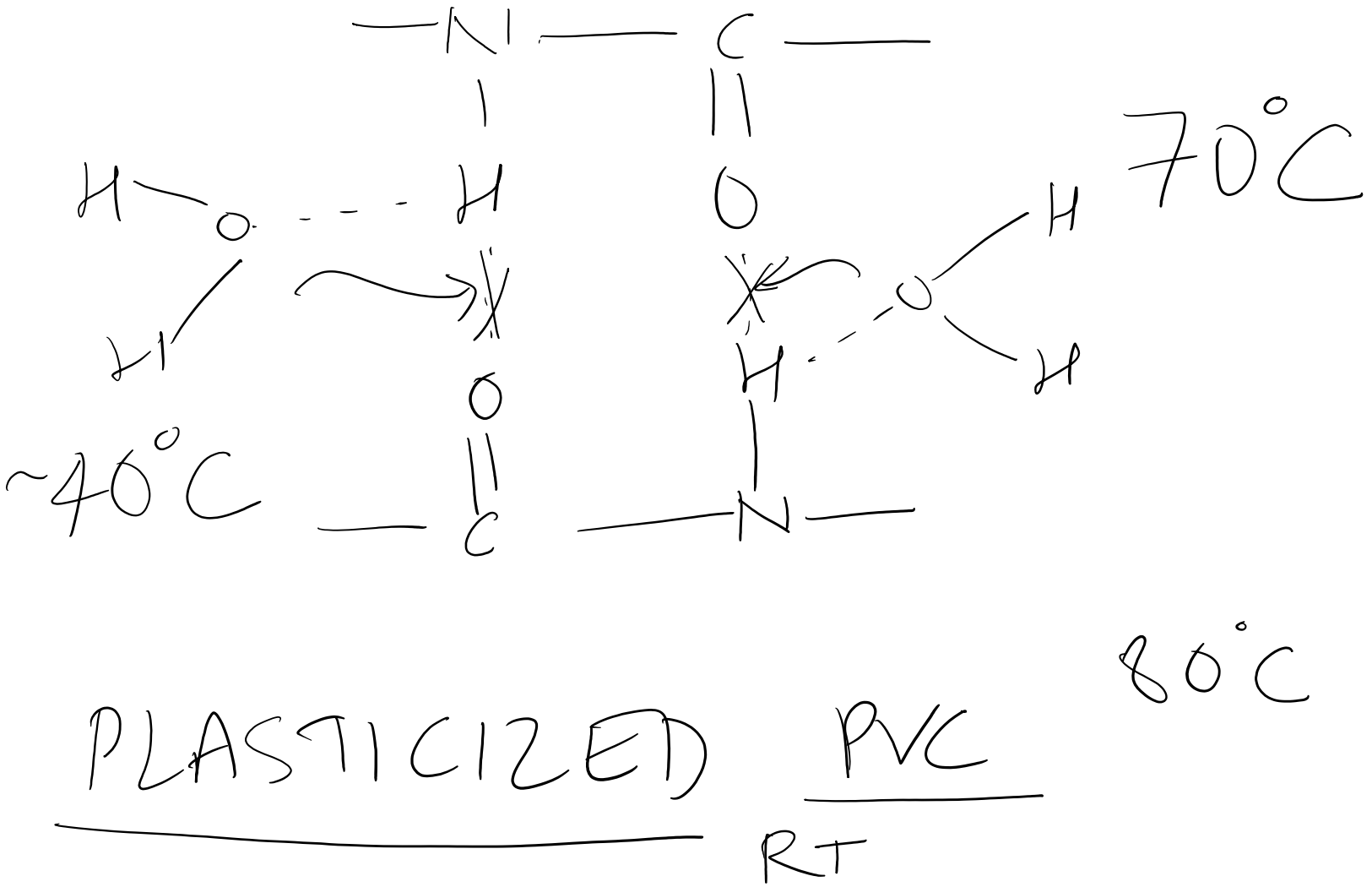
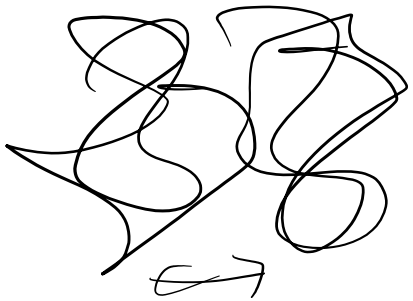
TXL211
Lecture 7

Factors affecting Tg

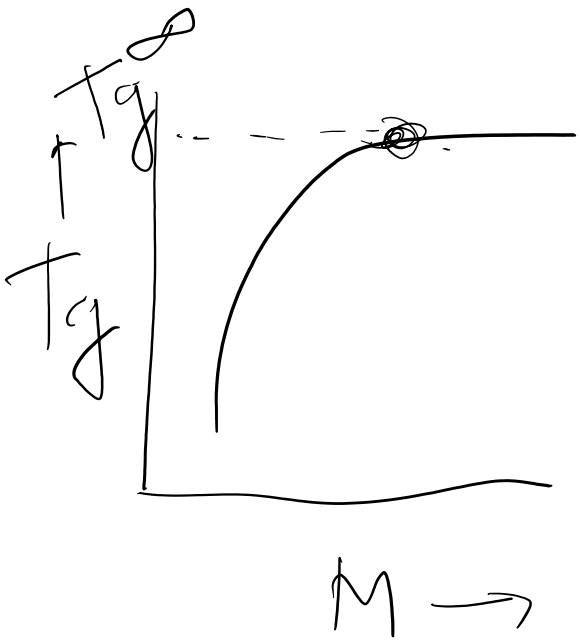
Plasticizer

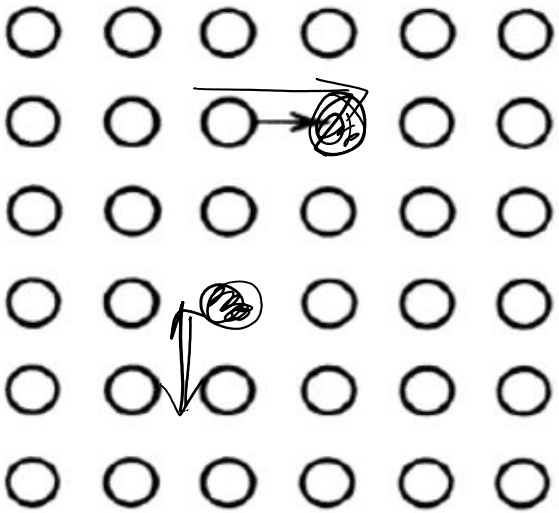


What is the effect of molecular weight and crosslinking on Tg?



1 MOLECULE
TgX





The Free Volume Theory

TOTAL VOLUME
= OCCUPIED VOLUME + FREE VOLUME

The concept of Free Volume

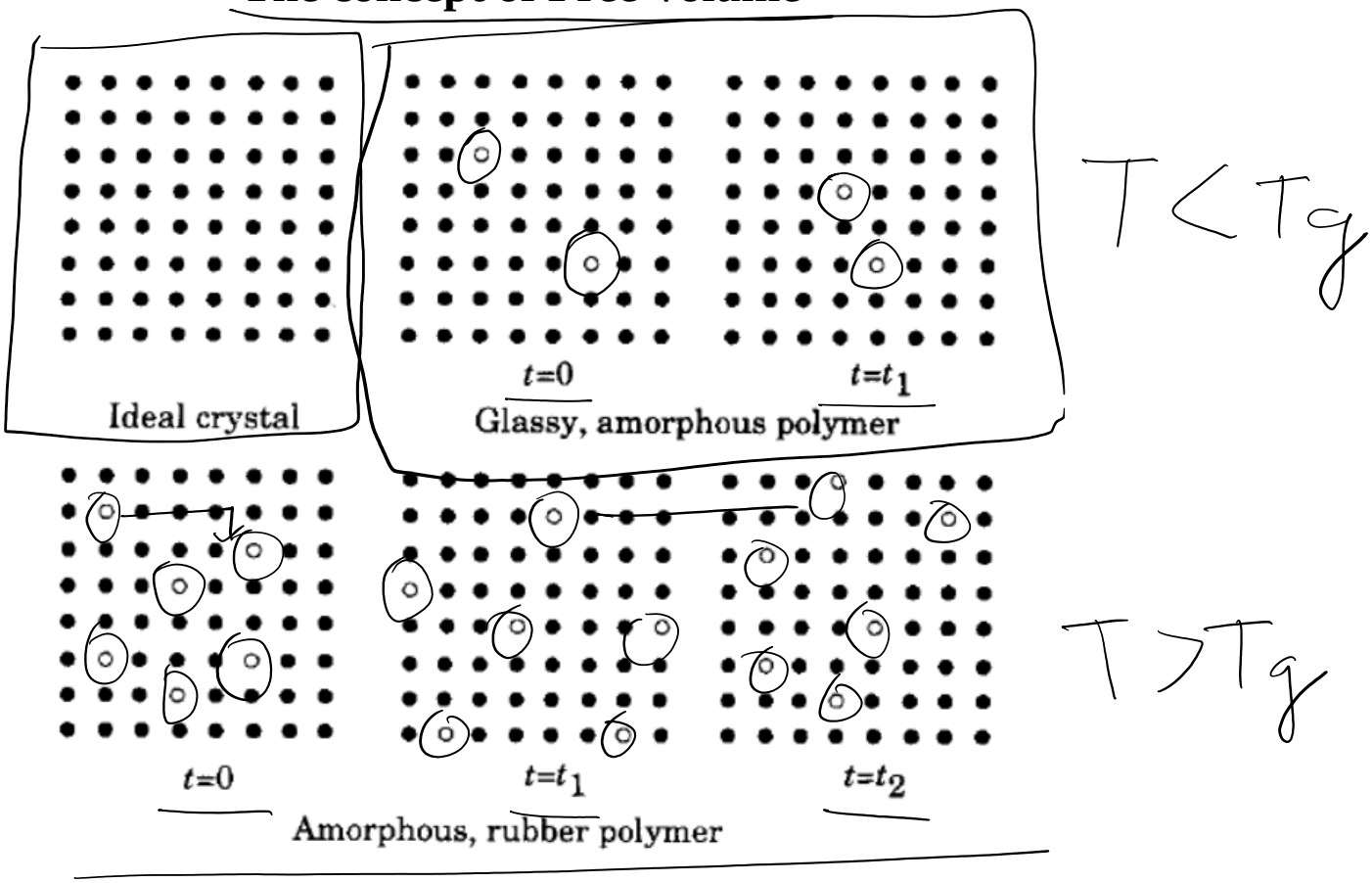
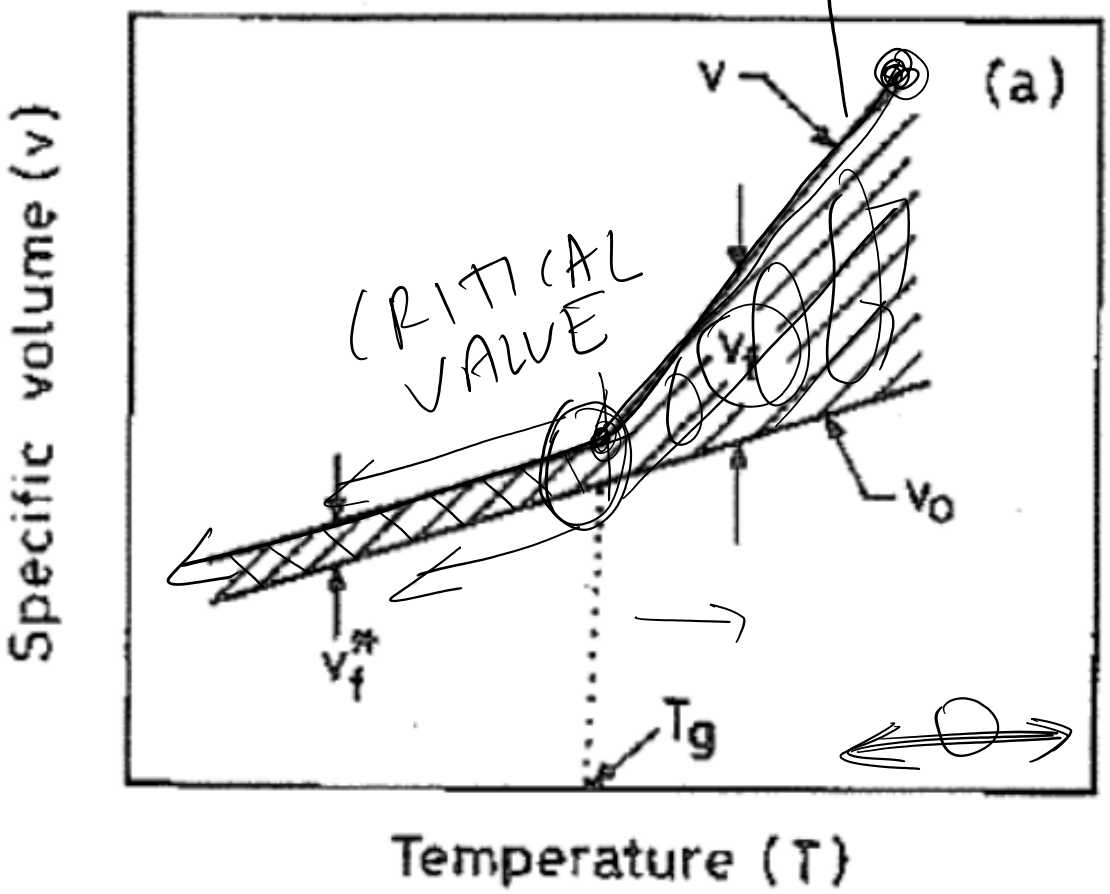


Illustration of the free volume concept. Occupied volume is marked by filled circles and free volume (hole) by open circles. Snapshots are taken at different times (t).

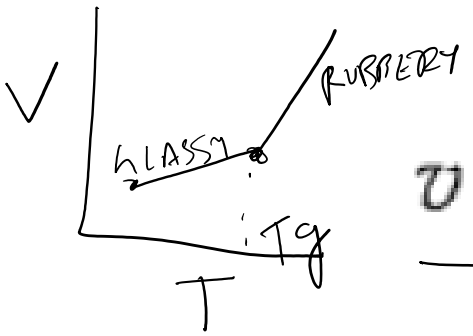
Molecular motion cannot take place without the presence of holes. These holes, collectively, are called free volume.

$V = V_0 + V_f$ FREE VOLUME THEORY

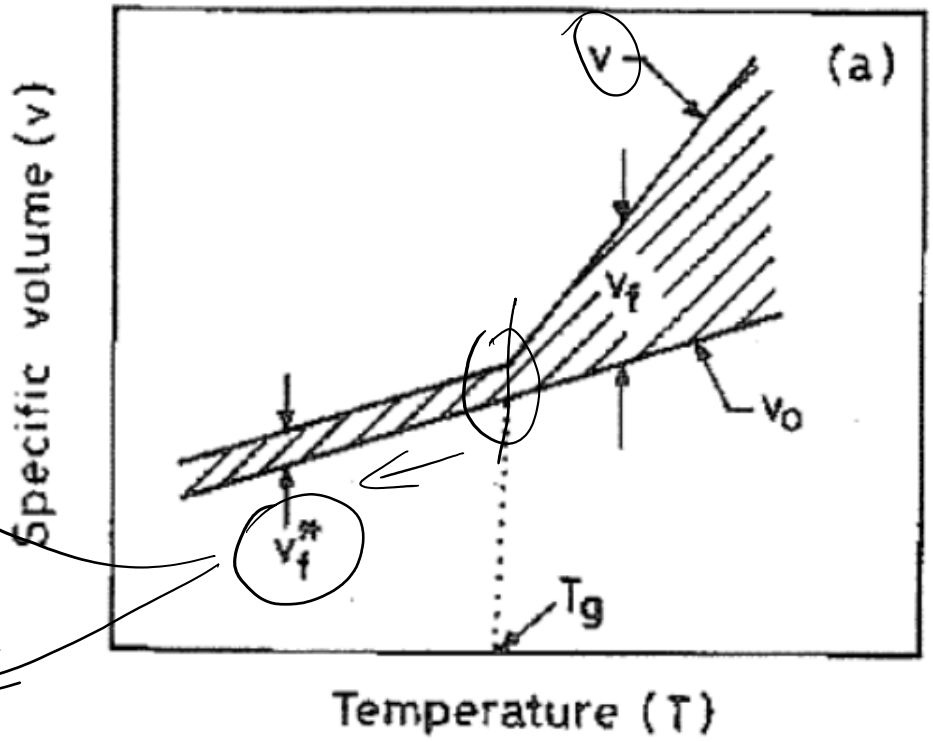


FRACTIONAL FREE VOLUME

$f = \frac{V_f}{V}$



$$v = v_0 + v_f$$



$f_g = \frac{v_f^*}{v}$

CONSTANT

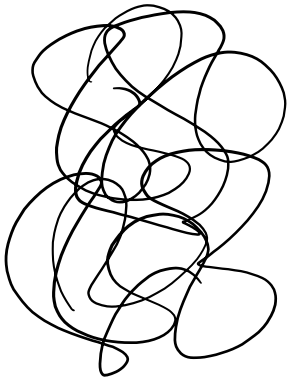
$T > T_g$

$$\Rightarrow v_f = \left[v_f^\star + (T - T_g)(\partial v/\partial T) \right] \frac{1}{v}$$

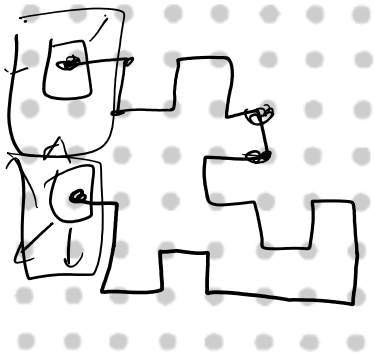
Dividing through by v gives

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

Effect of molecular weight on Tg

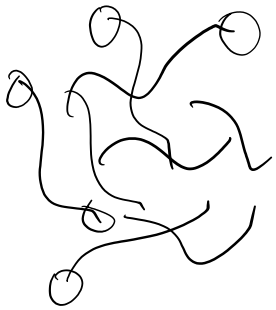


$$f = f^0 + \frac{C_2}{M}$$

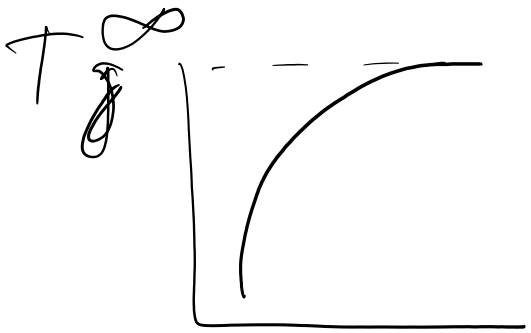


$$f \approx (C_3 + C_4 T) + \frac{C_2}{M}$$

$$f_e \propto \frac{1}{M} = \frac{C_2}{M}$$



$$f_g \approx C_3 + C_4 T_g + \frac{C_2}{M}$$

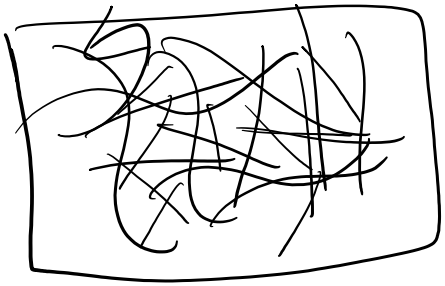


$$T_g \approx \frac{f_g - C_3}{C_4} - \frac{C_2}{C_4 M} = C_5 - \frac{C_6}{M}$$

Effect of crosslinking on Tg

$$f \approx f^0 - n_c C_7 = f^0 - \frac{C_8}{\bar{M}_c}$$

$$T_g \approx C_9 + \frac{C_{10}}{\bar{M}_c}$$



In a polymer which, prior to curing, has a molar mass of M, following glass transition equation is obtained:

$$T_g \approx C_4 - \frac{C_5}{\bar{M}} + \frac{C_9}{\bar{M}_c}$$

Isothermal Volume Recovery / Physical Aging

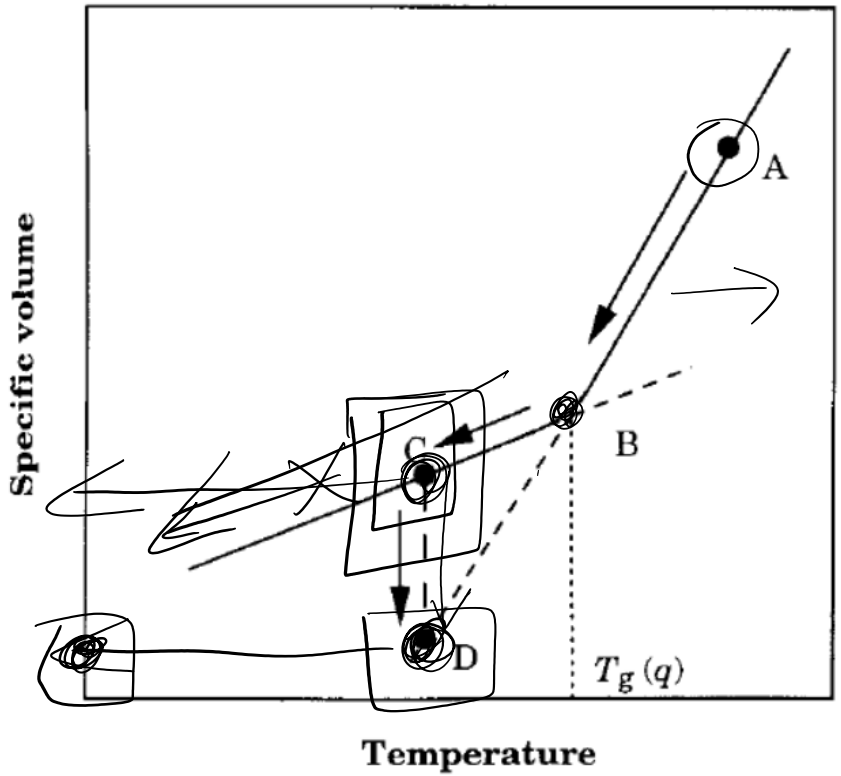
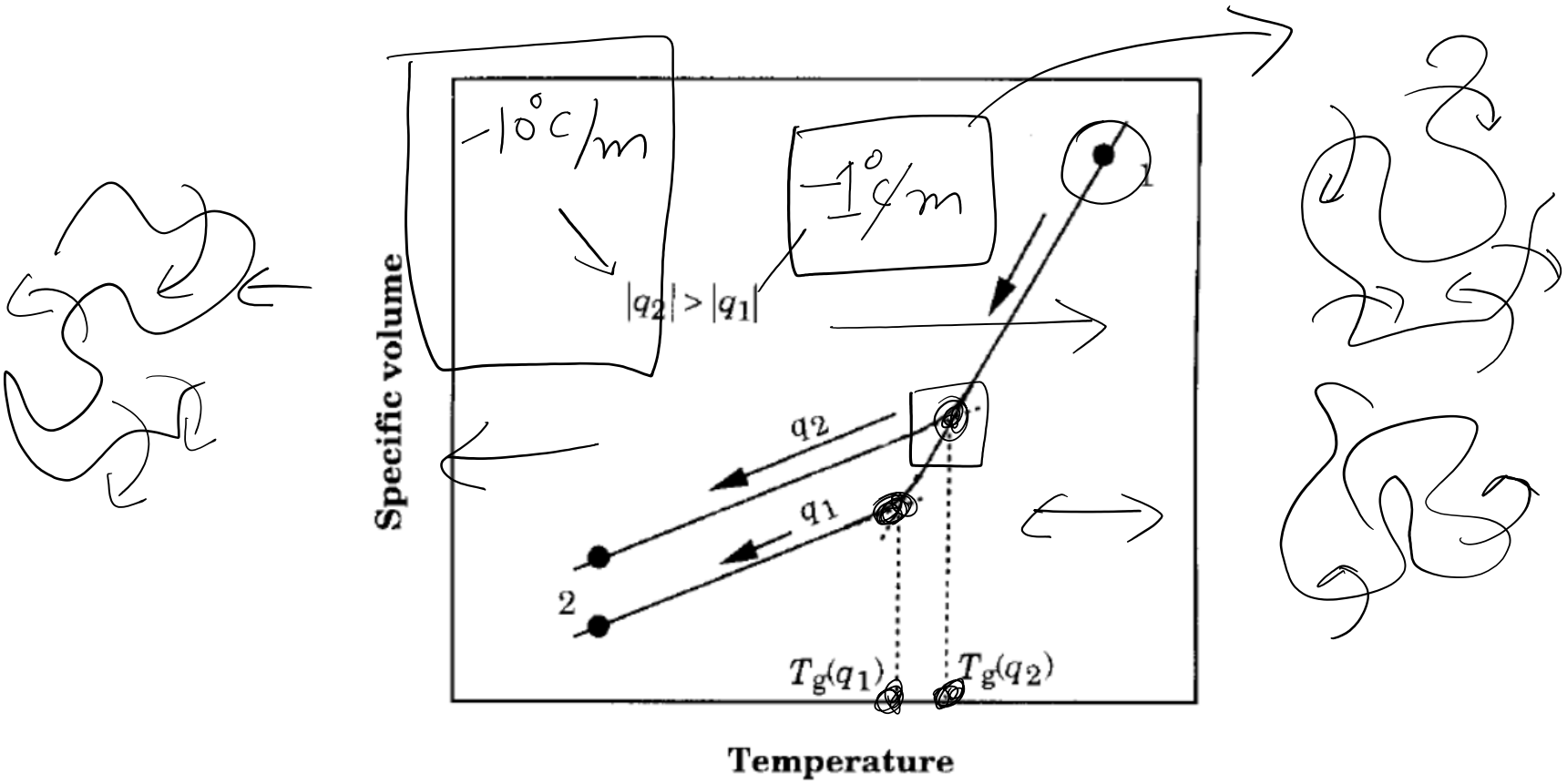


Illustration of the non-equilibrium nature of a glassy polymer.

Dependence of Tg on rate of cooling



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