}^{13}} \right) \\ &= \frac{1}{3k} \left(m v_{rms_0}^2 + \frac{2t}{n} \sum_{\substack{i=1 \\ i \neq j}}^n \frac{24\epsilon\sigma^6 (2\sigma^6 - r_{ij}^6)}{r_{ij}^{13}} \right) \end{aligned}$$

As the equation shows, the temperature of the system at some time t heavily relies on the average force between particles. If there are many particles very close together, one would expect that repulsive forces would dominate and the overall temperature of the system would drastically increase over time. The inverse is expected to be true in that few, sparsely populated particles would experience predominately attractive forces at the temperature of the system would decrease over some time.

- d. To model a cooling process, reducing the temperature of the system, add dissipation to the simulation by reducing the mean velocity of each particle by a fixed proportion each time step. Plotting the configuration of particle positions as they change over time, you should then see an initial gas-like behaviour transitioning to a condensed phase once the temperature is sufficiently low. Describe what you observe, and plot – with discussion – the pressure and temperature as a function of time. Determine the “ground-state” distribution, where the cooling has completely frozen the motion of the ensemble of particles.

The dissipation of velocity (as a percentage of initial velocity) per timestep was calculated using equations (6) and (7)

$$\begin{aligned}
 (1 - \text{Dissipation}) \cdot v_{rms_{initial}} &= \sqrt{v_x^2 + v_y^2} \\
 \Rightarrow v_{x_{final}} &= \sqrt{(1 - \text{Dissipation})^2 \cdot v_{rms_{initial}}^2 - v_{y_{initial}}^2} \\
 &= \sqrt{(1 - \text{Dissipation})^2 \cdot v_{x_{initial}}^2 + v_{y_{initial}}^2 ((1 - \text{Dissipation})^2 - 1)}
 \end{aligned}$$

To avoid any complex terms, the value inside the square root was taken as an absolute, and the whole term multiplied by the sign of the original velocity. So,

$$v_{x_{final}} = \frac{v_{x_{initial}}}{|v_{x_{initial}}|} \sqrt{|(1 - \text{Dissipation})^2 \cdot v_{x_{initial}}^2 + v_{y_{initial}}^2 ((1 - \text{Dissipation})^2 - 1)|} \quad (6)$$

$$v_{y_{final}} = \frac{v_{y_{initial}}}{|v_{y_{initial}}|} \sqrt{|(1 - \text{Dissipation})^2 \cdot v_{y_{initial}}^2 + v_{x_{initial}}^2 ((1 - \text{Dissipation})^2 - 1)|} \quad (7)$$

The updated code from Assignment 2 may be seen in Appendix 1, factoring in the interaction forces and dissipation of velocities.

As the intermolecular forces are still present even at miniscule temperatures, the distribution at true 0K could not be found in a reasonable timeframe, but at temperatures on the order of magnitude of 10^{-4}K , the distribution resembled that of Figure 1

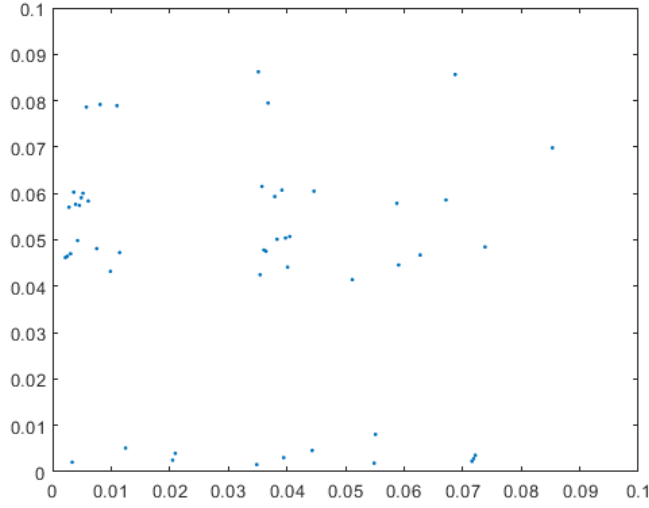


Figure 1: Approximate Ground-State Distribution of N₂ Particles

As can be seen, the particles form a few dense clusters resembling a solid (or dense liquid) phase. As can be seen, the program iteration had box dimensions of $0.1 \times 0.1 \text{ m}$, with 50 N₂ particles simulated. Due to the velocity falling each time step, one would expect the pressure to fall simultaneously. The relationship between temperature and pressure is described in Figure 2

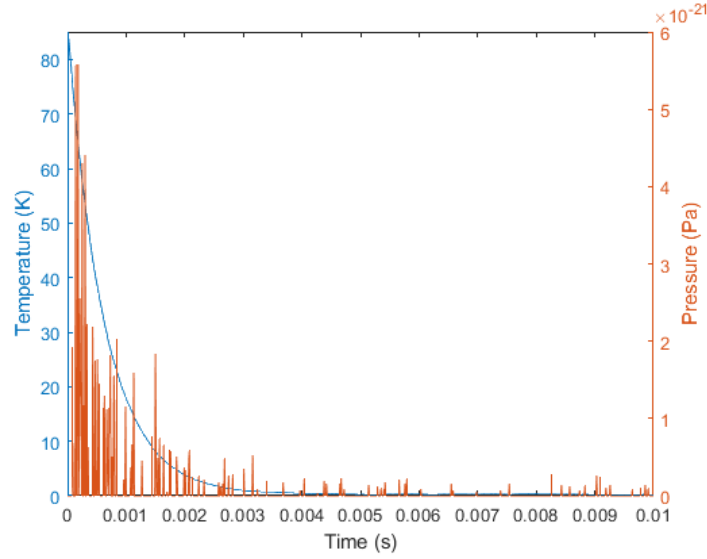


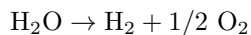
Figure 2: Relationship between Temperature and Pressure over Time

The figure shows relatively frequent wall collisions (high pressure) initially, which falls off in accordance with temperature, just as expected.

Question 2

(7 marks)

The electrolysis of liquid water into hydrogen and oxygen is given by the following chemical reaction



- a. In the electrolysis of water, what is the minimum electrical work required to separate one mole of water into hydrogen and oxygen gases?

The change in enthalpy over the reaction may be given by

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

Using the values given by the table of Thermodynamic Properties of Various Substances, this may be expanded to

$$\begin{aligned}\Delta H &= H_{\text{H}_2} + \frac{1}{2}H_{\text{O}_2} - H_{\text{H}_2\text{O}} \\ &= 0 + \frac{1}{2}0 - -285.83\text{kJ} \\ &= 285.83\text{kJ}\end{aligned}$$

and so approximately 286kJ of work is needed to convert one mole of H_2O into hydrogen and oxygen gas. Using the tabulated data for the entropies of each of these molecules, the change in entropy over the reaction is

$$\begin{aligned}\Delta S &= S_{\text{products}} - S_{\text{reactants}} \\ &= S_{\text{H}_2} + \frac{1}{2}S_{\text{O}_2} - S_{\text{H}_2\text{O}} \\ &= 130.68 + \frac{1}{2}205.14 - 69.91\text{J/K} \\ &\approx 163.3\text{J/K}\end{aligned}$$

and so the entropy increases by approximately 163.3J/K over the electrolysis reaction. Using the change in Gibbs free energy (and assuming electrolysis is taking place at room temperature, $T = 298\text{K}$), the minimum electric work required may be found by

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= 286\text{kJ} - 298\text{K} \cdot 163.3\text{J/K} \\ &\approx 237\text{kJ}\end{aligned}$$

and so a minimum of (approximately) 237kJ of electrical work is required to produce the electrolysis reaction of one mole of water.

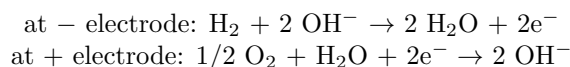
- b. How much energy in this case comes ‘for free’ as heat from the environment?

The heat from the environment may be found by the formula $\Delta S = \frac{Q}{T} \Rightarrow Q = T\Delta S$. Looking at the final two lines of the previous part of the question, it may be seen that the heat that enters the system is given by $286\text{kJ} - 237\text{kJ} = 49\text{kJ}$.

Question 3

(7 marks)

In a hydrogen fuel cell, the steps of the chemical reactions are



- a. Calculate the voltage of the cell

The electrical work of the cell may be found by the change in Gibbs free energy per electron. Expressed mathematically, that is

$$\begin{aligned}W &= \frac{\Delta G_{\text{reaction}}}{N_A \cdot \text{no. of electrons}} \\ &= \frac{G_{\text{products}} - G_{\text{reactants}}}{N_A \cdot \text{no. of electrons}}\end{aligned}$$

In this fuel cell, there are two electrons per product molecule, so

$$\begin{aligned}W &= \frac{G_{\text{products}} - G_{\text{reactants}}}{N_A \cdot 2} \\ &= \frac{G_{\text{H}_2\text{O}} - G_{\text{H}_2} - G_{\frac{1}{2}\text{O}_2}}{N_A \cdot 2}\end{aligned}$$

Using the tabulated data, this becomes

$$\begin{aligned}W &= \frac{-237.13\text{kJ} - 0 - 0}{2 \cdot 6.02 \times 10^{23}} \\ &= -1.97 \times 10^{-19} \text{ J}\end{aligned}$$

Since the sign is negative, the system is producing power. As one joule is $6.242 \times 10^{18} \text{ eV}$,

$$\begin{aligned}W &= 1.97 \times 10^{-19} \text{ J} \cdot 6.424 \times 10^{18} \frac{\text{eV}}{\text{J}} \\ &\approx 1.23 \text{ eV}\end{aligned}$$

and so each electron has an energy of 1.23 eV. As 1 volt is defined as the voltage needed to give an electron 1eV of energy, this means that the fuel cell has a voltage of $V = 1.23\text{V}$.

- b. What is the minimum voltage required for electrolysis of water? Explain briefly.

As the voltage produced by a hydrogen fuel cell is 1.23V, the electrolysis of water would also require such a voltage, as the reaction is running in reverse. This is assuming that the water is chemically pure, the reaction takes place at room temperature and in 1 atmosphere of pressure.

Question 4

(14 marks)

Thermodynamics of radiation

Consider a system consisting of electromagnetic radiation in thermal equilibrium at temperature T inside a sphere of volume V .

According to the Stefan-Boltzmann law the internal energy is given by

$$U(V, T) = \frac{4\sigma}{c} VT^4$$

where $\sigma = 5.67 \times 10^{-8} \text{ W}/(\text{m}^2 \text{ K}^4)$ is the Stefan-Boltzmann constant and c is the speed of light.

- a. Obtain an expression for the entropy of system, $S(T, V)$.

The thermodynamic identity is given by

$$dU = TdS - PdV + \mu dN \quad (8)$$

Taking the volume and number of particles of the system as a constant in equation (8),

$$\begin{aligned} dU &= TdS \\ dS &= \frac{dU}{T} \end{aligned}$$

Substituting in the internal energy given by the Stefan-Boltzmann law,

$$\begin{aligned} dS &= \frac{d\left(\frac{4\sigma}{c} VT^4\right)}{T} \\ S &= \frac{4\sigma}{c} VT^3 + d \end{aligned}$$

Where the integration constant d could be found by analysing the boundary conditions of the system. As a system with a temperature of 0K still has entropy, this baseline entropy would be the value of d . Treating residual entropies as negligible, the system can be taken to be at its lowest-energy state as described by the first law to be $d = S(0\text{K}) = 0\text{J/K}$, and the equation becomes

$$S = \frac{4\sigma}{c} VT^3 \quad (9)$$

And so the entropy of some system according to the thermodynamic identity and the Stefan-Boltzmann law is as shown in equation (9).

- b. Suppose that an adiabatically isolated system of blackbody radiation has temperature T_0 and volume V_0 . Find what thermodynamic states are accessible by (i) reversible processes, and (ii) irreversible processes. Sketch these states in the $V - T$ plane.

As the system is adiabatically isolated, it can be taken that there is no change in internal energy, or change in the number of particles present in the system. The resultant thermodynamic identity is then

$$PdV = TdS$$

- Reversible processes are defined as those with no change in entropy, $\Delta S = 0$. For a thermodynamic state to be accessible in this situation, $V_f T_f^3 = V_i T_i^3$.
- Irreversible processes are defined as those with $\Delta S > 0$. In this case, any positive change in volume and/or temperature may result in a positive change in entropy.

These two processes may be seen in Figure 3:

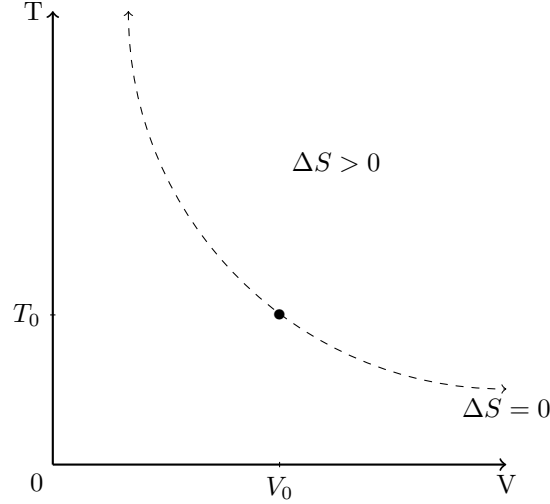


Figure 3: Possible Thermodynamic States for Reversible and Irreversible Processes on the $V - T$ Plane

Where the dashed line represents any reversible process $\Delta S = 0$, and the area above the line represents any irreversible process $\Delta S > 0$.

- c. Photons in the Cosmic Microwave Background (CMB) currently have a temperature of 2.73 K. These photons were last scattered by matter when the temperature of the universe was approximately 3000 K. Assume that the CMB then underwent reversible adiabatic expansion. Make an estimate of how much the “radius” of the universe has increased since the epoch of “last scattering”.

Since the change in entropy is assumed to be 0 (as the expansion was reversible), the ‘final’ and ‘initial’ entropic states of the universe can be equated, yielding

$$\begin{aligned}\frac{4\sigma}{c}V_f T_f^4 &= \frac{4\sigma}{c}V_i T_i^4 \\ V_f T_f^4 &= V_i T_i^4 \\ \frac{V_f}{V_i} &= \left(\frac{T_i}{T_f}\right)^4\end{aligned}$$

The left hand side of the relation describes how much larger the universe is in it’s current state than it was in it’s state at an average temperature of 3000K. Substituting in the two known temperatures yields

$$\begin{aligned}\frac{V_f}{V_i} &= \left(\frac{3000}{2.73}\right)^4 \\ V_f &\approx 1.46 \times 10^{12} V_i\end{aligned}$$

Based on the assumption that the expansion of the universe was a reversible process, the universe is approximately 1.46×10^{12} times larger than when the Cosmic Microwave Background photons were last scattered.

- d. Find an expression for the Helmholtz free energy $F(T, V) = U - TS$ and use it to obtain an expression for the radiation pressure. Compare the magnitude of the pressure of the CMB to atmospheric pressure.

Question 5

(7 marks)

- a. Sketch a qualitative phase diagram (pressure vs temperature) for H_2O .

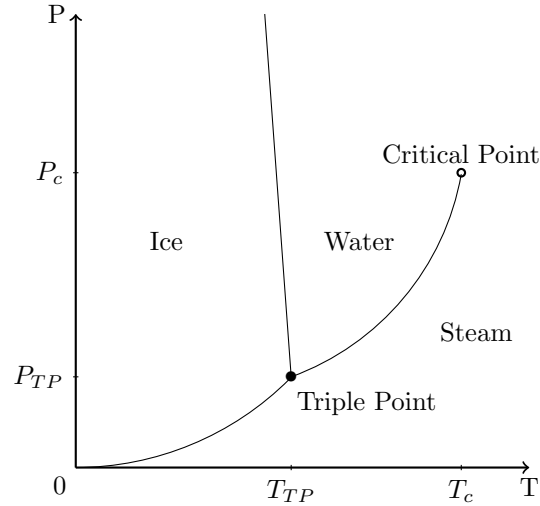


Figure 4: Qualitative Phase Diagram of H_2O

- b. Use the Clausius-Clapeyron relation to explain why the slope of the phase boundary between water and ice is negative.

The Clausius-Clapeyron relation describes the relationship between the pressure and temperature of a substance along one of its phase boundaries (the slope of the boundary on the phase diagram)

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

It is well understood that liquid water is more dense than solid ice, so as ice melts its volume decreases. In terms of the variables above, $\Delta T > 0 \Rightarrow \Delta V < 0$. This results in the gradient of the phase boundary being negative, and represented by equation (10)

$$\left(\frac{dP}{dT}\right)_{s \rightarrow l} = -\frac{L}{T\Delta V} \quad (10)$$

- c. Given that the density of ice is 917 kg/m^3 and the latent heat of fusion of water is 333 kJ/kg , how much pressure would you have to put on an ice cube to make it melt at -1°C ?

Firstly, density is given by

$$\rho = \frac{m}{V} \Rightarrow V = \frac{m}{\rho}$$

The change in pressure required to melt ice with respect to change in temperature is given by equation (10). For some mass m , the change required is

$$\begin{aligned} \left(\frac{dP}{dT}\right)_{s \rightarrow l} &= -\frac{mL}{T\Delta V} \\ &= -\frac{mL}{T\left(\frac{m}{\rho_{solid}} - \frac{m}{\rho_{liquid}}\right)} \\ &= -\frac{L}{T\left(\frac{1}{\rho_{solid}} - \frac{1}{\rho_{liquid}}\right)} \end{aligned}$$

At a temperature of 272.13K ,

$$\begin{aligned} \left(\frac{dP}{dT}\right)_{s \rightarrow l} &= -\frac{333000}{272.13\left(\frac{1}{917} - \frac{1}{1000}\right)} \text{ Pa/K} \\ &\approx -133.46 \text{ Bar/K} \end{aligned}$$

As the pressure required to melt ice at -1°C is to be found,

$$\begin{aligned} P(272.13\text{K}) &= -\int_{273.13}^{272.13} 133.46 dT \\ &= -133.46 \times (272.13 - 273.13) \text{ Bar} \\ &= 133.46 \text{ Bar} \end{aligned}$$

Therefore, at -1°C , it would take approximately 133.45 Bar of pressure to melt a cube of ice.

Appendices

Appendix 1: Interaction and Cooling MATLAB Script

```
clear all;

%following statements are initialising propeties of gas
m = 2 * 14 * 1.6735575 * 10^(-27); %Mass of each particle, value is for N2
k = 1.38064852 * 10^(-23); %Boltzmann's Constant
Temp = 70; %Temperature of gas
SD = sqrt((k * Temp) / m); %Standard deviation of gas speed
N = 100; %total number of particles
Dissipation = 0.008; %percentage loss of speed each timestep
Particles = zeros(4, N);

%initialise box dimensions, time
dt = 10^(-5); %Time step for particle trajectories
t = 0.01; %Total time to simulate particles
Box_Size = 0.1;
[x_min, y_min, elapsed, hits] = deal(0);
[x_max, y_max] = deal(Box_Size);

%create impulse (J), Pressure (P), Temp (T) and time arrays for graphing
[J, P, T, Time] = deal(zeros(round(t / dt), 1));

%following for loop determines values for particle variables
for n = 1:N
    Particles(1, n) = Box_Size .* rand(1); %x_ini
    Particles(2, n) = Box_Size .* rand(1); %y_ini
    Particles(3, n) = SD .* randn(1); %vx
    Particles(4, n) = SD .* randn(1); %vy
end

%particle simulation:
for i = 1:length(Time)
    for n = 1:N
        %initialise properties for particle calculation
        x_ini = Particles(1, n);
        y_ini = Particles(2, n);
        vxi = Particles(3, n);
        vyi = Particles(4, n);
        %following applies dissipation to velocity
        vx = (vxi / abs(vxi)) * sqrt(abs((1 - Dissipation)^2 * vxi^2 + vyi*((1 - Dissipation)^2 - 1)));
        vy = (vyi / abs(vyi)) * sqrt(abs((1 - Dissipation)^2 * vyi^2 + vxi*((1 - Dissipation)^2 - 1)));
        %following applies interaction forces
        for j = 1:N
            if j ~= n
                dx = Particles(1, j) - Particles(1, n); %find x distance between two particles
                dy = Particles(2, j) - Particles(2, n); %find y distance between two particles
                [dvx, dvy] = force_interaction(dt, m, dx, dy);
                vx = vx + (dt * dvx); %apply acceleration to x speed
                vy = vy + (dt * dvy); %apply acceleration to y speed
            end
        end
    end
end
```

```

end
x_new = x_ini + vx * dt;
y_new = y_ini + vy * dt;
%following if statements check if particle collides with wall
if x_new > x_max
    x_new = x_max - (x_new - x_max);
    J(i) = J(i) + (2 * abs(m * vx));
    hits = hits + 1;
    vx = -1 * vx;
end
if y_new > y_max
    y_new = y_max - (y_new - y_max);
    vy = -1 * vy;
end
if x_new < x_min
    x_new = x_min + (x_min - x_new);
    vx = -1 * vx;
end
if y_new < y_min
    y_new = y_min + (y_min - y_new);
    vy = -1 * vy;
end
%assign new properties for next iteration
Particles(1, n) = x_new;
Particles(2, n) = y_new;
Particles(3, n) = vx;
Particles(4, n) = vy;
end
vrms = sqrt(mean(Particles(3, 1:N).^2 + Particles(4, 1:N).^2));
apparent_temp = (m / (2 * k)) * vrms^2;
T(i) = apparent_temp;
P(i) = J(i) / (Box_Size^2);
%uncomment following lines for movie
% plot(Particles(1,:), Particles(2,:), '.');
% axis([0 Box_Size 0 Box_Size]);
% M(i) = getframe;

elapsed = elapsed + dt;
Time(i) = elapsed;
end

Force = J(end) / t; %average force on wall
Pressure = Force / (Box_Size^2) %average pressure of gas

%following calculations used to find apparent temperature
vrms = sqrt(mean(Particles(3, 1:N).^2 + Particles(4, 1:N).^2));
apparent_temp = (m / (2 * k)) * vrms^2;

%plot temperature, pressure vs time graph
yyaxis left
plot(Time, T); %plot of temperature v time
axis([0, t, 0, inf]);
xlabel('Time (s)');
ylabel('Temperature (K)');
yyaxis right
plot(Time, P);

```

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ylabel('Pressure (Pa)');

%plot impulse graph.
% plot(Time, J); %plot of impulse v time
% axis([0, t, 0, inf]);
% xlabel('Time (s)');
% ylabel('Total Impulse (kg.m/s)');
% movie(M, 1, 1 / dt); %uncomment for movie

function [ax, ay] = force_interaction(dt, m, dx, dy)
    sig = 3.715 * 10^(-8);
    eps = 10^-4;
    ax = 24 * (1 / m) * eps * sig^6 * (1 / dx^(13)) * (2*(sig^6) - dx^6); %acceleration in x
    % direction
    ay = 24 * (1 / m) * eps * sig^6 * (1 / dy^(13)) * (2*(sig^6) - dy^6); %acceleration in y
    % direction
    if dt * abs(ax) > 10 %checks if acceleration is abnormally large, sets to 0 if so
        ax = 0;
    end
    if dt * abs(ay) > 10 %checks if acceleration is abnormally large, sets to 0 if so
        ay = 0;
    end
end
end

```

References

- [1] Powles J.G., Gubbins K.E., 1975. *The Intermolecular Potential for Nitrogen* Chemical Physics Letters vol. 38, no. 3. Accessed 14/05/2020