RANDOM POLYMERS

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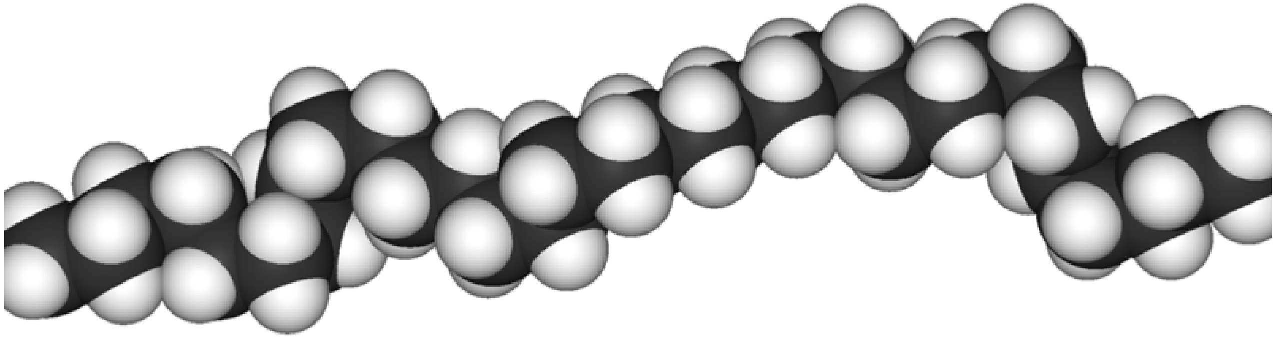
§ WHAT IS A POLYMER?

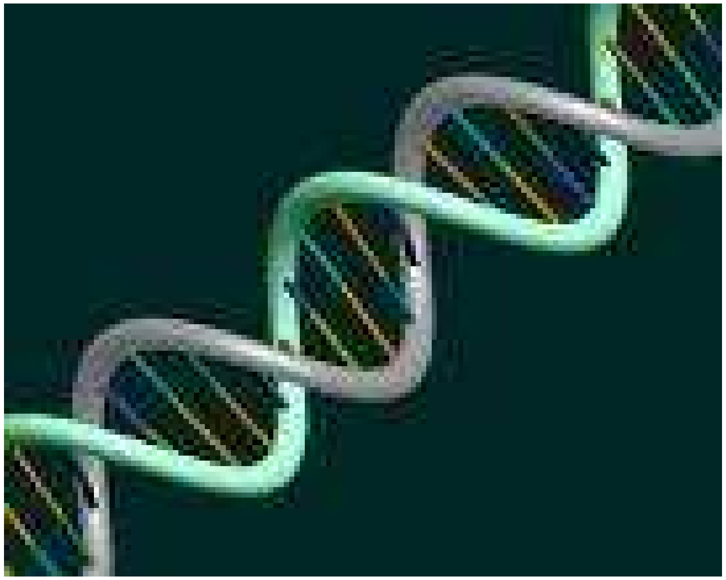
A polymer is a large molecule consisting of monomers that are tied together by chemical bonds.

The monomers can be either small units (such as CH_2 in polyethylene) or large units with an internal structure (such as the adenine-thymine and cytosine-guanine base pairs in the DNA double helix).

Polymers abound in nature because of the multivalency of atoms like carbon, oxygen, nitrogen and sulfur, which are capable of forming long concatenated structures.



Polyethylene



DNA

§ WHAT TYPES OF POLYMERS OCCUR IN NATURE?

Polymers come in two varieties:

(1) homopolymers, with all their monomers identical (such as polyethylene);

(2) copolymers, with two or more different types of monomer (such as DNA). The order of the monomer types in copolymers can be either periodic or random.

A further classification is into synthetic polymers (such as nylon and polystyrene) and natural polymers. Major subclasses of the latter are:

(a) proteins (strings of amino-acids),
(b) nucleic acids (DNA, RNA),
(c) polysaccharides (agar, carrageenan, cellulose),
(d) rubber.

Synthetic polymers typically are homopolymers, natural polymers typically are copolymers (with notable exceptions). Bacterial polysaccharides tend to be periodic, plant polysaccharides tend to be random.

Yet another classification is into linear polymers and branched polymers. These occur when the monomers have, respectively, one reactive group (such as CH_2) or two or more reactive groups (such as $O(HO)^2$).

Most natural polymers are linear, like proteins, DNA, RNA, and the polysaccharides agar, carrageenan and cellulose. Some polysaccharides are branched, like amylopectin. Many synthetic polymers are linear, and many are branched. An example of a branched polymer is rubber, both natural and synthetic.

§ WHAT ARE THE TYPICAL SIZE AND SHAPE OF A POLYMER?

The chemical process of building a polymer from monomers is called polymerization. The size of a polymer may vary from 10^3 up to 10^{10}. Human DNA has $10^9 - 10^{10}$ base pairs, lignin consists of $10^6 - 10^7$ phenyl-propanes, while polysaccharides carry $10^3 - 10^4$ sugar units.

Both in synthetic and in natural polymers, the size distribution may either be broad, with numbers varying significantly from polymer to polymer (e.g. nylons, polysaccharides), or be narrow (e.g. proteins, DNA). In synthetic polymers the size distribution can be made narrow through specific polymerization methods.

The length of the monomer units varies from $1.5\,\text{Å}$ (for CH_2 in polyethylene) to $20\,\text{Å}$ (for the base pairs in DNA), with $1\,\text{Å} = 10^{-10}\,\text{m}$.

The chemical bonds in a polymer are flexible, so that the polymer can arrange itself in many different shapes. The longer the chain, the more involved these shapes tend to be.

The polymer may:

- wind around itself to form a knot,
- inflate itself due to repulsive forces caused by excluded-volume,
- collapse to a ball due to attractive van der Waals forces,
- interact with a surface,
- be subjected to a force applied to one of its endpoints.

A variety of models have been proposed to describe such situations.

§ WHAT QUESTIONS MAY A MATHEMATICIAN ASK AND HOPE TO ANSWER?

The majority of mathematical research deals with linear polymers. Examples of quantities of interest are:

- number of different spatial configurations,
- end-to-end distance (subdiffusive/diffusive/superdiffusive),
- fraction of monomers adsorbed onto a surface,
- force needed to pull the polymer away from a surface,
- effect of randomness in the interactions,

all typically in the limit as the polymer gets long.

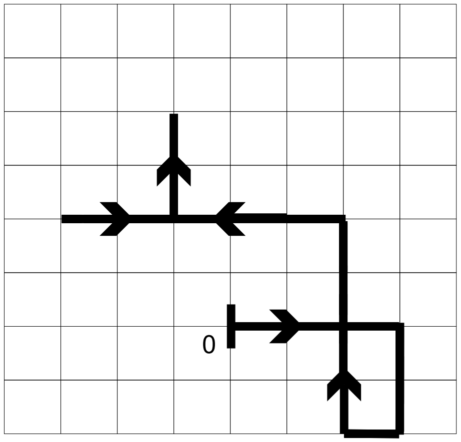
Of special importance are phase transitions, signalling drastic changes in the behavior of the polymer when interaction parameters cross critical values.

Literature: F. den Hollander, Random Polymers, Lecture Notes in Mathematics, Vol. 1974, Springer, Berlin, 2009, xiii + 258 pp., ISBN 978-3-642-00332-5

... and some 300 references therein.

§ WHAT IS THE MODEL SETTING?

In mathematical models polymers often live on a lattice, like $\mathbb{Z}^d$, $d \geq 1$, and are modelled as random paths, where the monomers are the vertices in the path, and the chemical bonds connecting the monomers are the edges in the path.



- Paths and energies:

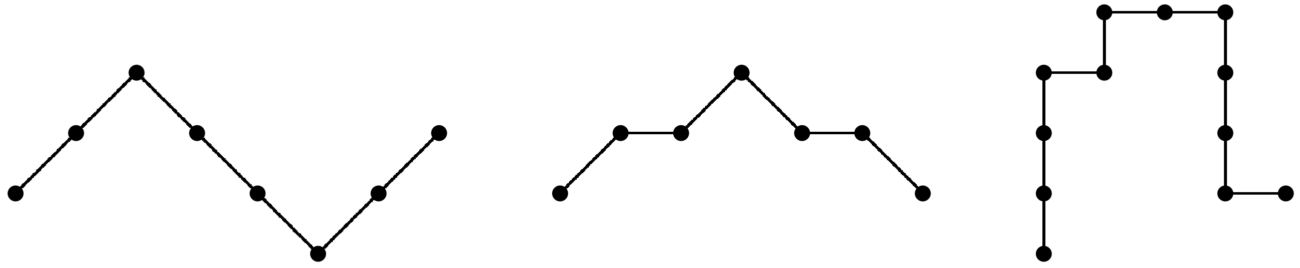
Choosing a polymer model amounts to fixing

- $\mathcal{W}_n$, a set of allowed n-step paths w on $\mathbb{Z}^d$,

- H_n, a Hamiltonian that associates an energy to each path $w \in \mathcal{W}_n$,

for each $n \in \mathbb{N}$. The choice depends on the particular situation to be described.

In W_n we may allow directed or undirected paths, possibly with some geometric constraints.



Three examples of directed paths on $\mathbb{Z}^2$.

The choice of H_n captures the interaction of the polymer with itself and/or its surroundings. Typically, H_n depends on one or two parameters, including temperature.

- Gibbs measure:

For each $n \in \mathbb{N}$, the law of the polymer of length n is defined by assigning to each $w \in \mathcal{W}_n$ a probability given by

$$P_n(w) = \frac{1}{Z_n}\,\mathrm{e}^{-H_n(w)}, \qquad w \in \mathcal{W}_n,$$

where Z_n is the normalizing partition sum. This is called the Gibbs measure associated with the pair $(\mathcal{W}_n, H_n)$, and it describes the polymer in equilibrium with itself and/or its surroundings.

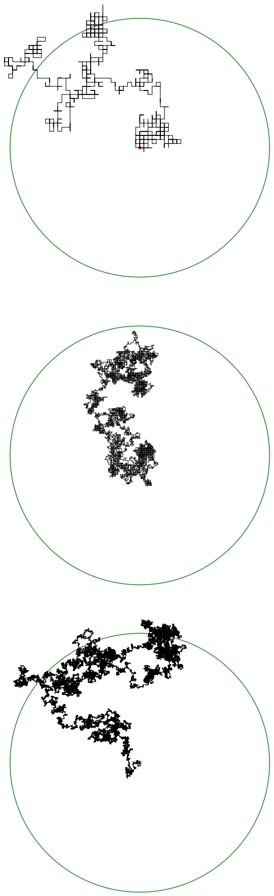
In some models H_n also depends on a random environment ω, describing e.g. a random ordering of the monomer types or a random field of charges. Accordingly, we write H_n^ω and P_n^ω.

In the remainder of this talk we take snapshots of four models of polymer chains exhibiting a phase transition.

§ A FREE POLYMER

Simple random walk (SRW) models a polymer chain without interaction:

$$\begin{aligned}\mathcal{W}_n &= \{\text{set of } n\text{-step paths on } \mathbb{Z}^d\},\\ H_n(w) &= 0 \;\forall\, w \in \mathcal{W}_n,\\ P_n &= \{\text{uniform distribution on } \mathcal{W}_n\}.\end{aligned}$$



Simulation of SRW on $\mathbb{Z}^2$ with $n = 10^3$, 10^4 and 10^5 steps. The circles have radius $\sqrt{n}$ in units of the step size.

A distinctive feature of SRW is that it exhibits diffusive behavior, i.e.,

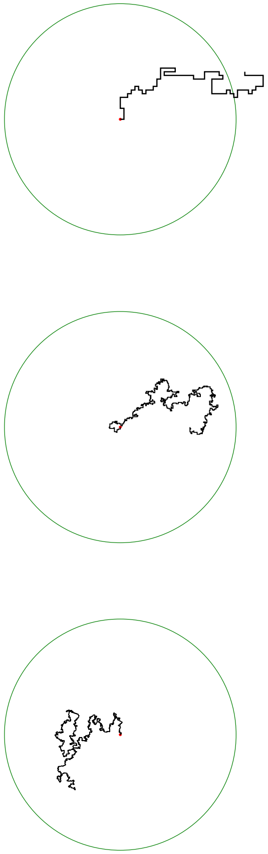
$$E_n(S_n^2) = n, \qquad n \in \mathbb{N}.$$

In fact, the path of the polymer scales to Brownian motion.

§ SELF-REPELLENT POLYMER

Self-avoiding walk (SAW) models a polymer chain with self-repellence:

$$\begin{aligned} \mathcal{W}_n &= \{\text{set of } n\text{-step non-intersecting paths on } \mathbb{Z}^d\}, \\ H_n(w) &= 0 \;\forall\, w \in \mathcal{W}_n, \\ P_n &= \{\text{uniform distribution on } \mathcal{W}_n\}. \end{aligned}$$



Simulation of SAW on $\mathbb{Z}^2$ with $n = 10^2$, 10^3 and 10^4 steps. The circles have radius $n^{3/4}$ in units of the step size.

The mean-square displacement is believed to scale like

$$E_n(S_n^2) \asymp \begin{cases} n^{2\nu}, & d \neq 4, \\ n(\log n)^{\frac{1}{4}}, & d = 4, \end{cases}$$

with ν a critical exponent given by

$$\nu = 1\ (d=1), \quad \tfrac{3}{4}\ (d=2), \quad 0.588\ldots\ (d=3), \quad \tfrac{1}{2}\ (d \geq 5).$$

Thus, SAW is

$d = 1$: ballistic
$d = 2, 3, 4$: subballistic & superdiffusive
$d \geq 5$: diffusive

Intuition:

In high dimensions, loops are rare and so the excluded-volume effect is short-ranged.

§ POLYMER COLLAPSE

A model for a polymer in a hostile solvent is

$$\mathcal{W}_n = \{\text{set of } n\text{-step paths on } \mathbb{Z}^d\},$$
$$H_n(w) = \beta I_n(w) - \gamma J_n(w), \quad w \in \mathcal{W}_n,$$

where $\beta, \gamma \in (0, \infty)$ and

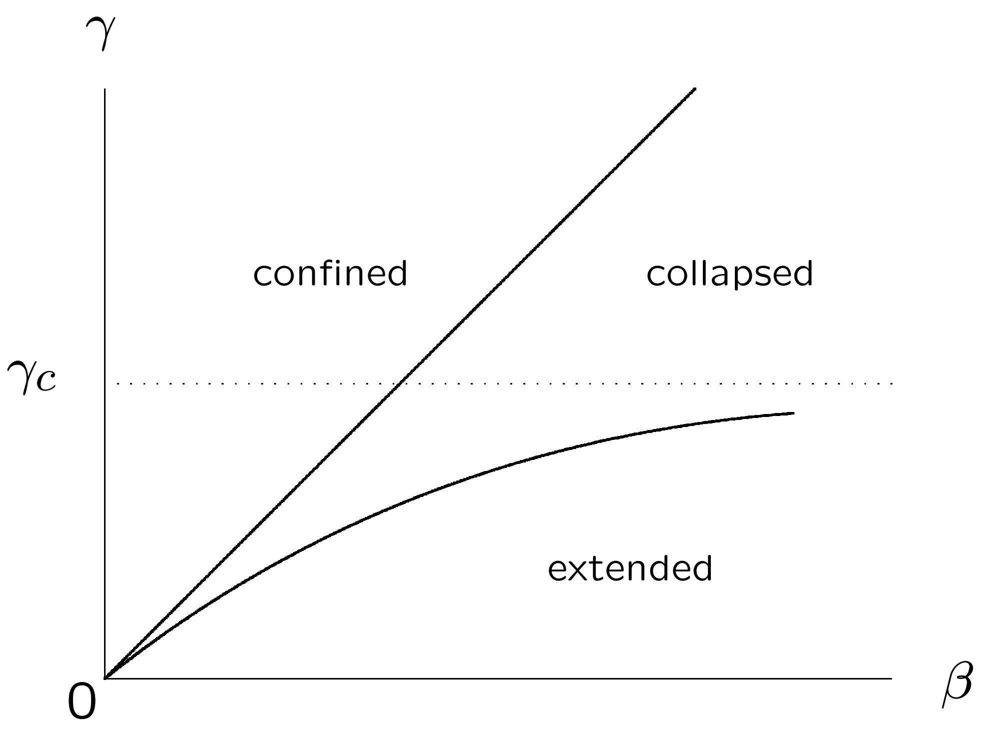
$$I_n(w) = \text{number of self-intersections of } w,$$
$$J_n(w) = \text{number of self-touchings of } w.$$

Under the Gibbs measure P_n, self-intersections are penalized while self-touchings are rewarded. We expect:

$\beta \gg \gamma$: polymer is a random coil,
$\gamma \gg \beta$: polymer is a compact ball.

An example is polystyrene dissolved in cyclohexane. At temperatures above 35 degrees Celsius the cyclohexane is a good solvent, at temperatures below 30 it is a poor solvent. When cooling down, the polystyrene collapses from a random coil to a compact ball.

For $d \geq 2$ there are actually three phases: extended, collapsed and confined:



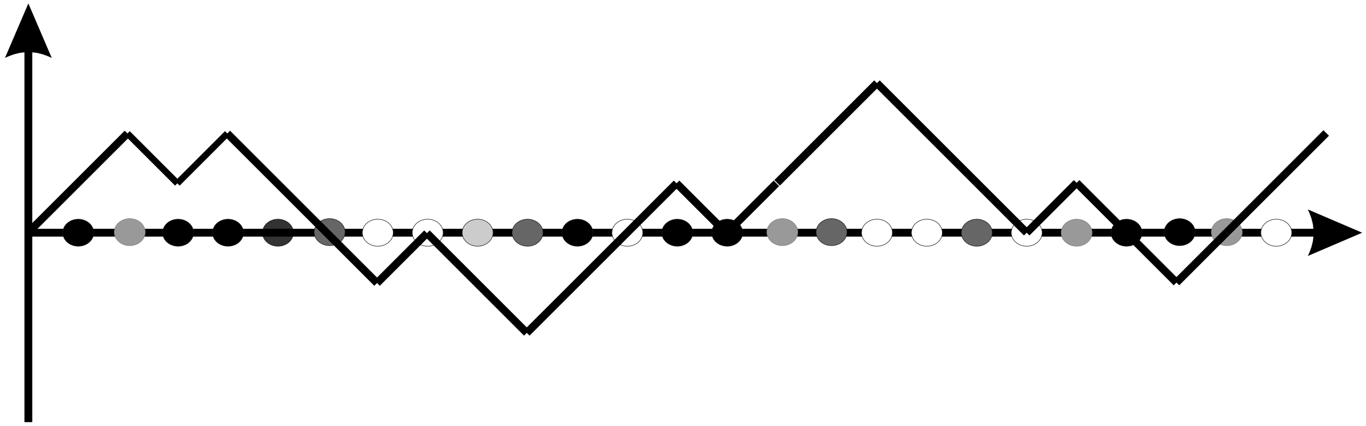
§ A POLYMER PINNED BY RANDOM CHARGES

A directed polymer near a linear interface carrying random charges $\omega = (\omega_i)_{i \in \mathbb{N}}$ is modeled by:

$$\mathcal{W}_n = \{\text{set of } n\text{-step directed paths on } \mathbb{N} \times \mathbb{Z}^d\},$$

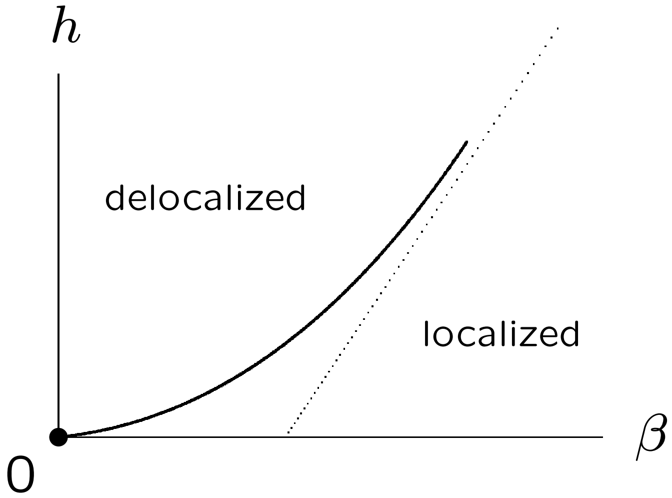
$$H_n^\omega(w) = \sum_{i=0}^{n} (\beta\omega_i - h)\, 1_{\{w_i = 0\}},$$

where $\beta, h \in (0, \infty)$ are the interaction strength and bias.



Different shades represent different disorder values.

There are two phases, localized and delocalized, separated by a critical curve:



DNA is a string of AT and CG base pairs forming a double helix: A and T share two hydrogen bonds, C and G share three. If we think of the two strands as performing random walks in three-dimensional space subject to the restriction that they do not cross each other, then the distance between the two strands is a random walk in the presence of a wall.

This view of DNA is called the Poland-Sheraga model. The localized phase corresponds to the bounded phase of DNA, where the two strands are attached. The delocalized phase corresponds to the denaturated phase of DNA, where the two strands are detached.

Upon heating, the hydrogen bonds that keep the base pairs together can break and the two strands can separate, either partially or completely. This is called denaturation.

§ CONCLUSION

Random polymers represent a research area where the following disciplines meet:

mathematics
physics
chemistry
biology.

Mathematics contributes ideas and techniques from

probability theory
functional analysis
combinatorics
ergodic theory.