통계물리 겨울학교

Statistical physics of polymers

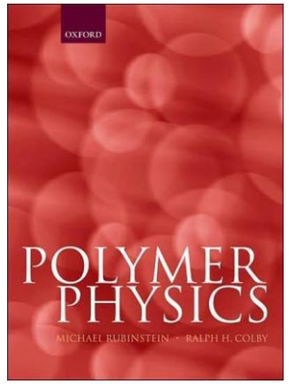
Part I: Polymer Physics and Polymer Field Theory

2025. 01. 06

Jaeup Kim (UNIST)

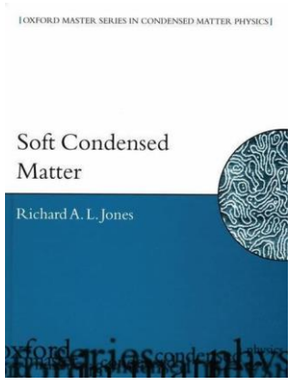


Textbooks and References



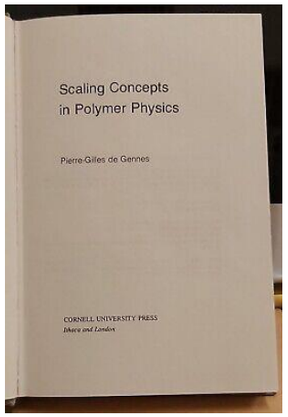
Polymer Physics Michael Rubinstein

고분자물리에 대한 입문서로 적당하다.



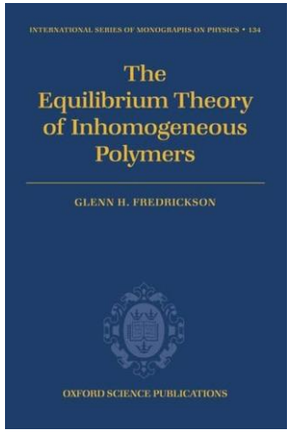
Soft Condensed Matter R. A. L. Jones

Soft Matter에 대한 입문서. Chapter 5에서 고분자를 소개한다.
학부 고학년/대학원생 비전공자들에게도 적합한 난이도이다.



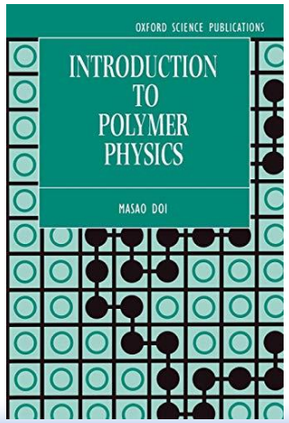
Scaling Concepts in Polymer Physics de Gennes

얇고 내용이 얼마 없어 보이지만 실제로는 깊이가 있는 책이다.
어느 정도 고분자물리에 익숙해지지 않으면 읽기 쉽지 않다.



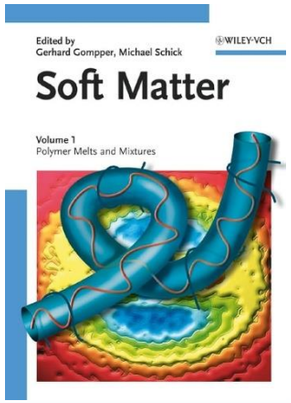
The Equilibrium Theory of Inhomogeneous Polymers
G. H. Fredrickson

본격적으로 고분자 이론연구를 하고 싶은 학생들에게 좋은 출발점.



Introduction to Polymer Physics M. Doi

고분자 물리 이론에 대해 가볍게 소개하는 책.
(사실 책이 얇을 뿐, 내용의 난이도는 낮지 않다.)



Soft Matter, Volume 1: Polymer Melts and Mixtures
Chapter: Self-consistent field theory and its applications
M.W. Matsen, edited by G.Gompper and M. Schick

본격적으로 고분자이론 연구를 하고 싶은 학생들에게 좋은 출발점.
특히 SCFT에 대해서는 (출판 시점에서 봤을 때) 완벽에 가까운 리뷰를 제공한다.

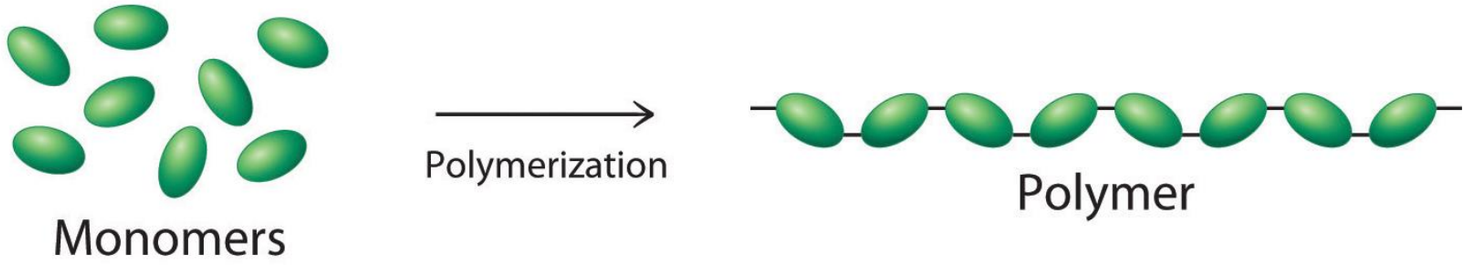
Polymer Age

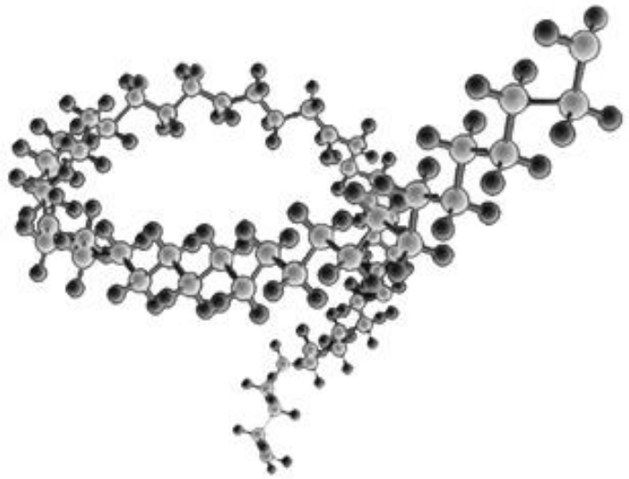
- 20세기는 화학과 재료공학의 발전을 통해 합성 고분자(polymer)의 발견과 상용화가 급격히 이루어진 시기였다.
- 폴리머는 천연 물질인 셀룰로스와 천연고무뿐만 아니라, 인류가 새롭게 합성한 나일론, 폴리에틸렌, 폴리프로필렌 같은 소재까지 포함한다.
- 고분자는 가벼우면서도 내구성이 뛰어나고 다양한 용도로 활용 가능하다는 점에서 20세기 기술 혁신의 중심에 있었다.
- 특히, 산업 및 일상생활에서 필수적인 플라스틱, 합성섬유, 고무 제품들은 고분자과학의 발전 없이는 불가능했을 것이다.
- 이러한 배경 속에서 20세기를 고분자가 인류 문명을 재정의하고 현대 생활의 기반을 제공한 “Polymer Age”라고 부르곤 했다. (21세기 들어서는 아무도 그런 주장을 하지 않는다.)

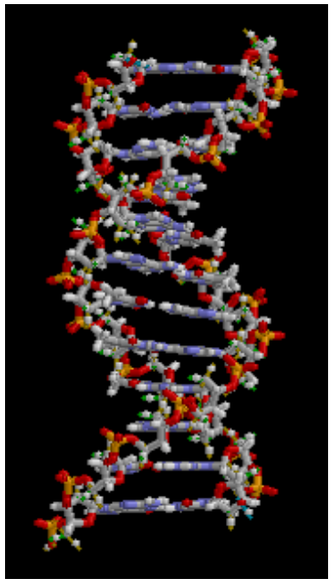
Introduction to Polymers

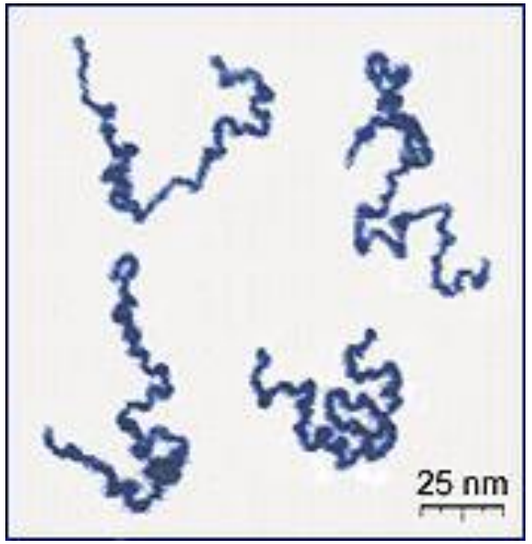
What is a polymer?

A polymer is a large molecule (macromolecule) composed of repeating structural units (monomer).



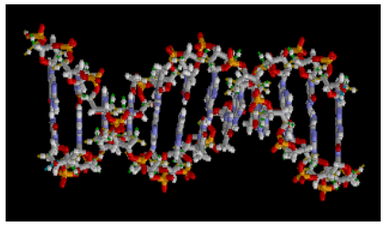


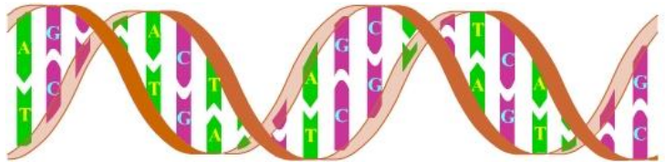




Polymeric materials form a large and important class of soft condensed matter.

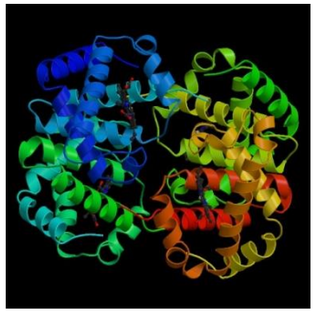
Natural Polymers





DNA, RNA

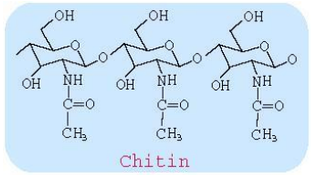
Polynucleotides

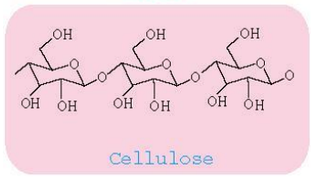


http://www.pdb.org
PDB ID : 1A3N
(J. Tame and B. Vallone)

Proteins

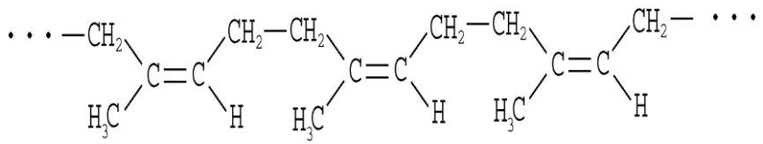
Polypeptides





Starch (Potatoes , Wheat)
Cellulose (Wood, Paper, Cotton)

Polysaccharides



Natural Rubber
(Sap of Hevea Braziliensis tree)

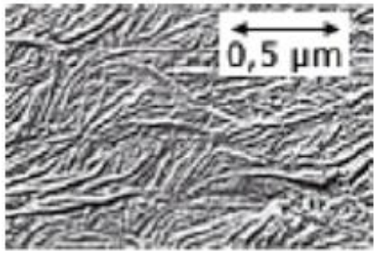
Polyisoprene

What are polymers?

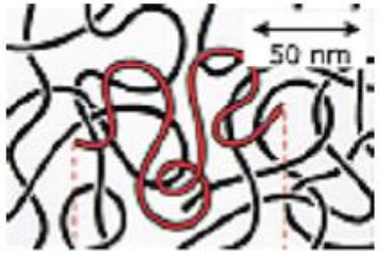


Photo: L. Falk

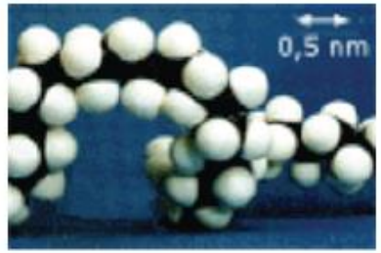
Plastic, rubber, plexiglas, gels and textile fibres such as nylon and polyester are all synthetic materials made of polymer molecules.



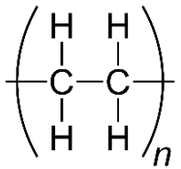
A Frisbee is a mixture of crystalline (ordered) and amorphous (disordered) polymer structures.
This makes the material both strong and flexible.



Each polymer molecule consists of linked basic units called monomers. The number of monomers in a chain can be very large, from thousands to several millions. The chains may be entangled like spaghetti (as above) or be ordered in crystalline formations.



The monomer is specific for every polymer and determines the name of the substance. A Frisbee is made of polyethylene which consists of linked ethylene (CH_2CH_2) monomers.

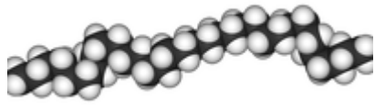


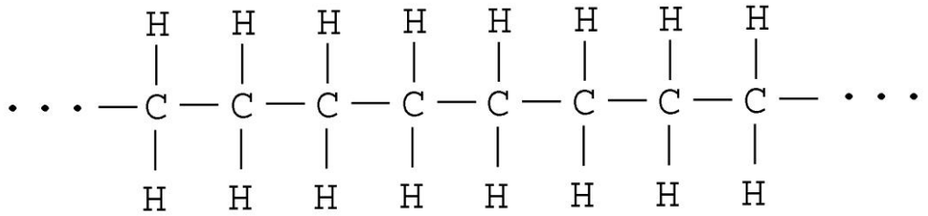
from http://nobelprize.org/nobel_prizes/physics/laureates/1991/illpres/polymers.html

Applications: plastics, paint, adhesives, fibers, fabrics, tires, flooring(vinyl and carpeting), molding, packaging, automotive, pipes, valves, tanks, electronics, lubricants, sports goods, shampoo, cosmetics, agriculture, optics, CD's, etc.

Synthetic Polymers

Polymers may be synthetic in origin; plastics such as polystyrene (PS) and polyethylene (PE) are polymers, as are the components of many glues, fibers, and resins (수지).





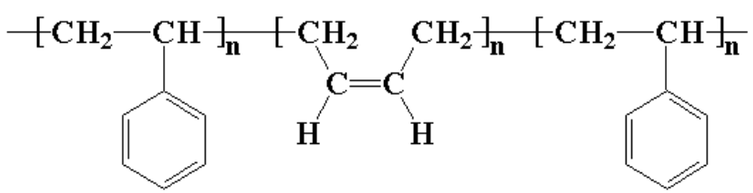
Polyethylene

Bags, bottles, …
Bullet proof vests







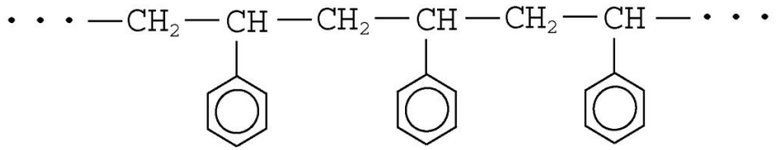


Poly(styrene-butadiene-styrene)

SBS rubber (Tyre treads)







Polystyrene

Car interiors, etc





PMMA Paints, Ultratough glass (e. g. plexiglass)

Polyvinylacetate(PVA) Adhesives Coatings

PVC Pipes

The Variety of Polymeric Materials

- A polymer is a giant molecule made up of many repeat units **covalently joined** together in the form of a long chain.

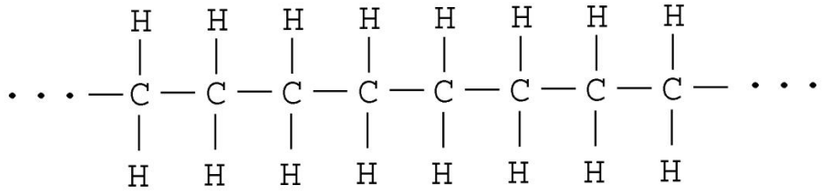
- In some long-chain, the objects, the subunits, are joined not by covalent bonds, but by **physical ones**. Examples of this are the giant worm-like micelles formed in some amphiphile solutions and the actin filaments.

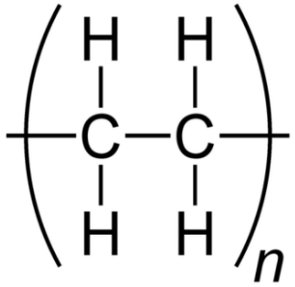
- Such objects are sometimes called **living polymers** and they can change their length in response to changes in the environment. This contrasts with the more usual covalently linked polymers, in which the length of the molecules is fixed during the polymerization process.

- In this lecture, we restrict our attention to covalently linked polymers, but even here we find tremendous variety. For the time being, let us review this variety, before discussing those polymer properties that are more universal.

Polymer Chemistry

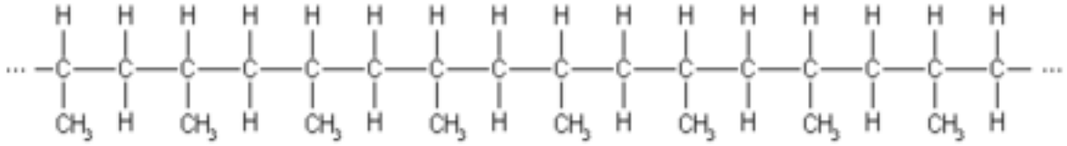
The repeating units are called monomers.

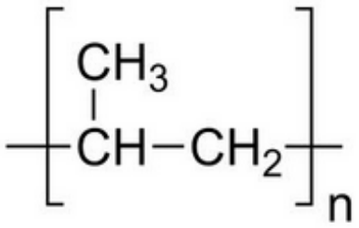




-A-A-A-A-A-A-A-A-

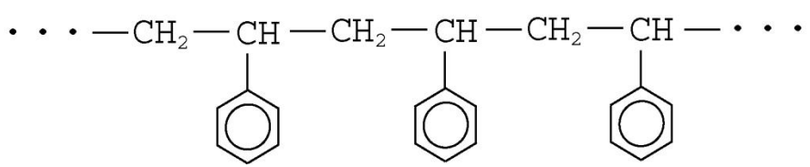
Polyethylene (PE)

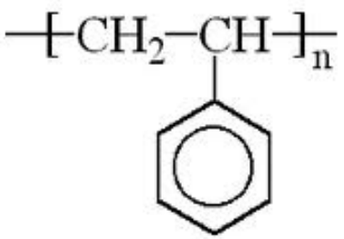




-B-B-B-B-B-B-B-B-

Polypropylene (PP)





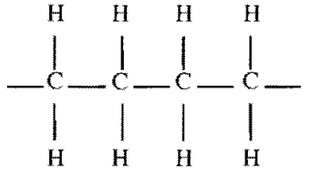
-C-C-C-C-C-C-C-C-

Polystyrene (PS)

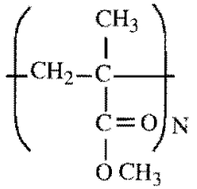
Polymer Chemistry

- Polymer chemistry is a predominant branch of organic chemistry; **most polymers are based on carbon**. But even with this distinction, there is a huge variety of possible structures and the polymers follow different properties from the different structures.
- Some examples are shown in the figure. the simplest chemical structure is a carbon main chain with two hydrogen atoms per carbon—PE.
- The main chain can incorporate atoms which are not carbon, i.e. nylon 6-10.
- The main chain can involve loops, such as **amylose**, or it can be multiply connected, forming a ladder structure, such as poly(dioctylfluorene).
- Some polymers do not involve carbon in their main chain at all, such as poly(dimethyl siloxane).
- Here we don't mention of the many **synthetic routes** by which polymers are made at all. However, physicists should recognize the tremendous intellectual and practical achievements of polymer chemists, who have **devised synthetic routes allowing precise control of polymer composition and architecture**. Without these developments, few of the advances in understanding made by polymer physics would have been possible.

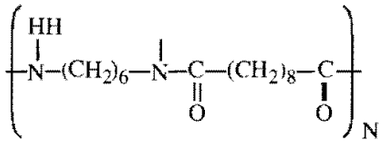
Polyethylene



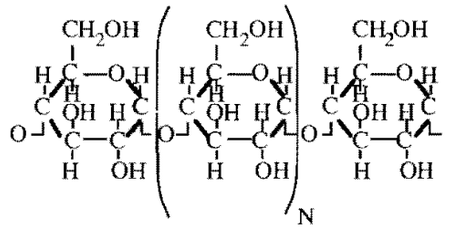
Polymethyl methacrylate



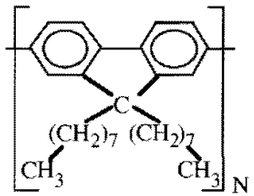
Nylon 6-10



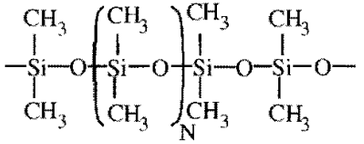
Amylose



Poly(di-octyl fluorene)

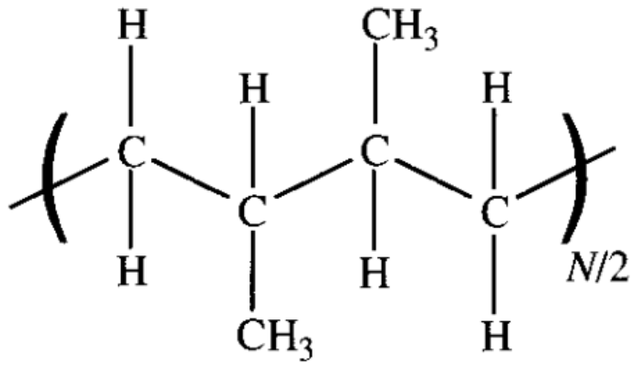


Polydimethyl siloxone

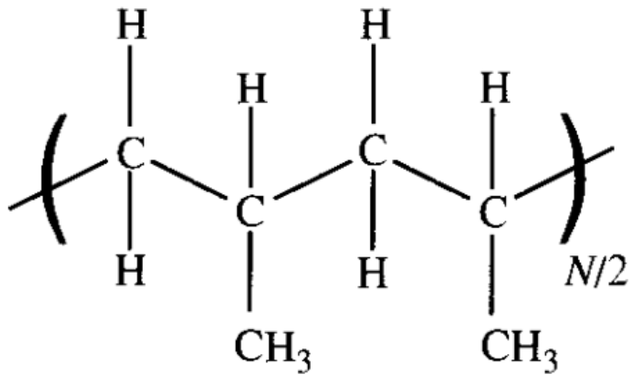


Sequence and Structural Isomerism

Example of **sequence isomerism** are shown in the figure.
(head-to-head isomer and head-to-tail isomer of polypropylene)

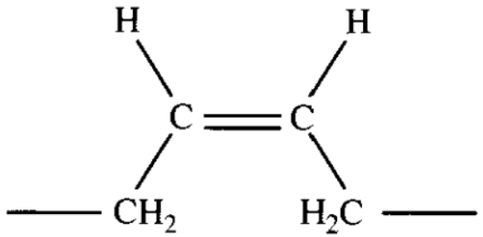


Head-to-head polypropylene

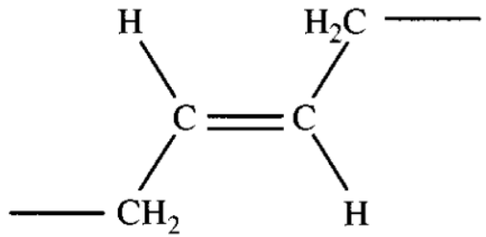


Head-to-tail polypropylene

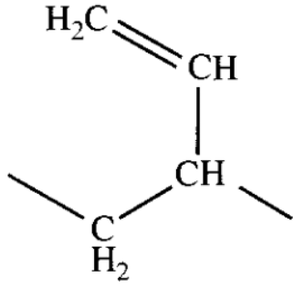
Polymers that contain a double bond in their backbone can exhibit **structural isomerism**.
Cis-, **trans-** and **vinyl-**polybutadiene are shown in the figure.



cis



trans

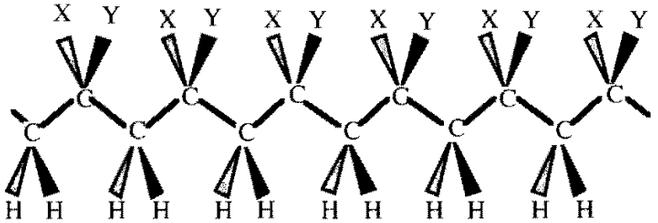


vinyl

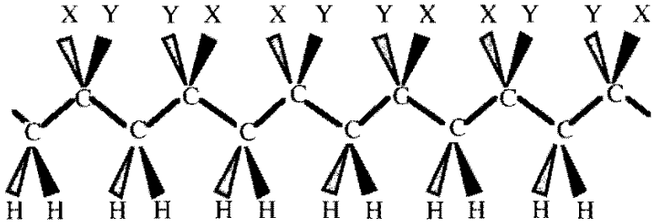
Stereoisomerism

If a polymer has more than one type of chemical groups attached to each main chain carbon atom, different arrangements of the groups are possible. The figure below shows three possible arrangements of a simple carbon main chain polymer with two different groups per carbon atom. For example, if X is a hydrogen atom and Y is CH_3, this would be polypropylene.

There are two regular arrangements of side groups: these are called **isotactic** and **syndiotactic**. In these, the similar side groups appear on the same side of the chain or on alternate sides, respectively. If the arrangement of the groups is **random**, then we have an **atactic** polymer.

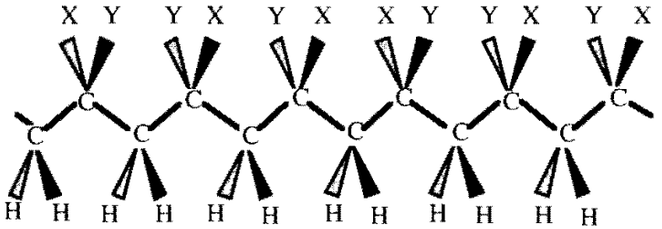


Isotactic



Syndiotactic

The importance of the atactic arrangement is that it involves **quenched disorder**. The energy barriers to rotation of the side groups are so large that once the arrangement is set in place during the synthesis of the polymer, no rearrangement of the groups occurs. **Thus even at absolute zero, there will still be some residual disorder.** The quenched disorder inherent in atactic polymers means that these molecules usually find it impossible to crystallize—at low temperatures these materials form **glasses**.



Atactic

Structure of Polymers

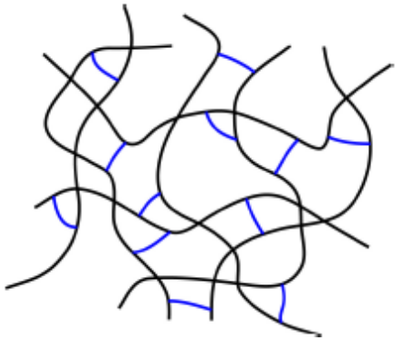
- **Linear Polymer**
  - Linear polymer consists of a long chain of skeletal atoms to which are attached the substituent groups.
  - Examples: PVC, PMMA, PE, Nylon
- **Branch Polymers**
  - Linear polymers with branches.
- **Network Polymers**
  - Chemical linkages exist between the chains.
- **Star Polymers**
  - Have arms (3 or more) radiating from a common core.
- **Ladder Polymers**
  - Consist of linear molecules in which two skeletal strands are linked together in a regular sequence by crosslinking units.



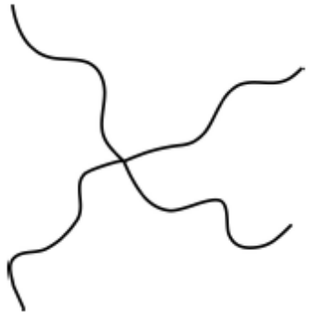
linear polymer



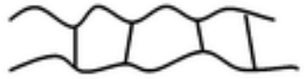
branched polymer



network polymer



star polymer



Ladder polymer

Copolymers

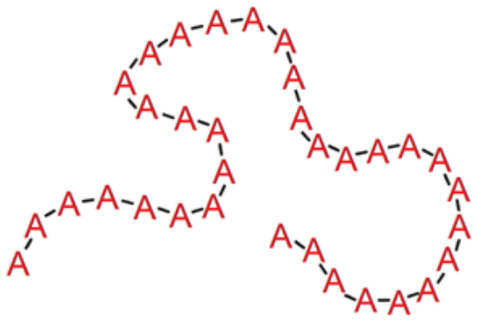
In many polymers, the molecule is formed from a **single type of repeat unit**—such molecules are called **homopolymers**.

However, other polymers are composed of **more than one type of repeat unit**. They are called **copolymers**. Copolymer molecules consist of two or more chemically distinct monomer units.

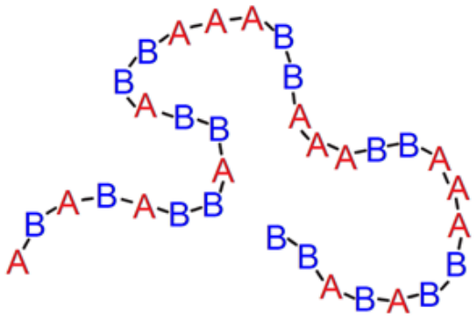
Molecules with strikingly different properties are obtained according to the way in which the different repeat units are arranged.

A purely random arrangement of repeat units gives a **random copolymer**. Once again, the random distribution of groups gives a molecule with quenched disorder and this generally prevents these materials from crystallizing well.

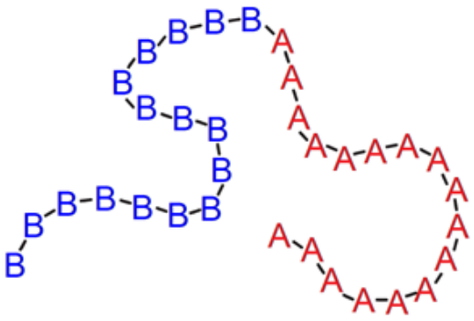
Apart from this, the properties of such random copolymers are often found to be intermediate between the properties of the two homopolymers formed from the two repeating units.



Homopolymer

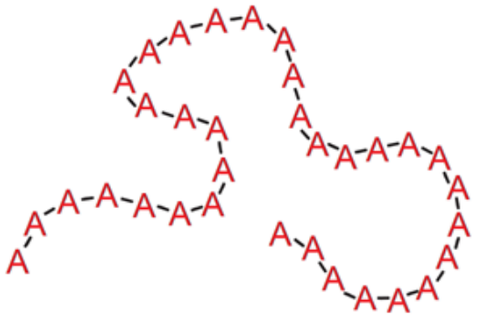


AB Random Copolymer

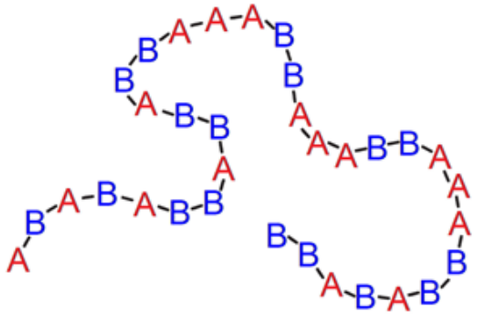


AB Diblock Copolymer

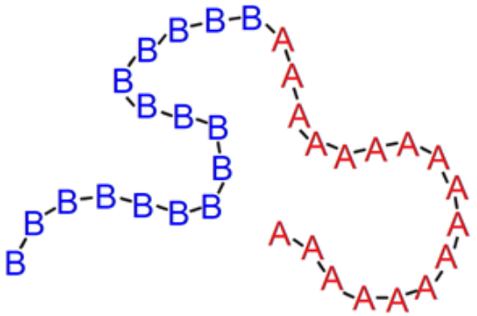
Copolymers



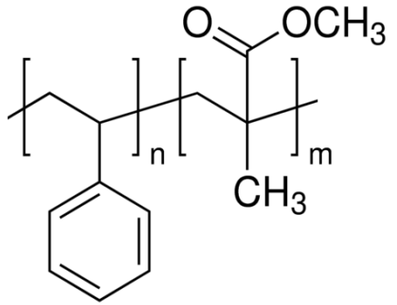
Homopolymer



AB Random Copolymer



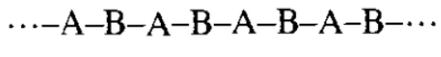
AB Diblock Copolymer



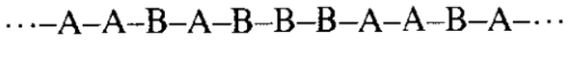
PS-PMMA
Block Copolymers

Dramatically new properties emerge if the **different repeating units are arranged in blocks**. In such a **block copolymer**, if the two (or more) types of repeating unit are very different chemically, they may have a tendency to phase-separate.

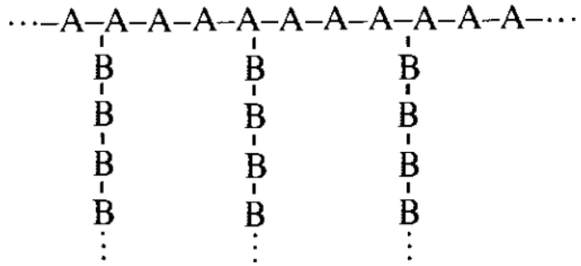
But because the blocks are covalently linked, complete macroscopic phase separation is not possible. Instead, they **microphase separate** into a wide variety of possible complex morphologies (see later slides).



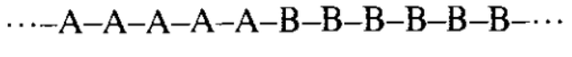
Alternating



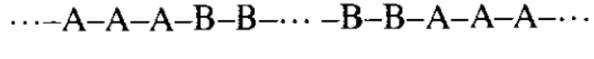
Random



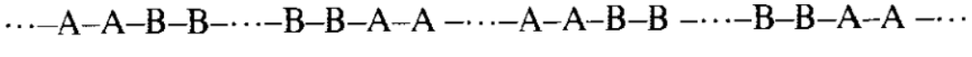
Graft



Diblock



Triblock



Multiblock

Copolymers

A final, very special class of copolymer is formed by the biopolymers **DNA and proteins**.

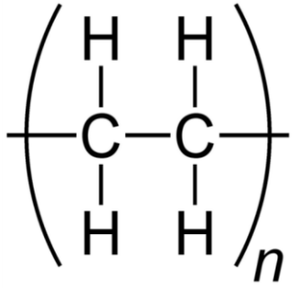
These are made up from repeating subunits of different chemical types which are arranged in a strictly prescribed, but non-periodic sequence.

At first sight, such **sequenced copolymers** are similar to random copolymers, but there is a profound difference.

The synthesis of a sequenced copolymer produces just one arrangement—a sequence that has been selected by evolution to have a particular property.

In the case of many proteins, this property is the ability of a single molecule to self-organize into a **complex but well-defined three-dimensional structure**.

Molecular Weight



According to the way in which they are synthesized, chains may be linear or branched. Examples of linear polymers are high-density polyethylene and most simple proteins.

Linear polymers are completely characterized by the number of repeat units present in the chain, the **degree of polymerization, *N***. This is proportional to the relative **molecular mass of the chain, *M***: the mass of one mole of these molecules.

For example, a polyethylene molecule consisting of $N = 1000$ chemical monomers, each with molar mass $M_{\text{mon}} = 28\ \text{gmol}^{-1}$, has a molar mass $M = 28000\ \text{gmol}^{-1}$. It is often stated that $M = 28000$ Da (Daltons), where

$$1\ \text{Da} = 1.66053906892(52) \times 10^{-27}\ \text{kg}$$

모노머 20개 정도 이하인 분자를 oligomer라고 따로 분류하기도 한다.

Molecular Weight

Almost all synthetic polymers are made by processes that yield not a single degree of polymerization, but a distribution. This distribution can be characterized by various averages, of which the most important are the **weight average** and the **number average**.

The **number average molecular mass** M_n is the ordinary arithmetic mean of the molecular masses of the macromolecules. Assuming that for each i, the number of molecules of molecular mass M_i is N_i,

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

The mass average molar mass or **weight average molar mass** M_w is calculated by

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

Q. why do we care the latter?

A. It can be easily measured experimentally via static light scattering, small angle neutron scattering, X-ray scattering, and sedimentation velocity.

Dispersity

The ratio of these two averages shows the broadness of the chain length distribution, and is known as the **dispersity *Đ*** (previously called polydispersity index, PDI).

$$Đ = \frac{M_w}{M_n}$$

The dispersity of synthetic polymers, particular those that are commercially available in large quantities, poses substantial difficulties in understanding their properties. Fortunately, for the point of view of fundamental studies, **chemists have been able to devise synthetic routes to obtain polymers with narrow distributions**.

If the polymers are monodisperse (all chains have the same length), the dispersity $Đ = 1$.
As the chain length distribution becomes broader, its value increases.

Problem: Consider a mixture containing number fraction 0.5 of chains with molar mass 10^5 gmol^{-1} and number fraction 0.5 of chains with molar mass 2×10^5 gmol^{-1}. Calculate its dispersity Đ.

$$M_n = 0.5 \times (10^5 + 2 \times 10^5) = 1.5 \times 10^5 \text{ gmol}^{-1}$$

$$M_w = \frac{0.5 \times (10^{10} + 4 \times 10^{10})}{1.5 \times 10^5} = 1.67 \times 10^5 \text{ gmol}^{-1}$$

$$Đ = \frac{10}{9}$$

Both synthetic and natural polymers may be branched. For example, **low-density polyethylene contains many branches**. Once again, these branched points introduce quenched disorder and hinder the formation of crystals. The presence of branches also has profound effects on their rheology as we see later.

As more and more branch points are introduced to a polymer system, one can create a **network that spans a macroscopic volume**. In this case, the polymer molecule essentially assumes macroscopic dimensions. Examples of such networks include vulcanized rubber and cured epoxy resins. Curing is a chemical process producing toughening or hardening of a polymer material by cross-linking of polymer chains.

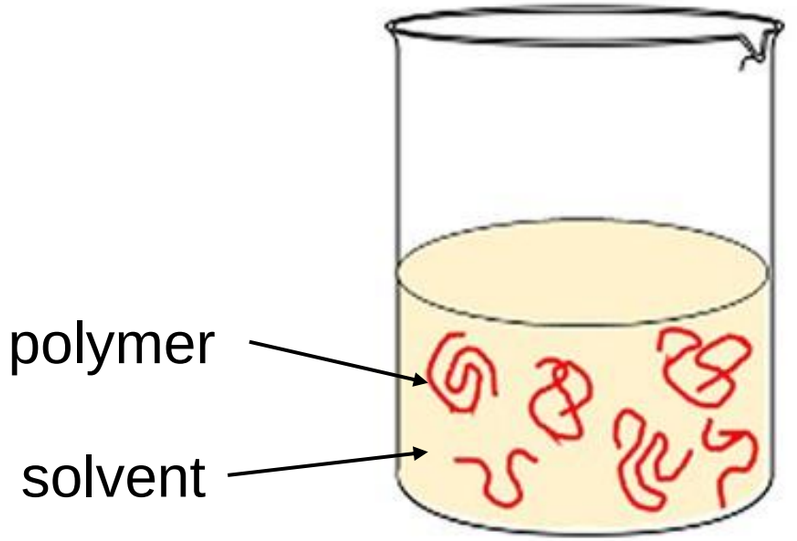
Polymeric Liquids

Polymer solution = polymer solute + solvent

Polymer solution은 고분자(polymer)가 용매(solvent)에 녹아 형성된 균일한 혼합물이다.

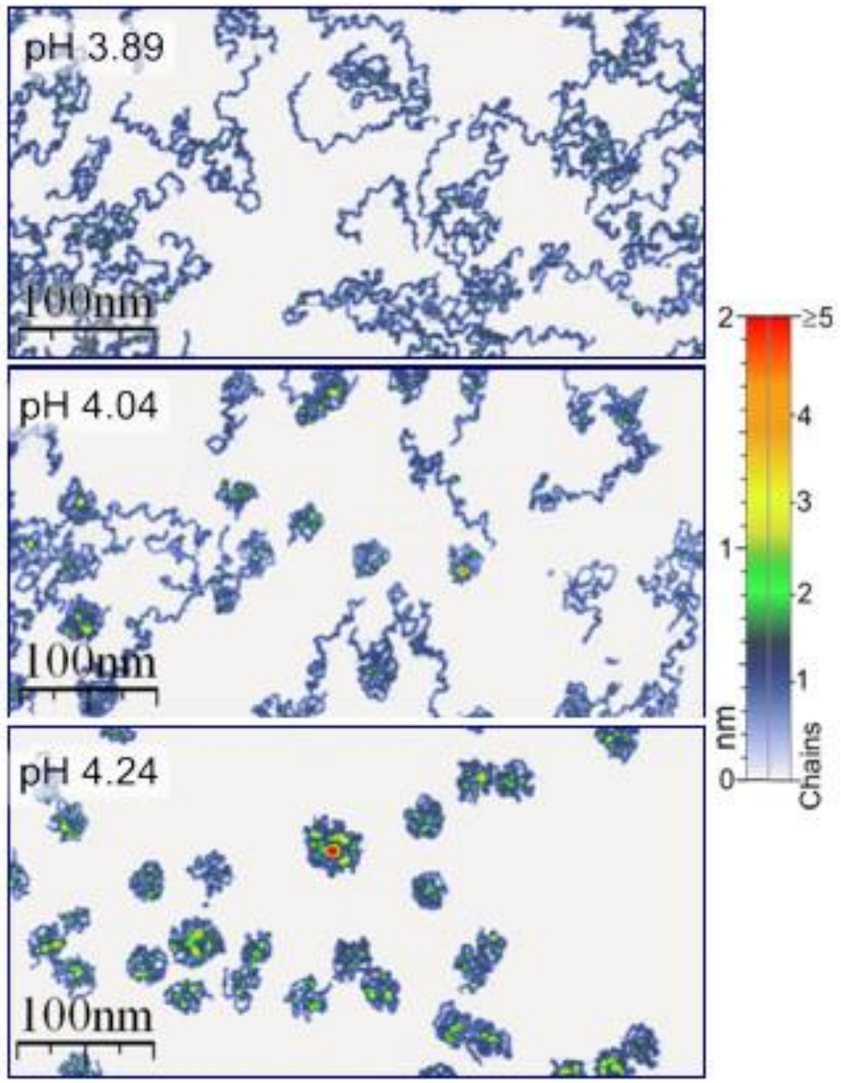
이 용액은 고분자 사슬이 용매 분자와 상호작용하며 분산된 상태로 존재하는 시스템으로, 고분자의 농도와 분자량, 용매의 종류, 온도 등에 따라 독특한 물리적 성질을 나타낸다.

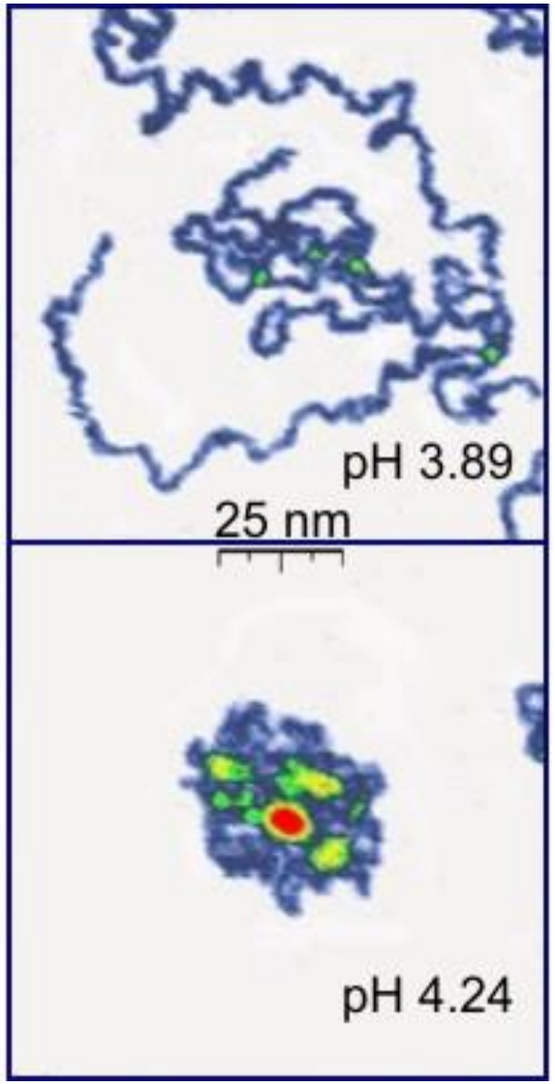
일반적인 저분자 용액과 달리, 고분자 용액은 점도 증가, 고분자 사슬의 코일링 현상, 그리고 상분리 현상 등 고분자 특유의 거동을 보여준다.



본 강연에서는 polymer solution의 이론에 대해서는 기본적인 소개만 할 것이다.

Polymeric Liquids





Single polymer molecule images recorded using a MultiMode microscope equipped with a fluid cell.

A sharp coil-to-globule transition of a poly(2-vinylpyridine) molecule upon pH change has been observed in this AFM images. (Roiter, Y. and Minko, S., J. Am. Chem. Soc. 2005)

Polymeric Liquids

- **Polymer melts** : In the absence of solvent, polymers become liquids above the melting temperature.

- They can be considered as **incompressible fluids**.



R. Hoy/University of South Florida; M. Kröger/ETH Zurich

Polymer melt는 고분자가 용매 없이 가열되어 녹은 상태로, 고분자 사슬이 액체와 유사한 움직임을 가지는 점성 상태를 가리킨다.

이 상태에서는 (원칙적으로) 고분자 분자가 자유롭게 움직일 수 있지만, 긴 사슬 구조로 인해 일반적인 저분자 액체와는 다른 점탄성(viscoelastic) 거동을 보인다.

고분자 용융체는 고분자 가공 공정(예: 사출 성형, 압출, 블로우 몰딩)에서 중요한 역할을 하며, 온도와 고분자의 분자량, 분자 구조에 따라 점도와 유동 특성이 크게 달라진다.

Phase Transition and Melting Temperature

유리 전이 온도(T_g)

고분자의 비결정(amorphous) 영역에서 고분자 사슬의 운동성이 제한된 경직 상태(glassy state)에서 더 유연한 상태(rubbery state)로 변환되는 온도이다. 이 전이는 고분자 사슬의 운동성이 제한된 상태에서 부분적으로 자유로워지는 과정을 나타낸다.
모든 고분자에서 관찰되며, 비결정성 고분자 또는 결정성 고분자의 비결정 부분에서 발생한다.

유리 전이 온도(T_g)는 고분자의 화학 구조, 분자량, 가소제의 유무 등에 따라 달라지며, 고분자의 기계적 성질, 열적 안정성 및 가공성을 결정짓는 중요한 특성 중 하나이다.
T_g 이상에서는 고분자가 더 유연하고 연성이 높은 반면, T_g 이하에서는 딱딱하고 깨지기 쉬운 특성을 보인다.
예: 폴리스티렌(PS), 폴리카보네이트(PC) 등.

녹는점(T_m)

고분자의 결정(crystalline) 영역이 열에 의해 녹아 액체로 변하는 온도.

고도로 규칙적인 사슬 배열을 가진 고분자(결정성)가 일정한 T_m을 가진다.

예: 폴리에틸렌(PE), 폴리프로필렌(PP) 등

고분자	T_g (°C)	T_m (°C)
폴리에틸렌(PE)	−125	137
폴리프로필렌(PP)	−10	160
폴리스타이렌(PS)	100	비결정성, T_m 없음
폴리테트라플루오로에틸렌(PTFE)	127	327

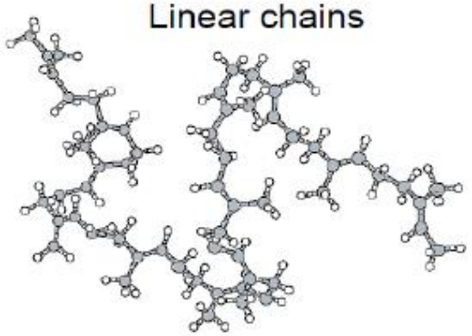
Physical state

At a given temperature and processing route, polymeric materials can be found in a variety of physical states.

- **Liquid**
  - Polymer **melts and solutions** are liquids, but they often are very viscous and show marked viscoelastic properties. **Dilute solvent and melt are fundamentally different**.
- **Glass**
  - Because of the difficulty of crystallizing polymers, **polymer glasses are very common**. Familiar examples include PS and PMMA.
- **Crystalline**
  - **Polymers sometimes can crystallize**, but usually, crystallization is not complete, owing to the kinetic limitations and the presence of quenched disorder.
  - In such **semi-crystalline materials**, very small crystals exist in a matrix of amorphous material, which can be in either a liquid-like or glassy state. Familiar examples of semi-crystalline materials include synthetic polymers such as PE as well as natural materials like starch.
- **Liquid crystalline**
  - Some polymers are rather rigid molecules, which can line up to form liquid crystalline phases. These can form the basis of very strong engineering materials, like Kevlar.

Polymers

Linear chains

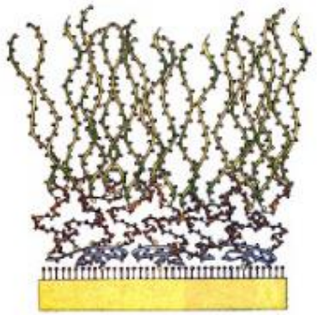




Branched chains

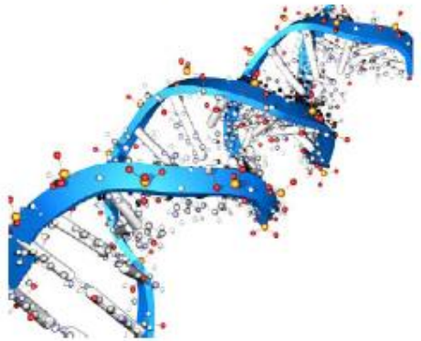
Dendrimers

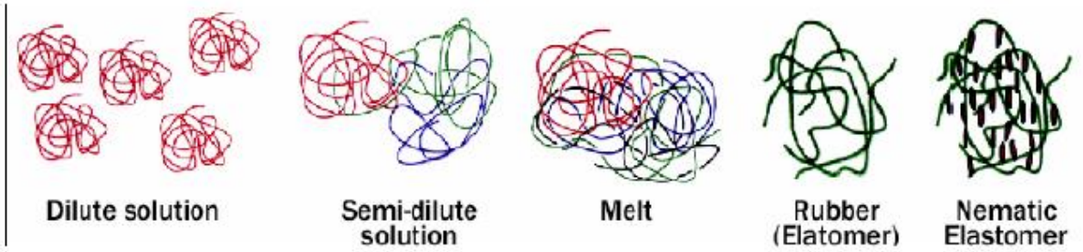




Grafted polymers

Polyelectrolytes





- monomer;
- oligomer;
- polymer;

Statistical Physics of Polymers

In order to understand the properties of polymer, which is a large assembly of molecules, we need to use **statistical physics** to calculate the characteristics of **an isolated polymer**.

A polymer molecules has many internal degrees of freedom, for example the rotational freedom about each C-C bond in the polyethylene molecule, and so it can take on many different configurations.

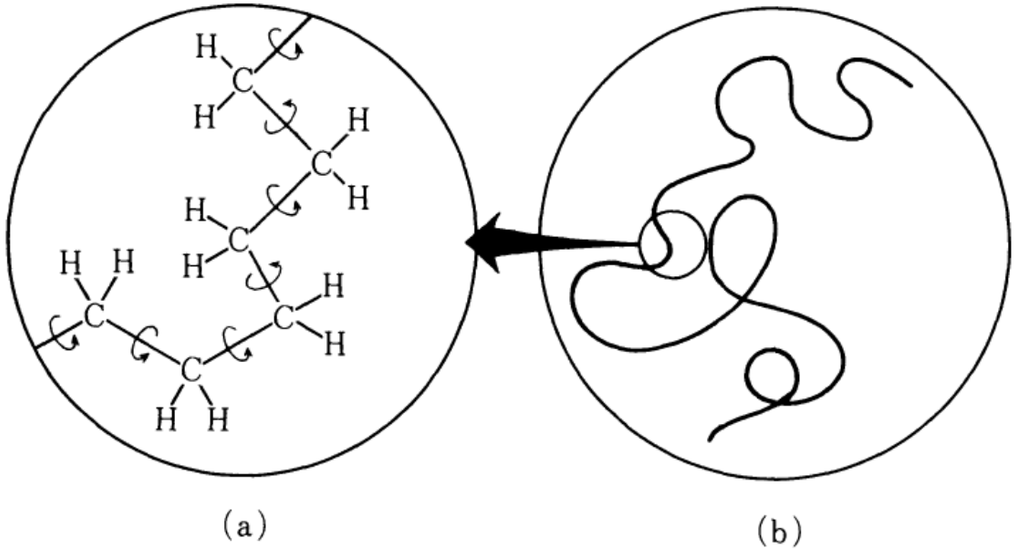
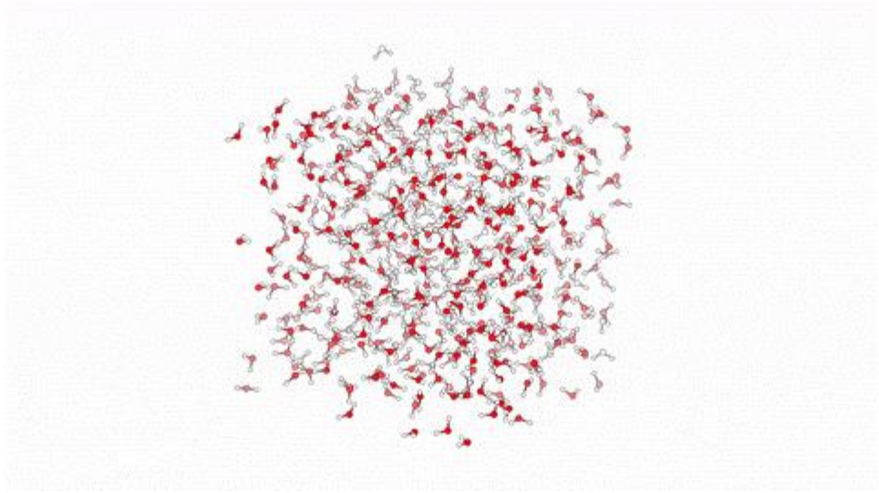


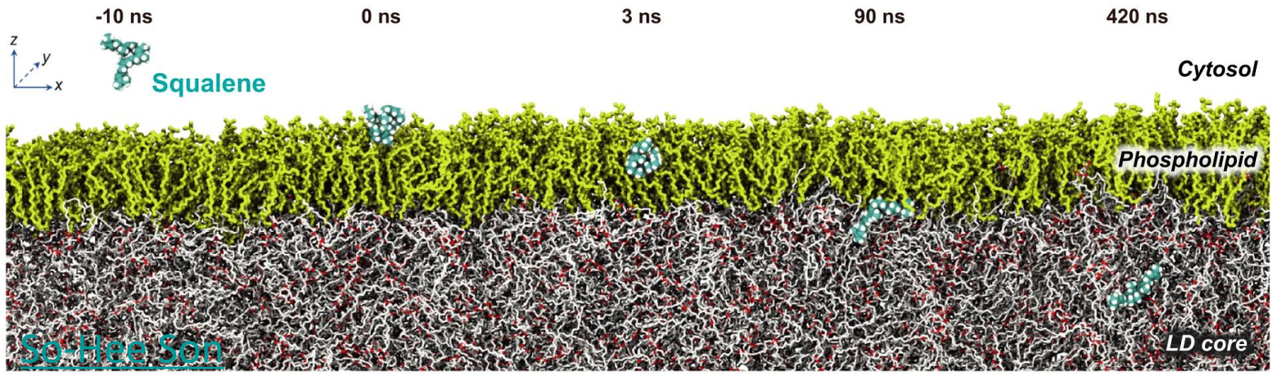
Fig. 1.1 (a) The atomic structure of the polyethylene molecule. (b) An overall view of the molecule. There is rotational freedom about each C–C bond, so the molecule as a whole resembles a long, flexible piece of string.

How do we model and simulate polymers?

1. Consider all the atoms as particles with given interaction.
2. Throw in all the atoms in the box and do molecular dynamics (MD) or Monte Carlo(MC) simulation.



All-atom MD simulation of water molecules (from Wikipedia)



So-Hee Son et. al. Nature Comm., 13, 3612 (2022)

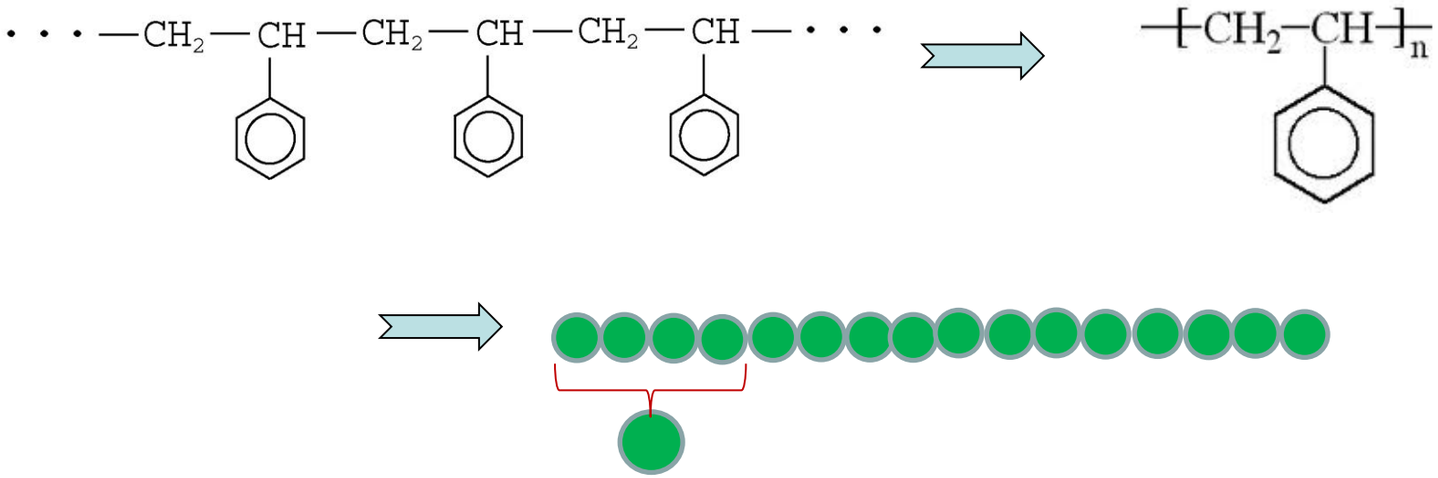
Possible Simulation Tools:

GROMACS, AMBER, CHARMM, OpenMM, in-house codes, etc.

Coarse-Graining of Polymers

2. Coarse grain the molecules (cow is spherical, right?), then perform simulations with “beads” and “springs”.





- Major parameters
  - N : Polymerization index (segment number)
  - a : Segment length
  - ρ_0^{-1}: Segment volume

One long polymer is a collection of many monomers. Each monomer can be represented by a bead. Here, a green bead is used for one styrene monomer in a polystyrene (PS) chain.

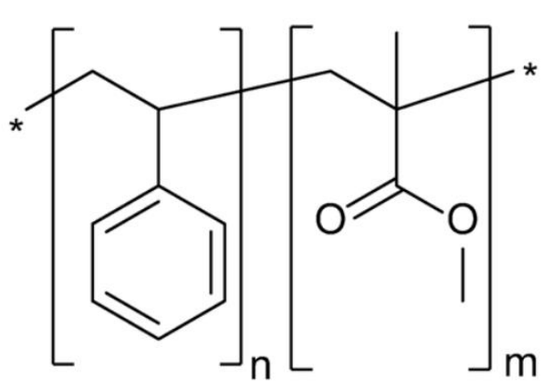
Usually, we collect a few monomers to call it a segment, and then, a polymer is a collection of N segments of statistical segment length a. and each segment has volume $1/\rho_0$.

When the discrete nature matters, a more convenient choice is to consider that a chain consists of $N+1$ segments connected by N equal bonds.

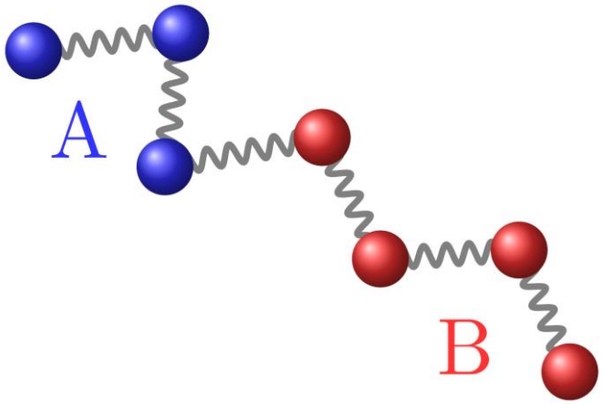
Possible Simulation Tools:
HOOMD-Blue, LAMMPS,
in-house codes, etc.

Coarse-Graining of Block Copolymers

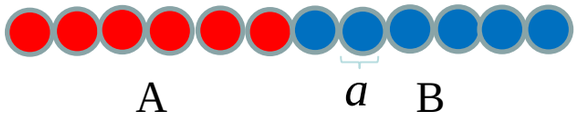
- Diblock copolymers consist of two (A and B) distinct blocks joined together.
- f is used to represent the fraction of A in the polymer, $1-f$ is the fraction of B.
- χN represents the incompatibility between blocks.



Coarse-graining



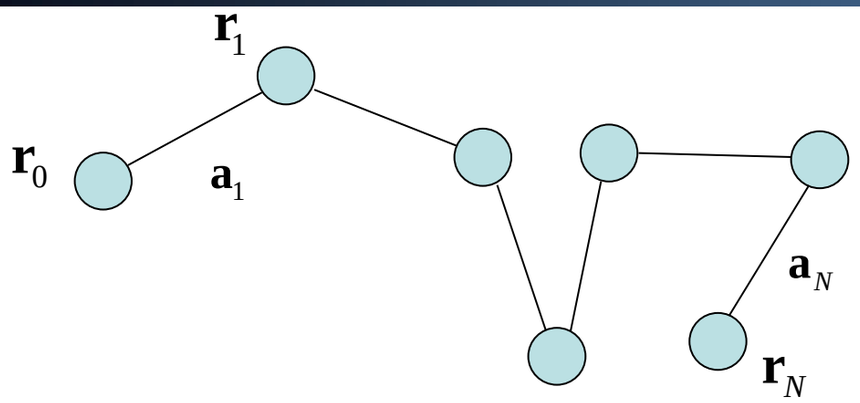
Diblock Copolymer



$N = 12, \quad N_A = 6, \quad f = N_A/N = 0.5$

- Major parameters
  - N : Polymerization index (segment number)
  - f : Volume fraction of A block
  - χN : Incompatibility between A and B block
  - a : Segment length
  - ρ_0^{-1}: Segment volume

Freely Jointed Chain (FJC) Model



$$\mathbf{a}_i \equiv \mathbf{r}_i - \mathbf{r}_{i-1}$$
$$|\mathbf{a}_i| = a$$

$$g(\mathbf{R}) \equiv \frac{\delta(|\mathbf{R}| - a)}{4\pi a^2}$$

Only nonzero at the surface of a sphere of radius a.

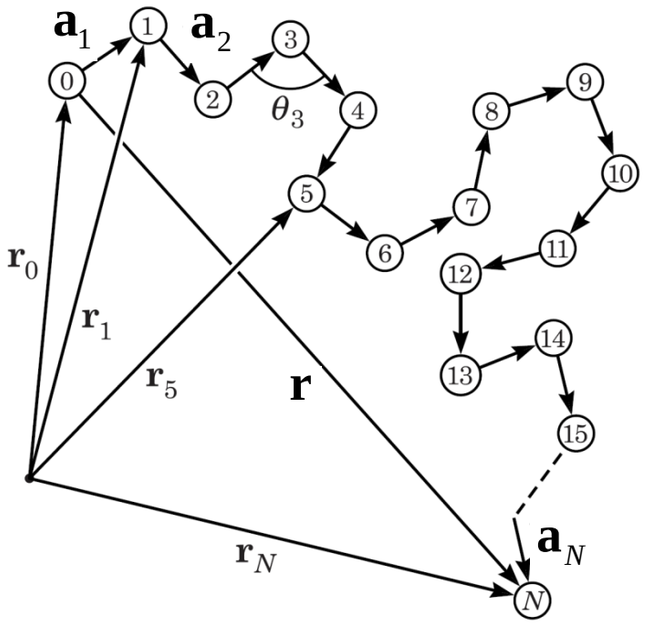
- Idea: In one polymer chain, there are N+1 segments. The segments can be treated as beads taking the mass of the polymer, and the length between the beads is fixed; Essentially, the ***N*+1 beads are connected by *N* rigid rods of length *a***. The position of each bead is labeled as $\mathbf{r}_i$ (i = 0,1, …,N).
- Essentially, we are separating **parts determining volume (beads) and length (rod)**.
- We assume the **rods are completely flexible** so that the energy does not depend on the joint angle. You may think that this model is unreasonable considering its chemical structure. The well-established universality of polymers allows one to fit a long enough polymer to this model by adjusting N and segment length a.
- Additional interaction between beads can be added later using a proper potential energy term.
- If no such potential energy is given, it simply becomes **3D random walk problem**.

Random walks and the dimensions of polymer chains

Let us find the universal behavior of polymers in terms of the overall dimensions of a polymer chain, and how these are related to its degree of polymerization N. Here is an extremely simple model quantitatively accounting for many properties of polymer chains and provides the starting point for much of the physics of polymers. This model is that of an **ideal random walk**, which is realized in the idealization of a **freely jointed chain**.

The freely jointed chain and its Gaussian limit

In this model we consider a chain with ***N* links**, each of which has **length *a*** (hence there are ***N*+1 segments**). The different links have independent orientations. Thus the path of the polymer in space is a **random walk**. The end-to-end vector $\mathbf{r}$ is simply the sum of the N jump vectors $\mathbf{a}_i$ which represent the direction and size of each link in the chain:



$$\mathbf{r} = \mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3 + \cdots + \mathbf{a}_N = \sum_{i=1}^{N} \mathbf{a}_i$$

The average of the **end-to-end vector** is zero. The average of its square is

$$\langle \mathbf{r} \rangle = 0 \qquad \langle \mathbf{r}^2 \rangle = \langle \mathbf{r} \cdot \mathbf{r} \rangle = \left\langle \sum_{i=1}^{N} \mathbf{a}_i \cdot \sum_{j=1}^{N} \mathbf{a}_j \right\rangle = \left\langle \sum_{i,j} \mathbf{a}_i \cdot \mathbf{a}_j \right\rangle$$

Picking out the N cases where $i = j$ we have $\left\langle \mathbf{r}^2 \right\rangle = \left\langle \sum_i \mathbf{a}_i^2 \right\rangle + \left\langle \sum_{i \neq j} \mathbf{a}_i \cdot \mathbf{a}_j \right\rangle$

If the chain is freely jointed, the directions of different links are completely uncorrelated and the cross-terms disappear when the average is taken. We recover the familiar random walk result

$$\left\langle \mathbf{r}^2 \right\rangle = Na^2 \qquad \text{or} \qquad R_0 \equiv \sqrt{\left\langle \mathbf{r}^2 \right\rangle} = N^{1/2} a \qquad a \equiv \left| \mathbf{a}_i \right|$$

The overall size of a random walk (the natural size of a polymer, R_0) is proportional to the square root of the number of steps.

What is distribution of possible end-to-end distances?
In the limit of large *N*, the **probability distribution function** $P(\mathbf{r}, N)$ is given by the Gaussian function. (Proof in next slide)

$$P(\mathbf{r}, N) = \left(\frac{3}{2\pi N a^2} \right)^{3/2} \exp\left(-\frac{3\mathbf{r}^2}{2Na^2} \right)$$

This expression is very important in understanding the physics of polymers. The **configurational entropy** $S(\mathbf{r})$ of a polymer chain as a function of its elongation is

$$S(\mathbf{r}) = -\frac{3k_B \mathbf{r}^2}{2Na^2} + \text{constant}$$

Central Limit Theorem for 3D FJC

j-th monomer of the freely jointed chain has uniform orientational distribution from the (*j*−1)-th monomer.

$$P(\mathbf{r}, j) = \frac{1}{4\pi}\int d\mathbf{n} P(\mathbf{r} - a\mathbf{n}, j-1)$$

$$f(\mathbf{r}) = \frac{1}{(2\pi)^3}\int d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{k})$$

This relationship can be recursively applied in the Fourier space,

$$P(\mathbf{k}, j) = \frac{1}{4\pi}\int d\mathbf{n} e^{-ia\mathbf{k}\cdot\mathbf{n}} P(\mathbf{k}, j-1) = j_0\left(a|\mathbf{k}|\right) P(\mathbf{k}, j-1)$$

$$j_0(\mathbf{x}) \equiv \frac{\sin \mathbf{x}}{\mathbf{x}} \quad \text{(Spherical Bessel function)}$$

$$P(\mathbf{k}, N) = \left[j_0\left(a|\mathbf{k}|\right)\right]^N P(\mathbf{k}, 0) \qquad P(\mathbf{r}, 0) = \delta(\mathbf{r}), \quad P(\mathbf{k}, 0) = 1$$

$$P(\mathbf{r}, N) = \frac{1}{(2\pi)^3}\int d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} \left[j_0\left(a|\mathbf{k}|\right)\right]^N$$

$$\approx \frac{1}{(2\pi)^3}\int d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} \left[1 - \frac{\left(a|\mathbf{k}|\right)^2}{6}\right]^N$$

$$\approx \frac{1}{(2\pi)^3}\int d\mathbf{k} \exp\left(-\frac{\left(a|\mathbf{k}|\right)^2}{6} N + i\mathbf{k}\cdot\mathbf{r}\right)$$

$$\int d\mathbf{x} \exp(-A\mathbf{x}^2 + \mathbf{b}\cdot\mathbf{x}) = \left(\frac{\pi}{A}\right)^{3/2} \exp\left(\frac{b^2}{4A}\right)$$

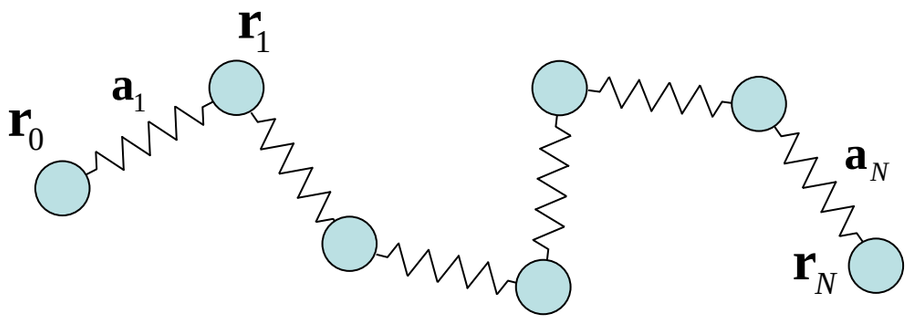
$$P(\mathbf{r}, N) \approx \left(\frac{3}{2\pi N a^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{r}^2}{2Na^2}\right)$$

When **we stretch a polymer chain, its entropy is lowered**. (How can you do that? Maybe one can use optical tweezers.) This results in an increase in the free energy $F(\mathbf{r})$:

$$F\left(\mathbf{r}\right)=\frac{3k_{\mathrm{B}}T\mathbf{r}^{2}}{2Na^{2}}+\text{constant}\qquad \mathrm{f}\left(\mathbf{r}\right)=-\nabla F\left(\mathbf{r}\right)=-\frac{3k_{\mathrm{B}}T}{Na^{2}}\mathbf{r}$$

A polymer chain behaves like a spring with **spring constant** $-3k_{\mathrm{B}}T/Na^{2}$; if it is stretched beyond its ideal random walk value there is a restoring force proportional to the extension. This restoring force does not arise from an increase of internal energy of the polymer, as it would for a spring. The origin of the force is entirely **entropic**. There are fewer possible configurations of the polymer chain when it is stretched compared to the random walk state.

Beads – Spring Chain (BSC) Model



$$g(\mathbf{R}) \equiv \left(\frac{3}{2\pi a^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2a^2}\right)$$

$\mathbf{R} = 0$에서 확률이 최대가 되는 함수임에 주의.

- Basic Idea: Again, the **volume is contained in the *N*+1 beads**.
- As the distance between two beads increases, there is higher entropy loss. This can be represented by a **spring potential**. (Now the restoring force arises from an increase of internal energy of the polymer.)

$$V = \sum_{i=0}^{N-1} \frac{k}{2}(\mathbf{r}_{i+1} - \mathbf{r}_i)^2 = \sum_{i=0}^{N-1} \frac{3}{2a^2}(\mathbf{r}_{i+1} - \mathbf{r}_i)^2$$

- By appropriately setting $k = 3/2a^2$, we can make the RMS length of each bond to be a. By using the potential as Boltzmann factor, the above bond function can be obtained.
- 모노머간의 추가적인 interaction energy 역시 추후에 적절한 포텐셜항으로 집어넣을 수 있다.

Central Limit Theorem for 3D BS Chain

The probability distribution function of the end-to-end vector **R** of the chain consisting of N segments :

$$P(\mathbf{R},N)=\int d\mathbf{a}_1\int d\mathbf{a}_2\cdots\int d\mathbf{a}_N\;\delta\left(\mathbf{R}-\sum_{n=1}^{N}\mathbf{a}_n\right)\prod_{n=1}^{N}P_1(\mathbf{a}_n)$$

$$P_1(\mathbf{r})\equiv\left(\frac{3}{2\pi a^2}\right)^{3/2}\exp\left(-\frac{3\mathbf{r}^2}{2a^2}\right)$$

$$\delta(\mathbf{r})=\frac{1}{(2\pi)^3}\int d\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{r}}$$

Gaussian integral
(refer to a book, Doi and Edwards, Appendix 2.I)

$$P(\mathbf{R},N)=\frac{1}{(2\pi)^3}\int d\mathbf{a}_1\int d\mathbf{a}_2\cdots\int d\mathbf{a}_N\int d\mathbf{k}\exp\left(i\mathbf{k}\cdot\left(\mathbf{R}-\sum_{n=1}^{N}\mathbf{a}_n\right)\right)\prod_{n=1}^{N}P_1(\mathbf{a}_n)$$

$$=\frac{1}{(2\pi)^3}\int d\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{R}}\int d\mathbf{a}_1\int d\mathbf{a}_2\cdots\int d\mathbf{a}_N\prod_{n=1}^{N}\exp(-i\mathbf{k}\cdot\mathbf{a}_n)P_1(\mathbf{a}_n)$$

$$=\frac{1}{(2\pi)^3}\int d\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{R}}\left[\int d\mathbf{r}\exp(-i\mathbf{k}\cdot\mathbf{r})P_1(\mathbf{r})\right]^N$$

$$=\frac{1}{(2\pi)^3}\left(\frac{3}{2\pi a^2}\right)^{3N/2}\int d\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{R}}\left[\int d\mathbf{r}\exp\left(-i\mathbf{k}\cdot\mathbf{r}-\frac{3\mathbf{r}^2}{2a^2}\right)\right]^N$$

$$=\frac{1}{(2\pi)^3}\int d\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{R}}\left[\exp\left(-\frac{a^2\mathbf{k}^2}{6}\right)\right]^N$$

$$=\frac{1}{(2\pi)^3}\int d\mathbf{k}\exp\left(-\frac{Na^2\mathbf{k}^2}{6}+i\mathbf{k}\cdot\mathbf{R}\right)$$

$$=\left(\frac{3}{2\pi Na^2}\right)^{3/2}\exp\left(-\frac{3\mathbf{R}^2}{2Na^2}\right)$$

∴ End distance is also Gaussian

$$\int d\mathbf{x}\exp(-A\mathbf{x}^2+\mathbf{b}\cdot\mathbf{x})=\left(\frac{\pi}{A}\right)^{3/2}\exp\left(\frac{b^2}{4A}\right)$$

Real polymer chains—short-range correlations

The freely jointed chain model has the appearance of being rather unphysical. We know from elementary chemistry that successive links in a polymer chain are not free to rotate, but instead are constrained to have certain definite bond angles.

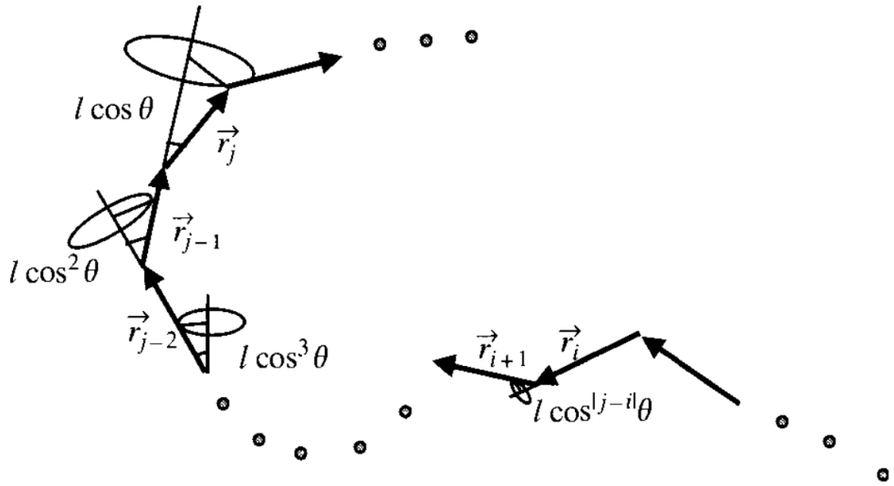
In this case, the cross-terms describing the correlations of neighboring bonds do not disappear. The surprising and important result of more careful calculations is that the presence of these **short-range correlations does not alter the basic random walk character of the polymer chain statistics**. It simply leads to an altered effective step size.

Consider, for example, a model in which the bond (with size b) is free to rotate (**freely rotating chain model**), but has a definite bond angle θ. Now, if we redo the previous calculation we find the cross-terms to be,

$$\mathbf{a}_i \cdot \mathbf{a}_{i-1} = b^2 \cos\theta \qquad \left\langle \mathbf{a}_i \cdot \mathbf{a}_{i-1} \right\rangle = b^2 \cos\theta$$

What about the relation between $\mathbf{a}_i$ and $\mathbf{a}_{i-2}$? The only correlation between the $\mathbf{a}_i$ and $\mathbf{a}_{i-1}$ that is transmitted down to the chain is the component of $\mathbf{a}_i$ along the bond vector $\mathbf{a}_{i-1}$. This value is $b \cos\theta$. Because the angle between $\mathbf{a}_{i-1}$ and $\mathbf{a}_{i-2}$ is again θ, the leftover memory of $\mathbf{a}_i$ when it reaches to $\mathbf{a}_{i-2}$ is $b\cos^2\theta$. Generalizing this, one can conclude that

$$\left\langle \mathbf{a}_i \cdot \mathbf{a}_{i-m} \right\rangle = b^2 \cos^m \theta$$



Real polymer chains—short-range correlations

As cos θ is always less than unity, the correlation dies away along the chain. The mean-square end-to-end distance is now

$$\left\langle \mathbf{r}^2 \right\rangle = \sum_{i,j} \left\langle \mathbf{a}_i \cdot \mathbf{a}_j \right\rangle = \sum_{i=1}^{N} \left(\sum_{j=1}^{i-1} \left\langle \mathbf{a}_i \cdot \mathbf{a}_j \right\rangle + \left\langle \mathbf{a}_i^2 \right\rangle + \sum_{j=i+1}^{N} \left\langle \mathbf{a}_i \cdot \mathbf{a}_j \right\rangle \right)$$

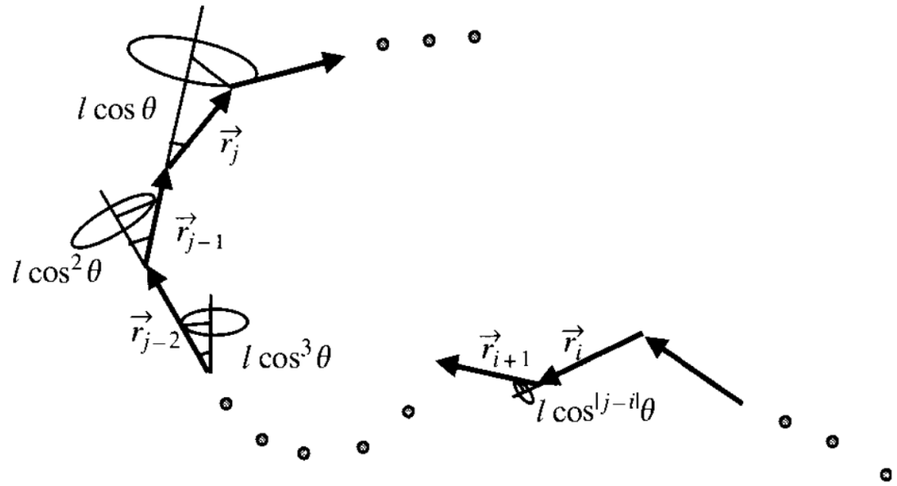
$$= Nb^2 + b^2 \sum_{i=1}^{N} \left(\sum_{k=1}^{i-1} \cos^k \theta + \sum_{k=1}^{N-i} \cos^k \theta \right)$$

Assuming the chain is long enough so that for most cases the summation can be replaced by the infinite summation as follows,

$$\sum_{i=1}^{N} \left(\sum_{k=1}^{i-1} \cos^k \theta + \sum_{k=1}^{N-i} \cos^k \theta \right) \cong 2 \sum_{i=1}^{N} \sum_{k=1}^{\infty} \cos^k \theta = \frac{2N \cos\theta}{1 - \cos\theta}$$

Finally, the mean-square end-to-end distance is

$$\left\langle \mathbf{r}^2 \right\rangle = Nb^2 \frac{1+\cos\theta}{1-\cos\theta} = Na^2 \qquad a \equiv b\sqrt{\frac{1+\cos\theta}{1-\cos\theta}}$$



Real polymer chains—short-range correlations

Thus, at least for the R_0 calculation, we can **regard that it is a freely-jointed chain with *N* bonds each with statistical step length *a* (Kuhn length)**.

If one knows the chemical details of the polymer, the statistical step length may be calculated.

More practically, one can extract their values for a given polymer from experimental data on chain dimensions.

There exist many other chain models such as “worm-like chain model”, “hindered rotation model” and “rotational isomeric state model”. (See Rubinstein pages 57~60)

Whichever model we take, as long as the interaction is short-ranged, one can always conclude that

$$\left\langle \mathbf{r}^2 \right\rangle = C_\infty N b^2 = N a^2 \qquad a \equiv \sqrt{C_\infty} b$$

with a proper constant C_∞ that depends on the model.

모든 short range self-interaction은 결국 C_∞에 흡수되어 사라지게 된다. 그런 의미에서 short range self-interaction은 계의 파라미터를 변화시킬 뿐, 계가 속한 universality class를 바꾸지는 않는다고 할 수 있다.

Real polymer chains—short-range correlations

Kuhn 길이는 실제 고분자의 복잡한 분자 구조와 구속을 고려하여 이를 **등가의 FJC로 모델링**한 결과이다.

많은 reference들이 비슷한 의미의 용어로 persistence length(l_p)를 사용하는데 이상적인 고분자의 경우 $a = 2l_p$이다.

Table 2.2 Assumptions and predictions of ideal chain models: FJC, freely jointed chain; FRC, freely rotating chain; HR, hindered rotation; RIS, rotational isomeric state

Models	FJC	FRC	HR	RIS
Bond length l	Fixed	Fixed	Fixed	Fixed
Bond angle θ	Free	Fixed	Fixed	Fixed
Torsion angle φ	Free	Free	Controlled by $U(\varphi)$	$t, g+, g-$
Next φ independent?	Yes	Yes	Yes	No
C_∞	1	$\frac{1+\cos\theta}{1-\cos\theta}$	$\left(\frac{1+\cos\theta}{1-\cos\theta}\right)\left(\frac{1+\langle\cos\theta\rangle}{1-\langle\cos\varphi\rangle}\right)$	Specific

Here is another approach to understand the statistical behavior of polymers using a simplified model. We can conceive of **collecting g segments** to create one large imaginary segment whose bond vector directions are practically uncorrelated.

Now there exists $N' = N/g$ **large segments with volume** $1/\rho'_0 = g/\rho_0$ and the effective statistical step length of each bond a' is given by

$$\left\langle \mathbf{r}^2 \right\rangle = Na^2 = N'a'^2 \qquad a' = a\sqrt{\frac{N}{N'}} = a\sqrt{g}$$

N'에 대한 하나의 선택이 다른 것보다 우월하다고 말하기는 쉽지 않다. 다만 한 자연스러운 g의 선택은 $a'^3\rho'_0 = 1$이 되게 하는 것이다. 그때의 N이 바로 다음의 **invariant degree of polymerization $\bar{N}$** 인데 분자량, 고분자 농도, 및 용매의 성질과 무관하게 결정되는 무차원적인 값이다.

$$\bar{N} \equiv a^6\rho_0^2 N$$

$\bar{N}$가 큰 계는 일반적으로 고분자의 길이가 길어 요동효과(fluctuation)가 작고 $\bar{N}$가 작아지면서 fluctuation의 영향이 커진다. 실험에서 보통 사용하는 합성고분자의 $\bar{N}$는 세자리수 정도일 때가 많다. 뒤에 소개할 SCFT와 같은 평균장 이론은 $\bar{N} = \infty$에서 정확한 이론이고, 요동효과를 넣을 수 있는 L-FTS와 같은 시뮬레이션은 $\bar{N} = 5000$ 정도 이상이 되어야 안정적으로 돌아간다.

One valuable question is if the actual polymer behavior can be properly described by these models (either N monomers with size a or N' monomers with size a'). The answer is not always yes, but the concept of universality established by de Gennes and others suggest that many polymer properties can be explained by such simple models.

This simple example shows the typical way in which polymer physics tries to proceed: **the long-range structure** (in this case the size of the chain specified by R_0) is given by statistics and is **universal** (i.e. independent of the chemical details of the polymer in question). **All these chemical details go into a few parameters**, which may be either calculated on the basis of detailed theory at the atomic level, or extracted from experiments.

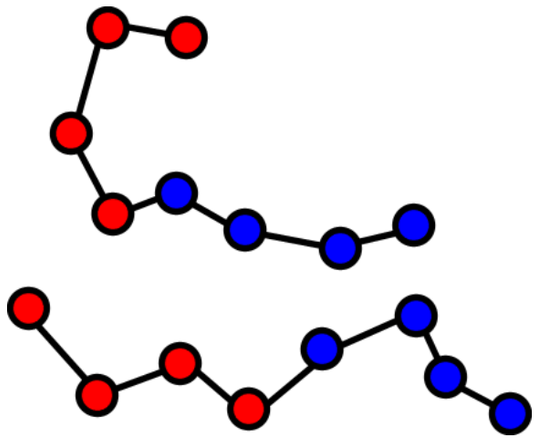
Universality

본질적으로 복잡한 고분자 사슬의 random walk을 이렇게 가우시안 분포로 단순화시켜서 설명하는 것이 실제 고분자의 거동을 얼마나 잘 설명할 수 있을까 의문을 가질 수 있다.

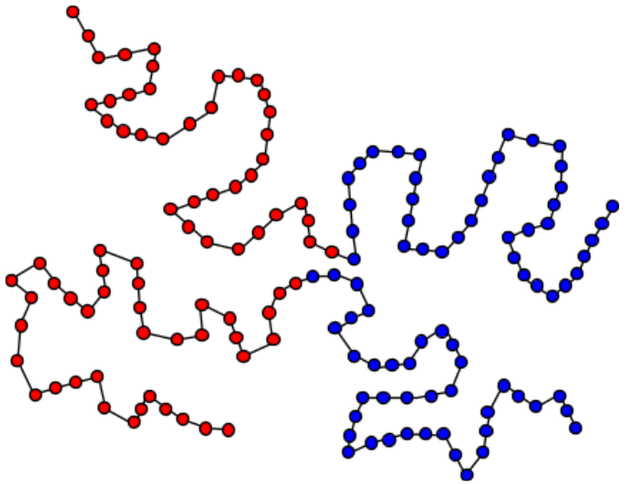
또한 고분자의 모노머들간의 현실적인 interaction은 아주 short range에서의 hard core repulsion 그리고 그보다 약간 긴 영역에서의 복잡한 (isotropic하지도 않은) repulsion 또는 attraction으로 주어지게 된다. 뒤에 이론 전개를 할 때 이것 역시 contact interaction으로 단순화시켜서 모델링하게 된다.

$$\frac{H_{\text{int}}}{k_{\text{B}}T} = \chi\rho_0 \int d\mathbf{r}\hat{\phi}_{\text{A}}(\mathbf{r})\hat{\phi}_{\text{B}}(\mathbf{r})$$

At small N, things such as the range of the interactions and the persistence length of the polymer chains are important



At large N, the range of the interactions and the persistence length become negligible relative to the size of the molecules



Thus, all systems reduce to the standard Gaussian chain model with contact interaction in the limit of $\bar{N} \to \infty$.

Excluded volume, the theta temperature, and coil-globule transitions

In the above analysis, we accounted for interactions between neighboring links of the chain, but we neglected **interactions between distant points on the chain**.

It turns out that these interactions are important for an isolated chain, and the long-range structure of the chain strongly depends on them.

At the simplest level, we know that **the chain cannot intersect itself**; the monomer units have finite volume and two cannot be in the same place at the same time; i.e. we have a **self-avoiding walk**.

The mathematics of self-avoiding walks is much more complicated than for simple random walks; instead of $\langle \mathbf{r}^2 \rangle^{1/2} = aN^{1/2}$, self-avoiding walk results $\langle \mathbf{r}^2 \rangle^{1/2} = aN^{\nu}$ where the **exponent** $\nu > 0.5$. The effect of excluded volume is to swell the polymer chain over the random walk value.

True polymers will have long-ranged repulsion and attraction in addition to the short-ranged correlations.

One may think that the exponent ν is a complicated function of the details of the interaction potential, but it turns out that **for long enough chain, it only depends on the nature of the overall interaction (repulsive or attractive) and the dimension of the polymer**.

Excluded volume, the theta temperature, and coil-globule transitions

We can estimate the exponent for the repulsive case using a very simple argument due to Flory.

We consider **a polymer chain in solvent**. the polymer molecule to be a gas of N segments **confined to a volume $V \sim r^3$**, where r is the radius of the polymer coil that we need to determine. The concentration of segments, c, is now given by

$$c = N / V \sim N / r^3$$

Consider a gas of N atoms confined to a volume V. If each atom occupies a **volume v which is inaccessible to the other atoms**, the entropy per atom is reduced by a factor of $k_B vN/2V$. (Factor 1/2 is from the double counting.)

In our polymer coil there is a positive contribution to the free energy due to the excluded volume F_{rep} which we can write as

$$F_{rep} = k_B T v \frac{N^2}{2V} \sim k_B T v \frac{N^2}{2r^3}$$

In this way, segments within the chain repel each other as a result of the excluded volume effect, and it tends to make the chain expand. But this expansion is opposed by the effect of configurational entropy introduced earlier. Its free energy expression is

$$F_{el} = \frac{3k_B T r^2}{2Na^2}$$

Excluded volume, the theta temperature, and coil-globule transitions

If we now minimize the total free energy ($F_{tot} = F_{rep}+F_{el}$) with respect to r, we find

$$r^5 \sim N^3 v a^2$$

Thus, the optimum size of the real chain in the Flory theory is

$$R_F \sim v^{1/5} a^{2/5} N^{3/5}$$

Often one assume that the exclude volume $v = a^3$ for simplicity. Then $R_F \sim aN^{3/5}$

Thus, **Flory's argument suggests $\nu = 3/5$**. The size of long real chains is much larger than that of ideal chains, $\frac{R_F}{aN^{1/2}} \sim \left(\frac{v}{a^3} N^{1/2}\right)^{1/5}$

Regardless of the solvent quality (as long as it is good enough) and details of the polymer chain, one gets a **universal power law** dependence of polymer size on the segment number, $R \sim N^{\nu}$

In a more general theory in d-dimension, $F \sim \frac{r^2}{N} + \frac{N^2}{R^d}$

and its minimization leads to $R \sim N^{3/(d+2)}$

which suggests that $\nu = \frac{3}{d+2}$

At $d = 2$, $\nu = 3/4$, and at $d = 4$, $\nu = 1/2$. It recovers the ideal chain exponent at $d \geq 4$. At the **critical dimension, $d_c = 4$**, there are actually log correction such as $R^2 \sim N(\log N)^{\alpha}$.

Excluded volume, the theta temperature, and coil-globule transitions

The success of the Flory theory is due to the cancellation of errors.

i) Computer simulation of random walks with excluded volume show that the number of contacts between monomers that are far apart along the chain does not grow with N.

ii) The elastic energy is also overestimated because the ideal chain conformational entropy is assumed.

More sophisticated theories using **renormalization group** provides accurate scaling exponent of the swollen chain in three dimension, $\nu = 0.5877$ ... (0.588 to three decimal places).

Experimentally, the chain dimensions of very dilute chains in **good solvents** are found to be swollen in the way predicted (though available experimental precision can barely distinguish between the Flory value of 3/5 and the more exact value).

Excluded volume, the theta temperature, and coil-globule transitions

In the above argument, we have neglected any **energetic interaction** between neighboring polymer segments or between polymer segments and neighboring solvent molecules.

Here is a simple way to introduce such interactions. We basically assume that **the segment of a polymer and a solvent molecule has the same volume, and they fill in the space while making contact with *z* neighbors**.

상당히 primitive한 모델로 보이겠지만, 앞에서 설명한 보편성을 생각하면, 고분자의 길이가 무한이 되는 극한에서는 이렇게 유도한 이론이 exact한 결과를 준다고 생각할 수 있다.

We take the energy of interaction between two neighboring polymer segments as ε_{pp}, between two neighboring solvent segments as ε_{ss}, and between a neighboring polymer and solvent segment as ε_{ps}.

If we assume that the polymer segments are uniformly distributed within the coil with a concentration $c = N/V$, $\phi = ca^3 \simeq cv$

is the dimensionless density of the polymer in the coil, or **the probability that a neighbor of a polymer segment turns out to be another polymer segment**.

Now we can **estimate the number of contacts** between different polymer segments N_{pp}, between solvent segments N_{ss}, and between polymer and solvent segments N_{ps}, as

$$N_{pp} = \frac{1}{2} zN\phi \qquad N_{ps} = zN(1-\phi) \qquad N_{ss} = N_{ss}^{0} - \frac{1}{2} zN\phi - zN(1-\phi)$$

where N_{ss}^{0} is number of solvent-solvent contact when there was no polymer. Writing down the interaction energy, we obtain

Excluded volume, the theta temperature, and coil-globule transitions

$$U_{\text{int}} = \frac{1}{2} zN\phi\varepsilon_{pp} + zN\left(1-\phi\right)\varepsilon_{ps} + \varepsilon_{ss}\left(N_{ss}^{0} - \frac{1}{2} zN\phi - zN\left(1-\phi\right)\right)$$

$$= N_{ss}^{0}\varepsilon_{ss} + \frac{1}{2} zN\phi\left(\varepsilon_{pp} + \varepsilon_{ss} - 2\varepsilon_{ps}\right) + zN\left(\varepsilon_{ps} - \varepsilon_{ss}\right)$$

We can **combine the interaction energies into a single interaction parameter χ**, given by

$$\chi k_{\text{B}}T \equiv \frac{1}{2} z\left(2\varepsilon_{ps} - \varepsilon_{pp} - \varepsilon_{ss}\right)$$

Now the interaction energy can be written as ($\phi \approx cv \approx vN/V$)

$$U_{\text{int}} = -\chi Nk_{\text{B}}Tcv + \text{const} = -\chi Nk_{\text{B}}Tv\frac{N}{V} + \text{const}$$

This equation has exactly the same functional form for the repulsive free energy due to excluded volume. Combining the two terms, we have

$$F_{\text{rep}} + U_{\text{int}} = k_{\text{B}}Tv\frac{N^2}{2V} - \chi Nk_{\text{B}}Tv\frac{N}{V} = k_{\text{B}}Tv\left(1-2\chi\right)\frac{N^2}{2V}$$

Thus, according to the value of χ, we have three different kinds of behavior:

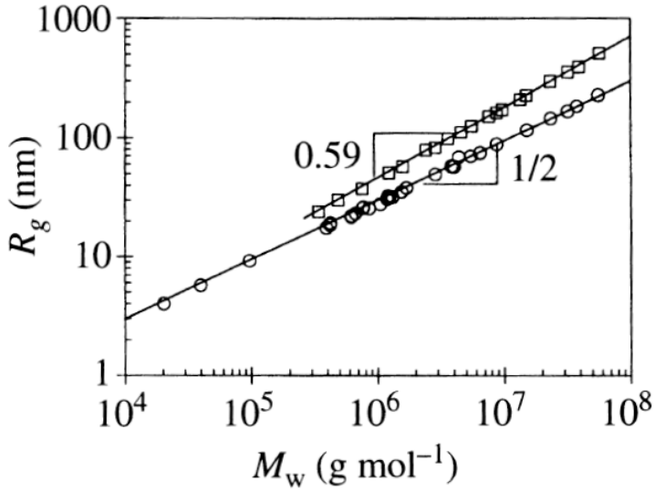
1. $\chi < 1/2$: the repulsion is dominant and the polymer chain is expanded with a radius $r \sim N^{3/5}$. This is referred to as **good solvent** behavior. (More precisely, the exponent is 0.588.)

Excluded volume, the theta temperature, and coil-globule transitions

2. $\chi = 1/2$: the repulsive effect of excluded volume is exactly cancelled by the attractive effect of the polymer/solvent interactions. The polymer chain makes an ideal random walk, with $r \sim N^{1/2}$. This situation is known as the **theta condition**.

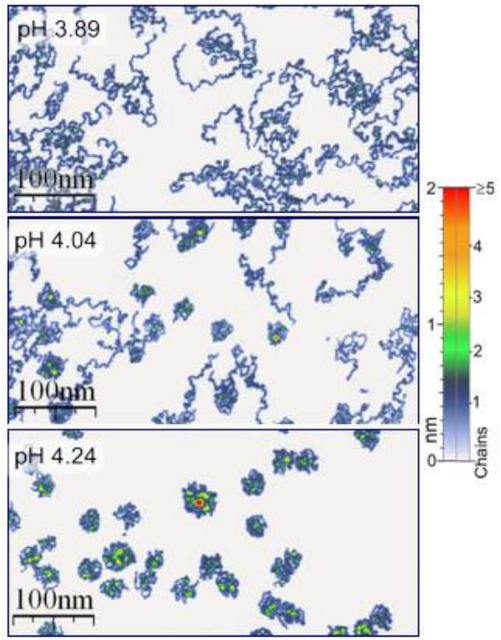
3. $\chi > 1/2$: the attractive effect of the polymer/solvent interaction out-weighs the repulsive excluded volume interaction, and the chain collapses to form a compact **globule**. The exponent for the globule is usually $\nu = 1/3$ in three dimension. ($1/d$ in d-dimension.)

Experimental measurements of chain size



Radius of gyration of polystyrene in a θ-solvent (cyclohexane at 34.5°C) and in a good solvent (benzene at 25°C)

From Fetters et al., *J. Phys. Chem. Ref Data* **23**, 619 (1994)



As the value of the interaction parameter χ between a polymer and a solvent is changed, for example by changing the temperature, the polymer undergoes a transition from an expanded chain, or coil, through the theta temperature to a collapsed coil. This is known as the **coil-globule transition**.

Note that for typical polymers, its temperature dependence of χ is experimentally known as

$$\chi = A + \frac{B}{T}$$

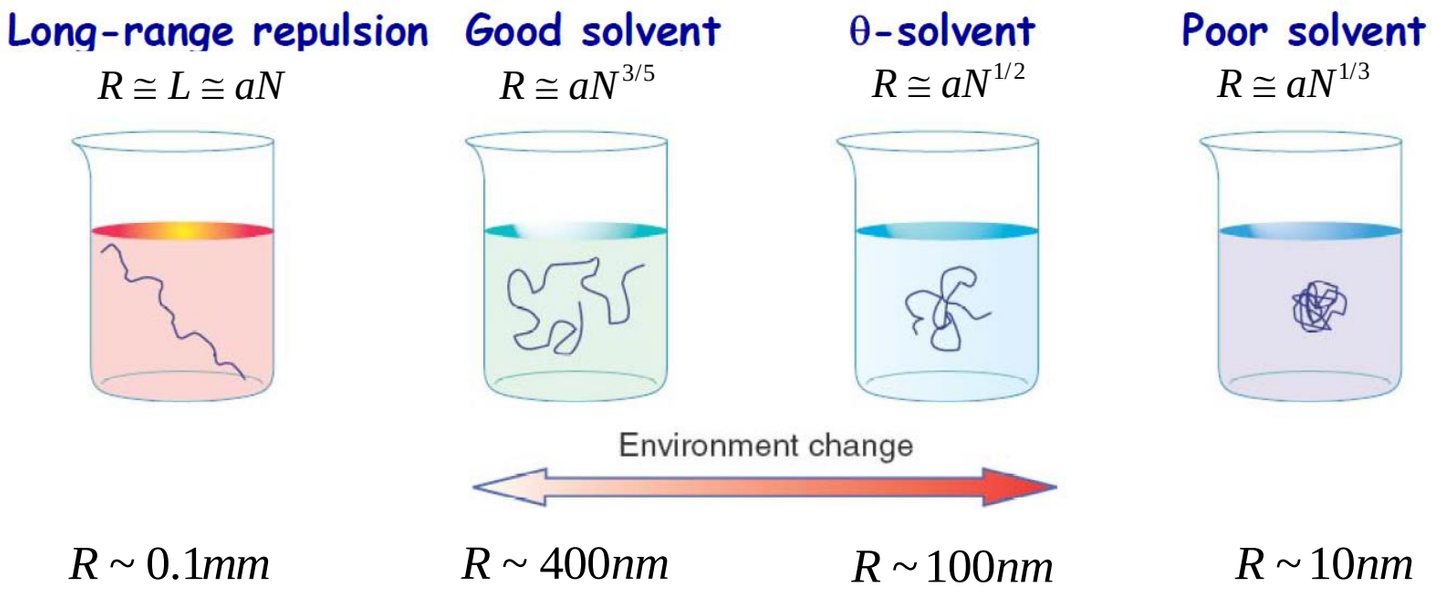
where A and B are some constants. The figure shows the case that pH controls the χ parameter.

Excluded volume, the theta temperature, and coil-globule transitions

At a special intermediate temperature, called the ***θ* temperature**, chains are in nearly ideal conformations because the attractive and repulsive parts of monomer-monomer interaction cancel each other.

Segment size $a \sim 0.1nm$

Number of Segments $N \sim 10^2 - 10^{10}$. Consider the case $N = 10^6$.

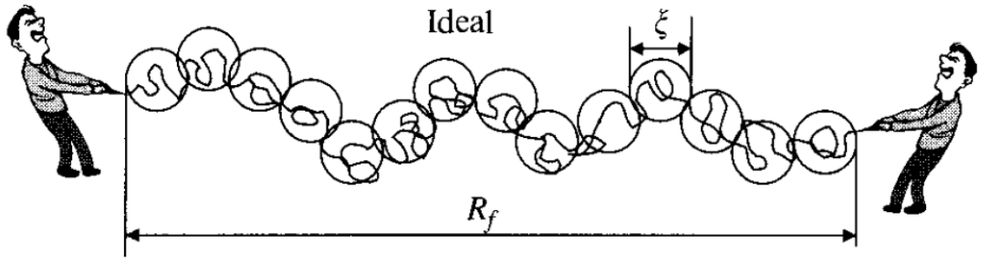


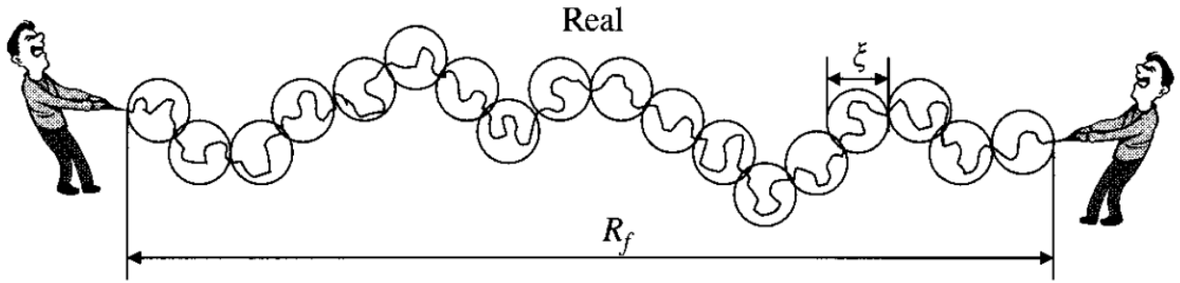
Our treatment of excluded volume and the interaction energy is too crude to allow us to deduce the details of the shape of the transition, but a more sophisticated treatment reveals that **the transition is a thermodynamic phase transition in the limit of long chains, $N \to \infty$**; the transition may be first or second order according to the stiffness of the chains.

Polymer Under Tension

In order to emphasize the difference between ideal and real chains, let us compare their **behavior under tension**.
Consider a polymer containing N monomers of size a, under tension in two different solvents:
i) a θ solvent and **ii) an athermal (good) solvent with excluded volume $v \approx a^3$**.

A convenient tool for this type of problem is the **blob picture**. Due to tension f, the long chain divides into linearly connected blobs, and inside each blob, the monomers are practically making random walks of the given nature.





Assuming a blob of size ξ contains g monomers,

$$\xi \approx a g^{1/2} \qquad \text{ideal}$$
$$\xi \approx a g^{3/5} \qquad \text{real}$$

The extended size of the chain is

$$R_f \approx \frac{\xi N}{g} \approx \frac{N a^2}{\xi} \approx \frac{R_0^2}{\xi} \qquad \text{ideal}$$
$$R_f \approx \frac{\xi N}{g} \approx \frac{N a^{5/3}}{\xi^{2/3}} \approx \frac{R_F^{5/3}}{\xi^{2/3}} \qquad \text{real}$$

The free energy cost for stretching the chains is of order $k_B T$ per tension blob (so that the monomer statistics is unperturbed inside a blob):

Polymer Under Tension

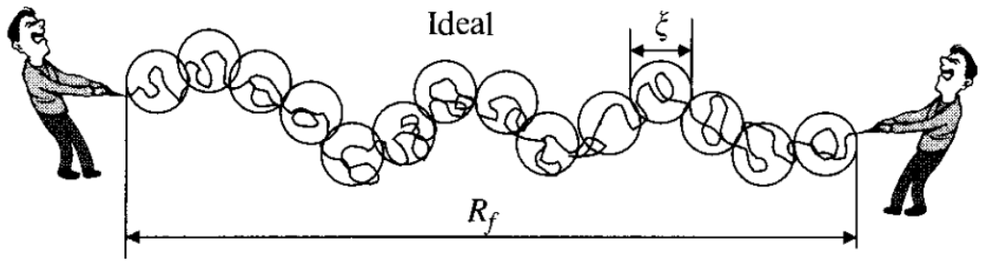
$$F(N,R_f) \approx k_B T \frac{N}{g} \approx k_B T \frac{R_f}{\xi} \approx k_B T \left(\frac{R_f}{R_0}\right)^2 \qquad \text{ideal}$$

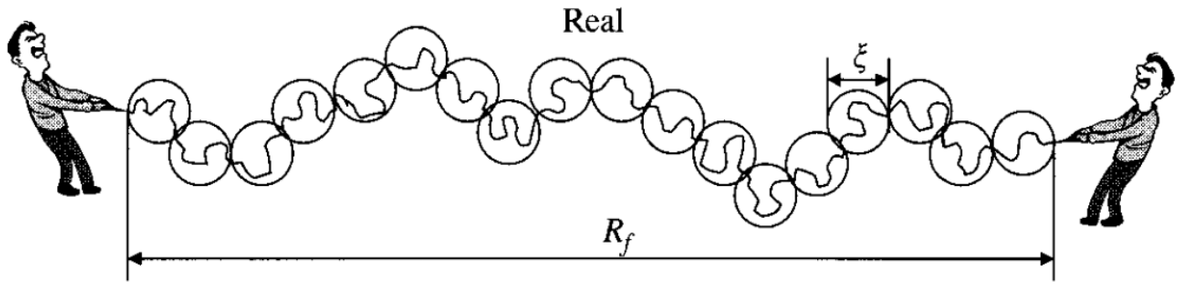
$$F(N,R_f) \approx k_B T \frac{N}{g} \approx k_B T \frac{R_f}{\xi} \approx k_B T \left(\frac{R_f}{R_F}\right)^{5/2} \qquad \text{real}$$

The force necessary to stretch the chain to end-to-end distance R_f can be estimated as

$$f \approx \frac{k_B T}{\xi} \approx \frac{k_B T}{R_0}\frac{R_f}{R_0} \qquad \text{ideal}$$

$$f \approx \frac{k_B T}{\xi} \approx \frac{k_B T}{R_F}\left(\frac{R_f}{R_F}\right)^{3/2} \qquad \text{real}$$

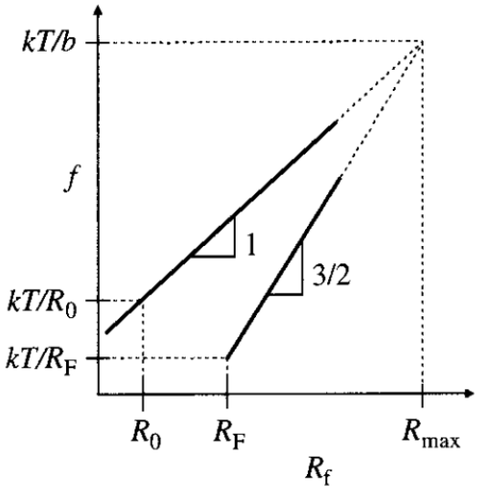




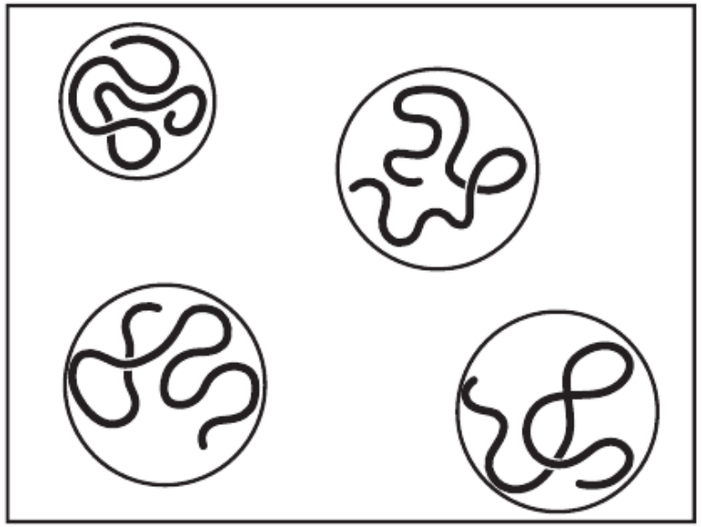
The same result can be obtained by differentiation of the free energy with respect to R_f.

Ideal chains satisfy Hooke's law with **force f linearly proportional to elongation R_f**. For real chains the dependence is **non-linear with the exponent 3/2 for $\nu = 3/5$**. This was first derived by Pincus and tension blobs are often called Pincus blobs.

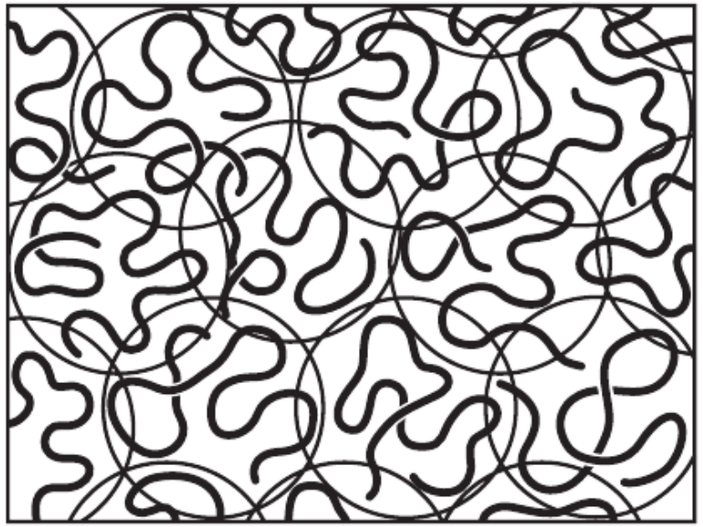
This type of **blob analysis** is very helpful in solving may polymer problems. Sometimes the derivation of important physical laws using scaling theory looks like an art.



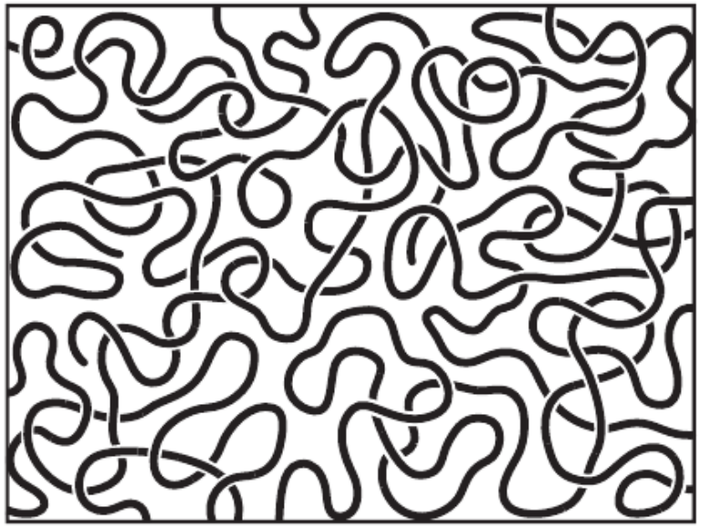
Excluded volume, the theta temperature, and coil-globule transitions



Dilute ($C < C^*$)



Overlap ($C = C^*$)



Semi-dilute ($C > C^*$)

Good solvent 안에 낮은 농도의 고분자가 있는 경우가 dilute regime이다. 이때의 고분자의 크기는 $R \sim aN^{\nu}$로 주어진다. 용액의 점도는 단일 고분자 사슬에 의존하며 농도와 선형적으로 비례한다.

고분자의 농도가 C^*보다 높아지면 각 코일의 영역이 겹치기 시작한다. Semi-dilute regime에서 용액의 점도는 농도에 비선형적으로 증가하기 시작한다.

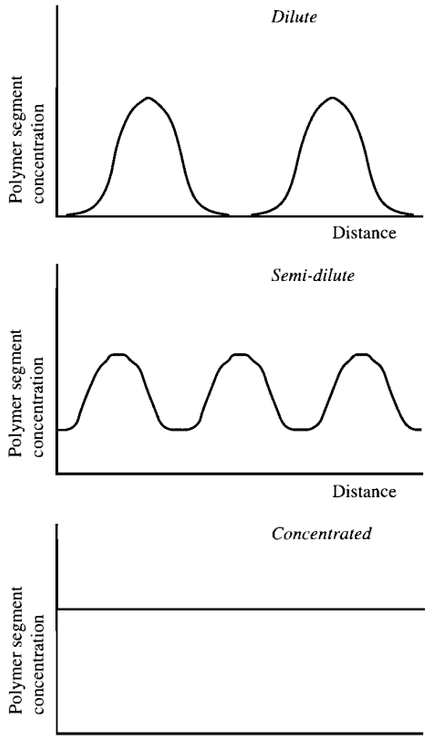
$$C^* \sim \frac{N}{R^3} \sim \frac{N^{1-3\nu}}{a^3} \qquad C^* \sim N^{-4/5} \text{ when } \nu = 3/5$$

용매가 없는 상태에서 고분자 사슬이 매우 높은 농도로 밀집되어 있는 상태가 고분자 melt이다. 점도는 고분자 사슬의 분자량의 3.4제곱 정도에 비례한다.

Chain statistics in polymer melts—the Flory theorem

Under good solvent environment, polymers do not follow random walk statistics in dilute solution because the chain is swollen. What happens as we make the solution more concentrated, ultimately arriving at the polymer melt? Counterintuitively, rather than becoming more complicated, **things become more simple: chains follow ideal random walk statistics in melt**!

This was first realized in 1949 by Flory and put on a sound theoretical footing by Edwards in 1966, when he introduced the idea of screening. Here is a simple plausibility argument. Consider schematic plots of the segment concentration c across a section through space. For a dilute solution, chains are isolated and segments do not interact with segments from different chains.



The effect of the excluded volume interaction is to include an unfavorable energy proportional to the probability of two segments being close together; that is, proportional to c^2. This leads to a force on the segments proportional to cdc/dx, which tends to make the chain expand. Now as the concentration is increased chains start to overlap; dc/dx is smaller and the repulsive force is reduced.

Finally, **in the melt, the concentration of segments is essentially uniform; thus there is no repulsive force between the segments and the chain follows ideal random walk statistics**. This result was confirmed by neutron scattering in the early 1970s.

Measuring the size of polymer chains

The **dimensions of polymer chains are most directly measured by scattering**. This method relies on the interference of waves scattered from different parts of an extended scattering object. What a scattering experiment usually measure is the **radius of gyration** R_g which is formally defined as

$$R_g^2 = \frac{1}{N+1}\sum_{i=0}^{N}\left(\mathbf{r}_i - \mathbf{r}_{\mathrm{CM}}\right)^2 \qquad \mathbf{r}_{\mathrm{CM}} \equiv \frac{1}{N+1}\sum_{i=0}^{N}\mathbf{r}_i$$

where $\mathbf{r}_i$ is the position of the ith monomer. The radius of gyration can be written in the alternative form.

$$R_g^2 = \frac{1}{2\left(N+1\right)^2}\sum_{i=0}^{N}\sum_{j=0}^{N}\left(\mathbf{r}_i - \mathbf{r}_j\right)^2$$

One can see that this is essentially the same as the moment of inertia of an object.

Table 2.4 Square radii of gyration of rigid objects: uniform thin disc of radius R, uniform sphere of radius R, thin rod of length L, and uniform right cylinder of radius R and length L

Rigid objects	Disk	Sphere	Rod	Cylinder
R_g^2	$R^2/2$	$3R^2/5$	$L^2/12$	$(R^2/2)+(L^2/12)$

For a random walking polymer, it can be shown that $R_g = R_0/\sqrt{6}$ at large N limit. Here is the proof.

Calculation of the Radius of gyration

When $|n-m|$ is large, $\mathbf{R}_n - \mathbf{R}_m$ of an ideal chain has a Gaussian distribution with variance $|n-m|a^2$

$$P(\mathbf{R}_n - \mathbf{R}_m) = \left(\frac{3}{2\pi |n-m| b^2}\right)^{3/2} \exp\left(-\frac{3(\mathbf{R}_n - \mathbf{R}_m)^2}{2|n-m|a^2}\right) \qquad \left\langle (\mathbf{R}_n - \mathbf{R}_m)^2 \right\rangle = |n-m| a^2$$

Therefore,

$$R_g^2 = \frac{1}{2N^2}\sum_{n=1}^{N}\sum_{m=1}^{N}\left\langle (\mathbf{R}_n - \mathbf{R}_m)^2 \right\rangle = \frac{1}{2N^2}\sum_{n=1}^{N}\sum_{m=1}^{N} |n-m| a^2$$

For large N, the summation can be replaced by an integration

$$R_g^2 = \frac{a^2}{2N^2}\int_0^N dn \int_0^N dm\, |n-m|$$

$$\therefore R_g^2 = \frac{a^2}{2N^2}\frac{N^3}{3} = \frac{1}{6}Na^2 = \frac{1}{6}R_0^2$$

$$\int_0^N dn \int_0^N dm\, |n-m| = \int_0^N dn \int_{n-N}^{n} dx\, |x| \qquad (n-m \equiv x)$$

$$= \int_0^N dn \left[\frac{x^2}{2}\Big|_0^n + \frac{x^2}{2}\Big|_0^{n-N}\right] = \int_0^N dn \left[\frac{n^2}{2} + \frac{(n-N)^2}{2}\right] = \frac{N^3}{3}$$

Measuring the size of polymer chains

In deciding what kind of radiation to use for the scattering experiment, we have to consider two factors:

wavelength—the radiation must have a wavelength comparable to the size of the object, so that we can detect scattering from the object;
contrast—the radiation must interact differently with the object than with the medium it is immersed in.

The possible types of radiation are as follows:

Visible light—here contrast is based on refractive index differences between the scattering object and its environment. The relatively long wavelength compared to molecular sizes means that even quite large polymers scatter to wide angles.

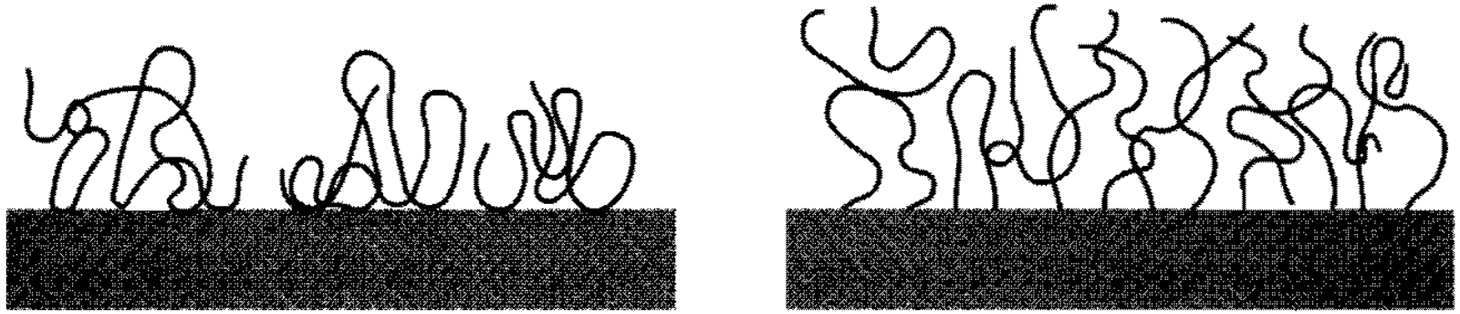
X-rays—here the contrast is based on differences in electron density between the scattering object and its environment. This means that the scattering object must contain atoms of relatively large atomic number compared to the surroundings. The smaller wavelength than visible light means that objects with sizes typical of polymer molecules scatter at small angles.

Neutrons—here the contrast is based on differences in nuclear interactions. As it happens, the scattering of neutrons is very different for hydrogen and deuterium, allowing one to distinguish a polymer molecule from a chemically very similar environment by **deuterium labeling**. The wavelength of thermal neutrons is similar to X-rays.

Although neutron scattering is expensive, the fact that it can distinguish between hydrogen and deuterium means that **it can measure chain dimensions in concentrated solutions and melts**—this cannot be done any other way. (Something very easy in simulation can sometimes be extremely difficult in experiment.)

Polymers at interfaces—adsorbed and grafted chains

Polymer chains bound to surfaces can profoundly modify the interactions between such surfaces, giving a mechanism for the **stabilization of colloidal dispersions**. We are now in a position to understand the physics underlying this steric stabilization in more detail.



(a) (b)

Two important ways in which polymers can interact with a surface are illustrated in the figure. In (a), **adsorbed homopolymers**, relatively weak interactions between an individual segment and the surface anchor the chain firmly to the surface.

The conformation of the polymer chain must be perturbed by its interaction with the surface, and more severely perturbed conformations are observed for higher energies of interaction. However, it is a difficult subject to quantify the relationship between the adsorption energy and the overall conformation of the whole chain.

Polymer Brush

The situation in which chains are attached by one end to an interface turns out to be much more easily dealt with theoretically, as well as being relevant to a number of practical situations. If the grafting density is high enough, the polymers are **stretched** outwards, and we call it a **polymer brush**. There are two types of polymer brushes. The first type is a brush immersed in solvents and the second type is a brush made by polymer melts.

Let us estimate the height h of the brush in solvents. Suppose we have polymers of degree of polymerization N, and their grafting density is σ; i.e. the average area for one chain is $1/\sigma$. and the volume per chain is h/σ. The stretching energy of a chain is estimated as

$$F_{\text{el}} = \frac{3}{2} k_{\text{B}} T \frac{h^2}{Na^2}$$

the combined excluded volume and interaction energy per chain is

$$F_{\text{rep}} + U_{\text{int}} = k_{\text{B}} T v \left(1 - 2\chi\right) \frac{N^2}{2V} = k_{\text{B}} T a^3 \left(1 - 2\chi\right) \frac{N^2 \sigma}{2h}$$

Finding the value of the brush height h that minimizes the total energy gives us $h \sim \left[\left(1-2\chi\right)\sigma a^2\right]^{1/3} Na$

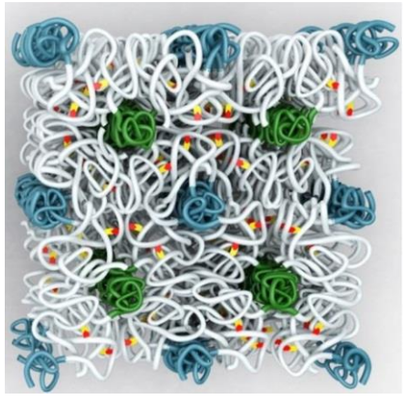
This reveals that a chain end-grafted to a polymer surface at high enough densities is stretched—the chain dimensions vary not as $N^{3/5}$ but as a **linear function of *N***.

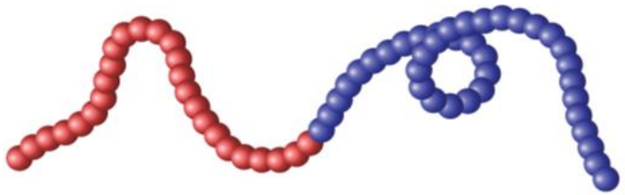
For the polymer melt case, the brush height is more easily calculated. The volume of each chain is approximately Na^3 and this must be equal to h/σ. Thus

$$h \sim \sigma N a^3$$

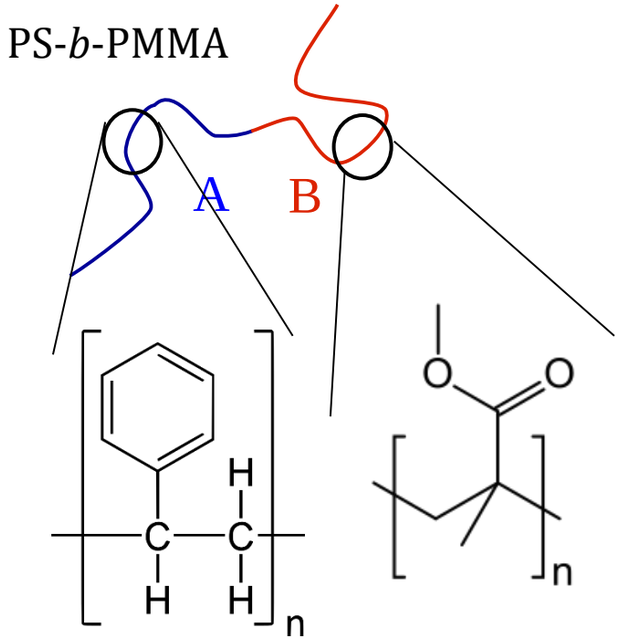
Block Copolymers (BCPs)

AB Block Copolymers

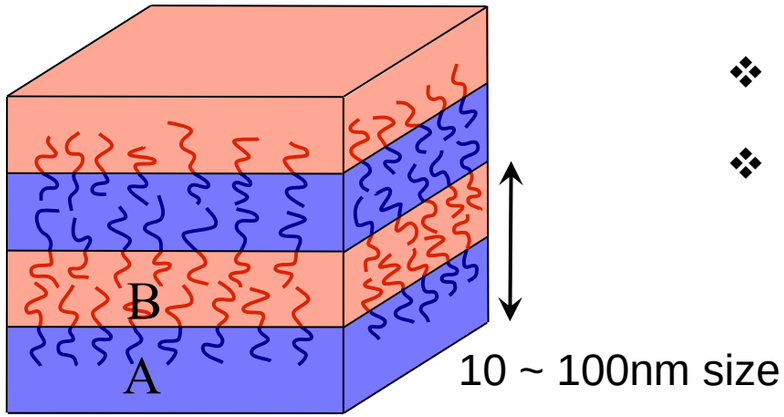




❖ Two chemically distinct polymer blocks joined together ➡ **AB block copolymer formation**



Incompressible melt of AB Diblock Copolymer Phase Behavior in Bulk

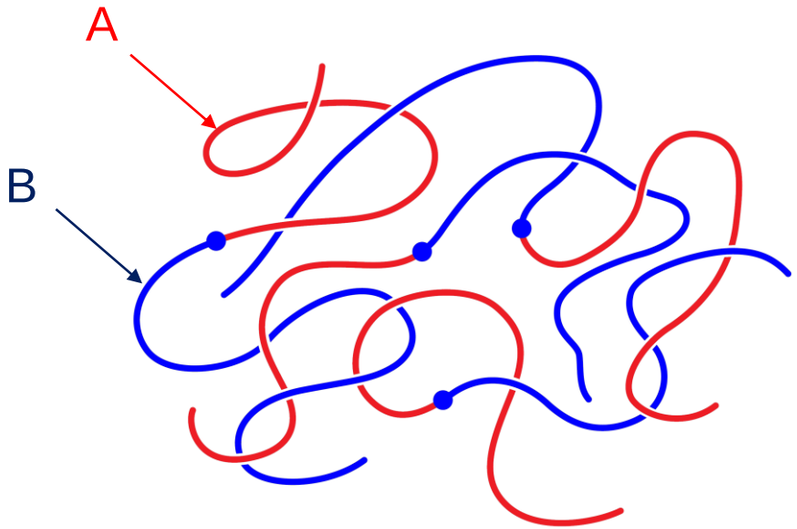


❖ The repulsion between A and B results in the formation of nanometer scale structures.

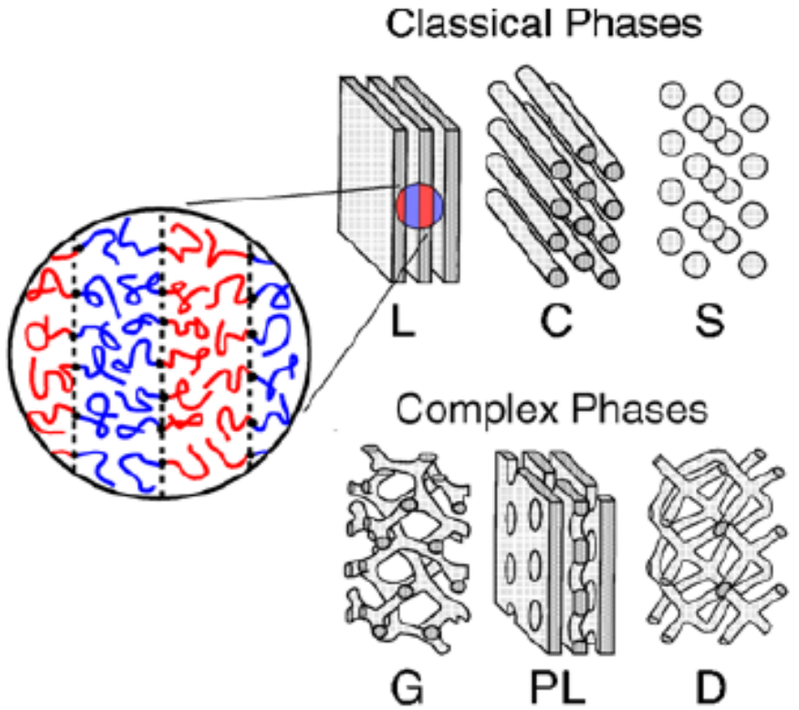
❖ Symmetric block copolymers form microstructure consisting of alternating lamellae of thin A- and B-rich domains with period of D = 10 ~ 100 nm.

Other Microphases are available

Block Copolymers



Microphase Separation



M. W. Matsen, 2006
M. W. Matsen, *J. Phys.: Condens. Matter*, **14**, R21 (2002)

- For a diblock copolymer, f is used to represent the fraction of A in the polymer, $1 - f$ is the fraction of B.
- Depending on f and χN parameters, the domains tend to form highly-ordered periodic geometrics, of which the lamellar phase of alternating thin layers is the simplest. (χ represents the degree of repulsion between segments.)
- This ability to self-assemble into **ordered nanoscale morphologies** of different geometries is used to create **nanostructures** that are applicable for various high-tech applications.

Major parameters
N : Polymerization index
f : Volume fraction of A block
χN : Incompatibility between A and B block
a : Statistical segment length

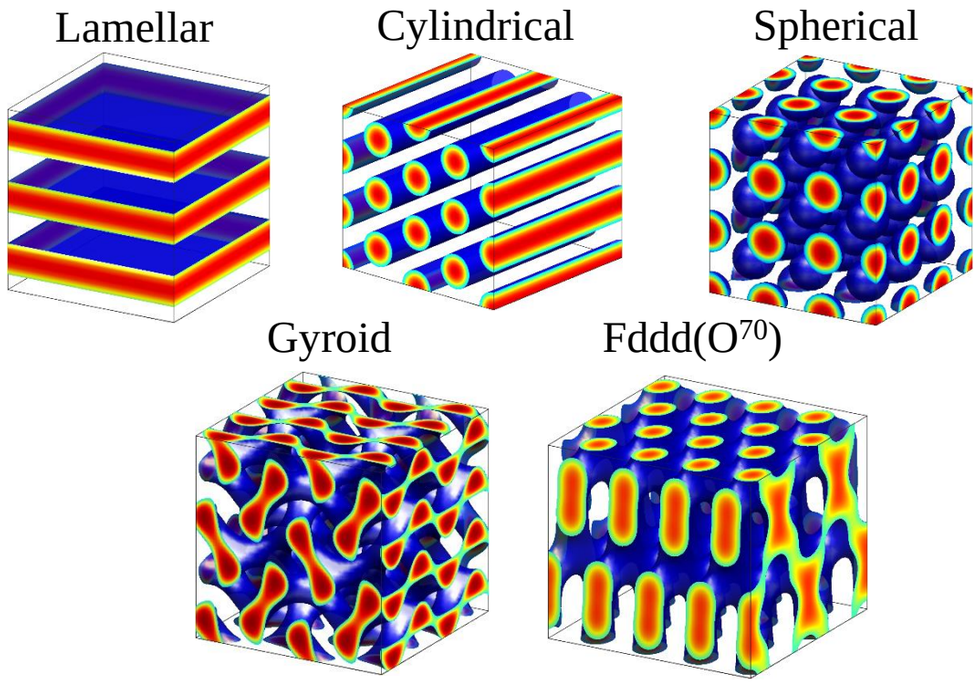
Phase diagram of AB diblock Copolymer Melts

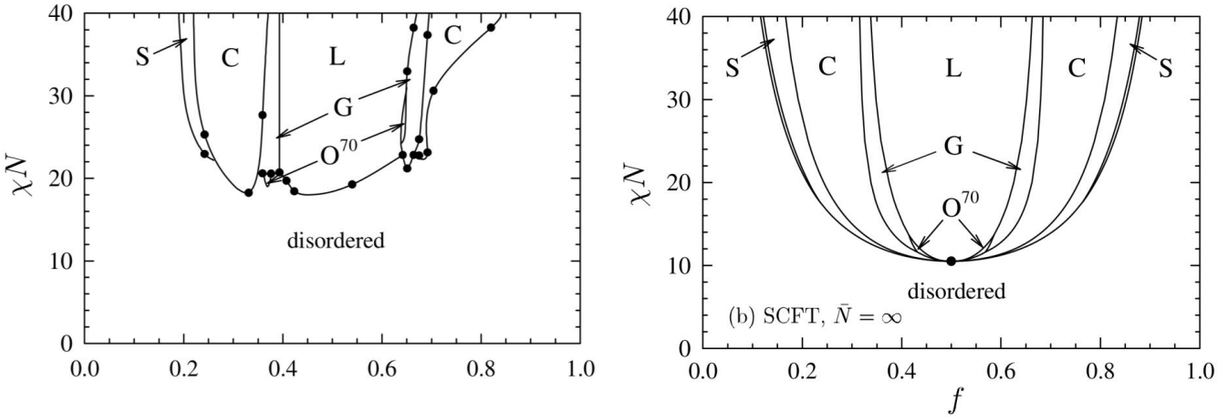
Microphase Separation of Block Copolymers

- Various microphases are experimentally observed and theoretically confirmed to be stable.
- Common phases: Lamellar (L), Cylindrical (C), Gyroid (G), Spherical (S). **Other Microphases are available**

What is a Phase Diagram?

- A map of stable BCP phases. Statistical mechanics is a tool to investigate the phase behavior of polymers.
- This phase diagram obtained by **Self-Consistent Field Theory (SCFT)**, Spectral Method.
- SCFT has provided a useful tool predicting the morphological behavior of polymer materials.



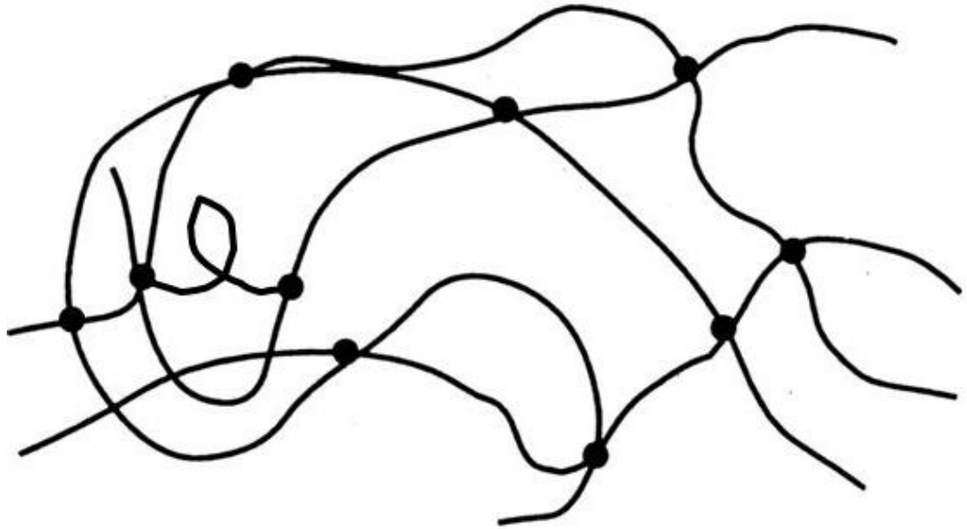


Phase diagram of PI-PS BCP (left), theoretical phase diagram using SCFT(right)

Matsen, M. W.; Beardsley, T. M.; Willis, J. D. Fluctuation-Corrected Phase Diagrams for Diblock Copolymer Melts. Phys. Rev. Lett. 2023, 130 (24), 248101.

Rubber Elasticity

The first statistical mechanical theory of the mechanical properties of a polymeric material was the classical theory of rubber elasticity. Chemical bonds between polymer molecules are called “crosslinks”.



A **rubber** is a polymer melt in which randomly placed cross-links bond the chains together to form a macroscopic network.

Sulphur can crosslink natural rubber. To observe “stretchiness”, the temperature should be above T_g for the polymer.

At a local level, the material behaves like a liquid; in particular the bulk modulus is rather high and to a first approximation the material may be taken as incompressible. However, the cross-links mean that macroscopic bulk flow cannot take place, and the material has a **finite shear modulus**. The classic theory of rubber elasticity uses statistical mechanics to calculate the shear modulus.

To calculate the modulus, we start by making an important assumption: when the rubber is deformed each individual cross-link point moves in proportion to the deformation of the whole sample. This is the assumption of **affine deformation**.

Thus if the initial dimensions of the sample are l_x, l_y, and l_z, and after deformation these dimensions become $\lambda_x l_x$, $\lambda_y l_y$ and $\lambda_z l_z$, the position of a point at coordinates (x, y, z) transforms to $(\lambda_x x, \lambda_y y, \lambda_z z)$.

If we consider a single strand between two cross-link points, one of which is initially at the origin, and the other is at the coordinates (x, y, z), we find its initial mean end-to-end distance is $r_0^2 = x^2 + y^2 + z^2$.

After deformation, the new mean end-to-end distance $r_1^2 = \lambda_x^2 x^2 + \lambda_y^2 y^2 + \lambda_z^2 z^2$. Using the relation for the entropy of a Gaussian chain given in Section 5.3.1, we find the change in entropy per strand on deformation, ΔS_{strand}, to be given by

$$\Delta S_{\text{strand}} = \frac{-3k_B}{2Na^2}\left[\left(\lambda_x^2 - 1\right)x^2 + \left(\lambda_y^2 - 1\right)y^2 + \left(\lambda_z^2 - 1\right)z^2\right]$$

If there are n strands per unit volume, we can use the relation $\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle = Na^2/3$ to write the total entropy change per unit volume ΔS_{volume} that results from the deformation as

$$\Delta S_{\text{volume}} = \frac{-nk_B}{2}\left[\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right]$$

Let us take the simplest case of deformation, a simple elongation in the x direction, and assume that rubber is **incompressible**, $\lambda_x = \lambda$, $\lambda_y = \lambda_z = 1/\sqrt{\lambda}$, we find

$$\Delta S_{\text{volume}} = \frac{-nk_B}{2}\left[\lambda^2 + \frac{2}{\lambda} - 3\right] \qquad \Delta F_{\text{volume}} = \frac{nk_BT}{2}\left[\lambda^2 + \frac{2}{\lambda} - 3\right]$$

This is simply the elastic work done during the deformation. From this, we can obtain the relation between tensile stress τ and strain e by noting that $\lambda = 1+e$, and $\tau = dF/de$. Thus

$$\tau = nk_{\mathrm{B}}T\left[(1+e) - \frac{1}{(1+e)^2}\right]$$

This is a non-Hookean stress/strain behavior, but we can expand for small strain to find that

$$\tau \cong 3nk_{\mathrm{B}}Te \qquad E = \tau / e = 3nk_{\mathrm{B}}T$$

where E is the Young's modulus. Once again assuming incompressibility (and thus a Poisson ratio = transverse strain / axial strain of 0.5) this gives for the shear modulus G the very simple relation (proof not shown here)

$$G = nk_{\mathrm{B}}T$$

Another convenient way to express this result, which we will use later, is in terms of M_x, the average relative molecular mass between cross-links, and the density ρ:

$$G = \frac{\rho RT}{M_x}$$

where R is the gas constant. This remarkable result indicates that the mechanical properties of a rubber are functions only of the temperature and cross-link density. As long as the chains behave in a liquid-like way (i.e. not glass-like) the chemistry of the polymer chains and the nature of the cross-links are not relevant.

Viscoelasticity in polymers and the reptation model

Polymer melts are usually highly viscous, but they also show very marked viscoelastic behavior. In this section we will review the basic phenomenology of polymer viscoelasticity, before introducing a powerful and simple model that allows us to understand and make quantitative predictions of polymer viscoelasticity from a molecular point of view. This model is the theory of **reptation**.

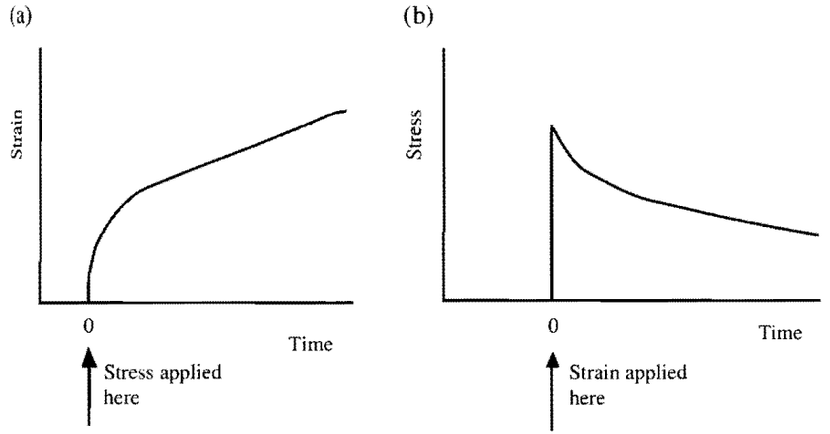
Characterizing the viscoelastic behavior of polymers

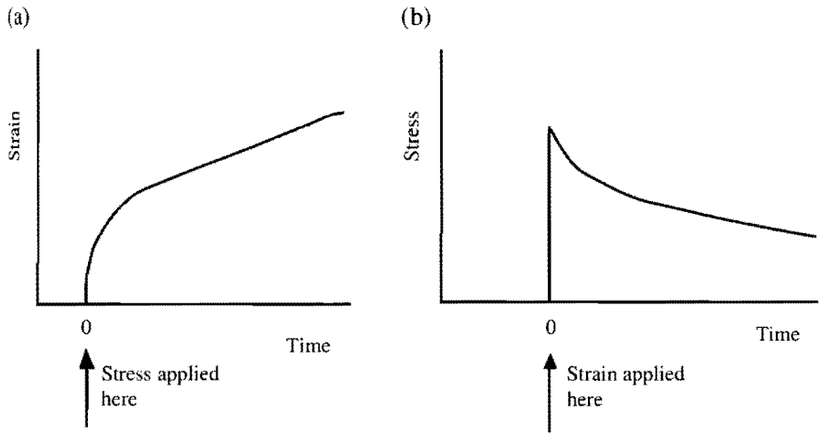
Viscoelastic liquids can behave either elastically or viscously, depending on the timescale over which they are deformed. Here we define measured functions that can characterize the observed viscoelastic properties.

The **creep compliance** $J(t)$ is defined with reference to an experiment in which a stress σ_0 is applied at time $t = 0$ and held constant, and the strain $e(t)$ is followed as a function of time. The creep compliance is then given by

$$e(t) = \sigma_0 J(t)$$

The form of this function for a typical viscoelastic material is sketched in Fig. (a). After an initial fast, elastic response, the sample slowly creeps before settling down to long-term viscous behavior in which the strain rate is constant.





The **stress relaxation modulus** $G(t)$ is defined by an experiment in which a strain e_0 is applied at time $t = 0$ and held constant, and the stress $\sigma(t)$ followed as a function of time. The stress relaxation modulus is then given by

$$\sigma(t) = e_0 G(t)$$

A typical shape for the stress relaxation modulus is sketched in Fig. (b). The initial response is elastic; as the material starts to flow the stress falls away to zero. An extremely important type of deformation, both experimentally and for theoretical considerations, is an oscillatory deformation at a certain frequency ω. If an oscillatory strain of the form

$$e(t) = e_0 \cos(\omega t)$$

is applied, then (for small amplitudes) the resulting stress can be written as

$$\sigma(t) = e_0\left[G'(\omega)\cos\omega t - G''(\omega)\sin\omega t\right]$$

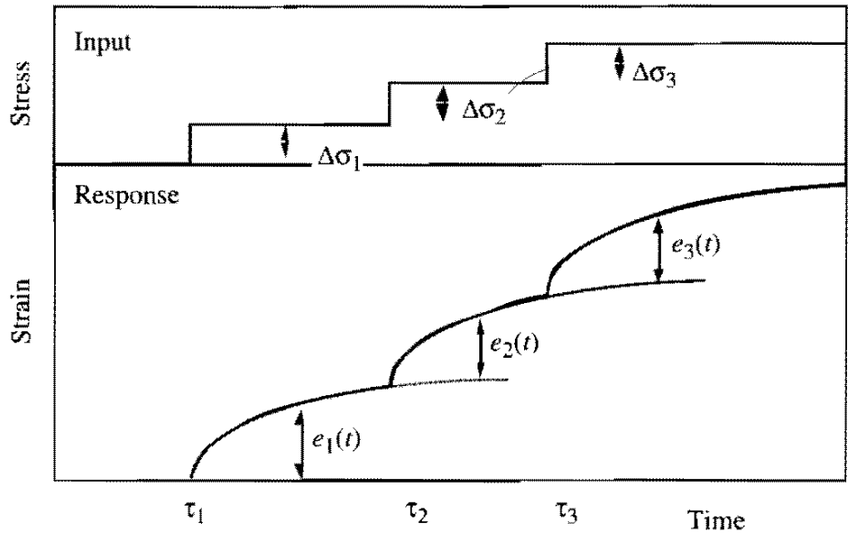
where $G^*(\omega) = G'(\omega) + iG''(\omega)$ is the **complex modulus**. The complex modulus $G^*(\omega)$ is essentially the Fourier transform of the stress relaxation modulus $G(t)$.

The complex modulus G^* thus tells us about both the elastic response and the viscous response at any given frequency. The real part, G', is the elastic component of the response, and is known as the **storage modulus**. The imaginary part, G'', is the viscous component of the response and is known as the **loss modulus**.

This analysis is analogous to the damped harmonic oscillator or the optical system with complex dielectric constant. The phase angle of the response, δ, is given by $\tan\delta = G''/G'$. A material with a $\tan\delta$ greater than one will exhibit more damping than a material with a $\tan\delta$ less than one.

Linear viscoelasticity and the Boltzmann superposition principle

For small deformations one can assume that each loading step makes an independent contribution to the total loading history, and the final deformation is simply the sum of the response to each step, as illustrated in Fig. 5.6; i.e. we are basically assuming the response is **linear**.



Thus it follows that we can write the strain as an integral involving the creep compliance $J(t)$

$$e(t) = \int_{-\infty}^{t} J(t-\tau)\, d\sigma(\tau) = \int_{-\infty}^{t} J(t-\tau) \frac{d\sigma(\tau)}{d\tau} d\tau$$

and, similarly, the stress as a function of time as an integral involving the stress relaxation modulus $G(t)$

$$\sigma(t) = \int_{-\infty}^{t} G(t-\tau) \frac{de(\tau)}{d\tau} d\tau$$

In the special case where the shear rate is constant this recovers Newton's law of viscosity $\sigma(t) = \eta_0 \dot{e}$ and gives us a useful relationship between the viscosity η_0 and the stress relaxation modulus:

$$\eta_0 = \int_{-\infty}^{t} G(t-\tau)\, d\tau = \int_{0}^{\infty} G(t)\, dt$$

The viscosity η_0 is called the **zero shear viscosity** to emphasize that this relation relies on the assumptions of linear viscoelasticity. It is common to go beyond the linear regime in experiments, but the theory of non-linear viscoelasticity is extremely complex and beyond the scope of this book.

The temperature dependence of viscoelastic properties: time-temperature superposition

We have seen that viscoelastic quantities are intrinsically a function of time. Experimentally, one also finds that the viscoelastic properties of polymers are a strong function of temperature; for example, a very viscous polymer solution or melt will become less viscous on being warmed.

It turns out experimentally that the dependences of viscoelastic quantity on time and temperature can be factorized. Taking the stress relaxation modulus as a function of time t and temperature T, $G(t, T)$ empirically follows

$$G\left(t,T\right)=G\left(a_T t,T_0\right) \qquad \log a_T=\frac{-C_1\left(T-T_0\right)}{C_2+\left(T-T_0\right)}$$

where a_T is a temperature-dependent shift factor.

It is common to use the glass transition temperature as the reference temperature T_0, in which case the constants C_1 and C_2 take values which are rather similar for many different polymers. Taking the logarithm as being to base 10, as is usual in the polymer literature, these quasi-universal values are $C_1^g = 17.4$ and $C_2^g = 51.6$ K. This expression is known as the WLF equation, after Williams, Landel, and Ferry.

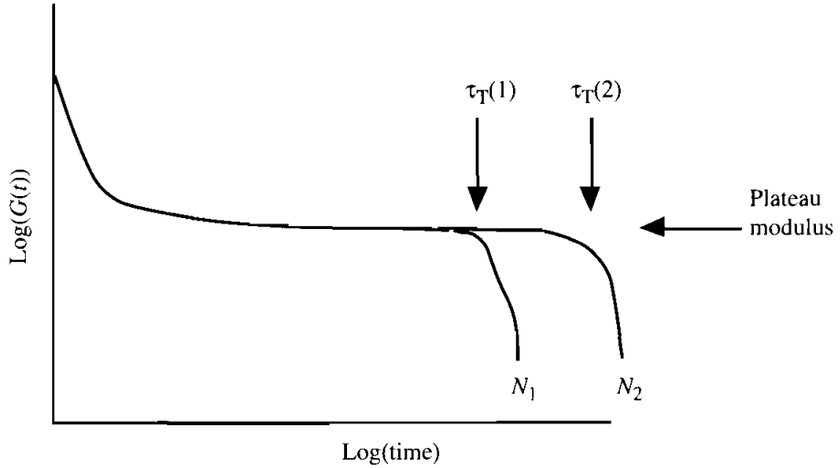
The fundamental significance of time-temperature superposition is that it tells us that in the problem of viscoelasticity all the microscopic timescales scale in the same way with temperature. We can anticipate that in any microscopic theory of viscoelasticity the temperature will enter via a single temperature-dependent parameter.

The specific form of the WLF relation for the shift factor given in the previous page can be shown to be equivalent to the statement that polymers have dynamics obeying the Vogel-Fulcher law, like most other glass-forming liquids.

In addition to its theoretical significance, the principle of time-temperature superposition is very useful experimentally, as it allows us to build up data sets covering very wide effective ranges of timescales on instruments whose actual range of accessible times is much smaller.

Viscoelasticity: experimental results for monodisperse linear polymer melts

Viscoelasticity is best understood for melts of linear polymers in which the distribution of relative molecular masses is rather narrow. For such materials the quantities characterizing linear viscoelasticity show a strong universal character. In the figure, the stress relaxation modulus $G(t)$ is shown for two chemically identical polymers with different degrees of polymerization.



At short times, the curve is independent of degree of polymerization. At intermediate times there is a wide range of times for which the modulus is essentially constant—this is the **plateau modulus**. The value of the plateau modulus does not depend on the degree of polymerization. The plateau ends at a **terminal time** τ_T, which does depend strongly on degree of polymerization, according to a power law $\tau_T \sim N^m$, where the exponent $m \approx 3.4$.

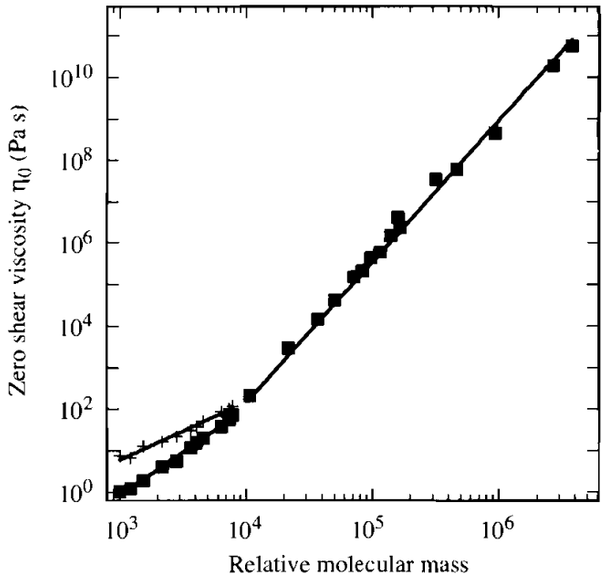
$$\sigma(t) = e_0 G(t)$$

$$e(t) = \sigma_0 J(t)$$

$$\eta_0 = \int_0^\infty G(t)\,dt$$

In the plateau part of the curve, the polymer behaves like an elastic solid. In fact, the numerical value of the modulus is comparable to that of a lightly cross-linked rubber. After the terminal time the polymer flows in an essentially viscous manner; here the creep compliance $J(t) \sim t$. The zero-shear viscosity η_0 is related to the terminal time and the plateau modulus G_p as $\eta_0 \sim \tau_T G_p$.

As the plateau modulus is independent of degree of polymerization, the molecular weight dependence of the viscosity should be the same as that of the terminal time. Thus we expect $\eta_0 \sim N^m$, where the exponent $m \approx 3.4$. This dependence of viscosity on degree of polymerization is exactly what is observed whenever the degree of polymerization is above a certain critical value N_c.



This is illustrated in the figure, which shows the dependence of zero shear viscosity on relative molecular mass for polybutadiene. Very similar curves are found for all linear polymers; below N_c the viscosity is proportional to N, while above N_c we find $\eta_0 \sim N^{3.4}$.

Entanglements

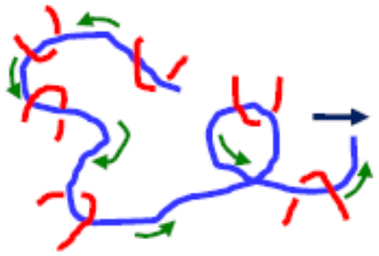
The striking features of polymer viscoelasticity can be understood at a qualitative level by the intuitively appealing notion of entanglement:

- Elastic property of rubber is from the permanent cross-links.
- Viscoelastic property of polymer melts is due to entanglement.

Polymer chains are linear objects which cannot pass through one another; it is easy to imagine that in a melt of long interpenetrating chains, shearing the melt will lead to the chains becoming tangled up with each other.

In this picture, one can interpret the rubber-like plateau in the shear modulus as indicating that entanglements behave like **temporary cross-links**. We can use the theory of rubber elasticity to estimate the density of entanglements. As the plateau modulus is independent of degree of polymerization, this quantity is a material constant for a given polymer. Adapting the earlier equation, we find



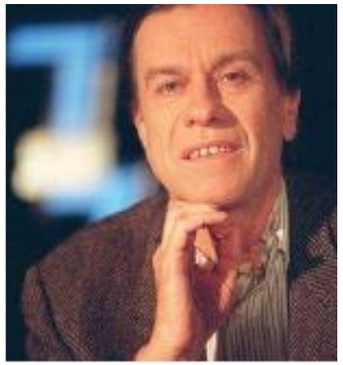


$$G = \frac{\rho RT}{M_e}$$

M_e: average relative molecular mass between entanglements
ρ: its density

These entanglements are not permanent—we imagine that they can disentangle with a characteristic timescale comparable to the terminal time τ_T. It is reasonable at a qualitative level that long chains will take longer to disentangle than shorter chains, but can we make this idea quantitative enough to explain the experimental result that $\tau_T \sim N^{3.4}$?

To make progress towards a quantitative theory of viscoelasticity we need to make the idea of entanglements slightly more well defined. This has been achieved in the **tube model** and the idea of reptation, due to Edwards, de Gennes and Doi.



Pierre Gilles de Gennes
(1932–2007)



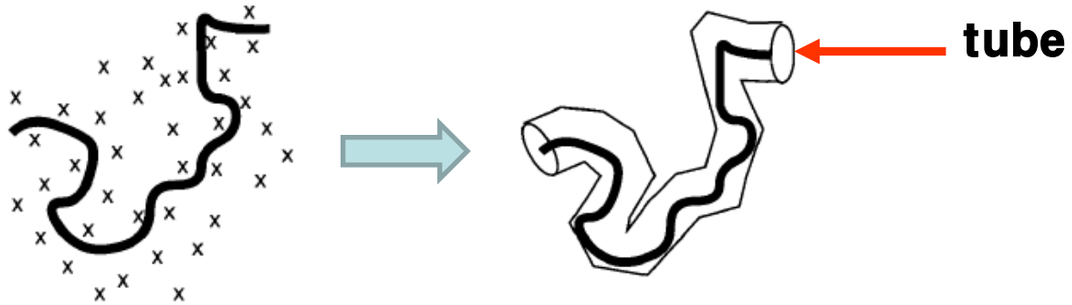
Samuel Edwards
(1928–2015)



Masao Doi

The tube model and the theory of reptation

How is the motion of one chain constrained by the presence of all the other chains with which it is strongly entangled? The basic constraint is that no chains can cross each other's path. One can imagine that each chain is effectively restricted to a **tube**.



The motion of a chain in a tube is severely constrained laterally, but it is still free to wriggle along the length of the tube, like a snake moving through long grass (see the figure). This type of motion is called **reptation**.

Entanglement된 고분자의 dynamics를 설명하는 다른 이론도 존재한다. Slip-link 등의 모델은 reptation 모델과 competing하는 동시에 서로를 보완적인 역할도 있다.

We can now associate the terminal time with the time it takes the polymer to move completely out of its original tube. We can estimate this by assuming that the motion is purely viscous within the tube; i.e. if we were able to move a segment of the chain through the tube it would feel a resistance force proportional to its velocity.

Thus we can define a segment mobility μ_{seg}. Here, the mobility is defined such that the velocity v under viscous fluid is given as $v = \mu_{seg}F$. If we were to pull a chain with N segments through the tube we would expect the viscous resistance felt by each segment to be additive, so mobility of the whole chain would be simply $\mu_{tube} = \mu_{seg}/N$.

Because the chain is an object in a viscous fluid, it will undergo constant Brownian motion; the chain will randomly wriggle backwards and forwards within the tube until it has completely escaped. Using Einstein's relation we can write down a diffusion coefficient D_{tube} to describe this Brownian motion:

$$D_{\text{tube}} = k_{\text{B}}T\,\mu_{\text{tube}} = \frac{k_{\text{B}}T\,\mu_{\text{seg}}}{N}$$

The chain is doing what is essentially a one-dimensional random walk within the tube, so if the length of the tube is L, the time taken to escape the tube, which we now identify with the terminal time τ_T (reptation time), is given by

$$\tau_T = \frac{L^2}{D_{\text{tube}}}$$

Since the length of the tube is proportional to the degree of polymerization N, we thus find that

$$\tau_T \sim N^3$$

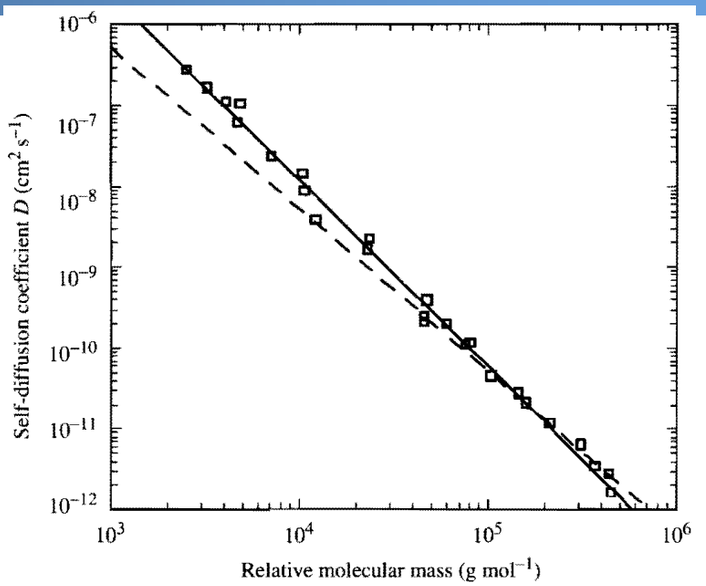
This is quite close(?) to the experimental result of $\tau_T \sim N^{3.4}$

We can also derive another testable prediction from this theory, for the variation of the **self-diffusion coefficient** of a polymer chain in a polymer melt. Each chain has diffused a distance comparable to its own end-to-end distance during the terminal time. Using the random walk result for chain end-to-end distance, we find

$$D_{\text{self}} = \frac{Na^2}{\tau_T} \qquad D_{\text{self}} \sim N^{-2}$$

The experimental situation is illustrated in the figure. Self-diffusion coefficients do obey a power law. A more recent reevaluation of the data (Lodge 1999) suggests that the exponent is slightly higher than 2; in fact the data seems to be best fitted by

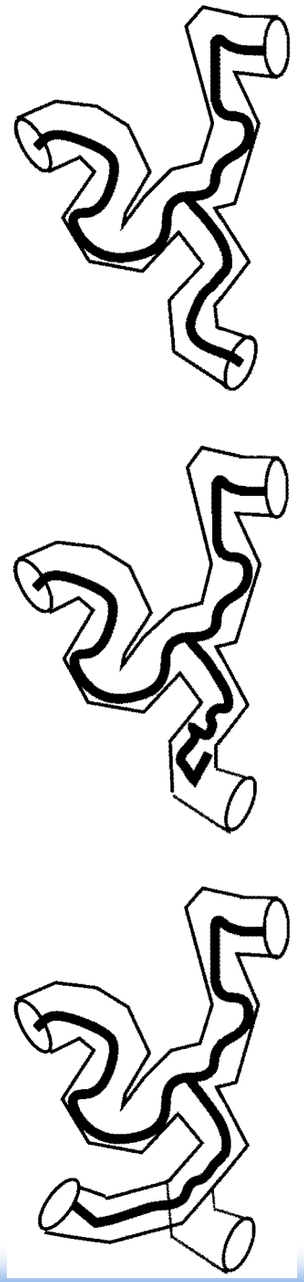
$$D_{\text{self}} \sim N^{-2.30}$$



Modifications to reputation theory

Thus experimental data for viscosity, terminal time, and self-diffusion seems to be reasonably consistent with a single scaling of the terminal time of $\tau_T \sim N^{(3.3–3.4)}$, while the simple reptation theory predicts $\tau_T \sim N^3$. What is the cause of this discrepancy? It turns out that the reptation prediction must be modified by the inclusion of two other ways in which the tube constraint may be relaxed. These are:

1. **Constraint release**. In the tube model, it is assumed that the constraints that are described by the tube are immobile. In fact these constraints are themselves chains which are also reptating, so the tube must have a finite lifetime.
2. **Contour length fluctuation**. The length of the tube is defined, in effect, by the end-to-end distance of the polymer chain given by $a\sqrt{N}$ on average. As the chain undergoes Brownian motion, this end-to-end distance will fluctuate. We can imagine the chain withdrawing into the tube, and then when it expands back to its average size some of the original constraints on it will have relaxed.



It is now believed that incorporation of these two corrections—particularly contour length fluctuations—can account for the discrepancy between experiment and the reptation prediction. The most striking implication of these effects comes from a consideration of the dynamics of non-linear polymers such as **star** and **branch** polymers.

The importance of these non-reptative relaxation modes for non-linear polymers is illustrated in the figure. A star molecule is confined to a non-linear lube from which it cannot escape by reptation. Instead, if one of the arms is retracted into its tube by a contour length fluctuation, the tube can relax.

For this type of motion, one expects a relaxation time that is an **exponential** function of the arm length N_{arm}, rather than the power law dependence of a linear molecule. This emphasizes the importance of **architecture** in polymer physics.

A linear polymer and a set of branched polymers of similar overall relative molecular mass, but with different degrees of branching, are chemically almost identical, but their physical properties, such as their melt viscosities, will be very different.

Statistical Physics of Polymers

For the rest of this lecture, let us develop statistical physics of **incompressible polymer melt system**.
Some degree of coarse-grained picture is necessary, and thus we make two major assumptions.

1) Each chain is an infinitely flexible **Gaussian chain**. It means that any small fragment of the chain exhibit Gaussian statistics.
2) There exists only **contact interaction** proportional to the polymer density at the position; i.e. the interaction Hamiltonian for AB system can be written as

$$\frac{H_{\text{int}}}{k_{\text{B}}T} = \chi\rho_0 \int d\mathbf{r}\hat{\phi}_{\text{A}}(\mathbf{r})\hat{\phi}_{\text{B}}(\mathbf{r})$$

where $\hat{\phi}_i(\mathbf{r})$ is the *i*-type segment density at position $\mathbf{r}$.

Both assumption are justified in the long chain limit where the universality is recovered.

Even the incompressibility and contact interaction conditions can be released in a generalized theory, and other chain models such as FJC can also be used when discretized theory is adopted.

Universality Hypothesis

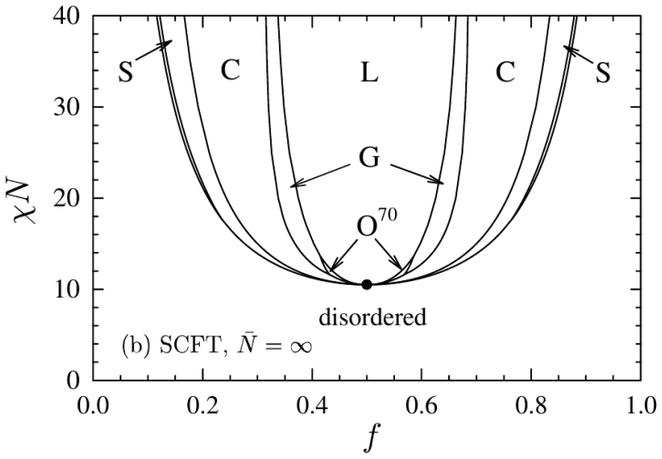
For long enough AB diblock copolymers, its mean field (SCFT) behavior is completely determined only by a few parameters:

$f = N_A/N$ is the A fraction (where $N = N_A + N_B$)

a_A/a_B is ratio of segment lengths (we assume it is 1 throughout this lecture)

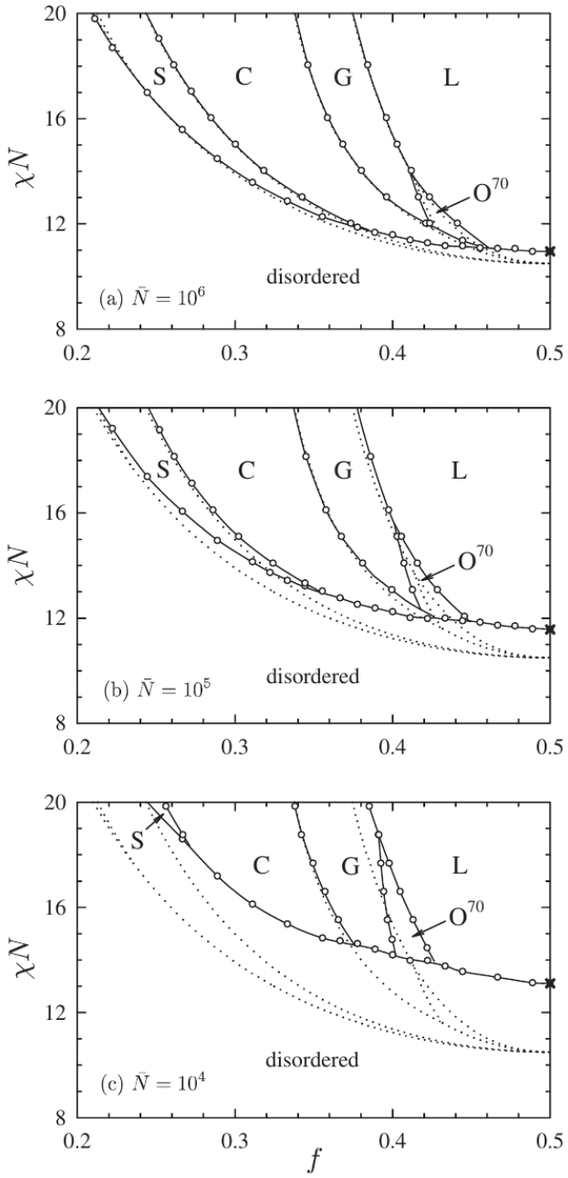
χN is the Flory-Huggins interaction parameter

In addition, $\bar{N} = a^6\rho_0^2 N$ (where $a^2 = f a_A^2 + (1-f)a_B^2$ is the average segment length) controls the fluctuation corrections to SCFT



Mark W. Matsen , Tom M. Beardsley and James D. Willis, Phys. Rev. Lett (2023)

L-FTS ($\bar{N}$ from 10^6 to 10^4)



As the invariant polymerization index $\bar{N}$ increases, the mean field approximation becomes more accurate.

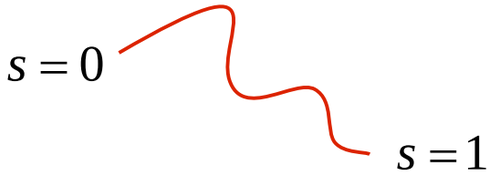
Particle- and Field-based Model

- **Coarse Grained Particle-Based Simulation (PBS)**:
  - Coarse grained model is commonly used in polymer physics.
  - ex) Monte Carlo (MC) and molecular dynamics (MD) simulations.
  - Interaction between segments : effective pairwise potential such as Lennard-Jones potential.
  - The physical and chemical details of polymers are embedded in the model.
  - System size is limited by computational demands.

- **Field-Based Calculation**:
  - Degree of freedom: Fields of local density.
  - Intermolecular interactions are indirectly represented by the fields.
  - Highly coarse-gained calculation requires only a few invariant parameters.

    (i.e. χN, natural end-to-end distance of polymer $aN^{1/2}$, invariant degree of polymerization $\bar{N}$).
  - One good example is the self-consistent field theory (SCFT) which is a mean field theory.
  - Another example is the field-theoretic simulation (FTS) which can account for the fluctuation effects.

Consider a polymer chain having N segments each with statistical segment length a and segment volume $1/\rho_0$.



Let us assume that the chain is an infinitely thin string like material. Its path can be represented by a space curve $\mathbf{r}_\alpha(s) \quad (0 \le s \le 1)$

s = 0 point is at one end. s = 1 at the other end. One may think the curve follows the backbone of the chain.

a : statistical segment length

N : degree of polymerization

ρ_0^{-1} : segment volume

Segment density due to this chain is

$$\hat{\phi}_\alpha(\mathbf{r}) = \frac{N}{\rho_0}\int_0^1 ds\,\delta(\mathbf{r}-\mathbf{r}_\alpha(s))$$

The above equation claims that the density must be zero everywhere except on the curve itself.
The prefactor can be explained by

$$\int d\mathbf{r}\hat{\phi}_\alpha(\mathbf{r}) = \int d\mathbf{r}\frac{N}{\rho_0}\int_0^1 ds\,\delta(\mathbf{r}-\mathbf{r}_\alpha(s)) = \frac{N}{\rho_0}\int_0^1 ds\int d\mathbf{r}\delta(\mathbf{r}-\mathbf{r}_\alpha(s)) = \frac{N}{\rho_0}\int_0^1 ds = \frac{N}{\rho_0}$$

It correctly represent the volume of one chain. (위의 density는 volume의 어떤 fraction을 고분자가 차지하고 있는지를 알려 주는 dimensionless number이다.)

Statistical Physics of Gaussian Chains

Assuming the chain is an **infinitely flexible Gaussian chain**, the free energy of a segment $[s_1,s_2]$ is



$$E[\mathbf{r}_\alpha; s_1, s_2] = \int_{s_1}^{s_2} ds \left(\frac{3}{2a^2 N} |\mathbf{r}'_\alpha(s)|^2 + w(\mathbf{r}_\alpha(s)) \right)$$

The first term represent the **entropic penalty** (다음 슬라이드 참조) while the second term is the **energy penalty** where w is the potential field acting on the αth chain.

a : statistical segment length

N : degree of polymerization

ρ_0^{-1} : segment volume

Note that we use E instead of F, because i) F is reserved for the total free energy of the system. ii) One usually forget that the origin of the first term is the entropy of chain stretching. (SBC와 같은 모델을 사용하면 이 term 이 실제 에너지가 될 때도 있다.)

The partition function of a polymer segment of length sN, with its two ends fixed at $\mathbf{r}_0$ and $\mathbf{r}$ is formally defined as

$$q(\mathbf{r}, \mathbf{r}_0, s) \propto \int \mathcal{D}\mathbf{r}_\alpha \exp\left(-\frac{E[\mathbf{r}_\alpha; 0, s]}{k_\mathrm{B}T} \right) \delta(\mathbf{r}_\alpha(0) - \mathbf{r}_0) \delta(\mathbf{r}_\alpha(s) - \mathbf{r})$$

with proper normalization,

$$q(\mathbf{r}, \mathbf{r}_0, 0) = (a^2 N)^{3/2} \delta(\mathbf{r} - \mathbf{r}_0)$$

This is a functional integral over all polymer configurations whose weight is given by the Boltzmann factor and the two ends are fixed by the delta functions.

At a glance it looks hopeless to calculate this directly. There is a simpler method to evaluate it.

Entropic Penalty Due to Stretching

앞에서 보았듯이 infinitely flexible한 길이 N인 고분자의 end-to-end length의 rms식은 다음과 같고 그 확률분포는 가우시안이다. $R_0 = N^{1/2}a$

고분자의 길이라 sN이라면, $R_0(s) = (sN)^{1/2}a$

The probability of a Gaussian polymer segment of length sN, with its two ends fixed at $\mathbf{r}_0$ and $\mathbf{r}$ is

$$P(\mathbf{r}, \mathbf{r}_0, s) = \frac{1}{(a^2N)^{3/2}}\left(\frac{3}{2\pi s}\right)^{3/2} \exp\left(-\frac{3|\mathbf{r}-\mathbf{r}_0|^2}{2a^2sN}\right)$$

By confirming the following relations, one can show that it is indeed the Gaussian function with the proper standard deviation.

$$\int P(\mathbf{r}, \mathbf{r}_0, s)d\mathbf{r} = 1 \qquad \int (\mathbf{r}-\mathbf{r}_0)^2 P(\mathbf{r}, \mathbf{r}_0, s)d\mathbf{r} = sNa^2$$

Assume s is small. If the polymer is uniformly stretched so that after sN step, $\mathbf{r} - \mathbf{r}_0 = l$, then the probability drop with respect to the case $\mathbf{r} - \mathbf{r}_0 = 0$ is $\exp\left(-\frac{3l^2}{2a^2sN}\right)$

Log of this expression must be the entropy decrease,

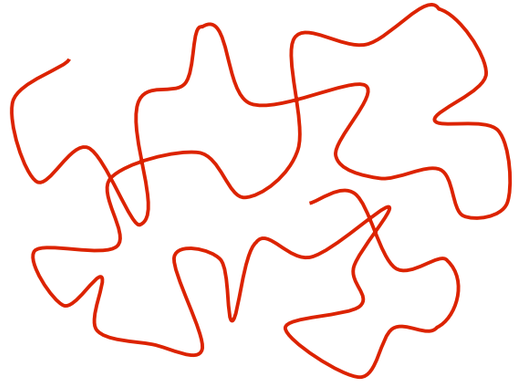
$$-\Delta S = \frac{3l^2}{2a^2sN} = \frac{3}{2a^2N}\left(\frac{l}{s}\right)^2 s = \int_0^s dt \frac{3}{2a^2N}\left|\mathbf{r}'_\alpha(t)\right|^2$$

This expression confirms the validity of the free energy expression.

Partition Function for Gaussian Chains

The probability of a Gaussian polymer segment of length sN, with its two ends fixed at $\mathbf{r}_0$ and $\mathbf{r}$ is

$$P(\mathbf{r},\mathbf{r}_0,s)=\frac{1}{(a^2N)^{3/2}}\left(\frac{3}{2\pi s}\right)^{3/2}\exp\left(-\frac{3|\mathbf{r}-\mathbf{r}_0|^2}{2a^2sN}\right)$$



The partition function is proportional to the probability density. If the field is turned off, we know the probability of a polymer segment of length sN, with its two ends fixed at $\mathbf{r}_0$ and $\mathbf{r}$.

$$q(\mathbf{r},\mathbf{r}_0,s)=\left(\frac{3}{2\pi s}\right)^{3/2}\exp\left(-\frac{3|\mathbf{r}-\mathbf{r}_0|^2}{2a^2sN}\right)$$

a : statistical segment length

N : degree of polymerization

ρ_0^{-1} : segment volume

The prefactor guarantees that $q(\mathbf{r},\mathbf{r}_0,s)$ is a dimensionless quantity and $q(\mathbf{r},\mathbf{r}_0,0)=\left(a^2N\right)^{3/2}\delta(\mathbf{r}-\mathbf{r}_0)$

Real chains are in a complicated field $w(\mathbf{r})$. (w is the energy penalty)
But at least, we know the short chain partition function in the field

$$q(\mathbf{r},\mathbf{r}_0,\varepsilon)\approx\left(\frac{3}{2\pi\varepsilon}\right)^{3/2}\exp\left(-\frac{3|\mathbf{r}-\mathbf{r}_0|^2}{2a^2\varepsilon N}-\varepsilon w(\mathbf{r})\right)$$

$w(\mathbf{r})$ is the field representing molecular interactions

Here is another weapon we have. The partial partition function satisfies the recurrence relation.

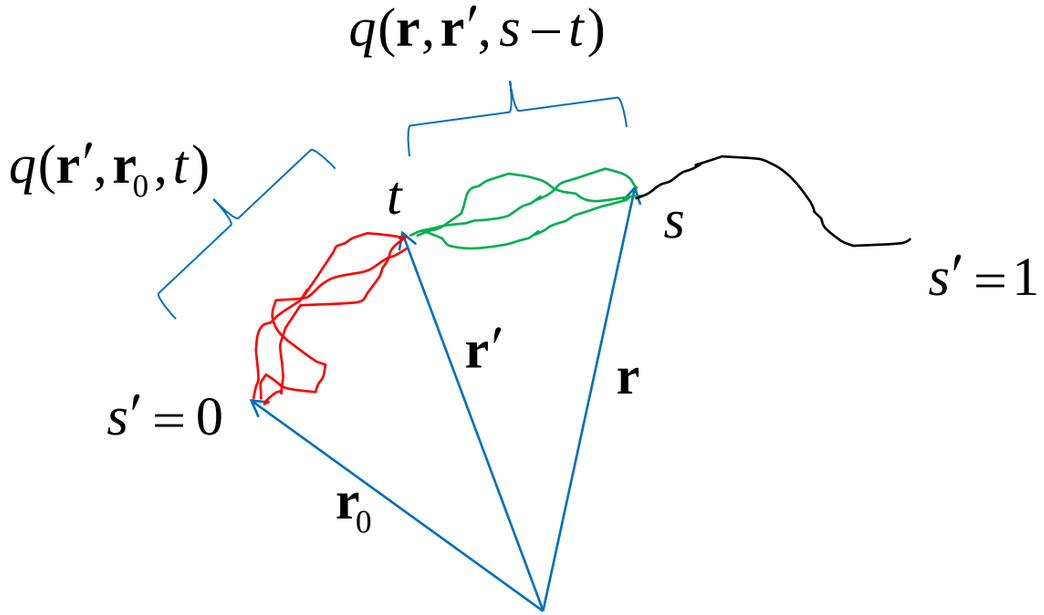
$$q(\mathbf{r},\mathbf{r}_0,s+\varepsilon)=\frac{1}{(a^2N)^{3/2}}\int d\mathbf{r}_\varepsilon q(\mathbf{r},\mathbf{r}+\mathbf{r}_\varepsilon,\varepsilon)\,q(\mathbf{r}+\mathbf{r}_\varepsilon,\mathbf{r}_0,s)$$

Recurrence Relation

Partial partition function, $q(\mathbf{r},\mathbf{r}_0,s)$, can be rewritten in terms of the partition function of the two shorter fragments. (**recursive relation**)

$$q(\mathbf{r},\mathbf{r}_0,s) = \frac{1}{(a^2N)^{3/2}}\int d\mathbf{r}'\, q(\mathbf{r},\mathbf{r}',s-t)\, q(\mathbf{r}',\mathbf{r}_0,t) \qquad (0<t<s)$$

(proportionality constant makes $q(\mathbf{r},\mathbf{r}_0,s)$ dimensionless.)



If we plug in $t = 0$,

$$q(\mathbf{r},\mathbf{r}_0,s) = \frac{1}{(a^2N)^{3/2}}\int d\mathbf{r}'\, q(\mathbf{r},\mathbf{r}',s)\, q(\mathbf{r}',\mathbf{r}_0,0)$$

$$= \frac{1}{(a^2N)^{3/2}}\int d\mathbf{r}'\, q(\mathbf{r},\mathbf{r}',s)\left[\left(a^2N\right)^{3/2}\delta(\mathbf{r}_0-\mathbf{r}')\right]$$

$$= q(\mathbf{r},\mathbf{r}_0,s)$$

Note the similarity to the path integral formalism of quantum physics.

Recurrence Relation

$$\frac{1}{(a^2N)^{3/2}}\int d\mathbf{r}'\, q(\mathbf{r},\mathbf{r}',s-t)\, q(\mathbf{r}',\mathbf{r}_0,t)$$

$$=\frac{1}{(a^2N)^{3/2}}\int d\mathbf{r}'\int \mathcal{D}\mathbf{r}_\alpha \exp\left(-\frac{E\left[\mathbf{r}_\alpha;0,t\right]}{k_{\mathrm{B}}T}\right)\delta\left(\mathbf{r}_\alpha(0)-\mathbf{r}_0\right)\delta\left(\mathbf{r}_\alpha(t)-\mathbf{r}'\right)\int \mathcal{D}\mathbf{r}_\beta \exp\left(-\frac{E\left[\mathbf{r}_\beta;t,s\right]}{k_{\mathrm{B}}T}\right)\delta\left(\mathbf{r}_\beta(t)-\mathbf{r}'\right)\delta\left(\mathbf{r}_\beta(s)-\mathbf{r}\right)$$

By performing the $\mathbf{r}'$ integral,

$$=\int \mathcal{D}\mathbf{r}_\alpha \exp\left(-\frac{E\left[\mathbf{r}_\alpha;0,s\right]}{k_{\mathrm{B}}T}\right)\delta\left(\mathbf{r}_\alpha(0)-\mathbf{r}_0\right)\delta\left(\mathbf{r}_\beta(s)-\mathbf{r}\right)=q(\mathbf{r},\mathbf{r}_0,s)$$

Those who are worried about the treating of the delta function at the joining point and the normalization factor may **confirm that there is no problem in its discretized version**.

양자역학의 한 포말리즘인 Path Integral로부터 슈뢰딩거 방정식을 유도하는 방법을 기억하고 있는 학생들은 다음 페이지부터의 내용이 익숙하게 느껴질 것이다.

$$\left\langle x_N,t_N\middle|x_1,t_1\right\rangle=\int dx_{N-1}\left\langle x_N,t_N\middle|x_{N-1},t_{N-1}\right\rangle\left\langle x_{N-1},t_{N-1}\middle|x_1,t_1\right\rangle$$

Partition Function for Gaussian Chains

위에서 구한 식들을 1차원 형태로 써 보자.

$$q(x, x+x_\varepsilon, \varepsilon) \approx \left(\frac{3}{2\pi\varepsilon}\right)^{1/2} \exp\left(-\frac{3x_\varepsilon^2}{2a^2N\varepsilon} - \varepsilon w(x)\right)$$

$$q(x, x_0, s+\varepsilon) = \frac{1}{(a^2N)^{1/2}} \int dx_\varepsilon q(x, x+x_\varepsilon, \varepsilon) q(x+x_\varepsilon, x_0, s)$$

위의 식을 가운데 항에 대입하면,

$$q(x, x_0, s+\varepsilon) = \frac{1}{(a^2N)^{1/2}} \int dx_\varepsilon \left(\frac{3}{2\pi\varepsilon}\right)^{1/2} \exp\left(-\frac{3x_\varepsilon^2}{2a^2N\varepsilon} - \varepsilon w(x)\right) q(x+x_\varepsilon, x_0, s)$$

그 다음엔 맨 뒤의 partition function을 Taylor series로 전개하자.

$$q(x, x_0, s+\varepsilon) = \frac{1}{(a^2N)^{1/2}} \int dx_\varepsilon \left(\frac{3}{2\pi\varepsilon}\right)^{1/2} \exp\left(-\frac{3x_\varepsilon^2}{2a^2N\varepsilon} - \varepsilon w(x)\right)$$
$$\times \left(q(x, x_0, s) + x_\varepsilon \frac{\partial}{\partial x} q(x, x_0, s) + \frac{x_\varepsilon^{\,2}}{2} \frac{\partial^2}{\partial x^2} q(x, x_0, s) \right)$$

일견 식이 복잡해 보이지만, 적분 자체는 x_ε에 대한 단순한 적분이다.

Partition Function for Gaussian Chains

$$q(x,x_0,s+\varepsilon)\approx\frac{\exp(-\varepsilon w(x))}{(a^2N)^{1/2}}\left(\frac{3}{2\pi\varepsilon}\right)^{1/2}\int dx_\varepsilon\exp\left(-\frac{3x_\varepsilon^2}{2a^2N\varepsilon}\right)\left(q(x,x_0,s)+x_\varepsilon\frac{\partial}{\partial x}q(x,x_0,s)+\frac{x_\varepsilon{}^2}{2}\frac{\partial^2}{\partial x^2}q(x,x_0,s)\right)$$

이 계산을 위해서는 세 번의 적분이 필요한데, 그 적분의 형태를 잘 살펴보자.

일단, $B=\dfrac{3}{2a^2N\varepsilon}$ 이라 하면, $\int\exp\left(-Bx_\varepsilon^2\right)dx_\varepsilon=\sqrt{\dfrac{\pi}{B}}$

$\int x_\varepsilon\exp\left(-Bx_\varepsilon^2\right)dx_\varepsilon=0$ Odd function 적분이므로 0이다.

$\dfrac{1}{2}\int x_\varepsilon^2\exp\left(-Bx_\varepsilon^2\right)dx_\varepsilon=\dfrac{\sqrt{\pi}}{4}B^{-3/2}$

다시 이것들을 맨 위의 식에 적용해서 넣어보면,

$$q(x,x_0,s+\varepsilon)\approx\frac{\exp(-\varepsilon w(x))}{(a^2N)^{1/2}}\left(\frac{3}{2\pi\varepsilon}\right)^{1/2}\left(q(x,x_0,s)\sqrt{\frac{2a^2N\varepsilon\pi}{3}}+0+\frac{\sqrt{\pi}}{4}\left(\frac{2a^2N\varepsilon}{3}\right)^{3/2}\frac{\partial^2}{\partial x^2}q(x,x_0,s)\right)$$

$$=\exp(-\varepsilon w(x))\left(q(x,x_0,s)+\frac{a^2N\varepsilon}{6}\frac{\partial^2}{\partial x^2}q(x,x_0,s)\right)$$

Partition Function for Gaussian Chains

이번에는 $\exp(-\varepsilon w(x))$ 를 Taylor 정리를 이용해서 표현하면,

$$q(x,x_0,s+\varepsilon)\approx\left(1-\varepsilon w(x)\right)\left(q(x,x_0,s)+\frac{a^2N\varepsilon}{6}\frac{\partial^2}{\partial x^2}q(x,x_0,s)\right)$$ ε에 대한 2차항은 무시한다.

$$\approx\left(q(x,x_0,s)+\frac{a^2N\varepsilon}{6}\frac{\partial^2}{\partial x^2}q(x,x_0,s)-\varepsilon w(x)q(x,x_0,s)\right)$$

이번에는 왼쪽 항을 s의 함수로 보고 Taylor 정리를 이용한다면,

$$q(x,x_0,s+\varepsilon)\approx\left(q(x,x_0,s)+\varepsilon\frac{\partial}{\partial s}q(x,x_0,s)\right)$$

$$q(x,x_0,s)+\varepsilon\frac{\partial}{\partial s}q(x,x_0,s)=q(x,x_0,s)+\frac{a^2N\varepsilon}{6}\frac{\partial^2}{\partial x^2}q(x,x_0,s)-\varepsilon w(x)q(x,x_0,s)$$

ε에 대한 first order만 비교해 보면 partition function이 만족하는 미분방정식을 얻을 수 있다.

$$\frac{\partial}{\partial s}q(x,x_0,s)=\frac{a^2N}{6}\frac{\partial^2}{\partial x^2}q(x,x_0,s)-w(x)q(x,x_0,s)$$

3차원 식은 다음과 같다. $\frac{\partial}{\partial s}q(\mathbf{r},\mathbf{r}_0,s)=\left[\frac{a^2N}{6}\nabla^2-w(\mathbf{r})\right]q(\mathbf{r},\mathbf{r}_0,s)$ $q(\mathbf{r},\mathbf{r}_0,0)=\left(a^2N\right)^{3/2}\delta(\mathbf{r}-\mathbf{r}_0)$

3차원 식의 유도(간략히 설명한 버전)

Recursive Relation for the Partition Function

$$q(\mathbf{r},\mathbf{r}_0,s)=\frac{1}{a^3N^{3/2}}\int d\mathbf{r}_1 q(\mathbf{r}_1,\mathbf{r}_0,t)q(\mathbf{r},\mathbf{r}_1,s-t)$$

The corresponding equation in quantum mechanics

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{x},t)=-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{x},t)+V(\mathbf{x})\psi(\mathbf{x},t)$$

Now let us build up partition function for a long chain from short chain fragments:

$$q(\mathbf{r},\mathbf{r}_0,s+\varepsilon)=\frac{1}{a^3N^{3/2}}\int d\mathbf{r}_\varepsilon q(\mathbf{r}+\mathbf{r}_\varepsilon,\mathbf{r}_0,s)q(\mathbf{r},\mathbf{r}+\mathbf{r}_\varepsilon,\varepsilon)$$

Expand the second term using Taylor expansion:

$$q(\mathbf{r},\mathbf{r}_0,s+\varepsilon)=\frac{1}{a^3N^{3/2}}\int d\mathbf{r}_\varepsilon q(\mathbf{r},\mathbf{r}+\mathbf{r}_\varepsilon,\varepsilon)\left[1+\mathbf{r}_\varepsilon\cdot\nabla+\frac{1}{2}\mathbf{r}_\varepsilon\mathbf{r}_\varepsilon:\nabla\nabla\right]q(\mathbf{r},\mathbf{r}_0,s)$$

The left hand side is $q(\mathbf{r},\mathbf{r}_0,s+\varepsilon)\approx\left[1+\varepsilon\frac{\partial}{\partial s}\right]q(\mathbf{r},\mathbf{r}_0,s)$

The integral on the right hand side can be evaluated as (The odd term cancels by symmetry)

$$q(\mathbf{r},\mathbf{r}_0,s+\varepsilon)\approx e^{-\varepsilon w(\mathbf{r})}\left[1+\frac{a^2N}{6}\varepsilon\nabla^2\right]q(\mathbf{r},\mathbf{r}_0,s)\approx\left[1+\frac{a^2N}{6}\varepsilon\nabla^2-\varepsilon w(\mathbf{r})\right]q(\mathbf{r},\mathbf{r}_0,s)$$

Comparing the first order terms:

$$\frac{\partial}{\partial s}q(\mathbf{r},\mathbf{r}_0,s)=\left[\frac{a^2N}{6}\nabla^2-w(\mathbf{r})\right]q(\mathbf{r},\mathbf{r}_0,s)$$

Partition Function for Gaussian Chains

Now the partial partition function is shown to satisfy the partial differential equation:

$$\frac{\partial}{\partial s} q(\mathbf{r}, \mathbf{r}_0, s) = \left[\frac{a^2 N}{6} \nabla^2 - w(\mathbf{r}) \right] q(\mathbf{r}, \mathbf{r}_0, s)$$

Integrating the previous partial partition equation with respect to $\mathbf{r}_0$,

$$q(\mathbf{r}, s) \equiv \frac{1}{(a^2 N)^{\frac{3}{2}}} \int d\mathbf{r}_0 q(\mathbf{r}, \mathbf{r}_0, s) \propto \int \mathcal{D}\mathbf{r}_\alpha \exp\left(-\frac{E[\mathbf{r}_\alpha; 0, s]}{k_\mathrm{B} T} \right) \delta(\mathbf{r}_\alpha(s) - \mathbf{r})$$

$$\frac{\partial}{\partial s} q(\mathbf{r}, s) = \left[\frac{a^2 N}{6} \nabla^2 - w(\mathbf{r}) \right] q(\mathbf{r}, s)$$

Also by integrating the initial condition, $q(\mathbf{r}, 0) = 1$.

Partial partition function for a chain fragment with a free end.



The partition function of a chain segment starting from the other end (with length $(1-s)N$)

$$-\frac{\partial}{\partial s} q^\dagger(\mathbf{r}, \mathbf{r}_1, s) = \left[\frac{a^2 N}{6} \nabla^2 - w(\mathbf{r}) \right] q^\dagger(\mathbf{r}, \mathbf{r}_1, s)$$

$$-\frac{\partial}{\partial s} q^\dagger(\mathbf{r}, s) = \left[\frac{a^2 N}{6} \nabla^2 - w(\mathbf{r}) \right] q^\dagger(\mathbf{r}, s)$$

$$q^\dagger(\mathbf{r}, \mathbf{r}_1, s) \propto \int \mathcal{D}\mathbf{r}_\alpha \exp\left(-\frac{E[\mathbf{r}_\alpha; s, 1]}{k_\mathrm{B} T} \right) \delta(\mathbf{r}_\alpha(s) - \mathbf{r}) \delta(\mathbf{r}_\alpha(1) - \mathbf{r}_1)$$

$$q^\dagger(\mathbf{r}, s) \equiv \frac{1}{(a^2 N)^{3/2}} \int d\mathbf{r}_1 q^\dagger(\mathbf{r}, \mathbf{r}_1, s) \propto \int \mathcal{D}\mathbf{r}_\alpha \exp\left(-\frac{E[\mathbf{r}_\alpha; s, 1]}{k_\mathrm{B} T} \right) \delta(\mathbf{r}_\alpha(s) - \mathbf{r})$$

$$q^\dagger(\mathbf{r}, 1) = 1$$

Partition Function for Gaussian Chains

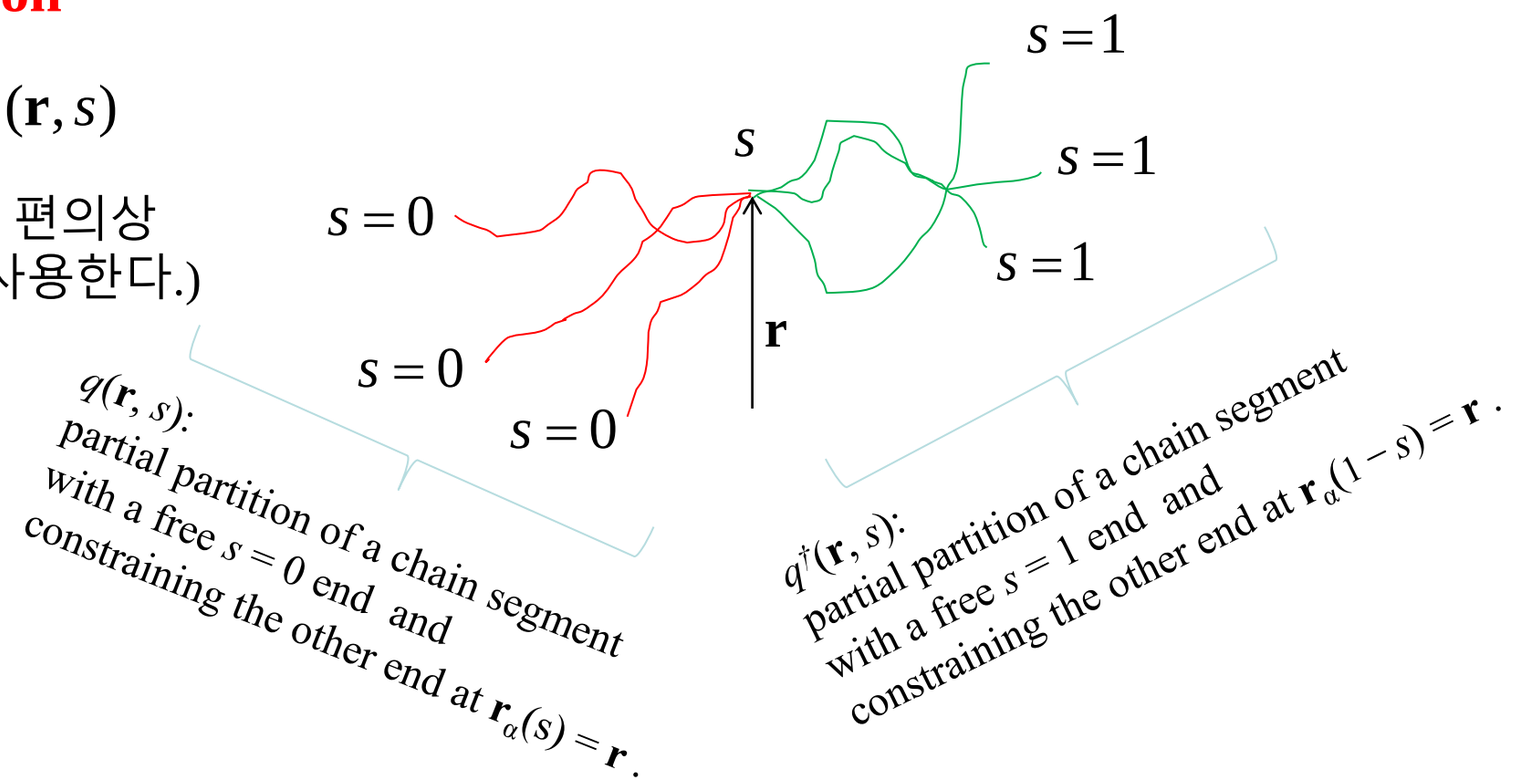
$$q(\mathbf{r},s) \propto \int \mathcal{D}\mathbf{r}_\alpha \exp\left(-\frac{E[\mathbf{r}_\alpha;0,s]}{k_\mathrm{B}T}\right)\delta(\mathbf{r}_\alpha(s)-\mathbf{r})$$

$$q^\dagger(\mathbf{r},s) \propto \int \mathcal{D}\mathbf{r}_\alpha \exp\left(-\frac{E[\mathbf{r}_\alpha;s,1]}{k_\mathrm{B}T}\right)\delta(\mathbf{r}_\alpha(s)-\mathbf{r})$$

Total partition function

$$Q[w] = \frac{1}{V}\int d\mathbf{r}\; q(\mathbf{r},s)\, q^\dagger(\mathbf{r},s)$$

(배포한 프로그램 등에서는 편의상 $1/V$를 곱하지 않은 표현을 사용한다.)



Density Calculation for Polymer Field Theory

대부분의 통계물리 문제에서는 partition function이 곧바로 밀도에 비례하게 되지만, polymer field theory에서는 고분자 밀도 계산에 주의를 기울여야 한다.

고분자 n개가 부피 V를 채우는 homopolymer melt의 고분자 밀도 계산을 해 보자.
먼저 field $w(\mathbf{r})$ 속에 있는 고분자의 total partition function은 다음과 같이 계산된다.

$$V = \frac{nN}{\rho_0}$$

$$Q[w] \equiv \frac{1}{V}\int d\mathbf{r}\, q(\mathbf{r},s)q^{\dagger}(\mathbf{r},s) = \frac{1}{V}\int \mathcal{D}\mathbf{r}_\alpha \exp\left(-\frac{E[\mathbf{r}_\alpha;0,1]}{k_{\mathrm{B}}T}\right)$$

α번째 고분자의 앙상블 평균 고분자 밀도는 다음과 같이 표현된다.

$$\phi_\alpha(\mathbf{r}) \propto \frac{V}{Q[w]}\int \mathcal{D}\mathbf{r}_\alpha \hat{\phi}_\alpha(\mathbf{r}) \exp\left(-\frac{E[\mathbf{r}_\alpha;0,1]}{k_{\mathrm{B}}T}\right) = \frac{NV}{\rho_0 Q[w]}\int_0^1 ds \int \mathcal{D}\mathbf{r}_\alpha \delta(\mathbf{r}-\mathbf{r}_\alpha(s)) \exp\left(-\frac{E[\mathbf{r}_\alpha;0,1]}{k_{\mathrm{B}}T}\right)$$

$$\phi_\alpha(\mathbf{r}) = \frac{NV}{\rho_0 Q[w]}\int_0^1 ds q(\mathbf{r},s)\, q^{\dagger}(\mathbf{r},s)$$

Continuous version에서는 델타함수의 개수와 prefactor 등이 좀 헷갈릴 수 있다.
Discrete chain에 대한 포말리즘으로 확인해 보면 위의 식이 정확하다.

See “Numerical Implementation of Pseudo-spectral Method in Self-consistent Mean Field Theory for Discrete Polymer Chains”, So Jung Park, Daeseong Yong, Yeongyoon Kim, and Jaeup U. Kim*, J. Chem. Phys. **150**, 234901 (2019).

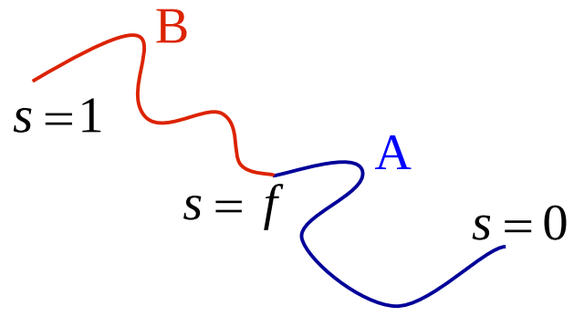
모든 chain의 contribution을 더하면

$$\phi(\mathbf{r}) = \frac{nNV}{\rho_0 Q[w]}\int_0^1 ds q(\mathbf{r},s)\, q^{\dagger}(\mathbf{r},s) = \frac{1}{Q}\int_0^1 ds q(\mathbf{r},s)\, q^{\dagger}(\mathbf{r},s)$$

$$\hat{\phi}_\alpha(\mathbf{r}) = \frac{N}{\rho_0}\int_0^1 ds \delta(\mathbf{r}-\mathbf{r}_\alpha(s))$$

Density Calculation for Polymer Field Theory

오른쪽 그림의 AB diblock copolymer의 경우의 고분자의 밀도 계산식은 다음과 같다.



$$Q[w] \equiv \frac{1}{V}\int d\mathbf{r}\, q(\mathbf{r},s)q^{\dagger}(\mathbf{r},s) \propto \frac{1}{V}\int \mathcal{D}\mathbf{r}_{\alpha} \exp\left(-\frac{E[\mathbf{r}_{\alpha};0,1]}{k_{\mathrm{B}}T}\right)$$

$$\phi_{\mathrm{A}}(\mathbf{r}) = \frac{1}{Q}\int_0^f ds\, q(\mathbf{r},s)q^{\dagger}(\mathbf{r},s) \qquad \phi_{\mathrm{B}}(\mathbf{r}) = \frac{1}{Q}\int_f^1 ds\, q(\mathbf{r},s)q^{\dagger}(\mathbf{r},s)$$

위 식을 잘 관찰해 보면, 적분되는 항은 s번째 segment가 특정 지점 $\mathbf{r}$에 있을 확률이다. 모든 A segment $(0 \le s \le f_A)$에 대해 이 확률을 더하면, 그 지점 $\mathbf{r}$에서의 A 고분자의 밀도가 된다.

비례상수는 다음과 같이 확인할 수 있다.

$$\int d\mathbf{r}\phi_{\mathrm{A}}(\mathbf{r}) = \frac{1}{Q}\int d\mathbf{r}\int_0^f ds\, q(\mathbf{r},s)q^{\dagger}(\mathbf{r},s) = \frac{1}{Q}\int_0^f ds \int d\mathbf{r} q(\mathbf{r},s)q^{\dagger}(\mathbf{r},s) = \frac{1}{Q}\int_0^f dsVQ = fV$$

즉, 밀도 함수를 모든 공간에서 적분하면, A 고분자의 부피가 나온다. (앞에서 설명했듯이 위의 밀도 함수는 질량 밀도가 아니라 부피 밀도이다.) 마찬가지로 $\int d\mathbf{r}\phi_{\mathrm{B}}(\mathbf{r}) = (1-f)V$

Density Calculation for Polymer Field Theory

$$Q[w] \equiv \frac{1}{V}\int d\mathbf{r}\, q(\mathbf{r},s)q^{\dagger}(\mathbf{r},s) = \frac{1}{V}\int \mathcal{D}\mathbf{r}_{\alpha} \exp\left(-\frac{E[\mathbf{r}_{\alpha};0,1]}{k_{\mathrm{B}}T}\right)$$

Total partition function Q의 적분되는 항은, 특정 지점에 sN번째 segment가 존재할 확률이므로 전체 공간에 대해 적분하면, 이 segment가 공간 어딘가에 존재할 확률에 비례하는 값이 된다.

그러므로 Q의 값은 s에 무관하여야 한다. 실제로 numerical하게 계산을 하다 보면, Q 값이 s에 따라 조금씩 변하는 경우가 생기는데, 그 경우 고분자의 양을 전부 더하면 시스템의 부피 V값과 조금씩 달라진다.

이러한 mass conservation error 테스트는 프로그램이 정상적으로 작동하는지 확인하는 주요한 방법 중의 하나이다.

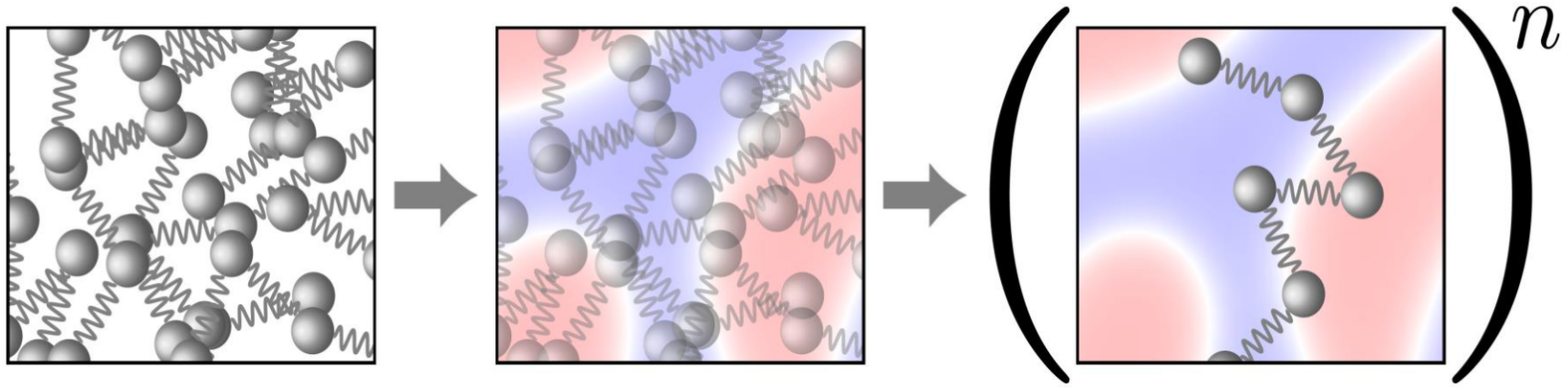
See “Finite volume method for self-consistent field theory of polymers: Material conservation and application ”, Daeseong Yong and Jaeup U. Kim, Phys. Rev. E, **96**, 063312 (2017).

이제 포텐셜 w(**r**)이 어떻게 결정되는지 알아볼 순서이다.

When there is no material, there is no potential. The potential is generated by the presence of the material.

Polymer Field Theory

Many-Body Problem → Statistical mechanics of single polymer chain in external fields



Decoupling interactions using the field transformation

- Our purpose of field transform is to develop an **effective Hamiltonian of AB diblock copolymer melt** as a functional of **two fluctuating fields, W_+ and W_-**.

Single chain partition function

$$\beta H[W_-, W_+] = -n \ln Q[W_-, W_+] + \rho_0 \int d\mathbf{r} \left(\frac{W_-^2}{\chi_b} - W_+ \right)$$

$$W_+ = (W_A + W_B)/2,$$
$$W_- = (W_A - W_B)/2.$$

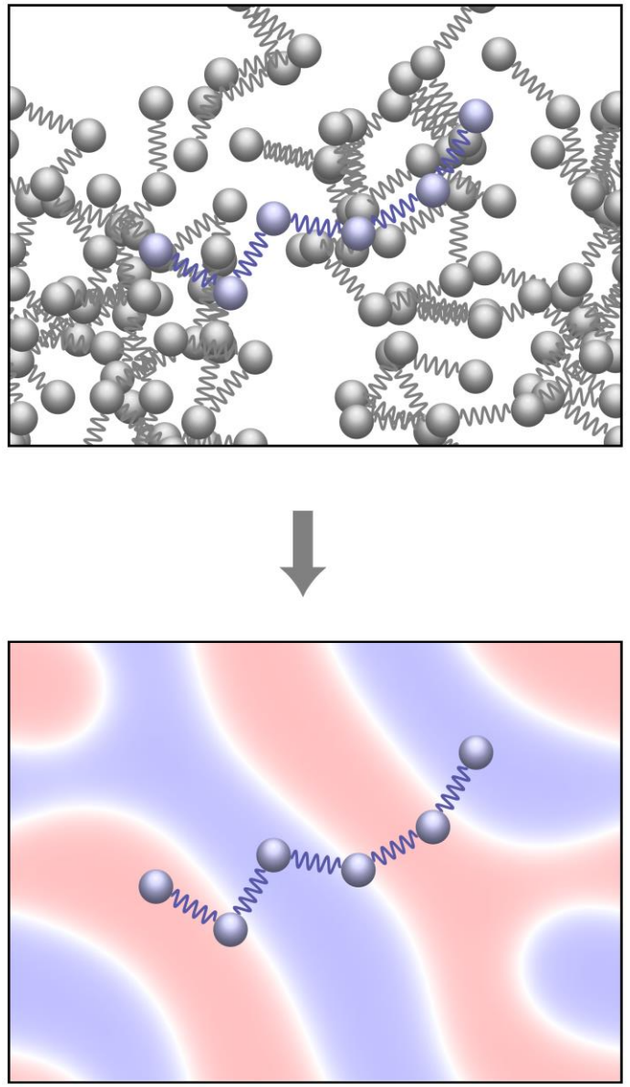
- W_-: exchange field
- W_+: pressure field
- n: # of polymers
- ρ_0: segment density
- χ_b: Flory-Huggins interaction parameter

Polymer Field Theory

- The interaction a polymer chain experiences in a sea of other chains is replaced by a field in the **polymer field theory**.
- The canonical partition function of incompressible AB diblock copolymer melt is given as follows

$$\mathcal{Z} = \frac{1}{n!}\prod_{\alpha=1}^{n}\int \mathcal{D}\mathbf{r}_\alpha \exp\left(-\beta H_p[\mathbf{r}_\alpha]\right) \times \delta[\hat{\rho}_A + \hat{\rho}_B - 1]$$

여기에서 $H_p[\mathbf{r}_\alpha]$는 각 chain의 path에 따른 모든 에너지 또는 자유에너지의 합인 particle based Hamiltonian이다. (chain stretching entropy penalty와 segment들간의 포텐셜 등을 포함.)



Polymer Field Transform

$\phi_+ \equiv \phi_A + \phi_B$
$\phi_- \equiv \phi_A - \phi_B$

- Let us consider a system with n incompressible diblock copolymers. Its partition function is given by

$$Z = \frac{1}{n!}\int \prod_{\alpha=1}^{n} \mathcal{D}\mathbf{r}_\alpha \exp\left(-\frac{H_p}{k_B T}\right)\delta\left(1-\hat{\phi}_A-\hat{\phi}_B\right) \qquad \frac{H_p}{k_B T} = \chi\rho_0 \int d\mathbf{r}\,\hat{\phi}_A(\mathbf{r})\hat{\phi}_B(\mathbf{r}) + \frac{3}{2Na^2}\sum_{\alpha=1}^{n}\int_0^1 ds|\mathbf{r}'_\alpha|^2$$

- Just to make life simpler, we absorb the last integral into the functional integral definition so that

$$Z = \frac{1}{n!}\int \prod_{\alpha=1}^{n} \mathcal{D}\tilde{\mathbf{r}}_\alpha \exp\left(-\frac{\tilde{H}_p}{k_B T}\right)\delta\left(1-\hat{\phi}_+\right) \qquad \frac{\tilde{H}_p}{k_B T} = \chi\rho_0 \int d\mathbf{r}\,\hat{\phi}_A(\mathbf{r})\hat{\phi}_B(\mathbf{r}) = \frac{\chi\rho_0}{4}\int d\mathbf{r}\left(\hat{\phi}_A(\mathbf{r})+\hat{\phi}_B(\mathbf{r})\right)^2 - \left(\hat{\phi}_A(\mathbf{r})-\hat{\phi}_B(\mathbf{r})\right)^2 = \frac{\chi\rho_0}{4}\int d\mathbf{r}(1-\hat{\phi}_-^2(\mathbf{r}))$$

- Note that the delta function should be understood as a functional version $\int \mathcal{D}\psi\,\delta(\hat{\phi}-\psi)f[\psi] = f[\hat{\phi}]$

- Let us now start from the introduction of W_- field. The one dimensional Gaussian integral is given as $\int_{-\infty}^{\infty} dz \exp\left(\frac{-az^2}{2}+jz\right) = \left(\frac{2\pi}{a}\right)^{1/2}\exp\left(\frac{j^2}{2a}\right)$

- Multivariable version of this equation is $\int_{-\infty}^{\infty} d\mathbf{z}\exp\left(-\frac{\mathbf{z}^T\mathbf{A}\mathbf{z}}{2}+\mathbf{J}^T\mathbf{z}\right) = \frac{(2\pi)^{N/2}}{(\det\mathbf{A})^{1/2}}\exp\left(\frac{\mathbf{J}^T\mathbf{A}^{-1}\mathbf{J}}{2}\right)$

where $\mathbf{A}$ is a symmetric and positive definite $N\times N$ matrix, and $\mathbf{J}$ is a real-valued vector.

$\mathbf{r}_\alpha$: path of α_{th} chain
$\hat{\phi}_i$: density of i type segments
N : polymerization index
a : segment length
ρ_0^{-1} : segment volume
n: total number of polymers
χ : Flory-Huggins interaction parameter
V : system volume

Polymer Field Transform

$$\phi_+ \equiv \phi_A + \phi_B$$
$$\phi_- \equiv \phi_A - \phi_B$$

By using Hubbard-Stratonovich identity,

$$\exp\left(\frac{\chi\rho_0}{4}\int d\mathbf{r}\hat{\phi}_-^2(\mathbf{r})\right) = \frac{\int \mathcal{D}W_- \exp\left(-\frac{\rho_0}{N}\int d\mathbf{r}\left(\frac{W_-^2(\mathbf{r})}{\chi N} + \hat{\phi}_-(\mathbf{r})W_-(\mathbf{r})\right)\right)}{\int \mathcal{D}W_- \exp\left(-\frac{\rho_0}{N}\int d\mathbf{r}\frac{W_-^2(\mathbf{r})}{\chi N}\right)}$$

Assume that the functional integral is defined so that the denominator is equal to 1.

- Now it's time to introduce the $W_\#$ field.
- The one dimensional Fourier transform of delta function is $\delta(k) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dz \exp(-ikz)$
- Its functional version is $\delta(1-\hat{\phi}_+) = \int \mathcal{D}W_\# \exp\left(-\frac{i\rho_0}{N}\int d\mathbf{r}(\hat{\phi}_+(\mathbf{r})-1)W_\#(\mathbf{r})\right)$

Again, any missing proportionality factor is absorbed in the definition of the functional integral.

- We finally have a field theoretic version of the partition function: (Note the functions $W_\#$ and W_- are real)

From this formula

$$\int_{-\infty}^{\infty} dz \exp\left(\frac{-az^2}{2} - jz\right) = \left(\frac{2\pi}{a}\right)^{1/2} \exp\left(\frac{j^2}{2a}\right)$$

set $a = \frac{2}{\chi\rho_0}$, $j = \hat{\phi}_-(\mathbf{r})$, $W_- = \frac{zN}{\rho_0}$

The last variable change will introduce additional factors in the functional integral, but we assume that such factors are all absorbed while setting the denominator to be 1.

$\mathbf{r}_\alpha$: path of α_{th} chain
$\hat{\phi}_i$: density of i type segments
N : polymerization index
a : segment length
ρ_0^{-1} : segment volume
n: total number of polymers
χ : Flory-Huggins interaction parameter
V : system volume

Polymer Field Transform

$$\phi_+ \equiv \phi_{\mathrm{A}} + \phi_{\mathrm{B}}$$
$$\phi_- \equiv \phi_{\mathrm{A}} - \phi_{\mathrm{B}}$$

$$Z = \int \prod_{\alpha=1}^{n} \mathcal{D}\tilde{\mathbf{r}}_\alpha \int \mathcal{D}W_{\#} \int \mathcal{D}W_{-} \exp\left(-\frac{\rho_0}{N} \int d\mathbf{r} \left(\frac{W_{-}^2(\mathbf{r})}{\chi N} + \hat{\phi}_{-}(\mathbf{r}) W_{-}(\mathbf{r}) + i\hat{\phi}_{+}(\mathbf{r}) W_{\#}(\mathbf{r}) - iW_{\#}(\mathbf{r}) + \frac{\chi N}{4} \right) - \ln n! \right)$$

$$= \int \prod_{\alpha=1}^{n} \mathcal{D}\tilde{\mathbf{r}}_\alpha \int \mathcal{D}W_{\#} \int \mathcal{D}W_{-} \exp\left(-\frac{\rho_0}{N} \int d\mathbf{r} \left(\frac{W_{-}^2(\mathbf{r})}{\chi N} + \hat{\phi}_{\mathrm{A}}(\mathbf{r}) \left(iW_{\#}(\mathbf{r}) + W_{-}(\mathbf{r}) \right) + \hat{\phi}_{\mathrm{B}}(\mathbf{r}) \left(iW_{\#}(\mathbf{r}) - W_{-}(\mathbf{r}) \right) - iW_{\#}(\mathbf{r}) + \frac{\chi N}{4} \right) - \ln n! \right)$$

By setting $iW_{\#} + W_{-} = W_A$, $iW_{\#} - W_{-} = W_B$ and $Q = \int \mathcal{D}\tilde{\mathbf{r}}_\alpha \exp\left(-\frac{\rho_0}{N} \left(\int_0^f ds W_{\mathrm{A}}(\mathbf{r}_\alpha(s)) + \int_f^1 ds W_{\mathrm{B}}(\mathbf{r}_\alpha(s)) \right) \right)$

(This equation requires some time to digest. Because of this conversion, the (seemingly arbitrarily named) fields W_A and W_B gains the physical meaning of fields acting on A and B type segments.

$$Z = \left(\frac{\rho_0 V}{N} Q \right)^n \int \mathcal{D}W_{\#} \int \mathcal{D}W_{-} \exp\left(-\frac{\rho_0}{N} \int d\mathbf{r} \left(\frac{W_{-}^2(\mathbf{r})}{\chi N} - iW_{\#}(\mathbf{r}) + \frac{\chi N}{4} \right) - \ln n! \right) \equiv \int \mathcal{D}W_{\#} \int \mathcal{D}W_{-} \exp\left(-\frac{H_f}{k_{\mathrm{B}}T} \right)$$

Still, some non-trivial factor is floating and they are absorbed into the functional integral.

Now the field-theoretic Hamiltonian H_f becomes,

$$\frac{H_f[W_{-}, W_{\#}]}{k_{\mathrm{B}}T} = -n \ln \frac{\rho_0 V Q}{N} + \ln n! + \frac{\rho_0}{N} \int \left(\frac{W_{-}^2(\mathbf{r})}{\chi N} - iW_{\#}(\mathbf{r}) + \frac{\chi N}{4} \right) d\mathbf{r}$$
$$= -n \left(\ln \frac{\rho_0 V Q}{N n} + 1 \right) + \frac{\rho_0}{N} \int \left(\frac{W_{-}^2(\mathbf{r})}{\chi N} - iW_{\#}(\mathbf{r}) + \frac{\chi N}{4} \right) d\mathbf{r}$$

$\mathbf{r}_\alpha$: path of α_{th} chain
$\hat{\phi}_i$: density of i type segments
N : polymerization index
a : segment length
ρ_0^{-1} : segment volume
n: total number of polymers
χ : Flory-Huggins interaction parameter
V : system volume

Polymer Field Transform

$$\phi_+ \equiv \phi_A + \phi_B$$
$$\phi_- \equiv \phi_A - \phi_B$$

We finally have

$$\frac{H_f[W_-, W_\#]}{k_B T} = -n(\ln Q + 1) + \frac{\rho_0}{N}\int\left(\frac{W_-^2(\mathbf{r})}{\chi N} - iW_\#(\mathbf{r}) + \frac{\chi N}{4}\right)d\mathbf{r}$$

The SCFT (mean field) solution of $W_\#$ is a purely imaginary function. It must be so because $iW_\#$ is the mean potential field enforcing the total segment density ϕ_+ to become 1 everywhere. (At least people believed that for 30 years.)

Thus, we often define $W_+ = iW_\#$ so that

$$\frac{H_f[W_-, W_+]}{k_B T} = -n(\ln Q + 1) + \frac{\rho_0}{N}\int\left(\frac{W_-^2(\mathbf{r})}{\chi N} - W_+(\mathbf{r}) + \frac{\chi N}{4}\right)d\mathbf{r}$$

See "Characteristics of the Complex Saddle Point of Polymer Field Theory", Wonjun Kang, Daeseong Yong, and Jaeup U. Kim; Macromolecules, **57**, 3850–3861 (2024).
and "Complex Implications of Translational Invariance in Polymer Field Theory", Jaeup U. Kim, Mark W. Matsen, David C. Morse, and James D. Willis; Macromolecules, **57**, 9900–9910 (2024).

Also see $\mathcal{PT}$ symmetric system in Quantum Physics.

$\mathbf{r}_\alpha$: path of α_{th} chain
$\hat{\phi}_i$: density of i type segments
N : polymerization index
a : segment length
ρ_0^{-1} : segment volume
n_i : i-type polymer number
n: total number of polymers
χ : Flory-Huggins interaction parameter
V : system volume

Self-Consistent Field Theory (SCFT)

$$\phi_+ \equiv \phi_A + \phi_B$$
$$\phi_- \equiv \phi_A - \phi_B$$
$$w_+ = (w_A + w_B)/2$$
$$w_- = (w_A - w_B)/2$$

- For more than two decades, **self-consistent field theory (SCFT) has become a standard tool of the field-based simulation**.
- By using the saddle-point approximation for both W_+ and W_- fields, we look for the **self-consistent mean field solution**.

$$\longrightarrow \quad Z = \int \mathcal{D}W_{\#} \int \mathcal{D}W_- \exp\left(-\frac{H_f}{k_B T}\right) \approx \exp\left(-\frac{H_f[W_+, W_-]}{k_B T}\right) \qquad \frac{H_f[W_-, W_+]}{k_B T} = -n(\ln Q + 1) + \frac{\rho_0}{N}\int \left(\frac{W_-^2(\mathbf{r})}{\chi N} - W_+(\mathbf{r}) + \frac{\chi N}{4}\right) d\mathbf{r}$$

$$\left.\frac{\delta H_f}{\delta W_\pm}\right|_{W_\pm = w_\pm} = 0$$

produces two equations

$$g_+[w_-, w_+](\mathrm{r}) \equiv \phi_+[w_-, w_+](\mathbf{r}) - 1 = 0,$$

Incompressibility condition

$$\phi_-[w_-, w_+](\mathbf{r}) + \frac{2w_-(\mathbf{r})}{\chi N} = 0$$

Equation showing how polymer density field produces exchange potential proportional to $\chi N \phi_-$.

- From now on, the pressure and exchange fields satisfying these two conditions are denoted as lower case $w_\pm(\mathbf{r})$.

- One may feel it weird that **W_+ is introduced as a purely imaginary field, but we discuss saddle points on the real axis**.
- It is somewhat analogous to the integral of function on the real axis, which is essentially determined by the poles of its analytic continuation far from the real axis.

Field-Based Simulations: SCFT

$$\phi_+ \equiv \phi_A + \phi_B$$
$$\phi_- \equiv \phi_A - \phi_B$$
$$w_+ = (w_A + w_B)/2$$
$$w_- = (w_A - w_B)/2$$

- In SCFT, it is more common to use A and B notation instead of + and −. Then, the self-consistency equations become

$$\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = 1$$

$$w_A(\mathbf{r}) = \chi N \phi_B(\mathbf{r}) + \xi(\mathbf{r}), \qquad w_B(\mathbf{r}) = \chi N \phi_A(\mathbf{r}) + \xi(\mathbf{r})$$

where, $\xi(\mathbf{r})$ is the **implicitly determined pressure field** that enforces the first equation.

The field-theoretic Hamiltonian H_f now becomes the SCFT free energy. It is common to use the following expression.

$$\frac{F}{nk_BT} = -\log Q - 1 + \frac{1}{V}\int d\mathbf{r}\left(\chi N \phi_A(\mathbf{r})\phi_B(\mathbf{r}) - w_A(\mathbf{r})\phi_A(\mathbf{r}) - w_B(\mathbf{r})\phi_B(\mathbf{r})\right)$$

- To find the self-consistent solution, iterations are necessary.

Problem Solving Strategy

1. Assume an initial potential field, because we do not know the true field until the last step.

2. Solve the diffusion equations for the two partition functions.

3. Calculate the polymer concentration, and hence the output fields.

$$\phi_{\mathrm{A}}(\mathbf{r}) = \frac{1}{Q}\int_0^f ds\, q(\mathbf{r},s)\, q^{\dagger}(\mathbf{r},s)$$

Total partition function:

$$Q = \frac{1}{V}\int d\mathbf{r}\, q(\mathbf{r},s)\, q^{\dagger}(\mathbf{r},s)$$

V: The system volume

4. Compare the input and output fields. From the given result, create a new input field.

5. Go back to step 1 and continue iterations until the field equations and the incompressibility equation ($\phi_{\mathrm{A}} + \phi_{\mathrm{B}} = 1$) are self-consistently satisfied.

The exact mean-field polymer configuration and its energy is now obtained

There are two important tasks in this process.

1. For an unbiased research, one may feel like to use **random initial fields**. However, there are certain BCP morphologies that one can never find without an **educated guess**. Making a proper guess is one important part of the research.

2. For the creating of a new input field, the simplest approach is the **steepest descent method**. There are many established approaches to make a better guess for the next field. Even **Deep Learning** is used nowadays.

$$w_{\mathrm{in}}^{\mathrm{new}} = (1-\lambda)w_{\mathrm{in}} + \lambda w_{\mathrm{out}}$$

Problem Solving Strategy (Gaussian Chain Model)

Diffusion equation

$$\frac{\partial}{\partial s}q(\mathbf{r},s)=\left(\frac{a^2N}{6}\nabla^2-\omega(\mathbf{r})\right)q(\mathbf{r},s)$$

$$-\frac{\partial}{\partial s}q^{\dagger}(\mathbf{r},s)=\left(\frac{a^2N}{6}\nabla^2-\omega(\mathbf{r})\right)q^{\dagger}(\mathbf{r},s)$$

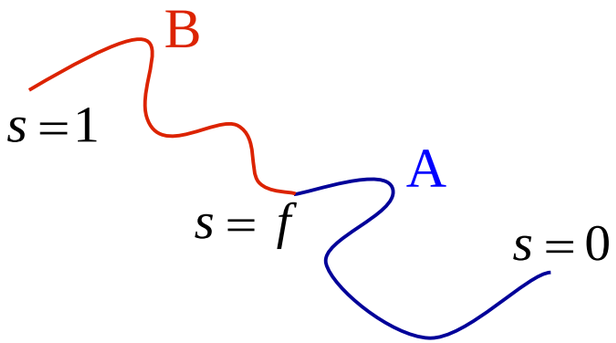
$q(\mathbf{r},s)$

Find partition function

$$\phi_{\mathrm{A}}(\mathbf{r})=\frac{1}{Q}\int_0^f ds\, q(\mathbf{r},s)\, q^{\dagger}(\mathbf{r},s)$$

$$\phi_{\mathrm{B}}(\mathbf{r})=\frac{1}{Q}\int_f^1 ds\, q(\mathbf{r},s)\, q^{\dagger}(\mathbf{r},s)$$

$$Q=\frac{1}{V}\int d\mathbf{r}q(\mathbf{r},s)\, q^{\dagger}(\mathbf{r},s)$$



$w_{\mathrm{in}}(\mathbf{r})$

Set input field
(first randomly)

$\phi(\mathbf{r})$

Find segment density

$$\frac{F}{nk_{\mathrm{B}}T}=-\log Q-1+\frac{1}{V}\int d\mathbf{r}\left(\chi N\phi_{\mathrm{A}}(\mathbf{r})\phi_{\mathrm{B}}(\mathbf{r})-w_{\mathrm{A}}(\mathbf{r})\phi_{\mathrm{A}}(\mathbf{r})-w_{\mathrm{B}}(\mathbf{r})\phi_{\mathrm{B}}(\mathbf{r})\right)$$

To find self consistent mean field solution

Simple mixing method

$$w_{\mathrm{in}}^{\mathrm{new}}=(1-\lambda)w_{\mathrm{in}}+\lambda w_{\mathrm{out}}$$

$w_{\mathrm{out}}(\mathbf{r})$

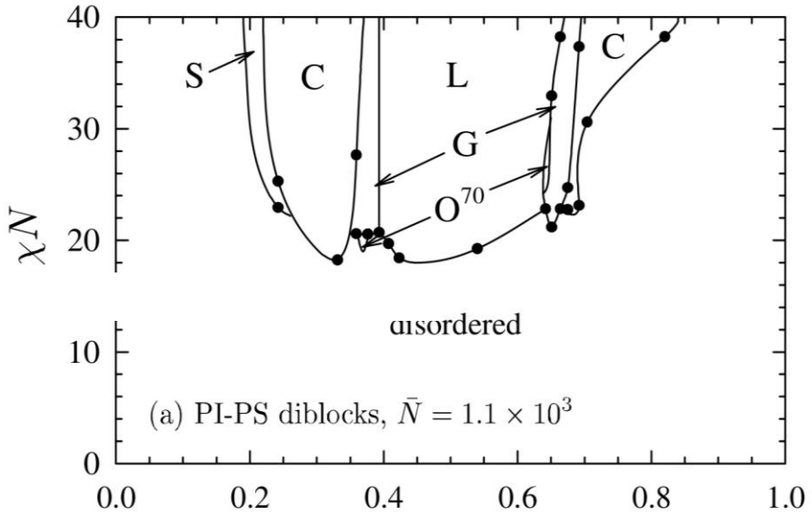
Find output field

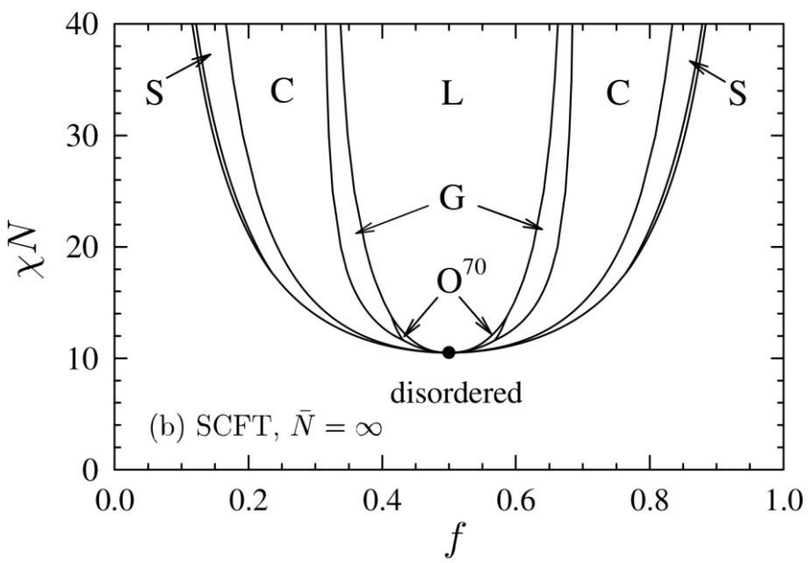
$$\phi_{\mathrm{A}}(\mathbf{r})+\phi_{\mathrm{B}}(\mathbf{r})=1$$

$$w_{\mathrm{A}}(\mathbf{r})=\chi N\phi_{\mathrm{B}}(\mathbf{r})+\xi(\mathbf{r})$$

$$w_{\mathrm{B}}(\mathbf{r})=\chi N\phi_{\mathrm{A}}(\mathbf{r})+\xi(\mathbf{r})$$

SCFT Phase Diagram



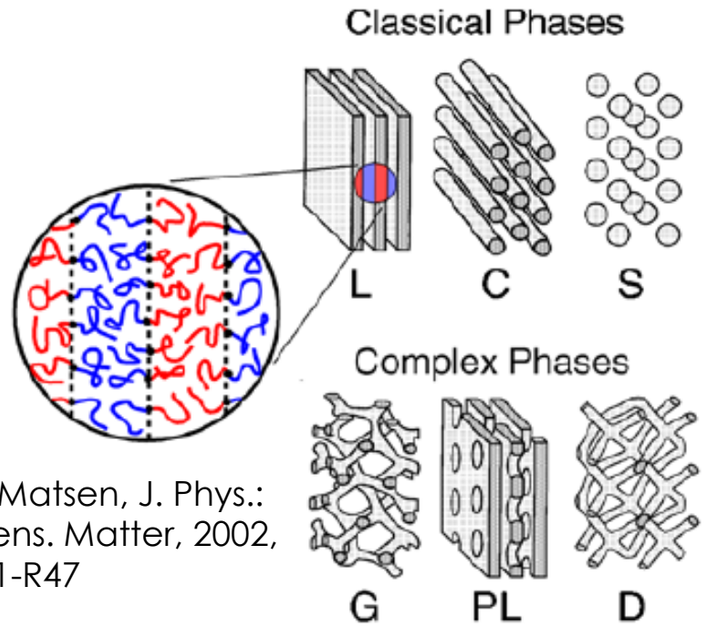


$$\bar{N} \equiv a^6 \rho_0^2 N$$

Phase diagram of PI-PS BCP (left)
theoretical phase diagram using SCFT(right)

Matsen, M. W.; Beardsley, T. M.; Willis, J. D. Fluctuation-Corrected Phase Diagrams for Diblock Copolymer Melts. Phys. Rev. Lett. 2023, 130 (24), 248101.

As the invariant polymerization index $\bar{N}$ increases (i.e. as the chain length increases), the mean field approximation becomes more accurate.



M. W. Matsen, J. Phys.: Condens. Matter, 2002, **14**, R21-R47

Field-Based Simulations: CL-FTS

$$Z \propto \int\int \exp\left(-\frac{H[W_+, W_-]}{k_B T}\right) \mathcal{D}W_+ \mathcal{D}W_-$$

$$\phi_+ \equiv \phi_A + \phi_B$$
$$\phi_- \equiv \phi_A - \phi_B$$
$$W_+ \equiv (W_A + W_B)/2$$
$$W_- \equiv (W_A - W_B)/2$$

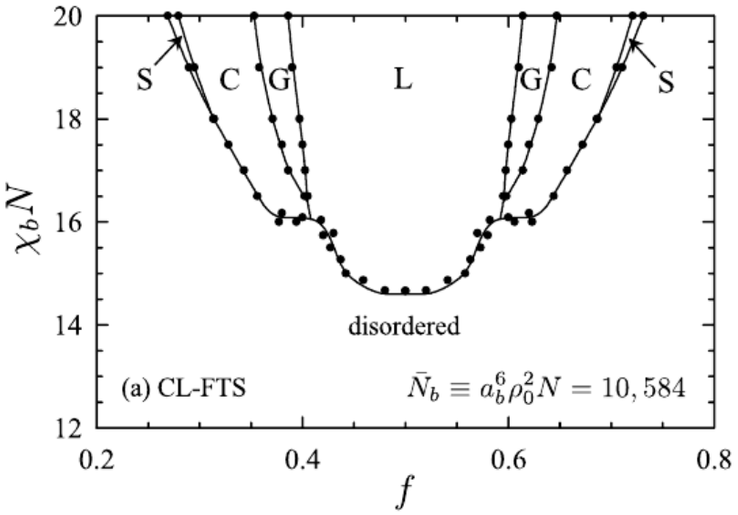
- Although field-theoretic representation of the partition function cannot be calculate exactly, it is possible to simulate it.
- In **Complex Langevin (CL)-FTS, both fields are permitted to sample the entire complex plane**. (τ is the fictitious time.)

$$\frac{\partial W_-(\mathbf{r};\tau)}{\partial \tau} = -\lambda_- \frac{\delta H}{\delta W_-} + \mathcal{N}_-,$$

$$\frac{\partial W_+(\mathbf{r};\tau)}{\partial \tau} = \lambda_+ \frac{\delta H}{\delta W_+} + i\mathcal{N}_+,$$

Gaussian noise

- With the advance of computer hardware and software, it is becoming manageable, but the **computational demand is still enormous**.
- Also, it is known that **instabilities** can be significant even at intermediate invariant polymerization index $\bar{N}$ regime. (This parameter determines the level of fluctuation.)



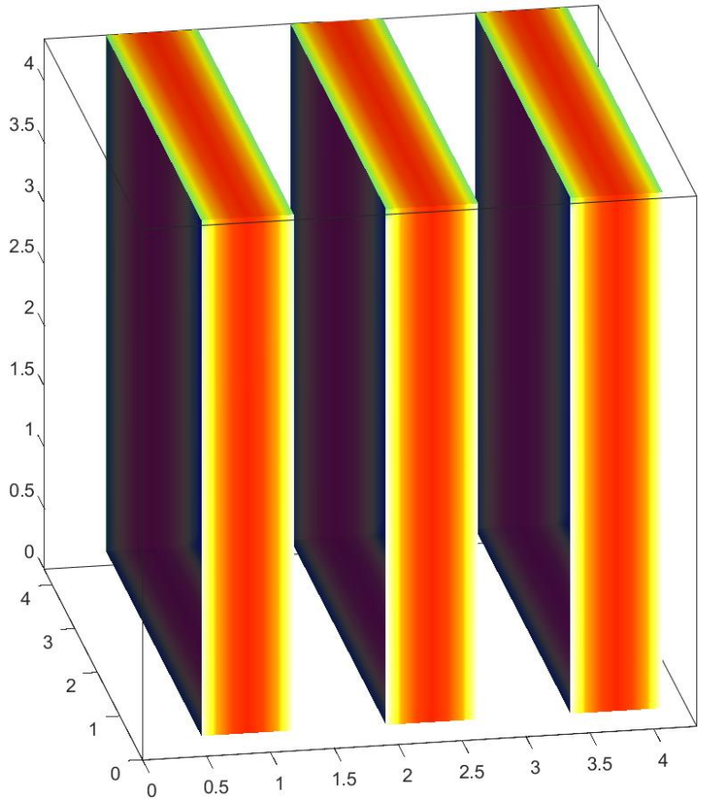
CL-FTS based block copolymer phase diagram

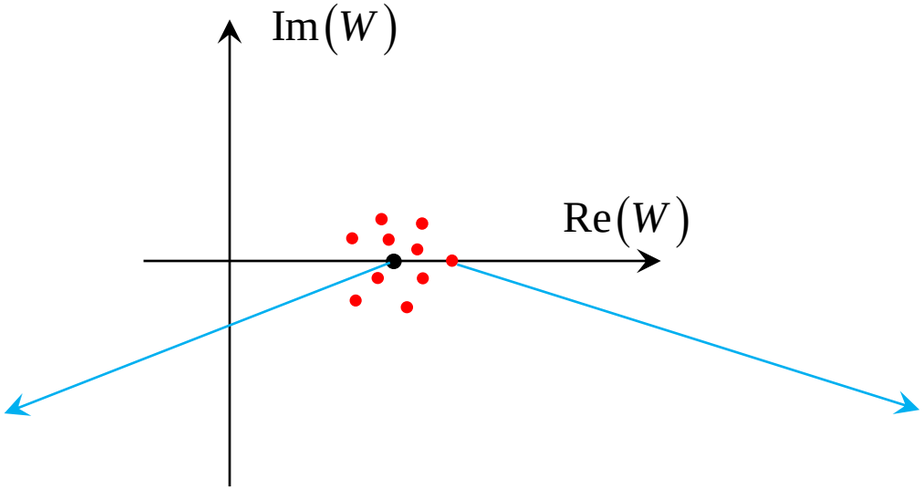
K. T. Delaney and G. H. Fredrickson,
J. Phys. Chem. B (2016)

CL-FTS and SCFT

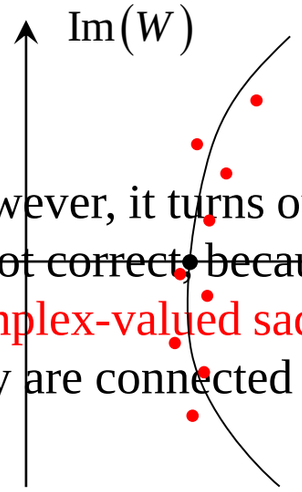
Block copolymer,
random copolymer mixture
(85%:15%)

Real Saddle Point
(SCFT solution)





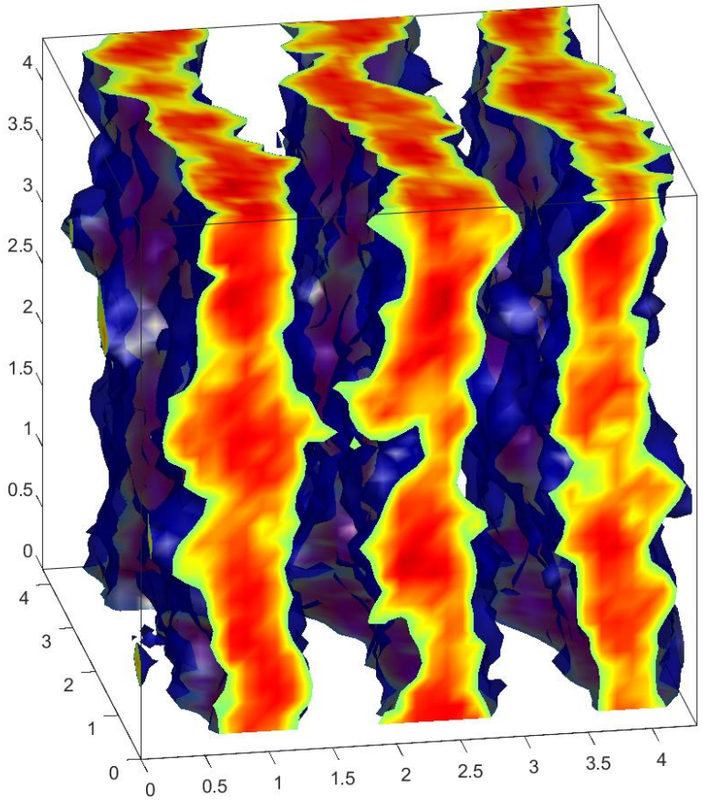
Traditional viewpoint for CL-FTS



However, it turns out that this view is not correct because there exists complex-valued saddle points and they are connected to the real one.

What CL-FTS actually does

Fluctuating Field Configuration
Around the Read Saddle Point



Field-Based Simulations: L-FTS

See T. M. Beardsley and M.W. Matsen, *Polymers*, 2437 (2021), for the details of L-FTS.

- In Langevin field-theoretic simulation (L-FTS), the **saddle point approximation** is applied only for W_+, $\longrightarrow$ $\mathcal{Z} \propto \int \mathcal{D}W_- \exp(-H[w_+, W_-])$
- It means we **iteratively** find the solution satisfying the **incompressibility condition** for polymer melts,

$$g_+[W_-, w_+](\mathbf{r}) = \phi_+[W_-, w_+](\mathbf{r}) - 1 = 0 \qquad (\phi_+ \equiv \phi_A + \phi_B)$$

- The pressure field that satisfies the incompressibility condition is denoted as lower case $w_+(\mathbf{r})$.
- Exchange fields ***W*_ evolves according to Langevin equation, and it is always a real function**.

Langevin Equation $$\frac{\partial W_-(\mathbf{r};\tau)}{\partial \tau} = -\lambda \frac{\delta H}{\delta W_-}\bigg|_{W_+ = w_+} + \mathcal{N},$$ → Gaussian noise

- Discretized equation using simple Euler method is

$$W_-(\mathbf{r};\tau + \Delta\tau) = W_-(\mathbf{r};\tau) - g_-[W_-, w_+](\mathbf{r})\Delta\tau + \mathcal{N}(0,\sigma)\,.$$

We later use predictor-corrector method or Leimkuhler-Matthews (LM) method when applying deep learning.

$\Delta\tau$: Fictitious time step

$\mathcal{N}(0,\sigma)$: Gaussian noise with zero mean and deviation σ.

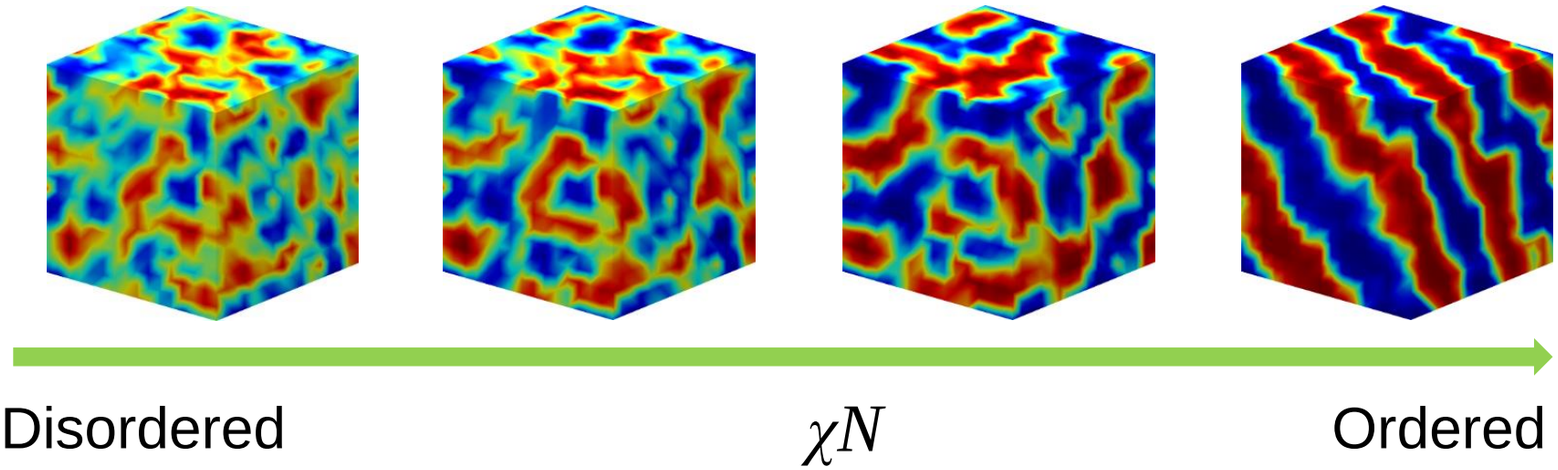
$$\sigma = \sqrt{2\Delta\tau/(\Delta_x\Delta_y\Delta_z\rho_0)}$$

Δ_α : grid size along α-axis

- In L-FTS, the most time consuming task is to **find w_+ for the given W_-** iteratively in each Langevin step.

Field-Based Simulations: L-FTS

- Here is a snapshot of the simulation after an equilibrium is reached (~100,000 Langevin time steps are required). Fluctuation around the mean field is now visible.



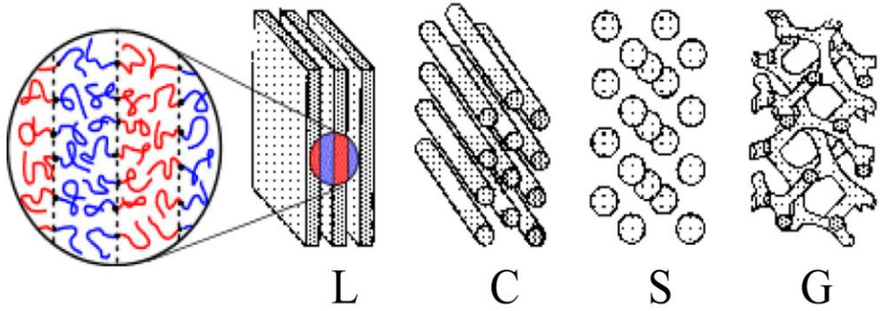
- For the calculation of physical quantities, we need to perform ensemble average of them after a long simulation (up to a million time steps).
- The ensemble average composition and two-point correlation is given by

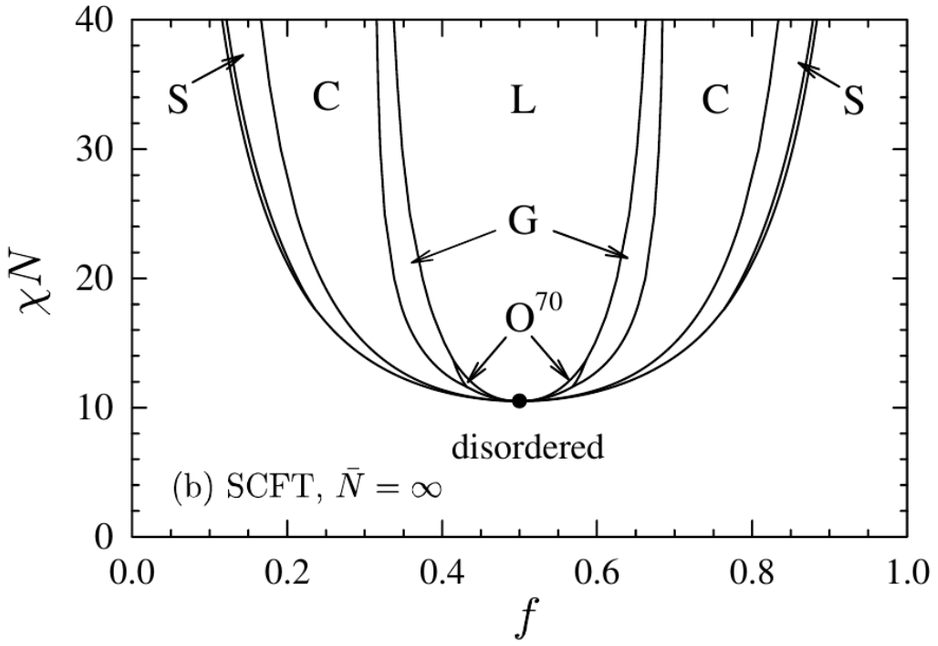
$$\langle \hat{\phi}_-(\mathbf{r}) \rangle = \frac{2}{\chi} \langle W_-(\mathbf{r}) \rangle, \qquad \langle \hat{\phi}_-(\mathbf{r}) \hat{\phi}_-(\mathbf{r}') \rangle = \frac{4}{\chi^2} \langle W_-(\mathbf{r}) W_-(\mathbf{r}') \rangle - \frac{2N^2 \delta(\mathbf{r}-\mathbf{r}')}{\chi \rho_0}.$$

- In addition, we need to perform calibration of bare $\chi_b N$ to renormalized χN.

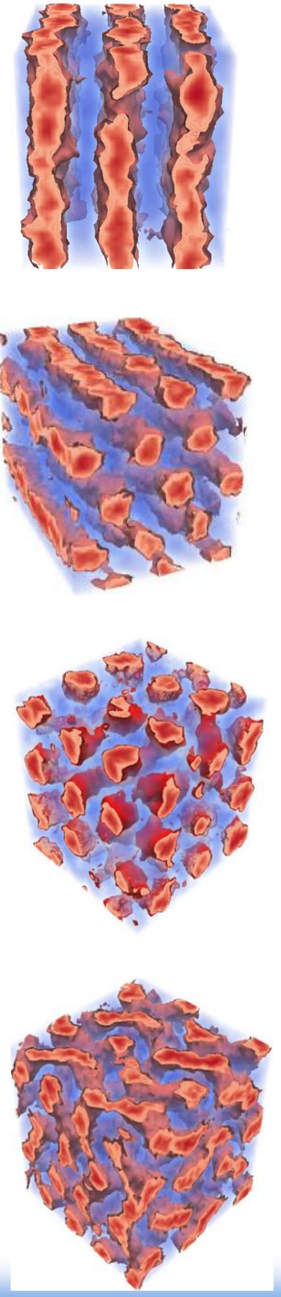
Examples of SCFT and L-FTS results

SCFT phase diagram

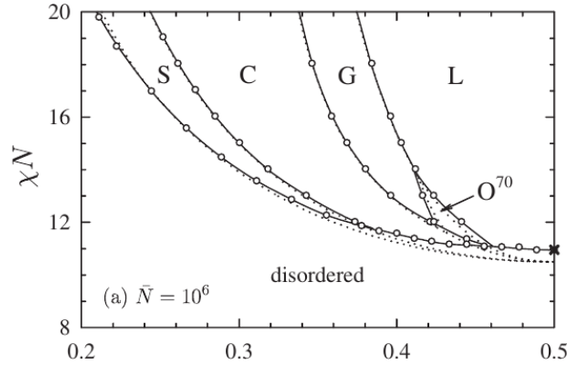


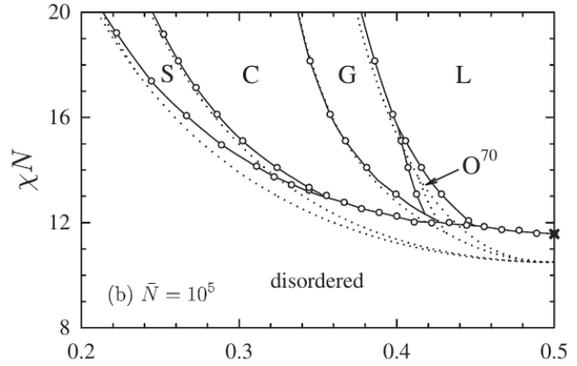


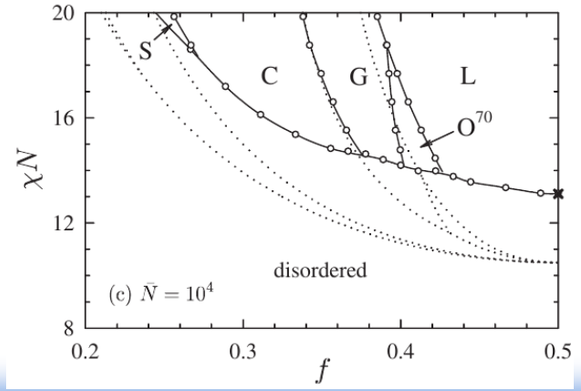
Mark W. Matsen , Tom M. Beardsley and James D. Willis, Phys. Rev. Lett (2023)



L-FTS phase diagram







Deep Learning Boosted L-FTS

$$g_+[W_-, W_+](\mathbf{r}) = \phi_+[W_-, W_+](\mathbf{r}) - 1$$

- The key point of our L-FTS acceleration is the **use of DL for the reduction of partial saddle point computation time** through **improved estimation of** w_+.





- Our NN (**DeepLab**) is based on NN models for the **semantic segmentation**, which are fully convolutional. PyTorch-Lightning is used as the DL framework.

- Inputs are W_- and g_+ rescaled by $\sigma(g_+)$ which is the standard deviation of g_+. The ground truth is $\Delta w_+^{\text{final}}$ which is iteratively computed by Anderson mixing method. The loss function is the mean square error function. Output is ΔW_+.

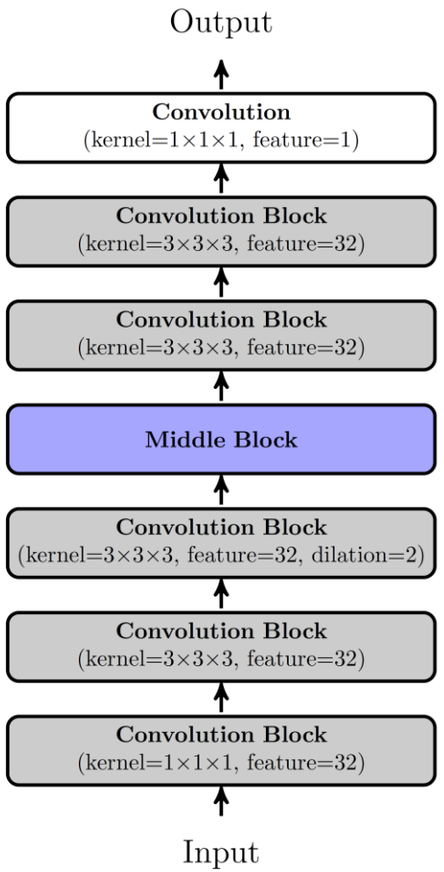
- For this supervised learning, training data are gathered in the first stage of L-FTS (during 1×10^4 time steps) without using DL.

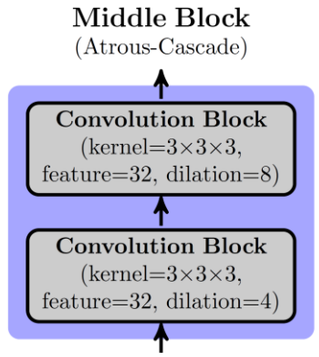
Architecture of Neural Network

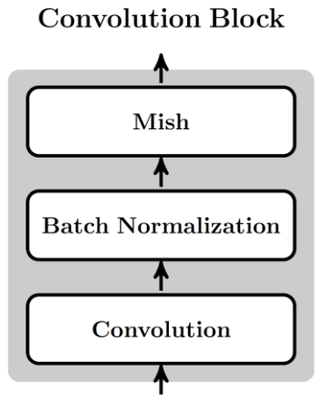
- The architecture of our DNN is shown here.



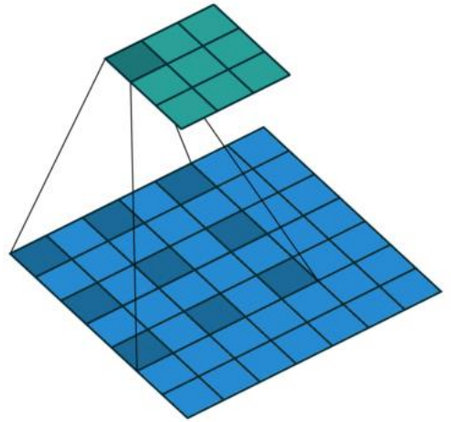








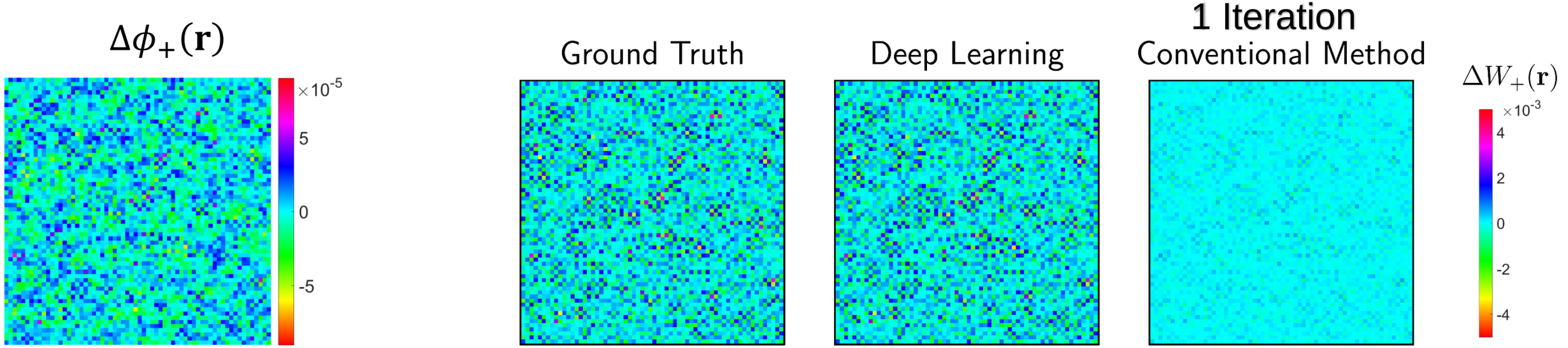
Atrous Convolution



Example of Semantic Segmentation. https://pytorch.org/

Results

- We developed a method to train deep neural network (DNN) that can boost the simulation. The prediction of DL is almost same as the ground truth, whereas single iteration of conventional method is quite different from the ground truth.



- After the training, DL assisted L-FTS is performed by using predictor-corrector method.
- We achieve speedup of factor 6 including the inference time.

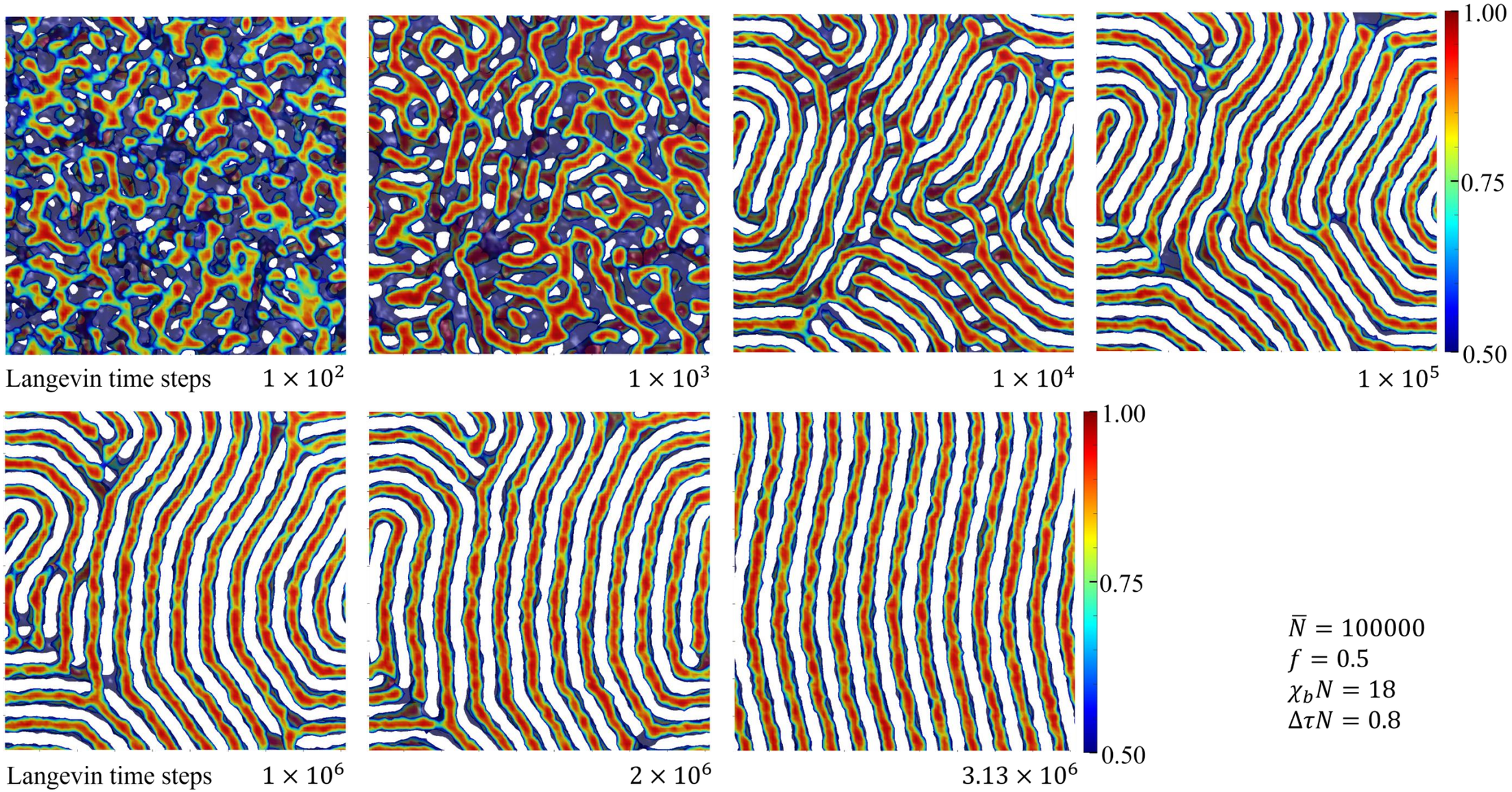
https://github.com/yongdd/langevin-fts
https://github.com/yongdd/deep-langevin-fts

Morphology	Speedup	Iterations Reduction
Spheres	5.97	9.09
Cylinders	6.19	9.37
Gyroid	6.19	8.64
Lamellae	5.99	8.44

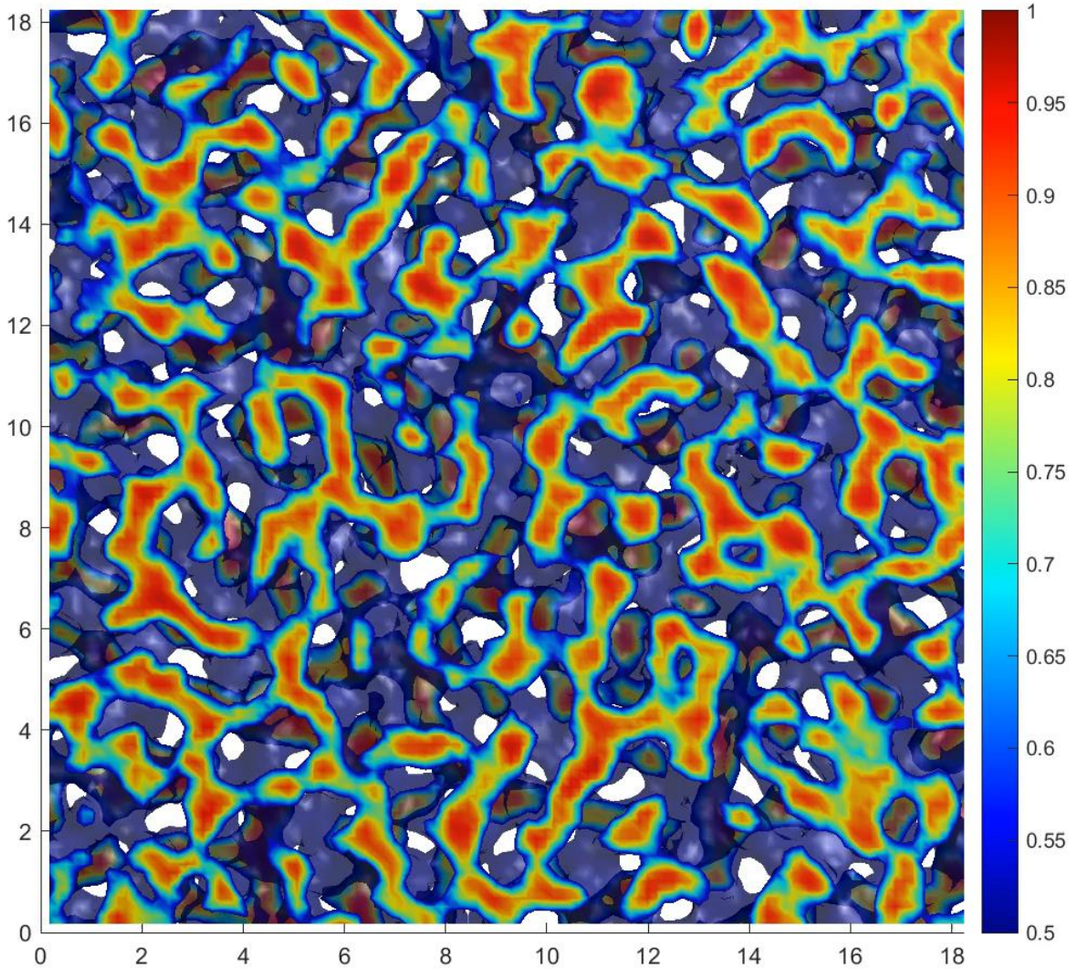
- Open source library for SCFT and L-FTS (utilizing Deep Learning).

Lamella-Forming Diblock Copolymer Thin Film

Segment density of diblock copolymers (only A domains shown)



Lamella-Forming Diblock Copolymer Thin Film



Discrete chain model

$\chi N_b = 15, \chi N = 14.3355, f_A = 0.50$

$\Delta x = 0.1689,$

$[L_x, L_y, L_z] = [18.24, 18.24, 2.02665] \approx \left[12R_0, 12R_0, {}^{4}/_{3}\, R_0\right]$

$ds = 0.01, \bar{N} = 10^5$

Multi Species Polymer Mixture System

In a system composed of two or more polymer species, the effective total number of polymers, n, is defined to ensure consistency with systems containing a single polymer species. For a polymer species i, the number of polymers is denoted as n_i. Assuming that the monomer volume is identical for all polymer species, n can be defined as

α_i is the length of the polymer chain of species i

$$n \equiv \alpha_1 n_1 + \alpha_2 n_2 + \alpha_3 n_3 + \cdots$$

Performing the field transform, the partition function of the system becomes

$$\mathcal{Z} = \frac{1}{n_1! n_2! n_3! \cdots} \left(\frac{\rho_0 V Q_1}{N}\right)^{n_1} \left(\frac{\rho_0 V Q_2}{N}\right)^{n_2} \left(\frac{\rho_0 V Q_3}{N}\right)^{n_3} \cdots = \frac{1}{n_1! n_2! n_3! \cdots} (nQ_1)^{n_1} (nQ_2)^{n_2} (nQ_3)^{n_3} \cdots$$

Q_i is total partition function of the polymer chains for species i

By using the Stirling approximation, the free energy of the system is

$$\frac{F}{k_B T} = \ln(n_1!) + \ln(n_2!) + \ln(n_3!) + \cdots - n_1 \ln Q_1 - n_2 \ln Q_2 - n_3 \ln Q_3 + \cdots$$
$$\approx n_1 \left(\ln \frac{n_1}{Q_1 n} - 1\right) + n_2 \left(\ln \frac{n_2}{Q_2 n} - 1\right) + n_3 \left(\ln \frac{n_3}{Q_3 n} - 1\right) + \cdots$$

The free energy of system per effective number of polymers can be expressed in terms of $\Phi_i \equiv \alpha_i n_i / n$, the global volume fraction of polymer species i,

$$\frac{F}{n k_B T} = \frac{n_1}{n}\left(\ln \frac{n_1}{Q_1 n} - 1\right) + \frac{n_2}{n}\left(\ln \frac{n_2}{Q_2 n} - 1\right) + \frac{n_3}{n}\left(\ln \frac{n_3}{Q_3 n} - 1\right) + \cdots = \frac{\Phi_1}{\alpha_1}\left(\ln \frac{\Phi_1}{\alpha_1 Q_1} - 1\right) + \frac{\Phi_2}{\alpha_2}\left(\ln \frac{\Phi_2}{\alpha_2 Q_2} - 1\right) + \frac{\Phi_3}{\alpha_3}\left(\ln \frac{\Phi_3}{\alpha_3 Q_3} - 1\right) + \cdots$$

Multi Species Polymer Mixture System: BCPs + HPs

Q_h: the total partition function of the HP chain
Φ_h: the global volume fraction of HPs
α_h: the length of the HP chain

For a binary **mixture of AB BCPs and A HPs**, the system's free energy is expressed as ($\alpha_c = 1$):

$$\frac{F}{nk_{\mathrm{B}}T} = \Phi_c\left(\ln\frac{\Phi_c}{Q_c} - 1\right) + \frac{\Phi_h}{\alpha_h}\left(\ln\frac{\Phi_h}{\alpha_h Q_h} - 1\right) + \frac{1}{V}\int d\mathbf{r}\,[\chi N\phi_{\mathrm{A}}(\mathbf{r})\phi_{\mathrm{B}}(\mathbf{r}) - w_{\mathrm{A}}(\mathbf{r})\phi_{\mathrm{A}}(\mathbf{r}) - w_{\mathrm{B}}(\mathbf{r})\phi_{\mathrm{B}}(\mathbf{r})]$$

The partition function of the HP chain is given as

$$Q_r = \frac{1}{V}\int q_h(\mathbf{r},s)q_h^{\dagger}(\mathbf{r},s)d\mathbf{r}$$

If the HPs are made of A-type segments, the modified diffusion equation for partial partition function is

$$\frac{\partial}{\partial s}q_r(\mathbf{r},s) = \frac{a^2N}{6}\nabla^2 q_h(\mathbf{r},s) - w_{\mathrm{A}}(\mathbf{r})q_h(\mathbf{r},s)$$

It is easy to confirm that

$$q_h^{\dagger}(\mathbf{r},s) = q_h(\mathbf{r},1-s)$$

The density of A and B blocks, incorporating contributions from both BCPs and HPs, are

$$\phi_{\mathrm{A}}(\mathbf{r}) = \frac{\Phi_c}{Q_c}\int_0^f q_c(\mathbf{r},s)q_c^{\dagger}(\mathbf{r},s)ds + \frac{\Phi_h}{\alpha_h Q_h}\int_0^{\alpha_h} q_h(\mathbf{r},s)q_h^{\dagger}(\mathbf{r},s)ds \qquad \phi_{\mathrm{B}}(\mathbf{r}) = \frac{\Phi_c}{Q_c}\int_f^1 q_c(\mathbf{r},s)q_c^{\dagger}(\mathbf{r},s)ds$$

Multi Species Polymer Mixture System: A+B HPs

Φ_i: the global volume fraction of I type HPs
α_i: the length of the *i* type chain

For the **binary mixture of A-type and B-type HPs**, the free energy can be expressed as:

$$\frac{F}{nk_BT} = \frac{\Phi_A}{\alpha_A}\left(\ln\frac{\Phi_A}{\alpha_A Q_A} - 1\right) + \frac{\Phi_B}{\alpha_B}\left(\ln\frac{\Phi_B}{\alpha_B Q_B} - 1\right) + \frac{1}{V}\int d\mathbf{r}\,[\chi N\phi_A(\mathbf{r})\phi_B(\mathbf{r}) - w_A(\mathbf{r})\phi_A(\mathbf{r}) - w_B(\mathbf{r})\phi_B(\mathbf{r})]$$

$$Q_A = \frac{1}{V}\int q_A(\mathbf{r},s)q_A^\dagger(\mathbf{r},s)d\mathbf{r} \qquad Q_B = \frac{1}{V}\int q_B(\mathbf{r},s)q_B^\dagger(\mathbf{r},s)d\mathbf{r}$$

The partial partition functions $q_A(\mathbf{r},s)$ and $q_B(\mathbf{r},s)$ are calculated by the following modified diffusion equations,

$$\frac{\partial}{\partial s}q_A(\mathbf{r},s) = \frac{a^2N}{6}\nabla^2 q_A(\mathbf{r},s) - w_A(\mathbf{r})q_A(\mathbf{r},s) \qquad \frac{\partial}{\partial s}q_B(\mathbf{r},s) = \frac{a^2N}{6}\nabla^2 q_B(\mathbf{r},s) - w_B(\mathbf{r})q_B(\mathbf{r},s)$$

The densities of A and B segments are calculated as

$$\phi_A(\mathbf{r}) = \frac{\Phi_A}{\alpha_A Q_A}\int_0^{\alpha_A} q_A(\mathbf{r},s)q_A^\dagger(\mathbf{r},s)ds$$

$$\phi_B(\mathbf{r}) = \frac{\Phi_B}{\alpha_B Q_B}\int_0^{\alpha_B} q_B(\mathbf{r},s)q_B^\dagger(\mathbf{r},s)ds$$

Phase Separation of A and B Mixture

Let us consider the **mixture of incompressible A and B homopolymers which have the same length, $\alpha_A = \alpha_B = 1$**.

$$\frac{F}{nk_{\mathrm{B}}T} = \Phi_{\mathrm{A}}\left(\ln\frac{\Phi_{\mathrm{A}}}{Q_{\mathrm{A}}} - 1\right) + \Phi_{\mathrm{B}}\left(\ln\frac{\Phi_{\mathrm{B}}}{Q_{\mathrm{B}}} - 1\right) + \frac{1}{V}\int d\mathbf{r}\,[\chi N\phi_{\mathrm{A}}(\mathbf{r})\phi_{\mathrm{B}}(\mathbf{r}) - w_{\mathrm{A}}(\mathbf{r})\phi_{\mathrm{A}}(\mathbf{r}) - w_{\mathrm{B}}(\mathbf{r})\phi_{\mathrm{B}}(\mathbf{r})]$$

If they form a **homogeneous mixture with A fraction ϕ** (and of course B fraction is $1-\phi$). We can easily find a trivial self-consistent solution, $w_{\mathrm{A}}(\mathbf{r}) = w_{\mathrm{B}}(\mathbf{r}) = 0$, which makes $q_{\mathrm{A}}(\mathbf{r}, \mathrm{s}) = q_{\mathrm{B}}(\mathbf{r}, \mathrm{s}) = Q_{\mathrm{A}} = Q_{\mathrm{B}} = 1$.

We now have a free energy expression,

$$\frac{F}{nk_{\mathrm{B}}T} = \phi(\ln\phi - 1) + (1-\phi)(\ln(1-\phi) - 1) + \chi N\phi(1-\phi)$$

This is the famous expression for the material mixture model. You probably have seen its derivation starting from a toy model with a cubic lattice and pair interaction. Such a **simplified model can produce an exact(!) result in the long chain limit**, where the universality conquers in the end.

For the analysis of the phase, we can drop out some linear terms:

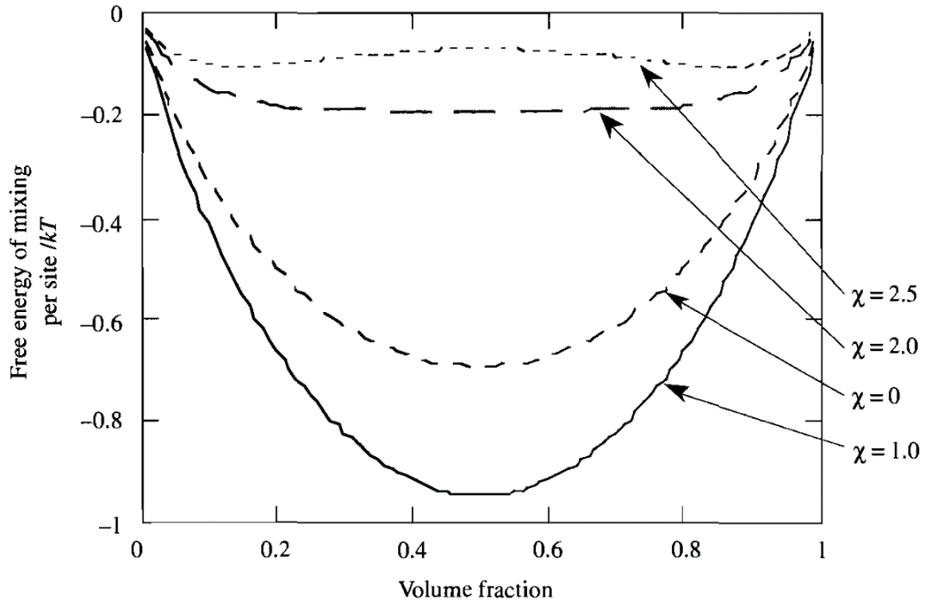
$$\frac{F_{\mathrm{mix}}}{nk_{\mathrm{B}}T} = \phi\ln\phi + (1-\phi)\ln(1-\phi) + \chi N\phi(1-\phi)$$

Phase Separation of A and B Mixture

The free energy of polymer mixing $\frac{F_{\text{mix}}}{nk_{\text{B}}T} = \phi \ln \phi + (1-\phi)\ln(1-\phi) + \chi N \phi(1-\phi)$

We can understand the phase behavior of our mixture by looking at the way the shape of the curves of free energy against composition change with varying values of χN.

For negative and small positive values of χN, the curve has a single minimum at $\phi_A = \phi_B = 0.5$. For values of $\chi N > 2$, we find two minima, and a (local) maximum at $\phi_A = \phi_B = 0.5$. To understand the physical significance of this, we must look at the two possible situations in more detail.



Phase Separation of A and B Mixture

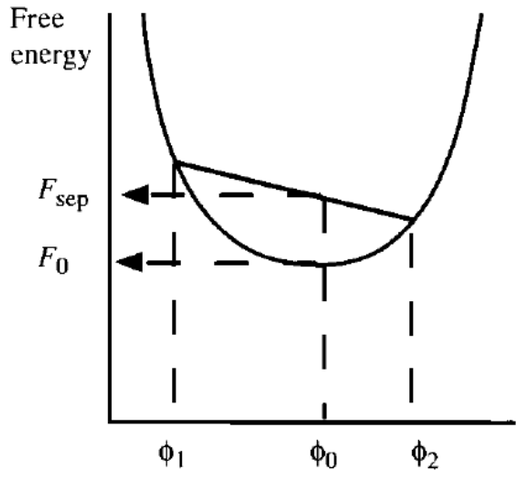
Suppose we have a volume V_0 of mixture whose starting volume fraction of A is ϕ_0. (All volume fractions refer to A) Now assume this mixture separates into a volume V_1 with volume fraction ϕ_1 and a volume V_2 with volume fraction ϕ_2. To conserve the total amount of A and B, $\phi_0 V_0 = \phi_1 V_1 + \phi_2 V_2$. We can also write

$$\phi_0 = \eta_1 \phi_1 + \eta_2 \phi_2 \qquad \eta_1 + \eta_2 = 1$$

where η_1 ($=V_1/V_0$) and η_2 ($=V_2/V_0$) are the relative proportions of the two phases. The total energy of the phase-separated system is

$$F_{\text{sep}} = \eta_1 F_{\text{mix}}(\phi_1) + \eta_2 F_{\text{mix}}(\phi_2) = \frac{\phi_0 - \phi_2}{\phi_1 - \phi_2} F_{\text{mix}}(\phi_1) + \frac{\phi_1 - \phi_0}{\phi_1 - \phi_2} F_{\text{mix}}(\phi_2)$$

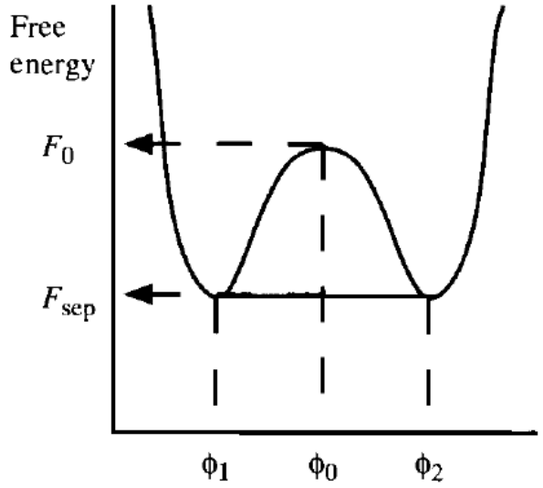
This equation is best interpreted graphically. In the figure, an initial composition ϕ_0 phase separates into two phases ϕ_1 and ϕ_2. The total free energy of these two phases, F_{sep}, can be read off the straight line joining $F(\phi_1)$ and $F(\phi_2)$ where the volume fraction takes the value ϕ_0.



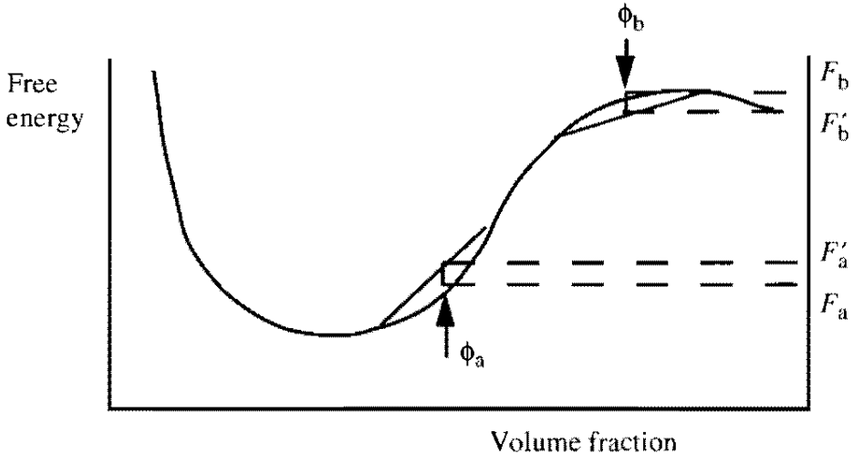
For the **concave curve**, the free energy resulting from phase separation into any pair of volume fractions ϕ_1 and ϕ_2 is always higher than the free energy of the starting composition F_0, so the **mixture is stable**.

Phase Separation of A and B Mixture

On the other hand, if there is any region in which the curve is convex, as shown in the figure, then there are some starting compositions which, if they phase separate, can lead to a lowering of free energy. The limiting compositions which bound this region of phase separation are those compositions joined by a **common tangent**, ϕ_1 and ϕ_2.



These compositions are known as the coexisting compositions, and the locus of these compositions as the temperature, and thus the interaction parameter, is changed, is known as the **coexistence** curve or the **binodal**.



If we look in more detail at the free energy curve for compositions that fall within the coexistence curve, we find another important distinction: the curvature of the free energy function, $d^2F/d\phi^2$ may be either positive or negative.

At a composition ϕ_b, phase separation to two compositions close to ϕ_b results in a lowering of free energy from F_b to F'_b. At this composition, the system is unstable with respect to small fluctuations in composition, and will immediately begin to phase-separate. This composition is unstable.

Phase Separation of A and B Mixture

However, at composition ϕ_a, a similar small change in composition leads to an increase in free energy from F_a to F'_a; the system is **locally stable** with respect to such small composition fluctuations. It is still **globally unstable** with respect to separation into the two coexisting phases. There is an energy barrier the system must overcome to achieve the global energy minimum associated with phase separation. This composition is **metastable**.

The limit of local stability is defined by the condition that the curvature $\mathrm{d}^2F/\mathrm{d}\phi^2 = 0$; the locus of these points is known as the **spinodal**.

Finally, we note that a critical χN (or temperature in most experiment) usually separates the two types of situation for which mixtures are always stable and situations for which there are compositions which will phase separate.

In the former, the curvature is always positive, while in the latter $\mathrm{d}^2F/\mathrm{d}\phi^2$ is negative within a certain range of ϕ. The **critical point is thus defined by the condition that $\mathrm{d}^2F/\mathrm{d}\phi^2 = \mathrm{d}^3F/\mathrm{d}\phi^3 = 0$, and it is the point at which the coexistence curve and spinodal line meet**.

Let us apply this analysis for our free energy $$f(\phi) = \frac{F_{\mathrm{mix}}}{nk_{\mathrm{B}}T} = \phi \ln \phi + (1-\phi)\ln(1-\phi) + \chi N \phi(1-\phi)$$

A solubility gap occurs when there exists a region that its second derivative becomes negative. Calculating the second derivative,

Phase Separation of A and B Mixture

$$\frac{d^2 f(\phi)}{d\phi^2} = -2\chi N + \frac{1}{\phi} + \frac{1}{1-\phi} \qquad \text{and} \qquad \frac{1}{\phi} + \frac{1}{1-\phi} \geq 4$$

If χN is negative or less than 2 (it usually happens when $T > T_c$ in many experimental systems), the second derivative is positive at any ϕ value. If χN is larger than 2 (or $T < T_c$) there exists a region with the solubility gap. Because it is a symmetric case, the coexistence curve is determined by the following condition.

$$\frac{df}{d\phi} = 0 \qquad \frac{d}{d\phi}\left(\phi \log\phi + (1-\phi)\log(1-\phi) + \chi N \phi(1-\phi)\right) = 0$$

$$\log\phi - \log(1-\phi) + \chi N(1-2\phi) = 0 \qquad \chi N = \frac{1}{2\phi - 1}\log\left(\frac{\phi}{1-\phi}\right)$$

Analytic expression is not available for ϕ, but the solution is shown in the figure. The spinodal line is obtained by solving

$$\frac{1}{\phi} + \frac{1}{1-\phi} = 2\chi \qquad \phi = \frac{1}{2} \pm \frac{1}{2}\sqrt{1 - \frac{2}{\chi}}$$

It is also shown in the figure. The critical point shown in the figure is $\phi = 0.5$ and $(\chi N)_c = 2$.

