THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 108, NUMBER 47, NOVEMBER 25, 2004

LETTERS

Virial Expansion Providing of the Linearity for a Unit Compressibility Factor

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Received: August 10, 2004; In Final Form: September 21, 2004

We show that the law of linearity for a unit compressibility factor testifying a lot of experimental data for many substances can be provided by appropriate procedure following from the rigorous consequences of statistical mechanics, namely, the virial expansion. An equation of state that includes the terms up to the fourth power of density is obtained by using second and third virial coefficients. The critical point parameters, phase densities, and pressure along the liquid−gas coexistence curve for the Lennard-Jones (6−12) (LJ) and Buckingham (exp6) potentials are defined. The results corresponding to the LJ potentials are in good agreement with the solution of integral equations and simulation results. For the Buckingham potentials, our predictions agree well with the experimental data for the group of real substances, satisfying the law of corresponding states.

The law of linear dependence between density and temperature along the line of unit compressibility factor $Z = 1$ (recently christened the Zeno line) has been verified experimentally for many substances.[1−4] Unfortunately, this law is less known in comparison with the corresponding states law, despite the fact that the linearity of the Zeno line has no less experimental confirmations than the law of corresponding states. The high accuracy and wide domain of applicability of the linearity for Zeno line indicates that this law may be a generic property of matter, and it is advantageous to incorporate it in the equations of state model. Nowadays there is a large variety of various equations of state. However, only one equation of state, namely, the virial equation of state, is the rigorous consequence of statistical mechanics. This equation relates the intermolecular potential for a given state of matter with its macroscopic parameters. The well-known form of the virial equation of state

$$Z(\rho,T) = \sum_{k=0}^{\infty} \frac{\rho^k}{k!} \frac{\partial^k Z(0,T)}{\partial \rho^k} = 1 + \rho B_2(T) + \rho^2 B_3(T) + \rho^3 B_4(T) + \cdots \quad (1)$$

is an expansion of the compressibility factor $Z = P/\rho T$ in the series of density, where B_k is the kth virial coefficient.

In this paper, we analyze whether the law of linearity for a unit compressibility factor could be deduced from the virial equation of state. We consider a model system that describes the Lennard-Jones (LJ) potential and group of real substances, which obey the law of corresponding states, with the Buckingham (exp6) potential

$$\varphi(r, a) = \frac{1}{1 - \dfrac{6}{a}} \left\{ \frac{6}{a} \exp[a(1 - r)] - \left(\frac{1}{r}\right)^6 \right\} \quad (2)$$

Here, the constant $a = 15.6$. (See the text below.)

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10.1021/jp046417z CCC: $27.50

Batschinski[5] noted that there are two consequences straightforwardly following from the van der Waals equation written in the dimensionless units ($\tilde{\rho} = \rho/\rho_c$, $\tilde{T} = T/T$, where ρ is the density, T is the temperature, and subscript c indicates the critical point). The first consequence, obtained by van der Waals himself, relates to the well-known law of corresponding states, claiming that the pressure in the reduced units does not depend on the nature of the substance. The second (lesser-known) consequence deals with the compressibility factor $Z = P/\rho T$ (here P is the pressure), which has the following expression

$$Z = \frac{P}{\rho T} = 1 + \frac{27\tilde{\rho}\left(\frac{\tilde{\rho}}{3} + \frac{8\tilde{T}}{27} - 1\right)}{(3 - \tilde{\rho})8\tilde{T}} \tag{3}$$

Equation 3 states that density-versus-temperature curve is a straight line for $Z = 1$. It intersects the temperature axis at the Boyle point $T = T_B = 27/8$ and the density axis at the point $\tilde{\rho}_B = 3$. Therefore, for dimensionless Boyle-point parameters ($\rho_1 = \rho/\tilde{\rho}_B$, and $\theta_1 = T/T_B$), eq 3 can be rewritten as

$$Z = 1 + \frac{\rho_1(\rho_1 + \theta_1 - 1)}{(1 - \rho_1)\theta_1} \tag{4}$$

It is evident that on the straight line $\rho_1 + \theta_1 = 1$ the compressibility factor must be equal to unity.

In Figure 1 a the pressure and b the phase equilibrium densities versus temperature along the phase coexistence curves for the substances that satisfy the law of corresponding states are plotted in dimensionless units. The dimensional parameters are, for the pressure, D/σ^3, for the temperature, D, and for the density, σ^{-3}. Here, D is the depth of the potential, σ is the minimum distance at which the potential is zero. For the plots shown in Figure 1, we used the values (denoted by symbols) of thermodynamic functions for noble gases tabulated in refs1 and 6. The latter are consistent with the entire body of experimental data on thermal properties of noble gases. Sets of reliable interaction potentials between two atoms of a noble gas have been published earlier.[7−10] The resulting parameters $r_{\min}$ and D for Ne, Ar, Kr, and Xe and the critical point parameters in absolute and reduced units are given in Table 1. One can see that the law of corresponding states is valid. The experimental data for the Zeno lines are also shown in these phase diagrams. The density at this line decreases as the temperature increases linearly for all substances in hand. We note that the change in the pressure along the $Z = 1$ line is small as the temperature increases.

The linearity of the line $Z = 1$ has been observed for other substances such as hydrocarbons C_2H_6, C_3H_6, C_3H_8, and C_4H_{10} in ref2 and water and other liquids in ref3.

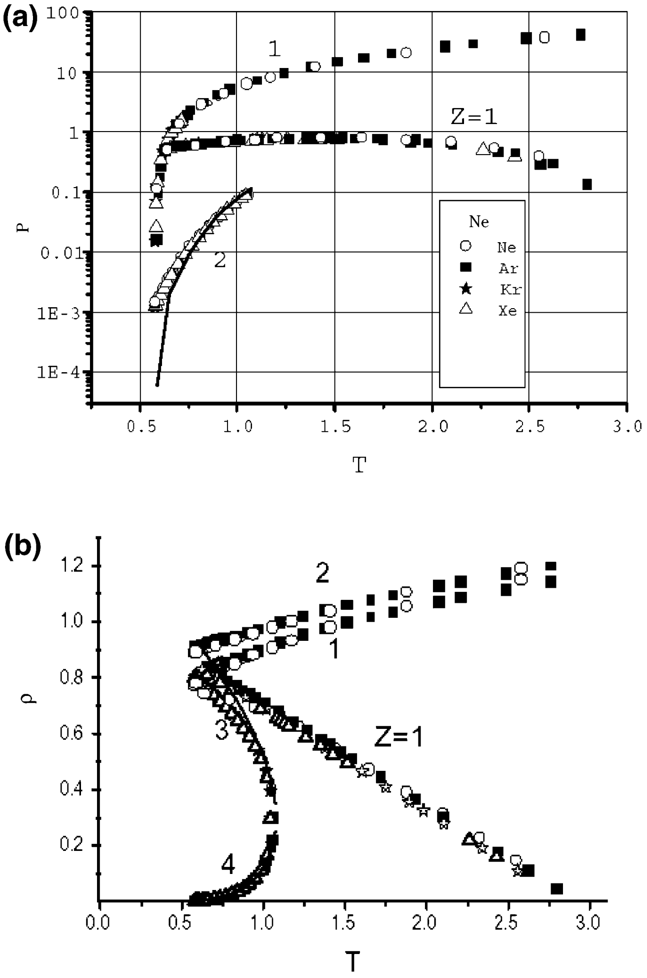

Figure 1. (a) Reduced pressure and (b) equilibrium densities versus reduced temperature along the phase coexistence curves and Zeno line ($Z = 1$). Symbols correspond to the values of pressure and equilibrium phase densities tabulated in refs1 and 6 for Ar, Ne, Kr, and Xe. In a, plots 1 and 2 correspond to the solid−liquid coexistence curve and liquid−gas coexistence curve, respectively. In b, plots 1, 2, 3, and 4 correspond to the solidification curve, melting curve, vaporization curve, and condensation curve, respectively. Solid lines are calculations of this paper.

TABLE 1

substance parameter	Ne	Ar	Kr	Xe
$r_{\min} = 2^{1/6}\sigma$, A^0	3.09	3.76	4.01	4.36
D, meV	3.64	12.3	17.3	24.4
D, K	42	143	200	278
m, au	20.18	39.95	83.8	131.3
$p_0 = D/\sigma^3$, atm	286	525	608	666
$\rho_0 = m/\sigma^3$, g/cm^3	1.61	1.76	3.05	3.72
T_c, K	44.4	150.9	209.4	289.7
	(1.05)[a]	(1.06)[a]	(1.04)[a]	(1.02)[a]
p_c, atm	27.6	49	55	58.4
	(0.097)[a]	(0.093)[a]	(0.0905)[a]	(0.087)[a]
ρ_c, g/cm^3	0.484	0.535	0.919	1.11
	(0.30)[a]	(0.304)[a]	(0.301)[a]	(0.298)[a]

[a] The values in parentheses are given in reduced units.

First, we analyze the validity of linearity of $Z = 1$ line depending on the number of the virial terms taken into account. It is shown that the best results are obtained when we take into account the four terms of the virial series. In this case, the $Z = 1$ line begins at the Boyle point and is very close to the straight line in a very wide range of temperature. Deviations from the straight line increase when the subsequent terms of the virial series are taken into account. However, the experiment shows that the $Z = 1$ line must be a straight line in the dense-fluid region as it nears the triple point. Therefore, we corrected the four-term virial equation get a direct Zeno line. As a result, we obtained the equation of state that includes the terms up to the fourth power of density, where the fourth virial coefficient is expressed by a combination of second and third coefficients and the Zeno line parameters. This equation can be used for the determination of the critical point parameters, the initial branch of the binodale curve, and the pressure on this binodale for LJ and (exp6) potentials. The calculated thermodynamical functions are compared with the results of integral equation solutions, computer simulations, and experimental data.

The reduced virial coefficients $B_k^* = B_k(3/2\pi)^{k-1}$ for $k = 2-5$ are given in Figure 2 for the LJ potential, calculated

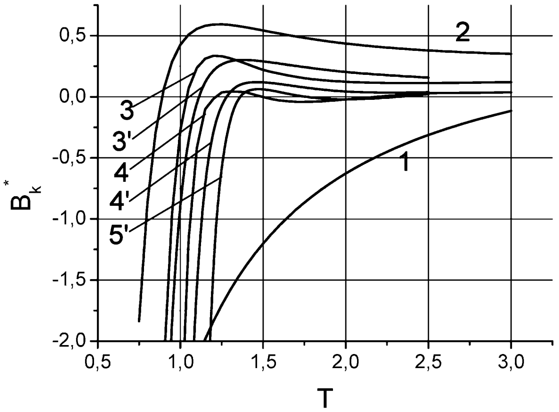

Figure 2. Dependence of the reduced virial coefficients on temperature for LJ potential, Lines 1-B_2, 2-B_3,[11] 3-B_4, and 4-B_5.[12] Lines 3′-B_4, 4′-B_5, and 5′-B_6 are calculations of this paper by the MV method[13].

according to refs 11 and 12 by the group integral method. Additionally, we show values of 3−6 virial coefficients, calculated in this work by the Martynov−Vompe (MV) method.[13] The latter is based on the expansion in power series of the density of the Ornstein−Zernike equation. According to the MV method, the second and third coefficients coincide with that calculated in the framework of the group integral method.[11]

One can see that the fourth and the fifth coefficients calculated by the MV method quantitatively differ a little from the values calculated by Barker.[12] However, the difference is not too large. The MV method gives the possibility to calculate the higher terms in the virial series, which would present a challenge if calculated by the group integral method. In Figure 2, there is the sixth virial coefficient, calculated by MV method.

We note that for $T < T_c$ the absolute values of B_k^* increase steeply with the decrease in temperature. A minimal value of temperature when the virial coefficients are equal to zero approaches the critical temperature with the growth of virial term number. This fact has also been confirmed by the calculations for generalized the LJ potentials ($m-n$) and rectangular well potential.[13]

The equation for the line $Z = 1$, following from the virial expansion eq 1, has the form

$$B_2(T) + \rho B_3(T) + \rho^2 B_4(T) + \rho^3 B_5(T) + \cdots = 0 \qquad (5)$$

Solutions of this equation are presented in Figure 3, where the number of virial terms is increased in a consecutive manner. Line 1 in Figure 3 corresponds to the limiting case, when $\rho \to 0$ and $T \to T_B$ ($T_B = 3.418$ for the LJ potential). In this case,[4] the dependence

$$\rho_B = -\left(\frac{dB_2(T)}{dT}\right)_{T=T_B} \frac{T - T_B}{B_3(T_B)} \qquad (6)$$

is a straight line (1) that starts at the Boyle point. Lines 2, 3, 4, and 5 correspond to cases where the terms (B_2, B_3), (B_2, B_3, B_4), (B_2, B_3, B_4, B_5), and (B_2, B_3, B_4, B_5, B_6) are accounted for, respectively. It is seen that the whole set of solutions coincides with the asymptotic eq 5 when the temperature tends to the Boyle point. The solution with only two terms (Line 2, Figure 3) noticeably deviates from the straight line (Line 1, Figure 3) with the decrease in temperature. The best solution with respect to the validity of Batschinski's law is the solution with four terms of the virial series. The addition of the fifth and sixth terms results in the increase in the deviation from the straight line (1). Generally, it can be shown that if we substitute the density in the form $\rho = A - BT$ (A and B are constants) in eq 5, then only the condition $B_2 = B_3 = \cdots = B_k = 0$ provides the validity of this equation, where k is the number of the higher virial term taken into account. This condition has no physical meaning.

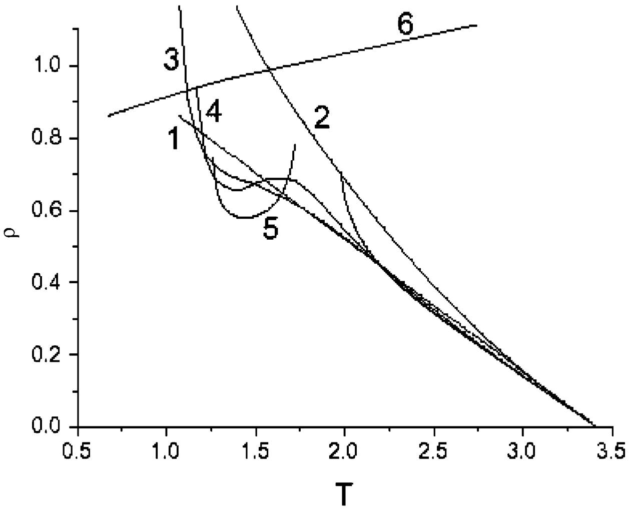

Figure 3. Line $Z = 1$. Line 1 was calculated from eq 7, and lines 2−5 were calculated from eq 6. Line 2 by taking into account B_2 and B_3, line 3 , B_2, B_3, and B_4, line 4, B_2, B_3, B_4, and B_5, and line 5, B_2, B_3, B_4, B_5 and B_6. Line 6 is the crystallization line.[15]

TABLE 2

	$T = 2.74$		$T = 2.0$		$T = 1.35$	
ρ	MC	8	MC	8	MC	8
0.1	0.97	0.973			0.72	0.72
0.2	0.99	0.982			0.50	0.5
0.3	1.04	1.03			0.35	0.356
0.4	1.19	1.129			0.27	0.3
0.5	1.46	1.26			0.31	0.342
0.6	1.9	1.45	1.40	1.154	0.55	0.496
0.7	2.586	1.678	2.11	1.421	1.175	0.774

Nevertheless, experimental evidence suggests that the Zeno line must be a straight line for low temperatures too (at least up to the intersection with the line of crystallization; see line 6, Figure 3). To satisfy this condition, we kept in eq 4 only three virial coefficients and introduce an effective fourth virial coefficient

$$B^*{}_4(T) = -\frac{B_2(T) + B_3(T)\rho_B(T)}{\rho_B(T)^2} \qquad (7)$$

Here, ρ_B is determined by eq 6. The equation of state then reads

$$Z(\rho, T) = 1 + \rho B_2(T)\left(1 - \frac{\rho^2}{\rho_B^2}\right) + \rho^2 B_3(T)\left(1 - \frac{\rho}{\rho_B}\right) \qquad (8)$$

This form of equation of state guarantees the linearity of the line $Z(\rho, T) = 1$ in the $\rho-T$ plane.

Let us discuss the consequences resulting from this equation. First, we consider the systems with LJ intermolecular potential. The compressibility factors for the LJ potential, calculated by the MC method[14] and by means of eq 8, are given in Table 2. Our calculations are in good agreement with MC data up to $\rho \leq 0\sigma$. The latter value apparently determines the upper boundary of validity of the method considered here.

We can determine the critical point parameters using the conditions $\partial P/\partial\rho = 0$, $\partial^2 P/\partial\rho^2 = 0$, and eq 8. As a result, we

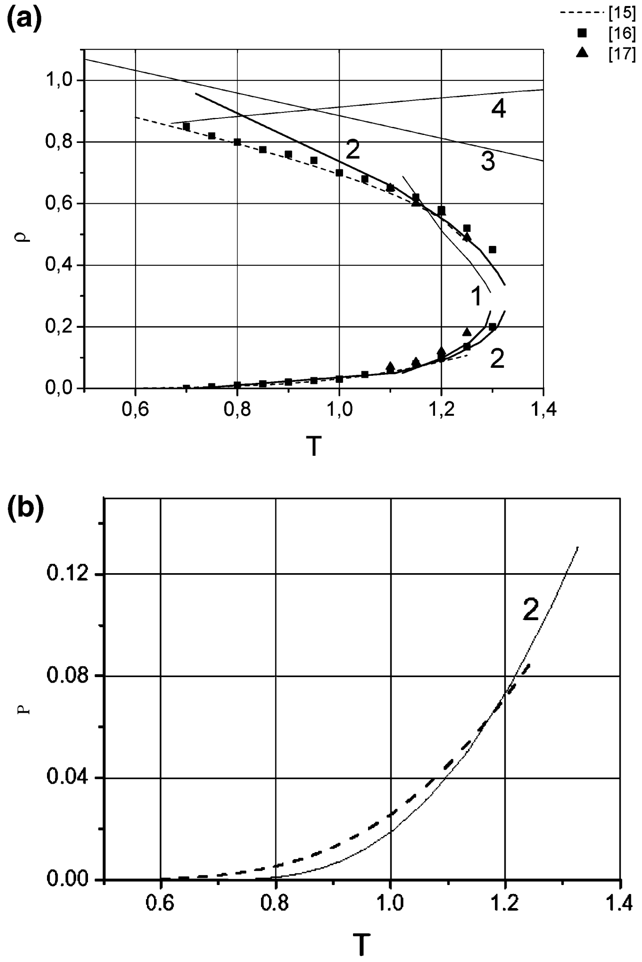

Figure 4. Dependence of equilibrium phase densities (a) and pressure (b) on temperature for LJ systems. Solid lines are calculations of this work: line 1 is the original virial expansion with five terms, and line 2 is the modified virial expansion, eq 9. Line 3 is $Z = 1$, and line 4 is crystallization line.[14] Dashed lines are integral equations.[15] Symbols are numerical experiments.[16,17]

obtain a set of two equations that must be solved to get T_c and ρ_c with the known values of the virial coefficients

$$4\rho_c B_2(T_c)/3 + \rho_c^2 B_3(T_c) = -1, \qquad 2\rho_c^3 B_4^*(T_c) - \rho_c B_2(T_c) = 1 \tag{9}$$

Substituting the value $B_4(T)$ following from the group expansion in eq 9, we obtain $\rho_c = 0.268$ and $T_c = 1.3$. If the effective value $B_4^*(T)$ is used, then these values for the critical parameters will be equal to $\rho_c = 0.284$ and $T_c = 1.33$. The latter quantities are close to the values $\rho_c = 0.34 \pm 0.02$ and $T_c = 1.34 \pm 0.02$, which have been obtained by solving integral equations[15] and computer simulations.[16−17] The critical point parameters found here are also close to the values $\rho_c = 0.25 \pm 0.05$ and $T_c = 1.28 \pm 0.5$ obtained in ref 13 based on the investigation of the convergence of the virial series.

We used the relation between the chemical potential μ and the pressure $d\mu_{T=\text{const}} = (1/\rho)(\partial P/\partial \rho)_T d\rho$. After the substitution of eq 8 into this relation and performing integration, we obtain

$$\mu(\rho, T) = T\ln(\rho) + T\rho\left(2B_2(T)\left(1 - \frac{2\rho^2}{3\rho_{\text{Bl}}^2}\right) + \frac{3B_3(T)\rho}{2}\left(1 - \frac{8\rho}{9\rho_{\text{Bl}}}\right)\right) \tag{10}$$

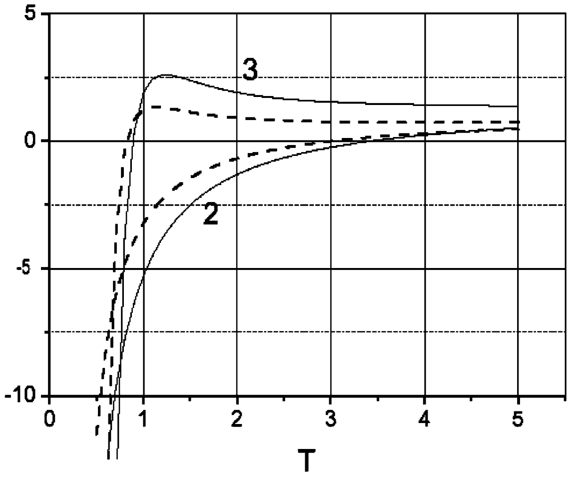

Figure 5. Dependence of the second (2) and third (3) virial coefficients on temperature. Solid lines denote the LJ potential, and dashed lines denote the (exp6) potential.

Solving the system of equations $\mu(\rho_1, T) = \mu(\rho_2, T) \prod P(\rho_1, T) = P(\rho_2, T)$, we find the phase densities at the equilibrium coexistence curve (Figure 4a and b). We can see that the gas branch of this curve is described well within the whole range of temperature. The coincidence of the liquid branch is quite satisfactory up to $T \geq 0.9$. For too low temperatures, the domain of liquid state is located near the crystallization line (2) and the expansions in the form eq 3 become, apparently, invalid. An analogous comparison of the pressure dependence on the temperature along the phase coexistence curve is shown in Figure 4b. One can see that there is acceptable agreement between our calculations and data.[15]

It follows from Figure 1b that the experimental value of the Boyle point is equal to $T_B \cong 3$ for the substances that obey the law of corresponding states. The LJ potential gives $T_B \cong 3.4$, and from this point of view, this potential is unsuitable for a description of thermodynamics of these substances. For this purpose, we use the Buckingham (exp6) potential eq 4. The values of the second and third virial coefficients for LJ and (exp6) potentials are presented in Figure 5. As can be seen, the second virial coefficient for the exp6 potential with $a = 15.6$ is equal to zero at the temperature $T_B = 3$. The latter value corresponds to the experimental one (Figure 1b). The third virial coefficient for the exp6 potential was calculated by the MV method.[13] These data appear sufficient to repeat the calculation carried out above for the LJ systems. Results of these calculations are presented in Figure 1a and b as solid lines. The calculated binodale coincides with experimental up to $\rho \leq 0.6$. The calculated pressure along the phase coexistence line is also in a good agreement with the experiment. The deviations begin at temperatures below $T \leq 0.7$.

We emphasize that the equation of state developed here closely describes the experimental values for the critical point parameters for the group of real substances. These values are equal to $T_c = 1.07$, $\rho_c = 0.3$, and $P_c = 0.11$ and are in excellent agreement with the corresponding experimental data from Table 1.

Acknowledgment. This study was supported by the Russian Foundation for Basic Research, project nos. 02-02-17255, 02-02-17376, 04-02-17292, NSh-1953-2003.2, and NSh-2045.2003.2.

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