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Nonlinear fluctuating hydrodynamics and sequence of time scales of relaxation in supercooled liquids

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Abstract. Nonlinear fluctuating hydrodynamic (NFH) models for relaxation in the supercooled liquid are considered. Recent results on self consistent mode coupling theory for the slow relaxation of density fluctuations are analyzed to explain the glassy dynamics. The relaxation mechanisms for different types of models with and without wave vector dependences are discussed. For the schematic models where all wave vector dependences are dropped a sequence of time scales enters the relaxation process. For the non-ergodicity parameter very close to the ideal transition point is scaled by an exponent equal to $1/2$. This is demonstrated here through an analysis of the mode-coupling equations for the wave vector dependent models that follow from equations of NFH.

Keywords. Glass transition; ergodicity; correlation function.

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1. Introduction

In the last ten years a good amount of progress has been achieved on the understanding of the dynamics of supercooled liquids using models derived from the nonlinear fluctuating hydrodynamic equations for the compressible fluid [1, 2]. In these models the transport coefficients for the supercooled liquid are obtained in terms of self-consistent expressions of the hydrodynamic correlation functions. This constitute a feedback mechanism [3, 4] giving rise to slow relaxation in the supercooled liquid. In the self consistent mode coupling models for glass transition, the feed back effects from the terms involving the slowly decaying density fluctuations are analyzed assuming that they produce the dominant contribution at supercooled states. In this paper we will focus our discussion on the nonlinear hydrodynamic models, specially with structural effects taken into account.

The present form of the mode-coupling theory (MCT) for supercooled liquid dynamics was initiated from the work of Leutheusser by showing that a model obtained from the kinetic theory of dense fluids exhibits an ergodic-nonergodic transition which has features similar to a liquid-glass transition. The model leads to a viscosity which diverges as $(T - T_0)^{-\alpha}$ as the temperature T approaches the ideal glass transition T_0. The exponent α was found to take values $\alpha \sim 2$. Later it was demonstrated [5] that the sharp transition is cutoff due to a mechanism arising from coupling of density and current fluctuations in a compressible fluid and this keeps the system ergodic at all temperatures. However the analysis done in ref. [5] also showed that the feed back mechanism from the coupling of density fluctuations does cause a substantial enhancement of the viscosity. Thus although the sharp transition is cutoff there are some strong remnants of it with a qualitative change in the supercooled liquid dynamics around a temperature T_0 higher than the usual glass transition temperature. Indeed such behavior was observed in a number of liquids [6, 7] termed as the fragile liquids. In a number of subsequent works [7] the cutoff mechanism responsible for ergodic behavior at the longest time scale in the supercooled liquid was simply ignored and the relaxation behavior around the point which involves a sharp transition from ergodic to non ergodic behavior was analyzed. The simplest example of this type is the Leutheusser model which consider a schematic form of the mode-coupling theory with all q dependence being dropped, but only the main characteristics of the dynamic instability being preserved. A sequence of time scales enter the relaxation process in the schematic model. However, when the full wave vector dependence in the models are taken into account , through a realistic static structure factor this aspect changes somewhat. We discuss these in the present work by presenting a simple analysis of the wave vector dependent model here.

We will divide the discussion mainly into two parts namely the idealized models with a sharp transition and the fully self-consistent model in which there is no sharp transition in the dynamic behavior of the liquid. In § 2 we first discuss the nonlinear fluctuating hydrodynamic equations for a compressible fluid with a simple choice of conserved densities as slow variables and discuss how the mode coupling model is obtained from these equations. In § 3, we discuss the idealized model which has a dynamic instability giving rise to the so called glass transition and discuss the various time scales that enter the relaxation process. In the next section we discuss the fully self consistent model with the cutoff mechanism for restoring ergodicity and discuss some recent results regarding the nature of the kernel for the cutoff mechanism. We end the paper with a small discussion.

2. Fluctuating hydrodynamics of compressible liquid

In the present work we will consider the set of hydrodynamic variables [5] as the mass density ρ, the momentum density $\mathbf{g}$, and the flow velocity $\mathbf{v}$ defined through the nonlinear constraint

$$\mathbf{g} = \rho\mathbf{v}. \tag{1}$$

The equations of motion for the hydrodynamic variables, are obtained using the well known Zwanzig–Mori [8] formalism and are valid for small and finite wavelengths. The equation for ρ is given by

$$\frac{\partial\rho}{\partial t} = -\nabla\cdot\mathbf{g} \tag{2}$$

and that for $\mathbf{g}$ is the generalized nonlinear Navier Stokes equation with thermal noise

$$\frac{\partial g_i}{\partial t} = -\rho\nabla_i\frac{\delta F_u}{\delta\rho} - \sum_j \nabla_j(g_i v_j) - \sum_j \int \mathrm{d}x' L_{ij}(x-x')\frac{\delta F}{\delta g_j(x')} + \Theta_i, \tag{3}$$

where $F_u[\rho(x)]$ is the potential energy part of the effective Hamiltonian F defined [9] as

$$F = \frac{1}{2}\int \mathrm{d}^3x g^2(x)/\rho(x) + F_u. \tag{4}$$

Following the usual forms common in the density functional theories, F_u is taken as an expansion of an inhomogeneous equilibrium liquid

$$(\beta m)F_u[\rho(x)] = \int \mathrm{d}x\rho(x)\{\ln[\rho(x)/\rho_0] - 1\}, +F_{\mathrm{int}}[\rho], \tag{5}$$

where the first term is the ideal gas entropy term and the interaction term F_{int} to lowest order can be obtained (up to a constant) as

$$F_{\mathrm{int}}[\rho] = -\frac{1}{2m}\int \mathrm{d}^3x\mathrm{d}^3x' c^{(2)}(x - x')\delta\rho(x)\delta\rho(x') \tag{6}$$

with $\delta\rho(x,t) = \rho(x,t) - \rho_0$ and $\beta = 1/k_BT \cdot c(x)$ is the equilibrium two particle correlation function for the liquid. In an isotropic fluid the bare transport matrix $L_{ij}(\mathbf{x})$ is related to the Gaussian noise Θ_i through the fluctuation dissipation relation

$$\langle\Theta_i(\mathbf{x},t)\Theta_j(\mathbf{x}',t')\rangle = 2k_BTL_{ij}(\mathbf{x})\delta(\mathbf{x} - \mathbf{x}')\delta(t - t'). \tag{7}$$

For an isotropic fluid the bare transport matrix $L_{ij}(\mathbf{x})$ or its Fourier transform

$$L_{ij}(q) = \int \mathrm{d}x\, \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{x}} L_{ij}(x) \tag{8}$$

can be expressed in terms of two independent transport coefficients given by

$$L_{ij}(q) = q_iq_j\Gamma^0(q) + [q^2\delta_{ij} - q_iq_j]\eta^0(q). \tag{9}$$

In the small wavenumber limit, $\Gamma^0(q)$ and $\eta^0(q)$ are the bare longitudinal and shear viscosities respectively. Since we will be applying these equations for finite wavelengths here, more generalized expressions for these quantities are obtained with the use of Enskog type models [10]. These reflect the short time properties referring to uncorrelated random collisions in the system.

In order to investigate the effects the nonlinearities in the hydrodynamic equations will have on the transport properties of the fluid, a field theory of the Martin–Siggia–Rose (MSR) [11] type was used in ref. [5]. The advantage of using the MSR field theory here is that the renormalized expressions for the various quantities are obtained in a self consistent manner in terms of the full correlation functions and is very useful in demonstrating the feedback mechanism that results in slow relaxation at supercooled densities. The field theoretic treatment of the problem is done following the techniques developed in the theories of dynamical critical point phenomena and for this the interested reader is referred to the papers cited under ref. [11]. For the analysis as applied to the theory of the compressible fluids see ref. [5, 12]. In the present discussion we give a very brief account of the steps used in obtaining the mode coupling models as applied for supercooled liquids. The fully renormalized theory of the hydrodynamic correlation functions are obtained in terms of the self energy matrix Σ defined through the Dyson equation

$$G^{-1}(\mathbf{q},\omega) = G_0{}^{-1}(\mathbf{q},\omega) - \Sigma(\mathbf{q},\omega), \tag{10}$$

where G_0 refers to the matrix of correlation functions obtained from the equations of linearized hydrodynamics. The main quantity of interest here is the density auto correlation function whose Fourier transform is defined as

$$G_{\rho\rho}(q,t) = \int d(\mathbf{x}-\mathbf{x}')e^{i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')}\langle\delta\rho(\mathbf{x},t)\delta\rho(\mathbf{x}',0)\rangle, \tag{11}$$

where the angular bracket refers to the average over the stationary states. In ref. [5] the following form for the Fourier–Laplace transform of $G_{\rho\rho}(\mathbf{x},t)$ normalized with respect to its equal time value is obtained in the small q and ω limit

$$\phi(q,z) = \frac{z + iD_L{}^R(q,z)}{z^2 - \Omega_q^2 + iD_L{}^R(q,z)[z + i\gamma(q,z)]}. \tag{12}$$

Here $\Omega_q^2 = q^2[\beta m S(q)]^{-1}$ and $D_L{}^R(q,z)$ is the renormalized longitudinal viscosity. The Laplace transform of $\phi(t)$ is defined as

$$\phi(z) = (-i)\int_0^\infty dt\, e^{izt}\phi(t), \quad \mathrm{Im}(z) > 0. \tag{13}$$

Similarly the Laplace transform for the transverse current fluctuation (normalized with respect to its equal time value) is given by

$$\phi^T(q,z) = \frac{1}{z + i\eta^R(q,z)}, \tag{14}$$

where $\eta^R(q,z)$ is the renormalized shear viscosity. In the formulation of the MSR type field theory the renormalized memory kernels on the R.H.S of (12) and (14) have the mode coupling contributions at the one loop level respectively given by

$$\begin{aligned} D_L{}^{mc}(q,t) =& \lambda_0 \int \frac{d\mathbf{k}}{(2\pi)^3}[\{\hat{q}\cdot\mathbf{k}\}c(k) + \{\hat{q}\cdot(\mathbf{q}-\mathbf{k})\}c(|\mathbf{q}-\mathbf{k}|)]^2 \\ & \times G_{\rho\rho}(\mathbf{q}-\mathbf{k},t)G_{\rho\rho}(\mathbf{k},t) \end{aligned} \tag{15}$$

and

$$\eta^{mc}(q,t) = \lambda_0 \int \frac{d\mathbf{k}}{(2\pi)^3}[c(k) - c(\mathbf{q}-\mathbf{k})]^2 k^2(1-u^2)G_{\rho\rho}(\mathbf{q}-\mathbf{k},t)G_{\rho\rho}(\mathbf{k},t), \tag{16}$$

where $\lambda_0 = (2\beta m^4\rho_0)^{-1}$ and $u = \hat{q}\cdot\hat{k}$ while $\hat{q}$ is the unit vector along the direction of $\mathbf{q}$. The quantity $\gamma(q,z)$ in the R.H.S of (12) arises from the coupling between the density fluctuations and current fluctuations in a compressible fluid. In the asymptotic limit when the viscosity become large due to the feedback coming from mode coupling contributions, the density autocorrelation function given by (12) develops a pole at

$$z + i\gamma(q,z) = 0. \tag{17}$$

Thus ergodicity is restored over a time scale of $1/\gamma(0,0)$, representing the longest time scale in the relaxation of the density correlation function. However, in the simple model where all the nonhydrodynamic corrections coming from time scales of the order of q^2

are ignored the simplified model has a dynamic instability similar to the liquid-glass transition. In the next section we will consider this model first to demonstrate the several relaxation processes that can be included in the context of mode coupling theory and the consequences of a proper wave vector dependence in the theory.

3. Effects of the feedback mechanism and sequence of time scales of relaxation

3.1 *Schematic models without wavevector dependence*

In this section we consider the simple model with the sharp instability showing a transition to an ideal glassy phase. In this regard several different types of models have been investigated. First we consider the schematic models where all the wave vector dependences in the mode coupling kernels for transport coefficients are dropped and the density autocorrelation function $\phi(z)$ following (12) is given by the functional equation

$$\frac{-\Omega_0^2\phi(z)}{1-z\phi(z)} = z + iD_L(z), \tag{18}$$

where Ω_0 is a microscopic frequency. In the schematic models the renormalized expression for the viscosity $D_L(z)$ is obtained as

$$D_L(z) = D_L^0 + \Omega_0^2 \int_0^\infty \mathrm{d}t\, \mathrm{e}^{izt} H[\phi(t)], \tag{19}$$

where D_L^0 is the bare viscosity governing the microscopic dynamics. In studying the feedback mechanism for slow relaxation in the supercooled liquid the memory kernel H is expressed as a functional of the density correlation function $\phi(t)$ [7, 13] given by

$$H[\phi(t)] = \sum_{n=1}^{N} c_n \phi^n(t). \tag{20}$$

In the model considered by Leutheusser $H[\phi] = c_2\phi^2$. The more general model with $c_1 = 0$ was first introduced in ref. [1]. The importance of the linear term was first pointed out by Goetze [14]. In the above expressions for the memory kernel all wave vector dependences are assumed to be weak and are suppressed. The basic assumption in the analysis of the equation (18) is that depending on the the kernel $H[\phi]$ i.e. the coefficients c_ns there is a time range over which $\phi(t)$ is approximately time independent following the form

$$\phi(t) = f + (1-f)\phi_\nu(t), \tag{21}$$

where f is the value of $\phi(t)$ in some metastable state which is yet to be specified. For time scales where the inequality $|z\phi_\nu(z)| \ll 1$ is valid, we obtain to leading order from equation (18)

$$\frac{\Delta_0}{z} + \Delta_1\phi_\nu(z) - (1-f)H'(f)z{\phi_\nu}^2(z) + \frac{(1-f)^2}{2}H''(f)L_z[{\phi_\nu}^2(t)] = 0 \tag{22}$$

with

$$\Delta_0 = H(f) - \frac{f}{1-f},$$
$$\Delta_1 = \frac{\partial}{\partial f}[(1-f)H(f) - f]. \tag{23}$$

We have used the notation $H''(f) = (\partial^2 H(f))/\partial f^2$ etc. and L_z stands for the Laplace transform of the function in the argument as defined in equation (13) with variable z. An ideal metastable state is obtained when both Δ_0 and Δ_1 are zero giving a solution for the decaying function $\phi_\nu(t)$. We can determine f by setting $\Delta_1 = 0$. This is obtained for

$$H(f) + 1 = \frac{C}{(1-f)}, \tag{24}$$

with C is a constant not depending on f. At this condition $\Delta_0 = (C-1)/(1-f)$. An ideal state is obtained when for a given set of c_n we have $\Delta_0(c_n) = 0$. Thus the ideal transition takes place with for $C = 1$ giving $\Delta_0 = 0$. For the Leutheusser model we obtain that $f = 1/2$ and c_2 has a critical value of $c_2^* = 4$. For the model by Goetze [14] we have linear term in the kernel, i.e.

$$H[\phi] = c_1\phi + c_2\phi^2, \tag{25}$$

with a line of critical values satisfying

$$c_1^* = 2\sqrt{c_2^*} - c_2^*. \tag{26}$$

For higher order models there are critical surfaces. Note that with $\Delta_1 = 0$ the equation (22) can be written as

$$\frac{\Delta_0}{z} - \frac{C}{(1-f)} z\phi_\nu^2(z) + \frac{(1-f)^2}{2} H''(f) L_z[\phi_\nu^2(t)] = 0. \tag{27}$$

For the high frequency region where the term proportional to Δ_0 can be neglected i.e.

$$(|\Delta_0|)^{1/2} \ll |z\phi_\nu(z)| \tag{28}$$

the above equation reduces to the simple form,

$$z\phi_\nu^2(z) - \lambda L[\phi_\nu^2(t)] = 0 \tag{29}$$

with $\lambda = ((1-f)^3/2C)\, H''(f)$. This equation is satisfied by the function

$$\phi_\nu(t) = A(t\Omega_0)^{-a}. \tag{30}$$

The exponent a is given in terms of the parameter λ by the equation

$$\frac{\Gamma^2(1-a)}{\Gamma(1-2a)} = \lambda, \tag{31}$$

where Γ is the gamma function. The inequality (28) and the solution (30) obviously holds in the time region

$$\Omega_0{}^{-1} \ll t \ll \tau_a \equiv |\Delta_0|^{-1/2a}. \tag{32}$$

The time scale τ_a diverges at the ideal transition point i.e. $\Delta_0 = 0$. Therefore $\phi(t)$ decays algebraically towards the metastable value f. For $\Delta_0 \neq 0$ i.e. points away from the transition the dynamics is quite different for the cases $\Delta_0 > 0$ and $\Delta_0 < 0$. For $\Delta_0 > 0$, equation (27) has the solution $\phi_\nu(z) \sim \Delta_0^{1/2}/z$ as $z \to 0$ and

$$f = f_0 + c(\Delta_0)^{1/2} + O(\Delta_0), \tag{33}$$

where f_0 is the value of f at the ideal transition point and c is a constant. For $\Delta_0 < 0$ we have from equation (27) a solution for $\phi_\nu(z)$ which is more singular that $1/z$ as $z \to 0$ and has the following form in the time regime

$$\phi_\nu(t) = -B(t/\tau_\alpha)^b, \tag{34}$$

where B is a positive constant. Similar to a in (30), b satisfies the equation

$$\frac{\Gamma^2(1+b)}{\Gamma(1+2b)} = \lambda. \tag{35}$$

Equation (34) is referred to as the von-Schweidler relaxation law. However this relaxation eventually violates the inequality $|z\phi_\nu(z)| \ll 1$ and this decay mechanism is valid in the region

$$\tau_a \ll t \ll \tau_\alpha, \tag{36}$$

where τ_α is given by

$$\tau_\alpha = |\Delta_0|^{-(1/2a+1/2b)}. \tag{37}$$

For $t \geq \tau_\alpha$, the system enters into the α relaxation regime. In these regime a fully analytic solution of the mode coupling equations is still not available. Numerical solution for a set of parameters [13] has shown that the solution is well fit by a stretched exponential

$$\phi(t) = f\,\mathrm{e}^{-(t/\tau_\alpha)^\beta}. \tag{38}$$

The final decay of the correlation function takes place over the time scale, given by $1/\gamma$. We show in figure 1 the sequence of times scales that enter the relaxation process in the mode coupling models that uses the schematic forms for the memory kernel in terms of the density correlation function.

3.2 *Effects of including proper structure factor*

In this case we consider the set of equations (for different q values),

$$\frac{-\Omega_q^2\phi(q,z)}{1 - z\phi(q,z)} = z + iD_L(q,z), \tag{39}$$

where the memory kernel representing the transport behavior is given by

$$D_L(q,z) = D_L^0(q) + \Omega_0^2 \int_0^\infty \mathrm{d}t\,\mathrm{e}^{izt} H_q[\phi(q,t)], \tag{40}$$

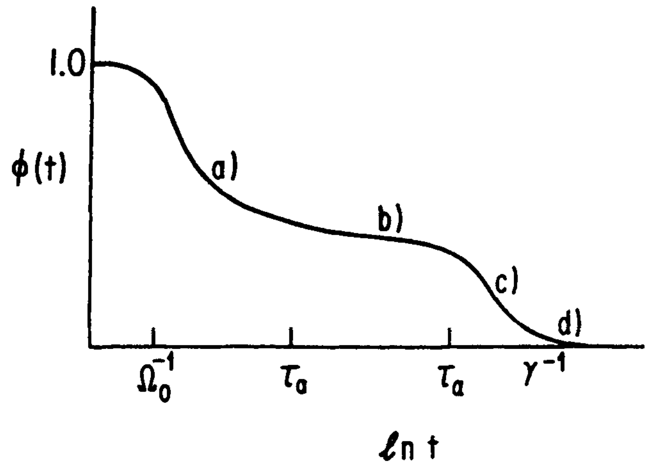

Figure 1. Schematic plot of the sequence of time scales in the relaxation predicted by MCT; (**a**) power-law decay t^{-a}, (**b**) von Schweidler relaxation $-Bt^b$, (**c**) primary relaxation $e^{-(t/\tau)^\beta}$, (**d**) exponential relaxation $e^{-\gamma t}$.

where $D_L^0(q)$ is the bare viscosity [15] governing the microscopic dynamics over length scale corresponding to wave vector q. The function $H_q[\phi]$ now depends on all the values of ϕ at different q values. In general we can have the kernel in the form

$$\begin{aligned} H_q[\phi(t)] &= \sum_{k_1} V^{(1)}(q,k_1)\phi(k_1,t) + \sum_{k_1,k_2} V^{(2)}(q,k_1,k_2)\phi(k_1,t)\phi(k_2,t) \\ &\quad + \sum_{k_1,k_2,k_3} V^{(3)}(q,k_1,k_2,k_3)\phi(k_1,t)\phi(k_2,t)\phi(k_3,t) + \cdots . \end{aligned} \tag{41}$$

In the model obtained using the nonlinear fluctuating hydrodynamics described in equation (15) $V^{(1)}$ happens to be zero. Subsequently, Kim [16] has considered models of fluctuating hydrodynamics that obtains a term in the kernel linearly proportional to the density correlation function. We look for a solution of the above equations in the form

$$\phi(q,t) = f_q + (1-f_q)\phi_\nu(q,t). \tag{42}$$

If f_q happens to be a nonzero set of values beyond a certain density then this corresponds to an ideal non ergodic state where the density correlation function decays to a finite value instead of decaying to zero. Following an analysis similar to what is described in the previous section for the schematic model, we obtain an equation

$$\begin{aligned} &\frac{\Delta_0^q}{z}\left[\sum_k (1-f_k)\frac{\partial H_q}{\partial f_k}\phi_\nu(k,z) - (H_q(f)+1)\phi_\nu(q,z)\right] \\ &\quad + \frac{1}{2}\sum_{k,k'}(1-f_k)(1-f_{k'})L_z[\phi_\nu(k,t)\phi_\nu(k',t)]\frac{\partial^2 H_q}{\partial f_k \partial f_{k'}} - \frac{C_q}{1-f_q} z\phi_\nu^2(z) = 0 \end{aligned} \tag{43}$$

with

$$\Delta_0^q = H_q(f) - \frac{f_q}{1-f_q}. \tag{44}$$

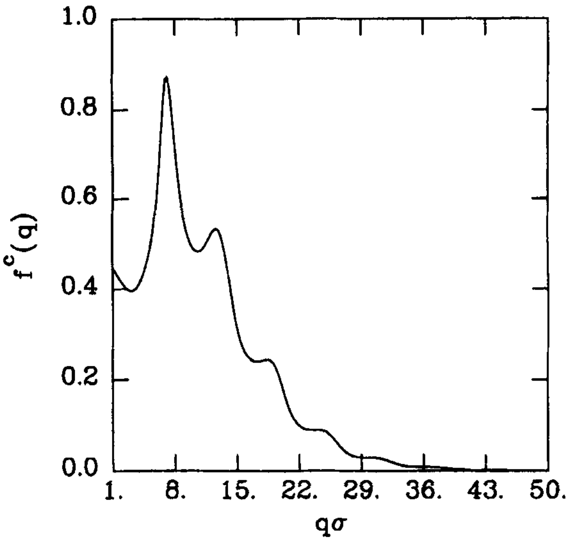

Figure 2. The long time limit of the density correlation function f_q, computed from the simple model at the density $n^* = 0.99$.

As in the other case here also we determine the f_q's by choosing the term linear in ϕ_ν to be vanishing. This gives rise to the condition that

$$H_q + 1 = \frac{C_q}{1 - f_q}, \tag{45}$$

where C_q are constants. Consequently, with this choice we can write

$$\Delta_0^q = \frac{C_q}{1 - f}. \tag{46}$$

For the ideal transition point one has the condition $\Delta_0^q = 0$ i.e. $C_q = 1$. Thus we obtain the following condition for f_q's,

$$f_q = \frac{H_q}{H_q + 1}. \tag{47}$$

In figure 2 we show the solution for f_q that is obtained using the model described by the kernel in equation (15). For the density $n^* \equiv n\sigma^3$ below $0.99 f_q$s' all are zero showing that the dynamic instability signifying transition to the nonergodic phase takes place at this density. In obtaining this equation we get the static structure factor or the direct correlation function that appear in the mode coupling integrals using the Percus Yevick (PY) solution [10] for the hard sphere system. For the points away from the transition we see that with $\Delta_0^q > 0$ the function $\phi_\nu(q,z) \sim (\Delta_0^q)^{1/2}/z$. Thus the nonergodicity parameter giving the strength of the $1/z$ pole in the density correlation function has the behavior

$$f_q = f_q^0 + c_q \epsilon^{1/2} + O(\epsilon), \tag{48}$$

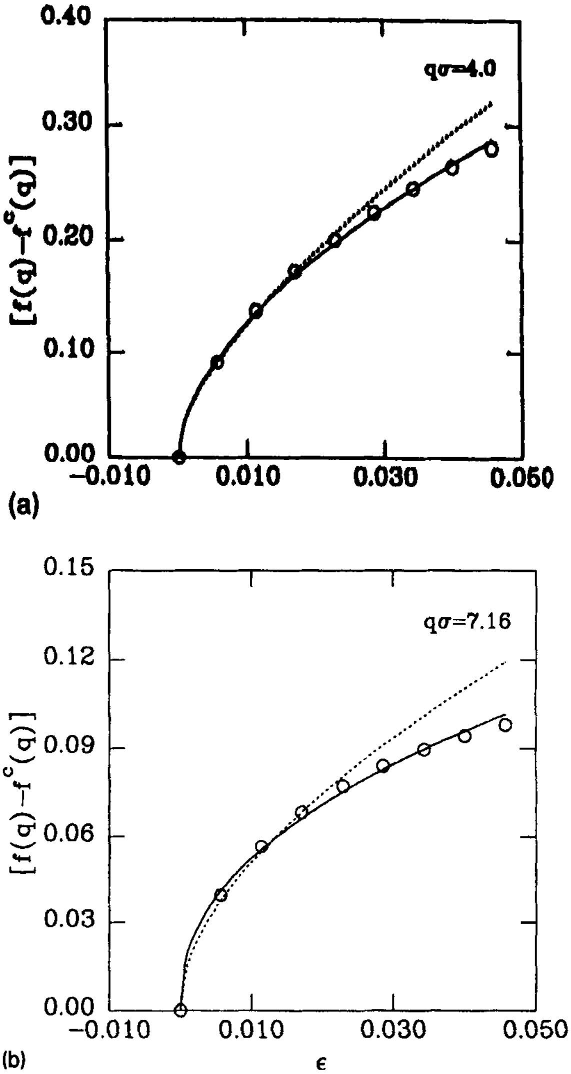

Figure 3. The nonergodicity parameter $[f_q - f_q^0]$ vs. ϵ for (**a**) $q\sigma$ = 4.00; (**b**) $q\sigma$ = 7.16. The dashed line is for the exponent $\frac{1}{2}$ and the solid line for a q dependent exponent.

where ϵ denotes the distance from the ideal transition point. Such a behavior was also found by numerical solution of the integral equations (47) giving f_q's. In figures 3(a) and 3(b) we show the fit for a power law with exponent $1/2$ (dashed line) and a wave vector dependent exponent (solid line) for two different values of the wave vector $q\sigma = 4.00$ and 7.16 respectively. For distances (in temperature or density) from the transition which are very small the square root law seems to work but for large ϵ this seems to break down. This square root law with the non ergodicity parameter is indeed seen in a polymeric liquid [17] where the transition point is found to be T_0 =216 K, about 35 K above the phenomenological glass transition point. This observation has been viewed as important evidence in favor of mode coupling theory. The important implication is that above T_g there exists a specific temperature T_0, above and below which the dynamics are quite different. However for the other side of the transition the exponents of relaxation are dependent on the wave vector q and this was investigated in ref. [18] from numerical solution of the mode coupling equations.

4. The self-consistent model with the ergodicity restoring mechanism

If the quantity $\gamma(q,z)$ is maintained then the system shows ergodicity over long time scales. In ref. [5] it was demonstrated that the quantity $\gamma(q,z)$ can be obtained in terms of the hydrodynamic correlation functions by analyzing the self energy matrix element $\Sigma_{\hat{v}_i\hat{v}_j}$ introduced in (10) in the form

$$\gamma(q,t) = \int \frac{d\mathbf{k}}{\rho_0^2(2\pi)^3} \left([u_1^2 G_{gg}^{\mathrm{L}}(\mathbf{q}-\mathbf{k},t) + (1-u_1^2) G_{gg}^{\mathrm{T}}(\mathbf{q}-\mathbf{k},t)] G_{\rho\rho}(\mathbf{k},t) \right.$$
$$\left. + u u_1 G_{g\rho}(\mathbf{k},t) G_{g\rho}(\mathbf{q}-\mathbf{k},t)\right) \qquad (49)$$

with definition $u \equiv \hat{k}\cdot\hat{q}$ and $u_1 = \hat{q}(\mathbf{q}-\mathbf{k})/|\mathbf{q}-\mathbf{k}|$ and the superscripts L and T respectively refer to longitudinal and transverse parts of the corresponding quantities in the isotropic fluid. This self consistent expression for γ was also used [12] for obtaining a close set of functional equations for the density and current correlation functions. The time scales of relaxation that followed from numerical solution of these equations demonstrated good agreement with computer simulation results [19]. Indeed if γ would self-consistently reduce to very small values, the supercooled dynamics is pushed to very long times. Hence the exact form of the kernel $\gamma(q,z)$ representing the cutoff mechanism for eliminating the glass transition singularity is important. In ref. [12] this issue was considered through a self-consistent solution of (39) and (49). In figure 4 we show the behavior of the static longitudinal viscosity $D_{\mathrm{L}}(0,0) = \bar{\Gamma}$ with the reduced density in a hard sphere system. Initially the viscosity shows a power law increase (with exponent close to 2) but for higher densities the sharp transition is cutoff. This work demonstrated that the relaxation time increases by two to three orders of magnitude showing a change in the dynamics but it did not give rise to any diverging time scales around this mode coupling singularity.

The question regarding the behavior of the quantity γ i.e. how small it can be pushed to produce extremely slow relaxation has also been investigated. This is done by using a lower cutoff time in the computation of the mode coupling effects. The argument for this cutoff time is as follows: the mode coupling contribution to the memory function computes effects due to correlated collisions or cooperative dynamics in the supercooled liquid. The long time and short time contributions to the viscosity can be separated according to

$$D_{\mathrm{L}}^{mc}(q,z) = \int_0^{t_0} dt\, e^{izt} D_{\mathrm{L}}^{mc}(q,t) + \int_{t_0}^{\infty} dt\, e^{izt} D_{\mathrm{L}}^{mc}(q,t), \qquad (50)$$

where the time t_0 sets the scale beyond which cooperative dynamics is effective. The first integral on the right side of (50) represents short time dynamics and is taken into account

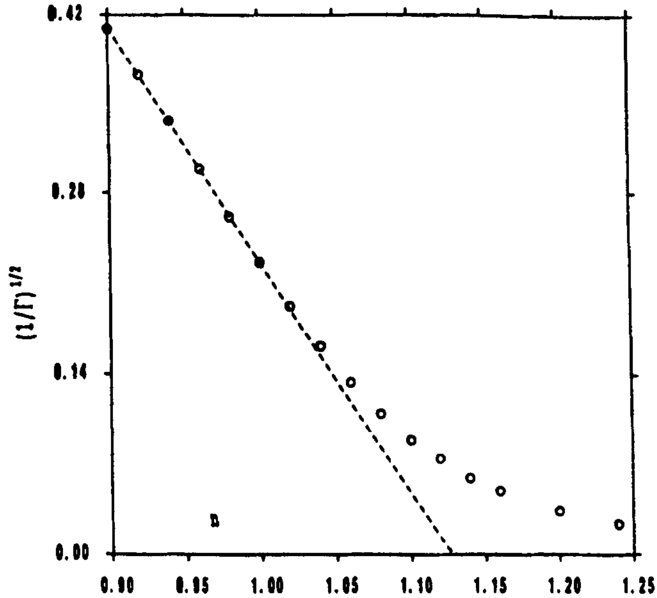

Figure 4. Square root of the inverse of the normalized longitudinal viscosity $\bar{\Gamma}$ vs. density. The dashed line shows the power law fit for intermediate densities.

through the bare transport coefficients. The mode coupling contribution to the viscosity is to a good approximation given by approximating it by the second integral in (50) and ignoring the first one since the bare transport coefficient already takes short time dynamics into account. For supercooled densities the same cutoff time is included in the expression for the kernel γ [20, 13]. The cutoff time t_0 in the theory can be estimated by fitting the value of the integrand with the computer simulation results on transport coefficients [15, 21]. For a hard sphere system good agreement with simulation data near freezing densities were obtained with $t_0 = 10t_E$ where t_E is the Enskog time [22] referring to the time scale for short time dynamics for the hard sphere liquid. For supercooled densities however, the mode coupling contribution to the viscosity is not very sensitive to t_0, but γ does get influenced by the cutoff time. In a number of recent works [23] the experimental data for relaxation in supercooled systems has been used to obtain an estimation of the cutoff function. In this respect the computation of the cutoff function from a fully self-consistent approach is relevant. It has been observed that even if the short time part of the dynamics is excluded from the mode coupling contribution through t_0, the self-consistent calculation does not produce any drastic change in the relaxation time as is seen in the strong liquids. In a number of recent works [23] the cutoff mechanism, smoothing off the ideal glass transition in the framework of mode coupling theory, has been incorporated with the use of experimental data. The strength of the cutoff function is estimated there through an analysis of the data. In ref. [16] Kim investigated the behavior of the cutoff function in a schematic model where all q dependences are dropped from the model and obtained an expression of the form

$$\gamma = \int_{t_0}^{\infty} \mathrm{d}t[\dot{\phi}(t)]^2. \tag{51}$$

It was found [16] that if t_0 was chosen sufficiently large ($t_0 \equiv 5{\Omega_0}^{-1}$), γ is greatly suppressed. Therefore the suppression of γ is obtained once the cutoff time exceeds the microscopic value. In the fully q dependent theory we see a qualitatively similar but less enhanced effect. With reasonable approximations for t_0 relevant for the short time dynamics, does not give rise to the very strong enhancement of the viscosity. It does indicate a slowing down of the relaxation over two to three orders of magnitudes over a temperature or density range higher than the glass transition temperature. This is similar to what has been termed in literature [24] as fragile liquids. It does not however give rise to, within sensible approximations, in the framework of a self consistent calculation the very sharp increase in viscosity seen in the strong liquids. Thus the basic results for the relaxation time does not change drastically with the introduction of the cutoff time t_0 in the framework of the fully self-consistent calculation.

5. Discussion

In this paper we discuss the nonlinear fluctuating hydrodynamic equations for compressible liquid, and how they were used for obtaining the mode coupling models for the supercooled liquid dynamics. The theory demonstrated existence of a characteristics temperature T_0 higher than the calorimetric glass transition temperature T_G such that within a narrow temperature range around T_0 there is a freezing out of the large scale structural rearrangements involving collective motion of many molecules. At this temperature there is a qualitative change in the collective dynamics in the liquid although there is no sharp glass transition characterized by a diverging viscosity. The temperature T_0 [27, 7, 23] is a signature of the dynamic singularity due to mode coupling effects. In a careful analysis [5] of the NFH equations it was demonstrated that ergodicity is maintained at all densities. In the Das and Mazenko analysis the role of the $1/\rho$ nonlinearities appearing in the equations were implemented in the field theoretic analysis through the constraint $\mathbf{g} = \rho\mathbf{v}$. The cutoff mechanism responsible for the absence of the sharp transition is a direct consequence of this [29]. Ergodicity was also demonstrated [25] in the asymptotic dynamics obtained in similar mode coupling models obtained from microscopic approaches. In a subsequent work Schimitz De and Dufty [26] (hereafter referred to as SDD) has also considered the equations of nonlinear fluctuating hydrodynamics to obtain a self consistent mode coupling theory for supercooled liquids extending it to short wavelengths. The analysis presented by these authors demonstrate the absence of a sharp transition to an ideal glassy phase similar to the earlier work by Das and Mazenko. In the work by SDD the role of the nonlinearities in the fluctuating hydrodynamic equations are investigated with the underlying microscopic dynamics being constrained by the detailed balance condition. The authors show that special nonlinearities of density ρ and momentum field $\mathbf{g}$ which appear in the continuity equation to maintain detailed balance, do eliminate a complete structural arrest that would have occurred if only coupling of density fluctuations were considered. In a recent work [28] it was demonstrated that both the works gives the identical result for the final relaxation process. The absence of the sharp glass transition in the mode coupling models is linked to the fact that with the increase of density the kernel γ [5] does not self consistently reduce to zero and the density correlation function decays to zero in the long time limit.

Indeed such an effect is also observed in a wide range of systems showing a qualitative change in dynamics of the supercooled liquid around a characteristics temperature higher than the calorimetric glass transition temperature although there is no sharp transition to an ideal glassy phase. γ however gets small, indicating a two/three orders of magnitude rise in the value of transport coefficients. In ref. [30] the authors have used a sophisticated form of scaling in α-relaxation of supercooled liquids. From the measurements of the dielectric susceptibility of a variety of glass forming liquids they observed that the data for all the sample liquids studied can be scaled so that they fall on top of one another over 13 decades of frequency. The curve is described by two parameters, the peak frequency ν_p and the normalized width W (with respect to the Debye width $= 1.14$) of the imaginary part of the dielectric susceptibility. While the observed scaling does fit very well to the stretched exponential form for low frequencies it deviates significantly from the stretched exponential form on the high frequency side. In a subsequent analysis by Kim and Mazenko [13] demonstrated the existence of a cross over temperature in the data of Nagel *et al* by plotting inverse of the peak frequency ν_p with temperature. The high frequency data again fits well to the form $(T - T_0)^2$ and $T_0 = 270\,\mathrm{K}$ for salol. These authors have also argued that the high frequency tail observed in Nagel's scaling curve is a realization of the von-Schweidler relaxation in the mode coupling theory if one assumes a relation between the exponent β of stretched exponential relaxation with the exponent b of von-Schweidler relaxation. Such a relation does not however follow from the mode coupling models obtained from simple nonlinear hydrodynamic models. Thus while the mode coupling models has led to considerable progress in understanding the sequence of time scales associated with relaxation near glass transition, there remain still significant questions for further research.

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