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Foundations of Linear Viscoelasticity*

BERNARD D. COLEMAN

Mellon Institute, Pittsburgh, Pennsylvania

AND

WALTER NOLL

Department of Mathematics, Carnegie Institute of Technology, Pittsburgh, Pennsylvania

1. INTRODUCTION

THE classical linear theory of viscoelasticity was apparently first formulated by Boltzmann[1] in 1874. His original presentation covered the three-dimensional case, but was restricted to isotropic materials. The extension of the theory to anisotropic materials is, however, almost immediately evident on reading Boltzmann's paper, and the basic hypotheses of the theory have not changed since 1874. Since that date, much work has been done on the following aspects of linear viscoelasticity: solution of special boundary value problems,[2a] reformulation[3,4] of the one-dimensional version of the theory in terms of new material functions (such as "creep functions" and frequency-dependent complex "impedances") which appear to be directly accessible to measurement, experimental determination[2b] of the material functions for those materials for which the theory appears useful, prediction of the form of the material functions from molecular models, and, recently, axiomatization[5,6] of the theory. In this article, instead of being concerned with these matters, we reexamine the fundamental hypotheses of linear viscoelasticity in the light of recent advances in nonlinear continuum mechanics.

The basic assumption of the classical linear theory of viscosity is a constitutive equation relating the stress tensor $T(t)$ at time t to the history of the infinitesimal strain tensor $E(t-s)$, $0\leq s<\infty$. This assumption asserts that if $E(t-s)$, taken relative to a natural reference configuration corresponding to zero equilibrium stress, is *small* in magnitude for *all* s, then

$$T(t)=\mathbf{\Omega}\{E(t)\}+\mathbf{\Phi}(0)\{E(t)\}+\int_0^\infty \dot{\mathbf{\Phi}}(s)\{E(t-s)\}ds, \tag{1.1}$$

where

$$\dot{\mathbf{\Phi}}(s)=(d/ds)\mathbf{\Phi}(s), \tag{1.2}$$

and $\mathbf{\Phi}$ is such that

$$\lim_{s\to\infty}\mathbf{\Phi}(s)=0. \tag{1.3}$$

Here $\mathbf{\Phi}(s)\{\ \}$ (for each s) and $\mathbf{\Omega}\{\ \}$ are linear transformations of the space of symmetric tensors into itself. As a function of time, $\mathbf{\Phi}$ has a simple physical significance and is called the "stress relaxation function." For if we consider a deformation history such that the material is kept in its natural reference configuration ($E=0$) for all times $t<0$ and has the strain E^* for all times $t\geq 0$, then for such a history Eq. (1.1) yields

$$T(t)=\begin{cases}0 & \text{if } t<0\\ \mathbf{\Phi}(t)\{E^*\}+\mathbf{\Omega}\{E^*\} & \text{if } t\geq 0.\end{cases} \tag{1.4}$$

In the familiar special case of an isotropic material, $\mathbf{\Phi}(t)$ is completely determined by two scalar-valued functions of time: the stress relaxation functions for shear and dilatation. The linear transformation $\mathbf{\Omega}$ characterizes the "linear equilibrium stress-strain law" of infinitesimal elasticity theory; i.e., Eqs. (1.3) and (1.4) yield

$$\lim_{t\to\infty}T(t)=\mathbf{\Omega}\{E^*\}. \tag{1.5}$$

For an isotropic solid, $\mathbf{\Omega}$ is determined by the two Lamé constants.

We refer to the classical linear theory based on Eqs. (1.1)–(1.3) as *infinitesimal viscoelasticity* because, roughly speaking, it can be applicable only to those situations in which the strain is small at all times.

In Sec. 4 we show how Eq. (1.1) must be modified when the reference configuration is arbitrary and not necessarily one in which the equilibrium stress is zero. In particular, in the case of a fluid, $T(t)$ should be replaced by $T(t)+p_rI$, where p_r is the equilibrium hydrostatic pressure corresponding to the reference configuration, and I denotes the unit (or identity) tensor. For a fluid $\mathbf{\Omega}$ is determined by the equilibrium compressibility.

It is often claimed that the theory of infinitesimal viscoelasticity can be derived from an assumption that on a microscopic level matter can be regarded as composed of "linear viscous elements" (also called

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[1] S. Boltzmann, Sitzber. Akad. Wiss. Wien, Math. naturw. Kl. **70**, 275 (1874); Pogg. Ann. Phys. **7**, 624 (1876).

[2] (a) E. H. Lee, in *Viscoelasticity*, edited by J. T. Bergen (Academic Press, Inc., New York, 1960), p. 1; (b) J. D. Ferry and K. Ninomiya, *ibid.*, p. 55.

[3] B. Gross, *Mathematical Structure of the Theories of Viscoelasticity* (Hermann & Cie., Paris, 1953). A summary of relationships between those material functions which occur in the one-dimensional formulation of the theory is given in this reference and in reference 4.

[4] H. Leaderman, Trans. Soc. Rheol. **1**, 213 (1957).

[5] E. R. Love, Australian J. Phys. **9**, 1 (1956).

[6] H. Konig and J. Meixner, Math. Nachr. **19**, 265 (1958).

"dashpots") and "linear elastic elements" (called "springs") connected together in intricate "networks."[7] The motivation behind some of the recent work on spring and dashpot networks appears to be the hope that the consideration of such readily visualized models will suggest a formalism for immersing viscoelasticity in a general thermodynamical theory of irreversible processes.

We feel that the physicist's confidence in the usefulness of the theory of infinitesimal viscoelasticity does not stem from a belief that the materials to which the theory is applied are really composed of microscopic networks of springs and dashpots, but comes rather from other considerations. First, there is the observation that the theory works for many real materials. But second, and perhaps more important to theoreticians, is the fact that the theory looks plausible because it seems to be a mathematization of little more than certain intuitive prejudices about smoothness in macroscopic phenomena. It is natural to assume that the dependence of the stress on the history of the deformation should be, in some sense, a *smooth dependence*. (Smoothness assumptions are usually so "natural" to physicists that they are seldom made explicit.) Since we know that in small neighborhoods smooth dependences are approximately *linear*, it is felt that if only small deformations are considered, the stress should be given by a linear functional of the deformation history, and that this functional should yield the form exhibited in Eqs. (1.1)–(1.3).

This article tries to make precise these observations about smoothness, and in so doing seeks to obtain a mathematical derivation of infinitesimal viscoelasticity from plausible macroscopic assumptions. To do this one must first presume a nonlinear theory of the mechanical behavior of materials with memory, and, if the undertaking is to be at all worthwhile, the presumed nonlinear theory must rest on constitutive equations based only on very general physical principles. Our development starts with the recently formulated general theory[8] of "simple materials" (i.e., materials for which the stress depends in an arbitrary way on the history of the first spatial gradient of the displacement). The theory of simple materials is outlined in Sec. 3.

To make precise the notion of smoothness we must introduce a topology into the space of functions characterizing the history of the deformation; i.e., we must have a way of knowing when two histories are close to each other. We do this by defining a *norm*. The particular norm used here is one of those considered in our paper on memory functionals.[9] This norm has two important properties: first, it makes our space of histories a Hilbert space; second, it places greater emphasis on the deformations which occurred in the recent past than on those which occurred in the distant past. We believe that this second property is essential if one is to formulate a smoothness assumption for macroscopic phenomena that is compatible with the everyday observation that memories are imperfect. The memory of a macroscopic object for its past deformations fades in the sense that deformations which occurred in the distant past have a smaller effect on the present forces than have more recent deformations.

We mathematize the notion of smoothness by assuming that the constitutive functionals which give the stress in a simple material are ***Fréchet differentiable*** in our Hilbert space of histories.

In considering finite deformations in simple materials, it is often convenient to take the present configuration as the reference configuration for describing the history of the deformation. Indeed, when dealing with a fluid, this is the natural thing to do, because a fluid has no preferred configurations. However, we can do this even for solids, provided we maintain in the constitutive equations a tensor parameter which tells how the present configuration is related to a preferred configuration.

The function space norm which we use has the property that the norm of a history is small if the deformations have been small at all times in the past; indeed, our derivation of infinitesimal viscoelasticity is a combination of this fact with our differentiability assumption. However, when one takes the present state as a reference, the deformation at the present time is zero, and if one further notes that the distant past is of little importance, it becomes clear that there are several ways in which a history can be small in norm. In particular, any history for which the motion has been *slow* in the recent past has a small norm. This observation has suggested to us the consideration of a new linear approximation for the general constitutive functionals of simple materials. We call the theory based on this new approximation *finite linear viscoelasticity*; it includes the classical infinitesimal theory as a special case, but has the advantage of being meaningful in situations involving finite deformations. The arguments presented in Secs. 3 and 5 show that finite linear viscoelasticity furnishes a complete first-order approximation to the theory of simple materials in the limit in which the history of the deformation, taken relative to the present configuration, is small in norm.

The smoothness considerations presented can be extended to obtain higher order approximations to the general constitutive equations of simple materials. In Sec. 6 we discuss a second-order theory of viscoelasticity for incompressible simple fluids.

2. KINEMATICS

We present a brief outline of the kinematics required for a discussion of simple materials. For a more complete

[7] D. R. Bland, *The Theory of Viscoelasticity* (Pergamon Press, New York, 1960), Chap. 2.
[8] W. Noll, Arch. Ratl. Mech. Anal. **2**, 197 (1958).
[9] B. D. Coleman and W. Noll, Arch. Ratl. Mech. Anal. **6**, 356 (1960).

presentation which goes back to first principles, see Noll.[8]

Consider a particular material point X of a body $\mathcal{B}$. Suppose that X occupies the position $\mathbf{X}$ in Euclidean space $\mathcal{E}$ when $\mathcal{B}$ is in a reference configuration. Let $\boldsymbol{\xi}$ be the position of X in $\mathcal{E}$ at time τ. For the dependence of $\boldsymbol{\xi}$ on $\mathbf{X}$ and τ, we write

$$\boldsymbol{\xi}=\chi(\mathbf{X},\tau). \tag{2.1}$$

The gradient $F(\tau)$ of $\chi(\mathbf{X},\tau)$ with respect to $\mathbf{X}$,

$$F(\tau)=\nabla\chi(\mathbf{X},\tau), \tag{2.2}$$

is called the *deformation gradient* at the material point X at time τ. It is a tensor which possesses an inverse $F(\tau)^{-1}$. (Here the term "tensor" is used a synonym for "linear transformation of the three-dimensional Euclidean vector space into itself.") The value of $F(\tau)$ at each point of $\mathcal{B}$ is affected not only by the configuration of $\mathcal{B}$ at time τ but also by our choice of a reference configuration for $\mathcal{B}$. This reference configuration may be chosen for convenience and need not necessarily be a configuration actually occupied by the body during its motion.

It is often useful to employ the configuration at the present time t, rather than a fixed configuration, as the reference. The corresponding deformation gradient is denoted by $F_t(\tau)$ and called the *relative deformation gradient*. The deformation gradients enjoy the following important property, which is a direct consequence of the chain rule for the differentiation of composite vector-valued functions:

$$F(\tau)=F_t(\tau)F(t), \tag{2.3}$$

where the indicated multiplication is the usual composition of linear transformations (matrix product).

An immediate consequence of the definition of $F_t(t)$ is that

$$F_t(t)=I, \tag{2.4}$$

where I is the unit (or identity) tensor. From Eq. (2.3) we obtain the relation

$$F_t(\tau)=F(\tau)F(t)^{-1}. \tag{2.5}$$

Let $\rho(\tau)$ give the mass density at X as a function of τ; it follows from a theorem of kinematics that

$$\det F_t(\tau)=\rho(t)/\rho(\tau). \tag{2.6}$$

If $F(\tau)$ is independent of X, we say that the configuration of $\mathcal{B}$ at time τ and the reference configuration of $\mathcal{B}$ are related by a *homogeneous deformation*. If $F=F(\tau)$ is orthogonal, i.e., if

$$F^TF=FF^T=I, \tag{2.7}$$

in which F^T denotes the transpose of F, then this "homogeneous deformation" represents a rigid rotation of the body. If F is symmetric positive-definite, then the body has been subjected to a *pure stretch*; in this case the proper vectors of F give the principal directions of stretch and the proper numbers of F are the principal stretch ratios.

A theorem of algebra, called the *polar decomposition theorem*, states that any invertible tensor F can be written in two ways as the product of a symmetric positive-definite tensor and an orthogonal tensor:

$$F=RU, \tag{2.8}$$

$$F=VR. \tag{2.9}$$

Furthermore, the orthogonal tensor R and the symmetric positive-definite tensors U and V in these decompositions are uniquely determined by F and obey the following relations:

$$U^2=F^TF\equiv C, \tag{2.10}$$

$$V^2=FF^T\equiv B, \tag{2.11}$$

$$U=R^TVR. \tag{2.12}$$

Equations (2.8) and (2.9) have the following significance in kinematics: Any homogeneous deformation with deformation gradient F may be regarded as being the result of a pure stretch U followed by a rigid rotation R, or a rigid rotation R followed by a pure stretch V. These interpretations uniquely determine the pairs R, U and R, V. The rigid rotations entering these two interpretations are the same; however, the pure stretches U and V can be different. It follows from Eq. (2.12) that although these stretches may have different principal directions, they must yield the same stretch ratios. We call the tensor R the *rotation tensor* and the tensors U and V, respectively, the *right* and *left stretch tensors*. The symmetric positive-definite tensors C and B, defined by Eqs. (2.10) and (2.11), are called, respectively, the *right* and *left Cauchy-Green tensors*; they obviously contain the same information as the corresponding stretch tensors, and their components are often easier to compute.

The rotation tensor, the stretch tensors, and the Cauchy-Green tensors computed from the relative deformation gradient F_t are denoted by R_t, U_t, V_t, C_t, and B_t. The modifier *relative* is used to indicate that the present configuration (time t) is used as the reference. For example, $C_t(\tau)$, is called the *relative right Cauchy-Green tensor*.

The following formulas are consequences of Eq. (2.4):

$$U_t(t)=V_t(t)=C_t(t)=B_t(t)=R_t(t)=I. \tag{2.13}$$

For simplicity we have emphasized the interpretation for *homogeneous deformations* of the tensors defined by Eqs. (2.8)–(2.11). These definitions obviously apply also to nonhomogeneous deformations, and similar interpretations can be given to them in the nonhomogeneous case if one merely first observes that the deformations considered in continuum mechanics are sufficiently smooth to be approximately homogeneous in small regions of $\mathcal{B}$.

We note that there is no unique way to measure "the strain" corresponding to an arbitrary finite deformation.

We now establish the connection between the kinematics of *finite deformations* sketched in the foregoing and the more familiar kinematics of *infinitesimal deformations*.

The *magnitude* $|A|$ of a tensor A is defined by

$$|A|^2=\mathrm{Tr}(AA^T), \tag{2.14}$$

where Tr denotes the trace of a tensor. If Cartesian coordinates are used, then $|A|^2$ is the sum of the squares of the elements of the 3×3 matrix corresponding to A. We also use the definition (2.14) or magnitude when A is replaced by a linear transformation $\mathbf{\Gamma}$ of the six-dimensional space of symmetric tensors. In this case, the square of the magnitude $|\mathbf{\Gamma}|$ of $\mathbf{\Gamma}$ is the sum of the squares of the 6×6 matrix corresponding to $\mathbf{\Gamma}$.

Let a motion with deformation gradient $F=F(\tau)$ be given. We put

$$H=F-I \tag{2.15}$$

and

$$\epsilon=\sup_{\tau}|H(\tau)|. \tag{2.16}$$

H is the gradient of the displacement vector field. We say that the deformation corresponding to $F(\tau)$ is *infinitesimal at all times* τ if

$$\epsilon\ll1. \tag{2.17}$$

The *infinitesimal strain tensor* $E=E(\tau)$ is defined by

$$E=\tfrac{1}{2}(H+H^T). \tag{2.18}$$

In the following we consider functions of τ which are determined by $H(\tau)$ and which have the property that for each τ their magnitude is less than $K\epsilon^n$, where K is a number independent of τ, the function $H(\tau)$, and ϵ. Any such function is denoted by the order symbol $O(\epsilon^n)$; i.e.,

$$|O(\epsilon^n)|<K\epsilon^n. \tag{2.19}$$

It is easy to show that

$$F=I+H=I+O(\epsilon), \tag{2.20}$$

$$F^{-1}=I-H+O(\epsilon^2)=I+O(\epsilon). \tag{2.21}$$

Also, it is not difficult to establish the following relations between the stretch tensors U, V and Cauchy-Green tensors C, B, on the one hand, and the infinitesimal strain tensor E, on the other hand:

$$U-I=E+O(\epsilon^2)=O(\epsilon), \tag{2.22}$$

$$V-I=E+O(\epsilon^2)=O(\epsilon), \tag{2.23}$$

$$C-I=2E+O(\epsilon^2)=O(\epsilon), \tag{2.24}$$

$$B-I=2E+O(\epsilon^2)=O(\epsilon). \tag{2.25}$$

Thus, if terms of order $O(\epsilon^2)$ can be neglected, the stretch tensors U, V and Cauchy-Green tensors C, B can be expressed in terms of E. For finite deformations, however, the infinitesimal strain tensor E is devoid of kinematical significance.

Finally, we note the following relations between the *infinitesimal rotation tensor* W, defined by

$$W=\tfrac{1}{2}(H-H^T), \tag{2.26}$$

and the finite rotation tensor R:

$$R=I+W+O(\epsilon^2)=I+O(\epsilon),$$
$$R^T=R^{-1}=I-W+O(\epsilon^2)=I+O(\epsilon). \tag{2.27}$$

In order to find an expression for the relative Cauchy-Green tensor $C_t(\tau)$, we first substitute Eqs. (2.20) and (2.21) into Eq. (2.5) and obtain

$$F_t(\tau)=I+H(\tau)-H(t)+O(\epsilon^2). \tag{2.28}$$

Equation (2.10), written for the relative tensors F_t and C_t, reads

$$C_t(\tau)=F_t(\tau)^TF_t(\tau). \tag{2.29}$$

Substitution of Eq. (2.28) into Eq. (2.29) and use of Eq. (2.18) yield

$$C_t(\tau)=I+2[E(\tau)-E(t)]+O(\epsilon^2)=I+O(\epsilon). \tag{2.30}$$

For finite deformations there is no simple relation between $C_t(\tau)$, $C(\tau)$, and $C(t)$.

3. FADING MEMORY

The theory of simple materials is based on the following physical assumption: *The present stress is given by a functional of the past history of the deformation gradient.*

Suppose the deformation gradient $F(\tau)$ is given (for all $\tau\leq t$) computed relative to a fixed reference configuration. The right Cauchy-Green tensor $C(t)$ and rotation tensor $R(t)$ corresponding to $F(t)$ are determined by Eqs. (2.8) and (2.10). On using Eqs. (2.5) and (2.29) we can compute the relative Cauchy-Green tensors $C_t(\tau)$ for all $\tau\leq t$. We now put

$$\bar{C}_t(\tau)=R^T(t)C_t(\tau)R(t). \tag{3.1}$$

If the material has always been at rest, we have, by Eqs. (2.13) and (3.1),

$$\bar{C}_t(\tau)\equiv I \quad \text{for } \tau\leq t. \tag{3.2}$$

The principle of material objectivity, which states that the properties of a material should appear the same to all observers, can be used to show that the general constitutive equation for simple materials reduces to the form

$$\bar{T}(t)\equiv R^T(t)T(t)R(t)=\underset{s=0}{\overset{\infty}{\mathfrak{K}}}(\bar{C}_t(t-s);C(t)), \tag{3.3}$$

where $T(t)$ is the stress tensor at time t and the symbol $\mathfrak{K}$ denotes a functional. [This may be compared with reference 8, Eq. (22.8). Here we use a somewhat more suggestive notation.]

It is useful to put Eq. (3.3) into a slightly different form by writing the right-hand side as the sum of an "equilibrium term" $\mathfrak{h}(C(t))$ and a term which vanishes when the material has always been at rest, i.e., when Eq. (3.2) holds:

$$\bar{T}(t)=\mathfrak{h}(C(t))+\overset{\infty}{\underset{s=0}{\mathfrak{F}}}(\bar{C}_t(t-s)-I;C(t)), \tag{3.4}$$

$$\overset{\infty}{\underset{s=0}{\mathfrak{F}}}(0;C(t))=0. \tag{3.5}$$

For present purposes it is sufficient to regard the constitutive equation (3.4) as the definition of a simple material.

We now add a new physical assumption: *The memory of a simple material fades in time.*

There is no unique way to give this statement a precise meaning. We consider a particular mathematical interpretation of it. For this purpose we first introduce the concept of an influence function which is used to characterize the rate at which the memory fades. (This definition of an influence function is slightly different and somewhat less technical than the one we gave in reference 9.) A function h is called an *influence function* of order $r>0$ if it satisfies the following conditions:

(a) $h(s)$ is defined for $0\leq s<\infty$ and has positive real values: $h(s)>0$.

(b) $h(s)$ decays to zero according to

$$\lim_{s\to\infty} s^r h(s)=0 \tag{3.6}$$

monotonically for large s. For example,

$$h(s)=(s+1)^{-p}$$

is an influence function of order r if $r<p$. An exponential

$$h(s)=e^{-\beta s}, \quad \beta>0$$

is an influence function of any order.

Any function $G(s)$, defined for $s\geq 0$ and with values which are symmetric tensors, is called a *history*. The argument function $G(s)=\bar{C}_t(t-s)-I$ of the functional $\mathfrak{F}$ of Eq. (3.4) is a history. The tensor $C(t)$ in Eq. (3.4) plays the role of a parameter.

Let an influence function $h(s)$ be given. We then define the norm $\|G(s)\|$ of a history $G(s)$ by

$$\|G(s)\|^2=\int_0^\infty |G(s)|^2 h(s)^2 ds, \tag{3.7}$$

where $|G(s)|$ is the magnitude of the tensor $G(s)$ defined by Eq. (2.14). The influence function $h(s)$ determines the influence assigned to the values of $G(s)$ in computing the norm $\|G(s)\|$. Since $h(s)\to 0$ as $s\to\infty$, the values of $G(s)$ for small s (recent past) have a greater weight than the values for large s (distant past).

The collection of all histories with finite norm (3.7) forms a Hilbert space $\mathfrak{H}$. A history $G(s)$ belongs to the space $\mathfrak{H}$ if it does not grow too fast as $s\to\infty$.

Consider now an influence function h and a functional

$$\overset{\infty}{\underset{s=0}{\mathfrak{F}}}(G(s))$$

which is defined on a neighborhood of the zero history in the Hilbert space $\mathfrak{H}$ corresponding to h and whose values are symmetric tensors. Assume that the value of $\mathfrak{F}$ for the zero history is zero, i.e., that

$$\overset{\infty}{\underset{s=0}{\mathfrak{F}}}(0)=0. \tag{3.8}$$

We say that $\mathfrak{F}$ is *Fréchet-differentiable* at the zero history if there is a continuous linear functional $\delta\mathfrak{F}$ such that

$$\overset{\infty}{\underset{s=0}{\mathfrak{F}}}(G(s))=\overset{\infty}{\underset{s=0}{\delta\mathfrak{F}}}(G(s))=\overset{\infty}{\underset{s=0}{\mathfrak{R}}}(G(s)), \tag{3.9}$$

where the "remainder" $\mathfrak{R}$ is of order $o(\|G(s)\|)$ in the sense that

$$\lim_{\|G(s)\|\to 0}\|G(s)\|^{-1}\overset{\infty}{\underset{s=0}{\mathfrak{R}}}(G(s))=0. \tag{3.10}$$

The linear functional $\delta\mathfrak{F}$ is called the *first variation* or *Fréchet differential* of $\mathfrak{F}$ at the zero history.

We now translate our physical assumption of fading memory into the following mathematical requirement:

(F) *There exists an influence function $h(s)$ of an order $r>\frac{1}{2}$ such that, for each value of the tensor parameter C, the functional $\mathfrak{F}$ of the constitutive equation* (3.4) *is Fréchet-differentiable at the zero history in the Hilbert space $\mathfrak{H}$ corresponding to $h(s)$.*

If we indicate the dependence on the tensor parameter C, Eq. (3.9) becomes

$$\overset{\infty}{\underset{s=0}{\mathfrak{F}}}(G(s);C)=\overset{\infty}{\underset{s=0}{\delta\mathfrak{F}}}(G(s);C)+\overset{\infty}{\underset{s=0}{\mathfrak{R}}}(G(s);C). \tag{3.11}$$

We now invoke the theorem of the theory of Hilbert spaces which states that every continuous linear functional may be written as an inner product. It follows from this theorem that the first variation $\delta\mathfrak{F}$ has an integral representation of the form

$$\overset{\infty}{\underset{s=0}{\delta\mathfrak{F}}}(G(s);C)=\int_0^\infty \mathbf{\Gamma}(s;C)\{G(s)\}ds. \tag{3.12}$$

Here $\mathbf{\Gamma}(s;C)\{\ \}$, for each s and each C, is a linear transformation of the space of symmetric tensors into itself with the property that

$$\int_0^\infty |\mathbf{\Gamma}(s;C)|^2 h(s)^{-2} ds<\infty, \tag{3.13}$$

where $|\boldsymbol{\Gamma}(s;C)|$ is the magnitude of $\boldsymbol{\Gamma}(s;C)$ as defined by Eq. (2.14). The property (3.13) shows that $\boldsymbol{\Gamma}(s;C)$ must approach zero at a faster rate than the influence function $h(s)$ as $s\to\infty$. Substitution of Eqs. (3.12) and (3.11) into Eq. (3.4) yields

$$\bar{T}=\mathfrak{h}(C)+\int_0^\infty \boldsymbol{\Gamma}(s;C)\{G(s)\}ds+\underset{s=0}{\overset{\infty}{\mathfrak{R}}}(G(s);C), \quad (3.14)$$

where

$$G(s)=\bar{C}_t(t-s)-I. \quad (3.15)$$

It is understood that the variables $\bar{T}$, C, and $G(s)$ depend on the present time t.

It seems natural to add to the requirement (F) the following two assumptions:

(F′) *The Fréchet-differentiability of* $\mathfrak{F}$ *postulated in* (F) *is uniform in the tensor parameter* C.

(D) *The tensor function* $\mathfrak{h}(C)$ *of* (3.14) *is continuously differentiable.*

By the assumption (F′) we mean that the first variation

$$\underset{s=0}{\overset{\infty}{\delta\mathfrak{F}}}(G(s);C)$$

depends continuously on C in the strong sense and that the convergence in Eq. (3.10) is uniform in C.

4. INFINITESIMAL VISCOELASTICITY

We first remark that any function of order $O(\epsilon^n)$ in the sense of Eq. (2.19) is also a function of order $O(\epsilon^n)$ with respect to the Hilbert-space norm (3.7); i.e., there is a constant $\bar{K}$, independent of ϵ, such that

$$\|O(\epsilon^n)\|<\bar{K}\epsilon^n. \quad (4.1)$$

In order to prove this inequality we substitute $O(\epsilon^n)$ for $G(s)$ in the definition (3.7) of the norm and use the inequality (2.19):

$$\|O(\epsilon^n)\|^2=\int_0^\infty |O(\epsilon^n)|^2 h(s)^2 ds<(K\epsilon^n)^2\int_0^\infty h(s)^2 ds. \quad (4.2)$$

The requirement (F) of Sec. 3 ensures that the number r of Eq. (3.6) is greater than $\frac{1}{2}$. It follows that the integral $\int_0^\infty h^2(s)ds$ is finite and hence that the inequality (4.1) holds with

$$\bar{K}=K\left(\int_0^\infty h(s)^2 ds\right)^{\frac{1}{2}}. \quad (4.3)$$

This remark shows that the order symbols in Eqs. (2.20)–(2.30) may be interpreted in terms of the convergence in the Hilbert space of histories defined in Sec. 3. This interpretation must be used to justify most of the subsequent considerations.

By combining Eqs. (3.1), (2.30), and (2.27), we find the following expression for the history

$$G(s)=\bar{C}_t(t-s)-I$$

which enters the constitutive equation (3.4) of a simple material:

$$G(s)=2[E(t-s)-E(t)]+O(\epsilon^2)=O(\epsilon). \quad (4.4)$$

On substituting Eq. (4.4) into Eq. (3.11) and using Eq. (3.10) and the linearity and continuity of the first variation $\delta\mathfrak{F}$, we obtain

$$\underset{s=0}{\overset{\infty}{\mathfrak{F}}}(G(s);C)=2\,\underset{s=0}{\overset{\infty}{\delta\mathfrak{F}}}(E(t-s)-E(s);C)+o(\epsilon), \quad (4.5)$$

where the order symbol $o(\epsilon)$ is used in the sense that

$$\lim_{\epsilon\to 0}\epsilon^{-1}|o(\epsilon)|=0. \quad (4.6)$$

It is not difficult to prove that the uniformity assumption (F′) of Sec. 3 implies that Eq. (4.5) remains valid if, on the right-hand side, the tensor $C=I+O(\epsilon)$ is replaced by the unit tensor I:

$$\underset{s=0}{\overset{\infty}{\mathfrak{F}}}(G(s);C)=2\,\underset{s=0}{\overset{\infty}{\delta\mathfrak{F}}}(E(t-s)-E(s);I)+o(\epsilon). \quad (4.7)$$

We now substitute the integral representation (3.12), for $C=I$, into Eq. (4.7), and obtain

$$\underset{s=0}{\overset{\infty}{\mathfrak{F}}}(G(s);C)=\int_0^\infty 2\boldsymbol{\Gamma}(s)\{E(t-s)\}ds-\int_0^\infty 2\boldsymbol{\Gamma}(s)ds\{E(t)\}+o(\epsilon). \quad (4.8)$$

On defining $\boldsymbol{\Phi}(s)$ by

$$\boldsymbol{\Phi}(s)=-2\int_s^\infty \boldsymbol{\Gamma}(\sigma)d\sigma,\quad \dot{\boldsymbol{\Phi}}(s)=\frac{d}{ds}\boldsymbol{\Phi}(s)=2\boldsymbol{\Gamma}(s), \quad (4.9)$$

we may rewrite Eq. (4.8) in the form

$$\underset{s=0}{\overset{\infty}{\mathfrak{F}}}(G(s);C)=\boldsymbol{\Phi}(0)\{E(t)\}+\int_0^\infty \dot{\boldsymbol{\Phi}}(s)\{E(t-s)\}ds+o(\epsilon), \quad (4.10)$$

where

$$\lim_{s\to\infty}\boldsymbol{\Phi}(s)=0. \quad (4.11)$$

Assumption (D) of Sec. 3 and Eq. (2.24) imply that the equilibrium term $\mathfrak{h}(C)$ of Eq. (3.4) has the form

$$\mathfrak{h}(C(t))=T_r+\boldsymbol{\Omega}\{E(t)\}+o(\epsilon). \quad (4.12)$$

Here, the linear transformation $\boldsymbol{\Omega}\{\ \}$ of the space of symmetric tensors is the gradient of the tensor function $\mathfrak{h}(C)$ at $C=I$. The tensor

$$T_r=\mathfrak{h}(I) \quad (4.13)$$

is the *residual stress*, i.e., the stress the material would sustain if it had been held in the reference configuration at all times in the past.

Substitution of Eqs. (4.10) and (4.12) into the constitutive equation (3.4) yields

$$\bar{T}(t)=T_r+[\mathbf{\Omega}+\mathbf{\Phi}(0)]\{E(t)\} + \int_0^\infty \dot{\mathbf{\Phi}}(s)\{E(t-s)\}ds+o(\epsilon). \quad (4.14)$$

Finally, going back to the definition (3.3) of $\bar{T}$ and using Eqs. (2.27), we obtain the following expression for the stress tensor $T(t)$:

$$T(t)-T_r=W(t)T_r-T_rW(t)+[\mathbf{\Omega}+\mathbf{\Phi}(0)]\{E(t)\} + \int_0^\infty \dot{\mathbf{\Phi}}(s)\{E(t-s)\}ds+o(\epsilon). \quad (4.15)$$

When ϵ, given by Eq. (2.16), is small enough, the remainder term $o(\epsilon)$ can be neglected in comparison with the other terms on the right-hand side of Eq. (4.15), which are of order $O(\epsilon)$. Thus, the *constitutive equation of infinitesimal viscoelasticity* reads

$$T(t)-T_r=W(t)T_r-T_rW(t)+[\mathbf{\Omega}+\mathbf{\Phi}(0)]\{E(t)\} + \int_0^\infty \dot{\mathbf{\Phi}}(s)\{E(t-s)\}ds. \quad (4.16)$$

When the reference configuration is a natural state, we have $T_r=0$, and Eq. (4.16) reduces to the classical equation (1.1). Equation (4.16), with $T_r\neq 0$, applies to infinitesimal deformations superposed on a large deformation from an unstressed natural state. In this case, the reference configuration is not the natural state but the deformed state with equilibrium stress T_r. If T_r is a hydrostatic pressure $T_r=-pI$, the terms involving $W(t)$ in Eq. (4.16), cancel. The stress relaxation function $\mathbf{\Phi}(s)$ depends not only on the material but also on the configuration which has been taken as the reference.

We remark that the special case $\mathbf{\Phi}(s)\equiv 0$ of Eq. (4.16) corresponds to the theory of infinitesimal elastic deformations superposed on large deformations. The special case $\mathbf{\Phi}(s)\equiv 0$ and $T_r=0$ corresponds to the classical theory of infinitesimal elasticity.

5. FINITE LINEAR VISCOELASTICITY

Motivation

Let us return to Eq. (3.14), which, under our hypothesis (F), is equivalent to the fundamental constitutive equation (3.4). It follows from Eq. (3.10) that the remainder term of Eq. (3.14) is small compared to the term involving the integral, provided the history $G(s)=\bar{C}_t(t-s)-I$ has a small Hilbert-space norm. Thus, the equation

$$\bar{T}=\mathfrak{h}(C)+\int_0^\infty \mathbf{\Gamma}(s;C)\{G(s)\}ds \quad (5.1)$$

approximates the general constitutive equation of a simple material in the limit

$$\|G(s)\|\rightarrow 0, \quad (5.2)$$

and the error approaches zero faster than $\|G(s)\|$. We call the theory based on Eq. (5.1) *finite linear viscoelasticity.*

One way of achieving the limit (5.2) is to let ϵ, defined by Eq. (2.16), go to zero. The discussion of Sec. 4 shows that, in this case, Eq. (5.1) reduces to the constitutive equation (4.16) of infinitesimal viscoelasticity.

When we consider, however, the definition (3.7) of the norm $\|G(s)\|$, we see that the limit (5.2) may be achieved even when ϵ does not approach zero. In order for $\|G(s)\|$ to be small, it is not necessary that the deformation (relative to the configuration at the present time t) be small at *all* past times $\tau<t$, but only that the deformation be small in the *recent* past. In particular, $\|G(s)\|$ is small for "slow" motions. To make this remark precise we consider a history $G(s)$ which has finite norm and corresponds to a deformation which makes no jump at the present, so that

$$\lim_{s\rightarrow 0} G(s)=0. \quad (5.3)$$

We then construct for each α, $0<\alpha\leq 1$, a "retarded" history

$$G_\alpha(s)=G(\alpha s). \quad (5.4)$$

It follows from Eq. (3.21) of reference 9 that

$$\lim_{\alpha\rightarrow 0}\|G_\alpha(s)\|=0, \quad (5.5)$$

i.e., that the limit (5.2) may be achieved by retardation of a given process.

Aside from the fact that the finite theory based on Eq. (5.1) applies to a much larger class of problems than the infinitesimal theory, there is a fundamental difference between the two theories. The infinitesimal theory is physically meaningless for finite deformations because it does not have the invariance properties required by the principle of material objectivity. The finite linear theory, on the other hand, enjoys the correct invariance. Thus, it is conceivable that there exists *some* material which obeys Eq. (5.1) for *arbitrary* finite deformations. The infinitesimal theory cannot possibly apply to *any* material when finite deformations are considered.

Finally, we remark that in the derivation of Eq. (5.1) no assumption has been made about the magnitude of the tensor parameter C. Hence, the finite theory based on Eq. (5.1) is applicable when the present and the reference configuration are related by an arbitrary large deformation.

Isotropic Materials

When dealing with isotropic materials it is convenient to take the reference configuration to be *undis-*

torted. (A precise definition of this term is given in reference 8.) Then the equilibrium stress is hydrostatic. Furthermore, the results in Sec. 22 of reference 8 show that the constitutive equation (5.1) reduces to

$$T=\mathfrak{h}(B)+\int_0^\infty \mathbf{\Gamma}(s;B)\{J(s)\}ds, \tag{5.6}$$

where $B=B(t)$ is the left Cauchy-Green tensor, defined by Eq. (2.11), and the history $J(s)$ is given by

$$J(s)=C_t(t-s)-I. \tag{5.7}$$

Furthermore, the tensor function $\mathfrak{h}$ and the linear functional given by the integral in Eq. (5.6) are *isotropic* in the sense that they obey the identities

$$Q\mathfrak{h}(B)Q^T=\mathfrak{h}(QBQ^T), \tag{5.8}$$

$$Q\int_0^\infty \mathbf{\Gamma}(s;B)\{J(s)\}ds\, Q^T =\int_0^\infty \mathbf{\Gamma}(s;QBQ^T)\{QJ(s)Q^T\}ds \tag{5.9}$$

for all orthogonal tensors Q. A fundamental theorem of the theory of isotropic tensor functions (for an elegant recent proof see reference 10, Sec. 59) states that $\mathfrak{h}$ has a representation

$$\mathfrak{h}(B)=h_0I+h_1B+h_2B^2, \tag{5.10}$$

where h_0, h_1, and h_2 are scalar invariants of B. Also, it can be shown that the identity (5.9) implies the following representation for $\mathbf{\Gamma}$:

$$\mathbf{\Gamma}(s;B)\{J(s)\}=\mathfrak{k}_1(s;B)J(s)+J(s)\mathfrak{k}_1(s;B) +\mathfrak{k}_2(s;B)\,\mathrm{Tr}[J(s)\mathfrak{k}_3(s;B)]. \tag{5.11}$$

Here, for each s, the tensor functions $\mathfrak{k}_i(s;B)$ are isotropic in the sense of Eq. (5.8) and hence have representations of the form (5.10). The proof of this result is too technical to be included here. Equations (5.10) and (5.11) and the representations for the $\mathfrak{k}_i$ may be used to render the constitutive equation (5.6) explicit. The resulting formula shows that, in the finite theory of linear viscoelasticity, the behavior of an isotropic material is determined by 11 independent scalar material functions; three of these depend on three variables and the remaining eight on four variables. The assumption of isotropy alone yields no further simplification. The special case $\mathbf{\Gamma}\equiv 0$ of Eq. (5.6) corresponds to the theory of finite (nonlinear) isotropic elasticity.

Fluids

We now consider materials which not only obey a constitutive equation of the form (5.1) but which are also *simple fluids* in the sense of the definition given in reference 8. (Coleman and Noll[11] give a summary of the general theory of simple fluids with emphasis on physical applications.) Such materials are isotropic, and hence Eqs. (5.6)–(5.9) apply. Moreover, the functions $\mathfrak{h}(B)$ and $\mathbf{\Gamma}(s;B)$ in Eq. (5.6) depend on B only through the determinant of B or, equivalently, only through the present density $\rho=\rho(t)$. Thus, for a fluid, Eq. (5.6) becomes

$$T=\mathfrak{h}(\rho)+\int_0^\infty \mathbf{\Gamma}(s;\rho)\{J(s)\}ds. \tag{5.12}$$

The isotropy identities (5.8) and (5.9) may be written in the form

$$Q\mathfrak{h}(\rho)Q^T=\mathfrak{h}(\rho), \tag{5.13}$$

$$\int_0^\infty Q[\mathbf{\Gamma}(s;\rho)\{J(s)\}]Q^T -\mathbf{\Gamma}(s;\rho)\{QJ(s)Q^T\}ds=0. \tag{5.14}$$

Since Eq. (5.13) is valid for all orthogonal tensors Q, it follows that $\mathfrak{h}(\rho)$ must reduce to a scalar multiple of the unit tensor:

$$\mathfrak{h}(\rho)=-p(\rho)I. \tag{5.15}$$

We call $p(\rho)$ the *equilibrium pressure*; it is the pressure the fluid would be supporting if it had remained at rest in its present configuration at all times in the past.

Equation (5.14) is valid for all orthogonal Q and for all possible histories $J(s)$ belonging to the Hilbert space $\mathcal{H}$. The only element of a Hilbert space which is orthogonal to all elements of the space is the zero element. This fact implies that the integrand in Eq. (5.14) must be identically zero. Hence, the transformation $\mathbf{\Gamma}(s;\rho)\{\ \}$ satisfies the identity

$$Q[\mathbf{\Gamma}(s;\rho)\{J\}]Q^T=\mathbf{\Gamma}(s;\rho)\{QJQ\} \tag{5.16}$$

for all orthogonal tensors Q and all symmetric tensors J. In other words, for each s and ρ, $\mathbf{\Gamma}(\rho;s)\{\ \}$ is an *isotropic* linear transformation of the space of symmetric tensors. The representation theorem for such isotropic transformations [special case of the theorem embodied in Eq. (5.10) (see reference 10, Sec. 59)] states that $\mathbf{\Gamma}(s;\rho)\{J(s)\}$ must be of the form

$$\mathbf{\Gamma}(s;\rho)\{J(s)\}=\mu(s;\rho)J(s)+\lambda(s;\rho)(\mathrm{Tr}\,J(s))I, \tag{5.17}$$

where $\mu(s;\rho)$ and $\lambda(s;\rho)$ are scalar functions of the time lapse s and the present density ρ. On substituting Eqs. (5.15) and (5.17) into Eq. (5.12), we obtain the following *constitutive equation of a simple fluid in the theory of finite linear viscoelasticity*:

$$T=-p(\rho)I+\int_0^\infty \mu(s;\rho)J(s)ds +\left[\int_0^\infty \lambda(s;\rho)\,\mathrm{Tr}\,J(s)ds\right]I. \tag{5.18}$$

[10] J. Serrin, "Mathematical principles of classical fluid mechanics," in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1959), Vol. VIII/1.

[11] B. D. Coleman and W. Noll, Ann. N. Y. Acad. Sci. **89**, 672 (1961).

In this theory, the mechanical behavior of a fluid is determined by the three scalar material functions $p(\rho)$, $\mu(s;\rho)$, and $\lambda(s;\rho)$.

If the fluid under consideration is *incompressible*, certain modifications must be made in this analysis. In incompressible materials, the motion determines the stress only up to a hydrostatic pressure. In other words, the constitutive equation gives only the *extra stress*

$$T_e = T + pI, \tag{5.19}$$

where p is an indeterminate pressure. In the incompressible case, the two terms in Eq. (5.18) which are scalar multiples of the unit tensor I may be absorbed into the indeterminate pressure term pI. From these remarks we see that in finite linear viscoelasticity the stress in an incompressible fluid is given by the remarkably simple equation

$$T_e = T + pI = \int_0^\infty \mu(s) J(s) ds, \tag{5.20}$$

where, since the density is constant, $\mu(s)$ is a function of only the time lapse s.

The "relaxation function" $\phi(s)$ determined by rheologists from measurements of the decay of shearing tractions for simple (infinitesimal) shear in incompressible fluids is related to the material function $\mu(s)$ as follows:

$$\phi(s) = -2\int_s^\infty \mu(\sigma) d\sigma, \quad \mu(s) = \tfrac{1}{2}(d/ds)\phi(s). \tag{5.21}$$

Thus, the relaxation function $\phi(s)$ is sufficient to determine the mechanical behavior of incompressible fluids in the theory of finite linear viscoelasticity.

For simple fluids, the property (3.13) is equivalent to the conditions

$$\int_0^\infty |\mu(s;\rho)|^2 h(s)^{-2} ds < \infty,$$
$$\int_0^\infty |\lambda(s;\rho)|^2 h(s)^{-2} ds < \infty. \tag{5.22}$$

These conditions relate the rate of decay of the influence function to the rate of decay of the material functions $\mu(s;\rho)$ and $\lambda(s;\rho)$ as $s \to \infty$.

6. SECOND-ORDER VISCOELASTICITY

In Sec. 3 we showed, on the basis of our assumption (F), that the (nonlinear) functional $\mathfrak{F}$ giving the stress in a simple material may be approximated by a *linear* functional. The error in this approximation approaches zero faster than the Hilbert-space norm $\|G(s)\|$ of the history (3.15). The analysis of Sec. 3 may be generalized if the assumption (F) is replaced by a stronger assumption which requires that the functional $\mathfrak{F}$ be not just once but n times Fréchet differentiable at the zero history. It is then possible to approximate $\mathfrak{F}$ by a *polynomial* functional of degree n with an error that approaches zero faster than the nth power of the norm $\|G(s)\|$. For example, when $n=2$, we find the following generalization of Eq. (3.14):

$$\bar{T} = \mathfrak{h}(C) + \int_0^\infty \mathbf{\Gamma}(s;C)\{G(s)\} ds + \mathop{\mathfrak{Q}}_{s=0}^{\infty}(G(s);C) + \mathop{\mathfrak{R}'}_{s=0}^{\infty}(G(s);C). \tag{6.1}$$

Here, $\mathfrak{Q}$ is a continuous *quadratic* functional depending on the tensor parameter C; the remainder $\mathfrak{R}'$ is of order $o(\|G(s)\|^2)$, i.e.,

$$\lim_{\|G(s)\|\to 0} \|G(s)\|^{-2} R'(G(s);C) = 0. \tag{6.2}$$

Relation (6.1) shows that the equation

$$\bar{T} = \mathfrak{h}(C) + \int_0^\infty \mathbf{\Gamma}(s;C)\{G(s)\} ds + \mathop{\mathfrak{Q}}_{s=0}^{\infty}(G(s);C) \tag{6.3}$$

approximates the general constitutive equation of a simple material in the limit $\|G(s)\| \to 0$, and the error approaches zero faster than $\|G(s)\|^2$. We call the theory based on Eq. (6.3) *second-order viscoelasticity*.

The quadratic functional $\mathfrak{Q}$ of Eq. (6.3) may be expressed in terms of a bounded symmetric operator on the Hilbert space of histories. It is not possible, in general, to represent $\mathfrak{Q}$ by integrals. However, an integral representation does exist if the operator corresponding to $\mathfrak{Q}$ is completely continuous. We consider only this special case.

Explicit forms of the constitutive equations for isotropic materials and for simple fluids in second-order viscoelasticity may be obtained by an analysis similar to the one given in Sec. 5 in finite linear viscoelasticity. The resulting formulas are too complicated to be included here in full. Without giving the details of the derivation, we state the *constitutive equation of an incompressible fluid in the second-order theory of viscoelasticity*:

$$T + pI = \int_0^\infty \mu(s) J(s) ds + \int_0^\infty \int_0^\infty [\alpha(s_1,s_2) J(s_1) J(s_2) + \beta(s_1,s_2)(\mathrm{Tr}\, J(s_1) J(s_2)] ds_1 ds_2. \tag{6.4}$$

Here, p is an indeterminate pressure, $J(s)$ is the history given by Eq. (5.7), and $\mu(s)$, $\alpha(s_1,s_2)$ and $\beta(s_1,s_2)$ are scalar material functions. The function $\mu(s)$ is the same as in Eq. (5.23). The functions α and β are symmetric, i.e.,

$$\alpha(s_1,s_2)=\alpha(s_2,s_1), \quad \beta(s_1,s_2)=\beta(s_2,s_1). \tag{6.5}$$

In order to illustrate the behavior predicted by Eq. (6.4), we consider a class of motions called *simple shearing motions*. These motions are defined by the property that the velocity field $\mathbf{v}(\mathbf{x})=\{v_x,v_y,v_z\}$, in some Cartesian coordinate system x, y, z, has the components

$$v_x=0, \quad v_y=v(x,t), \quad v_z=0. \tag{6.6}$$

It follows from Eqs. (5.6), (5.8), and (5.10) of reference 11 that the matrix function corresponding to the history $J(s)$ defined by Eq. (5.7) has the form

$$[J(s)]=\lambda_t(s)\left\|\begin{matrix}0&1&0\\1&0&0\\0&0&0\end{matrix}\right\|+\lambda_t(s)^2\left\|\begin{matrix}1&0&0\\0&0&0\\0&0&0\end{matrix}\right\|, \tag{6.7}$$

where

$$\lambda_t(s)=\int_0^s \frac{d}{dx}v(x,t-\sigma)d\sigma. \tag{6.8}$$

In order to obtain the components T_{xx}, T_{xy}, etc., of the stress tensor T, we substitute Eq. (6.7) into Eq. (6.4). After a simple calculation, we find

$$T_{xy}=\int_0^\infty \mu(s)\lambda_t(s)ds+\int_0^\infty\int_0^\infty \gamma(s_1,s_2) \times\lambda_t(s_1)^2\lambda_t(s_2)ds_1ds_2, \tag{6.9}$$

$$T_{xx}-T_{yy}=\int_0^\infty \mu(s)\lambda_t^2(s)ds+\int_0^\infty\int_0^\infty \gamma(s_1,s_2) \times\lambda_t(s_1)^2\lambda_t(s_2)^2ds_1ds_2, \tag{6.10}$$

$$T_{yy}-T_{zz}=\int_0^\infty\int_0^\infty \alpha(s_1,s_2)\lambda_t(s_1)\lambda_t(s_2)ds_1ds_2, \tag{6.11}$$

where

$$\gamma(s_1,s_2)=\alpha(s_1,s_2)+\beta(s_1,s_2). \tag{6.12}$$

Equations (6.9)–(6.11), together with Cauchy's equations of motion, lead to a rather complicated system of integro-differential equations.

We now consider the special case when

$$\epsilon=\sup_{s>0}|\lambda_t(s)| \tag{6.13}$$

is small. Physically, this case corresponds to shearing motions with the property that the configuration of the fluid at *all* past times differs from the present configuration only by a small deformation. Shearing vibrations of small amplitude have this property. It is clear from Eqs. (6.13) and (6.7) that the Hilbert space norm $\|J(s)\|$ is of order $O(\epsilon^2)$. But the terms involving double integrals in Eqs. (6.9) and (6.10) are of order $O(\epsilon^3)$ and $O(\epsilon^4)$, respectively. Therefore, for small ϵ, Eqs. (6.9) and (6.10) reduce to

$$T_{xy}=\int_0^\infty \mu(s)\lambda_t(s)ds, \tag{6.14}$$

$$T_{xx}-T_{yy}=\int_0^\infty \mu(s)\lambda_t^2(s)ds. \tag{6.15}$$

Equation (6.14) for the shearing stress T_{xy} is the same as the corresponding equation in the theory of infinitesimal viscoelasticity. The normal stress differences given by Eqs. (6.15) and (6.11), zero in the infinitesimal theory, do not vanish in the second-order theory. Equations (6.11) and (6.15) may be used, for example, for the interpretation of data on normal stresses obtained in experiments involving shearing vibrations of small amplitude. It is remarkable that the normal stress difference (6.15) depends only on the material function $\mu(s)$ or, equivalently, the shear relaxation function $\phi(s)$ given by Eq. (5.24).

These results on simple shearing motions can easily be generalized to motions that have a form similar to (6.6) in an appropriate curvilinear orthogonal coordinate system. (The method to be employed is analogous to the one used in Sec. 2 of reference 12.)

7. FINAL REMARKS

In our considerations in Secs. 3–6 we have used the relative right Cauchy-Green tensor C_t as a measure of strain. As we remarked at the end of Sec. 2, there is no unique "strain tensor" when finite deformations are considered. Instead of C_t we could also have used the relative right stretch tensor $U_t=(C_t)^{\frac{1}{2}}$, the inverse C_t^{-1}, $\log C_t$, or any other tensor related to C_t by a smooth one-to-one transformation. To different choices of the measure of strain correspond different theories of finite linear viscoelasticity. However, the difference of the stresses computed using two different such theories is of order $o(\|G(s)\|)$. Hence, since any finite linear theory can be expected to be accurate only when terms of order $o(\|G(s)\|)$ can be neglected, we can say that the various theories corresponding to the various measures of strain are equivalent.

To different choices of the measure of strain also correspond different theories of second-order viscoelasticity. These different theories are equivalent in the sense that the corresponding stresses differ only by terms of order $o(\|G(s)\|^2)$.

On the basis of a molecular model for certain incompressible fluids, Lodge[13] has derived a constitutive equation corresponding to Eq. (5.23) when $J(s)$ is

[12] B. D. Coleman and W. Noll, Arch. Ratl. Mech. Anal. **4**, 289 (1959).

[13] A. S. Lodge, Trans. Faraday Soc. **52**, 120 (1956).

computed using C_t^{-1} rather than C_t as a measure of strain. Our analysis shows that any other molecular model must give the same or an equivalent result, provided only that terms of order $o(\|G(s)\|)$ may be neglected.

As we have remarked in Sec. 5, the norm $\|G(s)\|$ is small in particular for "slow" motions, and hence the finite linear theory applies in this case. For slow flows in simple fluids, the finite linear theory is actually equivalent to the classical theory of Newtonian fluids, provided that the influence function h satisfies the relation (6.3) with $r>\frac{3}{2}$. This fact and analogous results for fluids of higher order are proved in reference 9.

Rivlin and his co-workers[14] in recent years have developed memory theories involving multiple integrals similar to the second-order theory proposed in Sec. 6. The emphasis in their work has been on the representation theorems following from material objectivity anp symmetry. In particular, the representations mentioned here in Secs. 5 and 6 can be derived using their results. An investigation of higher order theories of viscoelasticity based on the existence and complete continuity of Fréchet differentials of order >2 would make much more use of such representation theorems.

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Quantum-Mechanical and Semiclassical Forms of the Density Operator Theory of Relaxation*

PAUL S. HUBBARD

Department of Physics, University of North Carolina, Chapel Hill, North Carolina

1. INTRODUCTION

NUCLEAR magnetic resonance and relaxation involves the interaction of nuclear spins with each other, with externally applied magnetic fields, and with the molecular surroundings of the spins. The Hamiltonian of the system of spins and their molecular surroundings can be written in the form

$$\mathcal{H}=\hbar[E(s,t)+F(q)+G(s,q)], \tag{1}$$

where $\hbar E(s,t)$ is the part of the Hamiltonian that depends only on the spin variables s and the time (for example, the interaction energy of the nuclear magnetic moments with the time-dependent externally applied magnetic fields), $\hbar F(q)$ is the energy of the molecular degrees of freedom q, and $\hbar G(s,q)$ is the energy of interaction of the spins and the molecular surroundings. Since the system represented by this Hamiltonian is in general quite complicated, consisting of many nuclei and molecules, it can be appropriately treated by considering an ensemble of such systems and calculating the average behavior by the methods of statistical mechanics.

Bloch[1] has used the density operator formalism of quantum statistical mechanics to derive a differential equation for a reduced density operator $\sigma(s,t)$ in terms of which the ensemble average of the expectation value of any spin operator $Q(s)$ is given by

$$\langle Q\rangle=\mathrm{Tr}[\sigma(s,t)Q(s)]. \tag{2}$$

Redfield[2] has independently derived a similar theory, but it is limited to the case in which E does not depend explicitly on the time. Tomita has developed more specialized density operator theories of magnetic resonance saturation[3] and magnetic double resonance.[4]

Redfield[2] has also derived an equation for σ by formulating the problem in another manner, considering an ensemble of systems with Hamiltonians

$$\mathcal{H}=\hbar[E(s)+G(s,t)], \tag{3}$$

where $G(s,t)$ is a random function of the time. The random time dependence of G is usually the result of the random variation with time of coordinates q upon G depends:

$$G(s,t)=G(s,q(t)). \tag{4}$$

Since the time dependence of the $q(t)$ is usually determined by considering the q to be coordinates of a system whose motion is calculated classically, the resulting relaxation theory is called semiclassical. The transition probability method introduced by Bloembergen, Purcell, and Pound[5] (BPP) for the calculation of nuclear magnetic relaxation is in effect a special case of Redfield's semiclassical theory, involving only the diagonal elements of σ between eigenstates of E, these diagonal elements being proportional to the probable relative populations of the energy levels of E as a

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[1] F. Bloch, Phys. Rev. 105, 1206 (1957).

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[3] K. Tomita, Progr. Theoret. Phys. (Kyoto) 19, 541 (1958).

[4] K. Tomita, Progr. Theoret. Phys. (Kyoto) 20, 743 (1958).

[5] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948). Hereafter referred to as BPP.