

Williams-Landel-Ferry (WLF) Equation

1. Time-Temperature Superposition

The mechanical response of amorphous polymers in the transition zone (around T_g) depends strongly on both temperature and on the observation timescale. Viscoelastic processes that occur over seconds near T_g may occur in microseconds at higher temperature, a manifestation of the **time-temperature equivalence principle**.

For *thermorheologically simple* polymers, where all relaxation modes share the same temperature dependence and no structural changes occur in the relevant temperature range, this principle allows one to construct a **master curve** for viscoelastic properties (e.g. modulus) by shifting isothermal measurements horizontally along the logarithmic time or frequency axis.

The corresponding **horizontal shift factor** a_T expresses how much the timescale of molecular motion changes with temperature:

$$a_T = \frac{t(T)}{t(T_{\text{ref}})} = \frac{\tau(T)}{\tau(T_{\text{ref}})}, \quad (1)$$

where T_{ref} is an arbitrarily chosen reference temperature, often taken near T_g .

Empirically, Williams, Landel, and Ferry (1955) found that the logarithm of a_T follows a nearly universal form for amorphous polymers in the temperature range $T_g < T < T_g + 100$ °C:

$$\log a_T = -\frac{C_1(T - T_{\text{ref}})}{C_2 + T - T_{\text{ref}}}, \quad (2)$$

with constants C_1 and C_2 that adopt “universal” values $C_1 = 17.44$ and $C_2 = 51.6$ K for many amorphous polymers when $T_{\text{ref}} = T_g$.

2. Physical Interpretation and Connection to Free Volume

The origin of the WLF equation can be understood within the framework of the **free volume theory**. Early work by **Doolittle** proposed that the viscosity η of simple liquids (e.g., *n*-alkanes) increases exponentially with the ratio of occupied to free volume:

$$\eta = \eta_0 \exp\left(\frac{Bv_0}{v_f}\right), \quad (3)$$

where v_0 is the occupied (hard-sphere) volume per molecule, v_f the average free volume available for molecular motion, B an empirical constant, and η_0 the limiting viscosity at infinite free volume. Since viscosity and the characteristic molecular relaxation time τ are proportional,

$$\tau = \tau_0 \exp\left(\frac{Bv_0}{v_f}\right). \quad (4)$$

Later, Cohen and Turnbull provided a microscopic justification for the Doolittle equation: in a dense amorphous material, molecular rearrangement requires a local free-volume fluctuation (“hole”) of volume v^* into which a segment can move. Assuming that the distribution of local free volumes follows an exponential (Poisson-like) law, the probability of finding a hole larger than v^* is:

$$P(v > v^*) \sim \exp\left(-\frac{v^*}{v_f}\right). \quad (5)$$

If the jump frequency (and thus molecular mobility) is proportional to this probability, the relaxation time is inversely proportional to it:

$$\tau = \tau_0 \exp\left(\frac{v^*}{v_f}\right). \quad (6)$$

This expression is identical in form to the Doolittle equation if $v^* = Bv_0$. Thus, the exponential dependence reflects the statistical rarity of sufficiently large local voids that permit molecular rearrangement.

Accordingly, **free volume controls the ease of molecular rearrangements**: as the temperature decreases, v_f shrinks, segmental motion becomes exponentially rarer, and the viscosity (or relaxation time) rises sharply, ultimately leading to vitrification near T_g . The free volume is commonly assumed to increase linearly with temperature above the hypothetical equilibrium glass transition temperature T_0 :

$$v_f = v_0 (T - T_0)\Delta\alpha. \quad (7)$$

where $\Delta\alpha$ is the difference between the thermal expansion coefficients of the liquid and glassy states (see our course on Free Volume Theory). Substituting Equation (7) into (6) gives:

$$\tau = \tau_0 \exp\left(\frac{B\Delta\alpha^{-1}}{T - T_0}\right). \quad (8)$$

If we define $T_0 = T_g - A$, where A is the temperature difference between T_g and T_0 , this becomes:

$$\tau = \tau_0 \exp\left(\frac{B\Delta\alpha^{-1}}{A + T - T_g}\right), \quad (9)$$

and at the glass transition temperature:

$$\tau(T_g) = \tau_0 \exp\left(\frac{B\Delta\alpha^{-1}}{A}\right). \quad (10)$$

Using Equation (1) to define the horizontal shift factor,

$$\ln a_T = \ln \tau - \ln \tau(T_g) = \frac{B\Delta\alpha^{-1}}{A + T - T_g} - \frac{B\Delta\alpha^{-1}}{A} = \frac{AB\Delta\alpha^{-1} - B\Delta\alpha^{-1}(A + T - T_g)}{(A + T - T_g)A}, \quad (11)$$

and simplifying gives:

$$\ln a_T = - \frac{A^{-1}B\Delta\alpha^{-1}(T - T_g)}{A + T - T_g}. \quad (12)$$

This expression has **the same mathematical form** as the empirical WLF equation, with $C_1 \approx A/(2.303B\Delta\alpha)$ and $C_2 = A$. Both the Doolittle and WLF equations describe the steep temperature dependence of polymer relaxation times near T_g . Their apparent equivalence relies on three key assumptions:

- Local free-volume fluctuations follow an exponential distribution.
- Segmental mobility is proportional to the probability of finding a “hole” of critical size v^* .
- The average free volume increases linearly with temperature.

While these assumptions are physically plausible, they are not derived from first-principles molecular dynamics. Hence, **the WLF equation should be regarded as a phenomenological expression consistent with the free-volume concept** rather than a strict theoretical consequence.

3. Shift Factor Analysis

In time-temperature superposition experiments, the frequency dependence of viscoelastic functions such as the storage modulus G' and the loss modulus G'' is measured at different temperatures in the transition zone. The resulting data can be horizontally shifted along the logarithmic frequency (or time) axis to form a **master curve** at a chosen reference temperature. This master curve extends the experimentally accessible range by many decades in time and frequency, allowing one to predict the material’s mechanical behavior in otherwise inaccessible regimes.

- low-frequency regime (from high- T data): provides information relevant to creep, stress relaxation, long-term aging.
- high-frequency regime (from low- T data): corresponds to short-time responses such as high-speed impacts, mechanical vibrations, or acoustic excitations.

For quantitative analysis, the required shift factors a_T are determined from the horizontal displacements applied to superimpose the curves. **According to the WLF equation**, a plot of $\log a_T$ versus T (or $T - T_{\text{ref}}$) yields the material-specific constants C_1 and C_2 . In light of Equation (12), these constants can be related to microscopic parameters of the free volume model, allowing estimates of the thermal expansion coefficient difference $\Delta\alpha$ and the hypothetical temperature T_0 corresponding to zero free volume.

For most amorphous polymers, the WLF description holds well between T_g and $T_g + 100\text{--}150$ °C. At higher temperatures, however, deviations may occur as free-volume effects diminish and molecular mobility becomes governed by a fixed activation energy.

At sufficiently high temperatures, the temperature dependence of molecular relaxation follows an **Arrhenius relation**, which reflects thermally activated conformational motion rather than free-volume constraints:

$$\eta(T) = \eta_0 \cdot e^{(E_a/RT)} \quad , \quad (13)$$

where E_a is the activation energy for flow, R is the gas constant, and η_0 the pre-exponential factor. Because the shift factor a_T can also be expressed as the ratio of viscosities (or relaxation times) at T and a reference temperature T_{ref} ,

$$a_T = \frac{\eta(T)}{\eta(T_{\text{ref}})} \quad , \quad (14)$$

substitution of Equation (13) gives the **Arrhenius form for the shift factor**:

$$\ln a_T = \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \quad . \quad (15)$$

Thus, a plot of $\ln a_T$ versus $1/T$ yields a straight line with slope E_a/R . **The Arrhenius analysis therefore provides an estimate of the activation energy of segmental motion.** Deviations from linearity as the temperature approaches T_g reflect the onset of **free-volume-controlled dynamics, for which the empirical WLF equation again offers a more accurate description.**