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Second Virial Coefficient of a Gas from Sound-Velocity Measurements*

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Measurements of the velocity of sound as a function of pressure yield an inhomogeneous differential equation for the second virial coefficient. The formal solution of this equation is presented and the possible importance of the homogeneous solution of the equation for ^{4}He data below 20°K is discussed.

I. INTRODUCTION

Measurements of the sound velocity as a function of pressure in a gas have been used[1-3] to determine the second virial coefficient $B(T)$. The coefficient of the linear term in the pressure is the inhomogeneous term in a linear differential equation for $B(T)$. The object of this note is to display the formal solution of this equation, and to discuss the possible importance of the solution of the homogeneous version of this equation.

The solution of the differential equation for $B(T)$ is presented in Sec. II together with some mathematical comments on the analysis of experimental data. An application of this solution to ^{4}He data in the 2°K to 20°K temperature range is given in Sec. III. Section IV contains a discussion.

II. FORMAL SOLUTION FOR $B(T)$

For a nonideal gas the expansion[1] of the square of the sound velocity W in powers of the pressure p,

$$W^2 = W_0{}^2[1+(2/RT)fp+\cdots] , \tag{1}$$

has coefficients which are related to the absolute temperature T, the gas constant R, the ratio of ideal-gas specific heats γ_0, the atomic weight M, and the virial coefficients. For a monatomic gas, the coefficient of the linear pressure term depends on $B(T)$ through the relation

$$f(T) = B(T) + \tfrac{2}{3}T\,dB/dT + \tfrac{2}{15}\,T^2d^2B/dT^2 . \tag{2}$$

This is an inhomogeneous differential equation for $B(T)$ in terms of $f(T)$. It has both a homogeneous solution (B real)

$$B_h(T) = (\alpha/T^2)\cos[(7/2)^{1/2}\ln T + \phi] \quad , \tag{3}$$

with α and ϕ constants to be determined by the boundary conditions, and a particular solution

$$B_p(T) = \frac{15}{\sqrt{14}}\frac{1}{T^2}\int_\tau^T dt\; tf(t)\sin\left((7/2)^{1/2}\ln\frac{T}{t}\right) \quad , \tag{4}$$

where τ is an arbitrary constant.

The complete solution of Eq. (2) is thus

$$B(T) = \frac{\alpha(\tau)}{T^2}\cos\left((7/2)^{1/2}\ln\frac{T}{\tau} + \phi\,(\tau)\right)$$
$$+\frac{15}{\sqrt{14}}\,\frac{1}{T^2}\int_\tau^T dt\; t\,f(t)\sin\left((7/2)^{1/2}\ln\frac{T}{t}\right). \tag{5}$$

The constants in Eq. (5) are to be specified by information additional to that contained in $f(T)$.[4]

These results may be extended to the case[1] where a dilute-gas specific heat is nearly constant in some temperature range. The numerical coefficients in Eq. (2) are then modified, but there is a solution similar to Eq. (5). If the specific heat is strongly temperature dependent, this form of the solution is not applicable.

The usual method[1-3] of solving Eq. (2) has been to assume an expansion of $B(T)$ in a finite series of inverse powers of T,

$$B \sim \textstyle\sum_n a_n T^{-n} , \tag{6}$$

and to determine the coefficients in this expansion by a least-squares fit to the experimental values of $f(T)$. This does not make any explicit treatment of the homogeneous term, Eq. (3).[4]

However, in the limit of zero temperature, theoretical considerations[5,6] require that $B(T)$ has the following functional dependences:

$$B \sim C_1/T^{3/2} + C_2/T + C_3 + \cdots . \tag{7}$$

Neither the expansion Eq. (6) nor the homogeneous term Eq. (3) are adequate representations of $B(T)$ for this limit. ($T^{1/2}$ does not have an expansion in powers of T.) However, this is not sufficient reason to reject these functions in applications to finite temperature data.

For fitting data over a range of finite temperatures, Eq. (6) may be reinterpreted. In this view, the function $B(T)$ is expanded about some temperature T_0 in a power series in $(1/T - 1/T_0)$, the series is truncated, and the terms in it are rearranged to give the functional form Eq. (6). However, if the coefficients in this form are determined by Eq. (2), $B_h(T)$ might be introduced into $B(T)$ since it, too, has an expansion in powers of $(1/T - 1/T_0)$. Thus over some range of finite temperatures, $B(T)$ could be represented by a combination of Eqs. (3) and (6), although in practice these functional forms need not be particularly useful.

III. APPLICATION TO ^{4}He DATA

Prior determinations[1-3] of $B(T)$ from Eq. (2) have proceeded by assuming a functional form for $B(T)$ and then adjusting the coefficients in this form to fit the experimental values of $f(T)$ over some limited temperature range. Equation (5) may be used to evaluate $B(T)$ from such data without assuming a functional form for $B(T)$.

As an example of such a calculation, the data of Grimsrud and Werntz,[2] Plumb and Cataland,[7] and Keller[8] are used to specify the constants in Eq. (5). The experimental values[2,7] of $f(T)$ are shown in Fig. 1. Here τ is taken to be 2.15°K, the temperature of Keller's E isotherm.[8] The integrand of Eq. (5) is shown in Fig. 2 for two temperatures ($T_A = 3.95$°K and $T_B = 3.34$°K) of other Keller isotherms.[8] The integral is evaluated graphically for these temperatures, and then α and ϕ are determined by fitting Eq. (5) to Keller's values[8] for $B(T)$ at 2.15°K and either 3.95°K (Case A) or 3.34°K (Case B). The results are

$$\begin{aligned}&\text{(A)}\quad \alpha \approx -935\ \mathrm{cm^3(^\circ K)^2/mole}, \quad \phi \approx -0.51\ \mathrm{rad}, \\ &\text{(B)}\quad \alpha \approx -880\ \mathrm{cm^3(^\circ K)^2/mole}, \quad \phi \approx -0.39\ \mathrm{rad}.\end{aligned} \tag{8}$$

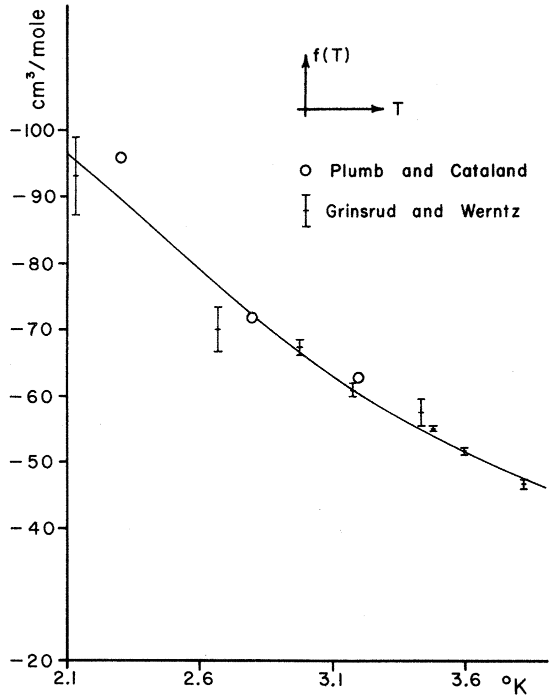

FIG. 1. $f(T)$[Eq. (1)] as a function of absolute temperature T. The data of Grimsrud and Werntz, Ref. 2, are shown with the statistical errors assigned by those authors. The data of Plumb and Cataland, Ref. 7, were derived from their Table II. The smooth line was drawn by eye through the data for use in interpolations.

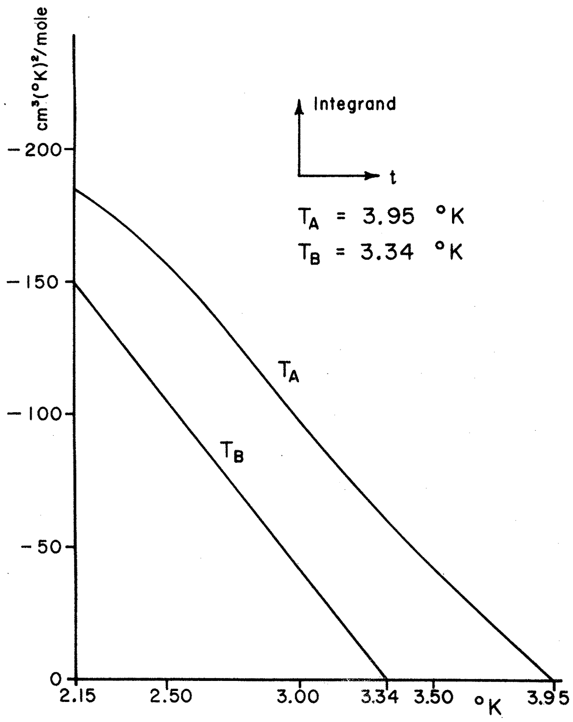

FIG. 2. The integrand of Eq. (5) is shown as a function of t (in °K) for two values of T. The values of $f(t)$ were obtained from the smooth line interpolation in Fig. 1. The value of the integral in Eq. (5) is given by the area under these curves.

These values could be combined with further measurements of $f(T)$ to determine $B(T)$ at higher temperatures.

This calculation does not specify the magnitude of the homogeneous term which should be added to a solution of the form of Eq. (6). To estimate this effect, the Boyd, Larsen, and Plumb[3] solution for $B(T)$ is compared with extrapolations of Keller's values[8] to 2 and 4°K, assuming no experimental error in either determination. Then, by ascribing the difference between these $B(T)$ values to a term $B_h(T)$, its coefficients are determined to be (with $\ln T$ replaced by $\ln(T/2)$, i.e., using a τ of 2°K)

$$\alpha \approx 125\ \mathrm{cm^3(^\circ K)^2/mole}, \quad \phi \approx -0.9\ \mathrm{rad}. \tag{9}$$

Boyd, Larsen, and Plumb[3] found, in the 2 to 10°K range, the coefficients in an assumed functional form

$$B(T) = a + b/T + c/T^2. \tag{10}$$

Their value of c was (69 ± 42) cm^3(°K)^2/mole. The α term is comparable to this; using the values of Eq. (9) it contributes about -0.6 cm^3/mole to $B(T)$ at 10°K. This is about a 3% effect.

A similar calculation for ^{3}He using Keller's values[9] for $B(T)$ and the Grimsrud and Werntz[2] solution from $f(T)$ shows a 1% effect at 10°K. This and the values in Eq. (9) are very sensitive to errors in the experimental values used.

IV. DISCUSSION

Grimsrud and Werntz[2] and Boyd, Larsen, and Plumb[3] have recently analyzed sound-velocity measurements on gaseous helium to obtain values for $B(T)$ which agree to within about 10% with values obtained by Keller[8,9] directly from isotherm measurements. These analyses have essentially obtained particular solutions to Eq. (2) without considering the homogeneous solution.

The result obtained here is that a difference between $B(T)$ derived from isotherm measurements and from sound velocity measurements is not necessarily to be ascribed to experimental error in either set of measurements. There is a possible difference between these values of $B(T)$ which varies roughly as the inverse square of the temperature. The numerical magnitude of this effect is not determined precisely with the present accuracy of the measurements, but it may amount to 3% in $B(T)$ for ^{4}He at 10°K.

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