Microscopic Theory II: Mass Action Kinetic Equations

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1 Phenomenology

- Chemical reactions are described by mass action kinetic equations that specify how the mean concentrations of chemical species vary with time. Under what circumstances is such a description possible? How may one compute the values of the rate constants that enter these equations from a knowledge of the microscopic properties of the system?

- Consider a reaction among n chemical species $X_i,\ i = 1, \ldots, n$ of the form

$$\nu_1 X_1 + \nu_2 X_2 + \cdots \nu_n X_n \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \bar{\nu}_1 X_1 + \bar{\nu}_2 X_2 + \cdots \bar{\nu}_n X_n \ , \tag{1}$$

characterized by the forward and reverse rate constants k_f and k_r.

  - The stoichiometric coefficients are ν_i and $\bar{\nu}_i$ for reactants and products, respectively. The mass action rate law for the average numbers $\bar{N}_i$ of the chemical species is

$$\frac{d\bar{N}_i(t)}{dt} = (\nu_i - \bar{\nu}_i)\left[-k_f \prod_{j=1}^{n} \bar{N}_j^{\nu_j}(t) + k_r \prod_{j=1}^{n} \bar{N}_j^{\bar{\nu}_j}(t)\right] = (\nu_i - \bar{\nu}_i) J \ , \tag{2}$$

    The second equality defines the reaction rate J which is independent of the species label in view of the constraints on the particle number changes implied by Eq. (1).

  - Note that in equilibrium, $d\bar{N}_i(t)/dt = 0$, and hence

$$\left[-k_f \prod_{j=1}^{n} \left(\bar{N}_j^{eq}\right)^{\nu_j} + k_r \prod_{j=1}^{n} \left(\bar{N}_j^{eq}\right)^{\bar{\nu}_j}\right] = 0. \tag{3}$$

  - Equation (2) can be used to define the progress variable $\bar{\chi}(t)$ which characterizes the extent of reaction [1]:

$$\frac{d\bar{\chi}(t)}{dt} = (\nu_i - \bar{\nu}_i)^{-1} \frac{d\bar{N}_i(t)}{dt} = J \ . \tag{4}$$

    This equation may be integrated from time t to $t = \infty$, where the system is in equilibrium and $\bar{\chi}(\infty) = 0$, to obtain

$$\bar{\chi}(t) = (\nu_i - \bar{\nu}_i)^{-1}(\bar{N}_i(t) - \bar{N}_i^{eq}) \ . \tag{5}$$

    Only a single dynamical variable $\bar{\chi}$ is needed to characterize the extent of reaction.

- Expanding the average particle numbers in terms of the progress variable and linearizing in $\bar{\chi}$ and using (3), we obtain

$$\frac{d\bar{\chi}(t)}{dt} = -k\bar{\chi}(t) \tag{6}$$

- The rate constant k is given by

$$k = \sum_{j=1}^{n}(\nu_j - \bar{\nu}_j)\left[k_f \prod_{i=1}^{n}(\bar{N}_i^{eq})^{\nu_i}\frac{\nu_j}{\bar{N}_j^{eq}} - k_r \prod_{i=1}^{n}(\bar{N}_i^{eq})^{\bar{\nu}_i}\frac{\bar{\nu}_j}{\bar{N}_j^{eq}}\right] . \tag{7}$$

- The deviations of average particle number is driven by the chemical affinity

$$\mathcal{A}(t) = \sum_{i=1}^{n}\mu_i(t)(\nu_i - \bar{\nu}_i) , \tag{8}$$

  which vanishes in equilibrium when $\mu_i(t) = \mu_i$.

- Finally, we note that Eq. (6) may be integrated to yield

$$\bar{\chi}(t) - \bar{\chi}(0) = -k\int_0^t dt'\bar{\chi}(t-t') , \tag{9}$$

2 Microscopic description

2.1 Nonequilibrium initial ensemble

- We assume that the system adjusts quickly to the slow chemical process, so that a kind of constrained equilibrium applies for the system. We therefore require that the thermodynamic driving force, the chemical affinity $\mathcal{A}(t)$ is small.

- We consider an initial nonequilibrium ensemble where only the progress variable is constrained to deviate from its zero equilibrium value.

- The nonequilibrium ensemble for the system at constant temperature T and volume V may be constructed from the usual canonical distribution by appending an additional term $\chi\mathcal{A}$ to the Hamiltonian H of the system:

$$\hat{\rho}(0) = \frac{e^{-\beta(H-\chi\mathcal{A})}}{\int d\mathbf{x}^{(N)}\, e^{-\beta(H-\chi\mathcal{A})}} , \tag{10}$$

  where $\beta = (kT)^{-1}$ as usual. It then follows that the average value of the progress variable is given by

$$\bar{\chi}(t) = \int d\mathbf{x}^{(N)}\, \chi(t)\hat{\rho}(0) . \tag{11}$$

  - This type of *local equilibrium* distribution can be obtained by requiring the initial ensemble average of the progress variable is constrained to be $\bar{\chi}(0)$.
  - Generalizations to this equation to include local concentrations may be used in which the average particle numbers $\bar{N}_i$ depend on the position in the system.

- Since the affinities $\mathcal{A}$ are assume to be small,

$$e^{-\beta(H-\chi\mathcal{A})} = e^{-\beta H}\ (1+\beta\chi\mathcal{A}+\cdots)\,, \tag{12}$$

and we may write the linearized form of $\hat{\rho}(0)$ as

$$\rho(0) = \rho_e\ (1+\beta\chi\mathcal{A}+\ldots)\,, \tag{13}$$

from which it follows that

$$\bar{\chi}(t) = \langle\chi(t)\chi\rangle\,\beta\mathcal{A}\,, \tag{14}$$

where $\langle\cdot\rangle$ denotes the equilibrium average and we have used the fact that

$$\langle\chi(t)\rangle = \int d\mathbf{x}^{(N)}\chi(t)\rho_e = (\nu_i-\bar{\nu}_i)^{-1}\left(\langle\bar{N}_i(t)\rangle - \bar{N}_i^{eq}\right) = 0.$$

Here ρ_e is the equilibrium distribution function,

$$\rho_e = \frac{e^{-\beta H}}{\int d\mathbf{x}^{(N)}\,e^{-\beta H}}\,. \tag{15}$$

- From Eq. (14) one observes that near equilibrium the nonequilibrium average of $\hat{\chi}(t)$ is given by the autocorrelation function describing the fluctuations of the progress variable about equilibrium.

2.2 Rate law derivation

- To derive the chemical rate law, one starts from the equations of motion of the progress variable:

$$\frac{d\chi(t)}{dt} = \mathcal{L}\chi(t) = e^{\mathcal{L}t}\mathcal{L}\chi\,, \tag{16}$$

and extracts the evolution proportional to $\chi(t)$ using projection operator methods. [2, 3]

- In view of the above considerations, an appropriate projection operator is

$$\mathcal{P}\mathcal{B} = \langle\mathcal{B}\chi\rangle\,\langle\chi\chi\rangle^{-1}\,\chi \tag{17}$$

since $\mathcal{P}$ just projects $\mathcal{B}$ onto χ.

- Substituting the operator identity

$$e^{\mathcal{L}t} = \int_0^t d\tau\,e^{\mathcal{L}(t-\tau)}\mathcal{P}\mathcal{L}e^{\mathcal{Q}\mathcal{L}\tau} + e^{\mathcal{Q}\mathcal{L}t}\,, \tag{18}$$

where $\mathcal{Q} = 1-\mathcal{P}$, into the last equality in Eq. (16), we obtain the generalized Langevin equation for $\chi(t)$:

$$\frac{d\chi(t)}{dt} = -\int_0^t d\tau\,\tilde{k}(\tau)\chi(t-\tau) + R(t)\,, \tag{19}$$

where the rate kernel is defined as

$$\tilde{k}(\tau) = \left\langle\left(e^{\mathcal{Q}\mathcal{L}t}\mathcal{L}\chi\right)\,\mathcal{L}\chi\right\rangle\langle\chi\chi\rangle^{-1}\,. \tag{20}$$

- The random reactive flux $R(t)$ is

$$R(t) = e^{\mathcal{Q}\mathcal{L}t}\mathcal{L}\chi \ . \tag{21}$$

  - Since $\langle\dot{\chi}\rangle = 0$, it follows that $\mathcal{Q}\dot{\chi} = \dot{\chi}$.
  - By construction, $R(t) = \mathcal{Q}R(t)$, and since

$$\langle(\mathcal{Q}B)\,\chi\rangle = \langle B\chi\rangle - \langle B\chi\rangle\,\langle\chi\chi\rangle^{-1}\,\langle\chi\chi\rangle = 0,$$

    we see that $\int d\mathbf{x}^{(N)}\,\rho(0)R(t) = 0$.

- From this property, the average of Eq. (19) over the initial nonequilibrium ensemble yields the generalized chemical rate law,

$$\frac{d\chi(t)}{dt} = -\int_0^t d\tau\,\tilde{k}(\tau)\bar{\chi}(t-\tau) \ . \tag{22}$$

  Using Eq. (14), we also note that this equation can be written as

$$\frac{dC_\chi(t)}{dt} = -\int_0^t d\tau\,\tilde{k}(\tau)C_\chi(t-\tau) \ , \tag{23}$$

  where $C_\chi(t) = \langle\chi(t)\chi\rangle\langle\chi\chi\rangle^{-1}$ is the normalized progress variable autocorrelation function.

  - This equation establishes the fact that we may monitor either the decay of the progress variable fluctuations about equilibrium or the decay of nonequilibrium initial states to determine the rate constant.

- It is convenient to integrate Eq. (22) over time in order to express the time evolution of the progress variable as

$$\bar{\chi}(t) - \bar{\chi}(0) = -\int_0^t dt'\tilde{K}(t')\bar{\chi}(t-t') \ , \tag{24}$$

  which involves the new rate kernel

$$\tilde{K}(t) = \int_0^t d\tau\tilde{k}(\tau) = \left\langle e^{\mathcal{Q}\mathcal{L}t}\chi\mathcal{L}\chi\right\rangle\langle\chi\chi\rangle^{-1} \ . \tag{25}$$

- We next consider the conditions under which the generalized rate laws, Eqs. (22) or (24), reduce to their phenomenological forms, Eqs. (6) or (9), respectively. In order to do this we need to examine the structure of the rate kernels.

2.3 Structure of the rate kernel

- Since $\langle\chi\mathcal{L}\chi\rangle = 0$ we see from Eq. (25) that the initial value of the rate kernel is zero, $\tilde{K}(0) = 0$.

- The projection operator $\mathcal{P}$ was constructed to project out of the dynamics of any operator that part which is proportional to the progress variable χ. Consequently, since the reactive flux autocorrelation function $\tilde{k}(t)$ evolves by projected dynamics $\mathcal{Q}\hat{\mathcal{L}}$, it will decay to zero on a microscopic time scale provided there are no other slowly varying degrees of freedom in the system other than $\chi(t)$.

- In this circumstance $\chi(t)$ will decay much more slowly than $\tilde{k}(t)$ and we may take $\hat{\chi}(t)$ out of the integral in Eq. (22) for times $t >> t_{mic}$, the microscopic decay time of $\tilde{k}(t)$.

- If t^* is a time such that $t_{mic} << t^* << t_{chem}$ we may write

$$\frac{d\bar{\chi}(t)}{dt} \simeq -\left[\int_0^{t^*} d\tau \tilde{k}(\tau)\right] \bar{\chi}(t) \ . \tag{26}$$

By time t^*, $\tilde{k}(t)$ will have decayed essentially to zero and we may extend the integral to infinity and identify the rate constant k by the infinite time integral of the reactive flux autocorrelation function,

$$k = \int_0^{\infty} dt \tilde{k}(t) \ , \tag{27}$$

in analogy with autocorrelation function expressions for other thermal transport coefficient expressions. Similarly, on the basis of these considerations, we see that the generalized rate law, Eq. (24), will reduce to the phenomenological form, Eq. (9), for times longer than t_{mic} where $\tilde{K}(t)$ assumes its asymptotic value k and may be removed from under the integral:

$$\begin{aligned} \bar{\chi}(t) - \bar{\chi}(0) &= -\int_0^t dt' \tilde{K}(t') \bar{\chi}(t-t') \ , \\ &\rightarrow -k \int_0^t dt' \bar{\chi}(t-t') \ , \quad (t >> t_{mic}) \ . \end{aligned} \tag{28}$$

So we have $\tilde{K}(\infty) = k$.

- Next, we consider the consequences of replacing projected dynamics by ordinary dynamics

$$e^{\mathcal{Q}\mathcal{L}t}\chi \rightarrow e^{\mathcal{L}t}\chi \equiv \chi(t) \ , \tag{29}$$

in the rate kernel expressions so that the rate kernel $\tilde{K}(t)$ takes the form

$$K(t) = \langle \chi(t) \mathcal{L}\chi \rangle \langle \chi\chi \rangle^{-1} \ , \tag{30}$$

while $\tilde{k}(t)$ becomes

$$k(t) = \langle \mathcal{L}\chi(t) \mathcal{L}\chi \rangle \langle \chi\chi \rangle^{-1} \ . \tag{31}$$

The tilde will be dropped when the operators or variables evolve by ordinary dynamics.

- To establish a relationship between the reactive flux rate kernels $\tilde{k}(t)$ and $k(t)$ for projected and unprojected dynamics, respectively we differentiating Eq. (23) to obtain

$$k(t) = -\tilde{k}(t) - \int_0^t d\tau \tilde{k}(\tau) \frac{d}{dt} C_\chi(t-\tau) \ , \tag{32}$$

whose Laplace transform is

$$k(z) = -\tilde{k}(z) - \tilde{k}(z)[zC_\chi(z) - 1] \ . \tag{33}$$

Here the Laplace transform of any function $f(t)$

$$f(z) = \int_0^{\infty} dt e^{-zt} f(t) \ , \tag{34}$$

is denoted by the same symbol but with argument z.

– Using the fact that

$$C_\chi(z) = (z + \tilde{k}(z))^{-1} \ , \tag{35}$$

we obtain

$$k(z) = \frac{z\tilde{k}(z)}{z + \tilde{k}(z)} \ . \tag{36}$$

– Note that since

$$\lim_{z\to 0} \tilde{k}(z) = \int_0^\infty d\tau \tilde{k}(\tau) \equiv \tilde{K}(t=\infty) = k \ , \tag{37}$$

we have

$$\lim_{z\to 0} K(z) = K(t=\infty) = 0 \ : \tag{38}$$

the rate kernel with unprojected dynamics decays to zero rather than to the rate constant k.

– The long time decay of $K(t)$ may be determined from the small z behavior of Eq. (36):

$$\tilde{k}(z) \approx k \ , \ \ K(z) = \frac{k(z)}{z} \approx \frac{k}{z+k} \ , \tag{39}$$

from which it follows that

$$K(t) \approx ke^{-kt} \ . \tag{40}$$

– Since $\tilde{k}(z) = zk(z)/(z - k(z))$, the large frequency behavior of both kernels is the same, $\tilde{k}(z) \approx k(z)$ (z large), so that the short time structure of both kernels is the same.

– Costley and Pechukas [4] showed that $C_\chi(t) \sim t^{3/2}$ for short times so $\tilde{K}(t) \sim t^{1/2}$ and $K(t) \sim t^{1/2}$ and both kernels grow parabolically.

– Similarly, both $\tilde{k}(t)$ and $k(t)$ diverge as $t^{-1/2}$ for short times.

- As a result of these considerations we may sketch the graphs of both $\tilde{K}(t)$ and $K(t)$ and these are shown in Fig. 1.

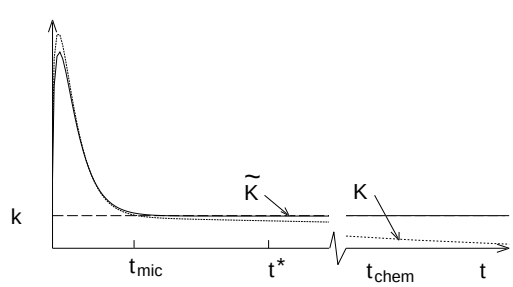

Figure 1: Sketch of projected $\tilde{K}(t)$ and unprojected $K(t)$ rate kernels versus time for a quantum mechanical system.

- Thus, provided the chemical relaxation time is much longer than any microscopic relaxation time in the system, $t_{chem} = k^{-1} >> t_{mic}$, $K(t)$ will first decay on a time scale t_{mic} to a plateau value given by $K(t^*)$, $t_{mic} << t^* << t_{chem}$, followed by a slow decay to zero. [5] In this circumstance

$$k \approx K(t^*) = \langle \chi(t^*) \mathcal{L} \chi \rangle \langle \chi \chi \rangle^{-1} \tag{41}$$

- Should such time scale separation not obtain, then the generalized rate law, Eqs. (22) or (24), must be used and the rate kernel evolution must be computed using projected dynamics.

3 Application of reactive flux formalism

In order to examine the structure of the classical rate kernel consider a simple system with a single reactive degree of freedom q governed by a double-well free energy potential $W(q)$ shown in Fig. 2.

- One can define the progress variable to monitor if the coordinate q lies to the left (species A) or to the right (species B) of the transition state at $q^\ddagger$:

$$\chi(q) = \theta(q - q^\ddagger) - \langle \theta(q - q^\ddagger) \rangle \ . \tag{42}$$

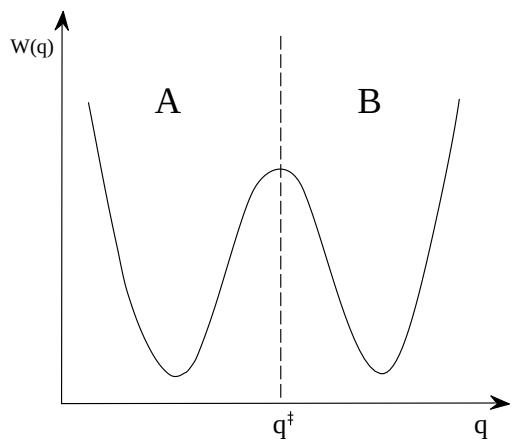

Figure 2: Free energy along the reaction coordinate showing the reactant and product regions separated by a free energy barrier at $q^\ddagger$.

  - Here $\theta(q)$ is the Heaviside function.

- For this progress variable, the rate kernel may be written more explicitly as

$$K(t) = \left\langle \dot{q} \delta(q - q^\ddagger) \theta(q(t) - q^\ddagger) \right\rangle \langle \chi \chi \rangle^{-1} \ . \tag{43}$$

- The $t = 0^+$ limit of $K(t)$ yields the transition state theory expression for the rate constant. [6]

– For short times $t = \epsilon$, $(\epsilon > 0)$, one has $q(t) \approx q^{\ddagger} + \epsilon\dot{q} + \mathcal{O}(\epsilon^2)$ and

$$\lim_{\epsilon \to 0} K(\epsilon) = \langle \dot{q}\delta(q - q^{\ddagger})\theta(\dot{q})\rangle \langle \chi\chi\rangle^{-1} = \langle \dot{q}\theta(\dot{q})\rangle \langle \delta(q - q^{\ddagger})\rangle \langle \chi\chi\rangle^{-1} \equiv k^{\mathrm{TST}} \ . \tag{44}$$

– We may identify this quantity with the transition state theory expression for the rate constant since

$$\langle \delta(q - q^{\ddagger})\rangle = \frac{e^{-\beta W(q^{\ddagger})}}{\int dq\, e^{-\beta W(q)}} \ , \tag{45}$$

thus, we have

$$k^{\mathrm{TST}} = \frac{\langle |\dot{q}|\rangle}{\langle \chi\chi\rangle} \frac{e^{-\beta W(q^{\ddagger})}}{\int dq\, e^{-\beta W(q)}} \ . \tag{46}$$

- The relationship between the rate kernel and the TST value of the rate constant is sketched in Fig. 3.

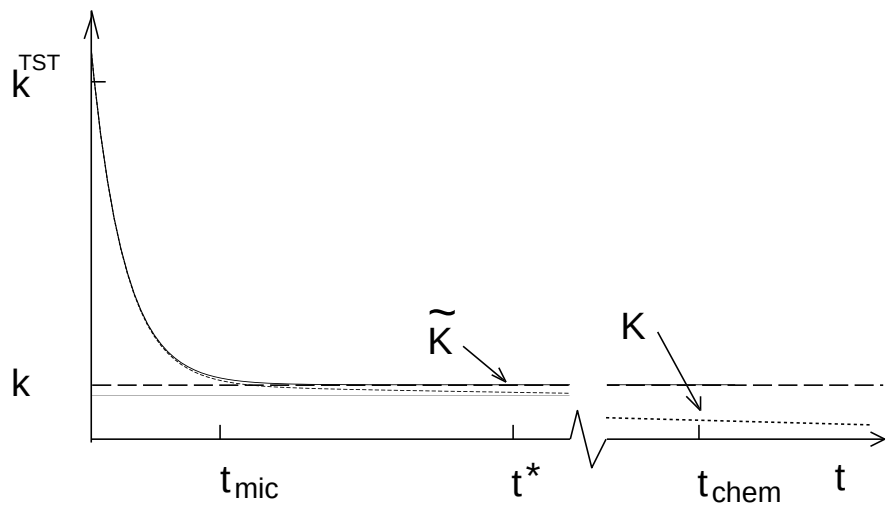

Figure 3: Sketch of projected $\tilde{K}(t)$ and unprojected $K(t)$ rate kernels versus time for a classical system.

- The above results may be generalized to any many-body reaction coordinate $\xi(R)$. In this case the progress variable is defined analogously to Eq. (42),

$$\chi(\xi(R)) = \theta(\xi(R) - \xi^{\ddagger}) - \langle \theta(\xi(R) - \xi^{\ddagger})\rangle \ . \tag{47}$$

where the generalized reaction coordinate $\xi(R)$ takes the place of q.

- The formal expressions for the rate kernel are similar to those derived above:

$$K(t) = \left\langle \dot{\xi}\delta(\xi - \xi^{\ddagger})\theta(\xi(t) - \xi^{\ddagger})\right\rangle \langle \chi\chi\rangle^{-1} \ ; \tag{48}$$

- In principle, the transition state result does not always assume a simple form since it may not be possible to factor the coordinate and velocity parts of this expression as was done in Eq. (46).

- Equation (48) forms the basis for a computational algorithm for evaluating the rate constant for rare reactive events. [6]

  - The rate kernel may be written as the product of the transition state rate constant, k^{TST}, and a time dependent transmission coefficient, $\kappa(t)$,

$$K(t) \equiv k^{\mathrm{TST}}\kappa(t) \ . \tag{49}$$

  - Once the coordinate $\xi(R)$ has been selected, the first step in the calculation is the determination of the free energy along the generalized reaction coordinate.
  - The minima in the free energy may be identified with the stable chemical species and the maxima (saddle points) with the transition states separating these species. The transition state rate constant is given by the $t = 0^+$ value of the rate kernel,

$$k^{\mathrm{TST}} = \langle \dot{\xi}\theta(\dot{\xi})\delta(\xi - \xi^{\ddagger})\rangle\langle\chi\chi\rangle^{-1} \ . \tag{50}$$

  - The transmission coefficient can be calculated by selecting configurations with the system constrained to the barrier top, $\xi = \xi^{\ddagger}$, releasing the constraint and determining the recrossing correction from

$$\kappa(t) = \frac{\langle \dot{\xi}\delta(\xi - \xi^{\ddagger})\theta(\xi(t) - \xi^{\ddagger})\rangle}{\langle \dot{\xi}\theta(\dot{\xi})\delta(\xi - \xi^{\ddagger})\rangle} \ . \tag{51}$$

- If $\kappa(t)$ is observed to decay to a plateau value on a microsopic time scale, well separated from the chemical relaxation time, the rate constant k can be determined directly from this plateau. If such a plateau is not observed this signals the breakdown of the phenomenological rate description and projected dynamics must be used to describe the rate kernel evolution.

3.1 Diffusive barrier crosssing: projected versus ordinary dynamics

In order to quantitatively examine some of the features of projected dynamics we consider again the double well free energy discussed above but assume the that full molecular dynamics is replaced by a diffusion model via the Smoluchowski equation discussed earlier:

$$\frac{\partial\rho(q,t)}{\partial t} = -\frac{\partial}{\partial q}[F(q)\rho(q,t)] + D\frac{\partial^2}{\partial q^2}\rho(q,t) \equiv \mathcal{L}_{FP}\rho(q,t) \ . \tag{52}$$

This equation defines the Fokker-Planck operator $\mathcal{L}_{FP}$.

- Here $F(q) = -dW(q)/dq$ is the mean force.

- The equation of motion for the progress variable $\chi(q,t) = \chi(t)$ (or any other dynamical variable) is

$$\frac{d\chi(t)}{dt} = \mathcal{L}^{\dagger}_{FP}\chi(t) \ , \tag{53}$$

  where the adjoint Fokker-Planck operator is

$$\mathcal{L}^{\dagger}_{FP} = F(q)\frac{\partial}{\partial q} + D\frac{\partial^2}{\partial q^2} \ . \tag{54}$$

- The classical formulas derived above apply directly to this problem if the classical Liouville operator $\mathcal{L}$ is replaced by the adjoint Fokker-Planck operator $\mathcal{L}_{FP}^{\dagger}$ and the phase space equilibrium averages are replaced by configuration space averages over the stationary distribution of Eq. (52):

$$\langle \cdots \rangle = \int_{-\infty}^{\infty} dq \rho_e(q) \cdots \ , \tag{55}$$

where

$$\rho_e(q) = \frac{e^{-W(q)/D}}{\int dq e^{-W(q)/D}} \ . \tag{56}$$

- In order to compute the rate kernels $\tilde{K}(t)$ and $K(t)$ we need to consider the eigenvalue problems for the $\mathcal{QL}_{FP}$ and $\mathcal{L}_{FP}$ operators as well as the $(\mathcal{QL}_{FP})^{\dagger}$ and $\mathcal{L}_{FP}^{\dagger}$ adjoint operators:

$$\mathcal{L}_{FP}\psi_n(q) = -\lambda_n \psi_n(q) \ , \quad \mathcal{QL}_{FP}\phi_n(q) = -\mu_n \phi_n(q) \ , \tag{57}$$

and

$$\mathcal{L}_{FP}^{\dagger}\psi_n^{\dagger}(q) = -\lambda_n \psi_n^{\dagger}(q) \ , \quad (\mathcal{QL}_{FP})^{\dagger}\phi_n^{\dagger}(q) = -\mu_n \phi_n^{\dagger}(q) \ . \tag{58}$$

- The Fokker-Planck operator $\mathcal{L}_{FP}$ has a zero eigenvalue and eigenfunction $\psi_0(q) = \rho_e(q)$, corresponding to total number conservation.
  - If the $A \rightleftharpoons B$ interconversion process is activated we expect that $\lambda_1 \approx 0$ and all higher eigenvalues will be well separated from λ_1 if $\chi(q)$ is the only slow dynamical variable.
  - In contrast, $\mathcal{QL}_{FP}$ ($(\mathcal{QL}_{FP})^{\dagger}$) has a doubly degenerate zero eigenvalue corresponding to total number and species conservation since the slow species variable $\chi(q)$ dynamics has been projected out of the evolution.
- For a symmetric double well one may establish that [7]

$$\mu_{2n} = \lambda_{2n} \ , \quad (n > 0) \ , \tag{59}$$

and

$$\lambda_{2n} < \mu_{2n+1} < \lambda_{2n+1} \ . \tag{60}$$

- The two eigenvalue spectra are sketched schematically in Fig. 4.
- We may now write the rate kernel in terms of the eigenvalues and eigenfunctions of $\mathcal{QL}_{FP}$:

$$\begin{aligned} \tilde{K}(t) &= \langle \chi\chi \rangle^{-1} \sum_{m=0}^{\infty} \langle \chi | \mathcal{L}_{FP} | \phi_{2m+1} \rangle \langle \phi_{2m+1} | \chi | \psi_0 \rangle e^{-\mu_{2m+1} t} \ , \\ &\equiv k + \sum_{m=1}^{\infty} \tilde{c}_m e^{-\mu_{2m+1} t} \ , \end{aligned} \tag{61}$$

where we have used an abstract notation: $\langle A|B \rangle = \int dq A(q) B(q)$.

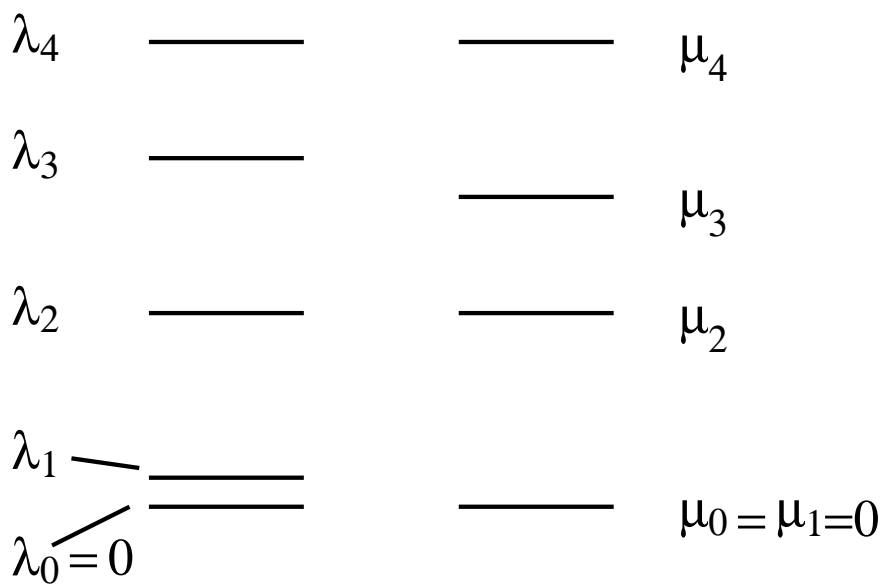

Figure 4: Eigenvalue spectra for the projected and unprojected Fokker-Planck operators.

- The even eigenstates do not contribute to the sum in view of the symmetry of the potential.
- For long times only the smallest non-zero eigenvalue determines the behavior. Since $\mu_1 = 0$, this eigenvalue is μ_3 and we have

$$\tilde{K}(t) \approx k + ce^{-\mu_3 t} \ . \tag{62}$$

- We see that as expected $\tilde{K}(t)$ decays to its plateau value k on a time scale determined by μ_3.

- The rate kernel has been computed for a quartic potential $W(q) = bq^4/4 - aq^2/2$, with $a = b = 1$ and diffusion coefficient $D = 50$. The decay occurs on a time scale $t_{mic} = \mu_3^{-1} \approx 0.02 << t_{chem} = k^{-1} \approx 0.10$. Since t_{mic} is roughly five times smaller than t_{chem} the phenomenological rate law holds approximately. For small barrier heights such time scale separation no longer holds and the rate law breaks down.

- The rate constant k can be read off as the $m = 0$ coefficient in Eq. (61) and is given by

$$k = \langle \chi\chi \rangle^{-1} \langle \chi | \mathcal{L}_{FP} | \phi_1 \rangle \langle \phi_1 | \chi | \psi_0 \rangle = 2D\phi_1'(0) \ , \tag{63}$$

where the second line follows from the explicit computation of the matrix elements. The eigenvector $\phi_1(q)$ may be computed analytically and is given by [7]

$$\phi_1(q) = \mathcal{N} e^{-W(q)/D} \int_0^q dq' e^{W(q')/D} \left[1 - 4 \int_0^{q'} dq'' \chi(q'') \rho_e(q'') \right] \ , \tag{64}$$

where $\mathcal{N}$ is the normalization constant:

$$\mathcal{N} = \left\{ 2 \int_0^\infty de^{-W(q)/D} \int_0^q dq' e^{W(q')/D} \left[1 - 4 \int_0^{q'} dq'' \chi(q'') \rho_e(q'') \right] \right\}^{-1} \ , \tag{65}$$

- In the limit of a high barrier, $D << 1$ and $a, b = \mathcal{O}(1)$, we find

$$k = \frac{2a}{\sqrt{2}\pi} e^{-a^2/4bD} = 4\pi\omega\omega^{\ddagger} e^{-\Delta W(q^{\ddagger})/D} \ , \tag{66}$$

  where $\Delta W(q^{\ddagger}) = a^2/4b$ is the barrier height and ω and $\omega^{\ddagger}$ are the frequencies at the minima and barrier top, respectively. This is just Kramers' solution of the Smoluchowski equation. [8]

- One may also evaluate $K(t)$ by expanding in eigenvalues and eigenfunctions of the unprojected operators:

$$K(t) = \langle \chi\chi \rangle^{-1} \sum_{m=0}^{\infty} \langle \chi | \mathcal{L}_{FP} | \psi_{2m+1} \rangle \langle \psi_{2m+1} | \chi | \psi_0 \rangle e^{-\lambda_{2m+1} t} \ . \tag{67}$$

- Since $\lambda_1 \neq 0$ we have $\lim_{t\to\infty} K(t) = 0$ as expected. For long times we may approximate $K(t)$ by the $m = 0$ term

$$K(t) \approx \langle \chi\chi \rangle^{-1} \langle \chi | \mathcal{L}_{FP} | \psi_1 \rangle \langle \psi_1 | \chi | \psi_0 \rangle e^{-\lambda_1 t} \ . \tag{68}$$

- In the small diffusion limit the eigenfunctions and eigenvalues of $\mathcal{Q}\mathcal{L}_{FP}$ tend to those of $\mathcal{L}_{FP}$ so we may use ϕ_1 as an approximation for ψ_1 in a perturbation calculation of λ_1:

$$\lambda_1 \approx \langle \phi_1 | \mathcal{P} L_{FP} | \phi_1 \rangle = 2D\phi_1'(0) = k \ . \tag{69}$$

  Thus, $K(t) \simeq ke^{-kt}$ as obtained earlier in the general case.

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