

Joint Scientific Session of the Division of General Physics and Astronomy, USSR Academy of Sciences, with the Division of Physico-Technical and Mathematical Sciences, Moldavian Academy of Sciences (Kishinev, 3-5 October, 1973)

Usp. Fiz. Nauk 113, 330-351 (June 1974)

A joint excursion scientific session of the Division of General Physics and Astronomy of the USSR Academy of Sciences with the Division of Physico-technical and Mathematical Sciences of the Moldavian Academy of Sciences was held on 3-5 October 1973 at Kishinev. The session opened with an introductory address by the President of the Moldavian Academy, Corresponding Member of the USSR Academy of Sciences Ya. S. Grosul. Welcoming remarks were delivered by the Academician-Secretary of the Division of General Physics and Astronomy of the USSR Academy of Sciences, Academician of the USSR Academy of Sciences A. M. Prokhorov, and by V. A. Andrunakievich, the Vice President of the Moldavian Academy, the Academician-Secretary of its Division of Physico-technical and Mathematical Sciences, and an Academician of that Academy. The following papers were presented:

1. I. M. Lifshitz and A. Yu. Grosberg, The phase Diagram of the Polymer Globule and the Problem of Self-Organization of its Spatial Structure.
2. Yu. A. Osip'yan, Interaction of Dislocations with Electrons in Solids.
3. G. A. Smolenskiĭ, Phase Transitions in Certain Magnetically Ordered and Ferroelectric Crystals.
4. L. V. Keldysh, Condensation of Excitons.
5. V. L. Ginzburg, Surface Excitons of the Electron-Hole Type.
6. Zh. I. Alferov, Heterotransitions in Semiconductors.
7. B. R. Lazarenko, Structure and Directions of Scientific Activity of the Institute of Applied Physics, Moldavian Academy of Sciences.
8. S. I. Radautsan, Investigation of Compound Semiconductive Materials in the Moldavian SSR.
9. T. I. Malinovskii, Interpretation of the Structures

of Complex Compounds with Heavy Atoms.

10. V. A. Moskalenko, The Theory of Superconductors with Overlapping Energy Bands.
11. Yu. E. Perlin and B. S. Tsukerblat, Dichroism Effects in Systems with Dynamic Jahn-Teller Coupling.
12. V. A. Kovarskiĭ, Features of the Absorption, Emission, and Scattering of Light by Atoms and Impurity Centers of Crystals with Degenerate Energy Spectra in a Strong Electromagnetic Field.
13. S. A. Moskalenko, Collective Properties of Excitons and Biexcitons.
14. D. V. Gitsu, Features of Transfer Phenomena in Crystals of The Bismuth Type.
15. V. V. Sobolev, Spectroscopy of Intrinsic Energy Levels of Solids.

The participants in the excursion session toured the Institute of Applied Physics of the Moldavian Academy and a number of physics laboratories of the Kishinev State University and the Kishinev Polytechnic Institute.

The joint resolution of the excursion session took note of the high scientific level and pertinence of the theoretical and experimental research being done in the scientific laboratories of the Moldavian Academy of Sciences and in the Republic's higher educational institutions in the fields of solid-state physics, semiconductor physics and chemistry, and new applications of electricity in the national economy.

We publish below brief contents of ten of the papers.

I. M. Lifshitz and A. Yu. Grosberg, The Phase Diagram of the Polymer Globule and the Problem of Self-Organization of its Spatial Structure. It is known that biopolymer chains are so long that each individual molecule is a statistical system. From this standpoint, the organization of the spatial tertiary structure of the

polymer chain should be regarded as a phase transition from the coiled state to the globular state.

In^[1], one of us constructed a consistent statistical-thermodynamic theory of polymer chains with volume interaction. It was shown that the macrostate of a polymer chain in a suspended state in a solution is a state of partial equilibrium with a fixed "linear memory" (i.e., a primary structure). In the simplest case of a homopolymer, the linear memory involves only memory of the position of each link in linear sequence along the chain; this linear memory is described by the correlations g_j between the coordinates of neighboring links. In the simplest model, that of "interacting beads on a flexible string," the correlations reduce to a single function that depends only on the distance between adjacent links:

$$g_j = g(|x_j - x_{j+1}|).$$

We stress that this model can describe a polymer whose primary structure is statistically homogeneous to a sufficient degree, while the strongly interacting monomers are separated by long segments of chain; but for description of polymers with highly specific primary structure, such as proteins, this model requires refinement or modification.

The phase state of the chain in the absence of an external field is determined by the volume interaction of its links, which may be separated by long chain segments but are brought close to one another at random when the chain bends. This interaction is relatively weak at comparatively high temperatures, and the chain remains in the state of a loose, irregularly pulsating coil. Although an average density distribution does exist in the coiled state, it is not a thermodynamically reliable characteristic, since the density fluctuations are on the order of the density itself.

The importance of the interaction increases as the temperature falls, and at a certain point the chain collapses into a dense globule in which the number density distribution $n(\mathbf{x})$ becomes a thermodynamically reliable quantity, i.e., one with small fluctuations. In an ordinary system without linear memory, the density n_0 in the condensed phase is determined by the characteristic direct interaction radius r_0 , which is equal in order of magnitude to the atomic dimension. In our case, there is, in addition to r_0 , another parameter (a) with the dimensions of length; it determines the correlation radius associated with the linear memory and is in most cases much larger than r_0 : $a \gg r_0$.

Since the order of magnitude of the globule volume V is determined by the density n_0 in its condensed core (i.e., r_0) and by the total number N of monomers: $V \sim N/n_0$, it is natural to distinguish among all macroscopic globules (for which $V \gg r_0^3$) the extreme cases of very large ($V \gg a^3$) and very small ($V \ll a^3$) globules. These cases must be considered separately.

We stress once again that the density distribution in the globule is nonlocal because monomers at a distance $\sim a$ are found to be correlated due to the linear memory. It is precisely this fact that determines all of the peculiarities in the statistics of the polymer chain. But in the first approximation in the parameter r_0/a , the direct volume interaction can be described by a local self-consistent field $\mu^*(n(\mathbf{x})) = \mu(n, T) - T \ln n$, where $\mu(n, T)$ is the chemical potential of the equivalent system of disconnected links with the same volume inter-

action at the density n and the temperature T . Here the nonlocalism is described by the entropy term in the free energy.

Since the solvent influences the nature of the volume interaction between monomers, $\mu(n)$ is an effective quantity that includes the indirect interaction of the links via the solvent; only when the density n is very small (so small that there is no interaction at all) and when the density is large (so that solvent molecules do not penetrate between monomer links) does the function $\mu(n)$ approach the conventional chemical potential.

The equilibrium density distribution in the globule is determined by the system of equations derived in^[1] from the minimization condition for the free energy $\mathcal{F}\{n\}$ as a functional of the density distribution. It follows from these equations that the local chemical potential $\mu(n)$ must be a continuous function of the coordinates. Thus, at temperatures below the critical temperature of the system of disconnected links $T < T_c$, when separation into two phases becomes possible in this system and, accordingly, $\mu(n)$ breaks up into two branches, the density distribution in the globule becomes discontinuous (Fig. 1a). The interface separates the dense (condensed) core of the globule from an open gaslike envelope.

The density of the gaslike fringe of the globule decreases with decreasing temperature. But since longitudinal bonds limit the size of the fringe, the entropy gain from formation of the fringe as the temperature is lowered is too small, and the fringeless globule appears (Fig. 1b).

The influence of the solvent on the monomer density distribution is taken into account through the dependence of the effective chemical potential $\mu(n)$ on the state of the solvent; here the spatial inhomogeneity of solvent state is treated as an external field.

The effective chemical potential depends, in particular, on the pressure \mathcal{P} in the solvent. We do not, of course, know any details of this relationship. However, the principal dependence on \mathcal{P} results from the fact that on collapse of the chain into a dense globule the volume of solvent displaced by the links of the polymer changes by an amount ΔV , and, consequently, the chain must perform a work $\mathcal{P}\Delta V$ against the external pressure to form the globule. This effect can be taken into account independently.

It is easily understood that in the presence of an external pressure \mathcal{P} on the solvent, the equilibrium state of the polymer chain is determined not by the minimum of the free energy $\mathcal{F}\{n\}$ (it is given by formulas (2.2) and (2.3) of^[2]), but by the minimum of a quantity analogous to the thermodynamic potential:

$$\Phi\{n\} = \mathcal{F}\{n\} + \mathcal{P}\Delta V.$$

We denote by $v(n)$ the volume of solvent displaced by a single monomer link in a region where the link den-

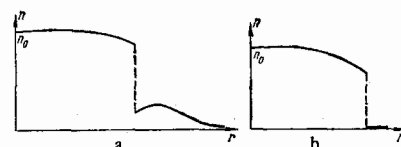


FIG. 1. Radial density distribution in a globule with a fringe (a) and without a fringe (b).

sity equals n . At high density, solvent does not penetrate between monomers and $v(n) \approx 1/n$; at low density, $v(n)$ becomes equal to the effective volume of the monomer link, $v(n) \approx v_0$. Using this notation

$$\Delta V = \int n(x) [v(n) - v_0] d^3x.$$

On minimizing $\Phi\{n\}$, it is easily verified that the influence of external pressure on the density distribution in the globule can be included in the self-consistent field, by virtue of which this field is equal in the presence of an external pressure to

$$\mu^*(n(x)) + \mathcal{P} [v(n) - v_0 + nv'(n)].$$

Density distributions for the two extreme cases of large and small globules were derived in [2] (where all formulas were written for the case $\mathcal{P} = 0$). The results appear simplest for a small globule without a fringe: in this globule, density is determined by the condition $p(n_0, T) = \mathcal{P}$ [$p(n, T)$ is the pressure in the system of disconnected links], and for the large globule, in which the role of the surface is a relatively minor one, since the density in the core does not depend on the presence or absence of the fringe and is determined by the equality $p(n_0, T) - n_0 T = \mathcal{P}$. The physical meaning of these results is obvious.

The boundary condition defining the density discontinuity at the boundary between the core of the globule and its fringe should be determined by minimizing the thermodynamic potential with respect to core volume. It does not follow from general considerations that this minimization will result in a local-pressure continuity condition, since the longitudinal bonds can transmit a mechanical force over a distance $\sim a$. However, as can be verified by direct variation of the free energy (formula (2.8) of [2]), the condition of local-pressure continuity that is characteristic for the system without linear memory is preserved in the present approximation, when the volume interaction is described solely by a self-consistent field of the form indicated above. Thus the densities on the boundary between the core of the globule and its fringe, n_- on the core side and n_+ on the fringe side, are determined by the conditions

$$\begin{aligned} \mu(n_-) &= \mu(n_+), \\ p(n_-) &= p(n_+) + \mathcal{P}. \end{aligned}$$

Similarly, the density on the boundary of a globule without a fringe is determined by

$$p(n_-) = \mathcal{P}.$$

This simplifies many results of [2], and some new ones, which will be published separately, can also be obtained.

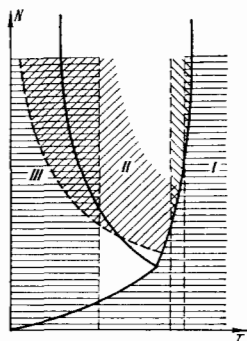
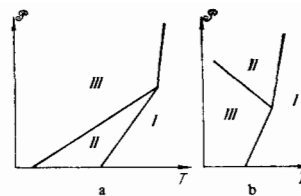


FIG. 2. Phase diagram of polymer chain at constant external pressure. Region I corresponds to the coil, II to the globule with fringe, and III to the globule without the fringe. Regions in which self-organization of the tertiary structure is impossible for one reason or another are shaded; horizontal shading indicates that the solvent is in the solid or gaseous state or that the polymer is in the coil state; oblique shading slanted to the right indicates a high probability of local topological disturbance; shading slanted to the left indicates that restructuring of the tertiary structure as a whole is thermodynamically favored.

FIG. 3. Phase diagram of polymer chain with constant length. Region I corresponds to the coil, region II to the globule with fringe, and region III to the globule without fringe.



Thus, the chain may be in any of three different phase states, depending on the number of monomers N , the temperature T , and the external pressure \mathcal{P} on the solvent: the coil, the fringed globule, or the unfringed globule. The transitions between these states are first-order phase transitions.

It is easily verified that the qualitative form of the phase diagram in the T, N plane ($\mathcal{P} = \text{const}$) does not depend on the pressure \mathcal{P} ; such a diagram appears in Fig. 2. Analytical expressions for all equilibrium curves were derived in [2] for the case $\mathcal{P} = 0$ and can easily be extended to other values of \mathcal{P} .

It is admissible at sufficiently small \mathcal{P} to neglect the influence of pressure on the effective chemical potential. It is then possible to construct a phase diagram in the T, \mathcal{P} plane ($N = \text{const}$); such a diagram appears in Fig. 3 for the case

$$N - \bar{N} = \delta N \ll \bar{N},$$

where the chain length \bar{N} corresponds to the triple point at $\mathcal{P} = 0$. The form of this diagram depends strongly on the relations between the system parameters (cases a and b in Fig. 3). Turning to analysis of the self-organization problem, we note first of all that for self-organization of the tertiary structure to be possible it is necessary that the microstructure of the equilibrium globule be similar in its ordering to the structure of the aperiodic crystal.

It is obvious that a sufficiently low temperature is in any event necessary if this is to occur, since otherwise a mixture of many substantially different conformational states will be thermodynamically favored, i.e., a liquid-like structure will appear. However, even if this condition is satisfied, local violations of order can also occur in the system, usually involving topological disturbances in the disposition of the chain segments, and hence requiring full conformational restructuring of the chain. Since local disturbances may occur over the entire length of the chain, the requirement for stability under these disturbances imposes a limit on chain length:

$$N \ll N_c \sim \exp\left(\frac{U_D}{T}\right),$$

where U_D is the characteristic defect energy.

In addition to all this, it can evidently be stated that for reliable self-organization, the thermodynamic equilibrium conformation must be the one that is kinetically most rapidly attainable. In a long chain, organization proceeds most rapidly if it can advance independently in various segments of the chain. This is possible only when the resulting steric structure has an extremely simple topology, i.e., if it has a zero number of nodes.

Only a very small fraction of all possible primary structures satisfy all of these conditions. But since the biochemical functioning of the globule is determined by its spatial structure, it is these primary sequences that were selected in the process of prebiological evolution.

¹I. M. Lifshitz, Zh. Eksp. Teor. Fiz. 55, 2408 (1968) [Sov. Phys.-JETP 28, 1280 (1969)].

²I. M. Lifshitz and A. Yu. Grosberg, Zh. Eksp. Teor. Fiz. 65, 2399 (1973) [Sov. Phys.-JETP 38, 1198 (1974)].

G. A. Smolenskii. Phase Transitions in Certain Magnetically Ordered and Ferroelectric Crystals.

Investigation of phase transitions is one of the central problems of contemporary physics. Substantial progress has been made in this field during recent years. The thermodynamic theory of second-order phase transitions has been improved and developed, a scaling theory has been created, specific models have been calculated, including the Ising model, the productive notion of the "soft" mode is being developed successfully, critical indices have been determined for various substances, etc.

It is therefore interesting to accumulate experimental data from study of phase transitions in various crystals. This paper briefly illuminates the results of studies of phase transitions in certain magnetically ordered substances and ferroelectrics.

It is known that a compensation point is observed, in accordance with Neel's theory, in rare-earth ferrimagnetics with garnet-type structure. This point is not a critical point in the absence of a magnetic field. But when an external magnetic field is applied, induced phase transitions appear near the compensation point. A theoretical analysis of this problem was carried out first for an isotropic ferrimagnetic, and then with consideration of magnetic anisotropy.

Two induced phase transitions were observed in terbium iron garnet in^[1]. As the temperature was raised, a transition occurred from one collinear ferrimagnetic phase to a noncollinear (antiferromagnetic) phase and then to another collinear ferrimagnetic phase. These transitions are accompanied by sign reversal of magnetic birefringence, and light scattering by fluctuations of the magnetic moment is observed.

Another example of the phase transitions studied is the spin reorientation in rare-earth orthoferrites with rhombic structure of the perovskite type. At temperatures above 10°K, only the magnetic moments of the iron ions form a magnetically ordered structure. These substances belong to the class of weak ferrimagnetics. At high temperatures, the magnetic-moment vector is directed along the c axis, and the antiferromagnetism vector along the a axis. As the temperature is lowered, a continuous transition occurs in many of these crystals, with the magnetic-moment vector stabilizing along the a axis and the antiferromagnetism vector along the c axis. K. P. Belov et al. showed that second-order phase transitions correspond to the beginning and end of the reorientation range. Investigation of the spin mode corresponding to joint oscillations of the magnetic-sublattice vectors in the a-c plane showed that the frequency of these oscillations drops to zero at the beginning and end of the reorientation range. The appearance of a "soft" spin mode results from the change in magnetic symmetry and not from a change in crystallographic symmetry, as is the case in ferroelectrics.

Studies of the elastic and magnetoelastic properties of various orthoferrites were investigated in^[2] in the frequency range 50 - 1500 MHz. It was shown that the velocity and damping of elastic waves decrease noticeably in the reorientation range along certain crystal-

lographic directions, owing to the coupling of the elastic waves with the soft spin mode.

Experiments were also carried out with magnetostrictive excitation of a high-frequency magnetic field at the fundamental and second-harmonic frequencies by elastic waves. Effective excitation was observed only in the spin-reorientation range.

It was necessary to consider not only the magnetoelastic energy, but also the piezomagnetic energy in order to explain the experimental data on the basis of a thermodynamic analysis.

In contrast to classical ferroelectrics, no distinct phase transition is observed in ferroelectrics of complex composition with perovskite-type structure, such as RbMg_{1/3}Nb_{2/3}O₃. This gave rise to the term "ferroelectric with smeared phase transition." A relaxation type of dielectric polarization is observed in the region of the phase transition in ferroelectrics of this group^[3]. These and other experimental facts can be explained if it is assumed that the smearing of the phase transition is governed by composition fluctuations. In this view, different regions of the crystal (of linear dimension ~ 100 Å) have different Curie points. It is assumed that the relaxation is due to: 1) motion of the boundaries between polar and nonpolar phases or 2) the production and vanishing of polar regions. The latter mechanism was calculated in^[4], in which the Debye theory was generalized to the case in which the number of relaxors varies with temperature (with a maximum at the average Curie point T_{av}). It is then possible to explain a number of experimental facts, including the experimentally observed temperature dependence of ϵ : $1/\epsilon = A + B(T - T_{av})^2$.

¹G. A. Smolensky, R. V. Pisarew, and I. G. Siny, Proc. of Intern. Conference, Japan, July 1970, p. 389.

²A. N. Grishmanovskii, V. V. Lemanov, G. A. Smolenskii, A. N. Balbashev, and N. Ya. Chervonenkis. Tezisy dokladov na Mezhdunarodnoĭ konferentsii po magnetizmu (Abstracts of Papers at International Conference on Magnetism), Nauka, Moscow, 1973.

³G. A. Smolensky, J. Phys. Soc. Japan, Suppl. 28, 26 (1969) (Proc. of the 2nd Intern. Meeting on Ferroelectricity).

⁴V. V. Kirillov and V. A. Ysupov, Ferroelectrics 5, 3 (1973).

V. L. Ginzburg. Surface Excitons of the Electron-Hole Type. It is obvious even from highly general considerations that various surface states (levels) whose populations correspond to the appearance of excitations or quasiparticles (surface phonons, excitons, magnons, electrons at surface levels, etc.) can exist on the surfaces of solids and liquids. It is also natural to assume the possibility of observing surface (i.e., two-dimensional or quasi-two-dimensional) analogs of ferromagnetism, ferroelectricity, superconductivity, superfluidity, etc.

Unfortunately, the investigation of this circle of problems is usually very complex because of the difficulty of obtaining sufficiently perfect surfaces or homogeneous surface layers, because of masking of surface phenomena by bulk effects, and for certain other reasons. As a result, clarification of numerous questions has dragged out over decades; an example is found