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Nonequilibrium dynamics of a supercooled liquid using schematic and structural models

Shankar P. Das *, Bhaskar Sen Gupta, Sunil P. Singh

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

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ABSTRACT

The glassy aging data of dielectric relaxation fits to a modified Kohlrausch–Williams-Watts (MKWW) form $exp\left[-\left(t_{age}/\tau_{age}\right)^{\beta_{age}}\right]$. The relaxation time $\tau_{age}(t_{age})$ and the stretching exponent β_{age} are both independent of the frequency of the corresponding data. We discuss two theoretical models to study this non equilibrium dynamics. First we discuss a schematic soft-spin model in which the aging behavior follows the MKWW form similar to the above dielectric data. The nature of the modified fluctuation-dissipation relation (FDR) is also studied in the time as well as correlation windows. Second, we solve numerically the equations of fluctuating nonlinear hydrodynamics (FNH) generalized to short wave lengths for a simple Lennard–Jones liquid. The correlation of density fluctuations at two and four points level are studied using the same density fluctuation data. The respective equilibration of both two point and four point functions follow the MKWW form with relaxation times (dependent of t_{age}) which are very different in the two cases.

1. Introduction

Understanding the dynamics of the supercooled liquid in the non equilibrium state is a topic of intense research in condensed matter physics. The supercooled liquid, when cooled fast enough, the dynamics of its constituent particles gets confined in a specific part of the phase space and the system cannot reach a state of thermal equilibrium. In this situation the time needed to relax to equilibrium increases far beyond the time scale of the experiment. Analysis of the dynamics of the liquid in the non-equilibrium state reveals a variety of phenomena like aging and memory effects [1, 2]. Theoretical approaches like computer simulations [3] and studies of simple dynamical models [4] have been used for understanding the complex relaxation behavior in the non-equilibrium state. An important question in this regard is whether the dynamics in the non-equilibrium state can be understood as an extrapolation of the alpha relaxation process characteristics of the equilibrium states at temperatures above the calorimetric glass transition temperature T_g [1]. The supercooled liquid falls out of equilibrium over laboratory time scales at the calorimetric glass transition temperature T_g. In the non-equilibrium system is not time translation invariant and correlations of fluctuations at two different times depend on both times. The initial time t_w at which the fluctuation is considered for correlation will be referred to as the waiting or aging time. In a recent work, Lunkenheimer et al. [5] studied over a range of frequency ω the dielectric response function $\chi_\omega(t_w)$ at temperature $T < T_g$. The aging time ($\equiv t_w$) dependence of χ follows a modified Kohlrausch–Williams–Watts (MKWW) function $\widetilde{f}(t_w) = exp\left[-(t_w/\tau(t_w))^{\beta_{age}}\right]$. The relaxation time $\tau(t_w)$ and the stretching exponent β_{age} are identical for all frequencies. The collapse of the data for different frequencies for the scaled function is displayed in Fig. 1. It has been shown [6] (inset of Fig. 1) that the aging time dependence of $\tau(t_w)$ can be obtained with the stretching exponent β_{age} being *different* from that of the corresponding α-relaxation β_α [6]. This conforms to a scenario in which the nature of the relaxation and heterogeneity controlling the aging process is different from that of the equilibrium structural relaxation.

For understanding the nonequilibrium dynamics in a supercooled liquid from a theoretical approach we study the relaxation phenomena in terms of suitable correlation functions. In the present paper, we discuss the calculation of the correlation function using two different theoretical models. In the first model the correlation and response functions are expressed in terms of soft spins. The glassy state is taken as a frozen solid (up to times scales of relaxation) and with the motion of its constituent particles being localized around randomly distributed sites. A variety of phenomena like aging and memory effects [1, 2] are observed from the analysis of the dynamics in this nonequilibrium glassy state. We discuss here a soft-spin type model, which is defined in terms of the displacements of the particles around a corresponding set of random lattice points. Important progress in understanding the nonequilibrium dynamics of the disordered systems has been made in recent years from the study of simple mean field spin glass models. In the multi-spin interaction models, the non-linearities in the Langevin dynamics give rise [7] to a ergodic–nonergodic transition. The basic mechanism for this transition is very similar to that present in the

* Corresponding author.
E-mail address: shankar0359@yahoo.com (S.P. Das).

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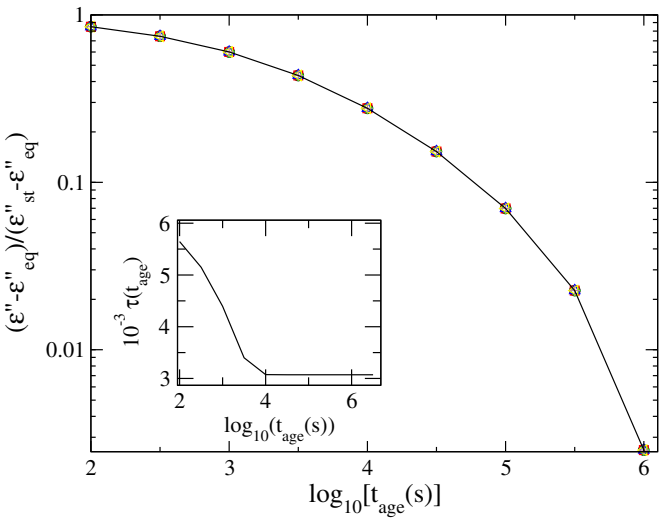

Fig. 1. Scaling of the dielectric data for glycerol at 179 K for frequencies 1–10^5 kHz. Solid line shows MKWW fit (see text) inset show the best fit $\tau(t_{age})$ vs. t_{age} (in sec) for glycerol [6].

models for the dynamics of supercooled liquids [8]. Weak ergodicity breaking [9] in a spherical p-spin ($p > 2$) interaction model [10] over the asymptotic time scales has been observed [4]. The dynamics crosses over from a regime of time translational invariance to that of aging behavior was demonstrated analytically. Low temperature properties of glassy systems, e.g., thermal conductivity and specific heat [27–29], have also been studied with models [11] for the structural glass with similar spin models. The aging behavior in the nonequilibrium glassy state is described by a modified KWW function similar to that obtained in Ref. [5] as discussed above. We also study in the model system how the standard fluctuation dissipation relation is followed for a system out of equilibrium over respective time ranges.

The second model we present here obtains the correlation functions in terms of the conserved modes of the liquid state. The conserved densities of mass, momentum, and energy constitute the simplest set of slow modes characteristic of the isotropic liquid. The dynamics of these slow modes with nonlinear differential equations of FNH having regular and stochastic parts. The regular parts involve nonlinear coupling of slow modes while the random parts represent noise. The most widely studied theoretical model for the slow dynamics in a supercooled liquid approaching vitrification follows from the FNH equations and is termed as the self-consistent mode coupling theory (MCT) [8, 12]. In a strongly interacting dense liquid the couplings of density fluctuations in the basic equations of generalized hydrodynamics produce the dominant effect on dynamics. The MCT involves a nonlinear feedback mechanism [13] of density fluctuations producing strong enhancement of the viscosity of the supercooled liquid. In its simplest version the MCT predicts that above a critical density the long time limit of the time correlation $C(t)$ of density fluctuations is nonzero. This signifies an ergodic-nonergodic transition (ENE) in the liquid and is a precursor to the liquid-glass transition. We study the slow dynamics of a dense monatomic Lennard-Jones liquid by numerically solving the stochastic equations of FNH. The non-perturbative calculation shows good agreement with the computer simulation results of the same system in equilibrium. We report here the results on the dynamics of the density fluctuations under nonequilibrium conditions by analyzing two and four point functions.

The paper is organized as follows. In the next section we discuss the schematic models using soft spins. We demonstrate in the two respective subsections the basics of the model and how the system reaches equilibrium or falls out of it on both sides of an ideal ergodicity-nonergodicity transition which occurs as a result of the dynamic coupling of the soft modes. In the section we describe a model for the supercooled liquid with proper structure. We describe computation of the correlations in equilibrium and non-equilibrium states from numerical solution of the equations of FNH. We end the paper with a discussion of the results.

2. The schematic model

2.1. Description of the model

The present model for an amorphous solid can be obtained from a semi-microscopic basis. Let r_i be the coordinates of the i-th particle in the solid. For the amorphous solid, $\{r_i^0\}$ constitutes a random structure corresponding to a local minimum of potential energy and u_i is the displacement of the i-th particle from its parent site, i.e., $r_i = r_i^0 + u_i$. We take the potential energy $U(\{r_i\})$ as a sum of two body potentials, $U = \sum_{i<j}\phi_{ij}$. A Born von Karman type expansion of the coordinates $\{r_i\}$ of the N particles around $\{r_i^0\}$ obtains,

$$U = G(u_i) + \sum_{ij}{}' J_{ij}^{(2)} u_i u_j + \sum_{ijk}{}' J_{ijk}^{(3)} u_i u_j u_k + \ldots, \tag{1}$$

with the single site potential $G(u_i)$ [11] being included in the amorphous system with random structure. The primes in the summations in the RHS indicate that the terms having all the corresponding running indices i, j, k etc. being the same are absent. The expansion in terms of u_i is valid over the time scale of the structural relaxation. The potential energy is obtained in the translational invariant form

$$H = \sum_{p=2}^{\infty}\sum_{i\neq j} J_{ij}^{(p)}\left(u_i - u_j\right)^p, \tag{2}$$

by assuming

$$J_{ijk}^{(3)} = J_{ij}^{(3)}\delta_{jk} + J_{jk}^{(3)}\delta_{ki} + J_{ki}^{(3)}\delta_{ij}, \tag{3}$$

where $J_{ji}^{(p)} = (-1)^p J_{ij}^{(p)}$ etc. For the amorphous solid, the interaction matrix $J_{ij}^{(p)}$ is assumed to be random following a gaussian probability distribution of zero mean and variance J_p^2/N. For reaching the expression (2) the coefficients of the single site term is chosen of the form

$$G(u_i) = \sum_i \left\{ w_{2i}u_i^2 + w_{3i}u_i^3 + \ldots \right\} \tag{4}$$

are chosen as: $w_{2i} = -\Sigma_j{}' J_{ij}^{(2)}$, $w_{3i} = -\Sigma_{j,k}' J_{ijk}^{(3)}$, etc. The time evolution of $u_i(t)$ is given by the dissipative Langevin equation,

$$\Gamma_0^{-1}\frac{\partial u_i}{\partial t} = -\beta\frac{\delta H}{\delta u_i} - z(t)u_i + \xi_i(t). \tag{5}$$

Γ_0 is the bare kinetic coefficient related to the variance of the gaussian white noise ξ_i through the fluctuation-dissipation relation

$$\langle \xi_i(t)\xi_j(t')\rangle = 2\beta^{-1}\Gamma_0\delta_{ij}\delta(t-t'). \tag{6}$$

$z(t)$ is a Lagrange's multiplier used enforcing the constraint $N^{-1}\sum_i \langle u_i^2(t)\rangle = 1$. In the present context of the amorphous solid state this is equivalent to having a constant Lindemann parameter at a fixed temperature T.

The time correlation and response functions of the displacement variable u_i is obtained by constructing the standard Martin-Siggia-Rose (MSR) [14] field theory in terms of the field u and $\hat{u}_i$. The hatted field $\hat{u}_i$ conjugate to u_i is introduced in the MSR theory to average over the Gaussian noise ξ_i. Correlation between u_i and $\hat{u}_j$ represents the linear