Criticisms of the recently proposed analysis and methods of 'thermoviscoelasticity'

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Thermoelasticity or force–temperature measurements on elastomeric networks are generally conducted in such a way that viscous effects can be assumed to be of negligible importance. Specifically, the deformed networks are permitted to relax for relatively long periods of time at high temperatures, and the measurements of the elastic force are then carried out at a series of lower temperatures using significantly shorter time intervals. These techniques have recently been criticized, with the recommendation that they be replaced with a time-dependent 'thermoviscoelasticity' analysis. Re-examination of this general problem shows the earlier approach to have a sound theoretical foundation and the time-dependent analysis to be misguided and very seriously flawed.

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INTRODUCTION

Crosslinked networks of amorphous polymers exert retractive forces f that are largely entropic in origin with a usually small energy contribution f_e to the force. With an elastic equation of state f_e can be partitioned between intra- and intermolecular interactions. To this end the Gaussian theory of elasticity has been widely used[1]. This theory asigns the ratio f_e/f in its entirety to intramolecular interactions stemming from polymer chain backbone rotational energies.

A massive amount of experimental data validates the Gaussian theory as being at least semiquantitatively reliable[2-10], and recent theoretical work is moving it closer to the quantitative realm[11-13]. Traditional problems in elasticity have generally been of two kinds: theoretical deficiencies of the Gaussian theory, and experimental failures to achieve equilibrium. Both problems could impact the field of thermoelasticity in major ways.

Since the Gaussian theory is quantitatively inexact, how much error is associated with its use to evaluate f_e/f? Short of an exact theory, it might appear that this question can be avoided by resort to a phenomenological approach involving only experimental quantities: force f, length L, volume V and temperature T. Unfortunately, this simply is not possible. Only if an experimental constraint of constant volume is imposed on the system can the phenomenological approach lead to an evaluation of f_e/f; even so, an interpretation of f_e/f is not supplied. And the condition of constant volume, difficult to maintain, is rarely used[14] in favour of the readily accessible condition of constant pressure. But constant-pressure experiments require absolutely an equation of state even to evaluate f_e/f, much less to interpret it. Thus, accuracy of the Gaussian theory is an issue that cannot be avoided. Studies of swollen[15] and unswollen[16] networks, and experiments at constant volume[14], indicate that thermoelasticity (force–temperature behaviour) is not dramatically sensitive to deficiencies of the Gaussian theory. In fact, the only networks in which non-Gaussian effects[7,17] are unambiguously present are probably those having very unusual bimodal distributions specifically designed to emphasize limited-chain extensibility[9,18]. Also, if such non-Gaussian effects were important, then f_e/f should exhibit its largest dependence on elongation at high elongations. However, when this ratio varies at all, it generally does so at low elongations (because of difficulties in measuring rest lengths), and at higher elongations only when strain-induced crystallization occurs[16,19,20]. It must be admitted, nonetheless, that this issue is by no means entirely settled.

The second problem is the inability of stretched networks to reach equilibrium. Slow relaxation can continue indefinitely and may not indicate a close approach to equilibrium. In fact, such a system could be far from equilibrium if its relaxation, or retardation, spectrum is skewed towards the region of long relaxation times. Are thermoelastic results then seriously affected by slow relaxation in the long-time region? Experimental results to date indicate that they are not, provided relaxation is so slow that reversibility is nearly achieved over the time of the experiment. For example, thermoelastic results for rubber networks are indifferent to an increase in relaxation time from 20 min to 8 h[16]. Also, swollen and unswollen networks fail to display problematic time effects, if they exist, which might be expected because of the greatly reduced internal viscosity of swollen networks[15]. More specifically, themoelastic measurements on networks swollen to volume fractions of polymer as low as 0.18 give essentially the same values of the temperature coefficient $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ of the unperturbed mean-square end-to-end distance of the

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network chains as do measurements on the same networks in the totally unswollen state[21]. Since the large viscoelastic responses generally present in unswollen networks are greatly reduced or eliminated at high degrees of swelling, this strongly suggests that thermoelastic measurements as presently conducted over relatively long time intervals are not very sensitive to time-dependent effects. Also relevant in this regard is the fact that viscosity–temperature data extrapolated to infinite dilution generally give values of $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ in very good agreement with thermoelastic results on the same polymer, including those obtained on the undiluted networks[21,22].

In two recent publications[23,24], N. G. McCrum dismisses all prior work on thermoelasticity on the grounds that viscoelastic effects are extensive and the Gaussian theory (invariably used) is incorrect—i.e. on the two grounds of traditional concern. In lieu of the 'irrational' methods of the past, he has proposed a new method of thermoviscoelasticity claimed to solve both problems. His method eliminates time, permitting even rapid experimental relaxation, and removes equations of state from the analysis even at constant pressure. In view of the importance of these two issues, his claims are certainly interesting, but we believe his method of thermoviscoelasticity and his analysis are incorrect.

DISCUSSION OF McCRUM'S CLAIMS

Thermoviscoelasticity

We consider first the thermoviscoelasticity argument[24]. McCrum discusses two small perturbations imposed upon a network stressed by an amount σ. Prior to either perturbation the stressed network is considered to have reached equilibrium so that its modulus, or compliance, is that of the equilibrium state. Actually, he does not require that this initial stressed state be at equilibrium, only that changes with time are slight throughout the experimental program. His calculations, however, refer to an equilibrium state and we will follow suit.

McCrum restricts his considerations to linear elasticity; a stress σ generates an equilibrium strain $\gamma(T,\sigma)$ at temperature T of amount:

$$\gamma(T,\sigma)=J(T)\sigma \tag{1}$$

where $J(T)$ is the equilibrium compliance. A small perturbation is imposed on this stretched state by suddenly increasing the stress by a small amount $\Delta\sigma$. When equilibrium is reached the perturbation $\Delta\sigma$ produces a change in strain $\Delta\gamma$ of amount:

$$\Delta\gamma(T,\Delta\sigma)=J(T)\Delta\sigma \tag{2}$$

But if sufficient time is not allowed for the perturbation to reach equilibrium, viscous retardation will diminish the strain increment after a time lapse t by a factor $X(t,T)$, so that:

$$\Delta\gamma(t,T,\Delta\sigma)=\Delta\gamma(T,\Delta\sigma)X(t,T) \tag{3}$$

or

$$\Delta\gamma(t,T,\Delta\sigma)=J(t,T)\Delta\sigma \tag{4}$$

where $J(t,T)$ is written for $J(T)X(t,T)$.

Next, McCrum considers a small strain increment at constant stress generated by a small sudden temperature perturbation ΔT. The network is first brought to equilibrium under the stress σ at temperature $T'=T-\Delta T$:

$$\gamma(T-\Delta T,\sigma)=J(T-\Delta T)\sigma \tag{5}$$

If the temperature is now abruptly changed by an amount ΔT to T, the new equilibrium state is described by (1), and the jump in strain, $\Delta\gamma(T,\sigma\Delta T)$, generated by the jump in temperature is the difference between (1) and (5):

$$\Delta\gamma(T,\sigma\Delta T)=\gamma(T,\sigma)-\gamma(T-\Delta T,\sigma) \tag{6}$$

or

$$\Delta\gamma(T,\sigma\Delta T)=[J(T)-J(T-\Delta T)]\sigma$$

which for a small variation ΔT is:

$$\Delta\gamma(T,\sigma\Delta T)=J(T)\frac{\mathrm{d}\ln J(T)}{\mathrm{d}T}\sigma\Delta T \tag{7}$$

If, however, this temperature-generated perturbation is not allowed to reach equilibrium, McCrum states that it will be retarded after a time lapse t by the same factor $X(t,T)$ as for the isothermal experiment involving a perturbation of stress. He argues this must be so because creep in both experiments occurs at the same temperature T. Therefore, multiplying both sides of (7) by $X(t,T)$, we have in complete agreement with McCrum:

$$\Delta\gamma(t,T,\sigma\Delta T)=J(t,T)\frac{\mathrm{d}\ln J(T)}{\mathrm{d}T}\sigma\Delta T \tag{8}$$

The ratio of the strain variations of the two experiments, at the same time t, is independent of time and involves only equilibrium quantities; (8) divided by (4) is:

$$\frac{\Delta\gamma(t,T,\sigma\Delta T)}{\Delta\gamma(t,T,\Delta\sigma)}=\frac{\mathrm{d}\ln J(T)}{\mathrm{d}T}\sigma\frac{\Delta T}{\Delta\sigma} \tag{9}$$

which does not involve time in any fashion.

No doubt McCrum has proffered a simple and unique expedient for eliminating the effects of viscoelastic creep on thermoelasticity, provided his analysis is correct. We do not think it is. It seems strange that a creep factor $X(t,T)$ applicable to an *isothermal* process could also apply to a *non-isothermal* isotonic process, as McCrum claims. His argument that the temperature change $T'\rightarrow T$, abrupt at $t=0$, which is all right as a working approximation, allows creep when $t>0$ only at temperature T encourages him to write, in effect, for a network initially at temperature $T'=T-\Delta T$ changing isotonically to temperature T, a change of strain of:

$$\Delta\gamma(t,T,\sigma\Delta T)=\gamma(T,\sigma)X(t,T)-\gamma(T',\sigma)X(t,T) \tag{10}$$

Time t is that elapsed since the inception of ΔT. But this clearly is not in accord with Boltzmann's superposition principle, which applies to problems of successive stresses and corresponding strains, this one being no exception. Consider the first experiment, an isothermal strain variation produced by a small change in stress from σ' to

σ. Boltzmann's principle tells us that $\Delta\gamma(t,T,\Delta\sigma)$ at time t following the stress variation $\Delta\sigma=\sigma-\sigma'$ is the strain $\gamma(t,T,\sigma)$ a time t after loading the unloaded sample at temperature T with the stress σ minus the strain $\gamma(t,T,\sigma')$ a time t after loading the unloaded sample at temperature T with the stress σ'. That is:

$$\Delta\gamma(t,T,\Delta\sigma)=\gamma(t,T,\sigma)-\gamma(t,T,\sigma') \qquad (11)$$

The two strains, both referred to the unstretched sample length, are simply the strains at T produced by the independent stresses σ and σ' after time t has elapsed from the respective independent loadings of the unstressed sample. Expanding (11) in a Taylor series to the first power of $\Delta\sigma$ gives:

$$\Delta\gamma(t,T,\Delta\sigma)=\frac{\partial\gamma(t,T,\sigma)}{\partial\sigma}\Delta\sigma=J(t,T)\Delta\sigma \qquad (12)$$

which is identical to (4), in agreement with McCrum.

The isotonic process must be treated in an exactly similar way. Since the change here is generated by the transition $T'\rightarrow T$, we must write:

$$\Delta\gamma(t,T,\sigma\Delta T)=\gamma(t,T,\sigma)-\gamma(t,T',\sigma) \qquad (13)$$

This strain perturbation is the strain $\gamma(t,T,\sigma)$ a time t after loading the unloaded sample at temperature T with the stress σ minus the strain $\gamma(t,T',\sigma)$ a time t after loading the unloaded sample at temperature $T'=T-\Delta T$ with the same stress σ. Expanding (13) to the first power of ΔT yields:

$$\Delta\gamma(t,T,\sigma\Delta T)=\frac{\partial\gamma(t,T,\sigma)}{\partial T}\Delta T \qquad (14)$$

Because $\gamma(t,T,\sigma)=J(t,T)\sigma$, it follows that:

$$\Delta\gamma(t,T,\sigma\Delta T)=J(t,T)\frac{\partial\ln J(t,T)}{\partial T}\sigma\Delta T \qquad (15)$$

which is very different from McCrum's result expressed by (8). The ratio of the isotonic to isothermal strain variations is not in fact independent of time, but instead:

$$\frac{\partial\ln J(t,T)}{\partial T}\sigma\frac{\Delta T}{\Delta\sigma} \qquad (16)$$

Consequently, the temperature derivative of the equilibrium compliance $J(T)$ *cannot* be obtained in general by combining the two experiments in this fashion, and this negates completely McCrum's concept of thermoviscoelasticity.

Gaussian approximation

We turn now to McCrum's second claim to have eliminated the necessity for an equation of state, specifically the Gaussian equation of state, from thermoelasticity analysis. Since it is not necessary to include time in this discussion, we follow McCrum and consider only the equilibrium situation. McCrum starts with a general stress–deformation equation:

$$\sigma=G(T)F(\lambda) \qquad (17)$$

The modulus $G(T)$ equals $1/J(T)$ and $F(\lambda)$ is a general function of the deformation ratio λ (length/initial length). McCrum believes the modulus $G(T)$ is the same as that of the Gaussian theory, but he leaves $F(\lambda)$ unspecified. From (17) he arrives at a result equivalent to, at constant pressure p:

$$\left(\frac{\partial L}{\partial T}\right)_{p,f}-L\beta_{\mathrm{L}}^{0}=f\left(\frac{\partial L}{\partial f}\right)_{p,T}\left(\frac{\mathrm{d}\ln J(T)}{\mathrm{d}T}-2\beta_{\mathrm{L}}^{0}\right) \qquad (18)$$

where L is the length, and β_{L}^{0} is the linear thermal expansion coefficient of the undeformed network. Actually McCrum writes the derivatives $(\partial L/\partial T)_{p,f}$ and $(\partial L/\partial f)_{p,T}$ as finite ratios $\Delta L/\Delta T$ and $\Delta L/\Delta f$, respectively. A precise delineation of the terms, however, is preferred if confusion is to be avoided. Equation (18) contains nothing of $F(\lambda)$, which makes it appear to be independent of an equation of state. A plot of $(\partial L/\partial T)_{p,f}$ against $f(\partial L/\partial f)_{p,T}$ is linear with a slope determined in part by the derivative of $J(T)$. Since McCrum claims $G(T)$ to be the Gaussian modulus, (18) is not really independent of the Gaussian theory as he states. But this is not the most serious error here.

The really important trouble is bound up with (17), which is not a correct general stress–strain representation. Actually, it is nothing more than a functional representation of the Gaussian theory (insofar as only reasonably realistic theories are considered). Without doubt, neither the non-Gaussian theory of finite deformations[25] nor the Mooney–Rivlin treatment[10,26] can be represented by (17). The problem is that equations of state cannot in general be factored in this way. The correct general factorization includes volume V as well as T and λ:

$$\sigma=G(T,V)F(T,V,\lambda)$$

and this leads to something quite different from (18). But since factorization is unnecessary anyway, let us start with the simplest of all representations of the force f, rather than the stress σ, as a function of T,V,L:

$$f=f(T,V,L) \qquad (19)$$

We want to know how $(\partial L/\partial T)_{p,f}$ is related to $(\partial L/\partial f)_{p,T}$. This is directly obtained by differentiating (19) at constant pressure p and force f:

$$\left(\frac{\partial f}{\partial L}\right)_{VmT}\left(\frac{\partial L}{\partial T}\right)_{p,f}+\left(\frac{\partial f}{\partial V}\right)_{L,T}\left(\frac{\partial V}{\partial T}\right)_{p,f}+\left(\frac{\partial f}{\partial T}\right)_{L,V}=0$$

Rearranging this to the form similar to that of (18), we have:

$$\left(\frac{\partial L}{\partial T}\right)_{p,f}-L\beta_{\mathrm{L}}^{0}=-f\left(\frac{\partial L}{\partial f}\right)_{V,T}\left[\left(\frac{\partial\ln f}{\partial T}\right)_{L,V}+V\beta\left(\frac{\partial\ln f}{\partial V}\right)_{L,T}+L\beta_{\mathrm{L}}^{0}\left(\frac{\partial\ln f}{\partial L}\right)_{V,T}\right]$$

where $\beta=(\partial\ln V/\partial T)_{p,f}$ is the volume thermal expansion coefficient. The volume V of an elastomer is essentially independent of its length L, so β can be replaced by $3\beta_{\mathrm{L}}^{0}$

and:

$$\left(\frac{\partial L}{\partial f}\right)_{V,T}=\left(\frac{\partial L}{\partial f}\right)_{p,T}$$

Thus, we have:

$$\left(\frac{\partial L}{\partial T}\right)_{p,f}-L\beta_{\mathrm{L}}^{0}=-f\left(\frac{\partial L}{\partial f}\right)_{p,T}\left\{\left(\frac{\partial \ln f}{\partial T}\right)_{L,V}+\beta_{\mathrm{L}}^{0}\left[3V\left(\frac{\partial \ln f}{\partial V}\right)_{L,T}+L\left(\frac{\partial \ln f}{\partial L}\right)_{V,T}\right]\right\} \qquad (20)$$

Equation (20), not (18), is perfectly general. But it is of little value without an equation of state to evaluate the various partial derivatives, particularly those enclosed by braces. It certainly cannot be assumed that a plot of $(\partial L/\partial T)_{p,f}$ vs. $f(\partial L/\partial f)_{p,T}$ is linear; indeed, it is not in the general case if equations of state other than the Gaussian can be used as a guide, although deviations from linearity may not be large. Use of the Gaussian theory leads back from (20) in a stepwise fashion to (18) and ultimately to Shen's equation[27]. McCrum's result, equation (18), is simply an intermediate step in applying the Gaussian theory to (20) to obtain Shen's important Gaussian result. Equation (18) is not at all a general equation independent of the Gaussian theory as claimed.

A related point

Finally, it is useful to include a general comment on systems not at equilibrium. The force is now dependent on time, i.e.:

$$f=f(T,V,L,t)$$

Limiting the time interval to a definite value t, $\mathrm{d}t=0$, we have:

$$\left(\frac{\partial L}{\partial T}\right)_{p,f,t}-L\beta_{\mathrm{L}}^{0}=-f\left(\frac{\partial L}{\partial f}\right)_{p,T,t}\left\{\left(\frac{\partial \ln f}{\partial T}\right)_{L,V,t}+\beta_{\mathrm{L}}^{0}\left[3V\left(\frac{\partial \ln f}{\partial V}\right)_{L,T,t}+L\left(\frac{\partial \ln f}{\partial L}\right)_{V,T,t}\right]\right\} \qquad (21)$$

This equation shows clearly that (1) an equation of state, actually a dynamical equation including time, is necessary to proceed beyond equation (21), and (2) time cannot be removed as a contributing factor unless it is great enough to establish equilibrium, in which case the dependence on t fades from each term in (21). At times short of equilibrium yet still large, we have little or no indication that the terms in (21) are seriously affected. It seems likely that the terms in square brackets are independent of time, or very nearly so. The quantity $(\partial \ln f/\partial T)_{L,V,t}$, however, should depend upon t, although it could be somewhat insensitive unless t is small.

CONCLUSIONS

We conclude from this analysis that traditional thermoelasticity studies in general are valid, not irrational, and not seriously affected by conditions of non-equilibrium except in impatiently carried out experiments where insufficient relaxation might have been a factor. Thermoelasticity cannot be analysed without an equation of state, the most acceptable and useful one to date being the Gaussian. Suggested methods of thermoviscoelasticity which purport to eliminate time from the analysis are without an acceptably rigorous theoretical foundation.

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