Equation of State for Free Energy of Homogeneous Nucleation in Supersaturated Lennard-Jones Vapor Phase Derived by Monte Carlo Simulations

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ABSTRACT

Monte Carlo simulations were carried out to estimate the free energy of homogeneous nucleation in supersaturated Lennard-Jones vapor phase. We suggested a simple model for the homogeneous nucleation as phase transition between the cluster phase and the supersaturated vapor phase. The Monte Carlo simulations were performed to obtain the cluster phase and the vapor phase separately, and we estimated the free energy of the nucleation as a difference between the free energies of the each phase. The Helmholtz free energy was obtained by the thermodynamic integration. Such simulations were performed among 2-80 of the number of particles, 0.01-1.00 ε/k of the temperature, besides 30, 43.2, 90, 240, and 1000 σ^3 of the volume per particle; where the symbols ε and σ are the Lennard-Jones potential parameters. From the simulation results, we assumed the equation of state for the Helmholtz free energy of the nucleation as a function of the number of particles, temperature, and volume per particle. The equation of state gave the maximum against the number of particles; the maximum corresponds to the size and the free energy of the critical nucleus. Moreover, we rearranged the equation of state for estimating Gibbs free energy of the nucleation as a function of the number of particles, temperature, and pressure by taking into consideration the volume dependence of the thermodynamic properties. It was concluded that the equation of state could represent Gibbs free energy of the homogeneous nucleation except for the high-pressure region.

A part of this work is reported:

- Yosuke Kataoka and Yuri Yamada, *Fluid Phase Equilibria,* **194**-**197**, 207-217 (2002): Chapter 2.
- Yuri Yamada and Yosuke Kataoka, *Bull. Chem. Soc. Jpn.,* **76**, 81-88 (2003): Chapter 3.
- Yuri Yamada and Yosuke Kataoka, *Bull. Chem. Soc. Jpn.,* (2003), in publishing: Chapters 4 and 5.

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CONTENTS