Molecular simulation of Ar, CH_4, C_2H_6 with MC algorithm in Python

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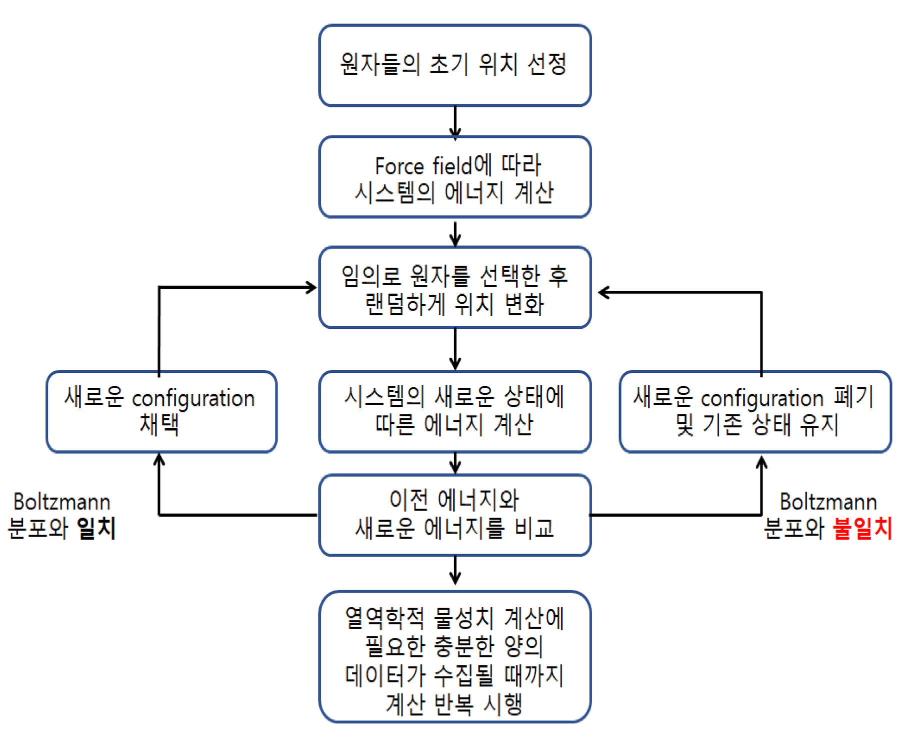
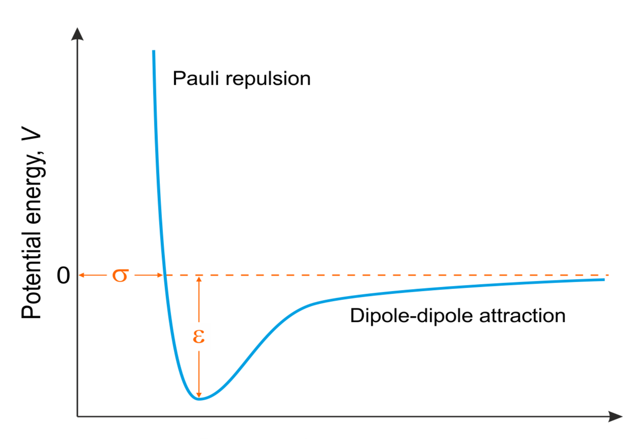
Abstract

Monte Carlo molecular simulation

Previously, several EOS (equations of state) were used to figure out thermodynamic properties of materials. However, it has the disadvantages of molecules having polarity or supercritical phase.
MC algorithm using randomness is implemented in Python to estimate thermodynamic properties of Ar, CH_4, and C_2H_6 more accurately than EOS. Internal energy and Pressure are estimated using NVT ensemble and heat capacity derived to compare the accuracy to EOS.

Project – Conceptual design





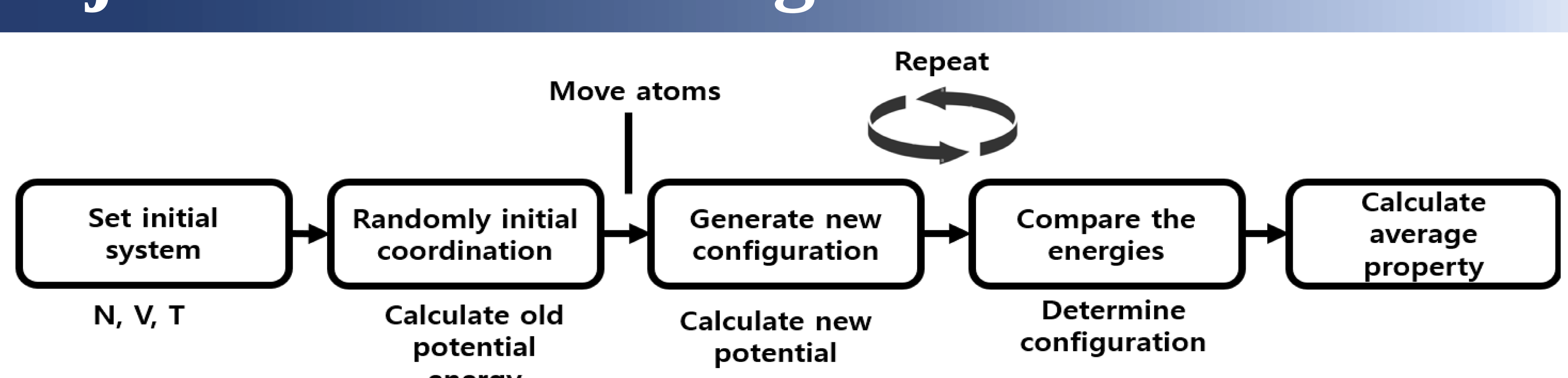
$$V_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Lennard-Jones potential model

$$V = \sum_{bonds}\frac{1}{2}k_r(r_{ij}-r_0)^2 + \sum_{angles}\frac{1}{2}k_\theta(\theta_{ijk}-\theta_0)^2 + \sum_{torsions}\sum^{n}k_{\phi,n}[\cos(n\phi_{ijkl}+\delta_n)+1]$$
$$+ \sum_{non-bonded\ pairs}\left[\frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}}\right]$$

Force field

Project – Detailed design

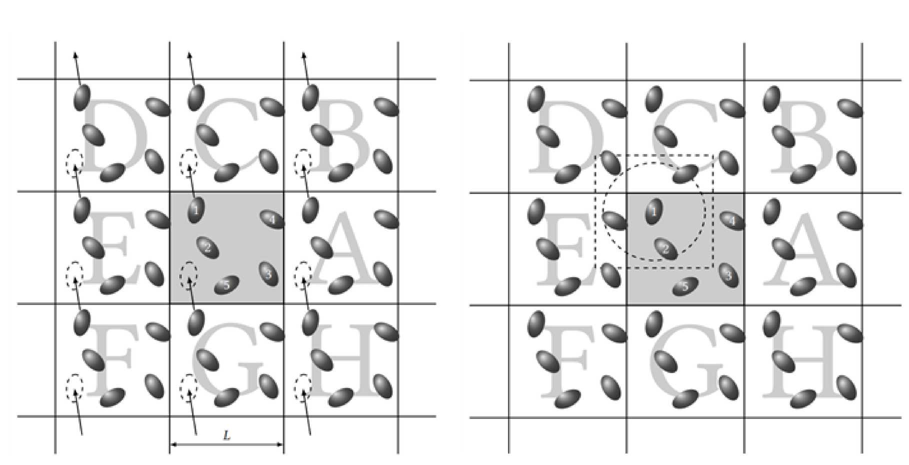



```
if(U_new > U_old):
    prob = np.exp((U_old - U_new) / (k * T))
    P = np.random.rand()
    if(prob > P):
        acc = acc + 1
        x[i] = x_new
        y[i] = y_new
         z[i] = z_new
     else :
        rej = rej + 1
else:
    x[i] = x_new
    y[i] = y_new
    z[i] = z_new
    acc = acc + 1
```

Boltzmann distribution

```
x_new = x + (2.0 * np.random.rand() - 1.0) * dr_max
y_new = y + (2.0 * np.random.rand() - 1.0) * dr_max
z_new = z + (2.0 * np.random.rand() - 1.0) * dr_max
if(x_new > BL):
    x_new = x_new - BL
if(x_new < 0):
    x_new = x_new + BL
if(y_new > BL):
    y_new = y_new - BL
if(y_new < 0):
    y_new = y_new + BL
if(z_new > BL):
    z_new = z_new - BL
if(z_new < 0):
    z_new = z_new + BL
move_ratio = acc/(acc+rej)
            if (move_ratio > 0.55):
                dr_max = dr_max * 1.05
            if (move_ratio < 0.45):
                dr_max = dr_max * 0.95
```

Optimization of accept ratio

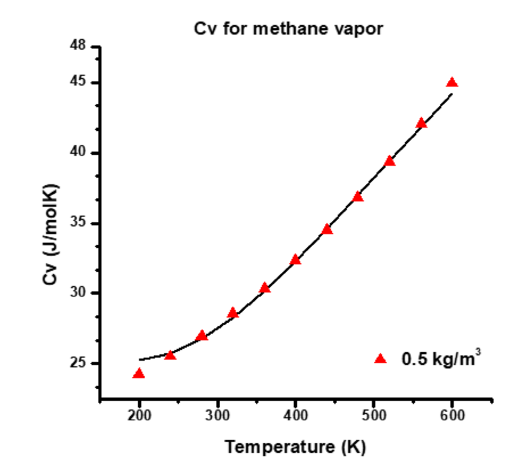


```
for i in range(N):
        for j in range(i+1, N):
            dx = abs(x[i]-x[j])
            dy = abs(y[i]-y[j])
            dz = abs(z[i]-z[j])
            if dx > BL/2:
                dx = dx - BL * round(dx/BL)
            if dy > BL/2:
                dy = dy - BL * round(dy/BL)
            if dz > BL/2:
                 dz = dz - BL * round(dz/BL)
            r = sqrt(pow(dx, 2) + pow(dy, 2) + pow(dz, 2))
            if (r > r_cut):
                continue
```

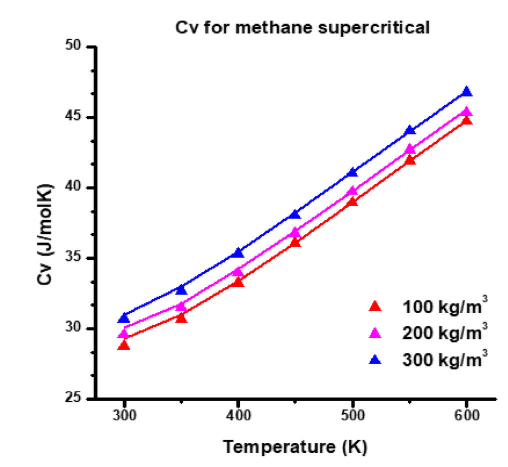
PBC condition
& Minimum image convention

Project - Results

- Heat capacity from Internal energy



Methane vapor

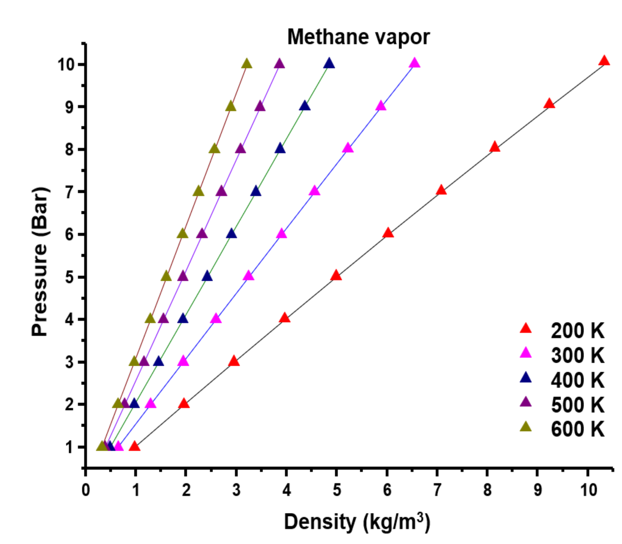


Methane supercritical

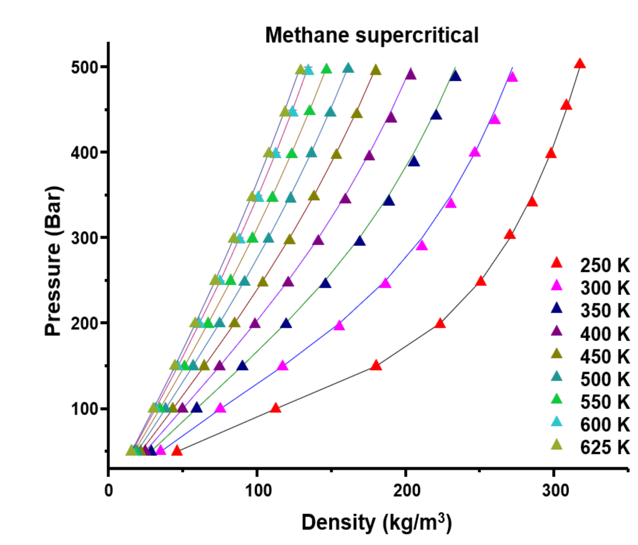
$$\frac{E}{nRT} = \frac{6}{2} + \sum_{j=1}^{3n-6}\left\{\frac{\Theta_{vj}}{2T} + \frac{\frac{\Theta_{vj}}{T}}{\exp\left(\frac{\Theta_{vj}}{T}\right)-1}\right\}$$

Statistical energy

- Pressure vs Density graph

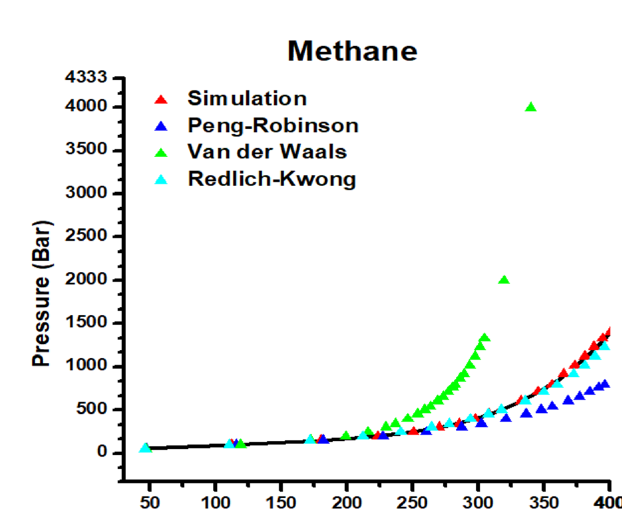


Methane vapor



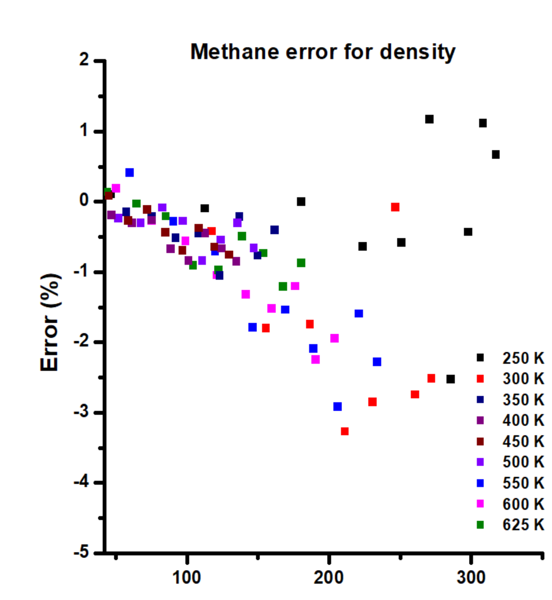
Methane supercritical

- Comparison with EOS

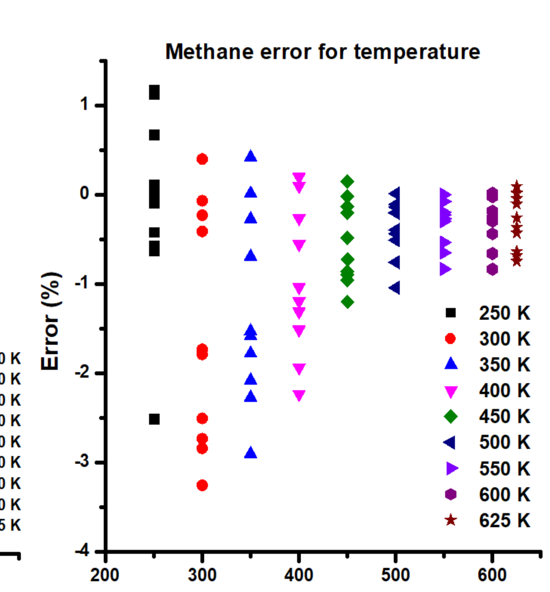


More accurate than EOS for supercritical phase

- Relative error

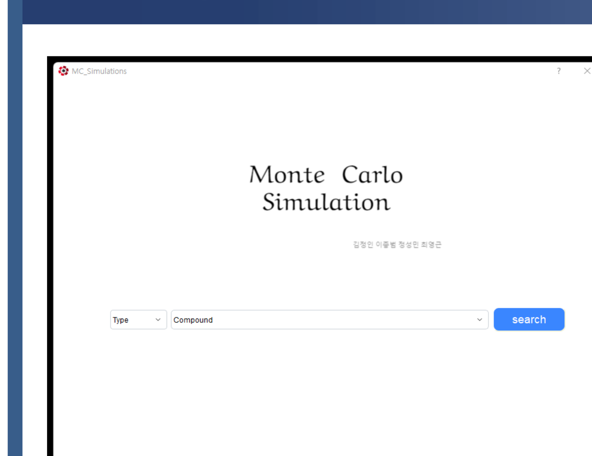


Density

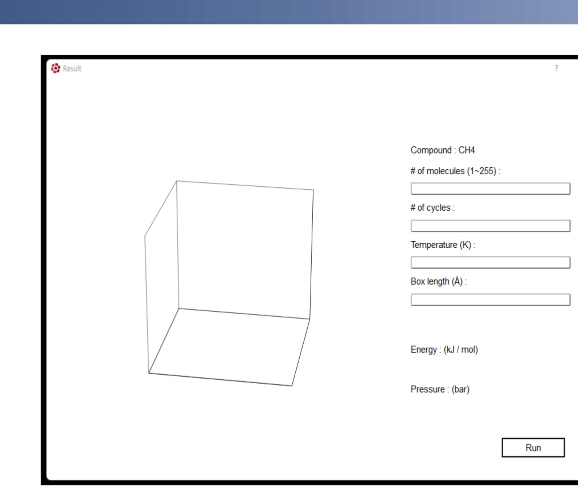


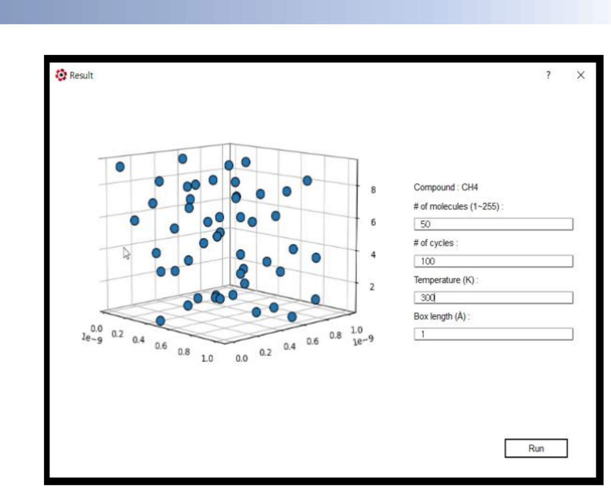
Temperature

Project – UI design



Initial Page





Result Page

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