Generalized Langevin Equation

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Abstract

This text describes the derivation and interpretation of the Generalized Langevin equation for classical and quantum observables, following the lines of R. Zwanzig's textbook "Nonequilibrium statistical mechanics" [1].

1 Time evolution of classical and quantum observables

1.1 Liouville operator in classical mechanics

A classical mechanical Hamiltonian system is described by a set of generalized coordinates and associated momenta, $\{q_k, p_k\}$ ($k = 1, \ldots, n$). The dynamics of these variables is described by Hamilton's equations of motion,

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \tag{1}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}, \tag{2}$$

where $H(p, q)$ is the Hamilton function of the system. We use the notation p and q for the ensemble of all momenta and coordinates, respectively. For a closed system the Hamilton function does not explicitly depend on time and has usually the form

$$H(p, q) = \frac{1}{2} a_{ij}(q) p_i p_j + U(q), \tag{3}$$

where the quadratic form in the momenta is the kinetic energy and $U(q)$ is the potential energy. Here and in the following we use Einstein's summation convention, where summation over pairwise equal indices is implicitly assumed.

In classical mechanics, any observable is a function of the coordinates and momenta, $A \equiv A(p, q)$, and its time evolution is obtained from the equation of motion

$$\frac{dA}{dt} = \dot{q}_i \frac{\partial A}{\partial q_i} + \dot{p}_i \frac{\partial A}{\partial p_i} = \frac{\partial H}{\partial p_i} \frac{\partial A}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial A}{\partial p_i},$$

where A is supposed not to depend explicitly on time, such that $\partial_t A = 0$. Introducing the Poisson bracket

$$\{A, B\} = \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} - \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i}, \tag{4}$$

and the Liouville operator

$$\mathscr{L} = \{H, .\}, \tag{5}$$

the equation of motion for A can thus be written in the compact form

$$\frac{dA}{dt} = \mathscr{L} A. \tag{6}$$

It has the formal solution

$$A(t) = e^{t\mathscr{L}} A(0), \tag{7}$$

where $A(t) \equiv A(p,q;t)$ and $A(0) \equiv A(p,q)$. Considering that $A(\delta t) \approx A(0) + \delta t\, dA(t)/dt|_{t=0}$ for a small increment in time, δt, it follows from the equation of motion (6) that Liouville operator is the generator of the time evolution described by $e^{t\mathscr{L}}$,

$$A(\delta t) \approx (1 + \delta t \mathscr{L}) A(0). \tag{8}$$

Using that $\exp(x) = \lim_{n\to\infty} \left(1 + \frac{x}{n}\right)^n$, a finite displacement in time can be written in the alternative form

$$A(t) = \lim_{n\to\infty} \left(1 + \frac{t}{n}\mathscr{L}\right)^n A(0), \tag{9}$$

i.e. as a succession of an infinite number of infinitely small displacements.

1.2 Quantum Liouville operator

In quantum mechanics one has to distinguish between state vectors describing the state of a quantum system and operators, which can be divided into unitary (norm-conserving) operators transforming the state vector of the system and hermitian operators corresponding to physical observables. The mean value for the measurement of a physical observable, A, is given by

$$\overline{A(t)} = \langle \psi(t) | \hat{A} | \psi(t) \rangle, \tag{10}$$

where the real eigenvalues of the hermitian operator $\hat{A}$ are the possible outcomes of a measurement and $|\psi(t)\rangle$ is the time-dependent state vector of the system. The bra-ket notation $\langle a|b\rangle = \langle b|a\rangle^*$ is used for a scalar product. The dynamics of the state vector is determined by the Schrödinger equation,

$$i\hbar \partial_t |\psi(t)\rangle = \hat{H} |\psi(t)\rangle, \tag{11}$$

where $\hat{H}$ is the Hamilton operator, and the formal solution of (11) is given by

$$|\psi(t)\rangle = e^{-\frac{it}{\hbar}\hat{H}} |\psi(0)\rangle, \tag{12}$$

where $\exp(-\frac{it}{\hbar}\hat{H})$ is the unitary operator describing the time-evolution of the state vector. Inserting the formal solution (19) into the Formula (10) for the mean value of A and using that $\hat{H}$ is Hermitian, i.e. $\langle \phi | \hat{A}\phi \rangle = \langle \hat{A}\phi | \phi \rangle$, we find that

$$\overline{A(t)} = \langle \psi(0) | e^{\frac{it}{\hbar}\hat{H}} \hat{A} e^{-\frac{it}{\hbar}\hat{H}} | \psi(0) \rangle. \tag{13}$$

This defines the time-dependent operator

$$\hat{A}_H(t) = e^{\frac{it}{\hbar}\hat{H}} \hat{A} e^{-\frac{it}{\hbar}\hat{H}} \tag{14}$$

describing the dynamics of quantum mean values in the "Heisenberg picture". An equation of motion for $\hat{A}_H(t)$ can be derived by differentiating (14) with respect to t, where it is, again, assumed that the operator $\hat{A}$ does not explicitly depend on time. Defining the commutator

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}, \tag{15}$$

and the quantum Liouville operator

$$\hat{L} = \frac{i}{\hbar}[\hat{H}, .], \tag{16}$$

the equation of motion for $\hat{A}_H(t)$ reads

$$\frac{d\hat{A}_H(t)}{dt} = \hat{L}\hat{A}_H(t), \tag{17}$$

and its formal solution can again be written in exponential form,

$$\hat{A}_H(t) = e^{t\hat{L}}\hat{A}_H(0). \tag{18}$$

All practical calculations in quantum mechanics are performed with matrix representations of operators and state vectors. The state vectors are elements of a Hilbert space, which is endowed with an orthonormal basis, $\{|u_k\rangle\}$, whose elements satisfy $\langle u_k|u_l\rangle = \delta_{kl}$. For simplicity we assume that the basis vectors are enumerable and that the Hilbert space has finite dimension, n. The matrix representation of the state vector $|\psi(t)\rangle$ is then a n-dimensional column vector $\boldsymbol{\psi}(t)$, where $\psi_k(t) = \langle u_k|\psi(t)\rangle$, and all operators, $\hat{A}$, are represented by $(n \times n)$-matrices, $\boldsymbol{A}$, whose elements are $A_{kl} = \langle u_k|\hat{A}|u_l\rangle$. Using the completeness relation $\sum_k |u_k\rangle\langle u_n| = \hat{1}$, one finds for example that matrix representation of Eq. (19) reads

$$\boldsymbol{\psi}(t) = e^{-\frac{it}{\hbar}\boldsymbol{H}}\boldsymbol{\psi}(0), \tag{19}$$

where $(\boldsymbol{H})_{kl} = \langle u_k|\hat{H}|u_l\rangle$. From Eq. (18) one obtains instead

$$\boldsymbol{A}_H(t) = e^{t\mathscr{L}}\boldsymbol{A}_H(0), \tag{20}$$

where $\mathscr{L} = (\mathscr{L}_{kl,mn})$ has four indices, since $e^{t\mathscr{L}}$ maps a matrix $\boldsymbol{A}_H(0)$ onto a matrix $\boldsymbol{A}_H(t)$, and each of these matrices has two indices. Expression (20) is the equivalent of Expression (7) for classical observables and the equivalent of Expression (19) for quantum state vectors. The concrete form of the time evolution operator $e^{t\mathscr{L}}$ acting on matrices can be obtained from Eq. (14), writing

$$(\boldsymbol{A}_H(t))_{kl} = \left(e^{t\mathscr{L}}\boldsymbol{A}\right)_{kl} = \left(e^{\frac{it}{\hbar}\boldsymbol{H}}\right)_{km} A_{mn} \left(e^{-\frac{it}{\hbar}\boldsymbol{H}}\right)_{nl},$$

where it has been used that $\boldsymbol{A}_H(0) = \boldsymbol{A}$. It follows then that

$$\left(e^{t\mathscr{L}}\right)_{kl,mn} = \left(e^{\frac{it}{\hbar}\boldsymbol{H}}\right)_{km} \left(e^{-\frac{it}{\hbar}\boldsymbol{H}}\right)_{nl}. \tag{21}$$

From this equation one derives the coefficients $\mathscr{L}_{kl,mn}$ through

$$\mathscr{L}_{kl,mn} = \frac{d}{dt}\left(e^{t\mathscr{L}}\right)_{kl,mn}\Big|_{t=0} = \frac{i}{\hbar}\left(H_{km}\delta_{nl} - \delta_{km}H_{nl}\right). \tag{22}$$

2 Generalized Langevin equation

2.1 Classical Langevin equation for Brownian motion

The Langevin equation for a Brownian particle [2],

$$\dot{\boldsymbol{v}}(t) + \gamma\boldsymbol{v}(t) = \boldsymbol{F}^{(s)}(t)/M \tag{23}$$

is the prototype of an equation of motion in which a "relevant" dynamical variable – the velocity $\boldsymbol{v}(t)$ of the Brownian particle – is separated from the "irrelevant" dynamical variables describing the surrounding solvent molecules, which are not explicitly considered. The frequent collisions of the Brownian particle with the surrounding solvent molecules are described by the stochastic force, $\boldsymbol{F}^{(s)}(t)$, which is modeled as white noise in order to account for the time scale separation between the slow motions of the heavy Brownian particle and the fast motions of the much lighter solvent molecules. The amplitude of the stochastic force is chosen such that the energy loss resulting from the friction of the Brownian particle with the surrounding solvent is compensated. The friction is here modeled by the friction force $-\gamma\boldsymbol{v}(t)$ ($\gamma > 0$). The time scale separation between the relevant and irrelevant variables leads to an absence of correlations between the velocity of the Brownian particle and the stochastic force,

$$\langle \boldsymbol{v}(0) \cdot \boldsymbol{F}^{(s)}(t)\rangle \approx 0. \tag{24}$$

The symbol $\langle \ldots \rangle$ denotes here an equilibrium ensemble average over all initial velocities, $\boldsymbol{v}(0)$. It follows from (24) and the Langevin equation (23) that the velocity autocorrelation function (VACF) of the Brownian particle, which is defined through

$$c_{vv}(t) = \langle \boldsymbol{v}(0) \cdot \boldsymbol{v}(t) \rangle, \tag{25}$$

fulfills the closed differential equation

$$\frac{d}{dt} c_{vv}(t) + \gamma c_{vv}(t) = 0. \tag{26}$$

The solution is an exponential function,

$$c_{vv}(t) = c_{vv}(0) e^{-\gamma t}, \tag{27}$$

where $c_{vv}(0) = \langle \boldsymbol{v} \cdot \boldsymbol{v} \rangle = 3v_{th}^2$ and $v_{th} = \sqrt{k_B T/M}$ is the thermal velocity. Time scale separation thus leads to exponentially decaying (auto)correlation functions.

2.2 Generalized Langevin equation through projection

2.2.1 Projectors in the Hilbert space of dynamical variables

In the following we describe the derivation of a generalized Langevin equation, where the dynamics of relevant and irrelevant and dynamical variables is separated by projection techniques. The goal is to avoid the assumption of a time scale separation, as the one expressed through Eq. (24). In order to construct projection operators onto the space of "relevant" dynamical variables, we define a scalar product of two dynamical variables U and V through the ensemble averages

$$(U, V) = \begin{cases} \int d^{2n}X \, \rho_{eq}(X) U^*(X) V(X) & \text{for classical systems,} \\ \text{tr} \left\{ \boldsymbol{\rho}_{eq} \cdot \boldsymbol{U}^\dagger \cdot \boldsymbol{V} \right\} & \text{for quantum systems.} \end{cases} \tag{28}$$

Here $X \equiv \{p, q\}$ is the ensemble of phase space variables for a classical system with n generalized coordinates and momenta, respectively, and $\rho_{eq}(X) = \exp(-\beta H(X))/Z_{cl}$ is the equilibrium distribution function. As usual, $\beta = (k_B T)^{-1}$ and $Z_{cl} = \int d^{2n}X \, \exp(-\beta H(X))$ is the classical partition function. In the quantum case $\boldsymbol{\rho}_{eq} = \exp(-\beta \boldsymbol{H})/Z$ is the density matrix and $\boldsymbol{U}$ and $\boldsymbol{V}$ are matrix representations of the observables U and V, respectively. Here "tr" stands for the trace and $Z = \text{tr} \{\exp(-\beta \boldsymbol{H})\}$ is the quantum partition function. It follows from the definition (28) of the scalar product that

$$(U, V)^* = (V, U). \tag{29}$$

It should be noted that the definition of a scalar product in the space dynamical variables according to Eq. (28) is chosen such that Expression (24) appears as (approximate) orthogonality of the velocity of a Brownian particle and the stochastic force. Time correlation functions are then scalar products of the form

$$C_{UV}(t) = (U, V(t)). \tag{30}$$

We suppose now that the relevant dynamical variables to be considered are $A_1, \ldots, A_f$. They can be considered as basis vectors spanning an f-dimensional subspace $\mathbb{V}_\parallel$ of the infinite dimensional Hilbert space of all dynamical variables. Using the definition (28) for the scalar product of two dynamical variables, we can construct a projector on that subspace through (we assume again the Einstein summation convention)

$$\mathscr{P} = A_k (G^{-1})_{kl} (A_l, .), \tag{31}$$

where $(G^{-1})_{kl}$ are the elements of the inverse of the matrix $\boldsymbol{G}$, where

$$G_{ij} = (A_i, A_j). \tag{32}$$

In the language of tensor analysis the matrix $\boldsymbol{G}$ is the matrix representation of the metric tensor. The projection of a dynamical variable U onto the subspace $\mathbb{V}_{\|}$ spanned by $A_1, \ldots, A_f$ is then given by

$$\mathscr{P}U = A_k (G^{-1})_{kl} (A_l, U) \tag{33}$$

and for $U = A_j$ one obtains in particular

$$\mathscr{P}A_j = A_k (G^{-1})_{kl} \underbrace{(A_l, A_j)}_{G_{lj}} = A_k \delta_{kj} = A_j. \tag{34}$$

Here we have used a common notation for classical and quantum systems and we note that one would write explicitly

$$\mathscr{P}U = \begin{cases} A_k(X)(G^{-1})_{kl}(A_l, U) & \text{for classical systems,} \\ \boldsymbol{A}_k (G^{-1})_{kl}(A_l, U) & \text{for quantum systems.} \end{cases} \tag{35}$$

This emphasizes that the projection of U onto $\mathbb{V}_{\|}$ is a linear combination of the dynamical variables $A_k(X)$ in case of classical systems and a linear combination of the matrix representations $\boldsymbol{A}_k$ of the observables A_k in case of quantum systems.

2.2.2 Deriving the Generalized Langevin Equation

To derive a "universal" generalized Langevin equation (GLE) for the dynamical variables of interest we split the Liouville operator into two orthogonal components,

$$\mathscr{L} = \mathscr{P}\mathscr{L} + (1 - \mathscr{P})\mathscr{L}, \tag{36}$$

where $\mathscr{P}\mathscr{L}$ generates an infinitesimal displacement in time in the subspace $\mathbb{V}_{\|}$ and $(1 - \mathscr{P})\mathscr{L}$ a corresponding displacement in the orthogonal complement, $\mathbb{V}_{\perp}$, spanned by the "noise variables". The total time evolution operator can then be written as [1]

$$e^{t\mathscr{L}} = e^{t(1-\mathscr{P})\mathscr{L}} + \int_0^t d\tau \, e^{(t-\tau)\mathscr{L}} (\mathscr{P}\mathscr{L}) e^{\tau(1-\mathscr{P})\mathscr{L}}, \tag{37}$$

which is proven in the Appendix. Following Zwanzig [1], we act with this operator on $(1 - \mathscr{P})\mathscr{L}A_j$,

$$e^{t\mathscr{L}}(1 - \mathscr{P})\mathscr{L}A_j = e^{t(1-\mathscr{P})\mathscr{L}}(1 - \mathscr{P})\mathscr{L}A_j + \int_0^t d\tau \, e^{(t-\tau)\mathscr{L}} (\mathscr{P}\mathscr{L}) e^{\tau(1-\mathscr{P})\mathscr{L}} (1 - \mathscr{P})\mathscr{L}A_j,$$

which yields an equation of motion for A_j,

$$\begin{aligned} \frac{d}{dt} \underbrace{(e^{t\mathscr{L}} A_j)}_{A_j(t)} - \underbrace{e^{t\mathscr{L}} A_k}_{A_k(t)} \underbrace{(G^{-1})_{kl}(A_l, \mathscr{L}A_j)}_{\Omega_{kj}} \\ = \underbrace{e^{t(1-\mathscr{P})\mathscr{L}}(1 - \mathscr{P})\mathscr{L}A_j}_{f_j^{\perp}(t)} + \int_0^t d\tau \, e^{(t-\tau)\mathscr{L}} (\mathscr{P}\mathscr{L}) \underbrace{e^{\tau(1-\mathscr{P})\mathscr{L}}(1 - \mathscr{P})\mathscr{L}A_j}_{f_j^{\perp}(\tau)}. \end{aligned}$$

Defining the "projected force",

$$\boxed{f_j^{\perp}(t) = e^{t(1-\mathscr{P})\mathscr{L}}(1 - \mathscr{P})\mathscr{L}A_j} \tag{38}$$

and the matrix $\boldsymbol{\Omega}$,

$$\boxed{\Omega_{kj} = (G^{-1})_{kl}(A_l, \mathscr{L}A_j)} \tag{39}$$

the equation of motion for A_j becomes

$$\frac{d}{dt}A_j(t) - \Omega_{kj}A_k(t) = f_j^\perp(t) + \int_0^t d\tau\, e^{(t-\tau)\mathscr{L}}\mathscr{P}\left\{\mathscr{L}f_j^\perp(\tau)\right\}.$$

With the explicit form for the projector $\mathscr{P}$ we obtain

$$\frac{d}{dt}A_j(t) - A_k(t)\Omega_{kj} = f_j^\perp(t) + \int_0^t d\tau\, e^{(t-\tau)\mathscr{L}}A_k(G^{-1})_{kl}\left(A_l, \mathscr{L}f_j^\perp(\tau)\right)$$

and noting that $\exp((t-\tau)\mathscr{L})A_k = A_k(t-\tau)$ and that $\mathscr{L}$ is skew-hermitian,

$$(U, \mathscr{L}V) = -(\mathscr{L}U, V), \tag{40}$$

the above equation of motion for A_j can be written in the alternative form

$$\frac{d}{dt}A_j(t) - A_k(t)\Omega_{kj} = f_j^\perp(t) - \int_0^t d\tau\, A_k(t-\tau)\underbrace{(G^{-1})_{kl}\left(\mathscr{L}A_l, f_j^\perp(\tau)\right)}_{M_{kj}(\tau)}.$$

This equation defines the *memory kernel*,

$$M_{kj}(t) = (G^{-1})_{kl}\left(\mathscr{L}A_l, f_j^\perp(t)\right), \tag{41}$$

which can be brought to a more convenient form observing that $f_l^\perp(0) = (1-\mathscr{P})\mathscr{L}A_l$ and therefore

$$\left(f_l^\perp(0), f_l^\perp(t)\right) = \left((1-\mathscr{P})\mathscr{L}A_l, f_j^\perp(t)\right) = \left(\mathscr{L}A_l, (1-\mathscr{P})f_j^\perp(t)\right) = \left(\mathscr{L}A_l, f_j^\perp(t)\right),$$

since $\mathscr{P}f_l^\perp(t) = 0$ by construction. Expression (41) is thus equivalent to

$$\boxed{M_{kj}(t) = (G^{-1})_{kl}\left(f_l^\perp(0), f_j^\perp(t)\right)} \tag{42}$$

which shows that the memory kernel is the correlation matrix of the projected forces, pre-multiplied by the inverse of metric matrix, $\boldsymbol{G}$. With these prerequisites the equation of motion for A_j takes the final form of a generalized Langevin equation,

$$\boxed{\frac{d}{dt}A_j(t) - A_k(t)\Omega_{kj} + \int_0^t d\tau\, A_k(t-\tau)M_{kj}(\tau) = f_j^\perp(t)} \tag{43}$$

which is an *exact* equation of motion that has been obtained by purely mathematical arguments. It *ressembles* though the Langevin equation, considering that $f_j^\perp(t)$ plays the role of a stochastic force and the convolution term the role of a (negative) friction force. An interpretation of the coefficients Ω_{kj} will be discussed in Section 2.4.

2.3 Correlation functions

2.3.1 Memory function equation

In many situations one is interested in time correlation functions of the relevant dynamical variables, $A_1, \ldots, A_f$, and not in the trajectories which are obtained by solving the GLE for given initial conditions. This concerns in particular the interpretation of spectroscopic experiments, where one measures usually the Fourier transform of time correlation functions. A closed equation of motion for time correlation functions can be derived from the GLE by noting that

$$\left(A_i(0), f_j^\perp(t)\right) = 0, \tag{44}$$

since $A_i(0) \equiv A_i \in \mathbb{V}_\parallel$ and $f_j^\perp(t) \in \mathbb{V}_\perp$ are in orthogonal subspaces. Eq. (44) corresponds to the time separation condition (24) of the Langevin equation, but in the context of the GLE time scale separation needs not to be assumed since Eq. (44) holds by construction. It follows then from (44) and from the GLE (43) that the time correlation functions

$$C_{ij}(t) = (A_i(0), A_j(t)) \tag{45}$$

verify the closed equation

$$\boxed{\frac{d}{dt}C_{ij}(t) - C_{ik}(t)\Omega_{kj} + \int_0^t d\tau\, C_{ik}(t-\tau)M_{kj}(\tau) = 0} \tag{46}$$

in which the projected force does not appear anymore. Eq. (46), which is referred to as memory function equation, is a very powerful tool for modeling time correlation functions by assuming a particular form for the memory kernel [3].

2.4 Orthonormal dynamical variables and the role of Ω

Starting from a set of arbitrary dynamical variables, $A_1, \ldots, A_f$, it is always possible to introduce a set of new dynamical variables, $\tilde{A}_1, \ldots, \tilde{A}_f$, such that

$$\boxed{(\tilde{A}_k, \tilde{A}_l) = \delta_{kl}, \quad \text{and therefore} \quad \tilde{\Omega}_{kj} = -\tilde{\Omega}^*_{jk}} \tag{47}$$

Such variables are in particular useful to understand the role of the coefficients Ω_{kj} in the GLE (43) and the associated equation of motion (46) for the correlation matrix $C_{ij}(t)$. The new variables, $\tilde{A}_1, \ldots, \tilde{A}_f$, can always be found be introduced by performing a Gram-Schmidt orthogonalization of the basis $\{A_i\}$, and technically this can be realized by a Cholesky-decomposition of the positive definite matrix $\boldsymbol{C}(0)$. Writing

$$A_i = T_{ki}\tilde{A}_k,$$

where T_{kl} are constant coefficients, we obtain

$$C_{ij}(0) = (T_{ki}\tilde{A}_k, T_{lj}\tilde{A}_l) = T^*_{ki}\underbrace{(\tilde{A}_k, \tilde{A}_l)}_{\delta_{kl}}T_{lj} = T^*_{ki}T_{kj},$$

which is indeed obtained by a Cholesky-factorization [4],

$$\boldsymbol{C}(0) = \boldsymbol{T}^\dagger \cdot \boldsymbol{T},$$

where $\boldsymbol{T}$ has upper triangular form.

In the new variables the memory function equation (46) takes the matrix form

$$\frac{d}{dt}\tilde{\boldsymbol{C}}(t) - \tilde{\boldsymbol{C}}(t)\cdot\tilde{\boldsymbol{\Omega}} + \int_0^t d\tau\, \tilde{\boldsymbol{C}}(t-\tau)\cdot\tilde{\boldsymbol{M}}(\tau) = \boldsymbol{0}, \tag{48}$$

where

$$\tilde{\boldsymbol{C}}(0) = \boldsymbol{1} \quad \text{and} \quad \tilde{\boldsymbol{\Omega}}^\dagger = -\tilde{\boldsymbol{\Omega}}. \tag{49}$$

We assume now that[1]

$$\tilde{\boldsymbol{\Omega}} \neq \boldsymbol{0} \quad \text{and that} \quad \tilde{\boldsymbol{M}}(t) \approx \boldsymbol{0}, \tag{50}$$

[1]One may well have the situation $\tilde{\boldsymbol{\Omega}} = \boldsymbol{0}$ (see Section 2.5), but in this case the memory kernel should not vanish, too, since this would lead to the trivial and uninteresting result $\tilde{\boldsymbol{C}}(t) = \boldsymbol{1}$ for all times.

i.e. that the memory function is negligible. In this case, the correlation matrix $\tilde{\boldsymbol{C}}(t)$ fulfills approximately the equation of motion of a rotation matrix,

$$\frac{d}{dt}\tilde{\boldsymbol{C}}(t) = \tilde{\boldsymbol{C}}(t) \cdot \tilde{\boldsymbol{\Omega}}, \tag{51}$$

where $\boldsymbol{\Omega}$ is a constant "angular velocity" matrix. The solution for the initial condition $\tilde{\boldsymbol{C}}(0) = \mathbf{1}$ is

$$\tilde{\boldsymbol{C}}(t) = e^{t\tilde{\boldsymbol{\Omega}}} \tag{52}$$

and $\tilde{\boldsymbol{C}}(t)$ fulfills indeed the orthogonality relation

$$\tilde{\boldsymbol{C}}^{\dagger}(t) \cdot \tilde{\boldsymbol{C}}(t) = \left(e^{t\tilde{\boldsymbol{\Omega}}}\right)^{\dagger} \cdot e^{t\tilde{\boldsymbol{\Omega}}} = e^{t\tilde{\boldsymbol{\Omega}}^{\dagger}} \cdot e^{t\tilde{\boldsymbol{\Omega}}} = e^{-t\tilde{\boldsymbol{\Omega}}} \cdot e^{t\tilde{\boldsymbol{\Omega}}} = \mathbf{1}, \tag{53}$$

since $\tilde{\boldsymbol{\Omega}}$ is skew-hermitian. Using the Frobenius (Euclidean) matrix norm [4],

$$\|\tilde{\boldsymbol{C}}(t)\| \equiv \sqrt{\mathrm{tr}\left\{\tilde{\boldsymbol{C}}^{\dagger}(t) \cdot \tilde{\boldsymbol{C}}(t)\right\}}, \tag{54}$$

it follows from Eq. (52) that

$$\|\tilde{\boldsymbol{C}}(t)\| = f, \tag{55}$$

and solving the exact equation of motion (51) for the correlation matrix, leads to "damping effects"[2] produced by the memory kernel, such that

$$\|\tilde{\boldsymbol{C}}(t)\| \overset{t\to\infty}{=} 0, \tag{56}$$

with the initial value $\|\tilde{\boldsymbol{C}}(0)\| = f$. In the general case, which includes the memory kernel, Eq. (51) is only valid at $t = 0$, which shows that

$$\tilde{\boldsymbol{\Omega}} = \frac{d}{dt}\tilde{\boldsymbol{C}}(t)\bigg|_{t=0}, \tag{57}$$

since $\tilde{\boldsymbol{C}}(0) = \mathbf{1}$.

2.5 Retrieving the Langevin equation for Brownian motion from the GLE

Brownian dynamics, as described by the Langevin equation, is a stochastic model for a Brownian particle, whereas the GLE is by construction an exact equation of motion, where the underlying dynamics is *deterministic*. Considering a classical mechanical system for the Brownian particle and the solvent molecules in which it is immersed, the dynamics of the total system is described by Hamiltonian mechanics for $3N$ coordinates q_k and $3N$ associated momenta p_k, where N is the total number of particles in the system. Choosing the the first three coordinates and velocities to be those of the Brownian particle, the "relevant" dynamical variables, A_k, are the components of the velocity of the Brownian particle in a Cartesian coordinate system,

$$A_j = v_j, \quad j = 1, 2, 3. \tag{58}$$

To go from the Hamiltonian dynamics of the Brownian we make the basic assumption is that the projected force varies much faster than the velocity of the Brownian particle, such that the projected forces are delta-correlated,

$$\left(f_l^{\perp}(0), f_j^{\perp}(t)\right) = a\delta_{lj}\delta(t). \tag{59}$$

[2]Strictly speaking, the term "damping" should be replaced by "decay" or "effective damping" since the GLE is a deterministic equation of motion.

The constant a is here still to be determined by the requirement that friction and fluctuation mut be balanced, such that the energy of the Brownian particle is conserved on average. Here the components of the metric matrix read (see Appendix C),

$$G_{kl} = (v_k, v_l) = \delta_{kl}(v_k, v_k) = v_{\text{th}}^2 \delta_{kl}, \tag{60}$$

where $v_{\text{th}}^2 = k_B T/M$ is the mean squared velocity of the Brownian particle in an arbitrary direction. It follows then from Eq. (42) that the memory kernel takes the form

$$M_{kj}(t) = a v_{\text{th}}^{-2} \delta_{kj} \delta(t), \tag{61}$$

expressing "memory-less" dynamics. In the framework of classical mechanics of a tagged Brownian particle we have moreover (see Appendix C)

$$\Omega_{kj} = 0 \tag{62}$$

if one assumes a Hamilton function of the standard form, $H(p,q) = T(p) + U(q)$, where $p_k = M_k v_k$ and $T(p)$ and $U(q)$ are, respectively, the kinetic and the potential energy. On account of Eqs. (42) and (59) the equation of motion for v_j becomes then

$$\frac{d}{dt} v_j(t) + \underbrace{\int_0^t d\tau \, v_k(t-\tau) a v_{\text{th}}^{-2} \delta_{kj} \delta(\tau)}_{\approx a v_{\text{th}}^{-2} v_j(t)/2} = f_j^{\perp}(t),$$

noting that the integral $\int_0^t d\tau \, \ldots$ includes half a delta function for any $t > 0$. Setting

$$\gamma = a v_{\text{th}}^{-2}/2 \tag{63}$$

we obtain the approximated equation of motion

$$\frac{d}{dt} v_j(t) + \gamma v_j(t) = f_j^{\perp}(t), \tag{64}$$

which is identical with the Langevin equation (23) if one sets $f_j^{\perp}(t) = F_j^{(s)}(t)/M_j$. Eq. (63) fixes $a = 2 v_{\text{th}}^2 \gamma$ and assures that the mean (kinetic) energy of the Brownian particle is constant. It follows from (64) and from the orthogonality relation

$$\Big(v_i, f_j^{\perp}(t) \Big) = 0 \tag{65}$$

that the components of the velocity correlation matrix of the Brownian particle,

$$c_{ij}(t) = \left(v_i(0), v_j(t) \right), \tag{66}$$

satisfy the equation of motion

$$\frac{d}{dt} c_{ij}(t) + \gamma c_{ij}(t) = 0. \tag{67}$$

The solution is

$$c_{ij}(t) = \begin{cases} v_{\text{th}}^2 e^{-\gamma t} & \text{if } i = j, \\ 0 & \text{if } i \neq j, \end{cases} \tag{68}$$

where it has been used that $c_{ij}(0) = (v_i, v_j) = 0$ for $i \neq j$. We note in this context that is has been shown by computer simulation and by simple scaling arguments that the velocity autocorrelation function of a tagged particle in a simple liquid becomes close to exponential if its mass is raised by a factor of 10 and more compared to the mass of the remaining "solvent molecules" [5, 6].

A Proof of formula (37)

Formula (37) can be proven by Laplace transform.[3] Using the convolution theorem[4] one obtains

$$\frac{\hat{1}}{s-\hat{L}} = \frac{\hat{1}}{s-\hat{Q}\hat{L}} + \frac{\hat{1}}{s-\hat{L}}(\hat{P}\hat{L})\frac{\hat{1}}{s-\hat{Q}\hat{L}}. \tag{69}$$

The righthand side of (69) may be rearranged to give

$$\begin{aligned}\frac{\hat{1}}{s-\hat{Q}\hat{L}} + \frac{\hat{1}}{s-\hat{L}}(\hat{P}\hat{L})\frac{\hat{1}}{s-\hat{Q}\hat{L}} &= \frac{\hat{1}}{s-\hat{L}}(s-\hat{L})\frac{\hat{1}}{s-\hat{Q}\hat{L}} + \frac{\hat{1}}{s-\hat{L}}(\hat{P}\hat{L})\frac{\hat{1}}{s-\hat{Q}\hat{L}} \\ &= \frac{\hat{1}}{s-\hat{L}}(s-\hat{L}+\hat{P}\hat{L})\frac{\hat{1}}{s-\hat{Q}\hat{L}} = \frac{\hat{1}}{s-\hat{L}}(s-(\underbrace{\hat{P}+\hat{Q}}_{=\hat{1}})\hat{L}+\hat{P}\hat{L})\frac{\hat{1}}{s-\hat{Q}\hat{L}} \\ &= \frac{\hat{1}}{s-\hat{L}}(s-\hat{Q}\hat{L})\frac{\hat{1}}{s-\hat{Q}\hat{L}} = \frac{\hat{1}}{s-\hat{L}}.\end{aligned}$$

This proves Eq. (69) and finally Eq. (37) by inverse Laplace transform.

B Proof of the symmetry relation (40)

B.1 Classical systems

Here we distinguish explicitly between generalized coordinates and momenta and write

$$(U, \mathscr{L}V) = \frac{1}{Z_{cl}} \int\int d^n p d^n q \, e^{-\beta H(p,q)} A_l^*(p,q) \mathscr{L}V(p,q),$$

where $Z_{cl} = \int\int d^n p d^n q \, \exp(-\beta H(p,q))$ is the classical partition function. It follows then that

$$\begin{aligned}(U, \mathscr{L}V) &= \frac{1}{Z_{cl}} \int\int d^n p d^n q \, e^{-\beta H(p,q)} U^*(p,q) \mathscr{L}V(p,q) \\ &= \int\int d^n p d^n q \, e^{-\beta H(p,q)} U^*(p,q) \left\{ \frac{\partial H}{\partial p_i}\frac{\partial V(p,q)}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial V(p,q)}{\partial p_i} \right\} \\ &\quad - \int\int d^n p d^n q \, e^{-\beta H(p,q)} V(p,q) \left\{ \frac{\partial H}{\partial p_i}\frac{\partial U^*(p,q)}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial U^*(p,q)}{\partial p_i} \right\} = -(\mathscr{L}U, V).\end{aligned}$$

Here partial integration has been used for the transition from the second to the third line, assuming that all phase space functions vanish at infinity. It thus follows that

$$(U, \mathscr{L}V) = -(\mathscr{L}U, V) \quad \square$$

B.2 Quantum systems

Noting that $\boldsymbol{\rho}_{eq} = \exp(-\beta \boldsymbol{H})/Z$, where $Z = \mathrm{tr}\{\exp(-\beta \boldsymbol{H})\}$, we write

$$(U, \mathscr{L}V) = \frac{1}{Z}\mathrm{tr}\left\{ e^{-\beta \boldsymbol{H}} \cdot \boldsymbol{U}^\dagger \cdot \left(\frac{i}{\hbar}[\boldsymbol{H}, \boldsymbol{V}] \right) \right\} = \frac{1}{Z}\mathrm{tr}\left\{ e^{-\beta \boldsymbol{H}} \cdot \boldsymbol{U}^\dagger \cdot \left(\frac{i}{\hbar}(\boldsymbol{H}\cdot\boldsymbol{V} - \boldsymbol{V}\cdot\boldsymbol{H}) \right) \right\}.$$

[3] The Laplace transform of an arbitrary function $f(t)$ is defined as $\hat{f}(s) = \int_0^\infty dt \, e^{-st} f(t)$, with $\Re\{s\} > 0$, and for the time derivative of $f(t)$ one obtains the correspondence $f'(t) \leftrightarrow s\hat{f}(s) - f(0)$. The inverse Laplace transform is defined through $f(t) = \frac{1}{2\pi i} \oint ds \, e^{st} \hat{f}(s)$.

[4] The convolution theorem of the Laplace transform reads $\int_0^t f(t-\tau) g(\tau) \leftrightarrow \hat{f}(s)\hat{g}(s)$.

Starting from this definition, we obtain

$$
\begin{aligned}
(U, \mathscr{L}V)^* &= \frac{1}{Z}\mathrm{tr}\left\{\left(-\frac{i}{\hbar}(\boldsymbol{V}^\dagger\cdot\boldsymbol{H}-\boldsymbol{H}\cdot\boldsymbol{V}^\dagger)\right)\cdot\boldsymbol{U}\cdot e^{-\beta\boldsymbol{H}}\right\} \\
&= \frac{1}{Z}\mathrm{tr}\left\{e^{-\beta\boldsymbol{H}}\cdot\left(-\frac{i}{\hbar}(\boldsymbol{V}^\dagger\cdot\boldsymbol{H}-\boldsymbol{H}\cdot\boldsymbol{V}^\dagger)\right)\cdot\boldsymbol{U}\right\} = \frac{1}{Z}\mathrm{tr}\left\{e^{-\beta\boldsymbol{H}}\cdot\left(-\frac{i}{\hbar}(\boldsymbol{V}^\dagger\cdot\boldsymbol{H}\cdot\boldsymbol{U}-\boldsymbol{H}\cdot\boldsymbol{V}^\dagger\cdot\boldsymbol{U})\right)\right\} \\
&= \frac{1}{Z}\mathrm{tr}\left\{e^{-\beta\boldsymbol{H}}\cdot\left(-\frac{i}{\hbar}(\boldsymbol{V}^\dagger\cdot\boldsymbol{H}\cdot\boldsymbol{U}-\boldsymbol{V}^\dagger\cdot\boldsymbol{U}\cdot\boldsymbol{H})\right)\right\} \\
&= \frac{1}{Z}\mathrm{tr}\left\{e^{-\beta\boldsymbol{H}}\cdot\boldsymbol{V}^\dagger\cdot\left(-\frac{i}{\hbar}[\boldsymbol{H},\boldsymbol{U}]\right)\right\} = -(V, \mathscr{L}U),
\end{aligned}
$$

where it has been used that

$$
\frac{1}{Z}\mathrm{tr}\left\{e^{-\beta\boldsymbol{H}}\cdot\boldsymbol{H}\cdot\boldsymbol{V}^\dagger\cdot\boldsymbol{U}\right\} = \frac{1}{Z}\mathrm{tr}\left\{\boldsymbol{H}\cdot e^{-\beta\boldsymbol{H}}\cdot\boldsymbol{V}^\dagger\cdot\boldsymbol{U}\right\} = \frac{1}{Z}\mathrm{tr}\left\{e^{-\beta\boldsymbol{H}}\cdot\boldsymbol{V}^\dagger\cdot\boldsymbol{U}\cdot\boldsymbol{H}\right\}.
$$

With $(V, \mathscr{L}U) = (\mathscr{L}U, V)^*$, we have finally

$$
(U, \mathscr{L}V) = -(\mathscr{L}U, V) \quad \square
$$

C Proof of Eq. (62)

We consider classical Hamiltonian mechanics with a Hamilton function of the standard form

$$
H(p,q) = \sum_{k=1}^{3N}\frac{p_k^2}{2M_k} + U(q_1,\ldots,q_{3N}) \equiv T(p) + U(q), \tag{70}
$$

where $T(p)$ is the kinetic energy and the $U(q)$ the potential energy. The equilibrium phase space distribution function factorizes as

$$
\rho_{eq}(p,q) = \frac{e^{-\beta T(p)}}{Z_p}\frac{e^{-\beta U(q)}}{Z_q}, \tag{71}
$$

where $Z_p = \int d^n p\, \exp(-\beta T(p)$ and $Z_q = \int d^n q\, \exp(-\beta U(q)$. Supposing that the coordinates of the Brownian particle are the first three coordinates and that $M_1 = M_2 = M_2 = M$, we have

$$
G_{kl} = (v_k, v_l) = M^{-2}\int d^n p\, \exp(-\beta T(p)) p_k p_l = v_{th}^2\delta_{kl}, \tag{72}
$$

where $v_{th} = \sqrt{k_B T/M}$, and therefore

$$
\Omega_{kj} = (G^{-1})_{kl}(v_l, \mathscr{L}v_j) = (\delta_{kl}/v_{th}^2)(v_l, \mathscr{L}v_j), \quad k,j = 1,2,3.
$$

Using that $(v_l, \mathscr{L}v_j) = (p_l, \mathscr{L}p_j)/M^2$, we compute

$$
(p_l, \mathscr{L}p_j) = -(p_l, \partial H(p,q)/\partial q_j) = -(p_l, \partial U(q)/\partial q_j).
$$

With (71) the last term becomes

$$
-(p_l, \partial U(q)/\partial q_j) = \underbrace{\left(Z_p^{-1}\int d^{3N}p\, p_l e^{-\beta T(p)}\right)}_{=0}\underbrace{\left(Z_q^{-1}\int d^{3N}q\, e^{-\beta U(q)}\left(-\frac{\partial U}{\partial q_j}\right)\right)}_{\text{mean force}=0} = 0,
$$

where $l, j = 1,2,3$. Therefore

$$
\Omega_{kj} = 0 \quad \square \tag{73}
$$

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