Séminaire de Chimie Théorique

Salle conference 3eme Est, Bat. A12
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The magic of transition state theory (TST), as independently introduced by Marcelin, Wigner and Eyring, lies in the replacement of the dynamics of all the trajectories between reactants and products with a simple geometric calculation. Although the TST rate formula is not generally exact, the order of magnitude of the rates is usually correct, and that has been of significant use in describing chemical reactions. In energy conserving systems, it is possible to do better. Rigorously non-recrossing dividing surfaces can be constructed from normal form theory, and have the structure of a normally hyperbolic invariant manifold. In dissipative systems, Kramers showed that naive transition state theory overestimates the rate at low friction (because reactants are not sufficiently activated) and at high friction (because reactants are slowed down before they reach the barrier). The mechanisms involved in these errors can be accounted for in modern transition state theory formulations, but the recrossing problem still persists. We will discuss recent novel methods for extending these exact geometric reformulations to reactions in the condensed phase. In addition, we will discuss the diffusion of colloidal particles in complex dynamic environments. Such a milieu can consist of static or dynamic spheres, rods, or even structured colloids (such as Janus particles). The emergent behavior of the dynamics of probes within these environments has been probed by simulations, and we are also able to synthesize it within dynamical theories motivated by TST.

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