PHYSICS OF OUR DAYS

Fluctuation kinetics of reactions

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The fluctuation kinetics of reactions corresponds to a description of the reacting systems at a mesoscopic level. In this approach, a description is written in terms of concentration distributions which are continuous but fluctuating. The basic principles and methods of fluctuation kinetics are illustrated by several specific examples. Particular emphasis is placed on cases in which powerful mechanisms intensify microscopic fluctuations associated with the atomistic nature of the individual reaction events to the point that they determine the outcome of events at macroscopic scales. The situation is analogous to macroscopic quantum effects. In the first main section of the paper, the induction period of a branching chemical reaction is calculated under the assumption of a complete mixing of the reactants and also for the case with spatially inhomogeneous fluctuations. The second section of the paper discusses fluctuations in the course of a two-particle recombination reaction. The third section takes up the spontaneous breaking of chiral symmetry in the course of biological evolution and a possible role of fundamental weak interactions. Appendix I gives the solution of the general problem in which the point of a second-order phase transition in a distributed system is traversed at a finite rate. Appendix II describes mathematical methods of the fluctuation kinetics of reactions.

Induction period of a branching chemical reaction. Recombination of various radicals. Spontaneous breaking of chiral symmetry in biology; fluctuations and pseudoscalar crystals.

INTRODUCTION

Classical chemical kinetics operates with large numbers of atoms and molecules which are participating in a reaction. Under such conditions there is no need to consider the individual atoms or molecules: Their concentration or total number can be treated as a continuous variable. In this manner, differential equations are obtained: ordinary differential equations for a reaction in a well-mixed volume or partial differential equations if concentration depends on the coordinates, and transport of matter by diffusion or by a general motion of the medium must be taken into account.

Classical chemical kinetics takes its place along with chemical thermodynamics as part of the foundation underlying some remarkable practical achievements in chemical technology. Nevertheless, the atomistic nature of the reacting substances does manifest itself in certain specially arranged conditions in the laboratory. Furthermore, there is the possibility that classical kinetics will be incapable of describing the reactions which are responsible for the most unusual—and ultimately the most important—process: the appearance of life.

In this paper, without any specific applications in mind, we will examine certain typical situations in which it is important to allow for the atomistic nature of events. This field is usually called "fluctuation kinetics." The name stems from the circumstance that the atomistic nature of events usually leads to fluctuations in observable quantities from the behavior described by a determinate solution of the classical equations. Furthermore, the word "atomistic" has

deep roots in the sense of the atomic structure of molecules. Its application to kinetics might result in some misunderstanding.

Questions pertaining to the role of fluctuations in the kinetics of chemical reactions have been discussed previously by several investigators.[1-7] It is not our purpose here to offer a comprehensive review of that research. Our intention is instead to suggest to the reader a chain of examples and specific situations which in our opinion illustrate the fundamental principles of fluctuation kinetics. If it is permissible to speak in terms of an essay as a genre of scientific paper, we would prefer to have this paper classified as such.

1. INDUCTION PERIOD OF A BRANCHING CHEMICAL REACTION

We consider a reaction for which the classical equation is, according to Semenov,

$$\frac{dn}{dt} = \alpha n - \beta n + w, \tag{1.1}$$

or

$$\frac{dn}{dt} = \gamma n + w, \tag{1.1'}$$

if we introduce $\gamma = \alpha - \beta$. Here w is the rate at which the particles of interest (e.g., free radicals) are generated, the coefficient α is a measure of the speed at which these particles are bred, and the coefficient β is the rate at which they are consumed.

A solution of Eq. (1.1) under the initial condition $n(t = 0) = 0$ with $\gamma > 0$ is

$$n = \frac{w}{\gamma}(e^{\gamma t} - 1). \tag{1.2}$$

We would speak in terms of an "explosion" if n reached a certain critical value n_c at which the reaction rate became so high that a visible glow appeared, the temperature and pressure rose, there was a significant change in the quantities

of the basic components, etc.

The explosion induction period τ is determined by the condition $n(t = \tau) = n_c$ [under the initial condition $n(t = 0) = 0$], so we find (at a large value of n_c)

$$\tau \approx \frac{1}{\gamma} \ln \frac{\gamma n_c}{w} . \tag{1.3}$$

However, we would like to study this problem from the fluctuation approach. For a chain explosion the rate w at which the active centers are generated is typically small, so the spontaneous formation of an active center (of the S→X type) would generally require an activation energy many times that of a branching reacton (of the type Y + X→Z + 2X). Here X is the chemical symbol of the centers, whose concentration is n.

In classical expression (1.3) the coefficient w appears inside a logarithm. The fluctuation approach leads to a different result. If the chain reaction is to begin, at least one active center must initially be spontaneously created in volume V. The probability for such an event per unit time is wV, and the average time required for the formation of the first center is

$$\tau_1 = \frac{1}{wV} . \tag{1.4}$$

Once an active center has been produced, it begins to breed rapidly. As the chain avalanche grows, one can of course ignore the improbable spontaneous production of new active centers. In this stage of the process the number of active centers increases as $e^{\gamma t}$, so the average induction period is [here we are using $n(t = \tau_1) = 1/V$]

$$\bar{\tau} = \frac{1}{wV} + \frac{1}{\gamma} \ln (V n_c). \tag{1.5}$$

The variance in τ is large:

$$\overline{(\tau - \bar{\tau})^2} \approx \frac{1}{(wV)^2} . \tag{1.6}$$

If the first term dominates expression (1.5) for the induction period, then we have $(\tau - \bar{\tau})^2 \approx \bar{\tau}^2$.

Actually, this is again an approximate expression; specifically, it is an underestimate. When there is branching, characterized by the coefficient α, and rupture of bonds (a consumption of active centers), characterized by β, an active center, considered separately, will convert at a probability $\frac{\alpha}{\alpha + \beta}$ into two centers, while it will be consumed at a probability $\frac{\beta}{\alpha + \beta}$. By following the fate of successive generations one finally finds the probability that an isolated center will give rise to an unquenched chain reaction[1]:

$$\xi = 1 - \frac{\beta}{\alpha} . \tag{1.7}$$

The corrected value of the average induction period is thus[8]

$$\bar{\tau} = \frac{\alpha}{\gamma} \frac{1}{wV} + \frac{1}{\gamma} \ln (V n_c). \tag{1.8}$$

Near the threshold, with $\gamma \ll \alpha, \beta$, incorporating this circumstance leads to a significant increase in $\bar{\tau}$.

Finally, if the volume V is large, the spontaneous appearance of separate active centers will lead to the formation of independent ignition points and to the propagation of a flame away from these points. In this case we would expect to see the appearance of an unusual spatial structure for the reaction. To determine the structure we need to find the ve-

locity at which the reaction propagates away from an ignition point which arises locally.

The well-known solution of the problem of chain propagation in its biological formulation was found back in 1937, independently by Kolmogorov, Petrovskiĭ, and Piskunov in the USSR[9] and by Fisher in England.[10] They considered specifically an unstable medium with a diffusion described by the equation

$$\frac{\partial n}{\partial t} = \gamma n + D \Delta n. \tag{1.9}$$

Since the spontaneous-creation term [i.e., w; see Eq. (1.1')] has been discarded, the mixture will react only if new active centers enter it from the outside, by diffusion. We know that the propagation velocity, i.e., the coefficient v_0 in a solution of the type $n = f(x - v_0 t)$, is given by

$$v_0 = 2 (D\gamma)^{1/2}. \tag{1.10}$$

When the initial equation is used, it is always presupposed that the reaction comes to a halt at $n > n_c$. Whether it comes to a halt abruptly $\left(\frac{dn}{dt} = 0 \text{ at } n > n_c \right)$ or smoothly $\left(\frac{dn}{dt} \sim n(n_c - n) \right)$ is unimportant for the propagation velocity.

The flame spans the entire medium when the flame ignition points grow together. This problem is similar to that of the crystallization of a supercooled liquid, which was solved back in 1938 by Kolmogorov.[11] The idea embodied in the derivation of this approximate formula is to determine the volume which is traversed from a given center (the first ignition center) until a new center of this sort is found within the volume. It is easy to see that the volume of an individual flame ignition region by the time at which these regions merge is of specifically this order of magnitude.

We assume that the unknown volume satisfied $V \sim l^3$. It can be seen from (1.8) that the average time over which an ignition center appears in volume V and gives rise to an unquenched chain reaction is $\alpha/\gamma wV$. This time must be the same as the lifetime of the original ignition region, l/v_0. We then find

$$\frac{l}{v_0} \sim \frac{\alpha}{\gamma w l^3} , \tag{1.11}$$

and thus

$$l \sim \left[\frac{\alpha (D/\gamma)^{1/2}}{w} \right]^{1/4} . \tag{1.12}$$

Let us rewrite the quantities of interest here in a unified way in terms of molecular kinetics. Let the density of the gas (the primary component of the gas) be N. This quantity varies only slowly in the course of the reaction, in contrast with n, the concentration of the active centers, which we are following. The gas-kinetics cross section is denoted by σ; the mean free path is then $\lambda = (N\sigma)^{-1}$. We denote by c the average velocity of the molecules.

The reaction rate is described by dimensionless coefficients: the ratios of the reaction cross sections to the gas-kinetics cross section. Specifically, we set

$$\alpha = a\sigma cN, \quad \beta = b\sigma cN, \quad \gamma = \Gamma\sigma cN, \quad w = g c \sigma N^2. \tag{1.13}$$

We are referring the reaction rate to the number of collisions per unit time, with the gas-kinetics cross section of molecules having an average gas-kinetics velocity c. The differ-

ence between the velocity of collisions which result in a reaction and the average velocity c is contained in the factors a, b, and Γ. Within a dimensionless coefficient we can set $D = c\lambda = c(N\sigma)^{-1}$.

We finally find

$$l = \frac{a^{1/4}N^{-1/2}\sigma^{-1/4}}{g^{1/4}(a-b)^{1/8}}. \qquad (1.14)$$

It is instructive to compare this quantity with the mean free path:

$$\frac{l}{\lambda} = \frac{N^{1/2}\sigma^{3/4}}{g^{1/4}} \cdot \frac{a^{1/4}}{(a-b)^{1/8}} \sim \frac{a^{1/4}}{\Gamma^{1/8}g^{1/4}} \cdot \frac{\rho_{gas}}{\rho_{liq}}. \qquad (1.15)$$

In the last expression we have taken the average distance between liquid molecules to be of the order of the gas-kinetics radius $r_{kin} = \sigma^{-1/2}$. We then find the estimate $N_{liq} \sim r_{kin}^{-3} \sim \sigma^{-3/2}$ and then the expresion written above. We wish to stress that the theory is meaningful only under the condition $l/\lambda \gg 1$. Since the density of a gas is always lower than that of a liquid, we require

$$\frac{a^{1/4}}{\Gamma^{1/8}g^{1/4}} \ll 1. \qquad (1.16)$$

This inequality can be satisfied if the branching is slow ($\Gamma \ll 1$) and/or the creation of active centers is rare ($g \ll 1$).

The theory contains yet another distance, and associated with it is yet another dimensionless quantity. We find the characteristic width of the flame front:

$$h = \frac{D}{v_0} \sim \left(\frac{D}{\gamma}\right)^{1/2}. \qquad (1.17)$$

Again reducing all quantities to the cross section, the molecular velocity, and the dimensionless coefficient, we easily find

$$\frac{h}{\lambda} = \frac{1}{\Gamma^{1/2}}. \qquad (1.18)$$

This is a well-known result: The width of a flame front is equal in order of magnitude to the mean free path of a molecule multiplied by the square root of the number of collisions required for a reaction. A continuum description is valid only in the case $h \gg \lambda$, i.e., only if the branching is slow ($\Gamma \ll 1$).

Expression (1.8) for the induction period, which was derived in the approximation of complete diffusive mixing, thus becomes inapplicable once the dimensions of the vessel become greater than l. The induction period is instead given by the following expression, which holds within logarithmic corrections, in order of magnitude (the induction period is now to be understood as the time which elapses until the entire mixture is in flame):

$$\bar{\tau} \sim \frac{l}{v_0} \sim \frac{1}{\gamma^{5/8}}\left(\frac{\alpha}{wD}\right)^{1/4}. \qquad (1.19)$$

The induction period ceases to depend on the volume of the vessel.

The basic idea of fluctuations in the induction period was expressed in Ref. 8. Other questions dealing with fluctuations in media with an explosive instability were discussed in Refs. 7, 12, and 13 (in particular, these questions involved a fluctuation lowering of the threshold for an explosion or of the limit of a chain reaction; see Ref. 12). Similar arguments were used in Ref. 14 in a study of multiple generation and the competition among sources of oscillations (guiding centers) in active media.

2. RECOMBINATION OF VARIOUS RADICALS

Let us consider the equilibrium or steady-state situation for the reaction

$$A + B \rightleftarrows C. \qquad (2.1)$$

This reaction is at equilibrium if it goes in both directions as a result of thermal motion. In this case the concentrations A, B, and C are related by the thermodynamic law of mass action:

$$\frac{AB}{C} = f(T). \qquad (2.2)$$

We note in particular that this model has no pair recombination: $A + A \neq A_2$, $B + B \neq B_2$.

The steady-state situation differs in that A and B are formed as a result of a continuous influx of energy, e.g., when the system is irradiated with photons ν:

$$A + B \rightleftarrows C + \nu. \qquad (2.3)$$

In this case we have

$$\frac{AB}{C} = K\nu \qquad (2.4)$$

and the coefficient K is determined by kinetic and optical quantities.

We asume that we have $A = B = 0$ and $C = C_0$ at the initial time. During the relaxation, equal amounts of the substances then appear ($A = B$). We now assume that the temperature decreases instantaneously and identically throughout the volume, so that beginning at $t = 0$ we have $f = 0$, or we have turned off irradiation instantaneously.[2)] Let us examine the bimolecular recombination

$$A + B \rightarrow C \qquad (2.5)$$

which then occurs, adopting the initial condition $A = B = A_0$. We assume that this process goes in a liquid or at a constant impurity of an inert gas, so that we need not be concerned about the removal of energy and momentum or about ternary collisions.

In the macroscopic approximation the problem is trivial:

$$\frac{dA}{dt} = -\varkappa AB = -\varkappa A^2, \qquad (2.6)$$

$$A = \frac{A_0}{1 + \varkappa A_0 t} \rightarrow \frac{1}{\varkappa t} \quad \text{at} \quad \varkappa A_0 t \gg 1. \qquad (2.7)$$

Result (2.7), however, is incorrect in the asymptotic limit $t \rightarrow \infty$. The correct result can be found only by fluctuation kinetics incorporating the natural nonuniformity of the distributions of A and B.

Let us examine in more detail the initial stage, before the radiation is turned off. Even if we were to prepare beforehand a completely homogeneous distribution of the molecules A and B, random inhomogeneities would appear in it because of diffusion (i.e., because of a random Brownian motion). The atomistic nature of the recombination reaction and of the inverse reaction will also generate random inhomogeneities in the distributions of molecules A and B.

If the distance which molecules A and B move apart during their pair generation involving the absorption of a photon is small, of the order of the radius of the binary recombination reaction, diffusion will play a leading role in the formation of a random spatial distribution of the molecules. The A and B molecules become distributed in accordance

with a Poisson law as a result of diffusion; these distributions for the different molecules are established independently. In a small volume (but a volume which is still large enough that the number of A molecules in it is much greater than one), the deviations are, on the average, of such a nature that we can write

$$[(w - \overline{w})^2]^{1/2} = \overline{w}.$$ (2.8)

A spectral decomposition of a random distribution of this sort results in a flat spectrum. Specifically, an isolated A molecule is described by a function $\delta(\mathbf{r} - \mathbf{r}_A)$ which obviously has a flat spectrum:

$$a_k = \frac{1}{V^{1/2}} \int \delta(\mathbf{r} - \mathbf{r}_A) e^{-i\mathbf{k}\mathbf{r}} \, d\mathbf{r} = \frac{1}{V^{1/2}} e^{-i\mathbf{k}\mathbf{r}_A},$$
$$|a_k|^2 = \frac{1}{V}.$$ (2.9)

If we have many molecules, the Fourier component a_k will be given by the sum

$$a_k = \frac{1}{V^{1/2}} \sum_j e^{-i\mathbf{k}\mathbf{r}_j}.$$ (2.10)

In a Poisson distribution all the molecules occupy uncorrelated positions, so the phases in some (2.10) are random and independent. The spectrum of the distribution of A molecules will thus be flat (i.e., will be the sum of square of moduli)

$$\langle |a_k|^2 \rangle = \frac{\overline{N}}{V} = \overline{A}.$$ (2.11)

The spectrum of the distribution of B molecules will be of the same nature.

The subsequent course of events after the lowering of the temperature or the cutoff of the radiation is described as a reaction for arbitrary spatial distributions $A(\mathbf{r}, t)$ and $B(\mathbf{r}, t)$:

$$\frac{\partial A}{\partial t} = -\varkappa AB + D \Delta A,$$
$$\frac{\partial B}{\partial t} = -\varkappa AB + D \Delta B.$$ (2.12)

For simplicity we assume $D_A = D_B$.

The local difference between the two concentrations, $s = A - B$, satisfies the pure diffusion equation

$$\frac{\partial s}{\partial t} = D \Delta s.$$ (2.13)

Avoiding the mathematical details, we consider a limiting case. After a certain time we can assume that the B molecules disappear completely from regions with an initial excess of A molecules:

$$A - B = s > 0, \quad A = s, \quad B = 0.$$ (2.14)

In other regions, only B molecules remain:

$$A - B = s < 0, \quad A = 0, \quad B = -s.$$ (2.15)

Consequently, the entire medium in which the recombination reaction proceeds can be partitioned into regions of two types, filled exclusively with A molecules or filled exclusively with B molecules.

How can we find the average dimensions of these regions and the average A and B concentrations in the regions of each type? The magnitude of the difference $s = A - B$ does not depend on the chemical reaction. According to the diffusion equation (2.13), the individual Fourier compo-

nents evolve in time in accordance with

$$s_k(t) = s_k(0) e^{-Dk^2 t};$$ (2.16)

in other words, the spectrum is effectively cut off at $k > (Dt)^{-1/2}$ at each instant. We also note that the spectrum is initially flat (at $t = 0$):

$$\langle |s_k(0)|^2 \rangle = \overline{A} + \overline{B} = 2A_0;$$ (2.17)

(since the positions of all the A and B molecules are uncorrelated).

Since the spectrum $\langle |s_k(t)|^2 \rangle$ contains only a single characteristic length, $(Dt)^{1/2}$, it is this length which will determine the typical dimensions of the A and B regions.

Since the A and B molecules are separated in different spatial regions, we have $\langle AB \rangle = 0$. Consequently, by virtue of the completeness theorem for a Fourier integral we can write

$$\int (A^2 + B^2) \, dV = V(\overline{A^2} + \overline{B^2}) = \int \langle |s_k|^2 \rangle \, d\mathbf{k}.$$ (2.18)

Also using (2.16), we find the law describing the decrease in $\overline{A}$ and $\overline{B}$ with time:

$$\overline{A^2} = \overline{B^2} \sim A_0 (Dt)^{-3/2},$$ (2.19)

and therefore

$$\overline{A} = \overline{B} \sim A_0^{1/2} (Dt)^{-3/4}.$$ (2.20)

This difference between the asymptotic decay laws was first pointed out in a note[15] published in 1977. We recall that classical kinetics, without fluctuations yields the asymptotic behavior $\overline{A} = \overline{B} \sim t^{-1}$ after a long time.

These results were subsequently derived by more rigorous methods in Refs. 5 and 16. In addition, a study was made of the more complicated case in which the A and B molecules initially move apart a large distance when they are formed, so that in practice they can be assumed to be produced one by one. In such a production process, the distribution of A molecules (and that of the B molecules) which is established does not have a flat spectrum: If k is not too large, the spectrum is a power-law spectrum[3]

$$\langle |a_k|^2 \rangle \sim \frac{1}{k^2}.$$ (2.21)

After the generation is terminated, the quantities $\overline{A}$ and $\overline{B}$ then vary in accordance with some other asymptotic law. We will not go into this situation in detail here; we refer the reader to Ref. 17.

We now consider the geometric structures which arise in the problem. In the one-dimensional case, it is sufficient to imagine a smooth random function $s(x)$ which has a flat spectrum, cut off at $k > (Dt)^{-1/2}$, and a zero mean value. This funciton obviously crosses zero (i.e., intersects the abscissa) many times. Each such crossing represents a boundary between a region occupied by A molecules and a region with B molecules. For brevity we will call these regions "A-regions" and "B-regions," respectively.

To find the velocity at which the boundary moves we note that the position of the boundary at time t is determined by the equality $s(x_0(t), t) = 0$. Differentiating it with respect to the time, we find

$$\frac{dx_0}{dt} \frac{\partial s}{\partial x}\bigg|_{x_0} + \frac{\partial s}{\partial t}\bigg|_{x_0} = 0.$$ (2.22)

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On the other hand, s obeys a diffusion equation, so we can write

$$\frac{\partial s}{\partial t}\Big|_{x_0} = D\,\frac{\partial^2 s}{\partial x^2}\Big|_{x_0}. \qquad (2.23)$$

Substituting (2.23) into (2.22), we find the displacement velocity of the boundary:

$$\frac{dx_0}{dt} = -D\,\frac{\partial^2 s/\partial x^2}{\partial s/\partial x}\Big|_{x=x_0(t)}. \qquad (2.24)$$

To illustrate equation (2.24), we consider the displacement of a boundary in the particular case in which two regions with maximum concentrations A_m and B_m and characteristic linear dimensions L_A and L_B, respectively adjoin each other. This situation corresponds, for example, to the $s(x)$ dependence

$$s = \frac{A_m\,(e^{x/L_A}-1)-B_m\,(e^{-x/L_B}-1)}{e^{x/L_A}+e^{-x/L_B}}. \qquad (2.25)$$

Carrying out some calculations on the basis of (2.24), we find

$$\frac{dx_0}{dt} = -\frac{1}{2}\,D\,\frac{A_m-B_m}{A_m L_B+B_m L_A}. \qquad (2.26)$$

As an order-of-magnitude estimate, expression (2.26) obviously holds even when the detailed distributions of the concentrations in the adjoining A- and B-regions are different. According to (2.26) if the maximum concentration (A_m) in the A-region is higher than the maximum concentration B_m then the boundary will shift to the right, and the A-region will grow at the expense of a shrinkage of the B-region. Since the concentration of molecules in a region is usually higher, the greater the linear dimension of the region, we are led to the conclusion that as time elapses the large regions will eat up the small regions, and the total number of regions will decrease.

In the two- and three-dimensional cases, the motion of a boundary between A- and B-regions will also be affected by a curvature of this boundary. We introduce a coordinate system whose z axis runs perpendicular to the boundary and whose x and y axes run along the principal axes of the curvature tensor of the interface. After the simple introduction of the Laplacian written in terms of these coordinates, we find

$$\frac{dz_0}{dt} = -D\,\frac{\partial^2 s/\partial z^2}{\partial s/\partial z}\Big|_{z=z_0(t)} - D\left(\frac{1}{R_1}+\frac{1}{R_2}\right), \qquad (2.27)$$

where R_1 and R_2 are the two principal radii of curvature of the interface at the point under consideration.[4]

The meaning of the terms which depend on the curvature is a smoothing of sharp A tentacles which penetrate into the B-region and also a rapid annihilation of small A islands in B or of small B islands in A.

In practice, therefore, there will be general decrease in the sizes of the regions and a decrease in the number of A- and B-regions as time elapses.

Actually, the partitioning into A- and B-regions is an idealization. As time elapses the A and B molecules react, and this reaction is obviously possible only if there is some overlap at the boundary. This overlap between two annihilating components which are transported by diffusion from the exterior into the reaction zone was actually studied[18] back in 1948 as part of a study of the combustion of unmixed gases. A corresponding analysis was recently undertaken[19]

in connection with an astrophysical problem.

At the boundary we have $s = 0$, so we can set $s = \mu x$ in a small neighborhood of the boundary. The reaction does not appear in the equation for s, so the displacement of the boundary and the change in the coefficient μ are determined by a far slower diffusion process. In calculating the overlap zone we can assume that the position of the boundary and the value of μ remain constant.

For the sum $q = A + B$ we find from (2.12)

$$\frac{\partial q}{\partial t} = -\frac{1}{4}\,\varkappa\,(q^2-s^2)+D\,\frac{\partial^2 q}{\partial x^2}. \qquad (2.28)$$

Taking account of the comments made above, we write the following equation for the behavior of q in the overlap zone:

$$D\,\frac{d^2 q}{dx^2} = \frac{1}{4}\,\varkappa\,(q^2-\mu^2 x^2) \qquad (2.29)$$

with the boundary condition $q\to\mu|x|$ as $x\to\pm\infty$.

Introducing the dimensionless variables

$$q = \left(\frac{D\mu^2}{\varkappa}\right)^{1/3}\tilde{q},\quad x = \left(\frac{D}{\varkappa\mu}\right)^{1/3}\tilde{x} \qquad (2.30)$$

we can put this equation in the form

$$\tilde{q}'' = \frac{1}{4}(\tilde{q}^2-\tilde{x}^2), \qquad (2.31)$$

where $\tilde{q}\to|\tilde{x}|$ as $\tilde{x}\to\pm\infty$.

The width of the overlap zone is thus given in order of magnitude by

$$l_v = \left(\frac{D}{\varkappa\mu}\right)^{1/3}, \qquad (2.32)$$

and the concentrations A and B in this zone are given in order of magnitude by

$$A(0) = B(0) \sim \left(\frac{D\mu^2}{\varkappa}\right)^{1/3}. \qquad (2.33)$$

The overlap zone becomes narrower, and the concentration of molecules in it smaller, as the recombination becomes more rapid, i.e., as the recombination rate $\varkappa$ increases.

Equations (2.32) and (2.33) contain μ, which can be found on the basis of the following considerations. As we mentioned earlier, the characteristic dimension of the A- and B-regions at a time t after the irradiation is cut off will be $L(t) \sim (Dt)^{1/2}$, while the characteristic concentration of the A and B molecules in these regions will be $\overline{A}=\overline{B} \approx A_0^{1/2}(Dt)^{-3/4}$ [see (2.20)]. Adopting $\overline{A}/L$ as an estimate of μ, we find

$$\mu(t) \sim A_0^{1/2}(Dt)^{-5/4}. \qquad (2.34)$$

By the time t the width of the overlap zone thus becomes

$$l_0 \sim \left(\frac{D^2}{\varkappa^2 A_0}\right)^{1/6}(Dt)^{5/12}. \qquad (2.35)$$

As time elapses, the boundary layer broadens, but at a slightly slower pace than the dimensions of the A- and B-regions grow:

$$\frac{l_0}{L} \sim \left(\frac{D^2}{\varkappa^2 A_0}\right)^{1/6}(Dt)^{-1/12}. \qquad (2.36)$$

We wish to emphasize that (2.36) applies to the case of a three-dimensional medium. For a two-dimensional medium we would have

$$\overline{A}(t) \sim A_0^{1/2}(Dt)^{-1/2}, \qquad (2.37)$$

and thus

$$l_0 \sim \left(\frac{D^2}{\varkappa^2 A_0}\right)^{1/6} (Dt)^{1/3}; \quad \frac{l_0}{L} \sim \left(\frac{D^2}{\varkappa^2 A_0}\right)^{1/6} (Dt)^{-1/6}. \quad (2.38)$$

In the one-dimensional case we find

$$\bar{A}(t) \sim A_0^{1/2} (Dt)^{-1/4},$$

$$l_0 \sim \left(\frac{D^2}{\varkappa^2 A_0}\right)^{1/6} (Dt)^{1/4}, \quad \frac{l_0}{L} \sim \left(\frac{D^2}{\varkappa^2 A_0}\right)^{1/6} (Dt)^{-1/4}. \quad (2.39)$$

As time elapses, the approximate description in terms of A- and B-regions becomes progressively more accurate, since the relative width of the overlap zone decreases.

Let us examine in more detail the properties of the spatial structure which is formed by these regions. Generally speaking, the spatial picture of a distribution has a hierarchical nature. Inside a closed B-region one may find closed A-regions; inside the latter one may find even smaller closed B-regions; etc.—down to a length scale $L = (Dt)^{1/2}$. If we do not reach this limiting length scale, then the set of regions occupied by the A (or B) molecules forms (in the sense of an intermdiate asymptotic behavior) an exceedingly complicated fractal structure.

The primary quantitative characteristic of this fractal structure is the size distribution of the closed regions.

A closed region can be characterized by its volume. We consider a large section of the medium. In it we count the number of closed A-regions with volumes between Ω and $\Omega + d\Omega$ (ignoring whether these closed regions are nested inside some larger A-regions in this section of the medium). Taking counts of this sort for various sections of the medium, we can construct a distribution in volume, $\nu_A(\Omega)$, such that $\nu_A(\Omega)d\Omega$ tells us the number of closed A-regions which have volumes between Ω and $\Omega + d\Omega$ per unit volume of the medium.

Since we are now considering regions with spatial dimensions far greater than $(Dt)^{1/2}$, the spectrum of the distribution can be assumed flat: $\langle |s_k|^2 \rangle = \text{const.}$ In other words, in this interval of dimensions spatial modes with all wave vectors are equiprobable, and there is no distinctive spatial dimensions. Consequently, the picture of the A- and B-regions should have the property of self-similarity.

Let us consider some volume V of the medium. In it there will be $dN = V\nu_A(\Omega)d\Omega$ closed A-regions with volumes between Ω and $\Omega + d\Omega$. We then consider the volume $V' = V/2^3$, with linear dimensions half as large. Inside it there will be $dN' = V'\nu_A(\Omega')d\Omega'$ closed A-regions with volumes between $\Omega' = \Omega/2^3$ and $\Omega' + d\Omega'$ where $d\Omega' = d\Omega/2^3$. Invariance under a spatial scale transformation requires $dN' = dN$. We thus find the functional equation

$$\nu_A(\Omega) = \frac{1}{2^6} \nu_A\left(\frac{\Omega}{2^3}\right). \quad (2.40)$$

It is not difficult to verify that this equation is satisfied only by a distribution $\nu_A(\Omega) = C/\Omega^2$ with a coefficient C which we do not know at this point. The equality $\bar{A} = \bar{B}$ means that we have $\nu_B(\Omega) = \nu_A(\Omega)$.

Because of the hierarchical nature of the picture, one finds inside any closed A-region smaller B-regions of various sizes. If we subtract from the total volume Ω of the A-region the total volume of all of its subregions containing exclusively B particles, and if we average the result over all the A-regions with a volume Ω, we find the quantity $\Lambda_A(\Omega)$, which

is the average pure volume filled with A particles inside an A-region of volume Ω. In a corresponding way, we can determine $\Lambda_B(\Omega)$.

For these quantitites we can write the integral equation

$$\Lambda_A(\Omega) = \Omega - \int_0^{\Omega} \nu_B(\Omega') \Lambda_B(\Omega') \Omega' \, d\Omega'. \quad (2.41)$$

Scale invarinace means that under the equality $\bar{A} = \bar{B}$ the A molecules in any closed region will, on the average, occupy exactly half the volume, as will the B molecules. We can thus write $\Lambda_A(\Omega) = \Lambda_B(\Omega) = \Omega/2$. Substituting this relation into (2.41), we finally find

$$\nu_A(\Omega) = \frac{1}{\Omega^2}. \quad (2.42)$$

Let us discuss this result. First, it shows that there is a finite probability for finding closed regions of arbitrarily large volume in the spatial picture. This conclusion means that self-averaging does not occur when we scale up to very large sections of the medium: There exists a nonzero probability that this entire section will be occupied by a single closed region.

The spatial picture is of a fractal nature down to a resolution of the order of $(Dt)^{1/2}$, which is the minimum size of the regions which survive to time t after irradiation has been cut off. As time elapses, progressively larger regions disappear, but in other respects the pattern retains its self-similarity properties at large scales.[5]

In chemistry the effects described above occur only at very low concentrations of neutral A and B molecules. If A and B are charged particles (e.g., A^+ and B^- ions), electrostatic forces will sharply reduce the charge fluctuations; i.e., the value of $s = A^+ - B^-$. A length of the order of the Debye length becomes the characteristic length.

There is a simple way out here, however: adding an inert electrolyte. In particular, to Ag^+ and Cl^- ions we might add an excess of $NaNO_3$ (which yields Na^+ and NO^-_3 ions in solution). Without influencing the $Ag^+ + Cl^- = AgCl$ reaction, the sodium ions and the NO^-_3 ions make possible thermodynamic fluctuations of the Ag^+ and Cl^- at a level typical of neutral molecules.

3. SPONTANEOUS BREAKING OF CHIRAL SYMMETRY IN BIOLOGY; FLUCTUATIONS AND PSEUDOSCALAR CRYSTALS

The question of a possible breaking of chiral symmetry (the dextrorotatory and levorotatory forms of molecules) is presently a subject of intense interest in organic chemistry. The interest stems from the asymmetry of proteins and DNA in all known varieties of life on earth.[6] The breaking of chiral symmetry is thus related to the exceedingly important problem of the appearance of life.

There are two fundamentally different answers to the question of biological asymmetry:

I) The origin of life is an exceedingly improbable process, which has occurred only once, with a definite sign of chirality. The propagation of this life has altered the conditions, and the appearance of life with a different chirality has become impossible.

II) At the lower levels of biosynthesis various physical factors associated with breaking of parity lead to a slight

violation of the chiral symmetry of the system as a whole (slight but still not zero, and having a definite sign). Autocatalytic effects subsequently amplify the slight asymmetry, raising it to 100% chiral purity of the biological world.

Let us examine this second possibility in more detail.

About 30 years ago it was suggested that there exists an interaction which breaks the chiral symmetry of the forces which connect electrons to a nucleus.[21,22] This form of the weak interaction has now been proved completely and comprehensively by experiments. The Z^0 boson, with a mass almost 100 times the mass of a proton, has been found: the mediator of a parity-breaking interaction. It is specifically this large mass which keeps the corresponding interaction small. Parity-breaking "chiral" effects have been found in the scattering of electrons.[23] After a prolonged debate, it was established that the polarization plane of light can be rotated by an atomic vapor of bismuth.[24-28] In vapor form, bismuth is monatomic; this particular substance was chosen because in heavy nuclei the electron wave function has a maximum density at the nucleus, and the interaction of interest is of short range.

For organic molecules of the amino acid type the difference between the energies of the dextrorotatory and levorotatory forms is about[29] 10^{-17} of the thermal energy at room temperature (i.e., $\Delta\mathscr{E}/k_B T \sim 10^{-17}$). We would thus need about 10^{17} molecules if the average number of dextrorotatory molecules is to deviate by one from the number of levorotatory molecules. However, 10^{34} molecules are required if the excess of dextrorotatory molecules over levorotatory molecules is to reach a value of the order of the average fluctuation in the total number of particles in such a volume.

Another factor which would cause an asymmetry is the kinetics of radiolysis processes. There is the well-known effect[30] (see also Ref. 31), and *not a small effect*, of a difference in the rates of photochemical reactions for the cases in which the light has different circular polarizations. The spin of an electron becomes polarized in β-decay processes. This polarization of electrons leads to a difference by a factor of the order to $\hbar\omega/k_B T \sim 10^5$—$10^6$ in a photochemical effect. However, it is difficult to estimate the relative importance of radiolysis in biological synthesis reactions. If this relative importance is some 1–10%, for example, the asymmetry effect will outweigh the fluctuations at 10^{12}–10^{16} molecules. The effect is much greater (under these assumptions) than the statistical effect mentioned above, but still it is very small.

Consequently, by itself an asymmetry of the weak interaction cannot explain the chiral purity of biological organisms. This purity must stem from nonlinear amplifying factors of some sort.

For systems which are at thermodynamic equilibrium and which consist of ideal gases it would be an easy matter to prove the intuitively obvious theorem that an equilibrium state is unique.[32] A small change in the thermodynamic or kinetic parameters will cause a correspondingly small change in the equilibrium state.

Under conditions to which this theorem applies, small changes in the energy or rate of a reaction of right-handed isomers in comparison with that for left-handed isomers thus could not cause anything in the way of a significant chirality in a system.

In order to explain the observed asymmetry we would need a sharp violation of at least one of the assumptions on which the theorem is based.

We first consider a very nonideal system, specifically, a liquid or solid phase, rather than a gas. Let us recall some basic facts. From a racemic mixture of d and l salts of tartaric acid, the d and l salts crystallize separately. We know that it was from specifically these crystals that Pasteur was able to select d forms and l forms separately (distinguishing them on the basis of their facets at corners).

We see in this example that the d-d and l-l affinity is greater than the d-l affinity. The advantage here stems from the geometry and relative arrangement of the molecules. The advantage is of the order of a few times $k_B T$ and has no bearing on effects associated with the breaking of chiral symmetry at the level of the electron-nucleus interaction.

Back in 1974 one of us[33] suggested the possibility that pseudoscalar liquid crystals might exist. For a pseudoscalar crystal the order parameter would be the chirality field of the molecules making up the liquid, i.e., the local difference between the concentrations of the d and l isomers (or a chirality-asymmetric arrangement of molecules), in contrast with the situation in ordinary liquid crystals, where the order parameter is the spatial orientation of the liquid molecules.

Any ordering involves a breaking of symmetry. An ordinary solid crystal violates both spatial isotropy and homogeneity, i.e., all the elements of the Poincaré group. A liquid crystal allows a common displacement but is characterized by a distinct direction of the director; the rotation group of three-dimensional space is violated. The pseudoscalar liquid crystal under discussion (if it existed) would violate the reflection point group.

We recall that objects which violate reflection symmetry undoubtedly exist: We started from that position. One such object is sweet water, i.e., a solution of ordinary sugar. (Is it not miraculous that beet sugar and cane sugar are identical in this regard.) In a weak solution, however, these systems are undoubtedly not at equilibrium. They undergo racemization in the presence of a suitable catalyst, with an entropy advantage of $R \ln 2$ per mole. A concentrated solution or a molten solution, however, may behave in a different way! Intermolecular forces may cause such a solution or melt to stratify into right-handed and left-handed pseudoscalar liquid crystals.

The picture of the phenomenon depends on the rate of the racemization process. If the probality for the conversion of one mirror isomer into the other is negligibly small, we are dealing with the problem of stratification of two immiscible liquids. A racemic mixture of two isomers decomposes into regions occupied by isomers of different chirality.

The situation changes if there are rapid conversions between isomers. Stereoselective interactions make a chirally pure state—levorotatory or dextrorotatory—more favorable from the thermodynamic standpoint. As a result, there is a spontaneous breaking of chiral symmetry throughout the liquid, and a nonzero average order parameter arises. The appearance of a pseudoscalar crystal of this sort upon a change in the parameters of a medium would occur through a second-order phase transition.

The parity-nonconserving weak interaction creates an external field associated with the order parameter. As was mentioned above, however, this field is so weak that it would

ordinarily not have to be taken into consideration. In nonliving nature there is nothing in the way of a significantly expressed chirality of molecules.

The principal biological molecules are very stable with respect to racemizing conversions. Opposite mirror isomers usually cannot participate in the finely fitted biochemical reactions in a living cell, where frequently one molecule is obliged by its very shape to fit into another molecule as a key in a lock (see, for example, the interesting paper which Gol'danskiĭ et al.[34] recently published). Racemization would have resulted in malfunctions of the operation of a cell. Consequently, it is to the advantage of a living organism to construct itself from chirally pure molecules, which are stable with respect to racemization: This tendency is strengthened genetically and is passed on from generation to generation.

We wish to stress that the pioneering studies carried out by Morozov and Goldanskiĭ played a major role in the formulation of the problem of the causes and paths to the development of the chiral purity of the biosphere. The results of their studies[35-41] are set forth in detail in a recent review.[42] These questions have also been discussed in several papers by Prigogine and his colleagues.[43-47]

Life on earth had a beginning. When it arose, the chiral symmetry characteristic of nonliving nature was violated. Whether this violation was a random event or imposed by the asymmetry of the weak interaction is one of the most profound puzzles.[7] In either case, some powerful mechanisms would have to come into play to amplify a small initial asymmetry.

We have only indirect data regarding the processes which occurred during the initiation of life. The situation here is somewhat similar to that of the appearance of the universe. The only possibility is to construct various scenarios of events and to compare their remote consequences with observable effects.

Various scenarios for the appearance of life have been proposed.[48-50] We would like to call the reader's attention to the recent book by Dyson,[51] which advances a new and fairly plausible scheme of events, developing ideas expressed by A. I. Oparin.

According to Dyson, the first stage in the initiation of life consisted of random selection of combinations of organic molecules which were of such a nature that they were capable of a cooperative catalysis in some of the coacervates or droplets floating in the primordial world ocean. These combinations began to perform a chemical conversion of substances in the world ocean. These organic molecules became the first enzymes. A metabolism process, i.e., an exchange of substances—the most important property of all life—began.

These "living" droplets were initially not yet capable of reproduction. Molecular mechanisms of reproduction and inheritance appeared only in a later second stage. Because of random mutations, some of the enzymes in some of the "living" droplets acquired autocatalytic properties.[8] Through replication they began to produce similar entities. A chain reproduction of molecules of an inheritance nature began. The growing droplets broke up; their number increased; a competition for the nourishing substrate arose; a pollution of the environment with reaction products occurred; and these processes were accompanied by natural selection.

The first "living" droplets, which consisted of enzymes alone and which were incapable of reproduction, appeared in a random manner from a racemic solution, so their mirror forms occurred with identical frequencies. Also identical were the probabilities for the appearance through mutations of reproducing molecules of the two mirror forms. The breaking of chiral symmetry occurred in the second stage of the initiation of life, when reproduction chain reactions arose, and powerful amplifying factors associated with these chain reactions also arose. We can construct a very simple model for this phenomenon. We of course do not know the details of the enzymatic reactions and the replication processes during the initiation of life. The model will therefore be purely phenomenological.

We denote by $n_d(\mathbf{r},t)$ and $n_l(\mathbf{r},t)$ the concentrations of the dextrorotatory and levorotatory molecules resulting from reproduction. In actuality, of course, these molecules are parts of separate droplets or coacervates. However, we will use a continuous description and assume that there are many such droplets in a physically small element of the medium. The time evolution of the concentrations is governed by the equations

$$\frac{\partial n_d}{\partial t} = (\gamma - \alpha n_d - \beta n_l) n_d + D \Delta n_d + \mu (n_l - n_d),$$
$$\frac{\partial n_l}{\partial t} = (\gamma - \alpha n_l - \beta n_d) n_l + D \Delta n_l + \mu (n_d - n_l). \quad (3.1)$$

The rate of the chain reproduction of dextrorotatory molecules, $K_d = \gamma - \alpha n_d - \beta n_l$, depends on the concentrations n_d and n_l for two reasons. First, the nourishing substrate is expended on the reproduction, and the replenishment of this substrate (e.g., through the eruption of volcanoes or by photochemical synthesis) is rather slow. An increase in the concentration of molecules resulting from reproduction leads to a depletion of the environment and to a depression of the chain reaction. If the substrate were completely common to the levorotatory and dextrorotatory replicating molecules (i.e., if the substrate were achiral or underwent racemization rapidly), the two mirror forms would have been indistinguishable with respect to this substrate, and the coefficients α and β would have been the same. As we will see below, under the condition $\alpha = \beta$ system (3.1) does not break chiral symmetry. Actually, however, the composition of the substrate may include molecules with a very slow racemization rate. This circumstance is equivalent to the presence, in addition to the common component, of unshared components of the substrate, which are drawn from separately by the levorotatory and dextrorotatory replicating molecules. Because of this effect, the coefficient α can exceed β.

The second reason is that the chiral intermediate products of the autocatalysis of dextrorotatory molecules pass through the common medium into the coacervates where levorotatory molecules are synthesized, and vice versa. They interfere in this synthesis and, because of the high stereoselectivity of enzymatic reactions, disrupt the synthesis, i.e., they serve as a poison. Consequently, the processes of chain reproduction of the molecules of the two mirror forms have a cross depressing effect on each other. This cross depression introduces an additional positive contribution to the value of the coefficient β.

Model (3.1) also incorporates a spatial diffusion of the molecules of the two mirror forms and their spontaneous conversion into each other. The rate of a racemic conversion of this sort, μ, is very small, but it turns out that in special

situations (specifically, near a bifurcation point) this process plays an important role.

With Eqs. (3.1) we can associate the following hypothetical scheme of chemical reactions (here S represents a substrate or food):

$$d + S \leftrightarrows d + d, \quad l + S \leftrightarrows l + l, \quad d + l \rightarrow 0, \quad d \leftrightarrows l. \tag{3.2}$$
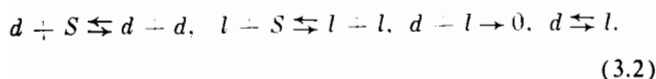
The model thus includes both reproduction reactions and an effective annihilation.

We begin by considering the case in which the diffusion is so rapid that it keeps the reacting molecules completely mixed and the distribution of concentrations uniform. We can then ignore the terms with spatial derivatives in Eqs. (3.1).

If the possibility of racemizing conversions is ignored ($\mu = 0$), a simple analysis shows that under the condition $\beta < \alpha$ a stable state of the system is symmetric and corresponds to the coexistence of the two mirror forms on an equal footing:

$$n_l = n_d = \frac{\gamma}{\alpha - \beta} . \tag{3.3}$$

In the case $\beta > \alpha$, the symmetric state is unstable, and the stable states are two purely asymmetric states, with exclusively dextrorotatory or exclusively levorotatory molecules:

$$n_l = 0, \quad n_d = \frac{\gamma}{\alpha} \quad \text{or} \quad n_l = \frac{\gamma}{\alpha}, \quad n_d = 0. \tag{3.4}$$

In the case $\alpha = \beta$, in this model, the levorotatory and dextrorotatory molecules are indistinguishable and can coexist in any proportions, so we have

$$n_l + n_d = \frac{\gamma}{\alpha} . \tag{3.5}$$

The value $\beta = \alpha$ is therefore a bifurcation value, but the bifurcation itself is degenerate. This degeneracy is lifted when racemizing conversions are taken into consideration (more on this below).

We turn now to spatial effects.

If a seat of the reproduction of levorotatory or dextrorotatory molecules has arisen at random in an initially empty medium ($n_d = n_l) = 0$), then this seat will generate the population wave which was studied by Kolmogorov, Petrovskiĭ, and Piskunov.[9] If the front of this wave is planar, it will move at a velocity $v_0 = (2D_\gamma)^{1/2}$; if the front instead has a radius of curvature R, the propagation velocity will be

$$v = v_0 - \frac{D}{R} , \quad R \gg \left(\frac{D}{\gamma} \right)^{1/2} . \tag{3.6}$$

What happens when two population waves, which are being followed by molecules of opposite chirality, collide? We first consider the one-dimensional problem, i.e., the collision of two waves with plane fronts. After the collision, a steady-state distribution is established. If we ignore the small probability for racemic conversions, and if we introduce the dimensionless variables

$$n_d = \frac{\gamma}{\alpha} n, \quad n_l = \frac{\gamma}{\alpha} m, \quad x = \left(\frac{D}{\gamma} \right)^{1/2} \xi. \tag{3.7}$$

then we can describe the steady-state distribution in terms of these variables by means of the equations

$$\frac{d^2 n}{d\xi^2} + (1 - n - \varkappa m) \, n = 0,$$
$$\frac{d^2 m}{d\xi^2} + (1 - m - \varkappa n) \, m = 0. \tag{3.8}$$

where $\varkappa = \beta / \alpha$.

We assume $\varkappa \gg 1$; i.e., the cross depression is far stronger than the direct depression. A distribution with a narrow overlap zone will then be established. The width of this zone, l_0, and the concentration of molecules in it can be found without difficulty from (3.8), when we note that in this case the equations are dominated by the terms $\varkappa m n$, so we return to the recombination problem of §2. As a result we find

$$l_0 \sim \left(\frac{D}{\gamma} \right)^{1/2} \varkappa^{-1/3},$$
$$n_d(0) = n_l(0) \sim \frac{\gamma}{\alpha} \varkappa^{-1/3}. \tag{3.9}$$

As $\varkappa$ decreases, the width of the overlap zone and the concentration of molecules in it increase. The critical value is $\varkappa = 1$. As this value is approached, the depth of the mutual penetration becomes infinite:

$$l_0 \approx \left(\frac{D}{\gamma} \right)^{1/2} \frac{1}{\varkappa - 1}, \quad \varkappa > 1. \tag{3.10}$$

If $\varkappa < 1$, the two chain reactions will become completely mixed, and a homogeneous steady state will be established:

$$n_d = n_l = \frac{\gamma/\alpha}{1 + \varkappa}, \quad \varkappa < 1. \tag{3.11}$$

Racemization effects become important near the critical point; we will return to a more detailed discussion of this question a bit further on.

The situation thus depends very strongly on the relation between the extent of the direct and cross depression of the chain reactions. In this connection we can postulate two distinct scenarios of an evolutionary explosion which results in the formation of a chirally pure biosphere:

a) In the case of a strong cross depression, large regions dominated by molecules of one chirality or the other should have initially formed on the earth. This geometric picture of regions would subsequently change because of the cross depression in the contact zones; certain regions would displace others; and ultimately one form of life would be completely annihilated.

b) The second scenario presupposes that the cross depression was initially quite weak, that the reproducing molecules of the two chiralities were completely mixed, and that the two chain reactions coexisted. However, the cross depression subsequently strengthened; the coefficient $\varkappa$ increased; and at a certain time it crossed the critical value $\varkappa = 1$. A complete homogeneous coexistence ceased to be possible. The chiral symmetry is violated through a second-order "phase transition" (analogous to the formation of a pseudoscalar liquid crystal). The choice of the specific chirality is determined by random fluctuations, and, possibly, the effect of the weak interaction.

Let us examine each of these two scenarios in more detail.

We assume that the cross depression is *pronounced* ($\varkappa \gg 1$). Two waves with plane fronts which have collided then come to a stop and form a fixed interface. If, however, the waves were not plane waves, and the interface which was

formed was curved, the interface would begin to move over time at a velocity

$$v_b = -\frac{D}{R}, \qquad (3.12)$$

where R is the local radius of curvature of the interface [which is large in comparison with the diffusion length $(D/\gamma)^{1/2}$]. The direction in which the interface moves is determined by the condition that the interface tends to reduce in length. As a result, an enclosed region which is entirely surrounded by a region with molecules of the other chirality will disappear completely over a time of order L_0^2/D, where L_0 is the initial dimension of the region.

It is useful to compare the propagation velocity of a free population wave $[v_0 = (2D\gamma)^{1/2}]$ with the velocity at which the interface moves, (3.12). These two velocities are of the same order of magnitude only if the radius of curvature is very small $[R \sim (D/\gamma)^{1/2}]$. If $R \gg (D/\gamma)^{1/2}$, the interface between the regions moves very slowly in comparison with the free propagation of waves. The course of the evolution can thus be divided into two stages. Initially, points of a chain reproduction arise in the ocean. Population waves propagate away from these points rapidly, and the entire ocean is soon divided into regions which contain only levorotatory or only dextrorotatory reproducing molecules. In the following, and slower, stage all the bends in the boundaries between regions are smoothed out, and all the closed regions which are surrounded by molecules of different chirality gradually disappear. One region, with a definite chirality, eventually covers the entire earth.[9]

In this scenario, the outcome of the evolutionary explosion depends strongly on the random initial geometry of the levorotatory and dextrorotatory regions, i.e., on the random process by which the chain-reaction points are initiated.

We studied the effect of the weak interaction on the motion of interfaces between regions with different chirality in Ref. 52. That effect contributes a correction of the order of $\varepsilon = \Delta\mathscr{E}/k_B T$ to the interface velocity $v_b = D/R$. This correction is so small, however, that even if the radii of curvature of the interface are comparable to the radius of the globe the correction can be ignored. In this scenario, the weak interaction is not capable of influencing the choice of chirality in the biosphere.

According to another evolutionary scenario, the cross depression was initially quite weak, so the levorotatory and dextrorotatory forms of life coexisted in a completely mixed symmetric state. Later, the intensity of the cross depression (i.e., the magnitude of the coefficient β) began to increase, a bifurcation occurred, and the system underwent a second-order phase transition into an asymmetric state with a definite predominant chirality.

Let us assume the course of events in this scenario. It is convenient here to introduce a dimensionless order parameter η and a dimensionless time τ:

$$\eta = \frac{\alpha}{\gamma}(n_d - n_l), \quad \tau = \gamma t. \qquad (3.13)$$

Near the bifurcation point, we find the following approximate equation for the order parameter from (3.1):

$$\frac{d\eta}{d\tau} = \frac{1}{2}(\varkappa - \varkappa_{cr})\eta - 2\theta\eta^3 + \varepsilon + f(\tau). \qquad (3.14)$$

Here $\varkappa_{cr} = 1 + 4\theta$. The coefficient $\theta = \mu/\gamma$ is very small and characterizes the probability for a racemic conversion of

an individual molecule over the average time between two sequential replication events of this molecule. The quantity ε characterizes the relative difference in the reproduction rates of the levorotatory and dextrorotatory molecules. If this difference stems from a difference in the ground-state energies of the levorotatory and dextrorotatory molecules due to the weak fundamental interaction, then we would have

$$\varepsilon \approx \Delta\mathscr{E}/k_B T \sim 10^{-17}.$$

In the derivation of (3.14), it was assumed that the order parameter is small: $|\eta| \ll 1$. If the small racemization probability is ignored, and if we set $\theta = \eta/\gamma = 0$, then we find that at $\varkappa > 1$ this equation describes an initial exponential stage of the decay of a completely mixed symmetric state. Equation (3.14) is identical in form to the time-dependent Ginzburg-Landau equation in the theory of second-order phase transitions at thermal equilibrium.[53] The quantity ε is playing the role of an external field.

The random function $f(\tau)$ in Eq. (3.14) incorporates the noise associated with the atomistic nature of the consumption and reproduction reactions. This noise is analyzed systematically in Appendix II; we will content ourselves here with some cruder arguments in order to find some estimates.

If independent reactions in which individual particles are consumed and reproduce occur in a system of N particles, the number (ΔM) of reaction events over a certain time interval Δt is a random quantity with a Poisson distribution and with a mean square value of $1/\Delta M$ of the relative fluctuations. At dynamic equilibrium, the number of consumption events is equal to the number of reproduction events over the same time interval, so we can write $\Delta M \sim \gamma N \Delta t$, where γ is the probability for the reproduction of some particular molecule per unit time. The noise intensity S, defined by

$$\langle f(\tau) f(\tau') \rangle = S\delta(\tau - \tau'), \qquad (3.15)$$

is equal in order of magnitude to the mean square value of the relative fluctuations in the number of reaction events per unit time, i.e., over a time $\Delta t = 1/\gamma$. We thus have $S \sim 1/N$, where N is the total number of reacting molecules of the left-handed and right-handed chirality.

If the noise is ignored, Eq. (3.14) has the steady-state solutions shown in Fig. 1. Under the condition

$$(\varkappa - \varkappa_{cr}) > (6\sqrt{3}\varepsilon\theta^{1/2})^{2/3} \qquad (3.16)$$

the system has two stable steady states, with order parameters opposite in sign.

Let us analyze the process by which the steady state is chosen as the critical point is crossed.[10] We can carry out this analysis by discarding from (3.14) the nonlinear term $2\theta\eta^3$, which leads to a limitation on the exponential growth at large values of the order parameter η.

It is not difficult to see that in the absence of noise the system will always, as it crosses the critical point, go from an initial symmetric state ($\eta = 0$) to a state with an order parameter whose sign is imposed by the external field. The question is how is this choice affected by the noise associated with the atomistic nature of the reaction events.

Since we are interested in simply order-of-magnitude estimates, we will assume that the system was initially (at

$\tau = 0$) at the critical point $\varkappa = \varkappa_{cr}$ in a symmetric state ($\eta = 0$), and then the parameter $\varkappa$ began to increase linearly with time:

$$\varkappa = \varkappa_{cr} + c\tau. \qquad (3.17)$$

Working from Eq. (3.14) without the nonlinear term, we can derive two equations describing the time evolution of the average value of the order parameter, $\langle \eta \rangle$, and of the mean square value of its fluctuations:

$$\frac{d}{d\tau} \langle \eta \rangle = \frac{1}{2} c\tau \langle \eta \rangle + \varepsilon, \qquad (3.18)$$

$$\frac{d}{d\tau} \langle \delta\eta^2 \rangle = c\tau \langle \delta\eta^2 \rangle + S. \qquad (3.19)$$

It follows from (3.18) and (3.19) that as long as the conditions $c\tau\langle\eta\rangle \ll \varepsilon$ and $c\tau\langle\delta\eta^2\rangle \ll S$ hold these quantities will grow over time in accordance with

$$\langle \eta \rangle = \varepsilon\tau, \quad \langle \delta\eta^2 \rangle = S\tau. \qquad (3.20)$$

The linear growth continues up to the time $\tau^* \sim c^{-1/2}$; at later times, $\tau \gg \tau^*$, the onset of an exponential instability becomes dominant, and the effects of the noise and the external field can now be ignored. In other words, if the order parameter had, say, a positive sign at $\tau = \tau^*$ then it will remain positive also at later times. The noise is thus capable of affecting the choice of the sign of the order parameter only in the time interval $0 < \tau < \tau^*$.

According to (3.20), in the case $0 < \tau < \tau^*$ the average value of the order parameter increases linearly with time, but fluctuations in it also increase simultaneously. The noise is not capable of influencing the choice of the sign of the order parameter if the mean square fluctuations in the order parameter by the time τ^* are smaller than the mean value of the order parameter. We thus have the condition

$$\tau^* \gg \frac{S}{\varepsilon^2}. \qquad (3.21)$$

Returning to dimensional units of time, and using $S \sim 1/N$, we find an inequality for the transition time $t_{tr} = \tau^*/\gamma$:

$$t_{tr} \gg \frac{1}{\gamma N \varepsilon^2}. \qquad (3.22)$$

If this condition holds, the asymmetry of the weak interaction would be sufficient to impose the sign of the chirality in the biosphere.

Let us attempt to find an estimate, even if quite crude, of the minimum transition time determined by inequality (3.22).

Since we do *not* know the characteristics or the number of the first living organisms, we will draw on some corre-
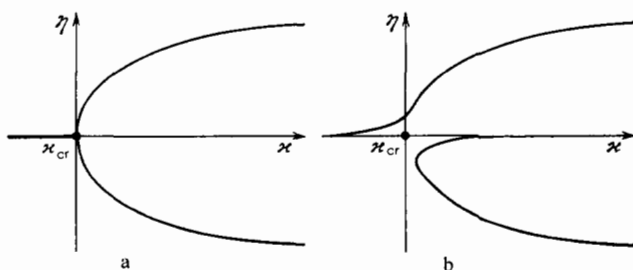

FIG. 1. Steady-state solutions of Eq. (3.14). a — $\varepsilon = 0$; b — $\varepsilon > 0$. The symmetric state with $\eta = 0$ above the critical point $\varkappa_{cr}$ is unstable.

sponding data for the present stage of biological evolution.[11] In one cubic meter of the surface layer of the ocean today there are about 10^7 living cells, in each of which there is a single DNA molecule. If we take the depth of the populated layer to be of the order of 100 m, we find the crude estimate $N \sim 10^{23}$ as the total number of reproducing molecules in the world ocean. The time interval between successive divisions in modern single-cell microorganisms ranges from 1 to 100 h; for an estimate we adopt $\gamma = 1$ h^{-1}. We also assume that the differences between the reproduction rates of the levorotatory and dextrorotatory molecules stem from a difference in their binding energies due to the asymmetry of the weak interaction. In other words, we assume $\varepsilon \sim 10^{-17}$. Substituting these values into (3.22), we find that the minimum duration of the transition which would be sufficient to allow the weak interaction to impose the sign of the chirality in the biological world would be about 10^7 yr. This estimate is *completely realistic since the total duration of biological evolution has been of the order of 10^9 yr*. Nevertheless, these estimates are so inaccurate that they may actually be one or two orders of magnitude too high or too low. Furthermore, they apply to only one of the postulated scenarios of evolutionary development. We can thus conclude only that an analysis of this question *does not rule out* the possibility that the chirality of biomolecules was determined by the asymmetry of the weak interaction.

CONCLUSION

Fluctuations associated with the atomistic nature of the individual events of a chemical reaction are usually manifested only at the microscopic level, in processes and effects with relatively small length and time scales. Nevertheless, the examples which we have discussed here show that there can also be situations in which some powerful nonlinear mechanism amplifies this initially weak microscopic noise to the point that it determines the outcome of macroscopic observable events. To some extent the situation is analogous to macroscopic quantum effects.

APPENDIX I

In this Appendix we consider the general problem of the behavior of fluctuations when the point of a second-order phase transition is crossed at a finite rate. We will derive the conditions which must be satisfied by the crossing rate if the medium is not to break up into domains of opposite phases after a transition in a given external field.

The time evolution of the real order parameter η in the case of an equilibrium second-order phase transition is described by[12] the Ginzburg–Landau equation[53]

$$\dot{\eta} = a\eta - b\eta^3 + g\,\Delta\eta + h + f\,(\mathbf{r},\,t). \qquad (I.1)$$

The random Gaussian force $f(\mathbf{r},t)$ in this equation incorporates the noise effect of the heat reservoir. Its intensity is determined by the temperature of the medium, T:

$$\langle f\,(\mathbf{r},\,t)\,f\,(\mathbf{r}',\,t')\rangle = 2T\delta\,(\mathbf{r}-\mathbf{r}')\,\delta\,(t-t'). \qquad (I.2)$$

The bifurcation coefficient a in Eq. (I.1) is determined by the external conditions. We will assume here that it varies linearly with time, and as the origin for the time scale we choose the instant at which the critical point is crossed:

$$a = ct. \tag{I.3}$$

In a steady-state regime, with a constant value of a, the correlation radius of the order parameter, r_c, and its correlation time t_c become infinite as $a \to 0$. This result means in particular that relaxation to thermal equilibrium requires progressively more time as we move closer to the critical point. It is thus obvious that when the critical point is crossed at a finite rate there is always a time interval during which the system is characterized by a probability distribution which is greatly different from that at thermal equilibrium.

For definiteness we assume that the system starts at the time $t = 0$ directly from the critical point, and we assume that the order parameter is initially equal to zero throughout the medium.[13] Fluctuations appear at $t > 0$ because of the noise of the heat reservoir, i.e., because of the random force $f(\mathbf{r},t)$ in Eq. (I.1). Because of its microscopic origin, this random force is δ-correlated in terms of the spatial coordinates. The onset of spatial correlations for the fluctuations of the order parameter is thus caused exclusively by the interaction with the different regions; this interaction is described by a term of the diffusion type, $-g\Delta n$, in Eq. (I.1). Over a finite time interval t this interaction is capable of establishing correlations only within a volume element with a linear dimension no greater than the diffusion length $r_d(t) = (gt)^{1/2}$.

The diffusion length $r_d(t)$ should be compared with the value of the correlation radius $r_c(t)$ at the instantaneous value of the bifurcation coefficient $a = ct$ at the corresponding time. If the condition $r_d(t) \gg r_c(t)$ holds, we can apply the adiabatic approximation, and the fluctuations of the order parameter at time t are the same as at thermal equilibrium with the value $a = ct$ of the bifurcation coefficient. On the other hand, in the nonadiabatic region, with $r_d(t) \ll r_c(t)$, the fluctuations are qualitatively different from equilibrium fluctuations.

We know quite well that in analyzing equilibrium fluctuations near a second-order phase transition we can distinguish a fluctuation region and a region in which the mean-field theory is applicable. The mean-field approximation is valid far from the tansition point, where the following condition holds[54]:

$$a \gg \frac{T^2 b^2}{g^3} . \tag{I.4}$$

At thermal equilibrium, the fluctuations in this region are small; more precisely, the mean square value of the fluctuations in the order parameter in a volume with a size equal to the correlation radius is small in comparison with the square of the mean value of the order parameter. Closer to the critical point there is a fluctuation region, in which the relative fluctuations of the order parameter at thermal equilibrium are large.

As the criticl point is crossed at a finite rate, the entire picture of events depend strongly on whether the nonadiabatic region spans *the entire* fluctuation region. In other words, an important question is whether the value of the bifurcation parameter $a^* = ct^*$ at the time t^*, at which the condition $r_d(t^*) = r_c(t^*)$ holds, satisfies inequality (I.4).

If we find ourselves in a fluctuation region when we leave the nonadiabatic region, then it is actually irrelevant to what extent the fluctuations have grown by this time: Large or small, they will subsequently become strong in the adiabatic regime. Far more interesting is the case in which the system, as it leaves the nonadiabatic region, goes immediately into the region in which the mean-field theory applies.

Since the correlation radius is given by the expression $r_c = (g/a)^{1/2}$ in the mean-field approximation, the duration of the nonadiabatic region is $t^* = c^{1/2}$, and the value of the bifurcation parameter by the time at which this region ends is $a^* = c^{1/2}$. The nonadiabatic region spans the entire fluctuation region if

$$c \gg \left(\frac{T^2 b^2}{g^3} \right)^2 . \tag{I.5}$$

Outside the fluctuation region [i.e., under inequality (I.4)] the creation, as a result of equilibrium thermal fluctuations, of macroscopic domains of opposite phases with dimensions greater than the correlation radius is an exponentially rare event. If the medium was originally broken up into domains with opposite signs of the order parameter, a process of relaxation to a final thermal equilibrium would begin in it. In the course of this relaxation, there would be shifts of the boundaries between domains, so that domains of a metastable phase would disappear.

It is not difficult to show that the radius (R) of a spherical domain which is immersed in the opposite phase has a time evolution determined by

$$\frac{dR}{dt} = -\frac{2g}{R} \pm \xi \frac{hg^{1/2}b^{1/2}}{a} , \tag{I.6}$$

where the numerical factor ξ is of the order of unity. We need to use the pluse sign in this equation if the relation $\eta > 0$ holds in the domain, and in the opposite case would use the minus sing.

It follows from (I.6) that all the metastable-phase domains ($\eta < 0$) contract over time and ultimately disappear. A spherical domain of a stable phase ($\eta > 0$) in a region filled with a metastable phase grows over time if its radius is greater than the critical value $R_{kp} \sim (a^2 g/hb)^{1/2}$.

Outside the fluctuation region, any arbitrarily weak external field h will eventually put the entire medium in a state with a definite sign of the order parameter, which the field imposes. For this to happen, however, sufficient time must elapse after the crossing of the transition point. In addition, processes by which the metastable domains disappear—if they occur—must have time to go to completion. Since the velocity of a plane interface vanishes as $h \to 0$, it is clear that for very weak fields the duration of this last stage can be exceedingly long and can exceed the very time over which the system exists. In this situation there is no phase stratification only if there are no macroscopic domains of a metastagle phase in the system upon the arrival at the mean-field region. In the problem involving the crossing of the point of the phase transition at finite rate this assertion means that as we go out of the nonadiabatic region into the region in which the mean-field approximation applies the fluctuations in a volume of the correlation radius must be small in comparison with the mean value of the order parameter, imposed by the external field.

What happens in the nonadiabatic region, i.e., at $t \ll t^*$? It is easy to see that under condition (I.5) the original Ginzburg-Landau equation, (I.1) can be simplified substantially

in this region; it reduces to the form

$$\dot{\eta} = g\,\Delta\eta + h + f\,(\mathbf{r},\ t). \tag{I.7}$$

Using (I.7), we find that at $t \ll t^*$ the mean value of the order parameter increases over time in accordance with

$$\langle\eta\rangle = ht, \tag{I.8}$$

and the mean square value of the fluctuations $\delta\eta = \eta - \langle\eta\rangle$, in the volume V, i.e., the quantity

$$\langle(\delta\eta^2)_V\rangle \equiv \frac{1}{V^2} \int\!\!\!\int\limits_{(V)} \langle\delta\eta\,(\mathbf{r},\ t)\,\delta\eta\,(\mathbf{r}',\ t')\rangle\,d\mathbf{r}\,d\mathbf{r}', \tag{I.9}$$

increasing with time in accordance with

$$\langle(\delta\eta^2)_V\rangle = \frac{Tt}{V}\ . \tag{I.10}$$

We require that the fluctuations in a volume V_c with the correlation radius $r_c(t^*) = (gt^*)^{1/2} = (g^2/c)^{1/4}$ be small by the time t^*. In other words, we require that the following condition hold:

$$\langle(\delta\eta^2)_{V_c}\rangle \ll \langle\eta\rangle^2. \tag{I.11}$$

Using (I.9) and (I.10), we find that this requirement implies the requirement

$$c \ll \left(\frac{h^2 g^{3/2}}{T}\right)^{4/5}. \tag{I.12}$$

We have thus obtained limitations on the rate at which the point of a second-order phase transition is crossed. These limitations have the effect of preventing the system from ever breaking up into regions with opposite phase throughout the crossing process.[14] These limitations are given by inequalities (I.5) and (I.12). In the general case of an arbitrary dimensionality of the medium, d, these limitations take the form

$$(h^2 g^{d/2} T^{-1})^{4/(d+2)} \gg c \gg (bT g^{-d/2})^{4/(4-d)}. \tag{I.13}$$

If the fields are too weak, the two inequalities in (I.13) are incompatible. There thus exists a minimum strength of the external field at which the system can cross the transition point without breaking up into a mixture of domains of two opposite phases. For a three-dimensional medium, this minimum value is given in order of magnitude by

$$h_{\min} = \frac{T^3 b^{5/2}}{g^{9/2}}\ . \tag{I.14}$$

The analysis above can be generalized in a natural way to the case of nonequilibrium second-order phase transitions, as an example of which we might cite the transition which we studied in §3 and which involved the breaking of the chiral symmetry of the biosphere. The only distinction is that now the random force $f(\mathbf{r},t)$ in Ginzburg-Landau equation (I.1) is slightly different in nature.

In the reactions which occur in a liquid medium, hydrodynamic noise and fluctuations associated with the atomistic nature of reactions and diffusion contribute to the random force $f(\mathbf{r},t)$ (see Appendix II for more details). For the transition analyzed in §3 the leading role is played by the fluctuations which stem from the atomistic nature of reactions. These fluctuations actually determine the effective

temperature T_{eff} which must be used to replace T in (I.2). It can be shown that in this case we have $T_{\text{eff}} \sim 1/N_0$, where $N_0 = n_0 l^3$ is the number of reproducing molecules in a volume element with a length $l = (D/\gamma)^{1/2}$. When spatially inhomogeneous fluctuations are taken into account, (3.22) is replaced by the following inequality for the duration of the transition:

$$t_{\text{tr}} \gg \frac{1}{\gamma\,(N_0 \varepsilon^2)^{2/5}}\ . \tag{I.15}$$

Under this condition, the medium does not break up after the transition into domains with opposite chirality of the reproducing molecules.

However, relation (I.15) is hardly applicable for describing processes which occur in the earth's biosphere. Over transition times of the order of 10^7 yr, the dominant role will be played by the large-scale turbulent transport of the reacting substances—a transport which is not described by a diffusion equation. A more natural assumption is that there is complete turbulent mixing over such times; this is the assumption which was made in §3.

APPENDIX II

In this mathematical Appendix we will discuss methods for describing fluctuations in reacting systems with diffusion. We recall that the formal kinetic equations of chemical reactions are written for nonfluctuating concentrations $n(\mathbf{x})$ of the reacting particles. In a comprehensive microscopic description of a reacting system, on the other hand, we need to introduce a set of distribution functions $\{P_N(\mathbf{x}_1, \ldots, \mathbf{x}_N; t)\}$, each of which gives the probability for finding $N = 0, 1, 2, \ldots$ particles in the system, at the points with coordinates $\mathbf{x}_1, \ldots, \mathbf{x}_N$. The time evolution of these functions due to reactions and the diffusion of particles is described by governing equations. There are many methods which could be used to work directly from these microscopic governing equations in order to solve kinetic problems (for example, one could construct a perturbation-theory diagram technique[55-59]). In this paper, however, we will focus on the intermediate (or *mesoscopic*) description level, where the description is formulated in terms of smooth distributions of the concentrations $n(\mathbf{x})$, but the fluctuations caused in these concentrations by the atomistic nature of the individual reaction events and by the diffusion process are taken into account.

We begin with the simplest case. We assume that the reaction consists of a single production of particles in a vessel, at a probability w_0 per unit time. The following exact governing equation then holds for the time evolution of the probability $p(n)$, which is the probability for finding n particles in the vessel:

$$\frac{\partial p(n)}{\partial t} = w_0 p(n-1) - w_0 p(n). \tag{II.1}$$

If the number of particles in the vessel is sufficiently large, the quantity n can be approximated by a continuously varying variable, and we can write

$$p(n-1) = p(n) - \frac{\partial p}{\partial n} + \frac{1}{2}\frac{\partial^2 p}{\partial n^2} + \cdots\ . \tag{II.2}$$

For smooth distributions $p(n)$ the terms with higher derivatives in expansion (II.2) can be ignored. Substituting (II.2)

into (II.1) we find an approximate Fokker-Planck equation for this reaction:

$$\frac{\partial p}{\partial n} = -\frac{\partial}{\partial n}(w_0 p) + \frac{1}{2}\frac{\partial^2}{\partial n^2}(w_0 p). \qquad (II.3)$$

We turn now to the decay reaction $X \to R$. We denote by w_1 the probability for the decay of an individual X particle per unit time. The corresponding governing equation is

$$\frac{\partial p(n)}{\partial t} = w_1(n+1)p(n+1) - w_1 p(n). \qquad (II.4)$$

Carrying out an exapnsion of $p(n+1)$ at large values of n by analogy with (II.2), we again find a Fokker-Planck equation:

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial n}(w_1 np) + \frac{1}{2}\frac{\partial^2}{\partial n^2}(w_1 np). \qquad (II.5)$$

Finally, for the breeding reaction $X \to 2X$ the governing equation is written

$$\frac{\partial p(n)}{\partial t} = w_2(n-1)p(n-1) - w_2 np(n), \qquad (II.6)$$

where w_2 is the probability for a doubling of an individual X particle per unit time. Corresponding to this case is the following approximate Fokker-Planck equation:

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial n}(w_2 np) + \frac{1}{2}\frac{\partial^2}{\partial n^2}(w_2 np). \qquad (II.7)$$

A distributed medium can be described approximately as a set of vessels or "boxes" in each of which production, decay, or breeding reactions are occurring. Furthermore, the particles can move at random from one box to others, with the result that there is a diffusion of particles. To simplify the analysis we first examine the processes which occur in a one-dimensional distributed medium, which may be thought of as a linear chain of boxes with indices $j = 0, \pm 1, \pm 2, \ldots$. The state of such a system is specified by specifying the set of the numbers of particles in each of the boxes.

If there is no diffusion (i.e., if particles do not go from one box to another), the number of particles in each of the boxes, n_j, will vary independently in accordance with the particular reactions which are occurring ($S \to X$, $X \to R$, or $X \to 2X$). The joint distribution function $p(\{n_j\})$ will then obey the approximate Fokker-Planck equation

$$\frac{\partial p(\{n_j\})}{\partial t} = -\sum_j \frac{\partial}{\partial n_j}[(w_0 - w_1 n_j + w_2 n_j)p(\{n_j\})]$$
$$+ \frac{1}{2}\sum_j \frac{\partial^2}{\partial n_j^2}[(w_0 + w_1 n_j + w_2 n_j)p(\{n_j\})]. \qquad (II.8)$$

We now consider the fluctuations caused by diffusion. We assume that there is a probability w that a particle will, in a unit time, hop into one of the neighboring boxes in the chain. The governing equation for this random process is

$$\frac{\partial p(\{n_j\})}{\partial t} = w \sum_j [(n_j + 1)p(/n_{j-1}-1, \ n_j+1/)$$
$$+ (n_j + 1)p(/n_j + 1, \ n_{j+1} - 1/)$$
$$- 2n_j p(\{n_j\})] \quad . \qquad (II.9)$$

Here we are using the notation $p(/n_{j-1} - 1, \ n_j + 1/)$, which shows that in the set of occupation numbers $\{n_j\}$ there are changes of ± 1 only in the numbers of particles in boxes $j - 1$ and j.

If the occupation numbers n_j are sufficiently large, they can be treated as continuous variables, and we can write the approximation

$$p(/n_{j-1}-1, \ n_j+1/) \approx p - \frac{\partial p}{\partial n_{j-1}} + \frac{\partial p}{\partial n_j} + \frac{1}{2}\frac{\partial^2 p}{\partial n_j^2}$$
$$+ \frac{1}{2}\frac{\partial^2 p}{\partial n_{j-1}^2} - \frac{\partial^2 p}{\partial n_j \partial n_{j-1}}. \qquad (II.10)$$

A similar expression holds for $p(/n_j + 1, n_{j+1} - 1/)$. Substituting these expressions into (II.9), we find a Fokker-Planck equation for the distribution function:

$$\frac{\partial p}{\partial t} = -w\sum_j \frac{\partial}{\partial n_j}[(n_{j+1} + n_{j-1} - 2n_j)p]$$
$$+ \frac{1}{2}w\sum_j \frac{\partial^2}{\partial n_j^2}[(2n_j + n_{j+1} + n_{j-1})p]$$
$$- \frac{1}{2}w\sum_j \frac{\partial^2}{\partial n_j \partial n_{j-1}}(2n_j p) - \frac{1}{2}w\sum_j \frac{\partial^2}{\partial n_j \partial n_{j+1}}(2n_j p). \qquad (II.11)$$

The next step is to switch from the discrete description, in which the medium is partitioned into a sequence of boxes, to a continuous description in terms of a smooth concentrtion $n(x)$. The multidimensional distribution function $p(\{n_j\})$ then converts into a functional $p[n(x)]$, which gives the probability density of the various realizations of the concentration field $n(x)$. Multidimensional Fokker-Planck equation (II.11) transforms into a functional Fokker-Planck equation. As will be shown below, this equation is

$$\frac{\partial p}{\partial t} = -D\int dx \frac{\delta}{\delta n(x)}\left(\frac{\partial^2 n}{\partial x^2}p\right)$$
$$+ D\int\int dx\, dy \frac{\delta^2}{\delta n(x)\,\delta n(y)}$$
$$\times \left[\frac{\partial^2}{\partial x\,\partial y}(n(x)\delta(x-y))p\right], \qquad (II.12)$$

where $D = wl^2$ is the diffusion coefficient (l is the size of one of the individual initial boxes).

To demonstrate the validity of equation (II.12), we transform from it to Eq. (II.11) by switching to a discrete description. We do this separately for the terms with the first and second functional derivatives.

After the switch to a discrete description, the first term turns out to be

$$D\int dx \frac{\delta}{\delta n(x)}\left(\frac{\partial^2 n}{\partial x^2}p\right) = w\sum_j \frac{\partial}{\partial n_j}[(n_{j+1} + n_{j-1} - 2n_j)p] \qquad (II.13)$$

and is therefore the same as the first term in (II.11).

The switch to a discrete description in the second term is a more complicated procedure. We first introduce the notation $\hat{A}(x) \equiv \delta/\delta n(x)$ and $\hat{A}(y) \equiv \delta/\delta n(y)$, so this term is written in the form

$$J = D\int\int dx\, dy\, \hat{A}(x)\,\hat{A}(y)\frac{\partial^2}{\partial x\,\partial y}(n(x)\delta(x-y))p. \qquad (II.14)$$

Now integrating by parts in (II.14), we find

$$J = D\int\int dx\, dy\, \frac{\partial \hat{A}(x)}{\partial x}\frac{\partial \hat{A}(y)}{\partial y}n(x)\delta(x-y)p$$

$$= D\int dx\left(\frac{\partial \hat{A}}{\partial x}\right)^2 np. \qquad (II.15)$$

We note that we have

$$\left(\frac{\partial \hat{A}}{\partial x}\right)^2 n = \frac{\partial \hat{A}}{\partial x} \frac{\partial}{\partial x} (\hat{A}n) - \frac{\partial \hat{A}}{\partial x} \hat{A} \frac{\partial n}{\partial x}$$

$$= \frac{\partial A}{\partial x} \frac{\partial}{\partial x} (\hat{A}n) + \frac{1}{2} \hat{A}^2 \frac{\partial^2 n}{\partial x^2} - \frac{1}{2} \frac{\partial}{\partial x} \left(\hat{A}^2 \frac{\partial n}{\partial x}\right) .$$

(II.16)

The last term here is a total derivative and disappears after integration over x. We finally find that the term in which we are interested can be put in the form

$$J = D \int dx \frac{\partial}{\partial x} \frac{\delta}{\delta n(x)} \frac{\partial}{\partial x} \left(\frac{\delta}{\delta n(x)} n(x)\right) p$$

$$+ \frac{1}{2} D \int dx \frac{\delta^2}{\delta n^2(x)} \left(\frac{\partial^2 n}{\partial x^2} p\right),$$

(II.17)

where the operators which perform a differentiation with respect to x only on the expressions in parentheses which follow them immediately.

It is now a convenient point at which to induce a discrete description. We then find

$$J = w \sum_j \left(\frac{\partial}{\partial n_{j+1}} - \frac{\partial}{\partial n_j}\right) \left[\frac{\partial}{\partial n_{j+1}} (n_{j+1}p) - \frac{\partial}{\partial n_j} (n_j p)\right]$$

$$+ \frac{1}{2} w \sum_j \frac{\partial^2}{\partial n_j^2} [(n_{j+1} + n_{j-1} - 2n_j) p]$$

$$= \frac{1}{2} w \sum_j \frac{\partial^2}{\partial n_j^2} [(n_{j+1} + n_{j-1}) p] + w \sum_j \frac{\partial^2}{\partial n_{j+1}^2} (n_{j+1} p)$$

$$- w \sum_j \frac{\partial^2}{\partial n_{j+1} \partial n_j} (n_j p) - w \sum_j \frac{\partial^2}{\partial n_j \partial n_{j+1}} (n_{j+1} p).$$

(II.18)

It is easy to verify that this expression becomes the same as the last term in (II.11) after a change of summation indices.

Consequently, functional Fokker-Planck equation (II.12) does indeed describe the fluctuations of the concentration field which are caused by the atomistic nature of the diffusion.

In the general case in which the medium is three-dimensional, and production, decomposition, and breeding reactions are occurring in it simultaneously, along with diffusion, the functional Fokker-Planck equation is

$$\frac{\partial p}{\partial t} = - \int d\mathbf{r} \frac{\delta}{\delta n(\mathbf{r})} \{(K_0 - K_1 n + K_2 n + D \Delta n) p\}$$

$$+ \frac{1}{2} \int \int d\mathbf{r} \, d\mathbf{r}' \frac{\delta^2}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}$$

$$\times \{[(K_0 + K_1 n + K_2 n) \delta(\mathbf{r} - \mathbf{r}')$$

$$+ \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} (2Dn \delta(\mathbf{r} - \mathbf{r}'))] p\},$$

(II.19)

where K_0 is the probability for the production of a particle per unit time per unit volume (i.e., $K_0 = w_0/l^3$), $K_1 = w_1$, and $K_2 = w_2$.

We know from the theory of random processes[60] that a Fokker-Planck equation can be associated unambiguously with a stochastic Langevin equation. For a fluctuating concentration field, this Langevin equation is

$$\dot{n} = K_0 - K_1 n + K_2 n + D \Delta n + f_0(\mathbf{r}, t) + (K_1 n)^{1/2} f_1(\mathbf{r}, t)$$

$$+ (K_2 n)^{1/2} f_2(\mathbf{r}, t) + \text{div} [((2Dn)^{1/2} \mathbf{f}(\mathbf{r}, t)],$$

(II.20)

where the Gaussian random forces f_0, f_1, f_2 and $\mathbf{f}$ are independent and have the correltion functions

$$\langle f_0(\mathbf{r}, t) f_0(0, 0)\rangle = \langle f_1(\mathbf{r}, t) f_1(0, 0)\rangle$$

$$= \langle f_2(\mathbf{r}, t) f_2(0, 0)\rangle$$

$$= \delta(\mathbf{r}) \delta(t), \quad \langle f^{(\alpha)}(\mathbf{r}, t) f^{(\beta)}(0, 0)\rangle$$

$$= \delta(\mathbf{r}) \delta(t) \delta_{\alpha\beta}, \quad \alpha, \beta = 1, 2, 3.$$

(II.21)

Stochastic differential equation (II.20) should be interpreted in the Ito sense.

[1] We denote by ξ_1 the probability that a center, considered separately, will not initiate an infinite chain of divisions. This quantity is the sum of the probabilities for two independent events: the probability that a center will be consumed without undergoing a single division and the probability that it will undergo one division, but the two centers which appear after it will fail to initiate an infinite chain. The quantity ξ_1 thus satisfies the equation

$$\xi_1 = \frac{\beta}{\alpha + \beta} + \frac{\alpha}{\alpha + \beta} \xi_1^2.$$

Solving it, and assuming $\xi = 1 - \xi_1$, we find the result (1.7).
[2] In an experiment it is obviously easier to turn off the radiation than to cool the entire volume instantaneously and uniformly.
[3] The power law holds down to $k \sim 1/a$, where a is the radius to which the molecules initially move apart. When k is smaller, the spectrum becomes flat again.
[4] Here R_1 and R_2 are positive if the surface is convex in the direction toward the z axis; in the opposite case they are negative.
[5] Related questions dealing with the formation of structures by random fields are discussed in the review in Ref. 20.
[6] Specifically, only dextrorotatory (d) sugar molecules and only levorotatory (l) amino acid molecules occur in living organisms.
[7] Amino acid and sugar molecules in living organisms have precisely that chirality which is favored by the weak interaction, but this could be a random coincidence (the probability differs too slightly from 1/21).
[8] According to the present data,[61] several RNA molecules have an enzymatic capability. In a recent theoretical paper, Farmer et al.[62] examined a chemical system in which polymer molecules undergo splitting and connection reactions catalyzed by other polymers from the existing set. It was shown in Ref. 62 that under certain conditions the number of polymers progressively larger molecular weights would spontaneously begin to increase without bound. In other words, an autocatalytic graph would form. It would be interesting to generalize the results of Ref. 62 to the case in which the set of polymers might contain molecules of the same chemical composition but with different chiralities of the constituent monomers.
[9] Simplified equations (3.1) no longer apply in this last stage, since the physical conditions in various regions on the globe are very different.
[10] These questions are studied in Refs. 46 and 47. We would also like to call the reader's attention to a recent paper[63] on the crossing of a bifurcation point at a finite rate in the presence of noise.
[11] We wish to thank V.V. Alekseev for assistance in making these estimates.
[12] We are expressing the time in units of the reciprocal relaxation rate of the order parameter, γ.
[13] This assumption is not very important. The final results hold in the general case in which the system crosses the critical point at a finite rate, moving from the symmetric state into the region with broken symmetry.
[14] More precisely, the probability for the appearance of domains of a metastable phase in the course of the transition is exponentially small.

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