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Mori-Zwanzig projection operator formalism: particle-based coarse-grained dynamics of open classical systems far from equilibrium

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ABSTRACT

We present a new generalized Langevin equation (GLE) of motion that governs exactly the time evolution of phase-space observables in finite open systems described by classical Hamiltonians with explicitly time-dependent potentials. This formalism is based on the Mori-Zwanzig projection operator (PO) method with a time-independent Zwanzig PO within a Heisenberg (Lagrangian) picture and reduced description of Hamiltonian systems in terms of canonical relevant and irrelevant coordinates. We demonstrate that, similarly to closed systems, GLE dynamics in Hamiltonian systems in the presence of time-dependent potentials is determined by conservative, dissipative memory, and projected force fields, and that the memory functions relate to the projected force, which is a two-time process, in a way that is reminiscent of the equilibrium second fluctuation-dissipation relation. We further show that, in the most general case, the memory kernel depends on the relevant momentum gradients of the (Boltzmann) entropy of the irrelevant subsystem. Using two Zwanzig operators which are, respectively, functionals of the canonical and generalized canonical probability densities, we then derive what we call canonical and generalized canonical GLEs. Further, we can formulate the particle-based, coarse-grained (CG) GLE dynamics by transitioning to the Jacobi coordinates that corresponds to a particle set partitioning of the Hamiltonian system. The obtained canonical CG GLE of motion for the relevant momenta is a generalization of the CG equation of motion known for closed systems. Also, using a Markovian approximation of the canonical CG GLE, we can extend the dissipative particle dynamics (DPD) equation to open systems. A distinctive feature of our extension is a use of explicitly time-dependent frictions, which reflect the changes in the dissipation rate caused by time-dependent coupling to an external bath. Our GLE formalism and workflow constitute a general and viable framework that can be readily used as a starting point to rigorously formulate microscopically informed CG treatments for a variety of phenomena in externally forced systems far from equilibrium.

I. INTRODUCTION

The projection operator (PO) formalism [1-14] remains one of the most powerful tools in statistical physics that prescribes how first-order equations of motion (e.g., Hamiltonian equations for observables or Liouville equations for probability densities) can be mapped onto reduced-dimensionality equations of motion. In statistical physics, the notion of POs was put forward by Nakajima [1] and then formalized by Mori and Zwanzig who introduced, in particular, the specific operators suitable to formulate a reduced description for classical and quantal systems. For this reason, PO theory is often referred to as the Mori-Zwanzig (MZ) theory. In general, the MZ formalism can be used within a Heisenberg (or Lagrangian) picture [15,16] to derive the equations of motion for the observables. These equations commonly appear in a time-convolution (generalized Langevin) form. Equally, the MZ method can be used within a Schrödinger (Eulerian) picture [9,14] to obtain the equations of motion for the probability densities (e.g., Fokker-Plank [9] and master [17] equations).

The MZ approach is widely used as a rigorous theoretical basis for treating nonequilibrium phenomena in many fields: transport theories [6,18-20], hydrodynamics and theories of liquids [15,21-24], theories of glasses [25], response theories [26,27], theories of nonlinear constitutive relations [6], damping theory [28], polymer physics [29-31], plasma physics [32], active matter [33], time-series analysis [34], classical density-functional theory [35,36], mode-coupling theory [22-25,37], correlation functions [6,38], relaxation phenomena [12], (active) probe dynamics [39], theory of turbulence [40], and the physics of phase transitions [41]. An important, and relatively recent, application of the MZ formalism is a

bottom-up particle-based, coarse-grained (CG) treatment where microscopic (Hamiltonian) systems are replaced with dynamically equivalent systems of CG particles [42,43] representing particle sets (clusters) in the Hamiltonian systems. Published applications have demonstrated that the time evolution of the translational degrees of freedom (d.f.) of the particle clusters composing a closed Hamiltonian system can be described by a (CG) generalized Langevin equation (GLE) of motion [31,44-53]. These works provided clear microscopic foundations for the dissipative particle dynamics (DPD) method, showing that the DPD equations arise as a Markovian case of CG GLE dynamics [31,48,51,54,55]. Applications of the MZ formalism encompass the bottom-up principles of a variety of particle-based CG models including hybrid-resolution models [51,56].

Open classical systems are usually understood as small Hamiltonian systems (i.e. with a finite number of d.f.) in contact with an external system (bath) [57]. The open classical systems are permeable to energy and not to matter and are always in nonequilibrium. The Hamiltonians can be explicitly time-dependent for open systems. Although the generalizations of the MZ formalism toward systems with time-dependent Hamiltonians have been topics of much research [58-60], the bottom-up particle-based CG GLE is not formulated for these systems. This is a consequence of many challenges faced by the MZ formalism to obtain practically useful CG equations of motion from time-dependent Hamiltonians. Those equations, however, are relevant for many scenarios which include soft-matter systems subjected to time-dependent external driving forces [39,61], systems of charged particles in external time-varying electromagnetic fields [62], and nonlinear response [15,27,63,64]. The formulation of GLE

dynamics for open systems is equivalent to the derivation of the second fluctuation-dissipation relation (FDR) for these systems [27,38]. The equilibrium FDRs can be rigorously derived within linear response theory [65]. Their validity in off-equilibrium situations, however, has been extensively discussed in the literature [66]. Consequently, the top-down applications of the equilibrium GLE and DPD models (in which the dissipative and projected forces are explicitly related via the equilibrium second FDR [67]) to states beyond equilibrium [68,69] are probing the boundaries of applicability of linear response theory [27,66]. Furthermore, the equilibrium GLE has to be properly extended with new terms to deal with the nonequilibrium. For example, the nonequilibrium conditions give rise to transport processes driven by the additional forces (transport terms) [9,50] which are required in the extended GLE. The constant energy variant of DPD (DPD-E method) suitable to treat energy transport in systems with a temperature gradient is an example of a top-down transport extension of the equilibrium GLE of motion [55,70,71].

In this work, we address the need for a framework to derive practical CG GLEs that rigorously project dynamics in the open classical systems with time-dependent Hamiltonians far from equilibrium. On the methodological side, the existence of such a framework is highly valued because: (1) it provides the structure of CG equations of motion which may be difficult, if not impossible, to guess from top-down considerations; (2) it clearly indicates the crucial points where approximations are required and provides the basis to apply these approximations systematically and consistently; and (3) it serves as a starting point to develop strategies for systematic parameterization of CG models which are tailored to study systems and states of interest. We limit ourselves to open systems which are described by Hamiltonians in the

presence of a time-dependent potential (i.e. the external force is the potential force). The reason for such a limitation is that Hamiltonians with more general system-bath coupling involving particle momenta give rise to a CG GLE with a far more complex memory term which cannot be reduced to a practical form. Our derivation follows the MZ formalism within a Heisenberg picture, which can be naturally extended to handle the systems with time-dependent Hamiltonians. The MZ formalism with time-dependent POs has been applied in the past to treat open quantal and classical systems far from equilibrium [38,59,60], as well as non-Hamiltonian systems [72]. In this paper, we show that GLE for the open Hamiltonian systems can be formulated using a time-independent Zwanzig PO, which simplifies the calculus and allows us to take the formalism to the point of obtaining practical, important CG equations of motion. In the reminder of the Introduction, we review the necessary preliminaries of the PO and MZ methods for classical systems.

The general problem addressed by the PO method in a Heisenberg picture for the open systems of interest is as follows. We consider an *n*-particle system with a phase space $\Gamma = \{r, p\}$, where the coordinates $r = \{r_i\}_{i=1}^n$, $p = \{p_i\}_{i=1}^n$ are the particle positions and momenta, respectively, and the following explicitly time-dependent Hamiltonian

$$H(\Gamma, t) = \sum_i \frac{p_i^2}{2m_i} + u(r,t) \tag{1}$$

where m_i is the *i*th particle mass. The term $u(r,t) = u_{int}(r) + u_{ext}(r,t)$ includes the interparticle interaction potential $u_{int}(r)$ and the external time-dependent potential $u_{ext}(r,t)$ which describes the coupling to external (potential) fields $F_{ext}(t) = -\nabla_r u_{ext}(r,t)$. The systems with coordinates

p, r coupled to external fields can be described by the Hamiltonian with a more general potential term $u_{ext}(\Gamma,t)$ when the corresponding external forces are momentum–dependent [9,15,28] (e.g. forces experienced by charged particles in a magnetic field). These systems are beyond the scope of the present work. We consider a sufficiently broad class of observables $\{B(\Gamma)\}$ which are functions of Γ with no explicit time dependence (the Hamiltonian obviously does not belong to this class, but the coordinates of the centers of mass of particle sets, for example, do). The flow of the observables, $B(\Gamma^t)$, along the system's phase space trajectory $\Gamma^t = \{r^t, p^t\}$ initiated at $t=0$ in the state Γ^0 is determined by the Liouville equation [15,16,73]:

$$\frac{d}{dt}B = iL(\Gamma^t,t)B \tag{2}$$

with the *p*-Liouvillian operator $iL(\Gamma,t)\cdot = \{\cdot, H(\Gamma,t)\}_\Gamma$, where $\{\cdot,\cdot\}_\Gamma$ are Poisson brackets in the Γ coordinates. We consider then the L^2 Hilbert space of the observables, $O = \{B(\Gamma^0)\}$, equipped with the inner product

$$\langle G;F\rangle_\rho \equiv \langle GF\rangle_\rho = \int d\Gamma^0 \rho(\Gamma^0,0)G(\Gamma^0)F(\Gamma^0), \tag{3}$$

where the weighting function is the specified probability density $\rho(\Gamma^0,t)$ at $t=0$, which, in general, can be non-stationary. A reduced description of the system dynamics is achieved by introducing a relevant set of independent observables: $A^0 = \{A_I(\Gamma^0)\}_{I=1}^N$, $A^0 \in O$, $N \square\ n$. The space $O_A = \{B_A(A^0)\}$ of the L^2 functions defined on A^0 is a subspace of the relevant

observables in O: $O_A \in O$. The PO method in a Heisenberg picture prescribes how to decompose the Hamiltonian vector field $iL\left(\Gamma^t, t\right)B$ [Eq. (2)] into the relevant $iL_A\left(t\right)B \in O_A$ and orthogonal (projected) $B^Q(t) \perp O_A$ contributions:

$$\frac{d}{dt}B = iL_A\left(t\right)B + B^Q\left(t\right) \ . \tag{4}$$

In terms of the inner product, the orthogonality property renders to

$$\left\langle B^Q(t); B_A \right\rangle_\rho = 0 \ , \tag{5}$$

where $\forall B_A \in O_A$, which can be interpreted as a lack of linear correlation between the projected force $B^Q(t)$ and the relevant dynamics in the ρ ensemble. This fact constitutes one of the major motivations to finding the decomposition in Eq. (4), as the $B^Q(t)$ term can be treated statistically with an equivalent stochastic process, which has a vanishing linear correlation with the relevant dynamics. An assumption that the A coordinates are "slow" is often made [9,13], however, it is not a necessary prerequisite for the orthogonality condition in Eq. (5). For the slow A, the relevant and irrelevant dynamics decorrelate on characteristic time scales of the A dynamics, which is advantageous when transitioning to a stochastic treatment of the projected force [31].

The PO P^0, $\mathrm{P}^{02} = \mathrm{P}^0$, is defined on O with the image in O_A. Using a Heisenberg picture, we consider the projection $\mathrm{P}^0 B^t$ of the flow $B^t = B\left(\Gamma^t\right)$, which belongs to O_A. The operator P^0 has a representation in a certain projection (though not necessarily complete) basis $\{\psi_i\}$ in O_A [5,9,74]:

$$\mathrm{P}^{0} B^{t} = \sum_{i} \left\langle B^{t}; \tilde{\psi}_{i} \right\rangle_{\rho} \psi_{i} \left(A^{0} \right) \tag{6}$$

where $\{\tilde{\psi}_i\}$ is the dual basis: $\left\langle \tilde{\psi}_i; \psi_j \right\rangle_{\rho} = \delta_{ij}$. The PO P^{0} in Eq. (6) has no explicit time-dependence if the basis $\{\psi_i\}$ and hence $\{\tilde{\psi}_i\}$ are stationary. In this case, the time evolution of the projection is carried out solely by B^t [48,50]. In fact, the difference between the POs (in a Heisenberg picture), which has been introduced in the past, can be expressed in terms of the different basis sets used in the representation in Eq. (6) [38]. Furthermore, for a similar reason, not all POs are equivalent and, in particular, not all operators can be used to obtain the exact equations of motion for an arbitrary observable $B(\Gamma)$, as per Eq. (4). For example, the Mori operator [4] has a representation in the basis $\{\psi_i\} = A^0$, which is incomplete in O_A and results in $iL_A(t)B$ being a linear functional of A (the so-called a-linear GLE [5]). Other operators are explicitly time-dependent (e.g., from Robertson [10-12], Kawasaki and Glunton [6], Ochiai [75], Willis and Picard [76], Grabert [7,13], McPhie et al. [59], Koide [19], Latz [77], Xing and Kim [72], and Meyer et al. [38]), as those operators can be represented effectively on an explicitly time-dependent basis $\{\psi_i\}$ [59], which somewhat complicates the resulting formalism. In this light, the Zwanzig PO (cf. Eq. (9.46) in Ref. [9]) seems to offer several important advantages. For the Zwanzig projection, the basis $\{\psi_i\}$ in Eq. (6) is complete in O_A [74]; consequently, the reduced equations of the motion in Eq. (4) are an exact representation of the Hamiltonian equations of motion in Eq. (2) [9,74,78]. For open and non-stationary systems inclusively, the Zwanzig PO can be made formally time-independent by using a

representation with a stationary basis $\{\psi_i\}$ [Eq. (6), also see Eq. (21)] [50]. Finally, the application of the Zwanzig PO is facilitated if A^0 is chosen to be a subset of the new canonical coordinates $\{A^0, \xi^0\}$ with a curvilinear mapping $\Gamma^0 = g(A^0, \xi^0)$ where ξ^0 is a canonical complement [48,50,51].

In this paper, we follow the previously described formalism to obtain the GLE for open CG systems. We start in Sec. II by discussing the Liouville propagator for open systems and introduce particle-based coarse-graining using the Jacobi coordinates. In Sec. III, following the formal PO calculus used in Refs. [13,20,49,79-82], which is more transparent for open systems compared to the Dyson decomposition [15,74] or Kawasaki identity [5], we obtain the time-convolution decomposition of the dynamics in open Hamiltonian systems. In Sec. IV, we describe an explicitly time-independent Zwanzig PO in a Heisenberg picture. In Sec. V, we pursue this development using the general canonical coordinates, a subset of which is considered the relevant observables, and the Zwanzig PO. We derive the most general GLE governing the nonequilibrium time evolution of the microscopic observables in open far-from-equilibrium systems. In the new GLE, the dissipative term is related to the projected term by the second FDR. Additionally, the dissipative term is determined by the relevant momentum gradients of the Boltzmann entropy of the irrelevant subsystem. Finally in this section, utilizing two Zwanzig operators which are, respectively, functionals of the canonical and generalized canonical probability densities, we derive what we refer to as canonical and generalized canonical GLEs. In Sec VI, we formulate CG GLE that describes the particle-based CG dynamics in the Jacobi

coordinates, which, for the canonical Zwanzig PO and closed systems, lead to known CG equations of motion. The Markovian approximation allows us to derive a DPD-type equation of motion for open systems. Finally, conclusions and outlook are given in Sec VII.

II. LIOUVILLE PROPAGATOR FOR OPEN SYSTEMS AND PARTICLE-BASED COARSE-GRAINING

The solution to the Liouville Eq. (2) can be written formally as [15,16,63,73,83]

$$B\left(\Gamma^t\right)=U_R(0,t)B\left(\Gamma^0\right). \tag{7}$$

The Liouville *p*-propagator $U_R(0,t)$, which we need to determine, satisfies the following operator equation [16]:

$$\frac{\partial}{\partial t}U_R(0,t)=U_R(0,t)iL(\Gamma^0,t). \tag{8}$$

Indeed, applying Eq. (8) to $B\left(\Gamma^t\right)$, we recover the Liouville equation in Eq. (2) as

$$\frac{d}{dt}B\left(\Gamma^t\right)=U_R(0,t)iL(\Gamma^0,t)B\left(\Gamma^0\right)=iL(\Gamma^t,t)B\left(\Gamma^t\right). \tag{9}$$

The formal iterative solution of Eq. (8) is the right time-ordered exponential (e_R):

$$U_R(0,t)=\sum_{n=0}^{\infty}\int_0^t ds_1\int_0^{s_1}ds_2\ldots\int_0^{s_{n-1}}ds_n iL(\Gamma^0,s_n)\ldots iL(\Gamma^0,s_2)iL(\Gamma^0,s_1)\equiv e_R^{\int_0^t dsiL\left(\Gamma^0,s\right)}, \tag{10}$$

$t>s_1>s_2>\cdots>s_n$. Provided the *p*-Liouvillian is explicitly time-independent, $iL(\Gamma^0,t)=iL(\Gamma^0)$ (e.g., the system is closed), we have

$$U_R(0,t)=e^{iL(\Gamma^0)t}. \tag{11}$$

We transition to a reduced description by combining the canonical relevant (CG) coordinates $A=\{R,P\}$ and their canonical irrelevant complement $\xi=\left\{r_\xi,p_\xi\right\}$ with, in general, a curvilinear coordinate mapping $\Gamma=g\left(A,\xi\right)$. A specific choice of coordinates $\left\{A,\xi\right\}$ is

prescribed by particle-based coarse-graining [42,43] when the system is partitioned into N non-overlapping particle clusters with masses $\{M_I\}_{I=1}^N$, $M_I = \sum_{i\in I} m_i$ and the coordinates $R = \{R_I\}_{I=1}^N, P = \{P_I\}_{I=1}^N$ describe translational d.f. of the clusters. A most common and convenient choice of $\{R,P\}$ is the center of mass (c.m.) positions of the clusters and their translational momenta, respectively:

$$R_I(r) = \frac{\sum_{i\in I} m_i r_i}{M_I},\ P_I(p) = \sum_{i\in I} p_i\ . \tag{12}$$

The generalized forces $F = \{F_I\}_{I=1}^N$,

$$F_I(r,t) = \dot{P}_I = \sum_{i\in I} f_i\ , \tag{13}$$

which are explicitly time-dependent, are easily computable linear mappings of the particle forces $f_i = \dot{p}_i$. The canonical coordinates of which the c.m. coordinates are a subset are the Jacobi coordinates, which for the Ith set are

$$\begin{aligned} r_{\xi,i_k} &= \frac{\sum_{i\le i_k | i\in I} m_i r_i}{\sum_{i\le i_k | i\in I} m_i} - r_{i_{k+1}},\ \ i_k, i_{k+1}\in I,\ k<|I| \\ r_{\xi,i_{|I|}} &= R_I \end{aligned} \tag{14}$$

($|I|$ denotes here a cardinality of set I). Therefore, $r_\xi = \{r_{\xi I}\}_{I=1}^N$, where $r_{\xi I} = \left\{ r_{\xi,i_k} \middle| i_k \in I, k<|I| \right\}$, can be chosen as the irrelevant canonical coordinates. Particle-based coarse-graining using the Jacobi coordinates is an example of the point transformation [84] (when the new position coordinates are functions of the old position coordinates only). The point transformation $R(r)$, $r_\xi(r)$ can always be inverted as $r(R, r_\xi)$. For the point transformation,

the complete set of conjugate momenta $\{P, p_\xi\}$ is [84] $\{P, p_\xi\} = \left\| \partial\left(R, r_\xi\right)/\partial r \right\|^{-1} p$. Furthermore, the Jacobi transformation $\{R(r), r_\xi(r)\}$ is linear and hence the transformation to Jacobi momenta $\{P(p), p_\xi(p)\}$ is also linear. For a canonical transformation, the Jacobian $\left|\partial\Gamma/\partial(A,\xi)\right| = 1$ and hence the volume measure is invariant:

$$d\Gamma = dAd\xi = dRdPdr_\xi dp_\xi \ . \tag{15}$$

For linear $R(r)$, $r_\xi(r)$ such as the Jacobi coordinates, the mass matrix of the system in the new coordinates is not a function of the old coordinates. If we assume that, additionally, the mass matrix associated with the relevant coordinates is diagonal, $\hat{M} = [M_I \delta_{IJ}]$, which is true for the Jacobi coordinates, then the Hamiltonian in Eq. (1) in the new coordinates becomes

$$H(A,\xi,t) = \sum_I \frac{P_I^2}{2M_I} + \frac{1}{2} p_\xi^T \hat{m}_\xi^{-1} p_\xi + u\left(R, r_\xi, t\right), \tag{16}$$

where $\hat{m}_\xi$ is the irrelevant mass matrix and $u\left(R, r_\xi, t\right) \equiv u\left(r\left(R, r_\xi\right), t\right)$. The new $H(A,\xi,t)$ is the canonical Hamiltonian which can be interpreted as describing the evolution of the c.m. coordinates of the particle clusters immersed into a sea of irrelevant d.f. in an external potential field. The $H(A,\xi,t)$ does not contain terms coupling the P and ξ coordinates. As we discuss, this property leads to far simpler and more standard GLEs.

III. TIME-CONVOLUTION DECOMPOSITION OF THE LIOUVILLE PROPAGATOR

Using the PO formalism, the Liouville dynamics [Eq. (7)] can be cast exactly into the reduced-dimensionality dynamics [Eq. (4)], in which the term $iL_A(t)B$ has time-convolution memory integrals [78]. This is achieved in two steps. First, Eq. (9) is transformed to a time-convolution equation (TCE), which retains the same mathematical structure for any (including time-dependent) PO P^0 and the complementary projector $\mathrm{Q}^0 = I - \mathrm{P}^0$ defined on $O = \left\{B\left(\Gamma^0\right)\right\}$. To obtain a general TCE, we use the formal operator approach [20,49,79-82] to perform a time-convolution decomposition of the dynamics in a Heisenberg picture. This approach works for generic (including time-dependent) POs and time-dependent Hamiltonians [79], so, for open systems, it seems advantageous compared to a Dyson decomposition or Kawasaki identity [5]. We begin with the two identities derived from Eq. (8):

$$\begin{aligned} \frac{\partial}{\partial t}U_R(0,t) &= U_R(0,t)\left(\mathrm{P}^0+\mathrm{Q}^0\right)iL(\Gamma^0,t) \\ \frac{\partial}{\partial t}U_R(0,t)\mathrm{Q}^0 &= U_R(0,t)\left(\mathrm{P}^0+\mathrm{Q}^0\right)iL(\Gamma^0,t)\mathrm{Q}^0 \end{aligned} \quad . \tag{17}$$

The second line, which is obtained by operating on the first line with Q^0 on the right and hence describes the irrelevant (projected) dynamics, is a nonhomogeneous linear operator equation with respect to $U_R(0,t)\mathrm{Q}^0$. Substituting its formal solution

$$U_R(0,t)\mathrm{Q}^0 = e_R^{\int_0^t ds\mathrm{Q}^0 iL\left(\Gamma^0,s\right)}\mathrm{Q}^0 + \int_0^t d\tau U_R(0,\tau)\mathrm{P}^0 iL(\Gamma^0,\tau)e_R^{\int_0^{t-\tau} ds\mathrm{Q}^0 iL\left(\Gamma^0,s\right)}\mathrm{Q}^0 \tag{18}$$

into the first line of Eq. (17), while transforming $\mathrm{Q}^0 e_R^{\int_0^t ds iL\left(\Gamma^0,s\right)\mathrm{Q}^0} = e_R^{\int_0^t ds \mathrm{Q}^0 iL\left(\Gamma^0,s\right)}\mathrm{Q}^0$ and then applying the resultant equation on $B\left(\Gamma^0\right)$, we obtain the following TCE:

$$\frac{d}{dt}B\left(\Gamma^t\right) = U_R(0,t)\mathrm{P}^0 iL(\Gamma^0,t)B\left(\Gamma^0\right) + \int_0^t d\tau U_R(0,t-\tau)\mathrm{P}^0 iL(\Gamma^0,t-\tau)B^{\mathrm{Q}}\left(\tau,t\right) + B^{\mathrm{Q}}\left(t,t\right). \quad (19)$$

In this equation, the first term in the right-hand side is the conservative force $B^C\left(t\right)$, the second term is the dissipative force $B^D\left(t\right)$, and the projected force is

$$B^{\mathrm{Q}}\left(\tau,t\right) = e_R^{\int_0^\tau ds \mathrm{Q}^0 iL\left(\Gamma^0,s\right)}\mathrm{Q}^0 iL(\Gamma^0,t)B\left(\Gamma^0\right). \quad (20)$$

Note, that in addition to being a function of the past time τ, the force $B^{\mathrm{Q}}\left(\tau,t\right)$ is an explicit function of the present time t as a result of the explicit time-dependence of $iL(\Gamma^0,t)$. The force $B^{\mathrm{Q}}\left(\tau,t\right)$ can be interpreted as the projected force of the system in the configuration $\left(\Gamma^\tau,t\right)$, that is, the system in the (past) state Γ^τ but where the external force is taken at the (present) time moment t (cf. Sec. 7.7 in [15]). Finally we note that the TCE in Eq. (19) holds for the time-dependent P^0, Q^0. In this case, the time ordering of the projection operations is taken care of by the exponent e_R in Eq. (20).

IV. ZWANZIG PROJECTION OPERATOR

In the second stage of the GLE derivation, we have to specify the PO. Our theory is based on a Zwanzig PO (cf. Eq. (9.46) in Ref. [9]) [31,44,47,49-51] in a Heisenberg picture

[15,16,74]. The corresponding Zwanzig projection of the flow $B\left(\Gamma^t\right)$ is the following thermodynamic conditional expectation given an initial A^0:

$$\mathrm{P}^{\,0}B\left(\Gamma^t\right)\equiv\left\langle B\left(\Gamma^t\right)\right\rangle_{\rho;A^0}^{cond}=\frac{\int d\Gamma^0\rho(\Gamma^0,0)\delta\left(A\left(\Gamma^0\right)-A^0\right)B\left(\Gamma^t\right)}{\int d\Gamma^0\rho(\Gamma^0,0)\delta\left(A\left(\Gamma^0\right)-A^0\right)}\ , \tag{21}$$

with integration over a given probability density $\rho(\Gamma,t)$ taken at $t=0$. The ensemble average is given by the unconditional thermodynamic expectation

$$\left\langle B\left(\Gamma^t\right)\right\rangle_\rho=\int d\Gamma^0\rho(\Gamma^0,0)B\left(\Gamma^t\right)\ . \tag{22}$$

It is convenient to work in terms of the conditional probability density

$$\rho\left(\Gamma\mid A,t\right)=\frac{\rho\left(\Gamma,t\right)}{\int d\Gamma\rho(\Gamma,t)\delta\left(A\left(\Gamma\right)-A\right)}\ , \tag{23}$$

which in coordinates $\Gamma=g\left(A,\xi\right)$ is denoted as

$$\rho_A\left(\xi,t\right)=\frac{\rho\left(g\left(A,\xi\right),t\right)}{\int d\xi\rho\left(g\left(A,\xi\right),t\right)} \tag{24}$$

where we to use Eq. (15). The Zwanzig projection in Eq. (21) then becomes

$$\mathrm{P}^{\,0}B\left(\Gamma^t\right)=\int d\xi^0\rho_{A^0}\left(\xi^0,0\right)B\left(\Gamma^t\right)\ . \tag{25}$$

The PO $\mathrm{P}^{\,0}$ is explicitly time-independent and the time-dependence of the projection is carried out solely by the time-evolution of $B\left(\Gamma^t\right)$. By expanding integral in Eq. (25) into the complete basis set $\left\{\psi_i\left(A^0\right)\right\}$, we can obtain the representation in Eq. (6). The majority of time-dependent POs that have been introduced in the past are functionals of $\rho\left(\Gamma,t\right)$ which is allowed to evolve

in time [13,17]. Since the projections are linear functionals of both the observable and $\rho(\Gamma,t)$, the projection basis $\{\psi_i\}$ in Eq. (6), in general, is explicitly time-dependent.

V. GLE FOR A GENERAL $\rho(\Gamma,t)$

A CG GLE for open systems is derived from the TCE in Eq. (19) using the explicit expression for a Zwanzig PO, Eqs. (21) and (25). The GLE force field is the sum of the conservative, dissipative, and projected force field terms:

$$\frac{d}{dt}B\left(\Gamma^t\right)=B^C\left(t\right)+B^D\left(t\right)+B^Q\left(t\right)\equiv iL^{GLE}\left(\left[\rho\right],t\right)B\left(\Gamma^t\right)\ . \tag{26}$$

The relevant contribution [Eq. (4)] is $iL_A\left(t\right)B=B^C\left(t\right)+B^D\left(t\right)$. In Eq. (26), we introduced the operator functional $iL^{GLE}\left(\left[\rho\right],t\right)$ to compactly denote the GLE force field. This notation reflects that the GLE is obtained for the PO using ρ and hence the GLE force field is a (linear) functional of ρ. The identicality of the Liouville and GLE dynamics can then be formulated as

$$iL^{GLE}\left(\left[\rho\right],t\right)=iL\left(t\right). \tag{27}$$

The mathematical form of the GLE is uniquely determined by the ρ and hence we may refer to the GLE by the name of the ensemble which the ρ represents (e.g. "equilibrium GLE" for equilibrium probability density ρ_{eq}). Following Zwanzig [3], we can use the equivalence of microscopic and GLE dynamics [Eq. (27)], and hence the independence of the GLE dynamics on ρ, to derive additional forces (transport terms) which are introduced to the equilibrium GLE to account for the transport of the averages of dynamical variables, $\left\langle B(t)\right\rangle_{\rho_{eq}}$.

Let us briefly outline this approach: we represent the quasi-equilibrium ρ as $\rho = \rho_{eq} + \delta\rho$ where $\delta\rho$ is a small perturbation; we can perturbatively expand the iL^{GLE} as

$$iL^{GLE}\left([\rho],t\right) = iL^{GLE}\left(\left[\rho_{eq}\right],t\right) + \int d\Gamma \delta\rho \frac{\delta}{\delta\rho} iL^{GLE}\left(\left[\rho_{eq}\right],t\right) + o([\delta\rho]) \ ; \tag{28}$$

it then follows from the equivalence in Eq. (27) that the terms linear in $\delta\rho$ are the additional forces necessary to add to $iL^{GLE}\left(\left[\rho_{eq}\right],t\right)$ to account for the transport phenomena in the quasi-equilibrium [39]. The transport equations for $\langle B(t)\rangle_{\rho_{eq}}$ are then obtained by averaging Eq. (26) over ρ_{eq}. This approach was used in Ref. [41] to derive the constant energy variant of the GLE.

In the remainder of this section, we derive expressions defining $B^C(t)$ and $B^D(t)$ in terms of conditional expectations $\langle\cdot\rangle_A^{cond}$ and then write down the GLE. The derivation of $B^D(t)$ holds for the canonical transformation $\Gamma = g(A,\xi)$, which does not lead to the terms in $H(A,\xi,t)$, which couple P and ξ [see the discussion of Eq. (16)]. The derivation for a general $H(A,\xi,t)$ is possible; however, the resulting GLE ought to adopt a more complex and less familiar form.

1. Conservative term

The conservative term $B^C(t)$ can be derived easily using the rule in Eq. (7), which for the relevant projection $A^t \equiv A^t(\Gamma^0)$ of trajectory Γ^t becomes $A^t = U_R(0,t)A^0$. Thus, we have

$$B^C(t) = U_R(0,t)\mathrm{P}^0 iL(\Gamma^0,t)B\left(\Gamma^0\right) = \left\langle iL(\Gamma^0,t)B\left(\Gamma^0\right)\right\rangle^{cond}_{\rho;A^0\to A^t} \ . \tag{29}$$

where, for clarity, in this equation, we use the previous, more explicit notation $iL(\Gamma^0,t)$.

If $B(\Gamma)=A(\Gamma)$, then the conservative term

$$A^C(t)=\hat{\Omega}_N\left\langle\nabla_{A^0}H\left(\Gamma^0,t\right)\right\rangle^{cond}_{\rho;A^0\to A^t}\ , \tag{30}$$

where $\hat{\Omega}_N$ is the $2N\times 2N$ simplectic matrix. For a closed system in the canonical equilibrium $\rho(\Gamma,0)=\rho_c(\Gamma)$,

$$\rho_c(\Gamma)=\frac{e^{-H(\Gamma)/k_BT}}{Z}\ , \tag{31}$$

we obtain

$$A^C(t)=\hat{\Omega}_N\nabla_{A^t}H^{rel}(A^t)\ . \tag{32}$$

Here, the relevant Hamiltonian

$$H^{rel}(A)=-k_BT\ln\Gamma_A^h\left\langle\delta\left(A(\Gamma^0)-A\right)\right\rangle_{\rho_c} \tag{33}$$

is the restricted Helmholtz free energy where Γ_A^h is a normalizing factor of dimensions of the volume element dA to cancel the dimensions of the average (e.g. for identical CG particles and the Jacobi coordinates, $\Gamma_A^h=h^{3N}N!$). Equation (32) justifies calling the term B^C the conservative force. For coarse-graining using the Jacobi coordinates and similar linear point coordinate transformations [see discussion of Eq. (16)], we have

$$H^{rel}(P,R)=\sum_I\frac{P_I^2}{2M_I}+W_{PMF}(R)+F_{id}^{irr}\ , \tag{34}$$

where $W_{PMF}(R)=-k_BT\ln V_\xi^{-1}\int dr_\zeta e^{-u\left(R,r_\xi\right)/k_BT}$ is the all-particle potential of mean force (PMF) and a constant $F_{id}^{irr}=-k_BT\ln h^{-3(n-N)}g_\xi^{-1}V_\xi\int dp_\xi e^{-p_\xi^T\hat{m}_\xi^{-1}p_\xi/(2k_BT)}$ is the ideal gas contribution from

the irrelevant momenta (here, $V_\xi = \int dr_\xi$ is the volume and g_ξ is the degeneracy factor for the irrelevant d.f.). For open systems, the term corresponding to $W_{PMF}(R)$ in Eq. (34) cannot be introduced. More generally, $H^{rel}(A,t)$, which is used to calculate a conservative term similar to Eq. (32) for closed systems, cannot be used in open systems. As we discuss in Sec. V.3, for GLE describing the time evolution of A, the potential $H^{rel}(A,0)$ can still be introduced if the GLE is derived using a canonical PO, i.e., in which $\rho(\Gamma,0) = Z^{-1}e^{-H(\Gamma,0)/k_BT}$. However, in this case, the potential H^{rel} can be related to A^C only at $t=0$ and, additionally, it appears in the dissipative term $B^D(t)$.

2. Dissipative term

The derivation of the dissipative term $B^D(t)$ in the GLE is more cumbersome but essentially follows the derivation for closed systems in a canonical ensemble [50]. During the course of the derivation, the anti-Hermitian property of iL must be replaced with

$$\langle iLO;B\rangle_\rho = -\langle O;iLB\rangle_\rho - \langle O;BiL\ln\rho(0)\rangle_\rho \,, \tag{35}$$

$\rho(0) \equiv \rho(\Gamma,0)$, which is obtained from integration by parts. Below, for a clarity, we use a vector component notation B_s to indicate that the observable $B = \{B_s\}$ may be a set of observables themselves. First, we express the memory term $B^D(t)$ in the TCE [Eq. (19)] in the following form:

$$B^D(t) = \int_0^t d\tau U_R(0,t-\tau)\left\langle iL(t-\tau)B^Q(\tau,t)\right\rangle^{cond}_{\rho;A^0} \,, \tag{36}$$

where following the definition of P^0 in Eq. (21), we express the projection $\mathrm{P}^0 iL(t-\tau)B^{\mathrm{Q}}$ as the conditional expectation. We expand

$$\left\langle iL(t-\tau)B^{\mathrm{Q}}(\tau,t)\right\rangle_{\rho;A^0}^{cond} = \sum_i b_i^{\mathrm{Q}}(\tau,t)\psi_i\left(A^0\right) \tag{37}$$

using the functional basis $\left\{\psi_i\left(A^0\right)\right\}_{i=1}^{\infty}$, which is orthonormal,

$$\left\langle \psi_i\left(A^0\right)\psi_j\left(A^0\right)\right\rangle_\rho = \delta_{ij}, \tag{38}$$

and complete [see Eq. (6)]. The expansion coefficients are

$$b_i^{\mathrm{Q}}(\tau,t) = \left\langle \left\langle iL(t-\tau)B^{\mathrm{Q}}(\tau,t)\right\rangle_{\rho;A^0}^{cond}\psi_i\left(A^0\right)\right\rangle_\rho = \left\langle iL(t-\tau)B^{\mathrm{Q}}(\tau,t);\psi_i\left(A^0\right)\right\rangle_\rho . \tag{39}$$

Integrating by parts in the thermodynamic average in the right-hand side of Eq. (39) [see Eq. (35)], we obtain

$$b_i^{\mathrm{Q}}(\tau,t) = -\left\langle B^{\mathrm{Q}}(\tau,t)iL(t-\tau)\psi_i\right\rangle_\rho - \left\langle B^{\mathrm{Q}}(\tau,t)\psi_i iL(t-\tau)\ln\rho(0)\right\rangle_\rho \tag{40}$$

(for clarity, we have eliminated the notation of the explicit dependence on A^0 in the averaging). For an equilibrium ρ, the last term in Eqs. (35) and (40) vanishes and hence $iL(t)$ is anti-Hermitian. We recall that in the canonical coordinates $\{A,\xi\}$, the canonical form of $iL(t)$ is preserved:

$$iL(t)\psi_i = \left\{\psi_i, H\left(\Gamma^0,t\right)\right\}_{\Gamma^0} = -\nabla_{R^0}H\left(\Gamma^0,t\right)\cdot\nabla_{P^0}\psi_i + \nabla_{P^0}H\left(\Gamma^0,t\right)\cdot\nabla_{R^0}\psi_i . \tag{41}$$

If we assume that $H(\Gamma,t)$ does not contain terms coupling P to the ξ coordinates [see discussion of Eqs. (1) and (16)], then the second term in Eq. (41) is the CG phase-space observable and thus is orthogonal to $B^{\mathrm{Q}}(\tau,t)$:

$$\left\langle B^{\mathrm{Q}}\left(\tau,t\right)\nabla_{P^0}H\left(\Gamma^0,t-\tau\right)\cdot\nabla_{R^0}\psi_i\left(A^0\right)\right\rangle_\rho\equiv 0\,. \tag{42}$$

Therefore, we are able to transform the expansion in Eq. (37) [with b_i^{Q} from Eq. (39)] into

$$\left\langle iL\left(t-\tau\right)B^{\mathrm{Q}}\left(\tau,t\right)\right\rangle_{\rho;A^0}^{cond}=$$
$$-\sum_i\left\{\left\langle B^{\mathrm{Q}}\left(\tau,t\right)\left[-\nabla_{\tilde{R}^0}H\left(\tilde{\Gamma}^0,t-\tau\right)\cdot\nabla_{\tilde{P}^0}\right]\psi_i\left(\tilde{A}^0\right)\right\rangle_\rho+\left\langle\psi_i\left(\tilde{A}^0\right)B^{\mathrm{Q}}\left(\tau,t\right)iL\left(t-\tau\right)\ln\rho\left(0\right)\right\rangle_\rho\right\}\psi_i\left(A^0\right), \tag{43}$$

where we assume the averaging is over the tilde coordinates $\left\{\tilde{A}^0,\tilde{\xi}^0\right\}$. The basis $\left\{\psi_i\right\}$ is complete:

$$\sum_i\psi_i\left(\tilde{A}^0\right)\psi_i\left(A^0\right)=\frac{\delta\left(\tilde{A}^0-A^0\right)}{\left\langle\delta\left(\tilde{A}^0-A^0\right)\right\rangle_\rho}\,. \tag{44}$$

We note that $\rho\left(A^0\right)=\left\langle\delta\left(\tilde{A}^0-A^0\right)\right\rangle_\rho$ in Eq. (44) is a weighting function for the inner product in the A^0 subspace. After we perform the summation over i in Eq. (43) using Eq. (44), we obtain

$$\left\langle iL\left(t-\tau\right)B^{\mathrm{Q}}\left(\tau,t\right)\right\rangle_{\rho;A^0}^{cond}=-\frac{\left\langle B^{\mathrm{Q}}\left(\tau,t\right)\left[-\nabla_{\tilde{R}^0}H\left(\tilde{\Gamma}^0,t-\tau\right)\cdot\nabla_{\tilde{P}^0}\right]\delta\left(\tilde{A}^0-A^0\right)\right\rangle_\rho}{\left\langle\delta\left(\tilde{A}^0-A^0\right)\right\rangle_\rho}$$
$$-\frac{\left\langle\delta\left(\tilde{A}^0-A^0\right)B^{\mathrm{Q}}\left(\tau,t\right)iL\left(t-\tau\right)\ln\rho\left(0\right)\right\rangle_\rho}{\left\langle\delta\left(\tilde{A}^0-A^0\right)\right\rangle_\rho}\,. \tag{45}$$

Next, in the first term of Eq. (45), making use of the known properties $B^{\mathrm{Q}}\left(\tau,t\right)\equiv\mathrm{Q}^0B^{\mathrm{Q}}\left(\tau,t\right)$, $\nabla_{\tilde{P}^0}\delta\left(\tilde{A}^0-A^0\right)=-\nabla_{P^0}\delta\left(\tilde{A}^0-A^0\right)$, and the Hermicity of Q^0, $\left\langle\mathrm{Q}^0B^{\mathrm{Q}};B\right\rangle_\rho=\left\langle B^{\mathrm{Q}};\mathrm{Q}^0B\right\rangle_\rho$, we transform the transpose of Eq. (45) as

$$\left\langle iL\left(t-\tau\right)B^{\mathrm{Q}}\left(\tau,t\right)\right\rangle_{\rho;A^0}^{cond\ T}=\frac{\nabla_{P^0}^{T}\left\langle\delta\left(\tilde{A}^0-A^0\right)B^{\mathrm{Q}}\left(\tau,t\right)\otimes\mathrm{Q}^0\left[-\nabla_{\tilde{R}^0}H\left(\tilde{\Gamma}^0,t-\tau\right)\right]\right\rangle_{\rho}^{T}}{\left\langle\delta\left(\tilde{A}^0-A^0\right)\right\rangle_{\rho}}$$
$$-\frac{\left\langle\delta\left(\tilde{A}^0-A^0\right)B^{\mathrm{Q}}\left(\tau,t\right)iL\left(t-\tau\right)\ln\rho\left(0\right)\right\rangle_{\rho}^{T}}{\left\langle\delta\left(\tilde{A}^0-A^0\right)\right\rangle_{\rho}}$$
$$=\frac{\nabla_{P^0}^{T}\left\langle\delta\left(\tilde{A}^0-A^0\right)\right\rangle_{\rho}\left\langle\delta\left(\tilde{A}^0-A^0\right)B^{\mathrm{Q}}\left(\tau,t\right)\otimes\mathrm{Q}^0\left[-\nabla_{\tilde{R}^0}H\left(\tilde{\Gamma}^0,t-\tau\right)\right]\right\rangle_{\rho}^{T}}{\left\langle\delta\left(\tilde{A}^0-A^0\right)\right\rangle_{\rho}^{2}}$$
$$+\nabla_{P^0}^{T}\frac{\left\langle\delta\left(\tilde{A}^0-A^0\right)B^{\mathrm{Q}}\left(\tau,t\right)\otimes\mathrm{Q}^0\left[-\nabla_{\tilde{R}^0}H\left(\tilde{\Gamma}^0,t-\tau\right)\right]\right\rangle_{\rho}^{T}}{\left\langle\delta\left(\tilde{A}^0-A^0\right)\right\rangle_{\rho}}$$
$$-\frac{\left\langle\delta\left(\tilde{A}^0-A^0\right)B^{\mathrm{Q}}\left(\tau,t\right)iL\left(t-\tau\right)\ln\rho\left(0\right)\right\rangle_{\rho}^{T}}{\left\langle\delta\left(\tilde{A}^0-A^0\right)\right\rangle_{\rho}} \tag{46}$$

where the symbol $\otimes$ denotes the outer product. Finally, in the vector component notation $B=\left\{B_s\right\}$, we introduce the memory tensor functions

$$\hat{\gamma}_{sJ}\left(\tau,t,A^0\right)=\frac{1}{k_B}\frac{\left\langle\delta\left(\tilde{A}^0-A^0\right)B_s^{\mathrm{Q}}\left(\tau,t\right)\otimes\mathrm{Q}^0\left[-\nabla_{\tilde{R}^0}H\left(\tilde{\Gamma}^0,t-\tau\right)\right]\right\rangle_{\rho}}{\left\langle\delta\left(\tilde{A}^0-A^0\right)\right\rangle_{\rho}}$$
$$=\frac{1}{k_B}\left\langle B_s^{\mathrm{Q}}\left(\tau,t\right)\otimes\left[-\mathrm{Q}^0\nabla_{\tilde{R}^0}H\left(\tilde{\Gamma}^0,t-\tau\right)\right]\right\rangle_{\rho;A^0}^{cond} \tag{47}$$

We observe that in this equation, the force $-\mathrm{Q}^0\nabla_{R_J}H\left(\Gamma,t\right)$ is the projected force from Eq. (20) for $B\left(\Gamma^0\right)=P^0$ [when $iL(\Gamma^0,t)P^0=-\nabla_{R^0}H$]:

$$F_J^{\mathrm{Q}}\left(\tau,t\right)=-e_R\int_0^{\tau}ds\mathrm{Q}^0 iL\left(\Gamma^0,s\right)\mathrm{Q}^0\nabla_{R_j^0}H\left(\Gamma^0,t\right) \tag{48}$$

taken at $\tau=0$. The memory function in Eq. (47) then adopts a more familiar form:

$$\hat{\gamma}_{sJ}\left(\tau,t,A^0\right)=\frac{1}{k_B}\left\langle B_s^{\mathrm{Q}}\left(\tau,t\right)\otimes F_J^{\mathrm{Q}}\left(0,t-\tau\right)\right\rangle_{\rho;A^0}^{cond}. \tag{49}$$

This equation is analogous to the equilibrium second FDR, but it holds for arbitrary out-equilibrium states processes [38]. In terms of the memory function in Eq. (49) and the vector component notation, Eq. (46) becomes

$$\begin{aligned}\left\langle iL\left(t-\tau\right)B_s^{\mathrm{Q}}\left(\tau,t\right)\right\rangle_{\rho;A^0}^{cond}=&-\sum_J\left\{\hat{\gamma}_{sJ}\left(\tau,t,A^0\right)\nabla_{P_J^0}S_B\left(A^0\right)-k_B\left[\nabla_{P_J^0}^T\hat{\gamma}_{sJ}^T\left(\tau,t,A^0\right)\right]^T\right\}\\&-\left\langle B_s^{\mathrm{Q}}\left(\tau,t\right)iL(t-\tau)\ln\rho(0)\right\rangle_{\rho;A^0}^{cond}\end{aligned}. \tag{50}$$

Here, the potential

$$S_B\left(A\right)=-k_B\ln\Gamma_A^h\left\langle\delta\left(A\left(\Gamma^0\right)-A\right)\right\rangle_\rho=-k_B\ln\Gamma_A^h\int d\Gamma^0\rho\left(\Gamma^0,0\right)\delta\left(A\left(\Gamma^0\right)-A\right) \tag{51}$$

is the Boltzmann entropy of the irrelevant subsystem [31] where Γ_A^h is the normalizing factor as in Eq. (33). This interpretation follows from the equality $\left\langle\delta\left(A\left(\Gamma^0\right)-A\right)\right\rangle_\rho=1/\Gamma_A^0$ where Γ_A^0 is the volume of the microscopic phase space Γ^0 associated with the macrostate A and the fact that the corresponding number of irrelevant microstates is $W_A=\Gamma_A^0/\Gamma_A^h$. Therefore, $S_B\left(A\right)=k_B\ln W_A$. Substituting Eq. (50) into Eq. (36), we finally obtain the general expression for the dissipative term:

$$B_s^D(t) =$$
$$-\int_0^t d\tau \left(\sum_J \left\{ \hat{\gamma}_{sJ}\left(t-\tau,t,A^\tau\right) \nabla_{P_J^\tau} S_B\left(A^\tau\right) - k_B \left[\nabla_{P_J^\tau}^T \hat{\gamma}_{sJ}^T \left(t-\tau,t,A^\tau\right) \right]^T \right\} + \left\langle B_s^Q\left(t-\tau,t\right) iL(\tau) \ln \rho(0) \right\rangle_{\rho;A^\tau}^{cond} \right)$$

. (52)

3. GLE and canonical GLE

Putting Eqs. (29) and (52) into vector component notation, we obtain the following GLE:

$$\frac{d}{dt} B_s\left(\Gamma^t\right) = \left\langle iL(t) B_s\left(\Gamma^0\right) \right\rangle_{\rho;A^0 \to A^t}^{cond}$$
$$-\int_0^t d\tau \left(\sum_J \left\{ \hat{\gamma}_{sJ}\left(t-\tau,t,A^\tau\right) \nabla_{P_J^\tau} S_B\left(A^\tau\right) - k_B \left[\nabla_{P_J^\tau}^T \hat{\gamma}_{sJ}^T \left(t-\tau,t,A^\tau\right) \right]^T \right\} + \left\langle B_s^Q\left(t-\tau,t\right) iL(\tau) \ln \rho(0) \right\rangle_{\rho;A^\tau}^{cond} \right)$$
$$+B_s^Q\left(t,t\right)$$

(53)

where the memory function is given by Eq. (47) and the projected force $B_s^Q\left(\tau,t\right)$ is given by Eq. (20) [see also Eq. (48)]. The less general but perhaps more practically useful GLE is obtained for $B \equiv A$, and choosing the $\rho(0)$ to be of the canonical form [compare to Eq. (31)],

$$\rho_c\left(\Gamma,0\right) = \frac{e^{-H(\Gamma,0)/k_B T}}{Z(0)} \ . \tag{54}$$

From the definition of S_B in Eq. (51) and the definition of H^{rel} in Eq. (33) where $\rho_c\left(\Gamma,0\right)$ is used, we have the following relation

$$\nabla_{P^0} S_B\left(A^0\right) = \frac{1}{T} \nabla_{P^0} H^{rel}\left(A^0,0\right). \tag{55}$$

Furthermore, the last term in the dissipative force [Eqs. (52) and (53)] vanishes. This leads to the following (canonical) CG GLE:

$$\begin{aligned}&\frac{d}{dt}A_s\left(\Gamma^t\right)=\hat{e}_{ss}\hat{\Omega}_N\left\langle\nabla_{A^0}H\left(\Gamma^0,t\right)\right\rangle^{cond}_{\rho_c;A^0\to A^t}\\&-\int_0^t d\tau\sum_J\left\{\hat{\gamma}_{sJ}\left(t-\tau,t,A^\tau\right)\nabla_{P_J^\tau}H^{rel}\left(A^\tau,0\right)-k_BT\left[\nabla^T_{P_J^\tau}\hat{\gamma}^T_{sJ}\left(t-\tau,t,A^\tau\right)\right]^T\right\}+A_s^{\mathrm{Q}}\left(t,t\right)\end{aligned}\tag{56}$$

($\hat{e}_{ss}$ is the $2N\times 2N$ single-entry matrix) with the memory tensor being scaled down by T

$$\hat{\gamma}_{sJ}\left(\tau,t,A^0\right)=\frac{1}{k_BT}\left\langle A_s^{\mathrm{Q}}\left(\tau,t\right)\otimes F_J^{\mathrm{Q}}\left(0,t-\tau\right)\right\rangle^{cond}_{\rho_c;A^0}\ .\tag{57}$$

It is interesting that although the system can be out of equilibrium, the notion for temperature can be still naturally introduced to the GLE. However, the use of temperature in Eq. (57) (which resembles the equilibrium second FDR) is rather superfluous and, in principle, can be eliminated: the canonical GLE dynamics is an exact map of the deterministic Hamiltonian dynamics and therefore does not rely on the notion of temperature.

For systems weakly influenced by external fields or which are in quasi-equilibrium where there is a set $\left\{X_l^{rel}\left(\Gamma\right)\right\}$ of relevant variables which evolve slowly, it is more appropriate to use the probability density of generalized canonical form $\rho_{gc}(\Gamma,t)=e^{-k_B^{-1}\Phi(t)-\sum_l\beta_l(t)X_l^{rel}(\Gamma)}$ [14], where $\Phi(t)=k_B\ln\int d\Gamma e^{-\sum_l\beta_l(t)X_l^{rel}(\Gamma)}$ is the Massieu–Planck function. The ρ_{gc} maximizes the Gibbs entropy functional $S_G[\rho]=-k_B\int d\Gamma\rho(\Gamma,t)\ln\rho(\Gamma,t)$. The Gibbs entropy then is $S_G(t)=\Phi(t)+k_B\sum_l\beta_l(t)x_l^{rel}(t)$, where $x_l^{rel}\left(t\right)=\int d\Gamma\rho_{gc}\left(\Gamma,t\right)X_l^{rel}\left(\Gamma\right)$. The conditional probability density is obtained following Eqs. (23) and (24): $\rho_{gc;A}\left(\xi,t\right)=e^{-k_B^{-1}\Phi(A,t)-\sum_l\beta_l^{rel}(t)X_l^{rel}(\Gamma)}$

with the conditional Massieu-Planck function $\Phi(A,t) = k_B \ln \int d\xi e^{-\sum_l \beta_l^{rel}(t) X_l^{rel}(\Gamma)}$. The thermodynamic state of the irrelevant subsystem is described by the variables $x_l^{rel}(A,t) = \int d\xi \rho_{gc;A}(\xi,t) X_l^{rel}(\Gamma)$, $x_l^{rel}(A,t) = -k_B^{-1} \delta\Phi(A,t)/\delta\beta_l(t)$ and their conjugates $\beta_l(t) = \delta S_G(A,t)/\delta x_l^{rel}(A,t)$ where the conditional Gibbs entropy is $S_G(A,t) = \Phi(A,t) + k_B \sum_l \beta_l(t) x_l^{rel}(A,t)$. From Eq. (51), it follows

$$\nabla_{P^0} S_B(A^0) = k_B \sum_l \beta_l(0) \nabla_{P^0} x_l^{rel}(A^0,0) - \nabla_{P^0} S_B(A^0) \sum_l \beta_l(0) x_l^{rel}(A^0,0) \tag{58}$$

from which we can find $\nabla_{P^0} S_B(A^0)$. The generalized canonical GLE can then be straightforwardly obtained from Eq. (53). In many applications, it is convenient and justifiable to choose $\{X_l^{rel}(\Gamma)\}_l = B$ if the B are slow variables.

VI. PARTICLE-BASED CANONICAL CG DYNAMICS AND MARKOVIAN ASSUMPTION

The particle-based canonical CG equations of motion are obtained from Eq. (56) in which $A = \{R,P\}$ are the Jacobi coordinates [Eqs. (12) and (14)]. Formally, the GLE can be written for the R coordinates; however, this GLE must be equivalent to $dR_I/dt = \nabla_{P_I} H^{rel} = M_I^{-1} P_I$, $I = 1,\ldots,N$, where the Hamiltonian H^{rel} is given in Eq. (34). Therefore, in the GLE for R, the memory and projected terms must vanish. The nontrivial GLE is obtained for the momenta P. From Eq. (55), we have

$$\nabla_{P^0} S_B(A^0) = \frac{1}{T} \left\{ \frac{P_I^0}{M_I} \right\}_{I=1}^{N}. \tag{59}$$

From Eqs. (56) and (1), we then obtain the following canonical CG GLE:

$$\begin{aligned}&\frac{d}{dt}P_I^t=-\left\langle\nabla_{R_I^0}u\left(r^0,t\right)\right\rangle_{R^0\to R^t}^{cond}\\&-\int_0^t d\tau\sum_J\left\{\hat{\gamma}_{IJ}\left(t-\tau,t,R^\tau,P^\tau\right)\frac{P_J^\tau}{M_J}-k_BT\left[\nabla_{P_J^\tau}^T\hat{\gamma}_{IJ}^T\left(t-\tau,t,R^\tau,P^\tau\right)\right]^T\right\}+F_I^{\mathrm{Q}}\left(t,t\right)\end{aligned}\tag{60}$$

with

$$\hat{\gamma}_{IJ}\left(\tau,t,R^0,P^0\right)=\frac{1}{k_BT}\left\langle F_I^{\mathrm{Q}}\left(\tau,t\right)\otimes F_J^{\mathrm{Q}}\left(0,t-\tau\right)\right\rangle_{R^0,P^0}^{cond}\tag{61}$$

where we dropped ρ_c in the expectation notation. The projected force is orthogonal to the P as

$$\left\langle P_{I,i}^t F_{J,j}^{\mathrm{Q}}\left(\tau,t\right)\right\rangle=0\,,\ t\geq\tau\geq 0,\ \ \forall I,J;\ \ i,j=1,2,3\tag{62}$$

where i , j indicate the vector components. Equations (47), (61) are both second FDR which is already known to hold for microscopic Hamiltonian systems in nonequilibrium states [27]. Equations (47), (61) prescribe a consistent procedure for generalization of the equilibrium second FDR (which can be derived within linear response theory) to open systems.

A generalized Markovian approximation can be introduced for open systems [60]. For CG dynamics in closed systems in equilibrium, a Markovian approximation is a major assumption, leading to the DPD equations of motion. We show that while a Markovian approximation can be introduced for open systems, the friction tensors approximating the memory functions become explicitly time-dependent, which reflects a change in the strength of the dissipative interactions caused by time variations in the strength of the coupling of the irrelevant subsystem to the external field. Using a Markovian approximation amounts to neglecting the memory effects in Eq. (60) and is justified when there is a strong separation

between characteristic time scales for the slow relevant and fast irrelevant dynamics. In this scenario the scale for the decay in τ of the memory functions $\hat{\gamma}_{IJ}(\tau,t,R^0,P^0)$ in Eq. (61) becomes short compared to the characteristic scale for the $A(\tau)$ trajectory evolution and we can use the following approximation

$$\hat{\gamma}_{IJ}\left(\tau,t,R^0,P^0\right)\approx\delta(\tau)2\hat{\bar{\gamma}}_{IJ}(t,R^0,P^0) \tag{63}$$

where

$$\hat{\bar{\gamma}}_{IJ}(t,R^0,P^0)=\frac{1}{k_BT}\int_0^\infty d\tau\left\langle F_I^{\mathrm{Q}}(\tau,t)\otimes F_J^{\mathrm{Q}}(0,t-\tau)\right\rangle_{R^0,P^0}^{cond} \tag{64}$$

are friction tensors expressed in the Green-Kubo form [31]. The next standard approximation we use is an assumption that $\hat{\bar{\gamma}}_{IJ}$ is not an explicit function of $\left\{R^0,P^0\right\}$. In this approximation, the conditional expectation $\langle\cdot\rangle_{R^0,P^0}^{cond}$ in Eq. (64) can be replaced with unconditional averaging $\langle\cdot\rangle$ while the gradient term $\nabla_{P_J}^T\hat{\bar{\gamma}}_{sJ}^T$ vanishes [see Eq. (60)] [47-50]. An additional observation of DPD is that the dissipative and projected forces are momentum conserving: $\sum_J F_J^{\mathrm{Q}}(0,t)=0$ and thus $\hat{\bar{\gamma}}_{II}(t)=-\sum_{J\neq I}\hat{\bar{\gamma}}_{IJ}(t)$. These approximations lead to the following DPD equation for open systems:

$$\frac{d}{dt}P_I^t=-\left\langle\nabla_{R_I^0}u\left(r^0,t\right)\right\rangle_{R^0\to R^t}^{cond}+\sum_{J\neq I}\hat{\bar{\gamma}}_{IJ}(t)\left(\frac{P_I^t}{M_I}-\frac{P_J^t}{M_J}\right)+F_I^{\mathrm{Q}}(t,t)\ . \tag{65}$$

where the friction tensors $\hat{\bar{\gamma}}_{IJ}$ and the projected forces F_I^{Q} are related by the following second FDR:

$$\left\langle F_I^{\mathrm{Q}}(\tau,t)\otimes F_J^{\mathrm{Q}}(0,t)\right\rangle=\delta(\tau)2k_BT\hat{\bar{\gamma}}_{IJ}(t)\ ,\ t\geq\tau\geq 0,\ I\neq J\ . \tag{66}$$

Note, here the friction tensors $\hat{\bar{\gamma}}_{IJ}$ are negative-definite which is a result of a sign convention on the average in Eq. (64) that has been adopted in the literature [31,85]. The FDR in Eq. (66) is internally consistent with describing τ evolution of the $F^{\mathrm{Q}}(\tau,t)$ by additive white noise $F^S(\tau)=\left\{F_I^S(\tau)\right\}_{I=1}^N$ (e.g., superposition of Gaussian white noises [67]). Furthermore, Eq. (66) implies that the τ and t scales are also separated (e.g. the characteristic time scale for the variation of the external forces is much longer compared to the characteristic scale for the intrinsic irrelevant dynamics). Therefore, when transitioning to a DPD description, we can go further and represent the projected force $F^{\mathrm{Q}}(t,t)$ in Eq. (65) by the following linear combination of Gaussian white noises [67,86]: $F_I^S(t)=\sum_J B_{IJ}(t)dW_J(t)/dt$, where $W_J(t)$ are Wiener processes [17,28] and $B_{IJ}(t)$ are deterministic processes satisfying $\sum_K B_{IK}(t)B_{JK}(t)=2k_BT\hat{\bar{\gamma}}_{IJ}(t)$. We are then able to satisfy the DPD FDR in Eq. (66) as:

$$\left\langle F_I^S(t)\otimes F_J^S(t')\right\rangle=\delta(t-t')2k_BT\hat{\bar{\gamma}}_{IJ}(t)\ ,\ t\geq t' \tag{67}$$

where we used the stationarity of $F_I^S(t)$.

Applying the DPD framework to open systems [Eqs. (65) and (67)] is complicated by the fact that the friction tensors, and consequently the FDR, are explicitly time-dependent. The frictions and the respective stochastic process designed to model the projected force must reflect the effect of the external force on the irrelevant dynamics. To assess our assumption that the CG dynamics in a microscopic system are Markovian, we compare the decay time of the

autocorrelations $C_F(t) = \left\langle F\left(r^t, t\right) \cdot F(r^0, 0)\right\rangle$ of the generalized forces [Eq. (13)] with the characteristic scale of the CG dynamics as commonly determined by the decay time of the P autocorrelations, $C_P(t) = \left\langle P^t \cdot P^0 \right\rangle$ [31,86]. $C_F(t)$ decaying faster than $C_F(t)$ would indicate that $F^{\mathrm{Q}}\left(t,t\right)$ can be treated stochastically within the FDR in Eq. (67). This, in turn, requires that the characteristic timescale of the external force may be large compared to the characteristic scale of the CG dynamics. This disparity in the characteristic timescales is a hallmark of Markovian behavior [31,86].

VII. SUMMARY AND OUTLOOK

We have shown that for classic Hamiltonian systems which are influenced by the external explicitly time-dependent potentials (we refer to such systems as open systems) and are far from equilibrium, the MZ formalism with a time-independent Zwanzig PO $\mathrm{P}^0\left[\rho\right]$ in a Heisenberg picture [Eq. (21)] can perform an exact time-convolution decomposition of the dynamics into relevant (CG) and irrelevant parts [Eq. (19)]. To develop our formalism, we required that together the CG and irrelevant coordinates form a canonical set. At this stage, we kept the formalism very general and obtained the GLE [Eq. (53)], which describes exactly the Hamiltonian time evolution [Eqs. (2) and (4)] of the microscopic observables without explicit time-dependence. The dynamics was determined by a GLE with time-reversible conservative [Eq. (29)], time-irreversible dissipative [Eq. (52)], and projected [Eq. (20)] force terms. The projected force [Eq. (20)] can be viewed as a two-time process with the first timescale determined by the phase trajectories Γ^τ and the second timescale determined by the explicit

time-dependence of the Hamiltonian [Eq. (1)]. The dissipative force takes a time-convolution form and can be expressed through memory tensor functions related to the projected force through the second FDR [Eqs. (49), (57), and (61)]. Furthermore, in general, the dissipative force depends linearly on the gradients of the (Boltzmann) entropy $S_B(A)$ of the irrelevant subsystem [Eq. (51)]. For closed systems and canonical Zwanzig $\mathrm{P}^0[\rho]$ (i.e., which corresponds to the canonical ρ), the $S_B(A)$ can be related to the relevant (CG) Helmholtz free energy [Eq. (33)]. Our framework using the canonical $\mathrm{P}^0[\rho]$ leads to a CG GLE [Eq. (56)] that is an extension of the known CG GLE but to open systems. The further generalization of the canonical CG GLE is obtained by using the ρ of the generalized canonical form. The main application we seek for our formalism is particle-based coarse-graining of open Hamiltonian systems, which is accomplished by transitioning to the Jacobi coordinates [Eqs. (12) and (14)] considering the c.m. coordinates [Eq. (12)] of the particle clusters as the CG coordinates. This is followed by the derivation of the particle-based CG GLE, which governs exactly the time evolution of the CG coordinates (the relevant Jacobi momenta) in open classical systems [Eq. (60)]. The obtained expressions for the particle-based CG GLE memory tensors through the projected force correlations [Eq. (61)] can be viewed as an open-system generalization of the second FDR known for closed systems in the equilibrium. This extension has not been previously reported.

We have also shown that in the Markovian limit, the particle-based CG GLE is a memoryless equation of motion of the DPD type with frictions that are explicitly time-

dependent. The time dependence of the frictions reflects a time-variable dissipation rate caused by coupling of the irrelevant subsystems to an external time-dependent bath. We have formulated criteria to determine whether the CG dynamics in open systems can be considered Markovian, and hence can use the stochastic differential equation (SDE) approach, where the projected force is modeled using additive Gaussian white noise.

Regardless of the $\rho(\Gamma,0)$ which determines the $\mathrm{P}^{0}[\rho]$, the presented CG GLE time evolution must be an exact map of the microscopic Liouville evolution and, as such, can serve as a starting point when considering CG dynamics in various approximations including those for transport equations [see Eq. (28)], response theories, DPD and its variants, the nonequilibrium statistical operator method [17]. An important application envisaged is the internal energy transport in open molecular systems. Energy transport processes can be described by the coupled set of GLEs governing the evolution of the position, momentum, and internal energy of thermal blobs representing entire complex molecules at the CG level [50,87]. Considering that the Jacobi conjugate momenta can be calculated analytically, the present generalizations of the CG GLE theory emerge as a tractable framework to study a range of other transport processes. Potential applications include bottom-up formulations of more complex coupled CG dynamics to describe the evolution of various properties of microscopic systems and in various ensembles. Many of these properties are not feasible to calculate from the CG trajectories alone due to loss of information upon coarse-graining.

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