Takahasi Nearest-Neighbour Gas Revisited; Stockmayer Gases with a Hard Core

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Some thermodynamic quantities for the Stockmayer potential $(12, 6, 3)$ with a hard core are analytically evaluated at an isobaric process. The parameters of polar gases for 16 substances are obtained. Also some thermodynamic quantities for H_2O are calculated numerically and drawn graphically. The inflexion point of the length L 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 compared with experimental data. The behaviour of L suggests the chance of a first-order phase transition in one-dimension.

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

1. Introduction

It has been pointed out by Takahasi that the coexistence of two phases is impossible in one-dimensional substances for any choice of the potential. In a system between two neighbouring molecules, the Gibbs free energy $G(T,P)$ and the length dG/dT are mathematically analytic functions applied to the properties of the Laplace transform, and must be single-valued functions of P [1, 2]. Although Gürsey [3] concluded that a single partition function is an analytic function of the pressure and the temperature from the Laplace transform, changes of phase were physically discussed illustrating the isotherms for the square-well potential [3, 4]. The Gibbs free energy is consequently replaced by the function of two intensive variables, namely T and P.

From the viewpoint of an isobaric process, this may be significant to provide the behaviours of thermodynamic quantities for the Stockmayer potential $(12, 6, 3)$ discussing physically the phase transition between gaseous and liquid phases. The Stockmayer potential $(12, 6, 3)$ [5, 6] is the sum of the Lennard-Jones potential $(12, 6)$ and an additional angle-dependent term to account for the electrostatic interaction of two dipoles while the dipole-dipole function includes the long-range interaction.

In this work, the parameters for Stockmayer gases $(12, 6, 3)$ with a hard core are obtained. The length

$(dL/dT)_p$, enthalpy, and heat capacity are analytically represented as the two intensive variables T and P. These thermodynamic quantities are determined by numerical calculations and are graphically displayed at atmospheric pressure for H_2O. The chance of the first-order phase transition for the Stockmayer potential at boiling points and at atmospheric pressure is discussed.

2. Second Virial Coefficients for the Stockmayer Potential $(12, 6, 3)$ with a Hard Core

For rigid spheres of distance σ, the Stockmayer potential $(12, 6, 3)$ is based upon the Stockmayer potential [5, 6]

$$U(r) = \begin{cases} \infty, & \text{for } r < \sigma, \\ \lambda \left[\left(\dfrac{\sigma}{r} \right)^{12} - \left(\dfrac{\sigma}{r} \right)^6 \right] - \dfrac{\mu^2 g}{r^3}, & \text{for } r > \sigma, \end{cases} \quad (1)$$

where μ is the permanent dipole moment and $g(\theta_1, \theta_2, \varphi)$ is the angular dependence of the dipole-dipole interaction, namely

$$g = 2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\varphi. \quad (2)$$

In this expression, θ_1 and θ_2 are the inclinations of the two dipole axes to the intermolecular axis and φ is the azimuthal angle between them. Substituting $r = \sigma x$, the potential (1) is replaced by

$$U(x) = \lambda [x^{-12} - x^{-6} - dgx^{-3}], \quad x > 1, \quad (3)$$

where

$$d = \frac{\mu^2}{\lambda \sigma^3}. \tag{4}$$

The second virial coefficients for angle-dependent potentials may be found, in classical statistics, from the well-known formula

$$B(T) = \frac{1}{4} N_A \sigma^3 \int_0^\infty \int_\Omega (1 - \exp[-\beta U(x)]) x^2 \mathrm{d}x \mathrm{d}\Omega, \tag{5}$$

where

$$\int_\Omega \mathrm{d}\Omega = \int_0^\pi \int_0^\pi \int_0^{2\pi} \sin\theta_1 \sin\theta_2 \mathrm{d}\theta_1 \mathrm{d}\theta_2 \mathrm{d}\varphi = 8\pi. \tag{6}$$

N_A is the Avogadro number and $\beta = 1/kT$. The second virial coefficients for polar gases $(12, 6, 3)$ with rigid spheres are expressed as

$$B(T) = \frac{2}{3} \pi N_A \sigma^3 \left[1 - \sum_{n=1}^\infty \frac{u^n}{n!} \sum_{k=0}^{k \leq n/2} {}_nC_{2k} d^{2k} G_k \right.$$
$$\left. \cdot \sum_{j=0}^{n-2k} {}_{n-2k}C_j \frac{(-1)^j}{2n - 2k + 2j - 1} \right], \tag{7}$$

where the integral is calculated by

$$G_k = \frac{1}{8\pi} \int_\Omega g^{2k} \mathrm{d}\Omega = \frac{1}{2k+1} \sum_{m=0}^{m=k} {}_kC_m \frac{3^m}{2m+1}. \tag{8}$$

Here $u = \beta\lambda$, and ${}_nC_{2k}$, ${}_{n-2k}C_j$, and ${}_kC_m$ are binominal coefficients.

3. Thermodynamic Functions of Stockmayer Gases $(12, 6, 3)$ with a Hard Core at Isobaric Process

Now, the particles and the gas constants in one dimension are calculated as follows [7]. The particles are obtained using the cubic root of the Avogadro number N_A, thus

$$N_1 = 0.84446 \times 10^8, \tag{9}$$

and, consequently, a gas constant is

$$R_1 = kN_1 = 1.1659 \times 10^{-15} \ \mathrm{JK}^{-1}. \tag{10}$$

Another gas constant corresponds to

$$R_1 = 0.122233 \ \mathrm{atm\,\mathring{A}\,K}^{-1}, \tag{11}$$

which is obtained by applying $T = 273.15$ K, $P = 1$ atm, and $L = (22414)^{1/3}$ cm $= 28.1951$ cm.

The configurational partition function for the Stockmayer potential may be defined as

$$Q(T,P) = \int_1^\infty \exp[-\beta f(x)]\mathrm{d}x, \tag{12}$$

where

$$f(x) = U(x) + P\sigma x. \tag{13}$$

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

$$Y(T,P,N_1) = \left(\frac{2\pi mkT}{h^2} \right)^{N_1/2} Q(T,P)^{N_1}. \tag{14}$$

The Gibbs free energy is derived from (14):

$$G(T,P) = -N_1 kT \left[\log \frac{(2\pi mkT)^{\frac{1}{2}}}{h} + \log Q(T,P) \right]. \tag{15}$$

Substituting $q = P\sigma/R_1 T$, then the configurational partition function can be explicitly represented as

$$Q = \int_1^\infty \mathrm{e}^{-qx} \mathrm{d}x$$
$$+ \sum_{n=1}^\infty \frac{u^n}{n!} \int_1^\infty (-x^{-12} + x^{-6} + dgx^{-3})^n \mathrm{e}^{-qx} \mathrm{d}x, \tag{16}$$

$$Q = \frac{\mathrm{e}^{-q}}{q} + \sum_{n=1}^\infty \frac{u^n}{n!} \sum_{k=0}^{k \leq n/2} {}_nC_{2k} d^{2k} G_k$$
$$\cdot \sum_{j=0}^{n-2k} {}_{n-2k}C_j (-1)^j F(6n - 6k + 6j, q), \tag{17}$$

where $F(m,q)$ is calculated by the primitive integrals and the exponential integral,

$$F(m,q) = \int_1^\infty x^{-m} \mathrm{e}^{-qx} dx$$
$$= \mathrm{e}^{-qx} \sum_{k=0}^{m-2} \frac{(-q)^k}{(m-1)(m-2)\cdots(m-1-k)} \tag{18}$$
$$- \frac{(-q)^{m-1}}{(m-1)!} \mathrm{Ei}(-q),$$

where $\mathrm{Ei}(-q)$ is a exponential integral and explicitly obtained as

$$\mathrm{Ei}(-q) = \gamma + \log q - \mathrm{e}^{-q} \sum_{n=1}^\infty \frac{q^n}{n!} \sum_{k=1}^n \frac{1}{k} \tag{19}$$

with the Euler constant γ.

Table 1. Parameters for the polar gas $(12, 6, 3)$ with hard core determined from experimental data of the second virial coefficients [8]. As dipole moments data of [9] are used.

Substance	μ/Debye	(λ/k)/K	σ/Å
$CHCl_3$	1.04	4731.48	2.67
HCl	1.1086	1519.88	2.61
CH_3NH_2	1.27	2880.57	2.59
NH_3	1.468	1197.36	2.52
$C_2H_2Cl_2$	1.62	2668.27	2.70
SO_2	1.634	1442.75	2.68
CH_3OH	1.690	2044.13	2.45
CH_3Br	1.797	1977.62	3.22
CH_3F	1.8471	743.57	3.18
CH_3Cl	1.892	1302.37	2.94
H_2O	1.94	979.12	2.46
C_2H_5Cl	2.05	1656.10	3.00
CH_3CHO	2.69	1195.69	3.61
CH_3COCH_3	2.93	1212.77	3.59
CH_3NO_2	3.46	802.71	3.84
CH_3CN	3.913	1143.74	4.23

The equation of state in one dimension is expressed as

$$L - N_1\sigma = \left(\frac{\partial G}{\partial P}\right)_T$$
$$= \frac{R_1 T}{P} \frac{1}{Q} \int_1^\infty qx\exp[-\beta f(x)]dx. \tag{20}$$

The derivative of L with respect to T can be derived from (20) to

$$\left(\frac{\partial L}{\partial T}\right)_P = \frac{R_1}{P}\left[\frac{1}{Q}\int_1^\infty qx\beta f(x)\exp[-\beta f(x)]dx\right.$$
$$\left. - \frac{1}{Q^2}\int_1^\infty qx\exp[-\beta f(x)]dx \right. \tag{21}$$
$$\left. \cdot \int_1^\infty \beta f(x)\exp[-\beta f(x)]dx\right].$$

Now the enthalpy is obtained as

$$H - PN_1\sigma = -T^2\left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right]_P$$
$$= R_1 T\left[\frac{1}{2} + \frac{1}{Q}\int_1^\infty \beta f(x)\exp[-\beta f(x)]dx\right]. \tag{22}$$

The heat capacity at constant pressure can be easily derived from (22) to

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$
$$= R_1\left[\frac{1}{2} + \frac{1}{Q}\int_1^\infty \{\beta f(x)\}^2\exp[-\beta f(x)]dx\right. \tag{23}$$
$$\left. - \frac{1}{Q^2}\left\{\int_1^\infty \beta f(x)\exp[-\beta f(x)]dx\right\}^2\right].$$

The integrals in (20), (21), (22), and (23) can be explicitly calculated by using (18).

4. Numerical Results

The parameters of the Stockmayer potential $(12, 6, 3)$ with a hard core for 16 substances are presented, λ and σ are determined from the experimen-
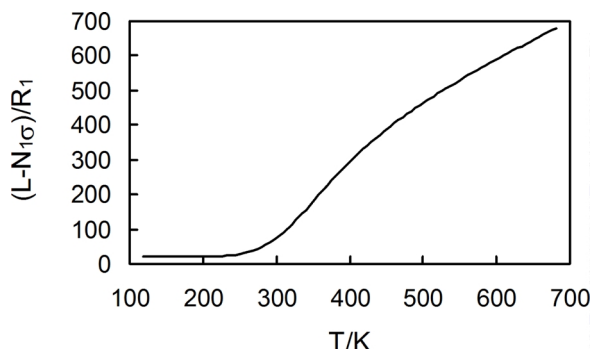

Fig. 1. Length L for H_2O vs. temperature at $P = 1$ atm; $T_B = 355.8$ K.
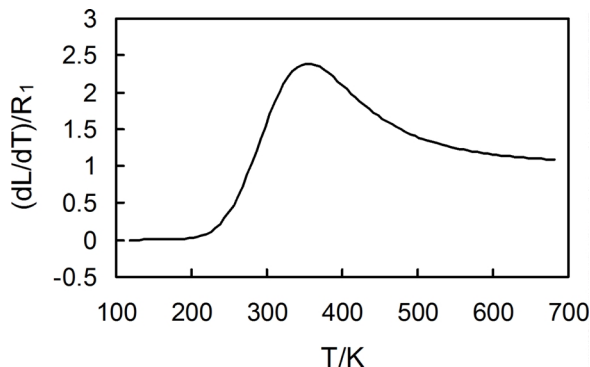

Fig. 2. Derivative $(dL/dT)_P$ for H_2O vs. temperature at $P = 1$ atm; $T_B = 355.8$ K.
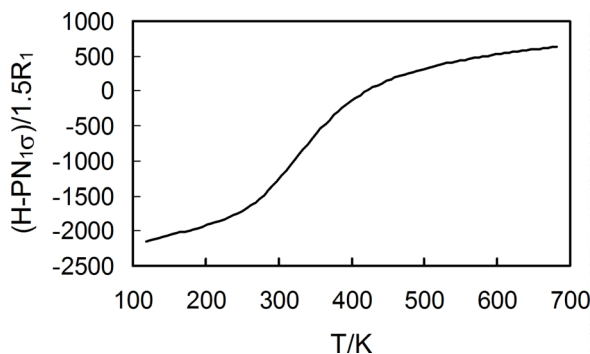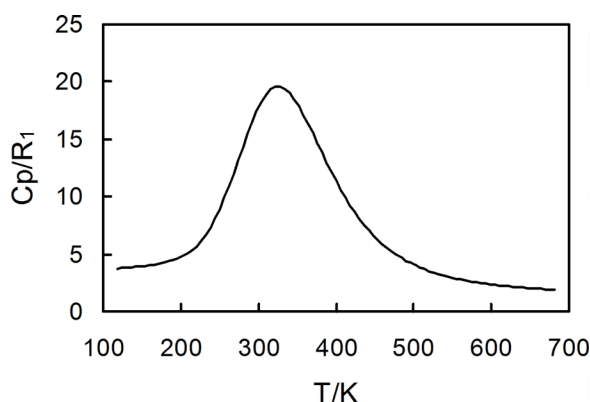

Fig. 3. Enthalpy H for H_2O vs. temperature at $P = 1$ atm; $T_B = 355.8$ K.

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

Substance	Polar gas (12, 6, 3)		Exp. result [13]
	T_1/K	T_B/K	T_B/K
CHCl$_3$	254	306	334.3
HCl	139	166	188.1
CH$_3$NH$_2$	208	243	266.8
NH$_3$	200	225	239.7
C$_2$H$_2$Cl$_2$	241	276	313.0
SO$_2$	212	240	263
CH$_3$OH	284	316	337.8
CH$_3$Br	187	220	276.7
CH$_3$F	161	185	194.8
CH$_3$Cl	213	241	248.9
H$_2$O	325	354	373,2
C$_2$H$_5$Cl	239	270	285.4
CH$_3$CHO	230	262	293.6
CH$_3$COCH$_3$	266	299	329.4
CH$_3$NO$_2$	289	322	374.4
CH$_3$CN	289	325	354.8

Fig. 4. Heat capacity C_p for H$_2$O vs. temperature at $P = 1$ atm; $T_B = 355.8$ K.

tal data of the second virial coefficients [8] and the dipole moments [9] by the least squares method as shown in Table 1. Numerical results obtained with the length $(dL/dT)_p$, enthalpy, and heat capacity for H$_2$O at atmospheric pressure are displayed in Figures 1 – 4.

As shown in Figure 2, the curve of $(dL/dT)_p$ in (21) has 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 the enthalpy H. The enthalpy reaches the behaviour of ideal gases at higher temperature beyond T_1. The heat capacity reaches 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 infinity according to three-dimensional models [10 – 12]. This point of L, however, corresponds physically to 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. This fact seems to be caused by the long-range interaction that includes the dipole-dipole function for the Stockmayer potential (12, 6, 3).

The differences of temperatures for two inflexions of L and H are about 30 K for 16 substances in Table 2. 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 the gaseous phase at the boundary of the boiling point in three-dimensional models [10 – 12]. Assuming that boiling temperature, T_B is physically equivalent to the inflexion point of L, T_2, the boiling temperatures for 16 polar substances indicate reasonable values comparing with experimental data [13] 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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