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STOCHASTIC EFFECTS IN THE BISTABLE HOMOGENEOUS SEMENOV MODEL*

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We present the mesoscopic description of stochastic effects in a thermochemical bistable diluted gas system subject to the Newtonian heat exchange with a thermostat. We apply the master equation including a transition rate for the Newtonian thermal transfer process, derived on the basis of kinetic theory. As temperature is a continuous variable, this master equation has a complicated integro-differential form. We perform Monte Carlo simulations based on this equation to study the stochastic effects in a homogeneous Semenov model (which neglects reactant consumption) in the bistable regime. The mean first passage time is computed as a function of the number of particles in the system and the distance from the bifurcation associated with the emergence of bistability. An approximate analytical prediction is deduced from the Fokker–Planck equation associated with the master equation. The results of the master equation approach are successfully compared with those of direct simulations of the microscopic particle dynamics.

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1. Introduction

Fluctuations in far-from-equilibrium chemical systems are often responsible for qualitatively new effects which are not predicted by the description of the dynamics at the macroscopic level. One of well-known phenomena of this kind are transitions between stable states in nonlinear systems which

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exhibit multistability. The master equation approach [1–3] appears as a particularly effective framework in studies of such stochastic properties. This approach is well developed for reaction-diffusion processes in isothermal systems [4], for which application of the master equation has been justified by careful comparisons with the results of microscopic simulations [5–7]. However, for thermal processes the mesoscopic treatment is much less advanced. The master equation has been previously formulated for energy fluctuations in a system with a uniform temperature gradient [8] and in a simple model with the Knudsen mechanism of transport [9, 10]. Recently, using the kinetic theory of gases we have derived the master equation which includes stochastic effects in the Newtonian energy exchange between a diluted gas system and a thermostat [11]. In this paper, we apply this description to the thermochemical system in the bistable regime.

We consider a closed reactor of volume V and surface S containing a reactive 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 [12] introduced the simplest feasible chemical reaction $A + A \to$ products+heat (Q), in which the 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 [11]. According to scheme (1), the total number N of particles in the system and the concentration n remain constant. The deterministic equation of energy balance reads:

$$\frac{d\mathcal{E}}{dt} = k_{\mathrm{r}} V n^2 Q - k_{\mathrm{a}} n k (T - T_{\mathrm{w}})\,, \tag{2}$$

where k_{r} and k_{a} are respectively the rate constants for reaction (1) and accommodation of particles at the walls. The expression of 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 [11, 13]:

$$k_{\mathrm{r}} = 2\sigma s_{\mathrm{r}} \sqrt{\frac{kT}{\pi m}} \exp\left(-\frac{E^*}{kT}\right)\,, \qquad k_{\mathrm{a}} = S s_{\mathrm{a}} \sqrt{\frac{2kT}{\pi m}}\,, \tag{3}$$

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, and are related to steric conditions for these processes. For the ideal gas, temperature is related to energy by the equation $\mathcal{E} = \frac{3}{2}NkT$. Equation (2) leads then to the following equation for the reduced temperature $\theta = T/T_\mathrm{w}$:

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

In order to reduce the number of parameters, we have introduced above the dimensionless time and activation energy

$$t\, 4n\sigma s_\mathrm{r}\left(\frac{kT_\mathrm{w}}{\pi m}\right)^{1/2}\frac{Q}{kT_\mathrm{w}} \to t\,, \qquad \varepsilon = \frac{E^*}{kT_\mathrm{w}}\,, \tag{5}$$

and we have defined a reduced coefficient for the Newtonian heat exchange

$$\gamma = \frac{S\lambda}{V}\frac{kT_\mathrm{w}}{Q}\frac{s_\mathrm{a}}{s_\mathrm{r}}\,. \tag{6}$$

Here, $\lambda = (\sqrt{2}n\sigma)^{-1}$ 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 $\sqrt{\theta}$ 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 [14,15].

Depending on the parameter values controlling the production of reaction heat and the Newtonian cooling, different dynamical regimes are observed. As shown in Fig. 1, the line $\gamma(\theta - 1)$ and the curve $\exp(-\varepsilon/\theta)$ can have either one or three intersection points [12] which correspond to the stationary solutions of Eq. (4). Thus, the system has either a unique stable steady state or two stable states $\theta_1 < \theta_2$, separated by an unstable one θ_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 ε, this condition yields the following critical values of γ:

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

Bistability can appear only if $\varepsilon > 4$, in the range of γ bounded by the critical values, $\gamma_\mathrm{c}^{+} < \gamma < \gamma_\mathrm{c}^{-}$. Outside this domain, the system possesses only a single stable stationary state which lies either on the extinction (lower) branch for $\gamma > \gamma_\mathrm{c}^{-}$, or on the combustion (higher) branch for $\gamma < \gamma_\mathrm{c}^{+}$. In this paper, we focus on the description of stochastic effects in the bistable regime.

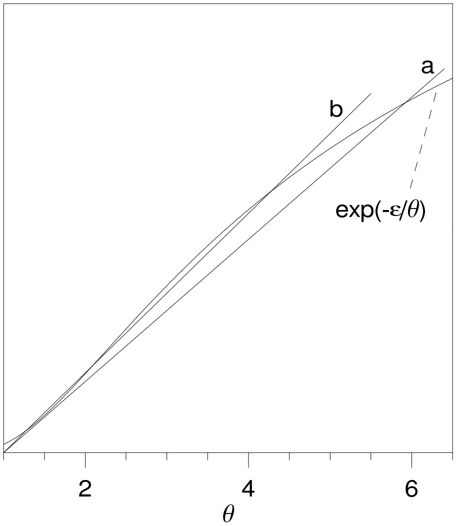

Fig. 1. The two terms of the right-hand side of the deterministic equation (4): $\exp(-\varepsilon/\theta)$ for $\varepsilon = 4.5$, and the line $\gamma(\theta - 1)$ for (a) $\gamma = 0.095$ and (b) $\gamma = 0.1066$. Case (a) corresponds to the explosive regime with a single intersection point of the two curves, *i.e.* a unique stable state on the combustion branch. Case (b) corresponds to the bistable regime with three intersection points, the two extreme ones are stable stationary solutions while the intermediate one is an unstable state.

2. Master equation

In this section, we give the main steps of the derivation of the master equation for the Semenov thermochemical system reported in our recent paper [11]. The basic assumption is that elastic collisions are much more frequent than reactive ones, so that the velocity distribution function retains the Maxwellian form, corresponding to an instantaneous temperature T of the system. In this section we employ simple, unscaled time t and temperature T, because the derivation involves expressions from the kinetic theory of gases which are more familiar in their original forms.

Energy exchange between the system and the thermostat is due to inelastic collisions between particles and the walls of the container. The velocity distribution function $\nu_{\text{out}}(\boldsymbol{v})$ of particles hitting the total surface of the container wall in a unit time is given by

$$\nu_{\text{out}}(\boldsymbol{v}) = Sn\left(\frac{m}{2\pi kT}\right)^{3/2} v_{\perp} \exp\left(-\frac{mv^2}{2kT}\right), \quad v_{\perp} > 0\,, \tag{8}$$

where n denotes the number density of particles, and $v_\perp$ is a component of velocity along outer normal to the surface (a particular orientation is not relevant here since the Maxwellian distribution is isotropic). Integration of distribution (8) over velocities yields the total collision frequency between particles and the walls. From another point of view, this equation indicates that particles striking the wall have a biased Maxwellian velocity distribution, that is the Maxwellian one scaled by velocity $v_\perp$. The particles hitting the wall are accommodated with a probability s_a to the temperature T_w of the wall. The accommodated particles are immediately emitted from the wall and the normalized probability distribution of their velocities $\boldsymbol{v}'$ is given consistently by the biased Maxwellian related to the temperature T_w of the wall

$$\phi_\mathrm{w}(\boldsymbol{v}') = \frac{1}{2\pi}\left(\frac{m}{kT_\mathrm{w}}\right)^2 |v'_\perp| \exp\left(-\frac{mv'^2}{2kT_\mathrm{w}}\right)\,, \quad v'_\perp < 0\,. \tag{9}$$

The transition rate for the system energy from $\mathcal{E}$ to $\mathcal{E}'$ includes the rates of transitions ($\boldsymbol{v} \to \boldsymbol{v}'$) for all combinations of initial and final velocities allowed by the energy constraint $\mathcal{E} - \mathcal{E}' = \frac{1}{2}mv^2 - \frac{1}{2}mv'^2$. By means of Eqs. (8) and (9), the rate of energy transitions in the Newtonian heat exchange is calculated as follows:

$$\begin{aligned} w_e(\mathcal{E} \to \mathcal{E}') \;=\; & S s_\mathrm{a} n \int\limits_{v_\perp > 0} \left(\frac{m}{2\pi kT}\right)^{3/2} v_\perp \exp\left(-\frac{mv^2}{2kT}\right) \\ & \times \int\limits_{v'_\perp < 0} \frac{1}{2\pi}\left(\frac{m}{2kT_\mathrm{w}}\right)^2 |v'_\perp| \exp\left(-\frac{mv'^2}{2kT_\mathrm{w}}\right) \\ & \times \delta\Big(\tfrac{1}{2}(mv^2 - mv'^2) - (\mathcal{E} - \mathcal{E}')\Big) d\boldsymbol{v} d\boldsymbol{v}'\,. \end{aligned} \tag{10}$$

As can be noticed, our treatment of stochastic effects in the Newtonian heat transfer is different from the approach applied usually to diffusive transfer in the master equation [1,4]. In that standard description (extended also to thermal processes [8–10]) rates of transitions depend only on local thermodynamic variables, while $w_e(\mathcal{E} \to \mathcal{E}')$ in Eq. (10) is a function of both the temperature of the system and the thermostat. After a change of variables from energy to temperature, integration of Eq. (10) yields finally the following rate of temperature transition $\Delta T = T' - T$ in the Newtonian thermal exchange

$$w_e(T \to T+\Delta T) = S\, s_{\rm a} n \left(\frac{kT}{2\pi m}\right)^{1/2} \frac{TT_{\rm w}}{(T+T_{\rm w})^3}$$
$$\times \left(2 + \frac{(T+T_{\rm w})(\frac{3}{2}N)|\Delta T|}{TT_{\rm w}}\right)\frac{3}{2}N \begin{cases} \exp\left(-\frac{3}{2}N\frac{|\Delta T|}{T}\right) & \text{for } \Delta T<0\,, \\ \exp\left(-\frac{3}{2}N\frac{\Delta T}{T_{\rm w}}\right) & \text{for } \Delta T>0\,. \end{cases} \tag{11}$$

This transition function is mostly confined to the narrow interval $-T/N < \Delta T < T_{\rm w}/N$, because a relative change of energy in a single inelastic particle–wall collision is of the order of $kT/\mathcal{E}$ $(kT_{\rm w}/\mathcal{E})$ which for the ideal gas results in the $1/N$ scaling. The mean value of temperature transition calculated by means of Eq. (11) yields the deterministic description of the Newtonian heat transfer [11].

The transition function w_e for the Newtonian heat exchange gives a continuous spectrum of temperature changes ΔT, unlike discrete changes of particle numbers involved in standard master equations for reaction-diffusion systems [1, 4]. Discretization of energy transfer can be applied as the very first approximation for the stochastic description of the Newtonian cooling [16]. This simplest approach consists in assuming discrete temperature jumps of some fixed length, but the frequency of such hopping can only be determined by matching average rates to the deterministic description [16].

In contrast to the Newtonian heat transfer, exothermal reaction (1) gives discrete transitions of T, since a fixed portion of energy is always released in a reactive collision. The reaction heat Q results in the increase of temperature by

$$\Delta T_{\rm r} = \frac{Q}{\frac{3}{2}Nk}\,. \tag{12}$$

The transition rate for T is determined by the rate of the thermally activated reaction (1) which according to Eqs. (2), (3) is given by

$$W_{\rm r}(T \to T+\Delta T_{\rm r}) = 2Vn^2\sigma\left(\frac{kT}{\pi m}\right)^{1/2} s_{\rm r}\exp\left(-\frac{E^*}{kT}\right)\,. \tag{13}$$

The master equation can be cast to a simple form with the use of the complete transition function w, which includes both w_e for continuous transitions ΔT and $W_{\rm r}$ for fixed shifts $\Delta T_{\rm r}$:

$$w(T \to T+\Delta T) = w_e(T \to T+\Delta T) + W_{\rm r}(T \to T+\Delta T_{\rm r})\delta(\Delta T - \Delta T_{\rm r})\,. \tag{14}$$

Using this complete transition function defined for the continuous variable ΔT, the master equation for the distribution function of temperature in the thermochemical system has the following form

$$\begin{aligned} \frac{\partial}{\partial t} P(T,t) &= \int\limits_{\Delta T < T} d(\Delta T) P(T-\Delta T, t) w(T-\Delta T \to T) \\ &\quad - P(T,t) \int\limits_{\Delta T > -T} d(\Delta T) w(T \to T + \Delta T) \, . \end{aligned} \tag{15}$$

The above master equation is the basic theoretical result on which our description of fluctuations in the Semenov system is founded. However, its complicated integro-differential form prevents any more rigorous analytical treatment. We study the stochastic effects in the thermochemical system by means of Monte Carlo simulations appropriately based on Eq. (15). The simulation method of stochastic dynamics governed by a master equation for discrete populations of chemical species is well-founded [17]; in the recent paper [11] we presented a generalization of this method, necessary for an equation of the form (15) which involves a continuous variable.

The simulation algorithm consists of the rule for generation of a single elementary transition, in which the system passes from an initial temperature T at time t to a final $T + \Delta T$ reached at $t + \Delta t$. The total rate of escape from the initial state is

$$\begin{aligned} W_{\mathrm{tot}}(T) &= \int d(\Delta T) w(T \to T + \Delta T) \\ &= S\, s_{\mathrm{a}} n \left(\frac{kT}{2\pi m} \right)^{1/2} + V n^2 \sigma \left(\frac{4kT}{\pi m} \right)^{1/2} s_{\mathrm{r}} \exp\left(-\frac{E^*}{kT} \right) \, , \end{aligned} \tag{16}$$

where the first term results from the Newtonian heat exchange and the second one from the exothermal reaction. Consequently, the waiting time to exit from the state with temperature T is $\Delta t = 1/W_{\mathrm{tot}}(T)$ (more exactly, it can be sampled from the exponential distribution $W_{\mathrm{tot}}(T) \exp(-W_{\mathrm{tot}}(T)\Delta t)$ characteristic for the Markovian processes [18]). While time is incremented by Δt, a process effective for the transition is chosen with the probability proportional to its contribution to the total transition rate given in Eq. (16). Thus, the chance to select the reaction is $W_{\mathrm{r}}/W_{\mathrm{tot}}$, as given in the standard method [17], and the associated temperature increment is ΔT_{r}. Accordingly, selection of a Newtonian heat exchange process means a choice of a temperature change ΔT sampled according to the probability distribution $w_e(\Delta T)/W_{\mathrm{tot}}$ for the continuous variable ΔT. Details of the later sampling procedure can be found in the previous paper [11]. After the transition is performed, the next step is generated starting from the updated temperature $T' = T + \Delta T$ at current time $t' = t + \Delta t$. The sequence of transitions forms then a stochastic trajectory of $T(t)$, and the averages are calculated for ensembles of such trajectories.

The results based on the mesoscopic dynamics are verified by comparison with the 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 [19] to simulate particle collisions in the diluted gas system. We employ the molecular model of reactive hard spheres, widely used in microscopic simulations [20,21] and kinetic theory studies [22–24] of chemical systems. The total cross section σ is like for hard spheres, but a part of it corresponds to reaction. A collision is reactive (*i*) with the probability given by the steric factor s_{r}, and (*ii*) if the relative velocity $(\boldsymbol{v}_k - \boldsymbol{v}_l)$ along the direction connecting 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. (13) with the activation energy $E^* = \frac{1}{2}\mu g^{*2}$, 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. Generating collisions of particles with the system boundaries, we assume that the container is cubic, and so collisions with the walls 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. In fact, 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 normalized biased Maxwellian distribution (9), appropriate for the collision direction.

3. Fokker–Planck approximation

Since the range of ΔT decreases like $1/N$, for large systems the master equation (15) can be expanded to the Fokker–Planck differential equation, which is much easier for analytical treatment. The Fokker–Planck equation for the dimensionless variables has the following form:

$$\frac{\partial}{\partial t}P(\theta,t) = -\frac{\partial}{\partial \theta}\Big(\alpha(\theta)P(\theta,t)\Big) + \frac{\partial^2}{\partial \theta^2}\Big(\beta(\theta)P(\theta,t)\Big). \qquad (17)$$

The coefficients α and β in the differential terms of the Fokker–Planck equation are given by the moments of the transition function:

$$\begin{aligned}\alpha(\theta) &= \int w(\theta \to \theta + \Delta\theta)\Delta\theta d(\Delta\theta)\\ &= \frac{1}{3}\sqrt{\theta}\left(\exp\left(-\frac{\varepsilon}{\theta}\right) - \gamma(\theta-1)\right) \qquad (18)\\ \beta(\theta) &= \frac{1}{2}\int w(\theta \to \theta + \Delta\theta)(\Delta\theta)^2 d(\Delta\theta)\\ &= \frac{1}{9N}\sqrt{\theta}\left(q\exp\left(-\frac{\varepsilon}{\theta}\right) + \gamma(3-4\theta+3\theta^2)\right), \qquad (19)\end{aligned}$$

where we have introduced a dimensionless heat release as $q = \frac{Q}{kT_{\mathrm{w}}}$. The coefficient β of the second, diffusive term in Eq. (17) is scaled by the $1/N$ factor, so that fluctuations are relatively weaker for large systems. It should be noted that the previous treatment of the stochastic thermochemical system [25] yielded the Fokker–Planck equation (17) with the following coefficient in the diffusive term:

$$\beta_1(\theta) = \frac{1}{9N}\sqrt{\theta}\left(q\exp\left(-\frac{\varepsilon}{\theta}\right) + \gamma(1+\theta^2)\right). \qquad (20)$$

The difference between Eqs. (19) and (20) comes only from the different stochastic descriptions of Newtonian heat exchange. It becomes larger when θ increases.

The Fokker–Planck equation can be used to easily evaluate fluctuations around the stable stationary state for large N. The equation for the stationary distribution function P_{s} has the form

$$\begin{aligned}&-\sqrt{\theta}\left(\exp\left(-\frac{\varepsilon}{\theta}\right) - \gamma(\theta-1)\right)P_{\mathrm{s}}(\theta)\\ &+\frac{\partial}{\partial\theta}\left[\frac{1}{3N}\sqrt{\theta}\left(q\exp\left(-\frac{\varepsilon}{\theta}\right) + \gamma(3-4\theta+3\theta^2)\right)P_{\mathrm{s}}(\theta)\right] = 0\,. \qquad (21)\end{aligned}$$

Since P_{s} is confined for large N mostly in a narrow interval around θ_{s}, the coefficients of the two terms can be expanded around the stationary state θ_{s}. For α, two terms of the expansion must be retained, because the lowest term vanishes at the stationary state, $\alpha(\theta_{\mathrm{s}}) = 0$. Thus, the approximation for $\alpha(\theta)$ can be written as

$$\alpha(\theta) \approx \left.\frac{d\alpha}{d\theta}\right|_{\theta_{\mathrm{s}}}(\theta-\theta_{\mathrm{s}}) + \ldots = \left[\frac{\varepsilon}{\theta_{\mathrm{s}}^2}\gamma(\theta_{\mathrm{s}}-1) - \gamma\right](\theta-\theta_{\mathrm{s}})\,. \qquad (22)$$

The expression $\exp(-\varepsilon/\theta_{\rm s})$ has been eliminated from the above term by means of the equation $\alpha(\theta_{\rm s}) = 0$. The variation of the second coefficient in the vicinity of $\theta_{\rm s}$ can be neglected with respect to variation of $P_{\rm s}(\theta)$ itself; this coefficient is approximated simply by $\beta(\theta) \approx \beta(\theta_{\rm s})$. Under these approximations, Eq. (21) has the form

$$\left[\frac{\varepsilon}{\theta_{\rm s}^2}(\theta_{\rm s}-1)-1\right](\theta-\theta_{\rm s})P_{\rm s}(\theta) = \frac{1}{3N}\left[q(\theta_{\rm s}-1)+(3-4\theta_{\rm s}+3\theta_{\rm s}^2)\right]\frac{\partial}{\partial\theta}P_{\rm s}(\theta)\,. \qquad (23)$$

The solution of this equation is the Gaussian around the mean $\theta_{\rm s}$ and the dispersion is given by

$$\sigma_\theta = \frac{1}{N}\,\frac{q(\theta_{\rm s}-1)+(3-4\theta_{\rm s}+3\theta_{\rm s}^2)}{3\left[1-\dfrac{\varepsilon}{\theta_{\rm s}^2}(\theta_{\rm s}-1)\right]}\,. \qquad (24)$$

The previous description of the thermochemical system [25] predicts the following dispersion of fluctuations:

$$\sigma_{1\theta} = \frac{1}{N}\,\frac{q(\theta_{\rm s}-1)+(1+\theta_{\rm s}^2)}{3\left[1-\dfrac{\varepsilon}{\theta_{\rm s}^2}(\theta_{\rm s}-1)\right]}\,. \qquad (25)$$

Both equations certainly recover the well-known result for temperature fluctuations in the equilibrium system ($\theta = 1$) under constant volume. However, the difference between the two descriptions becomes pronounced in nonequilibrium conditions, as θ increases. Figure 2 shows the predictions of the two theories for the steady states in the range $3 < \theta_2 < 14$, obtained by varying γ at the constant activation energy $\varepsilon = 4.5$. Such high temperatures may be not completely realistic, because the Semenov assumption of maintaining constant reagent concentration is likely to fail for fast reactions at high θ. Nevertheless, these extreme conditions can be used to examine the validity of the two descriptions of fluctuations by comparison with the appropriate simulations at the microscopic level. The divergence between the present and the previous approaches in this range of high θ is clear in Fig. 2. Simultaneously, the results of the microscopic simulations unambiguously point out that the treatment developed in Ref. [11] and the present paper correctly describe the fluctuations in a thermochemical system.

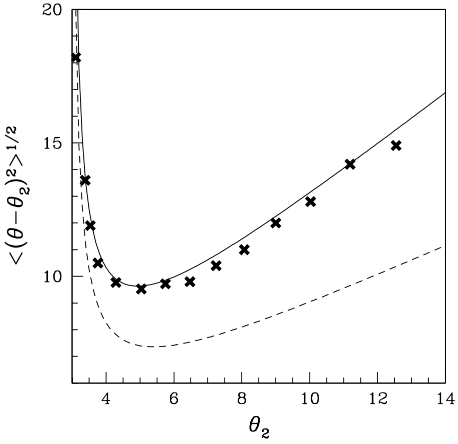

Fig. 2. Standard deviation (scaled by $\sqrt{N}$) of reduced temperature around θ_2 *versus* stationary state of high temperature θ_2. The crosses depict the results obtained from microscopic DSMC simulations for variable γ and for reduced activation energy $\varepsilon = 4.5$, reduced heat release $q = 5$, reaction steric factor $s_{\rm r} = 0.01$, number of particles $N = 10000$, ratio of mean free path and length of the system $\lambda/L = 0.5$. The solid line (resp. dashed line) is the analytical prediction deduced from the Fokker-Planck equation with our expression of $\beta(\theta)$ (resp. previous expression $\beta_1(\theta)$ of Baras *et al.* [25]).

4. Fluctuation-induced transitions in the bistable regime

Stochastic effects are manifested most prominently in regimes sensitive to even small perturbations, like the vicinity of bifurcations [1,4]. Fluctuation-induced transitions between stable states in bistable systems [2, 26, 27] are widely studied stochastic phenomena of this kind. In the bistable domain and for initial conditions in the basin of attraction of the stationary state θ_1, the deterministic description predicts an unavoidable relaxation toward the stationary state at low temperature θ_1. However, if the level of fluctuations is sufficient, the escape over the potential barrier and the final relaxation toward the stationary state of high temperature θ_2 may be observed as shown in Fig. 3 for stochastic trajectories deduced from MC simulations of the master equation. Using the Fokker–Planck equation given in Eq. (17), we wish to determine an analytical expression of the mean first passage time τ from θ_1 to θ_2. Standard calculations [26, 28, 29] lead to the following expression of $\tau(\theta)$ for a motion starting from θ between a reflecting barrier at $\theta_{\rm refl}$ and an absorbing barrier at $\theta_{\rm abs}$:

$$\tau(\theta) = \int\limits_{\theta}^{\theta_{\rm abs}} \exp(U(\theta'))d\theta' \int\limits_{\theta_{\rm refl}}^{\theta'} \frac{\exp(-U(\theta''))}{\beta(\theta'')} d\theta'' \,, \tag{26}$$

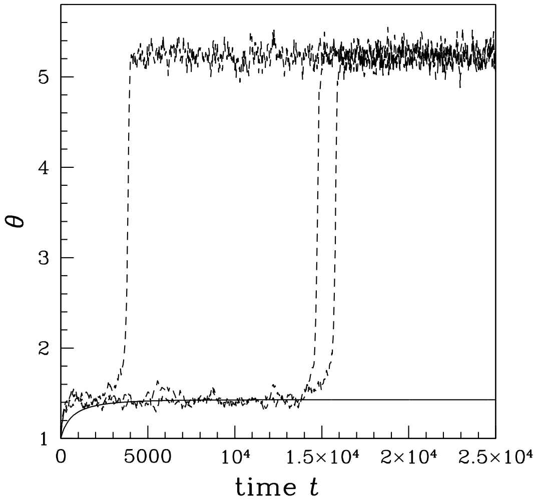

Fig. 3. Temperature θ as a function of time in the bistable domain with $\varepsilon = 4.5$ and $\gamma = 0.1$. The dashed lines are three stochastic realisations obtained by MC simulations of the master equation for $N = 10000$. The solid line is the deterministic evolution.

where function $U(\theta)$ is defined as:

$$\frac{dU}{d\theta} = -\frac{\alpha(\theta)}{\beta(\theta)} \,. \tag{27}$$

We calculate the mean escape time in a bistable system from the bottom of the left hand well, *i.e.* for $\theta = \theta_1$. Noting that a particle, in going over the barrier to the right well, takes most of the time in actually surmounting the barrier, function $U(\theta)$ is evaluated in the first integral by its expansion around θ_u:

$$U(\theta) \simeq U(\theta_u) - \frac{\alpha'(\theta_u)}{2\beta(\theta_u)}(\theta - \theta_u)^2 \,, \tag{28}$$

where $\alpha'(\theta) = \frac{d\alpha}{d\theta}$. In the second integral, function $U(\theta)$ is evaluated by its expansion around the local minimum θ_1 as follows:

$$U(\theta) \simeq U(\theta_1) - \frac{\alpha'(\theta_1)}{2\beta(\theta_1)}(\theta - \theta_1)^2 \,. \tag{29}$$

Following the standard steepest descent approximation, we extend the limits of the two integrations in Eq. (26) from $-\infty$ to $+\infty$. We finally obtain the following approximate value for the mean first passage time:

$$\tau = 2\pi \sqrt{\frac{\beta(\theta_u)}{\beta(\theta_1)|\alpha'(\theta_1)|\alpha'(\theta_u)}} \exp\Big(U(\theta_u) - U(\theta_1)\Big) \,. \tag{30}$$

The explicit expressions of the drift $\alpha(\theta)$ and diffusion term $\beta(\theta)$, given in Eqs. (18), (19), and the definition of function U, given in Eq. (27), have been used to compute τ in Fig. 4 for different values of particle number N. Four different approaches are compared in this figure showing the results of microscopic simulations using DSMC method, MC simulations of the master equation (15), the analytical prediction given in Eq. (30) and deduced from Fokker–Planck equation, and finally, the analogous analytical prediction deduced from the previous works of Baras *et al.* [25]. Figure 4 exhibits the expected exponential dependence of τ with the number of particles N.

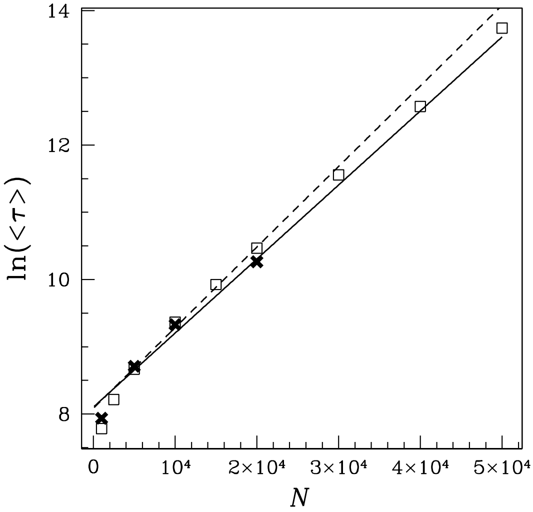

Fig. 4. Logarithm of mean first passage time $\langle\tau\rangle$ *versus* number of particles N. The squares show the results of MC simulations based on the master equation, the crosses depict the results obtained from microscopic DSMC simulations for the following parameter values: reduced activation energy $\varepsilon = 4.5$, Newtonian exchange coefficient $\gamma = 0.1$, reduced heat release $q = 5$, reaction steric factor $s_{\mathrm{r}} = 0.01$, ratio of mean free path and length of the system $\lambda/L = 0.5$. The solid line (resp. dashed line) is the analytical prediction deduced from the Fokker–Planck equation with our expression of $\beta(\theta)$ (resp. previous expression $\beta_1(\theta)$ of Baras *et al.* [25]).

The good agreement between the results of the master equation and microscopic simulations confirms the validity of the transition probabilities given in Eq. (11). However, the also satisfying agreement between these two approaches on one hand, and the approximate analytical results deduced from Fokker–Planck equations on the other, prove that the mean first passage time is not a very discriminating quantity. Note that the explicit expression of the transition rate for the Newtonian heat exchange is used to compute the diffusion term $\beta(\theta)$ in the Fokker–Planck equation. However, the deviation between the value of $\beta(\theta)$ deduced from our master equation and the previous results [25] $\beta_1(\theta)$ is not sufficient to lead to noticeable variations of the mean first passage time τ considered as a function of the number of particles N.

In the bistable domain, the height of the potential barrier between θ_1 and θ_2 increases with the coefficient for the Newtonian heat exchange γ. Accordingly, Eq. (30) predicts a rapid increase of τ with γ as shown in Fig. 5. As for the dependence on the number of particles, the analytical predictions for τ deduced from the Fokker–Planck equation, using either our expression of $\beta(\theta)$ or the previous value $\beta_1(\theta)$ of Baras *et al.* [25] are in good agreement with the mean first passage time deduced from MC simulations of the master equation (15). It is to be noted that the deviation between the analytical predictions of $\beta(\theta)$ and $\beta_1(\theta)$ increases with θ. In Section 3, these different approaches have already been used to characterize the fluctuations in the vicinity of the stationary state of high temperature, θ_2. They lead to well-defined differences and their comparison can be considered as a more reliable test of our expression of the master equation.

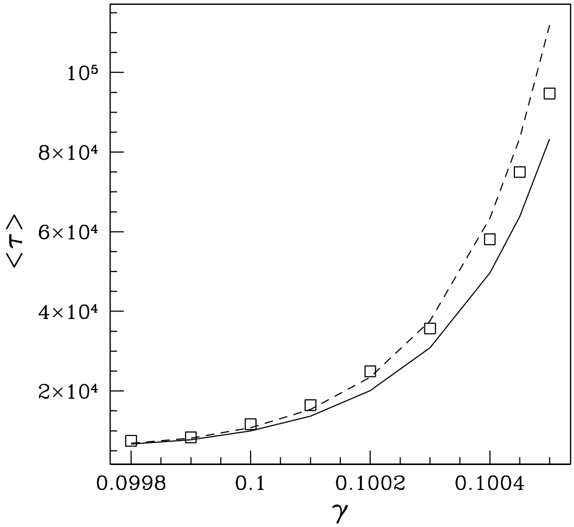

Fig. 5. Mean first passage time $\langle\tau\rangle$ *versus* distance from the bifurcation controlled by Newtonian exchange coefficient γ. The squares show the results of MC simulations based on the master equation for the following parameter values: reduced activation energy $\varepsilon = 4.5$, particle number $N = 10000$. The solid line (resp. dashed line) is the analytical prediction deduced from the Fokker–Planck equation with our expression of $\beta(\theta)$ (resp. previous expression $\beta_1(\theta)$ of Baras *et al.* [25]).

In order to directly check the major hypothesis on which our expression of the master equation relies, *i.e.*, the Maxwellian form of the distribution of particle velocities, we estimate in Fig. 6 the amplitude of the non equilibrium effects appearing when the chemical reaction and the cooling at the walls become faster. The control parameter chosen is the steric factor s_r for chemical reaction. Then the steric factor s_a for thermal accommodation follows from Eq. (6). All the other parameters are constant. In particular, the number of particles, *i.e.*, the fluctuation level is fixed. Using microscopic simulations based on DSMC method, we compute the kinetic energy of the particles when the system is stabilized around the stationary state of high temperature: we find that the absolute value of the relative deviation of temperature from its deterministic prediction, θ_2, increases with s_r. Moreover, the fourth order cumulant of the particle velocity distribution or kurtosis

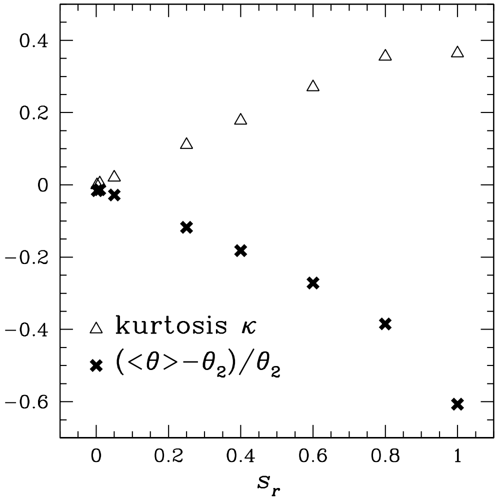

Fig. 6. Evaluation of the departure from partial equilibrium in microscopic DSMC simulations for the following parameter values: reduced activation energy $\varepsilon = 4.5$, Newtonian heat exchange coefficient $\gamma = 0.1$, reduced heat release $q = 5$, particle number $N = 1000$, ratio of mean free path and length of the system $\lambda/L = 0.5$. Variations with chemical steric factor s_r of the kurtosis κ of the particle velocity distribution (open triangles) and of the relative deviation $(\langle\theta\rangle - \theta_2)/\theta_2$ of the high temperature stationary state from its deterministic prediction θ_2 (crosses).

$$\kappa = \frac{\langle v^4\rangle - \frac{5}{3}\langle v^2\rangle^2}{\langle v^2\rangle^2} \tag{31}$$

increases with the speed of the processes. These nonvanishing values of the kurtosis reveal the lost of the Maxwellian shape of the particle velocity distribution in relation with the departure from partial equilibrium. Corrections to the deterministic temperature and kurtosis smaller than 1% are observed when the steric factor obeys $s_{\mathrm{r}} \leq 0.01$. The results of the microscopic simulations using DSMC method that are given in this paper have been obtained for the value $s_{\mathrm{r}} = 0.01$, which imposes already very slow processes and increases accordingly the duration of the simulations.

5. Conclusions

We have performed a mesoscopic description [11] of a thermochemical gaseous Semenov system in the bistable regime. Our approach is based on a master equation including a term for stochastic energy transfer, derived from the statistics of inelastic collisions between the gas particles and the thermostated walls. This transition rate takes into account the continuous spectrum of energy transferred in the Newtonian heat exchange, unlike transition functions for discrete populations of species in standard reaction-diffusion master equations. Consequently, the stochastic equation for the thermochemical system has a complicated integro-differential form, making hopeless any more rigorous analytical treatments. In order to solve this master equation for a continuous stochastic variable, we have extended the method of Monte Carlo simulations developed by Gillespie [17] for discrete variables in reaction-diffusion processes.

We have investigated the stochastic effects observed in the bistable regime and analyzed fluctuation-induced transitions between the two stable stationary states of the system. Different methods were used to compute the mean first passage time from one stationary state to another one: we have compared the results obtained from the master equation approach with those of microscopic simulations of the particle dynamics. The good agreement between the two series of results confirms the validity of the presented mesoscopic description. An analytical expression for the mean first passage time is determined using the Fokker–Planck equation deduced from the master equation. This approximate analytical treatment gives satisfying results, comparing well with the Monte Carlo simulations of the master equation.

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