Validity of Macroscopic Rate Equations in Exothermic Chemical Systems

F. Baras and M. Malek Mansour
Faculté des Sciences, CP 231, Université Libre de Bruxelles, Boulevard du Triomphe,
B-1050 Brussels, Belgium
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A molecular-dynamics computer experiment is set up to study the stationary properties of an exothermic gas-phase chemical system. A discrepancy is observed between the results of the simulation and predictions from macroscopic chemical kinetics. The origin of this discrepancy is found to arise from the deformation of the Maxwell distribution by reactive collisions. Quantitative agreement with the corrected rate law is established.

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The traditional formulation of macroscopic physics rests on the strict validity of the local equilibrium assumption. The theoretical description of most of the familiar phenomena of nonlinear physics, such as hydrodynamical and chemical instabilities, turbulence, combustion, etc., is based on this fundamental hypothesis. In this paper we show for a particular, though representative case, that deviations from local equilibrium can nevertheless be expected.

Consider first a dilute mixture of molecules undergoing the isothermal reaction:

$$A+A\xrightarrow{k}B+C\,, \tag{1}$$

where the rate constant k obeys the Arrhenius law,

$$k\sim\exp\{-E/k_BT\}\,, \tag{2}$$

E and k_B being the activation energy and the Boltzmann constant, respectively. A reactive collision occurs if the colliding particles have "enough" energy, i.e., if the kinetic energy of the relative motion before collision exceeds some threshold related to the activation energy E. This will give rise to a transfer of translational energy from the reacting particles A to the outgoing particles B and C. If the ratio E/k_BT is large enough, the rate of reactive collisions is much smaller than the elastic ones and the high-velocity tail of the Maxwell-Boltzmann distribution is replenished as fast as it is depleted by reactive encounters. There exists, however, a range of activation energy (or temperature) for which the rate of reaction can become comparable to the rate of thermal equilibration. Consequently, one may expect a slowing down of the reaction speed as compared to the usual macroscopic rate law, based on the equilibrium hypothesis.

Pioneering calculations along these lines were made by Prigogine and Xhrouet,[1] who solved the Boltzmann equation for the reaction scheme (1) to obtain a first-order correction to the corresponding reaction-rate formula. Further work by Present[2] and by Ross and Mazur[3] has led essentially to the same results. The main conclusion was that for realistic systems the deviations from equilibrium theory remain within the uncertainties associated with collision diameters and steric factors.

The situation may be different for nonisothermal reactions. Consider, for instance, the following exothermic gas-phase reaction,

$$F+S\xrightarrow{k}B+S+\text{heat}\,, \tag{3}$$

expressing the transformation of "fuel" particles F to "burned" particles B through the reactive collisions with "solvent" particles S. In addition to the above-mentioned effects, the heat released by the reaction will further increase the energy of the S particles which may well recollide with another F particle before being completely thermalized. If the reaction is fast enough, this continuous flow of energy from F to S particles may cause a non-negligible perturbation of the equilibrium distribution which in turn can modify significantly the phenomenological rate equations. This problem was analyzed in detail by Prigogine and Mahieu in 1950, using a Chapman-Enskog type of approach[4] (see also Ref. 1). In addition to the deformation of the Maxwell distribution occurring already in the isothermal case, it was found that further deviations from the usual rate law are now scaled by the value of heat of reaction relative to the thermal energy. It is reasonable to expect that such effects can become important, particularly in explosive systems where, in addition, the reaction is strongly accelerated.

To our knowledge there exists so far no experimental evidence for these effects. Indeed, combustion in exothermal chemical systems is, in general, quite difficult to handle, partly because it is often accompanied with the appearance of flame fronts or of hydrodynamic effects, and partly because the precise knowledge of the underlying mechanism is very difficult to establish. A deviation from a given macroscopic theory can thus always be attributed to the incomplete knowledge of the reaction mechanism or, perhaps, to the intervention of transport or hydrodynamic effects. One alternative for overcoming these difficulties is to perform molecular-dynamics (MD) computer experiments.

With the ever increasing computational power of modern computers, the MD techniques are becoming a valuable tool in bridging the gap between the analysis of large-scale macroscopic phenomena and their modeling at the microscopic level. For a long time the main effort has been concentrated in the study of nonreactive fluids.[5] A first attempt to simulate isothermal chemical reactions was done in 1975 by Portnow.[6] More complete work by Ortoleva and Yip[7] and by Boissonade[8] followed in 1976 and 1979, respectively, in which measurement of the composition fluctuations in nonequilibrium isothermal chemical systems has been reported (see also Ref. 9).

The first MD simulation of an exothermic chemical system was performed by Chou and Yip[10] for a hard-disk system in contact with thermal reservoirs and undergoing the following reaction:

$$A+A \xrightarrow{k} A+A+\text{heat}. \qquad (4)$$

The above scheme simulates optimally the so-called Semenov model of combustion in which the consumption of reacting particles is neglected.[11] Although the observed temperature profiles were in qualitative agreement with the macroscopic predictions, an important quantitative discrepancy was noted by the authors. A possible suggestion for this discrepancy was the nonnegligible temperature slip at the thermal walls. Our principal objective here is to show that the deviations from macroscopic law observed by Chou and Yip can be explained by the deformation of the local equilibrium distribution.

Despite its extreme simplicity, the Semenov model exhibits much of the complexity of realistic systems. In particular, for sufficiently low reservoir temperature, it leads to two stable states corresponding to "normal" and explosive behavior of the system.[12] For this reason, we concentrate our study on the model of Eq. (4). For the simulation, we use the Bird algorithm[13] which is especially well adapted for the study of dilute gases. Its main difference with the traditional MD experiments consists in a stochastic treatment of the collision processes which increases significantly the efficiency of the computation.

We consider a system made of an assembly of $N = 4000$ hard spheres of diameter d confined in a rectangular box of length $L_X = 20\lambda$ in the X direction and cross section $(1\times 1)\lambda^2$ in the Y and Z directions, leading to a number density of $n = 200/\lambda^3$. Here λ denotes the mean free path. The walls located at $X=0$ and $X=L_X$ act as thermal reservoirs: Each time a particle hits one of these walls, it is reinjected into the system having its velocity sampled from a local Maxwellian at the reservoir temperature. Periodic boundary conditions are assumed in the other directions. In what follows, the energy will be scaled by the equilibrium (reservoir) thermal energy so that the reservoir temperature $T_R = 1$. For the reactive cross section, we use a procedure set up by Present[2] which is slightly different from the one described in Refs. 1 and 4. It has the advantage of leading to the correct Arrhenius law in dilute systems.[14] The system is further divided into forty "statistical" cells in the X direction over each of which a space averaging is performed to give instantaneous values of the basic mechanical quantities. A time averaging then leads to the local macroscopic quantities, such as temperature, pressure, etc.

We start our simulation by considering a heat reaction $q = 2k_BT_R$. The activation energy will always be set to $E = 7k_BT_R$. It can be checked from macroscopic analysis of the Semenov model that for the above values of the parameters the system exhibits two well separated stable states corresponding to "cool" and "hot" (explosive) behavior.[11] The study of the transition between these states is an interesting problem which will be addressed in another communication. Here we concentrate on the properties of the cool state which can be reached by setting the initial value of the system's temperature close to the reservoir temperature.[15]

The program was run in a Cyber 855 and a time average over the last 10^5 collisions per particle (CPP) was performed, after the stationary state has been reached (about 10^4 CPP). The measured temperature profile is presented in Fig. 1 where the macroscopic result is also depicted. The statistical error, estimated from successive runs of 10^4 CPP, does not exceed 0.2%. As can be seen, there exists a large temperature slip at the boundaries and a significant difference with the macroscopic profile, all in qualitative agreement with the results of Ref. 10. A simple way to deal with the temperature slip is to set

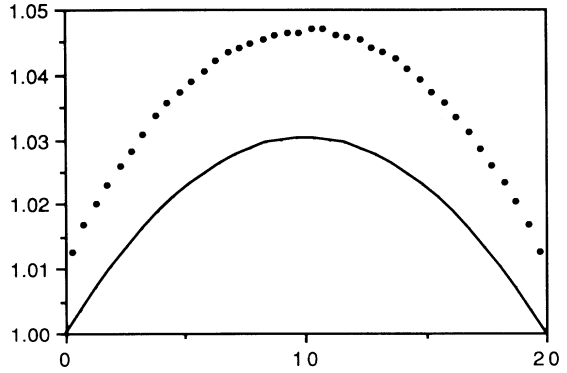

FIG. 1. Stationary temperature distribution for the model (4). The solid circles denote the MD data while the solid line represents the numerical solution of the macroscopic equation:

$$qv_0 + (\partial/\partial x)\kappa(\partial/\partial x)T = 0,$$

where $\kappa = (75/64d^2)(k_B^3T/\pi m)^{1/2}$ represents the thermal conductivity coefficient. $q/k_BT_R = 2$, $L_X = 20\lambda$, and v_0 is given by Eq. (6).

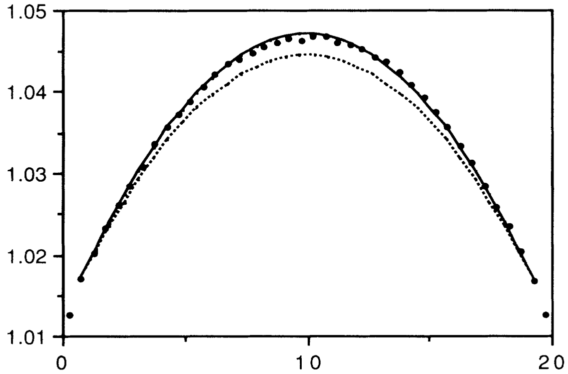

FIG. 2. Stationary temperature distribution for the model (4). The solid circles denote the MD data while the solid and the dashed lines represent the numerical solution of the macroscopic equation with and without correction, Eq. (5), respectively. The parameters are the same as in Fig. 1.

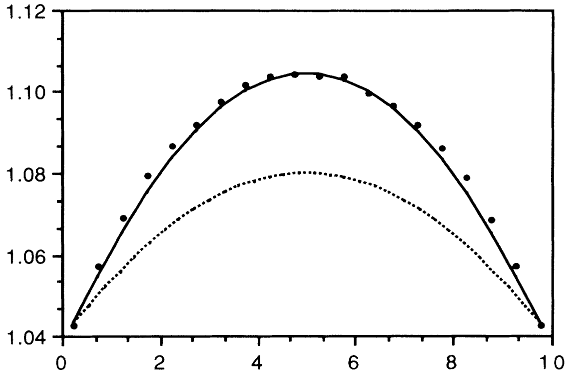

FIG. 3. Stationary temperature distribution for the model (4), with $q/k_BT_R=8$ and $L_X=10\lambda$. See captions of Figs. 1 and 2 for details.

the boundary-value problem in the macroscopic equation according to the actual value of the temperature measured in the extreme cells. As can be seen in Fig. 2, much better results are obtained by this procedure, which confirm partly the conclusions presented in Ref. 10. However, the improvement is not enough to resolve the discrepancy with the simulation data. This is particularly clear in Fig. 3, where the results obtained for a larger value of the heat of reaction, $q=8k_BT_R$, are depicted. Note that in order to remain in the "nonexplosive" state, we had to reduce the system size to $L_X=10\lambda$ ($N=2000$) in this latter case.

One possibility for the explanation of the simulation results is the interference with hydrodynamical effects. To check this, we first note that although microscopically we are dealing with a three-dimensional system, the measured macroscopic data concern effectively a one-dimensional system since $L_X \gg L_Y, L_Z$. A transport by advection will therefore affect necessarily the pressure profile in the X direction. The latter is found to be constant in all our computer experiments, thus eliminating the possibility of the presence of pressure waves across the system. Besides, one of the principal factors at the origin of thermal convection, namely the gravitational field, is absent in our simulations. To be complete, we have also measured the static velocity-temperature correlation function in the X direction and found it to be zero. We therefore conclude that the hydrodynamical effects, if any, could not exceed the statistical error (0.2%), which is far below the observed discrepancy, especially for $q=8k_BT_R$ (see Fig. 3).

To proceed further, we compute the correction to the macroscopic rate law, using the method described in Ref. 4. The calculations are tedious and lengthy and will be reported elsewhere. We report only the final result for the corrected reaction rate:

$$v=v_0\left\{1+X_A^2\frac{e^{-E/k_BT}}{8}\left(\frac{E}{k_Bt}\right)^2\frac{q}{k_BT}\left[\left[\left(\frac{E}{k_BT}-\frac{3}{2}\right)+\frac{1}{2}\left(\frac{q}{k_BT}\right)\right]\right]\right\}, \tag{5}$$

where X_A denotes the molar fraction of the reacting particles A. Since we are dealing with a one-component system, $X_A=1$. v_0 represents the usual macroscopic rate law:

$$v_0=\tfrac{1}{2}\nu n e^{-E/k_BT}, \tag{6}$$

where ν is the collision frequency, $\nu=4nd^2(\pi k_BT/m)^{1/2}$, and the factor $\frac{1}{2}$ takes account of the fact that the reaction involves a pair of the same particles. Note that the correction to v_0 increases with the heat of reaction, as was expected from our earlier discussion of model (3). Indeed, the correction is about 1% for $q=2k_BT_R$ and increases to 6% for $q=8k_BT_R$. The macroscopic temperature profile computed from the corrected rate law (5) is now in very good agreement with the simulation result (see Figs. 2 and 3). This is also the case for one further simulation that we have performed ($q/k_BT_R=6$, $L_X=10\lambda$).

Our result clearly establishes the deformation of the Maxwellian distribution and its implication in limiting the validity of the usual macroscopic rate law. It also demonstrates the applicability of the Chapman-Enskog perturbation techniques to handle the problem. The above conclusions, however, leave many questions open. For example, is it likely that even more important deviations from equilibrium theory occur during the explosion stage? Are the chemical processes influencing the transport coefficients? How are the results modified in more dense media?

The last two questions have been considered recently by Cukrowski and Popielawski in a series of papers dealing with isothermal chemical systems.[16] Interesting results concerning the modification of transport coefficients have been derived for reactive Boltzmann and Enskog gases.[17] The above results, however, show some quantitative discrepancy with previous work where the Grad moment technique has been used.[18,19] Molecular dynamics is certainly one of the simplest ways to check the validity of these results and to clarify eventually the origin of the discrepancy between the different approximation techniques. Work on this direction is in progress.

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