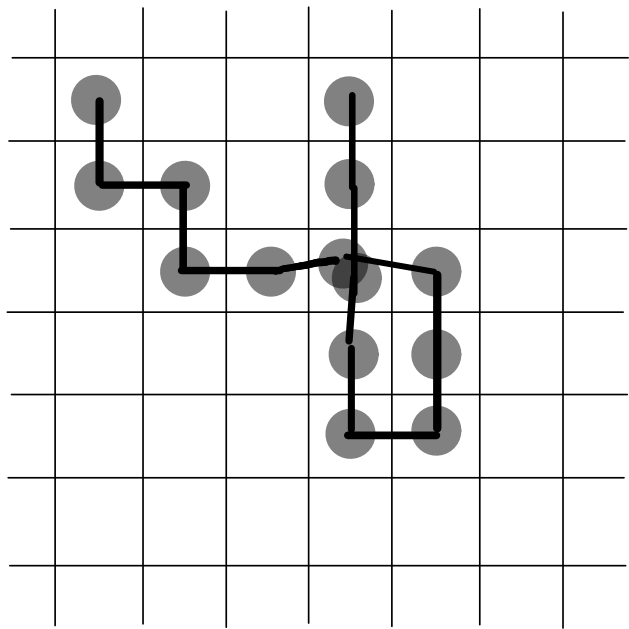


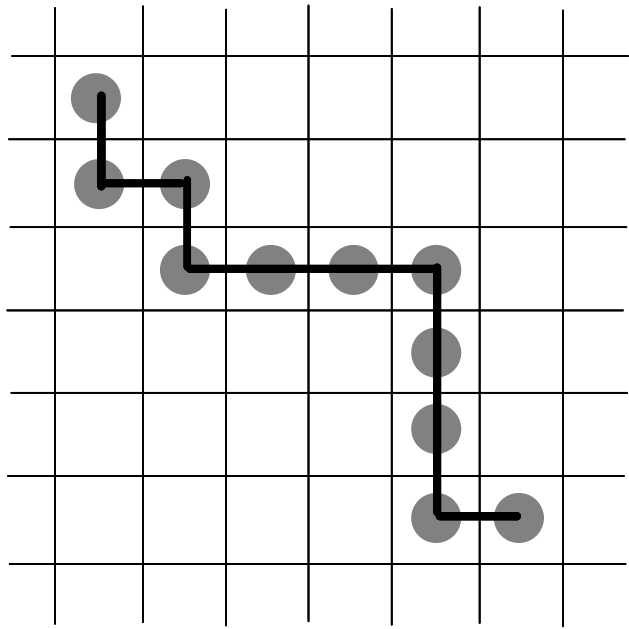
MODELLI SU RETICOLO



RW
discreto

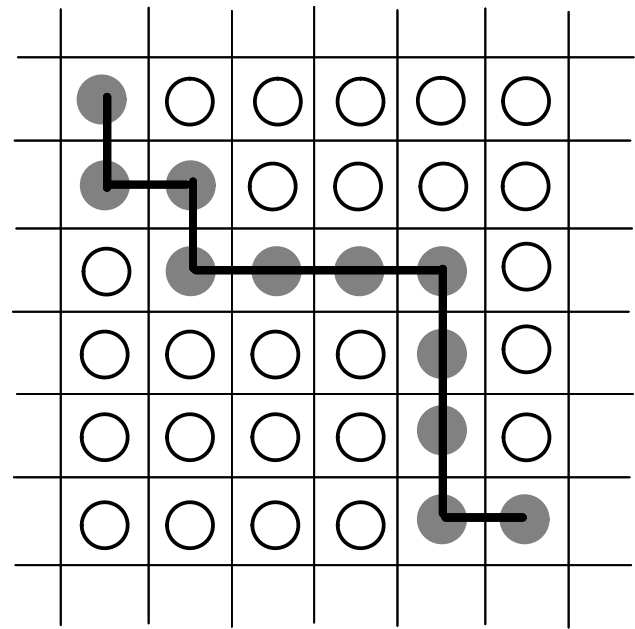
$$\langle |\vec{R}|^2 \rangle \sim N$$

$$R_g \sim N^{1/2}$$



SAW
Self-avoiding walk

$$R_g \sim N^{3/5}$$



Ruolo del solvente
effetti energetici

- \swarrow $\nu = 3/5$ good
- \leftarrow $\nu = 1/2$ θ
- \searrow $\nu = 1/3$ poor

SAW

- N monomeri
- reticolo: connettività z , volume cella $v = a^3 \rightarrow$ volume escluso
- bassa densità: monomeri indipendenti
- $N \gg 1$

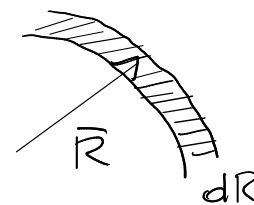
Goal: numero di conformazioni compatibili con il vincolo volume escluso

Catena ideale: $N \gg 1$

$$p_{id}(\vec{R}) = \left(\frac{3}{2\pi a^2 N} \right)^{3/2} \exp\left(-\frac{3|\vec{R}|^2}{2a^2 N}\right)$$

Numero di conformazioni con $|\vec{R}|$ tra R e $R+dR$

$$\Omega_{id}(R) = Z^N \cdot 4\pi R^2 dR p_{id}(\vec{R})$$



Fisso una regione di estensione lineare R , monomeri indipendenti

Prob. assenza overlap tra 2 monomeri

$$\left(1 - \frac{v}{R^3}\right)$$



Prob. che N monomeri non si sovrappongano

$$p(R) = \left(1 - \frac{v}{R^3}\right)^{\frac{N(N-1)}{2}} = \exp\left[\frac{1}{2}N(N-1) \ln\left(1 - \frac{v}{R^3}\right)\right] \stackrel{N \gg 1}{\approx} \exp\left(-\frac{1}{2} \frac{v}{R^3} N^2\right)$$

$$\Omega(R) = \Omega_{id}(R) \cdot p(R) \sim R^2 \exp\left(-\frac{3}{2a^2N} R^2 - \frac{vN^2}{2} \frac{1}{R^3}\right)$$

Distanza EZE tipica \equiv più probabile

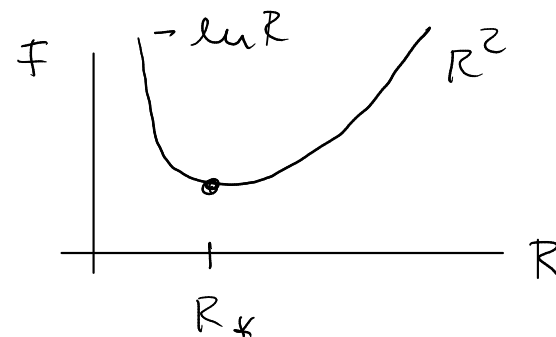
Energia libera

$$F(R) = -k_B T \ln[\Omega(R)] = \frac{3k_B T}{2a^2N} R^2 + \frac{k_B T v N^2}{2} \frac{1}{R^3} - 2k_B T \ln R$$

Caso ideale

$$\frac{dF}{dR} = \frac{3k_B T}{a^2N} R_* - \frac{2k_B T}{R_*^4} = 0 \Rightarrow R_*^2 = \frac{2a^2}{3} N \sim \langle R^2 \rangle$$

$$R_* \sim N^{1/2}$$



SAW

$$\frac{dF}{dR} = \frac{3k_B T}{a^2N} R_* - \frac{2k_B T}{R_*^4} - \frac{3k_B T v N^2}{2} \frac{1}{R_*^4} = 0$$

$$\frac{3}{a^2 N} R_*^2 - \frac{3\nu N^2}{2} \frac{1}{R_*^3} = 2 \quad \text{assumo } R_* \sim N^\nu$$

$$O(N^{2\nu-1}) \quad O(N^{2-3\nu}) \quad O(1) \quad \Rightarrow \begin{cases} 2\nu - 1 > 0 \\ 2 - 3\nu > 0 \end{cases} \Rightarrow \begin{cases} \nu > 0.5 \\ \nu < 2/3 = 0.\bar{6} \end{cases}$$

Trascuro RHS

$$\frac{R_*^2}{N} \sim \frac{N^2}{R_*^3} \Rightarrow R_*^5 \sim N^3 \Rightarrow R_* \sim N^{3/5} \quad \nu = 3/5 = 0.6 \quad \text{esponente di Flory}$$

Teoria gruppo rinormalizzazione: $\nu = 0.588$

$$R_* \sim N^{\frac{3}{d+2}} \quad \text{in } d \text{ dimensioni} \quad d = 1, 2, 3$$

EFFETTI ENERGETICI

- ~ Interazioni : monomero - monomero ϵ_{mm}
- monomero - solvente ϵ_{ms}
- solvente - solvente $\epsilon_{ss} = 0$

- Approssimazione campo medio \rightarrow trascuro fluttuazioni

Energia interazione per conformazione data α

$$U_\alpha = \frac{1}{2} \sum_{i=1}^N \epsilon_{mm} n_{mm}^{(i)} + \sum_{i=1}^N \epsilon_{ms} n_{ms}^{(i)}$$

\uparrow
 n_{vicini}

Energia media per R fissata

$$U(R) = \frac{1}{2} \sum_{i=1}^N \epsilon_{mm} \langle n_{mm} \rangle + \sum_{i=1}^N \epsilon_{ms} \langle n_{ms} \rangle = \frac{1}{2} N \epsilon_{mm} \langle n_{mm} \rangle + N \epsilon_{ms} \langle n_{ms} \rangle$$

Prob. conformazione con distanza $E2E$ R, approssimazione campo medio: $U_\alpha = U(R)$

$$P(R) \sim \underbrace{\Omega(R)}_{\text{SAW}} \exp[-\beta U(R)] \leftarrow \frac{\text{Tr}_\alpha [e^{-\beta U_\alpha} \delta(R_\alpha - R)]}{\text{Tr}_R [\text{Tr}_\alpha [e^{-\beta U_\alpha} \delta(R_\alpha - R)]]} = \frac{e^{-\beta U(R)}}{\text{Tr}_R [e^{-\beta U(R)}]} \sim e^{-\beta U(R)}$$

Energia libera

$$F(R) = F_{\text{SAW}}(R) + U(R) = -k_B T \ln [P(R)]$$

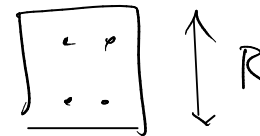
Regione di dim. lineare R

$$\langle n_{mm} \rangle = z \cdot \phi$$

$$\langle n_{ms} \rangle = z \cdot (1 - \phi)$$

Concentrazione monomeri

$$\phi = \frac{N}{R^3/v} = \frac{v}{R^3} N$$



$$\begin{aligned} U(R) &= \frac{1}{2} z \epsilon_{mm} \frac{v}{R^3} N^2 + z \epsilon_{ms} \left(1 - \frac{v}{R^3} N\right) N = \frac{1}{2} z (\epsilon_{mm} - 2\epsilon_{ms}) \frac{v}{R^3} N^2 + z \epsilon_{ms} N \\ &= -\frac{1}{2} z \epsilon \frac{v}{R^3} N^2 + \text{cost}(N) \end{aligned}$$

$$F(R) = F_0(N) + \frac{2 k_B T}{3 a^2 N} R^2 - 2 k_B T \ln R + \frac{1}{2} k_B T \frac{v}{R^3} \left(1 - \frac{z \epsilon}{k_B T}\right) N^2$$

Ruolo del solvente

$$v_{\text{eff}} = v \left(1 - \frac{z\epsilon}{k_B T} \right)$$

↑
parametro Flory-Huggins

vdw
↓

$$\epsilon = - \left(\underset{< 0}{\epsilon_{mm}} - 2 \underset{> 0}{\epsilon_{ms}} \right) \gtrsim 0$$

- $k_B T > z\epsilon$ ($v_{\text{eff}} > 0$) → "buon solvente"

→ SAW rinormalizzato $R_g \sim N^{3/5}$

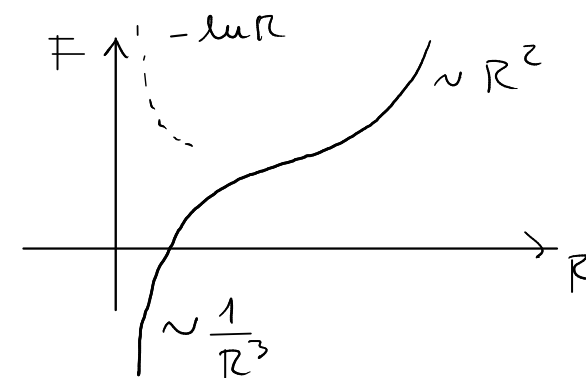
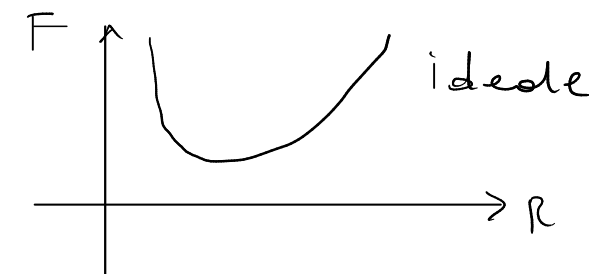
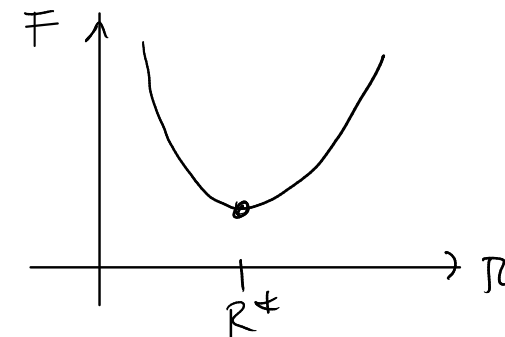
- $k_B T = z\epsilon$ ($v_{\text{eff}} = 0$) temperatura "Θ" → "solvente Θ"

→ catena ideale $R_g \sim N^{1/2}$

- $k_B T < z\epsilon$ ($v_{\text{eff}} < 0$) → "cattivo solvente"

→ collasso catena $R_g \sim N^{1/3}$ $\beta = \frac{N}{R_g^3}$

Transizioni di fase: coil-globule transition



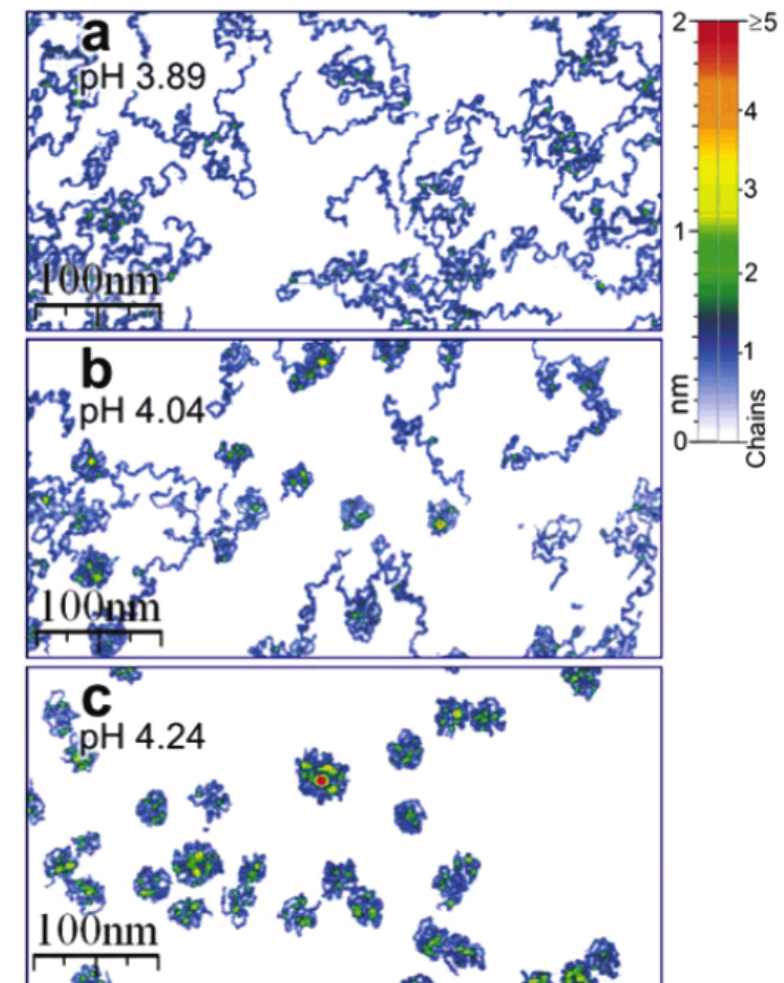


Figure 2. AFM-visualized conformations of adsorbed P2VP molecules: (a) pH 3.89, extended coils; (b) pH 4.04, intermediate state; (c) pH 4.24, compact coils. Z-scale bar shows a number of superposed chains assuming the height increment of 0.4 nm.

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