A Thermochemical Instability.
II. Inhomogeneous Fluctuations

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The behavior of coupled stochastic fields near a cusp bifurcation is studied. The results are applied to a thermochemical model and the possibility of observing nonclassical critidal behavior is discussed.

1. INTRODUCTION

We study the behavior of coupled stochastic fields $\phi_i(t, \mathbf{r})$ near a simple instability of their evolution equations. The situation is that in which the matrix associated with the linearized problem has one simple eigenvalue zero, while the others have negative real parts.

In Section 2, we treat the problem in detail for the case of two fields and indicate the generalization to n fields, which is direct. We show how to eliminate the "noncritical" fields and reduce the problem to a simple model which gives the behavior of the critical field near the instability. This problem is nontrivial: it depends on the dimensionality of the system. For example, for the simple situation in which only the homogeneous steady state becomes marginally stable (cusp bifurcation), the adiabatic elimination can only be performed for dimension $d \geqslant 3$. In this case, we recover the Landau–Ginzburg potential for the critical field. For $d \leqslant 2$, our method does not allow to eliminate the noncritical fields.[4]

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[4] The problem of adiabatic elimination for the homogeneous case was solved in Ref. 1.

In Section 3, we apply these results to the study of a thermochemical model, considered previously by van den Broeck,[2] in the absence of diffusion (zero-dimensional case). We determine explicitly the coefficients of the Landau–Ginzburg potential in terms of the variables of the problem (temperature, activation energy, etc.) and we evaluate the width of the non-classical critical region by applying the Landau–Ginzburg criterion.

Finally, we summarize in the Appendix the functional integral formalism for stochastic fields obeying Langevin equations.[2] This is done to make the paper self-contained and also because we felt that a simple and direct presentation of the results we needed here was not readily available in the current literature.

2. ADIABATIC ELIMINATION OF THE NONCRITICAL FIELD

We consider the stochastic fields $(\phi_1(t, \mathbf{r}), \phi_2(t, \mathbf{r}))$ in d-dimensional space, $\mathbf{r} = (r_1, ..., r_d)$, obeying the coupled Langevin equations,

$$\begin{bmatrix} \dot{\phi}_1(t, \mathbf{r}) \\ \dot{\phi}_1(t, \mathbf{r}) \end{bmatrix} = (\hat{L}_0 + \hat{D}\nabla^2) \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix} + \begin{bmatrix} \bar{G}_1 \\ \bar{G}_2 \end{bmatrix} + \begin{bmatrix} f_1 \\ f_2 \end{bmatrix} \tag{2.1}$$

In (1), $\hat{L}_0$ is a (2×2) real matrix of elements L_{ij} depending on a set of parameters $\{\mu_\alpha\}$ and $\hat{D}$ is a diagonal diffusion matrix of elements $D_i \delta_{ij}$, $D_i > 0$, ∇^2 is the d-dimensional Laplacian $\nabla^2 \equiv \partial_\mu \partial_\mu$, $\partial_\mu = \partial/\partial r_\mu$, G_j are the nonlinear terms.

$$\bar{G}_j = - \sum_{m+n \geqslant 2} b_{mn}^j \phi_1^n \phi_2^n, \qquad j = 1, 2 \tag{2.2}$$

and $f_j(t, \mathbf{r})$ is a Gaussian noise (white in time) with

$$\{ f_j(t, \mathbf{r}) f_l(t', \mathbf{r}) \} = \bar{b}_{jl}(1 + \bar{b}\nabla^2)\, \delta^{(d)}(\mathbf{r} - \mathbf{r}')\, \delta(t - t') \tag{2.3}$$

Here $\bar{b}_{jl}$ is a constant positive matrix, $\bar{b}$ a negative constant, and $\delta^{(d)}(\mathbf{r} - \mathbf{r}')$ the d-dimensional δ-function.

Let us suppose now that for the values $\{\bar{\mu}_\alpha\}$ of the parameters, $\hat{L}_0$ has an eigenvalue zero with multiplicity one and a second eigenvalue $(-\lambda) < 0$, i.e., we have det $\hat{L}_0(\{\bar{\mu}_\alpha\}) = 0$, Tr $\hat{L}_0(\{\bar{\mu}_\alpha\}) < 0$.

If Λ' is the matrix that diagonalizes $\hat{L}_0(\bar{\mu}_\alpha)$, one has at this critical point

$$\begin{bmatrix} \dot{\psi}_1 \\ \dot{\psi}_2 \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 0 & -\lambda \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} + \Lambda'\hat{D}\Lambda'^{-1}\nabla^2 \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} + \Lambda' \begin{bmatrix} \bar{G}_1 \\ \bar{G}_2 \end{bmatrix} + \Lambda' \begin{bmatrix} f_1 \\ f_2 \end{bmatrix} \tag{2.4}$$

where $\psi_i = \Lambda'_{ij}\phi_j$. For values $\{\mu_\alpha\}$ of the parameters near the critical point $\{\bar{\mu}_\alpha\}$, we denote by $(-\delta)$ the smallest eigenvalue of $\hat{L}_0$, i.e., $\delta = \delta(\{\mu_\alpha\})$

and $\delta(\{\bar{\mu}_\alpha\}) = 0$. Then, to first order in δ, a matrix $\Lambda'' = \Lambda' + O(\delta)$ will diagonalize $\hat{L}_0$, and putting now $\psi_i' = \Lambda_{ij}'' \phi_j$, we have

$$\begin{bmatrix} \dot{\psi}_1' \\ \dot{\psi}_2' \end{bmatrix} = \begin{bmatrix} -\delta & 0 \\ 0 & -\lambda' \end{bmatrix} \begin{bmatrix} \psi_1' \\ \psi_2' \end{bmatrix} + \Lambda'' D \Lambda''^{-1} \nabla^2 \begin{bmatrix} \psi_1' \\ \psi_2' \end{bmatrix} + \Lambda'' \begin{bmatrix} \bar{G}_1 \\ \bar{G}_2 \end{bmatrix} + \Lambda'' \begin{bmatrix} \bar{f}_1 \\ \bar{f}_2 \end{bmatrix}$$

$$(2.5)$$

with $\lambda' = \lambda + O(\delta)$. We suppose that in the space of parameters there is a domain Δ in the neighborhood of $\{\bar{\mu}_\alpha\}$ where one has $\delta > 0$. Taking the Fourier transform of (1), we see that the associated linear problem is determined by the matrix $\hat{L}_p = \hat{L}_0 - \hat{D} \mathbf{p}^2$, $\mathbf{p}^2 = p_1^2 + \cdots + p_d^2$, and one has

$$\det \hat{L}_p = \det \hat{L}_0 - \mathbf{p}^2 (D_1 L_{22} + D_2 L_{11}) + \mathbf{p}^4 D_1 D_2 \qquad (2.6)$$

$$\operatorname{Tr} \hat{L}_p = \operatorname{Tr} \hat{L}_0 - \mathbf{p}^2 (D_1 + D_2) \qquad (2.6')$$

If we consider the situation where

$$D_1 L_{22} + D_2 L_{11} < 0 \qquad (2.7)$$

we see that in the domain Δ all modes will be stable, since $\operatorname{Tr} \hat{L}_p < 0$ and $\det \hat{L}_p > 0$. Moreover, when $\delta \to 0^+$ the only mode with zero eigenvalue will be the one with $\mathbf{p}^2 = 0$. Let $\Lambda(p^2) = \Lambda'' + O(p^2)$ be the matrix that diagonalizes $\hat{L}_p$ in the domain we are considering; then we obtain from (2.1) for the fields $\psi_i = \Lambda_{ij}(\nabla^2) \phi_j$ the following equation:

$$\begin{bmatrix} \dot{\psi}_1 \\ \dot{\psi}_2 \end{bmatrix} = \begin{bmatrix} -[\delta + h_1(\nabla^2)] & 0 \\ 0 & -[\lambda' + h_2(\nabla^2)] \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix}$$

$$+ \Lambda(\nabla^2) \begin{bmatrix} \bar{G}_1 \\ \bar{G}_2 \end{bmatrix} + \Lambda(\nabla^2) \begin{bmatrix} \bar{f}_1 \\ \bar{f}_2 \end{bmatrix} \qquad (2.8)$$

where $h_1(-p^2) > 0$ and $\lambda' + h_2(-p^2) > 0$.

Putting $G_i = \Lambda(\nabla^2)_{ij} \bar{G}_j$, one has

$$G_i = \sum_{m+n \geq 2} \bar{a}_{mn}^i \psi_1^m \psi_2^n \qquad (2.9)$$

with

$$\bar{a}_{mn}^i = \bar{a}_{mn}^i(\nabla^2) = a_{mn}^i + O(\delta) + O(\nabla^2)$$

where a_{mn}^i is the coefficient of $\psi_1^m \psi_2^n$ in $G_i' = \Lambda_{ij}' \bar{G}_j$. The new white noises $f_i = \Lambda(\nabla^2)_{ij} \bar{f}_j$ have the following correlation function:

$$\{ f_i(t, \mathbf{r}) f_j(t', \mathbf{r}') \} = b_{ij}'[1 + b(\nabla^2)] \delta^{(d)}(\mathbf{r} - \mathbf{r}') \delta(t - t') \qquad (2.10)$$

where

$$b'_{ij} = b_{ij} + O(\delta), \qquad b_{ij} = A'_{ik} A'_{jl} \bar{b}_{kl}, \qquad b(\nabla^2) = \sum_{n \geq 1} b_n (\nabla^2)^n$$

We conclude that the set of equations (2.8) takes the form

$$\begin{bmatrix} \dot{\psi}_1(t, \mathbf{r}) \\ \dot{\psi}_2(t, r) \end{bmatrix} = \begin{bmatrix} -[\delta + h_1(\nabla^2)] & 0 \\ 0 & -[\lambda' + h_2(\nabla^2)] \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} + \begin{bmatrix} G_1 \\ G_2 \end{bmatrix} + \begin{bmatrix} f_1 \\ f_2 \end{bmatrix}$$

(2.11)

and we shall study them for $\delta \to 0^+$. We note that the original problem of Eq. (2.1) in the vicinity of $\{\bar{\mu}_\alpha\}$ corresponds to the loss of stability of the homogeneous solution $\psi_i = 0$. If we can realize the cusp bifurcation (two new real stable solutions appear after crossing the critical point $\delta = 0$), we must have $a^1_{20} = 0$, i.e., in the equation for the critical field ψ_1 the nonlinear term in ψ_1^2 has a coefficient $O(\delta)$, which means that we are now studying an instability of codimension two.

We can now use the results of the Appendix to write down the generating functional of correlation and response functions [see (A36)]:

$$\begin{aligned} Z[\mathbf{J}, \mathbf{J}^*] = \int_{\gamma_1(0)} \mathscr{D}\psi \, \mathscr{D}\Pi \exp i \int_{-\infty}^\infty dt \int d\mathbf{r} \, \Big\{ & \Pi_1(\dot{\psi}_1(t, \mathbf{r})) \\ & + [\delta + h_1(\nabla^2)] \, \psi_1 + \Pi_2(\dot{\psi}_2 + [\lambda' + h_2(\nabla^2)] \, \psi_2) \\ & - \Pi_k \sum_{m+n \geq 2} \bar{a}^k_{mn} \psi_1^m \psi_2^n \\ & + \tfrac{1}{2} b_{kl}[1 + b(\nabla^2)] \, \Pi_k \Pi_l + J_k \psi_k + J_k^* \Pi_k \Big\} \end{aligned}$$

(2.12)

The perturbation expansion of $Z[\mathbf{J}, \mathbf{J}^*]$ can be obtained as explained in the Appendix. The propagators [see (A40), (A41)] are ($\lambda_1 = \delta$, $\lambda_2 = \lambda'$)

$$\Delta^{kl}(\omega, \mathbf{P}) = \frac{1}{(2\pi)^{d+1}} \frac{b'_{kl}[1 + b(-\mathbf{p}^2)]}{\{\omega + i[\lambda_k + h_k(-\mathbf{p}^2)]\}\{\omega - i[\lambda_l + h_l(-\mathbf{p}^2)]\}} \qquad (2.13)$$

$$S^k_l(\omega, \mathbf{p}) = -\delta^k_l \frac{1}{(2\pi)^{d+1}} \frac{1}{\omega + i[\lambda_k + h_k(-\mathbf{p}^2)]} \qquad (2.14)$$

and in the calculations the ω integration is to be done first by the residue theorem. We are interested in the long-distance behavior when $\delta \to 0^+$, i.e., in the small $\mathbf{p}^2$ region, and in this limit we only keep the dominant contribution to (2.12). We can then make the following replacements in (2.13) and (2.14): the numerator of (2.13) is replaced by b_{kl}, $[\lambda' + h_2(-\mathbf{p}^2)]$ by λ,

and $[\delta + h_1(-\mathbf{p}^2)]$ by $(\delta + D\mathbf{p}^2)$. In the denominators $(\omega \pm i\lambda)$ we also eliminate the ω dependence, replacing it by $\pm i\lambda$, which amounts to suppressing in (2.12) the term $\Pi_2\dot{\psi}_2$. We can now eliminate the couplings that give finite contributions (nondivergent when $\delta \to 0^+$) at each order of the perturbation theory. By power counting, we see then that we can replace $\bar{a}_{mn}^k$ by a_{mn}^k and keep only the linear terms in ψ_2 for dimension $d > 2$. Since we are interested in the critical fields ψ_1 and Π_1, we put $J_2 = J_2^* = 0$ and we do the ψ_2 integration. This gives a functional δ-function,

$$\delta\left[\Pi_2\left(\lambda - \sum_{m \geqslant 1} a_{m1}^2 \psi_1^m\right) - \Pi_1 \sum_{m \geqslant 1} a_{m1}^1 \psi_1^m\right] \tag{2.15}$$

which allows us to eliminate Π_2 by integration

$$\Pi_2 = \lambda^{-1}\Pi_1[a_{11}^1 \psi_1 + (a_{21}^1 + \lambda^{-1}a_{11}^1 a_{11}^2)\,\psi_1^2 + \cdots] \tag{2.16}$$

The terms $b_{12}\Pi_1\Pi_2$ and $b_{22}(\Pi_2)^2$ in (2.12) will generate couplings $\Pi_1^2\psi_1^m$, $m \geqslant 1$, which are not relevant (give finite corrections for $\delta \to 0^+$) for $d > 2$ and can be dropped. The final result for the generating functional $Z[J_1, J_1^*]$ is

$$Z[J_1, J_1^*] = \int_{\gamma_1(0)} \mathscr{D}\psi_1\,\mathscr{D}\Pi_1 \exp i \int dt \int d\mathbf{r}[\Pi_1(\dot{\psi}_1 + (\delta - D\nabla^2)\,\psi_1$$

$$+ \tfrac{1}{2}b_{11}\Pi_1^2 - \Pi_1(b_2\psi_1^2 + b_3\psi_1^3 + b_4\psi_1^4 + \cdots) + J_1\psi_1 + J_1^*\Pi_1] \tag{2.17a}$$

with

$$b_2 = a_{20}^1, \qquad b_3 = a_{30}^1 + \lambda^{-1}a_{11}^1 a_{20}^1$$

$$b_4 = \lambda^{-1}[a_{11}^1 a_{30}^2 + (a_{21}^1 + \lambda^{-1}a_{11}^1 a_{11}^2)\,a_{20}^2] \tag{2.17b}$$

and so on.

By power counting, we can see from (2.17a) that the critical behavior will be determined by the coupling $b_m\Pi_1\psi_1^m$ for the lowest m with non-vanishing coefficient b_m. The cusp bifurcation appears here as a codimension-two instability when $b_2 = a_{20}^1 = O(\delta)$ and $b_3 \leqslant 0$. Then the dominant term near the critical point $\delta = 0$ will be $b_3\Pi_1\psi_1^3$ and we have the well-known behavior of the ψ^4 model with stationary probability[3]

$$P_{st}[\psi_1] = \exp -\frac{1}{b_{11}} \int d\mathbf{r}\left[D(\nabla\Psi)^2 + \delta\psi^2 - \frac{b_3}{2}\psi^4\right] \tag{2.18}$$

If the original problem [Eq. (2.8)] has the symmetry $\psi_1 \to -\psi_1$, the coefficient b_2 vanishes identically and the cusp bifurcation has codimension one.

The generalization to n fields is straightforward. Now in (1), $\phi = (\phi_1, \phi_2,..., \phi_n)$, $\hat{L}_0$ is an $(n \times n)$ real matrix, and we suppose that at $\{\bar{\mu}_\alpha\}$, L_0 admits an eigenvalue zero of multiplicity one and $n - 1$ simple eigenvalues λ_i with negative real parts. Instead of (2.6) we have

$$\det \hat{L}_p = \det \hat{L}_0 + \sum_{m=1}^{n-1} (\mathbf{p}^2)^m \alpha_m(D_i, L_{ij}) + (-\mathbf{p}^2)^n D_1 D_2 \cdots D_n \quad (2.19)$$

and condition (2.7) will be replaced by the $n - 1$ inequlities $\alpha_m > 0$ if n is even, $\alpha_m < 0$ if n is odd. The rest of the analysis is the same.

3. APPLICATION TO A THERMOCHEMICAL INSTABILITY

Let us now apply the results obtained in Section 2 to a thermo-chemical instability, which was previously studied by van den Broeck.[2] In the latter paper, the system was considered to be perfectly homogeneous. However, even in a well-stirred chemical reactor, concentration and thermal diffusion have to be taken into account on a length scale smaller then the Kolmogorov length, characterizing the size of the smaller turbulent eddies. Our model equations are therefore those for the homogeneous system, supplemented with thermal and molecular diffusion:

$$\partial_t x = -kx - \alpha(x - x_e) + D_1 \nabla^2 x + F_1(t, \mathbf{r})$$
$$\partial_t T = rkx - \beta(T - T_e) + D_2 \nabla^2 T + F_2(t, \mathbf{r}) \quad (3.1)$$

where $x(t, \mathbf{r})$ and $T(t, \mathbf{r})$ are, respectively, the concentration (in mole/cm^3) and temperature at the position $\mathbf{r}$ at time t, $k(T) = k_0 \exp(-U/k_B T)$ is the time-dependent rate constant of the exothermal chemical reaction

$$X \xrightarrow{k} A + \Delta H \quad (3.2)$$

r is the temperature increase per mole, and D_1 and D_2 are the concentration and thermal diffusion coefficients respectively. The terms $\alpha(x - x_e)$ and $\beta(T - T_e)$ represent the decay of the long-wavelength perturbations due to the coupling with the externally fixed reference concentration x_e and temperature T_e. The decay of the short-wavelength inhomogeneities is described by the molecular and thermal diffusion contributions $D_1 \nabla^2 x$ and $D_2 \nabla^2 T$. Such a phenomenological decomposition into long-wavelength decay incorporating boundary effects and short-wavelength contributions is very analogous to the decomposition of the pressure drop through porous media as the sum of a viscous term $(-\eta \nabla^2 u)$ and a term $-\beta u$ representing in a phenomenological way the effect of the boundaries (Darcy's law).[5]

Note that the term $-\alpha(x - x_e)$ can also be thought of as representing a linear chemical reaction

$$X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \tag{3.3}$$

with $k_1 = \alpha$ and $k_2 b = \alpha x_e$ (b is the constant concentration of species B). The quantities F_1 and F_2 represent the effect of the noise associated with the dissipative processes that take place in the system. As is usual,[6] we suppose that they are Gaussian white noise fields with mean value zero and correlation[6,7]

$$\{F_k(t, \mathbf{r}) F_l(t', \mathbf{r}')\} = \bar{b}_{kl} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t')$$

$$+ 2 \frac{\partial}{\partial \mathbf{r}} \frac{\partial}{\partial \mathbf{r}'} D_k \delta_{k,l}^{Kr} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \tag{3.4}$$

The coefficients $\bar{b}_{kl}$ are supposed to be constants, and can be roughly evaluated by considering the chemical reactor operating under equilibrium conditions and applying the fluctuation-dissipation theorem. For instance, $\bar{b}_{11}$ can be evaluated by considering the chemical reactions (3.2) and (3.3) operating under equilibrium conditions in an isolated reactor. One finds

$$\bar{b}_{11} = (1/N_A)(k + \alpha)\langle x \rangle^{st} \tag{3.5}$$

The concentration is expressed in mole/cm^3 and N_A is the Avogadro number. Our control parameters will be the concentration x_e of X in an external reservoir supplying X and the external temperature T_e. The homogeneous stationary state (x_{st}, T_{st}) is

$$x_{st} = \frac{\alpha x_e}{k(T_t) + \alpha} \tag{3.6}$$

$$f(T_{st}, T_e, x_e) = T_{st} - T_e - \frac{r\alpha k(T_{st}) x_e}{\beta[k(T_{st}) + \alpha]} = 0 \tag{3.7}$$

We shall be interested in the critical stationary state (x_{st}^c, T_{st}^c), which satisfies in addition to (3.6) and (3.7) the conditions

$$f'(T_{st}^c, T_e^c, x_e^c) = 0, \qquad f''(T_{st}^c, T_e^c, x_e^c) = 0 \tag{3.8}$$

where primes denote derivatives with respect to T_{st}, and we have written (x_e^c, T_e^c) for the values of the external parameters at the critical point. The four equations (3.6)-(3.8) determine $(x_{st}^c, T_{st}^c, x_e^c, T_e^c)$ and we see then that

we are in a codimension-two situation. These four equations can be written as follows[2] $[k_c = k(T_{st}^c)]$:

$$x_{st}^c / x_e^c \cong \tfrac{1}{2}\gamma/(\gamma - 2) \tag{3.9a}$$

$$T_{st}^c / T_e^c = \gamma/(\gamma - 2) \tag{3.9b}$$

$$\alpha/k_c = \gamma(\gamma - 4) \tag{3.9c}$$

$$\beta/k_c = \rho\gamma/4 \tag{3.9d}$$

where

$$\rho = \frac{r x_e^c}{T_e^c}, \qquad \gamma = \frac{U}{k_B T_e^c}, \qquad k_c = k_0 \exp\left(-\frac{U}{k_B T_{st}^c}\right) \tag{3.10}$$

Clearly, these equations can only be satisfied for $\gamma > 4$. Let $x_{st} = x_{st}^c + \Delta x_{st} = T_{st}^c + \Delta T_{st}$ be the stationary state corresponding to the values $(x_e^c + \Delta x_e, T_e^c + \Delta T_e)$ of the parameters. We choose to approach the critical point $(x_e^c, \subset T_e^c)$ along the line

$$\frac{\Delta T_e}{T_e^c} + \frac{2}{\gamma - 2} \frac{\Delta x_e}{x_e^c} = 0 \tag{3.11}$$

in order to realize a cusp bifurcation. Indeed, one has along this line that ΔT_{st} satisfies the equation[2]

$$\frac{\Delta T_{st}}{T_{st}^c} \left[\frac{\Delta T_e}{T_e^c} + \frac{1}{6}(\gamma - 2)\left(\frac{\Delta T_{st}}{T_{st}^c}\right)^2 \right] = 0 \tag{3.12}$$

Putting

$$x(t, \mathbf{r}) = x_{st}^c + \Delta x_{st} + \delta x(t, \mathbf{r}), \qquad T(t, \mathbf{r}) = T_{st}^c + \Delta T_{st} + \delta T(t, \mathbf{r})$$

we obtain from (1) for δx and δT the equation

$$\partial_t \begin{bmatrix} \delta x(t, \mathbf{r}) \\ \delta T(t, \mathbf{r}) \end{bmatrix} = (\Gamma + \hat{D}\nabla^2) \begin{bmatrix} \delta x \\ \delta T \end{bmatrix} + \text{nonlinear terms} + \begin{bmatrix} \bar{F}_1 \\ \bar{F}_2 \end{bmatrix} \tag{3.13}$$

where

$$\Gamma = \begin{bmatrix} -[k(T_{st}) + \alpha] & -k'(T_{st})\, x_{st} \\ r k(T_{st}) & r k'(T_{st})\, x_{st} - \beta \end{bmatrix} \tag{3.14}$$

and $\hat{D}$ is the diagonal matrix $\hat{D}_{ij} = \delta_{ij} D_i$. One finds along the bifurcation line (3.11) that

$$\det \Gamma = k_c^2 \frac{\rho\gamma(\gamma - 2)^2}{4(\gamma - 4)} \frac{\Delta T_e}{T_e^c} \tag{3.15}$$

clearly, det $\Gamma = 0$ at the critical point (x_e^c, T_e^c) and Eq. (3.13) takes the form

$$\partial_t \begin{bmatrix} \phi_1(t, \mathbf{r}) \\ \phi_2(t, \mathbf{r}) \end{bmatrix} = \left(\hat{L}_0 + \frac{\hat{D}}{k_c} \nabla^2 \right) \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix} + \text{nonlinear terms} + \begin{bmatrix} \bar{f}_1 \\ \bar{f}_2 \end{bmatrix} \quad (3.16)$$

where

$$\phi_1 = \frac{\delta x}{x_{st}^c}, \quad \phi_2 = \frac{\delta T}{T_{st}^c}, \quad \bar{f}_1 = \frac{F_1}{k_c x_{st}^c}, \quad \bar{f}_2 = \frac{F_2}{k_c T_{st}^c}$$

and

$$\hat{L}_0 = \begin{bmatrix} -2(\gamma - 2)/(\gamma - 4) & -(\gamma - 2) \\ \rho/2 & \rho(\gamma - 4)/4 \end{bmatrix} \quad (3.17)$$

We place ourselves now on the bifurcation line (3.11), where only one free parameter remains, which we choose to be ΔT_e. There is one vanishing eigenvalue $[-\delta(\Delta T_e)]$, which vanishes for $\Delta T_e \to 0$, and a second $(-\lambda')$, which remains finite in this limit.

One has $[\lambda' = \lambda + O(\delta)]$

$$\lambda = 2 \frac{\gamma - 2}{\gamma - 4} - \rho \frac{\gamma - 4}{4} \quad (3.18)$$

$$\delta = \frac{1}{\lambda} \frac{\rho \gamma (\gamma - 2)^2}{4(\gamma - 4)} \frac{\Delta T_e}{T_e^c} \quad (3.19)$$

and the condition $\lambda > 0$ imposes $\gamma < 4\rho^{-1}[(\rho + 1) + (\rho + 1)^{1/2}]$. The matrix Λ that diagonalizes $\hat{L}_0$ is

$$\Lambda = \begin{bmatrix} 1 & 4(\gamma - 2)/\rho(\gamma - 4) \\ 2/(\gamma - 4) & 1 \end{bmatrix} \quad (3.20)$$

and near the critical point $\{T_e^c\}$ one has for $\psi_i = \Lambda'_{ij} \psi_j$, $\Lambda' = \Lambda + O(\delta)$,

$$\partial_{k_c t} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = \begin{bmatrix} -\delta & 0 \\ 0 & -\lambda' \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} + \Lambda' \frac{\hat{D}}{k_c} \Lambda'^{-1} \nabla^2 \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix}$$

$$+ Z \begin{bmatrix} \gamma/(\gamma - 4) \\ \rho/2 - 2(\gamma - 4) \end{bmatrix} + \Lambda' \begin{bmatrix} \bar{f}_1 \\ \bar{f}_2 \end{bmatrix} \quad (3.21)$$

where

$$Z = -\frac{\rho^3 (\gamma - 2)^3}{96 \lambda^3} \psi_1^3 + a_{20} \psi_1^2 + a_{11} \psi_1 \psi_2 + a_{02} \psi_2^2 + \cdots \quad (3.22)$$

with $a_{20} = O(\delta)$, since we are in a cusp bifurcation. In the notation of Section 2 one has

$$a_{30}^1 = -\frac{\rho^3 \gamma (\gamma - 2)^3}{96 \lambda^3 (\gamma - 4)} + O(\delta) \tag{3.23a}$$

$$a_{30}^2 = \frac{\rho^3 (\gamma - 2)^2}{96 \lambda^3} \left(\frac{\rho}{2} - \frac{2}{\gamma - 4} \right) + O(\delta) \tag{3.23b}$$

Condition (2.7) is here

$$D_2 - D_1 \frac{\rho (\gamma - 4)^2}{8(\gamma - 2)} > 0 \tag{3.24}$$

and it guarantees that for $\delta > 0$ all modes will be stable. If (3.24) is violated, i.e., if $D_1 L_{22} + D_2 L_{11} = \alpha$ becomes positive, then we see from (2.6) that at $\delta = 0$ all the modes with $\mathbf{p}^2$ between zero and

$$\frac{\alpha}{D_1 D_2} = \frac{\rho k_c (\gamma - 4)}{4 D_2} \left[1 - \frac{8(\gamma - 2)}{\rho (\gamma - 4)^2} \frac{D_2}{D_1} \right] > 0 \tag{3.25}$$

become unstable and we cannot apply the results of Section 2. If (3.24) holds, then we conclude that the behavior of the critical field ψ_1 will be determined by a reduced model with generating functional $Z[J_1, J_1^*]$ given by (2.17). The parameter δ is defined in (3.19). For the other parameters D, b_3, and b_{11} one obtains

$$D = \left(A \frac{\hat{D}}{k_c} A^{-1} \right)_{11} = \frac{1}{k_c} \frac{2(\gamma - 2)}{\lambda(\gamma - 4)} \left[D_2 - D_1 \frac{\rho(\gamma - 4)^2}{8(\gamma - 2)} \right] > 0 \tag{3.26}$$

$$b_3 = -\frac{2}{3} \frac{\rho^3 \gamma (\gamma - 2)^3 (\gamma - 4)^2}{[8(\gamma - 2) - \rho(\gamma - 4)^2]^3} > 0 \tag{3.27}$$

$$b_{11} \approx \frac{\bar{b}_{11}}{k_c (x_{st}^c)^2} \approx \frac{2}{N_A x_{st}^c} \tag{3.28}$$

The reduced model corresponds to a Langevin equation

$$\partial_t \psi_1 = (-\delta + D\nabla^2) \psi_1 + b_3 \psi_1^3 + f_1(t, \mathbf{r}) \tag{3.29}$$

with

$$\{ f_1(t, \mathbf{r}) f_1(t', \mathbf{r}') \} = b_{11} \delta(k_c(t - t')) \delta^{(d)}(\mathbf{r} - \mathbf{r}')$$

The Fokker–Planck equation corresponding to (3.22) is

$$\frac{\partial}{\partial t} p[\psi_1, t | ...]$$

$$= \int d\mathbf{r} \frac{\delta}{\delta\psi_1(\mathbf{r})} \left\{ [\psi_1(\mathbf{r}) \delta + D\nabla^2\psi_1(\mathbf{r}) - b_3\psi_1(\mathbf{r})^2] \right.$$

$$\left. + \frac{b_{11}}{2} \frac{\delta}{\delta\psi_1(\mathbf{r})} \right\} p[\psi_1, t | ...] \qquad (3.30)$$

The stationary probability $p_{st}[\psi_1]$ corresponding to (3.30) reads

$$p_{st}[\psi_1] \approx \exp\left(-\int d\mathbf{r} \left\{ \frac{1}{2} \left[\frac{\delta}{b_{11}} \psi_1^2 + \frac{D}{b_{11}} (\nabla\psi_1)^2 \right] + \frac{b_3}{4! \, b_{11}} \psi_1^4 \right\} \right) \quad (3.31)$$

4. THE GINZBURG CRITERION

In order to estimate the range of validity of a mean-field type of approximation, we use the Ginzburg criterion.[4] In terms of the parameters δ, D, b_3, and b_{11}, the condition for observing nonclassical critical behavior reads

$$\frac{3b_{11}|b_3|}{D_2} \pi^{d/2} \frac{\Gamma(\varepsilon/2)}{\varepsilon} \left(\frac{\delta}{D}\right)^{d/2-2} > 1 \qquad (4.1)$$

where d is the dimension, $d = 4 - \varepsilon$. Combining this result with the explicit expressions (3.13) and (3.26)–(3.28), one obtains the following delimitation of the region characterized by nonclassical critical behavior:

$$\frac{\Delta T_c}{T_e^c} < \frac{\rho^5\gamma(\gamma-2)(\gamma-4)^4}{[8(\gamma-2)-\rho(\gamma-4)^2]^2} \left[\left(\frac{k_c}{K}\right)^{3/2} \frac{1}{N_A x_{st}^c} \right]^2 \qquad (4.2)$$

with

$$K = D_2 - D_1 \frac{\rho(\gamma-4)^2}{8(\gamma-2)} > 0 \qquad (4.3)$$

As expected, the vicinity of the critical point where nonclassical critical behavior will be observed becomes smaller as the "noncritical" correlation length

$$l_c = (K/k_c)^{1/2} \qquad (4.4)$$

becomes larger. The difficulty of observing nonclassical critical behavior in nonequilibrium transitions has been associated with the fact that this length is typically much larger in the case of nonequilibrium. systems. However, in the case of chemical nonequilibrium instabilities, it was argued that the large variability of the chemical rate constants makes these systems the best candidate for the observation of nonequilibrium nonclassical indices.[9] This same remark seems to apply to the presently discussed thermochemical instability: for a large value of k_c, the correlation length l_c may become comparable to atomic distances and nonclassical critical behavior is expected.

In addition, the result (4.2) suggests that one can markedly broaden the nonclassical critical region by considering reactions with a large specific heat of reaction, thereby increasing the value of ρ. Both these arguments, however, present serious drawbacks. First, it follows from the result (4.9d) that $\beta > \rho k_c$ (since $\gamma > 4$). Hence, a large value of k_c and/or of ρ implies a large value of β, which seems physically unattainable. Indeed, we have not been able to construct a simple internal temperature control device similar to the reaction scheme (4.3) for the concentration control. The parameter β thus cannot be associated with a chemical rate, but it represents a much slower rate describing the decay of the long-wavelength temperature inhomogeneities through thermal coupling with the boundaries, which are kept at a constant temperature. Second, the region in which a cusp bifurcation occurs without the interference of other instabilities becomes very narrow as the value of ρ increases $\{4 < \gamma < 4\rho^{-1}[\rho + 1 + (\rho + 1)^{1/2}]\}$, so that it seems very difficult to exploit the ρ^5 dependence in order to promote nonclassical critical behavior.

5. CONCLUSION

We have investigated the critical behavior in the vicinity of a nonequilibrium thermochemical instability for the simple case of a cusp bifurcation in a crude model [Eqs. (3.1)] of a linear exothermal reaction. The width of the nonclassical critical region is found to be proportional to the sixth power of the chemical reaction rate k_c and to the fifth power of the heat of reaction. Although large values of these parameters are possible, one cannot exploit this feature to propose a thermochemical experiment in which nonclassical critical behavior could be observed. First, for large values of k_c and ρ the critical point lies in a region of parameter space that is unattainable for practical purposes (e.g., large values of the temperature coupling constant β). Second, for these values of k_c and ρ, other instabilities (such as a transition to a limit cycle behavior) will interfere

with the cusp bifurcation. It remains to be seen whether these difficulties are inherent to the specific model discussed in this paper and can be surmounted in the case of more complex thermochemical systems.

APPENDIX

For simplicity, we explain the method in the case of one degree of freedom (for more details, see Ref. 3). Let $q(t)$ be the continuous Markov process, obeying the following Langevin equation:

$$\dot{q}(t) + A(q(t)) = f(t) \tag{A1}$$

where $f(t)$ is a Gaussian white process with

$$\{f(t)\} = 0, \qquad \{f(t)f(t')\} = c\,\delta(t - t') \tag{A2}$$

The bracket $\{\cdot\}$ stands for the average over the different realizations of f.

The solution $q^f(t)$ of (A1) is a functional of $f(t)$. Let us discretize the interval $[t_0, T]$ in $N + 1$ intervals of length ε, $t_j = t_0 + j\varepsilon$, $j = 0,\dots, N + 1$, $t_{N+1} = T$.

Setting $q_j = q(t_j)$ and

$$f_j = \frac{1}{\varepsilon} \int_{t_{j-1}}^{t_j} f(t)\, dt$$

[to be more rigorous, one should replace εf_j by $dw_j = w_j - w_{j-1}$, where $w(t)$ is the Wiener process[3]], one finds for the discretized version of (A1)

$$\frac{q_j^f - q_{j-1}^f}{\varepsilon} + A(q_{j-1}^f) = f_j, \qquad 1 \leqslant j \leqslant N + 1 \tag{A3}$$

This set of equations give us recursively q_j^f in terms of q_{j-1}^f. We will take the intial condition $q_0^f = Q_0$. Note that the f_j, $j = 1,\dots, N + 1$, are independent Gaussian random variables with joint probability distribution W given by

$$W(f_1, f_2,\dots, f_{N+1}) = \prod_{j=1}^{N+1} \left(\frac{\varepsilon}{2\pi c}\right)^{1/2} \exp\left(-\frac{\varepsilon f_j^2}{2c}\right) \tag{A4}$$

Let $F[q^f(t)]$ be a functional of $q^f(t)$, hence of $f(t)$. Its discretized form is a function $\tilde{F}(q_0^f,\dots, q_{N+1}^f)$. The values q_i^f are determined by (A3); hence, one can write

$$\tilde{F}(q_0^f,\dots, q_{n+1}^f)$$

$$= \int \prod_{i=0}^{N+1} dq_i \prod_{j=1}^{N+1} \delta(q_j - q_{j-1} + \varepsilon A(q_{j-1}) - \varepsilon f_j)\, \delta(q_0 - Q_0)$$

$$+ \tilde{F}(q_0,\dots, q_{N+1}) \tag{A5}$$

We remark that the Jacobian $|\det(\partial q_j/\partial q_k)|$ that should appear in (A5) is one, since we have discretized $A(q(t))$ as $A(q_{j-1})$, i.e., in the prepoint. Using $\delta(x) = (1/2\pi) \int dp \, e^{ipx}$, we can write (A5) as

$$\int \prod_{i=0}^{N+1} dq_i \int \prod_{j=1}^{N+1} \frac{dp_j}{2\pi} \exp i \left\{ \sum_{j=1}^{N+1} [P_j(q_j - q_{j-1} + \varepsilon A(q_{j-1})) - \varepsilon f_j] \right\}$$

$$\times \delta(q_0 - Q_0) \tilde{F}(q_0,..., q_{N+1}) \tag{A6}$$

where we have used $\delta(x) = (1/2\pi) \int dp \, e^{ipx}$.

From (A5) and (A6) we can write symbolically in the limit $N \to \infty$

$$F[q^f(t)] = \int_{\gamma_1(0)} \mathscr{D}q \, \mathscr{D}p \exp i \int_{t_0}^{T} dt \, p(t)[\dot{q} + A(q(t)) - f(t)]$$

$$\times \delta(q(t_0) - Q_0) F[q(t)] \tag{A7}$$

The functional integral in (A7) is defined as the limit for $N \to \infty$ of the discretized form (A6). Note that the discretized form of $p(t) A(q(t))$ is $p_j A(q_{j-1})$ and we call this the prepoint discretizaton, indicated by the symbol $\gamma_1(0)$.[3]

The next step is to evaluate the average of a functional of f over the different realizations. This can be very easily done using the discretized form (A6) for a functional and the simple Gaussian law (A4) for the random variables f_j. Using

$$\int \exp(ikx) \frac{1}{(2\pi)^{1/2} \sigma} \exp\left(-\frac{x^2}{2\sigma^2}\right) dx = \exp\left(-\frac{1}{2} k^2 \sigma^2\right) \tag{A8}$$

one obtains

$$\{\tilde{F}(q_0^f,..., q_{N+1}^f)\}$$

$$= \int \prod_{i=0}^{N+1} dq_i \int \prod_{j=1}^{N+1} \frac{dp_j}{2\pi}$$

$$\times \exp i \left[\sum_{j=1}^{N+1} p_j(q_j - q_{j-1} + \varepsilon A(q_{j-1})) - \varepsilon f_j \right]$$

$$\times \delta(q_0 - Q_0) \tilde{F}(q_0,..., q_{N+1}) \tag{A9}$$

The result (A9) gives us in principle the solution to our problem. Unfortunately, in general the integrals cannot be performed, due to the nonlinearities in $A(q_j)$ and due to the presence of $\tilde{F}$, and we have to use a perturbative approach.

We write $A(q_j) = \lambda q_j + \bar{A}(q_j)$, where $\bar{A}(q_j)$ is nonlinear in q_j. Furthermore, the problematic terms can be taken out of the integral in (A9) using the standard trick

$$\int f(q)\, g(q)\, dq = \int f(q)\, g(q)\, e^{iJq}\, dq \big|_{J=0}$$

$$= f\left(\frac{1}{i}\frac{\partial}{\partial j}\right) \int g(q)\, e^{iJq}\, dq \big|_{J=0} \tag{A10}$$

One has to perform this trick on both the p_j and q_j variables. We thus obtain

$$\{\tilde{F}(q_0^f, \ldots, q_{N+1}^f)\}$$

$$= \tilde{F}\left(\frac{1}{i\varepsilon}\frac{\partial}{\partial J_0}, \ldots, \frac{1}{i\varepsilon}\frac{\partial}{\partial J_{N+1}}\right)$$

$$\times \prod_{j=1}^{N+1} \exp\left[\varepsilon\frac{\partial}{\partial J_j^*}\,\bar{A}\left(\frac{1}{i\varepsilon}\frac{\partial}{\partial J_{j-1}}\right)\right] Z_0(\mathbf{J}, \mathbf{J}^*)\bigg|_{\mathbf{J}=\mathbf{J}^*=0} \tag{A11}$$

with

$$Z_0(\mathbf{J}, \mathbf{J}^*)$$

$$= \int \prod_{i=0}^{N+1} dq_i \int \prod_{j=1}^{N+1} \frac{dp_j}{2\pi}$$

$$\times \exp i \sum_{j=1}^{N+1}\left[p_j(q_j - q_{j-1} + \varepsilon\lambda q_{j-1}) + \frac{i\varepsilon c}{2}p_j^2 + \varepsilon J_j q_j + \varepsilon J_j^* p_j\right]$$

$$\times [\exp(i\varepsilon J_0 q_0)]\,\delta(q_0 - Q_0) \tag{A12}$$

Z_0 involves Gaussian integrals only, and can be computed exactly:

$$Z_0(J, J^*) = \exp\left\{iQ_0 \int_{t_0}^{T} dt'\,[\exp \lambda(t_0 - t')]\, J(t')\right.$$

$$- \int_{t_0}^{T} dt' \int_{t_0}^{T} dt''\, J(t')\left[\frac{1}{2}\Delta(t', t'')\, J(t'')\right.$$

$$\left.\left. + S(t' - t'')\, J^*(t'')\right]\right\} \tag{A13}$$

with

$$S(t) = iD(t); \qquad D(t) = \theta(t)\, e^{-\lambda t}$$

$$\Delta(t', t'') = \frac{c}{2\lambda}\left\{D(t' - t'') + D(t'' - t') - \exp[-\lambda(t' + t'' - 2t_0)]\right\} \tag{A14}$$

In this way, the calculation of averages is reduced to the calculation of functional derivatives (or partial derivatives in the discrete form) of the generating functional Z_0. We can interpret this functional as the characteristic functional for the linear Langevin equation:

$$\dot{q}(t) + \lambda q(t) + J^*(t) = f(t) \tag{A15}$$

From now on, we shall use the more compact path integral formulation, whose meaning is made precise by specifying the prepoint discretization rule $\gamma_1(0)$.

It is thus clear that the quantity $J^*(t)$ can be interpreted as a time-dependent external field. Note also that

$$Z[J(t), J^*(t)]$$

$$= \lim_{\varepsilon \to 0^+} \exp \int_{t_0}^{T} dt \, \frac{\delta}{\delta J^*(t+\varepsilon)} \, \bar{A}\left(\frac{1}{i} \frac{\delta}{\delta J(t)}\right) Z_0[J(t), J^*(t)] \tag{A16}$$

is the characteristic functional for the corresponding nonlinear Langevin equation [with $\lambda q(t)$ replaced by $A(q(t)) = \lambda q(t) + \bar{A}(q(t))$]. The $\varepsilon \to 0^+$ comes from the $\gamma_1(0)$ discretization and is necessary to define in an unambiguous way the action of the functional derivatives on $Z_0[J, J^*]$. As is well known, the characteristic functional is also a moment-generating function; e.g.,

$$\{q(t_1) \cdots q(t_n) \, p(t'_1) \cdots p(t'_m)\}$$

$$= \frac{1}{i^{m+n}} \frac{\delta^{n+m} Z[J(t), J^*(t)]}{\delta J(t_1) \cdots \delta J(t_n) \, \delta J^*(t'_1) \cdots \delta J^*(t'_m)}\bigg|_{J = J^* \equiv 0} \tag{A17}$$

For example, we obtain in the case of a linear Langevin equation

$$\{q(t_1) \, q(t_2)\}_L = -\frac{\delta^2}{\delta J(t_1) \, \delta J(t_2)} Z_0[J(t), J^*(t)]\bigg|_{J = J^* \equiv 0}$$

$$= Q_0^2 \exp[-\lambda(t_1 + t_2 - 2t_0)] + \varDelta(t_1, t_2) \tag{A18}$$

a result that can be obtained straightforwardly from the Langevin equation itself.

Often, one is interested in the long-time results only. This can be achieved by letting the initial time t_0 go to $-\infty$. Since $T > t_0$ is arbitrary, we put $T = +\infty$. In many cases, the system will reach a stationary state characterized by properties independent of the initial condition Q_0. In this case, the generating functional takes the following stationary state form Z^{st}:

$$Z^{st}[J(t), J^*(t)]$$

$$= \exp i \int_{-\infty}^{+\infty} dt \, \frac{1}{i\delta J^*(t)} \, \bar{A}\left(\frac{1}{i\delta J(t)}\right) Z_0^{st}[J(t), J^*(t)] \tag{A19}$$

with

$$Z_0^{\text{st}}[J(t), J^*(t)]$$

$$= \exp\left\{ -\int_{-\infty}^{+\infty} dt' \int_{-\infty}^{+\infty} dt'' \right.$$

$$\left. \times \frac{c}{4\lambda} J(t')[D(t'-t'') + D(t''-t')] J(t'') + iJ(t') D(t-t'') J^*(t'') \right\}$$

(A20)

We make here some remarks concerning our use of the prepoint discretization $\gamma_1(0)$. Indeed, any discretization can be used and the final result will be the same, as is shown in detail in Ref. 8 (see also Chapter IV of Ref. 3). For instance, if we use the $\gamma_1(\alpha)$ discretization, which discretiezs $A(q)$ as $A(q_{j-1} + \alpha(q_1 - q_{j-1}))$, the Jacobian involved in formula (A5), which was unity in the $\gamma_1(0)$, case is now

$$\exp \varepsilon \alpha \sum_j \frac{\partial A}{\partial q_j} \to \exp \alpha \int_{T_0}^{T} dt \frac{\partial A(q(t))}{\partial q}$$

This changes then in formula (A.7) the argument of the exponential to $p(\dot{q} - A(q) - i\alpha \, \partial A/\partial q)$, but at the same time we must change the prescription (A.16) to

$$\lim_{\varepsilon \to 0^+} i \int_{T_0}^{T} dt \left| p(t+\varepsilon) \, \bar{A}(q(t+\varepsilon) + \alpha(q(t+\varepsilon) - q(t)) - i\alpha \frac{\partial A(q(t))}{\partial q} \right|$$

with

$$p(t) \to \frac{1}{i} \frac{\delta}{\delta J^*(t)}, \quad q(t) \to \frac{1}{i} \frac{\delta}{\delta J(t)}$$

and $Z_0[J, J^*]$ remains the same. Then all the α dependence cancels in the perturbation expansion, which is the same as the $\gamma_1(0)$ one. Let us also note that one should treat the white noise $f(t)$ as the derivative of the Wiener process $w(t)$, which amounts to replacing f_j by $(w_j - w_{j-1})/\varepsilon$ in (A3). This point is discussed carefully in Chapter VII of Ref. 3, where the equivalence of discretizations is also shown.

It is straightforward to generalize the previous results to the case of a set of coupled Langevin equations:

$$\dot{q}^\mu(t) + A^\mu(q(t)) = f^\mu(t)$$

(A21)

with

$$\{f^\mu(t)\} = 0; \qquad \{f^\mu(t)\, f^\nu(t')\} = c^{\mu\nu}\delta(t - t') \qquad (A22)$$

One has

$$Z[\mathbf{J}, \mathbf{J}^*] = \int_{\gamma_1(0)} \mathscr{D}\mathbf{q}\ \mathscr{D}\mathbf{p} \exp i \int_{t_0}^{T} dt \left[p_\mu(\dot{q}^\mu + A^\mu(q)) \right.$$

$$\left. + \frac{1}{2} c^{\mu\nu\eta} p_\mu p_\nu + J_\mu q^\mu + J^{*\mu} p_\mu \right] \delta(\mathbf{q}(t_0) - Q_0)$$

$$= \exp i \int_{t_0}^{T} dt\ p_\mu \bar{A}^\mu(\mathbf{q}) \Bigg|_{\substack{p_\mu = (1/i)\,\delta/\delta J^{*\mu} \\ q_\mu = (1/i)\,\delta/\delta J_\mu}} Z_0[\mathbf{J}, \mathbf{J}^*] \qquad (A23)$$

and

$$Z_0[\mathbf{J}, \mathbf{J}^*] = \exp \left\{ i \sum_{\mu=1}^{n} Q_0^\mu \int_{t_0}^{T} dt \exp[\lambda_{(\mu)}(t_0 - t')] \cdot J_\mu(t') \right.$$

$$- \sum_{\mu,\nu=1}^{n} \int_{t_0}^{T} dt'\, dt''\, J_\mu(t')$$

$$\left. \times \left[\frac{1}{2} \Delta^{\mu\nu}(t', t'')\, J_\nu(t'') + S_\nu^\mu(t' - t'') \right] J^{*\nu}(t'') \right\} \qquad (A24)$$

with

$$S_\nu^\mu(t) = i\, \delta_\nu^\mu D_{(\mu)}(t), \qquad D_{(\mu)}(t) \equiv \theta(t) \exp(-\lambda_{(\mu)}t)$$

and

$$\Delta^{\mu\nu}(t', t'') = \frac{c^{\mu\nu}}{\lambda_{(\mu)} + \lambda_{(\nu)}} \{ D_{(\mu)}(t' - t'') + D_{(\nu)}(t'' - t')$$

$$- \exp[-(\lambda_{(\mu)}t' + \lambda_{(\nu)}t'') + (\lambda_{(\mu)} + \lambda_{(\nu)})\, t_0] \} \qquad (A25)$$

The above techniques become particularly interesting in the case of an infinite set of variables, i.e., in the case of stochastic fields

$$\phi(t, \mathbf{r}) = (\phi_1(t, \mathbf{r}),..., \phi_m(t, \mathbf{r}))$$

in d-dimensional space $\mathbf{r} = (r_1,..., r_d)$ (we use the notations $\partial_\mu \equiv \partial/\partial r_\mu$, $\nabla^2 \equiv \partial_\mu \partial_\mu$). All one has to do is to replace the index μ in $q^\mu(t)$ by the pair of indices $(l, \mathbf{r})$, where l is discrete, $l = 1, 2,..., m$, and $\mathbf{r}$ is continuous. The Langevin equations (A21) are now

$$\dot{\phi}_l(t, \mathbf{r}) + A_l(\phi(t, \mathbf{r}), \partial_\mu \phi(t, \mathbf{r})) = f_l(t, \mathbf{r}) \qquad (A26)$$

with $\{f_l(t, \mathbf{r})\} = 0$ and

$$\{f_k(t, \mathbf{r}) f_l(t', \mathbf{r}')\} = c_{kl}(\nabla^2) \, \delta^{(d)}(\mathbf{r} - \mathbf{r}') \, \delta(t - t')$$

where $c_{kl}(\nabla^2)$ is a matrix, which can depend on ∇^2 acting on the d-dimensional δ-function $\delta^{(d)}(\mathbf{r} - \mathbf{r}')$.

Since $\mu \to (l, \mathbf{r})$, a sum over μ will be replaced as $\sum_m \to \sum_l \int d\mathbf{r}$ and from (A28) we obtain

$$Z[\mathbf{J}, \mathbf{J}^*] = \int_{\gamma_l(0)} \mathscr{D}\boldsymbol{\phi} \, \mathscr{D}\Pi_k$$

$$\times \exp i \int_{-\infty}^{\infty} dt \int d\mathbf{r} \left\{ \Pi_k(t, \mathbf{r})[\dot{\phi}_k(t, \mathbf{r}) \right.$$

$$+ A_k(\boldsymbol{\phi})] + \frac{1}{2} c_{kl}(\nabla^2) \, \Pi_k(t, \mathbf{r}) \, \Pi_l(t, \mathbf{r})$$

$$\left. + J_k \phi_k + J_k^* \Pi_k \right\} \tag{A27}$$

where we have replaced $J_\mu(t) \to J_l(t, \mathbf{r})$, $J^{*\mu}(t) \to J_l^*(t, \mathbf{r})$, and $p_\mu(t) \to \Pi_l(t, \mathbf{r})$. In the discrete version of (A28) the measure is now

$$\mathscr{D}\boldsymbol{\phi} = \prod_j \prod_{l,\mathbf{r}} d\phi_l(t_j, \mathbf{r}), \qquad \mathscr{D}\Pi = \prod_j \prod_{l,\mathbf{r}} \frac{d\Pi_l(t_j, \mathbf{r})}{2\pi}$$

We put

$$A_k(\boldsymbol{\phi}(t, \mathbf{r})) = \lambda_{(k)}(\nabla^2) \, \phi_k(t, \mathbf{r}) + \bar{A}_k(\boldsymbol{\phi})$$

$$\mathbf{x} = (t, \mathbf{r}), \qquad d\mathbf{x} = dt \, d\mathbf{r}$$

The perturbation expansion for $Z[\mathbf{J}, \mathbf{J}^*]$ is

$$Z[\mathbf{J}, \mathbf{J}^*] = \lim_{\varepsilon \to 0^+} \exp i \int d\mathbf{x} \, \Pi_k(t + \varepsilon, \mathbf{r})$$

$$\times \bar{A}_k(\boldsymbol{\phi}(\mathbf{x})) \Big|_{\substack{\boldsymbol{\phi} = (1/i) \, \delta/\delta\mathbf{J}(\mathbf{x}) \\ \Pi = (1/i) \, \delta/\delta\mathbf{J}^*(\mathbf{x})}} Z_0[\mathbf{J}, \mathbf{J}^*]$$

with Z_0 given by [see (A24)]

$$Z_0[\mathbf{J}, \mathbf{J}^*] = \exp - \sum_{k,l=1}^{m} \int d\mathbf{x}' \, d\mathbf{x}'' \, J_k(\mathbf{x}') \left[\frac{1}{2} \Delta^{kl}(\mathbf{x}' - \mathbf{x}'') \, J_l(\mathbf{x}'') \right.$$

$$\left. + S_l^k(\mathbf{x}' - \mathbf{x}'') \, J_l^*(\mathbf{x}'') \right]$$

It is convenient to set up the expansion in terms of the Fourier transforms $\Delta^{kl}(\omega, \mathbf{p})$, $S_l^k(\omega, \mathbf{p})$ of the propagators,

$$F(\mathbf{x}) = \int d\mathbf{p}[\exp(-i\mathbf{p} \cdot \mathbf{x})]\, F(\mathbf{p})$$

$$\mathbf{p} = (\omega, \mathbf{p}), \qquad \mathbf{p} \cdot \mathbf{x} = \omega t - \mathbf{p} \cdot \mathbf{r})$$

which are [see (A25)]

$$S_k^l(\omega, \mathbf{p}) = \delta_k^l \frac{1}{(2\pi)^{d+1}} \frac{1}{\omega + i\lambda_{(l)}(-\mathbf{p}^2)} \tag{A28}$$

$$\Delta^{kl}(\omega, \mathbf{p}) = \frac{1}{(2\pi)^{d+1}} \frac{c_{kl}(-\mathbf{p}^2)}{[\omega + i\lambda_{(k)}(-p^2)][\omega - i\lambda_{(l)}(-\mathbf{p}^2)]} \tag{A29}$$

ACKNOWLEDGMENTS

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