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The apparent activation energy for mechanical and dielectric relaxation in glass-forming (polymeric) liquids: a misconception?

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It is shown that the well-known concept of an apparent activation energy (Q_{app}) is confusing. Much of the problem with the application of thermal activation theory to glass transition disappears when the concept is abandoned and replaced by a strict application of the Arrhenius formula with temperature dependent activation energy, $Q \neq Q_{\text{app}}$. © 1997 Elsevier Science Ltd. All rights reserved.

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Introduction

In the temperature range just above glass temperature (T_g), the viscosity and the mechanical or dielectric relaxation times change rapidly with temperature[1–3]. In general*, the behaviour cannot be described by an Arrhenius formula:

$$\ln \tau/\tau_0 = Q/RT \qquad (1)$$

where τ_0 is the limiting relaxation time at infinite temperature (generally of the order of 10^{-14} s), Q the activation energy (independent of T), R the gas constant and T the absolute temperature. A more satisfactory description is achieved by the WLF equation[7]:

$$\log a_T = \log(\tau/\tau_g) = -c_{1g}(T - T_g)/[c_{2g} + T - T_g] \qquad (2)$$

where $\log a_T$ is the ^{10}log of the ratio of the relaxation time τ (or viscosity) at temperature T and that (τ_g) at T_g whilst c_{1g} and c_{2g} are constants (subscript g denotes that T_g was taken as reference temperature). The WLF equation is equivalent to the Fulcher–Tammann–Hesse–Vogel equation[1]:

$$\ln \tau = A + B/(T - T_\infty) \qquad (3)$$

in which A, B and T_∞ are constants. The relations between the coefficients of equations (2) and (3) are given in ref. 6.

For a process obeying Arrhenius formula, the $\ln \tau$ vs $1/T$ plot is linear and the activation energy can be found from:

$$Q = R\,\mathrm{d}\ln\tau/\mathrm{d}(1/T) \qquad (4)$$

This formula has a straightforward meaning only when Q is independent of T. However, it is often applied to the non-Arrhenius behaviour at and above T_g (see for example refs 1 and 7–9). One then obtains the so called *apparent activation energy* (Q_{app}):

$$Q_{\text{app}} = R\,\mathrm{d}\ln\tau/\mathrm{d}(1/T) \qquad (5)$$

which is R times the (varying) slope of the curved $\ln \tau$ vs $1/T$ plot. For non-Arrhenius behaviour, Q_{app} necessarily varies with temperature. For example, when τ follows the WLF equation, equations (2) and (5) yield[6]:

$$Q_{\text{app}} = 2.303Rc_{1g}c_{2g}T^2/[c_{2g} + T - T_g]^2 \qquad (6)$$

A plot of the WLF equation is given in *Figure 1*, together with the course of Q_{app}. Obviously, Q_{app} is very large: about 1000 kJ mol^{-1} at T_g. This is larger than the energy to break a covalent C–C bond, and much larger than the activation energies observed for secondary relaxations below T_g (10–100 kJ mol^{-1})[10]. Furthermore, Q_{app} rapidly changes with temperature, decreasing by a factor of 5 between T_g and $T_g + 100$°C. The occurrence of such very high, temperature dependent activation energies prompted the well-known belief that the relaxation at T_g is due to the cooperative motion of a large (temperature-dependent) number of monomer segments and cannot be described by thermal activation theory. The last point was further substantiated by the success of the free-volume model[1].

It should however be realized that the use of an apparent activation energy is a half-hearted attempt to describe non-Arrhenius behaviour with Arrhenius formulas. The formalism of equation (1) is partially maintained (in differential form, see equation (5)) and it is accepted that the activation energy is temperature dependent. We therefore propose to go a step further and to maintain the formalism of equation (1) fully. Equation (1) is then replaced by:

$$\ln \tau/\tau_0 = Q(T)/RT \qquad (7)$$

in which $Q(T)$ is now a (real) activation energy depending on T.

If $Q(T)$ is independent of T, equations (5) and (7) lead to the same results. However, if $Q(T)$ varies with T (non-Arrhenius behaviour), Q will differ from Q_{app}. In equation (7), a change in T affects τ via the denominator as well as the numerator. If the last effect is omitted, differentiation of equation (7) results in equation (5). Performing the differentiation correctly, equation (7) yields:

$$\begin{aligned}\mathrm{d}\ln\tau/\mathrm{d}(1/T) &= (1/R)[Q - T\mathrm{d}Q/\mathrm{d}T] \\ &= (Q/R)[1 - \mathrm{d}\ln Q/\mathrm{d}\ln T] \qquad (8)\end{aligned}$$

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* Some glass-forming liquids (e.g. SiO_2 and GeO_2) show Arrhenius behaviour over the whole temperature range above T_g[4,5]. Thus, liquid–glass transition is not synonymous with non-Arrhenius or WLF behaviour

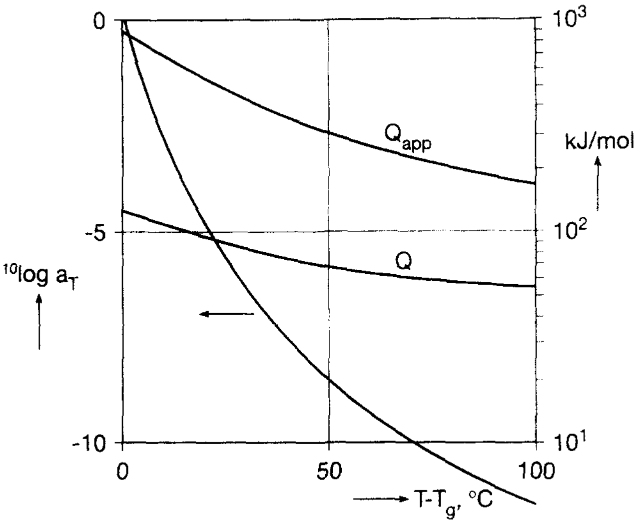

Figure 1 Plots of: shift log a_T according to the WLF equation with the 'universal' constants $c_{1g} = 17.4$ and $c_{2g} = 51.6$°C and a T_g-value of 100°C; apparent activation energy Q_{app} corresponding to this WLF equation and calculated with equation (6); activation energy Q, corresponding to this WLF equation and calculated with equation (11)

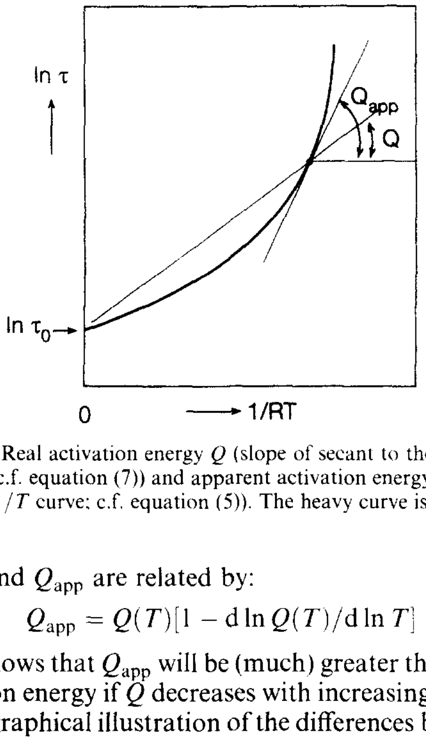

Figure 2 Real activation energy Q (slope of secant to the $\ln(\tau/\tau_0)$ vs $1/T$ plot; c.f. equation (7)) and apparent activation energy Q_{app} (slope of $\ln\tau$ vs $1/T$ curve; c.f. equation (5)). The heavy curve is schematical

and Q and Q_{app} are related by:

$$Q_{app} = Q(T)[1 - \mathrm{d}\ln Q(T)/\mathrm{d}\ln T] \qquad (9)$$

which shows that Q_{app} will be (much) greater that the real activation energy if Q decreases with increasing temperature. A graphical illustration of the differences between Q and Q_{app} is given in *Figure 2*.

In the example of WLF behaviour, equation (7) gives:

$$Q(T)/RT = \ln(\tau_g/\tau_0) - 2.303c_{1g}(T - T_g)/[c_{2g} + T - T_g] \qquad (10)$$

The $\ln(\tau_g/\tau_0)$ term can be expressed in terms of c_{1g} if the WLF equation is assumed to hold over the whole temperature range above T_g, i.e. up to $T \to \infty$*. Quantity $\ln(\tau/\tau_g)_{T\to\infty}$ then equals $-2.303\,c_{1g}$ and $\tau_{T\to\infty}$ equals the τ_0 of equation (1). Thus $\ln(\tau_g/\tau_0) = 2.303\,c_{1g}$. Substituting this into equation (10), we obtain:

$$Q(T) = 2.303Rc_{1g}c_{2g}T/[c_{2g} + T - T_g] \qquad (11)$$

which replaces equation (6). Note that equations (6) and (11) have the same form, except that the squares in equation (6) are replaced by first powers in equation (11). Note further that equations (2), (6) and (11) are identical in that they all describe the same $\ln\tau$ vs T behaviour; the differences lie in the definition of the activation energies used (Q_{app} vs Q). Note finally that, if WLF applies over the whole temperature range above T_g, the same holds for equations (6) and (11).

The course of activation energy, Q vs T corresponding to WLF is also given in *Figure 1*. We observe that Q is much lower than Q_{app}, much less depending on T and of the same magnitude as that for secondary processes. So, most of the erratics in the activation behaviour above T_g have disappeared.

An interesting result is obtained by calculating T_g by means of equation (7). T_g is defined as the temperature where τ reaches some characteristic value τ_g of about 1000 s (see below). So, T_g is the solution of the equation: $Q(T)/RT = \ln(\tau_g/\tau_0)$ which has a single, well-defined root when $\ln(\tau/\tau_0) = Q(T)/RT$ decreases with increasing temperature as usual. Denoting the Q value at T_g by Q_g (note that Q_g depends on the time τ_g chosen), equation (11) yields:

$$T_g = Q_g/(2.303Rc_{1g}) = Q_g/332 \qquad (12)$$

in which we substitute the 'universal' c_{1g} value of 17.4 whilst Q_g is expressed in J mol^{-1}. Equation (12) shows that T_g is proportional to the activation energy Q_g, just as found for the transition temperatures of secondary processes, and should be expected when the τ_0 in equation (1) has a 'universal' value of 10^{-14} s[2,3,11,12].

Remarkably, the proportionality constant (transition temperature/Q) is the same as for secondary processes. For T_g, the WLF equation leads to a value of 1/332 (equation (12)). To find the corresponding constant for secondary relaxations (see ref. 11) we have to compare the transitions at equal values of the characteristic time or frequency; so we need to know time/frequency for the glass transition. This can be found from Kovacs' paper[13], where it is shown that T_g, as defined from the intercept of the volume curves of liquid and glass, corresponds to a relaxation time τ_g of about $2.3/q$ in which q is the cooling rate in °C s^{-1}. This order of magnitude estimation agrees with experimental data. For example, Peyser[14] measured the relaxation time at T_g after cooling a polystyrene sample at 10°C min^{-1}; he found a time of 11 s which compares well with Kovacs' order of magnitude estimate of 14 s for 10°C min^{-1}. Since T_g is usually determined for cooling rates of 0.1–1°C min^{-1}, we arrive at a characteristic time of 140–1400 s, which agrees with Kauzmann's order of magnitude estimate of several minutes to hours[15]†. Since[17] time t corresponds to a frequency ν of about $1/(2\pi t)$, the characteristic frequency for T_g is 10^{-3} Hz at $q = 1$°C min^{-1} and 10^{-4} Hz at $q = 0.1$°C min^{-1}. Substituting this into Heijboer's equation[18], we find a proportionality constant of 1/306 for 1°C min^{-1} and 1/325 for 0.1°C min^{-1}. This agrees very well with equation (12) which was independently derived from the WLF equation with $c_{1g} = 17.4$. So, glass transition and thermal activation theory appear less antagonistic than usually assumed.

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[*] This is not entirely correct. In general, the WLF behaviour breaks down at about 100° above T_g and changes into an Arrhenius behaviour[1-3]. The effect of this on the present argument is limited

[†] O'Reilly's[16] data however strongly deviate. He finds relaxation times τ_g at T_g varying between 1 and 10^8 s (up to 3 years). He also finds τ_0 values of 10^{-27}–10^{-268} s. These unrealistic values probably reflect inconsistencies in the Narayanaswamy equation used for analysing the differential scanning calorimetry data of polymers

Conclusions

1. For non-Arrhenius relaxation processes above T_g, the concept of an apparent activation energy Q_{app}, defined as the slope of the $\ln \tau$ vs $1/T$ curve is a half-hearted attempt to describe non-Arrhenius behaviour with an Arrhenius formalism.
2. Full application of the Arrhenius formalism leads to an activation energy Q that is much smaller and much less temperature dependent than Q_{app}. The Q values found at and above T_g compare with those for secondary relaxation processes below T_g. Moreover, for the glass transition, the ratio between transition temperature and activation energy is the same as for secondary transitions below T_g (provided that the frequencies are taken as equal).
3. As a consequence of conclusion 2, we conclude that much of the well-known problems with the application of thermal activation theory to glass transition disappears when the Q_{app} concept is abandoned.

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