Deterministic Continuous Molecular-Dynamics-Simulation of a Chemical Oscillator *

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A macroscopic chemical oscillator involving 3 autocatalytic second-order reactions is simulated microscopically. A deterministic Newtonian simulation involving 1024 particles with a smooth $1/r$ potential in two dimensions is presented.

It is an old challenge going back to Boltzmann to simulate a nontrivial (recurrent) macroscopic chemical system from microscopic first principles. So far, apparently, no fully deterministic Newtonian example of this kind has been presented in the literature. An important step – a nonrecurrent autocatalytic reaction – has been simulated using 400 hard disks in 1983 by Heinrichs and Schneider [1].

An oscillatory reaction system of the Goodwin-Kerner-Chernavsky type has recently been simulated by means of a partially nondeterministic (Bird-algorithm-like) method by Gorecki [2]. In the following it is shown that the same reaction system can also be simulated in a purely deterministic fashion.

The reaction system used is the following one,

$$\begin{aligned} A + B &\longrightarrow 2A \\ B + C &\longrightarrow 2B \\ C + A &\longrightarrow 2C, \end{aligned} \tag{1}$$

with rate constants $k_1 = k_2 = k_3 = 6.1$.

There are no formal back reactions, and there is no energy-yielding substrate present as needed to satisfy the Wegscheider conditions. Moreover, the above reaction system is not realistic also from a mathematical point of view since it is non-dissipative and therefore structurally unstable on the macro level. More realistic systems meeting all the still lacking constraints can, however, also be simulated in the same fashion and work just as well (in preparation).

Figure 1 shows the time behavior of the concentration of the first variable (A) over 2.5 time units. One sees a nondecaying, more or less periodic macroscopic oscillation. The deviation from strict periodicity is due to the fairly small number of particles employed in the simulation. The fluctuations nevertheless are relatively small.

1024 particles were used in the plane. The size of the plane is two units (-1 to 1) in both directions. The particles were initially randomly distributed, with a Maxwell-like distribution of their moments. Total energy 4064. They are point-like, of unit mass, and subject to a smooth repulsive ϵ/r potential, where r is the interparticle distance and $\epsilon = 0.005$ is the force factor in the Hamiltonian.

The simulation of this Hamiltonian system is based on the well-known Verlet algorithm, cf. [3]. The latter is particularly appropriate for the reversible simulation of symplectic systems [4]. The above "gas" was confined to the plane, at the walls, not by a smooth potential but by a rule implemented in the Verlet algorithm that, whenever the next position is outside the plane, the momentum normal to the boundary is reversed. This rule, which mimics a hard billiard boundary, is exactly invertible (which is why it was chosen). It can be replaced by other rules or a smooth potential, respectively.

A "color code" transforms this mechanical gas into a chemically reacting one. At first, a gauge curve was set up to determine the ratio between kinetic constants as a function of the critical collision energy set as a threshold for a color change. A rough proportionality of the rate constant to $r \exp(-c/r)$, with r the threshold distance, was empirically found to apply. For example, a threshold distance of 0.008 generated $k = 6.1$ (the value chosen above), a threshold distance of 0.005 led to $k = 2.85$, 0.01 generated $k = 7.38$, and a threshold distance of 0.02 yielded $k = 19.23$. However, since in the reaction scheme (1) all rate constants are

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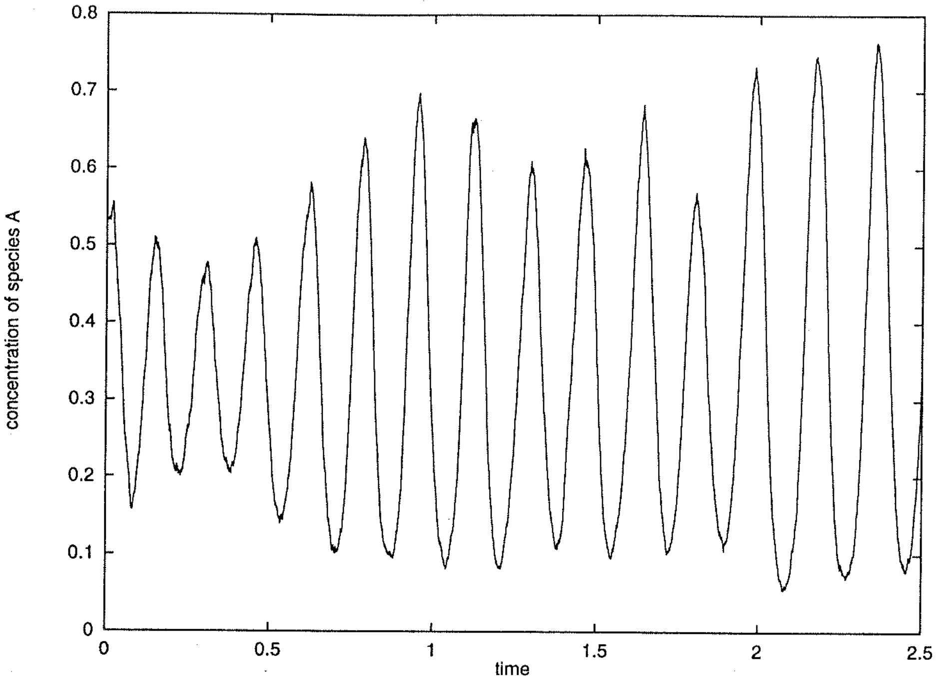

Fig. 1. Concentration of species A as a function of time in the reaction scheme (1), simulated in a plane using 1024 smoothly repulsive point particles. Initial conditions (macroscopic): A(0) = 496/1024, B(0) = 204/1024, C(0) = 324/1024. The concentrations of B and C showed a very similar behavior (displaced by a third of a period). Simulation performed on an Indigo workstation. For details about the Hamiltonian and the algorithm, cf. text.

equal this finding (which is not completely understood so far) is only mentioned for future use. Several simulations with a smaller *k* were also run, with analogous results.

To conclude, a marginally unrealistic chemical oscillator has been successfully reproduced from microscopic deterministic first principles, on both the macro and the micro level. Studies like this are of interest in the context of a complete understanding of a computer-simulated world that contains an observing subsystem.

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