V. I. Gol'danskiĭ and Yu. F. Krupyanskiĭ. *Dynamics of biopolymers and the glass model of proteins and* DNA. If the basic characteristics of matter are taken to be the presence (+) or absence (−) of order (i.e., definite structure), periodicity, and geometric single-valuedness of the ground state [here (+) corresponds to entropy tending to zero for $T \to 0$ and (−) corresponds to $S \neq 0$, $T \to 0$], we may conclude that a perfect crystal (+ + +) and glass (− − −) are complete antipodes. Moreover, analysis of the dynamic properties of biopolymers leads to the conclusion that they typically exhibit peculiar combinations of the properties of crystals and glasses.

As long as forty years ago, Schroedinger[1] characterized polymers as aperiodic crystals, and looked upon their order as the *main* functional activity factor. It became clear subsequently that the dynamic properties of polymers played a no less important role in manifestations of their reactivity.[2–4].

For a long time, traditional x-ray analysis led to the conclusion that polymer globules could be looked upon as molecules with geometrically unique positions of atoms in the ground state (+ − +). The conformational mobility observed, for example, in experiments on H–D exchange or luminescent tracer quenching, is usually described by considering short-lived fluctuations in the basic structure which, like any other excited states, have much lower statistical weights.

A fundamentally new approach to the dynamic structure of polymers emerged with the advent of dynamic x-ray analysis (DXA).[5,6] This method has been used to determine the root mean square amplitudes $\langle x^2 \rangle$ of displacements of atoms in the core and the side chains of polymer globules, to detect the presence of "quasisolid" ($\langle x^2 \rangle \lesssim 0.04$ Å^2) and "liquid-like" ($\langle x^2 \rangle$ up to about 1 Å^2) regions in these globules, i.e., the conformational heterogeneity of biopolymers, and thus investigate the temperatue dependence of $\langle x^2 \rangle$ between 300 K (Ref. 5) and 80 K (Ref. 7). The DXA method has substantially extended our ideas on the dynamic properties of polymers and has established the presence of conformational substrates (CS) or, more precisely, quasidegenerate conformational states (QDCS),[5] which corresponds to the designation of the biopolymer molecules as (+ − −). The conformational substrates are understood to be varieties of the same basic growth structure of a particular polymer molecule that are equivalent, or almost equivalent, in energy, but differ very slightly in local configurations (irreversible rotations relative to σ-bonds, shifts of hydrogen ridges, fluctation break-up and restoration of hydrogen bonds and, as a consequence, small shifts of large molecular groups or fragments relative to other portions of a globule). It is precisely transitions between the QDCS that are responsbile for the large values of $\langle x^2 \rangle$ observed by DXA. The idea of QDCS's and transitions between them has provided an explanation of the sharp change in the temperature dependence of the Mössbauer probability f', i.e., its rapid fall for $T \gtrsim 200$ K, first noted for proteins as far back as 1973.[8] This idea was subsequently confirmed quantitatively in new experiments based on *M*össbauer spectroscopy (MS)[9] and Rayleigh scattering of Mössbauer radiation (RSMR).[10,11] All the data ob-

tained by DXA, MS, and RSMR methods were, however, interpreted on the assumption that transitions between QDCS's occurred above the barrier.

On the other hand, it is quite easy to conclude that the presence of the QDCS's should lead to the appearance of a similarity not only between the structural characteristics of the biopolymer (+ − −) and glass (− − −), but between their dynamic properties as well.

According to the model advanced by Anderson *et al.*[12] and Phillips,[13] the linear dependence of specific heat on temperature that is characteristic for amorphous bodies, and is observed for $T \simeq 0.1$–0.4 K in many cases,[14] is due to a departure from equilibrium, the presence of residual entropy as $T \to 0$, and, consequently, the presence of quasiequilibrium positions (QEP) of certain atoms or groups of atoms and glasses. Transitions between these positions occur at low temperatures[12,13] and preferentially by tunneling but, since this tunneling requires resonance between the energy levels in the potential wells in the initial and final states, it is "assisted" by the excitation (emission or absorption) of phonons (this is the so-called phonon-assisted tunneling).

Transitions between the QEP are responsible for the appearance of the linear term $C_1 T$ in the specific heat

$$C_v = C_1 T + C_3 T^3 + C_E f_E \left(\frac{\theta_E}{T} \right) \quad (1)$$

in addition to the second (Debye) and third (Einstein) terms, where $C_1 + (\pi^2/6) \cdot K_B^2 \cdot n(0)$ is related to the QEP energy density $n(E)$ for $E \to 0$ and K_B is Boltzmann's constant.

Analysis of published data on low-temperature specific heats of biopolymers[15] has shown that $C_v(T)$ can be described by (1), where the linear term C_1 and, consequently, the QEP energy density in the globule are much higher than for inorganic and polymeric glasses.[16]

Thus, the analogy with the QEP in amorphous bodies enables us to achieve a more detailed understanding of the biopolymer QDCS's and transitions between them. While the use of DXA has led to the abandonment of the concept of geometric uniqueness of the ground state of biopolymer molecules (i.e., to a change for + − + to + − −), analysis of data on the low-temperature specific heat of biopolymers has led to the conclusion that transitions between the QDCS's occur not only above the activation-type energy barriers, but also by tunneling (in fact, phonon-assisted tunneling), which brings biopolymers closer to glasses not only according to structural but also dynamic characteristics.[16]

At the same time, this conclusion results in a substantial expansion of our ideas on the importance of tunneling by atoms and groups of atoms in different transformations in matter.[17]

At the atomic level, each QDCS corresponds to the occupation by each atom in the macromolecule of one of its degenerate or comparable-energy QEP's. Phonon-assisted tunneling by the smallest atomic groups, such as CH_2, NH, and so on, between the QEP's leads to the appearance of the linear term in the low-temperature specific heat.

Thus, DXA and specific heat data suggest that native polymer macromolecules or DNA macromolecules may be looked upon as a peculiar heterogeneous glass, i.e., an ensemble of regions with different glass transition temperatures, both above and below room temperature. This analogy presupposes a degenerate correspondence between the primary structure and spatial configuration of biopolymers. RSMR experiments indicate that the main factor governing the QEP density in polymers is hydration. Thus an increase in the degree of hydration is accompanied by a sharp increase in the number of QEP's at room temperature.[18] Analysis of transitions by groups of atoms between the QEP's, using RSMR data,[18] shows that, in all probability, tunneling will predominate above activation-type transitions between the QEP's up to room temperature. In addition to studies of biopolymer dynamics by DXA, MS, and RSMR, there is considerable interest in extending the range of experiments on the specific heats of biopolymers in the temperature range between room temperature and the lowest attainable temperatures. Since analysis of the phonon-assisted tunneling probability will yield the parameters of activation-type barriers for biopolymer transformations, low-temperature properties of these materials will yield additional information for the description of functional properties under physiological conditions. As a further confirmation of the importance of this topic, we note that a conference on the low-temperature studies and functions of biomolecules at room temperature is being planned in the USA.

A complete version of this paper will be found in Refs. 11, 16, and 18.

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