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Derivation of a generalized Langevin equation from a generic time-dependent Hamiltonian

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Abstract

The traditional Mori–Zwanzig formalism yields equations of motion, so-called generalized Langevin equations (GLEs), for phase-space observables of interest from the microscopic dynamics of a many-body system governed by a time-independent Hamiltonian using projection techniques. By using time-ordered propagators and time-independent projection operators, we derive the GLE for a scalar observable from a generic time-dependent Hamiltonian. The only restriction in our derivation is that the time-dependent part of the Hamiltonian and the observable of interest depend on spatial phase-space variables only. If the observable obeys Gaussian statistics and the time-dependent part of the Hamiltonian can be expressed as an odd power of the observable, the friction memory kernel in the GLE becomes proportional to the second moment of the complementary force, as is the case for a time-independent Hamiltonian in the Mori–Zwanzig formalism.

Supplementary material for this article is available online

Keywords: Mori–Zwanzig formalism, generalized Langevin equation, time-dependent Hamiltonian, non-equilibrium physics

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1. Introduction

For decades, physicists have been developing the theoretical description of non-equilibrium phenomena [1–7] with the aim to adapt and extend formalisms that work for equilibrium systems. In this paper, we focus on the Mori–Zwanzig formalism, which is a theoretical framework based on operator and projection techniques that allows to derive equations of motion for an observable of interest from the microscopic dynamics of the considered system [8–22].

To set the stage, we first review the equilibrium generalized Langevin equation (GLE) for a scalar observable of interest $A(\omega,t)$ derived from the equilibrium, i.e. time-independent, Hamiltonian $H_0(\omega)$ by Mori projection [23, 24]. The GLE is given by

$$\ddot{A}(\omega,t) = -K(A(\omega,t) - \langle A(\omega,t_0)\rangle) - \int_{t_0}^{t} ds\,\Gamma(t-s)\dot{A}(\omega,s) + F(\omega,t-t_0) \tag{1}$$

where

$$\langle X(\omega,t)\rangle \equiv \int_{\Omega} d\omega\,\rho_0(\omega)X(\omega,t) \tag{2}$$

defines the ensemble average over the phase space Ω of the general phase-space function $X(\omega,t)$ and

$$\rho_0(\omega) = \frac{e^{-\beta H_0(\omega)}}{Z(\beta)} \tag{3}$$

is the Boltzmann distribution determined by the Hamiltonian $H_0(\omega)$. Here $\beta \equiv 1/(k_B T)$ is the inverse thermal energy and $Z(\beta)$ denotes the partition function. The time-dependent Heisenberg observable satisfies the initial condition $A(\omega,t_0) = A_S(\boldsymbol{R})$, where $A_S(\boldsymbol{R})$ denotes the time-independent Schrödinger-type observable that only depends on spatial variables $\boldsymbol{R}$ and t_0 is the time at which the projection is performed. Thus, equation (1) is an equation of motion for the observable $A(\omega,t)$ in phase space Ω, K is the stiffness of an effective harmonic force, $\Gamma(t-s)$ is the friction memory kernel, and $F(\omega,t-t_0)$ the complementary force that takes into account the dynamics orthogonal to the projection space. $F(\omega,t-t_0)$ and $\Gamma(t-s)$ are related by

$$\Gamma(t-s) = \frac{\langle F(\omega,0)F(\omega,t-s)\rangle}{\langle \dot{A}(\omega,t_0)^2\rangle}, \tag{4}$$

which is often considered equivalent to the fluctuation dissipation theorem and is useful to reconstruct numerically the statistics of $F(\omega,t)$ from trajectories of $A(\omega,t)$.

While the derivation of GLEs for observables of interest from generic time-dependent Hamiltonian or Liouvillian dynamics often involves time-dependent projection operators [25, 26], it has been recently shown that if one adds to the time-independent Hamiltonian $H_0(\omega)$ a time-dependent part $H_1(\boldsymbol{R},t) = h(t)A_S(\boldsymbol{R})$, then one can derive the non-equilibrium Mori GLE for $A(\omega,t)$ from the total Hamiltonian $H(\omega,t) = H_0(\omega) - h(t)A_S(\boldsymbol{R})$ using time-independent projection operators [27]. In this paper we consider a much more general time-dependent Hamiltonian $H_1(\boldsymbol{R},t)$ that depends on all positional phase-space degrees of freedom $\boldsymbol{R}$, and show that the derivation of the non-equilibrium Mori GLE from $H(\omega,t) = H_0(\omega) - H_1(\boldsymbol{R},t)$ is still possible by using time-independent projection operators. We thus provide a Hamiltonian-based derivation of a non-equilibrium GLE, which in applications is typically introduced in an ad-hoc fashion [28–30]. Moreover, we show that if the observable $A(\omega,t)$ obeys Gaussian statistics and if the Hamiltonian satisfies certain conditions, the simple relation equation (4) is recovered. This finding is relevant, since many observables in complex systems exhibit Gaussian statistics [31, 32].

We illustrate our results by the example of a molecule that is embedded in a solvent and confined in a harmonic time-dependent external potential $H_1(\boldsymbol{R},t) = K_{ext}(t)(A_S(\boldsymbol{R}) - \langle A_S(\boldsymbol{R})\rangle)^2/2$, where $A_S(\boldsymbol{R})$ is the position of the center of mass of the molecule. This system has been previously studied by simulations in the limit of a time-independent confinement strength K_{ext}, [33], where it was shown that the friction memory kernel depends on K_{ext} in a non-trivial manner. Our formalism can in principle be used to analytically derive the dependence of the friction memory kernel on K_{ext}, as we outline later on.

The structure of our paper is the following: section 2 contains the complete derivation of the Mori GLE for the observable $A(\omega,t)$ from the microscopic dynamics of the system and can be skipped by a reader not interested in technical details. Section 3 discusses the properties of the GLE and shows how to recover a non-equilibrium version of equation (4) from the friction memory kernel when $A(\omega,t)$ is a Gaussian observable. Finally, section 4 presents a short discussion and an outlook.

2. Derivation of the non-equilibrium Mori GLE

2.1 Time-dependent Hamiltonian, Liouville operator, and microscopic dynamics of the system

We consider a classical system of N particles in three-dimensional space, characterized by particle masses, positions, and momenta. The core idea of the Mori–Zwanzig formalism is to derive an effective equation of motion for a time-dependent Heisenberg observable of interest $A(\omega,t)$ from the microscopic dynamics of this system, where $\omega \equiv (\boldsymbol{R},\boldsymbol{P})$ is a microscopic state, Ω the corresponding $6N$-dimensional phase space, and $\boldsymbol{R}$ and $\boldsymbol{P}$ are the generalized position and momentum vectors, which consist of the positions and momenta of all particles of the system.

The microscopic dynamics of the system are determined by a time-dependent Hamiltonian

$$H(\omega,t) = H_0(\omega) - H_1(\boldsymbol{R},t) \tag{5}$$

where $H_1(\boldsymbol{R},t)$ is the time-dependent contribution to $H(\omega,t)$ which we assume not to depend on $\boldsymbol{P}$, and $H_0(\omega)$ is the Hamiltonian of the equilibrium system which we assume to split into a kinetic and an interaction part according to [16, 23, 34–36]

$$H_0(\omega) = \sum_{n=1}^{3N} \frac{P_n^2}{2m_n} + V(\boldsymbol{R}). \tag{6}$$

For the above-mentioned example of a confined solvated molecule, $H_0(\omega)$ would be the Hamiltonian describing the interactions and kinetic energy of the solvent and the molecule, while $H_1(\boldsymbol{R},t)$ would consist of the external confinement potential acting on the molecule.

The microscopic dynamics of the non-equilibrium system are described by the Liouville equation

$$\partial_t \rho(\omega,t) = -\mathcal{L}(\omega,t)\rho(\omega,t), \tag{7}$$

a partial differential equation for the probability density $\rho(\omega,t)$ of a state ω in Ω at time t. It involves the Liouville operator

$$\mathcal{L}(\omega,t) = \sum_{n=1}^{3N} \left(\left[\partial_{P_n} H(\omega,t)\right] \partial_{R_n} - \left[\partial_{R_n} H(\omega,t)\right] \partial_{P_n} \right), \tag{8}$$

a partial differential operator that is linear in $H(\omega,t)$ and thus splits into

$$\mathcal{L}(\omega,t) = \mathcal{L}_0(\omega) - \mathcal{L}_1(\omega,t), \tag{9a}$$

where

$$\mathcal{L}_0(\omega) = \sum_{n=1}^{3N} \left(\frac{P_n}{m_n} \partial_{R_n} - \left[\partial_{R_n} V(\boldsymbol{R})\right] \partial_{P_n} \right) \tag{9b}$$

is the Liouville operator associated to $H_0(\omega)$ and

$$\mathcal{L}_1(\omega,t) = -\sum_{n=1}^{3N} \left[\partial_{R_n} H_1(\boldsymbol{R},t)\right] \partial_{P_n} \tag{9c}$$

is the Liouville operator associated to $H_1(\boldsymbol{R},t)$. All Liouville operators are anti-self-adjoint.

To solve the Liouville equation, we integrate equation (7) over time from t_0 to t and obtain

$$\rho(\omega,t) = \rho(\omega,t_0) - \int_{t_0}^{t} dt_1\, \mathcal{L}(\omega,t_1)\, \rho(\omega,t_1), \tag{10}$$

a recursive equation for $\rho(\omega,t)$ whose solution can be written as

$$\rho(\omega,t) = \exp_S\left(-\int_{t_0}^{t} dt' \mathcal{L}(t') \right) \rho(\omega,t_0). \tag{11a}$$

We defined a Schrödinger-type propagator

$$\exp_S\left(-\int_{t_0}^{t} dt' \mathcal{L}(t') \right) \equiv \mathcal{I} + \sum_{n\geqslant 1} (-1)^n \left(\prod_{k=1}^{n} \int_{t_0}^{\delta_{k,1}t+(1-\delta_{k,1})t_{k-1}} dt_k \prod_{j=1}^{n} \mathcal{L}(t_j) \right), \tag{11b}$$

where $\mathcal{I}$ is the identity operator and

$$\prod_{k=1}^{n} \int_{t_0}^{\delta_{k,1}t+(1-\delta_{k,1})t_{k-1}} dt_k \equiv \int_{t_0}^{t} dt_1 \ldots \int_{t_0}^{t_{n-1}} dt_n \tag{11c}$$

is a nested product of integrals and

$$\prod_{j=1}^{n} \mathcal{L}(t_j) \equiv \mathcal{L}(t_1) \ldots \mathcal{L}(t_n) \tag{11d}$$

is a time-ordered product of $\mathcal{L}(t)$. In order to simplify our notation, we have suppressed the dependency of $\mathcal{L}(t)$ on ω.

2.2 Schrödinger and Heisenberg observables

The expectation value of a scalar observable $A_S(\omega)$ is given by

$$a(t) \equiv \int_\Omega d\omega\, \rho(\omega,t) A_S(\omega), \tag{12}$$

where $A_S(\omega)$ denotes a scalar time-independent Schrödinger observable. By using that all Liouville operators are anti-self-adjoint, we rewrite equation (12) as

$$a(t) = \int_\Omega d\omega\, \rho(\omega,t_0) A(\omega,t) = \langle A(\omega,t)\rangle, \tag{13a}$$

where we introduced the Heisenberg observable

$$A(\omega,t) \equiv \exp_H\left(\int_{t_0}^{t} dt' \mathcal{L}(t')\right) A_S(\omega) \tag{13b}$$

and defined a Heisenberg-type propagator

$$\exp_H\left(\int_{t_0}^{t} dt' \mathcal{L}(t')\right) \equiv \mathcal{I} + \sum_{n\geqslant 1}\left(\prod_{k=1}^{n}\int_{t_0}^{\delta_{k,1}t+(1-\delta_{k,1})t_{k-1}} dt_k \prod_{j=n}^{1}\mathcal{L}(t_j)\right). \tag{13c}$$

The Heisenberg observable has the initial value

$$A(\omega,t_0) = A_S(\omega), \tag{14}$$

as follows from equation (13b). In order to simplify the notation, we do not specify the dependency of $A(\omega,t)$ on t_0.

Since $\mathcal{L}(t)$ and $\mathcal{L}(t')$ for $t \neq t'$ in general do not commute and the order of the operator products in equation (13c) is reversed in comparison with equation (11b), the propagator in equation (13c) is different from the one in equation (11b). By analogy with quantum mechanics, we call them Schrödinger and Heisenberg propagators and distinguish them by the S and H subscripts. If we replace the initial density distribution $\rho(\omega,t_0)$ by $\delta(\omega-\omega_0)$ in equation (13a), it is easily seen that $A(\omega,t)$ is nothing but the conditional expectation of $A_S(\omega)$ at time t, given that the initial state of the physical system is ω_0.

Using the rules for computing the time-derivatives of the Heisenberg propagator with respect to t [27], the first and second time derivatives of $A(\omega,t)$ are given by

$$\dot{A}(\omega,t) = \exp_H\left(\int_{t_0}^{t} dt' \mathcal{L}(t')\right) \mathcal{L}(t) A_S(\omega) \tag{15a}$$

and

$$\ddot{A}(\omega,t) = \exp_H\left(\int_{t_0}^{t} dt' \mathcal{L}(t')\right) \left(\mathcal{L}^2(t) + \partial_t \mathcal{L}(t)\right) A_S(\omega), \tag{15b}$$

which involve $\mathcal{L}(t)$ and its time derivative

$$\partial_t \mathcal{L}(t) = -\partial_t \mathcal{L}_1(t) = \sum_{n=1}^{3N} \left[\partial_{R_n} \partial_t H_1(\boldsymbol{R}, t)\right] \partial_{P_n}. \tag{16}$$

Since in this paper we consider an observable of interest that does not depend on $\boldsymbol{P}$, meaning that $A_S(\omega) = A_S(\boldsymbol{R})$, the actions of $\mathcal{L}(t)$ and $\partial_t\mathcal{L}(t)$ on $A_S(\boldsymbol{R})$ are $\partial_t\mathcal{L}(t)A_S(\boldsymbol{R}) = 0$ and $\mathcal{L}(t)A_S(\boldsymbol{R}) = \mathcal{L}_0 A_S(\boldsymbol{R})$, reducing equations (15*a*) and (15*b*) to

$$\dot{A}(\omega, t) = \exp_H\left(\int_{t_0}^{t} dt' \mathcal{L}(t')\right) \mathcal{L}_0 A_S(\boldsymbol{R}) \tag{17a}$$

and

$$\ddot{A}(\omega, t) = \exp_H\left(\int_{t_0}^{t} dt' \mathcal{L}(t')\right) \mathcal{L}(t) \mathcal{L}_0 A_S(\boldsymbol{R}), \tag{17b}$$

where in particular we see that $\dot{A}(\omega, t_0) = \mathcal{L}_0 A_S(\boldsymbol{R})$.

2.3 Projection and decomposition procedure: how to derive the non-equilibrium GLE

We introduce two time-independent projection operators, $\mathcal{P}$ and $\mathcal{Q}$, such that $\mathcal{I} = \mathcal{P} + \mathcal{Q}$, remembering that $\mathcal{I}$ is the identity operator. Using the fact that the propagator is a linear operator, equation (17*b*) can be written as

$$\begin{aligned}\ddot{A}(\omega, t) = &\exp_H\left(\int_{t_0}^{t} dt' \mathcal{L}(t')\right) \mathcal{P}\mathcal{L}(t) \mathcal{L}_0 A_S(\boldsymbol{R}) \\ &+ \exp_H\left(\int_{t_0}^{t} dt' \mathcal{L}(t')\right) \mathcal{Q}\mathcal{L}(t) \mathcal{L}_0 A_S(\boldsymbol{R}).\end{aligned} \tag{18}$$

We next rewrite the propagator in front of $\mathcal{Q}\mathcal{L}(t)\mathcal{L}_0 A_S(\boldsymbol{R})$ using a generalization of the Dyson operator identity [37]

$$\begin{aligned}\exp_H\left(\int_{t_0}^{t} dt' \mathcal{L}(t')\right) = &\exp_H\left(\mathcal{Q}\int_{t_0}^{t} dt' \mathcal{L}(t')\right) \\ &+ \int_{t_0}^{t} ds \exp_H\left(\int_{t_0}^{s} dt' \mathcal{L}(t')\right) \mathcal{P}\mathcal{L}(s) \exp_H\left(\mathcal{Q}\int_{s}^{t} dt' \mathcal{L}(t')\right),\end{aligned} \tag{19}$$

with which the expression for $\ddot{A}(\omega, t)$ becomes

$$\begin{aligned}\ddot{A}(\omega, t) = &\exp_H\left(\int_{t_0}^{t} dt' \mathcal{L}(t')\right) \mathcal{P}\mathcal{L}(t) \mathcal{L}_0 A_S(\boldsymbol{R}) \\ &+ \int_{t_0}^{t} ds \exp_H\left(\int_{t_0}^{s} dt' \mathcal{L}(t')\right) \mathcal{P}\mathcal{L}(s) F(\omega, s, t) + F(\omega, t_0, t),\end{aligned} \tag{20}$$

where $F(\omega, t_0, t)$ is defined as

$$F(\omega, t_0, t) \equiv \exp_H\left(\mathcal{Q}\int_{t_0}^{t} dt' \mathcal{L}(t')\right) \mathcal{Q}\mathcal{L}(t) \mathcal{L}_0 A_S(\boldsymbol{R}). \tag{21}$$

Since the projection operator $\mathcal{P}$ has not been specified yet, equation (20) is the general form of a GLE derived for the observable of interest $A(\omega,t)$ from $H(\omega,t)$ using time-independent projection. The three terms on the right hand side correspond respectively to the Markovian relevant force, the non-Markovian memory friction, and the complementary force, which stays in the complementary space, i.e. $\mathcal{P}F(\omega,t_0,t) = 0$. We notice that $\mathcal{P}$ in equation (20) acts to the right of the Heisenberg propagator. Therefore, we define the Mori projection operator, acting on a generic scalar observable $B(\omega,t)$, using the time-independent Schrödinger observable $A_S(\boldsymbol{R})$ as

$$\mathcal{P}B(\omega,t) = \langle B(\omega,t)\rangle + \frac{\langle(\mathcal{L}_0 A_S(\boldsymbol{R}))B(\omega,t)\rangle}{\langle(\mathcal{L}_0 A_S(\boldsymbol{R}))^2\rangle}\mathcal{L}_0 A_S(\boldsymbol{R}) + \frac{\langle(A_S(\boldsymbol{R}) - \langle A_S\rangle)B(\omega,t)\rangle}{\langle(A_S(\boldsymbol{R}) - \langle A_S\rangle)^2\rangle}(A_S(\boldsymbol{R}) - \langle A_S\rangle), \tag{22}$$

where $\langle\cdot\rangle$ denotes the expectation value defined in equation (13*a*) with

$$\rho(\omega,t_0) = \rho_0(\omega), \tag{23}$$

which is the stationary normalized solution of the time-independent Liouville equation using $\mathcal{L}_0$, given in equation (3). By this, it follows that the right-hand-side of the GLE (20) is a functional of $A(\omega,t)$ and $\dot{A}(\omega,t)$ and thus the GLE is an equation of motion for the acceleration $\ddot{A}(\omega,t)$ in terms of $A(\omega,t)$ and $\dot{A}(\omega,t)$. Details on the derivation are presented in the supplementary material.

3. Properties of the non equilibrium Mori GLE

3.1 Generic time-dependent Hamiltonian $H_1(\boldsymbol{R},t)$

Computing each term of equation (20) using the Mori projection equation (22), the non equilibrium GLE is explicitly given as

$$\ddot{A}(\omega,t) = D(t) - K(t)(A(\omega,t) - \langle A_S\rangle) + \int_{t_0}^{t} ds\,\Gamma_0(s,t) + \int_{t_0}^{t} ds\,\Gamma_1(s,t)(A(\omega,s) - \langle A_S\rangle) - \int_{t_0}^{t} ds\,\Gamma_2(s,t)\dot{A}(\omega,s) + F(\omega,t_0,t). \tag{24}$$

The GLE contains a time-dependent force

$$D(t) = \beta\langle[\mathcal{L}_0 A_S(\boldsymbol{R})]\mathcal{L}_0 H_1(\boldsymbol{R},t)\rangle \tag{25}$$

and a harmonic force with time-dependent stiffness

$$K(t) = K_0 - K_1(t), \tag{26a}$$

where

$$K_0 = \frac{\langle(\mathcal{L}_0 A_S(\boldsymbol{R}))^2\rangle}{\langle(A_S(\boldsymbol{R}) - \langle A_S\rangle)^2\rangle} \tag{26b}$$

and

$$K_1(t) = \beta \frac{\langle (A_S(\boldsymbol{R}) - \langle A_S \rangle)[\mathcal{L}_0 A_S(\boldsymbol{R})] \mathcal{L}_0 H_1(\boldsymbol{R}, t) \rangle}{\langle (A_S(\boldsymbol{R}) - \langle A_S \rangle)^2 \rangle}. \tag{26c}$$

Next there are three terms that involve integrals over memory kernels. The first memory kernel produces a time-dependent force that is independent of the observable or its derivative and is given by

$$\Gamma_0(s,t) = \beta \langle [\mathcal{L}_0 H_1(\boldsymbol{R}, s)] F(\omega, s, t) \rangle. \tag{27}$$

The second kernel

$$\Gamma_1(s,t) = \beta \frac{\langle (A_S(\boldsymbol{R}) - \langle A_S \rangle)[\mathcal{L}_0 H_1(\boldsymbol{R}, s)] F(\omega, s, t) \rangle}{\langle (A_S(\boldsymbol{R}) - \langle A_S \rangle)^2 \rangle} \tag{28}$$

couples to the observable. The third kernel

$$\Gamma_2(s,t) = \Gamma_{FF}(s,t) - \Delta\Gamma(s,t) \tag{29a}$$

couples to the time derivative of the observable and splits into two terms, one proportional to the autocorrelation function of the complementary force

$$\Gamma_{FF}(s,t) = \frac{\langle F(\omega, s, s) F(\omega, s, t) \rangle}{\langle (\mathcal{L}_0 A_S(\boldsymbol{R}))^2 \rangle} \tag{29b}$$

and a non-equilibrium correction term

$$\Delta\Gamma(s,t) = \beta \frac{\langle [\mathcal{L}_0 A_S(\boldsymbol{R})][\mathcal{L}_0 H_1(\boldsymbol{R}, s)] F(\omega, s, t) \rangle}{\langle (\mathcal{L}_0 A_S(\boldsymbol{R}))^2 \rangle}. \tag{29c}$$

Note that $\Gamma_{FF}(s,t)$ is the non-equilibrium version of equation (4). Obviously, in the limit $H_1(\boldsymbol{R}, t) \to 0$, the GLE in equation (24) becomes identical to the GLE in equation (1).

3.2 *Gaussian observables*

Previously [27], it was shown that if $A(\omega, t)$ displays Gaussian statistics, the correction term $\Delta\Gamma(s,t)$ in equation (29c) as well as $K_1(t)$, $\Gamma_0(s,t)$ and $\Gamma_1(s,t)$ vanish and we recover the relation in equation (4). This was shown for the specific time-dependent Hamiltonian of the form $H_1(\boldsymbol{R}, t) = h(t) A_S(\boldsymbol{R})$. Here, we investigate if a generic condition on $H_1(\boldsymbol{R}, t)$ exists such that $\Delta\Gamma(s,t)$, $K_1(t)$, $\Gamma_0(s,t)$ and $\Gamma_1(s,t)$ vanish.

We first observe that the expressions for $\Delta\Gamma(s,t)$, $K_1(t)$ and $\Gamma_1(s,t)$ correspond to three-point correlations of $A(\omega, t)$, $H_1(\boldsymbol{R}, t)$ and $F(\omega, t_0, t)$. The guiding idea is to find conditions for which these correlation functions become odd moments of the observable A, in which case they would vanish if A follows a multivariate Gaussian distribution.

To proceed, we define the deviatory observable, $\Delta A(\omega, t) = A(\omega, t) - a(t)$, which describes the deviation of $A(\omega, t)$ from its expectation defined in equation (12). By definition, when

$A(\omega,t)$ is a Gaussian observable, $\Delta A(\omega,t)$ is also a Gaussian observable and has a vanishing mean, i.e. $\langle \Delta A(\omega,t)\rangle = 0$. The GLE for $\Delta A(\omega,t)$ follows from equation (24) as

$$\Delta \ddot{A}(\omega,t) = -K(t)\,\Delta A(\omega,t) + \int_{t_0}^{t} ds\,\Gamma_1(s,t)\,\Delta A(\omega,s) - \int_{t_0}^{t} ds\,\Gamma_2(s,t)\,\Delta \dot{A}(\omega,s) + F(\omega,t_0,t)\,. \tag{30}$$

Based on equation (30), we see that $F(\omega,t_0,t)$ is linear in ΔA, $\Delta\dot{A}$ and $\Delta\ddot{A}$ without a contribution independent of ΔA. We now assume that $H_1(\boldsymbol{R},t)$ factorizes according to

$$H_1(\boldsymbol{R},t) = h(t)\;C_S(\boldsymbol{R})\,. \tag{31}$$

Using that $A_S(\boldsymbol{R}) - \langle A_S\rangle = \Delta A(\omega,t_0)$ and $\mathcal{L}_0 A_S(\boldsymbol{R}) = \Delta\dot{A}(\omega,t_0)$, we can rewrite the GLE parameters as

$$K_0 = \frac{\langle \Delta\dot{A}(\omega,t_0)^2\rangle}{\langle \Delta A(\omega,t_0)^2\rangle}, \tag{32a}$$

$$K_1(t) = \beta h(t)\,\frac{\langle \Delta A(\omega,t_0)\,[\mathcal{L}_0 C_S(\boldsymbol{R})]\Delta\dot{A}(\omega,t_0)\rangle}{\langle \Delta A(\omega,t_0)^2\rangle}, \tag{32b}$$

$$\Gamma_0(s,t) = \beta h(s)\,\langle [\mathcal{L}_0 C_S(\boldsymbol{R})] F(\omega,s,t)\rangle, \tag{32c}$$

$$\Gamma_1(s,t) = \beta h(s)\,\frac{\langle \Delta A(\omega,t_0)\,[\mathcal{L}_0 C_S(\boldsymbol{R})] F(\omega,s,t)\rangle}{\langle \Delta A(\omega,t_0)^2\rangle}, \tag{32d}$$

$$\Gamma_{FF}(s,t) = \frac{\langle F(\omega,s,s)\,F(\omega,s,t)\rangle}{\langle \Delta\dot{A}(\omega,t_0)^2\rangle}, \tag{32e}$$

and

$$\Delta\Gamma(s,t) = \beta h(s)\,\frac{\langle \Delta\dot{A}(\omega,t_0)\,[\mathcal{L}_0 C_S(\boldsymbol{R})] F(\omega,s,t)\rangle}{\langle \Delta\dot{A}(\omega,t_0)^2\rangle}. \tag{32f}$$

Since $F(\omega,t_0,t)$ is linear in ΔA, we see that if we assume $C_S(\boldsymbol{R})$ to be given by powers in $\Delta A(\omega,t_0)$ according to

$$C_S(\boldsymbol{R}) = (A_S(\boldsymbol{R}) - \langle A_S\rangle)^n = \Delta A(\omega,t_0)^n\,, \tag{33}$$

the functions $K_1(t)$, $\Gamma_1(s,t)$ and $\Delta\Gamma(s,t)$ in equations (32b), (32d) and (32f) vanish if n is odd and $A(\omega,t)$ is a Gaussian observable. In this case, the non-equilibrium version of the relation in equation (4), which reads

$$\Gamma_2(s,t) = \Gamma_{FF}(s,t) = \frac{\langle F(\omega,s,s)\,F(\omega,s,t)\rangle}{\langle (\mathcal{L}_0 A_S(\boldsymbol{R}))^2\rangle}, \tag{34}$$

holds (details on the derivation are given in the supplementary material) and thus the GLE governing the dynamics of the fluctuating observable ΔA is formally equivalent to the standard Mori equilibrium GLE. Turning this around, if a non-equilibrium system satisfies relation (34), we know that the observable of interest ΔA is in fact a Gaussian variable and that the time-dependent Hamiltonian $H_1(\boldsymbol{R},t)$ has the functional form given in equations (31) and (33) with n odd. If $n = 1$, also Γ_0 in equation (32c) vanishes because the complementary force is orthogonal to $\mathcal{L}_0 A_S$.

4. Summary and discussion

In this paper, we have shown that for a non-equilibrium system whose microscopic dynamics are determined by the sum of a time-dependent Hamiltonian $H_0(\omega)$ and a time-dependent Hamiltonian of the form $H_1(\boldsymbol{R},t)$, it is possible to use a time-independent projection operator, such as the Mori projection operator in equation (22), to derive the effective equation of motion for the Heisenberg observable of interest $A(\omega,t)$, defined in equation (13*b*), in the form of a GLE (24). Moreover, we have demonstrated that it is possible to recover a non-equilibrium version of the relation between the friction memory kernel and the autocorrelation function of the complementary force in equation (4) from this non-equilibrium GLE if $A(\omega,t)$ is a Gaussian observable (or more generally an observable for which all odd correlation correlation functions vanish) and if $H_1(\boldsymbol{R},t)$ is given as an odd power of the observable ΔA according to equations (31) and (33).

A key point of our derivation of the non-equilibrium Mori GLE is that the Mori projection contains phase-space integrals involving the functions $1, A_S(\boldsymbol{R})$, and $\mathcal{L}_0 A_S(\boldsymbol{R})$ which are linear in $A_S(\boldsymbol{R})$. In the future, it will be interesting to study GLEs that follow from a time-dependent Hamiltonian also for more complicated non-linear projections [23, 24], i.e. when observables are projected on non-linear functions of $1, A_S(\boldsymbol{R})$, and $\mathcal{L}_0 A_S(\boldsymbol{R})$. We note that there is a certain freedom involved in choosing the distribution $\rho(\omega,t_0)$ used for projection in equation (23). In the future it might be interesting to investigate how the non-equilibrium Mori GLE (24) changes if the projection distribution in equation (23) is modified.

At the end we come back to the example of a solvated molecule that is confined by an external time-dependent harmonic potential $H_1(\boldsymbol{R},t) = K_{ext}(t)(A_S(\boldsymbol{R}) - \langle A_S(\boldsymbol{R})\rangle)^2/2$. This scenario corresponds to the case where $h(t) = K_{ext}(t)/2$ and $n = 2$ in equations (31) and (33). Since n is even, the friction memory kernel $\Gamma_2(s,t)$ in equation (29*a*) does not reduce to $\Gamma_{FF}(s,t)$, thus, the correction factor $\Delta\Gamma(s,t)$ is expected to explicitly depend on $K_{ext}(t)$, irregardless of whether $\Delta A(\omega,t)$ is a Gaussian observable or not. Both contributions to $\Gamma_2(s,t)$ in equation (29*a*) involve correlations of $F(\omega,t_0,t)$ with itself or with $\Delta A(\omega,t_0)$ or $\Delta\dot{A}(\omega,t_0)$. Since the complementary force $F(\omega,t_0,t)$ in equation (21) depends via $\mathcal{L}(t)$ on $K_{ext}(t)$, $\Gamma_2(s,t)$, the friction kernel acting on a harmonically confined molecule in a solvent, is expected to depend on the confinement strength $K_{ext}(t)$, even if $K_{ext}(t)$ is time-independent. This explains the numerical results in [33], where the friction memory kernel of a harmonically confined methane molecule in water was found to depend significantly on the strength of a time-independent harmonic confinement potential.

Data availability statement

No new data were created or analysed in this study.

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