

Final Technical Report
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THEORY AND EXPERIMENTS ON CHEMICAL INSTABILITIES

by

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I. Research accomplishments during the period March, 1994 to December 1996.

We have made extensive progress in the theory and experiments on nonlinear kinetics; on studies of complex reaction mechanisms, including systematic approaches to their determination from measurements; and have written a review on propagating and stationary patterns in reaction-transport systems.

A. Theory and Experiments on Nonlinear Kinetics

1. Experimental stabilization of unstable steady states in oscillatory and excitable systems

A feedback method is used to stabilize unstable stationary states in experiments with the chlorite-iodide reaction. The unstable stationary states occur in oscillatory and excitable regions of constraint space. Stabilization of unstable steady states provides information about these states and may be of practical importance. An analytical study of a model mechanism of this reaction is consistent with the experiments. This feedback method does not create new stationary states but stabilizes unstable stationary states present in the autonomous system. Unlike "thermostat" type methods, knowledge of the exact location of the unstable stationary states of the autonomous system is not required to implement this feedback method. Published in the J. Phys. Chem. (308).

2. Stabilization of unstable spatial structures in an optically bistable system

We stabilize the unstable steady state of a spatially inhomogeneous optically bistable ZnSe interference filter and measure the average intensity of the light transmitted and reflected by the filter. We also image the spatial structures which are the stable and unstable steady states by spatially resolving the transmitted light. We further measure relaxations from the unstable branch to the two stable branches. Relaxations to the low-temperature branch occur homogeneously while relaxations to the high-temperature branch occur by the propagation of a front. The results are in agreement with calculated predictions of a deterministic model of this system. A comparison is also made to nonlinear reaction-diffusion systems. Published in the J. Phys. Chem. (309).

3. Fluctuation-dissipation relations for chemical systems far from equilibrium

A new fluctuation-dissipation relation is suggested for constant step, one intermediate chemical processes far from equilibrium. It establishes a relationship between the net reaction rate $\dot{\tau}(x)$, the probability diffusion coefficient $D(x)$ in the composition space and the species-specific affinity $A(x)$: $\dot{\tau}(x) = 2D(x) \tanh(-A(x)/2kT)$, where x is the concentration of the active intermediate, k is Boltzmann's constant and T is the absolute temperature. The theory is valid for nonlinear fluctuations of arbitrary size. For macroscopic systems the fluctuation-dissipation relation may be viewed as a force-flux relationship. We distinguish four fluctuation-dissipation regimes which correspond to the decrease of the absolute value of the species-specific affinity. The passage from high $|A(x)|$ to small $|A(x)|$ corresponds to a crossover from a linear dependence of the species-specific dissipation rate $\dot{\phi}(x)$ on $|A(x)|$, $\dot{\phi}(x) \sim -|A(x)|$, to a square one $\dot{\phi}(x) \sim -A^2(x)$. A main feature of the fluctuation-dissipation relation is its symmetry with respect to the contributions of the forward and backward chemical processes to fluctuation and relaxation. Two new physical interpretations of the probability diffusion coefficient are given: one corresponds to a measure of the strength of fluctuations at a steady state, and the other to a measure of the instability of a given fluctuation state. The dispersion of the number q of reaction events in a given time interval is given by a generalized Einstein relation $\langle \Delta q^2 \rangle = 2VD(x)t$, where V is the volume of the system. The diffusion coefficient $D(x)$ is proportional to the reciprocal value of the mean age $\langle \tau(x) \rangle$ of a fluctuation state characterized by the concentration x : $D(x) = 1/(2V\langle \tau(x) \rangle)$. These

interpretations are not related to the use of a Fokker-Planck approximation of the chemical master equation. Published in the J. Chem. Phys. (314).

4. Thermodynamic and stochastic theory of nonequilibrium systems: Fluctuation probabilities and excess work.

For a nonequilibrium system described at the mesoscopic level by the master equation, we prove that the probability of fluctuations about a steady state is governed by a thermodynamic function, the "excess work." The theory applies to systems with one or more nonequilibrium steady states, for reactions in a compartment that contains intermediates X_j of variable concentration, along with a reactant A and product B whose concentrations are held constant by connection of the reaction chamber to external reservoirs. We use a known relation between the stationary solution $P_S(X)$ of the master equation and an underlying stochastic Hamiltonian H: to logarithmic accuracy, the potential that gives $P_S(X)$ is the stochastic action S evaluated along fluctuational trajectories, obtained by solving Hamilton's equations of motion starting at a steady state. We prove that the differential action dS equals a differential excess work $d\phi^\circ$, and show that $d\phi^\circ$ can be measured experimentally in terms of total free energy changes for the reaction compartment and the reservoirs. Thus we connect the probability of concentration fluctuations in an open reaction compartment to thermodynamic functions for the entire closed system containing the compartment. The excess work $d\phi^\circ$ is the difference between the total free energy change for a specified change in the quantities of A, X, Y, and B in the state of interest, and the free energy change for the same changes in species numbers, imposed on the same system in a reference state (A, X° , Y° , B). The reference-state concentration for species X_j is derived from the momentum p_j canonically conjugate to X_j along the fluctuational trajectory. For systems with linear rate laws, the reference state (A, X° , Y° , B) is the steady state, and ϕ° is equivalent to the deterministic excess work ϕ^*_{det} introduced in our previous work. For nonlinear systems, (A, X° , Y° , B) differs from the deterministic reference state (A, X^* , Y^* , B) in general, and $\phi^\circ \neq \phi^*_{\text{det}}$. If the species numbers change by ± 1 or 0 in each elementary step and if the overall reaction is a conversion $A \rightarrow X \rightarrow Y \rightarrow B$, the reference state (A, X° , Y° , B) is the steady state of a corresponding linear system, identified in this work. In each case, $d\phi^\circ$ is an exact differential. Along the fluctuational trajectory away from the steady state, $d\phi^\circ > 0$. Along the deterministic kinetic trajectory, $d\phi^\circ \leq 0$, and ϕ° is a Liapunov function. For two-variable systems linearized about a steady state, we establish a separate analytic relation between $P_S(X)$, ϕ^*_{det} , and a scaled temperature T^* . This work is a substantial advance beyond our earlier studies in this field since we identify a non-equilibrium thermodynamic potential, ϕ° , for multi-component systems. Published in the J. Chem. Phys. (321).

5. Thermodynamic and stochastic theory of nonequilibrium systems: A Lagrangian approach to fluctuations and relation to excess work

The dynamics of fluctuations in systems approaching a non-equilibrium steady state, with or without detailed balance, are investigated by means of a Lagrangian function, which is derived from the generator of time displacement (Hamiltonian) of the mesoscopic evolution equation. In the thermodynamic limit, the stationary probability distribution for the fluctuating variables is expressed in terms of the action of this stochastic Lagrangian along the fluctuational trajectory, the most probable path of infinite duration for the generation of a particular fluctuation away from the steady state. The fluctuational trajectory is related by a gauge-like transformation to the deterministic trajectory, which is the most

probable path for the relaxation of the macroscopic system to the steady state. This framework is applied to the analysis of one-variable chemical reactions modeled by a constant step master equation, and to two-variable systems in the linearized region around the steady state, where the fluctuations are described by a linear Fokker-Planck equation. In these examples, the thermodynamic significance of the action along the fluctuational trajectory is established by relating the irreversible (odd under time inversion) part of the Lagrangian and the time derivative of a deterministic excess work. Published in the J. Chem Phys. (322).

6. Entrainment, phase resetting, and quenching of chemical oscillations

We examine the effect of periodic and discrete perturbations on the phase of an oscillatory chemical reaction system near a Hopf bifurcation. Discrete perturbations reset the phase of the oscillation and periodic perturbations entrain the frequency of the oscillation for perturbation frequencies in a small range about each rational multiple of the natural frequency. These phase responses may be determined from time series of a single essential species. The new phase resulting from discrete perturbations and the relative phase between the oscillation and the forcing of an entrained oscillation are described by the same response function, which is a simple sinusoid. We show that for single species perturbations, the amplitude and phase offset of this response function equal the magnitude and the argument, respectively, of the corresponding component of the adjoint eigenvector of the Jacobi matrix (that corresponds to a pure imaginary eigenvalue). These phase response methods are simpler than quenching studies for determining the adjoint eigenvectors, and in addition yield the local isochrons of the periodic orbit. Published in the J. Chem. Phys. (334).

7. Lyapunov functions and relative stability in reaction-diffusion systems with multiple stationary states

In prior work on a thermodynamic and stochastic theory of chemical systems far from equilibrium, the excess work (a Lyapunov function) was shown to predict relative stability of stationary states in reaction-diffusion systems with multiple stationary states. This theory predicts equistability when the excess work from one stationary state to the stable inhomogeneous concentration profile separating the two stable stationary states equals the excess work from the other stable stationary state to that profile. Here we prove that any Lyapunov function of the deterministic reaction-diffusion equations of a given form can be used to predict equistability. Further, we show that the spatial derivative of any Lyapunov function for these equations, which is simpler to calculate, can also be used to predict relative stability. Published in the J. Phys. Chem. (342).

8. Fluctuations near limit cycles in chemical reaction systems

We investigate fluctuational properties near a limit cycle for a homogeneous chemical reaction system using a master equation approach. Our method of solution is based on the WKB expansion of the probability density in the inverse of the system size. The first two terms of this series give the leading asymptotic behavior. The eikonal equation for the leading order term has the structure of a Hamilton-Jacobi equation. Its solutions are determined by the associated characteristic equations, which also give fluctuational trajectories. In the vicinity of the limit cycle, the characteristic equations are the variational equations for the associated Hamiltonian system and its solutions may be expressed as linear combinations of Floquet eigenfunctions. These eigenfunctions fall into three sets according to whether the real part of the characteristic exponent is less than, equal to, or greater than zero. Eigenfunctions corresponding to characteristic exponents with real part less than zero span the stable subspace; they describe exponentially fast relaxation to the limit cycle in the deterministic system. Eigenfunctions corresponding to characteristic exponents with real part greater than zero span the unstable subspace; they describe most probable fluctuational trajectories away from the limit cycle. The remaining

two eigenfunctions are associated with a double zero characteristic exponent and span the center subspace. One is due to the translational invariance of the periodic orbit and the other (generalized eigenfunction) to the one-parameter family of periodic orbits in Hamiltonian systems. The generalized eigenfunction describes diffusion along the limit cycle of a probability distribution front for which the gradient is perpendicular to the isochrons of the limit cycle. We develop an explicit formula for the time evolution of an initially localized density based on all these eigenfunctions. We show that relaxation of the density is exponentially fast in directions transverse to the limit cycle and slow (linear in time) along the limit cycle. In addition, we give a simple formula for the probability diffusion coefficient that characterizes dephasing along the orbit. A formula for the stationary distribution is obtained from the non-stationary density by removing the center and stable subspace. For this density, we give a new derivation of an identity: the marginal probability density along the limit cycle equals a constant times the inverse of the speed on the cycle, which is the invariant density along the limit cycle of the deterministic system. Published in the *J. Chem Phys.* (344).

9. Rate statistics and thermodynamic analogies for relaxation processes in systems with static disorder. Application to stretched exponential

The paper deals with the relationships between the total rate of a relaxation process occurring in a system with static disorder and the decay rates attached to the different individual reaction channels. It is proven that the models of relaxation constructed on the basis of these two types of rates are equivalent to each other. From an experimentally observed relaxation curve it is possible to evaluate only the density of channels characterized by different relaxation rates and the overall probability distribution of the total relaxation rate. For evaluating the probability density of the individual relaxation rates attached to different channels an approach based on the maximum information entropy principle is suggested. A statistical thermodynamic formalism is developed for the relaxation time of a given channel, i.e., for the reciprocal value of the individual relaxation rate. The probability density of the relaxation time is proportional to the product of the density of channels to an exponentially decreasing function similar to the Boltzmann's factor in equilibrium statistical mechanics. The theory is applied to the particular case of stretched exponential relaxation for which the density of channels diverges to infinity in the limit of large relaxation times according to a power law. The extremal entropy of the system as well as the moments and the cumulants of the relaxation times and of the relaxation rates are evaluated analytically. The probability of fluctuations can be expressed by a relationship similar to the Greene-Callen generalization of Einstein's fluctuation formula. In the limit of large rates the density of channels and the probability density of individual rates have the same behavior: both functions have long tails of the negative power law type characterized by the same fractal exponents; for small rates, however, their behavior is different: the probability density tends to zero in the limit of very small rates whereas the density of channels displays an infrared divergence in the same region and tends to infinity. Although in the limit of small rates the density of channels is very large the probability of occurrence of these channels is very small; the compensation between these two opposite factors leads to the self-similar features displayed by the stretched exponential relaxation. The thermodynamic approach is compared with a model calculation for the problem of direct energy transfer in finite systems. The connections between stretched exponential relaxation and the thermal activation of the channels are also investigated. It is shown that stretched exponential relaxation corresponds to a distribution of negative and positive activation energies of the Gompertz type. Accepted for publication in the *J. Chem. Phys.* (347).

10. Stochastic approach to nonequilibrium chain reactions in disordered systems:
Breakdown of eikonal approximation

A stochastic description of chain reactions occurring in disordered systems is suggested by considering a statistical distribution of time-dependent rate coefficients. The possibilities of constructing a thermodynamic formalism for nonequilibrium chain reactions are investigated by testing the validity of the eikonal approximation in the thermodynamic limit. If the fluctuations of the rate coefficient are restricted to a finite range then for large systems the probability of concentration fluctuations obeys the eikonal scaling condition, which makes possible the development of a nonequilibrium thermodynamic formalism. For an infinite range of variation of the rate coefficient, however, the eikonal scaling does not hold anymore: the probability of concentration fluctuations has a long tail of the negative power law type and the system displays statistical fractal features. The passage from the stochastic eikonal behavior to the fractal scaling is characterized by a change in the deterministic kinetic equations of the process: in the eikonal regime the effective reaction order with respect to the active intermediate is one whereas for fractal scaling it is equal to two. Due to this change in the effective reaction order for fractal scaling the reaction is much faster than in the eikonal regime and the explosion threshold may be reached after a finite time interval. Accepted for publication in the International J. Thermophys. (348).

11. Deterministic and stochastic asymptotic behavior for nonequilibrium chemical systems with time-dependent rate coefficients

We analyze the long time limit of the nonequilibrium solutions of a system of multivariable nonlinear kinetic equations with time-dependent rate coefficients, as achieved, for example, by temporal variation of the temperature. If the characteristic time scale attached to the change of rate coefficients is smaller than the relaxation time to equilibrium, then the system is constrained to evolve away, possibly far from equilibrium. However, after a sufficiently large time the system forgets its past: in the long run all solutions of the kinetic equations tend towards a special (normal) solution which depends on the previous values of the rate coefficients but it is independent of the initial state of the system. The normal solution may be very different from the equilibrium solution. The occurrence of this type of time-dependent normal regime for the deterministic kinetic equations is intimately connected to a similar behavior of the stochastic evolution equation of the system. In the long run all solutions of the stochastic equation for the state probability also tend towards a normal form which is independent of the initial preparation of the system. The logarithm of the normal form of the state probability is a Lyapunov function of the system of deterministic kinetic equations and plays the role of a generalized thermodynamic potential which may be used for developing a thermodynamic description of the chemical process. A Gibbsian ensemble description is introduced in terms of a multi-replica stochastic master equation. The logarithm of the large time solution of the multi-replica stochastic master equation is also a Lyapunov function, one for the stochastic evolution equations of the system. A kinetic experiment is suggested for checking the existence of normal solutions for chemical systems with time-dependent rate coefficients.
To be submitted. (352).

12. Fluctuation dynamics, thermodynamic analogies and ergodic behavior for nonequilibrium independent rate processes with dynamical disorder

The stochastic properties of the sojourn times attached to a Markov process in continuous time and with a finite number of states are described by using a statistical ensemble approach. This approach is applied for investigating the large time behavior of independent rate processes with dynamical disorder. The large time behavior of the system is described in terms of an effective transport operator which can be expressed as a static average with respect to the stochastic properties of the sojourn times. The method is illustrated by a generalization of the Van den Broeck approach to the generalized Taylor diffusion. Explicit formulas for the effective transport coefficients and for the fluctuations of the concentration fields are derived. The results are used for extending the nonequilibrium generalized thermodynamic formalisms suggested by Keizer and by Ross, Hunt and Hunt, to systems with dynamical disorder. It is shown that the logarithm of the probability density functional concentration fluctuations is a Lyapunov functional of the effective transport equation. This Lyapunov functional plays the role of a generalized nonequilibrium thermodynamic potential which may serve as a basis for a thermodynamic description of the average behavior of the system. The existence and stability of a steady state can be expressed as an extremum condition for the Lyapunov functional. For Taylor diffusion in an external electric field different from zero the generalized potential has a structure similar to the Helmholtz free energy rather than to the entropy. A generalized chemical potential is derived as the functional derivative of the Lyapunov functional with respect to the concentration field; the gradient of this generalized chemical potential is the driving force which determines the structure of the effective transport equation. Submitted for publication in *Physica A*. (353).

13. Jump statistics, sojourn times, fluctuation dynamics and ergodic behavior for Markov processes in continuous time with a finite number of states

A general approach is introduced for describing the time evolution of a Markov process in continuous time and with a finite number of states. The total number of transition events from one state to other states and of the total sojourn times of the system in the different states are used as additional state variables. The large time behavior of these two types of stochastic state variables is investigated analytically by using a stochastic Liouville equation. It is shown that the cumulants of first and second order of the state variables increase asymptotically linearly in time. A set of scaled sojourn times is introduced which in the limit of large times have a Gaussian behavior. For long times the total average sojourn times are proportional to the stationary state probability of the process and, even though the relative fluctuations decrease to zero, the relative cross correlation functions tend towards finite values. The results are used for investigating the connections with Van Kampen's approach for investigating the ergodic properties of Markov processes. The theory may be applied for studying fluctuation dynamics in stochastic reaction diffusion systems and for computing effective rates and transport coefficients for nonequilibrium processes in systems with dynamical disorder. Submitted for publication in *Physica A*. (354).

B. Theoretical and Experimental Studies of Complex Reaction Mechanisms

1. Formulation of oscillatory reaction mechanisms by deduction from experiments

A number of experiments are reviewed and some new ones suggested for the deduction of information about the reaction mechanisms from the experiments. These studies include the characterization of oscillations, amplitude relations, phase relations, concentration shift regulation, concentration shift destabilization, qualitative and quantitative pulsed species responses, delay experiments, quenching, phase response experiments, among others. The deduction of the basic elements of oscillatory reaction mechanisms from such experiments is analyzed including the role of essential and

nonessential species in the reaction mechanism, connectivity of the essential species and the categorization of the oscillatory reaction mechanism. Published in Adv. Chem. Phys. (313).

2. New Measurements on the Chlorite-Iodide Reaction and Deduction of Roles of Species and Categorization

We present the results of new experiments on the chlorite-iodide reaction and use these results to determine the roles of various chemical species in the reaction mechanism. We simultaneously monitor three species, I^- , ClO_2^- , and I_2 , and determine the relative phases of oscillations in these species. We use perturbations in these species and the additional species $NaOCl$, IO_3^- , Cl^- , HIO_2 , and H_2OI^+ to perform qualitative pulsed-species response, concentration shift regulation, and concentration shift destabilization experiments. Within a scheme of categorization of oscillatory reaction mechanisms, we determine that the chlorite-iodide system is a category 1CX or 1CW oscillator. Further, we distinguish essential and nonessential species, and identify ClO_2^- as a type Z essential species, I^- as a type Y essential species, and $HOC1$ as an essential species of type X or W. HOI and HIO_2 are essential species whose roles we were unable to identify from these measurements. I_2 and IO_3^- are identified as nonessential species of type B, while Cl^- is a nonessential species of type C. Our assignments of the mechanistic roles of the essential species show complete agreement with those predicted by the Citri-Epstein mechanism. However, that model mechanism predicts that I_2 is a nonessential species of type C and that Cl^- is a nonessential species of type B. Published in the J. Phys. Chem. (327).

3. Further measurements on the oscillatory cool-flame oxidation of acetaldehyde and comparison with reaction mechanism models

Experimental and theoretical studies are reported on oscillatory cool flame oxidation of acetaldehyde by oxygen in a CSTR. Several experimental tests are designed to provide information about the reaction mechanism. The concentrations of acetaldehyde, oxygen, methane, methanol, carbon dioxide, water, hydrogen peroxide and formaldehyde are measured as a function of time with mass spectrometry. Relative amplitude of oscillation, relative phase of oscillation, and the regulation of several species in response to a step perturbation of either acetaldehyde or oxygen inflow are computed from the measurements of concentration. These quantities are calculated for two models of the acetaldehyde reaction. Measurements suggest the eight cited species are chemical "nonessential" variables (their concentrations can be individually fixed while other variables oscillate). Calculations indicate that the "essential" variables in each model are a short-lived chemical species and several radicals. Calculations present mixed evidence for whether gas temperature is essential or nonessential. The measurements of concentration shift regulation of the eight cited species, in response to step perturbations of acetaldehyde or oxygen inflow, and the calculations made with the two models agree except for the responses of carbon dioxide and water to a step perturbation of acetaldehyde inflow. The concentration shift regulation of nine variables for a step perturbation of the bath temperature is inferred from the literature. Calculations of concentration shift regulation for the first model show agreement for three variables and disagreement for four variables; calculations for the second model show agreement for six variables and disagreement for two variables. Measurements and calculations of the relative phases of oscillation between acetaldehyde, oxygen, methane, methanol, internal temperature, and hydroxyl radical agree. Both models are "category 2" oscillators. The "negative feedback" species is peracetic acid in the first model and methylhydroperoxide in the second. The "autocatalytic" species in both models are groups of radical intermediates. Published in the J. Phys. Chem. (336).

C. Propagating and Stationary Patterns in Reaction Transport Systems

1. The variety of origins, structures and occurrences of nonlinear waves in reaction-transport systems is reviewed. Generic mechanisms of wave and pattern development are shown to be closely associated with underlying mathematical structure such as multiplicity in steady-state behavior, chemical oscillations, small-amplitude instabilities, and inherent degeneracies such as occurs when several species behave similarly chemically. Cellular automata and adaptive gridding approaches to the analysis of waves and other patterns are contrasted. The types of phenomena that can occur in two and three spatial dimensions are noted to be spirals and rotors and static, periodic and aperiodic knotted structures. The influence of wave velocity, dispersion and curvature are discussed.

The electrical response and autonomous behavior of electrolyte systems is reviewed, as are applications in biological and geological systems. Published in *Advances in Porous Media*, Vol. 2, Chapter 2, 107, edited by M. Yavuz Corapcioglu (Elsevier, 1994). (295).

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