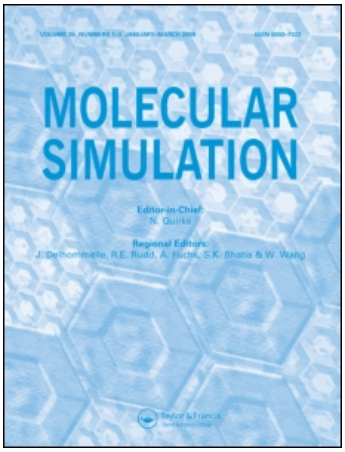

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Fluid-fluid Transition and Negative Expansion in 2 Step-function Molecules System by Statistical Mechanics

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Fluid–fluid Transition and Negative Expansion in 2 Step-function Molecules System by Statistical Mechanics

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In order to perform the statistical mechanical calculations, we adopt the periodic cubic system with two molecules in the unit cell. Our model potential function consists of a step-function and the hard sphere wall. We assume the minimum image convention and get the canonical partition function. We find the fluid–fluid phase transition and the negative thermal expansion in the system. We discuss the thermodynamic properties vs. temperature plots under the constant volume. We show some results of the Monte Carlo (MC) simulations on the system with the same potential function under the periodic cubic boundary condition for a comparison. The theoretical results on *pVT* relations are in agreement with the MC simulations on the two-molecule system. The results of 108-molecule system with the MC simulations are expected to have the similar phase transition near the state in the case of the two-molecule system.

Keywords: Step-function; Canonical partition function; Fluid–fluid phase transition; Negative thermal expansion; Monte Carlo simulation

INTRODUCTION

Computer simulations on a small number of molecules are frequently performed. We can use such that small systems to study the macroscopic properties by the periodic boundary conditions [1]. We are interested in the smallest system that consists of two molecules, because it is expected that the thermodynamic properties of the smallest system with the periodic boundary condition are in agreement with the ones of the larger system at least qualitatively.

The above system is the periodic system. In opposite, there are another small molecular systems where the periodicity is not always necessary. One example is the small molecular cluster. We consider the cluster structure as the condensed phase, for simplicity. We can say that the phase transition-like transformation of the structure [2] occurs between the cluster and the monomer states when the system is expanded at constant temperature [3,4]. Another interesting system is the small molecular system confined in the box. Two hard disks in a rectangular cell show the phase transition [5,6].

We study the thermodynamic properties of the small, infinitely periodic, system by the statistical mechanics because this demands smaller cost than the molecular simulations. In order to perform the statistical mechanical calculations, we adopt two-molecule ($N = 2$) system. The reason why we study the two-molecule system on the periodic boundary condition is that we can calculate the thermodynamic properties in detail, for example, the thermal expansion coefficient. Because the results are only on the two-molecule system, we cannot extrapolate them to the macroscopic system. We expect, however, some of the calculated properties are common with the macroscopic one qualitatively. It must be examined carefully which parts are common. One of the practical methods for the examination is to use Monte Carlo (MC) simulation on the several hundred molecules with periodic boundary conditions.

Our model potential function consists of a step-function and the hard sphere wall. As this potential has the step-function with a finite energy, the model system has the thermodynamic properties, which depend on the temperature. Similar models are studied to investigate the negative thermal expansion

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[7,8]. As this interaction has a short range, the canonical partition function will be obtained by the minimum image convention [1]. The pVT relation and other thermodynamic properties will be calculated and compared with the MC results. At the end of this work, the $N = 108$ system, examined by MC, will be shown that it is similar to the $N = 2$ system, qualitatively.

MODEL AND FORMULATION

Potential Function

Now we introduce potential function, the step-function. We assume the intermolecular interaction $u(r)$ as a function of only the intermolecular distance r:

$$u(r) = \infty, (r \le \sigma)$$
$$u(r) = \varepsilon, (\sigma < r \le \lambda\sigma) \quad (1)$$
$$u(r) = 0, (\lambda\sigma < r), \lambda = 1.5.$$

Here, ε and σ are potential constants. They have the dimensions of energy and length, respectively. Figure 1 shows the potential function $u(r)$.

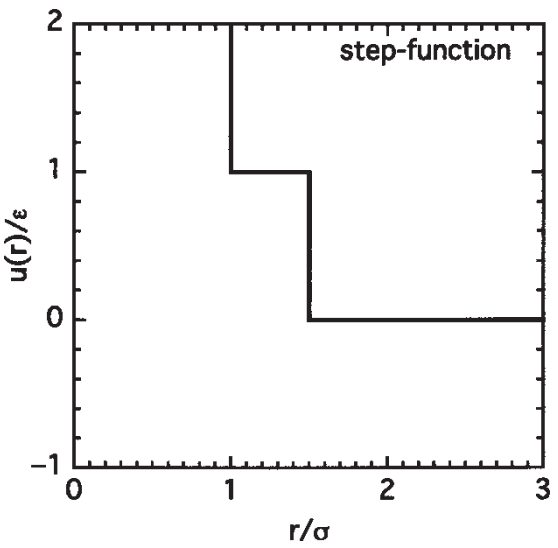

FIGURE 1 The step-function potential $u(r)$ is plotted as a function of the intermolecular distance r.

Partition Function of 2-Molecule System with the Step-Function

We assume two identical spherical molecules and consider the canonical ensemble of the two-molecule system with the periodic boundary condition at temperature T and volume V with the above potential function. We can fix the first molecule at the center of the unit cell because the potential function depends only on the molecular distance. The canonical partition function Q is the product of the ideal gas part Q_{id} and the interaction one Q_e [9,10].

$$Q = Q_{id} Q_e. \quad (2)$$

As the interaction energy depends only on the molecular distance, the interaction part is the next integral in the cube V_{cube} by the minimum image convention (see Fig. 1 in Ref. [1] and Fig. 2):

$$Q_e = \frac{1}{V} \int_{V_{cube}} \exp[-\beta u(r)]\, dv, \quad \beta = \frac{1}{kT}. \quad (3)$$

Here k is the Boltzmann constant, V is the volume of the system, and r is the molecular distance between the first and the second molecules. The position of the second molecule is confined in the minimum image cube where the first one is fixed at the center in the integration Eq. (3). The interaction is truncated outside the minimum image. Because the interaction has no long tail, this truncation is usually adopted in the molecular simulations.

We define the following common region V_s of the cube and the sphere (Fig. 2) and its volume $V_s(V,r)$ as a function of the half cell-length a and the radius r to obtain the partition function Eq. (3):

$$V_s = V_{cube} \cap V_{sphere}, \quad V_{cube} = V = 8a^3,$$
$$V_{sphere} = \frac{4\pi}{3} r^3. \quad (4)$$

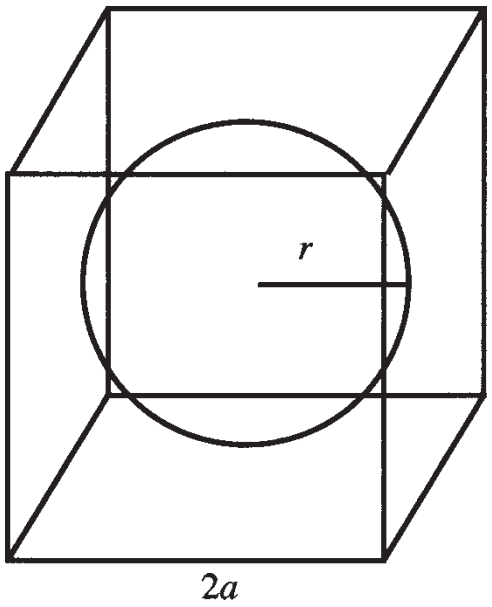

FIGURE 2 The minimum image convention in the cubic cell is described. We put the first molecule at the center of the cube, which has the same size and shape as unit cell. The other molecule is found in the cube. The circle indicates the sphere with radius r. This sphere is used in the integration to obtain the partition function.

The function $V_s(V,r)$ is obtained by the geometry,

$$V_s(V,r) = \frac{4\pi}{3} r^3, \quad r \le a$$

$$V_s(V,r) = \frac{2\pi}{3}(-3a^3 + 9ar^2 - 4r^3), \quad a \le r \le \sqrt{2}a$$

$$V_s(V,r) = \frac{2}{3}\left\{ \begin{array}{l} -a^3\pi + 3a\pi r^2 + 12a^2\sqrt{r^2-2a^2} + 4(a^3 - 3ar^2)\cos^{-1}\left(\frac{a}{\sqrt{r^2-a^2}}\right) \\ +(6a^3 - 6ar^2 + 8r^3)\cot^{-1}\left(\frac{a}{\sqrt{r^2-2a^2}}\right) - 8r^3\cot^{-1}\left(\frac{r\sqrt{r^2-2a^2}}{a^2}\right) \\ +(-4a^3 + 12ar^2)\tan^{-1}\left(\frac{a}{\sqrt{r^2-2a^2}}\right) - (2a^3 + 6ar^2)\tan^{-1}\left(\frac{\sqrt{r^2-2a^2}}{a}\right) \end{array} \right\}, \quad \sqrt{2}a \le r \le \sqrt{3}a. \tag{5}$$

Because the function $u(r)$ consists of three constant functions (see Eq. (1)), we can express the integration by the function $V_s(V,r)$ as follows:

$$\begin{aligned} &Q_e = 0, \quad V < V_1 \equiv \frac{8\sigma^3}{\sqrt{27}}, \\ &Q_e = \frac{1}{V}[e^{-\beta\varepsilon}(V - V_s(V,\sigma))], \\ &V_1 \le V < V_2 \equiv \frac{8\lambda^3\sigma^3}{\sqrt{27}}, \\ &Q_e = \frac{1}{V}[V - V_s(V,\lambda\sigma) \\ &\qquad + e^{-\beta\varepsilon}(V_s(V,\lambda\sigma)) - V_s(V,\sigma))], \\ &V \ge V_2. \end{aligned} \tag{6}$$

The Helmholtz free energy A has the following expression:

$$\begin{aligned} A &= -kT\ln(Q) = A_{id} + A_e \\ &= -kT\ln(Q_{id}) - kT\ln(Q_e). \end{aligned} \tag{7}$$

We adopt the next form for A_{id}, simply:

$$\begin{aligned} &A_{id} = -kT\ln(Q_{id}), \quad Q_{id} = \left(V_r T_r^{3/2}\right)^2, \\ &T_r = \frac{kT}{\varepsilon}, \quad V_r = \frac{V}{\sigma^3}. \end{aligned} \tag{8}$$

This means, the internal energy and the entropy have the following form, respectively:

$$U_{id} = 3kT, \quad S_{id} = 3k + k\ \ln\left(\left(\frac{V}{\sigma^3}\right)^2\left[\frac{kT}{\varepsilon}\right]^3\right). \tag{9}$$

The pressure p is also the next form, because our system is an effective two-molecule, infinitely periodic, one:

$$p = \frac{2kT}{V} = p_e. \tag{10}$$

We obtain the interaction part p_e by the formula:

$$p_e = kT\left(\frac{\partial \ln Q_e}{\partial V}\right)_T. \tag{11}$$

We can calculate the other thermodynamic properties by the standard way [11].

RESULTS

Fluid–Fluid Transition

The pVT relation (Fig. 3) shows that there is a phase transition-like behavior at the low temperatures around the volume V_2 because the isothermal compressibility is negative near this volume. The dense phase is the condense one and it is difficult to distinguish the solid or liquid ones in the $N = 2$ system. Then, we assign this transition tentatively as fluid–fluid transition because of their densities. The phase boundary between them will be examined in the following work.

Figure 4 shows the spinodal line by the solid line in the (V,T) domain. The critical constants are:

$$\begin{aligned} &T_c = 0.332\varepsilon/k, \quad V_c = 6.256\sigma^3, \\ &p_c = 0.225\varepsilon/\sigma^3. \end{aligned} \tag{12}$$

The dashed lines will be described in the next section.

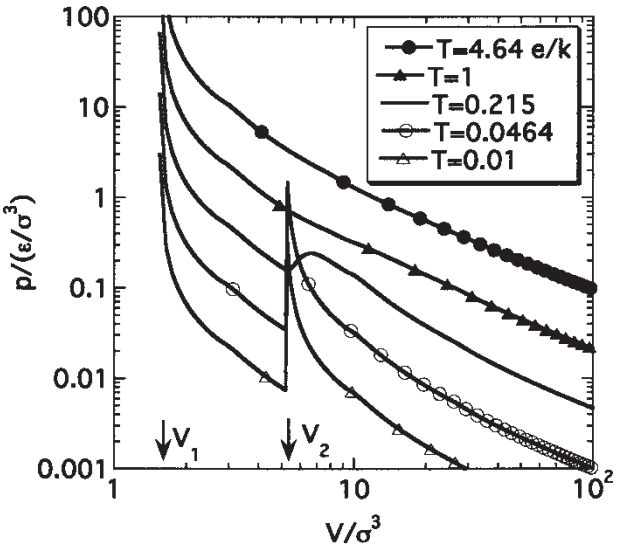

FIGURE 3 The isotherm of pressure p in the step-function system is plotted as a function of the volume V.

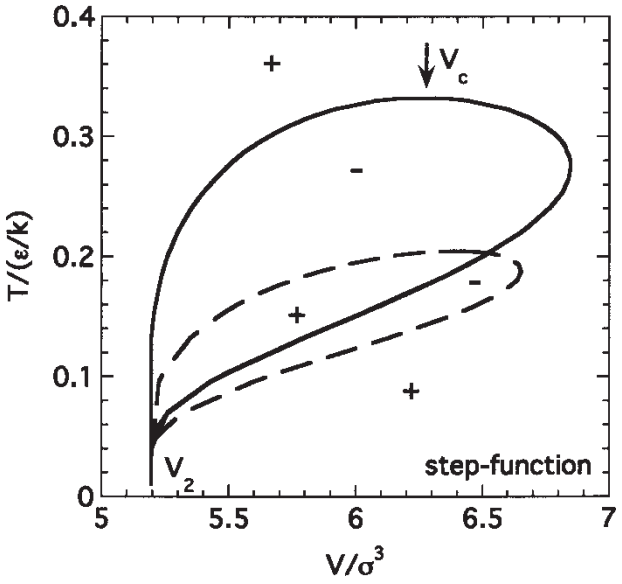

FIGURE 4 The spinodal line is shown by the solid line in the volume–temperature domain. The region, where the thermal expansion coefficient is negative or positive, is divided by the dashed and the solid lines. The sign of the thermal expansion coefficient is also depicted.

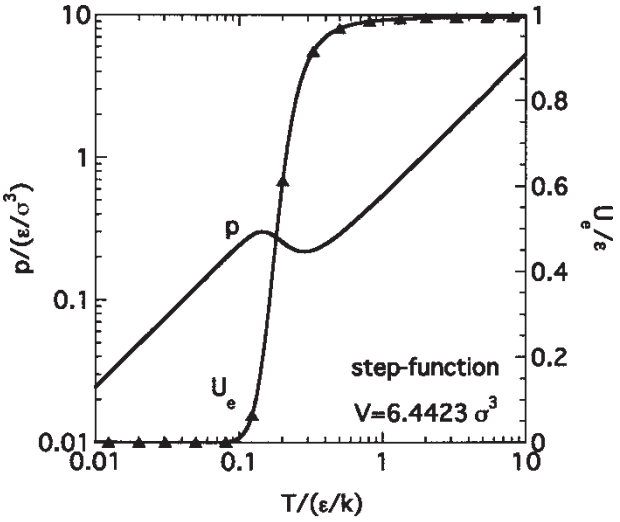

FIGURE 6 The interaction part of the internal energy U_e and pressure p are shown against the temperature at the volume $V = 6.4423\,\sigma^3$.

Thermal Expansion Coefficient

Figure 5 shows the thermal expansion coefficient α as a function of temperature at $V = 6.4423\,\sigma^3$. We see that the thermal expansion coefficient is negative in the two temperature-regions at this volume.

The physical reason of the negative expansion coefficient is easy to understand by the pressure vs. temperature plot at the constant volume as shown in Fig. 6. The averaged potential energy U_e is also shown in Fig. 6. The averaged potential energy shows that the state changes from $U_e = 0$ to ε around the temperature $T = 0.15\ \varepsilon/k$. At low temperature, the intermolecular distance r is prevented to shorten by the step of $u(r)$, therefore, the effective available volume is V_2 up to 6.4423 σ^3. While around the temperature $T = 0.15\ \varepsilon/k$, the effective available volume will be able to expand because the molecules gain the sufficient thermal energy to climb up the step of $u(r)$. Accordingly, the pressure begins to decrease against the temperature. Such behavior corresponds to the negative expansion coefficient under the condition of the constant pressure. The negative expansion coefficient has been calculated by a similar model [7,8].

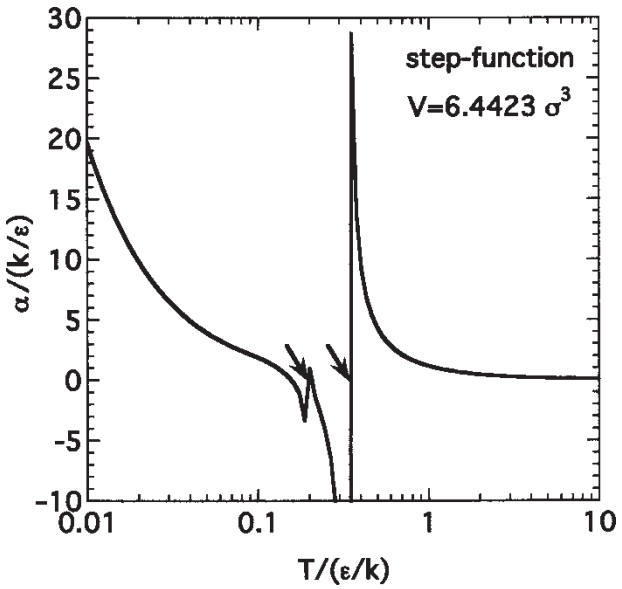

FIGURE 5 The thermal expansion coefficient vs. the temperature plot at constant volume $V = 6.4423\,\sigma^3$. The zero points shown by arrows correspond to the spinodal line, and the other zero points correspond to the dashed line in Fig. 4.

The zero points of the thermal expansion coefficient are shown by the solid and the dashed lines in Fig. 4. This means that the spinodal line coincides with one of the zero lines of the thermal expansion coefficient. The thermal expansion coefficient is negative in the two regions as shown in Figs. 4 and 5. One of them is located in the unstable states, inside of the spinodal line. The other is outside them. The reason why the thermal expansion coefficient is negative in the two regions is understood by the following equation:

$$\alpha = -\frac{1}{V}\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial p}\right)_T = \kappa_T \left(\frac{\partial p}{\partial T}\right)_V . \qquad (13)$$

This equation shows that the thermal expansion coefficient may be zero by one of the two reasons. These are shown by the dashed and the solid lines in Fig. 4. The zero points shown by arrows correspond to the spinodal line in Fig. 5. The other zero points correspond to the minimum and the maximum of

the pressure as a function of temperature under the constant volume condition as shown in Fig. 6.

Monte Carlo Simulations

We show the MC simulation results on the $N = 2$ system at $T = 0.2\,\varepsilon/k$ with the same potential. In the MC case, the cubic periodic boundary condition is assumed and the minimum image convention is applied. The corrections on the long tail terms are not adopted for the present purpose of comparison. In the initial configuration, one molecule is put at the center of the unit cell and the other at one of the corners. Our MC run consists of equilibration stage and the average one. The length of run in each stage is the same. The typical length of the sampling is $10^7 - 10^8$ MC steps where 1 MC step is N trial moves in the N-molecule system. The pressure is obtained by the following virial equation [12]:

$$\frac{pV}{NkT} = 1 + \frac{2\pi N}{3V} \times \sigma^3\{g(\sigma_+) - g(\lambda\sigma_-)(1 - \exp(\beta u(\lambda\sigma_-)))\lambda^3\}, \quad (14)$$

$$g(\sigma_+) = g(\sigma + \delta),\ \delta \to 0,\ (\delta > 0),$$

$$g(\lambda\sigma_-) = g(\lambda\sigma - \delta),\ \delta \to 0,\ (\delta > 0).$$

Figure 7 is the pVT relation vs. volume plot for the $N = 2$ system by MC and theoretical calculations. These results are in agreement within the errors in the numerical calculations excluding only very dense state ($V \sim \sigma^3$); such dense state is difficult to simulate by MC.

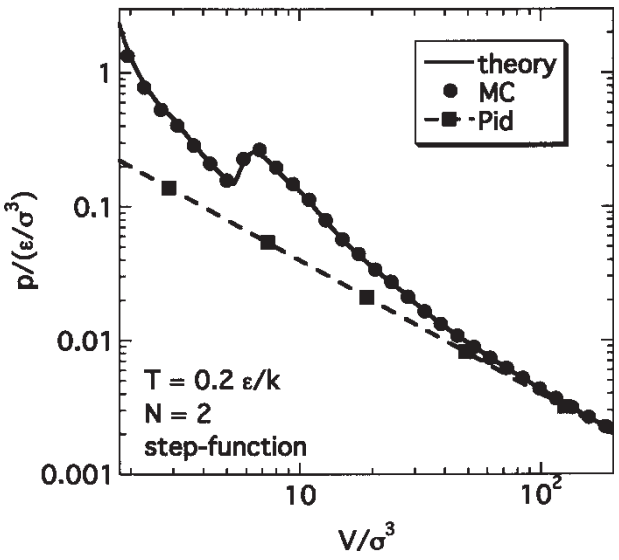

FIGURE 7 The theoretical isotherm of pressure p of $N = 2$ with the step-function system is compared with the MC results as a function of the volume at $T = 0.2\,\varepsilon/k$. The pressure of the ideal gas p_{id} is also shown for comparison.

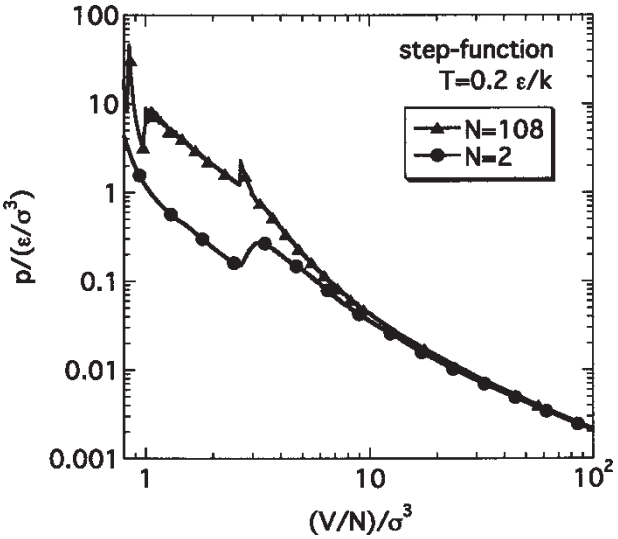

FIGURE 8 Comparison of the isotherm of the pressure p between the MC results of $N = 2$ and 108 systems as a function of the volume per particle V/N at $T = 0.2\,\varepsilon/k$.

The MC results on the $N = 108$ system at $T = 0.2\ \varepsilon/k$ is compared with those of the $N = 2$ system with the same potential function in Fig. 8. The initial configuration is FCC in this case. The other conditions in MC simulation are essentially the same as the $N = 2$ case. Other than the low-density state, the pressure of the $N = 108$ system does not coincide with that of the $N = 2$ system because the nearest neighbor numbers are different in these two systems. However, we see some common features in these two cases: the sharp change of the pressure as a function of the volume in $N = 108$ system corresponds to the p–V curve at lower temperatures in the $N = 2$ system as shown in Fig. 3. The isothermal compressibility is negative around $V/N = 2.6\ \sigma^3$ in the $N = 108$ system. A similar behavior is already seen in the $N = 2$ system. Incidentally, the transition around the volume $V/N = 1\ \sigma^3$ in the $N = 108$ system corresponds to the solid–fluid transition which is reasoned from the pair correlation functions in these phases.

CONCLUSION

We study the two-molecule periodic system with the statistical mechanical calculations. Our model potential function consists of a step-function and the hard sphere wall. The canonical partition function is obtained by the minimum image convention. We find the fluid–fluid phase transition and the negative expansion coefficient. The spinodal line is obtained in the (V,T) domain, and the negative expansion coefficient is found in the stable state. The theory gives the same pVT relation with the MC simulations. The 108-molecule system examined by MC also gives a similar pVT relation to the two-molecule systems qualitatively.

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