Critical Fluctuations in a Thermochemical Instability. I. Mean Field Description

C. Van den Broeck[1,2]

We calculate the temperature and concentration fluctuations in a homogeneous thermochemical model in the vicinity of a transition point towards a multiple steady state regime. Enhanced fluctuations of 0.1% are predicted at a distance of 10^{-3} °K from the critical point in a volume element of 10^{-3} mm^3.

1. INTRODUCTION

Systems far from equilibrium can undergo transitions associated with the bifurcation of new branches of solutions of the macroscopic evolution equations.[1–3] Much attention has been devoted to the behavior of the fluctuations in the vicinity of such nonequilibrium transitions. Reaction diffusion systems have been among the privileged examples for which many results have been obtained. Most of these results are limited to the behavior of the composition variables.[4] A large number of macroscopic phenomena involve, however, thermochemical processes, in which the internal energy or the temperature is the key variable. These problems have been studied in great detail in engineering sciences,[5,6] but only recently has attention been paid to the effect of fluctuations.[7] Apart from their theoretical interest, nonequilibrium thermochemical instabilities could be of experimental interest in that one could expect to observe anomalous fluctuations associated with the instability. As far as we know such fluctuations have been

---

[1] Aangesteld Navorser Nationaal Fonds Wetenschappelijk Onderzoek België.
[2] Departement Natuurkunde, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussel.

153

observed only in an indirect way in a nonequilibrium hydrodynamic instability.[8]

In this paper, we study the fluctuations in a simple thermochemical model where the coupling between the composition and the thermal variable leads to the possibility of a transition towards a multiple steady states regime (cusp bifurcation). A similar model was discussed by Nitzan and Ross[9] who, however, did not take into account the effect of fluctuations. We will restrict ourselves here to the case of a well-stirred homogeneous system. Hence, we can apply the general theory for the study of critical fluctuations in a homogeneous system near a cusp bifurcation elaborated in previous papers.[4,10] These results will be reviewed in Section 2. The deterministic thermochemical model under consideration is introduced in Section 3 and the values of the control parameters (external temperature, feeding rate of the reactor, . . .) at the bifurcation point are calculated in terms of the characteristics of the chemical mixture (rate constants, heat of reaction, . . .). In Section 4, the effect of homogeneous thermodynamic fluctuations is studied using the results expounded in Section 2. It is shown that enhanced fluctuations of the order of 0.1% may occur in the case of a typical exothermal reaction in gaseous phase at a distance of 10^{-3} °K from the critical point in a volume element of 10^{-3} mm^3. It should be noted, however, that inhomogeneous fluctuations can be important since they can modify the characteristics of a transition (for instance the critical exponents) or even rule out the possibility of a transition. These questions will be considered in a forthcoming paper.

2. MEAN FIELD FLUCTUATIONS IN THE VICINITY OF A CUSP BIFURCATION: GENERAL RESULTS

In an ideal gas at equilibrium, fluctuations are known to obey a Poisson law.[11] Hence, if X stands for the number of particles in a given volume V, one has

$$\frac{\langle \delta X^2 \rangle}{\langle X \rangle^2} = \frac{1}{\langle X \rangle} \tag{1}$$

where $\delta X = X - \langle X \rangle$. The average number of particles $\langle X \rangle$ in the volume V can also be written as $N_A V x$, where x is the (average) concentration (in mol/cm^3) and N_A is the Avogadro number. From (1), one concludes that for a gas under standard conditions in equilibrium ($x \simeq 10^{-4}$), fluctuations will be of the same importance as the average value in volume elements of the order $V \simeq 10^{-19}$ cm^3. Clearly such fluctuations will not be perceived macroscopically.

When the system is subject to a nonequilibrium constraint, the thermo-dynamic state of the system can eventually lose its stability in favor of new macroscopic states. The vicinity of this instability or bifurcation point is generally speaking characterized by an enhancement of the fluctuations. Hence, the following two questions arise:

    1. How large are the enhanced fluctuations (i.e., in how large a volume element will they be of the same importance as the average value)?

    2. How close to the bifurcation point do they appear?

In this section, we give a general answer to these questions for the simplest type of bifurcation in a homogeneous system: a cusp bifurcation or bifurcation towards multiple steady states. The basic point to note is that, according to our previous work,[10] one can identify a slow (intensive) variable u, whose probability density P obeys the following equation:

$$\partial_t P(u, t) = \left[-\frac{\partial}{\partial u}(-\delta u - bu^3) + Q\frac{\partial^2}{\partial u^2}\right] P(u, t) \tag{2}$$

We suppose here $b \neq 0$, i.e., we do not consider the case of a so-called tricritical point or a higher-order instability. The stationary solution of (2) is a quartic:

$$P_{\text{st}}(u) \sim \exp\left(-\frac{\delta u^2}{2Q} - \frac{bu^4}{4Q}\right) \tag{3}$$

The results (2) and (3) are general. The characteristics of the physical problem enter only through the dependence of the variables δ, b, and Q on the parameters present in the original problem.

From (3), it is straightforward to obtain the exact value of the mean square fluctuation:

$$\langle \delta u^2 \rangle = \langle \delta u^2 \rangle_G f(q) \tag{4}$$

Here

$$\langle \delta u^2 \rangle_G = Q/\delta \tag{5}$$

is the value of the mean square deviation in the Gaussian approximation ($b = 0$). Note that $\langle \delta u^2 \rangle_G$ diverges at the approach of the critical point $\delta \to 0$. In this limit, the fourth-power term in the exponential of (3) comes into play and one obtains the following result at the critical point ($\delta = 0$):

$$\langle \delta u^2 \rangle_c = 2\frac{\Gamma(3/4)}{\Gamma(1/4)}\left(\frac{Q}{b}\right)^{1/2} \tag{6}$$

Since, generally speaking, the noise amplitude Q is proportional to a small number (typically $Q \sim 1/VN_A$), the critical fluctuations (6) are several orders of magnitude larger than the Gaussian fluctuations (5). Note also the

different dependence on the volume:

$$\langle \delta u^2 \rangle_G \sim V^{-1} \quad \text{and} \quad \langle \delta u^2 \rangle_c \sim V^{-1/2}$$

The transition from the Gaussian result (5) to the result (6) at the critical point is described by the fluctuation enhancement function $f(q)$:

$$f(q) = 4q \left[\frac{K_{3/4}(q)}{K_{1/4}(q)} - 1 \right] \tag{7}$$

where K_ν stands for the modified Bessel function and q is the dimensionless variable which measures the relative importance of the Gaussian coefficient δ and the non-Gaussian parameter b, respectively:

$$q = \frac{\delta^2}{8Qb} \tag{8}$$

The function $f(q)$ has the following properties:

$$\lim_{q \to +\infty} f(q) = 1 \qquad \text{(Gaussian limit)} \tag{9a}$$

and

$$f(q) \overset{q \to 0}{\sim} 4 \frac{\Gamma(3/4)}{\Gamma(1/4)} (2q)^{1/2} \qquad \text{(critical limit)} \tag{9b}$$

The above results allow us to answer the two questions raised at the beginning of this section:

    1.   The amplitude of the critical fluctuations is given by (6).

    2.   The distance from the critical point at which critical behavior will be observed is determined by the requirement that $f(q)$ may be approximated by its limiting form (9b). This is valid for $q < 1$.

    Of course, the above results have to be interpreted in terms of the original variables of the problem. In the following sections, we will show how they apply in the case of a thermochemical instability in a continuously stirred tank reactor.

3. A MODEL FOR A THERMOCHEMICAL INSTABILITY IN A WELL STIRRED TANK REACTOR

    The most common thermochemical processes are oxidation reactions in a continuously stirred tank reactor (CSTR). In this case, a constant flow of the chemical mixture passes through a reactor in which it is consumed. Since a realistic description of fluctuations under the above circumstances is difficult, we will consider here a conceptually simpler situation. Specifically, we suppose that the relevant chemical species X is consumed in the

reactor by a monomolecular reaction:

$$X \xrightarrow{k} A + \Delta H \tag{10}$$

where ΔH stands for the heat of reaction and k is the chemical rate constant. (We are interested primarily in exothermal reactions, for which $\Delta H > 0$). Moreover, we model the supply of X by incorporating a constraint expressing the nonequilibrium condition under which the reaction takes place. This is realized in a simple way by coupling the above system with an external reservoir whose concentration is fixed at a value x_e, the rate of exchange being controlled by a coupling constant α. The macroscopic equation of evolution for the concentration x of the chemical species X thus reads:

$$\partial_t x = -kx - \alpha(x - x_e) \tag{11}$$

The composition variable x is coupled to the temperature T through the rate constant k:

$$k = k(T) = k_0 \exp\left(-\frac{U}{k_B T}\right) \tag{12}$$

where U stands for the activation energy (we have neglected the temperature dependence of the preexponential factor). It is thus necessary to consider the equation of evolution for the temperature. We will again simplify matters and suppose that the temperature is homogeneous inside the reactor and heat flows out at the boundaries. If we call c the specific heat per unit volume of the reactive mixture, K the conductivity of the reactor wall, S its surface, and d its thickness, V_R the reactor volume, and T_e the external temperature, then we obtain

$$\partial_t T = rkx - \beta(T - T_e) \tag{13}$$

where

$$r = \frac{\Delta H}{c}, \qquad \beta = \frac{KS}{cV_R d} \tag{14}$$

Equations (11), (12), and (13) are the equations for our simplified model of the CSTR.

Let us now show that these equations give rise to a bifurcation leading to multiple steady states. The steady state values x_{st} and T_{st} are given by

$$x_{st} = \frac{\alpha x_e}{k(T_{st}) + \alpha} \tag{15}$$

and

$$f(T_{st}, T_e, x_e) = T_{st} - T_e - \frac{r\alpha k(T_{st}) x_e}{\beta[k(T_{st}) + \alpha]} = 0 \tag{16}$$
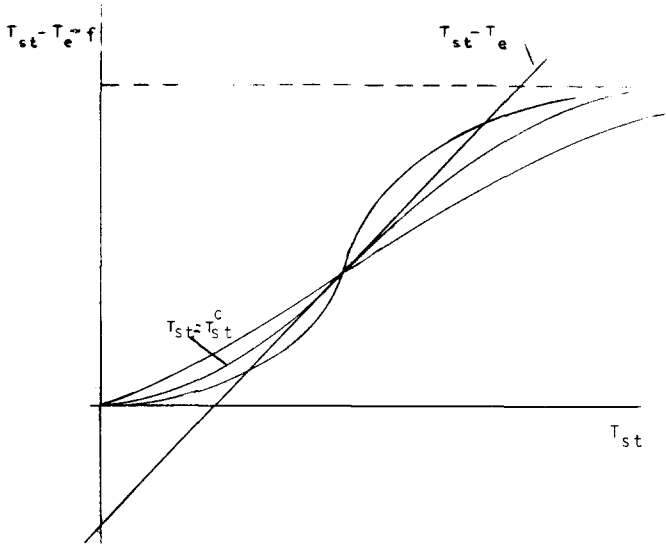
Fig. 1.   Existence of multiple steady states, solution of the transcendental equation (16).

From a graphical solution of the transcendental equation (16) (see Fig. 1), it is clear that a transition to a regime with multiple steady states can occur. The bifurcation point is characterized by the fact that the stationary temperature T_{st}^c is a triply degenerate solution of Eq. (16), i.e., f and its first two derivatives towards T_{st} vanish identically at the critical point. Setting

$$k(T_{st}^c) = k_c, \qquad \frac{dk(T_{st}^c)}{dT_{st}^c} = k_c'$$

and so on, one obtains

$$(k_c + \alpha)(T_{st}^c - T_e) = \frac{r\alpha x_e}{\beta} k_c \qquad (17a)$$

$$(k_c + \alpha) + k_c'(T_{st}^c - T_e) = \frac{r\alpha x_e}{\beta} k_c' \qquad (17b)$$

$$2k_c' + k_c''(T_{st}^c - T_e) = \frac{r\alpha x_e}{\beta} k_c'' \qquad (17c)$$

Before proceeding further, it is useful to note that one can distinguish the following seven dimensionless variables in the set of equations (11)–(13):

$$\tau = k_0 t, \qquad \frac{x}{x_e}, \qquad \frac{T}{T_e}, \qquad \frac{\alpha}{k}, \qquad \frac{\beta}{k}, \qquad \rho = \frac{r x_e}{T_e}, \qquad \gamma = \frac{U}{k_B T_e}$$

$$(18)$$

The time parameter τ does not appear in a steady state analysis. The steady state conditions (15) and (17a) and the bifurcation conditions (17b) and (17c) yield four equations involving the last six quantities. After lengthy but straightforward algebra, these equations can be recast into the following simple form:

$$\frac{x_{st}^c}{x_e} = \frac{1}{2} \frac{\gamma}{\gamma - 2} \tag{19a}$$

$$\frac{T_{st}^c}{T_e} = \frac{\gamma}{\gamma - 2} \tag{19b}$$

$$\frac{\alpha}{k_c} = \frac{\gamma}{\gamma - 4} \tag{19c}$$

$$\frac{\beta}{k_c} = \frac{\rho\gamma}{4} \tag{19d}$$

One notes from (19c) that $\gamma > 4$, in order to obtain a physically acceptable solution. Consequently, one obtains from (19a) and (19b) that

$$\frac{x_e}{2} < x_{st}^c < x_e, \qquad T_e < T_{st}^c < 2T_e \tag{20}$$

Of course, the inequalities $x_{st}^c < x_e$ and $T_e < T_{st}^c$ are trivial since we consider an exothermal reaction which consumes the substance X. From (19c) and (19d), one concludes

$$k_c < \alpha, \qquad k_c < \frac{\beta}{\rho} \tag{21}$$

Let us now consider a certain chemical reaction (for which k_0, U, and r are known) taking place in a given reactor (for which the exchange parameters α and β are known). Then it follows that the remaining parameters x_{st}, T_{st}, x_e, and T_e are completely determined by the equations (19) at the critical point. We will denote these values by x_{st}^c, T_{st}^c, x_e^c, and T_e^c. In order to investigate the vicinity of the critical point, we consider values of the control parameters, the external temperature T_e, and concentration x_e, close to their critical values T_e^c and x_e^c:

$$T_e = T_e^c + \Delta T_e, \qquad x_e = x_e^c + \Delta x_e \tag{22}$$

with $\Delta T_e / T_e^c$ and $\Delta x_e / x_e^c$ small. In order to calculate the corresponding change ΔT_{st} in the reactor temperature:

$$T_{st} = T_{st}^c + \Delta T_{st} \tag{23}$$

we remember that f and its first two derivatives towards T_{st} vanish at the critical point:

$$f(T_{st}^c, T_e^c, x_e^c) = \frac{\partial f}{\partial T_{st}}(T_{st}^c, T_e^c, x_e^c) = \frac{\partial^2 f}{\partial T_{st}^2}(T_{st}^c, T_e^c, x_e^c) = 0 \tag{24}$$

Hence by Taylor expansion, one has:

$$0 = f(T_{st}, T_e, x_e) \simeq \frac{1}{6} \frac{\partial^3 f}{\partial T_{st}^3}(T_{st}^c, T_e^c, x_e^c)\Delta T_{st}^3$$

$$+ \frac{\partial f}{\partial T_e}(T_{st}^c, T_e^c, x_e^c)\Delta T_e$$

$$+ \frac{\partial f}{\partial x_e}(T_{st}^c, T_e^c, x_e^c)\Delta x_e + \text{higher order terms in } \Delta T_{st}$$

$$(25)$$

From an explicit calculation of the partial derivatives using the bifurcation conditions (19), one has

$$\frac{1}{12}\gamma(\gamma - 2)\left(\frac{\Delta T_{st}}{T_{st}^c}\right)^3 \simeq \frac{\Delta T_e}{T_e^c} + \frac{2}{\gamma - 2}\frac{\Delta x_e}{x_e^c} \qquad (26)$$

The corresponding change in the concentration

$$x_{st} = x_{st}^c + \Delta x_{st} \qquad (27)$$

is obtained from (15):

$$\frac{\Delta x_{st}}{x_{st}^c} = -\frac{\gamma - 4}{2}\frac{\Delta T_{st}}{T_{st}^c} \qquad (28)$$

We conclude that in the vicinity of our bifurcation point, internal and external variables are related by a cubic law, reminiscent of the van der Waals equation of state at the critical point. Note also that (as $\gamma > 4$), the reactor temperature and concentration are always more sensitive to a change of the external temperature than to a change of the external concentration, particularly for large values of the activation energy ($\gamma \gg 4$). It is important to realize that the Taylor expansion (25) does not allow one to cross the critical point along the singular line of approach leading into the region of multiple steady states in the $x_e T_e$ plane (see Fig. 2). Therefore one has more generally to expand f only with respect to the reactor temperature:

$$f(T_{st}^c, T_e, x_e) + \frac{\partial f}{\partial T_{st}}(T_{st}^c, T_e, x_e)\Delta T_{st} + \frac{1}{6}\frac{\partial^3 f}{\partial T_{st}^3}(T_{st}^c, T_e^c, x_e^c)\Delta T_{st}^3 = 0$$

$$(29)$$

where we have taken into account that $(\partial^2 f/\partial T_{st}^2)(T_{st}^c, T_e, x_e)$ is identically zero and where we have evaluated the third derivative $\partial^3 f/\partial T_{st}^3$ at the critical point (since it is nonvanishing). From the explicit expression (16) for
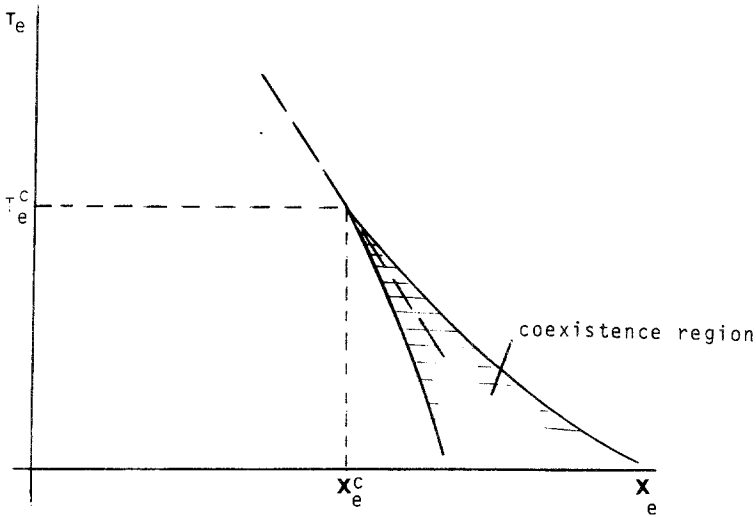
Fig. 2.   Cusp bifurcation in the x_e, T_e plane.

f and using the results (17), one obtains from (29)

$$-\Delta T_e - \frac{2}{\gamma - 2} T_e^c \frac{\Delta x_e}{x_e^c} - \Delta T_{st} \frac{\Delta x_e}{x_e^c} + \frac{\Delta T_{st}^3}{(T_{st}^c)^3} \frac{1}{12} (\gamma - 2)^2 T_{st}^c = 0$$

(30)

From this result it follows that the bisector, marking the entrance in the region of multiple steady states is given by

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

(31)

Along this line, the stationary solution is $\Delta T_{st} = 0$ before bifurcation, i.e., the reactor temperature remains a constant equal to its critical value T_{st}^c. At the crossing of the critical point, the coefficient of ΔT_{st} in (30) becomes negative: two new stable solutions

$$\frac{\Delta T_{st}}{T_{st}^c} = \pm \left(- \frac{6}{\gamma - 2} \frac{\Delta T_e}{T_e^c} \right)^{1/2}$$

arise whereas the original solution $\Delta T_{st} = 0$ becomes unstable. Note that along the bisector (31), the concentration does not remain a constant. One indeed finds from (15) that

$$\frac{\Delta x_{st}}{x_{st}^c} = \frac{\Delta x_e}{x_e^c} \qquad \text{for} \quad \Delta T_{st} = 0$$

The nonlinear law (26) is clearly a consequence of the marginal stability of the stationary state at the critical point. Another consequence will be the slowing down of the dynamics. Indeed, for small deviations:

$$\delta x = x - x_{\text{st}}, \qquad \delta T = T - T_{\text{st}} \tag{32}$$

one has

$$\partial_t \begin{bmatrix} \delta x \\ \delta T \end{bmatrix} = \begin{bmatrix} -(k + \alpha) & -k'x_{\text{st}} \\ rk & rk'x_{\text{st}} - \beta \end{bmatrix} \begin{bmatrix} \delta x \\ \delta T \end{bmatrix} + \text{nonlinear terms} \tag{33}$$

It is easy to verify that the determinant of the linear regression matrix Γ appearing in the right-hand side of (33) is zero at the critical point [use bifurcation conditions (17)]. More precisely, one finds that $\det \Gamma \sim \Delta T_{\text{st}}^2 / (T_{\text{st}}^c)^2$ in the close vicinity of the critical point. Note that $\det \Gamma$ remains positive as long as one does not follow a line of approach leading into the region of multiple steady states. Indeed, in this case $\Delta T_{\text{st}} = 0$ and one has to calculate higher-order terms. Using again the conditions (19), one finds

$$\frac{\det \Gamma}{k_c^2} = \frac{\rho\gamma(\gamma - 2)^2}{4(\gamma - 4)} \frac{\Delta T_e}{T_e^c} \tag{34}$$

valid along the bifurcation line defined by (31). Hence, the determinant changes sign upon entering the coexistence region (following the bisector): the original stationary state looses its stability.

From the vanishing of $\det \Gamma$ at the critical point, we conclude that, in order to describe the dynamics of perturbations, even small ones, in the close vicinity of the bifurcation point, one has to take into account the effect of nonlinear terms. Such small deviations will arise in every physical system due to the presence of thermal fluctuations. As they are only weakly damped near the critical point, their effect can become important in the close vicinity of this point. The purpose of the next section is to study the effect of fluctuations and dominant nonlinearities on the behavior of the system, and to answer the two questions discussed in Section 2 concerning the appearance of critical behavior.

4. MEAN FIELD FLUCTUATIONS AT THE THERMOCHEMICAL INSTABILITY

In order to introduce the effect of thermal fluctuations, we add stochastic forces to the macroscopic equations of evolution (11) and (13)[3]

$$\partial_t x = -k(T)x - \alpha(x - x_e) + F_x \tag{35a}$$

$$\partial_t T = rk(T)x - \beta(T - T_e) + F_T \tag{35b}$$

---

[3] For a justification of this procedure, see for instance Ref. 4.

Furthermore, we suppose that F_x and F_T are Gaussian white noises with correlation function:

$$\langle F_x(t)F_x(t')\rangle = Q_x\delta(t-t') \qquad (36a)$$

$$\langle F_x(t)F_T(t')\rangle = Q_{xT}\delta(t-t') \qquad (36b)$$

$$\langle F_T(t)F_T(t')\rangle = Q_T\delta(t-t') \qquad (36c)$$

The noise strength factors Q_x, $Q_{x,T}$, and Q_T are determined for a system in equilibrium by the fluctuation dissipation theorem. Note, however, that we introduced a nonequilibrium constraint here by adding dissipative transport terms in Eqs. (35). Therefore stochastic forces and dissipating terms will no longer obey the equilibrium fluctuation dissipation relation. Nevertheless, we expect that the thermal noise will be of the same order of magnitude as in equilibrium (see for instance Refs. 12 and 13), and we will use the equilibrium result to obtain approximate values of the noise strength Q. For instance we know that the fluctuations of the concentration variable (neglecting its coupling to the temperature variable) at equilibrium are given by[11] [compare with (1)]

$$\langle \delta x^2\rangle = \frac{Q_x}{k} = \frac{1}{N}\frac{k_B T}{(\partial\mu/\partial x)_{P,T}} \underset{\substack{\text{ideal} \\ \text{system}}}{=} \frac{\langle x\rangle}{VN_A} \qquad (37)$$

where N is the number of particles X in the system. It is clear from this example that the stochastic forces are proportional to a small parameter $N^{-1/2}$. This feature will allow us to solve the coupled set of Langevin equations (35) for large value of N, i.e., in the weak noise limit.

Let us now consider a stationary state on the bisector (31) close to, but before bifurcation. Under influence of the stochastic forces, the concentration and temperature will fluctuate in the course of time around these stationary values:

$$x = x(t) = x_{st}^c + \Delta x_{st} + \delta x(t) \qquad (38a)$$

$$T = T(t) = T_{st}^c + \Delta T_{st} + \delta T(t) \qquad (38b)$$

From (35), one obtains the following equations of evolution for these fluctuations:

$$\partial_{k_c t}\begin{bmatrix} \dfrac{\delta x}{x_{st}^c} \\[2mm] \dfrac{\delta T}{T_{st}^c} \end{bmatrix} = \begin{bmatrix} -2\dfrac{\gamma-2}{\gamma-4} & -(\gamma-2) \\[2mm] \dfrac{\rho}{2} & \rho\dfrac{\gamma-4}{4} \end{bmatrix}\begin{bmatrix} \dfrac{\delta x}{x_{st}^c} \\[2mm] \dfrac{\delta T}{T_{st}^c} \end{bmatrix} + Z\begin{bmatrix} -1 \\[2mm] \dfrac{\rho}{2} \end{bmatrix} + \begin{bmatrix} F_x \\[2mm] \dfrac{F_T}{k_c T_{st}^c} \end{bmatrix}$$

$$+ O\left(\frac{\Delta T_e}{T_e^c}\right) + O\left(\left(\frac{\delta T}{T_{st}^c}\right)^4, \left(\frac{\delta T}{T_{st}^c}\right)^3\frac{\delta x}{x_{st}^c}\right) \qquad (39)$$

with

$$
Z = \frac{1}{6}(\gamma - 2)\frac{\delta T}{T_{st}^c}\left[3(\gamma - 4)\frac{\delta T}{T_{st}^c} + 6\frac{\delta x}{x_{st}^c} \right.
$$

$$
\left. + 3(\gamma - 4)\frac{\delta x}{x_{st}^c}\frac{\delta T}{T_{st}^c} + (\gamma^2 - 10\gamma + 22)\left(\frac{\delta T}{T_{st}^c}\right)^2 \right] \quad (40)
$$

Let us now introduce the linear transformation which diagonalizes the linear regression matrix appearing in (39):

$$
\begin{bmatrix} u \\ v \end{bmatrix} = \begin{bmatrix} 1 & \dfrac{4(\gamma - 2)}{\rho(\gamma - 4)} \\ \dfrac{2}{\gamma - 4} & 1 \end{bmatrix}\begin{bmatrix} \dfrac{\delta x}{x_{st}^c} \\ \dfrac{\delta T}{T_{st}^c} \end{bmatrix} = \Lambda \begin{bmatrix} \dfrac{\delta x}{x_{st}^c} \\ \dfrac{\delta T}{T_{st}^c} \end{bmatrix} \quad (41)
$$

From (39)–(41) one obtains after lengthy but straightforward calculations:

$$
\partial_{k_c t}\begin{bmatrix} u \\ v \end{bmatrix} = \begin{bmatrix} -\delta & 0 \\ 0 & -\lambda \end{bmatrix}\begin{bmatrix} u \\ v \end{bmatrix} + Z\begin{bmatrix} \dfrac{\gamma}{\gamma - 4} \\ \dfrac{\rho}{2} - \dfrac{2}{\gamma - 4} \end{bmatrix} + \Lambda\begin{bmatrix} \dfrac{F_x}{k_c x_{st}^c} \\ \dfrac{F_T}{k_c T_{st}^c} \end{bmatrix} \quad (42)
$$

with eigenvalues

$$
\lambda = 2\frac{\gamma - 2}{\gamma - 4} - \rho\frac{\gamma - 4}{4} \quad (43)
$$

and

$$
\delta = \frac{1}{\lambda}\frac{\rho\gamma(\gamma - 2)^2}{4(\gamma - 4)}\frac{\Delta T_e}{T_e^c} \quad (44)
$$

The results (43) and (44) are obtained from the properties that $k_c(\lambda + \delta)$ $= -\operatorname{tr}\Gamma$ and $k_c^2\lambda\delta = \det\Gamma$.[4] Note that the linear stability of the stationary state requires that $\lambda > 0$ (for a more detailed discussion, see Ref. 6), hence

$$
4 < \gamma < 4\frac{\rho + 1 + (\rho + 1)^{1/2}}{\rho} \quad (45)
$$

where we have added the condition $\gamma > 4$ which is a consequence of the bifurcation condition (19c). In terms of the new variables, Z takes the

---

[4] The result (44) can be obtained from (39) by including explicitly the terms of order $\Delta T_e/T_e^c$.

following form:

$$Z = -\frac{\rho^3(\gamma - 2)^3}{96\lambda^3} u^3 + O\left(\frac{\Delta T_e}{T_e^c}\right)u^2 + \text{terms in } uv, v^2, u^2v, uv^2, v^3, \ldots$$

$$(46)$$

We now want to investigate the properties of the two coupled Langevin equations (42) in the limit of weak noise. A general analytic study of (42) is impossible due to the complicated nonlinear coupling and the absence of detailed balance. However, in the limit of a large volume size, the strength of the thermodynamic forces and therefore also of the fluctuations δx and δT (i.e., u and v) is small. For this reasoning a restricted number of nonlinear terms play a role to dominant order in the volume. For instance, the term $O(\Delta T_e/T_e^c)u^2$ is negligible in the equation for u compared to the linear terms $O(\Delta T_e/T_e^c)u = \delta u$. On the other hand the rate of change of the u variable is much smaller than the rate of change of the v variable since $\delta \to 0$ at the approach of the critical point. Therefore, v is a fast variable and can be eliminated adiabatically. A detailed proof of the above intuitive arguments can be found in Ref. 10. For the present problem, one verifies that to dominant order in the volume, the equation for the critical variable u is decoupled from the equation for v, and the dominant nonlinear term is the cubic term:

$$\partial_{k_c t} u = -\delta u - bu^3 + F_u \qquad (47)$$

Here δ is defined by (44), and b is given by

$$b = \frac{2}{3} \frac{\rho^3\gamma(\gamma - 2)^3(\gamma - 4)^2}{\left[8(\gamma - 2) - \rho(\gamma - 4)^2\right]^3} \qquad (48)$$

The scaled random force

$$F_u(t) = F_x(t/k_c)/k_c x_{st}^c$$

has a strength Q [use (36)]

$$Q = 1/N \qquad (49)$$

where $N = \langle x \rangle V N_A$ is the average number of particles in the volume element under consideration. Note that always $b > 0$, which guarantees the existence of a normalizable stationary solution. We have thus reduced the problem to the standard form discussed in Section 2.

The relation between u and the original variables can be found by inverting (41). Moreover, as the u variable is the only variable which develops enhanced, non-Gaussian fluctuations, it gives the dominant contribution to the fluctuations of composition and thermal variable. Therefore, for the purpose of calculating the second moment of these variables,

it will be sufficient to consider the contribution of the critical variable u in (41):

$$\frac{\delta x}{x_{st}^c} \approx \frac{\rho(\gamma - 4)^2}{\rho(\gamma - 4)^2 - 8(\gamma - 2)} u \tag{50}$$

$$\frac{\delta T}{T_{st}^c} \approx -\frac{2}{\gamma - 4} \frac{\delta x}{x_{st}^c} \tag{51}$$

Let us now apply the results of Section 2. The fluctuations of x and T at the critical point are given by [cf. Eq. (6)]

$$\left[\frac{\langle dx^2 \rangle_c}{(x_{st}^c)^2} \right]^{1/2} = \left[2 \frac{\Gamma(3/4)}{\Gamma(1/4)} \right]^{1/2} \left[\frac{g_x(\rho, \gamma)}{N} \right]^{1/4} \tag{52}$$

$$\left[\frac{\langle \delta T^2 \rangle_c}{(T_{st}^c)^2} \right]^{1/2} = \left[2 \frac{\Gamma(3/4)}{\Gamma(1/4)} \right]^{1/2} \left[\frac{g_T(\rho, \gamma)}{N} \right]^{1/4} \tag{53}$$

with

$$g_x(\rho, \gamma) = \frac{3}{2} \frac{\rho(\gamma - 4)^6}{\left[8(\gamma - 2) - \rho(\gamma - 4)^2 \right] \gamma(\gamma - 2)^3} \tag{54}$$

$$g_T(\rho, \gamma) = \left(\frac{2}{\gamma - 4} \right)^4 g_x(\rho, \gamma) \tag{55}$$

The onset of the critical regime characterized by a dependence of the fluctuations in $N^{-1/4}$ [see (52) and (53)] is determined by

$$q = \frac{\delta^2}{8Qb} < 1$$

Hence:

$$\frac{\Delta T_e}{T_e^c} < \left[\frac{g_c(\rho, \gamma)}{N} \right]^{1/2} \tag{56}$$

with

$$g_c(\rho, \gamma) = \frac{16}{3} \frac{(\gamma - 4)^2}{\gamma(\gamma - 2) \left[8(\gamma - 2) - \rho(\gamma - 4)^2 \right]} = \frac{32}{9} \frac{(\gamma - 2)^2}{\rho(\gamma - 4)^4} g_x(\rho, \gamma) \tag{57}$$

In Fig. 3 we have represented the logarithm of g_x, g_T, and g_c as a function of γ for the value $\rho = 1$. The latter value is typical for an oxidation
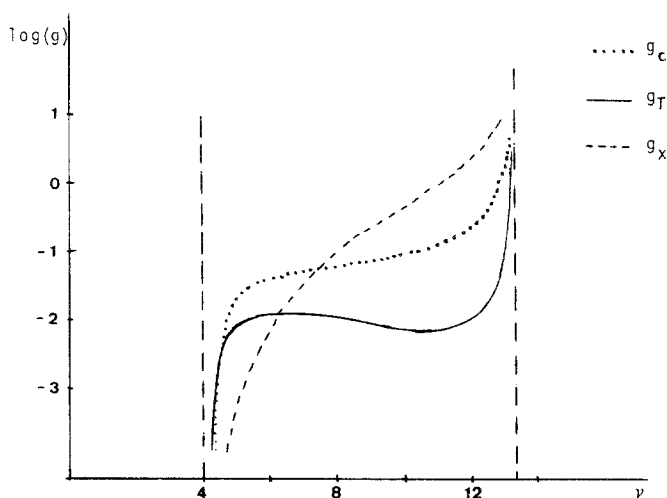
Fig. 3. The functions g_x, g_T, and g_c determining the enhancement of the fluctuations [Eqs. (52) and (53)] and the width of the critical region [Eq. (57)], respectively.

reaction in gaseous phase ($x_e \simeq 10^{-5}$ mole/cm^3, $T_e \simeq 10^3$ °K and $r \simeq 10^8$ °K cm^3/mole). From these results one concludes that in a volume element containing $N = 10^{12}$ particles, enhanced critical fluctuations of the order of 0.1% can occur. The distance from the critical point at which critical behavior sets in is of the order $\Delta T_e \approx 10^{-6} \, T_e^c$, hence for $T_e^c \approx 10^3$ °K, ΔT_e should be 10^{-3} °K.

5. CONCLUSION

We have shown that for a typical oxidation reaction taking place in a CSTR in gaseous phase, enhanced fluctuations of the order of 0.1% occur at a distance of 10^{-3} °K from the critical temperature in a volume element of the order of 10^{-3} mm^3 ($N = 10^{12}$). Such volume elements can be scanned by laser light spectroscopy. However, it is questionable whether in an experimental setup sufficient control over temperature and concentration can be achieved in order to actually perceive these enhanced fluctuations. Moreover, hydrodynamic effects may interfere with chemical and thermal fluctuations. In this paper, we focused on the critical behavior near a cusp bifurcation in a thermochemical system. However, the latter systems exhibit more complicated bifurcations such as bifurcation towards a limit cycle behavior or towards inhomogeneous steady states. It would be interesting to investigate the critical properties in these more complicated and typically nonequilibrium situations.

ACKNOWLEDGMENTS

REFERENCES

1. G. Nicolis and I. Prigogine, *Self Organization in Non-Equilibrium Systems* (Wiley, New York, 1977).
2. H. Haken, *Synergetics. An Introduction* (Springer-Verlag, Berlin, 1977).
3. N. G. Van Kampen, *Adv. Chem. Phys.* **34**:245 (1976).
4. M. Malek Mansour, C. Van den Broeck, G. Nicolis, and J. W. Turner, *Ann. Phys. (Leipzig)* **131**(2):283 (1981).
5. N. V. Kondratiev and E. E. Nikitin, *Gas-Phase Reactions* (Springer-Verlag, Berlin, 1981).
6. A. Uppal, W. H. Ray, and A. B. Poore, *Chem. Eng. Soc.* **29**:967 (1974).
7. G. Nicolis, F. Baras, and M. Malek Mansour in *Nonlinear Phenomena in Chemical Dynamics*, A. Pacault and C. Vidal, Eds. (Springer-Verlag, Berlin, 1981).
8. D. Beysens and M. Gbadamassi, *Phys. Rev. A* **22**:2250 (1980).
9. A. Nitzan and J. Ross, *J. Chem. Phys.* **59**(1):241 (1973).
10. C. Van den Broeck, M. Malek Mansour, and F. Baras, *J. Stat. Phys.* **28**(3):557 (1982).
11. L. Landau, E. Lifshitz, *Physique Statistique* (MIR, Moscow, 1967).
12. J. Swift and P. C. Hohenberg, *Phys. Rev. A* **15**(1):319 (1977).
13. S. Grossmann, *J. Chem. Phys.* **65**(5):2007 (1976).