CURRENT TRENDS IN THE SCIENCE AND TECHNOLOGY OF GLASS

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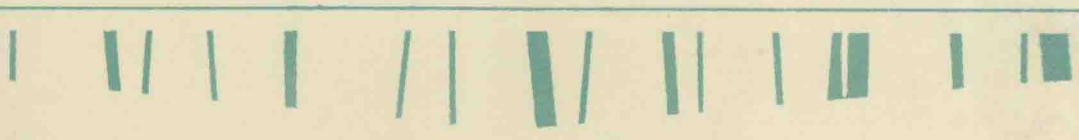

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PREFACE

It was the Spring of 1986 in New Delhi and the occasion was the XIV International Congress on Glasses, when a few participants started talking about the impact of the Congress on glass science and technology in India. As a result, a need was recognized for in-depth discussions on selected topics to continue the enthusiasm generated at the Congress. At that point Dr. E. C. Subbarao suggested the possibility of organizing an Indo-US Workshop. At this Workshop experts from the two countries would review the latest developments in a specific area of glass science or technology, which in turn would nucleate lengthy open discussions. Eventually a Workshop, with the added goal of enhancing interactions between the glass research communities of the two countries, was successfully held in Bangalore, India from November 13 to 20, 1988. Primary support for the Workshop was provided by the Department of Science and Technology, Government of India, and the U.S. National Science Foundation.

The overview papers at the Workshop were presented at the level of first year graduate student. It was felt that many others with an interest in science and technology of glass could benefit from the publication of these papers, hence this book which includes most of the Workshop papers. Because the purpose of the Workshop was to conduct in-depth discussions, only selected areas of glass research could be included in the program or this book.

We strived to publish this book soon after the Workshop and in doing so depended on the help of several individuals. In particular, we appreciate quick response from the contributors who also served as reviewers for the papers. Financial support by the National Science Foundation towards this publication and its distribution to the participants is also gratefully acknowledged.

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CONTENTS

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MODELS OF THE GLASS TRANSITION

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Abstract

Key features of the glass transition pheonomenon and three models of glass transition (the order parameter model, the free-volume model and the configurational entropy model) are critically reviewed. It is concluded that
(i) the order parameter model, representing an application of non-equilibrium thermodynamics to glass transition phenomenon, provides a rational basis for building the phenomenology of glass transition,
(ii) the free-volume model fails in several respects. It must be rejected as a viable model of glass transition, and
(iii) the Adam-Gibbs model explains most of the features of glass transition. Inspite of its few shortcomings it appears to represent a step in the right direction.

I. INTRODUCTION

A viable model of a phenomenon must explain most (and preferably all) of its key features. These features are those which are sufficiently general (i.e., almost always present whenever the phenomenon is observed), which are reasonably complete to distinguish and define the phenomenon, and which are seemingly independent of each other. Clearly it is necessary for a discussion of the models to first establish the set of key features for the phenomenon under consideration.

What are the key features of the glass transition? About five years ago Professor K. J. Rao, our chief host and one of the coordinators of

this workshop, and two of his colleagues attempted to answer this question in a review paper (1) entitled "The Glass Transition: Salient Facts and Models." As the most important feature they stated "more or less discontinuous changes from solid-like to liquid-like values in the second derivatives of the Gibbs free energy." Goldstein (2) in 1984, in an article entitled "The Signature of the Glass Transition," lists six features none of which contain the one mentioned by Rao. Goldstein argued that loss of degrees of freedom leading to a drop in specific heat cannot be considered a signature of the glass transition. He states that " a little thought will show that behavior resembling this will be observed when the rate of any physical or chemical process that shifts its equilibrium with temperature slows down to the point of unobservability. Not every such kinetic freezing out process can properly be called a glass transition." A lively discussion of this and other related issues is published as the panel discussion in a 1986 volume of the Annals of the N. Y. Academy of Sciences (3). As the leader of the discussion panel Angell asked "what are the criteria on which we should insist before recognizing some structural "freezing" phenomenon as a "vitrification" leading to a vitreous or glassy state. --- Let me direct this question to Dr. Moynihan." Moynihan replied, "I have no really good definition of a glass in the broadest sense." It is clear that in spite of the apparent naivete of the question of the key features of the glass transition, the answer is not simple unless the field of kinetically arrested phenomena is confined in some sense. In this paper attention will be limited to the glass transition in liquids.

When a liquid is cooled below its equilibrium melting point, it tends to crystallize. Since cystallization proceeds by nucleation and growth, it is possible by sufficiently rapid cooling to supercool a liquid to temperatures where the crystallization times are extremely large so that it is effectively suppressed. A supercooled liquid behaves in a manner which can be predicted by the analytic continuation of the equilibrium liquid from above the melting point to temperatures below it. This is because the probability for the system to be in the part of the phase space which consists of crystalline configurations is extremely small at temperatures above the melting point and below the

melting point the time allowed for the system to jump over the barrier to visit this part of the phase space is too small. Therefore a supercooled liquid in the context of glass transition is referred to simply as the equilibrium liquid.

As a liquid cools its structure continuously rearranges to maintain equilibrium with temperature. The low energy configurations with increased short range order become increasingly more probable with decreasing temperature. The description of the kinetics of the structural rearrangement process requires a distribution of relaxation times, i.e., it is non-exponential (or non-Debye) in nature. These structural relaxation times increase rapidly with decrease in temperature. The slowing down of the structural relaxation modes at low temperatures leads to a separation of time scales for the fast vibrational modes and the slow configurational (i.e., structural) modes. The three time scales in a glass-forming liquid are shown schematically as a function of temperature in Figure 1. The structural relaxation process is represented by a band of relaxation times which is narrow at high temperatures and becomes wider at lower temperatures. The average relaxation time is dominated by the slowest of the processes and is effectively represented by the upper edge of the band.

At a sufficiently low temperature (called the glass transition temperature, Tg) the average structural relaxation time becomes equal to the experimental time of observation (usually of the order of seconds to minutes in typical relaxation experiments). Below Tg, a liquid is sufficiently viscous that it behaves essentially like a solid and is called a glass. The faster modes of structural relaxation freeze-in gradually at lower temperatures allowing relaxation to occur below the glass transition temperature.

Clearly there are three aspects of the glass transition: (i) the behavior (both thermodynamic and kinetic) of the liquid state in the high viscosity range near Tg; (ii) the changes in properties associated with the liquid to glass transition; and (iii) the behavior (both static and dynamic) of the glassy state. Table I lists the important features of each of these. In Section II some of these features are discussed in more detail.

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Not surprisingly, there exist a large number of models explaining different aspects of the glass transition phenomenon. Table II is a crude attempt to arrange some of the more widely known models in a manner which shows their domains of applicability and classifies them by the degree of microscopic detail contained in each. Models which are phenomenological have wide applicability. They can explain the general features irrespective of the molecular nature of the system, but cannot provide microscopic details. For example,the order parameter model (4, 5) is an extension of classical thermodynamics to systems with relaxing degrees of freedom. It cannot provide detailed physical meaning of order parameters. That meaning must come from some more microscopic model. Similarly the statistical-mechanical model based on broken ergodicity (6, 7) is an extension of conventional statistical mechanics to systems which are non-ergodic. Its results are applicable to all kinetically arrested systems. The second class of models contains semi-microscopic models such as the Adam-Gibbs (8) or the free-volume (9, 10) models for the average structural relaxation time of a liquid. These, inspite of some vague mathematical approximations, find wide popularity because they provide some physical insight and give results which can be tested by experiments. The last class contains microscopic models such as the various Ising Spin models (11, 20). These can be formulated precisely but are difficult to solve exactly. Application of these models to relaxation in liquids requires vague physical interpretations of key concepts such as spins and transition probabilities. The usefulness of such models lies in the fact that they can be solved by Monte Carlo techniques (12) to a sufficient degree of accuracy and thereby can be used to test the predictions of the second class of models.

Models trying to explain the thermodynamic properties are conceptually simpler than the models describing the kinetics. Scherer (23) has categorized the dynamic models as rheological when they explain the behavior of the average relaxation time and as relaxational when they aim to explain the non-exponential aspect of the relaxation. In the latter category there exist two types of models: (i) those describing relaxation as a set of elementary processes taking place in

parallel with each other and (ii) those describing relaxation in terms of a sequence of elementary relaxation processes, each of which requires the completion of the preceding one. These latter ones are called "heirarchically constrained models" (13, 14).

In the last five years, several publications have appeared which review the field of glass transition and the associated models (23-28). In particular Jackle's paper (25) is an excellent and exhaustive review of the field. In addition to these publications there are many publications on specific models. References to various models are given in Table II. In this work shop, Dr. Ramaswami (29) has given a presentation on the mode coupling theory and Dr. Bagchi (30) has discussed models of non-exponential relaxation. Therefore attention, in this paper will be focussed mainly on the order parameter model and the two semi-microscopic models (Adam-Gibbs and free volume models) with brief remarks about the facilitated Ising spin models. A comparison of these models is presented in Section III.

II. FEATURES OF THE GLASS TRANSITION

A. Metastable Liquid State

1. Average Structural Relaxation Time.

Perhaps the most well known aspect of glass forming liquids is the rapid increase of the shear viscosity, η, with decrease in temperature. It is no surprise that Goldstein (2) lists as first in his list of features characterizing the glass transition, "a high apparent activation energy for molecular mobility at the glass transition temperature." Viscosity measurements as a function of temperature have been made on a large number of glass forming liquids (31, 32). Viscosity typically follows, over a large range, the Vogel-Fulcher (VF) equation:

$$\ln \eta = \ln \eta_\infty + \frac{A}{T-T_o} \qquad (1)$$

where the three parameters η_∞, A, and T_o are constants with respect to temperature. There remains a question, however, about the applicability of Equation (1) at high viscosities. Uhlmann (33), and others (34) have shown that for viscosities greater than about 10^7 poise the temperature dependence for some liquids shifts to an Arrhenius type with a high value for the activation enthalpy. This is significant, particularly in view of the facts that the distinction between the VF and Arrhenius equations is most pronounced at low temperatures in the vicinity of T_o and the non-divergence of the relaxation time has serious implications on some of the models. Does the Arrhenius dependence of η translate into a VF dependence for the average shear relaxation time, τ_s($= \eta/\mu_\infty$) if the temperature dependence of the infinite frequency shear modulus, μ_∞, is taken into account? The T-dependence of μ_∞ is given by a relation of the type (36):

$$\mu_\infty(T)^{-1} = \mu_\infty^{-1}(T_C) + a(T-T_C)$$

where a and T_c are constants. Using this equation and an Arrhenius form for η it can be shown that the temperature dependence of τ_s departs from the Arrhenius behavior in a direction opposite to that for the VF behavior.

It is reasonable to ask about the role of shear viscosity in the process of structural relaxation. Davies and Jones (37), more than thirty years ago, stated that "ordinary viscosity refers to shearing motion while there is no need for shearing motion to occur during stabilization. It is clear that what is required is an appropriately defined volume viscosity." The existence of a volume viscosity was recognized by Stokes in 1845 (38). The volume viscosity, η_v, can be measured by ultrasonic absorption spectroscopy (39). Litovitz and Davis (39) have published values of volume and shear viscosities for a variety of liquids. The ratio η_v/η_s is rarely greater than 20 or less than 0.1. More importantly according to Litovitz and Davis (39) "the temperature dependence of η_v is close to that of η_s". Similar results were reported by Davies and Jones (37) for glucose and glycerol and more

recently by Simmons and Macedo (40) for an oxide glass. Based on these observations it is generally believed that the average structural relaxation time, τ, follows same temperature dependence as the average shear relaxation time, τ_s. Recently Angell (41) has raised the possibility of decoupling at low temperatures of the shear and structural relaxation times so that the time for structural relaxation , the slower of the two processes, may not switch from VF to Arrhenius behavior and may follow the VF behavior all the way to the glass transition temperature.

Angell (32) has noted a strong though not perfect correlation between departures from the Arrhenius behavior and the magnitude of the heat capacity jump (ΔC_p) at the glass transition temperature. This correlation was first pointed out by Moynihan and Cantor (35). Liquids whose behavior is close to being Arrhenius have low values of ΔC_p and are referred by Angell as "strong." The other end of the spectrum contains liquids which depart significantly from the Arrhenius behavior and have large values of ΔC_p. These are termed "fragile." This correlation between temperature dependence of viscosity and ΔC_p, provides a strong support (as will be discussed later) for the Adam-Gibbs theory.

While the shear viscosity of most equilibrium liquids increases with increase in pressure, there are some glass forming liquids which exhibit a negative pressure dependence (42). Although only a small number of liquids show the anomalous behavior, the fact that it is possible is a powerful test for models of the liquid state (43). For example the negative pressure dependence of the viscosity is incompatible with the free-volume theory of liquids (44). But the Adam-Gibbs model permits such behaviour and suggests a correlation between the pressure dependence of viscosity and the magnitude of the jump in the expansion coefficient at the glass transition temperature (43).

2. Structural Relaxation Behavior.

When an equilibrium liquid is subjected to a sudden change in temperature or pressure its properties (volume, shear viscosity,

enthalpy, etc.) exhibit an instantaneous change which is followed by a slower and gradual change to the new equilibrium values. The instantaneous change takes place because of the rapid relaxation ($\tau_{vib} \simeq 10^{-13}$ seconds) of the vibrational states of the system. The slower change occurs due to rearrangement of the structure. The relaxation function $\phi_p(t)$ for a property, p, is defined as fraction unrelaxed at time t:

$$\phi_p(t) = \frac{p(t) - p(\infty)}{p(0^+) - p(\infty)} \qquad (2)$$

Here $p(0^+)$ is the value of the property at time zero after the instantaneous change, and p(t) is the value at time t. As defined $\phi_p(0) = 1$ and $\phi_p(\infty) = 0$. There are three aspects of the relaxation function which are commonly observed:

(i) Non-linearity

This is perhaps the most important aspect of relaxation in glass-forming liquids. The relaxation function in temperature jump experiments depends on the sign and magnitude of the temperature jump. As an example Figure 2 (taken from Reference 24) shows density relaxation following a temperature jump in a sample of plate glass. Two identical samples were held isothermally at 530°C after equilibrating one at 500°C and the other at 560°C. Both samples approach the same value of density after sufficiently long time. However the one equilibrated at the higher temperature relaxes at a faster rate than the sample equilibrated at the lower temperature.

The reason for the non-linearity is that the relaxation time (i.e. viscosity) depends on the structure. Consequently the relaxation time changes as the structure changes. In fact the change in viscosity following a temperature jump has been directly measured by Mazurin and his colleagues (45) for a number of glasses. The results show an instantaneous change in viscosity followed by a gradual change with time. These results are similar to the classic results of Lillie (46).

Non-linearity is always observed in experiments measuring enthalpy relaxation following a temperature jump because present instruments are

not sensitive enough to follow relaxation for ΔT values less than a few degrees (23). Recently Birge and Nagel (47) have developed a method (called specific heat spectroscopy) for measuring enthalpy relaxation in the linear regime using a sinusoidal temperature variation of extremely small amplitude and frequency which can be varied over six order of magnitude.

(ii) Non-exponentiality

The relaxation function is generally not exponential. It follows rather closely the stretched exponential (or the KWW) function (24):

$$\phi(t) = \exp[-(t/\tau)^{\beta}] \qquad (3)$$

where the exponent β has a value between 0 and 1. The corresponding distribution of relaxation times is asymmetric and is skewed toward short relaxation times. When $\beta = 1$, Equation (3) is a single exponential. The width of the distribution increases as β decreases. Ngai (48) and Douglas (49) have shown that the KWW equation provides a good fit to data obtained on a wide variety of materials. Birge and Nagel (47) find best fit for the peak shapes of their heat capacity data using the KWW equation. It is important to realize that while the KWW equation fits the data rather closely over short periods of time, a single value of β is not sufficient to fit data over large range of time (50). According to Scherer (24), "the measurements by Kurkjian (1963) of the shear relaxation function of a soda-lime-silicate glass are probably the best data available". Figure 3, taken from the work of Rekhson (51), shows a systematic deviation of Kurkjian's data from the KWW equation.

(iii) Thermo-rheological simplicity

The non-exponential relaxation functions of liquids near a glass transition exhibit a scaling property. Although the relaxation time changes with temperature over many orders of magnitude, the form of the relaxation function remains unchanged. Therefore relaxation curves which have been measured at different temperatures can be made to fall on a single master curve by scaling the time with an appropriate average relaxation time. For the KWW function this scaling principle, generally

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