polymer

The τ-effective paradox revisited: an extended analysis of Kovacs' volume recovery data on poly(vinyl acetate) [☆]

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Abstract

In 1964 Kovacs (Kovacs, AJ, Transition vitreuse dans les polymères amorphes. Etude phénoménologique. Fortschr Hochpolym-Forsch 1964;3:394–507) published a paper in which he analyzed structural (volume) recovery data in asymmetry of approach experiments. Kovacs used a parameter referred to as τ-effective (τ_{eff}) which is defined in terms of the volume departure from equilibrium δ as $\tau_{\text{eff}}^{-1} = -1/\delta \, \mathrm{d}\delta/\mathrm{d}t$. In plots of the $\log(1/\tau_{\text{eff}})$ vs. δ Kovacs observed an apparent paradox in that the values of τ_{eff} did not converge to the same point as δ approached zero (i.e. equilibrium). Hence the equilibrium mobility of the structural recovery seemed path dependent. Also, the apparent paradox was accompanied by a spreading of the curves for τ_{eff} in the up-jump experiments which has come to be known as the expansion gap. While it is currently accepted that the paradox itself does not exist because the curves will converge if the measurements are made closer to $\delta = 0$ (Kovacs' estimates of τ_{eff} were made for values as small as $\delta \approx 1.6 \times 10^{-4}$), the existence of the expansion gap is still a subject of dispute. This is particularly relevant today because recent models of structural recovery have claimed 'success' specifically because the expansion gap was predicted. Here we take the data Kovacs published in 1964, unpublished data from his notebooks taken at the same time, as well as more recent data obtained at the Institut Charles Sadron under his tutelage in the late 1960s and early 1980s. We then examine them using several different statistical analyses to test the following hypothesis: the value of τ_{eff} as $|\delta| \rightarrow 1.6 \times 10^{-4}$ for a temperature jump from T_i to T_0 is significantly different from the value obtained for the temperature jump from T_j to T_0. The temperatures T_i or T_j can be either greater or less than T_0. If the hypothesis is rejected, the τ_{eff}-paradox and expansion gap need to be rethought. If the hypothesis is accepted, then the argument that reproduction of the expansion gap is an important test of structural recovery models is strengthened. Our analysis leads to the conclusion that the extensive set of data obtained at 40°C support the existence of an expansion gap, hence an apparently paradoxical value of τ_{eff}, for values of $|\delta| \geq 1.6 \times 10^{-4}$. However, at smaller values of $|\delta|$ it appears that the values of τ_{eff} are no longer statistically different and, in fact, the data suggest that as $|\delta| \rightarrow 0$ all of the τ_{eff} values converge. In addition, data for experiments at 35°C do not have sufficient accuracy to support the expansion gap for such small values of $|\delta|$ because the duration of the experiments is significantly longer than those at 40°C. Consequently the data readings taken at 35°C were made at longer time intervals and this leads to dramatically reduced error correlations. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Structural recovery; Volume recovery; Expansion gap

1. Introduction

In 1964, Kovacs [7] published a paper in which he analyzed structural recovery data in asymmetry of approach experiments using a parameter that he referred to as τ-effective (τ_{eff}). τ_{eff} was defined in terms of the volume departure from equilibrium δ as $\tau_{\text{eff}}^{-1} = (-1/\delta)\mathrm{d}\delta/\mathrm{d}t$. In plots of the $\log(1/\tau_{\text{eff}})$ vs. δ, Kovacs observed an apparent paradox in that the values of τ_{eff} did not converge to the same point as δ approached zero (i.e. equilibrium), hence the equilibrium mobility of the structural recovery seemed path dependent. Also, the apparent paradox was accompanied by a spreading of the curves for τ_{eff} in up-jump experiments which has come to be known as the expansion gap. While it is currently accepted that the paradox itself does not exist because the curves [10] converge if the measurements are made closer to $\delta = 0$ (Kovacs' estimates of τ_{eff} went only to values of $\delta = 1.6 \times 10^{-4}$), the existence of the expansion gap (apparent paradox) is still a subject of dispute
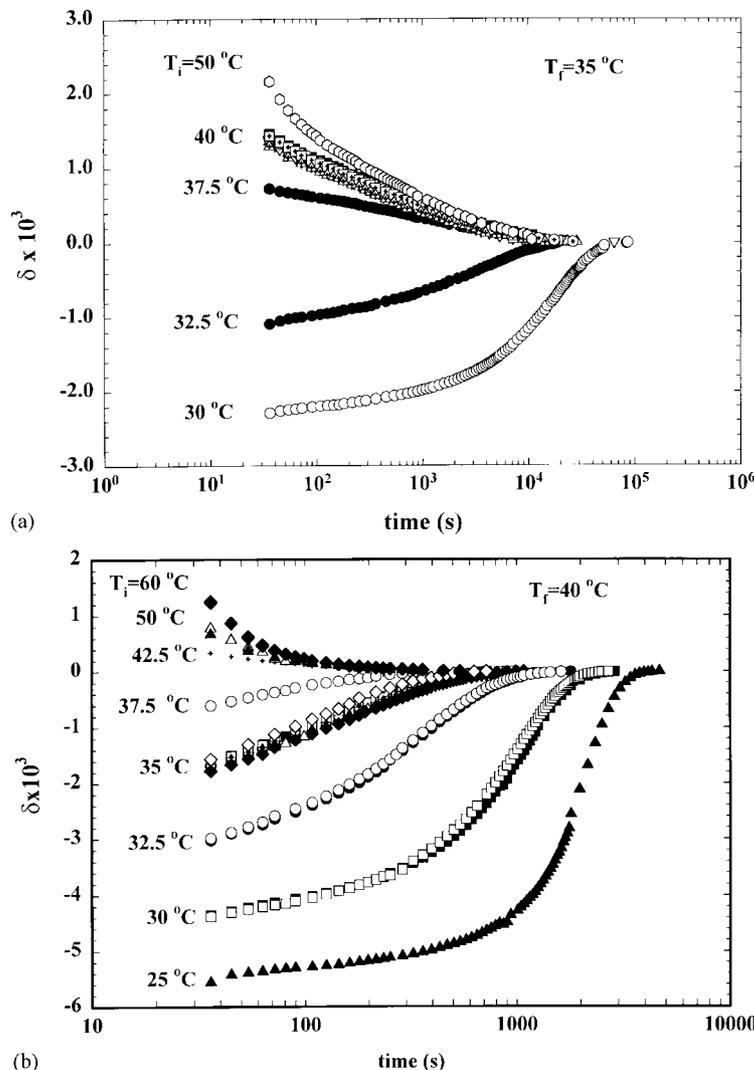
Fig. 1. Asymmetry of approach data for volume recovery of Poly(vinyl acetate) from Kovacs [7] as well as unpublished data of Kovacs as described in the text. The final temperatures are (a) $T_f = 35°C$ and (b) $T_f = 40°C$ and the initial temperatures T_i are as indicated in the drawing.

([12,13,16,19]. This is particularly relevant today because recent models [8,17] of structural recovery have claimed 'success' specifically because the expansion gap is obtained. Conversely, Struik [19] claims that the Kovacs' data do not support the expansion gap (or paradox) because the errors in the volume measurements propagate such that the errors in τ_{eff} become greater than the gap itself at values of $|\delta| \leq 5 \times 10^{-4}$. It is interesting to remark that Kovacs and co-workers in subsequent work [6,22] agonized over the expansion gap/ paradox and the fact that the reduced time models of structural recovery that they had developed did not seem to predict it. Struik's [19] arguments concerning the Kovacs [7] data would actually support the validity of the simple reduced time models.

Here we take the data Kovacs published in 1964, unpublished data of the same era from his notebooks, and data obtained later (1969–1982) at the Institut Charles Sadron under his tutelage, and subject them to a rigorous statistical analysis. We test the following

hypothesis: the value of τ_{eff} as $|\delta| \rightarrow 1.6 \times 10^{-4}$ for a temperature jump from T_i to T_0 is significantly different from the value obtained for the temperature jump from T_j to T_0. The temperatures T_i and T_j can be either greater or less than T_0. If this hypothesis is rejected, the τ_{eff}-paradox and expansion gap need to be rethought. If this hypothesis is accepted, then the argument that reproduction of the expansion gap is an important test of structural recovery models is strongly supported. We come to the conclusion that the data taken at 40°C support the existence of an expansion gap: hence, a paradoxical τ_{eff} when $|\delta| \geq 1.6 \times 10^{-4}$. However, at smaller values of $|\delta|$, it appears that the values of τ_{eff} are no longer statistically different and, in fact, the data suggest that as $|\delta| \rightarrow 0$ all of the τ_{eff} values converge. In addition, data for experiments at 35°C do not have sufficient accuracy to support the expansion gap for such small values of $|\delta|$ because the duration of the experiments is significantly longer than those at 40°C
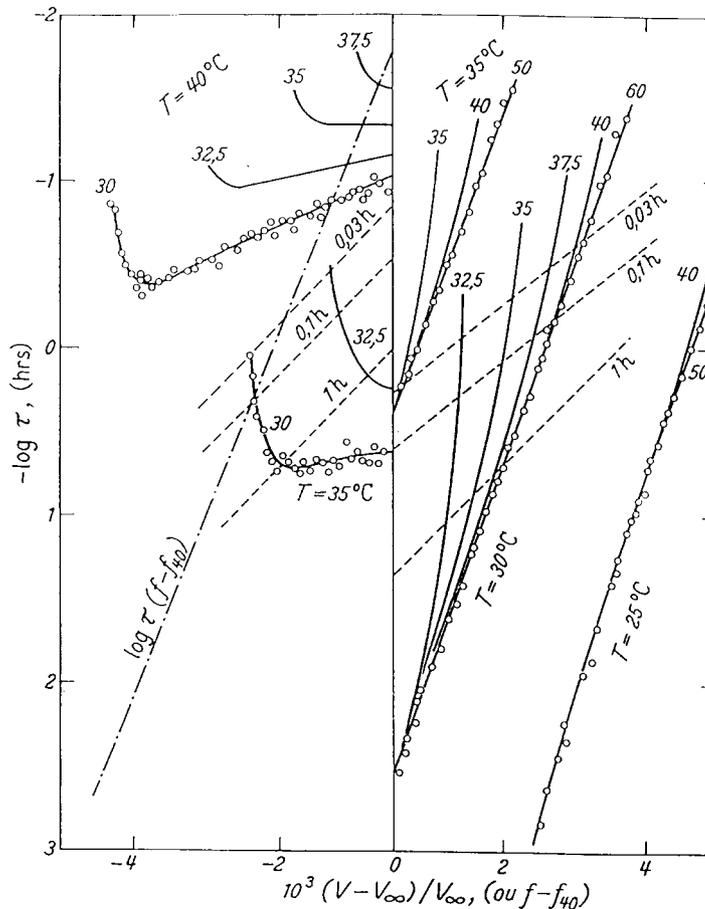
Fig. 2. Original τ-effective plot from Kovacs [7] in which expansion gap and apparent τ_{eff}-paradox are evidenced. See text for discussion. (Figure courtesy of A.J. Kovacs.)

and the data readings were made at longer time intervals which leads to dramatically reduced error correlations.

2. Asymmetry of approach experiments

In an asymmetry of approach experiment, a glass forming material is equilibrated at some temperature, T, that is greater than or less than the final temperature of test, T_0, by an amount ΔT. Subsequent to the equilibration a Temperature Jump (T-jump) is performed to the final temperature and the sample structural recovery is followed. Kovacs performed many such experiments for volumetric recovery, and the results of experiments to final temperatures of 35 and 40°C are depicted in Fig. 1(a) and 1(b) for different values of the initial temperature (or ΔT). The asymmetry arises when the up- and down-jump results for the same value of ΔT are not mirror images of one another. This is clear in the figures, and one sees that the approach towards equilibrium for the down-jump results is characterized by a small initial departure from equilibrium $\delta = (v - v_\infty)/v_\infty$ compared with that for the up-jump experiment.

We note that v is the specific volume at the time of measurement and v_∞ is the value in equilibrium. An explanation for the behavior seen in Fig. 1 has been given [7,9,11,14,20] as a structure (volume) dependent relaxation time. Hence, in the down-jump experiment, the initial response relaxes very rapidly because the departure from equilbrium is initially high and subsequently slows as the volume decreases. In the up-jump experiment, the initial departure is negative, hence the relaxation is slow initially and, as the volume increases towards equilibrium, the mobility increases. Therefore, the approach to equilibrium from below and above is asymmetric.

The asymmetry of approach experiment is itself relatively well understood and has been widely interpreted in terms of either the Tool–Narayanaswamy–Moynihan [11,14,20] fictive temperature based model of structural recovery or the mathematically equivalent KAHR [22] model which is based on the structural departure from equilibrium. However, the phenomenon described by Kovacs [7] as the τ-effective paradox is not explained within the context of these models [6]. In the next section we define τ-effective and examine the 'paradox', and its precursor the expansion gap.
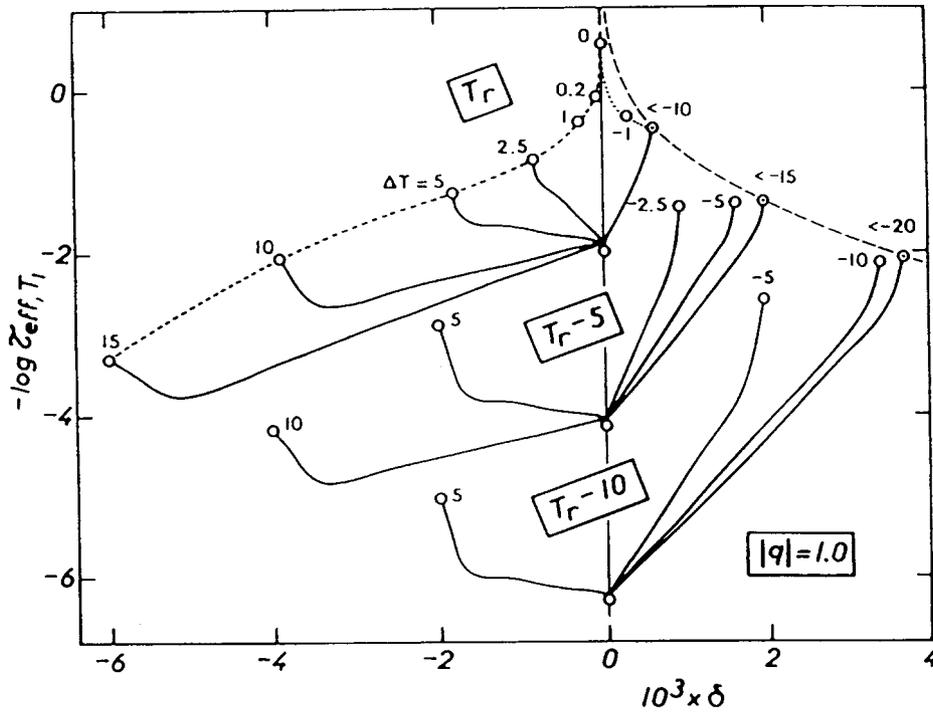
Fig. 3. τ_{eff} plot showing calculation from KAHR model showing no expansion gap and merging of the τ_{eff} values at $\delta = 0$. See text for discussion. (Figure from ref. 22, republished with permission of J. Wiley.)

3. Definition of τ-effective and the Kovacs τ-effective paradox

Let $\delta(t) = \delta_0 e^{-t/\tau}$ be an exponential decay function. Then the relaxation time τ is determined by taking the logarithmic derivative of $\delta(t)$ with respect to time, i.e.

$$\tau^{-1} = -\frac{1}{\delta}\frac{d\delta}{dt} = -\frac{d(ln|\delta|)}{dt} = \tau_{\text{eff}}^{-1}. \qquad (1)$$

For non-exponential decay functions the definition of τ becomes less clear. In volume recovery experiments, Kovacs [7] defined, as in Eq. (1), an effective rate or retardation time τ-effective or τ_{eff} whose deviations from constancy should be indicative of the non-exponentiality of the decay process.

In his studies on the kinetics of structural recovery, Kovacs performed many types of experiments that evidenced the nonlinear, non-exponential nature of the decay process. It is the asymmetry of approach experiment that interests us here because, in this experiment, Kovacs [7] observed the so-called τ-effective paradox. Kovacs took sets of data of the sort depicted in Fig. 1 and calculated τ_{eff}. The results that he presented in 1964 are shown in Fig. 2 as $-\log(\tau_{\text{eff}})$ vs. δ. There are several things to note from this figure. First, the up-jump results are to the left of $\delta = 0$ (i.e. negative departures from equilibrium) and the down-jumps are to the right of $\delta = 0$ (i.e. positive departures from equilibrium). Second, there are data for final temperatures of 40, 35, 30 and 25°C. The latter two temperatures are for down-jumps only and there are data at

Fig. 4. Plot of $\log|\delta|$ vs. t in T-jump experiments for a final temperature $T_f = 40$°C for the initial temperatures T_i indicated in the figure. $\log|\delta|$ is multiplied by the sign of δ in order to separate the up- and down-jump sets of experiments.

Fig. 5. Plot of $\log|\delta|$ vs. t in T-jump experiments for a final temperature of $T_f = 40°C$ for the initial temperatures T_i indicated in the figure. The data have been shifted to intersect at $\delta = 1 \times 10^{-4}$ to emphasize the trend of increasing slope with increasing initial temperature. Hatched area represents $\delta < 3.2 \times 10^{-5}$.
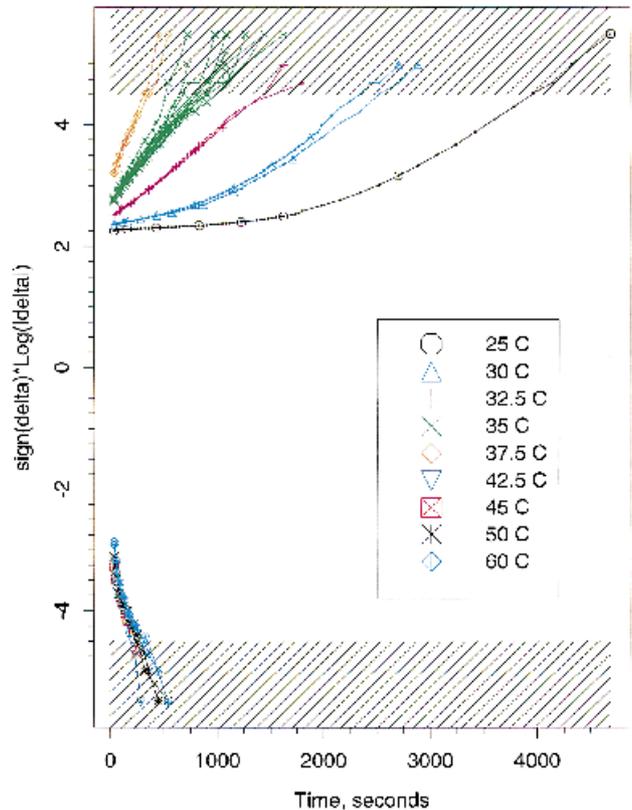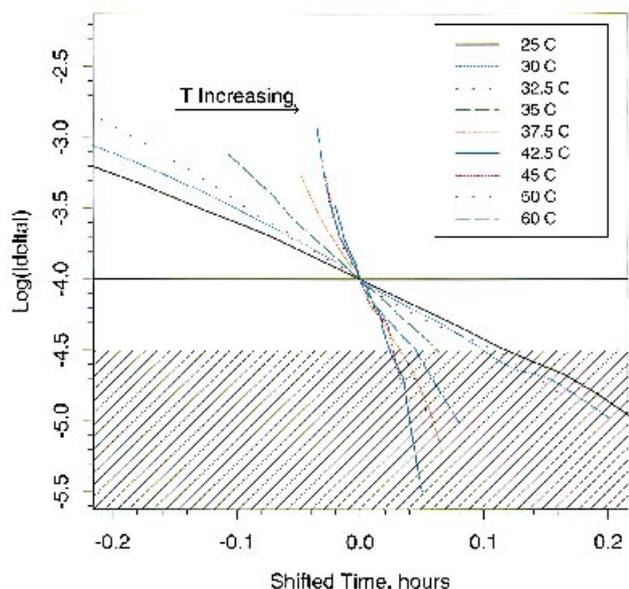

Fig. 6. Plot of $\log|\delta|$ vs. t in T-jump experiments for a final temperature of $T_f = 35°C$ for the initial temperatures T_i indicated in figure. The data have been shifted to intersect at $\delta = 1 \times 10^{-4}$ to emphasize the trend of increasing slope with increasing initial temperature. Hatched area represents $\delta < 3.2 \times 10^{-5}$.

40°C only for the up-jumps. The feature of interest in the figure is the apparent lack of convergence of curves at the same final temperature as $\delta \rightarrow 0$. Hence, the family of curves at $T = 40°C$ seems to fan with the order of the results following the magnitude of the initial temperature 30C $\Rightarrow$ 32.5 $\Rightarrow$ 35 $\Rightarrow$ 37.5°C. Similarly, the data at a final temperature of 35°C follow in sequence for the up-jumps 30 $\Rightarrow$ 32.5°C and the apparent final value for 30°C is different from the single value seen for all of the down-jump experiments. The behavior seen here is what Kovacs [7] referred to as the τ-effective paradox because the extrapolation of the curves to $\delta = 0$ results in an apparent path dependence of the equilibrium value of τ_{eff}. There has been some work [10] in which experiments were performed very close to equilibrium (with, perhaps, an order of magnitude better accuracy and resolution than seen in the Kovacs [7] data) which seems to establish that there is no paradox. However, the observation that the curves do not converge in the range of δ measured by Kovacs and shown in Fig. 2, is still perceived to be an important observation and has become known as the expansion gap. (The data of McKenna et al. [10] were taken over a much smaller range of δ, hence the expansion gap is not so clearly defined. Further, the data were obtained for a different reason and hence are not nearly as complete as those of Kovacs.)

4. The expansion gap

It is very important to establish the existence of the expansion gap in the Kovacs [7] data for several reasons.
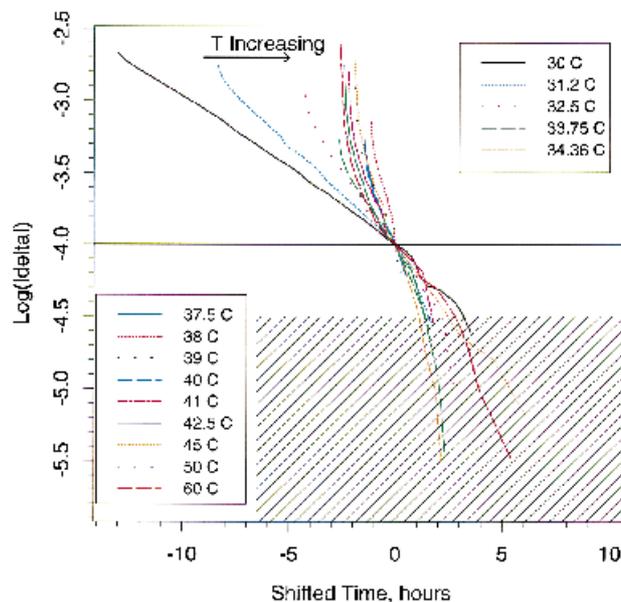
First, the existent Tool–Narayanaswamy–Moynihan and KAHR models [11,14,20,21] do not seem to give the gap [6] and a good example of this is shown in Fig. 3 in which the KAHR model was used to predict data similar to those of Fig. 2 (note the rapid convergence of the curves). Moreover, two models have appeared in the literature [8,17] in which the ability to predict the expansion gap has been taken as support for the validity of the models. In addition, there have for a long time been questions, in particular in the inorganic glass community, about the accuracy and precision of Kovacs' 1964 data and their ability to support the existence of the expansion gap [12,13,16]. Also, Haggerty [5], in studies of inorganic glass, did not see a significant expansion gap because of insufficient experimental accuracy. Goldstein and Nakonecznyi [4] did not see an expansion gap in $ZnCl_3$ and speculated that polymers might be exhibiting behavior that differs from inorganic glasses because they have a broader spectrum of retardation times. Finally, in a recent paper, Struik [19] has claimed that the data Kovacs published in 1964 do not support the existence of the expansion gap and he has put forth a propagation of errors argument to justify his claim.

The purpose of this paper is to examine rigorously the original Kovacs data. We consider not only the 'representative' data that he published, but also unpublished data taken at the same time. Further, data using the same dilatometer were taken later (1969–1982) under Kovacs' tutelage and we consider these in our analysis. In the following, we first describe the experiment of Kovacs and the sources of uncertainty in the measurements. We then perform two types of analysis on the data to estimate the point at which the value
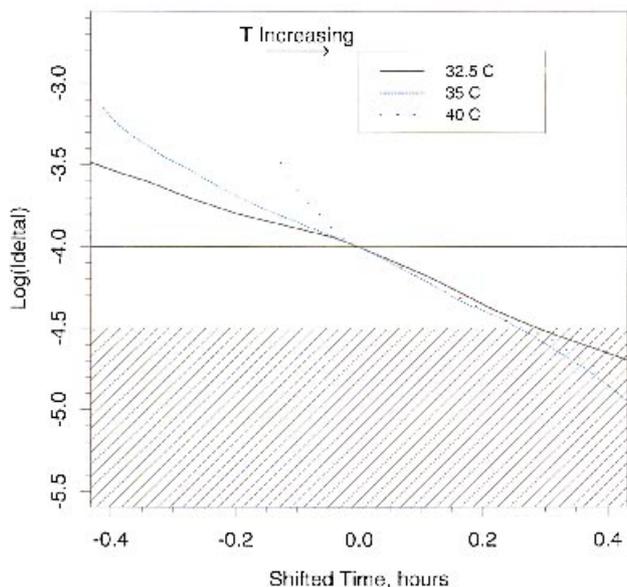
Fig. 7. As in Figs. 5 and 6 but now for $T_f = 37.5°C$.

Fig. 8. As in Figs. 5–7 but now for $T_f = 42.5°C$.

of τ_{eff} can no longer be said to be different between experiments run at different values of initial temperature. In the first data analysis, we analyze the slopes of curves of $\ln|\delta|$ vs. t, which are, in fact, $-\tau_{\text{eff}}^{-1}$. Secondly, we consider an analysis using a propagation of errors approach in which we consider correlated errors – something not considered by Struik [19]. From these two analyses we come to the conclusion that the expansion gap is real and establish limits on the minimum value of δ for which this can be said.

5. The Kovacs experiments

A major aspect of the determination of the statistical validity of the difference between values of τ_{eff} for different starting temperatures is to accurately estimate the sources of error in the data. Hence we describe these in some detail.

Kovacs performed dilatometry using Bekkedahl-type dilatometers [1] in which a poly(vinyl acetate) sample of approximately 1.25 cm^3 volume is placed into a glass tube which is sealed. The tube is attached to a capillary having a diameter of approximately 0.454 mm. The capillary is graduated by marks engraved at 1 mm intervals. The system is evacuated and then filled with mercury. Changes in volume of the sample are measured as changes in the height of the mercury in the capillary.

One source of error in the measurements is the resolution of the reading of the mercury height. This was done using a magnifying device having a low power lens and a reticle which was attached to the capillary. The mercury level could be read to within 0.10 mm using this device. This corresponds to a resolution of 1.6×10^{-5} cm^3, or a resolution in δ of 1.3×10^{-5}.
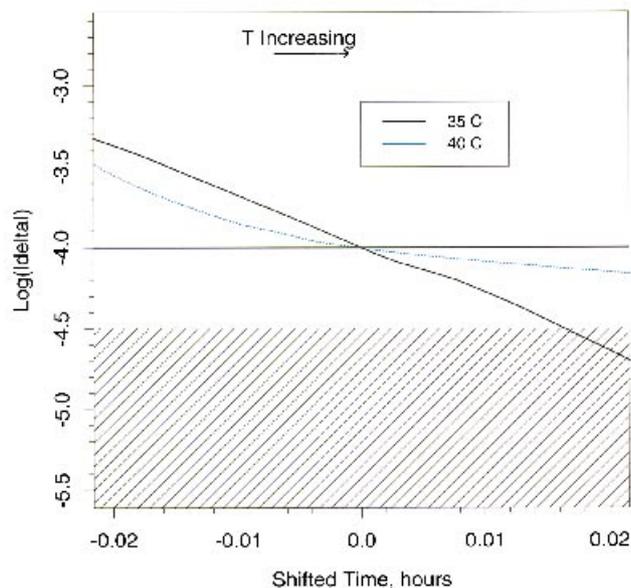
A second source of error arises in the temperature

fluctuations which are of the order of 0.015 K over a period of 100 h. This leads to an uncertainty in δ of approximately 1.7×10^{-5}.

One piece of information to address is the absolute temperature of the baths at T_0. Errors in T_0 do not affect the determination of τ_{eff} for a given experiment (i.e. errors in slope determination). However, they do affect the 'true' value of τ_{eff}, because τ_{eff} is temperature dependent. If the temperature of a bath was changed, the mercury relay thermometer could not be reset to exactly the same temperature, hence it is important to have measured the absolute temperature with some accuracy. The data we have chosen to analyze are of two sorts. In the earliest experiments the temperature was measured with a mercury thermometer that was calibrated by the Bureau International des Poids et Mesures in Sèvres, France. For data obtained after 1965, a Hewlett-Packard quartz thermometer was used, and a different calibration factor was obtained. Therefore, we have chosen to compare data at the nominal temperatures related to the 1950 calculation. Importantly, the temperature dependence of τ_{eff} itself is not a major source of error. As one expects τ_{eff} to vary approximately 1 order of magnitude per 3°C [23], an error of 0.1°C leads to an error of $10^{1/30} - 1 = 0.072$ – hence less than 10% which is significantly less than the size of the expansion gap which can be as much as an order of magnitude. This can be seen in Fig. 2. Therefore, this aspect of error is not considered further.

Finally, an important problem in the analysis of τ_{eff} is the fact that this is a derivative in the data, hence the correlations in errors in δ have an impact on the actual uncertainty in τ_{eff}. We come back to this in more detail when we quantitatively estimate the uncertainty using a propagation of errors analysis. First, however, we examine the data using a method that allows us to look at them as they are and to
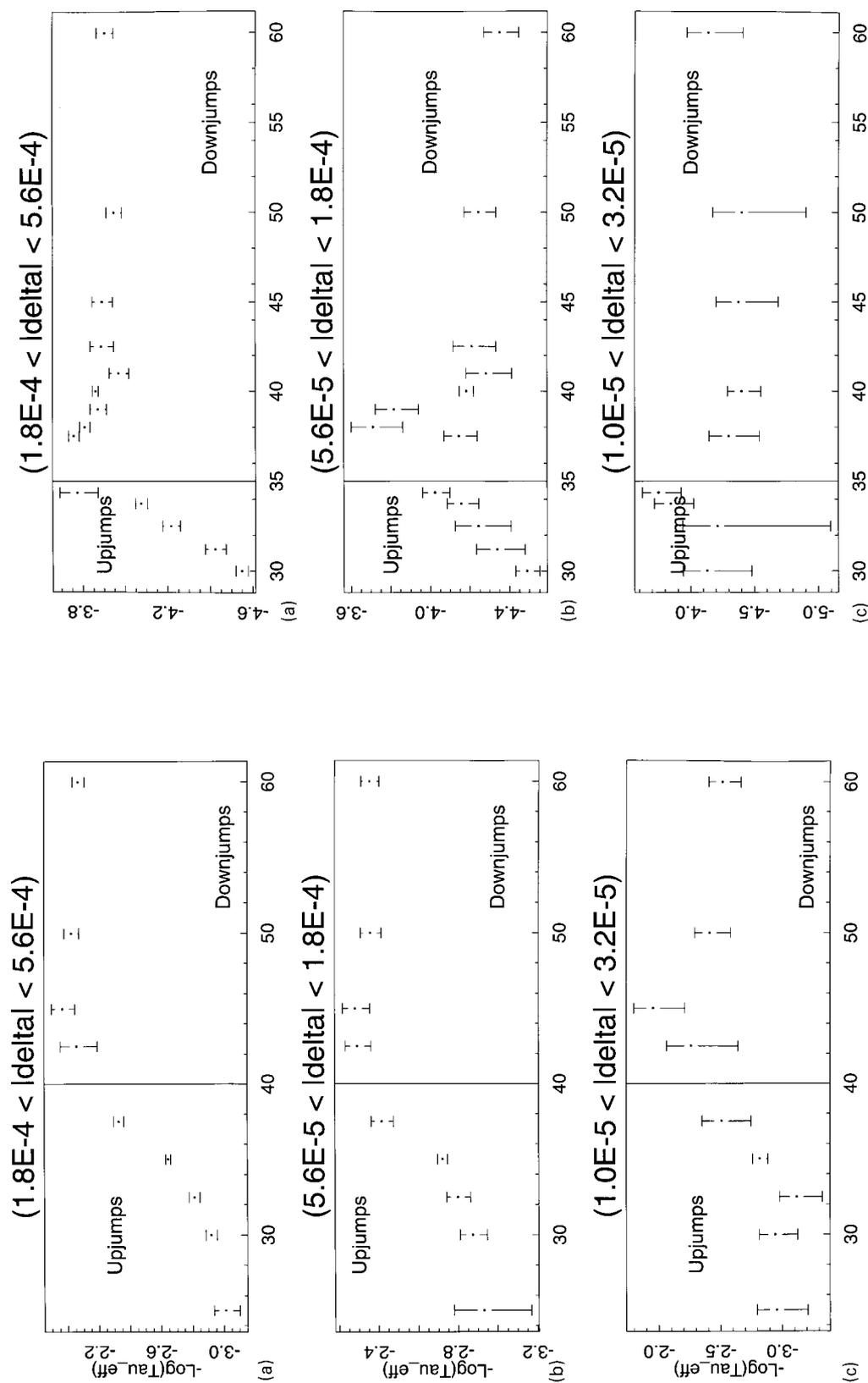
Fig. 9. Plots of $-\log(\tau_{eff})$ vs. initial temperature T_i for a final temperature $T_f = 40°C$ determined in the interval (a). $1.8 \times 10^{-4} < |\delta| < 5.6 \times 10^{-4}$; (b). $5.6 \times 10^{-5} < |\delta| < 1.8 \times 10^{-4}$; (c). $1.0 \times 10^{-5} < |\delta| < 3.2 \times 10^{-5}$. Plots compare up- and down-jump conditions. Error bars represent two standard errors of estimate of slope. See text for discussion.

Fig. 10. (a)–(c). Same as Fig. 9(a)–(c) but for 35°C.
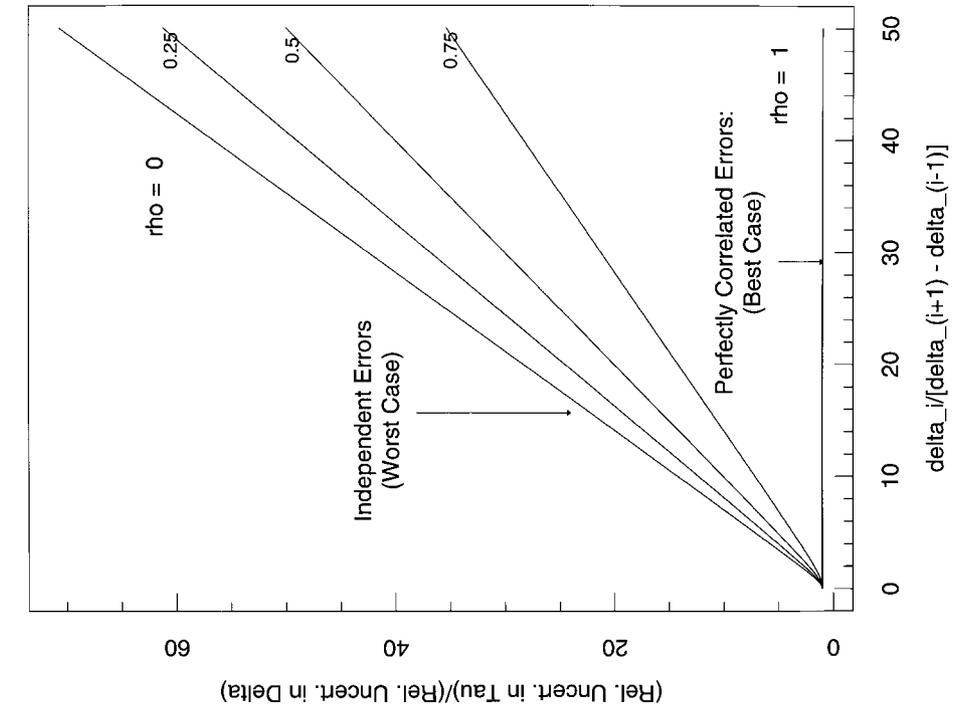
Fig. 12. Plot that shows the effect of error correlation on the ratio of the relative errors in τ_{eff} to those in δ from Eq. 4. See text for discussion.
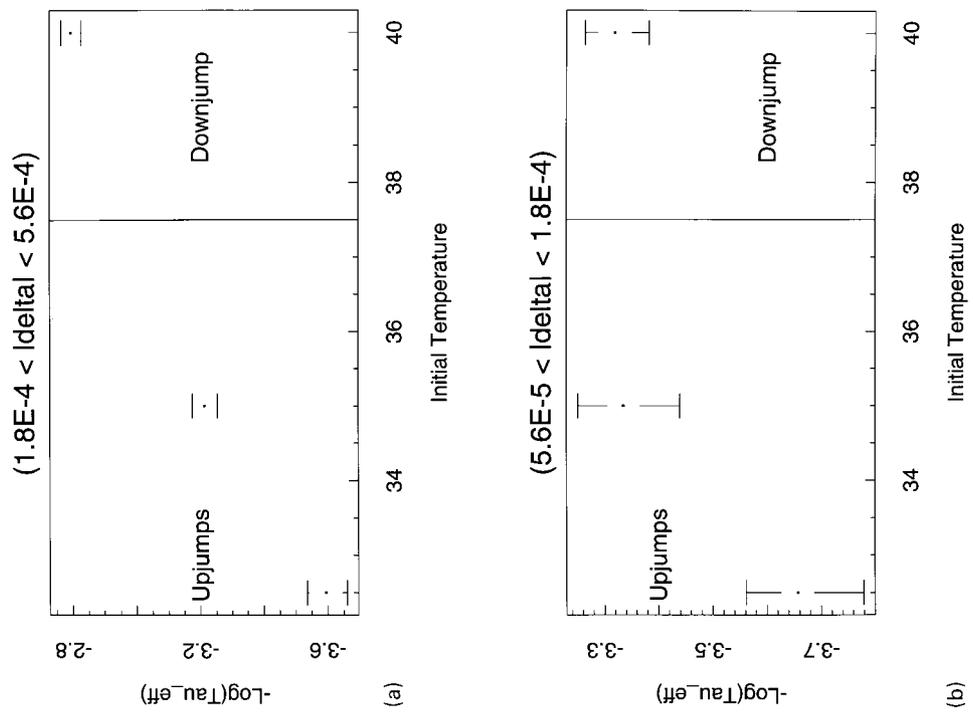
Fig. 11. a–b. Same as Fig. 9(a)–(c) but for 37.5°C.

T_0 = 40; T_f = 35, 11 Curves
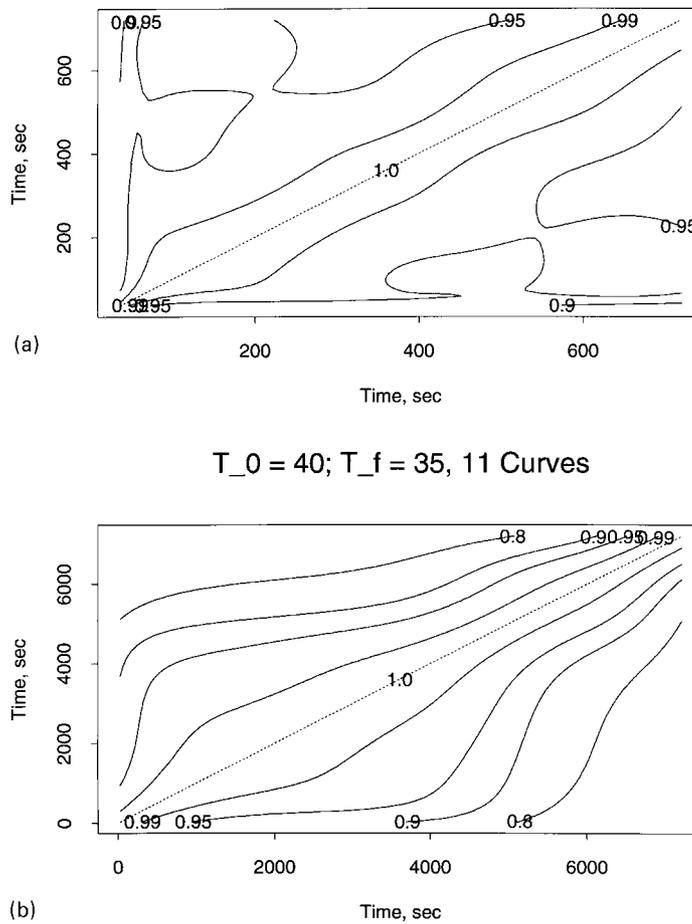
Fig. 13. Contour plot for error correlations with time between readings for (a) temperature jump from $T_i = 30°C$ to $T_f = 40°C$. Perfect correlation would follow the dashed line. (b). Same as (a) except that $T_i = 40°C$ and $T_f = 35°C$. See text for discussion.

thereby gain some insight into the meaning of τ_{eff}, the expansion gap and the behavior of the volume recovery as $\delta \rightarrow 0$. This approach, in fact, implicitly includes the error correlations.

6. The data

The original Kovacs [7] data represented only a partial set of the data that Kovacs had taken during the course of his studies. Further, subsequent work in the Laboratories at the Institut Charles Sadron (formerly Centre de Recherches sur les Macromolécules) was carried out, and we use these data to improve the statistics for repeat tests – an important aspect of the data quality because it provides another estimate of reproducibility beyond the within-test estimates of uncertainty given before. The data obtained from the Kovacs notebooks was taken down as both mercury height in the capillary and as a final calculated δ. We treat the data from the stage of δ as the two are directly related. In any given experiment, however, we do note that there is some potential arbitrariness in the value of $\delta = 0$. This is the limit of accuracy of the measurements as discussed before.
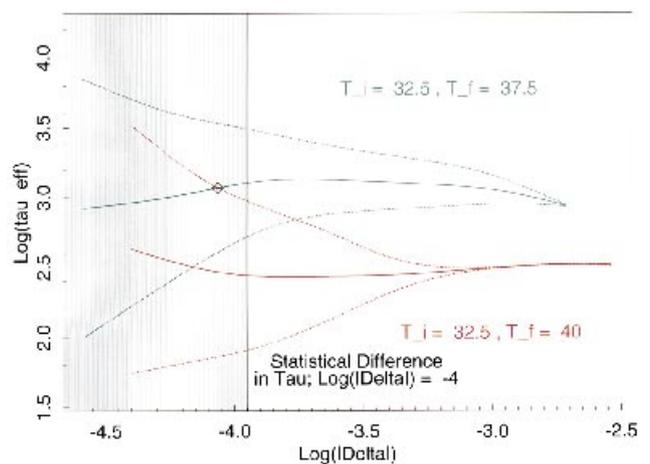
Fig. 14. Plot of $\log(\tau_{eff})$ vs. $\log|\delta|$ for T-jumps from 32.5°C to different final temperatures T_f of 37.5 and 40°C. Solid lines are mean values and dashed lines give the 95% confidence limits assuming appropriate error correlation functions. The vertical line and shading represent the values of $\log|\delta|$ below which one is no longer confident (at the 95% level) that the values of $\log(\tau_{eff})$ are different. See text for discussion.

Fig. 15. Plot of $\log(\tau_{\text{eff}})$ vs. $\log|\delta|$ for *T*-jumps from $T_i = 37.5°C$ and 35°C to the same final temperature $T_f = 40°C$. Solid lines are mean values and dashed lines give the 95% confidence limits assuming appropriate error correlation functions. The vertical line and shading represent the values of $\log|\delta|$ below which one is no longer confident (at the 95% level) that the values of $\log(\tau_{\text{eff}})$ are different. See text for discussion.

Fig. 16. Plot of $\log(\tau_{\text{eff}})$ vs. $\log|\delta|$ for two up-jumps from initial temperatures of 35°C and 37.5°C to a final temperature $T_f = 40°C$. Solid lines are mean values and dashed lines give the 95% confidence limits assuming appropriate error correlation functions. The vertical line and shading represent the values of $\log|\delta|$ below which one is no longer confident (at the 95% level) that the values of $\log(\tau_{\text{eff}})$ are different. See text for discussion.
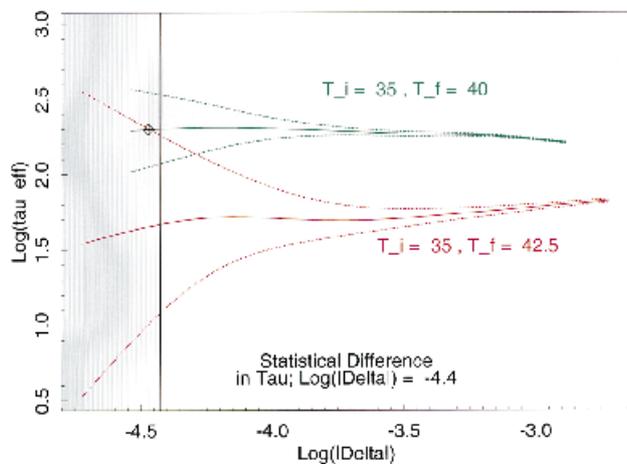
We consider up-jump and down-jump experiments to final temperatures of 35, 37.5, 40 and 42.5°C from multiple initial temperatures at which the samples had been equilibrated. We also examine down-jump experiments to 30°C, which provide important information about the reproducibility of the data and the error correlation in down-jump conditions. Table A1, presented in the Appendix, details the test conditions examined. Table A2, also in the Appendix, summarizes the test conditions. As can be seen, there are over 90 experiments considered. We note that Kovacs also performed many other experiments for other thermal histories than the asymmetry of approach type of experiment that is being examined here.

Finally, for completeness, we note that there were 4 experiments that we do not consider for temperature jumps to 35°C from 35.6, 36.0, 36.2 and 37°C because these were obvious outliers in that they recovered much too fast into equilibrium for the final temperature of 35°C. All of the other data were included, even when noisy. It is evident that Kovacs was meticulous in accepting certain experiments prior to thinking them as high enough quality for publication. With the exception aforementioned, we do not make such a judgement here.

7. A logarithmic representation of δ vs. t

One potential source of error in the Kovacs calculation of τ_{eff} is the determination of the slope of the data from a three point estimate. Further, plots of δ vs. t or δ vs. $\log t$ do not give a direct visualization of the way in which τ_{eff} is changing with time (or δ) throughout an experiment. An obvious, in retrospect, method of presenting the data is to plot $\log|\delta|$ vs. t. The slope of such a plot gives $-\tau_{\text{eff}}^{-1}$ to within a constant. Hence, one can see very dramatically in a
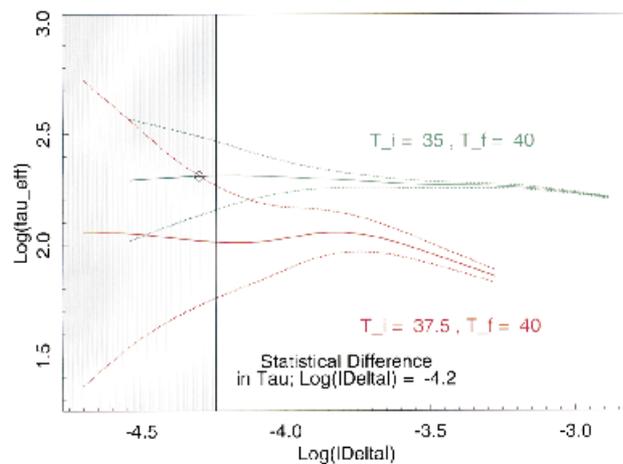
given series of experiments how the slopes of curves vary as, e.g. the initial temperature is changed. Such a plot is shown in Fig. 4 for a final temperature $T_0 = 40°C$. Note that the hatched area corresponds to an uncertainty in δ of 2×10^{-5}. The data for the up- and down-jumps are separated for clarity by multiplying by the sign of δ. We see several things in the figure. We see clearly that the data for the down-jumps come into equilibrium very quickly relative to the up-jumps, and the down-jump experiments seem to come into the hatched area with about the same slope – hence the same τ_{eff} values. However, the up-jump data do not come together and the slopes are not obviously all the same. It is also interesting to note that there is a relatively long portion of the up-jump data that seems to be linear on the plot, which would be true for a single relaxation process.

A better depiction of the changes in slope as the initial temperature changes is seen in Fig. 5 where we have now shifted all of the curves to intersect at $|\delta| = 10^{-4}$ and we plot $\log|\delta|$ vs. t on an expanded scale, so that the up- and down-jump data can be directly compared. It is very clear from the data that, as the initial temperature increases, the slopes of the curves increase and begin to merge as T_0 is approached and, for values corresponding to the down-jump conditions, the curves become virtually indistinguishable. Hence, an implication is that, at least until $|\delta| = 10^{-4}$, there is a difference in τ_{eff} that depends on the initial temperature for up-jumps and approaches that obtained in the down-jumps as the magnitude of the jump decreases. This supports the original interpretation of the data as presented by Kovacs in 1964 in his τ_{eff} plots for the data obtained at $T_0 = 40°C$.

Figs. 6–8 show similar depictions of $\log|\delta|$ vs. t for the final temperatures of 35, 37.5 and 42.5°C. For the 35°C data (Fig. 6) there is a slight trend similar to that seen in the 40°C data, but it is clear that the differences among the curves is slight. The results do show, strongly, that the final value of τ_{eff} seems to
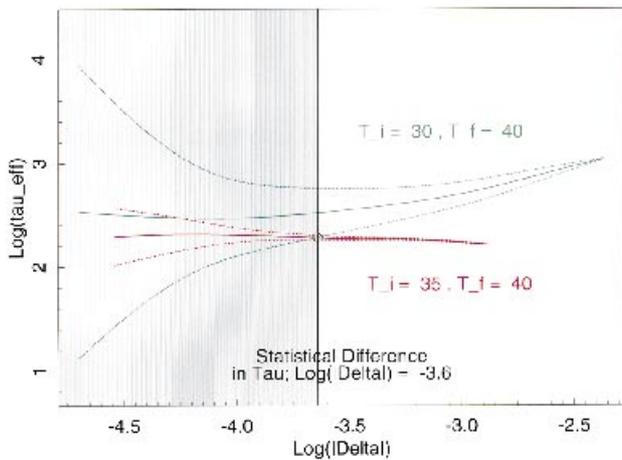
Fig. 17. Same as Fig. 16, but now $T_i = 30$ and $35°C$.

Fig. 18. Same as Fig. 16, but now $T_i = 42.5$ and $60°C$.

become independent of initial temperature for the down-jump conditions. For the other two temperatures the data are sparse, but the same trend of increasing slope with increasing intitial temperature as evident in the $40°C$ data is seen.

It is interesting to note that the differences in slopes persist more clearly until small values of δ in the $T_0 = 40°C$ data (Fig. 5) than for the other final temperatures. There may be other reasons for this, but our feeling is that the data taken for a final temperature of $40°C$ are "better" because the equilibration times are relatively short and the individual data readings were taken relatively close together in time even as δ becomes small. This leads to greater error correlation between data points taken at small values of δ and, therefore, to less uncertainty in the slopes of the lines and corresponding values of τ_{eff}. This issue is addressed directly in a subsequent section.

Although the representations of the data given in Figs. 4–8 are very striking, they do not answer directly the question whether or not the slopes, i.e. τ_{eff}, are statistically different for different initial temperatures, nor do they answer the question "at what magnitude of $|\delta|$ do the values of τ_{eff} become indistinguishable?". In order to address this question directly we estimated the uncertainty in the slopes (related to τ_{eff}^{-1}) by dividing the data into $|\delta|$ ranges. This approach assumes that for small intervals in $|\delta|$ the functions $\log(|\delta(t)|)$ are nearly linear. We fit a straight line model, with possibly different slopes for different initial temperatures, and allowing for different intercepts for each experimental curve. The deviations in the data from the straight line model are assumed to be Gaussian, with components of variance owing to variability between curves and within a curve. As replicated curves are available for several initial temperatures (at each final temperature), the uncertainties in the slopes ($-\tau_{eff}^{-1}$) can be estimated from the data. From these we determine the uncertainty in $-\log(\tau_{eff})$ as a standard error of estimate. In Fig. 9 we show the data for the estimates in $\log(\tau_{eff})$ and the uncertainties for four intervals of $|\delta|$ for the final temperature of $40°C$. The results are very intriguing. It can be seen that for the largest values of $|\delta|$ there is no doubt that the values of $\log(\tau_{eff})$ differ
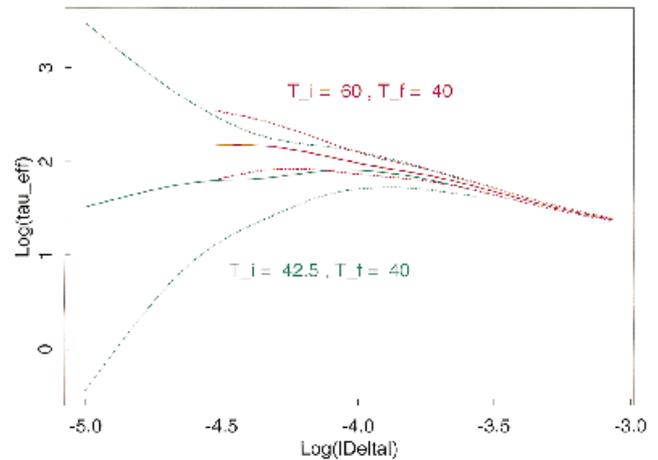
with initial temperature. Similar results are shown in Figs. 10 and 11 for the final temperatures of 35 and $37.5°C$. It is also seen that as $|\delta|$ decreases, the values of $\log(\tau_{eff})$ become less dependent on temperature and, in the interval $1.0 \times 10^{-5} < |\delta| < 5.6 \times 10^{-5}$, the $\log(\tau_{eff})$ values at the different starting temperatures become indistinguishable – hence showing that the Kovacs data themselves resolve the τ_{eff}-paradox. The data at $40°C$ support the existence of the expansion gap beginning in the range of values of $5.6 \times 10^{-5} < |\delta| < 1.8 \times 10^{-4}$ and for the ranges above this. For the $35°C$ data the results are less convincing, though there is a definite suggestion of a trend in the $\log(\tau_{eff})$ values that is similar to that seen in the $40°C$ data. At $37.5°C$, the results are consistent with the existence of the expansion gap.

Examination of the Figs. 9–11 also shows an interesting feature in that the plots of $\log(\tau_{eff})$ vs. T_i seem to be sigmoidal in shape. At large values of $|\Delta T|$ (lower temperatures) in the up-jump experiments the values of $\log(\tau_{eff})$ seem to be slowly changing until about $2°C$ from the final temperature, where they rapidly drop to the values observed in the down-jump experiments. The reasons for this are unclear. The results do show the kinetics of the structural recovery that lead to the expansion gap, perhaps simply reflecting the sensitivity of the up-jump experiment to long time relaxations [4,18,19] in the structural recovery process, or the different physics implicit in the constitutive models of Rendell et al. [17] or Lustig et al. [8] vis à vis the TNM–KAHR type models.

8. A propagation of errors analysis

8.1. Importance of the analysis

In a recent paper, Struik [19] used a propagation of errors analysis to argue that the Kovacs 1964 data do not support the expansion gap (or apparent paradox in τ_{eff}). One of the reasons for our disagreement with Struik's analysis resides in his assumption that the errors in the estimation of δ are

uncorrelated. In the analysis which follows, results similar to his would be obtained if there were no correlation in the errors in Kovacs' measurements. However, simple examination of the data show that this is untrue, and a more rigorous analysis allows us to estimate the correlation in the data. Considering correlation in the data leads to conclusions similar to those discussed before, and not in agreement with those of Struik [19]. Further, the replication of Kovacs' experiments improves the statistics and increases our confidence that the expansion gap exists.

What do we mean by uncorrelated and correlated data? If the data are uncorrelated, this implies that the uncertainties in measurements made over time are independent. Hence, if the errors are uncorrelated, the absolute error in the difference of δ measurements made 1 s apart are the same as the errors in measuremnts made 10 h apart. More formally, taking a measurement at time t_i followed by one at t_{i+1} would have the same relative error as taking the measurement at t_i followed by one at t_{i+n}. Clearly, in measurements of the sort described in the experimental section where readings are taken manually and in which bath temperature fluctuations are likely to occur over a relatively long time-scale the errors in the data will be correlated. The effect on error correlations of the temperature fluctuation uncertainty is one that is readily understood. Imagine that the bath temperature fluctuates as a result of daily temperature cycles as damped by the thermal mass and control system for the bath temperature. Then, in the limit that $\Delta t = t_{i+1} - t_i \rightarrow 0$, clearly the error in the height reading because of the bath temperature being different from one reading to the next vanishes. In this case, the estimate of τ_{eff}, which comes from the slope of the height vs. time ($\log|\delta|$ vs. t), will be completely as a result of the change in sample volume, hence will have no error even though the absolute measurement is somewhat in error because of the temperature uncertainty. One would expect that the correlation of the errors would decrease as the time interval Δt between readings increases. It is more difficult to define what the source of correlation among errors arising from the meniscus reading procedure itself might be, however, it is clear from the data themselves that such a correlation must exist because even where the data are changing very slowly (short times in the up-jumps, see Fig. 1) the data change monotonically. In the following, we first derive the expression for the error in τ_{eff} as a function of the error in the measurement of δ including a term for the correlation of the errors. We show how the errors in the estimate of τ_{eff} are dramatically larger for the case of uncorrelated errors than for the case of perfectly correlated errors. We then analyze data for a set of up-jump and a set of down-jump experiments for which there is substantial replication in order to estimate the error correlation as a function of time between readings. With the appropriate correlation functions we then estimate the magnitude of δ at which the values of $\log(\tau_{\text{eff}})$ are significantly different with 95% confidence for the Kovacs data discussed before. This analysis

results in similar conclusions to those discussed in the previous section.

8.2. The error analysis

We consider the divided-difference approximation that Kovacs likely used to estimate τ_{eff}^{-1} [19]. Using a linear Taylor series approximation, the uncertainty in an estimate of τ_{eff}^{-1} is related to the uncertainties in the δ measurements. Struik [19] provides a conservative a-priori estimate for the standard deviation of the uncertainty in δ. Estimates of τ_{eff}^{-1} can be obtained empirically and plausible measures of the correlations among the δ estimates in the divided difference approximations to τ_{eff}^{-1} can be estimated using replicated data sets. Taken together, the Taylor series approximation, and estimates of the correlations among δ estimates taken close together in time enable one to estimate τ_{eff}^{-1} curves as functions of time along with approximate 95% confidence bands. By examining these curves in pairs, we can estimate the smallest values of δ for which τ_{eff}^{-1} are statistically significantly different.

The data from each experiment consist of successive measurements of relative volume change from equilibrium $(d_1, d_2, \ldots, d_n)$, and corresponding elapsed times after the temperature jump $(t_1, t_2, \ldots, t_n)$. We assume that the measurement uncertainty in d_i's is much greater than the uncertainty in the times, so that the error made by treating the t_i values as if they are known is negligible. For the measured d_i's, in contrast, let $d_i = \delta_i + e_i$, where δ_i is the 'true' value which one would observe if there were no measurement uncertainty. The 'errors' e_i are assumed to be Gaussian with mean zero and standard deviation σ_d.

If Kovacs estimated τ_{eff}^{-1} using a three-point divided difference method, then one can express the 'true' quantity being estimated as

$$(\tau_{\text{eff}}^{-1})_i = \frac{\delta_{i+1} - \delta_{i-1}}{\delta_i(t_{i+1} - t_{i-1})}, \qquad (2)$$

and the estimate as

$$(t_{\text{eff}}^{-1})_i = \frac{d_{i+1} - d_{i-1}}{d_i(t_{i+1} - t_{i-1})}. \qquad (3)$$

We use the propagation of errors approach [2,3] to approximate the standard deviation of τ_{eff}^{-1}, σ_τ, in terms of σ_d, the t_i's, and the δ_i's. Finally, the unknown δ_i's are estimated from the measured d_i's. The propagation-of-errors approximation to the relative uncertainty in τ_{eff}^{-1} is then

$$\left(\frac{\sigma_\tau/\tau_{\text{eff}}^{-1}}{\sigma_d/d}\right)_i \approx \sqrt{1 + 2(1 - \rho_{i-1,i+1})\left(\frac{\delta_i}{\delta_{i+1} - \delta_{i-1}}\right)^2} \qquad (4)$$

where $\rho_{i-1,i+1}$ is the correlation between measurements made at times t_{i-1} and t_{i+1} on the same curve. This correlation is apparently assumed to be zero in the analysis of Struik [19]; as seen later, for the data here it is non-zero and often close to one for the time intervals that were typical of data collection in the Kovacs experiments. From Fig. 12,
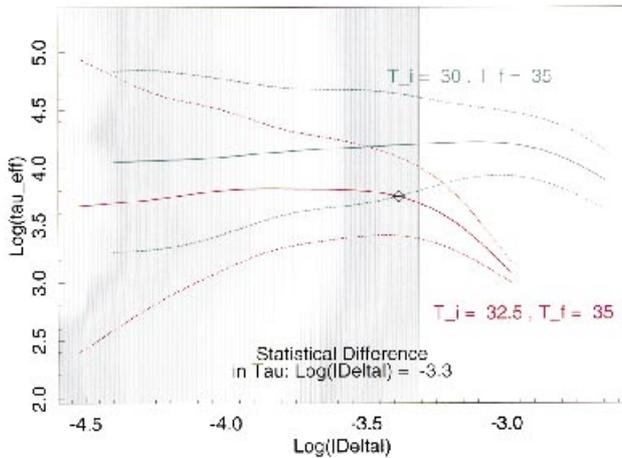
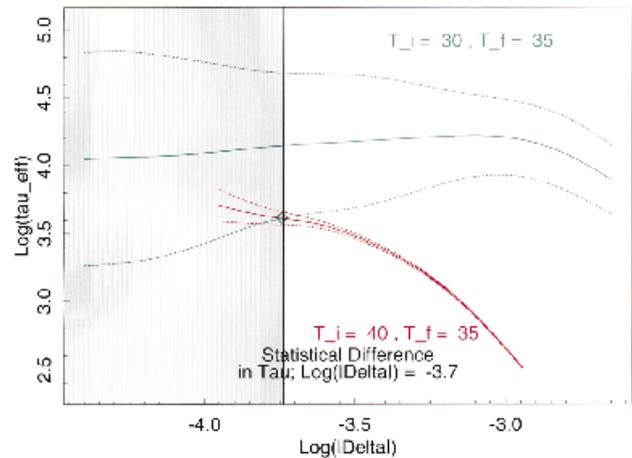Fig. 19. Same as Fig. 16, but now $T_f = 35°C$ with $T_i = 30$ and $32.5°C$.

Fig. 20. Same as Fig. 16, but now $T_f = 35°C$ with $T_i = 30°C$ and $40°C$.

where we present the ratio of Eq. (4) for different values of the correlation parameter $\rho_{i-1,i+1}$, it is clear that the impact of $\rho_{i-1,i+1}$ on the estimated value of the uncertainty in τ_{eff}^{-1} is dramatic.

We have given our estimates of the uncertainty in Kovacs' data as mentioned previously, they are not greatly different from those estimated by Struik [19], we use Struik's estimate to avoid further confusion. Struik [19] estimated the 'uncertainty' in δ to be $\pm 2 \times 10^{-5}$. We take this to represent $\pm 2\sigma_d$. Hence, we estimate $\sigma_d \approx 1 \times 10^{-5}$. Of course, the unknown true δ_{i+1} and δ_{i-1} are estimated by d_{i+1} and d_{i-1}, respectively. To estimate the correlation of the data $\rho_{i-1,i+1}$ we use replicated curves for the Kovacs experiments for T-jumps from 35 to 40°C and from 40 to 35°C. The correlation functions which we estimated using the methods of Ramsey and Silverman [15] are presented in Fig. 13 and discussed in the following paragraph. There were only three temperature pairs for which there is adequate replication of the experiments to estimate $\rho_{i-1,i+1}$. Those relevant to the current analysis are the 35–40°C data which we used to estimate $\rho_{i-1,i+1}$ for all of the up-jump curves. The 40–35°C estimates of $\rho_{i-1,i+1}$ are used for all of the down-jump curves. There are 15 data sets for the jump from 35 to 40°C and 11 for the jump from 40 to 35°C.

Fig. 13(a) and (b) show the correlation in the deviations of the Kovacs volume recovery data from a mean line fit to the replicate sets of data for the 35–40°C and the 40–35°C experiments. What can be seen from these data is that in the up-jump experiments the data correlation is very high ($\rho_{i-1,i+1} \gtrsim 0.90$) for data points taken up to approximately 600 s apart. For the down-jump case, the high correlation extends to data readings taken approximately 4500 s apart. Whether the differences in the times for the correlations to begin decreasing is a function of the specific experiment, i.e. down- vs. up-jump, or the final test temperature, is unclear. The other set of data available to perform such an analysis is the temperature jump from 40 to 30°C, and there the high

correlation is retained for times to approximately 2000 s. In any event, we used the correlations shown in Fig. 13(a) for our up-jump calculations and the correlations of Fig. 13(b) for the down-jump calculations discussed in the following.

8.3. Limiting values of δ for which τ_{eff} values are different

In the previous sections in which we estimated the limits for which the values of τ_{eff} for temperature jumps to the same final temperature are different, the analyses did not explicitly include correlation of errors, although the procedures for taking the slopes of the plots of $\log|\delta|$ vs. t included any such correlations implicitly. Here we take the error correlations determined before for the 'representative' up- and down-jump experiments and apply them so that we can compare T-jump results from different starting temperatures to the same final temperatures. In particular, how small is the smallest $\log|\delta|$ for which we have 95% confidence that the τ_{eff} values from two experiments are different? We examine temperature jumps to 35 and 40°C – the final temperatures originally considered by Kovacs. In addition, there were sufficient data for T-jumps to 37.5 and 42.5°C in the Kovacs notebooks to ask the same question. From examination of Fig. 2 we argue that the expansion gap should be significant for temperature jumps from two different initial temperatures when the τ_{eff} values are different when $|\delta| \leq 1.6 \times 10^{-4}$ or $\log|\delta| \leq -3.8$. This number is chosen because it is approximately the value of δ for the last data point in Fig. 2 for the T-jump from 30°C to 35°C. It is also in the region in which the curvature for the T-jump from 32.5°C to 35°C is changing into the flat line that looks as if it were extrapolating into the $\delta = 0$ line. It appears to be the limit for which Kovacs [7] trusted the data. As we go through the analysis that follows, these are the numbers to keep in mind.

The analysis of each set of two curves was performed by recognizing that we can estimate $\log \tau_{eff}$ as a function of δ from the data for each experiment using the divided
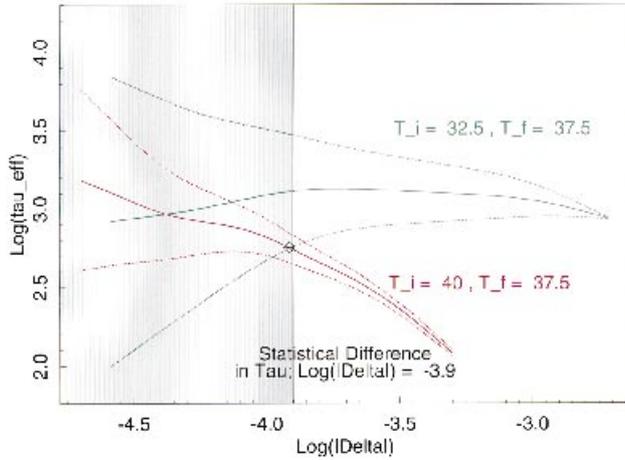
Fig. 21. Same as Fig. 16, but now $T_f = 37.5°C$ with $T_i = 32.5$ and 40°C.

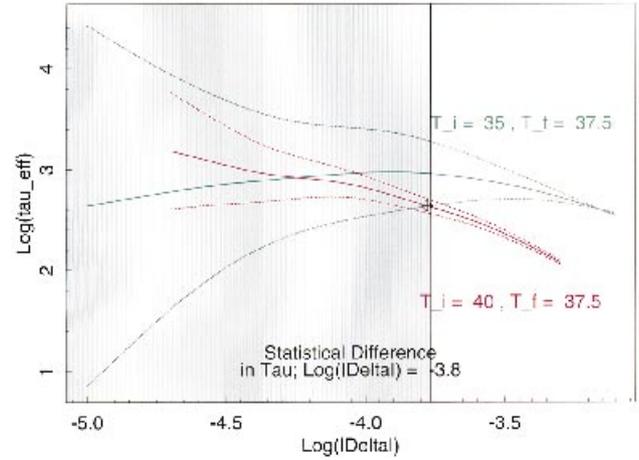Fig. 22. Same as Fig. 16, but now $T_f = 37.5°C$ with $T_i = 35$ and 40°C.

difference approximation (Eq. (2)). The correlation between d_{i+1} and d_{i-1} are then approximated using the correlation for the 35–40°C (up-jump) data, or the corresponding functions for the 40–35°C (down-jump) data. All of these estimates are then substituted into the propagation of errors formula (Eq. (4)) in order to estimate the standard error of τ_{eff} as a function of δ. From this one can easily determine the standard error of $\log \tau_{eff}$.

To estimate the limiting value of δ at which two curves become statistically indistinguishable we define this limiting value to be the largest value of d for which the absolute difference in the corresponding $\log \tau_{eff}$ estimates, divided by the standard error of this difference, is greater than 2. That is we require that

$$q_i = \frac{\left|[log(\hat{\tau}_{eff})]_{i+1} - [log(\hat{\tau}_{eff})]_i\right|}{[(\sigma_{\tau_{eff}})_{i+1}^2 + (\sigma_{\tau_{eff}})_i^2]^{1/2}} \geq 2 \qquad (5)$$

where the $\log(\hat{\tau}_{eff})$ refer to the estimated values for $\log \tau_{eff}$. Eq. (5) is closely related to the well-known two-sample t-test used to test for a statistically significant difference between two means. Typically, the largest value of d for which $q \geq 2$ will be slightly greater than the largest value of d for which one of the estimated mean curves is within the approximate 95% confidence interval for the other mean curve. This approach is used in the following discussion.

8.4. Temperature jumps to different final temperatures

The first comparison that we make is for two final temperatures that are close together and for up-jump conditions: $T_f = 37.5$ and 40°C for the same $T_i = 32.5°C$. The comparison is shown in Fig. 14 and we see that the value of the departure from equilibrium for which we have 95% confidence that the $\log \tau_{eff}$ values for the $T_f = 40°C$ differ from those at $T_f = 37.5°C$ is at $\log|\delta| = -4.1$, ($\delta = 7.9 \times 10^{-5}$) which is clearly smaller than the limit that we described above. This is expected since the values of τ_{eff} should vary with temperature. When the final temperatures

are 40 and 42.5°C and $T_i = 35°C$ we find that the limiting value of $\log|\delta| = -4.5$, ($\delta = 3.2 \times 10^{-5}$) as seen in Fig. 15 Here the statistics are undoubtedly better because of the fact that there are many replicates ($N = 15$) for the experiment in which the temperature was changed from 35 to 40°C.

8.5. Temperature jumps to 40°C

Next we compare the up-jump data for different initial temperatures for a final temperature of 40°C – the data most extensively analyzed by both Kovacs [7] and Struik [19]. As there are so many pairs of comparison to be made, we show three sets and the rest of the results are tabulated in Table A3. Fig. 16 shows the results from experiments performed in the up-jump to 40°C from initial temperatures that are close together and close to the final temperature: $T_i = 37.5°C$ and $T_i = 35°C$. Here it is clear that these two data sets are different to very small values of $\log|\delta| = -4.2$, ($|\delta| = 6.3 \times 10^{-5}$). However, (Fig. 17), when $T_i = 30°C$ is compared to $T_i = 35°C$ we find that the curves are different only when $\log|\delta| > -3.6$, ($\delta > 2.5 \times 10^{-4}$), which would suggest that these two curves are not coming in to different limiting values as $|\delta| \to 1.6 \times 10^{-4}$. This supports the observation made previously that τ_{eff} seems to follow a sigmoidal response in going from relatively large up-jumps towards small up-jumps and to the down-jump condition of a constant value of τ_{eff}. In Fig. 18 we depict the comparison of two down-jumps to 40°C: for $T_i = 42.5$ and 60°C. Here we see that there is no difference over the range of available data. Finally, upon examination of the data in Table A3 (see Appendix), we see that the results observed with the previous analyses in which error correlation is implicit, rather than explicit as here, the values of τ_{eff} are indistinguishable for adjacent large up-jumps, which are different from all of the down-jumps and there is a transition in which τ_{eff} changes and becomes indistinguishable between the small up-jumps and the down-jump experiments: hence, the existence of an expansion gap is supported by the
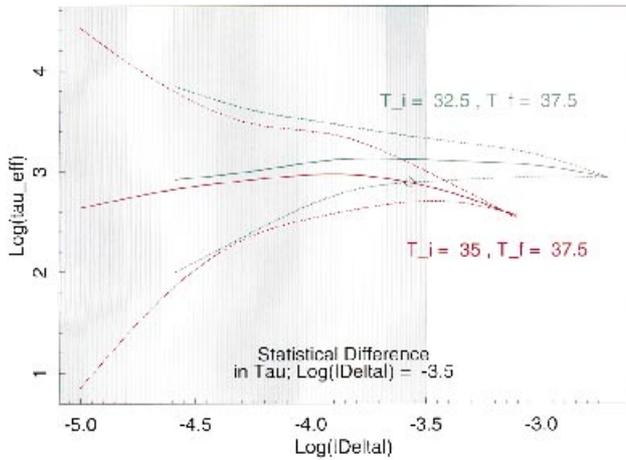
Fig. 23. Same as Fig. 16, but now $T_f = 37.5°C$ with $T_i = 32.5$ and $35°C$.

Fig. 24. Same as Fig. 16, but now $T_f = 42.5°C$ with $T_i = 35°C$ and $40°C$.

Kovacs data in asymmetry of approach experiments at 40°C. As an additional point, we call the reader's attention to the fact that for the comparisons between the large up-jumps and all of the down-jumps the values of τ_{eff} are different at the 95% confidence level or better based on the aforementioned criterion.

8.6. Temperature jumps to 35°C

Upon examination of Fig. 2 we see that for a final temperature of 35°C, Kovacs only showed results for initial temperatures of 30 and 32.5°C. In addition to τ_{eff} appearing different between these two initial temperatures, the data for the jump from 30°C seems to come in to zero departure from equilibrium at a value of τ_{eff} very different from the values in the down jump experiments from 35, 40 and 50°C. Hence, we can treat the data as in the previous section to ask what is the limiting value of $\log|\delta|$ (or $|\delta|$) below which the values of τ_{eff} are no longer different. This comparison is shown in Fig. 19 for the initial temperatures of 30 and 32.5°C. Two things can be seen from this figure. First, the 95% confidence limits are very large and the limiting behavior is for $\log|\delta| = -3.3$, ($|\delta| = 5.0 \times 10^{-4}$), a value somewhat larger than observed for the experiments at 40°C. The result is also affected by the small number of replicate experiments. If, however, we compare the experiment for $T_i = 30°C$ with that for $T_i = 40°C$, for which there are 11 replicates, the result changes: As shown in Fig. 20, there is a significant difference between τ_{eff} until $\log|\delta| = -3.7$, ($\delta = 2.0 \times 10^{-4}$). This is, then, similar to what was found above for the temperature jumps to 40°C. When we look at the full set of results in Table A3, in the Appendix, it is clear that the data for T-jumps to 35°C do not support the existence of an expansion gap except, perhaps, for the 30°C T-jump relative to some of the down-jumps. The explanation for the difference here and for the evidence obtained in the experiments at 40°C is that the times required for δ to approach zero (or the value of 1.6×10^{-4}) is at least ten times as long in the 35° C experiments as in the 40°C experiments. As a result,
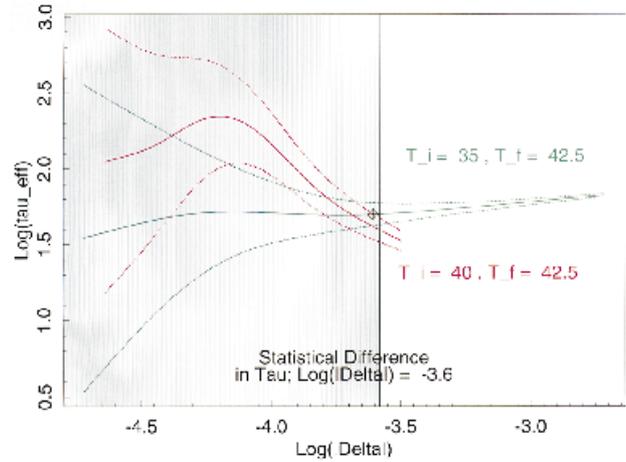
the error correlations when the time intervals between readings are longer decrease dramatically and the data have greater uncertainty. Of course, this does not mean that the "expansion gap" does not exist in the 35°C experiments, but that the Kovacs' 1964 data is insufficiently accurate to determine whether or not the expansion gap exists. This is important, because Rendell et al.[17] used the 35°C data, not the 40°C data as support for their model.

8.7. Temperature jumps to 37.5°C

The data for temperature jumps to 37.5°C that are presented and analyzed here were not reported in the original Kovacs [7] work. As shown next, these results uphold the contention of Kovacs that the data in the up-jump experiments show an expansion gap to very small values of δ.

In Fig. 21 we depict the curves from initial temperatures of 32.5°C and 40°C to the final temperature of 37.5°C along with the 95% confidence intervals. The values of $\log|\delta|$ at which the τ_{eff} are no longer different occurs when the 95% confidence line for the $T_i = 32.5°C$ intersects the mean curve for $T_i = 40°C$ at $\log|\delta| = -3.9$, ($|\delta| = 1.3 \times 10^{-4}$). Similarly, in Fig. 22 the curves for $T_i = 35°C$ and $T_i = 40°C$ are different until $\log|\delta| = -3.8$, ($|\delta| = 1.6 \times 10^{-4}$). Fig. 23 shows the comparison for the two up-jump experiments. We see that, in this case, they are different until values below $\log|\delta| = -3.6$, ($|\delta| = 2.5 \times 10^{-4}$), which does not support the existence of the expansion gap. However, because these two initial temperatures are close together, the results imply similar behavior to that seen in the 40°C data, i.e. the up-jumps are systematically different from the down-jumps, hence supporting the gap. However, up-jump experiments from temperatures close together are not necessarily going to show a difference at the 95% confidence limit required here. The experiments of interest, T-jumps from lower temperatures, were not performed.

8.8. Temperature jumps to 42.5°C

The data for temperature jumps to 42.5°C that are presented and analyzed here were not reported in the original Kovacs [7] work. In Fig. 24 we depict the curves from initial temperatures of 35 and 40°C to the final temperature of 42.5°C along with the 95% confidence intervals. The values of $\log|\delta|$ at which the τ_{eff} are no longer different occurs when the 95% confidence line for the $T_i = 40$°C interesects the mean curve for $T_i = 35$°C at $\log|\delta| = -3.6$, ($|\delta| = 2.5 \times 10^{-4}$). These data are not supportive of the existence of the expansion gap under the above defined criterion. However, it should be recalled that there are no replicate data for these experiments, which would greatly improve the statistics. Also, there are no down-jump data here for comparison.

9. Summary and conclusions

In 1964 Kovacs published a set of data from structural recovery experiments in which he made the observation that a plot of $\log(\tau_{eff})$ vs. δ exhibits an apparent τ_{eff}-paradox and an expansion gap. As there is some controversy in the literature concerning both the apparent paradox and the expansion gap, we have returned to the original Kovacs notebooks to analyze data that were taken at the same time as the data published in 1964, as well as subsequent data taken at the same laboratory under Kovacs' tutelage. Two different data analyses have been presented that demonstrate convincingly that the expansion gap exists to values of $\delta \approx 1.6 \times 10^{-4}$. This is true for both analyses in which the final temperature of test is 40°C and for which the data error correlations are expected to be the greatest. A simple analysis in which plots of $\log|\delta|$ vs. t (slope $\propto \tau_{eff}$) are made, shows very strongly that there is a systematic trend in the slopes with increasing initial temperature in the experiments. This supports the original contention of Kovacs that there exists an expansion gap or apparent τ_{eff}-paradox.

In an analysis of the data in which an estimate was made of the actual correlation of the errors in the experiments the results are unambiguous for the experiments with a final temperaure of 40°C. This is undoubtedly the best data set for two reasons. It is very extensive and the time-scale of the experiments was such that the manual reading procedures resulted in data being taken at time intervals such that the error correlation remained high. In contrast, the data at 35°C is far less convincing even though it, too, is an extensive data set. One reason for this is that the times required for the experiments were such that the manual reading procedures lead to long time intervals between data points such that the error correlations became very weak. The data at 37.5°C and 42.5°C are a bit ambiguous, with the former supporting the expansion gap and the latter not doing so at the 95% confidence level. However, neither of these data sets was very extensive.

The conclusions drawn here disagree with the argument of Struik [19] who uses a propagation of errors argument in which the uncertainties are assumed to be uncorrelated. Importantly, his analysis focused on the 40°C data. Our analysis shows a correlation of the error in the data which is, first, not unexpected and, second, sufficient to allow a sophisticated error propagation analysis that includes the correlation of the uncertainties.

An interesting feature of the up-jump curves in $\log|\delta|$ vs. t is that they remain linear for long stretches in time, which may have implications for the development of the constitutive models and their description of the expansion gap visible in the original Kovacs data and the expanded data shown here.

This brings us to the two final points of the paper. First, although the data originally published by Kovacs in 1964 does not in its entirety support the existence of the expansion gap (apparent τ_{eff}-paradox), the analyses presented here show that it definitely exists for the data obtained at a final temperature of 40°C, and has a strong likelihood of being found at the other temperatures if data were taken at closer intervals in time. This is because for data taken at shorter time intervals the errors would be more strongly correlated and there would also result more replicate data which would improve other aspects of the statistics. This being said, then, there is still a need to explain the expansion gap. Earlier we alluded to several possibilities for the explanation. One is the need for better constitutive equations than those of the Tool–Narayanaswamy–Moynihan et al. [11,14,20,21] (TNM) or KAHR models. Rendell et al. [17] and Lustig et al. [8] have suggested such equations. However, it may be that the expansion gap is merely a manifestation of the longest relaxation time processes occurring in the polymer glass. Goldstein and Nakonecznyj [4] first intimated this possibility. More recently Schultheisz and McKenna [18] have explicitly considered this possibility and Struik [19] in his work questioning the expansion gap also seems to suggest such a possibility. Clearly, then, the expansion gap is important and better measurements of its nature and improved models to explain and describe it are needed.

Appendix A. Tables A1–A3 describing Kovacs' experiments and their interpretation

Tables A1–A3

Table A1
Dilatometric experiments on poly(vinyl acetate) performed in the Laboratories of the Centre de Recherches sur les Macromolecules (now Institut Charles Sadron) by Kovacs and co-workers between 1959 and 1981 and analyzed in this work. The first column denotes the nominal final temperature of the *T*-jump experiment. The second column denotes the nominal initial temperature. The third through fifth columns denote the temperature according to the 1950 Sèvres calibration, 1965 Sèvres calibration, or quartz thermometer reading respectively. In instances in which the temperatures are italicized, there is no record in the notebooks of actual reading, only the nominal temperature is given. The final column presents the date of the measurement as day/month/year – followed by the fill number for the dilatometer used in all of these experiments. Where a Fig. number is indicated, it is known that these data were used in the 1964 Kovacs paper and the figure number refers to that reference

Final temp.	Initial temp.	Tleg(1950)	Tleg(1968)	Quartz thermometer	Date of exp – fill #.
42.5°C	40°C	*39.97*°C to *42.50*°C	*39.97*°C to *42.50*°C	—	15/02/60 – 1
42.5°C	35°C	34.97– .99°C to 42.38°C	34.87– .89°C to 42.26°C	—	16/06/60 – 2
40°C	37.5°C	37.47°C to 40°C	37.36°C to 40°C	—	11/01/60 – 1 (Fig. 23)
40°C	37.5°C	*37.5* to *40*°C	*37.5* to *40*°C	—	12/01/60 – 1
40°C	35°C	*35* to *40*°C	*35* to *40*°C	—	11/01/60 – 1 (Fig. 23)
40°C	35°C	34.84–.96°C to 39.95°C	34.74–.86°C to 39.84°C	—	08/01/60 – 1
40°C	35°C	34.94–35.01°C to 39.98°C	34.84–.91°C to 39.87°C	—	01/06/60 – 2
40°C	35°C	34.96–.98°C to 39.99°C	34.86–.88°C to 39.88°C	—	14/06/60 – 2
40°C	35°C	34.90–.93°C to 39.96–.97°C	34.80–.83°C to 39.85–.86°C	—	18/10/62 – 3
40°C	35°C	35.00–.01°C to 40.04–.05°C	34.90–.91°C to 39.93–.94°C	—	06/12/62 – 3
40°C	35°C	35.01°C to 40.00°C	34.86°C to 39.89°C	—	06/12/62 – 3
40°C	35°C	—	—	34.97–.99°C to 39.94–.95°C	24/01/69 – 5
40°C	32.5°C	32.5°C to *40*°C	32.4°C to *40*°C	—	24/12/59 – 1 (Fig. 23)
40°C	32.5°C	32.46°C to *40.05*°C	32.36°C to *40.05*°C	—	06/01/60 – 1
40°C	30°C	29.94–.98°C to 40.00–.01°C	29.84–.88°C to 39.89–.90°C	—	03/01/63 – 3 (Fig. 23)
40°C	30°C	29.95–.98°C to *39.97*°C	29.85–.88°C to *39.97*°C	—	15/02/60 – 1
40°C	25°C (1500 h)	25.00°C to 39.98°C	24.9°C to 39.87°C	—	25/05/60 – 2
40°C'	42.5°C	*42.5*°C to *40.0*°C	—	—	15/02/60 – 1
40°C	50°C	*50.0*°C to *40.0*°C	—	—	11/01/60 – 1
40°C	50°C	—	—	49.99–50.00°C to 39.94°C	23/01/69 – 5
40°C	60°C	60.15–.18°C to *40.0*°C	59.99–60.02°C to *40.0*°C	—	15/02/60 – 1
40°C	60°C	*60.0*°C to *40.0*°C	—	—	17/03/60 – 2
40°C	35°C	—	—	35.00–.02°C to 40.00°C	08/10/80 – 6
40°C	35°C	—	—	35.00°C to 40.00°C	09/10/80 – 6
40°C	35°C	—	—	34.99–35.01°C to 40.00°C	17/10/80 – 6
40°C	35°C	—	—	35.00°C to 40.00°C	22/10/80 – 6
40°C	35°C	—	—	35.00–.01°C to 40.00°C	24/10/80 – 6
40°C	35°C	—	—	34.99–35.01°C to 40.00–.01°C	30/10/80 – 6
40°C	35°C	—	—	34.99–35.01°C to 40.00–.01°C	07/01/81 – 6
40°C	45°C	—	—	44.99–45.00°C to 40.00°C	14/10/80 – 6
40°C	50°C	—	—	49.96°C to 40.00–.02°C	07/10/80 – 6
40°C	60°C	—	—	60.00°C to 40.00°C	16/10/80 – 6
38°C	35°C	34.98°C to 37.95°C	34.88°C to 37.84°C	—	23/06/60 – 2
37.5°C	32.5°C	—	—	32.51–.53°C to 37.52–.54°C	03/06/69 – 5
37.5°C	40°C	*40*°C to 37.46°C	*40*°C to 37.36°C	—	11/01/60 –1
37.5°C	40°C	*40*°C to *37.5*°C	*40*°C to *37.5*°C	—	11/01/60 – 1
37.5°C	40°C	—	—	40.00°C to 37.48–.50°C	08/10/80 – 6
37.5°C	35°C	—	—	35.00°C to 37.50°C	13/04/81 – 6
37.5°C	35°C	—	—	35.00°C to 37.50°C	14/04/81 – 6
37.5°C	32.5°C	—	—	32.48–.50°C to 37.47–.49°C	27/04/81 – 6
37°C	35°C	34.97–.99°C to 36.95–37.01°C	34.87–.89°C to 36.85–.91°C	—	25/06/60 – 2
35°C	32.5°C	32.49–.52°C to 34.91–.94°C	32.39–.42°C to 34.81–.84°C	—	13/06/63 – 4 (Fig. 23)

Table A1 (continued)

Final temp.	Initial temp.	Tleg(1950)	Tleg(1968)	Quartz thermometer	Date of exp – fill #.
35°C	30°C	29.95–.97°C to 35°C	29.85–.87°C to 35°C	—	04/12/62 – 3 (Fig. 23)
35°C	37°C	36.96–37.02°C to 34.97°C	36.85–.91°C to 34.87°C	—	27/06/60 – 2 (Fig. 23)
35°C	40°C	40.04–.05°C to 35°C	39.93–.94°C to 35°C	—	06/12/62 – 3 (Fig. 23)
35°C	40°C	40.03°C to 34.87–.89°C	39.92°C to 34.77–.78°C	—	30/01/63 – 3 (Fig. 23)
35°C	40°C	40.05°C to 34.93–.96°C	40.05°C to 34.83–.86°C	—	07/01/60 – 1
35°C	40°C	40°C to 34.84–.96°C	40°C to 34.74–.86°C	—	08/01/60 – 1
35°C	40°C	39.98°C to 34.96–.98°C	39.87°C to 34.86–.88°C	—	13/06/60 – 2
35°C	40°C	39.99°C to 34.97–.99°C	39.88°C to 34.87–.89°C	—	14/06/60 – 2
35°C	40°C	39.95–.96°C to 34.93°C	39.84–.85°C to 34.83°C	—	17/10/62 – 3
35°C	40°C	—	—	39.94°C to 34.97–.99°C	23/01/69 – 5
35°C	50°C	50°C to 34.96°C	50°C to 34.86°C	—	21/06/60 – 2 (Fig. 23)
35°C	32.5°C	—	—	32.48–.50°C to 35.00°C	21/10/80 – 6
35°C	30°C	—	—	29.98–30.02°C to 35.00°C	22/12/80 – 6
35°C	37.5°C	—	—	37.48–.50°C to 35.00°C	08/10/80 – 6
35°C	37.5°C	—	—	37.48°C to 35.00°C	15/10/80 – 6
35°C	40°C	—	—	40.00–.01°C to 34.99–35.01°C	07/10/80 – 6
35°C	40°C	—	—	40.00°C to 34.99–35.00°C	09/10/80 – 6
35°C	40°C	—	—	40.00°C to 35.00°C	13/04/81 – 6
35°C	50°C	—	—	50.00°C to 35.00°C	10/10/80 – 6
35°C	60°C	—	—	60.00°C to 35.00°C	13/10/80 – 6
35°C	42.5°C	42.38°C to 34.97°C	42.26°C to 34.87°C	—	16/06/60 – 2
35°C	45°C	44.98°C to 34.96–97°C	44.85°C to 34.86–87°C	—	20/06/60 – 2
35°C	41°C	40.98°C to 34.98°C	40.87°C to 34.88°C	—	22/06/60 – 2
35°C	39°C	38.99°C to 34.98°C	38.88°C to 34.88°C	—	22/06/60 – 2
35°C	38°C	37.95°C to 34.97–.99°C	37.84°C to 34.87–.89°C	—	24/06/60 – 2
35°C	38°C	37.99°C to 34.97–.99°C	37.88°C to 34.87–.89°C	—	24/06/60 – 2
35°C	37°C	36.95–37.01°C to 34.97°C	36.85–.91°C to 34.87°C	—	27/06/60 – 2
35°C	36°C	36°C to 34.98°C	36°C to 34.88°C	—	05/07/60 – 2
35°C	33.75°C	—	—	33.75°C to 35.00°C	31/03/80 – 6
35°C	36.2°C	—	—	36.18°C to 35.00°C	01/04/81 – 6
35°C	31.2°C	—	—	31.19–.20°C to 35.00°C	12/06/81 – 6
35°C	34.36°C	—	—	34.35–36°C to 35.00°C	19/06/81 – 6
35°C	35.6°C	—	—	35.62–.63°C to 35.00°C	29/06/81 – 6
32.5°C	40°C	39.97°C to 32.49–.52°C	39.86°C to 32.39–.42°C	—	07/06/63 – 4
32.5°C	40°C	—	—	40.00°C to 32.49–.50°C	17/10/80 – 6
32.5°C	40°C	—	—	40.00°C to 32.48–.50°C	16/04/81 – 6
32.5°C	37.5°C	—	—	37.49–.52°C to 32.49–.53°C	16/05/69 – 5
32.5°C	37.5°C	—	—	37.52–.54°C to 32.50–.53°C	04/06/69 – 5
32.5°C	37.5°C	—	—	37.52°C to 32.52–.53°C	10/06/69 – 5
32.5°C	37.5°C	—	—	37.52°C to 32.52–.53°C	17/06/69 – 5
30°C	60°C	59.9°C to 29.97–.98°C	59.9°C to 29.87–.88°C	—	08/03/60 – 1 (Fig. 23)
30°C	40°C	39.90–40.00°C to 29.93°C	39.79–39.89°C to 29.83°C	—	15/12/59 – 1
30°C	40°C	40.0°C to 29.92–.98°C	40.0°C to 29.82–.88°C	—	13/01/60 – 1
30°C	40°C	39.98°C to 29.94–.99°C	39.87°C to 29.84–.89°C	—	10/03/60 – 1
30°C	40°C	39.98°C to 29.92–.98°C	39.87°C to 29.82–.88°C	—	16/10/62 – 3
30°C	40C	39.96°C to 29.93–.98°C	39.85°C to 29.83–.88°C	—	18/10/62 – 3
30°C	40°C	40.00–.01°C to 29.96–.98°C	39.89–.90°C to 29.86–.88°C	—	03/01/63 – 3 (Fig. 23)

Table A1 (*continued*)

Final temp.	Initial temp.	Tleg(1950)	Tleg(1968)	Quartz thermometer	Date of exp – fill #.
30°C	40°C	—	—	39.94–.95°C to 30.02–.08°C	24/01/69 – 5
30°C	37.5°C	*37.48*°C to 29.98°C	*37.48*°C to 29.88°C	—	24/02/60 – 1 (Fig. 23)
30°C	35°C	34.97°C to 29.95–.99°C	34.87°C to 29.85–.89°C	—	26/02/60 – 1 (Fig. 23)
30°C	35°C	34.87–.89°C to 29.93–.95°C	34.77–.79°C to 29.83–.85°C	—	31/01/63 – 3
30°C	32.5°C	32.36°C to 29.96–30.00°C	32.26°C to 29.86–.90°C	—	04/03/60 – 1 (Fig. 23)
30°C	40°C	—	—	40.00°C to 30.00–.01°C	16/10/80 – 6
30°C	40°C	—	—	40.00°C to 29.99–30.01°C	22/10/80 – 6
30°C	40°C	—	—	40.00°C to 29.98–30.01°C	24/10/80 – 6
30°C	40°C	—	—	40.00–.01°C to 29.99–30.01°C	30/10/80 – 6
30°C	40°C	—	—	40.00°C to 29.98–30.02°C	05/11/80 – 6
30°C	40°C	—	—	40.00°C to 29.99–30.01°C	06/01/81 – 6
30°C	40°C	—	—	40.00°C to 29.99–30.01°C	07/01/81 – 6
30°C	40°C	—	—	40.00°C to 29.99 –30.00°C	22/07/81 – 6
30°C	45°C	—	—	45.06°C to 30.31–.32°C	24/10/68 – 5

Table A2
Summary of *T*-jump volume recovery experiments. T_i is the initial (nominal) temperature of the experiment and T_f is the final (nominal) temperature. Numerals represent number of replicate experiments for each experimental condition

T_i				T_f			
	30°C	35°C	37°C	37.5°C	38°C	40°C	42.5°C
25°C						1	
30		2				2	
31.2		1					
32.5	1	2		2		2	
33.75		1					
34.36		1					
35	2		1	2	1	15	1
35.6		1					
36		1					
36.2		1					
37		2					
37.5	1	2				2	
38		2					
39		1					
40	15	11		3		1	
41		1					
42.5		1			1		
45	1	1			1		
50		2				3	
60	1	1				3	

Table A3
Limiting values of $\log|\delta|$ and $|\delta|$ for which τ_{eff} values are different between two different temperature jumps from T_i to T_f. NA implies curves were different for all values of δ. Ind implies that the data were indistinguishable over the full range of the experiments. The qualifying column that tells "Same" or "Different" is our choice to set $\log|\delta| \leq -3.8$ or $|\delta|$ 1.6×10^{-4} as the limit at which τ_{eff} values from two different experiments are different at the 95% confidence level

Compare T_i to T_f	with T_i to T_f	Log$|\delta|$	$|\delta|$	"Same" or "Different"
$T_f = 30°C$				
32.5°C to 30°C	35°C to 30°C	-3.1	7.9×10^{-4}	Same
32.5°C to 30°C	37.5°C to 30°C	-3.1	7.9×10^{-4}	Same
32.5°C to 30°C	40°C to 30°C	No overlap	No overlap	Insufficient data
32.5°C to 30°C	45°C to 30°C	NA	NA	Different
32.5°C to 30°C	60°C to 30°C	-3.1	7.9×10^{-4}	Same
35°C to 30°C	37.5°C to 30°C	-2.9	1.3×10^{-3}	Same
35°C to 30°C	40°C to 30°C	Overlap to -2.8	Overlap to 1.6×10^{-3}	Insufficient data
35°C to 30°C	45°C to 30°C	Data different to -3.2	Data different to 6.3×10^{-4}	Insufficient data
35°C to 30°C	60°C to 30°C	-2.9	1.3×10^{-3}	Same
37.5°C to 30°C	40°C to 30°C	Overlap to -2.8	Overlap to 1.6×10^{-3}	Insufficient data
37.5°C to 30°C	45°C to 30°C	-3.0	1.0×10^{-3}	Same
37.5°C to 30°C	60°C to 30°C	-2.8	1.6×10^{-3}	Same
40°C to 30°C	45°C to 30°C	Overlap to -2.8	Overlap to 1.6×10^{-3}	Insufficient data
40°C to 30°C	60°C to 30°C	-2.6	2.5×10^{-3}	Same
45°C to 30°C	60°C to 30°C	-2.7	2.0×10^{-3}	Same
$T_f = 35°C$				
30°C to 35°C	31.2°C to 35°C	-2.8	1.6×10^{-3}	Same
30°C to 35°C	32.5°C to 35°C	-3.3	5.0×10^{-4}	Same
30°C to 35°C	33.75°C to 35°C	-3.4	4.0×10^{-4}	Same
30°C to 35°C	34.36°C to 35°C	-3.6	2.5×10^{-4}	Same
30°C to 35°C	37.5°C to 35°C	-3.8	1.6×10^{-4}	Different
30°C to 35°C	38°C to 35°C	NA	NA	Insufficient data
30°C to 35°C	39°C to 35°C	-3.6	2.5×10^{-4}	Same
30°C to 35°C	40°C to 35°C	-3.7	2.0×10^{-4}	Same
30°C to 35°C	41°C to 35°C	-3.6	2.5×10^{-4}	Same
30°C to 35°C	42.5°C to 35°C	-3.6	2.5×10^{-4}	Same
30°C to 35°C	45°C to 35°C	-3.7	2.0×10^{-4}	Same
30°C to 35°C	50°C to 35°C	-3.6	2.5×10^{-4}	Same
30°C to 35°C	60°C to 35°C	-3.6	2.5×10^{-4}	Same
31.2°C to 35°C	32.5°C to 35°C	-3.2	6.3×10^{-4}	Same
31.2°C to 35°C	33.75°C to 35°C	-3.4	4.0×10^{-4}	Same
31.2°C to 35°C	34.36°C to 35°C	-3.6	2.5×10^{-4}	Same
31.2°C to 35°C	37.5°C to 35°C	-3.7	2.0×10^{-4}	Same
31.2°C to 35°C	38°C to 35°C	NA	NA	Insufficient data
31.2°C to 35°C	39°C to 35°C	-3.6	2.5×10^{-4}	Same
31.2°C to 35°C	40°C to 35°C	-3.6	2.5×10^{-4}	Same
31.2°C to 35°C	41°C to 35°C	-3.5	3.2×10^{-4}	Same
31.2°C to 35°C	42.5°C to 35°C	-3.6	2.5×10^{-4}	Same
31.2°C to 35°C	45°C to 35°C	-3.6	2.5×10^{-4}	Same
31.2°C to 35°C	50°C to 35°C	-3.6	2.5×10^{-4}	Same
31.2°C to 35°C	60°C to 35°C	-3.5	3.2×10^{-4}	Same
32.5°C to 35°C	33.75°C to 35°C	-3.3	5.0×10^{-4}	Same
32.5°C to 35°C	34.36°C to 35°C	-3.5	3.2×10^{-4}	Same
32.5°C to 35°C	37.5°C to 35°C	-3.5	3.2×10^{-4}	Same
32.5°C to 35°C	38°C to 35°C	-3.4	4.0×10^{-4}	Same
32.5°C to 35°C	39°C to 35°C	-3.4	4.0×10^{-4}	Same
32.5°C to 35°C	40°C to 35°C	-3.4	4.0×10^{-4}	Same
32.5°C to 35°C	41°C to 35°C	-3.3	5.0×10^{-4}	Same
32.5°C to 35°C	42.5°C to 35°C	-3.3	5.0×10^{-4}	Same
32.5°C to 35°C	45°C to 35°C	-3.3	5.0×10^{-4}	Same
32.5°C to 35°C	50°C to 35°C	-3.3	5.0×10^{-4}	Same
32.5°C to 35°C	60°C to 35°C	-3.4	4.0×10^{-4}	Same

Table A3 (*continued*)

Compare T_i to T_f	with T_i to T_f	Log$|\delta|$	$|\delta|$	"Same" or "Different"
$T_f = 35°C$				
33.75°C to 35°C	34.36°C to 35°C	− 3.3	5.0×10^{-4}	Same
33.75°C to 35°C	37.5°C to 35°C	Ind	Ind	Same
33.75°C to 35°C	38°C to 35°C	Ind	Ind	Same
33.75°C to 35°C	39°C to 35°C	Ind	Ind	Same
33.75°C to 35°C	40°C to 35°C	Ind	Ind	Same
33.75°C to 35°C	41°C to 35°C	Ind	Ind	Same
33.75°C to 35°C	42.5°C to 35°C	Ind	Ind	Same
$T_f = 35°C$				
33.75°C to 35°C	45°C to 35°C	Ind	Ind	Same
33.75°C to 35°C	50°C to 35°C	Ind	Ind	Same
33.75°C to 35°C	60°C to 35°C	Ind	Ind	Same
34.36°C to 35°C	37.5°C to 35°C	− 3.5	3.2×10^{-4}	Same
34.36°C to 35°C	38°C to 35°C	− 3.5	3.2×10^{-4}	Same
34.36°C to 35°C	39°C to 35°C	− 3.5	3.2×10^{-4}	Same
34.36°C to 35°C	40°C to 35°C	− 3.5	3.2×10^{-4}	Same
34.36°C to 35°C	41°C to 35°C	− 3.5	3.2×10^{-4}	Same
34.36°C to 35°C	42.5°C to 35°C	− 3.5	3.2×10^{-4}	Same
34.36°C to 35°C	45°C to 35°C	− 3.5	3.2×10^{-4}	Same
34.36°C to 35°C	50°C to 35°C	− 3.5	3.2×10^{-4}	Same
34.36°C to 35°C	60°C to 35°C	− 3.5	3.2×10^{-4}	Same
37.5°C to 35°C	38°C to 35°C	− 3.6	2.5×10^{-4}	Same
37.5°C to 35°C	39°C to 35°C	− 3.7	2.0×10^{-4}	Same
37.5°C to 35°C	40°C to 35°C	− 3.6	2.5×10^{-4}	Same
37.5°C to 35°C	41°C to 35°C	− 3.6	2.5×10^{-4}	Same
37.5°C to 35°C	42.5°C to 35°C	− 3.6	2.5×10^{-4}	Same
37.5°C to 35°C	45°C to 35°C	− 3.6	2.5×10^{-4}	Same
37.5°C to 35°C	50°C to 35°C	− 3.7	2.0×10^{-4}	Same
37.5°C to 35°C	60°C to 35°C	− 3.5	3.2×10^{-4}	Same
38°C to 35°C	39°C to 35°C	− 3.6	2.5×10^{-4}	Same
38°C to 35°C	40°C to 35°C	− 3.3	5.0×10^{-4}	Same
38°C to 35°C	41°C to 35°C	− 3.7	2.0×10^{-4}	Same
38°C to 35°C	42.5°C to 35°C	− 3.5	3.2×10^{-4}	Same
38°C to 35°C	45°C to 35°C	− 3.5	3.2×10^{-4}	Same
38°C to 35°C	50°C to 35°C	NA	NA	Insufficient data
38°C to 35°C	60°C to 35°C	− 3.4	4.0×10^{-4}	Same
39°C to 35°C	40°C to 35°C	− 3.2	6.3×10^{-4}	Same
39°C to 35°C	41°C to 35°C	− 3.4	4.0×10^{-4}	Same
39°C to 35°C	42.5°C to 35°C	− 3.3	5.0×10^{-4}	Same
39°C to 35°C	45°C to 35°C	− 3.3	5.0×10^{-4}	Same
39°C to 35°C	50°C to 35°C	− 3.4	4.0×10^{-4}	Same
39°C to 35°C	60°C to 35°C	− 3.2	6.3×10^{-4}	Same
40°C to 35°C	41°C to 35°C	− 3.5	3.2×10^{-4}	Same
40°C to 35°C	42.5°C to 35°C	− 3.5	3.2×10^{-4}	Same
40°C to 35°C	45°C to 35°C	− 3.5	3.2×10^{-4}	Same
40°C to 35°C	50°C to 35°C	− 3.7	2.0×10^{-4}	Same
40°C to 35°C	60°C to 35°C	− 3.4	4.0×10^{-4}	Same
41°C to 35°C	42.5°C to 35°C	− 3.1	7.9×10^{-4}	Same
41°C to 35°C	45°C to 35°C	− 3.1	7.9×10^{-4}	Same
41°C to 35°C	50°C to 35°C	− 3.1	7.9×10^{-4}	Same
41°C to 35°C	60°C to 35°C	− 3.2	6.3×10^{-4}	Same
42.5°C to 35°C	45°C to 35°C	− 3.0	1.0×10^{-3}	Same
42.5°C to 35°C	50°C to 35°C	− 2.9	1.3×10^{-3}	Same
42.5°C to 35°C	60°C to 35°C	− 3.2	6.3×10^{-4}	Same
45°C to 35°C	50°C to 35°C	− 2.9	1.3×10^{-3}	Same
45°C to 35°C	60°C to 35°C	− 3.3	5.0×10^{-4}	Same
50°C to 35°C	60°C to 35°C	− 3.3	5.0×10^{-3}	Same
$T_f = 40°C$				
25°C to 40°C	30°C to 40°C	− 2.6	2.5×10^{-3}	Same
25°C to 40°C	32.5°C to 40°C	− 3.5	3.2×10^{-4}	Same
25°C to 40°C	35°C to 40°C	− 3.9	1.3×10^{-4}	Different
25°C to 40°C	37.5°C to 40°C	− 4.1	7.9×10^{-5}	Different

Table A3 (*continued*)

Compare T_i to T_f	with T_i to T_f	$\mathrm{Log}|\delta|$	$|\delta|$	"Same" or "Different"
$T_f = 34°C$				
25°C to 40°C	42.5°C to 40°C	− 4.2	6.3×10^{-5}	Different
25°C to 40°C	45°C to 40°C	− 4.1	7.9×10^{-5}	Different
25°C to 40°C	50°C to 40°C	− 4.1	7.9×10^{-5}	Different
25°C to 40°C	60°C to 40°C	− 4.1	7.9×10^{-5}	Different
30°C to 40°C	32.5°C to 40°C	− 3.2	6.3×10^{-4}	Same
30°C to 40°C	35°C to 40°C	− 3.6	2.5×10^{-4}	Same
30°C to 40°C	37.5°C to 40°C	− 4.1	7.9×10^{-5}	Different
30°C to 40°C	42.5°C to 40°C	− 4.2	6.3×10^{-5}	Different
30°C to 40°C	45°C to 40°C	− 4.1	7.9×10^{-5}	Different
30°C to 40°C	50°C to 40°C	− 4.1	7.9×10^{-5}	Different
30°C to 40°C	60°C to 40°C	− 4.1	7.9×10^{-5}	Different
32.5°C to 40°C	35°C to 40°C	− 3.5	3.2×10^{-4}	Same
32.5°C to 40°C	37.5°C to 40°C	− 3.7	2.0×10^{-4}	Same
32.5°C to 40°C	42.5°C to 40°C	− 3.9	1.3×10^{-4}	Different
32.5°C to 40°C	45°C to 40°C	− 3.9	1.3×10^{-4}	Different
32.5°C to 40°C	50°C to 40°C	− 3.9	1.3×10^{-4}	Different
32.5°C to 40°C	60°C to 40°C	− 3.9	1.3×10^{-4}	Different
35°C to 40°C	37.5°C to 40°C	− 4.2	6.3×10^{-5}	Different
35°C to 40°C	42.5°C to 40°C	− 4.3	5.0×10^{-5}	Different
35°C to 40°C	45°C to 40°C	− 4.2	6.3×10^{-5}	Different
35°C to 40°C	50°C to 40°C	− 4.3	5.0×10^{-5}	Different
35°C to 40°C	60°C to 40°C	− 4.2	6.3×10^{-5}	Different
37.5°C to 40°C	42.5°C to 40°C	− 3.9	1.3×10^{-4}	Different
37.5°C to 40°C	45°C to 40°C	− 3.8	1.6×10^{-4}	Different
37.5°C to 40°C	50°C to 40°C	− 3.8	1.6×10^{-4}	Different
37.5°C to 40°C	60°C to 40°C	− 3.9	1.3×10^{-4}	Different
42.5°C to 40°C	45°C to 40°C	− 3.5	3.2×10^{-4}	Same
42.5°C to 40°C	50°C to 40°C	− 3.5	3.2×10^{-4}	Same
42.5°C to 40°C	60°C to 40°C	− 3.6	2.5×10^{-4}	Same
45°C to 40°C	50°C to 40°C	− 3.4	4.0×10^{-4}	Same
45°C to 40°C	60°C to 40°C	− 3.6	2.5×10^{-4}	Same
50°C to 40°C	60°C to 40°C	− 3.6	2.5×10^{-4}	Same
$T_f = 37.5°C$				
32.5°C to 37.5°C	35°C to 37.5°C	− 3.5	3.2×10^{-4}	Same
32.5°C to 37.5°C	40°C to 37.5°C	− 3.9	1.3×10^{-4}	Different
35°C to 37.5°C	40°C to 37.5°C	− 3.8	1.6×10^{-4}	Different
$T_f = 42.5°C$				
35°C to 42.5°C	40°C to 42.5°C	− 3.6	2.5×10^{-4}	Same

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