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Comments Concerning a Simple Equation of State of the van der Waals Form

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ABSTRACT

When the Carnahan-Starling equation of state for hard spheres is combined with a simple attractive term, the molecular size parameter b for argon (as obtained from critical data) is much closer to the "correct" value than that obtained from the empirical Redlich-Kwong equation.

For the critical isotherm for argon, the best simple form of the attractive term lies between the two common forms, proposed by van der Waals and by Redlich. At constant temperature, the attractive contribution to the compressibility factor is proportional to $(v+0.2b)^{-1}$ where v is the molar volume. This proportionality is in agreement with results for a square-well fluid recently reported by Sandler.

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Since van der Waals presented his equation of state in 1873, numerous attempts have been made to improve that equation while retaining its physical significance and its algebraic simplicity. This note discusses some of these attempts and presents a slightly new modification which, perhaps, offers some advantages over those presented earlier.

The essence of van der Waals' equation is separation of the compressibility factor z into two parts; the first arises from repulsive forces (finite size of the molecules) and the second from a potential field (attractive forces between molecules) as discussed in depth by Kac[1] and Rowlinson[2]. Thus

$$z = \frac{Pv}{RT} = z^{rep} + z^{att} \tag{1}$$

where P is pressure, v is volume per mole and RT has its usual meaning.

As discussed in numerous texts, van der Waals proposed that

$$z^{rep} = \frac{v}{v-b} \tag{2}$$

and

$$z^{att} = \frac{a}{RTv} \tag{3}$$

where $b=(2/3)\pi N_{Av}\sigma^3$ (N_{Av} = Avogadro's number and σ = molecular diameter) and a is a constant which reflects the strength of the intermolecular attractive potential.

Martin's review articles[3] indicate that while only a few authors have been concerned with significant changes in Equation (2), many proposals have been made to change Equation (3). In

this context, "significant" means changes in the volume dependence of z; we are not now concerned with possible effects of temperature on "constants" a and b although we briefly return to that effect later.

In the engineering literature, the best known significant empirical variations in z^{att} are those by Redlich and Kwong[4] and by Peng and Robinson[5]. Some others are discussed by Martin[3], by Abbott[6], and by Fuller[7]. All of these authors are concerned with maintaining an equation of state such that pressure P is a cubic function of v at constant temperature. A cubic function is desirable so that when P and T are fixed, it is possible to find v analytically.

A truly significant change in z^{rep} follows from the theoretical work of Percus and Yevick as given by Carnahan and Starling[8] who write

$$z^{rep} = \frac{1+\xi+\xi^2-\xi^3}{(1-\xi)^3} \tag{4}$$

where $\xi \equiv \frac{b\rho}{4}$ and molar density $\rho = v^{-1}$.

We refer to Equation (4) with notation z^{cs}. Equation (4) reduces to Equation (2) for small values of reduced density ρb, but for most reduced densities, the difference between Equations (2) and (4) is very large as shown in Figure 1, whenever the same value of b is used in both equations. However, this difference can be somewhat reduced by using in Equation (2) an "effective" value for b, designated by b' in Figure 1. In this illustrative example 2b'=b.

The serious theoretical deficiencies in Equation (2) were recognized by van der Waals and coworkers more than 80 years ago; there were several early attempts to remove these deficiencies but no satisfactory result was obtained until Percus and Yevick's work based on the Ornstein-Zernike equation for the direct correlation coefficient. There is no question about the theoretical superiority of Equation (4), compared to Equation (2), as shown by computer-simulation studies of Ree and Hoover[9]. Nevertheless, as lamented by Henderson[10], Equation (2) persists, in part because Equation (4) does not lead to a cubic equation when P is a function of v.

In an oft-quoted paper, Carnahan and Starling[11] discussed two realistic equations of state

$$z^{csvdw} = z^{cs} - \frac{a}{RTv} \tag{5}$$

and

$$z^{csrk} = z^{cs} - \frac{a}{RT^{3/2}(v+b)} \tag{6}$$

The second part of Equation (5) is van der Waals' original Equation (3) and the second part of Equation (6) is from the equation of Redlich and Kwong. Constants a and b are found from the critical conditions; at the critical point (designated by subscript c),

$$\left[\frac{\partial P}{\partial v}\right]_{T_c} = \left[\frac{\partial^2 P}{\partial v^2}\right]_{T_c} = 0 \tag{7}$$

For Equation (5), $a=1.38RT_c v_c$ and $b=0.5216v_c$. Further, $z_c=\frac{P_c v_c}{RT_c}=0.359$. Therefore, we can also write $a=0.4954R^2T_c^2/P_c$ and

$b=0.1873RT_c/P_c$.

For Equation (6), $a=1.463RT_c^{3/2}v_c$ and $b=0.3326v_c$. Further, $z_c=0.316$. Therefore, we can also write $a=0.4619R^2T_c^{5/2}/P_c$ and $b=0.105RT_c/P_c$.

Since the theoretical value of z_c is not equal to the experimental value, constants a and b evaluated from experimental T_c and v_c, are not equal to constants a and b evaluated from experimental T_c and P_c. To illustrate, Figures 2, 3, and 4 show calculated critical isotherms for argon; these are compared with experimental compressibility factors taken from IUPAC[12].

Figure 2 shows the critical isotherm for argon calculated with the Redlich-Kwong equation and with the Peng-Robinson equation. The Redlich-Kwong equation uses Equation (2) and the second part of Equation (6).

Also shown in Figures 2, 3, and 4 are numerical values of b for argon. We compare these to the "correct" value as obtained from the detailed study by Dymond and Alder[13] who reduced extensive second-virial-coefficient and dilute-gas transport data to obtain a "true" value of $\sigma=0.328$nm for argon. We note that b (Redlich-Kwong) is much too small, about one-half that obtained from Dymond and Alder's work. In other words, the Redlich-Kwong equation uses an effective b (as shown in Figure 1) whose physical significance is doubtful.

When Equations (5) and (6) are used, the numerical values of b are "better" than that of Redlich and Kwong in the sense that

they are closer to the "correct" b of Dymond and Alder.

Figure 4 shows that for densities to about the critical, there is no significant difference between Equations (5) and (6) but at higher densities, the difference becomes large. Since T is a constant along the critical isotherm, the difference follows from using (v+b) in the second part of Equation (6) rather than v in the second part of Equation (5). When compared to experiment at high densities, z (Eq.5) is too high and z (Eq.6) is too low. Therefore, it appears reasonable to postulate an equation for the critical isotherm of the form

$$z = z^{cs} - \frac{a}{RT(v+nb)} \tag{8}$$

where n is a constant such that $0<n<1$.

We can obtain n empirically but before we do so, it is helpful to consider first a new semi-theoretical equation of state proposed by Sandler[14] which is

$$z = z^{cs} - \frac{n^{(0)}\gamma b}{v+n^{(1)}\gamma b} \tag{9}$$

where

$$\gamma = \exp(\varepsilon/2kT) - 1$$

$$n^{(0)} = n^{(1)} Z_{max},$$

and

$$n^{(1)} = \text{a constant} = \frac{3}{2\pi\sqrt{2}}$$

Here Z_{max} is the maximum coordination number, i.e. the coordination number at high density; ε is a characteristic potential-

energy parameter and k is Boltzmann's constant.

When the critical condition (Eq.7) is applied, we obtain $\varepsilon/kT_c=0.7977$ and $b=0.4656v_c$. Since $z_c=0.348$, we can rewrite $b=0.1620RT_c/P_c$; for argon, we obtain $b=41.49cm^3/mole$.

The critical isotherm which follows from Equation (9) is

$$z = z^{cs} - \frac{2.9786b}{v+0.1655b} \qquad (10)$$

which suggests that in Equation (8), n should be 0.1655. Empirically, when attention is confined to the critical isotherm of argon, it is not possible to specify n to more than one significant figure. We therefore suggest that the simplest and in some sense "best" van der Waals-type equation of state is Equation (8) with n=0.2.

Figures 5 and 6 compare experimental with calulated compressibility factors for the critical isotherm of argon; calulations are based on Sandler's equation first, using constants found from experimental values for T_c and v_c and second, using experimental values for T_c and P_c.

When the critical condition (Eq.7) is applied to Equation (8) with n=0.2, we find that $b=0.15787RT_c/P_c$ and $a=0.48055R^2T_c^2/P_c$. Figure 7 shows experimental and calculated compressibility factors for argon along the critical isotherm; calculations are based on Equation (8) with n=0.2. We note that the value for b is only 10% below that given by Dymond and Alder. We find that if we set n at some value below 0.2, the critical isotherm becomes too steep at high densities; if we set n equal to some value above 0.2, the

isotherm becomes too flat at high densities. Setting n=0.2 represents a reasonable compromise.

It appears that all simple equations of the van der Waals form are likely to exhibit serious deficiencies along the critical isotherm at densities between the critical and about twice the critical.

While temperature-independent values of a and b give a reasonable representation of thermodynamic properties at temperatures other than the critical, significantly improved agreement with experiment can be obtained by allowing both constants to decrease with rising temperature. We do not here discuss an optimized fit but conclude with a reasonable first approximation

$$\frac{a}{a_c} = 1 - 0.23052(1-T_c/T)$$

$$\frac{b}{b_c} = 1 - 0.12902(1-T_c/T)$$

where a_c and b_c are the values of a and b at the critical isotherm. These relations for a and b are based on experimental vapor-pressure data from the triple point to about $0.92T_c$ and on density data to 1000 bar in the temperature region 200 to 1000K. With these results we obtain good vapor pressures and liquid volumes as well as good supercritical compressibility factors for argon.

The goodness of fit for vapor pressures is about 6%; for saturated liquid volumes it is about 7% and for supercritical densities it is about 2%. Calculated second virial coefficients

agree well with experiment but they are somewhat too positive at low temperatures.

For temperatures below the critical, this goodness of fit is a little worse than that obtained with the algebraically much simpler Soave-Redlich-Kwong equation; at temperatures above the critical, the goodness of fit is about the same.

It appears that the original van der Waals form for z^{rep} [Equation (2)] has remarkable empirical value even though -- as van der Waals recognized many years ago -- it is in serious error at high densities if its physical (hard-sphere) significance is taken seriously. In the Soave-Redlich-Kwong equation, the significance of constant b is obscure; it is somehow related to molecular size but it is <u>not</u> correctly given by the usual formula relating b to molecular diameter σ when a "correct" value of σ is used. By contrast, constant b in the Carnahan-Starling formula [Equation (4)] has a meaningful definition, as indicated by the near equality of b in Equation (8) with the "correct" result of Dymond and Alder. If our object is to represent thermodynamic properties of a pure fluid, then there is little justification for using Equation (4) instead of Equation (2). But it may be that when we try to represent the properties of fluid mixtures, an equation of state using a (nearly) "correct" b will give better results. That tentative conclusion is supported by computer-simulation studies[14] but it will be difficult to persuade practical-minded engineers unless evidence can also be obtained to show that a "correct" b is truly superior to an "effective" b for thermodynamic calculations

applied to real mixtures. The theoretical superiority of Equation (4) over Equation (2) is beyond doubt. Efforts at Berkeley are now in progress to determine if that superiority also holds for engineering applications.

Nomenclature

a	a constant which reflects the strength of the intermolecular attractive potential
b	a constant which reflects the finite size of the molecules
k	Boltzmann's constant
n	constant (Eq. 8)
$n^{(0)}$	constant (Eq. 9)
$n^{(1)}$	constant (Eq. 9)
N_{Av}	Avogadro's number
P	pressure
R	gas constant
T	temperature
v	molar volume
z	compressibility factor
Z_{max}	maximum coordination number

Greek Letters

γ	a function of temperature (Eq. 9)
ε	energy parameter
ξ	reduced density
ρ	molar density
σ	molecular diameter

Subscripts

c	critical

Superscripts

att	attractive
cs	Carnahan-Starling
csrk	Carnahan-Starling/Redlich-Kwong
csvdw	Carnahan-Starling/van der Waals
rep	repulsive

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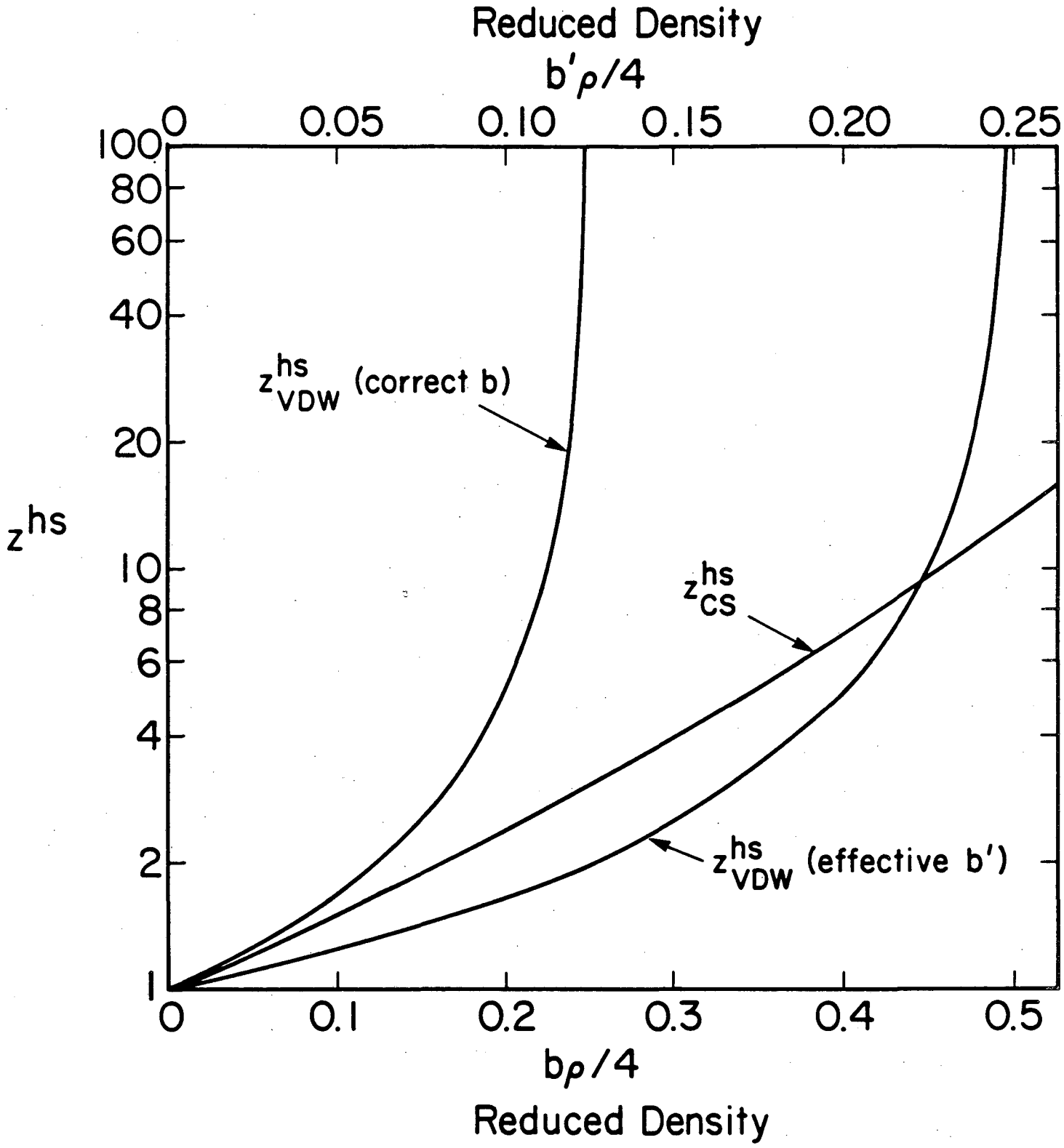
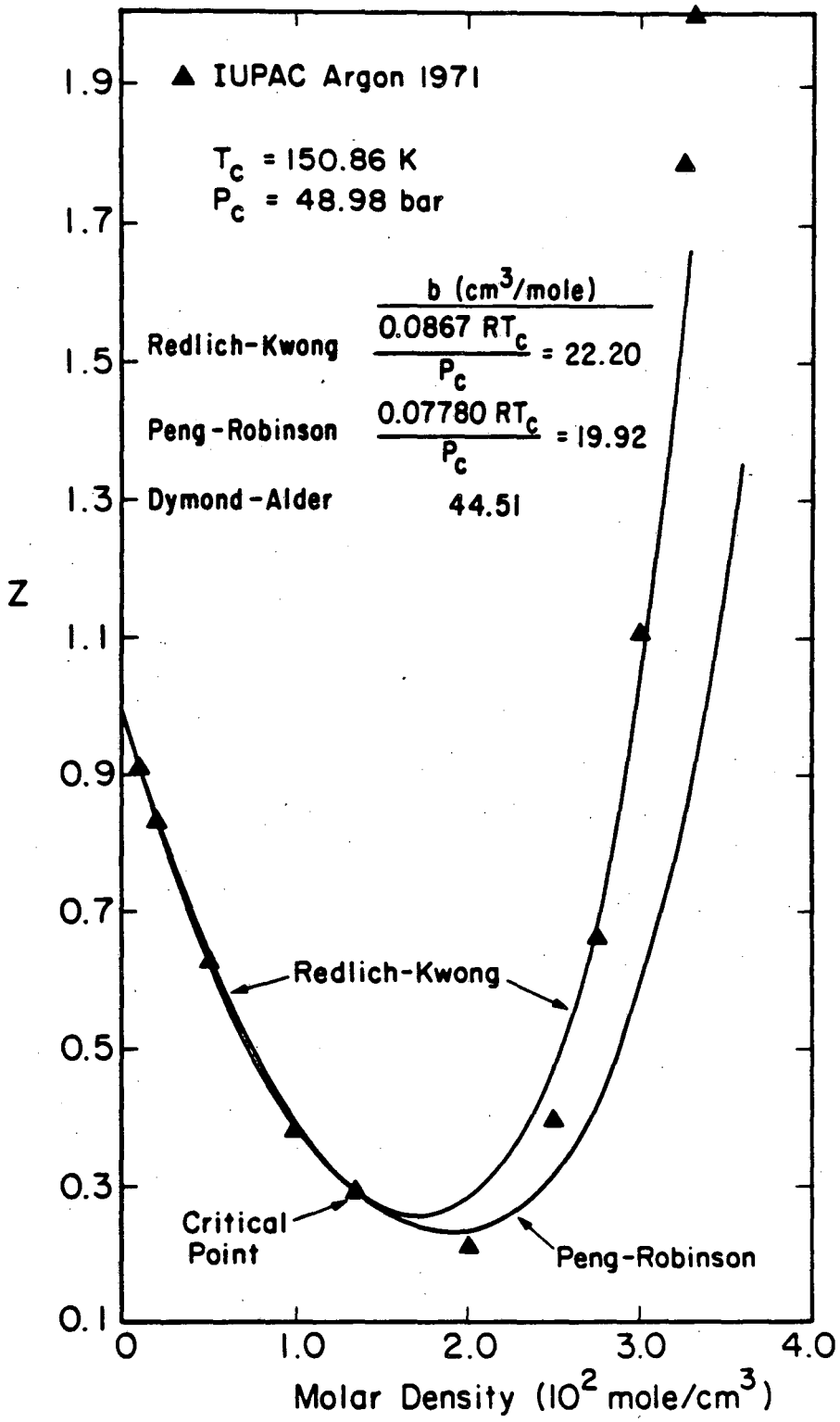


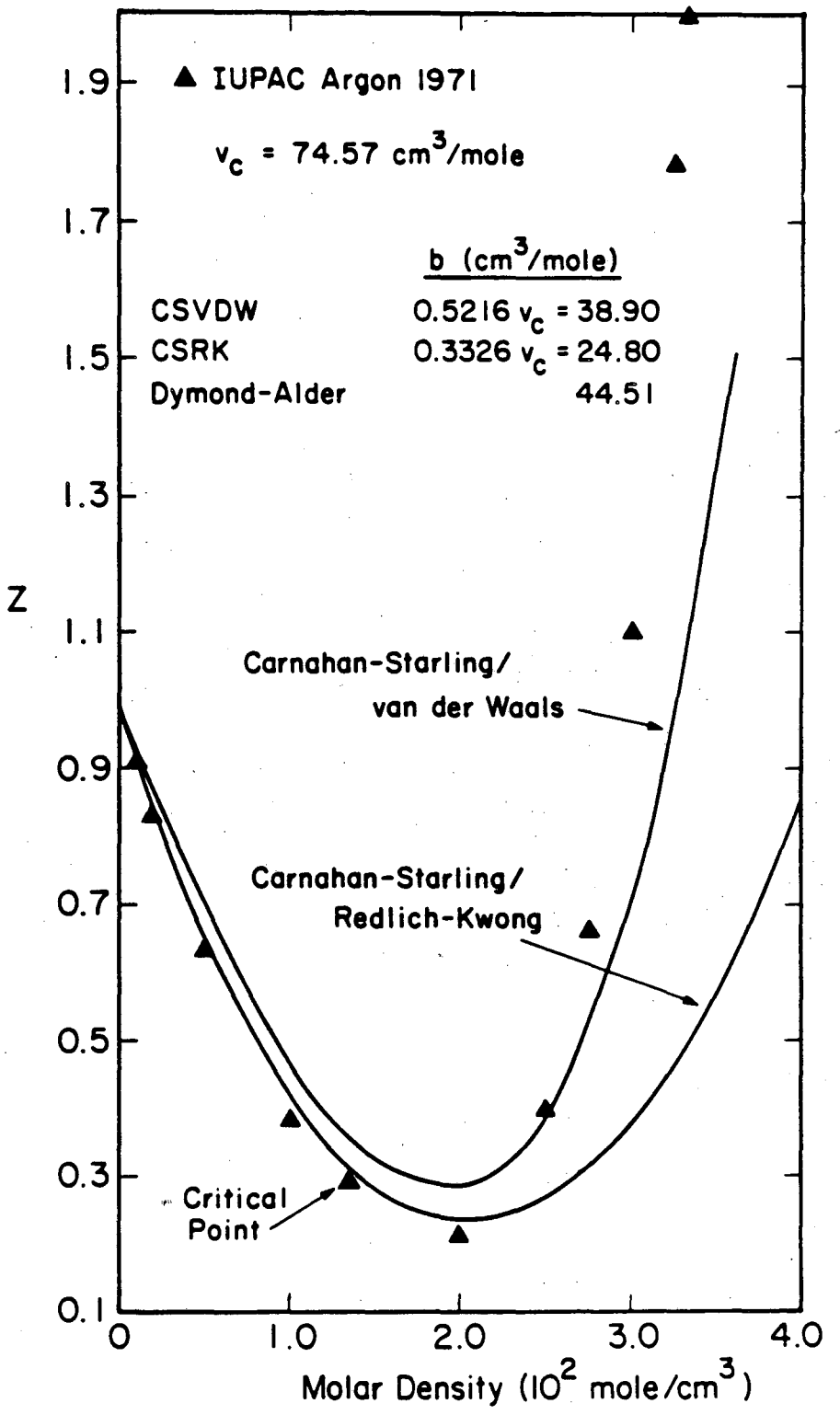
Compressibility Factor for a Hard-Sphere (hs) Fluid. Comparison of Carnahan-Starling (CS) and van der Waals (VDW) Equations at the Same Density ρ.

Figure 1



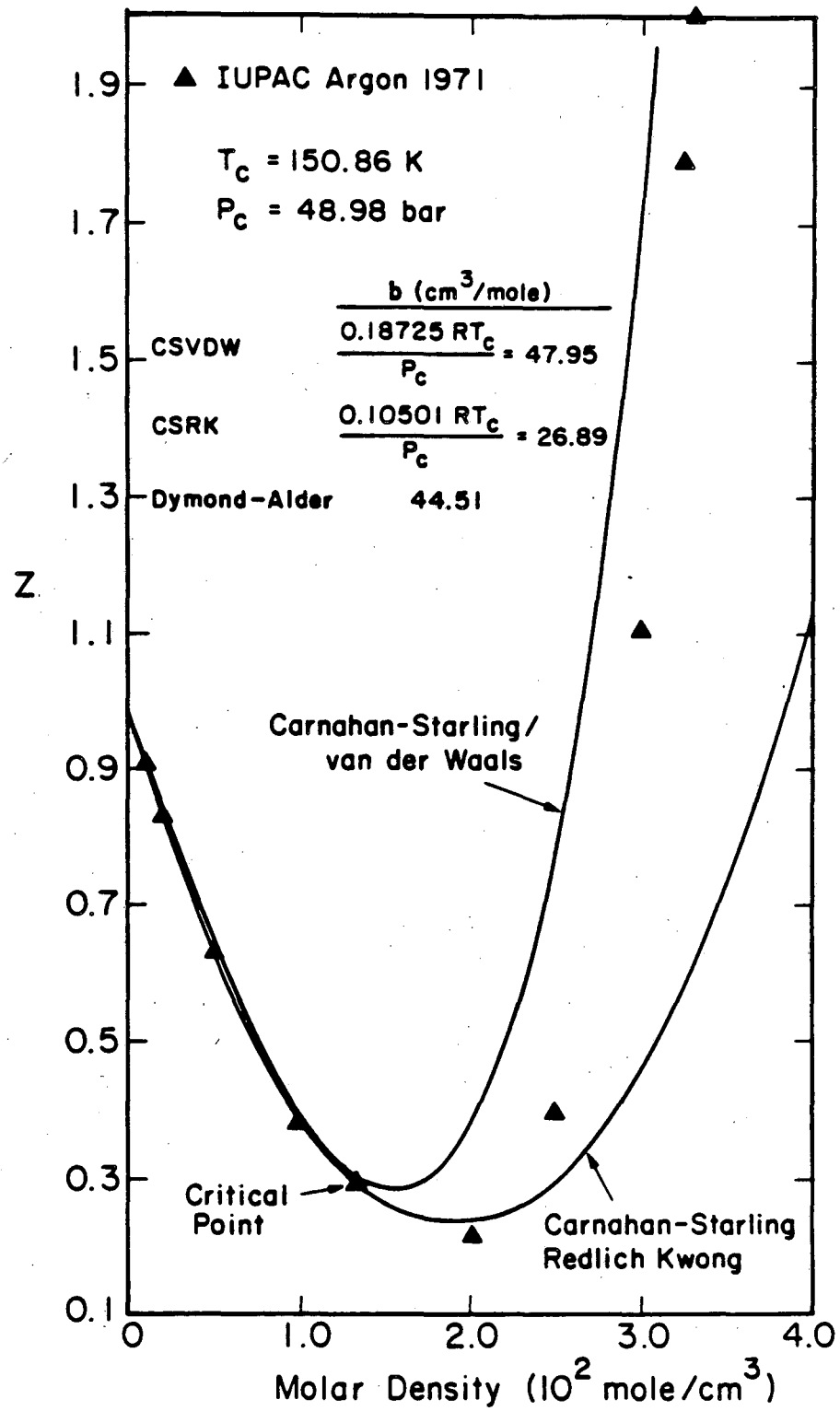
COMPRESSIBILITY FACTOR Z FOR ARGON
ALONG THE CRITICAL ISOTHERM

Figure 2



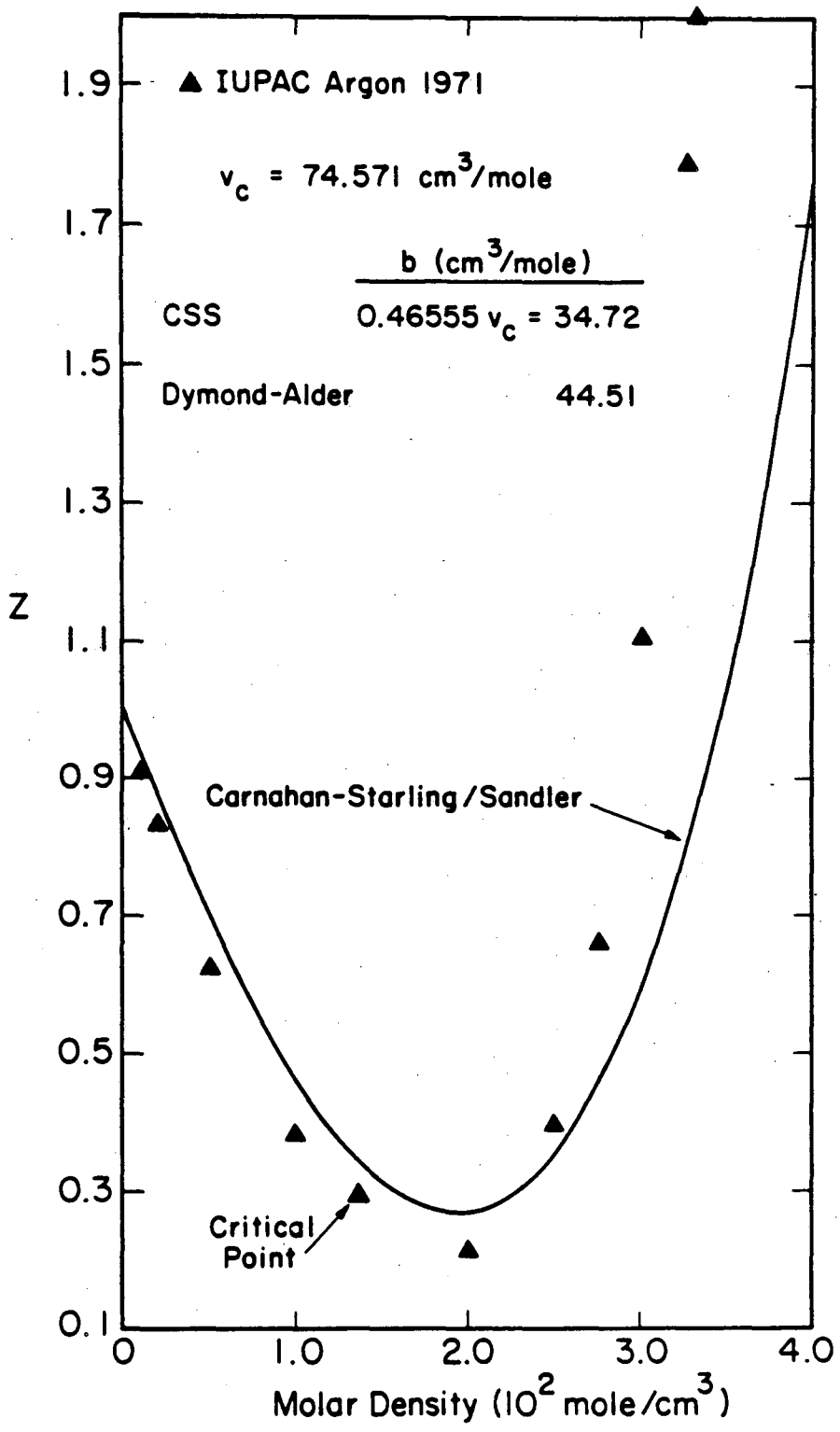
COMPRESSIBILITY FACTOR Z FOR ARGON ALONG THE CRITICAL ISOTHERM

Figure 3



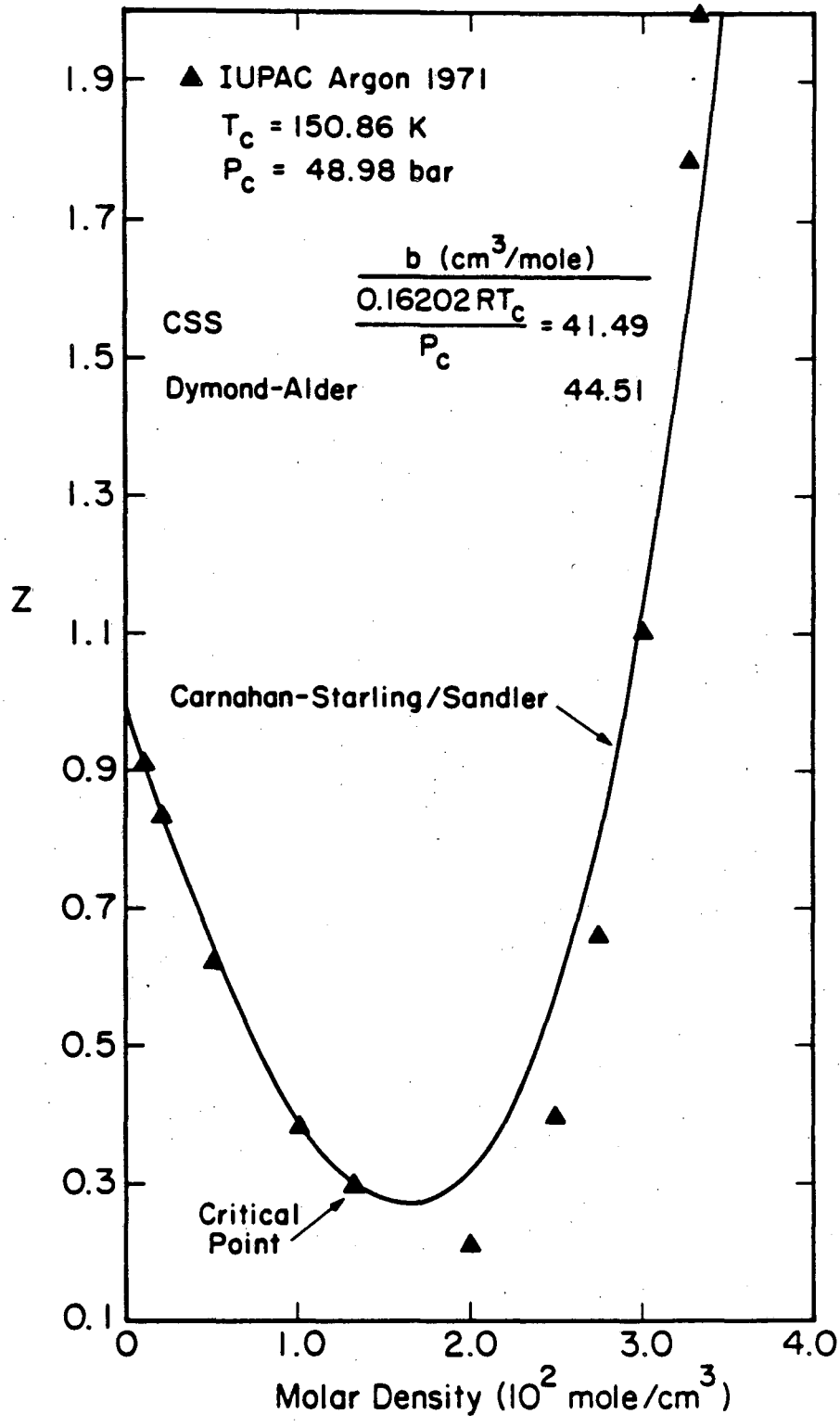
COMPRESSIBILITY FACTOR Z FOR ARGON
ALONG THE CRITICAL ISOTHERM

Figure 4



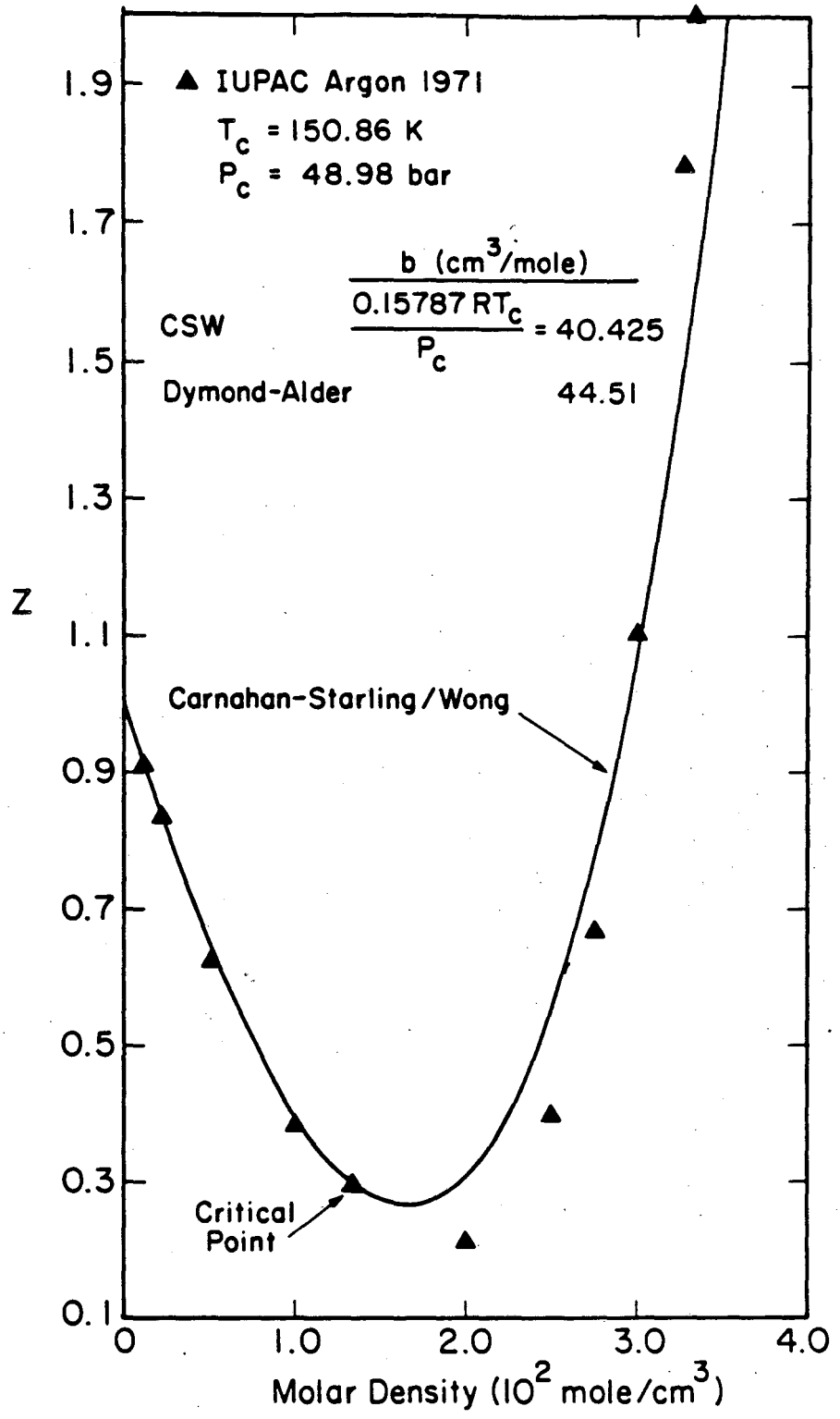
COMPRESSIBILITY FACTOR Z FOR ARGON ALONG THE CRITICAL ISOTHERM

Figure 5



COMPRESSIBILITY FACTOR Z FOR ARGON ALONG THE CRITICAL ISOTHERM

Figure 6



COMPRESSIBILITY FACTOR Z FOR ARGON ALONG THE CRITICAL ISOTHERM

Figure 7

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