Stochastic Process of Nucleation in the Early Stage

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The nonlinear relaxation processes from unstable or metastable states have been studied with keen interest by physicists in the field of statistical physics. As is well known in such non-stationary processes, there appears transiently a certain regime where the deterministic description by rate equations breaks down completely. In the present note we concern ourselves with the early stage of the organization process of the final stable state in the framework of the birth-and-death type markoffian process.

Let us consider the following situation appeared in the relaxation process from initial unstable state: At the initial time \( t=t_0 \), the distribution \( P(x, t) \) has only one most probable peak around the unstable state. Here \( x \) denotes the state variable. With the attenuation and the broadening of the initial unstable distribution \( P(x, t_0) \), the second small peak appears locally around the point of \( x=x_c \) at \( t=t_c \) for the first time. In this paper we call the organization of this second small peak "nucleation". This small local peak (or nucleus) can be considered to be a germination of the most probable peak in the final stable distribution \( P(x, t) \). The nucleating point \( (t_c, x_c) \) may be depending on the initial unstable distribution \( P(x, t_0) \) as well as on the system under consideration. Nevertheless, it is expected that the time evolution of the nucleus in the very early stage obeys a universal law once the nucleus has been organized in the system under consideration. In this paper, however, we do not specify the system because the formulations obtained in the present article are applicable to every system in which the initial distribution function can develop such a local peak as was mentioned above. The concrete system will be studied in a forthcoming paper.

The scaled intensive variable \( x \) satisfies the following generalization Fokker-Planck equation:

\[
\frac{\partial P}{\partial t} = \sum_{n=1}^{\infty} \frac{1}{n!} (-\partial / \partial x)^n c_n P, \quad (1)
\]

where \( P \) is the probability density function, and \( c_n \) is the \( n \)-th transition moment of the markoffian process. Hence \( c_n \) is of \( (n-1) \)-th order of inverse system size \( N^{-1}(=\varepsilon) \). When we introduce the generalized potential \( \phi \) by the relation \( P=\exp (-\phi) \), \( \phi \) satisfies the following relation:

\[
-\frac{\partial^2 \phi}{\partial t^2} = (-\partial c_1 / \partial x + \cdots)
\]

where \( \cdots \) denotes the higher order quantities of \( \varepsilon \) than that of the first term in each bracket \( (\ ) \), but here we have not yet assumed that \( \phi \) is of order \( O(N^{-1}) \). By expanding the potential \( \phi \) into a power series of \( x \) around the local peak point of \( P(x, t) \), i.e., \( x=y(t) \),

\[
\phi = a_0(t) + a_2(t) (x-y(t))^2 + a_3(t) (x-y(t))^3 + \cdots, \quad (3)
\]

we can get the coupled equations of \( a_k(t) \) and \( y(t) \) from Eq. (2). For example, the equation of \( dy/dt \) becomes as follows:
where only the dominant terms are taken into account and \( \cdots \) denotes the contribution arising from the higher order transition moments. \( y(t) \) must satisfy the following condition, \( y(t_c) = x_c \). In such nonstationary process as the nucleation under consideration, \( a_k \) is not necessarily of order \( N^t \), in addition, in the very early stage of nucleation \( a_2(t) \) goes to zero as \( t \to t_c \), because the curvature of the potential \( \phi \) is zero at the nucleating point \( (x_c, t_c) \). Consequently, the right-hand side of Eq. (4) becomes quite simple. In the equation of \( dy/dt \), the second term of the r.h.s. is most dominant, provided that the first transition moment does not have any singularities. Namely, in the early stage of nucleation the motion of the local peak \( y(t) \) is described by the following equation:

\[
\frac{dy}{dt} = - \frac{1}{2a_2} G(y, \{a_j\}).
\]

(5)

By the same consideration as used in the derivation of Eq. (5), the equation of \( da_k/dt \) is approximated by the most dominant terms including the factor \( a_2(t)^{-1} \) as appeared in the expression of \( dy/dt \). The solution of \( a_2(t) \) is derived as follows:

\[
a_2(t) = \sqrt{K(t-t_c)}, \quad K = -3a_2(t_c)G(x_c, \{a_j\}).
\]

(6)

This solution shows the birth or death of the nucleation for \( K > 0 \) or \( K < 0 \), respectively. By the use of Eqs. (5) and (6), the motion of the local peak \( y(t) \) is given as follows:

\[
y(t) = x_c + \sqrt{H(t-t_c)}, \quad H = K/(3a_1(t_c))^2.
\]

(7)

When \( a_2 \) becomes zero at the nucleating point \( t = t_c \), we must seek the other solution than Eqs. (6) and (7), because the solution of Eq. (7) loses its physical meanings in the case of \( a_2(t_c) = 0 \). To this end we will consider the following general case where \( a_k(t) \to 0 \) as \( t \to t_c \) \((k=2, 3, \ldots, n+1)\), and \( a_{n+2}(t_c) \) is finite. Then Eq. (2) in the early stage of nucleation gives the following relations:

\[
\frac{da_k}{dt} = \frac{(k+1)a_{k+1}}{(k+2)a_{k+2}} \frac{da_{k+1}}{dt},
\]

\[
\frac{dy}{dt} = \frac{da_2}{3a_1}.
\]

(8)

The solution of Eq. (8) are obtained as

\[
a_k(t) = A_k(t-t_c)^{\nu_k}, \quad y = x_c + \tilde{H}(t-t_c)^{\nu}, \quad \nu = \frac{1}{n+1}, \quad \nu_k = \frac{n-k+2}{n+1}, \quad \tilde{H} = - (n+1)G(x_c, \{a_j(t_c)\})/\nu, \quad A_k = \alpha/\nu (x_c, \{a_j(t_c)\})^{k-1} \times \left( \nu-\frac{1}{2} \right) \times \left( \nu-\frac{2}{3} \right) \times \cdots \times \left( \nu-\frac{k-3}{k-2} \right)^{k-1},
\]

(9)

where we have used the two parameters, \( 2A_2 = \alpha \) and \( \mu_k = \nu \).\(^3\)

In this note we have showed that dynamics of fluctuations satisfies the universal relation in the early stage of nucleation. Our discussion has been limited to the case where the nucleation is created by the internal fluctuation of the system, but we can also generalize the same kind of law as Eq. (8) to the case of the nucleation driven by an external noise and of the multivariate system. The recent results of numerical simulations carried out near the critical point of the chemical reaction seem to support the relation given by Eq. (7). Detailed results will be reported elsewhere.\(^3\)
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