

Linear Free Energy Relations and Reversible Stretched Exponential Kinetics in Systems with Static or Dynamical Disorder

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Stretched exponential relaxation is the result of the existence of a large number of relaxation channels, any of them having a very small probability of being open. It is shown that the stretched exponential kinetics obeys a type of linear free energy relation. The configuration entropy generated by the random distribution of channels is a linear function of the activation energy of the channel with the slowest relaxation rate and highest energy barrier. This property of stretched exponential relaxation is used for studying the multichannel first-order relaxation kinetics of reversible processes. By combination of the linear free energy relationship with the principle of detailed balance, a generalized kinetic law of the stretched exponential type is derived, which provides a theoretical justification for its prior use in the literature for fitting experimental data. The theory is extended to reversible processes with dynamical disorder. In this case there is no simple analogue of the free energy relationship suggested for systems with static disorder; however, stretched exponential kinetics can be investigated by using a stochastic Liouville equation. It is shown that for a process with dynamical disorder it is possible that in the long time limit the system evolves toward a nonequilibrium frozen state rather than toward thermodynamic equilibrium. We also study the concentration fluctuations for reversible chemical processes in systems with static or dynamical disorder. A set of fluctuation–dissipation relations is derived for the factorial moments of the number of molecules, and it is shown that for both types of disorder the composition fluctuations are intermittent. For the global characterization of the average kinetic behavior of reversible processes occurring in disordered systems we introduce an average lifetime distribution of the transient regime and an effective rate coefficient. The analytic properties of these two functions are investigated for systems with both static and dynamical disorder. Finally, the theory is extended to the case of one-channel thermally activated processes with random energy barriers. We emphasize that our theoretical approach, unlike other theories of stretched exponential relaxation, does not make use of the steepest descent approximation for computing the average kinetic curves: our results are exact in a limit of the thermodynamic type, for which the total number of relaxation channels tends to infinity and the probability that a relaxation channel is open tends to zero, with the constraint that the average number of open channels is kept constant.

1. Introduction

Chemical reactions and relaxation processes occurring in systems with static disorder involve statistical distributions of individual processes characterized by random rates. Many of these processes can be described by a kinetic curve of the stretched exponential type:^{1–3}

$$\langle \text{survival} \rangle = \exp[-(\omega t)^\alpha] \quad (1)$$

where $\langle \text{survival} \rangle$ is the average survival function at time t , ω is a characteristic frequency, and α is a positive dimensionless scaling exponent between zero and unity. For a first-order irreversible chemical reaction the survival function $\langle \text{survival} \rangle$ is simply equal to the ratio of the average concentration of a chemical at time t , $C(t)$, to the concentration of the same chemical at time $t = 0$, $C(0)$, that is, $\text{survival}(t) = C(t)/C(0)$.

A general formulation of the theory of first-order irreversible processes in systems with static disorder has been suggested a

decade ago.⁴ According to this formulation the average relaxation function of the process can be expressed as

$$\langle \text{survival} \rangle = \exp\left\{-\int_0^\infty \rho_k(k)[1 - \exp(-kt)] dk\right\} \quad (2)$$

where $\rho_k(k) dk$ is the average number of channels with an individual rate between k and $k + dk$. Rigorous derivations of eq 2 based on the theory of random point processes have been suggested.⁵

The purpose of this article is to show that the stretched exponential law (1) is a simple consequence of the general equation (2) provided that the relaxation process obeys a type of free energy relation,⁶ which is commonly encountered in chemical kinetics. We shall use this linear free energy relationship as a basis for generalizing the stretched exponential to the case of reversible reactions.

2. Linear Free Energy Relationships for Irreversible Processes

We formulate our theory in terms of two variables: the individual relaxation time of a channel

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$$\tau = 1/k \quad (3)$$

and the total number of channels

$$\Omega(\tau) = \int_{k=1/\tau}^{\infty} \rho_k(k) dk \quad (4)$$

with a relaxation time between 0 and τ . In terms of these two variables the general relaxation law (2) can be rewritten as

$$\langle \cdot / (t) \rangle = \exp \left\{ - \int_0^{\infty} \frac{\partial \Omega(\tau)}{\partial \tau} [1 - \exp(-t/\tau)] d\tau \right\} \quad (5)$$

In this article we limit ourselves to the particular case where the system is in a state of “local equilibrium” and the individual relaxation processes are thermally activated and obey the Arrhenius law:

$$\tau = \nu^{-1} \exp[E/(k_B T)] \quad (6)$$

where ν is the maximum frequency of relaxation corresponding to activation energy zero, E is the height of the energy barrier corresponding to a given channel, k_B is Boltzmann's constant, and T is the temperature of the system. The total number $\Omega(\tau)$ of relaxation channels with a relaxation time between 0 and τ can be interpreted as a number of microstates generated by the disorder in the system. From it we can evaluate a configurational entropy

$$S_{\text{conf}} = k_B \ln \Omega(\tau) \quad (7)$$

By making an analogy with the free energy relationships in physical organic chemistry,⁶ we assume that this configurational entropy is a monotonically increasing function of the range of variation of the activation energies in the ensemble of channels considered. If there is only one channel with relaxation time equal to zero ($\tau = 0$, $E = 0$), then $\Omega = 1$, and the configurational entropy is equal to zero, $S_{\text{conf}} = 0$. As the maximum value of the relaxation τ increases, the number $\Omega(\tau)$ of microstates also increases, and according to eq 6, so does the maximum activation energy E . Thus, it is plausible to assume that S_{conf} is an increasing function of E , that is

$$S_{\text{conf}} = S_{\text{conf}}(E) \quad \text{with} \quad [\partial S_{\text{conf}}(E)/\partial E] > 0 \quad (8)$$

In the first approximation the dependence $S_{\text{conf}} = S_{\text{conf}}(E)$ can be approximated by a linear Taylor expansion:

$$S_{\text{conf}}(E) \cong S_{\text{conf}}(0) + \left[\frac{\partial S_{\text{conf}}(E)}{\partial E} \right]_{E=0} E \quad (9)$$

By combining eqs 6–9, we come to a power law for the number $\Omega(\tau)$ of microstates

$$\Omega(\tau) = (\nu\tau)^{T\partial S_{\text{conf}}(0)/\partial E} \exp[S_{\text{conf}}(0)/k_B] \quad (10)$$

By inserting eq 10 into eq 5, it is easy to check that the integral over the values of the relaxation time in eq 5 converges if

$$T < 1/[\partial S_{\text{conf}}(0)/\partial E] \quad (11)$$

If this condition is fulfilled, then the integral in eq 5 can be easily evaluated, resulting in the stretched exponential law (1), where

$$\alpha = T[\partial S_{\text{conf}}(0)/\partial E] \quad (12)$$

$$\omega = \nu \left\{ \Gamma \left[1 - T \frac{\partial S_{\text{conf}}(0)}{\partial E} \right] \right\}^{1/T[\partial S_{\text{conf}}(0)/\partial E]} \times \exp \left\{ \frac{S_{\text{conf}}(0)}{k_B T [\partial S_{\text{conf}}(0)/\partial E]} \right\} \quad (13)$$

and $\Gamma(x) = \int_0^{\infty} t^{x-1} \exp(-t) dt$, $x > 0$ is the complete gamma function. From the inequalities (8) and (11) it follows that the scaling exponent α must be between zero and one, $1 > \alpha > 0$, as expected for a stretched exponential.

3. Reversible Processes with Static Disorder. General Analysis

Most of the work on stretched exponential kinetics presented in the literature refers to irreversible processes. In the following we extend the theory of stretched exponential kinetics to reversible processes. We consider a first-order chemical reaction of the type



taking place in a system with static order. We assume that there is a large number of reaction channels leading to the transformation of X to Y and vice versa. To a channel j correspond two opposite processes characterized by a forward rate coefficient k_j^+ describing the kinetics of transformation of X to Y and by a backward rate coefficient k_j^- describing the reverse transformation, of Y to X , respectively. According to the principle of detailed balance, at equilibrium the net rate of transformation for each channel equals zero, that is

$$k_j^+ C_X^{\text{equil}} = k_j^- C_Y^{\text{equil}} \quad j = 1, 2, \dots \quad (15)$$

where C_X^{equil} and C_Y^{equil} are the equilibrium concentrations of Y and X , respectively. The ratio of these two concentrations should be equal to the thermodynamic equilibrium constant of the reaction (14):

$$K_{\text{equil}} = C_Y^{\text{equil}}/C_X^{\text{equil}} \quad (16)$$

By combining eqs 15 and 16, we come to

$$K_{\text{equil}} = k_1^+/k_1^- = k_2^+/k_2^- = \dots = k_j^+/k_j^- = \dots \quad (17)$$

Equation 17 has a very important consequence: even though for a given channel the forward and backward rate coefficients may have random values, their ratio is nonrandom and equal to the thermodynamic equilibrium constant of the process. It follows that, if we denote by $\rho_{k^+}(k^+)$ and by $\rho_{k^-}(k^-)$ the average densities of forward and backward rates, respectively, we have the following relations:

$$\rho_{k^-}(k^-) = \int \delta(k^- - k^+/K_{\text{equil}}) \rho_{k^+}(k^+) dk^+ = K_{\text{equil}} \rho_{k^+}(K_{\text{equil}} k^-) \quad (18)$$

$$\rho_{k^+}(k^+) = \int \delta(k^+ - k^-/K_{\text{equil}}) \rho_{k^-}(k^-) dk^- = (K_{\text{equil}})^{-1} \rho_{k^-}(k^+/K_{\text{equil}}) \quad (19)$$

If N_1 channels are characterized by the rates k_1^{\pm} and N_2 channels are characterized by the rates k_2^{\pm} , ..., then we can

write the following overall kinetic equation for the component X:

$$dC_X(t)/dt = -C_X(t) \sum_j N_j k_j^+ + [C_X(0) + C_Y(0) - C_X(t)] \sum_j N_j k_j^- \quad (20)$$

and a similar relationship for the component Y. The survival function of the process can be expressed as a configurational average of the ratio

$$\langle / (t) \rangle = C_X(t)/C_\Sigma \quad \text{with} \\ C_\Sigma = C_X(0) + C_Y(0) = C_X(t) + C_Y(t) = \text{constant} \quad (21)$$

over the different possible rates attached to different channels, that is,

$$\langle / (t) \rangle = \sum_{N_1} \sum_{N_2} \dots P(N_1, N_2, \dots) [C_X(t)/C_\Sigma] \quad (22)$$

where $P(N_1, N_2, \dots)$ is the distribution of the numbers N_1, N_2, \dots of channels characterized by different individual rates. A reasonable approximation for $P(N_1, N_2, \dots)$ is given by a multivariate Poissonian.^{7,8}

$$P(N_1, N_2, \dots) = \prod_{j \geq 1} \left\{ \frac{\langle N_j \rangle^{N_j}}{N_j!} \exp(-\langle N_j \rangle) \right\} \quad (23)$$

By solving the differential equation (20), inserting the result into eq 22, and evaluating the sums over N_1, N_2, \dots , we obtain

$$\langle / (t) \rangle = \frac{1}{K_{\text{equil}} + 1} + \left[\langle / (0) \rangle - \frac{1}{K_{\text{equil}} + 1} \right] \times \exp \left\{ - \int_0^\infty dk_\Sigma \rho_\Sigma(k_\Sigma) [1 - \exp(-tk_\Sigma)] \right\} \quad (24)$$

where

$$k_\Sigma = k_+ + k_- \quad (25)$$

$$\rho_\Sigma(k_\Sigma) = \sum_j \langle N_j \rangle \delta[k_\Sigma - (k_j^+ + k_j^-)] \quad (26)$$

are the total rate of relaxation attached to a given channel and the average density of states attached to the total rate, respectively.

From eqs 17, 25, and 26 we can express the average density of states $\rho_\Sigma(k_\Sigma)$ of the total rate k_Σ in terms of the individual average densities $\rho_{k^\pm}^\pm$ of the rates k^\pm attached to the forward and backward processes

$$\rho_\Sigma(k_\Sigma) = \sum_j \langle N_j \rangle \delta[k_\Sigma - k^\pm (1 + (K_{\text{equil}})^{\mp 1})] = [(K_{\text{equil}})^{\mp 1} + 1]^{-1} \rho_{k^\pm}^\pm(k_\Sigma [(K_{\text{equil}})^{\mp 1} + 1]^{-1}) \quad (27)$$

By using eqs 27 and 28, we can express the average survival function in terms of the individual average densities of states $\rho_{k^\pm}^\pm(k_\pm)$

$$\langle / (t) \rangle = \frac{1}{K_{\text{equil}} + 1} + \left[\langle / (0) \rangle - \frac{1}{K_{\text{equil}} + 1} \right] \times \exp \left\{ - \int_0^\infty dk^\pm \rho_{k^\pm}^\pm(k^\pm) \left[1 - \exp \left(- \frac{tk^\pm}{1 + (K_{\text{equil}})^{\mp 1}} \right) \right] \right\} \quad (28)$$

Equations 24–28 make possible the evaluation of the average densities $\rho_\Sigma(k_\Sigma)$ and $\rho_{k^\pm}^\pm(k_\pm)$ of the rates k_Σ and k_\pm , from experiments. For doing that we introduce an effective time-dependent rate coefficient of the process $k_{\text{eff}} = k_{\text{eff}}(t)$, and an effective rate equation for the average survival function $\langle / (t) \rangle$:

$$d\langle / (t) \rangle / dt = k_{\text{eff}}(t) [\langle / (\infty) \rangle - \langle / (t) \rangle] \quad (29)$$

where

$$\langle / (\infty) \rangle = 1/(K_{\text{equil}} + 1) \quad (30)$$

is the equilibrium value of the average survival function $\langle / (t) \rangle$. The solution of eq 29

$$\langle / (t) \rangle = \langle / (\infty) \rangle + [\langle / (0) \rangle - \langle / (\infty) \rangle] \exp \left[- \int_0^t k_{\text{eff}}(t') dt' \right] \quad (31)$$

has a form similar to eqs 24 and 28. By comparison of eqs 24 and 28 with eq 31 it follows that

$$k_{\text{eff}}(t) = \int_0^\infty k_\Sigma \rho_\Sigma(k_\Sigma) \exp(-tk_\Sigma) dk_\Sigma \quad (32)$$

$$k_{\text{eff}}(t) = \frac{1}{1 + (K_{\text{equil}})^{\mp 1}} \int_0^\infty \rho_{k^\pm}^\pm(k^\pm) k^\pm \times \exp \left(- \frac{k^\pm t}{1 + (K_{\text{equil}})^{\mp 1}} \right) dk^\pm \quad (33)$$

If the time dependence of the average survival function $\langle / (t) \rangle$ is known from experiment, then the effective rate coefficient $k_{\text{eff}}(t)$ and the equilibrium constant K_{equil} can be evaluated from eqs 29 and 30. It follows that the average densities of states $\rho_\Sigma(k_\Sigma)$ and $\rho_{k^\pm}^\pm(k_\pm)$ can be evaluated from the integral equations 32 and 33, which can be solved by means of inverse Laplace transformation. We express $k_{\text{eff}}(t)$ as the Laplace transform of a complex function $\chi(\theta)$:

$$k_{\text{eff}}(t) = \int_0^\infty \chi(\theta) \exp(-\theta t) dt \quad \text{i.e.,} \\ \chi(\theta) = \mathcal{L}_t^{-1} k_{\text{eff}}(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} k_{\text{eff}}(t) \exp(\theta t) dt \quad (34)$$

where θ is the inverse Laplace variable conjugate to the time t and \mathcal{L}_t^{-1} denotes the inverse Laplace transformation with respect to the time t . The function $\chi(\theta)$ can be evaluated from $k_{\text{eff}}(t)$ by means of inverse Laplace transformation. From eqs 32–34 we notice that the densities of states $\rho_\Sigma(k_\Sigma)$ and $\rho_{k^\pm}^\pm(k_\pm)$ can be expressed in terms of $\chi(\theta)$ as

$$\rho_\Sigma(k_\Sigma) = \chi(k_\Sigma)/k_\Sigma \quad (35)$$

$$\rho_{k^\pm}^\pm(k_\pm) = \frac{1}{k_\pm} \chi \left[\frac{k_\pm}{1 + (K_{\text{equil}})^{\mp 1}} \right] \quad (36)$$

4. Reversible Processes with Static Disorder. Linear Free Energy Relations

The results derived in the preceding section are general, in that they apply for any first-order reversible reaction occurring in a disordered system with static disorder. In this section we use this general approach for deriving the following generalization of stretched exponential for reversible processes:

$$\langle / (t) \rangle = \langle / (\infty) \rangle + [\langle / (0) \rangle - \langle / (\infty) \rangle] \exp[-(\omega t)^a] \quad (37)$$

The shape of the graphical representation of the kinetic law (37) is the same as the shape of a stretched exponential law for irreversible processes, with the difference that for long times the survival function tends toward a finite value, $\langle \cdot \rangle / \langle \cdot \rangle_\infty$, which is generally different from zero. We mention that eq 37 has been already used in the literature for fitting experimental data, without a firm theoretical basis.⁹ By using the general theory developed in the preceding section, it is easy to show that in this case the average densities of states $\rho_\Sigma(k_\Sigma)$ and $\rho_{\lambda_\pm}^\pm(k_\pm)$ obey the following self-similar scaling laws

$$\rho_\Sigma(k_\Sigma) = \alpha[\Gamma(1 - \alpha)]^{-1}(\omega)^\alpha(k_\Sigma)^{-(1+\alpha)} \quad (38)$$

$$\rho_{\lambda_\pm}^\pm(k_\pm) = \alpha[\Gamma(1 - \alpha)]^{-1}[1 + (K_{\text{equil}})^{\mp 1}]^\alpha(\omega)^\alpha(k_\pm)^{-(1+\alpha)} \quad (39)$$

If the channel statistics is generated by a random distribution of energy barriers, then the kinetic law (37) and the corresponding scaling conditions may be generated by a free energy linear relation similar to eq 9 introduced in section 2. In terms of the total relaxation rate k_Σ of a channel, eqs 25 and 26, we introduce the total relaxation time

$$\tau_\Sigma = 1/k_\Sigma \quad (40)$$

and the total number

$$\Omega_\Sigma(\tau) = \int_{k_\Sigma=1/\tau_\Sigma}^{\infty} \rho_\Sigma(k_\Sigma) dk_\Sigma \quad (41)$$

of channels with a total relaxation time between 0 and τ_Σ , expressed in terms of τ_Σ . The configurational entropy generated by the random distribution of channels is given by

$$S_{\text{conf}} = k_B \ln \Omega_\Sigma(\tau) \quad (42)$$

The temperature dependence of the forward and backward rate coefficients, k_\pm , is assumed to be given by the Arrhenius formula:

$$k_\pm = \nu_\pm \exp[-E_\pm/(k_B T)] \quad (43)$$

where E_\pm are the corresponding activation energies and the preexponential factors, ν_\pm , are assumed to be temperature independent. The equilibrium constant K_{equil} is the same for all individual channels and is equal to

$$K_{\text{equil}} = k_+/k_- = (\nu_+/\nu_-) \exp[-\Delta H/(k_B T)] = \exp[-\Delta G^0/(k_B T)] = \text{constant} \quad (44)$$

where

$$\Delta H = E_+ - E_- \quad (45)$$

is the enthalpy variation of the reaction and ΔG^0 is the change of the Gibbs free energy in the reaction.

By invoking the same type of arguments as in section 2 we postulate that the configurational entropy S_{conf} is a nondecreasing function of the maximum individual activation energies E_\pm :

$$S_{\text{conf}} = S_{\text{conf}}(E_+, E_-) \quad \text{with} \quad [\partial S_{\text{conf}}(E_+, E_-)/\partial E_\pm] > 0 \quad (46)$$

and that the dependence (47) can be approximated by a linear relationship similar to eq 9. For generalizing eq 9 for a reversible process we should take into account that the activation energies E_\pm are not independent random variables but are related to each

other by the linear relationship given by eq 45. Two different formulations of the theory can be given, in terms of E_+ or E_- , respectively. As expected, both formulations lead to the stretched exponential kinetic law (37). In this paper we use the activation energy E_+ of the forward reaction as the main variable. In terms of E_+ the generalization of the linear free energy relation (9) is

$$S_{\text{conf}}(E_+, E_+ - \Delta H) \cong S_{\text{conf}}(0, -\Delta H) + \left[\frac{\partial S_{\text{conf}}(0, -\Delta H)}{\partial E_+} + \frac{\partial S_{\text{conf}}(0, -\Delta H)}{\partial E_-} \right] E_+ \quad (47)$$

After some calculations, from eqs 38–47 we get the following expressions for the average densities of states:

$$\rho_\Sigma(k_\Sigma) = \xi T \exp[S_{\text{conf}}(0, -\Delta H)/k_B] \times [\nu_+(1 + K_{\text{equil}})/K_{\text{equil}}]^{\xi T} (k_\Sigma)^{-(1+\xi T)} \quad (48)$$

$$\rho_{k_+}^+(k_+) = \xi T \exp[S_{\text{conf}}(0, -\Delta H)/k_B] (\nu_+)^{\xi T} (k_+)^{-(1+\xi T)} \quad (49)$$

$$\rho_{k_-}^-(k_-) = \xi T \exp\left[\frac{S_{\text{conf}}(0, -\Delta H) - \xi \Delta H}{k_B}\right] (\nu_-)^{\xi T} (k_-)^{-(1+\xi T)} \quad (50)$$

with

$$\xi = \frac{\partial S_{\text{conf}}(0, -\Delta H)}{\partial E_+} + \frac{\partial S_{\text{conf}}(0, -\Delta H)}{\partial E_-} \quad (51)$$

By inserting eqs 48–50 into eqs 24–28 we recover the incomplete stretched exponential law (37) where the kinetic parameters α and ω are given by

$$\alpha = \xi T \quad (52)$$

$$\omega = [\nu^+(1 + K_{\text{equil}})/K_{\text{equil}}][\Gamma(1 - \xi T)]^{1/\xi T} \times \exp\left[\frac{S_{\text{conf}}(0, -\Delta H)}{k_B T \xi}\right] \quad (53)$$

5. Reversible Processes with Dynamical Disorder. General Analysis

The analysis presented in section 3 for a first-order chemical reaction of the type (14) can be easily extended for systems with dynamical disorder.^{10,11} For a system with dynamical disorder the forward and backward rate constants, k_j^\pm , are random functions of time, $k_j^\pm(t)$, which obey the detailed balance condition. In particular, eq 17 becomes

$$K_{\text{equil}} = k_1^+(t)/k_1^-(t) = k_2^+(t)/k_2^-(t) = \dots = k_j^+(t)/k_j^-(t) = \dots \quad (54)$$

The average density of states, $\rho_{k_+}^+(k^+)$ and $\rho_{k_-}^-(k^-)$, become functional densities $\rho_{k_+}^+[k^+(t)]$ and $\rho_{k_-}^-[k^-(t)]$, which fulfill a set of consistency relations similar to eqs 18 and 19:

$$\rho_{k_-}^-[k^-(t)] \triangleleft [k^-(t)] = \triangleleft [k^-(t)] \int \int \delta[k^-(t') - k^+(t')/K_{\text{equil}}] \rho_{k_+}^+[k^+(t')] \triangleleft [k^+(t')] = \triangleleft [k^-(t)] K_{\text{equil}} \rho_{k_+}^+[K_{\text{equil}} k^-(t')] \quad (55)$$

and

$$\rho_{k^+}^+[k^+(t')] \Delta[k^+(t')] = \overline{\Delta[k^+(t')] \int \delta[k^+(t') - k^-(t')/K_{\text{equil}}] \rho_{k^-}^-[k^-(t')] \Delta[k^-(t')] = \Delta[k^+(t')](K_{\text{equil}})^{-1} \rho_{k^-}^-[k^+(t')/K_{\text{equil}}]} \quad (56)$$

where $\overline{\int}$ stands for the operation of path integration and $\Delta[k^\pm(t')]$ are suitable integration measures over the space of functions $k^\pm(t')$. Equation 20 remains also valid, with the difference that the individual rates are random functions of time. We solve eq 20 for a set a realizations of the random functions and use the expression (21) for the instantaneous value of the survival function. After some calculations we come to

$$\langle \lambda(t) \rangle = \frac{1}{K_{\text{equil}} + 1} + \left[\langle \lambda(0) \rangle - \frac{1}{K_{\text{equil}} + 1} \right] \times \exp\left\{-\sum_j N_j \int_0^t [k_j^+(t') + k_j^-(t')] dt'\right\} \quad (57)$$

We average eq 25 over all possible values of the numbers of channels N_1, N_2, \dots . We assume that the distribution of channels is Poissonian and obeys eq 23. By averaging eq 57 over N_1, N_2, \dots , we come to

$$\langle \lambda(t) \rangle = \frac{1}{K_{\text{equil}} + 1} + \left[\langle \lambda(0) \rangle - \frac{1}{K_{\text{equil}} + 1} \right] \times \exp\left\{-\overline{\int \int \rho_\Sigma[k_\Sigma(t')] \Delta[k_\Sigma(t')] \{1 - \exp[-\int_0^t k_\Sigma(t') dt']\}}\right\} \quad (58)$$

where

$$k_\Sigma(t') = k_+(t') + k_-(t') \quad (59)$$

$$\rho_\Sigma[k_\Sigma(t')] \Delta[k_\Sigma(t')] = \sum_j \langle N_j \rangle \delta\{[k_\Sigma(t') - ([k_j^+(t') + k_j^-(t')])]\} \Delta[k_\Sigma(t')] \quad (60)$$

are the total rate of relaxation for a system with dynamic disorder and the average functional density of channels attached to the total rate, respectively.

Equation 58 is the dynamic analogue of the general kinetic equation (31) derived in section 3 for systems with static disorder. The main difficulty related to the application of this general kinetic equation is related to the evaluation of the path integral:

$$\langle \lambda(t) \rangle = \overline{\int \int \rho_\Sigma[k_\Sigma(t')] \Delta[k_\Sigma(t')] \{1 - \exp[-\int_0^t k_\Sigma(t') dt']\}} \quad (61)$$

The evaluation of the path integral in eq 61 can be easily done if the functional density of states $\rho_\Sigma[k_\Sigma(t')] \Delta[k_\Sigma(t')]$ has a Gaussian behavior. Unfortunately, the Gaussian form for $\rho_\Sigma[k_\Sigma(t')] \Delta[k_\Sigma(t')]$ must be ruled out because it does not include the stretched exponential as a particular case. A general solution to the problem can be given by introducing an average probability density functional of the relaxation rates $k_\Sigma(t')$

$$\varphi_\Sigma[k_\Sigma(t')] \Delta[k_\Sigma(t')] = \rho_\Sigma[k_\Sigma(t')] \Delta[k_\Sigma(t')]/\langle \mathcal{N} \rangle \quad (62)$$

with the normalization condition

$$\overline{\int \int \varphi_\Sigma[k_\Sigma(t')] \Delta[k_\Sigma(t')] = 1} \quad (63)$$

and where

$$\langle \mathcal{N} \rangle = \overline{\int \int \rho_\Sigma[k_\Sigma(t')] \Delta[k_\Sigma(t')]} \quad (64)$$

is the total average number of reaction channels involved in the process. The factor $\langle \lambda(t) \rangle$ in eq 61 can be expressed in terms of the dynamical average of the random function

$$\lambda[k_\Sigma(t')] = \exp[-\int_0^t k_\Sigma(t') dt'] \quad (65)$$

We have

$$\langle \lambda(t) \rangle = \langle \mathcal{N} \rangle \{1 - \langle \lambda(t') \rangle\} \quad (66)$$

where the dynamical average $\langle \lambda(t') \rangle$ is given by

$$\langle \lambda(t) \rangle = \overline{\int \int \exp[-\int_0^t k_\Sigma(t') dt'] \rho_\Sigma[k_\Sigma(t')] \Delta[k_\Sigma(t')]} \quad (67)$$

In this paper we limit ourselves to the simplest case of dynamical disorder for which the random process corresponding to the average probability density functional $\varphi_\Sigma[k_\Sigma(t')] \Delta[k_\Sigma(t')]$ is Markovian. Moreover, we consider that the average effective number of channels, $\langle \mathcal{N} \rangle$, is time independent, $\langle \mathcal{N} \rangle = \text{constant}$. Under these circumstances the average probability density functional $\varphi_\Sigma[k_\Sigma(t')] \Delta[k_\Sigma(t')]$ can be represented in the following form:

$$\begin{aligned} \varphi_\Sigma[k_\Sigma(t')] \Delta[k_\Sigma(t')] = & \lim_{\substack{m \rightarrow \infty \\ (\Delta t \rightarrow 0)}} \{ \varphi_\Sigma(k_\Sigma^{(m)}; m\Delta t | k_\Sigma^{(m-1)}; (m-1)\Delta t) dk_\Sigma^{(m)} \times \\ & \varphi_\Sigma(k_\Sigma^{(m-1)}; m\Delta t | k_\Sigma^{(m-2)}; (m-2)\Delta t) dk_\Sigma^{(m-1)} \times \\ & \dots \varphi_\Sigma(k_\Sigma^{(2)}; 2\Delta t | k_\Sigma^{(1)}; \Delta t) dk_\Sigma^{(2)} \varphi_\Sigma(k_\Sigma^{(1)}; \Delta t | k_\Sigma^{(0)}; 0) dk_\Sigma^{(1)} \times \\ & \varphi_{\Sigma(st)}(k_\Sigma^{(0)}) dk_\Sigma^{(0)} \} \quad t \geq t' \geq 0 \quad (68) \end{aligned}$$

where

$$m = t/\Delta t \quad (69)$$

$$\varphi_\Sigma^{st}(k_\Sigma) dk_\Sigma \quad \text{with} \quad \int \varphi_\Sigma^{st}(k_\Sigma) dk_\Sigma = 1 \quad (70)$$

is the average one-time stationary probability density of an individual relaxation rate attached to a given channel corresponding to static disorder and

$$\varphi_\Sigma(k_\Sigma; t | k_\Sigma'; t') dk_\Sigma \quad \text{with} \quad \int \varphi_\Sigma(k_\Sigma; t | k_\Sigma'; t') dk_\Sigma = 1 \quad (71)$$

is the average conditional probability density of the relaxation rate k_Σ at time t provided that at time t' the relaxation rate was k_Σ' . For a Markov process both $\varphi_\Sigma^{st}(k_\Sigma) dk_\Sigma$ and $\varphi_\Sigma(k_\Sigma; t | k_\Sigma'; t') dk_\Sigma$ are the solutions of an evolution equation of the type

$$\partial \varphi / \partial t = \mathbf{L} \varphi \quad (72)$$

where \mathbf{L} is a linear Markovian evolution operator of the Liouville, Fokker–Planck, or the master equation type. In this case the probability $\varphi_\Sigma^{st}(k_\Sigma) dk_\Sigma$ is the stationary solution of eq 72 whereas the conditional probability $\varphi_\Sigma(k_\Sigma; t | k_\Sigma'; t') dk_\Sigma$ is the Green function of eq 72 corresponding to the initial condition

$$\varphi_\Sigma(k_\Sigma; t = t' | k_\Sigma'; t') = \delta(k_\Sigma - k') \quad (73)$$

For these Markovian systems there is a general method for computing dynamical path averages of the type (67) without the explicit evaluation of a path integral. This method is based on the observation that a realization of the function $\dot{\lambda}(t) = \dot{\lambda}(k_{\Sigma}(t))$ given by eq 65 obeys a multiplicative stochastic differential equation with a random coefficient

$$d\dot{\lambda}(t)/dt = -k_{\Sigma}(t) \dot{\lambda}(t) \quad \text{with} \quad \dot{\lambda}(t=0) = 1 \quad (74)$$

Since eq 74 is local in time and the rate coefficient $k_{\Sigma}(t)$ is Markovian, it follows that the pair of random variables $(k_{\Sigma}(t), \dot{\lambda}(t))$ is also Markovian and the one-time joint probability density,

$$P_{\Sigma}(k_{\Sigma}, \dot{\lambda}, t) dk_{\Sigma} d\dot{\lambda} \quad \text{with} \quad \int \int P_{\Sigma}(k_{\Sigma}, \dot{\lambda}, t) dk_{\Sigma} d\dot{\lambda} = 1 \quad (75)$$

obeys a compound stochastic Liouville equation¹²

$$\frac{\partial}{\partial t} P_{\Sigma}(k_{\Sigma}, \dot{\lambda}, t) = \frac{\partial}{\partial \dot{\lambda}} \{k_{\Sigma} \dot{\lambda} P_{\Sigma}(k_{\Sigma}, \dot{\lambda}, t)\} + \mathbf{L} P_{\Sigma}(k_{\Sigma}, \dot{\lambda}, t) \quad (76)$$

with the initial condition

$$P_{\Sigma}(k_{\Sigma}, \dot{\lambda}, t=0) = \delta(\dot{\lambda}-1) \varphi_{\Sigma}^{st}(k_{\Sigma}) \quad (77)$$

The dynamical average $\langle \dot{\lambda}(t) \rangle$ can be expressed as an average value corresponding to the joint probability $P_{\Sigma}(k_{\Sigma}, \dot{\lambda}, t) dk_{\Sigma} d\dot{\lambda}$

$$\langle \dot{\lambda}(t) \rangle = \int \int \dot{\lambda} P_{\Sigma}(k_{\Sigma}, \dot{\lambda}, t) dk_{\Sigma} d\dot{\lambda} = \int \mathcal{F}(k_{\Sigma}; t) dk_{\Sigma} \quad (78)$$

where

$$\mathcal{F}(k_{\Sigma}; t) = \int \dot{\lambda} P_{\Sigma}(k_{\Sigma}, \dot{\lambda}, t) d\dot{\lambda} \quad (79)$$

is a marginal average. We multiply eqs 76 and 77 by $\dot{\lambda}$ and integrate over $\dot{\lambda}$. After a partial integration we obtain a closed equation for the marginal average $\mathcal{F}(k_{\Sigma}; t)$

$$\frac{\partial}{\partial t} \mathcal{F}(k_{\Sigma}; t) + k_{\Sigma} \mathcal{F}(k_{\Sigma}; t) = \mathbf{L} \mathcal{F}(k_{\Sigma}; t) \quad (80)$$

with the initial condition

$$\mathcal{F}(k_{\Sigma}; t=0) = \varphi_{\Sigma}^{st}(k_{\Sigma}) \quad (81)$$

In the following section we try to apply this general method of evaluating dynamical averages to the particular case of reversible stretched exponential kinetics.

6. Reversible Stretched Exponential Kinetics with Dynamical Disorder

For a thermally activated process with dynamical disorder the fluctuations of the rate coefficient $k_{\Sigma}(t)$ are due to the fluctuations of the activation energies $E_{\pm}(t)$ of the forward and backward processes corresponding to the different channels. Due to the constraints generated by detailed balance, the fluctuations of these two activation energies are related to each other. We have

$$E_{+}(t) - E_{-}(t) = \Delta H = \text{constant} \quad (82)$$

It follows that the theory can be developed in terms of only one activation energy. For consistency with the choice made in section 4 we use the forward activation energy, E_{+} , as the main random variable of the theory. E_{+} is related to the rate coefficient $k_{\Sigma}(t)$ by means of the relationship

$$k_{\Sigma} = \left(\frac{K_{\text{equil}}}{1 + K_{\text{equil}}} \right) \nu_{+} \exp \left[-\frac{E_{+}}{k_{\text{B}} T} \right]; \quad E_{+} = k_{\text{B}} T \ln \left\{ \left(\frac{1 + K_{\text{equil}}}{K_{\text{equil}}} \right) \frac{\nu_{+}}{k_{\Sigma}} \right\} \quad (83)$$

Equation 83 allows us to switch from the joint probability $P_{\Sigma}(k_{\Sigma}, \dot{\lambda}, t) dk_{\Sigma} d\dot{\lambda}$ expressed in terms of k_{Σ} to the joint probability

$$P_{E_{+}}(E_{+}, \dot{\lambda}, t) dE_{+} d\dot{\lambda} \quad \text{with} \quad \int \int P_{E_{+}}(E_{+}, \dot{\lambda}, t) dE_{+} d\dot{\lambda} = 1 \quad (84)$$

expressed in terms activation energy E_{+} of the forward step.

We describe the fluctuations of the activation energy E_{+} by a Markovian master equation

$$\frac{\partial}{\partial t} \varphi_{E_{+}}(E_{+}; t) = \int [\varphi_{E_{+}}(E'_{+}; t) \mathcal{W}(E'_{+} \rightarrow E_{+}) - \varphi_{E_{+}}(E_{+}; t) \mathcal{W}(E_{+} \rightarrow E'_{+})] dE'_{+} \quad (85)$$

where

$$\varphi_{E_{+}}(E_{+}; t) dE_{+} \quad \text{with} \quad \int \varphi_{E_{+}}(E_{+}; t) dE_{+} = 1 \quad (86)$$

is the one-time probability distribution of the forward activation energy and $\mathcal{W}(E_{+} \rightarrow E'_{+})$ is the transition (renewal) rate from an activation energy E_{+} to an activation energy between E'_{+} and $E'_{+} + dE'_{+}$.

In this paper we limit ourselves to the study of strong dynamical disorder for which the transition rate $\mathcal{W}(E_{+} \rightarrow E'_{+})$ depends only on the final state of the system:

$$\mathcal{W}(E_{+} \rightarrow E'_{+}) = \mathcal{W}(E'_{+}) \quad \text{independent of } E_{+} \quad (87)$$

This type of assumption is commonly used in the literature of stochastic rate processes and is called “the strong collision hypothesis”.¹³ In this particular case it is easy to compute the stochastic operator \mathbf{L} and to evaluate the average survival function analytically. We express the probability $\varphi_{E_{+}}(E_{+}; t) dE_{+}$ in terms of the rate coefficient k_{Σ} and make use of eq 83. We obtain

$$\varphi_{E_{+}}(E_{+}; t) = \frac{\varphi_{\Sigma}(k_{\Sigma}; t)}{|dE_{+}(k_{\Sigma})/dk_{\Sigma}|} = \frac{k_{\Sigma} \varphi_{\Sigma}(k_{\Sigma}; t)}{k_{\text{B}} T} \quad (88)$$

By inserting eqs 87 and 88 into eq 85, we obtain

$$\frac{\partial}{\partial t} \varphi_{\Sigma}(k_{\Sigma}; t) = \frac{k_{\text{B}} T}{k_{\Sigma}} \left\{ \mathcal{W} \left[k_{\text{B}} T \ln \left\{ \left(\frac{1 + K_{\text{equil}}}{K_{\text{equil}}} \right) \frac{\nu_{+}}{k_{\Sigma}} \right\} \right] \right\} - \lambda \varphi_{\Sigma}(k_{\Sigma}; t) \quad (89)$$

where

$$\lambda = \int \mathcal{W}(E_{+} \rightarrow E'_{+}) dE'_{+} = \int \mathcal{W}(E'_{+}) dE'_{+} \quad (90)$$

is the total transition (renewal) rate from a given initial value of the activation energy to any final values. From eq 89 we notice that

$$\mathbf{L} \dots = \frac{k_{\text{B}} T}{k_{\Sigma}} \left\{ \mathcal{W} \left[k_{\text{B}} T \ln \left\{ \left(\frac{1 + K_{\text{equil}}}{K_{\text{equil}}} \right) \frac{\nu_{+}}{k_{\Sigma}} \right\} \right] \right\} - \lambda \dots \quad (91)$$

and eq 80 for the marginal average $\mathcal{F}(k_{\Sigma}; t)$ can be solved analytically. To save space, the details of the computation are

not presented here. By inserting the resulting expression for $\mathcal{F}(k_\Sigma; t)$ into eq 78, we come to

$$\langle \mathcal{L}(t') \rangle = \int_0^\infty \left\{ \varphi_\Sigma^{\text{st}}(k_\Sigma) \exp[-(\lambda + k_\Sigma)t] + \frac{\tilde{\mathcal{W}}(k_\Sigma)}{k_\Sigma + \lambda} \{1 - \exp[-(\lambda + k_\Sigma)t]\} \right\} dk_\Sigma \quad (92)$$

where

$$\tilde{\mathcal{W}}(k_\Sigma) = \left| \frac{dE_+(k_\Sigma)}{dk_\Sigma} \right| \mathcal{W}(E_+) = \frac{k_B T}{k_\Sigma} \left\{ \mathcal{W} \left[k_B T \ln \left\{ \left(\frac{1 + K_{\text{equil}}}{K_{\text{equil}}} \right) \frac{\nu_+}{k_\Sigma} \right\} \right] \right\} \quad (93)$$

is the transition rate for the activation energy expressed in terms of the rate coefficient k_Σ .

Now we notice the following difficulty. In our computation the initial condition corresponds to a system with static disorder displaying stretched exponential relaxation. In section 4 we have shown that for such a system the average density of states is given by eq 48. The exponent in eq 48 is given by eq 52, i.e., $\alpha = \xi T$. Since for a stretched exponential we have $\alpha < 1$, from eq 48 it follows that for static disorder the average number of channels is infinite:

$$\langle \mathcal{N} \rangle = \int_0^\infty \rho_\Sigma(k_\Sigma) dk_\Sigma = \infty \quad (94)$$

Due to the time independence of the total number of channels for systems with dynamical disorder, the divergent behavior carries over for systems with dynamical disorder. This divergence is, however, spurious because the corresponding integral expressions for the averages are well behaved. By using a technique commonly used in quantum field theory and stochastic mechanics, the problem can be solved by introducing an infrared cutoff $k_\Sigma^* \neq 0$ and by passing to the limit $k_\Sigma^* \rightarrow 0$ after the computations are performed.

For a cutoff value $k_\Sigma^* \neq 0$ the total average number of channels is finite. From eq 48 we come to

$$\langle \mathcal{N} \rangle = \int_{k_\Sigma^*}^\infty \rho_\Sigma(k_\Sigma) dk_\Sigma = [\Gamma(1 - \xi T)]^{-1} \left(\frac{k_\Sigma^*}{k_\Sigma^*} \right)^{\xi T} \quad (95)$$

and the stationary probability density $\varphi_\Sigma^{\text{st}}(k_\Sigma)$ is given by

$$\varphi_\Sigma^{\text{st}}(k_\Sigma) dk_\Sigma = \rho_\Sigma(k_\Sigma) dk_\Sigma / \int_{k_\Sigma^*}^\infty \rho_\Sigma(k_\Sigma) dk_\Sigma = \xi T (k_\Sigma^*)^{\xi T} (k_\Sigma)^{-(1+\xi T)} dk_\Sigma \quad (96)$$

After some calculations we get the following expression for the average survival function:

$$\begin{aligned} \langle \mathcal{L}(t) \rangle = & \frac{1}{K_{\text{equil}} + 1} + \left[\langle \mathcal{L}(0) \rangle - \frac{1}{K_{\text{equil}} + 1} \right] \times \\ & \exp \left\{ - \int_{k_\Sigma^*}^\infty \left[1 - \frac{\tilde{\mathcal{W}}(k_\Sigma)}{(\lambda + k_\Sigma) \varphi_\Sigma^{\text{st}}(k_\Sigma)} \right] \{1 - \exp[-t(\lambda + k_\Sigma)]\} \times \right. \\ & \left. \rho_\Sigma(k_\Sigma) dk_\Sigma \right\} \quad (97) \end{aligned}$$

Equation 97 can be further simplified by expressing the stationary probability distribution $\varphi_\Sigma^{\text{st}}(k_\Sigma)$ in terms of the

transition rate $\tilde{\mathcal{W}}(k_\Sigma)$. It is easy to check that for a system with strong dynamical disorder, obeying the constraint (86), the stationary solution of the master equation (85) is given by

$$\varphi_{E_+}^{\text{st}}(E_+) dE_+ = \mathcal{W}(E_+) dE_+ / \int \mathcal{W}(E_+) dE_+ = \mathcal{W}(E_+) dE_+ / \lambda \quad (98)$$

from which, by passing from the activation energy E_+ to the total rate k_Σ we come to

$$\varphi_{E_+}^{\text{st}}(k_\Sigma) dk_\Sigma = \tilde{\mathcal{W}}(k_\Sigma) dk_\Sigma / \lambda \quad (99)$$

By combining eqs 48, 52, 97, and 99, we can rewrite the dynamical average (97) in a very simple form:

$$\langle \mathcal{L}(t) \rangle = \frac{1}{K_{\text{equil}} + 1} + \left[\langle \mathcal{L}(0) \rangle - \frac{1}{K_{\text{equil}} + 1} \right] \exp\{-\mathcal{L}(t)\} \quad (100)$$

where the time factor $\mathcal{L}(t)$ is given by

$$\begin{aligned} \mathcal{L}(t) = & \int_{k_\Sigma^*}^\infty \left[\frac{k_\Sigma}{\lambda + k_\Sigma} \right] \{1 - \exp[-t(\lambda + k_\Sigma)]\} \rho_\Sigma(k_\Sigma) dk_\Sigma = \\ & \frac{\alpha \omega^\alpha}{\Gamma(1 - \alpha)} \int_{k_\Sigma^*}^\infty \left[\frac{1 - \exp[-t(\lambda + k_\Sigma)]}{(\lambda + k_\Sigma)(k_\Sigma)^\alpha} \right] dk_\Sigma \quad (101) \end{aligned}$$

and the frequency factor ω is given by eq 53. As expected, the last integral in eq 101 converges in the limit $k_\Sigma^* \rightarrow 0$. In this limit the integral can be evaluated analytically. For computing it, we differentiate eq 101 term by term with respect to the time variable t and express the resulting integral in terms of the complete gamma function. After this operation we reintegrate the resulting expression with respect to the time variable and express the time integral in the final expression in terms of the incomplete gamma function. The result of these mathematical transformations is the following:

$$\begin{aligned} \langle \mathcal{L}(t) \rangle = & \frac{1}{K_{\text{equil}} + 1} + \\ & \left[\langle \mathcal{L}(0) \rangle - \frac{1}{K_{\text{equil}} + 1} \right] \exp \left\{ - \alpha \left(\frac{\omega}{\lambda} \right)^\alpha \gamma(\alpha, \lambda t) \right\} \quad (102) \end{aligned}$$

where

$$\gamma(a, x) = \int_0^x x^{a-1} \exp(-x) dx \quad x \geq 0, \quad a > 0 \quad (103)$$

is the incomplete gamma function.

If in eq 102 the time of observation t is smaller than the time scale $\tau = 1/\lambda$ for the regression of activation energy fluctuations, then the system is very close to a state of static disorder and eq 102 reduces to the generalized stretched exponential law (37) derived in section 4 for systems with static disorder:

$$\langle \mathcal{L}(t) \rangle \sim \langle \mathcal{L}(\infty) \rangle + [\langle \mathcal{L}(0) \rangle - \langle \mathcal{L}(\infty) \rangle] \exp[-(\omega t)^\alpha] \quad \text{for } \lambda t < 1 \quad (104)$$

For large times, however, the systems with static and dynamic disorder display two different types of dynamic behavior. A system with static disorder evolves toward a state of thermodynamic equilibrium that is independent of the initial preparation of the system

$$\langle \cdot(t) \rangle \rightarrow \langle \cdot(\infty) \rangle = 1/(K_{\text{equil}} + 1) = \text{independent of } \langle \cdot(0) \rangle \quad (105)$$

On the other hand, according to eq 102 for a system with dynamical disorder, in the long run the process evolves toward a nonequilibrium stationary state that still contains some residual information about the initial state of the system. For systems with dynamical disorder investigated in this section the state of thermodynamic equilibrium cannot be reached even after an infinitely long period of time!

$$\langle \cdot(t) \rangle \rightarrow \frac{1}{K_{\text{equil}} + 1} + \left[\langle \cdot(0) \rangle - \frac{1}{K_{\text{equil}} + 1} \right] \times \exp \left\{ -\left(\frac{\omega}{\lambda} \right)^\alpha \Gamma(1 + \alpha) \right\} \quad \text{as } t \rightarrow \infty \quad (106)$$

Although at first sight this result might seem surprising, it is not totally unexpected. In the literature there are reports that dynamical disorder may slow down the kinetics.¹⁴ The physical explanation of this effect is simple: for a process with dynamical disorder the efficiency of channels with large relaxation rates is smaller than in a system with static disorder.

7. Fluctuation–Dissipation Relations for Rate Processes in Disordered Systems

Until now we have taken into account only the random fluctuations of the rate coefficients. We have neglected the statistical fluctuations of the numbers of molecules. In a real disordered system both types of fluctuations occur and their interaction leads to interesting effects. In this section we extend the theory developed in the previous sections by taking into account the fluctuations of numbers of molecules.

Our analysis proceeds in two steps. First we consider a set of random realizations of the rate coefficients and study the fluctuations of the numbers of molecules for this set of realizations. The second step consists in taking a configurational average over all possible values of the rate coefficients. These developments are similar both for systems with static and dynamical disorder. In the following we focus on the problem of dynamical disorder that includes the static disorder as a particular case.

We consider an ensemble of channels characterized by the multiplicities N_1, N_2, \dots and by the rate coefficients $k_1^\pm(t), k_2^\pm(t), \dots$. For a given realization of the numbers of channels N_1, N_2, \dots and of the rate coefficients $k_1^\pm(t), k_2^\pm(t), \dots$ we can describe the composition fluctuations in the system by means of a chemical master equation

$$\begin{aligned} \frac{\partial}{\partial t} \mathcal{B}_{\text{realiz}}(X; t) = & \left[\sum_j N_j k_j^+ \right] \{ \mathcal{B}_{\text{realiz}}(X+1; t)(X+1) - \mathcal{B}_{\text{realiz}}(X; t)(X) \} + \\ & \left[\sum_j N_j k_j^- \right] \{ \mathcal{B}_{\text{realiz}}(X_\Sigma - X + 1; t)(X_\Sigma - X + 1) - \\ & \mathcal{B}_{\text{realiz}}(X; t)(X_\Sigma - X + 1) \} \quad (107) \end{aligned}$$

where

$$X_\Sigma = X(0) + Y(0) = X(t) + Y(t) = \text{constant} \quad (108)$$

is the total number of molecular species present in the system, $X(t)$ and $Y(t)$ are the number of molecules of type X and Y present in the system at time t , respectively, and

$$\mathcal{B}_{\text{realiz}}(X; t) \quad \text{with} \quad \sum_{X=0}^{X_\Sigma} \mathcal{B}_{\text{realiz}}(X; t) = 1 \quad (109)$$

is the probability that, for a given realization of the parameters N_1, N_2, \dots and $k_1^\pm(t), k_2^\pm(t), \dots$ at time t , the systems contain X molecules of type X. If the disordered structure of the system is taken into account, then the composition fluctuations can be described by the configurational average of the probability $\mathcal{B}_{\text{realiz}}(X; t)$

$$\mathcal{P}(X; t) = \langle \mathcal{B}_{\text{realiz}}(X; t) \rangle \quad (110)$$

where the average $\langle \dots \rangle$ is taken over all possible values of the random parameters N_1, N_2, \dots and $k_1^\pm(t), k_2^\pm(t), \dots$. Unfortunately, the evaluation of the averaged probability $\mathcal{P}(X; t)$ is a very tough problem that in general does not have a simple analytic solution. It is possible however to derive an analytic expression for the generating function of this probability:

$$\mathcal{G}(s; t) = \sum_{X=0}^{X_\Sigma} s^X \mathcal{P}(X; t) \quad \text{with} \quad |s| \leq 1 \quad (111)$$

By using this expression for the generating function $\mathcal{G}(s; t)$ we can derive a general class of fluctuation–dissipation relations that makes it possible to compute all moments of the random variable X .

We transform the master equation (107) by using the conditions of detailed balance (54) and apply the generating function transformation

$$\mathcal{C}(s; t) = \sum_{X=0}^{X_\Sigma} s^X \mathcal{B}_{\text{realiz}}(X; t) \quad \text{with} \quad |s| \leq 1 \quad (112)$$

to the resulting equation. After some calculations we come to

$$\begin{aligned} \frac{\partial}{\partial \sigma} \mathcal{C}(s; \sigma) = & \frac{(1-s)(K_{\text{equil}} + s)}{(K_{\text{equil}} + 1)} \frac{\partial}{\partial s} \mathcal{C}(s; \sigma) - \\ & \frac{X_\Sigma(1-s)}{(K_{\text{equil}} + 1)} \mathcal{C}(s; \sigma) \quad (113) \end{aligned}$$

with the initial condition

$$\mathcal{C}(s; \sigma = 0) = \mathcal{C}^0(s) \quad (114)$$

where

$$\mathcal{C}^0(s) = \sum_{X=0}^{X_\Sigma} s^X \mathcal{B}_{\text{realiz}}(X; t = 0) \quad (115)$$

and

$$\sigma(t) = \int_0^t \left\{ \sum_j N_j [k_j^+(t') + k_j^-(t')] \right\} dt' \quad (116)$$

is an intrinsic time scale depending on the fluctuations of the rate coefficients.

The partial differential equation (113) can be solved exactly by using the method of characteristics. The calculations are lengthy but standard, and to save space, they are not presented here. The solution corresponding to the initial condition (114) is the following:

$$\mathcal{C}(s; \sigma) = \left\{ \frac{K_{\text{equil}} + \exp(-\sigma) + s[1 - \exp(-\sigma)]}{K_{\text{equil}} + 1} \right\}^{X_{\Sigma}} \times \mathcal{C}_0 \left\{ \frac{K_{\text{equil}}[1 - \exp(-\sigma)] + s[1 + K_{\text{equil}} \exp(-\sigma)]}{K_{\text{equil}} + \exp(-\sigma) + s[1 - \exp(-\sigma)]} \right\} \quad (117)$$

The only parameter in eq 117 depending on the random rate coefficients is the intrinsic time scale $\sigma(t)$, which simplifies the operation of computing the configurational average. Due to the linearity of the definitions of the generating functions we have

$$\mathcal{G}(s; t) = \langle \mathcal{C}(s; \sigma(t')) \rangle = \left\{ \left\{ \frac{K_{\text{equil}} + e^{-\sigma} + s[1 - e^{-\sigma}]}{K_{\text{equil}} + 1} \right\}^{X_{\Sigma}} \times \mathcal{G} \left\{ \frac{K_{\text{equil}}[1 - e^{-\sigma}] + s[1 + K_{\text{equil}} e^{-\sigma}]}{K_{\text{equil}} + e^{-\sigma} + s[1 - e^{-\sigma}]} \quad t = 0 \right\} \right\} \quad (118)$$

For computing the configurational average we try to express eq 118 as a linear series expansion of different powers of factors of the type

$$\Phi_m(t) = \langle \exp(-\sigma) \rangle = \langle \exp\{-m \int_0^t \{ \sum_j N_j[k_j^+(t') + k_j^-(t')] \} dt' \} \rangle \quad (119)$$

These factors can be easily evaluated by using the Poissonian distribution of channels (23) resulting in

$$\Phi_m(t) = \langle \exp(-m\sigma) \rangle = \exp[-\int_m(t)] \quad (120)$$

where the phase factors $\int_m(t)$ are given by the path integrals

$$\int_m(t) = \int \int \rho_{\Sigma}[k_{\Sigma}(t')] \mathcal{D}[k_{\Sigma}(t')] \times \{1 - \exp[-m \int_0^t k_{\Sigma}(t') dt']\} \quad (121)$$

These integrals can be evaluated by using the technique developed in section 5.

We introduce the factorial moments of the number of X particles attached to the probability distribution $\mathcal{P}(X; t)$:

$$F_m(t) = \sum_{X=0}^{X_{\Sigma}} X(X-1)\dots(X-m+1) \mathcal{P}(X; t) \quad m \leq X_{\Sigma} \quad (122)$$

These factorial moments can be expressed in terms of the generating function $\mathcal{G}(s; t)$ of the probability distribution $\mathcal{P}(X; t)$. We have

$$F_m(t) = (\partial^m \mathcal{G}(s; t) / \partial s^m)|_{s=1} \quad (123)$$

From eq 123 it follows that we can represent the generating function $\mathcal{G}(s; t)$ as a power expansion

$$\mathcal{G}(s; t) = 1 + \sum_{m=1}^{X_{\Sigma}} F_m(t) \frac{(s-1)^m}{m!} \quad (124)$$

By applying eq 124 for $t = 0$ and inserting the result in eq 118, it is possible to express the configurational average in eq 118 in terms of the functions given by eqs 119 and 120. After lengthy manipulations involving the expansion of the different terms as powers of $s - 1$, changing the summation variables and the order of summation, etc., eq 118 can be put in the form (124), where the factorial moments $F_m(t)$ are given by

$$F_m(t) = \sum_{q=0}^m \exp(-\int_q(t)) \frac{m!}{(m-q)!(X_{\Sigma}-m)!} \times \sum_{n=0}^q F_n(0) \frac{(-1)^{q-n}(X_{\Sigma}-n)!}{n!(K_{\text{equil}}+1)^{m-n}(q-n)!} \quad (125)$$

Equation 125 is the fluctuation-dissipation relation that establishes a relationship between the macroscopic behavior of the system, expressed by the time dependence of the average number of molecules, $\langle X(t) \rangle = F_1(t)$, or by the corresponding average survival function, $\langle \int(t) \rangle = \langle X(t) \rangle / X_{\Sigma}$, and the dynamics of the fluctuations, expressed by the superior moments. These equations may be used to compute central moments and the cumulants of the number of molecules by using a method based on the use of Stirling numbers of the first and second kind.¹⁵ Equation 125 may be used as a basis for developing semi-numerical approaches for computing the fluctuations of different orders. The numerical algorithms that can be developed by using these equations are going to be very simple because the most difficult operation, the dynamical averaging over all possible values of the rate coefficients has been carried out analytically.

For applying eq 125 it is necessary to evaluate the dynamical damping factors $\Phi_m(t)$ defined by eq 119. Here we give the expressions of these factors in the particular case of stretched exponential kinetics. For a system with dynamical disorder they are given by

$$\Phi_m(t) = \exp[-\int_m(t)] = \exp\left\{-\alpha \left(\frac{m\omega}{\lambda}\right)^{\alpha} \gamma(\alpha, \lambda t)\right\} \quad (126)$$

The expressions for the $\Phi_m(t)$ system with static disorder can be derived as a particular case from eq 126 by passing to the limit $\lambda \rightarrow 0$. We have

$$\Phi_m(t) = \exp[-\int_m(t)] = \exp\{-(mt\omega)^{\alpha}\} \quad (127)$$

Equations 126 and 127 have been derived by using the method of the stochastic Liouville equation developed in section 5 for the evaluation of the phase factor $\int(t)$ defined by eq 61. By examining the main steps of the derivation developed in section 5, it is easy to notice that the passage from the simple phase factor $\int(t)$ to the multiple phase factors $\int_m(t)$ defined by eq 121 corresponds to the substitutions

$$\int(t) = \int_1(t) \rightarrow \int_m(t) \quad \lambda \rightarrow \lambda/m \quad t \rightarrow mt \quad (128)$$

By applying the scale transformation (128) to eq 101 and evaluating the integral in the resulting equation in the limit $k_{\Sigma}^* \rightarrow 0$, we come to eq 125.

For a rate process occurring in an ordered system (for example, in an ideal crystal) in the thermodynamic limit the relative fluctuations become negligible and the deterministic evolution equations provide a very accurate description of the process. In nonequilibrium statistical physics it is generally agreed that a deterministic description is valid in the thermodynamic limit and the process fulfills the condition of statistical nonintermittence. For testing this condition it is necessary to evaluate the relative fluctuations of the numbers of molecules, expressed as the ratios of the cumulants of the different orders of the number of molecules divided by the successive powers of the average number of molecules. These ratios bear the name of relative fluctuations of different orders. We have

$$\rho_m = \langle\langle X^m \rangle\rangle / \langle\langle X \rangle\rangle^m \quad m = 2, 3, \dots \quad (129)$$

where $\langle\langle X^m \rangle\rangle$, $m = 1, 2, \dots$ are the cumulants of different orders of the random variable X , ρ_m is the relative fluctuation of order m , and the double brackets denote cumulant averages. If the population fluctuations are statistically nonintermittent in the thermodynamic limit, then as $\langle\langle X \rangle\rangle \rightarrow \infty$, the relative fluctuations of different orders must decay to zero:

$$\rho_m = \langle\langle X^m \rangle\rangle / \langle\langle X \rangle\rangle^m \rightarrow 0 \quad \text{as} \quad \langle\langle X \rangle\rangle \rightarrow \infty \quad (130)$$

Otherwise, if the relative fluctuations tend toward values different from zero or even diverge to infinity, the fluctuations are statistically intermittent. For a system displaying statistical intermittence a pure deterministic description is not appropriate.

In the following we test for statistical intermittence in reversible rate processes occurring in disordered systems. For simplicity we only investigate the asymptotic behavior of the relative fluctuation of order 2. In order to avoid the algebraic complexities generated by arbitrary initial conditions, we assume that at time $t = 0$ there is no intermediate X present in the system, i.e.

$$F_m(t=0) = 0 \quad m = 1, 2, \dots \quad (131)$$

If eq 130 holds, then the average value and the dispersion of the number of X molecules at time t can be easily evaluated from eq 125. We have

$$\langle X(t) \rangle = F_1(t) = X_\Sigma [1 - \Phi_1(t)] / (K_{\text{equil}} + 1) \quad (132)$$

and

$$\begin{aligned} \langle \Delta X^2(t) \rangle &= \langle X^2(t) \rangle - \langle X(t) \rangle^2 = F_2(t) + F_1(t)[1 - F_1(t)] = \\ &= \frac{(X_\Sigma)^2 \{ \Phi_2(t) - [\Phi_1(t)]^2 \} - X_\Sigma [1 - 2\Phi_1(t) + \Phi_2(t)]}{(K_{\text{equil}} + 1)^2} + \\ &\quad \frac{X_\Sigma [1 - \Phi_1(t)]}{K_{\text{equil}} + 1} \end{aligned} \quad (133)$$

From eqs 132 and 133 it is easy to check that in the thermodynamic limit the relative fluctuation of order 2 of the number of X molecules tends toward a finite value different from zero; that is, the fluctuations are intermittent:

$$\rho_2(t) \rightarrow \frac{\Phi_2(t) - [\Phi_1(t)]^2}{[1 - \Phi_1(t)]^2} > 0 \quad \text{as} \quad \langle X(t) \rangle \rightarrow \infty \quad (134)$$

The positivity of the right-hand side (rhs) of eq 134 can be easily proven by using the expression (126) for the damping factors $\Phi_m(t)$ and by using the Cauchy inequality. We notice that, according to eq 134, the intermittence occurs both for systems with static and dynamic disorder.

Finally, we remark that for vanishing initial conditions the average probability distribution for composition fluctuations, $\mathcal{P}(X; t)$, can be evaluated analytically. According to the definition (111) of the generating function $\mathcal{G}(s; t)$ we have

$$\mathcal{P}(X; t) = \frac{1}{X!} \frac{\partial^X}{\partial s^X} \mathcal{G}(s; t) \Big|_{s=0} \quad (135)$$

For vanishing initial conditions we have

$$\mathcal{B}_{\text{realiz}}(X; t=0) = \delta_{X0} \quad \text{and} \quad \mathcal{C}(s; t=0) = 1 \quad (136)$$

By combining eqs 118, 135, and 136, and after lengthy calculations, we obtain an analytic expression for the ensemble

average of the state probability:

$$\mathcal{P}(X; t) = \mathcal{P}_{\text{equil}}(X) \chi(X; t) \quad (137)$$

where $\mathcal{P}_{\text{equil}}(X)$ is the binomial distribution of the number of X molecules corresponding to thermodynamic equilibrium:

$$\mathcal{P}_{\text{equil}}(X) = \frac{X_\Sigma!}{X!(X_\Sigma - X)!} \left(\frac{K_{\text{equil}}}{K_{\text{equil}} + 1} \right)^X \left(\frac{1}{K_{\text{equil}} + 1} \right)^{X_\Sigma - X} \quad (138)$$

and

$$\begin{aligned} \chi(X; t) &= \left\langle \left(1 + \frac{\exp(-\sigma)}{K_{\text{equil}}} \right)^X (1 - \exp(-\sigma))^{X_\Sigma - X} \right\rangle = \\ &= \sum_{m_1=0}^X \sum_{m_2=0}^{X_\Sigma - X} \Phi_{m_1+m_2}(t) \frac{(K_{\text{equil}})^{-m_1} (-1)^{m_2} X!(X_\Sigma - X)!}{m_1!(X - m_1)! m_2!(X_\Sigma - X - m_2)!} \end{aligned} \quad (139)$$

is a correction factor which expresses the nonequilibrium effects.

Equations 137 and 138 may serve as a basis for developing a thermodynamic description of nonequilibrium systems with dynamical disorder, which is a generalization of the thermodynamic and stochastic theory by Ross, Hunt, and Hunt.¹⁶ We intend to investigate this problem in our future research.

8. Lifetime Distributions in Systems with Static or Dynamical Disorder

The theoretical study and the experimental measurement of the average lifetimes and of the corresponding lifetime distributions of reaction intermediates are important topics in the kinetic analysis of complex systems. In this context different approaches have been developed. For a number of chain reactions, for example, for radical polymerizations, the average lifetimes of the active intermediates is a measurable quantity that can be used for testing the validity of different reaction mechanisms and for the evaluation of the kinetic parameters of the process.¹⁷ In biochemistry the transition and transit times and their statistical properties are important factors characterizing the dynamical behavior of complex metabolic reaction networks. In the case of chemical reactions occurring in disordered systems the lifetime distributions have been used for developing the method of kinetic spectrum analysis, which has played an important role in conducting kinetic experiments in environmental chemistry and heterogeneous catalysis.¹⁸

We have developed a semistochastic technique for studying stationary as well as nonstationary lifetime distributions in complex chemical systems.¹⁹ These studies include analytical and numerical techniques for computing the time distributions and suggest a type of tracer experiment that may be used for the evaluation of these functions, both for stationary and time dependent regimes. In this section we apply some of these techniques for the theoretical study of lifetime distribution in systems with static or dynamical disorder.

Our purpose is to compute the average distribution of the duration of the transient regime of the process, that is, the distribution of the time necessary for the process to reach its final state. In the particular case of the stretched exponential kinetics studied in this article, there are two different types of final states. (1) A state of thermodynamic equilibrium, for systems with static disorder, for which the average survival function is given by eq 30, $\langle \rangle_{\infty} = \langle \rangle_{\text{equil}}$, where

$$\langle \rangle_{\text{equil}} = 1/(K_{\text{equil}} + 1) \quad (140)$$

(2) A frozen nonequilibrium state, characterized by systems with dynamical disorder, for which the final value of the survival function depends on the initial state of the system:

$$\langle \gamma(\infty) \rangle = \langle \gamma_{\text{equil}} \rangle + [\langle \gamma(0) \rangle - \langle \gamma_{\text{equil}} \rangle] \Phi(\infty) \quad (141)$$

where $\Phi(\infty)$ is the final value of the dynamical damping factor of order 1, given by eqs 120 and 121, applied for $m = 1$. In the particular case of systems with strong dynamical disorder, studied in section 6, $\Phi(\infty)$ is given by

$$\Phi(\infty) = \exp\left\{-\left(\frac{\omega}{\lambda}\right)^\alpha \Gamma(1 + \alpha)\right\} \quad (142)$$

(see eq 106). In order to introduce a properly defined lifetime distribution of the transient regime for static as well as for dynamical disorder, it is necessary to introduce a scaled average survival function, $\langle \tilde{\gamma}(t) \rangle$, which fulfills the following conditions:²⁰ (1) it is equal to unity for $t = 0$, (2) its final value of $\langle \tilde{\gamma}(\infty) \rangle$ is equal to zero, and (3) it is a nonincreasing function of time. These three conditions can be expressed as

$$\langle \tilde{\gamma}(t=0) \rangle = 1 \quad \langle \tilde{\gamma}(\infty) \rangle = 0 \quad \frac{d}{dt} \langle \tilde{\gamma}(t) \rangle \leq 0 \quad (143)$$

It is easy to check that a suitable scaled form is given by the homographic transformation

$$\langle \tilde{\gamma}(t) \rangle = [\langle \gamma(t) \rangle - \langle \gamma(\infty) \rangle] / [\langle \gamma(0) \rangle - \langle \gamma(\infty) \rangle] \quad (144)$$

which is commonly used in the literature for fitting experimental data.⁹ We rewrite the general kinetic equation in the form

$$\langle \gamma(t) \rangle = \langle \gamma_{\text{equil}} \rangle + [\langle \gamma(0) \rangle - \langle \gamma_{\text{equil}} \rangle] \Phi(t) \quad (145)$$

and apply the scale transformation (143), resulting in

$$\langle \tilde{\gamma}(t) \rangle = \frac{\Phi(t) - \Phi(\infty)}{1 - \Phi(\infty)} \quad (146)$$

It is easy to check that the scaled survival function $\langle \tilde{\gamma}(t) \rangle$, given by eqs 144–146, fulfills by construction the first two restrictions (143). The last restriction, i.e., $d\langle \tilde{\gamma}(t) \rangle/dt \leq 0$, is fulfilled only if the phase factor $\gamma(t)$, defined by eq 61, is a nondecreasing function of time:

$$\zeta(t) = d\gamma(t)/dt \geq 0 \quad (147)$$

that is, if the phase velocity $\zeta(t)$ is nonnegative. Although we do not have a formal proof for the constraint (147), we notice that it is automatically fulfilled for systems with strong dynamical disorder studied in section 6 for which

$$\zeta(t) = d\gamma(t)/dt = \alpha\omega^\alpha t^{\alpha-1} \exp(-\lambda t) > 0 \quad (148)$$

In terms of the scaled survival function $\langle \tilde{\gamma}(t) \rangle$ we can introduce the probability distribution of the transient lifetimes

$$\psi(t) dt \quad \text{with} \quad \int_0^\infty \psi(t) dt = 1 \quad (149)$$

We have

$$\psi(t) dt = -\frac{\partial}{\partial t} \langle \tilde{\gamma}(t) \rangle dt = -\frac{1}{1 - \Phi(\infty)} \frac{\partial}{\partial t} \Phi(t) \times dt = \frac{\Phi(t) \zeta(t) dt}{1 - \Phi(\infty)} \quad (150)$$

It is easy to check that, if the phase velocity $\zeta(t)$ is nonnegative,

then the function given by eq 150 is a properly defined probability density, that is, nonnegative for any real value of the lifetime t of the transient state and it is normalized to unity.

Another useful function for the study of lifetime distributions is the scaled effective rate of relaxation, $\tilde{k}_{\text{eff}}(t)$, which, according to the definitions used in the literature,^{5,20} is equal to the logarithmic derivative, with changed sign, of the scaled survival function $\langle \tilde{\gamma}(t) \rangle$

$$\begin{aligned} \tilde{k}_{\text{eff}}(t) dt &= \left[-\frac{\partial}{\partial t} \ln \langle \tilde{\gamma}(t) \rangle \right] dt = \frac{\psi(t) dt}{\langle \tilde{\gamma}(t) \rangle} = \\ &= -\frac{1}{\Phi(t) - \Phi(\infty)} \frac{\partial}{\partial t} \Phi(t) dt = \frac{\Phi(t) \zeta(t) dt}{\Phi(t) - \Phi(\infty)} = \\ &= \frac{\zeta(t)}{1 - \exp[\gamma(t) - \gamma(\infty)]} \quad (151) \end{aligned}$$

(see also eq 29).

In the particular case of stretched exponential kinetics in systems with static disorder, the functions $\psi(t)$ and $\tilde{k}_{\text{eff}}(t)$ are given by

$$\psi(t) = \alpha\omega^\alpha t^{-(1-\alpha)} \exp\{-(\omega t)^\alpha\} \quad (152)$$

and

$$\tilde{k}_{\text{eff}}(t) = \alpha\omega^\alpha t^{-(1-\alpha)} \quad (153)$$

Both functions have a singularity of the negative power law type for $t \rightarrow 0$, and as time increases, they decrease monotonically to zero. All positive moments of the lifetime of the transient state exist and are finite. We have

$$\langle t^m \rangle = \int_0^\infty t^m \psi(t) dt = \omega^{-m} \Gamma(1 + m/\alpha) \quad m \geq 0 \quad (154)$$

For dynamical disorder the time evolution the functions $\psi(t)$ and $\tilde{k}_{\text{eff}}(t)$ is more complicated. We obtain

$$\begin{aligned} \psi(t) &= \alpha\omega^\alpha t^{-(1-\alpha)} \left\{ 1 - \exp\left[-\alpha\left(\frac{\omega}{\lambda}\right)^\alpha \Gamma(\alpha)\right] \right\}^{-1} \times \\ &\quad \exp\left\{-\lambda t - \alpha\left(\frac{\omega}{\lambda}\right)^\alpha \gamma(\alpha, \lambda t)\right\} \quad (155) \end{aligned}$$

and

$$\begin{aligned} \tilde{k}_{\text{eff}}(t) &= \alpha\omega^\alpha t^{-(1-\alpha)} \times \\ &\quad \exp(-\lambda t) \left\{ 1 - \exp\left[-\alpha\left(\frac{\omega}{\lambda}\right)^\alpha [\gamma(\alpha, \lambda t) - \Gamma(\alpha)]\right] \right\}^{-1} \quad (156) \end{aligned}$$

Figures 1 and 2 display graphical representations of the dimensionless forms of these two quantities:

$$\psi_\tau(\tau) d\tau = \psi(t) dt \quad \text{and} \quad \tilde{k}_{\text{eff}}^*(\tau) = \tilde{k}_{\text{eff}}(t)/\omega \quad (157)$$

as functions of the dimensionless time

$$\tau = \omega t \quad (158)$$

and of the dimensionless renewal rate of the activation energy,

$$f = \lambda/\omega \quad (159)$$

For a renewal rate equal to zero, $f = 0$, Figures 1 and 2 display the behavior of a system with static disorder. As the renewal rate increases, the probability distribution of the lifetime becomes broader and broader. The physical interpretation of this result is simple. By taking into account that the renewal

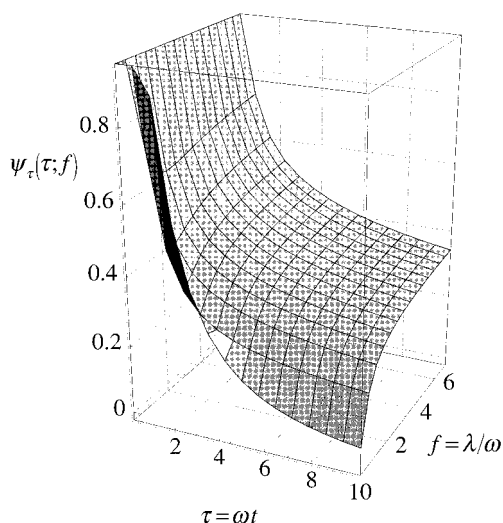


Figure 1. Graphical representation of the dimensionless form of the lifetime distribution for stretched exponential kinetics with dynamical disorder, $\psi_\tau(\tau; f)$, as a function of dimensionless time, $\tau = \omega t$, and of the dimensionless renewal rate of the activation energy, $f = \lambda/\omega$. The surface is evaluated for a value of the scaling exponent of the stretched exponential $\alpha = 0.7$.

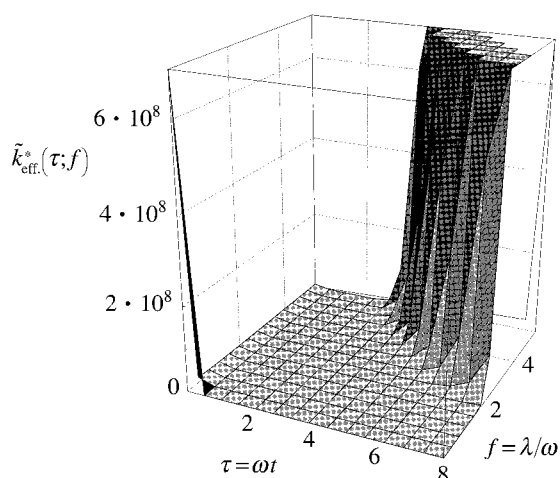


Figure 2. Graphical representation of the dimensionless effective rate coefficient for stretched exponential kinetics with dynamical disorder, $\tilde{k}_{eff}^*(\tau; f)$, as a function of dimensionless time, $\tau = \omega t$, and of the dimensionless renewal rate of the activation energy, $f = \lambda/\omega$. The surface is evaluated for a value of the scaling exponent of the stretched exponential $\alpha = 0.7$.

rate is a measure of the strength of dynamical disorder, it follows that the broadening of the lifetime distribution with the increase of the renewal rate is due to the slowing down of the process caused by dynamical disorder.

The effective rate of relaxation, $\tilde{k}_{eff}^*(\tau)$, has an interesting behavior. For small times and small frequencies it has very large values. With the increase of time and of the renewal frequency it decreases quickly toward small values very close to zero. For large values of time and of the renewal frequency it increases abruptly, taking again very large values. This type of behavior characterized by large exit rates for small and large values of the lifetime, and for low exit rates for intermediate lifetimes, is not very often encountered in physics or chemistry; however, it is quite common in vital statistics and reliability theory.²⁰ For example the mortality force in humans, which is a notion similar to the effective ratio of relaxation, is characterized by

large values for young and old ages and it is low and approximately constant for intermediate ages. Similarly, the rate of failure of an electronic component is very large at the beginning or at the end of its lifespan and low for intermediate times. This final increase of the effective rate of relaxation has, however, a negligible contribution, because it occurs only for the region of the state space characterized by large renewal rates f , which are very rare.

Finally, we summarize the main results derived in this section. We have introduced a systematic approach for computing lifetime distributions and effective rate constants based on the use of the homographic transformation (144) that leads to properly defined frequency distributions, which are never negative and preserve the condition of normalization to unity. Our approach provides a theoretical basis to the empirical adjusting of the experimental data to a stretched exponential by subtracting the “baseline” from the observed kinetic curves.⁹ Another advantage of our approach is that it makes it possible to generalize the kinetic spectrum analysis to reversible processes occurring in disordered systems. Work on this last problem is in progress and the corresponding results will be presented elsewhere.

9. Reversible Kinetics for One-Channel Thermally Activated Processes in Disordered Systems

As the final topic of this article we investigate the reversible kinetics of thermally activated processes with one channel with a random distribution of activation energies. For irreversible processes this is a popular model used for explaining the occurrence of long time tails, for rate processes of first order.^{1–3,21} For irreversible processes with static disorder one assumes that a realization of the survival function obeys a kinetic equation of first order

$$d/(t)/dt = -k_+/(t) \quad \text{with} \quad /(t=0) = 1, \\ \text{i.e., } /(t) = \exp(-k_+t) \quad (160)$$

where the rate coefficient obeys the Arrhenius equation

$$k_+ = \nu_+ \exp(-E_+/k_B T) \quad (161)$$

and the activation energy E_+ is a random variable that obeys a “frozen” Maxwell–Boltzmann distribution corresponding to a characteristic temperature $T^* \geq T$, bigger than the actual temperature T of the system

$$\eta^{\text{st}}(E_+) dE_+ = (k_B T^*)^{-1} \exp(-E_+/(k_B T^*)) dE_+ \quad \text{with} \\ \int_0^\infty \eta(E_+) dE_+ = 1 \quad (162)$$

Under these circumstances the average survival function has a long tail of the negative power law type:

$$\langle /(t) \rangle = \int_0^\infty \eta^{\text{st}}(E_+) \exp\{-\nu_+ \exp[-E_+/(k_B T)]t\} dE_+ = \\ \beta(\nu_+ t)^{-\beta} \gamma(\beta, \nu_+ t) \sim \Gamma(1 + \beta)(\nu_+ t)^{-\beta} \quad \text{as} \quad t \rightarrow \infty \\ \text{with} \quad \beta = T/T^* \leq 1, \quad \beta > 0 \quad (163)$$

Equation 163 has been applied to various physical and chemical problems, such as protein kinetics, exotic dielectric relaxation in molecular liquids, and the theory of dispersive transport in xerographic films. Although the theory has been extended to certain types of processes with dynamical disorder, no attempts have been made yet to study reversible processes.

In the following we attempt to extend the one-channel model with a random distribution of energy barriers by using the techniques developed in this article for multichannel systems. To save space, we start out with the investigation of the sampling fluctuations in systems with dynamical disorder and study the properties of systems with static disorder as a particular case. For one-channel systems most of the general relations derived in this article remain valid. The main difference is the way in which the random behavior of the disordered medium influences the kinetics of the process. For a one-channel process with dynamical disorder there is only one pair of forward and backward rate coefficients, $k_+(t)$ and $k_-(t)$, which obey a constraint similar to eq 54, necessary for consistency with the condition of thermodynamic equilibrium:

$$K_{\text{equil}} = k_+(t)/k_-(t) \quad (164)$$

which leads to a relationship between the forward and backward activation energies similar to eq 82

$$E_+(t) - E_-(t) = \Delta H = \text{constant} \quad (165)$$

The random properties of the disordered medium can be described in terms of the probability density functional of one of the activation energies, e.g., $E_+(t)$:

$$\mathcal{A}[E_+(t')] \mathcal{L}[E_+(t')] \quad \text{with} \quad \overline{\int \int \mathcal{A}[E_+(t')] \mathcal{L}[E_+(t')] = 1} \quad (166)$$

Considering a given realization of the random function $E_+(t)$, the master equation (107) becomes

$$\begin{aligned} \frac{\partial}{\partial t} \mathcal{B}_{\text{realiz}}(X; t) = & k_+(t) \{ \mathcal{B}_{\text{realiz}}(X+1; t)(X+1) - \mathcal{B}_{\text{realiz}}(X; t)(X) \} + \\ & k_-(t) \{ \mathcal{B}_{\text{realiz}}(X_{\Sigma} - X + 1; t)(X_{\Sigma} - X + 1) - \\ & \mathcal{B}_{\text{realiz}}(X; t)(X_{\Sigma} - X + 1) \} \end{aligned} \quad (167)$$

We use the thermodynamic constraint (164) and express in eq 167 the forward and backward rate constants $k_{\pm}(t)$ in terms of the total rate constant $k_{\Sigma}(t) = k_+(t) + k_-(t)$. After introducing the generating function (112) and after some algebraic transformations, we come to the partial differential equation (113) with the difference that now the intrinsic time scale $\sigma(t)$ is given by

$$\sigma(t) = \int_0^t k_{\Sigma}(t') dt' \quad (168)$$

It follows that the fluctuation–dissipation relations (125) and the expressions (137)–(139) for the probability of composition fluctuations derived in section 7 remain valid, with the difference that now the damping factors $\Phi_m(t)$ are given by

$$\begin{aligned} \Phi_m(t) = \langle \exp[-m \int_0^t k_{\Sigma}(t') dt'] \rangle = \overline{\int \int \mathcal{A}[E_+(t')] \times} \\ \mathcal{L}[E_+(t')] \exp\left[-m \int_0^t \left(\frac{K_{\text{equil}}}{1 + K_{\text{equil}}}\right) v_+ \exp\left[-\frac{E_+(t')}{k_B T}\right] dt'\right] \end{aligned} \quad (169)$$

The expressions (132) and (133) for the average value and the dispersion of the number of X molecules remain valid, and according to eq 124 for the relative fluctuations of order 2, in the thermodynamic limit the composition fluctuations are intermittent.

For evaluating the damping factors $\Phi_m(t)$, we develop a technique similar to the one developed in section 5 for the average survival function. We reduce the evaluation of the dynamical average (169) to the solving of a stochastic Liouville equation. The initial condition of this stochastic Liouville equation is chosen in such a way that at a given moment the distribution of the activation energies is given by the Maxwell–Boltzmann distribution (162). Moreover, we assume that the fluctuation activation energies are described by a renewal process in the strong collision limit, characterized by a set of transition rates characterized only by the final states of the system, and are consistent with the stationary distribution (162). The main steps of the computation are outlined in Appendix A. We come to the following expressions for the damping factors:

$$\begin{aligned} \Phi_m(t) = \int_0^{\infty} \eta^{\text{st}}(E_+) \times \\ \left\{ 1 - \frac{mk_{\Sigma}(E_+)}{\lambda + mk_{\Sigma}(E_+)} [1 - \exp(-(\lambda + mk_{\Sigma}(E_+))t)] \right\} dE_+ = \\ \frac{\beta}{(\nu_{\Sigma})^{\beta}} \int_0^{\nu_{\Sigma}} (k_{\Sigma})^{\beta-1} \left\{ \frac{\lambda}{\lambda + mk_{\Sigma}} + \frac{mk_{\Sigma}}{\lambda + mk_{\Sigma}} \times \right. \\ \left. \exp[-t(\lambda + mk_{\Sigma})] \right\} dk_{\Sigma} \end{aligned} \quad (170)$$

where the stationary distribution $\eta^{\text{st}}(E_+) dE_+$ of the activation energies is given by the Maxwell–Boltzmann law (162), the dependence of the total relaxation rate k_{Σ} on the activation energy E_+ is given by eq 83, and the maximum value ν_{Σ} of the total rate k_{Σ} is given by

$$\nu_{\Sigma} = \left(\frac{K_{\text{equil}}}{1 + K_{\text{equil}}} \right) v_+ \quad (171)$$

and other variables have the same significance as in section 6.

The systems with static disorder correspond to the particular case when the total rate of renewal of the disordered system, λ , tends to zero, $\lambda \rightarrow 0$. In this limit the expressions (188) for the damping factors $\Phi_m(t)$ become

$$\Phi_m(t) = \beta(\nu_{\Sigma} m t)^{-\beta} \gamma(\beta, \nu_{\Sigma} m t) \sim \Gamma(1 + \beta)(\nu_{\Sigma} m t)^{-\beta} \quad \text{as} \quad t \rightarrow \infty \quad (172)$$

For large times the damping factors decay to zero according to a scaling law of the negative power law type. In particular, by applying the fluctuation dissipation relation (125) for the particular case of the average value ($m = 1$), we get the following expression for the average survival function for systems with static disorder.

$$\begin{aligned} \langle \cdot / (t) \rangle = \langle X(t) \rangle / X_{\Sigma} = \frac{1}{K_{\text{equil}} + 1} + \\ \left[\langle \cdot / (0) \rangle - \frac{1}{K_{\text{equil}} + 1} \right] \beta(\nu_{\Sigma} t)^{-\beta} \gamma(\beta, \nu_{\Sigma} t) \sim \frac{1}{K_{\text{equil}} + 1} + \\ \left[\langle \cdot / (0) \rangle - \frac{1}{K_{\text{equil}} + 1} \right] (\nu_{\Sigma} t)^{-\beta} \Gamma(1 + \beta) \rightarrow \frac{1}{K_{\text{equil}} + 1} \quad \text{as} \\ t \rightarrow \infty \end{aligned} \quad (173)$$

For large times a system with static disorder approaches the state of thermodynamic equilibrium according to a kinetic law of the negative power law type.

For dynamical disorder, $\lambda \neq 0$, the behavior of the system is different. The damping factors $\Phi_m(t)$ decay toward positive

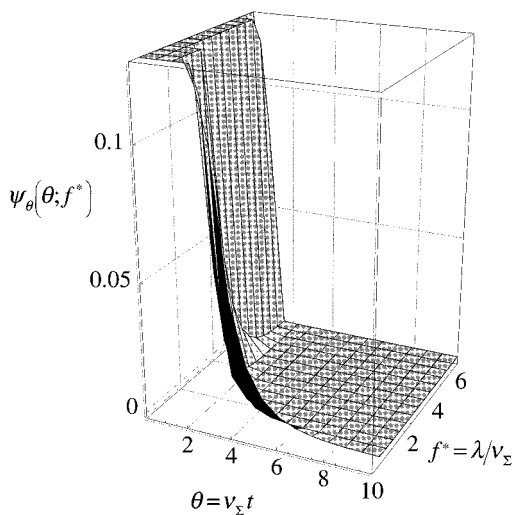


Figure 3. Graphical representation of the dimensionless form of the lifetime distribution for one-channel kinetics with dynamical disorder, $\psi_\theta(\theta; f^*)$, as a function of dimensionless time, $\theta = \nu_\Sigma t$, and of the dimensionless renewal rate of the activation energy, $f^* = \lambda/\nu_\Sigma$. The surface is evaluated for a values of the scaling exponent of the survival function $\beta = 0.7$.

values different from zero

$$\Phi_m(t) \rightarrow \frac{\beta \lambda^\beta}{m(\nu_\Sigma)^\beta} B\left(\beta, 1 - \beta, \frac{m\nu_\Sigma}{\lambda + m\nu_\Sigma}\right) > 0 \quad (174)$$

and the system evolves toward a frozen nonequilibrium state rather than toward thermodynamic equilibrium

$$\begin{aligned} \langle \nu(t) \rangle &= \frac{1}{K_{\text{equil}} + 1} + \left[\langle \nu(0) \rangle - \frac{1}{K_{\text{equil}} + 1} \right] \Phi_1(t) \rightarrow \\ &\frac{1}{K_{\text{equil}} + 1} + \left[\langle \nu(0) \rangle - \frac{1}{K_{\text{equil}} + 1} \right] \frac{\beta \lambda^\beta}{(\nu_\Sigma)^\beta} B\left(\beta, 1 - \beta, \frac{\nu_\Sigma}{\lambda + \nu_\Sigma}\right) \\ &\text{as } t \rightarrow \infty \quad (175) \end{aligned}$$

where

$$B(p, q; x) = \int_0^x y^{p-1} (1-y)^{q-1} dy \quad p, q > 0 \quad (176)$$

is the incomplete Eulerian function of the β type.

The general relationships (150) and (151) for the probability distribution of the lifetime, $\psi(t) dt$, and for the scaled effective rate of relaxation, $\tilde{k}_{\text{eff}}(t)$, remain valid, with the difference that now the damping function $\Phi(t)$ must be computed from eq 170, applied for $m = 1$. In the particular case of systems with static disorder, we obtain

$$\begin{aligned} \psi(t) &= \beta(\nu_\Sigma)^{-\beta} t^{-(1+\beta)} \gamma(1 + \beta, \nu_\Sigma t) \sim \\ &\begin{cases} [\nu_\Sigma t / (1 + \beta)] \exp(-\nu_\Sigma t) & \text{as } t \rightarrow 0 \\ \beta(\nu_\Sigma)^{-\beta} t^{-(1+\beta)} \Gamma(1 + \beta) & \text{as } t \rightarrow \infty \end{cases} \quad (177) \end{aligned}$$

and

$$\begin{aligned} \tilde{k}_{\text{eff}}(t) &= \beta t^{-1} \left\{ 1 + \frac{(\nu_\Sigma t)^\beta \exp(-\nu_\Sigma t)}{\gamma(\beta + 1, \nu_\Sigma t)} \right\}^{-1} \sim \\ &\begin{cases} \nu_\Sigma \beta / (1 + \beta) & \text{as } t \rightarrow 0 \\ \beta / t & \text{as } t \rightarrow \infty \end{cases} \quad (178) \end{aligned}$$

The behavior described by eqs 177 and 178 is different from

the one characteristic of stretched exponential kinetics. Both functions, $\psi(t)$ and $\tilde{k}_{\text{eff}}(t)$, do not have singularities at $t = 0$, but rather positive values that are finite. For large times both the lifetime distribution and the effective rate of relaxation tend slowly to zero and have long tails of the negative power law type. Due to the long tail of $\psi(t)$, all positive moments of the lifetime are infinite

$$\langle t^m \rangle = \int_0^\infty t^m \psi(t) dt = \infty \quad (179)$$

(Compare to eq 154 for the stretched exponential.) This is a typical feature of statistical fractal distributions²² that is missing in the case of stretched exponential kinetics.

For dynamic disorder the lifetime distribution $\psi(t)$ and the effective rate coefficient $\tilde{k}_{\text{eff}}(t)$ can be computed in a similar way. We obtain

$$\begin{aligned} \psi(t) &= t^{-(1+\beta)} \beta \exp(-t\lambda) \gamma(1 + \beta, \nu_\Sigma t) \times \\ &\left[(\nu_\Sigma)^\beta - \beta \lambda^\beta B\left(\beta, 1 - \beta, \frac{\nu_\Sigma}{\lambda + \nu_\Sigma}\right) \right]^{-1} \sim t^{-(1+\beta)} \beta \times \\ &\exp(-t\lambda) \Gamma(1 + \beta) \left[(\nu_\Sigma)^\beta - \beta \lambda^\beta B\left(\beta, 1 - \beta, \frac{\nu_\Sigma}{\lambda + \nu_\Sigma}\right) \right]^{-1} \\ &\text{as } t \rightarrow \infty \quad (180) \end{aligned}$$

$$\tilde{k}_{\text{eff}}(t) = t^{-(1-\beta)} \gamma(1 + \beta, \nu_\Sigma t) \left\{ \int_0^{\nu_\Sigma} \frac{(k_\Sigma)^\beta}{\lambda + k_\Sigma} \exp[-tk_\Sigma] dk_\Sigma \right\}^{-1} \quad (181)$$

We notice that for the one-channel system, the dynamical disorder leads to a narrowing of the lifetime distribution: for $\lambda > 0$ the tail of $\psi(t)$ is short and has an exponential shape. This narrowing effect is clearly displayed by Figure 3, which shows the dependence of the dimensionless lifetime distribution

$$\psi_\theta(\theta) d\theta = \psi(t) dt \quad (182)$$

as functions of the dimensionless time

$$\theta = \nu_\Sigma t \quad (183)$$

and of the dimensionless renewal rate of the activation energy,

$$f^* = \lambda/\nu_\Sigma \quad (184)$$

Figure 4 displays graphical representation of the dimensionless effective rate coefficient defined by

$$\tilde{k}_{\text{eff}}^{**}(\theta) = \tilde{k}_{\text{eff}}(t)/\nu_\Sigma \quad (185)$$

as a function of the dimensionless time and renewal frequency. We notice that the effective rate coefficient decreases monotonically with the increase of dimensionless time and increases with the increase of the dimensionless renewal frequency.

In conclusion, the techniques developed in this article for the study of stretched exponential relaxation can be easily extended to the study of one-channel reversible processes with a random distribution of activation energy barriers. The physical behavior of the two types of models is very different. The most striking difference is the different type of response of the two types of systems to dynamical disorder: whereas for stretched exponential relaxation the dynamical relaxation leads to a broadening of the lifetime distribution, for a one-channel system with a random energy barrier the effect of dynamical disorder is just the opposite (the lifetime distributions become narrower). This

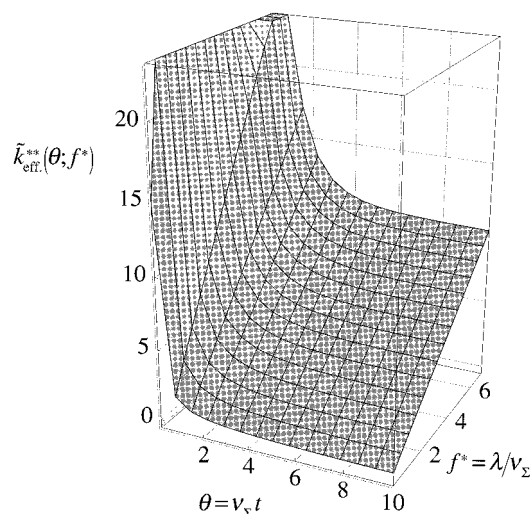


Figure 4. Graphical representation of the dimensionless effective rate coefficient for one-channel kinetics with dynamical disorder, $\tilde{k}_{\text{eff}}^{**}(\theta; f^*)$, as a function of dimensionless time, $\theta = \nu_{\Sigma} t$, and of the dimensionless renewal rate, $f^* = \lambda/\nu_{\Sigma}$, of the activation energy. The surface is evaluated for a value of the scaling exponent of the survival function $\beta = 0.7$.

qualitative difference between the two types of models may serve as a basis for selecting a given reaction mechanism starting out from experimental data. Another difference is related to the two fractal scaling exponents, α and β , which characterize the two types of processes. Apparently, according to their definitions, eqs 12 and 163, they are both linear functions of the absolute temperature of the system, T . In the particular case of irreversible processes, there is evidence in the literature^{1–3,21} that this is indeed the case for one-channel processes with random energy barriers. For stretched exponential kinetics, however, it seems that such a simple rule does not exist. Actually, in eq 12, the proportionality coefficient of the temperature may depend on other parameters of the system, which are temperature dependent, resulting in a nonlinear dependence $\alpha(T)$.

10. Discussion and Conclusions

The main object of study for our research in the kinetics of reversible rate processes in systems with dynamical disorder. However, in order to gain the physical insight necessary for the understanding of these complicated physico-chemical processes, we started out with the study of rate processes in systems with static disorder. The first system investigated is a multichannel irreversible first-order reaction occurring in a system with static disorder. For a given range of channels with different relaxation times we have introduced a configurational entropy that is proportional to the logarithm of the number of channels within the considered range. We have shown that if the logarithm of the configurational entropy is proportional to the activation energy of the slowest channel, then the kinetics of the process is described by a stretched exponential. This linear relationship between the configurational entropy and the activation energy is similar to other linear free energy relationships used in chemical kinetics.⁶

We have extended the multichannel model for the kinetics of rate processes in disordered systems to the case of reversible processes. We have assumed that for each individual channel there are two opposite processes, a forward process and a backward process and that at equilibrium each channel obeys detailed balance. By assuming that the individual channels obey

Poissonian statistics, we have derived an exact expression for the configurational average of the survival function defined by eq 21. The average kinetic curve depends on three different variables: (1) the initial concentrations in the system, (2) the equilibrium thermodynamic properties of the system, expressed by the equilibrium constant of the process, and (3) the average density of channels, which describes the distribution of the rates attached to the different individual channels.

By combining the suggested model for reversible relaxation with the assumption that a type of free linear energy relaxation also holds for reversible processes, we have derived a generalization of the stretched exponential law for reversible processes. We have derived an averaged kinetic equation that has been already used in the literature on an empirical basis for fitting the experimental data.⁹

We have generalized our approach to systems with dynamical disorder for which the individual rate coefficients are random functions of time. In this case the evaluation of the average survival functions for reversible chemical reactions is reduced to solving a stochastic Liouville equation. We have derived an explicit solution for systems with strong dynamical disorder that obey the strong collision hypothesis. We have shown that for this type of system the dynamical disorder decreases the efficiency of the reaction and that for long times the process evolves toward a “frozen” nonequilibrium state rather than to thermodynamic equilibrium.

We have also investigated the interference of composition fluctuations, described by a chemical master equation, with the fluctuations of the rate coefficients, which are generated by disorder in the reaction environment. We have developed a double averaging procedure based on the combined use of the generating function of the chemical master equation and of the stochastic Liouville equations, which describe the fluctuations of the disordered medium. We have derived an infinite chain of fluctuation–dissipation relations that relate the fluctuations of the concentrations of the chemicals, expressed by the factorial cumulants of the number of reacting molecules, and the macroscopic relaxation properties of the system, expressed by the average survival function. By using these fluctuation–dissipation relations we have shown that both for static and dynamic disorder the interference of the composition fluctuations with the fluctuations of the rate coefficients leads to a statistical intermittent behavior in the thermodynamic limit.

Another topic studied in the article is the statistics of lifetime distributions for stretched exponential kinetics in systems with static or dynamical disorder. We have shown that dynamical disorder has a broadening effect on the lifetime distribution. The effective rate of relaxation has very large values for small times and renewal frequencies, then decreases toward a relatively constant value for moderately large values of these two variables, and eventually increases again for large values of the lifetime and renewal frequency.

Finally, we have investigated the reversible kinetics of one-channel thermally activated processes with a random distribution of activation energy barriers. The kinetics of this type of process is described by time functions of the negative power law type rather than by stretched exponentials. The mathematical treatments of these types of processes presented in the literature are very different from the one used for investigating stretched exponential kinetics. Despite these differences we have shown that the techniques introduced in this article for the analysis of stretched exponentials can be adapted for the study of one-channel reaction kinetics in disordered systems. Although for one-channel kinetics there is no simple analogue of the free

energy relations introduced for stretched exponential kinetics, the averaging techniques based on stochastic Liouville equations can be easily applied to both types of problems. We have shown that multichannel and one-channel kinetics share some important features: both systems obey the same type of fluctuation–dissipation relations and, in the presence of dynamical disorder, in the long run both processes evolve toward a frozen nonequilibrium state rather than toward thermodynamic equilibrium. The statistical properties of the lifetime distributions are, however, different for the two types of systems. For stretched exponentials the lifetime distributions are nonfractal, characterized by short tails and finite moments, whereas the one-channel kinetics is characterized by statistical fractal lifetime distributions with long tails and infinite moments.

Most theories of stretched exponential relaxation presented in the literature make use of the steepest descent approximation. Many scientists do not trust these derivations because they create the impression that the stretched exponential kinetics is the result of a mathematical artifact, without a clear physical significance. We emphasize that our approach does not make use of the steepest descent approximation. Within the framework of our approach the mechanism of generation of stretched relaxation is clear; it is the result of occurrence of a large number of parallel relaxation channels, any of them having a very small probability of being open. The stretched exponential emerges as a universal asymptotic law in the limit where the total number of channels tends to infinity and the probability that a channel is open tends to zero, with the constraint that the average total number of open channels is kept constant. This type of limit is similar to the thermodynamic limit in equilibrium statistical mechanics. The resulting limit statistics for the number of open channels is Poissonian, and this Poissonian distribution is the direct cause of stretched exponential relaxation.

We emphasize that there is an important difference between the type of linear free energy relationships introduced in this article and the conventional linear free relationships used in physical organic chemistry.⁶ In physical organic chemistry a linear free energy relationship establishes a connection between the thermodynamic properties of a series of similar substances, expressed by the free energy changes attached to a series of similar reactions, and the kinetic properties of the same substances, expressed by the activation energies of the different chemical reactions studies. In our case the analogue of the series of different reactions studied are the individual processes attached to the different relaxation channels and in both cases the activation energies play similar roles. The difference is that for a disordered system our configurational entropy $\Omega(\tau)$ is not an equilibrium thermodynamic function in the conventional sense. Despite this difference we consider that the use of linear energy relationship introduced in this paper is a useful tool for studying the kinetics rate processes in disordered systems. In addition to the example of linear reversible processes presented in this article we intend to extend the method for deriving a nonlinear analogue of the stretched exponential law to rate processes with a reaction order bigger than 1.²³

The main emphasis of our approach is on dynamic disorder. Recent experimental research reported in the literature has shown that dynamical disorder is commonly encountered in systems obeying stretched exponential relaxation kinetics. Recent experimental studies reporting the existence of dynamic disorder deal with intrachain diffusion of unfolded cytochrome c^{24} and geminate rebinding and conformational dynamics of myoglobin embedded in a glass at room temperature.²⁵ An interesting example is the case of gas forming liquids. Recent

NMR measurements of two-, three-, and four-time correlation functions for supercooled ortho-terphenyl at low temperatures (10–15 K) have shown the existence of a dynamic heterogeneous structure.²⁶ The main features of the observed dynamic heterogeneous structure have been successfully explained by using a random walk approach in an energy landscape. The model of dynamic disorder suggested for the description of dynamic heterogeneities is similar to the strong collision approach suggested by us in section 6 for the description of reversible stretched exponential kinetics with dynamical disorder. We intend to explore these analogies in our future research.

Finally, we mention two different theoretical approaches reported in the literature which are related to our approach. Saven and Wolynes²⁷ discuss a statistical mechanical model for the combinatorial synthesis and analysis of folding molecules. Although their study focuses mainly on the equilibrium properties of folded molecules, it is an important step in the clarification of the origin of static as well as dynamical disorder in biochemical reactions involving proteins. Another recent study²⁸ deals with the path integral description of rate processes with dynamical disorder. In this last study the authors use the notion of instanton for describing complex reaction paths for rate processes with dynamical disorder. The instanton technique makes possible the development of approximate analytical methods for computing average survival functions for a complex rate process with dynamical disorder. In our future research we intend to combine the instanton approach with our method of describing reversible rate processes with dynamical disorder.

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Appendix A

We express the functions $\Phi_m(t)$ as dynamic averages of a set of first-order differential equations

$$\Phi_m(t) = \langle \Theta_m(t) \rangle \quad (\text{A.1})$$

where $\Theta_m(t)$ are the solutions of

$$\frac{d}{dt} \Theta_m(t) = -m \left(\frac{K_{\text{equil}}}{1 + K_{\text{equil}}} \right) \nu_+ \exp \left[-\frac{E_+(t)}{k_B T} \right] \Theta_m(t) \quad \text{with} \\ \Theta_m(t=0) = 1 \quad (\text{A.2})$$

Now we assume that the fluctuations of the activation energy $E_+(t')$ are described by a time-homogeneous Markovian process characterized by the evolution equation:

$$\frac{\partial}{\partial t} \eta = L \eta \quad (\text{A.3})$$

with

$$\eta(E_+; t = t' | E'_+; t') + \delta(E_+ - E'_+) \quad (\text{A.4})$$

where

$$\eta \, dE_+ = \eta(E_+; t | E'_+; t') \, dE_+ \quad \text{with} \\ \int_0^\infty \eta(E_+; t | E'_+; t') \, dE_+ = 1 \quad (\text{A.5})$$

is the conditional probability density of the activation energy E_+ at time t provided that at time t' the activation energy was

E'_+ and L is a time-independent Markovian evolution operator. In this case the probability density functional $\mathcal{A}[E_+(t')]$ $\mathcal{A}[E_+(t')]$ can be formally represented as

$$\begin{aligned} \mathcal{A}[E_+(t')] \mathcal{A}[E_+(t')] = \\ \lim_{\substack{m \rightarrow \infty \\ (\Delta t \rightarrow 0)}} \{ \eta(E_+^{(m)}; m\Delta t | E_+^{(m-1)}; (m-1)\Delta t) dE_+^{(m)} \times \\ \eta(E_+^{(m-1)}; (m-1)\Delta t | E_+^{(m-2)}; (m-2)\Delta t) dE_+^{(m-1)} \dots \\ \eta(E_+^{(2)}; 2\Delta t | E_+^{(1)}; \Delta t) dE_+^{(2)} \times \\ \eta(E_+^{(1)}; \Delta t | k_{\Sigma}^{(0)}; 0) dE_+^{(1)} \eta^{st}(E_+^{(0)}) dE_+^{(0)} \} \quad t \geq t' \geq 0 \quad (A.6) \end{aligned}$$

where $\eta^{st}(E_+) dE_+$ is the stationary solution of the evolution equation (A.3). We use the formal representation

$$\eta(E_+; t | E'_+; t') = \exp[-(t - t')L] \delta(E_+ - E'_+) \quad (A.7)$$

of the solution of eq A.3. From eqs 169 and A.6 we notice that the evaluation of the damping factors $\Phi_m(t)$ can be reduced to the evaluation of the joint probability density

$$P_m(E_+, \Theta_m; t) dE_+ d\Theta_m \quad \text{with} \\ \int_0^1 \int_0^\infty P_m(E_+, \Theta_m; t) dE_+ d\Theta_m = 1 \quad (A.8)$$

This joint probability density is the solution of the stochastic Liouville equation

$$\begin{aligned} \frac{\partial}{\partial t} P_m(E_+, \Theta_m; t) = \\ m \left(\frac{K_{\text{equil}}}{1 + K_{\text{equil}}} \right) v_+ \frac{\partial}{\partial \Theta_m} \left\{ P_m(E_+, \Theta_m; t) \Theta_m \exp \left[-\frac{E_+}{k_B T} \right] \right\} + \\ L P_m(E_+, \Theta_m; t) \quad (A.9) \end{aligned}$$

Since our approach should include the description of systems with static disorder as a particular case, we must assume that the initial distribution of the activation energy is given by the stationary law $\eta^{st}(E_+) dE_+$ and thus the initial condition of the stochastic Liouville equation (A.9) must be

$$P_m(E_+, \Theta_m; t = 0) = \eta^{st}(E_+) \delta(\Theta_m - 1) \quad (A.10)$$

In a way similar to the approach developed in section 5, the damping factors $\Phi_m(t)$ can be expressed in terms of the marginal average:

$$\mathcal{A}_m(E_+; t) = \int_0^1 \Theta_m P_m(E_+, \Theta_m; t) d\Theta_m \quad (A.11)$$

We have

$$\begin{aligned} \Phi_m(t) = \int_0^1 \int_0^\infty \Theta_m P_m(E_+; \Theta_m; t) dE_+ d\Theta_m = \\ \int_0^\infty \mathcal{A}_m(E_+; t) dE_+ \quad (A.12) \end{aligned}$$

Since in eq 178 the linear operator L does not depend on Θ_m , from this equation we can derive an evolution equation for $\mathcal{A}_m(E_+; t)$. We multiply each term of eq A.9 by Θ_m and integrate over Θ_m . After a partial integration we come to

$$\begin{aligned} \frac{\partial}{\partial t} \mathcal{A}_m(E_+; t) + m \left(\frac{K_{\text{equil}}}{1 + K_{\text{equil}}} \right) v_+ \exp \left[-\frac{E_+}{k_B T} \right] \mathcal{A}_m(E_+; t) = \\ L \mathcal{A}_m(E_+; t) \quad (A.13) \end{aligned}$$

The initial condition for eq A.13 can be derived from eq A.10.

We obtain

$$\mathcal{A}_m(E_+; t = 0) = \eta^{st}(E_+) \quad (A.14)$$

As in section 6, we assume that the fluctuations of the activation energy E_+ can be described by a Markovian renewal process in the strong collision limit, described by the master equation:

$$\begin{aligned} \frac{\partial}{\partial t} \eta(E_+; t | E'_+; t') = \int [\eta(E'_+; t | E'_+; t') \mathcal{W}(E'_+ \rightarrow E_+) - \\ \eta(E_+; t | E'_+; t') \mathcal{W}(E_+ \rightarrow E'_+)] dE'_+ \quad (A.15) \end{aligned}$$

with

$$\mathcal{W}(E_+ \rightarrow E'_+) = \mathcal{W}(E'_+) \quad \text{independent of } E_+ \quad (A.16)$$

The functional form of the transition rate $\mathcal{W}(E'_+)$ can be determined by requiring that the stationary solution $\eta^{st}(E_+)$ of the master equation (A.16) is given by the Maxwell–Boltzmann distribution (162). We obtain

$$\mathcal{W}(E_+) = \lambda \eta^{st}(E_+) = \lambda (k_B T^*)^{-1} \exp(-E_+ / (k_B T^*)) \quad (A.17)$$

where λ , the total transition rate from an initial value of the activation energy to any final values, is given by eq 90. From eqs A.15–A.17 it follows that the linear evolution operator L is given by

$$L \dots = \lambda (k_B T^*)^{-1} \exp(-E_+ / (k_B T^*)) - \lambda \dots \quad (A.18)$$

We insert eq A.18 into eq A.13, solve the resulting differential equation for $\mathcal{A}_m(E_+; t)$, and substitute the result into eq 181. We obtain

$$\begin{aligned} \mathcal{A}_m(E_+; t) = \\ \eta^{st}(E_+) \left\{ 1 - \frac{mk_{\Sigma}(E_+)}{\lambda + mk_{\Sigma}(E_+)} [1 - \exp(-t(\lambda + mk_{\Sigma}(E_+)))] \right\} \quad (A.19) \end{aligned}$$

By inserting eq A.19 into eq A.12 we come to eq 170.

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