DRAGOSLAV STOILJKOVIĆ
University of Novi Sad, Faculty of Technology
21000 Novi Sad, Bul. Cara Lazara 1, Serbia
e-mail: dragos@uns.ns.ac.yu

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

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", as early as in the 18th century, pointed out that the spiral atomic chains could be formed. He also pointed that the shape of the chain could be markedly changed due to slight changes of the distances among the atoms. The elastic properties of the chains have been stressed. The author of this article also presented some examples of the applications of Boscovich's theory for the interpretation of free-radical polymerization of compressed ethylene gas and liquid methyl methacrylate. The priority of Boscovich's macromolecular hypothesis is doubtless and his theory is still applicable in the current polymer science.

Key words: Roger Boscovich, theory of natural philosophy, macromolecular hypothesis, high-pressure polymerization of ethylene, polymerization of methyl methacrylate.

ZNACZENIE TEORII NATURALNEJ FILOZOFII BOSCOVICHA DLA WIEDZY O POLIMERACH

Streszczenie — Na podstawie przeglądu literatury z okresu XVIII—XXI wieku wykazano, że Roger Boscovich, autor fundamentalnej teorii filozofii (rys. 1), już w XVIII w., w ramach tej teorii, jako pierwszy przewidział możliwość formowania się spiralnych łańcuchów atomowych — których kształt w znacznym stopniu zależy od bardzo niewielkich zmian odległości pomiędzy atomami — a także możliwość występowania elastycznych właściwości takich łańcuchów (rys. 2—5). Przedstawiono również niektóre potwierdzone przez zespół Autora niniejszego artykułu przykłady owocnych zastosowań teorii Boscovicha do interpretacji wyników rodnikowej wysokociśnieniowej polimeryzacji gazowego etylenu oraz polimeryzacji ciekłego metakrylanu metylu (rys. 9—11). Priorytet makromolekularnej hipotezy Boscovicha nie podlega żadnej wątpliwości a jego teoria może wciąż jeszcze znajdować zastosowanie w interpretacji osiągnięć współczesnej nauki o polimerach.

Słowa kluczowe: Roger Boscovich, teoria filozofii naturalnej, hipoteza makromolekularna, wysokociśnieniowa polimeryzacja etylenu, polimeryzacja metakrylanu metylu.

The hypothesis that high polymers are composed of covalent structures many times greater in extent than those occurring in simple compounds, and that this feature alone accounts for the characteristic properties which set them apart from the other forms of matter, is in large measure responsible for the rapid advances in the chemistry and physics of these substances observed in recent years. It is generally accepted that the macromolecular hypothesis was presented for the first time by Hermann Staudinger in 1920 [1]. »Dear Colleague, leave the concept of large molecules well alone... there can be no such things as a macromolecule« was a comment on Staudinger's evidences on the macromolecule concept [2]. This elementary concept did not gain widespread acceptance before 1930, and vestiges of contrary views remained for more than a decade thereafter.

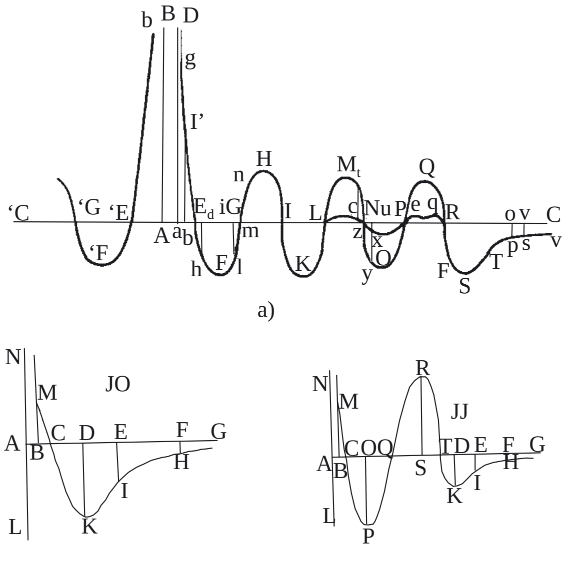
In this article, however, we would like to show that Roger Boscovich (1711-1787) was very first one who announced a macromolecular hypothesis in his famous "Theoria philosophia naturalis" [3] as early as in 1758. Hence, an outline of his theory and its confirmation by contemporary science achievements, the macromolecular hypothesis of Boscovich as well as some our applications of the theory are 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 non-extended points. Depending on the distance between the points, there are the determinations between

---

*) A part of the article has been presented on the conference "The past and the future of polymer engineering, technology, and science" organized on the occasion of 70th birthday of Prof. Igor Čatič, Society of Plastics and Rubber Engineers, Zagreb (Croatia), April, 27—28th, 2006.



a)

(b) (c)

Fig. 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 [3, 4]

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 in a distance, however, the repulsion force appears, than the attractive force again and thus several times (Fig. 1a) [3]. At very small distances the force is repulsive and prevents a contact of the particles. The number of attractive and repulsive arches, their height and shape can be different (Fig. 1b and 1c). These curves were published by Boscovich for the first time [4] in 1745 and explained in more detail [3] 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 force law (Fig. 1) can explain the interaction between them.

Boscovich emphasized the importance of distances at which the curve crosses the abscissa (E, G, I, L, N, P and R), *i.e.* the attractive and repulsive forces are equal. Should the particle find itself at point R and recede a little towards F, it would return towards R because it would have found itself in a region where the force was attractive. If, conversely, it recedes from R towards Q, it will again return towards R because it is now in the region of the repulsive force. The distances R, N, I and E represent the stable positions, named by Boscovich as the limits of cohesion.

The case of point P is different. Namely, if a particle at P should recede towards Q, it would find itself in the region of the repulsive force, and it would recede from P and approach R. If it should recede from P toward O, it would find itself in the region of the attractive force, and would approach N. The distances P, L and G are the unstable positions, named by Boscovich as the limits of non-cohesion.

REFLECTIONS OF BOSCOVICH'S NATURAL PHILOSOPHY IN CURRENT SCIENCE

In 1902 Lord Kelvin noted that different properties of the atom may be explained by Boscovich's theory: "...and as we are assuming the electrons to be all alike, we must fall back on Father Boscovich, and require him to explain the difference of quality of different chemical substances by different laws of forces between the different atoms." In 1907 Lord Kelvin was already quite sure that Boscovich's theory could be applied to explain phenomena in the interior of the atom, and declared: "My present assumption is Boscovichianism pure and simple" [5].

Joseph John Thompson (1856-1940) was inspired by Boscovich's theory to propose the structure of atom. If Boscovich's law of forces is applied on the atomic scale, the electrons may find themselves at the distances from the positively charged nucleus that will correspond to the distances of Boscovich's limits of cohesion. In those cases the electrons will be in equilibrium with the nucleus and will remain stable in the circular orbits. This model of atom was experimentally confirmed in 1909—1911 by Ernest Rutherford and further developed by Niels Bohr that also accepted the concepts of discrete orbits of electrons. Accordingly, Kelvin's and Thompson's hypothesis, based on Boscovich's ideas, inspired the studies and conclusions of Rutherford and Bohr. Boscovich's theory can thus be said to have indirectly contributed to the development of modern concepts of electronic structure of atoms [5].

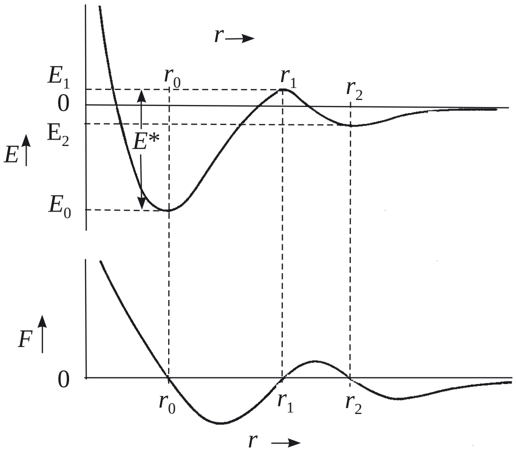


Fig. 2. Potential energy diagram that illustrates the dependence of the potential energy E on the distance of separation r of two atoms [8]. The bottom diagram is the corresponding force F acting between the atoms, obtained from the relation $F = -\partial E/\partial r$

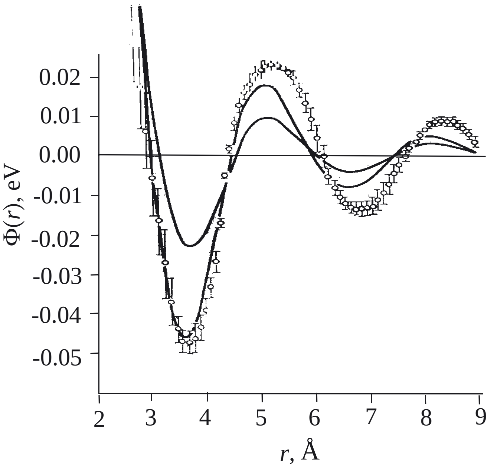


Fig. 3. Change of potential energy $\phi(r)$ as a function of the distance r between two atoms of liquid sodium [9] (solid lines are the theoretical calculations; the points are the experimental values)

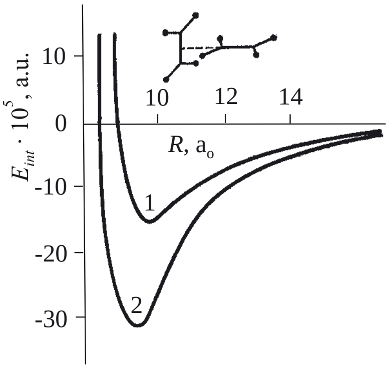


Fig. 4. Curves of potential energy E_{int} as a function of distance R between two ethylene molecules [10] (the curves 1 and 2 are theoretically calculated by two different methods); E_{int} is in atomic units (A.U.), where A.U. = $2.6253 \cdot 10^6$ kJ/mole; R is in a_0 units, where $a_0 = 5.2918 \cdot 10^{-7}$ cm

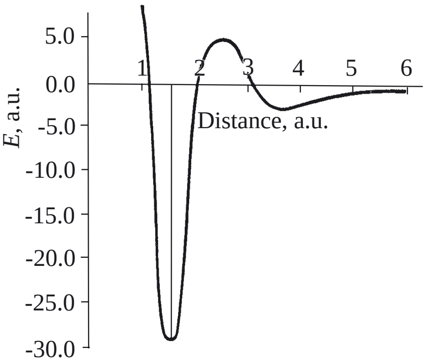


Fig. 5. Potential energy E as a function of the distance between an adsorbate molecule from the surface, i.e. transition from the physical to the chemisorption [11] (arbitrary units for E and distance)

Numerous achievements of modern science show that Boscovich was right in many respects, especially where his curve of forces is concerning. New scientists usually no longer mention Boscovich, and perhaps they no longer find him a source of stimulation in their explanations of specific phenomena, but there is no doubt that their results can be remarkably related to Boscovich. Several dozens of examples have been presented [5—7] to confirm the similarity of Boscovich curves (Fig. 1) with the corresponding curves found in the literature published in 20th and 21st century.

These curves describe the interactions of particles in a wide range of the hierarchy of matter: the interaction of nucleons, the interaction of nucleon and lambda hyperon, the fission of heavy atomic nuclei, the chemical (Fig. 2) and physical (Fig. 3) interactions of atoms, the interactions of molecules (Fig. 4), the adsorption phenomena (Fig. 5), the interaction of charged colloidal particles as well as the interaction of two clay particles, etc. The similarity of the current interaction curves with Boscovich's curves (Fig. 1) is evident. The only difference is that the energy (E) is presented on ordinates, instead of force (F) as it was done by Boscovich. Knowing that there is relation $F = -\partial E/\partial r$, however, an energy curve can be easily transformed to force curve: the minimum and maximum values of energy curves correspond to the limits of cohesion and non-cohesion on Boscovich's force curve (Fig. 2).

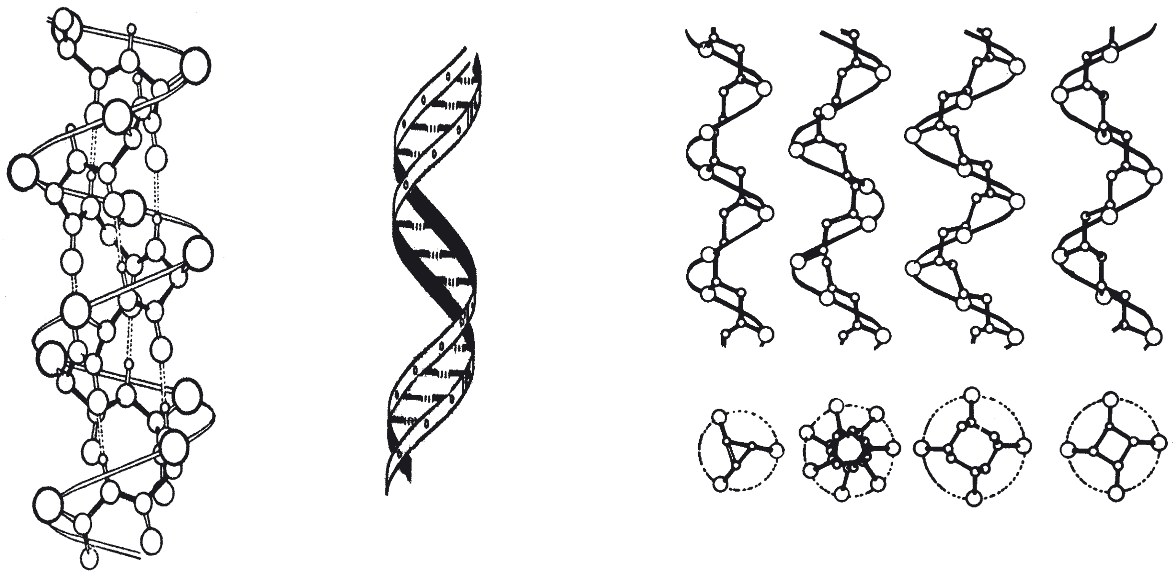
On the base of Boscovich's theory the great contributions have been made in mathematics, astronomy, theory of relativity, optics and physics of elementary particles [5, 12], so it is quite reasonable to conclude that he was the forerunner of modern physical theories, as it was done by Gill [13].

MACROMOLECULAR HYPOTHESIS IN BOSCOVICH'S THEORY OF NATURAL PHILOSOPHY

Having in mind his force-distance curves, Boscovich suggested (paragraph 440 in ref. [3]) 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, there would be experienced *a very great elastic force or propensity for expansion*." 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 bendings*." (In these citations some words are in italic given by the author of this text).

Let us consider some details of these Boscovich's statements. He suggested that *long series of points* could be formed, the shape of which might be *like spirals* of atoms. This is a macromolecular hypothesis, indeed. Today we know that such structures have been confirmed in the natural and the synthetic polymers, too (Fig. 6).

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



Protein structure Double helix of DNA Poly-α-olefins

Fig. 6. Spiral structures of some natural and synthetic macromolecular chains

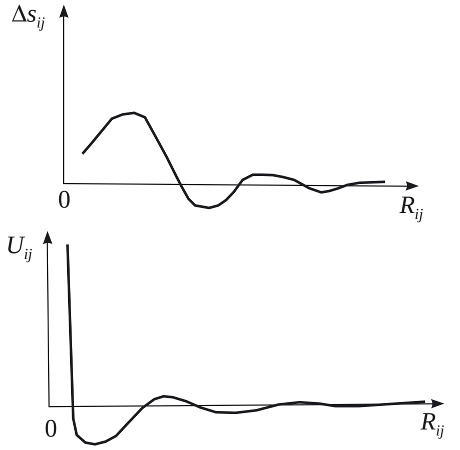


Fig. 7. Entropy (Sij) and enthalpy (Uij) changes with a distance (R) of two macromolecular chains (i and j) [14]

A *slight change of each distance* and the *slight bendings* 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.

Thus, Boscovich suggested all the basic characteristics of macromolecules: the chain structure, 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 had been done almost two centuries before Staudinger launched his macromolecular hypothesis.

But, how the interaction between the two macromolecular chains is explained by the current polymer science? It is presented in Fig. 7. The current explanation of interaction enthalpy and entropy is the same as Boscovich's curve (Fig. 1)!

OUR APPLICATIONS OF BOSCOVICH'S THEORY OF NATURAL PHILOSOPHY

Several times we have applied Boscovich's theory 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

It has been explained that Kelvin, Rutherford, Thompson and Bohr accepted Boscovich's law of forces, applied it in the atomic scale and suggested that the electrons may find themselves on the distances from the positively charged nucleus that will correspond to the distances of Boscovich's limits of cohesion. This is physical meaning of cohesion limits on the intra-atomic scale. Here we presented several examples (Fig. 2—5, 7) that Boscovich curve is valid in the higher scales, too: interatomic, molecular, supra-molecular and macromolecular scales. The examples for the lower then atomic scales have been presented elsewhere [5—7]. There are also cohesion and non-cohesion limits in these scales. It was quite reasonable for us to propose that these limits should have some physical meanings, too.

We applied and adopted the theory of Savich-Kashanin [15] to derive a very simple mathematical model for the calculation of specific volume of matter whose molecules were at the cohesion or at the non-cohesion limits (Fig. 8) [16]. The left side of each step corresponds to some cohesion, the right side — to some non-cohesion

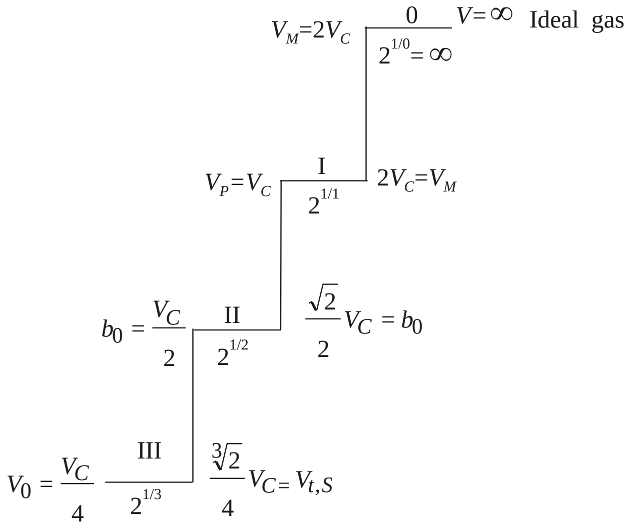


Fig. 8. Specific volume of matter which molecules are at the cohesion and non-cohesion limits (V_M — volume occupied by molecule rotation, V_C — critical volume, b_o — hard sphere volume, b — co-volume in the van der Waals equation of state, $V_{t,s}$ — volume of the solid phase at the triple point, V_o — volume at absolute zero temperature) [16]

limit. We have proved for 92 substances that the outermost cohesion limit (position R in Fig. 1a) corresponded to the volume at critical point (V_c). The other volumes represent the characteristic volumes of a matter, *i.e.* inherent properties of a matter, which do not depend on the pressure and temperature. It was proved for 143 substances that there was very good agreement of the empirical values with calculated ones by the model presented in Fig. 8 [16].

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): $R\bullet + CH_2{=}CH_2 \rightarrow R{-}CH_2{-}CH_2\bullet$. This process was discovered in 1933 by the ICI company. 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. A 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 the many decades after the process has been discovered. It was noticed by Hunter [17] that the density of ethylene gas at polymerization condition was about 0.46 g/cm^3. This value exceeds the density of the randomly and loosely packed ethylene molecules, *i.e.* 0.28 g/cm^3. Hunter concluded that ethylene molecules were regularly packed, properly oriented and highly distorted at polymerization conditions. He suggested that a supra-molecular organization of ethylene is a prerequisite for polymerization.

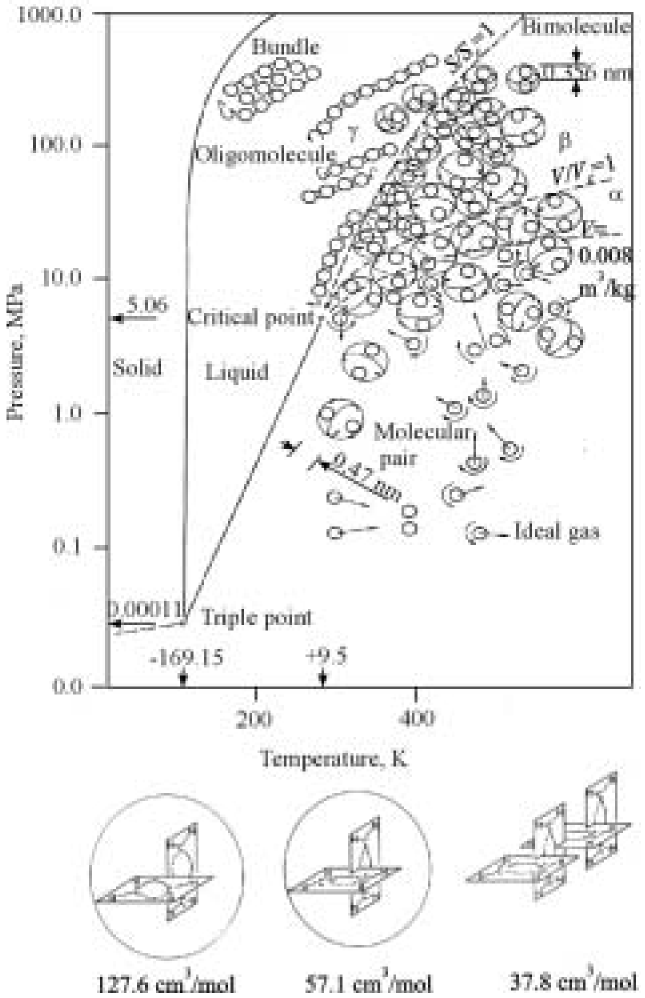


Fig. 9. Phase state (top) and supra-molecular species (bottom) and their volumes (empirical values) of compressed ethylene gas (molecular pair, bimolecule and oligomolecule, respectively) [18—23]

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 curve presented in Fig. 4 and to the Boscovich curve presented in Fig. 1b (published in 1745). The empirical value of the distance between the ethylene molecules at minimum potential energy is r_e = 0.466 nm. At lower distances, a high repulsive force is usually expected. The density of ethylene having the molecules separated by 0.466 nm is 0.22 g/cm^3. This value is two times lower than the density at polymerization conditions. It means that ethylene molecules could come at distance lower than 0.466 nm. Hence, we proposed that Boscovich's curve presented in Fig. 1c or 1a should be more appropriate. On the base of that proposal, the supra-molecular particles of compressed ethylene were suggested (Fig. 9). Their volumes were calculated by our mathematical model (Fig. 8) and amount 127.6, 63.8 and 40 cm^3/mole for the molecular pair, the bimolecule and the oligomolecule, respectively. These values are very close to the empirical values for these particles: 127.6, 57.1 and 37.8 cm^3/mole, respectively. 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 in [18—23].

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 the continuity published by Boscovich [24] 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 (Fig. 10) [23].

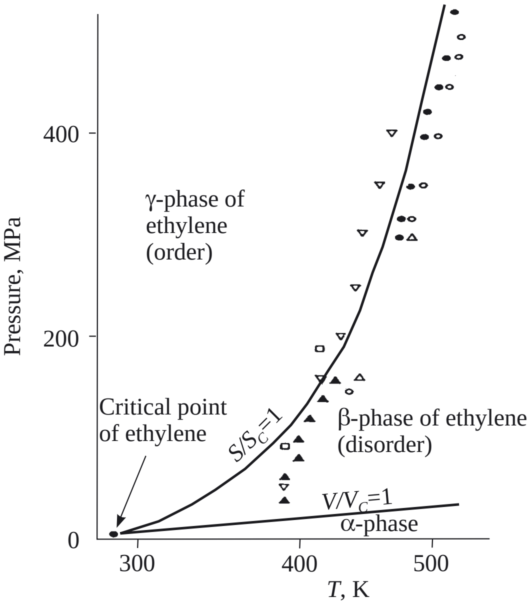


Fig. 10. Phase transitions in compressed ethylene gas (solid line S/S$_c$ = 1) and in compressed polyethylene (points) [23]

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 phenomenon 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 Fig. 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 presented in Fig. 8, it was possible to calculate the fractions of ordered and disordered domains in MMA (Fig. 11) [25]. Then we polymerized MMA at different temperatures. According to the theory of organized monomer polymerization [26], initially the monomer molecules in disordered domains should polymerize followed by polymerization of monomer in ordered domains. We have proved experimentally that the calculated fractions are equal to the experimentally determined fractions of polymerized monomer in ordered and disordered domains (points in Fig. 11). In addition to that, some other characteristic points at monomer conversion — time curve were theoretically predicted and confirmed experimentally.

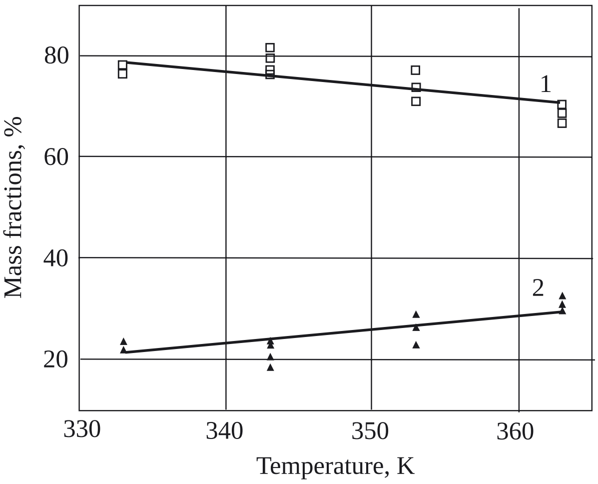


Fig. 11. Fractions of ordered (line 1) and disordered (line 2) domains of liquid MMA at different temperatures predicted by calculation; points experimentally determined by polymerization [25]

CONCLUSION

It is shown in this article that Roger Boscovich, in his monumental work "Theory of natural philosophy", as early as in the 18th century, pointed out that the spiral atomic chains could be formed. He also pointed that the shape of the chain could be markedly changed due to slight changes of the distances among the atoms. The elastic properties of the chains have been stressed. Furthermore, the interaction between two polymer chains is described by Boscovich's curve. The priority of Boscovich's macromolecular hypothesis is doubtless and his theory is still applicable in the current polymer science.

Here we presented only the scientific issues of Boscovich's theory and its importance for polymer science. His theory is of the greatest significance for the other scientific fields, such as the particle theory [27—29], the electric and magnetic field theory [30] and the quantum mechanics [31]. Very important is the philosophical background of his theory. It is out of scope of this article to brief on this issue. A good insight in Boscovich's philosophy has been presented elsewhere [32—34]. Attraction and repulsion are the essence of the matter not only for Boscovich, but for Kant, Hegel and Engels, too [35].

We would like also to mention that Werner Heisenberg in 1958 placed even greater emphasis on the importance of Boscovich's ideas for 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 the Boscovich's ideas were 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 were the philosophical views which guided Boscovich in his studies in the natural sciences" [5].

REFERENCES

1. Flory P.: "Principles of Polymer Chemistry", Cornell University Press, Ithaca, New York, 1953, p. 3.
2. Billmayer F. W.: "Texbook of Polymer Science", Wiley, New York, 1970.
3. Boscovich J. R.: (a) "Theoria philosophia naturalis redacta ad unicam legem virium in natura existentium", first (Wien, 1758) and second (Venetiis, 1763) edition in Latin language; (b) "A Theory of Natural Philosophy", in English, The M.I.T. Press, Massachusetts Institute of Technology, Cambridge, Massachusetts and London, England, 1966; (c) "Teorija prirodne filozofije svedena na jedan jedini zakon sila koje postoje u prirodi", bilingual in Latin and in Croatian languages, Liber, Zagreb, 1974.
4. Boscovich J. R.: "De viribus vivis", Komarek, Romae, 1745.
5. Dadić Ž: "Ruđer Bošković", bilingual in English and in Croatian languages Školska knjiga, Zagreb, 1987.
6. Stoiljković D.: *Polimeri* 1983, **4**, No. 9—10, p. 289.
7. Stoiljković D.: *Vasiona* 2005, **53**, No. 2—3, p. 77.
8. Benson S. W.: "The Foundations of Chemical Kinetics", McGraw-Hill, New York, 1960, p. 213.
9. Croxton C. A.: "Liquid State Physics — A Statistical Mechanical Introduction", Cambridge University Press, Cambridge, 1974, p. 227.
10. Kaplan I. G.: "Vvedenie v teoriyu mezhdumolekulyarnikh vzaimodeistvii", Nauka, Moskva, 1982, p. 175.
11. Gaylord N. G., Mark H.: "Linear and Stereoregular Addition Polymers", Interscience, New York, 1959.
12. White L. L.: "Roger Joseph Boscovich", George Allen and Unwin, London, 1961.
13. Gill H. V.: "Roger Boscovich — Forerunner of Modern Physical Theories", M. H. Gill and Sons, Dublin, 1941.
14. de Gennes P. G.: "Scaling Concepts in Polymer Physics", Cornell University Press, Ithaca, 1979.
15. Savić P., Kašanin R.: "The Behaviour of the Materials under High Pressures", Serb. Acad. Sci. Arts, Monographs, Section for natural sciences and mathematics, Belgrade, 1962, Vol. 351, No. 29.
16. Stoiljković D., Macanović R., Pošarac D.: *J. Serb. Chem. Soc.* 1995, **60**, No. 1, p. 15.
17. Hunter E. in: "Polythene" (ed. Renfrew A., Morgan P.), Illife and Sons, London, 1957, Chapter 3.
18. Stoiljković D., Jovanović S.: *J. Polym. Sci., Polymer Chem. Ed.* 1981, **19**, 741.
19. Stoiljković D., Jovanović S.: *Makromol. Chem.* 1981, **182**, 2811.
20. Stoiljković D., Jovanović S.: *Angew. Makromol. Chem.* 1982, **106**, 195.
21. Stoiljković D., Jovanović S.: *Brit. Polymer J.* 1984, **16**, 291.
22. Stoiljković D., Jovanović S.: *Makromol. Chem.* 1985, **186**, 671.
23. Stoiljković D., Jovanović S.: *Acta Polymerica* 1988, **39**, 70.
24. Boscovich R.: (a) "De Continuitatis Lege", in Latin language, Typographia Generosi Salomoni, Romae, 1754.; (b) "O zakonu kontinuiteta i njegovim posledicama u odnosu na osnovne elemente materije i njivoe sile", in Serbian language, Matematički Institut, Beograd, 1975; (c) "O zakonu neprekinutosti", bilingual in Latin and in Croatian languages, Školska knjiga, Zagreb, 1996.
25. Radičević R., Korugić Lj., Stoiljković D., Jovanović S.: *J. Serb. Chem. Soc.* 1995, **60**, No. 5, 347.
26. Stoiljković D., Pilić B., Radičević R., Bakočević I., Jovanović S., Panić D., Korugić-Karasz L.: *Hem. ind.* 2004, **58**, No. 11, 479.
27. White L. L.: *Nature* 1957, **179**, 284.
28. Silbar M. L.: *Analog* 1982, **102**, 52.
29. Rinard P. M.: *Am. J. Phys.* 1976, **41**, No. 7, 704.
30. Williams P. L.: *Proc. Roy. Inst. Great Brit.* 1960—1961, **38**, 245.
31. Stoiljković D.: *Arhe* 2005, **2**, No. 4, 181.
32. Oster M.: "Roger Joseph Boscovich als Naturphilosoph", Inaugural-Dissertation, Philosophischen Fakultaet der Rheinischen Friedrich-Wilhelms-Universitaet zu Bonn, Coeln, 1909.
33. "The Philosophy of Science of Ruđer Bošković" (Ed. Macan I). Two volumes: one in English, the other in Croatian, Institute of Philosophy and Theology, Croatian Province of the Society of Jesus, Zagreb, 1987.
34. *Filozofska istraživanja* 1989, **32—33**, No. 5—6, 1459—1638.
35. Stoiljković D.: *Filozofska istraživanja* 1989, **32—33**, No. 5—6, 1567.

Received 27 VII 2006.