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Irreducible memory function and slow dynamics in disordered systems

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We show how the irreducible memory function can be obtained in a rather straightforward way, and that it can be expressed in terms of two contributions representing two parallel decay channels. This representation should be useful for treating systems with a slow time dependence and where eventually some internal degrees of freedom enters in the relaxation process, and cuts off an underlying ideal ergodic to nonergodic transition. We also show how the irreducible memory function under certain mild conditions defines a regenerative stochastic process, or a two level stochastic system. This leads to a picture with dynamical heterogeneities, where the statistical properties asymptotically are ruled by limit processes. This can explain the universal behavior observed in many glass-forming systems.

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I. INTRODUCTION

In recent years there has been a lot of interest in systems with slow relaxation processes. Examples of such systems are supercooled liquids, glasses, colloidal suspensions, dense polymer solutions, melts, etc. [1–3]. Many experimental and theoretical investigations on such systems have been stimulated by the mode coupling theory (MCT) developed for simple liquids, where the density correlation function $C(\mathbf{q},t)=\langle n^{*}(\mathbf{q},t)n(\mathbf{q},0)\rangle$ is the fundamental object of study. Here $n(\mathbf{q})$ denotes the microscopic density fluctuations $n(\mathbf{q})=\Sigma_j \exp[-i\mathbf{q}\cdot\mathbf{r}_j]$. The fluctuating forces entering in a generalized friction kernel are approximated in terms of products of density fluctuations, and this leads to a closed system of equations for $C(\mathbf{q},t)$. The solution to these has been successfully compared with experiments on many systems, even if there are still open problems which motivate further studies [4–6]. The most successful application of the MCT so far is for the glass transition observed in dense colloidal suspensions [7]. Here there has been either a full microscopic approach starting from the Liouvillian and treating the suspension essentially as an atomic system [8,9], or a coarse grained description starting from the Smoluchowski operator with or without hydrodynamic interactions [10–19]. In the latter approach it was necessary to introduce the so-called irreducible memory function in order to avoid unphysical results with possibly negative values for the viscosity [13,14].

In the above so-called ideal MCT there appears an ergodic to nonergodic transition at a certain temperature T_c or density n_c. Since this ideal glass transition with an absolute structural arrest is not observed for molecular glass systems or even for hard sphere colloidal systems, extended versions of the MCT including couplings to current fluctuations have been introduced [20–25]. This coupling gives rise to a smearing out of the ideal transition and introduces the so-called activated hopping processes.

The ideal transition arises from the cage effect which leads to a selfconsistent trapping mechanism. The coupling to currents in the extended theory can be viewed as a backflow around any particle. This backflow is built up from repeated correlated collisions between a particle and the surrounding ones constituting the cage. Such correlated collisions eventually destroy the cage and result in a relaxation to the equilibrium state. However, in complex molecular systems or in colloidal suspensions it is not clear how currents influence the relaxation process for long times. In these systems such fluctuations decay within a typical time $\tau_B=m/\zeta$ where ζ is a bare friction coefficient. The typical time scale for structural relaxations τ_R is much longer than τ_B. Therefore in complex liquids other modes except currents may be more important for the structural relaxation process for long times. Some important aspects of this issue were recently discussed in the literature [26–28].

Mode coupling approximations have also been applied to various spin systems [29–35] and compared with simulation results. In this case the agreement between the ideal theory and simulations is not very convincing. In some of these systems there is no apparent underlying ergodic-nonergodic transition. This raises the question how to formulate an extended version of MCT for more general situations. For some spin-systems this has partly been achieved through a systematic diagrammatic theory [35]. There are also several other interesting attempts to extend the theory starting either from a density functional formulation [36–38], or by approximating higher order memory functions [39].

For dense fluids undergoing the glass transition, one is primarily concerned with local fluctuations where the dynamics occurs on a characteristic length scale of a few Å. Such local fluctuations or rearrangements of molecules will, except for translational motions, involve vibrational and rotational motions. In an almost arrested or frozen structure, where the center-of-mass motion is frozen out, such local rotational and vibrational motions can accumulate in time and after a sufficiently long time lead to a relaxation of the structure. In colloidal solutions the hydrodynamic interactions will induce currents in the medium which can then couple to other particles.

In this paper we will show how such local or other relevant fluctuations can be extracted from the irreducible memory function in a rather systematic way. The resulting expression is formally identical to previous results and it follows that structural relaxations can decay via two parallel channels. If one of the channels become blocked, by freezing out of the center-of-mass motion for instance, there is still the possibility of decay via local fluctuations such as vibrations or rotations or some other local modes depending on the system of interest. The present approach is nonperturbative, and can be applied to a stochastic operator or the microscopic Liouville operator.

The irreducible memory function seems to be the natural starting point for systems described by a stochastic equation [13,32–34]. This function is under certain rather general assumptions directly connected to an underlying regenerative stochastic process, which is essentially a stochastic two level system. General limit theorems can then be applied to get the asymptotic behavior of the correlation function.

II. GENERAL FORMULATION

A. Memory function

The derivation of the memory function is well established, and the essential steps are repeated here just in order to introduce the notations for the further development. We will follow the conventional lines of Zwanzig [40,41], Mori [42], Nordholm and Zwanzig [43], and Kawasaki [32].

We consider a system described by a probability distribution in some state space and satisfying the equation

$$\frac{\partial}{\partial t}f(t;\Gamma) = \Omega(\Gamma)f(t;\Gamma). \tag{1}$$

Here Γ denotes a set of state variables and Ω is some stochastic operator such as the Smoluchowski operator or the Liouville operator $\Omega = -i\mathcal{L}$. We will be interested in averages of some relevant dynamical variable $A(\Gamma)$ given by

$$\langle A(t)\rangle = \int d\Gamma A(\Gamma)f(t;\Gamma) = \int d\Gamma A(t;\Gamma)f(0;\Gamma). \tag{2}$$

Here we will consider a single variable but A could in the general case denote a column vector. $A(t;\Gamma)$ satisfies the equation

$$\frac{\partial}{\partial t}A(t;\Gamma) = \Omega^{\dagger}(\Gamma)A(t;\Gamma) \tag{3}$$

and $\Omega^{\dagger}$ denotes the adjoint operator.

The variable A has zero equilibrium average, and we introduce a projection operator P defined as

$$PX(\Gamma) = A(\Gamma)\langle A^{*}X\rangle \quad \text{or} \quad P = |A\rangle\langle A^{*}|, \tag{4}$$

where the asterisk denotes the complex conjugate variable. Here the bracket notation is given by [32]

$$\langle A| = \int d\Gamma A(\Gamma)\cdots$$

$$|A\rangle = \int \cdots A(\Gamma)f_{\mathrm{eq}}(\Gamma)d\Gamma, \tag{5}$$

where the ellipsis stands for another arbitrary function of the state variables Γ or in some case an operator. We will deal with a normalized variable A such that the equilibrium static correlation function is unity,

$$S = \langle A^{*}A\rangle = \int A^{*}(\Gamma)A(\Gamma)f_{\mathrm{eq}}(\Gamma)d\Gamma = 1. \tag{6}$$

In calculating the average values of the variable A only the part $Pf(t;\Gamma)$ enters, and we make the common decomposition

$$f(t;\Gamma) = Pf(t;\Gamma) + Qf(t;\Gamma) = f_1(t;\Gamma) + f_2(t;\Gamma), \tag{7}$$

where $Q = 1 - P$. This leads to the coupled equations

$$\begin{aligned}\frac{\partial}{\partial t}f_1(t;\Gamma) &= P\Omega Pf_1(t;\Gamma) + P\Omega Qf_2(t;\Gamma)\\ &= \Omega_{11}f_1(t;\Gamma) + \Omega_{12}f_2(t;\Gamma),\end{aligned} \tag{8}$$

$$\begin{aligned}\frac{\partial}{\partial t}f_2(t;\Gamma) &= Q\Omega Qf_2(t;\Gamma) + Q\Omega Pf_1(t;\Gamma)\\ &= \Omega_{22}f_2(t;\Gamma) + \Omega_{21}f_1(t;\Gamma).\end{aligned} \tag{9}$$

Solving Eq. (9) gives

$$f_2(t;\Gamma) = \int_0^t e^{\Omega_{22}(t-s)}\Omega_{21}f_1(s;\Gamma)ds + e^{\Omega_{22}t}f_2(0;\Gamma). \tag{10}$$

Substituting this into Eq. (8) gives

$$\begin{aligned}\frac{\partial}{\partial t}f_1(t;\Gamma) - \Omega_{11}f_1(t;\Gamma) + \int_0^t ds\hat{M}(t-s)f_1(s;\Gamma)\\ = \Omega_{12}e^{\Omega_{22}t}f_2(0;\Gamma),\end{aligned} \tag{11}$$

where the operator $\hat{M}$ is given by

$$\hat{M}(t) = -\Omega_{12}e^{\Omega_{22}t}\Omega_{21} = -\Omega_{12}R(t)\Omega_{21} \tag{12}$$

and $R(t) = \exp(\Omega_{22}t)$. Taking now the scalar product with $\langle A^{*}|$ from the left and inserting the expression for the projection operator gives the conventional equation [40–42]

$$\begin{aligned}\frac{\partial}{\partial t}\langle A^{*}(t)\rangle + \omega_A\langle A^{*}(t)\rangle + \int_0^t dsM(t-s)\langle A^{*}(s)\rangle\\ = \langle A^{*}\Omega QR(t)Q\rangle.\end{aligned} \tag{13}$$

Here the frequency ω_A is given by

$$\omega_A = -\langle A^{*}\Omega A\rangle \tag{14}$$

and the memory function by

$$M(t) = -\langle A^{*}\Omega QR(t)Q\Omega A\rangle. \tag{15}$$

For the correlation function

$$C(t) = \langle A^{*}(t)A(0)\rangle \tag{16}$$

this leads to the equation

$$\frac{\partial}{\partial t}C(t) + \omega_A C(t) + \int_0^t dsM(t-s)C(s) = 0. \tag{17}$$

A Laplace transformation then gives

$$C(z) = \frac{1}{z + \omega_A + M(z)}. \tag{18}$$

B. Irreducible memory function

For a stochastic operator such as the Smoluchowski operator Cichocki and Hess [13] argued that Eq. (18) was not the best starting point for approximations on the memory function $M(z)$ since it may lead to negative values for the viscosity. They introduced an additional projection operator and obtained in this way a further reduction to an irreducible memory function $M^{\mathrm{irr}}(z)$. Later Kawasaki [32,33] showed how this reduction could be generalized to a whole class of operators. A straightforward way of obtaining the irreducible memory function is to solve for $f_1(t;\Gamma)$ in Eq. (8) and insert into Eq. (9). This gives

$$f_1(t;\Gamma) = (\Omega_{11})^{-1}\frac{\partial}{\partial t}f_1(t;\Gamma) - (\Omega_{11})^{-1}\Omega_{12}f_2(t;\Gamma). \qquad (19)$$

The "inverse" operator $(\Omega_{11})^{-1}$ is defined via

$$(\Omega_{11})^{-1} = (P\Omega P)^{-1} = -|A\rangle\omega_A^{-1}\langle A^*| \qquad (20)$$

and satisfies

$$(P\Omega P)^{-1}(P\Omega P) = (P\Omega P)(P\Omega P)^{-1} = P. \qquad (21)$$

Here we assume that the inverse ω_A^{-1} exists. Equation (9) now reads

$$\frac{\partial}{\partial t}f_2(t;\Gamma) - Q(\Omega - \Omega_0)Qf_2(t;\Gamma) = \Omega_{21}(\Omega_{11})^{-1}\frac{\partial}{\partial t}f_1(t;\Gamma), \qquad (22)$$

where

$$\Omega_0 = \Omega P(P\Omega P)^{-1}P\Omega. \qquad (23)$$

This result was obtained by Kawasaki by splitting the operator Ω as

$$\Omega = \Omega_0 + \Omega_1, \qquad (24)$$

where $\Omega_1 = \Omega - \Omega_0$ is the irreducible operator first introduced by Cichocki and Hess for the Smoluchowski operator. We notice that $P\Omega_1 = \Omega_1 P = 0$ or that $Q\Omega_1 = \Omega_1 Q = \Omega_1$. Therefore the irreducible operator Ω_1 acts only in the space orthogonal to the variable A, and in this sense it is irreducible.

Solving Eq. (22) as before and inserting the solution in Eq. (8) gives

$$\frac{\partial}{\partial t}C(t) + \omega_A C(t) + \int_0^t ds M^{\mathrm{irr}}(t-s)\frac{\partial}{\partial s}C(s) = 0. \qquad (25)$$

The new irreducible memory function is given by

$$M^{\mathrm{irr}}(t) = \langle A^*\Omega Q R_1(t) Q\Omega A\rangle\omega_A^{-1} \qquad (26)$$

with

$$R_1(t) = e^{Q\Omega_1 Qt} \qquad (27)$$

and the time-dependence is now given by the operator $Q\Omega_1 Q = \Omega_1$. For the Laplace transform this gives

$$C(z) = \left[z + \frac{\omega_A}{1 + M^{\mathrm{irr}}(z)}\right]^{-1}. \qquad (28)$$

From Eqs. (18) and (28) one also gets the relation

$$M(z) = -\omega_A\frac{M^{\mathrm{irr}}(z)}{1 + M^{\mathrm{irr}}(z)}. \qquad (29)$$

The simple derivation above shows how the irreducible memory function can be obtained in a straightforward way by solving $f_1(t)$ in terms of its derivative from Eq. (8). By doing this we include the information contained in Eq. (8) into Eq. (9), with the effect of replacing Ω with Ω_1. The effect for the correlation function is that, instead of renormalizing the frequency ω_A by $M(z)$, one rather renormalizes the relaxation time by M^{irr} as argued by Kawasaki [32,44].

From Eq. (8) there are of course other possibilities. We can formally solve Eq. (8) for f_1, i.e.,

$$f_1(t) = e^{\Omega_{11}t}f_1(0) + \int_0^t ds e^{\Omega_{11}(t-s)}\Omega_{12}f_2(s)$$

and insert this into Eq. (9), which then gives an equation for $f_2(t)$ with a memory function which contains information on how the dynamics of $f_1(t)$ influences $f_2(t)$. We can solve this equation for $f_2(t)$ and insert this back into Eq. (8). Eventually this procedure leads us back to Eq. (18).

We can also iterate Eq. (19) as

$$f_1(t;\Gamma) = -(\Omega_{11})^{-1}\Omega_{12}f_2(t;\Gamma) - (\Omega_{11})^{-2}\Omega_{12}\frac{\partial}{\partial t}f_2(t;\Gamma) + (\Omega_{11})^{-2}\frac{\partial^2}{\partial t^2}f_1(t;\Gamma) = -\sum_{n=0}^{\infty}\Omega_{11}^{-n-1}\Omega_{12}\frac{\partial^n}{\partial t^n}f_2(t).$$

Introducing the first equality into Eq. (9) renormalizes again Ω to Ω_1 and the prefactor in front of its derivative. The second derivative of f_1 now appears on the right hand side as a driving term. However, the usefulness of such an approach has to be further investigated.

C. Further decomposition

The two memory functions $M(t)$ and $M^{\mathrm{irr}}(t)$ are certain correlation functions of fluctuation forces. However, they are quite different since $M(t)$ renormalizes a frequency while M^{irr} renormalizes a relaxation time. We are here interested in systems where the correlation function $C(t)$ decays very slowly and eventually can have a $1/z$ dependence for small frequencies. This implies that $M(z)$ have to exactly cancel the regular frequency ω_A, while $M^{\mathrm{irr}}(z)$ must also have a $1/z$ dependence for small z. Actually this singular behavior in $C(z)$ and $M^{\mathrm{irr}}(z)$ is eventually removed by some residual slow processes in the system.

Introducing the fluctuating forces $F(\Gamma) = Q\Omega A(\Gamma)$ and $\tilde{F} = Q\Omega^{\dagger}A(\Gamma)$ we have $M(t) = -\langle\tilde{F}^{\dagger}R(t)F\rangle$ and correspondingly for M^{irr}. The generalized forces F and $\tilde{F}$ are identical when Ω is self-adjoint. We can separate the forces as [42,44]

$$F = F_1[A(s)] + F_2,$$

where the first part is some nonlinear functional of the variable A and the second term contains fluctuations from other variables. Considering a simple liquid with spherical atoms for instance, the forces can be expressed in terms of a product of two density fluctuations. When we take the density as the variable A this gives the first term above. However, the forces also couple to the product of for instance two current fluctuations [45], and such additional fluctuations will then be included in the second term F_2.

In complex fluid systems the dynamics contains in general contributions from different kinds of forces. Except for intermolecular excluded volume forces which couple to pair of density fluctuations contained in F_1, there can also appear intramolecular or other types of forces where rotational and vibrational degrees of freedom can be important. These latter forces will then appear in F_2. In a colloidal solution made up of spherical particles for example, there are the direct interaction between the particles but also an indirect coupling via hydrodynamic interactions. When a particle moves it drags the surrounding fluid particles with it and creates a hydrodynamic disturbance which can propagate and induce an interaction on other particles. In the same way when the particles are more or less localized a rotation of a molecule disturbs the surrounding fluid and the resulting hydrodynamic flow gives a force on other particles which may result in a motion. In this way there can be a coupling between rotational and translational motions [46].

Similarly, in polymer solutions or melts there are, except for the excluded volume forces, intramolecular forces due to the covalent bonds within the chain. The latter forces are of an elastic nature and couple to the displacements of the molecules. In a dense system, where the excluded volume forces tend to form a tube around any single chain, this may result in a reptationlike motion, which eventually will lead to a translation of the whole chain. In a system with molecules of arbitrary shape and internal constraints one can introduce the center of mass coordinate $\mathbf{r}_i^c$ and some internal degrees of freedom $Q_1, Q_2, \ldots, Q_d$ and the position vector of atom or bead α in molecule i is given by $\mathbf{r}_i^\alpha = \mathbf{r}_i^c + \mathbf{R}_i^\alpha(Q_1, \ldots, Q_d)$. Similarly the forces consist of excluded volume forces which essentially couple to the center of mass motion and some internal forces which couple to the internal degrees of freedom Q_s, $s=1,d$ [47].

The memory function $M(z)$ can now be split into two terms

$$M(z) = M_0(z) + \Delta(z),$$

where $\Delta(z) = -\langle \widetilde{F}_2^\dagger R(z) F_2 \rangle$ will be referred to as a back-flow term. This also defines M_0 as $M_0 = M - \Delta$. The contributions from F_2 are expected to be small. The term M_0 is in leading order given by some functional of $C(t)$, which have to be determined, i.e.,

$$M_0(t) = \mathcal{F}[C(s)]$$

even if there will also be contributions from F_2 in M_0. For $M_0(z)$ we have the small frequency expansion $M_0(z) = -\omega_A + az + \cdots$ while $\Delta(z) = \delta_0 + \delta_1 z + \cdots$. Therefore due to the cancellation of ω_A the backflow term $\Delta(z)$ is responsible for the final decay of $C(t)$. The difference in signs between the leading contributions to M_0 and Δ was noted by Kawasaki [44].

For M^{irr} the fluctuating forces should also give two distinct contributions, but we now rather expect that $1/M^{\mathrm{irr}}(z)$ can be decomposed as

$$\frac{1}{M^{\mathrm{irr}}(z)} = \frac{1}{M_0^{\mathrm{irr}}(z)} + \Delta_1(z).$$

Again the first part is in the leading order some functional of the correlation function itself

$$M_0^{\mathrm{irr}}(t) = \mathcal{F}^{\mathrm{irr}}[C(s)].$$

From Eq. (29) we can find relations between $\mathcal{F}$ and $\mathcal{F}^{\mathrm{irr}}$ and also between Δ and Δ_1.

A very successful approximation for M_0^{irr} has been the mode-coupling approximation

$$M_0^{\mathrm{irr}}(t) = \nu\delta(t) + \sum_{n=1}^{\infty} v_n C^n(t) = \nu\delta(t) + m(t), \tag{30}$$

where the bare friction includes all fluctuations not included in $m(t)$ and $\Delta_1(t)$. The solution to Eqs. (28) and (30) with $\Delta_1 = 0$, gives an ergodic-nonergodic transition at some values v_n^c of the coupling coefficients. For small frequencies this implies that $m(z) \simeq 1/z$, and dominates over the white noise term.

However, we may argue that even if $m(z)$ becomes large and the resulting decay channel blocked there could still be a mechanism present for the relaxation, and even if this represents a small effect, it may accumulate in time and eventually be important. A useful picture of the slow relaxation processes is in terms of a potential landscape with large barriers between metastable states. These large barriers are created self-consistently by the dominant fluctuations in $m(t)$, and when the system is partially trapped in a deep valley some local fluctuations contained in $\Delta_1(t)$ rules the dynamics. Such fluctuations may for sufficiently long times take the system into a new metastable state and so on.

A structure of the equations where both these mechanisms were considered, was obtained by summing repeated collision terms in a kinetic theory formulation [21–23], a general field theory [20], and a general mode-coupling approximation [25]. In this case there appears two different contributions to the memory function with quite different behavior.

In Eq. (22) for $f_2(t)$ the irreducible frequency Ω_1 contains all dynamics in the space orthogonal to the variable A. In particular it contains the processes included in F_1 which appear in $m(t)$ but also other processes like those in F_2 as shown by Kawasaki [36]. The contributions from the latter fluctuations can be extracted and treated separately. The resolvent $R_1(t) = \exp(Q\Omega_1 Qt)$ satisfies the equation of motion

$$\frac{\partial}{\partial t} R_1(t) - Q\Omega_1 Q R_1(t) = 0 \tag{31}$$

or

$$\frac{\partial}{\partial t} R_1(t) - Q\Omega Q R_1(t) = -Q\Omega_0 Q R_1(t) \tag{32}$$

with the initial value $R_1(0) = 1$. We can solve for R_1 in terms of $R(t) = \exp(Q\Omega Qt)$ as

$$R_1(t) = R(t) - \int_0^t ds R(t-s) Q\Omega_0 Q R_1(s) \tag{33}$$

which is essentially Eq. (29). If we iterate the right-hand side (RHS) in Eq. (32) this gives

$$Q\Omega_0 Q R_1(t) = Q\Omega_0 Q R(t) + \int_0^t ds \Sigma_0(t-s) R_1(s), \tag{34}$$

where

$$\Sigma_0(t) = -Q\Omega_0 Q R(t) Q\Omega_0 Q = \Omega_{21}(\Omega_{11})^{-1}\hat{M}(t)(\Omega_{11})^{-1}\Omega_{12} \tag{35}$$

with $\hat{M}$ defined in Eq. (12).

At this point it is possible to extract the contribution from F_2 contained in $\hat{M}(t)$, where $\hat{M}(t)=\hat{M}_0(t)+\hat{\Delta}(t)$. We will now separate out the back-flow term $\hat{\Delta}$ from the irreversible operator Ω_1 and treat it as a small term on the RHS. In this way the local fluctuations contained in F_2 will be considered explicitly. Therefore, we introduce the operator

$$\Omega^c(t) = \Omega_1 \delta(t) + \Omega P(\Omega_{11})^{-1}\hat{\Delta}(t)(\Omega_{11})^{-1} P\Omega, \tag{36}$$

which is the irreducible operator Ω_1, but with the local variables extracted in the second term. The equation for $R_1(t)$ becomes

$$\frac{\partial}{\partial t} R_1(t) - \int_0^t ds Q\Omega^c(t-s) Q R_1(s)$$
$$= - \int_0^t ds \Omega_{21}(\Omega_{11})^{-1}\hat{\Delta}(t-s)(\Omega_{11})^{-1}\Omega_{12} R_1(s), \tag{37}$$

with the solution

$$R_1(t) = R^c(t) - \int_0^t ds \int_0^s du R^c(t-s)\Omega_{21}(\Omega_{11})^{-1}$$
$$\times \hat{\Delta}(s-u)(\Omega_{11})^{-1}\Omega_{12} R_1(u). \tag{38}$$

Here $R^c(t)=[\partial/\partial t - \int_0^t ds \Omega^c(t-s)]^{-1}$. For the irreducible memory function $M^{\mathrm{irr}}(t)=\langle A^* \Omega Q R_1(t) Q \Omega A\rangle \omega_A^{-1}$ this gives

$$M^{\mathrm{irr}}(t) = M_0^{\mathrm{irr}}(t) - \int_0^t ds \int_0^s du M_0^{\mathrm{irr}}(t-s)\Delta(s-u)\omega_A^{-1} M^{\mathrm{irr}}(u) \tag{39}$$

or

$$M^{\mathrm{irr}}(z) = \frac{M_0^{\mathrm{irr}}(z)}{1 + M_0^{\mathrm{irr}}(z)\Delta(z)\omega_A^{-1}}. \tag{40}$$

Here we identify M_0^{irr} as

$$M_0^{\mathrm{irr}}(t) = \langle A^* \Omega Q R^c(t) Q \Omega A\rangle \omega_A^{-1}. \tag{41}$$

M_0^{irr} is therefore the irreducible function but without the local variables which have been extracted in the back-flow term $\Delta(t)$. M_0^{irr} contains essentially the contributions from the forces F_1 and with a mode-coupling approximation on this part we get Eq. (30).

For the memory function $M(z)$ we now find from Eq. (29)

$$M(z) = -\omega_A \frac{M_0^{\mathrm{irr}}(z)}{1 + M_0^{\mathrm{irr}}(z)(1 + \Delta(z)\omega_A^{-1})}. \tag{42}$$

In the limit of small z where $|M_0^{\mathrm{irr}}(z)| \gg 1$ and $|\Delta(z)| \ll 1$ this gives

$$\omega_A + M(z) = \omega_A \frac{1 + M_0^{\mathrm{irr}}(z)\Delta(z)\omega_A^{-1}}{1 + M_0^{\mathrm{irr}}(z)[1 + \Delta(z)\omega_A^{-1}]}$$
$$\approx \frac{\omega_A}{1 + M_0^{\mathrm{irr}}(z)} + \Delta(z). \tag{43}$$

Therefore the dynamics will for small z values be dominated by the processes entering in F_2 which were neglected in the ideal theory.

III. REGENERATIVE PROCESS

To make further progress, the two contributions to the irreducible memory function above have to be approximated. However, from the structure found in Eq. (28) there is, under rather mild conditions, an interesting connection with basic stochastic limit processes. We will therefore make some assumptions about the properties of M^{irr} which eventually have to be verified for any particular approximation. The first assumptions are that $M^{\mathrm{irr}}(t) > 0$, $-(d/dt)M^{\mathrm{irr}} \geq 0$, and $M^{\mathrm{irr}}(t=0) < \infty$, i.e., that M^{irr} is positive and nonincreasing. These conditions are fulfilled for M_0^{irr} given by Eq. (30) and $\Delta(z)=\delta_0$ a constant [48]. This leading order approximation for $\Delta(z)$ has been found to give some reasonable results when analyzing experimental data on propylene carbonate [49]. For a more complex hopping term with an explicit frequency dependence the assumptions above have to be verified.

We can extract the hopping term by introducing the function $\phi(t)$

$$C(t) = e^{-\delta_0 t}\phi(t/\tau_0),$$

where $\tau_0=(1+\nu)/\omega_A$ is a microscopic relaxation time. $\phi(z)$ then satisfies the equation

$$\phi(z) = \left[z + \frac{1}{1 + \tilde{m}(z)} \right]^{-1}$$

with

$$\tilde{m}(t) = e^{\hat{\delta}_0 t} \sum_n \tilde{v}_n e^{-n\hat{\delta}_0 t}\phi^n(t),$$

where $\tilde{v}_n = v_n/\omega_A$ and $\hat{\delta}_0 = \delta_0 \tau_0$. These closed equations for the function $\phi(t)$ define a so-called regenerative stochastic process, i.e., a process with two states, say 0 and 1 [50,51]. The time axis is divided into random intervals A and B where the process is "on," and "off," respectively. Here the A intervals have an exponential distribution with an average $1/\tilde{m}(0)$ and the B intervals have a distribution given by

$$P(t) = 1 - \tilde{m}(t)/\tilde{m}(0).$$

In this case the memory function $\tilde{m}$ therefore corresponds to a waiting time distribution $\Pr\{X \leq t\} = P(t)$ where X is the lifetime of a cage built up of the surrounding particles. A particle is trapped during a random time X giving the length of a random interval B, thereafter it is free to relax. This two step process then repeats itself with a new trapping period and so on. The corresponding density function is $p(t) = -\tilde{m}'(t)/\tilde{m}(0)$, and it will show the qualitative features recently observed in computer simulations [52–57].

In Fig. 3 in Berthier and Garrahan [57] we see that in the liquid state $p(t)$ has a single rather sharp peak at some characteristic microscopic time. When the liquid is supercooled there first appears a two peak structure signalling the onset of the α-relaxation process. With lowering temperature, this process dominates the behavior of $p(t)$ which show a broad peak moving to longer times with decreasing temperatures.

These qualitative features are reproduced by $p(t) = -\tilde{m}'(t)/\tilde{m}(0)$. For short times $m(t)/m(0) = 1 - ct^2$ provided the dynamics is treated microscopically. In the liquid state $m(t)$ decays exponentially at longer times, resulting in a single sharp peak for $p(t)$. As the liquid is supercooled, the characteristic feature of the β and α processes appear with two peaks and a minimum in between with two power law wings representing the critical decay and the von Schweidler law. At further decrease of the temperature, the memory function develops a plateau region followed by the final α-decay. The latter is well described by a KWW law $\tilde{m}(t) = m_0 e^{-(t/\tau_\alpha)^\beta}$. This implies that $p(t) \approx 0$ up to the α region where $p(t) \propto t^{\beta-1}/\tau_\alpha^\beta e^{-(t/\tau_\alpha)^\beta}$. It can be shown that the KWW law is obtained as a limit solution to the MCT equations [58].

It is possible to define an indicator process

$$Z(t,\omega) = \begin{cases} 1 & \text{on } A \text{ intervals,} \\ 0 & \text{on } B \text{ intervals,} \end{cases} \tag{44}$$

where ω denotes a realization of the process. $Z(t)$ is therefore a random step function. In terms of $Z(t)$ one can define four other processes $\{H,T,U,V\}$ [59–61]. Here

$$H(t,\omega) = \int_0^t Z(u,\omega)du, \tag{45}$$

and T is the inverse process

$$T(v,\omega) = \sup\{t{:}H(t,\omega) \leq v\}. \tag{46}$$

Also $U(v,\omega) = T(v,\omega) - v$, and V is the inverse process to U; $V(t,\omega) = \sup\{v : U(v,\omega) \leq t\}$. $H(t,\omega)$ is a local time process, and measures the amount of time for which $Z(t) = 1$ during $[0,t]$.

These processes have a direct relevance for understanding the time dependence of $C(t)$ or $\phi(t)$ [51]. We find that the relaxation function $\phi(t)$ can be expressed in terms of the local time process H as

$$\phi(t) = \langle e^{-H(t,\omega)} \rangle, \tag{47}$$

where $\langle \cdots \rangle$ denotes the average over the realizations of the process. Therefore the relaxation function ϕ is for every realization an exponential decay, but where the time t is replaced with a stochastic time $H(t)$. The local time $H(t)$ increases like actual time t on the A intervals, while when the particle is trapped on the B intervals $H(t)$ is constant. The local clock therefore only runs when the particle can escape its surrounding cage. Equation (47) implies a heterogeneous time decay ruled by the statistical properties of A and B intervals.

The V process enter in a similar way for the longest times or smallest frequencies. Since $|\tilde{m}(z)| \gg 1$ for $z \to 0$ we find the equation

$$\phi(z) = 1/[z + 1/\tilde{m}(z)]. \tag{48}$$

$\phi(t)$ is now given by

$$\phi(t) = \langle e^{-V(t,\omega)} \rangle, \tag{49}$$

i.e., the relaxation function is the characteristic function of the point-process V. Since the A intervals in the limit $|\tilde{m}(z)| \to \infty$ effectively shrinks to points, the drift term in the H process plays no role and the H process goes over to the V process which increases in jumps. The relaxation now occurs on a fractal time set.

The limiting behavior of the four processes H, T, U, and V were studied by Bingham, and ergodic limits were found in terms of the self-similar stable process $Y_a(v)$, where

$$\langle e^{-sY_a(v)} \rangle = e^{-vs^a} \tag{50}$$

and its inverse process $X_a(u)$ where

$$X_a(t) = \sup\{v{:}Y_a(v) \leq t\}. \tag{51}$$

This latter process is given by the Mittag-Leffler distribution $G_a(t)$, where the Laplace transform is given by the Mittag-Leffler function

$$\int_0^\infty e^{-tx} dG_a(x) = M_a(t) = \sum_{n=0}^\infty \frac{(-t)^n}{\Gamma(1+an)} \tag{52}$$

and

$$\langle e^{-sX_a(t)} \rangle = M_a(st^a). \tag{53}$$

The fundamental results found by Bingham reads

$$\lim_{v\to\infty} \frac{H(vt)}{h(v)} = X_a(t), \quad \lim_{v\to\infty} \frac{T(vt)}{k(v)} = Y_a(t) \tag{54}$$

provided $h(v) = v^a$ and k is the inverse function to h, $k(v) \sim v^{1/a}$. Here we can replace H with V and T with U, i.e., the pair of processes have the same limit process. A sufficient and necessary condition for these limits to exist is that

$$\tilde{m}(v) \simeq 1/v^a, \quad v \to \infty. \tag{55}$$

These conditions are satisfied at the critical point v_n^c, with a given by the critical exponent. Around this point, the process H has an ergodic limit given by X_a, and since $H(u)/u^a \sim X_a(1)$ we find

$$\phi(t) = \langle e^{-t^a X_a(1)} \rangle = M_a(t^a). \tag{56}$$

The corresponding susceptibility is given by the Cole-Cole law

$$\chi(z) = 1 - z\phi(z) = \frac{1}{z^a + 1}. \tag{57}$$

For the V and U processes the limit $v \to \infty$ can be replaced with $v \to 0$, and it is possible to also analyze the initial decay of the α-relaxation process, i.e., the von Schweidler decay, in terms of the limit processes above [51], except that the exponent a is replaced with the von Schweidler exponent b. The presence of a Δ term in M^{irr} will cut off these power law decays, and the scaling function may decay faster than the Mittag-Leffler function outside a certain time window.

The Cole-Cole law has been observed repeatedly in complex liquids [62]. Recently, it has also been observed in several molecular liquids by OKE measurements [63,64]. These experimental results were successfully interpreted by Götze and Sperl [65] within MCT theory, and were explained by the β-peak phenomenon [66,67], which is generically described by the Cole-Cole law. The β-peak show up in a strongly coupled system and is, together with the critical decay and the von Schweidler decay, a manifestation of the cage effect. The analysis above shows that the molecular motions originating from the cage effect, where one particle is trapped by surrounding ones for some time, eventually are described by underlying limit processes $X_a(t)$ and $X_b(t)$. Since we expect the cage effect to be generally active in dense disordered systems, this implies a universal behavior for the time dependence of such systems up to the initial decay of the α-relaxation process.

IV. DISCUSSION

In this paper we obtained the reduction of the memory function to the irreducible one together with a further reduction including the coupling to local degrees of freedom in a quite general manner. These local degrees of freedom become active when the system becomes trapped in a long lasting metastable state corresponding to high potential barriers, and they induce a type of backflow in the system. The barriers are dynamical and arise from hard core excluded volume interactions.

The present formulation is formally exact, but its eventual usefulness must be verified from approximations on various complex systems, where at least two relaxation mechanisms are important. We notice that the operator Ω_0 plays a fundamental role in the derivation. This appears naturally when combining Eqs. (8) and (9), and enters as an effective coupling constant in Σ_0 in Eq. (35).

A schematic model for the two contributions $M_0^{\mathrm{irr}}(t)$ and $\Delta(t)$ would be $M_0^{\mathrm{irr}}(z) = \nu + m(z)$ with $m(t)$ as in Eq. (30) and

$$\Delta(t) = \sum_{n=1}^{K} w_n C_B^n(t), \tag{58}$$

where $C_B(t)$ is a correlation function for a variable describing some local fluctuations. This equation has to be supplemented with some expression for $C_B(t)$ or some equation for it. There may also appear cross correlations C_{AB}, and terms such as $C_B^k(t)C(t)$ in $\Delta(t)$.

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