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Determination of Thermodynamic Properties from the Speed of Sound[1]

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We describe methods by which all of the observable thermodynamic properties of a compressed gas, including the compressibility factor and the isochoric heat capacity, may be determined from sound speed data by numerical integration of a pair of partial differential equations. The technique may be employed over a wide range of conditions. Initial values are required, but we demonstrate that values specified on an isotherm close to the critical temperature are sufficient for application of the method to the entire homogeneous fluid region at subcritical densities. The method may also be extended to higher densities at temperatures above the critical. The effects of errors in both the initial values and the speed of sound are examined in detail by means of analytic and numerical results. The results indicate that all of the observable thermodynamic properties may be obtained with an uncertainty equal to or less than that achievable by the best available alternative techniques.

KEY WORDS: equation of state; speed of sound; thermodynamic properties.

1. INTRODUCTION

The accurate experimental determination of thermodynamic properties of fluids, coupled with the representation of these data by equations of state, remains an important task. For a number of pure fluids, wide-ranging equations of state have been developed which represent accurately all of the thermodynamic properties of the fluid [1, 4]. Certain information is

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considered to be essential in the formulation of these equations of state. In particular, the vapor pressure curve, densities of the saturated liquid and vapor, and wide-ranging (p, ρ_n, T) measurements in the single-phase regions are required. Knowledge of the perfect-gas properties is of course also essential. In principle, this information is sufficient to establish an equation of state, but in practice it is found that second derivatives of the Helmholtz free energy are not well defined and that some heat capacity and/or sound speed results are also desirable to constrain these derivatives [1]. The use of acoustic results in the formulation of equations of state is particularly attractive since, with modern instrumentation, the speed of sound may be measured over a wide range of conditions with outstanding accuracy.

It is also possible to obtain all of the observable thermodynamic properties of a fluid phase directly from the speed of sound in advance of adopting any particular empirical representation of the thermodynamic surface. This may be achieved by integration, subject to specified initial conditions, of the partial differential equations which link the speed of sound with the other thermodynamic properties. In this paper we describe a practical algorithm for this purpose which is appropriate to the gas phase. We investigate in detail the propagation of errors arising from uncertainties in both the initial conditions and the speed of sound.

2. THEORY

The speed of sound u in a homogeneous fluid at zero frequency is given by

$$u^2 = (\partial p/\partial \rho)_S \tag{1}$$

where p is the pressure, ρ is the mass density, and S denotes entropy. It is convenient to eliminate the isentropic partial derivatives in favor of isothermal and either isobaric or isochoric terms. Taking temperature T and pressure p as the independent variables and introducing the compressibility factor $Z = Mp/\rho RT$, we have

$$u^{-2} = (M/RTZ^2)[\{Z - p(\partial Z/\partial p)_T\} - (R/C_{p,\mathrm{m}})\{Z + T(\partial Z/\partial T)_p\}^2] \tag{2}$$

where R is the gas constant and M is the molar mass. In the perfect-gas limit, we have $(RT/Mu^2) = 1 - (R/C_{p,\mathrm{m}}^{\mathrm{pg}})$, from which the perfect-gas isobaric molar heat capacity $C_{p,\mathrm{m}}^{\mathrm{pg}}$ may be obtained. The isobaric molar heat capacity of the compressed gas may be written

$$C_{p,\mathrm{m}} = C_{p,\mathrm{m}}^{\mathrm{pg}} + \int_0^p (\partial C_{p,\mathrm{m}}/\partial p)_T \, dp \tag{3}$$

where

$$(\partial C_{p,\mathrm{m}}/\partial p)_T = -(R/p)\{2T(\partial Z/\partial T)_p + T^2(\partial^2 Z/\partial T^2)_p\} \tag{4}$$

Equations (2) and (4) may then be solved simultaneously to obtain $Z(T, p)$ and $C_{p,\mathrm{m}}(T, p)$ over the region in which $u(T, p)$ is known.

If, instead of (T, p), we take (T, ρ_n) as the independent variables, where ρ_n is the amount-of-substance density, the following equations are obtained:

$$u^2 = (RT/M)[\{Z + \rho_n(\partial Z/\partial \rho_n)_T\} + (R/C_{V,\mathrm{m}})\{Z + T(\partial Z/\partial T)_{\rho_n}\}^2] \tag{5}$$

and

$$(\partial C_{V,\mathrm{m}}/\partial \rho_n)_T = -(R/\rho_n)\{2T(\partial Z/\partial T)_{\rho_n} + T^2(\partial^2 Z/\partial T^2)_{\rho_n}\} \tag{6}$$

Equations (5) and (6) may also be solved simultaneously to obtain Z and $C_{V,\mathrm{m}}$ over the region in which u is known even when (u, T, p) are the measured quantities.

Clearly, initial values or boundary values are required for the integration of either pair of equations, and since we have a second-order partial differential equation, two independent sets of values will be required. Based on the form of Eq. (1), we argue that the initial conditions must be

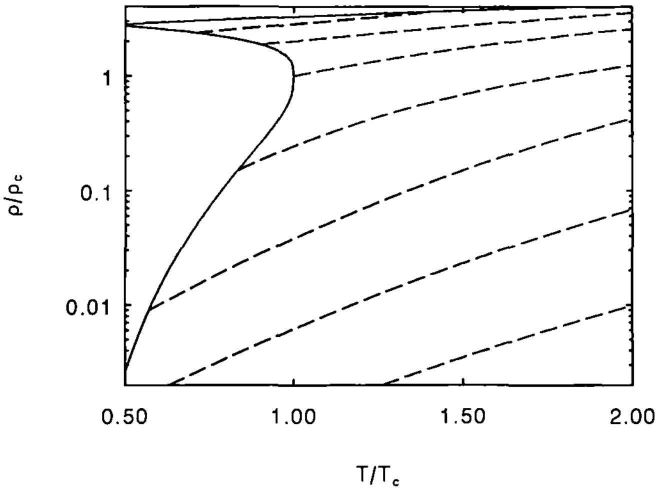

Fig. 1. Isentropes in fluid methane from Ref. 1. (-----) Isentropes; (——) phase boundaries.

specified along, or at least near to, a path which crosses all of the isentropes that pass through the region in which the solution is sought. The general form of the isentropes is illustrated in Fig. 1, where results for fluid methane are shown on a temperature-density diagram. If the integration region is a rectangular space in (T, ρ_n) or (T, p), then the only path that satisfies our criterion is the isotherm at the lowest temperature. The integration then proceeds toward higher temperatures. However, by our criterion, it should also be possible to generate a stable solution at temperatures below that of the initial isotherm provided that the domain of the integration is progressively restricted to pressures or densities which fall with decreasing temperature at least as rapidly as do the isentropes. These argument will be substantiated below using both analytic and numerical results concerning the sensitivity of the solution to the errors in the initial conditions.

3. NUMERICAL METHODS

We now turn to numerical algorithms for obtaining all of the thermodynamic properties of a gas from the speed of sound. A practical method for the case in which (T, p) are the independent variables has been described in detail by Trusler and Zarari [2]. Here we consider an alternative method appropriate to a rectangular space with (T, ρ_n) as the independent variables. We shall also indicate how either method may be adapted to cope with a subcritical region bounded by a line parallel to the saturation curve.

3.1. (T, ρ_n) as Independent Variables

In this case we are interested in solving Eqs. (5) and (6) and we have devised a strategy for this which is similar to the predictor-corrector algorithm of Trusler and Zarari [2]. Values of Z and $(\partial Z/\partial T)_{\rho_n}$ are required at the initial temperature T_0 and these are used together with the speed of sound to determined $C_{V,m}$ along the that isotherm from Eq. (5). Differentiation of $C_{V,m}$ with respect to ρ_n then permits determination of $(\partial^2 Z/\partial T^2)_{\rho_n}$ from Eq. (6) for use in the predictor step of the algorithm. In this step, Z and $(\partial Z/\partial T)_{\rho_n}$ are estimated at the temperature $T_1 = T_0 + \delta T$ by means of Taylor's series expansions truncated after the second temperature derivative of Z. The calculation is then repeated at T_1 to obtain $(\partial^2 Z/\partial T^2)_{\rho_n}$ at that temperature and, hence, the mean value of the second temperature derivative on the interval $[T_0, T_1]$. The corrector step of the algorithm is then employed in which improved values of Z and $(\partial Z/\partial T)_{\rho_n}$ at T_1 are obtained; in this step, the truncated Taylor's series are again used but now with the mean value of $(\partial^2 Z/\partial T^2)_{\rho_n}$ on the interval $[T_0, T_1]$ in place of the value at T_0. This has the effect of reducing the truncation error of the method and permits the use of larger temperature increments. The procedure then restarts at T_1 and continues until the upper experimental temperature is reached.

This method may be applied even when u, T, and p are the experimental quantities because, whenever it is necessary to employ a value of u, Z has already been determined at that point and the pressure corresponding to the specified temperature and density may be evaluated. Typically, measurements might be made along a set of isotherms with the greatest pressure on each chosen to lie approximately on a specified isochore. An interpolation method is required in practice to obtain u at the larger number of grid points used in the calculation from the, presumably, much smaller set of experimental results.

The method has been tested numerically using simulated results for argon obtained from the equation of state of Stewart and Jacobsen [3]. The tests were carried out in the reduced temperature range $1.0 \leqslant T/T^{\mathrm{c}} \leqslant 5.0$, where T^{c} is the critical temperature, and at densities up to one-half of the critical. With 30 evenly spaced densities and temperatures steps of order $T^{\mathrm{c}}/10^3$, the method was found to be stable and efficient with a numerical accuracy of order $\pm 10^{-5}$ in Z and $\pm 10^{-4}$ in $C_{V,\mathrm{m}}/R$. Higher numerical accuracy may be obtained with a finer grid.

3.2. Application to Subcritical Conditions

The methods described above may be applied without modification to gases at subcritical temperatures as long as a positive temperature increment δT is used. However, we have devised a more useful procedure, in which a negative temperature increment is used but neither isobars nor isochores are followed. Instead, the path of the integration is chosen to be parallel with the saturation curve so that, when (T, p) are the independent variables, one uses a set of pressures which are each specified fractions of the vapor pressure. With (T, ρ_n) as the independent variables, densities which are specified fractions of the saturated vapor density may be used. In either case, the path of the integration is such that all of the isentropes pass through the isotherm at the highest temperature. We have tested this method also with simulated results for argon in the reduced temperature range $0.7 \leqslant T/T^{\mathrm{c}} \leqslant 1.0$ and with densities up to half of the critical. The initial conditions were specified on the critical isotherm and the accuracy and stability of the method was the same as that described above.

4. PROPAGATION OF ERRORS

Errors in the thermodynamic properties obtained from the speed of sound will arise from errors in both u itself and the initial conditions. We shall take (T, ρ_n) as the independent variables for the purposes of this discussion and denote the "true" solution of Eqs. (5) and (6) by Z_0. If the equations are solved, with values of the speed of sound and initial conditions each burdened by small errors, then an erroneous solution for Z will be obtained which we denote by $Z_0 + Z_1$, where Z_1 may be termed a parasitic function. We suppose that initial conditions are specified at $T = T_0$ as follows:

$$Z = Z_0 + \varepsilon_0(\rho_n) \tag{7}$$

and

$$T_0(\partial Z/\partial T)_{\rho_n} = T_0(\partial Z_0/\partial T)_{\rho_n} + \varepsilon_1(\rho_n) \tag{8}$$

where ε_0 and ε_1 are functions which represent the experimental errors. We further suppose that the experimental values of u^2 are burdened by some small fractional error δ, which is a smooth function of temperature and density. When the errors are small (ε_0, ε_1, δ each $\ll 1$), Z_1 will also be small compared with Z_0 and we may linearize Eqs. (5) and (6) to obtain the equation obeyed by Z_1 in that regime:

$$\begin{aligned}(Mu^2/RT)\delta = {} & \{Z_1 + \rho_n(\partial Z_1/\partial \rho_n)_T\} + 2a\{Z_0 + T(\partial Z_0/\partial T)_{\rho_n}\} \\ & \times \{Z_1 + T(\partial Z_1/T)_{\rho_n}\} + a^2\{Z_0 + T(\partial Z_0/\partial T)_{\rho_n}\}^2 \\ & \times \int_0^{\rho_n} \{2T(\partial Z_1/\partial T)_{\rho_n} + T^2(\partial^2 Z_1/\partial T^2)_{\rho_n}\}\, \rho_n^{-1}\, d\rho_n \end{aligned} \tag{9}$$

Here $a = R/C_{V,m}$. We next assume that δ may be represented by the double-power series expansion

$$\delta = \sum_j b_j \rho_n^{n_j} (T/T_0)^{\alpha_j} \tag{10}$$

in which n_j and α_j are exponents and the b_j are constants. Exact analytic solution of Eq. (9) is possible only in the special case where $Z_0 = 1$ and hence $(Mu^2/RT) = (1 + a)$. It is also convenient to assume that a is constant, in which case the general solution is given by [4]

$$\begin{aligned}Z_1 = {} & \sum_j (b_j/\chi_j)\, \rho_n^{n_j} (T/T_0)^{\alpha_j} \\ & + \sum_k [c_k \cos\{\gamma_k \ln(T/T_0)\} + d_k \sin\{\gamma_k \ln(T/T_0)\}](T/T_0)^{-\beta_k} \rho_n^{m_k}\end{aligned} \tag{11}$$

In Eq. (11), χ_j is given by

$$\chi_j = \{n_j(n_j + 1) + 2an_j(1 + \alpha_j) + a^2\alpha_j(1 + \alpha_j)\}/\{(1 + a)\, n_j\} \tag{12}$$

c_k and d_k are arbitrary constants, m_k is an exponent, and β_k and γ_k are given by

$$\beta_k = \tfrac{1}{2}\{1 + (2m_k/a)\} \tag{13}$$

$$\gamma_k^2 = \{(1 + a)/a^2\}\, m_k - \tfrac{1}{4} \tag{14}$$

The corresponding error $\Delta C_{V,\mathrm{m}}$ in the isochoric molar heat capacity is then given by

$$\begin{aligned}\Delta C_{V,\mathrm{m}}/R = {} & -\sum_j (b_j/\chi_j)(\rho_n^{n_j}/n_j)\,\alpha_j(\alpha_j + 1)(T/T_0)^{\alpha_j} \\ & + \sum_k \{c_k(\gamma_k^2 - \beta_k^2 + \beta_k) + d_k(2\beta_k - 1)\,\gamma_k\} \\ & \times \cos\{\gamma_k \ln(T/T_0)\}(T/T_0)^{-\beta_k}(\rho_n^{m_k}/m_k) \\ & + \sum_k \{d_k(\gamma_k^2 - \beta_k^2 + \beta_k) - c_k(2\beta_k - 1)\,\gamma_k\} \\ & \times \sin\{\gamma_k \ln(T/T_0)\}(T/T_0)^{-\beta_k}(\rho_n^{m_k}/m_k)\end{aligned} \tag{15}$$

The first term in Eq. (11) is the particular solution corresponding to the assumed fractional error in the speed of sound, while the second term is the solution of the corresponding homogeneous equation [4]. The particular solution is completely determined by δ, and the constants c_k, d_k, and m_k should be adjusted to satisfy the initial conditions at $T = T_0$. This result indicates that the particular solution has exactly the same functional form as δ itself. Furthermore, since χ_j is generally of order unity, errors in the speed of sound propagate into errors in Z of the same order. However, two special cases are worth mentioning. The first is when δ is constant, in which case the corresponding error in Z vanishes (but there will be an error in the derived heat capacity). The second special case is when the function δ contains a term with values of n_j and α_j such that χ_j vanishes; the effect of such an error in u^2 is catastrophic. However, the equation $\chi_j = 0$ has a real root only when $n_j = a^2/\{4(1 + a)\}$ and $\alpha_j = -(2 + 3a)/\{4(1 + a)\}$; this value of n_j always corresponds to a term which is nonanalytic in the limit $\rho_n \to 0$. For example, with a monatomic gas n_j is 1/15 (and $\alpha_j = -3/5$). Provided that the fractional error in the speed of sound may be represented by terms which are analytic functions of the density, the conclusion that Z_1 is of the same order as δ is strictly valid. With current measurement techniques, this source of error may be one order of magnitude smaller than typical uncertainties in direct (p, ρ_n, T) measurements. For real gases, the precise propagation of errors from u^2 to Z will differ somewhat from the ideal-gas solution but the same general conclusion applies.

We now turn to the effects of errors in the initial conditions alone with $\delta = 0$. Since at $T = T_0$

$$Z_1 = \varepsilon_0 = \sum_k c_k \rho_n^{m_k} \tag{16}$$

and

$$T_0(\partial Z_1/\partial T)_{\rho_n} = \varepsilon_1 = \sum_k (\gamma_k d_k - \beta_k c_k)\, \rho_n^{m_k} \tag{17}$$

the parameters c_k, d_k, and m_k are determined completely by the functions ε_0 and ε_1. It follows from Eq. (14) that, provided $m_k \geqslant a^2/4(1+\alpha)$, γ_k and β_k are both positive-real, and the kth term in the series for the parasitic solution has the form of a damped oscillation which ultimately decays to zero along an isochore as $T \rightarrow \infty$. On the other hand, terms for $\beta_k < 0$ diverge with increasing T and it is therefore essential to ensure that the series representations of ε_0 and ε_1 do not contain such terms. In practice this should be fairly easy as the functional form of Z is known to be that of the virial series in the low-density limit. We note that along a path with $\rho_n \propto T^x$, the term $(T/T_0)^{-\beta_k} \rho_n^{m_k}$ ensures that Z_1 ultimately decays for all m_k only if $x < a^{-1}$. The case $x = a^{-1}$ corresponds to the isentropic path for the ideal-gas model with $C_{V,m}$ constant and represents a limit of stability. This is exactly the result anticipated earlier.

For moderately dense real gases, the most interesting errors terms are those proportional to positive integer powers of ρ_n. Typical behavior is illustrated in Fig. 2 by the results for a polyatomic gas with $a = \frac{1}{3}$. We show here the effects of errors in the initial values of Z (with $\varepsilon_1 = 0$) and also the effects of errors in the initial values of $T(\partial Z/\partial T)_{\rho_n}$ (with $\varepsilon_0 = 0$). Terms with $m_k = 1$, 2, and 3 are shown in both cases. The results are shown along an isochore on which either $\varepsilon_0 = 2 \times 10^{-4}$ or $\varepsilon_1 = 2 \times 10^{-3}$; these values were chosen to correspond to achievable experimental accuracies in Z and $T(\partial Z/\partial T)_{\rho_n}$. We see that the effects of an initial error in Z decay rather rapidly, especially for larger values of the exponent m_k. For the case of initial errors in $T(\partial Z/\partial T)_{\rho_n}$, the situation is slightly less satisfactory because the propagated errors at first grows before eventually decaying. However, in this example the greatest error does still not exceed 2×10^{-4}. We note that, in all cases, the propagated error decays more rapidly for smaller values of a and that the accuracy required of the initial values of $T(\partial Z/\partial T)_{\rho_n}$ is most demanding for the case of a monatomic gas. The effects of both kinds of error in the initial conditions on the values of $C_{V,m}$ obtained are greatest at the initial temperature and decay rapidly at higher temperatures. For example, the terms with $m_k = 1$ give rise to errors of

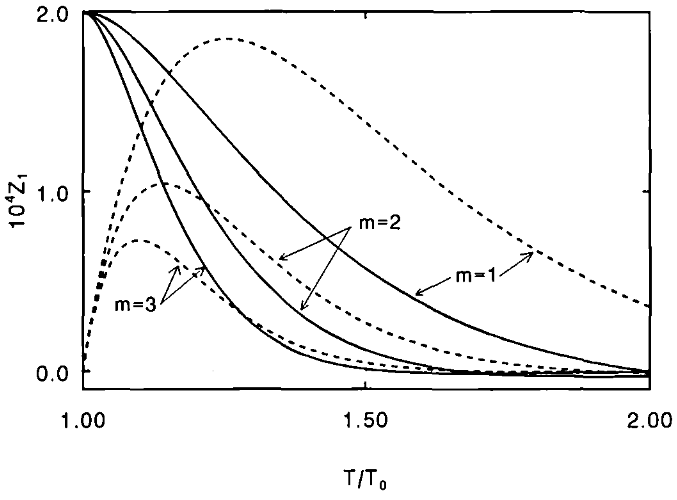

Fig. 2. Parasitic contribution Z_1 to Z along an isochore for a gas with $a = 1/3$ resulting from errors in the initial conditions proportional to ρ_n^m. (——) $Z_1 = 2 \times 10^{-4}$ at T_0; (-----) $T(\partial Z_1/\partial T)_{\rho_n} = 2 \times 10^{-3}$ at T_0.

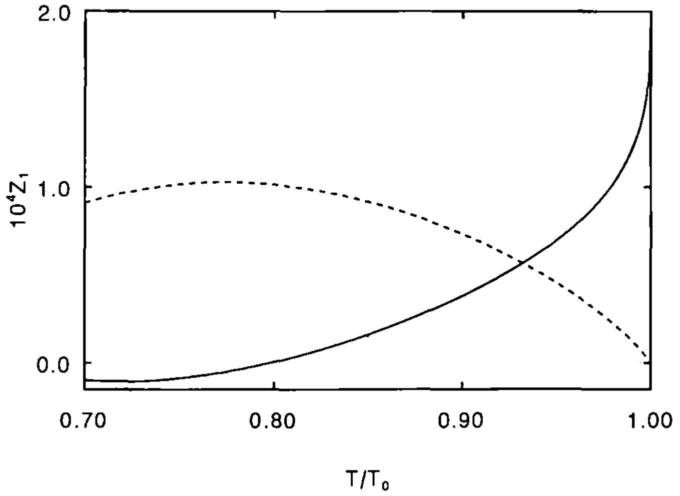

Fig. 3. Parasitic contribution Z_1 to Z along a line at a constant fraction of the saturation density for a gas with $a = 1/3$ resulting from errors in the initial conditions proportional to ρ_n. (——) $Z_1 = 2 \times 10^{-4}$ at T_0; (-----), $T(\partial Z_1/\partial T)_{\rho_n} = -2 \times 10^{-3}$ at T_0.

about 0.2% at T_0 but the propagated error is less than 0.1% at all temperatures above $1.1T_0$.

It is of course possible numerically to generate a solution at temperatures below T_0 but Eq. (11) shows that the parasitic errors will exhibit oscillatory behaviour with exponential growth as the temperature is reduced along an isochore. However, over a short interval, useful results may be expected. When the solution is generated with a negative temperature increment but in a region bounded by an upper density equal to a specified fraction of the saturated vapour density, the parasitic terms again decay. This is illustrated in Fig. 3 for the case of a polyatomic gas with $a = 1/3$ and errors in the initial conditions proportional to ρ_n.

The analytic model used above is of course based on the erroneous assumptions that Z_0 is unity and a is constant, but as we shall see, the results are qualitatively correct. The analytic solution correctly predicts the damped oscillatory behavior of Z_1 at temperatures above T_0, that the effects of errors in the initial conditions proportional to $\rho_n^{m_k}$ decay increasingly rapidly as the exponent m_k increases, and that the effects of errors in the initial conditions decay more rapidly for polyatomic gases ($a \leqslant 1/3$) than they do for monatomic gases ($a = 2/3$). By setting

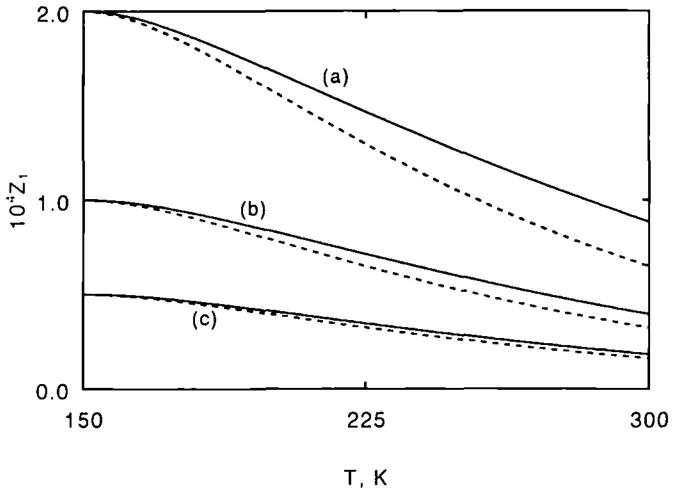

Fig. 4. Parasitic contribution Z_1 to Z along isochores for argon gas resulting from an error in the initial values of Z given by $\varepsilon_0 = 4\times10^{-4}(\rho_n/\rho_n^c)$, where ρ_n^c is the critical density. (a) $\rho_n = \rho_n^c/2$; (b) $\rho_n = \rho_n^c/4$; and (c) $\rho_n = \rho_n^c/8$. (——), Numerical solution of Eq. (9) with properties from Ref. 3; (-----), Eq. (11).

$a = R/C^{\mathrm{pg}}_{V,\mathrm{m}}(T_0)$ and neglecting variation of this quantity with temperature, one effectively overestimate slightly the propagation of errors for polyatomic gases at $T > T_0$.

The effects of approximating Z_0 by unity have been tested by comparing the analytic error model with the results of numerical solutions of Eq. (9). In Fig. 4 we show the results of calculations performed for argon gas along isochores at one-half, one-quarter, and one-eight of the critical density with the initial temperature close to T^c. For the numerical solution, all properties were calculated from the equation of state of Stewart and Jacobsen [3]. We see that the actual propagated error determined numerically is generally rather greater that the analytic model predicts but that the differences are not too large and the agreement gets better, as expected, at lower densities. If we compare instead Z_1/Z, then we find that the analytic model gives an upper bound of the relative error.

5. CONCLUSIONS

The results in this paper show that the compression factor of a gas may be obtained from the speed of sound with an accuracy controlled mainly be the accuracy of the initial conditions. The isochoric and isobaric heat capacities may be obtained also with outstanding accuracy. For the gas phase, initial conditions on an isotherm near to T^c are sufficient to apply the method along isochores (or isobars) to higher temperatures and along paths parallel to the saturation curve at lower temperatures. For many polyatomic gases, values of Z along two closely spaced isotherms should be sufficient to determine the initial conditions but, for monatomic gases, several isotherms may be needed to determine $T(\partial Z/\partial T)_{\rho_n}$ with sufficient accuracy for the results to equal or exceed the accuracy of direct measurements.

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