Use of The Velocity of Sound in Predicting the PVT Relations

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ABSTRACT

Thermodynamic properties of fluids are generally calculated from the PVT relations through equations of state. The majority of existing equations of state require the critical properties or intermolecular potential energy parameters as their input data. In many cases, such properties are neither available nor they can be accurately estimated.

One accessible and accurately measurable property of substances is the velocity of sound. In this report a method is introduced through which one can predict the PVT behavior of fluids using the velocity of sound data. A general mathematical relationship,

$$c^2 = c^2_{hs} + \frac{-v^2}{M} \int_T^\infty \left(\frac{\partial^2 T}{\partial v^2}\right)_s \left(\frac{\partial s}{\partial T}\right)_v dT$$

expressing the velocity of sound, c, in terms of the hard-core velocity of sound, c_{hs}, and thermodynamic properties is derived. One may use this equation to extract PVT data from cVT data, or vice versa. As an example the virial coefficients, the Lennard-Jones intermolecular potential parameters, and the constants of the van der Waals equation of state for a number of pure fluids are calculated using the velocity of sound data. Utility of this method is particularly attractive for such compounds as heavy hydrocarbons, unstable fluids, and newly designed molecules for which intermolecular parameters and critical properties are not available.

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INTRODUCTION

Equations of state are generally used to estimate thermodynamic properties of gases, liquids, and solids necessary in design and phase behavior calculations.   In most of the equations of state such as the van der Waals, Redlich-Kwong equations, etc., critical properties or intermolecular potential energy parameters are needed as input data to estimate constants in the equations. Properties calculated through equations of state are sensitive to the values of input data used as demonstrated by various investigators (Whitson, 1984; Chorn and Mansoori, 1988). Measured values of critical properties are available for some compounds, but for heavy materials such data cannot accurately be predicted. The main objective of this work is to look at another property, the velocity of sound, which is directly measurable and can be used for evaluation of constants in equations of state instead of critical constants or intermolecular potential energy parameters. Colgate, et al. (1992) have shown how the velocity of sound can be used to predict critical properties. In this work, we show how velocity of sound data can replace the critical constants to estimate the virial coefficients, the van der Waals constants, the Lennard-Jones potential parameters and other equation of state constants.

The basic thermodynamic relation for the velocity of sound in a medium is:

$$c^2 = \frac{-v^2}{M}\left(\frac{\partial P}{\partial v}\right)_s \tag{1}$$

where c is the velocity of sound, v is the molar volume and M is the molecular weight. Using thermodynamic property relations (Prausnitz, et al., 1986) it can be shown that eq. 1 is equivalent to:

$$c^2 = (-\gamma v^2/M)(\partial P/\partial v)_T = (\gamma/M)(\partial P/\partial \rho)_T \tag{2}$$

in which γ is the heat capacities ratio ($= C_p/C_v$) and ρ is the molar density ($= 1/v$) Considering that the isothermal compressibility, κ_T, is defined as:

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \tag{3}$$

The velocity of sound in terms of isothermal compressibility becomes:

$$c^2 = \frac{\gamma}{M\rho\,\kappa_T} \tag{4}$$

Knowing that the velocity of sound is a state function, an equation of state can be developed for the velocity of sound in terms of temperature and density as the independent thermodynamic variables.

VELOCITY OF SOUND EQUATION OF STATE

It was shown by Alem and Mansoori (1984) that the expression for the entropy departure of a hard-sphere fluid can be used for entropy departure of a real fluid provided the hard-sphere diameter is taken to be dependent on temperature and density. Using the Carnahan-Starling equation of state for a hard-sphere fluid the entropy departure from the ideal gas can be derived,

$$\left(s - s^{id}\right)_{hs} = -\frac{R\eta(4 - 3\eta)}{(1-\eta)^2} \tag{5}$$

in which η is the dimensionless packing fraction defined as:

$$\eta = (\pi/6) N_a \rho d^3 \tag{6}$$

N_a is the Avogadro number, d is the hard-sphere diameter, and ρ is the molar density. As shown by Alem and Mansoori (1984) for non-associating fluids, d, in general, can be taken as a linear function of $1/T$ and ρ, i.e., $d = d_0 + d_1\rho + d_2/T + d_3\rho/T$. From eq. 5 we have:

$$s = f(T, v) \tag{7}$$

Since c is a state function, we can write:

$$c = c(s, v) \tag{8}$$

Differentiating eq. 1 with respect to s at constant v gives:

$$2c\,dc = \frac{-v^2}{M}\left\{\frac{\partial}{\partial s}\left[\left(\frac{\partial p}{\partial v}\right)_s\right]_v\right\}ds \qquad \textit{at constant v} \tag{9}$$

From eq. 7 we have:

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT \qquad \textit{at constant v} \tag{10}$$

We also have the following mathematical identity:

$$\frac{\partial}{\partial s}\left[\left(\frac{\partial p}{\partial v}\right)_s\right]_v = \frac{\partial}{\partial v}\left[\left(\frac{\partial p}{\partial s}\right)_v\right]_s \tag{11}$$

and from the Maxwell relations:

$$\left(\frac{\partial p}{\partial s}\right)_v = -\left(\frac{\partial T}{\partial v}\right)_s \tag{12}$$

Substituting eqs. 10, 11 and 12 into eq. 9 we get:

$$2\,cdc = \frac{v^2}{M}\left\{\frac{\partial}{\partial v}\left[\left(\frac{\partial T}{\partial v}\right)_s\right]_s\right\}\left(\frac{\partial s}{\partial T}\right)_v dT \qquad \text{at constant } v \tag{13}$$

where $\left(\dfrac{\partial T}{\partial v}\right)_s$ can be determined from eq. 7:

$$\left(\frac{\partial T}{\partial v}\right)_s = -\frac{(\partial s/\partial v)_T}{(\partial s/\partial T)_v} \tag{14}$$

When $T\to\infty$ we have $c\to c_{hs}$, and integrating eq. 13 gives:

$$c^2 = c^2_{hs} + \frac{-v^2}{M}\int_T^\infty \left(\frac{\partial^2 T}{\partial v^2}\right)_s\left(\frac{\partial s}{\partial T}\right)_v dT \tag{15}$$

c_{hs} can be estimated from either eq. 1 or eq. 2 using the Carnahan-Starling hard-sphere equation of state. Eq. 15 is a general mathematical relationship for the velocity of sound equation of state which has the following general form:

$$c = c(T, v) \tag{16}$$

One can use Eq. 15 to extract PVT data from cVT data, or vice versa. Also provided the PVT equation of state for a substance is available one can use Eq. 15 to obtain the parameters of that equation of state from the velocity of sound, cVT data.

ESTIMATION OF EQUATION OF STATE CONSTANTS FROM THE VELOCITY OF SOUND

Although eq. 15 can be applied to any PVT relation, here as an example, we use the virial and Carnahan-Starling modified version of the Lennard-Jones equations of state to obtain their constants from velocity of sound data. Assuming equality of the hard-sphere and real fluid entropy departures is valid, the packing fraction of hard-spheres can be calculated from entropy data (eq. 5):

$$\eta = (\pi/6)\, \rho\, N_a d^3 = \left\{2 - (s - s^{id})/R - [4 - (s - s^{id})/R]^{1/2}\right\} / \left\{3 - (s - s^{id})/R\right\} \tag{17}$$

Calculated values of d from eq. 17 in the gas phase indicate the following simpler relation between the hard-core diameter, d, and T:

$$d = d_0 + d_1/T \tag{18}$$

Using the virial equation, truncated after the third term, we get:

$$Z = \frac{pv}{RT} = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} \tag{19}$$

For a hard-sphere fluid (when $T \to \infty$) we have:

$$Z_{hs} = \lim_{T \to \infty} Z = 1 + \frac{B_{hs}}{v} + \frac{C_{hs}}{v^2} \tag{20}$$

Since entropy departure from the ideal gas reference state of unit pressure is equal to:

$$s - s^{id} = \int_{\infty}^{v} \left[\left(\frac{\partial p}{\partial T}\right)_v - \frac{R}{v} \right] dv \tag{21}$$

by applying eqs. 19 and 20 into eq. 21 we get:

$$\left[\frac{s - s^{id}}{R} \right]_{real\ fluid} = -\left\{ \ln p + \frac{B + TB'}{v} + \frac{C + TC'}{2v^2} \right\} \tag{22}$$

$$\left[\frac{s - s^{id}}{R} \right]_{hard\ sphere} = -\left\{ \ln p + \frac{B_{hs}}{v} + \frac{C_{hs}}{2v^2} \right\} \tag{23}$$

where B' and C' are the first order derivatives of B and C with respect to

temperature. Equating the right-hand-sides of eqs. 22 and 23 results in the following relations:

$$TB' + B = B_{hs} \tag{24}$$

$$TC' + C = C_{hs} \tag{25}$$

For a hard-sphere fluid, the Carnahan-Starling equation of state gives the following relations for the second and the third virial coefficients (Walas, 1985):

$$B_{hs} = (2/3) \pi N_a d^3 \tag{26}$$

$$C_{hs} = (5/18) \pi^2 N_a{}^2 d^6 \tag{27}$$

Non-homogeneous differential equations 24 and 25 can be solved using eqs. 18, 26, and 27. The final solutions for B and C are in the following forms:

$$B(T) = q_0 \frac{\ln T}{T} + \sum_{n=0}^{3} \frac{P_n}{T^n} \tag{28}$$

$$C(T) = q_1 \frac{\ln T}{T} + \sum_{n=0}^{6} \frac{L_n}{T^n} \tag{29}$$

Parameters q_n, P_n and L_n are defined in Table 1. As it is shown in Table 1 since parameters k_1, k_2, d_0 and d_1 are all known, only parameters p_1 and L_1 are unknown. These may be determined from velocity of sound data. Substituting eq. 19 into eq. 2 would result in the following relation for the velocity of sound:

$$c^2 = \frac{\gamma RT}{M} [1 + \rho (2B + 3C\rho)] \tag{30}$$

From thermodynamic relations for C_p and C_v when eq. 19 is used for the PVT relation, the following expressions can be derived for the heat capacities:

$$C_p = C_p{}^{id} - R \left[\frac{T^2 B''}{v} - \frac{(B - TB')^2 - C + TC' - T^2 C''/2}{v^2} \right] \tag{31}$$

$$C_v = C_v{}^{id} - R \left[\frac{2TB' + T^2 B''}{v} - \frac{TC' + T^2 C''/2}{v^2} \right] \tag{32}$$

B" and C" are the second derivatives of B and C with respect to temperature

which can be obtained by differentiating eqs. 28 and 29.

Using experimental data of the velocity of sound, parameters p_1 and L_1 can be determined from eq. 30. From these parameters, complete forms of B(T) and C(T) will be determined from eqs. 28 and 29.

TABLE 1

Algebraic Expressions of Parameters of Equations 28 & 29

Equation 28	Equation 29
$k_1 = (2/3)\pi N_a = 1.26 \times 10^{24}$	$k_2 = (5/18)\pi^2 N_a^2$
$q_0 = 3k_1 d_0^2 d_1$	$q_1 = 6k_2 d_0^5 d_1$
$P_0 = k_1 d_0^3$	$L_0 = k_2 d_0^6$
$P_1 = $ Integration constant from eq. 24	$L_1 = $ Integration constant from eq. 25
$P_2 = -3k_1 d_0 d_1^2$	$L_2 = -15k_2 d_0^4 d_1^2$
$P_3 = -(1/2)k_1 d_1^3$	$L_3 = -10k_2 d_0^3 d_1^3$
	$L_4 = -5k_2 d_0^2 d_1^4$
	$L_5 = -(3/4)k_2 d_0 d_1^5$
	$L_6 = -(1/5)k_2 d_1^6$

THE LENNARD-JONES CONSTANTS

The Carnahan-Starling modified form of the Lennard-Jones equation of state is in the following form (Rao and Dutta, 1983; Rao and Gupta, 1985):

$$P = \frac{RT}{v}\left[\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} - \frac{32\epsilon\eta}{3k_BT}\right] \tag{33}$$

where k_B is the Boltzman constant, σ is the molecular size parameter and ϵ is the molecular energy parameter in the Lennard-Jones potential. Here the packing fraction, η, is defined in terms of parameter σ:

$$\eta = (\pi/6)\rho N_a \sigma^3 \tag{34}$$

Using eq. 33 for the PVT relation, the velocity of sound, c, can be estimated through eq. 2 in a similar way as for the virial equation of state.

Eq. 15 can also be applied to any other equation of state such as the van der Waals equation in a similar manner.

RESULTS AND DISCUSSION

The data for methane as reported by Goodwin (1974) are used to obtain the virial coefficients and the Lennard-Jones potential parameters from the velocity of sound data as discussed in the previous sections. Using the reported data for entropy of methane, the methane hard-core diameter was calculated through eq. 17. Values of d_0=2.516 [10^{-10}m] and d_1=554.16 [10^{-10}m x °K] appearing in eq. 18 were determined from the methane entropy data. With the knowledge of d_0 and d_1 all the parameters in eqs. 28 and 29 except p_1 and L_1 can be determined using the equations reported in Table 1. For simplicity we use the virial equation truncated after its second term and from eq. 30 parameter p_1 in eq. 28 can be determined by minimizing the differences between values of c from eq. 30 and the experimental values. Value of p_1 for methane in the temperature range of 90-500 K and pressure up to 100 bar was determined to be -81. Therefore, from eq. 28 and Table 1, the following relation for the second virial coefficient of methane can be derived:

$$B(T) = 13.274\frac{\ln T}{T} + 0.0201-81/T-2.924\times10^3/T^2-0.1073\times10^6/T^3 \tag{35}$$

where B is in m^3/kmol. Predicted values of c from eq. 30 using eq. 35 for B are within 0.4% of experimental values for the 200 data points tested. Eq. 35 can be further simplified into the following form for the gas phase:

$$B(T) = 28.54\frac{\ln T}{T} - 0.0194-165.82/T \tag{36}$$

Predicted values of the velocity of sound from eq. 36 are within 0.47% of the experimental values. The second virial coefficient for methane from eq. 36 versus the data reported by Dymond and Smith (1969) are shown in Fig. 1. Except at some intermediate temperatures, good agreement exists between eq. 36, which is derived from the velocity of sound, and the experimental data reported by Dymond and Smith. Predicted compressibilities from eq. 36 and Dymond and Smith data are compared with the experimental values in Fig. 2. For over 200 data points eq. 36 gives an average deviation of 0.5% while Dymond and Smith data produce Z values within 0.8% of the experimental values reported by Goodwin (1974).

The second virial coefficients in the form of Eq. 36 were also determined for ethane and propane from the data on the velocity of sound. The results as well as the data sources are given in Table 2.

The Carnahan-Starling modified version of the Lennard-Jones equation of state (eq. 34) is used to obtain the Lennard-Jones parameters from

the velocity of sound data as it was discussed earlier in this report. Values obtained for these parameters from the velocity of sound as well as those obtained from the viscosity and the second virial coefficient reported by Hirschfelder et al. (1964) for methane, ethane and propane are reported in Table 3. Absolute average deviations for estimating compressibility factors from the Lennard-Jones parameters are also reported in Table 3.
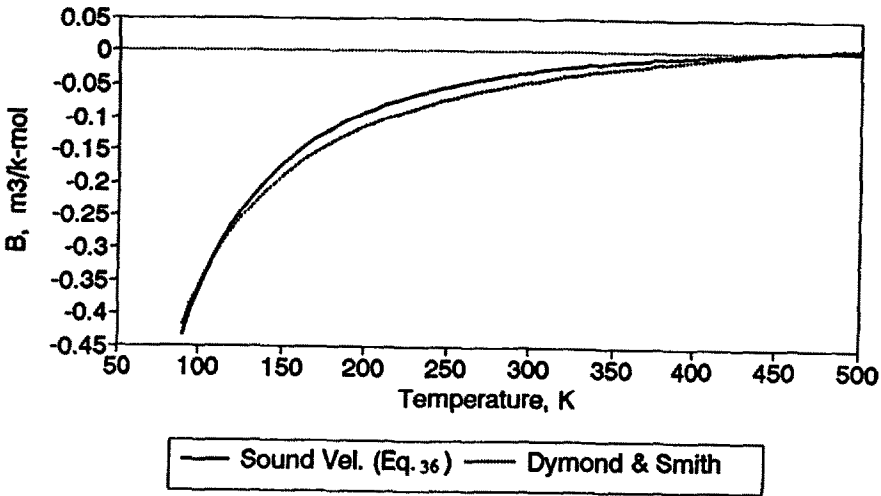
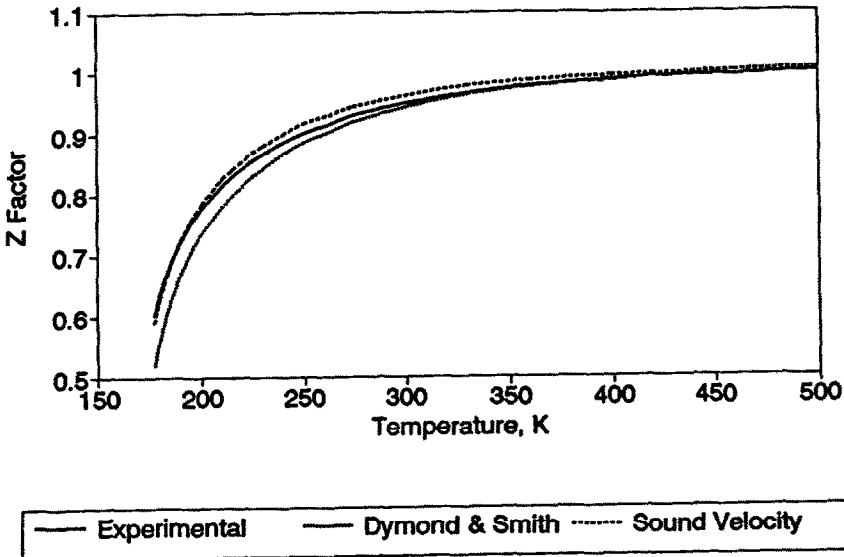Fig. 1. Second Virial Coefficient for Methane.

Fig. 2. Compressibility Factor for Methane at 30 Bar.

A graphical comparison for propane at 30 bar is shown in Figure 3.
        Data on the velocity of sound for methane, ethane and propane were
also used to obtain the van der Waals (vdW) constants. These constants as
well as the vdW constants obtained from the critical properties are given in
Table 4. Accuracy of constants on prediction of compressibility factors (Z) is
also shown in Table 4. For methane and ethane, graphical comparisons for
prediction of Z from van der Waals EOS are shown in Figures 4 and 5,
respectively. We believe the larger deviation for Z prediction shown in Fig. 5
is basically due to the inaccuracies of the van der Waals equation of state.
        Results obtained for the virial coefficient, the Lennard-Jones potential
parameters andthe van der Waals constants show that it is possible to obtain
PVT data from cVT data with reasonable degree of accuracy. However, as
mentioned earlier, the major goal of this work was to see how the
measurable velocity of sound data can be used to obtain the PVT relations.
This work does not indicate that the velocity of sound is merely the only
appropriate property for such a purpose. There are some other properties,
such as the refractive index, which could also be used to obtain parameters of
the equations of state.

TABLE 2

The Second Virial Coefficient Calculations from the Velocity of Sound Data

$B \, [m^3/Kmole] = a \, lnT/T + b + c/T; \quad T[=^\circ K]$

Compound	a	b	c	% AAD for Z
Methane	28.54	-0.0194	-165.82	0.5
Ethane	160.0	-0.25	-880.0	1.1
Propane	220.0	-0.23	-1290.0	1.4

Number of Data Points used: 150 for each compound (Goodwin, 1974; Goodwin, et al.,
1976; Goodwin and Haynes, 1982). Pressure Range: 0.01-20 MPa (0.1 - 200 bar);
Temperature Range: From saturation temperature up to $500^\circ K$ for methane, up to
$600 \, ^\circ K$ for ethane and up to $700 \, ^\circ K$ for propane.

CONCLUSIONS

        Based on the statistical and classical thermodynamics, coefficients of
the equations of state such as the virial coefficients, the Lennard-Jones
parameters, the van der Waals constants, etc. can be determined from the
velocity of sound data. A generalized cVT relation (eq. 15) is derived which
can be used for this purpose. In addition, a new temperature-dependent
correlation in the form of eq. 35 is developed for the virial coefficients. In the
present report for the demonstration of the technique and due to the
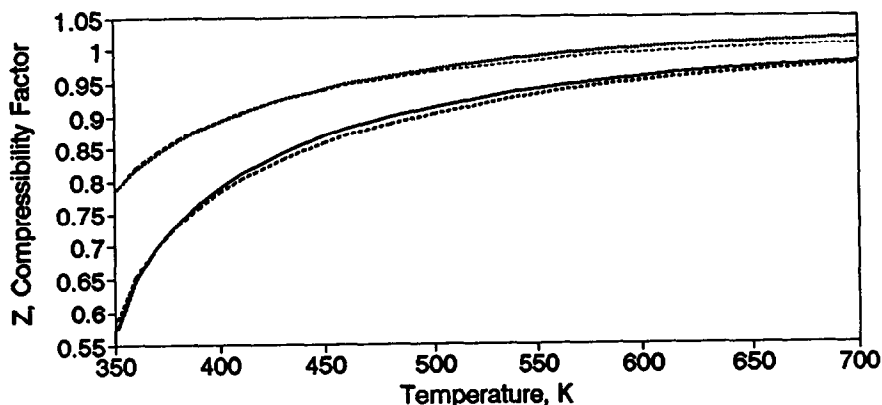availability of both experimental PVT and cVT data, only a few light

substances are examined. However, the proposed technique is applicable for heavy, complex or newly designed molecules for which the velocity of sound measurements are readily accessible, but their PVT relations may not be available.

TABLE 3

The Lennard-Jones Potential Parameters from the Velocity of Sound Data and Other Sources

Source of Data	ϵ / k_B (°K)	σ (°A)	%AAD for Z
Methane:			
Velocity of Sound	178.1	3.97	0.8
Second Virial Coefficient	148.2	3.817	4.0
Viscosity	144.0	3.796	4.7
Ethane:			
Velocity of Sound	300.0	4.25	0.5
Second Virial Coefficient	243.0	3.954	3.0
Viscosity	230.0	4.418	3.4
Propane:			
Velocity of Sound	350.0	5.0	1.1
Second Virial Coefficient	242.0	5.637	11.5
Viscosity	254.0	5.061	8.0

Data sources for the velocity of sound and PVT data and the temperature and pressure ranges are given in Table 2. The LJ parameters are based on the second virial coefficient and viscosity data and are taken from Hirschfelder, et al. (1964). $1°A = 10^{-10}$m.

Fig. 3. Compressibility Factor for Modified LJ EOS for Propane at 30 Bar.

TABLE 4

The van der Waals Constants from the Velocity of Sound and the Critical Properties Data*

Compounds	a $m^6/(Kmole^2.MPa)$	b $m^3/Kmole$	%AAD for Z
Methane:			
Velocity of Sound	0.188583	0.04478	1.0
Original Constants	0.227209	0.04305	0.8
Ethane:			
Velocity of Sound	0.384613	0.05718	1.8
Original Constants	0.549447	0.05198	2.4
Propane:			
Velocity of Sound	0.834060	0.09051	1.4
Original Constants	0.926734	0.09051	1.5

Data sources and the Pressure and temperature ranges are given in Table 2. The LJ parameters are based on the second virial coefficient and viscosity data and are taken from Hirschfelder, et al. (1964). Original constants for the vdW equation of state were determined through the use of the critical temperature and pressure.
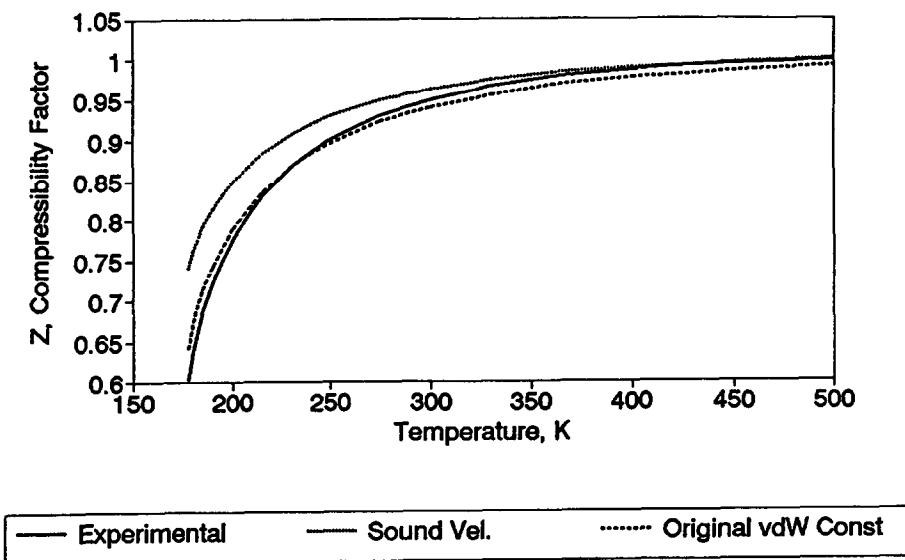

Fig. 4. Compressibility Factor from van der Waals EOS for Methane at 30 Bar.
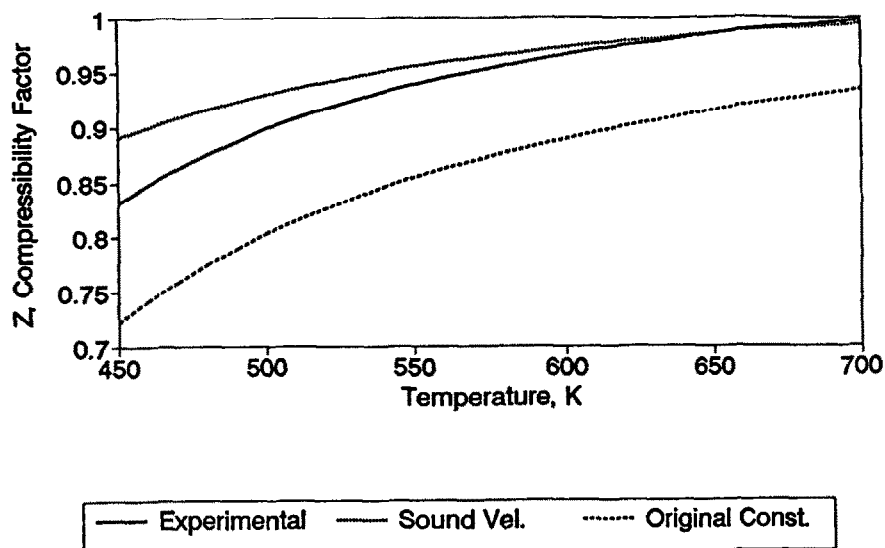
Fig. 5. Compressibility Factor from van der Waals EOS for Ethane at 100 Bar.

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NOMENCLATURE:

B	=	Second virial coefficient
B'	=	dB/dT = First derivative of B with respect to temperature
B''	=	d^2B/dT^2 = Second derivative of B with respect to T
C	=	Third virial coefficient
C'	=	dC/dT = First derivative of C with respect to temperature
c	=	Velocity of sound
C_p	=	Constant pressure heat capacity
C_v	=	Constant volume heat capacity
d	=	hard-sphere diameter
d_0 & d_1	=	Constants in eq. 18
k_B	=	Boltzman constant
L_n	=	Constant in eq. 29
M	=	Molecular weight
N_a	=	Avogadro number
p	=	Pressure
P_n	=	Constants in eq. 28
q_n	=	Constants in eqs. 28 & 29
R	=	Gas constant
s	=	Entropy
T	=	Temperature
v	=	Molar volume
Z	=	Compressibility factor

Greek Letters:

σ	=	Size parameter in the Lennard-Jones potential
ϵ	=	Energy parameter in the Lennard-Jones potential
ρ	=	Molar density
γ	=	Heat capacity ratio
κ_T	=	Isothermal compressibility
η	=	Packing fraction

Superscripts:

id	=	Ideal gas reference state of unit pressure

Subscript:

hs	=	hard-sphere