Glass-Rubber Transition

A Second order Transition Important in Polymeric Systems
Change in Specific Volume

**Figure 5.1** Cooling of a liquid following routes a (crystallization) or b (forming a glassy amorphous structure).
Effect of structure, side chain effect

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H} \\
\text{X} \\
\text{H}
\end{array}
\]

\[n\]

\[X = \text{CH}_3 \quad \text{C} \quad \text{CH}_3 \quad \text{C} \quad \text{C} \quad \text{C}\]

\[-10 \quad 100 \quad 115 \quad 135 \quad 145\]

\[T_g(\degree C)\]

**Figure 5.3** Glass transition temperatures of different vinyl polymers showing the influence of the size of the pendant group. Data from Eisenberger (1984).
Effect of structure, flexible side chains

Figure 5.4 Glass transition temperature of polyacrylates and polymethacrylates as a function of number of carbons $n$ in the oligo-methylene (R) group. Drawn after data from Rogers and Mandelkern (1957) (polymethacrylates) and Shetter (1963) (polyacrylates).
Effect of structure, chlorine effect

Figure 5.5 Effect of chlorine content on the glass transition temperature of chlorinated polyethylene. Data for polyvinylchloride (PVC) and polyvinylidene chloride (PVDC) are shown for comparison. Drawn after data from Schmieder and Wolf (1953).

Figure 5.6 Repeating unit of polyvinylidene chloride and schematic representation of the resulting dipole moment.
Effect of structure, cohesive energy density

\[ T_g = \frac{2\delta^2}{mR} + C_1 \]

where \( \delta^2 \) is the CED, \( m \) is a parameter which describes the internal mobility of the groups in a single chain, \( R \) is the gas constant and \( C_1 \) is a constant. The CED provides an integrated measure of the strength of the secondary bonds in a compound. Materials with strong secondary bonds show high CED values.
Effect of structure, cohesive energy density

\[ T_g = \frac{2\delta^2}{mR} + C_1 \]

Beaman (1953) and Boyer (1954) noticed in the early 1950s that both \( T_g \) and the melting point \( T_m \) of crystallizable polymers increased with decreasing chain flexibility and increasing CED. They established the following empirical correlations:

\[
\frac{T_g}{T_m} = \frac{1}{2} \quad \text{(symmetrical molecules)} \quad (5.2)
\]

\[
\frac{T_g}{T_m} = \frac{2}{3} \quad \text{(asymmetrical molecules)} \quad (5.3)
\]

According to more recent data, about 80% of the data for symmetrical and asymmetrical polymers are within the \( T_g/T_m \) limits 0.5–0.8.
Figure 5.2 The effect of molecular and thermal factors on the structure of the solidified polymer.
1. Types of Transitions

Ehrenfest Classification

- Classification of Transitions into:
  - First-order, first derivative of chemical potential with respect to $T$ is discontinuous during the transition.
  - Second-order first derivative of chemical potential with respect to $T$ remain continuous during the transition.
2. Glass-Rubber Transition

• The state of a polymer depends on temp. and time allotted
• At low enough temps. Amorphous polymers are stiff and brittle (glassy State)
• Warming cause the polymer soften in the glass-rubber transition temp.
• “the glass transition temp. is perhaps the most important parameter that determines the application of many noncrystalline polymers”, (Eisenburg’s statement)
2.1 The Glassy Region

Glass transition region

Glassy state

Rubbery plateau

Rubbery flow

Liquid flow
2.2. Glassy region

- $E$, $3 \times 10^{10}$ dyne/cm² ($3 \times 10^9$ Pa) for most polymers
- Molecules have restricted motion and vibration
2.3. Glass Transition Region

- The modulus drops a factor of 1000 over 20-30 °C range
- $T_g$ is often taken at the maximum turndown
- $T_g$ is defined as thermal expansion coefficient undergoes a discontinuity
- The onset of long-range molecular motions
- The glass-transition temp varies with structure and other parameters
<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g, ^\circ C$</th>
<th>Number of Chain Atoms Involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(dimethyl siloxane)</td>
<td>−127</td>
<td>40</td>
</tr>
<tr>
<td>Poly(ethylene glycol)</td>
<td>−41</td>
<td>30</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>+100</td>
<td>40–100</td>
</tr>
<tr>
<td>Polyisoprene</td>
<td>−73</td>
<td>30–40</td>
</tr>
</tbody>
</table>
2.3. The Rubbery Plateau Region

- Typical \( E = 2 \times 10^7 \) dyne/cm\(^2\) (2 \( \times \) 10\(^7\) Pa)

The exact elastomeric behavior (long-range elasticity)

Two regions are distinguished
- Linear polymers (poor elastic properties)
- Cross-linked polymers (improved elastic properties)

Figure 8.3 Effect of molecular weight on length of plateau (16). PB = polybutadiene.
2.3. The Rubbery Plateau Region

- The effect of crystallinity:
- If a polymer is semicrystalline, the dashed line in Figure 8.2 is followed.
- The height of the plateau is governed by the degree of crystallinity.
- This is so because of two reasons: first, the crystalline regions tend to behave as a filler phase, and second, because the crystalline regions also behave as a type of physical crosslink, tying the chains together.
2.4. The Rubbery Flow Region

- Rubber elasticity and flow properties.
- Rubber in short time experiments.
- Chain assemblies flow in long term experiments.
- This region does not appear for cross-linked polymers until decomposition temp. is reached.
2.4. The Rubbery Flow Region

A striking example of the rate dependence of these viscoelastic properties is furnished by Silly Putty. Slowly pulling on two parts of the Silly Putty stretches it apart until it very slowly separates. Placing the Silly Putty on a table and hitting it with a hammer will shatter it.

Slowly
Deformed

Rapidly
Deformed
The brittle fracture via scanning electron microscopy (SEM). The fracture surface exhibited classic brittle crack features, including a generally smooth morphology with hackle marks. The fracture surface contained features normally observed on amorphous thermoplastic materials. Amorphous thermoplastics are used at temperatures below their glass transition temperature, and as such the similarity in fracture surface morphology between such materials and the subambient rubber represents the glassy, brittle state of the material, and not the composition of the material.
2.5. The Liquid Flow Region

- Polymer flows easily
- A composite modulus is observed for semi-crystalline polymers. The amorphous portions go through the glass transition, but the crystalline portion remains hard.
3. The Effect of Plasticizers

- Plasticizers are nonvolatile molecules dissolved in polymer (soften it).
- The glass-transition temp is lowered and rubbery plateau modulus is lowered.
- In semi-crystalline polymers lower the melting point or lower the crystallinity.

Adding a small amount of plasticizer to PVC can lower the $T_g$ to –40 degrees C. This addition renders the PVC a soft, flexible material at room temperature, ideal for applications such as garden hoses. A plasticized PVC hose can, however, become stiff and brittle in winter. In this case, as in any other, the relation of the $T_g$ to the ambient temperature is what determines the choice of a given material in a particular application.
4. Methods Of Measuring Transitions

• Definitions of the Terms “Transition,” “Relaxation,” and “Dispersion”.
  – The term “transition” refers to a change of state induced by changing the temperature or pressure.
  – The term “relaxation” refers to the time required to respond to a change in temperature or pressure. It also implies some measure of the molecular motion, especially near a transition condition.
  – The term “dispersion” refers to the emission or absorption of energy—that is, a loss peak—at a transition. In practice, the literature sometimes uses these terms somewhat interchangeably.
4. Methods Of Measuring Transitions

Figure 8.5  Idealized variations in volume, $V$, enthalpy, $H$, and storage shear modulus, $G'$ as a function of temperature. Also shown are $\alpha$, the volume coefficient of expansion, and $C_p$, the heat capacity, which are, respectively, the first derivatives of $V$ and $H$ with respect to temperature, and the loss shear modulus, $G''$ (8).
### 4.1. Experimental Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Representative Instrumentation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dilatometry</strong></td>
<td></td>
</tr>
<tr>
<td>Volume-temperature</td>
<td>Polymer confined by mercury (home made)</td>
</tr>
<tr>
<td>Linear expansivity</td>
<td>TMS + computer</td>
</tr>
<tr>
<td><strong>Thermal</strong></td>
<td></td>
</tr>
<tr>
<td>DSC</td>
<td>Modulated DSC 2920 (TA Instruments)</td>
</tr>
<tr>
<td>DTA</td>
<td>DuPont 900</td>
</tr>
<tr>
<td>Calorimetric, $C_p$</td>
<td>Perkin-Elmer modulated DSC, Pyris 1</td>
</tr>
<tr>
<td><strong>Mechanical</strong></td>
<td></td>
</tr>
<tr>
<td>Static</td>
<td>Gehman, Clash-Berg</td>
</tr>
<tr>
<td>Dynamic</td>
<td>Rheometrics RDA2 (Rheometrics Scientific)</td>
</tr>
<tr>
<td><strong>Torsional Braid Analysis</strong></td>
<td>TBA (Plastics Analysis Instruments)</td>
</tr>
<tr>
<td><strong>Dielectric and magnetic</strong></td>
<td></td>
</tr>
<tr>
<td>Dielectric loss</td>
<td>DuPont Dielectric Analyzer, DEA 2920</td>
</tr>
<tr>
<td>Broad-line NMR</td>
<td>Joel JNH 3H60 Spectrometer</td>
</tr>
<tr>
<td>Melt viscosity</td>
<td>Weissental Rheogoniometer</td>
</tr>
<tr>
<td>TGA</td>
<td>HiRes TGA 2950 (TA Instruments)</td>
</tr>
</tbody>
</table>
4.1.1. Dilatometry Studies

A mercury-based dilatometer. Bulb A contains the polymer (about 1 g), capillary B is for recording volume changes (Hg + polymer), G is a capillary for calibration, sealed at point F. After packing bulb A, the inlet is constricted at E, C contains weighed mercury to fill all dead space, and D is a second constriction.
Figure 8.9 Dilatometric studies on branched poly(vinyl acetate) (23).
4.1.2. DSC Method

Some measurements that the DSC can make are:
- Glass Transitions
- Melting and Boiling Points
- Crystallisation time and temperature
- Percent Crystallinity
- Heats of Fusion and Reactions
- Specific Heat and Heat Capacity
- Oxidative Stability
- Rate and Degree of Cure
- Reaction Kinetics
- Percent Purity
- Thermal Stability
4.1.2. DSC Method

Figure 8.10 Example of a differential scanning calorimetry trace of poly(ethylene terephthalate-stat-p-oxbenzoate), quenched, reheated, and cooled at 0.5 K/min through the glass transition, and reheated for measurement at 10 K/min (28). \( T_g \) is taken at the temperature at which half the increase in heat capacity has occurred. The width of the glass transition is indicated by \( \Delta T \). Note that \( \Delta H_c \) and \( \Delta H_f \) are equal in magnitude but opposite in sign.
The thermal behavior of an EPDM rubber mixture was measured between \(-125\) and \(160\)°C at 10 K/min. The glass transition was detected at \(-52.5\)°C. The melting above the glass transition (peak temperature at \(31.4\)°C) is typical for the behavior of a sequence-type EPDM. The further endothermal effects (at \(98.6\) and \(110\)°C) are due to the evaporation of processing agents. The presentation in the separate window clearly shows the high sensitivity of the DSC 200 *F3 Maia* even for small energetic effects (0.43 J/g).
TMA / DSC Results

-57.13°C(I)  
-0.05473W/g  
25.00°C  
Alpha = 212.μm/m°C

-100.00°C  
Alpha = 64.3μm/m°C  
-51.05°C
4.1.3. Mechanical Methods

- Because of softening, mechanical methods are important
- Static or quasistatic methods (stress relaxation)
- Dynamic methods (dynamic mechanical spectroscopy, torsional braid analysis TBA)
4.1.4. A DMS (DMA) Study

Figure 8.11 Dynamic mechanical spectroscopy on polystyrene cross-linked with 2% divinyl benzene. Data taken with a Rheovibron at 110 Hz. Note that the tan δ peak occurs at a slightly higher temperature than the $E''$ peak (30). Experiment run by J. J. Fay, Lehigh University.
4.1.4. A DMS (DMA) Study

Polyisoprene
4.1.5. A TBA Study

**Definition:** A method of performing torsional tests on small amounts of materials in states in which they cannot support their own weight, e.g., liquid thermosetting resins. A glass braid is impregnated with a solution of the material to be tested. After evaporation of the solvent, the impregnated braid is used as a specimen in an apparatus which measures motion of the oscillating braid as it is being heated at programmed rate in a controlled atmosphere.
4.1.5. A TBA Study
4.1.6. Dielectric and Magnetic Methods
Dielectric methods are using sample as an electric capacitor.

Figure 8.13 Mechanical and dielectric loss tangent $\tan \delta$ and NMR absorption line width $\delta H$ (maximum slope, in gauss) of polytrifluorochloroethylene (Kel-F) (40).
4.1.7. Magnetic Methods (Using NMR)

Figure 8.14  Broad-line NMR spectra of a cured epoxy resin. (a) Broad line at 291 K; (b) motionally narrowed line at 449 K ($T_g + 39$ K) (38).
Other Transitions

• As the temperature of a polymer is lowered continuously, the sample may exhibit several second-order transitions.

• By custom, the glass transition is designated the as $\alpha$ transition, and successively lower temperature transitions are called the $\beta$, $\gamma$, . . . transitions.

• One important second-order transition appears above $T_g$, designated the $T_{ll}$ (liquid–liquid) transition.

• *If the polymer* is semicrystalline, it will also melt at a temperature above $T_g$. 
The Schatzki Crankshaft Mechanism:  
a) *Main-Chain Motions*

- There appear to be two major mechanisms for transitions in the glassy state: Main chain and Side chain Motions.

Schatzki’s crankshaft motion requires at least four —CH2— groups in succession. As illustrated, for eight —CH2— groups, bonds 1 and 7 are collinear and intervening —CH2— units can rotate in the manner of a crankshaft.
The transition of polyethylene occurring near -120°C is thought to involve the Schatzki mechanism.
b) Side-Chain Motions

• Many polymers have considerable side-chain “foliage,” and these groups can, of course, have their own motions.

• A major difference between main-chain and side-chain motions is the toughness imparted to the polymer.
• Low-temperature main-chain motions act to absorb energy much better than the equivalent side-chain motions, in the face of impact blows. When the main-chain motions absorb energy under these conditions, they tend to prevent main-chain rupture.
The $T_{\parallel}$ Transition

• The $T_{\parallel}$ transition occurs above the glass transition and is thought to represent the onset of the ability of the entire polymer molecule to move as a unit.

• Although there is much evidence supporting the existence of a $T_{\parallel}$, it is surrounded by much controversy.

• The observed (in TBA analysis) $T_{\parallel}$ transition may be related to reptation.
ANIONIC POLYSTYRENE
$M_n = 20,200$

$T_g = 38\, K\ (0.6\, Hz)$

HELUM ATMOSPHERE
$\Delta T/\Delta t = \pm 1.5^\circ C/min.$

PREHISTORY (DRYING): $25^\circ C \rightarrow 200^\circ C$
EXPERIMENT: $200^\circ C \rightarrow 195^\circ C \rightarrow 200^\circ C$
DATA SHOWN: $200^\circ C \rightarrow 80^\circ C$
$80^\circ C \rightarrow 200^\circ C$
Many polymers show evidence of several transitions besides $T_g$.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Transitions</th>
<th>Polystyrene Mechanism</th>
<th>General Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>433 K (160°C)</td>
<td>$T_{ll}$</td>
<td>Liquid$_1$ to liquid$_2$</td>
<td>Boundary between rubber elasticity and rubbery flow states</td>
</tr>
<tr>
<td>373 K (100°C)</td>
<td>$T_g$</td>
<td>Long-range chain motions, onset of reptation</td>
<td>Cooperative motion of several Kuhn segments, onset of reptation</td>
</tr>
<tr>
<td>325 K (50°C)</td>
<td>$\beta$</td>
<td>Torsional vibrations of phenyl groups</td>
<td>Single Kuhn segment motion</td>
</tr>
<tr>
<td>130 K</td>
<td>$\gamma$</td>
<td>Motion due to four carbon backbone moieties</td>
<td>Small-angle torsional vibrations, 2–3 mers</td>
</tr>
<tr>
<td>38–48 K</td>
<td>$\delta$</td>
<td>Oscillation or wagging of phenyl groups</td>
<td>Small-angle vibrations, single mer</td>
</tr>
</tbody>
</table>

The onset of de Gennes reptation is probably associated with $T_g$, the motions being experimentally identified at $T_g + 20^\circ C$. 
5. Theories of Glass Transition

- The Free-Volume Theory
- The Kinetic Theory
- Thermodynamic Theory
5.1. The Free-Volume Theory

Figure 8.21 A quasi-crystalline lattice exhibiting vacancies, or holes. Circles represent molecules; arrow indicates molecular motion.
The important point is that molecular motion cannot take place without the presence of holes. These holes, collectively, are called free volume.
5.1.1. Iso-Free Volume State

**Fox and Flory Eq.** In 1950 Fox and Flory (74) studied the glass transition and free volume of polystyrene as a function of molecular weight and relaxation time. For infinite molecular weight, they found that the specific free volume, \( v_f \), could be expressed above \( T_g \) as:

\[
v_f = K + (\alpha_R - \alpha_G)T
\]

\( v_f \) = specific free volume, \( K \) is related to free volume at \( 0^\circ K \), \( \alpha_R \) and \( \alpha_G \) cubic expansion in rubbery and glassy state.

They concluded that (a) below \( T_g \) the *local* conformational arrangement of the polymer segments was independent of both molecular weight and temperature and (b) the glass transition temperature was an iso–free-volume state.
5.1.1. Iso-Free Volume State

Simha and Boyer then postulated that the free volume at $T = T_g$ should be defined as

$$v - (v_{0,R} + \alpha_G T) = v_f$$
Figure 8.22  A schematic diagram illustrating free volume as calculated by Simha and Boyer.
\[ \nu - (\nu_{0,R} + \alpha_G T) = \nu_f \]

\[ \nu = \nu_{0,R} + \alpha_R T \]

\[ (\alpha_R - \alpha_G)T_g = K_1 \]

\[ K_1 = (\alpha_R - \alpha_G)T_g = 0.113 \]
Table 8.7 Glass transition temperature as an iso-free-volume state (71)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$, K</th>
<th>$\alpha_G \times 10^4$ K$^{-1}$</th>
<th>$\alpha_R \times 10^4$ K$^{-1}$</th>
<th>$\alpha_R T_g$</th>
<th>$(\alpha_R - \alpha_G)$</th>
<th>$(\alpha_R - \alpha_G)T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>143</td>
<td>7.1</td>
<td>13.5</td>
<td>0.192</td>
<td>7.4</td>
<td>0.105</td>
</tr>
<tr>
<td>Poly(dimethyl siloxane)</td>
<td>150</td>
<td>—</td>
<td>12</td>
<td>0.180</td>
<td>9.3</td>
<td>0.140</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>160</td>
<td>3.0</td>
<td>8.3</td>
<td>0.133</td>
<td>7.0</td>
<td>0.112</td>
</tr>
<tr>
<td>Polybutadiene</td>
<td>188</td>
<td>—</td>
<td>7.8</td>
<td>0.147</td>
<td>5.8</td>
<td>0.109</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>199.4</td>
<td>—</td>
<td>6.18</td>
<td>0.123</td>
<td>4.70</td>
<td>0.094</td>
</tr>
<tr>
<td>Hevea rubber</td>
<td>201</td>
<td>—</td>
<td>6.16</td>
<td>0.124</td>
<td>4.1</td>
<td>0.082</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>213</td>
<td>—</td>
<td>8.02</td>
<td>0.171</td>
<td>6.04</td>
<td>0.129</td>
</tr>
<tr>
<td>Poly(vinylidene chloride)</td>
<td>256</td>
<td>—</td>
<td>5.7</td>
<td>0.146</td>
<td>4.5</td>
<td>0.115</td>
</tr>
<tr>
<td>Poly(methyl acrylate)</td>
<td>282</td>
<td>—</td>
<td>5.6</td>
<td>0.158</td>
<td>2.9</td>
<td>0.082</td>
</tr>
<tr>
<td>Poly(vinyl acetate)</td>
<td>302</td>
<td>2.1</td>
<td>5.98</td>
<td>0.18</td>
<td>3.9</td>
<td>0.118</td>
</tr>
<tr>
<td>Poly(4-methyl pentene-1)</td>
<td>302</td>
<td>3.4</td>
<td>7.61</td>
<td>0.23</td>
<td>3.78</td>
<td>0.114</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>355</td>
<td>2.2</td>
<td>5.2</td>
<td>0.185</td>
<td>3.1</td>
<td>0.110</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>373</td>
<td>2.0</td>
<td>5.5</td>
<td>0.205</td>
<td>3.0</td>
<td>0.112</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>378</td>
<td>2.6</td>
<td>5.1</td>
<td>0.182</td>
<td>2.80</td>
<td>0.113</td>
</tr>
</tbody>
</table>


Note: The quantity $\alpha$ represents the volume coefficient of expansion. The linear coefficients of expansion are approximately $1/3$ of the volume coefficients of expansion. The quantities $\alpha_G$ (determined at 20°C) and $\alpha_R$ represent the glassy and rubbery states, respectively, the former being a typical value for the polymer (semicrystalline for polyethylene and polytetrafluoroethylene) while the latter is calculated for the 100% amorphous polymer. However, the quantities $\alpha_R - \alpha_G$ and $(\alpha_R - \alpha_G)T_g$ are calculated on the basis of 100% amorphous polymer.
5.1.2. The WLF Equation (Williams-Landel-Ferry)

\[
\log \left( \frac{\eta}{\eta_g} \right) = -\frac{B}{2.303 f_0} \left[ \frac{(T - T_g)}{f_0/\alpha_f + (T - T_g)} \right]
\]

\[
\frac{B}{2.303 f_0} = 17.44
\]

\[
\frac{f_0}{\alpha_f} = 51.6
\]

\(B\), a constant, \(f_0\) fractional free volume at \(T_g\), \(\alpha_f\) expansion coefficient of free volume
Suppose a polymer has a glass transition temperature of 0°C. At 40°C, it has a melt viscosity of $2.5 \times 10^5$ poises (P) ($2.5 \times 10^4$ Pa·s). What will its viscosity be at 50°C?

First calculate $\eta_g$:

$$\log \left( \frac{\eta}{\eta_g} \right) = -\frac{17.44(T - T_g)}{51.6 + (T - T_g)}$$

$$\log \eta_g = \log 2.5 \times 10^5 + \frac{17.44(313 - 273)}{51.6 + (313 - 273)}$$

$$\log \eta_g = 13.013$$

Polymers often have melt viscosities near $10^{13}$ P at their glass transition temperature, $1.03 \times 10^{13}$ P in this case.
Now calculate the new viscosity:

\[
\log \eta = 13.013 - \frac{17.44(323 - 273)}{51.6 + (323 - 273)}
\]

\[
\eta = 2.69 \times 10^4 \text{ Pa} \quad \text{or} \quad 2.69 \times 10^3 \text{ Pa} \cdot \text{s}
\]

Thus a 10°C increase in temperature has decreased the melt viscosity by approximately a factor of 10 in this range. The WLF equation can be used to calculate shift factors (Section 8.6.1.2), failure envelopes (Section 11.2.5.2), and much more.
5.2. The Kinetic Theory

\( T_g \) values obtained for a polymeric systems depends on experiment time scale, showing that free-volume theory is also Kinetic nature. Slower experiment results in lower \( T_g \)

\[
\log A_T = \log \left( \frac{t}{t_g} \right) = -\frac{17.44(T - T_g)}{51.6 + T - T_g}
\]

if the time frame of an experiment is decreased by a factor of 10 near \( T_g \),

\[
\lim_{T \to T_g} \left( \frac{\log A_T}{T - T_g} \right) = -0.338
\]

\[
\ln \left( \frac{\eta}{\eta_0} \right) = \ln A_T = \ln \left( \frac{t}{t_0} \right)
\]

\[
T - T_g = \frac{-1.0}{-0.338} = 3.0
\]
5.3. Thermodynamic Theory

What about infinite time allotted to establish a quiet equilibrium?

The Gibbs and DiMarizo Theory: In infinitely slow experiments a glassy phase will eventually emerge whose entropy is negligibly higher than that of crystal.
Summary of the Theories

• Free-Volume theory provides relationships between coefficients of expansion below and above Tg and yields equations relating viscoelastic motion to the variables of time and temp.

• The kinetic theory defines Tg as the temp. at which the relaxation time for the segmental motions in the main polymer chain is of the same order of magnitude as the time scale of experiment.
Summary (contd.)

• The thermodynamic theory introduce the notion of equilibrium and the requirements for a true second-order transition.
Glass transition theory box scores

<table>
<thead>
<tr>
<th>Theory</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free-volume theory</td>
<td>1. Time and temperature of viscoelastic events related to $T_g$</td>
<td>1. Actual molecular motions poorly defined</td>
</tr>
<tr>
<td></td>
<td>2. Coefficients of expansion above and below $T_g$ related</td>
<td></td>
</tr>
<tr>
<td>Kinetic theory</td>
<td>1. Shifts in $T_g$ with time frame quantitatively determined</td>
<td>1. No $T_g$ predicted at infinite time scales</td>
</tr>
<tr>
<td></td>
<td>2. Heat capacities determined</td>
<td></td>
</tr>
<tr>
<td>Thermodynamic theory</td>
<td>1. Variation of $T_g$ with molecular weight, diluent, and cross-link density predicted</td>
<td>1. Infinite time scale required for measurements</td>
</tr>
<tr>
<td></td>
<td>2. Predicts true second-order transition temperature</td>
<td>2. True second-order transition temperature poorly defined</td>
</tr>
</tbody>
</table>
6. Effect of Molecular Weight on $T_g$

a) Linear Polymers

$$T_g = T_{g\infty} - \frac{K}{(\alpha_R - \alpha_G)M}$$

PS as an example:

$$T_g = 106 - \frac{2.1 \times 10^5}{M_n}, \text{ at low heating rates}$$

$$T_g = 100 - \frac{1.8 \times 10^5}{M_n}, \text{ at normal heating rates}$$
Figure 8.26  The glass transition temperature of polystyrene as a function of $1/M_n$ (102).
8. Effect of Copolymerization on $T_g$

(one phase system)

\[ \ln T_g = \frac{M_1 \Delta C_{p1} \ln T_{g1} + M_2 \Delta C_{p2} \ln T_{g2}}{M_1 \Delta C_{p1} + M_2 \Delta C_{p2}} \]

\[ T_g \approx \frac{M_1 \Delta C_{p1} T_{g1} + M_2 \Delta C_{p2} T_{g2}}{M_1 \Delta C_{p1} + M_2 \Delta C_{p2}} \]
If $\Delta C_{p1} \approx \Delta C_{p2}$

or

$$\frac{1}{T_g} = \frac{M_1}{T_{g1}} + \frac{M_2}{T_{g2}}$$

$$\ln T_g = M_1 \ln T_{g1} + M_2 \ln T_{g2}$$

$$T_g = M_1 T_{g1} + M_2 T_{g2}$$
Two-phase system

Figure 8.29 Dynamic mechanical behavior of polystyrene–block–polybutadiene–block–polystyrene, a function of the styrene–butadiene mole ratio (112,113).
9. Dependence of $T_g$ on Chemical Structure

- Factors that increase the energy required for onset of molecular motions Increase $T_g$
- Those that decrease energy requirements decrease $T_g$

<table>
<thead>
<tr>
<th>Table 8.11  Factors affecting $T_g$ (131)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase $T_g$</td>
</tr>
<tr>
<td>Intermolecular forces</td>
</tr>
<tr>
<td>High CED</td>
</tr>
<tr>
<td>Intrachain steric hindrance</td>
</tr>
<tr>
<td>Bulky, stiff side groups</td>
</tr>
</tbody>
</table>
10. Effect of Side Chains

11. Effect of Tacticity

Table 8.12  Effect of tacticity on the glass transition temperatures of polyacrylates and polymethacrylates (137)

<table>
<thead>
<tr>
<th>Side Chain</th>
<th>Polyacrylates</th>
<th>Polymethacrylates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Isotactic</td>
<td>Dominantly Syndiotactic</td>
</tr>
<tr>
<td>Methyl</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>Ethyl</td>
<td>-25</td>
<td>-24</td>
</tr>
<tr>
<td>n-Propyl</td>
<td>—</td>
<td>-44</td>
</tr>
<tr>
<td>Iso-Propyl</td>
<td>-11</td>
<td>-6</td>
</tr>
<tr>
<td>n-Butyl</td>
<td>—</td>
<td>-49</td>
</tr>
<tr>
<td>Iso-Butyl</td>
<td>—</td>
<td>-24</td>
</tr>
<tr>
<td>Sec-Butyl</td>
<td>-23</td>
<td>-22</td>
</tr>
<tr>
<td>Cyclo-Hexyl</td>
<td>12</td>
<td>19</td>
</tr>
</tbody>
</table>

$T_g$ (°C)
12. Definition of Elastomers, Plastics, Adhesives and Fibers

- **An Elastomer** is a cross-linked, amorphous polymer above its Tg. (A rubber Band)
- **Adhesive** is a linear or branched amorphous above its Tg. It must be able to flow on a molecular scale to grip surfaces.
- **A plastic** is usually below its Tg if its amorphous. Crystalline plastics may be either above or below their Tg’s.
- **Fibers** are always composed of crystalline polymers, their Tg is usually near to ambient temperature
End of Chapter 3