**Stochastic birth and death equations to treat chemistry and nucleation in small systems**

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Chemical and nucleation processes taking place in very small open systems do not necessarily proceed at the scaled down rates of similar processes taking place in large systems. For example, reactions taking place on the surface of a particle of area 1 nm² will not proceed at one millionth of the rate of the same process on a particle of area 1 μm². In making this claim, we are not appealing to differences in surface properties, such as curvature. The crucial difference is that the populations of reactants in the smaller system are lower, and therefore more susceptible to statistical fluctuations which can alter the reaction rate in an important way. Normal classical chemical kinetics fail, as do the usual Becker-Döring birth and death equations for nucleation. The chemical and activation properties of ultrafine aerosols can therefore differ from expectations. The effect of this small system stochasticity was explored by Lushnikov, Bhatt and Ford (2003) and Bhatt and Ford (2003).

The reaction A+A→C can provide a simple illustration of the reason for the failure of traditional kinetics. The rate for such a two-body process is proportional to the square of the population of reactant A. The mean reaction rate is therefore proportional to the time-average of the squared reactant population. However, traditional kinetic equations employ the square of the mean reactant population, rather than the mean of the square, and these quantities differ for small systems. Mathematically, the evolution of N, the mean population of A-molecules, is given by

\[ \frac{dN}{dt} = j - \lambda N - \frac{1}{2} \kappa N^2 \]  

where \( \lambda \) is the reaction rate to form product C, and the first two terms describe gain and loss rates to and from the open system, respectively. For nucleation, the growth rate of a molecular cluster is normally taken to be proportional to the product of mean populations of monomer and cluster, and this assumption is similarly flawed.

In order to treat population fluctuations correctly, we can replace mean population dynamics with a description using master equations. These describe the evolution of the full probability distribution of the reactant population. However, except in some special cases, the equations are too complicated to be solved exactly, and numerical methods are very cumbersome. We have therefore explored a procedure to reduce master equations to traditional rate equations, but with additional stochastic terms that take account of fluctuations. The methods used are similar to treatments of quantum mechanical systems, where the fluctuations are due to quantum uncertainty, rather than the population uncertainty associated with a small, open, classical system.

The master equations may be cast in the form of a path integral (Doi 1976), which is a weighted sum of contributions from all possible time-histories of a complex quantity \( \phi(t) \). The path integral plays a similar role to the partition function in equilibrium statistical mechanics, in that it provides a means for calculating average quantities, such as mean populations and reaction rates. The key step (Tauber et al 2005) is then to convert the weighted integration over all paths into an averaging of system quantities over histories of \( \phi(t) \) computed according to a stochastic differential equation

\[ \frac{d\phi}{dt} = j - \lambda \phi - \frac{1}{2} \kappa \phi^2 + \xi(t) \]  

where \( \xi(t) \) is a complex white noise term.

The correspondence between equations (1) and (2) is quite clear and suggests that the real part of \( \phi(t) \) averaged over all noise histories corresponds to the mean population \( N \). Fluctuations are described by the noise term in the rate equation.

The formalism provides a simplified means for solving master equation kinetics, using Monte Carlo sampling of stochastic histories. The systems that can be described include cases of heterogeneous chemistry as well as much more complicated mechanisms for nucleating systems.

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