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On the rejuvenation of physically aged polymers by mechanical deformation

L. C. E. Struik
DSM Research, PO Box 18, 6160 MD Geleen, The Netherlands
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Experimental results obtained by volume measurements during mechanical deformation are compared with the author's tentative suggestion (*Physical Aging in Amorphous Polymers and Other Materials*, Elsevier, Amsterdam, 1977, pp. 83–96) that large mechanical deformation processes, even shear, may generate free volume. The experimental data appear to confirm the suggestion in detail. © 1997 Elsevier Science Ltd.

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INTRODUCTION

In a number of papers[1–9], McKenna and co-workers critized the author's suggestion[10] (pp. 83–96) that large deformations in glassy polymers may influence the state of physical ageing. The author's idea was that large-scale segmental motion, induced by mechanical stress, creates free volume, irrespective of whether the stress is tensile, compressive (uniaxial) or shear. Since ageing is supposed to be due to a gradual collapse of free volume, deformation-induced free volume will erase part of the previous ageing (rejuvenation).

McKenna and co-workers' criticism originates from their beautiful data, reproduced in *Figure 1*. We observe that the volume recovery of an epoxy glass ($T_g = 42.4°C$) quenched from 44 to 33.5°C and then periodically subjected to a shear deformation of 0.03. The shear was applied at 1800, 3600, 7200, ... s after quenching and removed after, respectively, 180, 360, 720, ... s (loading time smaller than 10% of the ageing time at the moment of straining). The volume shows peaks, both at strain application and at removal. The volume peaks last only a short time and the volume-recovery 'base-line' is hardly influenced (compare with the curve measured at the much smaller deformation of $\gamma = 0.0025$). So, McKenna and co-workers conclude that the author's suggestion is wrong and that the thermodynamic volume-recovery process is not basically influenced by mechanical deformation. In this paper we will consider whether this conclusion is justified.

COMPARISON OF MCKENNA AND CO-WORKERS' DATA WITH THE REJUVENATION HYPOTHESIS

First of all, McKenna and co-workers' data (*Figure 1*) confirm the very existence of a dilatation by shear[10] (p. 84). It should be realized that the literature is confusing about this effect. Wang *et al.*[11] reported positive as well as negative volume changes upon twisting PMMA and PC rods at room temperature (see also Pixa *et al.*[12]) and the discussion in ref. 3. Thus, the only point made here is that McKenna and co-workers' data confirm the author's suggestion instead of disproving it. These data further confirm that the dilatation occurs on application as well as on removal of strain, a feature predicted on page 90 of ref. 10. Moreover, on strain removal, the dilatation is larger than on strain application, an effect already explained[10] (p. 90) in connection with Turner's creep-recovery anomaly[13].

Sharpness of the volume peaks

First, there is no disagreement between the experimental data of McKenna and co-workers and those of the author. Take, e.g. Figure 74 of ref. 10, which was reproduced as Figure 8 in ref. 9. We see that a high stress pulse causes rejuvenation followed by reactivated ageing. The rejuvenation (increase in free volume) is not permanent, but fades away. In Figure 74 of ref. 10 this disappearance looks to be smeared out over a much

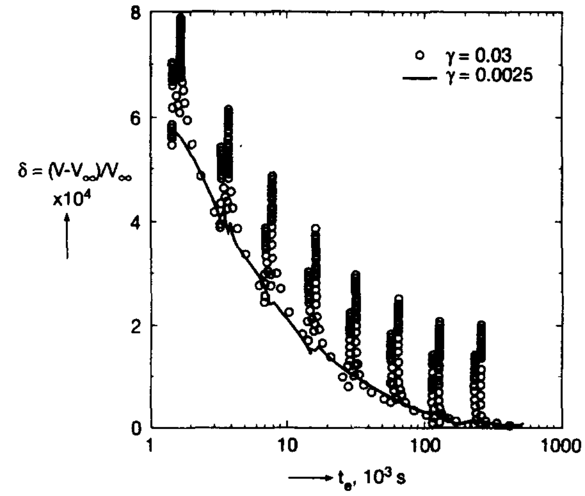

Figure 1 Volume recovery of epoxy glass: t_e is the time after the quench, minus the 450 s required for thermal equilibration, v denotes specific volume, and v_∞ its value at equilibrium. Reproduced with permission from Waldron *et al.*[9]. For details see text

longer period of time than in *Figure 1*. However, this difference is merely caused by the manner of plotting: when our data are replotted on a time scale similar to the one used by McKenna and co-workers, the peak has a similar sharpness (*Figure 2*).

Let us now consider the sharpness of the peaks from a theoretical point of view. The present author never succeeded in finding a satisfactory theoretical description of the coupled volume/mechanical relaxation. Both kinds of relaxation are characterized by wide distributions of relaxation times; it was not clear how to couple the distributions and how to distribute the deformation-induced volume over the various elements in the distribution. Therefore, in ref. 10 we used a simplified model with only a single relaxation time. This is well suited for down-quenching. As can easily be verified, for such tests, the differences between a one-parameter theory and the much better multi-parameter theories[14,15] are only small. In fact, for down-quenching, the volume recovery is dominated by the non-linear, self-retarding effects; the distribution of relaxation times is much less important than in an up-quench or in a down up-quench revealing maxima in the volume–recovery curve. It is for this reason that Lillie[16] and Kovacs[17] were successful with the application of the one-parameter model to simple down-quenches.

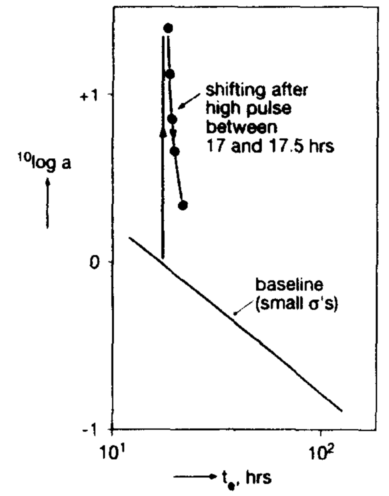

Figure 2 Rejuvenation and reactivation of ageing after a short application of high mechanical stresses (between 17 and 17.5 h after quenching). Data from Figure 74 of ref. 10 replotted on a time scale similar to the one used by McKenna and co-workers

Consider now *Figure 3*. The curve denoted by $v_s(t_e)$ represents the spontaneous volume recovery (no strain; subscript 's' stands for spontaneous). By rapid deformation at time t_{e1}, we 'pump in' an excess volume; just after t_{e1}, the volume has the value v_1 (see *Figure 3*). Curve $v'(t_e)$ denotes the volume recovery after this deformation.

For a one-parameter system (also in the non-linear case), the momentary rate is uniquely given by the momentary volume:

$$\mathrm{d}v/\mathrm{d}t_e = -(v - v_\infty)/\tau(v) \qquad (1)$$

where τ is the volume-dependent time constant.

As is well known, the solution of such a first-order differential equation is uniquely determined by the initial value of v; thus,

$$v'(t_e - t_{e1}) = v_s(t_e - t^*_{e1}); \qquad t_e > t_{e1} \qquad (2)$$

where t^*_{e1} is the time for which the spontaneous recovery $v_s(t_e)$ shows a volume v_1 (see *Figure 3*; t^*_{e1} is defined by $v_s(t^*_{e1}) = v_1$). Equation (2) shows that the curves for v_s and v' are mutually shifted on a linear time scale and that the deformation process at t_{e1} shifts the ageing back to the state attained at time t^*_{e1} during spontaneous relaxation.

On a logarithmic time scale, the simple shifting [equation (2)] is distorted and the recovery v' after t_{e1} looks strongly accelerated. This can be illustrated with the numerical values used in *Figure 3*. In the spontaneous recovery, t_e has to increase from 1 to 30 h to obtain a decrease in $\delta = v - v_\infty$ from 3 to 1.5 (see *Figure 3*). For $v'(t_e)$ the same decrease occurs between $100 + 1 = 101$ and $100 + 30 = 130$ h, i.e. over a much narrower interval

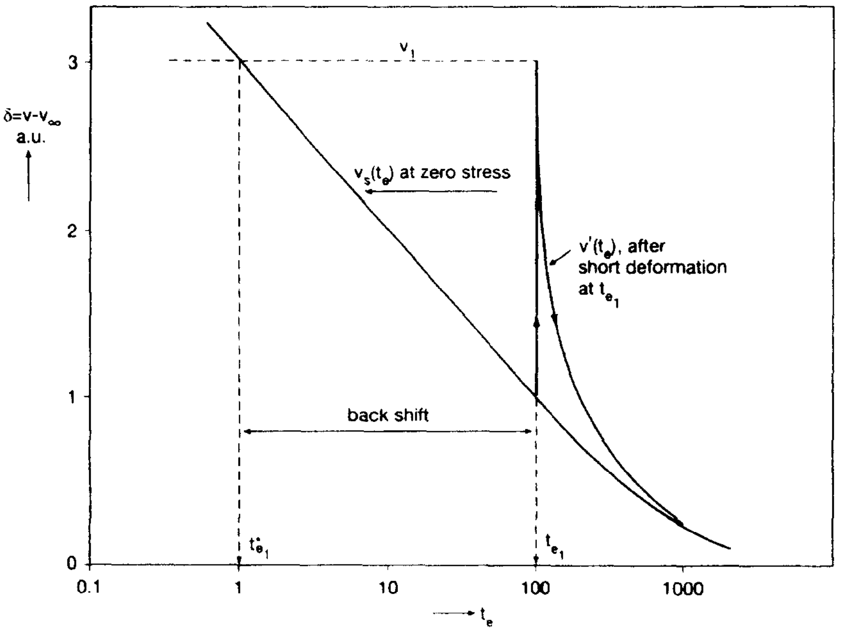

Figure 3 Spontaneous (no mechanical stress) volume relaxation $v_s(t_e)$ and relaxation $v'(t_e)$ after rapid deformation at $t_e = t_{e1}$; for explanation see text. Note that here, the notation is $\delta = v - v_\infty$ instead of $\delta = (v - v_\infty)/v_\infty$ as in *Figure 1*

on the $\log t_e$ scale. As a consequence, the deformation-induced dilatation fades away rapidly on the $\log t_e$ scale and hardly any effect remains for times three to five times greater than the time of stress application, just as found by McKenna and co-workers.

The above also explains McKenna and co-workers' finding (see, e.g. Figure 5 of ref. 9) that the time required to reach equilibrium at temperatures close to T_g is not influenced by the level of stress. Because the deformation-induced volume effects fade away rapidly, the 'base-line' of the volume recovery on the $\log t_e$ scale is hardly changed and the equilibration time will remain the same.

Peak height

Figure 1 shows that the height of the successive volume peaks is more or less constant. This can be explained with the effective-time theory for volume recovery[10] (pp. 118 and 128). We write:

$$\lambda = \int_0^{t_e} a(\xi)\,\mathrm{d}\xi \qquad (3)$$

where t_e is the (real) time elapsed after quenching, ξ an integration variable on the t_e time scale, λ the effective time, and a the acceleration factor, which depends on time via v and T, the latter being assumed constant here. The reference state ($a = 1$) can be chosen arbitrarily; we do not need to specify it here.

As in ref. 10, we assume that acceleration factor a is the same for volume and mechanical relaxation[10,18]. It then follows that on a λ-time scale all non-linear effects, i.e. stress and volume dependences disappear. The volume relaxation can be written as (crude one-parameter model of ref. 10):

$$\mathrm{d}\delta/\mathrm{d}\lambda' = -\delta/\tau_0 + \beta\Phi(\lambda') \qquad (4)$$

where $\lambda' = \lambda(t_e) - \lambda(t_{e1})$ is the increase in effective time since the moment of stress application, $\delta = v - v_\infty$, τ_0 is the (fixed) volume relaxation time in the reference state, and $\beta\Phi(\lambda')$ is the rate at which volume is generated by deformation. The magnitude, β, depends on stress level, but the time dependence, $\Phi(\lambda')$, is fixed and determined by the time dependence of the relaxation properties in the reference state; so, $\Phi(\lambda')$ is independent of stress or time of stress application. In ref. 10 we suggested that the free-volume production rate, $\beta\Phi$, is proportional to the dissipation rate of mechanical energy. This dissipation rate is a little bit complicated to calculate. For clarification purposes only, we therefore consider the simplified example of a free-volume production rate which is proportional to the absolute value of the strain rate. For creep under a constant stress σ, we then have: $\beta\Phi = \kappa|\sigma|\ \mathrm{d}J(\lambda')\,\mathrm{d}\lambda'$, where $|\sigma|$ is the absolute value of the stress, κ is a constant and $J(\lambda')$ is the creep compliance in the reference state. The last is independent of the moment, t_{e1}, of loading and of the level of stress; the same thus holds for Φ and this conclusion can be generalized to models in which the free-volume production rate depends on the deformation properties in a more complicated way than simply via the strain rate. The essence remains that, on the effective λ' time scale, the properties, including $\Phi(\lambda')$, are fixed, equal to those in the reference state and independent of t_{e1} or stress level.

The solution of equation (4) can be found in standard textbooks on calculus:

$$\delta(\lambda') = \delta_0 \exp(-\lambda'/\tau_0) + \beta \int_0^{\lambda'} \exp[(\zeta - \lambda')/\tau_0]\,\Phi(\zeta)\,\mathrm{d}\zeta \qquad (5)$$

where ζ is an integration variable on the λ' time scale and δ_0 the δ value at $\lambda' = 0$ (moment at stress application). The first term on the right-hand side is the spontaneous volume recovery (base-line) and the second the volume peak generated by deformation.

The only variable in equation (5) that depends on the age (t_{e1}) is δ_0; all other quantities are fixed. So, the volume peak [second term in equation (5)] does not depend on time, t_{e1}. Consequently, the successive peaks have the same height on the λ time scale. The same holds for the t_e time scale because, by changing from λ to t_e, we only distort the time scale, but do not change the volume values. So the height of the successive peaks on the t_e time scale will be the same, just as found by McKenna and co-workers.

It should be realized that the above discussion is based on a crude one-parameter model for volume recovery. Therefore, it is not surprising that subtle deviations are observed in the detailed volume-recovery data reported in ref. 4.

Sharpening of the volume peaks

The constancy of the peak height directly explains why the peaks have about constant sharpness on the $\log t_e$ scale of *Figure 1* for the period that v decreases at constant rate (with $\log t_e$) and narrow when v reaches equilibrium (see *Figure 1*).

We first apply the crude model of *Figure 3* in which it was assumed that a volume $m = v_1 - v_s(t_{e1})$ is generated instantaneously by rapid deformation at t_{e1}. Constant peak height implies that m is the same for all successive tests. Thus:

- Time range with constant $\mathrm{d}v/\mathrm{d}\log t_e$. The back-shift $\log(t_{e1}/t_{e1}^*) = m/[-\mathrm{d}v/\mathrm{d}\log t_e]$ will be constant because m and $\mathrm{d}v/\mathrm{d}\log t_e$ are constant. According to the earlier discussion, the sharpness of the peak on the $\log t_e$ scale is determined by the ratio t_{e1}/t_{e1}^*. This ratio being constant, the same holds for the peak sharpness.
- Equilibrium state. Dilatation, m being constant, the volume-recovery process is shifted back to the same point t_{e1}^*, independent of the value of t_{e1} (see *Figure 3*). Thus, the peak ratio t_{e1}/t_{e1}^* increases proportionally with t_{e1} and the peak narrows correspondingly, just as seen in *Figure 1*.

Similar, but more detailed, conclusions follow from the more refined model used in equation (5). The second term (volume peak) is independent of t_{e1}; so, the peak has a constant width $\partial = \partial\lambda'$ on the λ' time scale (this width is arbitrarily defined by, e.g. the time (on the λ' scale) at which 90% of the deformation-induced volume change has disappeared). Equation (3) gives: $\mathrm{d}t'/\mathrm{d}\lambda' = 1/a(t_e)$, where $t' = t_e - t_{e1}$. In equilibrium we have $a = a_\infty =$ constant. So, $\Delta t'/\Delta$ is constant and with increasing t_{e1} (moment of load application), the relative peak width $\Delta t'/t_{e1} = \Delta/(a_\infty t_{e1})$ is inversely proportional to t_{e1} (peak sharpening). During volume relaxation, we usually have[10]: $\mathrm{d}\log a/\mathrm{d}\log t_e = -\mu$, with $\mu \approx 1$ for large deviations from equilibrium. This means: $a = \alpha/t_{e1}^{\mu}$ where α is a constant. So, the width $\Delta t'$ will be given by $\Delta t' = \Delta\lambda'/a = [t_{e1}^{\mu}/\alpha]\Delta$. For the relative width on the $\log t_e$ scale we find: $\Delta t'/t_{e1} = [\Delta/\alpha]t_{e1}^{1-\mu}$; it will be constant for $\mu = 1$ and slowly decreasing with increasing t_{e1} for $\mu < 1$.

DECREASE OF SHIFT RATE μ WITH STRESS

McKenna and co-workers' results have an interesting consequence on the interpretation of the finding that the shift rate $\mu = -\mathrm{d}\log a/\mathrm{d}\log t_e$ decreases with increasing stress (see, e.g. pp. 69–70 of ref. 10 or ref. 9).

Suppose, as usual, that the sensitivity of molecular mobility to volume is not influenced by the stress. This means that the effects of v and σ on the shift factor, a, are separable:

$$a = F(v)G(\sigma) \tag{6}$$

or

$$\log a = \log F(v) + \log G(\sigma) \tag{7}$$

and

$$\mathrm{d}\log a/\mathrm{d}v = \mathrm{d}\log F/\mathrm{d}v = \text{independent of stress} \tag{8}$$

If this holds, the constancy of the volume peaks, seen in *Figure 1* and explained by equation (5), implies that, for each of the successive loadings, $\log a$ deviates in the same manner and at equal amounts from the $\log a$ *versus* t_e curve at zero stress. This is identical with saying that shift rate μ is not influenced by the stress level, which obviously contradicts experiment.

The contradiction is not due to the absence of a direct effect of stress on $\log a$; such effect is included in equation (6). Actually, the contradiction arises from the separability, i.e. from the assumption that the σ and v affect $\log a$ independently.

That such an independence is unrealistic was shown in ref. 19. It was argued that the non-linear deformation process close to yield basically differs from that at small strains. In amorphous polymers, high stresses (close to yield) lead to a kind of fracture of the van de Waals bonds that does not require any free volume or thermal activation at all (athermal fracture due to gross overloading of the bonds). So, the effect of v at small strains ($\sigma = 0$) must be different from and greater than that at stresses close to yield; in other words, separability is an unrealistic assumption.

A schematic illustration is given in *Figure 4*. At low stresses, the mechanical relaxation time τ is determined by ageing (free volume) and temperature. At the athermal yield stress, $\sigma_{\max}$, any dependence on free volume and temperature disappears and τ will be about equal to the molecular vibration time τ_0 of about 10^{-14} s. The lines, drawn for two values of t_e are only schematic; the real course is unknown. The only thing known (and understood) is that the two curves will merge at $\sigma = \sigma_{\max}$. Consequently, shift rate μ decreases and becomes zero for $\sigma = \sigma_{\max}$.

In fact, it is physically absurd to assume that the large effect of v on $\log\tau$, seen at small strains, will persist for large σ values. The τ value can never become smaller than $\tau_0 \approx 10^{-14}$ s. So, if τ has already been reduced by stress to a value close to τ_0, a further substantial reduction is impossible, however large the changes in free volume might be. So, $\mathrm{d}\log a/\mathrm{d}v$ must go to zero for $\sigma \to \sigma_{\max}$.

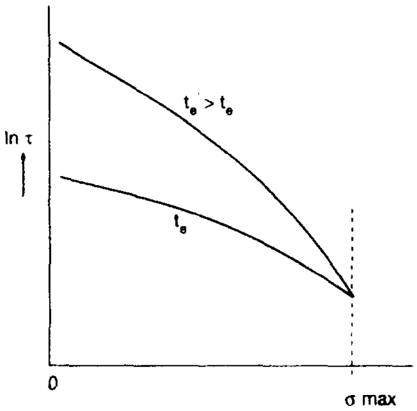

Figure 4 Course of mechanical relaxation time τ with stress for two values of t_e (age); $\sigma_{\max}$ is the athermal yield stress; for explanation see text. To some extent, this figure mimics Figure 13 of ref. 6

The above suggests that equations (6)–(8) should be replaced by

$$\log a = [\Psi(\sigma/\sigma_{\max})]\log F(v) \tag{9}$$

which leads to

$$\mu = \mu_0\Psi(\sigma/\sigma_{\max}) \tag{10}$$

in which function $\Psi(\sigma/\sigma_{\max})$ is unity for $\sigma = 0$ and zero for $\sigma = \sigma_{\max}$. If the lines in *Figure 4* were linear, we would have $\Psi = 1 - \sigma/\sigma_{\max}$ and $\mu_\sigma = \mu_0(1 - \sigma/\sigma_{\max})$ where μ_0 is the shift rate at zero stress and μ_σ that at stress σ.

The above also implies that the decrease of μ with stress is not due to the deformation-induced volume changes seen in *Figure 1*. For both equations (8) and (9), the constancy in height of the successive volume peaks leads to constant deformation-induced accelerations. For equation (9), these are smaller than for equation (8), but they are still constant and it is exactly this constancy that leads to the independence of μ on σ. So, in agreement with McKenna and co-workers, we conclude that the decrease of μ with σ has another origin, viz. the direct effect of stress on $\mathrm{d}\log a/\mathrm{d}v$ [equation (9)].

Although the deformation-induced volume changes do not explain the decrease in μ, it should not be concluded[9] that these volume effects have no importance and that non-linear viscoelastic behaviour and volume relaxation are completely uncoupled. Counter-examples have been discussed earlier. For example, in high-stress creep (see Section 11.5 of ref. 10), the reactivated ageing leads to a considerable shortening of the apparent t_e. Consequently, the constant-slope region (strain *versus* $\log t$) starts much earlier than in creep at small strains. In fact, the short-time creep curves in the high-stress region have the appearance of long-term creep curves at small strains, simply because of the coupling and the reactivated ageing. Other examples have been given in Section 8.6 of ref. 10.

VAN DIJK'S RESULTS[20]

Another criticism came from van Dijk who performed constant rate tests in tension and compression, simultaneously measuring specific volume. He found that, in uniaxial compression, the volume first decreases linearly with the compressive strain. Close to the yield point, the decrease is accelerated (the material is said to 'implode'), which seems to disagree with rejuvenation (increase in free volume at yield). The actual situation, however, is a little bit complicated. First, the accelerated volume decrease at yield is exactly what should be expected when the rejuvenation hypothesis would not have been made. Approaching the yield point, the relaxation rates are increased and the compressive response to the positive hydrostatic component of the applied stress will be accelerated. The material's compressibility changes from the low value characteristic for the glassy state to the high value of the rubbery/liquid state. Just as in tension (cold-drawing) or shear, liquid-like deformation processes set in at the yield point. So, the increase in volume due to rejuvenation is not the only effect; it is superimposed on a quite natural accelerated decrease in volume. The relative magnitudes of the two effects being unknown, it is not possible to say whether van Dijk's experiments agree or disagree with the rejuvenation hypothesis.

The 'implosion' reported by van Dijk has also been found by McKenna and co-workers[21,22] and might be connected with the stress acceleration of ageing as reported by Sternstein and co-workers[23,24] and the author[25].

DISCUSSION AND CONCLUSIONS

Surprisingly, the tentative and crude model of ref. 10 is able to give a straightforward prediction of the experimental results of McKenna and co-workers[1–9], even in the following details: existence of the shear induced dilatation, dilatation at application as well as at removal of strain, larger dilatation at strain removal, sharpness of the volume peaks, absence of an effect on the volume-recovery base-line, independence of the equilibration time t^+ on stress, constancy of the peak height, about constant sharpness during volume recovery and sharpening when the volume comes close to equilibrium. Although other details were not considered, it appears that McKenna and co-workers criticism against the model is unjustified. To be careful, we would like to stress that this is the only claim made in this paper. We admit that the author's model is crude, that free volume is an ill-defined (almost heuristic) quantity and that changes in mobility, as measured by superposition of small on large strains can also be observed in melts[1,2] or tyxotropic dispersions. So, we do not advocate that the model of ref. 10 is physically sound; we only claim that McKenna and co-workers' results can be explained from the model and do not disprove it.

In agreement with McKenna and co-workers, we conclude that the decrease in shift rate μ with increasing stress cannot be explained from the deformation-induced volume changes. It must be due to a reduction in the sensitivity of molecular mobility to volume ($\mathrm{d}\log a/\mathrm{d}v$) with increasing stress[19]; this sensitivity drops to zero at the athermal yield stress.

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