

# Empirical Regularity of the Thermal Pressure Coefficient for Dense Fluids

Zhi-Yong Zeng,<sup>†,‡</sup> Yuan-Yuan Xu,<sup>†</sup> Xiao-Sen Li,<sup>‡</sup> and Yong-Wang Li<sup>\*,†</sup>

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, People's Republic of China, and Key Laboratory of Renewable Energy and Gas Hydrate, Center for Gas Hydrate Research, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, 510640 Guangzhou, People's Republic of China

In this paper, an empirical regularity has been proposed for dense fluids, namely, that the thermal pressure coefficient is a near-parabola function of pressure. The regularity has been tested with experimental data for both associating and nonassociating compounds. The applicable ranges have also been investigated widely. It is found that the regularity holds well from the freezing temperature to critical temperature, and no obvious limits were found for pressure and compound type. Moreover, parameters of the thermal pressure coefficient expression were regressed from experimental data for *n*-alkanols, and the statistical results show it is an accurate correlation equation. Further, on the basis of the Lennard-Jones (12–6) potential function, the theoretical analysis was given to confirm the existence and uniqueness of the peak point for Lennard-Jones fluids.

## 1. Introduction

The thermal pressure coefficient,  $(\partial P/\partial T)_V$ , is one of the most important fundamental properties; it is closely related to various properties, such as internal pressure, sonic velocity, the entropy of melting, isothermal compressibility, and isobaric expansibility.<sup>1</sup> Thus, the study of thermal pressure coefficient could provide a useful basis for understanding the nature of liquid. Since it is normally difficult to obtain the properties by thermodynamic and statistical mechanics methods due to complex interactions among molecules, experimental methods have attracted much attention. Lots of experimental data,<sup>2–5</sup> simple regularities and theoretical results<sup>6–14</sup> have been obtained in previous research. Moeini<sup>11</sup> reported that the quantity  $[(\partial E/\partial V)_T/\rho RT]V^2$  is linear with  $\rho^2$ , where  $(\partial E/\partial V)_T$  is the internal pressure. This regularity pointed out the relation of internal pressure and volume. Goharshadi and Nazari<sup>12</sup> used a statistical mechanical equation of state to compute the internal pressure of different liquids and investigated the relation of internal pressure and external pressure. Siepmann et al.<sup>13</sup> found the parabola pressure function from simulations of the internal pressure for various compounds and provided additional structural information (pressure dependence of radial distribution functions and hydrogen bonding). These results were applied widely in industry and further accelerated the development of thermodynamic theory.

Generally, the thermal pressure coefficient may be expressed as a function of temperature, pressure, or volume. Equations of state (EoS) are often used to study the thermal pressure coefficient. As a function of volume, there are two main types to our knowledge: one is the virial type and its derivatives,  $(\partial P/\partial T)_V = A/V + B/V^2 + C/V^3 \dots$ , including virial, Martin–Hou, Benedict–Webb–Rubin, linear isotherm regularity (LIR)<sup>15</sup> EoS, and so on. The other is the van der Waals type and its derivatives,  $(\partial P/\partial T)_V = A/(V - b) - B/(V^2 + ubV + wb^2)$ , including van der Waals, Redlich–Kwong,<sup>16</sup> Soave,<sup>17</sup> Peng–Robinson EoS,<sup>18</sup> and so on.

\* To whom correspondence should be addressed. Tel.: (+86)351-7560831. Fax: (+86)351-7560668. E-mail: ywl@sxicc.ac.cn.

<sup>†</sup> State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences.

<sup>‡</sup> Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences.

As a temperature function of the thermal pressure coefficient, there are several variations in its development. In the early stage, it was proposed that the thermal pressure coefficient is only a function of density in the van der Waals EoS, which was certainly not a precise one. Then, Redlich and Kwong proposed a new EoS, and the thermal pressure coefficient became a linear function of  $T^{-1.5}$ . Later, Soave<sup>17</sup> found the function of the attraction parameter based on the experimental data:  $\alpha(T) = \alpha_c[1 + m(1 - T_r^{0.5})]^2$ , so the thermal pressure coefficient turned into the linear function of  $T^{-0.5}$ . From then on, this function was adopted by many other equations of state such as Peng–Robinson EoS<sup>18</sup> and Patel–Teja EoS.<sup>19</sup> Moreover, Deiters<sup>7</sup> and Song and Mason<sup>8</sup> observed experimentally that it is near the linearity of  $P$  vs  $T$  at constant density over the entire range from the perfect gas to the dense fluids.

Although there are many experimental findings, the pressure function of the thermal pressure coefficient has not been studied widely. In fact, the pressure dependence function was very important. At the simplest level, pressure–volume–temperature ( $PVT$ ) properties closely correlate and could transform each other through equations of state; thus, the regularity of the pressure function of the thermal pressure coefficient could be used to derive other  $PVT$  relations. Moreover, pressure as a variable was usually adopted in other properties, such as internal pressure; it would make for unifying variables.

The purpose of this paper is to present an empirical regularity that the thermal pressure coefficient is a near-parabola function of pressure and to validate it by the experimental data of various compounds. The applicable ranges of the regularity were investigated, including temperature, pressure, and compound type. Moreover, parameters of the pressure function would be studied for *n*-alkanol. Finally, more discussion and analysis on this regularity is given in the end of this paper.

## 2. Theoretical Background

The isobaric thermal expansivity  $\alpha_P$  and the isothermal compressibility  $\kappa_T$  are defined as

$$\alpha_P = V^{-1}(\partial V/\partial T)_P \quad (1)$$

$$\kappa_T = -V^{-1}(\partial V/\partial P)_T \quad (2)$$

The ratio between them is known as the thermal pressure coefficient,

$$(\partial P/\partial T)_V = \frac{\alpha_P}{\kappa_T} \quad (3)$$

$\alpha_P$  and  $\kappa_T$  have been measured experimentally for various fluids; thus, values of the thermal pressure coefficient were calculated from experimental data of isobaric thermal expansivity and isothermal compressibility in this work.

Moreover, the internal pressure  $\pi$  is defined as

$$\pi = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad (4)$$

On the basis of the definition, it is easy to obtain

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\pi + P}{T} \quad (5)$$

It shows clearly that the thermal pressure coefficient is contributed by a sum of internal and external pressures.

It has been found experimentally that the internal pressure increases initially, reaches a maximum, and then falls off. Typical experimental data<sup>20</sup> are shown in Figure 1. It is possible that the internal pressure is an even power function of pressure. Considering the representative experimental phenomena in Figure 1 and shortening the expression, the lowest order even power function was selected for study in this work, namely, the parabola function. It is expressed as

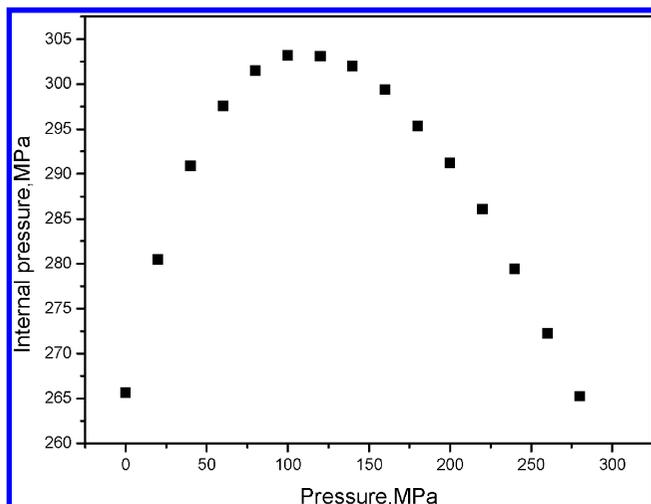
$$\pi = A' + B'P + C'P^2 \quad (6)$$

Combining with eq 5,  $(\partial P/\partial T)_V$  can be expressed as

$$\left(\frac{\partial P}{\partial T}\right)_V = A + BP + CP^2 \quad (7)$$

where

$$A = A'/T \quad (8)$$



**Figure 1.** Experimental internal pressure as a function of pressure for methanol at  $T = 333.15$  K, all experimental data from ref 20.

$$B = (B' + 1)/T \quad (9)$$

$$C = C'/T \quad (10)$$

where  $A'$ ,  $B'$ ,  $C'$ ,  $A$ ,  $B$ , and  $C$  are the temperature-dependent parameters.

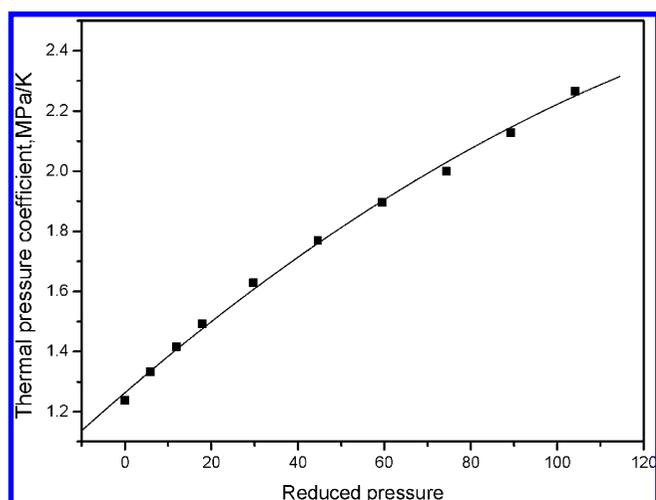
### 3. Results and Discussion

**3.1. Examining the Pressure Function of the Thermal Pressure Coefficient.** Some specific issues were focused on in this paper. First, the pressure and temperature ranges were investigated where the function holds well. Second, the type of fluids was studied for whether the proposed function is valid for all substances.

At the beginning, the pressure range was investigated. Ethyl butyrate and ethyl propionate served as our primary test fluids because their experimental data of  $\alpha_P$  and  $\kappa_T$  cover the pressure range from 1 to 3500 bar.<sup>21</sup> For convenience only, the pressure and temperature have been reduced by the critical properties. Figure 2 shows the  $(\partial P/\partial T)_V$  as a parabola function of reduced pressure at  $T = 288.15$  K. It can be seen that the experimental data are found to coincide essentially with the parabola function except for trivial deviations at the maximum and minimum pressure. Therefore, there appears to be no obvious pressure limits in the liquids (namely,  $T < T_C$  in this work) for the considered experimental data.

Then, the temperature range was studied with ethylene because its experimental data, given by Calado et al.,<sup>22</sup> cover the reduced temperature range from 0.39 to 0.99. The results are summarized in Table 1. The standard error is used to characterize the deviations. From these values, it appears that the parabola pressure function has a good consistency with the experimental data. Thus, the lower temperature limit is the freezing temperature as far as the experimental data are concerned. Due to the shortage of the experimental data at  $T > T_C$ , it cannot get the upper temperature limit definitely. However, it is certain that the regularity holds well between the freezing point and the critical point.

Moreover, in order to investigate whether the regularity is limited to a certain type of fluid or is generally true, different fluids were investigated over wide temperature and pressure ranges, including both associating and nonassociating compounds.<sup>20,23–32</sup> The results are shown in Table 2. It is clear that the parabola pressure function of  $(\partial P/\partial T)_V$  holds well for



**Figure 2.** Experimental thermal pressure coefficient<sup>21</sup> as a function of reduced pressure for ethyl propionate at  $T = 288.15$  K.

**Table 1. Results of Fitted Parameters of Equation 7, Pressure Range ( $\Delta P$ ) of the Data, and the Standard Error ( $\sigma$ ) at Different Temperatures for Ethylene**

$T/T_C$	$\Delta P$ (MPa)	$A$	$B$	$C \times 10^5$	$\sigma \times 10^2$ (MPa/K)
0.39	0.5–40	2.36910	0.00712	1.3369	1.6733
0.43	0.5–120	2.25413	0.00692	-0.18728	0.04202
0.46	0.5–130	2.05018	0.00684	-0.66055	0.08871
0.50	0.5–130	1.84451	0.00694	-0.97694	0.17425
0.53	0.5–130	1.66085	0.00707	-1.17438	0.9999
0.57	0.5–130	1.50063	0.00723	-1.34179	0.3067
0.60	0.5–130	1.36067	0.00737	-1.53767	0.6164
0.64	0.5–130	1.23457	0.00752	-1.57728	0.4117
0.67	0.5–130	1.11942	0.00759	-1.60326	0.5838
0.73	1.0–130	0.95941	0.00798	-1.8779	0.6052
0.78	1.0–130	0.80644	0.00845	-2.1689	0.8338
0.83	2.5–130	0.66633	0.00882	-2.3774	0.9522
0.89	2.5–130	0.51235	0.00983	-2.9809	1.7342
0.94	10–130	0.4198	0.00929	-2.63087	1.5883
0.99	20–130	0.34596	0.00856	-2.1985	0.7029

**Table 2. Results of the Average Standard Error in the Entire Range ( $\bar{\sigma}$ ), the Pressure and Temperature Ranges, and the Number of Points (NP) for Different Fluids**

fluid	ref	$\Delta P$ (MPa)	$\Delta T$ (K)	NP	$\bar{\sigma} \times 10^2$ (MPa/K)	
1-alkanol	methanol	Machado and Streett <sup>23</sup>	0.1–100	298.00–453.00	120	0.2153
		Sun et al. <sup>20</sup>	0.1–180	273.15–333.15	105	0.2348
	ethanol	Takiguchi and Uematsu <sup>24</sup>	1.0–190	340.00–460.00	202	0.2063
		Verdier and Andersen <sup>25</sup>	0.1–20	303.15–303.15	11	0.3022
	<i>n</i> -propanol	Zuniga-Moreno and Galicia-Luna <sup>36</sup>	0.5–25	313.15–362.77	160	0.0784
	<i>n</i> -butanol	Outcalt et al. <sup>37,a</sup>	0.5–50	270.00–470.00	165	0.1454
	<i>n</i> -pentanol	Garg et al. <sup>26,a</sup>	0.1–10	323.15–373.15	60	0.0042
	<i>n</i> -hexanol	Garg et al. <sup>26,a</sup>	0.1–10	323.15–373.15	60	0.0014
	<i>n</i> -heptanol	Dzida <sup>27</sup>	0.1–100	293.15–318.35	66	0.5514
		Garg et al. <sup>26,a</sup>	0.1–10	323.15–373.15	60	0.0014
	<i>n</i> -octanol	Dzida <sup>27</sup>	0.1–100	293.15–318.35	66	0.3715
	<i>n</i> -nonanol	Garg et al. <sup>26,a</sup>	0.1–10	323.15–373.15	60	0.0092
		Dzida <sup>27</sup>	0.1–100	293.15–318.35	66	0.2118
	<i>n</i> -decanol	Garg et al. <sup>26,a</sup>	0.1–10	323.15–373.15	60	0.0029
Dzida <sup>27</sup>		0.1–60	293.15–318.35	47	0.1715	
<i>n</i> -dodecanol	Garg et al. <sup>26,a</sup>	0.1–10	323.15–373.15	60	0.0021	
	Garg et al. <sup>26,a</sup>	0.1–60	293.15–318.35	47	0.1715	
<i>n</i> -alkane	<i>n</i> -pentane	Pecar and Dolecek <sup>28</sup>	0.1–40	298.15–348.15	15	0.4345
			0.1–40	298.15–348.15	15	0.4020
			0.1–40	298.15–348.15	15	0.3621
			1.0–20	278.15–353.15	63	0.5716
			0.1–20	303.15–303.15	11	0.4822
alkaene	ethylene	Calado et al. <sup>22</sup>	0.5–130	110.00–280.00	242	0.7542
			0.5–130	110.00–280.00	242	0.7542
others	cyclohexane	Sun et al. <sup>30</sup>	0.1–85	288.15–323.06	90	0.2525
			0.1–170	288.14–323.13	88	0.3186
	chlorobenzene	Easteal et al. <sup>31</sup>	0.1–275	278.15–338.15	60	0.5468
	1,2-dichlorobenzene		0.1–150	278.15–338.15	40	0.4875
	dimethyl carbonate	Lugo et al. <sup>29</sup>	1.0–20	278.15–353.15	63	0.5677
	ethyl propionate	Malhotra and Woolf <sup>21</sup>	0.1–350	278.15–333.15	60	0.6254
	ethyl butyrate	Malhotra and Woolf <sup>21</sup>	0.1–350	278.15–333.15	60	0.7534
	1,2-propanediol	Zorębski et al. <sup>33,34</sup>	0.1–100	293.15–313.15	55	0.0574
	1,3-propanediol		0.1–100	293.15–318.15	66	0.0891
	1,2-butanediol		0.1–100	293.15–318.15	56	0.1622
	1,3-butanediol		0.1–100	293.15–318.15	66	0.1315
	2,3-dimethylbutane	Garcia Baonza et al. <sup>32</sup>	0.1–100	208.15–298.15	70	0.0874
	water	Chen et al. <sup>35</sup>	0.0–100	273.18–373.15	231	0.3421

<sup>a</sup> These data were calculated from the fitted volume correlations.

all studied compounds. Therefore, it could be concluded that there are no known fluid limits.

**3.2. Study of the Parameters.** This part would further study the parameters of eq 7. As is mentioned above, the thermal pressure coefficient is temperature-dependent; thus, the parameters of eq 7 would be temperature-dependent, too. For examining this point, experimental data were correlated with different functions. A typical result is shown in Figure 3. Three linear functions of  $T$ ,  $T^{-0.5}$ , and  $T^{-1.5}$  were used to fit the experimental data,<sup>22</sup> it is clear that the linear function of  $T^{-0.5}$  has a better description of the experimental data than others. Therefore, the linear function of  $T^{-0.5}$  is adopted in this work.

Moreover, on the basis of the experimental data, the different substances have characteristic thermal coefficients at the same

condition; thus, the parameters of eq 7 are also substance-dependent. The experimental data of homologues were examined in this work, mainly for *n*-alkanols. The typical results are shown in Figure 4. It is obvious that the carbon number ( $C_n$ ) function of the thermal coefficient is a near-linear relation for 1-alkanols. Thus, the linear function of  $C_n$  is adopted for homologues in this work.

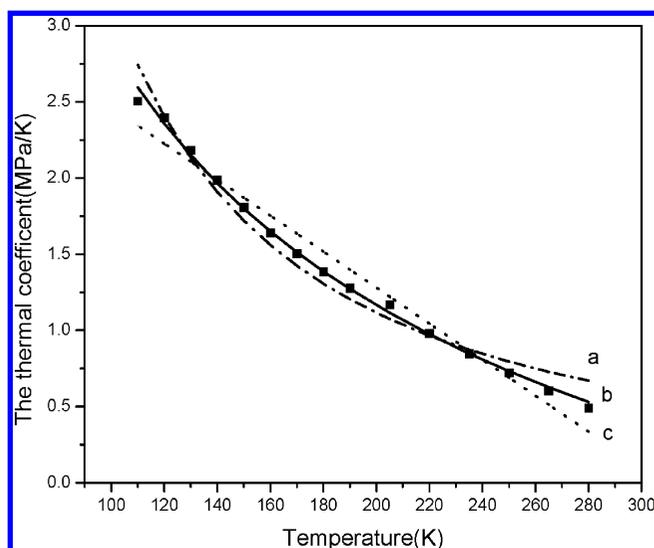
On the basis of the above results, the parameters of eq 7 could be expressed as the functions of carbon number and temperature for homologues. In this work, the parameters of *n*-alkanol were studied. Using the experimental data, the expressions of parameters of eq 7 could be regressed, and the detailed information is shown in eqs 11–13. The statistical results are shown in Table 3. The average values of standard deviations

**Table 3. Statistical Results of Fitting the Parameters of Equation 7 from Experimental Data**

fluid	ref	NP	$\Delta P$ (MPa)	$\Delta T$ (K)	$\sigma \times 10^2$ (MPa/K)
methanol	Machado and Streett <sup>23</sup>	120	0.1–100	298.00–453.00	0.5522
	Sun et al. <sup>20</sup>	105	0.1–180	273.15–333.15	0.3825
ethanol	Takiguchi and Uematsu <sup>24</sup>	202	1.0–190	340.00–460.00	0.8531
	Verdier and Andersen <sup>25</sup>	11	0.1–20	303.15–303.15	0.5614
<i>n</i> -propanol	Zuniga-Moreno and Galicia-Luna <sup>36,a</sup>	160	0.5–25	313.15–362.77	0.2865
<i>n</i> -butanol	Outcalt et al. <sup>37,a</sup>	165	0.5–50	270.00–470.00	0.1064
<i>n</i> -pentanol	Garg et al. <sup>26,a</sup>	60	0.1–10	323.15–373.15	0.4157
<i>n</i> -hexanol	Garg et al. <sup>26,a</sup>	60	0.1–10	323.15–373.15	0.3081
<i>n</i> -heptanol	Garg et al. <sup>26,a</sup>	60	0.1–100	293.15–318.35	0.1987
	Dzida <sup>27</sup>	66	0.1–10	323.15–373.15	0.1248
<i>n</i> -octanol	Garg et al. <sup>26,a</sup>	60	0.1–100	293.15–318.35	0.1203
	Dzida <sup>27</sup>	66	0.1–10	323.15–373.15	0.1445
<i>n</i> -nonanol	Garg et al. <sup>26,a</sup>	60	0.1–100	293.15–318.35	0.2304
	Dzida <sup>27</sup>	66	0.1–10	323.15–373.15	0.1885
<i>n</i> -decanol	Dzida <sup>27</sup>	47	0.1–60	293.15–318.35	0.2116
<i>n</i> -dodecanol	Garg et al. <sup>26,a</sup>	60	0.1–10	323.15–373.15	0.3074

av: 0.3122

<sup>a</sup> Values of thermal pressure coefficient were calculated by their PVT correlations in literatures.



**Figure 3.** Temperatures function of the thermal pressure coefficient of ethylene at  $P = 20$  MPa. ■ denotes the experimental data.<sup>22</sup> The solid line b represents the linear function of  $T^{-0.5}$ . The dotted line a represents the linear function of  $T$ . The dashed–dotted line c represents the linear function of  $T^{-1.5}$ .

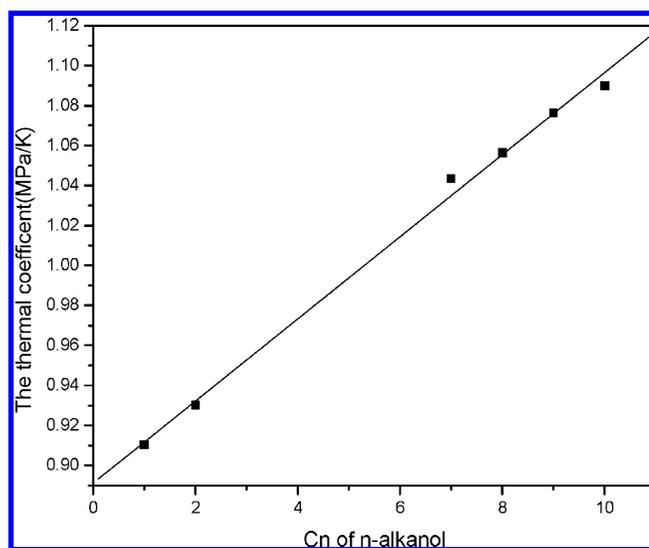
are small for the considered fluids, which indicate that the fitted parameters are accurate and reliable.

$$A = 2.3635 + 1.778 \times 10^{-2} C_n - 7.4625 \times 10^{-2} T^{0.5} - 4.5615 \times 10^{-4} C_n T^{0.5} \quad (11)$$

$$B = 1.97 \times 10^{-2} - 5.45 \times 10^{-3} C_n - 9.21 \times 10^{-4} T^{0.5} + 3.17 \times 10^{-4} C_n T^{0.5} \quad (12)$$

$$C = -1.10 \times 10^{-4} + 6.35 \times 10^{-5} C_n + 6.11 \times 10^{-6} T^{0.5} - 3.72 \times 10^{-6} C_n T^{0.5} \quad (13)$$

**3.3. Discussion of the Regularity.** Since the preceding results confirmed the validity of the thermal pressure coefficient as a parabola function of pressure, and the thermal pressure coefficient is related to the internal pressure according to eqs 4 and 5, it could be concluded that the internal pressure is also a parabola function of pressure in the considered ranges. For every parabola function, there exists one and only one peak point. The purpose of this part is to find the peak point and show its uniqueness.



**Figure 4.** Carbon number ( $C_n$ ) function of the thermal pressure coefficient for *n*-alkanols at  $T = 303.15$  K and  $P = 0.1$  MPa. ■ denotes the experimental data.<sup>20,25,27</sup> The straight line is regressed from the experimental data.

The internal pressure was defined as follows:

$$\pi = \left( \frac{\partial U}{\partial V} \right)_T \quad (11a)$$

When eq 11 was carried out for the isothermal differentiation with respect to pressure, it resulted in

$$\left( \frac{\partial \pi}{\partial P} \right)_T = \left( \frac{\partial U / \partial V}{\partial P} \right)_T \quad (12a)$$

Then,

$$\left( \frac{\partial U / \partial V}{\partial P} \right)_T = \left( \frac{\partial U / \partial V}{\partial V} \right)_T \left( \frac{\partial V}{\partial P} \right)_T = \left( \frac{\partial^2 U}{\partial V^2} \right)_T \left( \frac{\partial V}{\partial P} \right)_T \quad (13a)$$

The internal energy includes the kinetic part and potential part. Among of them, the kinetic energy does not change when the temperature holds constant; thus, only the potential energy is influenced as it experiences a small isothermal expansion. Therefore, the partial derivative of internal energy in eq 13 turns into the derivative of potential energy with respect to volume in the process.

In this work, the average potential energy was approximated by summing the contribution from nearest neighbors only. Then, the well-known Lennard-Jones (12–6) potential function was adopted; it is expressed as

$$U = (N/2)z(\rho)\left[\frac{C_n}{r^{12}} - \frac{C_m}{r^6}\right] \quad (14)$$

where  $U$  is the total potential energy among  $N$  molecules and  $r$  is the average distance between nearest molecules.  $z(\rho)$  is the average number of nearest neighbors. It is well-known that  $z(\rho)$  is proportional to  $\rho$ , and it is approximated that  $z(\rho)$  holds constant in the tiny expansion.

The volume of fluid is expressed as  $V \approx N(4\pi r^3/3)$  approximately, and then eq 14 can be transformed into

$$U = (N/2)z(\rho)\left[\frac{(4\pi N/3)^4 C_n}{V^4} - \frac{(4\pi N/3)^2 C_m}{V^2}\right] \quad (15)$$

Further, through eq 15 was carried out the second-order differentiation with respect to volume isothermally; it could be written as

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_T = (N/2)z(\rho)\left[\frac{20(4\pi N/3)^4 C_n}{V^6} - \frac{6(4\pi N/3)^2 C_m}{V^4}\right] \quad (16)$$

In this work, the regularity is only applied in the temperature range from freezing point to critical point. ON the basis of the classic thermodynamic and experimental data, there is no extremum in the  $P$ – $V$  relation in this temperature range. Therefore, combining with eq 13, when  $(\partial\pi/\partial P)_T = 0$  at the extremum, it must be

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_T = 0 \quad (17)$$

According to eq 16, it could be obtained as

$$\frac{20(4\pi N/3)^4 C_n}{V^6} = \frac{6(4\pi N/3)^2 C_m}{V^4} \quad (18)$$

Simplify eq 18 and combining the volume definition  $V \approx N(4\pi r^3/3)$ , it turns out

$$\left(\frac{1}{r}\right)^6 = \frac{3C_m}{10C_n} \quad (19)$$

where both  $C_m$  and  $C_n$  are positive numbers; thus, there is only one real answer for eq 19,

$$r = \sqrt[6]{10C_n/3C_m} \quad (20)$$

Therefore, the pressure function of the internal pressure has exactly one peak point over the temperature range from the freezing point to critical point, which coincides with the demand of the probable function.

#### 4. Conclusions

In this work, an empirical regularity of the thermal pressure coefficient was derived; that is,  $(\partial P/\partial T)_V = A + BP + CP^2$ . The experimental data, calculated with values of isobaric thermal expansivity and isothermal compressibility, were taken to check

its validity. The results showed high correlation coefficients for all of the experimental data.

The applicable ranges of temperature, pressure, and the type of compounds were investigated. It turned out that the regularity holds well in the temperature range from the freezing point to the critical point, and no obvious limits were found for pressure and the type of compounds.

Moreover, the parameters of eq 7 were regressed from experimental data for  $n$ -alcohol. Good agreement was found between the experimental and calculated data.

Further, the existence of one peak point in the pressure function for Lennard-Jones fluids was confirmed. The maximum of the internal pressure appears at  $r = (10C_n/3C_m)^{1/6}$ , where  $C_n$  and  $C_m$  are constants of the Lennard-Jones potential model.

The present result provides a reliable approach to correlate the thermal pressure coefficient and the internal pressure with external pressure. It would benefit the development of equations of state for dense fluids.

#### Acknowledgment

The authors gratefully acknowledge the financial support from Key Program of National Natural Science Foundation of China (Grant 20590361), the National Outstanding Young Scientists Foundation of China (Grant 20625620), and the Key Project of Chinese National Programs for Fundamental Research and Development (973 program: Grant 2009CB219507).

#### Literature Cited

- (1) Flory, P. J. Statistical Thermodynamics of Liquid Mixtures. *J. Am. Chem. Soc.* **1965**, *87* (9), 1833–1838.
- (2) Few, G. A.; Rigby, M. Thermal Pressure Coefficient and Internal Pressure of 2,2-Dimethylpropane. *J. Phys. Chem.* **1975**, *79*, 1543–1546.
- (3) Fortune, G. C.; Malcolm, G. N. Thermal Pressure Coefficient and the Entropy of Melting at Constant Volume of Isotactic Polypropylene. *J. Phys. Chem.* **1967**, *71*, 876–879.
- (4) Malcolm, G. N.; Ritchie, G. L. D. The Thermal Pressure Coefficient and the Entropy of Melting at Constant Volume of Polyethylene Oxide. *J. Phys. Chem.* **1962**, *66*, 852–854.
- (5) Bolotnikov, M. F.; Neruchev, Y. A. Temperature Dependence of the Thermophysical Properties of 1-Chlorohexane, 1-Iodohexane, 1-Iodoheptane, and 1-Chlorononane at Saturation Condition. *J. Chem. Eng. Data* **2004**, *49*, 202–207.
- (6) Lee, H.-Y.; Liu, G. a Generalized Equation of State for Liquid Density Calculation. *Fluid Phase Equilib.* **1995**, *108* (1–2), 15–25.
- (7) Deiters, U. a New Semiempirical Equation of State for Fluids—I: Derivation. *Chem. Eng. Sci.* **1981**, *36* (7), 1139–1146.
- (8) Song, Y.; Mason, E. A. Statistical-Mechanical Theory of a New Analytical Equation of State. *J. Chem. Phys.* **1989**, *91* (12), 7840–7853.
- (9) Smith, E. B. Equation of State of Liquids at Constant Volume. *J. Chem. Phys.* **1962**, *36* (5), 1404–1405.
- (10) Pant, N.; Chaturvedi, C. V.; Chaturvedi, G. D. Thermal Pressure Coefficient, Internal-Pressure and Solubility Parameter of Hard-Sphere Fluids. *Z. Phys. Chem. (Leipzig)* **1983**, *264* (3), 513–524.
- (11) Moeni, V. A New Regularity for Internal Pressure of Dense Fluids. *J. Phys. Chem. B* **2006**, *110*, 3271–3275.
- (12) Goharshadi, E. K.; Nazari, F. Computation of Internal Pressure of Liquids Using a Statistical Mechanical Equation of State. *Fluid Phase Equilib.* **2001**, *187*–188, 425–431.
- (13) Siepmann, J. I.; Schultz, N. E.; Ross, R. B. Pressure Dependence of the Hildebrand Solubility Parameter and the Internal Pressure: Monte Carlo Simulations for External Pressures up to 300 MPa. *J. Phys. Chem. C* **2007**, *111*, 15634–15641.
- (14) Zeng, Z. Y.; Xu, Y. Y.; Li, Y. W. Calculation of Solubility Parameter Using Perturbed-Chain SAFT and Cubic-Plus-Association Equations of State. *Ind. Eng. Chem. Res.* **2008**, *47*, 9663–9669.
- (15) Parsafar, G.; Mason, E. A. Linear Isotherms for Dense Fluids: A New Regularity. *J. Phys. Chem.* **1993**, *97*, 9048–9053.
- (16) Redlich, O.; Kwong, J. N. S. On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions. *Chem. Rev.* **1949**, *44*, 233–244.

- (17) Soave, G. Equilibrium Constants from a Modified Redlich-Kwong Equation of State. *Chem. Eng. Sci.* **1972**, *27* (6), 1197–&.
- (18) Peng, D.-Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15* (1), 59–64.
- (19) Patel, N. C.; Teja, A. S. A New Cubic Equation of State for Fluids and Fluid Mixtures. *Chem. Eng. Sci.* **1982**, *37* (3), 463–473.
- (20) Sun, T.; Biswas, S. N.; Trappeniers, N. J.; Ten Seldam, C. A. Acoustic and Thermodynamic Properties of Methanol from 273 to 333 K and at Pressures to 280 MPa. *J. Chem. Eng. Data* **1988**, *33*, 395–398.
- (21) Malhotra, R.; Woolf, L. A. PVT Property Measurements for the Liquids Ethyl Propionate and Ethyl Butyrate from (278 to 338) K and (0.1 to 380) MPa. *J. Chem. Eng. Data* **1996**, *41*, 1371–1374.
- (22) Calado, J. C. G.; Clancy, P.; Heintz, A.; Streett, W. B. Experimental and Theoretical Study of the Equation of State of Liquid Ethylene. *J. Chem. Eng. Data* **1982**, *27* (4), 376–385.
- (23) Machado, J. R. S.; Streett, W. B. Equation of State and Thermodynamic Properties of Liquid Methanol from 298 to 489 K and Pressures to 1040 bar. *J. Chem. Eng. Data* **1983**, *28*, 218–223.
- (24) Takiguchi, Y.; Uematsu, M. Densities for Liquid Ethanol in the Temperature Range from 310 to 480 K at Pressures up to 200 MPa. *J. Chem. Thermodyn.* **1996**, *28* (1), 7–16.
- (25) Verdier, S.; Andersen, S. I. Internal Pressure and Solubility Parameter as a Function of Pressure. *Fluid Phase Equilib.* **2005**, *231* (2), 125–137.
- (26) Garg, S. K.; Banipal, T. S.; Ahluwalia, J. C. Densities, Molar Volumes, Cubic Expansion Coefficients, and Isothermal Compressibilities of 1-Alkanols from 323.15 to 373.15 K and at Pressures up to 10 MPa. *J. Chem. Eng. Data* **1993**, *38*, 227–230.
- (27) Dzida, M. Speeds of Sound, Densities, Isobaric Thermal Expansion, Compressibilities, and Internal Pressures of Heptan-1-ol, Octan-1-ol, Nonan-1-ol, and Decan-1-ol at Temperatures from (293 to 318) K and Pressures up to 100 MPa. *J. Chem. Eng. Data* **2007**, *52*, 521–531.
- (28) Pecar, D.; Dolecek, V. Isothermal Compressibilities and Isobaric Expansibilities of Pentane, Hexane, Heptane and Their Binary and Ternary Mixtures from Density Measurements. *Fluid Phase Equilib.* **2003**, *211* (1), 109–127.
- (29) Lugo, L.; Comunas, M. J. P.; Lopez, E. R.; Fernandez, J. (p, V-m, T, x) Measurements of Dimethyl Carbonate plus Octane Binary Mixtures I. Experimental Results, Isothermal Compressibilities, Isobaric Expansivities and Internal Pressures. *Fluid Phase Equilib.* **2001**, *186* (1–2), 235–255.
- (30) Sun, T. F.; Kortbeek, P. J.; Trappeniers, N. J.; Biswas, S. N. Acoustic and Thermodynamic Properties of Benzene and Cyclohexane as a Function of Pressure and Temperature. *Phys. Chem. Liq.* **1987**, *16* (3), 163–178.
- (31) Easteal, A. J.; Back, P. J.; Woolf, L. A. PVT Property Measurements for Liquid Chlorobenzene and 1,2-Dichlorobenzene from (278 to 338) K and (0.1 to 300) MPa. *J. Chem. Eng. Data* **1997**, *42*, 1261–1265.
- (32) Garcia Baonza, V.; Caceres Alonso, M.; Nunez Delgado, J. Study of the Equation of State of Liquid 2,3-Dimethylbutane at High Pressures. *J. Phys. Chem.* **1993**, *97*, 2002–2008.
- (33) Zorębski, E.; Dzida, M.; Piotrowska, M. Study of the Acoustic and Thermodynamic Properties of 1,2- and 1,3-Propanediol by Means of High-Pressure Speed of Sound Measurements at Temperatures from (293 to 318) K and Pressures up to 101 MPa. *J. Chem. Eng. Data* **2007**, *53*, 136–144.
- (34) Zorębski, E.; Dzida, M. Study of the Acoustic and Thermodynamic Properties of 1,2- and 1,3-Butanediol by Means of High-Pressure Speed of Sound Measurements at Temperatures from (293 to 318) K and Pressures up to 101 MPa. *J. Chem. Eng. Data* **2007**, *52*, 1010–1017.
- (35) Chen, C. T.; Fine, R. A.; Millero, F. J. Equation of State of Pure Water Determined from Sound Speeds. *J. Chem. Phys.* **1977**, *66* (5), 2142–2144.
- (36) Zuniga-Moreno, A.; Galicia-Luna, L. A. Densities of 1-Propanol and 2-Propanol via a Vibrating Tube Densimeter from 313 to 363 K and up to 25 MPa. *J. Chem. Eng. Data* **2001**, *47*, 155–160.
- (37) Outcalt, S. L.; Laesecke, A.; Fortin, T. J. Density and Speed of Sound Measurements of 1- and 2-Butanol. *J. Mol. Liq.* *151* (1), 50–59.

Received for review February 3, 2010

Revised manuscript received June 8, 2010

Accepted June 21, 2010

IE100271C