Derivation of the WLF Equation from the Theory of Rate Process*

by

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ABSTRACT

The WLF equation is derived from the theory of rate processes in conjunction with the theory of liquefied significant structures. The empirical parameters in the WLF equation are discussed and compared with the corresponding quantities in the derived equation.

1. INTRODUCTION

In the past years, many studies were published on the temperature dependence of viscosities for glass forming liquids.*†‡ Among them, the successful semiempirical relation, which is often called the WLF equation after the authors' name, Williams, Landel, and Ferry, (3) is represented as

\[ \ln(\eta/\eta_g) = 40(T - T_g)/(T_g - T_g) \]

where \( \eta \) denotes the viscosity at temperature \( T \), and the quantities with the suffix \( g \) indicate the corresponding quantities at the glass transition. In this paper, the WLF equation is derived from the theory of rate processes,*†‡ and the empirical parameters such as 40 and 52 in equation (1) are correlated with the quantities appeared in the derived equation.

2. DERIVATION OF THE WLF EQUATION

The shear viscosity equation*§ developed by Ree, Ree and Eyring starting from the significant liquid-
structure concept\(^{(14-11)}\) and the theory of rate processes\(^{(10)}\) has the following form:
\[
y = \frac{V_S}{V} \eta_2 + \frac{V - V_S}{V} \eta_3 \quad \text{at} \quad T \quad \text{and} \quad \bar{T}
\]
where \(V_S\) and \(V\) are the molar volumes of the solid and liquid, respectively, \(\eta_2\) and \(\eta_3\) are the viscosities of the of the solid and gaseous states. The quantity \(\eta_3\) which is derived from the kinetic theory\(^{(11)}\) has the form, \(\eta_3 = (5/16\pi) \left( \frac{m^3 k T}{e} \right)^{\eta_3}\), where \(m\) and \(d\) are the molecular mass and diameter, respectively. The expression for \(\eta_3\) is as follows:\(^{(3)}\)
\[
\eta_3 = \frac{V}{V_S} \left( \frac{m k T}{2(V - V_S) x_a} \right)^{\frac{1}{2}} \exp \left[ \frac{-a V_Z g a}{(V - V_S)^{2k T}} \right]
\]
(3)
Here \(x_a\) is the free distance between nearest neighbors, \(x\) is a transmission coefficient, \(a\) is a proportionality constant, \(g(a)\) is an intermolecular potential function, \(Z\) is the number of nearest neighbors, \(k\) is Boltzmann's constant, and \(N\) is Avogadro's number.

Since \(\eta_3\) is quite small, this contribution (0 to 2\%) can be neglected. Thus, introducing equation (3) into (1), one obtains
\[
y = \frac{(m k T)^{\frac{1}{2}} N_l}{2(V - V_S)^2} \exp \left[ \frac{-a V_Z g a}{(V - V_S)^{2k T}} \right]
\]
(4a)
\[
= B_{1} \frac{E_S V_S}{(V - V_S)^{2k T} r_T}
\]
and \(E_S\) is the sublimation energy. Equation (4a) is represented as
\[
\log y = \log B + \frac{E_S V_S}{(V - V_S)^{2k T} r_T} \quad \text{at} \quad T \quad \text{and} \quad \bar{T}
\]
(4b)
Consider the viscosities of a liquid at two different temperatures, \(T_1\) and \(T_2\). From equation (4b), the following is resulted:
\[
\eta_2 = \frac{E_S V_S}{R} \left[ \frac{1}{(V_1 - V_S)^{2k T_1}} - \frac{1}{(V_2 - V_S)^{2k T_2}} \right]
\]
(5)
where it is assumed that the temperature dependence of \(B\) is very small for certain temperature ranges. Using the relation, \(X_2 = X_1 + a X_1 (T_2 - T_1)\), where \(X = V/V_S\) and \(a\) is the expansion coefficient for the glass-forming liquid (\(a\)) minus that for the glass (\(\eta_2\)),\(^{(13-15)}\) equation (5) is transformed into
\[
\ln \eta_2 = \frac{E_S V_S}{R} \left[ \frac{1}{(X_2 - 1)^{2k T_2}} - \frac{1}{(X_1 - 1)^{2k T_1}} \right]
\]
(6)
Rearranging Eq. (6) and assuming \(T_2 \gg \frac{1}{T_1 T_2}\), one obtains
\[
\ln \frac{\eta_2}{\eta_1} = \frac{E_S}{R} \left( \frac{1}{X_2 - 1} - \frac{1}{X_1 - 1} \right) \frac{T_2}{T_1} \quad \text{at} \quad T \quad \text{and} \quad \bar{T}
\]
(7)
where the suffix 1 was changed to \(g\), and the quantities suffixed 2 were unsuffixed. Equation (7) is exactly equal to the WLF equation, if the following relations hold:
\[
\frac{E_S}{R} \left( \frac{1}{X_2 - 1} \right) \approx 40 \quad \text{at} \quad T \quad \text{and} \quad \bar{T}
\]
(8)
\[
(X_2 - 1)/\pi X_2 \approx 52 \quad \text{at} \quad T \quad \text{and} \quad \bar{T}
\]
(9)

3. DISCUSSION

(1) First we consider the relation represented by equation (9).

The left-hand side of the latter is rewritten as
\[
\frac{X_2 - 1}{\alpha X_2} - \frac{V_S - V}{\alpha V_S} = \frac{V_{fl}}{\alpha V_f} \quad \text{at} \quad T \quad \text{and} \quad \bar{T}
\]
(10)
where \(V_{fl}/V_f\) is the fraction of free volume at \(T\), and it was estimated as about 1/40 by many authors.\(^{(13-15)}\) Recent data on polystyrene and polyisobutylene\(^{(14)}\) and polyethylene\(^{(15)}\) also indicate that the estimated value is substantially correct. The value of \(\alpha\) is about 5 X 10^{-4}/deg for most high polymers.\(^{(13-15)}\) Thus, the \(V_{fl}/\alpha V_f\) becomes 52 in agreement with the WLF equation.

In equation (10), \(V_f\) is considered to be the liquid volume at \(T_f\) occupied by a mole of segments of the polymer molecule, and \(V_S\) is understood as the volume of a mole of the segments at the solid state. According to the rate theory of flow processes,\(^{(16)}\) a hole (or free volume), the size of which must at least be \(V_S\) per mole, should exist next to the segment, otherwise the hopping of the segment is unsuccessful, consequently flow does not occur. Since \(V_{fl}/V_f = (V_{fl}/V_S)/(V_f/V_S) = 1/40\), the value of \(V_{fl}/V_f\) becomes 1/39 because \(V_f/V_S = 40/39\). Thus at \(T_f\), the average free volume per mole of segments \((V_f - V_{fl})\) is only 1/39 the necessary hole size \((V_S)\) per mole of segments. This means that the jumping
(flow) process becomes very hard at \( T_s \) in agreement with the experimental fact, \( \eta_s \approx 10^3 \).

(2) Next we consider the relationship represented by equation (8).

The left-hand-side term of the latter is rewritten in the following form:

\[
\frac{a' E_s}{RT_s} \frac{1}{(X_s - 1)} = \frac{a' E_s}{RT_s} \frac{V_f}{V_s} \frac{V_s}{V_f} = 39 \frac{a' E_s}{RT_s}, \quad \text{(11)}
\]

where the relations, \( V_{fs}/V_s = 1/40 \) and \( V_s/V_{fs} = 39/40 \) were substituted. From equation (4b), the first left-hand-side term of equation (11) is understood as the reduced activation energy at \( T_s \) of the flow process. Below, the activation energy is discussed in more detail.

In deriving equation (1), it was assumed that the activation energy \( E^* \) is proportional to \( E_i \) and inversely proportional to \( n_h \) (the number of holes around a jumping segment). i.e.,

\[
E^* = a' E_i n_h = a' E_i [V_s/V_f], \quad \text{(12)}
\]

where a molecule of mass was assumed, and \( a' \) is a proportionality constant. Thus, \( a' E_i \) is considered as the activation energy when \( n_h = 1 \). If there is one hole adjacent to a segment, and the latter has a thermal energy, \( RT_s \), it will be able to jump into the hole. Thus, the activation energy \( a' E_i \) will be equal to \( RT_s \), i.e., the relation,

\[
a' E_i / RT_s = 1, \quad \text{(13)}
\]

is considered to be very reasonable. Introducing equation (13) into (11), one readily obtains equation (8) since \( 39 \approx 40 \) in our approximation. Equation (13) is also a natural consequence from equation (8) if \( V_{fs}/V_s = 1/40 \). Thus, equation (13) seems to be a general relation for glass-forming liquids.

In connection with the activation energy, the following discussion will be of interest. Let \( \Delta S_s \) be the entropy change associated with the glass transition. The following values of \( \Delta S_s \) were reported in the literature: \( \Delta S_s \approx 1.6 \) to 2.3 e.u./mole for polyethylene, \( \approx 1.2 \) e.u./mole for polypropylene, \( \approx 1.7 \) e.u./mole for polystyrene. \( \approx 1.5 \) The average value of \( \Delta S_s \), 2 e.u./mole, is very close to the \( \Delta S \) for fusion of Ar (3 e.u./mole). From this fact, it may be concluded that the polymer segments behave at \( T_s \) like nonpolar symmetrical molecules. Thus, the above-mentioned discussion concerning equation (13) seems plausible.

(3) From equations (12) and (13), the following equation is derived:

\[
E^* = RT_s V_f/V_s, \quad \text{(14)}
\]

The activation energy \( E^*_s \) at \( T_s \) is calculated from equation (14), i.e.,

\[
E^*_s = RT_s V_f/V_s, \quad \text{(15)}
\]

For polyethylene \( (T_s = 188^\circ K) \), polypropylene \( (T_s = 255^\circ K) \), polystyrene \( (T_s = 373^\circ K) \), and polyisobutylene \( (T_s = 203^\circ K) \), the values of \( E^*_s \) are 14.5, 19.6, 28.8 and 15.7 kcal/mole, respectively.

Previously, we noted that \( \Delta S_s \) for the glass transition is about 2 e.u./mole which is similar to \( \Delta S \) for melting of Ar (3 e.u./mole). This fact indicates that a partial Brownian motion of polymer segments starts at \( T_s \). The motion will be not only a translational but also an internal molecular motion associated with the "trans-gauche" isomerism if the latter is possible. Since \( \Delta S_s \) is 2e.u./mole, \( \Delta E_s \) (energy change for the glass transition) is about 2\( T_s \) if the glass transition is an equilibrium phenomenon. Comparing \( \Delta E_s \) with \( E^*_s \), one immediately notices that the latter is also about 40 times as large as the former. Thus, it seems that at \( T_s \) the flow motion occurs with a great hardness.

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