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# Sensitivity of explosion to departure from partial equilibrium

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We study a thermochemical gaseous system in the vicinity of the bifurcation related to the emergence of bistability. Corrections to the standard deterministic dynamics induced by the perturbation of the particle velocity distribution are obtained from the solution of the Boltzmann equation. Using these results, analytical expressions including the nonequilibrium effects are derived for the ignition time in the explosive regime and mean first passage time in the bistable regime. It is demonstrated that a departure from partial equilibrium can shift the bifurcation point. The system which was bistable according to the standard deterministic approach, can become monostable and explosive in the presence of nonequilibrium effects. Even when the system remains in the bistable regime, the mean first passage time can be changed by several orders of magnitude. In the monostable domain, the ignition time can be about ten times smaller than the unperturbed value. These analytical predictions agree well with the results of the microscopic simulations of the dilute gas system.

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## I. INTRODUCTION

Kinetic theory studies based on the Boltzmann equation have revealed that a chemical reaction may lead to a departure of the particle velocity distribution from the equilibrium shape [1–6]. This microscopic phenomenon, known as a departure from partial or incomplete equilibrium [7], influences the macroscopic dynamics of the gaseous chemical systems. In this paper we address the case of an exothermal reaction taking place in a closed vessel in contact with a thermostat. We consider the model introduced by Semenov [8] in order to describe the temperature evolution of such a reactive gas mixture. It is the simplest model reproducing the transition between a regime of slow oxidation and a flame, i.e., allowing for studying the bifurcation between bistable and monostable regimes. In the monostable domain, the system possesses an explosive character: the temperature evolution has a typical sigmoidal shape, revealing a long induction period followed by a violent increase and a relaxation toward the single stationary state. The large fluctuations growing during the induction stage have been investigated in detail [9–11]. In the bistable domain, the deterministic evolution reproduces a slow reaction associated with a small temperature increase. However, in the presence of fluctuations, transitions through the potential barrier are observed and we already studied the probability distribution of the first passage time [11].

The effects of the perturbation of velocity distribution on the temperature profile in an inhomogeneous exothermal chemical system have already been analyzed [12], but the studied deviations from the equilibrium predictions were small. The propagation velocity and the shape of isothermal chemical waves in inhomogeneous media can also be affected by a departure from partial equilibrium. The cases of pulled [13] and pushed [14] fronts have been both characterized. For these isothermal systems, the departures from the equilibrium predictions do not exceed a few percent when the activation energy of the reaction is larger than $4kT$. In homogeneous isothermal chemical systems [15] the vicinity of the bifurcation associated with bistability has been studied and the distortion of the particle velocity distribution has been shown to induce a deformation of the bifurcation diagram. In the case of an exothermal reaction we expect here large nonequilibrium effects on ignition time and mean first passage time due to their extreme sensitivity to the activation barrier. We calculate the nonequilibrium corrections to the macroscopic description using the Boltzmann equation and take into account these perturbations in the analysis of the stochastic behavior of the system. These analytical predictions are compared with the results of microscopic simulations based on the direct simulation Monte Carlo (DSMC) method [16].

The paper is organized as follows. We first give in Sec. II the macroscopic equation governing the evolution of temperature in the Semenov model. Section III is devoted to a perturbative treatment of the Boltzmann equation for particle velocity distribution. The nonequilibrium corrections to the macroscopic equation for temperature are then derived. The most technical parts of the calculation are presented in the Appendix. The microscopic simulation method is presented in Sec. IV. The analytical predictions deduced from the Boltzmann equation and the simulation results are compared in Sec. V. Nonequilibrium effects on ignition time in the explosive regime and mean first passage time in the bistable domain are discussed. Section VI contains conclusions.

## II. DETERMINISTIC APPROACH TO THE SEMENOV MODEL

We consider a closed reactor of volume $V$ containing a reactive dilute gas. The gas is subject to an energy balance due to an exothermal reaction in the bulk and to 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 model [8] introduces the simplest feasible chemical reaction $A+A \rightarrow \text{products} + \text{heat}\, Q$ and neglects the consumption of reactant *A*. It amounts to considering the following scheme:

$$A+A \rightarrow A+A+\text{heat}\, Q \tag{1}$$

in the presence of an external light source. Hence, the total number of particles, *N*, in the system is constant. The deterministic equation of energy balance reads [8]

$$\frac{d\mathcal{E}}{dt'} = k_r \frac{N^2}{V} Q - k_a \frac{N}{V} 2k(T-T_w), \tag{2}$$

where $t'$ is time; $k_r$ and $k_a$ are, respectively, the rate constants of reaction and accommodation at the walls. Their expressions are deduced from the frequencies of collisions either in the bulk or with the walls of the reactor. Standard results of kinetic theory yield [17,16,10]

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

$$k_a = S s_a \sqrt{\frac{kT}{2\pi m}}, \tag{4}$$

where $\sigma$ is the total collisional cross section in the bulk, *m* is the mass of particle *A*, $E^*$ is the activation energy of reaction (1); $s_r$ is a steric factor related to an independent geometric condition for reaction, *S* is the surface of the walls, and $s_a$ is a steric factor for thermal accommodation. For the reduced temperature, $\theta = T/T_w$, Eq. (2) leads to

$$\frac{d\theta}{dt} = \frac{1}{3}\sqrt{\theta}\left[\exp\left(-\frac{\varepsilon}{\theta}\right) - \gamma(\theta-1)\right], \tag{5}$$

where we have used the dimensionless time and heat variables

$$t = 4n\sigma s_r \left(\frac{kT_w}{\pi m}\right)^{1/2} q t', \quad \varepsilon = E^*/kT_w, \quad q = \frac{Q}{kT_w}, \tag{6}$$

and we have introduced a reduced coefficient for Newtonian heat exchange

$$\gamma = \frac{S\lambda}{V} \frac{s_a}{s_r q}. \tag{7}$$

Here, $\lambda = (\sqrt{2} n\sigma)^{-1}$ denotes the molecular mean free path. Parameter $\gamma$ gives some measure of the efficiency of Newtonian cooling with respect to heat production by the exothermal reaction. The prefactor $\sqrt{\theta}$ of the two terms in Eq. (5) appears because the kinetic theory calculation reveals the dependence of collision rates on the square root of temperature [17]. In the standard macroscopic description of the Semenov model [8], this weak dependence on $\sqrt{\theta}$ is omitted, but it has already been included in previous microscopic treatments of thermochemical systems [12,18,10].

Depending on the parameter values controlling the production of reaction heat and Newtonian cooling, different dynamical regimes are observed. The line $\gamma(\theta-1)$ and the curve $\exp(-\varepsilon/\theta)$ can have either one or three intersection points [8] which correspond to the stationary solutions of Eq. (5). Thus, the system has either a unique stable steady state or two stable states, $\theta_1 < \theta_2$, separated by an unstable one, $\theta_u$. The bistability arises and vanishes at bifurcation points, at which the line $\gamma(\theta-1)$ becomes tangential to $\exp(-\varepsilon/\theta)$. For a given $\varepsilon$, this condition yields the following critical values of $\gamma$:

$$\gamma_c^{\pm} = \frac{1}{4}\varepsilon\left(1 \pm \sqrt{1-\frac{4}{\varepsilon}}\right)^2 \exp\left[-\frac{1}{2}\varepsilon\left(1 \pm \sqrt{1-\frac{4}{\varepsilon}}\right)\right]. \tag{8}$$

Bistability can appear only if $\varepsilon > 4$, in the range of $\gamma$ bounded by the critical values, $\gamma_c^+ < \gamma < \gamma_c^-$. For higher values, $\gamma > \gamma_c^-$, the system evolves at moderate rate towards a single stationary temperature which lies on the extinction (lower) branch of the steady states denoted by $\theta_1$. The opposite, below-bistability domain $\gamma < \gamma_c^+$ is the explosion region: after a long induction period, the temperature of the system grows in a characteristic, explosive manner and reaches the stable steady state $\theta_2$ on the combustion (upper) branch.

## III. THE BOLTZMANN EQUATION AND NONEQUILIBRIUM CORRECTIONS TO MACROSCOPIC EQUATIONS

Many kinetic theory studies of gaseous chemical systems [1–3,6] have demonstrated that a reaction may induce a significant perturbation of the particle velocity distribution, and that such a deformation influences the system dynamics. The velocity distribution function is obtained from the Boltzmann equation which for the Semenov system can be written in the form

$$\frac{\partial f}{\partial t} = \int [f(\mathbf{v}')f(\mathbf{v}_1') - f(\mathbf{v})f(\mathbf{v}_1)]|\mathbf{v}-\mathbf{v}_1| d\sigma^e d\mathbf{v}_1 + \left(\frac{\partial f}{\partial t}\right)_r^+ - \left(\frac{\partial f}{\partial t}\right)_r^- + \left(\frac{\partial f}{\partial t}\right)_w^+ - \left(\frac{\partial f}{\partial t}\right)_w^-. \tag{9}$$

$f(\mathbf{v},t)$ is the distribution function for particles *A* [only velocities are indicated explicitly as arguments of *f* in Eq. (9)]. The first term on the right-hand side of this equation is the integral for elastic collisions and $d\sigma^e$ is the usual differential cross section for elastic collisions [19]. Velocities $\mathbf{v}'$ and $\mathbf{v}_1'$ correspond to an inverse collision in which $\{\mathbf{v}',\mathbf{v}_1'\}$ are transformed into $\{\mathbf{v},\mathbf{v}_1\}$. The next two terms on the right-hand side of Eq. (9) describe the effect of inelastic collisions related to reaction (1). The loss part has the usual form

$$\left(\frac{\partial f}{\partial t}\right)_r^- = \int f(\mathbf{v})f(\mathbf{v}_1)|\mathbf{v}-\mathbf{v}_1| d\sigma^* d\mathbf{v}_1, \tag{10}$$

where $\sigma^*$ is the cross section for reaction (1). The gain counterpart

$$\left(\frac{\partial f}{\partial t}\right)_r^+ = \int f(\mathbf{v}'')f(\mathbf{v}_1'')|\mathbf{v}''-\mathbf{v}_1''|d\sigma^* \frac{\partial(\mathbf{v}'',\mathbf{v}_1'')}{\partial(\mathbf{v},\mathbf{v}_1)} d\mathbf{v}_1 \quad (11)$$

involves the rule of inverse collision: $\mathbf{v}''$ and $\mathbf{v}_1''$ are such initial velocities that yield $\mathbf{v}$ and $\mathbf{v}_1$ after a reactive collision. Equation (11) must include the factor $\partial(\mathbf{v}'',\mathbf{v}_1'')/\partial(\mathbf{v},\mathbf{v}_1) \neq 1$ which gives the change of a volume element of velocities in an inelastic collision [1,20]. Finally, the two last terms of Eq. (9) account for inelastic collisions of particles with the boundary walls, related to the exchange of energy with the thermostat. We omit the elastic collisions with the walls, because they do not change the speed of a particle, and consequently do not contribute to the Maxwellization of the speed distribution. The loss term is simply determined by the frequency of inelastic collisions, which for the cubic container has the form

$$\left(\frac{\partial f}{\partial t}\right)_w^- = s_a \frac{S}{6}\frac{1}{V} f(\mathbf{v})(|v_x|+|v_y|+|v_z|). \quad (12)$$

The associated gain portion provides the rate of appearing of particles $A$ with velocity $\mathbf{v}$ after bouncing from the wall of the reactor. After thermal accommodation at the boundary wall, the bounced particles have the (biased) Maxwellian velocity distribution with temperature $T_w$ of the thermostat, and the influx of particles from the walls is given by

$$\left(\frac{\partial f}{\partial t}\right)_w^+ = s_a \frac{S}{6}\frac{1}{V} f_{T_w}^{(0)}(|v_x|+|v_y|+|v_z|), \quad (13)$$

where $f_{T_w}^{(0)} = n_w(m/2\pi k T_w)^{3/2}\exp(-mv^2/2kT_w)$ denotes the Maxwellian distribution at temperature $T_w$ of bounced particles. Concentration $n_w$ in $f_{T_w}^{(0)}$ is determined from the condition of vanishing of the mass flux through the walls

$$\int_{v_\perp<0} f_{T_w}^{(0)}(\mathbf{v})|v_\perp|d\mathbf{v} = \int_{v_\perp>0} f(\mathbf{v})v_\perp\, d\mathbf{v}, \quad (14)$$

where $v_\perp$ is the velocity component perpendicular to the wall. Thus, Eq. (13) involves (implicitly) the distribution function $f$. Since $f$ and $f_{T_w}^{(0)}$ are isotropic in the homogeneous system, the orientation of $v_\perp$ is irrelevant; we may put $v_\perp = v_x$ and calculate explicitly the integral in the influx term on the left-hand side of Eq. (14).

The relation between the kinetic energy of the particles and the gas temperature

$$\int f(\mathbf{v})\frac{mv^2}{2}d\mathbf{v} = \frac{3}{2}nkT \quad (15)$$

allows us to obtain the evolution equation for temperature from the Boltzmann equation, after multiplying by $\frac{1}{2}mv^2$ and integration over velocities. In the lowest approximation, $f$ is the Maxwellian distribution corresponding to the instantaneous system temperature $T(t)$,

$$f^{(0)}(\mathbf{v},t) = n(m/2\pi kT)^{3/2}\exp(-mv^2/2kT). \quad (16)$$

This function is used to obtain the lowest approximation for the dynamics of temperature by means of Eq. (15).

In order to calculate the contribution to energy balance due to the reaction we must specify the reaction cross section $\sigma^*$. We use the molecular model of reactive hard spheres [21], which attributes a part of the hard sphere cross section to reactive collisions. A collision can be reactive if the relative velocity $\mathbf{g}$ of colliding molecules satisfies the following condition:

$$\mathbf{e}\cdot\mathbf{g} \geqslant g^*, \quad (17)$$

where $\mathbf{e}$ denotes the unit vector along the line connecting the centers of hard spheres at the instant of impact, and $g^*$ is the threshold relative velocity. The condition given in Eq. (17) implies that the activation energy for reaction in this model is given by

$$E^* = \frac{\mu g^{*2}}{2}, \quad (18)$$

where $\mu = m/2$ is the reduced mass of two identical molecules. Provided the energetic condition is satisfied, the collision is actually reactive with the probability $s_r$, which follows from steric constraints.

The contribution of reactive collisions to the dynamics of temperature is obtained by means of Eq. (15) from integrals (10) and (11) with $f^{(0)}$. For the model of reactive hard spheres, the result has the following form in the dimensionless variables:

$$\left(\frac{d\theta}{dt}\right)_r^{(0)} = \frac{1}{3}\sqrt{\theta}\exp\left(-\frac{\varepsilon}{\theta}\right). \quad (19)$$

Equation (14) in the lowest approximation reads $n_w^{(0)}\sqrt{T_w} = n\sqrt{T}$, and the calculation of the energy exchange terms gives then

$$\left(\frac{d\theta}{dt}\right)_w^{(0)} = -\frac{1}{3}\sqrt{\theta}\gamma(\theta-1). \quad (20)$$

The elastic collisions integral never gives a contribution to $d\theta/dt$ because energy is conserved in elastic collisions. Thus, in the lowest order approximation the sum of the two terms given in Eqs. (19) and (20) yields the dynamics of temperature given by Eq. (5).

However, the simple Maxwellian distribution is not the solution of the Boltzmann equation; the exact distribution function $f$ contains the perturbation of the Maxwellian (16) induced by the reaction and the thermal exchange process. The departure from the Maxwellian distribution results in the correction to the standard equation [Eq. (5)]. The solution for $f$ can be obtained by means of the Chapman-Enskog method [22], which is valid if the relaxation of the velocity distribution by elastic collisions is much faster than all the other processes. For chemical systems it means that reactions are relatively slow [3,6], and for the Semenov model this condition includes as well energy transfer through the boundaries. The distribution function is assumed in the form of an expansion in Sonine polynomials [22], and it was shown [23] that the few first terms can provide satisfactory approximation. If the perturbation is represented by one term of the expansion, the correction to the deterministic equation (5) can be presented in the following form:

$$\left(\frac{d\theta}{dt}\right)_1^{(1)}=\left(\frac{d\theta}{dt}\right)_r^{(0)}\frac{1}{16}\frac{s_r q}{\theta}r_2[\exp(-\varepsilon/\theta)\phi_{2r}-\gamma\phi_{2w}]+\left(\frac{d\theta}{dt}\right)_w^{(0)}\frac{1}{16}\frac{s_r q}{\theta}w_2[\exp(-\varepsilon/\theta)\phi_{2r}-\gamma\phi_{2w}]. \tag{21}$$

The two-term expansion gives the following extended correction:

$$\begin{aligned}\left(\frac{d\theta}{dt}\right)_2^{(1)}=&\left(\frac{d\theta}{dt}\right)_1^{(1)}+\left(\frac{d\theta}{dt}\right)_r^{(0)}\frac{1}{480}\frac{s_r q}{\theta}(4r_3+r_2)\\&\times[\exp(-\varepsilon/\theta)(\phi_{2r}+4\phi_{3r})-\gamma(\phi_{2w}+4\phi_{3w})]\\&+\left(\frac{d\theta}{dt}\right)_w^{(0)}\frac{1}{480}\frac{s_r q}{\theta}(4w_3+w_2)\\&\times[\exp(-\varepsilon/\theta)(\phi_{2r}+4\phi_{3r})-\gamma(\phi_{2w}+4\phi_{3w})].\end{aligned} \tag{22}$$

In these equations, $r_i$ ($i=2,3$) are given by Eqs. (A13) in the Appendix, $w_i$ by Eqs. (A15), $\phi_{ir}$ by Eqs. (A20), and $\phi_{iw}$ by Eqs. (A22); these coefficients are simple polynomials of $\varepsilon/\theta$ and $q/\theta$.

It is to be noted that the corrections to the macroscopic evolution induced by a deviation from equilibrium velocity distribution do not vanish for large systems, unlike the perturbations due to fluctuations. For systems of mesoscopic size, these two kinds of effects interfere. The perturbations of the deterministic dynamics due to a departure from equilibrium influence as well the stochastic evolution. In recent papers [10,11] we developed the master equation which governs the stochastic dynamics of the thermochemical Semenov model. The expansion of this master equation for systems with large particle number $N$ gives the following Fokker-Planck equation [11] for the probability distribution of temperature $P(\theta,t)$:

$$\frac{\partial}{\partial t}P(\theta,t)=-\frac{\partial}{\partial\theta}[\alpha(\theta)P(\theta,t)]+\frac{1}{2}\frac{\partial^2}{\partial\theta^2}[\beta(\theta)P(\theta,t)]. \tag{23}$$

The coefficient $\alpha$ in the Fokker-Planck equation is related to the deterministic dynamics; it is equal to the right-hand side of the deterministic equation given in Eq. (5). The simplest way to include the nonequilibrium effects in the mesoscopic description is to introduce the corrections given in Eq. (21) or Eq. (22) in the coefficient $\alpha$ in the Fokker-Planck equation (23). The coefficient $\beta$ describes the dispersion of the temperature distribution due to fluctuations according to [11]

$$\beta(\theta)=\frac{2}{9N}\sqrt{\theta}\left[q\exp\left(-\frac{\varepsilon}{\theta}\right)+\gamma(3-4\theta+3\theta^2)\right]. \tag{24}$$

Note that $\beta$ contains the scaling factor $1/N$, which indicates that fluctuations are relatively weaker for large systems. The Fokker-Planck equation gives a simple analytical expression [24] for the mean first passage time $\langle\tau(\theta)\rangle$ in a bistable system:

$$\langle\tau\rangle=2\pi\left(\frac{\beta(\theta_u)}{|\alpha'(\theta_1)|\alpha'(\theta_u)\beta(\theta_1)}\right)^{1/2}\exp[U(\theta_u)-U(\theta_1)], \tag{25}$$

where $\theta_1$ is the stable steady state of low temperature, $\theta_u$ the unstable steady state, $\alpha'(\theta)=d\alpha/d\theta$ is the derivative of $\alpha(\theta)$, and $U$ is defined by $dU/d\theta=-\alpha(\theta)/\beta(\theta)$.

## IV. MICROSCOPIC SIMULATION METHOD

We use the DSMC method developed by Bird [16] to simulate particle collisions in a dilute gas. Assuming that the system is homogeneous, we disregard the positions of the particles and only follow the evolution of their velocities. 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. A standard acceptance-rejection method is used to choose actual encounters. The collisions between two randomly chosen particles $k$ and $l$ are accepted proportionally to their relative velocity $(\mathbf{v}_k-\mathbf{v}_l)$. As in the analytical treatment of the Boltzmann equation, we choose the molecular model of reactive hard spheres. An accepted collision between particles $k$ and $l$ is reactive, with the probability given by the steric factor $s_r$, if their relative velocity along the direction connecting their centers at impact exceeds a certain threshold value, $g^*$. This threshold is related to the activation energy of the reaction by Eq. (18). 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 $T_w$:

$$f_w(\mathbf{v})=\frac{1}{2\pi}\left(\frac{m}{kT_w}\right)^2|v_\perp|\exp\left(-\frac{mv^2}{2kT_w}\right), \tag{26}$$

where $v_\perp$ is the component of velocity perpendicular to the wall chosen for collision. Starting from particles at the wall temperature $\theta=1$, we follow the evolution of their kinetic energy and determine time $\tau$ necessary for the temperature to reach the value $\theta=3$, close to the unstable stationary state in the bistable domain. Depending on the value of Newtonian exchange coefficient $\gamma$, the system is either explosive or bistable. In the explosive regime, mean time $\tau$ is called ignition time. In the bistable case and in the presence of fluctuations, it is called mean first passage time and defined as the time necessary to overcome the potential barrier between the two stable stationary states. We previously checked using a master equation approach [25,11] that the mean first passage time obeys Eq. (25) for sufficiently large particle numbers $N>5000$. At smaller $N$, specific fluctuation effects alter the behavior of $\tau$. To remain in the domain of validity of Eq. (25), we perform microscopic simulations for a sufficiently large particle number, but nevertheless as small as possible to reduce computation time. The chosen value, $N=10\,000$, offers a good compromise.

## V. NONEQUILIBRIUM EFFECTS ON IGNITION TIME AND MEAN FIRST PASSAGE TIME

We now compare the analytical predictions, with or without nonequilibrium corrections, with the results of the microscopic simulations. The amplitude of the corrections given in Eq. (21) or Eq. (22) depends in a nontrivial manner on the perturbations induced by cooling and reaction. For a fixed value of Newtonian exchange coefficient $\gamma$ controlling the distance from the bifurcation, the nonequilibrium corrections induced by reaction prevail when the activation energy reaches $\varepsilon=5$ and they increase with heat release $q$. Corrections of both origins are comparable for the parameter choice $\varepsilon=4.5$ and $q=5$ examined later.

We first study the behavior of the system in the explosive regime. Following an analogous procedure as for microscopic simulations, the ignition time values are obtained by integrating the unperturbed and corrected deterministic equations over a time such that temperature varies from $\theta=1$ to $\theta=3$. As shown in Fig. 1 for $\varepsilon=5$ and $q=8$, the nonequilibrium perturbations qualitatively affect the behavior of the system around the emergence of bistability and strongly change the value of ignition time. When using one (two) Sonine polynomial(s) in the calculation of nonequilibrium corrections, the critical value of $\gamma$, associated with the divergence of ignition time, is 10% (13%) higher than the unperturbed prediction. In a large interval defined by $0.071<\gamma<0.077$, the uncorrected deterministic equation ensures that the temperature of the system will remain small whereas explosion is predicted when taking into account the nonequilibrium corrections. In the explosive regime, the microscopic simulations qualitatively confirm the analytical predictions given in Eqs. (21) and (22). Their quantitative agreement with the nonequilibrium corrections calculated with one Sonine polynomial according to Eq. (21) is excellent. The discrepancy with the unperturbed deterministic prediction is very large: near the bifurcation point, for $\gamma=0.07$, the modified value of the ignition time is about ten times smaller than the unperturbed value. In the bistable domain, we use the expression of mean first passage time given in Eq. (25) and deduced from the Fokker-Planck equation, to compute the unperturbed value of $\langle\tau\rangle$ depicted in Fig. 1. The variations of mean first passage time including nonequilibrium effects are obtained by introducing corrected values of $U$ and $\alpha'$ in Eq. (25). The nonequilibrium corrections to the diffusion term $\beta$ are supposed to be negligible.

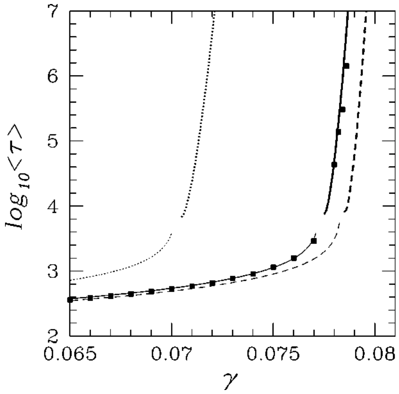

FIG. 1. Logarithm of the ignition time and mean first passage time $\langle\tau\rangle$ vs Newtonian exchange coefficient $\gamma$. Thin lines are predicted by deterministic equations in the explosive regime. Thick lines are deduced from Fokker-Planck equations in the bistable regime. Dotted lines are obtained without nonequilibrium corrections, solid (dashed) lines include nonequilibrium corrections predicted with one (two) Sonine polynomial(s). The solid squares depict the results obtained from microscopic DSMC simulations for the following parameter values: reduced activation energy $\varepsilon=5$, reaction steric factor $s_r=1$, reduced heat release $q=8$, particle number $N=10\,000$, ratio of mean free path and length of the system $\lambda/L=0.5$.

In the bistable domain, thanks to the presence of fluctuations in a system of $N=10\,000$ particles, the potential barrier, separating the two stationary states, is overcome and explosion is observed. As shown in Fig. 1, the variation with $\gamma$ of the results of the microscopic simulations in the bistable domain agrees very well with the stochastic predictions including nonequilibrium corrections with one Sonine polynomial. Due to the shift of the bifurcation to higher values of $\gamma$, the discrepancy between results taking nonequilibrium effects into account and the unperturbed predictions is enormous and can reach several orders of magnitude.

Exothermic chemical systems near a bifurcation present an exacerbate sensitivity to *a priori* small disturbances of microscopic origin. As shown here in the case of a bistable system, the macroscopic consequences of a departure from partial equilibrium may be dramatic: explosion occurs in an extended domain of parameters where unperturbed macrosocpic equations predict a soft evolution without explosion.

The origin of the discrepancy between microscopic simulations and standard deterministic approach can be clearly attributed to nonequilibrium effects as revealed by the variation of ignition time with steric factor for reaction, $s_r$, in the monostable domain. The results of the different approaches are given in Fig. 2. The unperturbed deterministic equation (5) does not depend on $s_r$. For given values of $\varepsilon$, $q$, and $\gamma$, the ignition time tends to the unperturbed value predicted by Eq. (25) when the steric factor tends to zero. For parameter values where nonequilibrium effects are dominated by the

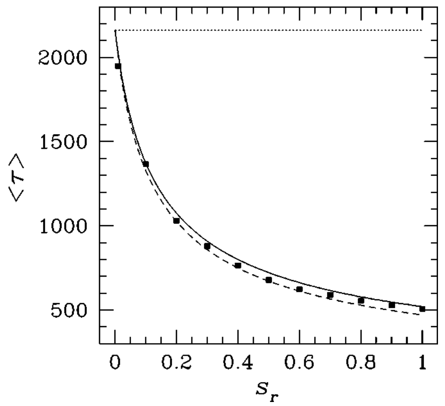

FIG. 2. Ignition time $\langle\tau\rangle$ vs reaction steric factor $s_r$ in the explosive regime for Newtonian exchange coefficient $\gamma = 0.0695$. The values of the other parameters are the same as in Fig. 1. Dotted line is the prediction of the deterministic equation without nonequilibrium corrections. Solid (dashed) line is the deterministic prediction including nonequilibrium corrections for one (two) Sonine polynomial(s). The solid squares depict the results obtained from microscopic DSMC simulations.

contribution of reaction, departure from partial equilibrium monotonically decreases as the perturbations induced by reaction become weaker. We also study in Fig. 3 the variation of ignition time with $s_r$, but for a higher value of $\gamma$. For $s_r = 1$, the nonequilibrium corrections predict that the system is monostable, but as $s_r$ decreases, the bifurcation point is crossed. In the bistable domain, the predictions of the mean first passage time, deduced from Fokker-Planck equation for nonequilibrium corrections including two Sonine polynomials, agree rather well with the microscopic simulation results.

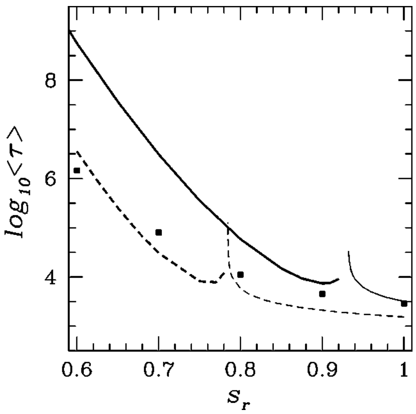

FIG. 3. Logarithm of the ignition time and mean first passage time $\langle\tau\rangle$ vs reaction steric factor $s_r$ for Newtonian exchange coefficient $\gamma = 0.077$. The values of the other parameters are the same as in Fig. 1. Equation (25) without nonequilibrium corrections predicts $\tau = 1.8 \times 10^{29}$ whatever $s_r$. Thin lines are predicted by deterministic equations with nonequilibrium corrections in the explosive regime. Thick lines are deduced from Fokker-Planck equations in the bistable regime. Solid (dashed) lines include nonequilibrium corrections predicted with one (two) Sonine polynomial(s). The solid squares depict the results obtained from microscopic DSMC simulations.

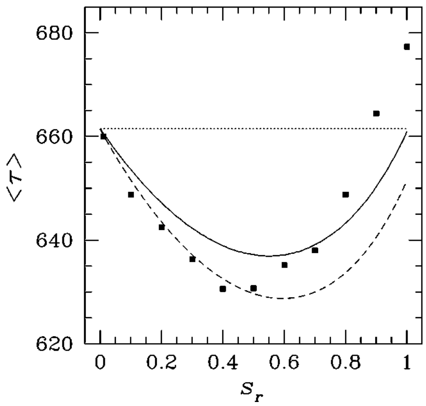

FIG. 4. Same as Fig. 2, but for the following parameter values: reduced activation energy $\varepsilon = 4.5$, Newtonian exchange coefficient $\gamma = 0.0942$, reduced heat release $q = 5$, particle number $N = 10\,000$, ratio of mean free path and length of the system $\lambda/L = 0.5$.

In order to check more precisely our analytical predictions, and in particular the expression of the nonequilibrium terms induced by the cooling at the walls, we perform a second series of simulations for smaller values of activation energy, $\varepsilon = 4.5$, and heat release, $q = 5$. For these parameter values, the corrections induced by reaction are smaller than in the previous series at $\varepsilon = 5$ and $q = 8$. The order of magnitude of the two sources of nonequilibrium, i.e., exothermic reaction and cooling at the walls, become comparable, but the two contributions have an opposite sign as shown in Eqs. (21) and (22). Whereas nonequilibrium effects for high values of $\varepsilon$ and $q$ clearly result in a decrease in ignition time and postpone the emergence of bistability for higher values of $\gamma$, more intricate results are obtained in Fig. 4 for $\varepsilon = 4.5$ and $q = 5$. As expected, the simulation results and the analytical predictions tend to the unperturbed deterministic ignition time as the reaction steric factor $s_r$ tends to zero. However, as $s_r$ increases, the nonequilibrium corrections predict a nonmonotonic evolution of $\tau$ confirmed by the simulation results: the ignition time goes through a minimum for $s_r \simeq 0.5$ and then increases. For $s_r = 1$, the simulation results even lead to an ignition time larger than the unperturbed deterministic prediction. Note that the agreement between simulation and analytical predictions observed in Fig. 4 constitutes a fine discriminating test of theory: we check variations of ignition time smaller than 5%. Obtaining Fig. 4 required a higher precision than Fig. 2 for the determination of the simulation results: the average values of $\tau$ were obtained from samples of 1500 runs whereas averaging over 200 runs was sufficient for the precision needed in Fig. 2.

## VI. CONCLUSION

An exothermal reactive system has been studied in the vicinity of the bifurcation leading to bistability. We obtained the analytical corrections to the macroscopic dynamics induced by a perturbation of particle velocity distribution. Our theoretical predictions agree well with the results of the microscopic simulations. These nonequilibrium effects have been shown not only to influence the deterministic evolution but also the stochastic behavior. We have demonstrated that a departure from Maxwellian velocity distribution may induce qualitative changes of the system properties. Whereas the system was bistable according to the standard deterministic approach, it can become monostable in the presence of nonequilibrium effects. It means that explosion may occur in a parameter domain that was considered safe in the standard description. Even when the system remains in the same regime, the quantitative effects can be enormous. In the bistable domain, the mean first passage time can be diminished by several orders of magnitude. In the explosive regime, the ignition time can be, for example, decreased by nearly a factor of 10. Contrary to the corrections introduced in the deterministic dynamics by mesoscopic fluctuations [9,26,10,11,25], these nonequilibrium effects induce macroscopic perturbations that do not vanish in the limit of large systems.

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## APPENDIX: CHAPMAN-ENSKOG SOLUTION OF THE BOLTZMANN EQUATION (9)

The basic assumption of the method is that elastic collisions are the dominant process in the system. Accordingly, the time derivative and the terms related to inelastic collisions in Eq. (9) are treated as perturbations of the elastic collision integral. The lowest order solution for $f$ is given by the Maxwellian distribution in Eq. (16). Introducing this function in the reaction and exchange terms of the Boltzmann equation and integrating according to Eq. (15), we obtain the contributions to the rate equation for temperature. For the model of reactive hard spheres, the terms connected to reaction and energy exchange are, respectively, given by

$$\left(\frac{d}{dt}\frac{3}{2}nkT\right)_r^{(0)} = 2Q\sigma n^2\left(\frac{kT}{\pi m}\right)^{1/2} s_r \exp\left(-\frac{E^*}{kT}\right), \quad \text{(A1)}$$

$$\left(\frac{d}{dt}\frac{3}{2}nkT\right)_w^{(0)} = -s_a\frac{S}{V}n\left(\frac{2kT}{\pi m}\right)^{1/2}(kT-kT_w). \quad \text{(A2)}$$

In the dimensionless variables (6) and (7), these equations have the form of Eqs. (19) and (20).

In the next order approximation, $f^{(0)}$ is used to calculate the perturbation terms in the Boltzmann equation; for example, the time derivative of $f$ has the form

$$\left(\frac{\partial f}{\partial t}\right)^{(0)} = \left(\frac{\partial f^{(0)}}{\partial T}\right)\left(\frac{dT}{dt}\right)^{(0)}. \quad \text{(A3)}$$

In the higher order approximation, $f$ contains the perturbation of the Maxwellian distribution

$$f = f^{(0)}(1+\psi). \quad \text{(A4)}$$

In the homogeneous system, $f$ is an isotropic function which depends only on $v^2$. Correction $\psi$ is assumed in the form of an expansion in Sonine polynomials [22]. The two first polynomials are excluded due to conservation of particle number and energy in elastic collisions. It has been shown that sufficiently accurate approximation can be obtained with the expansion containing the two first terms only [23]

$$\psi = a_2 S_{1/2}^{(2)}(c^2) + a_3 S_{1/2}^{(3)}(c^2), \quad \text{(A5)}$$

where the Sonine polynomials of $c^2 = mv^2/2kT$ used here are given by

$$S_{1/2}^{(2)}(c^2) = \frac{15}{8} - \frac{5}{2}c^2 + \frac{1}{2}c^4,$$

$$S_{1/2}^{(3)}(c^2) = \frac{35}{16} - \frac{35}{8}c^2 + \frac{7}{4}c^4 - \frac{1}{6}c^6. \quad \text{(A6)}$$

The equations for coefficients $a_2$ and $a_3$ in expansion (A5) are obtained by integrating over velocities the Boltzmann equation multiplied by the Sonine polynomials $S_{1/2}^{(i)}(c^2)$, for $i=2,3$. Only the terms that are linear with respect to the perturbation $\psi$ are retained in the kinetic equation in this approximation. The equations for coefficients $a_i$ are

$$-R_i - W_i = \sum_{k=2,3} a_k J_{ik}, \quad i=2,3, \quad \text{(A7)}$$

where $R_i$, $W_i$, and $J_{ik}$ denote the following collision integrals:

$$R_i = \frac{1}{2}\int f^{(0)} f_1^{(0)} \left(S_{1/2}^{(i)}(c_r^2) + S_{1/2}^{(i)}(c_{1r}^2) - S_{1/2}^{(i)}(c^2) - S_{1/2}^{(i)}(c_1^2)\right)|\mathbf{v}-\mathbf{v}_1|\, d\sigma^* d\mathbf{v}_1 d\mathbf{v}, \quad \text{(A8)}$$

$$W_i = n\frac{S}{V}\left(\frac{2kT}{\pi m}\right)^{1/2}\int_{c>0} \exp(-c^2)\left[S_{1/2}^{(i)}\left(\frac{T_w}{T}c^2\right) - S_{1/2}^{(i)}(c^2)\right]c^3 dc, \quad \text{(A9)}$$

$$J_{ik} = -\frac{1}{4}\int f^{(0)} f_1^{(0)} \left(S_{1/2}^{(k)}(c'^2) + S_{1/2}^{(k)}(c_1'^2) - S_{1/2}^{(k)}(c^2) - S_{1/2}^{(k)}(c_1^2)\right) \times \left[S_{1/2}^{(i)}(c'^2) + S_{1/2}^{(i)}(c_1'^2) - S_{1/2}^{(i)}(c^2) - S_{1/2}^{(i)}(c_1^2)\right]|\mathbf{v}-\mathbf{v}_1|\, d\sigma d\mathbf{v}_1 d\mathbf{v}. \quad \text{(A10)}$$

In the $R_i$ integral for reaction, $\mathbf{c}_r$ and $\mathbf{c}_{1r}$ are the final velocities obtained from initial ones $\mathbf{c}$ and $\mathbf{c}_1$ after a reactive collision. Specifically for the Chapman-Enskog method, the term of the time derivative vanishes upon integration over velocities.

The integrals $J_{ik}$ for elastic collisions can be extended on the entire, unperturbed cross section $\sigma$ for elastic hard spheres [6]. It is then convenient to represent all the collision integrals in Eqs. (A7) in the dimensionless form, obtained by scaling by $\sigma n^2(kT/\pi m)^{1/2}$. The elastic collision terms are [21]

$$J_{22}=-4,\quad J_{23}=J_{32}=1,\quad J_{33}=-\frac{31}{4}. \tag{A11}$$

The reaction terms are given by

$$R_i=\frac{s_r q}{\theta}\exp\left(-\frac{\varepsilon}{\theta}\right) r_i\,, \tag{A12}$$

where

$$r_2=-\frac{1}{2}+\frac{1}{2}\frac{q}{\theta}+\frac{\varepsilon}{\theta},$$

$$r_3=-\frac{3}{16}+\frac{3}{4}\frac{\varepsilon}{\theta}-\frac{1}{4}\left(\frac{\varepsilon}{\theta}\right)^2+\frac{3}{8}\frac{q}{\theta}-\frac{1}{4}\frac{\varepsilon}{\theta}\frac{q}{\theta}-\frac{1}{12}\left(\frac{q}{\theta}\right)^2. \tag{A13}$$

The terms related to the energy exchange at the walls have the form

$$W_i=\gamma s_r q\left(\frac{1-\theta}{\theta}\right) w_i \tag{A14}$$

with

$$w_2=\left(\frac{3-2\theta}{\theta}\right),\quad w_3=\left(\frac{-16+26\theta-9\theta^2}{4\theta^2}\right). \tag{A15}$$

Using the above expressions for the collision terms, we obtain the explicit solution for coefficients $a_i$ for the model of reactive hard spheres. If only one term is included in expansion (A5), the solution of Eq. (A7) has the form

$$a_{2(1)}=\frac{1}{4}\frac{s_r q}{\theta}\exp\left(-\frac{\varepsilon}{\theta}\right) r_2+\frac{1}{4}\gamma s_r q\left(\frac{1-\theta}{\theta}\right) w_2\,. \tag{A16}$$

The corresponding correction to $n_w^{(0)}$ following from the condition of vanishing of the mass flux is $n_w^{(1)}\sqrt{T_w}=-a_{2(1)}n\sqrt{T}/8$. For the expansion (A5) containing two terms, the solution is given by

$$a_{2(2)}=a_{2(1)}+\frac{1}{120}s_r q\left[\frac{1}{\theta}\exp\left(-\frac{\varepsilon}{\theta}\right)(r_2+4r_3)+\gamma\left(\frac{1-\theta}{\theta}\right)(w_2+4w_3)\right], \tag{A17}$$

$$a_{3(2)}=\frac{1}{30}s_r q\left[\frac{1}{\theta}\exp\left(-\frac{\varepsilon}{\theta}\right)(r_2+4r_3)+\gamma\left(\frac{1-\theta}{\theta}\right)(w_2+4w_3)\right]. \tag{A18}$$

The condition for vanishing of the mass flux gives in this case $n_w^{(1)}\sqrt{T_w}=-(a_{2(2)}+\frac{1}{2}a_{3(2)})n\sqrt{T}/8$.

Using this solution for $\psi$, the correction to the equation of temperature dynamics can be obtained from the Boltzmann equation by means of Eq. (15). The needed reactive collisions' integrals have the following form [scaled to $\sigma n^2(kT/\pi m)^{1/2}$]:

$$\int f^{(0)}f_1^{(0)}\left(S_{1/2}^{(i)}(c^2)+S_{1/2}^{(i)}(c_1^2)\right)(c_r^2-c^2)|\mathbf{v}-\mathbf{v}_1|d\sigma^* d\mathbf{v}_1 d\mathbf{v} =\frac{1}{2}\frac{s_r q}{\theta}\exp\left(-\frac{\varepsilon}{\theta}\right)\phi_{ir}\,, \tag{A19}$$

where [21]

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

$$\phi_{3r}=-\frac{1}{16}-\frac{3}{8}\frac{\varepsilon}{\theta}+\frac{3}{4}\left(\frac{\varepsilon}{\theta}\right)^2-\frac{1}{6}\left(\frac{\varepsilon}{\theta}\right)^3. \tag{A20}$$

The terms for the energy exchange are calculated by means of the integral

$$s_a\frac{S}{V}\int_{v_x>0}f^{(0)}\left(\frac{2^{-(i+1)}}{\theta}+S_{1/2}^{(i)}(c^2)\right)v_x c^2 d\mathbf{c}=-\frac{1}{2}\gamma\frac{s_r q}{\theta}\phi_{iw} \tag{A21}$$

with

$$\phi_{2w}=\frac{3\theta+1}{2},\quad \phi_{3w}=\frac{\theta+1}{4}. \tag{A22}$$

The one-term expansion gives the following correction to the temperature dynamics:

$$\left(\frac{d}{dt}\frac{3}{2}nk\theta\right)_1^{(1)} =\left(\frac{d}{dt}\frac{3}{2}nk\theta\right)_r^{(0)}\frac{1}{16}\frac{s_r q}{\theta}r_2[\exp(-\varepsilon/\theta)\phi_{2r}-\gamma\phi_{2w}] +\left(\frac{d}{dt}\frac{3}{2}nk\theta\right)_w^{(0)}\frac{1}{16}\frac{s_r q}{\theta}w_2[\exp(-\varepsilon/\theta)\phi_{2r}-\gamma\phi_{2w}]. \tag{A23}$$

If two terms of the expansion are included, the extended correction has the form

$$\left(\frac{d}{dt}\frac{3}{2}nk\theta\right)_2^{(1)}=\left(\frac{d}{dt}\frac{3}{2}nk\theta\right)_1^{(1)}+\left(\frac{d}{dt}\frac{3}{2}nk\theta\right)_r^{(0)}\frac{1}{480}\frac{s_rq}{\theta}(4r_3+r_2)[\exp(-\varepsilon/\theta)(\phi_{2r}+4\phi_{3r})-\gamma(\phi_{2w}+4\phi_{3w})]$$
$$+\left(\frac{d}{dt}\frac{3}{2}nk\theta\right)_w^{(0)}\frac{1}{480}\frac{s_rq}{\theta}(4w_3+w_2)[\exp(-\varepsilon/\theta)(\phi_{2r}+4\phi_{3r})-\gamma(\phi_{2w}+4\phi_{3w})]. \tag{A24}$$

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