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Volume viscosity in fluids with multiple dissipative processes

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The variational principle of Hamilton is applied to derive the volume viscosity coefficients of a reacting fluid with multiple dissipative processes. The procedure, as in the case of a single dissipative process, yields two dissipative terms in the Navier–Stokes equation: The first is the traditional volume viscosity term, proportional to the dilatational component of the velocity; the second term is proportional to the material time derivative of the pressure gradient. Each dissipative process is assumed to be independent of the others. In a fluid comprising a single constituent with multiple relaxation processes, the relaxation times of the multiple processes are additive in the respective volume viscosity terms. If the fluid comprises several relaxing constituents (each with a single relaxation process), the relaxation times are again additive but weighted by the mole fractions of the fluid constituents. A generalized equation of state is derived, for which two special cases are considered: The case of “low-entropy production,” where entropy variation is neglected, and that of “high entropy production,” where the progress variables of the internal molecular processes are neglected. Applications include acoustical wave propagation, Stokes flow around a sphere, and the structure and thickness of a normal shock. Finally, it is shown that the analysis presented here resolves several misconceptions concerning the volume viscosity of fluids. © 2009 American Institute of Physics. [DOI: 10.1063/1.3085814]

I. INTRODUCTION

Previously the authors applied Hamilton’s principle of least action to derive expressions for the volume viscosity in fluids, and demonstrated that the analysis leads to two dissipative terms in the Navier–Stokes equation: the traditional volume viscosity term, proportional to the rate of dilatation, and a “pressure relaxation” term, proportional to the (material) time rate of change of the pressure gradient.^{1,2} Both dissipative processes can be delineated in acoustics where frequency-dependent dissipation and volume-viscous effects are elements of classical theory. In the previous work, we showed that separating pressure relaxation from volume viscosity resulted in a modified Navier–Stokes equation that included both dissipative transport processes, removing them from the acoustic equation of state. Isolation of those effects in acoustics is relatively straightforward because pressure signals are generally of small amplitude compared with the total pressure and the decomposition of radiated acoustic pressure fluctuations into spectral components with associated frequency-dependent dissipation is an accepted characterization procedure. This is not the case in fluid dynamics.

In fluid dynamics, radiated sound is considered generally to be a nuisance that is part of the local fluid pressure for flows over objects. Furthermore, fluid flows with streamwise strain rates comparable in magnitude to shear rates are rare making it difficult to isolate and separate volume-viscous and pressure relaxation effects. Stationary normal shock

waves will be addressed later in this paper as a notable exception, but that type of flow exhibits strong convective nonlinearities. Indeed, the nonlinear contributions to material derivatives in flowing systems preclude straightforward spectral decomposition of velocity or pressure for purposes of isolating volume-viscous and pressure relaxation effects.

Lichtenstein³ may have been the first to apply Hamilton’s least action principle to fluid systems. Concurrently, Bateman⁴ utilized a variational principle based on Clebsch’s equations,⁵ with virtually the same mathematical formalism, for a class of two-dimensional, isentropic compressible flows. Serrin⁶ employed Lagrange multipliers to incorporate conservation of mass, energy, and particle identity in his study of perfect fluids and showed that the constraint on the entropy variation produced a somewhat puzzling thermodynamic relationship. He observed that because the material rate of change in that Lagrange multiplier for the entropy equation was equal to temperature, that material rate of change could be equated to the isochoric variation in internal energy with entropy, i.e., $[D\beta/Dt = T \equiv (\partial u / \partial s)_\rho]$. The temperature relationship appears to imply that the Lagrange multiplier for a fluid particle traveling in an isothermal fluid will increase linearly with time. However, as Serrin’s thermodynamic identity implies, the material rate of change in this multiplier is actually a function of temperature, and this constraint is similar to the implied thermodynamic relationship between the volume viscosity and the material rate of change in density.

Recently, Anthony⁷ and Scholle⁸ utilized Noether’s first theorem,⁹ relating differentiable symmetries of Lagrangian integrals to the conservation laws, to define valid flux-flux density constitutive relationships in applying Hamilton’s ac-

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tion principle to reversible and irreversible processes in continuum mechanics. Scholle⁸ was able to generalize the use of Galilean invariance in constructing the necessary invariance principles for a range of applications.

Here, we have extended Hamilton's action principle for dissipative fluids to fluids subject to multiple dissipative processes. For convenience, equation numbers taken from Ref. 1 are preceded by "I."

II. THE VARIATION

We assume that the dissipative processes are independent, each occurring as though all the others were absent. The Einstein summation convention is used for indices (i, j, k, l, m) designating coordinates, but not for indices (λ, μ, ν) designating reactions. The Lagrangian (I-25) remains

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

but the updated set of constraints (I-26 to I-28) is rewritten as follows:

Conservation of mass

$$\frac{D\rho}{Dt} + \rho \frac{\partial v_k}{\partial x_k} = 0, \quad (k = 1, 2, 3). \quad (2)$$

Conservation of reacting species

$$\frac{D\xi_\lambda}{Dt} - L_\lambda A_\lambda = 0, \quad (\lambda = 1, 2, \dots, n). \quad (3)$$

Material entropy constraint

$$\frac{DS}{Dt} - \frac{1}{T} \sum_{\lambda=1}^n L_\lambda A_\lambda^2 = 0, \quad (4)$$

where ρ , U , Ω , S , and T are the density, internal energy, body force potential function, entropy, and temperature of the fluid; x_k and v_k the k th components of particle position and velocity; ξ_λ , A_λ , and L_λ the progress variable, affinity, and a constant associated with the λ th process; t the time, n the number of processes; and D/Dt the material time derivative.

The variational integral (I-26) is accordingly modified to the following:

$$\begin{aligned} \delta \int_{t_0}^{t_1} \int_V \int \left[\frac{1}{2}\rho v_k v_k - \rho(U + \Omega) - \varphi \left(\frac{D\rho}{Dt} + \rho \frac{\partial v_k}{\partial x_k} \right) \right. \\ \left. - \rho \sum_{\lambda=1}^n \alpha_\lambda \left(\frac{D\xi_\lambda}{Dt} - L_\lambda A_\lambda \right) - \rho \beta \left(\frac{DS}{Dt} - \frac{1}{T} \sum_{\lambda=1}^n L_\lambda A_\lambda^2 \right) \right] dV dt \\ = 0. \end{aligned} \quad (5)$$

The independent variations of the velocity components, density, entropy, and equilibrium departures (I-30–I-33) then yield

δv_k :

$$v_k = \frac{\partial \phi}{\partial x_k} + \beta \frac{\partial S}{\partial x_k} + \sum_{\lambda=1}^n \alpha_\lambda \frac{\partial \xi_\lambda}{\partial x_k}, \quad (6)$$

$\delta \rho$:

$$\frac{D\phi}{Dt} = \frac{1}{2}v_k v_k - (U + \Omega) - \frac{P}{\rho}, \quad (7)$$

δS :

$$\frac{D\beta}{Dt} = T, \quad (8)$$

$\delta \xi_\lambda$:

$$\frac{D\alpha_\lambda}{Dt} = -A_\lambda. \quad (9)$$

Equation (6) is a modified Clebsch representation for the velocity⁸ and Eq. (7) a modified Bernoulli's equation.⁷ As will be shown later, Eqs. (8) and (9) ensure that the variational procedure will determine the stationarity of the solutions for the temperature and affinity. Following the same procedure leading to the equation of motion [Eq. (I-40)] for a single dissipative process, we find for multiple dissipative processes

$$\rho \frac{Dv_k}{Dt} = -\rho \frac{\partial \Omega}{\partial x_k} - \frac{\partial P}{\partial x_k} + \rho \frac{\partial}{\partial x_k} \left[\sum_{\lambda=1}^n \alpha_\lambda \frac{D\xi_\lambda}{Dt} + \beta \frac{DS}{Dt} \right]. \quad (10)$$

Let $(\xi_1, \xi_2, \dots, \xi_n, P, S)$ be the independent variables. Then $\rho = \rho(\xi_1, \xi_2, \dots, \xi_n, P, S)$ and

$$\begin{aligned} \rho - \rho_0 = \sum_{\lambda=1}^n \left(\frac{\partial \rho}{\partial \xi_\lambda} \right)_{PS\xi'_\lambda} (\xi_\lambda - \xi_{\lambda 0}) + \left(\frac{\partial \rho}{\partial P} \right)_{S\xi} (P - P_0) \\ + \left(\frac{\partial \rho}{\partial S} \right)_{P\xi} (S - S_0), \end{aligned} \quad (11)$$

where the subscript 0 indicates a value at equilibrium, the primed subscript ξ'_λ indicates a differentiation with all ξ 's held constant except ξ_λ , and unprimed subscript ξ indicates a differentiation with all ξ 's held constant. Upon taking the material time derivative of Eq. (11) we find

$$\sum_{\lambda=1}^n \left(\frac{\partial \rho}{\partial \xi_\lambda} \right)_{PS\xi'_\lambda} \frac{D\xi_\lambda}{Dt} = \frac{D\rho}{Dt} - \left(\frac{\partial \rho}{\partial P} \right)_{S\xi} \frac{DP}{Dt} - \left(\frac{\partial \rho}{\partial S} \right)_{P\xi} \frac{DS}{Dt}. \quad (12)$$

Now assume

$$\left(\frac{\partial \rho}{\partial \xi_\lambda} \right)_{PS\xi'_\lambda} \frac{D\xi_\lambda}{Dt} = f_\lambda \left[\frac{D\rho}{Dt} - \left(\frac{\partial \rho}{\partial P} \right)_{S\xi} \frac{DP}{Dt} - \left(\frac{\partial \rho}{\partial S} \right)_{P\xi} \frac{DS}{Dt} \right], \quad (13)$$

where f_λ is a constant (constrained by $\sum_\lambda f_\lambda = 1$), and let

$$\alpha_\lambda = -\frac{C_\lambda}{f_\lambda \rho} \left(\frac{\partial \rho}{\partial \xi_\lambda} \right)_{PS\xi'_\lambda}. \quad (14)$$

Then, it follows that

$$\sum_{\lambda=1}^n \alpha_{\lambda} \frac{D\xi_{\lambda}}{Dt} = \sum_{\lambda=1}^n C_{\lambda} \left[-\frac{1}{\rho} \frac{D\rho}{Dt} + \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_{S\xi} \frac{DP}{Dt} + \frac{1}{\rho} \left(\frac{\partial \rho}{\partial S} \right)_{P\xi} \frac{DS}{Dt} \right]. \quad (15)$$

Further, we eliminate the progress variable ξ_{λ} and entropy S from the equation of motion (10) by letting

$$\beta = - \sum_{\lambda=1}^n C_{\lambda} \frac{1}{\rho} \left(\frac{\partial \rho}{\partial S} \right)_{P\xi}. \quad (16)$$

Then substituting Eqs. (15) and (16) into Eq. (10), we get

$$\frac{Dv_k}{Dt} = - \frac{\partial \Omega}{\partial x_k} - \frac{1}{\rho} \frac{\partial P}{\partial x_k} + \frac{\partial}{\partial x_k} \sum_{\lambda=1}^n C_{\lambda} \left[-\frac{1}{\rho} \frac{D\rho}{Dt} + \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_{S\xi} \frac{DP}{Dt} \right]. \quad (17)$$

Two cases will be considered here: Multiple species each containing a single process or a single species containing multiple processes. The case of multiple species containing multiple processes is beyond the scope of this work.

In the former case the contribution of a relaxing degree of freedom in any species is diluted by the presence of the other species. In the acoustical literature this effect is taken into account by multiplying the associated specific heat by the mole fraction of the species—a procedure not applicable to general flows because the specific heat *per se* does not always appear as a parameter. Instead, the mole fraction is included here in the governing equations directly. In the latter case, since there is only a single species, the mole fraction associated with each process is simply equal to unity, as noted on page 130 of Bauer.¹⁰

Compatibility with the equations of acoustical wave propagation requires that

$$C_{\lambda} = X_{\lambda} \frac{\tau'_{\lambda}}{\kappa_{\infty}^0} = X_{\lambda} \frac{\tau_{\lambda}}{\kappa_S^0} = X_{\lambda} \tau_{\lambda} \rho_0 a_0^2, \quad (18)$$

where τ_{λ} and τ'_{λ} are the isentropic relaxation times for the λ th process at constant pressure and constant volume, respectively, X_{λ} is the mole fraction of the species containing the λ th process, κ_{∞}^0 and κ_S^0 are the frozen and unfrozen isentropic compressibilities, and a_0 is the unfrozen (low-frequency) speed of sound of the mixture. The term “unfrozen” implies that all degrees of freedom contribute to the specific heat; the term “frozen” implies that the relaxing degrees of freedom do not contribute to the specific heat.

Upon inserting

$$\frac{1}{\rho} \frac{D\rho}{Dt} = - \frac{\partial v_j}{\partial x_j} \quad (19)$$

and

$$\kappa_S^{\infty} = \frac{1}{\rho} \left(\frac{D\rho}{DP} \right)_{S\xi} \quad (20)$$

together with Eq. (18) into Eq. (17), and including the shear terms, we find the modified Navier–Stokes equation for multiple dissipative processes,

$$\rho \frac{Dv_k}{Dt} = - \rho \frac{\partial \Omega}{\partial x_k} - \frac{\partial P}{\partial x_k} + \frac{\partial}{\partial x_k} \sum_{\lambda=1}^n X_{\lambda} \left[\tau_{\lambda} \rho_0 a_0^2 \frac{\partial v_j}{\partial x_j} + \tau'_{\lambda} \frac{DP}{Dt} \right] + \frac{4}{3} \mu \frac{\partial^2 v_j}{\partial x_k \partial x_j} - \mu \varepsilon_{ikm} \varepsilon_{ijl} \frac{\partial^2 v_l}{\partial x_m \partial x_j}, \quad (21)$$

where μ is the shear viscosity and ε_{ijk} is the permutation symbol or alternator. Consequently, the volume viscosity coefficients for multiple processes are

$$\eta_V = \rho_0 a_0^2 \sum_{\lambda=1}^n X_{\lambda} \tau_{\lambda} \quad (22)$$

and

$$\eta_P = \sum_{\lambda=1}^n X_{\lambda} \tau'_{\lambda}. \quad (23)$$

The determination of the volume viscosity coefficients from relaxation parameters is described in Appendix A, and values of the volume viscosity coefficients for multiple relaxations in selected fluids are found in Table I. Results (8) and (9) of the variational procedure, together with the assigned relationships (14), (16), and (18) for the parameters α_{λ} , β , and C_{λ} , ensure stationary solutions for the temperature and affinity, as shown in Appendix B.

III. THE DYNAMIC EQUATION OF STATE

A. Preliminary remarks

The dynamic equation of state is a relationship among a set of state variables such as (ξ_{λ}, ρ, S) and their material time derivatives. It is derived from the principles of irreversible thermodynamics, using Eqs. (3), (11), and (12), along with appropriate Maxwell relations. The derivation for acoustical flows is well established in literature^{10,12,16,17} but cannot be applied to the general flows considered here for three basic reasons.

First, the acoustical derivation includes multiplication by a factor such as $(1 + i\omega\tau_{\lambda})^{-1}$, a step that conveniently permits the grouping of the parameters of a specific process into a single term (called “localization” for future reference). Here ω is the acoustical angular frequency. The equivalent factor in the time domain would be the operator $(1 + \tau_{\lambda} D/Dt)^{-1}$, but this is an undefined operator and cannot be used. Consequently, the comparable procedure for general flows necessitates successive material time differentiations.

Second, acoustical methodology places the dissipative terms in the acoustical equation of state, but the volume viscosity representation transfers these terms to the equation of motion, as indicated in Eq. (21). Further, the fact that the volume viscosity terms therein are independent of each other must be taken into account in the dynamic equation of state.

TABLE I. Values of the volume viscosity coefficients for multiple relaxations [other than translation (see Table II)] in selected fluids. RH=relative humidity. S =salinity in parts per thousand.

Fluid	Conditions	η_p (μ s)	η_v (Pa s)	Relaxation strength ε	Relaxation process
Air ^a 0% RH	$P=1$ atm	6640	944	0.000 675 4	O ₂ vibration
	$T=293.15$ K	17 700	2512	0.000 126 6	N ₂ vibration
Air, 50% RH	$P=1$ atm	4.47	0.635	0.000 664 8	O ₂ vibration
	$T=293.15$ K	478	67.8	0.000 124 6	N ₂ vibration
Air, 100% RH	$P=1$ atm	1.97	0.280	0.000 654 2	O ₂ vibration
	$T=293.15$ K	242	34.3	0.000 122 6	N ₂ vibration
Air ^b	$P=1$ atm	0.0033	0.000 56	0.148	O ₂ , N ₂ rotation
	$T=293.15$ K				
Sea water ^c	$P=1$ atm	142	3.23×10^5	5.642×10^{-6}	B(OH) ₃ ionization
	$T=283.16$ K	2.08	4739	2.751×10^{-5}	MgSO ₄ ionization
	$S=35$	2.97×10^{-7}	6.52×10^{-3}	0.8963	H ₂ O structural
Methane ^d	$P=1$ atm	1.86	0.257	0.02105	Vibration, ν_4 mode
	$T=298.15$ K	1.1×10^{-3}	4.9×10^{-4}	0.6955	Rotation

^aSee Ref. 11.^bSee Ref. 12, pp. 121–127, and Ref. 13, pp. 153–157. The best estimate $Z_{\text{rot}}=5$ for the rotational collision numbers of O₂ and N₂ is used for both constituents of air. Humidity dependence is ignored in the determination of the rotational coefficients.^cSee Ref. 14.^dSee Ref. 15.

Finally, acoustical derivations are based on the assumption of negligible entropy production ($S-S_0=0$), which obviously is not valid for general flows (although admittedly an excellent approximation for acoustical flows). The approach taken here is to examine two limiting cases, as illustrated by the substitution of Eq. (4) into Eq. (12),

$$\begin{aligned} \frac{D\rho}{Dt} = & \left(\frac{\partial\rho}{\partial P} \right)_{S\xi} \frac{DP}{Dt} + \sum_{\lambda=1}^n \left(\frac{\partial\rho}{\partial\xi_\lambda} \right)_{PS\xi'} \frac{D\xi_\lambda}{Dt} \\ & + \frac{1}{T} \sum_{\lambda=1}^n \frac{1}{L_\lambda} \left(\frac{\partial\rho}{\partial S} \right)_{P\xi} \left(\frac{D\xi_\lambda}{Dt} \right)^2. \end{aligned} \quad (24)$$

We define a “transition parameter” as the ratio of the terms under the last two respective summations. Hence, we can use the definition and chain rule to write

$$\chi_\lambda = \frac{1}{L_\lambda T} \frac{\left(\frac{\partial\rho}{\partial S} \right)_{P\xi} \left(\frac{D\xi_\lambda}{Dt} \right)^2}{\left(\frac{\partial\rho}{\partial\xi_\lambda} \right)_{PS} \frac{D\xi_\lambda}{Dt}} = - \frac{1}{L_\lambda T} \left(\frac{\partial\xi_\lambda}{\partial S} \right)_{P\rho} \frac{D\xi_\lambda}{Dt}. \quad (25)$$

The condition $|\chi_\lambda| \ll 1$ corresponds to the (acoustical) approximation of low-entropy production, in which case the term $S-S_0$ and its time derivative are omitted from the equation of state. The condition $|\chi_\lambda| \gg 1$ corresponds to the approximation of high entropy production, in which case the entropy terms are retained but the term $\xi_\lambda - \xi_{\lambda 0}$ and its time derivative are correspondingly omitted. This case will prevail at high Mach numbers because $|\chi_\lambda|$ increases with flow speed, which appears in the material time derivative. We derive the dynamic equation of state for each limiting case.

B. The dynamic equation of state for the limiting case of low-entropy production

The derivation of the dynamic equation of state for this case is well documented in literature¹⁸ and is not repeated here. In keeping with the first preliminary remark of Sec. III A, we write this equation for n dissipative processes in the following manner:

$$\begin{aligned} & \frac{1}{a_0^2} (D_1 D_2, \dots, D_n) (P - P_0) \\ & = [W_n (D_1 D_2, \dots, D_n) + N_1 (D_2 D_3, \dots, D_n) \\ & \quad + N_2 (D_1 D_3, \dots, D_n) + \dots + N_n (D_1 D_2, \dots, D_{n-1})] \\ & \quad \times (\rho - \rho_0), \end{aligned} \quad (26)$$

where

$$D_\lambda = 1 - \tau_\lambda'^2 \frac{D^2}{Dt^2}, \quad (27a)$$

$$N_\lambda = 1 - \tau_\lambda \tau_\lambda' \frac{D^2}{Dt^2}, \quad (27b)$$

and

$$W_n = 1 - n \quad (27c)$$

for the case of n processes in a single species, but

$$W_n = 0 \quad (27d)$$

for the case of a single process in each of n species. We note that in the special case of harmonic excitation all terms are real. For the case of a single dissipative process ($n=1$), Eq. (26) becomes

$$\frac{1}{a_0^2} D_\lambda (P - P_0) = N_\lambda (\rho - \rho_0), \quad (28)$$

which agrees with Eq. (I-52) of Ref. 1. Equation (26) yields the correct dispersion, or real part of the sound speed, in the traditional acoustical analysis, but is not applicable to the volume viscosity approach described herein, as suggested in the second preliminary remark. The reason is that Eq. (26) contains the dissipative terms of all n processes, but Eq. (28) must be used for the respective terms under the summation in Eq. (21).

We adopt the convention that $\lambda=0$ for the volume-inviscid terms in Eq. (21). Then the dynamic equation of state, allowing for the localization of the dissipative terms, combines Eqs. (26), (27a)–(27d), and (28) and takes the following form:

$$\frac{1}{a_0^2} \prod_{\mu=1}^n D_\mu (P - P_0) = \left\{ \begin{array}{l} \delta(\lambda) \left[W_n \prod_{\mu=1}^n D_\mu + \sum_{\nu=1}^n N_\nu \prod_{\mu=1}^n 'D_\mu \right] \\ + \delta(\lambda - \nu) \sum_{\nu=1}^n N_\nu \prod_{\mu=1}^n 'D_\mu \end{array} \right\} (\rho - \rho_0), \quad (29)$$

where a prime on a product excludes the value $\mu=\nu$, and $\delta(\)$ is a delta function that has the value unity for zero argument and zero otherwise. In sum, Eq. (29) gives the respective dynamic relationship between $(P-P_0)$ and $\rho-\rho_0$ for the volume-inviscid terms ($\lambda=0$) as well as the volume-viscous terms ($\lambda \neq 0$). The volume-viscosity representation, Eqs. (21) and (29), is applied to acoustical wave propagation, as an example, in Sec. IV A.

C. The dynamic equation of state for the limiting case of high-entropy production

For convenience we choose (ξ_λ, P, T) as the independent state variables. In accord with the final remark of Sec. III A, we assume that the terms in $\xi_\lambda - \xi_{\lambda 0}$ and their derivatives can be ignored when compared to the entropy terms. Then the entropy, its material time derivative, and the affinity for process λ are expanded about their equilibrium points as follows:

$$S - S_0 = \left(\frac{\partial S}{\partial P} \right)_{\xi T} (P - P_0) + \left(\frac{\partial S}{\partial T} \right)_{\xi P} (T - T_0), \quad (30)$$

$$\frac{DS}{Dt} = \left(\frac{\partial S}{\partial P} \right)_{\xi T} \frac{DP}{Dt} + \left(\frac{\partial S}{\partial T} \right)_{\xi P} \frac{DT}{Dt}, \quad (31)$$

$$A_\lambda = \left(\frac{\partial A_\lambda}{\partial P} \right)_{\xi T} (P - P_0) + \left(\frac{\partial A_\lambda}{\partial T} \right)_{\xi P} (T - T_0). \quad (32)$$

The entropy production is written

$$T \frac{DS}{Dt} = \sum_{\lambda, \mu} L_{\lambda\mu} A_\lambda A_\mu = \sum_{\lambda} L_\lambda A_\lambda^2, \quad (33)$$

in which $L_{\lambda\mu}=0$ for $\lambda \neq \mu$ since the reactions are independent. Then inserting Eq. (32) into Eq. (33) yields

$$T \frac{DS}{Dt} = \sum_{\lambda} L_\lambda \left[\left(\frac{\partial A_\lambda}{\partial P} \right)_{\xi T} (P - P_0) + \left(\frac{\partial A_\lambda}{\partial T} \right)_{\xi P} (T - T_0) \right]^2. \quad (34)$$

Upon comparing Eq. (34) with Eq. (31) we find the dynamic equation of state for the case of high entropy production:

$$\begin{aligned} \left(\frac{\partial S}{\partial P} \right)_{\xi T} \frac{DP}{Dt} + \left(\frac{\partial S}{\partial T} \right)_{\xi P} \frac{DT}{Dt} \\ = \frac{1}{T} \sum_{\lambda} L_\lambda \left[\left(\frac{\partial A_\lambda}{\partial P} \right)_{\xi T} (P - P_0) + \left(\frac{\partial A_\lambda}{\partial T} \right)_{\xi P} (T - T_0) \right]^2. \end{aligned} \quad (35)$$

Equation (35) can be expressed in terms of phenomenological quantities:

$$\left(\frac{\partial S}{\partial P} \right)_{\xi T} = - \left(\frac{\partial V}{\partial T} \right)_{\xi P} = -V\theta^\circ, \quad (36)$$

where θ° is the frozen isobaric thermal expansion coefficient, and it can be related to the unfrozen thermal expansion coefficient as follows:¹⁷

$$\theta^\circ = \theta^0 - \frac{C_P^0}{C_P^\infty V} \sum_{\lambda} L_\lambda \tau_\lambda \Delta H_\lambda \Delta V_\lambda, \quad (37)$$

where superscripts 0 and ∞ indicate unfrozen and frozen conditions. Here C_P is the specific heat at constant pressure, ΔH_λ the reaction enthalpy at constant pressure, and ΔV_λ the volume change of a (dissociation) reaction per unit change in ξ_λ . The constant L_λ is equal to (V/RT) multiplied by the forward reaction rate,^{10,17} or equivalently, the backward reaction rate at equilibrium. If the reaction has no volume change, then for an ideal gas

$$\theta^\circ = \theta^0 = \frac{1}{T}. \quad (38)$$

Further,

$$\left(\frac{\partial S}{\partial T} \right)_{\xi P} = \frac{C_P^\infty}{T}, \quad (39)$$

$$\left(\frac{\partial A}{\partial P} \right)_{\xi T} = - \left(\frac{\partial V}{\partial \xi_\lambda} \right)_{TP} = -\Delta V_\lambda, \quad (40)$$

$$\left(\frac{\partial A}{\partial T} \right)_{\xi P} = \left(\frac{\partial S}{\partial \xi_\lambda} \right)_{TP} = \frac{\Delta H_\lambda}{T}. \quad (41)$$

Upon substituting Eqs. (36)–(41) into Eq. (35), we obtain

$$\begin{aligned} -V\theta^\circ \frac{DP}{Dt} + \frac{C_P^\infty}{T} \frac{DT}{Dt} \\ = \frac{1}{T} \sum_{\lambda=1}^n L_\lambda \left[-\Delta V_\lambda (P - P_0) + \frac{\Delta H_\lambda}{T} (T - T_0) \right]^2. \end{aligned} \quad (42)$$

As pointed out by Bauer,¹⁰ in a dissociation reaction both ΔV_λ and ΔH_λ are positive definite; thus the two effects are in opposition.

It is often more convenient to express the equation of state in terms of (P, ρ) instead of (P, T) . We expand the specific volume accordingly:

$$V - V_0 = \left(\frac{\partial V}{\partial P} \right)_{\xi T} (P - P_0) + \left(\frac{\partial V}{\partial T} \right)_{\xi P} (T - T_0), \quad (43)$$

in which

$$\left(\frac{\partial V}{\partial P} \right)_{\xi T} = -V\kappa_T^\infty, \quad (44)$$

$$\left(\frac{\partial V}{\partial T} \right)_{\xi P} = V\theta^\infty. \quad (45)$$

Upon solving Eq. (43) for $T - T_0$, taking the material time derivative, and noting the reciprocal relationship $\rho = 1/V$, we rewrite Eq. (42) as follows:

$$\begin{aligned} & \left(-\frac{T}{\rho}\theta^\infty + \frac{C_p^\infty \kappa_T^\infty}{\theta^\infty} \right) \frac{DP}{Dt} - \frac{C_p^\infty}{\rho \theta^\infty} \frac{D\rho}{Dt} \\ &= \sum_{\lambda=0}^n L_\lambda \left[\left(-\Delta V_\lambda + \frac{\Delta H_\lambda \kappa_T^\infty}{T \theta^\infty} \right) (P - P_0) - \frac{\Delta H_\lambda}{T \rho \theta^\infty} (\rho - \rho_0) \right]^2. \end{aligned} \quad (46)$$

We adopt the convention that $\lambda=0$ corresponds to the case of no volume change (no dissociative reactions, i.e., $\Delta V_0=0$). The difference between the frozen and unfrozen isothermal compressibilities comprises a relationship similar to Eq. (37),

$$\kappa_T^\infty = \kappa_T^0 - \frac{C_p^0}{C_p^\infty V} \sum_{\lambda} L_\lambda \tau_\lambda (\Delta V_\lambda)^2. \quad (47)$$

If the reaction has no volume change, then for an ideal gas

$$\kappa_T^\infty = \kappa_T^0 = \frac{1}{P}. \quad (48)$$

Two limiting cases are of interest. First, consider a very rapidly varying flow, in which the time-dependent terms in Eq. (46) are much greater in magnitude than the time-independent terms. Then

$$\frac{DP/Dt}{D\rho/Dt} = \frac{1}{\rho_0 \kappa_T^\infty} \frac{C_p^\infty}{C_p^\infty - \frac{T(\theta^\infty)^2}{\rho \kappa_T^\infty}},$$

which for a reaction in an ideal gas with no volume change becomes

$$\frac{DP/Dt}{D\rho/Dt} = \frac{1}{\rho_0 \kappa_T^\infty} \frac{C_p^\infty}{C_p^\infty - \frac{P}{\rho T}} = \frac{1}{\rho_0 \kappa_T^\infty} \frac{C_p^\infty}{C_p^\infty - R} = \frac{\gamma_\infty}{\rho_0 \kappa_T^\infty} = a_\infty^2, \quad (49)$$

the frozen adiabatic sound speed squared. Here R is the ideal gas constant in units J/(kg K). In this class of flows the continuum flow speed is so high that the internal degrees of freedom can be considered frozen, corresponding to the acoustical case of frequencies well above the internal relaxation frequencies. Dissipation is due to the equilibration of

the translational degrees of freedom, in which case the specific heat ratio assumes the value $\gamma_\infty=5/3$ for all gases, in agreement with Bhatia.¹⁹ The application to shock structure is illustrated in Sec. IV C.

If, on the other hand, the flow is nearly steady such that the material time dependent terms are negligible, it follows that

$$\frac{P - P_0}{\rho - \rho_0} = \frac{1}{\rho_0 \kappa_T^\infty} \frac{\sum_{\lambda} \Delta H_\lambda}{\sum_{\lambda} \left(\Delta H_\lambda - \frac{T \theta^\infty}{\kappa_T^\infty} \Delta V_\lambda \right)}. \quad (50)$$

In the case of no volume change, this relation can be simplified to

$$\frac{P - P_0}{\rho - \rho_0} = \frac{1}{\rho_0 \kappa_T^\infty} = (a_T^\infty)^2 = RT, \quad (51)$$

which is the ideal gas law. If there is a volume change, this case will apply, for example, to dissociative reactions in flows with slow variations.

IV. APPLICATIONS

A. Acoustical wave propagation.

For simplicity consider the case of two independent relaxations ($\lambda=0, 1, 2$). For small-signal, one-dimensional, harmonic wave propagation, the Navier–Stokes Eq. (21), together with the continuity Eq. (2), takes the form

$$-\omega^2 \rho_a + k^2 P_a + k^2 \sum_{\lambda=1}^2 X_\lambda (a_0^2 i \omega \tau_\lambda \rho_a - i \omega \tau'_\lambda P_a) = 0, \quad (52)$$

where ρ_a and P_a are harmonic wave amplitudes of the density and pressure, ω the angular frequency, and k the complex wave number. Recalling that $\lambda=0$ designates the first two terms of Eq. (52), and $\lambda=1, 2$ the respective volume-viscous terms, we write the dynamic equation of state (29) for each value of λ for the single-species case, for example, vibrational and rotational relaxations in a diatomic gas,

$$\lambda = 0: P_a = a_0^2 \left(-1 + \frac{1 + \omega^2 \tau_1 \tau'_1}{1 + \omega^2 \tau_1'^2} + \frac{1 + \omega^2 \tau_2 \tau'_2}{1 + \omega^2 \tau_2'^2} \right) \rho_a, \quad (53a)$$

$$\lambda = 1: P_a = a_0^2 \left(\frac{1 + \omega^2 \tau_1 \tau'_1}{1 + \omega^2 \tau_1'^2} \right) \rho_a, \quad (53b)$$

$$\lambda = 2: P_a = a_0^2 \left(\frac{1 + \omega^2 \tau_2 \tau'_2}{1 + \omega^2 \tau_2'^2} \right) \rho_a. \quad (53c)$$

Upon inserting Eqs. (53a)–(53c) into Eq. (52) we find the complex sound speed,

$$\begin{aligned} \frac{a^2}{a_0^2} = \frac{\omega^2}{a_0^2 k^2} = & -1 + \frac{1 + \omega^2 \tau_1 \tau'_1}{1 + \omega^2 \tau_1'^2} + \frac{1 + \omega^2 \tau_2 \tau'_2}{1 + \omega^2 \tau_2'^2} + \frac{i\omega(\tau_1 - \tau'_1)}{1 + \omega^2 \tau_1'^2} \\ & + \frac{i\omega(\tau_2 - \tau'_2)}{1 + \omega^2 \tau_2'^2}, \end{aligned} \quad (53d)$$

which after some rearrangement agrees with Eq. (5.4.15) of

Ref. 19 and Eq. (21-16) of Ref. 16. For the case of single relaxations in two species (e.g., vibrational relaxation of nitrogen and oxygen in air), Eq. (53a) becomes

$$\lambda = 0: P_a = a_0^2 \left(1 + X_1 \frac{\omega^2 \tau_1' \tau_1'}{1 + \omega^2 \tau_1'^2} + X_2 \frac{\omega^2 \tau_2' \tau_2'}{1 + \omega^2 \tau_2'^2} \right) \rho_a, \quad (54a)$$

with the result

$$\frac{a^2}{a_0^2} = \frac{\omega^2}{a_0^2 k^2} = 1 + X_1 \frac{\omega^2 \tau_1' (\tau_1 - \tau_1')}{1 + \omega^2 \tau_1'^2} + X_2 \frac{\omega^2 \tau_2' (\tau_2 - \tau_2')}{1 + \omega^2 \tau_2'^2} + X_1 \frac{i\omega (\tau_1 - \tau_1')}{1 + \omega^2 \tau_1'^2} + X_2 \frac{i\omega (\tau_2 - \tau_2')}{1 + \omega^2 \tau_2'^2}. \quad (54b)$$

The analysis accordingly yields the correct expressions for the acoustical dispersion and absorption and therewith satisfies a necessary condition for a viable theory of the volume viscosity.

B. Stokes flow around a sphere

Stokes flow assumes an incompressible fluid and neglects the material time derivative of the velocity.²⁰ The equation of motion, including the pressure relaxation component of the volume viscosity, is then

$$\nabla \left[P - \eta_P \left(v_r \frac{\partial P}{\partial r} + \frac{v_\theta}{r} \frac{\partial P}{\partial \theta} \right) \right] = \mu \nabla^2 \mathbf{v}, \quad (55)$$

in which (v_r, v_θ) are the radial and azimuthal components of the velocity \mathbf{v} and μ the shear viscosity. Upon defining

$$P' = P - \eta_P \left(v_r \frac{\partial P}{\partial r} + \frac{v_\theta}{r} \frac{\partial P}{\partial \theta} \right), \quad (56)$$

we reduce Eq. (55) to the familiar form

$$\nabla P' = \mu \nabla^2 \mathbf{v}, \quad (57)$$

with known solutions

$$v_r = V_S \cos \theta \left(1 - \frac{3a}{2r} + \frac{a^3}{2r^3} \right), \quad (58a)$$

$$v_\theta = V_S \sin \theta \left(1 - \frac{3a}{4r} - \frac{a^3}{4r^3} \right), \quad (58b)$$

$$P' = - \frac{3\mu V_S a \cos \theta}{2r^2}, \quad (59)$$

where V_S is the free-stream velocity and a the radius of the sphere. The presence of the volume viscosity term does not change the velocity components nor the boundary conditions. Insertion of Eqs. (58a), (58b), and (56) into Eq. (59) yields

$$P - \eta_P V_S \cos \theta \left(1 - \frac{3a}{2r} + \frac{a^3}{2r^3} \right) \frac{\partial P}{\partial r} + \eta_P V_S \sin \theta \left(1 - \frac{3a}{4r} - \frac{a^3}{4r^3} \right) \frac{1}{r} \frac{\partial P}{\partial \theta} = - \frac{3\mu V_S a \cos \theta}{2r^2}. \quad (60)$$

Restricting our analysis to the far-field ($r \gg a$) for simplicity, we reduce Eq. (60) to

$$\frac{\partial P}{\partial r} - \frac{1}{L_P \cos \theta} P = \frac{3\mu V_S a}{2L_P r^2}, \quad (61)$$

where a “relaxation length” is defined as $L_P = \eta_P V_S$. With the aid of Eqs. (3.351.4) and (8.215) of Ref. 21, we find the solution to Eq. (61) in the following form:

$$P = - \frac{3\mu V_S a}{2L_P} e^{qr} \left[q \text{Ei}(-qr) + \frac{e^{-qr}}{r} \right], \quad (q > 0) \quad (62)$$

in which $q = (L_P \cos \theta)^{-1}$ and $\text{Ei}(\cdot)$ is the exponential integral function. Substitution of an explicit series for the latter yields the solution for the pressure P :

$$P = - \frac{3\mu V_S a \cos \theta}{2r^2} \times \left[1 - \frac{2! L_P \cos \theta}{r} + \frac{3! (L_P \cos \theta)^2}{r^2} - + \dots \right], \quad (r \gg a). \quad (63)$$

The first term, independent of volume losses, remains valid for all r and leads to the familiar Stokes expression for the drag. The volume losses in Stokes flow have no effect upon the velocity distribution, and serve only to accelerate the pressure drop with distance from the sphere. As seen from Eq. (23), the processes with the longer relaxation times will make the greater contributions. Since the boundary conditions require the velocity components to vanish at the surface of the sphere, the material time derivative there is zero, and as a result the volume viscosity makes no contribution to the drag. This conclusion will be true for Stokes flow around any obstacle. This example illustrates that it is possible to have volume losses in an incompressible flow.

C. Structure and thickness of a normal shock

The development of a normal shock in supersonic flow is assumed to conform to the condition of “high entropy production,” for which the dynamic equation of state is given by Eq. (49). In other words, at sufficiently high Mach numbers dissipation due to the translational processes overwhelms the internal molecular processes. Then the (one-dimensional) equations of continuity, momentum (modified Navier–Stokes), state, and thermal transport are, respectively,

$$\rho v = \rho_1 v_1, \quad (64)$$

$$\rho v^2 + P - \eta_V' \frac{dv}{dx} - \eta_P v \frac{dP}{dx} = \rho_1 v_1^2 + P_1, \quad (65)$$

$$P - P_1 = a_\infty^2 (\rho - \rho_1), \quad (66)$$

$$C_v^0 \frac{dT}{dx} - \frac{K}{\rho} \frac{d^2T}{dx^2} = \frac{P}{\rho^2} v \frac{d\rho}{dx}, \quad (67)$$

where (C_v^0, K, r, v, P) are the unfrozen specific heat at constant volume, thermal conductivity, density, velocity, and pressure; coordinate x is in the direction of the flow, and the subscript “1” refers to far upstream values. Further, we define

$$\eta'_V = \eta_V + \frac{4}{3}\mu. \quad (68)$$

Note that Eq. (66) is the integrated version of Eq. (49). The present analysis differs from those in the past^{22–25} by the inclusion of the volume viscosity terms in the momentum Eq. (65), which will be shown to be essential to a comprehensive understanding of the shock structure.

The nonequilibrium and equilibrium sound speeds for a diatomic gas are related by

$$a_\infty^2 = \frac{\gamma_\infty}{\gamma_1} a_1^2 = \frac{5/3}{7/5} a_1^2 = \frac{25}{21} a_1^2, \quad (69a)$$

in which the γ 's are the specific heat ratios. The temperature dependence of the shock properties are contained in the sound speed,

$$a_\infty^2 = a_{\infty 1}^2 \frac{T}{T_1}. \quad (69b)$$

Upon substituting Eqs. (64) and (66) into Eqs. (65) and (67) to eliminate ρ and P , we obtain the following equations for the velocity and temperature:

$$\frac{\left(-\eta'_V + \eta_P a_\infty^2 \rho_1 \frac{v_1}{v}\right) d\left(\frac{v_1}{v}\right)}{\frac{v_1}{v} \left[1 - \left(1 + \frac{a_\infty^2}{v_1^2}\right) \frac{v_1}{v} + \frac{a_\infty^2 v_1^2}{v_1^2 v^2}\right]} = \rho_1 v_1 dx, \quad (70)$$

$$\frac{dT}{dx} = -\frac{(P_1 - a_\infty^2 \rho_1)}{\rho_1 C_v^0} \frac{d(v/v_1)}{dx} - \frac{a_\infty^2}{C_v^0} \frac{d \ln(v/v_1)}{dx}. \quad (71)$$

In Eq. (71) the thermal diffusion term found in Eq. (67) is neglected. To simplify notation, let

$$z = \frac{v}{v_1} = \frac{\rho_1}{\rho} < 1 \quad (72a)$$

and

$$\psi = \frac{a_\infty^2}{v_1^2} = \frac{\gamma_\infty}{\gamma_1 M^2} < 1, \quad (72b)$$

in which M is the Mach number. (Sherman²² calls the reciprocal of ψ the “monatomic Mach number.”) Substitution of Eqs. (72a) and (72b) into Eqs. (70) and (71) yields the following differential equations:

$$\frac{(-\eta'_V z + \eta_P a_\infty^2 \rho_1) dz}{(z-1)(z-\psi)} = -\rho_1 v_1, \quad (73)$$

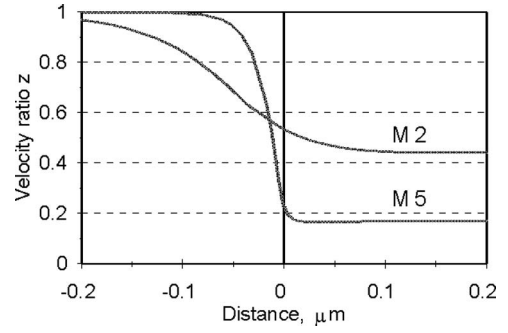


FIG. 1. Profile of a normal shock in air at Mach numbers $M=2$ and 5 at upstream temperature and pressure of 293.15 K and 1 atm according to Eqs. (75) and (76).

$$\frac{dT}{dx} = -\frac{(P_1 - a_\infty^2 \rho_1)}{\rho_1 C_v^0} \frac{dz}{dx} - \frac{a_\infty^2}{C_v^0} \frac{d \ln(z)}{dx}, \quad (74)$$

with the boundary conditions $v=v_1$, $T=T_1$, and vanishing spatial derivatives as $x \rightarrow -\infty$.

The solutions to Eqs. (73) and (74), satisfying the boundary conditions, are

$$\begin{aligned} & -\left(\frac{\eta'_V - \eta_P a_\infty^2 \rho_1}{1-\psi}\right) \ln(1-z) + \left(\frac{\eta'_V \psi - \eta_P a_\infty^2 \rho_1}{1-\psi}\right) \ln(z-\psi) \\ & = -\rho_1 v_1 (x+x_0), \end{aligned} \quad (75)$$

$$T = T_1 - \frac{(P_1 - a_\infty^2 \rho_1)}{\rho_1 C_v^0} (z-1) - \frac{a_\infty^2}{C_v^0} \ln(z). \quad (76)$$

The constant of integration (x_0) permits us to adjust the x -axis origin arbitrarily and is set to $x_0=0$ for present purposes. Based on an iterative procedure, the shock profile obtained from Eqs. (75) and (76) is plotted in Fig. 1 for Mach numbers $M=2$ and $M=5$, using the volume viscosity values for air listed in Table II.

The shock thickness δx is defined in terms of the maximum velocity ratio z_{\max} , the minimum ratio z_{\min} , and the maximum magnitude of the slope $|dz/dx|_{\max}$,

$$\delta x = \frac{z_{\max} - z_{\min}}{\left|\frac{dz}{dx}\right|_{\max}}. \quad (77)$$

Here

$$z_{\max} = 1, \quad (78a)$$

TABLE II. Contributions to the volume viscosity of dry air due to the translational relaxation of its major constituents (see Ref. 26 for the properties of air). $T=293.15$ K. $P=1$ atm.

Constituent	Mole fraction	η_P (μs)	$\eta'_V = \eta_V + \frac{4}{3}\mu$ (Pa s)
Argon	0.01	-8.9×10^{-6}	5.0×10^{-5}
Oxygen	0.21	-2.1×10^{-6}	3.8×10^{-5}
Nitrogen	0.78	-3.2×10^{-6}	3.3×10^{-5}
Air ^a	1.00	-3.0×10^{-6}	3.4×10^{-5}

^aSee Eqs. (22) and (23).

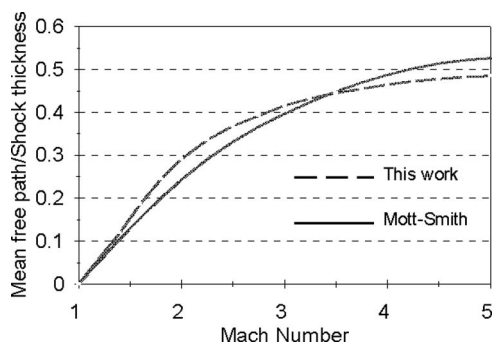


FIG. 2. Ratio of mean free path to shock thickness at upstream temperature and pressure of 293.15 K and 1 atm. Solid line: theory of Mott-Smith (Ref. 27) based on a solution to the Boltzmann equation. Dashed line: theory based on Eqs. (70), (71), (72a), (72b), (73)–(77), (78a), and (78b) of this work.

$$z_{\min} = \psi, \quad (78b)$$

and the value of the maximum slope (magnitude) is found numerically from Eqs. (73) and (74) for several Mach numbers. In Fig. 2 the ratio of mean free path to shock thickness as a function of Mach number is compared to that derived by Mott-Smith,²⁷ based on a solution to the Boltzmann transport equation. The solution presented here, based on Eqs. (70), (71), (72a), (72b), (73)–(77), (78a), and (78b) and the volume viscosity values listed in Table II, contains *no* adjustable parameters. The mean free path is corrected for temperature and pressure, the upstream value taken to be $\ell_1 = 6.5 \times 10^{-8}$ m at 293.15 K and 1 atm. This example illustrates the role of the equation of state for the case of high entropy production.

The $M=5$ case is interesting because it is considered by many to be the lower Mach number limit for the so-called hypersonic flow regime and, although the fluid behind that normal shock continues to obey an ideal gas compressibility (of unity) model, thermally induced chemical effects can be detected and the property variations across a normal shock wave cannot be modeled accurately with elementary gas dynamics normal shock wave relations (where the velocity ratio at $M=5$, would be 0.2 in Fig. 1). Huber²⁸ investigated the thermally dissociating normal shock behavior for air at altitudes as low as 10.9 km ($T=217$ K and $P=0.222$ bar), and determined that the velocity ratio across a $M=5$, normal shock would be 0.186.

V. MISCONCEPTIONS CONCERNING THE VOLUME VISCOSITY OF FLUIDS

The results presented here together with those of Ref. 1 permit us to resolve several misconceptions concerning the volume viscosity of fluids.

First, a single constitutive constant is inadequate to describe volume losses in fluids; rather two different effects are needed: one to represent the thermodynamic deviations from equilibrium equations of state, the other to represent the transport processes associated with the kinetics of a volume-dissipative process. A single constitutive coefficient, for ex-

ample, leads to expressions for acoustical dispersion and absorption that are valid only in the low-frequency limit (with limited accuracy even then).

Second, the volume viscosity coefficients of a monatomic gas are not zero. The prevailing dissipative process is heat conduction (as long as the flow is not isothermal). However, other processes may contribute to the volume losses. For example, near the liquid-gas phase boundary, dimerization or other aggregation processes may lead to volume losses, although the authors are unaware of any related measurements in monatomic fluids.

Finally, it is possible to have volume dissipation in incompressible flow (again, as long as the flow is not isothermal), for a pressure gradient in the fluid implies a temperature gradient. Molecules at an initial temperature convected to a region of a different temperature will strive to adjust their degrees of freedom to the new temperature. Consequently the fluid will incur volume losses.

VI. CONCLUSIONS

The Hamilton principle of least action is applied to fluids with multiple dissipative processes—subject to conservation of mass, conservation of reacting species, and material entropy constraints—to derive the volume viscosity in fluids. Under the assumption that the dissipative processes are independent of each other, the variational procedure therewith, as in the case of a single dissipative process, yields two volume-viscous terms in the Navier–Stokes equation: the conventional volume-viscosity term, proportional to the dilatational component of the velocity, and a “pressure relaxation” term, proportional to the material time derivative of the pressure gradient. Furthermore, the relaxation times associated with each process are additive in the respective volume-viscosity terms.

A generalized dynamic equation of state is derived from the principles of irreversible thermodynamics, allowing for dissociative reactions. In the limiting case of low-entropy production, where the entropy terms are ignored, the resulting equation of state and “modified” Navier–Stokes equation lead to the correct expressions for the dispersion and absorption of sound waves in fluids with multiple dissipative processes (e.g., vibrational relaxation of nitrogen and oxygen in air). In the limiting case of high entropy production, where the progress variables are ignored, the density and pressure are related by the “high-frequency” speed of sound, in which case the specific heat ratio is 5/3 for all gases. In the absence of dissociative reactions, the underlying process is relaxation of the translational degrees of freedom. Here the translational relaxation times of the fluid constituents are again additive when weighted by their mole fractions.

Three examples were presented to illustrate the role of the volume-viscosity terms in fluid flow. First, acoustical wave propagation exemplifies the case of low-entropy production, whereby the volume viscosity terms yield the correct solutions for the dispersion and absorption of sound in fluids with multiple dissipative processes—a necessary requirement for a viable theory of volume viscosity. Second, in Stokes (incompressible) slow viscous flow around a sphere,

the traditional volume viscosity term vanishes but the remaining “pressure relaxation” term illustrates that volume losses are possible in incompressible flow, even though these losses do not contribute to the drag. Finally, the formation of a normal shock in supersonic flow exemplifies the case of high entropy production. Here the volume-viscous terms are essential to describe the shock wave behavior between the upstream and downstream limits—a situation not possible with the traditional Rankine–Hugoniot equations.

Experimental data on acoustical relaxation processes in fluids remain the leading source of data for the volume viscosity coefficients, as explained in Appendix A.

APPENDIX A: DETERMINATION OF VOLUME VISCOSITY COEFFICIENTS FROM RELAXATION PARAMETERS

A single relaxation process is characterized by two of three parameters:^{10,17} the isentropic relaxation time at constant pressure τ_{PS} , the isentropic relaxation time at constant volume τ_{VS} , and the relaxation strength ε . These are related by

$$\varepsilon = \frac{\tau_{PS} - \tau_{VS}}{\tau_{PS}}. \quad (\text{A1})$$

The relaxation strength is determined from thermodynamic considerations. For a de-excitation reaction it is given by

$$\varepsilon = \frac{RC_i}{C_P^\infty C_V^0}, \quad (\text{A2})$$

and for a dissociation reaction (e.g., of a diatomic molecule) by

$$\varepsilon = \frac{RC_i}{C_P^\infty C_V^0} \left[1 - \frac{\Delta VC_P^0}{\Delta HV\theta^0} \right]^2, \quad (\text{A3})$$

where C_i is the specific heat of the relaxing degree of freedom or the “excess” specific heat of the dissociation reaction, respectively; the other parameters are defined in the text. A relaxation time τ_a determined from an absorption experiment is equal to

$$\tau_a = (\tau_{PS}\tau_{VS})^{1/2} \quad (\text{A4})$$

and a relaxation time τ_d determined from a dispersion experiment is simply equal to

$$\tau_d = \tau_{VS}. \quad (\text{A5})$$

Usually an experimenter reports only one of the two relaxation times because the absorption and dispersion are rarely measured simultaneously. In this case the second relaxation time can be determined from Eq. (A1), together with a knowledge or estimate of the relaxation strength. The difference between the two relaxation times is important only when it appears as such in the expression for the flow dissipation, as, for example, in acoustical wave propagation.

These considerations are valid for the multiple relaxation model described here, because the relaxation processes are assumed independent. However, it is pointed out that, in a mixture, the appropriate relaxation time of a particular spe-

cies is that in the mixture, as opposed to that in the pure substance. In a binary mixture of two species A and B we have

$$\frac{1}{\tau} = \frac{X_A}{\tau_{AA}} + \frac{1 - X_A}{\tau_{AB}}, \quad (\text{A6})$$

in which X_A is the mole fraction of species A , τ_{AA} the relaxation time of species A due to self-de-excitation, τ_{AB} the relaxation time of species A due to de-excitation by species B , and τ the relaxation time of A in the mixture.

Once the relaxation times for each process λ are established, they are inserted into Eqs. (22) and (23) to yield the volume viscosity coefficients. In these equations τ'_λ and τ_λ represent the isentropic relaxation times due to process λ at constant volume (τ_{VS}) and constant pressure (τ_{PS}), respectively, and ρ_0 and a_0 are the density and sound speed at reference conditions. (In a mixture they are properties of the mixture). It is important to note that the relaxation times vary inversely with density, or in the case of an ideal gas, with pressure. The isentropic relaxation times may be appropriate for flows other than acoustical flows; in some cases the isothermal relaxation times may be more appropriate, for example, in flows through a narrow duct. At constant pressure the isothermal relaxation time is C_P^0/C_P^∞ times the isentropic relaxation time, and at constant volume this factor becomes C_V^0/C_V^∞ .

The equilibration of the translational degrees of freedom does not constitute a relaxation process per se, but can be represented as such at time scales exceeding the longest translational relaxation time.²⁹ Based on the continuity, momentum (Navier–Stokes), state, and thermal transport equations, the resulting relaxation times for translation, to a good approximation, are shown to be

$$\tau'_{tr} = \frac{(\gamma_0 - 1)(\tau_v - \tau_h)\tau_h}{\tau_v + (\gamma_0 - 1)\tau_h}, \quad (\text{A7})$$

$$\tau_{tr} = \tau'_{tr} + (\gamma_0 - 1)\tau_h, \quad (\text{A8})$$

where

$$\tau_v = \frac{4}{3} \frac{\mu}{\rho_0 a_0^2}, \quad (\text{A9})$$

$$\tau_h = \frac{K}{\rho_0 a_0^2 C_P^0}, \quad (\text{A10})$$

and K is the thermal conductivity. It is noted that $\tau'_{tr} < 0$ for nearly all gases because $\tau_v < \tau_h$ —a condition needed to conform to Truesdell’s conclusion that the sound speed increases without limit with increasing frequency.³⁰ Further, since $|\tau'_{tr}| \ll \tau_{tr}$, the first term on the right hand side of Eq. (A8) can be ignored.

Upon inserting Eqs. (A7)–(A10) into Eqs. (22) and (23), we find the volume viscosity coefficients for translational relaxation,

$$\eta_v = (\gamma_0 - 1) \frac{K}{C_P^0}, \quad (\text{A11})$$

$$\eta_P = \frac{1}{\rho_0 a_0^2} \left[\frac{\left(\frac{4}{3} \mu - \frac{K}{C_p^0} \right)}{1 + \frac{4}{3} \frac{\mu C_p^0}{(\gamma_0 - 1)K}} \right]. \quad (\text{A12})$$

In Eq. (A11) the term τ'_{ir} is ignored.

APPENDIX B: STATIONARITY OF THE SOLUTIONS FOR THE TEMPERATURE AND AFFINITY

Here we treat the question of compatibility between the variational solutions Eqs. (8) and (9) and the variational parameter assignments (16) and (14), respectively. The analysis differs for gases and liquids because of the nature of their respective relaxation times. We start with the expression for β [Eq. (16)]. In the case of gases, we specify the value of the relaxation time at a reference temperature $\tau_\lambda = \tau_\lambda(T_0)$ and note the invariance of the relaxation time-density product,

$$\tau_\lambda(T_0)\rho_0 = \tau_\lambda(T)\rho, \quad (\text{B1})$$

where $\tau_\lambda(T)$ is the relaxation time and ρ the density at temperature T . Then we make use of a Maxwell relation, the reciprocal relationship $\rho = 1/V$, and Eqs. (38) and (39) to write

$$\left(\frac{\partial \rho}{\partial S} \right)_{P\xi} = -\rho^2 \left(\frac{\partial V}{\partial S} \right)_{P\xi} = -\rho^2 \left(\frac{\partial T}{\partial P} \right)_{S\xi} = -\frac{\rho^2 V \theta^\infty T}{C_p^\infty} = -\frac{\rho}{C_p^\infty}. \quad (\text{B2})$$

Upon substituting Eqs. (B1) and (B2) into Eqs. (8) and (16) and then expanding the density [Eq. (12)], we arrive at the following:

$$\begin{aligned} \frac{D\beta}{Dt} &= \sum_\lambda \frac{\tau_\lambda(T) a_0^2 D\rho}{C_p^\infty Dt} \\ &= \sum_\lambda \frac{\tau_\lambda(T) a_0^2}{C_p^\infty} \left[\left(\frac{\partial \rho}{\partial P} \right)_{S\xi} \frac{DP}{Dt} + \left(\frac{\partial \rho}{\partial S} \right)_{P\xi} \left(\frac{\partial S}{\partial T} \right)_{P\xi} \frac{DT}{Dt} \right. \\ &\quad \left. + \left(\frac{\partial \rho}{\partial \xi_\lambda} \right)_{PS} \frac{D\xi_\lambda}{Dt} \right] \\ &= T. \end{aligned} \quad (\text{B3})$$

After rearranging Eq. (B3), substituting Eqs. (B1) and (B2), and writing out the material time derivative, we obtain the following one-dimensional partial differential equation for the temperature:

$$\tau_T \left[\frac{\partial T}{\partial t} + v(x) \frac{\partial T}{\partial x} \right] + T = T_\infty(x, t), \quad (\text{B4})$$

where

$$\tau_T = \sum_\lambda \frac{\tau_\lambda(T) \rho a_0^2}{C_p^\infty T} = \sum_\lambda \frac{\tau_\lambda \rho_0 a_0^2}{C_p^\infty T} > 0, \quad (\text{B5})$$

$$T_\infty(x, t) = \sum_\lambda \frac{\tau_\lambda \rho_0 a_0^2 T}{C_p^\infty \rho} \left[\left(\frac{\partial \rho}{\partial P} \right)_{S\xi} \frac{DP}{Dt} + \left(\frac{\partial \rho}{\partial \xi_\lambda} \right)_{PS} \frac{D\xi_\lambda}{Dt} \right]. \quad (\text{B6})$$

Because the sound speed squared a_0^2 varies linearly with temperature, the thermal time constant τ_T [Eq. (B5)] is independent of temperature except for a weak dependence of the relaxation time τ_λ , which is ignored. The first term in Eq. (B6) represents a generating term due to gas compression/rarefaction, and the second term due to the reaction. We note that Eqs. (B3)–(B6) are valid for a nonreacting gas ($\xi_\lambda = 0$).

The solution to Eq. (B4) is the following:³¹

$$T = \exp\left(-\frac{t}{\tau_T}\right) \left[\Phi(u) + \frac{1}{\tau_T} \int_{t_0}^t T_\infty(t', u) \exp\left(\frac{t'}{\tau_T}\right) dt' \right], \quad (\text{B7})$$

where $u = x - v(x)t$ (u treated as a parameter of the integration) and $\Phi(u)$ is an arbitrary function.

It is easily shown that T reaches a stationary solution after a sufficiently long time, as long as $\Phi(u)$ is well behaved and T_∞ is bounded (as required by physical considerations). If the first condition is true, then the first term vanishes asymptotically. If the second condition is true, then let T_B be the bound on T_∞ and we have as $t \rightarrow \infty$

$$\begin{aligned} &\exp\left(-\frac{t}{\tau_T}\right) \frac{1}{\tau_T} \int_{t_0}^t T_\infty(t', u) \exp\left(\frac{t'}{\tau_T}\right) dt' \\ &\leq \exp\left(-\frac{t}{\tau_T}\right) \frac{1}{\tau_T} \int_{t_0}^t T_B \exp\left(\frac{t'}{\tau_T}\right) dt' \\ &= T_B. \end{aligned} \quad (\text{B8})$$

Thus Eq. (8) leads to a stationary value of the temperature.

In the case of liquids, since liquid densities are only weak functions of temperature, the temperature dependence of β is controlled almost exclusively by the temperature dependence of the relaxation time. As pointed out on page 403 of Ref. 16, the relaxation time has a negative temperature coefficient, thus leading to the temperature variation described by Eq. (B4) and the same conclusion regarding stationarity.

The analysis for the affinity A_λ follows a similar line. Here we use the chain rule [Eq. (94) of Ref. 10] and Eq. (41) to write

$$\begin{aligned} \left(\frac{\partial \rho}{\partial \xi_\lambda} \right)_{PS} &= -\rho^2 \left(\frac{\partial V}{\partial \xi_\lambda} \right)_{PS} \\ &= -\rho^2 \left[\left(\frac{\partial V}{\partial \xi_\lambda} \right)_{PT} + \left(\frac{\partial V}{\partial T} \right)_{P\xi_\lambda} \left(\frac{\partial T}{\partial S} \right)_{P\xi_\lambda} \left(\frac{\partial S}{\partial \xi_\lambda} \right)_{PT} \right] \\ &= -\rho^2 \left(\Delta V_\lambda - \frac{V \theta^\infty T \Delta H_\lambda}{C_p^\infty T} \right) \\ &= \rho \left(-\frac{\Delta V_\lambda}{V} + \frac{\Delta H_\lambda}{C_p^\infty T} \right). \end{aligned} \quad (\text{B9})$$

Upon substituting Eqs. (B1) and (B9) into Eqs. (9) and (14),

and then expanding the density [Eq. (12)], we arrive at the following:

$$\begin{aligned} \frac{D\alpha_\lambda}{Dt} &= -\frac{\tau_T(T)a_0^2}{f_\lambda} \frac{D\rho}{Dt} \\ &= -\frac{\tau_T(T)a_0^2}{f_\lambda} \left[\left(\frac{\partial\rho}{\partial P} \right)_{S\xi_\lambda} \frac{DP}{Dt} + \left(\frac{\partial\rho}{\partial S} \right)_{P\xi_\lambda} \frac{DS}{Dt} \right. \\ &\quad \left. + \left(\frac{\partial\rho}{\partial\xi_\lambda} \right)_{PS} \left(\frac{\partial\xi_\lambda}{\partial A_\lambda} \right)_{PS} \frac{DA_\lambda}{Dt} \right] \\ &= -A_\lambda. \end{aligned} \quad (\text{B10})$$

After rearranging Eq. (B10), substituting Eqs. (B1) and (B9), and writing out the material time derivative, we obtain the following one-dimensional partial differential equation for the affinity:

$$\tau_A \left[\frac{\partial A_\lambda}{\partial t} + v(x) \frac{\partial A_\lambda}{\partial x} \right] + A_\lambda = A_\lambda^\infty, \quad (\text{B11})$$

where

$$\begin{aligned} \tau_A &= \frac{\tau_\lambda(T)a_0^2}{f_\lambda} \left(-\frac{\Delta V_\lambda}{V} + \frac{\Delta H_\lambda}{C_p^T} \right) \left(\frac{\partial\rho}{\partial\xi_\lambda} \right)_{PS} \left(\frac{\partial\xi_\lambda}{\partial A_\lambda} \right)_{PS} \\ &= \frac{L_\lambda \tau_\lambda \rho_0 a_0^2}{f_\lambda} \left(-\frac{\Delta V_\lambda}{V} + \frac{\Delta H_\lambda}{C_p^T} \right)^2 \\ &> 0, \end{aligned} \quad (\text{B12})$$

$$\begin{aligned} A_\lambda^\infty &= \frac{\tau_\lambda \rho_0 a_0^2}{f_\lambda} \left(-\frac{\Delta V_\lambda}{V} + \frac{\Delta H_\lambda}{C_p^T} \right) \\ &\quad \times \left[\left(\frac{\partial\rho}{\partial P} \right)_{S\xi_\lambda} \frac{DP}{Dt} + \left(\frac{\partial\rho}{\partial S} \right)_{P\xi_\lambda} \frac{DS}{Dt} \right]. \end{aligned} \quad (\text{B13})$$

The solution, similar to Eq. (B7), will permit conclusions to be drawn about the stationarity of the affinity.

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