

# Physics of annealed and quenched copolymers.

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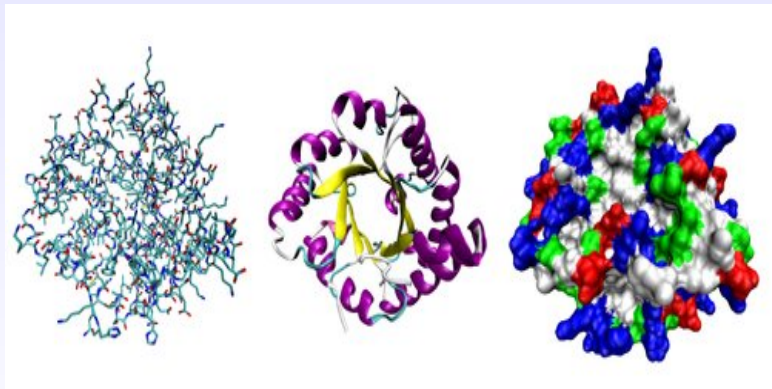
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<sup>1</sup>Collaboration with A.Halperin, D.Bicout, and N.Yoshinaga.

# Copolymers are polymers with two (or more) chemically different monomers.

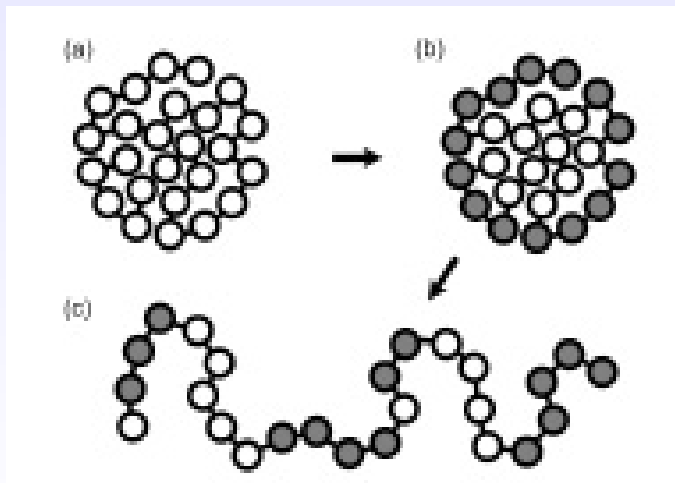
- Proteins are notorious representative of copolymers ;
- In a globular (native) state biological functionality is related to amino acid sequence ;
- Natural proteins are natural quenched copolymers.

# Three representations of protein structure.



**FIG.:** Left : all atoms ; Middle : backbone secondary structure ; Right : Solvent-accessible surface representation (acidic residues - red, basic residues - blue, polar - green, nonpolar - white).

# Artificial design of protein-like copolymers.



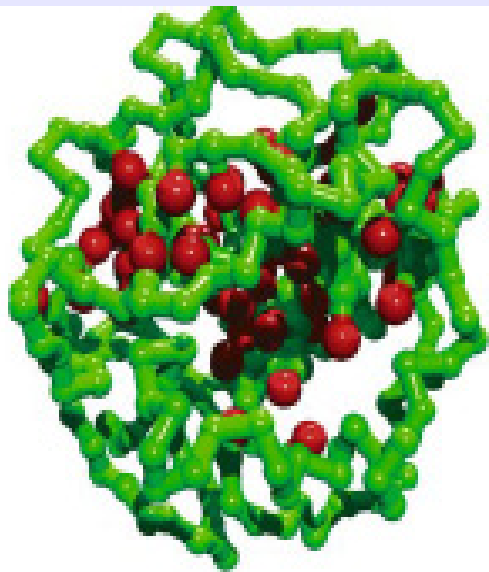


FIG.: Globular conformation of protein-like copolymers with hydrophobic (*H*) and polar (*P*) monomers

# Annealed copolymers.

- Two states ( $H$  and  $P$ ) of their monomers can be inter-converted  $P \rightarrow H$  and  $H \rightarrow P$  thermodynamically ;
- Transition probabilities :

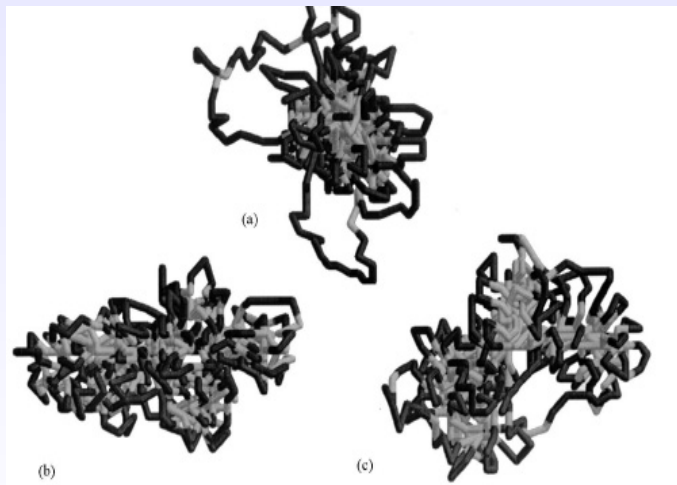
$$p(H \rightarrow P) = p(P \rightarrow P) = \frac{1}{2} \exp(-\Delta\epsilon/T) ;$$

$$p(P \rightarrow H) = p(H \rightarrow H) = 1 - \frac{1}{2} \exp(-\Delta\epsilon/T) .$$

# Experimental examples and motivation

- Observations of stable diluted solutions of the collapsed *PEO* and *PNIPAM* globules in the equilibrium with non-collapsed polymers.
- Internal bulk energy for the both states is more or less the same, but in the collapsed state the surface contribution  $\propto N^{2/3}$  should be added.
- For a typical  $N \simeq 10^5$  concentration of stable globules  $\propto \exp(-N^{2/3})$  is unrealistically small.

# Quenched case examples.



**FIG.:** protein-like copolymer (a) ; random copolymer (b) ; random-block copolymer (c) (block lengths are determined by the Poisson distributions adjusted to achieve the same composition and the same average block length as for (a))



# Simple (but yet nontrivial) theoretical model

- We assign a numerical variable  $u_i$  to each monomer along the copolymer chain :  $u_i = 1$  if the monomer  $i$  is  $H$ , and  $u_i = 0$  if the monomer is  $P$ .
- The average  $\langle u_i \rangle$  is trivially determined by the overall sequence composition.
- To compute dispersion  $D_n$  one can choose the window of length  $n$

$$D_n^2 = \sum_{i,j=k}^{k+n} [\langle u_i u_j \rangle - \langle u_i \rangle \langle u_j \rangle]$$

- For a completely random  $H, P$  sequence  $D_n \propto n^{1/2}$ , and deviation from this scaling  $D_n \propto n^\alpha$  with  $\alpha \neq 1/2$  would then manifest correlations.
- Since the sequence is uniquely determined by the parent globular conformation (e.g., with all  $P$  monomers on the surface), the statistics of sequences reflects the parent conformation.

# Flory theorem states that globular conformation is ideal (Gaussian).

- Dilute polymer chain in a good solvent is swollen, and its size  $R_F \propto N^{3/5}$  rather than  $N^{1/2}$  as it would be the case for an ideal chain.
- When one squeezes the chains together and reach a dense concentrated solution or melt, we might expect the situation to become even more complicated.
- The correct conclusion is different, and in a denser system of chains each chain is ideal because fluctuations of the total concentrations are very weak, and therefore the chain experiences almost no force and remains ideal.

# More details on artificial designed conformations.

- Core with  $H$  monomers is a sphere of radius  $R^* < R$ ;
- In a shell  $R^* < r < R$   $P$  monomers are predominantly concentrated ;
- $p_H(k)$  - probability that the Gaussian chain (Flory theorem) has a loop of  $k$  monomers entirely confined in the  $H$  region with ends on the separation surface.

$$p_H(k) \propto k^{-3/2}, \text{ if } 1 < k < (R^*/a)^2$$

- For larger  $k$ ,  $p_H(k)$  decays exponentially with  $k$ ;
- Similar relations hold for  $p_P(k)$  with  $R^* \rightarrow R - R^*$  ;
- To have 1 : 1  $H - P$  composition,  $R^* = 2^{-1/3}R \simeq 0.8R$ ;
- Polymer collapses into a globular conformation at volume fraction  $\phi$  independent of  $N$ , and when it happens

$$R \simeq 0.6aN^{1/3}\phi^{-1/3}$$

- Therefore crossover from power law (long range) correlations to short range (exponential) ones occurs for  $H$  specie

$$k_H \simeq 0.25N^{2/3}\phi^{-2/3}$$

and for  $P$  specie at

$$k_P \simeq 0.04N^{2/3}\phi^{-2/3}$$

- Protein-like sequence can be thought of as an alternating succession of  $H$  and  $P$  stretches with lengths of the stretches taken independently from the corresponding distributions  $p_H(k)$  and  $p_P(k)$ .
- This mathematical scheme is called a Levy flight.

- When one has  $k^{-3/2}$  behavior, the average block length diverges ! It means that dispersion is controlled by the longest block, yielding to ballistic law

$$D_n \propto n$$

- In the regime with short range correlations

$$D_n \propto n^{1/2}$$

# Dispersion of the number of $H$ -units in the fragment of size $l$

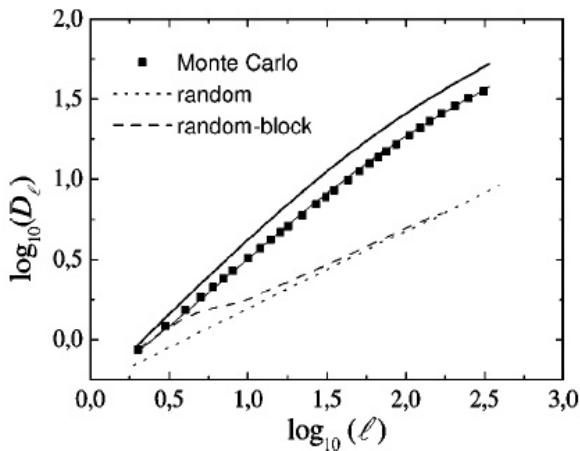


FIG.: For a random block copolymer  $f(x) = \exp(-\lambda)\lambda^x/x!$  where  $x = 0, 1, \dots, \lambda$ , where  $\lambda$  is a mean block size for protein-like sequence

- We arrive at a conclusion almost without any calculation that if  $1 < l < k_p^{cr} \simeq 0.04N^{2/3}\phi^{-2/3}$  then  $D_l \propto l$ ;
- In the regime with short range correlations, when  $l > 0.24N^{2/3}\phi^{-2/3}$   $D_l \propto l^{1/2}$

# The same but with analytical theory

- $P_H(k)$  is the probability that the random walker enters a sphere of the radius  $R^*$  (core) and then arrives to the boundary for the first (!) time after time  $k$ .
- Statistical weight of all such trajectories obeys time-dependent "Schroedinger" (diffusion) equation

$$\frac{\partial G(r, k|r_0)}{\partial k} = \frac{a^2}{6} \nabla^2 G(r, k|r_0) + \delta(k)\delta(r - r_0)$$

supplemented by the boundary condition  $G(r = R^*, k|r_0) = 0$ .

- Then

$$P_H(k) = \left| \int dA \frac{a^2}{6} \frac{\partial G}{\partial r} \Big|_{r=R^*} \right|$$

(integration along separating core from shell surface, and  $a$  is m.s. length of one step).

- and finally  $D_n$

$$\langle u_i u_j \rangle \propto \int d^3 r \int d^3 r_0 G(r, |i - j||r_0)$$



# Situation is completely different in annealed case

- First consider one chain in a good solvent. Then  $PH$  sequence is modeled by an ideal 1d mixture

$$F_0 = x\mu_H^0 + (1-x)\mu_P^0 + T[x \ln x + (1-x) \ln(1-x)]$$

with  $\mu_i^0$  standard chemical potentials, and  $x$  is the fraction of  $H$  monomers

- In the equilibrium

$$\frac{1-x_0}{x_0} = \exp\left(-\frac{\Delta\mu^0}{T}\right) \equiv K^0$$

- In the globular core  $F_0$  should be supplemented by

$$\frac{E_{core}}{T} = -\frac{Z}{2}[x\epsilon_{HH} + (1-x)\epsilon_{PP}] + x(1-x)\chi_{PH}$$

where

$$\chi_{PH} = Z \left[ \frac{\epsilon_{HH} + \epsilon_{PP}}{2} - \epsilon_{PH} \right]$$

- minimizing

$$\frac{1 - x_c}{x_c} = \exp[-(\Delta\mu^0/T) - (z/2)(\epsilon_{HH} - \epsilon_{PP}) + (1 - 2x_c)\chi_{PH}]$$

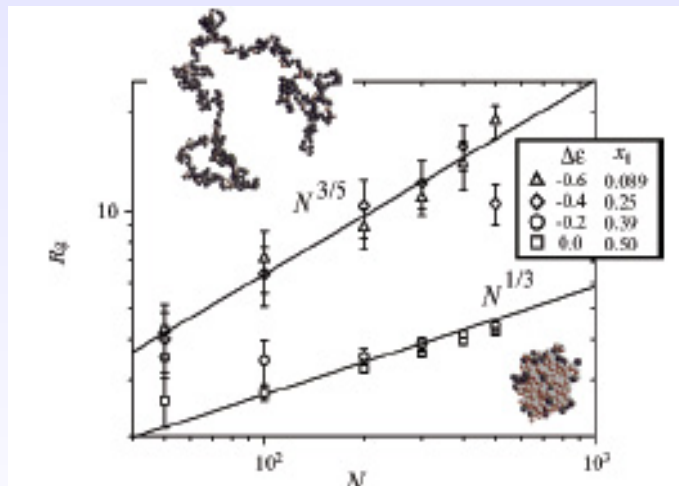
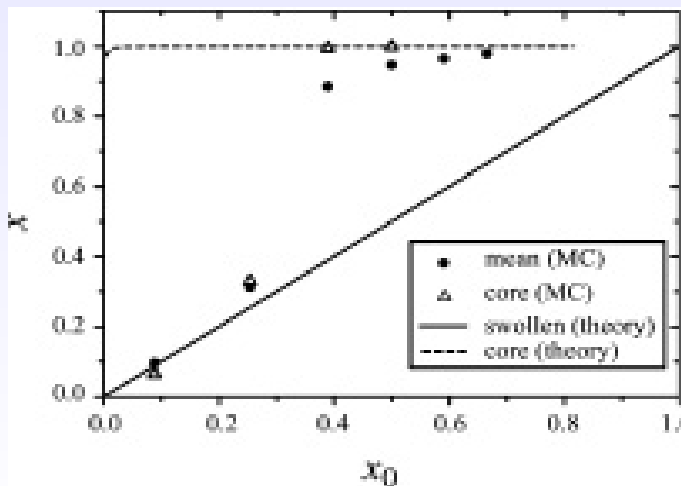
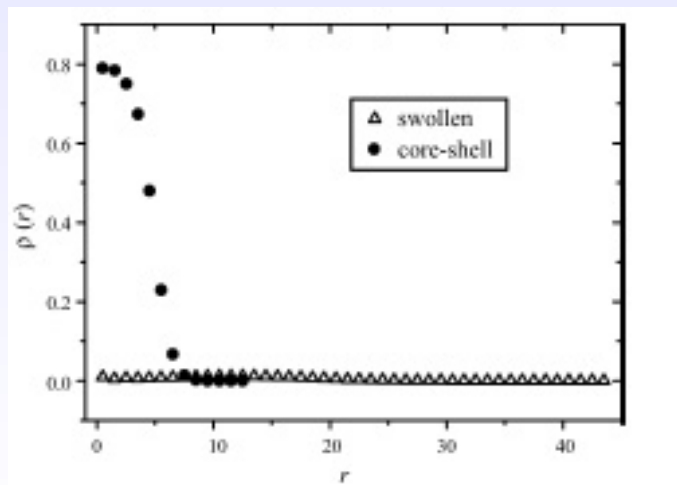


FIG.: Plots of  $\ln R$  vs  $\ln N$

# Comparison of our simple theory with MC simulations for the core region.



# Radial monomer density manifesting core-shell structure.



## Shell region.

- Two ingredients distinguish shell from the dense core : i) missing exterior neighbors ; and (ii) possibility of incomplete occupation of the interfacial layer ; Then if a fraction  $Y \leq 1$  of the surface sites is occupied

$$\frac{E_{shell}}{T} = -\frac{z_s}{2} Y^2 [x_s \epsilon_{HH} + (1 - x_s) \epsilon_{PP}] + Y^2 x_s (1 - x_s) \frac{z_s}{z} \chi_{PH} \\ + \frac{z - z_s}{4} Y [x_s \epsilon_{HH} + (1 - x_s) \epsilon_{PH}]$$

the 1-st two terms account for the in-plane interaction energy,  $(z_s/z)\chi_{PH}$  replaces  $\chi_{PH}$  to allow for the lower coordination number, and  $\epsilon_{ij}$  is replaced by  $\epsilon_{ij}/2$  to avoid double counting.

- Adding also an ideal solution term in the shell

$$\tilde{F}_0 = Y [x_s \mu_H^0 + (1 - x_s) \mu_P^0] + \\ T [(1 - Y) \ln(1 - Y) + Y \ln Y + Y x_s \ln x_s + Y (1 - x_s) \ln(1 - x_s)]$$

- minimizing

$$\frac{1 - x_s}{x_s} = \exp \left[ -\frac{\Delta\mu_0}{T} - Y \frac{z_s}{2} (\epsilon_{HH} - \epsilon_{PP}) + \right. \\ \left. Y(1 - 2x_s) \frac{z_s}{2} \chi_{PH} - \frac{z - z_s}{4} (\epsilon_{HH} - \epsilon_{PH}) \right]$$

# Plots of $x_s$ vs $x_0$ for different $Y$ values

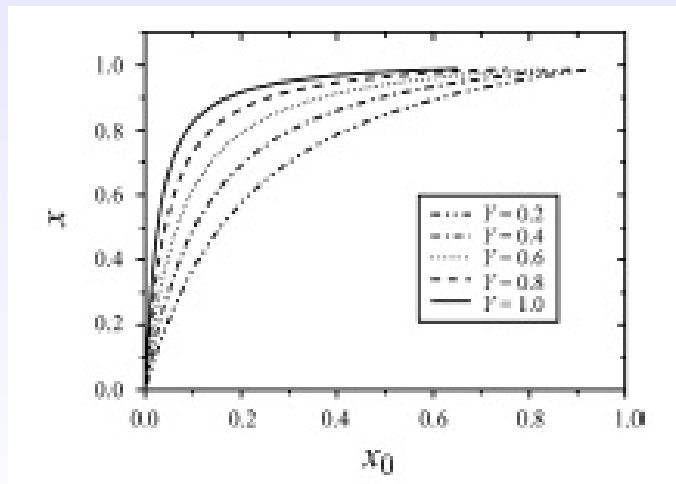
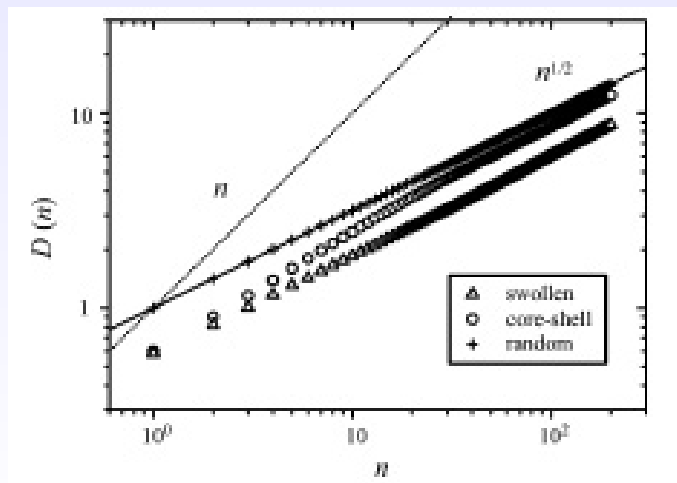


FIG.:  $\epsilon_{HH} = 1$ ,  $z = 12$  and  $z_s = 6$



# $\ln D_n$ vs $\ln n$ plots of swollen and collapsed core-shell configurations.



# Results and perspectives

- Annealed copolymers show collapsed globular state having core-shell structures ;
- In these, the core is mostly solvophobic, while the core boundary contains an excess of solvophilic monomers ;
- The statistics of the monomeric states along the chain vary with the degree of chain swelling, and different from quenched copolymers ( $\alpha < 1$ ) designed to create water soluble globules (though both systems involve a core-shell structure).
- The  $P - H$  interconversion opposes block structure.
- The overall  $H$  fraction is not fixed but varies with the configuration.

# Where to go further on.

- Clever materials with tunable properties ;
- Macromolecules consisting of  $P - H$  dimer units : concentration and orientation correlations ;
- Adsorption of quenched and annealed copolymers ;
- Microphase separation and various forms of aggregation

