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SECOND COEFFICIENT OF VISCOSITY IN AIR

By

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SECOND COEFFICIENT OF VISCOSITY IN AIR

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Abstract

Acoustic attenuation measurements in air have been analyzed in order to estimate the second coefficient of viscosity. Data over a temperature range of 11°C to 50°C and at relative humidities between 6 percent and 91 percent were used. This analysis has shown that the second coefficient of viscosity varied between 1900 and 20,000 times larger than the dynamic or first coefficient of viscosity over the temperature and humidity range of the data. In addition, the data have shown that the molecular relaxation effects, which are responsible for the magnitude of the second coefficient of viscosity, place severe limits on the use of time-independent, thermodynamic equations of state. Compressible flows containing large streamwise velocity gradients, like shock waves, which cause significant changes in particle properties to occur during time intervals shorter than hundredths of seconds, must be modeled using dynamic equations of state. The dynamic model approach has been described briefly.

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Introduction

When the stress tensor is symmetric, continuum theory limits the number of arbitrary constitutive constants to two for a linear, isotropic material. While solid mechanics handbooks tabulate pairs of material constants (Young's modulus and Poisson's ratio) relating stress to strain, fluid mechanics handbooks tabulate only one constant - - dynamic viscosity - - relating stress to rate of strain. Because many important fluid flows can either be treated as incompressible flows or boundary layer flows, the influence of a second coefficient of viscosity on the equations of motion can be eliminated from the formulation and the problem is avoided. However, current research for a variety of vehicle systems in air require analyses of flow fields which are neither incompressible nor amenable to boundary layer approximations. While limited experimental data are available, the purpose of this work is to examine recent acoustical data in order to estimate the magnitude of the second coefficient of viscosity in air.

Since the second coefficient of viscosity appears as a linear combination with the dynamic viscosity in many tensor manipulations, the linear combination is often referred to as the *bulk viscosity* or *volume viscosity*. Furthermore, since the trace of the stress tensor is an invariant, an average normal stress or pressure force is predicted for most compressible fluid flows which occurs in addition to thermodynamic pressure. That problem is avoided when the ratio of the second coefficient of viscosity to the dynamic viscosity is negative two thirds. In 1845, C.G. Stokes suggested that using a second coefficient equal to $-2/3\mu$ was a convenient way to avoid uncertainties in the meaning of pressure in a flowing fluid. *Stokes' hypothesis* can be justified for monatomic molecules like helium, but no such arguments exist for mixtures of polyatomic molecules like air.

White¹ has provided a good review of the second coefficient of viscosity problem in fluid mechanics. Since normal shock waves produce large velocity gradients in the direction of flow, shock thickness measurements can be used to determine the influence of second coefficient of viscosity. Unfortunately, shock waves produce strong gradients in all of the thermodynamic variables and if the second coefficient of viscosity varies with temperature, the accuracy of those

estimates are limited. However, the early shock wave thickness measurements of Sherman² which employed thermocouples and position indicators for the measurements, showed that the second coefficient of viscosity in air was a positive value (not equal to $-2/3\mu$).

Bulk viscous effects in air are of major concern to acousticians. Attenuation of radiated sound waves is controlled for the most part by bulk viscosity. However, because frequency dependent thermophysical properties violate the fundamental laws of continuum mechanics, the acoustics literature is nearly void of references to bulk viscous effects. Acousticians use *total sound attenuation* (in nepers/meter, where nepers are dimensionless) and tabulate that property. Total sound attenuation in air varies strongly with acoustic frequency, relative humidity and temperature. As productive engineers, acousticians have been concerned more with propagation models than with the frequency dependent property inconsistencies.

The second coefficient of viscosity controversy may have reached maximum intensity in 1954, when Rosenhead³ convened a meeting of some of the leading authorities in continuum theory and fluid mechanics in an attempt to sort out the problem. A prominent contributor to the controversy has been Truesdell,^{4,5} who showed rigorously that bulk viscous effects in simple fluids cannot vary with frequency. The stature of the scholars involved in that controversy may have restricted the rate at which others contributed information to the subject. Goldstein,⁶ was willing to discuss the dilemma in 1972, but his publication was rather obscure.

Acousticians made major strides in unraveling the controversy in the mid 1960's. Bauer and Roesler⁷ reported on the slow rate at which mixtures of nitrogen and oxygen returned to thermal equilibrium. The reason for slow relaxation rates could be attributed to the vibrational degrees of freedom possessed by both oxygen and nitrogen molecules. They found that up to 20 million collisions were required to re-equilibrate vibrationally excited molecules. Those measurements showed that equilibrium based equations of state could not be used in mixtures of nitrogen and oxygen for processes with characteristic frequencies in excess of a few hundred hertz. Subsequently, Bauer⁸ and Kneser⁹ developed rigorous models for these systems using ideas from non-equilibrium thermodynamics (see deGroot and Mazur¹⁰). While rigorous, the

models are cumbersome and demand additional thermodynamic relaxation data that were not available for air.

The implications of this previous work for compressible, non-boundary layer flows in air are profound. First, if bulk viscosity fails to obey Stokes hypothesis, a great deal of computational analysis is flawed. Second, if molecular relaxation effects are important at frequencies higher than a few hundred hertz, simple continuum theory models are restricted severely in both space (mean-free-path constraints) and time. Finally, attenuation data suggest that the second coefficient of viscosity in air may be free of frequency dependent, non-equilibrium relaxation effects only at low frequencies.

Fortunately, the situation in air may not be as bad as it sounds, which is probably why the controversy persists. First, as will be discussed later, water vapor accelerates the return to equilibrium of nitrogen and oxygen molecules. Hence, below altitudes of 10.5km (35,000 ft.) water vapor levels are often high enough to increase the collision-driven, upper frequency limit to several thousand hertz (see Bass et al.¹¹). Second, most computational fluid dynamics codes have used artificial viscosity to control computational stability and in some cases those adjustments may be consistent with air data. Also, as mentioned previously, incompressible flows and boundary layer flows are not influenced by bulk viscosity, although constraints on boundary layer approximation limits are more severe.

Recently, Marcy¹² has reported estimates of the bulk viscosity in air. He employed the correlations of Bass et al.¹¹, who used data from Zuckerwar and Meredith^{13,14}, to develop estimates of bulk viscosity over a wide range of temperatures and relative humidities. This study has employed Zuckerwar's experimental data directly to establish the accuracy of the empirically based predictions.

The present work will start with the basic formulations from acoustics and fluid mechanics, for the purpose of unifying the constitutive constants. Using the acoustic and fluid mechanical interpretations, Zuckerwar's measurements have been translated into bulk viscosity data for air. Finally, a brief discussion of non-equilibrium thermodynamic effects has been included.

Formulation

The stress tensor, σ_{ij} is assumed related to the rate of strain tensor by:

$$\sigma_{ij} = \mu \left[\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \gamma_{II} \frac{\partial u_k}{\partial x_k} \delta_{ij} \right] \quad (1.)$$

where μ is the dynamic viscosity, the u_i are the Cartesian velocity components, γ_{II} is the dimensionless form of the second coefficient of viscosity and δ_{ij} is the Kronecker delta. The Einstein summation convention is used throughout.

Since the trace of a second rank tensor is invariant, an average pressure contribution, p' , due to viscous effects is given by:

$$p' = -\sigma_{kk}/3 = -\mu(2/3 + \gamma_{II}) \frac{\partial u_k}{\partial x_k}, \quad (2.)$$

or from conservation of mass, the divergence of velocity is given by:

$$\frac{\partial u_k}{\partial x_k} = -\frac{1}{\rho} \frac{D\rho}{Dt}, \quad (3.)$$

so that viscous pressure fluctuations can be represented by

$$p' = \nu (2/3 + \gamma_{II}) \frac{D\rho}{Dt}, \quad (4.)$$

where ν is the kinematic viscosity and $\frac{D\rho}{Dt}$ is the material time derivative of density in an Eulerian system.

The bulk viscosity, β , is defined by

$$\beta \equiv \mu (2/3 + \gamma_{II}) \quad (5.)$$

and the dimensional form of the second coefficient of viscosity is often designated as λ ($=\mu\gamma_{II}$).

Acoustic disturbances are normally very small compared to other fluid mechanical effects. If consideration is given to a weak, plane acoustic wave, travelling in the x-direction, the position of an air "particle" translates across a reference location by some amount $\xi(x, t)$, where the particle

translations can be influenced by distance from the acoustic source - - say x . Furthermore, if a steady wave train is considered, the conservation of mass can be approximated by

$$\frac{\rho - \rho_0}{\rho_0} \equiv \Delta(t) \approx -\frac{\partial \xi}{\partial x}, \quad (6.)$$

where ρ_0 is the undisturbed density and ρ is the instantaneous density.

If the speed of sound is c , acoustic pressure fluctuations, \tilde{p} , are related to density fluctuations by:

$$\tilde{p} \approx \rho_0 c^2 \Delta \approx -\rho_0 c^2 \frac{\partial \xi}{\partial x}. \quad (7.)$$

The linearized conservation of momentum equation for a viscous fluid obeying Eq. (1.) can be written in terms of local particle displacement as

$$\frac{\partial^2 \xi}{\partial t^2} = -\frac{1}{\rho_0} \frac{\partial \tilde{p}}{\partial x} + \frac{\partial \sigma_{11}}{\partial x} = c^2 \frac{\partial^2 \xi}{\partial x^2} + \nu(2 + \gamma_{II}) \frac{\partial^2}{\partial x^2} \left(\frac{\partial \xi}{\partial t} \right), \quad (8.)$$

where variations of ν and γ_{II} with temperature have been neglected.

For an acoustic plane-wave being generated continuously at $x=0$,

$$\xi = \xi_0 e^{-\alpha x} e^{i(\omega t - kx)} \quad (9.)$$

satisfies the governing equations where α is called the *total sound attenuation* (in nepers/meter) by acousticians. Substitution of equation (9.) into equations (7.) and (8.) yields

$$\frac{\alpha}{\omega} = \frac{1}{c\sqrt{2}} \frac{\epsilon}{\sqrt{(1 + \epsilon^2) + (1 + \epsilon^2)^{3/2}}} \quad (10.)$$

$$\text{where } \epsilon \equiv \nu(2 + \gamma_{II}) \omega / c^2 \quad (11.)$$

In most acoustics applications, it is presumed that ϵ is small so that to a good approximation, Eq. (10.) becomes

$$\frac{\alpha}{\omega^2} \approx \frac{\nu(2 + \gamma_{II})}{2c^3}. \quad (12.)$$

When the approximation is met and the viscosities are constant, it is seen that acoustic attenuation increases quadratically with frequency. In fact, a great deal of experimental attenuation data are plotted as α/f^2 where f is frequency. It should be noted that Stokes derived this relation for $\gamma_{II} = -2/3$ in 1845.

Air is composed primarily of oxygen and nitrogen with variable amounts of water vapor. Both oxygen and nitrogen are diatomic molecules with one vibrational, two rotational and three translational degrees of freedom. On the other hand water vapor is triatomic and is classified as an *angular triatomic* molecule⁹. Bass et al.¹¹ have tabulated the various types of molecular relaxation processes which can occur when significant populations of vibrationally excited (out of equilibrium) molecules are present in air. Both vibrationally excited oxygen and nitrogen molecules relax slowly in air. Surprisingly, water vapor molecules can interact with either excited nitrogen or excited oxygen molecules to accelerate their relaxation. Unfortunately, water vapor levels of less than 0.01% are insufficient to "catalyze" the relaxation process effectively and hence, using the U.S. Standard Atmosphere¹⁵ and calculating maximum water content, dry air must be assumed at altitudes above 10,500 m (35,000 ft.). Acousticians have developed empirical data to estimate attenuation over a range of temperature, pressure and humidity conditions and a typical correlation is discussed subsequently.

If ϕ is used as a measure of the mole fraction of water in air, then

$$\phi \equiv (\text{Relative Humidity in percent}) \times P_w / P_{\text{atm}} \quad (13.)$$

where P_w is the saturation pressure of water corresponding to the atmospheric temperature and P_{atm} is the atmospheric pressure. The influence of water vapor, ambient pressure and temperature on total sound attenuation have been correlated empirically by Bass et al.¹¹ using ϕ as an independent variable. When pressures are normalized using atmospheres and absolute temperature, in degrees Kelvin, is normalized with respect to 293.15K, i.e.

$$\Theta = T / 293.15 \text{ K}, \quad (14.)$$

Bass et al.¹¹ reported total sound attenuation data correlations for air, given by:

$$\frac{\alpha}{\omega^2} = \frac{1}{(2\pi)^2} \left\{ 1.83 \times 10^{-11} \frac{\Theta^{1/2}}{P} + \Theta^{-5/2} \left[0.01278 \frac{e^{-7.638/\Theta}}{f_{r,o} + \frac{\omega^2}{(2\pi)^2 f_{r,o}}} + 0.1069 \frac{e^{-11.43/\Theta}}{f_{r,N} + \frac{\omega^2}{(2\pi)^2 f_{r,N}}} \right] \right\} \quad (15.)$$

where

$$f_{r,o} = P \left[24 + 44,100 \phi \frac{0.05 + \phi}{0.391 + \phi} \right] \quad (16.)$$

and

$$f_{r,N} = P (9 + 200\phi) \quad (17.)$$

which are the relaxation frequencies for oxygen and nitrogen, respectively. Hence, if α/ω^2 or α/f^2 is a constant in an acoustical total sound attenuation plot and ϵ , from Eq. (11), is small,

$$\gamma_{II} = 2c^3/\nu \left(\frac{\alpha}{\omega^2} \right) - 2 \quad (18.)$$

Otherwise, Eq. (10.) and (15.) can be used to find ϵ and

$$\gamma_{II} = \frac{c^2 \epsilon}{\omega \nu} - 2 \quad (19.)$$

Equation (15.) has been used to calculate γ_{II} , which has been compared to the experimental data. At high altitudes, dry air can be assumed and Marcy¹² has used the data of Bass et al.¹¹ to calculate the second coefficient of viscosity for dry air.

Reduction of Acoustic Data

A typical total attenuation plot from Zuckerwar and Meredith¹³ is shown in Figure 1. If ϵ , defined in Eq. (11.), is small, then from Equation (12.), acoustic attenuation, which is controlled by simple continuum theory, should vary quadratically with frequency. Furthermore, as frequency is increased, vibrational non-equilibrium effects become significant and a simple, time-independent, continuum theory cannot be used. Hence, a straight line has been drawn through the low frequency portion of the data, in Figure 1 showing how the quadratic approximation fits. The appearance of noticeable vibrational non-equilibrium effects are indicated with an arrow where the data cease to follow the quadratic line. From those data, second coefficient of

viscosity can be determined. The data in Table I are a summary of the results from Zuckerwar's measurements along with a comparison of estimates of γ_{Π} using Eq. (15).

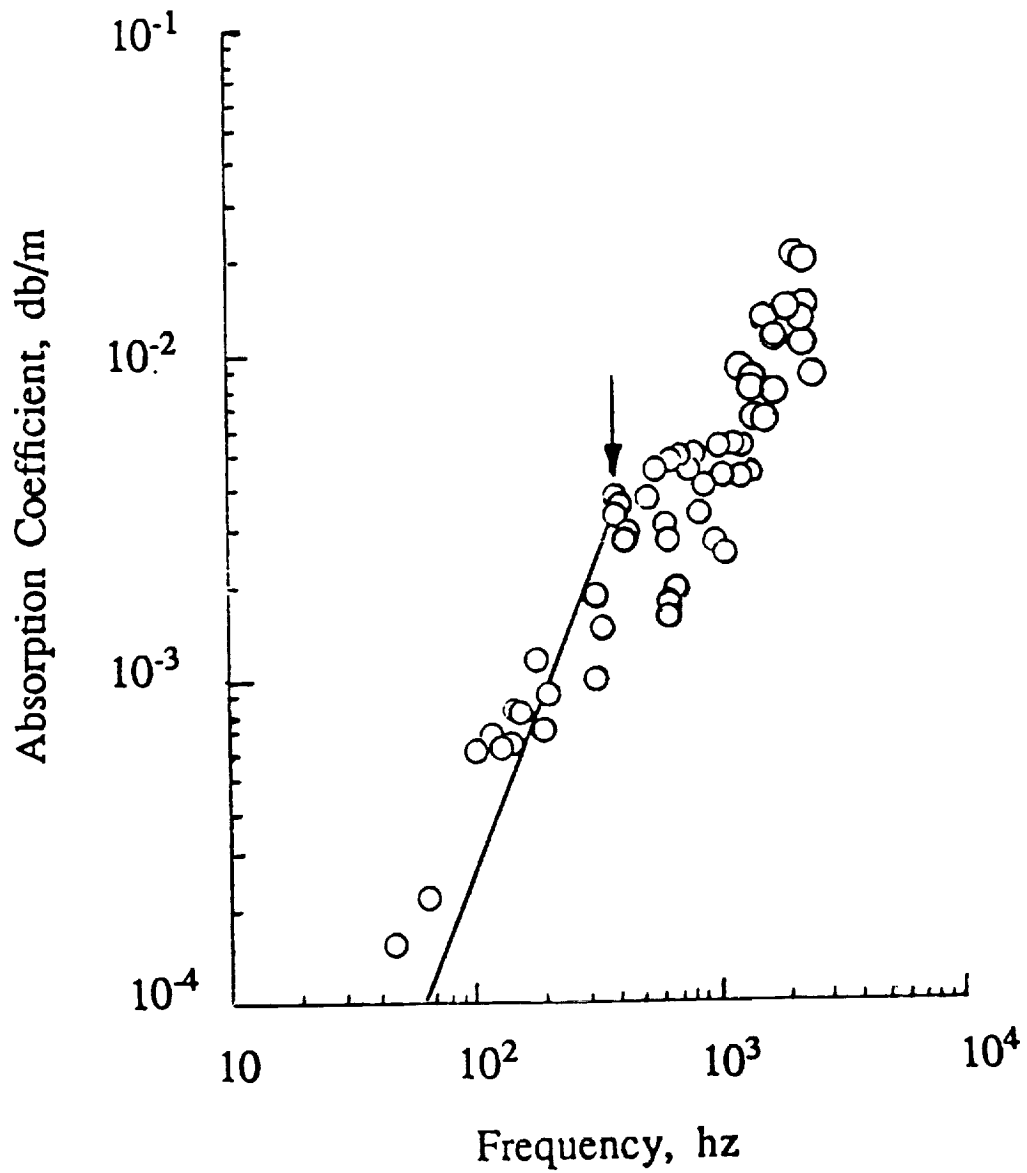


Figure 1 Typical Attenuation Curve

TABLE I
Second Coefficient of Viscosity
for Air, Calculated from Zuckerwar¹³

Experimental Conditions								
T	P	Relative Humidity	$\frac{\alpha}{\omega^2} \times 10^{10}$	$\nu \times 10^5$	fmax	γ_{II}	$\epsilon_{max} \times 10^4$	Error in Eq. 15
11.5°C	1.0009 atm	9.7%	37.5	1.456 m ² /s	70 hz	19,900	11.1	-16%
19.6	1.0104	7.9	14.4	1.495	170	7,770	9.14	156
19.8	1.0036	65.3	5.17	1.531	410	2,730	10.6	-71
20.0	1.0138	7.1	17.6	1.494	130	9,520	9.88	134
20.7	1.0104	28.3	9.73	1.514	180	5,210	7.56	-34
20.9	1.0172	73.5	3.95	1.526	420	2,100	7.16	-71
21.1	1.0104	20.4	11.0	1.514	180	5,900	8.54	3
21.7	1.0261	35.5	7.04	1.504	400	3,820	12.1	-76
21.8	1.0145	45.8	5.83	1.527	420	3,120	10.6	-54
21.8	0.9458	91.2	3.95	1.661	480	1,940	8.20	-80
29.8	0.9744	24.2	12.5	1.662	200	6,390	11.0	-41
29.8	1.0179	38.3	7.04	1.602	320	3,730	9.88	-57
30.0	1.0118	52.1	5.17	1.625	410	2,700	9.30	-67
30.2	1.0091	46.0	5.17	1.626	490	2,700	11.1	-58
30.3	0.9934	13.7	12.5	1.627	180	6,540	9.88	43
30.7	1.0084	65.5	3.95	1.649	500	2,040	8.68	-73
39.2	0.9989	25.7	6.59	1.725	480	3,400	14.1	-21
39.4	1.0125	47.9	5.17	1.734	500	2,650	11.5	-70
39.6	1.007	9.4	20.7	1.695	130	10,900	12.0	28
39.6	1.0132	16.5	10.5	1.693	230	5,520	10.8	7
40.0	1.0132	32.9	5.83	1.719	500	3,030	13.0	-46
49.1	1.0091	28.8	5.17	1.834	850	2,620	19.9	-37
49.8	1.007	17.4	10.1	1.821	500	5,180	22.8	-18
50.2	1.0234	6.2	20.7	1.769	180	11,000	16.8	97

It can be seen from Table I that estimated values for γ_{II} range from 1940 at 21.8°C, 91.2% relative humidity up to 19,900 at 11.5°C, 9.7% relative humidity. The data in Table I are plotted as γ_{II} vs temperature in Figure 2. Because of the extreme influence of moisture content on γ_{II} at a given temperature, the measured value of relative humidity is indicated beside each data point. In addition, the upper, dry-air limit line and lower, saturated air limit line, developed by Marcy¹² are shown. While the table shows that Eq. (15) is not very accurate in correlating

γ_{II} calculated from Zuckerwar and Meredith's¹³ experiments, the variation of γ_{II} with humidity, which covers more than two orders of magnitude at a given temperature, can produce much larger differences than those resulting from use of Eq. (15). It is important to recognize further that the experimental data are self consistent, showing decreases in γ_{II} with increases in water content, and that the data fall comfortably within the limit curves predicted by Marcy¹².

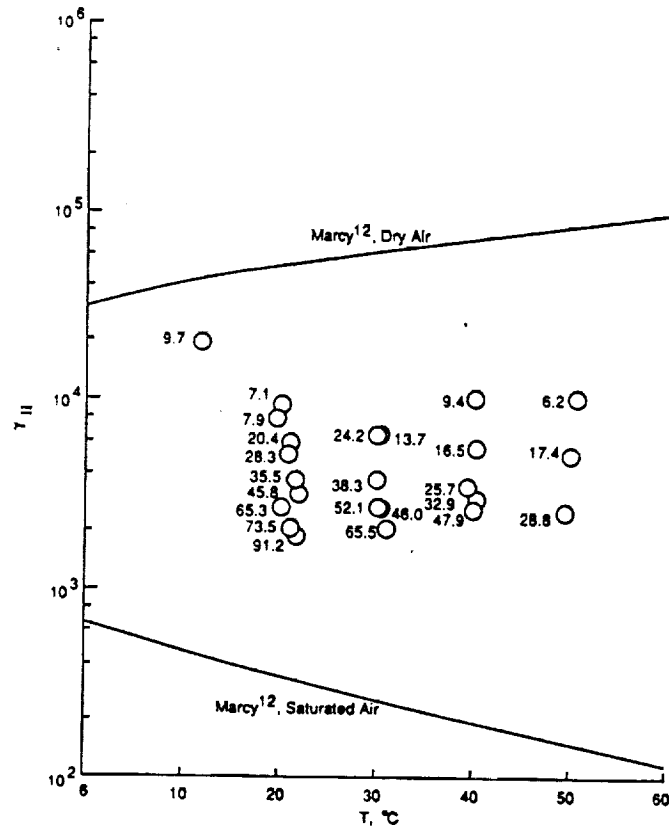
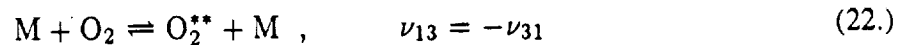
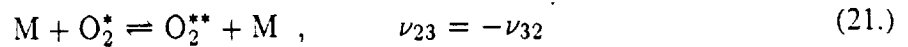
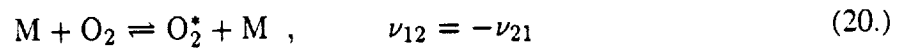


Figure 2 Variation of non-dimensional second coefficient of viscosity with temperature and relative humidity

When the more subtle frequency limitations indicated in Table I, are included, it should be recognized that both the simple time independent continuum model and the implied (from Eq. (12)) value of bulk viscosity cease to represent the flow physics fully for a variety of unsteady flow conditions. When flow events occur in air with characteristics times on the order of milliseconds, molecular relaxation effects must be included directly in the flow model. A brief discussion of how relaxation effects can be included follows.

Thermodynamic Considerations

The data discussed thus far suggest that non-equilibrium processes occur during acoustic excitations above a few hundred hz in ambient air. Acousticians are concerned primarily with higher frequencies and must model relaxation processes directly. Here, non-equilibrium is assumed to mean a process which occurs so rapidly that individual molecules do not have time to re-establish equilibrium energy distributions over the length scales associated with the process. Relying on irreversible thermodynamics, Bauer⁸ formulated a dynamic equation of state which includes relaxation effects. For the purposes of this discussion, suppose we consider a molecule like oxygen which can exist in a rotationally excited state -- say O_2^* -- and a vibrationally excited state -- O_2^{**} . Then, the following "excitation reactions" are possible due to collisions:



where M represents any colliding molecule, and the ν_{ij} will be used to designate the degree to which each of the oxygen reactions proceeds. Obviously, excitation reactions with other molecules are also possible (see Bass et al.¹¹). Furthermore, when significant populations of excited molecules are present, thermodynamic temperature ceases to be a unique quantity. In order to develop an appropriate model for high frequency acoustic waves, shock waves or other flows where bulk viscous effects are important, the second law of thermodynamics must be employed. That development has been discussed thoroughly by deGroot and Mazur¹⁰. They showed that the rate of entropy production, Γ , is given by:

$$\Gamma = q_i \frac{\partial}{\partial x_i} \left(\frac{1}{T} \right) - \frac{1}{T} \sum_{K=1}^N J_{K_i} \left[T \frac{\partial}{\partial x_i} \left(\frac{\mu_K}{T} \right) - F_{K_i} \right] - \frac{1}{T} \sigma_{ij} \frac{\partial u_i}{\partial x_j} - \frac{1}{T} \sum_{I=1}^M R_I A_I \quad (23.)$$

where \vec{q} is the heat flux vector, \vec{J}_K is the diffusion flux of the Kth species, given by:

$$\vec{J}_K = \rho_K (\vec{u}_K - \vec{u}), \quad (24.)$$

μ_K is the thermodynamic or chemical potential of the Kth species (out of N total species), \vec{F}_K is the body force acting on the Kth species, σ_{ij} is given by Eq. (1.), R_I is the reaction rate (in mass production rate per unit volume) of the Ith species, out of M possible reactions, and the chemical affinity, A_I , is defined by

$$A_I \equiv \sum_{K=1}^N \nu_{KI} \mu_K \quad (25.)$$

where the ν_{IJ} are the degrees of reaction (indicated in Eqs. (20)–(22)). Capital letter subscripts do not employ the Einstein summation convention.

If attention is focused on a single reaction - - say Eq. (20.) - - in a multi-component system, and viscous effects are ignored, it is possible to develop a dynamic energy equation model which incorporates relaxation effects. Under the single reaction, no viscous effects assumptions, $R_I = r$ and all other R_I are ignored. Furthermore,

$$A \equiv A_I = \sum_{k=1}^N \nu_{kI} \mu_k \quad (26.)$$

Eq. (23) simplifies to:

$$\Gamma = -\frac{rA}{T} \quad (27.)$$

with

$$\rho \frac{\partial C_I}{\partial t} = \nu_{I1} r, \quad (28.)$$

where

$$C_I = \rho_I / \rho \quad \text{and} \quad \rho = \sum_{I=1}^N \rho_I. \quad (29.)$$

Now the ν_{I1} are the degrees of reaction from species "I" to "1" and are positive if "1" is a product and negative if it is a reactant. It is assumed that the ν_{I1} are normalized with respect to the molecular weight of I (M_I) such that

$$\sum_{I=1}^q \nu_{I1} = -1, \quad \sum_{I=q+1}^N \nu_{I1} = 1, \quad \text{and} \quad \sum_{I=1}^N \nu_{I1} = 0, \quad (30.)$$

where the ν_{I1} are arranged so that reactants are indicated for $I \leq q$ and products for $I > q$.

From Equation (28.)

$$r = \frac{\rho}{\nu_{I1}} \frac{\partial C_I}{\partial t}, \quad I = 1, 2, \dots, N,$$

we can define a new variable, ζ , by

$$\frac{1}{\nu_{I1}} \frac{\partial C_I}{\partial t} \equiv \frac{\partial \zeta}{\partial t} = \frac{r}{\rho}, \quad (31.)$$

and integration yields

$$\zeta(t) = \frac{C_I(t) - C_I(0)}{\nu_{I1}}. \quad (32.)$$

We see that for any known C_I , all other $C_I(t)$ are known when the initial distributions of $C_I(0)$ are known. Also, we note that any null value for a ν_{J1} results in a requirement that $C_J(t) = C_J(0)$. Since $C_J \leq 1$ for all t , from the definition Eq. (36.),

$$\begin{aligned} \frac{1 - C_I(0)}{\nu_{I1}} \leq \zeta \leq -\frac{C_I(0)}{\nu_{I1}} & \quad 1 \leq I \leq q \\ \text{and} & \\ -\frac{C_I(0)}{\nu_{I1}} \leq \zeta \leq \frac{1 - C_I(0)}{\nu_{I1}} & \quad q < I \leq N \end{aligned} \quad (33.)$$

Now from Gibbs equation,

$$de = Tds - pdv + \sum_{I=1}^N \frac{\mu_I}{T} dC_I, \quad (34.)$$

where e is the specific internal energy, we can incorporate Eq.s (26), (29) and (31) and differentiate with respect to time to write:

$$\frac{Ds}{Dt} = \frac{1}{T} \frac{De}{Dt} + \frac{p}{T} \frac{Dv}{Dt} - \frac{A}{T} \frac{D\zeta}{Dt} \quad (35.)$$

Hence, from the exact differential properties of thermodynamic variables,

$$A = -T \left(\frac{\partial s}{\partial \zeta} \right)_{v, \dots} = \left(\frac{\partial e}{\partial \zeta} \right)_{s, v}, \quad (36.)$$

$$= \left(\frac{\partial h}{\partial \zeta} \right)_{s,p} = \left(\frac{\partial a}{\partial \zeta} \right)_{v,T} = \left(\frac{\partial g}{\partial \zeta} \right)_{p,T} \quad (37.)$$

using Maxwell relations, where h is enthalpy, a is Helmholtz free energy and g is Gibbs free energy. It is also noted that $A=0$ at equilibrium.

From elementary thermodynamics, an equilibrium can be determined for any gas mixture at a prescribed state. Let ζ^{eq} be the equilibrium value for ζ corresponding to any pair of independent thermodynamic variables. If we assume that the system is perturbed away from equilibrium and that it returns to equilibrium via a constant density (specific volume) and entropy process, we can write:

$$A \approx \left(\frac{\partial A}{\partial \zeta} \right)_{v,s}^{\text{eq}} \Delta \zeta = \left(\frac{\partial^2 e}{\partial \zeta^2} \right)_{s,v}^{\text{eq}} \Delta \zeta \quad (38.)$$

where $\Delta \zeta = \zeta - \zeta^{\text{eq}}$. Hence, from Eq. (31)

$$\frac{r}{\rho} = \frac{\partial \zeta}{\partial t} \quad (39.)$$

and deGroot and Mazur¹⁰ (p 34) have shown that

$$r = - \sum_{J=1}^M l_{1J} A_J / T \equiv - \frac{lA}{T} = \frac{l}{T} \left(\frac{\partial^2 e}{\partial \zeta^2} \right)_{s,v}^{\text{eq}} \quad (40.)$$

for a constant volume (or temperature) process. As a consequence,

$$\frac{\partial \zeta}{\partial t} = - \frac{l}{\rho T} \left(\frac{\partial^2 e}{\partial \zeta^2} \right)_{s,v}^{\text{eq}} \Delta \zeta \quad (41.)$$

or defining

$$\tau_{s,v} \equiv \frac{\rho T}{l \left(\frac{\partial^2 e}{\partial \zeta^2} \right)_{s,v}^{\text{eq}}} \quad (42.)$$

we have

$$\Delta \zeta = \Delta \zeta(0) e^{-t/\tau_{s,v}} \quad (43.)$$

This is an expression for the relaxation time required to re-equilibrate a fluid undergoing a single excitation reaction which is not too far from equilibrium.

Bauer⁸ has shown that the relaxation times of the type displayed in Eq. (42) can be incorporated in a dynamic equation of state. If it is assumed that $z = z(x,y)$ where z is the dependent thermodynamic variable ($e, h, s, g, \text{etc.}$) and x and y are the independent state variables ($x = v$ or $-p, y = s$ or T) and subscripts o are used to indicate equilibrium states,

$$\begin{aligned} \left[1 + \tau_{xy} \frac{D}{Dt}\right] (z - z_o) = & \left[\left(\frac{\partial z}{\partial x}\right)_{A,y} + \left(\frac{\partial z}{\partial x}\right)_{\zeta,y} \tau_{xy} \frac{D}{Dt} \right] (x - x_o) \\ & + \left[\left(\frac{\partial z}{\partial y}\right)_{A,x} + \left(\frac{\partial z}{\partial y}\right)_{\zeta,x} \tau_{xy} \frac{D}{Dt} \right] (y - y_o) \end{aligned} \quad (44.)$$

Further simplifications can be made for acoustic waves, but they do not apply to shock waves or vortices.

Relaxation time constant measurements which could be used in a dynamic equation of state like Eq. (44) are limited. Bauer and Roesler⁷ measured relaxation constants for mixtures of nitrogen and oxygen at 300 K. Their measurements showed that the internal temperature, T_i , relaxed toward its equilibrium temperature, T_{i0} ($=T$), for an isothermal, constant pressure process according to:

$$T_i(t) - T_{i0} = [T_i(0) - T_{i0}] e^{-\frac{C_p^o}{C_p^\infty \tau^o} t} \quad (45.)$$

where C_p^o is the steady-state, constant-pressure specific heat and C_p^∞ is the instantaneous, infinite frequency limit, specific heat. For a mixture of 21 percent oxygen and 79 percent nitrogen, their measurements suggest that the isothermal response constant was $\tau^o = 0.032$ s.

Adiabatic relaxation processes are of more interest than isothermal processes because an external energy source is not generally available to maintain isothermal conditions. In that case (see Kneser⁹):

$$C_p^\infty \frac{DT_i}{Dt} = -\frac{1}{\tau^o} \left[C_p^o (T_i - T_{i0}) - RT \left(1 - \frac{p_o}{p} \right) \right] \quad (46.)$$

where the constant pressure specific heats, C_p^∞ and C_p^o correspond to the instantaneous (infinite frequency) and steady-state (zero frequency) specific heats, respectively. Furthermore, if attention is restricted to an isentropic process, we can write⁹:

$$\left[1 + \tau_{ps} \frac{D}{Dt}\right] (\rho - \rho_o) = \left[\left(\frac{\partial \rho}{\partial p}\right)_{As} + \tau_{ps} \left(\frac{\partial \rho}{\partial p}\right)_{\zeta_s} \frac{D}{Dt} \right] (p - p_o) \quad (47.)$$

where

$$\tau_{ps} = C_p^\infty \tau^o / C_p^o \quad (48.)$$

Acousticians identify the two density derivatives as equilibrium and infinite frequency sonic speed quantities, where

$$\left(\frac{\partial \rho}{\partial p} \right)_{A,s} \equiv 1/c_o^2 \quad \text{and} \quad \left(\frac{\partial \rho}{\partial p} \right)_{\zeta,s} \equiv 1/\bar{c}^2 \quad (49.)$$

and recognizing that $p-p_o$ is the sound pressure, \tilde{p} , along with incorporating Eq. (6) in Eq. (47), they write:

$$- \left[1 + \tau_{ps} \frac{D}{Dt} \right] \rho_o \frac{\partial \xi}{\partial x} = \left[\frac{1}{c_o^2} + \frac{\tau_{ps}}{\bar{c}^2} \frac{D}{Dt} \right] \tilde{p} \quad (50.)$$

They consider the linearized form of Eq. (50), along with the inviscid momentum equation ($\nu=0$ in Eq. (8)) to be a complete set. Hence, they assume relaxation effects are controlling and neglect bulk viscous effects in the conservation of momentum equation.

Conclusions

The analysis presented here supports the contention that molecular relaxation processes occurring in air result in bulk viscous effects which invalidate Stokes' hypothesis. Viscous dilatational stresses become important in compressible flows and can easily exceed viscous shear stresses in flows with significant streamwise velocity gradients. Due to the strong influence of moisture content on bulk viscosity, great care is required in comparing theoretical predictions with experiment.

This work has shown that a serious concern to the aeronautics community should be the limited range of compressible flow conditions over which time independent equations of state can be employed. The influence of dilatational effects on pressure, along with the slow vibrational relaxation rate for oxygen and nitrogen molecules in air, must be accounted for in dynamic energy and momentum equation formulations.

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