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Some Properties of Gases with Vibrational Relaxation when Viewed as Materials with Memory

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Preface

In recent years there has been developed a general thermodynamics of materials for which the stress, temperature, and energy depend on the histories of the strain and another variable, such as the entropy. Here we discuss the compatibility of that thermodynamical theory with a special theory of mechanical dissipation which has been successfully used in physical gas dynamics: the theory of gases with vibrational relaxation. Granting, without detailed study, certain technical points involving the uniqueness and stability of solutions of a class of non-linear integral equations, we observe that the theory of relaxing gases can be imbedded in the framework of the thermodynamics of materials with memory, provided only that we identify "the temperature" of the thermodynamical theory with the "translational" or ("active-mode") temperature of the internal-relaxation theory.

We conclude our discussion with a report of a calculation we have made of the isentropic, pressure-volume, relaxation function exhibited by a gas with vibrational relaxation when regarded as a linearly viscoelastic material.

!• Materials with Memory

To place the theory of gases with vibrational relaxation within the domain of the thermodynamics of materials with memory[1], we do not need the memory theory in its full generality. We may focus our attention on materials for which the stress tensor reduces to pure hydrostatic pressure and for which the pressure p(t), the temperature d(t), and the specific internal energy e(t) (per unit mass) at a material point X are given by functionals of the histories up to time t of the specific volume *x>* • 1/p and specific entropy *r*\ at X:

$$p(t) = \underline{\underline{P}}\,O)\wedge), \tag{l.i}$$

$$\theta(t) = \underline{\underline{t}}\,o\wedge n*), \tag{1.2}$$

$$\epsilon(t) = \underline{\underline{e}}\,0\wedge,\wedge). \tag{1.3}$$

In a flowing material the specific volume and the specific entropy (per unit mass) are functions of the material point X and the time T:

$$X> \gg D(X,T), \qquad T| = tl(X,T). \tag{1.4}$$

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[1] B. D. Coleman, Arch. Rational Mech. Anal. **17**, 1, 230 (1964).

The histories up to time t of x> and r\ at X are the functions $X)^t$ and $r\backslash^t$, over [0,oo), defined by

$$\hat{}(s) = u(X,t-s), \qquad ri^t(s) = T)(X,t-s), \qquad 0 \leq s < 00. \qquad (1.5)$$

We assume that the functionals £> £> an<* £ obey the principle of fading memory in the form proposed by Coleman and Noll[2,3]. To state this principle in our present context we let h denote an influence **function,** i.e. a positive, monotone[4], continuous function on [0,oo) decaying to zero fast enough to be square integrable, and we define the norm |JA^t]| of a pair of histories A^t = ('0^t,T]^t) by

$$IIA^{t}I = A0)^2 + \hat{}(0)^2 + \int_0 (\hat{}^t(s)^2 + T_1^t(s)^2)h(s)^2 ds. \qquad (1.6)$$

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[2] B. D. Coleman and W. Noll, Arch. Rational Mech. Anal. 6, 355 (1960).

[3] B. D. Coleman and W. Noll, Reviews Mod. Phys. 33, 239 (1961), erratum: ibid. 36, 1103 (1964).

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[4] Coleman and Mizel[5] have recently shown that conditions on h weaker than monotonicity suffice for most of the theory of fading memory.

[5] B. D. Coleman and V. J. Mizel, Arch. Rational Mech. Anal. 23, **87 (1966).**

The common domain of the functionals p, t, and e is taken to be an open subset Ju in the cone C of pairs A ^{t}of positive-valued functions V) ,^{t}r\ ^{t} with |A^{t}I finite. The principle of fading memory is the assertion that for some influence function h(which we need not specify) the functionals p, t, and e are continuously differentiable, in the sense of Fréchet, throughout &j with respect to the norm ||*||.

Let v^t be an arbitrary history in £3 and let Q be a number; the function V^Afl defined by

(t>7\fl)(s) - J (V(0) + fl, a - 0/ \V^z(S), 0 < S < ∞, (1.7)

is called the jump continuation of x>^{t} with jump SI. An analogous equation defines the history TJ^t/\H, given r\ and H. Jump continuations^1 may be used to define the "D-operators", D$_\upsilon$ and D$_\eta$, which play a central role in the thermodynamics of materials with memory. Let f be a functional standing for p, t, or e. Clearly, for a given pair \) ,^{t}r\ ^t_y the number f(x>^{t}\Q,T\ ^{t}) is determined by a function f of the jump Q:

f(fl) - fO^Afl,^). (1.8)

The assumption that f is differentiable over fj relative to the norm (1.6) implies that f(&) is a differentiable function of fl; i.e. that

35 £("W^ = ^f(fl) (1.9)

exists for each pair υ^t, η^t in $\mathcal{D}$ and for an interval of values of Ω including 0. The operator D_υ is defined by

$$D_{\upsilon}\underline{f}(\upsilon^t,\eta^t) = \frac{\partial}{\partial\Omega}\underline{f}(\upsilon^t\wedge\Omega,\eta^t)\Big|_{\Omega=0}, \tag{1.10}$$

and similarly

$$D_{\eta}\underline{f}(\upsilon^t,\eta^t) = \frac{\partial}{\partial\Xi}\underline{f}(\upsilon^t,\eta^t\wedge\Xi)\Big|_{\Xi=0}. \tag{1.11}$$

Since they represent partial differentiation with respect to present values holding the past history fixed, $D_\upsilon \underline{f}$ and $D_\eta \underline{f}$ are called the <u>instantaneous derivatives</u> of $\underline{f}$ with respect to υ and η, respectively. Working in a more general theory for which the stress tensor is not necessarily a pure pressure and which accounts for the presence of heat conduction, Coleman[6] has found the complete set of restrictions which the constitutive functionals must obey in order that the entropy production never be negative in a thermodynamic process. Among these restrictions are the following: $\underline{e}$ must determine $\underline{p}$ through the <u>pressure-relation</u>,

$$\underline{p} = -D_{\upsilon}\underline{e}, \tag{1.12}$$

and $\underline{t}$ through the <u>temperature relation</u>,

$$\underline{t} = D_{\eta}\underline{e}. \tag{1.13}$$

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[6] Reference 1, Thm. 1 on p. 19 and Thm. 6 on p. 33.

In other words, knowledge of a single functional $\underset{=}{e}$ suffices for the determination of the present values e(t), p(t), and 9(t), when the histories $X)^t$ and $T\backslash^t$ are given:

$$€(t) \ll \underset{=}{e}tf,\overset{\upsilon^t}{\wedge}), \qquad p(t) - -D\wedge'V), \qquad \theta(t) - D\wedge O\wedge T,*). \tag{1.14}$$

Let p_o be the pressure the fluid would exhibit had it always been at rest with some particular fixed specific volume u_o and fixed specific entropy $r\backslash_o$. We may write

$$P_o - \underset{=}{P}(0^+_o,T^+_o) \tag{1.15}$$

where $x\gamma^\dagger_o$ and $T\!I^\dagger_o$ are the constant histories defined by

$$\wedge<^s> \quad ^s \quad V \qquad \wedge l^M \quad ^s \quad V \qquad 0 \leq s < co. \tag{1.16}$$

If we now put

$$p^* = \underset{=}{p}(\upsilon^t,\eta^t_o) \tag{1.17}$$

where x^t is arbitrary, then it follows from the principle of fading memory that[7]

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[7] Vid. Coleman and Noll[3] and Coleman[1] (pp. 245-249), who give the general argument for the three-dimensional case; the present simpler case is discussed by Coleman and Gurtin[8] (pp. 272 and 289).

[8] B. D. Coleman and M. E. Gurtin, Arch. Rational Mech. Anal. 1£, 266 (196^)

$$P^{*} - P_o - G(0)\Delta\upsilon(t) + \int_0^{\infty} \mathrm{Ao}(t-s)\frac{d}{d}j\, G(s)ds + 0(6) , \qquad (1.18)$$

where

$$\mathrm{Av}>(t-s) - \wedge(s) - x>_Q - D(t-s) - x>_o \qquad (1.19)$$

may be called the <u>volume increment,</u> and 6, given by

$$6 \ll \mathrm{lA^{\wedge}i} \qquad (1.20)$$

is small if Ao has always been small. The function G, called the (isentropic) <u>pressure-volume relaxation function corresponding to</u> $x>_o$ <u>and</u> $i\backslash_o$, is determined when the functional p is specified. For a given material different choices of $J]_o$ and $x>_o$ give rise to different functions 6. The equation (1.18) states that if the entropy is held fixed and the volume increment is kept small, the pressure increment for a non-linear fluid with fading memory is given, approximately, by a constitutive equation of the type occurring in the linear theory of viscoelasticity.

It of course follows from (1.15) that p_o is given by a function $\hat{p}$ of D_o and $T)_o$ alone:

$$p_0 = \hat{p}(\upsilon_{KJ}, \eta_{\nabla}). \qquad (1.21)$$

This function $\hat{p}$ determines the equilibrium pressure-volume-entropy relation for the gas. It turns out that

$$G(\infty) = \lim_{s\to\infty} G(s) = \frac{\partial}{\partial\upsilon_o}\hat{p}(\upsilon_o, \eta_o) \qquad (1.22)$$

while

$$G(0) = \underline{P}\ \wedge,\eta_{0}^{\dagger}). \tag{1.23}$$

The inequality

$$G(0) \leq G(\sim) \tag{1.24}$$

follows from restrictions which the second law of thermodynamics places on our constitutive functionals.[9]

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[9] The inequality (1.24) is a corollary of a theorem given by Coleman in ref. 1 (p. 249). It is clear that Coleman's theorem remains valid if his "stress-relaxation modulus at constant temperature" is replaced by a stress-relaxation modulus at constant entropy.

2. Constitutive Equations for Relaxing Gases

The principle source of dissipation of mechanical energy in gases undergoing rapid compression is often the gradual transfer of molecular motion from translational modes, where the motion contributes to the pressure, to internal modes, where it does not. For diatomic molecules one can usually assume that the vibrational and rotational modes are in equilibrium and that a single relaxation process accounts for the transfer of energy from the translational mode to the vibrational mode.[10,11]

When such is the case, one expresses the specific internal energy of the gas as a sum

$$\epsilon = \epsilon_V + \epsilon_A \qquad (2.1)$$

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[10] Cf. K. F. Herzfeld and F. O. Rice, Phys. Rev. &, 691 (1928).

[11] For quantum statistical theories of this type of relaxation see Rutgers[12], Knesser[13], Landau and Teller[14], Rubin and Shuler[15], and Montroll and Shuler[16].

[12] A. J. Rutgers, Ann. Physik 16, 350 (1933).

[13] H. O. Knesser, Ann. Physik 16, 360 (1933).

[14] L. Landau and E. Teller, Physik. Z. Sowjetunion 10, 34 (1936).

[15] R. J. Rubin and K. E. Shuler, J. Chem. Phys. 25, 59 (1956).

[16] E. W. Montroll and K. E. Shuler, J. Chem. Phys. 26, 454 (1957).

of the energy $£_V$ associated with the vibrational mode and the combined energy $€_A$ of the translational and rotational modes, which are called active modes. Similarly, the specific entropy r\ of the gas may be expressed as a sum of a vibrational contribution $r\backslash_V$ and an active contribution $r\backslash_A$:[17]

$$\eta = \eta_V + \eta_A. \tag{2.2}$$

When discussing the dynamical behavior of gases with vibrational relaxation one makes constitutive assumptions equivalent to the following;

(1) $€_A$ is given by a function $\overline{€}_A$ of $r\backslash_A$ and the specific volume x>, while $€_V$ is given by a function $\overline{€}_V$ of $T\backslash_V$ alone:

$$\epsilon_A \;\text{''}\; \hat{}A\hat{}V\hat{} \qquad \epsilon_V = \bar{\epsilon}_V(\eta_V). \tag{2.3}$$

The functions $\overline{€}_A$ and $\bar{e}_V$ obey the inequalities

$$\frac{\partial\bar{\epsilon}_A}{\partial\eta_A} > 0, \qquad \frac{\partial\bar{\epsilon}_A}{\partial\upsilon} < 0, \qquad \frac{\partial^2\bar{\epsilon}_A}{\partial\eta_A^2} > 0, \qquad \frac{\partial^2\bar{\epsilon}_A}{\partial\upsilon^2} > 0, \tag{2.4}$$

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[17] Insofar as the researches of Rubin and Shuler[5] and Montroll and Shuler[6] justify the concept of a vibrational temperature 0_V, they also justify the concept of a vibrational entropy. For, having 6_V and e_V, we can define c_V by (2.JP) and then define $r\backslash_V$, to within a constant, as the integral of $-r\frac{\quad}{\sigma V}{}^{\theta}_{V}$. Similar remarks hold for 6_A, $€_A$, and TJ_A.

and

$$\frac{d\bar{\epsilon}_V}{d\eta_V} > 0 \,, \qquad \text{d \%} \quad \wedge \text{"} > 0 \tag{2_5}$$

for all TJ$_A$, V>, and T^.

(2) The pressure is given by

$$p = \bar{p}(\upsilon, \eta_A) = -\frac{\partial}{\partial \upsilon} \bar{\epsilon}_A(\upsilon, \eta_A) > 0. \tag{2.6}$$

(3) The active-mode temperature (or translational temperature) 6.$_A$ and the vibrational temperature 6$_V$ are given by

θ_A = A\` ′ 'A′ 'A

It is a consequence of (2.3), (2.4)$_{3;}$ (2.5)$_2$, and (2.7) that i"$_A$ and $\bar{e}$^ determine functions $\tilde{e}_A$ and $\tilde{e}_V$ such that

$$\epsilon_A = \tilde{\epsilon}_A(\upsilon, \theta_A), \qquad \epsilon_V = \tilde{\epsilon}_V(\theta_V). \tag{2.8}$$

(4) The material time-derivative of the vibrational energy obeys an equation of the form

$$\dot{\epsilon}_V = \kappa(\upsilon, \theta_A)\, l\tilde{\epsilon}_V(e_A) - \epsilon_V I \tag{2.9}$$

with K always positive.[18]

The active mode heat capacity (at constant volume) c_A and the vibrational heat capacity c_V are defined by

$$c_A = \frac{d}{d\theta_A}\tilde{\epsilon}_A(\upsilon,\theta_A) > 0, \qquad c_V = \frac{d}{d\theta_V}\tilde{\epsilon}_V(\theta_V) > 0. \qquad (2.10)$$

The positivity of c_A and c_V follows from $(2.4)_3$, $(2.5)_2$, and (2.7).

If the gas has always been at equilibrium then $\dot{\epsilon}_V \equiv 0$, and $(2.8)_1$ and (2.9) imply $\tilde{\epsilon}_V(\theta_A) = \tilde{\epsilon}_V(\theta_V)$; this fact, when combined with $(2.10)_2$, yields $\theta_A = \theta_V$; i.e. at equilibrium the temperatures of the active and vibrational modes must be equal.

Given the histories of υ and θ_A and the value $\epsilon_V(t_o)$ of ϵ_V at some arbitrary time t_o, we can use (2.9) to find the value of ϵ_V at any time t; for, (2.9) has the solution

$$\epsilon_V(t) = e^{-f(t)}\left\{\epsilon_V(t_o) + \int_{t_o}^{t}\kappa\big(\upsilon(\tau),\theta_A(\tau)\big)\tilde{\epsilon}_V\big(\theta_A(\tau)\big)e^{f(\tau)}d\tau\right\}, \qquad f(t) = \int_{t_o}^{t}\kappa\big(\upsilon(\tau),\theta_A(\tau)\big)d\tau. \qquad (2.11)$$

It follows from $(2.7)_1$ that K may be expressed as a function K of η_A

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[18] The studies of Rubin and Shuler,[15] and Montroll and Shuler[16] indicate that since (2.7) holds precisely for their harmonic oscillator model, it should hold near to equilibrium for more general models. Cf. Vincenti and Kruger.[19]

[19] W. G. Vincenti and C. H. Kruger, ~~Introduction to Classical Gas Dynamics~~, (John Wiley, New York, 1965), Chapter VII.

and "0:

$$\bar{\kappa}(\upsilon,\eta_A) \overset{\text{def}}{=} \kappa\left(\upsilon,\bar{\theta}_A(\upsilon,\eta_A)\right). \qquad (2.12)$$

Therefore, if we put $_o t$ • t— £ and use (2*2)^ (2*3)o^ and (2*7)i, we may cast (2.11) into the form

$$\left.\begin{aligned}\bar{\epsilon}_V\left(\eta_V(t)\right) &= e^{-f(t)}\left\{\bar{\epsilon}_V\left(\eta_V(t-\zeta)\right) + \int_{t-\zeta}^{t}\bar{\kappa}\left(\upsilon(\tau),\ \eta(\tau)-\eta_V(\tau)\right)\tilde{\epsilon}_V\left(\bar{\theta}_A\left(\upsilon(\tau),\ \eta(\tau)-\eta_V(\tau)\right)\right)e^{f(\tau)}d\tau\right\},\\ f(t) &= \int_{t-\zeta}^{t}\bar{\kappa}\left(\upsilon(\tau),\ \eta(\tau)-\eta_V(\tau)\right)d\tau.\end{aligned}\right\} \quad (2.13)$$

We make the reasonable assumption that the functions e $_V$ and /c are such that, given TJ$_V$ (t-£), the non-linear integral equation (2,13) has a unique solution for TJ$_V$(T), t-^ < T < t, whenever O(T) and T](T) are prescribed for all T in [t-£,t]. [A careful study of this point would involve some difficult analysis.] If v>^{t} and r\$^t$ describe histories of a material which has been out of equilibrium only for a time interval of length £, i^e. if x>^{t} and r\$^t$ are such that for some *$_o$,TJ$_o$, and £ > 0,

$$x>^l(s) \text{ « } D_Q, \quad t|^t(s) \text{ « } t|_o \quad \text{for} \quad s \geq g, \qquad (2.14)$$

then, since 0_A • Q_V at equilibrium, T]$_V$ (t-Q is a solution of

$$\bar{\theta}_A\left(\upsilon_o,\ \eta_o-\eta_V(t-\zeta)\right) = \bar{\theta}_V\left(\eta_V(t-\zeta)\right). \qquad (2.15)$$

Let us now observe that the present theory is compatible with the assertion that the vibrational entropy $T_V(t)$ is determined when the histories of the volume o and total specific entropy r\ are specified:

T|v(t) = HO*,!)*). (2.16)

Indeed, for histories of the type (2.14), the equations (2.13) and (2.15) give us a system of equations which can be used, in principle, to calculate H(D^t,T^t). Under the norm (1.6), functions of the type (2.14) are dense in the cone C of pairs A^t of positive-valued functions for which ‖A^t‖ < ∞. Hence, if the functional H is continuous over an open region Jj in G, knowledge of ¥L(\> ,T)) for functions of the type (2.14) determines H throughout & . We shall leave open the interesting problem of determining the smoothness properties given to H by the identity (2.13); instead we shall merely assume that H is continuously Frechet-differentiable relative to the norm (1.6).

It is clear that any functional H obeying (2.13) must be such that

$$D_\upsilon \underline{\underline{H}}(\upsilon^t,\eta^t) \overset{\text{def}}{=} \frac{\partial}{\partial\Omega} \underline{\underline{H}}(\upsilon^t\wedge\Omega,\eta^t)\Big|_{\Omega=0} = 0,$$

$$D_\eta \underline{\underline{H}}(\upsilon^t,\eta^t) \overset{\text{def}}{=} \frac{d}{d\Xi} \underline{\underline{H}}(\upsilon^t,\eta^t\wedge\Xi)\Big|_{\Xi=0} = 0. \qquad (2.17)$$

It follows from (2.1)-(2.3) and (2.16) that

€(t) « €.(u(t), Ti(t)-H(\3^t,TI^t)) + 7$_t$/H(\J^t,Ti^t)) =S= e(v»^{t},Ti^t): (2.18)

i.e. €(t) is given by an equation which can be regarded as a particular example of (1.3); the functions €$_A$ and €$_V$ appearing here are those in

(2.3). Similarly

$$P(t) = \bar{p}\big(\upsilon(t),\ \eta(t)-\underline{\underline{H}}(\upsilon^t,\eta^t)\big) \overset{\text{def}}{=\!=} \underline{\underline{p}}(\upsilon^t,\eta^t), \qquad (2.19)$$

and

$$e_A(t) = \bar{\theta}_A\big(\upsilon(t),\ \eta(t)-\underline{\underline{H}}(\upsilon^t,\eta^t)\big) \overset{\text{def}}{=\!=} \underline{\underline{t}}(\upsilon^t,\eta^t). \qquad (2.20)$$

where $\bar{p}$ and $\bar{\theta}_A$ are the functions occurring in $(2.6)_{1}$ and $(2.7)_{1}$.

Let us use (2.18), (1.10), and (2.17) to compute $D_{\underline{\underline{\upsilon}}}\underline{\underline{e}}$:

$$\begin{aligned} D_{\underline{\underline{\upsilon}}}\underline{\underline{e}}(\upsilon^t,\eta^t) &= \Big[\frac{\partial}{\partial\Omega}\,\bar{\epsilon}_A\big(\upsilon(t)+\Omega,\ \eta(t)-\underline{\underline{H}}(\upsilon^t\wedge\Omega,\eta^t)\big) + \frac{\partial}{\partial\Omega}\,\bar{\epsilon}_V\big(\underline{\underline{H}}(\upsilon^t\wedge\Omega,\eta^t)\big)\Big]_{SH)} \\ &= \Big[55\ \epsilon_A(\upsilon,\eta_A) + D_{\underline{\underline{\upsilon}}}\underline{\underline{H}}(\upsilon^t,\eta^t)\Big[\frac{-\partial}{\partial\eta_A}\,\epsilon_A(\upsilon,\eta_A) + \frac{d}{d\eta_V}\,\bar{«}_V(\eta_V)\Big]\Big]_{\substack{V\ -\ 13(t) \\ \eta_V=\underline{\underline{H}}(\upsilon^t,\eta^t) \\ \eta_A=\eta(t)-\underline{\underline{H}}(\upsilon^t,\eta^t)}} \\ &= \frac{\partial}{\partial\upsilon}\,€_A(\upsilon,\eta_A)\Big|_{\substack{\upsilon=\upsilon(t) \\ \eta_A=\eta(t)-\underline{\underline{H}}(\upsilon^t,\eta^t)}} \end{aligned} \qquad (2.21)$$

Hence, by $(2.6)_2$ and (2.19), we here have

$$D_{\underline{\underline{\upsilon}}}\underline{\underline{e}}(\upsilon^t,\eta^t) = -\bar{p}\big(\upsilon(t),\ \eta(t)-\underline{\underline{H}}(\upsilon^t,\eta^t)\big) = -\underline{\underline{p}}(\upsilon^t,\eta^t). \qquad (2.22)$$

This equation has precisely the form of the general pressure relation (1.12).

By an analogous argument, again using (2.18), (1.10), and (2.17), we get

$$D_{\underline{\underline{\eta}}}\underline{\underline{e}}(\upsilon^t,\eta^t) = \frac{\partial}{\partial\eta_A}\,\bar{\epsilon}_A(\upsilon,\eta_A)\Big|_{\substack{\upsilon=\upsilon(t) \\ \eta_A=\eta(t)-\underline{\underline{H}}(\upsilon^t,*!^t)}}\ , \qquad (2.23)$$

and therefore $(2.7)_1$ and (2.20) yield

$$D_{\eta}\underline{\underline{e}}(\upsilon^{t},\eta^{t}) = e_{A}(v»(t),\ \mathrm{TKO}-\underline{\underline{\mathrm{H}}}\mathrm{OJ}',\wedge)) - \underline{\underline{t}}\wedge,\wedge). \qquad (2.24)$$

This relation has the form of the temperature relation (1.13) provided that we identify the temperature *9* of (1.2) with our present active-mode temperature Q_A.

3. The Pressure-Volume Relaxation Function

The pressure-volume relaxation function G corresponding to a fixed volume "0_o and fixed entropy $r\backslash_o$ was defined in equations (1.15)-(1.20). Using the identity (2.13) for the functional $\underline{H}$ defined in (2.16) and appearing in (2.19), one may calculate G for gases with vibrational relaxation. We here report the results of such a calculation.

Let TJ^{*}_{A}. be the value taken by the active-mode entropy when the gas is in equilibrium with $X>$ « $x>_{o}$ and $t\backslash$ » $T]_{o}$. Of course, since 0_{A} » Q_{V} at equilibrium, T^{*}_{A} is the solution of the equation

$$e\,l = \bar{\theta}_{A}(\upsilon_{o},\eta^{*}_{A}) = \bar{\theta}_{V}(\eta_{o}-\eta^{*}_{A}) = \theta^{*}_{V} \tag{3.1}$$

We find that the initial value G(0) and initial slope G'(0) of G are given by **the** formulae

$$G(0) = \frac{\partial}{\partial\upsilon}\bar{p}(\upsilon,\eta_{A})\Big|_{\substack{\upsilon=\upsilon_{o}\\ \eta_{A}=\eta^{*}_{A}}} , \tag{3.2}$$

$$G'(0) = \frac{\kappa^{*} c^{*}_{V}}{\theta^{*}_{A}}\frac{\partial}{\partial\upsilon}\bar{\theta}_{A}(\upsilon,\eta_{A})\Big|_{\substack{\upsilon=\upsilon_{o}\\ \eta_{A}=\eta^{*}_{A}}} \tag{3.3}$$

where $\bar{p}$ and $\bar{0}_{A}$ are the functions occurring in $(2.6)_{1}$ and $(2.7)_{1}$, while c^{*}_{V} and $/c^{*}$ are the values of the vibrational heat capacity c_{v} and the rate coefficient κ in the equilibrium state υ_o, η_o:

$$c_V^* = \frac{d}{d\theta_V}\tilde{\epsilon}_V(\theta_V)\Big|_{\theta_V=\theta_V^*}, \tag{3.4}$$

$$\kappa^* = \kappa(\upsilon_o,\theta_A^*) = \bar{\kappa}(\upsilon_o,\eta_A^*). \tag{3.5}$$

The numbers G(0) and G'(0) occur frequently in theories of wave propagation in viscoelastic materials.

The complete formula for G(s), $s \in [0,\infty)$, turns out more complicated than expected; to state our result let us put

$$\left.\begin{aligned} \psi &= \frac{\left(\dfrac{\partial\bar{\kappa}}{\partial\upsilon}\right)\dfrac{\partial\bar{\theta}_A}{\partial\upsilon}}{\dfrac{\partial\bar{\kappa}}{\partial\eta_A}}\Bigg|_{\substack{\upsilon=\upsilon_o\\ \eta_A=\eta_A^*}}, \\ \alpha &= -\frac{\epsilon_V^*}{\theta_A^*}\frac{\partial\bar{\kappa}}{\partial\upsilon}\frac{\partial\bar{\theta}_A}{\partial\upsilon}\Bigg|_{\substack{\upsilon=\upsilon_o\\ \eta_A=\eta_A^*}}, \qquad \beta = \frac{\kappa^* c_V^*}{\theta_A^*}\frac{\partial\bar{\theta}_A}{\partial\eta_A}\Bigg|_{\substack{\upsilon=\upsilon_o\\ \eta=\eta_A^*}}. \end{aligned}\right\} \tag{3.6}$$

We find that the Laplace transform

$$F(q) = \int_0^\infty [G(0)-G(s)]e^{-sq}ds \tag{3.7}$$

obeys the formula

$$F(q) = \frac{\kappa^{*2}\alpha - G'(0)\kappa^* q - G'(0)q^2}{q[-(\kappa^{*2}\alpha/\psi) + \kappa^*\beta q + (\kappa^*+\beta)q^2 + q^3]}. \tag{3.8}$$

Letting $-\kappa_0, -\kappa_1$, and $-\kappa_2$ be the three roots of the following cubic equation in q,

$$q^3 + (\kappa^* + \beta)q^2 + \kappa^*\beta q - (\dot{\kappa}^{*2}\alpha/\psi) = 0, \tag{3.9}$$

and putting

$$\Gamma_i = \kappa_i^2 G'(0) - \kappa_i\kappa^* G'(0) - \kappa^{*2} a, \qquad i = 0,1,2, \tag{3.10}$$

one may invert (3.7) and (3.8) to obtain

$$G(s) = G(0) + \psi - \frac{\Gamma_0 e^{-\kappa_0 s}}{\kappa_0(\kappa_1-\kappa_0)(\kappa_2-\kappa_0)} - \frac{\Gamma_1 e^{-\kappa_1 s}}{\kappa_1(\kappa_0-\kappa_1)(\kappa_2-\kappa_1)} - \frac{\Gamma_2 e^{-\kappa_2 s}}{\kappa_2(\kappa_0-\kappa_2)(\kappa_1-\kappa_2)}\,. \tag{3.11}$$

Thus although the materials we are considering obey the simple relaxation formula (2.9) for the energy, when viewed as linearly viscoelastic materials their isentropic pressure-volume relations may be expected to exhibit <u>three</u> relaxation times, $1/\kappa_i$, i = 0,1,2. It follows from (3.11), (3.2) and $(3.6)_1$ that

$$G(\infty) = G(0) + \psi = \left[\partial\bar{p}/\partial v + \frac{(\partial\bar{\kappa}/\partial v)\partial\bar{\theta}_A/\partial v}{\partial\bar{\kappa}/\partial\eta_A}\right]_{\substack{v=v_0\\ \eta_A=\eta_A^*}} \tag{3.12}$$

Of course, the formulae $(3.6)_1$, (3.11), and (3.12) become meaningless in the special and physically unlikely case

$$\frac{\partial\bar{\kappa}}{\partial v} = \frac{\partial\bar{\kappa}}{\partial\eta_A} = 0. \tag{3.13}$$

When (3.13) holds, in place of (3.11) and (3*12) we obtain the simple expressions

$$G(s) = 6(0) + \frac{G'(0)}{\beta}(1 - e^{-\beta s}) \qquad (3.14)$$

and

$$G(«o) = G(0) + \underline{G'(0)} = \left[\partial\bar{p}/\partial\upsilon + \frac{(\partial\bar{\theta}_A/\partial\upsilon)^2}{\partial\bar{\theta}_A/\partial\eta_A}\right]_{\substack{\upsilon=\upsilon_o\\ \eta_A=\eta_A^*}} \qquad (3.15)$$

with G(0), G'(0), and 0 still given by (3.2), (3.3), and (3.6)$_{3>}$

We say that a relaxing gas is ideal if p » *RG./x>,* i.e. if

$$\upsilon\bar{p}(\upsilon,\eta_A) = R\bar{\theta}_A(\upsilon,\eta_A) \qquad (3.16)$$

where the constant R is equal to the ratio of the universal gas constant to the molceular weight of the gas. It is not difficult to show that for an ideal gas €$_A$ must be expressible as a function of d$_A$ alone[20]:

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[20] The argument to be used is that spelled out by R. Courant and K. 0. Friedrichs, Supersonic Flow and Shock Waves, (Interscience, New York, 1948), pp. 8 and 9; we assume, of course, that d$\bar{p}$/di) < 0 and that $\partial^2\bar{p}/\partial\upsilon^2 > 0$.

$$\epsilon_A = \tilde{\epsilon}_A(\theta_A). \qquad (3.17)$$

Putting

$$\gamma = \frac{R + c_A^*}{c_A^*}, \qquad c_A^* = \frac{d}{d\theta_A} \sim \theta_A)\Big|_{\theta_A=\theta_A^*}, \qquad (3.18)$$

we find that when the material is an ideal gas the formulae (3.2) and (3.3) yield

$$G(0) - -\frac{R9{*}7}{X)}f- , \qquad (3.19)$$

$$G'(0) = \frac{R^2\kappa^* c\,\mathrm{k}}{c_A^{*2}\upsilon_o^2}, \qquad (3.20)$$

and the numbers *ij/f a, ixxni* p are given by

$$\psi = -\frac{R0\,A^*}{c_A^*\upsilon_o}\,\frac{(\partial\bar{\kappa}/\partial\upsilon)}{(\partial\bar{\kappa}/\partial\eta_A)}\Bigg|_{\substack{\upsilon=\upsilon_o\\ \eta=\eta_A^*}}, \qquad \alpha = \frac{R\,2V\,c^*}{c_A^*\,V\,o}\,\frac{\partial\bar{\kappa}}{\partial\upsilon}\Bigg|_{\substack{\upsilon=\upsilon_o\\ \eta=\eta_A^*}}, \qquad \beta = \kappa^*\frac{c\,\gamma^*-£}{c_A}. \qquad (3.21)$$

For an ideal gas, in the special case (3.13) we have

$$G(s) = --\frac{R6^*}{X)_o}f\left[1 + (7^* - l)\exp\left(-\frac{\kappa^* c_V^*}{c_A^*}s\right)\right]. \qquad (3.22)$$

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In recent years there has been developed a general thermodynamics of materials for which the stress, temperature, and energy depend on the histories of the strain and another variable^ such as the entropy. Here we discuss the compatibility of that thermodynamical theory with a special theory of mechanical dissipation which has been successfully used in physical gas dynamics: the theory of gases with vibrational relaxation. Granting, without detailed study, certain technical points involving the uniqueness and stability of solutions of a class of non-linear integral equations, we observe that the theory of relaxing gases can be imbedded in the framework of the thermodynamics of materials with memory, provided only that we identify "the temperature" of the thermodynamical theory with the "translational" or ("active-mode") temperature of the internal-relaxation theory.

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