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Debye Fluid State Equation

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A new form of a fluid state equation, based on a conceptual extrapolation from the Debye equation for the specific heat of solid materials is described. The Debye characteristic temperature, Θ, which is nominally a constant for solids, becomes a function of the fluid density ρ. Further assuming $\Theta = c_1\rho^{2/3}(1+c_2\rho+c_3\rho^2+\cdots)$ yields the conventional fluid virial equation in the high-T and low-ρ limits for a monatomic fluid. Additional terms must be added to describe (a) the compressibility of the dense subcooled fluid and (b) properties in the near-critical range. Discussion of the Gruneisen parameter and other factors is included. This Debye fluid theory was used as a state equation for ^{3}He, continuous from 0.005 K to above room temperature.

KEY WORDS: Debye theory; helium isotope; specific heat; state equation.

1. INTRODUCTION

Fluid state equations have been developed as an accurate science through a variety of publications, exemplified, for example, by NIST's REFPROP computer code [1]. However, the wide range of ^{3}He thermodynamic data posses a unique problem, illustrated by the experimental isochoric specific heat data in Fig. 1. This figure neglects the ^{3}He superfluid range below 0.0026 K, but does display significant and continuous fluid properties above 0.005 K. For almost all other fluids, the lower limit

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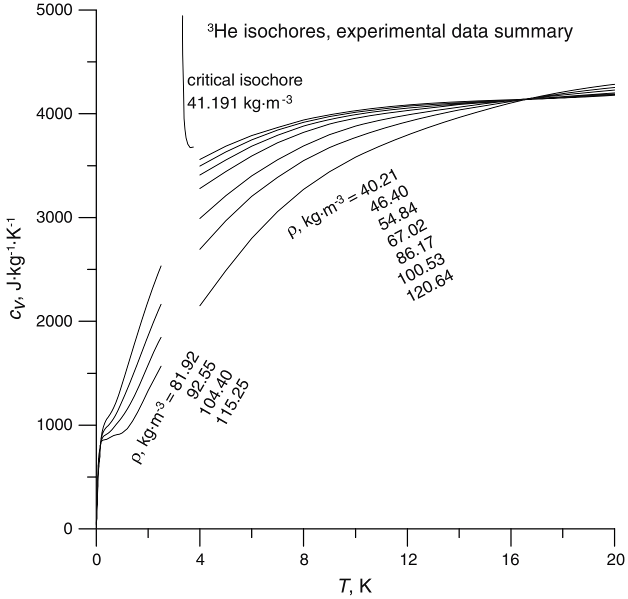

Fig. 1. Experimental isochoric specific heat of ^{3}He.

of the fluid state equation is roughly 1/4 to $1/2T_c$, limited by the formation of a solid at lower temperatures. For ^{4}He, the lower limit of the conventional state equation is again about $1/2T_c$, limited in this case by the transition to the unique superfluid state at lower temperatures. Dominant T_c/T terms in the generally accepted Helmholtz potential for fluids cannot be constrained to fit the ^{3}He data below about 2 K according to our limited test.

Our recent publication of a state equation for ^{3}He valid from 0.005 to 20 K (and probably to above 300 K, although ^{3}He data are not available to confirm this) [2,3] utilized a new Debye fluid state term in place of the more conventional equations. That paper focused on a combination of this Debye term with other terms describing nuclear spin alignment, the high-density fluid, and the near-critical behavior to obtain a reasonably satisfactory state equation. In this paper, we give a more comprehensive study of the fluid Debye equation itself, including tests and potential applications for other fluids.

2. CONCEPTUAL DEVELOPMENT

The Debye theory originated in the earliest days of quantum mechanics [4], with the study of vibrational motions within an atomic lattice.

It leads to relationships between energy and momentum of phonons in the low-frequency limit. These same excitational relationships have also been utilized in some studies of dynamics of atoms or molecules of a fluid, e.g., in neutron spectroscopy studies of liquid helium [5].

In the Debye theory, the specific heat at constant volume, c_v, is given by an integration over allowed excitation frequencies:

$$c_v = 9R_\mathrm{m}\zeta^3 \int_0^{1/\zeta} \frac{x^4 \mathrm{e}^x \mathrm{d}x}{(\mathrm{e}^x - 1)^2}, \tag{1}$$

where R_m is the molar gas constant, $\zeta = 1/x_\mathrm{D}$, and x_D is the Debye frequency, which is commonly defined as Θ/T. The parameter Θ is often spoken of as the "Debye characteristic temperature" or just "Debye theta." Θ is found to be approximately constant for many solids, e.g., 88 K for Pb, 315 K for Cu, and 1180 K for diamond [6]. A constant density is implicitly assumed.

In this work, it is convenient to use mathematical integrals of Eq. (1) related to entropy and Helmholtz energy. We define

$$H_2(\zeta) = c_v/\zeta \tag{2a}$$

$$H_1(\zeta) = \int_0^\zeta H_2(t)\mathrm{d}t \quad \text{or} \quad H_2 = \mathrm{d}(H_1(\zeta))/\mathrm{d}\zeta \tag{2b}$$

$$H_0(\zeta) = \int_0^\zeta H_1(t)\mathrm{d}t \quad \text{or} \quad H_1 = \mathrm{d}(H_0(\zeta))/\mathrm{d}\zeta \tag{2c}$$

$$H_{10} = \zeta H_1 - H_0. \tag{2d}$$

Equations (2a)–(2d) cannot be evaluated in closed form; thus, table look-ups and interpolation must be used for numerical calculations.

3. DEBYE FLUID STATE EQUATION

Our basic assumption (or approximation) is that Θ is a unique function of only the density, $\Theta(\rho)$, for a given fluid. It is convenient to use the notation:

$$\Theta' = \mathrm{d}\Theta/\mathrm{d}\rho \quad \text{and} \quad \Theta'' = \mathrm{d}^2\Theta/\mathrm{d}\rho^2. \tag{3}$$

We define the Debye fluid state equation from the Helmholtz potential,

$$A(\rho, T) = -\Theta H_0(\zeta). \tag{4a}$$

It follows from standard thermodynamics that

$$\text{Entropy}\, s = H_1(\zeta) \tag{4b}$$

$$\text{Specific heat}\, c_v = \zeta H_2(\zeta) \tag{4c}$$

$$\text{Pressure}\, p = \rho^2 H_{10}\Theta' \tag{4d}$$

$$(\partial p/\partial T)_\rho = \rho^2 \zeta H_2(\zeta)\Theta'/\Theta \tag{4e}$$

$$(\partial p/\partial \rho)_T = \rho[2H_{10} - \rho(\zeta^2 H_2(\zeta)(\Theta')^2/\Theta - H_{10}\Theta'')]. \tag{4f}$$

All other commonly defined fluid state properties can be derived from Eqs. (4a)–(4f).

An additional identification is important. Equations (4c) and (4e) can be combined to obtain an equation for the Gruneisen parameter Γ, defined as

$$\Gamma = (\partial p/\partial T)_\rho/(\rho c_v) = (\rho/T)(\partial T/\partial \rho)_s. \tag{5}$$

with the result

$$\Gamma = (\rho/\Theta)\mathrm{d}\Theta/\mathrm{d}\rho. \tag{6}$$

A further useful expression is the identity

$$c_p/c_v = \gamma = 1 + \alpha\Gamma, \quad \text{where } \alpha = -(T/\rho)(\partial\rho/\partial T)_p \tag{7}$$

Discussions related to Eq. (6) are included later in this paper. (Note that the Gruneisen parameter is often denoted as γ in the literature of solid-state properties. For fluid properties, we prefer to reserve the symbol γ for its customary definition(s) as (1) the ratio of specific heats, and/or (2) one of four critical-point scaling indices.)

4. FUNCTIONAL FORM OF $\Theta(\rho)$

The functional form for $\Theta(\rho)$ is conveniently obtained by considering the high-temperature limit. As $\zeta \to \infty$,

$$\begin{aligned} H_2(\zeta) &\to 3R_\mathrm{m}/\zeta \quad \text{or} \quad c_v \to 3R_\mathrm{m} \\ H_1(\zeta) &\to 3R_\mathrm{m}\log(\zeta) \\ H_0(\zeta) &\to 3R_\mathrm{m}(\zeta\,\log(\zeta) - 1) \\ H_{10}(\zeta) &\to 3R_\mathrm{m}\zeta, \end{aligned} \tag{8}$$

which agrees with the law of Dulong and Petit [7]. On the other hand, c_v for the ideal gas equals nR_{m}, where $n = 3/2$ for a monatomic gas and 5/2 for a diatomic gas. Hence, the right-hand side of Eq. (4) should be multiplied by a factor of $n/3$ to make units thermodynamically consistent. Considering the ideal-gas equation $p = \rho R_{\mathrm{m}} T$ and Eq. (4d) for pressure at this limit, we get

$$(n/3)\rho^2(3R_{\mathrm{m}})\zeta(\mathrm{d}\Theta/\mathrm{d}\rho) = \rho R_m T. \tag{9a}$$

Canceling the same variables on both sides, replacing ζ with T/Θ, and then integrating, we have

$$\Theta = \mathrm{c}_1\rho^{(1/\mathrm{n})}, \tag{9b}$$

which is valid in the limit of low density. At higher density it is reasonable to expect the following analytical form for helium isotopes:

$$\Theta = \mathrm{c}_1\rho^{(2/3)}(1 + \mathrm{c}_2\rho + \mathrm{c}_3\rho^2 + \cdots). \tag{9c}$$

Equation (4d) then becomes

$$p = \rho R_{\mathrm{m}} T(1 + (3/2)\mathrm{c}_2\rho + \mathrm{constant}\cdot\mathrm{c}_3\rho^2 + \cdots). \tag{10}$$

The density exponent in Eq. (9) is equal to the value of Γ in the ideal-gas (zero-density) limit. Equation (10) is a virial state equation, with the "first virial coefficient" = (3/2)c_2, a constant, in contrast to the temperature-dependent $B(T)$ for real fluids. Note that Eq. (10) is independent of the parameter c_1.

At less than high temperatures, the Debye equations are not analytic in the limit $\rho \to 0$, and Eq. (10) is not valid. For numerical work, it is convenient to define the second virial coefficient in the Debye approximation, B_{D}, as

$$B_{\mathrm{D}}(T) = (\partial^2 p/\partial\rho^2)_T/(nR_{\mathrm{m}}T/3) \text{ in the limit } \rho \to 0. \tag{11}$$

We have investigated Eq. (11) in comparison with accurate $B(T)$ data for both ^{3}He and ^{4}He [8]. For both of these fluids, $B(T)$ reaches a broad maximum at about 160–180 K and then slowly drops to about one-half of the peak value at 10,000 K. A practical problem is that numerical values from Eq. (11) become very sensitive to an accumulation of miscellaneous roundoff errors as $\rho \to 0$. Nevertheless, it is possible to find values of c_1 and c_2 that give satisfactory agreement between the reference $B(T)$ and calculated $B_{\mathrm{D}}(T)$ up to about 80 K for both ^{3}He and ^{4}He, as shown in Fig. 2. The optimized c_2 values for Fig. 2 differ significantly from those

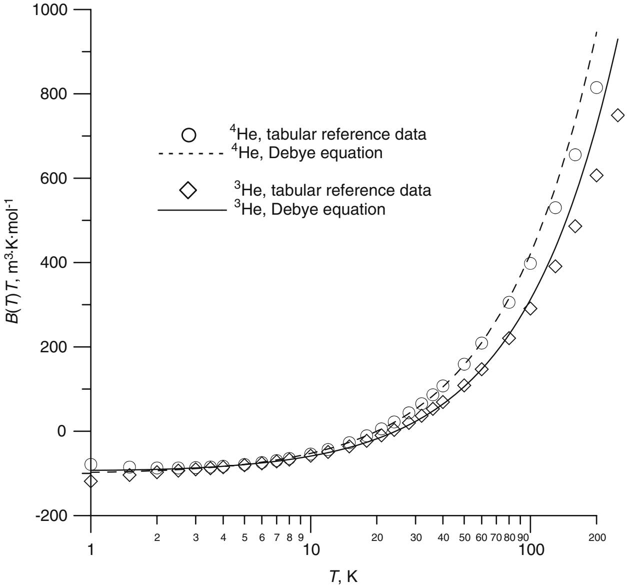

Fig. 2. Reference $B(T)$ and calculated $B_D(T)$ up to about 80 K for both ^{3}He and ^{4}He.

which could be estimated from Eq. (10). The low-temperature agreement becomes unacceptable if we try to force greater accuracy in the higher-temperature range, from 80 to 160 K. More generally we find that the calculated $B_D(T)$ is always positive and thus inconsistent with observed negative values of dB/dT for helium above 180 K. We further note that dB/dT is always positive at high T for other fluids in NIST's REFPROP compilation. For computer coding of state properties, it is reasonable to switch from a Debye equation to a virial equation at low density, e.g., when $\rho/\rho_c < 0.02$.

5. CRITICAL POINT

It is most important to realize that the Debye equations do not reference the critical point in any way. Thus, implementation of the Debye fluid state equation over the full (ρ, T) range requires additional terms to those of Eq. (5) in order to represent fluid properties in the vicinity of the critical point. The additional terms must be defined so as to have negligible effects in both the low- and high-temperature limits, where Eq. (5) hopefully will be accurate. We choose to write these critical terms as functions of the "distance" d from the critical point, empirically specified in the form,

$$A_{\mathrm{crit}}(d) = A_{\mathrm{crit}}((\delta^{j} - 1)^2 + a(\tau^{k} - 1)^2)^{0.5} = \mathrm{const}\cdot\exp(-\lambda d^2) \tag{12}$$

where j, K, a, and λ are adjustable parameters, $\delta = \rho/\rho_{\mathrm{c}}$, and $\tau = T/T_{\mathrm{c}}$. This scheme was reasonably satisfactory in our ^{3}He state equation [2] and in unpublished ^{4}He studies, but we recognize that other near-critical formulations could prove better in future work. A required mathematical constraint is that both $(\partial p/\partial\rho)_T = 0$ and $(\partial^2 p/\partial\rho^2)_T = 0$ at the critical point.

6. SUPERCRITICAL DENSITIES AND LOW *T*

In studies of both ^{3}He [2] and ^{4}He in the compressed superfluid [9], we find that a temperature-independent term must be added to Eq. (12), namely,

$$A(\rho, T) = -(n/3)\Theta H_0(T/\Theta) + A_{\mathrm{crit}}(d) + A_{\mathrm{HD}}(\rho) \tag{13}$$

where A_{HD} includes a factor that goes smoothly to zero when $\rho < \rho_{\mathrm{c}}$. This term is fitted to compressibility data in the dense cold liquid without serious disturbance of the lower density fit. We have used

$$A_{\mathrm{HD}} = (\mathrm{a}_1\rho^{-1} + \mathrm{a}_2\log(\rho) + \mathrm{a}_3\rho + \mathrm{a}_4\rho^2)F(\rho). \tag{14}$$

The $\mathrm{a}_i\rho^n$ series provides the primary compressibility data fit and F is either a Boltzman factor, $(1 - \exp(-\rho^n))$, or a Fermi factor, $1/(1 + \exp(n(\rho - \rho_{\mathrm{c}})))$, with n as an adjustable parameter. In practice, the Fermi term seems to provide a better fit to data in the transition region where $\rho \approx \rho_{\mathrm{c}}$.

7. GRUNEISEN PARAMETER, Γ

The assumption that Θ is independent of temperature is equivalent to the assumption that $\Gamma(\rho)$, defined in Eq. (6), is also independent of temperature. Γ in fluids has rarely been recognized or studied [10], although it is available as an output parameter in some computer programs for fluid properties, for example, by Arp [11].

Figure 3 shows $\Gamma(\rho)$ along selected isotherms of ^{4}He, at temperatures of 100 K or less, calculated from the NIST-12 standard reference code [12,13]. Differentials of pVT data provide the most support for the state equation in this region. Keeping in mind that ρ_{c} and T_{c} for ^{4}He

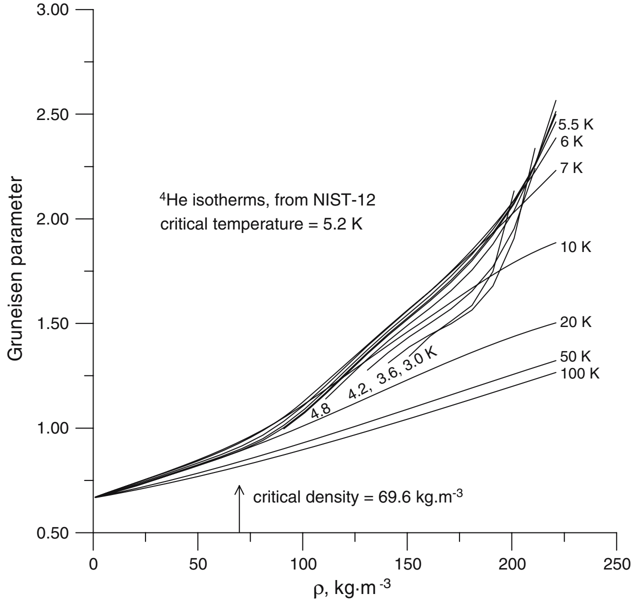

Fig. 3. $\Gamma(\rho)$ calculated from the NIST-12 code along selected isotherms of ^{4}He, with temperatures of 100 K or less.

are, respectively, about 5.2 K and 69 kg·m^{-3}, these curves show relatively little influence of the critical point. If we make some allowance for possible systematic error in the calculation of $\Gamma(\rho)$ from pVT data, it would be reasonable to conclude that $\Gamma(\rho)$ for ^{3}He or ^{4}He is approximately independent of temperature below about 10 K (down to about 3 K where the influence of superfluidity of ^{4}He at 2 K begins to be felt).

Figure 4 shows $\Gamma(\rho)$ from the same NIST reference code [12,13], with isotherms from 80 to 300 K. Supporting data for the state equation in this region are primarily from analysis of a single set of shock compression experiments [14] leading to densities up to eight times the critical density. Looking at Fig. 4 alone, it would be reasonable to conclude that $\Gamma(\rho)$ is nearly independent of temperature from 80 to 300 K. However, the quasi-temperature-independent $\Gamma(\rho)$ estimates from these two figures differ quite significantly from each other at densities above (roughly) 0.5 times the critical density. This difference could derive from incorrect high-density reference data, and/or it could reflect a substantial temperature dependence of $\Gamma(\rho)$ in the high-temperature region, roughly from 10 to 100 K.

Dugdale and Franck [15] estimate $\Gamma \approx 2.4$ in solid helium for both ^{3}He and ^{4}He. We have calculated $\Gamma = 2.86$ for superfluid ^{4}He below 0.3 K

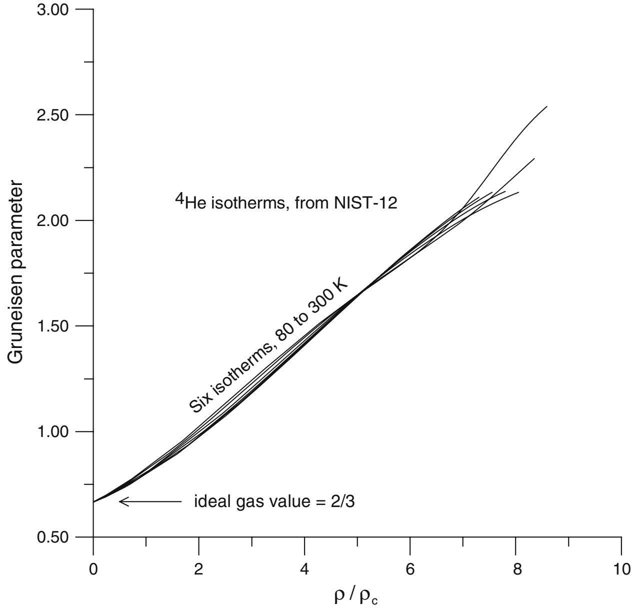

Fig. 4. $\Gamma(\rho)$ calculated from the NIST-12 reference code, with isotherms from 80 to 300 K.

(a region dominated by phonons) [9]. $\Gamma(\rho)$ curves from the standard equations of state for nitrogen and oxygen show significantly larger perturbations near their critical points than shown in Fig. 3. Overall, evidence for a temperature-independent $\Gamma(\rho)$, and hence a temperature-independent $\Theta(\rho)$, receives less than convincing support from available data, but it probably is not greatly in error (except possibly near the critical point). However, even small residual errors from this assumption certainly will detract from the overall accuracy of Debye fluid theory.

8. DEBYE FLUID EQUATIONS FOR ^{4}He

Reference data for ^{4}He used in this paper are calculated by the NIST-12 computer code [12,13]. In developing the ^{3}He properties code, we have developed an alternative Debye ^{4}He code for testing various math elements. Figure 5 shows the errors in the Debye calculated sound velocity along selected isotherms from 98 to 423 K. NIST-12 agrees with the original reference data [16] to better than 0.05%. The Debye equation, with just four fitted parameters in this temperature region, is seen to be in error by 1–2%. The conclusion from this figure applies to most of these

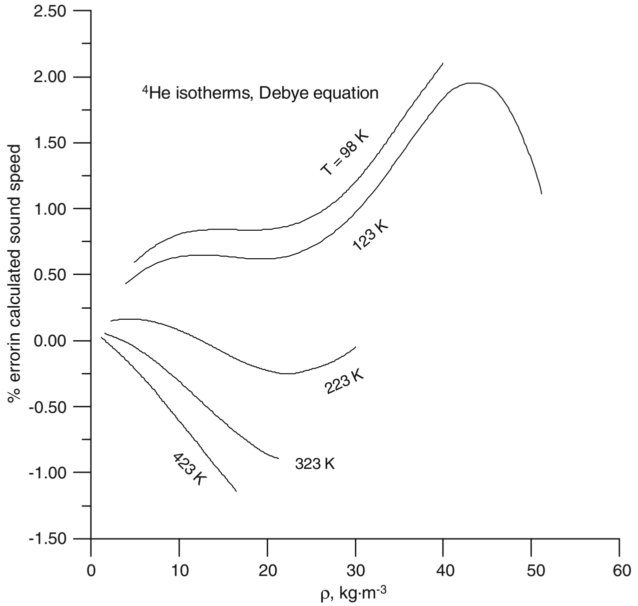

Fig. 5. Errors in the Debye calculated sound speed along selected isotherms from 98 to 423 K.

Debye tests: the Debye fluid equation does not compete with standard reference equations in absolute accuracy. The virtue of the Debye equation is its ability to fit fluid data far below the critical temperature ($\sim 0.001 T_c$) without gross loss of accuracy at high temperatures.

9. MAXIMUM ISOCHORIC SPECIFIC HEAT

The Debye theory includes a calculated upper limit for the quantum-mechanically allowed frequencies in the Fourier terms describing atomic motions. The maximum specific heat occurs when all allowed quantum states are occupied, each adsorbing $kT/2$ of energy spatial dimensions; the corresponding maximum specific heat is $c_v = 3NkT/2$, independent of temperature and density. Here k is Boltzmann's constant, and N is Avogadro's number. Larger observed specific heats are evidence of excitations not included in the Debye mathematics, perhaps related to optical frequency excitations or density fluctuations near the critical point. We point out that this limit appears to be exceeded by some published high-density data. Values of c_v/R up to 1.525 for ^{3}He and 1.585 for ^{4}He have been reported by Dugdale and Franck [15], and up to 1.59 by Glassford and

Smith [17]. In both cases their c_v data were derived from differentiation of pVT data. High-density specific-heat data in Fig. 1 seem to extrapolate to values a few percent above this theoretical limit at temperatures above about 15 K. The shock compression data discussed above are associated with values of c_v that rise from 20 to 100% above this Debye limit at densities of eight times critical. While it is possible that some, or all, of these higher-than-1.5 data are not accurate, collectively they form tentative evidence for high-density excitations that are inconsistent with basic Debye theory. This subject deserves further study.

10. THEORETICAL EXTENSIONS

In studies of the properties of solids, improved fits to experimental c_v data are obtained by allowing Θ to be a weak function of temperature. We have made some preliminary trials allowing $\Theta = \Theta(\rho, T)$, but a clear idea of irreducible deviations from the combination of fluid Debye theory with near-critical and supercritical density additions will be necessary before any real progress in this direction seems possible.

The math functions H_0, H_1, and H_2 are implicitly derived from the vibrational (or translational) motion of an isotropic atom in the three orthogonal dimensions of space. For a diatomic molecule, as an example, energies of rotational motions around two orthogonal axes must be added. Thus for the diatomic molecule, the factor of 3 in all of the above equations would be replaced by a factor of 5, e.g., $c_v = 5/2R_{\mathrm{m}}$ and $\Gamma = 2/5$ in the limit of zero density. Similar arguments can be made for other molecular geometries. With this change, the Debye theory outlined here possibly could be extended to a variety of higher molar mass compounds, although the accuracy of such extensions would have to be tested.

11. CONCLUSIONS

Debye fluid theory, outlined here, is a framework for equations for fluid properties that are asymptotically in agreement with known fluid properties at both zero temperature and ideal-gas limits. Empirical additions are required in order to fit both near-critical data and fluid compressibilities and those at high densities. With few adjustable constants, the Debye equations are inherently less accurate than standard reference fluid equations, but they may more easily bridge gaps in available reference data. The equations have been tested against ^{4}He data, and used in a ^{3}He state equation that is valid from 0.005 K to (probably) above room temperature.

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