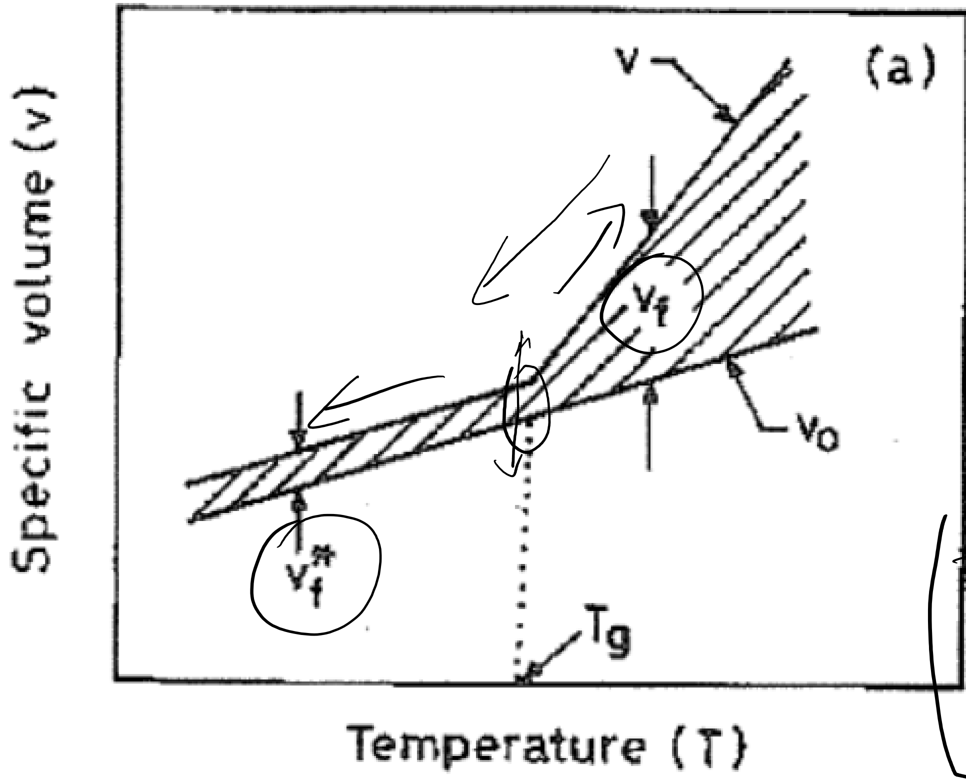
# TXL211
# Lecture 8




$$T_g = T_g^{\infty} - \frac{K}{M}$$

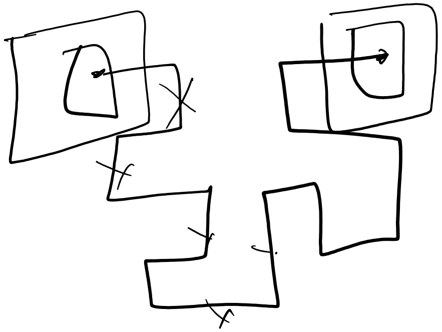
$$\boxed{T_g = C_5 - \frac{C_6}{M}} \uparrow$$

$$T_g = C_9 + \frac{C_{10}}{M_c} \downarrow$$

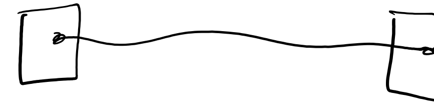
$$V = V_0 + V_f$$

$$V_f = V_f^* + (T - T_g)\left(\frac{\partial V}{\partial T}\right)$$

$$f_T = f_g + (T - T_g)\,\alpha_f$$



# Effect of Branching on Tg



$$T_g = T_{g,\infty} - K/M$$

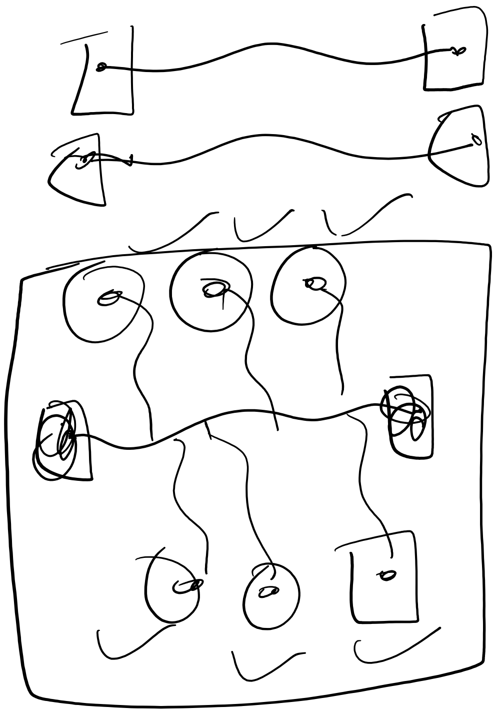
In a polymer sample of molecular weight $\overline{M}_n$ and density $\rho$ , the number of chains per unit volume is given by $\rho N_{Av}/\overline{M}_n$, where $N_{Av}$ is Avogadro's number, so the number of chain ends per unit volume is $\boxed{2\rho N_{Av}/\overline{M}_n}$.

If $\theta$ is the contribution of one chain end to the free volume then the total *fractional* free volume due to all chain ends, $f_c$, will be given by

$$f_c = 2\rho N_{Av}\theta/\overline{M}_n \quad (1)$$

$$f_c = \alpha_f(T_{g,\infty} - T_g) \quad (2)$$

① ② $f_c$



$$T_g = T_{g,\infty} - \frac{2\rho N_{Av}\theta}{\alpha_f \overline{M}_n}$$

$$T_g = T_g^{\infty} - \frac{K}{M}$$

$$T_g = T_{g,\infty} - \frac{y\rho N_{Av}\theta}{\alpha_f \overline{M}_n}$$

ACTUAL NO. OF BRANCHES $= y - 2$

# RESPONSE TIME

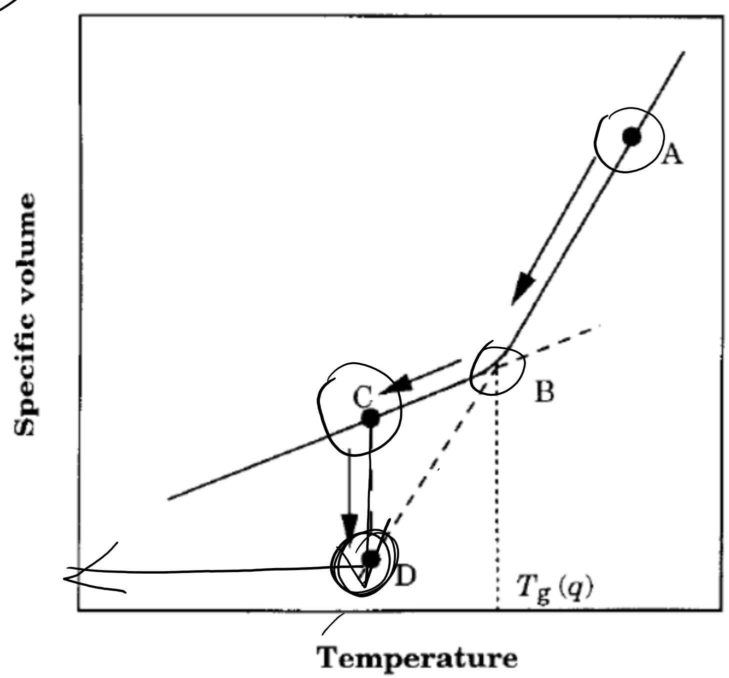
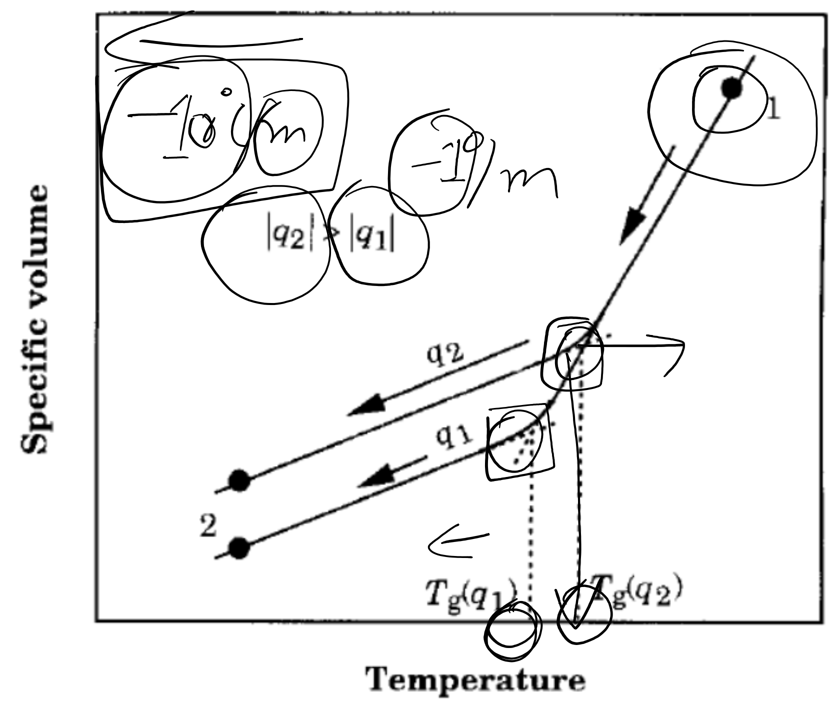
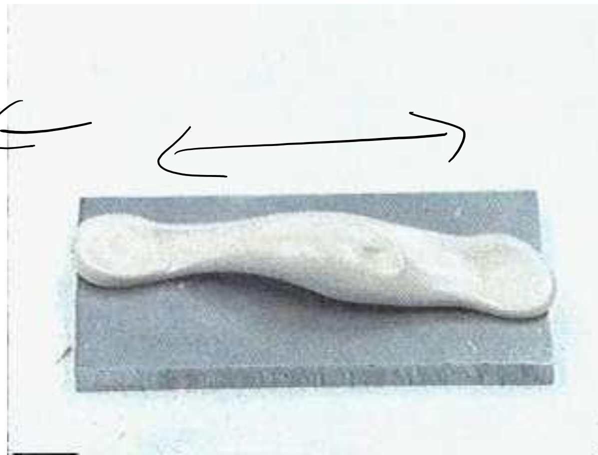
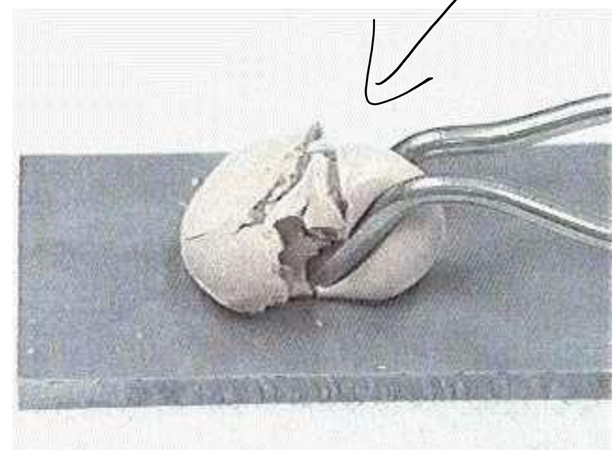



Illustration of the non-equilibrium nature of a glassy polymer.




Schematic curves showing the cooling rate dependence of the specific volume of a glass-forming wholly amorphous polymer.





**Slowly deformed**

**Rapidly deformed**

# Kinetic Theory

Predicts that the glass transition temperature is a purely kinetic phenomenon and that it appears when the response time of the system to reach equilibrium is of the same order as that of the time-scale of experiment.

$f$ = MOBILITY = $\eta$

$$\boxed{\eta = A \exp\left(\frac{B}{f}\right)}$$ DOOLITTLE EQ$^{N}$

WLF EQ$^{N}$

$$\log a_T = \frac{C_1(T - T_r)}{C_2 + T - T_r}$$

$a_T = \frac{\eta_T}{\eta_{T,r}} \approx \frac{T}{T_{T,r}}$

SHIFT FACTOR

$T_r = T_g$

$$\boxed{\log a_T = \frac{-17.44(T - T_g)}{51.6 + T - T_g}}$$ WLF EQ$^{N}$

WLF $\log a_T = \dfrac{C_1(T - T_r)}{C_2 + T - T_r}$

$$\eta = A \exp\left(\frac{B}{f}\right)$$

$$a_T = \frac{\exp\left(\frac{B}{f}\right)}{\exp\left(\frac{B}{f_r}\right)} = \exp\left(B\left(\frac{1}{f} - \frac{1}{f_r}\right)\right)$$

$T_r = T_g$

$f_r = f_g$

$$f = f_g + \alpha_f(T - T_g)$$

$$a_T = \exp\left(B\left(\frac{1}{f} - \frac{1}{f_g}\right)\right)$$

$$= \exp\left(B\left(\frac{1}{f_g + \alpha_f(T - T_g)} - \frac{1}{f_g}\right)\right)$$

$$= \exp\left(B\left(\frac{-\alpha_f(T - T_g)}{f_g(f_g + \alpha_f(T - T_g))}\right)\right)$$

$$= \exp\left(-\frac{B}{f_g}\left(\frac{\alpha_f(T-T_g)}{f_g+\alpha_f(T-T_g)}\right)\right)$$

$$= \exp\left(\frac{\left[-\frac{B}{f_g}\right](T-T_g)}{\left[\frac{f_g}{\alpha_f}\right]+T-T_g}\right)$$

$$\boxed{\log a_T \approx \frac{\left[\frac{-B}{2.303 f_g}\right](T-T_g)}{\left[\frac{f_g}{\alpha_f}\right]+T-T_g}}$$

2-5%

$$C_1 = -\frac{B}{2.303 f_g} = -17.44 \Rightarrow \boxed{f_g = 0.025} \quad (B=1)$$

$f_g$

$$C_2 = \frac{f_g}{\alpha_f} = 51.6\ \mathrm{K} \Rightarrow \alpha_f = \frac{f_g}{51.6} = \frac{0.025}{51.6} = \boxed{4.8\times10^{-4}\ \mathrm{K}^{-1}}$$

$\alpha_f$

WLF

The experimental value of $T_g$ depends on the time or frequency frame of the experiment. Calculate from the WLF equation the change that would be expected in the $T_g$ value if the time frame of an experiment is decreased by a factor of 100.

$$\log a_T = \frac{-17.44(T-T_g)}{51.6+T-T_g} \qquad a_T = \frac{1}{100}$$

$T \to T_g$

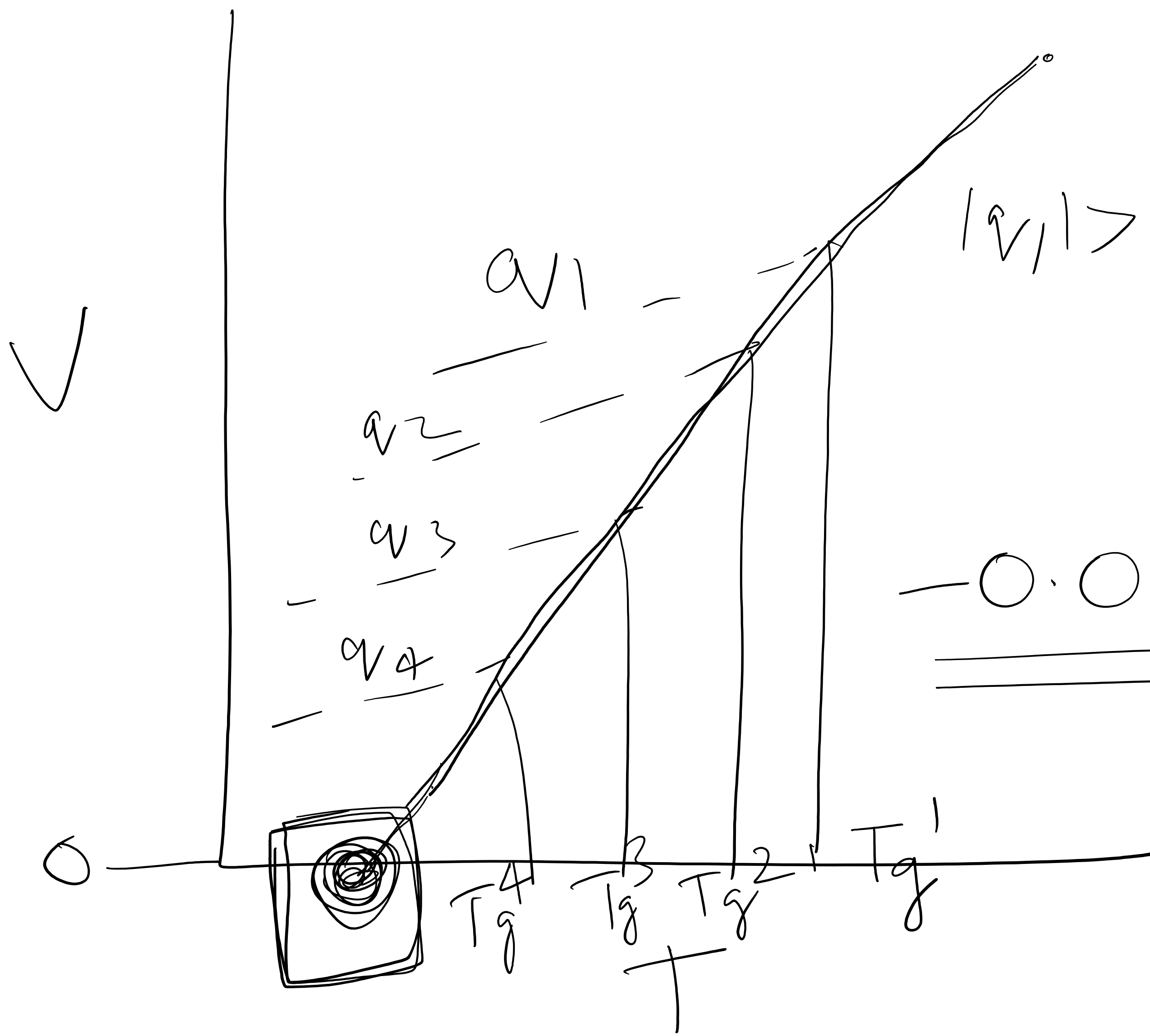
$$\lim_{T \to T_g}\left(\frac{\log a_T}{T - T_g}\right) = -17.44/51.6 = -0.338$$

Since the time frame of experiment is decreased by a factor of 100, the shift factor $a_T$ is 1/100. Therefore,

$$T - T_g = \frac{-2.0}{-0.338} \simeq 6°K$$

So the glass transition temperature would be raised by about 6°C. This is in agreement with experiment.

$$\frac{1}{10} \Rightarrow 3°C$$




$|q_1| > |q_2| > |q_3| > |q_4|$

$-0.001\,^\circ C/min$