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Nucleation Theory for a Model Bistable Chemical Reaction

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The theory of homogeneous nucleation is developed for a model nonlinear bistable chemical reaction driven far from equilibrium (trimolecular Schlögl model). The theory is restricted to the vicinity of the stable/unstable transition, where the nucleation barrier is small but nonvanishing. The nucleation rates are derived for two types of fluctuations: first, fluctuations due to a homogeneous external white noise source, and second, internal chemical fluctuations, described by a reastion-diffusion multivariate master equation. In the white noise case, a Landau–Ginzburg potential can be defined, and the standard nucleation formalism can be applied; this is not true for the internal case and a new result is used. The inhomogeneous chemical fluctuations, due to the coupling between the nonlinear reaction and diffusion, are shown to have an influence on the nucleation rate. Quantitative conditions are also given to evaluate the possibility of homogeneous nucleation in nonlinear chemical systems.

KEY WORDS: Nucleation; bistability; chemical reactions; fluctuations.

1. INTRODUCTION

Zaikin and Zhabotinskii(1) first showed, in 1970, that the Belousov–Zhabotinskii reactants, when prepared in a closed Petri dish, can spontaneously display striking spatial patterns, such as targets or spirals. Ever since, these structures have been extensively studied and discussed from both experimental and theoretical points of view (for a thorough review, see Vidal and Hanusse(2)). In recent years, chemical systems other than the BZ reaction have been investigated that also lead to spatial organization, for example, the arsenious acid–iodate reaction,(3,4) which appears as one of the most promising.

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The mechanism of propagation of the spatial patterns seems well understood within the frawework of solitary wave theories for bistable, excitable, or oscillatory reactions.(4–9) However, the mechanism of their creation from an initially uniform medium is still under discussion. Is it always a heterogeneous mechanism, due to pieces of dust or of catalyst present in solution? Or is there some room for a purely homogeneous nucleation process, initiated by the intrinsic internal fluctuations, which, although small, are always present in a macroscopic system? A theoretical answer, taking into account internal fluxtuations, has been given by Walgraef *et al.*(10) in the case of an oscillatory reaction. A careful experiment of Vidal *et al.*(11) using the BZ system does not confirm their predictions. As a side result, these authors did not detect any nucleation process in excitable conditions when careful filtering of the solution was performed. Their observation seems to support the idea of a purely heterogeneous mechanism of nucleation, at least in the BZ case, but does not give a definitive answer to the problem.

In this paper, we are interested in deriving a homogeneous nucleation rate formula for a chemically metastable system. We develop our theory with a simplified model of a bistable chemical reaction, the Schögl model; we have shown elsewhere(12) that our approach can easily be generalized to multispecies bistable and excitable reactions, as long as some time scale separation can be made in the kinetic mechanism. Most nonlinear chemical system belong to this category, and the BZ reaction in particular.(13,14) Note also that a mixture of iodate and arsenious acid, with an excess of iodate, provides a nice example of a one-variable, bistable reaction similar to the one of Shlögl.(15)

The Schlögl trimolecular model is presented in the next section. In a closed vessel, the theoretical starting point is a reaction-diffusion equation (RDE) associating mass transport and nonlinear chemical kinetics in the absence of convection.

In Section 3, we briefly present the deterministic theory of nucleation,(16) introducing the concept of nucleation nucleus, which is essential for the following stochastic treatment. Many general results given here are known in the literature, but have not been applied directly to nonlinear chemical systems. The deterministic analysis permits us to study the growth of the nucleus; however, it clearly does not account for the creation of the nucleation nucleus, which is due to the fluctuations: the next parts of the paper are devoted to this problem.

In Section 4, we develop a stochastic theory in order to derive the nucleation rate from an initially metastable chemical medium. In a first part, we suppose that the source of noise is external, which amounts to describing the fluctuation process by a simple multivariate Fokker–Planck equation, with an additive, diagonal noise matrix. Up to this point, our theory remains mainly based on the pioneering work of Langer on nucleation processes(17,18) and on the results of Landauer and coworkers.(16,19)

In the second part of Section 4, we consider the case of an internal fluxtuation mechanism. The adequate level of description this time is the multivariate master equation of Nicolic and Prigogine.(20) This equation accounts for inhomogeneous fluctuations due to the internal coupling between reaction and diffusion. Using a new generalization of the results of Langer to compute the nucleation rate, we find that the inhomogeneous fluctuations tend to lower the nucleation barrier, since they are responsible for long-range correlations, which have the same spatial extent as the width of the nucleation nucleus.

In the last part of Section 4, orders of magnitude are discussed from a chemical point of view. Conclusions are presented in Section 5.

2. MODEL

The second Schlögl model(21) has been introduced as the minimal elmentary mechanism giving rise to chemical bistability. Let A and B be two species whose concentrations are held constant, and X a variable species. The reaction reads

$$A + X \rightleftarrows 3X, \qquad X \rightleftarrows B \tag{2.1}$$

The first step is a trimolecular one, whose relevance from a chemical point of view is open to discussion. It may be understood as the reduction of several elementary steps where some quickly varying species have been adiabatically eliminated. On the other hand, as will be seen in this paper, this simple model permits us to obtain analytical results which can be quantitatively applied to more realistic situations (and even to multispecies systems(12)). The kinetic equation of reaction (2.1) is

$$dx/dt = F(x) = -dV(x)/dx \tag{2.2}$$

with

$$F(x) = -k_1 x^3 + k_2 x_A x^2 - k_3 x + k_4 x_B$$

x, x_A, an x_B are the concentrations of X, A, and B respectively. $V(x)$ is defined as the kinetic potential.

According to the imposed constraints, here the concentrations of A and B, Eq. (2.2) may have three stationary solutions, two of them stable, the third unstable. We suppose in the remaining of this paper that the bistability condition is fulfilled, and denote the stable concentrations by x_1 and x_3 and the unstable one by x_2 ($x_1 < x_2 < x_3$). The kinetic potential $V(x)$ has in this case the shape of a double well, with two minima at x_1 and x_3 and a maximum at x_2. Furthermore, we assume that x_1 is the metastable state and x_3 the stable one, in the sense that

$$V(x_1) < V(x_3) \tag{2.3}$$

The potential $V(x)$ is given in Fig. 1. If the Schlögl reaction takes place in a closed, one-dimensional vessel, a diffusional term is added to the kinetic equation (2.2) and yields the usual reaction-diffusion equation (RDE)

$$\frac{\partial x(\rho, t)}{\partial t} = F(x(\rho, t)) + \mathscr{D} \frac{\partial^2 x(\rho, t)}{\partial \rho^2} \tag{2.4}$$

where ρ is the spatial coordinate and $\mathscr{D}$ is the Fick diffusion coefficient. It will be convenient in the following to work with dimensionless concentration and time coordinates. If

$$u = x/x_1, \qquad \tau = t/\tau_c, \qquad D = \mathscr{D}\tau_c \tag{2.5}$$

with τ_c characteristic time of the reaction, $(k_1 x_1^2)^{-1}$, the RDE becomes

$$\frac{\partial u(\rho, t)}{\partial t} = f(u(\rho, t)) + D \frac{\partial^2 u(\rho, t)}{\partial \rho^2} \tag{2.6}$$

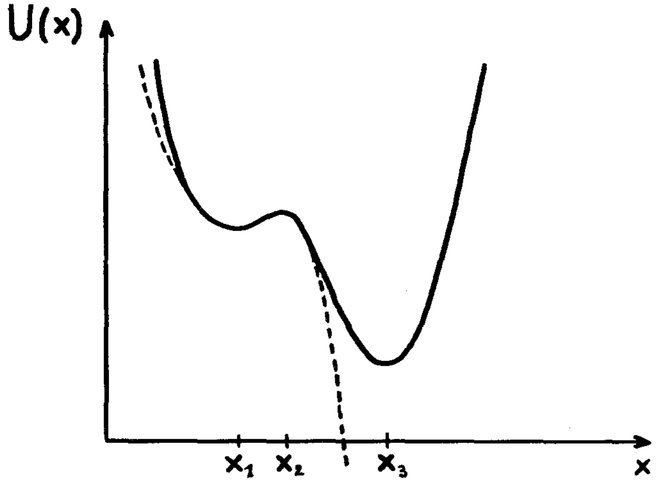

Fig. 1. Double-well potential $V(x)$ and (---) small-amplitude-nucleus limit.

with

$$f(u) = (1-u)(u_2-u)(u_3-u) = O(1)$$

Finally, we also find it convenient to move the concentration origin in the metastable state. With the convention

$$\xi = u - 1 = (x - x_1)/x_1 \tag{2.7}$$

the RDE takes the final form

$$\frac{\partial \xi}{\partial t} = D\frac{\partial^2 \xi}{\partial \rho^2} - b\xi + a\xi^2 - \xi^3 \tag{2.8}$$

with

$$b = |f'(1)| = (u_2-1)(u_3-1), \qquad a = \tfrac{1}{2}f''(1) = u_2 + u_3 - 2$$

3. DETERMINISTIC THEORY

3.1. Propagating Fronts and Nucleation

It is well known$^{(22,23)}$ that the RDE equation (2.8) admits kink–antikink solutions, which can be expressed as

$$\xi(\rho, t) = \xi_3\{1 + \exp[\pm\delta(\rho - \rho_0 \pm vt)]\}^{-1} \tag{3.1a}$$

with

$$\begin{gathered} \xi_3 = \tfrac{1}{2}[a + (a^2 - 4b)^{1/2}] \\ \delta^2 = \xi_3^2/2D, \; v = -(3b - a\xi_3)/2\delta \end{gathered} \tag{3.1b}$$

These solutions appear as fronts of constant profile, of width δ^{-1}, and moving at constant velocity v from the stable state, $\xi \equiv \xi_3$, to the metastable one, $\xi \equiv 0$ (v is positive when $V(0) > V(\xi_3)$, or, according to our notations, when $b < 2a^2/9$).

In this context, the nucleation of the stable "phase," $\xi \equiv \xi_3$, from an initially homogeneous metastable medium can be understood as the spontaneous creation of a kink–antikink pair, which later separates in each direction. When separated by a certain critical length κ, the kink and the antikink form a stationary profile, called a nucleation nucleus $\bar{\xi}(\rho)$, which represents an intermediate solution between the metastable and stable phases. This solution can be determined exactly as the product of a kink centered at $\rho = 0$ and an antikink at $\rho = -\kappa^{(23)}$ (see Fig. 2):

$$\bar{\xi}(\rho) = \xi_0 [1 + \exp(\delta\rho)]^{-1} \{1 + \exp[-\delta(\rho + \kappa)]\}^{-1} \tag{3.2}$$

where ξ_0 is the amplitude of the nucleus and δ^{-1} is the with of the diffusion front. Substitution of (3.2) in the RDE (2.8) makes it possible to determine the values of the three parameters κ, δ, and ξ_0,

$$\delta = \left(\frac{b}{D}\right)^{1/2}, \qquad \xi_0 = \frac{6b}{a + 3(b/2)^{1/2}}, \qquad \kappa = -\frac{1}{\delta} \ln \frac{a - 3(b/2)^{1/2}}{a + 3(b/2)^{1/2}} \tag{3.3}$$

When the kink and the antikink are separated by a distance less than κ, they tend to annihilate each other, and the concentration profile decays to the metastable homogeneous state. On the contrary, when the separation becomes greater than κ, the kink–antikink pair separates and the system evolves toward the homogeneous stable state. The nucleation nucleus can be interpreted in functional space as a saddle point solution between the attraction domains of the metastable solution, $\xi = 0$, and the stable one, $\xi = \xi_3$.

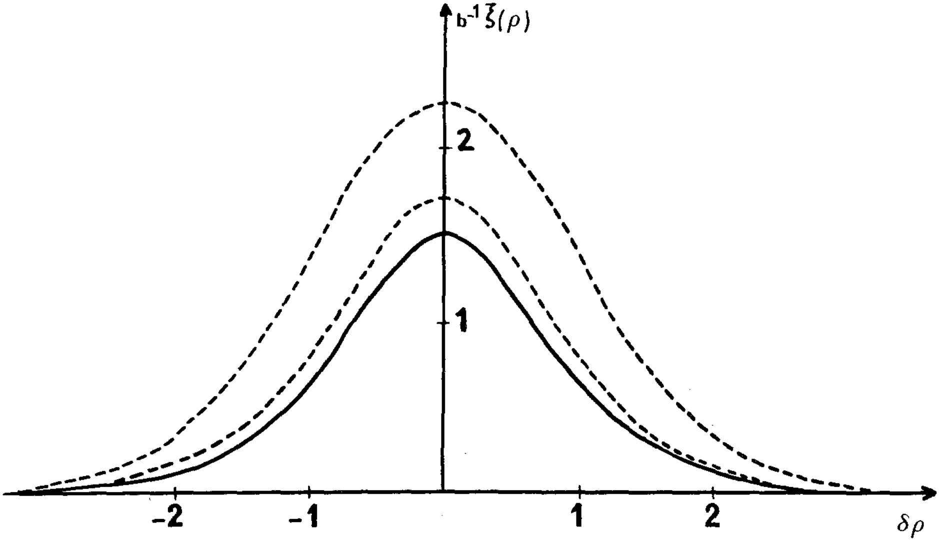

Fig. 2. Nucleation nucleus $b^{-1}\bar{\xi}(\rho)$ as a function of the reduced distance $\delta\rho$, for $a = 1$ and different values of the metastable well curvature b : $b = 0.01$ (SAN limit), $b = 0.1$, and $b = 0.2$.

3.2. Small-Amplitude Nucleus Limit

A limiting case of particular interest is obtained for a vanishing value of the kink–antikink distance ($\kappa = 0$); according to the terminology introduced by Büttiker and Landauer,(16) this limit is called the small-amplitude-nucleus (SAN) limit. The nucleation nucleus becomes

$$\bar{\xi}(\rho) = \frac{3b}{a}\,[1 + \cosh(\delta\rho)]^{-1} = \frac{3b}{2a}\operatorname{sech}^2\left(\frac{\delta}{2}\rho\right) \tag{3.4}$$

This expression can be shown to be a stationary solution of the equation

$$\frac{\partial\xi}{\partial t} = D\frac{\partial^2\xi}{\partial\rho^2} - b\xi + a\xi^2 \tag{3.5}$$

i.e., of the RDE (2.8), when the cubic term has been suppressed. The SAN limit amounts to retaining only a small deviation from the metastable state (so that $\xi^3 \ll \xi^2$). It is relevant near the marginal case, when b is small, $b \ll a^2$ (but positive, since we are studying the reaction beyond the threshold of bistability), which permits us to approximate the potential $V(\xi)$ by its cubic expansion around $\xi = 0$ up to the unstable concentration ($\xi = x_2/x_1 - 1$); a more refined analysis based on singular perturbations(12) confirms these considerations. In the present approximation, the stable part of the potential is replaced by an infinitely deep well (Fig. 1). The SAN theory is adequate to account for the early creation of the fronts, but not to describe their further propagation, when the cubic term should be involved.

The stability study of the nucleation nucleus can then be carried out explicitly. Substituting $\xi(\rho, t) = \bar{\xi}(\rho) + \psi(\rho)e^{-\lambda t}$ in the RDE and linearizing in ψ leads to the Schrödinger-like equation

$$-D\frac{\partial^2\psi}{\partial\rho^2} + [b - 2a\bar{\xi}(\rho)]\psi = \lambda\psi \tag{3.6}$$

or, according to the expression (3.4) of $\bar{\xi}(\rho)$,

$$-l_c^2\frac{\partial^2\psi}{\partial\rho^2} + \left[1 - 3\operatorname{sech}^2\left(\frac{\rho}{2l_c}\right)\right]\psi = \frac{\lambda}{b}\psi \tag{3.7}$$

where $l_c = \delta^{-1} = (D/b)^{1/2}$ defines a correlation length (namely the spatial extent of the nucleus). Equation (3.7) has explicit solutions(24); there are three bound states, given by

$$\begin{aligned}
\lambda_0 &= -\frac{5}{4}b, & \psi_0(\rho) &= \operatorname{sech}^3\left(\frac{\rho}{2l_c}\right)\\
\lambda_1 &= 0, & \psi_1(\rho) &= \frac{\sinh(\rho/2l_c)}{\cosh^2(\rho/2l_c)} \qquad (3.8a)\\
\lambda_2 &= \frac{3}{4}, & \psi_2(\rho) &= \frac{1-4\sinh^2(\rho/2l_c)}{\cosh^3(\rho/2l_c)}
\end{aligned}$$

plus a continuum of unbound states, corresponding to $\lambda_k/b = 1 + l_c^2 k^2$, and

$$\begin{aligned}
\psi_k(\rho) = e^{ik\rho}[&8ikl_c + 8ik^3 l_c^3 - (9 + 24k^2 l_c^2)\tanh(\rho/2l_c)\\
&- 30ikl_c \tanh^2(\rho/2l_c) + 15\tanh^3(\rho/2l_c)] \qquad (3.8b)
\end{aligned}$$

The stability analysis confirms the intuitive idea that the nucleation nucleus represents a saddle point solution in functional space. $\lambda_0 < 0$ corresponds to the unstable mode. $\lambda_1 = 0$ is a Goldstone mode, originating in the translational invariance of the nucleus; it is associated with the eigenvector $d\bar{\xi}/d\rho$.

In this work, we shall not go explicitly beyond the SAN case, although a complete analysis from the general formula (3.2) is not especially difficult.(12) It is in the SAN limit that the potential barrier between the metastable state and the nucleation nucleus is the lowest, and that the nucleation is the most probable. In the case of chemical systems, it will be seen that the nucleation process is certainly limited to a small range of control parameters around the metastable/unstable transition, in which conditions the SAN formulism is adequate.

3.3. Extension to Higher Space Dimension

For a space of general dimension ($d = 1, 2,$ or 3), the RDE reads

$$\frac{\partial\xi(\mathbf{r}, t)}{\partial t} = D\,\nabla_d^2\xi(\mathbf{r}, t) + f(\xi(\mathbf{r}, t)) \qquad (3.9)$$

where $\mathbf{r}$ is the d-dimensional Cartesian coordinate. For isotropic conditions, the solutions only depend on the radial coordinate ρ, and the RDE can be written

$$D\left[\frac{\partial^2\xi(\rho, t)}{\partial\rho^2} + \frac{p-1}{\rho}\frac{\partial\xi(\rho, t)}{\partial\rho}\right] + f(\xi(\rho, t)) = \frac{\partial\xi(\rho, t)}{\partial t} \qquad (3.10)$$

For $d = 2$ or 3, the ρ^{-1} term makes the search for exact analytical solutions intricate; approximate kink solutions have, however, been exhibited.(25,26)

As far as the nucleation nucleus is concerned, a fairly simple variational method is available.(27,28) The RDE can be set in a functional derivative form

$$\frac{\partial \xi}{\partial t} = -\frac{\delta \phi}{\delta \xi} \tag{3.11a}$$

where

$$\phi(\xi) = \int_{V(d)} d\mathbf{r} \{\tfrac{1}{2}D[\nabla \cdot \xi(\mathbf{r}, t)]^2 - \tfrac{1}{3}a\xi^3(\mathbf{r}, t) + \tfrac{1}{2}b\xi^2(\mathbf{r}, t) + \tfrac{1}{4}\xi^4(\mathbf{r}, t)\} \tag{3.11b}$$

$V(d)$ should be understood as the length L, the surface S, or the volume V of the system, for $d = 1, 2$, or 3. The nucleus is obtained by looking for a saddle point of ϕ in the space of parameters. In the SAN case, it is sufficient to take a trial function that depends only on two parameters, namely the amplitude and the width of the nucleus; more explicitly, one takes

$$\xi(\rho) = \mu g(\rho/\theta) \tag{3.12}$$

where $g(x)$ stands for an even function, decaying to zero with a width Δx of order one. The potential ϕ is a function of μ and θ,

$$\phi(\mu, \theta) = \gamma(d)\, \theta^{d-2}(\tfrac{1}{2}DI_1\mu^2 + \tfrac{1}{2}bI_2\theta^2\mu^2 - \tfrac{1}{3}aI_3\theta^2\mu^3) \tag{3.13}$$

with

$$I_1 = \int_0^\infty dx\, x^{d-1}g'(x), \qquad I_2 = \int_0^\infty dx\, x^{d-1}g(x)^2, \qquad I = \int_0^\infty dx\, x^{d-1}g(x)^3$$

and $\gamma(1) = 2$, $\gamma(2) = 2\pi$, $\gamma(3) = 4\pi$. Variation with respect to μ and θ gives for the nucleation nucleus

$$\bar{\mu} = \mu(d)b/a, \qquad \bar{\theta} = \theta(d)/(D/b)^{1/2} \tag{3.14}$$

For example, it is simple to make the calculations with a Gaussian trial function, $g(x) = \exp(-x^2)$. In this case, we find:

$$\begin{aligned} &\mu(1) = 1.47, \qquad \mu(2) = 2.25, \qquad \mu(3) = 3.7 \\ &\theta(1) = 1.10, \qquad \theta(2) = 1, \qquad \theta(3) = 0.87 \end{aligned} \tag{3.15}$$

Note that, irrespective of the precise expression of g, the nucleation nucleus scales as

$$\begin{gathered} \bar{\xi}(\rho) = (b/a)\, \bar{\zeta}(\rho/l_c) \\ l_c = (D/b)^{1/2}, \qquad \bar{\zeta}(x) = \mu(d)\, f(x/\theta(d)) \end{gathered} \tag{3.16}$$

It will be important in the following to also know the value of the "potential" ϕ at the saddle point $\xi(\rho)$. It is straightforward to get

$$\phi(\bar{\xi}) = \varphi(d)\, l_c^d b^3/a^2 = \varphi(d)\, D^{d/2} a^{-2} b^{3-d/2} \tag{3.17}$$

With the Gaussian trial function, we have $\varphi(1) = 1.21$ [instead of 1.20 when using the exact solution (3.4)] and $\varphi(2) = 8$, $\varphi(3) = 46$.

The stability analysis of the nucleus can be carried out in two and three dimensions, in the same way as in one dimension, and amounts to solving a Schrödinger-like equation similar to (3.7), this time including angular contributions, since the deviation from the unperturbed solution $\bar{\xi}(\rho)$ may not be isotropic. The qualitative aspect of the spectrum is unchanged, and is dominated by a negative, unstable mode λ_0 proportional to b, and d vanishing Goldstone modes $\lambda_1, \ldots, \lambda_{1+d} = 0$. The remaining eigenvalues are all positive and proportional to b. In terms of quantum mechanics, they describe the continuum of scatering states associated with the radial potential $V(\rho) = b - 2a\bar{\xi}(\rho)$.(12,27)

4. STOCHASTIC THEORY: EXPRESSION OF THE NUCLEATION RATES

4.1. Method of Evaluating the Nucleation Rates

The deterministic theory conveniently describes the propagation of fronts separating the metastable and stable regions; it also shows that in a homogeneous metastable medium the nucleation begins with the emergence of a nucleation nucleus. However, a stochastic treatment is necessary to study the creation of this nucleation nucleus as an effect of the chemical fluctuations of the medium. Following the method introduced by Kramers(31) and developed by Langer(17,27) and others,(29,30) we will identify the nucleation nucleus with a saddle point of the potential in the functional space of the concentration distributions. In passing from the metastable homogeneous state to the stable one, the system is most likely to cross this saddle point (or an equivalent one, corresponding to a translated nucleation nucleus); thus, one can estimate the nucleation rate by the steady-stade probability current flowing through the saddle point if a stationary situation is set up by artificially maintaining the metastable phase and evacuating the stable one.(17,37)

Clearly this method only accounts for the creation rate of the critical nuclei at the beginning of the process; however, this step is generally far longer than the subsequent growth of the nuclei and thus actually gives the time scale of the passage from the metastable to the stable state.

4.2. Homogeneous External Noise

The description of a homogeneous nucleation process requires the fluctuation process by which an initially metastable medium can spontaneously develop a nucleus of the stable "phase," which may grow and contaminate all the system.

As a preliminary step, we take the simplest possible stochastic process by adding a local homogeneous white noise source to the RDE (2.4). In Fokker–Planck language, this statement amounts to starting from an equation of the form

$$\frac{\partial p(\{x_r\},t)}{\partial t}=\sum_r\left\{-\frac{\partial}{\partial x_r}\left[\left(F(x_r)+\frac{\mathscr{D}}{\lambda^2}\sum_l{}'\,(x_{r+l}-x_r)\right)p\right]+\frac{\varepsilon}{2}Q_e\frac{\partial^2 p}{\partial x_r^2}\right\} \qquad (4.1)$$

The reactive medium has here been taken as a d-dimensional cube of dimension L. It has been coarse-grained in N^d cells of dimension $\lambda=L/N$. The index r has the meaning of an array of d integers $(r_1,\ldots,r_d)$, and locates cell "number" r. The deterministic drift in the Fokker–Planck operator is the coarse-grained version of the RDE (3.9); for each cell, the sum $\sum'$ runs over all adjacent cells. ε is the inverse of coarse-graining volume (ε^{-1} is equal to λs for a tube of small section s, $\lambda^2 h$ for a shallow layer of depth h, and λ^3 for a three-dimensional vessel). Finally, Q_e defines the strengh of the homogeneous external noise.

Use of dimensionles variables (2.5)–(2.7) and restriction for the deterministic part to the SAN approximation (3.5) transforms the FP equation (4.1) to

$$\frac{\partial p(\{\xi_r\},t)}{\partial t}=\sum_r\left\{\frac{\partial}{\partial\xi_r}\left[\frac{\partial\phi(\{\xi_r\})}{\partial\xi_r}\,p(\{\xi_r\}),t)\right]\right.$$
$$\left.+\frac{\varepsilon}{2x_1}Q_e\frac{\partial^2 p(\{\xi_r\},t)}{\partial\xi_r^2}\right\} \qquad (4.2)$$

where we have introduced the Landau–Ginzburg-type potential

$$\phi(\{\xi_r\})=\sum_r\frac{b}{2}\xi_r^2-\frac{a}{3}\xi_r^3+\frac{D}{4\lambda^2}\sum_l{}'\,(\xi_{r+l}-\xi_r)^2 \qquad (4.3)$$

Note that the potential ϕ is not normalizable as it stands, since it should be understood as a local expansion of the true potential around $\xi_r\equiv 0$. We let Z account for the complete normalization (quartic terms included), and in this context the stationary probability of (4.2) derives from a Landau–Ginzburg-type potential

$$P_{\mathrm{st}}(\{\xi_r\})=\frac{1}{Z}\exp\left[-\frac{2x_1}{\varepsilon Q_e}\phi(\{\xi_r\})\right] \qquad (4.4)$$

The derivation of the nucleation rate from an equation of this type has been given by Langer,(17,18) Brinkman,(29) and Landauer and Swansson,(30) generalizing the work of Kramers for one variable.(31) The result is

$$k=\frac{|\lambda_0|}{2\pi}\left(\frac{\pi\varepsilon Q}{x_1}\right)^{-d/2}\mathscr{A}\mathscr{B}\exp\left[-\frac{2x_1}{\varepsilon Q_e}\phi(\{\bar{\xi}_r\})\right] \tag{4.5}$$

where the notation has the following meaning:

(i) $\phi(\{\bar{\xi}_r\})$ is the value of the potential at the point $\{\bar{\xi}_r\}$, the discretized version of the nucleation nucleus $\bar{\xi}(\mathbf{r})$. It is related to the functional value $\phi(\bar{\xi})$ given in formula (3.17) by

$$\phi(\{\bar{\xi}_r\})=(1/\lambda^d)\,\phi(\bar{\xi})=\varphi(d)(l_c/\lambda)^d b^3/a^2 \tag{4.6}$$

(ii) The factor $\mathscr{B}$ is given by

$$\mathscr{B}^2=\prod_{p\geqslant 0}\lambda_p^{(0)}\Big/\prod_{p\geqslant 0}{}'\,\lambda_p \tag{4.7}$$

The λ_p are the normal modes of the potential $\phi(\{\bar{\xi}_r\})$ at $\{\bar{\xi}_r\}$, i.e., the eigenvalues of the matrix

$$\bar{\phi}_{rr'}=\frac{\partial^2\phi}{\partial\xi_r\,\partial\xi_{r'}}(\{\bar{\xi}_r\}) \tag{4.8}$$

or, according to the definition (4.3) of $\phi(\{\xi_r\})$,

$$\bar{\phi}_{rr'}=-\frac{D}{\lambda^2}\sum_l{}'\,(\delta_{r+l,r'}-\delta_{rr'})+(b-2a\bar{\xi}_r)\,\delta_{rr'} \tag{4.9}$$

This matrix is the coarse-grained, d-dimensional equivalent of the Schrödinger operator (3.6). Along the lines of our previous discussion, we have therefore

$$\lambda_0<0,\qquad \lambda_1\cdots\lambda_{1+d}=0,\qquad \lambda_p>0,\qquad p\geqslant d+2 \tag{4.10}$$

The symbol $\prod'$ in the denominator of $\mathscr{B}^2$ indicates that the null eigenvalues $\lambda_1\cdots\lambda_{1+d}$ have to be removed from the product. The $\lambda_p^{(0)}$ are the normal modes of the potential $\phi(\{\xi_r\})$ at the metastable state $\xi_r\equiv 0$, i.e., the eigenvalues of the matrix

$$\phi_{rr'}^{(0)}=-\frac{D}{\lambda^2}\sum_l{}'\,(\delta_{r+l,r'}-\delta_{rr'})+b\delta_{rr'} \tag{4.11}$$

It is easy to prove that

$$\lambda_p^{(0)} = \frac{4D}{\lambda^2} \sum_{i=1}^{d} \sin^2 \frac{\pi p_i}{N} + b, \qquad p = (p_1, ..., p_d) \tag{4.12}$$

or in the continuous limit $N \to \infty$, L fixed

$$\lambda_p^{(0)} = b(1 + l_c^2 k^2), \qquad k^2 = \frac{4\pi^2}{L^2} \sum_{i=1}^{d} p_i^2 \tag{4.13}$$

where l_c is again the characteristic length $(D/b)^{1/2}$

Thus, all the eigenvalues $\lambda_p^{(0)}$, like the λ, are proportional to b. Furthermore, the smallest ones $(k \to 0)$ can be taken equal to b. As a consequence, taking away $\lambda_1^{(0)} \cdots \lambda_{1+d}^{(0)} = b$ from the numerator in (4.7), $\mathscr{B}$ can be expressed as

$$\mathscr{B} = \beta(d)\, b^{d/2} \tag{4.14}$$

The b dependence has been separated, and $\beta(d)$ is a now a constant. This factor can be calculated exactly in one dimension(16) $[\beta(1) = (60)^{1/2}]$, and approximately in two and three dimensions, using semiclassical approximations for the continuous version of the Schrödinger-like equations (4.9) and (4.11).(12)

(iii) The factor $\mathscr{A}$ describes the contribution of the d null eigenvalues of $\{\phi_{rr'}\}$. According to an argument given by Langer (see Ref. 17, Appendix C), this factor is equal to

$$\mathscr{A} = \left\{ \frac{1}{d\lambda^d} \int_{L^d} d\mathbf{r} [\nabla \cdot \xi(\mathbf{r})]^2 \right\}^{d/2} L^d \tag{4.15}$$

Then, if the scaling (3.16) is used,

$$\begin{aligned} \mathscr{A} &= \alpha(d)\, \lambda^{-d^2/2} l_c^{d^2/2 - d} (b/a)^d L^d \\ &= \alpha(d)\, L^d \lambda^{-d^2/2}\, D^{d^2/4 - d/2} a^{-d} b^{3d/2 - d^2/4} \end{aligned} \tag{4.16}$$

with $\alpha(1) = 1.1$, $\alpha(2) = 8$, $\alpha(3) = 312$.

Finally, if we take care of the b dependance of $|\lambda_0|$, the contributions that we have described can all be put together in formula (4.5); this gives as a final expression of the nucleation rate, expressed here in dimensionless τ_c unit per cm^{-d},

$$\begin{aligned} k/L^d = {} & \Pr(d)(\varepsilon\lambda^d)^{-d/2}(Q_e/x_1)^{-d/2} a^{-d} D^{d^2/4 - d/2} b^{1 + 2d - d^2/4} \\ & \times \exp[-2\varphi(d)(\varepsilon\lambda^d)^{-1}(x_1/Q_e)\, D^{d/2} a^2 b^{3 - d/2}] \end{aligned} \tag{4.17}$$

The factor $\varphi(d)$ in the exponential is given by (3.17). The prefactor $\mathrm{Pr}(d)$ stands for

$$\mathrm{Pr}(d) = \frac{1}{2\pi^{1+d/2}} \frac{|\lambda_0|}{b} \alpha(d)\, \beta(d) \tag{4.18}$$

Finally, $(\varepsilon\lambda^d)^{-1}$ is equal to s, h, or 1 if the dimension d is 1, 2, or 3, respectively. Note that the nucleation rate tends to zero either when $b \to \infty$ or $b \to 0$. The limit $b \to 0$ applies in the immediate vicinity of the metastable/unstable transition, that is, in domain of spinodal decomposition, where the theory presented here should not be valid; the decrease of k/L^d in this limit is reminiscent of the critical slowing-down of fluctuations near the transition, which is well known in critical phenomena.(38–40) On the other hand, in the limit $b \to \infty$ the argument of the exponential (which we shall later call the activation factor and denote by A) becomes large and the nucleation process is impossible. The domain of nucleation is in fact limited to the case where the activation factor A remains of order unity.

4.3. Internal Noise

4.3.1. Multivariate Master Equation. We now turn to the case where the source of noise is an internal one, due to the intrinsic local fluctuations of concentration of the chemical species. The Brussels school, and Nicolis and Prigogine in particular,(20) have provided a formalism to account for internal fluctuations in a diffusing and reacting medium. The theory is based on the so-called multivariate master equation (MME). This equation holds in the same coarse-grained sense as the multivariate Fokker–Planck equation (4.1), and considers that the d-dimensional medium has been divided into N^d cells of dimension λ and volume ε^{-1}. Inside each cell, the chemical reaction is described as a birth-and-death Markovian process. The diffusion is mimicked by a stochastic jump process from cell to cell. In the case of the Schlögl reaction (2.1), the MME reads (here in terms of the concentration x_r of species X in cell r)

$$\begin{aligned} \varepsilon \frac{\partial p(\{x_r\}, t)}{\partial t} = \sum_r \Big\{ & W(x_r - \varepsilon)\, p(\dots, x_r - \varepsilon, \dots) \\ & - [W(x_r) + \bar{W}(x_r)]\, p(\dots, x_r, \dots) + \bar{W}(x_r + \varepsilon)\, p(\dots, x_r + \varepsilon, \dots) \\ & + \frac{\mathscr{D}}{\lambda^2} \sum_l{}' \, [(x_r + \varepsilon)\, p(\dots, x_{r+l} - \varepsilon, x_r + \varepsilon, \dots) \\ & - x_r\, p(\dots, x_{r+l}, x_r, \dots)] \Big\} \end{aligned} \tag{4.19a}$$

$W(x_r)$ and $\bar{W}(x_r)$ are the birth and death rates per unit volume in each cell

$$\begin{aligned} W(x_r) &= k_2 x_A x_r (x_r - \varepsilon) + k_4 x_B \\ \bar{W}(x_r) &= k_1 x_r (x_r - \varepsilon)(x_r - 2\varepsilon) + k_3 x_r \end{aligned} \tag{4.19b}$$

If we turn to the dimensionless variables (2.5), the MME becomes

$$\begin{aligned} \varepsilon' \frac{\partial p(\{u_r\}, t)}{\partial \tau} = \sum_r \Big\{ & w(u_r - \varepsilon')\, p(\dots, u_r - \varepsilon', \dots) \\ & - [w(u_r) + \bar{w}(u_r)]\, p(\dots, u_r, \dots) + \bar{w}(u_r + \varepsilon')\, p(\dots, u_r + \varepsilon', \dots) \\ & + \frac{D}{\lambda^2} \sum_l{}' \, [(u_r + \varepsilon')\, p(\dots, u_{r+l} - \varepsilon', u_r + \varepsilon', \dots) \\ & - u_r\, p(\dots, u_{r+l}, u_r, \dots)] \Big\} \end{aligned} \tag{4.20}$$

with $\varepsilon' = \varepsilon / x_1$ and, according to the definition of the parameters a and b,

$$\begin{aligned} w(u_r) &= (a+3)\, u_r (u_r - \varepsilon') + (a+b+1) \\ \bar{w}(u_r) &= u_r (u_r - \varepsilon')(u_r - 2\varepsilon') + (b + 2a + 3) u_r \end{aligned} \tag{4.21}$$

Note that $w(u) - \bar{w}(u)$ is, at dominant order in ε', the chemical kinetic term $f(u)$ introduced in (2.6). Furthermore, we define

$$\begin{aligned} Q(u) &= u^3 + (a+3)u^2 + (2a+b+3)u + (a+b+1) \\ &= w(u) + \bar{w}(u) \end{aligned} \tag{4.22}$$

The stationary solution $p_s(\{u_r\})$ of the MME cannot be found by simple arguments. It is possible to write it in the form

$$p_s(\{u_r\}) = (1/Z) \exp[-\varepsilon'^{-1} U(\{u_r\})] \tag{4.23}$$

This relation defines the stochastic potential $U(\{u_r\})$ [or $U(\{\xi_r\})$ if the variables $\xi_r = u_r - 1$ are used], which has to be distinguished from the determinisitc potential $\phi(\{\xi_r\})$ given by (4.3b). The potential U is not known exactly. However, Lemarchand(32-34) and Lemarchand and Nicolis(35) have derived a systematic method to provide a Taylor expansion of $U(\{u_r\})$ around any stationary deterministic solution $\hat{u}_r$, for example, in in our case around the metastable solution $\hat{u}_r \equiv 1$, and around the nucleation nucleus solution $\hat{u}_r \equiv \bar{u}_r = \bar{\xi}_r + 1$. We make extensive use of their method in the remainder of this work. However, in order to simplify the presentation, we postpone the discussion of the formalism and its application to our particular case (Appendix A). Let us just mention here that at first order the theory relates the second derivatives of the stochastic potential U to the second derivative of the deterministic potential ϕ via the formula

$$\boldsymbol{\phi}\mathbf{U}^{-1} + \mathbf{U}^{-1}\boldsymbol{\phi} - \mathbf{G} = 0 \tag{4.24}$$

with

$$\boldsymbol{\phi} = \{\phi_{rr'}\}, \qquad \mathbf{U} = (U_{rr'}\}, \qquad \mathbf{G} = \{G_{rr'}\}$$

and

$$\phi_{rr'} = \frac{\partial^2 \phi}{\partial u_r\, \partial u_{r'}}(\{\hat{u}_r\}), \qquad U_{rr'} = \frac{\partial^2 U}{\partial u_r\, \partial u_{r'}}(\{\hat{u}_r\})$$

From a Fokker–Planck point of view, $\mathbf{G}$ would be the noise matrix,⁽³⁶⁾ which reads in the case of the reaction-diffusion master equation (4.20)

$$G_{rr'} = \Big[Q(\hat{u}_r) + \frac{D}{\lambda^2} \sum_l{}' (\hat{u}_{r+l} + \hat{u}_r)\Big]\, \delta_{rr'} - \frac{D}{\lambda^2} \sum_l{}' (\hat{u}_{r+l} + \hat{u}_r)\, \delta_{r+l,r'} \tag{4.25}$$

where $Q(u)$ is fixed by (4.22).

However, it should be pointed out that the standard Fokker–Planck equation that can be derived from (4.20)⁽²⁰⁾ is only locally valid in the bistable case, and, for instance, does not yield a correct approximation of the stationary probability, in contrast to the method used in Appendix A.

4.3.2. Expression of the Nucleation Rates. We now go back to the nucleation problem. We have derived elsewhere⁽³⁷⁾ an equivalent of the nucleation rate formula (4.5), which applies to a general potential or nonpotential stochastic equation, and especially to the MME (4.20). Keeping similar notations as in (4.5), we find

$$k = \frac{|\lambda_0|}{(2\pi)^{1+d/2}} (\varepsilon')^{-d/2} \mathscr{A}\mathscr{B} \exp\left[-\frac{x_1}{\varepsilon} U(\{\bar{\xi}_r\})\right] \tag{4.26}$$

$U(\{\bar{\xi}_r\})$ is clearly the value of the stochastic potential at the nucleation saddle point $\bar{\xi}_r$. In the prefactor of the exponential, $|\lambda_0|$ and $\mathscr{A}$ have the same meaning and value as in formula (4.5), and express the contribution of the negative and null eigenmodes of the deterministic potential ϕ around $\{\bar{\xi}_r\}$. The factor $\mathscr{B}'$ has the same formal expression as $\mathscr{B}$,

$$\mathscr{B}'^2 = \prod_{p \geqslant 0} \omega_p^{(0)} \Big/ \prod_{p \geqslant 0}{}' \omega_p \tag{4.27}$$

but it involves this time the eigenmodes of the stochastic potential around $\xi_r \equiv 0$ and $\xi_r \equiv \bar{\xi}_r$, instead of those of the deterministic potential ϕ.

These different elements being settled, we now turn to the calculation of the two distinct parts that constitute the rate formula (4.26), that is, the prefactor of the exponential, and the activation factor itself, $A = \varepsilon'^{-1} U(\{\xi_r\})$. As in the remainder of this paper, we restrict the calculation to the SAN limit, where the smallness parameter b will make it possible to adopt a perturbational approach.

4.3.3. Calculation of the Prefactor. The prefactor relies in part on the eigenvalues ω_p of the matrix

$$\bar{U}_{rr'} = (\partial^2 U/\partial \xi_p \, \partial \xi_{r'})(\{\bar{\xi}_r\})$$

In order to calculate them, let us start from relation (4.24), expressed at the saddle point $u_r = \bar{\xi}_r + 1$. In terms of the variables $\bar{\xi}_r$, the deterministic matrix $\boldsymbol{\phi}$ is given by formula (4.9), and the noise matrix $\bar{\mathbf{G}}$ is

$$\bar{G}_{rr'} = \left[Q + Q'\bar{\xi}_r + \frac{Q''}{2} \bar{\xi}_r^2 + \bar{\xi}_r^3 + 2d \frac{D}{\lambda^2} (1 + \bar{\xi}_r) \right] \delta_{rr'}$$

$$- \frac{D}{\lambda^2} (1 + \bar{\xi}_r) \sum_l{}' \delta_{r+l,r'} \tag{4.28}$$

with

$$Q = Q(1) = 4a + 2b + 8, \qquad Q' = Q'(1) = 4a + b + 12$$

$$Q'' = Q''(1) = 2a + 12$$

Let $\psi_r^{(p)}$ be the set of vectors that diagonalize $\bar{\boldsymbol{\phi}}$, whose continuous, complex, one-dimensional version is given by formulas (3.8). Let $\mathbf{V}$ and $\boldsymbol{\Gamma}$ be the matrices $\bar{\mathbf{U}}$ and $\bar{\mathbf{G}}$ expressed in this new basis, i.e.,

$$\sum_{r,r'} \psi_r^{(p)} \bar{\phi}_{rr'} \psi_{r'}^{(q)} = \lambda_p \, \delta_{pq}, \qquad \sum_{r,r'} \psi_r^{(p)} \bar{U}_{rr'} \psi_{r'}^{(q)} = v_{pq} \tag{4.29a}$$

and

$$\sum_{r,r'} \psi_r^{(p)} G_{rr'} \psi_{r'}^{(q)} = \Gamma_{pq} \tag{4.29b}$$

In the new basis, the relation (4.24) can be expressed as

$$\boldsymbol{\Lambda} \mathbf{V}^{-1} + \mathbf{V}^{-1} \boldsymbol{\Lambda} - \boldsymbol{\Gamma} = 0 \tag{4.30}$$

or

$$V_{pq}^{-1} = \frac{\Gamma_{pq}}{\lambda_p + \lambda_q} \tag{4.31}$$

In the matrix **G** given by (4.28) we distinguish the homogeneous chemical part (at dominant order in b) from the remaining contributions

$$\bar{G}_{rr'} = Q_i \, \delta_{rr'} + P_{rr'}, \qquad Q_i = 4a + 8 \tag{4.32}$$

or in the $\boldsymbol{\psi}^{(p)}$ basis

$$\Gamma_{pq} = Q_i \, \delta_{pq} + \Pi_{pq} \tag{4.33}$$

and we treat the matrix $\mathbf{\Pi}$ as a perturbation. This procedure yields, to the first order,

$$V_{pq} = \frac{2\lambda_p}{Q_i} \delta_{pq} - \frac{4\lambda_p^2}{Q_i^2(\lambda_p + \lambda_q)} \Pi_{pq} \tag{4.34}$$

Using the usual perturbation theory of symmetric matrices, it is then straightforward to obtain the eigenvalues of **V** (or **U**). Up to first order

$$\omega_p = \frac{2\lambda_p}{Q_i} (1 - Q_i^{-1} \Pi_{pp}) \tag{4.35}$$

We show in Appendix B that in this formula, the perturbed term is of order b^2, while the dominant term is of order b, so that one can take

$$\omega_p = 2\lambda_p / Q_i + o(b^2) \tag{4.36}$$

The same perturbation calculation holds for the eigenmodes of the potential U at the metastable state, so that

$$\omega_p^{(0)} = 2\lambda_p^{(0)} / Q_i + o(b^2) \tag{4.37}$$

Now, substituting (4.36)–(4.37) in (4.26) yields, up to dominant order in b, the same prefactor as in the external noise formula (4.5). The dimensionless noise strengh Q_e simply has to be replaced by the internal chemical noise parameter $Q_i = 4(a + 2)$. Let us recall that this parameter is the value of the dimensionless, concentration-dependent chemical noise $Q(u) = w(u) + \bar{w}(u)$ taken at the metastable state: $u = x/x_1$ [see (4.22) and 4.28)].

In conclusion, we note that the prefactor in formula (4.17) also holds in the internal noise case, up to dominant order in the perturbation parameter b.

4.3.4. Calculation of the Activation Factor. The value of the stochastic potential at the saddle point $U(\xi_r\})$ can be obtained by a Taylor expansion of $U(\{\xi_r\})$ around the metastable state $\xi_r \equiv 0$, namely

$$U(\{\bar{\xi}_r\}) = \tfrac{1}{2} U^{rr'} \bar{\xi}_r \bar{\xi}_{r'} + \tfrac{1}{6} U^{rr'r''} \bar{\xi}_r \bar{\xi}_{r'} \bar{\xi}_{r''} \tag{4.38}$$

$U^{rr'\cdots}$ stands for the value of the derivative of $U(\{\xi_r\})$ with respect to $\xi_r, \xi_{r'},\ldots$ taken at $\xi_r = 0$. The notation used here implies summation over index $r, r',\ldots$. In the following, in agreement with the SAN condition that we have supposed to be true up to now, we shall discard terms of higher order than the cubic ones.

As mentioned earlier, Lemarchand and Nicolis$^{(32-35)}$ have developed a nice systematic method to calculate the expansion (4.38). In fact, their formalism works more conveniently in Fourier space. If

$$\xi_r = C_r^l \bar{\sigma}_l, \qquad U^{ll'} = U^{rr'\cdots} C_r^l C_{r'}^l \cdots \tag{4.39a}$$

with, in d dimensions,

$$r = (r_1,\ldots, r_d), \qquad l = (l_1,\ldots, l_d)$$

and

$$C_r^l = \exp\left(2\pi i \frac{l_1 r_1 + \cdots + l_d r_d}{N}\right) \tag{4.39b}$$

then $U(\{\xi_r\})$ is transformed to

$$U(\{\xi_r\}) = \tfrac{1}{2} U^{ll'} \bar{\sigma}_l \bar{\sigma}_{l'} + U^{ll'l''} \bar{\sigma}_l \bar{\sigma}_{l'} \bar{\sigma}_{l''} \tag{4.40}$$

The terms $U^{ll'}$, $U^{ll'l''}$ can be determined consistently, as sketched in Appendix A. Since $\bar{\sigma}_l$ is also known, by simple inverse Fourier transformation of ξ_r, the summation (4.40) can be fully achieved, at least numerically.

As a further simplification, we show in Appendix C that the parameter b acts once again as a perturbation parameter, so that $U(\{\xi_r\})$ can be expressed in the simple form

$$U(\{\xi_r\}) = \frac{2\phi(\{\xi_r\})}{Q_i} [1 - \varphi_i(d) b + o(b^2)] \tag{4.41}$$

where $\phi(\{\xi_r\})$ is the value of the deterministic potential, given by (4.6). Here $\varphi_i(d)$ is a positive coefficient of order one, whose expression is given in Appendix C. The term Q_i has the same meaning as in the preceding section, i.e., $Q_i = 4(a+2)$.

The latter relation, when generalized to any point ξ_r near $\xi_r \equiv 0$, shows a simple proportionality law between the stochastic and the deterministic potentials near the marginal transition ($b \to 0$). In this case the stochastic potential is, like the deterministic one, of the Landau–Ginzburg type; it is formaly analogous to the one obtained with a homogeneous external noice process, formula (4.3), Q_e being replaced by the intrinsic parameter Q_i. This fact was already recognized by Malek–Mansour *et al.*$^{(41)}$ using a singular perturbation expansion of the MME near a transition.

When b is increased, it can be seen that the stochastic potential at the saddle point is lowered with respect to the result of a simple Landau–Ginzburg theory, based on an homogeneous internal noise hypothesis. Far from the transition, Malek–Mansour *et al.*$^{(41)}$ have shown that the inhomogeneous fluctuations build in long-range correlations of order $l_c = (D/b)^{1/2}$, thus of the same size as the extent of the nucleation nucleus. On the nucleation point of view, the inhomogeneous fluctuations therefore act synergistically and make the formation of the nucleus easier.

4.4. Final Result and Discussion. At this point, whatever the internal or external character of the noise, we are able to provide a unified formula for the nucleation rate in the SAN limit. We express here all the parameters in usual units, i.e., length in centimeters, time in seconds, and concentration in moles per liter. From the discussion of the preceding section and from (3.17), we get

$$\frac{k}{L^d} = \mathrm{Pref} \cdot \exp\left\{ -2\varphi(d)(\varepsilon\lambda^d)^{-1} \frac{\mathscr{N}[\mathrm{X}]}{10^3} \times \frac{(\mathscr{D}\tau_c)^{d/2} a^{-d} b^{3-d/2}}{Q_{e,i}} [1 - \varphi_{e,i}(d) b] \right\} \tag{4.42a}$$

with the prefactor

$$\mathrm{Pref} = \tau_c^{-1} \Pr(d) \cdot (\varepsilon\lambda^d)^{-d/2} (\mathscr{N}[X]/10^3)^{d/2} Q_{e,i}^{-d/2} \times (\mathscr{D}\tau_c)^{d^2/4 - d/2} a^{-d} b^{1+2d-d^2/4} \tag{4.42b}$$

and $\varphi_e(d) = 0$, $\varphi_i(d) = o(1)$, $\mathscr{N}$ is the Avogadro number, and [X] the concentration of species X at the metastable state in moles per liter. Recall that $\mathscr{D}$ is the diffusion coefficient, and τ_c is the characteristic time of the reaction $\{\tau_c$ is here $(k_1[\mathrm{X}]^2)^{-1}$ if k_1 is expressed in $M^{-2}\,\mathrm{sec}^{-1}\}$.

As a conclusion of this section, let us discuss some orders of magnitude. As previously mentioned, the chemical nucleation process is confined to a range of physical parameters such that the activation factor A is of order 1. The condition $A \ll 1$ corresponds to the domain of spinodal decomposition, while for $A \gg 1$, the exponential predominates, and the nucleation cannot be observed. Note that, from an experimental point of view, the dimensionless parameter b gives an idea of the precision at which the external constraints should be monitored near the metastable/unstable transition. The numerical evaluation of these quantities shows that the observable nucleation should be limited to sharply defined values of the parameters, which makes experimentation quite difficult: the same remark usually holds for the nucleation from a metastable state, which has been widely studied in the case of phase transitions at equilibrium.(17,27,42,43)

As a matter of fact, if we take $D = 10^{-5}\,\mathrm{cm}^2/\mathrm{sec}$ and $a \sim 1$ for simplicity, the condition $A \sim 1$ is translated to

$$Q_{e,i}^{-1}\tau_c^{3/2}b^{3/2}[\mathrm{X}] \sim 10^{-15} \qquad d=3 \tag{4.43a}$$

$$Q_{e,i}^{-1}\tau_c b^2[\mathrm{X}]h \sim 10^{-17} \qquad d=2 \tag{4.43b}$$

$$Q_{e,i}^{-1}\tau_c^{1/2}b^{5/2}[\mathrm{X}]s \sim 10^{-19} \qquad d=1 \tag{4.43c}$$

It is difficult to consider here the external noise case, since the noise stength Q_e is not an intrinsic parameter and should be discussed on the basis of a precise experiment. In the internal case, on the contrary, all parameters are known ($Q_i = 4a + 8 \sim 12$). It can be easily seen that unless the product $\tau_c^{d/2} \cdot [\mathrm{X}]$ is very small, the nucleation conditions (4.43) imply that the control parameter b is itself very small. In the trimolecular Shlögl model, τ_c is equal to $(k_1[\mathrm{X}]^2)^{-1}$, so that the intrinsic homogeneous nucleation should be limited to reactions presenting a very fast trimolecular step and a large stationary concentration of the active species (except for $d=1$, where $\tau_c^{1/2} \cdot [\mathrm{X}] = k_1^{-1/2}$ is independent of $[\mathrm{X}]$). As an example, take $d=3$ and $[\mathrm{X}] = 10^{-3}\,\mathrm{M}$; in order that $b > 10^{-3}$, we should have $k_1 > 10^{10}\,\mathrm{M}^{-2}\,\mathrm{sec}^{-1}$. If k_1 is not large enough, the condition (4.43a) restricts b to a very narrow range around $b = 0$ and intrinsic homogeneous nucleation should be difficult to detect experimentally. Note that for models involving several chemical variables (like the Oregonator in excitable conditions(12)) τ_c and $[\mathrm{X}]$ are more likely to be independent. The conditions for the observation of homogeneous nucleation due to intrinsic fluctuations are then a fast reaction (small τ_c) and a low stationary concentration (small $[\mathrm{X}]$).

5. CONCLUSION

In this paper we have derived a rigorous formula for the homogeneous nucleation rate in a reacting-diffusing medium near its metastable/unstable transition. The theory has been given for both an external and an internal noise mechanism. The derivation of the nucleation rate for an internal stochastic equation such as the MME (4.19) is new, to our knowledge. This is important in the sense that the influence of internal noise on chemical systems driven far from equilibrium has often been discussed, although few quantitative predictions have been given. In many circumstances, it is still an open question whether the chemical structures can be initiated by internal noise or not. This question has already been addressed for oscillatory reactions, theoretically by Walgraef and co-workers(10) and experimentally by Vidal and co-workers.(11) The present work has the merit of giving a partial answer for bistable (or excitable) systems. On the other hand, it could also be useful for other nucleation situations in physical chemistry where an internal noise mechanism can be identified.

Practically, it appears that the nucleation due to the internal chemical fluctuations should in many cases be limited to a very narrow range of control parameters near the transition, and difficult to see experimentally. The external case is certainly more relevant from the practical point of view, since any experiment is subject to external disturbances, which easily may be greater than the internal fluctuations themselves. Furthermore, some attempts have already been made to impose a controlled external white noise on a reacting medium. This could be an interesting route to follow.

Finally, we have not treated in this work the problem of heterogeneous nucleation, which is certainly important in nonlinear chemical systems. It has been well established that, in certain cases, the chemical structures can be initiated by pieces of dust present in solution. However, to our knowledge, there are no clear statistical predictions of the influence of solid heterogeneities on a nonlinear chemical bistable or excitable system.

APPENDIX A

We briefly develop the formalism of Lemarchand and Nicolis,(32–35) which permits one to obtain an expansion of the stochastic potential around any deterministic stationary solution. The theory starts from the Hamilton–Jacobi equation associated with the MME (4.20). If $p_r = \partial U(\{u_r\})/\partial u_r$, the stationary version of (4.20) gives, up to first order in ε',

$$\begin{aligned} 0 &= H(\{u_r\}, \{p_r\}) \\ &= \sum_r w(u_r)(e^{p_r} - 1) + \bar{w}(u_r)(e^{-p_r} - 1) \\ &\quad + \frac{D}{\lambda^2} \sum_l{}' (e^{-p_r + p_{r+l}} - 1)u_r \end{aligned} \tag{A1}$$

We denote by $H^{jj' \cdots}_{rr' \cdots}$ the successive derivatives of H with respect to $u_{j'} u_{j'} \cdots$ and $p_{r'} p_{r'}, \ldots$ at a stationary point $\hat{u}_r$ [in this case, $\hat{p}_r = \partial U(\{\hat{u}_r\})/\partial u_r = 0$]. These derivatives are related by

$$\mathscr{S}\{H_r^j U_{jr}^{-1}\} + H_{rr'} = 0 \tag{A2a}$$

$$\begin{aligned}\mathscr{S}\{ & -H_r^{j_1}(U^{j_2 j_3 j_4} U_{j_2 r'}^{-1} U_{j_3 r''}^{-1} U_{j_4 j_1}^{-1}) \\ & + H_r^{j_1 j_2} U_{j_1 r'}^{-1} U_{j_2 r''}^{-1} + H_{rr'}^{j_1} U_{j_1 r''}^{-1}\} + H_{rr'r''} = 0\end{aligned} \tag{A2b}$$

and so on. The notation implies summation over conjugate indices. The symbol $\mathscr{S}$ indicates symmetrized expressions with respect to r, r', and r''.

It is easy to find that

$$H_r = 0 \tag{A3a}$$

$$H_{rr'} = \left[Q(\hat{u}_r) + \frac{D}{\lambda^2} \sum_l{}' (\hat{u}_{r+l} + \hat{u}_r) \right] \delta_{rr'} - \frac{D}{\lambda^2} \sum_l (\hat{u}_{r+l} + \hat{u}_r)\, \delta_{r+l,r'} \tag{A3b}$$

$$H_{rr'r''} = -\frac{D}{\lambda^2} \sum_l (\hat{u}_{r+l} - \hat{u}_r)(\delta_{rr'}\, \delta_{r+l,r''} + \delta_{r+l,r'}\, \delta_{r''r} - \delta_{r+l,r'}\, \delta_{r'r''}) \tag{A3c}$$

$$H_r^j = \left[f'(\hat{u}_r) - 2d\frac{D}{\lambda^2} \right] \delta_{rj} + \frac{D}{\lambda^2} \sum_l \delta_{r+l,j} \tag{A3d}$$

$$H_r^{jj'} = f''(\hat{u}_r)\, \delta_{rj}\, \delta_{rj'} \tag{A3e}$$

$$\begin{aligned} H_{rr'}^j = & \left[Q'(\hat{u}_r) + 2d\frac{D}{\lambda^2} \right] \delta_{rj}\, \delta_{r'j} \\ & - \frac{D}{\lambda^2} \sum_l (\delta_{rj}\, \delta_{r',j+l} + \delta_{r',r+l}\, \delta_{r'j} - \delta_{rr'}\, \delta_{r+l,j}) \end{aligned} \tag{A3f}$$

$Q(u_r)$ and $f(u_r)$ are defined by (2.6), (4.22). It is easy to verify that, in terms of the notation used in Section 4.2, $H_r^j = -\bar{\phi}_{rj}$ and $H_{rr'} = \bar{G}_{rr'}$, so that relation (A2a) is equivalent to the relation (4.24), connecting the stochastic potential to be deterministic one.

As far as a homogeneous steady state $\hat{u}$ is concerned, the formualism holds more conveniently in Fourier space. With (4.39) and the additional convention

$$H_{ll'\cdots}^{nn'\cdots} = C_l^{-1r} C_{l'\cdots}^{-1r'} H_{rr'\cdots}^{jj'\cdots} C_j^n C_{j'}^{n'} \cdots \tag{A4}$$

the relations (2) become

$$U_{ll'}^{-1} = \frac{H_{ll'}}{\lambda_l + \lambda_{l'}} \tag{A5a}$$

$$\begin{aligned} U^{ll'l''} = & -\frac{U^{ln} U^{l'n'} U^{l''n''}}{\lambda_n + \lambda_{n'} + \lambda_{n''}} \mathscr{S}\{H_n^{m'm''} U_{n'm'}^{-1} U_{n''m''}^{-1} \\ & + H_{nn'}^{m''} U_{n''m''}^{-1} + H_{nn'n''}\} \end{aligned} \tag{A5b}$$

with

$$\lambda_n = |f'(\hat{u})| + \frac{D}{\lambda^2}\mu_n$$

$$\mu_n = 4\sum_{i=1}^{d}\sin^2\frac{\pi n_i}{N}, \qquad n = (n_1,..., n_d)$$

From (A3) we get

$$\begin{aligned} H_l^n &= -\lambda_l\,\delta(l-n) \\ H_{ll'} &= N^{-d}\left[Q(\hat{u}) + 2d\frac{D}{\lambda^2}\hat{u}\mu_l\right]\delta(l+l') \\ H_l^{nn'} &= f''(\hat{u})\,\delta(n+n'-l) \\ H_{ll'}^n &= N^{-d}\left[Q'(\hat{u}) + \frac{D}{\lambda^2}(\mu_l + \mu_{l'} - \mu_n)\right]\delta(l+l'-n) \end{aligned} \tag{A6}$$

Substitution in (A5) gives

$$U^{ll'} = N^d w_l\,\delta(l+l') \tag{A7a}$$

$$\begin{aligned} U^{ll'l''} = -N^d\frac{\delta(l+l'+l'')}{\lambda_l+\lambda_{l'}+\lambda_{l''}}\Big\{ & f''(\hat{u})(\omega_l+\omega_{l'}+\omega_{l''}) \\ & + Q'(\hat{u})(\omega_l\omega_{l'} + \omega_{l'}\omega_{l''} + \omega_l\omega_{l''}) \\ & + \frac{D}{\lambda^2}\left[\omega_l\omega_{l'}(\mu_l+\mu_{l'}-\mu_{l''}) + \omega_{l'}\omega_{l''}(\mu_{l'}+\mu_{l''}-\mu_l)\right. \\ & \left. + \omega_l\omega_{l''}(\mu_l+\mu_{l''}-\mu_{l'})\right]\Big\} \end{aligned} \tag{A7b}$$

with

$$\omega_l = 2\frac{|f'(\hat{u})| + (D/\lambda^2)\mu_l}{Q(\hat{u}) + 2d(D/\lambda^2)\,\hat{u}\mu_l} \tag{A7c}$$

APPENDIX B

In continuous space variables $\mathbf{r}$, the matrix $\bar{\mathbf{G}}$ is transformed to the operator $\bar{G}$,

$$\bar{G} = Q + Q'\xi(\mathbf{r}) + \tfrac{1}{2}Q''\xi(\mathbf{r})^2 + \xi(\mathbf{r})^2 + \xi(\mathbf{r})^3 - 2d[1+\xi(\mathbf{r})]\,\nabla_{\mathbf{r}}^2 \tag{B1}$$

On the other hand, the continuous version of the matrix $\bar{\mathbf{\Phi}}$ is the Schrödinger operator (3.7a), whose real eigenvectors scales as

$$\psi^{(p)}(\mathbf{r}) = l_c^{-d/2}\varphi^{(p)}(\mathbf{x}), \qquad \mathbf{x} = \mathbf{r}/l_c \tag{B2}$$

so that

$$\int d\mathbf{x}\, \varphi^{(p)}(\mathbf{x})\, \varphi^{(q)}(\mathbf{x}) = \delta_{pq} \tag{B3a}$$

Recalling the scaling (3.16) of $\xi(\mathbf{r})$, $\bar{\xi}(\mathbf{r}) = (b/a)\,\bar{\zeta}(\mathbf{x})$, the matrix $\boldsymbol{\Gamma}$ can then be developed as a function of b, according to

$$\Gamma_{pq} = Q_i\, \delta_{pq} + \pi_{pq}$$

with

$$\pi_{pq} = b\left[2\delta_{pq} + 4\,\frac{a+3}{3}\int d\mathbf{x}\, \varphi^{(p)}(\mathbf{x})\, \bar{\mathscr{S}}(\mathbf{x})\, \varphi^{(q)}(\mathbf{x}) \right.$$
$$\left. -\,2d\int d\mathbf{x}\, \varphi^{(p)}(\mathbf{x})\, \nabla^2_{\mathbf{x}}(\varphi^{(q)}(\mathbf{x}))\right] + o(b^2) \tag{B3b}$$

So, the matrix ▮ is of order b, which justifies formulas (4.35)–(4.36).

APPENDIX C

In order to compute (4.40), we transform it into an integral. The continuous version of the definition (4.39) of $\bar{\sigma}_l$ is

$$\bar{\xi}(\mathbf{r}) = \left(\frac{L}{2\pi}\right)^d \int d\mathbf{k}\, [\exp(i\mathbf{k}\cdot\mathbf{r})]\, \bar{\sigma}(\mathbf{k}) \tag{C1a}$$

or

$$\bar{\sigma}(\mathbf{k}) = L^{-d}\int d\mathbf{r}\, [\exp(-i\mathbf{k}\cdot\mathbf{r})]\, \bar{\xi}(\mathbf{r}) \tag{C1b}$$

with

$$\mathbf{k} = (2\pi/L)(l_1,\ldots, l_d), \qquad \mathbf{r} = \lambda(r_1,\ldots, r_d)$$

The scaling law $\bar{\xi}(\mathbf{r}) = (b/a)\,\zeta(\mathbf{r}/l_c)$ becomes, for $\bar{\sigma}(\mathbf{k})$,

$$\bar{\sigma}(\mathbf{k}) = \left(\frac{l_c}{L}\right)^d \frac{b}{a}\int d\mathbf{x}\, [\exp(-i\mathbf{q}\cdot\mathbf{x})]\, \bar{\mathscr{S}}(\mathbf{x}) \tag{C2a}$$

with

$$\mathbf{q} = l_c\mathbf{k}, \qquad \mathbf{x} = \mathbf{r}/l_c$$

or

$$\bar{\sigma}(\mathbf{k}) = (l_c/L)^d(b/a)\, s(\mathbf{q}) \tag{C2b}$$

Note that since $\xi(\mathbf{r})\eta$is function of only the radial coordinate ρ, $\bar{\sigma}(\mathbf{k})$ is real and only depends on the scalar wavelength $k = |\mathbf{k}|$, that is,

$$\bar{\sigma}(k) = (l_c/L)^d (b/a)\, s(q), \qquad q = |\mathbf{q}| \tag{C3}$$

On the other hand, the factor $U^{ll' \cdots}$ in (4.40) can also be set in a continuous form. In the limit $N \to \infty$, L fixed, we obtain

$$\begin{aligned} \mu_l &= 4 \sum_{i=1}^{d} \sin^2 \frac{\pi l_i}{N} \\ &\sim \frac{4\pi^2}{N^2} \sum_{i=1}^{d} l_i^2 = \lambda^2 k^2 \end{aligned} \tag{C4}$$

using the definition (C1b) of $\mathbf{k}$. Thus, in this limit, the eigenvalues λ_l and ω_l used in formulas (7) of Appendix A can be written

$$\begin{aligned} \lambda_l &= b + Dk^2 \\ \omega_l &= 2\frac{b + Dk^2}{Q + 2dDk^2} \end{aligned} \tag{C5}$$

Recall that for the homogeneous metastable state $\hat{u} = 1$, we have denoted

$$\begin{aligned} f'(\hat{u}) = -b, \qquad f''(\hat{u}) = 2a, \qquad Q(\hat{u}) = 4(a+2) + 2b \\ Q'(\hat{u}) = 4(a+3) + b \end{aligned} \tag{C6}$$

Furthermore, the correlation length l_c is equal to $(D/b)^{1/2}$, so that λ_l, ω_l can be expressed as

$$\begin{aligned} \lambda_l &= \lambda(q) = b(1+q^2) \\ \omega_l &= \omega(q) = 2b(1+q^2)/(Q + 2dbq^2) \\ q &= l_c k \end{aligned} \tag{C7}$$

We see that, for b small,

$$\begin{aligned} \omega(q) &= \frac{2}{Q_i} \lambda(q) \left[1 - \frac{2d}{Q} q^2 b + o(b^2) \right] \\ &= \frac{2}{Q_i} \lambda(q) \left[1 - \frac{2}{Q_i} (1 + dq^2)\, b + o(b^2) \right] \\ &= \frac{2}{Q_i} [(1+q^2) b - A(q) b^2 + o(b^3)] \end{aligned} \tag{C8}$$

with

$$A(q) = \frac{2}{Q_i} (1+q^2)(1+dq^2)$$

From formulas (A7) we find therefore

$$U^{ll'} = U(\mathbf{q}, \mathbf{q}') = N^d \left[\frac{2}{Q_i} [(1+q^2)b - A(q)b^2]\, \delta(\mathbf{q}+\mathbf{q}') \right]$$

$$\begin{aligned} U^{ll'l''} &= U(\mathbf{q}, \mathbf{q}', \mathbf{q}'') \\ &= -N^d \frac{2}{Q_i} [2a + B(q, q', q'')b + o(b^2)]\, \delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}'') \end{aligned} \tag{C9}$$

where we have defined

$$\begin{aligned} B(q, q', q'') = \frac{2}{Q_i} [&(3+q^2+q'^2+q''^2)^{-1} \\ &\times \{-2a[(1+q^2)(1+dq^2)+(1+q'^2)(1+dq'^2) \\ &+(1+q''^2)(1+dq''^2)] + 4(a+3)[(1+q^2)(1+q'^2) \\ &+(1+q^2)(1+q''^2)+(1+q'^2)(1+q''^2)]\}] \end{aligned} \tag{C10}$$

Now, with the scaling (3), it is easy to prove that the summation (4.40) can be written in the form

$$U(\{\bar{\sigma}_l\}) = \frac{2}{Q_i} \lambda^{-d} l_c^d \varphi(d) \frac{b^3}{a^2} [1 - \varphi_i(d)b + o(b^2)] \tag{C11}$$

with

$$\begin{aligned} \varphi(d) = &\frac{(2\pi)^{-d}}{2} \int d\mathbf{q} (1+q^2)\, s(q)^2 \\ &-\frac{(2\pi)^{-2d}}{3} \int dq\, dq'\, dq''\, s(q)\, s(q')\, s(q'')\, \delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}'') \end{aligned}$$

$$\begin{aligned} \varphi_i(d) = \varphi(d)^{-1} \bigg[&\frac{(2\pi)^{-d}}{2} \int d\mathbf{q}\, A(q)\, s(q)^2 \\ &+\frac{(2\pi)^{-2d}}{6} \int d\mathbf{q}\, d\mathbf{q}'\, d\mathbf{q}''\, s(q)\, s(q')\, s(q'')\, B(q, q', q'')\, \delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}'') \bigg] \end{aligned}$$

The dominant part is exactly $2/Q_i \Phi(\{\xi_r\})$, with $\Phi(\{\xi_r\})$ being given by (4.6). Thus, we recover formula (4.41).

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