



ACCADEMIA NAZIONALE DEI LINCEI e FONDAZIONE «GUIDO DONEGANI»

INTERNATIONAL CONFERENCE

STATISTICAL THERMODYNAMICS AND CHEMICAL KINETICS: FAR AWAY FROM EQUILIBRIUM

25-26 JUNE 2019

# ABSTRACT

**Organizing Committee:** Vincenzo Aquilanti, Sergio Carrà, Tommaso Ruggeri

## PROGRAMME

*Celebrating 160 years from Arrhenius birthday and 130 years of remarkable success of his equation, open problems on its foundations and perspectives of future applications are under focus.*

One of the tasks of statistical mechanics is to provide the connection between the mechanics of the systems at a molecular level and the macroscopic behavior of matter.

The ongoing work in the field of non-equilibrium thermodynamics is inspired by Onsager (Nobel 1968), Prigogine (Nobel 1977) and Kramers. In this context some recent results obtained by the extended thermodynamics theory of gases provide a derivation of the mechanics of continuum from the classical kinetic theory of gases (at a mesoscopic level): remarkable advances regarding chemical kinetics are directly inspired by Maxwell, a predictive theory of reaction velocities and a detailed formulation of the reactivity at low temperatures, accounting for modern experimental and molecular dynamics results.

The interdisciplinary and transversal character of the topic of this conference, from mathematics and physics to chemistry and the science of materials, dates back to more than a century ago. Historically, statistical mechanics intends to provide the connection between the mechanics of atomic and molecular systems and the macroscopic behavior, in order to arrive at a microscopic theory of thermodynamic functions, accepting the challenge launched in one of the famous problems of Hilbert and concerning the state of mathematics: in particular the sixth problem concerns the relationship between discrete reality at the atomic and molecular level and that of the macroscopic continuum.

### **Tuesday, 25 June: Mathematical Physics**

14.00 Welcome address, Giorgio PARISI (Presidente dell'Accademia Nazionale dei Lincei)

14.15 Introduction by the Organizers

Chair: Francesco PEGORARO (Linceo, Università di Pisa)

14.30 Tommaso RUGGERI (Linceo, Università di Bologna): *New frontiers in non-equilibrium thermodynamics*

15.00 Masaru SUGIYAMA (Nagoya Institute of Technology): *A new link between kinetic theory and continuum thermo-mechanics*

15.30 Coffee break

Chair: Antonio SGAMELLOTTI (Linceo, Università di Perugia)

16.00 Constantino TSALLIS (Centro Brasileiro de Pesquisas Físicas, Rio de Janeiro): *Beyond Boltzmann-Gibbs in physics, chemistry and elsewhere*

16.30 Annalisa MARZUOLI (Università di Pavia): *Discrete vs Continuum: quantum to classical via semiclassical*

17.00 Andrea LOMBARDI, Federico PALAZZETTI (Università di Perugia) – Mikhail B. SEVRYUK (Academy of Sciences, Moscow): *Statistics of energy partitions for many-particle systems*

### **Wednesday, 26 June: Statistical Thermodynamics**

Chair: Tommaso RUGGERI (Linceo, Università di Bologna)

9.30 Ernesto P. BORGES (Universidade Federal da Bahia, Brazil): *From Boltzmann to non-Boltzmann distributions: strong to weak chaos*

10.00 Pier Luigi GENTILI (Università di Perugia): *Out-of-equilibrium chemical reactions in neuromorphic engineering*

10.30 Roger W. ANDERSON (University of California Santa Cruz): *Quantum reaction dynamics – Discrete algorithms*

11.00 Coffee break

Chair: Mario CAPITELLI (Università di Bari)

11.30 Massimo MORBIDELLI (ETH Zurich, Politecnico di Milano): *From polymer colloids to structural materials*

12.00 Paola DIOMEDE (Differ Institute, Eindhoven) - Savino LONGO (Università di Bari): *Fokker-Planck equation in chemical kinetics*

## Chemical Kinetics

Chair: Annibale MOTTANA (Lincoo, Università di Roma Tre)

14.00 Sergio CARRÀ (Lincoo, Politecnico di Milano): Introduction

14.20 Tiziano FARAVELLI (Politecnico di Milano): *Combustion kinetics and the environmental challenges*

14.50 Enrico TRONCONI (Politecnico di Milano): *Hunting for elusive intermediates in the selective catalytic reduction of NOx: how a fundamental study may result in a new exhaust after-treatment technology*

15.20 Vincenzo AQUILANTI (Lincoo, Università di Perugia): Panel presentations and conclusions, including:

Dario DE FAZIO (CNR, Roma) – Simona CAVALLI (Università di Perugia): *Exact quantum dynamics and kinetics for cold and ultracold reactions down to the Wigner's limit*

Danilo CALDERINI (ETH Zurich): *Path integral approach for partition function calculations*

Valter CARVALHO-SILVA (Universidade Estadual de Goiás, Anápolis, Brazil) – Nayara DANTAS-COUTINHO (Universidade de Brasília): *Rate processes on the verge of the thermodynamic and the kinetic limits*

Conference organized in collaboration with

Accademia Nazionale delle Scienze detta dei XL, Rome - Università di Perugia

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## Note the related event:

### OBSERVATORY FOR ASTROCHEMICAL KINETICS AND RELATED ASPECTS

Accademia Nazionale delle Scienze detta dei XL, Villa Torlonia, Rome: 27- 28 June 2019

Organizers: Vincenzo AQUILANTI, Andrea LOMBARDI, Federico PALAZZETTI

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## ***New frontiers in non-equilibrium thermodynamics***

Tommaso RUGGERI (Linceo, Università di Bologna)

In this survey, we first present a brief historical review of the still open problem that concerns the interrelationship between microscopic reversible dynamics of constituent molecules governed by Newton's law and macroscopic irreversible dynamics of the system composed of molecules under the entropy principle (second law of thermodynamics). Then we discuss some recent results obtained by extended thermodynamics of gases, in which we can establish a connection between two approaches of continuum mechanics and of the kinetic theory of gases at a mesoscopic level. This new theory has opened up new frontiers of research for a deeper understanding of non-equilibrium phenomena in gases with many applications both in the classical and relativistic cases.

## ***A new link between kinetic theory and continuum thermo-mechanics***

Masaru SUGIYAMA (Nagoya Institute of Technology)

Extended Thermodynamics (ET) of gases has been established as a theory to explore highly nonequilibrium phenomena beyond the local equilibrium assumption. ET takes count of the link to the kinetic theory of gases as its justification at mesoscopic level. For many years, ET has been confined within the study of rarefied monatomic gases.

Only recently ET of rarefied polyatomic gases has been constructed. The most typical one is the theory of 14 fields (ET<sub>14</sub>) of the mass density, the velocity, the temperature, the shear stress, the dynamic (nonequilibrium) pressure, and the heat flux. A remarkable feature of the theory is that it is composed of parallel hierarchical series of field equations of balance type, that is, the momentum series and the energy series. The theory is a natural extension of the well-known Navier-Stokes Fourier theory for viscous and heat-conducting fluids. By applying the constitutive theory of ET, the constitutive equations can be determined explicitly by the thermal and caloric equations of state together with the experimental data on the shear viscosity, the bulk viscosity, and the heat conductivity. The theory is fully consistent with the moment equations derived from the kinetic theory of polyatomic gases.

The purpose of the present talk is to make a review of the recent developments in the ET theory of polyatomic gases and also to show its applications to harmonic waves and the shock wave structure. Thereby we discuss about the descriptions of a gas from mesoscopic level to the macroscopic level, that is, from the kinetic theory to continuum thermo-mechanics. Lastly we mention briefly more refined version of the ET theory of rarefied polyatomic gases in which molecular rotational and vibrational relaxation processes are treated individually.

## ***Beyond Boltzmann-Gibbs in physics, chemistry and elsewhere***

Constantino TSALLIS (Centro Brasileiro de Pesquisas Físicas, Rio de Janeiro -  
Santa Fe Institute, New Mexico - Complexity Science Hub Vienna)

The celebrated Boltzmann-Gibbs statistical mechanics, based on its associated *additive* entropy  $S_{BG}$ , constitutes one of the pillars of contemporary theoretical physics. As well known, it enables the correct description of a wide variety of properties of uncountable so-called simple systems at their thermal equilibrium or close to it. It fails however when so-called complex systems are focused on at their stationary or quasi-stationary states. To cope with this type of limitations, a generalisation of the BG theory has been proposed in 1988 (Tsallis, *Journal of Statistical Physics*), based on a *nonadditive* entropy, currently referred to as  $S_q$ , which recovers  $S_{BG}$  as its  $q=1$  instance. This approach has been successful in very many natural, artificial and social systems, typically characterized by nonlinear dynamics whose maximal Lyapunov exponent vanishes, exhibiting generic long-range space-time correlations (e.g., many-body long-range-interacting classical Hamiltonian systems, strongly quantum entangled systems, asymptotically scale-free networks). A regularly updated Bibliography is available at <http://tsallis.cat.cbpf.br/biblio.htm> After a brief introduction of the grounding concepts, we shall exhibit several illustrative applications and verifications of theoretical predictions, with special emphasis on physics and chemistry, including some open problems such as the ground-state energies of all the elements of the entire Mendeleev table and of doped fullerenes, the recent  $q$ -generalisation of the Arrhenius law, and others.

## ***Discrete vs Continuum: quantum to classical via semiclassical***

Annalisa MARZUOLI (Università di Pavia)

Among the observables in Quantum Mechanics –associated with Hermitean operators- quantum angular momentum operators have discrete spectra, associated with integer or semi-integer quantum numbers in units of the Planck constant. Angular momentum functions –Wigner rotation matrices, Clebsch-Gordan coefficients, Racah coefficients,  $3nj$  symbols- actually provide complete sets of orthogonal polynomials of the hypergeometric type useful for a number of applications in atomic and molecular physics, theoretical and mathematical physics, and beyond (*cf.* the talk of Roger Anderson).

Interacting systems characterized by sharp angular momentum eigenstates are prototypical instances of quantum integrable systems, and their classical counterparts –depending on continuous dynamical variables- inherit this property (upon suitable interpretations). In this talk I shall refer to a particular angular momentum function, the  $6j$  symbol. The basic ingredient will be the asymptotic formula for the  $6j$  established by Ponzano and Regge in 1968: it represents the semiclassical limit of the symbol when all the angular momentum variables becomes larger and larger, thus approaching their classical vectorial counterparts. The WKB method (briefly reviewed) is the mathematical tool for achieving the goal of exploring this ‘quantum to classical transition’, providing the expressions of wave functions in terms of a slowly variable amplitude and a phase which contains the classical action of the underlying theory. I will focus on two types of applications/interpretations of the  $6j$  asymptotics, in discrete gravity models and in quantum computing (where the transition is between quantum-discrete and classical-analogic models of computation).

### ***Statistics of energy partitions for many-particle systems***

Andrea LOMBARDI (Consortium for Computational Molecular and Materials Sciences e Università di Perugia), Federico PALAZZETTI (Consortium for Computational Molecular and Materials Sciences, Perugia), Mikhail B. Sevryuk (Russian Academy of Sciences, Moscow)

The hyperspherical coordinate systems have been extensively adopted in the study of few-body scattering problems of nuclear and molecular physics, for example in the practical implementation of demanding quantum calculations typical of chemical reactions. The use of such formalism is limited to the treatment of three- or four-center problems, due to the exceedingly high computational cost of quantum dynamics calculations. To circumvent this restriction, a hyperspherical formulation has been developed in a series of works during the last years [1–3], suitable for the modeling of aggregates and large molecular systems. Such a hyperspherical formulation is based on classical definitions of the hyperangular momenta and invariant dynamical quantities leading to a set of partitions of the total kinetic energy into terms corresponding to various kinds of motion.

In this contribution, we first consider the statistics of these terms for clusters with the number of particles from 3 to 100 (at randomly selected particle coordinates and velocities) analyzing two limiting situations: those of particles of equal masses and particles whose masses vary randomly. Then we illustrate the application of the hyperspherical partitions to the specific heats of Lennard-Jones clusters [4].

## References

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## ***From Boltzmann to non-Boltzmann distributions: strong to weak chaos***

Ernesto P. BORGES (Universidade Federal da Bahia, Brazil)

Exponential and Gaussian distributions galore in nature. Examples of physical systems fall within Boltzmann-Gibbs statistics, that derives from the entropy functional  $S_{BG}$ . Non exponential and non Gaussian distributions are also usually found in physical, biological and social systems. Particularly there are plenty of examples with power laws. Tsallis statistics provides a framework that stems from a generalized entropic functional, parameterized by an index  $q$ . Boltzmann-Gibbs is recovered as a particular case ( $q=1$ ). The procedure of optimization with proper constraints and Lagrange multipliers yield probability distribution functions (PDF) named  $q$ -exponential and  $q$ -Gaussian that recover the usual exponential and Gaussian as special cases. These PDF asymptotically behave as power laws ( $q>1$ ), and thus they are able to interpolate between them within the same framework. Exponential and Gaussian PDF are a sort of signature for equilibrium states of ergodic systems, for which interactions, memory effects and/or correlations among the constituent elements are sufficiently weak, or even nonexistent. Nontrivial ergodicity breakdown may drag the system into out-of-equilibrium quasi-stationary states, and PDF that emerges from Tsallis formalism have been observed. We address some conservative low-dimensional dynamical systems, the standard map and the web map [1--3], that exhibit a crossover between Boltzmann-Gibbs and Tsallis statistics. The phase space of these dynamical systems is defined by their control parameter, and present coexistence of regions of finite positive Lyapunov exponent ( $\lambda > 0$ ), i.e., strong chaos regime, and regions with vanishingly small positive largest Lyapunov exponent ( $\lambda \approx 0$ ), weak chaos regime. Positive Lyapunov regions present mixing, leading to ergodicity, and Gaussian PDF emerge. PDF of time average variables taken within the zero Lyapunov regions present long-standing  $q$ -Gaussian behavior. The control parameter of the dynamical systems continuously changes the phase

space, and consequently determines a continuous crossing between Tsallis and Boltzmann-Gibbs statistics. It is remarkable that the  $q$ -Gaussian PDF obtained from the time averages taken inside the regions of zero Lyapunov attain the value of  $q=1.935$ , regardless the values of the control parameter, for both standard and web maps. These results point towards the domains of validity of Boltzmann-Gibbs and Tsallis statistics.

### **References**

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## ***Out-of-equilibrium chemical reactions in neuromorphic engineering***

Pier Luigi GENTILI (Università di Perugia)

Chemical reactions that are maintained out-of-equilibrium through external forces can exhibit diversified behaviors. They can reach either stable or unstable steady states; alternatively, they can give rise to either periodic or aperiodic chemical oscillations; finally, they can proceed in a chaotic regime. Some of these out-of-equilibrium reactions are suitable to mimic the dynamics of neurons [1]. The well-known Belousov-Zhabotinsky reaction can be used to simulate either pacemaker or tonic excitable neurons. If we use UV and visible radiation as signals for the communication among chemical systems, photochromic and fluorescent compounds can be employed as surrogates of phasic excitable neurons. Finally, the photo-response of photochromic and luminescent materials in the presence of the convective motions of the solvent can give rise to chaotic dynamics and mimic neurons in a chaotic regime [2]. We present experimental data and simulations [3, 4] showing that pairs of out-of-equilibrium chemical reactions can communicate through one or two optical signals as Artificial Neuron (AN) models, and triads of ANs can be arranged and behave as both feed-forward and recurrent networks. We show that the ANs, powered by the energy of electromagnetic radiation and/or chemically, can give rise to the emergent properties of in-phase, out-of-phase, anti-phase synchronizations, and phase-locking, mimicking the communication among real neurons, from a dynamical point of view. Our results trace a new path in the field of Neuromorphic Engineering that is focused on the design of brain-like computing machines, which could have a revolutionary impact in our societies [5].

## References

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## Complete discrete basis sets in quantum mechanics

Roger W. ANDERSON (University of California, Santa Cruz)

This presentation first discusses present status for the calculation and properties of ortho-normal discrete functions that form a convenient basis for quantum mechanical calculations. The discrete functions are ortho-normal for a sum over the Discrete Variable and for a sum over Order.

$$\sum_{x=x_{\min}}^{N-1+x_{\min}} U(x, y)U(x, y') = \delta_{yy'}, \quad \sum_{y=y_{\min}}^{N-1+y_{\min}} U(x, y)U(x', y) = \delta_{xx'}$$

Discrete ortho-normal functions are also used for pattern recognition, smoothing and compression of data, signal analysis, and other purposes.

The discrete functions seem to be best calculated by diagonalization of a  $N \times N$  symmetric real tridiagonal matrix whose elements are given by the difference equation for the functions or underlying polynomials. Several important tools are introduced to aid in the interpretation and application of the discrete functions: Caustics, Braun Potentials (1978), and Scaling (Neville 1971 and Braun). Caustics mark the boundaries between non-classical and classical behavior of the discrete functions, and the Braun potentials are particularly useful for identifying caustics and regions of parameter space for bound and resonance states. Scaling determines the magnitude of the discrete functions in terms of the elements of the tridiagonal matrix. All of the tools require the eigenvalues determined by the diagonalization.

We review some examples of discrete functions based on  $3j$  and  $6j$  symbols (single well potentials, 2 turning points, in Euclidean, Hyperbolic, and Spherical space). We also mention some recent work on the connections between Wigner  $d$  functions and  $3j$  and  $6j$  symbols.

The rest of the talk is devoted to new work on other finite difference methods: Elongation (curve crossing), New observations about the difference equation method for solving differential equations (Multiple well potentials and tunneling), and other features of finite difference equations. Elongation is a method to change



the separation between the Braun potentials for 3j or 6j systems in Euclidian and non-Euclidian space. This method is particularly interesting because some choices for the separation lead to curve crossings which are interpreted with screens of the elongated functions and Braun potentials. The new interpretation for the finite difference method reveals tunneling and four turning point regions for calculations two turning point bound states.

Examples illustrate the new and older work.

### ***From polymer nanoparticles to structured materials***

Massimo MORBIDELLI (ETH Zurich, Politecnico di Milano)

Emulsion polymerization is widely used at the industrial scale to produce aqueous dispersions of polymer colloids, with highly controlled size and polydispersity, in a variety of different chemical compositions and morphologies. Such nanoparticles are typically coagulated in appropriate devices to produce the desired polymeric materials in the form of dry powders.

Recent results in the theory of colloidal systems indicated the possibility to exploit the aggregation and breakage events occurring in these devices to produce supranano-structures, which cannot be achieved otherwise. Appropriate chemical reactions are then conducted to provide suitable functionalities as well as mechanical properties.

For example, one can mix dispersions of colloids of different composition and realize composites where the different phases retain the same size and morphology of the original colloidal particles. By controlling the gelation process, one can create percolating phases inside such composites, which allow transferring physicochemical properties from the nano to the macro scale.

Examples of different structured materials of interest for various applications are discussed. These include the production of controlled porous materials in the form of powders or monoliths, which can be used as adsorbents, vectors for drug delivery or as thermal insulators.

### ***Fokker-Planck equation in chemical kinetics***

Paola DIOMEDE (Differ Institute, Eindhoven) - P. VIEGAS, M.C.M. VAN DE SANDEN,  
Savino LONGO (Università di Bari)

The kinetics of internal level populations in the course of a chemical reaction is a very important and interdisciplinary topic with an impressive range of applications. For example, the dissociation (“activation”) of CO<sub>2</sub> is presently under

widespread investigation in the perspective of climate change mitigation. In the authors' approach<sup>1-2</sup>, the internal energy distribution  $f(\varepsilon)$  is a solution of a Fokker-Planck equation which is solved by numerical methods. The chemically meaningful particular solution is selected by matching the total flux with the reaction rate. Transport coefficients present in the equation are related in a rigorous way to the specific rate of energy exchange processes and partially derived from generalized forms of detailed balance. Similar approaches have been used discontinuously in the 70's-80's but our version includes several improvements. It has been validated against the state-to-state finite rate one, which is known to produce the exact solution. With respect to this last, our approach provides a lower computational cost, the possibility of application to systems with a very large number of internal states and finally, valuable insight into the reaction itself, which can be interpreted as a transport process in the energy space, and discussed using concepts like diffusion, drift and flux.

### **References**

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## **Combustion kinetics and the environmental challenges**

Tiziano FARAVELLI (Politecnico di Milano)

Despite the continuous increase of the use of renewable energies, combustion of fossil fuels is still the worldwide primary energy source and this leading role is expected to remain unchanged for the next 50 years or so. Several reasons are at the root of this situation. The old and consolidated tradition of the combustion processes, the consequent low expensive industrial devices and well distributed infrastructures, the relative low cost of the fuels and of their supply and, above all, the energy density of the liquid fuels make combustion difficult to be rapidly replaced by technologies with comparable efficiency.

Unfortunately, combustion has several drawbacks, which are becoming more and more evident. The most debated in these last years is the greenhouse effect of carbon dioxide, with the related global warming effects. Formation of pollutants, like nitrogen oxides, hydrocarbon polycyclic aromatics and particulate matter, is another example of the dangerous consequences of combustion. Finally, the growth of the energy demand results in a continuous depletion of natural sources.

In this not idyllic scenario, the investigation of the chemistry of combustion reveals to be a key tool to reduce the negative impacts of these processes. Combustion kinetics presents some peculiarities, which make its study a difficult task. In particular, the temperature ranges are very wide, moving from 300 K up to 2500 K and over. This variability strongly affects the reactions rates, because of the exponential effect of temperature, as included in the Arrhenius law. The time scales involved in combustion span over different orders of magnitudes: from microseconds up to seconds. Consequently, any thermodynamic approach is useless. Fast chemistry, like the one controlling CO evolution, could approach equilibrium in many cases. On the contrary, slow chemistry, typical of pollutants like NO<sub>x</sub> and particulate can never attain the equilibrium.

The main characteristic of combustion kinetics is its complexity. Even the combustion of a simple fuel, like methane, involves several hundreds of species and ten thousands of reactions. The description of this chemistry is then very challenging. Moreover, this complexity results in the appearance of unusual phenomena, sometimes called combustion pathologies. Negative temperature coefficient, dumped cool flames and oscillating behaviors can be observed in many cases. Those phenomena control processes like ignition in internal combustion engines or instabilities in flames and their understanding is of paramount importance to increase efficiency and reduce emissions.

Kinetics is then a very challenging topic, whose investigation can contribute to reduce the negative impact of the combustion, but it is also a nice example of the impact of theoretical and fundamental studies to real world application. As a further confirmation, some of the results and of the tools developed for the study of combustion kinetics have shown to be effective in other fields of science.

***Hunting for elusive intermediates in the Selective Catalytic Reduction of NO<sub>x</sub>: how a fundamental study may result in a new exhaust after-treatment technology***

Enrico TRONCONI (Politecnico di Milano)

The Selective Catalytic Reduction (SCR) of nitrogen oxides with ammonia/urea is nowadays recognized as the best available technology for the abatement of polluting emissions of NO<sub>x</sub> from Diesel vehicles. Although extensively implemented worldwide, the more and more stringent emission regulations call for a substantial improvement of the technology, particularly during the critical “cold start” transients. To meet this goal, a deeper fundamental understanding of the SCR catalytic chemistry is urgently needed.

At Politecnico di Milano we have used chemical trapping techniques as a novel tool to assess the nature of unstable reaction intermediates in the Standard SCR reaction at low temperature (120°C-200°C). For this purpose, we have run transient response experiments over mechanical mixtures comprising a metal-promoted zeolite SCR catalyst (Fe-ZSM-5 or Cu-CHA) and a NO<sub>x</sub> storage material (BaO/Al<sub>2</sub>O<sub>3</sub>), which is able to trap and stabilize highly reactive NO<sub>x</sub> species. Our results confirm that NO is oxidatively activated to form a gaseous intermediate, which acts as a nitrite precursor (e.g. HONO or N<sub>2</sub>O<sub>3</sub>, with oxidation state of N equal to +3) and is eventually stored onto BaO/Al<sub>2</sub>O<sub>3</sub>. In the presence of ammonia, the same species can react readily with NH<sub>3</sub> to form N<sub>2</sub>. Such an activated gaseous NO<sub>x</sub> species is therefore a key intermediate of the Standard SCR mechanism over metal-promoted zeolites.

We have further demonstrated that the capability of our chemical trapping mechanical mixtures to capture NO in O<sub>2</sub> at low temperature can be exploited also in practical applications for NO<sub>x</sub> emission control during the cold start transients of Diesel vehicles. In fact, these systems (SCR catalyst + NO<sub>x</sub> storage material) are characterized by an intrinsic dual functionality: they are able both to store NO<sub>x</sub> at low temperature, when the SCR catalyst is not active yet and urea cannot be injected (e.g. below 170°C), and to reduce the stored NO<sub>x</sub> with ammonia at higher temperatures in the same single device. Accordingly, we have renamed these mixtures Adsorption + Selective Catalytic Reduction (AdSCR) systems. We are currently developing the new AdSCR concept in collaboration with Daimler AG.

This talk will summarize major results achieved when implementing mechanical mixtures of NO<sub>x</sub> Adsorbers and SCR catalysts both to elucidate the Standard SCR catalytic mechanism and to engineer the abatement of cold start NO<sub>x</sub> emissions.

***Exact quantum dynamics and kinetics for cold and ultracold reactions down to the Wigner's limit***

Dario DE FAZIO (CNR, Roma) – Simona CAVALLI (Università di Perugia)

Recent attention to cold environments, either in the laboratory or under astrophysical and other conditions, is putting at the forefront the tunnel effect, a principal source of deviations from the Arrhenius rate law. Progress in theoretical chemical kinetics relies on accurate knowledge of potential energy surfaces, as provided by advanced quantum chemistry and tested against experiments [1]. To generate accurate rate data, quantum scattering calculations involve sophisticated algorithms to produce scattering matrix elements at given angular

momenta (to be summed to yield cross sections) and as a function of collision velocities (to be integrated to give rate constants and temperature dependencies). Here illustrated are these passages, a milestone having been benchmark temperature dependent rate constants for the prototypical F + H<sub>2</sub> reaction [2], recently validated by experiments in the moderate tunnelling regime [3]. The F+HD variant permits exploring tunnel as well as isotopic effects [4] and developing a phenomenology and interpretive ingredients down to the deep tunnelling regime [5,6] where the reactivity is strongly dominated by resonances and quantum effects.

In the conference we discuss and compare cold and ultra-cold reactive behaviours of the F+H<sub>2</sub> reaction and of its isotopic variants (F+HD and F+D<sub>2</sub>) to deeply understand its dependence by the entrance channel behaviour of the potential energy surface [7]-

Simplified dynamical treatments and ultra-cold theories will be employed to understand the various resonance features obtained by 'exact' quantum reactive scattering results and as they affect cross sections and kinetic behaviours.

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### ***Path integral approach for partition function calculations***

Danilo CALDERINI

Exploring the phase space of complex molecules has an exponential computational cost which can become even more challenging near Conical intersections. One of the most studied consequence, the Jahn-Teller effect, can cause molecules to become fluxional and rearrange their configuration via quantum tunneling pathways. When these pathways wind around conical intersections, the geometric (Berry) phase strongly influences the dynamics and spectrum.

We employ full-dimensional simulations to locate the tunneling pathways from first principles in the methane cation and its isotopologues.

Taking account of the geometric phase and the change in the molecular orientation along the pathway, we predict spectra in good agreement with experiment, confirming the previous analysis for  $\text{CH}_4^+$ ,  $\text{CD}_4^+$  and  $\text{CH}_3\text{D}^+$ . However, the calculations show that, contrary to expectation, increasing the overall amount of deuteration does not necessarily reduce the tunneling splitting, leading to a new interpretation of the dynamics of  $\text{CH}_2\text{D}_2^+$  and  $\text{CD}_3\text{H}^+$ . The theoretical approach described could also be used to study the geometric-phase effect in other, larger molecular systems.

***From kinetic theory of gases to the kinetics of chemical reactions:  
matter on the verge of the thermodynamical and kinetic limits***

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New experiments and computational molecular dynamics are expanding our understanding of rate processes at low temperatures where deviations from linearity of Arrhenius plots are revealed [1,2]. When molecular systems in a specific phase are embedded in extreme environments, their thermodynamical behavior emerges in a specific limit which is attained under conditions on large volume and number of particles at a given density, while the kinetic features range between the limiting temperatures determining by the existence of specific phases. Here, invoking the correspondence between the microcanonical and canonical ensemble from Darwin-Fowler formulation, we evaluate activation and averages energies in rate processes yielding a retarded access to the thermodynamical limit: mathematically, the involved analysis requires reconsideration of role of the Euler exponential succession in Poisson and Boltzmann distributions. Arguments are presented to demonstrate as universal behavior the decrease in rates that can be theoretically described and amply documented in increasingly wider contexts, including viscosities and glass transitions, biological processes, enzymatic catalysis, plasma catalysis, geochemical fluidity, chemical reactions involving collective phenomena.[4]. The statistical mechanics formulation is based on Tolman-Fowler evaluation of the activation of processes from averages energies and their derivatives, permitting the introduction of the “transitivity function” that accounts for the quantitative compactness of the phenomenological formulas. The velocity distribution function far from the thermodynamical limit is derived and illustrated for the description of the kinetics of low-temperature transitions and

of non-equilibrium reaction rates, also beyond the classical cases to include Fermi and Bose statistics.

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