

Numerical estimates for the bulk viscosity of ideal gases

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We estimate the bulk viscosity of a selection of well known ideal gases. A relatively simple formula is combined with published values of rotational and vibrational relaxation times. It is shown that the bulk viscosity can take on a wide variety of numerical values and variations with temperature. Several fluids, including common diatomic gases, are seen to have bulk viscosities which are hundreds or thousands of times larger than their shear viscosities. We have also provided new estimates for the bulk viscosity of water vapor in the range 380–1000 K. We conjecture that the variation of bulk viscosity with temperature will have a local maximum for most fluids. The Lambert-Salter correlation is used to argue that the vibrational contribution to the bulk viscosities of a sequence of fluids having a similar number of hydrogen atoms at a fixed temperature will increase with the characteristic temperature of the lowest vibrational mode. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4729611>]

I. INTRODUCTION

Shear viscosity plays a central role in the study of fluid dynamics. Ultimately, it is the source of all forms of loss and drag and gives rise to the instabilities which lead to flow turbulence. As a result, its molecular interpretation, variation with temperature and pressure, and numerical values can be found in nearly every reference on fluid mechanics. In contrast, the general understanding of the second or bulk viscosity

$$\mu_b \equiv \lambda + \frac{2}{3}\mu \quad (1)$$

is considerably less developed. Here $\mu_b = \mu_b(p, T)$, $\lambda = \lambda(p, T)$, and $\mu = \mu(p, T)$ are the bulk, second, and shear viscosities, respectively. The quantities T and p are the absolute temperature and pressure. The theoretical foundation of an equilibrium, i.e., zero-frequency, bulk viscosity has been known for over half a century. One of the first detailed studies is due to Tisza¹ who related the bulk viscosity to molecular energy storage and showed how the second and bulk viscosities found in the Navier-Stokes equations are obtained in the equilibrium limit. Further discussions of the relation of the bulk viscosity to classical fluid dynamics are found in Graves and Argrow² and Herzfeld and Litovitz.³ However, experimental data for μ_b are restricted to only a few fluids for a limited temperature range; see, e.g., the compilations by Karim and Rosenhead,⁴ Thompson,⁵ and Graves and Argrow.² The main goal of the present study is to extend the current data set as well as to illuminate the different temperature variations possible for μ_b .

Because the second and bulk viscosities are fundamental transport properties necessary for the full specification of the Navier-Stokes stress tensor, their values and variations with the thermodynamic variables are of obvious scientific interest. In addition, many technological applications involve complex, fully viscous and compressible flows which can only be described numerically. Accurate descriptions of such flows therefore require reasonably accurate estimates for the bulk viscosity. Examples include the flows in Rankine cycle power systems using steam as a working fluid as well as systems which employ non-aqueous working fluids. The latter working fluids tend to be advantageous when non-fossil fuel heat sources are used; see, for example, the studies of organic Rankine cycles by Curran,⁶ Devotta and Holland,⁷ Yan,⁸ Hung, Shai, and Wang,⁹ Liu, Chien, and

Wang,¹⁰ Wei *et al.*,¹¹ Saleh *et al.*,¹² and Shuster, Karellas, and Aumann¹³ or the studies of Dostal *et al.*,^{14,15} Dostal,¹⁶ Moiseyev,¹⁷ Moiseyev and Sienicki,¹⁸ and Sarkar^{19,20} on the use of CO₂ and N₂O for nuclear power systems. Even if the working fluid is steam, our examination of the literature indicates that no estimates of the bulk viscosity are currently available for water vapor. We believe that the present study provides the first explicit estimate of the bulk viscosity of water vapor. Other applications involving complex molecules and configurations include wind tunnel similarity studies and nanoparticle generation in the pharmaceutical industry. Examples of the former are the studies of SF₆ as a wind tunnel fluid by Anderson^{21,22} and Anders²³ to obtain a better match of Mach and Reynolds numbers between test and flight conditions. In the pharmaceutical industry, the rapid expansion of supercritical solution (RESS) process expands a dilute supersaturated mixture of a desired precipitate in a pressurized solvent, typically CO₂, through a capillary nozzle resulting in a precipitate of relatively uniform diameter; see, e.g., Tom and Debenedetti,²⁴ Eckert *et al.*,²⁵ and Turk *et al.*²⁶

The present study will focus on the estimation of the bulk viscosity for low pressure or dilute gases. Thus, the equation of state is the well known ideal gas law

$$p = \rho RT, \quad (2)$$

where R is the gas constant and ρ is the fluid density. As a result of the simplicity of (2), the energy per unit mass is a function of temperature only and can be written as the sum

$$e = e(T) = e_{tr} + \sum_{i=1}^N e_i,$$

where e_{tr} is the molecular translational energy and the e_i are the contributions due to the N internal energy modes, i.e., the energies associated with molecular rotation and vibration.

If the gas is monatomic, e.g., He, Ar, or Ne, the rotational and vibrational energies are regarded as negligible and changes to the gas are rapidly communicated by way of molecular collisions. Because a new equilibrium state is established within a few collisions, the time scale for the establishment of translational equilibrium is taken to be $\tau_c \equiv$ the average time between collisions. If the gas is polyatomic, changes in the internal energy modes are also driven by collisions. However, the probability that any particular collision results in a change in the rotational or vibrational state of either molecule depends on the details of the collision and the translational energy of collision relative to the lowest energy state of each internal mode. Thus, the number of collisions required to bring the internal energy modes into equilibrium with each other and with the translational modes may be more, sometimes many more, than the number required to establish translational equilibrium. The time scale associated with this process will be denoted as τ_i and will be referred to as the relaxation time for the i th internal mode. The relation of the bulk viscosity to these relaxation times was first established by Tisza.¹ In the notation used here, Tisza's near-equilibrium, i.e., zero-frequency, result can be written

$$\mu_b = (\gamma - 1)^2 \sum_{i=1}^N \frac{c_{vi}}{R} p \tau_i, \quad (3)$$

where

$$c_{vi} = c_{vi}(T) \equiv \frac{de_i}{dT} \quad (4)$$

is the isochoric specific heat associated with each internal mode and $\gamma = \gamma(T)$ is the ratio of specific heats. In the ideal gas limit considered here

$$\mu_b(p, T) \rightarrow \mu_b(T)$$

and each $p\tau_i = f(T)$ only. Tisza's result (3) is completely consistent with the idea that $\mu_b \equiv 0$ for monatomic gases for which all c_{vi} are taken to be zero. Furthermore, when the temperature is so low that the energy of collision is considerably lower than the energy associated with the i th energy mode, $c_{vi} \approx 0$ and the i th mode makes no significant contribution to the bulk viscosity. Since Tisza's paper

appeared, more sophisticated derivations of (3) have been carried out. A comprehensive discussion and review may be found in the text by Chapman and Cowling.²⁷

Previous estimates of the bulk viscosity of dilute gases have either used direct methods such as acoustic absorption measurements or have measured the relaxation time τ_i and then used (3) to deduce μ_b . One of the earliest studies to estimate μ_b directly from acoustic absorption data is that of Karim and Rosenhead,⁴ albeit for liquid, rather than gaseous, water. More recent estimates based on absorption are due to Prangma, Alberga, and Beenakker²⁸ for low pressure N_2 , CO , CH_4 , and CD_4 who found values of $\mu_b = 0.73 \mu$, 0.55μ , 1.33μ , and 1.17μ at 293 K, respectively. A second direct method is to infer the bulk viscosity from measurements of shock thickness. The latter method was used by Sherman²⁹ to deduce that $\mu_b \approx 0.67 \mu$ for low pressure N_2 . In both direct methods, the dilation rates must be low enough to ensure that the fluid is in local thermodynamic equilibrium (LTE) which, in turn, ensures the validity of the Navier-Stokes-Fourier equations. In the case of shock thickness measurements, it can be argued that LTE is guaranteed if the shock is weak. In the case of acoustic absorption the condition $\omega\tau_i|_{\max} \ll 1$, where ω is the acoustic frequency, is required. A significant advantage of the indirect method used here is that we only need accurate estimates of τ_i regardless of the frequency employed in its experimental determination. Substitution of the estimate for τ_i in (3) guarantees that the resultant estimate for μ_b is the desired zero-frequency transport property.

The first to apply (3) to estimate the low frequency bulk viscosity was Tisza¹ who estimated that μ_b is roughly 2000 times μ for both CO_2 and N_2O . Tisza also estimated that $\mu_b = 0(\mu)$ for air. More recent computations based on (3) were given by Emanuel³⁰ who gave $\mu_b \approx 3000 \mu$ for CO_2 at 303 K.

Efforts to estimate τ_i have also included theoretical studies. For example, Parker³¹ carried out a classical analysis to derive the following expression for the rotational relaxation times of diatomic gases:

$$Z_r \equiv \frac{\tau_r}{\tau_c} = Z_r^\infty \frac{4T'}{\pi(4 + \pi) + 2\pi^{\frac{3}{2}}(T')^{\frac{1}{2}} + 4T'}, \quad (5)$$

where Z_r^∞ is a nondimensional constant dependent on parameters characterizing the molecular interaction potential, $T' \equiv Tk/\epsilon'$, k is Boltzmann's constant, τ_r is the rotational relaxation time, and ϵ' is an energy characterizing the intermolecular potential used by Parker. The quantity Z_r is the collision number representing the number of collisions required to obtain rotational equilibrium. Parker's result corresponds to a gradual increase of Z_r with increasing temperature. If we assume the rotational mode is fully activated and that the vibrational portion of the specific heat is negligible so that $\gamma - 1 = R/c_v = 2/(f_r + 3)$ and if we estimate the viscosity by the exact hard-sphere model, i.e.,

$$\mu = \mu_{HS} = \frac{5}{4} p \tau_c, \quad (6)$$

we find that the rotational part of μ_b can be written

$$\frac{\mu_b}{\mu_{HS}} = \frac{8f_r}{5(f_r + 3)^2} Z_r, \quad (7)$$

where f_r denotes the number of relevant rotational modes. Because $f_r = \text{constant}$, the temperature variation of μ_b/μ is therefore expected to be the same as Z_r . If we employ the more accurate estimate for shear viscosity described in Sec. II, the increase in μ_b/μ with T suggested by (7) will be somewhat weakened.

One of the best known classical theories for vibrational relaxation is the Landau-Teller theory. An easily accessible description of the Landau-Teller theory can be found in Herzfeld and Litovitz.³ Landau-Teller theory is expected to be valid at temperatures which are so large that the long range attractive intermolecular forces are negligible during collisions. The repulsive part of the intermolecular potential was taken to be of the form $V_o \exp(\alpha r)$, where the constants V_o and α give a measure of the magnitude and steepness of the potential. The result of Landau and Teller's analysis

is that

$$Z_{10} \approx \text{constant } e^{\eta^{\frac{1}{3}}}, \quad (8)$$

where

$$\eta = \text{constant} \cdot \frac{m_e v^2}{\alpha^2 k T}. \quad (9)$$

In (9) the constant is a pure number, v is the lowest vibration frequency, and m_e is the effective molecular mass. The quantity Z_{10} represents the number of collisions required for a transfer of translational energy to the lowest vibrational mode. The relation of Z_{10} to the vibrational relaxation time τ_v is

$$Z_v \equiv \frac{\tau_v}{\tau_c} = \frac{Z_{10}}{1 - e^{-\frac{\theta_v}{T}}}. \quad (10)$$

The factor in the denominator of (10) accounts for the fact that collisions with molecules in the same vibrational state will result in no energy transfer. The constant θ_v is the characteristic temperature associated with the lowest vibrational energy level. It can be shown that η is proportional to the square of the ratio of the duration of collision (t_d) to the period of vibration of the lowest mode ($t_v \equiv v^{-1}$). Thus, at these temperatures, Z_{10} will decrease monotonically with increasing temperature.

Although (8)–(9) formally holds for only sufficiently large temperatures, experimental data for Z_v and $p\tau_v$ frequently fit straight line relations

$$\log_{10} Z_v \text{ or } \log_{10} p\tau_v = \text{constant} + \text{constant} \cdot T^{-\frac{1}{3}} \quad (11)$$

over a wide range of temperatures. Such a relation is used in many published curve-fits and will be employed for some of the fits presented here.

We note that the rapid decrease of Z_v with T suggested by (8)–(10) is likely to be stronger than any increase in the coefficient of $p\tau_i$ with temperature; see, e.g., the discussion of Sec. II. Because the shear viscosity of dilute gases increases with temperature, we should therefore expect both μ_b and the ratio μ_b/μ to ultimately decrease as the temperature increases when the Landau-Teller law holds.

At lower temperatures, forces neglected in the Landau-Teller theory become important. Models which include attractive forces were first described by Schwartz, Slawsky, and Herzfeld,³² Schwartz and Herzfeld,³³ and Tanczos;³⁴ see, also, Herzfeld and Litovitz³ for a comprehensive summary. The role of the long range attractive force is to increase the relative speed of the colliding particles, therefore decreasing t_d resulting in a more efficient transfer of energy from translation to vibration. Under these conditions, the Landau-Teller asymptote overpredicts the value of Z_v and the vibrational relaxation time. When the temperature is so low that the molecular kinetic energy is on the order of or much less than the minimum in the intermolecular potential, molecules can pair to form dimers which further increases the efficiency of the energy exchange and decreases the vibrational relaxation time; see, e.g., the discussion by Lambert.³⁵ As the temperature increases, the relative velocity of collision increases and dimers are less likely to form. Thus, at sufficiently low temperatures, the values of Z_v and vibrational relaxation times are expected to increase with increasing temperature. We would therefore expect the values of Z_v , $p\tau_v$, and the bulk viscosity to have a local maximum as the energy exchange process shifts from the low temperature increase with temperature to the strong decrease with temperature associated with the high temperature Landau-Teller regime.

When we consider polar fluids the additional effect of the dipole forces must be considered, particularly when the kinetic energy is on the order of or smaller than the energy associated with the dipole. At such temperatures, the dipoles tend to re-orient the molecules during the collision. The additional forces and the alignment of the dipoles yield a very efficient translational-vibrational energy transfer and the resultant vibrational relaxation times tend to be smaller than those of non-polar fluids. Thus, the bulk viscosities of polar fluids are also expected to be smaller than those of non-polar fluids. Furthermore, full re-alignment is less likely to occur as the molecular speeds increase. As a result, the values of Z_v and τ_v will increase with temperature. At higher temperatures, re-orientation does not have time to occur, the repulsive force dominates, and the Landau-Teller

theory will ultimately hold. Again, the variation of Z_v , τ_v , and μ_b with temperature is expected to exhibit a local maximum.

The aforementioned theories, and even their extensions, cannot yet provide accurate and comprehensive predictions of the relaxation times. Here our primary goal is to provide numerical estimates of the bulk viscosity for a variety of common fluids. We will also give simple formulas for the temperature variation of μ_b which can provide future researchers with formulas for use in design and computational studies. Hence, we will simply use the physics described above to interpret our results for the bulk viscosity and, in some cases, to guide our choices for curve-fits.

II. ASSUMPTIONS AND MODELS

In all that follows, we will assume that the rotational and vibrational modes relax independently, that all the rotational modes relax with a single relaxation time and all the vibrational modes also relax with a single time. Equation (3) can therefore be written as

$$\mu_b = \mu_b|_r + \mu_b|_v \quad (12)$$

with

$$\mu_b|_r \equiv (\gamma - 1)^2 \frac{f_r}{2} p \tau_r, \quad (13)$$

$$\mu_b|_v \equiv (\gamma - 1)^2 \frac{c_v|_v}{R} p \tau_v, \quad (14)$$

where $(\)|_r$ and $(\)|_v$ will denote rotational and vibrational contributions to the indicated quantity. Here f_r = the number of rotational degrees of freedom with

$$f_r = \begin{cases} 2 & \text{for linear molecules} \\ 3 & \text{otherwise,} \end{cases}$$

and τ_r = rotational relaxation time. The quantity

$$\frac{c_v|_v}{R} = \frac{c_v}{R} - \frac{f_r + 3}{2} \quad (15)$$

is the vibrational part of the scaled specific heat at constant volume. The quantity τ_v is the vibrational relaxation time. Within the experimental resolution currently available, many molecules satisfy the condition of a single relaxation time. However, the vibrational modes of some molecules, e.g., SO_2 , are known to possess distinct relaxation times.

Implicit in Eq. (13) is the assumption that the rotational modes are fully activated at the temperatures under consideration. This assumption is reasonable because most characteristic temperatures for rotation (denoted by θ_r) are only a few degrees Kelvin. The primary exception is $n - \text{H}_2$ for which $\theta_r \approx 88$ K. Although one should include the rotational contribution to μ_b at most temperatures, τ_r is typically only a few collision times and is normally much smaller than τ_v . Hence, if the vibrational modes are active, i.e.,

$$\frac{c_v|_v}{R} = O(1),$$

we will estimate the bulk viscosity using only the vibrational mode, i.e., $\mu_b \approx \mu_b|_v$. On the other hand, when the temperature is much less than the characteristic temperature for the lowest vibrational mode (denoted by θ_v), no significant translational-vibrational energy can be exchanged and we will estimate μ_b based on the rotational contribution (13) only. An important exception here is our estimate for the bulk viscosity of water vapor where both rotational and vibrational contributions will be included. The use of only one term or the other in (12) will clearly yield a lower bound for the true value of μ_b for the substance under consideration.

Data for the specific heats are readily available for the substances of interest here. In all that follows we will compute these from the polynomial curve-fit provided by Reid, Prausnitz, and

Poling.³⁶ In particular, the coefficients for their curve-fit for each fluid are those given in Appendix A of their book.

In this study, the estimates for μ_b will be presented as the ratio μ_b/μ , where μ is the shear viscosity. To calculate $\mu = \mu(T)$ we use the well known Chapman-Cowling result:

$$\mu = \frac{5}{16} \left(\frac{k}{\pi \tilde{N}} \right)^{\frac{1}{2}} \frac{(WT)^{\frac{1}{2}}}{\sigma^2 \Omega}, \quad (16)$$

where W is the molecular weight, σ is the molecular diameter, k is Boltzmann's constant, and \tilde{N} is Loschmidt's number $= 6.0225 \times 10^{26} (\text{kg mol})^{-1}$. The quantity $\Omega = \Omega(T)$ is the collision integral based on the 12-6 Lennard-Jones potential and is computed from

$$\Omega_{LJ} = A_1 T_*^{-A_2} + A_3 e^{-A_4 T_*} + A_5 e^{-A_6 T_*}, \quad (17)$$

$$\Omega = \Omega_{LJ} + \frac{0.2\delta^2}{T_*}, \quad (18)$$

where

$$T_* \equiv T/T_\epsilon,$$

$$T_\epsilon \equiv \frac{\epsilon}{k},$$

$$\delta \equiv \frac{\mu_p^2}{2\epsilon\sigma^3},$$

ϵ is the characteristic energy of the Lennard-Jones potential and μ_p is the molecular dipole moment. The second term in (18) represents the Stockmayer correction for polar fluids; details of the latter can be found in Reid, Prausnitz, and Sherwood.³⁷ A further discussion of (16)–(18) and the numerical values of A_i , $i = 1 \rightarrow 6$, are found in Reid, Prausnitz, and Poling.³⁶ The numerical values of T_ϵ and σ were taken from Appendix B of Reid, Prausnitz, and Poling³⁶ or Svehla's original report.³⁸ The values of W and μ_p were also obtained from Reid, Prausnitz, and Poling's³⁶ Appendix A.

Because $\gamma - 1 = R/c_v$ in the dilute gas limit employed here, we can use (15) to show that the coefficient of $p\tau_v$ in (14) is

$$\Delta \equiv (\gamma - 1)^2 \frac{c_v|_v}{R} = \frac{\frac{c_v|_v}{R}}{\left(\frac{f_r + 3}{2} + \frac{c_v|_v}{R} \right)^2}, \quad (19)$$

from which it is clear that Δ is proportional to $c_v|_v$ as $c_v|_v/R \rightarrow 0$ and that $\Delta \rightarrow 0$ as $c_v|_v/R \rightarrow \infty$. It is also easily verified that Δ vs $(c_v/R)|_v$ curves have a local maximum at

$$\frac{c_v|_v}{R} = \frac{f_r + 3}{2}, \quad \frac{c_v}{R} = f_r + 3$$

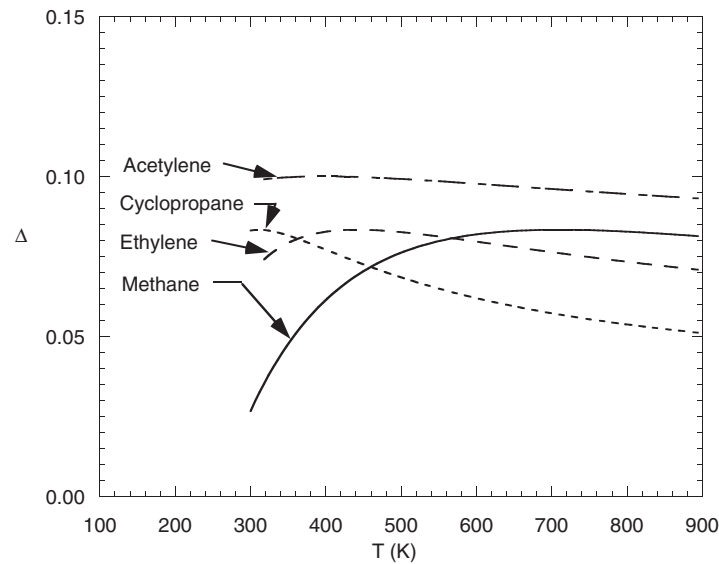
and the corresponding maximum value of Δ is

$$\Delta_{\max} = \frac{1}{2(f_r + 3)} = \begin{cases} \frac{1}{10} & \text{for } f_r = 2 \\ \frac{1}{12} & \text{for } f_r = 3. \end{cases}$$

Thus, any fluid for which

$$c_v > (f_r + 3)R$$

will also have a local maximum in the coefficient Δ at the temperature for which $c_v = (f_r + 3)R$. We note that the value of c_v for diatomic molecules varies monotonically from $5R/2$ to $7R/2 < 5R$ and

FIG. 1. Temperature variation of Δ for selected fluids.

no local maximum will be observed. For diatomic molecules, Δ will simply approach the limiting value of $4/49 < 1/12$ as $T \rightarrow \infty$. Thus, $\Delta \leq 1/10$ and the vibrational contribution to $\mu_b|_v$ will always be less than one-tenth of the value of $p\tau_v$. To illustrate the resultant temperature variation, we have plotted Δ vs T for acetylene ($f_r = 2$), cyclopropane ($f_r = 3$), ethylene ($f_r = 3$), and methane ($f_r = 3$) in Figure 1. Inspection of Figure 1 reveals relatively small values of Δ for methane for $T \approx 300$ K. The small values of Δ are due to the relatively low characteristic temperature for vibration ($\theta_v \approx 1880$ K); in fact, $c_v|_v \approx 0$ by $T = 257$ K. The significance of this decrease on the vibrational portion of the bulk viscosity of CH_4 will be discussed in Secs. IV and V.

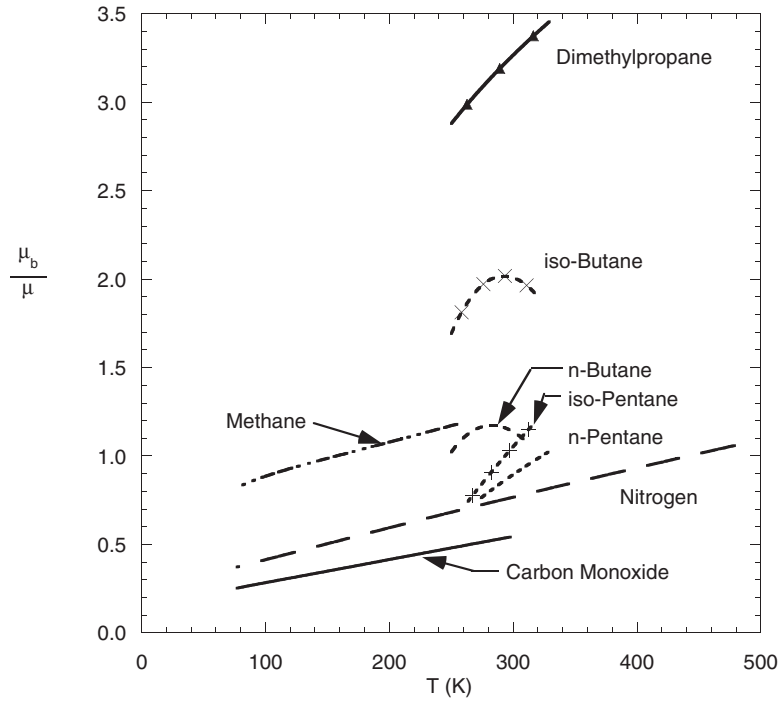
In Secs. III and IV, the sources of data for the relaxation times are described. Many of these sources present their data graphically rather than in tabular form. Because the original numerical values are frequently unavailable, we have extracted the data from many sources using a commercial graph digitizer. For plotting purposes and the convenience of future researchers, we then fit the extracted discrete data to various analytical formulas. These fits were always based on a conventional least-squares algorithm.

III. FLUIDS HAVING MODERATE BULK VISCOSITY

The temperature variation of μ_b/μ for a selection of fluids having $\mu_b = O(\mu)$ is depicted in Figure 2. The characteristic temperatures for the lowest vibrational modes of nitrogen (N_2), carbon monoxide (CO), and methane (CH_4) are approximately 3360 K, 3090 K, and 1880 K, respectively. We will therefore assume that the primary contribution to μ_b is that due to rotation, at least over the temperature range of the plot. This assumption would seem reasonable for N_2 and CO. However, an inspection of Figure 1 and the calculations of Sec. IV lead us to conclude that there will be some non-zero contribution of the vibrational mode to the total bulk viscosity of CH_4 at 300 K. Nevertheless, in this section we will present our results for the rotational contribution to the bulk viscosity of CH_4 without a detailed consideration of $\mu_b|_v$. The data for the bulk viscosities of CO and CH_4 were taken directly from the results reported by Prangma, Alberga, and Beenakker²⁸ and, following Emanuel,³⁹ fit to the following power-law representation:

$$\mu_b = \mu_{br} \left(\frac{T}{T_r} \right)^n, \quad (20)$$

where μ_{br} , T_r , n are constants. For N_2 the data of Prangma, Alberga, and Beenakker²⁸ were also employed, but were supplemented by the data for $p\tau_r$ of Winter and Hill⁴⁰ at 773 K and 1073 K;

FIG. 2. Temperature variation of μ_b/μ for fluids having moderate bulk viscosity.

these latter data were substituted into (13) to compute μ_b and the complete data set was fit to a power-law of the form (20). The values of μ_{br} , T_r , and n used for the plots of Figure 2 are

$$\mu_{br} = 0.778 \times 10^{-5} \text{ kg/(m s)}, \quad T_r = 200 \text{ K}, \quad n = 1.376 \text{ for } N_2,$$

$$\mu_{br} = 0.533 \times 10^{-5} \text{ kg/(m s)}, \quad T_r = 200 \text{ K}, \quad n = 1.461 \text{ for CO},$$

$$\mu_{br} = 0.836 \times 10^{-5} \text{ kg/(m s)}, \quad T_r = 200 \text{ K}, \quad n = 1.295 \text{ for CH}_4.$$

The formal range of validity for the curve-fits for CO and CH₄ is 77–293 K and the formal range of validity for the N₂ curve-fit is expected to be 77–1073 K. In spite of the fact that the formal upper bound on the range of validity of the CH₄ fit is 293 K, we have truncated the curve plotted in Figure 2 at $T = 257 \text{ K}$ which is the temperature at which we found $\Delta \rightarrow 0$.

The bulk viscosities and μ_b/μ for CO, CH₄, and N₂ are seen to increase gradually with temperature and the results for N₂ and CO are in agreement with values commonly quoted, e.g., $\mu_b \approx 0.73 \mu$ for N₂ at 293 K. The gradual increase of μ_b/μ is seen to be in qualitative agreement with the increase inherent in (5) and (7).

The remainder of the bulk viscosities plotted in Figure 2 are due to the vibrational modes only. For dimethylpropane we simply used the curve-fit provided by Ewing *et al.*⁴¹

$$\mu_b = A + BT, \quad (21)$$

who suggested $A = -12.9 \times 10^{-6} \text{ kg/(m s)}$ and $B = 0.122 \times 10^{-6} \text{ kg/(m s K)}$ and is expected to be valid for $250 \text{ K} \leq T \leq 325 \text{ K}$. The plots for *n*-pentane, and iso-pentane were generated by fitting a straight line to the $\rho\tau_v$ vs T data of Ewing, Goodwin, and Trusler,⁴² and Ewing and Goodwin,⁴³ respectively. The straight line fits for $\rho\tau_v$ were then converted to equations for $p\tau_v$ as follows:

$$p\tau_v = RT(\rho\tau_v) = AT + BT^2. \quad (22)$$

The values of $\rho\tau_v$ were then combined with (12), neglecting $\mu_b|_r$, to determine the variation of μ_b with T . The values of A and B in (22) were found to be

$$A = -4.594 \times 10^{-7} \text{ kg/(m s K)}, \quad B = 2.671 \times 10^{-9} \text{ kg/(m s K}^2\text{)} \text{ for } n\text{-pentane,}$$

$$A = -8.177 \times 10^{-7} \text{ kg/(m s K)}, \quad B = 4.190 \times 10^{-9} \text{ kg/(m s K}^2\text{)} \text{ for iso-pentane,}$$

which correspond to the authors' data in the ranges $270 \text{ K} \leq T \leq 330 \text{ K}$, and $260 \text{ K} \leq T \leq 320 \text{ K}$, respectively.

Data for n -butane and iso-butane were taken from Ewing *et al.*⁴⁴ and Ewing and Goodwin.⁴⁵ The data for n -butane showed evidence of a local maximum in μ_b and the data for iso-butane showed evidence of a local maximum in $\rho\tau_v$. Hence, these quantities were fit with second-order polynomials of the form

$$\mu_b = A_n + B_n T + C_n T^2 \text{ for } n\text{-butane,} \quad (23)$$

$$\rho\tau_v = A_{\text{iso}} + B_{\text{iso}} T + C_{\text{iso}} T^2 \text{ for iso-butane,} \quad (24)$$

where

$$A_n = -7.05 \times 10^{-5} \text{ kg/(m s)}, \quad B_n = 5.28 \times 10^{-7} \text{ kg/(m s K)}, \quad C_n = -8.85 \times 10^{-10} \text{ kg/(m s K}^2\text{)},$$

$$A_{\text{iso}} = -3.412 \times 10^{-4} \text{ (kg s)/m}^3, \quad B_{\text{iso}} = 2.584 \times 10^{-6} \text{ (kg s)/(m}^3 \text{ K)},$$

$$C_{\text{iso}} = -4.234 \times 10^{-9} \text{ (kg s)/(m}^3 \text{ K}^2\text{)}.$$

The fits (23) and (24) are expected to be valid for 250 K to 310 K and 250 K to 320 K, respectively. The computed values of μ_b , based on (23)–(24), for n -butane and iso-butane are plotted in Figure 3 along with the values of μ_b based on the authors' discrete experimental data for μ_b and $\rho\tau_v$. The scatter seen in Figure 3 is also typical of that for n -pentane, iso-pentane, and dimethylpropane.

The computed values of μ_b/μ for n -butane, iso-butane, n -pentane, iso-pentane, and dimethylpropane appear to correspond to the low temperature behavior described in Sec. I. That is, the vibrational relaxation times are relatively small and increase with increasing temperature.

Because the vibrational contribution to μ_b/μ is of order one for the fluids shown in Figure 2, it is natural to ask whether the rotational contribution to μ_b will have a significant impact on the total

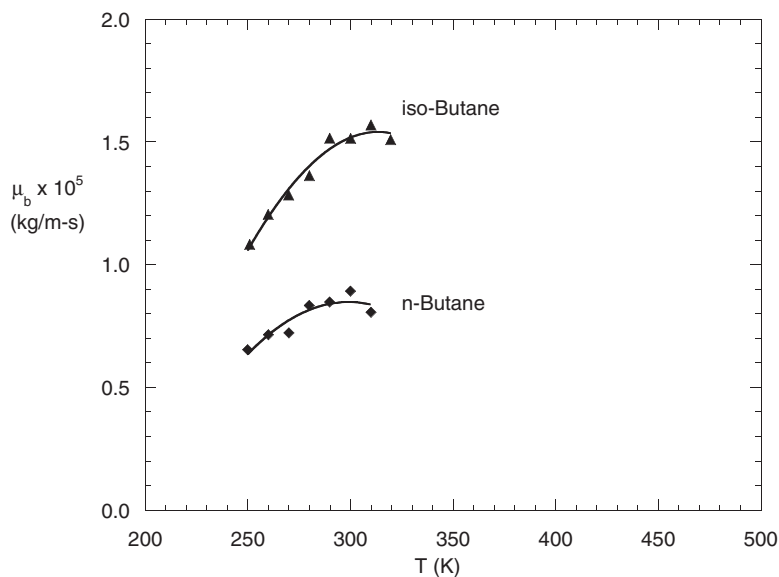


FIG. 3. Temperature variation of μ_b for iso-butane and n -butane. Solid lines denote our quadratic curve-fit and symbols denote values based on the experimental data of Ewing *et al.*⁴⁴ and Ewing and Goodwin.⁴⁵

μ_b . The relative size of these contributions is given by

$$\frac{\mu_b|_r}{\mu_b|_v} = \frac{f_r}{2} \frac{1}{\frac{c_v}{R} - \frac{f_r+3}{2}} \frac{Z_r}{Z_v}. \quad (25)$$

As an example, we consider *n*-pentane ($f_r = 2$) at 300 K. We find that $c_v = 13.53R$, $\gamma - 1 = R/c_v \approx 0.074$, $\Omega \approx 1.7$, $\mu_b|_v \approx 0.8953 \mu$. Thus, at 300 K, we have

$$Z_v \approx \frac{5}{4(\gamma - 1)^2 \Omega \frac{c_v|_v}{R}} \frac{\mu_b|_v}{\mu} \approx 10.9$$

and, from (25), we have

$$\frac{\mu_b|_r}{\mu_b|_v} \approx \frac{1}{120} Z_r.$$

Thus, if $Z_r \leq 5$, $\mu_b|_r$ will be less than 4% of $\mu_b|_v$. As a second example, we consider dimethylpropane at 300 K. By the same analysis as for *n*-pentane, we find that $Z_v \approx 55.3$ and

$$\frac{\mu_b|_r}{\mu_b|_v} \approx \frac{Z_r}{395}.$$

Holmes, Jones, and Lawrence⁴⁶ report a value of $Z_r \approx 3.7$ which suggests that the $\mu_b|_r$ is only 0.1% of $\mu_b|_v$ for dimethylpropane at 300 K. When we carry out the same calculations for *n*-butane, isopentane, and iso-butane we find that these yield similar estimates for $\mu_b|_r/\mu_b|_v$. We would therefore expect that the results plotted in Figure 2 will change very little if the rotational contribution to μ_b is included.

Data for the relaxation times of water vapor are surprisingly scant, are frequently scattered, and are sensitive to the effects of impurities. A discussion of many of the best known studies of sound absorption and relaxation times in water vapor has been provided by Bass, Olsen, and Amme⁴⁷ and Keeton and Bass.⁴⁸ The estimates for μ_b/μ presented here were computed using the data for $Z_v \equiv \tau_v/\tau_c$ and $Z_r \equiv \tau_r/\tau_c$ provided by Bass, Olsen, and Amme.⁴⁷ We assumed that Bass, Olsen, and Amme computed their Z_r and Z_v using the hard sphere collision time given by

$$\tau_c^{-1} = 4n\sigma_*^2\sqrt{\pi RT}, \quad (26)$$

where n = number density and σ_* is their value of the molecular diameter of H₂O. By combining (12)–(14), (16), and (26) we obtain

$$\frac{\mu_b}{\mu} = \frac{4}{5} \Omega (\gamma - 1)^2 \left[\frac{f_r}{2} Z_r + \frac{c_v|_v}{R} Z_v \right], \quad (27)$$

where we have assumed that Bass, Olsen, and Amme took the hard sphere molecular diameter σ_* to be the same as that reported by Svehla,³⁸ i.e., $\sigma_* = \sigma = 2.641 \text{ \AA}$. The values of Z_v were fit to the data presented in Figure 10 of Bass, Olsen, and Amme⁴⁷ yielding

$$Z_v = 0.003186 \exp\left(\frac{76.4}{T^{\frac{1}{3}}}\right), \quad (28)$$

where T is in degrees Kelvin. In this fit only the authors' six measured points between 380 K and 1000 K were used. The rotational collision number was obtained by fitting the data in the authors' Figure 11 to

$$Z_r = 29.31 - \frac{133.1}{T^{\frac{1}{3}}} \quad (29)$$

using the seven points between 380 K and 1000 K. The fit (28) is seen to be consistent with the Landau-Teller law (11) but, due to the degree of scatter, we regard (28) only as a convenient fit. Bass, Olsen, and Amme⁴⁷ and Lambert³⁵ suggest that there may be a local maximum in Z_v at lower temperatures. Thus, (28) should be used with caution as $T \rightarrow 300 \text{ K}$.

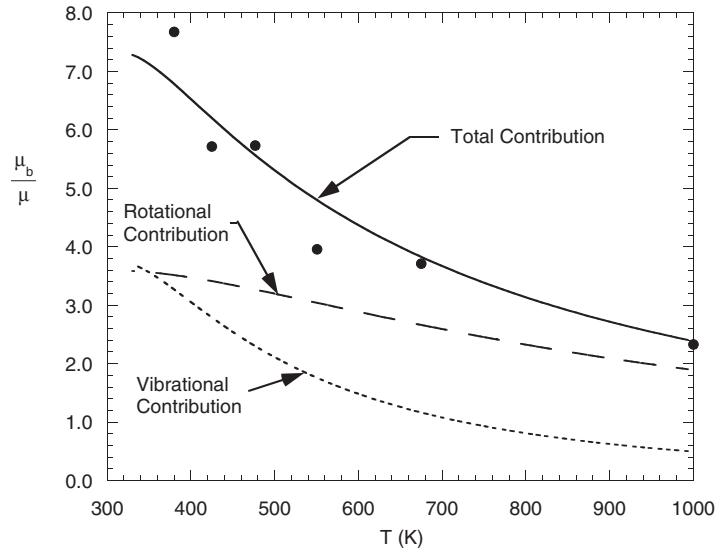


FIG. 4. Temperature variation of μ_b/μ for water vapor. The solid line represents our curve-fit for μ_b/μ , the long dashed line represents the rotational contribution to μ_b/μ , and the short dashed line represents the vibrational contribution to μ_b/μ . Symbols denote the values of the total μ_b/μ based on the experimentally determined values of Z_r and Z_v of Bass, Olsen, and Amme.⁴⁷

The resultant variation of μ_b/μ is plotted in Figure 4 along with the rotational and vibrational contributions to μ_b/μ , i.e.,

$$\frac{\mu_b|_r}{\mu} \equiv \frac{2}{5} \Omega (\gamma - 1)^2 f_r Z_r,$$

$$\frac{\mu_b|_v}{\mu} \equiv \frac{4}{5} \Omega (\gamma - 1)^2 \frac{c_v|_v}{R} Z_v.$$

In order to illustrate the scatter in the data we have also included the estimates for μ_b/μ based on Bass, Olsen, and Amme's reported Z_r and Z_v at their common temperature set. In order to identify the approximate temperature at which contributions of the rotational and vibrational modes are equal we have extended our curve-fits to 330 K in Figure 4. Inspection of Figure 4 reveals that μ_b/μ for H_2O decreases with increasing temperature. The rotational contribution to μ_b/μ is also seen to decrease with increasing temperature in spite of the fact that Z_r increases with temperature. The increase of Z_r is rather weak and the increase in $\mu = \mu(T)$ is sufficient to cause the ratio $\mu_b|_r/\mu$ to decrease. It is interesting to note that the vibrational and rotational contributions are roughly equal at low temperatures whereas the rapid decrease in Z_v causes the rotational contribution to dominate at higher temperatures.

IV. FLUIDS HAVING LARGE BULK VISCOSITIES

We now consider fluids having bulk viscosities which are large compared to their shear viscosities. The first fluid considered is molecular hydrogen H_2 which has a characteristic vibrational temperature of approximately 6000 K. Thus, at the temperatures considered here, the primary contribution to the bulk viscosity will be due to the rotational mode. Rotational relaxation in hydrogen is particularly slow due to the low moment of inertia of the H_2 molecule. The resultant rotational energy levels are therefore widely spaced compared to heavier molecules such as N_2 and O_2 . As a result, H_2 requires 200 or more collisions to establish equilibrium which is considerably more than the 5–10 collisions for N_2 . Herzfeld and Litovitz³ report values of α/α_{cl} for H_2 , where α is the measured acoustic absorption coefficient and α_{cl} is the $\mu_b = 0$ absorption coefficient, of 20–30 near room temperature which yields values of 36–55 for μ_b/μ . Here we have chosen the more recent data

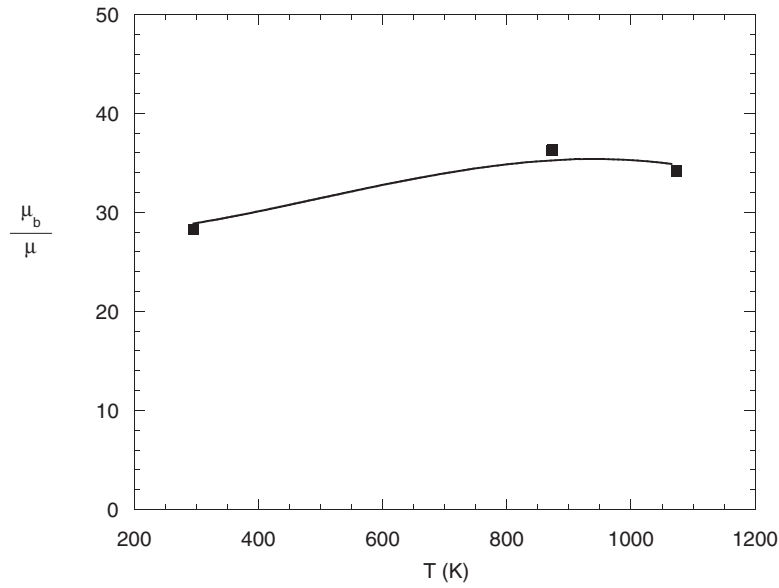


FIG. 5. Temperature variation of μ_b/μ of H_2 . The solid line denotes our curve-fit and the symbols denote values based on Winter and Hill's⁴⁰ data for $p\tau_r$.

of Winter and Hill⁴⁰ who report values of $p\tau_r$ for temperatures of 295 K, 873 K, and 1073 K. Their data were fit to a linear $p\tau_r$ vs T relation

$$p\tau_r = a + bT,$$

where $a = 1.822 \times 10^{-4} \text{ kg/(m s)}$ and $b = 4.641 \times 10^{-6} \text{ kg/(m s K)}$. We also fit Winter and Hill's data to a power-law for $p\tau_r$, but the exponent of T was very close to one and the simpler linear variation gives essentially the same results for μ_b/μ . We have plotted the resultant variation of μ_b/μ vs T for H_2 in Figure 5. We have also included the viscosity ratios computed based on Winter and Hill's discrete data. The values of μ_b/μ are seen to be somewhat lower than those based on the older data reported by Herzfeld and Litovitz,³ but nevertheless yield $\mu_b \approx 30 \mu$ in the vicinity of room temperature. Our calculations show that μ_b increases monotonically from $\approx 25 \times 10^{-5} \text{ kg/(m s)}$ at 295 K to $\approx 72 \times 10^{-5} \text{ kg/(m s)}$ at 1073 K. However, the increase in μ_b is slower than the increase in μ with increasing T resulting in a local maximum in μ_b/μ at 941 K.

In the remainder of this section we consider fluids having a vibrational characteristic temperature which is low enough to result in the vibrational mode being active at room temperature. The first set of fluids to be considered is methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), and cyclopropane ($c-C_3H_8$). Data for the vibrational relaxation times for each fluid were taken from Wang and Springer⁴⁹ who provided comparisons to previous studies and curve-fits for the values of $p\tau_v$. These fits were of the form of the Landau-Teller law and can be written as

$$p\tau_v = A \exp\left(\frac{B}{T^{\frac{1}{3}}}\right), \quad (30)$$

where

$$A = 429.3 \times 10^{-5} \text{ kg/(m s)}, \quad B = 21.07(\text{K})^{\frac{1}{3}} \text{ for methane,}$$

$$A = 1086 \times 10^{-5} \text{ kg/(m s)}, \quad B = 5.913(\text{K})^{\frac{1}{3}} \text{ for cyclopropane,}$$

$$A = 26.84 \times 10^{-5} \text{ kg/(m s)}, \quad B = 22.29(\text{K})^{\frac{1}{3}} \text{ for acetylene,}$$

$$A = 39.42 \times 10^{-5} \text{ kg/(m s)}, \quad B = 26.09(\text{K})^{\frac{1}{3}} \text{ for ethylene.}$$

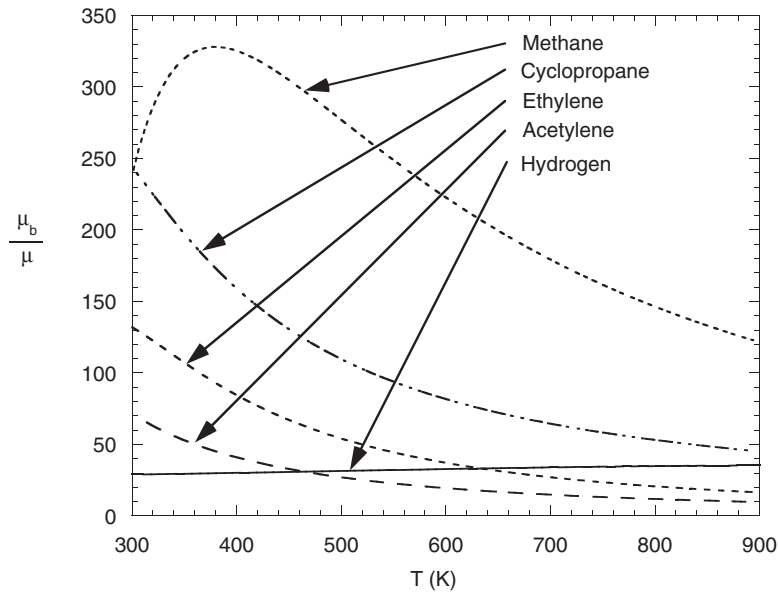


FIG. 6. Temperature variation of μ_b/μ for selected fluids having bulk viscosities which are large compared to their shear viscosities.

When the values of $p\tau_v$ are substituted in (14) we obtain the temperature variations of μ_b/μ plotted in Figure 6. For reference, we have also included the variation of H_2 in this figure.

Because of the strong decay of $p\tau_v$ with temperature inherent in the Landau-Teller variation (30), compounded with the increase in μ with increasing temperature, the values of μ_b and μ_b/μ decrease monotonically with increasing temperature for ethylene, cyclopropane, and acetylene. However, methane shows a local maximum in both μ_b and μ_b/μ at ≈ 450 K for μ_b and 378 K for μ_b/μ . The explanation for this non-monotone behavior can be seen by an inspection of the computed values of the coefficient (19). As pointed out in Sec. II, $\Delta \rightarrow 0$ near 257 K leading to the local maximum seen in Figure 6. We note that the magnitude of the slope of μ_b of ethylene also becomes relatively small at 300 K. If we employ (30) to compute μ_b for ethylene at temperatures slightly less than 300 K we find that ethylene also exhibits a non-monotone variation in μ_b with T . We note that use of the data of Holmes and Stott⁵⁰ for ethylene also gives rise to a local maximum in μ_b and μ_b/μ . In each case the reason for the local maximum is the decrease in $c_v|_v$ and Δ which overwhelms the increase in $p\tau_v$ as T decreases.

Because $\mu_b|_v$ will always vanish as $c_v|_v \rightarrow 0$ and, at large temperatures, the variation of $\mu_b|_v$ is controlled by the strong decrease associated with the Landau-Teller law, we conclude that the vibrational contribution to μ_b will have a local maximum. Because the rotational component of the bulk viscosity is always present, the total bulk viscosity will be given by the gradually increasing rotational component at temperatures so low that $c_v|_v \approx 0$. We have sketched the expected qualitative behavior of μ_b in Figure 7.

In Figure 8 we have plotted the variation of μ_b/μ of chlorine (Cl_2), fluorine (F_2), nitrous oxide (N_2O), sulfur hexafluoride (SF_6), and carbon tetrafluoride (CF_4). Each plot is based solely on the vibrational contribution to μ_b . The bulk viscosity for Cl_2 was computed using the curve-fit provided by Hurly.⁵¹ When cast in terms of $p\tau_v$ the fit for Cl_2 reads

$$p\tau_v = 0.7418 \times 10^{-5} T e^{\frac{1128.9}{T}}, \quad (31)$$

where $p\tau_v$ is in kg/(ms), T is in degrees Kelvin and the formal range of validity is 260–440 K. Vibrational relaxation times for chlorine have been obtained by a number of other authors. We have compared the values of μ_b/μ based on (31) to those based on the experimental data provided by Smiley and Winkler,⁵² Eucken and Becker,⁵³ and Schultz⁵⁴ in Figure 9. In each case, the data were taken from Smiley and Winkler's Figure 6. Inspection of Figure 9 reveals that Hurly's more recent

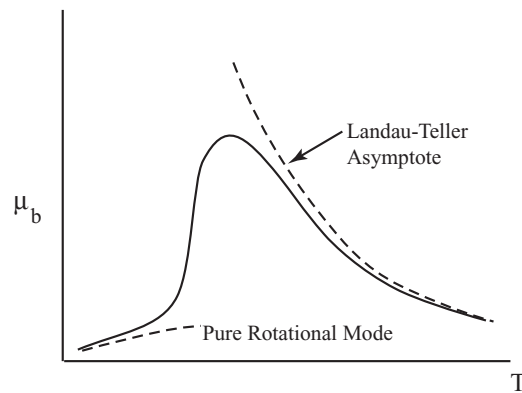


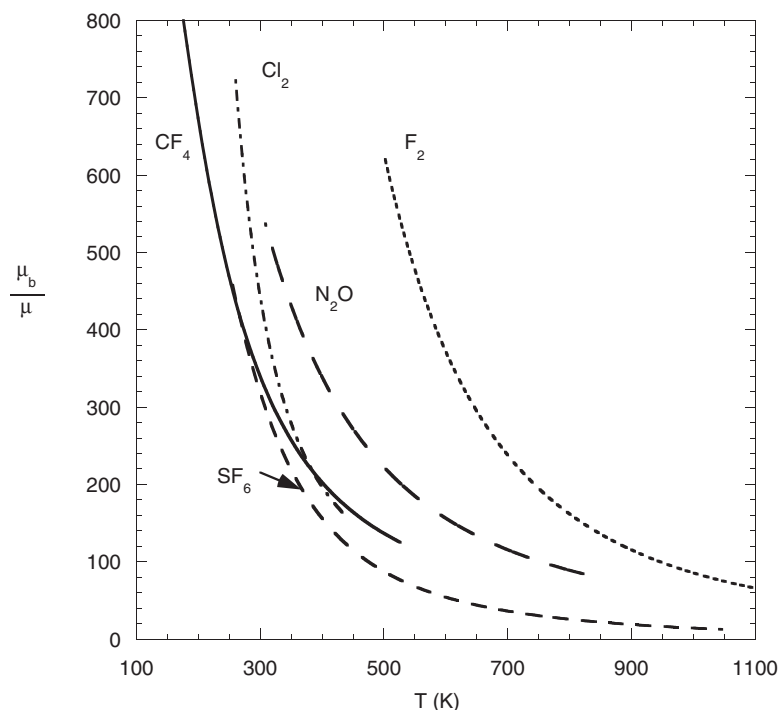
FIG. 7. Sketch of typical temperature variation of the bulk viscosity.

experiments yield $\mu_b \approx 440 \mu$ at 300 K whereas the older data correspond to considerably larger values of $p\tau_v$ and therefore μ_b/μ . For example, Eucken and Becker's data are about 50% larger than that of Hurly over roughly the same temperature range.

For F_2 we used the curve-fit of Diebold, Santoro, and Goldsmith⁵⁵ which can be written in the form (30) with

$$A = 9.502 \times 10^{-5} \text{ kg/(m s)}, \quad B = 65.20(\text{K})^{\frac{1}{3}} \quad (32)$$

and should be formally valid in the range 500–1300 K. Here we refer the reader to Diebold, Santoro, and Goldsmith's Eq. (4) and their Figure 3 for an indication of the scatter of their results. Because the formal lower limit of the validity of (32) is 500 K, it is of interest to determine what can be said about the values of μ_b at room temperature. In Figure 3 of their report, Diebold, Santoro, and Goldsmith extend their Landau-Teller fit to lower temperatures yielding reasonable agreement with

FIG. 8. Temperature variation of μ_b/μ for selected fluids having large bulk viscosity.

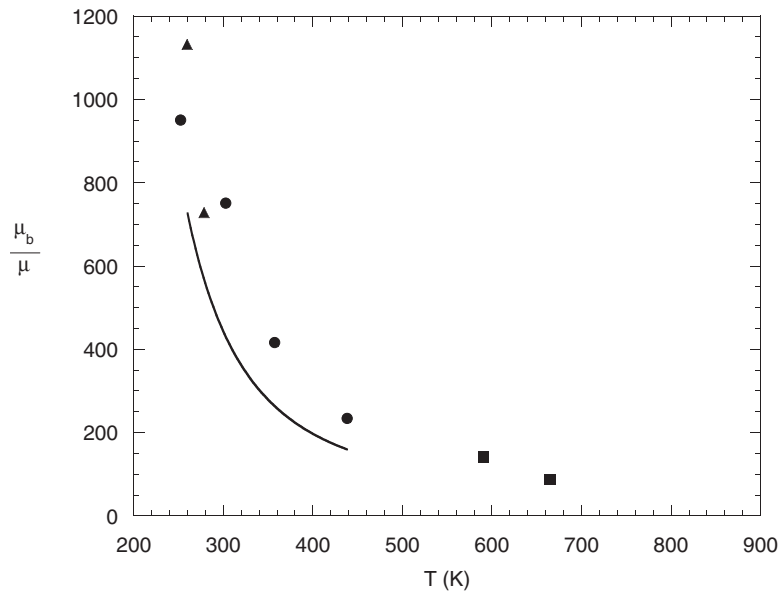


FIG. 9. Comparison of μ_b/μ for Cl_2 to the results of earlier studies. The solid line denotes our fit based on the formula by Hurly,⁵¹ ■ denotes values based on the experiments of Smiley and Winkler,⁵² ● denotes values based on the experiments of Eucken and Becker,⁵³ and ▲ denotes values based on the work of Schultz.⁵⁴

the data of Shields.⁵⁶ In particular, the difference in $p\tau_v$ is well within the suggested scatter of Diebold, Santoro, and Goldsmith's experiment. We assume that Shields' data for F_2 correspond to a pressure of 1 atm and obtain a result for $p\tau_v$ which is approximately that plotted by Diebold, Santoro, and Goldsmith⁵⁵ in their Figure 3. In Figure 10 we have plotted the values of μ_b/μ based on (32) and (30), but extended to 300 K along with values of μ_b/μ based on Shields' data. Again, the newer data yield a lower value of μ_b . Nevertheless, this extrapolated, but conservative, estimate suggests that $\mu_b > 2200 \mu$ at 300 K.

The bulk viscosities for sulfur hexafluoride were computed using the data of Holmes and Stott⁵⁰ and the curve-fit provided by Breshears and Blair.⁵⁷ The latter authors concluded that their experimental data conformed to the Landau-Teller law and could be represented by (30) with

$$A = 0.2959 \text{ kg/(m s)}, \quad B = 38(\text{K})^{\frac{1}{3}},$$

which was expected to be valid for $450 \text{ K} \leq T \leq 1050 \text{ K}$. In the fit used here, only the data from 251.15 K to 418.15 K of Holmes and Stott's report were included. To generate a single fit to both data sets we used Breshears and Blair's curve-fit to generate discrete "data" points and then fit the combined set to an equation of the form

$$p\tau_v = A \exp \left[\frac{B}{T^{\frac{1}{3}}} + \frac{C}{T^{\frac{2}{3}}} \right]. \quad (33)$$

The number of discrete points corresponding to Breshears and Blair's data was taken to be equal to the number of points used from Holmes and Stott. The resultant values of the constants in (33) were

$$A = 0.2064 \text{ kg/(m s)}, \quad B = 121(\text{K})^{\frac{1}{3}}, \quad C = -339(\text{K})^{\frac{2}{3}}.$$

A comparison of the bulk viscosities based on our fit, Breshears and Blair's fit, and the discrete data of Holmes and Stott is plotted in Figure 11. As can be seen, our fit agrees very well with the experimental data at 300 K. The maximum difference between our fit and the experimental data is about 13% at 418 K.

The plot for CF_4 is based on a curve-fit to the data of Corran *et al.*⁵⁸ and Ewing and Trusler.⁵⁹ All the data of Ewing and Trusler⁵⁹ were used. We assumed that the data of Corran *et al.* correspond to 1 atm and we also omitted the point at 588 K in our fit. This last point appeared to be an anomaly

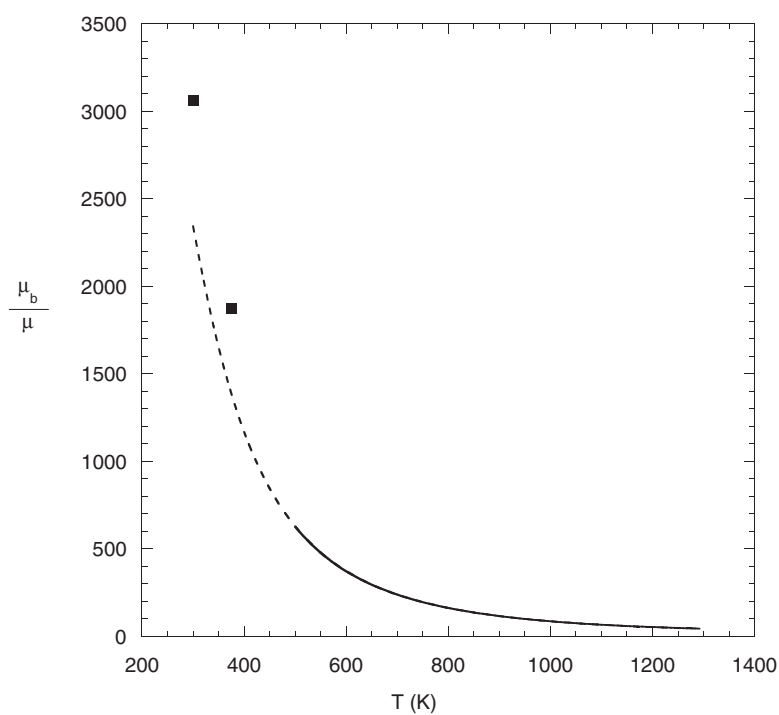


FIG. 10. Comparison of μ_b/μ for F_2 to the data of Shields.⁵⁶ The solid line represents our curve-fit, the dashed line represents the extension of our fit to 300 K, and the symbols denote values based on the experiments of Shields.⁵⁶

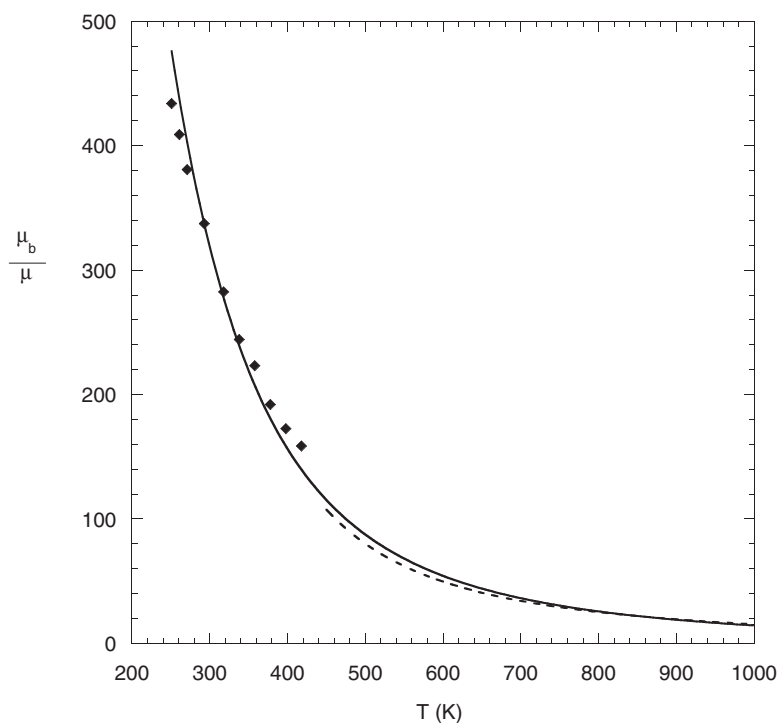


FIG. 11. Composite curve-fit of temperature variation for SF_6 . Solid line represents our curve-fit, symbols are based on the discrete data of Holmes and Stott,⁵⁰ and the dashed line represents the curve-fit provided by Breshears and Blair.⁵⁷

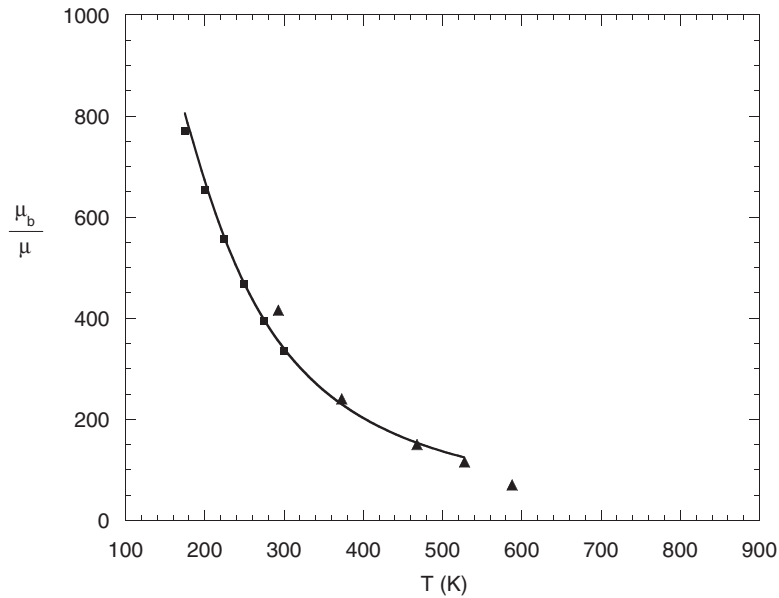


FIG. 12. Composite curve-fit of temperature variation of μ_b/μ for CF_4 . The solid line represents our curve-fit, ■ denotes the values based on the data of Ewing and Trusler,⁵⁹ and ▲ denotes values based on the data of Corran *et al.*⁵⁸

compared to the rest of Corran *et al.*'s data. Our fit was of the Landau-Teller type, i.e., (30), with

$$A = 497.8 \text{ kg/(m s)} \text{ and } B = 17.9(\text{K})^{\frac{1}{3}},$$

which is expected to be valid from 175 K to 518 K. A comparison of our fit to the discrete data is provided in Figure 12. This plot also includes the anomalous point at 588 K. Our fit agrees quite well with the data of Ewing and Trusler⁵⁹ near 300 K, whereas there is about a 14% discrepancy between our fit and Corran *et al.*'s⁵⁸ data point at 293 K.

The variation of μ_b/μ for nitrous oxide (N_2O) plotted in Figure 8 was computed using the shock tube data of Simpson, Bridgman, and Chandler⁶⁰ who carefully accounted for a dependence of the results on departures from equilibrium. The authors compared their results to previous investigations including the well known study of Griffith, Brickl, and Blackman.⁶¹ Simpson, Bridgman, and Chandler⁶⁰ reported their data as a single curve which presumably was a fit to discrete data. Using graph-digitizer software, we extracted $(p\tau_v, T^{\frac{1}{3}})$ points from their Figure 3 and, because their curve did not conform well to the Landau-Teller law, we then fit their points to a power-law of the form

$$p\tau_v = (p\tau_v)_{\text{ref}} \left(\frac{T}{T_{\text{ref}}} \right)^n, \quad (34)$$

where $(p\tau_v)_{\text{ref}} = 0.05305 \text{ kg/(m s)}$, $T_{\text{ref}} = 500 \text{ K}$, and $n = -1.178$. Our fit is expected to be valid over the same range covered by Simpson, Bridgman, and Chandler,⁶⁰ i.e., 320–850 K.

The final fluid to be considered is carbon dioxide (CO_2) which has historically been regarded as having $\mu_b/\mu = \mathcal{O}(10^3)$. The data used for our estimates are the relaxation time data of Simpson, Bridgman, and Chandler⁶² who accounted for departures from equilibrium on the reported value of the relaxation time, the sensitivity of the test gas to trace amounts of water vapor, and made comparisons to previous investigations. As in the case of N_2O , the authors report their results only as a single curve. We followed the same procedure as for N_2O and found that their curve could be represented by a power-law of the form (34) with

$$(p\tau_v)_{\text{ref}} = 0.19152 \text{ kg/(m s)}, \quad T_{\text{ref}} = 800 \text{ K}, \quad n = -1.353$$

which should be valid for $296 \text{ K} \leq T \leq 1711 \text{ K}$. We have plotted the values of μ_b/μ based on our curve-fit along with the values based on the points taken from Simpson, Bridgman, and Chandler's Figure 5 in Figure 13. We note that value of the bulk viscosity based on our power-law at 296.3 K

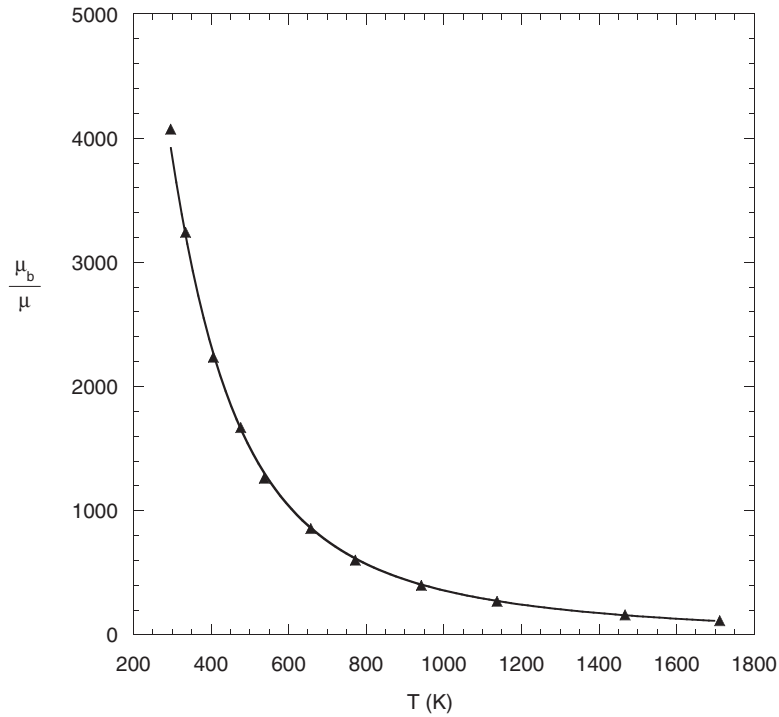


FIG. 13. Temperature variation of μ_b/μ for CO_2 . The solid line represents our curve-fit and the symbols are values based on data taken from Simpson, Bridgman, and Chandler.⁶²

was 3922μ whereas the value based on the data taken from Simpson, Bridgman, and Chandler's Figure 5 was 4073μ for a difference of $\approx 3.7\%$; this is the largest discrepancy in Figure 13.

At 300 K, we find that our fit yields $p\tau_v \approx 0.72 \text{ kg}/(\text{m s})$ which is only about 5% higher than the value of $p\tau_v$ used by Emanuel.³⁰ At 300 K, our estimates yield

$$c_v \approx 3.48R, \quad \mu \approx 1.52 \times 10^{-5} \text{ kg}/(\text{m s}), \quad \mu_b \approx 5845 \times 10^{-5} \text{ kg}/(\text{m s})$$

yielding a ratio $\mu_b/\mu = 3849$ which is about 8% larger than an estimate for μ_b/μ obtained by using Emanuel's data and the Planck-Einstein formula for the vibrational specific heat.

V. PREDICTIONS OF THE GENERAL SIZE OF THE BULK VISCOSITY

The estimates for μ_b found in Secs. III and IV have ranged from $\mu_b = O(\mu)$ to $\mu_b = O(10^3 \mu)$. In the design of experiments, power systems, and other technologies, it is useful to have a simple method for the estimation of the general size of μ_b/μ . Because the variability of μ_b from fluid to fluid is primarily due to the variability of the relaxation time, we believe that the Lambert-Salter⁶³ empirical correlation can provide a reasonable guide to the size of the ratio μ_b/μ .

The Lambert-Salter correlation relates the collision number Z_{10} to the characteristic temperature corresponding to the lowest vibrational mode as follows:

$$\log_{10} Z_{10} = K\theta_v, \quad (35)$$

where K is a constant taken to depend on the number of hydrogen atoms comprising the molecule and the temperature at which Z_{10} is evaluated, typically taken to be 300 K. The value of K for molecules having no hydrogen atoms is observed to be larger than that corresponding to molecules having two or more hydrogen atoms. An illustration of the Lambert-Salter correlation is provided in Figure 14. The values of Z_{10} were computed from our estimates of μ_b/μ at 300 K and (10) for *n*-butane, *n*-pentane, dimethylpropane, acetylene, ethylene, cyclopropane, and methane. The straight line fits seen in Figure 14 are based on a least-squares fit to the slope; because $Z_{10} \geq 1$, we

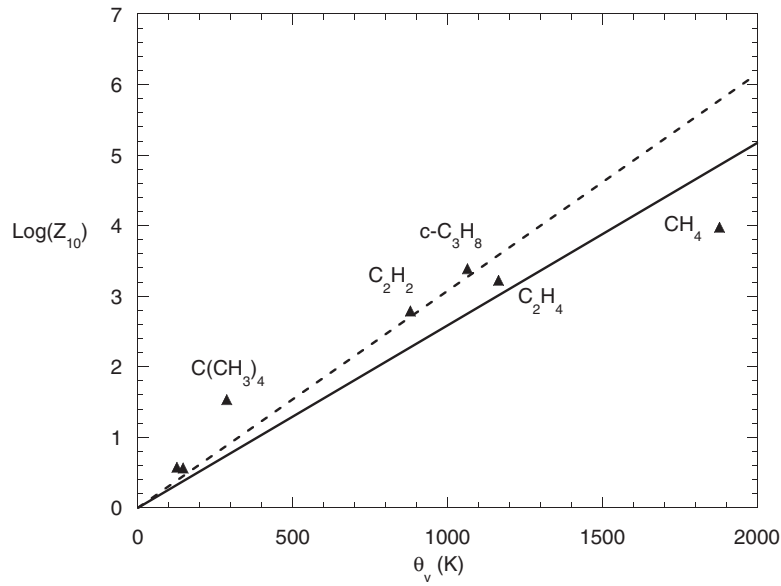


FIG. 14. Lambert-Salter plot for molecules containing two or more hydrogen molecules. The two substances having $\log(Z_{10}) < 1$ are n-butane ($\text{n-C}_4\text{H}_{10}$) and n-pentane ($\text{n-C}_5\text{H}_{12}$). The dashed line is a straight line fit to the data excluding CH_4 and the solid line is a straight line fit including CH_4 .

follow Lambert and Salter⁶³ and Lambert³⁵ in fixing $\log_{10} Z_{10} = 0$ at $\theta_v = 0$. As seen in the studies of Lambert,³⁵ methane falls below the line determined by the general grouping. Thus, we have provided straight line fits to our own more limited data set both including and excluding methane. The corresponding values of K were found to be $2.6 \times 10^{-3}(\text{K})^{-1}$ and $3.1 \times 10^{-3}(\text{K})^{-1}$, respectively.

The variation of μ_b/μ with θ_v at fixed temperature can be anticipated by considering the ratio

$$\frac{\mu_b|_v}{\mu_{HS}} = \frac{4}{5} \Delta Z_v, \quad (36)$$

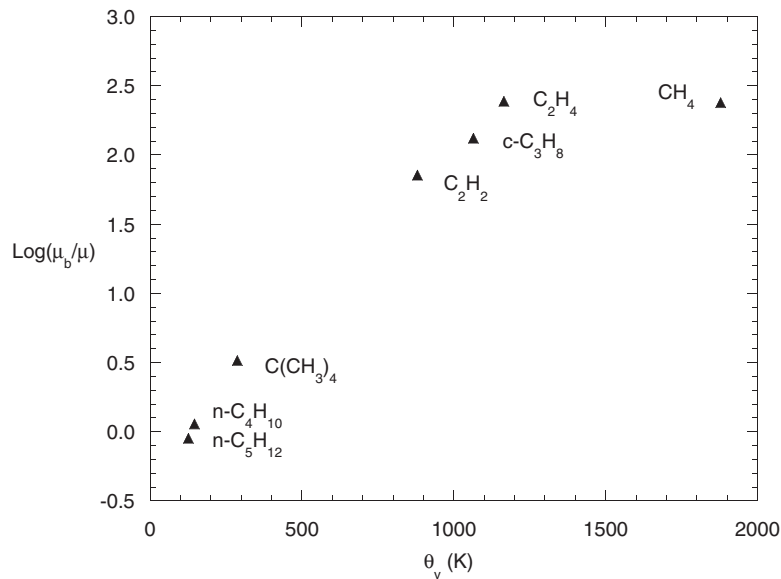
where μ_{HS} is the hard sphere approximation (6) for the shear viscosity. If we combine (35) with (10), we have

$$Z_v = \frac{10^{K\theta_v}}{1 - e^{-\frac{\theta_v}{T}}},$$

which is seen to have a local minimum at $\theta_v \approx 115\text{K}$ if we use $T = 300\text{K}$ and $K \approx 3.1 \times 10^{-3}(\text{K})^{-1}$. If we assume that $\Delta = \Delta(\theta_v)$ at fixed temperature, it is reasonable to conclude that

$$\frac{\mu_b|_v}{\mu_{HS}} = f(\theta_v).$$

If we use the more accurate estimate (16) for the viscosity, we must include the collision integral (18) in the numerator of (36). Because $\Omega = \Omega(T_\epsilon)$ at fixed temperature and T_ϵ is independent of θ_v , a pure correlation of μ_b/μ with θ_v is not strictly possible. However, the numerical value of Ω does not vary strongly from fluid to fluid and we would expect that some simple trend could nevertheless be observed. As partial support for this conjecture, we have plotted our computed values of $\log_{10}(\mu_b/\mu)$ against θ_v for the same fluids as were used in Figure 14 in Figure 15. Except for methane we see a clear increase in μ_b/μ with θ_v . The relatively low value of $\log_{10}(\mu_b/\mu)$ of methane is primarily due to the anomalous behavior of CH_4 with respect to the Lambert-Salter plot of Figure 14. A second contributing factor is the fact that the vibrational mode is becoming deactivated in the vicinity of 300 K. This decrease in $c_v|_v$ and Δ can be seen in Figure 1 and gave rise to the non-monotone variation of μ_b/μ with T in Figure 6.

FIG. 15. Variation of μ_b/μ with characteristic temperature of vibration at 300 K.

We have also verified that our calculations are consistent with Lambert and Salter's observation that fluids having no hydrogen atoms have a larger K -value and therefore have larger values of Z_{10} at the same value of θ_v . The estimates of μ_b/μ for fluids having no hydrogen atoms were also seen to be larger than those having hydrogen molecules at the same θ_v .

In conclusion, we believe that, at a given temperature, μ_b/μ can generally be regarded as an increasing function of θ_v . Fluids having no hydrogen atoms, e.g., CO₂, CF₄, SF₆, etc., are expected to have higher values of μ_b/μ for the same value of θ_v than fluids containing hydrogen atoms. However, this trend will become invalid at sufficiently large values of θ_v , i.e., when $T/\theta_v \rightarrow 0$. As $\theta_v \rightarrow \infty$, $\Delta \rightarrow 0$ and the vibrational modes become inactive, i.e., $\mu_b|_v \rightarrow 0$. Thus, there will be a local maximum in the $\mu_b|_v/\mu$ (or $\log_{10} \mu_b|_v/\mu$) vs θ_v curve.

In cases where $\mu_b|_v \ll \mu_b|_r$, i.e., $T \ll \theta_v$, the rotational contribution to μ_b is dominant and the general size of μ_b is $O(\mu)$; an important exception is H_2 for which μ_b is roughly 30 times μ at room temperature.

As discussed by Lambert and Salter⁶³ and Lambert,³⁵ polar fluids are expected to possess a more complicated behavior. However, if the strong dipole forces are large enough, the energy transfer will be highly efficient so that we would expect μ_b to be $O(\mu)$ for polar fluids. We expect that exceptions will occur if the energy associated with the dipole is weak compared to the kinetic energy at the temperature in question; examples are expected to include methyl chloride (CH₃Cl) and methyl fluoride (CH₃F) which, according to Table 3.5 of Lambert,³⁵ can have values of Z_{10} on the order of acetylene or higher at 300 K.

VI. SUMMARY

The primary objective of the present study is to provide estimates of the bulk viscosity (1) of dilute polyatomic gases using Tisza's formula (3) or (12)–(14) combined with published measurements of the vibrational and rotational relaxation times. Unlike the shear viscosities, the bulk viscosities can have a wide range of numerical values and temperature variations, even in the ideal gas limit. The discussion and analysis presented here suggests that the temperature variation of the bulk viscosity will always have a local maximum. At sufficiently low temperatures, the vibrational mode is deactivated and the bulk viscosity is due to the relaxation of the rotational mode typically yielding a bulk viscosity which is $O(\mu)$ and is gradually increasing with temperature. At sufficiently high temperatures, the vibrational mode is activated and the bulk viscosity is characterized by the

strong decay with temperature associated with the Landau-Teller theory. Hence, at least one local maximum must occur.

The largest values of the maximum value of μ_b/μ are likely to occur when the characteristic temperature of vibration is considerably larger than that where dipole moments or attractive forces are non-negligible. In this case, the local maximum will occur as the vibrational mode is activated and marks the transition between the Landau-Teller region and the region where the bulk viscosity is primarily due to its rotational contribution. If, on the other hand, θ_v is so low that attractive and dipole forces play a role after the vibrational modes are activated, the equilibration of the vibrational energy will be efficient and the resultant local maximum in μ_b will typically be $O(\mu)$.

In Sec. V we have employed the Lambert-Salter correlation to suggest that the numerical value of μ_b/μ at a given temperature can be inferred by a knowledge of θ_v . For example, it appears that fluids having similar numbers of hydrogen atoms and which have larger values of θ_v will also have larger values of μ_b/μ at the same temperature. The limitation of this tendency occurs when the chosen temperature is small compared to θ_v resulting in a deactivation of the vibrational mode. Although we provide no detailed supporting data, we believe that it is reasonable to conjecture that the variation of μ_b/μ with θ_v at constant temperature will always have a local maximum.

The general order of magnitude of μ_b/μ for substances such as N_2 , CO_2 , N_2O , and H_2 at room temperature is in reasonable agreement with the estimates provided in previous investigations. A contribution of the present study is to establish explicit estimates of μ_b for a wider range of fluids than considered previously. In doing so, it is seen that many common fluids, including diatomic gases, can have bulk viscosities which are hundreds to thousands of times larger than their shear viscosities.

The primary factor determining the accuracy of our estimates is the accuracy of the published relaxation times. Due to the difficulty of the measurements, scatter in excess of 10% is commonly observed. An important contribution to the determination of μ_b is the refinement of estimates for the relaxation times, particularly H_2O and other fluids of technological interest.

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