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Mode-coupling theory and the glass transition in supercooled liquids

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Mode-coupling theory is an approach to the study of complex behavior in the supercooled liquids which developed from the idea of a nonlinear feedback mechanism. From the coupling of slowly decaying correlation functions the theory predicts the existence of a characteristic temperature T_c above the experimental glass transition temperature T_g for the liquid. This article discusses the various methods used to obtain the model equations and illustrates the effects of structure on dynamics and scaling behavior over different time scales using a wave-vector-dependent model. It compares the theoretical predictions, experimental observations, and computer simulation results, and also considers phenomenological extensions of mode-coupling theory. Numerical solutions of the model equations to study the dynamics from a nonperturbative approach are also reviewed. The review looks briefly at recent observations from landscape studies of model systems of structural glasses and their relation to the mode-coupling temperature T_c. The equations for the mean-field dynamics driven by the p-spin interaction Hamiltonian are similar to those of mode-coupling theory for structural glasses. Related developments in the nonequilibrium dynamics and generalization of the fluctuation-dissipation relation for the structural glasses are briefly touched upon. The review ends with a summary of the open questions and possible future direction of the field.

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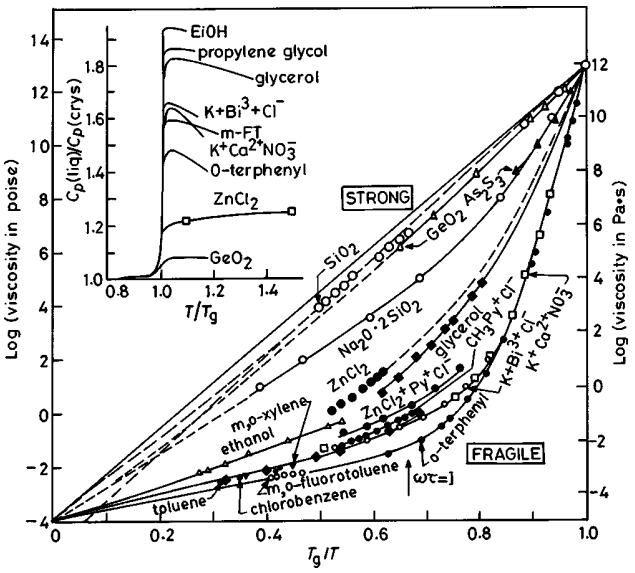

FIG. 1. Viscosity of various glass-forming liquids vs T_g/T. T_g is defined as the temperature at which the viscosity reaches 10^{14} P. From Angell, 1984.

I. INTRODUCTION

Almost every liquid undergoes a glass transition when supercooled below its freezing temperature, bypassing the formation of the crystalline state. The rapidly increasing viscosity of the liquid is a generic feature of the supercooled state. Many different expressions have been used to fit the experimentally observed temperature dependence of the viscosity. These include the standard Arrhenius form $\sim\exp(A/T)$, the Vogel-Fulcher form $\sim\exp[B/(T-T_{VF})]$, and the power-law behavior $\sim(T-T_o)^{-\gamma}$. Experimentally the temperature at which the viscosity reaches the value of 10^{14} P has usually been identified with the so-called calorimetric glass transition temperature T_g. An interesting plot of the data of glassy relaxation was made by Angell (1984) of viscosity η vs inverse temperature T_g/T scaled with T_g (see Fig. 1). The increase of viscosity in different materials occurs in different ways. One extreme is a slow growth of η with lowering of temperature T over the temperature range $T>T_g$ followed by a very sharp increase within a small temperature range close to T_g. In a number of systems described as *fragile liquids* a crossover in the temperature dependence of the viscosity η was observed. A more uniform increase is seen over the whole temperature range for strong liquids like B_2O_3 or SiO_2. This behavior has been quantified by defining a *fragility parameter* m as the slope of the viscosity-temperature curve as $m=d\ln\eta/dT$ at $T=T_g$ (Böhmer *et al.*, 1993). Thus, for example, $m=81$ (for o-terphenyl) and $m=20$ (for SiO_2) denote two extreme cases of fragile and strong systems.

Understanding the transformation of a normal liquid to an amorphous-solid-like state from the basic laws of statistical physics has been an area of strong research interest in recent times. The dynamics of the liquid state at the microscopic level are described by the classical equations of motion of a very large number of particles. Early theoretical work on the dynamics of the fluid state involved to a large extent the study of kinetic theories of hard spheres, following the approach of Maxwell and Boltzmann (Chapman and Cowling, 1970). Transport phenomena in the liquid were studied from the Boltzmann equation with Enskog corrections, which included only short-range uncorrelated binary collisions of the constituent particles. Theories of the fluid that consider only the time evolution of the microscopic states controlled by uncorrelated collisions lead to the conclusion that the fluctuations from equilibrium decay with an exponential dependence on time. Thus typical time-dependent measurements on the fluid could be understood in terms of simple exponential relaxations. Deviations from such behaviors appeared in subsequent studies. Typical examples of such cases are the density expansion of transport coefficients (Zwanzig, 1963; Kawasaki and Oppenheim, 1965; Ernst *et al.*, 1969) discovered to be nonanalytic, or computer simulation studies of hard-disk or hard-sphere fluids (Alder and Wainright, 1967, 1970) showing that the correlation of the velocity $v(t)$ of a tagged particle with the same quantity at an earlier time follows with a power-law decay ($t^{-d/2}$ in d dimensions). The traditional kinetic theories dealing with uncorrelated collisions of fluid particles were extended to study correlated motions in terms of ring and repeated-ring collision events between the fluid particles. The origin of these observed behaviors were collective or hydrodynamic effects (Zwanzig and Bixon, 1970; Pomeau and Résibois, 1975) on a semimicroscopic level. As the liquid is increasingly supercooled below its freezing point and approaches the glass transition, the role of correlated motions of the fluid particles becomes