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Dedicated to Prof. Igor Čatić, PhD, on his 70th birthday

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Importance of Boscovich's theory of natural philosophy for polymer science

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Summary

It has been generally accepted that the macromolecular hypothesis was for the first time presented by H. Staudinger (1920.). It is shown in this article, however, that Roger Boscovich, in his monumental work *Theory of natural philosophy*, pointed out, as early as the 18th century that the spiral atomic chains could be formed. He also pointed out that the shape of the chain could be considerably changed due to slight changes of the distances between atoms, as well as that these sequences of atoms have elastic properties. The author of this article also presented some examples of the applications of Boscovich's theory to the interpretation of free-radical polymerization of compressed ethylene gas and liquid methyl methacrylate. The priority of Boscovich's macromolecular hypothesis is unquestionable and his theory is still applicable in the current polymer science.

KEYWORDS:
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Roger Boscovich
theory of natural philosophy

KLJUČNE RIJEČI:
makromolekularna hipoteza
Ruđer Bošković
teorija prirodne filozofije

Važnost Boškovićeve teorije prirodne filozofije za polimerijske znanosti

Sažetak

Opće je prihvaćeno mišljenje da je otac hipoteze o postojanju makromolekula Nijemac Staudinger (1920.). Međutim, u ovom radu je pokazano da je Ruđer Bošković, još u 18. stoljeću, u svom monumentalnom djelu Teorija prirodne filozofije, ukazao na mogućnost nastajanja spiralnih nizova atoma i da se taj oblik može znatno mijenjati uslijed malih promjena razmaka između atoma te da ti nizovi atoma imaju elastična svojstva. Autor ovog rada je također naveo primjere primjene Boškovićeve teorije za tumačenje slobodno-radikalne polimerizacije stlačenog plinovitog etilena i kapljevitog metilmetakrilata. Nesumnjiv je primat Boškovićeve makromolekulske hipoteze, a njegova teorija je i danas primjenljiva u znanosti o polimerima.

Introduction

It is generally accepted that the macromolecular hypothesis was presented for the first time by Hermann Staudinger in 1920.[1] This elementary concept did not gain widespread acceptance before 1930, and vestiges of contrary views lingered on for more than a decade thereafter.

In this article, however, we would like to show that Roger Boscovich (1711-1787) was the very first one who announced a macromolecular hypothesis in his famous *Theoria philosophiae naturalis*[2] as early as in 1758. Hence, we will present an outline of his theory and its confirmation by the contemporary science achievements. The macromolecular hypotheses of Boscovich as well as some of our applications of the theory will also be presented here.

Boscovich's *Theory of natural philosophy*

Boscovich held the matter to be discrete. The elementary particles of which matter is built were held to be the *non-extended points*. Depending on the distance between the points, there are determinations between them to be attracted or repelled, i.e. there are the attractive or the repulsive forces. If the distance between the points is very large there is an attractive force between them. With the decrease of distance, however, the repulsion force appears, than the attractive force again and so on, several times (Figure 1a).[2] At very small distances the force is repulsive and prevents contact of the particles. The number of attractive and repulsive arches, their height and shape can be different (Figure 1b and 1c). These curves were published by Boscovich for the first time[3] in 1745 and explained in more detail[2] in 1758.

The elementary points are combined producing the more complex particles of first order; the first order particles are combined producing the second order particles, etc. Then atoms, molecules, bodies are formed. Whatever the level of the particles, the same law of forces (Figure 1) can explain the interaction between them.

Macromolecular hypothesis in Boscovich's theory of natural philosophy

Having in mind his force-distance curves, Boscovich suggested (paragraph 440 in ref. 2) that the atoms could be connected: »In such a way *atoms might be formed like spirals; and, if these spirals were compressed by a force, a very great elastic force or propensity for expansion* would be experienced.« Also, he wrote: »...by a very *slight change of each the distance* in a very *long series of points* there might be obtained a *bending of the figure of comparatively large amount, due to a large number of these slight bends.*« (In these citations some words are in italic given by DS.)

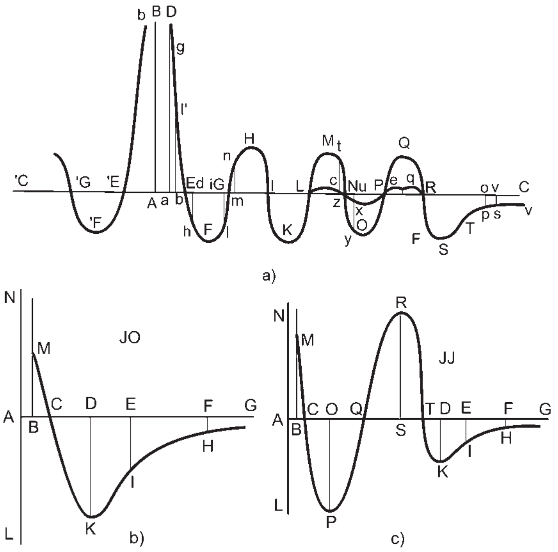

FIGURE 1. General (a) and some particular (b, c) shapes of Boscovich's curves that present the attractive and repulsive forces (bottom and upper ordinates, respectively) vs. distance (abscissa) between the elementary points of matter[2,3]

Let us consider some details of these statements of Boscovich. He suggested that the *series of points* and *spirals* of atoms could be formed. This is a macromolecular hypothesis, indeed. The statements that the series could be *long* and the large *number* of slight bends mean that Boscovich proposed a high degree of polymerization.

Furthermore, he proposed *a spiral* shape of the atomic chains, i.e. the spiral conformation of macromolecular chains. Today we know that such structures have been confirmed in the natural as well as the synthetic polymers (Figure 2.). A "*slight change of each distance*" and the "*slight bends*" in a "*very long series of points*" resulting in a "*bending of the figure of comparatively large amount*" could be understood as a change of macromolecular conformation due to the rotation around chemical bonds in the macromolecular chain backbone.

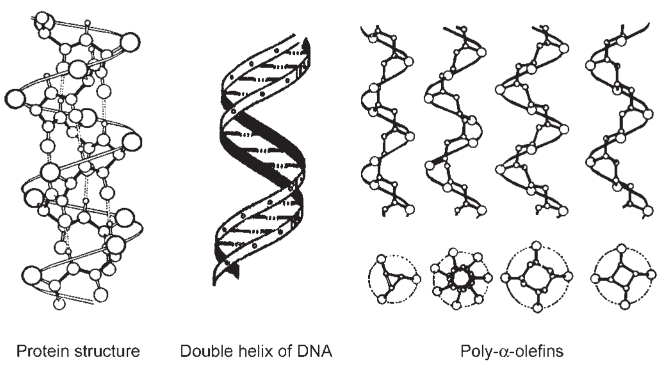

FIGURE 2. Spiral structures of some natural and synthetic macromolecular chains

Furthermore, the *elastic* properties as well as the *propensity of expansion*, suggested by Boscovich, are the well known characteristics of some macromolecular materials.

Thus, Boscovich suggested all the basic characteristics of macromolecules: the chain structure, the high degree of polymerization, the possibility of spiral chain conformation, the change of the conformation as a result of the slight bendings of chemical bonds and also the elastic properties of macromolecular materials. It was done almost two centuries before Staudinger launched his macromolecular hypothesis.

But, how is the interaction between the two macromolecular chains explained by the contemporary polymer science? It is presented in Figure 3. The modern explanation of interaction enthalpy and entropy is the same as Boscovich's curve (Figure 1)!

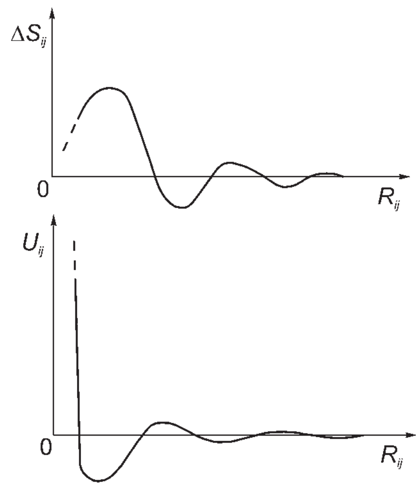

FIGURE 3. Entropy *(Sij)* and enthalpy *(Uij)* change by distance *(R)* between two macromolecular chains (*i* and *j*)[4]

Our applications of Boscovich's theory of natural philosophy

We have applied Boscovich's theory a number of times to solve some problems of polymer science and practice. Only a short outline of these applications will be presented here.

Physical meaning of cohesion and non-cohesion limits on the molecular scale

We applied and adopted the theory of Savić-Kašanin[5] to derive a very simple mathematical model for the calculation of specific volume of matter whose molecules are at the cohesion (Fig. 1, points E, I, N and R) or at the non-cohesion (Fig. 1, points G, L and P) limits.[6] It was proved for 143 substances that the cohesion and non-cohesion limits correspond to the characteristic states of matter such as critical point, triple point, absolute zero temperature etc. These states are the inherent properties of matter, which do not depend on the pressure and temperature.

Free radical polymerization of compressed ethylene gas

Ethylene molecule has a double bond and can be polymerized by a free radical mechanism producing low density polyethylene (PE-LD): R• + $CH_2{=}CH_2 \rightarrow R{-}CH_2{-}CH_2$. This process was discovered in 1933 by the company ICI. The peculiarity of this simple polymerization, however, is that it can be performed only if the ethylene gas is compressed to a very high pressure. Typical polymerization conditions in the industrial plants are in the ranges of 1 000-3 000 bar and 150-300 °C. Why it is necessary to have such high pressure was an open question for many decades after the process has been discovered. It was suggested by Hunter[7] that ethylene molecules were regularly packed, properly oriented and highly distorted at polymerization conditions. He concluded that a supra-molecular organization of ethylene is a prerequisite for polymerization.

There was no explanation, however, how the molecules were packed, oriented and distorted. Usually, the ethylene molecules interaction is presented by Lennard-Jones potential curve (published in 1924), which is similar to the Boscovich's curve presented in Figure 1b (published in 1745). Instead of that, we proposed that Boscovich's curve presented in Figure 1c or 1a should be more appropriate. On the basis of that proposal, the supra-molecular particles of compressed ethylene were suggested. The existence of these particles and the higher order phase transitions in compressed ethylene have been confirmed by the thermodynamic, physical and spectroscopic methods. The effects of the supra-molecular particles on the mechanism and kinetics of polymerization as well as on the structure and properties of polyethylene have been published by us.[8,9]

Effect of pressure on melting temperature of low density polyethylene (PE-LD)

Effect of pressure on melting temperature of PE-LD is of a great importance for PE-LD processing. Knowing the supra-molecular organization of compressed ethylene gas it was possible to predict this effect by the law of continuity published by Boscovich[10] in 1754: The phase transitions in compressed ethylene and in compressed polyethylene should occur at the same pressure-temperature conditions. This prediction has been confirmed by the empirical data.[9]

Supra-molecular organization and polymerization of liquid methyl methacrylate (MMA)

Free radical polymerization of liquid MMA has been frequently investigated because of the very pronounced auto-acceleration phenomena known as the *gel effect* or *Norrish-Trommsdorff effect*. Boscovich suggested that the interactions of particles in a liquid should be presented by curve presented in Figure 1c. According to the present knowledge, a liquid consists of ordered and disordered domains. Knowing the specific volume of liquid MMA and using the mathematical model,[6] the fractions of order and disorder domains in MMA were calculated.[11] Then we polymerized MMA and proved experimentally that the calculated fractions were equal to the experimentally determined fractions of polymerized monomer in ordered and disordered domains. In addition to that, some other characteristic points on the *monomer conversion - time* curve were theoretically predicted and confirmed experimentally.

Conclusion

This article shows that Roger Boscovich, in his monumental work *Theory of natural philosophy*, as early as in the18th century, pointed out that the spiral atomic chains could be formed. He also pointed out that the shape of the chain could be markedly changed due to slight changes of the distances between atoms. The elastic properties of the chains have been stressed. Furthermore, the interaction between two polymer chains could be as suggested here described by Boscovich's curve. The priority of Boscovich's macromolecular hypothesis is unquestionable and his theory is of some use, as it is shown here, in applications to the modern polymer science.

We have presented here only the scientific issues of Boscovich's theory and its importance for the polymer science. His theory is of greatest significance for other scientific fields, such as the particle theory[12-14], the electric and magnetic field theory[15] and the quantum mechanics.[16] Great contributions have been made to mathematics, astronomy, theory of relativity, optics and physics of elementary particles[17,18] on the basis of Boscovich's theory; it is quite reasonable to conclude (as was done by Gill[18]) that Boscovich is the forerunner of modern physical theories. Very important is the philosophical background of his theory, too. It is out of scope of this article to enlighten this issue. A good insight in Boscovich's philosophy has been presented elsewhere.[19-21] Attraction and repulsion are the essence of the matter not only for Boscovich, but for Kant, Hegel and Engels, too.[22] We would like also to mention that Werner Heisenberg in 1958 placed even greater emphasis on the importance of Boscovich's ideas for the 20th century science: *The remarkable concept that forces are repulsive at small distances, and have to be attractive at greater ones, has played a decisive role in modern atomic physics*. *Heisenberg* also stressed that *Boscovich's* ideas are still present in modern science: »His main work, *Theoria Philosophiae Naturalis* contains numerous ideas which have reached full expression only in modern physics of the past fifty years, and which show how correct the philosophical views were which guided Boscovich in his studies in the natural sciences.«[17]

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