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# Volume-recovery theory: 1. Kovacs' $\tau_{eff}$ paradox

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It is shown that there is nothing paradoxical in Kovacs' well-known $\tau_{eff}$ data. At small deviations from equilibrium ($|\delta| <$ a few times $10^{-4}$), the $\tau_{eff}$-values are inaccurate, should be rejected, and do not allow any conclusion about the behaviour of $\tau_{eff}$ for $\delta \rightarrow 0$. Thus, there has never been any physical evidence for a 'paradox' or an 'expansion gap' at equilibrium. The reliable part of the data ($|\delta| >$ a few times $10^{-4}$) can be described, within experimental error, by the phenomenological volume-recovery theory. A dependence of $\tau_{eff}$ on the initial temperature (at constant $\delta$) is a normal feature of linear and nonlinear systems with wide distributions of relaxation times. The dependence may even persist up to equilibrium; however, $\tau_{eff}$ then necessarily continues to increase (to $\infty$) with decreasing $|\delta|$ instead of approaching a finite limit as suggested by Kovacs' data. © 1997 Elsevier Science Ltd.

**(Keywords: volume recovery; volume relaxation; expansion gap)**

## INTRODUCTION

In 1964[1] Kovacs reported some volume-recovery data reproduced in part in *Figure 1*. The data refer to heating tests from thermodynamic equilibrium at initial temperature $T_0$ to final temperature $T$; $T_0$ and $T$ were varied. Quantity $\delta$ characterizes the deviation from equilibrium and is defined by

$$\delta = (v - v_\infty)/v_\infty \qquad (1)$$

where $v_\infty$ denotes the equilibrium specific volume at final temperature $T$.

Effective relaxation time $\tau_{eff}$ is defined by

$$\tau_{eff} = [(-\mathrm{d}\delta/\mathrm{d}t)/\delta]^{-1} = [\mathrm{d}\ln|\delta|/\mathrm{d}t]^{-1} \qquad (2)$$

in which the vertical bars denote absolute values. This relaxation time was introduced by Kovacs[1] as a *purely experimental quantity*. For linear processes with a single, constant, relaxation time $\tau_1$, $\delta$ follows an exponential decay curve and $\tau_{eff}$ is constant and equal to $\tau_1$. In all other cases, $\tau_{eff}$ may vary during the volume-recovery process, just as seen in *Figure 1*.

At first sight, the behaviour of *Figure 1* looks peculiar. The effective relaxation time $\tau_{eff}$, turns out to depend on the initial temperature $T_0$, even near equilibrium at final temperature $T$. So, near or at equilibrium at $T$, the material appears to remember the initial temperature $T_0$. This would violate the very idea of an equilibrium state at $T$, and therefore led to the term $\tau_{eff}$ *paradox*.

Another common phrase is *expansion gap*: the difference in $\log\tau_{eff}$ at equal $\delta$ and $T$ for recovery from different temperatures $T_0$ (see vertical arrow in *Figure 1* for the $T = 40$°C data). Usually, the phrase 'expansion gap' is reserved for the $T_0$-dependence of $\tau_{eff}$ at equilibrium ($\delta = 0$). In the present paper, the phrase is used in the wider sense of a $T_0$-dependence of $\tau_{eff}$ at arbitrary $\delta$ (vertical arrow in *Figure 1* refers to $\delta = -1.4 \times 10^{-3}$). The word 'paradox' however only refers to cases where the gap persists in the equilibrium state (a gap at $\delta \neq 0$ is not paradoxical at all; see Theory).

Several authors (see refs 2–14) have discussed the paradox and, for example, McKenna stated (p. 350 of ref. 3) that it cannot be explained by any of the existing theories for volume recovery[15–18], except, Ngai and coworkers' coupling model[9].

The present paper re-analyses the theory as well as the experimental results. It is shown that:

1) A dependence of $\tau_{eff}$ on $T_0$ (a gap) is a straightforward consequence of a wide distribution of relaxation times; it naturally occurs in linear systems. In such systems, the gap may even persist up to equilibrium. However, $\tau_{eff}$ then continues to increase (up to $\infty$) for $\delta \rightarrow 0$; there will be no finite limit as suggested by the data of *Figure 1*.
2) The conventional volume-recovery theory[15–18] predicts that the gap at given $\delta$ and $T$ is not affected by the nonlinear effects.
3) Quenching ($T_0 > T$) produces a 'contraction gap'. This is hardly seen in practice and not discussed in the literature, because volume recovery after quenching is strongly influenced by the non-ideality of the quench (finite cooling rates); this masks the contraction gap.
4) Kovacs' $\tau_{eff}$ data (*Figure 1*) are very inaccurate for small $\delta$s (< a few times $10^{-4}$) and should be rejected.
5) The reliable part of Kovacs' data can be described by the phenomenological volume-relaxation theory[15–18] within experimental error.

Thus, the idea that Kovacs' data reveal a paradox is wrong for two reasons: first, the data do not allow for any conclusion about $\tau_{eff}$ at $\delta$-values close to equilibrium (point 4). Secondly, the assumption that, at equilibrium, $\tau_{eff}$ should converge to a unique value, independent of

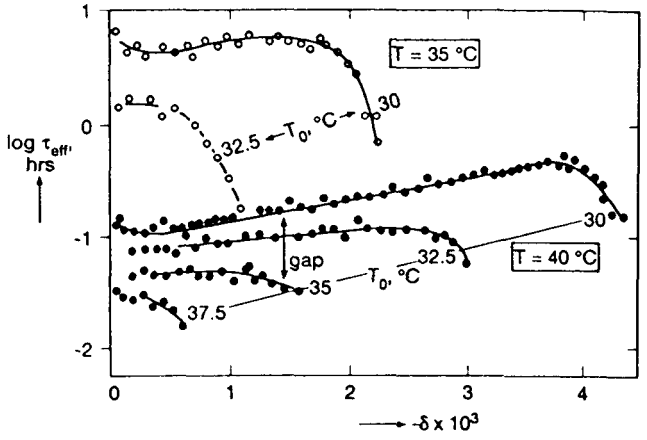


**Figure 1** Volume recovery after jumps (heating) from equilibrium states at initial temperatures $T_0$ to final temperatures $T$ of 40 (dots) and 35°C (circles). The horizontal axis gives the deviation $\delta$ from equilibrium as defined by equation (1), the vertical axis shows the effective relaxation time $\tau_{eff}$ defined by equation (2). Replotted with inverted log $\tau_{eff}$- and $\delta$-scales from Figure 6 of ref. 2; for the recovery after cooling, see *Figure 5*

initial temperature $T_0$ is wrong (point 1). The phrase paradox arose because Kovacs' data deviate from the expected behaviour; however, for $\delta \rightarrow 0$, the data are unreliable and the expectation wrong.

## THEORY

### *Linear relaxation; the origin of the gap**

As an example, we consider a *linear* volume-relaxation test. The material is in thermodynamic equilibrium at $T_0$ for $t < 0$; at $t = 0$, the temperature is suddenly raised to final temperature $T$. To get linear behaviour, $T$ and $T_0$ have to differ only slightly[19]. The deviation from equilibrium is given by $v(t) - v_\infty = v_\infty \delta(t) = [T_0 - T]\,\phi(t)$ in which $\phi(t)$ is the linear volume response[18]. As in *Figure 1*, we define $1/\tau_{eff} = -[1/\delta(t)]\mathrm{d}\delta(t)/\mathrm{d}t = -\mathrm{d}\ln|\delta|/\mathrm{d}t = -\mathrm{d}\ln\phi(t)/\mathrm{d}t$ and plot it vs the deviation $\delta$ from equilibrium. By varying $T_0$ we get different amplitudes (initial conditions of *Figure 1*).

If $\phi(t)$ relaxes according to a single exponential ($\phi(t) = A\,\mathrm{e}^{-t/\tau}$) in which $\tau$ is the relaxation time and $A$ the value for $t = 0$) we find: $\tau_{eff} = \tau =$ constant. Thus, in this case, variations in $\tau_{eff}$ as seen in *Figure 1* are impossible.

Usually, relaxation of polymers does not obey a single exponential but reveals a wide distribution of relaxation times. As an example, consider:

$$\phi(t) = A/(1 + t/\tau)^n \qquad (3A)$$

in which $n$ is a constant (generally $< 1$) and $A$ the initial value for $t = 0$. This equation is the well-known power law[20], slightly modified to avoid an infinite value at $t = 0$; usually, constant 1 in the nominator is omitted.

We find:

$$\tau_{eff} = (\tau + t)/n \qquad (3B)$$

With:

$$\delta/\delta_0 = (1 + t/\tau)^{-n} \qquad (3C)$$

this yields:

$$\tau_{eff} = (\tau/n)(\delta_0/\delta)^{1/n} \qquad (3D)$$

A graphical illustration is given in *Figure 2*. It shows that $\tau_{eff}$ depends on the initial conditions ($\delta_0$) over the whole relaxation period, up to equilibrium. We also see that $\tau_{eff}$ varies (increases†) with time and we clearly observe a gap that persists up to equilibrium. Thus, a quite usual linear system shows an 'anomaly' similar to that shown by Kovacs's volume-recovery data. The phrase 'paradox' should therefore be avoided. The confusion appears to originate from the implicit assumption that $\tau_{eff}$ is something like a state variable that, irrespective of the initial conditions, should converge to a unique value at equilibrium. The example above demonstrates that this is not the case, at least not in general.

Let us consider a second example. Relaxation (also volume recovery, see refs 3–5) at temperatures close to glass transition temperature ($T_g$) is often described by the Kohlrausch–Williams–Watts (KWW) equation

$$\phi(t) = A\exp(-(t/\tau)^n) \qquad (4)$$

where $\tau$ and $n < 1$ are constants, depending on temperature. The relaxation curve according to KWW is similar to that according to equation (3A), although the cut-off at long times is sharper (at equal values of $n$). For $\tau_{eff}$ we find:

$$\tau_{eff} = (\tau/n)[\ln(\delta_0/\delta)]^{-1+1/n} \qquad (5)$$

An illustration is given in *Figure 3*. We observe a

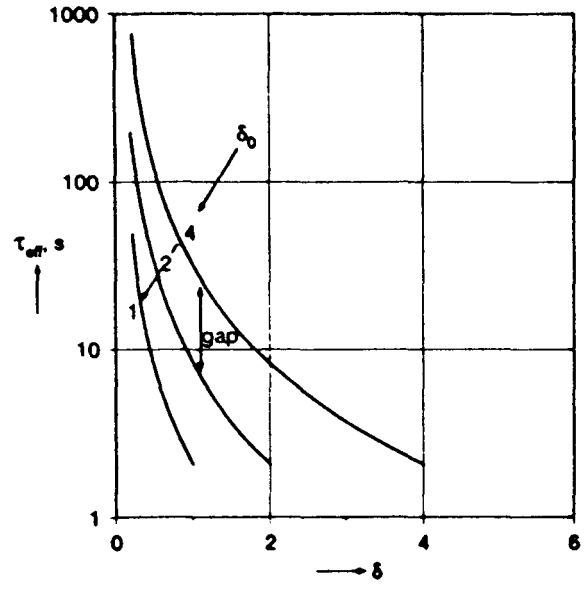


**Figure 2** $\tau_{eff}$ vs deviation, $\delta$, from equilibrium for linear relaxation according to equation (3A) with $n = 0.5$ and $\tau = 1$ s. The curves are given for three values of the initial deviation $\delta_0$. The gap is clearly visible and persists up to equilibrium ($t \rightarrow \infty$). For two values for $\delta_0$, viz. $\delta_{01}$ and $\delta_{02}$, the gap $g = \ln[\tau_{eff,\delta_{01}}/\tau_{eff,\delta_{02}}]$ is independent of $\delta$ and equal to $(1/n)\ln(\delta_{01}/\delta_{02})$ (see equation (3D))

* The theory is formulated for volume recovery; it equally applies to arbitrary linear relaxation processes, e.g. stress- or dielectric-relaxation

† The strong increase in log $\tau_{eff}$ with decreasing $\delta$, shown in *Figure 2*, is not observed in *Figure 1*. This difference is due to the strong nonlinear effects in the volume recovery of *Figure 1*. This point will be discussed later; here, we only aim at showing that a gap is a quite normal phenomenon, even for $\delta \rightarrow 0$

behaviour similar to that of *Figure 2*: $\tau_{eff}$ changes with $\delta$, but now the gap (effect of initial deviation) closes on approaching the equilibrium state. As shown in the right subfigure, this closure is very slow; at $\delta$s of only a few percent of the initial deviation $\delta_0$, the gap is still 0.1–0.2 decades wide. The gap will be the larger and the closure the slower, the lower the value of $n$.

The behaviour of linear systems can be summarized as follows: when time $t$ increases, $\tau_{eff}$ 'probes' all relaxation times of the system. If there is only one ($\tau_1$), $\tau_{eff}$ is constant and equal to $\tau_1$. If there is a distribution between a minimum value $\tau_{min}$ and a maximum $\tau_{max}$, $\tau_{eff}$ will gradually increase with $t$ from $\tau_{min}$ to $\tau_{max}$ and stay constant (at $\tau_{max}$) for $t \gg \tau_{max}$. If there is no maximum relaxation time, $\tau_{eff}$ continues to increase with $t$, as the width of distribution increases. For such systems, the phenomena observed by Kovacs (expansion gap, etc.) are not peculiar but in line with expectations. The closure of the gap critically depends on the long-time tail of the distribution, i.e. on the long-time tail of the $\delta$ vs $t$ curve. This tail is difficult to assess experimentally (small $\delta$-values).

*Remarks.* (a) The data of *Figure 1* do not fully agree with the above theory. *Figure 1* suggests that $\tau_{eff}$ goes to a finite limit for $\delta \to 0$. Thus, there must be a maximum relaxation time and the gap should close, in contrast with *Figure 1*. Later, we will show that Kovacs' data (*Figure 1*) have limited accuracy for small $\delta$s and do not allow any conclusion about the behaviour for $\delta \to 0$. (b) Kovacs' $\tau_{eff}$ is identical to the Bucci-relaxation time[21–23] in mechanical relaxation. Also here, confusion arose because some authors[21,22] did not realize that $\tau_{eff}$ varies with time. It is exactly for this reason that McCrum[23] has introduced a corrected Bucci-relaxation time $\tau_{B1/2}$, which is $\tau_{eff}$ at a given $\delta/\delta_0$-value.

*Nonlinear volume recovery*

For larger $T$-jumps (*Figure 1*), the volume recovery is strongly affected by nonlinear effects[1]. In the phenomenological volume-recovery theories[15–18] (which are basically identical but differ in formalism), these nonlinearities are *removed* by introducing the concept of a reduced time $\lambda$; the nonlinear volume recovery then reduces to the linear one of the previous section.

As discussed on pp. 117–122 of ref. 18, the recovery after an ideal (stepwise) jump from an equilibrium state at $T_0$ to final temperature $T$ can be described by:

$$v(\lambda) - v_\infty = (T_0 - T)\phi(\lambda) \tag{6}$$

with:

$$\phi(\lambda) = \psi(\infty) - \psi(\lambda) \tag{7}$$

where $\psi$ is the unit-step response defined on p. 117 of ref. 18 and $\lambda$ the reduced time given by:

$$\lambda = \int_0^t a(\xi)\,\mathrm{d}\xi \tag{8}$$

Quantity $\xi$ is an integration variable on the $t$-time scale and $a(v, T)$ the acceleration function depending on $t$ (or $\xi$) via the time dependence of $v$ and $T$. Function $a(v, T)$ increases with increasing temperature and (free) volume. As said before, the reduced time is introduced to remove the nonlinearities; thus, $\phi(\lambda)$ describes the linear volume response on $\lambda$-time scale and the results of the previous section can directly be applied to $\phi$.

For $\tau_{eff}$ we find:

$$1/\tau_{eff} = -(1/\delta)\,\mathrm{d}\delta/\mathrm{d}t = -(1/\delta)\,\mathrm{d}\delta/\mathrm{d}\lambda\;\mathrm{d}\lambda/\mathrm{d}t \tag{9}$$

Equation (8) yields:

$$\mathrm{d}\lambda/\mathrm{d}t = a[\delta(t)] \tag{10}$$

where $a(\delta)$ is a function only of $\delta$ because we deal with isothermal recovery at final temperature $T$.
Combining equations (6), (9) and (10) we obtain:

$$1/\tau_{eff} = -a(\delta)\,(1/\delta)\,\mathrm{d}\delta/\mathrm{d}\lambda = a(\delta)[-\mathrm{d}\ln\phi/\mathrm{d}\lambda] \tag{11}$$

or:

$$\log\tau_{eff} = -\log[a(\delta)] + \log\tau'_{eff} \tag{12}$$

where:

$$1/\tau'_{eff} = -\mathrm{d}\ln\phi/\mathrm{d}\lambda \tag{13}$$

refers to the linear system (on $\lambda$-time scale) to which the previous results can be applied.

Let us now compare up-jumps to the same final temperature $T$, starting from different initial temperatures $T_0 < T$. On $\lambda$-time scale, the behaviour is linear. Thus, we can plot $\log\tau'_{eff}$ vs $\delta$ as in *Figures 2* and *3* and obtain the expansion gap (see *Figure 4*). Equation (12) shows, however, that $\log\tau_{eff}$ and $\log\tau'_{eff}$ only differ by the factor $-\log a(\delta)$, which only depends on $\delta$. So, the expansion gap, at given $\delta$ is not influenced by the nonlinear effects; at given $\delta$ the correction due to the

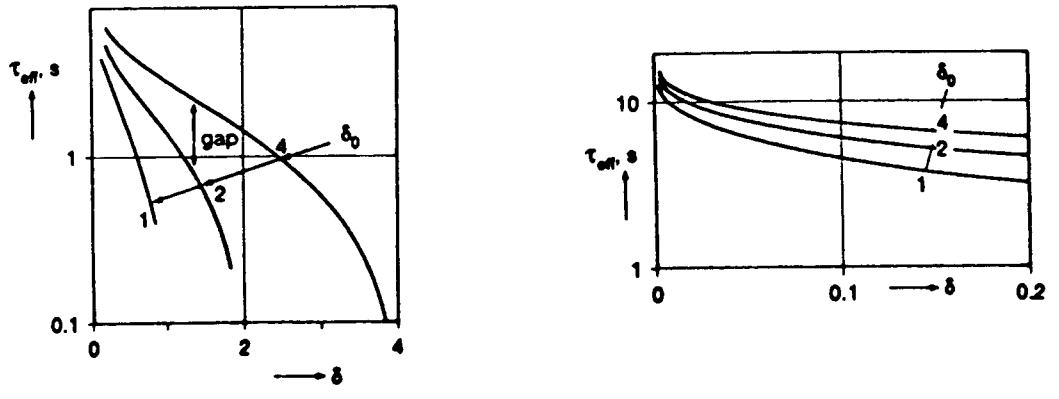


**Figure 3** As *Figure 2*, but now for relaxation according to equation (4) with $n = 0.5$ and $\tau = 1$ s. The gap slowly closes for $\delta \to 0$; see right subfigure with engarged $\delta$-scale

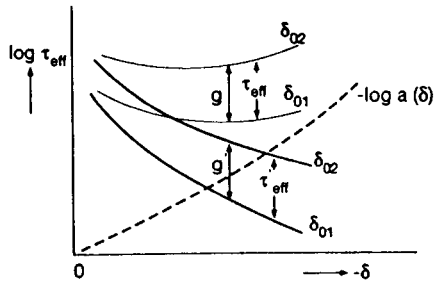


**Figure 4** Effect of nonlinearity on $\tau_{eff}$ for up-jumps to final temperature $T$ from $T_{01}$ and $T_{02}$ (initial deviations $\delta_{01}$ and $\delta_{02}$). $\log \tau'_{eff}$ refers to the linear behaviour on the $\lambda$-time scale; $a(\delta)$ is the acceleration function. The curves for $\log \tau_{eff}$ are obtained by adding $-\log a(\delta)$ to $\log \tau'_{eff}$ (see equation (12)). This addition has no effect on the expansion gap (denoted by $g$ and $g' = g$)

non-linear effects is the same for all tests (see *Figure 4*). The only effect of the nonlinearity is to tilt the curves; in the nonlinear case (*Figure 1*), the $\log \tau_{eff}$ vs $\delta$ curves have a (much) lower slope than in the linear case (*Figures 2* and *3*; see footnote on p. 4678).

*The contraction gap; the asymmetry between heating and cooling*

A point, generally not discussed, is the *contraction gap* for down-quenching. In the theory above, there is no effect of the sign of the deviation from equilibrium. Thus, the same gap should be expected for up- and down-quenching. In *Figure 5*, the contraction data appear to converge to the same point and the behaviour differs from that after heating.

The interpretation can be found by combining (i) the strong nonlinear aspects of volume recovery with (ii) the non-ideality of the temperature jumps (not real steps). Both points have been discussed in detail in refs 1, 2 and 15, and much of what follows in this section can be found there. The volume-recovery tests are done on samples placed in dilatometers. The sample and the dilatometer both have a thermal inertia and the jump is actually a cooling or heating process with finite rate. This process is characterized by a thermal equilibration time $t_d$ of the order of 100 s. On an $\lambda$-time scale, the step is also non-ideal; the corresponding transition time is denoted by $\lambda_d$. Now, the effect of non-ideal jumping dramatically differs for cooling and heating. After an up-jump, acceleration factor $a$ increases with $t$ and $\lambda$, so:

$$\lambda_d = \int_0^{t_d} a(\xi)\, d\xi < a(t_d) t_d \tag{14}$$

$$\lambda - \lambda_d = \int_{t_d}^{t} a(\xi)\, d\xi > a(t_d)\,[t - t_d] \tag{15}$$

which gives:

$$\lambda_d/\lambda < t_d/t \tag{16}$$

Consequently, we have $\lambda \gg \lambda_d$ for $t \gg t_d$. Applying the Boltzmann integral of equation (87) of ref. 18, it follows that the differences between ideal and non-ideal heating fade away for $t \gg t_d$. In other words, up-quenches give reliable results for $t \gg t_d$; it was exactly for this reason that we confined the theory of the previous Section to up-quenches.

After a down-quench, the acceleration factor decreases with time. The condition $t \gg t_d$ does not lead to $\lambda \gg \lambda_d$, which means that the effect of non-ideal cooling may persist for times which are very long compared to $t_d$. Thus, the recovery after down-quenching cannot be derived in a straightforward way; it depends on the details of the quenching process. However, we may argue as follows: for large temperature jumps, acceleration factor, $a$, decreases dramatically; according to WLF, (Williams, Landes and Ferry, see ref. 20) by a factor of 10 per few degrees Centigrade. During the earlier phases of cooling, the relaxation times are still

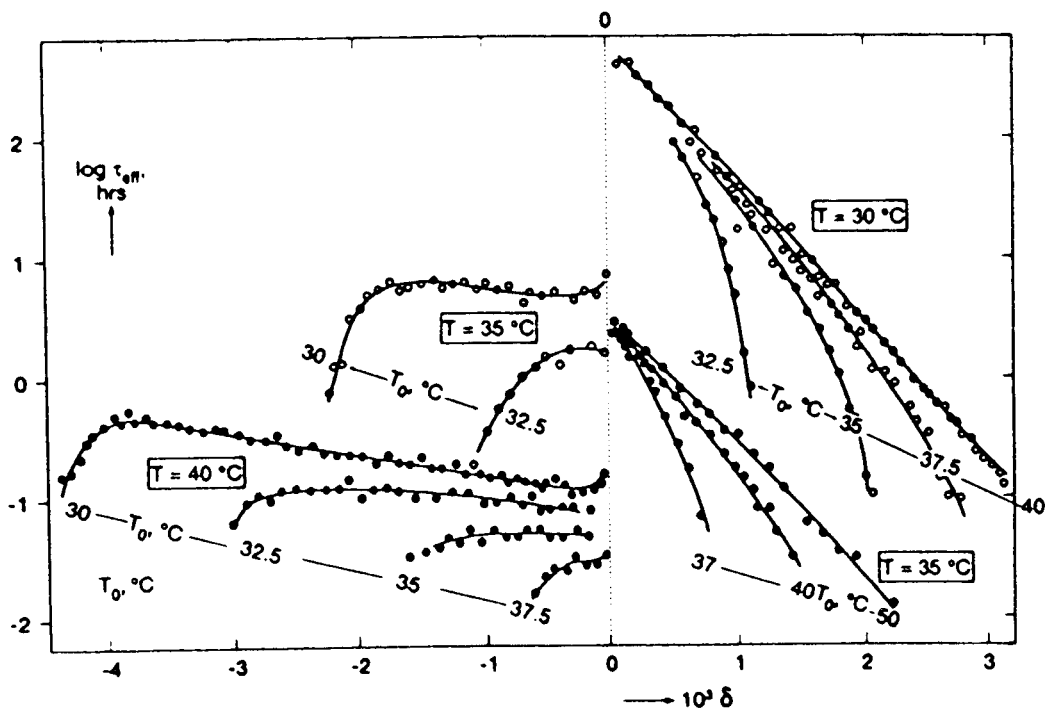


**Figure 5** As *Figure 1*, but now completed with Kovac *et al.*'s[2] contraction data (quenching from various temperatures $T_0$ to final temperatures $T$ of 30 and 35°C). Note that for the heating data (left), we now plot $\delta$ instead of $-\delta$ as in *Figure 1*

very short, and the material more or less follows the equilibrium line of the liquid above $T_g$, provided that $T_0$ lies sufficiently above $T_g$. The actual quenching temperature is not $T_0$, but some temperature $T_0^*$, almost independent of $T_0$. Consequently, the recovery after down-quenching only slightly depends on the initial temperature $T_0$ [1,24]; $\delta_0$ hardly depends on $T_0$ and the contraction gap will be reduced. Note that this is only due to the strong nonlinearities during non-ideal quenching; the contraction gap will appear if the jumps are sufficiently small.

Let us finally consider the asymmetry seen in *Figure 5* (cf. refs 1, 2 and 15): the contraction curves show a much higher slope than the expansion curves. As illustrated in *Figure 6*, this is a direct consequence of the nonlinear effects. The $\log \tau'_{eff}$ curves (linear behaviour on $\lambda$-time scale) are symmetrical, i.e. the same for up- and down-quenching. The $\log \tau_{eff}$ curves (nonlinear behaviour on $t$-time scale) are highly asymmetrical because the asymmetric function $-\log[a(\delta)]$ is added to $\log \tau'_{eff}$.

## THE ACCURACY OF KOVACS' $\tau_{eff}$ DATA

There is a serious accuracy problem in Kovacs' data because the experimental errors in $\tau_{eff}$ must go to infinity for $\delta \rightarrow 0$. This can be seen as follows. Let $\epsilon$ be the absolute accuracy of $\delta$. The absolute accuracy in rate $d\delta/dt$ is then proportional to $\epsilon$. On approaching equilibrium, $\delta$ and $d\delta/dt$ go to zero simultaneously. Consequently, the relative errors in $\delta$, $d\delta/dt$ and $\tau_{eff} = -\delta/[d\delta/dt]$ go to infinity.

Kovacs claims[25] that his $\delta$-values, measured with the techniques described in ref. 26, have an accuracy of $\pm 10^{-5}$. This appears to be a little bit optimistic, since:

- in ref. 26, Kovacs mentioned a stability of the thermostats (contact thermometer controlled; years 1950–1960) of $\pm 0.02$°C. With an expansion coefficient in the rubbery state of $6.9 \times 10^{-4}$ °C$^{-1}$ (PVAc data of Table 1 of ref. 1) the resulting (slow) volume fluctuations are $\pm 1.4 \times 10^{-5}$.
- the accuracy of the dilatometer scale reading was said[26] to be $\pm 1/20$ mm$^3$, which corresponds to a quite reasonable read-off error of 0.1 mm (height of the mercury column). With a sample volume of 1–2 cm$^3$ (see ref. 26), the random error in each $\delta$-reading equals $\pm 2.5$–$5 \times 10^{-5}$.
- careful inspection of magnifications of Figures 8 and 17 of ref. 1 shows that $\delta$ fluctuates by $\pm 2$–$3 \times 10^{-5}$ around the smooth curves drawn in these figures. We neglect the even larger deviations at short times ($t = 0.01$ h); these are most probably due to a delayed approach of thermal equilibrium.

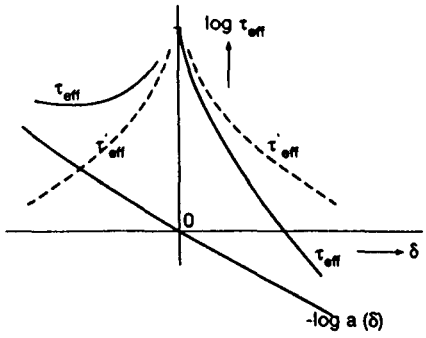


**Figure 6** Asymmetry of $\log \tau_{eff}$ vs $\delta$ curves for cooling (right) and heating (left). The $\log \tau'_{eff}$ vs $\delta$ curves (linear case; $\lambda$-time scale) are symmetrical; the asymmetry is introduced by quantity $-\log[a(\delta)]$ which is added to $\log \tau'_{eff}$ to obtain $\log \tau_{eff}$ (see equation (12))

So, as a more realistic value, we take $\epsilon = 2 \times 10^{-5}$. The conclusions to be reached below are not basically changed, however, if we would accept Kovacs' claim of $\epsilon = 10^{-5}$.

Let us now calculate the relative error in $\tau_{eff}$. The relative error in $\delta$ equals:

$$\Delta\delta/\delta = \pm\epsilon/\delta; \quad \text{with } \epsilon = 2 \times 10^{-5} \tag{17}$$

As argued below, Kovacs determined $\tau_{eff}$ by numerical differentiation of the $\delta - t$ curves, most probably by a formula of the type:

$$\tau_{eff}^{-1}(t_3) \approx (x_1 - x_2)/[(t_2 - t_1)x_3] \tag{18}$$

in which $x = -\delta$ ($x$ is positive and decreasing with time $t$). Times $t_1$, $t_2$ and $t_3$ are equidistant with $t_1 < t_3 < t_2$. Most probably, Kovacs performed the differentiation on a log time scale but, as can easily be verified, this does not change the argument. Equation (18) is based on a second-order polynomial and allows for curvature.

We now have:

a) the absolute error in $x_1 - x_2$ is $\pm 2\epsilon$.
b) since $x(t)$ decreases with increasing time, $x_1 - x_2$ will be smaller than $x_1$. Thus, the relative error in $x_1 - x_2$ will be $\pm 2u\epsilon/x_1$ with $u > 1$.
c) the relative error in $x_3$ is $\pm\epsilon/x_3$.
d) the relative error in the time values is assumed to be zero.
e) since the errors in $x_1$, $x_2$, and $x_3$ are independent (mainly capillary read-off errors or variations due to temperature fluctuations), the relative error in $(x_1 - x_2)/x_3$ is the sum of the errors mentioned under points (b) and (c), i.e. $\pm\epsilon[1/x_3 + 2u/x_1]$. The term in brackets exceeds $3/x_1$ since $x_3 < x_1$ and $u > 1$.
f) because of (d), the relative error mentioned under point (e) is equal to that of $\tau_{eff}$ (cf. equation (18)), provided that $x_1 \approx x_3 = \delta$ (points not too far removed). Thus, we have found the following *lower bound* for the relative error in $\tau_{eff}$:

$$\Delta\tau_{eff}/\tau_{eff} = \pm 3\epsilon/|\delta| \tag{19}$$

Note that equation (19) underestimates the real errors (see later).

*Figure 7* shows that the errors become very large for $\delta \rightarrow 0$. At $\delta = -10^{-4}$, the (underestimated) errors are comparable to the alleged expansion gap at equilibrium (cf. *Figure 1*). Thus, there is no and has never been any physical evidence for such a gap at equilibrium. A similar

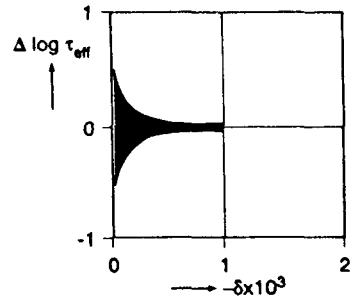


**Figure 7** Relative error according to equation (19) (underestimate) for $\epsilon = 2 \times 10^{-5}$. The black area gives the positive and negative fluctuation in $\log \tau_{eff}$. For $\delta \rightarrow 0$, any reliability in $\tau_{eff}$ disappears

conclusion follows for $\epsilon = 10^{-5}$ (Kovacs's claim; errors two times smaller).

A sharper estimate of the errors in $\log\tau_{eff}$ (*Figure 1*) can be obtained by a reconstruction of the way in which Kovacs calculated $\tau_{eff}$ from the original volume-relaxation curves of Figures 8 and 17 of ref. 1. The volume data for $T = 35°C$ (Figure 8 of ref. 1) are not complete since the curve for $T_0 = 32.5°C$ is missing. Therefore, we restrict the analysis to the $T = 40°C$ data (Figure 17 of ref. 1).

*Figure 1* shows a scatter in the $\tau_{eff}$ values. This implies that Kovacs did not derive $\tau_{eff}$ from an analytical equation fitted to the whole $\delta$ vs $t$ curve, but applied some numerical differentiation formula, e.g. a two-point forward difference formula $dv/dt \approx [v(t + \Delta t) - v(t)]/\Delta t$ or a three-point central difference formula $dv/dt \approx [v(t + \Delta t) - v(t - \Delta t)]/(2\Delta t)$. The volume-relaxation curves were originally obtained as $v$ vs $\log t$ plots, so the differentiation has logically been done on a $\log t$ scale. Since the curves show some curvature, the three-point formula (based on a second degree polynomial) is preferred over the two-point formula based on a straight line approximation. Since the calculation is just as easy for the three-point as for the two-point formula, Kovacs most probably used the three-point formula. Higher approximations are not required because, on a $\log t$-scale, the curvature is limited. So, we assume that Kovacs used the following formula:

$$r = d\delta/d\log t = [\delta(p + \log t) - \delta(-p + \log t)]/(2p) \quad (20)$$

where $p$ is the spacing on a $\log t$ scale. If Kovacs used a two-point formula, the errors derived below are two times too small; thus, we are at the safe side.

Spacing, $p$, can be estimated by counting the number of points in Figure 17 of ref. 1 and *Figure 1* of the present paper. It turns out that in both figures, the number of points per decade (in time) is about the same, except for:

- the last part ($10^3\delta$ increasing from $-1$ to 0) of the $T_0 = 32.5°C$ curve (10 points in *Figure 1* and 17 in Figure 17 of ref. 1)
- the last part ($10^3\delta$ from $-1$ to 0) of the curve for $T_0 = 35°C$ (10 points in *Figure 1* and 20 in Figure 17 of ref. 1)
- the whole curve at $T_0 = 37.5°C$ (Figure 17 of ref. 1) shows twice as many points as *Figure 1*)

So, we take $p$ equal to the spacing in Figure 17 of ref. 1, except for the cases mentioned above where the spacing is taken as twice as large. In other words, we assume that Kovacs calculated the rates from three successive data points or from six for the exceptions mentioned above; this corresponds to a spacing $2p$ of about 0.05–0.2 decades (cf. Figure 1 of ref. 1).

Since the absolute error in $\delta$ is $\pm\epsilon$ (with $\epsilon = 2 \times 10^{-5}$), the absolute error in the rate is given by (see equation (20)):

$$\Delta r = \pm\epsilon/p \quad (21)$$

We further have (see legend to *Figure 1* and remember that $d\delta/dt = [d\delta/d\ln t]/t = [d\delta/d\log t]/2.303t) = r/(2.303\,t)$:

$$\tau_{eff} = -\delta/[d\delta/dt] = -\delta\,2.303t/r \quad (22)$$

Combining equations (21) and (22) we find:

$$\Delta r/r = \pm\epsilon\tau_{eff}/[2.303tp|\delta|] \quad (23)$$

The final error in $\tau_{eff}$ is found by adding the relative error $\pm\epsilon/\delta$ in $\delta$ (see equations (17) and (22)). We then get:

$$\Delta\tau_{eff}/\tau_{eff} = \pm\{1 + \tau_{eff}/[2.303tp]\}\epsilon/|\delta| \quad (24)$$

Ratio $\tau_{eff}/t$ can be obtained by combining Figure 17 of ref. 1 with *Figure 1* of the present paper; spacing $p$ is found as described before. The final result is shown in *Figure 8*. As expected, the errors are greater than in *Figure 7*. For the central part of the curves, the calculated errors compare reasonably with the actual scatter seen in Kovacs' data. This gives some confidence in the above analysis, which, as should be admitted, is only a reconstruction. For $\delta \to 0$ the calculated errors are greater; here Kovacs' data are puzzling since the scatter *should* increase with decreasing $\delta$ (see before). Also for large deviations from equilibrium, the calculated errors are larger than the scatter in Kovacs' data. Also here, the almost constant scatter in Kovacs' data is puzzling since at large $\delta$s (short times), the rates $-d\delta/d\log t$ become small (see Figure 17 of ref. 1) and the relative error in $\tau_{eff}$ *must* increase.

The errors become infinite for $\delta \to 0$ (equations (19) and (24)). *Figure 8* shows that at $\delta = -2.5 \times 10^{-4}$ we have an error of ±30–40% (equation (19) gives 24%); at $\delta = -5 \times 10^{-4}$, we have ±20–30% (equation (19) gives 12%). So, in the next section, the analysis will be restricted to $-\delta \geq 5 \times 10^{-4}$.

Surprisingly, this high inaccuracy at small $\delta$-values has not received much attention in the literature, at least to the author's knowledge. It is immediately obvious that the relative errors must be very large for $\delta \to 0$. It is also well known that dilatometer experiments have an accuracy of a few times $10^{-5}$. So, a point like A in *Figure 8* with a $\delta$-value of $-3 \times 10^{-5}$ has relative errors in $\delta$, $d\delta/dt$ and $\tau_{eff}$ of 50–100% and there are more such highly unreliable points in *Figure 1*.

*Final remark.* Kovacs used non-ideal temperature jumps; the time $t_d$ to reach thermal equilibrium is 0.01–0.02 h[26]. Particularly for the higher $T_0$ values in *Figure 1* ($T_0 = 37.5$ or 35°C with $T = 40°C$) this leads to $t_d/t$ ratios which are not small compared to unity (compare Figure 17 of ref. 1, where it appears that the relaxation from 37.5°C is finished within 0.05–0.1 h which is only a few times $t_d$). As can easily be verified for the linear case ($a(\delta) = 1$), such non-ideal jumping

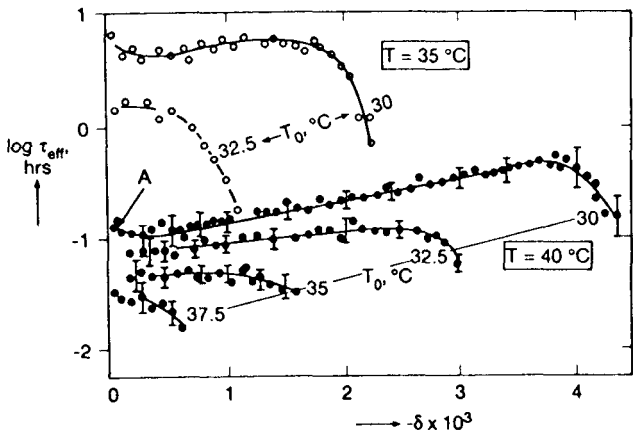


**Figure 8** Replot of *Figure 1*, but now with error bars as determined with equation (24); for explanation see text

leads to a decrease in $\tau_{eff}$. We disregard these effects here because the corrections are smaller than the errors discussed before[27].

## QUANTITATIVE TEST OF THE VOLUME-RELAXATION THEORY FOR THE $\tau_{eff}$ DATA

We are now ready for a quantitative comparison of theory and experiment. Theory predicts that we can transform *Figure 1* into a diagram in which all curves superimpose. The reasoning is as follows. When we add $\log[a(\delta)]$ to the vertical coordinate of *Figure 1*, the resulting quantity is $\log \tau'_{eff} = \log[-\mathrm{d}\ln\phi/\mathrm{d}\lambda]$ (see equations (11) and (12)). When we divide $\delta$ (horizontal coordinate) by $T_0 - T$, we get $\phi(\lambda)/v_\infty$ (see equation (6)). When these reduced quantities are plotted against each other, a unique curve will result, independent of $T_0$, because:

- $v_\infty$ is independent of $T_0$.
- as usual in relaxation theory[28], $\phi(\lambda)$ is assumed to be a total monotonic decreasing function of $\lambda$. Such functions can be described by a sum of (or integral over) positive exponentials with different positive relaxation times (see ref. 15 and pp. 118–122 of ref. 18). This implies that $-\mathrm{d}\ln\phi/\mathrm{d}\lambda$ monotonically decreases with increasing $\lambda$ (see Appendix). The monotony of both $\phi(\lambda)$ and $\mathrm{d}\ln\phi/\mathrm{d}\lambda$ implies that there exists a unique relationship between these quantities.

To find $\log[a(\delta)]$ we apply Kovacs' formula (equation (120b) of ref. 1):

$$\log a(\delta) = b\delta/[2.303 f_T(\delta + f_T)] = c\delta/[1 + \delta/k] \quad (25)$$

in which the plus sign is used instead of a minus[1] because here, $a$ is considered as an acceleration factor, increasing with fractional free volume $f$. Further, $f_T$ denotes the $f$-value at equilibrium at $T$ and $b$ the $b$-factor of the Doolittle equation. Obviously, we have:

$$c = b/[2.303 f_T^2] \quad (26)$$

$$k = f_T \quad (27)$$

Usually, $b$ is taken as unity, which leads to $f_T$-values of about 0.025 at $T_g$ and to $k = 1/\sqrt{(2.303c)}$. Substituting this in equations (26) and (27), we find: $c \approx 700$ and $k \approx 0.025$. To find the optimum $c$-value, we constructed the reduced plots as described before and varied $c$ until the scatter was minimum (for Doolittle's $b$-factor of unity).

The result is shown in *Figure 9*. As data points, we took the $\tau_{eff}$ values read from the curves in *Figure 1* for $-10^3\delta = 0.50,\ 0.75,\ 1.00, \ldots$, etc. We next varied $c$ between 400 and 1000, and found 600 as the best value. Finally, we plotted $\log \tau'_{eff}$ vs $\delta/[T_0 - T]$ and gave each point an error bar as determined in the previous section. Obviously, a single curve can be drawn through all error bars. Thus, there is no disagreement between theory and experiment, in contrast with the statements made in ref. 3.

As said earlier, the inaccurate points close to equilibrium ($|\delta| < 5 \times 10^{-4}$) were omitted. In fact, this pivot value of $5 \times 10^{-4}$ is arbitrary and, therefore, we now remove this restriction. In *Figure 10* we plotted all near-equilibrium points of *Figure 1* ($|\delta| < 5 \times 10^{-4}$). The $\log \tau_{eff}$ and $\delta$-values were read from (a magnified version of) *Figure 1* and the plot was constructed with the same values for $c$ and $b$ as in *Figure 9*. Also the curve of *Figure 9* is replotted in *Figure 10* and the data points were completed with error bars as described before. We observe that also the inaccurate points follow the curve of *Figure 9*, almost within experimental error.

At first sight, the result of *Figure 10* looks surprising. At equilibrium, we have $\log a(\delta) = 0$. Thus, the vertical shift, used to obtain superposition, is zero. Further, for $\delta \to 0$, division by $[T_0 - T]$ has no effect on the horizontal coordinate (0 divided by some number

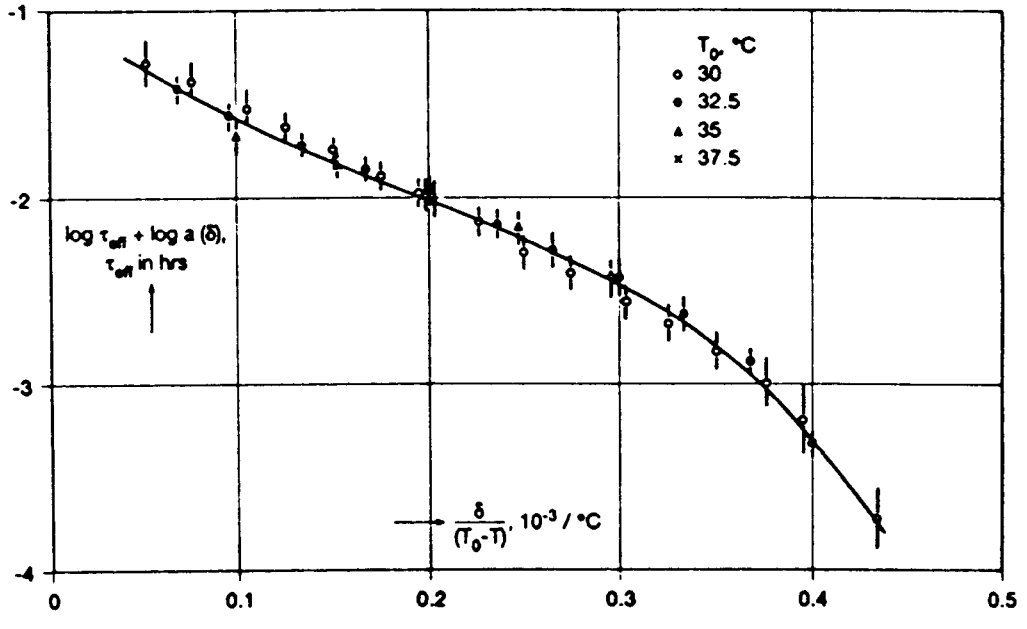


**Figure 9** Reduced plot derived from *Figure 1* (40°C data and $|\delta| > 5 \times 10^{-4}$) by shifting the points in a vertical direction by an amount $\log a(\delta)$ given by equation (25) and by changing the horizontal axis by plotting $\delta/[T_0 - T]$ instead of $\delta$. According to theory, the data should lie on a single curve. The error bars were taken from the previous section; for details, see text

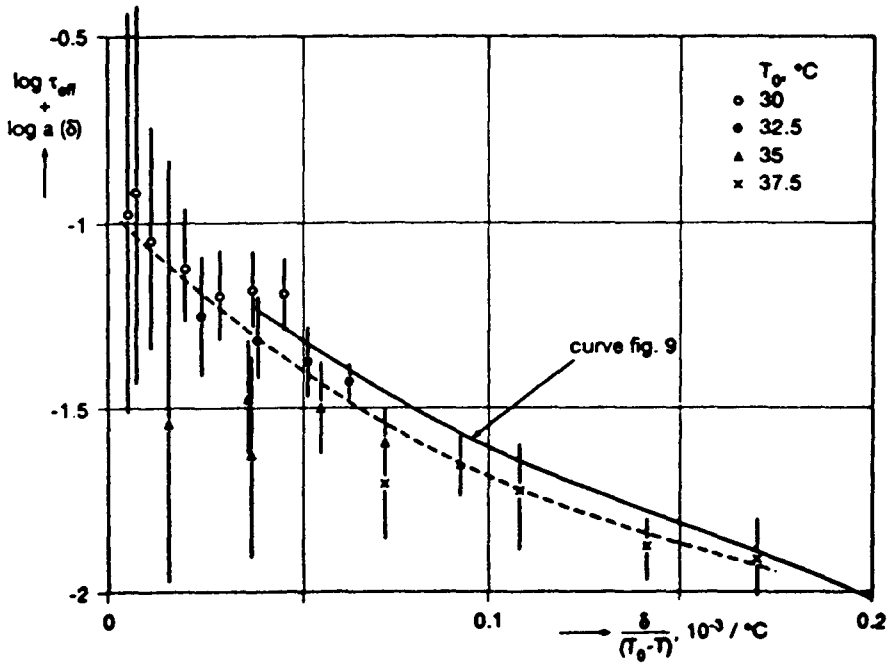


**Figure 10** As *Figure 9*, and with the same constants ($c = 600$, $b = 1$), but now for the inaccurate data points, rejected in *Figure 9*; for details see text

remains 0). Thus, our superposition method does not change the coordinates of points close to equilibrium and cannot remove an expansion gap at equilibrium. The superposition still works because the alleged gap is smaller than the large errors at $\delta \rightarrow 0$.

The procedure used to construct *Figure 9* does not lead to a sharp estimate of parameter $c$. The value of 600 gives the optimum fit, but the scatter in $\log \tau_{\text{eff}}$ is such that good fits are also possible for $c$-values ranging between 500 and 700 (note that Kovacs used $c = 670$ for constructing the dotted $\log a$ vs $\delta$ curve in Figure 6 of ref. 2). Even a model with $k = \infty$ ($\log a(\delta) = c\delta$) gives a reasonable fit. Consequently, by using rates, we have introduced so much scatter that a sharp estimation of $c$ and $k$ is impeded.

In a subsequent paper[27], we will analyse Kovacs' original $\delta$ vs $t$ curves and show that also these data can be described within experimental error ($\pm 2 \times 10^{-5}$) by the phenomenological volume relaxation theory.

## CONCLUSION

The $\tau_{\text{eff}}$-paradox does not exist. Kovacs' data at small $\delta$-values should be rejected because of large inaccuracies in $\tau_{\text{eff}}$; the rest of the data can be described by existing phenomenological volume relaxation theory. Moreover, even for linear relaxation, $\tau_{\text{eff}}$ does not necessarily converge to a single value at equilibrium.

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## APPENDIX

Assume that function $G(t)$ can be written as:

$$G(t) = \sum g_k \exp(-t/\tau_k) \qquad \text{(A1)}$$

with:

$$g_k > 0 \text{ and } \tau_k > 0 \tag{A2}$$

whilst the summation runs from $k = 1$ to $k = n > 1$ (unspecified). We then have:

$$R(t) = -\mathrm{d}\ln G(t)/\mathrm{d}t = \left\{\sum [g_k/\tau_k]\exp(-t/\tau_k)\right\}/\left\{\sum g_i \exp(-t/\tau_i)\right\} \tag{A3}$$

with $i$ and $k$ running from 1 to $n$.
Differentiation with respect to $t$ yields:

$$\mathrm{d}R/\mathrm{d}t = f(t)/g(t) \tag{A4}$$

$$f(t) = \sum g_k g_i [1/(\tau_i \tau_k) - 1/\tau_k^2]\exp[-t(1/\tau_i + 1/\tau_k)] \tag{A5}$$

$$g(t) = \left\{\sum g_i \exp(-t/\tau_i)\right\}^2 \tag{A6}$$

In the formula for $f(t)$, we can interchange $i$ and $k$ and get the same result. Adding this to that of equation (A5), we get:

$$f(t) = -1/2 \sum g_k g_i [1/\tau_i^2 + 1/\tau_k^2 - 2/(\tau_i \tau_k)] \times \exp[-t(1/\tau_i + 1/\tau_k)] \tag{A7}$$

which is obviously negative because the fist term in square brackets is a square. With $f(t)$ negative and $g(t)$ positive it follows that $R(t)$ must be a decreasing function of $t$.