

Non-Equilibrium Projection-Operator for a Quenched Thermostatted System

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Received November 21, 2001; accepted March 14, 2002

A projection operator formalism is presented which allows to derive an exact set of equations for correlation functions and susceptibilities in out of equilibrium situations of many particle systems. Explicitly considered is the case of an initial temperature quench in a simple liquid stabilized by a Gaussian thermostat. Implications for the violation of the fluctuation dissipation theorem in simple structural glass formers like Lennard–Jones glasses and colloidal glasses and the differences to the Kawasaki–Gunton projection operator are discussed.

KEY WORDS: Nonequilibrium dynamics; aging; projection operator; glasses; colloidal systems.

1. INTRODUCTION

One of the fundamental problems of non–equilibrium statistical physics is to find mathematical descriptions for systems which are by definition not in a unique state (the equilibrium) but in a transient, time dependent state. The first rigorous approach to this problem is due to Boltzmann with the famous Boltzmann equation for the phase space density $f(r, p, t)$. His ansatz lead to the development of powerful methods known as kinetic theory.^(1, 2) One of the highlights of this theory was the explanation of the long time tails and non analytic corrections to wave vector expansions of transport coefficients in dilute systems.^(3–8) Kinetic theory is often starting with a small density expansion and then trying with the help of sophisticated resummation techniques to extend the validity to higher densities.⁽⁴⁾

This article is dedicated to Bob Dorfman on the occasion of his 65th birthday.

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For more complicated systems or for very high densities where glass transitions occur or where solidification sets in, this systematic ansatz has natural limitations. Another approach to deal with systems lying beyond the reach of small density expansions and its systematic extensions is the projection operator techniques.⁽⁹⁻¹²⁾ Within this method one tries to isolate with physical intuition and general arguments like conservation laws the most relevant variables in order to derive exact generalized Langevin equations for those variables. All the unknown fluctuations or those considered as unimportant are buried in “memory functions” and “fluctuating forces” which are assumed to be simpler or just less important than the main variables. For these unknown functions approximations have to be made to obtain closed equations. For complicated systems the approximations are very often uncontrolled but the only possibility to make progress. In a few cases like the glass transition problem they can lead to astonishingly interesting even quantitatively correct results.⁽¹³⁻¹⁵⁾ In the glass transition problem an equilibrium projection operator, the Mori–Zwanzig projection operator is used to derive equations for the density–density correlation function of simple glass formers. The memory functions are approximated with the help of mode coupling approximations, first systemically explored by Kawasaki.^(16,17) This projection operator is only valid if the system to be described is in thermodynamic equilibrium. Ideal glasses do not fulfill this condition. Therefore, although a glass transition is predicted within the mode coupling theory of the glass transition,⁽¹⁸⁾ the equations are only justified as long as the system is in the supercooled state. Inconsistencies arise as soon as the ideal glass state is entered.⁽¹⁹⁾ Progress in this problem was first achieved by extending simple spin glass models which exhibit a glass transition analogous to the structural glass transition⁽²⁰⁻²²⁾ to non equilibrium situations with the help of field theoretic techniques.^(23,24) In this approach exact equations for the correlation functions and susceptibilities of the mentioned simple mean field p -spin models were derived without making any equilibrium assumption. This allowed to discuss the violation of the fluctuation dissipation theorem (FDT) in those spin glass systems and to identify interesting generalizations of the FDT in glasses. Since the validity of the FDT is implicitly assumed to be valid in the Zwanzig–Mori projection operator formalism even in the glassy regime, the mode coupling theory based on this approach⁽¹⁸⁾ leads to qualitatively incorrect results for the *idealized* glass state. It is only due to the existence of hopping processes which smear out the ideal glass transition and allow equilibration also below the glass transition temperature of the idealized theory transition, that some of the results for the idealized theory survive also below the glass transition. Notable exceptions where this argument is not applicable are colloidal systems which do not seem to exhibit hopping phenomena, and

numerical or experimental techniques which allow to perform experiments immediately after a quench within a time shorter than the nearly diverging time scale of the slowest relaxation in supercooled systems, the so called α - or structural relaxation time. If this time scale is long due to a complex molecular structure as, e.g., in polymers or in systems with hydrogen bonding⁽²⁵⁾ it is very likely to observe violations of the FDT and related non equilibrium phenomena like aging.⁽²⁶⁾ Unfortunately these kinds of systems are too complicated to be treated with the help of field theoretic techniques. It is therefore interesting to extend the projection operator approach to out of equilibrium situations. First steps with the help of the Kawasaki–Gunton (K–G) projection operator⁽²⁷⁾ have been done in ref. 28. Within this approach it is conceptually difficult to obtain *exact* equations for correlation functions and susceptibilities. This problem could be circumvented in ref. 29 where the final equations obtained by an alternative projection operator were evaluated in mode coupling approximation, obtaining violations of the FDT for structural glasses. It is the purpose of the present paper to derive explicitly this alternative non–equilibrium projection operator formalism and to discuss its differences from the K–G projection operator. To make the discussion not too abstract I will discuss the specific problem of quenching a simple liquid from the liquid into the glass and fixing its temperature with the help of a Gaussian thermostat.

2. EQUATION OF MOTION

I consider an N -particle system, which, in equilibrium, is described by a Hamilton function $H = \sum_j \vec{p}_j^2/2m + \frac{1}{2} \sum_{i \neq j} V(|\vec{r}_i - \vec{r}_j|)$. A convenient measure for the temperature is the average of the kinetic temperature per particle $3/(2\beta) = \langle \sum_j \vec{p}_j^2/2m \rangle / N := K$. It has been shown, that this definition is also applicable in out of equilibrium situations.^(30, 31) The physical situation I want to describe is a quench from an initial equilibrium state at temperature $T_i = 1/\beta_i$ to a final state at temperature $T = 1/\beta$. The overall density and the volume are kept constant. In practice this is achieved by changing the temperature of the heat bath coupled to the system under investigation. A simplified theoretical description is obtained under the plausible assumption that the kinetic energy is equilibrating very quickly with the external temperature. The non-equilibrium processes occurring in the system after the quench are, under this assumption, related only to relaxation of structural degrees of freedom. This ansatz was successfully used to describe time dependent thermodynamic derivatives in glassy systems.^(30, 31) Therefore it is justified to replace the original problem by a slightly simpler situation, where an artificial thermostat is coupled to each

individual particle such that the average of the total kinetic energy is kept strictly constant in time. This thermostat is the well known Gaussian thermostat, used in non-equilibrium molecular dynamic simulations.⁽³²⁾ The equation of motion for a function $A(\vec{r}_j(t), \vec{p}_j(t))$ of the phase space variables $\vec{r}_j(t), \vec{p}_j(t)$ can be modeled by a time dependent differential operator $L(t)$:

$$\frac{dA}{dt} = iU(t, 0) L(t) A(0) = U(t, 0) \left(iL_0 A + \sum_j \alpha(t) \vec{p}_j(0) \frac{\partial}{\partial \vec{p}_j(0)} A(\vec{r}_i, \vec{p}_i) \right) \quad (1)$$

where $U(t, 0) = T_+ \exp(i \int_0^t L(t') dt')$ is a time ordered product (time increases from left to right). $L_0 = -i\{H, \cdot\}$ is the Liouville operator. $\alpha(t)$ is the Gaussian thermostat which couples to each individual particle. It is adjusted such that $\langle \sum_j \frac{\vec{p}_j^2(t)}{2m} \rangle \frac{2}{3} = N/\beta$ for all times t . I used the notation $\{A, B\} = \sum_j \frac{\partial A}{\partial \vec{r}_j} \frac{\partial B}{\partial \vec{p}_j} - \frac{\partial A}{\partial \vec{p}_j} \frac{\partial B}{\partial \vec{r}_j}$ for the Poisson bracket. Applying (1) to the phase space variables leads to the well known equation of motion for a thermostated system

$$\frac{d\vec{r}_j(t)}{dt} = \vec{p}_j/m \quad (2)$$

$$\frac{d\vec{p}_j(t)}{dt} = -\frac{\partial V(\{\vec{r}(t)\})}{\partial \vec{r}_j(t)} + \alpha(t) \vec{p}_j(t) \quad (3)$$

The necessity of applying the thermostat arises since the initial probability density ρ_{ne} has to describe a situation where the kinetic energy is equilibrated at the lower temperature, $K(t=0) = 3/(2\beta)$, but the structural part of the partition function $Z_S = \langle \exp -\beta_i V \rangle$ is the one at the higher temperature $1/\beta_i$. This is achieved by choosing $\rho_{Ne} = \exp(-\beta K - \beta_i V)/Z$, where Z is the non-equilibrium partition function. An exact expression for $\alpha(t)$ is obtained by multiplying (3) from left with $\vec{p}_j(t)$, averaging over the non-equilibrium ensemble and using the requirement $m dK(t)/dt = \langle \vec{p}_j(t) d\vec{p}_j(t)/dt \rangle = 0$. The thermostat can therefore be expressed as

$$\alpha(t) = \frac{\beta}{3m} \langle \vec{p}_j(t) \partial V / \partial \vec{r}_j(t) \rangle = \frac{\beta}{3m} \left\langle \frac{dV}{dt} \right\rangle \quad (4)$$

The only possibility to study equations of motion like (2), (3) under the described boundary conditions “exactly” was the use of molecular dynamic simulations.⁽³³⁻³⁵⁾ These simulations show that quenching from a liquid state into a glassy state leads to interesting non-equilibrium phenomena

already on the level of two point density–density correlation functions and the corresponding susceptibilities.^(33–35) It is therefore interesting to study Eqs. (2) and (3) not directly, but its consequences on the density–density two point correlation function and susceptibilities.

The density and current fluctuations are defined by $n_q(t) = \sum_j e^{i\vec{q}\vec{r}_j(t)}$ and $j_q(t) = \sum_j \frac{\vec{q}\vec{p}_j}{qm} e^{i\vec{q}\vec{r}_j(t)}$. Here I chose only the longitudinal current fluctuations parallel to the external wave vector \vec{q} . With these two variables the particle conservation and the momentum conservation in the direction of \vec{q} is taken into account. In principle also the energy conservation could be dealt with explicitly.^(30,31) The equation of motion for the variables under consideration follows from (1):

$$\frac{dn_q(t)}{dt} = i \frac{q}{m} j_q(t) / m \quad (5)$$

$$\frac{dj_q(t)}{dt} = iU(t, 0) L_0 j_q(0) + \alpha(t) j_q(t) \quad (6)$$

The force fluctuation $U(t, 0) L_0 j_q(0)$ can be split into two contributions: one which is directly proportional to the density and current fluctuation and one “perpendicular” to it. If there were only a linear contribution with known coefficients the solution of the equation of motion were extremely simple. This is of course not the case in general. The most interesting physics is hidden in the “perpendicular” part. It is also obvious that the meaning of “perpendicular” is not unique but depends on the scalar product which we define in the space of fluctuations. The problem is to find the scalar product which is best adapted to the kind of problems to be solved. Having defined the scalar product which I will do below, the splitting can be achieved by introducing a projection operator $P(t)$, such that $U(t, 0) P(t) A_i(0) = A_i(t)$, where $A_i(0) = n_q(0), j_q(0)$ for $i = 1, 2$, respectively. To describe non-equilibrium fluctuations the projection operator is in general time-dependent, expressing the fact that the statistically relevant states are changing with time if not all degrees of freedom are in equilibrium with the external boundary conditions. The problem of defining the appropriate scalar product is therefore equivalent to defining an appropriate projection operator.

Since one of the goals of the theory is to discuss the fluctuation dissipation theorem in out of equilibrium situations it would be useful to derive a theory in which the correlation functions and susceptibilities occur explicitly without any additional approximation. The Kawasaki–Gunton projection operator $P_c(t) = |A_i(0)\rangle S_{ij}^{-1}(t) \langle A_j(t) | U(t, 0)$ ⁽²⁷⁾ used in ref. 28

does not fulfill this requirement. Here $S_{ij}(t) = (A_i(t) | A_j(t)) = \langle \delta A_i^*(t) \delta A_j(t) \rangle_{ne}$ is the equal time non-equilibrium correlation function of the fluctuations $\delta A_i^*(t) = A_i^*(t) - \langle A_i^*(t) \rangle$, where * means complex conjugation. It was noted in ref. 28 that with this projection operator based on the correlation functions the susceptibility can only be defined with help of memory functions. Only within a mode coupling ansatz the susceptibilities is directly related to an explicit entity of the theory, the fluctuation propagator $N_{jn}^c(t_1, t)$. $N_{jn}^c(t_1, t)$ can, within the Kawasaki-Guntton approach, exactly be written in terms of two time correlation functions and equal time correlation functions^(9, 28)

$$N_{jn}^c(t_1, t) = \mathbf{S}_{jj}^{-1}(t_1) C_{jn}(t_1, t) + \mathbf{S}_{jn}^{-1}(t_1) C_{mn}(t_1, t) \quad (7)$$

The susceptibility $\chi_q(t_1, t) = \langle \{n_q^*(t_1), n_q(t)\} \rangle_{ne} := [n_q(t_1) | n_q(t)]$ is then given by

$$\chi_q(t_1, t) = -i \frac{q}{m} N_{jn}^c(t_1, t) + iq \int_{t_1}^t dt' [n_q(t_1), F_q^c(t_1, t')] N_{jn}^c(t', t) \quad (8)$$

Here $F_q^c(t_1, t')$ is the random force of the K-G projection operator formalism which is uncorrelated with density and current fluctuations at t_1 , i.e., which fulfills the condition $(A_i(t_1) | F_q(t_1, t)) = 0$, where $A_i(t_1) = n_q(t_1), j_q(t_1)$, for $i = 1, 2$, respectively. It is important to note that the Poisson bracket of A_i with the random force occurring in (8) does not vanish in general. If we assume, that for long times $t_1, t \rightarrow \infty$ velocity fluctuations at time t and fluctuations of the spatial degrees of freedom at the same time are becoming uncorrelated again and that the velocity fluctuations are Maxwell distributed at the temperature of the heat bath, the equal time correlation of density and current fluctuations are simplifying considerably. It is then

$$\lim_{t \rightarrow \infty} \mathbf{S}(t) = N \begin{pmatrix} S_q^\infty & 0 \\ 0 & 1/\beta m \end{pmatrix} \quad (9)$$

S_q^∞ is the static structure factor reached for very long times and it was used that $\lim_{t \rightarrow \infty} S_{jn}(t) = (n_q(t) | j_q(t)) = 0$. Putting this form back into (8) and using $\partial C(t_1, t) / (\partial t_1) = -iq C_{jn}(t_1, t)$ leads to a generalization of the fluctuation dissipation theorem in the form

$$T \chi_q(t_1, t) = \frac{\partial C_{mn}(q; t_1, t)}{\partial t_1} - \int_{t_1}^t dt' \delta X_q(t_1, t') \frac{\partial C_{mn}(q; t', t)}{\partial t'} \quad (10)$$

where $\delta X_q(t_1, t') = m[n_q(t_1), F_q^c(t_1, t')]$. In equilibrium the FDT violation $\delta X_q(t_1, t')$ is exactly zero, since in equilibrium the average of the Poisson bracket of the density fluctuation at t_1 and the random force between t_1 and t vanishes due to $[n_q, F_q] = \beta(\{n_q, H\} | F_q) = -iq\beta(j_q | F_q) \equiv 0$. If in non-equilibrium situations the Poisson bracket with the random force were exactly given by its instantaneous Markovian part $\delta X_q^{\text{markov}}(t_1, t') = (1 - X_q) \delta(t_1 - t)$, the generalization $T\chi_q(t_1, t) = -X_q \partial C_m(q; t_1, t) / \partial t$ found for p -spin models and random manifolds⁽³⁶⁾ were obtained. Due to the existence of renormalized corrections $\delta X_q^{\text{renorm}}(t_1, t)$, deviations from this form are possible. The experimental verification of the Markovian form of (10) in simple glass formers^(33, 35, 37) might be related to the fact that any simple mode coupling approximation where the random force is expressed in terms of all possible pairs of density and current fluctuations $F_q(t_1, t) = Q_c(t_1) |n_{q-k}(t_1) n_k(t_1)\rangle R_{q,k}^{(1)}(t_1, t) + Q_c(t_1) |n_{q-k}(t_1) j_k(t_1)\rangle R_{q,k}^{(2)}(t_1, t) + Q_c(t_1) |j_{q-k}(t_1) j_k(t_1)\rangle R_{q,k}^{(3)}(t_1, t)$ leads to a vanishing renormalized part. The form of the $R^{(\alpha)}(t_1, t)$ is not important for the argument. The vanishing of the simplest mode coupling contributions can easily be checked by evaluating the Poisson brackets of $n_q(t_1)$ with all occurring pairs projected with $Q_c(t_1)$ perpendicular (in the K-G definition) to density and current fluctuations and averaging the result over the non-equilibrium ensemble.

With the K-G approach, we therefore recover the simplified Markovian form of the generalization of the FDT within mode coupling approximations, but a separate theory for the Markovian term is needed. Instead of doing this, it seems to be more reasonable to work out a projection operator formalism which leads immediately to separate equations for susceptibilities and correlation functions. This goal can be achieved by introducing a projection operator formalism which is based on Poisson brackets instead of correlation functions

$$P(t) = |A_i(0)\rangle \chi_{ij}^{-1}(t, t) [A_j(t) | U(t, 0) \equiv 1 - Q(t) \quad (11)$$

where $A_i(t) = n_q(t), j_q(t)$ for $i = 1, 2$, respectively. Its action on any function of the phase space variables $B(\vec{r}_i(t), \vec{p}_i(t))$ is given by $P(t) B(\vec{r}_i(0), \vec{p}_i(0)) = |A_i(0)\rangle \chi_{ij}^{-1}(t, t) [A_j(t) | U(t, 0) B(\vec{r}_i(0), \vec{p}_i(0))] = |A_i(0)\rangle \chi_{ij}^{-1}(t, t) [A_j(t) | B(\vec{r}_i(t), \vec{p}_i(t))]$. Contrary to the correlation functions the equal time susceptibilities can be evaluated exactly for all times t even in non-equilibrium

$$\chi(t, t) = N \begin{pmatrix} 0 & -iq/m \\ -iq/m & 0 \end{pmatrix} \quad (12)$$

The projection operator therefore has the simple form

$$P(t) = \frac{im}{Nq} (|n_q(0)\rangle [j_q(t) | U(t, 0) + |j_q(0)\rangle [n_q(t) | U(t, 0) \quad (13)$$

It has all the properties of a general time dependent projection operator listed in ref. 9. Especially to note are

$$P(t_1) P(t) = P(t) \quad (14)$$

$$\frac{dP(t)}{dt} = \dot{P}(t) = P(t) \dot{P}(t) Q(t) \quad (15)$$

These two conditions are used to derive equations of motion for the density and current fluctuations. The procedure is completely general.⁽⁹⁾

$$\frac{d \delta n_q(t)}{dt} = iq \delta j_q(t) \quad (16)$$

$$N \frac{d^2 \delta n_q(t)}{dt^2} = -NU(t, 0) L(t) \delta j_q(0) \quad (17)$$

$$\begin{aligned} &= -im \delta n_q(t) [j_q(t) | L(t) j_q(t)] - im \delta j_q(t) [n_q(t) | L(t) j_q(t)] \\ &+ m \int_{t_1}^t dt' \delta n_q(t') \Sigma_q(t', t) \\ &- NqU(t_1, 0) Q(t_1) G(t_1, t) L(t) \delta j_q(0) \end{aligned} \quad (18)$$

The time t_1 is an arbitrary time smaller than t . The memory function $\Sigma_q(t_1, t)$ is an explicit function of two times.

$$\Sigma_q(t_1, t) = [Lj_q(t_1) | U(t_1, 0) Q(t_1) G(t_1, t) L(t) \delta j_q(0)] \quad (19)$$

$$G(t_1, t) = \mathcal{F} \exp \left(i \int_{t_1}^t dt' L(t') Q(t') \right) \quad (20)$$

where the operator \mathcal{F} induces a time ordering from left to right. $\Sigma(t_1, t)$ is the average of the Poisson bracket of the force $L(t_1) j_q(t_1)$ at time t_1 and the fluctuating force

$$F_q(t_1, t) = U(t_1, 0) Q(t_1) G(t_1, t) L(t) \delta j_q(0) \quad (21)$$

between t_1 and t . It is very important to note that this fluctuation force is *not* uncorrelated with the fluctuations at t_1 , i.e., $(A_i(t_1) | F_q(t_1, t)) \neq 0$ in general. The name fluctuating force is justified since it is not susceptible to changes in the generalized chemical potentials $\mu_i(t_1)$ at t_1 which couple to density and current fluctuations respectively, i.e., its Poisson bracket with density and current fluctuations at t_1 are zero:

$$[n_q(t_1) | F_q(t_1, t)] = 0 \quad (22)$$

$$[j_q(t_1) | F_q(t_1, t)] = 0 \quad (23)$$

Due to this property the time dependent differential operator $L(t)$ can be replaced by the Liouville operator L_0 in the fluctuating force and in the memory functions since the thermostat leads to a term proportional to the current fluctuation in the force $L(t) j_q(0)$, i.e., $F_q(t_1, t) = U(t_1, 0) Q(t_1) G(t_1, t) L_0 j_q(0)$ and $\Sigma_q(t_1, t) = [L_0 j_q(t) | F_q(t_1, t)]$.

Equations (16) and (17) have the form of an inhomogeneous integro-differential equation, the random force $F_q(t_1, t)$ being the inhomogeneous term. This set of equations can successively be solved by first introducing a formal solution $N_{kl}(q; t_1, t)$ of the homogeneous equation where $k, l \in \{1 \equiv n_q, 2 \equiv j_q\}$ and then constructing the full solution with $N_{ij}(q; t_1, t)$ and the inhomogeneous term. The functions $N_{ij}(q, t_1, t)$ are defined by the homogeneous set of equations

$$\frac{\partial N_{k1}(q, t_1, t)}{\partial t} = iq N_{k2}(q, t_1, t) \quad (24)$$

$$N \frac{\partial^2 N_{k2}(q, t_1, t)}{\partial t^2} = -im N_{k1}(q, t_1, t) [j_q(t) | L_0 j_q(t)] + \alpha(t) q N_{k2}(q, t_1, t) + m \int_{t_1}^t dt' N_{k1}(q; t_1, t') \Sigma_q(t', t) \quad (25)$$

with the initial condition $N_{ij}(q; t_1, t_1) = \delta_{ij}$. I have also used $[n_q(t) | L_0 j_q(t)] = 0$ and $[j_q(t) | j_q(t)] = 0$ to simplify the linear terms in Eqs. (24) and (25). It can easily be checked that the full solutions are then given by

$$\delta n_q(t) = \delta n_q(t_1) N_{11}(q; t_1, t) + \delta j_q(t_1) N_{21}(q; t_1, t) + i \int_{t_1}^t F_q(t_1, t') N_{21}(t', t) \quad (26)$$

$$\delta j_q(t) = \delta n_q(t_1) N_{12}(q; t_1, t) + \delta j_q(t_1) N_{22}(q; t_1, t) + i \int_{t_1}^t F_q(t_1, t') N_{22}(t', t), \quad (27)$$

The homogeneous solutions are exactly related to the susceptibilities. Using Eqs. (22), (23), (26), and (27) the susceptibilities can be expressed by

$$\chi_{m}(q; t_1, t) = -i \frac{q}{m} N_{21}(q; t_1, t) \quad (28)$$

$$\chi_{jn}(q; t_1, t) = -i \frac{q}{m} N_{11}(q; t_1, t) \quad (29)$$

$$\chi_{nj}(q; t_1, t) = -i \frac{1}{q} \partial \chi_{m}(q; t_1, t) / \partial t \quad (30)$$

$$\chi_{jj}(q; t_1, t) = -i \frac{1}{q} \partial \chi_{jn}(q; t_1, t) / \partial t \quad (31)$$

This linear relation should be contrasted with the relation (8) in the Kawasaki–Gunton projection operator formalism.

The result for the correlation function can formally be obtained by multiplying Eqs. (26) and (27) from left with the fluctuations at t_1 and averaging over the non-equilibrium ensemble. By doing so they are expressed by the unknown equal time correlation functions and the unknown correlation of the fluctuations with the fluctuating force. To obtain a more satisfying result it is therefore useful to derive equations for the correlation functions from the equations for the fluctuations. Since only the initial state ($t_1 = 0$) is known, the time t_1 should be put to zero. Multiplying Eq. (17) from left with the density fluctuation $n_q^*(t_w)$ at some waiting time t_w from left and averaging over the non-equilibrium ensemble the equation for the density–density correlation function $C_{nn}(q; t_w, t)$ is obtained:

$$\begin{aligned} N \frac{\partial^2 C_{nn}(q, t_w, t)}{\partial t^2} &= -im C_{nn}(q, t_w, t) [j_q(t) | L_0 j_q(t)] + \alpha(t) q C_{nj}(q, t_w, t) \\ &+ m \int_0^t dt' C_{nn}(q; t_w, t') \Sigma_q(t', t) \\ &- N q (n_q(t_w) | Q(0) G(0, t) L(t) j_q(0)) \end{aligned} \quad (32)$$

The unknown correlation function $(n_q(t_w) | Q(0) G(0, t) L(t) j_q(0))$ can be simplified in two steps. First we use the K–G projection operator at time $t_1 = 0$ to express explicitly the direct correlation to the initial density and current fluctuations.

$$\begin{aligned}
& (n_q(t_w) | F_q(0, t)) \\
&= C_{nn}(q; t_w, 0) \frac{1}{S_{nn}(0)} (n_q(0) | F_q(0, t)) \quad (33)
\end{aligned}$$

$$+ C_{nj}(q; t_w, 0) \frac{1}{S_{jj}(0)} (j_q(0) | F_q(0, t)) + (n_q(t_w) | Q_c(0) F_q(0, t)) \quad (34)$$

With the help of Eqs. (26) and (28), the second part of Eq. (34) can then be transformed into

$$(n_q(t_w) | Q_c(0) F_q(0, t)) = \frac{m}{N} \int_0^{t_w} dt' \chi_{nn}^*(q; t', t_w) M_q(t', t) \quad (35)$$

Here $M_q(t', t)$ is the correlation function of the random forces between 0 and t' , and 0 and t respectively.

$$M_q(t', t) = (F_q(0, t') | Q_c(0) | F_q(0, t)) \quad (36)$$

The equation for the correlation function therefore reads

$$\begin{aligned}
N \frac{\partial^2}{\partial t^2} C_q(t_w, t) &= -imC_q(t_w, t)[j_q(t) | L_0 j_q(t)] \\
&\quad - im\alpha(t) \frac{\partial}{\partial t} C_q(t_w, t) + m \int_0^t dt' C_q(t_w, t') \Sigma_q(t', t) \\
&\quad + m \int_0^{t_w} dt' \chi_q^*(t', t_w) M_q(t', t) \\
&\quad - qC_q(t_w, 0) \frac{1}{S_q(0)} (n_q(0) | F_q(0, t)) \\
&\quad - qC_{nj}(q; t_w, 0) \frac{1}{S_{jj}(0)} (j_q(0) | F_q(0, t)) \quad (37)
\end{aligned}$$

Using Eqs. (24), (25), (28), and (29), the equation for the density-density susceptibility is

$$\begin{aligned}
N \frac{\partial^2}{\partial t^2} \chi_q(t_w, t) &= -im\chi_q(t_w, t)[j_q(t) | L(t) j_q(t)] \\
&\quad - im\alpha(t) \frac{\partial}{\partial t} \chi_q(t_w, t) + m \int_{t_w}^t dt' \chi_q(t_w, t') \Sigma_q(t', t). \quad (38)
\end{aligned}$$

The unknown thermostat can also be expressed in terms of correlation functions and memory functions. Since the thermostat is coupling to each individual particle it is necessary to repeat the presented derivation of the collective density and current fluctuations for the single particle density and current fluctuations, $n_q^s(t) = \exp(iq\vec{r}_s(t))$ and $j_q^s(t) = (\vec{q}/q) \vec{v}^s(t) \exp(iq\vec{r}_s(t))$, respectively. The procedure is completely analogous to the one for the collective fluctuations. Also the equations for single particle correlation functions and susceptibilities have exactly the same structure as the one for the collective fluctuations. An equation for the thermostat is then obtained from the requirement that the single particle current correlation function at equal times $(j_q^s(t) j_q^s(t)) = (\vec{v}^s(t) | \vec{v}^s(t))/3$ is constant equal to $1/(\beta m)$ due to the thermostat requirement. It is of course also possible to find other approximation strategies for the exact expression (4). For very long times the effect of the thermostat can be neglected since a simple scaling argument based on (4) shows that $\alpha(t)$ decays at least as $1/t$ since it is the time derivative of the total potential energy.

It was shown in ref. 29 that the set of Eqs. (37) and (38) leads in mode coupling approximation to a generalized theory for the fluctuation dissipation ratio originally introduced in ref. 23 for p -spin systems and it allows to formulate a theory for the structure factor of a glass $\lim_{t \rightarrow \infty} S_q(t) = S_q^\infty$, i.e., in the non-ergodic state. This structure factor does not only depend on the external thermodynamic parameters but also on the degree of non-ergodicity F_q measured in terms of the two point correlation functions $F_q = \lim_{t \rightarrow \infty} \lim_{t_w \rightarrow \infty} C_{nn}(q; t_w, t)$.

Here I want to show that Eqs. (37) and (38) reduce to the standard Mori equations for the correlation functions, if the initial state is an equilibrium state and the external heat bath temperature is the same as the temperature of the canonical equilibrium distribution. In this case the Gaussian thermostat can be put to zero, $\alpha(t) \equiv 0$.

In equilibrium the susceptibility and the correlation function are time translational invariant and they obey the fluctuation dissipation theorem $\frac{dC_q(t-t_w)}{dt} = -T\chi(t-t_w)$. This is a special case of the general relation

$$[A | B(t)]_{eq} = \beta(A | \{H, B(t)\}) = -\frac{d}{dt} (A | B(t))_{eq} = \beta(\dot{A} | B(t))_{eq} \quad (39)$$

which can easily be obtained by partial integrations in the canonical ensemble. It is also possible to show (see Appendix) that in equilibrium the memory functions $\Sigma(t-t_w)$ and $M(t-t_w)$ obey a FDT of the second kind.

$$\frac{dM_q(t-t_w)}{dt} = -T\Sigma_q(t-t_w) \quad (40)$$

Due to relation (39) the relation $(j_q(0) | F_q(0, t)) \propto [n_q(0) | F_q(0, t)] = 0$ is valid. The equation for the correlation function (37) can therefore be written (again making use of (39)) as

$$\begin{aligned}
 N \frac{\partial^2}{\partial t^2} C_q(t_w, t) &= -m\beta((L_0 j_q | L_0 j_q) - M(t, t)) C_{nn}(q; t_w, t) \\
 &\quad - m\beta \int_{t_1}^t dt' \frac{d}{dt'} C_{nn}(q; t' - t_w) M_q(t - t') \\
 &\quad + m \int_0^{t_w} dt' \left(\chi_q(t_w - t') - \beta \frac{d}{dt'} C_{nn}(q; t' - t_w) \right) M_q(t', t) \\
 &\quad - q C_q(t_w, 0) \left(\frac{1}{S_q(0)} (n_q(0) | F_q(0, t)) + \frac{m\beta}{q} M(0, t) \right) \quad (41)
 \end{aligned}$$

Using the definition of $M_q(t_w, t)$ (36) in equilibrium and the FDT for the correlation function it can be seen that the last two lines of Eq. (41) vanish and that the equation for the correlation function can be written as

$$\begin{aligned}
 \frac{\partial^2}{\partial t^2} C_q(t_w, t) &= -m\beta(L_0 j_q | P_c | L_0 j_q) C_{nn}(q; t_w, t) \\
 &\quad - m\beta \int_{t_1}^t dt' \frac{d}{dt'} C_{nn}(q; t' - t_w) M_q(t - t') \quad (42)
 \end{aligned}$$

Here it was used that $P_c = 1 - Q_c$. With $(L_0 j_q | P_c | L_0 j_q) = (L_0 j_q | n_q)(n_q | L_0 j_q) / S_{nn}(q) = (q/m\beta)^2 / S_{nn}(q)$ the standard Mori form of the equation of motion for the density–density correlation function is obtained.

3. CONCLUSION

I presented an alternative time dependent non-equilibrium projection operator formalism which allows to derive equation of motion not only for the correlation functions but also for susceptibilities. First interesting results using this new projection operator have been presented in ref. 29. The presented projection operator is based on Poisson brackets, i.e., on susceptibilities instead of on correlation functions as in the Kawasaki–Gunton projection operator used in ref. 28. It is important to realize, that there are no a priori arguments which allow to decide which approach is more appropriate. E.g., the Kawasaki–Gunton operator allows to derive the most general form of the FDT in non equilibrium situations (see Eqs. (8) and (10)), where the projection operator (11) ultimately leads in

mode coupling approximation to a theory for the Markovian contribution of the general FDT obtained with the K–G operator. Also in physical situations where the equal time correlation function does not reach a stationary state on human time scales and if there are, e.g., experimental informations or general scaling arguments for their time dependence available, it cannot be excluded that the K–G-approach is more appropriate since the equal time correlation function appears explicitly in the equation of motion for the two time density–density correlation functions. I also want to mention that there is another method available⁽³⁸⁾ to derive non-equilibrium equations of motion for the correlation functions which are structurally equivalent to the Equations obtained in ref. 28 with the K–G-operator. The origin of this equivalence was noted (on a very abstract level) in ref. 39.

To tackle the fundamentally and practically important problem of non-equilibrium relaxations in structural glasses and soft condensed matter it is crucial to have reliable starting points for approximations. It is the hope that the development of exact non-equilibrium equations of motion for density fluctuations in simple systems could be the guide to develop equations of motion, based on sound statistical concepts, for more complicated physical systems like polymers or structural glasses with internal degrees of freedom and also for more complicated physical situations like sheared driven systems.

APPENDIX. THE FLUCTUATION DISSIPATION THEOREM OF THE SECOND KIND

In equilibrium the projection operator $Q(t)$ is time independent $Q(t) \equiv Q$. The memory function $\Sigma(t-t')$ in equilibrium is given by

$$\Sigma(t-t') = [L_0 j_q(0) | Q \exp(iLQ(t-t')) | L j_q(0)] \quad (43)$$

$$= [Q \exp(iLQ t') L_0 j_q(0) | Q \exp(iLQ t) L_0 j_q(0)] \quad (44)$$

In the last equality it was used that Q and L are self adjoint operators with respect to $[\cdot | \cdot]$. By using $P(t_1) P_c(t) = P_c(t)$ and the general relation (39) we arrive at

$$\Sigma_q(t-t') = -\beta(Q_c Q \exp(iLQ t') L_0 j_q | \{\exp(iLQ t) L j, H\}) \quad (45)$$

$$= -\beta \frac{d}{dt} (Q \exp(iLQ t') L_0 j_q | Q_c \exp(iLQ t) L j) \quad (46)$$

$$= -\beta \frac{d}{dt} M_q(t-t') \quad (47)$$

It was used that $(Q_c A | B) = (A | Q_c B)$.

ACKNOWLEDGMENTS

It is a great pleasure to contribute to this volume in honor of the 65th birthday of Bob Dorfman. I had the privilege to spent two years as a post-doc with Bob. They belong to the most enriching and enjoyable years of my life as well in professional as in personal respect. Bob is combining in a truly unique way professional rigor with the best human qualities.

REFERENCES

1. L. Boltzmann, *Vorlesungen über Gastheorie* (Barth, Leipzig, 1896).
2. J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd Ed. (Academic Press, London, 1986).
3. B. J. Alder and W. Alley, *Physics Today* **37**:56 (1984).
4. E. G. D. Cohen, *Physics Today* **37**:64 (1984).
5. J. R. Dorfman and E. G. D. Cohen, *Phys. Rev. Lett.* **25**:1257 (1970).
6. M. H. Ernst and J. R. Dorfman, *Phys.* **61**:157 (1972).
7. M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuwen, *Phys. Rev. A* **4**:2055 (1971).
8. M. H. Ernst and J. R. Dorfman, *J. Statist. Phys.* **15**:311 (1976).
9. H. Grabert, *Projection Operator Techniques in Nonequilibrium Statistical Mechanics*, Springer Tracts in Modern Physics, Vol. 95, G. Höhler, ed. (Springer, Berlin, 1982).
10. S. Nakajima, *Prog. Theor. Phys.* **20**:948 (1958).
11. H. Mori, *Prog. Theor. Phys.* **33**:423 (1965).
12. R. Zwanzig, *J. Chem. Phys.* **33**:1338 (1960).
13. H. Z. Cummins, *J. Phys. Cond. Mat. A* **11**:95 (1999).
14. W. Götze, in *Liquids, Freezing and the Glass Transition*, J. P. Hansen, D. Levesque, and J. Zinn-Justin, eds. (North-Holland, Amsterdam, 1991).
15. W. Götze, *J. Phys. Cond. Mat. A* **11**:1 (1999).
16. K. Kawasaki, in *Phase Transitions and Critical Phenomena*, Vol. 5A, C. Domb and M. S. Green, eds. (Academic Press, London, 1976).
17. T. Keyes, in *Modern Theoretical Chemistry: Statistical Mechanics*, B. J. Berne, ed. (Academic Press, New York, 1977).
18. U. Bengtzelius, W. Götze, and A. Sjölander, *J. Phys. C* **17**:5915 (1984).
19. J. Jäckle, *J. Phys. Cond. Mat.* **1**:267 (1989).
20. T. R. Kirkparick and D. Thirumalai, *Phys. Rev. B* **36**:5388 (1987).
21. T. R. Kirkparick and D. Thirumalai, *Phys. Rev. B* **37**:5342 (1988a).
22. T. R. Kirkparick and D. Thirumalai, *Phys. Rev. A* **37**:4439 (1988b).
23. L. F. Cugliandolo and J. Kurchan, *Phys. Rev. Lett.* **71**:173 (1993).
24. A. Crisanti, H. Horner, and H. J. Sommers, *Z. Phys. B* **92**:257 (1993).
25. N. E. Israeloff and T. Grigera, *Europhys. Lett.* **43**:308 (1998).
26. L. C. E. Struick, *Physical Aging in Amorphous Polymers and Other Materials* (Elsevier, Houston, 1978).
27. K. Kawasaki and J. D. Gunton, *Phys. Rev. A* **4**(5):2048 (1973).
28. A. Latz, *J. Phys. Condens. Mat.* **12**:6353 (2000).
29. A. Latz, preprint, cond-mat/0106086 (2001b).
30. W. Götze and A. Latz, *J. Phys. Cond. Mat.* **1**:4169 (1989).
31. P. Scheidler, W. Kob, A. Latz, J. Horbach, and K. Binder, *Phys. Rev. B* **63** (2001).
32. D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Academic Press, London, 1990).

33. G. Parisi, *Phys. Rev. Lett.* **79**:3660 (1997).
34. W. Kob and J. L. Barrat, *Phys. Rev. Lett.* **78**:4581 (1997).
35. R. Di Leonardo, L. Angelani, G. Parisi, and G. Ruocco, *Phys. Rev. Lett.* **84**:6054 (2000).
36. L. F. Cugliandolo, J. Kurchan, and P. Le Doussal, *Phys. Rev. Lett.* **76**:2390 (1996).
37. J. L. Barrat and W. Kob, *Europhys. Lett.* **46**:637 (1999).
38. P. De Gregorio, F. Sciortino, P. Tartaglia, E. Zaccarelli, and K. A. Dawson, *preprint, cond-mat/0111018* (2001).
39. H. Furukawa, *Progr. Theoret. Phys.* **62**:70 (1979).