PVT성질의 분자 동역학적 모사

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Molecular Dynamics Simulation of PVT Property

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Introduction

Knowledge of *PVT* properties is important to the interpretation of physical and chemical processes. This information is usually obtained from experimental measurements. However, most measurements are limited to a relatively small temperature and pressure range. In some cases data have been extrapolated of interpolated by fitting to an equation of state(EOS). However, the reliability of an EOS is dependent on the form selected and comprehensiveness of experimental database because most EOSs are empirically based. From these points of view, molecular dynamics simulation is one of the best methods to supplement experimental data.

PVT data can be easily obtained from a simple equation($PV=NkT$) for ideal gas. For real gas, however, interaction energy between molecules should be considered for computing *PVT* data. Applying appropriate potential function, *PVT* data can be obtained by molecular dynamics simulation. In this study, pressure has been computed for a large range of temperature and molar volume.

Theory

A simple method of fixing the kinetic temperature of a system in molecular dynamics simulation is to rescale the velocities at each time step by a factor of $\chi = (T/\mathcal{T})^{1/2}$ where $\mathcal{T}$ is the current kinetic temperature, T is the desired thermodynamic temperature[1]. Constant kinetic temperature dynamics is generated by the equations of motion

$$\dot{\mathrm{r}} = \mathrm{p}/m$$

$$\dot{\mathrm{p}} = \mathrm{f} - \xi(\mathrm{r},\mathrm{p})\mathrm{p}$$

where r is a position vector, **p** is a momentum, *m* is mass, **f** is force and $\dot{\mathrm{r}}, \dot{\mathrm{p}}$ is a time derivative of r, p. The quantity $\xi(\mathrm{r},\mathrm{p})$ is a kind of friction coefficient which varies so as to constrain $\mathcal{T}$ to a constant value. The constraint is chosen so as to perturb as little as possible the classical equations of motion, by making ξ a Lagrange multiplier which minimizes the difference between the constrained and Newtonian trajectories. Finally a modified velocity equation in leap-frog scheme can be written as followed:

$$\dot{\mathrm{r}}\left(t+\frac{1}{2}\delta t\right) = (2\chi-1)\,\dot{\mathrm{r}}\left(t-\frac{1}{2}\delta t\right) + \chi \mathrm{f}\,(t)\,\delta t/m\ .$$

Pressure is defined as the force per unit area acting normal to the surface. In general, pressure is compose of two components: kinematic pressure(P_k) and dynamic pressure(P_d). Kinetic pressure is the momentum carried by the atoms themselves as they cross a unit area during *dt* and dynamic pressure is the momentum flux transferred as a result of forces acting between atoms that lie on different sides of the surface[3].

The kinetic pressure is usually derived in kinetic theory[2]. Imagine a cubic cell which contains N molecules. Under the kinetic theory, the average force on container walls has been determined to be

$$F_{avg} = \frac{mN\langle v_x^2\rangle}{L}$$

where <·> is time average. Then the pressure in a container can be expressed as

$$P_k = \frac{F_{avg}}{A} = \frac{mN\langle v^2\rangle}{3LA} = \frac{2N}{3V}\frac{m\langle v^2\rangle}{2}.$$

According to equipartition theory[6], pressure can be written as

$$P_k = \frac{NkT}{V}$$

where k is Boltzmann constant. This is equal to EOS of ideal gas[5].

The dynamic pressure is the total force acting normal to the surface A, where the forces are caused by atoms on one side of the surface interacting with atoms on the other side. It can be written as

$$P_d = \frac{1}{3V}\langle \sum\sum_{i<j} \mathbf{F}_{ij} \cdot \mathbf{r}_{ij} \rangle$$

where V is volume, $\mathbf{F}_{ij}$ is intermolecular force and $\mathbf{r}_{ij}$ is distance between molecules i and j [4].

Model and method of molecular dynamics simulation

In present study we conduct simulation in the canonical ensemble system(constant N, V, T). The molecules interact via Lennard-Jones potential,

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

The initial positions are the sites on a face-centered-cubic(fcc) lattice. The particle velocity follows the Maxwell-Boltzmann distribution. Periodic boundary condition and cutoff method are employed for reducing calculation time. 365 molecules are traced with leap-frog algorithm.

The simulation data have been used for calculation after the system get to equilibrium in order to remove an effect of fcc structure. The computer simulation values for pressure are calculated as follows:

$$P_{sim} = \frac{NkT}{V} - \frac{1}{3V}\left\langle \sum\sum_{i<j} r_{ij}\frac{du(r_{ij})}{dr_{ij}} \right\rangle.$$

The simulation is performed over some different temperature and molar volume.

Result and Discussion

The pressure of hydrogen is computed at each temperature of 100K, 300K and 500K. Simulation results are compared with Peng-Robinson EOS which is practically used. Comparison of compressibility factor(Z) between simulation data and calculation data from EOS is shown in Figure 1. As Z becomes larger, calculation data from EOS deviate from experimental data, but simulation results are fairly approximate.

Comparison of error between simulation data and calculation data from EOS is shown in Fig 2. Simulation data is more approximate to experimental data than calculation data through large range of molar volume.

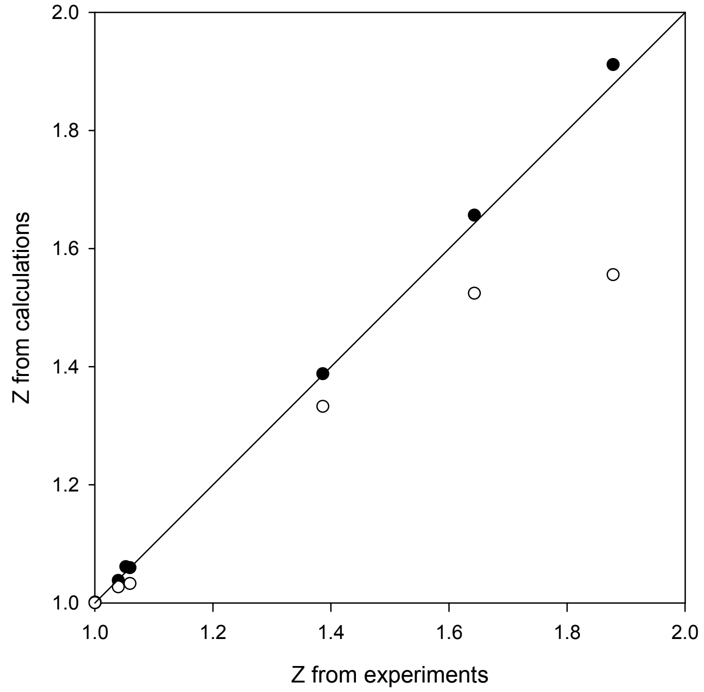

Fig 1. Comparison of compressibility factor. Black circles for MD simulation and white circles for P-R EOS. 100K≤T≤500K and 1≤P≤1000bar.

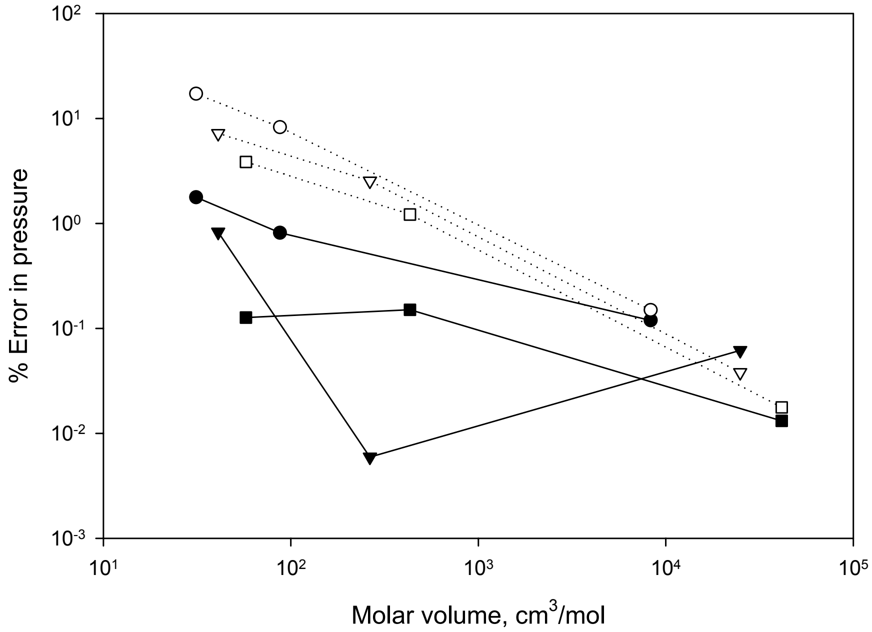

Fig 2. Comparison of simulation data with calculation data from EOS. Solid lines denote MD simulation and dotted lines denote P-R EOS. Circles = 100K, triangles = 300K, and squares = 500K.

Conclusion

The molecular dynamics simulation is a powerful method of physical property prediction and results from molecular dynamics simulation are very similar to experimental data. Therefore, we can predict many kinds of useful quantities like *PVT* property using molecular dynamics simulation without experiment. Actually, *PVT* data can be easily calculated by some EOSs but their applicable range is confined to finite temperature and pressure. Molecular dynamics simulation gives more accurate results of *PVT* properties applying to appropriate potential energy function.

Acknowledgment

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