Random Activation Energy Model and Disordered Kinetics, from Static to Dynamic Disorder[†]

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We suggest a unified path integral approach for random rate processes with random energy barriers, which includes systems with static and dynamic disorder as particular cases. We assume that the random component of the activation energy barrier can be described by a generalized Zubarev–McLennan nonequilibrum statistical ensemble that can be derived from the maximum information entropy approach by assuming that the time history of the fluctuations of the random components of the energy barrier are known. We show that the average survival function, which is an experimental observable in disorderd kinetics, can be computed exactly in terms of the characteristic functional of this generalized Zubarev–McLennan nonequilibrium statistical ensemble. We investigate different types of disorder described by our approach, ranging from static disorder with infinite memory to random processes with long or short memory, and finally to rapidly fluctuating independent random processes with no memory. We derive expressions of the average survival function for all these types of disorder and discuss their implications in the evaluation of kinetic parameters from experimental data. We illustrate our approach by studying a simple model of dynamic disorder of the renewal type. Finally we discuss briefly the implications of our approach in molecular biology and genetics.

1. Introduction

The random activation energy model (RAE) is widely used for describing the kinetics of rate processes in disordered systems.[1–4] The main assumption of this model is that the activation energies of the rate coefficients have random components selected from certain probability laws, typically frozen Maxwell–Boltzmann distributions. This model has been successfully applied to many physical, chemical, and biological problems, such dielectric and other molecular relaxation processes, the chemical transformations of active intermediates in radiation chemistry, the reaction kinetics on heterogeneous surfaces, the charge or mass transport in disordered systems, and the ligand–protein interactions in molecular biology.[1–4] In its simple form, the RAE assumes that a fluctuation of the activation energy barrier, once it occurs, lasts forever; in other words, the system displays static disorder. This is a reasonable assumption for low and moderate temperature systems. As the temperature increases, the disorder becomes dynamic[5] and the random components of the activation energy barriers become random functions of time. Similar situations occur in single-molecule kinetics.[6,7] Although various models of random activation barriers with dynamic disorder have been suggested in the literature,[1–4,8–10] they are based on various ad hoc assumptions and lack unity. The purpose of this article is the development of a unified approach for the RAE models, which describes any type of stochastic behavior of the random components of the random activation energy barriers, ranging from static disorder with infinite memory to long-range and short-range dynamic disorder, and finally extreme dynamic disorder with rapid, independent fluctuations. The structure of the paper is as follows. In section 2 we give a general formulation of the problem by starting from the classical form of RAE with static disorder with infinite memory. In section 3 we develop general methods for static and dynamic averaging based on the use of a generalized Zubarev–McLennan nonequilibrium ensemble approach.[11–12] In section 4 we apply the general theory for computing the average survival function, which is an experimental observable, for various types of static and dynamic disorder. In section 5 we illustrate our approach by considering a single type of dynamic disorder of the renewal type. In sections 6 and 7 we generalize the nonequilibrium ensemble approach to reversible reactions and apply the results to a desorption experiment reported in the literature. In section 8 we discuss the possible implications of our theory for interpreting experimental data. Finally, in section 9 we discuss the implications of our approach in molecular biology and genetics.

2. Formulation of the Problem

In this section we formulate the objective of this paper by starting out from the simplest version of the random activation energy model, which, in the language of chemical kinetics, corresponds to a first order process with a random activation energy barrier with static disorder. Both the classical RAE model as well as the dynamic generalizations introduced in this article can be easily extended to nonlinear kinetics. For first-order kinetics the evolution equation of the process is

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$$\partial \ell /\partial t = -k\ell, \quad \ell(t_0) = 1 \tag{1}$$

Here k is a rate coefficient and ℓ is an instantaneous, fluctuating survival function. In molecular relaxation, ℓ is the instantaneous, fluctuating probability that the relaxation process has not occurred from the initial moment t_0 until the current time t. In chemical kinetics ℓ is the ratio of the concentration of a chemical species at time t and the concentration of the species at the initial time t_0. The rate coefficient obeys the Arrhenius equation; that is,

$$k = A \exp\left[-\frac{E}{k_B T}\right] \tag{2}$$

where T is the temperature of the system, k_B is Boltzmann's constant, E is the activation energy of the process, and A is a preexponential amplitude factor which is (almost) independent of temperature. The activation energy of the process is assumed to be made up of two different components: a constant term E_0 and a random component ΔE that is selected from a given probability law,

$$E = E_0 + \Delta E \tag{3}$$

The constant term E_0 is assumed to be nonnegative, $E_0 \geq 0$, and the variable term ΔE is assumed to take any random value between zero and infinity. If we denote by $\eta(\Delta E) \, d\Delta E$ the probability that the random component ΔE has a value between ΔE and $\Delta E + d\Delta E$, we have

$$\int_0^\infty \eta(\Delta E) \, d\Delta E = 1 \tag{4}$$

The experimental observable of the model is the average survival function, $\langle \ell(t) \rangle$, which can be expressed as a static average:

$$\langle \ell(t) \rangle = \int_0^\infty \ell(t) \eta(\Delta E) \, d\Delta E \tag{5}$$

We solve eq 1, insert the result into eq 5, and use eqs 2–3, resulting in

$$\langle \ell(t) \rangle = \int_0^\infty \exp\{-k_0(T)\chi(\Delta E)t\}\eta(\Delta E) \, d\Delta E, \tag{6}$$

where

$$k_0(T) = A \exp\left[-\frac{E_0}{k_B T}\right] \tag{7}$$

is the constant, nonrandom component of the rate coefficient corresponding to $\Delta E = 0$ and

$$\chi(\Delta E) = \exp[-\Delta E/(k_B T)] \tag{8}$$

is a random transparence factor.

The simplest version of RAEM assumes that the probability density $\eta(\Delta E) \, d\Delta E$ is a Maxwell–Boltzmann distribution "frozen" at a temperature T^*, which is higher than the current temperature T of the system

$$\eta(\Delta E) \, d\Delta E = (k_B T^*)^{-1} \exp[-\Delta E/(k_B T^*)] \, d\Delta E \tag{9}$$

with $T^* > T$. The frozen Maxwell–Boltzmann distribution was introduced a long time ago in heterogeneous catalysis; subsequently, its use has expanded in other applications of the RAE model. By inserting eq 9 into eq 6 we come to

$$\langle \ell(t) \rangle = \frac{\alpha \gamma[\alpha, k_0(T)(t - t_0)]}{[k_0(T)(t - t_0)]^\alpha} \sim \frac{\alpha \Gamma(\alpha)}{[k_0(T)]^\alpha}(t - t_0)^{-\alpha} \quad \text{for } t \gg t_0 \tag{10}$$

where $\gamma(a,x) = \int_0^x x^{a-1} \exp(-x) \, dx$, $a, x > 0$ and $\Gamma(a,x) = \int_0^\infty x^{a-1} \exp(-x) \, dx$, $a > 0$ are the incomplete and the complete gamma functions, respectively, and α is a fractal scaling exponent given by $\alpha = T/T^*$. We note that for a Maxwell–Boltzmann distribution the RAE model leads to a fractal scaling law of the negative power law type; the experimental occurrence of this fractal scaling law is well documented in the literature.

For some systems, for example in the case of ligand–protein interactions,[13] the distribution of the random energy barriers is not always of the Maxwell–Boltzmann type. In this case, the probability density $\eta(\Delta E)$ of the random energy barrier can be evaluated from experimental data. It is convenient to introduce the probability density

$$p(k) \, dk \text{ with } \int p(k) \, dk = 1 \tag{11}$$

of the rate coefficient. We have

$$p(k) \, dk = dk \int \delta\{k_0(T)\chi(\Delta E) - k\}\eta(\Delta E) \, d\Delta E$$
$$= \begin{cases} k_B T \eta\left[k_B T \ln\left(\frac{k_0(T)}{k}\right)\right]\dfrac{dk}{k} & \text{for } k \leq k_0(T) \\ 0 & \text{for } k \geq k_0(T) \end{cases} \tag{12}$$

and eq 6 becomes

$$\langle \ell(t) \rangle = \int_0^\infty p(k) \exp(-kt) \, dk \tag{13}$$

in other words, the observed average survival function $\langle \ell(t) \rangle$ is the Laplace transform of probability density $p(k)$ of rate coefficient. It follows that $p(k)$ can be obtained from the observed survival function by means of an inverse Laplace transformation. After $p(k)$ is computed from the experimental data, the distribution of energy barriers can be evaluated from eq 12. We obtain

$$\eta(\Delta E) = \frac{k_0(T)}{k_B T} \exp\left(-\frac{\Delta E}{k_B T}\right) p\left[k_0(T) \exp\left(-\frac{\Delta E}{k_B T}\right)\right] \tag{14}$$

Now we can introduce a generalized RAE model that is valid both for static and dynamic disorder. In general, the random component ΔE of the energy barrier is a stochastic function of time, $\Delta E = \Delta E(t')$, $t_0 \leq t' \leq t$; its stochastic properties can be described by a probability density functional:

$$\mathscr{P}_{\Delta E}[\Delta E(t')]\mathscr{D}_{\Delta E}[\Delta E(t')] \text{ with}$$
$$\overline{\int\int}\mathscr{P}_{\Delta E}[\Delta E(t')]\mathscr{D}_{\Delta E}[\Delta E(t')] = 1 \tag{15}$$

where $\mathscr{D}_{\Delta E}[\Delta E(t')]$ is a suitable integration measure over the space of functions $\Delta E = \Delta E(t')$, $t_0 \leq t' \leq t$; and the symbol $\overline{\int\int}$ denotes the operation of path integration. Equation 6 for the average survival function is replaced by the more general formula

$$\langle \ell(t) \rangle = \langle \exp\{-k_0(T)\int_{t_0}^t \chi(\Delta E(t')) \, dt'\}\rangle \tag{16}$$

with

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$$\langle...\rangle = \overline{\int\int}...\mathscr{P}_{\Delta E}[\Delta E(t')]\mathscr{D}_{\Delta E}[\Delta E(t')] \quad (17)$$

which includes eq 1 as a particular case. To show that this is true, we discretize the time interval from t_0 into time intervals limited by the times t_u, $u = 0,1,...$ which have the lengths $\Delta t_u = t_u - t_{u-1}$, $u = 1,2,...$ By recalling that for static disorder a random selection of ΔE is made only once, at the beginning of the process and then that selection lasts forever, we obtain:

$$\mathscr{P}_{\Delta E}^{\text{static}}[\Delta E(t')]\mathscr{D}_{\Delta E}^{\text{static}}[\Delta E(t')] =$$

$$\lim_{\forall \Delta t_u \to 0}\{\eta(\Delta E(t_0))\,d\Delta E(t_0)\prod_{u>0}[\delta(\Delta E(t_u) -$$

$$\Delta E(t_{u-1}))]\,d\Delta E(t_u)\} \quad (18)$$

By inserting eq 18 into eq 17 we come to eq 6, as expected.

It follows that, for a unified approach to the RAE model, which includes both static and dynamic disorder as particular cases, we have to solve the following problems: (1) Find a suitable method for evaluating the probability density functional (eq 15) for the random energy barriers. (2) Develop methods for computing the average survival function of the process from eqs 16−17. (3) Use the theory for evaluating the kinetic parameters of the process from experimental data. These three problems are investigated in the remainder of this paper.

3. Nonequilibrium Ensemble Approach to Random Energy Barriers

The first problem to be solved is the introduction of a suitable representation for the probability density functional of the random energy barriers. Different approaches can be used for solving this problem. Our suggestion is to use a generalization of the method of nonequilibrium statistical ensembles introduced by Zubarev[11] and McLennan.[12] Compared to other methods, this approach has the advantage that it leads to the Maxwell−Boltzmann density as a particular case, which makes it possible to discuss the transition from static disorder to dynamic disorder by using a unified approach.

By using the Zubarev−Khalashnikov[11] version of the nonequilibrium ensemble theory, a nonequilibrium probability density functional for the energy barriers can derived from the maximum information entropy approach by requiring knowledge on the whole previous histories of the average height of the random energy barriers

$$\langle \Delta E \rangle = \langle \Delta E(t') \rangle,\ t \geq t' \geq t_0 \quad (19)$$

By using eq 19 as an isoperimetric condition, we arrive at a nonequilibrium ensemble which is a dynamic generalization of the static Maxwell−Boltzmann distribution of the random energy barriers. We shall show later that this dynamical Maxwell−Boltzmann ensemble can only describe the particular case of extremely fast dynamic disorder without memory. To consider the transition from static to dynamic disorder we need to use a more general type of nonequilibrium statistical ensemble. We use a generalization of the Zubarev−Khalashnikov method suggested by Vlad and Mackey.[14] This method consists of requiring knowledge not only of the previous history of the average values of the random variables but also of the history of various correlation functions. Applied to the problem of random energy barriers, this approach leads to the isoperimetric conditions

$$\langle \Delta E_1...\Delta E_m \rangle = \langle \Delta E(t_1')...\Delta E(t_m') \rangle$$

$$t \geq t_1',...t_m' \geq t_0,\ m = 1,2,... \quad (20)$$

The isoperimetric conditions (eq 20) can be determined either from theoretical considerations or from experimental data. The simplest choice is to assume that the moments (eq 20) have constant values for all times. By using the maximum information entropy principle we arrive at the following nonequilibrium ensemble:

$$\mathscr{P}_{\Delta E}[\Delta E(t')]\mathscr{D}_{\Delta E}[\Delta E(t')] = \mathscr{L}^{-1}[\lambda_1(t_1'),...,\lambda_m(t_{11}',...,t_{1m}'),..] \times$$

$$\exp\{-\sum_{m=1}^{\infty}\int_{t_0}^{t}\cdots\int_{t_0}^{t}\lambda_m(t_1',...,t_m')\Delta E(t_1')\,dt_1'...\Delta E(t_m')\,dt_m'\} \times$$

$$\mathscr{D}_{\Delta E}[\Delta E(t')] \quad (21)$$

where

$$\mathscr{L}[\lambda_1(t_1'),...,\lambda_m(t_1',...,t_m'),..] = \overline{\int\int}\exp\left\{-\sum_{m=1}^{\infty}\int_{t_0}^{t}\cdots\int_{t_0}^{t}\lambda_m \times\right.$$

$$\left.(t_1',...,t_m')\Delta E(t_1')\,dt_1'...\Delta E(t_m')\,dt_m'\right\}\mathscr{D}_{\Delta E}[\Delta E(t')] \quad (22)$$

is a partition functional and the Lagrange multipliers $\lambda_1(t_1'),...,\lambda_m(t_1',...,t_m'),...$ are determined by the functional equations

$$\langle \Delta E(t_1'')...\Delta E(t_m'') \rangle =$$

$$-\frac{\delta}{\delta\lambda_m(t_1'',...,t_m'')}\ln\mathscr{L}[\lambda_1(t_1'),...,\lambda_m(t_1',...,t_m'),..]. \quad (23)$$

The characteristic functional of the nonequilibrium ensemble (eq 22) is

$$\mathscr{G}_{\Delta E}[\sigma(t')] = \overline{\int\int}\exp\{i\int_{t_0}^{t}\sigma(t')\Delta E(t')\,dt_1'\} \times$$

$$\mathscr{P}_{\Delta E}[\Delta E(t')]\mathscr{D}_{\Delta E}[\Delta E(t')] \quad (24)$$

where $\sigma(t')$ is a test function conjugated to $\Delta E(t')$. The derivation of eqs 21−24 is long but standard; it is a straightforward functional generalization of the information theory approach to statistical mechanics. For a similar computation, see Vlad and Mackey.[14] This characteristic functional can be easily evaluated in terms of the partition functional (eq 22). By inserting eq 21 into eq 24 and using eq 22, we come to

$$\mathscr{G}_{\Delta E}[\sigma(t')] = \frac{\mathscr{L}[\lambda_1(t_1') - i\sigma(t'),\lambda_2(t_1',t_2'),...,\lambda_m(t_1',...,t_m'),..]}{\mathscr{L}[\lambda_1(t_1'),...,\lambda_m(t_1',...,t_m'),..]} \quad (25)$$

Now we can try to evaluate the dynamic average in eq 17. We notice that for dynamic disorder the rate coefficient k is a random function of time. It is convenient to introduce a probability density functional for the rate coefficient k:

$$\mathscr{P}_k[k(t')]\mathscr{D}_k[k(t')] \text{ with } \overline{\int\int}\mathscr{P}_k[k(t')]\mathscr{D}_k[k(t')] = 1 \quad (26)$$

and its characteristic functional

$$\mathscr{G}_k[\zeta(t')] = \overline{\int\int}\exp\{i\int_{t_0}^{t}\zeta(t')k(t')\,dt'\}\mathscr{P}_k[k(t')]\mathscr{D}_k[k(t')] \quad (27)$$

where $\mathscr{D}_k[k(t')]$ is a suitable integration measure over the space

of functions $k = k(t')$, $t_0 \leq t' \leq t$; and $\zeta(t')$ is a test function conjugated to $k(t')$.

The probability functional $\mathscr{P}_k[k(t')]\mathscr{D}_k[k(t')]$ and its characteristic functional $\mathscr{G}_k[\zeta(t')]$ can be derived from $\mathscr{P}_{\Delta E}[\Delta E(t')]\mathscr{D}_{\Delta E}[\Delta E(t')]$ and $\mathscr{G}_{\Delta E}[\sigma(t')]$ by means of a functional transformation:

$$k(t') = k_0(T)\chi(\Delta E(t')) \qquad (28)$$

We obtain

$$\mathscr{P}_k[k(t')]\mathscr{D}_k[k(t')] = \langle\delta[k(t') - k_0(T)\chi(\Delta E(t'))]\mathscr{D}_k[k(t')]\rangle =$$

$$\overline{\int\int}\{\delta[k(t') - k_0(T)\chi(\Delta E(t'))]\mathscr{D}_k[k(t')]\} \times$$
$$\mathscr{P}_{\Delta E}[\Delta E(t')]\mathscr{D}_{\Delta E}[\Delta E(t')] \quad (29)$$

and

$$\mathscr{G}_k[\zeta(t')] = \overline{\int\int}\,\overline{\int\int} \exp\{i\int_{t_0}^t \zeta(t')k(t')dt'\} \times \delta[k(t') -$$
$$k_0(T)\chi(\Delta E(t'))]\mathscr{D}_k[k(t')]\mathscr{P}_{\Delta E}[\Delta E(t')]\mathscr{D}_{\Delta E}[\Delta E(t')] =$$
$$\overline{\int\int} \exp\{i\int_{t_0}^t \zeta(t')k_0(T)\chi(\Delta E(t'))\,dt'\}\mathscr{P}_{\Delta E}[\Delta E(t')] \times$$
$$\mathscr{D}_{\Delta E}[\Delta E(t')] \quad (30)$$

By comparing eqs 16, 27, and 30, we notice that the average survival function $\langle\ell(t)\rangle$ can be expressed in terms of the characteristic functional $\mathscr{G}_k[\zeta(t')]$. We have

$$\langle\ell(t)\rangle = \mathscr{G}_k\{i[\vartheta(t' - t_0) - \vartheta(t - t')]\} \qquad (31)$$

where δ is a functional delta symbol and $\vartheta(x)$ is Heaviside's step function. Equation 31 makes it possible to evaluate the average survival function in terms of the characteristic functional $\mathscr{G}_k[\zeta(t')]$; in a few cases the characteristic functional $\mathscr{G}_k[\zeta(t')]$ can be evaluated exactly; otherwise, if the cumulants of the rate coefficient exist and are finite, $\mathscr{G}_k[\zeta(t')]$ can be expressed as cumulant expansion. These problems are investigated in detail in the following section.

4. Average Survival Functions for Different Types of Disorder

4.1. Extreme Dynamic Disorder. We start out by investigating the case of rapidly changing, independent fluctuating energy barriers. This is the simplest possible type of dynamic RAE model and corresponds to extreme, very strong dynamic disorder. Other types of disorder are intermediates between this extreme case of independent, dynamic disorder without memory and the classic RAE model with static disorder and infinite memory discussed in the literature and summarized in section 1. For rapid, independent fluctuations, the nonequilibrium ensemble is determined completely by the time evolution of the average value, $\langle\Delta E(t')\rangle$, $t \geq t' \geq t_0$ of the random component of the activation energy barrier. By applying the general theory developed in section 3, we come to the following expression of the probability density functional of $\Delta E(t')$:

$$\mathscr{P}_{\Delta E}[\Delta E(t')]\mathscr{D}_{\Delta E}[\Delta E(t')] =$$
$$\mathscr{L}^{-1} \exp\{-\int_{t_0}^t \lambda_1(t')\Delta E(t')\,dt'\}\mathscr{D}_{\Delta E}[\Delta E(t')] \quad (32)$$

In this case the Lagrange multiplier $\lambda_1(t')$ can be easily evaluated in terms of $\langle\Delta E(t')\rangle$, $t \geq t' \geq t_0$. We have

$$\lambda_1(t') = 1/\langle\Delta E(t')\rangle \qquad (33)$$

We notice that in this case the nonequilibrium ensemble can be expressed as the continuous limit of a product of independent Maxwell−Boltzmann probability densities:

$$\mathscr{P}_{\Delta E}[\Delta E(t')]\mathscr{D}_{\Delta E}[\Delta E(t')] =$$
$$\lim_{\forall\Delta t_u \to 0} \prod_u \{\langle\Delta E(t_u)\rangle^{-1} \exp[-\Delta E(t_u)/\langle\Delta E(t_u)\rangle]\,d\Delta E(t_u)\} =$$
$$\lim_{\forall\Delta t_u \to 0} \prod_u \{[k_B T^*(t_u)]^{-1} \exp[-\Delta E(t_u)/[k_B T^*(t_u)]]\,d\Delta E(t_u)\}$$
$$(34)$$

where

$$T^*(t_u) = \langle\Delta E(t_u)\rangle/k_B \qquad (35)$$

are characteristic temperatures corresponding to different intermediate times t_u. The nonequilibrium ensemble is the continuous limit of a product of Maxwell−Boltzmann distributions "frozen" at various characteristic temperatures $T^*(t_1), T^*(t_2),..., T^*(t_u),...$ This is a feature similar to the one displayed by the static RAE model discussed in section 2.

The average survival function, $\langle\ell(t)\rangle$, can be expressed as

$$\langle\ell(t)\rangle = \left\langle\exp\left\{-k_0(T)\int_{t_0}^t \exp\left[-\frac{\Delta E(t')}{k_B T}\right]dt'\right\}\right\rangle$$
$$= \overline{\int\int} \exp\left\{-k_0(T)\int_{t_0}^t \exp\left[-\frac{\Delta E(t')}{k_B T}\right]dt'\right\} \times$$
$$\mathscr{P}_{\Delta E}[\Delta E(t')]\mathscr{D}_{\Delta E}[\Delta E(t')] \quad (36)$$

In Appendix A we show that eqs 34−36 lead to the following expression for the average survival function:

$$\langle\ell(t)\rangle = \exp\left\{-k_0(T)\int_{t_0}^t \left[\frac{k_B T}{\langle\Delta E(t')\rangle + k_B T}\right]dt'\right\} \quad (37)$$

Equation 37 connects the average survival function, which is an experimental observable, to the temperature of the system, T, and to the kinetic parameters of the model, the nonrandom component of the rate coefficient, $k_0(T)$, and the previous average values of the random component $\langle\Delta E(t')\rangle$ of the activation energy barrier. The kinetic parameters in eq 37, $k_0(T)$ and $\langle\Delta E(t')\rangle$, can be evaluated by comparing eq 37 with experimental data.

To clarify the physical significance of eq 37 we consider a slight generalization of the independent Maxwell−Boltzmann nonequilibrium ensemble (eq 34). We replace in eq 34 the Maxwell−Boltzmann probability densities corresponding to different times by arbitrary, independent probability densities $\eta(\Delta E; t_u)$:

$$\mathscr{P}_{\Delta E}[\Delta E(t')]\mathscr{D}_{\Delta E}[\Delta E(t')] = \lim_{\forall\Delta t_u \to 0} \prod_u \{\eta(\Delta E(t_u); t_u)\,d\Delta E(t_u)\}$$
$$(38)$$

In Appendix B we show that the probability density functional (eq 38) leads to the following expression for the average survival function:

$$\langle\ell(t)\rangle = \exp\{-\int_{t_0}^t \langle k(t')\rangle\,dt'\} \qquad (39)$$

In the particular case of Maxwell−Boltzmann distributions, eq 39 reduces to eq 37. By differentiating eq 39 we come to

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$$\frac{\partial}{\partial t}\langle \ell(t)\rangle = -\langle k(t)\rangle\langle \ell(t)\rangle \tag{40}$$

that is, for rapid dynamic fluctuations the average survival function $\langle \ell(t)\rangle$ obeys the same evolution equation as the fluctuating survival function $\ell(t)$ (eq 1), with the difference that the fluctuating rate coefficient $k(t)$ is replaced by its average value $\langle k(t)\rangle$.

The physical significance of eqs 37−39 is clear: they are the integral kinetic laws derived from an averaged differential kinetic equation (eq 40) characterized by an averaged rate coefficient $\langle k(t)\rangle$. In particular, for a Zubarev−McLennan ensemble we have

$$\langle k(t')\rangle = \int_0^\infty k_0(T)\chi(\Delta E(t'))\langle \Delta E(t')\rangle^{-1} \exp[-\Delta E(t')/$$

$$\langle \Delta E(t')\rangle]\, \mathrm{d}\Delta E(t') = \frac{k_0(T)k_B T}{\langle \Delta E(t')\rangle + k_B T} \tag{41}$$

and eq 39 reduces to eq 37.

4.2. General Treatment of Dynamic Disorder. The generalization introduced above and developed in Appendix B also provides a clue about a possible way of generalizing eq 39 for an arbitrary type of dynamic disorder; it suggests to express the average kinetic curves in terms of the cumulants $\langle\langle k(t_1)....k(t_m)\rangle\rangle, m = 1,2,...$ of the rate coefficient. By assuming that these cumulants exist and are finite, the characteristic functional $\mathscr{G}_k[\zeta(t')]$ can be expressed as

$$\mathscr{G}_k[\zeta(t')] =$$
$$\exp\left\{\sum_{m=1}^\infty \frac{i^m}{m!}\int_{t_0}^t\cdots\int_{t_0}^t \langle\langle k(t_1')....k(t_m')\rangle\rangle\zeta(t_1')...\zeta(t_m')\, \mathrm{d}t_1'... \, \mathrm{d}t_m'\right\} \tag{42}$$

and eq 31 leads to

$$\langle \ell(t)\rangle = \exp\left\{\sum_{m=1}^\infty \frac{(-1)^m}{m!}\int_{t_0}^t\cdots\int_{t_0}^t \langle\langle k(t_1')....k(t_m')\rangle\rangle\, \mathrm{d}t_1'... \, \mathrm{d}t_m'\right\} \tag{43}$$

Equations 31 and 43 are exact equations for the average survival function. Unfortunaley, to apply these equations we need to evaluate the characteristic function $\mathscr{G}_k[\zeta(t')]$ of the total rate coefficient or the cumulants $\langle\langle k(t_1)....k(t_m)\rangle\rangle, m = 1,2,...$ in terms of the generalized nonequilibrium ensemble (eq 21) or the partition functional (eq 22). These quantities can be evaluated, at least in principle, by using perturbation approaches similar those used in quantum field theory, by starting out from the independent Zubarev−McLennan ensemble (32) and then evaluating corrections induced by the correlation functions of the energy barriers. In this article we do not attempt to carry out such computations; instead we try to analyze the general physicochemical implications of eqs 31 and 43.

We start out by discussing the problem of the time-dependence of the average of the random component of the energy barrier, $\langle\Delta E(t)\rangle$. From the theoretical point of view, such a dependence arises naturally from the application of the Zubarev−McLennan approach. However, for most experimental systems described by the RAE model, the disorder is stationary and thus such a time dependence can be ruled out. Time-dependent averages $\langle\Delta E(t)\rangle$ may be needed for describing the relaxation under the influence of external fields with a time dependent average. The time dependence of $\langle\Delta E(t)\rangle$ may complicate the analysis of experimental data. For example the

condition that $\langle\Delta E\rangle$ is constant applied to rapid, independent fluctuations of the Zubarev−McLennan type leads to exponential relaxation, with a constant rate $k_0(T)k_B T/[\langle\Delta E\rangle + k_B T]$. If $\langle\Delta E\rangle$ is linearly increasing in time:

$$\langle\Delta E(t)\rangle = \langle\Delta E(t_0)\rangle + b(t - t_0) \tag{44}$$

the kinetic curve displays a long tail with a scaling exponent $k_0(T)k_B T/b$:

$$\langle \ell(t)\rangle = \left[\frac{k_B T + \langle\Delta E(t_0)\rangle}{k_B T + \langle\Delta E(t_0)\rangle + b(t - t_0)}\right]^{k_0(T)k_B T/b} \tag{45}$$

Similarly, if $\langle\Delta E\rangle$ is a periodic function of time,

$$\langle\Delta E(t)\rangle = \langle\Delta E(t_0)\rangle + a\cos[\omega(t - t_0) + \varphi], \langle\Delta E(t_0)\rangle > a \tag{46}$$

then the relaxation function is given by

$$\langle \ell(t)\rangle = \exp\left\{-\frac{2k_0(T)k_B T}{\omega a\sqrt{c^2 - 1}}\left\{\mathrm{arctg}\left[\sqrt{\frac{c-1}{c+1}}\mathrm{tg}\left(\frac{\varphi}{2}\right)\right] - \mathrm{arctg}\left[\sqrt{\frac{c-1}{c+1}}\mathrm{tg}\left(\frac{\omega(t - t_0) + \varphi}{2}\right)\right]\right\}\right\} \tag{47}$$

where

$$c = [\langle\Delta E(t_0)\rangle + k_B T]/a > 1 \tag{48}$$

In this paper we do not discuss these cases in further detail. In the following, for simplicity, we assume that the stochastic process that describes the fluctuations of the energy barrier is stationary and therefore $\langle\Delta E\rangle$ is constant.

4.3. Relations between Static and Dynamic Disorder. Now we discuss the relations between static and dynamic disorder for RAE models. For simplicity we assume the case where the probability density of energy barriers $\eta(\Delta E)$ has an arbitrary shape but is time independent; this includes the case of Maxwell−Boltzmann profiles as a particular case. In Appendix C we show that, under these circumstances, for static disorder the cumulants and moments of the total rate coefficient are constant.

$$\langle k^m(t_0)\rangle = \langle k(t_1')....k(t_m')\rangle, t \ge t_1',...,t_m' \ge t_0 \tag{49}$$

$$\langle\langle k^m(t_0)\rangle\rangle = \langle\langle k(t_1')....k(t_m')\rangle\rangle, t \ge t_1',...,t_m' \ge t_0. \tag{50}$$

The physical interpretation of eqs 49−50 is clear: for the static RAE model, the moments and the cumulants of the rate coefficient do not decay; for any time they have the same value as at the initial moment t_0. Under these circumstances a fluctuation of the energy barrier and of the rate coefficient, once it occurs, lasts forever. It follows that the RAE model with static disorder has infinite memory.

Equations 49−50 make it possible to discuss the transition from static to dynamic disorder. Based on these equations, in Appendix C we show that

$$\langle \ell(t)\rangle_{\mathrm{static}} = G_k(t) = \int_0^\infty p(k)\exp(-kt)\, \mathrm{d}k \tag{51}$$

which is equivalent to eq 13, derived in section 1 for systems with static disorder. The transition from static to dynamic disorder can be understood in terms of two time scales, the kinetic (relaxation) time scale, which has the magnitude order

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$\tau_{\text{kinetic}} \sim 1/k_0(T)$, and the time scale characteristic for the decay of the fluctuations of the rate coefficient, τ_{decay}. If $\tau_{\text{decay}} \gg \tau_{\text{kinetic}}$, the cumulants of the rate coefficients decay very slowly and the transition from static to dynamic disorder is also very slow. From eqs 43, 50, and 51 it follows that

$$\langle \ell(t) \rangle = \exp \left\{ \sum_{m=1}^{\infty} \frac{(-1)^m}{m!} \langle\langle k^m(t_0) \rangle\rangle (t - t_0)^m \right\} \sim$$
$$\langle \ell(t) \rangle_{\text{static}}, \text{ for } \tau_{\text{decay}} \gg \tau_{\text{kinetic}}, \tau_{\text{decay}} \gg t - t_0 \quad (52)$$

That is, for small to intermediate times, the decay of fluctuations of the rate coefficient has little influence on the kinetics of the process and the average survival function is almost the same as the average survival function for a system with static disorder. For large times, however, the kinetics of the process is no longer dominated by the kinetic time scale, τ_{kinetic}, and the decay of the fluctuations of the process play a dominant role.

If the two time scales have the same order of magnitude, $\tau_{\text{decay}} \sim \tau_{\text{kinetic}}$, then there is a strong interaction between the kinetics of the process and the decay of the fluctuations. For a better understanding of this intermediate regime we consider a special type of cumulant of the rate coefficient that is capable of describing a wide range of types of disorder. Since we discuss only the case of stationary processes, it follows that the cumulants must obey the condition of time invariance:

$$\langle\langle k(t_1)....k(t_m) \rangle\rangle = \langle\langle k(t_1 - t_m^*)....k(t_m - t_m^*) \rangle\rangle \quad (53)$$

where $t_m^* = \min(t_1,...,t_m)$. Furthermore, we assume that the decay of the cumulants of a given order can be described in terms of a single damping function $g_m(t - t_m^*)$, which depends on the cumulant of order m:

$$\langle\langle k(t_1 - t_m^*)....k(t_m - t_m^*) \rangle\rangle = \kappa_m \prod_u g_m(t_u - t_m^*) \quad (54)$$

Simple shot noise models for dynamic disorder produce[15] cumulants of the type in eq 54. After some algebraic manipulations involving transformations of integration variables and domains, eqs 43 and 54 lead to the following expression for the survival function:

$$\langle \ell(t) \rangle =$$
$$\exp \left\{ \sum_{m=1}^{\infty} \frac{(-1)^m}{(m-1)!} \kappa_m \int_0^{t-t_0} ... \, d\theta [\int_0^{t-t_0-\theta} ... \, g_m(\tau) \, d\tau]^{m-1} \right\} \quad (55)$$

We consider two types of memory: long memory and short memory.

(a) Long Memory. If the damping functions $g(t - t_m^*)$ have long tails of the negative power law type, then the fluctuations of the rate coefficients have long memory. The simplest case of long memory corresponds to

$$g_m(\tau) \sim \tau^{-H_m}, \quad 1 > H_m > 0 \quad (56)$$

where H_m are fractal exponents attached to the different cumulants. By inserting eq 56 into eq 55 we obtain

$$\langle \ell(t) \rangle =$$
$$\exp \left\{ \sum_{m=1}^{\infty} \frac{(-1)^m \kappa_m (t - t_0)^{1+(m-1)(1-H_m)}}{(m-1)!(1 - H_m)^{m-1}(1 + (m-1)(1 - H_m))} \right\} \quad (57)$$

that is, the average survival function is given by a generalized stretched exponential.

(b) Short Memory. If the damping functions $g(t - t_m^*)$ decay fast and have short tails of the exponential type, then the fluctuations of the rate coefficients have short memory. The simplest case of short memory corresponds to

$$g_m(\tau) \sim \exp(-\nu_m \tau) \quad (58)$$

where ν_m are decay frequencies which depend on the cumulants of order m. In this case the amplitude factors κ_m are equal to the cumulants of the rate coefficient for static disorder:

$$\kappa_m = \langle\langle k^m(t_0) \rangle\rangle. \quad (59)$$

Equation 59 can be obtained from eqs 54 and 58 applied for $t_1,...,t_m = t_0$. The average survival function becomes

$$\langle \ell(t) \rangle = \exp \left\{ \sum_{m=1}^{\infty} \frac{(-1)^m \langle\langle k^m(t_0) \rangle\rangle}{(m-1)!} \int_0^{t-t_0} ... \, d\theta \times \right.$$
$$\left. \left[\frac{1 - \exp[-\nu_m(t - t_0)]}{\nu_m} \right]^{m-1} d\theta \right\} \quad (60a)$$

$$= \exp \left\{ \sum_{m=1}^{\infty} \frac{(-1)^m \langle\langle k^m(t_0) \rangle\rangle}{(m-1)!(\nu_m)^m} \left\{ \nu_m(t - t_0) - \right. \right.$$
$$\left. \left. \sum_{u=1}^{m-1} \frac{1}{u} [1 - \exp(-\nu_m(t - t_0))]^u \right\} \right\} \quad (60b)$$

In this case $\tau_{\text{decay}} \sim \max(1/\nu_m)$. According to eq 60b, for large times the average survival function decays exponentially

$$\langle \ell(t) \rangle = \exp[-(t - t_0)\Omega], \text{ for } t - t_0 \gg 0 \quad (61)$$

where

$$\Omega = \sum_{m=1}^{\infty} \frac{(-1)^{m-1}}{(m-1)!} \langle\langle k^m(t_0) \rangle\rangle (\nu_m)^{1-m} \quad (62)$$

is a characteristic frequency.

From eqs 60a–b we can also recover the two extreme types of disorder as particular cases. As expected, for $\tau_{\text{decay}} \gg \tau_{\text{kinetic}}$, eq 60a reduces to eq 51 valid for static disorder. In the other extreme, for $\tau_{\text{decay}} \ll \tau_{\text{kinetic}}$, we have $\nu_m \to \infty$ and eqs 60a–b reduce to

$$\langle \ell(t) \rangle = \exp[-\langle\langle k(t_0) \rangle\rangle (t - t_0)] \quad (63)$$

which is a particular case of eqs 37 and 39 valid for rapid, independent fluctuations described by the Zubarev–McLennan ensemble: eqs 37 and 39 reduce to eq 63 for $\langle \Delta E \rangle$ constant.

A popular approach for disordered kinetics is based on the use of multiplicative Gaussian, white noise[16] for describing the fluctuations of rate coefficients. Applied to the RAE model, such an approach is based on the assumption that the first cumulant of the rate coefficient, $\langle\langle k \rangle\rangle$, which is identical to the average value $\langle k \rangle$ is constant, the cumulant of second order is delta correlated and all other cumulants are equal to zero:

$$\langle\langle k \rangle\rangle = \text{constant}, \langle\langle k(t_1)k(t_2) \rangle\rangle =$$
$$\sigma_2 \delta(t_1 - t_2),..., \langle\langle k(t_1)...k(t_m) \rangle\rangle_{m>2} = 0 \quad (64)$$

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Despite its popularity, the Gaussian approximation (eq 64) leads to unphysical results for the RAE model, due to the fact that Gaussian probability laws are symmetric and make it possible for the rate coefficient to take negative values, which is incorrect. Although the probability of taking negative values is usually very small, its effect is increased by the multiplicative nature of the noise. This shortcoming can be easily overcome by introducing a generalized white noise for which all cumulants of order larger than one are delta correlated:[10]

$$\langle\langle k \rangle\rangle = \text{constant}, \quad \langle\langle k(t_1)...k(t_m) \rangle\rangle =$$
$$\sigma_m \prod_{u=1}^{m-1} \delta(t_u - t_{u+1}), \quad m = 2, 3,... \quad (65)$$

In the literature, kinetic systems obeying eqs 65 are usually described in terms of Langevin equations. However, in this paper we study the implications of eqs 65 by using the nonequilibrium ensemble approach, which leads to results compatible with the method of Langevin equations. We intend to investigate the connections between these two approaches in a separate publication.

The approach developed in this section is based on the assumption that the cumulants of the rate coefficient exist and are finite. It follows that, strictly speaking, a system with white noise described by eq 65 cannot be used; the normal approach for such systems is to use stochastic calculus of the Stratonovich or Ito type. In this article, however, we use an alternative approach suggested by Van Kampen and West[17] for other problems; such an approach has the advantage that we can use partial results developed in this section. We consider cumulants which lead to the delta correlated expressions (eq 65) for certain given values of some parameters, compute the average survival function for arbitrary values of the parameters and then pass to the limit which reproduces the delta-correlated cumulants (eq 65). Such an approach can be easily implemented by considering a slight modification of the damping functions (58)

$$g_m(\tau) = \nu_m \exp(-\nu_m \tau) \quad (66)$$

By introducing the preexponential frequency factor ν_m, the damping factor $g_m(\tau)$ has the formal structure of a probability density for the time difference τ; in the limit $\nu_m \to \infty$, the damping factor $g_m(\tau)$ tends toward a delta function. In this case eq 59 is replaced by

$$\kappa_m = \langle\langle k^m(t_0) \rangle\rangle (\nu_m)^{m-1} \quad (67)$$

and the cumulants described eqs 54 reduce to the delta correlated cumulants described by eqs 65 in the limit, $\forall \nu_m \to \infty$ with the constraint

$$\lim_{\forall \nu_m \to \infty} \kappa_m (\nu_m)^{1-m} = \sigma_m \quad (68)$$

For arbitrary ν_m the average survival function can be easily evaluated from eq 55

$$\langle\ell(t)\rangle = \exp\left\{ \sum_{m=1}^{\infty} \frac{(-1)^m \kappa_m(\nu_m)^{1-m}}{(m-1)!} \int_0^{t-t_0} ... \, d\theta \{ 1 - \right.$$
$$\left. \exp[-\nu_m(t-t_0)]\}^{m-1} \, d\theta \right\} \quad (69)$$

In the limit $\forall \nu_m \to \infty$ with the constraint (eq 68), eq 69 leads to an exponential law for the average survival function

$$\langle\ell(t)\rangle = \exp[-(t-t_0)\Omega^*] \quad (70)$$

where

$$\Omega^* = \sum_{m=1}^{\infty} \frac{(-1)^{m-1}\sigma_m}{(m-1)!} \quad (71)$$

It is interesting to compare the Zubarev−McLennan fluctuations with the case of white, non-Gaussian noise with delta correlated cumulants. In both cases the fluctuations of the energy barrier and rate coefficient are fast and statistically independent. Both types of fluctuations correspond to the limit case of very strong dynamic disorder. There is only one difference between the two: for Zubarev−McLennan fluctuations the cumulants of the rate coefficient exist and are finite, whereas for white noise the cumulants display delta type singularities. In both cases the average survival function decays exponentially; although the decay rates are different in the two cases, experiments based on measurement of average concentrations cannot make a distinction between these two types of dynamic disorder.

The typical pattern that emerges from the examination of the different types of dynamic disorder investigated in this section is that, for long times, the dynamics of activation energy fluctuation decays, prevails, and outweighs the contribution of the reaction kinetics. If the fluctuations are slowly decaying, the contribution of chemical kinetics can be seen in the shape of the average survival function for small to intermediate times; otherwise, if the decay of fluctuations is fast, the overall kinetics of the process is dominated by fluctuation dynamics. In the following section we illustrate the general results derived in this section by considering a simple example of an RAE model with dynamic disorder.

5. Example: RAE Models with Renewal-type Dynamic Disorder

We introduce a simple RAE model with dynamic disorder, based on the following assumptions. (1) The random component ΔE of the energy barrier is randomly selected from a time invariant probability density $\eta(\Delta E)$. Different values ΔE are selected at random times from the probability density $\eta(\Delta E)$; the selected value at a given time is independent of the other values of ΔE selected at previous times. (2) The time interval τ between two selection events is chosen from two probability laws: an initial probability density $\psi_0(\tau)$ for the time interval that elapses from the beginning of the process to the first selection event and a second probability density $\psi(\tau)$ for the time interval between two selection events. The RAE model defined by these two assumptions is a model of the continuous time random walk[18] type (CTRW), which is also referred to as a renewal process. CTRW (renewal) processes are commonly used for describing transport processes in disordered systems.[1−4] By using the general theory developed in this paper, in Appendix D, we show that the Laplace transform of the average survival function is given by

$$\mathscr{L}_t\langle\ell(t)\rangle = \int dk_0 \, p(k_0) \bar{\Psi}_0(k_0 + s) + $$
$$\frac{[\int dk_1 \, p(k_1)\bar{\Psi}(k_1 + s)][\int dk_0 \, p(k_0)\bar{\psi}_0(s + k_0)]}{1 - \int dk \, p(k)\bar{\psi}(s + k)} \quad (72)$$

where

$$\Psi_0(\tau) = \int_\tau^\infty \psi_0(\tau)\,d\tau, \ \Psi(\tau) = \int_\tau^\infty \psi(\tau)\,d\tau \quad (73)$$

the overbar and $\mathscr{L}_t$ denote the Laplace transformation, and s is the Laplace variable conjugated to the time variable.

From eq 72 we notice that the time dependent behavior of the average survival function is determined by the eigenvalues of the secular equation

$$I(s) = 1 - \int dk p(k)\bar{\psi}(s + k) = 0 \quad (74)$$

The eigenvalues of eq 74 depend only on the probability density $\psi(\tau)$ of the time interval between two arbitrary selection events and are independent of the probability density $\psi_0(\tau)$ attached to the first selection event. It follows that $\psi_0(\tau)$ may influence the values of amplitude factors present in the expression of the average survival function but does not influence the time dependence of this function. For this reason in the following we assume that

$$\psi_0(\tau) = \psi(\tau) \quad (75)$$

The approximation (eq 75) is commonly used in the CTRW literature and in most cases it does not lead to serious limitations.

We express the Laplace transforms $\bar{\Psi}(k + s)$ in terms of $\bar{\psi}(k + s)$. We have

$$\bar{\Psi}(k + s) = \int_0^\infty dt \exp[-(k + s)t]\int_t^\infty \psi(t')\,dt' =$$
$$\frac{1 - \bar{\psi}(k + s)}{k + s} \quad (76)$$

We also notice that the Laplace transform $\bar{\langle l}(s)\rangle_{\text{static}}$ of the average survival function for static disorder, $\langle l(t)\rangle_{\text{static}}$, can be expressed as

$$\langle \bar{l}(s)\rangle_{\text{static}} = \int_0^\infty \langle l(t)\rangle_{\text{static}} \exp(-st)\,dt =$$
$$\int_0^\infty \int p(k)\,dk \exp(-(s + k)t)\,dt = \int \frac{p(k)}{s + k}\,dk \quad (77)$$

By using eqs 75−77, eq 72 becomes

$$\mathscr{L}_t\langle l(t)\rangle = \frac{\langle \bar{l}(s)\rangle_{\text{static}} - \int dk p(k)\dfrac{\bar{\psi}(s + k)}{(s + k)}}{1 - \int dk p(k)\bar{\psi}(s + k)} \quad (78)$$

Equation 78 can be used for evaluating the average survival function for different types of disorder. The static disorder corresponds to the particular case where the time interval between two selection events tends toward infinity. We assume that the probability density $\psi(\tau)$ depends on the average value $\langle \tau \rangle$. Dimensional analysis requires $\psi(\tau)$ to be of the form

$$\psi(\tau) = \langle \tau \rangle^{-1}\varphi(\tau/\langle \tau \rangle) \quad (79)$$

where $\varphi(x)$ is a dimensionless probability density and $x = \tau/\langle \tau \rangle$ is a dimensionless time interval. We have

$$\bar{\psi}(s) = \int_0^\infty \exp(-\langle \tau \rangle xs)\varphi(x)\,dx \quad (80)$$

From eq 80 it follows that in the limit $\langle \tau \rangle \to \infty$ we have $\bar{\psi}(s) \to 0$, and from eq 78

$$\lim_{\langle \tau \rangle \to \infty}\langle l(t)\rangle = \langle l(t)\rangle_{\text{static}} \quad (81)$$

as expected.

In the other extreme of fast, independent fluctuations we have $\langle \tau \rangle \to 0$. We notice that $\langle x \rangle = \langle \tau \rangle/\langle \tau \rangle = 1$, that is, the average value of the dimensionless time interval x is equal to one and thus, according to eq 80, we have

$$1 = \langle x \rangle = \int_0^\infty x\varphi(x)\,dx = -\frac{\partial}{\partial z}\bar{\varphi}(0) \quad (82)$$

where

$$\bar{\varphi}(z) = \int_0^\infty \exp(-xz)\varphi(x)\,dx \quad (83)$$

is the Laplace transform of $\varphi(x)$ and z is the Laplace variable conjugated to the dimensionless time interval x. From eqs 78, 80, and 82−83 we obtain

$$\lim_{\langle \tau \rangle \to 0}\mathscr{L}_t\langle l(t)\rangle = \frac{-\int dk p(k)\dfrac{\partial}{\partial z}\bar{\varphi}(0)}{-\int dk p(k)(s + k)\dfrac{\partial}{\partial z}\bar{\varphi}(0)} = \frac{1}{s + \langle k \rangle} \quad (84)$$

from which, by coming back to the time variable, we come to

$$\langle l(t)\rangle = \exp[-\langle k \rangle t] \quad (85)$$

which is the same as eq 63 for the average survival function for independent, rapidly fluctuating Zubarev−McLennan fluctuations.

For studying the intermediate types of dynamic disorder, we need to know the solutions of the secular eq 74. We notice that

$$\int dk p(k)\bar{\psi}(s + k) =$$
$$\int dk p(k)\int_0^\infty \exp[-t(s + k)]\psi(t)\,dt = \chi(s) \quad (86)$$

where

$$\chi(s) = \int_0^\infty \exp(-st)\psi(t)\langle l(t)\rangle_{\text{static}}\,dt \quad (87)$$

and thus the secular eq 74 can be put in a form similar to Lotka's secular equation from mathematical demography, which has been extensively studied in the literature:[19]

$$\chi(s) = \int_0^\infty \exp(-st)\psi(t)\langle l(t)\rangle_{\text{static}}\,dt \quad (88)$$

It has been shown that if $\chi(s)$ is analytic in s then equations of type (88) have a single real root s_0, which is nonpositive.[19] We have

$$s_0 < 0 \text{ if } \chi(0) < 1 \text{ and } s_0 = 0 \text{ if } \chi(0) = 1 \quad (89)$$

Equation 88 can also have, at most, a countable number of complex roots $s_q = u_q \pm iv_q$, $q = 1,2,...$ with real parts u_q smaller or at least equal to the real root s_0 (ref 19)

$$u_q \leq s_0, \ q = 1,2,... \quad (90)$$

For simplicity, we assume that the complex eigenvalues $s_q = u_q \pm iv_q$ are simple and evaluate the inverse Laplace transform of eq 78. After lengthy algebraic manipulations we come to

$$\langle \ell(t) \rangle = \mathscr{A} \exp(-t|s_0|) + 2 \sum_q \frac{\mathscr{B}_q(t)}{(\mathscr{J}_q^+)^2 + (\mathscr{J}_q^-)^2} \exp(-t|u_q|)$$

$$(91)$$

where $\mathscr{A}$ and $\mathscr{J}_q^\pm$ are constants

$$\mathscr{A} = \frac{\int \frac{\mathrm{d}k p(k)}{s_0 + k} \int_0^\infty \mathrm{d}\theta \{1 - \exp[-\theta(s_0 + k)]\} \psi(\theta)}{\int \mathrm{d}k p(k) \int_0^\infty \mathrm{d}\theta \theta \exp[-\theta(s_0 + k)] \psi(\theta)} \quad (92)$$

$$\mathscr{J}_q^\pm = \int \mathrm{d}k' p(k') \int_0^\infty \mathrm{d}\theta' \theta' \exp[-\theta'(k' - |u_q|)] \times \begin{cases} \cos(w_q \theta') \\ \sin(w_q \theta') \end{cases} \psi(\theta') \quad (93)$$

and $\mathscr{B}_q(t)$ are periodic functions of time

$$\mathscr{B}_q(t) = \int \int \mathrm{d}k \, \mathrm{d}k' \int_0^\infty \int_0^\infty \mathrm{d}\theta \, \mathrm{d}\theta' \int_0^1 \mathrm{d}x \theta \theta' p(k) p(k') \times \\ \exp[-x\theta(k - |u_q|) - \theta'(k' - |u_q|)] \cos(w_q(t - x\theta)) \cos(w_q \theta') \psi(\theta) \psi(\theta') \quad (94)$$

For large times, the decay of the average survival function is exponential

$$\langle \ell(t) \rangle \sim \mathscr{A} \exp(-t|s_0|) \text{ for } t \gg 0 \quad (95)$$

a result that is consistent with the general analysis in section 4.

An interesting situation that was not considered in the general discussion in section 4 corresponds to the case where the probability density $\psi(\tau)$ of the time interval between two selections is also described by a rate process with a random activation energy barrier. More precisely, we assume that $\psi(\tau)$ is described by a superposition of exponential distributions:

$$\psi(\tau) = \int_0^\infty \mathrm{d}\Delta E_\mu \eta_\mu(\Delta E_\mu) \mu(\Delta E_\mu) \exp[-\tau \mu(\Delta E_\mu)] \quad (96)$$

where $\mu(\Delta E_\mu)$ is an activated rate coefficient for which the energy barrier has a random component ΔE_μ

$$\mu(\Delta E_\mu) = \mu_0(T) \exp\left[-\frac{\Delta E_\mu}{k_B T}\right] \text{ with } \mu_0(T) = A_\mu \exp\left[-\frac{E_{\mu 0}}{k_B T}\right] \quad (97)$$

and $\eta_\mu(\Delta E_\mu)$ is the probability density of the random component ΔE_μ of the energy barrier of the selection process. In this particular case, the model is similar to a master equation approach developed in a different physical context in ref 10. The kinetics of the process is represented by the superposition of two different static RAE models, one for the chemical process itself and the second for the selection process of the energy barriers. By combining eqs 78 and 97, after some algebraic manipulations we come to

$$\mathscr{L}_t \langle \ell(t) \rangle = \left[\int \int \frac{p(k) p_\mu(\mu)}{s + k + \mu} \, \mathrm{d}k \, \mathrm{d}\mu \right] \Big/ \int \int \frac{p(k) p_\mu(\mu)(s + k)}{s + k + \mu} \mathrm{d}k \, \mathrm{d}\mu \quad (98)$$

where $p(k)$ is given by eq 1 and $p_\mu(\mu)$ is given by

$$p_\mu(\mu) \, \mathrm{d}\mu = \mathrm{d}k \int \delta \left\{ \mu_0(T) \exp\left(-\frac{\Delta E_\mu}{k_B T}\right) - \mu \right\} \eta_\mu(\Delta E_\mu) \, \mathrm{d}\Delta E_\mu$$

$$= \begin{cases} k_B T \eta_\mu \left[k_B T \ln\left(\frac{\mu_0(T)}{\mu}\right) \right] \frac{\mathrm{d}\mu}{\mu} \text{ for } \mu \leq \mu_0(T) \\ 0 \text{ for } \mu \geq \mu_0(T) \end{cases}$$

$$(99)$$

Although not identical, eq 98 has a similar structure with eq 8.14 from ref 10. This similar structure can be used for evaluating the inverse Laplace transform in eq 98 for different types of distribution functions. By using this method we can identify different types of asymptotic regimes that can be used for the analysis of experimental data. We distinguish three different cases.

(1) We assume that the rate process is described by a Maxwell–Boltzmann distribution of activation energies and the selection process by a constant activation energy $E_\mu = E_{\mu 0}$. We have

$$p(k) \, \mathrm{d}k = \frac{\vartheta[k - k_0(T)]}{[k_0(T)]^\alpha} \alpha k^{\alpha - 1} \, \mathrm{d}k \quad (100)$$

$$p_\mu(\mu) \, \mathrm{d}\mu = \delta[\mu_0(T) - \mu] \, \mathrm{d}\mu \quad (101)$$

and the large time behavior of the average survival function is given by

$$\langle \ell(t) \rangle \sim \\ \frac{\Gamma(1 + \alpha)[k_0(T)]^{-\alpha}}{1 - \alpha[\mu_0(T)/k_0(T)]^\alpha B[\alpha, 1 - \alpha, k_0(T)/(k_0(T) + \mu_0(T))]} t^{-\alpha} \\ \exp[-\mu_0(T)t], \text{ for } t \gg 1/k_0(T) \quad (102)$$

where $B(p,q,x) = \int_0^x x^{p-1}(1 - x)^{q-1} \, \mathrm{d}x, p, q, x > 0$ is the incomplete beta function. According to eq 102, the beginning of the tail of the survival function, for $1/\mu_0(T) \gg t \gg 1/k_0(T)$, is described by a negative power law, whereas the end of the tail, for $t \gg 1/k_0(T)$ is described by an exponential function. Thus, for large times, the decay of the fluctuations determines the overall kinetics of the process, a result which is compatible with the general approach in section 4.

(2) The rate process is described by a Maxwell–Boltzmann distribution of activation energies and the selection process by a positive Gompertz law with a characteristic variation of the activation energy $\Delta E_{\mu 0}$

$$\eta_\mu(\Delta E_\mu) = \\ (\Delta E_{\mu 0})^{-1} \exp\{\Delta E_\mu/\Delta E_{\mu 0} - \exp(\Delta E_\mu/\Delta E_{\mu 0}) - 1\} \quad (103)$$

We get the following asymptotic expression for the large time behavior of the average survival function:

$$\langle \ell(t) \rangle \sim \Gamma(1 + \alpha)[k_0(T)]^{-\alpha} \mu_0(T) t^{1-\alpha} \exp[-(\xi t)^\epsilon] \quad (104)$$

where

$$\epsilon = k_B T/(\Delta E_{\mu 0} + k_B T) < 1 \quad (105)$$

is a second fractal exponent and

$$\xi = \mu_0(T) \left[1 + \frac{k_B T}{\Delta E_{\mu 0}} \right]^{1 + \Delta E_{\mu 0}/k_B T} \frac{k_B T}{\Delta E_{\mu 0}} \quad (106)$$

is a characteristic frequency. In this case, the beginning of the tail is given by a power law and the end of the tail by a stretched exponential.

(3) We assume that both the rate process and the dynamic fluctuations of the energy barriers are described by Maxwell–Boltzmann distributions. The probability density $\eta(\Delta E)$ is given by eq 9, and $\eta_\mu(\Delta E_\mu)$ is given by a similar exponential law

$$\eta_\mu(\Delta E_\mu) = [\langle\Delta E_\mu\rangle]^{-1} \exp[-\Delta E_\mu/\langle\Delta E_\mu\rangle] \quad (107)$$

where $\langle\Delta E_\mu\rangle$ is the average value of the random component of the energy barrier attached to the selection process. The probability density $p(k)$ of the reaction rate k is given by the power law (100) and the probability density $p_\mu(\mu)$ of the rate μ is given by a similar power law

$$p_\mu(\mu)\,d\mu = d\mu \int \delta\left\{\mu_0(T) \exp\left[-\frac{\Delta E_\mu}{k_B T}\right] - \mu\right\} \times$$
$$\eta_\mu(\Delta E_\mu)\,d\Delta E_\mu = \frac{\vartheta[\mu - \mu_0(T)]}{[\mu_0(T)]^{\alpha_\mu}}\alpha_\mu\mu^{\alpha_\mu-1}\,d\mu \quad (108)$$

and

$$\alpha_\mu = k_B T/\langle\Delta E_\mu\rangle \quad (109)$$

is a third scaling exponent between zero and unity. From eqs 98, 108, and 109 we get the following expression for the large time behavior of the average survival function:

$$\langle\ell(t)\rangle \sim \Gamma(1 + \alpha)\Gamma(1 + \alpha_\mu)[\mu_0(T)/k_0(T)]^\alpha \times$$
$$[\mu_0(T)t]^{-(\alpha+\alpha_\mu)} \text{ for } k_0(T) \gg \mu_0(T), t \gg [\mu_0(T)]^{-1} \quad (110)$$

In this case there are two RAE models, one for the rate process itself and the second one for the selection of the energy barriers which describes the decay of the dynamic fluctuations of the activation energy. In the long run, these two RAE models interfere, resulting in a fractal exponent $\alpha + \alpha_\eta$, which is the sum of the fractal exponents attached to the two processes.

In conclusion, in this section we have shown that continuous time random walk (renewal) models for dynamic disorder lead to results that are generally compatible with the general analysis in section 4: for small to moderately large times the process can be approximately described by a static RAE models, whereas for large times the decay of dynamic fluctuations of the energy barrier prevail. There is, however, one exception, corresponding to long memory of the decay of fluctuations of the energy barrier. In this case, the two RAE models interfere in the long run and the total fractal exponent of the resulting power tail is the sum of the fractal exponents corresponding to the two RAE processes.

6. Nonequilibrium Ensemble Approach to Reversible Chemical Processes

Until now we have focused on the simplest disordered rate process, a first-order irreversible reaction with static or dynamic disorder. In this section we consider a more complicated type of process, a reversible (quasi) reaction, involving a set of forward and backward steps:

$$A + B \rightleftharpoons C \quad (111)$$

Reaction 111 describes different types of experimental systems, for example, adsorption kinetics on a heterogeneous surface, where A is a chemical species in the gas or liquid phase, B is

a free adsorption site on a surface, and C is an occupied site on the surface. In the following we limit ourselves to the study of the adsorption problem; in the next section, an adsorption experiment reported in the literature is analyzed based on the theoretical results derived in this section.

We assume that the surface is energetically heterogeneous, the adsorption energy of the species A varies from place to place. By following the homottatic patch approximation, we assume that the surface can be divided into patches that are characterized by the same adsorption energy and that these patches are big enough so that a (quasi) macroscopic description of the adsorption is possible.

For each patch we have a set of local adsorption and desorption rate coefficients

$$k^\pm_{local}(E^\pm) = A^\pm_{local} \exp\left[-\frac{E^\pm}{k_B T}\right] \quad (112)$$

where $k^\pm_{local}(T)$ are the adsorption and desorption rate coefficients at temperature, T, $A^\pm_{local}$ are preexponential factors, and $E^\pm$ are adsorption and desorption activation energies, with random functions of time and position. For a given patch, the ratio between the two rate coefficients

$$K_{local}(\epsilon) = k^+_{local}(E^+)/k^-_{local}(E^-) =$$
$$[A^+_{local}/A^-_{local}] \exp\left[-\frac{E^+ - E^-}{k_B T}\right] = K^0_{local}\left[\frac{\epsilon}{k_B T}\right] \quad (113)$$

is a local equilibrium constant and

$$\epsilon = E^- - E^+ = -\Delta H \quad (114)$$

is the adsorption energy. In general, the activation energies $E^\pm$ are both random functions of time. Instead of carrying out dynamic averages over two random functions, E^+ and E^-, it is more convenient to use eq 114 and take an average over one of the two activation energies, say the activation energy for desorption, E^-, and the adsorption energy ϵ. This type of averaging is easier because the adsorption energy ϵ is a random number, not a random function, and the corresponding average is static.

We denote by $[A] = \rho$, the concentration of species in the bulk phase (liquid or gas), by $[B(\epsilon)] = b(\epsilon)d\epsilon$ the surface concentration of free sites with an adsorption energy between ϵ and $\epsilon + d\epsilon$, and by $[C(\epsilon)] = c(\epsilon)d\epsilon$ the corresponding surface concentration of occupied sites. We have the balanced equation

$$b(\epsilon)d\epsilon + c(\epsilon)d\epsilon = g(\epsilon)d\epsilon \quad (115)$$

where $g(\epsilon)d\epsilon$ is the total concentration of adsorption sites, free and occupied, that are characterized by an adsorption energy between ϵ and $\epsilon + d\epsilon$. The local coverage corresponding to an adsorption energy between ϵ and $\epsilon + d\epsilon$ is given by

$$\theta_{local}(\epsilon) = c(\epsilon)/g(\epsilon) \quad (116)$$

The kinetic equation for this local coverage is given by

$$\frac{\partial}{\partial t}\theta_{local}(\epsilon) = k^+_{local}(t)\rho(1 - \theta_{local}(\epsilon)) - k^-_{local}(t)\theta_{local}(\epsilon) \quad (117)$$

In typical adsorption experiments, the variation of the bulk concentration ρ is negligible and eq 117 can be easily solved, resulting in

$$\theta_{\text{local}}(\in,t) = \theta_{\text{local}}^{\text{equil}}(\in) + [\theta_{\text{local}}(\in,t_0) - \theta_{\text{local}}^{\text{equil}}(\in)] \exp[-(1 + K_{\text{local}}(\in)\rho) \int_{t_0}^{t} k_{\text{local}}^{-}(t') \, dt'] \quad (118)$$

where

$$\theta_{\text{local}}^{\text{equil}}(\in) = \frac{K_{\text{local}}(\in)\rho}{1 + K_{\text{local}}(\in)\rho} \quad (119)$$

is the local equilibrium coverage corresponding to an absorption energy between $\in$ and $\in + d\in$.

The experimental observable is the total coverage $\theta(t)$, which can be obtained from eq 118 by means of a double averaging procedure: (i) over all possible random functions $k_{\text{local}}^{-}(t')$ and (ii) over all possible equilibrium constants $K_{\text{local}}(\in)$, corresponding to different adsorption energies $\in$.

We rewrite eq 118 in a better form. The dynamic averaging over all possible random functions $k_{\text{local}}^{-}(t')$ can be easily carried out by using the nonequilibrium ensemble approach developed in section 3. Equation 119 can be expressed in terms of the modified survival function

$$\ell^*(t) = \exp[-\kappa_0^*(\in) \int_{t_0}^{t} \chi(\Delta E^{-}(t')) \, dt'] \quad (120)$$

where

$$\Delta E^{-} = E^{-} - E_0^{-} \quad (121)$$

is the random component of the desorption activation energy,

$$\kappa_0^*(\in) = k_{\text{local}}^{-}(E_0^{-})(1 + K_{\text{local}}(\in)\rho) \quad (122)$$

is an effective rate coefficient, and

$$\chi(\Delta E^{-}(t')) = \exp[-\Delta E^{-}(t')/k_{\text{B}}T] \quad (123)$$

is a random transparence factor similar to the one defined by eq 8. We have

$$\theta_{\text{local}}(\in,t) = \theta_{\text{local}}^{\text{equil}}(\in) + [\theta_{\text{local}}(\in,t_0) - \theta_{\text{local}}^{\text{equil}}(\in)]\ell^*(t) \quad (124)$$

By examining eq 124, we notice that the only term dependent on the fluctuations of the energy barrier $E^{-}(t')$ is $\ell^*(t)$ and that all terms in this equation depend on the adsorption energy $\in$. The total coverage $\theta(t)$ can be expressed as the double average

$$\theta(t) = \langle\langle\theta_{\text{local}}(\in,t)\rangle_{\Delta E^{-}(t')}\rangle_{\in} = \langle\theta_{\text{local}}^{\text{equil}}(\in,T)\rangle_{\in} +$$

$$\langle\theta_{\text{local}}(\in,t_0)\langle\ell^*(t)\rangle_{\Delta E^{-}(t')}\rangle_{\in} - \langle\theta_{\text{local}}^{\text{equil}}(\in,T)\langle\ell^*(t)\rangle_{\Delta E^{-}(t')}\rangle_{\in} \quad (125)$$

where the dynamic average $\langle\ell^*(t)\rangle_{\Delta E^{-}(t')}$ can be computed by using the nonequilibrium ensemble techniques developed in section 3 and the static average $\langle...\rangle_{\in}$ can be expressed in terms of the probability density $p_{\in}(\in) \, d\in$ of the adsorption energy:

$$\langle...\rangle_{\in} = \int \cdots p_{\in}(\in) \, d\in \quad (126)$$

As pointed out by a referee, for complex processes, the average concentrations or survival functions do not contain enough information for the determination of the kinetic parameters of the process. In some cases the evaluation of the statistical properties of the lifetime of a species provides the necessary information for determining the kinetics and mechanism of the process. In the following we compute the probability density of the lifetime τ of the species on the surface.

We introduce a joint density function for the adsorption heat and the trapping time:

$$\sigma(\tau,\in) \, d\tau \, d\in \quad \text{with} \quad c(\in) \, d\in = d\in \int \sigma(\tau,\in) \, d\tau \quad (127)$$

Here $\sigma(\tau,\in) \, d\tau \, d\in$ is the surface concentration of occupied sites with an adsorption energy between $\in$ and $\in + d\in$ and which have trapped a molecule for a time interval between τ and $\tau + d\tau$. The density function can be computed from the balance equations

$$\left(\frac{\partial}{\partial t} + \frac{\partial}{\partial \tau}\right)\sigma(\tau,\in) = -\sigma(\tau,\in)k_{\text{local}}^{-}(t) \quad (128)$$

$$\sigma(\tau = 0, \in) = \rho k_{\text{local}}^{+}(t)(1 - \theta_{\text{local}}(\in))g(\in) \quad (129)$$

In terms of the density function $\sigma(\tau,\in)d\tau \, d\in$, we can compute the conditional probability density

$$\varphi(\tau|\in;E^{-}(t')) \, d\tau = \frac{\sigma(\tau,\in) \, d\tau}{\int \sigma(\tau,\in) \, d\tau} \quad \text{with} \int \varphi(\tau|\in,E^{-}(t')) \, d\tau = 1 \quad (130)$$

of the trapping time corresponding for a given value of the adsorption energy. Finally, the unconditional probability density of the trapping times can be evaluated by averaging over all possible values of the adsorption energy and of the activation energy $E^{-}(t')$ of the desorption process:

$$\varphi(\tau) \, d\tau = d\tau \int \langle\varphi(\tau|\in;E^{-}(t'))\rangle_{\Delta E^{-}}(t')p_{\in}(\in) \, d\in = \langle\langle\varphi(\tau|\in;E^{-}(t'))\rangle_{\Delta E^{-}}(t')\rangle_{\in} \quad (131)$$

with $\int\varphi(\tau) \, d\tau = 1$.

In conclusion, in this section we have shown that the nonequilibrium ensemble approach can be easily extended to reversible chemical reactions involving a forward and backward step. For illustration we considered the case of adsorption kinetics on a heterogeneous surface. The obtained results are used in the following section for analyzing an experiment on desorption kinetics.[20]

7. Interpretation of Desorption Experiments by Drazer and Zanette

In their experiments, Drazer and Zanette[20] used nonconsolidated packings of relatively uniform, spherical, activated carbon grains obtained from apricot pits, with an average radius of $d = (0.13 \pm 0.01)$ cm. The carbon grains were packed in a 30 cm high, 2.54 cm inner diameter cylinder. In the experiments, the porous medium is initially filled up with aqueous 0.1M NaI solution tagged with I.[131] These authors carried out desorption experiments where the untagged NaI solution was replaced by distilled water and showed that for large times the concentration profiles of I[131] decrease slowly to zero according to a negative power law,

$$\rho(t) \sim t^{-\mu}, t \gg 0, \mu = 0.63 \quad (132)$$

characterized by a fractal exponent $\mu = 0.63$. Drazer and Zanette have also shown that the adsorption equilibrium at low concentrations is described by a Freundlich adsorption isotherm

$$\theta \sim \rho^{\nu}, \rho \text{ small}, \nu = \mu = 0.63 \quad (133)$$

where θ is the surface coverage and $\nu = \mu = 0.63$. The

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experimental results of the authors suggest that the displacement of the radioactive isotope I^{131} involves a very slow, dispersive (Montroll) diffusion processs.[18] The qualitative physical picture suggested by the authors[20] is the following: the motion of an atom of the radioactive isotope along the column can be represented by a hopping mechanism involving a succession of desorption and readsoption processes, which is basically a random walk in continuous time.[18] According to Montroll's theory of dispersive difffusion,[18] such a continuous time random walk may lead to concentration profiles with long time tails of the negative power law type if the probability density of the trapping time of the radioactive isotope in the adsorbed state on the surface has a long time tail.

In a previous article[21] we came up with a theoretical interpretation of Drazer and Zanette's experiment, based on the random activation energy model and on the assumption that the adsorption and desorption activation energies are related to each other through a linear free energy relation. In the following we shall show that, within the framework of the nonequilibrium ensemble approach developed in this article, the existence of a linear free energy relation between the adsorption and desorption activation energies is not necessary for explaining the experimental results of Drazer and Zanette; however, the linear free energy relation is compatible with their results.

By assuming that the generation of a concentration profile of the type $\rho(t) \sim t^{-\mu}$, $t \gg 0$, is due to a CTRW motion, it can be shown that the probability density of the lifetime of a molecule on the surface also has a long tail of the type[22]

$$\varphi(\tau) \sim \tau^{-(1+\mu)}, \tau \gg 0 \qquad (134)$$

Now we can apply the results derived in section 6 to the experiments of Drazer and Zanette. Although the whole column is in a nonequilibrium state, it is reasonable to assume that at each section of the column there is a local stationary state. By assuming static disorder, the stationary solutions of eqs 128 and 129 are given by

$$\sigma(\tau, \in) = \rho k_{\text{local}}^+(t)(1 - \theta_{\text{local}}(\in))g(\in) \times$$
$$\exp[-\tau k_{\text{local}}^-(E_0^-)\chi(\Delta E^-)] \quad (135)$$

where the transperance factor $\chi(\Delta E^-)$ is given by eq 123, applied to static disorder. By inserting eq 135 into eqs 130−131 we obtain

$$\varphi(\tau)d\tau = d\tau \int k_{\text{local}}^-(E_0^-)\chi(\Delta E^-) \times$$
$$\exp[-\tau k_{\text{local}}^-(E_0^-)\chi(\Delta E^-)]p_{\Delta E^-}(\Delta E^-)d\Delta E^- = -d\tau \frac{\partial}{\partial\tau}\prime^*(\tau) \quad (136)$$

where

$$\prime^*(\tau) = \int \exp[-\tau k_{\text{local}}^-(E_0^-)\chi(\Delta E^-)]p_{\Delta E^-}(\Delta E^-) \, d\Delta E^- \quad (137)$$

is an apparent survival function. We notice that eq 137 has the same structure as eq 6 from section 1. This analogy suggests that, if the probability density $p_{\Delta E^-}(\Delta E^-)$ of the random component of the desorption activation energy is of the Maxwell−Boltzmann type,

$$p_{\Delta E^-}(\Delta E^-)d\Delta E^- = \mu(k_B T)^{-1}\exp[-\Delta E^-\mu/(k_B T)]d\Delta E^- \quad (138)$$

then $\prime^*(\tau)$ and thus $\varphi(\tau)$ have long tails of the negative power law type. If we carry out the computations we come to

$$\varphi(\tau) = \frac{\mu\gamma(\mu + 1, k_{\text{local}}^-(E_0^-)\tau)}{[k_{\text{local}}^-(E_0^-)]^\mu \tau^{\mu+1}} \sim \frac{\mu\Gamma(\mu + 1)}{[k_{\text{local}}^-(E_0^-)]^\mu \tau^{\mu+1}}$$
$$\text{for } \tau \gg 1/k_{\text{local}}^- \quad (139)$$

a result which is consistent with the experiments of Drazer and Zanette.

Similarly, we can recover the Freundlich adsorption isotherm (eq 133) observed experimentally by Drazer and Zanette by applying eq 123 for large times, $t \to \infty$:

$$\theta = \int \theta_{\text{local}}^{\text{equil}}(\in, T)p_\in(\in)d\in = \int \frac{K_{\text{local}}(\in)\rho}{1 + K_{\text{local}}(\in)\rho}p_\in(\in)d\in \quad (140)$$

Equation 140 is a standard expression for the total coverage on a on a nonuniform surface,[23−24] which has been extensively studied in the literature. If the probability density $p_\in(\in)$ of the adsorption energy is also given by a Maxwell−Boltzmann distribution, then, in the limit of small concentrations, $\rho \to 0$ eq 140 leads to the Freundlich adsorption isotherm, eq 133. For consistency with our formalism, we express the adsorption energy $\in$ as the sum of a constant component $\in_0$ and a random component $\Delta\in$, which obeys a Maxwell−Boltzmann $p_{\Delta\in}(\Delta\in)$-$d\Delta\in$ distribution and varies between zero and infinity:

$$\in = \in_0 + \Delta\in \quad (141)$$

$$p_{\Delta\in}(\Delta\in)d\Delta\in = \nu(k_B T)^{-1}\exp[-\Delta\in\nu/(k_B T)]d\Delta\in \quad (142)$$

We insert eqs 141−142 into eq 140 and express the integral in terms of Eulerian beta functions.[21,24] The resulting expression makes it possible to evaluate the total coverage in the limit of small concentrations (see also eq 31 from ref 21):

$$\theta \sim (\rho K_{\text{local}}(\in_0))^\nu \frac{\pi\nu}{\sin(\pi\nu)} \quad \text{as } \rho \to 0 \quad (143)$$

Equation 143 is a Freundlich isotherm compatible with the experimental data of Drazer and Zanette.

In conclusion, our approach has shown that the experimental data of Drazer and Zanette can be described by assuming that the probability densities of the random components of the desorption activation energy and of the adsorption energy are described by the same Maxwell Boltzmann distribution, eqs 138 and 143, where $\nu = \mu = 0.63$. Unlike the case of our previous analysis of these experiments,[21] no linear free energy relations are necessary for data analysis.

To clarify the possible connections between our approach and linear free energy relations, we mention that the linear free energy relations from ref 21, compatible with the experimental data of Drazer and Zanette, are (see also Appendix E):

$$E^+ = \text{constant}, E^- = \in + \text{constant} \quad (144)$$

or, in terms of the random components ΔE^+, ΔE^-, and $\Delta\in$

$$\Delta E^+ = 0, \Delta E^- = \Delta\in \quad (145)$$

Note that the linear free energy relations (eqs 144, 145) imply that the probability densities for ΔE^- and $\Delta\in$ are identical; however, the reverse is not true. A brief analysis of the relationships between our approach and the linear free energy relations is presented in Appendix E. Linear free energy relations represent an extreme case of collective behavior, where a number of random variables are related to each other through
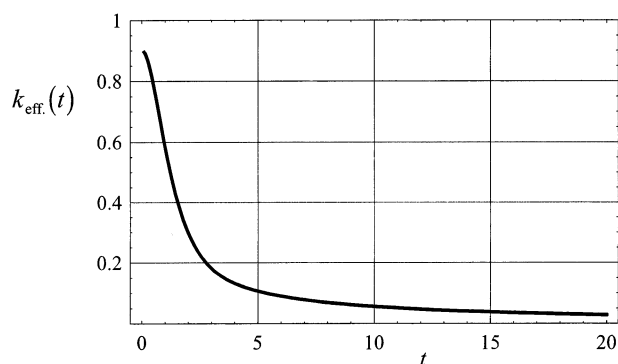
Random Activation Energy Model and Disordered Kinetics

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Figure 1. Typical plot of the effective decay rate $k_{eff}(t)$ as a function of time t for systems with static disorder. For large times $k_{eff}(t)$ tends toward zero hyperbolically (eqs 10 and 146).

a set of deterministic relations. It is generally accepted that such a strong collective behavior exists in heterogeneous catalysis. For other disordered kinetic systems a moderate collective behavior can be represented by joint probability densities of activation energies.

8. Extraction of Information from Experimental Data

The quantitative description disordered kinetics is a complicated problem. The general theory developed in this article has shown that different types of asymptotic behavior may emerge. Unfortunately, these asymptotic results cannot describe the whole time range of an experiment in disordered kinetics. For this reason we have focused on the qualitative analysis of the implications of our theory in the analysis of experimental data of disordered kinetics. Starting from our theory we have generated numerically a large number of kinetic curves and tried to identify the patterns which emerge due to different types of disorder. We examined regular ($\langle \ell(t) \rangle$ versus t), semilogarithmic (log $\langle \ell(t) \rangle$ versus t), as well as logarithmic (log $\langle \ell(t) \rangle$ versus log t), plots of the survival function as well as plots of the effective decay rate

$$k_{eff}(t) = -\frac{\partial}{\partial t}\ln\langle \ell(t) \rangle \qquad (146)$$

versus time t. The calculations were based both on the general equations derived in section 4 as well as on the renewal model from section 5. We have reached the following conclusions.

In most cases the examination of the plots of the effective decay rate versus time is more useful than the examination of the plots involving the survival function. A typical plot of the effective decay rate for static disorder as a function of time is displayed in Figure 1. For a system with static disorder, the effective decay rate tends hyperbolically to zero for large times. For a system with dynamic disorder with short memory, the effective decay rate decreases slower than in the case of static disorder (Figure 2), and for large times the effective decay rate tends toward a positive value, which expresses the contribution of the fluctuations of the energy barriers to the kinetics of the process. The presence of such a positive asymptotic value indicates the presence of dynamic disorder. This type of asymptotic behavior is characteristic for all types of dynamic disorder with short memory: exponential decay, independent Zubarev−McLennan fluctuations or multiplicative white noise. If the only experimental observable available is the average survival function, these types of dynamic disorder with short memory are indistinguishable.

The presence of dynamic disorder with long memory is much harder to identify, both in the case of correlations with long
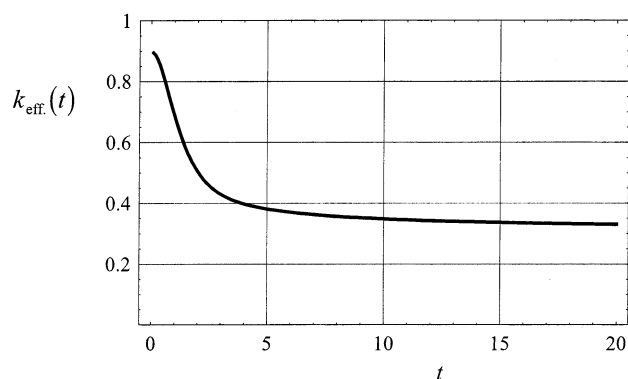

Figure 2. Typical plot of the effective decay rate $k_{eff}(t)$ as a function of time t for systems with dynamic disorder with short memory. For large times $k_{eff}(t)$ tends toward a positive value, which expresses the contribution of the dynamic fluctuations of the energy barrier to the kinetics of the process (eqs 60 and 146).
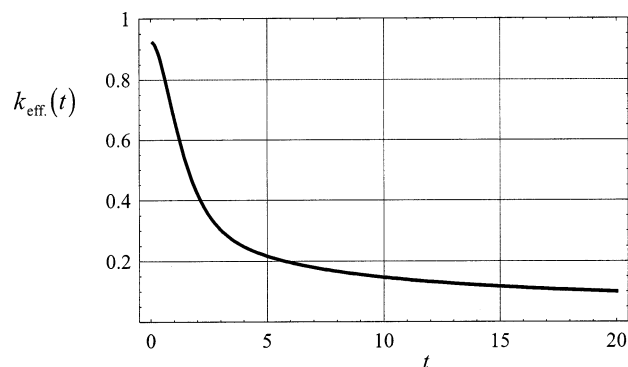

Figure 3. Typical plot of the effective decay rate $k_{eff}(t)$ as a function of time t for renewal systems with dynamic disorder with long memory. For large times, $k_{eff}(t)$ tends toward zero with a rate which is smaller than in the case of static disorder. The plot has the same qualitative features as the corresponding curve for static disorder (eqs 91 and 146).

tails and in the case of renewal processes. Figure 3 displays the time dependence of the effective decay rate for a renewal system with long memory. The plot has the same qualitative shape as the case of static disorder (Figure 1). For large times, the effective decay rate approaches the asymptotic value zero; compared to a system with static disorder the rate is approaching the asymptotic value zero with a slower rate. In general it is not possible to identify dynamic disorder with long memory from the qualitative analysis of the $k_{eff}(t)$ versus t plots.

The plots involving the survival function are not very useful for identifying the dynamic disorder with short memory. The main difficulty is that for short memory it is not possible to see both fingerprints of static and dynamic disorder in a single plot, two different types of plots, (log $\langle \ell(t) \rangle$ versus t), as well as (log $\langle \ell(t) \rangle$ versus log t), need to be used simultaneously. However, the dynamic disorder with long memory is easier to identify from these types of plots. The typical log $\langle \ell(t) \rangle$ versus log t plot for renewal systems with long memory is displayed in Figure 4. The first straight line is produced by static disorder, whereas the second one is the result of interference of the static disorder with the dynamic disorder. The presence of two different straight lines in a log $\langle \ell(t) \rangle$ versus log t plot signals the existence of dynamic disorder with long memory. Since this procedure involves a log−log plot, the experimental data needs to be accurate.

Once the type of disorder is determined from the analysis of the plots, some of the kinetic parameters of the process can be evaluated from the asymptotic laws derived in sections 4 and 5.
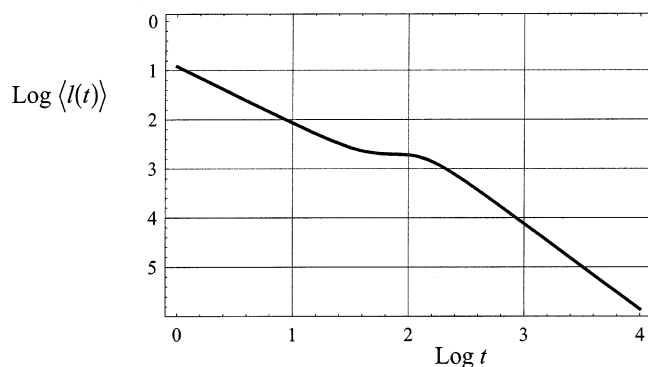
Figure 4. Typical plot of the logarithm of the average survival function, $\log \langle l(t) \rangle$ as a function of the logarithm of time, $\log t$, for renewal systems with dynamic disorder with long memory. The first straight line is the result of static disorder and the second straight line is the result of interaction between static and dynamic disorder. To display both straight lines, the graph should cover many orders of magnitude of the time variable (eqs 9, 98, 107).

For simplicity in most of this paper we restricted ourselves to the study of first order, irreversible rate processes. Much of the results derived in this paper can be easily extended for simple, nonlinear irreversible or reversible processes. Work on this problem is in progress.

9. Implications in Biochemistry and Genetics

Many complex reaction networks in biochemistry are sparsely connected; that is, only a small fraction of all possible connections among the chemical species present in the system actually exist in the system. A number of numerical alogrithms presented in the literature[25] take advantage of the sparse structure of large reaction networks.

The nonequilibrium ensemble approach developed in this article may serve as a basis for the statistical description of large biochemical networks with a sparse structure. It is possible to develop a statistical description of large reaction networks somewhat similar to random matrix theory from nuclear physics. Instead of describing a reaction network in terms of individual connections and rate coefficients, we consider statistical distributions of these parameters and study their statistical properties. The typical experimental input values for such studies are microarray data.[26] Our preliminary studies show that at least two different types of universal scaling laws emerge for large networks with sparse connection. These scaling laws show that the essential interactions in a sparse network can be described in a hierarchical way: there are clusters of nodes, which can be grouped into clusters of clusters and so on. We intend to continue this investigation and to explore the possible existence of other scaling laws.

The ultimate purpose of this research is to suggest suitable reaction mechanisms compatible with experimental data, more than to obtain laws for the statistical distribution of kinetic parameters. The statistical distribution can be used as a starting point for the derivation of suitable reaction mechanisms. The simplest application is the derivation of suitable reaction mechanisms for a small portion of a large reaction network. The first step of the analysis is the extraction from experimental data of statistical distribution laws for the whole network. The next step is to consider the interaction between the sub-network we are interested in and the rest of the network in a way similar with the system-thermostat interaction in statistical mechanics. The rest of the network is described statistically whereas properties of the sub-network we are interested in can be

obtained by applying suitable optimization algorithms. Work on this problem is in progress.

A biological application of the ensemble approach is related to the study of the influence of random drift on the geographical distribution of various mutations in human populations.[27–28] The purpose of this project is the elaboration of methods for evaluating the original position and original time of a mutation from the current geographical distribution of a mutation.[27] The method involves a combination of the nonequilibrium ensemble method with a generalization of the fundamental Fisher's theorem of natural selection,[28] which describes the combined effect of selection, mutations, and random drift on evolution. Another genetic application of the nonequilibrium ensemble method is the description of large gene regulation networks.

Appendix A

Equation 36 leads to

$$
\langle l(t) \rangle = \lim_{u \to \infty, \forall \Delta t_u \to 0} \prod_u \left\{ \int_0^\infty \exp\left\{ -k_0(T)\exp\left[-\frac{\Delta E(t_u)}{k_B T} \right] \Delta t_u - \right.\right.
$$
$$
\left.\left. \frac{\Delta E(t_u)}{\langle \Delta E(t_u) \rangle} \right\} \frac{\mathrm{d}\Delta E(t_u)}{\langle \Delta E(t_u) \rangle} \right\} =
$$
$$
\lim_{u \to \infty, \forall \Delta t_u \to 0} \prod_u \left\{ \frac{k_B T \gamma[k_B T/\langle \Delta E(t_u) \rangle, k_0(T)\Delta t_u]}{\langle \Delta E(t_u) \rangle [k_0(T)\Delta t_u]^{k_B T/\langle \Delta E(t_u) \rangle}} \right\} \quad (A.1)
$$

To evaluate the continuous limit of the product in eq A.1, we introduce the phase factor

$$
\Phi = -\ln\left\{ \prod_u \left\{ \frac{k_B T \gamma[k_B T/\langle \Delta E(t_u) \rangle, k_0(T)\Delta t_u]}{\langle \Delta E(t_u) \rangle [k_0(T)\Delta t_u]^{k_B T/\langle \Delta E(t_u) \rangle}} \right\} \right\} \quad (A.2)
$$

and evaluate it in the limit $\forall \Delta t_u \to 0$. By using the following expansion of the incomplete gamma function

$$
\gamma(a,x) = x^a \exp(-x) \sum_{n=0}^\infty \frac{\Gamma(a)}{\Gamma(a+n+1)} x^n \quad a,x > 0 \quad (A.3)
$$

we come to

$$
\Phi = k_0(T) \sum_u \Delta t_u \left[\frac{k_B T}{\langle \Delta E(t_u) \rangle + k_B T} \right] + \mathcal{O}[(\Delta t_u)^2] \quad (A.4)
$$

In the continuous limit, the average survival function can be expressed as

$$
\langle l(t) \rangle = \lim_{u \to \infty, \forall \Delta t_u \to 0} \exp(-\Phi) \quad (A.5)
$$

By combining eqs A.4 and A.5 we obtain eq 37.

Appendix B

By using eqs 30 and 38 we can compute the characteristic functional of the rate coefficient, $\mathcal{G}_k[\zeta(t')]$, in terms of $\eta(\Delta E; t_u)$. We obtain

$$\mathscr{G}_k[\zeta(t')] = \lim_{\forall \Delta t_u \to 0} \prod_u \{\int \exp\{i\zeta(t')k_0(T)\chi(\Delta E(t_u))\Delta t_u\} \times$$
$$\eta(\Delta E(t_u);t_u)\, d\Delta E(t_u)\} \quad (B.1)$$

We introduce the probability density of the total rate coefficient k at time t_u:

$$p(k;t_u)\, dk \quad \text{with} \int p(k;t_u)\, dk = 1 \quad (B.2)$$

and its characteristic function

$$G_k(\rho_u;t_u) = \int \exp(i\rho_u k)p(k;t_u)\, dk \quad (B.3)$$

where ρ_u is the Fourier variable conjugated to the rate coefficient k at time t_u. We have

$$p(k;t_u)\, dk =$$
$$dk \int \delta\{k_0(T)\chi(\Delta E(t_u)) - k\}\eta(\Delta E(t_u);t_u)\, d\Delta E(t_u)$$
$$= \begin{cases} k_B T \eta\left[k_B T \ln\left(\dfrac{k_0(T)}{k}\right);t_u\right]\dfrac{dk}{k} & \text{for } k \le k_0(T) \\ 0 & \text{for } k \ge k_0(T) \end{cases} \quad (B.4)$$

(see also eq 12, valid for static disorder) and

$$G_k(\rho_u;t_u) = \int \exp\{i\rho_u k_0(T)\chi(\Delta E)\Delta t_u\}\eta(\Delta E;t_u)\, d\Delta E \quad (B.5)$$

By combining eqs B.1–B.5 we come to

$$\mathscr{G}_k[\zeta(t')] = \lim_{\forall \Delta t_u \to 0} \prod_u \{G_k(\zeta(t_u)\Delta t_u;t_u)\} \quad (B.6)$$

Now we impose the restriction that the cumulants $\langle\langle k^m(t_u)\rangle\rangle$ of the total rate coefficient exist and are finite. It follows that the characteristic functions $G_k(\rho_u;t_u)$ can be represented by cumulant expansions

$$G_k(\rho_u;t_u) = \exp\left\{\sum_{m=1}^{\infty}\frac{1}{m!}[i\rho_u]^m\langle\langle k^m(t_u)\rangle\rangle\right\} \quad (B.7)$$

For evaluating the continuous limit in eq B.6 we introduce the phase factor

$$\Psi = i\ln\{\mathscr{G}_k[\zeta(t')]\} = i\sum_u \ln G_k(\zeta(t_u)\Delta t_u;t_u) \quad (B.8)$$

and evaluate it by using the cumulant expansions (B.7). We have

$$\Psi = i\sum_u \zeta(t_u)\langle\langle k(t_u)\rangle\rangle\Delta t_u + [(\Delta t_u)^2] \quad (B.9)$$

and therefore

$$\mathscr{G}_k[\zeta(t')] = \lim_{\forall \Delta t_u \to 0}\exp(i\Psi) = \exp\{i\int_{t_0}^t \zeta(t')\langle\langle k(t')\rangle\rangle\, dt'\} \quad (B.10)$$

We insert eq B.10 into eq 31, resulting in eq 39.

Appendix C

From eqs 18 and 30 it follows that for the static RAE model the generating functional of the rate coefficient is

$$\mathscr{G}_k[\zeta(t')] = \lim_{\forall \Delta t_u \to 0}\{\int \eta(\Delta E(t_0))\, d\Delta E(t_0) \times$$
$$\exp[ik_0(T)\chi(\Delta E(t_0))\sum_u \zeta(t_u)\Delta t_u]\} = \int \eta(\Delta E(t_0))\, d\Delta E(t_0) \times$$
$$\exp[ik_0(T)\chi(\Delta E(t_0))\int_{t_0}^t \zeta(t')\, dt'] \quad (C.1)$$

and thus

$$\mathscr{G}_k[\zeta(t')] = G_k(\int_{t_0}^t \zeta(t')\, dt') \quad (C.2)$$

where

$$G_k(\rho) = \int \exp\{i\rho k_0(T)\chi(\Delta E)\}\eta(\Delta E)\, d\Delta E =$$
$$\int \exp\{i\rho k\}p(k)\, dk \quad (C.3)$$

is the generating function of the probability density $p(k)$ of the rate coefficient (see also eqs 11, 12, and B.6–B.7) and ρ is the Fourier variable conjugated to the rate coefficient k. Now we assume that all moments and cumulants of the rate coefficient exist and are finite (it is easy to check that this is true in the case of Maxwell−Boltzmann energy barriers). We perform moments and cumulant expansions of both sides of eq C.2, resulting in

$$1 + \sum_{m=1}^{\infty}\frac{i^m}{m!}\int_{t_0}^t \cdots \int_{t_0}^t \langle k^m(t_0)\rangle\zeta(t_1')...\zeta(t_m')\, dt_1'...dt_m'$$
$$= 1 + \sum_{m=1}^{\infty}\frac{i^m}{m!}\int_{t_0}^t \cdots \int_{t_0}^t \langle k(t_1')...k(t_m')\rangle\zeta(t_1')...\zeta(t_m')\, dt_1'...dt_m' \quad (C.4)$$

and

$$\exp\left[\sum_{m=1}^{\infty}\frac{i^m}{m!}\int_{t_0}^t \cdots \int_{t_0}^t \langle\langle k^m(t_0)\rangle\rangle\zeta(t_1')...\zeta(t_m')\, dt_1'...dt_m'\right]$$
$$= \exp\left[\sum_{m=1}^{\infty}\frac{i^m}{m!}\int_{t_0}^t \cdots \int_{t_0}^t \langle\langle k(t_1')...k(t_m')\rangle\rangle\zeta(t_1')...\zeta(t_m')\, dt_1'...dt_m'\right]$$

From eqs C.3 and C.4 we come to eqs 49 and 50, respectively. By inserting eqs 50 into eq 43 we have

$$\langle \mathscr{I}(t)\rangle = \exp\left\{\sum_{m=1}^{\infty}\frac{(-1)^m}{m!}\langle\langle k^m(t_0)\rangle\rangle(t - t_0)^m\right\} = G_k(i(t - t_0)) \quad (C.5)$$

From eqs C.3 and C.5 we obtain eq 51.

Appendix D

Since we assume that the probability density $\eta(\Delta E)$ is time independent, we can assume without loss of generality, that $t_0 = 0$. The characteristic functional of the rate coefficient is

$$\mathscr{G}_k[\zeta(t')] = \overline{\int\int} \exp\{i\int_{t_0}^t \zeta(t')k_0(T)\chi(\Delta E(t'))\, dt'\} \times$$
$$\mathscr{P}_{\Delta E}[\Delta E(t')]\mathscr{D}_{\Delta E}[\Delta E(t')] = \lim_{\forall \Delta t_u \to 0}\sum_{m=0}^{\infty}\Theta_m \quad (D.1)$$

where

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$$\Theta_0 = \int d\Delta E_0 \eta(\Delta E_0) \exp\{i\zeta(0)k_0(T)\chi(\Delta E_0)\Delta t_0\}\Psi_0(t) \tag{D.2}$$

$$\Theta_1 = \int_0^t dt_1 \int\int \prod_{u=0}^1 [d\Delta E_u \eta(\Delta E_u)] \times$$
$$\exp\{i\sum_{u=0}^1 \zeta(t_u)k_0(T)\chi(\Delta E_u)\Delta t_u\}\psi_0(t_1)\Psi(t-t_1),..., \tag{D.3}$$

$$\Theta_m = \int_0^t dt_m...\int_0^{t_m} dt_2 \int_0^{t_2} dt_1 \int\cdots\int \prod_{u=0}^m [d\Delta E_u \eta(\Delta E_u)] \times$$
$$\exp\{i\sum_{u=0}^m \zeta(t_u)k_0(T)\chi(\Delta E_u)\Delta t_u\}\psi_0(t_1)\prod_{u=2}^m [\psi_u(t_u -$$
$$t_{u-1})]\Psi(t-t_m) \tag{D.4}$$

are contributions corresponding to different numbers of selection events and the functions $\Psi_0(\tau)$, $\Psi(\tau)$, are given by eqs 72.

The average survival function can be computed by combining eqs 31 and D.1−D.4:

$$\langle \ell(t) \rangle = \Psi_0(t) \int d\Delta E_0 \eta(\Delta E_0) \exp\{-tk_0(T)\chi(\Delta E_0)\} +$$
$$\int_0^t dt_1 \int\int \Psi_0(t-t_1)\psi(t_1)\prod_{u=0}^1 [d\Delta E_u \eta(\Delta E_u)] \times$$
$$\exp\{-k_0(T)[(t-t_1)\chi(\Delta E_1) + t_1\chi(\Delta E_0)]\} +$$
$$\sum_{m=2}^\infty \int_0^t dt_m...\int_0^{t_m} dt_2 \int_0^{t_2} dt_1 \int\cdots\int \psi_0(t_1)\prod_{u=2}^m [\psi_u(t_u -$$
$$t_{u-1})]\Psi(t-t_m)\prod_{u=0}^m [d\Delta E_u \eta(\Delta E_u)] \times \exp\{-k_0(T)[(t-$$
$$t_m)\chi(\Delta E_m) + \sum_{v=2}^m (t_v - t_{v-1})\chi(\Delta E_{v-1}) + t_1\chi(\Delta E_0)]\} \tag{D.5}$$

Although eq D.5 is rather complicated, its Laplace transform is easy to evaluate. We change the integration variables from ΔE_u to the corresponding rate coefficients k_u, notice that eq D.5 contains multiple nested convolution products and apply the Laplace transform, resulting in

$$\mathscr{L}\langle \ell(t) \rangle = \int dk_0 p(k_0)\bar{\Psi}_0(k_0 + s) + [\int dk_1 p(k_1)\bar{\Psi}(k_1 + s)] \times$$
$$[\int dk_0 p(k_0)\bar{\psi}_0(s + k_0)] + \sum_{m=2}^\infty [\int dk_m p(k_m)\bar{\Psi}(k_m + s)]\prod_{u=2}^m$$
$$[\int dk_{u-1} p(k_{u-1})\bar{\psi}(s + k_{u-1})][\int dk_0 p(k_0)\bar{\psi}_0(s + k_0)] \tag{D.6}$$

By evaluating the sum in eq D.6 we come to eq 73.

Appendix E

In this appendix we investigate the relations between the analysis of the experiments of Drazer and Zanette[20] presented in sections 6 and 7 and the analysis based on the use of linear free energy relations developed in ref 21. Following Drazer and Zanette, we assume that the system is with static disorder. The average coverage and lifetime distribution can be evaluated in terms of a joint probability density of the random components ΔE^+ and ΔE^- of the adsorption and desorption activation energies:

$$p_{\Delta E^\pm}(\Delta E^+, \Delta E^-) d\Delta E^+ d\Delta E^-, \text{ with } \int\int p_{\Delta E^\pm}$$
$$(\Delta E^+, \Delta E^-) d\Delta E^+ d\Delta E^- = 1 \tag{E.1}$$

For time-dependent processes, the average must be taken with respect to two random variables, such as ΔE^+ and ΔE^- or some other two transformed variables such as $\Delta\epsilon$ and ΔE^-. The assumption of local equilibrium leads to an important simplification: the total coverage depends only on $\Delta\epsilon$, whereas the lifetime distribution depends only on ΔE^-. For this reason, strictly speaking, the interpretation of the experiments of Drazer and Zanette can be done in terms of the marginal probabilities for $\Delta\epsilon$ and ΔE^-, and no linear free energy relations are needed. Nevertheless, the analysis of the implications of linear energy relations may provide useful information about the physics and chemistry of the process. The existence of the linear energy relations for adsorption kinetics has been well documented in the literature of heterogeneous catalysis, both experimentally and theoretically.[23] In the case of adsorption kinetics these relations are

$$\Delta E^\pm = -\beta^\pm \Delta\epsilon \tag{E.2}$$

where $\beta^\pm$ are scaling exponents (see also eqs 12 from ref 21). From eqs 114 and E.1 it follows that the scaling exponents are related to each other. We have

$$\beta^+ - \beta^- = 1 \tag{E.2}$$

Equations E.1 are deterministic relations among three random variables, $\Delta E^\pm$ and $\Delta\epsilon$. By taking eqs E.2 and E.3 into account, the joint probability density $p_{\Delta E^\pm}(\Delta E^+, \Delta E^-)^-$ can be expressed as

$$p_{\Delta E^\pm}(\Delta E^+, \Delta E^-) d\Delta E^+ d\Delta E^- =$$
$$d\Delta E^+ d\Delta E^- \int \delta\left(\Delta E^+ + \frac{\Delta\epsilon}{\beta^+}\right)\delta\left(\Delta E^- + \frac{\Delta\epsilon}{\beta^+ - 1}\right) \times$$
$$p_{\Delta\epsilon}(\Delta\epsilon) d\Delta\epsilon \tag{E.4}$$

In particular, if the probability density of the random component of the adsorption energy is given by the Maxwell−Boltzmann law (eq 142), we get the following expression for the marginal probability density of ΔE^-:

$$p_{\Delta E^-}(\Delta E^-) d\Delta E^- =$$
$$d\Delta E^- \int p_{\Delta\epsilon}(\Delta\epsilon)\delta\left(\Delta E^- + \frac{\Delta\epsilon}{\beta^+ - 1}\right) d\Delta\epsilon =$$
$$\frac{\nu}{(1 - \beta^+)k_B T} \exp\left[-\frac{\nu\Delta E^-}{(1 - \beta^+)k_B T}\right] \quad 1 - \beta^+ > 0 \tag{E.5}$$

The probability density of the lifetime corresponding to eq E.5 is given by

$$\varphi(\tau) =$$
$$\nu\tau^{-(1+\nu/1-\beta^+)}(k_{\text{local}}^-)^{-(\nu+\beta^+/1-\beta^+)}\gamma\left(\frac{1+\nu}{1-\beta^+}, \tau k_{\text{local}}^-\right) \sim$$
$$\nu\tau^{-(1+\nu/1-\beta^+)}(k_{\text{local}}^-)^{-(\nu+\beta^+/1-\beta^+)}\Gamma\left(\frac{1+\nu}{1-\beta^+}\right),$$
$$\text{for } \tau \gg 1/k_{\text{local}}^- \tag{E.6}$$

where

$$\frac{1-\nu}{2} > \beta^+ > -\nu \qquad (E.7)$$

By comparing eq E.6 with eq 134, it follows that, for the experimental data of Drazer and Zanette, we have

$$\beta^+ = 0, \beta^- = -1 \qquad (E.8)$$

By inserting eqs E.8 into eqs E.2, we obtain eqs 145.

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