## Single Polymer in Solution [pln49]

Polymer in the form of N monomers linked into a chain by covalent bonds.

Sources of entropy S:

- Relative angles (polar and azimuthal) between successive monomers may have several local energy minima. Depending on how energy barriers relate to  $k_{\rm B}T$ , angular coordinates are treated as discrete or continuous variables. Multiplicity of available conformational microstates contributes to entropy.
- Interface between polymer and solvent depends on polymer conformation (coil, helix, globule, ...). Solvent molecules bound to polymer in any particular conformation contribute negatively to entropy.

Sources of enthalpy H:

- Elastic energy between successive monomers (bending and stretching).
- Interactions between monomers that are distant or nearby on contour.
- Interactions between polymer and solvent molecules.

Gibbs free energy: G = H - TS.

- Coil conformation is most disordered. Conformational entropy has a maximum.
- To an application of tension between its ends, the polymer responds by stretching out, causing enthalpic and entropic changes. The macrostate settles such that G assumes a minimum.
- An attractive interaction between distant monomers may favor the formation of a polymeric globule, a form of intramolecular condensation. This brings an enthalpic gain,  $\Delta H < 0$ , but at an entropic cost,  $\Delta S > 0$ . The cost  $T\Delta S$  is bigger at high T than at low T.
- An attractive interaction between nearby monomers may favor the formation of a helix conformation (in polypetides), a form of intramolecular crystallization. Unlike globules, which are more or less amorphous in structure, the helix is highly ordered. Therefore, it is formed at a higher entropic price. The enthalpic gain is associated with the formation of internal H-bonds.
- Either conformational change also involves enthalpic and entropic contributions associated with the interaction interfacial structure between polymer and solvent.

Ideal polymer chain (mathematical model):

- chain of immaterial links between successive monomers,
- no interactions between more distant monomers,
- interactions with solvent molecules accounted for by random force.

Models of ideal polymer chains differ in link structure (constraints) and type of bonding (energies). Such models help us understand the constraints on thermal motion and the restrictions on conformational entropy of polymers.

Flexibility is a characteristic attribute of polymers, which is modeled in various ways including geometric constraints or energetic discriminations on link configurations.

For example, a model may allow one particular valence angle  $\gamma$  and a continuum of internal rotation angles  $\phi$  associated with a potential energy  $U(\phi)$ .



Measures of polymer size in common use:

Na: contour length, where N is the number of monomers of length a.

- $R_0$ : rms end-to-end distance,
- $R_{\rm g}:$  radius of gyration defined as the rms distance of a monomer from the center of mass.