Mode-coupling theory for the dynamic heterogeneity in an aging glass: How Do Glassy Domains Grow?

Saroj Kumar Nandi and Sriram Ramaswamy

Centre for Condensed Matter Theory, Department of Physics, Indian Institute of Science, Bangalore-560 012, India.

We construct the equations for the growth kinetics of an aging structural glass within mode-coupling theory through a non-stationary variant of the 3-density correlator defined in Phys. Rev. Lett. 97, 195701 (2006). We solve a schematic form of the resulting equations to obtain the coarsening of the dynamic heterogeneity, characterized via the 3-point correlator $\chi_3(t, t_w)$, as a function of waiting time $t_w$. For a quench into the glass, we find that $\chi_3$ attains a peak value $\sim t_w^{0.5}$ at $t - t_w \sim t_w^{0.5}$, providing a theoretical basis for the numerical observations of Parisi [J. Phys. Chem. B 103, 4128 (1999)] and Kob and Barrat [Phys. Rev. Lett. 78, 4581 (1997)]. The aging is not “simple”: the $t_w$ dependence cannot be attributed to an evolving effective temperature.

When a system is quenched below an ordering transition, domains of the ordered phase appear and begin to grow, with characteristic size given by the decay length of equal-time correlations of the order parameter. The corresponding issue for the glass transition has been examined numerically using susceptibilities and correlation lengths that capture the onset of amorphous freezing, but a quantitative theory of these observations has been lacking. Length-scale information similar to that obtained from the 4-density correlator and related overlap functions has been shown to be contained in a certain three-point correlator $\chi_3(t)$, whose peak value, and the time at which the peak is attained, diverge upon approaching the mode-coupling glass transition.

In this work we present a theory of the coarsening of glassy order, using a non-stationary generalization $\chi_3(t, t_w)$, whose peak value $\Omega(t_w)$ is the correlation volume as a function of the waiting time $t_w$ since the quench. We formulate our calculation in the framework of the fluctuating hydrodynamics of a dense liquid, and obtain results using mode-coupling theory (MCT), in a schematic approach. Figures summarize our results. We find that $\Omega(t_w)$ grows without bound for a quench into the MCT glass (Fig. 2), as $t_w^{0.5}$, and the relaxation time as $t_w$ (Fig. 3), in agreement respectively with the computer experiments of Parisi and Kob and Barrat. As effects beyond MCT cut off the transition, the coarsening in experiments, simulations, or a complete theory will cease at long enough times, but typical simulations do not explore these asymptotically long time scales and can therefore be compared usefully to our MCT coarsening predictions. The three-point function, Fig. 5 shows features incompatible with “simple aging” but qualitatively similar to 3. For a quench to a distance $\epsilon$ from the threshold value on the liquid side, $\Omega$ grows to saturation (Fig. 3), reaching an equilibrium value $\sim \epsilon^{-1}$, with a relaxation time $\sim \epsilon^{-1.8}$ (Fig. 4).

MCT is an analytically tractable approximation to equilibrium liquid-state dynamics that yields a glass transition in a homogeneous system, which is why it is so widely used despite its shortcomings. In order to extend MCT to describe non-stationary states such as coarsening we work with a general field-theoretic approach, taking care not to use results like the Kubo formulae and fluctuation-dissipation relations (FDR), which are justified only in equilibrium treatments. We start with the equations of fluctuating hydrodynamics for the velocity and density fields for an isothermal compressible fluid, extended to large wavenumbers so as to take into account the modes around the structure factor peak. In order to obtain an equation for the density field alone, we eliminate the velocity while retaining momentum conservation but ignoring inertia.

FIG. 1: The aging of the two-point function. The correlation function $C(t, t_w)$ as a function of $t$, for various waiting times $t_w$ shown in the legend. The decay with $t$ becomes progressively slower with increasing $t_w$. The final parameter values are $T = 1.0$ and $\lambda = 2.0$. Inset: Scaling $t - t_w$ by $t_w$ yields a data collapse in the $\alpha$-relaxation regime. Such “simple aging”, however, is not seen in the three-point function, Fig. 5.
This yields the dynamical equation
\[
\frac{\partial \rho_k(t)}{\partial t} + K_1 \rho_k(t) = \frac{K_2}{2} \int_q \mathcal{V}_{k,q} \delta \rho_q(t) \delta \rho_{-q}(t) + f_k(t), \tag{1}
\]
for the Fourier-transformed density fluctuation $\delta \rho_k(t)$ at wavevector $k$, with $\mathcal{V}_{k,q} = k \cdot (q + (k - q)c_{k-q})$, $K_1 = k_B T / S_k D_L$ and $K_2 = k_B T / D_L k^2$. Eq. (1) can be viewed as the no-inertia limit of Eq. (4.1) of [14]. Here $D_L = (\zeta + 4\eta/3)/\rho_0$ is the longitudinal damping, where $\zeta$ and $\eta$ are the bare shear and bulk viscosities, $k_B T$ is Boltzmann’s constant times temperature, $S_k$ and $c_k$ are the equilibrium static structure factor and direct correlation function respectively and the noise $f_k(t)$ obeys
\[
(f_k(t)f_k(t')) = \frac{2k_B T}{D_L} \rho_k(t) \delta(k + k') \delta(t - t'). \tag{2}
\]
From diagrammatic perturbation theory [11, 15], we construct the equations of motion for the correlation function $C_k(t, t_w) = \langle \delta \rho_k(t) \delta \rho_{-k}(t_w) \rangle$ and response function $R_k(t, t_w) = \langle \partial \delta \rho_k(t) / \partial f_{-k}(t_w) \rangle$:
\[
\frac{\partial C_k(t, t_w)}{\partial t} = -K_1 C_k(t, t_w) + \int_0^{t_w} ds D_k(t, s) R_k(t, s) \\
+ \int_0^t ds \Sigma_k(t, s) C_k(s, t_w), \tag{3a}
\]
\[
\frac{\partial R_k(t, t_w)}{\partial t} = \delta(t - t_w) - K_1 R_k(t, t_w) \\
+ \int_0^t ds \Sigma_k(t, s) R_k(s, t_w), \tag{3b}
\]
with $D_k(t, t') = (2k_B T / D_L) \rho_k(t') \delta(t - t') + M_k(t, t')$, $M_k(t, t') = (K_2^2/2) \int_q \mathcal{V}_{k,q}^2 C_k(t, t') C_{k-q}(t, t')$ and $\Sigma_k(t, t') = K_2^2 \int_q \mathcal{V}_{k,q}^2 \delta m_q(t, t') C_{k-q}(t, t')$. The contribution to $\Sigma$ from the first term in $D_k(t, t')$ vanishes due to causality. Franz and Hertz [12] obtained schematic equations similar to (3a) and (3b) for the Amit-Roginsky model [18].

How are the input quantities $K_1$ and $\mathcal{V}_{k,q}$ in equations (3a) and (3b) defined for the case of a quench? A comparison with the treatment of Zaccarelli et al. [17] is useful here. The $\mathcal{V}_{k,q}$ term in (3a) and (3b) involves the “residual interactions” in [17]. We define our quench to be an abrupt increase in the interaction strength, implying that $\mathcal{V}_{k,q}$ should be evaluated at the final parameter value. To determine $K_1$, which must now be a time-dependent quantity as we are dealing with a non-stationary state, we insist, as in [19], that for $\tau = (t - t_w) \ll t_w$ Eq. (3b) obeys time-translation invariance and the FDR. This leads, after some algebra, to
\[
K_1(t) S_k = T R_k(0) + K_2^2 \int_0^t \int_q \mathcal{V}_{k,q}^2 C_{k-q}(t, s) \times
\left[ \frac{1}{2} C_q(t, s) R_k(t, s) + R_q(t, s) C_k(t, s) \right] ds. \tag{4}
\]

In [17] the term corresponding to $K_1$ enters through the equal-time density correlator. The latter being time-dependent in a coarsening situation, it is natural that $K_1$ should change in time.

To obtain the equation of motion for the growth kinetics of glassy correlations, we look at the behaviour of our nonstationary generalization of the three-density correlation function $\chi_3$ mentioned above. We introduce in the free-energy functional a one-body term $\epsilon(r)\rho(r)$, coupling the density to an external potential $\epsilon(r)$ and leading on average to an inhomogeneous shift $\delta m(r)$ in the mean density field $\bar{\rho}$. We work in the limit where $\epsilon(r)$ and hence $\delta m(r)$ are uniform, so that the Fourier transform $\delta m_k$ has non-zero weight $\delta m_0$ only for wavevector $k = 0$. We will see that this suffices for the purpose of extracting the correlation volume. The resulting generalized Langevin equation for $\rho$, to first order in the background density $\delta m_0$ which encodes the effects of the field, is [21, 22]
\[
\frac{\partial \delta \rho_k(t)}{\partial t} + K_1(t) \delta \rho_k(t) - \frac{k_B T C_k \delta m_0}{D_L} \delta \rho_k(t) \\
= \frac{K_2}{2} \int_q \mathcal{V}_{k,q} \delta \rho_q(t) \delta \rho_{-q}(t) + f_k(t). \tag{5}
\]
Let $\tilde{C}_k(t, t_w)$ and $\tilde{R}_k(t, t_w)$ denote the $\delta m_0$-dependent two-point correlation and response functions implied by (5). As we are working in a non-stationary state, we must define separate 3-point quantities analogous to $\chi_3$ in [9] for $\tilde{C}_k$ and $\tilde{R}_k$: $\tilde{\chi}_3^c(t, t_w) = \partial \tilde{C}_k(t, t_w) / \partial \delta m_0 \delta m_0 \to 0$ and $\tilde{\chi}_3^r(t, t_w) = \partial \tilde{R}_k(t, t_w) / \partial \delta m_0 \delta m_0 \to 0$, with equations of
FIG. 3: Evolution of three-point function following a quench to a point close to but on the liquid side of the transition. Growth to saturation of $\chi_C(t, t_w)$ as a function of $t$ for various $t_w$ for $\lambda = 0.75$, corresponding to a quench into the liquid.

Inset: The two-point correlator, for the same parameter values, shows a relaxation time that grows progressively with increasing $t_w$ but approaches a finite value.

can clearly be seen in the behaviour of $C(t, t_w)$ in Fig. 4. Second and more important is the characteristic non-monotone behavior of $\chi_C(t, t_w)$, and its dependence on $t_w$ and interaction strength $\lambda$ (Fig. 2). For a fixed initial condition corresponding in our schematic approach to a liquid with negligible correlations, we examine in particular how $\chi_C(t, t_w)$ as a function of $t$ changes with $t_w$, for values of $\lambda$ corresponding to the liquid and the glass phase. Recall that $\lambda$ defines the point to which the system is quenched. For $\lambda$ in the liquid phase but close to the transition we find, as expected, that $\chi_C(t, t_w)$ attains a peak value $\chi_C^P$ at a time $t_{peak}$, with both $\chi_C^P$ and $t_{peak}$ growing with $t_w$ but saturating to finite values as shown in Fig. 3. The final peak value of $\chi_C(t, t_w)$ grows as $(\lambda - \lambda_c)^{-1}$ and $\chi_C^P \sim t_{peak}^{0.56}$ (Fig. 4). These final values, obtained at $t_w \rightarrow \infty$ are the equilibrium values of the corresponding quantities. In the notation of 9 we are working at $q_0 \rightarrow 0$ and our results are consistent with theirs in that limit. A more detailed comparison with 0 or 28, including an estimate of the correlation length requires a calculation of the sensitivity of two-point functions to a spatially varying potential.

For a quench into the glassy region, $\lambda = 2.0$, as shown in Fig. 2 $\chi_C^P$ grows without bound. In more detail (Fig. 5), $\chi_C^P \sim t_{peak}^{0.8}$ at a time $t_{peak} \sim t_{peak}^{1/4}$ with increasing $t_w$. The exponents $a \approx 0.5$ in agreement with simulations 2 and $b \approx 0.8$. From the two-point correlator $C(t, t_w)$ we find a relaxation time $t_r \approx t_{peak}/4$ close to the transition. Thus our result implies $t_r \sim t_{peak}^{0.8}$ in agreement with the numerical experiment of Ref. 1; the relation between $t_r$ and $t_{peak}$ remains to be tested. $\chi_C^P$ measures an effective correlation volume, so that its growth is the claimed coarsening of glassy structure, and is consistent
with the idea of a growing "domain size". Regardless of the precise values obtained, it is significant that our theory and the simulations of [2, 3], all find a total structure factor \( \chi^p \) growing very sublinearly in time. Our scaling laws differ quantitatively (Fig. 5) from those of [2, 3], perhaps because we measure different quantities. However, if we scale \( \chi_C(t, t_w) \) by \( \chi^p_C(t_w) \) and plot them as a function of \( 1 - C(t, t_w) \), data collapse is obtained in the \( \alpha \)-relaxation regime (Fig. 5). We do not claim to understand the origin of this scaling or, for that matter, that of Ref. [1]. A similar calculation [20] for the three-point correlation function for a 3-spin spin-glass model with \( p = 3 \) finds again a growing \( \chi^p_C \), but slower than for the present problem.

We emphasize that the \( t_w \)-dependent properties we extract do not correspond to those of an equilibrium system at an evolving \( \lambda \) or temperature. Had it been so, scaling \( \chi_C(t, t_w) \) by \( \chi^p_C(t_w) \) and time by \( t_{peak} \) would have given data collapse for all \( t_w \) as for the equilibrium case (Fig. 4). Fig. 4 shows the absence of such collapse even for larger \( t_w \). It would appear that the 3-point correlator is more sensitive to departures from "simple aging", and an interpretation in terms of an evolving effective temperature, than the two-time correlation function [4, 14] (see inset of Fig. 4). Perhaps the monotone decay of the latter masks such deviations or, more likely, \( \chi_C \) carries additional, independent information.

We close by summarising the achievements of this work. We have shown that mode-coupling theory adapted to describe non-stationary states captures the key features of the emergence and coarsening of glassy order from a liquid. Through the evolution of a three-point function we have shown that the glassy correlation volume grows as \( t_w^{0.5} \) with waiting time \( t_w \), slower than domain volumes in conventional coarsening, and the relaxation time of the glass grows as \( t_w^{0.8} \). These theoretical growth laws are supported by simulation studies [2, 4], and the broad features we observe are similar to those in [4]. In an experimental realization, if the quench is below the MCT transition but above a putative ideal glass transition at, say, the Kauzmann temperature \( T_K \), activated processes [29] outside the scope of MCT should cut off the growth. Presumably a quench below \( T_K \) will give indefinite growth of a different glassy length scale [30–32] with a form not predicted by MCT. In results to be presented separately [20] we find further that an imposed shear-rate \( \gamma \) cuts off aging and coarsening at \( t_w \sim 1/\dot{\gamma} \) in the glassy region and \( t_w = \min(t_r, 1/\dot{\gamma}) \) in the fluid. Since the relaxation time goes as \( t_w^{0.8} \), this should imply that \( t_r \) or \( t_{peak} \) should vary as \( \dot{\gamma}^{-0.8} \). We look forward to experimental tests of our results.

We thank C. Dasgupta for valuable suggestions and a critical reading of our paper and N. Menon for enlightening comments. We also thank S.M. Bhattacharyya, B. Kim, K. Miyazaki, S. Sastry, D. Sen, S.P. Singh and E. Zaccarelli for discussions. SKN was supported in part by the University Grants Commission and SR by a J.C. Bose Fellowship from the Department of Science and Technology.

Supplementary information (SI)

The schematic form of the equations and the source terms

The schematic form of the equations (3a) and (3b), is obtained by following the outline given in the paper. The
we present in detail here. To proceed, let us define
\[
\omega(t) = T + 6\lambda \int_0^t C^2(t, s) R(t, s) ds.
\]
Eqs. (7a) and (7b) contain two “source” terms which we present in detail here. To proceed, let us define
\[
\omega_k(t) = \frac{K_k^2}{S_k} \int_0^t \int_q \chi_{k,q}^R(t, s) \left\{ \frac{1}{2} C_q(t, s) R_k(t, s) + R_q(t, s) C_k(t, s) \right\} ds
+ C_{k-q}(t, s) \left\{ \frac{1}{2} \chi_q^C(t, s) R_k(t, s) + \frac{1}{2} C_q(t, s) \chi_k^C(t, s) + \chi_q^R(t, s) C_k(t, s) + R_q(t, s) \chi_k^R(t, s) \right\} ds.
\]

Then the source terms can be written in the form
\[
S_k^R(t, t_w) = \frac{k_B T c_k}{D_L} R_k(t, t_w) - \omega_k(t) R_k(t, t_w),
\]
\[
S_k^C(t, t_w) = \frac{k_B T c_k}{D_L} C_k(t, t_w) - \omega_k(t) C_k(t, t_w)
\]

The equations for the three-point correlators are also schematised in a similar way as stated in the paper. The final schematic forms of equations (7a) and (7b) will be
\[
\frac{\partial C(t, t_w)}{\partial t} = -\mu(t) C(t, t_w) + 2\lambda \int_0^{t_w} C^2(t, s) R(t_w, s) ds
+ 4\lambda \int_0^t C(t, s) R(t, s) C(s, t_w) ds,
\]
\[
\frac{\partial R(t, t_w)}{\partial t} = \delta(t - t_w) - \mu(t) R(t, t_w)
+ 4\lambda \int_{t_w}^t R(t, s) C(t, s) R(s, t_w) ds
\]
where \(\mu(t)\) is the schematic version of \(K_1(t)\):
\[
\mu(t) = T + 6\lambda \int_0^t C^2(t, s) R(t, s) ds.
\]

The equations for the three-point correlators are also schematised in a similar way as stated in the paper. The final schematic forms of equations (7a) and (7b) will be
\[
\frac{\partial \chi_R(t, t_w)}{\partial t} + \mu(t) \chi_R(t, t_w) = 4\lambda \int_0^{t_w} C(t, s) \chi_R(s, t_w) ds + 4\lambda \int_t^{t_w} R(t, s) \chi_C(t, s) R(s, t_w) ds
+ 4\lambda \int_0^t \chi_R(t, s) C(t, s) R(s, t_w) ds + S_R(t, t_w)
\]
\[
\frac{\partial \chi_C(t, t_w)}{\partial t} + \mu(t) \chi_C(t, t_w) = 4\lambda \int_0^{t_w} C(t, s) \chi_C(s, t_w) R(t_w, s) ds + 2\lambda \int_0^{t_w} C^2(t, s) \chi_R(t_w, s) ds
+ 4\lambda \int_0^t C(t, s) R(t, s) \chi_C(s, t_w) ds + 4\lambda \int_0^t \chi_C(t, s) R(t, s) C(s, t_w) ds
+ 4\lambda \int_0^t C(t, s) \chi_R(t, s) C(s, t_w) ds + S_C(t, t_w)
\]

with the source terms given as
\[
S_R(t, t_w) = [1 - \omega(t)] R(t, t_w) \quad \text{and} \quad S_C(t, t_w) = [1 - \omega(t)] C(t, t_w)
\]
where \(\omega(t)\), the schematic form of \(\omega_k(t)\), is given as
\[
\omega(t) = 12\lambda \int_0^t C(t, s) \chi_C(t, s) R(t, s) ds
+ 6\lambda \int_0^t C^2(t, s) \chi_R(t, s) ds.
\]
The aging of the time-decay of two-point density correlations has been studied in experiments [33], numerical simulations [4], mode-coupling theories [34] and generalized Langevin treatments [35] on structural glasses, and in related theoretical work on spin-glasses [14, 19, 26].

We introduce the external potential in the coarse-grained free-energy functional whereas [4] do so in the microscopic Hamiltonian, where it must affect all degrees of freedom, fast and slow.