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Commentary on the Self-Consistent Mode-Coupling Approximation

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A brief review of the recent developments of mode-coupling theory of dense fluids shows that the existing approximations can predict certain fundamental behavior of structural relaxation and transport that are characteristic of supercooled liquids, but fall short of providing a dynamical description of the liquid–glass transition. Limitations of the theory are best investigated in the temperature region of crossover dynamics (T_x), which is distinctly above the glass transition temperature (T_g).

KEY WORDS: Density Fluctuations; glass transition; mode coupling; supercoded liquids; structural relaxation.

1. INTRODUCTION

In recent years there has been much interest in the theoretical description of density fluctuations in fluids which have been either cooled or compressed beyond the freezing point. Because these fluids are now more dense than the normal liquids, the problem of analyzing the dynamics of density fluctuations in these systems is considered a formidable challenge. One reason for the current excitement is the discovery that a certain self-consistent mode-coupling approximation leads to a tractable description which shows a freezing transition where the system becomes nonergodic. The question is then raised as to whether one has achieved by this means a dynamical theory of the liquid–glass transition.

The purpose of this contribution is to comment on this development of the mode-coupling theory. Since the mode-coupling approximation can be regarded as an extension beyond the Enskog approximation in kinetic

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theory, and kinetic theory has been a dominant part of E. G. D. Cohen's scientific interest, it is perhaps appropriate to consider, on this special occasion, how far one has proceeded with such an approach. The views offered below are not new, nor are they intended to be different from those that have been put forth in the literature; nevertheless, it is hoped that they provide a useful perspective on the current status of an intriguing problem in nonequilibrium statistical mechanics.

2. MODE-COUPLING APPROXIMATIONS

The basic problem is to study the density fluctuations in an atomic fluid in equilibrium at arbitrary density n and temperature T.[2] For the present purpose we need consider only a schematic model of the mode-coupling formulation. Let $F(k, t)$ denote the Fourier transform of the space-time density correlation function $G(\mathbf{r}, t)$ and let $\varphi(z)$ be its Laplace transform

$$\varphi(z) = i \int_0^\infty dt\, e^{izt} F(t) \tag{1}$$

The wavenumber dependence will be suppressed, since it is not relevant to the discussion; if necessary, one can think of $F(k, t)$ at $k = k_0$, where k_0 is the wavenumber at the diffraction maximum.

The calculation of $\varphi(z)$ can be formulated in two ways. One is to derive a kinetic equation for the phase-space density correlation function whose momentum integral gives $\varphi(z)$.[3] Equivalently, one can adopt the memory function approach of Zwanzig and Mori by introducing the memory function $K(z)$,(1)

$$-\varphi(z)^{-1} = z + K(z) \tag{2}$$

and further express $K(z)$ in terms of its memory function $M(z)$,

$$-\Omega^2 K(z)^{-1} = z + M(z) \tag{3}$$

where $\Omega(k) = kv_0/\sqrt{S(k)}$ is a characteristic frequency of the fluid, v_0 being the thermal speed and $S(k)$ the static structure factor with its maximum at $k = k_0$.

In the self-consistent mode-coupling formulation one derives an approximate expression for $M(z)$ by essentially postulating that the decay

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[2] See ref. 1 for a general discussion of the problem of density fluctuations from various theoretical standpoints.

[3] See ref. 2 for a review of the kinetic theory approach to density fluctuations in fluids.

of the memory function $M(t)$ can be decomposed into two components, a short-time relaxation due to collisions among individual particles and a long-time decay associated with collective behavior such as motions of clusters of particles. The first component corresponds to the Enskog approximation where only uncorrelated binary collisions are considered. This part of $M(t)$ is well known.(2) The long-time decay is treated by coupling different hydrodynamic modes such as density, current, and temperature fluctations; it is this part which makes the theory applicable at high densities or low temperatures.

We shall be concerned here with two closely related but distinct mode-coupling approximations, which schematically can be written as

$$M(z) \simeq M_0(z) + m(z) \tag{4}$$

and

$$M(z) \simeq M_0(z) + \frac{m(z)}{1 - \Delta(z)\, m(z)} \tag{5}$$

with

$$M_0(t) = \nu\delta(t) \tag{6}$$

$$m(t) = \lambda_1 F(t) + \lambda_2 F^2(t) \tag{7}$$

$$\Delta(t) = \lambda_3 F(t)\, J(t) \tag{8}$$

The memory function $M_0(t)$ is the Enskog approximation, with ν being the collision frequency. To focus attention on the collective behavior, we have taken the relaxation to be instantaneous, thereby ignoring the dynamical features on the time scale of the duration of binary collisions. The relaxation function $m(t)$ is the simplest mode-coupling treatment of collective effects; in the present model the coupling involves only linear and quadratic density modes. The density- and temperature-dependent coupling coefficients λ_1 and λ_2 will be treated as constants here, but, when needed, explicit expressions for them can be given involving the interatomic potential function and the two- and three-particle radial distribution functions. The function $\Delta(t)$ arises when coupling between the density and longitudinal current fluctuations are taken into consideration, with $J(t)$ being the longitudinal current correlation function and λ_3 another coupling coefficient. The presence of Δ is the distinction between the two approximations, Eqs. (4) and (5).

The remarkable properties of the self-consistent mode-coupling approximation were first demonstrated using Eq. (4), with $\lambda_1 = 0$ in Eq. (7), by Leutheusser(3) and by Bengtzelius, Götze, and Sjölander.(4) It was shown that the memory function contribution $m(t)$ leads to an ergodic-to-nonergodic transition at a critical density n_c or temperature T_c, at which point the diffusivity vanishes and the shear viscosity diverges with the appearance of a nonzero shear modulus.[4] Further studies(6,7),[5] and an equivalent formulation in terms of a nonlinear fluctuating hydrodynamic theory(9) have confirmed that this relatively simple hypothesis is capable of giving a rich spectrum of nonlinear relaxation and transport properties. We will henceforth refer to Eqs. (4) and (7), in which $\lambda_1 = 0$, as the LBGS approximation.

The onset of nonergodicity signifies the freezing in of some of the structural degrees of freedom in the fluid, a transition that is regarded as a liquid-to-glass transition since the model contains no mechanism for crystallization.(3,4) The origin of this transition is purely dynamical and can be interpreted as arising from a nonlinear feedback mechanism which leads to the localization of the particles.(10,11) In the present formalism structural arrest occurs when $F(t \to \infty) = f$ is no longer zero, or, in view of Eq. (1), $\varphi(z)$ has a zero-frequency pole, $\varphi(z) \sim 1/z$. This can come about when $m(z) \sim 1/z$, so that $M(z)$ becomes likewise singular.

The second approximation, Eq. (5), results when one takes into account the coupling between density and current fluctuations in deriving the mode-coupling contribution to $M(z)$.(12,13) Thus, it can be regarded as an extension of the LBGS approximation. The effect of this coupling is seen to be a renormalization of the memory function such that the singular behavior of $M(z)$ is cutoff; in other words, when $\Delta \neq 0$, $M(z)$ no longer diverges like $1/z$ for small z even though $m(z) \sim 1/z$, so the system always remains ergodic. On the other hand, it does not mean that the two approximations (4) and (5) necessarily have to give different results in the intermediate-time domain where significant slowing down in the relaxation occurs due to collective edffects. The complexity of Eq. (5) has thus far precluded much analytical analysis of its properties; there exist limited numerical results(12,14,15) which suggest that in the time domains appropriate to neutron and light scattering measurements and molecular dynamics simulations, the two descriptions may be quite similar in the decay of $F(t)$.

3. COUPLING OF DENSITY FLUCTUATIONS

The basic hypothesis of the mode-coupling formulation is that the part of $M(t)$ representing the collective behavior, or the effects of correlated

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[4] See ref. 5 for a recent review of the theories of the liquid–glass transition.

[5] See ref. 8 for an application of the mode-coupling approximation to binary systems.

collisions in the formalism of renormalized kinetic theory,(16) can be expressed as products of two hydrodynamic modes. This hypothesis cannot be justified in the sense of obtaining an estimate of the leading corrections to the approximation. Thus, validation of the various approximations has to rely on the general reasonableness of the predictions and, when feasible, on the comparison of model results with experimental or computer simulation data.

Let us consider first those predictions of the LBGS model which are consistent with experiment or molecular dynamics simulation. At densities below n_c, the self-diffusion coefficient is predicted to have a power-law density dependence, $D \sim (n_c - n)^\alpha$, with exponent $\alpha \simeq 1.76$, and correspondingly the reciprocal of the shear viscosity η behaves in the same way.(3,4) There exist diffusivity data for the supercooled liquid methylcyclohexane and from simulation results on hard-sphere and Lennard-Jones fluids which can be fitted to this power law(4); also, there are several "fragile" liquids whose viscosity in the supercooled region follows a temperature variation $\eta \sim (T - T_0)^{-2}$, where T_0 is a temperature distinctly greater than the glass transition point T_g.(17) Thus, one may conclude that the density and temperature variation of the transport coefficients of simple fluids in the liquid and supercooled regions can be predicted reasonably well by the LBGS approximation. This by itself is already a significant improvement over the Enskog theory, which is generally valid up to about half the liquid density and is known to fail at around the triple-point density.(18)

Numerical calculations of the density correlation function $F(k, t)$ have been performed for the LBGS model(19) and the results at various densities directly compared with molecular dynamics simulation data on a Lennard-Jones system.(20,29) It is found that while both model and simulation results for the decay of $F(t)$ show a characteristic slowing down due to structural relaxation, the densities at which similar behavior sets in do not correspond very well; specifically, the model seems to predict the onset of structural arrest at a lower density compared to the simulation results.

The more general approximation of Eqs. (4) and (7) with nonzero λ_1 and λ_2 also has been analyzed in some detail.(7,21) It was shown that with $\lambda_1 \neq 0$ the model exhibits scaling and stretching behavior characteristic of the α relaxation,(22) behavior typical of systems near the liquid–glass transition. The property of scaling means $F(t)$ can be written in the form of $F(t) = A(t/\tau)$, where A is a universal or master function and relaxation time τ is a parameter which accounts for all the temperature dependence. Stretching, on the other hand, manifests in a nonexponential decay of $F(t)$, $F(t) = F_0 \exp[-(t/\tau)^\beta]$, with $0 < \beta < 1$. It is rather remarkable that the approximation of Eqs. (4) and (7) can predict such behavior,(7) which, moreover, have been found to have experimental correspondence in inelastic neutron scattering studies (ref. 23; also the discussion in ref. 26). If, instead of Eq. (7), one writes $m(t) = \Gamma(F(t))$, where Γ is a mode-coupling functional, a polynomial with nonnegative coefficients $\lambda_1, \lambda_2, \ldots$, then one can even discuss the phenomenon of β relaxation, which has been observed in dielectric loss spectra(24) and is also characterized by a broad distribution of relaxation rates.(25)

The present assessment of the validity of the mode-coupling approximation therefore finds the correct prediction of several fundamental features of relaxation and transport behavior which have been observed in supercooled liquids. The harder question of whether the ideal glass transition predicted by the LBGS model has anything to do with the glass transition observed experimentally has not been answered unambiguously. A major difficulty is that the definition of the latter depends on the physical property one is considering, and different changes in structural, thermodynamic, or transport properties have been used to characterize the glass transition in various measurements. Since the ideal glass transition is purely dynamical in origin, it seems natural to examine its relation to the behavior of a transport coefficient, the shear viscosity coefficient η. In this context it is conventional to define a glass transition temperature T_g as that at which η has the value of 10^{13} P. The question then becomes whether the transition predicted by the LBGS model is capable of describing the magnitude and the temperature variation of η in the region near T_g. In other words, is it reasonable to identify T_c with T_g?

When the question is posed in this manner it is clear that from the theoretical side the difference between the two approximations, Eqs. (4) and (5), can be quite important; moreover, one needs to obtain numerical results for η that can be compared with experiment or computer simulation data. From the experimental side it has been pointed out by Taborek *et al.*(17) that the shear viscosity coefficients of a number of supercooled liquids all show a typical behavior of following a power-law temperature variation, with exponent approximately 2, in the regime where η has increased to about 10 P, and that at lower temperatures η increases much more rapidly. It was noted that by extrapolating the data in the low-η region to infinite viscosity one obtains a characteristic temperature which these authors denoted as T_0. The significance of T_0 is that it is the "transition temperature" in the supercooled region separating the two characteristic behaviors of the shear viscosity. Thus, η behaves like the prediction of LBGS for $T > T_0$, while in the region of $T < T_0$, the data show an increase by several orders of magnitude until one reaches T_g. Furthermore, the latter increase occurs over a considerable range of temperature, so T_0 is well separated from T_g, and in some cases $T_0 \sim 2T_g$.(17)

To our knowledge, only one numerical calculation of η using an approximation similar to Eq. (5)(12) has been reported.(14) From the rather limited results obtained, one sees that relative to its value in the normal liquid state, η in the supercooled region can show increases of a factor of 10–100, but not several orders of magnitude. The implication is therefore that the existing mode-coupling approximation, in the form of either Eq. (4) or Eq. (5), cannot describe the sharp increase of η in the temperature region below T_0. This conclusion actually can be anticipated, since it is well recognized that activated-state dynamics is not taken into account in the LBGS model. For the extended model, Eq. (5), one may regard the presence of Δ as the one-phonon contribution to phonon-assisted hopping processes(26); nevertheless, it seems unlikely that the model can adequately describe the effects of particles hopping over local potential minima, motions which surely must dominate the dynamical behavior near T_g.

4. THE T_x PROBLEM

If it is correct that the present mode-coupling approximation does not apply to the laboratory glass transition, one may ask next, What is the significance of the temperature region near T_0? The behavior of η suggests that T_0 delineates a crossover region where the particle motions apparently change from continuous fluidlike displacements to barrier hopping between potential minima. Such a picture of viscous flow was considered some 30 years ago by Goldstein.(27) Within this scenario one may think of a broad dynamical transition which signals the onset of potential barriers. It has been suggested(28) to label the crossover transition by the temperature T_x instead of T_0 to avoid confusion with a parameter in the well-known Vogel–Fulcher expression for η or D.

There is evidence in various forms pointing to the existence of a crossover transition. A molecular dynamics study of compressed Lennard-Jones fluids has revealed such a behavior, the transition being charactyerized by a decrease in the compressibility, a change in the density variation of D, and the onset of a slowly decaying component in $F(t)$, all occurring at a density well below that required to bring the diffusivity down to typical values for glasses.(29) Another molecular dynamics study of local stress fluctuations in quenched liquids showed the onset of spatial correlation effects at a characteristic temperature considerably above T_g.(30) In recent studies of spin-glass models it has been found that two transition temperatures can be identified, a dynamical transition at higher temperature which is associated with the appearance of barriers in the local energy surface and an equilibrium transition at a lower temperature where the configurational entropy vanishes.(31)

5. CONCLUDING REMARKS

We will close this commentary with two thoughts. The first is that an appropriate test of the mode-coupling approach should be carried out in the supercooled region T_x and not in the region near T_g. The extended model, Eq. (5), should be studied to see if the effects of the cutoff of the nonergodic transition are numerically significant; in this respect comparison with molecular dynamics data on $F(t)$ will be valuable.

The second thought is that the mode-coupling approximation was first developed to treat the collective aspects of collisional dynamics which are not taken into account by the Enskog approximation in the kinetic theory of thermal fluctuations; in particular, the approximation of coupling to density and current fluctuations was not invoked just for the purpose of describing the liquid–glass transition. Therefore, one should not be disappointed that this approach thus far has not led to a theory of the glass transition. Moreover, given that the validity of the approached has been previously demonstrated in the analysis of viscoelastic behavior in dense hard-sphere fluids(32) and diffusion-localization transition in the Lorentz model,(10) its present success in describing the structural relaxation behavior of supercooled liquids is not without foundation.

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