

# Mode-coupling theory and the glass transition in supercooled liquids

Shankar P. Das\*

*School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067, India*

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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.

## CONTENTS

|  |     |   |     |
|--|-----|---|-----|
| I. Introduction                              | 786 | A. The one-component liquid                               | 801 |
| II. Classical Liquids: Some Preliminaries    | 788 | 1. The schematic model                                    | 801 |
| A. Equilibrium structure of the liquid       | 788 | a. Relaxation over different time scales                  | 801 |
| B. Time correlation functions                | 789 | b. The nonergodic phase $\Delta_0 \geq 0$                 | 802 |
| 1. Neutron-scattering experiments            | 789 | c. The ergodic phase $\Delta_0 < 0$                       | 802 |
| 2. Light-scattering experiments              | 789 | 2. Effects of structure on the dynamics                   | 802 |
| C. Linear response to perturbations          | 790 | a. The cusp behavior of the nonergodicity parameter       | 803 |
| 1. Fluctuation-dissipation theorem           | 790 | b. Scaling in power-law relaxations                       | 804 |
| 2. Linear transport coefficients             | 790 | c. The factorization property                             | 804 |
| III. Collective Modes in Classical Liquids   | 791 | d. Alpha-relaxation scaling                               | 805 |
| A. Hydrodynamic description                  | 791 | e. Viscoelastic behavior                                  | 805 |
| 1. Conservation laws and balance equations   | 791 | 3. Tagged-particle dynamics                               | 806 |
| 2. Macroscopic hydrodynamics                 | 791 | B. Extensions to more complex systems                     | 808 |
| a. Local equilibrium distribution            | 791 | 1. Mode-coupling theory for binary mixtures               | 808 |
| b. Dissipative dynamics                      | 792 | 2. The molecular liquid                                   | 809 |
| c. Hydrodynamic fluctuations                 | 792 | a. The memory function                                    | 810 |
| B. Beyond conventional hydrodynamics         | 793 | b. The glass transition scenario                          | 811 |
| 1. Generalized hydrodynamic modes            | 793 | VI. Absence of a Sharp Transition                         | 812 |
| a. The projection operator                   | 793 | A. Role of current fluctuations                           | 812 |
| b. The hard-sphere liquid                    | 794 | B. Ergodicity-restoring and "hopping" processes           | 814 |
| 2. Dynamics in the Markovian approximation   | 795 | VII. Evidence from Experiments                            | 816 |
| IV. Strongly Correlated Liquid               | 795 | A. The complex relaxation scenario                        | 816 |
| A. Mode-mode coupling: Some physical insight | 795 | 1. Signature of the dynamic transition                    | 816 |
| B. The renormalized theory                   | 796 | 2. Power-law relaxations                                  | 817 |
| 1. Memory function approach                  | 797 | a. The critical decay                                     | 817 |
| 2. Nonlinear dynamics of collective modes    | 797 | b. von-Schweidler relaxation                              | 817 |
| a. An example: Incompressible fluid          | 798 | 3. The $\alpha$ -relaxation regime                        | 820 |
| b. Compressible liquids                      | 798 | a. The temperature dependence of the $\alpha$ peak        | 820 |
| c. Renormalized transport coefficients       | 798 | b. The scaling in the $\alpha$ regime                     | 820 |
| C. Dynamic density-functional model          | 800 | B. The Nagel plot and mode-coupling theory                | 821 |
| V. Self-Consistent Mode-Coupling Theory      | 801 | C. Glass transition in colloids                           | 822 |
|  |     | VIII. Phenomenological Extensions of Mode-Coupling Theory | 823 |
|  |     | A. Hydrodynamics of solids                                | 823 |
|  |     | B. A model for structural relaxation                      | 825 |
|  |     | IX. Beyond Mode-Coupling Theory: Nonperturbative Approach | 826 |

\*Electronic address: shankar@mail.jnu.ac.in

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|--|-----|
| A. Numerical solution of the Langevin equations    | 826 |
| 1. Nature of the relaxation                        | 827 |
| 2. Dynamics in the free-energy landscape           | 827 |
| B. Mapping onto a lattice gas model                | 828 |
| X. Computer Simulation Results                     | 830 |
| A. Comparison with mode-coupling theory            | 830 |
| B. Mode-coupling $T_c$ : Landscape studies         | 831 |
| C. Generalized fluctuation-dissipation relation    | 833 |
| XI. Mode Coupling and Spin-Glass Models            | 834 |
| A. $p$ -spin interaction spin-glass model          | 834 |
| B. Nonequilibrium dynamics: Spherical model        | 836 |
| C. Generalization: Systems with intrinsic disorder | 837 |
| D. Comparison with the structural glass problem    | 838 |
| XII. Conclusions and Outlook                       | 839 |
| Acknowledgments                                    | 841 |
| Appendix: Deduction of the Self-Consistent Model   | 841 |
| 1. Analysis of the memory function                 | 841 |
| 2. The field-theoretic formulation                 | 842 |
| a. The renormalized perturbation theory            | 842 |
| b. Nonperturbative results                         | 843 |
| c. One-loop results                                | 844 |
| d. Simplified model in terms of the $\rho$ field   | 844 |
| References   | 845 |

## 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  $\sim (T-T_0)^{-\gamma}$ . 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  $\eta$  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  $\eta$  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  $\eta$  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

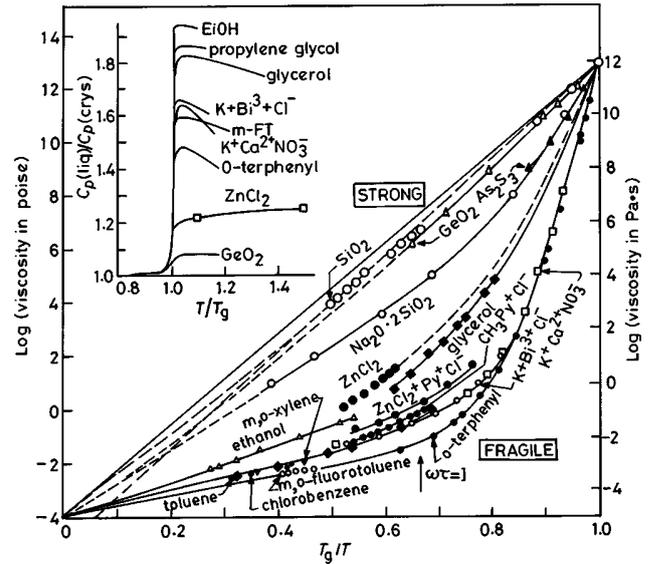


FIG. 1. Viscosity of various glass-forming liquids vs  $T_g/T$ .  $T_g$  is defined as the temperature at which the viscosity reaches  $10^{14}$  P. From Angell, 1984.

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