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Variational Approach to the Volume Viscosity of Fluids

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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, 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, the most general linear relationship between the second-order stress tensor \( \sigma_{ij} \) and the rate of strain tensor \( \dot{e}_{ij} \) for a simple, isotropic fluid is given by

\[
\sigma_{ij} = [-P + \lambda \delta_{kk}] \delta_{ij} + 2\mu \dot{e}_{ij},
\]

where \( \delta_{ij} \) 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.
(for repeated indices), and the rate of strain tensor is defined as

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

where $v_i$ represents the $i$th component of the velocity vector in an $(x_1, x_2, x_3)$ Eulerian, Cartesian coordinate system, with the linear coefficients $\lambda$ and $\mu$, 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 $\sigma_{kk}$ 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

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

Stokes (1845) postulated that setting the second coefficient of viscosity $\lambda$ 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 ($\partial v_i / \partial x_k = 0$). 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 $\eta_v$, where

$$\eta_v = \lambda + \frac{(2/3)\mu}{\partial x_k}.$$

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

$$\bar{\sigma}_V = \eta_v \frac{\partial v_k}{\partial x_k}.$$

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

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

or, recognizing that

$$\frac{\partial P}{\partial t} + v_j \frac{\partial P}{\partial x_j} = \frac{DP}{Dt},$$

where $DP/DT$ 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

$$\dot{e}_{ij} = -\frac{1}{\rho} \frac{DP}{Dt} = \frac{\partial}{\partial x_k} \left[ \frac{1}{2} \mu \frac{\partial v_j}{\partial x_i} - \frac{2}{3} \lambda \frac{\partial v_k}{\partial x_i} \right].$$

If one is interested primarily in fluid systems that have relatively small variations in temperature, one can assume that the volume viscosity $\eta_v$ and dynamic viscosity $\mu$ 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. 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.

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

\[ M_0 + M \rightleftharpoons M_1 + M, \]

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 tetroxide or acetic acid; or (3) the recombination of a pair of ions to form a neutral electrolyte,

\[ M^+ + N^- \rightleftharpoons MN; \]

(4) the transition between two states of a rotational isomer like 1,1,2-trichloroethane, or (5) the redistribution of the populations of structural complexes in a liquid, like water,

\[ n_1M_1 + n_2M_2 + \cdots \rightleftharpoons n'_1M'_1 + n'_2M'_2 + \cdots . \]

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

\[
\frac{dU}{dS} = TdS + \frac{P}{\rho}d\rho - ADd\xi,
\]

where \( U, T, S, \rho, P, \) and \( \xi \) 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

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

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:

\[
d\xi = \frac{d\xi}{dt},
\]

where \( n_i \) and \( v_i \) are, respectively, the molar concentration and stoichiometric coefficient of the \( i \)th species of the fluid. The foundation of the theory of irreversible thermodynamics is based on the hypothesis:

\[
\frac{d\xi}{dt} = LA,
\]

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

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

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

\[
\frac{d\xi}{dt} = -\xi - \xi_0. \]

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. 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 \((P, S, \xi)\) 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 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

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

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

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

\[
= -L \left[ \left( \frac{\partial A}{\partial \xi} \right)_{P,S} - \left( \frac{\partial V}{\partial \xi} \right)_{P,S} \left( \frac{\partial P}{\partial \xi} \right)_{V,S} \right],
\]

which uses the Maxwell relation

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

Now,
where \(\Delta V\) and \(\Delta P\) are the isentropic changes in volume and pressure per unit change of progress variable \(\xi\). Equation (11) can then be written

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

(14)

If the flow is incompressible (\(\Delta V=0\)) or isobaric (\(\Delta P=0\)), then \(\tau_{Vs}=\tau_{Ps}\), 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\(^\text{13}\) 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\(^\text{14}\) 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:

\[
\eta_v = (\gamma - 1)P \frac{C_i}{C_V^0} \tau_v,
\]

(15)

where \(\gamma\), \(P\), \(C_i\), \(C_V^0\), and \(\tau\) 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,\(^\text{15}\) Woods,\(^\text{16}\) and Emanuel.\(^\text{17}\)

DeGroot and Mazur\(^\text{18}\) applied the method of irreversible thermodynamics and arrived at the following expression, which is a combination of their Eqs. (119) and (168):

\[
\eta_v = P \frac{RC_i}{C_V^0} \tau_v.
\]

(16)

in which \(C_V^\infty\) 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\(^\text{19}\) started with the Boltzmann transport equation for a gas with internal degrees of freedom and ultimately arrived at the following:

\[
\eta_v = \frac{2}{3} \frac{P C_i}{C_V^0} \tau_v.
\]

(17)

in which the relaxation time \(\tau_v\) is related to the equilibration of the translational degrees of freedom. Their derivation is based on the erroneous supposition that the relaxation time \(\tau_v\) 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 \(\tau_v\).

Hirshfelder, Curtiss, and Bird\(^\text{20}\) also started with a “generalized Boltzmann equation,” from which they claimed to have derived the following:

\[
\eta_v = \frac{P R C_i}{(C_V^0)^2} \tau,
\]

(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\(^\text{21}\) 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

\[
\eta_v = \frac{2(d - 3)}{d^2} P \tau,
\]

(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 \(\tau\) 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\(^\text{22}\) 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 \(\tau_v / \beta_{rot}\), where \(\tau_v\) is the mean free time and \(\beta_{rot}\) a constant. If \(\beta_{rot}\) 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:
\[ \eta_v = \left( \frac{U_{\text{rot}}}{U} \right)^2 \eta, \]  

where \( U_{\text{rot}} \) 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

\[ \eta_v/\mu \approx 2/3. \]  

These treatments represent a microscopic approach to the relaxation of the translational degrees of freedom. Interestingly, the macroscopic (phenomenological) approach yields a ratio\(^{24}\)

\[ \frac{\eta_v}{\mu} = \left( \frac{3}{4} \right) (y-1) \left( \frac{R}{C_v} \right) \left( \frac{1}{P_r} \right), \]  

where \( C_v \) is the specific heat at constant volume and \( P_r \) the Prandtl number. With \( P_r \approx 2/3 \) 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 \( \tau_{hc} \) in terms of macroscopic properties is the following:\(^{24}\)

\[ \tau_{hc} = \frac{(y-1)\chi_T M}{\rho_0 a_0 C_p}, \]  

where \( \chi_T, M, \rho_0, a_0, \) 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 \( 1.3 \times 10^{10} \) 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

\[ \tau_v = \frac{1}{P \rho a_0} \left( \frac{4}{3} \mu + \frac{(y-1)\chi_T M}{C_p} \right), \]  

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\(^{15}\) 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 quasiirreversible 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

\[ L = \frac{1}{2} \rho v_i v_i - \rho (U + \Omega), \]  

where \( \Omega \) is the body force potential function, and a set of constraints.

Conservation of mass:
\[
\frac{Dp}{Dt} + \rho \frac{\partial v_k}{\partial x_k} = 0. \tag{26}
\]

Conservation of reacting species:
\[
\frac{D\xi}{Dt} - LA = 0. \tag{27}
\]

Material entropy constraint:
\[
\frac{DS}{Dt} = 0. \tag{28}
\]

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\textsuperscript{11} and by Herzfeld and Litovitz\textsuperscript{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
\[
\delta \int_{t_0}^{t_1} \int \int \left[ \frac{1}{2} \rho v_i v_i - \rho (U + \Omega) - \phi \left( \frac{Dp}{Dt} + \rho \frac{\partial v}{\partial x} \right) \right] - \rho \alpha \left( \frac{D\xi}{Dt} - LA \right) - \rho \beta \frac{DS}{Dt} \, dV \, dt = 0, \tag{29}
\]

where \( \varphi, \alpha, \) and \( \beta \) are Lagrange multipliers, \( V \) the volume, and the sign of \( \varphi \) has been changed to conform with the standard definition for the velocity potential function, as utilized by Serrin.\textsuperscript{27} The independent variations of the velocity components, density, entropy, and equilibrium departure then yield

\( \delta v_k: \)
\[
v_k = \frac{\partial \varphi}{\partial x_k} + \beta \frac{\partial S}{\partial x_k} + \alpha \frac{\partial \xi}{\partial x_k}, \tag{30}
\]

\( \delta p: \)
\[
\frac{D\varphi}{Dt} = \frac{1}{2} v_k v_k - (U + \Omega) - \frac{P}{\rho}, \tag{31}
\]

\( \delta S: \)
\[
\frac{DS}{Dt} = T, \tag{32}
\]

\( \delta \xi: \)
\[
\frac{D\xi}{Dt} = -A, \tag{33}
\]

where the Gibbs relation (5) has been utilized to evaluate the various partial derivatives of the internal energy:
\[
\left( \frac{\partial U}{\partial \xi} \right)_{\rho, S} = -A,
\]
\[
\left( \frac{\partial U}{\partial \rho} \right)_{\xi, S} = \frac{P}{\rho^2},
\]

(34)

\[
\frac{\partial \varphi}{\partial x_i} + \frac{\partial S}{\partial x_i} + \frac{\partial \xi}{\partial x_i} = \frac{\partial U}{\partial x_i} = T.
\]

From (31), one can write
\[
\frac{\partial \varphi}{\partial x_i} + v_k \left( \frac{\partial \varphi}{\partial x_k} - v_k \right) = - \frac{1}{2} v_k v_k - (U + \Omega) - \frac{P}{\rho}, \tag{34}
\]

Upon substituting (30) and differentiating with respect to \( x_i \), one obtains
\[
\frac{\partial}{\partial x_i} \left( \frac{v_k v_k}{2} \right) = v_k \frac{\partial v}{\partial x_i} + \epsilon_{ijk} v_j \left( \epsilon_{kmn} \frac{\partial \xi}{\partial x_m} \right) \tag{35}
\]

and
\[
\epsilon_{kml} \frac{\partial v}{\partial x_m} \epsilon_{kmn} = \epsilon_{kml} \epsilon_{nmk} = \delta_{m} \delta_{jn} - \delta_{m} \delta_{jn},
\]

leaving
\[
\frac{\partial}{\partial x_i} \left( \frac{v_k v_k}{2} \right) = v_k \frac{\partial v}{\partial x_i} + \frac{\partial S}{\partial x_i} + \frac{\partial \xi}{\partial x_i} - v_k \frac{\partial v}{\partial x_i} + \frac{\partial S}{\partial x_i} + \frac{\partial \xi}{\partial x_i} \tag{37}
\]

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

Consequently, one can write (34) as
\[
\frac{\partial}{\partial t} \left( \frac{\partial \varphi}{\partial x_i} \right) - \frac{\partial v_k}{\partial x_k} \left( \frac{\partial S}{\partial x_k} + \frac{\partial \xi}{\partial x_k} \right) - v_k \frac{\partial v}{\partial x_i} + \frac{\partial S}{\partial x_i} + \frac{\partial \xi}{\partial x_i} \tag{36}
\]

In addition, from (30) one can rewrite
\[
\frac{\partial}{\partial t} \left( \frac{\partial \varphi}{\partial x_i} \right) = \frac{\partial v_k}{\partial t} \frac{\partial v}{\partial x_i} + \frac{\partial S}{\partial x_i} + \frac{\partial \xi}{\partial x_i},
\]

so that (36) becomes
\[
\frac{D\mathbf{v}}{Dt} - \frac{D}{Dr} \left( \frac{D\mathbf{v}}{Ds} + \alpha - \frac{\partial \xi}{\partial x_i} \right) - \frac{\partial v_i}{\partial x_i} \left( \frac{D\mathbf{v}}{Dx} + \alpha - \frac{\partial \xi}{\partial x_k} \right) = - \frac{\partial U}{\partial x_i} - \frac{\partial \Omega}{\partial x_i} + P \frac{\partial P}{\rho^2} - \frac{1}{\rho} \frac{\partial P}{\partial x_i}.
\]

Now,
\[
\frac{D}{Dr} \left( \frac{D\mathbf{v}}{Ds} + \alpha - \frac{\partial \xi}{\partial x_i} \right) - \frac{\partial v_i}{\partial x_i} \left( \frac{D\mathbf{v}}{Dx} + \alpha - \frac{\partial \xi}{\partial x_k} \right) = T \frac{\partial \mathbf{v}}{\partial t} + \beta \left( \frac{\partial \mathbf{v}}{\partial t} + D \xi \right) + \frac{\partial v_i \partial S}{\partial x_i \partial x_k} = T \frac{\partial \mathbf{v}}{\partial t} + \beta D \xi + \frac{\partial v_i \partial S}{\partial x_i \partial x_k},
\]
and
\[
\frac{D}{Dr} \left( \alpha \frac{\partial \xi}{\partial x_i} \right) + \frac{\partial v_i}{\partial x_i} \alpha \frac{\partial \xi}{\partial x_k} = \alpha \frac{D}{Dr} \left( \frac{\partial \xi}{\partial x_i} \right) + \frac{\partial v_i \partial \xi}{\partial x_i \partial x_k} + \frac{\partial v_i \partial \xi}{\partial x_i \partial x_k} = A \frac{\partial \xi}{\partial x_i} + \alpha \left( \frac{\partial \xi}{\partial t} + v_i \frac{\partial \xi}{\partial x_k} \right) + \frac{\partial v_i \partial \xi}{\partial x_i \partial x_k} + \alpha \left( \frac{\partial \xi}{\partial t} + v_i \frac{\partial \xi}{\partial x_k} \right) = A \frac{\partial \xi}{\partial x_i} + \alpha \left( \frac{\partial \xi}{\partial t} + v_i \frac{\partial \xi}{\partial x_k} \right) + \frac{\partial v_i \partial \xi}{\partial x_i \partial x_k} + \alpha \left( \frac{\partial \xi}{\partial t} + v_i \frac{\partial \xi}{\partial x_k} \right) = A \frac{\partial \xi}{\partial x_i}.
\]

Collecting expressions, one has
\[
\frac{D\mathbf{v}}{Dt} - T \frac{\partial \mathbf{v}}{\partial x} - A \frac{\partial \xi}{\partial x_i} - \beta \frac{\partial D \xi}{\partial t} - \alpha \frac{\partial D \xi}{\partial x_i} = - \frac{\partial U}{\partial x_i} - \frac{\partial \Omega}{\partial x_i} + P \frac{\partial P}{\rho^2} - \frac{1}{\rho} \frac{\partial P}{\partial x_i}.
\]

When Eqs. (5) and (28) are inserted into (39), one finds
\[
\frac{D\mathbf{v}}{Dt} = - \frac{\partial \Omega}{\partial x_i} - \frac{1}{\rho} \frac{\partial P}{\partial x_i} + \alpha \frac{\partial D \xi}{\partial x_i}.
\]

or in vector notation
\[
\frac{D\mathbf{v}}{Dt} = - \nabla \Omega - \frac{1}{\rho} \nabla P + \alpha \nabla \left( \frac{D \xi}{Dt} \right).
\]

It is more useful to express the equation of motion in terms of \(\rho\) and \(P\) rather than \(\xi\). One proceeds by expanding the molar density \(\rho(\xi, P, S)\) about its equilibrium point:
\[
\rho - \rho_0 = \left( \frac{\partial \rho}{\partial \xi} \right)_{PS} (\xi - \xi_0) + \left( \frac{\partial \rho}{\partial P} \right)_{ES} (P - \rho_0) + \left( \frac{\partial \rho}{\partial S} \right)_{P \xi} (S - S_0).
\]

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
\[
\frac{D\xi}{Dt} = - \rho \nabla \cdot \mathbf{v} + \kappa_S \frac{D \rho}{D \xi}.
\]

where the high-frequency adiabatic compressibility
\[
\kappa_S = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial \xi} \right)_{PS}
\]

and continuity relationship (26)
\[
\frac{D\rho}{Dt} = - \rho \nabla \cdot \mathbf{v}
\]

were substituted into Eq. (41). Equation (40) then becomes
\[
\rho \frac{D\mathbf{v}}{Dt} = - \rho \nabla \cdot \mathbf{v} - \alpha \nabla \left( \frac{D \xi}{Dt} \right) - \frac{1}{\rho} \nabla \left( \frac{D \rho}{D \xi} \right)_{P S}.
\]

As will be shown below, compatibility with the equations of acoustical propagation leads to the following expression for the coefficient in Eq. (42):
\[
- \frac{\alpha \rho}{\kappa_S} = \frac{\tau_{PS} \rho_{\xi}^2}{\kappa_S} = \frac{\tau_{PS} \rho_{\xi}^2}{\kappa_S} = \frac{\tau_{PS} \rho_{\xi}^2}{\kappa_S},
\]

where \(\kappa_S^0\) and \(\alpha_0\) are the low-frequency isentropic compressibility and the low-frequency sound speed, respectively. One finds
\[
\rho \frac{D\mathbf{v}}{Dt} = - \rho \nabla \cdot \mathbf{v} - \nabla \left( \frac{\tau_{PS} \rho_{\xi}^2}{\kappa_S} \nabla \cdot \mathbf{v} + \tau_{VS} \frac{D \rho}{D \xi} \right).
\]

The first term in the square brackets is the traditional volume viscosity term with
\[
\eta_v = \tau_{PS} \rho_{\xi}^2,
\]
and the second is the additional needed term, called here the “pressure relaxation” term, with
\[
\eta_p = \tau_{VS}.
\]

The Navier-Stokes equation, modified to include the pressure relaxation term, then reads as follows:
\[
\rho \frac{D\mathbf{v}}{Dt} = - \nabla \left( 1 - \frac{D \rho}{D \xi} \right) P - \rho \nabla \Omega + \nabla \left( \frac{\eta_v}{3} \mu \right) \nabla \cdot \mathbf{v} + \nabla \times (\mu \nabla \times \mathbf{v}) + 2(\nabla \times (\mu \nabla \nabla)) \mathbf{v}.
\]

If we neglect variations in the coefficients of viscosity and pressure relaxation, this equation can be written:
\[
\rho \frac{D\mathbf{v}}{Dt} = - \nabla P + \eta_p \nabla \cdot \mathbf{v} + \eta_v \nabla \Omega + \left( \eta_v + \frac{4}{3} \mu \right) \nabla \cdot \mathbf{v}.
\]

A list of values of the volume viscosity coefficients \(\eta_p\) and \(\eta_v\) 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.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$\eta_v$ (μs)</th>
<th>$\eta_s$ (Pa s)</th>
<th>$\eta_{4/3}$ (Pa s)</th>
<th>Conditions</th>
<th>Relaxation process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air, $^c$ 0% RH</td>
<td>6640</td>
<td>944</td>
<td>$24.1 \times 10^{-6}$</td>
<td>$P=1$ atm</td>
<td>O$_2$ vibration</td>
</tr>
<tr>
<td>Air, 50% RH</td>
<td>4.47</td>
<td>0.635</td>
<td>$24.0 \times 10^{-6}$</td>
<td>$T=293.15$ K</td>
<td>Translation</td>
</tr>
<tr>
<td>Air, 100% RH</td>
<td>1.97</td>
<td>0.280</td>
<td>$23.9 \times 10^{-6}$</td>
<td>$P=1$ atm</td>
<td>MgSO$_4$ ionization</td>
</tr>
<tr>
<td>Argon $^{b,c}$</td>
<td>$-8 \times 10^{-6}$</td>
<td>$22 \times 10^{-6}$</td>
<td>$29.6 \times 10^{-6}$</td>
<td>$T=293.15$ K</td>
<td>Translation</td>
</tr>
<tr>
<td>Sea water $^{b,d}$</td>
<td>2.08</td>
<td>4739</td>
<td>$1.840 \times 10^{-3}$</td>
<td>$P=1$ atm</td>
<td>MgSO$_4$ ionization</td>
</tr>
<tr>
<td>Sea water $^{b,d}$</td>
<td>2.08</td>
<td>4739</td>
<td>$1.840 \times 10^{-3}$</td>
<td>$T=283.16$ K</td>
<td>MgSO$_4$ ionization</td>
</tr>
</tbody>
</table>

$^a$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 $\eta_v$ 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

$$
\begin{align*}
\rho &= \rho_0 + \rho_1 \exp \left( i \omega t - kx \right), \\
P &= P_0 + P_1 \exp \left( i \omega t - kx \right),
\end{align*}
$$

(47)

where $\rho_0$ and $P_0$ are the ambient density and pressure, respectively, and $\rho_1$ and $P_1$ acoustic amplitudes, $k$ the (complex) wave number, and $\omega$ 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

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

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 $\eta_v$ 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:

$$
\begin{bmatrix}
\frac{\partial^2}{\partial t^2} & - \frac{\partial}{\partial x} \\
1 + \tau_{PS} \frac{\partial}{\partial t} & - \frac{1}{\rho_0 \left( 1 + \tau_{VS} \frac{\partial}{\partial t} \right)}
\end{bmatrix}
\begin{bmatrix}
\rho_1 \\
P_1
\end{bmatrix} = 0.
$$

(48)

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

$$
\begin{bmatrix}
- \omega^2 & k^2 \\
1 + i \omega \tau_{PS} & - \frac{1}{\rho_0 \left( 1 + i \omega \tau_{VS} \right)}
\end{bmatrix}
\begin{bmatrix}
\rho_1 \\
P_1
\end{bmatrix} = 0.
$$

(49)

The resulting solution for the complex sound speed is

$$
\frac{1}{a^2} - \frac{k^2}{\omega^2} = \frac{1}{\rho_0 \left( 1 + i \omega \tau_{PS} \right)}
$$

(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):

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

and then

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

leading to

$$
\begin{bmatrix}
- \omega^2 + k^2 a_0^2 i \omega \tau_{PS} & k^2 (1 - i \omega \tau_{VS}) \\
1 + \omega^2 \tau_{PS} \tau_{VS} & - \frac{1}{\rho_0 \left( 1 + \omega^2 \tau_{VS} \right)}
\end{bmatrix}
\begin{bmatrix}
\rho_1 \\
P_1
\end{bmatrix} = 0.
$$

(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
\[
\left(1 - \frac{\tau p}{V S} \frac{D^2}{D t^2}\right)(p - p_0) = \frac{1}{\alpha_0} \left(1 - \frac{\tau p}{V S} \frac{D^2}{D t^2}\right)(P - P_0).
\]

(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 \(\xi\) 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 \(\eta_v\) and \(\eta_p\), 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.


14. L. Tisza, “Supersonic absorption and Stokes’ viscosity relation,” *Phys. Rev.* 61, 351 (1942). The substitution \(P = \rho \frac{\gamma}{\gamma - 1}\) was introduced into his Eq. (15) to obtain our Eq. (15).

15. See Ref. 4, p. 159.


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


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 \(\tau / \beta_m = \tau_i\) was introduced into his Eq. (10-7.10) to obtain our Eq. (20), where \(\tau_i\) is the mean free time between collisions and \(\beta_m\) the reciprocal rotational collision number.


30. H. J. Bauer, “Phenomenological theory of the relaxation phenomena in

31 See Ref. 4, p. 166.

