

Phenomenological Models for the Generic van der Waals Equation of State and Critical Parameters

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In this paper, phenomenological models for the generic van der Waals equation of state are proposed for the subcritical regime of a simple fluid by assuming empirical forms for the generic van der Waals parameters A and B . The models that are assumed are tested against the critical parameters. It is shown that quadratic and cubic models for A and B are shown to give good critical parameters. The quadratic and cubic models are then employed to calculate critical isotherms of argon and methane to determine which model is superior. It is found that the quadratic model yields excellent critical isotherms in comparison with experimental data and is much superior to the cubic model in the experimental range of density. The model equation of state is also used to determine the spinodal curve, which is shown to be closely related to the nonanalytic behavior of A and B with respect to temperature.

I. Introduction

It was shown in a previous paper¹ that if the interaction potential function consists of an attractive and a repulsive branch then the virial equation of state can be expressed in a form that looks like the van der Waals equation of state

$$[p + A(\rho, \beta)\rho^2][1 - B(\rho, \beta)\rho] = \rho\beta^{-1} \quad (1)$$

where p , ρ , and β are, respectively, the pressure, density, and $1/k_B T$, with T denoting the temperature and k_B , the Boltzmann constant. In this equation of state, $A(\rho, \beta)$ and $B(\rho, \beta)$ are generally functions of ρ and β , but as the density diminishes to zero, they become the van der Waals constants a' and b' of the van der Waals equation of state

$$(p + a'\rho^2)(1 - b'\rho) = \rho\beta^{-1} \quad (2)$$

provided that the Mayer function in the statistical mechanical formulas for A and B is approximated by its lowest-order term in the power series of β . For this reason, they are called the generic van der Waals (GVDW) parameters, and the equation of state (eq 1), the generic van der Waals equation of state. Since the form of the equation of state (eq 1) is generic to any fluid characterized by an interaction potential energy consisting of attractive and repulsive potential energies, it may be regarded as a canonical form of the equation of state for fluids obeying such potentials of interaction. Since this terminology is simple and short, we will henceforth refer to the equation of state in the form of eq 1 as the canonical equation of state.

The GVDW parameters can be calculated by using the pair correlation function of the fluid if their definitions given in ref 1 are employed. The canonical equation of state (eq 1) provides a well-defined statistical mechanical expression for free volume, and such an expression for free volume has been successfully

applied to calculate diffusion coefficients of liquids^{2–4} within the framework of the Cohen–Turnbull free-volume theory⁵ of diffusion in liquids. The statistical mechanical calculations of the GVDW parameters A and B performed for ref 1 and for its applications^{2–4} made later indicate that they are not only dependent on density and temperature but also piecewise continuous with a discontinuity bounded by the coexistence curve, displaying nonanalytic behavior characteristic of the equation of state for a fluid in the subcritical regime. This behavior has been verified¹ by means of the Percus–Yevick integral equation theory for the pair correlation function. Relying on this nonanalytic behavior of the GVDW parameters, we have assumed nonanalytic empirical formulas—consisting of irrational functions of density and temperature—for the GVDW parameters and have demonstrated⁶ that the equation of state thus constructed is capable of describing the critical behavior of the fluid in the vicinity of the critical point. In particular, it has been possible to show that the model for the equation of state is able to give the critical exponents from the empirically assumed nonanalytic forms for A and B since the critical exponents are directly related to the nonanalytic parts of A and B . However, the model assumed gives simply the critical parameters such as the critical density (ρ_c), temperature (T_c), and pressure (p_c), which are identical to the values predicted by the original van der Waals equation of state. Since the latter values are known to be unsatisfactory in comparison with the experimental values, it is clear that the model should be further improved so as to yield correct critical parameters. Improving the model in such a respect is one of the major aims of this work. The temperature-dependent parameters in the models can be partially determined from the information provided by spinodal curves. We show how this is possible to carry out by examining the spinodal curve near the critical point.

This paper is organized as follows. In section II, empirical models for A and B are proposed, and therewith the canonical equation of state is put into a reduced form free from the explicit

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dependence of the potential parameters. In section III, the critical parameters, namely, the critical pressure, density, and temperature, are calculated by using the models for A and B and are compared with their experimental values. The quadratic and cubic models for A and B both give an excellent critical compressibility factor, which may be regarded as a good gauge, apart from the critical exponents, for assessing the global quality of the equation of state in the subcritical regime. We then use the reduced equation of state to relate the spinodal curve to the nonanalytic temperature dependence of A and B , especially near the critical point in section IV. Concluding remarks are given in section V.

II. Empirical Canonical Equation of State

If the parameters A and B are assumed to be constants that are independent of density and temperature, then the van der Waals equation of state arises from eq 1 as mentioned earlier. This assumption is equivalent to the vanishing density limits of A and B :

$$\lim_{\rho \rightarrow 0} A(\rho, T) = a' + O(T^{-1}) \quad \lim_{\rho \rightarrow 0} B(\rho, T) = b' \quad (3)$$

The vanishing density limit of $A(\rho, T)$ is not generally independent of temperature, but if the Mayer function involved in the statistical mechanical formula¹ for A is expanded in a power series of β and only the leading term is retained, then the result is a constant van der Waals parameter a' . Although such constant parameters make the van der Waals equation of state simple to work with, the simplicity comes at the expense of accuracy. This loss of accuracy is felt even more acutely because the van der Waals theory is capable of qualitatively correctly describing most features of the thermodynamics of fluids, including critical phenomena. For example, it is well known that the critical parameters predicted by the van der Waals equation of state are poor in accuracy in comparison with experimental values, but all of the qualitative features are correctly in place. Another, perhaps more glaring, defect of the van der Waals equation of state other than the incorrect critical exponents is the appearance of the unstable states in the equation of state when the latter is plotted in the pressure–volume (or density) plane. These defects can be removed in part if the GVDW parameters A and B are assumed to be nonanalytic, as has been shown previously.⁶ In this work, we consider more general, nonanalytic empirical forms for A and B and analyze the behavior of the fluid near the critical point by employing the empirical canonical equation of state.

For the purpose of carrying out the desired analysis, it is convenient to use nondimensionalized variables. We define the following reduced variables:

$$p^* = \frac{pv_0}{\epsilon} \quad T^* = \frac{k_B T}{\epsilon} \quad \eta = v_0 \rho \quad (4)$$

$$A^* = \frac{A}{\epsilon v_0} \quad B^* = \frac{B}{v_0}$$

ϵ is the potential well depth, σ is the size parameter (the diameter of the molecule), and $v_0 \equiv \pi\sigma^3/6$ is the molecular volume of the hard sphere. They may be identified with the Lennard-Jones potential parameters. For studying the critical and subcritical behavior of the fluid, it is convenient to scale p^* , η , and T^* with the reduced critical parameters p_c^* , η_c , and T_c^* . Thus, with

the definitions of scaled reduced variables

$$\psi = \frac{p^*}{p_c^*} = \frac{p}{p_c} \quad y = \frac{\eta}{\eta_c} \quad \theta = \frac{T^*}{T_c^*} = \frac{T}{T_c}$$

we define reduced relative variables

$$\phi = \psi - 1 \quad x \equiv y - 1 \quad t \equiv \theta - 1 \quad (5)$$

These reduced relative variables vanish at the critical point. The critical parameters p_c^* , η_c , and T_c^* are as yet undetermined but will be expressed in terms of parameters making up A^* and B^* . We also define the dimensionless parameters

$$\nu \equiv B_c^* \eta_c \quad \tau \equiv \frac{A_c^* \eta_c^2}{p_c^*} \quad \zeta \equiv \frac{\eta_c T_c^*}{p_c^*} \quad (6)$$

where $A_c^* = A^*(x=0, t=0)$ and $B_c^* = B^*(x=0, t=0)$ are empirical constants whose meanings will become evident presently when the empirical formulas for A^* and B^* are given. They are constants independent of density and temperature and may be related to the van der Waals constants a' and b' in the van der Waals theory. The critical parameters then can be expressed in terms of these dimensionless parameters and A_c^* and B_c^* :

$$\eta_c = \frac{\nu}{B_c^*} \quad p_c^* = \frac{\nu^2 A_c^*}{\tau B_c^{*2}} \quad T_c^* = \frac{\zeta \nu A_c^*}{\tau B_c^*} \quad (7)$$

The reduced parameter ζ , being independent of A_c^* and B_c^* , is an important quantity that enables us to gauge the quality of models for the GVDW parameters A^* and B^* , as will be seen later. The critical parameters given in eq 7 should be compared with the corresponding parameters in the van der Waals theory given in terms of $a = a'/\epsilon v_0$ and $b = b'/v_0$:

$$(\eta_c)_{\text{vdw}} = \frac{1}{3b} \quad (p_c^*)_{\text{vdw}} = \frac{a}{27b^2} \quad (T_c^*)_{\text{vdw}} = \frac{8a}{27b} \quad (8)$$

Note that these parameters a and b are dimensionless in the present scheme of reducing variables and parameters. The constants A_c^* and B_c^* are qualitatively comparable to the reduced van der Waals constants a and b , respectively, and the dimensionless parameters ν , ν^2/τ , and $\zeta\nu/\tau$ should correspond, respectively, to the van der Waals theory values ($1/3$, $1/27$, $8/27$), as will be seen later. The structural similarities of the critical parameters in the van der Waals theory and the present canonical equation of state theory are an advantage of the latter because with simple models for A^* and B^* the canonical equation of state is capable of accounting for the critical phenomena in a relatively simple manner as the van der Waals theory does and also because the thermodynamics of fluids may be built on and around the van der Waals theory, which is capable of qualitatively describing most of the features of real fluids over the entire density range.

In a phenomenological thermodynamic theory of fluids in the critical regime, Sengers and collaborators^{7–9} propose the derivation of a crossover van der Waals equation of state from the Helmholtz free energy suitably constructed under a set of rules for transformations of density and temperature differences from the critical values to their forms predicted by the renormalization group theory.^{10–12} The equation of state so constructed is capable of correctly producing the coexistence curve and other thermodynamic observables of critical fluids.

There is a kindred spirit between the theory of Sengers and his collaborators and the approach taken in the present work insofar as the general aim of empirically treating fluids in the critical regime is concerned. Both make the van der Waals equation of state the reference equation of state in the treatment. The present approach, however, differs from the former in that models for the canonical equation of state are built by directly and empirically constructing the GVDW parameters without recourse to the free energy of the fluid. The two approaches mentioned are, in fact, opposite in the direction of approach since the present approach will provide an alternative empirical method for the same aim.

Upon using the aforementioned reduced variables and parameters ζ , ν , and τ , we can reduce the canonical equation of state (eq 1) with respect to the critical parameters and express them in the nondimensional form

$$[\phi + 1 + \tau(x + 1)^2 \mathcal{A}(x, t)][1 - \nu(x + 1) \mathcal{B}(x, t)] = \zeta(x + 1)(t + 1) \quad (9)$$

where

$$\mathcal{A}(x, t) = \frac{A^*}{A_c^*} \quad \mathcal{B}(x, t) = \frac{B^*}{B_c^*} \quad (10)$$

If $\mathcal{A} = 1$ and $\mathcal{B} = 1$, then eq 9 becomes the nondimensionalized (i.e., corresponding state) van der Waals equation of state. If \mathcal{A} and \mathcal{B} are functions of only x and t , which are truly independent of material parameters, then eq 9 will be in conformity with the law of corresponding states.

We will denote the reduced spinodal densities by z_{sl} and z_{sv} , where $z_{sl} = \eta_{sl}/\eta_c$ is the spinodal density η_{sl} of the liquid, which is reduced relative to the critical density, whereas $z_{sv} = \eta_{sv}/\eta_c$ is the spinodal density η_{sv} of the vapor, which is reduced relative to the critical density ($\eta_{sl} > \eta_{sv}$). It should be noted that

$$\lim_{T \rightarrow T_c} z_k = 1 \quad (k = sl, sv)$$

since the spinodal curve shares the same tangent with the critical isotherm at the critical point.

We now assume for A^* and B^* in the regime of $T \leq T_c$ the following empirical forms:

$$A^* = A_c^* [a_0^{(sl)}(t) + \sum_{i=1}^{l_a} a_i^{(sl)}(t)(y - z_{sl})^i + A_{na}^{(sl)}(t, y - z_{sl})] \quad \text{for } y > z_{sl}, t \leq 0 \quad (11)$$

$$= A_c^* [a_0^{(sv)}(t) + \sum_{i=1}^{l_a} a_i^{(sv)}(t)(y - z_{sv})^i + A_{na}^{(sv)}(t, y - z_{sv})] \quad \text{for } y < z_{sv}, t \leq 0$$

$$B^* = B_c^* [b_0^{(sl)}(t) + \sum_{i=1}^{l_b} b_i^{(sl)}(t)(y - z_{sl})^i + B_{na}^{(sl)}(t, y - z_{sl})] \quad \text{for } y > z_{sl}, t \leq 0 \quad (12)$$

$$= B_c^* [b_0^{(sv)}(t) + \sum_{i=1}^{l_b} b_i^{(sv)}(t)(y - z_{sv})^i + B_{na}^{(sv)}(t, y - z_{sv})] \quad \text{for } y < z_{sv}, t \leq 0$$

$a_i^{(k)}$ and $b_i^{(k)}$ ($k = sl, sv$) are temperature-dependent such that the liquid and vapor branches of the coefficients coincide with

each other at the critical temperature, namely,

$$a_i^{(l)}(0) = a_i^{(v)}(0) \equiv a_i \neq 0 \quad b_i^{(l)}(0) = b_i^{(v)}(0) \equiv b_i \neq 0 \quad (13)$$

$$\lim_{t \rightarrow 0} a_0^{(k)}(t) = 1 \quad \lim_{t \rightarrow 0} b_0^{(k)}(t) = 1 \quad (k = sl, sv)$$

and the terms $A_{na}^{(k)}$ and $B_{na}^{(k)}$ ($k = sl, sv$) are the nonanalytic parts that give rise to the nonanalytic behavior of the equation of state and the nonclassical critical exponents different from the mean field theory values. It must be emphasized that the presence of the nonanalytic components in A^* and B^* is *essential* for the equation of state to exhibit a discontinuity in the subcritical regime and thus describe the subcritical behavior of liquid–vapor systems. The upper limits l_a and l_b of the sums depend on the model chosen for A^* and B^* .

In previous work,⁶ we have assumed the following forms consisting of an irrational function of density for the nonanalytic terms:

$$A_{na}^{(k)} = \alpha_{na}^{(k)}(y - z_k)^3 |y - z_k|^{1+\delta} \quad (k = sl, sv) \quad (14)$$

$$B_{na}^{(k)} = \beta_{na}^{(k)}(y - z_k)^3 |y - z_k|^{1+\delta} \quad (k = sl, sv)$$

$\alpha_{na}^{(k)}$ and $\beta_{na}^{(k)}$ denote parameters that may depend on temperature t only but are constants on the critical isotherm in the same sense as for $a_i^{(k)}$ and $b_i^{(k)}$ in eq 13: $\alpha_{na}^{(sl)}(0) = \alpha_{na}^{(sv)}(0) \equiv \alpha_{na}$ and $\beta_{na}^{(sl)}(0) = \beta_{na}^{(sv)}(0) \equiv \beta_{na}$. The exponent δ is a fractional number that is less than unity and determined empirically. Because $\delta < 1$, functions $A_{na}^{(k)}$ and $B_{na}^{(k)}$ are irrational and hence nonanalytic. The particular forms given in eq 14 for nonanalytic parts $A_{na}^{(k)}$ and $B_{na}^{(k)}$ are suggested by the critical behavior of the fluid and the fact that the generic van der Waals parameters must exhibit a subcritical discontinuity because the equation of state should be discontinuous in the subcritical regime in (T, ρ, p) space. For example, the exponent $(4 + \delta)$ of $A_{na}^{(k)}$ and $B_{na}^{(k)}$ is intimately related to the $\phi \approx x^{4+\delta}$ behavior experimentally observed near the critical point. In fact, if we choose, for example, $\delta = 0.30$, then the critical exponent for ϕ is 4.30, in agreement with experiment.^{13–15}

Owing to the aforementioned properties of $a_i^{(k)}$, $b_i^{(k)}$, $A_{na}^{(k)}$, and $B_{na}^{(k)}$, the expansions for A^* and B^* in eqs 11 and 12 reduce, on the critical isotherm, to the forms

$$A^* = A_c^* [1 + \sum_{i=1}^{l_a} a_i x^i + \alpha_{na} x^3 |x|^{1+\delta}] \quad (t = 0) \quad (15)$$

$$B^* = B_c^* [1 + \sum_{i=1}^{l_b} b_i x^i + \beta_{na} x^3 |x|^{1+\delta}] \quad (t = 0) \quad (16)$$

For this model, constants A_c^* and B_c^* play the role of the van der Waals constants a and b in the sense that they yield critical parameters η_c , p_c^* , and T_c^* , but their numerical values differ from the values of a and b significantly, as will be seen.

In the previous paper⁶ on the critical exponents, the coefficients a_1 , a_2 , b_1 , and b_2 were taken to be equal to zero. As a consequence, the critical parameters were determined by A_c^* and B_c^* only, which give rise to exactly the same values as for the critical parameters in the van der Waals theory. Therefore, although the model yields nonclassical critical exponents arising from the nonanalytic terms, such as those in eqs 15 and 16, the critical parameters are not at all improved beyond the van der Waals theory. We will show that the present model represented

by eqs 11 and 12 reducing to eqs 15 and 16 on the critical isotherm yields improved results for the critical parameters. Of course, it also yields the critical exponents that are identical to those shown in a previous paper.⁶ The nonanalytic terms in A^* and B^* do not play a role in determining the critical parameters because their exponents are larger than 4, so they still vanish at the critical point after four differentiations with respect to density.

III. Critical Parameters

Since the definition of critical point must be modified to that of van Laar¹⁶ and Baehr¹⁷ according to our previous study⁶ if we are to obtain nonclassical exponents from the canonical equation of state, the first four density derivatives of pressure are set to vanish at the critical point. We therefore have five equations at the critical point

$$p_c^* \beta_c^* = \frac{\eta_c}{1 - B_c^* \eta_c} - \beta_c^* A_c^* \eta_c^2 \quad (17)$$

$$\left(\frac{\partial^i p^*}{\partial \eta^i} \right)_{T=T_c, \eta=\eta_c} = 0 \quad (i = 1, \dots, 4) \quad (18)$$

For the purpose of explicitly calculating these conditions, it is convenient to rearrange the reduced canonical equation of state (eq 9) to the form

$$\begin{aligned} P(x, t) &= \zeta(x+1)(t+1) - \\ &\quad [1 + \tau(x+1)^2 \mathcal{A}(x, t)][1 - \nu(x+1) \mathcal{B}(x, t)] \\ &= P_0 + P_1 x + P_2 x^2 + P_3 x^3 + P_4 x^4 + P_5 x^5 + \dots \end{aligned} \quad (19)$$

where $P(x, t)$ on the left is defined by

$$P(x, t) = \phi[1 - \nu(x+1) \mathcal{B}(x, t)] \quad (20)$$

We then observe that since $\phi = 0$ at the critical point and

$$\left(\frac{\partial^i p^*}{\partial \eta^i} \right)_{T_c, \eta_c} = \left(\frac{\partial^i \phi}{\partial x^i} \right)_c \quad (i = 1, \dots, 4)$$

where the subscript c denotes the critical point, the conditions (eqs 17 and 18) give rise to the equivalent conditions in terms of the derivatives of $P(x, t)$ evaluated at the critical point:

$$\left(\frac{\partial^i P}{\partial x^i} \right)_c = 0 \quad (i = 0, 1, \dots, 4) \quad (21)$$

The derivatives of $P(x, t)$ are then evaluated with eq 19 by using the formulas for A^* and B^* on the critical isotherm (eqs 15 and 16). It is straightforward to calculate the derivatives. We will calculate them for a few models for A^* and B^* in the following discussion. Notice that the nonanalytic part is proportional to a term with a fractional exponent of $(4 + \delta)$ ($0 < \delta < 1$) in the lowest order. It therefore does not play a role in determining the critical point according to the van Laar–Baehr definition^{16,17} of the critical point given earlier.

A. Linear Model. The simplest model beyond the van der Waals approximation for A^* and B^* , namely, taking the van der Waals constants a and b for A^* and B^* , is a linear model in which it is assumed that $a_i = 0$ and $b_i = 0$ for all $i \geq 2$ in the expansions given in eqs 15 and 16. Therefore, there are five unknowns: a_1 , b_1 , τ , ν , and ζ . For this model, we find that the

critical point is given by the five algebraic equations arising from eqs 17 and 21:

$$P_0 = \zeta - (1 + \tau)(1 - \nu) = 0$$

$$P_1 = \nu + \zeta + \tau(\nu b_1 - a_1 + \nu a_1 + 3\nu - 2) + \nu b_1 = 0$$

$$P_2 = \tau(3\nu a_1 - 2a_1 + 3\nu b_1 + a_1 \nu b_1 + 3\nu - 1) + \nu b_1 = 0 \quad (22)$$

$$P_3 = \tau(3\nu a_1 + \nu + 3\nu b_1 + 3a_1 \nu b_1 - a_1) = 0$$

$$P_4 = \tau \nu (a_1 + b_1 + 3a_1 b_1) = 0$$

Solving these algebraic equations for ν , τ , and ζ , we find

$$\nu = \frac{a_1}{1 + 3b_1 + 3a_1 + 3a_1 b_1} \quad (23)$$

$$\tau = \frac{a_1 b_1}{1 + 2a_1 + 3b_1 + 3a_1^2 + 6a_1 b_1 + 5a_1^2 b_1} \quad (24)$$

$$\zeta = (1 - \nu)(1 + \tau) \quad (25)$$

where a_1 and b_1 are solutions of the pair of algebraic equations

$$a_1 + b_1 + 3a_1 b_1 = 0$$

$$\varphi_2 b_1^2 + \varphi_1 b_1 + \varphi_0 = 0 \quad (26)$$

with φ_0 , φ_1 , and φ_2 defined by

$$\varphi_0 = 1 + 5a_1 + 9a_1^2 + 9a_1^3$$

$$\varphi_1 = 6 + 24a_1 + 38a_1^2 + 25a_1^3 \quad (27)$$

$$\varphi_2 = 9 + 27a_1 + 34a_1^2 + 17a_1^3$$

Solving eq 26 numerically for a_1 and b_1 , we find

$$a_1 \doteq -0.629 \quad b_1 \doteq -0.709 \quad (28)$$

which yields the reduced critical parameters in the linear model

$$\tau = 5.976 \quad \nu = 0.375 \quad \zeta = 4.359 \quad (29)$$

These results produce the critical temperature, packing fraction, and pressure as follows:

$$\begin{aligned} T_c^* &= 0.274 \frac{A_c^*}{B_c^*} & \eta_c &= \frac{0.375}{B_c^*} & p_c^* &= 2.35 \times 10^{-2} \frac{A_c^*}{B_c^{*2}} \\ \frac{p_c^*}{\eta_c T_c^*} &= 0.229 \end{aligned} \quad (30)$$

Here, we are free to choose suitable values for A_c^* and B_c^* . These parameters may be chosen such that two of the three critical parameters agree with the experimental values. For example, the empirical values for argon ($T_c = 150.69$ K and $\rho_c = 0.5356$ g/cm³)¹⁸ are

$$T_c^* = 2.17 \quad \eta_c = 0.134 \quad p_c^* = 0.198 \quad \frac{p_c^*}{\eta_c T_c^*} = 0.290 \quad (31)$$

where the square-well potential parameters¹⁹ $\sigma_{sw} = 0.3162$ nm

and $\epsilon_{sw} = 69.4k_B$ are used to reduce the variables. Then, we deduce

$$A_c^* = 31.9 \quad B_c^* = 4.23 \quad (32)$$

These results should be compared with the van der Waals theory values, which can be determined from the first three equations of eq 22 with $a_1 = b_1 = 0$, namely,

$$\begin{aligned} \zeta - (1 + \tau)(1 - \nu) &= 0 \\ \nu + \zeta - 2\tau &= 0 \\ \tau(3\nu - 1) &= 0 \end{aligned}$$

These equations yield the solutions

$$\nu = \frac{1}{3} \quad \tau = 3 \quad \zeta = \frac{8}{3} \quad (33)$$

and hence the critical parameters in the forms

$$\begin{aligned} T_c^* &= 0.296 \frac{a}{b} & \eta_c &= \frac{1}{3b} & p_c^* &= \frac{a}{27b^2} = 3.70 \times 10^{-2} \frac{a}{b^2} \\ & & & & \frac{p_c^*}{\eta_c T_c^*} &= 0.375 \end{aligned}$$

With the experimental critical parameters in eq 29, we obtain

$$a = 18.3 \quad b = 2.50$$

which should be compared with the values of A_c^* and B_c^* given in eq 32. Here, an important criterion for comparison is the critical compressibility factor $p_c^*/\eta_c T_c^*$, which does not depend on parameters A_c^* and B_c^* or a and b in the case of the van der Waals theory. The sets $(\nu, \tau, \zeta)_{lm}$ and $(\nu, \tau, \zeta)_{vdw}$ for the reduced critical parameters of the linear model and the van der Waals theory are also an indicator for the quality of the model, but both are universal, being independent of material parameters. Therefore, the equation of state obeys the law of corresponding states. For this reason, it is sufficient at this level of approximation to test the theory for a single representative substance, for example, argon in the case of simple fluids. The linear model is judged to be insufficiently accurate.

B. Quadratic Model. Let us now assume that coefficients a_i and b_i vanish for $i \geq 3$ in the analytic part of parameters A^* and B^* . That is, we assume that on the critical isotherm

$$\begin{aligned} \mathcal{A} &= \frac{A^*}{A_c^*} = 1 + \sum_{i=1}^2 a_i x^i + \alpha_{na} x^3 |x|^{1+\delta} \\ \mathcal{B} &= \frac{B^*}{B_c^*} = 1 + \sum_{i=1}^2 b_i x^i + \beta_{na} x^3 |x|^{1+\delta} \end{aligned} \quad (34)$$

For this quadratic model, P_0 and P_1 are given by the same expressions as those in eq 22 for the linear model whereas P_2 ,

P_3 , and P_4 are given by the equations

$$\begin{aligned} P_2 &= 2\tau\nu(b_2 + 3b_1 + b_1 a_1 + 3a_1 + 3 + a_2) \\ &\quad - 2\tau(a_2 + 2a_1 + 1) + 2\nu(b_2 + b_1) = 0 \\ P_3 &= 6\tau\nu(a_2 + 3a_1 + 3)b_1 + 6\tau\nu(3 + a_1)b_2 + 6\tau\nu \\ &\quad + 18\tau\nu(a_1 + a_2) - 6\tau(2a_2 + a_1) + 6\nu b_2 = 0 \end{aligned} \quad (35)$$

$$\begin{aligned} P_4 &= 24\tau\nu(1 + 3a_2 + 3a_1)b_1 + 24\tau\nu(a_2 + 3a_1 + 3)b_2 \\ &\quad + 24\tau\nu(a_1 + 3a_2) - 24\tau a_2 = 0 \end{aligned}$$

Since there are seven variables $a_1, a_2, b_1, b_2, \tau, \nu$, and ζ for five equations, two variables are undetermined and thus act as free variables, which can be used as adjustable parameters. Proceeding similarly to the linear model, these equations can be solved for the parameters ζ, τ , and ν in terms of a_1, a_2, b_1 , and b_2 , which form a pair of algebraic equations. Therefore, only two of the variables a_1, a_2, b_1 , and b_2 can be determined. For example, if we choose

$$a_1 = -0.336 \quad b_1 = -0.618$$

then the other two are determined from the pair of algebraic equations for a_1, a_2, b_1 , and b_2 :

$$a_2 = -0.360 \quad b_2 = 0.0436$$

It is worth mentioning how the aforementioned values of a_1 and b_1 have been estimated. First, the Monte Carlo simulations for a fluid obeying the square-well potential model with the potential parameters specified earlier is performed for the pair correlation function at $T = T_c$ and $\rho = \rho_c$. Then, B_c^* is estimated from the statistical mechanical representation¹ for B^* by using the Monte Carlo data for the pair correlation function. In the next step, an iterative solution of eq 35 and the equations for P_0 and P_1 in eq 22 is sought in such a way that $B_c^* = \nu/\eta_c$ (see eq 6) computed with η_c taken as an empirical input is in agreement with the simulated B_c^* and the critical compressibility factor ζ^{-1} is also in agreement with the experimental value. In this way, the values of a_1 and b_1 are uniquely estimated such that the critical parameters agree with experimental values because the experimental critical parameters supply two additional conditions that were missing initially in the equations for P_n ($n = 0, \dots, 4$) for the quadratic model. This procedure, of course, simultaneously determines a_2, b_2 , and A_c^* as well as τ, ν , and ζ from the equations listed earlier.

The aforementioned set of values for a_1, a_2, b_1 , and b_2 thus determined gives rise to the values of ν, τ , and ζ as follows:

$$\tau = 6.424 \quad \nu = 0.535 \quad \zeta = 3.448$$

which in turn yields

$$T_c^* = 0.287 \frac{A_c^*}{B_c^*} \quad \eta_c = \frac{0.535}{B_c^*} \quad \frac{p_c^*}{\eta_c T_c^*} = 0.290$$

The values of A_c^* and B_c^* can be obtained from the experimental values for the critical temperature and packing fraction. They are as follows:

$$A_c^* = 30.25 \quad B_c^* = 4.01$$

The square-well potential parameters for argon have been

employed for the reduction. These values vary considerably from those for the linear model because of the presence of the quadratic terms. However, the value of the critical compressibility factor, which is a gauge of the quality of the model for the critical parameters, is in excellent agreement with the experimental value. This model will be further tested later by calculating the critical isotherm in comparison with experimental data. This test, in fact, will enable us to choose between the quadratic model and the cubic model, which is studied in the following section.

C. Cubic Model. We now assume the following model for \mathcal{A} and \mathcal{B} on the critical isotherm:

$$\begin{aligned}\mathcal{A} &= 1 + a_1x + a_3x^3 + \alpha_{\text{na}}x^3|x|^{1+\delta} \\ \mathcal{B} &= 1 + b_1x + b_3x^3 + \beta_{\text{na}}x^3|x|^{1+\delta}\end{aligned}\quad (36)$$

Since in this cubic model the analytic part of \mathcal{A} and \mathcal{B} does not include a quadratic term, it must be regarded as a particular case of cubic polynomials. If the analytic part is a convergent series of x , then it is natural to include a quadratic term of x and show that the coefficient of the cubic terms is smaller than that of the quadratic term. However, if this approach is taken, then we have two more unknown parameters that cannot be uniquely determined by the procedure employed for the quadratic model. Such a situation is not desired in the present work in which we desire to develop a model for GVDW parameters A and B uniquely. For this reason, we have set the coefficients of the quadratic terms in eq 36 equal to zero.

For the present cubic model, we find that P_0 , P_1 , and P_2 are given by the same equations as those in eq 22 whereas P_3 and P_4 are given by the equations

$$\begin{aligned}P_3 &= 6\tau\nu(b_3 + 3b_1 + 3b_1a_1 + 1 + 3a_1 + a_3) \\ &\quad - 6(a_1 + a_3)\tau + 6b_3\nu = 0\end{aligned}\quad (37)$$

$$\begin{aligned}P_4 &= 24\tau\nu(b_1 + 3a_3 + 3b_3 + a_1 + 3b_1a_1 + b_3a_1 + b_1a_3) \\ &\quad - 48\tau a_3 + 24\nu b_3 = 0\end{aligned}$$

Using procedures similar to those used in previous cases, we find ζ , τ , and ν in terms of coefficients a_1 , a_3 , b_1 , and b_3 , which form a pair of algebraic equations. Solving the equations for a_3 and b_3 upon choosing the values for the pair (a_1, b_1) such that

$$a_1 = -0.546 \quad b_1 = -0.620$$

which have been estimated in the same manner as for the case of the quadratic model, we find that

$$a_3 = -1.865 \quad b_3 = 0.592$$

This set of values for a_1 , a_3 , b_1 , and b_3 produces

$$\nu = 0.288 \quad \tau = 3.847 \quad \zeta = 3.448$$

which yield the critical parameters

$$T_c^* = 0.258 \frac{A_c^*}{B_c^*} \quad \eta_c = \frac{0.288}{B_c^*} \quad \frac{p_c^*}{\eta_c T_c^*} = 0.290$$

If the experimental critical temperature and density for argon are used, then we find that

$$A_c^* = 18.12 \quad B_c^* = 2.16$$

TABLE 1: Summary of Critical and Associated Parameters for Argon

parameters	vdw	quadratic	cubic	exptl
a_1	0	-0.336	-0.546	
b_1	0	-0.618	-0.620	
a_2	0	-0.360	0	
b_2	0	0.0436	0	
a_3	0	0	-1.865	
b_3	0	0	0.592	
ν	$1/3$	0.535	0.288	
τ	3	6.424	3.847	
ζ	$8/3$	3.448	3.448	
A_c^*	$a = 18.3$	30.3	18.1	
B_c^*	$b = 2.50$	4.01	2.16	
$\zeta^{-1} = p_c^*/\eta_c T_c^*$	0.375	0.290	0.290	0.29

for which the square-well potential parameters have also been used for reduction. These values also deviate from those for the linear model because of the cubic term. The value of the critical compressibility factor $p_c^*/\eta_c T_c^*$, which is independent of constants A_c^* and B_c^* , is also found to be in excellent agreement with the experimental value. On the basis of the critical parameters and the critical compressibility factor alone, it is difficult to choose between the quadratic and cubic models. However, when the critical isotherm is calculated with the quadratic and cubic models, it is possible to choose between them, as will be shown.

The summary of the results for the critical parameters and associated coefficients is given in Table 1 for the ease of assessment of the models.

D. Critical Isotherm. With the coefficients determined as described in the previous subsections, GVDW parameters A^* and B^* for the critical isotherm are now summarized as follows:

$$A^* = A_c^* \left(1 + \sum_{i \geq 1}^3 a_i x^i + \alpha_{\text{na}} x^3 |x|^{1+\delta} \right) \quad (38)$$

$$B^* = B_c^* \left(1 + \sum_{i \geq 1}^3 b_i x^i + \beta_{\text{na}} x^3 |x|^{1+\delta} \right)$$

α_{na} and β_{na} are the parameters that can be determined by investigating the critical behaviors of various thermodynamic quantities other than the critical parameters considered earlier. It was shown that the nonanalytic term is capable of correctly accounting for the critical exponents if an appropriate choice is made for the value of δ .

We have seen that the quadratic and cubic models are excellent in predicting the critical compressibility factor ζ^{-1} , and on the basis of ζ alone, it is difficult to see which of the two models is better. To resolve this question, we have calculated the critical isotherms predicted by the models and have compared them with the experimental data. Argon data are used for this purpose in Figure 1.

In Figure 1, the density dependence of pressure at $T = T_c$, namely, the critical isotherm, is shown for argon. The solid curve has been calculated from the quadratic model (QM) with the nonanalytic terms included, for which $\alpha_{\text{na}} = 0.01$ and $\beta_{\text{na}} = -0.015$ have been used. The dotted curve (QM₀) has been calculated from the quadratic model but with $\alpha_{\text{na}} = \beta_{\text{na}} = 0$. Therefore, the dotted curve represents an analytic equation of state, which must be considered inappropriate in the neighborhood of the critical point (i.e., as $x \rightarrow 0$ and $t \rightarrow 0$) from the standpoint of principle because it implies a classical critical exponent. Nevertheless, it is considered here, first, to determine how it performs and, second, because the literature on the

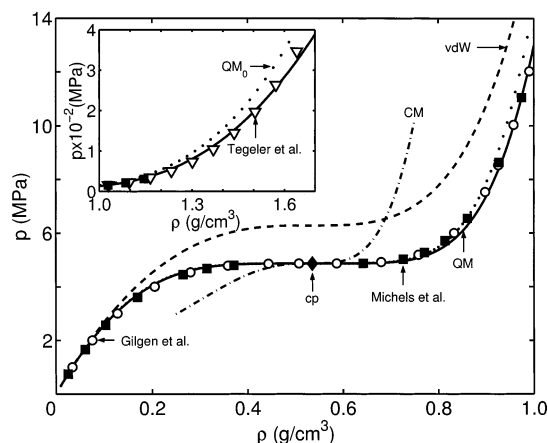


Figure 1. Critical isotherms for argon predicted by the quadratic and cubic models in comparison with experiment and the van der Waals equation of state. The filled diamond represents the critical point. The solid curve is for the quadratic model (QM) with the nonanalytic terms included, for which $\alpha_{na} = 0.01$ and $\beta_{na} = -0.015$. The dotted curve (QM₀) is the quadratic model without the nonanalytic terms, namely, $\alpha_{na} = \beta_{na} = 0$. The dashed curve (vdW) is for the van der Waals theory, and the dash-dotted (— · —) curve is for the cubic model (CM), for which $\alpha_{na} = 0.01$ and $\beta_{na} = -0.015$ have been used. The symbols are for the experimental data: ■ by Michels et al.²⁰ and ○ by Gilgen et al.²¹ The critical point is indicated by the filled diamond (◆), and the triangles in the inset (▽) (for the high-density regime) are computed by employing the empirical equation of state for argon proposed by Tegeler et al.¹⁸

equations of state is predominantly inclined to use analytic equations of state. The dashed curve (vdW) is from the van der Waals theory, and the dash-dotted (— · —) curve has been computed from the cubic model (CM), where $\alpha_{na} = 0.01$ and $\beta_{na} = -0.015$ have been employed. The linear model has been eliminated from consideration on the basis of the critical compressibility factor, which is found to be poor; see eq 30. The quadratic model is found to be excellent in comparison with experiment, and the inclusion of nonanalytic terms improves the numerical results in the high-density regime. Of course, they are essential for nonclassical critical exponents and for making the equation of state nonanalytic and discontinuous in the subcritical regime so as to be in accord with experiment.

The cubic model is evidently poor in describing the critical isotherm, which is good only in the neighborhood of the critical point. Thus, it can be eliminated from the list of candidates for phenomenological models for A and B . The poor performance of the particular cubic model indicates that a cubic model in which a quadratic term is absent does not properly represent the analytic part of A and B . If the quadratic model considered were extended by including a cubic term of x and by treating the cubic coefficients as adjustable parameters, then we would expect the cubic coefficients to be smaller than those of the quadratic terms and the critical isotherm to be as good as or better than that of the quadratic model. The main aim of this work, however, is to show that there exists a unique model for A and B that extends the original van der Waals equation of state for the critical parameters and isotherm. For this reason, we have set $a_2 = b_2 = 0$ in the cubic model considered.

The canonical equation of state considered in this work should be equally well applicable to polyatomic fluids, provided that the coefficients in the models are suitably chosen. The statistical mechanical reason for this assertion is that as long as non-spherical angle-dependent potential energies have repulsive and attractive branches the virial expression for the pressure of

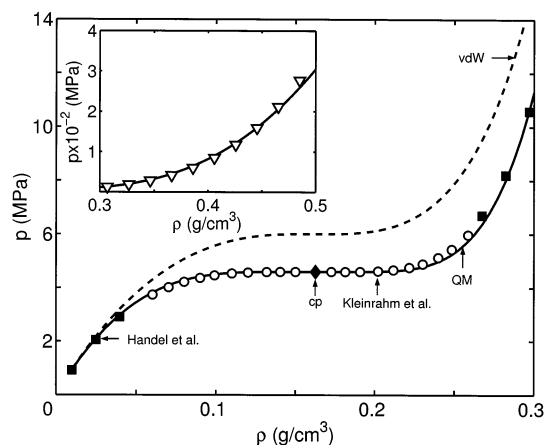


Figure 2. Critical isotherms for methane predicted by the quadratic model and the van der Waals theory in comparison with experiment. The solid curve is for the quadratic model (QM) with the nonanalytic terms included, for which $\alpha_{na} = 0.01$ and $\beta_{na} = -0.015$ have been used, and the dashed curve (vdW) is for the van der Waals theory. The symbols are for the experimental data: ■ by Händel et al.²² and ○ by Kleinrahm et al.²³ The critical point is indicated by the filled diamond (◆), and the triangles in the inset (▽) (for the high-density regime) are computed by employing the empirical equation of state for methane proposed by Setzmann and Wagner.²⁴

polyatomic fluids can be expressed by a canonical form similar to the canonical equation of state, eq 1, employed in this work. On the basis of this theoretical reasoning, we examine the critical isotherm of methane, which is, in fact, almost spherical. In Figure 2, we have shown the critical isotherm of methane calculated by employing the quadratic model with the following parameter values:

$$a_1 = -0.336 \quad b_1 = -0.618 \quad a_2 = -0.360 \quad b_2 = 0.0436$$

$$\sigma_{sw} = 0.345 \text{ nm} \quad \epsilon_{sw} = 115.0 k_B \quad A_c^* = 23.5 \quad B_c^* = 4.08$$

$$T_c = 190.56 \text{ K} \quad \rho_c = 0.163 \text{ g/cm}^3 \quad \zeta^{-1} = \frac{p_c^*}{\eta_c T_c^*} = 0.286$$

The potential parameters σ_{sw} and ϵ_{sw} are the square-well potential parameters. The values of the critical variables T_c , ρ_c , and p_c are from the literature.²² The solid curve has been calculated from the quadratic model (QM) with the nonanalytic terms included, for which the same values of $\alpha_{na} = 0.01$ and $\beta_{na} = -0.015$ as those used for Figure 1 have been employed whereas the dashed curve (vdW) has been calculated by the van der Waals theory. The cubic model was ruled out on the basis of the examination made in Figure 1. In the case of methane, the quadratic model also performs excellently in the range of density considered by experiment.

On the basis of the comparisons made in Figures 1 and 2, we are able to conclude that the quadratic model is the most favorable among the models tested. Application of the quadratic model to a study²⁵ of transport properties (e.g., viscosity) of glass-forming substances indicates that it is robust and capable of giving reliable results for transport properties.

IV. Canonical Equation of State and Spinodal Curve

In the subcritical regime of density and temperature, the thermodynamic conditions for equilibrium must be satisfied. Furthermore, the spinodal curve is the locus of vanishing first derivatives of isotherms. Thus, along the spinodal curve, there

holds the equation

$$0 = \beta^* \left(\frac{\partial p^*}{\partial \eta_{\text{sp}}} \right)_T = \frac{1}{(1 - B_{\text{sp}} \eta_{\text{sp}})^2} + \frac{\eta_{\text{sp}}^2}{(1 - B_{\text{sp}} \eta_{\text{sp}})^2} \left(\frac{\partial B_{\text{sp}}}{\partial \eta_{\text{sp}}} \right)_T - 2\beta A_{\text{sp}} \eta_{\text{sp}} - \beta^* \eta_{\text{sp}}^2 \left(\frac{\partial A_{\text{sp}}}{\partial \eta_{\text{sp}}} \right)_T \quad (39)$$

and along the liquid–vapor coexistence curve, there holds the equation

$$\frac{\eta_l}{1 - B_l \eta_l} - \beta^* A_l \eta_l^2 = \frac{\eta_v}{1 - B_v \eta_v} - \beta^* A_v \eta_v^2 \quad (40)$$

In these expressions

$$A_k = A^*(\eta_k, T^*) \quad B_k = B^*(\eta_k, T^*) \quad (k = \text{c, sp, l, v})$$

Here, c, sp, l, and v stand for critical, spinodal, liquid, and vapor, respectively.

With the definition of scaled GVDW parameters

$$\mathcal{A} = \frac{A^*}{A_{\text{c}}} \quad \mathcal{B} = \frac{B^*}{B_{\text{c}}} \quad (41)$$

the reduced equation of state is expressible in the form

$$\psi = \frac{\xi(t+1)y}{1 - \nu \mathcal{B}y} - \tau \mathcal{A}y^2 \quad (42)$$

By using this form of the equation of state, it is possible to formulate an algorithm to construct the spinodal and liquid–vapor coexistence curves in the (T, η) plane.

The spinodal curve is the locus of the points satisfying eq 39, which may be expressed in the reduced form

$$\frac{\xi(t+1)(1 + \nu y_k^2 \mathcal{B}_k^{(1)})}{(1 - \nu \mathcal{B}_k y_k)^2} - 2\tau \mathcal{A}_k y_k - \tau y_k^2 \mathcal{A}_k^{(1)} = 0 \quad (43)$$

where $k = (\text{sl}, \text{sv})$ and

$$\mathcal{A}_k = \mathcal{A}(y_k) \quad \mathcal{B}_k = \mathcal{B}(y_k) \quad \mathcal{A}_k^{(1)} = \left(\frac{\partial \mathcal{A}}{\partial y} \right)_k \quad \mathcal{B}_k^{(1)} = \left(\frac{\partial \mathcal{B}}{\partial y} \right)_k \quad (44)$$

Thus, on the liquid branch,

$$y_{\text{sl}} = z_{\text{sl}}$$

whereas on the vapor branch,

$$y_{\text{sv}} = z_{\text{sv}}$$

in the present system of notation. Therefore, it follows from eqs 11 and 12 that

$$\mathcal{A}_k = \mathcal{A}(y_k) = a_0^{(k)} \quad \mathcal{B}_k = \mathcal{B}(y_k) = b_0^{(k)} \quad (45)$$

$$\mathcal{A}_k^{(1)} = \left(\frac{\partial \mathcal{A}}{\partial y} \right)_k = a_1^{(k)}(t) \quad \mathcal{B}_k^{(1)} = \left(\frac{\partial \mathcal{B}}{\partial y} \right)_k = b_1^{(k)}(t) \quad (k = \text{sl}, \text{sv})$$

Since $y_k = z_k$ ($k = \text{sl}, \text{sv}$) on the spinodal curve, upon using these results eq 43 is written as

$$\frac{\xi(t+1)[1 + \nu z_k^2 b_1^{(k)}(t)]}{(1 - \nu z_k)^2} - \tau z_k [2a_0^{(k)} + z_k a_1^{(k)}(t)] = 0 \quad (46)$$

Since $z_k = 1$, $y_k = 1$, and $a_0^{(k)} = 1$ at the critical point, the corresponding equation is

$$\frac{\xi(1 + \nu b_1)}{(1 - \nu)^2} - \tau(2 + a_1) = 0 \quad (47)$$

Equation 46 determines z_k in terms of t , and the temperature dependence of the spinodal curve is determined by the coefficients $a_0^{(k)}(t)$, $a_1^{(k)}(t)$, and $b_1^{(k)}(t)$ of the zeroth- and linear-order terms in the expansions for \mathcal{A} and \mathcal{B} . To be specific about the coefficients, we assume for $a_0^{(k)}(t)$, $a_1^{(k)}(t)$, $b_0^{(k)}(t)$, and $b_1^{(k)}(t)$ the empirical forms

$$a_0^{(k)}(t) = 1 + a_{0k}|t|^\epsilon$$

$$b_0^{(k)}(t) = 1 + b_{0k}|t|^\epsilon$$

$$a_1^{(k)}(t) = a_1(1 + a_{1k}|t|^\epsilon)$$

$$b_1^{(k)}(t) = b_1(1 + b_{1k}|t|^\epsilon) \quad (48)$$

where $\epsilon > 0$ and a_{0k} , b_{0k} , a_{1k} , and b_{1k} are parameters. The liquid and vapor spinodal curves may have different values for the exponent ϵ , but we have assumed a single value for the simplicity of analysis. This assumption is easily removed. Since in the notation used in this work

$$z_k = x_k + 1$$

eq 46 may be written as

$$F(t, x_k) = 0 \quad (49)$$

where

$$F(t, x_k) = \frac{\xi[1 + \nu b_1(1 + b_{1k}|t|^\epsilon)(x_k + 1)^2]}{(1 - \nu - \nu x_k)^2} - \tau(x_k + 1)[2 + 2a_{0k}|t|^\epsilon + a_1(1 + a_{1k}|t|^\epsilon)(x_k + 1)] \quad (50)$$

Since we are interested in the behavior of the solution near the critical point, the function $F(t, x_k)$ may be expanded near $x_k = 0$; we thus obtain

$$F(t, x_k) = \sum_{n \geq 0} f^{(n)}(t) |t|^\epsilon x_k^n + t g^{(0)}(t) + \sum_{n \geq 1} g^{(n)}(t) x_k^n \quad (51)$$

where $f^{(n)}(t)$ and $g^{(n)}(t)$ are rational functions of t . Leading examples of them are as follows:

$$\begin{aligned}
f^{(0)}(t) &= \frac{\zeta \nu b_1 b_{1k}}{(1-\nu)^2} - \frac{\tau(2a_{0k} + a_1 a_{1k})}{1+t} \\
f^{(1)}(t) &= \frac{2\zeta \nu b_1 b_{1k}}{(1-\nu)^3} - \frac{2\tau(2a_{0k} + a_1 a_{1k})}{1+t} \\
g^{(0)}(t) &= \frac{\tau(2 + a_1)}{1+t} \\
g^{(1)}(t) &= \frac{2\zeta \nu(1 + b_1)}{(1-\nu)^3} - \frac{2\tau(1 + a_1)}{1+t}
\end{aligned} \quad (52)$$

Note that for $n \geq 3$ the coefficients $f^{(n)}$ and $g^{(n)}$ are independent of t . Therefore, in the neighborhood of $x_k = 0$, there holds the equation

$$[f^{(0)}(t) + f^{(1)}(t)x_k]|t|^\epsilon + tg^{(0)}(t) + g^{(1)}(t)x_k = 0 \quad (53)$$

which yields x_k in the neighborhood of $t = 0$

$$\begin{aligned}
x_k &= -\frac{[f^{(0)}(t) + tg^{(0)}(t)]|t|^\epsilon}{g^{(1)}(t) + f^{(1)}(t)|t|^\epsilon} \\
&\approx \left[\frac{(2a_{0k} + a_1 a_{1k})}{2 + a_1} - \frac{\zeta \nu b_1 b_{1kk}}{\tau(2 + a_1)(1-\nu)^2} \right] |t|^\epsilon + O(|t|^{2\epsilon}) \quad (54)
\end{aligned}$$

This result indicates that whereas a_1 and b_1 are determined from the critical parameters the parameters a_{0k} , a_{1k} , and b_{1k} can be determined from the information on the spinodal curve and vice versa. Therefore, the critical parameters and the spinodal curve completely determine the zeroth- and linear-order coefficients a_{0k} , $a_1^{(k)}$, and $b_1^{(k)}$ ($k = \text{sl, sv}$) of \mathcal{A} and \mathcal{B} . For wider ranges of x_k and t , eq 49 should be solved without expanding $F(t, x_k)$ in the neighborhood of the critical point. Such a solution can be obtained numerically.

V. Concluding Remarks

The van der Waals theory provides a fairly simple form of the equation of state that accounts for most fluid behaviors in a qualitatively correct manner. However, it has defects that should be removed and thus requires an improvement if quantitatively correct results are desired for various aspects of thermodynamic properties of matter. Because of the qualitatively correct features of the van der Waals theory, it would be advantageous if an improved theory were built on and around the van der Waals theory by incorporating the virtuous parts of the van der Waals theory into the improved theory. The present study is made in this spirit. We have shown in a previous paper¹ that the canonical equation of state provides a very good candidate for this purpose. In this paper, we have examined a few empirical models for the generic van der Waals parameters in the canonical equation of state in order to account for the critical parameters of simple fluids. The models for A and B consist of analytical and nonanalytical parts, the former being made up of a polynomial of density and the latter, of a term proportional to a density term with a fractional exponent—thus irrational and nonanalytic. We have shown that quadratic and cubic models for the analytical part yield excellent results for the critical compressibility factor, which is a reliable measure of the quality of empirical models for the equation of state. To distinguish between the quadratic and cubic models, we have calculated the critical isotherms for argon with the models and have found that the quadratic model performs excellently in

comparison with experiment whereas the cubic model is poor except in the neighborhood of the critical point. We have also calculated the critical isotherm for methane with the quadratic model and have found that it compares excellently with experimental data whereas the cubic model performs poorly. Therefore, it is possible to rule against the particular cubic model considered in this work in favor of the quadratic model as the model to use for studying the critical behavior of the fluid. A recent application of the quadratic model to calculate the viscosity²⁵ of supercooled liquids indicates that the model is reliable and robust, suggesting its potential application to the study of subcritical fluids.

We have also shown that the spinodal curve can be constructed in terms of the linear coefficients of the analytical parts of A and B , and the temperature dependence of coefficients a_{0k} , $a_1^{(k)}$, and $b_1^{(k)}$ ($k = \text{sl, sv}$) of A and B determine the temperature dependence of the spinodal curve and vice versa.

In effect, through the present work, we are putting forth the notion that the equation of state should be generally nonanalytic with respect to temperature and density. Furthermore, we have shown that there is a systematic algorithm for determining the expansion coefficients for the generic van der Waals parameters, which exploits the critical data and spinodal curves that hierarchically provide information on the expansion coefficients for A and B . In this work, we have shown how part of such information may be extracted for the coefficients a_{0k} , b_{0k} , $a_1^{(k)}$, and $b_1^{(k)}$ ($k = \text{sl, sv}$) from the critical data and spinodal curves. The liquid–vapor coexistence curves and other thermodynamic properties of subcritical fluids would provide additional information for other coefficients, but the investigation of this question, requiring extensive numerical analysis, is deferred to future work.

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References and Notes

- (1) Eu, B. C.; Rah, K. *Phys. Rev. E* **2001**, 63, 031203.
- (2) Rah K.; Eu, B. C. *J. Chem. Phys.* **2001**, 115, 2634.
- (3) Rah K.; Eu, B. C. *Phys. Rev. Lett.* **2002**, 88, 065901.
- (4) Rah K.; Eu, B. C. *J. Chem. Phys.* **2002**, 116, 7967.
- (5) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, 31, 1164.
- (6) Eu, B. C. *J. Chem. Phys.* **2001**, 114, 10899.
- (7) Chen, Z. Y.; Abbaci, T.; Sengers, J. V. *Phys. Rev. A* **1990**, 42, 4470.
- (8) Anisimov, M. A.; Kiselev, S. B.; Sengers, J. V. *Physica A* **1992**, 188, 487.
- (9) Kostrowicka Wyczalkowska, A.; Anisimov, M. A.; Sengers, J. V. *Fluid Phase Equilib.* **1999**, 158–160, 523.
- (10) Nicoll, J. F. *Phys. Rev. A* **1981**, 24, 2203.
- (11) Nicoll, J. F.; Albright, P. C. *Phys. Rev. B* **1985**, 31, 4576.
- (12) Brézin, E.; Le Guillou, J. C.; Zinn-Justin, J. In *Phase Transitions and Critical Phenomena*; Domb, C., Green, M. S., Eds.; Academic Press: New York, 1976; Vol. 6, p 125.
- (13) Egelstaff, P. A.; Ring, J. W. In *Physics of Simple Liquids*; Temperley, H. N. V., Rowlinson, J. S., Rushbrooke, G. S., Eds.; North-Holland: Amsterdam, 1968; Chapter 7.
- (14) Levelt Sengers, J. M. H.; Straub, J.; Vincentini-Missoni, M. J. *Chem. Phys.* **1971**, 54, 5034.
- (15) Sengers, J. V.; Levelt Sengers, J. M. V. H. In *Progress in Liquid Physics*; Croxton, C. A., Ed.; Wiley: New York, 1978; p 103.
- (16) van Laar, J. J. Z. *Phys. Chem. Stoechiom. Verwandtschaftsl.* **1893**, 11, 721. van Laar, J. J. Z. *Proc. Sci. Sec. Kon. ned. Akad. Wetensch.* **1912**, 14 II, 1091.
- (17) Baehr, H. D. *Forsch. Geb. Ingenieurwes.* **1963**, 29, 143.
- (18) Tegeler, Ch.; Span, R.; Wagner, W. *J. Phys. Chem. Ref. Data* **1999**, 28, 779.
- (19) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954; p 245.

- (20) Michels, A.; Levelt, J. M.; De Graaff, W. *Physica* **1958**, 24, 657.
- (21) Gilgen, R.; Kleinrahm, R.; Wagner, W. *J. Chem. Thermodyn.* **1994**, 26, 383.
- (22) Händel, G.; Kleinrahm, R.; Wagner, W. *J. Chem. Thermodyn.* **1992**, 24, 685.
- (23) Kleinrahm, R.; Duschek, W.; Wagner, W. *J. Chem. Thermodyn.* **1986**, 18, 1103.
- (24) Setzmann, U.; Wagner, W. *J. Phys. Chem. Ref. Data* **1991**, 20, 1061.
- (25) Rah, K.; Eu, B. C. To be submitted for publication.