Stability and relative stability in nonlinear driven systems

Autor(en): **Landauer, Rolf**

Stability and relative stability in nonlinear driven systems

Rolf Landauer
IBM Thomas J. Watson Research Center, Yorktown Heights,
New York 10598, (U.S.A.)

Abstract. Fluctuation activated escape from a metastable state to a more likely state has long been a subject of theoretical attention. We illustrate the existing methods by application to noise induced errors in underdamped Josephson junction circuits. Concern with escape from the metastable state has been extended, during the last two decades, to include a concern with relative stability in open systems. The sophistication of some of the recent theories may have obscured the simpler and more important physical aspects which are reviewed here. We emphasize the simplicity of transport in the most common one-dimensional situations. We discuss the two different forms for the diffusion current, $D\partial n/\partial x$ and $\partial(Dn)/\partial x$, commonly found in the literature. The more likely of several competing locally stable states cannot be identified by simple criteria which are only concerned with the states being compared. The detailed kinetics along the pathways connecting such states, where the system is rarely found, cannot be ignored. As a consequence we cannot expect to discuss the origin of life, or evolution, by reliance on thermodynamic or information theoretic criteria, without attention to the detailed pathways for the process.

1. Introduction

Escape from a metastable state, activated by thermal fluctuations, was studied long ago in such problems as thermionic emission from metals, or in the Becker-Döring theory of nucleation. We will regard such processes as Brownian motion. The motion of some of the principal degrees of freedom will be treated explicitly; their interaction with other degrees of freedom, and with the rest of the universe, will be represented by frictional effects and noise. Thus, deterministic equations of motion drive the system toward preferred states of local stability, and noise permits it to get away from there. This viewpoint is principally due to Kramers in a paper [1] which is frequently cited, but whose full content is often left unappreciated. Kramers' paper dealt with motion in a one-dimensional potential and was generalized to many-dimensions by Brinkman [2], Landauer and Swanson [3], and Langer [4]. We cite three recent notes [5] as an indication that this many-dimensional problem has not yet reached the settled and definitive state of the one-dimensional case. If, however, we consider a spatially extended system with translational invariance, e.g. an unlimited one-dimensional chain of coupled particles, all in the same potential, we regain some simplicity, despite the infinite

number of degrees of freedom. Such systems were the focus of an earlier review [6], and will occur only peripherally in the present discussion. Kramers' approach can also be broadened to more general dynamic systems, which do not necessarily represent motion in a potential, but nevertheless exhibit competing states of local stability. Early discussions include those by Stratonovich [7], and by this author [8]. In such systems the noise can be, and generally will be, a function of the state of the system. This was explicit in Refs. [7] and [8], but has been rediscovered in the recent literature via the use of new terminology, "multiplicative noise" and "external noise."

There are recent, clear, and detailed reviews of this field [9,10]. The purpose of this shorter item is different. I believe that the generality and formality of some recent contributions has served to obscure some of the simple and important aspects. This paper is, of course, devoted to a discussion of physics. Elsewhere [11] I have described the sociology of the field.

Fluctuations are important in the attempt to receive weak signals, or in the attempt to make precision measurements, and this led to the character of the early theory [12]. Fluctuations, however, can also determine the overall qualitative behavior of small systems, and this emphasis on small systems clearly takes us away from the "thermodynamic limit", characteristic of much of the literature in statistical mechanics. Fluctuations can play a key role in biological processes, particularly in the understanding of the early stages in the evolution of life [13]. Indeed, biological evolution is dependent on genetic mutations, and *these are fluctuations*. To cite another example: digital computer circuitry, using Josephson junctions, has become sufficiently miniaturized so that thermal noise, while perhaps still not crucial to design, is no longer totally irrelevant [14]. The effects of alpha particles and cosmic rays on integrated silicon circuitry are much more dramatic [15], and have been a matter of practical concern for some years, and can also be considered to be noise.

2. Escape from underdamped well; Josephson junctions

As a prototype problem, we briefly discuss an example taken from the analysis of Josephson circuits [16]. Essentially, the same equations also arise in the analysis of externally synchronized oscillators [6], and in the analysis of a particle in a tilted sinusoidal potential, as shown in Fig. 1. We shall here, for simplicity, emphasize the sinusoidal potential. The potential has the form

$$V = V_0(1 - \cos\theta) - F\theta, \tag{1}$$

where θ is the coordinate of motion. The particle in this potential is also assumed to be subject to viscous forces and to thermal noise. A particle in the metastable state at P_3 can be carried over the adjacent right hand barrier as a result of noise forces. If the system is heavily damped, then the particle will end up at P_1. If the system is lightly damped, the particle will continue past further barriers and end up in a state with continuing motion to the right. The equation of motion is

$$m\ddot{\theta} + \gamma\dot{\theta} = -\partial V/\partial\theta + \zeta, \tag{2}$$

with noise forces

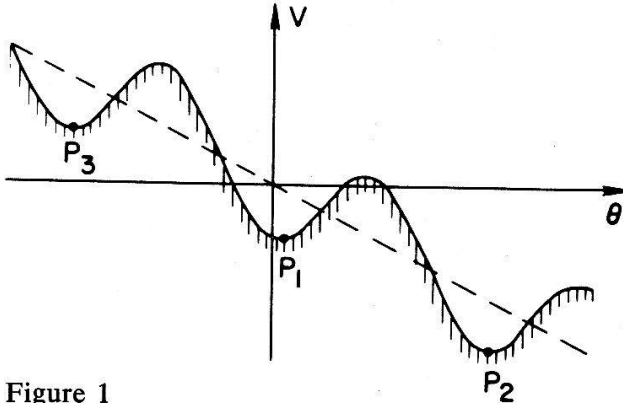$$\langle\zeta(t)\zeta(t')\rangle = 2\gamma kT\delta(t - t'). \tag{3}$$

Figure 1
Single particle potential of Eq. (1).

The rate of escape from a well is generally taken to be of the form $\nu\exp[-U/kT]$, where U is the height of the barrier relative to the minimum, and ν is a frequency. All of the sophisticated discussions in this subject concentrate on the description of ν. Uncertainties in this frequency can, in some problems, amount to many powers of ten [17]. Figure 2, taken from Ref. [16], illustrates the results of both theory, and of numerical simulation, describing the escape rate as a function of damping. The dimensionless damping constant in Fig. 2 is defined by $G = \gamma/(mV_0)^{1/2}$. The escape rate is measured in units defined in Ref. [16], and not needed for our purposes. For overdamped motion the escape occurs in a diffusive way across the bottleneck at the top of barrier. The escape rate decreases as the viscosity increases and as the diffusion coefficient decreases. A well known result for the escape rate, from Ref. 1, labelled KM in Fig. 2, and covering the case of heavy and moderate damping is

$$r = \frac{\omega_A}{2\pi|\omega_b|}\left(\left(\frac{1}{4}\eta^2 + |\omega_b|^2\right)^{1/2} - \frac{\eta}{2}\right)e^{-E_b/kT}. \tag{4}$$

Here r is the escape rate expressed as a probability of escape, per unit time, for particles in the initial well. $\eta = \gamma/m$ is the momentum relaxation rate. $\omega_A = \omega_p(1 - F^2/V_0^2)^{1/4}$ is the frequency associated with particle motion in the bottom of the initial well. $\omega_p = (V_0/m)^{1/2}$ is this frequency at F=0, called plasma frequency in the Josephson junction literature. ω_b is the analogous imaginary frequency associated with the unstable potential curvature at the barrier. At very low damping, however, it is clear that a particle executes almost conservative motion, and the escape up in energy, out of the well, must become difficult. This deviation from Eq. (4) was already understood by Kramers, who also derived the

result labeled KL in Fig. 2. Unfortunately, a good many later authors failed to appreciate Kramers' discussion of this extremely underdamped case. The KL result in Fig. 2 arises from the assumption that the particles are diffusing up along the energy or action coordinate, with the probability or population going to zero at the energy of the barrier peak. The unlabelled result in Fig. 2 is a recent refinement of Kramers' KL approximation [16]. It proceeds by treating the uphill diffusion, in the initial well, just as Kramers did, but in the range above the barrier peak assumes the presence of continued uphill diffusion *and* simultaneous flow out of the well, across the barrier.
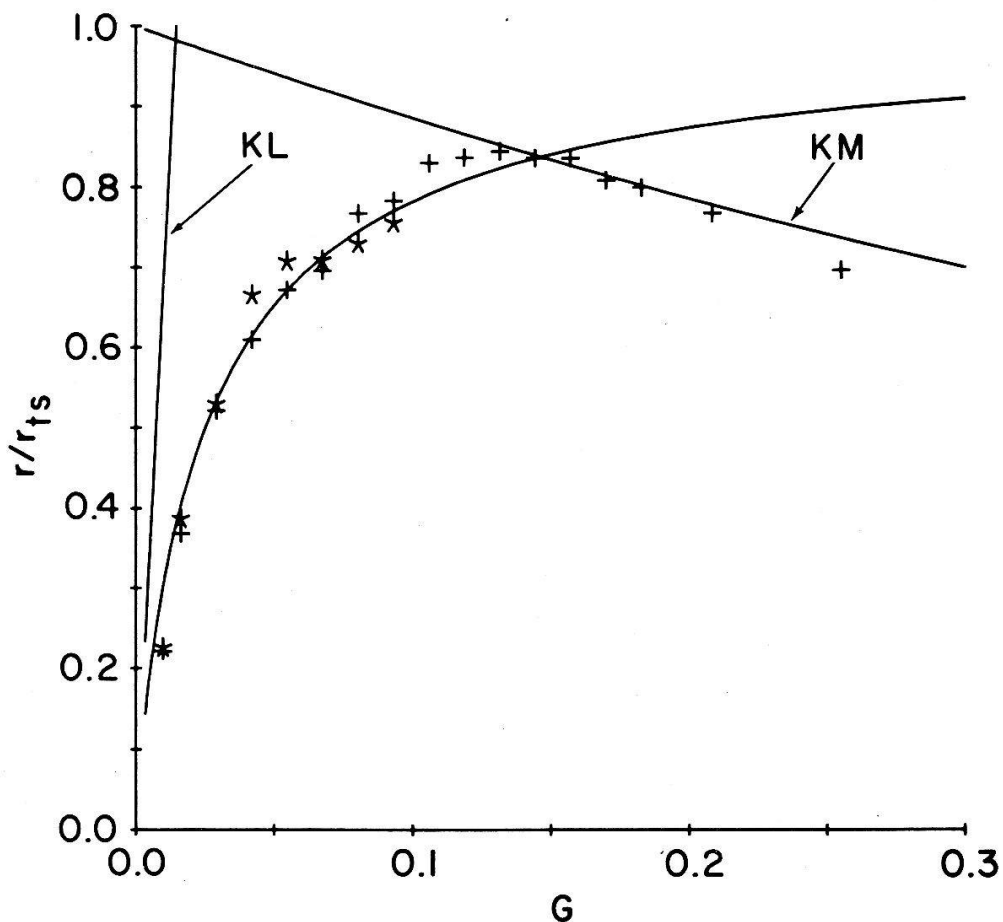
Figure 2

Escape rate for $F/V_0 = 0.985$, and a barrier height of 3.938 kT. The theoretical results described in the text are compared with computer simulations of escape events denoted by (+) and (✶).

3. Heavily damped case

Let us now turn explicitly to the heavily damped case, in which the inertial term in Eq. (2) becomes negligible. This leads to a Fokker-Planck equation for the probability distribution $\rho(\theta)$, often called the Smoluchowski equation. It has the form

$$\frac{\partial \rho}{\partial t} + \text{div } j = 0, \tag{5}$$

where the probability flux j is, in turn, given by

$$j = v\rho - D\partial\rho/\partial\theta. \tag{6}$$

Here v is the drift velocity, $v = -\mu\nabla V$ with $\mu = 1/\gamma$. The diffusion coefficient D and the mobity μ are related by the Einstein relation, $D = \mu kT$. We would like to make two observations about this case, and some of its minor modifications. The minor modifications include the case where motion occurs on a discretized one-dimensional lattice, and also includes the case where the motion is not that in a potential V, but represents some kind of more general system dynamics. We believe that in the steady state ($\partial\rho/\partial t = 0$), but a steady state which can include sources and sinks, this is an exceedingly simple problem. Furthermore, it is the steady state results which are needed most frequently. This point was discussed in in an Appendix to an earlier conference paper [6], and with the kind permission of the Editor of these Proceedings and of the Plenum Publishing Corporation, New York, include this material here as Table I. The material is adapted in its format, and also condensed slightly to eliminate overlap with the rest of this text. Note that Table I has its own separate citation list, at the end of Table I.

There is a one-dimensional case which is not trivial, and not usually discussed. Take the case where motion along the coordinate of interest, say θ, occurs via two different mechanisms. One mechanism causes jumps by a discrete amount, say $\pm 2\pi$. The other mechanism causes jumps over much smaller distances. Now assume that motion to the right, over some range of θ, occurs primarily by the large discrete jumps, whereas the counterbalancing motion to the left occurs mostly through the smaller jumps. We now have a one-dimensional situation where the steady state does not reflect detailed balance, and which will be more complex than the typical one-dimensional cases. The charges on a tunnel diode capacitance, leaking away through the diode, but charged through an ordinary series resistance, constitute an example of this situation [8].

The discussion in Table I is aimed primarily at the case where the transport properties vary smoothly, but it applies equally to the case where the jump probability between adjacent sites of a one-dimensional chain varies stochastically [18]. Even in that problem, the evaluation of long range mobilities or diffusion coefficients is trivial, unless we are interested in the case where the probability distribution for jumps between adjacent sites emphasizes relatively rare breaks in the chain, where the jump probability becomes very small.

4. Is the diffusion current $\partial(Dn)/\partial x$ or $D(\partial n/\partial x)$?

In Eq. (6) we invoked a form for the diffusive current in which the diffusion coefficient is not differentiated. Actually both of the forms, cited in the above Section title, occur in the literature. That may not be quite as silly as it sounds. Consider first the viewpoint of the hot-electron physicist [19]. Take a

Table I

Simplicity of Transport in the Smoluchowski Equation

Consider first a classical gas of noninteracting particles, overdamped in their motion, and spatially nonuniform in one direction. There are many papers on this subject, treating particles crossing single potential barriers, and also particles in sinusoidal potentials. Our key point: We invoke electrochemical potentials as the driving force for particle motion. This is hardly a new point, and is implicit, but not explicit, in Kramers' original paper (1940) on the thermally activated barrier crossing process. It is *the* prevalent method in the semiconductor device literature (Shockley, 1950). After all, an electron moving through a p region, in an npn structure, is crossing a potential barrier. Electrochemical potentials occur in many other places, e.g. in the literature dealing with the effect of activity coefficients on diffusion (Le Claire, 1949). The concept was particularly emphasized by Swanson (1957).

Consider particles with mobility μ and producing a flux

$$j = -\mu kT \frac{dn}{dx} - \mu n \frac{dU}{dx}, \qquad (T.1)$$

as a result of a concentration gradient and also as a result of a field induced drift term. In Eq. (T.1) we have implicitly used the Einstein relation, $D = \mu kT$. We can rewrite (T.1)

$$j = -\mu n \, kT \frac{d \log n}{dx} - \mu n \frac{dU}{dx} = -\mu n \frac{d}{dx}(U + kT \log n) = -\mu n \frac{d}{dx} \psi \qquad (T.2)$$

where ψ is the chemical potential of the particles. In equilibrium ψ is constant and its derivative vanishes. For small deviations from equilibrium we can, to first order in the deviations, take the n above, which multiplies $d\psi/dx$, as the equilibrium particle density $n_0(x)$. In the one-dimensional case, and in the steady state, j must be independent of x, and

$$\frac{d\psi}{dx} = -j/\mu n_0(x). \qquad (T.3)$$

The total drop in ψ, therefore, can be calculated by simply integrating this equation.

$$\psi(B) - \psi(A) = -j \int_A^B dx/\mu \, n_0(x). \qquad (T.4)$$

The extent to which the drop in ψ is composed of concentration gradients vs. applied fields is immaterial. We are essentially dealing with resistances in series and the driving force must be largest where the "conductivity" $\mu n_0(x)$ is smallest. Note that μ can be a function of x, it need not be constant. Furthermore, if j is kept inside the integral sign, it can also be a function of x, allowing for an arbitrary distribution of sources and sinks. Thus we can inject particles in one well, remove them from an adjacent well, and ask how much deviation from the equilibrium population distribution between the two wells is needed, to sustain the assumed flux over the barrier. We shall have occasion to refer again, later, to the possibility of simultaneously injecting and removing particles.

Table I

So far, in the utilization of Eq. (T.4), we have assumed small deviations from equilibrium. If, however, we are dealing with a linear diffusion problem, we can simply scale up the currents and concentration gradients, and thus describe large departures from equilibrium *exactly*. Note, however, that it is the concentration gradients, and concentration differences, that scale linearly, not the deviations in ψ. Thus, utilizing $\delta\psi = kT\delta n/n$, Eq. (T.4) becomes

$$kT\left(\frac{\delta n(A)}{n_0(A)} - \frac{\delta n(B)}{n_0(B)}\right) = -j\int_A^B dx/\mu\, n_0(x) \tag{T.5}$$

where $\delta n(A)$ and $\delta n(B)$ are the deviations from the equilibrium concentrations $n_0(A)$ and $n_0(B)$ maintained at A and B, respectively. Eq. (T.5) is now valid for large values of $\delta n(A)$, $\delta n(B)$, and j, as well as for small values. Note that $n_0(x)$, in Eq. (T.5), is independent of j, *and does not reflect the perturbed concentration profile and its shifted minimum*. If we consider the application of a large force, with or without simultaneous application of concentration changes, we can again return to Eq. (T.5) by choosing n_0 to be the equilibrium distribution characteristic of the potential *in the presence of the applied force*. Note that we obtained Eq. (T.5) indirectly, via Eq. (T.4), in order to make contact with concepts used in other fields. It is, of course, not necessary to do this.

For a high potential barrier, near which n_0 is very small compared to its value elsewhere, it has become common to invoke the approximation used by Kramers, in which the spatial variation of n_0 is represented only through the second derivative of the potential at the maximum. We can see, however, from the above result, that in the steady state case it is trivial to go beyond that.

If the particles are charged and interacting, the above equations are still valid. Now, however, the density perturbations and the field variation are no longer independent, but are related through Poisson's equation. It can then be shown (Landauer, 1978) that over large distances the drop in the applied voltage, multiplied by the particle's charge, must equal the drop in ψ.

If, instead of a one-dimensional continuum problem, we have a ladder of points, and the particles make transitions only between adjacent points, we can still write

$$j = g_{n,n+1}(\delta\psi_n - \delta\psi_{n+1}), \tag{T.6}$$

where $\delta\psi_n$ is a *small* deviation, in the electrochemical potential from its equilibrium value, at the nth point, and the "conductance" $g_{n,n+1}$ depends upon the jump rates. Then the total change in ψ, across a ladder of points, is just the sum of terms $j/g_{n,n+1}$, one per step.

Let us now go on to point out that the same methods apply to more general dynamic open systems, and to small departures from their steady state. Once again we can discuss a discrete ladder or, alternatively, a continuum system. To emphasize the analogy

Table I

with the equations already written down we will discuss the continuum case. We assume that there is a probability distribution $\rho(q)$, whose flux is j, with q denoting the stochastic variable of interest. We assume

$$j = \rho v(q) - D \partial \rho / \partial q \qquad (T.7)$$

where the first r.h.s. term represents the deterministic laws of motion, and the diffusive term represents the fact that ensemble members are not all compelled to follow that law. We will not pause to ask when the above equation will be a good approximation; that is a more subtle question than the things discussed in this Table.

From (T.7) we find that the steady state distribution function, at j=0, is

$$\rho_{ss} = c \exp \left(\int (v/D) dq \right). \qquad (T.8)$$

If we now assume $\rho = \beta(q) \rho_{ss}$, then

$$j = -D(\partial \beta / \partial q) \rho_{ss} = -D \beta^{-1} (\partial \beta / \partial q) \rho, \qquad (T.9)$$

or $j = -D(\partial \log \beta / \partial q) \rho$. Thus if we let $\psi = \log \beta$ then $j = -D(\partial \psi / \partial q) \rho$ or

$$\psi(q_2) - \psi(q_1) = -\int_{q_1}^{q_2} (j/D\rho) dq. \qquad (T.10)$$

If we are close to the steady state, then, to first order in j, we can replace ρ by ρ_{ss} in the above equation. Just as in the transition from (T.4) to (T.5) we can eliminate ψ, and thus find

$$\frac{\delta \rho(q_2)}{\rho_{ss}(q_2)} - \frac{\delta \rho(q_1)}{\rho_{ss}(q_1)} = -\int_{q_2}^{q_1} (j/D\rho_{ss}) dq \qquad (T.11)$$

without restrictions to small departures from ρ_{ss}.

Let us now break away from the steady state case for some more general remarks. Many authors discuss the "first passage time" question: How long does a particle now at x_0 take to get to x_1, for the first time? While this question exists for all the variants we have discussed above, let us use the specific language appropriate to a continuous coordinate x, and to motion in an overdamped potential, U. Let us insert a current j at point x_0, and remove the particles the moment they reach the location x_1. Thus if $x_1 > x_0$ we will have a solution of the equations, given at the beginning of this Table, in which ψ is constant, for $x < x_0$. At x_0 we must match on to a solution which corresponds to the injected current, and which vanishes at x_1. This matching requires continuity in ψ, or n, at x_0. The particles injected at x_0 will build up a total integrated density proportional to the time they spend in the space under consideration. Thus

Table I

$$j\tau = \int n\,dx, \tag{T.12}$$

where the integral is evaluated from the solution we have described, and gives us the desired averaged first passage time τ. If x_0 is near the bottom of a bistable potential, and x_1 is at the peak of the barrier, then $1/\tau$ is *not* the escape rate. A particle reaching the peak of the barrier has an equal probability of falling back into its original well and continuing on into the new well. This makes the escape rate $1/2\tau$. (This particularly simple explanation for the factor $1/2$ was pointed out to us by B. J. Matkowsky and Z. Schuss.)

The genuinely time-dependent problem, which departs from the steady state that we have discussed, is certainly more complex, and not without interest or importance. It is, however, the steady state result which is often the one that is really needed. Furthermore in the case of a long lived metastable state, the longest of the relaxation times found in the time-dependent problem, can easily be found from the solution of the steady state problem described above, where we inject particles into one well and remove them from the adjacent well (Landauer and Swanson, 1961).

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Figure 3
Complicated potential with many competing states of local stability.

situation in which the band bottom and doping are independent of space, so that the normal drift term is absent. Take the temperature spatially non-uniform, so that D is a function of the coordinate x along which diffusion occurs. Start with an initially uniform carrier density, i.e. $\partial n/\partial x = 0$. Then if we take $j = -D(\partial n/\partial x)$ no current will flow and the carrier distribution will remain uniform. We know, however, that is the wrong answer. Carriers in the hot region tend to leave it faster than they arrive, in turn, from the cold region. The hot regions will end up with a lower steady state carrier density. If, instead, we take $j = -\partial(Dn)/\partial x$, it gives us a carrier redistribution in the expected direction.

Now consider a system in which there is a single, space independent, temperature. Let μ and D be functions of x as a result of reflecting barriers, which have a higher density in one region of space, than in another. Let the barriers be thin enough so that they have no effect on the chemical potential of the carriers, but only on μ and D. If we now start with a spatially uniform carrier distribution, and a flat band bottom, then the carrier distribution should remain flat, i.e. $j = 0$. Only the form $j = -D\partial n/\partial x$ will give that result.

This paradox has been resolved [20], though the resolution doesn't seem to be well known. Briefly put: It is only the total current that is significant, not the diffusion term by itself. The drift term has a compensating ambiguity. Refs. [9,21,22] make it clear that the ambiguity discussed here involves terms with a formal similarity to the widely discussed Ito vs. Stratonovich question [23], but it is in fact a separate and distinct issue. As is made very clear in Ref. [23], the Ito vs. Stratonovich issue arises only if we attempt to start from a Langevin equation. Unfortunately, the distinction between the two questions is sometimes blurred, and we cite one recent example of that [24]. Eq. (2), used by us, is a Langevin equation, and if the temperature were taken to be a function of θ, would get us into the Ito vs. Stratonovich problem. Generally, however, it is possible and advisable to go directly from the physical kinetics to a "master equation" describing the time dependent probabilities, without going through the Langevin equation. Thus, for example, the solid state transport literature discussing motion of particles in a spatially variable potential, e.g. in a transistor, never invokes a Langevin equation.

The r.h.s. of Eq. (6) can be written in two ways

$$j = v\rho - D\frac{\partial\rho}{\partial\theta} = u\rho - \frac{\partial}{\partial\theta}(D\rho), \tag{7}$$

with $u = v + \partial D/\partial\theta$. Ref. [20] pointed to the physical interpretation which distinguishes between the two velocities, u and v. The velocity v measures the unbalance in the flow exchanged *between* nearby points, whereas u measures the unbalance in flow in the two directions away from a *given* point. We will, here, present a simplified version of the discussion in Ref. [20], applicable to the situation where we have a sequence of points on a line, and only allow jumps between adjacent points. We also assume that the occupation probability, P_n, of the nth point, varies only slightly between adjacent points, and make a similar assumption about the jump probabilities. In that case, we can expect to represent the time variation of P_n by a continuum approximation. n can, for example, represent the

number of molecules of a particular species present in an open chemical reaction, the number of quanta in a laser cavity, the number of electrons on a tunnel diode capacitance, or a biological population. Let $W_{n,n+1}$ represent the probability of a jump, per unit time, from the $(n+1)^{th}$ site to the nth site. Similarly $W_{n+1,n}$ represents departures from the nth site to $n+1$. Then the flux from n to $n+1$ is given by

$$j = -W_{n,n+1}P_{n+1} + W_{n+1,n}P_n. \tag{8}$$

Now let

$$W_g = \frac{1}{2}(W_{n+1,n} + W_{n,n+1}), \tag{9a}$$

$$W_u = \frac{1}{2}(W_{n+1,n} - W_{n,n+1}). \tag{9b}$$

Then Eq. (8) becomes

$$j = W_u(P_{n+1} + P_n) - W_g(P_{n+1} - P_n). \tag{10}$$

Clearly this has the form of Eq. (6), differing only as a result of the discretization. The first r.h.s. term of Eq. (10) corresponding to the first r.h.s. or *drift* term of Eq. (6) is proportional to the unbalance in jump rates *between* adjacent points, defined in Eq. (9b). The second r.h.s. term of Eq. (10) contains the population difference $P_{n+1} - P_n$, analogous to $\partial\rho/\partial\theta$, multiplied by W_g, a jump rate which weights jumps in both directions equally. Eq. (10) can also be written in the form:

$$j = \frac{1}{2}P_{n+1}[W_{n+2,n+1} - W_{n,n+1}] + \frac{1}{2}P_n[W_{n+1,n} - W_{n-1,n}] - \mathbf{D}. \tag{11}$$

$\mathbf{D}$ is given by

$$\mathbf{D} = \left[\frac{1}{2}(W_{n,n+1} + W_{n+2,n+1})P_{n+1} - \frac{1}{2}(W_{n+1,n} + W_{n-1,n})P_n\right]. \tag{12}$$

Consider the two r.h.s. terms which are written out in detail in Eq. (11). In the first of these P_{n+1} is multiplied by what is essentially an unbalance in velocities *away* from the point $n+1$. The next term has the same form, but is evaluated at n. The fact that Eq. (11) averages these two terms, evaluated respectively at $n+1$ and at n, is not significant. The basic point: the probability densities, in this term, are multiplied by the unbalance in velocities *away* from a given point, analogous to u. The final term, $\mathbf{D}$, given explicitly in Eq. (12), involves factors of the form $(W_{n,n+1} + W_{n+2,n+1})$. Once again, if the probabilities vary slowly with n, this does not differ seriously from $(W_{n+1,n+2} + W_{n+2,n+1})$. The latter, however, is the symmetrized expression of Eq. (9a), which we have already equated with the diffusion coefficient in our discussion of the second r.h.s. term of Eq. (10). Thus $\mathbf{D}$ has the form $\partial(D\rho)/\partial\theta$, and it is this term which, in Eq. (11), is accompanied by a drift term which contains u, rather than v.

The question which we have just belabored is discussed, with varying degrees of success, in a number of publications. We can cite only a few [25], without analysis of their exact relationship to our discussion.

5. Particle in tube of nonuniform temperature

Noise is not always as simple as in Eq. (3), where it is related to a space independent damping constant, but instead can depend on the state of the system. A simple and instructive example consists of charged particles, in a long thin insulating tube [26]. The particles are assumed to keep their charge unchanged when they bounce into the walls of the tube, but to take on a velocity characteristic of the local wall temperature, at each encounter with the wall. This temperature will be taken to be variable along the length of the tube. The charge on the particle permits us to put the particle in a force field, by depositing charges on the outside of the tube. At first, however, we assume that no such field is present. The cross-section of the tube, and therefore the mean free path, will be assumed to be small compared to the scale of variation along the tube. The particles will be taken to be noninteracting; they do not equilibrate through a gas pressure. Let us also assume the inelastic scattering at the wall to be completely diffuse, so that the direction of the reflected particle will be independent of its direction of incidence. Thus, the geometrical paths of the particles will be independent of the temperature profile; the temperature only influences their speed. The time the particles spend in a given portion of the tube will be inversely proportional to their velocity. Their density then varies a $1/T^{1/2}$. We can come to the same conclusion through the methods of the preceding section. The far r.h.s. form of j, as given in Eq. (7), is valid if u is the average velocity of particles *away* from a given point, rather than the velocity measured by the transitions *between* nearby points. Under the assumption of complete thermalization, u as used above, vanishes. Thus in the steady state $D\rho$ must be constant. Then, if the jump distance involved in the determination of D is temperature independent, it is only the jump frequency, proportional to particle velocity, and thus proportional to $T^{1/2}$, which causes D to vary. Thus, ρ varies as $1/D$, or as $1/T^{1/2}$.

We see, not surprisingly, that particles tend to gather preferentially in the cold parts of the tube. We can also, without further analytical details, assume that if the nonuniformities induced by the temperature variation are large compared to those caused by applied fields, at the typical temperature involved, then the temperature effects will predominate.

6. Open systems and biology

Consider an asymmetric bistable potential well, with two wells of unequal depth, separated by a barrier. In thermal equilibrium it is easy to discuss relative stability, i.e. the relative occupation of the two wells, through the use of the Boltzmann factor. Changing the behavior between the wells, at the barrier, can change the relaxation rate, i.e. the ease with which particles move over the barrier,

but won't change the relative probabilities of occupation between the two wells, in the steady state. More general dynamic systems, with several competing states of local stability, do not have such a simple behavior. These more general systems include the bistable potential well, if different parts of the well are allowed to have different temperatures, as in the case of the particle in the tube that we have just discussed. For such more general systems relative occupation probabilities depend on the detailed kinetics along the whole path between the wells, including the unlikely states near the barrier. This concept, already implicit in Ref. [8], was emphasized in later papers, and it seems superfluous to rederive this point, even though some of the physical chemistry literature was slow to accept it [27,28].

We do, however, want to repeat and stress one obvious consequence. In a multistable system, far from equilibrium, we cannot expect - at least not with great generality - to recognize the steady state distribution function, or the relative probability of the locally stable states, from any examination of the system which is limited to the neighborhood of the most likely states. Commonly advocated principles involving entropy maximization, entropy production, entropy curvature, etc., which typically disregard the behavior near states which are rarely occupied, just will not work. The most well known of these principles, that of minimal entropy production, is, of course, only intended to apply to systems close to thermal equilibrium. Even there, however, it has serious limitations [29], and if stated with sufficient care, cannot be regarded as a very general physical principle.

We have emphasized the need to take fluctuations along the whole pathway into account. There have been attempts to discuss relative stability through generalizations of Maxwell's equal area rule, as applied to the liquid gas phase transition. These attempts (See Ref. [26] for citations) invoke the deterministic equations of the system, without regard to fluctuations. Our viewpoint, stressing the role of fluctuations, is most clearly essential for small systems. In the case of large systems, transitions between relative states of stability occur by nucleation of a new phase, followed by expansion of the nucleus through domain wall motion. The kinetics of wall motion do not, generally, depend appreciably on the fluctuations [6,30]. Thus, in a large system, where there is opportunity for the formation of nuclei and domain walls, the favored phase is determined by the direction of wall motion and, therefore, not by fluctuations. On the other hand, the transition *rate* is determined by the number of nuclei, and these arise through fluctuations. We point out explicitly that if we are concerned with the origin of life, or with molecular biology, we are likely to be concerned with small systems, in which each item of information is contained in a few degrees of freedom.

We now go on to discuss the implications of our viewpoint for evolution, and for the origin of life, adopting an approach which P. W. Anderson [31] has labelled the spin glass view of evolution. In our case it stems from discussions with Charles Bennett, in 1974. We cite only the latest of the papers [32] presenting this view. Evolution is viewed as a progression through a series of states of local stability. Think of these as roughly analogous to the minima of the potential diagram shown in Fig. 3, located at the end of Table I. In contrast to Fig. 3, however, we are not dealing with motion in a potential, but with the time develop-

ment of a more complex open and dynamic system. Evolution, takes us from one long lived state, to another nearby one, through fluctuations. In the later stages of evolution these fluctuations take the form of genetic mutations. These replace the thermal fluctuations in Fig. 3, which can take us from one valley, to a deeper one. In a many dimensional case, corresponding to Fig. 3, the fluctuations typically have to take us far enough to develop a nucleus of the new favored phase; after that the coherent dynamics of the system, via motion of domain walls, can take over. The biological case is very similar. Not just any fluctuation will do, the right genetic mutation that will push us a little way toward the new state is required. After that, the deterministic biological mechanisms can take over. Note, also, that Fig. 3, drawn in one dimension, is misleading in its implication that a transition to a lower lying valley may require a transition toward a valley which is far away. Biological space has a huge number of dimensions, and each state of local stability is surrounded by a great many other states of local stability, and not just two, as in Fig. 3.

If biological evolution can be viewed as described, then the relative stability of locally stable states cannot be evaluated simply by comparing the two states. The kinetics along the pathways must be taken into account. We cannot expect to predict the more likely life forms, or states of ecology, toward which progress is likely to occur, by comparing these states, but must take the pathways into account. In particular, any attempt to invoke thermodynamic or information theoretic comparisons between the competing locally stable states cannot provide answers.

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