Lecture 1:
Macromolecular Engineering: Networks and Gels – Introduction

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1 Suggested reading

- *Polymer Physics* – Rubinstein and Colby: Chapter 1

- *Principles of Polymer Chemistry* – Flory: Chapter 1

- *Soft Condensed Matter* – Jones: Chapters 1 & 2

- Many of the lectures notes of this course owe a great debt to the lecture notes of A. Alexander-Katz (MIT, USA) from his excellent course on *Polymer Physics*.

2 Course overview

The purpose of this course is to provide an introduction to the physics and engineering of the fascinating class of materials composed of cross-linked polymeric materials. *Macromolecular Engineering: Network and Gels* will focus on the study of ***soft matter*** with a specific focus on polymeric networks and gels. Soft condensed matter or simply soft matter – a term coined by Pierre-Gilles de Gennes (Nobel Prize for Physics 1991) and Madeleine Veyssiè – is a broad term for the class of materials that includes polymers, networks, gels, colloids, liquid crystals, complex fluids, nanoparticles, and other 'soft' material systems. This course will focus primarily on polymers and polymeric materials; however, the governing physics that we will explore apply to soft matter in general. Further, most biological systems are composed predominantly of soft matter and a study of polymer physics will provide insight into aspects of biological physics as well. Biological gels compose a large fraction of the support material in living systems – extracellular matrix, mucus, and bacterial biofilms.

A critical aspect of the interesting properties of soft matter is that many of the intermolecular interactions in soft materials have energies on the scale of $\sim 1\ k_B T$. Here, k_B is the Boltzmann constant, T is the temperature of the system, and $k_B T$ is a measure of the typical thermal energy of an object in the system. In contrast, most hard materials, *e.g.*, metals, ceramics, are held together by much stronger bonds that have interaction energies on the order of ~ 10–$100\ k_B T$. Simply put, **weak intermolecular interactions are prevalent in soft matter**, and this leads to large fluctuations in thermodynamic quantities that impart interesting behavior in these systems. For example, intermolecular interactions can be disrupted with minimal applied stimuli such as pulling or pushing on the material. Further, the weak intermolecular interactions lead to a highly dynamic and adaptive nature of soft materials. Proteins in the body undergo large conformational changes to execute many functions, which is only possible because intermolecular interactions are weak compared to thermal energy. That said, as we will explore, soft materials are often comprised of large numbers of intermolecular interactions and even with relatively weak energies this can lead to very strong materials. Kevlar, for example, is composed of a synthetic polymer with a large number of hydrogen bonds and a rigid backbone that allows it to withstand high impact – it is a major component in bulletproof vests. The first section of this course will build physical intuition for how these weak interactions lead to many of the fascinating thermodynamic properties of polymers and soft materials. **The interplay of energy and entropy is essential**.

In polymeric networks and gels, we also introduce a small fraction of strong physical or covalent interactions into the system that cross-link the polymer chains into an 'infinite' molecular weight molecule. This combination of weak intermolecular forces and strong intramolecular linkages leads to another fascinating range of properties. Networks and gels can possess a wide range of elasticities and demonstrate viscoelastic properties. They are employed in a broad range of materials including the

rubber in your car tires, the material in your contact lenses, the absorbent in a baby's diaper, and many coating materials.

The learning objective of this course is to equip you with the tools to understand how macromolecular structure leads to macroscale properties in networks and gels and to provide you with insight into how to engineer this class of materials for a range of applications in industry and the biomedical sciences. We will build to this through the exploration of several **sub-themes**:

- properties of single polymer chains

- behavior of polymer solutions

- networks and rubber elasticity

- gels and swollen networks

- applications of networks and gels

Along the way we will need the following **tools**:

- thermodynamics

- statistical mechanics

- (a bit of) chemistry

- physics / mechanics

The world of soft matter – and especially the topics of networks and gels – is rich and fascinating. We live in a 'Polymer Age' and understanding the physics of soft matter is critical for engineering next-generation materials.

3   Brief history of polymer chemistry

Human history has often been categorized by the available materials: the Stone Age, the Bronze Age, and the Iron age. It is often argued that in the 20th century we entered the 'Polymer Age'.

Yet, long before this, humans have been engineering macromolecules without knowing it. This includes many food products in the production of cheeses, doughs, breads, and pastas. An excellent example of engineering with polymeric networks is found in Mesoamerican history. The Olmec, Maya, and Aztec civilizations were fabricating balls and shoes out of natural rubber (*e.g.*, latex from *Castilla elastica* mixed with juice from *Ipomoea alba*) as early as the 2nd millennium BCE. Evidence even suggests that they had engineered the ratio of the reactants to optimize the material properties of the resultant rubbers. In another example, ancient Egyptians employed photopolymerization during embalming in the mummification process.

Synthetic chemists have been producing macromolecules, or what we would now call polymers, since the middle of the 19th century, but they refused to accept that they were actually molecules of large molecular weight despite several experimental measurements. The accepted view was that these products formed were **colloids** – or physically associated clusters of small molecules.

In the 1920s, here at ETH Zürich, Hermann Staudinger (Nobel Prize for Chemistry 1953) proposed the **macromolecular hypothesis** stating that the colloids observed by himself and his colleagues were in fact large molecular weight molecules or **macromolecules** that were held together by covalent bonds. He introduced the terms **monomer**, **polymer**, and **polymerization** and was convinced that polymers were chains of similar monomers linked chemically through a polymerization reaction. In contrast to colloids, covalently linked polymer chains exhibit colloidal properties in all solvents – they cannot be dissolved into smaller constituents. He met significant resistance from his colleagues and

was told that he should abandon this work as it had already been proven wrong. He persisted and finally convinced the community that his view was correct and he was awarded the Nobel Prize in Chemistry for this work in 1953. This is an excellent lesson to always be skeptical of accepted dogma.

The introduction of the macromolecular hypothesis brought about great progress in the polymer chemistry field. By 1929, Wallace H. Carothers at Dupont had synthesized a range of well-defined polymers including Nylon and the 'Polymer Age' took off.

4   Interactions in soft matter

Molecules are classically held together by covalent bonds between atoms with many conformations available via rotational isomeric states. Molecular geometries are enabled by the rotation of atoms about these intramolecular bonds. This is true of the backbone structure of a polymer chain as well and enables conformational freedom in the chain. We will discuss this in more detail in the coming lectures. In addition to the intramolecular bonds, several weak intermolecular interactions play a key role in the physical behavior of soft matter:

- Lennard-Jones potential – *i.e.*, induced dipole interactions & Pauli repulsion.

- Coulombic interactions – *i.e.*, electrostatic attraction / repulsion between ionic species.

- Hydrogen bonding – *i.e.*, net dipole interactions.

- Hydrophobic effect – a largely entropic interaction (not pairwise like those above) caused by the restructuring of water around hydrophobic interaces.

In this course, we will not discuss in depth the origin of these interactions, many of which can be understood rigorously with quantum mechanics. For a thorough description, we recommend the book *Intermolecular and Surface Forces*, Jacob Israelichvili, Academic Press, 2011. Combinations of these interactions can lead to several different interactions between monomers in a polymer chain: *i.* attractive interaction, *ii.* zero effective interaction, *iii.* short-range repulsion, and *iv.* long-range repulsion. If we consider a model polymer chain with 10^{10} monomers each 1 cm in length, for these interactions the chain would *i.* fit inside of a lecture hall, *ii.* occupy the size of ETH Hönggerberg, *iii.* occupy the size of Zürich, and *iv.* stretch $\frac{1}{4}$ of the way to the moon.

5   Definitions

Throughout this course we will introduce a range of terms, many of which may be new to you. We will try to collect these terms and definitions in the lecture notes so that you can begin to build the language of this topic. If any term is unclear to you, please do not hesitate to ask for clarification.

In the early section of this course we will discuss single **polymer** chains. The word *poly-mer* means *many-parts* and refers to those molecules that consist of many base units, called **monomers**. For example, the polymer polyethylene (CH_3–$(CH_2)_N$–CH_3) is composed of the monomer ethylene (CH_2=CH_2). The polymer is built through a **polymerization** reaction wherein the monomers are covalently bonded together into a single chain. The number of monomers in the polymer is referred to as its **degree of polymerization** N. The **molar mass** M of a polymer is equivalent to the degree of polymerization times the molar mass M_{mon} of the monomer:

$$M = NM_{mon}. \tag{1}$$

If a molecule is comprised of a low degree of polymerization or a small number of monomers (typically, less than 20) it is called an **oligomer**. Linear polymers contain between 20 and 10 billion – the longest known chromosome – monomers and many physical properties of polymers and polymers in solution vary with the degree of polymerization. We can also synthesize other polymer topologies including

ring, star, *H*, comb, ladder, dendrimer, or randomly branched polymers. As we will discuss extensively later in the semester, cross-linking leads to the formation of **polymer networks** that are useful as soft solids or gels.

We often encounter polymers as liquids either as **polymer melts** or **polymer solutions**. In these scenarios, we often discuss the volume fraction ϕ, the ratio of the occupied volume of the polymer in the solution to the volume of the solution

$$\phi = \frac{c}{\rho} = c\frac{\mathrm{v_{mon}}\mathcal{N}_{\mathrm{Av}}}{M_{\mathrm{mon}}}, \tag{2}$$

where c is the mass concentration of polymer, ρ is the polymer density, $\mathrm{v_{mon}}$ is the occupied volume of a single monomer ($\mathrm{v_{mon}} \approx 100 \text{Å}^3$), and $\mathcal{N}_{\mathrm{Av}}$ is Avogadro's number.

The **pervaded volume** V is the volume of solution occupied by the polymer chain

$$V \approx R^3, \tag{3}$$

where R is the 'size' of the polymer chain. We will calculate R for different polymer chains in the coming lectures. Importantly, V is typically orders of magnitude larger than the occupied volume of the chain $\mathrm{v_{mon}}N$ and this means that most of the pervaded volume is occupied by solvent or other polymer chains.

We can then calculate the volume fraction of a single polymer chain inside of the volume that it spans and define this as the **critical volume fraction** ϕ^* as well as the corresponding **critical concentration** c^*:

$$\phi^* = \frac{N\mathrm{v_{mon}}}{V} \qquad c^* = \frac{\rho N\mathrm{v_{mon}}}{V} = \frac{M}{V\mathcal{N}_{\mathrm{Av}}}. \tag{4}$$

These properties define the critical concentration or volume fraction wherein a polymer solution transitions from a dilute regime with little intermolecular interactions to a regime with significant intermolecular interactions. These limits are also important in network and gel formation, as will be discussed later in the course. In general, these concentrations are quite low, 0.1–5 wt%.

A major feature of most synthetic polymers is that we are generally unable to produce a **uniform** sample and the materials we deal with are **disperse**, meaning that the sample is a collection of individual molecules that have a distribution of degrees of polymerization. Many natural polymers, such as proteins, are perfectly uniform but this is rare in synthetic systems and remains a 'holy grail' in polymer chemistry research. To describe disperse polymer samples, we often talk about the **molar mass distribution** often visualized as the **number fraction** n_N of chains containing N monomers plotted as a function of molar mass $M_N = M_{\mathrm{mon}}N$ of the chains. It is also often convenient to deal with the **weight fraction** w_N of chains with molar mass M_N:

$$w_N = \frac{n_N M_N}{\sum\limits_N n_N M_N} = \frac{c_N}{c}, \tag{5}$$

where c_N is the mass concentration of chains with degree of polymerization N.

It can be difficult to work with complete distributions and as such, we often characterize distributions by the **moments** of the distribution. For example, the 1st moment of a distribution is the mean. In general, we can define the kth moment, μ_k, of the number fraction distribution above as the sum of the products of the number fraction n_N of chains with degree of polymerization N and the corresponding molar mass M_N raised to the kth power:

$$\mu_k = \sum_N n_N M_N{}^k. \tag{6}$$

By definition, the zeroth ($k = 0$) moment is equal to unity.

In polymer physics, we often describe molar mass distributions by one or more average molar masses. The **number-average molar mass** M_n is defined as the ratio of the first ($k = 1$) to zeroth ($k = 0$) moments of the number fraction distribution:

$$M_n \equiv \frac{\sum\limits_{N} n_N M_N}{\sum\limits_{N} n_N} = \sum_{N} n_N M_N. \tag{7}$$

The number-average molar mass is controlled by the polymerization reaction and will often be listed on a chemical bottle of polymer as it is relatively easy to determine. The **weight-average molar mass** M_w is the ratio of the second moment to the first moment of the number fraction distribution:

$$M_w \equiv \frac{\sum\limits_{N} n_N M_N^2}{\sum\limits_{N} n_N M_N} = \frac{\sum\limits_{N} n_N M_N^2}{M_n} = \sum_{N} w_N M_N. \tag{8}$$

The weight-average molar mass is obtained by randomly selecting monomers and counting how long the the polymer chain is associated with that monomer. The weight-average molar mass can be determined experimentally by light scattering from a dilute polymer solution and the viscosity of polymer liquids correlates with M_w. As M_w biases for longer chains, by definition $M_w \geq M_n$. Finally, we often characterize the spread of a molar mass distribution with the **dispersity** ($Đ$), which is defined as the ratio of the weight-average molar mass to the number-average molar mass:

$$Đ \equiv \frac{M_w}{M_n} \geq 1. \tag{9}$$

Uniform samples have a $Đ$ of 1 and larger $Đ$ values correspond to broader molar mass distributions.