National Journal of Multidisciplinary Research and Development
ISSN: 2455-9040
Impact Factor: RJIF 5.22
www.nationaljournals.com
Volume 3; Issue 1; January 2018; Page No. 1356-1358

Statistical mechanics approach to elastomeric network

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Abstract

Polymers are studied in the fields of biophysics and macromolecular science, and polymer science (which includes polymer chemistry and polymer physics). Branched Polymer are those polymers in which one or more of the side chains are different, structurally or configurationally, from the main chain. In polymer chemistry, branching occurs by the replacement of a substituent. An elastomer is a polymer with viscoelasticity (colloquially "elasticity"), generally having low Young's modulus and high failure strain compared with other materials. The study of deformations in polymeric networks from the simplest models the phantom Gaussian network. The first theoretical molecular approach to the theory of rubber elasticity was done by Kuhn in late thirties.

Keywords: polymer, phantom network, elastomer

Introduction

A polymer is a large molecule, or macromolecule, composed of many repeated subunits, known as monomers. Because of their broad range of properties, both synthetic and natural polymers play an essential and global role in everyday life. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many monomers. Their consequently large molecular mass relative to small molecule compounds produces unique physical properties, including toughness, viscoelasticity, and a tendency to form glasses and semicrystalline structures rather than crystals.

The term "polymer" derives from the ancient Greek word (polus, meaning "many, much") and (meros, meaning "parts"), and refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. The units composing polymers derive, actually or conceptually, from molecules of low relative molecular mass. The term was coined in 1833 by Jöns Jacob Berzelius, though with a definition distinct from the modern IUPAC definition, The modern concept of polymers as covalently bonded macromolecular structures was proposed in 1920 by Hermann Staudinger, who spent the next decade finding experimental evidence for this hypothesis.

Polymers are studied in the fields of biophysics and macromolecular science, and polymer science (which includes polymer chemistry and polymer physics). Historically, products arising from the linkage of repeating units by covalent chemical bonds have been the primary focus of polymer science; emerging important areas of the science now focus on non-covalent links. Polyisoprene of latex rubber and the polystyrene of styrofoam are examples of polymeric natural/biological and synthetic polymers, respectively. In biological contexts, essentially all biological macromolecules i.e., proteins (polyamides), nucleic acids (polynucleotides), and polysaccharides are purely polymeric, or are composed in large part of polymeric components e.g., isoprenylated /lipid-modified glycoproteins, where small lipidic molecule and oligosaccharide modifications occur on the polyamide backbone of the protein.

Branched Polymer are those polymers in which one or more of the side chains are different, structurally or configurationally, from the main chain. In polymer chemistry, branching occurs by the replacement of a substituent, e.g., a hydrogen atom, on a monomer subunit, by another covalently bonded chain of that polymer; or, in the case of a graft copolymer, by a chain of another type. In cross- inking rubbe by vulcanization, short sulfur branches link polyisoprene chains (or asynthetic variant) into a multiply branched thermosetting elastomer. Rubber can also be so completely vulcanized that it becomes a rigid solid, so hard it can be used as the bit in a smoking pipe. Polycarbonate chains can be crosslinked to form the hardest, most impact-resistant thermosetting plastic, used in safety glasses. Branching may result from the formation of carbon-carbon or various other types of covalent bonds. Branching by ester and amide bonds is typically by a condensation reaction, producing one molecule of water (or HCl) for each bond formed. Polymers which are branched but not crosslinked are generally thermoplastic. Branching sometimes occurs spontaneously during synthesis of polymers; e.g., by free-radical polymerization of ethylene to form polyethylene. In fact, preventing branching to produce linear polyethylene requires special methods. Because of the way polyamides are formed, nylon would seem to be limited to unbranched, straight chains. But "star" branched nylon can be produced by the condensation of dicarboxylic acids with polyamines having three or more amino groups. Branching also occurs naturally during enzymatically-catalyzed polymerization of glucose to form polysaccharides such as glycogen (animals), and amylopectin, a form of starch (plants). The unbranched form of starch is called amylose. The ultimate in branching is a completely crosslinked network such as found in Bakelite, a phenol-formaldehyde thermoset resin.

An elastomer is a polymer with viscoelasticity (colloquially "elasticity"), generally having low Young's modulus and high failure strain compared with other materials. The term, which is derived from elastic polymer, is often used interchangeably with the term rubber, although the latter is preferred when referring to vulcanisates. Each of themonomers which link to form the polymer is usually made of carbon, hydrogen, oxygen and/or silicon. Elastomers are amorphous polymers existing above their glass transition temperature, so that considerable segmental motion is possible.

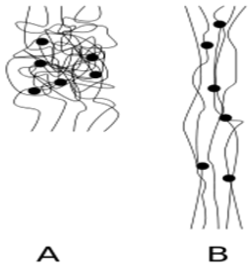

Fig 1: (A) is an unstressed polymer; (B) is the same polymer under stress. When the stress is removed, it will return to the A configuration. (The dots represent cross-links)

Overview of classical theories of rubber elasticity

Phantom Network

The study of deformations in polymeric networks from the simplest models the phantom Gaussian network. Consider a concentrated polymer solution or melt of Gaussian chains. If it assumed that a instantaneously formed a network from an equilibrium solution or melt. This can be achieved either by the instantaneous cross-linking or by the end linking of chains. After formation of the network, the chains “realize” that they are no longer free to move through the system but are constrained by the crosslinks. From now on a chain is defined as a linear section between two cross-links, even though it could have been a part of a multiply cross-linked original chain. The dangling ends of the network are not considered, because they can completely relax even in the stretched network and do not contribute to its elasticity. On consider the conformations of a test chain of N monomers. The only way the chain “knows” that it is a part of a phantom network is because its ends (cross-links) are no longer free but are localized and can only fluctuate around some average Positions.

There are two factors that define the amplitude of such fluctuations: the elasticity of the test chain and the elastic properties of the network at those places where the chain is connected to it (Figure 1a). Therefore it is convenient to consider the fluctuations of the network without the test chain. The local stiffness of such network at the two potential cross-link points can be described by the mean square amplitude $\xi_i{}^2$ of fluctuations of these potential cross-links, i) 1, 2, around their average positions Xi. One can represent the fluctuations of a potential cross-link by the fluctuations of the free end of an n_i-mer (“virtual chain”), the other end of which is attached at position Xi inside an elastic nonfluctuating solid (see Figure 1b). These attachment points displace affinely with the deformation of the network. The number of monomers $n1$ and $n2$ of such virtual chains represents the fluctuations ξ_1 and ξ_2 of the network at the places where the test chain is connected to it, $n_i=(\xi_i/b)^{1/2}$ for i) 1, 2, where b is the monomer size (persistence length). The monomers of virtual chains undergo thermodynamic fluctuations like the native chains of the network. Since the fluctuations of the cross-links are independent, the mean square fluctuations of the vector between these potential cross-links without the test chain attached to them is $\xi^2 = \xi_1{}^2 + \xi_2{}^2 = b^2n$, where $n = n_1 + n_2$ is the total number of monomers comprising the two virtual chains. The value ξ^2 defines the elastic free energy, $\_kT\mathrm{R}^2/\xi^2$, of deformations having a distance |R| between the two potential cross-links, and thus, the effective elastic modulus between these points is kT/ξ^2 (k is the Boltzmann coefficient, and T is the temperature). The local stiffness of the network varies from one region to another because of the irregularities of the network structure. These variations lead to corresponding variations of the values of ξ_1 and ξ_2 (or ξ) about their average values. In the case of networks prepared by cross-linking of linear chains, one can estimate the average elastic modulus between any two potential cross-links to be $kT(b^2N\mathrm{h})$, where Nh is the average number of monomers of the network chains. This estimate gives us the value of the mean-squared fluctuations of the distance between the potential crosslinks $\xi^2 = b^2N\mathrm{h}$ averaged over the volume of the network. Here the bar is used to distinguish averaging over the volume of the network from thermodynamic averaging. The distribution function of the fluctuation length $\hat{e}$ is peaked near its average value $(\xi^2)^{1/2}$ The width of the peak grows with increasing polydispersity of the chain lengths. A method of calculating this distribution function for a given network structure was proposed by Ball and Higgs on the basis of the analogy with the calculations of the conductivity of the resistor network.

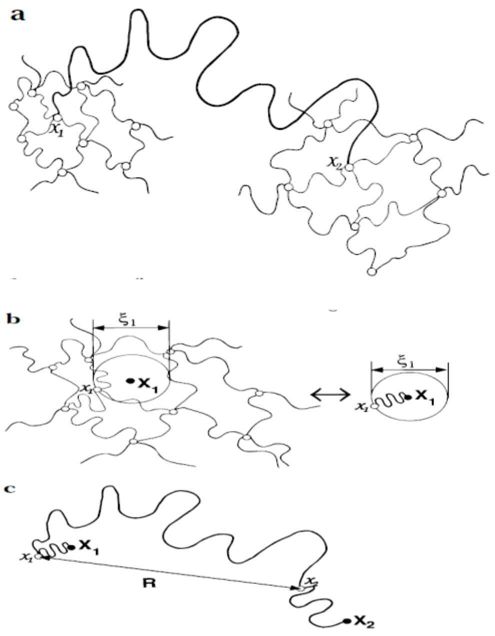

Fig 1: Combined chain of a phantom network.

a. A strand is connected to the network by its ends. The chains of the network, sketched by thin lines, are determining the local elastic environment at the ends of the strand.
b. The fluctuations of the potential cross-link $\mathbf{x}_1$ around its average position X_1 by a typical distance ξ_1 can be represented by a virtual chain. The number of monomers of the virtual chain is $n_1 = (\xi_1/b)$ [2].
c. The combined chain consists of the network strand of N monomers and two virtual chains of n_1 and n_2 monomers. The virtual chains connect the network strand to the nonfluctuating elastic solid at points X_1 and X_2.

Kuhn-Treloar Theory

The first theoretical molecular approach to the theory of rubber elasticity was done by Kuhn in late thirties. A very good review of history of early rubber elasticity was given by Flory. The theory Kuhn, Guth, Mark approach was further developed by Treloar. This element approach is based on the assumptions that the rubber network consists on v freely-jointed Gaussian chains. It is assumed that crosslinking of chains in the undeformed network does not change mean square end-to-end distance of chains in respect to the uncrosslinked polymer melt. This assumption is supported by data obtained from neutron scattering experiments. Another assumption is that the volume of the rubber network does not change during the stretching, and that positions of junctions (points of crosslinking) deform affinely upon deformation. It is also assumed that the total free energy of the network is the sum of free energies of all v chains.

The elastic free energy of the deformed network is

Equation

$$\Delta A_{\mathrm{el}} = \frac{3kT}{2\langle r^2\rangle_0}\sum_{\nu}(r^2 - \langle r^2\rangle_0) = \frac{3\nu kT}{2}\left(\frac{\langle r^2\rangle}{\langle r^2\rangle_0} - 1\right) \qquad (1)$$

Writing ⟨r2⟩ in terms of the Cartesian components of the deformation tensor **λ** we obtain:

Equation

$$\langle \mathbf{r}^2\rangle = \langle x^2\rangle + \langle y^2\rangle + \langle z^2\rangle = \frac{1}{3}\langle r^2\rangle_0\left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2\right) \qquad (2)$$

Which leads to

Equation

$$\Delta A_{\mathrm{el}} = \frac{1}{2}\nu kT\left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right) \qquad (3)$$

The elastic force f is then equation

$$f = \left(\frac{\partial \Delta A_{\mathrm{el}}}{\partial L}\right)_{T,V} = \frac{1}{L_0}\left(\frac{\partial \Delta A_{\mathrm{el}}}{\partial \lambda}\right)_{T,V} = \frac{\nu kT}{L_0}(\lambda - \lambda^{-2}) \qquad (4)$$

Where $\lambda = \lambda x$ is the x-component of the deformation tensor **λ** (assuming that the rubber is stretched in the $x$direction), and L_0 is the length of the undeformed rubber sample in the direction of stretch.

Conclusion

An elastomer is a polymer with elasticity generally having low Young's modulus and it is an amorphous polymer. An example of elastomer type of polymer is natural rubber. The classical theory of rubber elasticity is described with the help of phantom network. The first theoretical molecular approach to the theory of rubber elasticity was done by Kuhn Treloar theory.

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