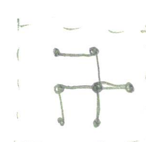
Lecture 5: Scaling theory

A. Self-Similarity

* Last time we talked about one theory of real chains called "Flory Theory." FT relied on what are called "mean-field" approximations. (ie FT is a "mean-field" theory.) In other words, we assumed that an average number of contacts governed the interactions.

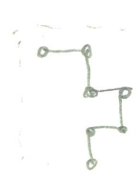
* Mean-field theories, like Flory theory, are not the only type of theory for the size of real chains. Another type of theory is called a "scaling theory." Before we learn about scaling theories, we need a bit of background.

* Recall in discussing ideal chains, we learned that an ideal chain is a random walk. We said it had some interesting properties:



  - A fractal object
  - Continuous, but non-differentiable pathway

* A "real" chain has some related properties. It is a self-avoiding walk (SAW). It's path is also a fractal object.

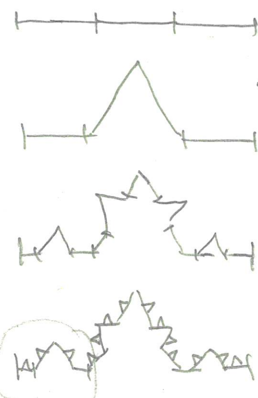


* let's be more precise about this. A fractal is an object that is self-similar.

self-similar – an object that is similar to part of itself.

Example: Koch curve (triadic)

(pronounce: like a can of Coke)



← equalateral triangle in middle third.

← repeat process

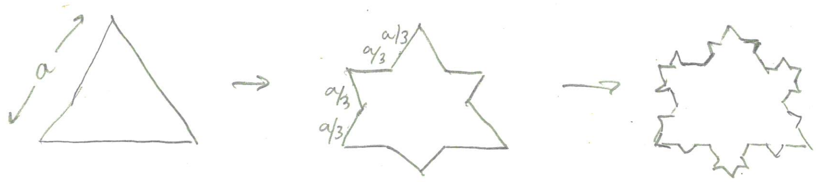
repeat on ad infinitum

(Koch curve is the limit of this process)

• If a smaller part is magnified, it looks just like the larger part

This is self-similarity

* Fractals are weird objects. Consider the Koch snowflake



$k=1$ $\qquad$ $k=2$ $\qquad$ $k=3$

• It has an infinite perimeter:

"Mandelbrot: can't define coast length of Britain"

$$p^{(1)} = 3a$$

$$p^{(2)} = 3 \cdot \tfrac{4}{3} a = 4a$$

$$p^{(3)} = 3 \cdot \left(\tfrac{4}{3}\right)\left(\tfrac{4}{3} a\right)$$

$$p^{(\infty)} = \lim_{k \to \infty} 3\left(\tfrac{4}{3}\right)^{k-1} a$$

diverges to ∞!

- But it obviously has a finite area.

(can compute, but not worth our time.
Here is derivation for completeness sake.)

$$A^{(1)} = \frac{\sqrt{3}}{4} a^2$$

$$A^{(2)} = \frac{\sqrt{3}}{4} a^2 + \frac{\sqrt{3}}{4} \cdot \left(\frac{a}{3}\right)^2 \cdot 3$$

$$A^{(3)} = \frac{\sqrt{3}}{4} a^2 + 3 \frac{\sqrt{3}}{4} \left(\frac{a}{3}\right)^2 + 4 \cdot 3 \frac{\sqrt{3}}{4} \left(\frac{a}{3^2}\right)^2$$

$$\vdots$$

$$A^{(\infty)} = \frac{\sqrt{3}}{4} a^2 + \sum_{k=1}^{\infty} 3 \cdot 4^{k-1} \cdot \frac{\sqrt{3}}{4} \left(\frac{a}{3^k}\right)^2$$

$$= \frac{\sqrt{3}}{4} a^2 \left[1 + \frac{3}{4} \sum_{k=1}^{\infty} \frac{4^k}{3^{2k}}\right]$$

$$= \frac{\sqrt{3}}{4} a^2 \left[1 + \frac{3}{4} \sum_{k=1}^{\infty} \left(\frac{4}{9}\right)^k\right]$$

recall, geometric series

$$\sum_{k=0}^{\infty} r^k = \frac{1}{1-r}$$

so,

$$\sum_{k=1}^{\infty} \left(\frac{4}{9}\right)^k = \sum_{k=0}^{\infty} \left(\frac{4}{9}\right)^k - \left(\frac{4}{9}\right)^0$$

$$= \frac{1}{1-\frac{4}{9}} - 1 = \frac{1}{\frac{5}{9}} - 1$$

$$= \frac{4}{5}$$

$$= \frac{\sqrt{3}}{4} a^2 \left[1 + \frac{3}{\cancel{4}} \cdot \frac{\cancel{4}}{5}\right] = \frac{\sqrt{3}}{4} \cdot \frac{8}{5} a^2 = \frac{2\sqrt{3}}{5} a^2$$

$$\boxed{A^{(\infty)} = \frac{2\sqrt{3}}{5} a^2}$$

- Ok, this is really weird. This is what we mean by "non-differentiable." Perimeter isn't definable by derivative of area or anything.

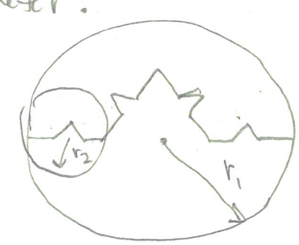
- This is a consequence of "scale invariance." what is the correct length scale for the koch curve? It has a whole spectrum of length scales!

* In real life, we (almost?) always have a finite "fractal perimeter." Can we somehow relate this to the area?

  - # of monomers of a polymer
  - path of a diffusing particle

  - The area gives us a measurable length scale!

  - How does the size (length scale) change with perimeter?



$r_1 = 3r_2$ → we know the lengths of the segments reduce by $1/3$rd)

$P_1 = 4P_2$ → There are 3 more $(1+3=4)$ segments in region 1 than 2.

suppose $P_1 = C \cdot r_1^D$ & $P_2 = C r_2^D$

$4P_2 = C(3r_2)^D \qquad P_2 = C r_2^D$

$$4(\cancel{c}\, r_2^D) = \cancel{c}\,(3r_2)^D$$

$$\ln 4 + \cancel{D \ln r_2} = D \ln 3 + \cancel{D \ln r_2}$$

$$\boxed{D = \frac{\ln 4}{\ln 3}} \simeq 1.262$$

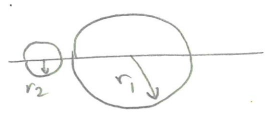
$$P \simeq r^{\ln 4/\ln 3} \quad \text{or} \quad r \simeq P^{\ln 3/\ln 4} \simeq P^{1/D}$$

perimeter   size

$$\boxed{r \simeq P^{1/D}}$$

- what is D?

  - suppose "fractal" was a simple line?

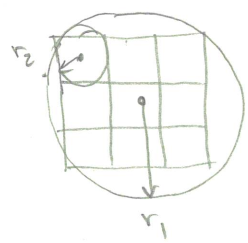


$r_1 = 3r_2$ $r_1 = C_r r_2$

$P_1 = 3P_2$ $P_1 = C_p P_2$

$$D = \frac{\ln C_p}{\ln C_r} = \frac{\ln 3}{\ln 3} = 1$$

  - suppose "fractal" is a square (P is now an area)



$r_1 = 3r_2$

$P_1 = 9P_2$

$$D = \frac{\ln 9}{\ln 3} = \frac{\ln 3^2}{\ln 3} = 2$$

  - D is the dimension of the shape

- Fractal objects have a <u>non-integer</u> dimension

* <u>Now to polymer chains</u>. what is the fractal dimension of a polymer chain

- An ideal chain : $R \simeq bN^{1/2}$

$\uparrow$ size $\quad$ $\uparrow$ "perimeter", path length of fractal curve

(*) Notation
= : equal
$\simeq$: drop constants
$\sim$: scales like, not dimensionally consistent

$$\boxed{R \sim N^{1/D} \qquad D = 2}$$

- A self avoiding walk : $R \simeq bN^{\nu}$, $D = 1/\nu$
  - F.T. predicts $\nu = 3/5$ or $D = 5/3$
  - More exact calculations (simulations, renormalization group theory) give $\nu = 0.588$

- For a SAW, it is not a 1D object or a 2D object. Like a koch curve, it is something in between.

B, Scaling theory

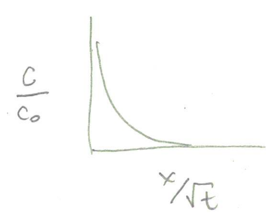
* When a physical problem has "no natural length scale", it's properties are usually (always?) invariant to a change in length scale.

- Deep property of nature. Like Galilean invariance, which says laws cannot depend on frame of reference.

- Is a limiting property. Usually only applies in limits (e.g. much bigger than molecule size)

- Examples:

  - Diffusive transport into semi-infinite medium

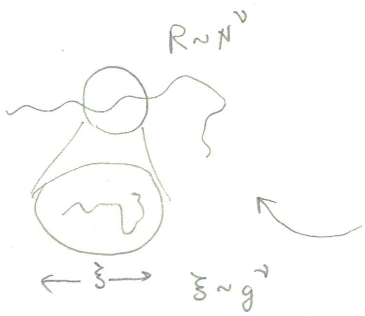


  - critical point in gas-liquid. Fluctuations at all length scales (above molecular)

  - turbulence (eddy sizes at all length scales)

  - Dimensionless quantities in relation to each other.

  - Polymer conformations (size of chain does not depend on the scale we are looking at)



* Scale invariance is expressed mathematically by the relationship:

$$f(\lambda x) = \lambda^{\Delta} f(x)$$

change of scale by λ — same function

- This kind of relationship is a "scaling law"
- We have already seen examples:

$$R \simeq bN^{\nu}$$

written as

$$R(Nb) = N^{\nu} b$$

- All monomials are scale invariant

$$f(x) = x^n$$

$$f(\lambda x) = (\lambda x)^n = \lambda^n x^n$$

← power laws. Think dimensional analysis here.

* Scaling laws give us a deeper understanding of universality. Universality applies to polymers in the limit that scaling laws describe behavior
  - Exponents & functional dependence is universal
  - Coefficients depend on microscale properties

$$R \simeq bN^{\nu}$$

← universal b/c of scale invariance.

microscale properties buried here

* what is a scaling theory?

- If the properties of polymers don't depend on length scale, we expect dimensionless ratios to be related by power laws.

Step 1: Dimensional Analysis

$$N_1 = f(N_2)$$ N_1 & N_2: dimensionless groups

Step 2: write as a power law

$$N_1 \simeq (N_2)^{\Delta}$$ Polymer properties are scale invariant.

Step 3: Postulate exponents based on physical intuition

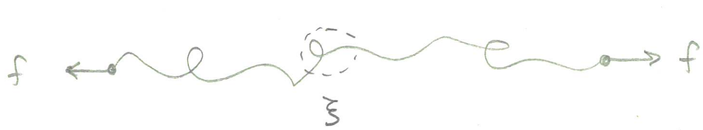
* Polymer Size:

(1) $\frac{R}{b}$, N (2) $\frac{R}{b} \simeq N^{\Delta}$ (3) $\Delta = \nu$ of a SAW

$$R \simeq bN^{\nu}$$

- Can give you a lot. But cannot give coefficients
- Does not neglect correlations. Different than mean-field theory!

* Example: Polymer under tension



(1) R_f : size under tension , N monomers

ξ : "tension blob" , g monomers

↑ size of the chain where tension force is $\simeq kT$, so the "blob" is not deformed , $\xi = bg^\nu$

($\nu = 1/2$ or $3/5$)

(2) $$\frac{R_f}{\xi} = f\left(\frac{N}{g}\right) = \left(\frac{N}{g}\right)^\Delta$$

(3) $\Delta = 1$, blobs are aligned along f.

$$R_f \simeq \xi \frac{N}{g} \leftarrow \text{get rid of } g : \quad g = \left(\frac{\xi}{b}\right)^{1/\nu}$$

$$R_f \simeq \xi \frac{b^{1/\nu} N}{\xi^{1/\nu}} \simeq \frac{(bN^\nu)^{1/\nu}}{\xi^{1/\nu - 1}} \simeq \frac{R^{1/\nu}}{\xi^{1/\nu-1}}$$

$$\frac{1}{\nu} - 1 = \frac{1-\nu}{\nu}$$

$$\xi^{1/\nu - 1} \simeq \frac{R^{1/\nu}}{R_f} \Rightarrow \boxed{\xi \simeq \frac{R^{1/1-\nu}}{R_f^{\nu/1-\nu}}}$$

for ideal: $\xi = \dfrac{R^2}{R_f}$

for real: $\xi = \dfrac{R^{5/2}}{R_f^{3/2}}$

- Now repeat for free Energy :

(1) F: free energy

kT: Thermal energy

(2) $$\frac{F}{kT} \simeq \left(\frac{N}{g}\right)^\Delta \simeq \frac{N}{g}$$

(3) $\Delta = 1$ $$\frac{F}{kT} \simeq \frac{N}{g} \simeq \frac{R_f}{\xi}$$

$$\Rightarrow \frac{F}{kT} \simeq R_f \cdot \frac{R_f^{\nu/1-\nu}}{R^{1/1-\nu}} = \left(\frac{R_f}{R}\right)^{1/1-\nu}$$

$$\boxed{F \simeq kT\left(\frac{R_f}{R}\right)^{\frac{1}{1-\nu}}}$$

ideal: $F \simeq kT\left(\frac{R_f}{R}\right)^{2}$

real: $F \simeq kT\left(\frac{R_f}{R}\right)^{5/2}$

* Example: Polymer under compression

(1) $R_{\parallel}$, D, N, g

D takes place of ξ "compression blob" size

$D \simeq b g^{\nu}$

$\rightarrow \quad g \simeq (D/b)^{1/\nu}$

(2) $\frac{R_{\parallel}}{D} \simeq f\left(\frac{N}{g}\right) \simeq \left(\frac{N}{g}\right)^{\Delta}$

case 1: Ideal chain

$\Delta = 1/2$, random walk of compression blobs

$\frac{R_{\parallel}}{D} \simeq \left(\frac{N}{g}\right)^{1/2} \qquad g \simeq (D/b)^2, \quad (\nu = 1/2)$

$\frac{R_{\parallel}}{D} \simeq \left(\frac{b^2 N}{D^2}\right)^{1/2} \Rightarrow \boxed{R_{\parallel} \simeq N b^{1/2}}$ Not affected!

- Deformation in 1 direction does not affect other dimensions

case 2: real chain

$\Delta = 1$, self-avoiding walk of compression blobs

$\frac{R_{\parallel}}{D} \simeq \frac{N}{g} \qquad g \simeq (D/b)^{5/3} \qquad \nu = 3/5$

$R_{\parallel} \simeq D \cdot \frac{N b^{5/3}}{D^{5/3}} \simeq \left(\frac{b}{D}\right)^{2/3} N b \qquad \boxed{R_{\parallel} \simeq \left(\frac{b}{D}\right)^{2/3} \cdot L}$

- Repeat for free Energy

(1) $F,\ kT\ ,\ N,\ g$ (2) $\frac{F}{kT} \simeq \left(\frac{N}{g}\right)^{\Delta}$

(3) let $\Delta = 1$, free energy is extensive in # of blobs

$$\frac{F}{kT} \simeq \frac{N}{g} \simeq \frac{N b^{1/\nu}}{D^{1/\nu}}$$

$$\boxed{\frac{F}{NkT} \simeq \left(\frac{b}{D}\right)^{1/\nu}}$$

ideal: $\frac{F}{NkT} \simeq \left(\frac{b}{D}\right)^{2}$

real: $\frac{F}{NkT} \simeq \left(\frac{b}{D}\right)^{5/3}$

* Compare the last to my paper.

* Scaling theory often seems really "loosey-goosey" to some theory people. The dimensional analysis seems ok, but then it feels made up.

All of this can be much more rigorously justified with <u>renormalization group theory</u> (RG).

without going into too many details.

(1) write down partition function for polymer
$G_B(R, N_0, u_0; a)$ (B: bare)

(2) Rescale important parameters (e.g. excluded volume)
(e.g. $u \to u_0$, $N \to N_0$, $L \to a$)

(3) write a scaling relation between scaled & unscaled partition function

Examples for Excluded volume problem
Freed & Kholodenko, J. Stat. Phys. 30, pp437-447 (1983)

$$G(\underline{R}, N, u; L) = Z\left(u, \tfrac{a}{L}\right) G_B(R, N_0, u_0; a)$$

(4) Use scale invariance:

$$L \frac{\partial}{\partial L} G_B(R, N_0, v_0; a) = 0$$

change of length scale $\Rightarrow$ should not change partition function

(5) Solve differential equation for G.

- This gives a partition function

$$G(R, N, u^*; L) = N^\Delta f\left(R/N^\nu\right)$$

- Rigorously justifies scaling theory assumptions
  - derives exponents
  - gets functions, even when not in scaling limits
  - gets numerical prefactors.

- Super messy math.
  - Sometimes the rescaled terms diverge & it causes problems.