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AUG 78 M GOLDSTEIN

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STUDIES IN SECONDARY RELAXATIONS IN GLASSES: INFLUENCE OF ANNEALING ON THE STRENGTHS OF RELAXATIONS.

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A study of the influence of annealing (as measured by the fictive temperature) on the strength of dielectric loss in glasses was studied on six molecular liquid glass-formers. A remarkable sensitivity of dielectric loss to fictive temperature was found (1-3 per cent per degree fictive). This sensitivity decreased as the temperature of measurement decreased. It was not possible to determine whether the changes in the β -relaxation region were greater than the changes in the background loss. The thermodynamic implications of these results for the glass transition are pointed out.

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Introduction

In this terminal report we repeat, in the interest of completeness, some material from a previously submitted Interim report covering the period March 1, 1975 to April 30, 1976.

The research carried on under this grant has involved both theoretical and experimental aspects, with the results of the theoretical analyses determining the direction taken in the experimental studies.

The theoretical program has focused on two closely related but different aspects of the glass transition: the first more narrowly concerned with the thermodynamic aspects, and the second on the molecular basis for the thermodynamics; i.e. on the statistical mechanics.

The experimental part of the program has been concerned with a quantitative study on the influence of structural state (fictive temperature) on the strength of secondary relaxations.

Theoretical Program

On the purely thermodynamics side, a careful re-examination of the standard thermodynamic treatment of the transition was undertaken in view of a critical analysis of it by E.A. DiMarzio (J. Appl. Phys. 45, 4143 (1974)), whose conclusion was that the standard treatment has overlooked certain of the logical consequences of its own premises, and if these consequences are taken into account, much of the previous analyses of the relevance of thermodynamic parameters such as free volume and configurational entropy to the observed transition temperature T_g would be in error.

Our re-examination led to the conclusion that DiMarzio's analysis is in error, and that the original thermodynamic treatment and the inferences drawn from its application are correct. This work formed part of an invited lecture to the Division of High Polymer Physics of the American Physical Society meeting in Denver in March 1975, and has been published with the Proceedings of the Meeting in the Journal of Applied Physics. A copy is appended to this report as Publication No. 1.

As part of a more general analysis of configurational thermodynamic properties of glass forming substances (specifically of entropy) because of their relevance to the evidence for a thermodynamic phase transition below T_g , to equation of state expressions for polymers, and to the pressure dependence of T_g , attention was paid to an ambiguity in their definition. In brief, it was concluded that although infinitesimal changes in these properties are operationally defined and are therefore independent of theories of the transition, the same need not be true for their total values. It was realized that this problem required a closer look at the molecular origin of the configurational properties.

An analysis of calorimetric data from the National Bureau of Standards on six glass forming substances, including selenium, two organic high polymers and three molecular glasses, was carried out. The conclusion was that the interpretation of the excess "configurational" heat capacity ΔC_p observed at T_g as arising solely from changes in the number of molecular configurations available to the liquid with changes in temperature is seriously in error. Only about half of ΔC_p arises from this source. Part of the remainder arises from changes in lattice vibrational frequencies with structure and part either from changes in

anharmonicity with structure, or changes in the number of molecular groups that are capable of engaging in secondary relaxations with structure. This work formed the remainder of the invited lecture given at the A.P.S. meeting in Denver, and is described in several papers, one which appeared in the Journal of Chemical Physics, a second in the Proceedings of a Conference on "The Glass Transition and the Nature of the Glassy State", held under the auspices of the New York Academy of Science in New York City in December 1975.

Copies of both are appended as Publications 2 and 3.

Additional development of the theoretical ideas about configurational entropy described in the Interim Report of April 30, 1976, were presented to the Fourth International Conference on Non-Crystalline Solids held September 1976, in Clausthal, Federal Republic of Germany, and are published in "Non-Crystalline Solids", G.H. Frischat, Editor, Transtech Publications, Rockport, Massachusetts, 1977, under the title, "Sources of the Configurational Specific Heat and Entropy of Liquids Near the Glass Transition". Unfortunately, I have not been given reprints, nor does my library possess a copy I could xerox the article from. It is listed as publication No. 4.

Currently theoretical models based on the above conclusions are under investigation. It appears that a thermodynamic transition of the Ehrenfest type, as has been inferred by Gibbs and DiMarzio from thermodynamic data and also derived by them from a statistical mechanical model based on configurational considerations, may also arise from the factors listed previously: changes in lattice frequencies, anharmonicity and numbers of "loose" molecular groups, as structure is changed.

Experimental Program

In the Interim Report of April 30, 1976 we reported the preliminary results of a study of the influence of annealing on dielectric loss in the glassy state.

In the period from that time to the termination of the grant Dr. James Haddad and I continued the experimental study of this problem. We studied six glass-forming molecular liquids, but we believe our results are consistent with the very small amount of qualitative observations on organic high polymers as well.

We have written up our results for publication, and our paper has been accepted by the Journal of Non-Crystalline Solids; a copy is appended to this report as publication No. 5.

Results of the Research

We can best summarize the results by first quoting the abstract of the paper verbatim, and then making a few additional comments.

"The influence of fictive temperature T_f (defined as the temperature in the transition range at which the sample was annealed to equilibrium) on dielectric loss tangent in the glassy state has been investigated in 6 molecular glass systems, of which 4 have well defined β -relaxations. The temperature range used extended from a little below the glass transition temperature T_g to 77.K, and the frequency range was from 300 Hz to 50 kHz. A tendency for some structural relaxation to occur at an appreciable rate below the transformation range, already reported by others, was apparent in our studies, and prevented a quantitative answer to the question of how much the β -relaxation strength depends on T_f . Qualitatively it was found that in two of the substances the β -relaxation strength decreased as T_f was lowered; in two others the

results were ambiguous. In all substances the background dielectric loss, a general feature of the glassy state on which secondary relaxations, when present, are superposed, was significantly dependent on T_f : The percentage change in $\tan \delta$ per degree change in T_f was about 1-3 per cent in most of the substances, and 5-8 percent in one of them, although in all cases it tended to decrease as temperature decreased. This is a remarkable sensitivity of T_f , compared to, for example glass density, which varies by .02 to .04 percent per degree change in T_f . The molecular origin of the background loss is not well understood, but it has been related to anharmonicity, which in turn has been suggested to make a significant contribution to the thermodynamics of the liquid at T_g ."

Additional Comments:

(1) The occurrence of appreciable structural relaxation well below the usual transition range is a phenomenon that has recently emerged in studies of thermal aging in polymers. However it could be avoided in future studies of the effect of annealing on the β -relaxation by the use of higher frequencies than our equipment permitted (100 kHz to 1 MHz).

(2) The background loss in dielectric studies of glasses, to which very little scientific attention has been paid until now, is seen to be of possibly great significance as an indicator of a characteristic excess anharmonicity of the amorphous state, which in turn may be of thermodynamic significance for the glass transition. This concept has provided the basis for a new model of the glass transition I have published in the Journal of Chemical Physics (67, 2246 (1977)).

LIST OF PUBLICATIONS

1. M. Goldstein "Validity of the Ehrenfest equation for a system with more than one ordering parameter: Critique of a paper by Di Marzio". J. Appl. Phys. 46 4153 (1975)
2. M. Goldstein "Viscous liquids and the glass transition. V. Sources of the excess specific heat of the liquid". J. Chem. Phys. 64 4767 (1976)
3. M. Goldstein "Statistical Thermodynamics of Configurational Properties". Annals N. Y. Acad. Sciences 279 68 (1976)
4. M. Goldstein "Sources of the Configurational Specific Heat and Entropy of Liquids Near the Glass Transition". in Non-Crystalline Solids G. H. Frischat, Ed. Transtech Publications, Rockport, Mass. 1977
5. J. Haddad and M. Goldstein "Viscous liquids and the glass transition. VIII Effect of fictive temperature on dielectric relaxation in the glassy state". J. Non-crystalline Solids, in press.