

# Negative Expansion in Two-Molecule System with the Step Function outside the Hard Sphere Wall in a Spherical Cell

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The canonical ensemble partition function is obtained for a two-molecule system with the repulsive step function outside the hard sphere wall in a spherical cell. Fluid-fluid phase transition-like behavior is evident at low temperatures. The spinodal line is obtained in the  $(V, T)$  domain and a negative expansion coefficient is found in the stable state. The theoretical  $pVT$  relationship is confirmed through Monte Carlo simulations. The periodic 108-molecule system examined by Monte Carlo simulations also provides a qualitatively similar  $pVT$  relationship to the two-molecule system.

**Keywords:** Negative Expansion, Canonical ensemble partition function, Repulsive step function, Monte Carlo simulations, Spinodal line

## 1 Introduction

Molecular systems containing the repulsive step function have the minimum and maximum points on the melting curve and solid-solid phase transitions [1]. These features on the observed phase diagram of cesium and cerium were compared [1]. The negative expansion is also reported for the liquid phase in a system with the step function [2], and even the low temperature properties of the liquid water were modeled by a similar potential function [3]. For these reasons, a molecular system with the repulsive step function outside a hard sphere wall is studied.

Statistical mechanical calculations on a periodic cubic system containing two molecules in the unit cell were reported [4], where the model potential was the step function. The minimum image convention [5] was assumed, resulting in the canonical partition function. When the interaction energy between the molecule 1 and the other molecules is calculated, only the closest periodic images of the other molecules interact with the molecule 1 in this approximation. The fluid-fluid phase transition-like behavior and negative thermal expansion was observed in the system. The theoretical  $pVT$  relationship results had properties similar to the Monte Carlo simulation [5] results for a periodic 108-molecule system with the same

potential function [4].

This work assumes a spherical cell without the periodic boundary condition. This shape is convenient because the canonical partition function can be obtained from statistical mechanics. There are two identical spherical molecules in the cell. The repulsive step function is assumed outside the hard sphere wall between the molecules. The present work is compared with the previous one in Table 1. The intent of this study is to provide basic information in the research on nanoporous materials [6]. The theoretical  $pVT$  relationship will be compared with Monte Carlo simulations performed with the same boundary condition. The effects of non-periodicity will also be observed by comparing the results with the periodic 108-molecule system examined by Monte Carlo simulations. It will be shown that the periodic system exhibits a qualitatively similar  $pVT$  relationship to the present two-molecule system.

The assumed potential function contains three constant parts and depends only on the molecular distance. The proposed method can be applied easily to other potential systems, like the hard sphere and the square well model, to obtain the thermodynamic properties of the two-molecule system in the spherical cell.

Table 1. The present work is compared with the previous one [4].

	The present work	The previous paper [4]
the potential function	the repulsive step function outside the hard sphere wall	the repulsive step function outside the hard sphere wall
the boundary condition	non-periodic	periodic
the shape of the cell	spherical	cubic
the number of molecules in the unit cell	2	2
the approximation	no	the minimum image convention [5]

## 2 Model and Formulation

**Potential Function.** Now the potential function, a step function, is introduced. The intermolecular interaction  $u(r)$  is assumed to be only a function of the intermolecular distance  $r$ :

$$\begin{aligned} u(r) &= \infty & (r \leq \sigma), \\ u(r) &= \varepsilon & (\sigma < r \leq \lambda\sigma), \\ u(r) &= 0 & (\lambda\sigma < r), \quad \lambda = 1.5. \end{aligned} \quad (1)$$

Here, quantities  $\varepsilon$  and  $\sigma$  are the potential constants, which have the dimensions of energy and length, respectively. Figure 1 shows the potential function  $u(r)$ .

**Partition Function of the Two-Molecule System with the Step-Function.** Two identical spherical molecules were assumed, and the canonical ensemble of the two-molecule system in the spherical cell at temperature  $T$  and volume  $V$  with the above potential function was considered, without the periodic boundary condition. The canonical partition function  $Q$  is the product of the ideal gas part  $Q_{id}$  and the interaction part  $Q_e$  [7, 8].

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

$$Q_e = \frac{1}{V^2} \int_V \int_V \exp[-\beta u(r_{12})] d^3r_1 d^3r_2. \quad (3)$$

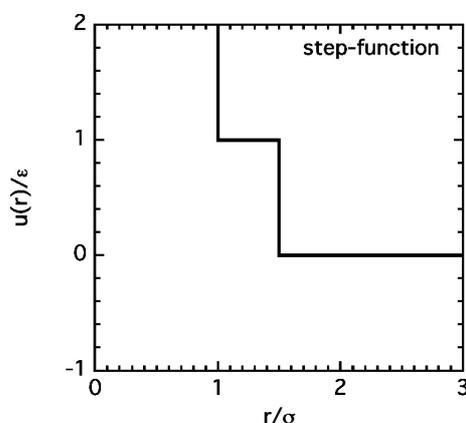


Figure 1. Step-function potential  $u(r)$  plotted as a function of the intermolecular distance  $r$ .

In Equation (3),  $\beta = 1/kT$ ,  $k$  is the Boltzmann constant. The positions of the two particles are denoted as  $r_1$  and  $r_2$  and the centers of mass are inside the cell. The volume of the cell is  $V$  and its radius is written as  $r_c$ . Two new constants  $V_1$  and  $V_2$  are defined as follows:

$$V_c = V = \frac{4\pi}{3}r_c^3, \quad V_1 = \frac{\pi}{6}\sigma^3, \quad V_2 = \frac{\pi}{6}(\lambda\sigma)^3. \quad (4)$$

The cell is referred to as  $\mathbf{V}_c$  and the sphere is centered at  $r_1$  with the radius  $s$ , written as  $\mathbf{V}_{(1)}$ . The volume of the common region  $\mathbf{V}_s$  between the cell  $\mathbf{V}_c$  and the sphere  $\mathbf{V}_{(1)}$  is written as  $V_s(s, r_c, r_1)$ , as depicted in Figure 2.

$$\mathbf{V}_s = \mathbf{V}_c \cap \mathbf{V}_{(1)} \quad (5)$$

The common volume  $V_s(s, r_c, r_1)$  is obtained by the geometry:

$$\begin{aligned} V_s(s, r_c, r_1) &= \frac{4}{3}\pi s^3 & (r_c - s \geq r_1 \geq 0), \\ V_s(s, r_c, r_1) &= \frac{\pi r_1^3}{12} - \frac{\pi r_1}{2}(r_c^2 + s^2) & (6) \\ &\quad - \frac{\pi}{4r_1}(r_c^2 - s^2)^2 + \frac{2\pi}{3}(r_c^3 + s^3) & \\ &\quad (r_c - r_1 < s \leq r_c + r_1). \end{aligned}$$

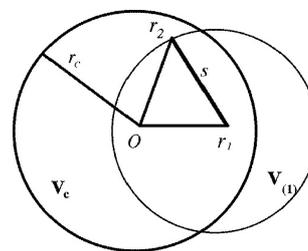


Figure 2. Cell  $\mathbf{V}_c$  and the sphere centered at  $r_1$  with the radius  $s$  is written as  $\mathbf{V}_{(1)}$ .

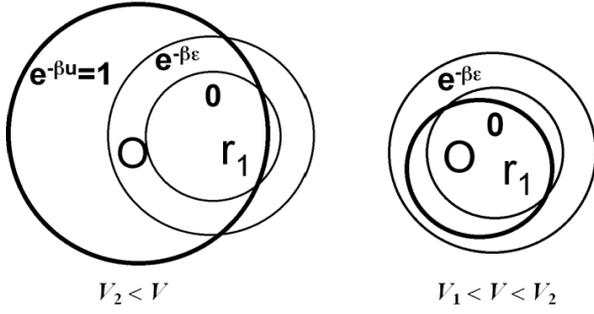


Figure 3. The space is classified into three regions where the Boltzmann factor is constant.

Because the interaction energy depends only on the molecular distance and the function  $u(r)$  consists of three constant functions (see Eq. (1)), the integration with respect to  $r_2$  can be performed as follows, as shown in Figure 3:

$$\int_V \exp[-\beta u(r_{12})] d^3 r_2 = V - V_s(\lambda\sigma, r_c, r_1) + \exp(-\beta\epsilon) [V_s(\lambda\sigma, r_c, r_1) - V_s(\sigma, r_c, r_1)] \quad (V_2 < V),$$

$$\int_V \exp[-\beta u(r_{12})] d^3 r_2 = \exp(-\beta\epsilon) [V - V_s(\sigma, r_c, r_1)] \quad (V_1 < V \leq V_2),$$

$$\int_V \exp[-\beta u(r_{12})] d^3 r_2 = 0 \quad (V \leq V_1).$$

The final stage is the integration with respect to  $r_1$ . This integration is performed using *Mathematica* [9].

$$Q_e = 0 \quad (V \leq V_1),$$

$$Q_e = e^{-\beta\epsilon} \left( 1 - \frac{\sigma^3}{r_c^3} + \frac{9\sigma^4}{16r_c^4} - \frac{\sigma^6}{32r_c^6} \right) \quad (V_1 < V \leq V_2),$$

$$Q_e = 1 - \frac{\sigma^3}{r_c^3} (e^{-\beta\epsilon} + \lambda^3 - e^{-\beta\epsilon}\lambda^3) + \frac{9\sigma^4}{16r_c^4} (e^{-\beta\epsilon} + \lambda^4 - e^{-\beta\epsilon}\lambda^4) - \frac{\sigma^6}{32r_c^6} (e^{-\beta\epsilon} + \lambda^6 - e^{-\beta\epsilon}\lambda^6) \quad (V_2 < V).$$

The Helmholtz free energy  $A$  has the following expression:

$$A = -kT \ln(Q) = A_{id} + A_e = -kT \ln(Q_{id}) - kT \ln(Q_e). \quad (9)$$

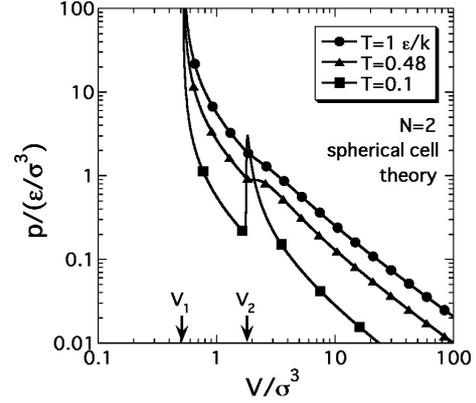


Figure 4. The isotherm of pressure  $p$  in the step-function system is plotted as a function of the volume  $V$ .

The following form for  $A_{id}$  is selected for its simplicity:

$$A_{id} = -kT \ln(Q_{id}),$$

$$Q_{id} = \left( V_r T_r^{3/2} \right)^2, \quad T_r = \frac{kT}{\epsilon}, \quad V_r = \frac{V}{\sigma^3}. \quad (10)$$

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

$$U_{id} = 3kT,$$

$$S_{id} = 3k + k \ln \left\{ \left( \frac{V}{\sigma^3} \right)^2 \left( \frac{kT}{\epsilon} \right)^3 \right\}. \quad (11)$$

Because the system is a two-molecule system, the pressure  $p$  can be written as:

$$p = \frac{2kT}{V} + p_e, \quad (12)$$

The interaction part  $p_e$  can be obtained by the formula:

$$p_e = kT \left( \frac{\partial \ln Q_e}{\partial V} \right)_T. \quad (13)$$

The remaining thermodynamic properties can be calculated the standard way [10].

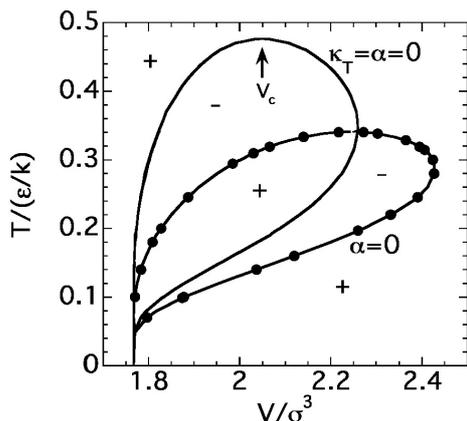


Figure 5. The spinodal line is depicted by the solid line in the volume-temperature domain. The positive and negative thermal expansion coefficient regions are divided by the solid line and the solid line with solid circles. The sign of the thermal expansion coefficient is also displayed.

### 3 Results

**Fluid-Fluid Transition.** The  $pVT$  relationship, shown in Figure 4, shows that there is a phase transition-like behavior at low temperatures around volume  $V_2$  because its isothermal compressibility  $\kappa_T$  is negative near this volume. The dense phase is the condense phase, making it difficult to distinguish the solid and liquid phases in the  $N = 2$  system. Then, this transition is tentatively assigned the fluid-fluid transition according to the densities. The phase boundary between them will be examined in a following work.

Figure 5 shows the spinodal line ( $\kappa_T = 0$ ) depicted by the solid line in the  $(V, T)$  domain. The critical constants are:

$$\begin{aligned} T_c &= 0.4764\varepsilon/k, V_c = 2.049\sigma^3, \\ p_c &= 0.8839\varepsilon/\sigma^3, \end{aligned} \quad (14)$$

The line with the solid circles will be described in the next section.

**Thermal Expansion Coefficient.** Figure 6 illustrates the thermal expansion coefficient  $\alpha$  as a function of the temperature at  $V = 2.3 \sigma^3$ . The thermal expansion coefficient is calculated using the following formula:

$$\alpha = -\frac{1}{V} \left( \frac{\partial p}{\partial T} \right)_V \left( \frac{\partial V}{\partial p} \right)_T = \kappa_T \left( \frac{\partial p}{\partial T} \right)_V. \quad (15)$$

It can be seen that the thermal expansion coefficient is negative in the range  $0.21 \varepsilon/k < T < 0.34 \varepsilon/k$  at this volume.

The physical reason for this negative expansion coefficient is evident from the pressure vs. temperature plot

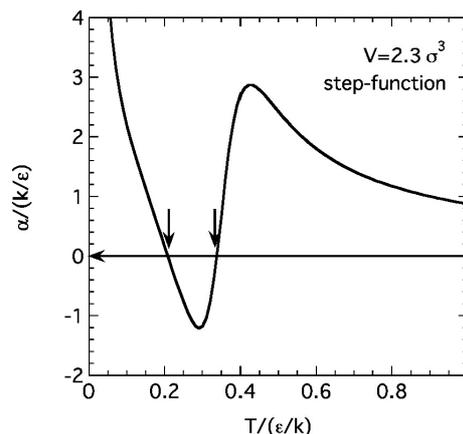


Figure 6. Thermal expansion coefficient vs. the temperature plot at constant volume  $V = 2.3 \sigma^3$ . The zero points indicated by arrows correspond to those shown by the solid line with the solid circles in Figure 5.

at constant volume, as shown in Figure 7. The averaged potential energy  $U_e$  is also shown in Figure 7 at  $V = 2.3 \sigma^3$ . The averaged potential energy reveals that the state changes from  $U_e = 0$  to  $\varepsilon$  around temperature  $T = 0.3 \varepsilon/k$ . At low temperatures, the intermolecular distance  $r$  is maintained by the step of the  $u(r)$ . Therefore, the effective available volume is  $V_2$  up to  $2.6 \sigma^3$ . Around temperature  $T = 0.3 \varepsilon/k$ , however, the effective available volume becomes capable of contracting because the molecules gain sufficient thermal energy to climb up the step of  $u(r)$ . Moreover, the pressure begins to decrease with the rising temperature. Such behavior corresponds to the negative expansion coefficient under the condition of the constant pressure. The negative expansion coefficient has also been calculated by similar models [2, 3].

The zero points of the thermal expansion coefficient  $\alpha$  are depicted by the lines with and without the solid circles in Figure 5. This means that the spinodal line coincides with one of the zero lines of the thermal expansion coefficient. In these two regions, the thermal expansion coefficient is negative, as shown in Figure 5 and Figure 8. One of them is located in the unstable states, inside the spinodal line, while the other is outside. The reason why the thermal expansion coefficient is negative in the two regions can be determined from Equation (15).

This equation shows that the thermal expansion coefficient may be zero for one of two reasons, which are represented by the two types of solid lines in Figure 5. The spinodal line corresponds to the zero points indicated by arrows in Figure 8. The other line corresponds to the minimum and the maximum of the pressure as a function of temperature under the constant volume condition, as shown in Figure 7.

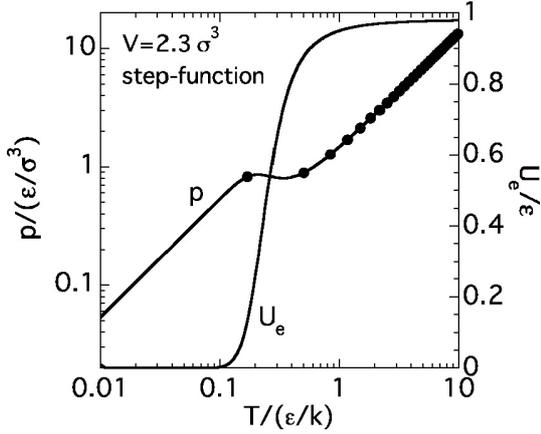


Figure 7. The interaction part of the internal energy  $U_e$  and pressure  $p$  plotted against the temperature at  $V = 2.3 \sigma^3$ .

The  $N = 2$  system is studied in the spherical cell. In addition, another interesting system is a small molecular system confined in a box. The phase transition has already been examined for a hard disk system. Two hard disks in a rectangular cell also exhibit the phase transition [12, 13].

## 4 Monte Carlo Simulations

This section reports the Monte Carlo (MC) simulation [5] results for the  $N = 2$  system at  $T = 0.2 \varepsilon/k$  with the same potential. In this MC simulation, the boundary condition is the same as the theoretical calculation. In the initial configuration, one molecule is put at the center of the spherical cell and the other is placed near the cell boundary. The MC run consists of the equilibration stage and the average stage. The length of the run in the stages 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 [11]:

$$\begin{aligned} \frac{pV}{NkT} &= 1 + \\ &\frac{2\pi N}{3V} \sigma^3 [g(\sigma_+) - g(\lambda\sigma_-) \{1 - \exp(\beta u(\lambda\sigma_-))\} \lambda^3], \\ g(\sigma_+) &= g(\sigma + \delta), \quad \delta \rightarrow 0 (\delta > 0), \\ g(\lambda\sigma_-) &= g(\lambda\sigma - \delta), \quad \delta \rightarrow 0 (\delta > 0), \end{aligned} \quad (16)$$

Figure 9 shows the  $pVT$  relationship vs. volume plot for the  $N = 2$  system determined by both MC and theoretical calculations. These results are in agreement within the margin of error when only the very dense state ( $V \sim V_1$ )

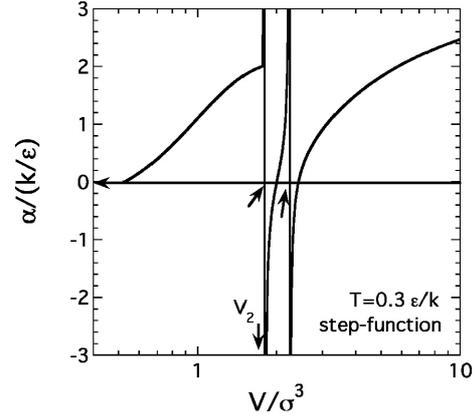


Figure 8. Thermal expansion coefficient vs. the volume plot at constant temperature  $T = 0.3 \varepsilon/k$ . The zero points indicated by arrows correspond to the spinodal line, and the others correspond to the other line with the solid circles in Figure 5.

for the numerical calculations is excluded; such a dense state is difficult to simulate by MC.

Next, the finite system is compared with the periodic, effectively infinite system simulated by the MC method. For this purpose, the cubic periodic boundary condition is assumed and the minimum image convention is applied in the MC. The corrections on the long tail terms are not adopted for the present purpose of comparison. For this case, the initial configuration is FCC. The other conditions in the MC simulation are essentially the same as for the  $N = 2$  cases.

The MC results for the periodic  $N = 108$  system at  $V/N = 2.9 \sigma^3$  are shown in Figure 10. The interaction part of the internal energy  $U_e$  and pressure  $p$  are plotted against the temperature. Then, these results are compared with those of the  $N = 2$  systems in the spherical, non-periodic cell with the potential function in Figure 7. The volume and internal energy are normalized by the number of molecules  $N$  in the unit cell in Figure 10. For these two cases, the figures exhibit some common features, including a sharp change in pressure as a function of the temperature in the  $N = 108$  system that corresponds to the floppy  $p$ - $T$  curve in the  $N = 2$  system shown in Figure 7. The internal energies in these figures also show phase transition-like behaviors. The other MC results on the  $pVT$  relationship on the periodic  $N = 108$  systems are shown in a previous work [4]. This system also contains a region where the isothermal compressibility is negative, as in Figure 4. In this sense, even the  $N = 2$  finite system has some features in common with the  $pVT$  relationship and the internal energy with very large systems like the periodic  $N = 108$  system.

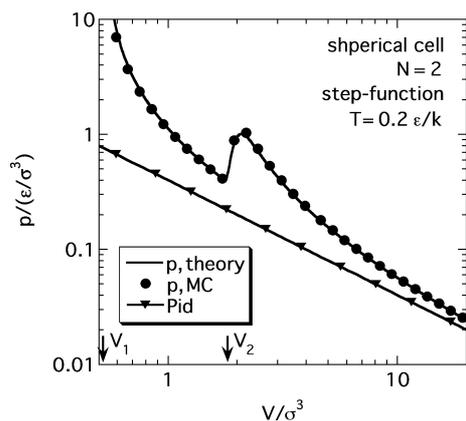


Figure 9. The theoretical isotherm of pressure  $p$  of  $N = 2$  with the step-function system is compared with the MC results as a function of the volume at  $T = 0.2 \epsilon/k$ . The pressure of the ideal gas  $p_{id}$  is also shown for comparison.

## 5 Conclusion

A two-molecule system is studied with statistical mechanical calculations. For these calculations, the model potential function consists of a step-function and the hard sphere wall. The canonical partition function is obtained by statistical mechanics. Fluid-fluid phase transition-like behavior and a negative expansion coefficient were discovered. The spinodal line is obtained in the  $(V, T)$  domain, and a negative expansion coefficient is found in the stable state. The theory generates the same  $pVT$  relationship as that determined by Monte Carlo simulations. The periodic 108-molecule system examined by MC also provides a qualitatively similar  $pVT$  relationship to the two-molecule system.

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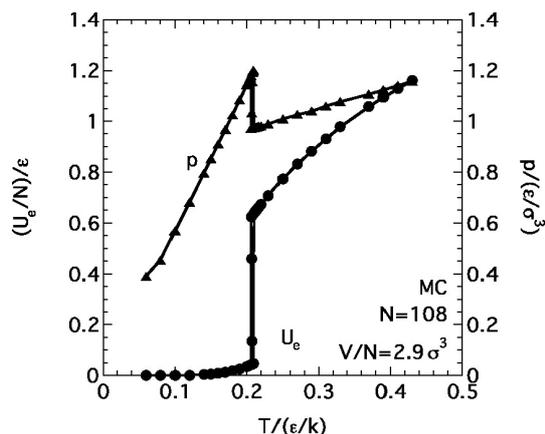


Figure 10. The MC results on the periodic cubic  $N = 108$  system: the interaction part of the internal energy  $U_e$  and pressure  $p$  are plotted against the temperature  $T$  at the volume per particle  $V/N = 2.9 \sigma^3$ .

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