Universal properties of aging in structural glasses

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I. INTRODUCTION

Glasses are important solids, which are by definition in an out of equilibrium state. Nevertheless in many experiments they can be dealt with as if they were in a time independent quasi equilibrium state. E.g. measurements of static structure factors and dynamic neutron or light scattering functions give reproducible results seemingly independent of the waiting time $t_w$ after the production of the glass. On the other side it is known, that properties of glasses depend on the procedure with which they are obtained and that they change on very long time scales. The later phenomenon is known as aging of glasses and there exists a vast experimental literature on this non equilibrium behavior \[1\]. So far it exists no microscopic theory of structural glasses, which contains the equilibrium and the non equilibrium aspects of glasses, including the influence of their non ergodic character on the structure and on the other side the influence of the structure on the dynamics. \[2\]. Although there are many theoretical investigations on the aging behavior of simple models \[3\], which are able to rationalize properties of simulations on models of simple liquids out of equilibrium \[3\], they cannot, due to their simplicity, address structural aspects of the aging dynamics. For supercooled liquids in equilibrium a microscopic theory, the mode coupling theory (MCT) of the glass transition, exists, which successfully describes the dynamic of such systems at temperatures above the critical glass transition temperature \[10,11\]. The applicability of this theory below the transition temperature is not obvious, since it is based on equilibrium considerations, which are not fulfilled a priori for non ergodic systems \[13\]. In this letter I will present a description of the dynamics of glasses, which unifies the non equilibrium aspects discussed in simple model systems and the detailed structural aspects of the (equilibrium) MCT of supercooled liquids. The theory allows to draw very general conclusions on the nature of aging in structural glasses.

The goal is to develop a theory, which allows to calculate dynamic correlation and response functions in space and time for glass. To describe the experimental situation, only the initial equilibrium state is assumed to be known. The final glassy state is a result of the dynamic reached for time $t \to \infty$ after the quench at $t = 0$. The variables relevant for the description of structural relaxation are density fluctuations $n_q(t) = \sum_j \exp(\imath \vec{q} \vec{r}_j(t))$ and longitudinal current fluctuations $j_q(t) = \sum_j (\vec{q} \vec{p}_j)/(q m) \exp(\imath \vec{q} \vec{r}_j(t))$. Here $\vec{r}_j$. $\vec{p}_j$ and $m$ are the position, the momentum and the mass of particle $j$. The density fluctuations contain the information about the spatio temporal distributions of the particle, whereas the momentum fluctuations are necessary to capture possible effects of global momentum conservation and to describe the rate of the spatio temporal changes. The equations of motion are given by the underlying Hamiltonian dynamics and the coupling to a thermostat, which guarantees, that the chosen thermodynamic parameters like density or temperature are kept constant after the quench. To be specific, I will choose in the following a temperature quench from an initial equilibrium state with temperature $T_i = 1/(\beta k_B)$ to a final temperature $T$. The temperature can be measured with the help of the kinetic energy $k_B T = 2/(3N) \sum_j p_j^2/(2m)$, where $N$ is the number of particles. The average $\langle \ldots \rangle$ is an ensemble average over the initial non equilibrium ensemble $ho_{ne} = \exp(-\beta \sum_j (p_j^2)/(2m) - \beta_i \sum_{i<j} V(|\vec{r}_i - \vec{r}_j|))$, where $V(|\vec{r}_i - \vec{r}_j|)$ is the interaction potential. This ensemble guarantees, that the value for the temperature, measured with the help of the velocity distribution is $k_B/\beta$ and that the spatial structure is the same as that of the liquid at the initial temperature $k_B/\beta_i$. The dynamics is given by a time dependent differential operator $L(t)$. For a variable $A(\vec{r}_i, \vec{p}_i)$ the equation of motion is: $dA/dt = iU(t, 0)A(0) := U(t, 0) \left( i L_0 A - \sum_j \alpha(t) \vec{p}_j(0) \partial A(\vec{r}_i, \vec{p}_j(0))/\partial \vec{p}_j(0) \right)$ where $U(t, 0) = T_+ \exp(i f_0 L(t')dt')$ is a time ordered product (time increases from left to right). $L_0 = -i\{H, \ldots\}$ is the Liouville operator, and $\{\ldots\}$ is the Poisson bracket. The Gaussian thermostat $\alpha(t)$ is adjusted such that
\( \sum_j (p_j^2(t)/(3Nm)) = 1/\beta \) for all times \( t \). Given these equations of motion for the phase space variables, one has to derive the equations of motion for the experimentally relevant correlation functions and, since a priori the validity of the FDT is not guaranteed, also for the susceptibilities. A suitable method to achieve this, is a non equilibrium projection operator formalism, using \( n_q(t) \) and \( j_q(t) \) as slow variables \([14]\). To obtain an exact equation for the susceptibilities, it is necessary to formulate the projection operator in terms of Poisson brackets instead of correlation functions \([14]\). With such a projection operator and the specified iso-kinetic dynamics the equation for susceptibility \( \chi_q(t_w, t) = \Theta(t - t_w)|n_q(t)|^2/n_q(t) || \) and the correlation function \( C_q(t_w, t) = (n_q(t_w)n_q(t))/N := \langle n_q^2(t_w), n_q(t) \rangle/N \) is broken. The equation for it reads

\[
\frac{\partial^2}{\partial t^2}C_q(t_w, t) = -\frac{m}{N} \chi_q(t_w, t)[j_q(t)L(t)j_q(t)]
- \im \alpha(t) \frac{\partial}{\partial t}C_q(t_w, t) + m \int_{t_w}^{t} dt' \chi_q(t_w, t') \Sigma_q(t', t).
\]  

The memory function \( \Sigma_q(t') \) is the average of the Poisson bracket of the true force at \( t = t' \) and the random force \( F_q(t', t) \) between \( t' \) and \( t \). This random force describes the dissipation of the gradient of the longitudinal stress at \( t' \) in non-hydrodynamic modes between \( t' \) and \( t \). The correlation function \( C_q(t_w, t) \) depends on all times between \( 0 \) and \( t \), since the time translational invariance is broken. The equation for it reads

\[
\frac{\partial^2}{\partial t^2}C_q(t_w, t) = -\frac{m}{N} C_q(t_w, t)[j_q(t)L(t)j_q(t)]
- \im \alpha(t) \frac{\partial}{\partial t}C_q(t_w, t) + m \int_{t_w}^{t} dt' C_q(t_w, t') \Sigma_q(t', t)
+ m \int_{0}^{t} dt' \chi_q(t_w, t') M_q(t', t)
- q C_q(t_w, 0) \frac{1}{N \Sigma_q(0)} \langle n_q(0)|F_q(0, t) \rangle
- q (n_q(t_w)|j_q(0) \rangle \frac{1}{N \langle j_q(0)|j_q(0) \rangle} (j_q(0)|F_q(0, t) \rangle)
\]  

The last two lines in Eq. \([3]\) describe the correlation to the initial state. The memory function \( M_q(t_w, t) \) is an autocorrelation function of random forces \( F_q(0, t_w) \) and \( F_q(0, t) \). The equation for the time dependent equal time correlation function \( S_q(t) = (n_q(t)|n_q(t) \rangle / N \), which describes the change in the structure of the liquid after the quench, is easily derived.

\[
\frac{1}{2} \frac{\partial^2}{\partial t^2} S_q(t) = (j_q(t)|j_q(t) \rangle / N - \frac{\partial^2}{\partial t^2} C_q(t_w, t)|_{t_w=t}.
\]  

If we make the assumption, that the velocities of different particles are as in equilibrium uncorrelated at every time \( t \), equation \([3]\) simplifies further, since \( (j_q(t)|j_q(t) \rangle / N = 1/(\beta m) \) in this case.

The set of equation \([3]\) are formally exact. If the initial state is an equilibrium state i.e. if there is no temperature quench, it can be exactly shown \([14]\), that the correlation function and susceptibilities fulfill the FDT

\[
\chi_q(t_w, t) = \chi_q^{eq}(t - t_w) = -1/T dC_q^{eq}(t - t_w)/dt \quad (4)
\]

and the memory functions \( \Sigma_q(t_w, t) \) and \( M_q(t_w, t) \) obey a FDT of the second kind

\[
\Sigma_q(t_w, t) = \Sigma_q^{eq}(t - t_w) = -1/T dM_q^{eq}(t - t_w)/dt \quad (5)
\]

The three equations \([1]\) \([2]\) and \([3]\) are reducing then to one equation for the correlation function \([4]\), which was the basis for the equilibrium MCT \([13]\).

A solvable theory is obtained by approximating the two unknown functions \( \Sigma_q(t_w, t) \) and \( M_q(t_w, t) \). The simplest non trivial approximation consistent with the mathematical requirement for the memory functions \([14]\) is a one loop type or mode coupling approximation. It has the form

\[
\Sigma_q(t_w, t) = q^2/(m^2 \beta^2) \sum_{k, \beta} \delta_{q, p+\mathbf{k}} \quad (6)
\]

\[
c_{qkp}(\{S_q(t_w)\}) \quad (7)
\]

The vertices \( c_{qkp} \) are functionals of the one time correlation function \( S_q(t) \). They are symmetric with respect to exchange of \( p \) and \( k \). Under this general condition, the FDT of the second kind \([1\] \([2]\) is automatically fulfilled in equilibrium. The explicit form of \( c_{qkp}(t) \) will determine the theory for the structure factor \( S_q(t) \). For asymptotically long times \( t_w, t \rightarrow \infty \) all correlation functions, which depend only on a single time can be replaced by their asymptotic value. If the quench was performed from an equilibrium liquid state, the functions \( C_q(t_w, 0) \) and \( (n_q(t_w)|j_q(0) \rangle \) in Eq. \([3]\) will vanish for \( t_w \rightarrow \infty \). It can also be shown \([14]\), that the influence of the thermostat \( \alpha(t) \) vanishes at least as \( 1/t \) and therefore the equations for the correlation functions and the susceptibilities in the long time limit depend only on the asymptotic value of the structure factor \( S_q^{\infty} \) and the vertices \( c_{qkp}(\infty) \).

If there were no wave vector dependencies, the structure of the resulting equations were similar to the equations for the spherical \( p \) - spin model \([1\] \([2]\) in the same asymptotic limit. As in this model I will make the ansatz, that there exist below the glass transition two different dynamic regimes. The FDT regime is characterized by the limit \( C_q^{FDT}(\tau) = \lim_{t_w \rightarrow \infty} C_q(t_w, t_w + \tau) \) with \( \chi_q^{FDT}(\tau) = (-1/T) dC_q^{FDT}(\tau)/dt \). The aging regime is
defined by the limit \( \hat{C}_q(\lambda) = \lim_{t \to \infty} C_q(\lambda t, t) \). This scaling behavior is called simple aging. There are more general scenarios which could so far only be ruled out for the \( p \)-spin model \[13\]. For notational simplicity I will concentrate on the ansatz of simple aging. I also will make the ansatz of a generalized FDT ansatz, known to be correct for the \( p \)-spin model \[3\]. It assumes, that the susceptibility \( \hat{\chi}_q(\lambda) = \lim_{t \to \infty} t \chi_q(\lambda t, t) \) is related to the correlation function by \( \hat{\chi}_q(\lambda) = (X_q/T)dC_q(\lambda)/d\lambda \) \[13\]. Astonishingly it turns out \[14\] that only a wave vector independent fluctuation dissipation ratio (FDR) \( 0 \leq X(T) \leq 1 \) will give compatible equations for correlation functions and susceptibilities in the aging regime.

With the definitions of normalized quantities \( \phi_q(t_w, t) = C_q(t_w, t)/S_q^\infty \), \( \chi_q(t_w, t) = \chi_q(t_w, t)/S_q^\infty \), \( f_q = F_q/S_q^\infty \), where \( F_q = \lim_{t \to \infty} C_q^\infty(\tau) = \hat{C}_q(1) \) and \( v_{kp} = \delta_{q,k}^\infty \beta \langle q_{kp} \rangle \), the following equations for the asymptotic structure factor \( S_q^\infty \) is obtained

\[
1/S_q^\infty = m\beta c_B^2 - 1/2 \sum_{k,p} v_{kp} \left\{ 1 - f_q f_p (1 - X) \right\} \tag{8}
\]

Here \( c_B^2 = \lim_{t \to \infty} im|j_q(t)|L_0 j_q(t)/q^2 \) is a bare wave vector dependent velocity, which will be renormalized by contributions from the vertices \( v_{kp} \). The equation for the correlation function in the FDT regime i.e.

\[
\frac{\partial^2}{\partial \tau^2} \phi^\infty_q(\tau) = -\beta \frac{d^2}{d\tau^2} \phi^\infty_q(\tau) = \left[ -c_B^2 \frac{q^2}{2m\beta} \sum_{k,p} v_{kp} \right] \phi^\infty_q(\tau) + \frac{q^2}{2m\beta} \sum_{k,p} v_{kp} \left\{ \int_0^\tau d\tau' \frac{d^2}{d\tau'^2} (\phi^\infty_{k'p}(\tau') - \phi^\infty_{kp}(\tau')) + f_q f_p (1 - X) \right\} \tag{9}
\]

With Eq. \[3\] and \[8\] it follows immediately that Eq. \[3\] reduces to the standard MCT equation for the supercooled liquid above the glass transition temperature \( T_c \), where \( f_q = 0 \) and \( X_q = 0 \). It is interesting to note, that like in the approach of Zaccarelli et al. \[19\], the mode coupling approach contains implicitly a theory for the structure factor of liquids. Below the glass transition the structure of the glass depends on the non ergodicity parameter i.e. the non ergodic nature of the glass also influences the equal time correlation function.

\[
0 = c_B^2 + 1/(2m\beta) \sum_{k,p} v_{kp} \left\{ (1 - f_k f_p) N_q(\lambda) \right\} \tag{10}
\]

\[
+ N_k(\lambda) \hat{\phi}_p(\lambda)(1 - f_q) + 1/\beta \int_\lambda^1 ds N_q(\lambda) N_k(s) \hat{\phi}_p(s) \}
\]

The Eq. for the non ergodicity parameter can be obtained from the \( t \to \infty \) limit of \[11\] and it is identical with the initial value \( \hat{\phi}_q(1) \). With the help of Eq. \[8\] it can be written

\[
f_q/(1 - f_q) = \sum_{k,p} v_{kp} f_k f_p (1 - (1 - X)(1 - f_q)) \tag{11}
\]

Since it can be shown, that \( X = 1 \) for \( T = T_c \) only, Eq. \[13\] reduces to the equation of the MCT of supercooled liquids only at \( T = T_c \). For \( T < T_c \) it is modified due to the breaking of the FDT (\( X \neq 1 \)).

A deeper insight in the meaning of the wave vector independence of \( X \) can be obtained by investigating the behavior of \( \phi_q(t_w, t) \) for times, where it is close to the non ergodicity parameter \( F_q \). A detailed analysis shows \[4\], that the Eqs. \[8\] and \[10\] can be simultaneously solved by the ansatz \( \phi_q(t_w, t) = f_q - e_q G(t_w, t) \) up to quadratic order in \( G(t_w, t) \). Here \( e_q \) is an eigenvector of a matrix \( D_{qk} \)

\[
0 = \sum_k D_{qk} \hat{G}_k'(1) \quad \text{with} \quad D_{qk} = -c_B^2 q^2 - (q^2/2m\beta) \sum_{kp} v_{kp} (1 - f_k f_p) \hat{\phi}_q k' \]

\[
+ (q^2/2m\beta) v_{kp} f_k f_p (1 - f_q). \tag{12}
\]

Eq. \[12\] is the solvability condition for \( \hat{N}_q(\lambda) = (X/T) dG_q(\lambda)/d\lambda \) by setting \( \lambda = 1 \) in Eq. \[14\].

The equations for \( G(t_w, t) \) in the FDT and the aging regime follow by multiplying the resulting equations from left with the left eigenvector \( \hat{e}_q \) to eigenvalue zero of \( D_{qk} \). i.e. \( \sum_k \hat{e}_q D_{qk} = 0 \):

\[
0 = \Lambda (G^\infty)^2(\tau) - d/d\tau \int_0^\tau d\tau' G^\infty(\tau - \tau') G^\infty(\tau') \tag{14}
\]

\[
0 = (\Lambda/X) \hat{G}^2(\lambda) - \int_\lambda^1 ds d\hat{G}(s) \hat{G}(s) \tag{15}
\]

where

\[
\Lambda = \frac{\sum_{kp} \hat{e}_q \hat{e}_k \lambda^2 v_{kp} (1 - f_k f_p) e_k e_p}{\sum_{kp} \hat{e}_q \hat{e}_k \lambda^2 v_{kp} e_k e_p f_k f_p} \tag{16}
\]

The microscopic structure of the system only enters via the exponent parameter \( \Lambda \), which is a complicated functional of the asymptotic structure factor \( S_q^\infty \). This behavior is very reminiscent of the \( \beta \) - relaxation phenomena in supercooled liquids above the glass transition. Eq. \[13\] has exactly the form of the \( \beta \) - scaling equation of the MCT of supercooled liquids at the critical temperature \[21\]. In this theory the glass transition is a critical bifurcation of codimension 1, in which the dynamics close to the transition temperature and for times, at which the correlation function is close to the non ergodicity parameter, is completely determined by the critical direction of the bifurcation. In the theory presented here, the additional solvability condition for aging Eq. \[12\]
forces the system always to be at the critical bifurcation for temperatures below $T_c$. Since this bifurcation is still of codimension 1, there is only one temperature dependent number to guarantee this self organized criticality, namely the fluctuation dissipation ratio $X(T)$. This is the deeper reason, why $X$ does not depend on wave vectors. Within the presented theory, aging is due to a self organized critical bifurcation scenario. Because of this criticality Eq. (14) and (15) can be solved exactly for all temperatures below the transition temperature $G^{FDT}(\tau) = \tau^{-a}$ for $t^* > \tau > \tau_0$ where $\tau_0$ is some microscopic correlation scale and $t^*(t_w)$ is the time where $\phi_q(t_w,t) = f_q [28]$. The exponent $a$ is determined by $\Lambda$:

$$\Lambda(T) = \Gamma^2(1-a)/\Gamma(1-2a),$$  \hspace{1cm} (17)

where $\Gamma$ is the Euler Gamma function. The form of this equation is known from the $\beta$- scaling theory of supercooled liquids [21]. But contrary to this theory Eq. (17) holds for all temperatures below the glass transition with a temperature dependent exponent parameter $\Lambda$ and thus a temperature dependent exponent $a$. Equation (15) is solved by $G(\lambda) = -(-\log \lambda)^b$ for $\lambda < 1$. Here $t_w(t_w)$ is a time characterizing the final decay of the correlation function The exponent $b$ is determined by an equation similar to (15):

$$\Lambda(T) = X(T) \Gamma^2(1+b)/\Gamma(1+2b)$$  \hspace{1cm} (18)

At the transition Eq. (18) reduces to the Equation for the von Schewlieder exponent of the $\beta$ scaling theory [21]. Below the transition relation (18) was also found in mean field theories [24], in which the dynamics reduces for all times to a single component theory. For models, in which simple aging does not hold, $\lambda = t_w/t$ has to be replaced by $\lambda' = h(t_w)/b(t)$, where $h(t)$ is a yet unspecified function (see e.g. the discussion in [17]). It is important to notice, that the decoupling of wave vector dependence and time dependence in the present theory does not apply once the condition $G^3(\lambda) \ll G^2(\lambda)$ is violated. In this case wave vector dependencies of the correlation functions are to be expected and the solution of (14) can only be found numerically ($X(T)$ of course remains wave vector independent). The predicted factorization property $\phi_q(t_w,t) = f_q + e_q G(t_w,t)$ was indeed found in simulations [3]. The presented theory allows for a systematic theoretical investigation of the dynamics of the glassy state of simple liquids as e.g. the colloidal hard sphere system, in which indication for aging was already observed [22] or the Lennard Jones systems of [33]. Especially it the foundation for a theory of the structure factor of glasses by specifying the vertices $e_q p(t)$ in Eqs. 3 and 5. This will be part of future work.

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