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## Non-equilibrium mode-coupling theory for supercooled liquids and glasses

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**Abstract.** A formally exact set of equations is derived for the description of non-equilibrium phenomena exhibited by classical liquids and glasses. With the help of a non-equilibrium projection operator formalism, the correlation functions and fluctuation propagators are expressed in terms of memory functions and time-dependent collective frequencies. This formally exact set of equations is approximated by applying mode-coupling approximations to the memory functions. The resulting set of equations for wave-vector-dependent correlation functions, fluctuation propagators and one-time structure factors  $S_q(t)$  generalizes the well known mode-coupling theory of the glass transition to situations far away from equilibrium.

### 1. Introduction

The mode-coupling theory (MCT) of the glass transition is based on the experimental and theoretical understanding of dense liquids. Although approximative in nature, mode-coupling theories were quite successful for describing quantitatively the dynamics of dense liquids close to the triple point. The dynamics of dense liquids is dominated by two mechanisms, the precursor of the cage effect and a complicated coupling of current fluctuations and density fluctuations. This coupling is the main cause of activated motion close to the glass transition [1, 2] and will not be considered further in this paper. The cage effect is a collective phenomenon caused by the mutual hindering of the motion of the atoms or molecules due to the strong repulsion of the cores of the atoms. Instead of a smooth flow-like motion, a kind of stop-and-go mechanism is observed in simulations of dense liquids. The particles tend to rattle in a cage formed by the surrounding atoms. To escape this cage an atom has to find a hole in the surrounding wall formed by the other atoms. The same is of course true for the atoms building the wall. Due to the thermal motion a situation will arise in which the particles can pass each other. This process will be repeated over and over again. In this way the motion of particles, which are nearby at some instant of time, will decorrelate slowly. In the process, a back-flow pattern is created. On increasing the density, the local cage effect will eventually lead to a complete blocking of long-range motion of the particles. They will be stuck in their local cages and thus form a glass. The details of how this is done—especially how this glassification affects the various spatial scales—are described by the idealized mode-coupling theory [3]. Within this theory it is e.g. possible to understand the effect of the stiffening of the local cages on the thermodynamics and hydrodynamics close to the glass transition [4]. Experimentally observed phenomena like the frequency-dependent specific heat are thus explained quite naturally in a unified framework.

The underlying mathematical mechanism of the glass transition in the idealized MCT is a bifurcation in the equation for the dynamics of the density–density correlation function of a system of  $N$  particles. Using a standard Mori projection operator formalism for the density and current fluctuation  $n_q(t)$ ,  $\vec{j}_q(t)$  with

$$n_q(t) = \exp(iLt)n_q(0) = \sum_i^N \exp(i\vec{q} \cdot \vec{r}_i(t)) \quad (1)$$

$$j_q(t) = \frac{\vec{q}}{q} \cdot \vec{j}_q(t) = \sum_i^N \frac{\vec{q}}{q} \cdot \vec{v}_i \exp(i\vec{q} \cdot \vec{r}_i(t)) \quad (2)$$

the following formally exact equations for the density correlation function  $\phi_q(t)$  can be derived:

$$\frac{d\phi(t)}{dt} = i\vec{q}\phi_{n,\vec{j}}(t) := iq\phi_{n,j} \quad (3)$$

$$\frac{d^2\phi(t)}{dt^2} = -\Omega_{nj}^2(q)\phi(t) - \int_0^t dt' \frac{d\phi(t')}{dt'} M(t-t'). \quad (4)$$

Here the correlation function  $\phi$  and the frequency  $\Omega_{nj}(q)$  are given as

$$\phi(t) \equiv \phi_{nm}(t) = \langle n_q | n_q(t) \rangle := \text{Tr}(\exp(-\beta H) n_q^*(0) n_q(t)) \quad (5)$$

$$\Omega_{nj} = q\sqrt{S_{jj}/S_q}. \quad (6)$$

$S_{jj}$  is the static current fluctuation function. In equilibrium it is given as

$$S_{jj} = Nk_B T/m \quad (7)$$

where  $m$  is the mass of an atom and  $T$  is the equilibrium temperature.  $L$  is the Liouville operator. Its action on a dynamic variable is defined by the Poisson bracket:

$$LA = -i \sum_i^N \{H, A\}. \quad (8)$$

By construction the memory function  $M$  is free of any hydrodynamic singularity and cannot be expressed as a linear functional of the correlation functions. Instead it can be written as a correlation function of fluctuation forces:

$$M_q(t) = \langle QLj_q | \exp(iLQt) QLj_q \rangle / S_{jj}. \quad (9)$$

In the mode-coupling approximation the fluctuating forces are approximated as a superposition of two-mode contributions [3]

$$QLj_q \approx \sum_{kp} v(q|kp) n_k n_p \quad (10)$$

$$v(q|kp) = \langle QLj_q | n_k n_p \rangle (S_k S_p)^{-1} = \delta_{\vec{p}, \vec{q}-\vec{k}} S_{jj} \hat{v}(k, q-k). \quad (11)$$

The second equality in equation (11) is due to momentum conservation.  $S_q$  is the static structure factor  $\phi(q, t=0)$ . The two-mode approximation can be qualitatively justified by the observation that forces can be exactly microscopically expressed as superpositions of products of density excitations. The bare coupling constant is proportional to the derivative of the interaction potential in the case of continuous potentials<sup>†</sup>. With the projection scheme used in equations (10), (11) an approximative static renormalization of the bare vertex is attempted, which can also be used for hard-core potentials.

<sup>†</sup> For hard-core potentials it is necessary to use pseudo-Liouville operators [5].

The renormalized vertex  $\hat{v}(k, q - k)$  can be evaluated in equilibrium. Neglecting static direct three-point correlation functions the memory function is given by [3]

$$M_q(t) = n(k_B T/m)^2 \frac{1}{2} \sum_k \hat{v}^2(k, q - k) \phi(q - k, t) \phi(k, t) \quad (12)$$

with

$$\hat{v}(k, q - k) = \left( \vec{k} \cdot \frac{\vec{q}}{q} c_k + (\vec{q} - \vec{k}) \cdot \frac{\vec{q}}{q} c_{q-k} \right)^2. \quad (13)$$

Here  $c_q$  is the (equilibrium) direct correlation function. Equations (4) and (12) form a closed set of equations for the density–density correlation function in equilibrium. The solution properties of the above equilibrium MCT (EMCT) equation are very well known [7]. They exhibit an ideal glass transition as a bifurcation scenario from an ergodic to a non-ergodic state. The transition temperature  $T_c$  (or density, pressure, . . .) is independent of the cooling rate since it is an equilibrium property of the system. If the temperature approaches  $T_c$ , the structural relaxation is dramatically slowing down, developing the typical two-step relaxation pattern of  $\beta$ - and  $\alpha$ -relaxation. The EMCT was quantitatively tested for an experimental realization of a hard-sphere system [8]. Without any fit factor (up to an overall scale factor) it is possible to reproduce with 20% accuracy the density–density correlation for the wave vector at the peak of the structure factor. With the same kind of approximations for memory functions the theory was also quantitatively tested for a binary Lennard-Jones systems [9], a system of dumb-bells [10] and a model system for water [11]. Any generalization to non-equilibrium situations should therefore in equilibrium reduce to the above set of equations (4) and (12).

The non-equilibrium situations to be described in this paper arise if one investigates the relaxation in a system which is not yet equilibrated. When cooling down from some temperature  $T_1 > T_c$  to  $T_2 > T_c$ , one has to wait at least for some time  $t_w$  comparable to a typical  $\alpha$ -relaxation time  $\tau_q(T_2)$  to guarantee equilibration at the temperature  $T_2$ . As indicated, the  $\alpha$ -relaxation time  $\tau_q$  depends on the wave vector  $q$ . To use the EMCT, density fluctuations for all wave vectors have to be equilibrated. For hard-sphere-like systems the largest  $\alpha$ -relaxation time is given by the wave vector at the peak of the structure factor, i.e. only for a time  $t_w > \tau(q_{max})$  are the above equations able to describe the density correlation functions. For times smaller than  $\tau(q_{max})$  non-equilibrium effects like breaking of time translation invariance are to be expected. For example, the one-time structure factor  $S_q(t) = \phi_q(t, t)$  is time dependent, since the probability density has not yet reached its equilibrium value.

As soon as the system is quenched to below  $T_c$ , the behaviour of the system changes qualitatively. In EMCT the  $\alpha$ -relaxation time is going to infinity for all wave vectors when  $T$  is approaching  $T_c$  from above, i.e. the system never reaches equilibrium for  $T \leq T_c$ . This means that e.g. even for infinitely long waiting time the one-time structure factor will be different from the value that it would reach in the presence of hopping processes. For real systems, where activated processes cannot be neglected, the waiting time has to be smaller than the inverse of the typical hopping rate, in order to see aging. Therefore the applicability of EMCT has to be reconsidered within the larger framework of a theory which is applicable also in non-equilibrium situations.

In the theory of spin glasses quite some progress in this direction has been made in recent years. Already Kirkpatrick and Thirumalai [12] have shown that the dynamics of an infinite-ranged  $p$ -spin system with  $p \geq 2$  and a disordered Potts system ( $p > 4$ ) exhibit great similarities to the dynamics of structural glasses at least close to the critical temperature  $T_c$  (which is in the spin-glass literature called  $T_D$ ). The equation for the correlation function for  $T > T_c$  reduce to a schematic EMCT model of the glass transition. For  $p = 3$  the dynamics

of the  $p$ -spin model is equivalent to the so-called Leutheusser model [13] above  $T_c$ . This model exhibits a glass transition, but its  $\alpha$ -relaxation is a simple exponential relaxation and therefore cannot explain the typical stretched relaxation observed in real glasses. In the context of supercooled liquids the Leutheusser model can only be motivated by the complete neglect of the wave-vector dependence in equations (4), (12). For the  $p$ -spin model the Leutheusser model is an exact theory above  $T_c$  due to the mean-field character of this system. Cugliandolo and Kurchan showed for the  $p$ -spin model that the EMCT is not valid any longer below  $T_c$ , for similar reasons to those explained above [14]. Instead they derived non-equilibrium mode-coupling equations for this model and solved them asymptotically below  $T_c$ . Contrary to the EMCT, the dynamics cannot be understood in terms of correlation functions alone; a coupled set of equations for the correlation functions  $\phi(t_w, t)$  and susceptibilities  $\chi(t_w, t)$  is necessary. The most interesting property of the solution of these equations is the separation of the dynamics into a short-time part, where the fluctuation-dissipation theorem (FDT) is obeyed, and an aging part, where FDT is violated in a very specific way<sup>†</sup>. In the aging regime the equations for  $\phi(t_w, t)$ ,  $\chi(t_w, t)$  can be reduced to a single equation for a function  $\hat{\phi}(\lambda)$  with  $\lambda = h(t_w)/h(t)$ . The susceptibility is given as

$$\chi(t_w, t) = \frac{h'(t_w)}{h(t)} \hat{\chi}(\lambda) \quad (14)$$

where

$$\hat{\chi}(\lambda) = \frac{x}{T} \frac{d\hat{\phi}}{d\lambda}.$$

The function  $h$  has to be determined by matching the FDT solution and the aging regime. So far its form is only known for the spin glass with  $p = 2$  [16]. The term  $T/x$  was interpreted as an effective temperature [17]. Since the important work of Cugliandolo and Kurchan a large number of papers have addressed the problem of non-equilibrium relaxations in mean-field models [18]. It was shown for general non-linear  $\Phi^n$  field theories that in the cases where NMCT equations are exact, a mapping to an equivalent disordered problem can be found [19]. This can also be achieved by deterministic but highly irregular interactions [20].

Simulations of binary liquids in the out-of-equilibrium regime [21–24] exhibit striking qualitative similarities to the dynamics found in the  $p$ -spin model. There is the separation into the FDT and aging regimes. Also the scaling behaviour (14) seems to be fulfilled. For describing the behaviour of real liquids the schematic models are not sufficient, since they lack the important wave-vector dependence, leading e.g. to non-exponential relaxation and experimentally testable results like wave-vector-dependent Kohlrausch exponents [25]. Equations for multicomponent models have been formulated on an abstract level [19, 26], but their relation to the theory of glass-forming liquids is not obvious. Additionally there are no equations for the one-time structure factor  $S_q(t)$  for real liquids. In the following, I am going to formulate a generalization of the EMCT for real liquids, which will enable the study of the dynamics of real liquids above and below  $T_c$  in equilibrium and non-equilibrium situations.

## 2. The non-equilibrium projection operator formalism

The main reason for the appearance of generic non-equilibrium relaxation is the inability of the system to equilibrate below  $T_c$  (if hopping is neglected, which I will assume in the following). To keep the formalism as simple as possible, I will consider a situation where the probability density  $\rho_{NE}$  is different from the canonical ( $\rho \neq \exp(-\beta H)$ ) or other equilibrium densities

<sup>†</sup> The possibility of FDT breaking in the  $p$ -spin model was first realized in [15].

but the microscopic dynamics is still Hamiltonian. The only requirement for not being in equilibrium is

$$\{\rho_{NE}, H\} \neq 0. \quad (15)$$

This situation may e.g. arise if the system is isolated after an initial quench from an equilibrated liquid above  $T_c$  to a glass below  $T_c$  (e.g. by coupling to an external heat bath, whose temperature is below  $T_c$ ). The system tries to get into equilibrium with the heat bath. As argued in [4] it can be expected that the kinetic energy is equilibrating on microscopic timescales. It is the potential energy which does not reach its equilibrium value due to its contribution from structural relaxations. After the initial quench we may therefore expect to describe the system with an initial density operator

$$\rho_{NE} = \exp(-(\beta_f K + \beta_I \epsilon^{pot})).$$

Here  $\beta_I$  is the inverse of the initial temperature before the quench and  $\beta_f$  is the inverse of the final temperature. With  $\beta_c = 1/(k_B T_c)$  the relation  $\beta_I < \beta_c < \beta_f$  is fulfilled.  $K, \epsilon^{pot}$  are the kinetic and potential energies respectively. If necessary, the formalism can also be developed by assuming a permanent coupling to an external heat bath by using a Gaussian thermostat to guarantee the average of the kinetic energy being constant at any time [27], but here I want to concentrate on the simpler case of an isolated system described by an initial non-equilibrium density operator.

As basic variables for the following projection operator formalism (POF)  $A_i(t)$ , I will again use density fluctuations (1) and current fluctuations (2). The energy fluctuations are neglected. They are of course influenced by the glass transition, but they do not qualitatively change the glass transition scenario [4]. The main idea of any projection operator formalism is to separate the dynamics of the variables into a part directly proportional to a chosen variable, a part which is given by the fluctuation of the variables in the past and a fluctuating force, whose dynamics is never directly proportional to the fluctuations of the basic variable  $\delta A_i(t)$ . The most direct generalization of the standard Mori formalism to situations in which also equal-time correlation functions are time dependent is obtained by using [29–31]

$$\begin{aligned} \bar{P}(t) &= \exp(-iLt) \delta A_i(0) \mathbf{S}_{ik}^{-1}(t) \delta A_k(t) \exp(iLt) \\ &:= \exp(-iLt) |A_i(0)\rangle \mathbf{S}_{ik}^{-1}(t) \langle A_k(t) | \exp(iLt) \end{aligned} \quad (16)$$

$$\bar{Q}(t) = 1 - \bar{P}(t). \quad (17)$$

Repeated indices are summed over. In equilibrium these projection operators reduce to the time-independent Mori projection operator in equilibrium. The matrix  $\mathbf{S}$  is the equal-time correlation matrix of the variables  $A_i$ :

$$\mathbf{S}_{ik} = (A_i(t) | A_k(t)) = \text{Tr}(\rho_{NE} (\exp(iLt) A_i(0)) | \exp(iLt) A_k(0)). \quad (18)$$

The projection operators have the following properties:

$$\begin{aligned} \bar{P}(t_1) \bar{P}(t_2) &= \bar{P}(t_2) \\ \bar{Q}(t_1) \bar{Q}(t_2) &= \bar{Q}(t_1) \\ \bar{Q}(t_2) \bar{P}(t_1) &= 0. \end{aligned} \quad (19)$$

With the help of (16), (17) a formally exact set of equations for the fluctuation of the density (1) and the current (2) can be derived:

$$\frac{dn_q(t)}{dt} = iqj_q(t) \quad (20)$$

$$\begin{aligned} \frac{dj_q(t)}{dt} = iLj_q = & (i\delta n_q(t)\Omega_{nj}^2(t) + i\delta j_q(t)\Omega_{jj}^2(t))/q \\ & - \int_{t_w}^t dt' \delta n_q(t') \mathbf{S}_{nj}^{-1}(t') M_q(t', t) - \int_{t_w}^t dt' \delta j_q(t') \mathbf{S}_{jj}^{-1}(t') M_q(t', t) \\ & + i \exp(iLt_w) \bar{Q}(t_w) G(t_w, t) L \delta j_q(0). \end{aligned} \quad (21)$$

The structure of the equation is very similar to that of the equilibrium equation. Equation (20) is simply the continuity equation for the density.  $\Omega_{nj}, \Omega_{jj}$  are generalized time-dependent frequencies. They are given by

$$\Omega_{nj}^2 = qS_{nn}^{-1}(t)(n_q(t)|Lj_q(t)) + qS_{nj}^{-1}(t)(j_q(t)|Lj_q(t)) \quad (22)$$

$$\Omega_{jj}^2 = qS_{jn}^{-1}(t)(n_q(t)|Lj_q(t)) + qS_{jj}^{-1}(t)(j_q(t)|Lj_q(t)). \quad (23)$$

In equilibrium,  $\Omega_{nj}$  reduces to (6) and  $\Omega_{jj}$  would be zero due to time translational invariance, but has to be kept in non-equilibrium for finite times. The memory function  $M_q$  is an explicit function of two times:

$$M_q(t_1, t) = (Lj_q(t_1)|\exp(iLt_w)\bar{Q}(t_w)G(t_w, t)L\delta j_q(0)) \quad (24)$$

$$G(t_1, t) = \mathcal{T} \exp\left(i \int_{t_1}^t dt' L\bar{Q}(t')\right) \quad (25)$$

where the operator  $\mathcal{T}$  induces a time ordering from left to right. It is important to note that in general the memory function (24) does not have the form of a correlation function of fluctuating forces, but is the correlation of the accumulated random force between  $t_1$  and  $t$  and the real force  $Lj_q(t_1)$  at time  $t_1$ . It describes the dissipation between  $t_1$  and  $t$  [30]. This will be important for finding appropriate approximations. The last term in (21) is a fluctuating force  $F_q(t_w, t)$ :

$$F_q(t_w, t) = \exp(iLt_w)\bar{Q}(t_w)G(t_w, t)Lj_q(0). \quad (26)$$

Due to the properties of the projection operators (19), the time-ordered product in (25) propagates the force  $Lj_q$  always in the space of functions perpendicular to density and current at every time step. The fluctuating force  $F_q(t_w, t)$  is not correlated with the fluctuation of density or current at time  $t_w$ .

Equations (20), (21) have the form of an inhomogeneous integro-differential equation. They can be solved formally by introducing fluctuation propagators  $N_{kl}$ , which obey the homogeneous part of equations (20), (21):

$$\frac{dN_{in}(q; t_1, t)}{dt} = iqN_{ij}(q; t_1, t) \quad (27)$$

$$\begin{aligned} \frac{dN_{ij}(q; t_1, t)}{dt} = & (iN_{in}(q; t_1, )\Omega_{nj}^2(t) + iN_{ij}(q; t_1, t)\Omega_{jj}^2(t))/q \\ & - \int_{t_w}^t dt' N_{in}(q; t_1, t') \mathbf{S}_{nj}^{-1}(t') M_q(t', t) \\ & - \int_{t_w}^t dt' N_{ij}(q; t_1, t') \mathbf{S}_{jj}^{-1}(t') M_q(t', t). \end{aligned} \quad (28)$$

The initial conditions are  $N_{ik}(q; t, t) = \delta_{ik}$ . If a density or current fluctuation is given at a time  $t_1$  e.g. by applying a known external field to the system, the fluctuations at all later times are then given by

$$\delta n_q(t) = \delta A_i(t_1)N_{in}(q; t_1, t) + i \int_{t_1}^t dt' F_q(t_1, t')N_{jn}(t', t) \quad (29)$$

$$\delta j_q(t) = \delta A_i(t_1)N_{ij}(q; t_1, t) + i \int_{t_1}^t dt' F_q(t_1, t')N_{jj}(t', t) \quad (30)$$

where  $F_q(t_1, t)$  is the random force defined in equation (26). The  $A_i$  are density and current respectively for  $i = 1, 2$ . This can easily be checked by replacing density and current in equations (20), (21) by (29), (30).

The fluctuation propagators are very closely related to the susceptibilities. These are given by Poisson brackets of the variables [30]:

$$\chi_{ik} = \langle \{ \delta A_i^*(t_1), \delta A_k(t) \} \rangle. \tag{31}$$

The density susceptibility can therefore be written with the help of equation (29) as

$$\chi_{nn}(t_1, t) = -iq N_{jn}(t_1, t) + i \int_{t_1}^t dt' \langle \{ n_q^*(t_1), F_q(t_1, t') \} N_{jn}(t', t) \rangle. \tag{32}$$

Here it was used that  $\chi_{nn}(t_1, t_1) = 0$  and  $\chi_{nj}(q; t_1, t_1) = -iq$ . In the mode-coupling approximation, the second term in (32) is zero [28]. The dynamical susceptibility can therefore be identified with the fluctuation propagator  $-iq N_{jn}(q; t_1, t)$ .

The equation for the density correlation function can be easily derived from equations (20), (21), (29):

$$\begin{aligned} \frac{d^2 \phi_q(t_1, t)}{dt^2} &= -\phi_q(t_1, t) \Omega_{nj}^2(t) + i \frac{d\phi_q(t_1, t)}{dt} \frac{\Omega_{jj}^2(t)}{q} - iq \int_0^t dt' \phi_q(t_1, t') \mathbf{S}_{nj}^{-1}(t') M_q(t', t) \\ &\quad - \int_0^t dt' \frac{\phi_q(t_1, t')}{dt'} \mathbf{S}_{jj}^{-1}(t') M_q(t', t) \\ &\quad + \int_0^{t_1} dt' (-iq N_{jn}(q; t', t_1)) \bar{M}_q(t', t). \end{aligned} \tag{33}$$

The function  $\bar{M}_q(t', t)$  is in general not identical to the memory function  $M_q(t_1, t)$  in (24), but it is the correlation function of the fluctuating forces:

$$\bar{M}_q(t_1, t) = (\bar{Q}(0) F_q(0, t_1) | \bar{Q}(0) F_q(0, t)). \tag{34}$$

Equations (33), (28) are a formally exact set of equations for the density correlation function and fluctuation propagators, which reduces to the response or integrated response within mode-coupling theory. If we assume equilibrium, i.e. if we use the canonical ensemble, the set of equations reduces exactly to the one in equilibrium [28]. Time translation invariance is restored, the fluctuation propagator  $N_{nn}(t_1, t)$  is identical to the normalized correlation function,  $\bar{M} = M$  and the equation (33) reduces to (4) with the equilibrium value (6) for  $\Omega_{nj}$ .

For non-equilibrium situations a further step has to be taken. In EMCT the only input needed is the static structure factor. The frequency  $\Omega_q$  can easily be calculated if  $S(q)$  is known. In non-equilibrium  $S(q)$  turns into a time-dependent function. For example, for quenches we only know the value of  $S_q(t = 0)$ , which is just the equilibrium structure factor of the liquid at the beginning of the quench. The equations presented so far do not provide an equation for the equal-time correlation function. It is easily possible to obtain an equation by differentiating  $S_q(t)$  twice:

$$\frac{d^2 S_q(t)}{dt^2} = 2q^2 (j_q(t) | j_q(t)) - 2 \text{Re } q ((n_q(t) | L j(t)). \tag{35}$$

Equations like this cannot be treated with the standard non-equilibrium projection operator formalism, since it is assuming implicitly that frequencies like  $q(n_q | L j_q)$  are known or can be simply calculated. This is not the case for liquids close to the glass transition in non-equilibrium. Since  $L\rho_{NE} \neq 0$ , the Liouville operator is not a self-adjoint operator like in equilibrium. Therefore  $(n_q | L j_q) \neq (L n_q | j_q)$  and can therefore not be simply calculated. One possibility is to express the frequencies  $\Omega_{nj}(t)$  and  $\Omega_{jj}(t)$  with the help of a modified



projection operator [28] in terms of the one-time structure factor, correlation functions and susceptibilities. Equation (35) can therefore be written in the form

$$\begin{aligned} \frac{1}{2} \frac{d^2 S_q(t)}{dt^2} = & q^2 S_{jj}(t) - \text{Re}[S_q(t)\Omega_{nj}(0) + S_{nj}(q; t)\Omega_{jj}(0)] \\ & + iq \int_0^t dt' \phi_{nl}(t, t') \mathbf{S}_{lm}^{-1}(0) W_{mj}(q; t', t) \\ & - q \int_0^t dt' \frac{\phi_{nl}(q; t, t')}{dt'} \mathbf{S}_{lm}^{-1}(0) U_{mj}(t', t) \\ & - \int_0^t dt' (-iq N_{jn}(q; t', t))^* \bar{M}_q(t', t). \end{aligned} \quad (36)$$

There appear four new memory functions  $W_{mj}$  and  $U_{mj}$  with  $m = 1, 2$  in this equation.  $W_{mj}$ ,  $U_{mj}$  are the correlation functions of the fluctuation of the variable  $A_m(0) \in (n_q, j_q)$  and the current of the fluctuating force  $LF_q(t', t)$  between  $t'$  and  $t$  or the fluctuating force, respectively, translated backwards in time to  $t = 0$ :

$$W_{mj}(t', t) = (A_m(0) | \exp(-iLt') LF_q(t', t)) \quad (37)$$

$$U_{mj}(t', t) = (A_m(0) | \exp(-iLt') F_q(t', t)). \quad (38)$$

In equilibrium the memory function  $U$  vanishes exactly. The fluctuating force  $F_q(t', t)$  is perpendicular to  $A_m(t')$  and

$$U_{mj}(t', t) \equiv (\exp(+iLt') A_m(0) | F_q(t', t)) \equiv 0.$$

The memory function  $W_{nj}$  is in equilibrium equal to the fluctuating force correlation function  $\bar{M}_q$ . Together with the fluctuation-dissipation theorem therefore the convolution integrals in time in (36) cancel. The first line in (36) vanishes, since in equilibrium  $\Omega_{jj} \equiv 0$  and  $\Omega_{nj} = q^2 S_{jj}/S_q$ . Equations (36), (33), (27) and (28) are an exact set of equations for one-time and two-time quantities, describing the change of the structure and the correlations and susceptibilities if, e.g. by an initial quench, a non-equilibrium probability density is imposed.

### 3. Approximations

To close the equations, closure relations for the memory functions  $M_q$ ,  $W_{mj}$ ,  $U_{mj}$  and the correlation function of fluctuation forces  $\bar{M}_q$  have to be found. There is no systematic way of calculating the memory function, since no small parameter is available for dense liquids close to the glass transition. The only guide available is the requirement that the equations should reduce to the equations (12) and (4) in equilibrium and that certain mathematical requirements intrinsic to the projection operator formalism are fulfilled. It is very plausible to express  $\bar{M}$  as a quadratic form of the correlation functions since it has the structure of a correlation function of fluctuating forces:

$$\bar{M}(q; t_1, t) = \frac{1}{2} S_{jj}^2(t) \sum_k v^2(k, q-k; t) \phi_k(t_1, t) \phi_{q-k}(t_1, t). \quad (39)$$

The vertex  $v(q; k, q-k; t)$  is the same as in (13) if the direct correlation functions are understood as time-dependent quantities. The memory function  $M$  describes the influence of a force fluctuation at  $t'$  on its surroundings integrated between  $t'$  and  $t$ . Since  $M$  cannot be written as a linear functional of the integrated response the next simple approximation possible is the following:

$$M(q; t_1, t) = M_q(t, t) - S_{jj}^2(t_1) \sum_k \int_{t_1}^t dt' v^2(k, q-k; t') (-ik) N_{jn}(k; t', t) \phi_{q-k}(t', t) \quad (40)$$

where  $N_{jn}(k; t', t)$  can be identified with the susceptibility as explained above. In equilibrium this guarantees that  $M_q = \bar{M}_q$ . Therefore the two last integrals in equation (33) cancel for times  $t_1 = t$ . This property has to be fulfilled rigorously [27]. It can therefore be used to calculate  $M(t, t)$  self-consistently. Although  $M$  and  $\bar{M}$  are equal in equilibrium, the formal expressions in non-equilibrium are different. Choosing  $M = \bar{M}$  has the consequence that a generalized fluctuation theorem of the second kind [30] would be fulfilled. It can be shown [27] that this immediately excludes the possibility of the aging properties found e.g. in simulations [22–24]. Only a transient aging phenomenon caused by the time dependence of the static structure factors would be observed in this case. Another possibility for introducing approximations is first to integrate the third integral in (33) by parts. This leads to

$$\begin{aligned} \frac{d^2\phi_q(t_1, t)}{dt^2} = & -\phi_q(t_1, t)\Omega_{nj}^2(t) + i\frac{d\phi_q(t_1, t)}{dt}\frac{\Omega_{jj}^2(t)}{q} - S_q(t)M(t, t) + \phi_q(t, 0)M(0, t) \\ & + \int_0^t dt' \phi_q(t_1, t')\Sigma(t', t) + \int_0^{t_1} dt' (-iqN_{jn}(q; t', t_1))\bar{M}_q(t', t) \end{aligned} \quad (41)$$

with

$$\Sigma(t', t) = \mathbf{S}_{jj}^{-1}(t')\frac{dM_q(t', t)}{dt'} - iq\mathbf{S}_{nj}^{-1}(t')M_q(t', t). \quad (42)$$

With the approximation

$$M(q; t_1, t) = S_{jj}^2(t_1) \sum_k v^2(k, q - k; t) N_{jn}(k; t_1, t) \phi(q - k; t_1, t) \quad (43)$$

the resulting structure of the theory is very similar to that of the  $p$ -spin model [14]. This is also true for the theory introduced by the approximations (39), (40). Both reduce to EMCT in equilibrium. Which of the approximations is more appropriate for real liquids has to be tested and is work for the future.

Similar approximations are possible for the new memory functions  $U$  and  $W$ . But since there are fewer mathematical boundary conditions to be fulfilled than for  $M$  and  $\bar{M}$  there is more freedom in the choice of the approximation. Different approximations will lead only to quantitatively and not qualitatively different results for  $S_q$ .

#### 4. Conclusions

With the help of non-equilibrium projection operator techniques it is possible to derive an exact set of equations for one-time quantities like the time-dependent equal-time structure factor and two-time quantities like correlation functions and fluctuation propagators. The memory functions can be approximated as in the EMCT by the correlation functions and response functions. It is interesting to note that in the formulation presented here, a theory for the equal-time structure factor (which is trivial in the  $p$ -spin model) and not the potential energy as in the  $p$ -spin model is derived. The structure factor is directly accessible to experiments and it would be especially interesting to study aging phenomena in colloidal hard-sphere glasses as is done for colloidal clays [32], where the structure factor can easily be measured within light scattering experiments. It is already obvious from the equations that the structure factor  $\lim_{t \rightarrow \infty} S_q(t)$  of the glass will not be the structure factor of the corresponding equilibrium liquid, but will depend on the non-ergodicity parameters, i.e. on  $\lim_{t \rightarrow \infty} \lim_{t_w \rightarrow \infty} \phi_q(t_w, t)$  via the memory functions  $W_{jj}$ ,  $U_{nj}$  and the correlation function of fluctuating forces  $M$ . The aging scenario to be expected from the equations presented here can be formulated within the bifurcation scenario of the glass transition derived from mode-coupling theory [7]. This picture can best be explained in discretized models, where only a discretized set of wave

vectors is used. In this case the wave-vector components of the equilibrium structure factor  $S_q^{equ}$  can be considered as control parameters of the mode-coupling models. In the space formed by the components there exists a critical hypersurface which separates the control parameter space into a liquid subset and a glassy subset. Since in the non-equilibrium case the value of  $S_q(t)$  for  $t \rightarrow \infty$  depends on the non-ergodicity parameters, the critical hypersurface will also depend on the two-time correlation function. A quench can now be considered in the following way. Starting in the liquid subset, the system, which can be considered as a point in the control parameter space, starts to flow towards the critical hypersurface. As it approaches this surface, relaxations become slower and slower. Due to the glass transition in the critical hypersurface the system cannot reach the point which would correspond to the thermodynamic parameters in equilibrium. Instead it will very probably be trapped on the (non-equilibrium) critical hypersurface, which also depends on the non-ergodicity parameters. In hard-core-like systems the glass transition is driven by the nearest-neighbour repulsion. This can be inferred from the fact that in the EMCT equations the glass transition occurs if the first peak of the structure factor becomes big enough. Therefore trapping on the critical hypersurface will lead to a drastic change in the sensitivity of the peak height to the quench temperature (or density), once the system is quenched below  $T_c$  (above  $n_c$ ). This qualitative aspect can be seen in simulations of binary Lennard-Jones systems [24]. In this simulation the area under the first peak of the radial distribution function  $g(r)$ , which roughly corresponds to the height of the first peak of the structure factor  $S_q$ , does not seem to increase beyond a certain threshold, if the system is quenched below  $T_c$ . As a next step, the details of the theory presented will be studied in simplified models before the properties of realistic glass-forming liquids are calculated. This will be included in future studies.

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