

Simple theory of relaxation from instabilities

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This paper gives a method for the study of relaxation at instabilities described by Langevin equations. The method uses backward-diffusion equations which are conditioned on the initial value of the dynamical variables, instead of the Fokker-Planck (forward) equation. By using the backward-diffusion equation, we obtain simple characterizations of relaxation properties such as the mean time to leave an observation region about the instability, the probability of reaching a preferred steady state, the mean time to reach it, and the rate of reaching it. Ensemble effects are included by averaging over the initial distribution. This kind of approach complements previous studies which were based on the Fokker-Planck equation. The interaction of noise, strength of the instability, and size of the observation region is studied. A number of examples are given (lasers, ferromagnets, classical molecular scattering, spontaneous optical resolution) and the methods developed here are applied to calculate properties of spontaneous optical resolution.

I. INTRODUCTION

The relaxation of physical, chemical, and biological systems from an unstable state received attention over the past few years (see, e.g., Suzuki's recent review article¹ for a summary of previous work). The essential ingredients of the problem are described as follows: By some means a system is prepared so that it is concentrated near an unstable steady state. [This can be accomplished by tuning some parameter appropriately (see below).] Since the state is unstable, any fluctuation will drive the system away from the initial state. In most cases, there is more than one stable steady state present and one asks which stable steady state does the system reach, how long does it take to get there, etc.? Fluctuations of any intensity cause the system to move from the unstable state, so the typical approach to these questions uses a combination of deterministic dynamics and fluctuations.

Most authors have relied on the Fokker-Planck equation.¹⁻⁸ The use of the Fokker-Planck equation proceeds as follows. An initial density $f_0(x)$, such that $f_0(x)dx$ is the probability of initially finding the system in $[x, x+dx]$, is given. The Fokker-Planck equation is used to characterize the density $f(x, t)$, defined so that $f(x, t)dx$ is the probability of finding the system in $[x, x+dx]$ at time t . One constructs a density $f(x, t)$ so that $f(x, t) \rightarrow f_0(x)$ as $t \rightarrow 0$. If $x_{s,i}$ denote the stable steady states of the system, then by observing $f(x_{s,i}, t)$ one gets an idea of how the system is relaxing toward the stable states. Unfortunately, a good deal of analysis is involved; since the initial density is not concentrated near $x_{s,i}$, local expansions about the stable states are ineffective.

The point of this paper is to introduce another approach which avoids some of these difficulties. This approach is based on *backward*-diffusion equa-

tions rather than the Fokker-Planck equation. For example, suppose $v(x, t)$ is the probability that the system has exited from some neighborhood of the unstable steady state going towards a specified stable state by time t , given that the system starts at x . The average of $v(x, t)$ against $f_0(x)$ gives a good idea of the relaxation of the system. This kind of approach complements the previous one and is somewhat simpler; together the two approaches give a firm theory for these phenomena.

We are interested in three parameters that characterize the system. The first, denoted by ϵ , is a measure of the intensity of the fluctuations. The second, denoted by β , is a measure of the strength of the instability. The third, denoted by L , is a measure of the *observation* scale. It characterizes the region around the unstable state where all the action is. Once the system leaves the region of size L , going towards a specified state the future evolution is clear, with probability close to one.

In the next section, we provide a number of physical examples of relaxation from instabilities. The classical optical (laser) examples are discussed first, followed by ferromagnets, spontaneous resolution of optical activity, and orbiting in molecule-ion molecule collisions. In Sec. III, we study the theory of relaxation in one dimension. After a description of the assumptions, we study the initial preparation of the system, the equilibrium distribution after the steady state becomes unstable, the mean relaxation times, and the rate of relaxation from the instability. These quantities are calculated by solving the *backward*-diffusion equations associated with the Langevin equations. The results of Sec. III are generalized to many dimensions in Sec. IV, where we consider laserlike and chemical-like instabilities. The results of Secs. III and IV are used in Sec. V to calculate properties of the spontaneous asymmetric synthesis models of Frank.

II. PHYSICAL EXAMPLES

We consider systems of moderate size that can be described by a continuous variable, assumed to satisfy a Langevin type of equation, where the noise may be multiplicative.

A. Lasers and nonlinear optics

Phenomena involving lasers provide many examples of the instabilities studied here; other kinds of optical instabilities are discussed in Graham's monograph.⁵ A simple model for the laser is the following.^{4,9,10} The field is represented by a vector $B(t) = (B_1(t), B_2(t))$, where $B_1(t)$ and $B_2(t)$ satisfy the Langevin equations

$$\frac{dB_i}{dt} = \beta B_i [d - (B_1^2 + B_2^2)] + (2q)^{1/2} \xi_i(t). \quad (2.1)$$

In this equation β and q are constants representing the properties of the laser and $\xi(t)$ is Gaussian white noise. The parameter d is a tunable parameter, representing the intensity of the pumping. If $d < 0$, the laser is below threshold. It is easy to see that $B(t) = 0$ is the only real steady state of (2.1) and it is stable. If one prepares a system with $d < 0$ and waits for a long enough time, the system will settle into a quasistationary distribution. This distribution is approximately Gaussian, with variance proportional to q . When $d = 0$ the laser is at threshold and when $d > 0$ the laser is above threshold. Above threshold, the origin is unstable and the system moves away from the origin. Further discussion of laser examples are found in^{4-7,9-11}

B. Ferromagnets

The following model of the mean-field ferromagnet^{12,13} also exhibits the kind of instability studied here. $X(t)$ is a continuous variable measuring the ordering of a magnet of N spins. When $X(t) = \pm 1$, the system is completely ordered; when $X(t) = 0$ the number of spins pointing up is equal to the number of spins pointing down. According to this model, $X(t)$ satisfies the Langevin equation

$$\frac{dX}{dt} = 2e^{\alpha/N} [\sinh(\alpha X + \delta) - X \cosh(\alpha X + \delta)] + [a(X)]^{1/2} \xi(t), \quad (2.2)$$

where

$$a(X) = \frac{1}{N} \left[(1 - X) \exp\left(\alpha X + \frac{\alpha}{N} + \delta\right) + (1 + X) \exp\left(-\alpha X + \frac{\alpha}{N} - \delta\right) \right]. \quad (2.3)$$

In these equations, α is proportional to the cou-

pling between spins and δ is proportional to the applied field. It is easy to show that as α switches from $\alpha < 1$ to $\alpha > 1$ for $\delta = 0$ the origin switches from a stable to an unstable state.^{12,13}

C. Spontaneous asymmetric synthesis

Frank¹⁴ proposed a model that describes the origin of optical activity in living systems. Extensions of this model form the basis of some models for morphogenesis¹⁵ and there is experimental evidence indicating that such resolutions are observable.¹⁶ Frank's model is summarized as follows. Let n_L and n_D represent the concentrations of a pair of enantiomers in a solution; thus if $n_L = n_D$ the system is racemic.

In the simplest model, we assume that n_L and n_D satisfy the Langevin equations

$$\begin{aligned} \frac{dn_L}{dt} &= n_L [(1 + \alpha) - \alpha n_D - n_L] \\ &\quad + [a_{1j}(n_L, n_D)]^{1/2} \xi_j(t), \\ \frac{dn_D}{dt} &= n_D [(1 + \alpha) - \alpha n_L - n_D] \\ &\quad + [a_{2j}(n_L, n_D)]^{1/2} \xi_j(t), \end{aligned} \quad (2.4)$$

with summation over j . The coefficients $a_{1j}(n_L, n_D)$ and $a_{2j}(n_L, n_D)$ can be determined by applying the birth-and-death formalism¹⁷ of chemical kinetics or Keizer's fluctuation dissipation postulates¹⁸ to give (also see Sec. V)

$$\begin{aligned} a_{11}(n_L, n_D) &= \frac{1}{V} n_L [(1 + \alpha) + n_L], \\ a_{12}(n_L, n_D) &= a_{21}(n_L, n_D) = \frac{1}{V} \alpha n_L n_D, \\ a_{22}(n_L, n_D) &= \frac{1}{V} n_D [(1 + \alpha) + n_D], \end{aligned} \quad (2.5)$$

where V is the size of the system.

Equations (2.4) have the following properties¹⁹: If $\alpha < 1$ the racemic state $n_D = n_L$ is stable. If $\alpha > 1$ the racemic state is unstable and the resolved states are stable.

D. Orbiting in molecule-molecule ion collisions

In Refs. 20 and 21, the collision of a molecule with a molecule ion is studied. In polar coordinates with the molecule at the center, $r(t)$ measuring molecule-to-molecule-ion distance and $\theta(t)$ measuring angle, classical scattering theory shows that

$$\begin{aligned} \frac{d}{dt} (r)^2 &= g \left(1 - \frac{b^2}{r^2} + \frac{Z\alpha e^2}{2r^4 E} \right), \\ \frac{d\theta}{dt} &= -\frac{gb}{r^2}. \end{aligned} \quad (2.6)$$

Here g is the initial velocity of the molecule ion, Z its valence, E its initial energy, α the polar-

izability of the molecule, and e is the electronic charge. The asymptotic center-to-center distance b is called the impact parameter. Set $b_c = (2Z\alpha e^2/E)^{1/4}$. If $b < b_c$, then the solution of (2.6) spirals into the origin; if $b > b_c$, then the solution of (2.6) approaches the origin and flies away on a hyperbolic trajectory. If $b = b_c$, the solution of (2.6) exhibits an unstable limit cycle, which is the instability. Quantum effects on the classical dynamics (2.6) can be studied by using Langevin equations

$$\begin{aligned} \frac{d}{dt} (R)^2 &= g \left(1 - \frac{b^2}{R^2} + \frac{Z\alpha e^2}{2R^4 E} \right) + \left(\frac{\hbar^2}{m} \right)^{1/2} \xi_1(t), \\ \frac{d}{dt} \theta &= -\frac{gb}{R^2} + \left(\frac{\hbar^2}{m} \right)^{1/2} \xi_2(t). \end{aligned} \quad (2.7)$$

Here \hbar is Planck's constant divided by 2π and m is the mass of the molecule ion.

III. THEORY OF RELAXATION IN ONE DIMENSION

In this section, we discuss the theory of relaxation in a one-dimensional system. The results derived here are exact and are used to motivate the approximate techniques used to study the relaxation in many dimensions.

In a recent paper,²² van Kampen studied some questions of relaxation from instabilities by Fokker-Planck methods. He finds it necessary to match various solutions of that equation. The procedure given here (especially Secs. III C–III F) avoids most of the difficulties he encountered.

A. Assumptions

$X(t)$ is the macrovariable describing the state of the system and is assumed to satisfy the Langevin equation

$$\frac{dX}{dt} = b(X, \alpha) + [\epsilon a(X, \alpha)]^{1/2} \xi(t). \quad (3.1)$$

In this equation, $\xi(t)$ is Gaussian white noise, or some approximation to it; ϵ is the reciprocal size of the system, we assume $\epsilon \ll 1$. In the absence of noise, $X(t)$ evolves according to $dX/dt = b(X, \alpha)$, where α is a parameter. We assume the following properties for $b(X, \alpha)$:

- (i) $X=0$ is a solution of $b(X, \alpha)=0$.
- (ii) If $\alpha < 0$, $b'(0, \alpha) < 0$ and $X=0$ is the only steady state.
- (iii) If $\alpha > 0$, $b'(0, \alpha) > 0$ and there are two other steady states $X_0 < 0 < X_1$ which are stable.

We define a potential $\Phi(X, \alpha)$ by

$$\Phi(x, \alpha) = \int^x b(s, \alpha) ds; \quad (3.2)$$

the potential is shown schematically in Fig. 1.

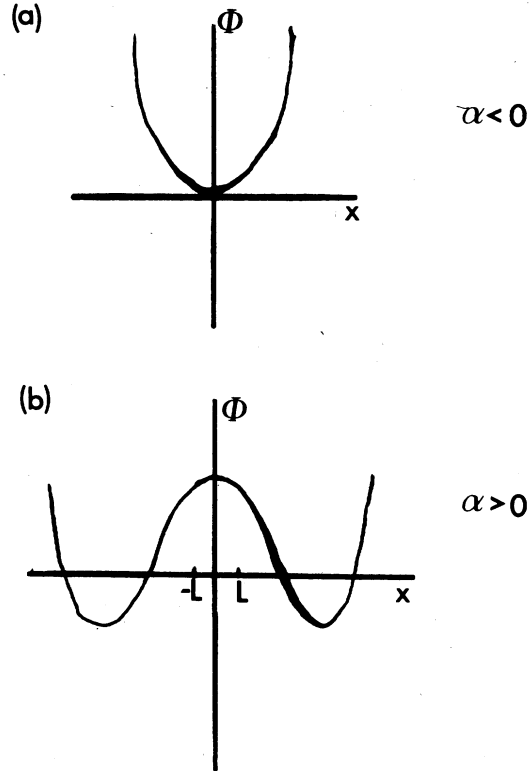


FIG. 1. Potential $\Phi(x)$ when the origin is stable (a) or unstable (b).

Our assumptions ensure that the potential is locally harmonic near $X=0$, thus critical type behavior does not occur^{13,19} (also see the Appendix here).

The functions $b(X, \alpha)$ and $\epsilon a(X, \alpha)$ are connected by the physical problem at hand. If $b(X, \alpha)$ represents the (scaled) mean of a single-step birth-and-death process, so that $b(X, \alpha) = b^+(X, \alpha) - b^-(X, \alpha)$, with $b^+(X, \alpha) > 0$, $b^-(X, \alpha) > 0$, then $a(X, \alpha) \propto b^+(X, \alpha) + b^-(X, \alpha)$.^{18,19} Otherwise, $b(X, \alpha)$ and $a(X, \alpha)$ need be connected by some kind of fluctuation formalism^{18,23} or limit theorem.²⁴

B. System preparation

We assume that at $t = -\infty$ the system is prepared with $\alpha < 0$. Thus, by time 0, the system is in a stationary, equilibrium distribution. This density $f_0(x)$ satisfies the Fokker-Planck equation.^{25,26}

$$\begin{aligned} 0 &= \frac{\epsilon}{2} \frac{\partial^2}{\partial x^2} [a(x, \alpha) f_0] \\ &\quad - \frac{\partial}{\partial x} \left[\left(b(x, \alpha) + \frac{\epsilon}{4} a'(x, \alpha) \right) f_0 \right]. \end{aligned} \quad (3.3)$$

In (3.3), $a'(x, \alpha) = (\partial/\partial x)[a(x, \alpha)]$ and we have used the Stratonovich interpretation of (3.1).

The solution of (3.3) is

$$f_0(x, \alpha) = \left(\frac{c}{a(x, \alpha)} \right) \times \exp \left[\int^x \frac{2}{\epsilon a(s, \alpha)} \left(b(s, \alpha) + \frac{\epsilon}{4} a'(s, \alpha) \right) ds \right]. \quad (3.4)$$

In (3.4), c is a normalization constant, assumed to be finite.²⁷ When ϵ is small, i.e., for moderately sized systems, the behavior of $f_0(x, \alpha)$ is asymptotically determined by the behavior of

$$\varphi(x, \alpha) = \int^x \frac{b(s, \alpha)}{a(s, \alpha)} ds. \quad (3.5)$$

The potential $\varphi(x, \alpha)$ has a critical point [$\varphi'(x, \alpha) = 0$] at $x=0$; set

$$-\gamma(\alpha) = \frac{1}{a(0, \alpha)} \frac{\partial}{\partial s} [b(s, \alpha)] \Big|_{s=0} \quad (3.6)$$

Then we find the leading order in ϵ ,

$$f_0(x, \alpha) \sim \frac{c}{a(0, \alpha)} \exp \left(-\frac{\gamma(\alpha)}{\epsilon} x^2 \right), \quad (3.7)$$

so that the system has a locally Gaussian density, with variance parameter $\epsilon/2\gamma(\alpha)$.

We assume that at $t=0$ the parameter α is switched from $\alpha < 0$ to $\alpha > 0$. The system, initially concentrated near $x=0$, will move toward X_0 or X_1 . Clearly, if in some sense $X(0) \gg \epsilon$ (a measure of the intensity of the noise), then $X(t) \rightarrow X_1$ with overwhelming odds; if $X(0) \ll -\epsilon$, $X(t) \rightarrow X_0$ with the same odds. The most interesting relaxation questions pertain to those points where $X(0) \approx 0$.

C. Equilibrium distribution

As $t \rightarrow \infty$, the system is concentrated near X_0 and X_1 . In order to estimate the fraction of systems near each stable state, we define

$$u(x, L, \alpha) = \text{Prob}\{X(t) \text{ exits } [-L, L] \text{ through } L | X(0) = x\}, \quad (3.8)$$

$$\frac{du(x)}{dL} \sim \frac{\exp\left(-\frac{b'(0)}{\epsilon a(0)} L^2\right)}{\int_{-L}^L \exp\left(-\frac{b'(0)}{\epsilon a(0)} s^2\right) ds} + \frac{-2 \int_{-L}^x \exp\left(-\frac{b'(0)}{\epsilon a(0)} s^2\right) ds}{\left[\int_{-L}^L \exp\left(-\frac{b'(0)}{\epsilon a(0)} s^2\right) ds \right]^2} \exp\left(-\frac{b'(0)}{\epsilon a(0)} L^2\right). \quad (3.13)$$

Rewriting the denominator as an integral from $-\infty$ to $+\infty$ minus twice an integral from L to ∞ gives

$$\frac{du(x)}{dL} \sim \exp\left(-\frac{b'(0)}{\epsilon a(0)} L^2\right) \left(\frac{b'(0)}{\pi \epsilon a(0)} \right)^{1/2} - 2 \exp\left(-\frac{b'(0)}{\epsilon a(0)} L^2\right) \int_{-L}^x \exp\left(-\frac{b'(0)}{\epsilon a(0)} s^2\right) ds \left(\frac{b'(0)}{\pi \epsilon a(0)} \right). \quad (3.14)$$

We conclude that if the observation scale $L \gg [\epsilon a(0)/b'(0)]^{1/2}$, then du/dL is exponentially small. Since the noise is small in systems of moderate size, as long as $b'(0) > 0$ the observation

We will study the dependence of $u(x, L, \alpha)$ on the observation scale L and this will show how to pick L . The equation that $u(x, L, \alpha)$ satisfies is a backward-diffusion equation since the conditioning is on $X(0)$; it is derived in a number of textbooks^{25, 26} and is

$$0 = \frac{\epsilon a(x, \alpha)}{2} \frac{\partial^2}{\partial x^2} u(x, L, \alpha) + \left(b(x, \alpha) + \frac{\epsilon}{4} a'(x, \alpha) \right) \frac{\partial}{\partial x} u(x, L, \alpha), \quad (3.9)$$

$$u(L, L, \alpha) = 1, \quad u(-L, L, \alpha) = 0. \quad (3.10)$$

In the sequel, we denote $a(x) = a(x, \alpha)$, $b(x) = b(x, \alpha)$, $u(x) = u(x, L, \alpha)$ for simplicity. The exact solution of (3.9) and (3.10) is

$$u(x) = \frac{\int_{-L}^x \exp\left(-\int^s \frac{2b(y)}{\epsilon a(y)} + \frac{a'(y)}{2a(y)} dy\right) ds}{\int_{-L}^L \exp\left(-\int^s \frac{2b(y)}{\epsilon a(y)} + \frac{a'(y)}{2a(y)} dy\right) ds}. \quad (3.11)$$

Since $b(0) = 0$ and $b'(0) > 0$, the main contribution to (3.11) comes from the origin. Hence we obtain the asymptotic result

$$u(x) \sim \frac{\int_{-L}^x \exp\left(-\frac{b'(0)}{\epsilon a(0)} s^2\right) ds}{\int_{-L}^L \exp\left(-\frac{b'(0)}{\epsilon a(0)} s^2\right) ds}. \quad (3.12)$$

When ϵ is small, there is an *internal boundary layer* around $x=0$ where $u(x)$ changes rapidly from zero to one. The width of this region is order $[\epsilon a(0)/b'(0)]^{1/2}$, so it decreases with increasing force of repulsion and increases with increasing intensity of noise at the instability.

From (3.12) we find

region of importance is one near the origin. Once the system reaches $-L$ or L it is approaching X_0 or X_1 , respectively, with probability one minus exponentially small terms.

Referring again to (3.8), $u(x, L, \alpha)$ is conditioned on $X(0) = x$. The equilibrium distribution is then obtained as an integral

$$u(L, \alpha) = \int_{-L}^L f_0(x, \alpha) u(x, L, \alpha) dx. \quad (3.15)$$

If $b(s)$ is symmetrical about $s=0$, then $u(L, \alpha) \sim \frac{1}{2}$; correction terms are order ϵ . If $b(s)$ is not symmetrical, so the potential is skewed, then $u(L, \alpha)$ need not be asymptotic to $\frac{1}{2}$.

D. Conditional relaxation time towards equilibrium

We define the relaxation time as the average time required for the system to leave the observation region $[-L, L]$. To find it, define $T(x)$ by

$$T(x) = E\{\text{mint: } X(t) \notin [-L, L] | X(0) = x\}. \quad (3.16)$$

$T(x)$ is the average time that it takes for the system to leave the observation region, given that it starts at x . If $T(x)$ is integrated against the initial density $f_0(x, \alpha)$, the overall relaxation time τ is obtained. The average relaxation rate is then $1/\tau$. $T(x)$

$$T(x) = \frac{2}{\epsilon} \int_{-L}^x e^{-B(s, \alpha)/\epsilon} ds \left(\frac{\int_{-L}^L e^{-B(s, \alpha)/\epsilon} \int_{-L}^s e^{B(z, \alpha)/\epsilon} \frac{dz ds}{a(z, \alpha)}}{\int_{-L}^L e^{-B(s, \alpha)/\epsilon} ds} \right) - \frac{2}{\epsilon} \int_{-L}^x e^{-B(s, \alpha)/\epsilon} \int_{-L}^s e^{B(z, \alpha)/\epsilon} \frac{dz ds}{a(z, \alpha)}. \quad (3.20)$$

Equation (3.20) is exact; it is easily evaluated numerically and the relaxation time is calculated by one more quadrature.

E. Conditional relaxation rate to a specified state

Consider the rate of relaxation towards a specified stable state, say X_1 . To do this, we calculate the average time to cross $X(t) = L$ for all systems that cross L before $-L$. Define $T_L(x)$ by

$$T_L(x) = E\{\text{mint: } X(t) \geq L | X(0) = x, X(t) \text{ exits } [-L, L] \text{ through } L\}; \quad (3.21)$$

$T_L(x)$ satisfies

$$-u(x, L, \alpha) = \frac{\epsilon a(x, \alpha)}{2} \frac{d^2 T_L}{dx^2} + \left(b(x, \alpha) + \frac{\epsilon}{4} a'(x, \alpha) \right) \frac{dT_L}{dx}. \quad (3.22)$$

In (3.22), $u(x, L, \alpha)$ is the equilibrium distribution function calculated in Sec. IIIC. An obvious boundary condition for (3.22) is $T_L(L) = 0$. For the second boundary condition, we set $dT_L/dx|_{-L} = 0$. This condition is motivated as follows. $T_L(x)$ assumes that the process exits through L . Any sys-

tem reaching $-L$ must thus be reflected at $x = -L$ and return through $x = 0$; the choice of boundary condition corresponds to this reflection.

$$-1 = \frac{\epsilon a(x, \alpha)}{2} \frac{d^2 T}{dx^2} + \left(b(x, \alpha) + \frac{\epsilon}{4} a'(x, \alpha) \right) \frac{dT}{dx},$$

$$T(L) = T(-L) = 0. \quad (3.17)$$

If ϵ were zero then $T(x)$ would be the solution of the macroscopic equation

$$t = \begin{cases} \int_x^L \frac{ds}{b(s, \alpha)} & \text{if } x > 0, \\ \int_x^{-L} \frac{ds}{b(s, \alpha)} & \text{if } x < 0, \end{cases} \quad (3.18)$$

and $T(0)$ would be infinite. Once again, we conclude that the important part of the observation region is a small neighborhood of the origin.

Define

$$B(x, \alpha) = \int^x \left(\frac{2b(s, \alpha)}{a(s, \alpha)} + \frac{\epsilon}{2} \frac{a'(s, \alpha)}{a(s, \alpha)} \right) ds; \quad (3.19)$$

so that the solution of (3.17) is

tem reaching $-L$ must thus be reflected at $x = -L$ and return through $x = 0$; the choice of boundary condition corresponds to this reflection.

Defining $B(x, \alpha)$ as in (3.19), we obtain the solution of (3.22) as

$$T_L(x) = \frac{2}{\epsilon} \int_x^L e^{-B(s, \alpha)/\epsilon} \times \int_{-L}^s \frac{e^{B(s', \alpha)/\epsilon}}{a(s', \alpha)} u(s', L, \alpha) ds' ds. \quad (3.23)$$

The average time of relaxation towards X_1 , τ_L , is the integral of $T_L(x)$ against the initial density $f_0(x, \alpha)$, and the average rate of relaxation is $1/\tau_L$.

F. Rate of relaxation to a specified state

The last theoretical quantity that we calculate is the rate of relaxation, rather than an average rate of relaxation. Define

$u(x, t, L) = \text{Prob}\{X(t) \text{ exits } [-L, L] \text{ through } L \text{ by time } t | X(0) = x\}.$ (3.24)

This probability satisfies the equation

$$\frac{\partial u}{\partial t} = \frac{\epsilon a(x, \alpha)}{2} \frac{\partial^2 u}{\partial x^2} + \left(b(x, \alpha) + \frac{\epsilon}{4} a'(x, \alpha) \right) \frac{\partial u}{\partial x}. \quad (3.25)$$

Equation (3.25) is the first partial differential equation that has appeared in the theory. It needs

both initial and boundary conditions; from (3.24) these are

$$\begin{aligned} u(x, 0, L) &= 0, \quad -L < x < L \\ u(-L, t, L) &= 0, \quad u(L, t, L) = 1. \end{aligned} \quad (3.26)$$

Clearly, as $t \rightarrow \infty$, $u(x, t, L) \rightarrow u(x, L, \alpha)$ calculated in Sec. III C. In order to calculate the rate of decay, we construct the asymptotic solution of (3.25) and (3.26) by exploiting the smallness of ϵ . Introducing Taylor expansions for $a(x, \alpha)$ and $b(x, \alpha)$ in (3.25) gives

$$\frac{\partial u}{\partial t} = \frac{\epsilon}{2} [a(0, \alpha) + a'(0, \alpha)x + O(x^2)] \frac{\partial^2 u}{\partial x^2} + \left(b'(0, \alpha)x + O(x^2) + \frac{\epsilon}{4} [a'(0, \alpha) + a''(0, \alpha)x] \right) \frac{\partial u}{\partial x}. \quad (3.27)$$

As in Sec. III C., we expect the most important part of the solution to come from a vicinity of $x=0$. We introduce a scale transformation $x = \sqrt{\epsilon}z$ so that (3.27) becomes

$$\begin{aligned} \frac{\partial u}{\partial t} &= \frac{1}{2} [a(0, \alpha) + a'(0, \alpha)\sqrt{\epsilon}z + O(\epsilon)] \frac{\partial^2 u}{\partial z^2} \\ &+ [b'(0, \alpha)z + O(\sqrt{\epsilon})] \frac{\partial u}{\partial z}. \end{aligned} \quad (3.28)$$

We use a perturbation expansion of the solution of (3.28), $u(z, t) = \sum_{n=0}^{\infty} \epsilon^n u_n(z, t)$; the leading term $u_0(z, t)$ satisfies

$$\frac{\partial u_0}{\partial t} = \frac{1}{2} a(0, \alpha) \frac{\partial^2 u_0}{\partial z^2} + b'(0, \alpha)z \frac{\partial u_0}{\partial z}, \quad (3.29)$$

with initial and boundary conditions determined from (3.26). These are found as follows. We expect that

$$\begin{aligned} u_0(z, t) &\rightarrow 1 \quad \text{as } z \rightarrow \infty, \\ u_0(z, t) &\rightarrow 0 \quad \text{as } z \rightarrow -\infty. \end{aligned} \quad (3.30)$$

Thus we set

$$u_0(z, t) = \frac{\int_{-\infty}^z \exp\left(-\frac{b'(0, \alpha)}{a(0, \alpha)} s^2\right) ds}{\int_{-\infty}^{\infty} \exp\left(-\frac{b'(0, \alpha)}{a(0, \alpha)} s^2\right) ds} - w(z, t), \quad (3.31)$$

where $w(z, t)$ is to be determined. The integral appearing on the right-hand side of (3.31) is a differently scaled version of (3.12), the asymptotic expansion of the equilibrium distribution.

The function $w(z, t)$ satisfies the equation

$$\frac{\partial w}{\partial t} = \frac{a(0, \alpha)}{2} \frac{\partial^2 w}{\partial z^2} + b'(0, \alpha)z \frac{\partial w}{\partial z}, \quad (3.32)$$

with initial condition

$$w(z, 0) = \frac{\int_{-\infty}^z \exp\left(-\frac{b'(0, \alpha)}{a(0, \alpha)} s^2\right) ds}{\int_{-\infty}^{\infty} \exp\left(-\frac{b'(0, \alpha)}{a(0, \alpha)} s^2\right) ds} = w_0(z), \quad (3.33)$$

and decay requirements as $z \rightarrow \pm\infty$. To solve (3.32), we set $w(z, t) = W(z e^{b'(0, \alpha)t}, a(0, \alpha)t) \equiv W(y, \tau)$ and obtain

$$\exp\left(-\frac{2b'(0, \alpha)}{a(0, \alpha)} \tau\right) \frac{\partial W}{\partial \tau} = \frac{1}{2} \frac{\partial^2 W}{\partial y^2} \quad (3.34)$$

Next we transform the time variable by setting

$$\eta = \frac{1 - \exp\left(\frac{2b'(0, \alpha)}{a(0, \alpha)} \tau\right)}{-\frac{2b'(0, \alpha)}{a(0, \alpha)}}, \quad (3.35)$$

so that

$$\frac{d\eta}{d\tau} = \exp\left(\frac{2b'(0, \alpha)}{a(0, \alpha)} \tau\right).$$

Since $\partial W / \partial \tau = (\partial W / \partial \eta)(d\eta / d\tau)$, (3.34) becomes

$$\frac{\partial W}{\partial \eta} = \frac{1}{2} \frac{\partial^2 W}{\partial y^2}. \quad (3.36)$$

The fundamental solution of (3.36) is

$$W(y, \eta) = \frac{1}{(2\pi\eta)^{1/2}} e^{-y^2/2\eta} \quad (3.37)$$

so that the solution with initial data $w_0(y)$ is

$$W(y, \eta) = \int w_0(\xi) \frac{1}{(2\pi\eta)^{1/2}} e^{-(y-\xi)^2/2\eta} d\xi. \quad (3.38)$$

Using (3.35) and $t = \tau / a(0, \alpha)$ we obtain

$$\begin{aligned} w(z, t) &= \int w_0(\xi) \left(\frac{b'(0, \alpha)}{\pi a(0, \alpha) (e^{2b'(0, \alpha)t} - 1)} \right)^{1/2} \\ &\times \exp\left(-\frac{(ze^{b'(0, \alpha)t} - \xi)^2 b'(0, \alpha)}{a(0, \alpha) (e^{2b'(0, \alpha)t} - 1)} \right) d\xi. \end{aligned} \quad (3.39)$$

Inspection of (3.39) shows that $w(z, t) \rightarrow w_0(\xi)$ as $t \downarrow 0$ and that $w(z, t) \rightarrow 0$ uniformly in z as $t \rightarrow \infty$.

Comparing (3.39) and (3.31) we see that $u_0(z, t)$ relaxes towards the equilibrium distribution at a rate determined by the macroscopic relaxation rate $b'(0, \alpha)$.

IV. THEORY OF RELAXATION IN MANY DIMENSIONS

The theory of the preceding section is one dimensional, and this allows exact calculation of many quantities of interest in relaxation. There are physical problems, however, which are fundamentally multidimensional and cannot be reduced to one-dimensional problems. In order to develop a theory of multidimensional relaxation, the smallness of ϵ must be exploited fully. Instead of obtaining exact answers and then analyzing them by asymptotic methods, we shall obtain asymptotic solutions from the start. For definiteness, we will be concerned with two-dimensional systems.

There are essentially no new *physical* ideas involved in the study of relaxation from multidimensional instabilities. The one-dimensional problems have given us all the physical insight. On the other hand, the *mathematical* difficulties involved by going from one to many dimensions are considerable. Some of the necessary mathematics are in Ref. 23; our goal in this section is to point out how the one-dimensional problems generalize and to sketch the mathematical methods.

A. Kinds of two-dimensional instabilities

The systems we study are now described by a pair of variables $X(t) = [X_1(t), X_2(t)]$, assumed to satisfy Langevin equations

$$\frac{dX_i}{dt} = b_i(X, \alpha) + [\epsilon a_{ij}(X, \alpha)]^{1/2} \xi_{ij}(t), \quad i, j = 1, 2 \quad (4.1)$$

with summation over repeated indices. As before, let $X = (0, 0)$ be a zero of the vector $b(X, \alpha) = [b_1(X, \alpha), b_2(X, \alpha)]$. Let

$$B \equiv \begin{pmatrix} \frac{\partial b_1}{\partial X_1} & \frac{\partial b_1}{\partial X_2} \\ \frac{\partial b_2}{\partial X_1} & \frac{\partial b_2}{\partial X_2} \end{pmatrix} \bigg|_{(0,0)} \quad (4.2)$$

An instability is called *laserlike* if when $\alpha > 0$ the matrix B has two positive eigenvalues, and *chemical-like* if when $\alpha > 0$, B has one positive and one negative eigenvalue. These definitions are motivated by Eqs. (2.1) and (2.4), respectively.

Consider a laserlike instability. Since B has two positive eigenvalues, there is repulsion from the origin in every direction [Fig. 2(a)]. For ex-

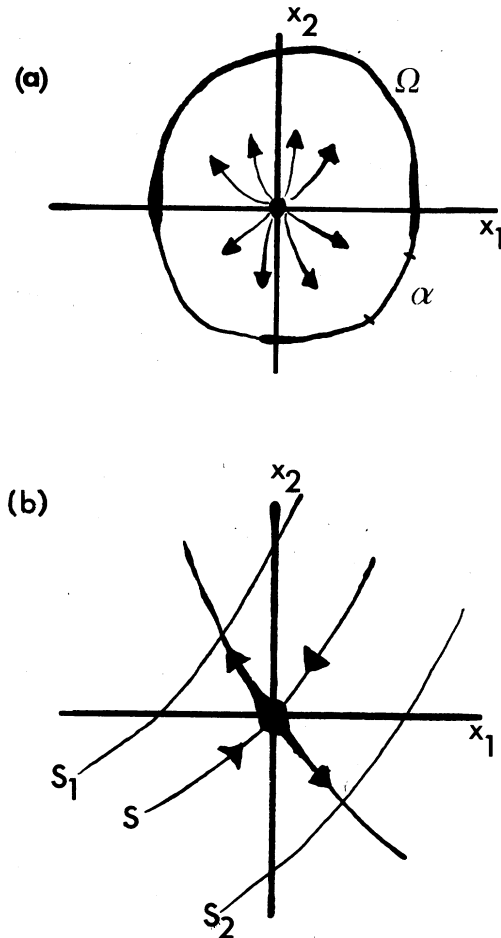


FIG. 2. Two kinds of two-dimensional instabilities: (a) laserlike and (b) chemical-like.

ample, if the laser equations, without noise, are rewritten in terms of $R = (B_1^2 + B_2^2)^{1/2}$ and $\theta = \arctan(B_1/B_2)$ then (2.1) becomes

$$\frac{dR}{dt} = \beta R(d - R^2), \quad \frac{d\theta}{dt} = 0. \quad (4.3)$$

For an instability such as this one, the most appropriate relaxation problem is the following. Surround the instability at $(0, 0)$ by some closed trajectory Ω (e.g., the circle $R = \sqrt{d}$ for the laser). One then asks for the distribution of exit points on Ω and for the probability of exiting through a specified arc, α , of Ω , given an initial point $X(0) = x$. The first question is adequately treated by Fokker-Planck methods.⁴⁻⁷ The second problem is not effectively treated by those methods.

Consider a *chemical-like* instability. The eigenvector corresponding to the negative eigenvalue of B gives rise to a deterministic separatrix²⁸ which separates the phase plane into two domains of attraction [Fig. 2(b)]. The observation region

$[-L, L]$ is now generalized to a band around the separatrix S bounded by two curves S_1 and S_2 which do not intersect S . We will study relaxation in the observation region bounded by S_1 and S_2 . In this paper, we will concentrate on chemical-like instabilities.

B. System preparation

As in Sec. III, we assume that the system is prepared so that $X=0$ is a stable state. We assume that when $\alpha < 0$, B given by (4.2) has two negative eigenvalues. At $t = -\infty$, the system is prepared with $\alpha < 0$. Thus, by $t=0$ a stationary distribution $f_0(x)$ is achieved; it is characterized by the Fokker-Planck equation

$$0 = \frac{\epsilon}{2} \sum_{i,j} \frac{\partial^2}{\partial x_i \partial x_j} [a_{ij}(x) f_0] - \sum_i \frac{\partial}{\partial x_i} \left[\left(b_i(x) + \frac{\epsilon}{4} \sum_j a_{ij}(x) \right) f_0 \right]. \quad (4.4)$$

There are many approximation schemes for the solution of (4.4).²⁹⁻³¹ All methods exploit the smallness of ϵ and obtain solutions of the form $f_0(x) \sim g(x, \epsilon) e^{-\varphi(x)/\epsilon}$, where $\varphi(x)$ satisfies a Hamilton-Jacobi equation and $g(x, \epsilon)$ is represented as a power series in ϵ . The coefficients of $g(x, \epsilon) = \sum g_k(x) \epsilon^k$ satisfy certain ordinary differential equations on the characteristics of the Hamilton-Jacobi equation.³⁰⁻³²

C. Equilibrium distribution for chemical-like instabilities

The generalization of the equilibrium distribution of III C is obtained as follows. Let

$u(x, \alpha) = \text{Prob}\{X(t) \text{ exits region bounded by}$

$$S_1 \text{ and } S_2 \text{ through } S_2 | X(0) = x\}. \quad (4.5)$$

The equilibrium distribution is then obtained by integrating $u(x, \alpha) f_0(x)$ over the region of interest. $u(x, \alpha)$ satisfies the elliptic equation

$$0 = \frac{\epsilon}{2} \sum_{i,j} a_{ij}(x, \alpha) \frac{\partial^2 u}{\partial x_i \partial x_j} + \sum_i \left(b_i(x, \alpha) + \frac{\epsilon}{4} \sum_j \frac{\partial}{\partial x_j} a_{ij}(x, \alpha) \right) \frac{\partial u}{\partial x_i}, \quad (4.6)$$

with boundary conditions

$$u(x, \alpha) = \begin{cases} 0, & x \in S_1 \\ 1, & x \in S_2 \end{cases}. \quad (4.7)$$

An approximate technique for solving this kind of equation is given in Ref. 23.

The results derived there show that

$$u(x, \alpha) = g(x, \epsilon) E(\psi(x, \alpha)/\sqrt{\epsilon}) + \epsilon^{1/2} h(x, \epsilon) E'(\psi(x, \alpha)/\sqrt{\epsilon}), \quad (4.8)$$

where $g(x, \epsilon)$ and $h(x, \epsilon)$ (to be determined) are power series in ϵ , $g(x, \epsilon) = \sum g_k(x) \epsilon^k$, $h(x, \epsilon) = \sum h_k(x) \epsilon^k$. $E(z)$ is the error function

$$E(z) = \int_z^\infty e^{-s^2/2} ds, \quad (4.9)$$

and $\psi(x, \alpha)$ is to be determined. The leading term in the asymptotic expansion (4.8) is

$$u(x, \alpha) \sim g_0(x) \int^{\psi(x, \alpha)/\sqrt{\epsilon}} e^{-s^2/2} ds, \quad (4.10)$$

which is an analog of (3.12). It turns out that $g_0(x)$ is a constant, given by

$$g_0(x) = \left(\int_{\psi_1(x, \alpha)/\sqrt{\epsilon}}^{\psi_2(x, \alpha)/\sqrt{\epsilon}} e^{-s^2/2} ds \right)^{-1}. \quad (4.11)$$

Here $\psi_i(x, \alpha)$ is the value that $\psi(x, L, \alpha)$ takes on boundary S_i . The function $u(x, \alpha)$ given by (4.8) asymptotically satisfies (4.6) if $\psi(x, \alpha)$ satisfies²³:

$$0 = \sum_i b_i(x, \alpha) \frac{\partial \psi}{\partial x_i} - \frac{\psi}{2} \sum_{i,j} a_{ij}(x, \alpha) \frac{\partial \psi}{\partial x_i} \frac{\partial \psi}{\partial x_j}. \quad (4.12)$$

Regularity of $\psi(x, \alpha)$ requires that $\psi(x, \alpha) = 0$ for $x \in S$, the deterministic separatrix.

The trajectory S in Fig. 2 plays the same role as the single point of instability in the one-dimensional problem. In particular, if S_1 and S_2 are far apart, we let $\psi_1(x, \alpha) \rightarrow -\infty$, $\psi_2(x, \alpha) \rightarrow \infty$, and then $u(x, \alpha) \sim \frac{1}{2}$ for points $x \in S$. This result accords with intuition and generalizes the result of Sec. III C that $u(x, L, \alpha) \sim \frac{1}{2}$ at the point of instability.

For points x not on S , but close to it, $\psi(x, \alpha)$ can be determined by a Taylor expansion, as follows. We switch from (x_1, x_2) to coordinate tangential and normal to the separatrix S . Since $\psi = 0$ on S , its tangential derivative vanishes. Equation (4.12) gives an equation for the normal derivative ψ_n :

$$\frac{d\psi_n}{dt} + \hat{b}\psi_n - \frac{\hat{a}\psi_n^3}{2} = 0. \quad (4.13)$$

Here b and a are coefficients involving the $b_i(x)$ and $a_{ij}(x)$.²³ The point is that (4.13) gives the normal derivative of ψ ; for points a distance δn from the separatrix $\psi \sim \psi_n \delta n$. Thus there is a symmetry in the value of ψ about the separatrix. This is the same kind of symmetry that allowed the asymptotic expansion of (3.11) to give the quotient of error functions. Such symmetry is not present at critical points in parameter space and more complicated asymptotic solutions are needed²³ (see the Appendix for a simple example).

The results presented in this section pertain only to the first part [$g_0 E(\psi(x)/\sqrt{\epsilon})$] of the expansion (4.8); other terms are calculated in a like fashion.

D. Relaxation times for chemical-like instabilities

As in Secs. II D and III E, we can consider two types of conditional relaxation rates. The first, denoted by $T_1(x)$, is the mean time to leave the region bounded by S_1 and S_2 given that $X(0)=x$. It satisfies the equation

$$-1 = \sum_{i,j} \frac{\epsilon}{2} a_{ij}(x, \alpha) \frac{\partial^2 T_1}{\partial x_i \partial x_j} + \sum_i \left(b_i(x, \alpha) + \frac{\epsilon}{4} \sum_j \frac{\partial}{\partial x_j} a_{ij}(x, \alpha) \right) \frac{\partial T_1}{\partial x_i}, \quad (4.14)$$

with the boundary conditions

$$T_1(x) = 0 \quad \text{if } x \in S_1 \text{ or } x \in S_2. \quad (4.15)$$

Equation (4.15) is the two-dimensional generalization of (3.17).

The second conditional relaxation time, denoted by $T_2(x)$, is the mean time to exit the region through S_2 given that $X(0)=x$ and that the process exits through S_2 . This time satisfies the equation

$$-u(x, \alpha) = \sum_{i,j} \frac{\epsilon}{2} a_{ij}(x, \alpha) \frac{\partial^2 T_2}{\partial x_i \partial x_j} + \sum_i \left(b_i(x, \alpha) + \frac{\epsilon}{4} \sum_j \frac{\partial}{\partial x_j} a_{ij}(x, \alpha) \right) \frac{\partial T_2}{\partial x_i}. \quad (4.16)$$

The boundary conditions that we apply to (4.16) are generalizations of the boundary conditions to (3.22):

$$T_2(x) = 0, \quad x \in S_2$$

$$\frac{\partial T_2(x)}{\partial n} = 0, \quad x \in S_1. \quad (4.17)$$

Here $\partial T_2/\partial n$ is the normal derivative of $T_2(x)$ on S_1 .

Let $T(x)$ represent either $T_1(x)$ or $T_2(x)$. We seek a solution of (4.14) or (4.16) in the form²³

$$T(x) \sim g(x, \epsilon) F(\psi(x)/\sqrt{\epsilon}) + \epsilon^{1/2} h(x, \epsilon) F'(\psi(x)/\sqrt{\epsilon}) + k(x, \epsilon). \quad (4.18)$$

Here $g(x, \epsilon)$, $h(x, \epsilon)$, $k(x, \epsilon)$ are power series in ϵ [e.g., $k(x, \epsilon) = \sum \epsilon^n k_n(x)$, etc.]. $F(z)$ is a special function defined by the differential equation

$$\frac{d^2 F}{dz^2} = -z \frac{dF}{dz} - 1 \quad (4.19)$$

[the error function (4.9) satisfies $d^2 E/dz^2 = -z dE/dz$].

In Ref. 23 it is shown that (i) $\psi(x)$ satisfies the equation (4.12) and (ii) g_0 is a constant determined so that the solution of the equation

$$\sum b_i(x, \alpha) \frac{\partial k_0}{\partial x_i} - \sum_{i,j} a_{ij} \frac{(x, \alpha)}{2} \frac{\partial \psi}{\partial x_i} \frac{\partial \psi}{\partial x_j} g_0 = Q \quad (4.20)$$

is regular at the instability. Here $Q = -1$ if $T = T_1$ and $Q = -u(x, \alpha)$ if $T = T_2$. The function k_0 is then determined by the method of characteristics.^{23,33}

As in Sec. III, the appropriate relaxation time is obtained by integrating $T_1(x)f_0(x, \alpha)$ or $T_2(x)f_0(x, \alpha)$ over the region bounded by S_1 and S_2 .

E. Rate of relaxation to a specified state

The last quantity we consider is a generalization of $u(x, t, L)$ given by (3.24). Let

$u(x, t) = \text{Prob}\{X(t) \text{ exits region bounded by}$

S_1 and S_2 through

$S_2 \text{ by time } t | X(0) = x\}$. (4.21)

This probability satisfies the equation

$$\frac{\partial u}{\partial t} = \frac{\epsilon}{2} \sum_{i,j} a_{ij}(x, \alpha) \frac{\partial^2 u}{\partial x_i \partial x_j} + \sum_i \left(b_i(x, \alpha) + \frac{\epsilon}{4} \sum_j \frac{\partial}{\partial x_j} a_{ij}(x, \alpha) \right) \frac{\partial u}{\partial x_i}, \quad (4.22)$$

with initial and boundary conditions

$u(x, 0) = 0, \quad x \in \text{region bounded by } S_1 \text{ and } S_2$

$$u(x, t) = \begin{cases} 0, & x \in S_1 \\ 1, & x \in S_2 \end{cases}. \quad (4.23)$$

As in Sec. III E, we seek a solution $u(x, t) \sim u(x) - w(x, t)$, where $u(x)$ satisfies (4.8) and $w(x, t)$ thus solves (4.22) with initial condition $w(x, 0) = u(x)$. A solution of (4.22) with this initial condition can be obtained by the method described in Sec. IV B.

V. SPONTANEOUS ASYMMETRIC SYNTHESIS

We conclude the paper by applying the methods of the preceding section to the problem of spontaneous asymmetric synthesis. Our goal in this section is

(i) to estimate the size of the region in which fluctuations are important (i.e., affect the outcome of the experiments);

(ii) to estimate the mean relaxation time to leave this region. Both of these quantities are

important if one tries to experimentally verify the occurrence of spontaneous asymmetric synthesis. The first condition indicates how precise the initial conditions must be and the second indicates how long one needs to wait to observe the asymmetric evolution.¹⁴

We start with the deterministic equations for spontaneous asymmetric synthesis. We assume n_L and n_D are two enantiomers that are catalysts for their own production and anticatalysts for the other enantiomer. They are assumed to satisfy mass action kinetics given by

$$\begin{aligned}\frac{dn_L}{d\tau} &= n_L(k_1 - k_2 n_D - k_3 n_L), \\ \frac{dn_D}{d\tau} &= n_D(k_1 - k_2 n_L - k_3 n_D).\end{aligned}\quad (5.1)$$

We now determine conditions on the rate constants so that the racemic state ($n_D = n_L$) is unstable. Define scaled variables $x = n_L/n^0$, $y = n_D/n^0$, $t = k_3\tau$ so that

$$\begin{aligned}\frac{dx}{dt} &= x\left(\frac{k_1}{k_3 n^0} - \frac{k_2}{k_3} y - x\right), \\ \frac{dy}{dt} &= y\left(\frac{k_1}{k_3 n^0} - \frac{k_2}{k_3} x - y\right).\end{aligned}\quad (5.2)$$

The scaling parameter n^0 is picked so that

$$\frac{k_2}{k_3} = \alpha \quad \text{and} \quad \frac{k_1}{k_3 n^0} = 1 + \alpha \quad (5.3)$$

[i.e., $n^0 = k_1/(k_2 + k_3)$]. The Eqs. (5.2) become

$$\begin{aligned}\frac{dx}{dt} &= x(1 + \alpha - \alpha y - x), \\ \frac{dy}{dt} &= y(1 + \alpha - \alpha x - y).\end{aligned}\quad (5.4)$$

The racemic state is $(x, y) = (1, 1)$. The eigenvalues of the matrix B given by (4.2) are $-1 \pm \alpha$, so that a sufficient condition for the racemic state to be an instability is that $\alpha > 1$ (i.e., $k_2/k_3 > 1$).

Introduce random variables N_L and N_D that satisfy the Langevin equation:

$$\begin{aligned}0 &= \frac{\epsilon}{2} \left(\frac{\partial^2 u}{\partial x^2} [(1 + \alpha)x + x^2] + 2 \frac{\partial^2 u}{\partial x \partial y} \alpha xy + \frac{\partial^2 u}{\partial y^2} [(1 + \alpha)y + y^2] \right) + \frac{\partial u}{\partial x} \left(x[(1 + \alpha) - \alpha y - x] + \frac{\epsilon}{4} [(1 + \alpha) + 2x + \alpha y] \right) \\ &+ \frac{\partial u}{\partial y} \left(y[(1 + \alpha) - \alpha x - y] + \frac{\epsilon}{4} [(1 + \alpha) + 2y + \alpha x] \right).\end{aligned}\quad (5.10)$$

We switch to the variables (z, w) . The equation (5.10) is transformed to

$$\begin{aligned}0 &= \frac{\epsilon}{2} \left[\frac{\partial^2 u}{\partial z^2} \left((1 + \alpha)w + \frac{1}{2}(z^2 + w^2) + \frac{\alpha}{2}(z^2 - w^2) \right) + 2 \frac{\partial^2 u}{\partial z \partial w} [(1 + \alpha)z + zw] \right. \\ &\quad \left. + \frac{\partial^2 u}{\partial w^2} \left((1 + \alpha)w + \frac{1}{2}(z^2 + w^2) + \frac{\alpha}{2}(w^2 - z^2) \right) \right] + \frac{\partial u}{\partial z} \left((1 + \alpha)z - wz + \frac{\epsilon}{4}(2w - \alpha z) \right) \\ &+ \frac{\partial u}{\partial w} \left[(1 + \alpha)w + \frac{\alpha}{2}(z^2 - w^2) - \left(\frac{w^2 + z^2}{2} \right) + \frac{\epsilon}{4}[2(1 + \alpha) + (2 + \alpha)z] \right]\end{aligned}\quad (5.11)$$

$$\begin{aligned}\frac{dN_L}{dt} &= N_L(k_1 - k_2 N_D - k_3 N_L) \\ &+ [a_{11}(N_L, N_D)]^{1/2} \xi_1(t) + [a_{12}(N_L, N_D)]^{1/2} \xi_2(t), \\ \frac{dN_D}{dt} &= N_D(k_1 - k_2 N_L - k_3 N_D) \\ &+ [a_{12}(N_L, N_D)]^{1/2} \xi_2(t) + [a_{22}(N_L, N_D)]^{1/2} \xi_3(t),\end{aligned}\quad (5.5)$$

Applying a birth-and-death formulation,¹⁹ we obtain

$$\begin{aligned}a_{11}(N_L, N_D) &= (k_1 N_L + k_3 N_L^2) \frac{1}{V}, \\ a_{12}(N_L, N_D) &= (N_L N_D k_2) \frac{1}{V}, \\ a_{22}(N_L, N_D) &= (k_1 N_D + k_3 N_D^2) \frac{1}{V}.\end{aligned}\quad (5.6)$$

Here V is a measure of the volume of the system.³⁴ Applying the scaling above (5.2) to (5.6) gives

$$\begin{aligned}a_{11}(x, y) &= [(1 + \alpha)x + x^2] \epsilon, \\ a_{12}(x, y) &= (\alpha xy) \epsilon, \\ a_{22}(x, y) &= [(1 + \alpha)y + y^2] \epsilon,\end{aligned}\quad (5.7)$$

where $\epsilon \equiv 1/V \ll 1$.

We first solve the backward equation (4.6) for the equilibrium distribution. A simpler set of variables [instead of (x, y)] is

$$z = x - y, \quad w = x + y. \quad (5.8)$$

From (5.4) it follows that the deterministic dynamics for z and w are

$$\frac{dz}{dt} = (1 + \alpha)z - zw, \quad (5.9)$$

$$\frac{dw}{dt} = (1 + \alpha)w + \frac{\alpha}{2}(z^2 - w^2) - \frac{1}{2}(z^2 + w^2).$$

The point $(0, 2)$ is a saddle point instability and the w axis (i.e., $z = 0$) is the separatrix.

The backward equation (4.6) in (x, y) variables is

The boundary conditions for (5.11) are $u(-L, w) = 0$, $u(L, w) = 1$.

We use the ansatz (4.8) to solve (5.11); the leading term is given by (4.10) and (4.11); from (4.11), $g_0 \sim 1/\sqrt{2\pi}$ so only $\psi(z, w)$ needs to be determined. To do this, we use (4.12). We differentiate (4.12) with respect to z and evaluate it on the separatrix $z = 0$, where $\psi = 0$ and thus $\psi_w = 0$. This gives an equation for ψ_z on $z = 0$:

$$\left((1 + \alpha)w - \frac{w^2}{2}(1 + \alpha) \right) \frac{d}{dw} \psi_z + \psi_z \left[(1 + \alpha) - w - \left(\frac{(1 + \alpha)w + \frac{w^2}{2}(1 + \alpha)}{2} \right) \psi_z^2 \right] = 0. \quad (5.12)$$

At the saddle point the first term vanishes. This gives an algebraic equation for ψ_z ($\psi_z = 0$ is rejected as a solution). Solving gives

$$\psi_z(w=2) = \left(\frac{\alpha - 1}{2(1 + \alpha)} \right)^{1/2}. \quad (5.13)$$

With this condition, (5.12) is solved by standard methods.^{23,35} We are not as interested in the exact solution as in the order of magnitude. Namely, from (5.13), the argument of the error function $[\psi(z, w)/\sqrt{\epsilon}]$ is order

$$\left(\frac{\alpha - 1}{2(1 + \alpha)} \right)^{1/2} z \frac{1}{\sqrt{\epsilon}}. \quad (5.14)$$

Let us reconsider (5.14) in the physical variables. It becomes

$$\begin{aligned} & \left(\frac{(k_2 - k_3)n_0}{2k_1} \right)^{1/2} \left(\frac{n_L - n_D}{n_0} \right) V^{1/2} \\ &= \left(\frac{k_2 - k_3}{2(k_2 + k_3)} \right)^{1/2} \left(\frac{(n_L - n_D)k_1}{k_2 + k_3} \right) V^{1/2}. \end{aligned} \quad (5.15)$$

As a measure of V , we take the total number of molecules in the sample; for a 20-mg sample of an optically active substance such as 1,1'-binaphthyl,¹⁶ this means that $V^{1/2} \sim 10^8$ to 10^9 . For the experiments in Ref. 16 the concentrations are about 10^{-3} molar. Let us fix $n_L - n_D/n_L$ at 0.01, say a 1% difference in optical activity. An estimate of k_1 is $O(10^{-1}/\text{sec})$.¹⁶ The probability integral goes from 0.01 to 0.99 as its argument goes from -1.3 to 1.3. This means that (5.15) should be $O(1)$ for the fluctuation effects to be observable. Assume that k_2, k_3 are $O(1)$. Then we need $[(k_2 - k_3)/2(k_2 + k_3)]^{1/2} \sim 10^{-2}$ to 10^{-3} . We conclude that the system must be strongly autocatalytic (i.e., k_1 "large") but weakly selective on the anticatalytic dynamics (i.e., $k_2 \approx k_3$, but $k_2 > k_3$).

We now estimate the observation time for the relaxation. To completely do the calculation, one needs to solve (4.14) using (4.18). We will estimate g_0 in (4.18) at the point of instability, using (4.20). We obtain

$$g_0 = \frac{2}{\alpha - 1} = \frac{2k_3}{k_2 - k_3}. \quad (5.16)$$

Using the estimate $(k_2 - k_3)/2(k_2 + k_3) \sim 10^{-6}$ gives

an estimate for $g_0 \sim 10^4$ to 10^6 sec (since $k_2 \sim k_3$). This estimate for the relaxation time is the same order of magnitude as the times observed in the experiments.¹⁶ This estimate also shows that spontaneous optical resolution should be experimentally observable.

VI. SUMMARY

We have seen in the previous sections that the backward-diffusion equations can provide a good deal of useful information about relaxation from instabilities. The questions that are easily answered by using the backward equation complement the equations that are easily answered by using the Fokker-Planck equation. For example, consider the mean time to leave an observation region in a one-dimensional problem, starting at the origin (which is assumed to be the instability). Using the backward equation, we find this time by solving an ordinary differential equation (3.17) by simple quadratures. If we approach this problem via the Fokker-Planck equation (see, e.g., Refs. 31 and 22), then a partial differential equation or a difficult eigenvalue problem must be solved. There are, of course, questions that cannot easily be answered by the methods of this paper and the backward equation techniques will never replace techniques using the Fokker-Planck equation. Instead, the two kinds of methods complement each other and provide the capability to study many interesting questions about relaxation at instabilities.

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APPENDIX: CRITICAL INSTABILITIES

Our analysis explicitly avoided critical points in the parameter space,¹³ i.e., points where $b(x_0, \alpha) = 0$ and $b'(x_0, \alpha) = 0$. In order to study fluctuations at these points, one cannot use Gaussian densities but more complicated densities are needed.^{13,23} To illustrate this idea, we will redo the calculation of Sec. III C near the critical

point $\alpha = 0$. We start with (3.11), and assume for notational convenience that $a(y) = 2$. Then (3.11) becomes

$$u(x) = \frac{\int_{-L}^x \exp\left(-\int_0^s \frac{b(y, \alpha)}{\epsilon} dy\right) ds}{\int_{-L}^L \exp\left(-\int_0^s \frac{b(y, \alpha)}{\epsilon} dy\right) ds}. \quad (\text{A1})$$

In Sec. III, we proceeded by expanding $b(y, \alpha)$ in a Taylor series around $y = 0$ and keeping only the first two terms. This will not work at a critical point. Instead we expand as follows:

$$\int_0^s b(y, \alpha) dy \approx \frac{1}{2} \frac{\partial b}{\partial y} \bigg|_{(0, \alpha)} s^2 + \frac{1}{3!} \frac{\partial^2 b}{\partial y^2} \bigg|_{(0, \alpha)} s^3 + \frac{1}{4!} \frac{\partial^3 b}{\partial y^3} \bigg|_{(0, \alpha)} s^4 \quad (\text{A2})$$

and assume that

$$\begin{aligned} \frac{\partial b}{\partial y} \bigg|_{(0, \alpha)} &= 2\alpha g_1(\alpha), \\ \frac{\partial^2 b}{\partial y^2} \bigg|_{(0, \alpha)} &\equiv 0, \\ \frac{\partial^3 b}{\partial y^3} \bigg|_{(0, \alpha)} &= 4! g_2(\alpha), \end{aligned} \quad (\text{A3})$$

where $g_2(0) > 0$. The assumption about the second derivative is made for convenience. Near the critical point, $\alpha = 0$, the numerator of (A1) is replaced by

$$\begin{aligned} \int_{-L}^x \exp\left(-\int_0^s \frac{b(y, \alpha)}{\epsilon} dy\right) ds \\ \approx \int_{-L}^x \exp\left(-\frac{\alpha g_1(\alpha) s^2 - g_2(\alpha) s^4}{\epsilon}\right) ds. \end{aligned} \quad (\text{A4})$$

In going from (3.11) to (3.12) we used Laplace's method, which requires that the s^2 term in (A4)

dominate the s^4 term in (A4). This is true as long as $\alpha g_1(\alpha)$ and $g_2(\alpha)$ are the same order. Near the critical point this condition fails, Laplace's method cannot be used and (A4) is the canonical integral for the asymptotic analysis.²³ When α is nonzero, but small, (A4) must still be used. To estimate the size of the region of non-Gaussian fluctuations, we proceed as follows. The main contribution to the integral in (A4) comes from a vicinity of the origin. Let us consider the value of s at which $\exp\{-[\alpha g_1(\alpha)/\epsilon] s^2\}$ is equal to $\exp(-N)$ where N is a suitable integer (e.g., $N=4$ implies $e^{-4} = 1.83 \times 10^{-2}$). The requisite value of s is

$$s^* = \pm \left(\frac{\epsilon N}{\alpha g_1(\alpha)} \right)^{1/2}. \quad (\text{A5})$$

The non-Gaussian term in (A4) can be ignored if the s^4 term in (A4) is much less than the s^2 term, when $s = s^*$. This means that

$$\frac{1}{\epsilon} g_2(\alpha) \left(\frac{\epsilon N}{\alpha g_1(\alpha)} \right)^2 \ll N. \quad (\text{A6})$$

This gives the requirement

$$\frac{g_2(\alpha)}{\alpha^2 g_1(\alpha)^2} \ll \frac{1}{\epsilon N}. \quad (\text{A7})$$

Equation (A7) provides a bound on the region of non-Gaussian fluctuations. For example, assume that $g_2(\alpha) = g_1(\alpha) = 1$ and $N=4$; then (A7) becomes

$$\frac{1}{\alpha^2} \ll \frac{1}{4\epsilon}$$

or

$$\alpha \gg 2\sqrt{\epsilon}, \quad (\text{A8})$$

i.e., if the parameter α satisfies (A8) then the fluctuations are adequately described by a Gaussian model.

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