

Stochastic effects in a thermochemical system with Newtonian heat exchangeB. Nowakowski^{1,*} and A. Lemarchand²¹*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*²*Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie, CNRS UMR 7600, 4, place Jussieu, 75252 Paris Cedex 05, France*

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We develop a mesoscopic description of stochastic effects in the Newtonian heat exchange between a diluted gas system and a thermostat. We explicitly study the homogeneous Semenov model involving a thermochemical reaction and neglecting consumption of reactants. The master equation includes a transition rate for the thermal transfer process, which is derived on the basis of the statistics for inelastic collisions between gas particles and walls of the thermostat. The main assumption is that the perturbation of the Maxwellian particle velocity distribution can be neglected. The transition function for the thermal process admits a continuous spectrum of temperature changes, and consequently, the master equation has a complicated integro-differential form. We perform Monte Carlo simulations based on this equation to study the stochastic effects in the Semenov system in the explosive regime. The dispersion of ignition times is calculated as a function of system size. For sufficiently small systems, the probability distribution of temperature displays transient bimodality during the ignition period. The results of the stochastic description are successfully compared with those of direct simulations of microscopic particle dynamics.

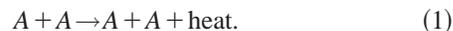
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I. INTRODUCTION

Fluctuations in far-from-equilibrium chemical systems are a subject of extensive studies due to their effects on nonlinear dynamics that are manifested at the macroscopic level. In investigations of stochastic properties, particularly convenient is the master equation formalism [1–3], which provides a description of fluctuations in terms of macroscopic coefficients—like reaction rates or diffusion constants—and allows us to avoid going into the complexity of underlying microscopic dynamics. This mesoscopic approach is well established for reaction-diffusion processes in isothermal systems [4], for which the master equation is extensively applied and verified by the results of microscopic simulations [5–7]. However, for thermal processes, the mesoscopic treatment is much less developed. The master equation has been formulated for energy fluctuations in a system with a uniform temperature gradient [8], but the result in its explicit form was inferred only with a reference to the deterministic dynamics. Along the lines applied to the description of diffusion process, fluctuating energy flows were expressed in terms of local thermodynamic variables. Another model of transport considered was the transfer of mass and energy in a diluted gas by the Knudsen mechanism [9,10]. The results obtained for spatial correlations of temperature in this simple system were successfully compared with the microscopic simulations [11]. For the fully microscopic level, molecular dynamics results were reported for oscillatory [12] and excitable [13] thermochemical systems in contact with a thermostat. A number of studies were also concerned with adiabatic chemical systems, but under the adiabatic constraint, the thermal state is not independent but is determined completely by chemical conditions.

In this paper, we develop a treatment of stochastic effects in the Newtonian energy exchange. We study, in particular, the Semenov thermochemical system [14]: A dilute gas closed in a container and subject to energy balance due to an exothermal chemical reaction in the bulk and the Newtonian heat transfer through a boundary surface. The temperature of walls of the container is assumed constant, fixed by an appropriately fast energy exchange with an external thermostat. As in the previous studies that focused on the stochastic thermal effects in chemical systems [9,10], it is convenient to consider the simplest feasible reaction scheme



Following the Semenov approximation, it amounts to neglect the depletion of reactants. In order to justify this approximation, one may regard Eq. (1) as an overall scheme for a two-step process: In a first step, the ground-state A_0 is excited to a higher-energy state A by irradiation by an external light source or interaction with the boundaries of container. The energy of excitation is subsequently released in bimolecular reactive collisions according to the second step $A + A \rightarrow A_0 + A + \text{heat}$. Reaction heat is transformed into translational energy of products. If the activation process is much faster than the second step, then the ground-state A_0 produced in this second step is immediately excited to A . Taking into account the disparity of time scales of the two steps, the intermediate form A_0 may be eliminated from the kinetic scheme [15], leading to the overall reaction (1). Accordingly, the intermediate species A_0 is also not considered in the stochastic approach. Note that the energy pumping from the exterior acts as a constraint maintaining the system out of equilibrium. The heat of reaction (1) is dissipated to the thermostat in the process of Newtonian cooling. In the Semenov

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model, the system is assumed homogeneous. For gaseous species, this approximation is justified if the mean free path is comparable with the size of the system so that the boundary layer extends over the whole volume. Then, a particle transfers energy between the wall and any part of the system effectively in a single free flight, without energy dissipation in intermediate collisions. Under such conditions, even the innermost parts of the system are effectively in direct thermal contact with the walls of the container. Considering this rarefied gas system, we neglect the effect of the temperature jump at the boundary [16], which must be included in the continuum description of thermal transfer in the inhomogeneous Semenov system [17].

In the next section, we derive the master equation for the probability distribution function of temperature of the gaseous Semenov system. Besides the usual term for the chemical reaction, it also includes a specific transition function related to the Newtonian heat exchange with the thermostat. As any analytical treatment of this equation is extremely difficult, we resort to Monte Carlo simulations. In Sec. III, we present the method of simulations based on the master equation, as well as simulations of the diluted gas system at the microscopic level, which was used to ascertain the developed stochastic description. In order to find conditions in which significant stochastic effects can be expected, we consider in Sec. IV the qualitative features of the deterministic dynamics of the Semenov system. The results of the two simulation methods for the system in the explosive regime are presented in Sec. V. Conclusions and the main results of this study are summarized in the last part of the paper.

II. THE MASTER EQUATION

Stochastic effects in the dynamics of the thermochemical system are related to the statistics of inelastic collisions of particles—either reactive with heat release or associated with accommodation and energy exchange with the walls of the container. Our main assumption is that inelastic collisions are much less frequent than elastic ones, which are thus sufficiently effective to maintain the Maxwellian form of the particle velocity distribution corresponding to the instantaneous temperature T of the system.

Inelastic collisions with the walls of the container contribute to energy transfer between the system and the thermostat, which is described by a specific, nonstandard term in the master equation. The rate, at which particles strike a unit surface of the wall, is given by the flux of particles in the outward direction at the wall surface. To be concrete, we take the positive x direction as outward normal to the surface element; a particular orientation is not relevant here since the Maxwellian distribution is isotropic. The rate $\nu_{out}(\mathbf{v})$ of collisions with the wall for particles with velocity around \mathbf{v} is then

$$\nu_{out}(\mathbf{v})d\mathbf{v} = n \left(\frac{m}{2\pi kT} \right)^{3/2} v_x \exp\left(-\frac{mv^2}{2kT} \right) d\mathbf{v}, \quad v_x > 0, \quad (2)$$

where n denotes the number density of particles. Alternatively, this equation indicates that particles striking the wall

have a biased Maxwellian velocity distribution, that is the Maxwellian one scaled by the velocity v_x normal to the wall. It is related to the effect that particles with a higher-velocity component in the x direction are more susceptible to collide with the wall. This is exactly the property expressed in the Boltzmann collision integral: the wall is “seen” by the gas molecules as a gigantic, immobile particle. The particles hitting the wall are accommodated to the temperature T_w of the wall with the probability s_a , which is a steric factor for thermal adaptation. Thus, $Ss_a\nu_{out}(\mathbf{v})d\mathbf{v}$ is a total accommodation rate of particles striking with velocity \mathbf{v} the entire surface S of the wall. The accommodated particles are immediately emitted from the wall and the distribution of their velocities \mathbf{v}' is given accordingly by the biased Maxwellian related to the temperature T_w of the wall. The normalized form of this distribution function is

$$\phi_w(\mathbf{v}') = \frac{1}{2\pi} \left(\frac{m}{kT_w} \right)^2 |v'_x| \exp\left(-\frac{mv'^2}{2kT_w} \right), \quad v'_x < 0. \quad (3)$$

The transition $\{\mathbf{v} \rightarrow \mathbf{v}'\}$ of particle velocity in an inelastic collision involves (i) accommodation of the particle at the wall surface and (ii) its subsequent emission with the corresponding final velocity. Consequently, the rate of transitions $w(\mathbf{v} \rightarrow \mathbf{v}')$ for particle velocities is composed of two factors: the total accommodation rate $Ss_a\nu_{out}(\mathbf{v})d\mathbf{v}$ for particles with incident velocities around \mathbf{v} , and the probability $\phi_w(\mathbf{v}')d\mathbf{v}'$ that after accommodation the particle emitted from the wall has a velocity around \mathbf{v}'

$$\begin{aligned} w(\mathbf{v} \rightarrow \mathbf{v}')d\mathbf{v}d\mathbf{v}' &= Ss_a\nu_{out}(\mathbf{v})d\mathbf{v} \times \phi_w(\mathbf{v}')d\mathbf{v}' \\ &= Ss_a n \left(\frac{m}{2\pi kT} \right)^{3/2} v_x \exp\left(-\frac{mv^2}{2kT} \right) \\ &\quad \times \frac{1}{2\pi} \left(\frac{m}{kT_w} \right)^2 |v'_x| \exp\left(-\frac{mv'^2}{2kT_w} \right) d\mathbf{v}d\mathbf{v}'. \end{aligned} \quad (4)$$

The transition rate for the system energy from \mathcal{E} to \mathcal{E}' includes the rates of transitions $w(\mathbf{v} \rightarrow \mathbf{v}')$ for all combinations of initial and final velocities that satisfy the energy constraint $\mathcal{E} - \mathcal{E}' = (1/2)(mv^2 - mv'^2)$. Thus, the rate of energy transitions in the Newtonian heat exchange is calculated from Eq. (4) as follows:

$$\begin{aligned} w_e(\mathcal{E} \rightarrow \mathcal{E}') &= Ss_a n \int_{v_x > 0} \left(\frac{m}{2\pi kT} \right)^{3/2} v_x \exp\left(-\frac{mv^2}{2kT} \right) \\ &\quad \times \int_{v'_x < 0} \frac{1}{2\pi} \left(\frac{m}{kT_w} \right)^2 |v'_x| \exp\left(-\frac{mv'^2}{2kT_w} \right) \\ &\quad \times \delta\left(\frac{1}{2}(mv^2 - mv'^2) - (\mathcal{E} - \mathcal{E}') \right) d\mathbf{v}d\mathbf{v}'. \end{aligned} \quad (5)$$

Due to the energy constraint in Eq. (5), the out- and in-flux of heat are not independent in the calculation of $w_e(\mathcal{E} \rightarrow \mathcal{E}')$. Rather, the heat influx from the thermostat arises as a response to the accommodation of energy at the boundary of

the system, and its magnitude is imposed by the energy constraint. Both of these flux components contribute jointly always to a single, elementary energy transition $\mathcal{E} \rightarrow \mathcal{E}'$. Therefore, our treatment of stochastic effects in the Newtonian heat transfer does not follow the approach applied usually to diffusion in the master equation [1,4]. In that usual description, adapted previously also to thermal processes [8–10], any volume element is treated as an independent source of outflux of matter (or energy), which results in an elementary transition. Rates of transitions depend then only on local thermodynamic variables for the volume element giving rise to the flux, unlike $w_e(\mathcal{E} \rightarrow \mathcal{E}')$ in Eq. (5), which depends on both the temperature of the system and the thermostat. For the assumed Maxwellian form of the velocity distribution, temperature is related to the energy of the ideal gas by $\mathcal{E} = (3/2)NkT$, where N is the number of particles in the system. Integration of Eq. (5) yields then the rate of temperature transition $\Delta T = T' - T$ in the Newtonian thermal exchange

$$w_e(T \rightarrow T + \Delta T) = S s_a n \left(\frac{kT}{2\pi m} \right)^{1/2} \frac{TT_w}{(T + T_w)^3} \times \left(2 + \frac{(T + T_w) \left(\frac{3}{2}N \right) |\Delta T|}{TT_w} \right) \times \frac{3}{2}N \begin{cases} \exp\left(-\frac{3}{2}N \frac{|\Delta T|}{T}\right) & \text{for } \Delta T < 0, \\ \exp\left(-\frac{3}{2}N \frac{\Delta T}{T_w}\right) & \text{for } \Delta T > 0. \end{cases} \quad (6)$$

The transition function given in Eq. (6) is mostly confined to the interval $-T/N < \Delta T < T_w/N$, which corresponds to an energy portion of the order of kT (kT_w), transferred in a single inelastic particle-wall collision. If $T > T_w$, transitions with $\Delta T < 0$ are more probable than the opposite ones with $\Delta T > 0$, and vice versa. This results in the average trend that constitutes the deterministic description of the Newtonian heat transfer: the temperature T of the system tends (at linear rate in the first approximation) to the thermostat temperature T_w . The deterministic dynamics is considered in some detail further in Sec. IV.

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]. That usual approach has been adopted in the very first approximation for the master equation with the term for Newtonian cooling [18]. The simplest description consists of assuming discrete temperature jumps of some fixed length, but the frequency of such hopping may only be determined by matching average rates to the deterministic description [18]. Reference to the deterministic dynamics was also necessary to obtain the explicit form for rates of thermal fluctuations in a system with uniform heat flow [8].

In contrast to the Newtonian heat transfer, exothermal reaction (1) gives discrete transitions of T , because always a

fixed portion of energy is released in a reactive collision. The reaction heat Q results in the increase of temperature by

$$\Delta T_r = Q / \frac{3}{2} Nk. \quad (7)$$

The transition rates are determined by the frequency of reactive collisions, calculated for the assumed Maxwellian velocity distributions of colliding particles. The rate of the thermally activated reaction includes the Arrhenius factor following from the barrier of activation energy E^* , and the steric factor s_r related to the probability of reaction imposed by the independent, steric condition. The transition rate for T due to chemical reaction (1) with these conditions is given by

$$W_r(T \rightarrow T + \Delta T_r) = V n^2 \sigma \left(\frac{4kT}{\pi m} \right)^{1/2} s_r \exp\left(-\frac{E^*}{kT}\right), \quad (8)$$

where σ denotes the total collisional cross section, and V is the volume of the system. The exclusion correction of the order of $1/N \ll 1$ has been omitted in Eq. (8).

It is convenient to introduce the complete transition function w , which includes both w_e for continuous transitions ΔT due to the heat exchange and W_r for fixed shifts ΔT_r related to reaction

$$w(T \rightarrow T + \Delta T) = w_e(T \rightarrow T + \Delta T) + W_r(T \rightarrow T + \Delta T_r) \times \delta(\Delta T - \Delta T_r). \quad (9)$$

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

$$\frac{\partial}{\partial t} P(T, t) = \int_{\Delta T < T} d(\Delta T) P(T - \Delta T, t) w(T - \Delta T \rightarrow T) - P(T, t) \int_{\Delta T > -T} d(\Delta T) w(T \rightarrow T + \Delta T). \quad (10)$$

The limits of the integrals in Eq. (10), imposed by the condition of positive temperatures, are rather formal as w_e is extremely small for $\Delta T \sim T, T_w$. The above master equation provides a well-founded ground to study fluctuations in the Semenov system, however, its complicated integro-differential form makes hopeless any more rigorous analytical treatment. We study the stochastic effects in the thermochemical system by means of Monte Carlo simulations appropriately based on Eq. (10). These mesoscopic results are verified by comparison with the simulations of the diluted gas system at the microscopic level, in which the velocity of each individual particle is followed.

III. METHODS OF MONTE CARLO SIMULATIONS

Monte Carlo (MC) simulations provide a convenient alternative approach when analytical results are not available. The simulation method of stochastic dynamics governed by a

master equation for discrete populations of chemical species is well founded [19]. However, it must be generalized here in the case of Eq. (10) which involves a continuous spectrum for temperature transitions due to the Newtonian heat exchange. Extending the standard approach, one may treat the integral over ΔT in Eq. (10) as a limit of sums over finite intervals $d(\Delta T)$. In this sense, ΔT is a continuous parameter for a variety of thermal processes, each with a specific fixed temperature change ΔT .

The simulation algorithm relies on 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 transition rate from the initial state is

$$W_{tot}(T) = \int d(\Delta T) w(T \rightarrow T + \Delta T) = S s_a n \left(\frac{kT}{2\pi m} \right)^{1/2} + V n^2 \sigma \left(\frac{4kT}{\pi m} \right)^{1/2} s_r \exp\left(-\frac{E^*}{kT}\right), \quad (11)$$

where the first term results from the Newtonian heat exchange and the second one from the exothermal reaction. Accordingly, the waiting time to exit from the state with temperature T is $\Delta t = 1/W_{tot}(T)$, or more exactly, it may be sampled from the exponential distribution $W_{tot}(T) \exp[-W_{tot}(T)\Delta t]$ characteristic for the Markovian processes [20]. 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. (11). Thus, the chance to select the reaction is W_r/W_{tot} , similar to the standard method [19], and the associated temperature increment is ΔT_r .

The selection of a transfer process related to the Newtonian heat exchange means a choice of temperature change ΔT sampled according to the continuous transition function w_e given by Eq. (6). To make the sampling easier, we can notice that w_e consists of two branches, one for positive and one for negative ΔT ; further, each of these two branches is a combination of the easy-for-sampling probability distributions $\exp(-x)$ and $x \exp(-x)$ for $x \sim |\Delta T|$. Using this partition in four (in total) functions, a two-step sampling following from the decomposition of probability distribution $w_e(\Delta T)/W_{tot}$ is easily applied. First, one of the four cases is selected with the probability g_i , which is the weight it contributes to W_{tot} , and subsequently, ΔT is sampled from the corresponding normalized probability distribution $p_i(\Delta T)$. Equation (6) yields the following probabilities g_i and distributions p_i of ΔT : For $\Delta T < 0$,

$$g_1 = S s_a n \left(\frac{kT}{2\pi m} \right)^{1/2} \frac{2T^2 T_w}{(T + T_w)^3} / W_{tot}, \quad (12)$$

$$p_1(x) = \exp(-x), \quad x = \frac{\frac{3}{2} N |\Delta T|}{T},$$

$$g_2 = S s_a n \left(\frac{kT}{2\pi m} \right)^{1/2} \frac{T^2}{(T + T_w)^2} / W_{tot},$$

$$p_2(x) = x \exp(-x), \quad x = \frac{\frac{3}{2} N |\Delta T|}{T}.$$

For $\Delta T > 0$,

$$g_3 = S s_a n \left(\frac{kT}{2\pi m} \right)^{1/2} \frac{2T T_w^2}{(T + T_w)^3} / W_{tot},$$

$$p_3(x) = \exp(-x), \quad x = \frac{\frac{3}{2} N \Delta T}{T_w},$$

$$g_4 = S s_a n \left(\frac{kT}{2\pi m} \right)^{1/2} \frac{T_w^2}{(T + T_w)^2} / W_{tot},$$

$$p_4(x) = x \exp(-x), \quad x = \frac{\frac{3}{2} N \Delta T}{T_w}. \quad (13)$$

The next transition is generated starting from the updated temperature $T' = T + \Delta T$ at current time $t' = t + \Delta t$, and the sequence of transitions forms then a stochastic trajectory of $T(t)$. The averages are calculated for ensembles of such trajectories.

The validity of the simulation results based on the master equation are examined by comparing with simulations of the dynamics at the microscopic level. We use the direct simulation Monte Carlo (DSMC) method developed by Bird [21] to simulate the evolution of the diluted gas system. In a homogeneous system, the positions of the particles may be disregarded, and their velocities are the only relevant variables. The form of the Boltzmann collision integral implies the rule of selection [21] of random $(1/2) V n^2 \sigma \langle |\mathbf{v}_k - \mathbf{v}_l| \rangle \Delta t$ pairs of particles (k, l) colliding in a time step Δt shorter than the mean time of free flight. We employ the molecular model of reactive hard spheres, widely used in microscopic simulations [22,23] and kinetic theory studies [24–26] of chemical systems. The total cross section $\sigma = \pi d^2$ is the same as for hard spheres with diameter d , but a part of it is connected with reaction. A collision is reactive (i) with the probability given by the steric factor s_r , and (ii) if the relative velocity $(\mathbf{v}_k - \mathbf{v}_l)$ 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. (8) 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 . In generation of 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. Treating the container walls just like an immobile target with a cross section S , random $(1/3) n S \langle |v_x| \rangle \Delta t$ particles are selected to collide with the surface normal to the x direction, and analogously for the two other orientations. Particles hitting the walls are either specularly reflected or thermally accommodated with the probability s_a . 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 given in Eq. (3) appropriate for collision direction.

Before proceeding to a description of the simulation results, we consider in more detail the properties of the dynamics of the thermochemical Semenov system. In particular, we are looking for the conditions in which considerable stochastic effects may be expected.

IV. REGIMES OF SYSTEM DYNAMICS

The features of the dynamics are easily captured in the framework of the deterministic description, which involves only the average rates of energy transitions. Heat production by the exothermal reaction (1) in the bulk yields a source term in the energy balance equation. The average frequency of reactive collisions gives the following rate of heat release:

$$\left\langle \left(\frac{d\mathcal{E}}{dt} \right)_r \right\rangle = QVn^2\sigma \left(\frac{4kT}{m} \right)^{1/2} s_r \exp\left(-\frac{E^*}{kT} \right). \quad (14)$$

The term related to the energy exchange with the thermostat is given by the average net energy flux at the wall surface. The average heat outflux accommodated on the walls of the container is calculated by means of the particle velocity distribution for temperature T of the system

$$\begin{aligned} \langle \mathcal{J}_E \rangle_{out} &= -Ss_{an} \int_{v_x > 0} \frac{mv^2}{2} v_x \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mv^2}{2kT} \right) d\mathbf{v} \\ &= -Ss_{an} \left(\frac{2kT}{\pi m} \right)^{1/2} kT. \end{aligned} \quad (15)$$

Similarly, the heat influx to the system is obtained from the velocity distribution at temperature T_w for particles emitted from the wall after accommodation

$$\begin{aligned} \langle \mathcal{J}_E \rangle_{in} &= Ss_{an_w} \int_{v_x < 0} \frac{mv^2}{2} |v_x| \left(\frac{m}{2\pi kT_w} \right)^{3/2} \exp\left(-\frac{mv^2}{2kT_w} \right) d\mathbf{v} \\ &= Ss_{an_w} \left(\frac{2kT_w}{\pi m} \right)^{1/2} kT_w. \end{aligned} \quad (16)$$

Concentration n_w in the distribution for emitted particles given in Eq. (16) is determined by the condition of vanishing of the mass flux. Equation $\langle v_x \rangle_{out} + \langle v_x \rangle_{in} = 0$ with the velocity distributions specific for the incident and emitted molecules results in the following relation:

$$n(kT)^{1/2} = n_w(kT_w)^{1/2}. \quad (17)$$

The source term (14) and the exchange terms (15) and (16), subject to condition (17), yield the following deterministic equation of energy balance:

$$\begin{aligned} \frac{d\mathcal{E}}{dt} &= n\sigma \left(\frac{4kT}{\pi m} \right)^{1/2} \left(QVn s_r \exp\left(-\frac{E^*}{kT} \right) \right. \\ &\quad \left. - \frac{1}{\sqrt{2}\sigma} Ss_a k(T - T_w) \right). \end{aligned} \quad (18)$$

As in the stochastic description, it is useful to introduce temperature instead of energy of the system. Convenient dimensionless thermal variables may be defined by

$$\theta = T/T_w, \quad (19)$$

$$\varepsilon = E^*/kT_w, \quad (20)$$

and

$$q = Q/kT_w. \quad (21)$$

Hereafter, we also use the dimensionless time scale

$$t4n\sigma s_r \left(\frac{kT_w}{\pi m} \right)^{1/2} \frac{Q}{kT_w} \rightarrow t. \quad (22)$$

Substitutions (19)–(21) and (22) reduce the number of independent relevant parameters. The deterministic equation in terms of the dimensionless variables has the following form:

$$\frac{d\theta}{dt} = \frac{1}{3} \sqrt{\theta} \left(\exp\left(-\frac{\varepsilon}{\theta} \right) - \gamma(\theta - 1) \right). \quad (23)$$

This equation involves only two parameters: the activation energy ε and the reduced coefficient for the Newtonian heat exchange

$$\gamma = \frac{S\lambda}{V} \frac{kT_w s_a}{Q s_r}, \quad (24)$$

where $\lambda = (\sqrt{2}n\sigma)^{-1}$ denotes the molecular mean free path. Parameter γ 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. (23) appears because the kinetic theory calculation reveals that the collision rates depend on the square root of temperature [16]. In the standard macroscopic description of the Semenov model, this weak dependence on $\sqrt{\theta}$ is omitted but it has already been included in previous microscopic treatments of thermochemical systems [17,12,13].

Equation (23) may also be obtained from the stochastic description. Using the master equation given in Eq. (10), the evolution of the average scaled temperature $\langle \theta \rangle$ is given by

$$\begin{aligned} \frac{d}{dt} \langle \theta \rangle &= \int_{\theta > 0} d\theta \int_{\Delta\theta < \theta} d(\Delta\theta) P(\theta - \Delta\theta, t) w(\theta - \Delta\theta \rightarrow \theta) \theta \\ &\quad - \int_{\theta > 0} d\theta P(\theta, t) \int_{\Delta\theta > -\theta} d(\Delta\theta) w(\theta \rightarrow \theta + \Delta\theta) \theta. \end{aligned} \quad (25)$$

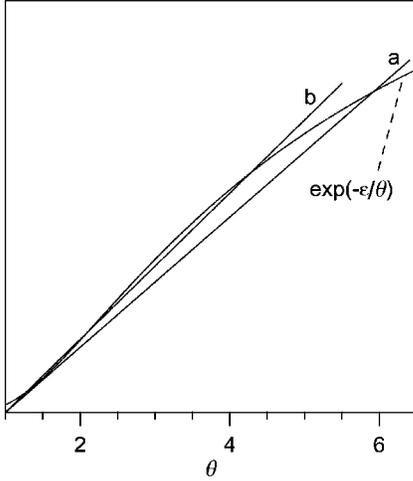


FIG. 1. The two terms of the right-hand side of the deterministic Eq. (23): $\exp(-\varepsilon/\theta)$ for $\varepsilon=4.5$, and the line $\gamma(\theta-1)$ for (a) $\gamma=0.095$ and (b) $\gamma=0.1066$. In case (a), the single intersection point of the two curves gives the unique stable state on the combustion branch. In case (b), there are three intersection points, the two extreme ones represent the stable stationary solutions (bistability), while the intermediate one corresponds to the unstable state.

After the change of variable $\theta' = \theta - \Delta\theta$ in the gain term, Eq. (25) may be transformed into

$$\frac{d}{dt}\langle\theta\rangle = \int_{\theta>0} d\theta P(\theta, t) \int_{\Delta\theta>-\theta} d(\Delta\theta) w(\theta \rightarrow \theta + \Delta\theta) \times [(\theta + \Delta\theta) - \theta]. \quad (26)$$

The deterministic dynamics is obtained by admitting that the probability distribution is extremely narrow so that the approximation $P(\theta, t) \sim \delta(\theta - \langle\theta\rangle)$ may be used. It reads

$$\frac{d}{dt}\langle\theta\rangle = \int_{\Delta\theta>-\theta} d(\Delta\theta) w(\langle\theta\rangle \rightarrow \langle\theta\rangle + \Delta\theta) \Delta\theta. \quad (27)$$

Using Eqs. (6), (8), and (9) for the transition rate, and performing integration over $\Delta\theta$, we obtain Eq. (23).

The schematic plot in Fig. 1 explains the well-known qualitative features [14,27,28] of the solution of deterministic Eq. (23). The regime of the deterministic dynamics depends on the relation between the production of reaction heat and the Newtonian cooling, given by the first and second term of the right side of Eq. (23), respectively. The line $\gamma(\theta-1)$ and the curve $\exp(-\varepsilon/\theta)$ may have either one or three intersection points [14] which correspond to the stationary solutions of Eq. (23). 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 the bifurcation points, at which the line $\gamma(\theta-1)$ becomes tangential to $\exp(-\varepsilon/\theta)$ at some θ_b . For a given ε , this condition yields the following critical values of γ :

$$\gamma_c^\pm = \frac{1}{4}\varepsilon \left(1 \pm \sqrt{1 - \frac{4}{\varepsilon}} \right)^2 \exp \left[-\frac{1}{2}\varepsilon \left(1 \pm \sqrt{1 - \frac{4}{\varepsilon}} \right) \right]. \quad (28)$$

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

V. STOCHASTIC EFFECTS IN THE EXPLOSIVE REGIME

Stochastic effects are manifested most prominently in regimes sensitive to even small perturbations, such as the vicinity of bifurcations [1,4]. Fluctuation-induced transitions between stable states in bistable systems [2,34] are widely studied stochastic phenomena of this kind. Less attention has been attracted by effects that may arise when system dynamics is in the vicinity of a bifurcation, but still in a monostable regime. This is the case we are interested in the present paper: we study the dynamics of the Semenov system for $|\gamma - \gamma_c^+| \ll \gamma$, though in the region $\gamma < \gamma_c^+$ below the bistability domain. As the system evolves from the initial condition $\theta(0) = 1$, the temperature increases, attracted by the unique stationary state on the combustion branch. However, the rate of this growth drastically falls down when the system passes through the region of θ where the two curves in Fig. 1 come nearly to the tangential point corresponding to bifurcation. At this instant, the right-hand side of Eq. (23) reaches the extreme, smallest values of the minimum, which is scaled by the small parameter $|\gamma - \gamma_c^+|$. The system passes then the induction stage, at which the dynamics of $\theta(t)$ is governed within the long-time interval by a slow mode. The characteristic violent evolution at the explosive stage comes only after the system has crossed the induction barrier. The effects of fluctuations on the system dynamics are the strongest in the induction period, when the deterministic trend is relatively the weakest. Stochastic properties of explosive thermochemical systems have been considered in theoretical [9,29] and experimental [30] works. In this paper on the features of stochastic explosive dynamics, we examine the validity of the master equation given by Eq. (10), which includes the specific term for the Newtonian cooling. In particular, we wish to check the predictions based on Eq. (10) by comparing them with the results of microscopic DSMC simulations.

We study the explosive system for $\varepsilon=4.5$, $q=5$, and $\gamma=0.096$, close to the bifurcation point $\gamma_c^+=0.09957, \dots$, for this ε . These parameters determine completely the conditions of the deterministic and stochastic dynamics. In the microscopic simulations, we take the length L of the cubic container equal to 2λ ; this fixes the geometrical factor in γ and consequently only one of the probability factors, let us choose s_r , is left as an independent parameter that scales the rates of the bulk and surface thermal processes. The reaction steric factor s_r should be small in order to ensure that reactive collisions are relatively rare, so that dominant elastic collisions are enough effective to restore the Maxwellian form of the velocity distribution function.

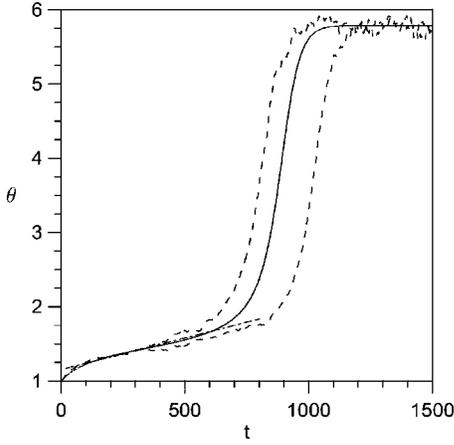


FIG. 2. Temperature θ as a function of time for the explosive system with $\varepsilon=4.5$ and $\gamma=0.096$. The solid line shows the solution of the deterministic Eq. (23), and the dashed lines give two examples of simulation results based on the master equation, for $N=10\,000$. The dashed-dotted line is a linear fit for $\theta(t)$ at the induction stage.

Figure 2 depicts $\theta(t)$ calculated from the deterministic Eq. (23) and two examples of stochastic trajectories obtained from the MC simulations based on the master equation. The long induction stage with its characteristic very slow evolution can be easily identified. The duration of the induction period diverges in the vicinity of the bifurcation point similar to $|\gamma_c - \gamma|^{-1/2}$ [9,31]. This slow mode is abruptly terminated as the system reaches the next, ignition stage, to which corresponds the steep slope of $\theta(t)$ demonstrating the violent increase of temperature. The high temperatures attained at the final, saturation stage 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, the model is useful to examine the description of fluctuations derived here in the Newtonian heat exchange. Moreover, our interest is mostly confined to the stochastic effects appearing at relatively low temperatures, at which the crossover from the induction to the ignition stage occurs. The slow deterministic dynamics in the induction period creates the most favorable conditions for development of significant fluctuation effects.

Figure 2 shows that even small fluctuation-induced deviations from the deterministic trajectory at the induction stage may result in a large dispersion of times at which the ignition temperature is reached. An approximate calculation may be used to evaluate the spread of stochastic trajectories around the deterministic (mean) value in the induction period. The following equations for the moments of the distribution function are easily derived from Eq. (10) in the same way as Eq. (26) for the mean temperature

$$\frac{d}{dt}\langle\theta^k(t)\rangle = \int d\theta P(\theta, t) \int d(\Delta\theta) w(\theta \rightarrow \theta + \Delta\theta) \times [(\theta + \Delta\theta)^k - \theta^k]. \quad (29)$$

In comparison to P , the transition rate w is a slowly varying function of θ and may be evaluated using the instantaneous

mean value $\langle\theta(t)\rangle$. Equation (29) yields then the following equation for the dispersion of stochastic trajectories around the mean value:

$$\frac{d}{dt}\langle(\theta^2(t)) - \langle\theta(t)\rangle^2\rangle = \int d(\Delta\theta) w(\langle\theta\rangle \rightarrow \langle\theta\rangle + \Delta\theta) (\Delta\theta)^2. \quad (30)$$

Further approximation may be applied in the induction period, because the temperature remains then nearly constant and the right-hand side of Eq. (30) may be evaluated at a mean value $\bar{\theta}$ in this time interval. Thus, Eq. (30) describes the diffusive spreading of θ around the mean value $\langle\theta\rangle$ according to

$$\frac{d}{dt}\langle(\theta - \langle\theta\rangle)^2\rangle = 2D_{\bar{\theta}}, \quad (31)$$

where the time-independent diffusion coefficient is calculated using the transition rate given in Eq. (9). It reads,

$$D_{\bar{\theta}} = \frac{1}{9N} \sqrt{\bar{\theta}} [\gamma(3 - 4\bar{\theta} + 3\bar{\theta}^2) + qe^{-\varepsilon/\bar{\theta}}]. \quad (32)$$

If the induction period lasts for time τ_n , then the final mean deviation from the deterministic temperature in this time interval reaches the value $\Delta\theta_n = \sqrt{2D_{\bar{\theta}}\tau_n}$. Even a small uncertainty $\Delta\theta_n$ may result in a relatively large dispersion Δt_g of times at which the system attains the ignition temperature θ_g and undergoes switching to the explosive evolution. This amplification effect of small stochastic perturbations is related to the slow dynamics at the induction stage. The spread of ignition times may be estimated on the basis of a simplified dynamics [32]. Let us approximate the deterministic trajectory at the induction stage by the linear growth of $\theta(t)$ with a characteristic small slope (cf. Fig. 2). At the induction period, temperature increases from θ_0 to the ignition temperature θ_g during the time τ_n , so the slope of $\theta(t)$ in this region is $\alpha = (\theta_g - \theta_0)/\tau_n$. The dispersion of ignition times may then be evaluated as follows:

$$\Delta t_g = \Delta\theta_n / \alpha = \left[\frac{2}{9N} \sqrt{\bar{\theta}} (\gamma(3 - 4\bar{\theta} + 3\bar{\theta}^2) + qe^{-\varepsilon/\bar{\theta}}) \right]^{1/2} \times \tau_n^{3/2} / (\theta_g - \theta_0), \quad (33)$$

where the diffusive spread $\Delta\theta_n$ is calculated using the diffusion coefficient given in Eq. (32). The predictions of this equations, in particular the scaling law $1/\Delta t_g \sim \sqrt{N}$, may be examined by the numerical results for the reciprocal $1/\Delta t_g$ in Fig. 3, obtained from the MC simulations for systems with various particle numbers N . From Fig. 2, we evaluate $\theta_0 = 1.25$, $\theta_g = 1.75$, $\bar{\theta} = 1.5$, and $\tau_n = 550$. Equation (32) then yields $D_n \approx 0.0833/N$, and relation (33) results in the scaling $1/\Delta t_g \approx 9.5 \times 10^{-5} \sqrt{N}$. This rough evaluation is in very good agreement with the fit $1/\Delta t_g = 9.9 \times 10^{-5} \sqrt{N}$ obtained from the MC results in Fig. 3. More exact statistics of ignition times could be calculated from the backward master equation [33], but it has a complicated integro-differential form simi-

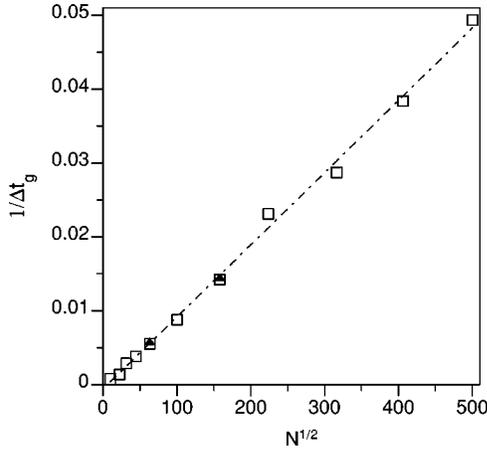


FIG. 3. Reciprocal $1/\Delta t_g$ of the standard deviation for ignition time, $\Delta t_g = \sqrt{\langle t_g^2 \rangle - \langle t_g \rangle^2}$, for systems with various particle numbers N . The squares show the results of MC simulations based on the master equation, the triangles depict the data obtained from the microscopic DSMC simulations for the following parameter values: reduced activation energy $\varepsilon=4.5$, Newtonian exchange coefficient $\gamma=0.096$, reduced heat release $q=5$, reaction steric factor $s_r=0.01$, ratio of mean free path and length of the system $\lambda/L=0.5$. The dashed-dotted line is a linear fit of $1/\Delta t_g$.

lar to Eq. (10). Figure 3 displays also the results of microscopic DSMC simulations obtained for the reaction steric factor $s_r=0.01$. The DSMC data agree with the corresponding results based on the master equation. Effectiveness of the microscopic simulations decreases in comparison to the mesoscopic simulations as the probability of inelastic collisions becomes smaller, since both elastic and reactive collisions must be generated in the microscopic approach. This prevented us from reaching in the DSMC simulations the range of such large N as in the mesoscopic treatment.

In order to study the peculiarity of the temperature distribution during the ignition process, we present in Figs. 4 and

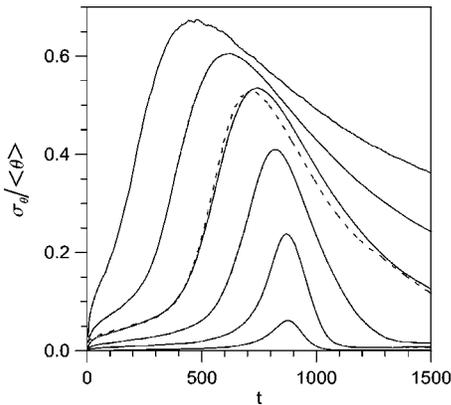


FIG. 4. Standard deviation of temperature distribution $\sigma_\theta = \sqrt{\langle \theta^2 \rangle - \langle \theta \rangle^2}$ scaled to the mean value $\langle \theta \rangle$ as a function of time. The solid lines from uppermost to lowermost show results of the MC simulations of the master equation for systems with the following particle numbers $N=100, 500, 2000, 10\,000, 50\,000, 1\,250\,000$. The dashed line gives the data from microscopic DSMC simulations for $N=2000$ and the same parameter values as in Fig. 3.

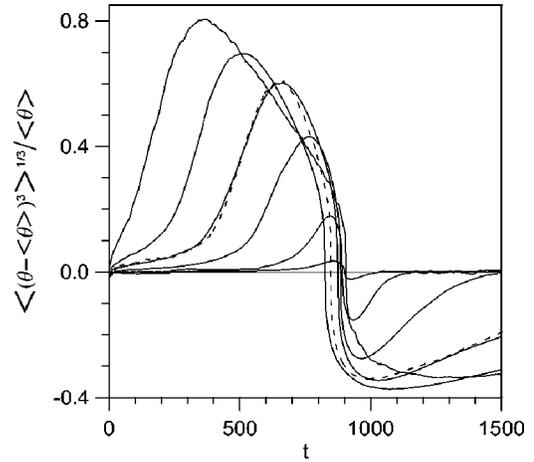


FIG. 5. Third central moment of temperature distribution $\langle (\theta - \langle \theta \rangle)^3 \rangle^{1/3}$ scaled to the mean value $\langle \theta \rangle$ as a function of time. Same notation and parameter values as in Fig. 4.

5 the evolution of quantities related to the second and third central moments of $P(\theta, t)$, respectively, for systems with various particle numbers N . The results are divided by $\langle \theta(t) \rangle$, because Eq. (32) implies the relation $D_\theta \sim \theta^2$ as a rough approximation for the dependence of temperature dispersion on θ . Due to the choice of the very low-reaction steric factor $s_r=0.01$, only the results for $N=2000$ particles have been available for us in the microscopic DSMC simulations, and these data agree very well with the results of the mesoscopic approach. For a system in a monostable regime, the method of large volume expansion [34] predicts that a distribution function of stochastic variable has the Gaussian shape (with a time-dependent dispersion) around a deterministic solution. Figure 4 shows that the dispersion increases at the ignition stage, what may be explained by the stretching of the temperature distribution by the fast dynamics in this period. However, the third central moment of P displayed in Fig. 5 does not remain always small, as it should for an approximately Gaussian distribution, but during the ignition period, it increases up to abnormally high values and is quite comparable to the dispersion. This effect evidently reveals a large deviation from the expected Gaussian shape of the distribution. It arises because the high-temperature tail of the distribution is extended by the fast dynamics in the ignition region. Considering the statistical ensemble at a certain moment in the induction period, it is easy to imagine that while most of the systems still remain in the induction stage, some of them reach the ignition temperature earlier and rapidly move away from the mainstream due to a fast temperature increase at the ignition stage. This high-temperature tail results in an asymmetry of the distribution, which is seen in Fig. 5 as a prominent positive value of the third central moment of the distribution.

Figure 6 displays the mean deviation of temperature at $t=650$ as a function of number N of particles in the system. According to the deterministic evolution depicted in Fig. 2, for this t , the system is about to finish the induction stage. For large systems, the data in Fig. 6 follow the scaling $\sigma_\theta / \langle \theta \rangle \sim 1/\sqrt{N}$, consistent with the Gaussian form of the dis-

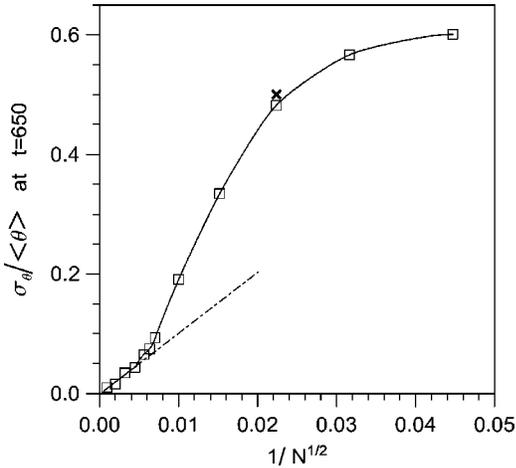


FIG. 6. Scaled standard deviation of temperature distribution $\sigma_\theta / \langle \theta \rangle$ at $t=650$ for systems with various particle numbers N . The squares represent the results of the MC simulations based on the master equation and the cross shows the data obtained from the microscopic simulations. The dashed-dotted line is a linear fit for the scaling $\sigma_\theta / \langle \theta \rangle \sim 1/\sqrt{N}$, calculated for $N \geq 50\,000$. Same parameter values as in Fig. 3.

tribution. However, the deviation from this asymptotic law develops abruptly beginning from $1/\sqrt{N} \approx 0.006$. For this $N \approx 3 \times 10^4$, Fig. 3 gives the dispersion of ignition times $\Delta t_g \approx 60$, so that some systems of the ensemble evolve already according to the advanced time $t' = t + \Delta t_g = 710$. This is approximately the moment that the deterministic solution in Fig. 2 begins the ignition stage. Thus, at $t=650$, the upper limit of temperature distribution for $N \approx 3 \times 10^4$ attains the ignition temperature and the high-temperature tail is formed due to the stretching by the fast ignition dynamics. Since the extension of the high-temperature part of distribution is eventually terminated by attraction of the “probability mass” to the unique stationary state, such evolution may result in the transient bimodality of the distribution function [35–37,29]; two maxima of P may temporarily coexist, one corresponding to the usual concentration around the deterministic solution at the induction stage and the other one related to the single dynamics’ attractor that gathers the systems that already passed the ignition stage. Such a specific effect may arise only if mean deviation of ignition times is larger than half the duration of the ignition stage. The deterministic solution in Fig. 2 gives for the latter one $\tau_g \approx 250$, and then Fig. 3 shows that the transient bimodality develops for systems with $N < 6000$.

The bimodality of the distribution may be demonstrated using the approximate distribution function, obtained by averaging P within several intervals

$$\bar{P}_i(t) = \frac{1}{\theta_i - \theta_{i-1}} \int_{\theta_{i-1}}^{\theta_i} P(\theta, t) d\theta. \quad (34)$$

If the intervals cover from θ_0 to $\theta_{i_{\max}}$, the whole range of θ , such defined function $\{\bar{P}_i(t)\}_{i=1, \dots, i_{\max}}$ gives a useful approximation for the full $P(\theta, t)$. The distribution function

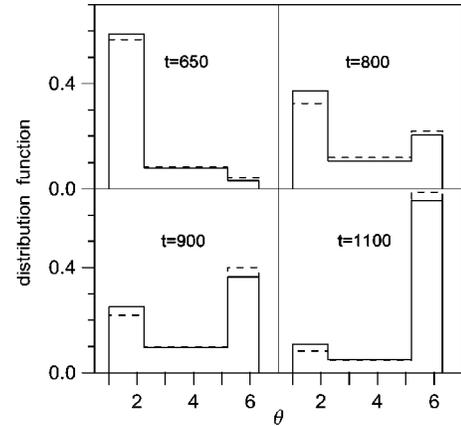


FIG. 7. Interval-averaged distribution function of temperature (34) at various times for the system with $N=2000$ particles. The solid lines depict the results of the MC simulations based on the master equation, and the dashed lines show the data obtained from the DSMC microscopic simulations for the same parameter values as in Fig. 3.

given in Eq. (34) may be calculated with a relatively good accuracy on the basis of a much smaller statistical ensemble than that necessary to obtain the detailed form of $P(\theta, t)$. The following limits of the intervals are suitable to show the bimodality of the distribution function during the ignition process: (i) from $\theta_0=1$ to $\theta_1=2.25$ for the range of θ at the induction stage, (ii) from θ_1 to $\theta_2=5.25$ for the region passed during the ignition period, and (iii) from θ_2 up to $\theta_3=6.3$ for the domain around the stable steady state at $\theta_s \approx 5.7856$. Figure 7 displays such interval-averaged distribution function \bar{P} for a system with $N=2000$ particles, at four times close to the mean ignition time. The bimodal form of the distribution function clearly arises for intermediate times, before the final collapse of the “probability mass” onto the unique attractor θ_s . Worth to note in Fig. 7 is the very good agreement between the results of the mesoscopic simulations and the data obtained from simulations at the microscopic level for $s_r=0.01$. This provides us a valuable confirmation of the validity of the developed mesoscopic treatment, because the shape of the distribution function (even the approximate one) is a sensitive test in calculation of stochastic variables.

VI. CONCLUSIONS

We have developed the mesoscopic description of a thermochemical gaseous system subject to the Newtonian heat exchange between the homogeneous system interior and the walls thermostated by the external medium. It is based on the master equation including the term for stochastic energy transfer, derived from the statistics of inelastic collisions between 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 solutions. In order to treat this master equation for the continuous stochastic variable, we extended the method of Monte Carlo simulations developed for discrete variables in reaction-diffusion processes.

We considered in detail the Semenov thermochemical model in the explosive regime; in particular, we investigated the stochastic effects in the ignition process. We calculated the dispersion of ignition times and two moments of the temperature distribution function that demonstrate the peculiarity of the stochastic evolution of the explosive system. The developed mesoscopic treatment of thermochemical systems allowed us to study such a subtle stochastic effect such

as transient bimodality of the temperature distribution function. The good agreement between the results deduced from the Monte Carlo simulations of the master equation and from the direct simulations of the microscopic particle dynamics confirms the validity of the presented mesoscopic description.

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