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Research Summary on Condensed Phase Chemical Reaction Dynamics

The generalized Langevin equation (GLE) was cast into canonical form in the classic paper by Mori, which provided a rigorous basis for treating *slow variable/ fast bath* phenomena like Brownian motion. But it was Adelman and Doll who first recognized that the GLE also provides a framework for rendering tractable the many body problems of condensed matter chemical dynamics. The idea was first developed for molecular collisions with solid surfaces. The Adelman-Doll technique had a very substantial impact since: (i) it was the first extension of gas phase chemical dynamics to condensed phases; (ii) it provided a basis for studying surface catalysis. The GLE method for surface chemistry has been extensively developed and applied to the interpretation of experiments by Prof. John Tully, and others.

Adelman next extended the GLE method to the much more difficult problem of reaction dynamics in liquids. Unlike surface reactions where the explicitly treated “primary zone” atoms are bound to the solid, in liquids the corresponding neighboring “solvation shell” molecules are unbound. This problem was solved by Adelman’s discovery of a new statistical mechanical identity, the equivalent chain equations. These replace the true local solvent environment by fictitious particles which rigorously simulate its effects. These particles are harmonically bound and thus do not “fly away” like real solvent molecules.

Far more important, is that the equivalent chain equations optimally represent the physics of the non-classical *fast variable/slow bath* timescale regime. The chain equations are as fundamental to the fast variable regime as Mori’s identity is to the opposite slow variable regime.

The fast variable regime is of prime importance in liquid phase chemistry. This follows from Arrhenius’ principle that only atypically fast molecules can surmount chemical activation barriers. Adelman first demonstrated the fast variable/slow bath timescale separation for reaction dynamics in 1977 model numerical studies. The timescale separation was definitively confirmed ten years later by Wilson and coworkers in their molecular dynamics (MD) simulations of a number of liquid phase reactions. Especially they confirmed Adelman’s basic “Einstein (or sudden) limit” concept by their observation of the dominance of the identical “frozen solvent” limit. Moreover they found reaction coordinate energies of thousands of degrees Kelvin, showing that solute reaction dynamics differs radically from solute thermal motions.

Adelman then recast the fast variable picture into standard potential energy form by formulating the *instantaneous potential (IP)*. It is the IP not the potential of mean force which governs chemical dynamics in liquids. The IP is the sum of the gas phase potential and the “frozen solvent” cage potential. It thus makes transparent the enhanced role of cage effects in liquid phase chemistry.

The IP gives a picture of early time liquid phase reaction dynamics, *which is opposite to and incompatible with that of the Kramers Brownian motion picture*. In the Kramers picture, in zeroth order the reaction is mediated by the *zero velocity* potential of mean force. In first order, this description is corrected for *small velocities* by the frictional force. In the new picture, in zeroth order the reaction is governed by the *infinite velocity* IP. In first order, this picture is corrected for finite velocity by a relaxation kernel which accounts for the response of the “frozen solvent” to the solute motion.

This IP picture was extended to all times by the new concept of *imperfect following*. Its basis is that the solvent cannot remain in thermodynamic equilibrium with the solute, since only the latter is driven by the very strongly accelerating gas phase potential. Reactions are thus dominated by the interplay between the gas phase driving forces which propel the system out of equilibrium and liquid state forces which (unsuccessfully) attempt to restore equilibrium.

To contact experiment, the short time equations must be augmented by methods for computing the liquid state quantities which appear in them, especially the cage potential and the relaxation kernel. The latter may be determined from the friction kernel.

Adelman's early work convinced him continuum models fail for molecular processes. So he developed *molecular friction methods* which were suggested by the forms of the rigorous fast variable equations of motion. The most powerful methods are based on Adelman's *partial clamping approximation*. In this approximation the chemically relevant generalized coordinates are held fixed while the remaining solution degrees of freedom move freely. The approximation may be readily implemented by MD. At least a dozen research groups from have carried out such implementations. Wilson, especially, has made detailed applications of partial clamping to solute activated barrier crossing and vibrational energy relaxation (VER).

Adelman next developed an analytical implementation of partial clamping. This work yields molecular formulas for both translational-rotational friction and (the previously unformulated) vibrational friction. The formulas are a vast advance over those of the hydrodynamic and dielectric friction models, since the latter ignore the molecular nature of the solvent including molecular shape effects.

The formulas were numerically applied to (VER) to yield a molecular basis for the isolated binary collision model. Recently Adelman proved that the wings of the frequency domain friction kernel are Gaussian-like not exponential-like, an essential result for VER theory including the validity of Adelman's analytic molecular friction method.