MEETINGS AND CONFERENCES

Scientific session of the Division of General Physics and Astronomy and of the Division of Nuclear Physics, Academy of Sciences of the USSR (19 December 1985)

A joint scientific session of the Division of General Physics and Astronomy and of the Division of Nuclear Physics, Academy of Sciences of the USSR, was held on 19 December 1985 at the S. I. Vavilov Institute of Physical Problems, Academy of Sciences of the USSR. The following reports were presented at the session:

1. *A. Yu. Grosberg and A. R. Khokhlov.* Phase transi-

tions in polymer and biopolymer systems.

2. *M. V. Vol'kenshteĭn.* Evolution of biopolymers and biological evolution.

3. *M. D. Frank-Kamenetskiĭ.* Topology and structural transitions in DNA.

The reports are summarized below.

A. Yu. Grosberg and A. R. Khokhlov. *Phase transitions in polymer and biopolymer systems.* A distinctive feature of polymer systems is that they consist of long chains of molecules, with the following consequences: a) There is the possibility of long-range correlations along the chains and thus of pronounced ("critical") fluctuations and anomalously high susceptibilities; b) Such systems are characterized by a long-term "topological," and "linear" memory of the synthesis conditions and of the prehistory of the motion ("topological" here means that the memory occurs because self-intersections of parts of the chains are forbidden; "linear" means that the memory is due to an immobilization of a sequence of units along the chain). These circumstances lead to a wide variety of phase transitions in polymers. The transitions which have been studied most thoroughly are ball–globule transitions,[1–3] with which we are concerned in the present paper, and also transitions which result from a liquid-crystal ordering[4,5] (see also Ref. 6).

Ball–globule transitions frequently occur in systems of ordinary synthetic polymers and play a special role in biopolymers, where they frequently lead to self-organization, i.e., to a structural implementation of genetic information. The modern theory of ball–globule transitions arose from work by I. M. Lifshitz.[1] This theory is set forth in detail in the review papers of Refs. 2 and 3 (see also Ref. 7).

The ball–globule transition which is simplest to observe experimentally is the collapse of chains connected by chemical bonds in a network (a gel), since this collapse is manifested as an abrupt and large change (often by a factor of tens) in the dimensions of a macroscopic sample of the network. This phase transition may be caused by changes in the temperature or composition of the solvent and also by an external pressure or load. According to the present theoretical understanding, the equilibrium dimensions of a polymer gel (i.e., its swelling or collapse) are determined by a balance between the specifically polymeric entropic elasticity of the network

and three-dimensional interactions of the units. If the chains of a network contain ionized groups, so that mobile counterions are present in the required number in the solvent, the Coulomb interaction of charge density fluctuations and the osmotic pressure of the gas of counterions also contribute to the free energy of the network. The theory[8] based on these considerations has successfully explained many observable[9] features, e.g., the sharp increase in the change in the dimensions with increasing fraction of charged units in the network and with decreasing ionic strength of the solution. The theory has also predicted several new effects, which have subsequently been observed experimentally[10]: the possibility of two successive phase transitions—a collapse and a decollapse—upon a monotonic change in the composition of the solvent; the fact that a phase transition in a network can be caused by an external tensile stress; and the sharpening of collapse upon the introduction of charged macromolecules in a neutral gel. Further study of the collapse of polymer networks is interesting from the standpoint of mechanochemical applications; it may also prove useful in the gel chromatography of polymers and in fine adjustments of the activity of enzymes.[11]

Among the many ball–globule transitions, that which is of the greatest fundamental interst in connection with biological problems is the collapse of an isolated long polymer chain in a dilute solution, which occurs as the solvent temperature is lowered and as the quality of the solvent becomes poorer. In recent years this phenomenon has been the subject of active experimental research,[12] and it has stimulated the development of the existing[1–3] qualitative theory of such transitions to a quantitative level (in Ref. 13). According to the theory, in the simplest case a ball–globule transition for flexible polymer chains is a second-order phase transition; for chains of elevated stiffness it is a first-order transition, with many properties similar to those of a second-order transition. The quantitative theory of this phenomenon can ex-
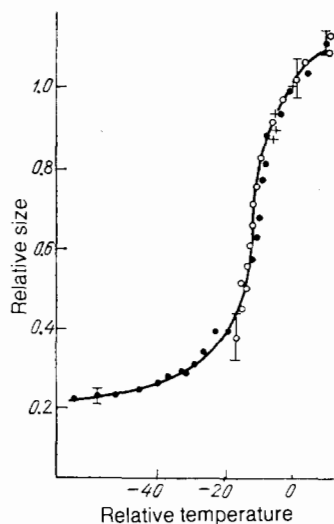
FIG. 1.

plain, for example, the fact that the picture of the transition is independent of the length of the polymer: A change in the length by a factor of x reduces to simply a change by a factor of $x^{1/2}$ in the scale along the temperature axis. The agreement between the theoretical and measured results on the temperature dependence of the inertial radius of a macromolecule which is demonstrated in Fig. 1, which summarizes data on chains differing in length by a factor of more than a thousand, confirms the applicability of the approximation of a self-consistent field—on which the theory is based—for the given phase transition. More precisely, we could say that in the case shown in Fig. 1 (polystyrene in cyclohexane) the Ginzburg parameter, which controls the applicability of this approximation for phase transitions of second order or nearly second order, is of the order of 10^{-2}.

The properties of the polymer globules which form are also extremely interesting. In terms of local structure, the core of a polymer globule might be an analogue of any condensed state of ordinary matter—a liquid or a liquid crystal, an amorphous or crystalline solid, or a solid or liquid solution; the state may be metastable ("vitrified"); a phase stratification is possible even within a single macromolecule; etc. Correspondingly, the following are predicted theoretically and observed experimentally: first, a mechanism for the ball–globule transition which is an alternative to that described above, consisting of a first-order phase transition accompanied by the simultaneous formation of a liquid-crystal, crystalline, or microstratified structure; second, globule–globule phase transitions involving changes in the local structure of the globule cores.[2-4,14]

Of particular interest are ball–globule transitions in macromolecules of biological polymers: DNA and proteins. The primary distinguishing feature of these systems is a heterogeneous sequence of units of different types. In DNA, however, the strands are woven in a double helix, so that the heterogeneous amino acid groups are inside the helix, and the double helix as a whole is an effective homopolymer with a very high flexural rigidity, which is distributed uniformly along the contour. The globulization of double-helix DNA occurs most effectively in a solution of balls of another flexible polymer, where it is of the nature of a fluctuational instability. A solution of balls is a strongly fluctuating system; the exchange of its fluctuations between the segments of the DNA leads to an effective attraction between them. The corresponding theory not only successfully explains the mechanism and the characteristics of the collapse of DNA but also correctly predicts the size and shape of the globular particles which result. These particles may be spheres or tori.[15]

For proteins, the problem of heterogeneity of the linear structure is an exceedingly important one. It has now been learned that, in addition to having a globular native state (a biologically active state) and a ball state, a protein molecule can also be in a state of a "molten globule."[16] A transition between the native state and the molten state is a first-order phase transition. The theory derived in Ref. 17 explains the type of melting of a heterogeneous globule in terms of the presence of additional kinetic constraints (in addition to the linear memory) in the native globular protein. Further progress in this field will require the derivation of a systematic theory for the equilibrium properties of globules for heteropolymers with a complex sequence of different units and also an analysis of those of their kinetic properties which are determined by the topological constraints.

[1] I. M. Lifshitz, Zh. Eksp. Teor. Fiz. 55, 2408 (1968) [Sov. Phys. JETP 28, 1280 (1969)].
[2] I. M. Lifshitz, A. Yu. Grosberg, and A. R. Khokhlov, Usp. Fiz. Nauk 127, 353 (1979) [Sov. Phys. Usp. 22, 123 (1979)].
[3] A. Yu. Grosberg and A. R. Khokhlov, in: Problems in Solid State Physics (eds. A. M. Prokhorov and A. S. Prokhorov), Mir Publishers, Moscow, 1984, p. 330.
[4] A. Yu. Grosberg and A. R. Khokhlov, Adv. Polym. Sci. 41, 53 (1981).
[5] A. R. Khokhlov and A. N. Semenov, J. Stat. Phys. 38, 16, 161 (1985).
[6] A. Yu. Grosberg and A. R. Khokhlov, in: O Nereshennykh problemakh statisticheskoĭ fiziki makromolekul (Unresolved Problems of the Statistical Physics of Macromolecules), NTsBI, Pusnchino, 1985.
[7] A. R. Khokhlov, in: Statisticheskaya fizika makromolekul (Statistical Physics of Macromolecules), Izd. Mosk. Univ., Moscow, 1985.
[8] A. R. Khokhlov, Polymer 21, 376 (1980); V. V. Vasilevskaya and A. R. Khokhlov, Matematicheskie metody dlya issledovaniya polimerov (Mathematical Methods for Studying Polymers), NTsBI, Pushchino, 1982, p. 45; V. V. Vasilevskaya and A. R. Khokhlov, Vysokomol. Soedin. A28, 316 (1986).
[9] T. Tanaka, Phys. Rev. Lett. 40, 820 (1978); T. Tanaka et al., Phys. Rev. Lett. 45, 1636 (1980); I. Ohmine and T. Tanaka, J. Chem. Phys. 77, 5725 (1982).
[10] S. Katayama, Y. Hirokawa, and T. Tanaka, Macromolecules 17, 2641 (1984); S. G. Starodubtsev and A. R. Khokhlov, Dokl. Akad. Nauk SSSR 282, 392 (1985); S. G. Starodubtsev, N. R. Pavlova, V. V. Vasilevskaya, and A. R. Khokhlov, Vysokomol. Soedin. B27, 485, 500 (1985).
[11] A. R. Khokhlov et al., Protsessy studneobrazovaniya v polimernykh sistemakh (Gel-Formation Processes in Polymer Systems), Izd. Sarat. Univ. Saratov, 1985, p. 78.
[12] S. T. Sun, I. Nishio, W. Swislow, and T. Tanaka, J. Chem. Phys. 73, 5971 (1980); P. Stepanek, C. Konak, and B. Sedlacek, Macromolecules 15, 1214 (1982); M. Nierlich, J. P. Cotton, and B. Farnoux, J. Chem. Phys. 69, 1379 (1978).
[13] A. Yu. Grosberg and D. V. Kuznetsov, Vysokomol. Soedin. B26, 701, 706 (1984); A. Yu. Grosberg, A. V. Zhestkov, and D. V. Kuznetsov, Vysokomol. Soedin. A28, (1986).

[14] A. Yu. Grosberg, Biofizika **29**, 569 (1984).

[15] A. Yu. Grosberg, I. Ya. Erukhimovitch, and E. I. Shakhnovitch, Biopolymers **21**, 2413 (1982); E. S. Nikomarov and S. P. Obukhov, Zh. Eksp. Teor. Fiz. **80**, 650 (1981) [Sov. Phys. JETP **53**, 328 (1981)]; A. Yu. Grosberg and A. V. Zhestkov, Biofizika **30**, 233 (1985); A. Yu. Grosberg and A. V. Zhestkov, Mol. Biol. **19**, 1153 (1985).

[16] R. I. Gil'manshin, D. A. Dolgikh, O. B. Ptitsyn, A. V. Finkel'shteĭn, and E. I. Shakhnovich, Biofizika **27**, 1005 (1982).

[17] E. I. Shakhnovich and A. V. Finkel'shteĭn, Dokl. Akad. Nauk SSSR **267**, 1247 (1982).