2006

Variational Approach to the Volume Viscosity of Fluids

Allan J. Zuckerwar

Robert L. Ash
Old Dominion University, rash@odu.edu

Repository Citation

Original Publication Citation

Variational approach to the volume viscosity of fluids

Allan J. Zuckerwar[a)]
NASA Langley Research Center, Mail Stop 238, Hampton, Virginia 23681

Robert L. Ash[b)]
Old Dominion University, Department of Aerospace Engineering, Norfolk, Virginia 23508

The variational principle of Hamilton is applied to develop an analytical formulation to describe the volume viscosity in fluids. The procedure described here differs from those used in the past in that a dissipative process is represented by the chemical affinity and progress variable (sometimes called "order parameter") of a reacting species. These state variables appear in the variational integral in two places: first, in the expression for the internal energy, and second, in a subsidiary condition accounting for the conservation of the reacting species. As a result of the variational procedure, two dissipative terms appear in the Navier-Stokes equation. The first is the traditional volume viscosity term, proportional to the dilatational component of velocity; the second term is proportional to the material time derivative of the pressure gradient. Values of the respective volume viscosity coefficients are determined by applying the resulting volume-viscous Navier-Stokes equation to the case of acoustical propagation and then comparing expressions for the dispersion and absorption of sound. The formulation includes the special case of equilibration of the translational degrees of freedom. As examples, values are tabulated for dry and humid air, argon, and sea water.
© *2006 American Institute of Physics.* [DOI: 10.1063/1.2180780]

I. INTRODUCTION

The shear or dynamic viscosity of a fluid can be measured unambiguously in a variety of viscometric apparatuses. By imposing a specific velocity gradient across a fluid and measuring the forces required to maintain that gradient, the shear viscosity can be deduced directly. That is not the case for the volume viscosity. From the general form of isotropic fourth-rank tensors, the second-rank stress tensor, when related linearly to rates of strain (Newtonian fluid), includes a volumetric dilatation term that alters the normal stresses. The linear coefficient characterizing that effect is called the volume viscosity. (Various algebraic representations of the volume viscosity have been termed *bulk viscosity* and *second coefficient of* viscosity, as will be mentioned in the text.) However, because of the need to utilize thermodynamic pressure and associated equations of state, the volume viscosity appears in the constitutive equation for a Newtonian fluid, where it must either include or be added to the thermodynamic pressure.

Consequently, it is not possible to model simple fluids using only shear viscosity when large axial velocity gradients (compared with transverse velocity gradients) exist in the flow. That is the case for flows with shock waves and in the study of acoustics, where transverse velocity gradients can be missing altogether and frequency-dependent attenuation effects must be modeled. In the case of shock waves, the axial flow gradients are confined to very small spatial distances (on the order of a molecular mean free path) and can

be modeled numerically as discontinuities for many types of flow studies, thus eliminating the need for constitutive stress-strain rate coefficients. Strong shock waves in air and gases such as carbon dioxide and nitrogen result in significant departures from thermodynamic equilibrium, requiring separate models for the various molecular degrees of freedom and making it extremely difficult to separate volume-viscous effects from nonequilibrium thermodynamic effects. Frequency-dependent attenuation of sound using a continuum constitutive model (i.e., shear and volume viscosities) can result in frequency-dependent coefficients that violate the so-called *frame independence* or *material indifference* requirement,[1] where observers moving with different reference speeds would need to use different attenuation constants. It was this dilemma that caused George Gabriel Stokes in 1845 to assume that the second coefficient of viscosity constant was related linearly to the shear viscosity (the so-called "Stokes hypothesis," which will be introduced later), in order to exclude volume-viscous effects from his equations of motion. In order to develop our volume viscosity approach, we will need to review the basic continuum model in order to synchronize our notation and illuminate the approach.

In the absence of rotational viscosity,[2] the most general linear relationship between the second-order stress tensor σ_{ij} and the rate of strain tensor $\dot{\varepsilon}_{ij}$ for a simple, isotropic fluid is given by

$$\sigma_{ij} = [-P + \lambda \dot{\varepsilon}_{kk}]\delta_{ij} + 2\mu\dot{\varepsilon}_{ij}, \tag{1}$$

where δ_{ij} is called the *Kronecker delta* (with the value of unity when i and j are the same indices, and zero otherwise) using index notation and the Einstein summation convention

[a)]Electronic mail: a.j.zuckerwar@larc.nasa.gov
[b)]Author to whom correspondence should be addressed. Electronic mail: rash@odu.edu

(for repeated indices), and the rate of strain tensor is defined as

$$\dot{\varepsilon}_{ij} \equiv \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right),$$

where v_i represents the ith component of the velocity vector in an (x_1, x_2, x_3) Eulerian, Cartesian coordinate system, with the linear coefficients λ and μ, defined as the second coefficient of viscosity and the dynamic viscosity, respectively. In agreement with solid mechanics, the diagonal stress tensor components are considered to be positive in tension; thus, absolute pressure is a negative quantity.

Introductory fluid mechanics texts tabulate the dynamic or shear viscosity for common liquids and gases. In fact, the shear viscosity can be estimated for monatomic gases using the Boltzmann equation with a restricted set of distribution functions that are slightly perturbed from Maxwellian form. On the other hand, the second coefficient of viscosity or volume viscosity, does not enjoy the same clarity. Firstly, we note that when the fluid is in thermodynamic equilibrium, in the sense that an equation of state in the form $P = P(\rho, T)$ can be used to relate temperature, pressure, and density, the trace of the stress tensor σ_{kk} must be equal to three times the average normal stress, and thus should yield $-3P$ (because the trace of the Kronecker delta is 3), and we have the requirement that the average normal stress $\bar{\sigma}$, given by

$$\bar{\sigma} = \frac{\sigma_{kk}}{3} = \left[-P + \lambda \frac{\partial v_k}{\partial x_k} \right] + \frac{2}{3}\mu \frac{\partial v_k}{\partial x_k} = -P + \left(\lambda + \frac{2}{3}\mu \right) \frac{\partial v_k}{\partial x_k}.$$

Stokes (1845)[1] postulated that setting the second coefficient of viscosity λ equal to $-(2/3)\mu$ resulted in the desired relationship between pressure and average normal stress. However, it could be argued that (measured) pressure and average normal stress are equivalent only when the measurement is made in the absence of any volumetric dilatation ($\partial v_k / \partial x_k = 0$). This requirement is actually enforced when fluid pressure or fluid temperature is measured using a solid sensing element, since the no-slip boundary condition on any solid surface creates a "no volumetric dilatation" condition on that surface. On the other hand, when optical techniques are used to measure local temperatures and pressures in a flowing fluid, nontrivial volumetric dilatation conditions can exist. The departures of the second coefficient of viscosity from $-(2/3)\mu$ have been defined as the *volume viscosity* η_V, where

$$\eta_V \equiv \lambda + (2/3)\mu.$$

The volume-viscous contribution to the average normal stress is then

$$\bar{\sigma}_V = \eta_V \frac{\partial v_k}{\partial x_k}. \tag{2}$$

Part of the volume viscosity measurement difficulty resides in the fact that for nonrelativistic systems, conservation of mass requires that

$$\frac{\partial \rho}{\partial t} + v_j \frac{\partial \rho}{\partial x_j} + \rho \frac{\partial v_j}{\partial x_j} = 0,$$

or, recognizing that

$$\frac{\partial \rho}{\partial t} + v_j \frac{\partial \rho}{\partial x_j} \equiv \frac{D\rho}{Dt}, \tag{3}$$

where $D\rho/Dt$ represents the *material time derivative* of density, or the rate of change of density for an infinitesimal volume of fluid moving through a spatial location in an Eulerian coordinate system at a given instant. Hence, we see that

$$\dot{\varepsilon}_{jj} = \frac{\partial v_j}{\partial x_j} = -\frac{1}{\rho}\frac{D\rho}{Dt} = \frac{D(1/\rho)}{Dt}$$

and therefore, the general stress tensor relationship can actually be written

$$\sigma_{ij} = -\left[P + \left(\eta_V - \frac{2}{3}\mu \right) \frac{1}{\rho}\frac{D\rho}{Dt} \right]\delta_{ij} + \mu\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right).$$

If one is interested primarily in fluid systems that have relatively small variations in temperature, one can assume that the volume viscosity η_V and dynamic viscosity μ are constants throughout the volume.

II. DISSIPATION OF MECHANICAL ENERGY IN FLUIDS

There are four recognized classes of processes by which nonrandom mechanical energy can be dissipated as random energy (heat) in matter: viscous, relaxation, resonance, and hysteretic.[3] The latter two have not been observed in simple fluids and will not be considered further, although hysteretic effects have been found in liquids in the glassy state.[4]

Viscous dissipation occurs in a fluid subjected to a shear stress. The relationship between the shear stress and the transverse velocity gradient is found from Eq. (1) for the case $i \neq j$. The process represented by Eq. (1) is characterized by a single constitutive constant μ, the absolute or dynamic viscosity of the fluid. This constant can be determined by a wide variety of experiments, can be derived from fundamental physical laws (e.g., Boltzmann transport equation), and is well tabulated in handbooks as a function of temperature, pressure, and fluid composition.[5] Noteworthy is the fact that the shear viscosity is a transport property, rather than an equilibrium property of the fluid.

A relaxation process, on the other hand, is the response of a fluid to a dilatational disturbance. It can manifest itself as (1) a transport process or (2) an equilibrium process, the latter rendering the return of the disturbed state of the fluid toward equilibrium without molecular transport. The transport process, known as "translational relaxation" (classical heat conduction), involves the redistribution of excess kinetic energy among all the velocity components. This will be discussed in more detail below. The second process involves the transition of a molecule or molecules M_i from one equilibrium state to another, as described by a reaction:

$$\sum_i \nu_i M_i \leftrightarrows \sum_i \nu_i' M_i', \quad (i = 1, 2, \dots), \tag{4}$$

where ν_i and ν_i' are the stoichiometric coefficients of the reactants M_i and products M_i', respectively. For example, Eq. (4) may represent (1) the excitation of a vibrational, rotational, or electronic degree of freedom of a fluid molecule,

$$M_0 + M \leftrightarrows M_1 + M,$$

where M_0 and M_1 represent the molecule in the ground and first excited levels, respectively; (2) the association of a dimer from a pair of monomers, as occurs in nitrogen tetraoxide[6] or acetic acid[7]
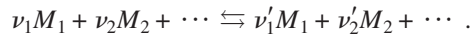
$$2M \leftrightarrows M_2,$$
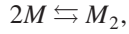
where M_2 represents the dimer; (3) the recombination of a pair of ions to form a neutral electrolyte,[8]

$$M^+ + N^- \leftrightarrows MN;$$
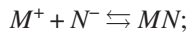
(4) the transition between two states of a rotational isomer like 1,1,2-trichloroethane,[9]

$$M \leftrightarrows M';$$
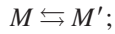
or (5) the redistribution of the populations of structural complexes in a liquid, like water,[10]

$$\nu_1 M_1 + \nu_2 M_2 + \cdots \leftrightarrows \nu_1' M_1 + \nu_2' M_2 + \cdots .$$

In equilibrium, the forward rate of Eq. (4) equals the backward rate, in which case the equilibrium concentrations of the reactants and products are determined by the law of mass action. In the event of a disturbance, the reaction proceeds to the right or to the left to strive toward a new equilibrium. The time delay between the excitation and response is the cause of mechanical dissipation in fluids.

The force that drives the reaction toward the new equilibrium is the affinity A, as defined by Gibbs. The affinity represents the reaction in all thermodynamic potential functions; for example

$$dU = TdS + \frac{P}{\rho^2} d\rho - A d\xi, \tag{5}$$

where U, T, S, ρ, P, and ξ are, respectively, the internal energy, temperature, entropy, molar density, pressure, and progress variable (sometimes called "ordering parameter") of the fluid. From Eq. (5), one finds

$$A = -\left(\frac{\partial U}{\partial \xi} \right)_{S, \rho}. \tag{6}$$

Upon the attainment of equilibrium, the affinity vanishes.

The progress variable, a measure of how far the reaction has proceeded toward the new equilibrium, is defined as follows:

$$d\xi = \frac{dn_i}{\Delta \nu_i}, \tag{7}$$

where n_i and ν_i are, respectively, the molar concentration and stoichiometric coefficient of the ith species of the fluid. The foundation of the theory of irreversible thermodynamics is based on the hypothesis:

$$\frac{d\xi}{dt} = LA, \tag{8}$$

where L is a constant and t is time. For small changes about equilibrium, the affinity A can be expanded as follows:

$$A = A(\xi, X, Y) = \left(\frac{\partial A}{\partial \xi} \right)_{X, Y} (\xi - \xi_0) + \left(\frac{\partial A}{\partial X} \right)_{\xi, Y} (X - X_0)$$
$$+ \left(\frac{\partial A}{\partial Y} \right)_{X, \xi} (Y - Y_0),$$

where X and Y are nonconjugate state variables, and subscript 0 refers to the value at equilibrium. A relaxation time can be then defined as

$$\frac{1}{\tau_{XY}} = -L \left(\frac{\partial A}{\partial \xi} \right)_{X, Y}, \tag{9}$$

which, when substituted into Eq. (8), leads to the familiar relaxation equation:

$$\frac{d\xi}{dt} = -\frac{\xi - \xi_0}{\tau_{XY}}.$$

Noteworthy is the fact that the relaxation time depends upon the relaxation path.

Meixner has demonstrated the generality of the formulation given by Eqs. (4)–(9), and has shown that it does not depend upon the molecular details of any specific processes.[11] It is the contention here that the processes governed by these equations are exhaustive. In other words, all known processes for the volume-dissipation of mechanical energy in fluids, with the exception of translational (classical) relaxation processes, are subject to and described by the physical laws outlined in the above equations.

For convenience, choose (P, S, ξ) to be the independent state variables. One may then write $A = A(P, S, \xi)$ In the remaining analysis, it will be assumed for simplicity that the applicable flows are adiabatic, for mixed flows (allowing heat conduction through the boundaries) depend upon the boundary conditions[12] and add a level of complexity that will obscure the physical principles leading to the derivation of the volume viscosity. The isobaric, isentropic relaxation time then becomes

$$\frac{1}{\tau_{PS}} = -L \left(\frac{\partial A}{\partial \xi} \right)_{P, S}, \tag{10}$$

and the isochoric (incompressible), isentropic relaxation time is given by

$$\frac{1}{\tau_{VS}} = -L \left(\frac{\partial A}{\partial \xi} \right)_{V, S} = -L \left[\left(\frac{\partial A}{\partial \xi} \right)_{P, S} + \left(\frac{\partial A}{\partial P} \right)_{\xi, S} \left(\frac{\partial P}{\partial \xi} \right)_{V, S} \right]$$
$$= -L \left[\left(\frac{\partial A}{\partial \xi} \right)_{P, S} - \left(\frac{\partial V}{\partial \xi} \right)_{P, S} \left(\frac{\partial P}{\partial \xi} \right)_{V, S} \right], \tag{11}$$

which uses the Maxwell relation

$$\left(\frac{\partial A}{\partial P} \right)_{\xi, S} = -\left(\frac{\partial V}{\partial \xi} \right)_{P, S}.$$

Now,

$$\left(\frac{\partial V}{\partial \xi}\right)_{P,S} = \Delta V \tag{12}$$

and

$$\left(\frac{\partial P}{\partial \xi}\right)_{V,S} = \Delta P \tag{13}$$

where ΔV and ΔP are the isentropic changes in volume and pressure per unit change of progress variable ξ. Equation (11) can then be written

$$\frac{1}{\tau_{VS}} = -L\left[\left(\frac{\partial A}{\partial \xi}\right)_{P,S} - (\Delta V)(\Delta P)\right] = \frac{1}{\tau_{PS}} + L(\Delta V)(\Delta P). \tag{14}$$

If the flow is incompressible ($\Delta V=0$) or isobaric ($\Delta P=0$), then $\tau_{PS}=\tau_{VS}$, and volume dissipation can be described by a single constitutive constant. In the general case of compressible flow with a pressure gradient, however, the two relaxation times are not equal, and volume dissipation accordingly requires two independent constitutive constants. This is the fallacy of relying on Eq. (2) alone to describe the volume dissipation in fluids.

The traditional expression for the volume viscosity [Eq. (2)] has led to much controversy and misunderstanding. Values for this constitutive property cannot be found in handbooks, because there are no accepted standards or even consensus for direct experimental measurement. The leading effort has been acoustic streaming, but as Nyborg[13] has shown, the results can be easily explained as conventional relaxation.

On the theoretical side, a variety of approaches have been undertaken. A partial list is reviewed here. The discussion is confined to a single dissipative process but can readily be extended to multiple processes. Tisza[14] applied the Navier-Stokes equation, containing the volume viscosity term, and continuity equation and compared the result to the known expression for acoustical dispersion. He was able to make the comparison in the limit to zero frequency and obtained the following for a gas with internal degrees of freedom:

$$\eta_V = (\gamma - 1)P\frac{C_i}{C_V^0}\tau, \tag{15}$$

where γ, P, C_i, C_V^0, and τ are the gas specific-heat ratio, pressure, molar specific heat of the relaxing degree of freedom, molar low-frequency specific heat at constant volume, and relaxation time, respectively. Later this expression was confirmed by Herzfeld and Litovitz,[15] Woods,[16] and Emanuel.[17]

DeGroot and Mazur[18] applied the method of irreversible thermodynamics and arrived at the following expression, which is a combination of their Eqs. (119) and (168):

$$\eta_V = P\frac{RC_i}{C_V^0 C_V^\infty}\tau, \tag{16}$$

in which C_V^∞ is the high-frequency specific heat at constant volume. Again, when applied to sound absorption, their derivation is valid only in the limit of zero frequency.

Wang Chang, Uhlenbeck, and de Boer[19] started with the Boltzmann transport equation for a gas with internal degrees of freedom and ultimately arrived at the following:

$$\eta_V = \frac{2}{3}P\frac{C_i}{C_V^0}\tau_\kappa, \tag{17}$$

in which the relaxation time τ_κ is related to the equilibration of the translational degrees of freedom. Their derivation is based on the erroneous supposition that the relaxation time τ_κ applies to both the translational and internal processes. The rigor of their development was lost when they, without justification, substituted the "relaxation time introduced in the theory of the dispersion of sound by Herzfeld and Rice" in place of τ_κ.

Hirshfelder, Curtiss, and Bird[20] also started with a "generalized Boltzmann equation," from which they claimed to have derived the following:

$$\eta_V = P\frac{RC_i}{(C_V^0)^2}\tau, \tag{18}$$

where R is the universal gas constant, but they do not show the derivation. Even though their derivation cannot be confirmed, their expression (18) actually agrees with Tisza's equation (15), but the authors do not mention any time-scale limitations.

Cowling and Chapman[21] applied the generalized Boltzmann equation to derive the traditional volume viscosity, but the solution contains an unknown indefinite integral, which they evaluated by comparison with an alternative derivation based on energy and continuity equations. In fact, they did not even need the Boltzmann equation at all. The result is

$$\eta_V = \frac{2(d-3)}{d^2}P\tau, \tag{19}$$

where d is the number of molecular degrees of freedom. For a diatomic molecule with frozen vibration, $d=5$, in which case Eq. (19) differs from (15) by a factor of $2/5$. Cowling and Chapman recognized that Eq. (19) was "valid only…when τ is small compared with the time scale of the expansion," and suggested a procedure for a derivation when the relaxation time is comparatively large; but they lacked the mathematical framework to cover the entire range of time scales. Further, their expression for the relaxation time does not conform to that of any known physical process.

Pierce[22] derived the volume viscosity from classical, phenomenological energy and continuity equations. For the special case of a rotational relaxation process (the only one treated), his derivation contains the quantity $\tau_c/\beta_{\rm rot}$, where τ_c is the mean free time and $\beta_{\rm rot}$ a constant. If $\beta_{\rm rot}$ is interpreted to be the reciprocal of the "collision number," that is, the number of collisions needed to effect a successful quantum transition, then his expression for the volume viscosity can be written as follows:

$$\eta_V = \left(\frac{U_{\text{rot}}}{U}\right)^2 P\tau, \tag{20}$$

where U_{rot} is the molecular rotational contribution to the total internal energy. For a diatomic molecule with frozen vibration, Eq. (20) agrees with (19) but not (15).

Recent treatments yield derivations by molecular-dynamics simulations based on fluctuation analysis. For example, Bertolini and Tari[23] find that when "k [wave number] goes to zero" the ratio of volume viscosity to shear viscosity is simply

$$\eta_V/\mu \approx 2/3. \tag{21}$$

These treatments represent a microscopic approach to the relaxation of the translational degrees of freedom. Interestingly, the macroscopic (phenomenological) approach yields a ratio[24]

$$\frac{\eta_V}{\mu} \approx \left(\frac{3}{4}\right)(\gamma - 1)\left(\frac{R}{C_V}\right)\left(\frac{1}{\text{Pr}}\right), \tag{22}$$

where C_V is the specific heat at constant volume and Pr the Prandtl number. With $\text{Pr} \approx 2/3$ for argon, the numerical value found for (22) is $\approx 1/2$, in fair agreement with that of (21).

The expressions (15)–(21) for the traditional volume viscosity are valid only in the limit of large time scales compared to the relaxation time, as pointed out by Cowling and Chapman, and in the special case of periodic (acoustical) flow do not yield the correct expressions for acoustical absorption and dispersion, even in the limit to zero frequency. There is no prior treatment that is valid over the entire range of time scales. The failure of these approaches to yield a comprehensive treatment of the volume dissipation in fluids illustrates the futility of attempts to describe a two-constant phenomenon with a single constitutive constant.

III. TRANSLATIONAL (CLASSICAL) DISSIPATION

A dilatational disturbance imparts an excess of translational energy to the constituent molecules of a fluid beyond its initial equilibrium value. The return to equilibrium leads to what is traditionally known as "heat conduction losses." The associated relaxation time τ_{hc} in terms of macroscopic properties is the following:[24]

$$\tau_{\text{hc}} = \frac{(\gamma - 1)\chi_T M}{\rho_0 a_0^2 C_P}, \tag{23}$$

where χ_T, M, ρ_0, a_0, and C_P are, respectively, the thermal conductivity, molar mass, ambient density, low-frequency speed of sound, and molar specific heat at constant pressure. For argon at 293.15 K, Eq. (23) yields a relaxation time of 1.3×10^{-10} s, suggesting that this loss will not be substantial except for extremely rapid excitation. It is important to note, however, that this loss occurs in all fluids, even in monatomic gases, and that it is erroneous to state that the volume viscosity coefficient in the latter is zero—a statement often found in the literature. For slow excitation, the heat conduction contribution to the losses will be small indeed, but not zero.

A uniaxial deformation, as generated by a piston stroke or an acoustical plane wave in a fluid, is composed of strongly coupled dilatational and shear deformations. The mathematically complex expression for the coupled dissipation can be approximated as a conventional relaxation, at time scales down to the translational relaxation time, by the method of Pade' approximants.[25] The relaxation strength is nearly, but not exactly, equal to unity, and there are two relaxation times—one much larger than the other. The larger relaxation time is that given by Eq. (23). When the shear contribution is included, then the translational relaxation time becomes

$$\tau_{\text{tr}} = \frac{1}{\rho_0 a_0^2}\left(\frac{4}{3}\mu + \frac{(\gamma - 1)\chi_T M}{C_P}\right), \tag{24}$$

as will be shown in Sec. V.

IV. THE VARIATION

Herivel[26] was able to deduce the equations of motion for an inviscid, incompressible fluid by way of Hamilton's principle. Serrin[27] showed subsequently, utilizing a particle identity constraint developed by Lin,[28] that the equations of motion could be evolved from Hamilton's principle for an inviscid, compressible fluid, without invoking an irrotationality restriction.

Here the Hamiltonian approach is extended to include molecular relaxation processes, using nonequilibrium thermodynamics formulations developed by Meixner[11] and later by deGroot and Mazur[18] and Woods.[29] Woods has discussed how the characteristic relaxation times of different types of processes can be modeled in the context of reversible and irreversible thermodynamics. We are interested particularly in differentiating between thermodynamic (translational) pressure relaxation, which can be modeled as a quasireversible phenomenological process, and dissipative volume viscous behavior that evolves naturally via the Newtonian fluid constitutive transport model. The resulting constraints on the variational problem are developed to allow molecular populations to depart from equilibrium.

If one restricts attention to a single degree of freedom (of nonequilibrium) for simplicity, it is possible to consider a uniform mixture of N molecular species where all of the species could contribute to the nonequilibrium state by way of the generalized chemical reaction (4). Hence, the dilatational fluctuations are controlled thermodynamically and we consider the limiting minimum entropy process where, to first order, $DS/Dt = 0$. Employing the Herivel methodology, and replacing Lin's particle identity constraint with Eq. (8), one can formulate a Lagrangian

$$\mathsf{L} \equiv \frac{1}{2}\rho v_k v_k - \rho(U + \Omega), \tag{25}$$

where Ω is the body force potential function, and a set of constraints.

Conservation of mass:

$$\frac{\mathrm{D}\rho}{\mathrm{D}t} + \rho\frac{\partial v_k}{\partial x_k} = 0. \tag{26}$$

Conservation of reacting species:

$$\frac{\mathrm{D}\xi}{\mathrm{D}t} - LA = 0. \tag{27}$$

Material entropy constraint:

$$\frac{\mathrm{D}S}{\mathrm{D}t} = 0. \tag{28}$$

Note that the conservation constraints are all written in terms of the material time derivative, as defined in Eq. (3), to allow for convective flows. An explanation for the constraint (28) is provided by Meixner[11] and by Herzfeld and Litovitz,[4] who point out that the entropy production is of "second order" (since the entropy at equilibrium is a maximum) and can be neglected for departures from equilibrium that are not too large.

Hamilton's principle can then be represented as

$$\delta\int_{t_0}^{t_1}\int\int\int_V\left[\frac{1}{2}\rho v_k v_k - \rho(U+\Omega) - \varphi\left(\frac{\mathrm{D}\rho}{\mathrm{D}t} + \rho\frac{\partial v_k}{\partial x_k}\right)\right.$$
$$\left. - \rho\alpha\left(\frac{\mathrm{D}\xi}{\mathrm{D}t} - LA\right) - \rho\beta\frac{\mathrm{D}S}{\mathrm{D}t}\right]\mathrm{d}V\mathrm{d}t = 0, \tag{29}$$

where φ, α, and β are Lagrange multipliers, V the volume, and the sign of φ has been changed to conform with the standard definition for the velocity potential function, as utilized by Serrin.[27] The independent variations of the velocity components, density, entropy, and equilibrium departure then yield

δv_k:

$$v_k = \frac{\partial\phi}{\partial x_k} + \beta\frac{\partial S}{\partial x_k} + \alpha\frac{\partial\xi}{\partial x_k}, \tag{30}$$

$\delta\rho$:

$$\frac{\mathrm{D}\phi}{\mathrm{D}t} = \frac{1}{2}v_k v_k - (U+\Omega) - \frac{P}{\rho}, \tag{31}$$

δS:

$$\frac{\mathrm{D}\beta}{\mathrm{D}t} = T, \tag{32}$$

$\delta\xi$:

$$\frac{\mathrm{D}\alpha}{\mathrm{D}t} = -A, \tag{33}$$

where the Gibbs relation (5) has been utilized to evaluate the various partial derivatives of the internal energy:

$$\left(\frac{\partial U}{\partial\xi}\right)_{\rho,S} = -A,$$

$$\left(\frac{\partial U}{\partial\rho}\right)_{\xi,S} = \frac{P}{\rho^2},$$

$$\left(\frac{\partial U}{\partial S}\right)_{\rho,\xi} = T.$$

From (31), one can write

$$\frac{\partial\phi}{\partial t} + v_k\left(\frac{\partial\phi}{\partial x_k} - v_k\right) = -\frac{1}{2}v_k v_k - (U+\Omega) - \frac{P}{\rho}.$$

Upon substituting (30) and differentiating with respect to x_i, one obtains

$$\frac{\partial}{\partial t}\left(\frac{\partial\phi}{\partial x_i}\right) + \frac{\partial}{\partial x_i}\left(-\beta\frac{\partial S}{\partial x_k} - \alpha\frac{\partial\xi}{\partial x_k}\right)v_k = -\frac{\partial}{\partial x_i}\left(\frac{v_k v_k}{2}\right)$$
$$- \frac{\partial}{\partial x_i}(U+\Omega) - \frac{\partial}{\partial x_i}\left(\frac{P}{\rho}\right). \tag{34}$$

Now,

$$\frac{\partial}{\partial x_i}\left(\frac{v_k v_k}{2}\right) = v_k\frac{\partial v_i}{\partial x_k} + \varepsilon_{ijk}v_j\left(\varepsilon_{kmn}\frac{\partial v_n}{\partial x_m}\right)$$

and

$$\varepsilon_{kmn}\frac{\partial v_n}{\partial x_m} = \varepsilon_{kmn}\left[\frac{\partial^2\phi}{\partial x_m\partial x_n} + \frac{\partial}{\partial x_m}\left(\beta\frac{\partial S}{\partial x_n}\right) + \frac{\partial}{\partial x_m}\left(\alpha\frac{\partial\xi}{\partial x_n}\right)\right], \tag{35}$$

where ε_{ijk} is the familiar alternating tensor, obeying the identity

$$\varepsilon_{ijk}\varepsilon_{kmn} = \varepsilon_{ijk}\varepsilon_{mnk} = \delta_{im}\delta_{jn} - \delta_{in}\delta_{jm},$$

leaving

$$\frac{\partial}{\partial x_i}\left(\frac{v_k v_k}{2}\right) = v_k\frac{\partial v_i}{\partial x_k} + (\delta_{jm}\delta_{kn} - \delta_{jn}\delta_{km})\left[v_j\frac{\partial}{\partial x_m}\left(\beta\frac{\partial S}{\partial x_m}\right)\right.$$
$$\left. + v_j\frac{\partial}{\partial x_m}\left(\alpha\frac{\partial\xi}{\partial x_m}\right)\right] = v_k\frac{\partial v_i}{\partial x_k} + v_j\frac{\partial}{\partial x_i}\left(\beta\frac{\partial S}{\partial x_j}\right.$$
$$\left. + \alpha\frac{\partial\xi}{\partial x_j}\right) - v_j\frac{\partial}{\partial x_j}\left(\beta\frac{\partial S}{\partial x_i} + \alpha\frac{\partial\xi}{\partial x_i}\right),$$

since the first term on the right-hand side of (35) vanishes identically.

Consequently, one can write (34) as

$$\frac{\partial}{\partial t}\left(\frac{\partial\phi}{\partial x_i}\right) - \frac{\partial v_k}{\partial x_i}\left(\beta\frac{\partial S}{\partial x_k} + \alpha\frac{\partial\xi}{\partial x_k}\right) - v_k\frac{\partial}{\partial x_i}\left(\beta\frac{\partial S}{\partial x_k} + \alpha\frac{\partial\xi}{\partial x_k}\right)$$
$$= -v_k\frac{\partial v_i}{\partial x_k} + v_k\frac{\partial}{\partial x_k}\left(\beta\frac{\partial S}{\partial x_i} + \alpha\frac{\partial\xi}{\partial x_i}\right) - v_k\frac{\partial}{\partial x_i}\left(\beta\frac{\partial S}{\partial x_k} + \alpha\frac{\partial\xi}{\partial x_k}\right)$$
$$= -\frac{\partial U}{\partial x_i} - \frac{\partial\Omega}{\partial x_i} + \frac{P}{\rho^2}\frac{\partial\rho}{\partial x_i} - \frac{1}{\rho}\frac{\partial P}{\partial x_i}. \tag{36}$$

In addition, from (30) one can rewrite

$$\frac{\partial}{\partial t}\left(\frac{\partial\phi}{\partial x_i}\right) = \frac{\partial v_i}{\partial t} - \frac{\partial}{\partial t}\left(\beta\frac{\partial S}{\partial x_i} + \alpha\frac{\partial\xi}{\partial x_i}\right),$$

so that (36) becomes

$$\frac{Dv_i}{Dt} - \frac{D}{Dt}\left(\beta\frac{\partial S}{\partial x_i} + \alpha\frac{\partial \xi}{\partial x_i}\right) - \frac{\partial v_k}{\partial x_i}\left(\beta\frac{\partial S}{\partial x_k} + \alpha\frac{\partial \xi}{\partial x_k}\right) = -\frac{\partial U}{\partial x_i}$$

$$-\frac{\partial \Omega}{\partial x_i} + \frac{P}{\rho^2}\frac{\partial \rho}{\partial x_i} - \frac{1}{\rho}\frac{\partial P}{\partial x_i}.$$

Now,

$$\frac{D}{Dt}\left(\beta\frac{\partial S}{\partial x_i}\right) + \frac{\partial v_k}{\partial x_i}\beta\frac{\partial S}{\partial x_k} = \beta\frac{D}{Dt}\left(\frac{\partial S}{\partial x_i}\right) + \frac{\partial S}{\partial x_i}\frac{D\beta}{Dt} + \frac{\partial v_k}{\partial x_i}\beta\frac{\partial S}{\partial x_k}$$

$$= T\frac{\partial S}{\partial x_i} + \beta\left[\frac{\partial}{\partial x_i}\left(\frac{\partial S}{\partial t} + v_k\frac{\partial S}{\partial x_k}\right)\right.$$

$$\left. - \frac{\partial v_k}{\partial x_i}\frac{\partial S}{\partial x_k}\right] + \beta\frac{\partial v_k}{\partial x_i}\frac{\partial S}{\partial x_k} = T\frac{\partial S}{\partial x_i}$$

$$+ \beta\frac{\partial}{\partial x_i}\left(\frac{DS}{Dt}\right) \tag{37}$$

and

$$\frac{D}{Dt}\left(\alpha\frac{\partial \xi}{\partial x_i}\right) + \frac{\partial v_k}{\partial x_i}\alpha\frac{\partial \xi}{\partial x_k} = \alpha\frac{D}{Dt}\left(\frac{\partial \xi}{\partial x_i}\right) + \frac{\partial \xi}{\partial x_i}\frac{D\alpha}{Dt} + \frac{\partial v_k}{\partial x_i}\alpha\frac{\partial \xi}{\partial x_k}$$

$$= A\frac{\partial \xi}{\partial x_i} + \alpha\left[\frac{\partial}{\partial x_i}\left(\frac{\partial \xi}{\partial t} + v_k\frac{\partial \xi}{\partial x_k}\right)\right.$$

$$\left. - \frac{\partial v_k}{\partial x_i}\frac{\partial \xi}{\partial x_k}\right] + \alpha\frac{\partial v_k}{\partial x_i}\frac{\partial \xi}{\partial x_k} = A\frac{\partial \xi}{\partial x_i}$$

$$+ \alpha\frac{\partial}{\partial x_i}\left(\frac{D\xi}{Dt}\right). \tag{38}$$

Collecting expressions, one has

$$\frac{Dv_i}{Dt} - T\frac{\partial S}{\partial x_i} - A\frac{\partial \xi}{\partial x_i} - \beta\frac{\partial}{\partial x_i}\left(\frac{DS}{Dt}\right) - \alpha\frac{\partial}{\partial x_i}\left(\frac{D\xi}{Dt}\right) = -\frac{\partial U}{\partial x_i} - \frac{\partial \Omega}{\partial x_i}$$

$$+ \frac{P}{\rho^2}\frac{\partial \rho}{\partial x_i} - \frac{1}{\rho}\frac{\partial P}{\partial x_i}. \tag{39}$$

When Eqs. (5) and (28) are inserted into (39), one finds

$$\frac{Dv_i}{Dt} = -\frac{\partial \Omega}{\partial x_i} - \frac{1}{\rho}\frac{\partial P}{\partial x_i} + \alpha\frac{\partial}{\partial x_i}\left(\frac{D\xi}{Dt}\right),$$

or in vector notation

$$\frac{D\boldsymbol{v}}{Dt} = -\nabla\Omega - \frac{1}{\rho}\nabla P + \alpha\nabla\left(\frac{D\xi}{Dt}\right). \tag{40}$$

It is more useful to express the equation of motion in terms of ρ and P rather than ξ. One proceeds by expanding the molar density $\rho(\xi, P, S)$ about its equilibrium point:

$$\rho - \rho_0 = \left(\frac{\partial \rho}{\partial \xi}\right)_{P,S}(\xi - \xi_0) + \left(\frac{\partial \rho}{\partial P}\right)_{\xi,S}(P - P_0)$$

$$+ \left(\frac{\partial \rho}{\partial S}\right)_{P,\xi}(S - S_0). \tag{41}$$

In equilibrium $(S = S_0)$ is an extremum, in which case first derivatives are zero and to first order the contribution can be dropped. It follows that

$$\frac{D\xi}{Dt} = \frac{-\rho\left[\nabla \cdot \boldsymbol{v} + \kappa_S^\infty\frac{DP}{Dt}\right]}{\left(\frac{\partial \rho}{\partial \xi}\right)_{P,S}},$$

where the high-frequency adiabatic compressibility

$$\kappa_S^\infty = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_{\xi,S}$$

and continuity relationship (26)

$$\frac{D\rho}{Dt} = -\rho\nabla \cdot \boldsymbol{v}$$

were substituted into Eq. (41). Equation (40) then becomes

$$\rho\frac{D\boldsymbol{v}}{Dt} = -\rho\nabla\Omega - \nabla P - \alpha\rho\nabla\left[\nabla \cdot \boldsymbol{v} + \kappa_S^\infty\frac{DP}{Dt}\right] \Big/ \left(\frac{\partial \rho}{\partial \xi}\right)_{P,S}. \tag{42}$$

As will be shown below, compatibility with the equations of acoustical propagation leads to the following expression for the coefficient in Eq. (42):

$$\frac{-\alpha\rho}{\left(\frac{\partial \rho}{\partial \xi}\right)_{P,S}} = \frac{\tau_{VS}}{\kappa_S^\infty} = \frac{\tau_{PS}}{\kappa_S^0} = \tau_{PS}\rho_0 a_0^2,$$

where κ_S^0 and a_0 are the low-frequency isentropic compressibility and the low-frequency sound speed, respectively. One finds

$$\rho\frac{D\boldsymbol{v}}{Dt} = -\rho\nabla\Omega - \nabla P + \nabla\left[\tau_{PS}\rho_0 a_0^2\nabla \cdot \boldsymbol{v} + \tau_{VS}\frac{DP}{Dt}\right].$$

The first term in the square brackets is the traditional volume viscosity term with

$$\eta_V = \tau_{PS}\rho_0 a_0^2, \tag{43}$$

and the second is the additional needed term, called here the "pressure relaxation" term, with

$$\eta_P = \tau_{VS}. \tag{44}$$

The Navier-Stokes equation, modified to include the pressure relaxation term, then reads as follows:

$$\rho\frac{D\boldsymbol{v}}{Dt} = -\nabla\left(1 - \eta_P\frac{D}{Dt}\right)P - \rho\nabla\Omega + \nabla\left[\left(\eta_V - \frac{2}{3}\mu\right)\nabla \cdot \boldsymbol{v}\right]$$

$$+ \nabla \times (\mu\nabla \times \mathbf{v}) + 2[\nabla \cdot (\mu\nabla)]\boldsymbol{v}. \tag{45}$$

If we neglect variations in the coefficients of viscosity and pressure relaxation, this equation can be written:

$$\rho\frac{D\boldsymbol{v}}{Dt} = -\nabla P + \eta_P\nabla\frac{DP}{Dt} - \rho\nabla\Omega + \left(\eta_V + \frac{4}{3}\mu\right)\nabla(\nabla \cdot \boldsymbol{v})$$

$$- \mu\nabla \times (\nabla \times \boldsymbol{v}). \tag{46}$$

A list of values of the volume viscosity coefficients η_P and η_V for selected fluids is given in Table I.

TABLE I. Values of the volume viscosity and $4/3 \times$ shear viscosity coefficients for selected fluids. RH =relative humidity. S=salinity in parts per thousand.

Fluid	η_P (μs)	η_V (Pa s)	$(4/3)\mu$ (Pa s)	Conditions	Relaxation process
Air,[a,b] 0% RH	6640	944	24.1×10^{-6}	$P=1$ atm	O_2 vibration
Air, 50% RH	4.47	0.635	24.0×10^{-6}	$T=293.15$ K	
Air, 100% RH	1.97	0.280	23.9×10^{-6}		
Argon[b,c]	-8×10^{-6}	22×10^{-6}	29.6×10^{-6}	$P=1$ atm	Translation
				$T=293.15$ K	
Sea water[b,d]	2.08	4739	1.840×10^{-3}	$P=1$ atm	$MgSO_4$ ionization
				$T=283.16$ K	
				$S=35$	

[a]See Ref. 32.
[b]For values of shear viscosity see Ref. 22 (air and sea water) and Ref. 33 (argon).
[c]See Ref. 24. This reference explains the negative value of η_P for argon and its physical consequences.
[d]See Ref. 34.

V. APPLICATION TO ACOUSTICAL WAVE PROPAGATION

The density and pressure for a small-signal, one-dimensional (plane) propagating wave are assumed to take the form

$$\begin{cases} \rho = \rho_0 + \rho_1 \exp i(\omega t - kx) \\ P = P_0 + P_1 \exp i(\omega t - kx) \end{cases}, \quad (47)$$

where ρ_0 and P_0 are the ambient density and pressure, respectively, and ρ_1 and P_1 acoustic amplitudes, k the (complex) wave number, and ω the angular frequency, with

$$\rho_1 \ll \rho_0, \quad P_1 \ll P_0.$$

In the absence of convection the material time derivative reduces to

$$\frac{\mathrm{D}}{\mathrm{D}t} = \frac{\partial}{\partial t}.$$

For molecular dissipative processes[4,11,30] it is assumed that in Eq. (46),

$$(4/3)\mu \ll \eta_V,$$

as is justified by comparison of the third and fourth columns of Table I. However, $(4/3)\mu$ must be added to η_V for translational processes, because the contributions of heat conduction and shear viscosity are comparable. In this case, Eq. (24) rather than Eq. (23) will be substituted into Eq. (43). The traditional Navier-Stokes equation (without the volume viscosity terms), together with the continuity equation (26) and the acoustical equation of state,[30,31] then lead to the following matrix equation:

$$\begin{bmatrix} \dfrac{\partial^2}{\partial t^2} & -\dfrac{\partial^2}{\partial x^2} \\[2mm] 1 + \tau_{PS}\dfrac{\partial}{\partial t} & -\dfrac{1}{a_0^2}\left(1 + \tau_{VS}\dfrac{\partial}{\partial t}\right) \end{bmatrix} \begin{bmatrix} \rho_1 \\ P_1 \end{bmatrix} = 0. \quad (48)$$

Upon substituting (47) into (48), one finds

$$\begin{bmatrix} -\omega^2 & k^2 \\[2mm] 1 + i\omega\tau_{PS} & -\dfrac{1}{a_0^2}(1 + i\omega\tau_{VS}) \end{bmatrix} \begin{bmatrix} \rho_1 \\ P_1 \end{bmatrix} = 0. \quad (49)$$

The resulting solution for the complex sound speed is

$$\frac{1}{a^2} = \frac{k^2}{\omega^2} = \frac{1}{a_0^2}\frac{1 + i\omega\tau_{VS}}{1 + i\omega\tau_{PS}}, \quad (50)$$

which yields the familiar expressions for sound dispersion and absorption.

If the Navier-Stokes equation includes the volume viscosity terms [Eq. (46)], then the resulting matrix must be equivalent to the square matrix in Eq. (48) in order to yield the solution (50). The equivalent matrix is easily found by application of the elementary column operations to Eq. (49):

$$a_0^2 i\omega\tau_{PS}C_2 + C_1 \to C_1$$

and then

$$(1 - i\omega\tau_{VS})C_2 \to C_2,$$

leading to

$$\begin{bmatrix} -\omega^2 + k^2 a_0^2 i\omega\tau_{PS} & k^2(1 - i\omega\tau_{VS}) \\[2mm] 1 + \omega^2\tau_{PS}\tau_{VS} & -\dfrac{1}{a_0^2}(1 + \omega^2\tau_{VS}^2) \end{bmatrix} \begin{bmatrix} \rho_1 \\ P_1 \end{bmatrix} = 0. \quad (51)$$

The top row is the Navier-Stokes equation containing the volume-viscous terms, and the bottom row is the corresponding dynamic equation of state. It is readily verified that Eq. (51) recovers the solution (50). The equation of state in the time domain is then

$$\left(1 - \tau_{PS}\tau_{VS}\frac{D^2}{Dt^2}\right)(\rho - \rho_0) = \frac{1}{a_0^2}\left(1 - \tau_{VS}^2\frac{D^2}{Dt^2}\right)(P - P_0).$$

$$(52)$$

It is noted that the equivalence operations remove the dissipative terms from the equation of state (52) and transfers them to the Navier-Stokes equation (46). The resulting dynamic equation of state (52) is valid for convective flows.

VI. CONCLUSIONS

The variational principle of Hamilton has been applied to derive expressions describing the volume-viscous dissipation in fluids. A dissipative process in a fluid that responds to a dilatational excitation is either a relaxation processes, or, in the case of translational relaxation, can be represented as such at time scales much larger than the translational relaxation time. A relaxation process is represented by the thermodynamic state variables ξ and A, the progress variable and affinity, respectively, in all the thermodynamic potential functions. These variables appear in the variational integral in two places: in the internal energy, and in a subsidiary constraint expressing the conservation of the participating reacting species. This feature was not included in past utilizations of the variational principle, which, although successful in deriving the traditional Navier-Stokes equation, could not account for the nonequilibrium processes occurring in a fluid. Consequently, the variational procedure as applied here introduces two terms into the Navier-Stokes equation: the traditional volume viscosity term and an independent second term, called here the pressure relaxation term, characterized by coefficients η_V and η_P, respectively. This result is consistent with the requirement that a volume-viscous process in a fluid must be represented by two independent constitutive constants.

When applied to acoustical propagation, the "modified" Navier-Stokes equation (including the volume viscosity terms) yields the known expressions for sound dispersion and absorption—another feature that has eluded past derivations of the volume viscosity. Thus, acoustical measurements serve as a leading source of data to evaluate the volume viscosity coefficients and their dependence upon ambient parameters, although other measurement methods (e.g., shock tube, impact tube, laser fluorescence, etc.) could serve the purpose as well.

Finally, it has been shown that the appearance of the volume-dissipative terms in the Navier-Stokes equation necessitates their removal from the dynamic equation of state. A simple matrix equivalence operation, designed to transfer the volume-dissipative terms from the dynamic equation of state to the Navier-Stokes equation, yields a new dynamic equation of state, which in the case of acoustical propagation allows for dispersion but not absorption of the propagating sound wave. The resulting dynamic equation of state is valid for convective as well as acoustical flows.

[1] C. Truesdall and R. A. Toupin, *The classical field theories*, in *Handbuch der Physik*, edited by S. Flugge (Springer Verlag, Berlin, 1960), Vol. III/1, pp. 226–793.

[2] L. C. Woods, *The Thermodynamics of Fluid Systems* (Clarendon, Oxford, 1975).

[3] H. G. van Bueren, *Imperfections in Crystals* (North-Holland, Amsterdam, 1960).

[4] K. F. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic, New York, 1959).

[5] J. O. Hirschfelder, C. F. Curtiss, and R. B. Byrd, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

[6] H. O. Kneser, "Molecular relaxation processes in gases," in *Physical Acoustics IIA*, edited by W. P. Mason (Academic, New York, 1965), p. 193.

[7] E. Freedman, "On the use of ultrasonic absorption for the determination of very rapid reaction rates at equilibrium: application to the liquid phase associate of carboxylic acids," J. Chem. Phys. **21**, 1784 (1953).

[8] M. Eigen and K. Tamm, "Sound absorption in electrolyte solutions due to chemical relaxation. I. Relaxation theory of multistage dissociation," Z. Elektrochem. **66**, 93 (1962).

[9] J. Lamb, "Ultrasonic relaxation due to rotational isomers," Z. Elektrochem. **64**, 136 (1960).

[10] A. Eucken, "The association of water," Z. Elektrochem. **52**, 255 (1948).

[11] J. Meixner, "Allgemeine Theorie der Schallabsorption in Gasen und Flussigkeiten unter Berucksichtigung der Transporterscheinungen," Acustica **2**, 101 (1952).

[12] G. B. Whitham, "The Navier-Stokes equations of motion," in *Laminar Boundary Layers*, edited by L. Rosenhead (Oxford at the Clarendon Press, Oxford, 1963), pp. 124–127.

[13] W. L. M. Nyborg, "Acoustic streaming," in *Physical Acoustics IIB*, edited by W. P. Mason (Academic, New York, 1965), pp. 265–339.

[14] L. Tisza, "Supersonic absorption and Stokes' viscosity relation," Phys. Rev. **61**, 531 (1942). The substitution $P = \rho_o a_o^2/\gamma$ was introduced into his Eq. (15) to obtain our Eq. (15).

[15] See Ref. 4, p. 159.

[16] See Ref. 2, p. 196.

[17] G. Emanuel, "Bulk viscosity of a dilute polyatomic gas," Phys. Fluids A **2**, 2252 (1990).

[18] S. R. deGroot and P. Mazur, "Viscous flow and relaxation phenomena," in *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962), Chap. 7, pp. 304–333. Explicit expressions for the adiabatic and isothermal compressibilities were introduced into their Eq. (168) to obtain our Eq. (16).

[19] C. S. Wang Chang, G. E. Uhlenbeck, and J. de Boer, "The heat conductivity and viscosity of polyatomic gases, Part C," in *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck (North-Holland, Amsterdam, 1964), pp. 241–268. The expression for the volume viscosity is their Eq. (72).

[20] See Ref. 5, p. 501. Molecular properties were converted to molar properties (related by Avogadro's number) in their Eq. (7.6-30) to obtain our Eq. (18).

[21] S. Chapman and T. G. Cowling, *The Mathematical Theory of Uniform Gases* (Cambridge University Press, Cambridge, U.K., 1970). The specific heats in their Eq. (12.5,1) were converted to molecular degrees of freedom to obtain our Eq. (19).

[22] A. D. Pierce, *Acoustics: An Introduction to Its Physical Principles and Applications* (Acoustical Society of America/American Institute of Physics, New York, 1989). The substitution $\tau_c/\beta_{rot} = \tau$ was introduced into his Eq. (10-7.10) to obtain our Eq. (20), where τ_c is the mean free time between collisions and β_{rot} the reciprocal rotational collision number.

[23] D. Bertolini and A. Tani, "On the generalized bulk viscosity behavior," J. Chem. Phys. **115**, 6285 (2001).

[24] A. J. Zuckerwar, "Phenomenological theory of the translational relaxation times in gases," J. Acoust. Soc. Am. **105**, 2210 (1999).

[25] *Handbook of Applicable Mathematics*, edited by R. F. Churchhouse (Wiley, New York, 1981), pp. 216–223.

[26] J. W. Herivel, "The derivation of the equations of motion of an ideal fluid by Hamilton's principle," Proc. Cambridge Philos. Soc. **51**, 344 (1955).

[27] J. Serrin, "Mathematical principles of classical fluid mechanics," in *Handbuch der Physik*, edited by S. Flugge (Springer-Verlag, Berlin, 1959), Vol VIII/1, pp. 144–150.

[28] C. C. Lin, "Hydrodynamics of helium II," *Proc. Int. School of Physics, Course XXI* (Academic, New York, 1963), pp. 93–146.

[29] L. C. Woods, *Thermodynamic Inequalities in Gases and Magnetoplasmas* (John Wiley and Sons, Chichester, 1996).

[30] H. J. Bauer, "Phenomenological theory of the relaxation phenomena in

gases," in *Physical Acoustics IIA*, edited by W. P. Mason (Academic, New York, 1965), pp. 47–131.

[31] See Ref. 4, p. 166.

[32] ANSI Standard S1.26-1995, "Method for calculation of the absorption of sound by the atmosphere" (Standards Secretariat of the Acoustical Society of America, New York, 1995).

[33] *Handbook of Chemistry and Physics*, 63rd ed., edited by D. R. Lide (CRC Press, Boca Raton, FL, 1983).

[34] F. H. Fisher and P. F. Worcester, "Essential oceanography," in *Encyclopedia of Acoustics*, edited by M. J. Crocker (Wiley Interscience, New York, 1997), Vol. I, p. 381.