

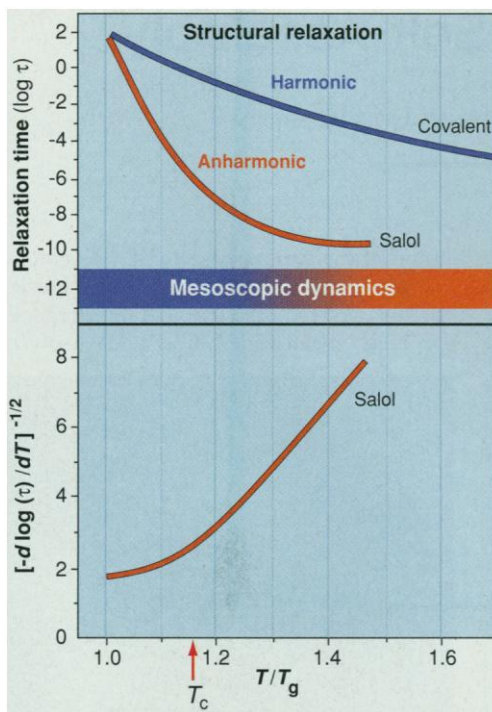
Why the Glass Transition Is Still Interesting

A. P. Sokolov

For thousands of years, it has been known that many liquids can form glasses upon cooling. Glass formation is a general property of liquids with strong covalently bonded structures, like ordinary window glasses; with hydrogen bonds, like glycerol; of alcohols, with weak van der Waals interactions; and of ionic liquids. Inorganic and organic compounds can form glasses, as can polymeric and metallic systems. Yet, in spite of its ubiquity, the nature of the glass transition is still not understood, even qualitatively. There has, however, been significant progress in this field during the last decade, strongly stimulated by achievements of the mode-coupling theory (MCT) of the glass transition (1). MCT is formulated in terms of nonlinear coupling between density fluctuation modes and predicts an ideal kinetic glass transition. Although the theory still has to overcome several problems, it highlights a few essential features in the dynamics of supercooled liquids and has stimulated many experimental efforts. What are these new details of the glass transition process learned during the last decade?

The most important finding is the existence of a crossover temperature T_c above the glass transition temperature T_g where qualitative changes in the dynamics occur. The MCT predicts that the dynamics of the glass-forming liquids should change significantly near T_c . The latter has been identified for some ionic and van der Waals liquids to be $\sim 1.15T_g$ to $1.2T_g$. Although the structural relaxation time τ does not show critical behavior around T_c (see figure, top panel), analysis of experimental results showed (2) that many properties of glass-forming liquids have explicit changes just at this temperature range: The decoupling of different relaxation processes occurs around T_c , and an additional relaxation process, the so-called Johari-Goldstein β process, appears at temperatures below T_c . The most pronounced demonstration of the existence of the crossover temperature has been done recently from analysis of the temperature variations of τ (3). The relaxation time τ varies more than

10 orders of magnitude in the temperature range of interest, and it is difficult to see any details of this variation from a direct analysis of τ (figure, top panel). Instead, the authors of (3) suggested taking the derivative $[d\log(\tau)/dT]^{-1/2}$, which immediately reveals a strong change in the temperature behavior of τ around T_c (figure, bottom panel). Thus,



Glass dynamics. (Top) Temperature variations of the structural relaxation time for a typical van der Waals glass-former salol [red, data from (3)] and for a typical covalently bonded system (blue). The region of the mesoscopic dynamics is marked to stress the great difference in time scales between these two processes. **(Bottom)** Temperature variation of the derivative of τ clearly shows a presence of some crossover temperature above T_g [salol, red, data from (3)].

the glass transition is not a monotonic process and qualitative changes in the dynamics occur at a certain crossover temperature. It seems that above this temperature, glass-forming systems behave as normal liquids, and at T_c , a transition to more and more pronounced solidlike behavior with spatial and dynamic heterogeneities starts. At present, the description of the temperature dependence of τ is a great challenge because neither MCT nor any other known theory of the glass transition can do it properly.

Another important detail is the role of fast dynamics—that is, excitations in the mesoscopic frequency range $\nu \sim 10$ to 1000 GHz (which is significantly below the frequency of a single-molecule vibration) in the glass transition scenario. It is well known that the excitation spectrum of glasses in this mesoscopic frequency range has two features (4): an anharmonic relaxation-like contribution, which is traditionally ascribed to motion in double well potentials (the famous tunneling states), and harmonic quasi-local vibrational excitations, which show up as the low-frequency so-called boson peak. Both contributions are believed to be collective excitations involving ~ 20 to 100 atoms.

Recent analysis showed (5) that the ratio of these two contributions to the dynamic spectrum in the mesoscopic frequency range correlates strongly with the behavior of the structural relaxation around T_g : If the vibrational contribution dominates the spectrum, the glass-forming system shows an Arrhenius-like temperature behavior of τ ; if, however, the anharmonic contribution dominates, the system shows a more complicated temperature variation of τ (figure, top panel). These correlations look exciting because at T_g the structural relaxation time is separated from the mesoscopic dynamics by more than 10 orders of magnitude. The temperature variations of the fast dynamics spectrum also show qualitative changes around T_c (1, 5, 6). These results strongly support the idea that the mesoscopic dynamics drives (or at least strongly influences) the dynamics of the glass transition. Also, MCT suggests that a fast process in the mesoscopic frequency range is a precursor of the slow structural relaxation. Although there are some suggestions (5, 7), it remains a challenge to find a relation between the mesoscopic dynamics and variations of the structural relaxation during the glass transition.

These two new features of the glass transition dynamics—qualitative changes at a certain T_c and the role of the fast dynamics—change significantly our vision of the glass transition process. In particular, it has been pointed out that the temperature range between T_c and T_g is rather short ($T_c \sim 1.15T_g$ to $1.2T_g$) for ionic and van der Waals systems but is very broad ($T_c \sim 1.7T_g$ to $1.6T_g$) for glass-forming systems with strong covalently bonded structure (5, 6). For B_2O_3 , it has been found (6) that $T_c \approx 850$ to 900 K is significantly higher than the melting point $T_m \approx 725$ K. One also notes that it is nearly impossible to crystallize supercooled B_2O_3 . These results lead us to speculate that liquids below the crossover temperature can be stable against crystallization.

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At present, understanding the glass transition phenomenon is one of the most intriguing puzzles in the physics of condensed matter. It may ultimately influence different fields, in particular biophysics and biochemistry (8). Biological macromolecules like proteins and DNA show many similarities with glasses in the mesoscopic frequency range (9): There are harmonic low-frequency vibrations, similar to the boson peak in glasses, and there is a fast anharmonic motion. Also, some crossover temperatures were identified for biological macromolecules (8–10). It could be that the stabilization of biological objects below some T_c , which may be achieved not only

by cooling but also by changes in the chemical composition of the solution (for example, by drying), is very important for their preservation, suppression of their degradation with time, and so on. Thus, the understanding of the glass transition phenomenon in relatively simple systems can bring new ideas in other fields of science and technology.

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Visualizing the Logic Behind RNA Self-Assembly

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Spliceosomes and ribosomes are the complex molecular machines that our cells use to assemble genetic messages and translate them into proteins. RNA, not protein, is the central player in both of these multicomponent complexes. Thus, the three-dimensional structure of RNA is key to our understanding of the chemistry at the heart of two essential processes catalyzed by living organisms: RNA splicing and protein synthesis. It may well also be the key to how the ancestors of life on Earth made a living, because large RNA molecules can carry out many of the catalytic functions previously believed to be specific to proteins. Although we know the three-dimensional structures of thousands of proteins, RNA crystallography has been slow to come of age. But we are now at a turning point; with two papers in this issue (1, 2), it will be the third consecutive year during which the crystal structure of a large RNA molecule has been published. And as is fitting for an Olympics year, the 160-nucleotide RNA, the structure of which is reported by Cate *et al.* (1, 2), shatters a 22-year-old record: transfer RNA, with a mere 76-odd nucleotide monomers, is no longer the largest RNA structure solved at atomic resolution.

This success can be attributed in part to the many theoretical and technical advances in macromolecular crystallography since the days of transfer RNA [for details on the reso-

lution of the structure, see (3)]. As is often the case with crystallography, this breakthrough also required considerable preparatory biochemical work. Cate *et al.* have solved

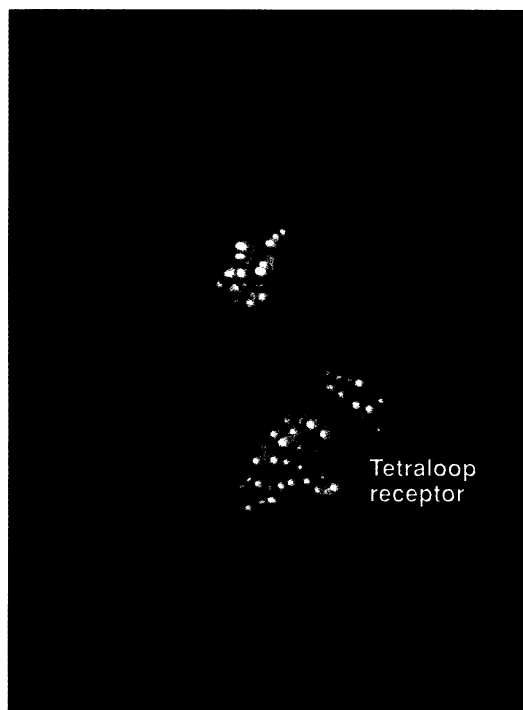


Image of a catalytic RNA. The 160-nucleotide domain of the *Tetrahymena* intron. The compactness of the structure is achieved through side-by-side helix packing and specific tertiary contacts in the shallow grooves of the RNA helices. The newly discovered A-A platform (white) occurs three times. One of the A-A platforms forms part of the 11-nucleotide receptor (yellow and white) for an apical GAAA tetraloop (red). This picture was made with DRAWNA (10) with the use of coordinates provided by Cate *et al.* (1).

the structure of a fragment of the celebrated *Tetrahymena* intron, which 14 years ago was the first RNA molecule found to have catalytic activity. The key step to success was the identification of this fragment as an autonomously folding domain (4). In fact, both the hairpinlike overall fold of this molecular domain and the two clamps that maintain its bent shape had been anticipated from the biochemical work. However, a blurred image has now been replaced by a sharp 2.8 Å resolution picture teeming with exciting detail.

It should come as no surprise that large catalytic RNA molecules, with only four nucleotide building blocks at hand, achieve the compact architectures that seem essential to their function by making intensive use of a small number of preferred motifs and their combinations. One example of these recurrent motifs is constituted by the so-called GNRA loops and their receptors. Four-nucleotide terminal loops with a GNRA sequence (R stands for A or G, and N can be any base) are frequent in large RNA molecules such as the ribosomal RNAs. A few years ago, it was proposed from sequence comparisons and model building (5) that the evolutionary success of GNRA loops reflects in part their ability to interact with specific sequence motifs in the shallow (minor) groove of RNA double helices. Since then, the existence of several varieties of GNRA loop–receptor pairs has been demonstrated. In one of these pairs, which was recently visualized as an intermolecular contact in crystals of the “hammerhead” RNA (6), the receptor consists essentially of two consecutive base pairs in a helix. But some receptors are larger; the one for GAAA loops, which is of special interest because of its particularly high affinity and remarkable abundance in large catalytic RNAs (7), comprises 11 nucleotides in its complete form. Because this particu-

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