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# Van der Waals type equation of state for Lennard-Jones fluid and the fluctuation of the potential energy by molecular dynamics simulations

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Molecular dynamics (MD) simulations of a Lennard-Jones system are performed to obtain the  $pVT$  and  $UVT$  relations. An extended van der Waals equation of state (EOS) is derived by statistical mechanics on the perturbation approximation. A hard sphere system is used as the reference system. The Ree–Hoover EOS is assumed for the hard sphere system. The attraction energy term in the canonical ensemble partition function is extended by a cluster expansion. The new EOS includes three parameters, two of which are the interaction parameters in the Lennard-Jones interaction. The last parameter is the effective volume of the hard sphere system as the reference. The extended van der Waals EOS reproduces the  $pVT$  and  $UVT$  relations, at least qualitatively, whereas the original van der Waals EOS can explain only the  $pVT$  relation. The present EOS can also explain the fluctuations of the potential energy as calculated by MD simulations with 1000 molecules in the unit cell. In this sense, the present EOS gives better heat capacities at constant volume  $C_v$ , even at lower temperatures than the original van der Waals EOS, which includes the attraction part of the equation, with no temperature dependence in the internal energy  $U$ .

**Keywords:** equation of state; molecular dynamics simulation; Lennard-Jones system; fluctuation of the potential energy

## 1. Introduction

The van der Waals equation of state (EOS) is often used in physical chemistry because of its simplicity and the fact that it explains the characteristics of a real gas [1]. The following  $pVT$  relation also explains the vapour-liquid critical point:

$$p(N, V, T) = \frac{NkT}{V - Nb} - a\left(\frac{N}{V}\right)^2, \quad (1)$$

where  $a$  and  $b$  are constants that characterise the molecular system. The variables  $p$ ,  $N$ ,  $V$  and  $T$  are the pressure, the number of molecules, the volume and the temperature of the system, respectively. The Boltzmann constant is denoted as  $k$ . The vapour-liquid transition point is calculated by the Maxwell construction in the van der Waals loop region in the  $pVT$  relation, where the unstable state is also found [1]. This loop appears because the van der Waals theory assumes a single phase. Conventional molecular simulation methods also treat the phase as a single phase.

In a previous paper, we had derived an extended van der Waals EOS by statistical mechanics on the perturbation approximation [2], and qualitative agreement with the molecular dynamics (MD) simulation results on a Lennard-Jones system was observed. This paper

introduces better  $pVT$  and  $UVT$  relations on such systems. A hard sphere system is used as the reference system. In the previous paper, we had used the simple pressure EOS of the hard spheres. In this study, the Ree–Hoover EOS [3] is assumed for the hard sphere system. The attraction energy term in the canonical ensemble partition function is extended by a cluster expansion, as described in the previous paper [2].

Another new aspect of this study is the fluctuation of the potential energy. The MD simulations reveal large fluctuations as functions of temperature and density. The fluctuations of the potential energy will also be calculated using the new EOS.

## 2. Extension of van der Waals EOS

A molecular system with  $N$  spherical molecules of mass  $m$  at temperature  $T$  and volume  $V$  is considered. The canonical partition function  $Q(N, V, T)$  is given as follows [4]:

$$Q(N, V, T) = \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} Z_N, \quad (2)$$

$$Z_N = \int_V e^{-U_N(r_1, \dots, r_N)/kT} dr_1 \dots dr_N. \quad (3)$$

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Here, the potential energy of the system is written as  $U_N(r_1, \dots, r_N)$ . The effect of the interaction energy is approximated by the van der Waals approximation. The statistical mechanical theory on the van der Waals-type EOS adopts the perturbation approximation. The total potential energy is divided into two parts:

$$U_N = U_N^{(0)} + U_N^{(1)}, \quad (4)$$

where  $U_N^{(0)}$  and  $U_N^{(1)}$  are the potential energy of the reference system and the potential energy of the perturbed system, respectively. The quantity  $\beta$  is the inverse of temperature:  $\beta = 1/kT$ . The configuration integral is as follows:

$$\begin{aligned} Z_N &= \int \dots \int e^{-\beta(U_N^{(0)} + U_N^{(1)})} dr_1 \dots dr_N \\ &= \int \dots \int e^{-\beta U_N^{(0)}} dr_1 \dots dr_N \\ &\quad \times \frac{\int \dots \int e^{-\beta(U_N^{(0)} + U_N^{(1)})} dr_1 \dots dr_N}{\int \dots \int e^{-\beta U_N^{(0)}} dr_1 \dots dr_N}. \end{aligned} \quad (5)$$

This equation can be rewritten as follows:

$$Z_N = Z_N^{(0)} \langle \exp(-\beta U_N^{(1)}) \rangle_0. \quad (6)$$

The reference system is a hard sphere system.

Ree and Hoover reported the following EOS [3]:

$$\begin{aligned} \frac{p}{\rho_{\text{HS}} kT} - 1 &= b\rho \frac{1 + 0.063507b_0\rho_{\text{HS}} + 0.017329b_0^2\rho_{\text{HS}}^2}{1 - 0.561493b_0\rho_{\text{HS}} + 0.081313b_0^2\rho_{\text{HS}}^2}, \\ \rho_{\text{HS}} &= \frac{Nb_0}{V}, \quad b_0 = \frac{2\pi}{3}\sigma_{\text{HS}}^3, \end{aligned} \quad (7)$$

where  $\sigma_{\text{HS}}$  is the diameter of the hard sphere and  $\rho_{\text{HS}}$  is the reduced density of the hard sphere system. We assume this EOS for the reference system. An explicit equation for the configuration integral  $Z_N^{(0)}$  is obtained by statistical mechanical integration. This integration will be presented in a future paper, in which the free energies will be discussed.

There may be monomers, dimers, trimers, etc. in the system depending on the temperature and density. The largest cluster in the system is assumed to be an  $M$ -mer. The structure and energy of the  $J$ -mer cluster are simplified as follows. The  $J$ -mer cluster has  $(J-1)$  bonds that start from the central molecule being considered. Each bond has energy  $-\varepsilon$ . The parameter  $\varepsilon$  is the energy parameter in the Lennard-Jones potential function. The energy of the  $J$ -mer cluster is then  $-(1/2)(J-1)\varepsilon$ . The factor  $1/2$  appears because the present theory is a one-body approximation, and this factor is necessary in order to obtain a reasonable total energy for the system. Therefore, in the present theory, the

$J$ -mer cluster has a Boltzmann factor of  $\exp((1/2)\beta(J-1)\varepsilon)$ , according to the temperature of the system. The geometric probability of its being found in the system is proportional to the pre-exponential factor  $(v_0/v)^{(J-1)/3}$ . Here,  $v$  is the volume per molecule, and  $v_0$  is the volume per molecule for the case of the closest packing. The values of  $M$  and  $v_0$  are fixed by the crystal structure. The closest packing structure in the Lennard-Jones system is face-centred cubic and it has 12 nearest neighbours. For this reason,  $M = 13$  and the volume  $v_0$  has the following value:  $\sigma^3/\sqrt{2}$ , where  $\sigma$  is the size parameter in the Lennard-Jones potential function. The exponent  $(J-1)/3$  is assumed because the probability of finding the  $J$ -mer cluster may be proportional to the ratio of the length of the closest packing structure to that of the characteristic length of the volume per molecule of the system. Based on this assumption, the partition function is written as follows:

$$Z_N = Z_N^{(0)} Z_N^{(1)}, \quad (8)$$

$$Z_N^{(1)} = \left[ \sum_{J=1}^M \left( \frac{v_0}{v} \right)^{(J-1)/3} \exp \left( \frac{1}{2} \beta (J-1) \varepsilon \right) \right]^N, \quad (9)$$

$$\begin{aligned} q_a &= [Z_N^{(1)}]^{1/N} = \sum_{J=1}^M \left( \frac{v_0}{v} \right)^{(J-1)/3} \\ &\quad \times \exp \left( \frac{1}{2} \beta (J-1) \varepsilon \right). \end{aligned} \quad (10)$$

Equation (9) shows our model, i.e. the independent  $J$ -mer with its energy  $-(J-1)\varepsilon$  and the probability proportional to  $(v_0/v)^{(J-1)/3}$  according to the density. This model will be justified only by the following comparison with the MD simulations.

For this molecular partition function, the attractive term of the internal energy  $\langle U_a \rangle$  is obtained as follows:

$$\begin{aligned} \frac{\langle U_a \rangle}{N} &= kT^2 \left( \frac{\partial \ln q_a}{\partial T} \right)_{N,v} \\ \frac{\langle U_a \rangle}{N} &= kT^2 \frac{1}{q_a} \sum_{J=1}^M \frac{1}{2} (J-1) \varepsilon \frac{-1}{kT^2} \left( \frac{v_0}{v} \right)^{(J-1)/3} \\ &\quad \times \exp \left( \frac{1}{2} \beta (J-1) \varepsilon \right). \end{aligned} \quad (11)$$

The attraction part of the heat capacity at constant volume  $C_{\text{ve}}$  is calculated by the fluctuation of the attraction energy as follows:

$$\begin{aligned} \frac{\langle U_a^2 \rangle}{N} &= \frac{1}{q_a} \sum_{J=1}^M \left\{ \frac{1}{2} (J-1) \varepsilon \right\}^2 \left( \frac{v_0}{v} \right)^{(J-1)/3} \\ &\quad \times \exp \left( \frac{1}{2} \beta (J-1) \varepsilon \right), \end{aligned} \quad (12)$$

$$\frac{\langle U_a^2 \rangle - \langle U_a \rangle^2}{N} = \frac{C_{\text{ve}}}{N} kT^2. \quad (13)$$

The contribution of the attractive interaction to pressure is as follows:

$$p_a = kT \left( \frac{\partial N \ln q_a}{\partial V} \right)_{N,T}, \quad (14)$$

$$p_a = kT \frac{1}{q_a} \left[ \sum_{J=1}^M \frac{-(J-1)}{3} \left( \frac{v_0}{v} \right)^{(J-1)/3} \frac{1}{v} \exp \left( \frac{1}{2} \beta (J-1) \varepsilon \right) \right]. \quad (15)$$

### 3. MD simulation

NTV MD simulations [5] on fluid argon are performed at several temperatures in order to obtain the average pressure  $p$  and internal energy  $U$  as a function of volume  $V$ . As shown in Table 1, the following Lennard-Jones potential Equation (16) is adopted:

$$u(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]. \quad (16)$$

The time step is 1 fs, and the standard MD length is 1,000,000 steps in the Gear method. The velocity scaling method is used to control the temperature. The number of molecules in the cell is 1000. A periodic boundary condition is assumed on the cubic basic cell [5]. The assumed initial configuration is a simple cubic lattice, in which only the density varies depending on the volume. The Materials Explorer<sup>TM</sup> (v4 and v5) programs are used for the present simulation (<http://software.fujitsu.com/jp/materials-explorer/>). The cut-off distance is the half of the basic cell length and the standard corrections are included.

The very long simulations are expected in the simulation to obtain the fluctuations. For this reason, the Hernandez method (<http://software.fujitsu.com/jp/materials-explorer/>) is used in the calculation on the fluctuation of the potential energy, where the standard MD length is 10,000,000 steps, and the time for one MD step is 10 fs. This algorithm gives the stable MD simulation even with a rather long MD step.

### 4. $pVT$ and $UVT$ relations in the extended van der Waals EOS

In this study, the parameter  $b_0$  in Equation (7) is an adjustable parameter that is chosen by trial and error to be

Table 1. Lennard-Jones potential parameters for argon (<http://software.fujitsu.com/jp/materials-explorer/>). The Boltzmann constant is denoted as  $k$ .

$\varepsilon$ (kcal/mol)	$\varepsilon/k$ (K)	$\sigma$ (m)
0.2483	125	3.43E-10

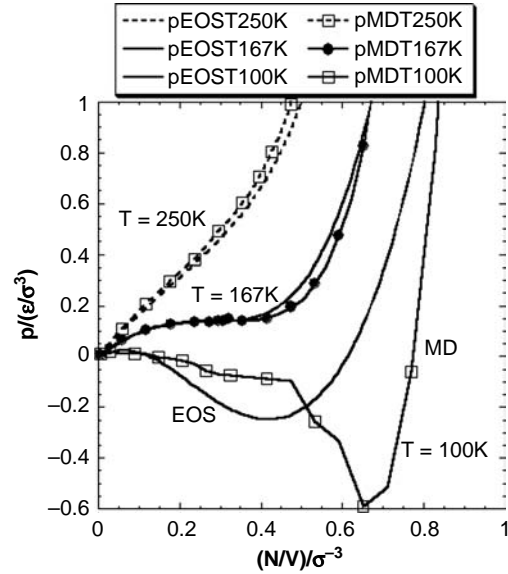


Figure 1.  $pVT$  relation as calculated by the extended van der Waals EOS and that obtained by MD simulation. The ordinate shows the pressure  $p$  in Lennard-Jones units  $\varepsilon/\sigma^3$ , and the abscissa shows the number density  $N/V$ . In addition, the constant temperature curves for  $T = 250$ , 167 and 100 K are shown.

$1.7\sigma^3$  through a comparison of the extended EOS with the results of MD simulation. The parameter  $\sigma$  is the size parameter in the Lennard-Jones potential in Equation (16). The fitted  $pVT$  and  $UVT$  relations are described in Figures 1

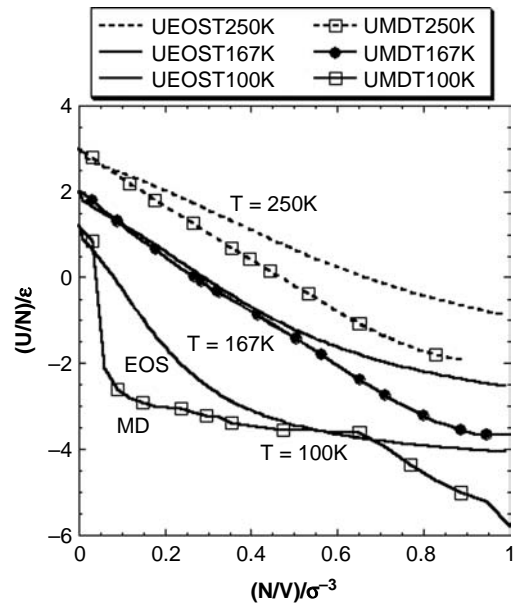


Figure 2.  $UVT$  relation as calculated by the extended van der Waals EOS and that obtained by MD simulation. The ordinate shows the internal energy per molecule in Lennard-Jones units  $\varepsilon$ , and the abscissa shows the number density  $N/V$ . In addition, the constant temperature curves for  $T = 250$ , 167 and 100 K are shown.



Table 2. Critical point as determined by the extended van der Waals EOS and the critical point in the fitted EOS of MD simulations on a Lennard-Jones system.

	$T_c$ ( $\epsilon/k$ )	$p_c$ ( $\epsilon/\sigma^3$ )	$\rho_c$ ( $\sigma^{-3}$ )
Nicolas et al. [6]	1.35	0.142	0.35
Kolafa and Nezbeda [7]	1.3396	0.1405	0.3108
Present study	1.34	0.139	0.27

	$T_c$ (K)	$p_c$ (atm)	$V_c$ ( $\text{cm}^3/\text{mol}$ )
Nicolas et al. [6]	169	61	69
Kolafa and Nezbeda [7]	167	60.4	78
Present study	167	59.7	90

and 2, respectively, and are compared with the extended van der Waals EOS. These figures indicate that the extended EOS can reproduce, at least qualitatively, the MD simulation results.

The critical point as determined by the proposed EOS is compared with that in the fitted EOS of the MD simulations on the Lennard-Jones system [6,7], as shown in Table 2. The obtained results agree fairly well with the fitted EOS, even with only three parameters in the proposed extended EOS.

### 5. Fluctuation of the potential energy

The MD results on the fluctuation of the potential energy are shown in Figure 3 for several temperatures as a function of the number density. The fluctuations at 130 K at a density of approximately  $0.095\sigma^{-3}$  are larger than

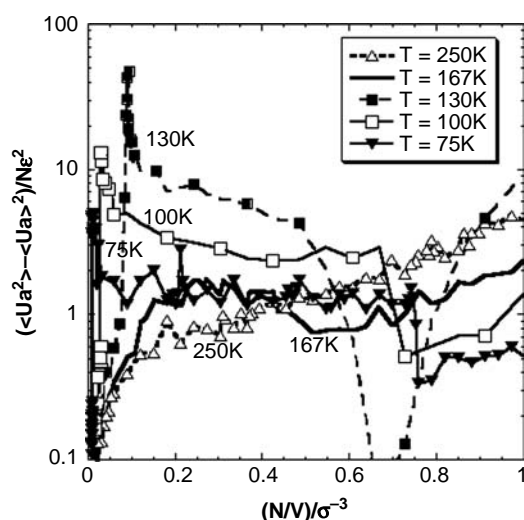


Figure 3. Fluctuations of the potential energy as obtained by MD simulations for several temperatures as a function of the number density. The ordinate shows the fluctuation of the potential energy (see Equation (13)) in Lennard-Jones units  $\epsilon^2$ , and the abscissa shows the number density  $N/V$ . In addition, the constant temperature curves for  $T = 250, 167, 130, 100$  and  $75$  K are shown.

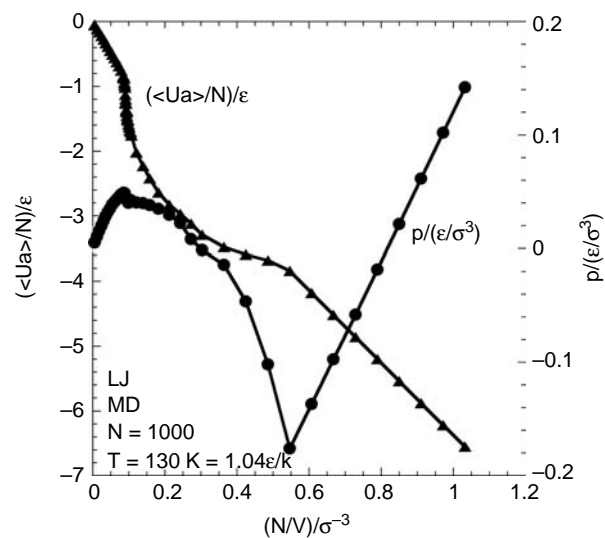


Figure 4. The average potential energy per molecule  $\langle U_a \rangle / N$  and pressure  $p$  as functions of number density  $N/V$  at  $T = 130$  K as obtained by MD simulations.

those at the critical temperature, 167 K, at a density of approximately  $0.3\sigma^{-3}$ , because the present calculation is performed in the  $NTV$  ensemble. Notable critical fluctuations are observed in the  $NTP$  ensemble. The state with large fluctuations of the potential energy corresponds to that with a peak in the pressure vs. density plot at 130 K. This state is found in the region in which the potential energy decreases steeply as a function of the density at 130 K. These features appear in Figure 4. An example of the molecular configuration in this region is shown in Figure 5. A large cluster appears in Figure 5.

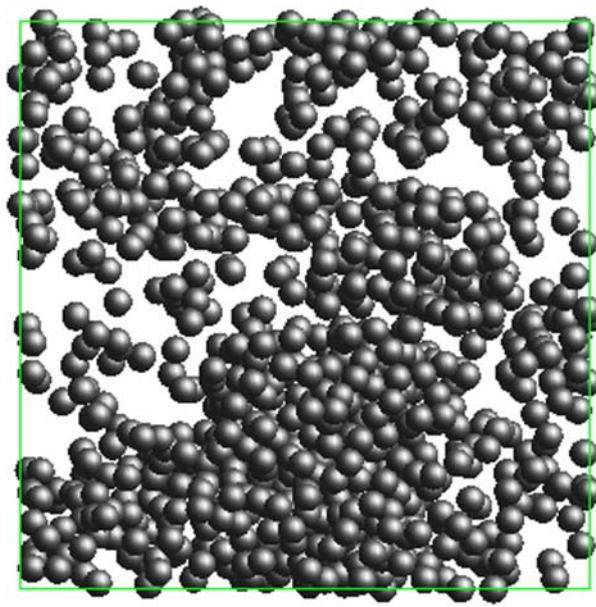


Figure 5. Example of the molecular configuration at  $T = 130$  K and a number density of  $N/V = 0.095\sigma^{-3}$ .

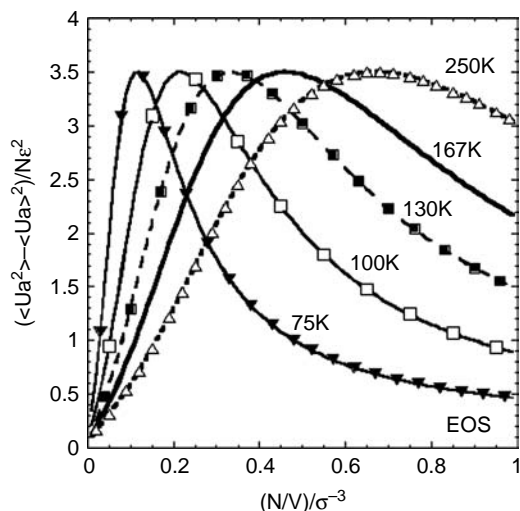


Figure 6. Fluctuations of the potential energy as obtained by the extended EOS for several temperatures as a function of the number density. The ordinate shows the fluctuation of the potential energy (see Equation (13)) in Lennard-Jones units  $\epsilon^2$ , and the abscissa shows the number density  $N/V$ . In addition, the constant temperature curves for  $T = 250, 167, 130, 100$  and  $75$  K are shown.

For comparison, the fluctuations of the potential energy are calculated by the extended EOS, as shown in Figure 6. In contrast to the MD results, the height of the maximum is always 3.5 in the proposed EOS. The density

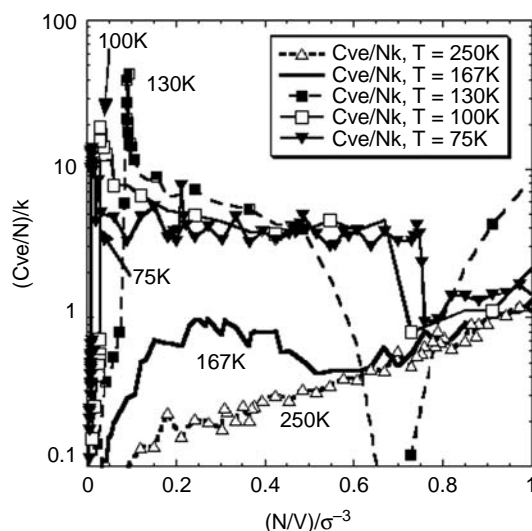


Figure 7. Heat capacities at constant volume from the potential energy as obtained by MD for several temperatures as a function of the number density. The ordinate shows the heat capacity at constant volume (see Equation (13)), and the abscissa shows the number density  $N/V$ . In addition, the constant temperature curves for  $T = 250, 167, 130, 100$  and  $75$  K are shown.

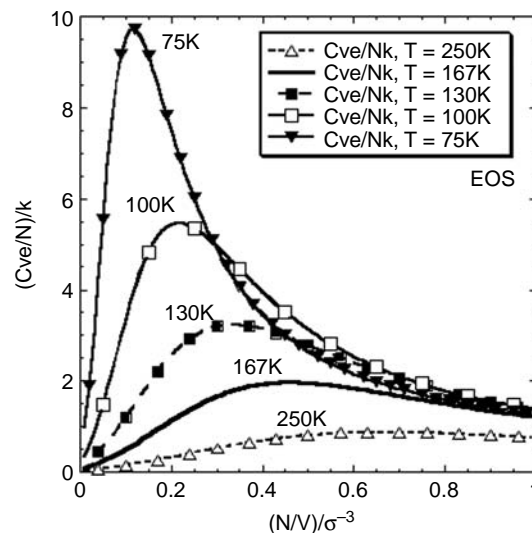


Figure 8. Heat capacities at constant volume from the potential energy as obtained by the extended EOS for several temperatures as a function of the number density. The ordinate shows the heat capacity at constant volume (see Equation (13)), and the abscissa shows the number density  $N/V$ . In addition, the constant temperature curves for  $T = 250, 167, 130, 100$  and  $75$  K are shown.

of the maximum fluctuations increases as a function of the temperature. This feature is the same in the MD results. The maximum value 3.5 is understood by the high temperature limit in the left-hand side of Equation (13) with  $\beta = 0$  at the volume  $v = v_0$ .

The heat capacities from the potential energy are shown in Figures 7 (MD) and 8 (EOS), as calculated using Equation (13). The density with the maximum heat capacity at constant volume increases as a function of the temperature in both figures. The orders of magnitude of the heat capacities in Figure 8 generally correspond to those in Figure 7. Since the theory behind the extended EOS essentially requires the one-body assumption, the effects of the short-range order in the molecular system are neglected. The extended EOS can explain the existence of a maximum in the heat capacity at constant volume as a function of the density, because large clusters develop around a particular density.

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