

음속의 열역학

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Thermodynamics of Sound Velocity

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ABSTRACT

The sound velocity measurements can permit much higher precision than that obtainable in the direct PVT experiments in addition to producing static and dynamic properties simultaneously, and thus the study on the sound velocity has been considered as another important approach to a fundamental understanding and description of the structure of fluids. This review deals with what have been done on studies of the sound velocity for evaluating thermodynamic properties with an emphasis on the development of the methods to extract the thermodynamic properties from the experimental data on sound velocity.

음속에 대한 실험값은 보통의 PVT 측정값보다 훨씬 정확하게 얻을 수 있고 또한 정적, 동적 성질을 동시에 얻을 수 있으므로 유체의 구조를 이해하는 방법으로 간주되어 오고 있다. 본 연구에서는 음속의 열역학적 성질에 대한 여러 이론을 기술하고 측정된 음속의 실험값들로부터 열역학적 성질을 추출해내는 여러 방법들에 대해 검토한다.

1. INTRODUCTION

A substantial amount of accurate data for thermodynamic and thermophysical properties of pure fluids and their mixtures are always essential to the design of chemical processes and the efficient operation and transportation of fuel gases. Also, such data can be useful in testing the theoretical models proposed such as perturbation and variational theories, and intermolecular potential models.

The important approach to obtaining

thermodynamic properties of a fluid has been via the direct measurements and the equations of state usually defined by the experimental determination of the PVT surface of the fluid. In spite of the great progress in the development of equations of state for predicting thermodynamic properties, there still remains difficulty evaluating constants or parameters present in the equations of state for some pure components such as complex, heavy, or newly designed molecules. When the thermodynamic properties of such components are not available or accessible only with difficulty by the direct measurements, other methods must be considered.

Like the Joule-Thompson coefficient, refractive index and dielectric constant, the sound velocity has been an important clue to different approaches to understanding thermodynamic properties of fluids. Any change of stress or

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pressure producing a local change in density or a local displacement from equilibrium in an elastic medium can serve as a source of sound. The science of sound, called acoustics, endeavors to describe and explain the phenomena associated with motional disturbances from equilibrium of elastic media. Modern acoustics has experienced enormous development by the invention of transducers which can precisely control the generation and detection of sound with respect to frequency and intensity. The sound propagation taking place through an elastic medium by means of wave motion can be related to the equilibrium value of medium through the principles of thermodynamics^[1].

The sound velocity c at zero-frequency limit is related to thermodynamic properties by the following equation.

$$c^2 = \frac{1}{\rho \chi_S} = \frac{\gamma}{\rho \chi_T} = \frac{1}{\rho} \frac{1}{\chi_H - \alpha_p / C_p} \quad (1)$$

where ρ is the density, V is the molar volume, M_w is the molecular weight, γ is the ratio of the isobaric and isochoric heat capacities (C_p/C_v), and χ_S , χ_T , and χ_H are the adiabatic, isothermal, and isenthalpic compressibilities, respectively. These compressibilities are defined and related to thermodynamic properties by

$$\chi_S \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S = \frac{1}{\rho c^2} \quad (2)$$

$$\chi_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{\rho c^2} + \frac{TV\alpha_p^2}{C_p} \quad (3)$$

$$\chi_H \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_H = \frac{1}{\rho c^2} + \frac{\alpha_p}{C_p} \quad (4)$$

where α_p is the thermal expansion coefficient ($= (\partial V / \partial T)_p / V$). Compressibilities χ_S , χ_T , and χ_H have numerous applications. For example, they appear to be very instrumental in characterizing the behavior of petroleum fluids during the various production: isothermal within the reservoir, at the level of chokes where expansion is isenthalpic, and at the level of the compressors and turboexpanders where the process is isentropic to the first order^[2]. Other forms of expressions for the sound velocity and

compressibilities are summarized in Appendix 1, where c_0 and γ_0 are the sound velocity and heat capacity ratio at the ideal gas state, and γ_v and γ_s are the thermal pressure coefficients at constant volume ($= (\partial P / \partial T)_v$) and along the saturation curve ($= (\partial P / \partial T)_s$), and Z is the compressibility factor ($= PV/RT$).

The physical theory of sound waves deals with systematic motions of material medium relative to an equilibrium state, thus comprises the vibrational aspects of elasticity and fluid dynamics. There are two types of elastic waves: (1) *longitudinal* wave where particles move in the direction of propagation. (2) shear (*transverse*) wave where the displacement of the particles of the medium is perpendicular to the direction of propagation of the wave. A longitudinal sound wave is mainly attenuated by two properties of the medium: (1) classical absorption (α_{cl}) by viscosity and heat conduction. (2) molecular absorption (α_{mo}) by molecular absorption and dispersion. The longitudinal motion of sound wave causes the collisions of molecules, which often result in rotational and vibrational motions of molecules. Each of absorption processes is characterized by a relaxation time, which measures the amount of time for the particular process to be completed to some degree. The sound velocity, thus, depends on the relative magnitude of the angular frequency $\omega (= 2\pi f)$ of the sound wave and relaxation time. When the angular frequency is large compared with $1/\tau$, the sound velocity becomes higher than that calculated from eqn (1)^[3].

As the attenuation data provides some direct information about dynamic behavior, one can know a lot about the mechanism involved from its dependency on frequency and temperature. On the other hand, the sound absorption and dispersion caused by the presence of viscosity and heat conduction can be related to thermophysical properties such as viscosity, conductivity, and surface tension.

In monoatomic gases and liquids, the sound attenuation can be explained due to shear and bulk viscosities and heat conduction. When the

dispersion to classical attenuation is assumed to be negligible for such fluids, the absorption coefficients α_s and α_{th} due to shear viscosity and thermal conduction, respectively, are given by^[4]

$$\alpha_s = \frac{8\pi^2}{3} \frac{\eta_s f^2}{\rho c^3} \quad (5)$$

$$\alpha_{th} = \frac{2\pi^2 k(\gamma-1)}{\rho \gamma C_V c^3} f^2 \quad (6)$$

where k is the thermal conductivity and η_s is the shear viscosity. Under another assumption that the classical absorption is additive, the classical absorption becomes

$$\alpha_{cl} = \frac{2\pi^2}{\rho c^3} \left[\frac{4}{3} \eta_s + \frac{(\gamma-1)k}{\gamma C_V} \right] f^2 \quad (7)$$

Polyatomic liquids, on the other hand, show additional attenuation due to two types of relaxations: (1) thermal relaxations which have been demonstrated for gases and nonassociated liquids and caused by an interchange between the longitudinal sound wave and the rotational and internal modes of motion of the gas or liquid molecules. (2) structural relaxations which occur for associated liquids, polymer liquids, and solids and take place when one part of the molecule moves from one position to another under the combined effect of the thermal energy and sound wave energy^[5].

The explicit expression of the sound velocity as a function of the angular velocity $\omega (= 2\pi f)$ is^[6]

$$\left[\frac{c(\omega)}{c(0)} \right]^2 = 1 + \frac{1}{4} X^2 [3 + 10(\gamma-1)Y - (\gamma-1)(7-3\gamma)Y^2] + O(X^4) \quad (8)$$

with X and Y dimensionless quantities defined as

$$X \equiv \frac{\omega(\eta_v + 4\eta_s/3)}{\rho c^2(0)} \quad (9)$$

$$Y \equiv \frac{kM_w}{(\eta_v + 4\eta_s/3)C_p} \quad (10)$$

where η_v is the volume viscosity.

Since the sound velocity, in general, is a function of the ultrasonic frequency (f) as mentioned above, eqn (1) is true only in the zero-frequency limit. However, the measured

sound velocities are known to be independent of f at sufficiently low frequencies. Even though such a low-limit frequency range differs from the components, the velocity measured in the range of 0.1 to 10 MHz can be taken as the zero-frequency limit under the assumption that the dispersion is shown to be negligible^[7].

Since the sound velocity is considered as purely thermodynamic quantity only when it is extrapolated to zero frequency and zero amplitude, it might not attract more attention than other PVT experiments. Despite that fact, the experiments on the sound velocity have several advantages over PVT experiments. The sound velocity experiments can be conducted more precisely than other direct thermodynamic measurements, particularly at extremely high pressure or in the neighborhood of phase transitions, and thus the sound velocity data may be used to check the data by other PVT measurements.

Also, for the components such as heavy hydrocarbons in which the critical constants used in most of equations of state are not available through the PVT experiments, these sound velocity data will be very useful to get the PVT data through thermodynamic relation between the PVT fundamental properties and sound velocity^[8]. Another advantage is that the sound velocity data produce the static and dynamic properties as well.

This paper summarizes the relations between the sound velocity and thermodynamic properties, which are based on the theoretical and/or empirical developments, and also reviews the methods to obtain thermodynamic properties from the experimental data on sound velocity for the primary object.

2. RELATIONS BETWEEN SOUND VELOCITY AND THERMO-DYNAMIC PROPERTIES

Since the sound velocity is a thermodynamic property as discussed in the previous chapter, it can be used as a criterium for theories proposed to predict thermodynamic properties, according to how well one theory predicts the sound

velocity.

Another important characteristic of the study on the sound velocity is that the information on the structure of fluid can be acquired. Several theories, proposed primarily from molecular basis to explain the state of liquid, will be reviewed in this chapter. It will be discussed later how several semi-empirical and empirical equations of state predict the sound velocity well.

2.1. Sound velocity in terms of the intermolecular potential energy and molecular distribution functions

The canonical partition function Q is related to the Helmholtz free energy A by

$$A = -k_B T \ln Q \quad (11)$$

where k_B is the Boltzmann constant. The partition function is factorized into a product of internal (Q_{int}) and external (Q_{ext}) parts as follows.

$$Q = Q_{ext} Q_{int} \quad (12)$$

where

$$Q_{int} = (q_t q_v q_r)^N \quad (13)$$

$$Q_{ext} = \Lambda^{-3N} Q_c$$

$$\text{where } \Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}} \quad (14)$$

In eqn (13), q_t , q_v , and q_r are the molecular translational, vibrational, and rotational partition functions, respectively, N is the number of molecules in the volume V , and Q_c is the configurational partition function which is related to the configurational integral Z_N by

$$Q_c = \frac{1}{N!} Z_N(V, T)$$

where

$$Z_N(V, T) = \int \exp(-\beta U) dp_N dq_N \quad (15)$$

in which p_N and q_N denote all the momenta and coordinates as usual.

With the assumption of the pairwise additivity, the pressure and internal energy from standard statistical thermodynamics are given by

$$\begin{aligned} P &= P^{id} + k_B T \left(\frac{\partial \ln Q_c}{\partial V} \right)_{T, N} \\ &= \rho_N k_B T - \frac{\rho_N^2}{6} \int_0^\infty u'(r) g(r) 4\pi r^3 dr \end{aligned} \quad (16)$$

and

$$\begin{aligned} U &= U^{id} + k_B T^2 \left(\frac{\partial \ln Q_c}{\partial T} \right)_{N, V} \\ &= U^{id} + \frac{\rho_N^2 V}{2} \int_0^\infty u(r) g(r) 4\pi r^2 dr \end{aligned} \quad (17)$$

where ρ_N is the number density and $g(r)$ is the radial distribution function whose physical meaning is the probability of finding a molecule at r if there is a molecule at the origin. Also, the isothermal compressibility is derived in terms of $g(r)$ without assuming the pairwise additivity of the intermolecular potential function.

$$\kappa_T = \frac{1}{k_B T} \left[\frac{1}{\rho_N} + \int_0^\infty [g(r) - 1] 4\pi r^2 dr \right] \quad (18)$$

With the above information, the sound velocity using eqn (A4) in Appendix 1 can be represented by intermolecular pair potential energy and radial distribution functions, and their derivatives as follows

$$\begin{aligned} c^2 &= \frac{1}{\rho} \left[\frac{\rho_N k_B T}{1 + \rho_N \int_0^\infty [g(r) - 1] 4\pi r^2 dr} \right. \\ &\quad \left. + \frac{N k_B T \left(1 - \frac{\rho_N}{6 k_B} \int_0^\infty u'(r) \left(\frac{\partial g}{\partial T} \right)_V 4\pi r^3 dr \right)^2}{C_v^{id} + (\rho_N^2 V / 2) \int_0^\infty u(r) \left(\frac{\partial g}{\partial T} \right)_V 4\pi r^2 dr} \right] \end{aligned} \quad (19)$$

For the ideal gas where $g(r)=1$ and $u(r)=0$, the RHS of eqn (19) becomes equal to $\gamma RT/M_w$, which is also derived directly from eqn (1). Eqn (19), however, cannot be used to produce the exact expressions for more realistic models because it is impossible to get the analytical forms of $g(r)$ and its temperature derivative for those models.

There are few theories for more realistic models, if ever, where the sound velocity is expressed in terms of the intermolecular potential and radial distribution functions. Even though the application is restricted to viscoelastic fluids, Rao and Gupta^[9], through

the use of those functions, calculated the sound velocity for several viscoelastic fluids taking advantage of some results on hydrodynamics and elasticity of materials, and their statistical mechanical derivations. The classical theory of elasticity and hydrodynamics classifies deformable substances into the idealized categories of the perfect elastic solids and the perfect viscous fluids according to their responses to the application of a stress. In an isotropic solid, a longitudinal wave propagating along the [100] direction of a cubic crystal, the longitudinal sound velocity c in that direction is related to the second-order elastic constant C_{11} by the expression^[10].

$$c^2 = \frac{C_{11}}{\rho} \quad (20)$$

When a mechanical force is applied suddenly to a fluid, the fluid responds elastically at first, just as if it were a solid body. The initial response may be described by two quantities, the high-frequency limit of the shear modulus G_∞ , and the bulk modulus K_∞ .

Assuming eqn (20) is valid for the longitudinal sound velocity in the long wave-length limit, Rao and Gupta evaluated the sound velocity of molten salts besides the shear and bulk viscosities, and the high-frequency limit of the shear modulus (G_∞) and the bulk modulus (K_∞) with the aid of the relations between the elastic constants and two structural integrals I_1 and I_2 as:

$$C_{11} = \rho_N k_B T \left(3 + \frac{2}{5} I_1 + \frac{1}{5} I_2 \right) \quad (21)$$

where I_1 and I_2 were defined by Schofield^[11] as follows:

$$I_1 = \frac{\rho_N}{2k_B T} \int_0^\infty f g(r) \frac{du(r)}{dr} 4\pi r^2 dr \quad (22)$$

$$I_2 = \frac{\rho_N}{2k_B T} \int_0^\infty r^2 g(r) \frac{d^2 u(r)}{dr^2} 4\pi r^2 dr \quad (23)$$

From the definition of the structure function in the long-wave limit, $S(0)$ ^[12], and the relation between $S(0)$ and I_1 and I_2 , it is known by

$$S(0) \equiv \frac{1}{1 - \rho_N \tilde{c}(0)} = \frac{1}{5/3 - 2I_1/9 + I_2/9} \quad (24)$$

where $\tilde{c}(0)$ is the Fourier transformation of the

known direct correlation function $c(r)$. With the help of $\gamma(\sigma)$, that is, $g(r)$ at $r = \sigma$, the integral I_1 for a particular potential can be evaluated. Once the two integrals in eqns (22) and (23) are evaluated for a given potential, the sound velocity can be easily calculated. Using the hard sphere potential, Rao and Gupta calculated the sound velocity for molten salts and their results were in good agreement with the experimental data.

It should be noted, however, that when $g(r)=1$ and $u(r)=0$ are inserted in eqns (22) and (23), the sound velocity expression for the ideal gas, $c^2 = \gamma RT/M_w$, can not be obtained from eqns (20) and (21). To allow quantitative theoretical treatment of viscoelastic behavior for simple liquids, the viscosity of liquids must be greater than 10^{-2} Ns/m² (10cP)^[4].

The several theories, which approximate to evaluate the partition function in eqn (11) and make use of the molecular collision parameters, or combine the molecular-based theories with the empirical relations, were developed. It will be used as a criterium for those theories proposed according to how well one theory predicts the sound velocity, for the sound velocity is also related to thermodynamic properties.

2.2. Approximation models

Several models based on molecular level were proposed to predict sound velocity from the molecular parameters. A very simple "free volume" model, based on a regular lattice structure composed of rigid spheres having their diameters σ with an intermolecular distance d , was developed by Kincaid and Eyring^[13]. The free volume V_f is defined as the volume available to the center of a molecule in its cell. Assuming the sound wave is transmitted with an infinite velocity in case of molecular collision and with the same velocity as in the ideal gas in the one-dimensional free space, the ratio (c^*) of the actual sound velocity in the liquid to the ideal gas velocity is given by

$$c^* = \frac{c}{c_0} = \left(\frac{V}{V_f} \right)^{1/3} = \frac{1}{1 - \sigma/d} = \frac{1}{1 - (\zeta/V^*)^{1/3}} \quad (25)$$

where V^* ($= V/N_A \sigma^3$) is the dimensionless volume and ζ is a constant which depends on the particular lattice considered. For simple cubic lattices ζ is 1, and for face-centered cubic and hexagonal close-packed lattices ζ is $\sqrt{2}$. As eqn (25) implies, the temperature effect on c^* at constant density is not taken into account, and the sound velocities calculated eqn (25) were found to be overestimated^[14].

Substituting the thermodynamic relations of $P = -(\partial A/\partial V)_T$ and $S = -(\partial A/\partial T)_V$, into eqn (A4) (see Appendix 1), the sound velocity can be expressed in terms of the Helmholtz free energy A as follows:

$$c^2 = \frac{V^2}{M_w} \left(\frac{\partial^2 A}{\partial T^2} \right)_V \left[\left(\frac{\partial^2 A}{\partial V^2} \right) \left(\frac{\partial^2 A}{\partial T^2} \right) - \left(\frac{\partial^2 A}{\partial T \partial V} \right)^2 \right] \quad (26)$$

Since the Helmholtz free energy is related to the partition function, the sound velocity can be calculated from determination of the partition function, which makes the sound velocity serve as a thermodynamic quantity used to test various models of fluids. The evaluation of the free energy expression for more realistic models of the liquid state is difficult and thus the determinations of the sound velocity become much more complicated. Here, several simple models for which the Helmholtz free energy can be easily determined are reviewed.

One of the simplest models is the simple cell theory^[15]. The partition function Q is approximated using the free volume V_f as

$$Q = V_f^N$$

$$\text{where } V_f = \frac{4\pi\zeta'}{3N} [V^{1/3} - V_0^{1/3}]^3 \quad (27)$$

where the constant ζ' also depends on the lattice of interest and V_0 is the volume corresponding to the closed packing for a given lattice structure. Substituting eqn (27) into eqn (11) gives

$$A = Nk_B T \ln \frac{3N}{4\pi\zeta'} - 3Nk_B T \ln [V^{1/3} - V_0^{1/3}]$$

(28)

From eqns (26) and (28) the corresponding sound velocity becomes

$$c^2 = \frac{RT}{M_w} \frac{1}{[1 - (V_0/V)^{1/3}]^2} \quad (29)$$

Modifying the above model, the "smearing" approximation was proposed^[16]. In the smearing approximation where the neighbors of a molecule are uniformly smeared on a sphere, the molar free energy A is given by^[17]

$$A = -\frac{3Nk_B T}{2} \ln \frac{2\pi m k_B T}{h^2} + Nk_B T \ln \frac{3N}{4\pi\sqrt{2}} - 3Nk_B T \ln (V^{1/3} - V_0^{1/3}) \quad (30)$$

Substituting eqn (30) into eqn (26) gives

$$c^2 = \frac{RT}{M_w} \left[\frac{1}{1 - (V_0/V)^{1/3}} \right]^2 \left[\frac{5}{3} - \frac{2}{3} \left(\frac{V_0}{V} \right)^{1/3} \right] \quad (31)$$

Van Dael and Van Itterbeek^[14] also discussed results obtained from the above theories and made comparisons with experimental data.

Eyring et al.^[18] calculated the sound velocity by making use of the "significant liquid structure" theory that has been believed to be quite successful in evaluating thermodynamic properties of liquids. According to the significant structure theory, the partition function of liquids is expressed as follows

$$Q_l = Q_s^{N(V_s/V)} Q_g^{N(V - V_s)/V} \quad (32)$$

where Q_s and Q_g are the partition functions for the solid-like degree of freedom and the gas-like degree of freedom, and V and V_s are the molar volumes of the liquid and solid, respectively. With the Helmholtz free energy from eqns (11) and (32) determined, a set of P , V_l , and V_g were determined by the slope of the common tangent of the Helmholtz free energy at V_l and V_g , and thus the sound velocity was evaluated. The significant structure theory was applied to predict the sound velocities for Ar, Kr, Xe and $TiCl_4$, and provided good agreement with experimental sound velocities^[19,20]. The significant structure theory, however, has been criticized due to the large number of parameters used^[21].

There are also two important theories based on the molecular collision parameters that are capable of calculating sound velocity. Making use of the concept "intermolecular free length", Jacobson^[22] proposed a method to calculate thermophysical properties. It is assumed the molecules in a liquid have the closest packing at $T=0$ °K with the molar volume of V_0 and the liquid is expanded as a whole through molecular oscillations without expansion of molecules themselves as temperature increases. Under that assumptions, the total surface area of all molecules per mole, designated as Y ($= \sqrt[3]{36\pi N V_0^2}$), is not changed and the increase in volume is equal to the available volume defined as

$$V_a = V_T - V_0 \quad (33)$$

where V_T and V_0 are the molar volumes at T °K and 0 °K, respectively. The intermolecular free length L_f between the surfaces of the molecules can be obtained from

$$L_f = \frac{2V_a}{Y} \quad (34)$$

From the experimental data on the isentropic compressibility for 54 non-associating liquids, it was found

$$\alpha_s = kL_f^p \quad (35)$$

where the temperature-dependent constants k and p are 2.082 and $10^{7.097}$ at 20°C .

Substituting eqn (35) into eqn (1) produces

$$c = \frac{K}{L_f^{p/2}\sqrt{\rho}} \cong \frac{K}{L_f\sqrt{\rho}} \quad (36)$$

where K is another temperature dependent constant.

The other one, the collision factor theory, was proposed by Schaaffs^[23]. From the experimental results on sound velocity for organic liquids and imposing several approximations, Schaaffs derived

$$c = c_\infty S Y_f = C_\infty \frac{SB}{V} \quad (37)$$

where S is the collision factor, B is the actual volume of the molecule per mole ($=4\pi r^3 N_A/3$), Y_f is the space-filling factor ($=B/V$), and c_∞ is taken as 1600 m/sec. The free length theory and collision factor theory would rather be used

to calculate the sound velocities of mixtures from those of pure fluids and to evaluate the molecular parameters such as free length, effective molecular radius, etc., as will be discussed later.

Next, we turn to another approach that combines the molecular-based theory and empirical relation. Flory^[24] derived the following reduced equation of state using the characteristic values, V° , T° , and P°

$$\frac{P^*V^*}{T^*} = \frac{V^{*1/3}}{V^{*1/3}-1} - \frac{1}{V^*T^*} \quad (38)$$

where P^* , V^* , and T^* are the reduced pressure, volume, and temperature, respectively. According to Flory, the characteristic pressure is determined by

$$P^\circ = \gamma_v T V^2 \quad (39)$$

At zero pressure, eqn (38) becomes

$$\frac{V^{*1/3}-1}{V^{*4/3}} = T^* \quad (40)$$

Differentiating eqn (40) with respect to T^* and using the definition of the thermal expansion coefficient α_p at $P=0$ give

$$V^{*1/3}-1 = \frac{\alpha_p T^*}{3(1+\alpha_p T^*)} \quad (41)$$

A reduced form of equation for surface tension based on the Flory's equation was derived by Prigogine and Saraga^[25] as follows:

$$\sigma^*(V^*) = M V^{*-5/3} - \frac{V^{*1/3}-1}{V^{*2}} \ln \frac{V^{*1/3}-0.5}{V^{*1/3}-1} \quad (42)$$

where M is the fraction of nearest neighbors which a molecule loses on moving from the bulk of the liquid to the surface and its most suitable value is found to be 0.29. Therefore, the surface tension of liquids in terms of the Flory theory may be represented by

$$\sigma = \sigma^\circ \sigma^*(V^*) \quad (43)$$

where the characteristic surface tension σ° was shown to be represented by the characteristic values T° and P° as follows^[26]:

$$\sigma^\circ = k_B^{1/3} P^{\circ 2/3} T^{\circ 1/3} \quad (44)$$

Auerbach^[27] derived the following empirical equation relating surface tension (in dyne/cm) to sound velocity (in m/sec) and density (in

g/cm³).

$$c^2 = \left[\frac{\sigma}{6.3 \times 10^{-4} \rho} \right]^{2/3} \quad (45)$$

Substituting eqn (43) along with eqns (42) and (44) into eqn (45) gives

$$\begin{aligned} c^2 &= \left[\frac{\sigma}{6.3 \times 10^{-4} \rho} \right]^{2/3} \\ &= \left[\frac{k_B^{1/3} P^{0.2/3} T^{0.1/3}}{6.3 \times 10^{-4} \rho} \right]^{2/3} \\ &\times \left[MV^{*-5/3} - \frac{V^{*1/3} - 1}{V^{*2}} \ln \frac{V^{*1/3} - 0.5}{V^{*1/3} - 1} \right]^{2/3} \end{aligned} \quad (46)$$

After calculating the characteristic values of P° , V° , and T° from eqns (39) through (41) together with experimental data, the sound velocities for noble gases (argon, krypton, and xenon) and nitrogen were computed by way of the surface tension. While the agreement between experimental and calculated sound velocities for noble gases was good (within 5 %), the results on nitrogen were not. Using the Auerbach's relation in eqn (45) and the surface tension data, Kannappau and Rajendran^[28] also calculated the sound velocities for fluorocarbons.

Thus far we have summarized the theories proposed on the sound velocity. The sound velocity expressions can be derived from a given equation of state because of its being directly related to the PVT relations. An emphasis in this chapter, however, has been placed on the nature that the sound velocity rather serves as an autonomous datum in direct relation to a fluid model proposed.

3. CALCULATIONS OF SOUND VELOCITY FROM EQUATIONS OF STATE

During the past several decades, since van der Waals proposed an equation of state representing liquids as well as gases, there have been enormous progress in developing equations of state to predict fluids in all phases. Since the sound velocity is related to thermodynamic properties, it is worthwhile to observe how well

an equation of state predicts the sound velocity.

Appendix 2 indicates the sound velocity expressions for various equations of state. Additional information on the values of the ideal gas heat capacities C_{p0} ($=C_{v0}+R$) as a function of T is required to calculate the sound velocity when an equation of state is given, because C_{p0} can not be determined from an equation of state, which provides the residual heat capacity properties, (C_v-C_{v0}) and (C_p-C_{p0}) . With C_{p0} determined, C_p and C_v can be calculated from the following equations:

$$C_v = (C_{p0} - R) - T \int_0^{\rho} \frac{1}{\rho^2} \left(\frac{\partial^2 P}{\partial T^2} \right)_o d\rho \quad (47)$$

$$\begin{aligned} C_p &= C_v + \frac{T}{\rho^2} \left(\frac{\partial P}{\partial T} \right)_\rho^2 / \left(\frac{\partial P}{\partial \rho} \right)_T \\ &= C_v - T \left(\frac{\partial P}{\partial T} \right)_V^2 / \left(\frac{\partial P}{\partial V} \right)_T \end{aligned} \quad (48)$$

The performance of equations of state to predict the sound velocity has been tested. The Carnahan-Starling equation of state^[29] for the hard sphere model was used to calculate the sound velocity for benzene, toluene, and chloroform^[30]. For C_p or C_v required to evaluate γ as shown in Appendix 1, the experimental heat capacity data were used, and the hard sphere diameter d needed to evaluate η was determined from the following empirical relation:

$$d^{5/2} = \frac{V}{7.210 \times 10^{19}} \left(\frac{\sigma}{T_c} \right)^{1/4} \quad (49)$$

where σ and V are the surface tension and molar volume, respectively. The calculated results were in good agreement with the experimental sound velocities, which demonstrated the validity of the Carnahan-Starling equation of state.

Using the Soave-Redlich-Kwong equation of state, Kouremonos and Antonopoulos^[31] calculated the values of c/c_0 for air over a wide range of temperature and pressure and plotted the generalized compressibility chart. Compared with the results of other thermodynamic properties, the calculated results of c/c_0 appeared to be underestimated. That may be partly due to their omission of the term, γ/γ_0 , in the expression for the sound velocity.

Sharif and Groves^[32] calculated γ/γ_0 and c/c_0 of argon, carbon dioxide and nitrogen in the gas state from three different equations of state (van der Waals, virial, Benedict-Webb-Rubin) to evaluate these equations. The BWR equation of state provided a better prediction of compressibility than other equations as expected because of the BWR equation of state being an empirical equation to fit thermodynamic data like density, pressure and thus compressibility. However, the predicted values of γ/γ_0 and c/c_0 by the BWR equation of state, which are related to the slope of thermodynamic properties, were found to be less accurate than those by the virial equation of state.

The sound velocities for hydrocarbons of up to n-C₁₆ and a few of aromatic compounds were calculated from six different equations of state and corresponding states relation to compare the results with the experimental data by Ye et al.^[2]. Starting from each P-T set for which the experimental velocity is contained, an equation of state was solved numerically for V or ρ , and then α_p , κ_T , and C_p needed for c were evaluated. They got the better results with the Lee-Kesler correlation than with several cubic and non-cubic equations of state.

Substitution of the virial form of equation of state into eqn (1) also gives eqns (A13) through (A21) in Appendix 2 relating the virial coefficients to the sound velocity^[14]. In the equations, B, C and D (or B', C' and D') are the second, third, and fourth virial coefficients, and A₂, A₃ and A₄ in eqn (A14) (or A₂', A₃' and A₄' in eqn (A19) when expressed in powers of pressure) are called the second, third, and fourth acoustic virial coefficients. Also, γ_0 is the ratio of the heat capacities at the pressure in the ideal gas state.

Lestz^[33] calculated the sound velocities of N₂, Ar, and Kr in the gas state from the virial equation of state based on the Lennard-Jones potential. The reduced form of the sound velocity equation truncated after the second acoustic virial coefficient becomes

$$c^2 = \frac{\gamma_0 RT}{M_w} \left[1 + \frac{K^*}{ZT^*} P^* \right] \quad (50)$$

where

$$Z = 1 + \frac{B^*}{T^*} P^* + \frac{(C^* - B^{*2})}{T^{*2}} P^{*2} \quad (51)$$

$$K^* = \left[2B^* + 2(\gamma_0 - 1)T^* \frac{dB^*}{dT^*} + \frac{(\gamma_0 - 1)^2}{\gamma_0} T^{*2} \frac{d^2B^*}{dT^{*2}} \right] \quad (52)$$

With the values for B* and its derivative with respect to T* from the well-tabulated results^[16] and the Lennard-Jones parameters, the sound velocities for argon and nitrogen were calculated. The results were in good agreement with the experimental data.

4. METHODS TO DERIVE THERMODYNAMIC PROPERTIES FROM THE SOUND VELOCITY DATA

Since the sound velocity has been known to be measured more accurately than any other thermodynamic quantity, it can be used not only to check PVT data independently, but also to deduce the PVT relations when it is difficult to measure those by the direct methods.

The methods to obtain PVT relations from the sound velocity data can be largely grouped into the empirical and theoretical methods. The methods based on the theoretical relations have been applied to gases at moderate pressures for evaluating the virial coefficients, and to fluids at high pressures for extracting useful information on the PVT relations and their temperature and pressure dependences.

4.1. Based on the empirical relations

Rao^[34] made an empirical relation between the derivative of sound velocity with respect to temperature and thermal expansion coefficient from the experimental sound velocity data.

$$\frac{1}{c} \left(\frac{\partial c}{\partial T} \right)_p = -k_1 \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (53)$$

with $k_1 = 3.0$

or after integration,

$$c^{1/k_1} V = R' \quad (54)$$

where R' is the Rao's constant and it is also

called the molar velocity. It was found that R' can not be a constant for all liquids and not even for a liquid over its whole range of temperature and pressure^[35].

Similar types of empirical relations for adiabatic compressibility^[36] and the pressure derivative^[37] of sound velocity were proposed as follows:

$$\frac{1}{\chi_T} \left(\frac{\partial \chi_T}{\partial T} \right)_P = -k_2 \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

with $k_2 = 1/7$ (55)

$$\frac{1}{c} \left(\frac{\partial c}{\partial P} \right)_T = -k_3 \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

with $k_3 = 3.0$ (56)

Although the three relations mentioned above have empirical origins, not confirmed by any convincing theoretical argument, they are sometimes supposed to be criteria for the normal behavior of a fluid^[14]. The Rao's rule has also been used to calculate the sound velocity of mixture.

Another type of approach is to take advantage of the corresponding states principle that provides a suitable method to get the generalized correlations and to predict thermodynamic properties of fluids from the correlations. Regardless of the abundant data on the experimental sound velocity, there have not been many attempts to correlate these data in the form of simple algebraic equations for thermodynamic analysis.

De Boer^[38] defined the reduced variables P^* , V^* , and T^* for fluids with the Lennard-Jones intermolecular potential to make a simple correlations of the sound velocity using the following characteristic values:

$$P_o = \frac{\epsilon}{\sigma^3}$$

$$V_o = N_A \sigma^3 \quad (57)$$

$$T_o = \frac{\epsilon}{k_B}$$

and the corresponding characteristic sound velocity becomes

$$c_o^2 = \frac{P_o V_o}{M_w} = \frac{N_A \epsilon}{M_w} \quad (58)$$

Then, the reduced sound velocity from eqn (1), which is independent of the molecular weight,

can be taken as

$$c^{*2} = -\gamma V^{*2} \left(\frac{\partial P^*}{\partial V^*} \right)_T \quad (59)$$

Another reduced expression of the sound velocity is the ratio of the actual sound velocity to the ideal gas value defined by

$$c^{*2} = \frac{c^2}{\gamma_o RT/M_w} \quad (60)$$

The advantage of eqn (60) over eqn (59) is that all pressure or density effects can be plotted on a scale where the trivial ideal gas temperature effect is eliminated. The corresponding state treatments on gases and liquids for several pure fluids using eqns (59) and (60) were discussed in details by Van Dael and Van Itterbeek^[14]. It was mentioned that the corresponding states principle using the above definitions of characteristic values could be successfully applied only to simple fluids.

Another form of definition on the characteristic temperature T_o , to apply the corresponding states principle to a bit more complex molecules, was proposed by Srivivisan and Krishna Murthy^[39] utilizing the saturated liquid density data as follows

$$\frac{\partial(T\rho_o)}{\partial T} = 0 \quad \text{at } T = T_o \quad (61)$$

In eqn (61), T_o can be defined as the temperature where the product $T\rho_o$ goes to a maximum for liquids. Rearranging eqn (61) shows that the thermal expansion coefficient α_o for the saturated liquid at T_o is the reciprocal of T_o , that is,

$$-\frac{1}{\rho_o} \left(\frac{\partial \rho_o}{\partial T} \right)_o = \frac{1}{T_o} \quad (62)$$

The sound velocity in the ideal gas state at T_o is used to define the corresponding reduced sound velocity as usual.

$$c^* = \frac{c}{c_o} \quad (63)$$

where

$$c_o = \sqrt{\gamma RT_o/M_w} \quad (64)$$

Srivivisan^[40] applied the above definition of T_o to obtain the correlations for several cryogenic liquids and refrigerants. It was shown that cryogenic liquids and ammonia fall into a

different category from the hydrocarbons and refrigerants, and the correlations fit the experimental data with an absolute average error of about 5%.

In spite of the fact that the sound velocity can be considered a thermodynamic property at low frequency, there has not been any attempt to introduce another parameter to explain the deviations from simple fluids such as the Pitzer's acentric factor, polar parameters, and shape factors. As expected, the corresponding states principle without such parameters can not transform the sound velocity into one form of expression with the dimensionless variables defined above.

4.2. Gas state

The sound velocity data also plays an important role in characterizing the virial coefficients and the ideal gas reference state heat capacities with greater precision than the direct PVT measurements. It is difficult and tedious to determine the thermodynamic properties as the ideal reference state experimentally. As mentioned earlier, the ideal gas heat capacity data are also required to calculate the sound velocity with an equation of state.

The results are analyzed in terms of an expansion of the sound velocity in powers of pressure P.

$$c^2 = \sum_{i=0} C_i P^i \quad (65)$$

where C_i 's are the constants to be fitted. From eqns (65) and (A19) in Appendix 2, the ideal gas heat capacities, the second (A_2) and third (A_3) acoustic virial coefficients are determined from

$$\gamma_0 = \frac{C_0 M_w}{RT} = \frac{1}{1 - R/C_{po}} \quad (66)$$

$$A_2 = \frac{C_1}{C_0} = \frac{M_w}{\gamma_0 RT} C_1 \quad (67)$$

$$A_3 = \frac{C_2}{C_0} = \frac{M_w}{\gamma_0 RT} C_2 \quad (68)$$

The regression of the results on C_{po} as a function of temperature can be represented by

$$C_{po} = a_0 + \frac{a_1}{T}, \text{ or } C_{po} = a_0 + \frac{a_1}{T} + \frac{a_2}{T^2},$$

$$\text{or } C_{po} = a_0 + \frac{a_1}{T} + a_2 T + a_3 T^2 \quad (69)$$

The above procedure was attempted by many researchers^[41,42,43,44]. The values of C_{po} obtained from the sound velocity data were in excellent agreement with the flow-calorimetric measurements^[45].

Once A_2 is determined, the second virial coefficient can be calculated from the following second order ordinary differential equation

$$2B + 2(\gamma_0 - 1)T \frac{dB}{dT} + \frac{(\gamma_0 - 1)^2}{\gamma_0} T^2 \frac{d^2B}{dT^2} = A_2 RT = A_2 \quad (70)$$

and third virial coefficient can be also computed similarly by

$$\frac{2\gamma_0 - 1}{\gamma_0} C + \frac{\gamma_0^2 - 1}{\gamma_0} T \frac{dC}{dT} + \frac{(\gamma_0 - 1)^2}{2\gamma_0} T^2 \frac{d^2C}{dT^2} = G \quad (71)$$

where G is independent of C and is given by

$$G = (A_2 + A_3 RT)RT - \left[B + (2\gamma_0 - 1)T \frac{dB}{dT} + (\gamma_0 - 1)T^2 \frac{d^2B}{dT^2} \right]^2 \frac{(\gamma_0 - 1)}{\gamma_0} \quad (72)$$

As shown in eqns (70) and (71), however, determination of the virial coefficients from the sound velocity measurements is not as straightforward as for the C_{po} . There have been many attempts to calculate the virial coefficients from eqn (70) after regression of the sound velocity data. At low pressure P, the sound velocity expression truncated after B(T) can be rearranged as

$$c^2 = c_0^2 \left[1 + \frac{2f(T)}{RT} P + \dots \right] \quad (73)$$

where

$$f(T) = \frac{A_2(T)}{2} = B + (\gamma_0 - 1)T \frac{dB}{dT} + \frac{(\gamma_0 - 1)^2}{2\gamma_0} T^2 \frac{d^2B}{dT^2} \quad (74)$$

Eqn (70) or (74) is the second order ordinary differential equation and it is evident that two boundary or initial conditions on $B(T)$ are necessary to solve eqn (74) for the complete solution. The term $f(T)$ in eqn (74), however, is only known numerically at a limited number of the experimental $f(T)$ data and hence eqn (74) should be evaluated by numerical integration after the interpolation of $f(T)$.

Instead of integrating eqn (74) numerically, early researchers assumed that $B(T)$ in certain T intervals is adequately represented by the function form

$$B(T) = b_1 + \frac{b_2}{T} \quad (75)$$

This, in turn, means that $f(T)$ is given by

$$f(T) = b_1 + \left(\frac{1}{\gamma_0}\right) \frac{b_2}{T} \quad (76)$$

By plotting $f(T)$ from the sound velocity data as a function of $1/T$, the coefficients b_1 and b_2 were determined and thus the second virial coefficient $B(T)$ was evaluated^[33,46,47]. Also, Ewing and coworkers^[41] obtained $B(T)$ based on the square well intermolecular potential.

$$B(T) = b_1 + b_2 \exp(b_3/T) \quad (77)$$

The three adjustable parameters were determined to fit the values of A_2' and γ_0 . Applying eqn (77) to several components^[42,43], they obtained accurate predictions for $B(T)$.

Provided a more general functional form for $B(T)$ in a finite series of $1/T$ is assumed as

$$B_n(T) = \sum_n b_n T^{-n} \quad (78)$$

Then the coefficients b_n can be determined by a least-square fit to the experimental values of the corresponding functional form for $f(T)$. Therefore, this method in which $B(T)$ has certain assumed functional forms, is called the "curve-fitting method" in contrast to the following method to try to get the analytical solution of eqn (70) or (74).

With the function G in eqn (72) evaluated using the $B(T)$ and its temperature derivatives, and the third acoustic virial coefficient A_3' , the third virial coefficient A_3 can be determined. It was concluded that even though the third virial coefficients calculated by this method show

large discrepancies, these are not unreasonable in view of the experimental difficulties in the direct measurements^[45].

There may have been several approaches to get the second virial coefficient solving eqn (74) without recourse to an assumed functional form on $B(T)$. Criticizing the curve-fitting method for not making explicit use of the solution of the homogeneous equation part of eqn (74) and using the fact that the numerical values for $f(T)$ at certain T from eqn (75) values are known, Bruch^[48] solved eqn (74) without assuming a functional form of $B(T)$ as in the curve-fitting methods to derive the following formal solution

$$B(T) = B_h + B_p \\ = \frac{\chi_1(\tau)}{T^2} \cos \left[\left(\frac{7}{2} \right)^{1/2} \ln \frac{T}{\tau} + \chi_2(\tau) \right] \quad (79) \\ + \frac{15}{\sqrt{14}T^2} \int_{\tau}^T \text{tf}(t) \sin \left[\left(\frac{7}{2} \right) \ln \frac{T}{t} \right] dt$$

where B_h and B_p are the homogeneous and particular solutions, respectively, and χ_1 and χ_2 are the integration constants depending on the choice of an arbitrary constant representing the integration range in eqn (79). Since $f(T)$ is only known numerically at a limited number of points, the integral in eqn (79) can be evaluated by numerical integration after taking a value of τ and regressing $f(T)$ from a finite number of the experimental $f(T)$ data. The results obtained by this procedure for gases helium (⁴He) agreed within 10 % with the values from the isothermal measurements by Keller^[49].

Inserting eqn (75), which was often employed for the curve-fitting method, into the integral of eqn (79), Boyd and Mountain^[50] derived the semi-empirically analytical particular solution.

$$B_p = A + \frac{C}{T} - \frac{\tau^2}{T^2} \cos \left[\left(\frac{7}{2} \right)^{1/2} \ln \frac{T}{\tau} + \chi_2(\tau) \right] \quad (80)$$

where

$$\chi_2(\tau) = \tan^{-1} \left[- \left(\frac{2}{7} \right)^{1/2} \frac{(2A + C/\tau)}{(A + C/\tau)} \right]$$

They also pointed out that choosing a form for $B(T)$ specifies an approximate differential equation for which the chosen form is the

complete solution and that Bruch's contention that the curve-fitting method chooses the particular integral without considering the homogeneous solution of eqn (74) is not correct.

Another method to solve eqn (74) was done by Ewing et al.^[41], who utilized an iterative data inversion formula to obtain the intermolecular pair potential as well as the second virial coefficient, simultaneously. Provided the homogeneous solution B_h of eqn (74) can be expressed in terms of linear combination of the two independent solutions B_{h1} and B_{h2} , the complete solution is

$$B = C_1 B_{h1} + C_2 B_{h2} + B_p \quad (81)$$

where C_1 and C_2 are constants to be determined from the initial conditions on B and dB/dT . Also, the 'well-width' function $\Delta(t)$ is defined as

$$\Delta(t) = r_L^3(t) - r_R^3(t) \quad (82)$$

where $t = (u + \epsilon)/\epsilon$, and r_R and r_L are the intermolecular separations on the inner and outer branches of $u(r)$. Then, taking the Laplace transform of eqn (81) gives

$$\begin{aligned} g_B(s) &\equiv L_s\{\Delta(t)\} \equiv \int_0^\infty \Delta(t) \exp(-st) dt \\ &= \left[\frac{3}{2\pi N_A \exp(s)} \right] (B_p + C_1 B_{h1} + C_2 B_{h2}) \\ &= g_p(s) + C_1 g_{h1}(s) + C_2 g_{h2}(s) \end{aligned}$$

$$\text{and BC's are } \begin{aligned} \Delta(t=0) &= 0 \\ \Delta(t=\infty) &= 0 \end{aligned} \quad (83)$$

where $s = \epsilon/kT$ and N_A is the Avogadro's constant. The expansion of the Pade approximant on the second acoustic virial coefficient in a series of positive and negative powers of T was employed to perform a numerical integration more accurately instead of the simple interpolation, that is,

$$\frac{A'_{2,o} - 2b_o}{A_{2,o} - 2b_o} = \sum_{n=0}^4 a_n T^{n-2} \quad (84)$$

where $b_o = 2\pi N_A \sigma_o^3/3$ at the collision diameter σ_o and $A'_{2,o}$ was determined from an approximate potential function with σ_o and an interpolation formula for γ_o . Both $B(T)$ and $u(r)$ were determined by this inversion method of

the second acoustic virial coefficient under the only assumption that $u(r)$ is spherically symmetrical. The results on $u(r)$ was found to be almost identical to that obtained by inversion of the true virial coefficients. It was mentioned, however, that the results on the second acoustic virial coefficient over a wide range of temperature were required.

Recently, Riazi and Mansoori^[8] developed a method to solve eqn (74) for $B(T)$ analytically and to obtain the parameters present in the equation of state using the sound velocity data. From the definition of the sound velocity in eqn (1), the sound velocity can be expressed in the general form of

$$c = c(S, V) \quad (85)$$

Differentiating eqn (1) with respect to S at constant V gives

$$2c dc = - \frac{V^2}{M_w} \left[\frac{\partial}{\partial S} \left(\frac{\partial P}{\partial V} \right)_S \right] dS \quad (86)$$

Substituting the thermodynamic relations of $dS = (\partial S/\partial T)_V dT$ and

$$(\partial P/\partial S)_V = -(\partial T/\partial V)_S$$

into eqn (86) and making use of the mathematical identity of derivatives yield

$$2c dc = \frac{V^2}{M_w} \left[\frac{\partial}{\partial V} \left(\frac{\partial T}{\partial V} \right)_S \right] \left(\frac{\partial S}{\partial T} \right)_V dT \quad (87)$$

On integration of eqn (87) with another mathematical identity on $(\partial T/\partial V)_S$, eqn (88) is derived.

$$c^2 - c_{hs}^2 = \frac{V^2}{M_w} \int_T^\infty \left(\frac{\partial^2 T}{\partial V^2} \right)_S \left(\frac{\partial S}{\partial T} \right)_V dT \quad (88)$$

where the subscript 'hs' denotes for the hard sphere property. Eqn (88) is a mathematical relationship for the following equation of state in the form of the sound velocity:

$$c = c(T, V) \quad (89)$$

Eqn (89) forms a basis for use of the sound velocity in obtaining PVT data. It has also been shown by Alem and Mansoori^[51] that the entropy of a hard sphere fluid becomes equal to that of a real fluid. For a hard sphere fluid the residual entropy is given by

$$(S - S_o)_{hs} = - \frac{R\eta(4-3\eta)}{(1-\eta)^2} \quad (90)$$

The residual entropy for ideal gas is equal to

$$S - S_0 = \int_{\infty}^V \left[\left(\frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV \quad (91)$$

Substituting the virial equation of state truncated after the third virial coefficient and its equation for hard sphere fluids into eqn (91), and making use of the equality of real fluids and hard sphere, the following ordinary differential equations for the second and third virial coefficients can be obtained.

$$T \frac{dB}{dT} + B = B_{hs} \quad (92)$$

$$T \frac{dC}{dT} + C = C_{hs} \quad (93)$$

where B_{hs} and C_{hs} are the second and third virial coefficients for the hard sphere equation of state. Since B_{hs} and C_{hs} are known for the Carnahan-Starling equation of state, the ordinary differential equations of eqns (92) and (93) were solved to give

$$B(T) = q_0 \frac{\ln T}{T} + \sum_{n=0}^3 \frac{p_n}{T^n} \quad (94)$$

$$C(T) = q_1 \frac{\ln T}{T} + \sum_{n=0}^6 \frac{l_n}{T^n} \quad (95)$$

The unknown parameters p_1 and l_1 in eqns (94) and (95), which are integration constants, were determined from the sound velocity data. The sound velocity expression for the virial equation of state becomes

$$c^2 = \frac{\gamma RT}{M_w} \left(1 + \frac{2B}{V} + \frac{3C}{V^2} \right) \quad (96)$$

With C_p and C_v for γ in eqn (96) expressed in terms of B and C , the parameter p_1 and l_1 were determined from the experimental sound velocity data. It might be interesting to note that the form of $B(T)$ has a term of $\ln T$, which has not been included in the curve-fitting method such as eqns (77) and (78).

$B(T)$ determined from eqn (94) for methane were in excellent agreement with the experimental data^[52]. While Dymond and Smith data produced the compressibility factor (Z) within around 0.8 % of the experimental values for more than 200 data points, $B(T)$ from eqn (94) gave an average deviation of 0.4 %. By the similar procedure the Lennard-Jones parameters σ and ϵ , and the parameters a and b in the van der Waals equation of state were also

evaluated. From the results on the compressibility factor (Z) obtained from the Lennard-Jones parameters, and parameters a and b in the van der Waals equation of state, it was concluded that the PVT relations could be extracted from the sound velocity data successfully.

4.3. Fluids at high pressures

The values of heat capacities over a wide range of pressure and temperature can be used to check the temperature derivatives of other thermodynamic properties and to test molecular theories of the behavior of thermodynamic properties. It is now known that errors of 1 or 2 parts per thousand in the PVT surface can lead to errors of 5 or 10 % in the first derivatives of the equation of state. At high pressures, where the pressure and temperature dependences of these derivatives are small, this can lead to larger errors, or sometimes even the wrong algebraic sign in the second derivatives used to calculate the pressure and volume dependence of heat capacities^[53].

Since the sound velocity measurements do not have any particular problem and can be done easily even at high pressures, where direct measurements are sometimes difficult, the sound velocity data can provide a check on the accuracy and precision of PVT data. The combination of sound velocity and PVT data can furnish a method to evaluate heat capacities without recourse to heat.

There are two groups of approaches to obtaining the thermodynamic properties of fluids at high pressures from the sound velocity data: (1) to derive the compressibilities and heat capacities directly with combination of the sound velocity and PVT data. (2) to extract PVT data (P-T isochores or P-r isotherms) from the sound velocity and other data at reference state by the successive integration procedures.

In the first method the adiabatic compressibility κ_S can be determined from eqn (1) once the sound velocity is measured as functions of density and temperature. The principal use of κ_S is to calculate κ_T and it

may be done through the following thermodynamic identity^[54]:

$$\alpha_T = \frac{\alpha_S C_\sigma + TV \alpha_\sigma (\alpha_\sigma + \alpha_S \gamma_\sigma)}{C_\sigma - TV \gamma_\sigma (\alpha_\sigma + \alpha_S \gamma_\sigma)} \quad (97)$$

when C_σ , α_σ , α_S , and γ_σ along the saturation curve are determined experimentally. After α_T is evaluated, the values of γ_v , α_p and γ can be calculated from the following relations in conjunction with PVT data.

$$\alpha_p = \alpha_\sigma + \alpha_T \gamma_\sigma \quad (98)$$

$$\gamma_v \equiv \left(\frac{\partial P}{\partial T} \right)_v = \frac{\alpha_p}{\alpha_T} \quad (99)$$

$$C_v = C_\sigma - TV \alpha_\sigma \gamma_v \quad (100)$$

$$C_p = C_\sigma - TV \alpha_p \gamma_\sigma \quad (101)$$

The calculated results on $(\partial \rho / \partial P)_T$ and heat capacities for saturated liquid oxygen, nitrogen, and argon, except hydrogen, agreed well with the experimental data^[55]. In order to calculate α_S and γ at elevated pressures, however, knowledge of density as a function of pressure must be given. This was obtained by using the following form of the Tait equation to describe the isothermal changes in the molar volume^[56]

$$\left(\frac{\partial V}{\partial P} \right)_T = - \frac{b_1}{b_2 + P} \quad (102)$$

where b_1 and b_2 are temperature dependent constants. Integrating eqn (102) yields

$$V_\sigma - V = b_1 \ln \frac{b_2 + P}{b_2 + P_\sigma} \quad (103)$$

Constants b_1 and b_2 were determined from two molar volumes at saturated vapor pressure P_σ and at some higher pressure P . With V determined, then, the adiabatic compressibility and heat capacities were evaluated by

$$\alpha_S = \frac{V}{M_w c^2} \quad (104)$$

$$C_p = \frac{TV \alpha_p^2}{\alpha_T - \alpha_S} \quad (105)$$

$$C_v = \frac{C_p \alpha_S}{\alpha_T} \quad (106)$$

This calculation method was applied to high pressure data in oxygen, nitrogen and hydrogen by Van Itterbeek and Van Dael^[56]. Theon et

al.^[57] used eqns (104) through (106) to calculate the thermodynamic properties of argon at pressures up to 500 atm and Streett^[53] extended these calculations for liquid argon up to its melting curve ($P_{\max} = 3000$ atm) at temperatures between 90 and 150 K.

When the sound velocity and all PVT data of interest are available, eqns (104) through (106) can be directly used to calculate the isothermal compressibility and heat capacities^[58,59,60,61]. When this procedure was applied to liquid krypton, for example, the results on C_p and C_v were accurate within about 5 % with the experimental values.

From the experimental data of density (ρ_σ) and pressure (P_σ) along the saturation curve, the sound velocity, and isobaric specific heat (C_p) instead of C_σ , the procedure of determining the values of α_T , γ , and C_v was developed by Blagoi et al.^[62]. Starting from the thermodynamic identity in eqn (98), the second term of the right hand side was considered negligible in the first run. With the approximated value of α_p in eqn (98) and sound velocity, the heat capacity ratio γ was determined from the following identity.

$$\gamma = 1 + \frac{T \alpha_p^2 c^2}{C_p} \quad (107)$$

Then, α_T was calculated from α_S and γ , and the calculation of α_p in the second run as carried out from α_T and γ_σ . By the successive approximations, the values of α_p , C_v , and γ were evaluated after the calculated value of α_p converged. This method was carried out over a limited range of high temperatures for krypton, xenon, and methane in the liquid state where γ_σ and α_T are so small that the error caused by the first approximation in eqn (98) leads to only less than 2%. The results on C_v deviated about 10% from the experimental data.

This technique to utilize the sound velocity data provides a means of calculating heat capacities without measuring a quantity of heat. The results on those calculated from the sound velocity agreed quite well with those by the

direct measurements for most components and were compiled by Rowlinson and Swinton^[54]. It should also be noticed that the above method presents real advantage compared with the relations using the second order derivatives commonly applied on PVT data, i.e.,

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P \quad (108)$$

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad (109)$$

It was shown that the calculated C_v curve had the general shape as the experimental results and was in excellent agreement with the experimental values^[56]. Streett^[53] also discussed that the sound velocity data together with the PVT relations could predict much better trend of the variation of C_p and C_v with a function of pressure.

Turning to the other approach, Davis and Gordon^[63] first developed an exact method by the stepwise integrations to calculate density change of Hg under high pressure as a function of P and T from the sound velocity data. The pressure dependence of the sound velocity was fitted to give

$$c = A + BP + DP^2 \quad (110)$$

where A , B , and D are adjustable parameters. As the first step to represent density as a function of T and P , the following thermodynamic identity comes from the definition of the sound velocity in Appendix 1.

$$\left(\frac{\partial \rho}{\partial P}\right)_T = \frac{1}{c^2} + \frac{T \alpha_p^2}{C_p} \quad (111)$$

They integrated eqn (111) at constant temperature T with respect to P .

$$\rho(P, T) = \rho(P^0, T) + \int_{P^0}^P \frac{1}{c^2(P)} dP + T \int_{P^0}^P \frac{\alpha_p^2}{C_p} dP \quad (112)$$

where P^0 is the pressure at the reference state (1 atm). On integration of eqn (112), the pressure interval $\Delta P (= P_2 - P_1)$ was kept small enough for $1/c^2(P)$ in the first integral to be assumed to vary linearly with pressure, and was determined to be about 125 bar for this system by a trial and error method. Provided

α_T is taken to be a polynomial function of temperature at P_1 , i.e., $\alpha_T = \sum a_n T^n$, the thermal expansion coefficient α_p in the second integral can be determined by using the following identity.

$$\left(\frac{\partial \alpha_p}{\partial P}\right)_T = -\left(\frac{\partial \alpha_T}{\partial T}\right)_P \quad (113)$$

With the initial slope of α_p vs. P determined from eqn (113), α_p over the interval ΔP was evaluated from

$$\alpha_p(P) = \alpha_p(P_1) + \left(\frac{\partial \alpha_p}{\partial P}\right)_{T, P_1} (P - P_1) \quad (114)$$

Using eqn (114) and its derivative with the respect to T , the pressure dependence of C_p in the second integral was approximated as follows:

$$\begin{aligned} \left(\frac{\partial C_p}{\partial P}\right)_T &= -\frac{T}{P} \left[\left(\frac{\partial \alpha_p}{\partial T}\right)_P + \alpha_p^2 \right] \\ &\approx -\frac{T}{\rho} \left[\left(\frac{\partial \alpha_p}{\partial T}\right)_{P_1} + \alpha_p^2 \right. \\ &\quad \left. + \frac{(\partial \alpha / \partial T)_{P_2} - (\partial \alpha / \partial T)_{P_1}}{P_2 - P_1} (P - P_1) \right] \end{aligned} \quad (115)$$

where $P_1 \leq P \leq P_2$

Integrating eqn (115) to observe ΔC_p , it was found that if ρ was assumed to be constant over ΔP , ΔC_p was small enough to be assumed constant for the integration over ΔP . Only the integral of α_p^2 along with eqn (114), therefore, was considered to compute the density variation in eqn (112).

Besides evaluating $\rho(P_2)$ from integrating eqn (112) with above information, C_p and α_p were determined as a function of T and P_2 from eqns (114) and (115). Once α_p was evaluated, α_T was also calculated as a function of T and P_2 from eqn (113). The thermodynamic properties such as ρ , α_p , C_p , α_S , and α_T , were obtained by repetition of the same procedure over ΔP at three different temperatures together with the experimental results on c , ρ , α_p , and C_p at 1 atm as the initial values to be needed for integration. An analytical repression for P - ρ

isotherms was shown to give a better representation than equations of state available. The error associated with each of the calculated values of the thermodynamic properties was estimated by placing appropriate perturbations on the input data and recording its effect on the final results.

A bit simpler method on integration of the second integral in eqn (112), where α_p was calculated directly from successive ρ -T isobars, was developed by Sun et al.^[64]. The density ρ^o and specific heat C_p^o at the reference state of 0.1 MPa (P^o) from the experimental data was fitted to give

$$\rho^o = a_0 + a_1 T + a_2 T^2 \quad (116)$$

$$C_p^o = b_0 + b_1 T + b_2 T^2 + b_3 T^3 \quad (117)$$

Under the assumption that the isobaric density at elevated pressures can also be represented by a second polynomial in T as in eqn (116),

$$\rho_{p1} = d_0(P) + d_1(P)T + d_2(P)T^2 \quad (118)$$

$\alpha_p(T) = -(\partial\rho/\partial T)_{p/\rho}$ at elevated pressures

was determined from ρ -T isobars in eqn (118). The first integral in eqn (112) was evaluated after fitting the sound velocity data to the following double polynomial equation:

$$P - P^o = \sum_{i=1}^m \sum_{j=1}^n A_{ij} T^i [c - c^o(T)]^j \quad (119)$$

where c^o is the sound velocity at P^o and A_{ij} 's are the coefficients to be fitted. The first integral $I = \int_{P^o}^{\infty} dP/c^2$, then, was expressed in the following form suitable for computer calculations:

$$I = \sum_{i=1}^m i \sum_{j=0}^n a_{ij} T^j \sum_{k=0}^{i-1} \frac{i-1-C_k}{k+1} (-c^o)^{i-k-1} \times [c^{k+1} - (c^o)^{k+1}] \quad (120)$$

This technique is simpler than the previous method by Davis and Gordon in that it does not need additional assumptions on $1/c^2$ and α_p for evaluating the first integral in eqn (112) and α_T , respectively. In addition to that, the more suitable form for the integral I in eqn (120) was used. By the error analysis composed of perturbations on the input data and monitoring

their effects on the results it was noted that accurate density data should be available for obtaining thermodynamic properties from the sound velocity data. The calculated results on density for ethanol at pressures of up to 280 MPa were found to show good agreement with the experimental data within 0.1% of average deviation. The same method was applied to toluene and n-heptane^[65].

ten Seldam and Biswas^[66], recently developed a new computational method of stepwise construction of P-T isochores starting from one experimental reference P- ρ isotherm, sound velocity data of the gas expressed as a function of P and T, and the heat capacity data fitted by the double polynomial expansion of temperature and density at lower pressures. Those are

$$\rho = A + \frac{B}{P} + CP + \frac{D}{P^2} + EP^m \quad (121)$$

$$P = \sum_{i=1}^m \sum_{j=1}^n A_{ij} T^i [c - c^o(T)]^j \quad (122)$$

$$C_v = C_{v0} + \sum_{k=1}^5 \sum_{l=1}^5 K_{kl} T^k \rho^l \quad (123)$$

where c^o is the sound velocity at $P^o = 0.1$ MPa and A, B, C, D, E, m, A_{ij} , and B_{ij} are adjustable parameters to fit the experimental data for the reference P- ρ isotherm, the sound velocity at the gas under investigation, and the specific heat of the gas.

Along with the values of P and $(\partial T/\partial T)_\rho$ calculated from eqn (122) at the reference temperature (298.15K) and at a number of selected densities, c at this pressure P and C_v were evaluated in eqns (122) and (123), respectively. The variation of C_v with density for all densities of study was determined by integrating the following relation.

$$\begin{aligned} \left(\frac{\partial C_v}{\partial \rho}\right)_T &= -\frac{T}{\rho^2} \left(\frac{\partial^2 P}{\partial T^2}\right)_\rho \\ &\approx -\frac{T}{\rho^2} \left[\left(\frac{\partial P}{\partial T}\right)_{\rho,T} \right. \\ &\quad \left. - \left(\frac{\partial P}{\partial T}\right)_{\rho,T-\Delta T}\right] / \Delta T \end{aligned} \quad (124)$$

At the next temperature T- ΔT with ΔT small (usually 1 K), the pressures corresponding to the selected densities were computed from

$$P(T - \Delta T) = P(T) - \left(\frac{\partial P}{\partial T} \right)_\rho \Delta T \quad (125)$$

Constructing the P-T isochores from eqn (112), the P- ρ isochores can also be developed simultaneously at temperatures with the temperature interval ΔT without an interpolation of procedure, and C_p and γ as well as C_v were also evaluated by using the thermodynamic relations:

$$C_p = \gamma C_v \quad (126)$$

$$\gamma = c^2 \left(\frac{\partial \rho}{\partial P} \right)_T \quad (127)$$

The average deviation of the density results for argon up to 1 GPa was be less than 0.1 % and was found to be within the experimental uncertainty of the direct measurements. Eqn (121), however, is not correct for low P as ρ blows out when $P \rightarrow 0$, which makes the application of this method restricted to high pressure regions where eqn (121) retains valid.

A computational method of constructing ρ -T isobars instead of P-T isochores was recently developed by the same group^[67]. It was needed to replace eqns (124) and (125) by

$$\left(\frac{\partial^2 V}{\partial T^2} \right)_\rho = \left[\left(\frac{\partial V}{\partial T} \right)_{\rho, T} - \left(\frac{\partial V}{\partial T} \right)_{\rho, T - \Delta T} \right] / \Delta T \quad (128)$$

$$\rho(T + \Delta T) = \rho(T) + \left(\frac{\partial \rho}{\partial T} \right)_\rho \Delta T \quad (129)$$

for evaluating ρ -T isobars.

We have discussed a series of methods to get the thermodynamic properties by integrating eqn (111) successively. In the stepwise integration methods, however, the gradual accumulation of errors is inevitable as the successive integrations proceed.

There was another type of approach to make use of the form of a secant bulk modulus. By using the bulk modulus K, which is the reciprocal of the isothermal compressibility κ_T , Fine and Millero^[68] determined the density and compressibility of water over the range of 0-100 °C and 0-1000 bar as functions of T and P from sound velocities. The second degree secant modulus equation is expressed in the following form^[69]

$$K \equiv \frac{1}{\kappa_T} = -\hat{V} \left(\frac{\partial P}{\partial \hat{V}} \right)_T \quad (130)$$

$$= \frac{P \hat{V}^\circ}{\hat{V}^\circ - \hat{V}} = K^\circ + A_1 P + A_2 P^2$$

where K, K° and \hat{V} , \hat{V}° are the bulk modulus and specific volumes at applied pressures P and 0, respectively. The values of K° and \hat{V}° can be fitted to give the polynomials in temperature from the experimental data. Rearranging eqn (130) gives the following expression for the specific volume:

$$\hat{V} = \hat{V}^\circ - \frac{\hat{V}^\circ P}{K^\circ + A_1 P + A_2 P^2} \quad (131)$$

Differentiation of eqn (131) with respect to P gives

$$\left(\frac{\partial \hat{V}}{\partial P} \right)_T = \frac{\hat{V}^\circ (K^\circ - A_2 P^2)}{(K^\circ + A_1 P + A_2 P^2)^2} \quad (132)$$

Eqn (132) is related to the sound velocity by the following thermodynamic relation

$$\left(\frac{\partial \hat{V}}{\partial P} \right)_T = \frac{\hat{V}^2}{c^2} + \frac{T \hat{V}^2 \alpha^2}{\hat{C}_p} \quad (133)$$

In eqn (133), \hat{C}_p° is calculated by integrating the thermodynamic relation of eqn (6.56).

$$\hat{C}_p = \hat{C}_p^\circ - T \int_1^P \left(\frac{\partial^2 \hat{V}}{\partial T^2} \right) dP \quad (134)$$

where \hat{C}_p° is the specific heat at 1 atm. Eqns (132) to (134) were combined to determine A_1 and A_2 as the polynomial functions of T. The specific volume was calculated from eqn (131), and the isothermal compressibility and thermal expansion coefficient of water, then, were determined from

$$\kappa_T = -\frac{1}{\hat{V}} \left(\frac{\partial \hat{V}}{\partial P} \right)_T = \frac{\hat{V}^\circ (K^\circ - A_2 P^2)}{\hat{V} (K^\circ + A_1 P + A_2 P^2)^2} \quad (135)$$

$$\alpha_p = \frac{1}{\hat{V}} \left(\frac{\partial \hat{V}}{\partial T} \right)_P$$

$$= \frac{1}{\hat{V}} \left(\frac{\partial \hat{V}^\circ}{\partial T} \right)_P - \frac{P (\partial \hat{V}^\circ / \partial T)_P}{\hat{V}^\circ (K^\circ + A_1 P + A_2 P^2)}$$

$$= P \hat{V}^\circ \frac{(dK^\circ/dT) + P(dA_1/dT) + P^2(dA_2/dT)}{\hat{V} (K^\circ + A_1 P + A_2 P^2)^2} \quad (136)$$

The calculated results for specific volumes by this approach were in good agreement within $2 \times 10^{-5} \text{ cm}^3/\text{g}$ with the experimental data. Chen et al.^[70] attempted the same method with more reliable data on the sound velocity at 1 atm. It was noticed that in spite of differences existing in the various fitting equations of sound velocity, the effects on the calculated specific volume were small.

Thus far several leading methods to obtain thermodynamic properties from the sound velocity data by the stepwise integrations have been reviewed. These techniques provide reliable information on thermodynamic properties and their temperature and pressure dependences and the accuracy of the computed PVT data, in general, is comparable to those obtained by the direct measurements. It was concluded that if the experimental density data at the reference state is accurate enough to make a smooth function of temperature over a wide range of temperature, an accurate equation of state for liquid can be extracted from the sound velocity data^[64].

5. CONCLUDING REMARKS

We have reviewed the relations between thermodynamic properties and sound velocity, and the methods to obtain thermodynamic properties from the sound velocity data.

Along with the complete PVT data, the sound velocity data can be very instrumental in checking the PVT data and in obtaining more accurate information on the temperature and pressure dependence of the important thermodynamic properties, such as thermal expansion coefficient, isothermal compressibility, and heat capacities. The measurement of the sound velocity also provides the methods to extract valuable information on thermodynamic properties which are accessible to direct measurement only with extreme difficulty. When it is difficult to determine the parameters in the equations of state for complex molecules, which are usually related to critical constants and other parameters, the sound velocity data will provide a promising tool for evaluating those.

The stepwise integration methods to take advantage of the sound velocity data have been applied to gases at moderate pressures, and liquids or supercritical fluids at high pressures with the reliable results. By reducing the gradual accumulation of errors during the successive integrations, the attempts to extend the stepwise construction technique to mixtures as well as to pure components over more wide range of conditions are to be desired.

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Appendix 1. Various expressions for sound velocity and compressibility

sound velocity

$$c^2 = \frac{1}{\rho x_s} = \frac{V}{M_w x_s} = -\frac{V^2}{M_w} \left(\frac{\partial P}{\partial V} \right)_s \quad (A1)$$

$$c^2 = \frac{\gamma}{\rho x_T} = \frac{\gamma V}{M_w x_T} = -\frac{\gamma V^2}{M_w} \left(\frac{\partial P}{\partial V} \right)_T \quad (A2)$$

$$c^2 = -\frac{\gamma ZRT}{M_w} \left(\frac{V}{P} \right) \left(\frac{\partial P}{\partial V} \right)_T \quad (A3)$$

$$c^2 = \frac{TV\gamma_V^2}{M_w C_V} + \frac{V}{M_w x_T} = \frac{V}{M_w} \left[\frac{TV\gamma_V^2}{C_V} + \frac{1}{x_T} \right] \quad (A4)$$

$$= \frac{T\gamma_\rho^2}{C_V \rho^2} + \left(\frac{\partial P}{\partial \rho} \right)_T$$

$$c^2 = \frac{V^2}{M_w} \left[\frac{T\gamma_V^2}{C_V} - \left(\frac{\partial P}{\partial V} \right)_T \right] \quad (A5)$$

$$= \frac{T}{\rho^2 C_V} \left(\frac{\partial P}{\partial T} \right)_\rho^2 + \left(\frac{\partial P}{\partial \rho} \right)_T$$

$$c^2 = \frac{RT}{M_w} \left[Z - V \left(\frac{\partial Z}{\partial V} \right)_T + \frac{R}{C_V} \left(Z + T \left(\frac{\partial Z}{\partial T} \right)_V \right)^2 \right] \quad (A6)$$

$$\left(\frac{c}{c_o} \right)^2 = -\frac{ZV}{P} \left(\frac{\gamma}{\gamma_o} \right) \left(\frac{\partial P}{\partial V} \right)_T = \left(\frac{\gamma}{\gamma_o} \right) \left[Z - V \left(\frac{\partial Z}{\partial V} \right)_T \right] \quad (A7)$$

compressibilities and ratio of heat capacities

$$\gamma = \frac{C_P}{C_V} = \frac{x_T}{x_s} = 1 + \frac{TVx_T\gamma_V^2}{C_V} = 1 + \frac{TV\alpha_P^2}{C_V x_T} \quad (A8)$$

$$\frac{1}{x_s} = \frac{1}{x_T} + \frac{TV\gamma_V^2}{C_V} \quad (A9)$$

$$x_T = x_s + \frac{TV\alpha_P^2}{C_P} = x_s + \alpha_P \left(\frac{\partial T}{\partial P} \right)_s \quad (A10)$$

Appendix 2. Sound velocity expressions for several equations of state

(1) Ideal gas law

$$PV = RT \quad (A11)$$

$$c^2 = c_o^2 = \frac{\gamma_o RT}{M_w} \quad (A12)$$

(2) Virial equation of state

$$P = \frac{RT}{V} \left(1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \right) \quad (\text{A13})$$

$$c^2 = \frac{\gamma_0 RT}{M_w} \left[1 + \frac{A_2}{V} + \frac{A_3}{V^2} + \frac{A_4}{V^3} + \dots \right] \quad (\text{A14})$$

where

$$A_2 = \left[2B + 2(\gamma_0 - 1)T \frac{dB}{dT} + \frac{(\gamma_0 - 1)^2}{\gamma_0} T^2 \frac{d^2B}{dT^2} \right] \quad (\text{A15})$$

$$A_3 = \left[B + (2\gamma_0 - 1)T \frac{dB}{dT} + (\gamma_0 - 1)T^2 \frac{d^2B}{dT^2} \right]^2 \frac{(\gamma_0 - 1)^2}{\gamma_0} \quad (\text{A16})$$

$$+ \frac{2\gamma_0 + 1}{\gamma_0} C + \frac{\gamma_0^2 - 1}{\gamma_0} T \frac{dC}{dT} + \frac{(\gamma_0 - 1)^2}{2\gamma_0} T^2 \frac{d^2C}{dT^2}$$

$$A_4 = \left(T \frac{dB}{dT} + T^2 \frac{d^2B}{dT^2} \right) \left[b + (2\gamma_0 - 1)T \frac{dB}{dT} + (\gamma_0 - 1)T^2 \frac{d^2B}{dT^2} \right]^2 \frac{(\gamma_0 - 1)^2}{\gamma_0} + \frac{1}{\gamma_0} \left[B + 2(\gamma_0 - 1)T \frac{dB}{dT} + (\gamma_0 - 1)T^2 \frac{d^2B}{dT^2} \right]^2 \times \left[2C + 2\gamma_0 T \frac{dC}{dT} + (\gamma_0 - 1)T^2 \frac{d^2C}{dT^2} \right] + \frac{2(\gamma_0 - 1)}{\gamma_0} D + \frac{2(\gamma_0 + 2)(\gamma_0 - 1)}{3\gamma_0} T \frac{dD}{dT} + \frac{(\gamma_0 - 1)^2}{3\gamma_0} T^2 \frac{d^2D}{dT^2} \quad (\text{A17})$$

or

$$P = \frac{RT}{V} (1 + B'P + C'P^2 + D'P^3 + \dots) \quad (\text{A18})$$

$$c^2 = \frac{\gamma_0 RT}{M_w} [1 + A_2'P + A_3'P^2 + A_4'P^3 + \dots] \quad (\text{A19})$$

where

$$B' = \frac{B}{RT}, \quad C' = \frac{C - B^2}{(RT)^2}, \quad D' = \frac{D - 3BC + 2B^2}{(RT)^3} \quad (\text{A20})$$

$$A_2' = \frac{A_2}{RT}, \quad A_3' = \frac{A_3 - BA_2}{(RT)^2}, \quad A_4' = \frac{A_4 - 2BA_3 + (2B^2 - C)A_2}{(RT)^3} \quad (\text{A21})$$

(3) Soave-Redlich-Kwong equation of state^[71]

$$P = \frac{RT}{V - b} - \frac{a\alpha}{V(V + b)} \quad (\text{A22})$$

$$\left(\frac{c}{c_0} \right) = \left(\frac{\gamma}{\gamma_0} \right) \left[\left(\frac{V}{V - b} \right)^2 - \left(\frac{V}{V - b} - Z \right) \left(1 + \frac{V}{V + b} \right) \right] \quad (\text{A23})$$

(4) Peng-Robinson equation of state^[72]

$$P = \frac{RT}{V - b} - \frac{a\alpha}{V(V + b) + b(V - b)} \quad (\text{A24})$$

$$\left(\frac{c}{c_0} \right) = \left(\frac{\gamma}{\gamma_0} \right) \left[\left(\frac{V}{V - b} \right)^2 - \left(\frac{V}{V - b} - Z \right) \left(1 + \frac{2V^2 + b^2}{V(V + b) - b(V - b)} \right) \right] \quad (\text{A25})$$