

# Dynamics of structural isomerization and evaporation of isolated small atomic clusters as multichannel chemical reactions and their characterization with "temperature"

Kazuo Takatsuka

Department of Basic Science, University of Tokyo, Japan

kaztak@mns2.c.u-tokyo.ac.jp

Isomerization dynamics of a small atomic (or van der Waals) cluster wandering from one molecular structures to another among many isomers shows many interesting phenomena that gives a link between the deterministic dynamics and macroscopic statistical mechanics [1]: melting (a prototype of the first order phase transition), loss of the memory in structural transitions, liquid-like dynamics that does not care about the so-called transition state, evaporation coupled with structural isomerization, and so on. This isomerization dynamics can be regarded as a prototype of multi-channel chemical reaction, which is far beyond the "transition state concept" having dominated the theory of rate process in the 20<sup>th</sup> century. In this talk, I discuss the characteristics of these isomerization dynamics from the following view points. (1) "Microcanonical temperature" to characterize the lifetime of isomers. (2) Successive bifurcation of the so-called reaction tube (a geometrical structure in phase space) to characterize the memory-loss rate. (3) Non-Euclidean mechanics inevitably introduced into shape-changing dynamics. (4) Extraction of collective coordinates for the structural change. (5) A novel statistical theory for evaporation of atom or diatomic molecule from the clusters, which coupled with the structural isomerization in a similar time scale. (6) Experimental determination of the canonical temperature in terms of kinetic energy released by the above evaporation.

A particular emphasis is placed on a novel *nonempirical* statistical theory to give reaction rate and the kinetic energy distribution of fragments for molecular evaporation from highly nonrigid atomic and van der Waals clusters, in which an efficient and accurate method to evaluate the absolute value of classical density of states (the Thomas-Fermi density in phase space) and the flux at the so-called dividing surface has been implemented [2]. It is shown numerically that the nonempirical statistical theory gives quite an accurate reaction rate. We also study the kinetic energy release (KER) arising from these evaporations and its Boltzmann-like distribution both for atomic and diatomic evaporation. This provides a general relation between the KER and temperature of the fragments [3].

## Reference

- [1] K. Takatsuka, Adv. Chem. Phys. **130**, 25 (2005) and references cited therein.
- [2] M. Fujii and K. Takatsuka, J. Chem. Phys. **128**, 114318 (2008).
- [3] M. Fujii and K. Takatsuka, J. Chem. Phys., **127**, 204309 (2007).