

# Takahasi Nearest-Neighbour Gas Revisited III; Lennard-Jones Gases

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Some thermodynamic quantities for the Lennard-Jones (12,6) potential are expressed as analytical formula at an isobaric process. The parameters of Lennard-Jones gases for 18 substances are obtained by the second virial coefficient data. Also some thermodynamic quantities for benzene are calculated numerically and drawn graphically. The inflexion point of the length  $L$  which depends on temperature  $T$  and pressure  $P$  corresponds physically to a boiling point.  $L$  indicates the liquid phase from lower temperature to the inflexion point and the gaseous phase from the inflexion point to higher temperature. The boiling temperatures indicate reasonable values comparing with experimental data. The behaviour of  $L$  suggests a chance of a first-order phase transition in one dimension.

*Key words:* Takahasi Nearest-Neighbour Gas; Lennard-Jones Potential; Boiling Temperature; Equation of State; Enthalpy; First-Order Phase Transition.

## 1. Introduction

In the previous papers the behaviours of the length  $L$  and the heat capacity  $C_p$  have suggested a chance of a first-order phase transition in one dimension for Stockmayer gases [1] and Morse gases [2] while Takahasi had pointed out that the coexistence of two phases is impossible in an one-dimensional substance for any choice of the potential over 70 years ago [3]. The first-order phase transition may be caused by the long-range interaction for Stockmayer and Morse gases. On the one hand, the Lennard-Jones potential has been called a commonly empirical intermolecular potential function for non-polar molecules which is due to the short-range interaction. The integral of the partition function for the Lennard-Jones potential in  $T$ - $P$  ensemble, however, can be hardly calculated up to now while a second-order phase transition for the Lennard-Jones potential may occur at the critical point [4]. From the viewpoint of an isobaric process, this may be significant to provide the behaviours of thermodynamic quantities for the Lennard-Jones potential discussing physically the phase transition between gaseous and liquid phases.

In this work, the parameters for Lennard-Jones gases are obtained by the second virial coefficients. The partition function is expressed as analytical for-

mula. The length  $L$ ,  $(dL/dT)_p$ , enthalpy, and heat capacity are analytically represented as the two intensive variables of  $T$  and  $P$ . These thermodynamic quantities are determined through numerical calculations, and are graphically displayed at atmospheric pressure for  $C_6H_6$ . The chance of the first-order phase transition for the Lennard-Jones potential at boiling points and atmospheric pressure is discussed.

## 2. Thermodynamic Functions of Lennard-Jones Gases at Isobaric Process

The Lennard-Jones potential is described by

$$U(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (1)$$

in which  $\varepsilon$  is the maximum energy of attraction, and  $\sigma$  is that value of the intermolecular separation  $r$  for which  $U(r) = 0$ . The configurational partition function for the Lennard-Jones potential may be defined as

$$Q_0(T, P) = \int_0^\infty \exp[-\beta U(r) - \beta Pr] dr, \quad (2)$$

where

$$\beta = 1/kT.$$

$Q_0(T, P)$  is converted using integration by parts as follows:

$$Q_0(T, P) = \frac{1}{\beta P} \int_0^\infty \exp[-\beta U(r) - \beta Pr] \cdot \left[ -\beta \frac{dU(r)}{dr} \right] dr \quad (3)$$

and

$$Q_0(T, P) = \frac{1}{\beta P} Q(T, P). \quad (4)$$

Introducing the new variables

$$u = 4\beta\varepsilon, \quad (5)$$

$$z = u \left( \frac{\sigma}{r} \right)^{12}, \quad (6)$$

$$q = \beta P \sigma u^{1/12}, \quad (7)$$

$$a = -\frac{1}{12}, \quad (8)$$

$$f(z) = z - \sqrt{uz} + qz^a, \quad (9)$$

and

$$g(z) = z - \frac{\sqrt{uz}}{2}. \quad (10)$$

The partition function  $Q(T, P)$  is rewritten as

$$Q(T, P) = \int_0^\infty \exp[-f(z)] g(z) z^{-1} dz. \quad (11)$$

The partition function in the  $T$ - $P$  grand canonical ensemble is expressed as the product of kinetic and configurational partition functions,

$$Y(T, P, N_1) = \left( \frac{2\pi mkT}{h^2} \right)^{N_1/2} Q_0(T, P)^{N_1}. \quad (12)$$

The Gibbs free energy is derived from (12):

$$G(T, P) = -R_1 T \left[ \log \frac{(2\pi m)^{1/2}}{h} - \frac{3}{2} \log \beta - \log P + \log Q(T, P) \right], \quad (13)$$

where  $R_1 = 0.103221 \text{ atm cm K}^{-1}$  [2].

The properties of ideal gases for one dimension in  $T$ - $P$  ensemble may be dependent on a part of functions  $(-3/2 \log \beta - \log P)$ , in (13) and  $Q(T, P)$  is shown as the configuration of intermolecular interaction.

The equation of state in one dimension is expressed as

$$L = \left( \frac{\partial G}{\partial P} \right)_T \quad (14)$$

$$= \frac{R_1 T}{P} \left[ 1 + \frac{q}{Q} \int_0^\infty \exp[-f(z)] g(z) x^{a-1} dz \right].$$

The derivative  $L$  with respect to  $T$  can be derived from (14):

$$\left( \frac{\partial L}{\partial T} \right)_P = \frac{R_1}{P} \left[ 1 + \frac{q}{Q} \int_0^\infty \exp[-f(z)] \cdot g(z) \{f(z) - 1\} z^{a-1} dz \right. \\ \left. - \frac{q}{Q^2} \int_0^\infty \exp[-f(z)] g(z) z^{a-1} dz \right. \\ \left. \cdot \int_0^\infty \exp[-f(z)] g(z) \{f(z) - 1\} z^{-1} dz \right]. \quad (15)$$

The enthalpy is obtained as

$$H = -T^2 \left[ \frac{\partial}{\partial T} \left( \frac{G}{T} \right) \right]_P \quad (16)$$

$$= R_1 T \left[ \frac{3}{2} + \frac{1}{Q} \int_0^\infty \exp[-f(z)] g(z) \{f(z) - 1\} z^{-1} dz \right].$$

The heat capacity at constant pressure can be easily derived from (16):

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P \quad (17)$$

$$= R_1 \left[ \frac{3}{2} + \frac{1}{Q} \int_0^\infty \exp[-f(z)] g(z) \cdot \{f(z)^2 - 2f(z)\} z^{-1} dz \right. \\ \left. - \frac{1}{Q^2} \left\{ \int_0^\infty \exp[-f(z)] g(z) \{f(z) - 1\} z^{-1} dz \right\}^2 \right].$$

The integrals in which (11), (14)–(17) are contained can be explicitly calculated in [5].

The second virial coefficients for the intermolecular potential  $U(r)$  may be found, for classical statistics, from the well-known formula [4]

$$B(T) = -\frac{2\pi N_A}{3} \int_0^\infty \beta \frac{dU(r)}{dr} \exp[-\beta U(r)] r^3 dr, \quad (18)$$

where  $N_A$  is the Avogadro number. The second virial coefficients for Lennard-Jones gases are expressed as

$$\begin{aligned}
 B(T) &= \frac{2}{3} \pi N_A u^{1/4} \sigma^3 \int_0^\infty \exp(-z + \sqrt{uz}) \\
 &\quad \cdot \left( z^{3/4} - \frac{1}{2} \sqrt{uz}^{1/4} \right) z^{-1} dz \quad (19) \\
 &= -\frac{\pi N_A u^{1/4} \sigma^3}{6} [\Gamma(-1/4)F(-1/4, 1/2; u/4) \\
 &\quad + \sqrt{u}\Gamma(1/4)F(1/4, 3/2; u/4)], \quad (20)
 \end{aligned}$$

where  $F(a, b; x)$  is a confluent hypergeometric function.

### 3. Numerical Results

The parameters  $\varepsilon$  and  $\sigma$  of the Lennard-Jones potential (12,6) for 18 substances are determined from the experimental data of the second virial coefficients [6]

by the least squares method as shown in Table 1. Numerical results obtained with the length,  $(dL/dT)_p$ , enthalpy, and heat capacity for  $C_6H_6$  at atmospheric pressure are displayed in Figures 1–4. As shown in Figure 2, the curve of  $(dL/dT)_p$  in (15) appears a maximum at the temperature  $T_2$  which is the inflexion point of the length  $L$ . This curve of  $(dL/dT)_p$  may reach asymptotically to 0 with decreasing  $T$  and to 1 with increasing  $T$  beyond  $T_2$ . Considering Figure 2, the curve of  $L$  in Figure 1 is definitely away from  $T_2$  and the behaviours of ideal gases. Also, similar to  $(dL/dT)_p$ , the curve of the heat capacity in Figure 4 shows a maximum at the temperature  $T_1$  which is the inflexion point of enthalpy  $H$ . The enthalpy reaches the behaviour of ideal gases at higher temperature beyond  $T_1$ . The heat capacity becomes asymptotically 1.5  $R_1$  at higher temperature than  $T_1$ .  $(dL/dT)_p$  and  $C_p$  are originally not maxima but must diverge to an infinite according to three-dimensional models [7–9]. This point of  $L$ , however, corresponds physically to

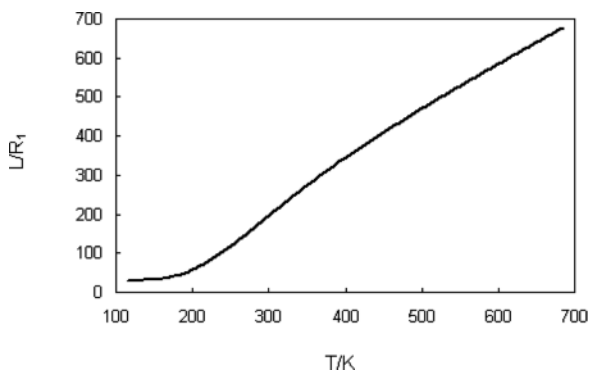


Fig. 1. Length  $L$  for  $C_6H_6$  vs. temperature at  $P = 1$  atm;  $T_B = 291$  K.

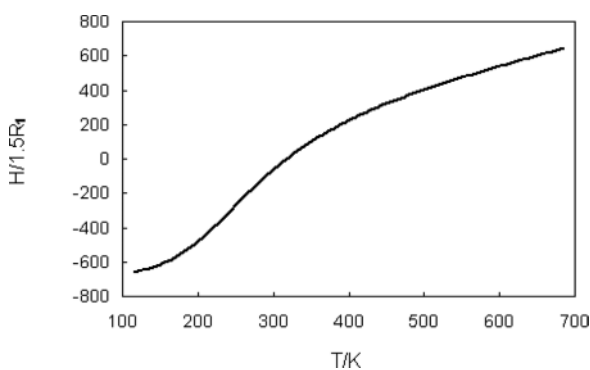


Fig. 3. Enthalpy  $H$  for  $C_6H_6$  vs. temperature at  $P = 1$  atm;  $T_B = 291$  K.

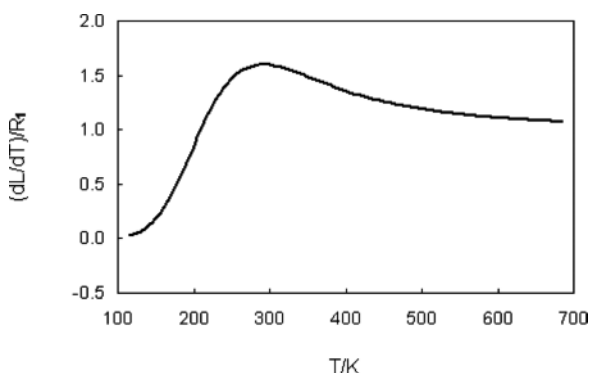


Fig. 2. Derivative  $(dL/dT)_p$  for  $C_6H_6$  vs. temperature at  $P = 1$  atm;  $T_B = 291$  K.

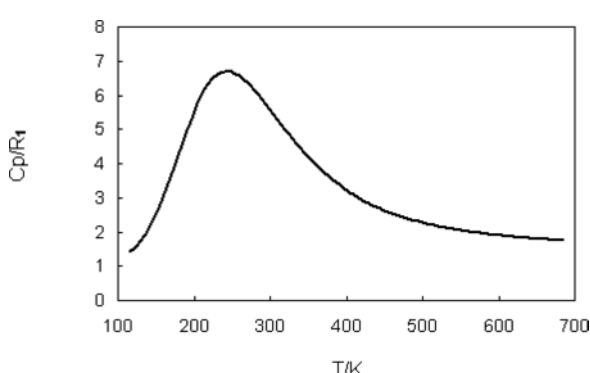


Fig. 4. Heat capacity  $C_p$  for  $C_6H_6$  vs. temperature at  $P = 1$  atm;  $T_B = 291$  K.

Table 1. Parameters for the Lennard–Jones (12,6) potential determined from experimental data of the second virial coefficients [5].

Substance	$(\epsilon/k)/\text{K}$	$\sigma/\text{\AA}$
Ne	35.086	2.737
Ar	118.63	3.446
Kr	164.89	3.669
Xe	224.80	4.053
N <sub>2</sub>	95.040	3.669
O <sub>2</sub>	119.37	3.454
CO	100.17	3.760
CS <sub>2</sub>	1038.59	2.746
CCl <sub>4</sub>	1217.65	2.987
CH <sub>4</sub>	149.07	3.798
C <sub>2</sub> H <sub>4</sub>	209.33	4.329
C <sub>2</sub> H <sub>6</sub>	232.06	4.395
C <sub>3</sub> H <sub>8</sub>	301.72	4.788
C <sub>4</sub> H <sub>10</sub>	786.33	3.374
C <sub>5</sub> H <sub>12</sub>	1016.02	3.181
C <sub>6</sub> H <sub>14</sub>	1202.93	3.186
c-C <sub>6</sub> H <sub>12</sub>	1160.67	3.144
C <sub>6</sub> H <sub>6</sub>	1143.91	3.196

Table 2.  $T_1$  (temperature for maximum of  $C_p$ ) and boiling temperature  $T_B$  for different substances at 1 atm.

Substance	Lennard–Jones gas		Exp. result [9]
	$T_1/\text{K}$	$T_B/\text{K}$	$T_B/\text{K}$
Ne	19	35	27.0
Ar	45	67	87.3
Kr	56	82	119.8
Xe	72	103	165.0
N <sub>2</sub>	38	62	77.4
O <sub>2</sub>	44	67	90.2
CO	40	64	81.7
CS <sub>2</sub>	219	261	319.4
CCl <sub>4</sub>	254	300	349.7
CH <sub>4</sub>	53	79	111.7
C <sub>2</sub> H <sub>4</sub>	69	101	169.4
C <sub>2</sub> H <sub>6</sub>	75	108	184.5
C <sub>3</sub> H <sub>8</sub>	93	131	231.1
C <sub>4</sub> H <sub>10</sub>	181	223	272.7
C <sub>5</sub> H <sub>12</sub>	221	266	309.2
C <sub>6</sub> H <sub>14</sub>	253	302	341.9
c-C <sub>6</sub> H <sub>12</sub>	246	293	353.9
C <sub>6</sub> H <sub>6</sub>	244	291	353.3

a boiling point, while  $L$  does not show a sudden change but a sluggish one in the neighbourhood of the inflexion point  $T_2$ .  $L$  in Figure 1 indicates the liquid phase from lower temperature to the inflexion point and the gaseous phase from the inflexion point to higher temperature.

In one dimension, the inflexion point of  $L$  does not agree with that of  $H$  though a jump for  $H$  is graphically observed from the liquid to gaseous phase at

the boundary of the boiling point in three-dimensional models [7–9]. Assuming that the boiling temperature  $T_B$  is physically equivalent to the inflexion point of  $L$ , the boiling temperatures  $T_2$  for Lennard-Jones substances indicate reasonable values comparing with experimental data [10] as shown in Table 2. The behaviour of  $(dL/dT)_P$  in the neighbourhood of the boiling point corresponds to a first-order phase transition in one dimension.

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