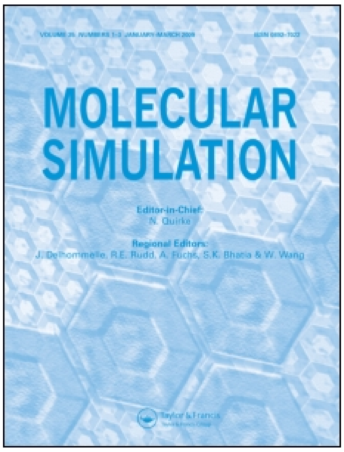

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Fluctuation-induced and Nonequilibrium-induced Bifurcations in a Thermochemical System

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We study the Semenov thermochemical model at different levels of description. This simple model of combustion includes the description of slow oxidation with stabilization of the system around a low temperature and thermal explosion leading the system to a high temperature. The results of the mesoscopic description based on the master equation and microscopic simulations of the particle dynamics reveal deviations from the macroscopic deterministic dynamics. Fluctuation effects observed in small systems change the domains of mono- and bistability of the system. These are noise-induced bifurcations, already known in isothermal chemical systems. Another effect is related to the departure of particle velocity distribution from its equilibrium shape. The departure from partial equilibrium originating at the level of the velocity distribution also leads to changes of the bifurcation diagram. By analogy, we call this phenomenon a nonequilibrium-induced bifurcation.

Keywords: Combustion; Fluctuations; Departure from partial equilibrium; Bifurcation; Bistability

PACS: 05.10.Gg; 82.33.Vx; 05.10.Ln; 82.20.Wt

INTRODUCTION

Thermochemical systems are governed by nonlinear dynamics and can therefore be highly sensitive to small perturbations. Consequently, their macroscopic behavior can be modified by weak disturbances of microscopic origin. The perturbations are relatively more important if the deterministic trend becomes weak, like in the vicinity of bifurcations [1]. Moreover, if the size of the system is small, the relative magnitude of fluctuations is higher and pronounced stochastic effects are expected [2,3]. Independent of fluctuation effects, the validity of the usual deterministic equations for the macroscopic variables can be questioned in a reactive medium. The standard macroscopic dynamics rely on the hypothesis of partial equilibrium. In this condition, the particle velocity distribution function is assumed to maintain a Maxwellian shape during the evolution of the effective temperature of the system at a rate imposed by chemistry and exchanges at the boundaries. However, kinetic theory studies based on the Boltzmann equation have revealed that a chemical reaction may induce a departure from partial equilibrium and influence the dynamics of gaseous chemical systems [4–13]. Indeed, the reactivity of a molecule depends on its kinetic energy. Consequently, a chemical process affects more strongly the reactant molecules with large velocities, leading to a deformation of velocity distributions.

In this paper, we use descriptions of a thermochemical system at different levels. We perform mesoscopic simulations of the master equation to study macroscopic consequences of the fluctuations. We also carry out microscopic simulations of the particle dynamics including both fluctuation and nonequilibrium effects. In order to compare the simulation results with analytical calculations, we choose the minimal model for thermochemical systems introduced by Semenov [14]. In this case, the macroscopic dynamics reduces to the evolution of a single variable. At the mesoscopic level, it allows for an analytical treatment of the Fokker–Planck

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equation deduced from the master equation. At the microscopic level, we use a perturbative solution of the Boltzmann equation for the particle velocity distribution. The paper is organized as follows: the macroscopic and mesoscopic descriptions of the Semenov model are discussed in second and third section. In the fourth section, the microscopic simulation method is described. The results of the different methods, obtained in the vicinity of bifurcations leading to bistability, are then analyzed in fifth section. The sixth section contains our conclusions.

MACROSCOPIC DESCRIPTION

We consider a closed reactor of volume V and surface S containing a dilute gas which is subject to an energy balance due to an exothermal reaction in the bulk and the Newtonian heat transfer through the walls of the reactor. The temperature of the walls is assumed to be fixed at T_w by fast energy exchanges with an external thermostat. In order to focus on thermal properties and to reduce the deterministic dynamics to the evolution of a single variable, Semenov [14] introduced the simplest feasible chemical reaction $A + A \to \text{products} + \text{heat}\ (Q)$, in which consumption of reactant A is neglected. It amounts to considering the scheme:

$$A + A \to A + A + \text{heat} \tag{1}$$

for example, in the presence of an external light source [15]. According to scheme (1), the total number N of particles in the system or equivalently the concentration n remains constant. The deterministic equation of energy balance reads:

$$\frac{d\mathcal{E}}{dt} = k_r V n^2 Q - k_a S n k (T - T_w) \tag{2}$$

where k_r and k_a are respectively the rate constants for reaction (1) and accommodation of particles at the walls, and k denotes the Boltzmann constant. The expression for k_r and k_a are deduced from the frequencies of particle collisions in the bulk or with the walls of the reactor. Standard kinetic theory calculations yield [15,16]:

$$k_r = 2\sigma s_r \sqrt{\frac{kT}{\pi m}} \exp\left(-\frac{E^*}{kT}\right), \quad k_a = s_a \sqrt{\frac{2kT}{\pi m}} \tag{3}$$

where σ is the cross section for collisions in the bulk, m is the mass of particle A, and E^* is the activation energy of reaction (1). The coefficients s_r and s_a are steric factors for reaction and accommodation, respectively. They give account for steric conditions, that are linked to internal degrees of freedom of molecules A. For an ideal gas system, the relation $\mathcal{E} = (3/2)NkT$ between energy and temperature allows to convert Eq. (2) to the following equation for the reduced temperature $\theta = T/T_w$:

$$\frac{d\theta}{d\tau} = \frac{1}{3}\sqrt{\theta}\left(\exp\left(-\frac{\varepsilon}{\theta}\right) - \gamma(\theta - 1)\right). \tag{4}$$

In order to reduce the number of parameters, we introduce a dimensionless time, reaction heat and activation energy as:

$$\tau = 4n\sigma s_r q t \left(\frac{kT_w}{\pi m}\right)^{1/2}, \quad q = \frac{Q}{kT_w}, \quad \varepsilon = \frac{E^*}{kT_w}. \tag{5}$$

We also define in Eq. (4), a reduced coefficient for the Newtonian heat exchange by

$$\gamma = \frac{S\lambda}{V}\frac{s_a}{s_r q}, \tag{6}$$

where $\lambda = (\sqrt{2}n\sigma)^{-1}$ denotes the mean free path of a gas molecule. Parameter γ gives some measure of the efficiency of the Newtonian cooling with respect to heat production by the exothermal reaction. The weak dependence on temperature given by $\sqrt{\theta}$ in Eq. (4) is usually omitted in the standard macroscopic description of the Semenov model but it has already been included in previous microscopic treatments of thermochemical systems [17–21].

Depending on the parameter values controlling the production of reaction heat and the Newtonian cooling, the Semenov system exhibits different dynamical regimes [14]. The line $\gamma(\theta - 1)$ and the curve $\exp(\varepsilon/\theta)$ can have either one or three intersection points which correspond to the stationary solutions of Eq. (4). Thus, the system has either a unique stable steady state or two stable states separated by an unstable one. The bistability arises and vanishes at bifurcation points, at which the line $\gamma(\theta - 1)$ becomes tangential to $\exp(\varepsilon/\theta)$. For a given ε, this condition yields the following critical values of γ:

$$\gamma_c^{\pm} = \frac{1}{4}\varepsilon\left(1 \pm \sqrt{1 - \frac{4}{\varepsilon}}\right)^2 \exp\left[-\frac{1}{2}\varepsilon\left(1 \pm \sqrt{1 - \frac{4}{\varepsilon}}\right)\right]. \tag{7}$$

Bistability can appear only if $\varepsilon > 4$, in the range of γ bounded by the critical values, $\gamma_c^+ < \gamma < \gamma_c^-$. Outside this domain, the system possesses only a single stable stationary state which lies either on the extinction (lower) branch for $\gamma > \gamma_c^-$, or on the combustion (higher) branch for $\gamma < \gamma_c^+$. In this paper, we focus on the description of macroscopic consequences of microscopic perturbations in the vicinity of the bifurcations appearing for $\gamma = \gamma_c^+$ and $\gamma = \gamma_c^-$.

MESOSCOPIC DESCRIPTION

In the stochastic approach, the state of the system is described by the distribution function $P(\theta,\tau)$ for the system temperature θ. The dynamics of P is governed by a master equation, which can be written in the following form:

$$\frac{\partial}{\partial\tau}P(\theta,\tau)=\int_{\Delta\theta<\theta}\mathrm{d}(\Delta\theta)P(\theta-\Delta\theta,\tau)w(\theta-\Delta\theta\rightarrow\theta)$$
$$-P(\theta,\tau)\int_{\Delta\theta>-\theta}\mathrm{d}(\Delta\theta)w(\theta\rightarrow\theta+\Delta\theta)\qquad(8)$$

The transition probability w for the Semenov model is a sum of two terms [15]:

$$w(\theta\rightarrow\theta+\Delta\theta)=w_{\mathrm{r}}(\theta\rightarrow\theta+\Delta\theta)\delta(\Delta\theta-\Delta\theta_{\mathrm{r}})$$
$$+w_{\mathrm{e}}(\theta\rightarrow\theta+\Delta\theta).\qquad(9)$$

where the term w_{e} is related to the Newtonian energy exchange and the term w_{r} is connected to reaction (1). The fixed, discrete temperature variation accompanying reaction (1) is related to reaction heat Q by:

$$\Delta\theta_{\mathrm{r}}=\frac{2Q}{3NkT_{w}}.\qquad(10)$$

The transition rate w_{r}, is determined by the rate of the thermally activated reaction (1) which, according to Eqs. (2) and (3), is given by

$$w_{\mathrm{r}}(\theta\rightarrow\theta+\Delta\theta)=\frac{N}{2q}\sqrt{\theta}\exp\left(-\varepsilon/\theta\right)\qquad(11)$$

The transition probability w_{e} for energy exchange is a continuous function of $\Delta\theta$. Its explicit expression has been recently derived [15]. It is based on the assumption that elastic collisions are much more frequent than reactive ones, so that the velocity distribution function retains the Maxwellian form, corresponding to the instantaneous temperature of the system. Using the dimensionless variables defined by Eqs. (5) and (6), w_{e} can be cast in the following form:

$$w_{\mathrm{e}}(\theta\rightarrow\theta+\Delta\theta)=\frac{N}{4}\gamma\sqrt{\theta}\omega(\theta)\qquad(12)$$

where

$$\omega(\theta)=\frac{\theta}{(\theta+1)^{3}}\left(2+\frac{(\theta+1)\left(\frac{3}{2}N\right)|\Delta\theta|}{\theta}\right)$$
$$\times\frac{3}{2}N\begin{cases}\exp\left(-\frac{3}{2}N\frac{|\Delta\theta|}{\theta}\right) & \text{for}\quad\Delta\theta<0\\ \exp\left(-\frac{3}{2}N\Delta\theta\right) & \text{for}\quad\Delta\theta>0\end{cases}\qquad(13)$$

It is not possible to obtain an analytical solution of the master equation which has an integrodifferential form given in Eq. (8). We study stochastic effects in the thermochemical system considered by means of the simulation of the processes described by this equation. The Monte Carlo simulation method of the master equation introduced by Gillespie [22,23] for discrete variables is well founded, and its appropriate modification for the continuous form of Eq. (8) has been recently presented [15].

The simulation algorithm consists in generating a single elementary transition, in which the system passes from an initial temperature θ at time τ to a final $\theta+\Delta\theta$ reached at $\tau+\Delta\tau$. The total escape rate from the initial state is

$$W_{\mathrm{tot}}(\theta)=\int\mathrm{d}(\Delta\theta)w(\theta\rightarrow\theta+\Delta\theta)$$
$$=\frac{1}{4}\gamma N\theta^{1/2}+\frac{N}{2q}\theta^{1/2}\exp\left(-\frac{\varepsilon}{\theta}\right),\qquad(14)$$

where the first term results from the surface process and the second one from the reaction in the bulk. Consequently, the waiting time to exit from the state θ is $\Delta\tau=1/W_{\mathrm{tot}}(\theta)$. More exactly, it can be sampled from the exponential distribution $W_{\mathrm{tot}}(\theta)\exp\left(-W_{\mathrm{tot}}(\theta)\Delta\tau\right)$ characteristic for the Markovian processes. While $\Delta\tau$ is the time increment, $\Delta\theta$ is chosen either from the probability density $w_{\mathrm{e}}/W_{\mathrm{tot}}$ for thermal accommodation, or from the probability density $w_{\mathrm{r}}/W_{\mathrm{tot}}$ for reaction. After the transition is performed, the next step is generated starting from the updated temperature $\theta'=\theta+\Delta\theta$ at current time $\tau'=\tau+\Delta\tau$. The sequence of transitions forms then a stochastic trajectory in the phase space θ.

The expansion of the master equation for systems with large particle number N gives the Fokker–Planck equation [24]:

$$\frac{\partial}{\partial\tau}P(\theta,\tau)=-\frac{\partial}{\partial\theta}(\alpha(\theta)P(\theta,\tau))$$
$$+\frac{1}{2}\frac{\partial^{2}}{\partial\theta^{2}}(\beta(\theta)P(\theta,\tau))\qquad(15)$$

The coefficient α in the Fokker–Planck equation is related to the deterministic dynamics; it is equal to the righthand side of Eq. (4):

$$\alpha(\theta)=\frac{\sqrt{\theta}}{3}\left(\exp\left(-\frac{\varepsilon}{\theta}\right)-\gamma(\theta-1)\right).\qquad(16)$$

The coefficient β describes the dispersion of the temperature distribution due to fluctuation according to [24]:

$$\beta(\theta)=\frac{2}{9N}\sqrt{\theta}\left(q\exp\left(-\frac{\varepsilon}{\theta}\right)+\gamma(3-4\theta+3\theta^{2})\right)\qquad(17)$$

Note that β contains the scaling factor $1/N$, which indicates that fluctuations are relatively weaker for large systems. Following the approach developed in Ref. [25], we look for stationary solutions of the Fokker–Planck equation obeying:

$$\frac{\frac{\partial}{\partial\theta}(\beta P_{\mathrm{s}})}{\beta P_{\mathrm{s}}}=\frac{2\alpha}{\beta}\qquad(18)$$

A solution of this equation can be written in the form:

$$P_s = C\exp(-U(\theta)) \tag{19}$$

where C is a constant and where the stochastic potential $U(\theta)$ is given by:

$$U(\theta) = -\int_0^{\theta} \frac{2\alpha}{\beta}\,\mathrm{d}\theta' + \ln\beta \tag{20}$$

The extrema of the stochastic potential gives the value of the stationary states including the corrections due to fluctuations. Deriving Eq. (20) and using the expressions for α and β given in Eqs. (16) and (17), we obtain:

$$\begin{aligned} &\exp\left(-\frac{\varepsilon}{\theta}\right)\left(1-\frac{q}{3N\theta}\left(\frac{1}{2}+\frac{\varepsilon}{\theta}\right)\right) \\ &\quad = \gamma\left(\theta - 1 + \frac{1}{6N}(-8+15\theta-4\theta^2+3\theta^3)\right) \end{aligned} \tag{21}$$

Depending on the parameter values, this equation has one or three solutions corresponding to the corrected steady states.

MICROSCOPIC SIMULATION METHOD

We wish to compare the results based on the mesoscopic dynamics with simulations of the system evolution at the microscopic level. In a homogeneous system, the positions of the particles can be disregarded, and their velocities are the only relevant variables. We use the direct simulation Monte Carlo (DSMC) method developed by Bird [26] to simulate particle collisions in the dilute gas system. Rather than exactly calculating collisions as in molecular dynamics, the DSMC method generates collisions stochastically with scattering rates and postcollision velocity distributions determined from the kinetic theory of a dilute gas [27]. The typical time resolution reached in DSMC is 0.1 ns.

A standard acceptance–rejection method is used to choose actual encounters. The collisions between two randomly chosen particles k and l are accepted proportionnally to their relative velocity $(v_k - v_l)$. We employ the molecular model of reactive hard spheres, widely used in microscopic simulations [28–31] and kinetic theory studies [6–8,32] of chemical systems. A part of the total cross section σ for hard spheres corresponds to reaction. A collision is reactive (i) with the probability given by the steric factor s_r and (ii) if the relative velocity $(v_k - v_l)$ along the direction connecting the centers of particles k, l at impact exceeds a certain threshold value g^*. The frequency of reactive collisions in this line-of-centers model is given by Eq. (11) with the activation energy $E^* = (1/2)\mu g^{*2}$, where $\mu = m/2$ is the reduced mass. After a reactive collision, the kinetic energy of the particles that reacted is increased by the value of the reaction heat Q.

The collisions of the particles with the walls of the reactor are treated as follows: we assume that the container is cubic so that collisions with the boundaries in x, y and z directions are chosen with equal probability. Particles hitting the walls are thermally accommodated with the probability s_a, otherwise they are specularly reflected. We neglect collisions with elastic reflection, because they do not have any thermal effect nor contribute to maxwellization of the particle velocity distribution. Velocities of particles emitted after thermal accommodation are sampled from the following biased Maxwellian distribution at temperature T_w:

$$f_w(v) = \frac{1}{2\pi}\left(\frac{m}{kT_w}\right)^2 |v_\perp| \exp\left(-\frac{mv^2}{2kT_w}\right) \tag{22}$$

where $v_\perp$ is the component of velocity perpendicular to the wall chosen for collision.

In the microscopic simulations, we compute the temperature of the system by calculating the kinetic energy of the particles. In addition to fluctuations, the results of the microscopic simulations contain the effects of the deformation of the particle velocity distribution. For a fixed activation energy, the rate of reaction (1) is controlled by the steric factor s_r, and departures from partial equilibrium may appear as s_r becomes sufficiently large. The departure from the Maxwellian distribution results in corrections to the deterministic equation given in Eq. (4). The velocity distribution function can be obtained by means of the Chapman–Enskog solution [33] of the Boltzmann equation. We recently showed [34] that the deterministic equation including nonequilibrium corrections is given by:

$$\begin{aligned} \frac{\mathrm{d}\theta}{\mathrm{d}\tau} &= \frac{1}{3}\sqrt{\theta}\exp\left(-\frac{\varepsilon}{\theta}\right) \\ &\quad \times \left(1 + \frac{s_r q}{16\theta} r_2 (\exp(-\varepsilon/\theta)\phi_{2r} - \gamma\phi_{2e})\right) \\ &\quad - \frac{1}{3}\sqrt{\theta}\gamma(\theta - 1) \\ &\quad \times \left(1 + \frac{s_r q}{16\theta} e_2 (\exp(-\varepsilon/\theta)\phi_{2r} - \gamma\phi_{2e})\right) \end{aligned} \tag{23}$$

with

$$r_2 = -\frac{1}{2} + \frac{q}{2\theta} + \frac{\varepsilon}{\theta}, \quad e_2 = \left(\frac{3-2\theta}{\theta}\right) \tag{24}$$

$$\phi_{2r} = -\frac{1}{4} - \frac{\varepsilon}{\theta} + \left(\frac{\varepsilon}{\theta}\right)^2, \quad \phi_{2e} = \frac{3\theta + 1}{2} \tag{25}$$

RESULTS

The dynamics of a system is more sensitive to small perturbations, for example, of microscopic origin, when the deterministic trend is weak. It is the case of the vicinity of bifurcations [1–3] where stochastic and nonequilibrium effects are more marked. We examine the behavior of the Semenov system for parameter values such that the bistable domain is small. The activation energy is chosen equal to $\varepsilon = 4.2$, slightly larger than 4. As shown in Fig. 1, the system undergoes two bifurcations for close values of the parameter γ. The system possesses a single stationary state of high temperature for $\gamma = 0.119$. It becomes bistable for $\gamma = 0.121$ and again has a single steady state of low temperature for $\gamma = 0.123$. The results of the master equation for a sufficiently large number of particles, $N = 5000$, and the microscopic simulation results for a sufficiently small steric factor, $s_r = 10^{-4}$, both agree with the deterministic predictions deduced from Eq. (4). According to Fig. 1, the histograms of visited temperatures are centered around the noncorrected deterministic steady states. In particular, we find a bimodal histogram in the bistable domain.

The evolution of the histograms observed in Fig. 2 as the particle number N increases is similar to the evolution obtained in Fig. 1 for the increasing control parameter γ. For fixed parameters, but a variable noise level, the same sequence of bifurcations is observed. According to deterministic predictions, the system should have a single steady state of high temperature. This behavior is obtained with the master equation for $N = 5000$.

When the fluctuation level is increased by decreasing the particle number, the system becomes bistable for $N = 2000$ and even monostable at low stationary temperature for $N = 500$. This specific effect of the fluctuations is called noise-induced transition [25]. The maxima of the histograms are now found close to the corrected steady state values calculated by means of Eq. (21) which includes the effects of fluctuations. The simulations based on the master equation are confirmed by the results of DSMC for a sufficiently small steric factor s_r.

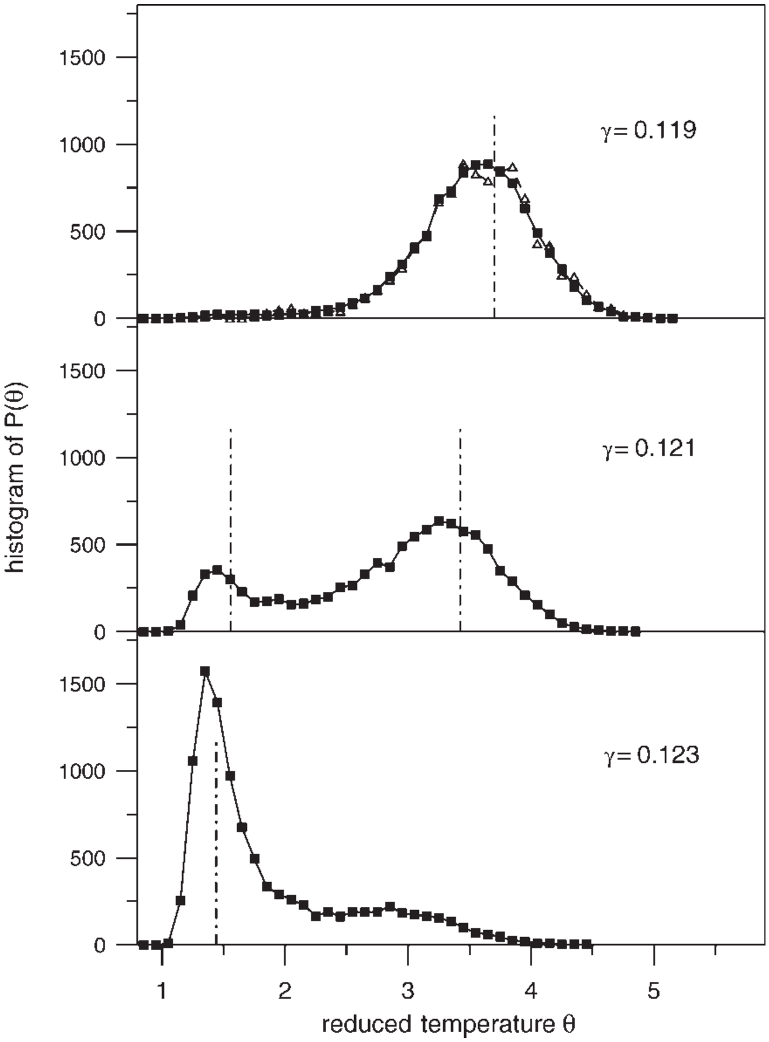

FIGURE 1 Histograms of the visited temperatures for different bifurcation parameter γ and fixed activation energy, $\varepsilon = 4.2$ and particle number, $N = 5000$. The results are deduced from simulations of the master equation (solid squares). In the case $\gamma = 0.119$, they are compared to the results of DSMC simulations (open triangles) for steric factor $s_r = 10^{-4}$ and for reduced heat release $q = 150$. The vertical dotted-dashed lines give the steady state values predicted by the deterministic equation.

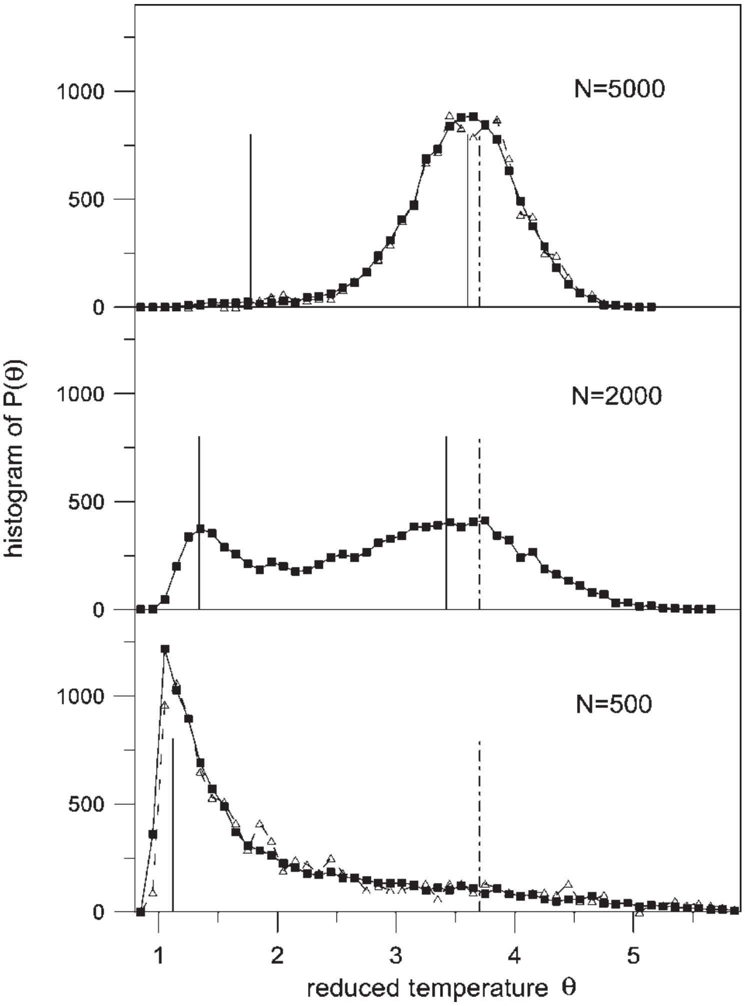

FIGURE 2 Histograms of the visited temperatures for different particle number N at fixed $\gamma = 0.119$ and $\varepsilon = 4.2$. The results are deduced from simulations of the master equation (solid squares). In the cases $N = 5000$ and 500, they are compared to the results of DSMC simulations (open triangles) for steric factor $s_r = 10^{-4}$ and for reduced heat release $q = 150$. The vertical dotted-dashed lines give the steady state values predicted by the deterministic equation. The vertical solid lines give the steady state values predicted by the Fokker–Planck equation.

We give in Fig. 3, the temperature histograms obtained by microscopic simulations for different values of the steric factors s_r, and s_a. All the other parameters are fixed. As the steric factor for reaction s_r, is varied, the steric factor for accommodation s_a is adjusted to keep constant the ratio s_a/s_r, so that coefficient γ defined in Eq. (6) remains unchanged. In these conditions, the parameters of the deterministic equation and the master equation are all imposed. Besides the effect of fluctuations presented in Fig. 2, the results given in Fig. 3 reveal another effect appearing at the microscopic level. As the steric factor s_r increases, the rate of the reaction increases, leading to a departure from the equilibrium particle velocity distribution [6–8,13,34], which affects the dynamics of the system at the macroscopic level. This nonequilibrium effect results in increasing deviations between the histograms obtained with the master equation and the histograms obtained with DSMC for increasing s_r. Figure 3 shows that this effect can be so strong that it can switch the stability of the system from the high to the low stationary temperature. By analogy to the phenomenon presented in Fig. 2, we call this effect a nonequilibrium-induced bifurcation. The corrected steady states including nonequilibrium effects can be calculated analytically using Eq. (23) that has been deduced from the Boltzmann equation. As shown in Fig. 3, the analytical perturbative results predict bistability in the proper s_r domain and lead to steady-state values close to the maxima of the histograms obtained by DSMC. In the studied case, both fluctuation and nonequilibrium effects give deviations from the deterministic prediction in the same direction, tending to stabilize the low temperature steady state. The agreement between the microscopic simulations and the master equation is reached for very low values of the steric factor. These values of s_r are one or two orders of magnitude smaller than typical values obtained for isothermal systems [35],

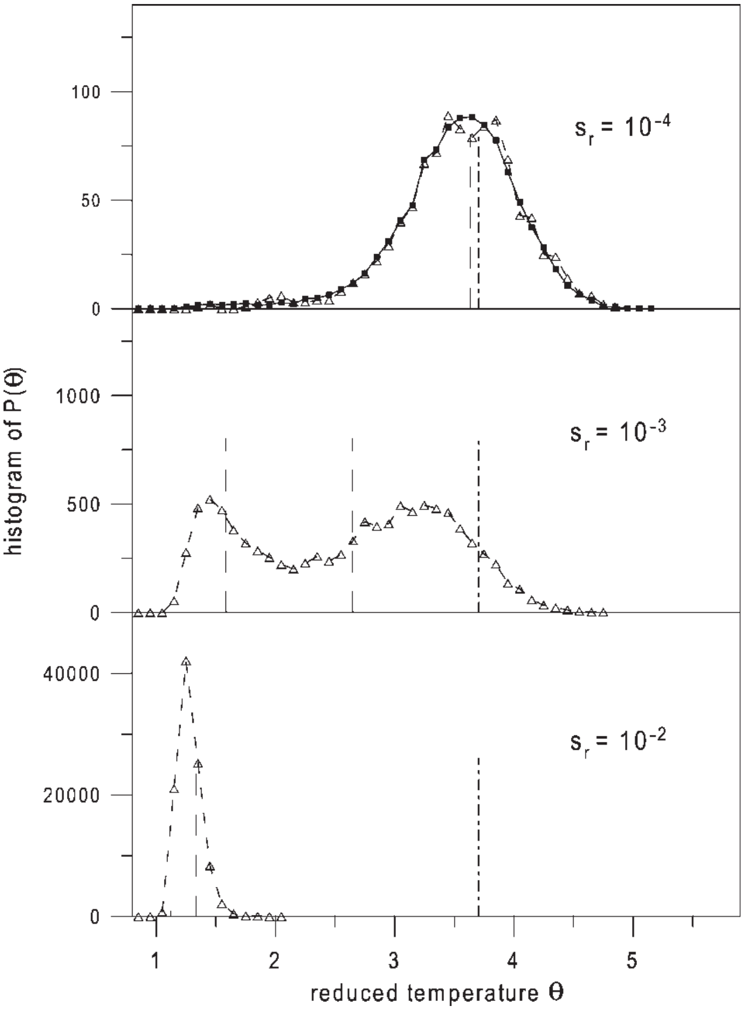

FIGURE 3 Histograms of visited temperatures for different steric factor for reaction, s_r, at fixed $q = 150$, $\varepsilon = 4.2$, $N = 5000$ and $\gamma = 0.119$. The steric factor for accommodation at the walls, s_a, is adjusted to keep γ constant for variable s_r. The results are deduced from DSMC simulations (open triangles). In the case $s_r = 10^{-4}$, they are compared to the results given by the master equation (solid squares). The vertical dotted-dashed lines give the steady state values predicted by the deterministic equation. The vertical long-dashed lines give the steady state values including the nonequilibrium corrections.

proving that nonequilibrium effects are much more important in thermochemical systems. We have observed similar effects in another model [36] involving two chemical species

$$A + A \rightarrow A + B + \text{heat} \quad \text{(in the bulk)}, \qquad (26)$$

$$B \rightarrow A \quad \text{(on the surface)}. \qquad (27)$$

In this case, the macroscopic dynamics involved two variables and it was not possible to obtain analytical corrections to the steady states, neither due to fluctuations nor to nonequilibrium effects.

CONCLUSION

We have studied Semenov thermochemical gaseous system using the master equation and microscopic simulations based on the DSMC method. We describe a succession of bifurcations in which the system enters and leaves the region of bistability. We have shown that the fluctuations growing in the system for small particle numbers can switch it from the monostable regime to the bistable one, or even can destabilize the steady state of high temperature to the benefit of the steady state of low temperature. The analytical corrections to the steady states deduced from the Fokker–Planck equation agree very well with the results of the simulation of the master equation. The observed behavior is characteristic of noise-induced bifurcations, previously predicted for isothermal chemical systems [25]. Moreover, the microscopic simulations reveal an analogous sequence of bifurcations when varying the steric factor of the reaction. As the reaction becomes faster, the deformation of particle velocity distribution results in deviations from the deterministic prediction. This departure from partial equilibrium originating at the level of velocity distribution leads, at the macroscopic level, to a deformation of the bifurcation diagram. By analogy with the phenomenon observed in the presence of fluctuations, we speak of nonequilibrium-induced bifurcations. The analytical nonequilibrium corrections to the steady states deduced from a perturbative solution of the Boltzmann equation agree reasonnably well with the results of the microscopic simulations. These effects observed for the simple Semenov model are similar to the effects recently reported for a bicomponent thermochemical model [36]. Only in the case of the one-variable Semenov model, we are able to compare the numerical results with analytical predictions. For both models, the effects of fluctuations and departure from partial equilibrium give deviations in the same direction. They tend to stabilize the stationary state of low temperature. If such an explosive gas mixture is used in an engine for parameter values close to bistable conditions, the microscopic perturbations reduce the efficiency of the combustion. However, if the goal is to store such a gas, both fluctuations and nonequilibrium effects have the tendency to reduce combustion hazards.

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