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Ergodicity and slow diffusion in a supercooled liquid

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HIGHLIGHTS

- Equations of Fluctuating Nonlinear hydrodynamics for the compressible liquid are considered.
- Role of density current couplings and an extra slow diffusive mode are both included.
- The viability of slow dynamics in presence of the above two competing effects is studied using field-theoretic approach.

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ABSTRACT

A model for the slow dynamics of the supercooled liquid is formulated in terms of the standard equations of fluctuating nonlinear hydrodynamics (FNH) with the inclusion of an extra diffusive mode for the collective density fluctuations. If the compressible nature of the liquid is completely ignored, this diffusive mode sets the longest relaxation times in the supercooled state and smooths off a possible sharp ergodicity–nonergodicity (ENE) transition predicted in a mode coupling theory. The scenario changes when the complete dynamics is considered with the inclusion of $1/\rho$ nonlinearities in the FNH equations, reflecting the compressible nature of the liquid. The latter primarily determines the extent of slowing down in the supercooled liquid. The presence of slow diffusive modes in the supercooled liquid do not give rise to very long relaxation times unless the role of couplings between density and currents in the compressible liquid is negligible.

1. Introduction

The Mode coupling theory(MCT) has been developed as a microscopic theory to understand the slow dynamics of a supercooled liquid. The basic mechanism that increases the viscosity was first identified [1–3] from kinetic theory of dense fluids. Subsequently equations of fluctuating nonlinear hydrodynamics (FNH) have been used to derive [4–7] the MCT. Generally, the defining expressions for these correlation functions are expressed in terms of space and time dependent transport coefficients. In the FNH formulation of the MCT, it is assumed that the crystallization process [8,9] does not interrupt and the transport coefficients are renormalized due to nonlinearities in the equations of motion for the slow modes and they are expressed in terms of hydrodynamic correlation functions. Nonlinear equations for the dynamics of the correlation functions are obtained from such definitions combined with the self consistent expressions for the transport coefficients. This gives rise to a feedback mechanism [2] for slow relaxation of correlations [10] in the supercooled liquid. As a consequence, the mode coupling theory (in its simplest form) predicts an ergodicity–nonergodicity (ENE) transition at a critical density n_c. The correlation function $\phi(q, t)$ of collective density fluctuations at wave vector q and time separation t is $f(q) \neq 0$ at the transition.

In Ref. [11] analysis of the fluctuating hydrodynamic equations for the compressible liquid showed how ergodicity is restored in the long time dynamics. The role of the $1/\rho$ [12] nonlinearities in the generalized equation for the momentum

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fluctuations in the compressible fluid played the key role in producing the ergodicity restoring mechanism. In a subsequent work Schimitz, Dufty, and De [13] has also considered a self-consistent mode coupling theory for supercooled liquids. The analysis presented by these authors demonstrates the absence of sharp transition to an ideal glassy phase [11] in the model. In both the versions of mode coupling theories, respectively described in Refs. [11,13], the density correlation 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 hydrodynamic correlation functions giving rise to a diffusive decay. Subsequent to these works several other phenomenological models [14] for the structural relaxation in a deeply supercooled glassy liquid [15] were developed. Models taking into account orientational degrees of freedom [16,17] have been proposed. From a qualitative level the breaking of the cage formation in the dense liquid is manifested through the couplings of current and density fluctuations. This process influences the dynamics and in particular mass transport in important ways. Orientational degrees of freedom have been included in description of the supercooled liquid to describe the process of cage formation and freezing at a local scale. In some of the works such phenomenological considerations were used to construct model [18–21] by extending the existing self-consistent formulation of the MCT. From a general viewpoint the effects of activated events in some of these models are incorporated in the dynamics by using the concepts from the random first order transition theory. The dynamic structure factor is modified by localized activated hopping [22] events termed in some works as instantons. Thus if we denote the density correlation function which acts like an order parameter in the MCT, as $\phi_{\mathrm{MCT}}(q, t)$, by including the so called hopping [23] it was modified as

$$\phi(q, t) \approx \phi_{\mathrm{MCT}}\phi_{\mathrm{hopp}}. \tag{1}$$

It is argued that close to the glass transition temperature, T_g, since the configurational entropy S_c is diminishing, the activated process slows down leading to an arrest of the structural relaxation. Beyond the mode coupling transition temperature, T_c, the density correlation is assumed to decay via the hopping channel. Thus the longitudinal viscosity, which is otherwise divergent in the idealized MCT, remains finite.

In the present work we propose a model in which instead of making a modification of standard MCT at the level of correlation function [18,24], with a diffusive mode, we modify the equations of FNH with the same, which forms the basis of the MCT. We include an extra diffusive process in the collective density fluctuations in addition to the standard MCT. If the extra diffusive mode is ignored then our model reduces to the standard extended MCT model. The latter refers to the full mode coupling model in which all the important nonlinearities of the original equations of FNH are present. These nonlinearities include those which give rise to an ergodicity–nonergodicity (ENE) transition at the simplest level, as well as the source of ergodicity restoring mechanism over longer time scales. The assumed diffusive mode is an additional mode in the system. Our analysis demonstrates the importance of the compressible nature of the liquid in determining the slow dynamics.

This basic model of extended MCT is obtained primarily from the conservation laws and the dynamics of the corresponding collective modes in the liquid. The Fluctuating Nonlinear Hydrodynamic model [13] is formulated in terms of two fluctuating variables $\mathbf{g}$ and ρ and without any $1/\rho$ nonlinearity present in the generalized equation for the momentum conservation. This involves simplifying the expression for the kinetic energy term F_K of the driving free energy functional for the system which determines the equilibrium state of the liquid [25]. Making this change violates the Galilean invariance of the FNH equations. Since our focus here is primarily on the slow dynamics produced due to dominant density fluctuations we assume that this is not too important in the present analysis. The FNH equations studied in the present work are also based on a purely Gaussian form of the driving free energy functional $F[\rho, g]$ like that of Ref. [13] and contain the same density and current coupling in the continuity equation as in Ref. [13]. In this model of extended MCT, the ENE transition is smeared off due to this density and current coupling appearing in the continuity equation. On ignoring this nonlinearity in the continuity equation, we get the basic MCT model which predicts an ENE transition at a critical density. As noted above additionally, we include here a diffusive mode as an extra slow process in the dense supercooled state of the liquid. With this the continuity equation is now modified and the corresponding current have contributions from the diffusive mode as well as the random noise. The form of a balance equation for the density variable is maintained. The dissipative term in the equation of motion for the collective density field $\rho(\mathbf{x}, t)$ is linear. If this diffusive mode and the related noise is ignored then our model reduces to the FNH model of Ref. [13]. The goal of the present analysis is to study how the simultaneous presence of the diffusive mode and $1/\rho$ nonlinearities affects the dynamics and determine their relative importance in producing the slow dynamics.

The paper is organized as follows. In Section 2 we discuss the construction of the basic equations of FNH using standard formalisms [26] but adopting a purely Gaussian free energy functional. This is followed in Section 3 by discussion of linearized dynamics and the noise averaged correlation functions. In Section 4 we construct the renormalized theory taking into account one loop expressions for the self energies renormalizing the transport coefficients. Section 5 discusses the numerical solution of the MCT equations and is followed by discussion section.

2. Model studied

The basic equations of the model for the dynamics of a fluid is obtained using the standard techniques [26–28] of fluctuating nonlinear hydrodynamics (FNH). The equation of motion for the coarse grained density $\rho(\mathbf{x}, t)$ is a continuity equation with the momentum density $\mathbf{g}(\mathbf{x}, t)$ as the current which itself is a conserved property. The current $\mathbf{g}(\mathbf{x}, t)$ satisfies the momentum conservation equation. The latter constitutes the generalized Navier–Stokes equation. We include in the