My memory of Prof. Shuichi Tasaki

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The first time I met with Shuichi was seventeen years ago, 1994, at the Institute for Fundamental Chemistry (IFC) founded in 1988 (currently, Fukui Institute for Fundamental Chemistry in Kyoto University) where I spent my first academic carrier as a postdoctoral research fellow. At that time, Shuichi served as one of three senior research staffs in the IFC (I had an overlap with Shuichi until I moved to University of Chicago in 1997). Some readers of this special volume might wonder why Shuichi had spent his carrier in an institute related to "chemistry." Here is the tale I heard from Shuichi. That is, while he was a postdoctoral researcher in Brussels, Professor Ilya Prigogine wondered which academic institution was appropriate for his next carrier and asked his friend, Professor Kenichi Fukui (Nobel Prize in Chemistry 1981), who had served as the director of that institute. Professor Fukui recommended Professor Prigogine to make Shuichi to join the IFC. Professor Fukui had encouraged especially young researchers to look deeper into the fundamental problems in chemistry (in a very broad sense) without restricting themselves to conventional territories of natural sciences which human kinds had determined (Professor Fukui himself devoted his research partially on the problem why the number of chemical elements is so small compared to the diverse number of chemical compounds by using Ramsey theory). I think that Shuichi was considered to be most well fitted to the perspectives of Professor Fukui as a key researcher who could not just only bring a new discipline or a seed to chemists but also conduct some researches not passively but rather actively to dig into fundamental problems in chemistry. Although Shuichi explored, e.g., optical properties of carbon nanotubes [1] by his own, he also actively interacted with young researchers in the IFC while he was there. I think that I was only the one who really enjoyed the benefits. When I joined the IFC in 1994, I organized a reading circle of A.J. Lichtenberg and M.A. Lieberman, *Regular and Chaotic Dynamics* (Springer-Verlag 1991) with other four postdoctoral research fellows who all received PhD in Theoretical Chemistry.

—— In those days chemists hardly appreciate chaos theories, and rather were very suspicious to what chaos could actually bring new insights to chemistry: most concepts and theories in

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Hamiltonian chaos are based on near-integrable systems to which perturbation theory can be applied, and most of all applications were of a few degrees of freedom. On the contrary, most systems chemists are dealing with are high dimensional (much more than just a few) with very complicated nonlinear interactions among the degrees of freedom, and were considered to be highly chaotic so that any perturbation theory might not work. Remember that a Poincaré section for Henon-Heiles Hamiltonian system at the threshold energy above which most trajectories escape from the potential well (i.e., reactions start to undergo) seemingly implies that any canonical perturbation theory does not work to capture the underlying phase space structure [2]. However, in 1980s, Professor Iwao Ohmine discovered [3], by using computer simulations, the existence of intermittent collective motions when the system exhibits transitions among potential energy basins in liquid water dynamics. His finding was enough to motivate me not to believe a simple stochastic process along the reaction process and to study chaos much more extensively than before. ——

Most time of the reading circle, Shuichi joined and gave us insightful comments. When I studied secular perturbation theory and Lie canonical perturbation theory in my turn and read the original papers of Lie canonical perturbation theory developed by Gen-ichiro Hori [4, 5], I came up with a new idea, that is, if Lie canonical perturbation theory can be applied to the region of rank-one saddles where only one hyperbolic degree of freedom exists and all the rest elliptic degrees of freedom that can be coupled with each other, one of the long-standing unresolved problems (more than 70 years!), the so-called nonrecrossing assumption, in chemical reaction theories can be resolved [6, 7, 8]. In short, this assumption originally proposed by Wigner [9] can be represented as follows: in a wide class of molecules in gas phase (i.e., many degrees of freedom Hamiltonian systems strongly coupled with each other highly nonlinearly) there exists a co-dimension one manifold in the phase space through which the reacting system crosses once and only once before being "captured" in the state of the product during the process of the reactions from the state of the reactant to the state of the product. This is what chemists have termed 'transition states [10].' Chemistry, originated from alchemy that had dreamed to transform all materials to gold, have been categorized for long duration as an *empirical* science. Even two decades ago, due to highly complicated, nonlinear interactions among atoms constituting molecules, most efforts for transition states in reaction dynamics were devoted just to practically elucidate the reaction rates by using this conceptual entity, and the very question, In what circumstance and where such co-dimension one manifold can exist for high-dimensional systems, has been untouched.

Note that the system is highly chaotic at such energies where reactions take place and any perturbation theory seems not to work. Nevertheless the reason why I can realize that still canonical perturbation theory should work was by a series of papers (1992-1993) on the analysis

of local Liapunov exponents for isomerization of atomic clusters [11, 12, 13] (whose numbers of atoms are from three to five) by Professor R. Stephen Berry in University of Chicago: They manifestly showed the appearance of a significant decrease of local Liapunov exponent while the system crosses the potential barrier linking two potential minima, suggesting the existence of local invariants in crossings.

The remaining problem to be rationalized was just what the corresponding action-angle variables associated with a hyperbolic degree of freedom are. However, most books on Hamiltonian chaos in 1990s (and even now) have explained canonical perturbation theory, if it exists, for the vicinity of an elliptic stable fixed point. When I have been looking for the action-angle variables associated with a hyperbolic degree of freedom, I explained that problem to Shuichi, may be at that corner at the second floor in the IFC where people can drink coffee and tea with chatting sciences. Shuichi promptly recommended me an old paper in *Faraday Discussions Chem. Soc.* in 1977 by Professor William H. Miller in Department of Chemistry, University of California in Berkeley [14]. *Why did Shuichi know this article in Faraday Discussions Chem. Soc.?* Shuichi was the person who had participated in several conferences/meetings in chemistry while he joined the IFC and knew that Professor Miller's semiclassical transition state theory defines the action-angle variables associated with a hyperbolic degree of freedom I have been seeking. Shuichi said that he himself had once checked whether Professor Miller's definition satisfies the canonical relation with the action-angle variables with the other elliptic degrees of freedom after he knew Professor Miller's presentation. This is just one of the examples that Shuichi was always an open minded researcher against the other disciplines or fields without assigning any boundary of sciences. There still exist many unresolved intriguing subjects in chemistry that have been seeking breakthrough from nonlinear physics viewpoints, e.g., whether can one predict the destination of reactions just by knowing the initial condition at time t equal to zero even under the existence of thermal noise in dissipative systems [15, 16, 17, 18]?, what is the origin of persistence of the predictability or the birth of stochasticity in reactions under the existence of high dimensional chaos [19, 20, 21]?, what is the essential difference between three degrees of freedom and the higher because most real systems in chemistry is not just a few dimensions?, what is the dynamical origin of the existence of Arrhenius relation (ergodic problems for "opened" systems escaping to another potential wells [22]) and so forth.

Shuichi was one of the very outstanding physicists who could share and understand the enthusiasm, with deep insights, for such fundamental problems actually not only in chemistry but also in physics. Hence, I can easily imagine that not only physics community but also the other disciplines such as chemistry community really missed him. I would also like to contribute a Japanese article in which we have just recently clarified [23] the mechanism of the breakdown of normally hyperbolic invariant manifold and its stable/unstable manifolds, which serve as

essential building blocks in high dimensional phase space to dominate all transport phenomena, all of which have originated from that chatting with Shuichi at the corner at the second floor in the IFC and that reading circle in Kyoto.

References

[1] S. Tasaki, K. Maekawa, and T. Yamabe. π-band contribution to the optical properties of carbon nanotubes -effects of chirality-. *Phys. Rev. B*, 57:9301, 1998.

[2] A. J. Lichtenberg and M. A. Lieberman. *Regular and Chaotic Dynamics*. Springer, New York, 2 edition, 1992.

[3] I. Ohmine and H. Tanaka. Fluctuation, relaxations, and hydration in liquid water. hydrogen-bond rearrangement dynamics. *Chem. Rev.*, 93:2545, 1993.

[4] G. Hori. *Pub. Astro. Soc. Japan*, 18:287, 1966.

[5] G. Hori. *Pub. Astro. Soc. Japan*, 19:229, 1967.

[6] T. Komatsuzaki and M. Nagaoka. Study on "regularity" of the barrier recrossing motion. *J. Chem. Phys.*, 105:10838, 1996.

[7] T. Komatsuzaki and M. Nagaoka. A dividing surface free from a barrier recrossing motion in many-body systems. *Chem. Phys. Lett.*, 265:91, 1997.

[8] T. Komatsuzaki. Deterministic property in the (thermally) fluctuating world -why does a reacting system pass through the saddle? -the solution of nonrecrossing assumption unresolved for 70 years-. *Bussei Kenkyu (Kyoto)*, 78:354, 2002.

[9] E. Wigner. Calculation of the rate of elementary association reactions. *J. Chem. Phys.*, 5:720–725, 1937.

[10] R. D. Levine. *Molecular Reaction Dynamics*. Cambridge University Press, Cambridge, 2005.

[11] C. Amitrano and R. S. Berry. Probability distributions of local liapunov exponents for small clusters. *Phys. Rev. Lett.*, 68:729–732, 1992.

[12] C. Amitrano and R. S. Berry. Probability distributions of local liapunov exponents for hamiltonian systems. *Phys. Rev. E*, 47:3158, 1993.

[13] R. J. Hinde and R. S. Berry. Chaotic dynamics in small inert gas clusters: The influence of potential energy saddles. *J. Chem. Phys.*, 99:2942, 1993.

[14] W. H. Miller. Semi-classical theory for non-separable systems:. construction of good action-angle variables for reaction rate constants. *Faraday Discussions Chem. Soc.*, 62:40–46, 1977.

[15] S. Kawai and T. Komatsuzaki. Dynamical reaction coordinate buried in thermal fluctuation i: time-dependent normal form theory for multidimensional underdamped langevin equation. *J. Chem. Phys.*, 131:224505, 2009.

[16] S. Kawai and T. Komatsuzaki. Dynamical reaction coordinate buried in thermal fluctuation ii: numerical examples. *J. Chem. Phys.*, 131:224506, 2009.

[17] S. Kawai and T. Komatsuzaki. Hierarchy of reaction dynamics in a thermally fluctuating environment. *Phys. Chem. Chem. Phys.*, 12:7626–7635, 2010.

[18] S. Kawai and T. Komatsuzaki. Nonlinear dynamical effects on reaction rate constants in thermally fluctuating environments. *Phys. Chem. Chem. Phys.*, 12:7636–7647, 2010.

[19] T. Komatsuzaki and R. S. Berry. Dynamical hierarchy in transitions states: Why and how does a system climb over the mountain? *Proc. Natl. Acad. Sci. USA*, 78:7666, 2001.

[20] C. B. Li, A. Shojiguchi, M. Toda, and T. Komatsuzaki. Definability of no-return transition states in the high-energy regime above the reaction threshold. *Phys. Rev. Lett.*, 97:028302, 2006.

[21] S. Kawai and T. Komatsuzaki. Robust existence of a reaction boundary to separate the fate of a chemical reaction. *Phys. Rev. Lett.*, 105(4):048304, Jul 2010.

[22] T. Komatsuzaki, A. Baba, S. Kawai, M. Toda, J.E. Straub, and R.S. Berry. Ergodic problems for real complex systems in chemical physics. *Adv. Chem. Phys.*, 2011.

[23] H. Teramoto, M. Toda, and T. Komatsuzaki. A dynamical switching of a reaction coordinate to carry the system through to a different product state at high energies. *Phys. Rev. Lett.*, 106:054101, 2011.