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LETTER TO THE EDITOR

Mode coupling and the microscopic derivation of a rate constant for isomerisations in liquids

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Abstract. We derive an effective perturbed Hamiltonian for a parabolic barrier with non-linear coupling between the reactive mode and the fast-relaxing modes. The coupling is introduced *perturbatively*. In the long-wavelength limit, the treatment yields the correct analytical form of the macroscopic rate constant for isomerisations in liquids provided the separation of relaxation timescales is consistent with the perturbation parameter.

A detailed knowledge of the coupling of fast-relaxing modes to reactive modes is paramount to understand deviations from transition state theory (TST) for rates of isomerisations in solution. Such an understanding does not necessarily entail a derivation of the macroscopic rate constant starting from the actual Hamiltonian of the system. To take into account the full phase space as a starting point might pose a formidable problem [1-3]. On the other hand, a derivation which makes use of a probability distribution $Q = Q(X, P_x, t)$, where X is the reaction coordinate and P_x its conjugated momentum, must be regarded as provisional insofar as a direct understanding of the coupling of fast modes to X and P_x is not available.

It is well established that a separation in the characteristic timescales for the slow dominant degree of freedom, τ_x , and the fast-relaxing variables, τ_F , does not in any way warrant the success of a TST treatment [4, 5]: the coupling of modes involved at the top of the reaction barrier is directly responsible for the deviations from TST. We shall introduce an effective Hamiltonian associated with a neighbourhood at the top of the barrier so that the coupling is included *perturbatively*. It is intuitively obvious that a consistency argument would require that the perturbation parameter be the small characteristic parameter for the system: $\varepsilon = \tau_F / \tau_x$. Thus, the question to be answered in this paper can be posed as follows: given that the solvent rearranges on the short timescale τ_F every time an infrequent isomerisation event occurs, how does its participation reflect itself in the perturbative mode coupling at the top of the barrier?

At this point, a digression is in order. The reaction coordinate X should be regarded as coincident with the internal coordinate in the gas phase, as is the case when the presence of the solvent merely renormalises the gas-phase free-energy surface [5, 6]. A distinctively different situation, not treated in this work, arises when X is a combination of an effective solvent coordinate and an internal solute coordinate (see for example [7]).

In order to address the issue of mode coupling, we need to consider a third timescale, besides the ones mentioned above. This one, denoted τ_b , corresponds to the motion along X in a neighbourhood of the barrier top [8]. The full set of inequalities that need to be satisfied so that our treatment is applicable is

$$\tau_F \ll \tau_b \ll \tau_x. \quad (1)$$

The strategy employed could be best defined as a partial inversion of the problem of integration of the Liouville equation in order to derive a time-dependent macroscopic distribution. The inversion is only partial since we do not intend to retrieve information from phase space [9]. More specifically, let $N_R(t)$ denote the number of molecules which remain as reactants at time t (reciprocally, $N_P(t)$ denotes the number of product molecules and $N_R + N_P = N$ is a constant in a closed system). Then, given a macroscopic distribution φ with

$$\varphi = \varphi(\delta N_R, t) \quad \delta N_R = N_R - \langle N_R \rangle \quad (2)$$

where the angular brackets denote thermal or statistical average, we search for a microscopic distribution $B(X, P_x, \{S_i, P_i\}, t) = B$, where S_i denotes generically a fast degree of freedom and P_i its conjugated momentum [9,10]. In general, the distribution B will not satisfy Liouville's equation but it must fulfil the following conditions.

(a) Let G be any functional (such as the number N_P of molecules which have reacted) of X and P_x ; then

$$\langle G \rangle_B = \langle G \rangle \quad (3)$$

where the subscript B denotes an average with respect to that distribution.

(b) There exists a projection operator U such that $UA = B$, where the distribution A satisfies the Liouville equation.

One can construct B as follows [10]:

$$B = \int I(\delta[\delta N'_R - \delta N_R])^{-1} \varphi(\delta N_R, t) \delta[\delta N'_R - \delta N_R] d\delta N_R \quad (4)$$

where $\delta N'_R$ is regarded as the macroscopic variable, in principle a function of the position and momenta for all particles, δN_R is a specific value of that variable and the symbol $I(\cdot)$ stands for integration over all phase space.

The motivation for implementing this route for inversion lies in the fact that we wish to compare the long-wavelength-limit behaviour of the dynamics projected by $(1 - U)$ with the macroscopic dynamics as defined by the memory kernel $K(t)$ associated with the time correlations of δN_R .

We are now in a position to state the problem we shall focus on more clearly. Assuming we have determined the correlation $C(t)$ for δN_R using as input data the macroscopic rate law and the separation of relaxation timescales, we aim at determining an effective Hamiltonian H_{eff} which has associated with it the distribution B . This is obviously an inversion problem, in general intractable except for the fact that the region of interest to us is a neighbourhood of the top of the barrier and, therefore, we should be able to introduce the coupling perturbatively.

The relevant transport coefficient in our approach is τ_x^{-1} , a quantity we wish to compare with the long-wavelength limit of the dynamics which results after applying the projector U . Given an arbitrary distribution A of microstates, the operator U is

defined as

$$UA = \int [I(\delta(\delta N'_R - \delta N_R))]^{-1} I(A\delta(\delta N'_R - \delta N_R)) \delta(\delta N'_R - \delta N_R) d\delta N_R. \quad (5)$$

The transport coefficient is related to the memory kernel $K(t)$ by [4, 11]

$$\tau_x^{-1} = \int_0^T dt K(t)[1 + O(\varepsilon)] \quad (6)$$

where T satisfies

$$\tau_F \ll T \ll \tau_x. \quad (7)$$

However, since we wish to introduce H_{eff} in a neighbourhood of the barrier top, T must satisfy the stronger condition

$$\tau_F \ll T \ll \tau_b. \quad (8)$$

The kernel $K(t)$ has been estimated for equilibrium considerations. Additional input data on the macroscopic rate law and the timescale separation are required. This yields [11]

$$K(t) = C(0)^{-1} \langle \dot{N}_R e^{ELt} \dot{N}_R \rangle \quad E = [1 - U] \quad (9)$$

where L is the Liouville operator.

This expression can be simplified further for the case of low solute concentration, where one can safely assume that isomerisation events are uncorrelated. In other words

$$N_R \sim N^{1/2} \chi_-(X - X_0) \quad (10)$$

where χ_- is the characteristic function for the negative real axis and X_0 is the coordinate value for the free energy maximum. Making use of this assumption, one obtains the nearly standard result

$$\tau_x^{-1} = (m_R m_P)^{-1} \langle P_x \delta(X - X_0) (1 - \chi_-)(X(T) - X_0) \rangle [1 + O(\varepsilon)] \quad (11)$$

where m_R and m_P are the mole fractions of reactant and product respectively. The quantities are fixed once the reaction has reached equilibrium.

The reason we can invert resides in the fact that $K(t)$ can be alternatively written in terms of the projector E . That is so since $K(t)$ relaxes on the timescale τ_F ; that is, it comprises the dynamics orthogonal to the slow motion. Thus we obtain (cf [10])

$$K(t) = I(M(\delta N_R) \delta(\delta N'_R - \delta N_R) \exp[EitL] M(N'_R)) \quad (12)$$

where $M(\delta N_R)$ is given by

$$M(\delta N_R) = E \delta(\delta N'_R - \delta N_R) iL \delta N'_R. \quad (13)$$

Thus, if φ is the distribution which yields $K(t)$ then B , being the microscopic distribution induced by φ , satisfies the integral equation

$$\varphi(\delta N_R, t) N^{1/2} \delta(X - X_0) = I_F \left(\int B dP_x \right) \quad (14)$$

where $I_F(\cdot)$ denotes integration over all fast variables. Equation (14) follows readily if one notices that, by definition of B , the following relation must be satisfied for any functional $F(\delta N_R(X)) = \bar{F}(X)$:

$$\langle F(\delta N_R(X)) \rangle_\varphi = \langle \bar{F}(X) \rangle_B. \quad (15)$$

Thus, the inversion problem is now reduced to finding a Hamiltonian $H_{\text{eff}} = H_{\text{eff}}(X, P_x, \{S_i, P_i\}, \varepsilon)$ which yields B .

Direct inspection of (14) reveals that it suffices to construct H_{eff} so that, after integration of the equations of motion along the non-reactive modes, we obtain the distribution D defined as

$$D(X, P_x, t) = I_{\mathcal{F}}(B). \quad (16)$$

We shall introduce H_{eff} as a Hamiltonian diagonal in the mass-weighted coordinates and momenta with perturbative coupling non-linear in the bath coordinates:

$$H_{\text{eff}} = \left(-w_{\text{na}}^2 X^2 + \frac{P_x^2}{2} \right) + \left(\sum_i w_i^2 S_i^2 + \frac{P_i^2}{2} \right) + \varepsilon XH(\mathbf{S}) \quad (17)$$

where $\tau_b^{-1} = w_{\text{na}}$; the bath is represented as a set of uncoupled harmonic oscillators and the coupling to the reaction coordinate is introduced perturbatively, via the term in ε , with $H(\mathbf{S})$ an analytic function. The non-adiabatic frequency corresponding to fast motion at the barrier top is w_{na} , while the frequencies for the bath oscillators are the w_i .

Following standard procedures to solve perturbatively for the bath coordinates, we obtain an *implicit* relation to be satisfied by the S_i [12]:

$$S_i(t) = S_i(0) \cos w_i t + \frac{S_i(0)}{w_i} \sin w_i t + \varepsilon \int_0^t \frac{\sin w_i(t-\tau)}{w_i} X(\tau) H_i(S(\tau)) d\tau \quad (18)$$

where $H_i = \delta H / \delta S_i$. Since H is analytic, we can write

$$H(\mathbf{S}) = \sum_{j, l_n} H_{i_1 \dots i_j}^{(j)} S_{i_1} \dots S_{i_j}. \quad (19)$$

The implicit relation (18) will now be solved perturbatively, in the form of a series expansion:

$$S_i(t) = S_i^{(0)}(t) + \varepsilon \delta S_i(t) + \varepsilon^2 \delta^2 S_i(t) + \dots \quad (20)$$

where the zeroth-order term is the solution obtained for a bath uncoupled to X (that is, taking the limit $\varepsilon \rightarrow 0$) and

$$\delta S_j(t) = - \int_0^t d\tau W_j(\mathbf{S}^{(0)}, t, \tau) P_x(\tau) + W_j(\mathbf{S}^{(0)}, t, t) X(t) - W_j(\mathbf{S}^{(0)}, t, 0) X(0) \quad (21)$$

where

$$W_j(\mathbf{S}, t, \tau) = \int_{\tau}^t d\tau' \frac{\sin w_i(t-\tau')}{w_i} H_i(\mathbf{S}(\tau')). \quad (22)$$

The perturbation expansion must be consistent with the fluctuation-dissipation theorem; thus, one must retain dissipative terms to order ε^2 if only fluctuating terms of order ε are considered. Thus, the lowest-order fluctuating term which contributes to \dot{P}_x is $\varepsilon H(\mathbf{S}^{(0)}) = \varepsilon f(t)$. The first dissipative term, of order ε^2 , is

$$\begin{aligned} & \varepsilon^2 \sum_j H_j(\mathbf{S}^{(0)}) \delta S_j \\ &= \varepsilon^2 X(t) [V(t, t) + \delta V(t, t)] - \varepsilon^2 X(0) [V(t, 0) + \delta V(t, 0)] \\ & \quad - \varepsilon^2 \int_0^t d\tau P_x(\tau) [V(t, \tau) + \delta V(t, \tau)] \end{aligned} \quad (23)$$

where

$$V(t, \tau) = \sum_j \langle H_j(\mathbf{S}^{(0)} W_j(\mathbf{S}^{(0)}, t, \tau) \rangle \quad (24)$$

and $\delta V(t, \tau)$ represents the deviation from the statistical average.

The term with $V(t, t)$ in (23) is a shift in the (X, P_x) -system potential energy that can be absorbed into a virtual Hamiltonian defined as

$$H_V(X, P_x) = -w_{na}^2 X^2 + \frac{P_x^2}{2} - \frac{\varepsilon^2}{2} V(t, t) X^2. \quad (25)$$

This reduction is possible only because $V(t, t)$ is actually independent of t , since $V(t, t') = V_0(t - t')$. The retention of the dissipative and fluctuating terms to lowest order in ε gives

$$\dot{P}_x = -\frac{\partial H_V}{\partial X} - \varepsilon^2 \int_0^t d\tau V(t, \tau) P_x(\tau) + \varepsilon f(t). \quad (26)$$

Thus, the distribution D satisfies the Fokker-Planck equation

$$\frac{\partial}{\partial t} D = -\left[\frac{\partial}{\partial X} P_x + \frac{\partial}{\partial P_x} \left(\frac{\partial}{\partial X} H_V + \frac{\varepsilon^2 V_0(0)}{2} P_x \right) + \varepsilon^2 V_0(0) k_B T \frac{\partial^2}{\partial P_x^2} \right] D. \quad (27)$$

In this equation, k_B is the Boltzmann constant and T the absolute temperature. Equation (27) is thermodynamically consistent since $\langle f^2(t) \rangle = k_B T V_0(0)$, and compatible with the timescale separation, since we have assumed the expansion parameter to be $\varepsilon = \tau_F / \tau_x$. Thus, the generalised Langevin equation obtained corresponds to an ε perturbation of the TST result.

References

- [1] Zwanzig R 1973 *J. Stat. Phys.* **9** 215
- [2] Mori H 1965 *Prog. Theor. Phys.* **33** 423
- [3] Fernández A 1988 *Phys. Rev. A* **38** 4256
- [4] Yamamoto T 1960 *J. Chem. Phys.* **33** 281
- [5] Kutz H D, Oppenheim I and Ben-Reuven A 1974 *J. Chem. Phys.* **61** 3313
- [6] Chandler D 1978 *J. Chem. Phys.* **68** 2959
- [7] Aleksandrov I V and Goldanskii V I 1984 *Chem. Phys.* **87** 455
- [8] Hynes J T 1985 *Theory of Chemical Reaction Dynamics* vol IV (Boca Raton, FL: CRC Press)
- [9] Bogolyubov N N 1978 *Physics of Elementary Particles and the Atomic Nucleus* **9** 501 (in Russian)
- [10] Fernández A 1987 *J. Phys. A: Math. Gen.* **20** L763
- [11] Hynes J T and Deutsch J M 1975 *Physical Chemistry, An Advanced Treatise* vol 11B, ed H Eyring, W Jost and D Henderson (New York: Academic)
- [12] Lindenberg K and Seshadri V 1981 *Physica* **109A** 483