Estimation of thermodynamic properties of Methane and Carbon dioxide by MC & PR EOS

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Abstract

Using molecular simulation software based on Monte carlo method, we calculate thermodynamic properties of Methane and Carbon Oxide. To prevent phase transition of materials, calculations are progressed by path that via supercritical fluid zone. In this research, we apply TraPPE-UA force field model to simulation. We get potential energy from simulation and calculate Helmholtz energy. So, we approve accuracy of this simulation through checking free energy change and comparing compressibility factors among simulation, PREOS and experimental values.

Theory

◇ Montecarlo simulation

- Random number generation (0 ~ 1)
- Convert random numbers to sample values
- Convert probability distribution to cumulative probability distribution
- Transform sample values and enter them into the model
- Record simulation results
- Repeat

◇ Lennard-Jones (L J)

$$u_{ij}(r) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] + \frac{q_i q_j}{4\pi\epsilon_0 r}$$

◇ Gibbs Duhem Integration

$$\frac{A(\rho_2,T)}{N} = \frac{A(\rho_1,T)}{N} + \int_{\rho_1}^{\rho_2} \frac{P(\rho)}{\rho^2} d\rho \text{ (At constant T)}$$

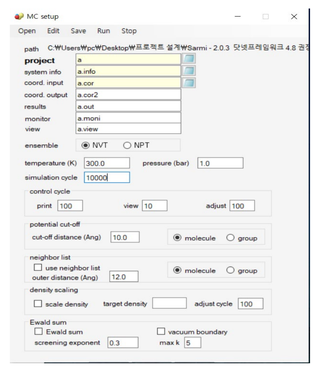
$$\frac{A(\rho,T_2)}{NT_2} = \frac{A(\rho,T_1)}{NT_1} + \int_{T_1}^{T_2} \frac{E(T)}{NT^2} dT \text{ (At constant } \rho)$$

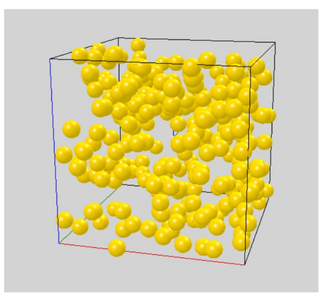
◇ PREOS

$$P = \frac{RT}{\underline{V}-b} - \frac{a(T)}{\underline{V}(\underline{V}+b)+b(\underline{V}-b)}$$

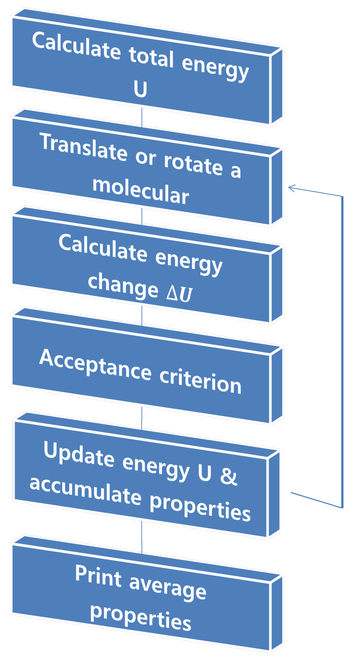
$$a(T) = 0.45724\,\frac{R^2 {T_c}^2}{{P_c}^2} \qquad b = 0.07780\,\frac{RT_c}{P_c}$$

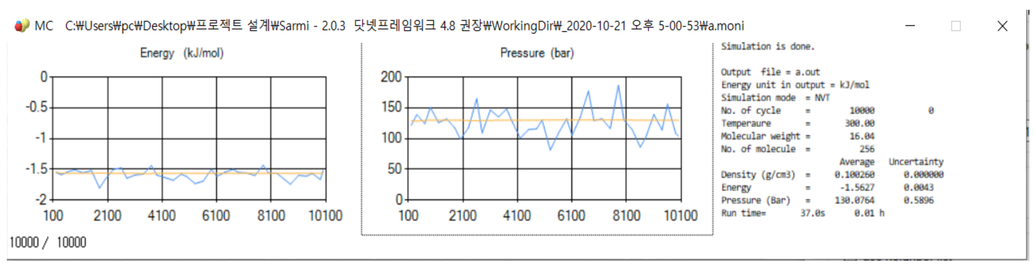
Project





- **Select Substance**
- **Select Ensemble(NVT , NPT)**
- **Set P, T, Cycle #**
- **At least 10,000 cycles**
- **3D coordinated**
- **number of particles is constant**
- **Simulation**
- **Calculate ρ, E, P**
- **Change ρ, T**
- **Repeat**





Discussion & Conclusion

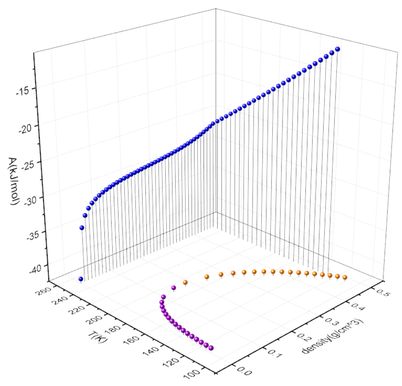


fig1. The Helmholz energy of Methane obtained from the gibbs Duhem integration. The path avoid 2-phase area, so can prevent phase transition in simulation. Lowest point is helmholtz energy of ideal gas methane 250k 1bar. At section1, density increase, and temperature is fixed. At section 2, density is fixed and temperature decrease. The entire path is shown bottom of graph.

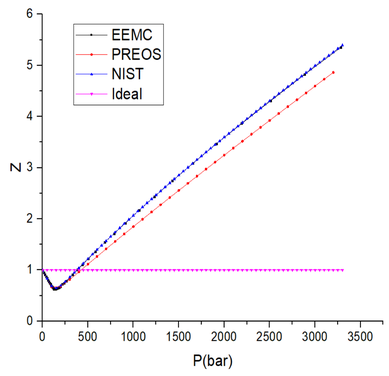


fig2. The compressibility factors of methane obtained from EEMC, PREOS, experimental data. At constant temperature condition, Z is lower than ideal value at low pressure, but at high pressure, it is higher than ideal value. EEMC data of methane show high precision as compared with experimental data

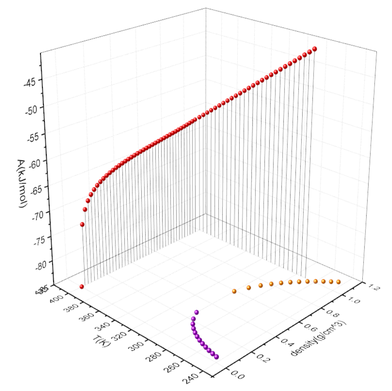


fig3. he Helmholz energy of Carbon dioxide obtained from the gibbs Duhem integration. The path avoid 2-phase area, so can prevent phase transition in simulation. Lowest point is helmholtz energy of ideal gas methane 400k 1bar. At section1, density increase, and temperature is fixed. At section 2, density is fixed and temperature decrease. The entire path is shown bottom of graph.

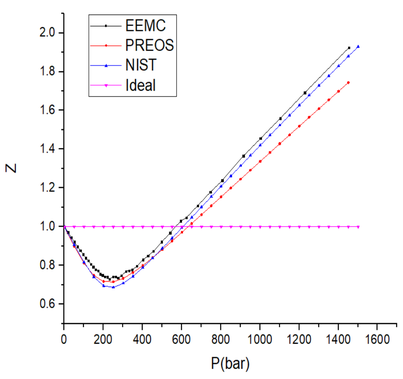


fig4. The compressibility factors of Carbon dioxide obtained from EEMC, PREOS, experimental data. At constant temperature condition, Z is lower than ideal value at low pressure, but at high pressure, it is higher than ideal value. EEMC data of Carbon dioxide show higher accuracy than PREOS data

Reference

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