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Viscoelastic Properties

Interrelations Between Relaxation Distribution Functions and Apparent Activation Energy of Flow

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Summary

Starting from both the three-dimensional diagram of viscoelastic properties in the reciprocal temperature - log frequency - space and the time-temperature interrelation via apparent activation energy of flow, the possibility of theoretical interpretation of the isochronal behaviour is demonstrated, in analogy to the isothermal one. The determinative apparent activation energy of local flow is related with the relaxation spectra over the entire range of validity of the time-temperature superposition principle. Thus a theoretical background is offered for the method recommended before for the evaluation of the apparent activation energy of flow, which is applicable to calculate both isotherm and isochrone shift factors.

The reciprocal relaxation - temperature spectrum

As it has been pointed out 1) within the range of validity of the time-temperature superposition principle the temperature dependence of viscoelastic functions tacidly includes the supposition that all relaxation times are governed by the same temperature law. It has been shown that this temperature dependence can be described in terms of EYRING's transition state theory, assuming at the same time a temperature variant 2) apparent activation energy of flow

$$\theta_P(T)/\theta_P(T_o) = \exp\{\int_{1/T_o}^{1/T} [E(T)/R]d(1/T)\} \quad . \qquad (1)$$

In equ. (1) P specifies the attribution of the respective relaxation time, θ, to a given individual relaxation process, P.

By definition isochrone curves comprise viscoelastic properties due to relaxation processes at different temperatures taking place, however, in the same time interval. At any given temperature the relaxation time of the slowest one of the possible processes will be equal than to the reciprocal frequency of measurement. Consequently, for a given frequency each relaxation process finally will become the slowest one relaxing to half of its stored stress at a specific temperature

$$\theta_P(T) = \theta_{P'} = 1/\omega_o \quad . \qquad (2)$$

P' represents this slowest process. By substituting $\theta_P(T)$ from equ. (1), equ. (3) results showing the time variable, $\theta_{P'}$, at the left and the temperature variable, $T_{P'}$, at the right hand

$$\theta_P(T_o) = (1/\omega_o)\ \exp\{\int_{1/T_P}^{1/T_o}[E(T)/R]d(1/T)\}\quad . \qquad (3)$$

The statement of equ. (3) means that each relaxation time correponds with a precise temperature. This temperature, $T_{P'}$, can be defined as the relaxation temperature of the choosen frequency of measurement, ω_o. It will be specified, therefore, as $T_P(\omega_o)$. In conditions of measurements, according to equation (3), the slowest relaxation process will be characterized by $T_{P'} = T_o$ and $\theta_{P'} = 1/\omega_o$. The above comprehension of attributing relaxation processes, times and temperatures, respectively, is illustrated by mutual interdependences → Accordingly, one has to distinguish between these three distribution functions, that of the relaxation processes, $h_r(P)$, that of the relaxation times, $F_r[\theta_P(T_o)]$, and that of the relaxation temperatures, $F_r[T_P(\omega_o)]$. As indicated by "r" all these functions have to be temperature and density reduced. Starting with the supposition imposed by the time-temperature superposition principle - that all relaxation processes and also all stress relaxations, consequently, have to be identical independently on the type of the distribution function considered - the following relations have to be valid

$$\begin{tikzcd}
 & \theta_P(T_o) \arrow[dd, leftrightarrow] \\
P \arrow[ur, leftrightarrow] \arrow[dr, leftrightarrow] & \\
 & T_P(\omega_o)
\end{tikzcd}$$

$$\int_{P=1}^{\infty} h_r(P)\,d(P) = \int_{\theta_P=0}^{\infty} F_r[\theta_P(T_o)]\,d\theta = \int_{T_P=0}^{\infty} F_r[T_P(\omega_o)]\,dT \quad . \qquad (4)$$

Taking into account, however, the practice of plotting viscoelastic functions either using the logarithmic time or the reciprocal temperature scale, the following distribution functions seem to be more suitable

$$\int_{P=1}^{\infty} h_r\,(P)\,d(P) = \int_{-\infty}^{\infty} H_r[\theta_P(T_o)]\,d\ln\theta = -\int_{0}^{\infty} H_r[T_P(\omega_o)]\,d(1/T) \quad . \qquad (5)$$

$H_r[\theta_P(T_o)]$ is now the T_o refered logarithmic relaxation time spectrum, whilst $H_r[T_P(\omega_o)]$ is the ω_o related reciprocal relaxation temperature spectrum

$$H_r[T_P(\omega_o)] = F_r[T_P(\omega_o)]\,T_P^2 \quad . \qquad (6)$$

Substituting $(d\ln\theta)_{T_o}$ in equ. (5) by $[E(T_P)/R]d(1/T)\big|_{T_P=T_o}$ according to the supposed temperature dependence in equ. (3), equation (7) results

$$\int_{0}^{\infty} H_r[T_P(\omega_o)]\,d(1/T) = \int_{0}^{\infty}[E(T_P)/R]\,H_r[\theta_P(T_o)]\Bigg|_{\theta_P(T_o)\,=\,f(\omega_o,\,T_P)} d(1/T) \quad . \qquad (7)$$

Consequently, if both the distribution functions are related with the same relaxation process P, the following correlation will be valid

$$\left[\frac{H_r[T_P(\omega_o)]}{H_r[\theta_P(T_o)]}\right]_P = E(T_P)/R \quad . \qquad (8)$$

It is evident that equ. (8) is generally valid and applies to the slowest relaxation process, P', too

$$\frac{H_r(T_{p'})}{H_r(\theta_{p'})} = \frac{[H_r(T_o)]_{\omega_o}}{[H_r(1/\omega_o)]_{T_o}} = E(T_o)/R \quad . \qquad (\ 9\ )$$

Related to the mastersurface in the reciprocal temperature - log frequency space this condition applies to any point on this surface, defined as $f_r(\omega_o, T_o)$, f_r being the chosen viscoelastic function 1).

Significance of the method of evaluation of the apparent activation energy of flow 1)

The problem which usually concerns all methods is the physical meaning of any implicated quantity. In this context the analyse of equ. (10) which has been recommended before for the evaluation of the apparent activation energy of flow 1) will be performed now

$$\frac{\partial(\log G')_{\omega_o} / \partial(1/T)_o}{\partial(\log G')_{T_o} / \partial(\log\omega)_o} = E(T_o)/2.303\,R \quad . \qquad (\ 10\ )$$

Mathematically this is equivalent to

$$\frac{\partial(G'_r)_{\omega_o} / \partial(1/T)_o}{\partial(G'_r)_{T_o} / \partial(\log\omega)_o} = E(T_o)/2.303\,R \quad . \qquad (\ 11\ )$$

Taking into account that, in the first approximation, the differentiation of the reduced storage modulus, G'_r, with respect to the logarithmic frequency is equivalent to the relaxation time spectrum

$$G'_r(\omega_o, T_o) \approx \int_{1/\omega_o}^{\infty} H_r[\theta(T_o)]\, d\ln\theta \quad , \qquad (\ 12\ )$$

equ. (13) may be formulated, finally

$$\partial(G'_r)_{T_o} / [2.303\,\partial(\log\omega)_o] \approx \{H_r[\theta(T_o)]\}_{\theta\,(T_o) = 1/\omega_o} \quad .$$

$$= (1/\omega_o)\,\{F_r[\theta(T_o)]\}_{\theta(T_o) = 1/\omega_o} = [H_r(1/\omega_o)]_{T_o} \quad . \qquad (\ 13\ )$$

The second and third approximations of relation (12) due to Williams and Ferry 3), and Tschoegl 4) 5), respectively, will not be analyzed here. According to Ferry, however, the approximation in equ. (13) can be written also in form of the equality in (14), "A" being a constant for a given relaxation process

$$H_r[\ (T_o)] = A\,\partial(G'_r)_{T_o} / \partial(\log\omega)_o \ \Big|_{\theta(T_o) = 1/\omega_o} \quad . \qquad (\ 14\ )$$

In order to make the connection of these relations with equ. (9) evidently it has to be stated only that condition $\theta(T_o) = 1/\omega_o$ means in fact the differentiation related to the slowest relaxation process occuring at a certain frequency, ω_o (see equ. (2)).

The solution of the system of relations (13), (11) and (9) yields

$$\partial(G'_r)_{\omega_o} / \partial(1/T)_o \approx H_r[T_P(\omega_o)] = [H_r(T_o)]_{\omega_o} \quad . \qquad (\ 15\ )$$

Using equ. (14) instead of (13) approximation (15) becomes

$$A\,\partial(G'_r)_{\omega_o}/\partial(1/T)_o = H_r[T_P(\omega_o)] = [H_r(T_o)]_{\omega_o} \quad . \qquad (16)$$

Therefore it is evident that equation (10) actually is equivalent to relation (9). That means that the apparent activation energy of flow according to the recommended method $^{1)}$ really is given by the ratio of the distribution functions. In practice the distribution functions are substituted by experimentally accesible quantities, i. e. the slopes of the respective isochrone and isotherm viscoelastic curves. It is also incontestable that the method is applicable to any viscoelastic function because they all are connected with the distribution functions.

In order to demonstrate the capacities of the above defined reciprocal relaxation temperature spectrum $H_r[T_P(\omega_o)]$ in describing the isochrone behaviour of linear viscoelastic bodies, some fundamental equations are presented in the following.

Isochronal view on viscoelastic functions

First it will be evidenced that besides from isothermal distribution functions, experimentally accessible viscoelastic data can be derived also from the isochronal ones. Starting with the well known isothermal relation, (17), which relates the storage modulus with the relaxation time spectrum, H_r, and substituting according to equations (3) and (8) $\theta_P(T_o)$, $(d\ln\theta)_{T_o}$ and $H_r[\theta_P(T_o)]$, respectively, the isochronal relation, (18), can be formulated

$$G'_r(\omega_o,T_o) = G'_{r\infty} + \int_{-\infty}^{\infty} H_r[\theta_P(T_o)]\,\frac{[\omega_o\theta_P(T_o)]^2}{1+[\omega_o\theta_P(T_o)]^2}\,d\ln\theta \qquad (17)$$

$$G'_r(\omega_o,T_o) = G'_{r\infty} + \int_{o}^{\infty} H_r[T_P(\omega_o)]\,\frac{\exp\{2\cdot\int_{1/T_P}^{1/T_o}[E(T)/R]\,d(1/T)\}}{1+\exp\{2\cdot\int_{1/T_P}^{1/T_o}[E(T)/R]\,d(1/T)\}}\,d(1/T) \quad . \qquad (18)$$

This relation can be simplified considering the storage modulus in the terminal zone only, when the activation energy of flow, E(T), is a constant

$$G'_r(\omega_o,T_o) = G'_{r\infty} + \int_{o}^{\infty} H_r[T_P(\omega_o)]\,\frac{\exp[2E/R(1/T_o-1/T_P)]}{1+\exp[2E/R(1/T_o-1/T_P)]}\,d(1/T) \quad . \qquad (19)$$

Consequently, it is evident that any frequency function turns by substitution into a temperature function. This temperature function accomplishes the same role as before the frequency function. The isochronal distribution function, however, is divided by the temperature function into a relaxed and an unrelaxed part. The temperature functions for different constant activation energies of flow, E, and for different temperatures of measurement, T_o' and T_o'', are plotted in Figure 1 for illustration. It is evident that the shape of the function is not depending on T_o. In a similar way, the isochronal distribution function H_r can be related with the loss modulus or with any other viscoelastic function too.

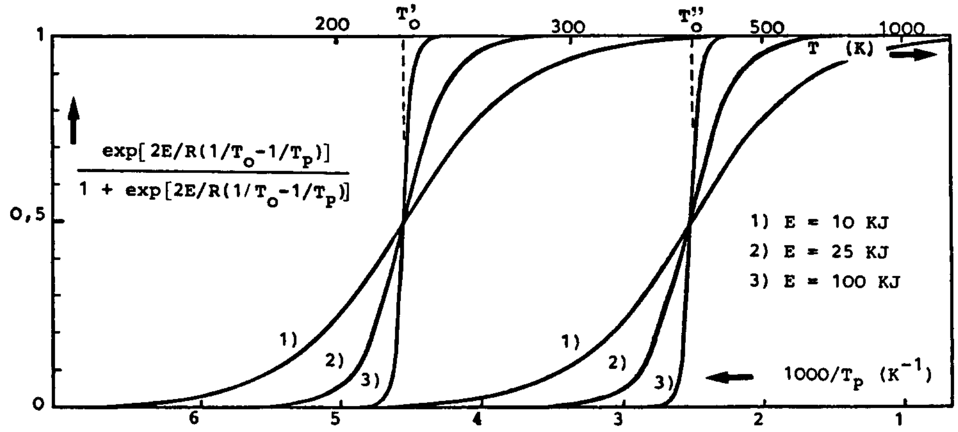

Figure 1: Temperature functions for different constant E and for T_o' and T_o'', respectively

Considering the Newtonian flow on macroscopic scale, than, in isochronal terms equation (19) has to be extrapolated to $1/T \to 0$. According to experimental findings E(T) becomes temperature independent in this region. Consequently, the following relations may be formulated for the zero shear viscosity and the loss modulus, respectively

$$\eta_{ro}(T_o) = \exp(E/RT_o)\int_0^\infty [(1/\omega_o)\exp(E/RT_p)]H_r[T_p(\omega_o)]\,d(1/T_p) = K\exp(E/RT_o) \qquad (20)$$

$$\ln[\eta_{ro}(T_o)] = \ln K + E/RT_o \qquad (21)$$

$$\ln[G''_{ro}(\omega_o,T_o)] = \ln[\omega_o\eta_{ro}(T_o)] = \ln K + \ln\omega_o + E/RT_o\ . \qquad (22)$$

As it has been already supposed [6] it is confirmed now by equ. (22) that in the Newtonian region of flow the slope of ln G''_{ro} versus $1/T$ is related directly with the apparent activation energy of flow. This statement is also in accordance with the proposed method [1] for the determination of activation energy. At the same time both the proposed methods and equation (22) evidence that the slope of ln G''_{ro} versus lnω has to be equal to unity.

In conclusion all isochronal considerations, the method for the determination of activation energy included, result in a consistent concept of analyzing viscoelastic properties in the reciprocal temperature - log frequency space. This statement may be understood also as an impuls for further development of isochronal measurements, especially in the region of constant activation energy of flow. In a further step invariant plots of viscoelastic functions may be realized by plotting versus E/RT. Application of this approach for relaxation processes with temperature-variable activation energies will be discussed in a following paper.

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