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Fluctuations and nonlinear irreversible processes

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The paper reexamines the relationship between fluctuations and nonlinear irreversible processes. The deterministic equations for nonlinear irreversible processes are shown to be derivable from a minimum principle, which permits the introduction of a set of variables η canonically conjugate to the macroscopic variables a. In terms of the action integral of the minimum principle and the conjugate variables η, we are able to construct a covariant expression for the conditional probability of the fluctuations for a small interval of time. The short-time conditional probability is used to construct the conditional probability for finite times as a path integral. This path integral is a generalization of a corresponding expression of Onsager and Machlup for the linear regime. An explanation for a difference with Graham's recent calculation is given. The conditional probability is shown to satisfy a Fokker-Planck equation, which has the form derived from statistical mechanics by one of us.

I. INTRODUCTION

The insight that there is intimate connection between fluctuations and the statistical-mechanical theory of irreversible processes began with Einstein,[1] developed through the work of a number of authors[2] and reached a certain conclusion in an earlier work of one of us (M.S.G.).[3] In this latter work it was proposed that irreversible processes can be represented by Markov processes governed by a Fokker-Planck equation whose coefficients are determined through certain statistical mechanical averages. Perhaps the most seminal expression of the relation of irreversible processes and fluctuations is the representation of the transition probability between two macroscopic states as a functional integral expression.[4] This so-called Onsager-Machlup functional gives a natural generalization to the time-dependent domain of Boltzmann's fundamental relationship between the entropy and the probability.

The work of Onsager and Machlup was limited to the linear regime in which the transport coefficients are independent of the macroscopic variables and in which the thermodynamic forces are linear in the deviations of the macroscopic variables from their equilibrium values. One of the challenges that this work presents is to extend the path integral concept to nonlinear irreversible processes.

This challenge has been addressed in the work of Graham[5] who has expressed the transition probability in functional form for a Fokker-Planck process with diffusion matrix and drift vectors that are arbitrary functions of the macroscopic variables. While Graham gives a rather complete answer to the question of the form of the nonlinear Onsager-Machlup functional, his basic Fokker-Planck process has a purely mathematical origin. The present work is motivated by the desire to put the nonlinear Onsager-Machlup functional in a physical rather than a mathematical context. This physical context is interesting in itself but it also has the advantage of putting the very complicated calculations in a framework that helps in their understanding. In our work the fluctuations are supposed to come from the underlying molecular nature of the system, which is primarily manifest in the form of the deterministic equations of motion as a linear relationship between fluxes and forces. Following Onsager and Machlup we start from these deterministic equations and make a hypothesis about the conditional probability for a small time interval. This hypothesis is a natural extension to nonlinear processes of an analogous assumption in their work..

The assumption leads to a functional representation for the conditional probability, as well as to a Fokker-Planck equation which agrees with the statistical mechanical Fokker-Planck equation.[3] The connection with the work[5] of Graham, who obtained a slightly different functional, will be discussed below.

The outline of the paper is the following:

In Sec. II, we discuss deterministic equations for the irreversible process that are nonlinear generalizations of Onsager's form.[2(b)] The fluxes are linear in the forces, but the proportionality coefficients, i.e., the transport coefficients, are not necessarily independent of the state, and the forces can be nonlinear functions of the variables. We demonstrate that these equations can be derived from a minimum principle. Because they are of first order in time this minimum principle differs from Hamilton's principle in classical mechanics. Whereas in Hamilton's principle only paths between determined initial and final states are considered, here the minimum is sought for among all paths starting out from a fixed initial state.

The method for determining the minimum path naturally divides into two steps. First the minimum path between fixed end points is determined by solving the Euler-Lagrange equations, and then the final state is varied. This introduces a new quantity η, which is in a sense a canonical conjugate to the macroscopic variables a. η must be set equal to zero to pick out the actual path among all solutions of the Euler-Lagrange equations.

In Sec. III, we turn to the problem of allowing for fluctuations around the deterministic path. It is natural to assume following Onsager and Machlup that the minimum value of the path integral of action as a function of fixed end points is connected with the logarithm of the transition probability $p(a'/a)\,da'$ from a state a to a state a' in the volume element da'. In the nonlinear case the correct determination of the volume element in state space is essential. As pointed out by Graham,[5] it is necessary that the probabilities transform correctly under arbitrary nonlinear transformations of the state variables. The action itself is invariant under such transformations. Using the invariance of the volume element of the conjugate pair a, η we are able to construct from the action a conditional probability with the correct transformation properties.

In Sec. IV we explicitly evaluate the expression for the conditional probability for a short time interval τ. Some of our manipulations are parallel to calculations carried out in a quantum-mechanical context.[6] We use this result in Sec. V to represent the conditional probability for finite times as a path integral. Since this integral is explicitly defined as the limit of a sequence of discrete approximations, no so-called discretization ambiguities arise. Further, we show that the conditional probability obeys a Fokker-Planck equation.

It is a consequence of the nonlinearity that there are two natural generalizations of the Onsager-Machlup functional, the functional whose minimum gives the deterministic path and the functional whose functional integral gives the conditional probability. Either one of these functionals, however, determines the other one completely. The fact that the functional in the path integral is determined by the deterministic equations can be viewed as the ultimate content of Onsager's hypothesis that the transport (deterministic) equations determine the process of spontaneous fluctuations.

II. DETERMINISTIC MOTION

A. Transport equations

Consider a system described by a set $a = (a^1, \ldots, a^i, \ldots, a^n)$ of macroscopic variables. The variables are assumed to be even in time.[7] Let $S(a)$ be the entropy of the system. The entropy is maximal for the equilibrium state. In a nonequilibrium state, the thermodynamic forces

$$\chi_i = S_{|i} \equiv \frac{\partial S}{\partial a^i} \tag{2.1}$$

drive the system towards equilibrium. The forces χ cause fluxes $\dot{a}$. The transport equations

$$\dot{a}^i = L^{ij}\chi_j \tag{2.2}$$

determine the fluxes in terms of the forces. Here and in the following we understand that a summation is to be carried out for repeated indices. Our system will be nonlinear in the sense that the transport coefficients L^{ij} may be functions of the state a, and the forces χ are not necessarily linear in a. For a system described by even variables the matrix L^{ij} is symmetric

$$L^{ij} = L^{ji}. \tag{2.3}$$

The second law requires that L^{ij} is positive definite. Given an initial nonequilibrium state the transport equations determine the future states with certainty, thus ignoring the fluctuations that take place in a realistic system. We shall refer to (2.2) also as deterministic equations. They describe the global behavior of macroscopic systems. In many cases, fluctuations are only a small correction to this global behavior.

B. Transformation properties

Instead of describing the system by the state variables a we might just as well have chosen a different set of state variables a^*, which are quite arbitrary functions of the a. Then, the fluxes associated with the new variables read

$$\dot{a}^{i*} = \frac{\partial a^{i*}}{\partial a^j}\dot{a}^j. \tag{2.4}$$

We introduce an affine geometry in state space and look upon a^i as a contravariant vector. Since the entropy is a function of the state only and does not depend on the chosen representation of the state we have

$$S^*(a^*) = S(a), \tag{2.5}$$

which means that the entropy is a scalar. Using (2.1) we see that the thermodynamic forces χ transform like a covariant vector

$$\chi_i^* = \frac{\partial a^j}{\partial a^{i*}}\chi_j \tag{2.6}$$

and from (2.2) we see with (2.4), (2.6) and $(\partial a^i/\partial a^{j*})(\partial a^{j*}/\partial a^k) = \delta^i_k$ that the matrix of transport coefficients is a contravariant tensor, i.e.,

$$L^{ij*} = \frac{\partial a^{i*}}{\partial a^k}\frac{\partial a^{j*}}{\partial a^l} L^{kl}. \qquad (2.7)$$

These transformation properties through which the covariance of the transport equations is manifest will be of some help below.

C. Variational principle

The deterministic equations of motion can be derived from a variational principle. Let us denote by L_{ij} the inverse of the transport matrix defined by

$$L_{ij}L^{jk} = L^{kj}L_{ji} = \delta_i^k. \qquad (2.8)$$

The L_{ij} form a covariant tensor. We now define a Lagrangian O by

$$O(a,\dot{a}) = \tfrac{1}{2}L_{ij}(\dot{a}^i - f^i)(\dot{a}^j - f^j), \qquad (2.9)$$

where

$$f^i = L^{ij}\chi_j \qquad (2.10)$$

is the deterministic drift. We also define an action functional A by

$$A(a(t), t_1 \le t \le t_2) = \int_{t_1}^{t_2} dt\, O(a(t), \dot{a}(t)). \qquad (2.11)$$

Given the state a of the system at time t_1 we may ask for the path $a(t)$, $t_1 \le t \le t_2$ with $a(t_1) = a$ that minimizes the functional A. The first variation of A is given by

$$\delta A = \int_{t_1}^{t_2} dt\left(\frac{\partial O}{\partial a^i} - \frac{d}{dt}\frac{\partial O}{\partial \dot{a}^i}\right)\delta a^i + \frac{\partial O}{\partial \dot{a}^i}\bigg|_{t=t_2}\delta a^i(t_2). \qquad (2.12)$$

The second term on the right-hand side appears because we allow for variations of the end point and fix only the initial state a. The minimum path[8] has to satisfy the Euler-Lagrange equations

$$\frac{d}{dt}\frac{\partial O}{\partial \dot{a}^i} = \frac{\partial O}{\partial a^i} \qquad (2.13)$$

as well as the condition

$$\frac{\partial O}{\partial \dot{a}^i}\bigg|_{t=t_2} = 0. \qquad (2.14)$$

From (2.9) we find

$$\frac{\partial O}{\partial a^i} = \tfrac{1}{2}L_{jk|i}(\dot{a}^j - f^j)(\dot{a}^k - f^k) - L_{jk}(\dot{a}^k - f^k)f^j{}_{|i} \qquad (2.15)$$

and

$$\frac{\partial O}{\partial \dot{a}^i} = L_{ij}(\dot{a}^j - f^j). \qquad (2.16)$$

If we introduce the covariant vector

$$\eta_i = \frac{\partial O}{\partial \dot{a}^i} = L_{ij}(\dot{a}^j - f^j) \qquad (2.17)$$

Eq. (2.15) can be written

$$\frac{\partial O}{\partial a^i} = -\tfrac{1}{2}L^{jk}{}_{|i}\eta_j\eta_k - f^j{}_{|i}\eta_j, \qquad (2.18)$$

where we have used (2.8) and

$$L_{jk|i}L^{kl} = -L_{jk}L^{kl}{}_{|i} \qquad (2.19)$$

and the Euler-Lagrange equations (2.13) can be transformed to

$$\dot{a}^i = f^i + L^{ij}\eta_j = L^{ij}(\chi_j + \eta_j), \qquad (2.20)$$

$$\dot{\eta}_i = -\tfrac{1}{2}L^{jk}{}_{|i}\eta_j\eta_k - f^j{}_{|i}\eta_j. \qquad (2.21)$$

These equations are of the canonical form

$$\dot{a}^i = \frac{\partial H}{\partial \eta_i}, \quad \dot{\eta}_i = -\frac{\partial H}{\partial a^i}, \qquad (2.22)$$

where the Hamiltonian H is given by

$$H(a,\eta) = \eta_i\dot{a}^i - O(a,\dot{a}) = \tfrac{1}{2}L^{ij}\eta_i\eta_j + f^i\eta_i. \qquad (2.23)$$

The condition (2.14) which comes from the variation of the final state reads

$$\eta_i(t_2) = 0. \qquad (2.24)$$

This condition extracts from (2.20) and (2.21) the special solution with $\eta(t) = 0$, and we see that the minimum path satisfies the deterministic equations (2.2).

By use of the transport equations (2.2) and Eq. (2.8) the time rate of change of the entropy can be written

$$\dot{S}(a) = \chi_i\dot{a}^i = L_{ij}\dot{a}^i\dot{a}^j = L^{ij}\chi_i\chi_j. \qquad (2.25)$$

Onsager's dissipation function

$$\phi(a,\dot{a}) = \tfrac{1}{2}L_{ij}\dot{a}^i\dot{a}^j \qquad (2.26)$$

expresses one-half of the rate of change of the entropy as a function of the state a and the fluxes $\dot{a}$. The explicit dependence of this function on the state a is a characteristic of nonlinear systems. Introducing the corresponding function of the forces

$$\Psi(a,\chi) = \tfrac{1}{2}L^{ij}\chi_i\chi_j \qquad (2.27)$$

the Lagrangian (2.9) can be written

$$O(a,\dot{a}) = \phi(a,\dot{a}) + \Psi(a,\chi) - \frac{d}{dt}S(a). \qquad (2.28)$$

This form coincides with that given by Onsager and Machlup.

III. HYPOTHESIS FOR THE CONDITIONAL PROBABILITY

A macroscopic system undergoes fluctuations that are neglected in the deterministic theory. In a stochastic theory we can not determine the future state of the system with certainty, but rather ask for a system in the state a at time t_1 for the probability $p_\tau(a'/a)da'$ to find it at time $t_2 = t_1 + \tau$ in the state a' in the volume element da'. For a closed system this conditional probability depends only on the time difference τ. The probability is normalized to

$$\int da' p_\tau(a'/a) = 1. \tag{3.1}$$

From the work of Onsager and Machlup, it is natural to consider a possible relationship of the conditional probability $p_\tau(a'/a)$ for a small time interval τ to the minimal increase of action associated with a change from the initial state a at time t_1 to the final state a' at time $t_1+\tau$. This is given by

$$A_\tau(a'/a) = \int_{t_1}^{t_1+\tau} dt\, O(a(t), \dot{a}(t))_{\min}, \tag{3.2}$$

where the minimum is taken with respect to all paths satisfying the boundary conditions

$$a(t_1) = a, \quad a(t_1+\tau) = a'. \tag{3.3}$$

The minimum path from a to a' obeys the Euler-Lagrange equations (2.13) but generally does not fulfill Eq. (2.14), which characterizes the deterministic path. Hence, the $\eta(t)$ are nonvanishing along a fluctuating path and we may say that the $\eta(t)$ cause the fluctuations. Since the $\eta(t)$ are just added to the thermodynamic forces in Eq. (2.20) we call them random forces.

Instead of characterizing the minimum path connecting a with a' by the initial and final states, we may just as well characterize it by the initial state a and the initial random forces η.[9] Then, we have to solve (2.20) and (2.21) with these initial values to obtain the final state as a function of these values

$$a' = a'(a, \eta, \tau). \tag{3.4}$$

Vice versa, we might express the initial random forces η as functions of a and a'

$$\eta = \eta(a', a, \tau). \tag{3.5}$$

From (3.2) we see with (2.9) and (2.17) that the minimal action can be written

$$A_\tau(a'/a) = \int_{t_1}^{t_1+\tau} dt\, \tfrac{1}{2} L^{ij}(a(t))\eta_i(t)\eta_j(t), \tag{3.6}$$

where the integral is along the minimum path. Since the random forces $\eta(t)$ vanish along the deterministic path, $A_\tau(a'/a)$ vanishes if a' is the final state according to the deterministic motion and it is positive for other states a'. We now assume that in the limit of a small time interval τ the action $A_\tau(a'/a)$ is a measure for the probability that a fluctuation from the state a to the state a' occurs within the time interval τ. More precisely, we make the hypothesis

$$p_\tau(a'/a)\,da' = \frac{\exp[-(1/2k)A_\tau(a'/a)]\,d\eta}{\int d\eta \exp[-(1/2k)A_\tau(a'/a)]}, \tag{3.7}$$

where k is Boltzmann's constant and η has to be viewed as a function of a' according to Eq. (3.5).

There are several comments in order: The normalization (3.1) of $p_\tau(a'/a)$ is fulfilled by construction of (3.7). Boltzmann's constant appears since the action has the dimension of the entropy such that A_τ/k is dimensionless. The probability $p_\tau(a'/a)da'$ has to be invariant under nonlinear transformations of the macrovariables. Since the Lagrangian O is a scalar, the exponential on the right-hand side of (3.7) is itself invariant. Hence, we cannot simply multiply the exponential with the differential da', which is not an invariant volume element. The invariance of the right-hand side of (3.7) is seen if one multiplies numerator and denominator by da. Then $da\,d\eta$ is a phase-space volume element that is invariant under any contact transformation and in particular under the point transformation generated by an arbitrary transformation of a. The invariance of (3.7) will be seen explicitly below.

If we denote by $\partial\eta/\partial a'$ the Jacobian of the transformation (3.5) with a and τ as parameters, we obtain

$$p_\tau(a'/a) = \frac{\exp[-(1/2k)A_\tau(a'/a)]\,\partial\eta/\partial a'}{\int d\eta \exp[-(1/2k)A_\tau(a,\eta)]} \tag{3.8}$$

for $\tau\to 0$, where $A_\tau(a,\eta) = A_\tau(a'/a)$ if η and a' are related by (3.5). We shall see that the stochastic process of the macroscopic variables is completely determined by this formula.

IV. CALCULATION OF THE CONDITIONAL PROBABILITY FOR SMALL τ

In this section the conditional probability is determined explicitly in the limit $\tau\to 0$. Though the algebraic manipulations involved are rather extensive the method used is very simple, so that we only present the basic steps. [The result of this calculation is given in Eq. (4.29).]

A. Action

Our first aim is an expression for $A_\tau(a,\eta)$ in the limit $\tau\to 0$. To this purpose we have to determine the solution of (2.20) and (2.21) with the initial conditions $a(t_1) = a$, $\eta(t_1) = \eta$. Choosing $t_1 = 0$ for simplicity, the Taylor series expansion of the solution reads

$$\begin{aligned} a^i(t) &= a^i + \dot{a}^i t + \tfrac{1}{2}\ddot{a}^i t^2 + \cdots, \\ \eta_i(t) &= \eta_i + \dot{\eta}_i t + \tfrac{1}{2}\ddot{\eta}_i t^2 + \cdots, \end{aligned} \tag{4.1}$$

where the coefficients follow from Eqs. (2.20) and

(2.21) and their derivatives as

$$\begin{aligned} \dot{a}^i &= f^i + L^{ij}\eta_j, \\ \dot{\eta}_i &= -\tfrac{1}{2}L^{jk}{}_{|i}\eta_j\eta_k - f^j{}_{|i}\eta_j, \\ \ddot{a}^i &= f^i{}_{|j}\dot{a}^j + L^{ij}{}_{|k}\dot{a}^k\eta_j + L^{ij}\dot{\eta}_j, \\ \ddot{\eta}_i &= -f^j{}_{|ik}\dot{a}^k\eta_j - f^j{}_{|i}\dot{\eta}_j - \tfrac{1}{2}L^{jk}{}_{|il}\dot{a}^l\eta_j\eta_k - L^{jk}{}_{|i}\eta_j\dot{\eta}_k, \end{aligned} \tag{4.2}$$

and so on.

To determine the action $A_\tau(a,\eta)$ we insert the expansion of $\eta(t)$ [(4.1)] and a Taylor series in $a(t)-a$ for $L^{ij}(a(t))$ into (3.6) and carry out the integral from $t_1=0$ to $t_2=\tau$ term by term. We immediately see from (3.6) that the leading contribution to $A_\tau(a,\eta)$ is given by $\frac{1}{2}L^{ij}\eta_i\eta_j\tau$. Whenever this remains finite in the limit $\tau\to 0$ it gives a contribution to (3.8). Hence, we have to consider initial random forces η that are of order $\tau^{-1/2}$. This determines the order of magnitude of the Taylor coefficients (4.2). We find

$$\begin{aligned} \eta_i, \dot{a}^i &= O(\tau^{-1/2}), \\ \dot{\eta}_i, \ddot{a}^i &= O(\tau^{-1}), \\ \ddot{\eta}_i, \dddot{a}^i &= O(\tau^{-3/2}). \end{aligned} \tag{4.3}$$

Using this, we obtain from (3.6) by systematic expansion

$$\begin{aligned} A_\tau(a,\eta) = {}& \tfrac{1}{2}L^{ij}\eta_i\eta_j\tau - \tfrac{1}{2}L^{ij}f^k{}_{|j}\eta_i\eta_k\tau^2 \\ & + \tfrac{1}{4}L^{ij}{}_{|k}f^k\eta_i\eta_j\tau^2 + O(\tau^{3/2}). \end{aligned} \tag{4.4}$$

Since the calculation is simple, we omit the details. Let us mention only that in the course of the calculation there also appear terms of fourth order in η that cancel. The action is invariant and the same should be true for the systematic approximation (4.4). The invariance is not manifest since the ordinary derivatives $f^i{}_{|j}$, $L^{ij}{}_{|k}$ do not transform like tensors. However, we may define a covariant derivative of a vector by

$$f^i{}_{;j} = f^i{}_{|j} + \left\{{}^{\,i}_{jk}\right\}f^k, \tag{4.5}$$

where

$$\left\{{}^{\,i}_{jk}\right\} = L^{il}\{jk,l\} \tag{4.6}$$

and

$$\{jk,l\} = \tfrac{1}{2}(L_{lj|k} + L_{lk|j} - L_{jk|l}). \tag{4.7}$$

This is the usual definition of a covariant derivative in a Riemannian space with metric tensor L_{ij}. It can be shown that $f^i{}_{;j}$ indeed transforms like a tensor with one contravariant and one covariant component. Using this, (4.4) may be written in a manifestly covariant form as

$$A_\tau(a,\eta) = \tfrac{1}{2}L^{ij}\eta_i\eta_j\tau - \tfrac{1}{2}L^{ij}f^k{}_{;j}\eta_i\eta_k\tau^2 + O(\tau^{3/2}). \tag{4.8}$$

B. Normalization factor

Now, we can determine the numerator on the right-hand side of Eq. (3.8). Since $\eta_i\eta_k\tau^2$ is of order τ we have

$$\begin{aligned} \exp\left(-\frac{1}{2k}A_\tau(a,\eta)\right) = {}& \exp\left(-\frac{\tau}{4k}L^{ij}\eta_i\eta_j\right) \\ & \times\left(1 + \frac{\tau^2}{4k}L^{ij}f^k{}_{;j}\eta_i\eta_k + O(\tau^{3/2})\right). \end{aligned} \tag{4.9}$$

The integral over η can easily be done with the result

$$\begin{aligned} \int d\eta \exp\left(-\frac{1}{2k}A_\tau(a,\eta)\right) = {}& \left(\frac{4\pi k}{\tau}\right)^{n/2}\frac{1}{L^{1/2}} \\ & \times\left(1 + \frac{\tau}{2}f^i{}_{;i} + O(\tau^{3/2})\right), \end{aligned} \tag{4.10}$$

where L is the determinant of the matrix of transport coefficients. The covariant divergence of the drift can be written more explicitly

$$f^i{}_{;i} = L^{1/2}(f^iL^{-1/2})_{|i}, \tag{4.11}$$

which follows from (4.5), (4.6) by use of

$$\left\{{}^{\,j}_{ij}\right\} = \tfrac{1}{2}L^{jk}L_{jk|i} = -\tfrac{1}{2}L^{jk}{}_{|i}L_{jk} = -(\ln L^{1/2})_{|i}. \tag{4.12}$$

C. Transformation from η to a'

Our next aim is an approximate expression for the transformations (3.4) and (3.5) from the η to the a' and vice versa. Since $a^{i'} = a^i(\tau)$ we obtain from (4.1)

$$a^{i'} = a^i + \dot{a}^i\tau + \tfrac{1}{2}\ddot{a}^i\tau^2 + \tfrac{1}{6}\dddot{a}^i\tau^3 + O(\tau^2), \tag{4.13}$$

where we used the order of magnitude (4.3) of the Taylor coefficients. The coefficients themselves follow from the Euler-Lagrange equations and the first two are listed in (4.2). By inserting the coefficients as functions of a and η in the needed accuracy into (4.13) we find

$$\begin{aligned} a^{i'} = {}& a^i + L^{ij}\eta_j\tau + f^i\tau + \tfrac{1}{2}(L^{ij}{}_{|k}f^k + L^{jk}f^i{}_{|k} - L^{ik}f^j{}_{|k})\eta_j\tau^2 \\ & + \tfrac{1}{6}(L^{ij}{}_{|pq}L^{pk}L^{ql} - \tfrac{1}{2}L^{ip}L^{jk}{}_{|pq}L^{ql} + \tfrac{1}{2}L^{ip}L^{jq}{}_{|p}L^{kl}{}_{|q} - L^{ip}{}_{|q}L^{qj}L^{kl}{}_{|p} \\ & + L^{ij}{}_{|p}L^{pk}{}_{|q}L^{ql} - \tfrac{1}{2}L^{ij}{}_{|p}L^{pq}L^{kl}{}_{|q})\eta_j\eta_k\eta_l\tau^3 + O(\tau^2). \end{aligned} \tag{4.14}$$

To determine the inverse transformation we first notice that we obtain in lowest order from (4.14),

$$\eta_i = (1/\tau) L_{ij} \Delta a^j + O(\tau^0), \tag{4.15}$$

where

$$\Delta a^i = a^{i\prime} - a^i . \tag{4.16}$$

This can be inserted into the terms of order τ on the right-hand side of (4.14) to yield a better approximation for η. Then, if we iterate once more we obtain

$$\eta_i = \frac{1}{\tau} L_{ij}(\Delta a^j - \tau f^j) + \frac{1}{2\tau}\{jk, i\}\Delta a^j \Delta a^k + \frac{1}{6\tau}(\{jk, i\}_{|l} - L^{pq}\{ij, p\}\{kl, q\}) \times \Delta a^j \Delta a^k \Delta a^l + O(\tau), \tag{4.17}$$

where we have used (4.7). Some terms cancel because of the form (2.10) of the deterministic drift and $\chi_{i|j} = \chi_{j|i} = S_{|ij}$.

D. Jacobian

As a next step, we calculate the Jacobian $\partial\eta/\partial a'$. With (4.17) we have

$$\frac{\partial \eta_i}{\partial a^{j\prime}} = \frac{1}{\tau} L_{ik}(\delta_j^k + M_j^k), \tag{4.18}$$

where

$$M_j^k = L^{kl}\{jr, l\}\Delta a^r + \tfrac{1}{6} L^{kl} \times (2\{jr, l\}_{|s} + \{rs, l\}_{|j} - L^{pq}\{rs, p\}\{jl, q\} - 2L^{pq}\{jr, p\}\{ls, q\})\Delta a^r \Delta a^s + O(\tau^{3/2}). \tag{4.19}$$

Since the determinant of a matrix has the properties

$$\det \vec{A}\vec{B} = \det\vec{A} \cdot \det\vec{B}, \quad \det\vec{A} = \exp(\operatorname{tr} \ln \vec{A}), \tag{4.20}$$

we obtain from (4.18)

$$\frac{\partial\eta}{\partial a'} = \frac{1}{\tau^n L} \exp[\operatorname{tr} \ln(\delta_j^i + M_j^i)] . \tag{4.21}$$

Note that M_j^i is at least of order $\tau^{1/2}$ so that (4.21) can be expanded to yield

$$\frac{\partial\eta}{\partial a'} = \frac{1}{\tau^n L}(1 + M_i^i + \tfrac{1}{2}(M_i^i)^2 - \tfrac{1}{2} M_j^i M_i^j + O(\tau^{3/2})). \tag{4.22}$$

If we insert (4.19) into (4.22) we find after some algebra

$$\frac{\partial\eta}{\partial a'} = \frac{1}{\tau^n L}[1 - (\ln L^{1/2})_{|i}\Delta a^i - \tfrac{1}{2}(\ln L^{1/2})_{|ij}\Delta a^i \Delta a^j + \tfrac{1}{2}(\ln L^{1/2})_{|i}(\ln L^{1/2})_{|j}\Delta a^i \Delta a^j - \tfrac{1}{6} R_{ij}\Delta a^i \Delta a^j + O(\tau^{3/2})], \tag{4.23}$$

where we have used (4.12) and where R_{ij} is given by

$$R_{ij} = L^{kl} R_{ikjl} \tag{4.24}$$

with

$$R_{ikjl} = \tfrac{1}{2}(L_{ij|kl} - L_{il|kj} - L_{kj|il} + L_{kl|ij}) + L^{pq}(\{ij, p\}\{kl, q\} - \{kj, p\}\{il, q\}). \tag{4.25}$$

The R_{ikjl} form the Riemann tensor of a Riemannian space with metric tensor L_{ij}. Equation (4.23) can be written in a more compact form if we notice that

$$\left(\frac{L}{L'}\right)^{1/2} = \exp(\ln L^{1/2} - \ln L'^{1/2}) = 1 - (\ln L^{1/2})_{|i}\Delta a^i + \tfrac{1}{2}(\ln L^{1/2})_{|i}(\ln L^{1/2})_{|j}\Delta a^i \Delta a^j - \tfrac{1}{2}(\ln L^{1/2})_{|ij}\Delta a^i \Delta a^j + O(\tau^{3/2}) \tag{4.26}$$

so that we may write

$$\frac{\partial\eta}{\partial a'} = \frac{1}{\tau^n (LL')^{1/2}}[1 - \tfrac{1}{6} R_{ij}\Delta a^i \Delta a^j + O(\tau^{3/2})] . \tag{4.27}$$

E. Conditional probability

Finally, we need the minimal action as a function of the end points a and a'. Let us insert η as given by Eq. (4.17) into the right-hand side of (4.4). Then, we find in the considered approximation

$$A_\tau(a'/a) = \frac{1}{2\tau} L_{ij}(\Delta a^i - \tau f^i)(\Delta a^j - \tau f^j) + \frac{1}{4\tau} L_{ij|k}\Delta a^i \Delta a^j \Delta a^k + \frac{1}{12\tau}(L_{ij|kl} - \tfrac{1}{2} L^{pq}\{ij, p\}\{kl, q\})\Delta a^i \Delta a^j \Delta a^k \Delta a^l - \tfrac{1}{2}(L_{ij} f^j)_{|k}\Delta a^i \Delta a^k + O(\tau^{3/2}). \tag{4.28}$$

We now insert (4.10) and (4.27) into (3.8) and obtain for the conditional probability

$$p_\tau(a'/a) = \frac{1}{(4\pi k\tau)^{n/2} L'^{1/2}} \exp\left(-\frac{1}{2k} A_\tau(a'/a)\right) [1 - \tfrac{1}{2}\tau f^i{}_{;i} - \tfrac{1}{6} R_{ij}\Delta a^i \Delta a^j + O(\tau^{3/2})] . \tag{4.29}$$

In this approximation $A_\tau(a'/a)$ is determined by (4.28). From this explicit form of the conditional probability we see that $p_\tau(a'/a)da'$ is in fact invariant. $da'/L'^{1/2}$ is an invariant volume element in state space. The minimal action $A_\tau(a'/a)$ is invariant as is most easily seen from Eq. (4.4). The expression (4.28) disguises the transformation properties to some extent. Note that Δa^i has vector character only in the lowest order in τ where it is approximated by $L^{ij}\eta_j\tau$. However, this approximation is sufficient in the term $R_{ij}\Delta a^i \Delta a^j$ on the right-hand side of (4.29) so that the terms in parenthesis form a scalar in the considered approximation.

V. PATH INTEGRAL AND FOKKER-PLANCK EQUATION

A. Modified Lagrangian

Let us now examine some properties of the conditional probability $p_\tau(a'/a)$ for small τ. If we insert (4.28) into (4.29) and make use of (4.26) we find

$$p_\tau(a'/a) = \frac{1}{(4\pi k\tau)^{n/2}L^{1/2}} \exp\left(-\frac{1}{4k\tau}L_{ij}(\Delta a^i - \tau f^i)(\Delta a^j - \tau f^j)\right)\left(1 - \frac{1}{8k\tau}L_{ij|k}\Delta a^i \Delta a^j \Delta a^k - (\ln L^{1/2})_{|i}\Delta a^i + O(\tau)\right). \tag{5.1}$$

Here we have omitted terms of order τ. These terms are important for the proper normalization of $p_\tau(a'/a)$, however, they will not contribute to the moments in order τ that we shall determine now. Using (5.1) and well-known properties of Gaussian integrals we find

$$\int da' \Delta a^{i_1} \cdots \Delta a^{i_m} p_\tau(a'/a) = O(\tau^{3/2}) \quad \text{for } m \geq 3,$$
$$\int da' \Delta a^i \Delta a^j p_\tau(a'/a) = 2kL^{ij}\tau + O(\tau^{3/2}), \tag{5.2}$$
$$\int da' \Delta a^i p_\tau(a'/a) = K^i\tau + O(\tau^{3/2}),$$

where

$$K^i = f^i + kL^{1/2}(L^{ij}L^{-1/2})_{|j}. \tag{5.3}$$

In determining the first moment we have made use of (2.19) and (4.12). For the zeroth-order moment we have to include the terms of order τ omitted in (5.1) and use the more accurate approximation (4.29). Naturally, we will obtain

$$\int da' p_\tau(a'/a) = 1 + O(\tau^{3/2}) \tag{5.4}$$

in this approximation, since the conditional probability is normalized by definition. To the normalization integral the term $-\frac{1}{6}R_{ij}\Delta a^i \Delta a^j$ on the right-hand side of (4.29) yields a contribution of $-\frac{1}{3}R_{ij}L^{ij}k\tau + O(\tau^{3/2})$. The normalization is the only place where this term gives a contribution of order τ. Hence, we can replace it by $-\frac{1}{3}R_{ij}L^{ij}k\tau$ and the conditional probability may be written

$$p_\tau(a'/a) = \frac{1}{(4\pi k\tau)^{n/2}L'^{1/2}} \times \exp\left(-\frac{1}{2k}\tilde{A}_\tau(a'/a)\right)[1 + O(\tau^{3/2})], \tag{5.5}$$

where

$$\tilde{A}_\tau(a'/a) = A_\tau(a'/a) + kf^i_{;i}\tau + \tfrac{2}{3}k^2R\tau \tag{5.6}$$

and

$$R = R_{ij}L^{ij}. \tag{5.7}$$

Here we have transferred terms of order τ to the exponent which gives only corrections of higher order, and have introduced a modified action $\tilde{A}_\tau(a'/a)$. With the modified Lagrangian

$$\begin{aligned}\tilde{O}(a,\dot{a}) &= O(a,\dot{a}) + kf^i{}_{;i} + \tfrac{2}{3}k^2R \\ &= \tfrac{1}{2}L_{ij}(\dot{a}^i - f^i)(\dot{a}^j - f^j) + kf^i{}_{;i} + \tfrac{2}{3}k^2R,\end{aligned} \tag{5.8}$$

the action $\tilde{A}_\tau(a'/a)$ may be written

$$\tilde{A}_\tau(a'/a) = \int_{t_1}^{t_1+\tau} dt\, \tilde{O}(a(t), \dot{a}(t))_{\min}, \tag{5.9}$$

where the integral is over the minimum path connecting a with a'. Of course, the new Lagrangian $\tilde{O}$ will also modify the Euler-Lagrange equations. However, this change does not show up in the action in the considered approximation neglecting terms of order $\tau^{3/2}$.

B. Path integral

It is shown in the Appendix that the conditional probability (4.29) fulfills the Chapman-Kolmogorov equation for small time intervals

$$\int da' \, p_{\tau''}(a''/a') p_{\tau'}(a'/a) = p_\tau(a''/a)[1 + O(\tau^{3/2})], \quad \tau = \tau' + \tau''. \quad (5.10)$$

Hence, we may look upon (4.29) as the short-time approximation of the conditional probability of a Markov process. Then, the conditional probability for a finite time difference s follows by repeated use of (5.10) as

$$p_s(a'/a) = \lim_{N\to\infty} \int da^1 \cdots da^{N-1} \times p_\tau(a'/a^{N-1}) p_\tau(a^{N-1}, a^{N-2}) \cdots p_\tau(a^1, a) \quad (5.11)$$

where $\tau = s/N$. On the right-hand side of (5.11) the approximations (4.29) or (5.5) for the conditional probability are sufficient since terms of order $\tau^{3/2}$ do not contribute in the limit $N\to\infty$. With (5.5) and (5.9) we obtain more explicitly

$$p_s(a'/a) = \frac{1}{L(a')^{1/2}} \lim_{N\to\infty} \frac{1}{(4\pi k\tau)^{nN/2}} \times \int \prod_{i=1}^{N-1} \frac{da^i}{L(a^i)^{1/2}} \exp\left(-\frac{1}{2k}\int_0^s dt \, \tilde{O}(a,\dot{a})_{\min}\right), \quad (5.12)$$

where $\tau = s/N$, and where the integral $\int_0^s dt\, \tilde{O}(a,\dot{a})_{\min}$ is over the minimum path satisfying $a(0) = a, a(i\tau) = a^i, a(s) = a'$.[10] This relation defines the conditional probability for arbitrary s.

Introducing a scalar measure of integration

$$D[a(t)] = \lim_{N\to\infty} \frac{1}{(4\pi k\tau)^{nN/2}} \prod_{i=1}^{N-1} \frac{da(i\tau)}{L(a(i\tau))^{1/2}} \quad (5.13)$$

we may write the right-hand side of (5.12) as a path integral

$$p_s(a'/a) = \frac{1}{L(a')^{1/2}} \int D[a(t)] \exp\left(-\frac{1}{2k}\int_0^s dt\, \tilde{O}(a,\dot{a})\right). \quad (5.14)$$

This has to be looked upon as a shorthand notation for the limit (5.12).

C. Fokker-Planck equation

The conditional probability $p_s(a'/a)$ and the initial single-event distribution $p_{t_0}(a)$ characterize the Markovian process of fluctuations completely. The single-event distribution at time t is given by

$$p_t(a) = \int da' \, p_{t-t_0}(a/a') p_{t_0}(a'). \quad (5.15)$$

It is known from the theory of stochastic processes[11] that for a Markov process with the properties (5.2) the single-event distribution $p_t(a)$ fulfills the Fokker-Planck equation

$$\frac{\partial}{\partial t} p_t(a) = \frac{\partial}{\partial a^i}\left(-K^i(a) + \frac{\partial}{\partial a^j} k L^{ij}(a)\right) p_t(a). \quad (5.16)$$

Further, the conditional probability is the Green's function of (5.16) so that the Fokker-Planck equation itself specifies the dynamics of fluctuations completely. By use of (5.3) and $f^i = L^{ij} S_{|j}$, Eq. (5.16) can be transformed to

$$\frac{\partial}{\partial t} p_t = \frac{\partial}{\partial a^i} k L^{ij}\left[\frac{\partial p_t}{\partial a^j} - p_t \frac{\partial}{\partial a^j}\left(\frac{S}{k} - \ln L^{1/2}\right)\right]. \quad (5.17)$$

From this form of the Fokker-Planck equation we see that

$$w(a) = \frac{1}{L(a)^{1/2}} \exp\left(\frac{1}{k} S(a) + \text{const}\right) \quad (5.18)$$

is the stationary distribution. The normalization constant can be absorbed by the entropy. Equation (5.18) relates the fluctuations in the stationary (equilibrium) state with the macroscopic state function entropy and can be viewed as a version of Boltzmann's principle. The factor $L(a)^{-1/2}$ is necessary in nonlinear systems in order that $w(a)\, da$ and $S(a)$ should both be independent of the chosen representation of the state.

D. $k \to 0$ limit

From the Fokker-Planck equation (5.16) we find for the average flux

$$\langle \dot{a}^i \rangle = \langle K^i \rangle = \langle f^i \rangle + k \langle L^{1/2} (L^{ij} L^{-1/2})_{|j} \rangle, \quad (5.19)$$

where $\langle\ \rangle$ is the average over $p_t(a)$. Generally $\langle f^i \rangle$ is different from $f^i(\langle a \rangle)$, however, in the limit $k \to 0$ the diffusion matrix kL^{ij} of the Fokker-Planck equation vanishes and there is no broadening of a distribution initially concentrated at one state. From Eq. (5.19), we see that the center of such a distribution will move in the limit $k\to 0$ according to

$$\dot{a}^i = f^i(a). \quad (5.20)$$

Hence, the deterministic theory is the limit $k \to 0$ of the stochastic theory.

This can also be seen from the path integral representation (5.14) of the conditional probability. Because of the factor of $1/2k$ in the exponent and

$$\lim_{k\to 0} \tilde{O}(a,\dot{a}) = O(a,\dot{a}) \quad (5.21)$$

the path probability concentrates in the limit $k \to 0$ sharply around the deterministic path and the fluctuations vanish.

VI. CONCLUSION

Starting with the deterministic equations of motion of an irreversible system we have examined the process of spontaneous fluctuations of the state variables. The stochastic theory was based on the "fluctuation hypothesis" (3.7). Logically, there is no reason why the approximate deterministic theory should determine the stochastic theory. Rather, the logical argument runs vice versa, the deterministic theory is a limiting case of the stochastic theory and the stochastic theory needs direct justification.

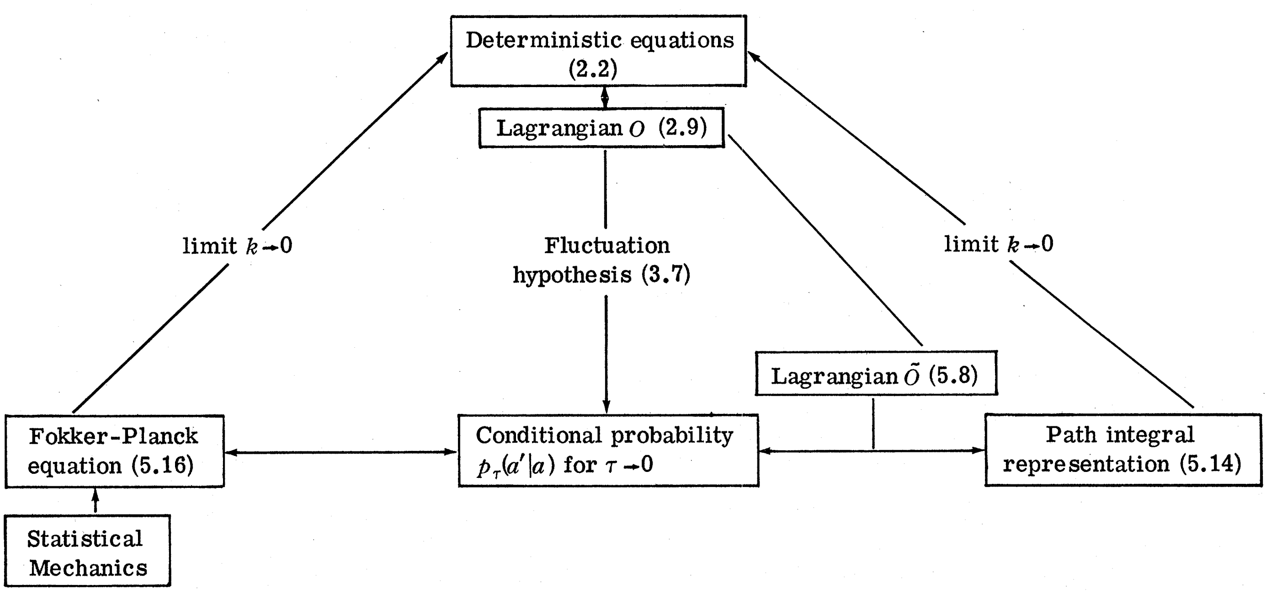
The Markovian process of spontaneous fluctuations has been considered from a statistical-mechanical point of view in an earlier paper by one of us.[3] There the Fokker-Planck equation[12]

$$\frac{\partial}{\partial t}p_t = \frac{\partial}{\partial a^i}\left(-w^{-1}\frac{\partial w\xi^{ij}}{\partial a^j} + \frac{\partial}{\partial a^j}\xi^{ij}\right)p_t \qquad (6.1)$$

is derived. $w(a)$ and the symmetric matrix ξ^{ij} are defined by molecular expressions. Contact with the phenomenological theory is made if we define the transport coefficients L^{ij} and the entropy S by

$$\xi^{ij} = kL^{ij}, \quad w = e^{S/k}/L^{1/2}. \qquad (6.2)$$

Note that Boltzmann's constant does not appear naturally in a statistical mechanical theory. With (6.2) the transport coefficients and the entropy are measured in the usual units of phenomenological thermodynamics. By use of (6.2) the Fokker-Planck equation (6.1) is easily brought into the form (5.17) or (5.16). Hence, the stochastic theory presented here can be based on statistical mechanics. The deterministic theory can now be looked upon as the $k\to 0$ limit of the stochastic theory and the fluctuation hypothesis (3.7) shows up to give the correct connection of the conditional probability for short times with the deterministic equations. The mutual dependence of the various equations can be summarized in a diagram:



As a special result our work gives the path-integral representation (5.14) of the Green's function of the Fokker-Planck equation (5.16). This problem has recently been considered by Graham.[5] In order to compare with Graham's result we have to put formally $k=\frac{1}{2}$. Then, the Fokker-Planck equation (5.16) coincides with Graham's Eq. (3.1) in Ref. 5(b) up to differences in notation. The Lagrangian $\tilde O$ defined in (5.8) reads for $k=\frac{1}{2}$

$$\tilde O(a,\dot a) = \tfrac{1}{2}L_{ij}(\dot a^i - f^i)(\dot a^j - f^j) + \tfrac{1}{2}f^i{}_{;i} + \tfrac{1}{6}R.$$

This differs from Graham's Lagrangian [Eq. (6.3) in Ref. 5(b)] in the last term where he obtained $\frac{1}{12}R$. The difference is due to Graham's use of the relation $\Delta a^i = \dot a^i\tau$, which is not accurate enough in nonlinear systems[13] but has to be replaced by

(4.14). The term $\frac{1}{6}R$ is completely determined by the proper normalization of the conditional probability which we take explicitly into account.

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APPENDIX: DERIVATION OF EQ. (5.10)

In order to verify (5.10) we have to show that

$$Z_{\tau'\tau''}(a''|a) = \int da'\, p_{\tau''}(a''|a')p_{\tau'}(a'|a) \tag{A1}$$

has in order $\tau=\tau'+\tau''$ the same moments as $p_\tau(a''|a)$. Because of (5.4) we find for the zeroth-order moment

$$\int da''\, Z_{\tau'\tau''}(a''|a) = 1+O(\tau'^{3/2})+O(\tau''^{3/2}) = 1+O(\tau^{3/2}). \tag{A2}$$

For the higher-order moments we can use the approximate expression (5.1) for the conditional probability, which can also be written

$$p_\tau(a'|a) = \frac{1}{(4\pi k\tau)^{n/2}L'^{1/2}} \times \exp\left(-\frac{1}{4k\tau}\,\overline{L}_{ij}(\Delta a^i-\tau f^i)(\Delta a^j-\tau f^j)\right) \times (1+O(\tau)), \tag{A3}$$

where $\overline{L}_{ij}$ is L_{ij} taken at the midpoint $\overline{a}=\frac{1}{2}(a+a')$ of its argument.

Inserting (A3) in the right-hand side of (A1), we find

$$Z_{\tau'\tau''}(a''|a) = \frac{1}{(4\pi k\tau)^{n/2}L''^{1/2}} \exp\left(-\frac{1}{4k\tau}\overline{L}_{ij}(\Delta a^i-\tau f^i)(\Delta a^j-\tau f^j)\right) \times \int d\alpha \frac{1}{(4\pi k\tau'\tau''/\tau)^{n/2}\overline{L}^{1/2}} \exp\left(-\frac{1}{4k}\frac{\tau}{\tau'\tau''}\overline{L}_{ij}\alpha^i\alpha^j\right)[1+O(\tau)] = p_\tau(a''|a)[1+O(\tau)]. \tag{A4}$$

Here $\overline{L}_{ij}$ is taken at the position $\frac{1}{2}(a+a'')$, and we have made use of the transformation

$$a' = \alpha + (\tau''a+\tau'a'')/\tau. \tag{A5}$$

By (A4) the first and higher moments of $Z_{\tau'\tau''}(a''|a)$ coincide in order τ with the corresponding moments of $p_\tau(a''|a)$. From this and (A2) we obtain Eq. (5.10).

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[1]A. Einstein, Ann. Phys. (Leipzig) 17, 549 (1905).

[2](a) N. Nyquist, Phys. Rev. 32, 110 (1928). (b) L. Onsager, *ibid.* 37, 405 (1931); 38, 2265 (1931). (c) J. G. Kirkwood, J. Chem. Phys. 14, 180 (1946). (d) H. B. Callen and T. A. Welton, Phys. Rev. 83, 34 (1951). (e) N. Hashitzume, Prog. Theor. Phys. 8, 461 (1952).

[3]M. S. Green, J. Chem. Phys. 20, 1281 (1952).

[4]L. Onsager and S. Machlup, Phys. Rev. 91, 1505 (1953); 91, 1512 (1953).

[5](a) R. Graham, Z. Phys. B 26, 281 (1977). (b) 26, 397 (1977).

[6]B. S. DeWitt, Rev. Mod. Phys. 29, 377 (1967); U. Weiss, Z. Phys. B 30, 429 (1978).

[7]The more-general case of variables with mixed time reversal symmetry will be considered in a subsequent publication.

[8]The extremum is a minimum because the matrix of transport coefficients is positive.

[9]We adopt the convention that unprimed quantities (a,η) refer to time t_1, whereas primed quantities (a',η') refer to time $t_1+\tau$. Whenever necessary we indicate the time dependence explicitly.

[10]The minimum path has $N-1$ points where the derivative $\dot{a}$ does not exist. The path is, however, continuous and the singular points are connected by analytic arcs having a Taylor-series expansion in time. Although the Lagrangian $\tilde{O}$ is undefined for a finite number of points, the action integral exists for each N and the limit (5.12) is well defined. The limiting paths are nevertheless typically nondifferentiable.

[11]R. L. Stratonovich, *Topics in The Theory of Random Noise*, (Gordon and Breach, New York, 1963).

[12]Equation (30) in Ref. 3, specialized to even variables by means of (54) and (56).

[13]The substitution $\Delta a=\dot{a}\tau$ would only hold if the limiting paths would be differentiable. Δa however is of order $\tau^{1/2}$. The rule $\Delta a=\dot{a}\tau$ also violates covariance because Δa is not a vector.