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Microscopic simulation of chemical oscillations in homogeneous systems

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A microscopic computer experiment is set up to investigate the statistical properties of far from equilibrium homogeneous chemical systems undergoing instabilities. Sustained periodic behavior of limit cycle type is observed. Both the frequency and the amplitude of the oscillations are found to be in good agreement with the macroscopic description. A comparison with the stochastic theory of chemical systems based on master equation formalism is also carried out. The dynamical and static correlation functions obtained by these two procedures are in very good agreement.

I. INTRODUCTION

There is a growing interest in molecular dynamics (MD) simulations of complex macroscopic systems.¹ So far, the main effort has been concentrated in hydrodynamic phenomena such as shock waves,² flow past an obstacle,³ or Bénard convection.⁴ The study of chemically reacting systems via MD has been primarily devoted to verifying fluctuation theory.⁵⁻⁸ In this paper we report on the observation of sustained chemical oscillations in a microscopic simulation involving a dilute gas of hard spheres.

In an oscillating system, the period of oscillation is a macroscopic quantity which depends on rate constants and chemical concentrations. The existence of such a macroscopic time scale implies that there are many reactive collisions per period and thus a high computational cost. To overcome this difficulty, we limit ourselves to the particular particle simulation method pioneered by Bird, which turns out to be 100 to 1000 times faster than traditional MD. Note that Bird's method is valid for a dilute Boltzmann gas. (For details of Bird's technique, see Ref. 9.)

The major problem with this algorithm is that it is restricted to binary collisions only, i.e., to second-order chemical reactions. On the other hand, simple chemical models yielding oscillations such as the Brusselator and generalized Schlögl models rely on trimolecular collisions.¹⁰ It has been shown that the trimolecular step can be approximated by a pair of bimolecular steps involving different time scales, such that an adiabatic elimination of a fast variable leads to an effective trimolecular step. Nevertheless, such a scheme is inappropriate for MD studies because the species represented by the slow variables undergo far fewer reactive collisions per unit time than those represented by fast variables. This results in much wasted bookkeeping with a corresponding waste of CPU time.

Thus with present day computers, we are left with two alternatives: either set up a microscopic model "mimicking" a three-body collision or search for a suitable second-order reaction scheme in which the difference of time scale between intermediate variables is as small as possible. The for-

mer alternative has already been considered successfully by Mareschal and De Wit for the Brusselator model.¹¹ In this paper we choose the second alternative and look for a chemical model satisfying the following three constraints: (i) it consists of binary collisions only; (ii) it has no significant separation of time scales; and (iii) it involves as few reactants as possible. In Sec. II a simple model satisfying these requirements is set up and its microscopic counterpart is formulated. The main results are presented in Sec. III.

II. MODEL AND MICROSCOPIC SIMULATION

We consider the following simple model:



The macroscopic rate equations for the above system in an isothermal continuous flow stirred tank reactor (CSTR) are

$$\frac{du}{dt} = -k_1 uw + \alpha(u_f - u), \quad (4)$$

$$\frac{dv}{dt} = k_1 uw - 2(k_2 v^2 - k_{-2} w) - k_3 v + \alpha(v_f - v), \quad (5)$$

$$\frac{dw}{dt} = k_2 v^2 - k_{-2} w, \quad (6)$$

where u , v , and w are the mole fractions of U , V , and W ; the $k_{\pm i}$ are the rate constants of the i th reaction; α is the inverse residence time or feed rate, and u_f and v_f are the feed mole fractions of u and v . The system is assumed impermeable to w .

For a certain range of parameter values, the system admits a multiplicity of steady states and limit-cycle oscillations. To our knowledge, this is the first model chemical oscillator in which there is no significant separation of time scales or trimolecular step. A full bifurcation analysis will be presented in a forthcoming paper.

Let us now turn to the microscopic simulation using Bird's technique. This technique consists of partitioning physical space into cells and monitoring the velocities of various particles in each cell. The molecules undergo free flight for a short time and subsequently each cell is examined for the purpose of identifying possible collision partners. The probability that a pair of molecules suffer a collision is proportional to their relative velocity (hard spheres gas) and is independent of the relative positions of the molecules within the cell. Our goal here is to model a CSTR. As the gas remains homogeneous in space, the problem may be regarded as "zero dimensional" and we have to consider the entire system as a single cell. The probability of a collision between a pair of molecules is thus independent of the positions of the molecules. This formulation is equivalent to the fluctuating homogeneous Boltzmann equation.

The usual procedure to include chemical reactions in a Boltzmann gas is to assume that a collision is reactive if the relative kinetic energy of the colliding particle exceeds some threshold related to the activation energy of the corresponding reaction. It has been shown that this may give rise to a deformation of the Maxwellian distribution which, in turn, can modify the macroscopic rate laws.¹²⁻¹⁴ A simple way to avoid this problem is by the following procedure. After a collision between two particles has occurred, we choose randomly \tilde{k} % of the collisions to be reactive, where \tilde{k} is related to the activation energy E of the reaction through the Arrhenius law

$$\tilde{k} = e^{-E/k_B T}. \quad (7)$$

In order to carry out MD simulations of the above CSTR system we introduce two more participants: "solvent" molecules S and molecules A . The solvent molecules undergo reactive collisions with the other species and participate, in addition, to reactions designed to mimic the feed terms. Every time a solvent particle is created (destroyed) in a collision with the other species, an $S(A)$ particle is chosen at random and replaced by an A (S) particle. Thus the solvent concentration remains fixed. Since the A molecules do not participate in any reactions, they merely constitute a reservoir of particles able to maintain the solvent concentration fixed.

The above process affects only reactions (2) and (3). Reactions (1)–(3) are thus replaced by



where the $\tilde{k}_{\pm i}$ are the fractions of reactive collisions corresponding to reactions (8)–(10). The feed terms are modeled by the following pair of reactions:



and



The forward reaction corresponds to inflow and the reverse reaction to outflow; a_{\pm} and b_{\pm} are the fractions of refractive collisions for these two reactions. Clearly, an S – S reaction can result in the production of either U or V molecules. The fraction of reactive S – S collisions resulting in the production of a U molecule is $u_f/(u_f + v_f)$ and the fraction of reactive collisions resulting in the production of a V molecule is then just $v_f/(u_f + v_f)$. We stress again that the number of S molecules is held fixed by the appropriate transformation of S and A molecules.

The full set of equations relevant for the microscopic simulations refers to the numbers of particles including the S species rather than to the mole fractions as in Eqs. (4)–(6). They read

$$\frac{dU}{dt} = -\tilde{k}_1 \frac{\nu}{N_T} UW + a_+ \frac{\nu}{2N_T} S^2 - a_- \frac{\nu}{N_T} SU, \quad (13)$$

$$\begin{aligned} \frac{dV}{dt} = & \tilde{k}_1 \frac{\nu}{N_T} UW - 2\left(\tilde{k}_2 \frac{\nu}{2N_T} V^2 - \tilde{k}_{-2} \frac{\nu}{N_T} SW\right) \\ & - \tilde{k}_3 \frac{\nu}{N_T} SV + b_+ \frac{\nu}{2N_T} S^2 - b_- \frac{\nu}{N_T} SV, \end{aligned} \quad (14)$$

$$\frac{dW}{dt} = \tilde{k}_2 \frac{\nu}{2N_T} W^2 - \tilde{k}_{-2} \frac{\nu}{N_T} SW, \quad (15)$$

where N_T represents the total number of particles and ν is the collision frequency. A comparison with the macroscopic equations (4)–(6) leads

$$\begin{aligned} \tilde{k}_1 &= \frac{k_1}{\nu}; \quad \tilde{k}_2 = \frac{2k_2}{\nu}; \quad \tilde{k}_{-2} = \frac{k_{-2}}{\nu s}; \quad \tilde{k}_3 = \frac{k_3}{\nu s} \\ a_+ &= \frac{2\alpha u_f}{\nu s^2}; \quad b_+ = \frac{2\alpha v_f}{\nu s^2}; \quad a_- = b_- = \frac{\alpha}{\nu s}, \end{aligned} \quad (16)$$

where s is the mole fraction of the S species. Note that the collision frequency is identical for all species involved since the particles have the same microscopic characteristics (i.e., same diameter and mass) and differ only by an index indicating their chemical identity.

The simulation procedure is thus completely specified in terms of kinetic constants, feed rate and the concentration of S particles.

III. RESULTS

It can be shown that for $k_1 = k_2 = k_{-2} = 1$, $k_3 = 10^{-1}/3$, $\alpha = 10^{-2}/3$, $u_f = 1$ and $v_f = 0.8/3$, Eqs. (4)–(6) admit limit cycle behavior. We have considered a system made of an assembly of 5000 hard spheres with $s = 0.1$. The results of the computer experiments for these values reproduce the sustained oscillations. We have performed two different types of analysis. First we consider 30 runs, all starting from the same macroscopic initial condition, extending over four periods of oscillations. A single run corresponds to about 50 million collisions. In Fig. 1 the en-

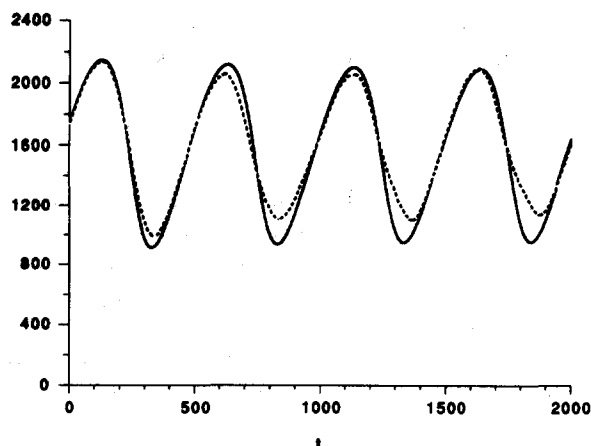


FIG. 1. Ensemble average of the microscopic trajectories of U species (dots) compared to the numerical solution of the deterministic equations (solid line).

semble average of the microscopic trajectories is compared to the numerical solution of the deterministic equations (4)–(6). Despite the small number of samples, the agreement is quite good. This procedure also allows for an estimation of the statistical errors which turn out to be of the order of 5%.

Next we have considered a single run of a total length of 120 oscillations (corresponding to a total number of collisions of about 10^9). A discrete time Fourier transform is performed and the power spectrum is computed by considering first the entire time series (dashed line in Fig. 2). We next divide the time series in six portions of 20 oscillations each. The solid line in Fig. 2 represents the average of the power spectrum over these six parts. In the same figure, we have also plotted the power spectrum corresponding to the macroscopic equations (vertical solid lines). We see that there is very good agreement for the location of the fundamental frequency and reasonable agreement for the first harmonic.

We can also compare the results of our computer experiments to the predictions of the stochastic theory of chemical reactions based on the master equation formalism. Here it is assumed that the chemical reactions define a “birth and death process” in the number of particles space. The evolution of the system can then be viewed as a random walk in a discrete phase space for which the transitions occur at randomly spaced time intervals. From the distribution of waiting times and the transition probabilities associated to each elementary chemical step, we can construct explicitly realizations of the process along the lines of a Monte Carlo simu-

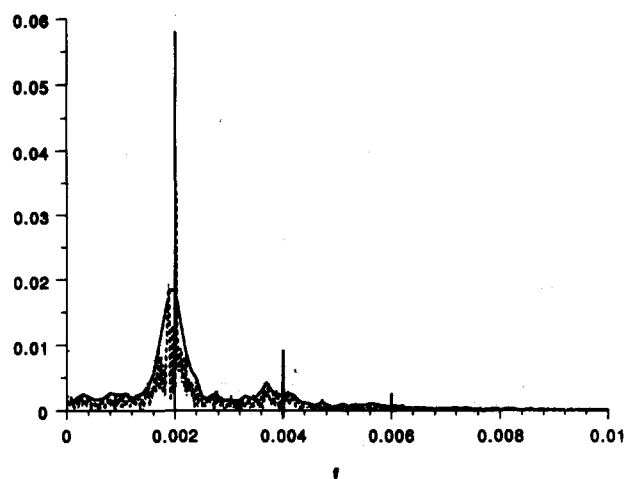


FIG. 2. Power spectrum of the microscopic signal: discrete time Fourier transform on the entire time series of 120 oscillations (dashed curve); average of the power spectrum over 6×20 oscillations (solid line) and power spectrum corresponding to the macroscopic equations (vertical solid lines).

lation of chemical systems. The standard techniques are described in Ref. 15. With the time series so obtained, we first computed the static properties of the process, i.e., equal time correlations. A comparison with the MD results is presented in Table I. We note that the deviations never exceed 5% which is within the expected statistical errors.

Next we have analyzed the dynamical properties by computing the time correlation function. In Fig. 3, we plot the time correlation function of the u species $\langle u(0)u(t) \rangle$ generated by Bird procedure and by simulation of the master equation. Again, we observe a very good agreement between the two curves. Note that the amplitude is decaying as a consequence of frequency fluctuations (phase diffusion). Simple theory, based on harmonic oscillators with random frequencies, predicts an exponential decay of the amplitude for long times.¹⁶ This is confirmed by our observations (see Fig. 4).

The technique developed in the present paper should prove useful in probing a number of open questions. Assuming perfect mixing and no hydrodynamic effects, an MD simulation of systems yielding deterministic chaos might shed some light on the question of whether the chemical chaos observed in the Belousov–Zhabotinsky reaction is of chemical or hydrodynamic origin.¹⁷ Chemical dynamics in spatially extended systems can also be addressed. In this con-

TABLE I. Comparison between microscopic results and master equation solution. Static mean values noted by $\langle \rangle$ for the species U , V , and W measured in number of particles units. Equal time fluctuations and correlations: $C_{ab} = (\langle ab \rangle - \langle a \rangle \langle b \rangle) / (\langle a \rangle \langle b \rangle)$.

	$\langle U \rangle$	$\langle V \rangle$	$\langle W \rangle$			
Bird	1587.36	425.83	41.16			
Master Eq.	1582.12	428.27	41.36			
	C_{uu}	C_{uv}	C_{uw}	C_{vu}	C_{vw}	C_{wv}
Bird	$9.10 \cdot 10^{-2}$	$1.38 \cdot 10^{-1}$	$5.99 \cdot 10^{-1}$	$-7.16 \cdot 10^{-2}$	$-1.43 \cdot 10^{-1}$	$2.74 \cdot 10^{-1}$
Master Eq.	$8.92 \cdot 10^{-2}$	$1.33 \cdot 10^{-1}$	$5.70 \cdot 10^{-1}$	$-6.96 \cdot 10^{-2}$	$-1.39 \cdot 10^{-1}$	$2.63 \cdot 10^{-1}$

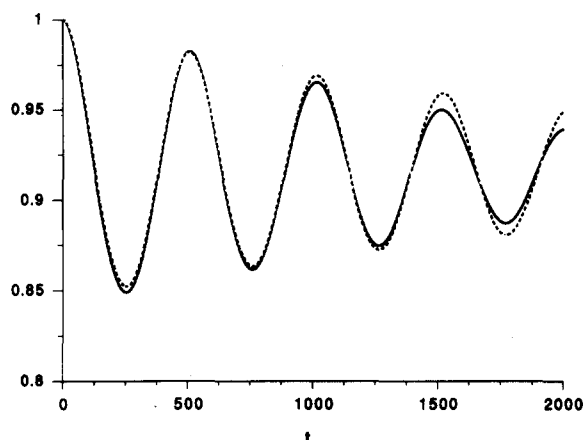


FIG. 3. Normalized time correlation function of U species generated by the microscopic simulation (solid line) and by master equation formalism (dashed line).

text, a basic question is the possibility of spontaneous symmetry breaking induced by the interplay between reactions and diffusion.¹⁸ Until recently time-independent chemical patterns have been observed as the result of externally imposed gradients.¹⁹ Quite recently evidence for stationary patterns displaying an intrinsic wavelength has been reported.²⁰ Molecular dynamics "experiments" on chemical pattern formation should help in further clarifying this important issue.

Our results also confirm the validity of the stochastic theory of chemical systems based on the master equation.

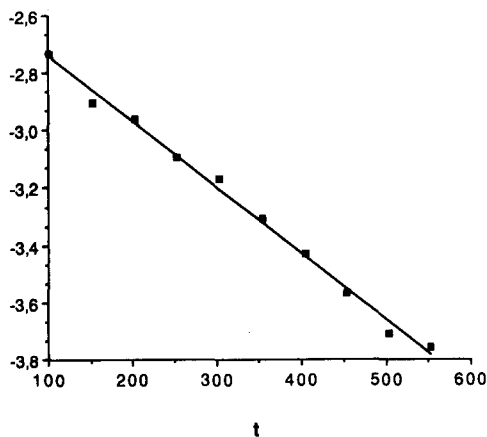


FIG. 4. Logarithm of the envelope of the time correlation function vs time.

This formalism can thus be used as a preliminary test in more complex situations dealing, for instance, with spatio-temporal patterns.

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- ¹ A nearly up to date account in this field is given in *Molecular Dynamics Simulation of Statistical Mechanical Systems*, edited by G. Ciccotti and W. G. Hoover (North Holland, Amsterdam, 1986).
- ² B. L. Holian, *Phys. Rev. A* **37**, 2562 (1988).
- ³ D. C. Rapaport and E. Clementi, *Phys. Rev. Lett.* **57**, 695 (1986); L. Hannon, G. Lie, and E. Clementi, *J. Sc. Comp.* **1**, 145 (1986); D. C. Rapaport, *Phys. Rev. A* **36**, 3288 (1987); E. Meiburg, *Phys. Fluids* **29**, 3107 (1986).
- ⁴ M. Mareschal and E. Kestemont, *Nature* **329**, 427 (1987); *J. Stat. Phys.* **48**, 1187 (1987); M. Mareschal, M. Malek Mansour, A. Puhl, and E. Kestemont, *Phys. Rev. Lett.* **61**, 22 (1988); A. Puhl, M. Malek Mansour, and M. Mareschal, *Phys. Rev. A* **40**, 1999 (1989); D. C. Rapaport, *Phys. Rev. Lett.* **60**, 2480 (1988).
- ⁵ J. Portnow, *Phys. Lett. A* **51**, 370 (1975).
- ⁶ P. Ortoleva and S. Yip, *J. Chem. Phys.* **65**, 2045 (1976).
- ⁷ J. Boissonade, *Phys. Lett. A* **74**, 285 (1979); *Physica A* **113**, 607 (1982); in *Nonlinear Phenomena in Chemical Dynamics*, edited by C. Vidal and A. Pacault (Springer, Berlin, 1981).
- ⁸ G. Nicolis, A. Amellal, G. Dupont, and M. Mareschal, *J. Mol. Liq.* **41**, 5 (1989).
- ⁹ G. A. Bird, *Molecular Gas Dynamics* (Clarendon, Oxford, 1976).
- ¹⁰ G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems* (Wiley, New York, 1977).
- ¹¹ M. Mareschal and A. De Wit (to be published).
- ¹² I. Prigogine and E. Xhrouet, *Physica XV*, 913 (1949); I. Prigogine and M. Mahieu, *Physica XVI*, 51 (1950).
- ¹³ R. D. Present, *J. Chem. Phys.* **35**, 747 (1959).
- ¹⁴ F. Baras and M. Malek Mansour, *Phys. Rev. Lett.* **63**, 2429 (1989).
- ¹⁵ D. T. Gillespie, *J. Comput. Phys.* **22**, 403 (1976); *J. Chem. Phys.* **81**, 2340 (1977).
- ¹⁶ R. Kubo, in *Fluctuation, Relaxation, and Resonance in Magnetic Systems*, edited by D. ter Haar, Scottish Universities Summer School in Physics (Oliver and Boyd, Edinburgh, 1962); R. Kubo and K. Tomita, *J. Phys. Soc. Jpn.* **9**, 888 (1954).
- ¹⁷ F. Argoul, A. Arneodo, P. Richetti, J.-C. Roux, and H. L. Swinney, *Acc. Chem. Res.* **20**, 436 (1987); L. Gyorgyi and R. Field, *J. Chem. Phys.* **92**, 7079 (1988).
- ¹⁸ J. E. Pearson and W. Horsthemke, *J. Chem. Phys.* **90**, 1588 (1989).
- ¹⁹ Q. Ouang, Thèse, Université de Bordeaux I, 1989; Q. Ouang, J. Boissonade, J. C. Roux, and P. de Kepper, *Phys. Lett. A* **134**, 282 (1989).
- ²⁰ V. Castets, E. Dulos, J. Boissonade, and P. De Kepper (to be published).