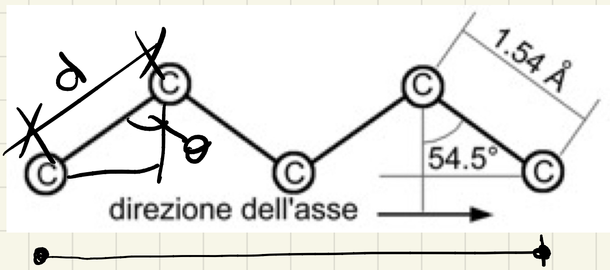
Lezione 8

## Struttura dei polimeri

- AMORFA ①
- SEMICRISTALLINA

Condizioni ①
- PRESENZA di GRUPPI LATERALI (ATATTICITÀ) → COMPOSIZIONE
- CATENE RAMIFICATE → CONFIGURAZIONE
- VELOCITÀ di RAFFREDDAMENTO

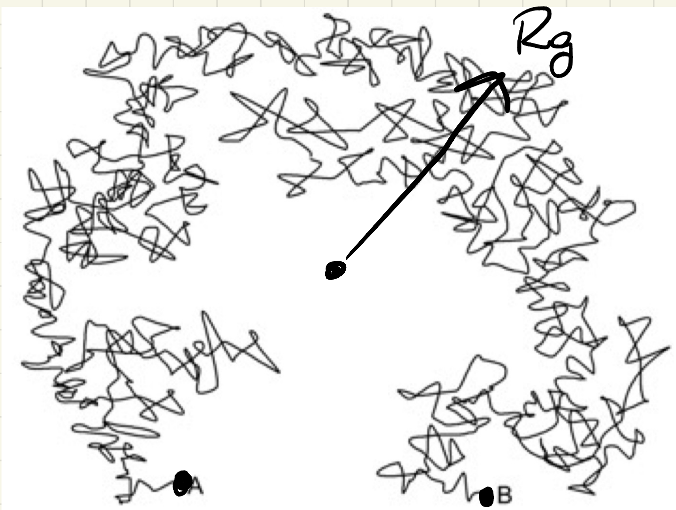
Condizioni ②
- ASSENZA di GRUPPI LATERALI (ISOTATTICO o SINDIOTATTICO)
- CATENE LINEARI
- BASSE VELOCITÀ di RAFFREDDAMENTO




$L = d \sin\theta \cdot N$

$L = 0.1 - 1\ \mu m$

RANDOM COIL




$L = d \sin\theta\, N^{1/2}$

(cammino libero)

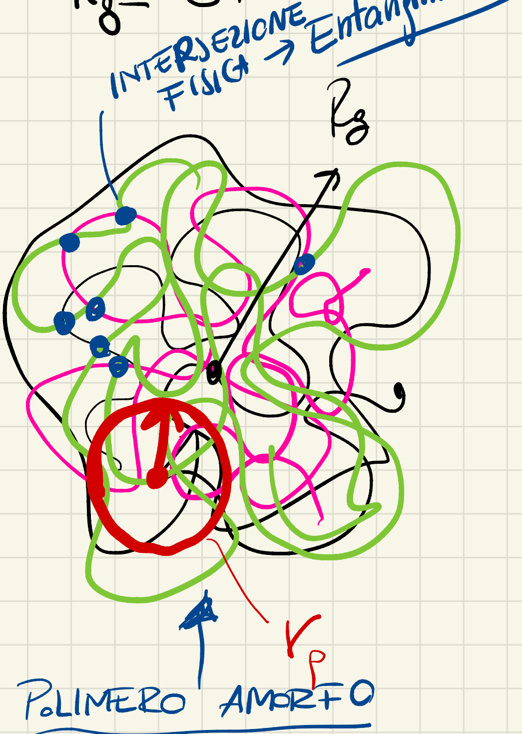
$$R_g \simeq 0.3 \sqrt{PM_n}$$

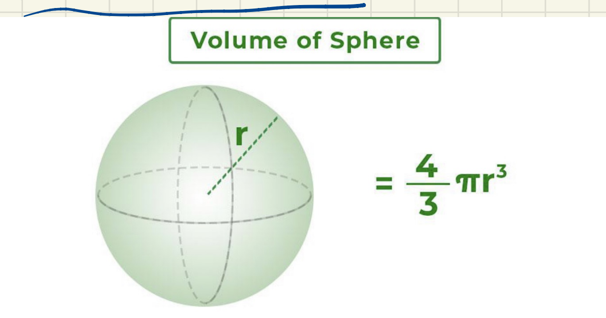
$R_g \simeq 1 - 10\ nm$

$PM_n = 10000\ g/mol$ (PS)

$L \simeq 750\ nm$

$R_g \simeq 3\ nm$




$\rho = 1\ g/cm^3$

$\rho = \frac{m}{V}$

$1g : 1cm^3 = \frac{10000g}{N_A} : V$

PM $\left[\frac{g}{mol}\right]$

$1\ mol \simeq 6 \times 10^{23}$

$1 : 1 = \frac{10^4}{6 \times 10^{23}} : V$

$V \simeq 10^{-18}\ cm^3$

$V = \frac{4}{3}\pi r^3$

$r = \sqrt[3]{\frac{10^{-18} \times 3}{4} \times \pi}$

$r < R_g$

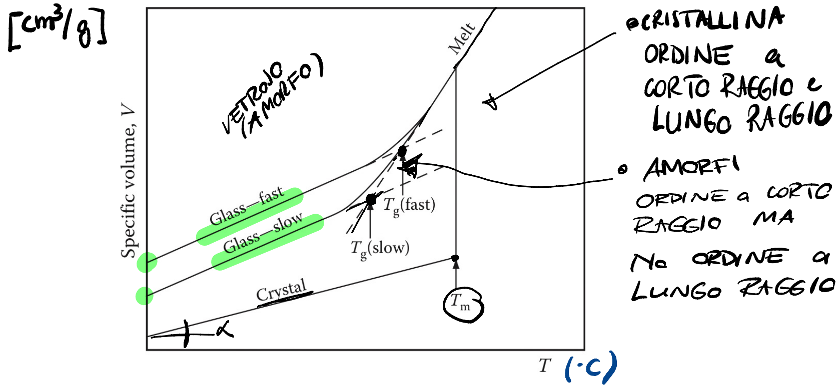
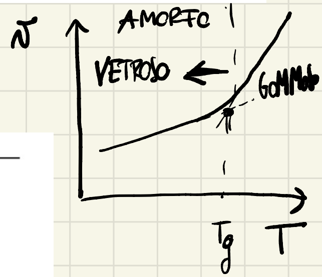
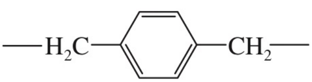
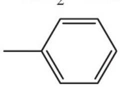



**FIGURE 16.2** Variation of the specific volume with temperature for different materials. Examples are shown for the formation of a glassy polymer, by either slow or fast cooling, and the melting of a crystalline material at a temperature $T_m$.




## TABLE 16.1
## Approximate Values of Glass Transition Temperature, $T_g$, for Various Polymers

| Repeat Unit | Polymer Name | $T_g$/°C |
|---|---|---|
| $-CH_2-CH_2-$ | Polyethylene | −130 to −10 |
| $-CH_2-CH_2-O-$ | poly(ethylene oxide) | −67 |
|  | poly(*p*-xylylene) | 80 |
| Vinyl polymers | Side group (X) | |
| $-CH_2-CHX-$ | $-CH_3$ | −23 |
| | $-CH_2-CH_3$ | −24 |
| | $-CH_2-CH_2-CH_3$ | −40 |
| | $-CH_2-CH(CH_3)_2$ | 30 |
| |  | 100 |
| | −Cl | 81 |
| | −OH | 85 |
| | −CN | 97 |

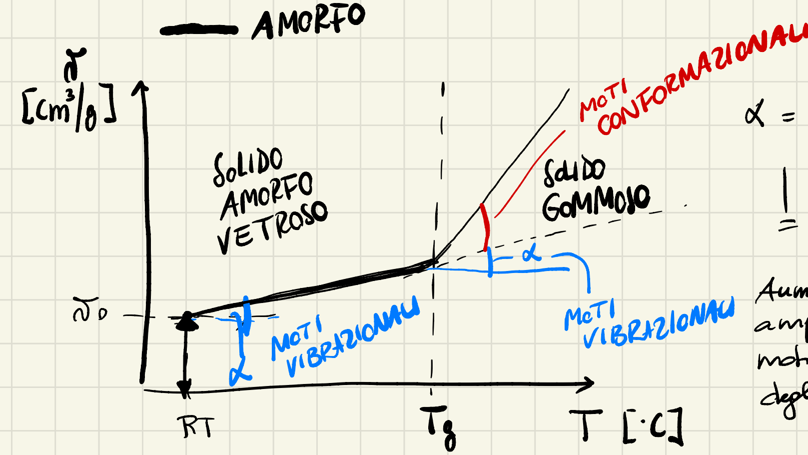
$\left( CH_2-CH_2 \right)_n$

$\left( CH_2-CH \right)_n$ with X

APPLICAZIONE a T > RT

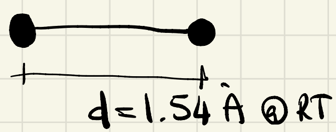
# TEMPERATURA di TRANSIZIONE VETROSA

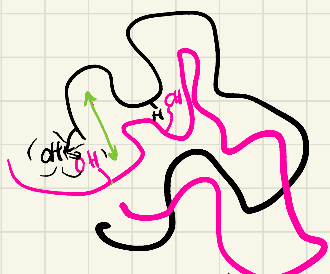
→ Temperatura in corrispondenza della quale sono possibili movimenti coordinati e continuativi di segmenti di catena

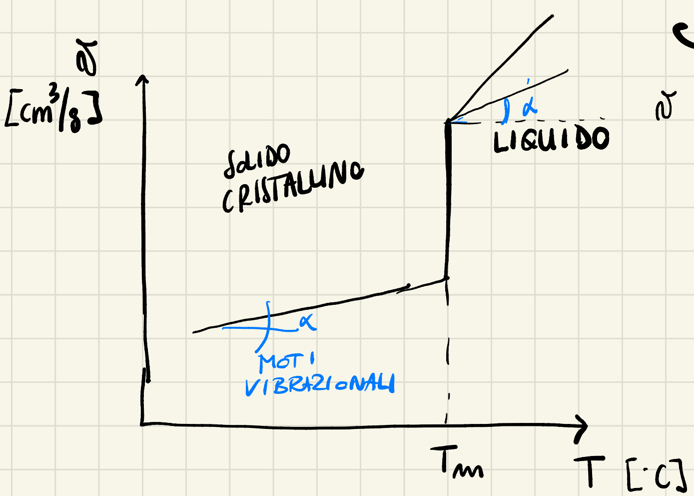



$\alpha$ = Coef. di dilatazione termica lineare $= \frac{\partial v}{\partial T}$ $[\cdot 10^{-6} \cdot °C^{-1}]$

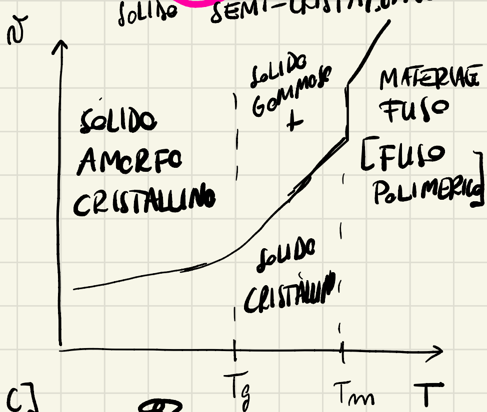
Aumento dell'ampiezza dei moti vibrazionali degli atomi.

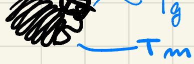



SOLIDO SEMI-CRISTALLINO



$$V = V_o + V_f \tag{16.8}$$

It is more convenient to talk in terms of fractional free volume $f_V$, which is defined as $f_V = V_f/V$. At and below the $T_g$, $f_V$ is given by $f_g = V_f^*/V$ and can be considered as being effectively constant. Above the $T_g$, there will be an important contribution to $V_f$ from the expansion of the melt. The free volume above $T_g$ is then given by

$$V_f = V_f^* + (T - T_g)\left(\frac{\partial V}{\partial T}\right) \tag{16.9}$$

2.5%

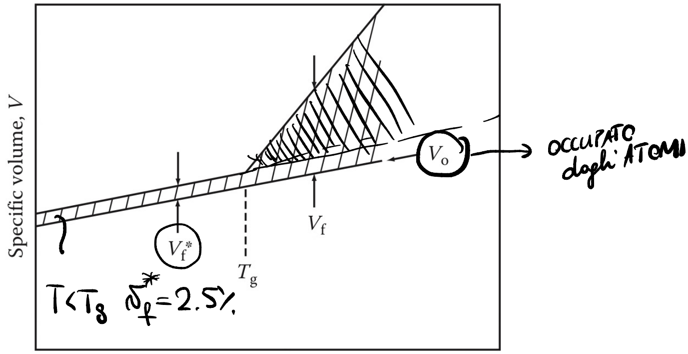



**FIGURE 16.4** Schematic illustration of the variation of the specific volume $V$ of a polymer with temperature $T$. The free volume is represented by the shaded area.

$\nu_f \leftrightarrow \eta$ → VISCOSITÀ

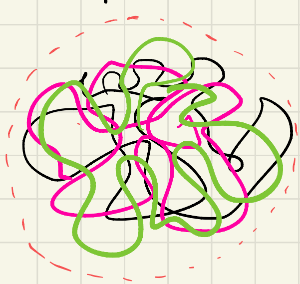
↳ VOLUME LIBERO

Determina l'interazione tra le macromolecole

**T < T_g**

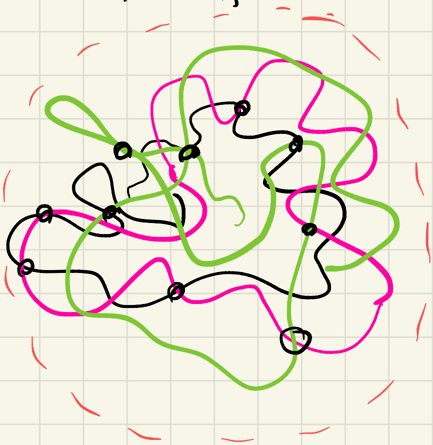
$\nu_f^* = 2.5\%$

Sono POSSIBILI Solo MOTI VIBRAZIONALI



- Sono PRESENTI Legami chimici secondari
- Sono presenti legami fisici (entanglements)

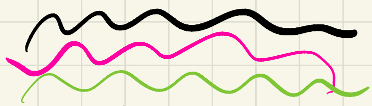
**T ≥ $T_g$**  $\nu_f > \nu_f^*$



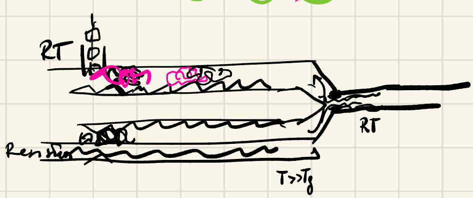
1 Sono possibili moti VIBRAZIONALI e CONFORMAZIONALI

→ Ho solo legami fisici (entanglement) fra le macromolecole

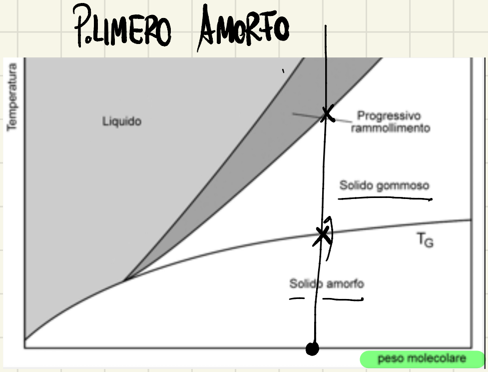
**T >> $T_g$**  Si rompono i legami fisici



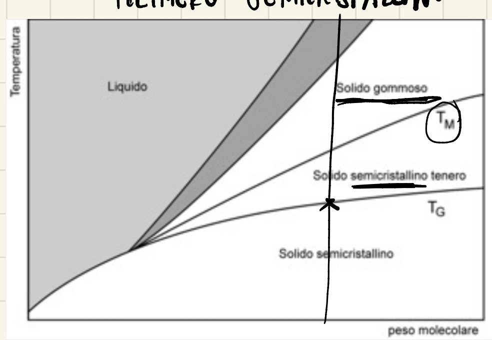
ESTRUSORE




POLIMERO AMORFO




POLIMERO SEMICRISTALLINO



# Tg dei copolimeri

$$f_V^A = f_g^A + (T - T_g^A)\alpha_f^A \quad (16.11)$$

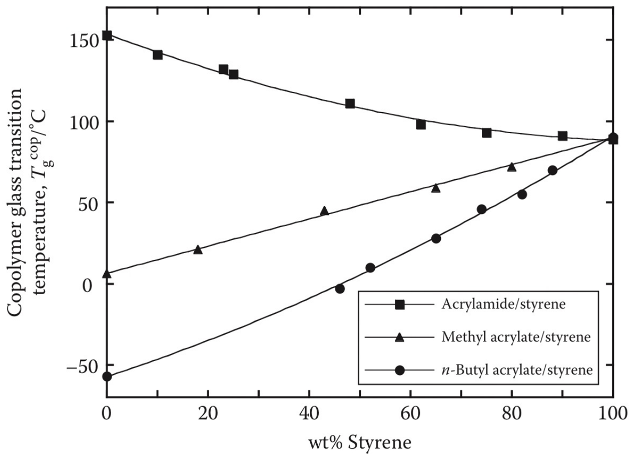



**FIGURE 16.5** Variation of copolymer glass transition temperature with the weight fraction of styrene for various styrene-based statistical copolymers. (Data taken from Illers, K.H., *Kolloid-Zeitschrift*., 190, 16, 1963.)