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Master Surfaces of Viscoelastic Functions in the Reciprocal Temperature-Frequency Space

1. Basic Considerations

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SUMMARY

Starting from EYRING's transition state theory it is demonstrated for systems obeying the superposition principle that the frequency shift factors of isotherm mastercurves of the viscoelastic functions as well as the temperature shift factors of the isochrone ones are unequivocally interrelated with the apparent activation energy of flow. The method for the evaluation of the activation energy from viscoelastic data is discussed, considering the moduli surfaces in the reciprocal temperature - frequency space. Experimental data prove the reliability of the approach. It is demonstrated that it is much more suitable to construct mastercurves as well as master surfaces in this way, because it is not necessary to apply measurements at low frequencies, which are unavoidable when the curves are constructed by empirical shift in the usual way.

SCOPE

Composite curves of viscoelastic functions generally are constructed by shifting the isotherm data empirically along the frequency axis. SCHNEIDER and CANTOW (1) have shown recently that those curves may be obtained too on the basis of isochrones, by a shift along the 1/T axis. This shift along 1/T is equivalent to the displacement of the isochrones of the dynamic viscosity along the slope of zero shear apparent activation energy of flow. It has been demonstrated that both types of shift are related to this zero shear activation energy of flow, so that an unique shift mechanism is effective in both cases. Isochrone mastercurves are favourable for studies on polymer blends particularly, because the problematical choice of reference temperatures is circumvented.

The approach discussed in the following has been motivated by three demands

- to determine activation energies in the frequency domain of non-Newtonian flow on macroscopic scale of linear viscoelastic bodies,
- to substitute the empirical shift procedures by theoretically supported ones
- to minimize the time required to realize experimentally reliable reduced data.

INTRODUCTION

Relaxation experiments on linear viscoelastic bodies may be described by the relaxation modulus

$$G(t) = \sigma(t)/\gamma_0 = \varphi(t) + G_\infty \qquad (1)$$

This equation is related to shear experiments, and it presents the relation between G(t) and relaxation stress, $\sigma(t)$, and shear, γ_0, resp., relaxation function, $\varphi(t)$, and equilibrium modulus, G_∞.

For dynamical relaxation experiments the following relationships are valid

$$\sigma(t)/\gamma(t) = G^* = G_\infty + G' + i\,G'' \qquad (2) \qquad\qquad G''/G' = \mathrm{tg}\,\delta \qquad (3)$$

$$\sigma(t)/[d\gamma(t)/dt] = \eta = G''/\omega \quad , \qquad (4)$$

with G^* the complex modulus, G' the storage modulus, G'' the loss modulus, η the dynamic viscosity, with $\mathrm{tg}\ \delta$ the loss factor and ω the angular velocity. Essentially, all these viscoelastic magnitudes are describing the sum of identical relaxation processes, which are caused by stressing mechanically a linear viscoelastic body. For macromolecules the generalized MAXWELL model is describing best these relaxation processes. The differing relaxation times θ for chain segments of different lengths are taken into account by the relaxation spectrum $F(\theta)$. Thus, with $H(\theta) = \theta F(\theta)$, the viscoelastic quantities may be written in the form

$$\varphi(t) = \int_{-\infty}^{\infty} H(\theta)\exp(-t/\theta)\,d\ln\theta \quad (5) \qquad G'(\omega) = \int_{-\infty}^{\infty} H(\theta)(\omega\theta)^2/[1+(\omega\theta)^2]\,d\ln\theta \quad (6)$$

$$G''(\omega) = \int_{-\infty}^{\infty} H(\theta)\,\omega\theta/[1+(\omega\theta)^2]\,d\ln\theta \quad (7) \qquad \eta = \int_{-\infty}^{\infty} \theta H(\theta)\,/\,[1+(\omega\theta)^2]\,d\ln\theta\,. \quad (8)$$

By $H(\theta)$ all viscoelastic properties of a body are determined. Its temperature dependence has to be known in order to derive the temperature dependence of the viscoelastic quantities. As a consequence of the superposition principle all relaxation times of a spectrum exhibit identical temperature dependence . It has to be noted that the overall viscosity η (Equ. 8) as well as the viscosity of the individual relaxation processes are assumed to be independent on strain and shear, resp. Thus Newtonian flow is assumed for the molecular flow processes although macroscopically no Newtonian flow is exhibited by the linear viscoelastic body. Newtonian flow is assumed at molecular scale of the viscoelastic body, which is subjected to deformation processes.

THEORETICAL BASIS

Temperature dependence of relaxation time and of dynamic viscosity

According to Equ. (8) η gets time independent for $\omega \to 0$

$$\lim_{\omega \to 0} \eta = \eta_0 \int_{-\infty}^{\infty} \theta(T)\,H[\theta(T)]\,d\ln\theta \quad . \quad (9)$$

For the Newtonian flow the ARRHENIUS equation is valid

$$\eta_0 = B\exp(E/RT) \quad . \quad (10)$$

As a consequence of the validity of the superposition principle $F(\theta)$ is directly proportional to the absolute temperature necessarily. Consequently, the exponential term has to be embodied in $\theta(T)$. Thus Equ.(9) may be written as Equ.(11), whereby for an individual relaxation process P of the spectrum, $\theta_P(T) = B'_P \exp\ (E/RT)$, is valid. B' will be related to the relaxation times of the processes, i. e. $B'[\theta(T)]$.

$$\eta_0 = \int_{-\infty}^{\infty} B'\,[\theta(T)]\exp(E/RT)H[\theta(T)]\,d\ln\theta = \exp(E/RT)\int_{-\infty}^{\infty} B'\,[\theta(T)]H[\theta(T)]\,d\ln\theta \quad , \quad (11)$$

Equ. (8) may be transformed also

$$\eta = \exp(E/RT)\int_{-\infty}^{\infty} B'\,[\theta(T)]\,H[\theta(T)]\,/\,\{1+[\omega\theta(T)]^2\}\,d\ln\theta = P(\omega,T)\,\exp(E/RT) \quad . \quad (12)$$

Equ. (12) differs from the ARRHENIUS equation only by the fact that the preexponential factor is also a function of time, for dynamical measurements a function of frequency.

This equation can be obtained too by applying the formalism of rate processes to the displacement events in relaxation processes. Assuming the zero order kinetics characteristic for the transport processes the rate equation is given by

$$(A \xrightarrow{k} B) \quad ; \quad d(B)/dt = k \quad ; \quad t = (B)\,k^{-1} \quad . \quad (13)$$

The rate constant may be expressed by the apparent activation parameters introduced by EYRING,

$\Delta^{\#}S$ and $\Delta^{\#}H$ 2) 3). Substituting the entropic term by the factor $B^* = (h/k_BT)\exp(-\Delta S^{\#}/R)$, the temperature dependence of the relaxation time may be written

$$\theta(T) = t(T) = (B)\,B^*\exp(\Delta H^{\#}/RT) \quad . \qquad (14)$$

In comparison with $\exp(\Delta H^{\#}/RT)$, B^* changes only slowly with temperature. Thus it may be assumed constant when evaluating measurements over a limited temperature range. $\Delta H^{\#}$ (indicated as E mostly) is the (apparent) activation energy of the process, of the relaxation processes in our case. Consequently, $(B) = Z(\theta)$ will be the number of elementary relaxations per unit volume, which belong to relaxation process P with the relaxation time θ. Introducing this relaxation time into Equ. (12) Equ. (15) is obtained, which gives the same evidence like Equ. (12)

$$\eta = B^*\exp(E/RT)\int_{-\infty}^{\infty} Z[\theta(T)]H[\theta(T)] / \{1+[\omega\theta(T)]^2\}\,d\ln\theta = P'(\omega,T)\,B^*\exp(E/RT) \quad . \qquad (15)$$

Temperature dependence of relaxation time spectrum and of shift factors

The viscoelastic properties depend on the relaxation time spectrum as well as on a function depending on the frequency of measurement. The relations for the viscoelastic magnitudes as functions of the logarithmic relaxation time spectrum are

$$G'(\omega,T) = \int_{-\infty}^{\infty} H[\theta(T)]\,[\omega\theta(T)]^2 / \{1+[\omega\theta(T)]^2\}\,d\ln\theta \qquad \text{Storage modulus} \qquad (16)$$

$$G''(\omega,T) = \int_{-\infty}^{\infty} H[\theta(T)]\,[\omega\theta(T)] / \{1+[\omega\theta(T)]^2\}\,d\ln\theta \qquad \text{Loss modulus} \qquad (17)$$

$$\eta(\omega,T) = \int_{-\infty}^{\infty} \theta(T)\,H[\theta(T)] / \{1+[\omega\theta(T)]^2\}\,d\ln\theta \qquad \text{Dynamic viscosity} \quad . \qquad (18)$$

From the frequency functions for G' and η (Figure 1) the following equations result

$$I' = \int_{-\infty}^{\infty} (\omega\theta)^2 / [1+(\omega\theta)^2]\,d\ln(\omega\theta) \qquad (19)$$

$$II' = \int_{-\infty}^{\infty} 1 / [1+(\omega\theta)^2]\,d\ln(\omega\theta) \qquad (20)$$

$$I' + II' = \int_{-\infty}^{\infty} d\ln(\omega\theta) \quad . \qquad (21)$$

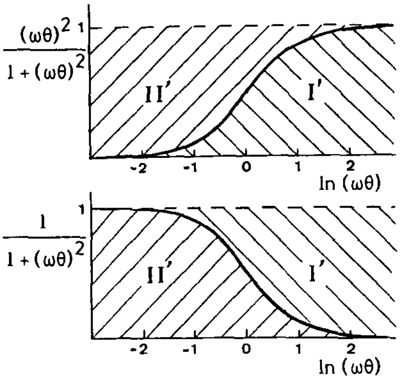


Figure 1: Frequency functions of G' and η versus ln(ωθ)

Applying these findings to the logarihmic relaxation spectrum (Figure 2), the latter may be splitted into a relaxed part (II) and an unrelaxed one (I). These parts are presented in integral form as areas as used in the functions of viscoelastic quantities. Area II enters in the viscosity and the loss modulus, whereas the storage modulus results from area I (Figure 2).

The relaxation time spectra b and c in Fig. 2 are reduced to temperature T_1 via temperature and density correction

$$H'[\theta(T_2)] = H[\theta(T_2)]\,T_1\rho_1 / T_2\rho_2 \qquad H'[\theta(T_3)] = H[\theta(T_3)]\,T_1\rho_1 / T_3\rho_3 \quad .$$

The ratios of the partial areas to the total frequency independent area are determined by the relative position of the frequency of measurement to the relaxation times of the spectrum. $[\ln(1/\omega_1) - \ln\theta_P]$ consequently is a function of the frequency at constant temperature according to

$$I = \int_{-\infty}^{\infty} H'[\theta(T)]\,[\omega_1\theta(T)]^2 / \{1+[\omega_1\theta(T)]^2\}\,d\ln\theta \qquad (22)$$

$$II = \int_{-\infty}^{\infty} H'[\theta(T)] / \{1+[\omega_1\theta(T)]^2\}\,d\ln\theta \quad (23) \qquad I + II = \int_{-\infty}^{\infty} H'[\theta(T)]\,d\ln\theta \quad . \quad (24)$$

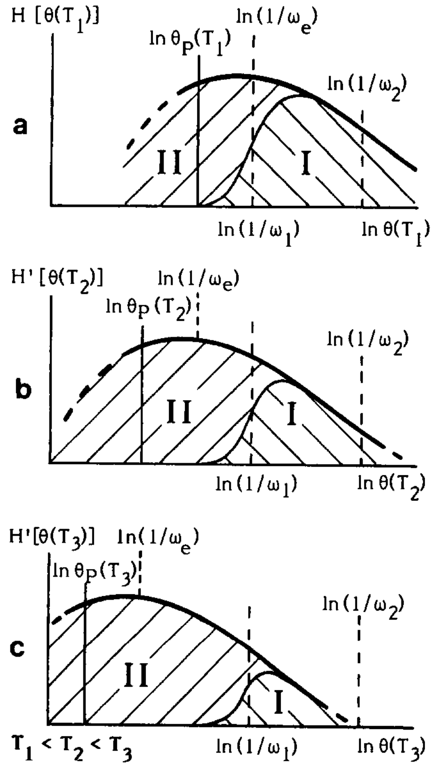


Figure 2: Split of the logarithmic relaxation spectrum into (II) relaxed and (I) unrelaxed part

The Figures show, how due to the temperature dependent shift of the relaxation spectrum a constant frequency of measurement, ω_1, changes its relative position to the relaxation times of the spectrum, implying synchronously a change of the areas I and II, of the loss and of the storage modulus. Supposing now the frequency of measurement, ω_2, one may assume for case c that the area II becomes equal the total area and will maintain that value at smaller frequencies and higher temperatures. This situation coincides to macroscopic Newtonian flow.

The applicability of the superposition priciple, which is valid for most macromolecular compounds, is the actual proof that all relaxation times of a spectrum exhibit identical temperature dependences. Consequently, the reduced spectrum, $H'[\theta_p(T)]$, in the form $H'[\theta_p(T) - \theta(T)]$, is a function, which is independent on temperature. Because it has to be related to an absolute value, $\theta(T) = 0$, due to the temperature dependences of the relaxation times, a horizontal shift of $H'[\theta(T)]$ by a quantity $\ln a_T$ along the logarithmic time axis will result.

$$\{\ln(1/\omega_1) - \ln[\theta_p T_2)]\} - \{\ln(1/\omega_1) - \ln[\theta_p(T_1)]\} = \ln[\theta_p(T_2)] - \ln[\theta_p(T_1)] = -\ln a_T \quad . \quad (25)$$

If asking for the frequencies at which identical partial areas, i.e. moduli, are obtained irrespective of the temperatures of the measurement, one concludes that these frequencies ω_e take a temperature independent fixed position relatively to shifting relaxation times of the spectrum. Thus Equ. (25) may be extended $\ln(1/\omega_e)_T - \ln[\theta_p(T)] = \text{const}$

$$\ln(1/\omega_1) - \ln(1/\omega_e)_{T_2} = \ln[\theta_p(T_1)] - \ln[\theta_p(T_2)] = -\ln(a_T)_{T_1/T_2} \quad (26)$$

$$\ln(1/\omega_1) - \ln(1/\omega_e)_{T_3} = \ln[\theta_p(T_1)] - \ln[\theta_p(T_3)] = -\ln(a_T)_{T_1/T_3} \quad . \quad (27)$$

These equations demonstrate the relation between relaxation times and shift factor a_T.

Starting with Equ. (14) one may introduce the temperature dependence of a_T (Fig. 3 b)

$$\ln a_T = \ln[\theta_p(T_2) / \theta_p(T_1)] = E/R\,(1/T_2 - 1/T_1) \quad , \quad (28)$$

with E the apparent activation energy of the relaxation processes.

Proceeding from the general conditions, which are required by the superposition principle, the same relationship is derived from the viscosity

$$[G'(\omega_1,T_1)\,T_2\rho_2] / [G'(\omega_e,T_2)\,T_1\rho_1] = [G''(\omega_1,T_1)\,T_2\rho_2] / [G''(\omega_e,T_2)T_1\rho_1] =$$
$$[\eta(\omega_1,T_1)T_2\rho_2] / [\eta(\omega_e,T_2)\,T_1\rho_1]\,\omega_1/\omega_e = 1 \quad . \quad (29)$$

$$\ln(a_T)_{T_1/T_2} = \ln(\omega_1/\omega_e) = \ln\{[\eta(\omega_e,T_2)\,T_1\rho_1] / [\eta(\omega_1,T_1)\,T_2\rho_2]\} =$$
$$\ln\{[P'(\omega_e,T_2)\,B^*\exp(E/RT_2)\,T_1\rho_1] / [P'(\omega_1,T_1)\,B^*\exp(E/RT_1)\,T_2\rho_2]\} \quad . \quad (30)$$

When the considerations concerning Fig. 2 are related to Equ. (15), relation (31) becomes valid, and (30) may be simplified to Equ. (32)

$$P'(\omega_1, T_1) = P'(\omega_e, T_2)\, T_1 \rho_1 / (T_2 \rho_2) \tag{31}$$

$$\ln (a_T)_{T_1/T_2} = \ln(\omega_1/\omega_e) = E/R(1/T_2 - 1/T_1) \quad . \tag{32}$$

The most important conclusions of these reflections may be summarized as follows:

- All statements are based on the validity of EYRING's transition state theory.
- The predicted exponential dependence of the viscosity on the reciprocal temperature is not limited to the Newtonian range of macroscopic deformation.
- The a_T-shift factors are identical for all viscoelastic functions so long as the superposition principle is applicable.
- a_T exhibits exponential dependence on the reciprocal absolute temperature too.
- Knowing $H'(\theta)_{T_0}$, $F'(\theta)_{T_0}$ and $a_T(T)$ all viscoelastic functions are defined within the time and temperature range, where the superposition principle is valid.

It may be noted finally that the free volume theory, which is based on DOOLITTLE's expression [4),

$$\eta = A' \exp (B_0 v_0 / v_f) \tag{33}$$

yields the well known WLF-equation[5) 6) 7)], which applies from T_g to $T_g + 100\,\mathrm{K}$ according to literature

$$\log (\eta / \eta_0) = \log a_T = [C_{1,g}(T - T_g)] / [C_{2,g} + (T - T_g)] \quad . \tag{34}$$

The shift factor is related here with the glass transition temperature as the reference. $C_{1,g}$ and $C_{2,g}$ can be expressed by thermal expansion coefficients and the specific volumes at T_g.

METHOD FOR THE DETERMINATION OF THE ACTIVATION ENERGY OF FLOW

From the theoretical standpoint viscoelastic functions are comparable in their reduced form only (compare Fig. 2). Consequently, any shift of measured curves is justified only after temperature and density correction. However, in many cases correction, especially density correction, is avoidable because of limited accuracy of the measurements.

Equ. (32) supports that a frequency shift is equivalent to a temperature change and, correspondingly, the shift factor a_F can be defined

$$a_F = (1/T_2 - 1/T_1) = (E/R)^{-1} \ln a_T \quad . \tag{35}$$

Consequently isochrone presentation of measured data is fully justified. Isochrone mastercurves for the range of constant activation energy of flow have been performed the first time by SCHNEIDER and CANTOW [1)]. Figure 3 shows the isotherm and the isochrone mastercurves for a poly(dimethylsiloxane), $P_n \sim 10000$, in a spatial presentation. For this polymer the apparent activation energy is constant within the applied temperature range. At a temperature around -70° C partial crystallization occurs, and measurements become not more reproducible. Fig. 3 shows the log G' surface, which is determined by the relaxation time spectrum and by temperature dependence of the relaxation processes. The shape of this surface is characteristic for the viscoelastic body and can be considered as invariant in its reduced form. By changing the temperature of reduction the entire surface is shifted along the Z-axis by the amount $\log(T_2/T_1)$ without changing its shape. The cut of the surface by the isotherm planes yields isotherm mastercurves. It should be pointed out that all isotherm mastercurves originated in this way still have to be reduced to their reference temperature in order to correspond to the usual mastercurves (excepted that with identical reduction and reference temperature). The cut of the isochrone planes by the surface $\log G'$ yields the isochrone mastercurves, all reduced to the same temperature.

By means of the surface in Fig. 3 some reflections may be done. A point $\log[G'(\log \omega_0, 1/T_0)]$ on this surface may be understood as the intersection of an isotherm with an isochrone curve. Figure 4 illustrates this conception.

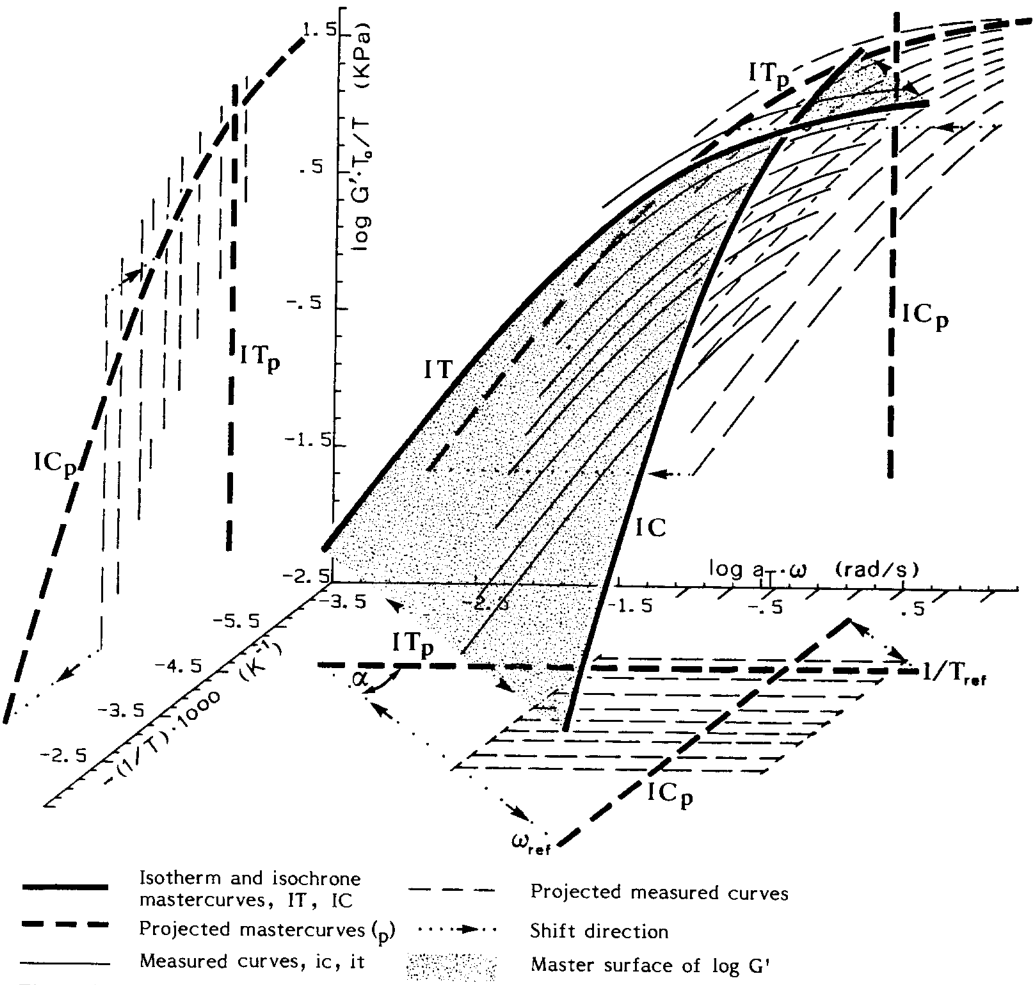


Figure 3: Spatial presentation of the storage modulus of poly(dimethysiloxane), $P_n \sim 10000$, $T_g = 142$ K, apparent activation energy of flow = 16 kJ mole^{-1}, reduced temp. = 273 K

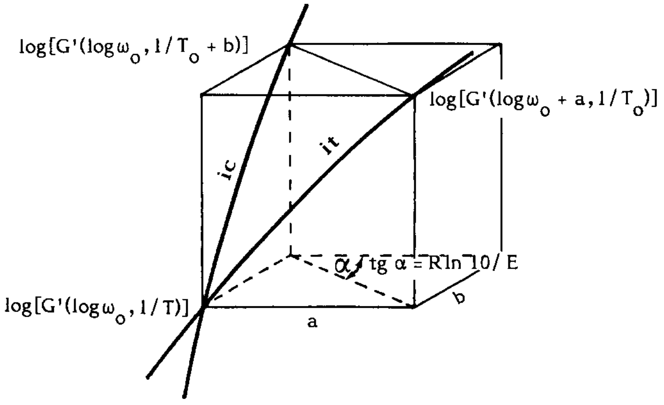


Figure 4: Intersection of an isotherm and an isochrone curve

Let $\log[G'(\log \omega_0 + a, 1/T_0)]$ and $\log[G'(\log \omega_0, 1/T_0 + b)]$ be two points on the isotherm and isochrone curve, resp., which would superpose according to the superposition principle and which are situated in the direct vicinity of an arbitrary point $\log[G'(\log \omega_0, 1/T)]$. a and b are the respective distances on the time and temperature axis from this assumed intersection point. Correspondingly, the following relations may be formulated:

$$\log[G'(\log\omega_0 + a, 1/T_0)] = \log[G'(\log\omega_0, 1/T_0 + b)] \qquad (36)$$

$$b/a = R \cdot \ln 10/E = \mathrm{tg}\,\alpha \qquad (37)$$

$$\{\log[G'(\log\omega_0 + a, 1/T_0)] - \log[G'(\log\omega_0,\ 1/T_0)]\}/a = \mathrm{tg}\,\alpha_1 \qquad (38)$$

$$\{\log[G'(\log\omega_0, 1/T_0 + b)] - \log[G'(\log\omega_0,\ 1/T_0)]\}/b = \mathrm{tg}\,\alpha_2 \qquad (39)$$

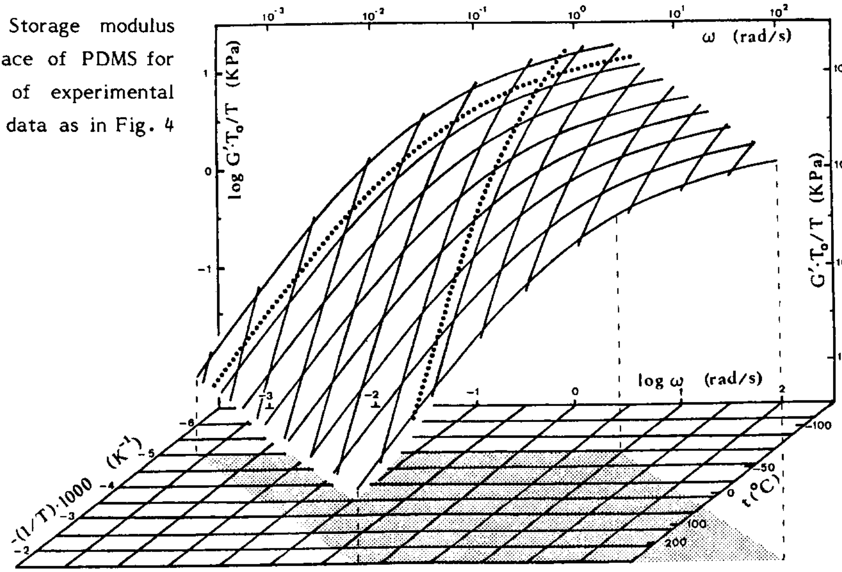
$$\mathrm{tg}\,\alpha = \mathrm{tg}\,\alpha_1/\mathrm{tg}\,\alpha_2 \quad . \qquad (40)$$

Equ. (38) and (39) may be written in a differential form. With (37) and (40) Equation (41) follows

$$\mathrm{tg}\,\alpha = \frac{\mathrm{tg}\,\alpha_1}{\mathrm{tg}\,\alpha_2} = \frac{\{\partial[\log(G')]_{T_0}/\partial(\log\omega)_0\}}{\{\partial[\log(G')]_{\omega_0}/\partial(1/T)_0\}} = R \cdot \ln 10/E \quad . \qquad (41)$$

Equation (41) represents the theoretical base for a novel insight into the viscoelastic properties of linear viscoelastic bodies. This equation makes the statement that the apparent activation energy of flow is determinable from the slopes of isotherm and isochrone curves reduced to identical temperature. Pre-condition is, however, that both slopes are known at the respective point. Consequently, a general method is offered not only for the determination of activation energies or, more generally, of the temperature dependences of the relaxation processes over the entire temperature range. It may be applied also for the construction of both isotherm and isochrone mastercurves and of spatial master surfaces. Fig. 5 presents such surface for direct estimation of temperature and frequency dependent storage moduli.

As known, the usual method of estimation of the activation energy of flow is based on viscosity measurements and is limited to the vicinity of zero shear rate, where the activation energy is constant. Whilst, the temperature dependence of the relaxation behaviour within the non-Newtonian range is described using additional data measurable within this range.Likewise the WLF equation is supported by the iso-free volume state supposition and the determination of the thermal expansion



<u>Figure 5:</u> Storage modulus master surface of PDMS for the range of experimental confidence, data as in Fig. 4

coefficients. Although the iso-free volume hypothesis tries to relate those quantities to the temperature dependences of the relaxation processes, one is left in practice to shift isotherm curves empirically.

The proposed method, based on Equ. (41), applies viscoelastic data exclusively, and no additional measurements or assumptions have to be made. The temperature dependence of the relaxation behaviour of the linear viscoelastic body will be reflected in a temperature dependence of the apparent activation energy given by these estimations. Thus the requirements for a consistent theory for the description of the time and temperature dependent viscoelastic behaviour of linear viscoelastic bodies are offered.

It may be noted that Equ. (41) is not limited to the storage modulus but applicable in analogeous manner for the loss modulus as well for the relaxation modulus. It may be useful for the interpretation of normal stress coefficients too.

TEMPERATURE DEPENDENCE OF THE SHIFT FACTORS

The relationship between the shift factors and activation energy is given by Equ. (32). As E is calculated at different temperatures, and a constancy of E is not imposed, the function $E(T)$ may be applied. $E(T)/R$ corresponds to the derivation of $\ln(a_T)$ versus $1/T$, i. e.

$$d\{\ln[a_T(T)]\} = [E(T)/R]\, d(1/T) \quad . \qquad (42)$$

Integration yields

$$\ln[a_T(T)] = \int_{1/T_{ref}}^{1/T} [E(T)/R]\, d(1/T) \quad . \qquad (43)$$

Using Equ. (43) the shift factor may be computed as a function of temperature so long as the applied reference temperature is situated within the range, where the apparent activation energy of flow has been determined.

Because the measured temperature dependence is independent of the type of exponential dependence of the relaxation processes on temperature, a discussion may be performed too concerning the applicability and the range of validity of DOOLITTLE's and EYRING's models.

Experimental verification of the proposed method on several polymers, with inclusion of the temperature dependence of the apparent activation energy of flow, will be published in near future.

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