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Generic van der Waals equation of state and statistical mechanical representations of the van der Waals parameters

Byung Chan Eu* and Kyunil Rah
Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec, Canada H3A 2K6

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In this paper, we show that in the case of the potential made up of a repulsive and an attractive part the virial equation of state can be put into a form similar to the van der Waals equation of state and thus the form of the van der Waals equation of state is generic to such a class of potentials. The derivation provides exact statistical mechanical representations for the van der Waals parameters. The generic van der Waals parameters are evaluated as functions of density and temperature by using the Percus-Yevick integral equation for the pair correlation function in the case of a square-well potential. They become disjointed functions of density, which are not defined in a density interval in the subcritical regime, if the temperature is less than the critical temperature. On the basis of the numerical solution results for the parameters we conjecture that they are irrational functions of density and thus nonanalytic.

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I. INTRODUCTION

The van der Waals equation of state has been serving not only as a practical model for description of liquids and gases but also as a prototype of, and a guide for, the equations of state subsequently proposed in the literature [1–3], which were attempts made to improve it from the phenomenological standpoints. Besides such older versions of equation of state that appear in the literature, in some relatively recent versions propositions [4,5] have been made to modify the excluded volume term in the van der Waals equation of state so as to make it perform better at high densities. However, such modifications are made intuitively without a firm statistical mechanical basis except that the resulting equations of state perform better than the original version of van der Waals in some respects. If the thermodynamic perturbation theories were pursued to all orders, one might in principle obtain some relations of the van der Waals parameters to the perturbation series for the distribution function. However, the resulting relations should be expected to be rather complicated and physically nonintuitive. In the absence of firm statistical mechanical foundations an *ad hoc* attempt at improvement of a very intuitive theory, such as the van der Waals theory, is bound to produce a result not sufficiently robust. One may therefore ask if there are reasonably simple representations of the van der Waals parameters, which are rigorously based on statistical mechanics, and, concurrently, if it is possible to remove the principal defect of the van der Waals equation of state, that is, to remove the appearance of the loop in the equation of state. Answering these questions would in effect amount to modifying the van der Waals equation of state to a form similar in mathematical structure but without the defect of the former.

In this work we would like to show that the form of the van der Waals equation of state is generic to all interaction potential models that have a hard core and a finite ranged attractive potential, or, more generally, a repulsive core and an attractive branch of interaction, provided that the density does not approach that of close packing. It is a canonical form for fluids obeying such a potential model. Therefore the form of the equation of state presented in this work in effect amounts to a derivation of an exact van der Waals-type equation of state. This viewpoint enables us to obtain exact statistical mechanical representations of the van der Waals parameters or, more precisely, generic van der Waals parameters, and thereby investigate the meanings of the original van der Waals parameters in a more precise manner and also to explore modifications of the original van der Waals equation of state to forms more suitable for study of the thermodynamic properties of fluids. To make the investigation as simple as possible and also to be more specific in investigation, we assume a square-well interaction potential and the Percus-Yevick closure [6] for the Ornstein-Zernike (OZ) equation for the pair correlation function. The Percus-Yevick closure, however, is not mandatory because any other closure can be used. The integral equation for the pair correlation function in the subcritical region of density and temperature provides not only integral equation representations for the van der Waals-type parameters, but also a way to obtain an equation of state free from the van der Waals loop. The generic van der Waals parameters defined are not analytic in the subcritical regime and may be represented by irrational functions of density and temperature. By assuming suitable irrational (nonanalytic) functions for the generalized van der Waals parameters in the subcritical regime, one can in fact show that the equation of state can yield nonclassical critical exponents for some relations of the thermodynamic variables near the critical point. We will report on this line of study elsewhere [7] in the near future.

In Sec. II we present the derivation of a generic form of the equation of state for a potential model that has a hard core and a finite ranged attractive potential. This derivation is rather simple if the virial form of the equation of state is

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*Also at the Centre for the Physics of Materials and Department of Physics, McGill University, and the Asia Pacific Center for Theoretical Physics, Seoul, Korea. Electronic address: eu@chemistry.mcgill.ca

used. It enables us to obtain the statistical mechanical representations of the generic van der Waals parameters. Then these representations are specialized to the case of a square-well potential. In Sec. III we numerically calculate the generic van der Waals parameters as functions of density and temperature by using the Ornstein-Zernike equation with the Percus-Yevick closure in the case of a square well model for the potential energy. The generic van der Waals parameters are found to be continuous functions of density over the entire density range as they should be, if the temperature is supercritical, but in the subcritical regime of temperature they are not defined in a domain of density and thus become disjointed, piecewise continuous functions of density. This disjointedness reflects the fact that the liquid and vapor phases are in equilibrium with each other, and the integral equation for the pair distribution function consequently does not have solutions in the range of density bounded by a temperature-density curve reminiscent of the liquid-vapor coexistence curve. The discontinuity of the generic van der Waals parameters implies that they are nonanalytic functions of density and temperature in the subcritical regime. In Sec. IV the generic van der Waals equation of state is organized to a form which we believe is more suitable for studying the thermodynamics of fluids in the subcritical regime so that we can avail ourselves to the basic methodology of the van der Waals theory for the subcritical behavior of fluids. The result of this line of study, which is not presented in this work, suggests that the generic van der Waals equation of state can be potentially useful for studying the thermodynamics of subcritical fluids and study of critical phenomena becomes tantamount to studying the nonanalyticity of the generic van der Waals parameters. In Sec. V the concluding remarks are given.

II. EQUATIONS FOR PRESSURE

A. Generic van der Waals equation of state

For a pair potential energy $u(r)$ the virial equation of state is given by [8,9]

$$\frac{\beta p}{\rho}=1-\frac{2\pi}{3}\beta\rho\int_0^\infty dr\, r^3 u'(r)\exp[-\beta u(r)]y(r,\rho,\beta), \tag{1}$$

where $u'(r)=du(r)/dr, \beta=1/k_BT$ with k_B denoting the Boltzmann constant, and $y(r,\rho,\beta)$ is the cavity function. The density and temperature dependence will be suppressed in the cavity function for brevity of notation, whenever convenient. Let us assume that the potential energy has the form

$$\begin{aligned} u(r)&=\infty \quad \text{for} \quad r<\sigma \\ &=u_a(r) \quad \text{for} \quad \sigma<r<\xi \\ &=0 \quad \text{for} \quad \xi<r. \end{aligned} \tag{2}$$

Here $u_a(r)<0$. Therefore the potential has a hard core and a finite ranged force of attraction. These conditions can be made less restrictive by removing the condition of finite range of the attractive potential and making the potential simply repulsive for $r<\sigma$; these relaxed conditions would not invalidate the conclusion on the generic form for the equation of state presented below. For the potential model presented earlier the virial equation of state takes the form

$$\frac{\beta p}{\rho}=1+\frac{2\pi\sigma^3}{3}\rho y(\sigma,\rho,\beta)+\frac{2\pi}{3}\rho\int_\sigma^\xi dr\, r^3 y(r,\rho,\beta)\frac{d}{dr}f(r), \tag{3}$$

where $f(r)$ is the Mayer function defined for $u(r)$ by

$$f(r)=\exp[-\beta u(r)]-1. \tag{4}$$

Define the following functions of density and temperature:

$$A(\rho,\beta)=-\frac{2\pi}{3\beta}\int_\sigma^\xi dr\, r^3 y(r,\rho,\beta)\frac{d}{dr}f(r), \tag{5}$$

$$B(\rho,\beta)=\frac{2\pi\sigma^3}{3}\frac{y(\sigma,\rho,\beta)}{1+\frac{2\pi\sigma^3}{3}\rho y(\sigma,\rho,\beta)}. \tag{6}$$

Then the virial equation of state in Eq. (3) can be written in the form

$$(p+A\rho^2)(1-B\rho)=\rho\beta^{-1}, \tag{7}$$

which has formally the same form as the van der Waals equation of state. This will be referred to as *the generic van der Waals equation of state*, and the coefficients *A* and *B the generic van der Waals parameters* in this work. This simple derivation, or rather a recasting of the virial equation of state, implies that the van der Waals equation of state is a canonical and generic form of equation of state for the class of potential models assumed, and Eqs. (5) and (6) are the exact statistical mechanical representations for the generic van der Waals parameters *A* and *B* in the canonical form of equation of state. As will be shown later, the generic form in Eq. (7) reduces to the original van der Waals equation of state as a special case holding in the limit of $\rho\rightarrow 0$, where $y(\sigma,\rho,\beta)\rightarrow 1$, or if the potential model is such that it yields *A* and *B* which are independent of density and temperature. The latter case, however, would take a rather special kind of the potential energy function. We will examine Eq. (7) together with Eqs. (5) and (6) in this paper. It must be noted that the parameter *B* is closely related to the hard core, and the parameter *A* to the attractive branch of the potential.

B. Square-well potential model

We assume a square-well potential model for the interaction potential energy for the simplicity it provides without loss of the essential physical contents of the idea:

$$\begin{aligned} u(r) &= \infty \quad \text{for} \quad r<\sigma \\ &= -\varepsilon \quad \text{for} \quad \sigma<r<\xi \\ &= 0 \quad \text{for} \quad r>\xi. \end{aligned} \tag{8}$$

Here ε is the well depth of the potential. For this potential the Mayer function takes the form

$$\begin{aligned} f(r) &= -1 \quad \text{for} \quad r<\sigma \\ &= \exp(\beta\varepsilon)-1 \quad \text{for} \quad \sigma<r<\xi \\ &= 0 \quad \text{for} \quad r>\xi. \end{aligned}$$

The interaction range parameter ξ and the well depth ε may be fixed such that the second virial coefficients computed with the van der Waals interaction ($-r^{-6}$ potential) and the square-well potential, respectively, match with each other so that ξ and ε are not independent parameters. The virial equation of state for the square-well potential is easily shown to be given by the expression

$$\begin{aligned} \frac{\beta p}{\rho} &= 1+\frac{2\pi\sigma^3}{3}\rho y(\sigma,\rho,\beta)-\frac{2\pi\sigma^3}{3}\rho[\exp(\beta\varepsilon)-1] \\ &\quad \times\left[\left(\frac{\xi}{\sigma}\right)^3 y(\xi,\rho,\beta)-y(\sigma,\rho,\beta)\right]. \end{aligned} \tag{9}$$

This equation of state may be put into the form given in Eq. (7) for which the parameters *A* and *B* are now given by the formulas

$$\begin{aligned} A(\rho,\beta) &= -\frac{2\pi}{3}\sigma^3\beta^{-1}[\exp(\beta\varepsilon)-1]\left[y(\sigma,\rho,\beta)\right. \\ &\quad \left.-\left(\frac{\xi}{\sigma}\right)^3 y(\xi,\rho,\beta)\right], \end{aligned} \tag{10}$$

$$B(\rho,\beta) = \frac{2\pi\sigma^3}{3}\,\frac{y(\sigma,\rho,\beta)}{1+\dfrac{2\pi\sigma^3}{3}\rho y(\sigma,\rho,\beta)}. \tag{11}$$

For the case of a square-well potential the form of parameter *B* remains unchanged from the case of the potential model (2).

III. DENSITY AND TEMPERATURE DEPENDENCE OF *A* AND *B*

To study the density and temperature dependence of the generic van der Waals parameters it is convenient to use reduced variables defined as follows:

$$\eta=\frac{\pi}{6}\rho^*, \quad \beta^*=T^{*-1}=\beta\varepsilon, \quad p^*=pv_0/\varepsilon, \quad \gamma=\xi/\sigma$$

together with $v_0=\pi\sigma^3/6$ and $\rho^*=\sigma^3\rho$. The equation of state for the square-well potential then may be put into the reduced form

$$(p^*+A^*\eta^2)(1-B^*\eta)=\eta\beta^{*-1}, \tag{12}$$

where with the definitions

$$A^*=\frac{A}{\varepsilon v_0}, \quad B^*=\frac{B}{v_0} \tag{13}$$

the reduced generic van der Waals parameters are given by the formulas

$$\begin{aligned} A^*(\beta^*,\eta) &= 4\beta^{*-1}(\exp\beta^*-1)[\gamma^3 y(\gamma,\beta^*,\eta) \\ &\quad -y(1,\beta^*,\eta)], \end{aligned} \tag{14}$$

$$B^*(\beta^*,\eta)=\frac{4y(1,\beta^*,\eta)}{1+4\eta y(1,\beta^*,\eta)}. \tag{15}$$

With *A* and *B* reduced to these forms, the generic van der Waals equation of state evidently does not explicitly depend on material parameters such as σ and ε. Therefore it is a corresponding-state equation of state, although not in the sense of that of the van der Waals theory, which yields a corresponding-state equation of state on scaling the equation of state with the critical parameters (p_c, v_c, T_c) defined by it.

To prepare for the comparison to be made of the equation of state presented in Eq. (12) with the original van der Waals equation of state, we present the latter in terms of the reduced variables introduced:

$$(p^*+a^*\eta^2)(1-b^*\eta)=\eta\beta^{*-1}. \tag{16}$$

Here the van der Waals parameters a' and b' are reduced as follows:

$$a^*=\frac{a'}{\varepsilon v_0}, \quad b^*=\frac{b'}{v_0}. \tag{17}$$

It should be noted that a' and b' are constants independent of temperature and density.

A. The cavity functions and the generic van der Waals parameters

On close examination of the equation of state (12) for the square-well potential, we see that the cavity function $y(1,\eta,\beta^*)$ is intimately related to the hard core of the potential whereas the cavity function $y(\gamma,\eta,\beta^*)$ must be more closely related to the attractive part of the potential than $y(1)$ is, as can be verified by a perturbation theory. The limiting behavior of the parameters A^* and B^* with regard to density can be readily deduced by observing that the cavity functions $y(1,\eta,\beta^*)$ and $y(\gamma,\eta,\beta^*)$ tend to unity as $\eta\rightarrow 0$. In this limit the reduced parameters therefore tend to constants

$$\begin{aligned} \lim_{\eta\rightarrow 0} A^*(\beta^*,\eta) &= 4\beta^{*-1}(\exp\beta^*-1)(\gamma^3-1)\approx 4(\gamma^3-1), \\ \lim_{\eta\rightarrow 0} B^*(\beta^*,\eta) &= 4. \end{aligned} \tag{18}$$

Note that the zero density limit of A^* generally depends on temperature. With this set of constant parameters the generic van der Waals equation of state becomes the original van der Waals equation of state, if we identify

$$a' = 4\varepsilon v_0(\gamma^3 - 1), \quad b' = v_0$$

for the square-well potential model. These parameters are independent of density and temperature. From the viewpoint of the present approach the van der Waals equation of state therefore is the zero density limit for the cavity functions and thus for B^* and A^* for which $\beta^{*-1}(\exp\beta^* - 1) \simeq 1$. This consideration suggests that the van der Waals equation of state will not arise as an exact statistical mechanical result, unless special models are taken for the potential as in the case of the studies made by Kac and others [10,11]. In the sense of the limits given in Eq. (18) the equation of state (12) is a generalized form of the original van der Waals equation of state, and it is justifiable to call it the generic van der Waals equation of state because of the similarity of the forms of Eqs. (12) and (16) and the generality of the former. The limiting behavior of A^* and B^* in Eq. (18) motivates us to investigate their density and temperature dependence and develop modified forms of the van der Waals equation of state. For this purpose we must investigate the integral equation for the cavity function.

B. Free volume

The density dependence of A^* and B^* discussed later indicates that in the high density regime A^* becomes negative beyond a density value, η_t, say, and B^* tends to a constant independent of density. In the density regime of $\eta > \eta_t$ it then is reasonable to write the equation of state in the form

$$p^*(1 - B_f\eta) = \eta\beta^{*-1}, \tag{19}$$

where

$$\begin{aligned} B_f &= \frac{B^* + (1 - B^*\eta)\chi}{1 + (1 - B^*\eta)\eta\chi}, \\ \chi &= -A^*(\beta^*, \eta)\beta^* > 0. \end{aligned} \tag{20}$$

The parameter χ is positive because $A^* < 0$ for $\eta > \eta_t$. This form of equation of state makes it natural to define the free volume v_f by the formula

$$v_f = v(1 - B_f\eta), \tag{21}$$

where $v = 1/\eta$. This is an exact statistical mechanical representation of free volume. The free volume is not easy to evaluate in general, and it remained elusive and unresolved for van der Waals himself according to Klein [12]. However, the present approach to the equation of state readily provides a natural statistical mechanical representation and a method of evaluating it as exactly as the evaluation of the cavity functions can be made by means of a suitable integral equation for the cavity function or the pair correlation function. This statistical mechanical representation of free volume makes the free volume concept precisely quantified and computable by means of the pair correlation function of the fluid instead of using models for it as is usually the case in the literature [13–15].

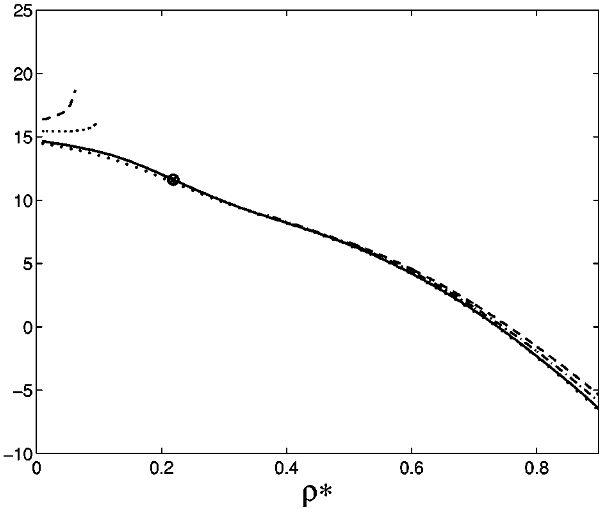

FIG. 1. Density dependence of A^*. The dotted curve is for $T^* = 1.25$; the solid curve is for $T^* = 1.218$; the dashed–dotted curve is for $T^* = 1.1$; and the broken curve is for $T^* = 1.0$. The last two curves are subcritical and undefined in an interval enclosing the critical point and thus disjointed. The symbol represents the critical point.

C. Numerical results for A^* and B^*

The cavity functions appearing in the expressions for the parameters A^* and B^* are computed from the solutions for the integral equation for the total correlation function by assuming the Percus-Yevick closure for the Ornstein-Zernike equation, namely, the Percus-Yevick integral equation [6]. The Fourier transform method is used for solving the integral equation.

Parameters A^* and B^* are calculated from the solution for the Percus-Yevick integral equation for $\gamma = 1.5$, and A^* is plotted as a function of density at various temperatures in Fig. 1. In the scale of the density axis A^* is a monotonically, and almost linearly, decreasing function of density with a weak temperature dependence above the critical temperature, but as the temperature becomes lower than the critical temperature, the integral equation for the pair correlation function ceases to yield a solution in the density intervals bounded within the coexisting densities. The parameter A^* thus becomes a disjointed, piecewise continuous function, which is not defined in the density range (η_1, η_2), where η_1 and η_2 are the maximum and minimum value, respectively, on the isotherm at which the integral equation does not yield the solution. These values are, respectively, larger and smaller than the coexisting vapor and liquid density of the isotherm. In the van der Waals theory this parameter A^*, and also B^*, is a constant and the equation of state admits an unstable portion in approximately the same interval as $\eta_1 < \eta < \eta_2$. In the figure the solid and dotted curves are iso-

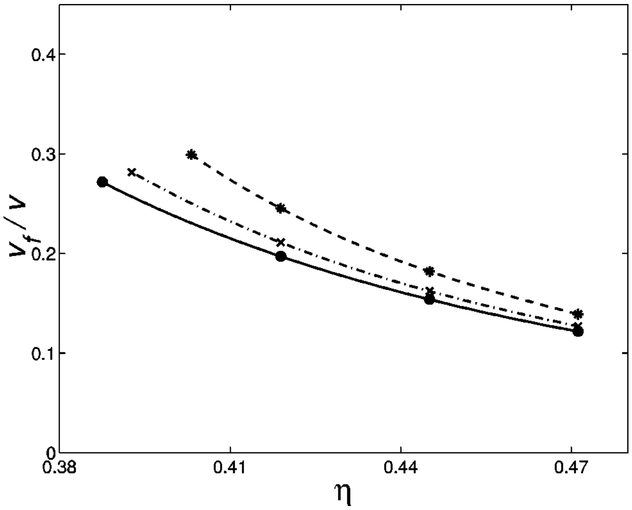

FIG. 2. Density dependence of free volume. The solid curve is for $T^*=1.25$; the dashed–dotted curve is for $T^*=1.1$; and the broken curve is for $T^*=0.9$.

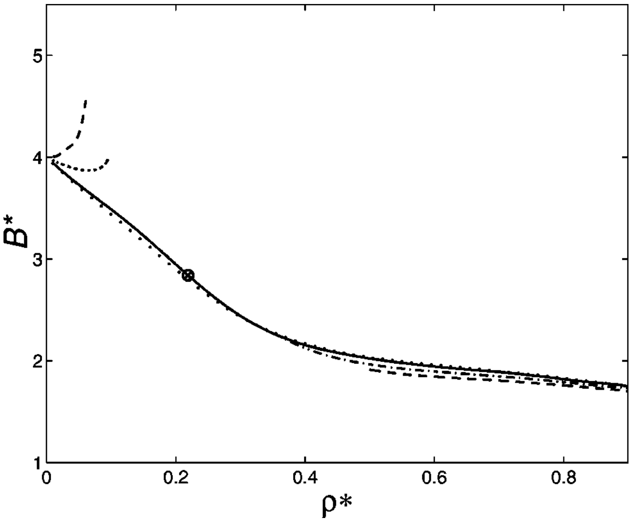

FIG. 3. Density dependence of B^*. The meanings of the curves are the same as in Fig. 1 for A^*.

therms above the critical point ($T_c^*\approx 1.2,\rho_c^*\approx 0.23$) which are continuous over the whole density range, whereas the broken and dashed–dotted curves are subcritical isotherms which are discontinuous. It is useful to remark that the nonexistence of solutions of the integral equation for the pair correlation function in the subcritical regime is not unique to the Percus-Yevick integral equation, since it happens to other integral equations such as the hypernetted chain integral equation, although the precise locations in the density–temperature plane where the solutions cease to exist depend on the closure taken for the Ornstein-Zernike equation. Therefore, the singular behavior of A^* and B^* is robust, although the domain of singular behavior, or the location of the singularity, in the density–temperature plane can vary, depending on with which integral equation the cavity function is calculated.

Another significant feature of the density dependence of A^* presented is that it becomes negative as the density crosses a value η_t, which occurs in the liquid density regime and weakly depends on temperature. This means that in the regime of the density beyond η_t it becomes meaningless to associate parameter A^* with the attractive part of the interaction potential, as is in the case of the van der Waals theory, but it instead must be associated with the repulsive force between the particles. This is because the attractive force is overpowered by the repulsive force as the particles are packed to a sufficiently high density. Thus in the range of density in question it makes sense to combine the parameter A^* with the parameter B^* and recast the equation of state in the form given in Eq. (19), which motivates us to define the free volume as given in Eq. (21). The density dependence of the free volume is plotted in Fig. 2 at various temperatures. In any case, the generic van der Waals equation of state provides a natural way of defining free volume, and the free volume so defined can be used to calculate the self-diffusion coefficient of liquids and glassy materials by applying various free volume theories for them [13–15]. Such a study of density dependence of the self-diffusion coefficient of liquids will be reported elsewhere [16].

In Fig. 3 parameter B^* is plotted as a function of density at various temperatures. The isotherms of this parameter above the critical temperature are also continuous for all η, but they are undefined and thus become discontinuous in the same density intervals as for the corresponding isotherms for A^*, as the temperature becomes less than the critical temperature. The meanings of the curves are the same as in Fig. 1. Notice that parameter B^* decreases almost linearly down to $\rho^*\approx 0.35$ and then levels off to an almost constant value on the order of σ^3. This region invariably occurs in the liquid branch of B^* in the high density regime. This suggests that in the high density liquid regime the van der Waals parameter B may be taken with unity in the reduced units, namely, in the units of σ^3. This choice was suggested by Nordholm and Haymet [4] on an intuitive ground, and the present result seems to support the idea.

The critical density, marked by the symbol ⊗ in Figs. 1 and 3, occurs around $\rho^*\approx 0.23$. It is useful to observe that both A^* and B^* appear to be approximately linear around the critical density when $T\gtrsim T_c$, but in the case of $T<T_c$ their behavior with respect to density and temperature is rather similar, although they have opposite signs for the curvature in the liquid regime. This density dependence appears to be traceable to the difference in their cavity function dependence; see their definitions in terms of the cavity functions. The similarity in the subcritical behaviors of A^* and B^* suggests that the values of $y(1)$ and $y(\gamma)$ share the same characteristic feature that they become singular, as the density value reaches the spinodal curve if $T<T_c$. (Here we use the term spinodal curve for want of a suitable terminology, but the curve appears to be related to the spinodal curve, but does not coincide with it.) The mathematical reason for such similarity of the behaviors of A^* and B^* is that they are the values at two different positions of a function obeying the same integral equation. This means that they are scaled by an identical function, which is singular with respect to density but multiplied by different regular functions of density and

temperature that produce the differences in their functionalities and magnitudes in different density regimes. Since the functions A^* and B^* do not exist as real functions in the interval $\eta_1 < \eta < \eta_2$, the singular part must be irrational, and as a consequence the equation of state is no longer analytic. We therefore conjecture that *the generic van der Waals equation of state is generally nonanalytic and, in particular, irrational with regard to the density dependence*. The statistical mechanical support of this conjecture must be sought in the solution of the integral equation for the cavity function for the potential model considered. However, this problem is not simple to resolve satisfactorily, because the solution cannot be obtained in closed form for the integral equation. We defer the study of this subject to future work.

D. Calculation of the chemical potential

As we have seen in the preceding subsection, to examine the functions A^* and B^* near the critical state it is necessary to locate the critical point. For this purpose the liquid-vapor coexistence curve must be constructed. We find it more convenient to use the chemical potential for the purpose. The statistical mechanical formula for the chemical potential is given by the formula [8]

$$\beta\mu(\rho,\beta) = \ln(\Lambda^3\rho) + \beta\mu_{ex}, \tag{22}$$

where $\Lambda = h/\sqrt{\pi m k_B T}$ and the excess chemical potential μ_{ex} is defined by the expression

$$\beta\mu_{ex} = 4\pi\beta\rho \int_0^1 d\lambda \int_0^\infty dr\, r^2 u(r) g(r,\lambda) \tag{23}$$

with λ denoting the charging parameter and $g(r,\lambda)$ the pair correlation function at charging parameter λ.

To calculate the chemical potential we first observe that since the charging parameter λ multiplies the potential energy strength ε, the temperature may be scaled with it, that is, $T \rightarrow T/\lambda$ in the Boltzmann factor appearing in the pair correlation function. Therefore the following variable change may be made in the charging parameter integral for the chemical potential:

$$\int_0^1 d\lambda\, F(\lambda/T) = T \int_T^\infty d\tau\, F(\tau^{-1}).$$

The chemical potentials consequently can be calculated from Eqs. (22) and (23) by computing the pair correlation functions at different temperatures ranging from the temperature in question to a sufficiently high value where the fluid behaves ideally. This procedure is equivalent to changing the charging parameter integral as indicated above. In the actual computation the excess chemical potential is split into the hard sphere and attractive potential contributions

$$\beta\mu_{ex} = \beta\mu_{ex}^{\mathrm{HS}} - 4\pi\beta\varepsilon\rho \int_0^1 d\lambda \int_\sigma^\xi dr\, r^2 g(r,\lambda)$$

and the Percus–Yevick theory results for the hard spheres have been used for μ_{ex}^{HS}.

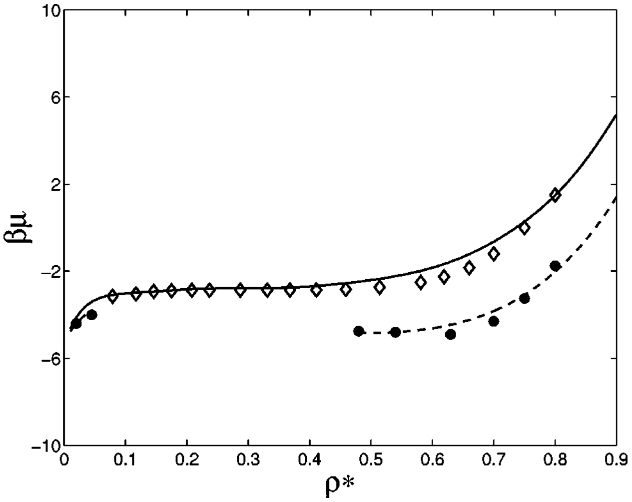

FIG. 4. Chemical potential vs density. The solid curve is for $T^* = 1.25$ and the broken curve is for $T^* = 0.9$. The symbols are the simulation data by Vörtler and Smith [18].

This method is different from the commonly used particle insertion method based on Widom's theory [17]. The chemical potentials, relative to $\ln(\Lambda^3/\sigma^3)$, thus computed for $\gamma = 1.5$ are plotted in Fig. 4 and compared with the simulation results. The solid and broken curves are the results by the present method and the symbols are the simulation results [18].

Both simulation results and the results by the present method, although probably for different reasons, yield vapor and liquid branches of an isotherm whose endpoints are not connected by a single horizontal tie line. To get around this difficulty we exploit the fact that

$$\oint \mu\, d\eta = 0.$$

By using this condition it is possible to perform a Maxwell construction for the coexisting values of the chemical potentials of vapor and liquid phases, and the liquid-vapor coexistence curve can be constructed thereby. The result is presented in Fig. 5, where the solid curve is the liquid-vapor coexistence curve computed by the method described and the symbols are the simulation values. The broken curve is the locus of densities where the integral equation for the pair correlation function fails to yield the solution. The comparison with simulations on the liquid side is poor. But in the liquid region the simulation values have also considerable lateral errors (i.e., in density) and also the Percus–Yevick integral equation is not sufficiently accurate in the neighborhood of the coexisting liquid densities. Nevertheless, it is possible to locate the critical point reasonably well by locating the maximum of the curve. In this way, we find $T_c^* \approx 1.2$ and $\rho_c^* \approx 0.23$ for $\gamma = 1.5$. These values have served as a guide for the calculation of A^* and B^* in the subcritical regime in this work.

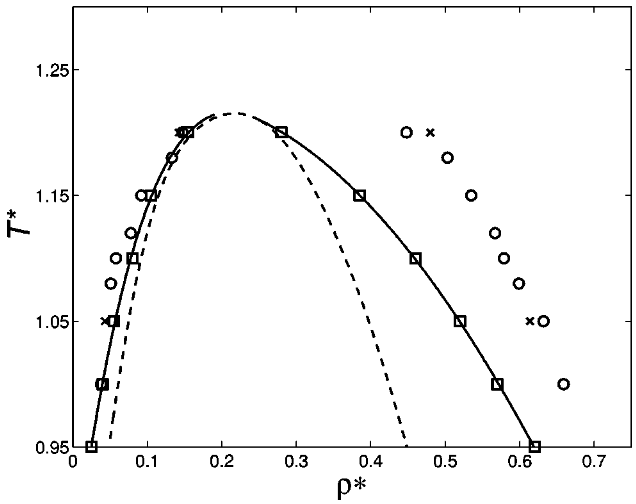

FIG. 5. Liquid-vapor coexistence curve and spinodal curve. The square (□) is the present theory results which are connected by the solid curve to guide the eyes. Other symbols are the simulation values [18]. The broken curve is the spinodal curve.

IV. REDUCED EQUATION OF STATE IN THE SUBCRITICAL REGIME

The virtue of the van der Waals equation of state is its ability to describe many aspects of liquid-vapor equilibrium. The generic van der Waals equation of state has also a promising potential for such capability. Here we would like to provide a glimpse of such a potential for the equation.

The numerical study of the generic van der Waals parameters made in the preceding section strongly suggests that they are nonanalytic functions of density if $T<T_c$. Therefore one may look for nonanalytic phenomenological forms for A^* and B^* and carry out study of the thermodynamics of subcritical fluids obeying the generic van der Waals equation of state. To this end it is useful to organize the generic van der Waals equation of state in a more suitable form, which is reminiscent of the similar equation in the van der Waals theory. By assuming nonanalytic forms for the parameters A^* and B^* we in fact have made a study of the subcritical behavior on the basis of the form of the generic van der Waals equation of state presented below. We hope to report on the details of the study elsewhere.

Let us introduce new reduced variables in reference to the critical state defined by parameters p_c^*, η_c, and T_c^*:

$$\phi=\frac{p^*}{p_c^*}-1, \quad x=\frac{\eta}{\eta_c}-1, \quad t=\frac{T^*}{T_c^*}-1.$$

Also define the following quantities:

$$\zeta^*=\frac{A_c\eta_c^2}{p_c^*}, \quad v^*=B_c\eta_c, \quad \tau^*=\frac{\eta_c T_c^*}{p_c^*},$$

$$\mathcal{A}=A^*/A_c, \quad \mathcal{B}=B^*/B_c,$$

where A_c and B_c are, respectively, A^* and B^* evaluated at the critical point:

$$A_c=A^*(x=0,t=0), \quad B_c=B^*(x=0,t=0).$$

Then the generic van der Waals equation of state can be written as

$$[1+\phi+\zeta^*\mathcal{A}(1+x)^2][1-v^*\mathcal{B}(1+x)]=\tau^*(1+x)(1+t). \tag{24}$$

In the case of the original van der Waals equation of state, $A^*=A_c$ and $B^*=B_c$, which are simply constants, and it can be shown that

$$\zeta^*=3, \quad v^*=\tfrac{1}{3}, \quad \tau^*=\tfrac{8}{3}.$$

The equation of state (24) can be rearranged to the form

$$\phi[1-v^*\mathcal{B}(1+x)]\equiv\Pi(x,t), \tag{25}$$

$$\Pi(x,t)=(D_0+\tau^*t)+(D_1+\tau^*t)x+D_2x^2+D_3x^3+R(x,t), \tag{26}$$

where

$$D_0=\tau^*-(1+\zeta^*)(1-v^*), \quad D_1=\tau^*-2\zeta^*+v^*+3\zeta^*v^*, \tag{27}$$

$$D_2=\zeta^*(3v^*-1), \quad D_3=\zeta^*v^*,$$

and

$$R(x,t)=R_0(x,t)+R_1(x,t)x+R_2(x,t)x^2+R_3(x,t)x^3,$$

with the definitions

$$\begin{aligned} R_0(x,t)&=\zeta^*v^*[\mathcal{A}(x,t)\mathcal{B}(x,t)-1]-\zeta^*[\mathcal{A}(x,t)-1]\\ &\quad+v^*[\mathcal{B}(x,t)-1],\\ R_1(x,t)&=3\zeta^*v^*[\mathcal{A}(x,t)\mathcal{B}(x,t)-1]-2\zeta^*[\mathcal{A}(x,t)-1]\\ &\quad+v^*[\mathcal{B}(x,t)-1],\\ R_2(x,t)&=3\zeta^*v^*[\mathcal{A}(x,t)\mathcal{B}(x,t)-1]-\zeta^*[\mathcal{A}(x,t)-1],\\ R_3(x,t)&=\zeta^*v^*[\mathcal{A}(x,t)\mathcal{B}(x,t)-1]. \end{aligned} \tag{28}$$

Therefore, apart from the term containing $\mathcal{B}$ on the left-hand side of Eq. (25), the R term represents the nonclassical correction to the van der Waals equation of state; every term in $R(x,t)$ is made up of the nonanalytic functions $\mathcal{A}$ and $\mathcal{B}$.

The critical point is defined by

$$\Pi(0,0)=0, \tag{29}$$

$$\Pi^{(1)}(0,0)=\left(\frac{\partial\Pi}{\partial x}\right)_0=0, \tag{30}$$

$$\Pi^{(2)}(0,0)=\left(\frac{\partial^2\Pi}{\partial x^2}\right)_0=0, \tag{31}$$

The derivatives $\Pi^{(1)}(0,0)$ and $\Pi^{(2)}(0,0)$ coincide with the density derivatives of ϕ, $(\partial\phi/\partial x)_0$, and $(\partial^2\phi/\partial x^2)_0$, at the critical point. Since $R(0,0)=0$ at the critical point, the conditions (29)–(31) mean the following:

$$D_0=0, \quad D_1+\left(\frac{\partial R}{\partial x}\right)_0=0, \quad 2D_2+\left(\frac{\partial^2 R}{\partial x^2}\right)_0=0. \tag{32}$$

If the equation of state is treated as a phenomenological expression these three conditions then impose constraints on the functions $\mathcal{A}$ and $\mathcal{B}$. We may further require that $\mathcal{A}$ and $\mathcal{B}$ are such that the third and fourth density derivatives of $\Pi(x,t)$ also vanish at the critical point:

$$\Pi^{(3)}(0,0)=6D_3+\left(\frac{\partial^3 R}{\partial x^3}\right)_0=0, \quad \Pi^{(4)}(0,0)=\left(\frac{\partial^4 R}{\partial x^4}\right)_0=0. \tag{33}$$

These derivatives also coincide with the vanishing third and fourth density derivatives of ϕ at the critical point. Therefore the definition of the critical point by Eqs. (32) and (33) coincides with that of Baehr [19] and others [20,21], who imposed the condition of vanishing first four density derivatives of ϕ at $x=0$ and $t=0$.

On use of the conditions (32) and (33) the right-hand side of the equation of state takes the form

$$\begin{aligned}\Pi(x,t)=&[R_0(x,t)-R_0^{(1)}x-\tfrac{1}{2}R_0^{(2)}x^2-\tfrac{1}{6}R_0^{(3)}x^3-\tfrac{1}{24}R_0^{(4)}x^4]\\&+\tau^*t+[R_1(x,t)-R_1^{(1)}x-\tfrac{1}{2}R_1^{(2)}x^2-\tfrac{1}{6}R_1^{(3)}x^3]x\\&+\tau^*tx+[R_2(x,t)-R_2^{(1)}x-\tfrac{1}{2}R_2^{(2)}x^2]x^2\\&+[R_3(x,t)-R_3^{(1)}x]x^3,\end{aligned} \tag{34}$$

where

$$R_i^{(j)}=\left(\frac{\partial^j R_i}{\partial x^j}\right)_0. \tag{35}$$

When expanded in x away from the singular points of $\mathcal{A}$ and $\mathcal{B}$, the function $\Pi(x,t)$ does not have first four expansion terms at the critical point and the estimate [7] of remainder of the expansion yields a nonclassical fractional exponent for x of the leading term because $\mathcal{A}$ and $\mathcal{B}$ are nonanalytic with respect to x. A nonclassical exponent of the leading term in the temperature expansion for (x_l-x_v), where x_l and x_v are the coexisting liquid and vapor density, respectively, can be shown [7] to arise also because of the nonanalytic $\mathcal{A}$ and $\mathcal{B}$.

In summary, the equation of state at $t=0$, namely, the critical isotherm, may be written as

$$\phi[1-v^*\mathcal{B}(1+x)]=\Pi(x,0) \tag{36}$$

with $\Pi(x,t)$ given by Eq. (34). This equation of state is exact as it stands. If it is to account for the experimental data near $x=0$, then $\Pi(x,0)$ must be nonanalytic with respect to x and its leading term in fact should behave like x^δ with the value of the exponent in the range 4.2–4.5 suggested by experiment. For the t^β behavior the power series in t of ϕ at x_l and x_v can be used with same nonanalytic forms for $\mathcal{A}$ and $\mathcal{B}$ as for the case of the $t=0$ isotherm. These nonclassical behaviors therefore impose certain conditions on A^* and B^* making up the function $\Pi(x,t)$. Therefore, by investigating the nonanalyticity of $\mathcal{A}$ and $\mathcal{B}$ it is possible to study the subcritical behavior of the fluid. This line of study will be reported elsewhere [7].

V. CONCLUDING REMARKS

The van der Waals equation of state expresses in a simple functional form the role of repulsive and attractive intermolecular forces in determining the fluid properties, although it has defects with regard to the critical behavior of the fluids. Despite the defects its great allure has been enduring because of its weightier virtues, and it is this strength of allure that has induced so much research on and with this equation of state for the properties of liquids, and the present work is one of them. The present work, however, is markedly different from the past investigations in the van der Waals equation of state in that we regard the original van der Waals equation of state as a special case of the generic van der Waals equation, which is exact because it is obtained by recasting the exact and formal virial equation of state given in terms of the pair correlation function under the condition that there are two distinctive branches, namely, repulsive and attractive, in the intermolecular force between a pair of particles in the fluid. The aforementioned recasting of the virial equation of state provides us with exact statistical representations of the generic van der Waals parameters A and B in the exact generic van der Waals equation of state, and the original van der Waals equation of state is recovered by taking the low density limit of the statistical expressions for A and B.

These generic van der Waals parameters are then calculated as functions of density and temperature in the case of a square-well potential model by using the Percus–Yevick integral equation for the pair correlation function. We could have readily used the more realistic Lennard-Jones potential model instead of the square-well model, but we have used the latter for some mathematical transparency it provides for the role of the cavity functions and some future analytical work planned. Therefore, on a superficial and cursory reading, it could be easily questioned, since in the present work we are simply recasting some well-known numerical results in another form, what is new after all? However, the recasting is precisely the point, since by recasting a well known statistical mechanical formula, not only are we putting a new light and thereby gaining a great deal of insight into the original van der Waals equation of state itself as well as acquiring a canonical form of equation of state for liquids. But also we are opening up a new way to structure the theory of liquids on and around the van der Waals equation of state, which is known to contain a major portion of truth about the nature of liquids, and to investigate thermodynamic properties of liquids from a fresh viewpoint. We find through the numerical study of the generic van der Waals parameters that the defects and weaknesses of the van der Waals equation of state are indeed removed because the parameters A and B become disjointed functions of density if the temperature is lower than the critical temperature, and thereby become nonanalytic in density and temperature. We believe that the appropriate understanding of nonanalyticity of A and B should enable us to comprehend the critical behavior of the fluids obeying the generic van der Waals equation of state. This will be an additional motivation for studying the generic van der Waals equation of state presented. The merits of the generic van der Waals equation of state lie in identifying the essential objects of study and in the economic way of developing a nonanalytic equation of state by two avenues of approach, phenomenological and statistical mechanical, and one should take these two approaches in parallel and in a synergetic manner. The forms for A and B remain important objects of theoretical investigations, which we hope to pursue further in the future.

To acquire more precise information on A and B in the statistical mechanics approach one needs first of all a better closure for the Ornstein-Zernike equation than the Percus-Yevick closure, which is adequate if the temperature is above the critical point, but is generally subject to errors. The thermodynamically consistent closure recently proposed [22] could be a good starting point in such investigations. Furthermore, numerical solutions of the Percus-Yevick integral equation are difficult to achieve in high precision as the temperature approaches the critical value. This difficulty also should be overcome. Therefore there is a considerable amount of work to be done on the aspects just mentioned.

The free volume in liquids is a difficult quantity to estimate, although the concept appears in many ways in condensed matter physics; examples are the cell and hole theories [13] of liquids, free volume theory [15] of diffusion, and so on. It, in fact, was a quantity that remained elusive to van der Waals himself, according to Klein [12]. The statistical representations of A and B, especially in the high density regime gives a quantitative method of evaluation of the elusive quantity. They can be used to compute the free volume from the molecular viewpoint instead of using it as an adjustable parameter in the theories mentioned. The latest calculation [16] made of the self-diffusion coefficients of liquids by applying the free volume concept based on the generic van der Waals equation of state indicates the utility, for even transport properties, of the equation of state presented in this work.

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