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Fluctuations and viscoelasticity

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Abstract. Viscoelasticity is exhibited by polymers, metals undergoing diffusion creep, etc. The strain is a linear functional of the stress, but there is no unique equilibrium relationship between them. Under a constant stress, the strain does not saturate to an equilibrium value. This divergence is the main difficulty facing a first-principles theory of viscoelasticity, in contrast to anelasticity which has already been understood as a relaxation process in terms of response theory, fluctuations and related concepts. We now present such a theory, based on the recognition that viscoelasticity occurs whenever the spontaneous fluctuations of the strain *rate*, but *not* of the strain, form a stationary random process. We give fundamental formulas for the creep function and the complex compliance, in terms of the spontaneous fluctuations of the strain rate, that apply to both viscoelasticity and anelasticity. A detailed stochastic analysis of the basic viscoelastic network equation corroborates and complements these results. The unphysical instantaneous response of the network is eliminated, and the network parameters are related to internal fluctuations. A certain functional form of the creep function is derived that is common to several physical situations, a few of which are mentioned. Detailed applications will be taken up elsewhere.

Keywords. Viscoelasticity; fluctuations; stochastic processes; linear response theory; creep; compliance; Maxwell network.

1. Introduction

Anelasticity is the simplest form of time-dependent mechanical behaviour. It is exhibited by a wide variety of solids, especially crystalline materials with defects, under low stress levels. In recent work (beginning with Balakrishnan *et al* 1978, referred to as I hereafter; and subsequent references), anelasticity has been successfully understood in terms of linear response theory (LRT), strain fluctuations, and related concepts. The application of these ideas to several specific mechanisms has also been carried out. Of considerable aid in this programme is the fact that anelasticity implies a unique equilibrium relationship between the stress and the strain. Under a constant stress, therefore, the strain creeps from zero to a saturation value. The system can be regarded as *relaxing* from one *equilibrium* configuration to another. The theoretical apparatus developed for other relaxation phenomena can be employed to study anelasticity. This is indeed what has been achieved, in some detail.

Viscoelasticity is a more complicated type of mechanical behaviour (see, e.g., Flory 1953; Ferry 1970; Lockett 1972; and the brief account in Markovitz 1975). Here there is no unique equilibrium relationship between stress and strain, meaning that permanent or irrecoverable plastic deformation is induced by an applied stress. As in Nowick and Berry (1972), we shall use the term viscoelasticity to cover only those

cases in which the stress-strain relationship continues to be linear.* A host of materials under diverse conditions display viscoelasticity. Polymers provide a prime example. Diffusion creep in metals at high temperatures is another. The chief difficulty in a fundamental theoretical analysis of viscoelasticity is that the system does *not* approach a new equilibrium state once it is perturbed from its initial equilibrium by an applied stress. Typically, a constant stress applied for a time t produces a strain that becomes proportional to t for large values of t. (However, in many instances, new mechanisms begin to operate as t is increased further, causing the strain to saturate ultimately. An example is the formation of cross links that inhibit the indefinite extension of long-chain molecules in polymers. We shall not be concerned with this sort of reversion to anelasticity.) It is the unbounded growth of the strain in viscoelastic creep that we tackle in this paper from a fundamental point of view.

It is helpful to state first the basic strategy that enables the problem to be brought under control. LRT relates the average strain under an applied stress to the autocorrelation of the strain in the *absence* of the applied stress, i.e., to the spontaneous fluctuations of the strain. If therefore $\langle \epsilon(t) \rangle \sim t$ for large values of t, it is clear intuitively that $\langle \epsilon^2(t) \rangle_0$ is also $\sim t$ in this limit, where the subscript zero stands for zero applied stress. (Recall the behaviour of the *position* of a particle undergoing Brownian motion.) Therefore the spontaneously fluctuating strain is not a stationary random variable, and one cannot define its power spectrum in the usual manner. On the other hand, this does not preclude the possibility that the strain *rate* may be a stationary random variable, with a well-defined power spectrum, like the velocity of a Brownian particle. One aims, therefore, at writing all formulas for the strain response in terms of the equilibrium fluctuations of the strain rate. The strain itself is an integral of a stationary random process. In other words, it is a process with stationary increments (Stratonovich 1963). This identification aids a stochastic analysis of the stress-strain relation for the basic viscoelastic network, the Maxwell model. Such an analysis corroborates and complements the LRT approach.

We develop our theory as follows. The notation is that of I. In § 2, we obtain formulas for the strain response to a static stress (the creep function) and to a dynamic stress (the complex compliance) in forms that are valid *for both viscoelasticity and anelasticity*. In §3, we analyse the constitutive relation of the Maxwell model as a stochastic equation in which random stress fluctuations drive the strain fluctuations. The autocorrelation of the strain rate can be calculated from this equation. When fed into the general formulas from LRT, the creep function of the Maxwell network is recovered. This verifies the validity of the formulas. We show further that the instantaneous or elastic response, an unphysical feature of the Maxwell model, is eliminated by our analysis. Not only do we relate the dissipative element of the network to the spontaneous fluctuations of the stress (the fluctuation-dissipation theorem), but also the reactive element. In terms of the stress relaxation function, we show that these results amount to a ' renormalisation ' of the relaxation time. This is dictated by the necessarily retarded nature of the response. In § 4, we derive a specific form for the creep function and the corresponding compliance. Different physical examples are cited to suggest that this form is rather general, in that it is common to a variety of problems. More detailed applications will be taken up separately.

*The plastic behaviour of main interest in metallurgy generally involves a highly *non-linear* stress-strain functional relationship. Evidently (linear) viscoelasticity must be fully understood before a similar first-principles theory of plasticity is attempted.

2. Formulas for the creep function and compliance

To keep the notation simple, we restrict ourselves to a single component σ of a homogeneous stress and the corresponding strain component ϵ. Generalisation to include spatial inhomogeneity and the tensor nature of the variables is possible as in the case of anelasticity (Balakrishnan 1978a). The most general linear relation between σ and ϵ is then

$$\epsilon(t) = \int_{-\infty}^{t} dt' \, \psi\,(t - t')\, \dot{\sigma}\,(t'). \tag{1}$$

The creep function $\psi\,(t)$ is the material property that we are primarily interested in. It is the strain response to a unit applied stress $\theta\,(t)$. The complex compliance $J\,(\omega)$ describes the response to a sinusoidal applied stress of frequency ω. It is easily shown that

$$J\,(\omega) = -i\omega\, \bar{\psi}\,(\omega), \tag{2}$$

where $\bar{\psi}\,(\omega)$ is the analytic continuation to $s = -i\omega$ of the Laplace transform of $\psi(t)$.

We now write down some of the results of paper I concerning anelasticity. Subsequently we shall generalise them to cover viscoelasticity as well. At $t = -\infty$, let the system be described a time-independent Hamiltonian H_0. Equilibrium averages $\langle\rangle_0$ are determined by the corresponding density matrix. In the presence of the applied stress $\sigma_{\text{ext}}(t)$, the Hamiltonian becomes

$$H = H_0 - V\epsilon\, \sigma_{\text{ext}}(t), \tag{3}$$

where V is the volume of the material. LRT, *together* with the assumption that the fluctuating strain is stationary in equilibrium, yields

$$\psi\,(t) = \beta\, V\, [\langle \epsilon^2 \rangle_0 - \langle \epsilon\,(0)\ \epsilon\,(t) \rangle_0], \ (\beta = 1/k_B\, T), \tag{4}$$

and also
$$J(\omega) = \beta\, V\, [\langle \epsilon^2 \rangle_0 + i\omega \int_0^{\infty} dt\, \langle \epsilon\,(0)\ \epsilon\,(t) \rangle_0 \exp\,(i\omega t)]. \tag{5}$$

The solution in any particular instance then reduces to the evaluation of the equilibrium autocorrelation $\langle \epsilon\,(0)\ \epsilon\,(t) \rangle_0$. If a stochastic approach is adopted for modelling the fluctuating strain $\epsilon\,(t)$, it may be more convenient to work with the associated power spectrum. This is defined as

$$S(\epsilon;\, \omega) = 2 \int_{-\infty}^{\infty} dt\, \langle \epsilon(0)\ \epsilon(t) \rangle_0 \exp\,(i\omega t). \tag{6}$$

One can then show that the creep function in (4) has the alternative representation

$$\psi(t) = (\beta V/\pi) \int_0^\infty d\omega \; S(\epsilon; \omega) \sin^2 (\omega t/2). \tag{7}$$

It is evident that

$$\text{Im } J(\omega) = \tfrac{1}{2} \beta V \omega \; S(\epsilon; \omega) \; (\omega \text{ real}). \tag{8}$$

This fluctuation-dissipation relationship, together with the dispersion relation obeyed by $J(\omega)$ by virtue of causality, leads to the spectral representation

$$J(\omega) = (\beta V/4\pi) \int_{-\infty}^\infty d\omega' \; \omega' \; S(\epsilon; \omega')/(\omega' - \omega - i0). \tag{9}$$

(See paper I for details. The boundary value prescription in (9) and in (16) below arises because $J(\omega)$ is a retarded response function.) As they stand, these formulas apply only to anelasticity. We seek to modify them so as to allow for viscoelastic behaviour. The results will continue to be valid for anelasticity as well.

At first sight, it might appear that a linearly time-dependent creep function is easy to produce, as an *approximation* to anelastic behaviour itself. Let us take the phenomenological Maxwell network as a concrete example. A spring of modulus E is put in series with a Newtonian dashpot of viscosity η. A stress σ_{ext} is applied to the network. For the spring, $\sigma_{\text{ext}} = E \; \epsilon$. For the dashpot, $\sigma_{\text{ext}} = \eta \; \dot{\epsilon}$. Since the stress is the same across both elements while the strains, i.e., the extensions, add up, it is easy to see that the network equation is

$$\dot{\epsilon} = \sigma_{\text{ext}}/\eta + \dot{\sigma}_{\text{ext}}/E. \tag{10}$$

The creep function for this network is therefore

$$\psi(t) = 1/E + t/\eta. \tag{11}$$

The first term represents the instantaneous or elastic response due to the spring. Let us now see how such a functional form could arise from microscopic considerations. The elastic response in a crystalline solid is essentially a property of the perfect crystal, or the host material. The time-dependent response is governed by the kinetics of the defect motion in it. Let us write the instantaneous, fluctuating strain as the sum $\epsilon(t) = \epsilon_h(t) + \epsilon_d(t)$ of the respective contributions, and assume that the two pieces are uncorrelated. Then (4) becomes

$$\psi(t) = \beta V \; [\langle \epsilon_h^2(0) \rangle_0 - \langle \epsilon_h(0) \; \epsilon_h(t) \rangle_0 + \langle \epsilon_d^2 \rangle_0 - \langle \epsilon_d(0) \; \epsilon_d(t) \rangle_0]. \tag{12}$$

Note that $\psi(0) = 0$, implying that there can be no truly instantaneous response. However, the correlation time of $\epsilon_h(t)$ is expected to be very small, as the fluctuations in

ϵ_h would arise from sources such as the thermal motion of the atoms of the crystal. For all practical purposes, therefore, $\langle \epsilon_h(0)\ \epsilon_h(t)\rangle_0$ can be dropped. If we assume also that $\epsilon_d(t)$ is exponentially correlated, we have

$$\psi(t) = \beta V \langle \epsilon_h^2 \rangle_0 + \beta V \langle \epsilon_d^2 \rangle_0\ [1-\exp(-t/\tau_d)],$$

$$\approx \beta V \langle \epsilon_h^2 \rangle_0 + \beta V \langle \epsilon_d^2 \rangle_0\ t/\tau_d, \tag{13}$$

correct to first order in t/τ_d. The final line in (13) has the form required by (11), although the preceding line describes anelasticity (the strain saturates as $t \to \infty$).

There are two reasons why the above is too facile a solution to the problem. First, viscoelastic behaviour includes cases in which $\psi(t) \sim t^\alpha$ with $0 < \alpha \leqslant 1$. Such non-integral exponents cannot arise from a power series expansion of $\exp(-t/\tau_d)$. But this is not a serious objection, because such exponents *can* occur in situations requiring a summation over an *infinite* set of correlation times $\tau_d^{(n)}$. An example is anelastic relaxation due to the Gorsky effect (Balakrishnan 1978b), where summation over such a set leads to a $t^{\frac{1}{2}}$ short-time behaviour of $\psi(t)$. A more striking example is provided by the theory of stress relaxation in glass (Majumdar 1971). Here the creep function can be shown to have a short-time behaviour proportional to t^α with $\alpha = 1/3$, $1/2$, or $3/5$, depending on the mechanism. The second point is a weightier one. True viscoelasticity is characterised by $\psi(t) \sim t^\alpha$ over a considerable range of t, and not just in the restricted region $t \lesssim \tau_d$. In fact, this behaviour extends to very *large* values of t, unless overridden by other mechanisms, such as cross linking in polymers. We really must deal with this ' run-away ' feature.

As already explained, we believe that this feature is intrinsic to the phenomenon of viscoelasticity. In other words, it is our contention that viscoelasticity rather than anelasticity occurs whenever the spontaneous fluctuations of the strain rate, *but not of the strain,* constitute a stationary random process. Fortunately, there is an easy way to modify the results of LRT so as to allow for this circumstance. One need not re-derive the formalism from the beginning, although this is possible. It suffices to observe that if $\epsilon(t)$ does happen to be a stationary random process, its derivative $\dot{\epsilon}(t)$ is also stationary. The corresponding power spectra are related according to

$$S(\epsilon; \omega) = S(\dot{\epsilon}; \omega)/\omega^2. \tag{14}$$

Here $S(\dot{\epsilon}; \omega)$ is defined exactly as in (6), with $\dot{\epsilon}$ standing in place of ϵ. All we have to do, then, is to substitute this relation in equation (7) for $\psi(t)$. The rest follows, provided some care is exercised. We cannot directly use (14) in (9), for instance; the integral will diverge if we did so. $J(\omega)$ must be found by going back to the basic equation (2). Let us now write down the new representations for the response functions in terms of the properties of $\dot{\epsilon}(t)$.

The creep function is given by

$$\psi(t) = (\beta V/\pi) \int_0^\infty d\omega\ S(\dot{\epsilon}; \omega)\ (\sin \tfrac{1}{2}\omega t/\omega)^2. \tag{15}$$

Constructing $\overline{\psi}(\omega)$ and using (2), we get after some algebra

$$J(\omega) = (\beta V/2\pi) \int_0^\infty d\omega' \, S(\dot{\epsilon}; \omega')/[\omega'^2 - (\omega + i\,0)^2]. \tag{16}$$

Provided $S(\dot{\epsilon}; \omega)$ vanishes sufficiently rapidly as $\omega \to \pm\infty$, it is not difficult to show that (16) can be written also as

$$J(\omega) = (\beta V/4\pi\omega) \int_{-\infty}^\infty d\omega' \, S(\dot{\epsilon}; \omega')/(\omega' - \omega - i\,0). \tag{17}$$

Formula (15) and the spectral representation (17) supplant (7) and (9) respectively. They are actually of wider applicability than the latter equations. They remain valid even when $\epsilon(t)$ is *not* a stationary random variable in equilibrium, in which case $S(\epsilon; \omega)$ cannot be defined and (7) and (9) make no sense. In a similar fashion, the fluctuation-dissipation theorem is

$$\text{Im}\, J(\omega) = (\beta V/4\omega) \, S(\dot{\epsilon}; \omega). \tag{18}$$

Besides (15), there is another, equivalent representation for $\psi(t)$; this turns out to be the most convenient one for practical applications. In addition, it is an expression in the time domain, and is therefore a generalisation of (4). The desired representation is found by substituting the definition of $S(\dot{\epsilon}; \omega)$ in (15) and carrying out the integration over ω. The result is

$$\psi(t) = \beta V \int_0^\infty dt' \, (t - t') \langle \dot{\epsilon}(0) \, \dot{\epsilon}(t') \rangle_0. \tag{19}$$

The analogy with classical diffusion is now quite evident. If the velocity of the diffusing particle stands in the place of $\dot{\epsilon}$, the integral in (19) is essentially its mean square displacement.

In like manner, the correct generalisation of (5) can be shown to be

$$J(\omega) = (i\beta V/\omega) \int_0^\infty dt \, \langle \dot{\epsilon}(0) \, \dot{\epsilon}(t) \rangle_0 \exp(i\omega t). \tag{20}$$

Equations (15) and (17), or equivalently (19) and (20), are the key results. We reiterate that they hold good for *both* viscoelasticity and anelasticity. In the latter case, $\epsilon(t)$ is also stationary in equilibrium. It may be verified that the previous set of formulas, (4), (5), (7) and (9), is then recovered. This set is inapplicable to viscoelasticity. Before this section is concluded, it is worth perceiving the difference between anelasticity and viscoelasticity in yet another way. The difference in the long-time behaviour of $\psi(t)$ is of course reflected in the low-frequency behaviour of $J(\omega)$. To determine the latter, let us separate the representation (17) into its real and imaginary

parts.* Now the principal value integral of $S(\dot{\epsilon}; \omega')/\omega'$ vanishes by virtue of symmetry. Hence, as $\omega \to 0$, the dominant contribution to $J(\omega)$ comes from its imaginary part. This is given by (18). The extreme of viscoelastic behaviour occurs when $S(\dot{\epsilon}; 0)$ is a non-vanishing number. In that case $J(\omega) \sim \omega^{-1}$, with a coefficient equal to $i\beta VS(\dot{\epsilon}; 0)/4$. At the other extreme the divergence at $\omega = 0$ actually disappears, because $S(\dot{\epsilon}; 0)$ vanishes. Anelasticity is the result. For, if ϵ is *itself* stationary in equillibrium,

$$S(\dot{\epsilon}; 0) = 4 \int_0^\infty dt \, \langle \dot{\epsilon}(0) \, \dot{\epsilon}(t) \rangle_0 = -4 \langle \dot{\epsilon}(0) \, \epsilon(0) \rangle_0 = 0. \tag{21}$$

It is easy to show that, in this situation,

$$J(0) = \psi(\infty) = \beta V \langle \epsilon^2 \rangle_0. \tag{22}$$

Finally, consider the behaviour of $J(\omega)$ as $\omega \to \infty$, or, equivalently, the $t \to 0$ behaviour of the creep function. This question is related to that of an elastic component in the response. In turn, this depends on whether or not a subtraction is needed in the dispersion relation (17). If it is, then of course $J(\omega)$ tends to a real constant as $\omega \to \infty$. If it is not,

$$J(\omega) \underset{\omega \to \infty}{\sim} i\beta V K/4\omega, \quad K = \lim_{\omega \to \infty} S(\dot{\epsilon}; \omega). \tag{23}$$

This corresponds to the linear dependence

$$\psi(t) \underset{t \to 0}{\to} \tfrac{1}{4} \beta V K t. \tag{24}$$

In some cases, K may vanish. $\psi(t)$ may then display a t^2 dependence for small t. All these remarks will become clearer in the light of the specific examples to be considered below.

3. Stochastic analysis of the network equation

We now come to a most important task. The modified response-theoretic formulas of §2 were motivated by the assertion, already made, that $\epsilon(t)$ is non-stationary while $\dot{\epsilon}(t)$ is stationary in the absence of an applied stress. In more formal language (van Kampen 1977), the macroscopic equation for $\epsilon(t)$ is supposed to be stable but not asymptotically stable, like that for the position of a Brownian particle. On the other hand, the macroscopic equation for $\dot{\epsilon}(t)$ is asymptotically stable, like that for the velocity of a Brownian particle. This basic assertion must now be substantiated explicitly. Only then can confidence be placed in the formal answers derived in § 2.

*It is worth remembering that $J(\omega)$ is a retarded susceptibility. It is not an analytic function of ω. The spectral representation (9) shows that it is the boundary value from above of an analytic function of ω. The latter has a cut along the real axis.

What must be done is as follows. A suitable macroscopic or phenomenological stress-strain constitutive equation that represents viscoelastic behaviour, must be chosen. Next, this relation must be regarded as a stochastic equation connecting the instantaneous fluctuating stress and strain. In the absence of an externally applied stress, the equation describes how random internal stress fluctuations drive the strain fluctuations.* Given the statistical properties of the former, the equilibrium autocorrelation of the strain rate may be computed. When substituted in the LRT formulas of § 2, the known response functions corresponding to the macroscopic constitutive relation must emerge correctly. These response functions relate the average strain to the external stress. Their determination from the properties of equilibrium (zero applied stress) fluctuations in $\dot{\epsilon}(t)$ constitute, therefore, a direct demonstration of our theory. Once this verification is achieved, attention may be diverted to applications.

The natural choice for the macroscopic constitutive relation corresponds to the Maxwell network. This is the simplest model of viscoelasticity. The stress-strain relation (10) and the creep function (11) have already been written down. The latter displays the typical runaway character of viscoelastic flow with increasing time. This will be reproduced from a consideration of the fluctuations. In addition, the unphysical instantaneous response occurring in the phenomenological model will be tamed. After the stochastic analysis of this archetypal model is completed, one need no longer lean upon any particular network equation to describe viscoelastic behaviour. Any convenient method of computing the equilibrium autocorrelation of the strain rate will suffice to solve the problem in each physical situation.

Let us begin, therefore, with the stochastic counterpart of the network equation (10), namely,

$$\dot{\epsilon}(t) = \sigma(t)/\eta + \dot{\sigma}(t)/E. \tag{25}$$

No external stress is applied. $\sigma(t)$ is the random internal stress. It is taken to be a stationary random process with $\langle \sigma(t) \rangle = 0$. Therefore $\dot{\epsilon}(t)$ is also a stationary random process with $\langle \dot{\epsilon}(t) \rangle_0 = 0$. On the other hand, integrating (25) with the initial condition $\sigma(t_0)=0$, say, gives

$$\epsilon(t) - \epsilon(t_0) = (1/\eta) \int_{t_0}^{t} dt' \sigma(t') + (1/E)\sigma(t). \tag{26}$$

The first term on the right arises from the dissipative element in the network, the dashpot in series. Its presence clearly shows that $\epsilon(t)$ is not a stationary process, but rather one with stationary *increments* (Stratonovich 1963). This is the property ultimately responsible for viscoelastic flow in the model.

*One could just as well adopt the complementary view: namely, that random internal *strain* fluctuations drive those in the stress. This would be a more natural standpoint, perhaps, if one could also ' apply ' external strain. And indeed this is effectively the case in a stress relaxation experiment. Moreover, the Maxwell model does exhibit an exponential stress relaxation. However, we have once and for all chosen to regard the stress as the 'external force' in the Hamiltonian, and the strain as the conjugate variable. No generality is lost by retaining this convention. In fact, our being able to handle viscoelastic creep directly, instead of considering stress relaxation, is an illustration of the power of the method of analysis used.

When applied to (25), the Wiener-Khinchin theorem gives

$$S(\dot{\epsilon};\,\omega)=(1/\eta^2+\omega^2/E^2)\,S(\sigma;\,\omega). \tag{27}$$

To go on, some further properties of the stochastic process $\sigma(t)$ must be specified. The simplest choice is a totally random $\sigma(t)$, a white noise—more specifically, a δ-correlated Gaussian Markov process. However, this is an idealisation not realisable in practice. There is also a technical difficulty in defining the corresponding derivative process $\dot{\sigma}(t)$, and the latter occurs in the stochastic equation. Finally, the factor ω^2 in (27) (associated with the instantaneously responding part of the network) leads to an unphysical divergence of $S(\dot{\epsilon};\,\omega)$ as $\omega\to\infty$, if $S(\sigma;\,\omega)$ has the flat spectrum corresponding to white noise. All these problems can be solved quite simply. After white noise, the simplest random process is a stationary Gaussian Markov process. We take $\sigma(t)$ to be such a process. It is then exponentially correlated:

$$\langle\sigma(0)\,\sigma(t)\rangle = \langle\sigma^2\rangle \exp(-\gamma t)\ (t>0). \tag{28}$$

The correlation time is $1/\gamma$. Further,

$$S(\sigma;\,\omega) = 4\langle\sigma^2\rangle\,\gamma/(\gamma^2+\omega^2). \tag{29}$$

The white noise case can also be recovered from the above, on letting $\langle\sigma^2\rangle\to\infty$, $\gamma^{-1}\to 0$ such that

$$\lim \langle\sigma^2\rangle/\gamma = \text{constant} = \Gamma/2. \tag{30}$$

We have then

$$\langle\sigma(0)\,\sigma(t)\rangle = \Gamma\,\delta(t),\ S(\sigma;\,\omega)=2\,\Gamma. \tag{31}$$

Let us return to (28) and (29). Substitute the latter in (27), and use the result in equation (15) for the creep function. Performing the required integration, we obtain

$$\psi(t)=\beta V\langle\sigma^2\rangle\,[t/\eta^2\gamma+(1/E^2-1/\eta^2\gamma^2)\,\{1-\exp(-\gamma t)\}]. \tag{32}$$

Except for the additional exponential term, this is functionally of the same form as (11), as required. Let us analyse (32) point by point. First, note that the exponential term ensures that $\psi(0)=0$. Hence there is no strictly instantaneous response, as long as the correlation time γ^{-1} is non-vanishing. If γ^{-1} is very small, then $\exp(-\gamma t)\to 0$ within a very short time period t. The system then *appears* to have an elastic response. The next point is crucial. For large values of t (such that $\gamma t \gg 1$), the term linear in t dominates $\psi(t)$. Likewise, the creep function (11) obtained from the macroscopic equation (10) is dominated by the linear term t/η. A comparison thus yields the equation

$$\eta = \beta V\langle\sigma^2\rangle/\gamma. \tag{33}$$

In the white noise limit (30), the above relation becomes

$$\Gamma = 2\eta k_B T/V. \tag{34}$$

Equation (33) and its special case (34) represent a very important consistency condition, the fluctuation-dissipation theorem. It relates the strength of the random internal stress to the parameter controlling the dissipation in the network, the dashpot viscosity η. Such a relation exists even though $\epsilon(t)$ is non-stationary because $\dot{\epsilon}(t)$ *is* stationary and the macroscopic equation for this latter variable is asymptotically stable. What is even more striking is the following observation. In paper I, a stochastic analysis of the Voigt network was given. This is the simplest model of anelasticity. It consists of a spring and dashpot in *parallel.* Here, $\epsilon(t)$ is itself stationary in equilibrium. The corresponding fluctuation-dissipation theorem happens to be precisely the one deduced above! (See equation (40) of I). There is a simple explanation for this ' coincidence '. After all, the fluctuation-dissipation connection should transcend the particular configuration in which the dissipative element occurs in the network.* Therefore this identity of result, obtained from two very different network equations describing two different types of mechanical behaviour, is gratifying. It serves as a further corroboration of our procedure.

Next, consider (32) once again in the region $\gamma t \gg 1$, so that the exponential term may be dropped. Comparing the constant term in the result with that in (11), we get the equation

$$1/E = \beta V\langle\sigma^2\rangle(1/E^2 - 1/\eta^2\gamma^2). \tag{35}$$

Solving for E, and using (33), we find that

$$E = (\sqrt{5} - 1)\beta V\langle\sigma^2\rangle/2 = (\sqrt{5} - 1)\eta\gamma/2. \tag{36}$$

Before commenting on the final equation in (36) let us record that (33) and (36) help write the true creep function (32) of the Maxwell network in the form

$$\psi(t) = (t/\eta) + (1/E)\,[1 - \exp(-\gamma t)]. \tag{37}$$

This replaces (11). The compliance corresponding to (37) is, using (2),

$$J(\omega) = (i/\eta\omega) + \gamma/E(\gamma - i\omega). \tag{38}$$

Since this expression vanishes as $\omega \to \infty$, no subtraction is needed in the spectral representation for $J(\omega)$. The limit $\gamma \to \infty$ takes us back to the instantaneous response situation, in which $J(\infty) = \psi(0) = 1/E$.

Let us now comment on the relation between E and η that appears to be expressed by the final equation in (36). At the phenomenological level, of course, these are two quite independent, unrelated network parameters. Now the compliance of the origi-

*Equation (34) is the mechanical equivalent of the Nyquist theorem for the thermal noise voltage in a resistor. The latter relation is clearly independent of whether a series or parallel effective LR circuit is used in deriving it.

nal Maxwell network is given by $(1/E)+(i/\eta\omega)$. One may be tempted to argue, therefore, that causality, i.e., a dispersion relation, does connect the real and imaginary parts of this expression. Once again, this is not so. The model is so simple that both the terms in the compliance are ' exceptions '. The real part is a subtraction term. The imaginary part is a zero-frequency pole. Both these are independent additions to the analytic part of the generalised susceptibility. It is the latter part that obeys a dispersion relation. In the present instance, this part happens to be absent, that is, identically zero. Hence E and η are not related.

What is the meaning, then, of (36)? The original Maxwell model exhibits stress relaxation. The stress required to maintain a given constant strain imposed at $t=0$ decreases exponentially with time. The stress relaxation function is $E \exp(-Et/\eta)$. The relaxation time is $\tau=\eta/E$. Equation (36) merely relates this to the correlation time $1/\gamma$ of the random internal stress, according to $\tau=(\sqrt{5}+1)/2\gamma$. However, τ should no longer be regarded as the actual relaxation time. We have shown that (37) and (38) are the true response functions of the model. Concurrently, the stress relaxation function is also modified.* It is given by $E' \exp(-t/\tau')$, where the relaxation strength decreases to $E'=2(\sqrt{5}-2)E/(\sqrt{5}-1) \simeq 0{\cdot}39\ E$. The relaxation time turns out to have the ' renormalised ' value

$$\tau' = (\sqrt{5}+3)/2\gamma = \tau + 1/\gamma. \tag{39}$$

The smearing out of the original instantaneous response thus slows down the stress relaxation.

4. A general form for ψ (t); other remarks

The creep function of the original Maxwell model is linear in t, with a slope $1/\eta$. According to the modified form (37), however, this is the asymptotic value of the slope. For very small values of $t(\gamma t \ll 1)$, $\psi(t)$ is again approximately linear in t. The slope is $(1/\eta)+(\gamma/E)=(\sqrt{5}+3)/2\eta \simeq 2{\cdot}62/\eta$.

$\psi(t)$ has a leading linear behaviour for small t because $\dot{\epsilon}(t)$ has a white noise component in the example under consideration. (Equations (27) and (29) show that $S(\dot{\epsilon};\omega) \to$ const. as $\omega \to \infty$.) It is necessary to point out that this will *not* be the case in most physical situations. $\dot{\epsilon}(t)$ can generally be related to some microscopic velocity or current. In a widc range of problems, the conditional probability density of the latter variable can be taken to obey a generalised Fokker-Planck equation. In a broad sense, we may say that the viscoelasticity of the material is ' diffusion-controlled '. As in various other situations (see, e.g., Balakrishnan 1978b), the advantage of the LRT approach is that only the external stress-free master equation need be considered in evaluating the creep function, compliance, etc. Quite generally, $\langle \dot{\epsilon}(0)\dot{\epsilon}(t)\rangle_0$ will turn out to be a damped exponential, or possibly a superposition of such terms. Unless there are questions of convergence in cases involving a super-

*To determine the stress relaxation function, we may use the fact that its Fourier-Laplace transform $\bar{\phi}(\omega)$ and that of the creep function, $\bar{\psi}(\omega)$, are related by $1+\omega^2\bar{\phi}(\omega)\bar{\psi}(\omega)=0$.

position of an infinite number of terms, the representation (19) enables us to deduce the leading small t behaviour

$$\psi(t) \underset{t\to 0}{\sim} \tfrac{1}{2}\beta V\langle \dot{\epsilon}^2\rangle_0 t^2. \tag{40}$$

This explains the comment made following (24). Similarly, the asymptotic behaviour of the creep function is given by

$$\psi(t) \underset{t\to\infty}{\sim} \beta V t \int_0^\infty dt' \langle \dot{\epsilon}(0)\, \dot{\epsilon}(t')\rangle_0. \tag{41}$$

As already shown in (21), this integral vanishes, and the strain therefore saturates, in the special case of anelasticity.

The rest is specific to the particular problem of interest. A few further remarks of a general nature may be made. An example of diffusion creep is Nabarro-Herring creep (see, e.g., Nowick and Berry 1972). This occurs in metals at high temperatures. The mechanism is the anisotropic intra-grain diffusion of vacancies under an applied stress. To determine the associated creep function *rigorously*, the equilibrium auto-correlation of the vacancy current must be computed. However, one may state on physical grounds that the basic time scale governing the correlation of this fluctuating current will be $\sim l^2/D$, where l is the average linear dimension of a grain and D is the vacancy diffusion constant. Of course, a whole spectrum of relaxation times, related to the basic time scale, may occur in the expression for $\langle\dot{\epsilon}(0)\dot{\epsilon}(t)\rangle_0$. This depends on the boundary conditions of the problem. A similar thing happens in the Rouse molecular theory of polymer viscoelasticity (Rouse 1953) as well as in subsequent refinements. Here each macromolecule is assumed to be made up of n ' submolecules '. The end-to-end displacement $\mathbf{r}_i$ of the ith submolecule is supposed to have a Gaussian distribution. A diffusion model is set up to describe the random motion of the points joining two submolecules. It turns out that n relaxation times occur in the problem, given by

$$1/\tau_r = (24\, Bk_BT/\overline{r_s^2}) \sin^2 [\pi r/2(n+1)].\ (r=1, 2,\ldots n). \tag{42}$$

Here B is a ' mobility ' constant, and $\overline{r_s^2}$ is the mean square end-to-end distance of a submolecule. In all the above cases, $\langle\dot{\epsilon}(0)\dot{\epsilon}(t)\rangle_0$ is a continuous or discrete superposition of damped exponentials. It is therefore interesting to see what the functional form of the corresponding creep function is. This form promises to be one of some generality.

Accordingly, let

$$\langle\dot{\epsilon}(0)\, \dot{\epsilon}(t)\rangle_0 = \sum_i c_i \exp(-\lambda_i t)\ (\lambda_i>0), \tag{43}$$

where the summation may be an integration in some cases. Oscillatory multiplicative factors (e.g., $\cos \omega_i t$) can be included if necessary without any difficulty. Pro-

vided certain easily-deduced convergence conditions are satisfied, the creep function is

$$\psi(t)=\beta V \sum_i (c_i/\lambda_i^2)\,[\lambda_i t-1+\exp(-\lambda_i t)]. \tag{44}$$

As expected, $\psi(t)$ begins with a leading t^2 short-time behaviour, and switches over to a linear asymptotic behaviour. This feature is quite universal. Many mechanisms of plastic deformation also share it. The asymptotic region of course corresponds to steady-state flow. In diffusion-controlled cases, the t^2 regime is a consequence of the familiar 'free-particle' short-time behaviour that dominates for $t \ll 1/\lambda_i$, i.e., before the 'friction' sets in to damp the motion. In plastic deformation due to dislocation motion, there is a rather similar reason for the existence of this regime. It occurs while the dislocation density is in the process of building up under the applied stress. The density is sufficiently small to permit unhindered dislocation glide. Once there is substantial interaction between the dislocations, the creep behaviour becomes more complicated. Work-hardening is said to occur. Thus, although plasticity with its non-linear σ-ϵ functional relationship is well outside the scope of this paper, the corresponding creep function shares, in many cases, some of the physical features present in (44).

Let us conclude by recording the expression for $J(\omega)$ associated with (43) and (44). This is

$$J(\omega)=i\beta V \sum_i c_i/\omega\,(\lambda_i-i\omega). \tag{45}$$

Consistent with the short-time t^2 dependence of $\psi(t)$, $J(\omega) \sim \omega^{-2}$ as $\omega \to \infty$. We reiterate that these conclusions can be altered drastically in certain cases. An infinite summation over the index i, or an integration over a continuous spectrum, may lead to fractional powers in the leading behaviour at either extreme of frequency (or time). The general formulas derived in §2 continue to hold good. A careful examination of these will yield the correct leading exponents in such cases.

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