

Soft Matter Physics and its Creator – Pierre-Gilles De Gennes (1932–2007) in Memoriam

Abstract

Pierre-Gilles de Gennes passed away on 18 May 2007. The Royal Swedish Academy of Sciences decided to award the 1991 Nobel Prize in physics to him “for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers” [1]. He is still the only scientist dealing with polymer science who has been a Nobel Prize winner in physics; therefore, it was justified to commemorate his work and achievements during the session of the Seventh International Conference on X-Ray Investigations of Polymer Structure.

Key words: *soft matter, polymers, surfactants, liquid crystals, colloids.*

Introduction

In the year 1995, P.G. de Gennes published the review article in the fundamental, three-volume book ‘Twentieth Century Physics’ [2]. It was entitled ‘Soft Matter: Birth and Growth of Concepts’. In this article, de Gennes – for the first time – used the notion of *soft matter*, and he defined the main characteristic of such materials. As examples of soft matter, he took into consideration polymers, liquid crystals, surfactants and colloids. Having in mind these four basic types of soft matter, it is worth learning something about the history of Nobel Prize winners for achievements in soft matter science. Such a list is presented below:

- Colloids: Ch, 1925, R.A. Zsigmondy; Ch, 1926, T. Svedberg
- Surfactants: Ch, 1932, I. Langmuir
- Polymers: Ch, 1953, H. Staudinger; Ch, 1963, K. Ziegler, G. Natta; Ch, 1974, P. Flory; Ch, 2000, A. MacDiarmid, H. Shirakawa and A. Heeger
- Polymers and liquid crystals: Ph, 1991, P.G. de Gennes.

(“Ch” denotes the Prize in chemistry, and “Ph” in physics).

The Royal Swedish Academy of Sciences decided to award the 1991 Nobel Prize in physics to de Gennes “for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers”. Therefore, the main aim of this article is to underline some selected achievements of de Gennes in the field of soft matter science, with special attention paid to polymer physics.

The meaning of ‘soft’: characteristics of soft matter

The most direct meaning of the word ‘soft’ in this context tells us that ‘soft materials’ are not as stiff and hard as common solid materials like metals and ceramics. Their elastic modulus may be several orders of magnitude less than for solids, for example the shear modulus might be of order 10 Pa for soft material, whereas it is of order 10^{10} Pa for metals. However, much more importantly, and as pointed out by de Gennes, a soft system gives large responses to very small perturbations. Moreover, this response may be strongly nonlinear, and these perturbations may represent a variety of types: electric field, magnetic field, temperature, composition and many others. The vulcanization of rubber, where less than 1% of the carbon atoms are attacked by sulphur atoms but the result is dramatic, is a good example of such an extremely strong response to a very small change in the composition.

The structures and objects typical of soft matter may show *mesoscopic* scales of dimensions: from atomic to macroscopic ones. Also, for all phenomena taking place in soft materials, the importance of thermal fluctuations, including Brownian motions, should be underlined. Finally, the typical behaviour of molecules in soft matter shows the fundamental importance of self-organization (*self-ordering, self-assembly*) phenomena and processes, leading to the creation of a variety of different phases, hierarchic structures and other fascinating objects.

Polymers: three selected ideas of de Gennes

The achievements of P.G. de Gennes in the field of polymer physics are so great that only three selected examples of his

work may be shown in this article. These achievements have been summarized in the very famous textbook ‘Scaling Concepts in Polymer Physics’ [3].

Polymer melts: molten chains are ideal – a self-consistent field argument

The basic points of de Gennes’s implication are as follows:

- consider a dense system of chains
- focus on one ‘white’ chain
- study the repulsive potential U experienced by the white monomer; it is proportional to the local concentration c_1 of monomers, so the force is pointing outwards:

$$F \sim -\partial U/\partial x;$$

- the ‘black’ potential creates an inward force, exactly equal to the force caused by the white monomers since U_{tot} is constant in space:

$$\partial U_{\text{tot}}/\partial x \equiv 0,$$

so the chain experiences no force and remains ideal.

Polymer solutions in good solvents: the notion of blobs

The ‘blob’ model of de Gennes states that a certain typical segment of a chain can move as if it were free, even in more concentrated solutions. The outline of his idea is explained below:

- consider the solution shown in a certain time – a network with an *average mesh size* ζ ;
- it is shown that $\zeta(\Phi) \approx a \Phi^{-3/4}$, where a – monomer size, Φ – polymer fraction;
- focus on one particular chain;
- one may visualize it as a succession of ‘blobs’ of size ζ ;
- inside one blob – from the definition of the mesh size – the chains do not interact with other chains;
- thus, inside one blob there are correlations of the excluded volume type;

- this implies that the number of monomeric units per blob g is related to ζ by the law of swollen coils:

$$\zeta \approx a g^{3/5}, \text{ so}$$

$$g = (\zeta/a)^{5/3} = \Phi^{-5/4} \text{ and}$$

$$g = c \zeta^3 \text{ (} c \text{ – concentration).}$$

- This equation says that the solution is essentially a *closely packed system of blobs*.
- If we take the blobs as the basic units, we go back to the molten chain problem, so from the Flory theorem that the chains are ideal on a large scale, their mean square end-to-end size can be estimated from the ideal chain formula for N/g blobs of size ζ :

$$R^2(\Phi) = (N/g) \zeta^2 \approx N a^2 \Phi^{-1/4}.$$

Dynamics of chains: reptation of a single chain

This is perhaps the most famous idea of de Gennes in the field of polymer physics. His model starts with the following observation:

- Assume that we have one linear chain moving in a given network, described by fixed obstacles;
- the chain can move in between in a wormlike fashion. We call this *reptation*.
- It is convenient to think of the chain as being trapped in a certain *tube*;
- of course, the chain leaves some parts of the tube, and it ‘creates’ some new parts.
- This allows the prediction of some scaling laws:
let μ_1 – mobility of one segment of a chain, μ_{tube} – mobility of a whole chain;
■ $\mu_{\text{tube}} = \mu_1 / N$, because the friction force v/μ_{tube} must be $\sim N$.
- From the relation of Einstein and Smoluchowski:

$$D_{\text{tube}} = \mu_1 kT / N$$

(D_{tube} – ‘tube diffusion coefficient’),

- Because the chain must progress by tube diffusion over a length comparable with its overall length L , the corresponding time is:
 $\tau_1 \approx L^2 / D_{\text{tube}}; L \sim N \rightarrow \tau_1 \sim N^3!$
- This implies that the viscosity coefficient $\eta \sim m^3$, where m – molar mass.

Liquid crystals

P.-G. de Gennes was always very interested in order – disorder transitions and relations. He was able to show that phase transitions in such apparently widely differing physical systems as magnets, superconductors, liquid crystals (LC) and polymer solutions can be described in mathematical terms of surprisingly broad generality.

Considering the achievements of de Gennes in the field of physics of liquid crystals, only a few points can be indicated here:

- One has the excellent example of the strong response, typical of soft matter, mentioned above: the molecules in a liquid crystal display are triggered every second by extremely small electric signals;
- The Landau–de Gennes theory of liquid-crystalline order is one of fundamental part of the physics of liquid crystals;
- ‘The Physics of Liquid Crystals’ – this textbook, written by de Gennes, is still one of the basic references in this field [4];

The problem of anisotropy of viscosity should be explained here. For the first time, it was solved by Dr Marian Mięśowicz (1907-1992) in the year 1935, working in the Department of Physics at the Academy of Mining (now: AGH-UST), Krakow. He performed some experiments with the oscillations of a balance, damped by a plate placed in LC. He was able to show that the viscosity coefficients of LC strongly depend on the orientation of molecules (which are possible to orientate by magnetic field). For *p*-azoxyphenetol, at the temperature $T = 144.4$ °C, he obtained: $\eta_1 = 1.3$ mPa s, $\eta_2 = 8.3$ mPa s and $\eta_3 = 2.5$ mPa s, for various orientations of LC molecules. These research works were reported in two articles published in ‘Nature’ (1935, 1946: ‘The Three Coefficients of Viscosity of Anisotropic Liquids’ [5]) and now in the literature so-called ‘Mięśowicz [Mięśowicz] coefficients’ are widely used. Here, the most interesting point is that, for the first time, this notion was introduced by P.-G. de Gennes in his textbook!

Surfactants

The term *surfactants* comes from the abbreviation of: ‘surface active agents’; the other name for this type of material is *amphiphiles*. Both names describe frustrated molecules, with one part that likes water (*hydrophilic*) and one part that likes oil and hates water (*hydrophobic* or *lipophilic*). Such molecules are attracted to an oil–water interface and also an air–water interface, where they significantly decrease the surface tension. Thus, they facilitate the making of foams, emulsions, etc. For increasing concentrations of surfactants, one finds that some associations occur, in the forms of: *spherical micelles*, *lamellar phases*, *vesicles (liposomes)* and *sponge phases*. It should be underlined that these problems are quite close to the field of biology, so the soft matter physics appears to be one of the main gateways to such interdisciplinary research.

Colloids

Colloid means ultra-divided matter: one phase is somehow dispersed in the other phase, and the average size of such dispersed particles is in the range of 1-100 nm. All basic types of colloids are collected in the following table:

dispersed in:	gas	liquid	solid
gas	–	foam	porous solid, aerogel
liquid	aerosol (fog)	emulsion	gel
solid	aerosol (smoke)	suspension, sol	–

At least two examples of colloidal soft material should be briefly underlined:

- Foams represent an extremely interesting phase for theoretical and experimental research. The problems related to the structure and evolution of foam still produce a lot of fundamental and important articles, published in the most prestigious journals (for example, see [6]).
- Porous solids and aerogels are excellent objects for SAXS measurements; therefore, during several conferences of the XIPS series, some very interesting results concerning this topic have been presented.

Concluding remarks

It is justifiable to conclude this commemorating paper with the citation of two sentences written by de Gennes at the end of his article, mentioned above [2]. Let these words represent the final conclusion:

- “Soft matter, as we defined it, represents the *science of everyday life* – and, as such, it should take an increasing share in our educational system”.
- “Insects (temporarily) lost their grasp on the Earth, because of their clumsy, hard, crust. Humans won when their **soft** hands allowed them to make tools; this ultimately led them to expand their brains, and to think. **Soft is beautiful.**”

References

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Received 23.05.2008 Reviewed 23.05.2008
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