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Macromolecules and Physics

A. J. Staverman, Leiden

Professor of Physical Chemistry at the University of Leiden. Former director of the Central Laboratory at Delft and presently advisor to TNO.

1. HISTORY

It may seem surprising that the European Physical Society has within its Division of the Physics of Condensed Matter a Section of Macromolecular Physics although no such section exists in IUPAP and also the national physical societies in many countries do not have a corresponding section. It is the purpose of this brief survey to indicate to physicists at large why a physicist could become interested in macromolecules and how the study of macromolecules by physicists not only can assist technologists in improving the quality of plastics, tyres and paints, but may provide fundamental information about the laws governing the structure and physical properties of condensed matter.

The fact that IUPAP has not provided a section for macromolecules is probably due to the circumstance that IUPAC has a very active division in this field, founded and inspired by Herman Mark in the fifties and active in all fields of chemistry, biology and physics where the structure and properties of macromolecules play a part. In Europe, however, it appears that specialists are more reluctant to cross interdisciplinary borderlines than in other parts of the world, which may well be caused by the history of this continent. One gets the impression that because polymers have been invented and prepared by chemists and are products of the chemical industry, most physicists consider polymer research as a domain of chemistry or of technology, not interesting for the pur sang physicist.

This is surprising in view of the fact that solid state physics is generally accepted as occupying a place in physics although here the materials are also prepared by chemists and many of these materials have also become industrial products.

Historically, physicists have been fascinated by polymers long before chemists had any idea about their molecular structure. In 1805 J. Gough[1]) observed that a slip of rubber develops heat on stretching and absorbes heat on contraction and that the length of a rubber slip under a constant force decreases in length with increasing temperature. These observations were confirmed by Joule in 1859[2]) after Kelvin in 1857[3]) had derived a quantitative relation between these two effects from the second law of thermodynamics.

From these experiments the conclusion emerges that the contractile force of rubber originates from a decrease of entropy on deformation. The molecular origin of this entropy of deformation remained obscure until 1934. By that time the basic chemical structure of rubbers had been elucidated. On that basis Mark and Guth[4]) suggested that the decrease of entropy on deformation corresponds to a decrease in the number of conformations* of macromolecules**.

Another incident in the history of the physics of macromolecules was the observation of the mechanical memory of rubber by Kohlrausch in 1876[5]). Kohlrausch subjected a rubber rod to a torsion over + 720° for 48 hours followed by a torsion -45° for 30 sec. After release of the force he observed a reversal of the torsion towards a position value, thereafter a gradual decrease towards zero. This experiment shows that the time scale of mechanical relaxation in rubbers extends at least into the range of minutes.

2. MECHANICAL PROPERTIES

It is difficult to understand why the study of physics of rubbers and other polymers was more or less interrupted from 1876 until 1934. After all, the first chapter in any general course of physics deals with mechanics, and polymers have unique mechanical properties which can be studied also without a clear picture of the molecular structure of the material.

Perhaps the interruption is due to the inability of chemists to procure well defined materials in a reproducible manner. Since 1934 and in particular since World War II, this situation has changed dramatically.

Polymers can be produced in the laboratory and industrially with well defined, accurately measurable and reproducible properties. Since that time the study of mechanical properties of polymers has made great progress.

Not only elastic materials like rubbers and glassy polymers, also viscoelastic liquids like molten polymers or polymer solutions have been subjected to all sorts of deformations and deformation histories. Generally these materials are non-Newtonian, the viscosity decreases at high rate of shear. In periodic deformations regions of

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* *By "conformations" of a molecule we understand the combinations of positions that its atoms can assume without breaking primary chemical bonds.*

Transitions between conformations occur through rotations around chemical bonds in which potential barriers not much larger than kT are involved.

** *By "macromolecules" we understand molecules consisting of many atoms, up to many thousands, connected by valence bonds as in organic molecules.*

If every atom is chemically bonded to two neighbours the macromolecule is called linear; if some of the atoms are bonded to more than two neighbours the macromolecule is branched or forms part of a network structure. In order to behave like a rubber it is essential that the material consists of macromolecules with many conformations as defined above.

Materials wholly or partly consisting of macromolecules are often called "polymers".

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high damping separated by regions of low damping have been formed over a very large time scale ranging from 10^4 to 10^{-9} sec and over large ranges of temperature. Also in simple shear deformation normal forces have been found perpendicular to the planes of shear and in superposition of a periodic and constant rate of shear even negative values of the real part of elasticity modulus have been found[6]).

These studies are generally reported in journals and symposia of Rheological Societies. The physical societies, in particular in Europe, apparently consider this branch of physics as a specialised borderline field, and leave its study to chemists and engineers.

3. STATISTICAL MECHANICS AND THERMODYNAMICS

Macromolecules are not only interesting objects of experimental studies, also theoretical physicists, in particular specialists in statistical mechanics, are challenged by the properties of molecules with large numbers of conformations. In several ways macromolecular materials are more versatile and also more complex than ensembles of molecules in gases or in magnetic materials which are the most popular examples of systems treated by statistical mechanics.

The first feature is that the number of internal degrees of freedom of a macromolecule is so large that a single molecule can be treated with statistical methods.

The number of the internal degrees of freedom of a macromolecule is proportional to the molecular weight in suitable chosen series of macromolecules. Since the average molecular weight can be controlled and determined rather accurately, this is a very convenient variable in experimental checks of theoretical studies. Series of macromolecules differing only in the number of chemical units in a molecule and not in the nature of these units are called homologous series.

Another very interesting feature of macromolecular systems is that their degrees of freedom fall in two classes, internal degrees of freedom and external degrees of freedom and that in either of these classes different types of order and disorder, and transitions between them, exist. This gives rise to the very versatile behaviour of macromolecular systems.

3.1 *Internal Degrees of Freedom*

The internal degrees of freedom represent the freedom of the macromolecule to pass through a large number of conformations by rotations around valence bonds. These conformations can be treated by statistical analysis of suitable models.

A series of models of increasing realism has been conceived:

- *a)* *the random flight chain;*
- *b)* the random chain with fixed valence bonds and *free rotation* around these bonds;
- *c)* the chain with fixed valence bonds and *rotation barriers;*
- *d)* the chain with fixed valence bonds, rotation barriers and interaction-energy between the rotation barriers of neighbouring units, and
- *e)* the same chain with interaction between units separated by a small number of other units in the chain.

These models show increasing *short range interaction,* that is interaction between units connected to each other via a small number of units in the chain.

A still more realistic model takes into account *long range interactions.* Those are the interactions between units of the chain separated by a large number of units on the chain. These interactions will be rather weak between two specific units but the number of these interactions is large *and depends on the molecular weight, M, of the molecule.* The long range interactions are comparable to the interactions between molecules in a non-ideal gas. They depend not only on the structure of the macromolecule but also on the environment. For the study of internal degrees of freedom dilute solutions of macromolecules are most suitable. For every solvent-solute combination one can find a specific temperature at which long range interactions disappear as a result of compensation of attractive and repulsive forces. This temperature is comparable to the Boyle-temperature in a non-ideal gas and is called the ϑ- temperature (or Flory-temperature) of a macromolecular solution.

Several experimental observations indicate that the various models have realistic features. For instance, the average square radius of gyration $<\sigma^2>$ of a macromolecule in a dilute solution can be determined from light scattering and also from viscosity measurements. For models without long range interactions the average square radius of gyration $<\sigma^2>$ is expected to be proportional to M for sufficiently large M. This is confirmed by experiments at ϑ- temperature.

For molecules with long range interaction, one expects that $<\sigma^2>$ will increase with M to a power somewhat larger than unity. This has been confirmed by experiments on solutions at temperature $T > \vartheta$. It is also satisfactory that one finds experimentally relations between $<\sigma^2>$ and the second virial coefficient A_2 of the solution which hold for a given macromolecule in very different solvents at different temperature, confirming the assumption that both quantities are determined by the interaction between units.

The effects of short range interaction are

1. to affect the quantitative value of $<\sigma^2>$ as computed from the distance and angles known from chemical and structural evidence, and
2. to give rise to temperature dependence of $<\sigma^2>$.

The quantitative comparison between experimental and calculated values of both quantities involves detailed knowledge of the energy differences between "rotational isomers" which is the designation of the conformations with minimum free energy. Conversely dimensions of macromolecules are very sensitive to the exact values of differences between energies of rotational isomers and thus suitable to obtain information on such energy differences. For a large number of macromolecules satisfactory agreement between theory and experiment has been obtained[7]).

If every unit can assume s different conformations (s is of the order of 3), the conformation of each unit can be considered as a vector of s dimensions. If the macromolecule consists of n units, then the total conformation is a vector of sn dimensions. The short range interactions occur in the statistical calculations as interaction tensors between the vectors of s units. If all the units are chemically identical and we number the units by 1....i,j .... n and the conformations by ξ,η,ϑ, then the free energy of the macromolecule can be written as the sum of the energies of the separate units plus the sum of interactions between nearest neighbours plus the sum of interactions between next to nearest neighbours and so on. The model thus used can be considered as a generalised Ising model, realistically adapted to chemical structures. An interesting result of this treatment is, that, by introducing short range interactions between units separated by chain parts of increasing length, one finds that *chain-transitions* can occur with an increasing *co-operative character.* These transitions are the *helix-coil-transitions* which have been found experimentally. In general the macromolecule will adopt the character of a helix if every unit or every sequence of 2, 3 or 4 units assumes the same rotational isomeric state. Thus, the helix structure is a one dimensional analogue of the crystal. If the different units occur in different states distributed over the chain according to probability factors, the molecule is said to be in the coil state comparable to the liquid state.

It is clear that helix-coil transitions and transitions between different helices are very sensitive to small changes in interaction parameters as induced by change of temperature or environment, p_H and other parameters. It is therefore particularly interesting that in living organisms many macromolecules appear to occur in helix conformations and that dramatic changes in the properties of these molecules can be induced by small chemical changes in the environment.

3.2 *External Degrees of Freedom*

It is certainly surprising that the original explanation of the entropy origin of the rubber elastic forces based upon the assumption of molecules with large numbers of conformations has produced such a large offspring in molecular interpretations of physical, chemical and biological phenomena. And it is equally surprising that the quantitative theory of rubber elasticity has made very little progress since its original conception of 1934.

Not only exists some controversy about the mathematically correct treatment of *networks* of macromolecules of which the internal statistics is known[8]). Also the effect of the external degrees of freedom and its dependence on temperature and pressure on the quantitative relation between the elastic force and the deformation are not completely understood. An additional difficulty in this field is the fact that chemical methods to determine the number of crosslinks in a network are much less reliable than methods to determine molecular weights in solutions. Moreover, the number of crosslinks as determined by chemical analysis need not be identical with the number of crosslinks which are effective in the production of the elastic force on deformation.

We know that it is more or less an accident that the rubber elastic force in natural rubber is for nearly 100 % of entropy origin. For other polymers one finds appreciable contributions from internal energy and this can be understood from the theory of interactions between internal degrees of freedom as discussed above. But also the external degrees of freedom will be important in a complete description of the dependence of the elastic force on deformation, on temperature and on pressure.

In undiluted polymers the external degrees of freedom will be subjected to restrictions as compared to polymers in solution. There is no general agreement as to the effect of these restrictions. There are strong arguments in favour of the assumption that in undiluted amorphous polymers the macromolecules are in the *random coil* conformation[9]). However, it is not clear how this model can produce a close packed phase. Therefore, another model, *the bundle model*, proposed by Kargin[10]) and co-workers on the basis of convincing experimental evidence, is supported by at least equally strong arguments[11]). In the bundle model, later refined and elaborated as the *meander model*[12]), the molecules exist in straight helical parts interrupted by folds and different molecules are aligned into bundles. Surprisingly it appears that from the meander model and the random coil model the same value for the radius of gyration is calculated in agreement with experimental values. Thus the conformation of macromolecules in the amorphous undiluted state is essentially an unsolved problem.

3.3 *Phase-transition*

Also for those physicists who consider molecular conformations as an object of study for chemists, macromolecules offer many challenging problems. Besides the helix-coil transition which is essentially a transition within isolated molecules, macromolecular substances can undergo transitions between crystals and liquids and between liquids and glasses.

The physical character of these transitions is very different and has also features differing from the behaviour of substances of low molecular weight. In the crystalline state the occurrence of *chain folding* is an essential structural element characteristic for macromolecules[13]).

In principle the crystalline state in polymers is of the same nature as in other substances, but polymers are more versatile. The rate of crystallisation, the degree of crystallisation and the number and nature of lattice defects all depend on specific details of the molecular structure and the crystallisation conditions.

As the molecular structure can be rather easily controlled in different respects, such as average molecular weight, m.w. distribution, branching, sequence of different monomers, polymers offer a wide scale of model substances to study the effects of molecular structure on crystallisation.

The *glass transition* is a transition of a character completely different from that of crystallisation.

Polymers are not the only substances showing a glass transition but they are very well suited to study this interesting phenomenon. With the exception of highly crystalline polymers, all polymers show a glass transition. It is not a thermodynamic transition in the sense that both phases are in thermodynamic equilibrium and, therefore, Ehrenfest's classification[14]) of phase transitions cannot be applied to it. In fact, the essential feature of the formation of a glass from a liquid or rubbery phase on decreasing the temperature, is that in the glass the true equilibrium state cannot be reached for kinetic reasons. The molecular processes are too slow at low temperature and the glass transition is very dependent on the time of experimentation. However, the frozen, glassy state can be characterised by thermodynamic functions, such as a free energy, a volume, a heat content, a specific heat, a compression modulus and a dilatation coefficient.

Theoretically and experimentally one can show[15]) that glass transitions have many traits of Ehrenfest's second order transitions. The transitions are characterised by equality of volume and entropy of the two phases in the transition point, but inequality of the second derivatives of the free energy with respect to temperature and pressure. Ehrenfest derived relations between the differences of these second derivatives for second order transitions. The validity or non-validity of those same relations for glass transitions yields information about the parameters freezing in the glass state and about the critical conditions for a glass transition.

The elastic modulus, considered earlier in this paper, is also a second derivative of the free energy and undergoes a dramatic change at the glass transition temperature. In extreme cases the modulus of the glass can be a hundred to a thousand times larger than that of the corresponding rubber.

4. CONCLUSIONS

Summarising we list the following properties in which systems with macromolecules are unique or at least outstanding.

4.1 *Rubber elasticity*
4.2 *Low entropy of solution*
4.3 *Helix-coil and helix-helix-transitions*
4.4 *Cristallinity variable from 0 % to 100 %*
4.5 *Glass transitions*
4.6 *Time dependence of mechanical and other properties over a very large range of times (and temperatures)*

It is impossible in this paper to treat in detail any of the interesting physical phenomena which are shown by polymers.

The main purpose of this brief review is to show that macromolecules and polymers not only deserve the attention of physicists because they are interesting by themselves, but also because their versatility makes it possible to use them as objects for study of physical phenomena and theories in general.

In several fields of theoretical physics macromolecules give rise to interesting extensions and applications. One such field is that of statistical thermodynamics with particular emphasis on generalised Ising models and phase transitions. [4.3 and 4.4]. Besides, also the theory of molecular forces [4.1 and 4.2] and of relaxation phenomena [4.5 and 4.6] acquires new possibilities in the study of macromolecules. Finally, since nature makes extensive use of macromolecules and their very specific intra- and intermolecular interactions, the physicists' contributions to the unraveling of the intricate ways in which nature realises the infinite variety of structures and functions in living matter will necessarily start with the study of macromolecules.

Besides, calling attention to the activities of the section on macromolecules of the European Physical Society, this short review will perhaps contribute to a change in the role of macromolecules in physics courses.

Perhaps macromolecules will not only be considered as interesting objects for study in borderline fields of physics, but will be given a central place in physics teaching and research.

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Letter to the Editor

Technology interacting with norms and values

Sir,

Stimulated by Casimir's article "Technology for the future" (Europhysics News, September 1974) as I always am by his writings, I venture to comment on the reasoning leading to his conclusion : "For the time being I do not see an indication on the necessity to limit the growth of electronics". He bases this conclusion on three arguments : (1) we cannot conserve anything like our present civilization without technology (including electronics) ; (2) electronics does not lead to waste, it may even reduce it; (3) it does not spoil environment.

But he also states that : "in developed countries part of the population is living at a level of energy consumption that seriously impairs their well-being and therefore lowers their standards of living". Could it then not be that, because of the growth of electronics, the same holds, for an even larger part of the population, as regards information consumption ? Moreover, might not the unrestricted growth of electronics and information techniques encourage the accumulation of centralized, bureaucratic power over individuals ? (In this respect it would have been more relevant to quote Orwell's "1984" than Huxley's "Brave New World").

The answers to such questions could have a bearing on our thinking on limits to growth. History has shown that the growth of science and technology has influenced norms and values. On the other hand scientists and spokesmen of public opinion, reasoning from the existing system of norms and values, are increasingly asking the question "Is this what we want ?" Should we not include in "the system" such immaterial things as norms and values and their interaction with the science and technology spiral (My Concise Oxford says that a system is an "organized body of material or immaterial things"...

Casimir's three arguments for not limiting the growth of electroncis leave open the question of whether, in the not too distant future, the values and norms of a society that respects human privacy, dignity and freedom might not themselves impose limits on this growth. Casimir's optimistic view of the future of electronics, which in many respects I endorse, should not, however, deter scientists working in this field from incorporating the latter interaction in their thinking about the consequences of their work. *G. Diemer, Eindhoven*

Society News

Divisions

The **Nuclear Physics** Board, at its first meeting, held at Legnaro, Italy, elected the officers of the Board and coopted members to ensure that all areas of nuclear physics and national regions are fully represented.

The Board at present has the following members:
C. van der Leun, Utrecht, (Chairman); A. Strzalkowski, Cracow, (Vice-Chairman); W.D. Hamilton, Brighton, (Secretary); K. Alder, Basel; K. Bethge, Heidelberg; N. Cindro, Zagreb; E. Cotton, Gif-sur-Yvette; P.G. Hansen, Geneva; M. Ivascu, Bucharest; T. Mayer-Kuckuk, Bonn; S.G. Nilsson, Lund; R.A. Ricci, Legnaro; I. Talmi, Rehovot.

The first Divisional Conference will be held at A.E.R.E. Harwell on 24-26 March 1975 with the title "Nuclear Interactions at Medium and Low Energies". The topics and principal speakers are:

Heavy Ion Nuclear Physics	M. Lefort and W.R. Phillips
Heavy Ion Non-Nuclear Physics	W. Greiner
Nuclear Fusion and Heavy Elements	H.J. Specht and a speaker to be announced
Nuclear Physics Aspects of Nuclear Astrophysics	D. Bodansky
Low Energy Neutron Interactions	H. Weigmann and M. Coates
Laser Fusion	D.E.T.F. Ashby
Accelerators	J.P. Blaser

Accommodation will be in Oxford Colleges. Further details are available from The Meetings Officer, The Institute of Physics, 47, Belgrave Square, London SW1X 8QX *(see also Meetings Issue, Vol 5, No. 11).*

Call for nominations. The Board of the **Plasma Physics Division** will be renewed this year for the term of office 1976-1978. The present board of the Division is preparing a list of candidates.

Members of the Division, i.e. Individual Ordinary Members, Constitution Article 4a) and 4c), and National Societies, Academies and Laboratories, Article 4b), can make proposals for candidates.

Any proposal for candidates should be sent before 28 February 1975 to:
Professor P. Vandenplas,
Chairman, Plasma Physics Division,
Ecole Royale Militaire,
Laboratoire de Physique des Plasmas,
30, avenue de la Renaissance,
B - 4 Brussels