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Thermal Bath Modeling in Open Quantum and Quantum-Classical Systems

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ABSTRACT

A predictive description of a chemical process in the condensed phase requires the elimination of the overwhelming majority of the degrees of freedom in favour of their averaged statistical influence upon a small set of retained coordinates. The quantity characterizing that influence differs according to whether the retained coordinates are propagated classically or quantum mechanically: the classical reduction retains a friction kernel, defined as a conditional equilibrium correlation function of the environmental force, whereas the quantum reduction retains the power spectrum of the bath operator to which the system couples. This thesis establishes the conditions under which these two descriptors characterize the same environment, quantifies the dynamical consequences of their violation, and measures the classical descriptor for a solvated molecular photoswitch.

A single projection-operator derivation yields both reductions and supplies microscopic definitions of the friction tensor and of the fluctuating force. A harmonic environment bilinearly coupled to the system coordinate relates the two descriptors exactly, and the conditions this model imposes are enumerated. The correspondence is then tested numerically upon a two-state photoisomerization model, propagated both by a vibronic Redfield equation and by the quantum-stochastic Liouville equation. The form of the system-bath coupling operator alone is found to determine the branching ratio, which spans the full accessible range at fixed bath parameters; quantitative agreement between the two descriptions is attainable, but only at a friction exceeding the value dictated by the correspondence by two orders of magnitude.

The descriptor is subsequently measured rather than postulated. A protocol extracting the conformation-dependent friction from the fluctuations of the generalized force along a restrained torsion is developed, validated upon a coarse-grained model, and applied to 4,4'-dihydroxyazobenzene in explicit water. The friction varies by a factor of 6.8 along the isomerizing coordinate, is maximal at the planar geometries and minimal at the perpendicular one, and is steric rather than dielectric in origin. This topology is the inverse of that implied by the coupling operators employed in the preceding benchmark, and thereby excludes them.

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ACRONYMS

BO	Born-Oppenheimer
CB	classical bath
CL	Caldeira-Leggett
COM	centre of mass
CS	classical subsystem
DOF	degrees of freedom
ES	excited state
FACF	force autocorrelation function
FC	Franck-Condon
FDT	fluctuation-dissipation theorem
FFT	fast Fourier transform
GLE	generalized Langevin equation
GS	ground state
HOMO	highest occupied molecular orbital
KMS	Kubo-Martin-Schwinger
LJ	Lennard-Jones
LUMO	lowest unoccupied molecular orbital
MD	molecular dynamics
NPT	isothermal-isobaric ensemble
NVT	canonical ensemble
PBC	periodic boundary conditions
PES	potential energy surface
PME	particle-mesh Ewald
PMF	potential of mean force
QCLE	quantum-classical Liouville equation
QS	quantum subsystem
QSLE	quantum-stochastic Liouville equation
RDO	reduced density operator
SMD	steered molecular dynamics
TST	transition-state theory
VACF	velocity autocorrelation function

INTRODUCTION

The improvement of a chemical process, whether through the identification of an alternative pathway, the design of a more efficient reagent, or the suppression of a competing channel, requires knowledge of the underlying mechanism by which that process occurs. Every branch of the discipline contributes to this understanding: analytical chemistry identifies the products and by-products; organic and inorganic chemistry supply the structural and reactivity principles governing candidate pathways; and physical chemistry provides the thermodynamic, kinetic, and spectroscopic observables for the rationalization of the process and its molecular interpretation. Although these fields provide useful information regarding the phenomenon of interest, none provides direct insight into the mechanism itself. A mechanism is a statement about how a molecular structure evolves in time, whereas every experimental technique reports a functional of that evolution, averaged over a macroscopic ensemble and projected upon the few coordinates to which the probe is sensitive. A rate constant reports the integrated flux across a dividing surface; a vibrational spectrum reports a set of frequencies; a transient absorption trace reports a population weighted by a transition dipole. Each constrains the underlying dynamics without determining it, and the inference from the observable to the motion that produced it is neither unique nor direct.

Reconstructing that temporal evolution is the domain of molecular dynamics (MD) simulation, which supplies the microscopic trajectories from which the measured projections may be constructed. Operating as a complement to experiment, simulation provides the information required to interpret complex physicochemical data. The reliability of the mechanistic conclusions drawn from these models depends upon the physical approximations they embody. The construction, evaluation, and validation of one specific class of those approximations form the subject of this thesis.

1.1 THE MULTISCALE CHALLENGE IN CONDENSED-PHASE CHEMISTRY

The objective of theoretical and computational chemistry is the identification of the simplest representation capable of reproducing the phenomenon under investigation. This task begins with isolating the relevant portion of the total system. The decision of which coordinates to retain precedes the choice of the formalism used to describe them. In the condensed phase, bridging the gap between this reduced representation and the direct propagation of the microscopic equations of motion presents significant challenges, primarily driven by dimensionality and computational cost.

A typical chemical system consists of a molecule of interest immersed in a solvent, and the objective is to extract mechanistic information concerning that solute. The surrounding environment contributes the overwhelming majority of the

degrees of freedom (DOF), resulting in a configuration space possessing a dimensionality several orders of magnitude greater than that of the species under study. Sampling this full phase space requires extensive computational resources, yet the individual identity of these solvent coordinates is irrelevant to the solute: they act upon it only collectively, through the statistical properties of their fluctuations.

This dimensional challenge is compounded by the cost inherent to a quantum mechanical treatment. Although the laws of quantum mechanics govern molecular systems, the exact numerical solution of the many-body Schrödinger equation scales exponentially with system size. This scaling restricts fully quantum treatments to small molecular fragments in vacuum, rendering them inapplicable to macroscopic assemblies or solvated systems without further reduction.

When investigating the dynamics of such composite systems, it becomes necessary to leverage the distinct characteristics of the constituent DOF. The separation of timescales between electronic and nuclear motion, resulting from their disparate masses, forms the basis of the Born-Oppenheimer (BO) approximation.[1–3] This framework allows the heavy nuclei to be propagated on a single potential energy surface generated by the fast electrons. However, in many photochemical processes, such as photoisomerization, strong non-adiabatic coupling governs the dynamics. The concept of motion on an isolated surface becomes invalid, requiring nuclear trajectories to be propagated across coupled electronic states.[4, 5] In these regimes, the disparity in mass motivates the development of mixed quantum-classical descriptions. Propagating the fast electronic coordinates quantum mechanically and a subset of the slower nuclear DOF classically reduces the computational cost.

These limitations share a common feature: the computational effort is dictated by the full microscopic specification of the system, whereas the physical and chemical content is localized within a small subset of coordinates. The remaining environmental DOF cannot simply be discarded, as their collective action thermalizes the reactive coordinates, drives energy dissipation, and dictates the reaction yield. Resolving this impasse requires a fundamental reformulation. The mechanistically critical coordinates must be retained and propagated explicitly, while the environment is eliminated in favour of its averaged statistical influence.

1.2 THE SYSTEM-BATH PARADIGM

That reformulation is not a mere theoretical approximation peculiar to condensed-phase simulation. It is the operation by which chemistry has always rendered molecules tractable, and its most familiar instance is one that no chemist regards as an approximation at all.

The BO separation partitions the constituents of a molecule by timescale. Coarse-grained models of macromolecular and biomolecular systems perform the same operation in the opposite direction, eliminating fast intramolecular coordinates in favour of effective interactions between the slow collective variables that remain.[6] The two constructions differ in which coordinates are retained and in the criterion by which the retention is decided; they do not differ in kind.

In its general form, this operation defines the system-bath paradigm, by which the dimensional reduction demanded by condensed-phase chemistry is achieved.

Rather than treating an entire molecular assembly on an equal footing, the macroscopic system is partitioned conceptually into a localized, relevant subsystem and a surrounding thermal bath. The environmental [DOF](#) are then eliminated in favour of their averaged statistical influence upon the retained subsystem. What must be supplied to complete the reduced description is a characterization of these eliminated [DOF](#): not their individual trajectories, which the reduction discards, but the statistical properties of the physical influence they exert. This characterization constitutes the bath descriptor, and its accurate formulation is the primary subject of this thesis.

This paradigm would be of limited interest were the environment merely a weak perturbation upon dynamics determined elsewhere. In a broad class of chemical processes, the bath is instead an active participant that dictates the mechanism and the outcome. Three well-established phenomena, drawn from distinct areas of chemistry, illustrate this environmental control. Each relies upon a system-bath partition, yet each requires a fundamentally different property of the bath to predict the experimental observable.

The first example is outer-sphere electron transfer, a ubiquitous process in solution chemistry where a donor and an acceptor exchange an electron without forming or breaking chemical bonds. Because the molecular structures remain largely intact, the reaction possesses no obvious intramolecular coordinate; Marcus recognized that the reaction coordinate is instead supplied by the solvent.[\[7, 8\]](#) Thermal fluctuations in the collective polarization of the medium modulate the electronic states of the solute, and the transfer occurs only at the transient solvent configuration that renders the donor and acceptor states degenerate. The activation barrier is dictated by the free-energy difference of the reaction alongside the reorganization energy, which quantifies the thermodynamic penalty of polarizing the solvent without transferring the electron. The resulting rate exhibits a non-monotonic dependence on the driving force that has been confirmed experimentally across biological and electrochemical systems.[\[9\]](#) In this context, the bath descriptor is a macroscopic thermodynamic quantity. When the solvent relaxes slowly compared to the electronic transition, the rate acquires a dependence upon the longitudinal relaxation time of the medium, elevating the descriptor from a static free energy to a dynamical property.[\[10\]](#)

The second phenomenon is the migration of excitation energy within photosynthetic light-harvesting complexes, which transfer absorbed solar energy to a reaction centre with near-unit efficiency. The chromophores within these biological networks possess mismatched site energies due to their varying local protein environments, hindering coherent exciton delocalization. The environment resolves this mismatch by assisting rather than disrupting the transport. Vibrational fluctuations driven by the protein scaffold suppress the destructive quantum interference that would otherwise localize the excitation, while simultaneously providing the specific energy quanta required to bridge the gaps between mismatched pigments.[\[11–13\]](#) Predicting this environment-assisted quantum transport requires a bath descriptor that captures the spectral distribution of the environmental fluctuations, resolved in frequency and evaluated at the specific energy gaps of the multichromophoric system.

The third example governs barrier crossings and transitions. Standard transition-state theory (TST) assigns to a barrier crossing a rate determined entirely by the equilibrium free-energy profile, on the assumption that a trajectory reaching the barrier top proceeds to products without return.[14] In solution, this assumption fails, and it fails in two opposite ways. Kramers showed that at strong coupling, the solvent randomizes the velocity of the reactive coordinate within the barrier region, causing the dividing surface to be recrossed repeatedly so that the rate falls as the friction rises. At weak coupling, the solvent supplies energy to the coordinate too slowly to maintain a thermal population near the barrier top, and the rate falls as the friction is reduced.[15] The rate is therefore non-monotonic in the friction, a behaviour observed in the pressure and viscosity dependence of isomerization rates and photoisomerization quantum yields in liquids and compressed gases.[16] For a photochemical process, the friction governs not only the rate but the identity of the product, since it dictates whether the excess energy released upon passage through the region of electronic degeneracy is dissipated before or after the system commits to one of the accessible minima.[17] The bath descriptor demanded here is a single scalar, the friction coefficient, and the outcome of the reaction depends upon it non-monotonically.

1.3 THESIS OBJECTIVES AND OUTLINE

The problem posed at the close of the preceding section is addressed here in a specific setting: the photoisomerization of a molecular switch about a double bond, in an explicit aqueous environment. The choice is deliberate. The process is non-adiabatic, meaning the retained coordinates cannot be treated by classical mechanics alone. Its outcome is decided during a passage through a region of electronic degeneracy, the duration of which is comparable to the time the environment requires to dissipate the released energy. Consequently, the bath acts neither as a static perturbation nor as a fully equilibrated reservoir. Furthermore, the reactive coordinate is a torsion, and therefore periodic, a geometric feature that proves incompatible with the assumptions upon which the standard formal correspondence between classical and quantum bath descriptors rests. The system is thus not merely an application of the theoretical framework, but a stringent stress test of its underlying assumptions.

Three objectives follow. The first is to establish, from a single microscopic derivation, exactly what each description retains of an eliminated environment, and under what conditions the resulting quantities are equivalent. The second is to determine whether two descriptions of the same process, one propagating the retained coordinates fully quantum mechanically and the other treating the nuclear coordinate classically, yield consistent dynamics when their bath parameters are related by that formal correspondence. The third is to replace the postulated theoretical bath with a measured one, extracting the descriptor directly from atomistic simulations of the solvated molecule rather than assigning it by parameterization.

Chapter 2 presents the elimination of the environment in both the classical and the quantum descriptions, using the same projection-operator construction. The classical treatment yields a generalized Langevin equation in which the friction is a conditional equilibrium correlation function of the environmental force.

The quantum treatment yields a Redfield equation in which the environment enters through the power spectrum of the coupling operator. The chapter concludes without establishing whether these two quantities characterize the same physical environment.

Chapter 3 constructs the theoretical model in which they demonstrably do—a bath of harmonic oscillators linearly coupled to the system coordinate—and enumerates the physical conditions that this model imposes. It then tests the formal correspondence numerically by propagating a two-state photoisomerization model in both a fully quantum and a mixed quantum-classical description. Comparing their response to their respective bath parameters identifies which features of the environment the two descriptions successfully represent, and which features are carried by an operator for which the classical formulation possesses no analogue.

Chapter 4 derives the classical descriptor directly from molecular dynamics. A computational protocol is developed to extract the conformation-dependent friction along a torsional coordinate from the fluctuations of the generalized force. The methodology is validated upon a coarse-grained model and applied to 4,4'-dihydroxyazobenzene in explicit water. The resulting atomistic friction profile is then confronted with continuum-hydrodynamic calculations and with the coupling operators assumed in the preceding quantum benchmark.

Chapter 5 draws the results together and sets out the theoretical developments required to complete the construction.

The original contributions of this work are the projection-operator derivation of Subsection 2.1.6 and Appendix A, presented at a level of generality that admits non-linear system-bath coupling; the implementation of the dissipative vibronic quantum dynamics of Subsection 3.3.2 and the non-adiabatic benchmark of Section 3.4; and the extraction protocol, atomistic simulations, and hydrodynamic analysis of Chapter 4.

What is offered in this thesis is a physical diagnosis, together with the components required to resolve the problem it identifies, rather than a closed multiscale computational scheme. The conditions under which the classical and quantum descriptions of the bath coincide are formally established, the dynamical consequences of their violation are quantified, and the descriptor is measured for a real solvated molecule. Returning that measured descriptor to the quantum dynamics framework requires further methodological developments, which Chapter 5 identifies and which lie beyond the present work.

THERMAL BATH MODELLING

As established in the preceding chapter, a predictive description of chemical processes in the condensed phase cannot rely on the explicit propagation of every microscopic DOF involved. Instead, the system-bath partition offers a computationally viable framework: a small manifold of chemically relevant coordinates (the *system*) is retained and propagated explicitly, while the remaining DOF (the *thermal bath*), being neither experimentally accessible nor of chemical interest, are eliminated in favour of their averaged statistical influence upon the retained coordinates.

This chapter outlines the two theoretical formulations required to model this environmental influence. Section 2.1 introduces the classical stochastic description of the thermal bath,[18–23] while Section 2.2 extends these concepts to the quantum regime, developing the description of an open quantum system.[24–26]

2.1 STOCHASTIC DESCRIPTIONS OF THE THERMAL BATH

The foundation of the system-bath paradigm can be traced back to the observation, made by the botanist Robert Brown in 1827, that particles released from pollen grains suspended in water exhibit an animated and irregular motion.[27] The phenomenon, subsequently termed Brownian motion, remained unexplained until the seminal works of Einstein[28] in 1905 and, independently in the following year, of Smoluchowski.[29]

Einstein’s solution rests upon two propositions. The first is dynamical: the irregular motion of the suspended grain originates from the incessant, random collisions with the molecules of the surrounding fluid. The second is methodological, and it is the more consequential. Because these collisions are exceedingly frequent and effectively uncorrelated on the timescale over which the displacement of the grain is resolved, their cumulative effect necessitates a probabilistic, rather than deterministic, description.

The formalism of Brownian motion extends well beyond the suspended particle. The «Brownian particle» can be abstracted to represent any collective variable of a macroscopic system that evolves on a timescale significantly slower than its environment. Examples range from the instantaneous concentration of a reacting species near equilibrium to the orientational relaxation of a dipolar molecule in a polar solvent.[30, 31]

The apparent randomness inherent to these processes arises from our adoption of a reduced description. By seeking a simplified representation of a complex process, we necessarily isolate a small subset of relevant observables, whether macroscopic, such as energy and pressure, or microscopic, such as a specific bond length or a centre-of-mass position. When the full, deterministic equations of motion are projected onto this reduced phase space, the microscopic influence of the numerous unobserved DOF manifests as random fluctuations.[18]

Consequently, every macroscopic physical quantity we observe is accompanied by inherent fluctuations arising from the microscopic motion of the underlying bath. While these fluctuations are often small relative to the ensemble average and can sometimes be neglected, they encode information regarding the microscopic dynamics and dissipative properties of the environment. Brownian motion is the first problem in which the properties of a high-dimensional, inaccessible bath are inferred through their statistical imprint on a single observable [DOF](#), and it is the historical origin of the system-bath paradigm. The remainder of this section develops that description in its classical form, beginning with the equation of motion proposed for the suspended particle itself.

2.1.1 The Langevin Equation

Despite its apparent stochasticity, Brownian motion arises from a system governed by the same equations of motion as any other dynamical system. Consider the one-dimensional motion of a Brownian particle of mass m and velocity v . Its evolution is governed by Newton's equation of motion

$$m \frac{dv}{dt} = F(t) \quad (2.1)$$

where $F(t)$ represents the instantaneous force exerted by the surrounding medium at time t .

In the phenomenological treatment of thermal environments, this environmental force is partitioned into two distinct contributions. This division rests upon a separation of time scales: the force exerted by the bath loses correlation on a timescale far shorter than that required for the velocity of the much heavier Brownian particle to change appreciably. The first component is therefore a systematic macroscopic dissipative term, $-\xi v$, characterized by a time-independent friction coefficient ξ . If this were the sole environmental influence, the dynamics would describe a monotonic dissipation of kinetic energy, driving the particle's velocity to zero within a characteristic relaxation time m/ξ . However, this purely deterministic decay violates the equipartition theorem, which mandates a finite mean thermal kinetic energy, $\langle v^2 \rangle_{\text{eq}} = k_B T/m$, at equilibrium.

To rectify this and maintain thermal equilibrium, a second component is introduced: a fluctuating stochastic force, $R(t)$, representing the microscopic collisions with the bath molecules. This term injects energy back into the system, counterbalancing the macroscopic dissipation. Retaining both components, Equation (2.1) yields the Langevin equation[\[32, 33\]](#)

$$m \frac{dv}{dt} = -\xi v + R(t) \quad (2.2)$$

which is historically significant as the first stochastic differential equation, i.e., a differential equation containing a random term. Because the driving force $R(t)$ is a random variable, the velocity $v(t)$ itself becomes a stochastic process. Each realization of the noise generates a unique trajectory, and macroscopic physical predictions are obtained as ensemble averages over these realizations.

When the particle moves in an external potential $V(x)$, which, for a coordinate embedded in a solvent, is to be understood as a potential of mean force (PMF), the same partition generalizes to

$$m \frac{dv}{dt} = -\frac{\partial V(x)}{\partial x} - \xi v + R(t) \quad (2.3)$$

which serves as the standard working equation for propagating a generalized reaction coordinate in condensed-phase systems.

The model is fully determined only once the statistical properties of the noise are specified. In this phenomenological limit, $R(t)$ is modelled as a stationary Gaussian white noise process.[34, 35] Physically, this is the limiting case of the separation of time scales invoked above, in which the correlation time of the environmental force is taken to zero. The noise is then completely characterized by its first two moments

$$\langle R(t) \rangle = 0 \quad \langle R(t)R(t') \rangle = 2B\delta(t - t') \quad (2.4)$$

where B quantifies the strength of the fluctuating force, and the Dirac delta enforces this memoryless limit. The noise is assumed to be statistically independent of the initial velocity (i.e., $\langle v(0)R(t) \rangle = 0$ for $t > 0$).

For the free particle, Equation (2.2) is a linear, first-order differential equation that can be formally integrated to yield[36, 37]

$$v(t) = v(0) e^{-\xi t/m} + \frac{1}{m} \int_0^t ds e^{-\xi(t-s)/m} R(s) \quad (2.5)$$

The first term dictates the deterministic decay of the initial velocity, while the second represents the cumulative diffusion driven by the thermal noise. Squaring Equation (2.5), averaging over the noise realizations using Equation (2.4), and taking the infinite-time limit to enforce the equipartition theorem relates the noise amplitude B to the friction coefficient[38, 39]

$$B = \xi k_B T \quad (2.6)$$

where k_B is the Boltzmann constant and T is the temperature of the bath.

Equation (2.6) is the fluctuation-dissipation theorem (FDT) of the second kind. It demonstrates that friction and noise are not independent phenomenological parameters; rather, they are two macroscopic manifestations of the exact same underlying microscopic interactions. Friction alone would freeze the system, while noise alone would heat it infinitely. The strict proportionality established by Equation (2.6) enforces the thermodynamic balance required to sustain a stationary thermal state at the temperature of the bath. This concept is one of the cornerstones of non-equilibrium statistical mechanics, and more general forms of this theorem will reappear throughout this thesis (see Subsection 2.1.5).

Despite its utility, this classical formulation suffers from two significant theoretical limitations. First, Equation (2.2) is constructed via physical intuition rather than rigorous derivation: ξ and B are introduced as phenomenological constants, and no methodology for computing either from a microscopic Hamiltonian has yet been given. Second, the assumption of purely delta-correlated Gaussian noise is a

mathematical idealization; no physical function of microscopic coordinates varies infinitely fast.

Both deficiencies will be resolved in Subsection 2.1.6 through projection operator techniques, which extract from Hamiltonian mechanics a generalized equation of identical structure, thereby providing microscopic definitions for both friction and noise. To support this derivation, the intervening subsections will first formalize the framework of stochastic processes.

2.1.2 Formalization of Stochastic Processes

The Langevin equation formulated in the preceding subsection was constructed without reference to any formal theory of random processes, yet it implicitly presupposes several of its central concepts: that the fluctuating force retains no memory of its own history, that its statistical properties do not themselves evolve in time, and that averages taken along a single trajectory may stand for averages over an ensemble. The present subsection names and defines these assumptions, and introduces the vocabulary required by the remainder of this chapter. A rigorous formulation of stochastic processes is beyond the present scope and can be found in standard treatments.[21, 23, 40]

A dynamical system whose evolution cannot be fully determined by deterministic equations of motion is termed a *stochastic process*. Instead of following a single, predictable trajectory, the state of the system is characterized by a set of time-dependent random variables, denoted collectively by the state vector $\mathbf{X}(t)$.

To describe the time evolution of $\mathbf{X}(t)$, two complementary perspectives are commonly employed. The single-system, or trajectory, perspective focuses on the evolution of an individual realization of the process, wherein $\mathbf{X}(t)$ represents just one outcome among the infinitely many permitted by the underlying dynamics. Alternatively, the statistical ensemble perspective describes the system probabilistically, shifting the focus from individual trajectories to the time-dependent probability density of finding an infinite ensemble of identically prepared systems at a generic point $\mathbf{x}$ in state space at time t .

In the statistical ensemble view, the stochastic process is completely specified by the hierarchy of joint probability densities

$$p(\mathbf{x}_1, t_1; \mathbf{x}_2, t_2; \mathbf{x}_3, t_3; \dots) \quad (2.7)$$

where $p d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_3 \dots$ is the probability that the process takes values within $d\mathbf{x}_i$ of $\mathbf{x}_i$ at each time t_i .

From these joint distributions, one can construct conditional probability densities

$$p(\mathbf{x}_1, t_1; \mathbf{x}_2, t_2; \dots | \mathbf{y}_1, \tau_1; \mathbf{y}_2, \tau_2; \dots) \equiv \frac{p(\mathbf{x}_1, t_1; \mathbf{x}_2, t_2; \dots; \mathbf{y}_1, \tau_1; \mathbf{y}_2, \tau_2; \dots)}{p(\mathbf{y}_1, \tau_1; \mathbf{y}_2, \tau_2; \dots)} \quad (2.8)$$

Conditional probabilities carry the predictive content of the theory. Assuming chronological time ordering (i.e., all t_i occur after all τ_i), they yield the probability of observing future configurations conditioned upon a known history of past states.

A stochastic process $\mathbf{X}(t)$ is formally defined as a *Markov process* if its conditional probability satisfies

$$p(\mathbf{x}_1, t_1; \mathbf{x}_2, t_2; \dots | \mathbf{y}_1, \tau_1; \mathbf{y}_2, \tau_2; \dots) = p(\mathbf{x}_1, t_1; \mathbf{x}_2, t_2; \dots | \mathbf{y}_1, \tau_1) \quad (2.9)$$

where τ_1 is the most recent observation time. In a Markovian system, the future evolution depends exclusively on the current state and is independent of the states visited at earlier times. This memorylessness is the approximation introduced phenomenologically in the previous subsection through the delta-correlated white noise of Equation (2.4). The identification requires care: delta-correlated noise renders the joint process in position and velocity Markovian, whereas the position alone retains memory through the momentum it has accumulated. It is for this reason that the equation of motion for the probability density must be formulated in the full phase space, as will be seen in Subsection 2.1.4.

Because of this property, the entire hierarchy of joint densities for a Markov process can be generated solely from the single-time probability density $p(\mathbf{x}_1, t_1)$ and the transition density $p(\mathbf{x}_1, t_1 | \mathbf{x}_2, t_2)$. By requiring that the probabilistic description remains consistent under the insertion of an intermediate observation time t_2 , and invoking Equation (2.9) to make the transitions before and after t_2 statistically independent, one obtains

$$p(\mathbf{x}_1, t_1 | \mathbf{x}_3, t_3) = \int d\mathbf{x}_2 p(\mathbf{x}_1, t_1 | \mathbf{x}_2, t_2) p(\mathbf{x}_2, t_2 | \mathbf{x}_3, t_3) \quad t_1 \geq t_2 \geq t_3 \quad (2.10)$$

which is the Chapman-Kolmogorov equation.[41, 42] It dictates that the transition probability from state $\mathbf{x}_3$ to $\mathbf{x}_1$ is the sum over all possible intermediate states $\mathbf{x}_2$ through which the system may have passed. It is the fundamental governing relation for Markov processes and serves as the starting point for deriving equations of motion for probability densities, as demonstrated in Subsection 2.1.4.

A Markov process is classified as *homogeneous* if its conditional probability density depends only on the time interval between observations, rendering it invariant under a uniform translation of the time axis

$$p(\mathbf{x}_1, t_1 + t_0 | \mathbf{y}_1, \tau_1 + t_0) = p(\mathbf{x}_1, t_1 | \mathbf{y}_1, \tau_1) \quad \forall t_0 \quad (2.11)$$

The process is further defined as *stationary* if it is homogeneous and its single-time probability density is also invariant with respect to time shifts

$$p(\mathbf{x}_1, t_1 + t_0) = p(\mathbf{x}_1, t_1) \quad \forall t_0 \quad (2.12)$$

Stationarity implies that the statistical properties of the system do not evolve over time. Because every thermal bath considered in this thesis is assumed to be at macroscopic thermodynamic equilibrium, all associated stochastic bath processes are stationary.

Finally, a stationary process is *ergodic*[43] if the time average of an observable $f(\mathbf{X})$ along an infinitely long single realization coincides with its ensemble average, denoted by $\langle f(\mathbf{X}) \rangle$

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt f(\mathbf{X}(t)) = \langle f(\mathbf{X}) \rangle \quad (2.13)$$

Equation (2.13) is the assumption that justifies equating time-averaged quantities, such as those computed from MD trajectories of finite duration, with equilibrium thermodynamic ensemble averages. This principle is invoked implicitly whenever numerical trajectory averages are reported in the subsequent chapters.

2.1.3 Time-Correlation Functions

Ergodicity, as expressed by Equation (2.13), makes the statistical characterization of a stochastic process accessible from a single trajectory. It remains to identify which statistical quantities carry the dynamical information of interest. Equilibrium statistical mechanics is built upon the partition function, from which all macroscopic thermodynamic properties of a statistical ensemble can be derived. However, there is no unique comparable object away from equilibrium, where a system can occupy many non-equilibrium states. In the statistical mechanics of irreversible processes, the dynamical properties of a system are instead encoded within the correlation functions of its fluctuations. Time-correlation functions occupy the central position held by the partition function in equilibrium theory; they determine the transport properties of the system (such as viscosity, thermal conductivity, and diffusion) and serve as the quantities through which the theory makes contact with observation.

A time-correlation function arises whenever we analyse the statistical behaviour of a time-dependent observable $A(t)$ measured over a long time. The first step in this analysis is to define the time-averaged value of the observable,

$$\bar{A} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt A(t) \quad (2.14)$$

from which we isolate the instantaneous fluctuation, $\delta A(t) = A(t) - \bar{A}$. While the mean and the variance provide a static statistical picture, they reveal little about the underlying dynamical memory of the system. To quantify the dynamical influence of a fluctuation at time s on a subsequent fluctuation at time $s + t$, one constructs the time-autocorrelation function, originally introduced by Taylor[44]

$$C_{AA}(t) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T ds \delta A(s) \delta A(s+t) \quad (2.15)$$

If the system under investigation is ergodic, Equation (2.13) permits the equivalence between this long-time trajectory average and an equilibrium ensemble average over the product of two fluctuations: $C_{AA}(t) = \langle \delta A(t) \delta A(0) \rangle$. Within a stationary equilibrium ensemble, C_{AA} depends only upon the absolute time difference and is an even function, $C_{AA}(t) = C_{AA}(-t)$. The value at coincident times, $C_{AA}(0) = \langle \delta A^2 \rangle$, yields the mean-square fluctuation. At sufficiently long times the fluctuation loses all statistical dependence upon its initial value, so that $C_{AA}(t)$ decays to zero. The rate of this decay defines the correlation time,

$$\tau_c = \frac{1}{C_{AA}(0)} \int_0^\infty dt C_{AA}(t) \quad (2.16)$$

which quantifies the characteristic interval over which the observable retains memory of its earlier states. This is the quantity invoked qualitatively in Subsection 2.1.1, where the correlation time of the bath force was assumed negligibly short.

Many experimental techniques, as well as theoretical analyses, probe not the correlation function itself, but its Fourier transform,

$$\tilde{C}_{AA}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} C_{AA}(t) \quad (2.17)$$

known as the power spectrum of the observable A . For example, the optical absorption spectrum of a molecule as a function of frequency is related to the time-correlation function of its total electric dipole moment.[45] The formal identification of the power spectrum of a stationary stochastic process with the Fourier transform of its autocorrelation function is established in the Wiener-Khinchin theorem.[46, 47] The evenness of $C_{AA}(t)$ ensures that $\tilde{C}_{AA}(\omega)$ is real, while its non-negativity follows from the positivity of the underlying physical measure.

Returning to the phenomenological models established previously, the Langevin equation and the [FDT](#) can be used to derive exact analytical expressions for various time-correlation functions. One of the most important is the velocity autocorrelation function ([VACF](#)) of a Brownian particle. Multiplying the formal solution of the Langevin equation (2.5) by $v(0)$, taking the ensemble average, and applying both $\langle v(0)R(t) \rangle = 0$ and $\langle v^2(0) \rangle = k_B T/m$, yields

$$C_{vv}(t) = \langle v(t)v(0) \rangle = \frac{k_B T}{m} e^{-\xi|t|/m} \quad (2.18)$$

where the absolute value enforces the evenness property, and the momentum relaxation time is identified as m/ξ . Time integration of Equation (2.18) yields the macroscopic diffusion coefficient of the Brownian particle

$$D = \int_0^{\infty} dt C_{vv}(t) = \frac{k_B T}{\xi} \quad (2.19)$$

which is the Einstein relation.[28] Equation (2.19) represents it in the Green-Kubo form: a macroscopic non-equilibrium transport coefficient expressed exactly as the time integral of a microscopic equilibrium correlation function.[48, 49]

Of equal importance to the remainder of this thesis is the force autocorrelation function ([FACF](#)) exerted upon the system by its environment, $C_{FF}(t) = \langle \delta F(t) \delta F(0) \rangle$, where $\delta F(t) = F(t) - \langle F \rangle$ denotes the deviation of that force from its mean value, and of which the white noise $R(t)$ of Equation (2.4) is the phenomenological limit. The Markovian approximation adopted there is equivalent to stating that C_{FF} decays on a timescale so short that it may be approximated by a Dirac delta function on the scale of the system's dynamics. By relaxing that idealization while preserving the thermodynamic balance dictated by Equation (2.6), the friction coefficient can be recovered analogously,[50] through

$$\xi = \frac{1}{k_B T} \int_0^{\infty} dt C_{FF}(t) \quad (2.20)$$

This relation, identical in its Green-Kubo structure to Equation (2.19), allows the friction coefficient to be computed from the microscopic dynamics of the environment, rather than assigned as a phenomenological constant. The integral in Equation (2.20) must be evaluated over an interval on which it attains a stable plateau, long compared to the correlation time of the bath, but short compared

to the relaxation time of the system coordinate itself.[51] Equation (2.20) constitutes a first and partial answer to the limitation identified in Subsection 2.1.1: the friction coefficient is no longer an adjustable parameter, but a computable equilibrium average over the fluctuations of the bath. It remains, however, a single number characterizing a memoryless process, and the derivation from which both friction and noise acquire their microscopic definitions has not yet been given; it is supplied in Subsection 2.1.6.

While correlation functions characterize a stochastic process through the statistics of individual trajectories, a complementary description exists in which the probability density of the system is propagated directly in time. This alternative formulation is developed in the following subsection.

2.1.4 The Fokker-Planck Equation

In this complementary formulation, a single equation of motion governs the entire ensemble distribution, from which any physical average can be extracted by integration, while the requirement that the equilibrium distribution be stationary imposes a constraint upon the coefficients of that equation.[20, 23]

For a continuous stochastic process characterized by a single Markovian variable x , the integral Chapman-Kolmogorov relation of Equation (2.10) can be recast into a differential equation by inserting the short-time transition density into the propagation of $p(x, t)$ and expanding the integrand about x . The result is the Kramers-Moyal expansion[15, 52]

$$\frac{\partial p(x, t)}{\partial t} = \sum_{n=1}^{\infty} \left(-\frac{\partial}{\partial x} \right)^n D^{(n)}(x, t) p(x, t) \quad (2.21)$$

The coefficients $D^{(n)}$ are the short-time moments of the displacement $\Delta = x(t + \tau) - x(t)$ taken per unit time, $D^{(n)}(x, t) = \lim_{\tau \rightarrow 0} \langle \Delta^n \rangle |_{x(t)=x} / (n! \tau)$, evaluated for a system known to occupy x at time t . The first two admit a direct physical interpretation: $D^{(1)}$ measures the systematic drift of the probability distribution, while $D^{(2)}$ quantifies the rate at which the distribution diffuses.

Equation (2.21) is exact but formally infinite, and it admits no arbitrary truncation. According to Pawula's theorem,[53] if the expansion is terminated at any finite order beyond the second, the resulting probability density fails to remain non-negative; the series must therefore either terminate after the second term or retain infinitely many. Truncation after the second term defines the Fokker-Planck equation[54, 55]

$$\frac{\partial p(x, t)}{\partial t} = \left[-\frac{\partial}{\partial x} D^{(1)}(x, t) + \frac{\partial^2}{\partial x^2} D^{(2)}(x, t) \right] p(x, t) \quad (2.22)$$

where $D^{(1)}$ is the drift coefficient and $D^{(2)} > 0$ the diffusion coefficient of the variable in which the expansion is carried out. The latter is not the macroscopic diffusion coefficient D of Equation (2.19): for the Brownian particle the expansion is performed in the velocity, so that $D_{vv}^{(2)}$ measures the spreading of the velocity distribution, whereas D measures the spreading of the particle in space.

This construction relies upon the Markov property, Equation (2.9), meaning it must be established exactly which variable, or set of variables, possesses this property. As noted previously in Subsection 2.1.2, the coordinate x of a Brownian particle is not Markovian on its own: two realizations passing through the same value of x with different velocities evolve differently thereafter, so the coordinate retains memory of its history through the momentum accumulated along the trajectory. The pair (x, v) , however, is Markovian, as the right-hand side of the underlying Langevin equation (2.3) depends only on the instantaneous values of x and v , driven by a memoryless noise. The Fokker-Planck framework must therefore be applied to the two-variable phase space, with the scalar derivatives replaced by derivatives with respect to each variable and the coefficients by their tensorial counterparts.

The necessary drift and diffusion coefficients can be computed directly from the short-time moments of the Langevin model. Evaluating the phase-space increments Δx and Δv over an infinitesimal interval τ yields the deterministic drift terms $D_x^{(1)} = v$ and $D_v^{(1)} = -(\partial V/\partial x + \xi v)/m$. The noise enters only the velocity equation, so the position increment is deterministic at leading order and contributes no diffusion, while the delta correlation of the stochastic force causes the variance of the velocity to increase linearly in τ ; the sole non-vanishing second-order coefficient is therefore $D_{vv}^{(2)} = B/m^2 = \xi k_B T/m^2$. Because the noise is Gaussian, every moment of Δv beyond the second is of order τ^2 or smaller, so all Kramers-Moyal coefficients with $n \geq 3$ vanish identically. For the Langevin model, the truncation mandated by Pawula's theorem is therefore not an approximation, but an exact property. Substituting these coefficients into the two-dimensional form of Equation (2.22) yields the Klein-Kramers equation[15, 56]

$$\frac{\partial p(x, v, t)}{\partial t} = \left[-v \frac{\partial}{\partial x} + \frac{1}{m} \frac{\partial V}{\partial x} \frac{\partial}{\partial v} + \frac{\xi}{m} \frac{\partial}{\partial v} \left(v + \frac{k_B T}{m} \frac{\partial}{\partial v} \right) \right] p \quad (2.23)$$

which represents the phase-space Fokker-Planck description of the Brownian dynamics introduced in Subsection 2.1.1.

One verifies directly that the Maxwell-Boltzmann distribution, $p_{\text{eq}}(x, v) \propto \exp[-\frac{1}{2}mv^2 + V(x)]/k_B T$, is a stationary solution to Equation (2.23): the purely mechanical streaming terms cancel one another, and the dissipative bracket annihilates p_{eq} . This exact cancellation occurs only if the noise strength satisfies $B = \xi k_B T$.

In the highly viscous (*overdamped*) regime, where the momentum relaxes on a timescale m/ξ that is negligibly short compared to the evolution of the spatial coordinate, the velocity can be eliminated. Under this condition, Equation (2.23) reduces to a single equation for the spatial probability density,

$$\frac{\partial p(x, t)}{\partial t} = \frac{1}{\xi} \frac{\partial}{\partial x} \left[\frac{\partial V}{\partial x} + k_B T \frac{\partial}{\partial x} \right] p \quad (2.24)$$

known as the Smoluchowski equation,[57] wherein the macroscopic diffusion coefficient of Equation (2.19) reappears as the prefactor of the second spatial derivative.

The probability density formulation thus provides a complete and independent description of the same physics contained in the Langevin equation. Furthermore, it delivers the FDT (2.6) a second time: whereas it was previously obtained by demanding velocity equipartition, it is recovered here by requiring the canonical

thermodynamic distribution to be stationary under the evolution of the probability density. This conceptual recurrence is not accidental; it is a manifestation of a much broader physical principle, which is generalized in the following subsection.

2.1.5 The Fluctuation-Dissipation Theorem

The recurrence noted at the end of the preceding subsection is an instance of a general relation between the manner in which a system responds to a weak external perturbation and the spontaneous fluctuations it exhibits at thermal equilibrium.[19, 58] In the literature, the **FDT** refers to two distinct, albeit related, statements, and it is convenient to separate them at the outset. The *theorem of the first kind* relates the macroscopic response of an observable to an equilibrium time-correlation function of that same observable; the *theorem of the second kind* constrains the friction and the stochastic noise that appear together in an effective equation of motion. Both have been encountered in specific limits thus far; the purpose of this subsection is to formalize the general statements of which those cases are instances.

Consider a system, initially in thermal equilibrium, that is perturbed by a weak external field $E(t)$ coupled linearly to a dynamical variable M , so that the Hamiltonian becomes $H - ME(t)$. Expanding the Liouville equation to first order in E , and exploiting the fact that the equilibrium distribution depends on the phase-space coordinates solely through the unperturbed Hamiltonian H , one finds that the non-equilibrium ensemble average of an arbitrary observable A deviates from its equilibrium value according to linear response theory[18, 49]

$$\delta \langle A(t) \rangle = \int_0^t ds \phi_{AM}(s) E(t-s) \quad (2.25)$$

where the response function is defined as

$$\phi_{AM}(t) = \beta \langle A(t) \dot{M}(0) \rangle_{\text{eq}} \quad (2.26)$$

with $\beta = 1/k_B T$. The derivation is elementary in classical mechanics because H and M are functions on phase space and therefore commute. The essential feature of Equations (2.25) and (2.26) is that the response function is an equilibrium property: it is determined entirely by the unperturbed dynamics and contains no reference to the perturbation that induces it. This constitutes the **FDT** of the first kind.

The Brownian particle furnishes an immediate application. Let the perturbation be a uniform external force acting upon the spatial coordinate, so that $M = x$, and let the observable be the velocity, $A = v$. Consequently $\dot{M} = v$, and the response function is $\phi_{vx}(t) = \beta C_{vv}(t)$. The mobility $\hat{\mu}(\omega)$, defined as the ratio of the steady-state mean velocity to an applied force oscillating at frequency ω , is the corresponding susceptibility, obtained as the one-sided Fourier transform of the response function

$$\hat{\mu}(\omega) = \beta \int_0^\infty dt e^{-i\omega t} C_{vv}(t) = \frac{1}{i\omega m + \xi} \quad (2.27)$$

where the second equality follows from substituting the Langevin **VACF**, Equation (2.18). At zero frequency, the static mobility is $\hat{\mu}(0) = 1/\xi$, and a direct comparison with Equation (2.19) yields $D = \hat{\mu}(0) k_B T$. The Einstein relation is thus

revealed not as an independent law, but as the zero-frequency limit of the theorem of the first kind, and the Green-Kubo structure identified previously is the canonical form that all such static transport relations assume.

The theorem can equivalently be cast in the frequency domain using the power spectrum introduced in Equation (2.17). Defining the complex susceptibility $\hat{\chi}_{AA}(\omega) = \chi'_{AA}(\omega) - i\chi''_{AA}(\omega)$ as the one-sided transform of the response function $\phi_{AA}(t)$, whose real and imaginary components are linked by the Kramers-Kronig relations,[59, 60] the dissipative component χ''_{AA} , which dictates the rate of energy absorption from the perturbing field, satisfies

$$\tilde{C}_{AA}(\omega) = \frac{2k_B T}{\omega} \chi''_{AA}(\omega) \quad (2.28)$$

The power spectrum of the spontaneous fluctuations of A therefore entirely determines the dissipation the system exhibits when driven at the corresponding frequency, and vice versa. This is the formal expression of Onsager's postulate,[31] which posits that a spontaneous microscopic fluctuation decays according to the same laws that govern the relaxation of a macroscopic deviation prepared deliberately.

In contrast, the theorem of the second kind concerns not an observable response, but the decomposition of an environmental force. In its most general form, it states that[38]

$$\langle R(t)R(t') \rangle = k_B T \xi(t - t') \quad (2.29)$$

where $\xi(t)$ is a memory friction kernel that replaces the constant coefficient ξ when the separation of timescales invoked in Subsection 2.1.1 is unavailable. The phenomenological Langevin requirement, Equation (2.6), is the Markovian limit wherein $\xi(t - t') = 2\xi\delta(t - t')$, where ξ on the right denotes the constant coefficient of Equation (2.2). Taking the one-sided Fourier transform of Equation (2.29) gives the frequency-resolved friction

$$\hat{\xi}(\omega) = \int_0^\infty dt e^{-i\omega t} \xi(t) = \beta \int_0^\infty dt e^{-i\omega t} C_{FF}(t) \quad (2.30)$$

which stands to the friction exactly as Equation (2.27) stands to the velocity, and of which Equation (2.20) is the zero-frequency limit. The two theorems are joined by the observation that the mobility of a particle subject to retarded friction is $\hat{\mu}(\omega) = [i\omega m + \hat{\xi}(\omega)]^{-1}$, of which Equation (2.27) is the Markovian case $\hat{\xi}(\omega) = \xi$. The kernel itself is defined, and Equation (2.29) obtained as an identity rather than imposed as a requirement, in Subsection 2.1.6.

As established by Kubo,[61] the two statements are not of equal theoretical standing. The theorem of the first kind relates an observable to a perturbation and emerges directly from the exact microscopic equations of motion adopted in linear response theory. The theorem of the second kind, however, presupposes that the total force acting upon the system has already been partitioned into a systematic dissipative part and a residual fluctuating noise. That partitioning is a construct of statistical mechanics rather than a fundamental law, and it is precisely the limitation identified in Subsection 2.1.1. The theorem of the first kind is therefore to

be regarded as fundamental, the second kind as a corollary dependent upon the effective equation of motion employed.

Three conditions circumscribe the formulation presented here. First, the bath must reside at thermal equilibrium, as the theorem asserts nothing about dissipative environments driven far from equilibrium. Second, the response must be linear, requiring the external perturbation to remain weak on the scale of the thermal energy. Third, this formulation is classical, valid only when the thermal energy is large compared with the relevant energy quanta of the bath motions.

The theorem constrains the relationship between friction and noise, but derives neither. The memory kernel $\xi(t)$ has been introduced, and its relation to the fluctuations of the environmental force established, yet the equation of motion in which it appears has not been written. The partitioning of the environmental force into systematic and fluctuating components remains an assumption rather than a result. Both deficiencies are resolved in the following subsection, where the bath **DOF** are eliminated exactly from a microscopic Hamiltonian, yielding microscopic definitions of the friction and the noise.

2.1.6 Projection Operators

The present subsection eliminates the environment from a microscopic Hamiltonian by means of the projection-operator formalism of Nakajima, Zwanzig and Mori.[62–66] Through this machinery the friction and the noise acquire microscopic definitions in terms of equilibrium averages over the bath **DOF**, and the relation between them, imposed in Equation (2.29) in order to enforce thermal equilibrium, emerges as a consequence of the construction.

Consider a molecular system whose configuration is specified by a set of slow coordinates $\mathbf{x}$ with conjugate momenta $\mathbf{p}$ and diagonal mass matrix $\mathbf{m}$. This system is immersed in an environment described by coordinates $\mathbf{y}$, momenta $\boldsymbol{\pi}$ and mass matrix $\mathbf{m}_B$. The total Hamiltonian is partitioned as

$$H = H_S(\mathbf{x}, \mathbf{p}) + H_B(\mathbf{y}, \boldsymbol{\pi}; \mathbf{x}) \quad (2.31)$$

with the system Hamiltonian defined as

$$H_S(\mathbf{x}, \mathbf{p}) = \frac{1}{2} \mathbf{p}^T \mathbf{m}^{-1} \mathbf{p} + V(\mathbf{x}) \quad (2.32)$$

and the bath Hamiltonian as

$$H_B(\mathbf{y}, \boldsymbol{\pi}; \mathbf{x}) = \frac{1}{2} \boldsymbol{\pi}^T \mathbf{m}_B^{-1} \boldsymbol{\pi} + u_B(\mathbf{y}) + u(\mathbf{x}, \mathbf{y}) \quad (2.33)$$

in which $V(\mathbf{x})$ is the bare potential acting upon the retained coordinates, $u_B(\mathbf{y})$ is the internal potential of the environment, and $u(\mathbf{x}, \mathbf{y})$ represents the interaction between the two subsystems. No assumptions are made regarding the functional form of u .

The interaction is grouped with H_B not because it is an exclusive property of the environment, but because H_B must generate the dynamics of the bath in the presence of the system held fixed at a specific configuration $\mathbf{x}$. The semicolon in Equation (2.33) indicates that $\mathbf{x}$ enters as a parametric variable rather than a

dynamical one. It is the equilibrium distribution associated with this constrained dynamics onto which the projection is subsequently made.

The full phase-space density obeys the Liouville equation

$$\frac{\partial}{\partial t} \rho(\mathbf{x}, \mathbf{p}, \mathbf{y}, \boldsymbol{\pi}, t) = -i\hat{\mathcal{L}} \rho(\mathbf{x}, \mathbf{p}, \mathbf{y}, \boldsymbol{\pi}, t) \quad (2.34)$$

whose Liouvillian operator decomposes as

$$i\hat{\mathcal{L}} = i\hat{\mathcal{L}}_S + i\hat{\mathcal{L}}_B \quad (2.35)$$

with

$$i\hat{\mathcal{L}}_S = (\mathbf{m}^{-1}\mathbf{p}) \cdot \frac{\partial}{\partial \mathbf{x}} + \mathbf{F}_S(\mathbf{x}, \mathbf{y}) \cdot \frac{\partial}{\partial \mathbf{p}} \quad (2.36)$$

$$i\hat{\mathcal{L}}_B = (\mathbf{m}_B^{-1}\boldsymbol{\pi}) \cdot \frac{\partial}{\partial \mathbf{y}} + \mathbf{F}_B(\mathbf{x}, \mathbf{y}) \cdot \frac{\partial}{\partial \boldsymbol{\pi}} \quad (2.37)$$

where the total forces acting upon the two sets of coordinates are

$$\mathbf{F}_S(\mathbf{x}, \mathbf{y}) = -\frac{\partial}{\partial \mathbf{x}} [V(\mathbf{x}) + u(\mathbf{x}, \mathbf{y})] \quad (2.38)$$

$$\mathbf{F}_B(\mathbf{x}, \mathbf{y}) = -\frac{\partial}{\partial \mathbf{y}} [u_B(\mathbf{y}) + u(\mathbf{x}, \mathbf{y})] \quad (2.39)$$

Equations (2.36) and (2.37) partition the phase-space flow by dynamical variable rather than by Hamiltonian. $i\hat{\mathcal{L}}_B$ is exactly the generator of H_B at fixed $\mathbf{x}$, and consequently annihilates the conditional equilibrium distribution defined below. Conversely, $i\hat{\mathcal{L}}_S$ is not the generator of H_S ; rather, it propagates the retained coordinates under the total force, preserving a dependence upon the instantaneous configuration of the bath.

The elimination of the bath is achieved via the projection operator

$$\hat{\mathcal{P}} = \rho_B(\mathbf{y}, \boldsymbol{\pi} | \mathbf{x}) \int d\mathbf{y} d\boldsymbol{\pi} \quad (2.40)$$

where

$$\rho_B(\mathbf{y}, \boldsymbol{\pi} | \mathbf{x}) = \frac{e^{-\beta H_B(\mathbf{y}, \boldsymbol{\pi}; \mathbf{x})}}{Z(\mathbf{x})} \quad (2.41)$$

is the equilibrium distribution of the environment conditional upon the retained coordinates, normalized by the constrained partition function

$$Z(\mathbf{x}) = \int d\mathbf{y} d\boldsymbol{\pi} e^{-\beta H_B(\mathbf{y}, \boldsymbol{\pi}; \mathbf{x})} \quad (2.42)$$

The choice of projector is a physical modelling decision. Projecting onto the equilibrium distribution of the environment *conditional* upon $\mathbf{x}$ ensures that every quantity surviving the integration becomes an equilibrium ensemble average evaluated at a specified configuration of the system. Thus, the reduced description acquires a parametric dependence upon $\mathbf{x}$.

Applying $\hat{\mathcal{P}}$ and its orthogonal complement $\hat{\mathcal{Q}} = 1 - \hat{\mathcal{P}}$ to Equation (2.34), and assuming that the environment is initially equilibrated at the initial configuration

of the retained coordinates (i.e., $\hat{Q}\rho(0) = 0$), yields the Nakajima-Zwanzig generalized master equation[62, 63]

$$\frac{\partial}{\partial t} \hat{\mathcal{P}}\rho(t) = -i\hat{\mathcal{P}}\hat{\mathcal{L}}\hat{\mathcal{P}}\rho(t) - \int_0^t d\tau \hat{\mathcal{P}}\hat{\mathcal{L}}e^{-i\hat{Q}\hat{\mathcal{L}}\tau}\hat{Q}\hat{\mathcal{L}}\hat{\mathcal{P}}\rho(t-\tau) \quad (2.43)$$

which is exact. The first term generates the reversible drift of the reduced probability density, while the memory integral carries the dissipative influence of the environment. The evaluation of both terms is elementary but lengthy, and is reported in full in Appendix A. Although the construction follows the standard treatments of Brownian motion in a molecular environment,[66, 67] it is set out here in the notation and at a level of generality that standard treatments do not supply and that the following chapters require. One substantive approximation is introduced there: assuming the environment relaxes rapidly in comparison to the system **DOF** permits the projected propagator $e^{-i\hat{Q}\hat{\mathcal{L}}\tau}$ to be replaced by the propagator $e^{-i\hat{\mathcal{L}}_B\tau}$ generated by H_B at fixed $\mathbf{x}$. It is this substitution that converts a propagation in the orthogonal subspace into the ordinary dynamics of a constrained bath, thereby making the resulting memory kernel computable.

Defining $\rho_S(\mathbf{x}, \mathbf{p}, t)$ as the reduced density obtained by integrating $\hat{\mathcal{P}}\rho$ over the environmental variables, the result is

$$\begin{aligned} \frac{\partial \rho_S(\mathbf{x}, \mathbf{p}, t)}{\partial t} = & -(\mathbf{m}^{-1}\mathbf{p}) \cdot \frac{\partial \rho_S}{\partial \mathbf{x}} + \frac{\partial \mathcal{A}(\mathbf{x})}{\partial \mathbf{x}} \cdot \frac{\partial \rho_S}{\partial \mathbf{p}} \\ & + k_B T \int_0^t d\tau \frac{\partial}{\partial \mathbf{p}} \cdot \left[\boldsymbol{\xi}(\mathbf{x}, \tau) \cdot \left(\frac{\partial}{\partial \mathbf{p}} + \beta \mathbf{m}^{-1}\mathbf{p} \right) \rho_S(\mathbf{x}, \mathbf{p}, t-\tau) \right] \end{aligned} \quad (2.44)$$

This is a generalized Klein-Kramers equation. It is the multidimensional, memory-retaining counterpart to Equation (2.23). It differs from the phenomenological formulation in three respects: the friction is now a tensorial quantity rather than a scalar, it depends explicitly upon the instantaneous configuration of the retained coordinates, and it acts non-locally in time via a memory integral.

Two fundamental identifications give Equation (2.44) its physical content, and both concern the interaction force exerted upon the system by the bath

$$\mathbf{F}(\mathbf{x}, \mathbf{y}) = -\frac{\partial u(\mathbf{x}, \mathbf{y})}{\partial \mathbf{x}} \quad (2.45)$$

The conditional ensemble average of this force is denoted $\langle \mathbf{F} \rangle_{\mathbf{x}}$, and its instantaneous fluctuation is $\delta \mathbf{F} = \mathbf{F} - \langle \mathbf{F} \rangle_{\mathbf{x}}$. The systematic force appearing in the drift is the sum of the external force and this conditional average. Because differentiating Equation (2.42) yields $\langle \mathbf{F} \rangle_{\mathbf{x}} = \beta^{-1} \partial \ln Z / \partial \mathbf{x}$, the total systematic force is exactly the negative gradient of

$$\mathcal{A}(\mathbf{x}) = V(\mathbf{x}) - \beta^{-1} \ln Z(\mathbf{x}) \quad (2.46)$$

which is the **PMF**. [68] The effective potential governing the reduced dynamics is therefore proven to be a free energy and not a bare potential energy, a distinction anticipated without justification in Subsection 2.1.1 and established here.

The second identification concerns the memory kernel, which is the tensorial autocorrelation function of the fluctuating part of the same force,[50] evaluated within the bath at fixed configuration $\mathbf{x}$

$$\xi(\mathbf{x}, t) = \beta \langle \delta \mathbf{F}(\mathbf{x}, 0) \delta \mathbf{F}(\mathbf{x}, t)^T \rangle_{\mathbf{x}} \quad (2.47)$$

This is the multidimensional, configuration-resolved counterpart to the [FACF](#) C_{FF} introduced in Subsection 2.1.3.

While Equation (2.44) propagates the probability density, the equivalent trajectory-based stochastic equation of motion follows from the correspondence established in Subsection 2.1.4. The memory integral separates into a retarded drag proportional to $\xi \cdot \mathbf{m}^{-1} \mathbf{p}$ and a diffusion in momentum with tensor $k_B T \xi$. The stochastic equation of motion generating precisely these two terms is the generalized Langevin equation ([GLE](#))

$$\mathbf{m} \ddot{\mathbf{x}}(t) = -\frac{\partial \mathcal{A}(\mathbf{x})}{\partial \mathbf{x}} - \int_0^t ds \xi(\mathbf{x}, t-s) \cdot \dot{\mathbf{x}}(s) + \delta \mathbf{F}(\mathbf{x}, t) \quad (2.48)$$

In this framework, the fluctuating force is the multidimensional counterpart to the random force $R(t)$ of Equation (2.2); it is no longer a postulated stochastic variable, but the exact deviation of a physical microscopic force from its conditional equilibrium average, with a time-correlation function governed by Equation (2.47). The correspondence between the probability density and trajectory formalisms is exact at the order to which the kernel was obtained, since characterizing the fluctuations solely by their two-time correlation function is equivalent to treating the noise as Gaussian.

As a result, the same tensor $\xi(\mathbf{x}, t)$ governs both the macroscopic retarded drag and the correlation of the microscopic fluctuating noise. This enforces the [FDT](#) of the second kind (2.29) in its tensor, memory-retaining, and configuration-dependent form. However, whereas in Subsection 2.1.1 this balance had to be imposed in order that the model sustain a thermal stationary state, here it is a consequence of the projection.

When the environmental correlations decay on a timescale extremely short compared with that over which $\dot{\mathbf{x}}$ evolves appreciably, the memory integral may be evaluated by pulling the velocity out of the integrand, rendering both descriptions local in time. Under this Markovian limit, Equation (2.48) reduces to a Langevin equation with a configuration-dependent friction tensor

$$\xi(\mathbf{x}) = \beta \int_0^\infty d\tau \langle \delta \mathbf{F}(\mathbf{x}, 0) \delta \mathbf{F}(\mathbf{x}, \tau)^T \rangle_{\mathbf{x}} \quad (2.49)$$

Equation (2.49) is the multidimensional generalization of the Green-Kubo expression found in Equation (2.20). The phenomenological models of the preceding subsections are thereby recovered as limiting cases of a single microscopic derivation. Whether the Markovian approximation is legitimate in a given application must be judged by comparing the decay of the kernel with the timescale of the motion it is intended to damp.

The assumptions upon which the foregoing rests may now be enumerated: (i) the environment is initially at equilibrium conditional upon the configuration of

the retained coordinates; (ii) the bath relaxes rapidly enough to permit the substitution of the constrained propagator at fixed $\mathbf{x}$; (iii) the bath is macroscopic, ensuring its correlations decay irreversibly; and (iv) the fluctuating force is Gaussian. None of these requires the interaction $u(\mathbf{x}, \mathbf{y})$ to be linear in the retained coordinates. The friction tensor of Equation (2.47) is exact in that respect, and its dependence upon $\mathbf{x}$ is a direct consequence of the fact that the coupling is in general not linear. The linear-response assumption enters only when a kernel of this form is subsequently represented by a bath of harmonic oscillators, a construction developed in Chapter 3.

Equations (2.48) and (2.49) are the central results of this section, and the derivation leading to them, presented in this subsection and in Appendix A, was carried out as part of the present work. They express the friction experienced by a set of system coordinates entirely in terms of an equilibrium time-correlation function of the environment, computable at any specified configuration, and thereby fulfil the goal stated at the end of Subsection 2.1.1: the PMF and the friction tensor are now defined microscopically from first principles, and the relation between friction and noise is a theorem rather than a constraint. Equation (2.47) provides the theoretical basis for the computational extraction protocol of Chapter 4. What remains is to establish how these quantities dictate the rate of a chemical process across a potential barrier. That is the subject of the following subsection.

2.1.7 Kramers Theory

Consider a single reaction coordinate evolving on the PMF $\mathcal{A}(\mathbf{x})$, with a metastable reactant minimum of angular frequency ω_0 separated from the product region by a barrier of height $\Delta\mathcal{A}$ and barrier frequency ω_b . Provided the barrier is high relative to the thermal energy, the reactant population relaxes to a quasi-stationary distribution far more rapidly than it escapes, the flux across the barrier attains a steady state, and a rate coefficient is well defined.[16, 20] TST assigns to this process the rate $k_{\text{TST}} = (\omega_0/2\pi) \exp(-\beta\Delta\mathcal{A})$, obtained under the assumption that every trajectory reaching the barrier top proceeds to products without return.[69, 70] The dynamical influence of the environment is conventionally collected into a dimensionless transmission coefficient, $\kappa = k/k_{\text{TST}}$, which corrects for the failure of this no-return assumption.[14]

Kramers established that this supposition fails at both extremes of the system-bath coupling, and by opposite mechanisms.[15] At strong coupling the process is *spatial-diffusion limited*: the velocity of the coordinate is randomized on the momentum relaxation time $\tau_v = m/\xi$ identified in Equation (2.18). When τ_v becomes short compared with the time required to traverse the barrier region the coordinate recrosses the dividing surface repeatedly before committing to either well. Treating the passage as a diffusive process governed by the Langevin equation gives

$$\kappa_K(\xi) = \sqrt{1 + \left(\frac{\xi}{2m\omega_b}\right)^2} - \frac{\xi}{2m\omega_b} \quad (2.50)$$

For $\xi \gg m\omega_b$, this coefficient decays asymptotically as $m\omega_b/\xi$. This asymptote represents the *overdamped*, or Smoluchowski, limit, wherein $\tau_v \ll \omega_b^{-1}$ and the

momentum may be eliminated altogether, as in Equation (2.24). It is a particular case of the spatial-diffusion regime; Equation (2.50) retains inertia and remains valid at moderate damping.

At weak coupling the failure is inverted, and the process becomes *energy-diffusion limited*. Here, the environment exchanges energy with the coordinate too slowly to maintain a thermalized Boltzmann population near the barrier top. Consequently, the rate is determined by the slow diffusion of energy (activation) rather than spatial passage, causing κ to grow in proportion to ξ . The transmission coefficient is therefore non-monotonic: it rises from zero at vanishing friction, passes through a maximum at intermediate damping, and decays thereafter, a behaviour known as the *Kramers turnover*.

Mel'nikov and Meshkov showed that these two branches combine multiplicatively, with the spatial-diffusion result being modulated by a depopulation factor that measures the energy exchanged with the environment during a single traversal of the barrier region relative to $k_B T$. [71, 72] While their exact factor takes the form of an integral, the interpolation

$$\kappa(\xi) = [1 - e^{-A\xi}] \left[\sqrt{1 + (B\xi)^2} - B\xi \right] \quad (2.51)$$

reproduces both asymptotic regimes and is commonly adopted. [16] The second bracket is Equation (2.50) with $B = (2m\omega_b)^{-1}$, while $A = \beta I_b/m$, where I_b is the action of the periodic orbit at the barrier energy and equals $2\pi\Delta\mathcal{A}/\omega_0$ for a harmonic well. Equation (2.51) correctly vanishes linearly with ξ as $\xi \rightarrow 0$ and recovers the $(2B\xi)^{-1}$ decay as $\xi \rightarrow \infty$.

With this the classical description of the thermal bath is complete. The following section constructs the counterparts of the same objects for a system whose retained DOF cannot be treated classically.

2.2 OPEN QUANTUM SYSTEMS

The reduction carried out in Section 2.1 rests upon a premise that was nowhere made explicit: that the DOF retained after the elimination obey classical mechanics, so that their state is faithfully represented by a probability density on phase space. This premise ceases to be adequate whenever the spacing of the system's energy levels is comparable with or larger than $k_B T$, whenever the process of interest is a transition between discrete quantum states, or whenever the phase relations between such states influence the evolution. In these circumstances, the object to be reduced is not a phase-space density but a density operator.

The architecture of the reduction is nevertheless unchanged. The procedure once again partitions the variables to be retained from those to be eliminated, defines a projection that specifies what is discarded, yields an exact equation of motion that is non-local in time, and recovers a memoryless description only when the correlation time of the environment is negligibly short compared with the timescale on which the system evolves. A fluctuation-dissipation relation again constrains the surviving environmental quantities, and again it is this relation that guarantees relaxation towards the correct thermodynamic state. What changes is the content of each of these steps.

The present section constructs the quantum counterparts in this same order. Subsection 2.2.1 introduces the reduced density operator (RDO); Subsection 2.2.2 partitions the Hamiltonian and identifies the single environmental quantity that survives the reduction; Subsection 2.2.3 performs the projection and takes the Markovian limit; and Subsection 2.2.4 develops the resulting Redfield equation and the secular approximation through which it is brought to a usable form. The treatment presented here follows the frameworks established in the literature.[20, 24–26]

2.2.1 The Reduced Density Operator

Consider the situation that a condensed-phase experiment actually presents: a molecule dissolved in a liquid is interrogated through a small number of DOF (a few electronic states, a reaction coordinate, or perhaps a handful of vibrational modes) while the surrounding solvent contributes many orders of magnitude more, which are neither observed nor controlled. The division mirrors the one drawn in Section 2.1: a relevant system S, whose evolution is the object of the theory, and an environment B, whose detailed state is neither accessible nor required. What changes is that the retained DOF must now be treated quantum mechanically, raising the immediate question of what the state of S means.

Let the total system be closed, governed by a total Hamiltonian partitioned as

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB} \quad (2.52)$$

where $\hat{H}_S$ and $\hat{H}_B$ describe the system and bath, respectively, and $\hat{H}_{SB}$ represents their coupling. Let the total state be the wavefunction $\Psi(\mathbf{x}, \mathbf{y}; t)$ depending upon the system coordinates $\mathbf{x}$ and the environmental coordinates $\mathbf{y}$. Because the two sets of coordinates are coupled, the total wavefunction does not factorize

$$\Psi(\mathbf{x}, \mathbf{y}; t) \neq \varphi_S(\mathbf{x}; t) \chi_B(\mathbf{y}; t) \quad (t > 0) \quad (2.53)$$

for any pair of functions φ_S and χ_B . Even a state prepared as a product ceases to be one after any finite interval; the coupling correlates the two parts, rendering them entangled. Consequently, there is no wavefunction for the system alone. Here the quantum problem departs from the classical one. In classical statistical mechanics, integrating out the environmental variables from a joint phase-space distribution always returns a valid probability density for the subsystem. In quantum mechanics, however, once the system and environment interact and entangle, the subsystem possesses, in general, no valid wavefunction at all. A description in terms of state vectors must therefore be abandoned at the outset, in favour of a formalism that represents the state by an operator.

That object is the density operator.[73, 74] For a statistical ensemble prepared in pure states $|\psi_k\rangle$ with classical probabilities p_k , it is defined as

$$\hat{\rho} = \sum_k p_k |\psi_k\rangle \langle\psi_k| \quad (2.54)$$

which is a Hermitian, positive semi-definite operator of unit trace. The expectation value of any physical observable $\hat{O}$ is obtained directly via the trace

$$\langle\hat{O}\rangle = \text{Tr} [\hat{\rho} \hat{O}] \quad (2.55)$$

The purity of the state is quantified by the trace of its square, $\text{Tr} [\hat{\rho}^2] \leq 1$. This quantity equals unity if the ensemble is described by a single pure state, and is less than one whenever the state is a statistical mixture.

The dynamical evolution of this total, closed state is obtained by applying the time-dependent Schrödinger equation to Equation (2.54), yielding the Liouville-von Neumann equation

$$\frac{d\hat{\rho}(t)}{dt} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}(t)] \equiv -i\hat{\mathcal{L}}\hat{\rho}(t) \quad (2.56)$$

which defines the quantum Liouvillian superoperator $\hat{\mathcal{L}} = \hbar^{-1} [\hat{H}, \cdot]$. This is the direct quantum mechanical counterpart to the classical Liouville equation (2.34). Its formal solution is unitary, meaning the total system evolves reversibly and its purity is conserved. Irreversible dissipation cannot originate in the exact equation of motion of the isolated whole; it emerges solely from the deliberate restriction of observation to an open subpart of it.

That restriction is achieved by taking the partial trace over the environmental DOF,

$$\hat{\rho}_S(t) = \text{Tr}_B [\hat{\rho}(t)] \quad (2.57)$$

from which the expectation value of any system observable follows as $\langle\hat{O}_S\rangle = \text{Tr}_S [\hat{\rho}_S \hat{O}_S]$. The RDO so defined is the quantum analogue of the reduced phase-space density $\rho_S(\mathbf{x}, \mathbf{p}, t)$ of Subsection 2.1.6. It retains all the physical information accessible to measurements upon S , while discarding the correlations between the system and its environment.

The physical content of $\hat{\rho}_S$ is most transparent when expanded in the energy eigenbasis of the isolated system, $\hat{H}_S |a\rangle = E_a |a\rangle$. In this representation, the matrix elements $\rho_{ab}(t) = \langle a|\hat{\rho}_S(t)|b\rangle$ divide into two classes. The diagonal elements,

$\rho_{aa} \geq 0$, are real and sum to unity; these are the *populations* of the system eigenstates, which directly correspond to the classical probabilities of Section 2.1. The off-diagonal elements, ρ_{ab} with $a \neq b$, are complex and quantify the degree to which a definite quantum phase relationship survives between different states. These are the *coherences*, which in the isolated system oscillate at the Bohr frequencies $\omega_{ab} = (E_a - E_b)/\hbar$. Coherences possess no classical analogue, representing the first major conceptual departure from the classical phase-space treatment.

With the reduced state defined, the core difficulty emerges when attempting to determine its temporal evolution. Taking the partial trace of the Liouville-von Neumann equation (2.56) yields

$$\frac{d\hat{\rho}_S(t)}{dt} = -\frac{i}{\hbar} [\hat{H}_S, \hat{\rho}_S(t)] - \frac{i}{\hbar} \text{Tr}_B [\hat{H}_{SB}, \hat{\rho}(t)] \quad (2.58)$$

where the isolated contribution of $\hat{H}_B$ vanishes due to the cyclic invariance of the trace. The first term describes the coherent evolution the system would undergo if isolated. The second term, however, is not a functional of $\hat{\rho}_S$ alone; evaluating the coupling commutator requires the full total density operator $\hat{\rho}(t)$, thus invoking the system-environment correlations that the partial trace was intended to discard. The RDO therefore obeys no closed equation of motion, reflecting the same situation encountered classically in Subsection 2.1.6. The route towards a closed equation is likewise analogous: it requires a projection that formalizes the elimination, yielding an exact, non-local master equation, followed by a memoryless limit that is legitimate only when the environment loses memory faster than the system evolves. The subsequent subsections execute these theoretical steps in turn, beginning with the formal definition of the environment itself.

2.2.2 System-Bath Coupling and the Bath Correlation Function

The theoretical reduction may now be given a concrete setting. Of the three terms of the partition introduced in Equation (2.52), only the coupling requires further specification; it is expanded throughout as a sum of separable products

$$\hat{H}_{SB} = \sum_u \hat{A}_u \otimes \hat{B}_u \quad (2.59)$$

where the Hermitian operators $\hat{A}_u$ act upon the system and the $\hat{B}_u$ upon the environment. One property of the environment must be made explicit, as the reduction relies upon it: its mode frequencies are assumed to form a continuous spectrum. An environment with a discrete spectrum will inevitably return to its initial state after a Poincaré recurrence time, and only as the spacing between modes becomes vanishingly small is this recurrence time pushed beyond every physically relevant timescale, allowing the system to relax irreversibly. The same requirement underlies the finite correlation time established in Subsection 2.1.3.

No assumption is made regarding the structure of $\hat{H}_B$ or the specific form of the operators $\hat{B}_u$. The harmonic realization of the environment, upon which Chapter 3 rests, is a specialization introduced there and is nowhere required in the general

formalism below. Two conventions complete the specification. First, the environment is taken to reside in the canonical equilibrium state

$$\hat{\rho}_B = \frac{e^{-\beta \hat{H}_B}}{Z_B} \quad (2.60)$$

where the environmental partition function is defined as

$$Z_B = \text{Tr}_B \left[e^{-\beta \hat{H}_B} \right] \quad (2.61)$$

This canonical form guarantees that the bath state is stationary under its own dynamics. Second, the coupling operators are taken to have vanishing mean in that state, $\langle \hat{B}_u \rangle_B = 0$. Any non-zero average exerts a static mean force upon the system and is therefore absorbed into $\hat{H}_S$, leaving only the fluctuating component of the coupling.

The entire influence of the environment upon the system is then encapsulated within a single object, the bath correlation function

$$C_{uv}(t) = \langle \hat{B}_u(t) \hat{B}_v(0) \rangle_B \quad (2.62)$$

where the environmental operators evolve in the interaction picture

$$\hat{B}_u(t) = e^{i\hat{H}_B t/\hbar} \hat{B}_u e^{-i\hat{H}_B t/\hbar} \quad (2.63)$$

Because the operators evolve under $\hat{H}_B$ alone, C_{uv} is a property of the unperturbed environment. Furthermore, since the ensemble average is taken over the stationary state defined in Equation (2.60), this function depends solely upon the time difference. This object is the quantum equivalent to the [FACF](#) $C_{FF}(t)$ of Subsection 2.1.3, and it occupies the same position in the theory: once the reduction has been performed, no other property of the environment survives. When a single coupling term suffices, the indices are suppressed and the correlation function is written simply as $C(t)$.

The key property of $C(t)$ is that it is complex. Because the operators $\hat{B}(t)$ and $\hat{B}(0)$ generally do not commute, the order of the factors in Equation (2.62) cannot be interchanged, and the function separates into real and imaginary components

$$C(t) = C'(t) + iC''(t) \quad (2.64)$$

where the symmetric and antisymmetric parts are respectively given by

$$C'(t) = \frac{1}{2} \langle \{ \hat{B}(t), \hat{B}(0) \} \rangle_B \quad (2.65)$$

$$C''(t) = \frac{1}{2i} \langle [\hat{B}(t), \hat{B}(0)] \rangle_B \quad (2.66)$$

Both C' and C'' are real. The symmetrized part C' is even in t and serves as the direct analogue of the classical correlation function, measuring the thermal fluctuations of the coupling operator. Conversely, C'' is odd in t , ensuring that $C(-t) = C^*(t)$. This antisymmetric component vanishes identically when the operators are replaced by commuting classical variables; it possesses no classical analogue, and it is this component that governs macroscopic dissipation. While

a classical environment is described by a single real, even function, a quantum environment requires two. The relation between them forms the content of the remainder of this subsection.

Moving to the frequency domain makes that relationship explicit. The power spectrum of the environment is defined via the Fourier transform

$$\tilde{C}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} C(t) \quad (2.67)$$

in exact parallel with the Wiener-Khinchin construction of Equation (2.17). Although $C(t)$ is complex in the time domain, $\tilde{C}(\omega)$ is real and non-negative. The complexity of $C(t)$ manifests instead as an asymmetry of $\tilde{C}(\omega)$ in the frequency domain, and the canonical form of the bath state (2.60) exactly fixes that asymmetry. Evaluating Equation (2.67) in the energy representation yields the detailed-balance, or Kubo-Martin-Schwinger (KMS), condition

$$\tilde{C}(-\omega) = e^{-\beta\hbar\omega} \tilde{C}(\omega) \quad (2.68)$$

Its physical interpretation is immediate. The transform at a positive argument weights those processes in which the environment absorbs a quantum of energy $\hbar\omega$, and at a negative argument it weights those in which it surrenders the same quantum. Equation (2.68) guarantees that the former outweighs the latter by the Boltzmann ratio. Since the system must lose exactly what the environment gains, transitions that carry the system downwards in energy are favoured over the corresponding upward transitions by this ratio. This asymmetry is absent from a classical description, which weights both directions equally. It is exactly this detailed-balance condition that drives the open quantum system towards a thermal distribution rather than towards infinite temperature.

Equation (2.68) represents the quantum FDT in the form required below, as becomes evident upon forming the ratio of the symmetric and antisymmetric parts of the power spectrum

$$\frac{\tilde{C}(\omega) + \tilde{C}(-\omega)}{\tilde{C}(\omega) - \tilde{C}(-\omega)} = \coth\left(\frac{\beta\hbar\omega}{2}\right) = \frac{2}{\hbar\omega} E_{\beta}(\hbar\omega) \quad (2.69)$$

the numerator and the denominator on the left being respectively twice the transform of $C'(t)$ and twice that of $iC''(t)$, both of which are real. Here, $E_{\beta}(\hbar\omega)$ represents the mean thermal energy of a quantum harmonic oscillator of angular frequency ω at temperature T , inclusive of the zero-point contribution, defined as

$$E_{\beta}(\hbar\omega) = \frac{\hbar\omega}{2} \coth\left(\frac{\beta\hbar\omega}{2}\right) \quad (2.70)$$

Equation (2.69) is Kubo's statement of the theorem: quantum fluctuation and dissipation stand in a fixed, frequency-dependent ratio determined solely by the temperature [49, 58, 75].

The classical limit of this theorem follows immediately, and deserves to be stated with care, as the methodology of later chapters relies upon it. For $\beta\hbar\omega \ll 1$, the hyperbolic cotangent expands to $2/\beta\hbar\omega$, causing $E_{\beta}(\hbar\omega)$ to approach the

thermal energy $k_B T$. Concurrently, the Boltzmann factor in Equation (2.68) tends to unity. As a result, $\tilde{C}(\omega)$ becomes symmetric, $C(t)$ becomes real and even, and the theorem reduces to the classical FDT established in Subsection 2.1.5.

The practical consequence of this frequency dependence is a division of the environmental modes. For the low-frequency, diffusive motions of a liquid solvent, whose spectral weight falls well within the limit $\beta\hbar\omega \ll 1$, the classical form is a valid approximation. For stiff intramolecular vibrations, whose frequencies violate that inequality at ordinary temperatures, it is a poor one. A complex environment may therefore behave classically with respect to some of its modes and quantum mechanically with respect to others, and whether a classical correlation function may legitimately be used to characterize such an environment is a question that must be settled mode by mode.

It remains to define the timescale that the reduction requires. The bath correlation time τ_B is the interval over which $C(t)$ decays, serving as the quantum counterpart to the correlation time τ_c of Equation (2.16). An environment whose mode spectrum is continuous, in the sense assumed above, possesses a finite τ_B . The justification for the Markovian approximation invoked in the subsequent subsection turns upon the fact that τ_B is negligibly short.

2.2.3 Projection Operators and the Born-Markov Approximation

The formal elimination of the environment may now be carried out. The instrument is the same as the one used in Subsection 2.1.6: a projection superoperator that separates the relevant part of the total density operator from the irrelevant part. Defining the projector and its complement as

$$\hat{\mathcal{P}}\hat{\rho} = \text{Tr}_B [\hat{\rho}] \otimes \hat{\rho}_B = \hat{\rho}_S \otimes \hat{\rho}_B \quad (2.71)$$

$$\hat{\mathcal{Q}}\hat{\rho} = \hat{\rho} - \hat{\mathcal{P}}\hat{\rho} \quad (2.72)$$

the operation in Equation (2.71) serves as the quantum counterpart to the classical projector of Equation (2.40), with the partial trace replacing the integration over the environmental variables, and the canonical operator $\hat{\rho}_B$ replacing the classical equilibrium environmental density. The relevant part, $\hat{\mathcal{P}}\hat{\rho}$, carries the information contained in $\hat{\rho}_S$, as the environmental factor is a fixed reference state. Conversely, the irrelevant part, $\hat{\mathcal{Q}}\hat{\rho}$, contains the system-environment correlations.

The convention $\langle \hat{B}_u \rangle_B = 0$ adopted in Subsection 2.2.2 guarantees that $\hat{\mathcal{P}}\hat{\mathcal{L}}\hat{\mathcal{P}} = 0$, since the mean coupling was completely absorbed into $\hat{H}_S$ at the outset. Because of this, every term of first order in $\hat{H}_{SB}$ drops out of what follows, exactly as the subtraction of the mean force removed the corresponding term in Subsection 2.1.6.

Applying $\hat{\mathcal{P}}$ and $\hat{\mathcal{Q}}$ to the Liouville-von Neumann equation (2.56), solving the resulting equation for $\hat{\mathcal{Q}}\hat{\rho}$ and substituting that solution back into the equation for $\hat{\mathcal{P}}\hat{\rho}$ yields the Nakajima-Zwanzig equation[62, 63]

$$\frac{d}{dt}\hat{\mathcal{P}}\hat{\rho}(t) = - \int_0^t d\tau \hat{\mathcal{P}}\hat{\mathcal{L}} e^{-i\hat{\mathcal{Q}}\hat{\mathcal{L}}\tau} \hat{\mathcal{Q}}\hat{\mathcal{L}} \hat{\mathcal{P}}\hat{\rho}(t-\tau) - i\hat{\mathcal{P}}\hat{\mathcal{L}} e^{-i\hat{\mathcal{Q}}\hat{\mathcal{L}}t} \hat{\mathcal{Q}}\hat{\rho}(0) \quad (2.73)$$

The algebra leading to Equation (2.73) is identical to that presented in Appendix A for the classical case, and thus not repeated; only the physical interpretation of the

symbols has changed. Equation (2.73) is exact. Its first term is the memory term, which plays the same role as the memory integral in Equation (2.43). The second term depends upon the correlations present at the initial instant. It is conventionally removed by the choice of initial condition, $\hat{Q}\hat{\rho}(0) = 0$, which is equivalent to assuming the total system is prepared in a factorized, uncorrelated state: $\hat{\rho}(0) = \hat{\rho}_S(0) \otimes \hat{\rho}_B$.

The exact memory kernel of Equation (2.73) is generally no more computationally tractable than the dynamics of the total system itself, and further progress requires an expansion in the coupling. The kernel is therefore truncated at second order in the coupling; this truncation is the Born approximation.[24] This assumes that the coupling between the system and the environment is sufficiently weak that the influence of the system upon the macroscopic bath remains negligibly small. The density operator of the bath $\hat{\rho}_B$ is unaffected by the interaction, and the state of the total system at time t may be approximately characterized by the tensor product

$$\hat{\rho}(t) \simeq \hat{\rho}_S(t) \otimes \hat{\rho}_B \quad (2.74)$$

with only the system factor evolving. This does not assert that the environment is never excited; rather, it asserts that whatever excitation the system produces decays within τ_B and leaves no lasting imprint upon $\hat{\rho}_B$. It is convenient at this point to pass to the interaction representation with respect to the non-interacting Hamiltonian $\hat{H}_0 = \hat{H}_S + \hat{H}_B$. In this frame, operators carrying an explicit time argument evolve under $\hat{H}_0$, while the **RDO**, denoted $\hat{\rho}_S^I$, evolves solely under the coupling. Inserting Equation (2.74) into Equation (2.73) gives a closed integro-differential equation for the **RDO**

$$\frac{d\hat{\rho}_S^I(t)}{dt} = -\frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B [\hat{H}_{SB}(t), [\hat{H}_{SB}(t-\tau), \hat{\rho}_S^I(t-\tau) \otimes \hat{\rho}_B]] \quad (2.75)$$

in which the environment enters exclusively through the bath correlation functions C_{uv} of Equation (2.62), which naturally emerge upon carrying out the partial trace. Equation (2.75) is not yet Markovian: the **RDO** still appears at the retarded time $t - \tau$, and the integration still runs over the history from 0 to t . Consequently, the evolution at time t remains determined by the prior history of the system. Equation (2.75) is the quantum counterpart to the memory integral of the **GLE** (2.48).

Equation (2.75) is simplified by the Markovian approximation, which rests upon the separation of timescales established in Subsection 2.2.2.[20] The bath correlation functions $C_{uv}(\tau)$ decay over the interval τ_B , whereas $\hat{\rho}_S^I$ changes appreciably only over the far longer relaxation time τ_S . When $\tau_B \ll \tau_S$, the retarded density operator may therefore be replaced by its value at the current time, and the upper limit of the integral may be extended to infinity, as the integrand has already decayed to zero. This yields the Markovian master equation

$$\frac{d\hat{\rho}_S^I(t)}{dt} = -\frac{1}{\hbar^2} \int_0^\infty d\tau \text{Tr}_B [\hat{H}_{SB}(t), [\hat{H}_{SB}(t-\tau), \hat{\rho}_S^I(t) \otimes \hat{\rho}_B]] \quad (2.76)$$

The time substitution $t - \tau \rightarrow t$ is made for $\hat{\rho}_S^I$ alone, and not for the coupling operators. The interaction-picture evolution of the coupling operators is generated

by $\hat{H}_S$ and oscillates rapidly at the Bohr frequencies of the system; that motion is not slow on the scale of τ_B , and suppressing it would discard the frequency selectivity upon which the following subsection depends.

The truncation at second order in the coupling and the subsequent removal of the memory together constitute the Born-Markov approximation. Equation (2.76) is the resulting Redfield equation. Expressing this equation explicitly in the energy eigenbasis of $\hat{H}_S$, and examining what its tensorial structure implies for the populations and coherences introduced in Subsection 2.2.1 is the subject of Subsection 2.2.4.

2.2.4 The Redfield Equation and the Secular Approximation

Equation (2.76) acquires its physical content once a basis is chosen, and the natural choice is the eigenbasis of the system Hamiltonian, $\hat{H}_S |a\rangle = E_a |a\rangle$. Writing $A_{ab}^{(u)} = \langle a | \hat{A}_u | b \rangle$ for the matrix elements of the system coupling operators, defined in Equation (2.59), and carrying out the trace over the environment, all reference to the environment collects into the memory matrix

$$M_{ab,cd}(t) = \frac{1}{\hbar^2} \sum_{u,v} C_{uv}(t) A_{ab}^{(u)} A_{cd}^{(v)} \quad (2.77)$$

The one-sided Fourier transforms of this matrix, denoted $\Gamma_{ab,cd}(\omega)$, are then evaluated at the Bohr frequencies of the system

$$\Gamma_{ab,cd}(\omega) = \int_0^\infty d\tau e^{i\omega\tau} M_{ab,cd}(\tau) \quad (2.78)$$

In terms of these spectral quantities, the equation of motion for the reduced density matrix elements $\rho_{ab} = \langle a | \hat{\rho}_S | b \rangle$ takes the compact form

$$\frac{d\rho_{ab}}{dt} = -i\omega_{ab} \rho_{ab} - \sum_{c,d} R_{ab,cd} \rho_{cd} \quad (2.79)$$

where the relaxation matrix, or Redfield tensor, is given by

$$R_{ab,cd} = \delta_{ac} \sum_e \Gamma_{be,ed}(\omega_{de}) + \delta_{bd} \sum_e \Gamma_{ae,ec}(\omega_{ce}) - \Gamma_{ca,bd}(\omega_{ab}) - \Gamma_{db,ac}(\omega_{ca}) \quad (2.80)$$

Equations (2.79) and (2.80) constitute the Redfield equation.[76, 77] Closely related formulations were given earlier by Wangsness and Bloch.[78, 79] The first term of Equation (2.79) is the coherent evolution of the isolated system; the second term encapsulates the whole influence exerted by the environment.

The transforms $\Gamma_{ab,cd}$ are complex. Their imaginary components induce Lamb-type shifts in the transition frequencies of the system;[80] the shift is conventionally absorbed into $\hat{H}_S$ via energy level renormalization. The real components govern the redistribution of amplitude among the elements of $\hat{\rho}_S$. As Equation (2.77) shows, this redistribution depends on the environmental correlation functions C_{uv} evaluated at the Bohr frequencies. The environment acts upon the system only

through its power spectrum, sampled at the frequencies at which the system is energetically capable of making a transition. In the classical theory, the Markovian friction tensor of Equation (2.49) evaluates the transformed memory kernel at zero frequency, whereas the quantum theory samples it at every transition frequency. This distinction clarifies the classical limit discussed in Subsection 2.2.2: when all relevant transition energies satisfy $\hbar\omega_{ab} \ll k_B T$, the environmental spectrum is symmetric across the sampled frequencies, and the two descriptions coincide.

The Redfield tensor elements fall into three distinct classes, based on the type of density-matrix elements they connect. Elements with $a = b$ and $c = d$ transfer population between energy eigenstates. Elements with $a = c$ and $b = d$ (where $a \neq b$) damp coherences. The remaining elements couple populations to coherences and transfer amplitude between distinct coherences. Because coherences themselves possess no classical analogue, both the second and third classes describe quantum-mechanical effects. However, it is specifically this third class that constitutes the target of the secular approximation.

Transforming Equation (2.79) to the interaction representation reveals the oscillatory behaviour of these couplings

$$\frac{d\rho_{ab}^I}{dt} = - \sum_{c,d} R_{ab,cd} e^{i(\omega_{ab}-\omega_{cd})t} \rho_{cd}^I \quad (2.81)$$

Each term carries a phase oscillating at the difference between two Bohr frequencies. Terms satisfying the condition

$$|\omega_{ab} - \omega_{cd}| \gg |R_{ab,cd}| \quad (2.82)$$

undergo rapid oscillations in the time before the density operator changes appreciably. Integrating over the coarse-grained time axis upon which the Markovian approximation is defined averages these contributions to zero. The secular approximation discards these rapidly oscillating terms.[24, 25] The surviving contributions are those satisfy $\omega_{ab} = \omega_{cd}$: population-transfer elements (where both frequencies vanish); coherence-damping elements (a trivial equality); and elements connecting degenerate transitions. Assuming the Bohr frequencies of $\hat{H}_S$ are non-degenerate, only the first two classes remain, decoupling populations from coherences.

In this fully secular case, the diagonal population elements $P_a = \rho_{aa}$ obey a closed differential equation

$$\frac{dP_a}{dt} = \sum_{b \neq a} (k_{b \rightarrow a} P_b - k_{a \rightarrow b} P_a) \quad (2.83)$$

with time-independent transition rates given by Fermi's golden rule[81]

$$k_{a \rightarrow b} = \frac{1}{\hbar^2} \sum_{u,v} \tilde{C}_{uv}(\omega_{ab}) A_{ab}^{(u)} A_{ba}^{(v)} \quad (2.84)$$

This is a Pauli master equation.[82] The coherences decouple and decay exponentially as $\rho_{ab}(t) \propto e^{-i\omega_{ab}t - \gamma_{ab}t}$, with dephasing rates

$$\gamma_{ab} = \frac{1}{2} \sum_{e \neq a} k_{a \rightarrow e} + \frac{1}{2} \sum_{e \neq b} k_{b \rightarrow e} + \gamma_{ab}^{pd} \quad (2.85)$$

where the pure dephasing contribution is

$$\gamma_{ab}^{\text{pd}} = -\frac{1}{\hbar^2} \sum_{u,v} \tilde{C}_{uv}(0) A_{aa}^{(u)} A_{bb}^{(v)} \quad (2.86)$$

Equation (2.85) dictates that any process depopulating either of the two levels destroys the phase relation between them, so energy relaxation is a source of dephasing. The pure dephasing term γ_{ab}^{pd} isolates coherence loss occurring without energy exchange. Governed by the environmental spectrum at zero frequency, this mechanism shifts the energy levels without inducing any transition between them. It requires non-vanishing diagonal coupling elements, $A_{aa}^{(u)} \neq 0$, and has no classical analogue.

The secular equations relax to the thermal equilibrium due to the KMS condition. Applying Equation (2.68) to the rates of Equation (2.84) gives the principle of detailed balance

$$\frac{k_{a \rightarrow b}}{k_{b \rightarrow a}} = e^{\beta \hbar \omega_{ab}} \quad (2.87)$$

Downward transitions exceed upward transitions by the Boltzmann factor, making the canonical thermal distribution $P_a \propto e^{-\beta E_a}$ the unique stationary solution of the Pauli master equation (2.83). This is the direct parallel to the verification in Subsection 2.1.4 that the Maxwell-Boltzmann distribution is stationary under the Klein-Kramers equation. In both descriptions, the relationship between fluctuation and dissipation drives the system to the correct thermal state.

The secular equation assumes Lindblad form, generating a completely positive dynamical map.[83, 84] This ensures the eigenvalues of $\hat{\rho}_S$ remain non-negative at all times and populations represent valid probabilities. The full Redfield equation lacks this property; numerical solutions of Equation (2.79) can yield negative populations, particularly at short times or under strong coupling.[85–87] Positivity in the Lindblad formulation is achieved by the secular approximation rather than by an extended domain of validity. A negative population in the full Redfield equation signals a breakdown of the underlying assumptions, whereas the Lindblad form masks this failure by returning mathematically well-behaved, yet physically inaccurate, density matrices.

The secular approximation requires well-separated Bohr frequencies relative to the scale of the relaxation rates. For near-degenerate transitions, $|\omega_{ab} - \omega_{cd}|$ is small, the corresponding terms oscillate slowly, and discarding them is unjustified. Enforcing the approximation under these conditions coarse-grains the time axis over the interval $|\omega_{ab} - \omega_{cd}|^{-1}$ rather than the shorter environmental correlation time τ_B . This eliminates the third class of tensor elements and the associated physics of coherence-driven population dynamics among near-degenerate transitions. Retaining these elements in a non-secular treatment preserves this physics at the cost of guaranteed positivity. The choice depends on the spectral separation of the system.

The reduction is now complete. The influence of the environment upon the system has been compressed into an equilibrium correlation function of the bath coupling operator, constrained by the temperature via Equation (2.68) and entering the dynamics only at the transition frequencies of $\hat{H}_S$. The two sections of

this chapter have thus reached the same destination by parallel routes, and they differ not in where the partition is drawn, but in what survives it. The classical elimination in Subsection 2.1.6 retains the friction tensor of Equation (2.49), the zero-frequency value of the transform of a [FACF](#). The quantum elimination retains the power spectrum of the coupling operator sampled at every Bohr frequency. Whether these two descriptors represent the same physical environment is settled by neither derivation, as each was obtained without reference to the other and no unified framework has been established.

BRIDGING QUANTUM AND CLASSICAL BATHS IN NON-ADIABATIC DYNAMICS

The preceding chapter concluded with an open question. The classical and quantum projections each yield a single environmental descriptor: the friction and the power spectrum of the coupling operator, respectively. Neither derivation references the other, leaving the physical consistency of these two quantities unresolved when applied to the same thermal bath.

A general correspondence between these descriptors cannot be formulated. The friction kernel of Equation (2.47) derives from the two-time statistics of a classical fluctuating force, whereas the Redfield tensor of Equation (2.80) relies on the ordered quantum correlation function of Equation (2.62). For an arbitrary environment, the classical correlation function cannot determine its quantum counterpart due to the lack of operator ordering information. A physical mapping requires a model where both descriptors are generated by a common set of parameters. An environment of harmonic modes bilinearly coupled to the system coordinate fulfills this requirement. Section 3.1 develops this harmonic model and establishes the analytical bridge between the classical and quantum descriptors.

Establishing a theoretical mapping does not alone constitute a comparison of the theories; assessing their consistency requires a numerical evaluation of the resulting formalisms. The remainder of this chapter evaluates both descriptions through a shared case study in non-adiabatic dynamics: photoisomerization. This model system features two electronic states coupled to a single torsional coordinate embedded in a thermal bath. Section 3.2 introduces the quantum-classical framework, treating the electronic DOF quantum mechanically while propagating the torsional coordinate as a classical stochastic variable. Section 3.3 specifies the model system and the two implementations through which it is treated. Section 3.4 reports the numerical benchmarks and identifies the physical regimes that produce quantitative agreement, should any exist. Subsection 3.4.7 evaluates the limitations of both the mapping and the constituent theories, outlining the conditions required for their resolution.

3.1 THE HARMONIC BATH AND THE ANALYTICAL BRIDGE

The present section constructs the harmonic environment model and extracts from it the relation between the classical and quantum bath descriptors.

3.1.1 *The Caldeira-Leggett Hamiltonian*

Let the system possess a single coordinate $\hat{q}$, with conjugate momentum $\hat{p}$ and inertial parameter M , and let the environment consist of a set of harmonic modes indexed by j , with masses m_j , frequencies ω_j , coordinates $\hat{x}_j$, and momenta $\hat{p}_j$.

The three terms of the partition (2.52) are specified as follows. The system is a particle moving in a generally anharmonic potential,

$$\hat{H}_S = \frac{\hat{p}^2}{2M} + V(\hat{q}) \quad (3.1)$$

the environment is the set of harmonic modes,

$$\hat{H}_B = \frac{1}{2} \sum_j \left[\frac{\hat{p}_j^2}{m_j} + m_j \omega_j^2 \hat{x}_j^2 \right] \quad (3.2)$$

and the interaction is linear in both the environmental coordinates and the system coordinate

$$\hat{H}_{SB} = -\hat{q} \sum_j c_j \hat{x}_j + \frac{1}{2} \Lambda \hat{q}^2 \quad (3.3)$$

where c_j measures the coupling strength of the j -th mode to the system coordinate, and the counterterm parameter is defined as

$$\Lambda = \sum_j \frac{c_j^2}{m_j \omega_j^2} \quad (3.4)$$

The linearity in the environmental coordinates relies on the assumption that the interaction of the system with any individual DOF of a macroscopic environment scales inversely with the bath volume and is therefore weak. The weak perturbation of any individual mode, however, does not imply that the aggregate dissipative influence of the macroscopic bath is weak.[26]

Comparing the first term of Equation (3.3) with Equation (2.59) identifies a single pair of coupling operators

$$\hat{A} = \hat{q} \quad \hat{B} = -\sum_j c_j \hat{x}_j \quad (3.5)$$

The convention $\langle \hat{B} \rangle_B = 0$ adopted in Subsection 2.2.2 is satisfied identically because $\hat{B}$ is linear in coordinates whose equilibrium distribution under $\hat{H}_B$ is centered upon the origin. This model therefore specializes the general framework of Section 2.2 to a harmonic environment where the relevant system operator is the coordinate itself.

Collecting the environmental and interaction terms yields the Caldeira-Leggett (CL) Hamiltonian[88–91]

$$\hat{H} = \frac{\hat{p}^2}{2M} + V(\hat{q}) + \frac{1}{2} \sum_j \left[\frac{\hat{p}_j^2}{m_j} + m_j \omega_j^2 \left(\hat{x}_j - \frac{c_j}{m_j \omega_j^2} \hat{q} \right)^2 \right] \quad (3.6)$$

a construction previously introduced by Magalinskii[92] and by Ford, Kac and Mazur.[93] The environment is formulated as a set of oscillators whose equilibrium positions are displaced in proportion to the instantaneous value of $\hat{q}$. The parameter Λ from Equation (3.4) is the exact quantity required to factor the Hamiltonian into this displaced harmonic form; this representation is possible only if the second term of Equation (3.3) is present with that specific strength.

The counterterm prevents an unphysical renormalization of the potential.[26] In Subsection 2.1.6, Equation (2.46) established that the effective potential governing the reduced dynamics is not the bare potential but the PMF, derived from the partition function of the environment. Evaluating the constrained partition function generated by the bracketed expression in Equation (3.6) requires only the translation $\hat{x}_j \rightarrow \hat{x}_j + c_j \hat{q}/m_j \omega_j^2$, a canonical transformation that leaves the trace invariant. Consequently,

$$Z(\hat{q}) = Z(0) \quad \text{and therefore} \quad \mathcal{A}(\hat{q}) = V(\hat{q}) \quad (3.7)$$

Without the counterterm, the environment would subtract a quadratic contribution ($\frac{1}{2} \Lambda \hat{q}^2$) from the bare potential, unphysically softening or eliminating the binding potential. The counterterm guarantees that the bare potential of Equation (3.1) acts as the free energy surface for the reduced dynamics.

The model may be verified by recovering the classical result of Subsection 2.1.6 exactly. The Heisenberg equation for the j -th mode represents a driven oscillator

$$m_j \ddot{\hat{x}}_j(t) = -m_j \omega_j^2 \hat{x}_j(t) + c_j \hat{q}(t) \quad (3.8)$$

Substituting its solution into the Heisenberg equation for $\hat{q}$, [93, 94] and integrating the driven term by parts, produces a contribution $\Lambda \hat{q}(t)$ that exactly cancels the counterterm. The resulting equation is [26, 93]

$$M \ddot{\hat{q}}(t) = -\frac{\partial V(\hat{q})}{\partial \hat{q}} - \int_0^t ds \, \xi(t-s) \dot{\hat{q}}(s) + \hat{\zeta}(t) \quad (3.9)$$

with the friction kernel

$$\xi(t) = \sum_j \frac{c_j^2}{m_j \omega_j^2} \cos(\omega_j t) \quad (3.10)$$

and the fluctuating force operator

$$\hat{\zeta}(t) = \sum_j c_j \left[\left(\hat{x}_j(0) - \frac{c_j}{m_j \omega_j^2} \hat{q}(0) \right) \cos(\omega_j t) + \frac{\hat{p}_j(0)}{m_j \omega_j} \sin(\omega_j t) \right] \quad (3.11)$$

The displacement is absorbed into the initial coordinates in Equation (3.11) so the fluctuating force possesses vanishing mean under the conditional equilibrium distribution (2.41). Note that Equation (3.10) defines $\xi(t)$ as an even function, conforming with the FDT requirement that equates the kernel to a FACF.

Equation (3.9) is the GLE (2.48) in operator form, derived without weak-coupling expansions or timescale separations. The drift potential remains the bare V , the fluctuating force has vanishing mean when the environment is equilibrated conditionally upon the initial system configuration, which is assumption (i) of Subsection 2.1.6, and the kernel (3.10) lacks any dependence upon $\hat{q}$. The bilinearity of the coupling eliminates the configuration dependence of the general friction kernel. Furthermore, $\xi(0) = \Lambda$, identifying the zero-time friction kernel with the counterterm strength.

3.1.2 The Spectral Density

The parameters c_j , m_j , and ω_j are not individually accessible, nor are they individually required, as they enter Equation (3.10) solely through the combination $c_j^2/m_j\omega_j^2$, evaluated at the mode frequencies. A spectral density is introduced to collect this combination into a single frequency-dependent function[26, 91]

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{m_j\omega_j} \delta(\omega - \omega_j) \quad (3.12)$$

Subsection 2.2.2 required the mode spectrum of the environment to be continuous, so that the Poincaré recurrence time exceeds every physically relevant interval; in that limit the delta functions merge into a smooth function, removing the discrete nature of the environment from the theory.

The bath correlation function follows from the equilibrium statistics of independent oscillators. Using the standard result for the position autocorrelation function of a single mode in a canonical state (2.60),[24] Equation (2.62) gives

$$C(t) = \frac{\hbar}{\pi} \int_0^\infty d\omega J(\omega) \left[\coth\left(\frac{\beta\hbar\omega}{2}\right) \cos(\omega t) - i \sin(\omega t) \right] \quad (3.13)$$

The real and imaginary components correspond to the symmetric (C') and anti-symmetric (C'') parts defined in Equations (2.65) and (2.66). Equation (3.13) shows that the temperature enters through C' alone, while C'' is determined by $J(\omega)$ and is independent of T . The dissipative response is a property of the environmental mode structure, while the fluctuations are thermally weighted. This is the microscopic content of the statement, made in Subsection 2.1.5, that friction and noise are two manifestations of one set of interactions.

Transforming Equation (3.13) according to the definition (2.67) gives the power spectrum

$$\tilde{C}(\omega) = 2\hbar J(\omega) [1 + n(\omega)] \quad (3.14)$$

where

$$n(\omega) = \frac{1}{e^{\beta\hbar\omega} - 1} \quad (3.15)$$

and $J(\omega)$ is continued to negative arguments as an odd function. Equation (3.14) is manifestly real and non-negative. Forming the ratio at $\pm\omega$ returns

$$\frac{\tilde{C}(-\omega)}{\tilde{C}(\omega)} = \frac{n(\omega)}{1 + n(\omega)} = e^{-\beta\hbar\omega} \quad (3.16)$$

recovering the KMS condition (2.68). The harmonic bath identically satisfies detailed balance, driving the system to the canonical distribution. Subtracting the values at $\pm\omega$ isolates the spectral density

$$J(\omega) = \frac{1}{2\hbar} [\tilde{C}(\omega) - \tilde{C}(-\omega)] \quad (3.17)$$

showing that $J(\omega)$ is the antisymmetric, temperature-independent part of the power spectrum. The spectral density is not an additional ingredient of the theory;

it is the temperature-independent content of the object that survived the reduction, separated from the thermal weighting that Equation (2.69) supplies.

This function enters the Redfield construction of Subsection 2.2.4. Specializing Equation (2.84) to the single coupling operator (3.5) gives the transition rates between the eigenstates of $\hat{H}_S$ as

$$k_{a \rightarrow b} = \frac{2}{\hbar} J(\omega_{ab}) [1 + n(\omega_{ab})] |q_{ab}|^2 \quad (3.18)$$

with $q_{ab} = \langle a | \hat{q} | b \rangle$. The spectral density is evaluated only at the system's Bohr frequencies, and the matrix elements of the system coordinate select which of them are sampled.

3.1.3 The Classical Limit and the Friction Kernel

The bridge sought emerges by comparing Equations (3.10) and (3.12). Expressing the kernel as an integral over the continuous spectrum yields

$$\xi(t) = \frac{2}{\pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega} \cos(\omega t) \quad (3.19)$$

Inverting the cosine transform expresses the spectral density directly through the friction[26]

$$J(\omega) = \omega \int_0^\infty dt \xi(t) \cos(\omega t) \quad (3.20)$$

Equivalently, using the one-sided transform (2.30), $J(\omega) = \omega \operatorname{Re} \hat{\xi}(\omega)$. Equations (3.19) and (3.20) are exact within the Hamiltonian (3.6); no limits or expansions are required because both quantities share identical fundamental parameters. The descriptor of the classical bath and the descriptor of the quantum bath are, within this model, two representations of one object.

It remains to establish in what sense the friction appearing in Equation (3.20) is the friction of Chapter 2, whose definition (2.47) is an equilibrium average over a classical environment. Assuming the classical limit $\beta \hbar \omega \ll 1$ holds for all frequencies at which $J(\omega)$ is non-negligible, the hyperbolic cotangent in Equation (3.13) expands to $2/\beta \hbar \omega$. The symmetric part reduces to

$$C'(t) \simeq \frac{2}{\pi \beta} \int_0^\infty d\omega \frac{J(\omega)}{\omega} \cos(\omega t) = k_B T \xi(t) \quad (3.21)$$

The antisymmetric part becomes negligible. Equation (3.21) represents the memory-retaining FDT of the second kind (2.29), identifying the classical FCF as the high-temperature limit of the symmetrized quantum correlation function. This establishes a theoretical mapping: a classically computed FCF determines $\xi(t)$ via Equation (2.20); $\xi(t)$ determines $J(\omega)$ through Equation (3.20); and $J(\omega)$ governs the Redfield tensor via Equation (3.18). Equation (3.20) itself requires no quantum correction. The classical approximation occurs during the extraction of ξ , requiring the restoration of the coth factor (2.70) to convert the classical FCF into the proper symmetrized quantum form.

Every spectral density employed below vanishes linearly as $\omega \rightarrow 0$. Its slope at the origin,

$$\eta = \lim_{\omega \rightarrow 0} \frac{J(\omega)}{\omega} = \hat{\xi}(0) = \int_0^\infty dt \xi(t) \quad (3.22)$$

is therefore defined for all of them, the three expressions being equal by Equation (3.20). The last identifies η with the constant friction coefficient of the Langevin equation (2.2), which by Equation (2.20) is the Green-Kubo integral of the [FACF](#). The Ohmic case is the one in which that slope extends to all frequencies,

$$J(\omega) = \eta \omega \quad (3.23)$$

Substituting this form into Equation (3.19) yields $\xi(t) = 2\eta \delta(t)$. The memory integral in Equation (3.9) collapses to $\eta \dot{q}(t)$, recovering the Langevin equation (2.3). The Ohmic form, while capturing strictly Markovian phenomenology, produces a linearly divergent counterterm Λ . Regularizing this with a cut-off frequency ω_c yields the Drude-Lorentz form[26, 95]

$$J(\omega) = \eta \omega \frac{\omega_c^2}{\omega^2 + \omega_c^2} \quad (3.24)$$

Evaluating Equation (3.19) with this spectrum produces an exponentially decaying kernel

$$\xi(t) = \eta \omega_c e^{-\omega_c |t|} \quad (3.25)$$

with finite $\xi(0) = \Lambda = \eta \omega_c$. The quantity ω_c^{-1} is the environmental correlation time τ_B defined in Subsection 2.2.2. The Markovian limit of the [GLE](#) requires the separation of timescales expressed by $\tau_B \ll \tau_S$, i.e., ω_c large compared with the characteristic frequencies of $\hat{H}_S$.

The spectral density is frequently parameterized by a reorganization energy,[25] in the form $J(\omega) = \Lambda \omega \omega_c / (\omega^2 + \omega_c^2)$, the reorganization energy being one half of the counterterm strength Λ of Equation (3.4).

3.1.4 Conditions of the Correspondence

The correspondence established by Equation (3.20) is exact within the model that generates it, and the question of its applicability to a molecular environment is therefore the question of whether that model is adequate. The required conditions are: (i) bilinear coupling between the system and environment; (ii) a configuration-independent friction kernel; (iii) Gaussian statistics for the fluctuating force; (iv) $\beta \hbar \omega \ll 1$ for all frequencies at which $J(\omega)$ is non-negligible, necessary when a classically derived kernel parametrizes the quantum spectral density; and (v) weak coupling consistent with the Born approximation.

These conditions are neither independent nor of equal standing. Condition (v) constrains the quantum master equation rather than the correspondence, as Equation (3.9) remains exact at any coupling strength. Condition (iv) concerns which modes of a complex environment carry the relevant spectral weight, and admits a

correction in the form of the coth factor. Conditions (i) and (ii) represent the critical requirement: the environment must couple linearly to the system coordinate. The harmonic representation is less restrictive than it appears; any environment with a linear response to the system coordinate exerts a Gaussian fluctuating force and is indistinguishable from a harmonic bath with the spectral density of Equation (3.20).^[94, 96]

Subsection 3.4.7 evaluates these conditions for the current model system, while Chapter 4 assesses them for a molecular solvent. The primary conclusion of this section is that the classical and quantum descriptors are related by Equation (3.20). This correspondence presupposes a framework in which friction enters as a parameter, which is developed in the following section.

3.2 THE QUANTUM-CLASSICAL FRAMEWORK

While the preceding section established an analytical mapping between the classical friction and the quantum spectral density, assessing their physical consistency requires a numerical comparison. The common ground for this evaluation is non-adiabatic dynamics propagated as a statistical ensemble. The comparison requires a description in which the friction appears as a macroscopic parameter. Because the system features discrete electronic states interacting non-adiabatically with relevant classical coordinates, a quantum-classical framework is the natural choice.

This section outlines the quantum-stochastic Liouville equation (QSLE), a multiscale, non-adiabatic, mixed quantum-classical method developed for molecular dynamics in condensed phases.[97–99] Its governing principle is to propagate the density matrix of a quantum subsystem and the phase-space probability density of a set of classical coordinates concurrently within a single equation of motion, while the remaining classical DOF are eliminated in favour of their statistical influence. Unlike on-the-fly trajectory-based methods, the QSLE requires pre-computed potential energy surfaces (PESs) and propagates an ensemble directly, rather than a sample, so that a single solution corresponds in principle to the average over a large number of independent trajectories. This ensemble propagation makes the framework structurally compatible with the Redfield equation of Subsection 2.2.4.

3.2.1 Hierarchical Partitioning of the Degrees of Freedom

The construction relies on a two-stage partitioning of the DOF based on independent criteria.[97, 100]

The first criterion is relevance to the physical observable under investigation. The nuclear DOF are divided into a relevant set and an irrelevant set. The irrelevant set, termed the classical bath (CB), comprises nuclear coordinates that are fast in comparison with the relevant ones and energetically uncoupled from the quantum core of the process. In a solvated molecule, the CB contains the solvent coordinates and the stiff internal modes of the solute.

The second criterion is dynamical character. Among the relevant DOF, the electronic coordinates $\mathbf{r}$ constitute the quantum subsystem (QS), while the relevant nuclear coordinates $\mathbf{x}$, with conjugate momenta $\mathbf{p}$ and diagonal mass matrix $\mathbf{m}$, constitute the classical subsystem (CS). The irrelevant coordinates are denoted $\mathbf{y}$, with momenta $\boldsymbol{\pi}$, matching the notation of Subsection 2.1.6. The two criteria are distinct: a coordinate may be relevant and yet be treated classically, which characterizes the reaction coordinate in the present model. Figure 3.1 provides an example of this separation for the azobenzene molecule.

Referred to the framework of Chapter 2, the union of QS and CS is the system and the CB is the thermal bath. The QSLE performs the same elimination as Sections 2.1 and 2.2, but differs in the internal constitution of the retained subsystem: whereas, for instance, Subsection 2.2.3 retained a set of quantum DOF, the present framework retains a QS coupled non-adiabatically to a classical one (CS).

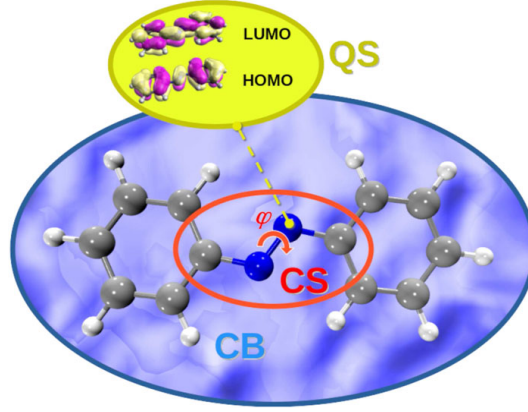


Figure 3.1: Schematic partitioning of the DOF for solvated azobenzene. The QS includes the electronic DOF responsible for the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The CS includes the rigid body roto-translations and the dihedral angle. All other molecular internal DOF and the solvent coordinates constitute the CB set.[97]

The BO approximation is applied exclusively to the CB coordinates. Non-adiabatic coupling is retained in full between QS and CS. This asymmetry manifests as an approximation upon the total potential energy,

$$\hat{V}(\mathbf{r}, \mathbf{x}, \mathbf{y}) \simeq \hat{V}_{\text{QS-CS}}(\mathbf{r}, \mathbf{x}) + V_{\text{CS-CB}}(\mathbf{x}, \mathbf{y}) \quad (3.26)$$

which neglects direct coupling between the electrons and the environment. The electronic states thereby become independent of $\mathbf{y}$; the adiabatic basis introduced below is parameterized by the CS configuration alone and does not require recomputation for each environmental configuration. The price is that the environment can no longer shift the electronic energies. Modulations of the energy surfaces by the solvent, such as solvatochromic shifts, lie outside this description. The environment influences the electronic subsystem only indirectly, via the classical coordinates to which the electrons are coupled.

3.2.2 The Quantum-Classical Liouville Equation

The starting point is the exact, unitary Liouville-von Neumann equation (2.56) for the total density operator. A partial Wigner transform is performed with respect to all nuclear coordinates,[101] followed by the heavy-mass limit.[102, 103] The outcome is the quantum-classical Liouville equation (QCLE)

$$\frac{\partial \hat{\rho}_W(t)}{\partial t} = -\frac{i}{\hbar} [\hat{H}_W, \hat{\rho}_W(t)] + \frac{1}{2} \left(\{ \hat{H}_W, \hat{\rho}_W(t) \} - \{ \hat{\rho}_W(t), \hat{H}_W \} \right) \quad (3.27)$$

in which $\{ \cdot, \cdot \}$ denotes the Poisson bracket with respect to the nuclear phase-space variables. The object $\hat{\rho}_W$ is an operator in the electronic Hilbert space and a continuous function over the nuclear phase space. It acts as the mixed quantum-classical equivalent of the total density $\rho(\mathbf{x}, \mathbf{p}, \mathbf{y}, \boldsymbol{\pi}, t)$ of Equation (2.34), from which it differs in carrying electronic indices. The commutator generates the coherent evolution of the electronic subsystem, while the antisymmetrized combination of Pois-

son brackets dictates the classical propagation of the nuclei and the energy exchange between the two subsystems.

Equation (3.27) is represented in the adiabatic basis, defined as eigenstates of the electronic Hamiltonian $\hat{h} = \hat{K}_{QS} + \hat{V}_{QS-CS}$ evaluated at a fixed configuration of the CS,[102]

$$\hat{h}(\mathbf{r}; \mathbf{x}) |\alpha; \mathbf{x}\rangle = E_\alpha(\mathbf{x}) |\alpha; \mathbf{x}\rangle \quad (3.28)$$

where the index α labels an electronic state and the semicolon denotes, as in Equation (2.33), a parametric dependence on the classical coordinates.

Writing $\rho_{\alpha\alpha'}(\mathbf{x}, \mathbf{p}, \mathbf{y}, \boldsymbol{\pi}, t) = \langle \alpha; \mathbf{x} | \hat{\rho}_W | \alpha'; \mathbf{x} \rangle$, Equation (3.27) becomes[104]

$$\frac{\partial \rho_{\alpha\alpha'}}{\partial t} = -i \left[\omega_{\alpha\alpha'}(\mathbf{x}) + \hat{\mathcal{L}}_{\alpha\alpha'} \right] \rho_{\alpha\alpha'} + \sum_{\beta\beta'} \hat{\mathcal{J}}_{\alpha\alpha',\beta\beta'} \rho_{\beta\beta'} \quad (3.29)$$

where $\omega_{\alpha\alpha'}(\mathbf{x}) = [E_\alpha(\mathbf{x}) - E_{\alpha'}(\mathbf{x})] / \hbar$ is the local Bohr frequency, now a function of the classical configuration. The classical Liouville operator is

$$i\hat{\mathcal{L}}_{\alpha\alpha'} = (\mathbf{m}^{-1} \mathbf{p}) \cdot \frac{\partial}{\partial \mathbf{x}} + \frac{1}{2} [\mathbf{F}_{\alpha\alpha}(\mathbf{x}) + \mathbf{F}_{\alpha'\alpha'}(\mathbf{x})] \cdot \frac{\partial}{\partial \mathbf{p}} \quad (3.30)$$

which has the same structure as Equation (2.36), with the total force replaced here by the mean of the forces exerted by the two surfaces involved. For a diagonal element, $\alpha = \alpha'$, the operator generates standard adiabatic propagation upon the surface E_α . For an off-diagonal element, it generates propagation upon the average of two surfaces, providing the mechanism by which separating surfaces induce decoherence. The forces are given by

$$\mathbf{F}_{\alpha\beta}(\mathbf{x}) = -\frac{\partial E_\alpha(\mathbf{x})}{\partial \mathbf{x}} \delta_{\alpha\beta} + \hbar \omega_{\alpha\beta}(\mathbf{x}) \mathbf{d}_{\alpha\beta}(\mathbf{x}) \quad (3.31)$$

incorporating the non-adiabatic coupling vectors

$$\mathbf{d}_{\alpha\beta}(\mathbf{x}) = \langle \alpha; \mathbf{x} | \frac{\partial}{\partial \mathbf{x}} | \beta; \mathbf{x} \rangle \quad (3.32)$$

The transition superoperator takes the form

$$\hat{\mathcal{J}}_{\alpha\alpha',\beta\beta'} = -D_{\alpha\beta} \left(1 + \frac{\mathbf{F}_{\alpha\beta}}{2D_{\alpha\beta}} \cdot \frac{\partial}{\partial \mathbf{p}} \right) \delta_{\alpha'\beta'} - D_{\alpha'\beta'} \left(1 + \frac{\mathbf{F}_{\alpha'\beta'}}{2D_{\alpha'\beta'}} \cdot \frac{\partial}{\partial \mathbf{p}} \right) \delta_{\alpha\beta} \quad (3.33)$$

where

$$D_{\alpha\beta}(\mathbf{x}, \mathbf{p}) = (\mathbf{m}^{-1} \mathbf{p}) \cdot \mathbf{d}_{\alpha\beta}(\mathbf{x}) \quad (3.34)$$

Equation (3.34) states the essential feature of the non-adiabatic coupling in a quantum-classical description: transitions are driven not by the coupling vector alone but by its projection upon the nuclear velocity. Consequently, a system passing slowly through a region of strong coupling undergoes fewer transitions. The adiabatic basis is assumed real throughout, so that $\mathbf{d}_{\alpha\beta}$ is antisymmetric in its indices and complex conjugations are omitted.

3.2.3 Elimination of the Coherences and the Momentum-Jump Approximation

Equation (3.29) couples populations and coherences. A projection operator is applied to eliminate the electronic coherences, relying on the assumption that they decay rapidly relative to population dynamics. A coherence propagating upon the mean of two separating surfaces accumulates phase at a rate determined by their energy difference and is destroyed within a decoherence time τ_{decoh} , which is short compared with the interval over which populations are transferred. Defining the projector onto the diagonal,

$$\left(\hat{\mathcal{P}}_d\right)_{\alpha\alpha',\beta\beta'} = \delta_{\alpha\alpha'} \delta_{\alpha\beta} \delta_{\alpha'\beta'} \quad (3.35)$$

and its complement,

$$\left(\hat{\mathcal{Q}}_d\right)_{\alpha\alpha',\beta\beta'} = (1 - \delta_{\alpha\alpha'}) \delta_{\alpha\beta} \delta_{\alpha'\beta'} \quad (3.36)$$

the procedure of Subsection 2.1.6 leads to the generalized master equation for the populations $\rho_\alpha \equiv \rho_{\alpha\alpha}$, [64, 104]

$$\frac{\partial \rho_\alpha(t)}{\partial t} = -i\hat{\mathcal{L}}_\alpha \rho_\alpha(t) + \int_0^t d\tau \sum_\beta \hat{\mathcal{M}}_{\alpha\beta}(\tau) \rho_\beta(t-\tau) \quad (3.37)$$

The memory kernel is constructed from the transition superoperator propagated in the subspace orthogonal to the populations

$$\hat{\mathcal{M}}_{\alpha\beta}(\tau) = \sum_{\nu\nu'} \sum_{\mu\mu'} \hat{\mathcal{J}}_{\alpha\alpha,\nu\nu'} \left(e^{-i\hat{\mathcal{Q}}_d \hat{\mathcal{L}} \tau} \right)_{\nu\nu',\mu\mu'} \hat{\mathcal{J}}_{\mu\mu',\beta\beta} \quad (3.38)$$

Equation (3.37) is the analogue of the Nakajima-Zwanzig equation (2.43), maintaining the same structure of a reversible drift and a dissipative memory integral. This step constitutes a secular approximation in the sense of Subsection 2.2.4, decoupling populations from coherences, though applied here at a different stage of the formal construction.

The evaluation of Equation (3.38) is simplified by the momentum-jump approximation.[102, 103, 105] The derivative with respect to the momenta appearing in Equation (3.33) may be recast as a finite translation of the nuclear momentum along the direction of the non-adiabatic coupling vector. Defining mass-scaled momenta $\tilde{\mathbf{p}} = \mathbf{m}^{-1/2} \mathbf{p}$ and the corresponding unit vector $\hat{\mathbf{d}}_{\alpha\beta}$ along the coupling direction $\mathbf{m}^{-1/2} \mathbf{d}_{\alpha\beta}$, the transition operator $\hat{\mathcal{J}}_{\alpha\rightarrow\beta}$ evaluates the phase-space density at the same spatial configuration but at a shifted momentum, replacing the component along the coupling direction according to

$$\hat{\mathbf{d}}_{\alpha\beta} \cdot \tilde{\mathbf{p}} \mapsto \text{sgn}(\hat{\mathbf{d}}_{\alpha\beta} \cdot \tilde{\mathbf{p}}) \sqrt{(\hat{\mathbf{d}}_{\alpha\beta} \cdot \tilde{\mathbf{p}})^2 + 2\Delta E_{\alpha\beta}(\mathbf{x})} \quad (3.39)$$

with $\Delta E_{\alpha\beta} = E_\alpha - E_\beta$, while all orthogonal momentum components remain unaltered.

Equation (3.39) enforces energy conservation transition by transition. A transition between surfaces is accompanied by a change in the nuclear kinetic energy: a downward electronic transition increases the nuclear momentum, while an upward transition draws upon it. An upward transition is forbidden if the available kinetic energy along the coupling direction is insufficient (rendering the radicand in Equation (3.39) negative).

3.2.4 Elimination of the Classical Bath

The second projection eliminates the environment and connects the formalism to Section 2.1. The relevant projector is [104, 106, 107]

$$\hat{\mathcal{P}}_B = \rho_B(\mathbf{y}, \boldsymbol{\pi} | \mathbf{x}) \int d\mathbf{y} d\boldsymbol{\pi} \quad (3.40)$$

where $\rho_B(\mathbf{y}, \boldsymbol{\pi} | \mathbf{x})$ is the equilibrium distribution of the environment conditional upon the CS configuration, as defined in Equation (2.41). This executes the Zwanzig-Mori elimination of Subsection 2.1.6 upon an equation of motion carrying an electronic index. The projection requires the environment to be initially equilibrated conditional upon the initial configuration of the relevant coordinates,

$$\rho_\alpha(\mathbf{x}, \mathbf{p}, \mathbf{y}, \boldsymbol{\pi}, 0) = \rho_\alpha(\mathbf{x}, \mathbf{p}, 0) \rho_B(\mathbf{y}, \boldsymbol{\pi} | \mathbf{x}) \quad (3.41)$$

which annihilates the inhomogeneous initial-condition term.

Under this projection, the drift term of Equation (3.37) acquires a memory integral. Under the Markovian approximation, this becomes a Fokker-Planck operator acting upon the classical phase space of a single surface [106]

$$\hat{\Gamma}_\alpha = -k_B T \begin{bmatrix} \partial/\partial \mathbf{x} \\ \partial/\partial \mathbf{p} \end{bmatrix}^T \begin{bmatrix} 0 & -1 \\ 1 & \boldsymbol{\xi} \end{bmatrix} \rho_\alpha^{\text{eq}} \begin{bmatrix} \partial/\partial \mathbf{x} \\ \partial/\partial \mathbf{p} \end{bmatrix} (\rho_\alpha^{\text{eq}})^{-1} \quad (3.42)$$

where ρ_α^{eq} is the equilibrium distribution upon the surface α and $\boldsymbol{\xi}$ is the friction tensor. Expanding Equation (3.42) yields

$$\begin{aligned} -\hat{\Gamma}_\alpha \rho_\alpha = & -(\mathbf{m}^{-1} \mathbf{p}) \cdot \frac{\partial \rho_\alpha}{\partial \mathbf{x}} + \frac{\partial \mathcal{A}_\alpha(\mathbf{x})}{\partial \mathbf{x}} \cdot \frac{\partial \rho_\alpha}{\partial \mathbf{p}} \\ & + \frac{\partial}{\partial \mathbf{p}} \cdot \left[\boldsymbol{\xi}(\mathbf{x}) \cdot \left(k_B T \frac{\partial}{\partial \mathbf{p}} + \mathbf{m}^{-1} \mathbf{p} \right) \rho_\alpha \right] \end{aligned} \quad (3.43)$$

This is the Markovian limit of the generalized Klein-Kramers equation (2.44), and hence the multidimensional analogue to Equation (2.23). Thus, the operator governing nuclear motion in the quantum-classical framework is identical to the operator derived in Chapter 2, applied independently to each adiabatic surface.

The surface appearing in the drift of Equation (3.43) requires comment, as the literature often defines it as the bare adiabatic energy E_α . Equation (2.46) established that environmental elimination produces a free energy, not a potential energy. The conditional average over the CB implicit in ρ_α^{eq} supplies this contribution, making the relevant surface the PMF upon state α : $\mathcal{A}_\alpha(\mathbf{x}) = E_\alpha(\mathbf{x}) - \beta^{-1} \ln Z_\alpha(\mathbf{x})$. This coincides with E_α only where the environmental contribution is independent of configuration.

The memory term of Equation (3.37) is treated by a second, independent Markovian approximation. Within the momentum-jump approximation introduced above, the kernel factorizes as $\hat{\mathcal{M}}_{\alpha\beta}(\tau) = \mathcal{M}_{\alpha\beta}(\tau) \hat{\mathcal{J}}_{\alpha \rightarrow \beta}$, the scalar memory function $\mathcal{M}_{\alpha\beta}$ carrying the time dependence and the jump operator the action upon the momenta. Averaged over the environment, the memory kernel decays on the timescale τ_{decoh} .

Provided the populations evolve slowly by comparison, the kernel is replaced by a delta function weighted by its time integral

$$m_{\alpha\beta}(\mathbf{x}) = \int_0^\infty d\tau \langle \mathcal{M}_{\alpha\beta}(\tau) \rangle_{\mathbf{x}} \quad (3.44)$$

the average being taken over the conditional distribution (3.40). Collecting Equations (3.42), (3.39) and (3.44) gives the final QSLE[97]

$$\begin{aligned} \frac{\partial \rho_\alpha(\mathbf{x}, \mathbf{p}, t)}{\partial t} = & -\hat{\Gamma}_\alpha \rho_\alpha(\mathbf{x}, \mathbf{p}, t) \\ & + \sum_\beta m_{\alpha\beta}(\mathbf{x}) \hat{\Gamma}_{\alpha \rightarrow \beta} \rho_\beta(\mathbf{x}, \mathbf{p}, t) - m_{\alpha\alpha}(\mathbf{x}) \rho_\alpha(\mathbf{x}, \mathbf{p}, t) \end{aligned} \quad (3.45)$$

The first term propagates the phase-space density stochastically upon the surface α , while the remaining terms transfer population between surfaces at configuration-dependent rates.

Equation (3.45) resembles a reaction-diffusion equation, with two key differences. First, the stochastic motion is inertial, rather than diffusive; momentum remains a dynamical variable because it mediates the energy exchange with the electronic subsystem at each transition. Second, the transitions are not vertical in phase space. The shift mandated by Equation (3.39) means population arriving on a lower surface carries excess momentum. The operator $\hat{\Gamma}_\alpha$ must subsequently dissipate this momentum at a rate governed by the friction tensor.

Evaluating the rates (3.44) demands an integral over the environmental phase space at each point in the classical phase space, which becomes prohibitive for high-dimensional relevant coordinates and requires further approximations in practice.[98] Additionally, the two independent Markovian approximations may fail independently. Neither is expected to hold under inertial conditions where friction is small and the memory kernel does not rapidly relax. The framework is therefore restricted to condensed-phase environments.

3.2.5 The Bath Descriptor of the Quantum-Classical Description

It remains to identify what survives of the environment in Equation (3.45), since it is this quantity that must be placed in correspondence with the spectral density of Subsection 3.1.2.

Three contributions of the CB survive the elimination process: it renormalizes each adiabatic surface into a PMF; it thermally weights the rates (3.44) through the conditional distribution over which they are averaged; and it supplies the friction tensor ξ in Equation (3.43). The first two contributions are static equilibrium averages. Only the friction tensor carries dynamical information regarding the environment. This friction is the quantity defined in Equation (2.49): the time integral of the FACF evaluated at a specified CS configuration, representing the zero-frequency value of the transform of the memory kernel.

The disparity with the quantum description is now apparent. The Redfield construction samples the environmental spectrum at every Bohr frequency of the system Hamiltonian, weighting upward and downward transitions asymmetrically through Equation (2.68). The QSLE samples the same spectrum exclusively at zero

frequency, and the asymmetry disappears with it. The environment enters the Redfield formulation as a frequency-dependent function, whereas it enters the [QSLE](#) formulation as a scalar value. The correspondence therefore requires a model of the kind constructed in Section [3.1](#), where both the function and the scalar are determined by a shared parameter set.

Further asymmetries influence the comparisons in Section [3.4](#). The nuclear coordinate carries no quantum properties within the [QSLE](#) framework: it possesses no zero-point energy, no discrete level structure, and no tunnelling. Barriers are crossed only by thermal activation. Additionally, the detailed balance guaranteed by Equation [\(2.87\)](#) in the fully quantum description is distributed across two mechanisms in the [QSLE](#): the Fokker-Planck operator maintains the canonical distribution upon each surface via the classical [FDT](#), while the detailed balance between surfaces is enforced by the energy conservation rules built into Equation [\(3.39\)](#).

The theoretical frameworks for the benchmark are now established. The following section specifies the model system and the numerical implementations required to evaluate these descriptions.

3.3 THE MODEL SYSTEM AND ITS TWO IMPLEMENTATIONS

The comparison undertaken in this chapter requires a physical system governed by a small number of electronic states and a single nuclear coordinate, so that the quantum treatment remains tractable. The coordinate must be coupled to a condensed-phase environment to define a macroscopic friction, and the dynamics must be non-adiabatic so that neither description may be replaced by a simpler one. Photoisomerization about a double bond satisfies these criteria.

This photochemical transformation is the primary photochemical event of vision, through retinal isomerization in rhodopsin,[108, 109] the photocycles of phytochromes, and the operation of synthetic photoswitches such as azobenzene.[17, 110] The defining observable is the quantum yield: the fraction of the excited population that reaches the product configuration rather than returning to the reactant, and the timescale upon which it does so. The theoretical challenge arises because the BO approximation fails where the outcome is decided. Torsion carries the system toward a conical intersection where adiabatic states mix, transferring population within a single vibrational period.[4, 111]

The environment is not a spectator. The large-amplitude torsion displaces surrounding solvent, generating macroscopic friction. The energy dissipation timescale is comparable to the passage timescale itself. The branching that determines the quantum yield occurs in a regime where the coordinate is neither freely inertial nor fully equilibrated. A photoswitch in a dissipative medium thus provides a physical regime where the differences between the bath descriptors examined in Section 3.1 become observable.

3.3.1 The Model System

The model system adopted is the minimal representation of ultrafast *cis-trans* photoisomerization introduced by Hahn and Stock, parameterized to reproduce the energetics of the retinal chromophore.[112, 113] It retains two electronic states and one nuclear coordinate, the dihedral angle φ about the isomerizing bond, treated as periodic.

DIABATIC REPRESENTATION. The model is specified in the diabatic electronic representation, in which the system Hamiltonian reads

$$\hat{H}_S = \sum_{n=0,1} |\psi_n\rangle \langle \psi_n| \otimes [\hat{T} + V_{nn}(\varphi)] + \lambda (|\psi_0\rangle \langle \psi_1| + |\psi_1\rangle \langle \psi_0|) \otimes \hat{\mathbb{I}} \quad (3.46)$$

where $|\psi_0\rangle$ and $|\psi_1\rangle$ are the diabatic electronic states, and the kinetic energy operator of the torsion is

$$\hat{T} = -\frac{\hbar^2}{2M_\varphi} \frac{\partial^2}{\partial \varphi^2} \quad (3.47)$$

with M_φ the moment of inertia conjugate to φ . The diabatic potentials are

$$V_{00}(\varphi) = \frac{1}{2}W_0 (1 + \cos \varphi) \quad (3.48)$$

$$V_{11}(\varphi) = E_1 - \frac{1}{2}W_1 (1 + \cos \varphi) \quad (3.49)$$

The diabatic coupling λ is independent of φ . The parameter values are $W_0 = 3.6$ eV, $W_1 = 1.09$ eV, $E_1 = 2.48$ eV, and $\lambda = 0.065$ eV.[112]

Equation (3.48) is the potential of a hindered rotor with a minimum at $\varphi = \pi$ (the *trans* configuration), where the barrier W_0 represents the π bond resisting torsion. Electronic excitation removes a portion of that bonding character, inverting the excited diabatic potential (3.49) so its minimum lies at $\varphi = 0$ (the *cis* configuration). The two curves cross, and λ converts this intersection into an avoided crossing, forming a one-dimensional section of a molecular conical intersection.

ADIABATIC REPRESENTATION. The dynamics are reported in the adiabatic representation to maintain consistency with the quantum-classical framework of Section 3.2. Diagonalizing the potential matrix at each value of φ gives the adiabatic surfaces

$$V_{0,1}(\varphi) = \frac{1}{2} (V_{00} + V_{11}) \mp \frac{1}{2} \sqrt{(V_{00} - V_{11})^2 + 4\lambda^2} \quad (3.50)$$

where V_0 denotes the lower surface and V_1 the upper. The corresponding electronic states $|0; \varphi\rangle$ and $|1; \varphi\rangle$ follow the parametric convention of Equation (3.28). Because the electronic space is two-dimensional and λ is real, the transformation between the two representations is an orthogonal rotation through a single angle

$$\tan 2\theta(\varphi) = \frac{2\lambda}{V_{00}(\varphi) - V_{11}(\varphi)} \quad (3.51)$$

The non-adiabatic coupling of Equation (3.32) is its derivative

$$d_{01}(\varphi) = \langle 0; \varphi | \frac{\partial}{\partial \varphi} | 1; \varphi \rangle = \frac{\partial \theta}{\partial \varphi} \quad (3.52)$$

Equation (3.52) holds exactly for a two-state model. It is required only by the quantum-classical calculation, which takes it as a tabulated input to the transition rates; the quantum calculation never evaluates it, the non-adiabatic coupling being carried implicitly and exactly by the vibronic eigenstates of Equation (3.46), which diagonalize the two surfaces together.

TOPOGRAPHY. The surfaces are illustrated in Figure 3.2. The avoided crossing lies at $\varphi \simeq \pm 87^\circ$, where the gap reaches its minimum value ($2\lambda = 0.13$ eV) and the magnitude of the coupling (3.52) peaks.

The lower surface V_0 possesses a global minimum at the *trans* configuration ($\varphi = \pi$) and a local minimum at the *cis* configuration ($\varphi = 0$), lying 1.39 eV above it. The barrier separating them, at the avoided crossing, stands 0.45 eV above the *cis* well. At 300 K the *cis* well lies 54 $k_B T$ above the *trans* minimum and is retained by a barrier of 17 $k_B T$, rendering the photoproduct metastable and thermal ground-state interconversion slow on the timescales considered here. The upper surface V_1 features equivalent minima situated at the avoided crossings. Excited state (ES) population is thus driven toward the region of strongest non-adiabatic coupling, which is the mechanism responsible for the efficiency of the process.

These topographic features impact the correspondence defined in Section 3.1. The coordinate is periodic, and every corresponding function reflects this symmetry. Furthermore, branching occurs after a descent of 0.51 eV from the point of

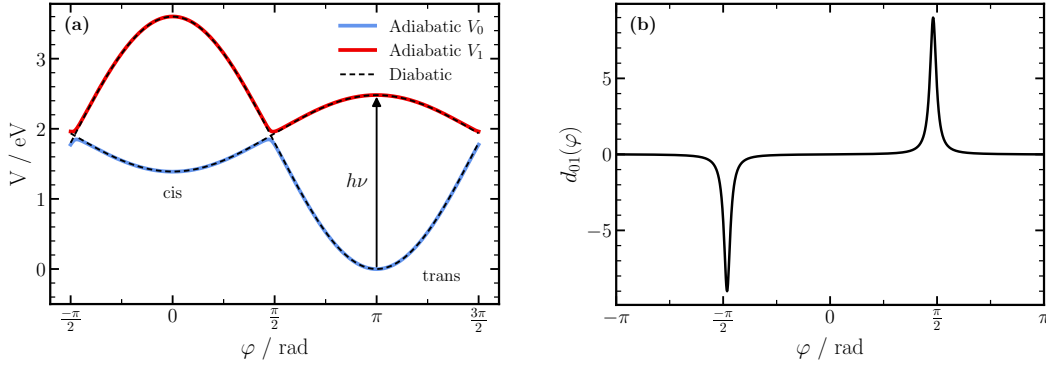


Figure 3.2: (a) Adiabatic surfaces V_0 and V_1 of Equation (3.50) (solid) and diabatic potentials V_{00} and V_{11} of Equations (3.48) and (3.49) (dashed), as functions of the dihedral angle. The *trans* minimum of V_0 at $\varphi = \pi$ and the *cis* minimum at $\varphi = 0$ are indicated, together with the vertical excitation defining the initial condition. (b) The non-adiabatic coupling $d_{01}(\varphi)$ of Equation (3.52), whose magnitude peaks at the avoided crossings near $\pm 87^\circ$.

preparation, meaning population arriving on the lower surface carries an excess kinetic energy. Whether this excess dissipates before or after the system commits to a specific well depends on the friction. Section 3.4 evaluates how the two descriptions handle this dissipation competition.

3.3.2 The Fully Quantum Implementation

The quantum treatment propagates the Redfield equation of Subsection 2.2.4 for the vibronic density matrix, quantizing the torsional coordinate alongside the electronic DOF. This implementation was developed as part of the present work; computational details are collected in Appendix B, and what follows specifies the model.

THE DISSIPATIVE HAMILTONIAN. The total Hamiltonian is partitioned following Equation (2.52), with $\hat{H}_S$ given by Equation (3.46). The environment is the harmonic bath of Equation (3.2), and the coupling retains the separable form of Equation (2.59) using a single operator pair

$$\hat{H}_{SB} = \hat{Q} \hat{B} \quad (3.53)$$

The environmental operator $\hat{B}$ is that of Equation (3.5) and is linear in the bath coordinates. However, the system operator $\hat{Q}$ is not the torsional coordinate itself. The choice of $\hat{Q}$ is the primary modelling decision of this implementation. Equation (3.53) departs from the CL Hamiltonian (3.6), and it omits the counterterm required to equate the bare potentials with the free-energy surfaces of the reduced dynamics.

BATH DESCRIPTORS. The environment enters the dynamics solely through the spectral density of Equation (3.12), taken in the Drude-Lorentz form (3.24). Its parameters are the coupling strength η , defined by Equation (3.22), and the cut-off

frequency ω_c , which fixes the environmental correlation time $\tau_B = \omega_c^{-1}$. Through Equation (3.20), this choice corresponds to the exponentially decaying friction kernel (3.25), and it is the point at which the quantum calculation is placed in correspondence with its classical counterpart.

The Redfield tensor requires the one-sided transform of the bath correlation function evaluated at the Bohr frequencies of $\hat{H}_S$. Its real part equals one half of the power spectrum (3.14), and its imaginary part is the dispersion function

$$S(\omega) = \frac{1}{2\pi} \mathcal{P} \int_{-\infty}^{\infty} d\omega' \frac{\tilde{C}(\omega')}{\omega - \omega'} \quad (3.54)$$

so that Equation (2.78) becomes

$$\Gamma(\omega) = \frac{1}{2} \tilde{C}(\omega) + i S(\omega) \quad (3.55)$$

While Subsection 2.2.4 observed that the imaginary part is conventionally absorbed into $\hat{H}_S$ as a Lamb-type renormalization, it is retained here to shift the oscillation frequencies during the propagation of the coherences. The populations remain governed by $\tilde{C}$ alone.

THE COUPLING OPERATOR. The environment of a solvated chromophore does not couple to the torsion in isolation, but to the electronic charge distribution, which shifts character along the reaction coordinate. Following Hahn and Stock, $\hat{Q}$ is constructed as the product of a diabatic electronic projector $\hat{P}_n = |\psi_n\rangle \langle \psi_n|$ and a periodic function of φ .^[113] The two elementary components are

$$\hat{Q}_I = \hat{P}_1 (1 + \cos \varphi) \quad (3.56)$$

$$\hat{Q}_{II} = \hat{P}_0 (1 - \cos \varphi) \quad (3.57)$$

each maximizing at the minimum of the diabatic surface upon which its projector acts, and vanishing at the opposite configuration. Their sum,

$$\hat{Q}_0 = \hat{Q}_I + \hat{Q}_{II} = \hat{1} + (\hat{P}_1 - \hat{P}_0) \cos \varphi \quad (3.58)$$

is the reference choice. It reduces to $2\hat{P}_0$ at $\varphi = \pi$ and $2\hat{P}_1$ at $\varphi = 0$, coupling the environment in each well to whichever diabatic state is locally lowest in energy; it reduces to the identity at the avoided crossings. Two alternative operators defined in the same work were also examined,^[113]

$$\hat{Q}_{III} = \hat{P}_0 (1 - \cos \varphi) + \hat{P}_1 \cos \varphi = \hat{P}_0 + (\hat{P}_1 - \hat{P}_0) \cos \varphi \quad (3.59)$$

$$\hat{Q}_{IV} = \hat{P}_1 (1 + \cos \varphi) - \hat{P}_0 \cos \varphi = \hat{P}_1 + (\hat{P}_1 - \hat{P}_0) \cos \varphi \quad (3.60)$$

The rightmost forms of Equations (3.58), (3.59) and (3.60) clarify their relationship: they share the same φ -dependent operator $(\hat{P}_1 - \hat{P}_0) \cos \varphi$ and differ only by a static electronic operator, $\hat{1}$, $\hat{P}_0$ and $\hat{P}_1$, respectively. Only the first operator is proportional to the identity and therefore confined to the diagonal of the vibronic eigenbasis. The projectors $\hat{P}_0$ and $\hat{P}_1$ mix the diabatic characters of the eigenstates, contributing to both population transfer and dephasing. Consequently, the three operators produce different dynamics despite their common dihedral dependence.

None of the operators (3.56) to (3.60) is linear in φ . According to Subsection 3.1.4, none satisfies the CL representation required for the correspondence in Equation (3.20). Two further choices that remove the electronic projectors

$$\hat{Q}_{\sin} = \hat{1}_2 \otimes \sin \varphi \quad \text{and} \quad \hat{Q}_{\varphi} = \hat{1}_2 \otimes \varphi \quad (3.61)$$

were examined in preliminary tests. The operator $\hat{Q}_{\varphi}$ is the coupling the CL model requires, but the angle is not single-valued upon the circle: $\hat{Q}_{\varphi}$ is defined only on the branch $-\pi/2 \leq \varphi < 3\pi/2$ and is discontinuous at its endpoints, so it is retained as a formal reference rather than as a physically admissible coupling. The operator $\hat{Q}_{\sin}$ is periodic and reduces to $\hat{Q}_{\varphi}$ in the neighbourhood of $\varphi = 0$, but it is not linear in φ either.

BASIS AND VIBRONIC EIGENSTATES. The torsional coordinate is expanded in the eigenstates of the free rotor,

$$\langle \varphi | k \rangle = \frac{e^{ik\varphi}}{\sqrt{2\pi}} \quad k \in \mathbb{Z} \quad (3.62)$$

truncated symmetrically at a finite $|k|$. This basis is dictated by the periodicity of the coordinate: it identically satisfies the boundary conditions, diagonalizes the matrix elements of $\hat{T}$, and ensures the cosine potentials and coupling operator only connect adjacent k values. Thus, $\hat{H}_S$ and $\hat{Q}$ form tridiagonal matrices in the torsional index, whose matrix elements are available in closed form. Diagonalizing $\hat{H}_S$ within the product of this basis with the two-dimensional electronic space yields the vibronic eigenstates $|a\rangle$ and energies E_a . These define the Bohr frequencies ω_{ab} at which, by Equation (3.18), the environmental spectrum is sampled and the matrix elements $Q_{ab} = \langle a | \hat{Q} | b \rangle$ that weight the coupling.

These states are the eigenstates of the coupled two-surface Hamiltonian. They belong to neither electronic surface nor configuration individually, distinguishing them from the adiabatic electronic states $|\alpha; \varphi\rangle$ of Equation (3.28), which are defined at fixed φ and carry no torsional quantization.

EQUATIONS OF MOTION. The full Redfield tensor of Equation (2.80) generates a number of elements scaling as the fourth power of the vibronic basis dimension. For a dense torsional basis, this exceeds available memory limits. The secular approximation of Subsection 2.2.4 is therefore invoked, decoupling the tensor into population and coherence blocks. The populations obey the Pauli master equation (2.83) governed by the rates of Equation (3.18)

$$k_{a \rightarrow b} = \tilde{C}(\omega_{ab}) |Q_{ab}|^2 / \hbar^2 \quad (3.63)$$

These time-independent rates permit propagation via direct matrix exponentiation. The coherences decay independently at the rates defined in Equation (2.85) (where sums over intermediate states include the state itself) and acquire the frequency shift defined in Equation (3.55).

This approximation is adopted for computational feasibility, not because the separation condition (2.82) is satisfied. The rates (3.63) depend upon the environment via $\tilde{C}(\omega_{ab})$ and are proportional to η ; the terminal thermal equilibrium is fixed by

detailed balance, Equation (2.87), independent of η . Within the secular treatment, the coupling strength scales the rate of the process but cannot alter its equilibrium outcome. Conversely, the matrix elements Q_{ab} determine which transitions are permitted to occur. The interplay between these roles is evaluated in Section 3.4.

INITIAL CONDITION. The system is prepared by vertical excitation of the lowest vibronic eigenstate,

$$|\Psi(0)\rangle = (\hat{\sigma}_x \otimes \hat{\mathbb{I}}) |\Psi_0\rangle \quad \hat{\rho}_S(0) = |\Psi(0)\rangle \langle \Psi(0)| \quad (3.64)$$

where $|\Psi_0\rangle$ is the ground state (GS) of $\hat{H}_S$ and $\hat{\sigma}_x$ exchanges the electronic labels while preserving the torsional wavefunction. Because $|\Psi_0\rangle$ is localized in the *trans* well, where the diabatic gap is 2.48 eV, Equation (3.64) is an effective Franck-Condon (FC) transition from V_0 to V_1 at $\varphi = \pi$, as indicated in Figure 3.2. The preparation places the entire population upon the upper surface in a state that is pure in the nuclear coordinate. Subsection 3.3.4 compares this initial state with the thermal distribution utilized in the quantum-classical calculation.

OBSERVABLES. The configuration is resolved using the spatial projectors

$$\hat{\Pi}^{\text{trans}} = \Theta(|\varphi| - \pi/2) \quad \hat{\Pi}^{\text{cis}} = \hat{\mathbb{I}} - \hat{\Pi}^{\text{trans}} \quad (3.65)$$

which map the neighbourhood of $\varphi = \pi$ to the *trans* region and $\varphi = 0$ to the *cis* region, with the dividing surfaces located at $\pm\pi/2$. The electronic state is resolved by the adiabatic projectors $\hat{\Pi}_\alpha = |\alpha; \varphi\rangle \langle \alpha; \varphi|$, constructed from the rotation (3.51) and therefore dependent upon φ . Evaluating the combined observable

$$P_\alpha^x(t) = \text{Tr} [\hat{\rho}_S(t) \hat{\Pi}_\alpha \hat{\Pi}^x] \quad \alpha = 0, 1 \quad x = \text{trans, cis} \quad (3.66)$$

yields the joint probability of occupying the adiabatic surface α in configuration x . These quantities are directly comparable with the quantum-classical results. Under this labelling, the initial state is $P_1^{\text{trans}} = 1$, and the photoproduct corresponds to P_0^{cis} (the population of the *cis* well on the lower surface). The quantum yield is identified with P_0^{cis} evaluated once the upper surface has been depleted but prior to the onset of thermal equilibration between the two wells of V_0 , a temporal window sustained by the 17 $k_B T$ barrier established in Subsection 3.3.1.

Beyond integrated populations, projecting the density matrix onto the coordinate grid gives the spatially resolved density $P_\alpha(\varphi, t) = \langle \varphi | \hat{\Pi}_\alpha \hat{\rho}_S(t) \hat{\Pi}_\alpha | \varphi \rangle$. This continuous spatial distribution is the primary metric for comparison against the phase-space density propagated by the quantum-classical method in Section 3.4.

3.3.3 The Quantum-Classical Implementation

The quantum-classical calculations were performed with QSLE-v1.0, a published implementation of the framework described in Section 3.2.[99] One point of departure from that presentation should be noted. Section 3.2 develops the QSLE for a generic set of classical nuclear coordinates, whereas the implementation is formulated in natural internal coordinates of the Z-matrix type, that is bond lengths,

bond angles and dihedral angles.[97, 106] The two are related by a change of variables, and the consequence for what follows is the appearance of the metric factors of Equation (3.69); nothing in the structure of Equation (3.45) is altered. The choice is natural for the present problem, the relevant coordinate being a dihedral angle.

The program propagates one classical nuclear coordinate alongside two electronic surfaces. Because the coordinate is treated as a periodic torsional angle, the model outlined in Subsection 3.3.1 integrates without modification. Unlike the Redfield implementation, the program was not developed as part of the present work. The underlying numerical algorithms and their validation are documented in the software’s primary reference, and the specific numeric parameters employed here are summarized in Appendix B; what follows is restricted to the physical elements required for the comparative benchmark.

Specializing Equation (3.45) to two surfaces and to the phase-space point $X = (\varphi, p_\varphi)$ gives

$$\frac{\partial \rho_0(X, t)}{\partial t} = -\hat{\Gamma}_0 \rho_0 + m_{01} \hat{J}_{0 \rightarrow 1} \rho_1 - m_{00} \rho_0 \quad (3.67)$$

$$\frac{\partial \rho_1(X, t)}{\partial t} = -\hat{\Gamma}_1 \rho_1 + m_{10} \hat{J}_{1 \rightarrow 0} \rho_0 - m_{11} \rho_1 \quad (3.68)$$

where ρ_0 and ρ_1 are the quantum-classical probability densities upon the adiabatic surfaces V_0 and V_1 of Equation (3.50). The two equations are coupled by the transition rates and momentum-jump operators.

STOCHASTIC PROPAGATION. When written out for a single spatial coordinate, the Fokker-Planck operator of Equation (3.42) reads

$$\hat{\Gamma}_\alpha = \frac{p_\varphi}{g_\varphi} \frac{\partial}{\partial \varphi} - \frac{\partial V_\alpha}{\partial \varphi} \frac{\partial}{\partial p_\varphi} - \frac{\xi_\varphi}{g_\varphi} \frac{\partial}{\partial p_\varphi} p_\varphi - k_B T \xi_\varphi \frac{\partial^2}{\partial p_\varphi^2} \quad (3.69)$$

where ξ_φ is the friction coefficient and g_φ is the conformational element of the covariant metric tensor generated by the transformation from Cartesian to curvilinear coordinates, evaluated for the dihedral angle.[106] For a torsion it plays the part of the moment of inertia, and it replaces the diagonal mass matrix $\mathbf{m}$ of Equation (3.43), which presumes Cartesian coordinates. The first two terms of Equation (3.42) generate deterministic classical propagation upon surface V_α . The third term exerts drag, while the fourth drives momentum diffusion. Equation (3.69) is the Klein-Kramers equation (2.23) in curvilinear form, consolidating the whole influence of the environment upon the nuclear motion into the scalar coefficient ξ_φ .

THE FRICTION COEFFICIENT. The implementation offers two routes to ξ_φ . It can be estimated with the DiTe2 library,[114] which is a software package for the calculation of the generalized friction tensor in flexible molecules. It adopts a hydrodynamic model of the solute, in which the molecule is represented as a set of beads subject to Stokes friction with hydrodynamic coupling between pairs, the generalized friction tensor being obtained by projecting the bead friction onto the generalized velocities and the element conjugate to the torsion extracted; alternatively it may be supplied as an external parameter. The second route is adopted

here, allowing the friction to serve as the independent variable for the benchmark in Section 3.4. The hydrodynamic value calculated for a four-bead representation of the model provides a physical reference against which the explored parameter range is evaluated.

Although ξ_φ is in general a function of the dihedral angle, QSLE-v1.0 holds the friction coefficient constant across the entire coordinate. The software cannot represent a configuration-dependent friction, effectively enforcing condition (ii) of Subsection 3.1.4 regardless of the underlying physical validity.

SURFACE HOPPING. The operator $\hat{J}_{\alpha \rightarrow \beta}$ evaluates the density at the same angle but at the shifted momentum

$$\bar{p}_\varphi^{\alpha\beta} = \text{sgn}(p_\varphi) \sqrt{p_\varphi^2 + 2 g_\varphi \Delta V_{\alpha\beta}(\varphi)} \quad (3.70)$$

with $\Delta V_{\alpha\beta} = V_\alpha - V_\beta$. This corresponds to Equation (3.39) specialized to one coordinate. A downward transition converts the electronic energy gap into torsional kinetic energy; an upward transition draws upon that energy and is frustrated whenever the radicand is negative. Population descending to V_0 near the avoided crossing arrives with the substantial excess momentum discussed in Subsection 3.3.1. Section 3.4 probes the dynamical competition between this momentum excess and the drag enforced by Equation (3.69).

The transition rates $m_{\alpha\beta}$ of Equation (3.44) are evaluated internally from the non-adiabatic coupling $d_{01}(\varphi)$ of Equation (3.52) and from a decoherence time τ . [98, 99] These rates are not treated as adjustable parameters in the present work, and no attempt was made to reconcile them with the quantum transition rates. The two formalisms drive transitions via distinct mechanisms: Equation (3.63) transfers population when the environment absorbs or supplies an energy quantum, while Equation (3.70) transfers population because nuclear momentum carries the system through a region of strong electronic coupling, independently of environmental action.

The parameterization of τ warrants attention. If no external value is supplied, the program defaults to $\tau = g_\varphi / \xi_\varphi$, evaluated where the non-adiabatic coupling peaks, operating under the assumption that coherence vanishes as torsional momentum loses correlation. The friction therefore enters the quantum-classical description twice: directly via the propagation drag in Equation (3.69), and indirectly via the surface-hopping rates. The quantum description avoids this parameter coupling; its rates (3.63) are linearly proportional to the spectral density, with dephasing rates following analytically.

INITIAL CONDITION AND OBSERVABLES. The initial state is a vertical excitation of the thermally equilibrated lower surface,

$$\rho_0(X, 0) = 0 \quad \rho_1(X, 0) \propto \exp[-H_0(X)/k_B T] \quad (3.71)$$

with $H_0 = p_\varphi^2/2g_\varphi + V_0(\varphi)$. Because the *cis* well lies far above the *trans* minimum on the scale of $k_B T$, the distribution (3.71) remains constrained to the *trans* region. This places the entire initial population upon V_1 near $\varphi = \pi$, mirroring the quantum preparation.

Configurational populations follow by integration over the phase space,

$$P_{\alpha}^x(t) = \int_x d\varphi \int dp_{\varphi} \rho_{\alpha}(\varphi, p_{\varphi}, t) \quad (3.72)$$

where the spatial integration spans the region x delimited by $\pm\pi/2$, matching the boundaries defined by the quantum projectors (3.65). Equations (3.66) and (3.72) output identical physical quantities, tracking the photoisomerization yield through P_0^{cis} . Marginalizing ρ_{α} across the momentum axis generates a spatial density that can be visually and quantitatively compared against the quantum $P_{\alpha}(\varphi, t)$ frame by frame. Furthermore, the unmarginalized $\rho_{\alpha}(X, t)$ enables direct visualization of the phase-space momentum distribution, an observable inaccessible within the standard quantum density matrix formalism.

3.3.4 Commensurability of the Two Calculations

Because the two implementations solve different equations representing different physical frameworks, establishing a baseline comparison requires classifying which ingredients are forced into agreement, which the correspondence of Section 3.1 would determine, and which remain fundamentally disconnected. Table 3.1 lists this classification, and the paragraphs below detail the implications.

SURFACES AND OBSERVABLES. Both calculations propagate upon the adiabatic surfaces (3.50) mapped from a shared set of diabatic parameters. The *trans* and *cis* regions are delimited by $\pm\pi/2$ in both formalisms. Consequently, Equations (3.66) and (3.72) extract equivalent physical probabilities, requiring no subsequent transformations to align the observables.

THE INERTIA. The quantum implementation parameterizes a constant M_{φ} obtained by averaging the inertial parameter $g_{\varphi}(\varphi)$ of the quantum-classical model over the torsional coordinate. Introducing a configuration-dependent inertia into the quantum solver would render the kinetic energy operator non-diagonal in the free-rotor basis (3.62), removing the closed-form matrix elements upon which the construction depends. Since QSLE-v1.0 enforces constant friction, holding the inertia constant across both models ensures comparability.

The direction of this adjustment carries physical implications. The inertia parameter was taken from the quantum-classical model and imposed upon the quantum solver, resulting in a substantially larger value than the original Hahn-Stock parameterization. The isolated effect of this shift on the quantum dynamics is evaluated in Subsection 3.4.2.

THE BATH DESCRIPTORS. The two descriptions do not align with the one-to-one mapping permitted by Section 3.1. While Equation (3.20) equates the scalar friction with the slope of the spectral density at the origin ($\xi_{\varphi} = \eta$), this identity rests upon the assumption of bilinear coupling. As established in Subsection 3.1.4, none of the coupling operators (3.56) through (3.60) satisfies this bilinear condition.

This asymmetry manifests directly in the equations of motion. The quantum rates (3.63) separate the environmental influence into two components: the spec-

Ingredient	Fully quantum	Quantum-classical
<i>Required to agree and made to agree</i>		
Diabatic parameters	W_0, W_1, E_1, λ	identical
Adiabatic surfaces	Eq. (3.50)	identical
Non-adiabatic coupling	implicit in $ \alpha\rangle$	tabulated, Eq. (3.52)
Temperature	300 K	300 K
Inertia	constant M_φ	g_φ , held constant
Configurational partition	Eq. (3.65)	same regions
Observables	Eq. (3.66)	Eq. (3.72)
Initial condition	Eq. (3.64)	Eq. (3.71)
<i>Bath descriptors, related by Section 3.1</i>		
Spectral content	$J(\omega)$, Eq. (3.24)	ξ_φ , Eq. (3.69)
Coupling strength	η	ξ_φ
Coupling operator	$\hat{Q}$, Eqs. (3.56)–(3.60)	no counterpart
<i>Without counterpart</i>		
Cut-off frequency	ω_c	Markovian by construction
Counterterm	omitted	not defined
Decoherence time	from $\tilde{C}$ and $\hat{Q}$	$\tau = g_\varphi / \xi_\varphi$
Transition mechanism	bath-induced, Eq. (3.63)	inertial, Eq. (3.70)

Table 3.1: Ingredients of the two calculations, classified by whether commensurability requires them to agree, whether the correspondence of Section 3.1 relates them, or whether one description possesses a quantity lacking a direct analogue.

tral density $\tilde{C}(\omega_{ab})$ scales the coupling, while the matrix element $|Q_{ab}|^2$ determines which specific transitions occur. The Fokker-Planck operator (3.69) merges these influences into a single scalar variable, ξ_φ , which scales both drag and momentum diffusion. The QSLE framework cannot accommodate an analogue for $\hat{Q}$ because the bilinear coupling assumption is built into the Klein-Kramers structure; the Fokker-Planck operator is inherently a $\hat{Q} = \varphi$ theory. Because a single parameter on one side attempts to map to a separated product pair on the other, the theoretical map admits no unique inverse.

Accordingly η and ξ_φ were not bound to each other in the calculations reported below. Each parameter was varied independently across its respective framework, treating any relationship between them as a result rather than a constraint.

QUANTITIES WITHOUT A COUNTERPART. The cut-off frequency is the most prominent disparity. The quantum-classical description is Markovian by construction. Its friction is a fixed scalar, meaning the finite ω_c employed by the quantum calculation lacks a counterpart in Equation (3.69). The formalisms align physically only in the limit $\omega_c \rightarrow \infty$, where Equation (3.24) collapses to the Ohmic form (3.23). The specific cut-off value adopted for the quantum solver yields a correlation time that is short relative to the full torsional period, but not negligible relative to the swift passage through the coupling region. The residual memory

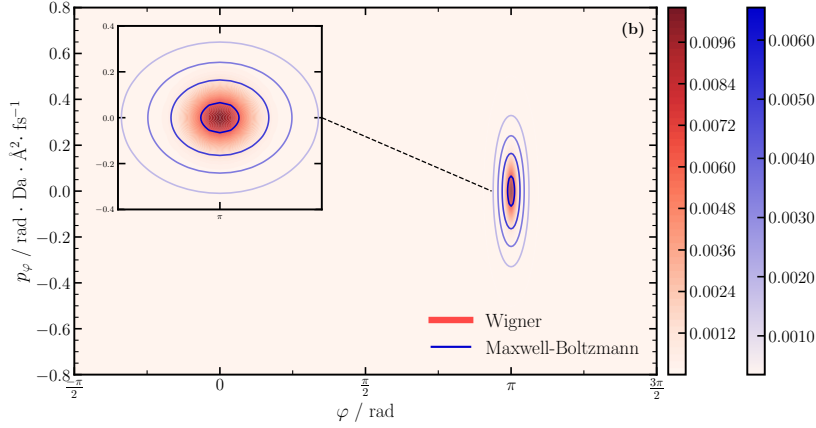


Figure 3.3: Initial phase-space distributions of the two calculations. Red: the Wigner distribution of the quantum initial state (3.64). Blue contours: the Maxwell-Boltzmann distribution (3.71) employed by the quantum-classical calculation. Both are centred on the *trans* minimum and confined to it; the inset magnifies that region. The ratio of their widths is derived in Appendix C.

retained by the quantum calculation introduces a systemic difference rather than an adjustable parameter offset.

The counterterm is a second discontinuity. The QSLE algorithm inserts the adiabatic surfaces directly into the deterministic drift of Equation (3.69). The quantum implementation deliberately omits the counterterm required by Equation (3.3). According to Equation (3.7), the surface driving the reduced quantum dynamics is essentially V_α renormalized by a term proportional to $\Lambda \hat{Q}^2$, with $\Lambda = \eta \omega_c$. Because this renormalization scales with coupling strength and progressively flattens the transition barrier, increasing η affects the potential landscape itself, not merely the rate of dissipation. This is a limitation of the present implementation.

The third disparity concerns decoherence. In the quantum formulation, the decoherence timescale emerges from the environment via Equation (2.85), drawing upon both $\hat{C}$ and $\hat{Q}$. In the quantum-classical formulation, it is tied to the friction by $\tau = g_\varphi / \xi_\varphi$. Varying ξ_φ shifts both the dissipation and the surface-hopping rate simultaneously. In contrast, varying η shifts the quantum dissipation and transition rates in proportion, but leaves the transition selection rules to $\hat{Q}$.

THE INITIAL STATE. The quantum calculation is prepared in the pure state defined in Equation (3.64), while the quantum-classical calculation initiates from the thermal distribution of Equation (3.71). These initializations occupy different state spaces; an exact correspondence is impossible because classical phase-space densities must remain non-negative, whereas Wigner functions may assume negative values. However, because the Wigner transform of Equation (3.64) is non-negative across the entire domain, a direct visual comparison with distribution (3.71) is presented in Figure 3.3. The transform is evaluated analytically in Appendix C, where the harmonic reduction of the *trans* well is carried out and the widths of the two distributions are related.

Both distributions centre upon the same phase-space point and remain narrow across the torsional coordinate, though they are not identical. Expanding the lower surface potential around the *trans* minimum gives a harmonic frequency $\omega_0 = \sqrt{W_0/2M_\phi}$, yielding $\beta\hbar\omega_0 \simeq 0.2$ at 300 K. The torsional mode therefore resides within the classical limit defined by condition (iv) in Subsection 3.1.4. Figure 3.3 verifies this condition for the present system, which is the assumption required to propagate the coordinate classically within the QSLE framework. According to the expansion driving Equation (3.21), the Wigner function of a true thermal state of the torsion aligns with Equation (3.71) within an error bound of $(\beta\hbar\omega_0)^2$.

The minor residual difference visible in Figure 3.3 is a variation in physical preparation rather than a quantum-classical failure: the quantum calculation initializes at the vibronic GS, whereas the quantum-classical solver samples a broader thermal ensemble. In this classical regime, these states differ in phase-space area by a factor of $2k_B T/\hbar\omega_0$. The impact of this discrepancy on the terminal observables is negligible. Population traversing the avoided crossing descends 0.51 eV from the point of preparation, meaning the momentum there is governed by the descent rather than the initial thermal spread. The thermal distribution generates a relative momentum spread of $\sqrt{k_B T/2\Delta V}$, and the GS introduces a spread scaling with $\sqrt{\hbar\omega_0/4\Delta V}$. Because both are small, the branching ratio remains insensitive to the preparation offset.

With both calculations specified, and the points of alignment and divergence identified, the quantitative benchmark can proceed.

3.4 BENCHMARK

3.4.1 Protocol

Every calculation reported below employs the surfaces of Equation (3.50) parameterized in Subsection 3.3.1, evaluated at 300 K. The inertial parameter is fixed at $M_\phi = 5.72 \times 10^4 \text{ eV}^{-1}$, obtained from the quantum-classical model. The quantum calculations employ a cut-off frequency of $\hbar\omega_c = 0.0175 \text{ eV}$. Within each description, a single bath parameter is varied: the coupling strength η in the Redfield model, and the friction ξ_ϕ in the quantum-classical one.

Because the torsional coordinate is dimensionless, both parameters carry the dimensions of a moment of inertia per unit time, equivalently of an action; they are reported in units of $\hbar$. The parameter sweeps cover $0.2 \leq \eta/\hbar \leq 5$ (quoted, as throughout, in units in which $\hbar = 1$) and $0.76 \leq \xi_\phi/\hbar \leq 4.34 \times 10^3$. The upper bound of the friction sweep corresponds to the hydrodynamic value ($4.58 \times 10^{-31} \text{ J s}$) computed for a four-bead representation of the model in n-hexane.[114] These parameter ranges overlap only at their lower limits, a result examined in Subsection 3.4.4.

All dynamics are evaluated at 100 ps. This choice is a necessary compromise for the quantum calculations: the upper surface is depleted before this time, but thermal redistribution between the two V_0 wells begins to encroach at later times, converting the kinetic branching ratio into an equilibrated population. At 100 ps, the quantum-classical computation retains approximately 7% of its population on the upper surface, compared to 0.2% for the quantum model. The models are therefore compared at slightly different degrees of completion, with the quantum yield being the closer of the two to its asymptote.

The inertia and the reference coupling operator $\hat{Q}_0$ were fixed in advance, on the criteria of Subsections 3.3.4 and 3.4.3. The two bath parameters were subsequently adjusted against the integrated populations alone. The spatially resolved densities were excluded from this calibration and examined only after it was complete. Whatever agreement they display is therefore a prediction of the calibrated model rather than a consequence of the calibration, and Subsection 3.4.6 reports it on that basis.

3.4.2 Inertia and the Semiclassical Limit

The QSLE framework assumes the dihedral evolves as a classical variable. While Subsection 3.3.4 established the static condition for this approximation ($\beta\hbar\omega_0 \simeq 0.2$ at the *trans* minimum), Figure 3.4 visualizes the dynamical implications.

The panels compare the dynamics across two inertial parameters: a low-mass regime approximating the original Hahn-Stock parameterization ($M_\phi \approx 2000 \text{ eV}^{-1}$), and the heavy-mass regime extracted from the quantum-classical model ($M_\phi \approx 50000 \text{ eV}^{-1}$). The harmonic frequency $\omega_0 = \sqrt{W_0/2M_\phi}$ sets the energy scale. The twenty-five-fold mass increase shifts $\hbar\omega_0$ from approximately 30 meV down to 6 meV, shifting $\beta\hbar\omega_0$ from 1.2 to 0.2. The two columns therefore lie on either side of the crossover from quantum to classical behaviour.

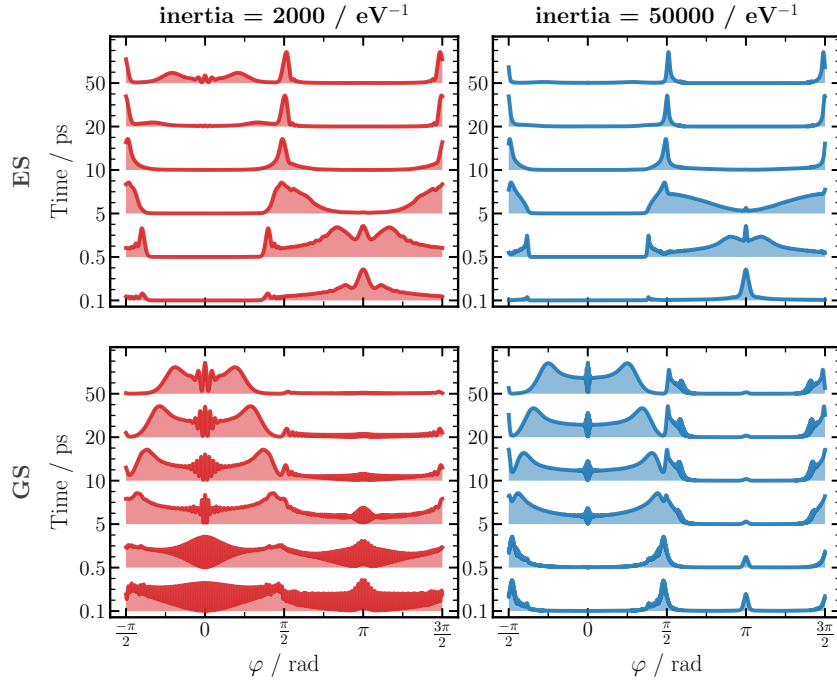


Figure 3.4: Spatially resolved population densities $P_\alpha(\varphi, t)$ upon the [ES](#), upper row, and the [GS](#), lower row, for two values of the inertial parameter. Within each panel the traces are stacked by time, the vertical offset giving the instant at which each is evaluated. Left: the low-inertia regime ($M_\varphi \approx 2000 \text{ eV}^{-1}$), close to the original Hahn-Stock parameterization, in which interference fringes persist in the *cis* well throughout. Right: the high-inertia regime obtained from the quantum-classical model ($M_\varphi \approx 5 \times 10^4 \text{ eV}^{-1}$), in which the fringes are suppressed and the density is smooth.

The spatially resolved densities capture this transition. In the low-inertia regime (left column), the ground-state distribution shows pronounced oscillatory interference, persisting as a stable fringe pattern in the *cis* well up to 50 ps. These fringes arise from quantum interference between wavepacket components arriving from opposite sides of the barrier. A classical phase-space density governed by Equation (3.69) cannot reproduce such structure, its solution being smooth and non-negative. In the high-inertia regime (right column), the interference is suppressed, yielding a smooth bimodal density. Residual oscillations are confined to the immediate vicinity of the avoided crossings and the $\varphi = 0$ minimum.

This suppression originates from the density of the torsional spectrum. The torsional energy level spacing scales as M_φ^{-1} . The heavier rotor supports a spectrum twenty-five times denser, generating tightly spaced Bohr frequencies. The wavepacket spans a proportionally larger number of these transitions, accelerating the environmental dephasing governed by Equation (2.85). Consequently, the interference pattern degrades within the first few picoseconds.

Imposing the classical inertia upon the quantum model forces the system into the semiclassical regime where the [QSLE](#) operates. Figure 3.4 does not establish agreement between the descriptions; rather, it establishes that the models are compared in a regime where agreement is possible, and it fixes the parameterization used throughout.

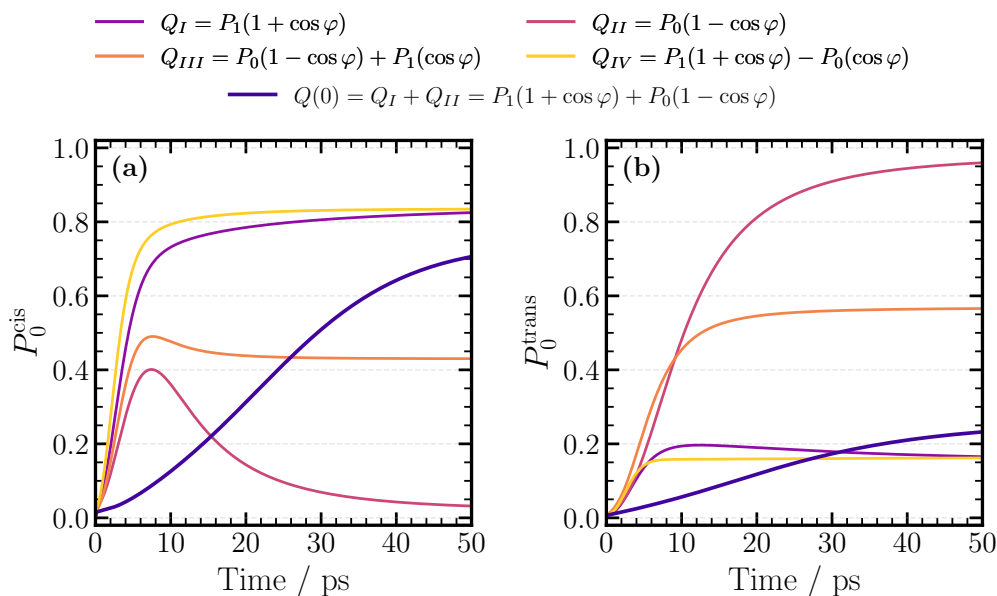


Figure 3.5: Ground-state populations under the five coupling operators of Equations (3.56) to (3.60), evaluated at $\eta = 4$. (a) The *cis* well, P_0^{cis} . (b) The *trans* well, P_0^{trans} . All other parameters match Subsection 3.4.1; values at 50 ps are recorded in Table 3.2.

3.4.3 The Coupling Operator Determines the Outcome

The five operators of Equations (3.56) to (3.60) were propagated at a fixed coupling strength of $\eta = 4$, with all other parameters held at the values established in Subsection 3.4.1. Figure 3.5 displays the resulting populations of the two ground-state wells, and Table 3.2 records their values at 50 ps.

The yields span the entire accessible range, from 3% to 83%, at a single coupling strength and upon a single pair of surfaces. Nothing in the energetics distinguishes the five calculations; the form of the coupling operator alone fixes the branching ratio.

The yields correlate with the relative weight the operator assigns to the excited diabatic projector $\hat{P}_1$ over $\hat{P}_0$. Specifically, $\hat{Q}_{II}$ lacks a $\hat{P}_1$ component and yields predominantly *trans* product. The operator $\hat{Q}_{III}$ introduces $\hat{P}_1$ weighted by $\cos \varphi$, which is positive only in the *cis* geometry. The reference $\hat{Q}_0$ weights $\hat{P}_1$ by $1 + \cos \varphi$ while retaining a $\hat{P}_0$ term. The operator $\hat{Q}_I$ uses the same $\hat{P}_1$ profile but eliminates $\hat{P}_0$, and $\hat{Q}_{IV}$ introduces a negative $\hat{P}_0$ admixture.

The mechanism underlying this ordering follows from the topography of the surfaces. In the *cis* well, $V_{11} < V_{00}$, so that the lower adiabatic surface is predominantly $|\psi_1\rangle$ there. The reverse ordering applies in the *trans* well, where V_0 is predominantly $|\psi_0\rangle$. An operator built upon $\hat{P}_1$ couples the environment to the system most strongly when the molecule occupies the *cis* region, whereas an operator built upon $\hat{P}_0$ localizes the coupling in the *trans* region. Population arriving on V_0 from the avoided crossing retains excess kinetic energy. It remains mobile until that energy is dissipated, and is therefore trapped preferentially in the well

Operator	Static term	p_0^{cis}	p_0^{trans}
$\hat{Q}_{\text{II}}$, Eq. (3.57)	—	0.032	0.960
$\hat{Q}_{\text{III}}$, Eq. (3.59)	$\hat{P}_0$	0.430	0.566
$\hat{Q}_0$, Eq. (3.58)	$\hat{1}$	0.706	0.232
$\hat{Q}_{\text{I}}$, Eq. (3.56)	—	0.825	0.165
$\hat{Q}_{\text{IV}}$, Eq. (3.60)	$\hat{P}_1$	0.834	0.162

Table 3.2: Ground-state populations at $t = 50$ ps for the five coupling operators, evaluated at $\eta = 4$ and ordered by increasing *cis* yield. The second column gives the static electronic term in the decomposition of Subsection 3.3.2, which applies to $\hat{Q}_0$, $\hat{Q}_{\text{III}}$ and $\hat{Q}_{\text{IV}}$ alone; $\hat{Q}_{\text{I}}$ and $\hat{Q}_{\text{II}}$ are the elementary components and admit no such decomposition.

where the environmental coupling is strongest. The coupling operator therefore controls the spatial distribution of dissipation along the reaction coordinate, directly governing the branching ratio.

Two consequences follow for the correspondence of Section 3.1. First, a scalar friction parameter cannot encode the spatial distribution of dissipation. The Fokker-Planck operator assigns identical dynamics to all five scenarios because they share the same parameters and surfaces. The essential physical information is carried by $\hat{Q}$, an operator degree of freedom that Equation (3.69) does not possess.

Second, the outcome is sensitive to the static electronic term. For example, $\hat{Q}_{\text{I}}$ and $\hat{Q}_{\text{IV}}$ differ only by the term $\hat{P}_0 \cos \varphi$ and produce nearly identical yields (0.825 versus 0.834). In contrast, $\hat{Q}_{\text{III}}$ and $\hat{Q}_{\text{IV}}$ differ by a factor of two (0.430 versus 0.834), despite differing solely by the static electronic projector ($\hat{P}_0$ versus $\hat{P}_1$). Static electronic operators fail to commute with both $\hat{H}_{\text{S}}$ and the configurational projectors. Their matrix elements between mixed vibronic eigenstates open population transfer channels inaccessible to a purely diagonal operator such as the identity matrix. The final branching ratio is thus sensitive to electronic features of the coupling operator that lack torsional dependence, and to which no friction kernel of the form (3.25) can correspond.

The transition rates in Equation (3.63) separate the environmental influence into the spectral density $\tilde{C}(\omega_{ab})$ and the matrix element $|Q_{ab}|^2$. While the present subsection evaluated variations in the coupling operator at a constant spectral density, the following one varies the spectral density scaling and compares the result against the response of the quantum-classical framework to its single friction parameter.

3.4.4 Response to the Bath Parameter

AN EXACT SCALING OF THE QUANTUM DYNAMICS. The response of the Red-field dynamics to the coupling strength is fixed analytically. Because the Drude-Lorentz spectral density (3.24) and the resulting power spectrum (3.14) are linearly proportional to η , the rates (3.63) may be written $k_{a \rightarrow b} = \eta \bar{k}_{a \rightarrow b}$, with $\bar{k}$ evalu-

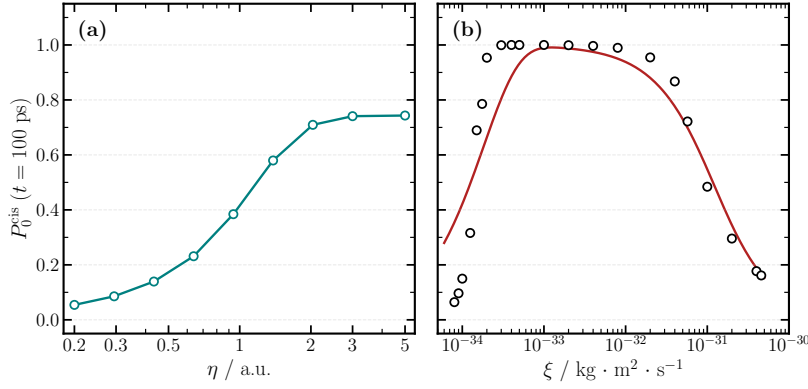


Figure 3.6: Photoisomerization yield at $t = 100$ ps as a function of the bath parameter. (a) Redfield calculation with $\hat{Q}_0$, against the coupling strength η . (b) Quantum-classical calculation against the friction ξ_φ , with a fit to the interpolation (2.51) (line), for which $A = 5.47 \times 10^{33} (\text{J s})^{-1}$ and $B = 6.39 \times 10^{30} (\text{J s})^{-1}$.

ated at unit coupling. The matrix W governing the populations in Equation (2.83) is linear in those rates, so that $W = \eta \bar{W}$ and

$$e^{Wt} = e^{\bar{W}\eta t} \quad (3.73)$$

The populations depend upon η and t through the product ηt alone. Within the secular treatment, the coupling strength rescales the kinetic clock but does not alter the underlying dynamics.

This scaling is subject to specific physical boundaries. While accurate for populations, it fails for the coherences. The coherent evolution incorporates a dephasing rate that scales with η and a Bohr frequency that does not. Because the observables (3.66) rely on configurational operators outside the diagonal of the vibronic eigenbasis, coherences contribute to the early dynamics; the scaling holds only after they have decayed. Furthermore, the scaling assumes a spectral density directly proportional to its strength parameter, a condition the Drude-Lorentz form satisfies. Finally, the scaling relies on the omission of the counterterm noted in Subsection 3.3.4. Retaining the counterterm from Equation (3.3) would introduce an η -dependence into $\hat{H}_S$, shifting the eigenvalues E_a and the matrix elements Q_{ab} , thereby breaking Equation (3.73).

Panel (a) of Figure 3.6 is a single kinetic time trace $P_0^{\text{cis}}(\eta t)$ sampled at a fixed observation time across nine values of η . The sigmoidal rise reflects the observation window overtaking the reaction kinetics, and the plateau is the branching ratio itself, attained once the process has run to completion within 100 ps.

Detailed balance, Equation (2.87), confirms why the terminal branching ratio remains independent of η : a uniform rescaling of W leaves the stationary state unchanged, as the ratio of forward to reverse rates is dictated by the temperature alone. The coupling strength in the quantum model governs the kinetics exclusively. The final product distribution is determined by the coupling operator $\hat{Q}$.

RESPONSE OF THE QUANTUM-CLASSICAL DESCRIPTION. The quantum-classical yield exhibits a different parameter dependence. As shown in panel (b) of Fig-

ure 3.6, the yield rises steeply from the lowest friction, passes through a broad maximum, and falls away at the hydrodynamic value, describing the non-monotonic response established in Subsection 2.1.7.

The line is the interpolation (2.51) of Mel'nikov and Meshkov, fitted to the computed points.[71] The turnover of panel (b) is thus not merely a curve possessing a maximum; it is the Kramers turnover of the surface upon which the dynamics proceeds.

One factor confounds this interpretation. Because the program derives the decoherence time from the friction, $\tau = g_\varphi/\xi_\varphi$, a sweep in ξ_φ alters both the dissipation and the surface-hopping rates of Equation (3.44). The two contributions are not separated by the present calculations, and a sweep at fixed τ would be required to separate them.

THE FAILURE OF THE CORRESPONDENCE, QUANTIFIED. Setting the two panels of Figure 3.6 side by side quantifies the divergence between the descriptions. Under the specific constraints of Section 3.1, Equation (3.20) maps η to ξ_φ , implying the plots should share a common abscissa. However, the profiles differ in both shape and range. The Redfield profile is monotonic and saturating, reflecting reaction kinetics at a fixed product outcome. The quantum-classical profile is non-monotonic, reflecting friction-dependent variations in the outcome itself.

The parameter ranges also differ. The Redfield calculation achieves its asymptotic branching ratio by $\eta \simeq 3 \hbar$, whereas the quantum-classical yield varies over three decades of friction, up to $4.3 \times 10^3 \hbar$. The intervals overlap exclusively in their lowest decade. Reproducing the quantum yield within the quantum-classical description requires a friction exceeding the originating coupling strength by two orders of magnitude. Furthermore, the physically grounded hydrodynamic value lies three decades beyond the explored range of η .

This is the quantitative content of the argument of Subsection 3.1.4. Equation (3.20) assumes a coupling bilinear in the system coordinate. Because the operators in Subsection 3.3.2 violate this condition, the theoretical identity $\xi_\varphi = \eta$ collapses. The classical friction represents the aggregate physical effect of both the coupling strength and the coupling operator in Equation (3.63). A single scalar variable derived from a bilinear model cannot be equated with either factor alone.

3.4.5 Kinetic and Thermodynamic Control

The turnover of the preceding subsection reflects the microscopic phase-space dynamics directly propagated by the quantum-classical description. Figure 3.7 compares two simulations differing only in the friction, the hydrodynamic value and that value reduced eightfold. The outcomes invert. At hydrodynamic friction, the excited surface depletes over 20 ps, accumulating population in the *trans* well and generating a *cis* yield of 0.16. At the reduced friction, depletion concludes within a few picoseconds, directing population into the *cis* well for a yield of 0.72. Adjusting a single macroscopic parameter exchanges the thermodynamic product for the kinetic product.

The lower panels map this divergence to the phase-space density on V_1 at 1 ps, when the excited surface still carries essentially the whole population and the

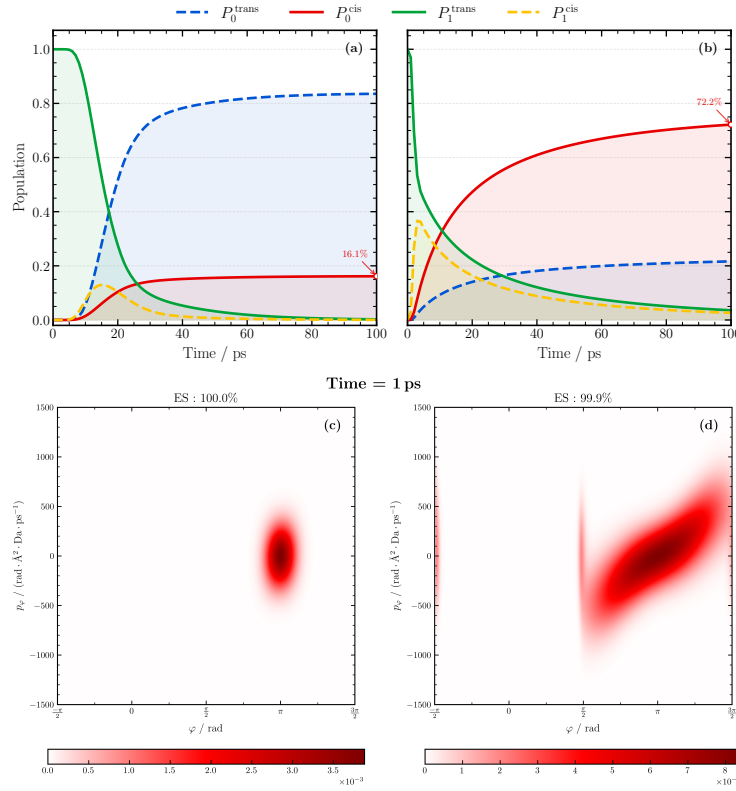


Figure 3.7: Quantum-classical dynamics at two frictions. (a,c) Hydrodynamic value $\xi_\phi = 4.58 \times 10^{-31}$ J s. (b,d) The same reduced by a factor of eight, $\xi_\phi = 5.73 \times 10^{-32}$ J s. Upper panels: populations of Equation (3.72). Lower panels: the phase-space density $\rho_1(\phi, p_\phi)$ upon the excited surface at $t = 1$ ps, before any appreciable surface hopping has occurred.

branching has not yet occurred. At hydrodynamic friction, the density remains a compact distribution centred at $\phi = \pi$ with a thermal momentum spread. The system is arrested at the FC geometry; the drag term of Equation (3.69) extracts the excess energy before the coordinate evolves. At reduced friction, the density spreads across the excited well toward the avoided crossings, elongated along a direction of positive correlation between angle and momentum. This correlation indicates ballistic propagation: population rolls down V_1 from $\phi = \pi$, converting potential energy into momentum several times the thermal spread.

Equation (3.70) translates this momentum into the branching outcome. Population reaching the crossing region with high momentum passes through the transition zone. Upon transferring to V_0 , it acquires the energetic gap released by the transition, entering the GS with significant velocity directed away from the crossing. Population arriving with thermal momentum is deposited near the crossing and relaxes according to the local gradient. The high-momentum regime represents kinetic control, where the transition trajectory dictates the outcome. The thermal-momentum regime represents thermodynamic control, where the relaxed topography of the GS dictates the outcome.

These two regimes define the physical boundaries of the Kramers turnover. At strong coupling, nuclear motion is quenched prior to the crossing, suppressing the

yield as friction increases. At weak coupling, the system retains momentum, but the environment dissipates energy too slowly to trap the molecule in the shallow *cis* well. The population coasts past the minimum and settles in the deeper *trans* well, suppressing the yield as friction decreases. The maximum yield occurs in the intermediate regime, where the system retains sufficient momentum to enter the *cis* well and experiences sufficient dissipation to remain trapped.

The quantum description resolves none of this. Its observables are configurational populations, and momentum influences the dynamics only implicitly via the vibronic spectrum. The secular Redfield formalism contains no analogue to the phase-space dynamics depicted in panels (c) and (d) of Figure 3.7 and no mechanism that responds to coupling strength with a turnover. As established by Equation (3.73), the quantum coupling strength rescales the kinetic timeline but cannot redirect the spatial branching. The classical friction redirects the branching by modulating the coordinate velocity at the transition point. Because the two parameters govern distinct physical processes within their respective frameworks, achieving numerical agreement requires identifying specific overlapping boundary conditions.

3.4.6 A Regime of Quantitative Agreement

Having established the independent parameter responses of both formalisms, this section evaluates whether a parameterization exists that forces the two models into quantitative agreement, and analyses the physical implications of that mapping.

CALIBRATION. The calibration fixes three fundamental parameters: the inertia, for the reasons of Subsection 3.4.2, the coupling operator $\hat{Q}_0$, and the quantum coupling strength at $\eta = 4$. As demonstrated in Figure 3.6(a), $\eta = 4$ lies safely on the kinetic plateau where the process reaches completion within the observation window, ensuring the measured yield is the asymptotic branching ratio. The calibration therefore relies on a single free parameter, the classical friction ξ_ϕ , which was adjusted to match the integrated populations in panel (a) of Figure 3.8.

The value obtained is $\xi_\phi = 5.5 \times 10^{-32}$ J s, equivalent to 522 $\hbar$. This value occupies the descending branch of the Kramers turnover, residing an order of magnitude below the hydrodynamic friction limit and an order of magnitude above the turnover maximum shown in Figure 3.6(b). Comparing this calibrated friction against the quantum coupling strength gives the ratio

$$\frac{\xi_\phi}{\eta} \simeq 130 \tag{3.74}$$

Under the conditions of Subsection 3.1.4, this ratio would be unity. Equation (3.74) quantifies the breakdown of the analytical correspondence for this specific model. The scalar friction must be inflated by two orders of magnitude to reproduce the branching ratio that the quantum description achieves via the structure of its coupling operator. While the absolute value is model-dependent, its substantial deviation from unity confirms the theoretical disconnect.

AGREEMENT OF THE POPULATIONS. Panel (a) tracks the four observables under both descriptions. The asymptotic *cis* yields differ by 2.1 percentage points, 74.3% against 72.2%. The agreement extends beyond the endpoint: both models deplete the excited surface monotonically, capture the transient rise and decay of P_1^{cis} on identical timescales, and accumulate *trans* population toward a comparable plateau. Minor kinetic deviations emerge, with the quantum-classical formulation depleting the excited surface faster at early times and slower at late times, retaining the residual 100 ps population noted in Subsection 3.4.1. Because the models employ different transition mechanisms and were calibrated against a single asymptotic endpoint, the global temporal alignment validates the quantum-classical framework's capacity to reproduce macroscopic reaction kinetics.

THE DENSITIES, AS PREDICTION. Panels (b) and (c) project the dynamics onto the spatial coordinate. These were examined only after the calibration was complete and entered it at no point; what they display is a prediction of the calibrated model rather than a consequence of the calibration.

At 0.5 ps, both descriptions localize the wavepacket on the excited surface in the *trans* region. By 5 ps, the population reaches the excited minima near the avoided crossings and initiates ground-state transfer. The ES populations agree within a ten-percent margin, and the ground-state densities develop corresponding bimodal distributions, with the *cis* well already dominating. At 20 ps, both models transfer comparable population fractions to the ground surface, matching the relative spatial distribution between the two wells. By 100 ps, the population predominantly occupies the *cis* well with a secondary accumulation in the *trans* geometry; the shapes of the distributions correspond closely.

Residual structural differences remain. The quantum densities exhibit oscillatory interference near $\varphi = 0$ and at the avoided crossings. This coherence effect cannot be replicated by the Fokker-Planck equation (3.69). Furthermore, the quantum ground-state densities skew asymmetrically within each well, diverging from the centred Gaussians generated by the QSLE. This asymmetry originates from the electronic projector $\hat{\Pi}_\alpha$ in the quantum observable (3.66), which varies across the coordinate space via the mixing angle (3.51). The quantum-classical observable (3.72) lacks this configuration-dependent weighting. The discrepancy therefore stems from the definition of the observable rather than divergent underlying dynamics.

The alignment of the spatial densities, achieved by tuning a single scalar parameter, establishes that the quantum-classical description successfully reproduces the full quantum spatial dynamics of this system. However, the scalar parameter required to achieve this alignment cannot be predicted a priori, and Equation (3.74) establishes its significant deviation from the value dictated by the theoretical correspondence of Section 3.1.

3.4.7 Limitations

The evaluations in this section rely on approximations spanning the analytical mapping, the theoretical formalisms, and the numerical implementations.

LIMITATIONS OF THE CORRESPONDENCE. Equation (3.20) assumes an environmental coupling bilinear in the system coordinate. As demonstrated in Subsection 3.4.3, violating this assumption alters the outcome: five operators sharing identical Fokker-Planck parameters yield different branching ratios. The coupling operator acts not as a refinement of the bath model, but as an independent descriptor; the classical friction represents the combined effect of both the coupling strength and the spatial distribution of the coupling operator.

The periodicity of the torsional coordinate makes this unavoidable. A periodic hindering potential demands a periodic coupling function, precluding a linear coordinate dependence on symmetry grounds. Eliminating the bath DOF for a generalized non-linear coupling $f(\hat{q})$ yields a coordinate-dependent friction kernel, reducing to $f'(q)^2\xi$ in the Markovian limit, and a spatially varying counterterm $\frac{1}{2}\Lambda f(q)^2$. [26] Because the standard Fokker-Planck operator cannot accommodate these features, both evaluated models resort to configuration-independent friction approximations. Section 3.4 therefore tests the consistency of two simplified bath models rather than their adequacy for representing a molecular solvent. Measuring configuration-dependent friction directly from the environment is addressed in Chapter 4.

LIMITATIONS OF THE TWO DESCRIPTIONS. The secular approximation imposes a severe constraint on the quantum formulation. Equation (3.73) dictates that the coupling strength rescales the kinetic timeline without altering the branching outcome.

The omission of the environmental counterterm compounds this issue. Restoring the counterterm from Equation (3.3) makes $\hat{H}_S$ dependent upon $\Lambda = \eta \omega_c$, which would carry an η -dependence into the eigenvalues E_a and the matrix elements Q_{ab} , and the rates (3.63) would cease to be proportional to η . At the couplings employed here the renormalization would amount to a fraction of the ground-state barrier, and it would act to lower it. Overcoming this limitation and restoring the η -dependence of the quantum yield requires reincorporating the counterterm.

The QSLE operates under corresponding classical limitations. The torsional coordinate lacks zero-point energy, discrete vibrational levels, and tunnelling mechanisms; energy barriers are crossed exclusively via thermal activation. The formalism relies on independent Markovian approximations applied to the drift and memory integrals. Furthermore, friction dictates the macroscopic drag in Equation (3.69) while simultaneously setting the decoherence time $\tau = g_\varphi/\xi_\varphi$ governing the surface-hopping rates. Sweeping ξ_φ varies dissipation and non-adiabatic hopping probability together; separating them would require a sweep at fixed τ .

THE NON-SECULAR TENSOR. The constraint imposed by Equation (3.73) is specific to the secular approximation. Retaining the full tensor of Equation (2.80) couples populations to coherences, and the population dynamics then depends on the coupling strength through mechanisms beyond a simple time-rescaling. A non-secular treatment therefore grants the branching ratio the freedom to respond to η .

Storing the complete tensor is computationally prohibitive. Sparse algorithms mitigate this by retaining only elements connecting transitions with near-degenerate Bohr frequencies.[115] The efficiency of such approaches relies on near-degeneracies being the exception within the vibronic spectrum. The present system violates this condition for the very reason that the comparison of this chapter was possible at all: the inertia adopted in Subsection 3.4.2, chosen to ensure semiclassical behaviour, generates a dense torsional spectrum in which near-degeneracies are not the exception but the rule. The sparsity these algorithms require is therefore absent, regardless of the numerical tolerance applied.

The non-secular formulation remains theoretically sound but computationally inaccessible for a semiclassical rotor expanded across the full angular coordinate. Progress requires reducing the vibronic dimensionality by restricting the calculation to a thermally accessible active space, rather than improving tensor storage capabilities.

Future development must also address two requirements: restoring the environmental counterterm, and examining couplings carried by the coordinate alone, such as $\hat{Q}_\varphi$ and $\hat{Q}_{\sin}$ of Equation (3.61). Preliminary calculations with these operators recover the smooth, classically shaped ground-state distributions absent from the projector-based results. Neither, however, restores the correspondence outright. The coupling $\hat{Q}_\varphi$ is bilinear in the torsion but is not single-valued upon the circle, and $\hat{Q}_{\sin}$ is bilinear in $\sin(\varphi)$. In the tests performed, the system reaches the thermodynamic product independently of η , consistent with Equation (3.73). A quantitative cross-evaluation against the quantum-classical description under these updated parameters remains a target for future work.

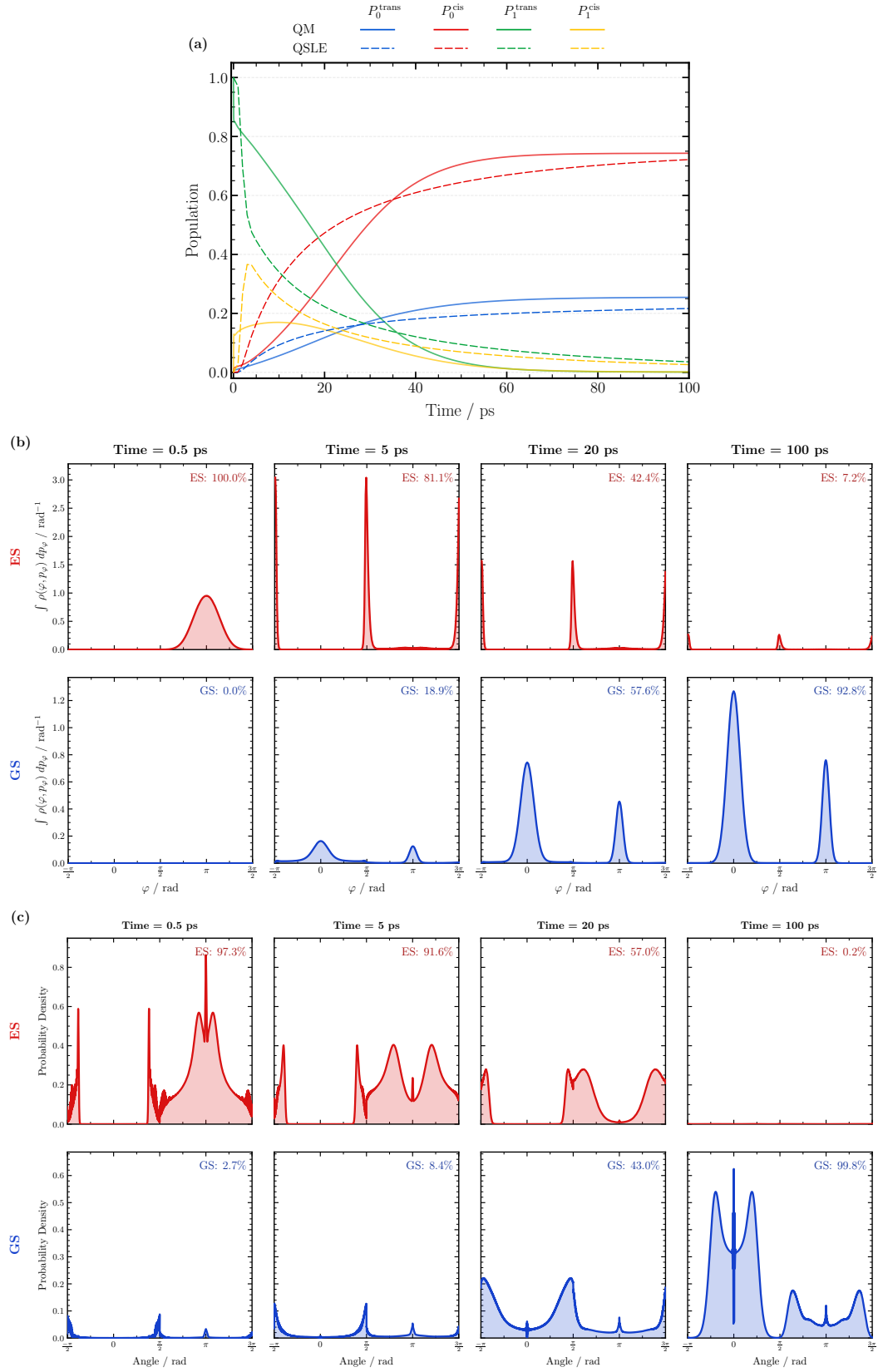


Figure 3.8: Comparison of the calibrated descriptions. (a) Populations of Equations (3.66) and (3.72): Redfield dynamics (solid) evaluated at $\eta = 4$ with $\hat{Q}_0$, quantum-classical dynamics (dashed) at $\xi_\varphi = 5.5 \times 10^{-32}$ J s. Spatially resolved densities of (b) the quantum-classical calculation and (c) the quantum calculation, displayed for the excited surface (upper row) and the ground surface (lower row) at four discrete times. Percentages indicate the total population residing upon each surface.

MICROSCOPIC DERIVATION OF THE THERMAL BATH FROM ATOMISTIC SIMULATIONS

The preceding chapters formulated the thermal bath descriptor by construction rather than direct measurement. While Subsection 2.1.6 defined friction microscopically as an equilibrium time-correlation function of the environmental force upon a retained coordinate, and Section 3.1 mapped this quantity to the spectral density of a quantum environment, neither provided a numerical value from first principles. In the benchmark of Section 3.4 the friction entered as an adjustable parameter. The value required to align the quantum-classical and fully quantum descriptions exceeded the analytical correspondence by two orders of magnitude. This discrepancy originates in the coupling operator. Five distinct operators, evaluated on identical surfaces with a shared bath parameter, yielded branching ratios spanning the accessible range, with no internal physical criterion to discriminate among them.

These limitations stem from a common assumption. A configuration-independent scalar friction cannot capture the spatial variation of dissipation along a reaction coordinate, and ad hoc coupling operators lack verification against the physical environment they represent. Equation (2.47) resolves this by defining friction as an equilibrium average over environmental fluctuations, conditional on the configuration of the retained subsystem. This formulation allows the extraction of configuration-dependent dissipation directly from atomistic MD trajectories.

This chapter carries out that computation. Section 4.1 translates the definition into a computational protocol, detailing the methodologies for extracting position-dependent friction from MD simulations. Section 4.2 applies this protocol to a coarse-grained 4-bead chain. The simplicity of this model permits cross-validation of the extraction methodologies; comparing simulations in vacuum against those in explicit water isolates the dissipative contribution of the solute's internal coordinates from the solvent friction. Section 4.3 extends the analysis to 4,4'-dihydroxyazobenzene in explicit water, yielding the friction profile along the photoisomerizing torsion. Section 4.4 compares these atomistic results against continuum-hydrodynamic calculations.

The extraction protocol, its implementation, the atomistic simulations, and the analytical pipeline bridging the atomistic and hydrodynamic tensors were developed as part of the present work.

4.1 A PROTOCOL FOR EXTRACTING POSITION-DEPENDENT FRICTION FROM MOLECULAR DYNAMICS

Let φ denote the dihedral angle about the isomerizing bond. Specializing the GLE (2.48) to this single retained coordinate gives[64, 65]

$$g_\varphi \ddot{\varphi}(t) = -\frac{\partial \mathcal{A}(\varphi)}{\partial \varphi} - \int_0^t ds \xi(\varphi, t-s) \dot{\varphi}(s) + \delta F(\varphi, t) \quad (4.1)$$

where $\mathcal{A}$ is the PMF of Equation (2.46), g_φ is the mass-metric element conjugate to the torsion introduced in Equation (3.69), and δF is the fluctuating part of the generalized force exerted upon φ by the bath DOF. The memory kernel is the one-dimensional reduction of Equation (2.47)[50]

$$\xi(\varphi, t) = \beta \langle \delta F(\varphi, 0) \delta F(\varphi, t) \rangle_\varphi \quad (4.2)$$

and the Markovian friction is its time integral

$$\xi(\varphi) = \beta \int_0^\infty dt \langle \delta F(\varphi, 0) \delta F(\varphi, t) \rangle_\varphi \quad (4.3)$$

Three features of Equations (4.2) and (4.3) dictate the measurement protocol.

First, the angular brackets denote an average conditional upon the configuration of the retained coordinate. In an atomistic simulation, this conditional ensemble is realized by applying a harmonic restraint to the dihedral and recording the generalized force, excluding the bias contribution. A restraint is used instead of a rigid constraint to preserve the canonical momentum distribution of the system coordinate and avoid metric tensor corrections. The restraint stiffness must be chosen to balance configurational confinement against environmental perturbation, a trade-off that will be quantified in Section 4.2.

Second, Equation (4.3) yields a marginal quantity. Because the fluctuating force δF is measured while all orthogonal molecular coordinates relax freely, the methodology extracts the generalized drag upon the torsion. The relationship mapping this marginal scalar to the full multidimensional dissipation tensor is deferred to Section 4.4, where atomistic results are compared against hydrodynamic models.

Third, because the dihedral is measured in radians, Equation (4.3) carries units of J s rad^{-2} . Since the radian is dimensionless, these values equate numerically to the J s units employed in Chapter 3. The angular label is retained to track the conversion from the native degree units of the simulation software.

4.1.1 Routes from a Trajectory to the Friction

Extracting friction from MD involves either inferring the kernel from an unconstrained trajectory or measuring the fluctuating force directly on a restrained trajectory. Application of these methodologies, evaluated in Section 4.2, reveals numerical limitations favouring the restrained approach.

THE UNCONSTRAINED ROUTE. Multiplying Equation (4.1) by the initial angular velocity $\dot{\varphi}(0)$ and averaging over the equilibrium ensemble eliminates the

fluctuating force. Approximating the [PMF](#) near its minimum by a harmonic form of curvature k_{eff} , and writing $\omega_0^2 = k_{\text{eff}}/g_\varphi$ for the resulting squared oscillation frequency, yields a Volterra integral equation of the second kind[[116](#), [117](#)]

$$\dot{C}_{vv}(t) = -\omega_0^2 C_{v\varphi}(t) - \frac{1}{g_\varphi} \int_0^t d\tau \xi(\tau) C_{vv}(t-\tau) \quad t > 0 \quad (4.4)$$

where $C_{vv}(t)$ is the velocity autocorrelation function and $C_{v\varphi}(t)$ the velocity-position cross-correlation. This expresses the friction through correlation functions computable from a free trajectory.[[22](#), [118](#)] As will be demonstrated in Section [4.2](#), numerical deconvolution of this equation proves unstable for bound coordinates in the underdamped regime ($\gamma \ll \omega_0$). In this limit, the terms $\dot{C}_{vv}$ and $\omega_0^2 C_{v\varphi}$ oscillate in antiphase, making their sum a small residual. Statistical noise in the correlation functions is thereby amplified, accumulating without bound in the running integral of the kernel.

THE LAPLACE LIMIT. Transforming Equation (4.4) and evaluating the zero-frequency limit avoids deconvolution, returning the Markovian coefficient without reference to the kernel

$$\xi = g_\varphi \frac{C_{vv}(0) - \omega_0^2 \int_0^\infty dt C_{v\varphi}(t)}{\int_0^\infty dt C_{vv}(t)} \quad (4.5)$$

As Section [4.2](#) will establish, this expression reduces to an indeterminate form for a bound coordinate. The denominator represents the diffusion coefficient, which vanishes for a torsion trapped in a deep potential well. Consequently, the cumulative integral oscillates without converging.

THE PARAMETRIC FIT. An alternative approach bypasses inversion by assuming a memoryless kernel, reducing Equation (4.1) to the Langevin equation of a damped harmonic oscillator. The friction is derived from the damping rate of the closed-form [VACF](#)

$$C_{vv}(t) = C_{vv}(0) e^{-\gamma t/2} \left[\cos(\Omega t) + \frac{\gamma}{2\Omega} \sin(\Omega t) \right] \quad t \geq 0 \quad (4.6)$$

where $\Omega = \sqrt{\omega_0^2 - \gamma^2/4}$. While numerically stable, this estimator forces multi-timescale friction into a single damping parameter, assuming the angular velocity corresponds to a single effective oscillator. Section [4.2](#) will show that this fitting procedure recovers the Markovian friction coefficient for the basic four-bead model. However, as Section [4.3](#) will demonstrate for 4,4'-dihydroxyazobenzene, the approximation fails when several structural relaxation timescales modulate the torsion. Furthermore, the approach returns a basin-averaged friction rather than a configuration-specific value.

THE RESTRAINED ROUTE. The reference methodology directly evaluates Equation (4.3) using a harmonically restrained trajectory.[[48–50](#)] The fluctuating force $\delta F(t)$ is recorded by subtracting the conditional mean of the total conjugate force,

removing the systematic potential gradient. The friction emerges from the running integral of the resulting [FACF](#).

This route circumvents the obstructions of the unconstrained routes. The measured quantity is a relaxing environmental correlation rather than an undamped coordinate correlation, preventing indeterminate limits and residual cancellations. It provides a model-free time series without parametric assumptions, enabling the extraction of friction localized at specified geometries, including non-equilibrium transition states inaccessible to free trajectories.

Its costs are a separate simulation for each point of the profile, and the residual perturbation that the restraint itself exerts upon the environment in the immediate vicinity of the solute. As demonstrated by Daldrop *et al.*,[\[119\]](#) harmonic restraints can modify the solvent structure and lead to an overestimation of the friction coefficient. The viability of this route therefore depends on identifying a compromise: a restraint stiff enough to localize the coordinate at selected geometries, yet soft enough to avoid perturbing the local dissipation. Sections [4.2](#) and [4.3](#) quantify this trade-off for their respective models. Provided this balance is achieved, the restrained route bypasses the structural limitations of the [VACF](#)-based computational approaches and is adopted as the primary method throughout this chapter.

4.1.2 Simulation Protocol

The methods of Subsection [4.1.1](#) were applied to two systems. The first is a coarse-grained four-bead chain, representing the carbon backbone of a generic alkene in the *trans* configuration, and introduced as a minimal realization of a torsional coordinate embedded in a solvent to establish the protocol. The second is 4,4'-dihydroxyazobenzene at atomistic resolution. Azobenzene constitutes a canonical molecular photoswitch whose relevance to non-adiabatic dynamics was established in Section [3.3](#); the 4,4'-dihydroxy derivative is selected here to ensure adequate aqueous solubility for explicit-solvent atomistic simulations. Both systems share a unified simulation pipeline, which is set out here once.

FORCE FIELDS. The four-bead chain is defined by harmonic bonds of force constant $K_b = 250.0 \text{ kcal mol}^{-1} \text{ \AA}^{-2}$ and equilibrium length $r_0 = 2.50 \text{ \AA}$, harmonic angles of force constant $K_\theta = 50.0 \text{ kcal mol}^{-1} \text{ rad}^{-2}$ and equilibrium value $\theta_0 = 120^\circ$, and Lennard-Jones ([LJ](#)) parameters $\epsilon = 0.100 \text{ kcal mol}^{-1}$ and $R_{\text{min}}/2 = 2.00 \text{ \AA}$. The central torsion is governed by a single cosine term of amplitude $K = 15.0 \text{ kcal mol}^{-1}$, multiplicity $n = 2$, and phase $\delta = 180^\circ$, generating minima at planar geometries separated by 30 kcal mol^{-1} barriers. At 300 K, this $50 \text{ k}_B\text{T}$ barrier precludes spontaneous isomerization on the sampled timescales. For 4,4'-dihydroxyazobenzene, parameters were assigned using the CGENFF program (version 4.0),[\[120, 121\]](#) with the central $\text{C}-\text{N}=\text{N}-\text{C}$ dihedral defining the reaction coordinate.

GENERATION OF INITIAL CONFIGURATIONS. Because extracting friction requires sampling non-equilibrium geometries, particularly the perpendicular transition state, initial coordinates were generated via steered molecular dynamics ([SMD](#)).[\[122\]](#) The dihedral was driven across its full domain, extracting snapshots at

target values of φ . Each snapshot independently seeded the subsequent pipeline, ensuring the steering protocol influenced only the initial coordinates and not the sampled ensemble.

THERMODYNAMIC PIPELINE. Each configuration was subjected to the same four stages. Energy minimization was performed for 5000 steps. The system was then thermally annealed from 60 K to 300 K in increments of 1 K. Solvated systems were equilibrated for 5 ns in the isothermal-isobaric ensemble (NPT) at 1 atm using a Langevin piston barostat,[123] maintaining periodic boundary conditions (PBC) and particle-mesh Ewald (PME) electrostatics.[124, 125] Production sampling spanned 20 ns in the canonical ensemble (NVT) at 300 K. The dihedral restraint was set to $0.5 \text{ kcal mol}^{-1} \text{ deg}^{-2}$ during minimization and annealing, before reduction to the equilibration and production value of $0.05 \text{ kcal mol}^{-1} \text{ deg}^{-2}$.

SIMULATION PARAMETERS. Trajectories were propagated in NAMD (version 3.0.3).[126] Bonds involving hydrogen were constrained in the atomistic azobenzene models,[127] removing the fastest vibrational modes of the solute and permitting an integration timestep of 2 fs; the same timestep was retained for the four-bead chain, whose stiffest bond vibration is considerably slower. Non-bonded interactions were truncated at 12 Å with a switching function activated at 10 Å, using a 14 Å pair-list and a 1 Å PME grid.[124, 125]

The four-bead model was simulated in TIP3P water and in vacuum; 4,4'-dihydroxyazobenzene was simulated in TIP4P water, with values obtained in TIP3P being indistinguishable from them.[128]

COLLECTIVE-VARIABLE DEFINITION AND CONTROLS. The dihedral was defined as a collective variable via the COLVARS module.[129] The bias-excluded total conjugate force was recorded every 20 fs. To isolate the physical origin of the dissipation, two control calculations were performed. The four-bead pipeline was repeated in vacuum, isolating the contribution of the remaining internal solute DOF. For azobenzene, solute-solvent electrostatic interactions were alchemically decoupled while retaining full LJ interactions, separating steric from dielectric solvent drag.[130, 131]

EXTRACTION. The recorded force time series is converted into a friction coefficient through a three-step protocol. The mean conditional force is subtracted to isolate the fluctuations. The autocorrelation function of this residual is computed via the Wiener-Khinchin relation (2.17) using a fast Fourier transform (FFT). The running integral (4.3) is evaluated via the trapezoidal rule. The Markovian friction is extracted as the average of this integral over the 5-20 ps interval, where it attains a stable plateau between the decay of the bath correlations and the structural relaxation of the coordinate itself.[51]

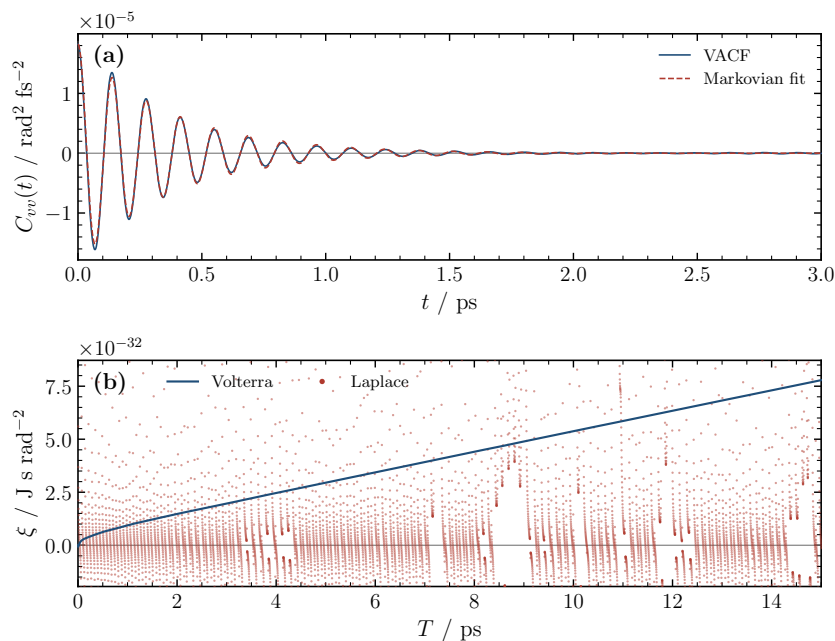


Figure 4.1: Three estimators of the friction coefficient applied to a single unconstrained four-bead trajectory. (a) Velocity autocorrelation function $C_{vv}(t)$ (solid blue) and the underdamped Markovian model fitted to it (dashed red), from which $\xi = 1.21 \times 10^{-33} \text{ J s rad}^{-2}$ is obtained. (b) Running friction coefficient obtained from the same trajectory by the two deconvolution routes, plotted against the upper limit of integration T : the Volterra recursion (solid blue line) and the Laplace-domain estimator (red points).

4.2 THE FOUR-BEAD MODEL

The four-bead chain is used for two purposes. It is simple enough that every approach of Section 4.1 can be applied to the same trajectory and their respective domains of validity compared. Furthermore, as a solvated molecule with a genuine torsional coordinate, it yields a configuration-dependent friction profile representative of molecular environments.

4.2.1 The Confinement Regime

The performance of each estimator depends upon the dynamical regime of the coordinate. Statistical analysis of an unrestrained trajectory confirms the system remains localized within the *trans* well, exhibiting a circular mean of $\varphi_{\text{eq}} = 180.0^\circ$ and a thermal standard deviation of $\sigma_\varphi = 5.8^\circ$. Applying equipartition relations to this trajectory gives the inertial parameter and the effective well curvature,

$$g_\varphi = \frac{k_B T}{\langle \delta \varphi^2 \rangle} \quad k_{\text{eff}} = \frac{k_B T}{\langle \delta \varphi^2 \rangle} \quad (4.7)$$

evaluating to $g_\varphi = 3.27 \times 10^4 \text{ kcal fs}^2 \text{ mol}^{-1} \text{ rad}^{-2}$ and $k_{\text{eff}} = 58.5 \text{ kcal mol}^{-1} \text{ rad}^{-2}$. This curvature matches the analytical second derivative of the torsional potential ($60 \text{ kcal mol}^{-1} \text{ rad}^{-2}$) to within three percent, confirming harmonic con-

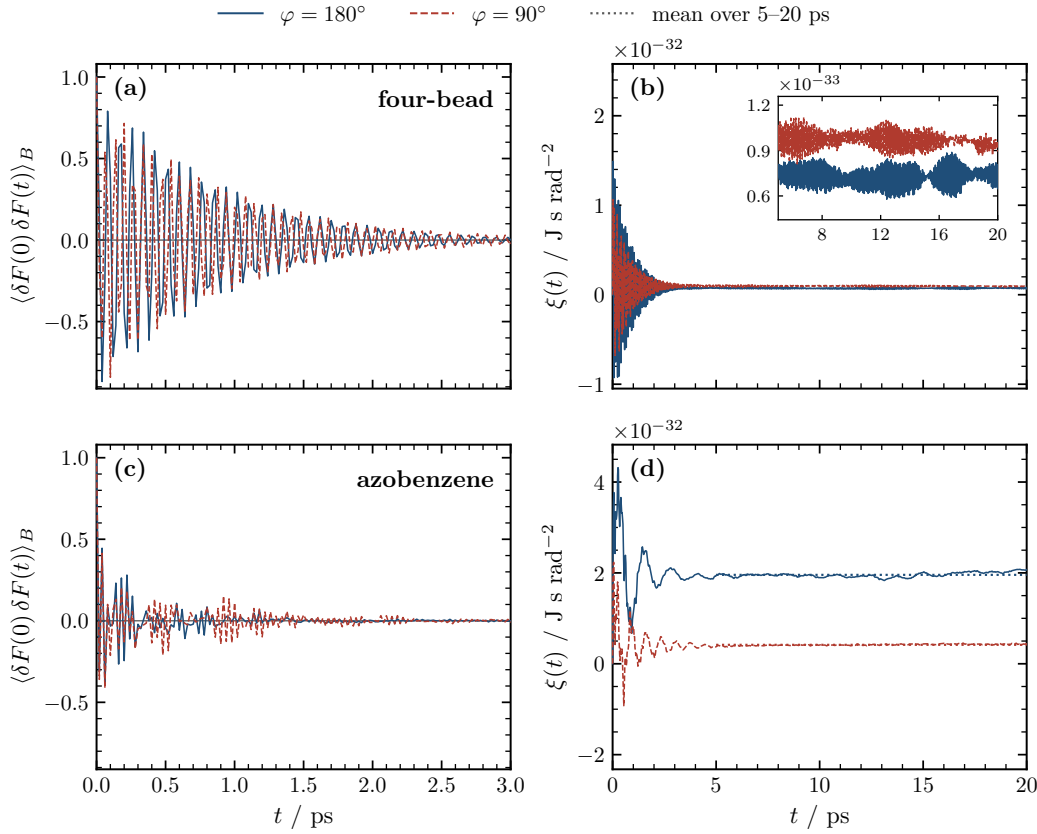


Figure 4.2: FAF and running Green-Kubo integral for the four-bead model (upper row) and for 4,4'-dihydroxyazobenzene (lower row), at the planar ($\varphi = 180^\circ$, solid blue) and perpendicular ($\varphi = 90^\circ$, dashed red) geometries. (a), (c) Autocorrelation function of the fluctuating force conjugate to the dihedral coordinate, normalized to its value at $t = 0$. (b), (d) Running integral where the dotted lines denote the mean over the 5-20 ps averaging window. The ordinate scales of (b) and (d) differ; those of (a) and (c) are common. The four-bead profiles in (b) are resolved in the inset.

finement. The corresponding oscillation frequency is $\omega_0 = 0.0423 \text{ fs}^{-1}$. The coordinate is therefore strongly confined and underdamped. This is the regime where unconstrained estimators are expected to fail, permitting their limitations to be observed directly.

4.2.2 Evaluation of the Unconstrained Extraction Methods

Equation (4.4) was discretized and solved via Volterra recursion. The derivative $\dot{C}_{vv}(t)$ was obtained from the exact identity $C_{vF}(t)/g_\varphi$, and the PMF gradient was evaluated in the harmonic approximation. As illustrated by the solid blue line in Figure 4.1(b), the recursion fails to extract a localized kernel. The physical residual driving the equation is small ($\gamma/\omega_0 = 0.13$), amplifying statistical errors in the correlation functions. This noise propagates through the convolution sum, causing the running integral to diverge linearly without attaining a plateau.

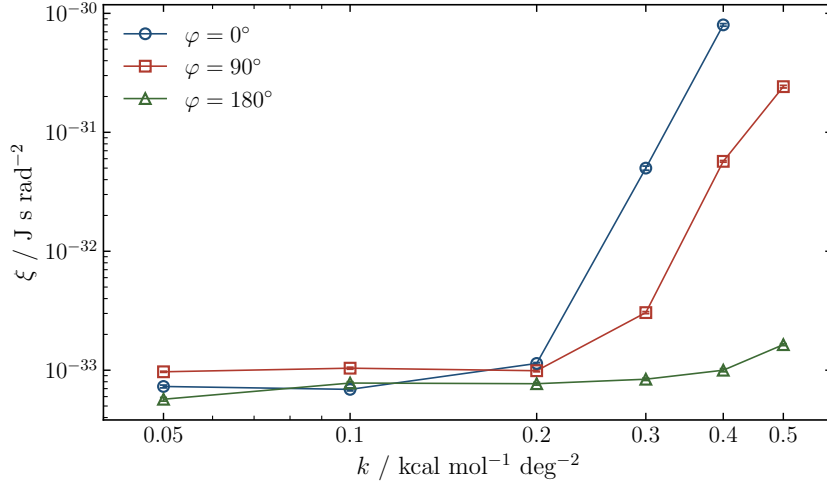


Figure 4.3: Friction coefficient of the four-bead model as a function of the harmonic restraint force constant k , at three values of the restrained dihedral angle: $\varphi = 0^\circ$ (blue circles), 90° (red squares) and 180° (green triangles). Both axes are logarithmic. Values are shown for $0.05 \leq k \leq 0.4$ at $\varphi = 0^\circ$ and for $0.05 \leq k \leq 0.5$ at the other two angles.

The Laplace-domain approach avoids deconvolution but fails structurally. Evaluating Equation (4.5) against a variable upper integration limit produces the oscillating point distribution in Figure 4.1(b). The denominator is the running integral of an oscillatory, weakly damped VACF, which periodically crosses zero. The estimator alternates in sign and diverges at half-period intervals. For a bound coordinate, the diffusion coefficient vanishes, rendering the zero-frequency limit indeterminate.

The parametric Markovian fit avoids these instabilities. Fitting Equation (4.6) to the measured VACF yields the dashed envelope in Figure 4.1(a), parameterized by a damping rate $\gamma = 5.32 \times 10^{-3} \text{ fs}^{-1}$ and a damped frequency $\Omega = 0.0422 \text{ fs}^{-1}$. The fitted frequency recovers the equipartition value, and the damping ratio ($\gamma/2\omega_0 = 0.063$) confirms the underdamped regime. The resulting friction coefficient is $\xi_{\text{VACF}} = g_\varphi \gamma = 1.21 \times 10^{-33} \text{ J s rad}^{-2}$.

4.2.3 The Constrained Force Correlation and Friction Profile

The restrained route bypasses the instabilities inherent to the unconstrained trajectory. Figure 4.2(a) displays the autocorrelation function of the fluctuating generalized force for the four-bead model at planar and perpendicular geometries. The correlation decays rapidly, allowing the running Green-Kubo integral in Figure 4.2(b) to converge to a plateau.

The restraint stiffness must first be chosen. Figure 4.3 maps the extracted friction against the harmonic force constant k at three configurations. For $k \leq 0.2 \text{ kcal mol}^{-1} \text{ deg}^{-2}$, the measured friction remains stationary. At higher values, the measurement rises by orders of magnitude, reflecting perturbation of the local solvent structure. A force constant of $k = 0.05 \text{ kcal mol}^{-1} \text{ deg}^{-2}$ ensures the coordinate

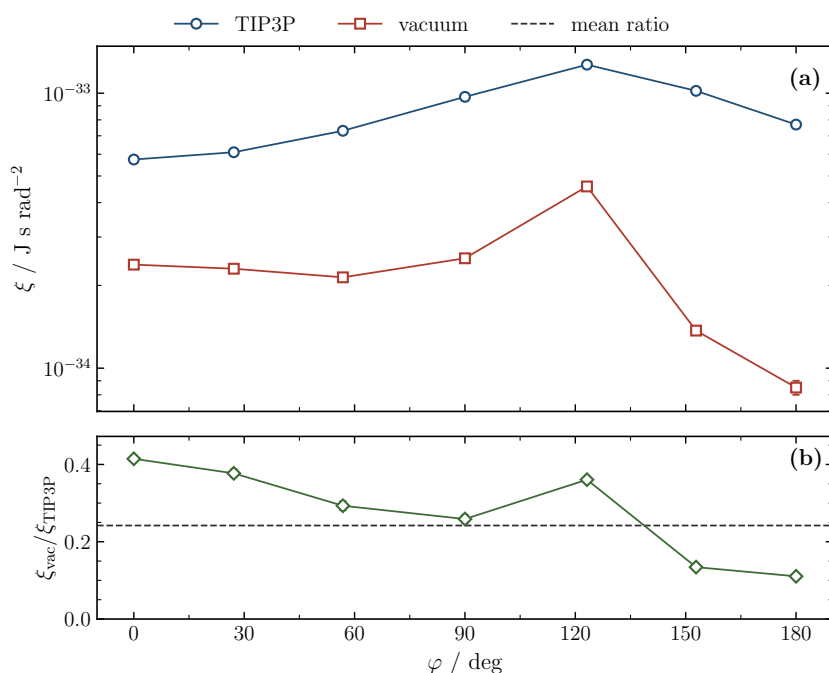


Figure 4.4: Friction profile of the four-bead model as a function of the restrained dihedral angle φ . (a) Friction coefficient in TIP3P water (blue circles) and in vacuum (red squares), on a logarithmic ordinate. (b) Ratio $\xi_{\text{vac}}/\xi_{\text{TIP3P}}$ at corresponding angles, on a linear ordinate; the dashed line marks the weighted mean of 0.24.

is localized to within 3° while residing safely on the unperturbed plateau. This value is adopted for all subsequent extractions.

Applying this protocol across the dihedral domain yields the configuration-dependent friction profile shown in Figure 4.4(a). In TIP3P water, the friction varies by a factor of 2.2, minimizing at the *cis*-planar geometry ($5.74 \times 10^{-34} \text{ J s rad}^{-2}$) and maximizing near 123° ($1.27 \times 10^{-33} \text{ J s rad}^{-2}$). The friction is therefore not a constant of the molecule, and a scalar substituted for this profile is in error by a factor of two at the extremes.

The vacuum control calculation in Figure 4.4(a) isolates the dissipative origin. With solvent removed, the friction retains 24% of its solvated magnitude and exhibits a more pronounced angular dependence, peaking at the same geometry. The internal DOF generate a structured dissipative contribution.[117, 132] Solvation scales the magnitude and alters the profile shape, as shown by the configuration-dependent ratio in Figure 4.4(b).

At the *trans*-planar geometry (180°), the constrained extraction in TIP3P yields $\xi_{\text{FACF}} = 7.69 \times 10^{-34} \text{ J s rad}^{-2}$. This value can now be evaluated against the parametric VACF estimate obtained in Subsection 4.2.2. The two values agree to within a factor of 1.6. The VACF overestimation aligns with its methodological constraints: it computes a basin-averaged friction across a $\pm 31^\circ$ sampling range rather than a local minimum, and it collapses multi-timescale dissipation into a single Markovian damping rate. This agreement validates the constrained method, establishing it as the robust protocol for extracting position-dependent friction profiles.

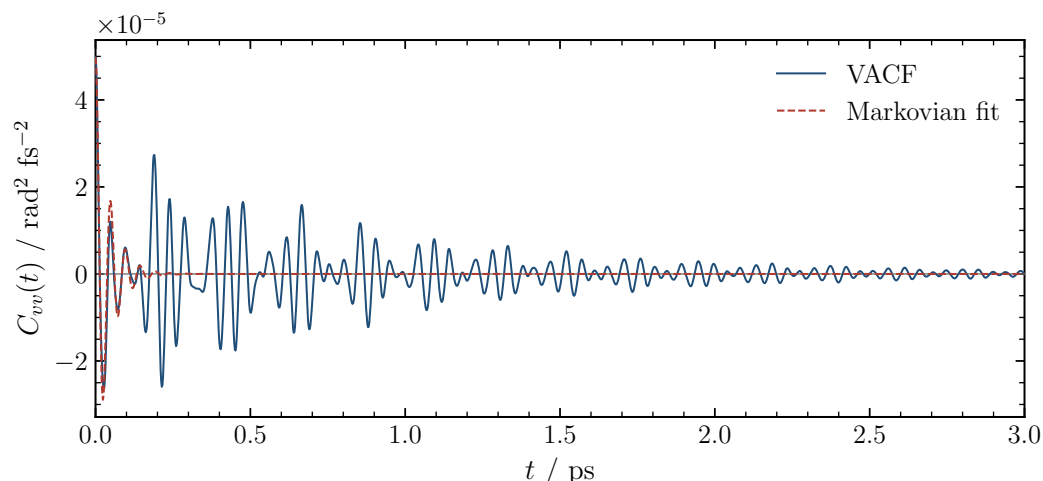


Figure 4.5: Velocity autocorrelation function of the dihedral coordinate of 4,4'-dihydroxyazobenzene in TIP4P water, extracted from an unconstrained trajectory about the *trans* minimum (solid blue), shown with the underdamped Markovian model fitted to it (dashed red). The fitted friction coefficient is $\xi = 3.77 \times 10^{-33} \text{ J s rad}^{-2}$.

4.3 4,4'-DIHYDROXYAZOBENZENE

The four-bead chain established that the restrained route extracts a configuration-dependent friction incorporating a substantial intramolecular component. To evaluate these findings in a chemical context, the protocol is applied here to 4,4'-dihydroxyazobenzene at atomistic resolution. This section assesses the performance of the extraction methodologies on a molecule with a dense internal vibrational spectrum, determines the friction profile along the C–N=N–C torsion, and evaluates the implications for the system-bath coupling assumed in Chapter 3.

4.3.1 Failure of the Unconstrained Extraction Methods

The inversion-based estimators fail for the reasons established in Section 4.2. The torsion is confined by a deep barrier and remains strongly underdamped, causing the Volterra recursion to amplify statistical noise and rendering the Laplace limit indeterminate.

The parametric fit to the unconstrained velocity autocorrelation function also fails, but through a distinct mechanism. As shown in Figure 4.5, fitting Equation (4.6) yields an envelope that decays within 0.1 ps, whereas the measured correlation function continues oscillating beyond 2 ps. The resulting friction coefficient is $\xi_{\text{VACF}} = 3.77 \times 10^{-33} \text{ J s rad}^{-2}$.

This failure originates in the fundamental assumption of Equation (4.6): that the dihedral angular velocity corresponds to a single effective oscillator. In an atomistic molecule, the dihedral velocity is modulated by fast, large-amplitude internal modes. The dominant oscillation in the measured VACF exhibits a period near 45 fs, characteristic of aromatic ring deformations rather than torsional motion about a double bond. Consequently, the equipartition relation severely underestimates the

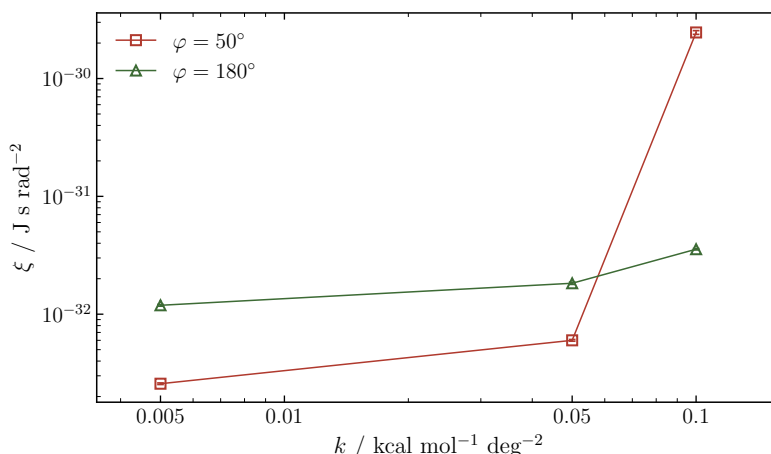


Figure 4.6: Friction coefficient of 4,4'-dihydroxyazobenzene in TIP4P water as a function of the harmonic restraint force constant k , evaluated at $\varphi = 50^\circ$ (red squares) and $\varphi = 180^\circ$ (green triangles). Both axes are logarithmic.

effective inertia. Because the extracted friction is the product of this underestimated inertia and the fitted damping rate, the resulting coefficient is suppressed. The unconstrained [VACF](#) route is therefore unusable for this complex molecule, and the restrained route is the only estimator applied below.

4.3.2 The Constrained Force Correlation and Restraint Dependence

Figure 4.2(c) displays the autocorrelation function of the fluctuating generalized force extracted via the restrained route. The correlation decays rapidly at both planar and perpendicular geometries, allowing the running Green-Kubo integral in Figure 4.2(d) to converge to a stable plateau.

The same harmonic restraint sweep was repeated for azobenzene. Figure 4.6 maps the extracted friction against the force constant k at $\varphi = 180^\circ$ and 50° , the latter a configuration selected because it exhibits the largest overestimation. At $k = 0.005 \text{ kcal mol}^{-1} \text{ deg}^{-2}$, the restraint is too weak: the angular standard deviation at 180° reaches 5.3° , and the mean angle at 50° drifts to 27° , failing to sample the target geometry. Increasing k beyond 0.05 artificially elevates the measured friction due to perturbation of the local solvent, raising the value by a factor of 1.9 at 180° and by over two orders of magnitude at 50° . The force constant $k = 0.05 \text{ kcal mol}^{-1} \text{ deg}^{-2}$ provides sufficient spatial confinement ($\sim 3^\circ$) without perturbing the surrounding bath, and is adopted for the full profile.

4.3.3 The Friction Profile and the Electrostatic Control

Evaluating the constrained protocol across seventeen configurations yields the friction profile in Figure 4.7. The dissipation varies by a factor of 6.8 along the coordinate, exhibiting maxima at the planar geometries ($2.80 \times 10^{-32} \text{ J s rad}^{-2}$ at 0° ; $1.95 \times 10^{-32} \text{ J s rad}^{-2}$ at 180°) and a broad, flat minimum across the perpendicular region ($4.10 \times 10^{-33} \text{ J s rad}^{-2}$ between 71° and 93°). The profile is asymmetric,

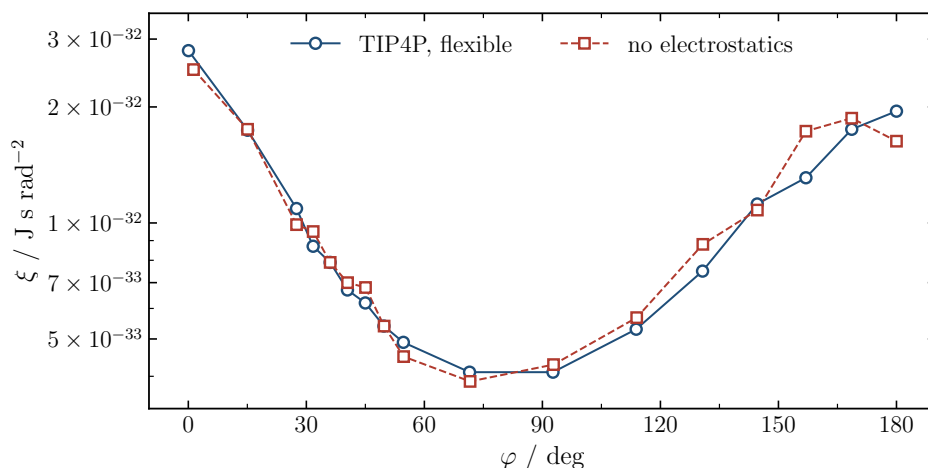


Figure 4.7: Friction profile of 4,4'-dihydroxyazobenzene as a function of φ . Data are shown for the fully flexible solute in TIP4P water (blue circles) and for a control simulation where solute-solvent electrostatic interactions are decoupled (red squares). The ordinate is logarithmic.

reflecting the differing excluded volumes and steric congestion generated by the hydroxyphenyl rings at the *cis* versus *trans* geometries.

The constrained extraction at 180° can now be compared against the parametric VACF estimate from Subsection 4.3.1. The VACF method underestimates the local friction by a factor of 5.2, confirming that the unconstrained methodology breaks down when applied to coordinates coupled to dense internal vibrational spectra.

To identify the origin of the dissipation, a control simulation decoupled all solute-solvent electrostatic interactions while retaining LJ parameters. As shown in Figure 4.7, the resulting profile is indistinguishable from that of the fully interacting system, establishing that friction along this torsion is overwhelmingly steric in origin; dielectric friction from the polar aqueous solvent contributes negligibly.

4.3.4 Consequences for the Coupling Operator

The measured profile imposes a physical constraint on the system-bath coupling operators evaluated in Chapter 3. As established in Subsection 3.4.7, a non-linear coupling $f(\hat{q})$ generates a configuration-dependent friction proportional to $f'(q)^2$.^[26]

The reference operator adopted in the quantum benchmark, $\hat{Q}_0$ whose torsional dependence is $\cos(\varphi)$, predicts a friction profile proportional to $\sin^2 \varphi$, which vanishes at planar geometries and maximizes at the perpendicular transition state. The atomistic measurement in Figure 4.7 yields the inverse topology: maxima at the planar configurations and a minimum at the perpendicular geometry.

The measured profile is qualitatively consistent with a coupling of the form $f = \sin \varphi$, which predicts $\xi(\varphi) \propto \cos^2 \varphi$. This corresponds to the operator $\hat{Q}_{\sin}$ introduced in Equation (3.61). While higher-order harmonics are required to capture the asymmetry of the atomistic profile, the fundamental topology dictates that the physical environment excludes the $\cos \varphi$ -based coupling operators upon which the prior quantum benchmark relied.

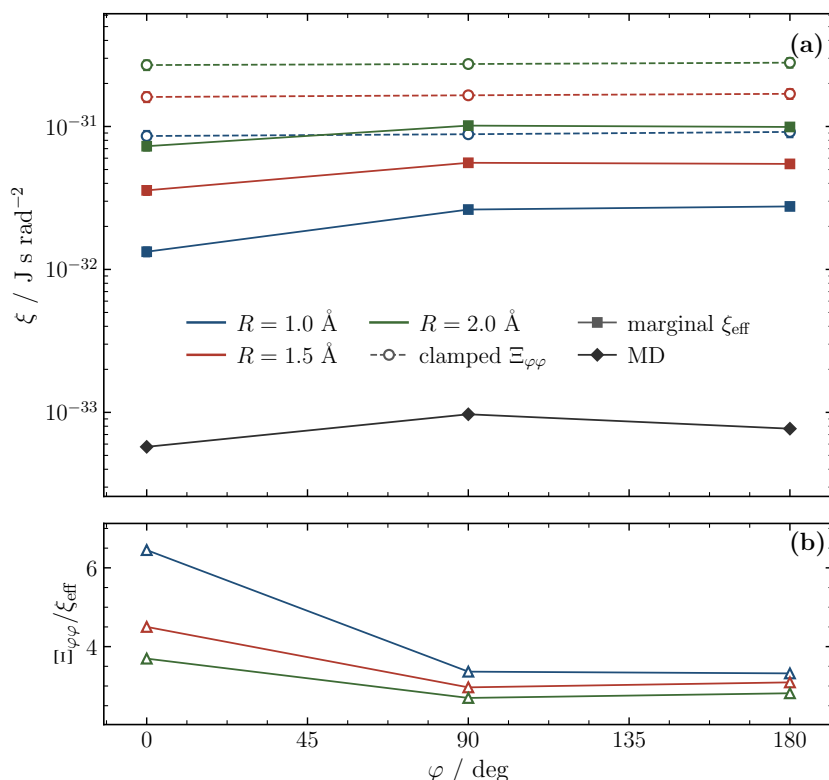


Figure 4.8: Four-bead model compared with the hydrodynamic prediction. (a) Friction coefficient against the dihedral angle on a logarithmic ordinate, for bead radii $R = 1.0, 1.5$ and $2.0 \text{ \AA}$ (blue, red and green). Open symbols joined by dashed lines give the clamped value $\Xi_{\varphi\varphi}$; filled symbols joined by solid lines give the marginal value ξ_{eff} . Black diamonds give the friction measured by MD in TIP3P water. (b) The ratio $\Xi_{\varphi\varphi} / \xi_{\text{eff}}$ at each angle, for the same three radii.

4.4 COMPARISON WITH HYDRODYNAMIC CALCULATIONS

The friction profiles in the preceding sections were extracted via explicit solvent simulations, incurring significant computational expense per configuration. An established alternative is to replace the atomistic environment with a viscous continuum, computing the drag directly from solute geometry. The comparison tests whether the environment of a rotating molecular fragment behaves as a macroscopic continuum. Because continuum models cannot capture the granular solvent displacement driven by internal DOF, reproducing the exact angular dependence of the atomistic profile is not to be expected. The objective of this comparison is to evaluate whether the hydrodynamic model, after appropriate subspace projection, recovers a friction coefficient of a consistent order of magnitude.

4.4.1 The Hydrodynamic Model

Continuum calculations were performed utilizing the DiTe2 framework,[114] which computes generalized friction and diffusion tensors from a bead-model representation.[133–136] Each atom is assigned a hydrodynamic radius R subject to Stokes

drag in a fluid of specified shear viscosity (0.89×10^{-3} Pa s for water). Hydrodynamic interactions between bead pairs are incorporated under stick boundary conditions.[137, 138]

The solver outputs the generalized friction tensor Ξ , encompassing translational, rotational, and internal coordinates. The bare diagonal element of the tensor, $\Xi_{\varphi\varphi}$, represents the clamped internal friction: the drag exerted on the torsion if global translation and orthogonal internal coordinates were pinned. In an unconstrained atomistic ensemble, macroscopic rigid-body modes thermalize and relax to accommodate internal conformational changes. The physically comparable observable is the coupled (marginal) internal friction, which accounts for this hydrodynamic relaxation.

This coupling is integrated by projecting out the orthogonal subspace via the block Schur complement

$$\xi_{\text{eff}} = \Xi_{\varphi\varphi} - \Xi_{\text{B}}^{\text{T}} \Xi_{\text{A}}^{-1} \Xi_{\text{B}} \quad (4.8)$$

where Ξ_{A} is the dissipation block governing all non-torsional modes and Ξ_{B} is the coupling vector. Because Ξ_{A} is positive definite, the coupling correction is non-negative, enforcing the physical requirement that orthogonal relaxation reduces overall drag ($\xi_{\text{eff}} \leq \Xi_{\varphi\varphi}$).

The projection is validated through the Kirkwood relation, $\mathbf{D} = k_{\text{B}}T \Xi^{-1}$. [139] Block inversion dictates the identity $(\Xi^{-1})_{\varphi\varphi} = 1/\xi_{\text{eff}}$, allowing the coupled friction to be independently derived from the diffusion tensor: $\xi_{\text{eff}} = k_{\text{B}}T/D_{\varphi\varphi}$. Across all sampled configurations, the Schur complement and diffusion-derived friction agree to within numerical precision, confirming the thermodynamic consistency of the projection.[140, 141]

To identify the specific orthogonal modes dissipating the torsional energy, dimensionless coupling coefficients are computed

$$\rho_{\varphi i} = \frac{\Xi_{\varphi i}}{\sqrt{\Xi_{\varphi\varphi} \Xi_{ii}}} \quad (4.9)$$

Bounded by the Cauchy-Schwarz inequality ($|\rho| \leq 1$), these coefficients isolate the dominant hydrodynamic screening mechanisms at each configuration.

4.4.2 The Four-Bead Model

The four-bead chain was evaluated with the full 12×12 tensor. The clamped friction at a bead radius of $1.0 \text{ \AA}$ is almost featureless, varying from 8.58×10^{-32} to $9.16 \times 10^{-32} \text{ J s rad}^{-2}$ across the whole coordinate, a range of seven per cent. Eliminating the eleven orthogonal coordinates gives a marginal friction that varies over the same interval from 1.33×10^{-32} to $2.76 \times 10^{-32} \text{ J s rad}^{-2}$, a factor of 2.1, and the reduction factor falls from 6.45 at the *cis* geometry to 3.36 and 3.32 at the perpendicular and *trans* geometries. As Figure 4.8 shows, the angular structure of the hydrodynamic prediction is generated by the coupling reduction and not by the bare torsional drag.

The coupling coefficients, collected in Table 4.1, identify the orthogonal modes performing the screening. At both planar geometries the dominant coupling is to

Rank	$\varphi = 0^\circ$		$\varphi = 90^\circ$		$\varphi = 180^\circ$	
	Mode	$\rho_{\varphi i}$	Mode	$\rho_{\varphi i}$	Mode	$\rho_{\varphi i}$
1	rotation, x	0.86	bond angle θ_1	0.75	rotation, y	0.77
2	translation, z	0.39	rotation, z	-0.63	rotation, x	-0.54
3	—	—	rotation, y	0.51	translation, z	-0.41

Table 4.1: Three largest hydrodynamic coupling coefficients (4.9) between the central torsion and the remaining coordinates of the four-bead chain, at a bead radius of 1.0 Å. Rigid-body axes refer to the principal frame of the molecule.

rigid-body rotation, and the drag upon the torsion is relieved by counter-rotation of the chain as a whole. At the perpendicular geometry the dominant coupling shifts to an internal bond angle, with rigid-body rotation falling below 0.63, while the coefficients associated with bond stretching remain negligible throughout. That the torsion should be screened by internal deformation at the barrier top and by rigid-body rotation at the minima corroborates the vacuum control of Section 4.2, and is consistent with the finding that the dihedral dynamics of small solutes in water is governed to a large extent by friction internal to the solute.[117, 132]

The comparison with the atomistic measurement nevertheless fails for this system, and by a wide margin. The marginal friction at $R = 1.0$ Å exceeds the values measured in TIP3P water by factors of between 23 and 36, and at $R = 2.0$ Å, the radius corresponding to the Lennard-Jones parameter of the beads, by factors of between 105 and 129. No radius within the range examined brings the two into agreement. Part of the discrepancy is attributable to the solvent, since the hydrodynamic calculation employs the viscosity of real water whereas TIP3P reproduces approximately a third of that value, but correcting for this leaves a residual disagreement of an order of magnitude. Two circumstances account for the remainder. The coarse-grained beads are not atoms, and their hydrodynamic radius is not determined by a Lennard-Jones parameter assigned without reference to solvent displacement; the choice of an effective hydrodynamic radius is in general the principal source of uncertainty in bead-model calculations for small solutes.[142, 143] The chain, moreover, possesses only five internal coordinates through which the torsion may be screened. The four-bead model therefore establishes the behaviour of the reduction, but does not constitute a test of the hydrodynamic magnitude.

4.4.3 4,4'-Dihydroxyazobenzene

Azobenzene was evaluated using two coordinate sets: a 7×7 tensor retaining global translation, rotation, and the central torsion, and a 70×70 tensor leaving all coordinates free. Eight dihedral angles are omitted from the 70×70 coordinate set. These are the torsions internal to the two phenyl rings, which are not independent: ring closure fixes them in terms of the remaining coordinates, so that rotation about any one of them is already accounted for by the constraints defining the ring.

The two reductions differ both in magnitude and in sense. Eliminating only the rigid-body coordinates gives reduction factors between 2.3 and 4.1 at $R = 1.0 \text{ \AA}$, and these rise from the *cis* to the *trans* geometry. Eliminating every non-torsional coordinate gives reduction factors between 19.5 and 13.6 at the same radius, reaching 39 at the smallest radius examined, and these fall from *cis* to *trans*. Figure 4.9(c) and (d) display the two trends. The internal DOFs of the molecule, and not its rigid-body motion, therefore perform the greater part of the screening, so that the rigid-body treatment constitutes an upper bound upon the marginal friction rather than an estimate of it.

Only the full reduction furnishes a quantity comparable with the atomistic measurement, in which the molecule translates, rotates and deforms freely about the restrained dihedral. Figure 4.9 bears this out. The 7×7 marginal friction exceeds the measured profile at every configuration and every radius examined, by roughly an order of magnitude at the planar geometries and by considerably more at the perpendicular one, even at the smallest radius. The 70×70 marginal friction at $R = 1.0 \text{ \AA}$ is $1.84 \times 10^{-32} \text{ J s rad}^{-2}$ at the *cis* geometry, 2.47×10^{-32} at the perpendicular geometry and 2.45×10^{-32} at the *trans* geometry, against measured values of 2.80×10^{-32} , 4.10×10^{-33} and $1.95 \times 10^{-32} \text{ J s rad}^{-2}$. At the two planar geometries the continuum calculation therefore agrees with the explicit-solvent measurement to within factors of 1.5 and 1.3, at a bead radius physically reasonable for a hydrodynamic sphere representing a carbon atom.[136, 142] At the perpendicular geometry it exceeds the measurement by a factor of 6.0.

The coupling coefficients of the full tensor, collected in Table 4.2, are structurally uniform along the coordinate. At every configuration the screening is dominated by rigid-body rotation about the long molecular axis together with two internal torsions, while every coefficient associated with a bond length or a bond angle remains below 0.10. The continuum model attributes the screening throughout to counter-rotation of the molecule and of its aromatic rings, and offers no mechanism by which that arrangement should change character at the perpendicular geometry.

Two conclusions follow. The first concerns the treatment of the tensor. An order-of-magnitude disagreement between hydrodynamic and explicit-solvent estimates of torsional friction is in large part an artefact of comparing a clamped quantity with a coupled one. Applying Equation (4.8) with every non-torsional coordinate eliminated brings the two descriptions into agreement within a small factor at the planar geometries of a flexible aromatic solute, at a physically admissible bead radius. The projection is not a refinement of the comparison but a precondition for it, and the necessity of treating internal coordinates explicitly is consistent with hydrodynamic treatments of flexible molecules developed for the interpretation of relaxation data.[144, 145]

The second concerns the residual disagreement, which is localized rather than systematic. The measured profile possesses a deep minimum at the perpendicular geometry, falling to fifteen per cent of its maximum, whereas the hydrodynamic profile rises by some thirty per cent from *cis* to *trans* and exhibits no minimum. A model representing the solute as a smooth envelope of spheres in a structureless fluid possesses no mechanism for the collapse in drag that accompanies the mutual perpendicularity of the two rings. The vacuum control of Section 4.2 indicates

Rank	$\varphi = 0^\circ$		$\varphi = 90^\circ$		$\varphi = 180^\circ$	
	Mode	$\rho_{\varphi i}$	Mode	$\rho_{\varphi i}$	Mode	$\rho_{\varphi i}$
<i>7 × 7 tensor, rigid solute</i>						
1	rotation, x	0.71	rotation, y	0.57	rotation, y	0.73
2	translation, z	0.37	translation, x	0.45	translation, z	−0.46
3	rotation, y	0.24	rotation, z	−0.40	—	—
<i>70 × 70 tensor, flexible solute</i>						
1	torsion τ_2	0.36	rotation, x	−0.42	rotation, x	−0.62
2	rotation, x	−0.35	torsion τ_2	0.33	torsion τ_2	0.38
3	torsion τ_1	0.28	torsion τ_1	0.26	torsion τ_1	0.30

Table 4.2: Three largest hydrodynamic coupling coefficients (4.9) between the central C–N=N–C torsion of 4,4′-dihydroxyazobenzene and the remaining coordinates, at a bead radius of 1.0 Å, for the two coordinate sets. The torsions τ_1 and τ_2 are the rotations of the two hydroxyphenyl rings about their C–N bonds. Rigid-body axes refer to the principal frame of the molecule.

why: a substantial and angularly structured fraction of the dissipation originates in the internal motion of the solute, which a hydrodynamic model omits by construction.[132] The consequence for the dynamics is that the hydrodynamic estimate departs from the atomistic measurement most severely at the perpendicular geometry, which is the region of the avoided crossing where the non-adiabatic dynamics of Chapter 3 is most sensitive to the friction.

A methodological asymmetry remains in how the two ensembles are constrained. The atomistic protocol evaluates the correlation function with the internal coordinate restrained while the molecule translates and rotates freely in the solvent, which is the condition the full reduction reproduces. A rigorous comparison against the 7 × 7 tensor would instead require atomistic simulations matching its boundary conditions, with the centre of mass (COM) and the molecular orientation held fixed and the internal coordinate actively sampled. In an isotropic and homogeneous environment, static orientational constraints would suffice; in an anisotropic environment such as a liquid crystal the orientational DOFs would have to be sampled explicitly.[144–146] Implementing such constraints within the atomistic extraction is a natural direction for further methodological work, and would place the two calculations upon identical boundary conditions.

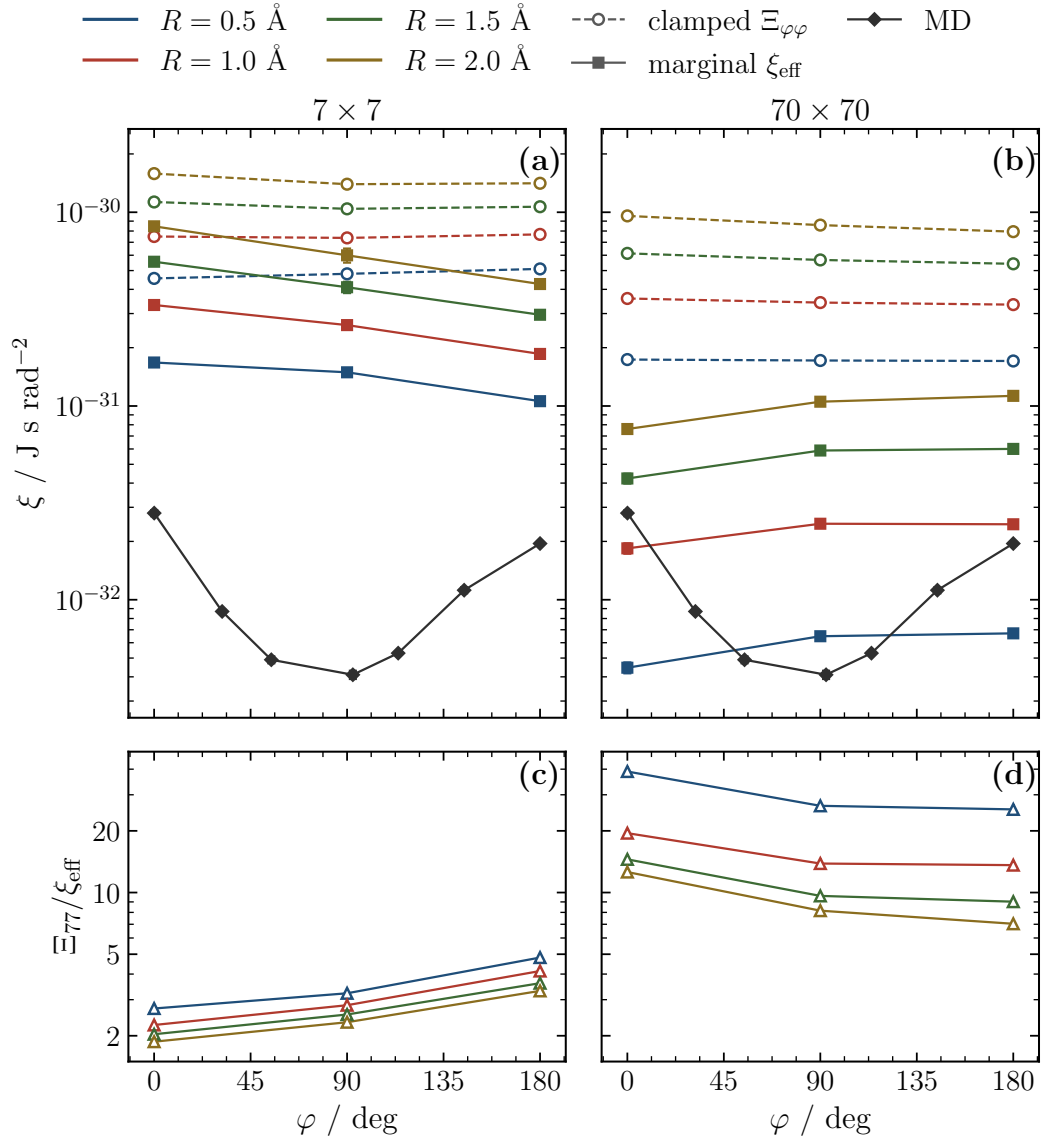


Figure 4.9: Azobenzene compared with the hydrodynamic prediction, for two levels of hydrodynamic detail: a 7×7 tensor in the left column, (a) and (c), and a 70×70 tensor in the right column, (b) and (d). (a), (b) Friction coefficient against the dihedral angle on a common logarithmic ordinate, for bead radii $R = 0.5, 1.0, 1.5$ and $2.0 \text{ \AA}$. Open symbols joined by dashed lines give the clamped value Ξ_{77} and filled symbols joined by solid lines the marginal value ξ_{eff} . Black diamonds give the MD friction. (c), (d) The ratio $\Xi_{\varphi\varphi}/\xi_{\text{eff}}$ for the same radii.

CONCLUSIONS AND PERSPECTIVES

5.1 SYNTHESIS

This thesis has examined what survives the elimination of a molecular environment, whether the surviving quantity is the same object in a classical and in a quantum description of the same process, and whether it can be measured rather than assigned.

Chapter 2 executed this elimination through a unified projection-operator framework. For classical systems, projecting the Liouville equation onto the conditional equilibrium bath distribution produces a GLE. The drift derives from a PMF, and the memory kernel is the configuration-dependent autocorrelation tensor of the fluctuating environmental force. By relaxing the assumption of linear system-bath coupling, the configuration dependence of the friction emerges as a consequence. For quantum systems, truncating the analogous projection at second order and invoking the Markovian limit yields the Redfield equation, characterizing the environment via the power spectrum of the coupling operator sampled at the system transition frequencies. These parallel derivations do not inherently guarantee that the classical zero-frequency transform and the quantum frequency-resolved spectrum describe identical environments.

Chapter 3 established their equivalence within a specific model: a harmonic bath bilinearly coupled to the system yields both descriptors from a common parameter set. Evaluating this correspondence on a non-adiabatic photoisomerization model revealed divergences. In the quantum description, the spatial distribution of dissipation is governed by the coupling operator, which dictates the branching ratio independently of coupling strength. Under the secular approximation, coupling strength rescales the kinetic timeline without altering product distribution. In the mixed quantum-classical framework, friction modulates both kinetics and branching, exhibiting Kramers turnover. Reproducing the quantum branching ratio required a classical friction exceeding the corresponding quantum coupling strength by two orders of magnitude, highlighting the breakdown of the analytical correspondence for periodic coordinates. Subject to this calibration, the two descriptions yielded matching asymptotic populations and spatially resolved densities.

Chapter 4 replaced the postulated descriptors with values extracted from atomistic MD. Estimators relying on unconstrained trajectories failed for a bound torsional coordinate: Volterra inversion amplified statistical noise, Laplace transformation yielded indeterminate limits, and parametric fitting collapsed multi-timescale relaxation into a single damping rate, underestimating the friction by a factor of 5.2. Evaluating the restrained FACF provided a configuration-resolved friction profile for 4,4-dihydroxyazobenzene in explicit water. The extracted friction varies by a factor of 6.8, maximizing at planar geometries and minimizing across the perpendicular region. Removing solute-solvent electrostatic interactions left the pro-

file unchanged, confirming its steric origin. This angular topology invalidates the cosine-based coupling operators assumed in the quantum benchmark, aligning instead with a sine-based coupling. Comparing atomistic results against continuum hydrodynamics demonstrated that projecting out orthogonal non-torsional coordinates via the Schur complement resolves the standard order-of-magnitude discrepancy, achieving near-quantitative agreement at planar geometries while localizing residual divergence at the perpendicular transition state.

5.2 SUMMARY OF ORIGINAL CONTRIBUTION

The primary theoretical contribution is the generalized projection-operator derivation of Subsection 2.1.6 and Appendix A, presented at a generality that standard treatments do not supply. This formulation does not impose linear system-bath interaction and therefore gives a configuration-resolved friction tensor and a fluctuation-dissipation relation emergent from the construction itself. That derivation is the basis of the extraction protocol developed subsequently.

The dissipative vibronic quantum dynamics of Subsection 3.3.2 was implemented as part of this work, as was the comparative protocol of Section 3.4, in which the parameters of the two descriptions are calibrated against integrated populations alone and the spatially resolved densities are reserved as a prediction. The benchmark quantifies the failure of the analytical correspondence for a periodic coordinate, and identifies the coupling operator as an independent bath descriptor for which the quantum-classical formalism possesses no analogue.

The extraction protocol of Section 4.1, its implementation, the atomistic simulations of Sections 4.2 and 4.3, and the analysis bridging the atomistic and hydrodynamic tensors of Section 4.4 were developed here. They furnish the configuration-resolved friction profile along the photoisomerizing torsion of a solvated azobenzene derivative, the identification of that dissipation as steric and intramolecular in origin, and the demonstration that the Schur projection is a precondition rather than a refinement of any comparison between continuum and atomistic methodologies.

5.3 OPEN CHALLENGES AND FUTURE OUTLOOK

Integrating the measured descriptor into the quantum dynamics framework presents specific challenges.

The secular approximation adopted in Chapter 3 precludes the turnover physics captured by the quantum-classical description. Restoring the full Redfield tensor couples populations to coherences and recovers the dependence of the branching ratio upon coupling strength. The dense vibronic spectrum generated by the semi-classical inertia renders sparse tensor algorithms inefficient, necessitating a reduction of the computational domain to a thermally accessible active space. Furthermore, the environmental counterterm must be restored to correctly renormalize the potential energy surfaces in proportion to the coupling strength.

A more fundamental limitation remains in the implementation of the bath descriptor. A non-linear coupling in the reaction coordinate generates a spatially

varying friction, yet current quantum-classical propagators assume a constant coefficient. Developing a quantum-classical propagator that admits configuration-dependent friction, together with the corresponding spatially varying counterterm on the quantum side, is the prerequisite for closing the pipeline. The friction of Subsection 3.4.6 and the value measured at the *trans* geometry in Chapter 4 agree to within a small factor, which suggests that the closure is within reach once the descriptor is admitted in its measured form rather than as a scalar. The agreement between the friction required for the benchmark in Subsection 3.4.6 and the measured atomistic friction at the planar geometry in Section 4.3 suggests this closure is physically attainable.

Several questions concerning the descriptor remain open. The Markovian approximation should be validated by comparing the measured decay time of the FACF against the correlation time $\tau_B = \omega_c^{-1}$ assumed in the benchmarks. The integration of conditional mean forces will yield the PMF, defining the correct free-energy surface for the reduced dynamics. A vacuum control calculation for azobenzene is needed to isolate the specific contributions of solvent and internal coordinates to the observed friction, raising the question of whether intramolecular dissipation should be grouped within the macroscopic bath.

Three further directions follow naturally. First, separating the friction from the decoherence time in the quantum-classical description, which the present implementation ties together through $\tau = g_\varphi / \xi_\varphi$, requires a parameter sweep at fixed decoherence time. Second, placing the atomistic and hydrodynamic calculations upon identical boundary conditions requires restrained simulations in which the COM and the molecular orientation are held fixed. Finally, the reduction of the multidimensional friction tensor to the marginal coefficient conjugate to a single reactive coordinate, performed here for the hydrodynamic tensor by the Schur complement, admits the same treatment atomistically, and would extend the description to processes in which more than one coordinate carries the chemistry.

GENERALIZED KLEIN-KRAMERS - APPENDIX

This appendix supplies the algebraic derivation omitted from Subsection 2.1.6, adopting the notation and physical assumptions established therein.

THE NAKAJIMA-ZWANZIG EQUATION

With $f = \hat{\mathcal{P}}\rho$, $g = \hat{\mathcal{Q}}\rho$ and $\hat{\mathcal{P}} + \hat{\mathcal{Q}} = 1$, Equation (2.34) separates into

$$\frac{\partial f}{\partial t} = -i\hat{\mathcal{P}}\hat{\mathcal{L}}f - i\hat{\mathcal{P}}\hat{\mathcal{L}}g \quad (\text{A.1})$$

$$\frac{\partial g}{\partial t} = -i\hat{\mathcal{Q}}\hat{\mathcal{L}}g - i\hat{\mathcal{Q}}\hat{\mathcal{L}}f \quad (\text{A.2})$$

Equation (A.2) is a linear, inhomogeneous differential equation in g , admitting the formal solution

$$g(t) = e^{-i\hat{\mathcal{Q}}\hat{\mathcal{L}}t} g(0) - \int_0^t d\tau e^{-i\hat{\mathcal{Q}}\hat{\mathcal{L}}\tau} i\hat{\mathcal{Q}}\hat{\mathcal{L}} f(t-\tau) \quad (\text{A.3})$$

Assuming the environment is initially equilibrated conditional upon the initial configuration of the system implies $\rho(0) = \rho_B \rho_S(0)$. This initial state is annihilated by $\hat{\mathcal{Q}}$, so that $g(0) = 0$. Substituting Equation (A.3) into Equation (A.1) yields the exact Nakajima-Zwanzig generalized master equation

$$\frac{\partial}{\partial t} \hat{\mathcal{P}}\rho(t) = -i\hat{\mathcal{P}}\hat{\mathcal{L}} \hat{\mathcal{P}}\rho(t) + \int_0^t d\tau \hat{\mathcal{P}} i\hat{\mathcal{L}} e^{-i\hat{\mathcal{Q}}\hat{\mathcal{L}}\tau} i\hat{\mathcal{Q}}\hat{\mathcal{L}} \hat{\mathcal{P}}\rho(t-\tau) \quad (\text{A.4})$$

THE REVERSIBLE DRIFT

To evaluate the systematic drift term $-i\hat{\mathcal{P}}\hat{\mathcal{L}}f$, we first expand the action of the full Liouvillian on the factorized state. Since ρ_B is stationary under $i\hat{\mathcal{L}}_B$ and ρ_S is independent of $(\mathbf{y}, \pi)$, only $i\hat{\mathcal{L}}_S$ contributes. Furthermore, since ρ_B is independent of $\mathbf{p}$, the product rule gives

$$i\hat{\mathcal{L}}(\rho_B \rho_S) = (\mathbf{m}^{-1}\mathbf{p}) \cdot \left(\frac{\partial \rho_B}{\partial \mathbf{x}} \right) \rho_S + \rho_B \left[(\mathbf{m}^{-1}\mathbf{p}) \cdot \frac{\partial \rho_S}{\partial \mathbf{x}} + \mathbf{F}_S \cdot \frac{\partial \rho_S}{\partial \mathbf{p}} \right] \quad (\text{A.5})$$

Because the parametric dependence of H_B on $\mathbf{x}$ resides entirely in $u(\mathbf{x}, \mathbf{y})$, differentiation of Equation (2.42) gives

$$\frac{\partial \ln Z}{\partial \mathbf{x}} = \frac{1}{Z} \int d\mathbf{y} d\pi \left(-\beta \frac{\partial u}{\partial \mathbf{x}} \right) e^{-\beta H_B} = \beta \langle \mathbf{F} \rangle_{\mathbf{x}} \quad (\text{A.6})$$

Consequently, differentiating the conditional density of Equation (2.41) provides

$$\frac{\partial \rho_B}{\partial \mathbf{x}} = \rho_B \frac{\partial}{\partial \mathbf{x}} (-\beta u - \ln Z) = \beta \rho_B (\mathbf{F} - \langle \mathbf{F} \rangle_{\mathbf{x}}) = \beta \rho_B \delta \mathbf{F} \quad (\text{A.7})$$

Applying $\hat{\mathcal{P}}$ to Equation (A.5) integrates over the environmental phase space $(\mathbf{y}, \boldsymbol{\pi})$ and restores the distribution ρ_B . The first term vanishes because $\langle \delta \mathbf{F} \rangle_{\mathbf{x}} = 0$; in the second term, the integration affects only the force, generating the gradient of the potential of mean force

$$\langle \mathbf{F}_S \rangle_{\mathbf{x}} = -\frac{\partial V}{\partial \mathbf{x}} + \langle \mathbf{F} \rangle_{\mathbf{x}} = -\frac{\partial}{\partial \mathbf{x}} [V(\mathbf{x}) - \beta^{-1} \ln Z(\mathbf{x})] = -\frac{\partial \mathcal{A}(\mathbf{x})}{\partial \mathbf{x}} \quad (\text{A.8})$$

so that the reversible drift evaluates to

$$-i\hat{\mathcal{P}}\hat{\mathcal{L}}f = \rho_B \left[-(\mathbf{m}^{-1}\mathbf{p}) \cdot \frac{\partial \rho_S}{\partial \mathbf{x}} + \frac{\partial \mathcal{A}}{\partial \mathbf{x}} \cdot \frac{\partial \rho_S}{\partial \mathbf{p}} \right] \quad (\text{A.9})$$

THE MEMORY KERNEL

Applying $\hat{\mathcal{Q}}$ to Equation (A.5) isolates the fluctuating component of the dynamics. Utilizing Equation (A.7) yields the source term for the memory integral

$$i\hat{\mathcal{Q}}\hat{\mathcal{L}}f(t) = \rho_B \delta \mathbf{F} \cdot \left(\frac{\partial}{\partial \mathbf{p}} + \beta \mathbf{m}^{-1} \mathbf{p} \right) \rho_S(t) \quad (\text{A.10})$$

Insertion of this source term into the memory integral of Equation (2.43) yields

$$\mathcal{J} = \int_0^t d\tau \hat{\mathcal{P}} i\hat{\mathcal{L}} e^{-i\hat{\mathcal{Q}}\hat{\mathcal{L}}\tau} \left[\rho_B \delta \mathbf{F} \cdot \left(\frac{\partial}{\partial \mathbf{p}} + \beta \mathbf{m}^{-1} \mathbf{p} \right) \rho_S(t-\tau) \right] \quad (\text{A.11})$$

Because the orthogonal propagator $e^{-i\hat{\mathcal{Q}}\hat{\mathcal{L}}\tau}$ is not available in closed form, the derivation invokes the assumption of a timescale separation. By assuming the environment relaxes rapidly compared to the system coordinates, the orthogonal propagator is replaced by $e^{-i\hat{\mathcal{L}}_B\tau}$, the propagator generated by H_B at fixed $\mathbf{x}$. This is the sole substantive dynamical approximation of the derivation, rendering the memory kernel computationally accessible as an equilibrium correlation function.

Under this bath propagator, ρ_B is stationary, and $(\partial/\partial \mathbf{p} + \beta \mathbf{m}^{-1} \mathbf{p}) \rho_S$ contains no environmental variables and therefore commutes with the propagator, so that

$$e^{-i\hat{\mathcal{L}}_B\tau} \left[\rho_B \delta \mathbf{F} \cdot \left(\frac{\partial}{\partial \mathbf{p}} + \beta \mathbf{m}^{-1} \mathbf{p} \right) \rho_S \right] = \rho_B \delta \mathbf{F}(-\tau) \cdot \left(\frac{\partial}{\partial \mathbf{p}} + \beta \mathbf{m}^{-1} \mathbf{p} \right) \rho_S \quad (\text{A.12})$$

where the Liouville propagator displaces the environmental fluctuating force backwards in time.

When applying $\hat{\mathcal{P}} i\hat{\mathcal{L}}$ to Equation (A.12), three of its four constituent terms vanish. The contribution of $i\hat{\mathcal{L}}_B$ vanishes because it is a total divergence in the closed phase space of the environment. The operators $(\mathbf{m}^{-1}\mathbf{p}) \cdot \partial/\partial \mathbf{x}$ and $-(\partial V/\partial \mathbf{x}) \cdot \partial/\partial \mathbf{p}$ contain no environmental variables, commuting with the integration to leave the isolated factor $\langle \delta \mathbf{F}(-\tau) \rangle_{\mathbf{x}}$, which is zero by definition. Only the term $\mathbf{F} \cdot \partial/\partial \mathbf{p}$ survives. Its mean part vanishes upon integration for the same reason, and since the instantaneous force $\mathbf{F}$ is independent of $\mathbf{p}$ it may be taken inside the derivative, giving

$$\mathcal{J} = \rho_B \int_0^t d\tau \frac{\partial}{\partial \mathbf{p}} \cdot \left[\mathbf{C}_{FF}(\mathbf{x}, -\tau) \cdot \left(\frac{\partial}{\partial \mathbf{p}} + \beta \mathbf{m}^{-1} \mathbf{p} \right) \rho_S(t-\tau) \right] \quad (\text{A.13})$$

with the memory tensor defined as

$$\mathbf{C}_{\text{FF}}(\mathbf{x}, \tau) = \left\langle \delta \mathbf{F}(\mathbf{x}, 0) \delta \mathbf{F}(\mathbf{x}, \tau)^T \right\rangle_{\mathbf{x}} \quad (\text{A.14})$$

Stationarity of the conditional equilibrium ensemble guarantees $\mathbf{C}_{\text{FF}}(-\tau) = \mathbf{C}_{\text{FF}}(\tau)^T$. Moreover, because $\mathbf{F}$ depends only upon configurational positions, it is invariant under reversal of the environmental momenta, mandating that $\mathbf{C}_{\text{FF}}$ is a symmetric tensor. Therefore, $\mathbf{C}_{\text{FF}}(-\tau) = \mathbf{C}_{\text{FF}}(\tau)$.

Adding Equations (A.9) and (A.13), dividing by ρ_B and setting $\xi(\mathbf{x}, \tau) = \beta \mathbf{C}_{\text{FF}}(\mathbf{x}, \tau)$ gives the generalized Klein-Kramers equation

$$\begin{aligned} \frac{\partial \rho_S(\mathbf{x}, \mathbf{p}, t)}{\partial t} = & -(\mathbf{m}^{-1} \mathbf{p}) \cdot \frac{\partial \rho_S}{\partial \mathbf{x}} + \frac{\partial \mathcal{A}(\mathbf{x})}{\partial \mathbf{x}} \cdot \frac{\partial \rho_S}{\partial \mathbf{p}} \\ & + k_B T \int_0^t d\tau \frac{\partial}{\partial \mathbf{p}} \cdot \left[\xi(\mathbf{x}, \tau) \cdot \left(\frac{\partial}{\partial \mathbf{p}} + \beta \mathbf{m}^{-1} \mathbf{p} \right) \rho_S(\mathbf{x}, \mathbf{p}, t - \tau) \right] \end{aligned} \quad (\text{A.15})$$

THE MARKOVIAN LIMIT

If $\xi(\mathbf{x}, \tau)$ decays to zero over a time interval sufficiently short that ρ_S does not vary appreciably, then $\rho_S(t - \tau) \simeq \rho_S(t)$ and the upper limit may be extended to infinity, so that the time integration acts upon the memory kernel alone

$$\int_0^\infty d\tau \xi(\mathbf{x}, \tau) = \xi(\mathbf{x}) \quad (\text{A.16})$$

Under this Markovian limit, Equation (2.44) becomes local in time,

$$\frac{\partial \rho_S}{\partial t} = \left[-(\mathbf{m}^{-1} \mathbf{p}) \cdot \frac{\partial}{\partial \mathbf{x}} + \frac{\partial \mathcal{A}}{\partial \mathbf{x}} \cdot \frac{\partial}{\partial \mathbf{p}} + \frac{\partial}{\partial \mathbf{p}} \cdot \xi(\mathbf{x}) \cdot \left(\mathbf{m}^{-1} \mathbf{p} + k_B T \frac{\partial}{\partial \mathbf{p}} \right) \right] \rho_S \quad (\text{A.17})$$

For a single coordinate, a friction independent of position, and $\mathcal{A}$ identified with V , Equation (A.17) reduces to Equation (2.23) and Equation (A.16) reduces to Equation (2.20).

COMPUTATIONAL DETAILS - APPENDIX

This appendix summarizes the numerical parameters defining the fully quantum and the quantum-classical implementations. The physical constants governing the system Hamiltonian are defined in Subsection 3.3.1, and the comparative simulation parameters are specified in Subsection 3.4.1.

THE FULLY QUANTUM IMPLEMENTATION

Basis Set and Spatial Grid

The torsional coordinate is expanded in the free-rotor basis of Equation (3.62), symmetrically truncated at a maximum plane-wave momentum $k_{\text{max}} = 250$. This truncation yields 501 basis functions per electronic surface, generating a total vibronic basis dimension of 1002. For the evaluation of the configuration-dependent observables defined in Equation (3.66) and the spatially resolved densities, the density matrix is projected onto a spatial grid comprising 1000 points uniformly distributed across the angular interval $[-\pi/2, 3\pi/2]$. The transformation between the momentum basis and the spatial grid is executed via discrete Fourier transform matrices.

Environmental Functions

The evaluation of the quantum dispersion function $\mathcal{S}(\omega)$ introduced in Equation (3.54) requires computing a principal value integral. For the Drude-Lorentz spectral density of Equation (3.24), this integral is resolved analytically utilizing a Matsubara frequency expansion.[147] The expansion is truncated at 500 terms to ensure numerical convergence across the sampled frequency range.

Propagation Protocol

The system Hamiltonian (3.46) is evaluated via full matrix diagonalization to extract the vibronic eigenstates. As detailed in Subsection 3.3.2, the master equation is decoupled into independent population and coherence blocks via the secular approximation. Because the population transition rates of Equation (3.63) are time-independent, the populations are propagated through direct matrix exponentiation. The coherences are updated concurrently via analytical exponential decay according to the rates defined in Equation (2.85). The equations of motion are integrated using a fixed time step of 0.05 ps up to a total simulation time of 100 ps.

THE QUANTUM-CLASSICAL IMPLEMENTATION

The quantum-classical calculations were executed utilizing the QSLE-v1.0 software package.[99] The physical variables, including the configuration-independent friction coefficient and the covariant metric tensor elements, are detailed in Subsection 3.3.3.

Phase-Space Grid

To resolve the Fokker-Planck operator of Equation (3.69) numerically, the continuous phase-space density is discretized upon a two-dimensional grid. The angular domain $[-\pi, \pi)$ is partitioned into 300 discrete points. The conjugate momentum domain is symmetrically truncated at a maximum absolute value of $1.5 \text{ amu } \text{\AA}^2 \text{ rad fs}^{-1}$ and partitioned into 301 points.

Propagation Protocol

The phase-space partial derivatives required to evaluate deterministic classical propagation, momentum diffusion, and frictional drag are computed using a finite difference method. The resulting discretized equations of motion, coupled to the surface-hopping probabilities defined in Equation (3.44), are integrated using a fixed time step of 0.005 fs.

Algorithmic details are documented in the user guide accompanying the original software release.[99]

THE WIGNER DISTRIBUTION OF THE INITIAL STATE

This appendix derives the phase-space distribution of the quantum initial state (3.64) and compares it with the Maxwell-Boltzmann distribution (3.71) employed by the quantum-classical calculation.

REDUCTION TO A SINGLE HARMONIC MODE

In the *trans* well the diabatic gap $V_{11}(\pi) - V_{00}(\pi) = E_1$ exceeds λ by a factor of nearly forty, so that the mixing angle (3.51) is negligible and the lowest eigenstate of Equation (3.46) factorizes as $|\Psi_0\rangle \simeq |\psi_0\rangle \otimes |\chi_0\rangle$. The operator $\hat{\sigma}_x$ in Equation (3.64) acts on the electronic factor alone; the nuclear state remains $|\chi_0\rangle$ following excitation, and the phase-space distribution of the initial state is that of χ_0 .

Defining $u = \varphi - \pi$ and expanding Equation (3.48) gives

$$V_{00} = \frac{1}{2}W_0 (1 + \cos \varphi) = \frac{1}{4}W_0 u^2 \left(1 - \frac{1}{12}u^2 + \dots\right) \quad (\text{C.1})$$

which yields the harmonic frequency of the *trans* well

$$\omega_0 = \sqrt{\frac{W_0}{2M_\varphi}} \quad (\text{C.2})$$

The adiabatic surface V_0 differs from V_{00} by $-\lambda^2/(V_{11} - V_{00})$. The curvature of this difference at $\varphi = \pi$ alters Equation (C.2) by a relative magnitude of $\lambda^2(W_0 + W_1)/E_1^2 W_0 \sim 10^{-3}$. The quartic term in Equation (C.1) contributes a comparable correction over the sampled range of u . Both corrections are neglected.

WIGNER TRANSFORM

The normalized ground state of Equation (C.1) is the Gaussian

$$\chi_0(u) = (2\pi\sigma_\varphi^2)^{-1/4} \exp(-u^2/4\sigma_\varphi^2) \quad (\text{C.3})$$

with $\sigma_\varphi^2 = \hbar/2M_\varphi\omega_0$. Its Wigner transform,

$$W_0(\varphi, p_\varphi) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} ds e^{-ip_\varphi s/\hbar} \chi_0^*\left(u - \frac{s}{2}\right) \chi_0\left(u + \frac{s}{2}\right) \quad (\text{C.4})$$

factorizes into a function of u and a Gaussian in s , evaluating to

$$W_0(\varphi, p_\varphi) = \frac{1}{\pi\hbar} \exp\left[-\frac{(\varphi - \pi)^2}{2\sigma_\varphi^2} - \frac{p_\varphi^2}{2\sigma_p^2}\right] \quad (\text{C.5})$$

with the respective variances

$$\sigma_\varphi^2 = \frac{\hbar}{2M_\varphi\omega_0} \quad \sigma_p^2 = \frac{\hbar M_\varphi\omega_0}{2} \quad (\text{C.6})$$

This distribution is normalized on the phase plane and saturates the uncertainty product, $\sigma_\varphi \sigma_p = \hbar/2$. Equation (C.5) is non-negative everywhere, satisfying Hudson's theorem for pure states with Gaussian wavefunctions,[148] permitting direct comparison with a classical phase-space density.

COMPARISON WITH THE CLASSICAL DISTRIBUTIONS

In the same harmonic approximation, the distribution (3.71) is a Gaussian centered upon the same point, with variances

$$\left(\sigma_\varphi^{\text{cl}}\right)^2 = \frac{k_B T}{M_\varphi \omega_0^2} \quad \left(\sigma_p^{\text{cl}}\right)^2 = M_\varphi k_B T \quad (\text{C.7})$$

Both classical widths exceed their quantum counterparts by the scaling factor

$$\frac{\sigma^{\text{cl}}}{\sigma} = \sqrt{\frac{2}{\beta \hbar \omega_0}} \quad (\text{C.8})$$

which is approximately three for $\beta \hbar \omega_0 \simeq 0.2$. This is the discrepancy visible in Figure 3.3. Equation (C.8) identifies its origin: it is the ratio of a thermal spread to a zero-point spread, and it is large because the mode is in the classical limit.

The discrepancy stems from preparation rather than representation, as demonstrated by the Wigner function for the thermal state of the same mode,

$$W_\beta(\varphi, p_\varphi) = \frac{1}{\pi \hbar} \tanh\left(\frac{\beta \hbar \omega_0}{2}\right) \exp\left[-\frac{2}{\hbar \omega_0} \tanh\left(\frac{\beta \hbar \omega_0}{2}\right) H_0(\varphi, p_\varphi)\right] \quad (\text{C.9})$$

with $H_0 = p_\varphi^2/2M_\varphi + \frac{1}{2}M_\varphi\omega_0^2(\varphi - \pi)^2$. Equation (C.9) reduces to Equation (C.5) as $T \rightarrow 0$ and to Equation (3.71) as $\hbar \rightarrow 0$. The high-temperature expansion $x \coth x = 1 + x^2/3 + \dots$ yields the variances relative to Equation (C.7) as

$$\frac{(\sigma^\beta)^2}{(\sigma^{\text{cl}})^2} = \frac{\beta \hbar \omega_0}{2} \coth\left(\frac{\beta \hbar \omega_0}{2}\right) = 1 + \frac{(\beta \hbar \omega_0)^2}{12} + \mathcal{O}[(\beta \hbar \omega_0)^4] \quad (\text{C.10})$$

which introduces a correction of approximately three parts in a thousand. This is the same high-temperature expansion utilized in Equation (3.21). A thermally prepared torsion is therefore represented by the Maxwell-Boltzmann distribution within this accuracy margin. The scaling factor of three in Equation (C.8) is attributable to the quantum calculation initializing in the vibronic ground state rather than sampling a thermal ensemble.

REMARK ON THE PERIODIC COORDINATE

Equation (C.4) is the Wigner transform for a coordinate on the real line, whereas φ is a periodic angle with a discrete conjugate momentum. The continuous and periodic formalisms differ by terms involving the overlap of χ_0 with its 2π -displaced

images. For $\sigma_\varphi \ll \pi$, these terms scale as $\exp(-\pi^2/2\sigma_\varphi^2)$ and remain negligible for this system. This conclusion applies equally to the classical density of Equation (3.71).

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