Fluctuating hydrodynamic models for supercooled liquids and development of long relaxation times

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(Received 31 January 1996)

Two fluctuating hydrodynamic models for the supercooled liquid are considered. The self-consistent mode coupling theory for the slow relaxation of density fluctuations are analyzed to explain the glassy dynamics. The density correlation function decays to zero in the long-time limit with diffusive kernels which are identical in both the models. The time scales introduced with the present formulation of the coupling of density fluctuations and current fluctuations shows agreement with behavior of a wide range of simulations and experiments. The renormalization of the various transport coefficients in the two models are also compared. [S1063-651X(96)04807-6]

PACS number(s): 64.70.Pf, 05.60.+w, 64.60.Cn

INTRODUCTION

Nonlinear fluctuating hydrodynamic equations were used [1–3] for obtaining the mode coupling models for the supercooled liquid dynamics. In these models the transport coefficients are obtained in terms of self-consistent expressions of the hydrodynamic correlation functions. This gives rise to a feedback mechanism [4,5] for slow relaxation in the supercooled liquid. In the self-consistent mode coupling models for glass transition the feedback effects from the terms involving the slowly decaying density fluctuations are analyzed since they produce the dominant contribution at supercooled densities. In Refs. [2,6] analysis of the fluctuating hydrodynamic equations for the compressible fluid was done to show how ergodicity is restored in the system in the very long-time limit. It was demonstrated that there is no sharp transition to an ideal glassy state due to the coupling between density fluctuations and current fluctuations in the compressible fluid. The role of the nonlinearities are investigated by introducing a velocity field $\vec{v}$ through the constraint $\vec{g}=\rho\vec{v}$ in the compressible fluid. This is essential in taking care of the $1/\rho$ nonlinearities that appear in the equations of motion [2,7]. Subsequently these models were extended [6,8] to include the structural effects by incorporating proper wave vector dependence and good agreement with computer simulation results were obtained. The theory demonstrated existence of a characteristics temperature T_O higher than the calorimetric glass transition temperature T_G such that within a narrow temperature range around T_o there is a feezing 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 system still remains ergodic over long enough time scales. Ergodicity was also demonstrated [9] in the asymptotic dynamics obtained in similar mode coupling models obtained from microscopic approaches [10].

In a subsequent work Schimitz, Dufty, and De (hereafter referred to as SDD) has also considered a self-consistent mode coupling theory for supercooled liquids extending it to short wavelengths. The analysis presented by these authors demonstrates the absence of a sharp transition to an ideal glassy phase similar to the earlier work by Das and Mazenko. Although the dynamic transition is cut off there are some strong remnants of the glass transition singularity. In both the versions of mode coupling theories, respectively described in Refs. [2] and [11], the density correlation function has an asymptotic behavior given by the form $[z+i\gamma(q,z)]^{-1}$, where the kernel $\gamma(q,z)$ can be expressed self-consistently in terms of the hydrodynamic correlation functions giving rise to a diffusive decay. This indicates that ergodicity is restored over a time scale of $1/\gamma(0,0)$. Indeed if γ would self-consistently reduce to very small values, the supercooled dynamics would be pushed to very long times. Hence the exact form of the kernel representing the cutoff mechanism eliminating the glass transition singularity is important. In Ref. [8] this issue was considered through a self-consistent calculation. This demonstrated that the relaxation time increases by two to three orders of magnitude showing a change in the dynamics but did not give rise to any diverging time scales around this mode coupling singularity. This behavior has been observed in computer simulations of simple liquids as well as for a wide class of systems called the fragile glasses through radiation experiments. The temperature T_C [12,10,13] is a signature of the dynamic singularity due to mode coupling effects.

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 $\vec{g}$ 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 the present work we compare the results of the two models presented in Refs. [2] and [11] and demonstrate that both the works gives the identical result for the final relaxation process. We also analyze the two models to compare the renormalization of transport coefficients and sound speeds in the two models. We end the paper with a small discussion.

FLUCTUATING HYDRODYNAMICS OF COMPRESSIBLE LIQUID

In the analysis by Das and Mazenko in Ref. [2] the set of hydrodynamic variables used are the mass density ρ, the momentum density $\vec{g}$, and the flow velocity $\vec{v}$ defined through the nonlinear constraint

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

The equations of motion for the hydrodynamic variables are obtained using the well known Zwangig-Mori [14] formalism and are valid for small and finite wavelengths. The equation for ρ is given by

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

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

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

where $F_u[\rho(x)]$ is the potential energy part of the effective Hamiltonian F defined [15] as

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

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

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

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

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

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

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

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) [16] type was used in Ref. [2]. 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 fully renormalized theory of the hydrodynamic correlation functions are obtained interms of the self-energy matrix Σ defined through the Dyson equation

$$G^{-1}(\vec{q},\omega)=G_o^{-1}(\vec{q},\omega)-\Sigma(\vec{q},\omega), \tag{8}$$

where G_o 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

$$G_{\rho\rho}(q,t)=\int d(\vec{x}-\vec{x}')e^{i\vec{q}\cdot(\vec{x}-\vec{x}')}\langle\delta\rho(\vec{x},t)\delta\rho(\vec{x}',0)\rangle, \tag{9}$$

where the angular brackets refer to the average over the stationary states. In Ref. [2] the following form for the Fourier-Laplac transform of $G_{\rho\rho}(\vec{x},t)$ normalized with respect to its equal time value is obtained in the small q and ω limit,

$$\psi(q,z)=\frac{z+iq^2\Gamma^R(q,z)}{z^2-q^2c^2(q)+iq^2\Gamma^R(q,z)[z+i\gamma(q,z)]}. \tag{10}$$

Here $c^2(q)=[\beta mS(q)]^{-1}$ and $\Gamma^R(q,z)$ is the renormalized longitudinal viscosity. Similarly the Laplac transform for the transverse current fluctuation (normalized with respect to its equal time value) is given by

$$\phi(q,z)=\frac{1}{z+iq^2\eta^R(q,z)}, \tag{11}$$

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 right-hand side (RHS) of Eqs. (10) and (11) have the mode coupling contributions at the one loop level, respectively, given by

$$q^2\Gamma^{mc}(q,t)=\lambda_o\int\frac{d\vec{k}}{(2\pi)^3}[\{\hat{\vec{q}}\cdot\vec{k}\}c(k)+\{\hat{\vec{q}}\cdot(\vec{q}-\vec{k})\}\times c(|\vec{q}-\vec{k}|)]^2G_{\rho\rho}(\vec{q}-\vec{k},t)G_{\rho\rho}(\vec{k},t) \tag{12}$$

and

$$q^2\eta^{mc}(q,t)=\lambda_o\int\frac{d\vec{k}}{(2\pi)^3}[c(k)-c(\vec{q}-\vec{k})]^2k^2\times(1-u^2)G_{\rho\rho}(\vec{q}-\vec{k},t)G_{\rho\rho}(\vec{k},t), \tag{13}$$

where $\lambda_o=(2\beta m^4\rho_o)^{-1}$ and $u=\hat{\vec{q}}\cdot\hat{\vec{k}}$ while $\hat{\vec{q}}$ is the unit vector along the direction of $\vec{q}$.

The quantity $\gamma(q,z)$ on the RHS of Eq. (10) arises from the coupling between the density fluctuations and current fluctuations in a compressible fluid. In the asymptotic limit when the viscosity becomes large due to the feedback coming from mode coupling contributions, the density autocorrelation function given by Eq. (10) develops a pole at

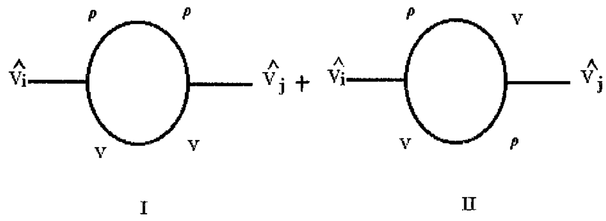

FIG. 1. The one loop diagram contributing to the self-energy $\Sigma_{\hat{v}_i\hat{v}_j}$.

$$z+i\gamma(q,z)=0. \tag{14}$$

In Ref. [2] it was demonstrated through the relation (6.59) 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 Eq. (8). The one loop diagrams for the self-energy $\Sigma_{\hat{v}_i\hat{v}_j}$ is shown in Fig. 1. On evaluating these diagrams the following self-consistent expression for γ in terms of density and current correlation functions is obtained.

$$\gamma(q,t)=\int \frac{d\vec{k}}{\rho_o^2(2\pi)^3}\big([u_1^2G_{gg}^L(\vec{q}-\vec{k},t) + (1-u_1^2)G_{gg}^T(\vec{q}-\vec{k},t)]G_{\rho\rho}(\vec{k},t) + uu_1G_{g\rho}(\vec{k},t)G_{g\rho}(\vec{k}-\vec{k},t)\big), \tag{15}$$

with definitions $u\equiv\hat{\vec{k}}\cdot\hat{\vec{q}}$ and $u_1=\hat{\vec{q}}(\vec{q}-\vec{k})/|\vec{q}-\vec{k}|$ 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 in Ref. [8] for obtaining a close set of functional equations for the density and current correlation functions. The time scales of relaxation that followed from the numerical solution of these equations demonstrated good agreement with the computer simulation results [17]. Here we compare the predictions of Refs. [2,8] with that of Ref. [11].

RESULTS FROM THE MODEL BY SDD

In this section we discuss the results by SDD as presented in Ref. [11] and compare them with the earlier works by Das and Mazenko. Following Ref. [11], the hydrodynamic correlation functions are expressed in terms of the appropriate memory functions, given by Eqs. (9) to (13) cited therein. We consider below memory functions M_0, M_1, M_2, and M_3 introduced in these expressions for analyzing the results of these authors.

(a) Memory kernel M_2 and M_3: The renormalization of longitudinal and shear viscosities of the supercooled liquid due to mode coupling effects are expressed, respectively, through the memory functions M_2 and M_3. The longitudinal viscosity is defined through the attenuation of the density auto correlation function. If we ignore nonlinearities appearing in the equations of motion due to coupling between density and momentum fields, and consider only those due to

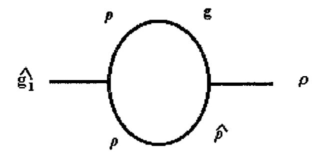

FIG. 2. The one loop diagram contributing to the self-energy $\Sigma_{\hat{g}_i\rho}$ due to the $\{\hat{\rho}g_i\rho\}$ vertex.

density fluctuations, the following expression for the density correlation function is obtained:

$$\psi(q,z)\equiv C_{00}(q,z)=\left[z+\frac{\Omega^2(k)}{z+M_2(q,z)}\right]^{-1}, \tag{16}$$

where $\Omega=k/[\beta mS(k)]$. The memory function M_2 is understood to have a short-time part denoted by σ in Ref. [11]. M_2 turns out to be identical to the expression for Γ^R given in Eq. (10). In the simple model where only coupling of density fluctuations are considered there is a dynamic instability at a critical density beyond which the liquid freezes into a nonergodic phase with the density correlation function decaying to a nonzero value in the long-time limit. Thus, beyond a critical density Eq. (16) for a range of q allows for a solution with a nonzero set of values for $\psi(q,t\rightarrow\infty)=f(q)$.

Similarly the decay of the transverse correlation function $C_{33}(q,z)$ or $\phi(q,z)$ given in Eq. (11) is determined by the the memory function $M_3(q,z)$ which is identical to the generalized shear viscosity given by (13). Thus in the models where all couplings between currents and density fluctuations are ignored, identical results are obtained in both the models of Ref. [2] and Ref. [11]. However, the difference in the *longitudinal* viscosity kernels in the two models show up when all the couplings between current and density fluctuations are taken into account. This is discussed below.

(b) Memory kernel M_1: This is of $o(q^2)$ in the small wave vector limit. In the work by Das and Mazenko the similar quantity is obtained through the $\hat{g}_\rho-\rho$ element of the self-energy matrix introduced in Eq. (8). This goes in the renormalization of the sound speed. Indeed it was shown in Ref. [2] at the one loop level the contribution $\Sigma_{\hat{g}\rho}/q$ is zero in the small q limit. The memory function M_1 stands for the correction to the sound speed in the finite wave vector or short wavelength regime. Its contribution in the hydrodynamic limit is zero since a Gaussian free energy functional has been used in the analysis. The contribution to M_1 comes from the diagram shown in Fig. 2. This is a consequence of the vertex that appears in the density equation as a result of detailed balance imposed on the microscopic dynamics.

(c) Memory kernel M_o: This memory kernel determines the asymptotic decay of the density correlation function. For very long times which corresponds to small z, the density correlation function develops a pole at $z=-M_o(q,z)$ and the dynamic instability showing the transition to a nonergodic phase is now absent since $M_o(0,0)\neq 0$. In fact M_0 expressed self-consistently in terms of the hydrodynamiccorrelation functions is *identical* to the result obtained by Das and Mazenko. Following Ref. [11] Eq. (13) we can express the kernel M_o as

$$M_o(q,z)=(2\pi)^{-3}\int_0^\infty dte^{-izt}\int d\vec{q}\Lambda_{\alpha\beta\gamma}(\vec{q}:\vec{k},\vec{q}-\vec{k})\times C_\beta(k,t)C_\gamma(|\vec{q}-\vec{k}|,t). \quad (17)$$

Using the expressions for Λ matrix given in Ref. [11] and the relation (15) we can simplify the above expressions obtaining

$$M_o(q,z)=i\gamma(q,z). \quad (18)$$

Thus the quantity M_0 expressed self-consistently in terms of the hydrodynamic correlation functions is *identical* to the result for the asymptotic decay of the density correlation function as obtained by Das and Mazenko. However, when the density and current couplings are kept, the memory kernel M_2 in the model by SDD has the form

$$M_2=\lambda_o\int\frac{d\vec{k}}{(2\pi)^3}[\{\hat{\vec{q}}\cdot\vec{k}\}S^{-1}(k)+\{\hat{\vec{q}}\cdot(\vec{q}-\vec{k})\}S^{-1}\times(|\vec{q}-\vec{k}|)]^2G_{\rho\rho}(\vec{q}-\vec{k},t)G_{\rho\rho}(\vec{k},t) \quad (19)$$

which is different from the result quoted in Eq. (12). When the current and density couplings are taken into account, i.e., the vertex function $U^{(2)}$ is included, the mode coupling contributions to the transport coefficients are *not identical* and this difference persists even in the small q and ω limit.

DISCUSSION

We have considered in detail here the two hydrodynamic models for supercooled liquids. The main conclusions are as follows:

(i) If the density nonlinearites in the equations of motion are only considered, then the model by SDD reduces to the standard form, which is also the q-dependent generalization of the Das and Mazenko model discussed in Ref. [8] where the result follows simply by ignoring nonhydrodynamic (higher in q) terms rather than picking up a certain set of nonlinearities in the equations of motion. This model contains a dynamic instability which freezes the liquid into a nonergodic phase, characterized by diverging transport coefficients.

(ii) Retaining the nonlinear terms coming from both the density fluctuations as well as current fluctuations, SDD shows that the dynamics controlled by the detailed balance eliminates the sharp transition into an ideal glassy phase mentioned above. Over very long-time scales the density correlation function develops a pole as $[z+M_o(q,z)]^{-1}$. The earlier analysis by Das and Mazenko obtains an identical behavior for the density autocorrelation function. The self-consistent expression for M_o in terms of the density and current correlation functions are shown to be *identical* in the two models. This is a key result of this paper. However, the quantitative behavior of the hydrodynamic correlation functions can be determined through the solution of the self-consistent mode coupling equations with proper mode coupling vertex functions. In Ref. [8] this was done for the wave vector dependent extension of the Das and Mazenko model with a choice of the standard free energy functional. The resulting expression for the renormalization of viscosity in the analysis of Ref. [8] is in agreement with other works [5]. In the model by SDD the mode coupling vertex, given by Eq. (19) for renormalizing the transport coefficients is different due to introduction of the new vertex function referred to as $U^{(2)}$ in the model in Ref. [11], arising from the detailed balance used in the model. The full quantitative implications of this can only be made by a numerical evaluation.

(iii) 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 $\vec{g}=\rho\vec{v}$. The cutoff mechanism responsible for the absence of the sharp transition is a direct consequence of this. The role of the Jacobian function in the field theoretic analysis with the three fields $\vec{g}$, $\vec{v}$, and ρ and that its implication on the dynamics is irrelevant was discussed in detail elsewhere by Mazenko and Yeo [7].

(iv) The expression $\gamma(q,z)$ in Eq. (10) in Ref. [2] was obtained through a nonperturbative analysis and taking the hydrodynamic limit of small q and ω. On the other hand, the work by SDD starts from a set of hydrodynamic equations which is not invariant under Galilean transformations. But their analysis does not involve the consideration of the hydrodynamic limit. This allows an extension of the theory into the short length scales.

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 [2] or M_o [11] does not self-consistently reduce to zero and the density correlation function always 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 or three orders of magnitude rise in the value of transport coefficients. The present work establishes the exact equivalence of the time scales predicted in two different hydrodynamic models for supercooled liquid.

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