CHEMICAL PHYSICS

Reaction Rates and Friction: Classical Activation and Quantum Tunneling

The activated passage of an effective particle over a barrier lies at the heart of many important processes in chemical physics. Examples include chemical reactions, thermal desorption, structural isomerizations in macromolecules, and the decay of metastable states. For many years the leading theory that describes the rates for such processes has been the Transition State Theory. This theory pictures the passage as a free flight over the barrier, with no dynamical influence arising from the solvent, lattice, or "bath" with which the particle is in contact.

The critical role of the surroundings in determining a barrier passage rate was first elucidated in a classic paper[1] by H. A. Kramers, who described a simple one-dimensional Markovian Brownian motion in terms of a friction constant. In recent years there has been a veritable flood of research testing, extending, and superseding the original Kramers theory, and significant advances have been made in connection with the influence of friction on aspects of the rate problem.[2–5]

One example is the effect of memory friction on reaction rates.[2] For a simple barrier passage, the friction constant in Kramers' theory for the diffusive transmission factor is replaced by a frequency-dependent friction,[2] a difference reflecting the fact that the rate is sensitive to the short time scale rather than the long time scale interaction of the reaction system with its surroundings. This effect is apparent in recent experimental isomerization studies.[3]

The multiple dimensions within the reacting system have also come under scrutiny.[4] In particular, internal molecular degrees of freedom can dramatically influence low-friction behavior. The reaction rate becomes determined by collisional energy activation. This phenomenon is revealed as a peak in a plot of the rate as a function of pressure or viscosity.

At lower temperatures, thermally activated "hopping" processes become rarer and the effect of quantum tunneling becomes increasingly important.[6–10] The crossover between thermal activation and quantum tunneling, which occurs at a temperature T_0, is marked by the softening of a fluctuation mode around the saddle point of the potential energy surface.[7] At temperatures lower than T_0, the rate is dominated by quantum tunneling.[8] In particular, a recent theory shows that at very low temperatures, the dissipation leads to a universal exponential T^2 thermal enhancement.[9] This T^2 law should be valid for all systems with finite low-frequency friction. In recent months this characteristic behavior has been observed in experiments on low temperature Josephson junction systems.[10]

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1. H. A. Kramers, Physica (The Hague) **7**, 284 (1940).
2. R. F. Grote and J. T. Hynes, J. Chem. Phys. **73**, 2715 (1980); P. Hanggi and F. Mojtabai, Phys. Rev. A 26, 1168 (1982).
3. S. P. Velsko, D. H. Waldeck, and G. R. Fleming, J. Chem. Phys. **78**, 249 (1983); B. Bagchi and D. Oxtoby, *ibid.* **78**, 2735 (1983).
4. A. G. Zawadzki and J. T. Hynes, Chem. Phys. Lett. **113**, 476 (1985); M. Borkovec and B. J. Berne, J. Chem. Phys. **82**, 794 (1985); A. Nitzan, *ibid.* **82**, 1614 (1985); S. H. Courtney and G. R. Fleming, Chem. Phys. Lett. **103**, 443 (1984); G. Maneke, J. Schroeder, J. Troe, and F. Voss, Ber. Bunsenges. Phys. Chem. (in press).
5. H. Frauenfelder and P. G. Wolynes, Science **229**, 337 (1985).
6. P. G. Wolynes, Phys. Rev. Lett. **47**, 968 (1981); P. Hanggi, H. Grabert, G. L. Ingold, and U. Weiss, *ibid.* **55**, 761 (1985).
7. H. Grabert and U. Weiss, Phys. Rev. Lett. **53**, 1787 (1984); A. I. Larkin and Yu N. Ovchinnikov, Sov. Phys. JETP **59**, 420 (1984); P. Riseborough, P. Hanggi, and E. Freidkin, Phys. Rev. A **32**, 489 (1985).
8. A. O. Caldeira and A. J. Leggett, Ann. Phys. (N.Y.) **149**, 374 (1983); **153**, 445 (1984).
9. H. Grabert, U. Weiss, and P. Hanggi, Phys. Rev. Lett. **52**, 2193 (1984).
10. S. Washburn, R. A. Webb, R. F. Voss, and S. M. Faris, Phys. Rev. Lett. **54**, 2712 (1985); D. B. Schwartz, B. Sen, C. N. Archie, A. K. Jain, and J. E. Lukens, IC-Squids 85, International Conference, Berlin, 1985; (preprint).