Introduction

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One contribution of 11 to a theme issue ‘Theoretical and computational studies of non-equilibrium and non-statistical dynamics in the gas phase, in the condensed phase and at interfaces’.

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In this Introduction, we show the basic problems of non-statistical and non-equilibrium phenomena related to the papers collected in this themed issue. Over the past few years, significant advances in both computing power and development of theories have allowed the study of larger systems, increasing the time length of simulations and improving the quality of potential energy surfaces. In particular, the possibility of using quantum chemistry to calculate energies and forces ‘on the fly’ has paved the way to directly study chemical reactions. This has provided a valuable tool to explore molecular mechanisms at given temperatures and energies and to see whether these reactive trajectories follow statistical laws and/or minimum energy pathways. This themed issue collects different aspects of the problem and gives an overview of recent works and developments in different contexts, from the gas phase to the condensed phase to excited states.
1. Introduction

How chemical reactions proceed in time and how phase space is visited is one of the main topics of physical chemistry. One of the most reliable and widely used models in reaction dynamics is transition state theory (TST) [1]. In the gas phase, a particularly powerful microcanonical-based theory is Rice–Ramsperger–Kassel–Marcus (RRKM) theory [2–4], from which the rate constant is easily obtained from the density and the sum of states of the reactant and the transition state (TS), respectively. This theory is based on statistical assumptions, as is TST, and it needs the knowledge of reactant and TS properties. This is simple when tight TSs are involved, but it is technically more complicated when the reaction proceeds through a loose TS. In this case, variational TST can be employed [5,6], or alternatively phase-space theory can be used [7–10], which does not need the molecular characterization of the TS but of the products. This last method is often used for cluster evaporation [11–13].

However, advances in experimental and theoretical methods have revealed the existence of non-statistical/non-equilibrium effects in a number of chemical reactions [14–22]. These effects cannot be taken into account by TST (or related theories), and although they sometimes may be neglected in the calculation of highly averaged macroscopic coefficients, as thermal rate constants, they are of key importance in the analysis of the reaction from a microscopic point of view.

In particular, assuming a gas-phase context (this implies that the reactions in other phases can be considered as a perturbation to gas-phase behaviours), we can distinguish two classes of non-statistical effects:

(i) non-RRKM, where the internal vibrational energy redistribution is not complete [23];
(ii) non-intrinsic reaction coordinate (non-IRC), when the reaction does not follow the IRC [24].

Their borders are not always sharp and other classifications have been suggested [25]. A close interplay between theory and simulations is necessary to understand these phenomena and to set up a well-defined approach to study and predict chemical selectivity.

Direct dynamics simulations are employed to study and identify non-statistical phenomena [26,27]. Thanks to increasing computer power, direct dynamics has been applied to large systems in the gas and condensed phases and in vacuum–solid interfaces. These simulations can improve existing theoretical models, which in general are based on statistical assumptions and on a reduced dimensionality potential energy surface (PES).

In the gas phase, there are examples of non-RRKM [28,29] and non-IRC behaviour [30,31] for unimolecular and bimolecular reactions. In the condensed phase, post-TS dynamics simulations can help us to understand the selectivity in organic reactions [32–35]. Non-statistical and non-equilibrium reaction dynamics often occur at the interface between gases and solids and liquids. Local heating of the solid or liquid can lead to non-statistical and non-equilibrium effects, before the system is equilibrated [36,37].

In this themed issue, we have collected together recent advances in the field based on a recent CECAM workshop organized in Paris, France, at the Institut Henri Poincaré (https://www.cecam.org/workshop-1241.html). In this workshop, overviews were presented of both theoretical developments and simulation results, which showed that equilibrium theories may not be sufficient to explain all the physics. Theoretical developments of analytical theories are still of major interest, because only with comparisons with correct and proper statistical treatments can one show if a phenomenon exhibits a real non-statistical effect, as applications of approximate theories may lead to quantitative deviations. In addition, we want to point out through the articles
collected in this themed issue that molecular simulations can not only be a source of information (i.e. of phenomenological data), but also a solid ‘experimental tool’ to verify and develop new molecular theories.

In this Introduction, we give a brief overview of the topics covered in this issue and use the occasion to underline some aspects which were discussed by the participants of the associated meeting.

2. Description of the themed issue

This themed issue starts with a perspective article by Ma & Hase [38] that provides an overview of what was done and understood in recent years on the non-statistical aspects of reaction dynamics. In particular, five classes of illustrative examples in which non-statistical dynamics play an important role are given: post-TS dynamics, unimolecular decompositions, non-IRC dynamics, bimolecular reactions and roaming dynamics. This perspective article provides the literature background introducing the field in which the following contributions are placed.

In this issue, we distinguish four important aspects, which are covered by contributed articles: (i) theoretical and algorithmic developments, (ii) reactivity in the gas phase, (iii) reactivity in the condensed phase and at interfaces, and (iv) excited state reactivity. We now provide the main insights of these topics as discussed in this issue.

(a) Theoretical and algorithmic developments

Developing theories for non-statistical and non-equilibrium effects entails going beyond the typical approaches based on statistical mechanics, like the aforementioned TS, phase-space and RRKM theories. Direct dynamics can give information on the statistical (or non-statistical) behaviour of a given system when results are compared with the appropriate theory. In some sense, if a comparison between simulation results and a quite approximate theory shows substantial deviations, one can argue for ‘dynamical’ (i.e. non-statistical or non-equilibrium) behaviour, while the problem may reside in the underlying theory. For example, TST is powerful and beautifully simple when applied to thermal reactions, but it becomes more complicated for state-to-state reactions [39]. Thus, theoretical developments are always important and still prevail. In the present issue, we show some recent examples based on TST and phase-space theory.

In the field of chemical kinetics, the Arrhenius law is surely (at least historically) one of the best known and most frequently used laws in chemistry [40]. The contribution of Aquilanti and co-workers [41] reviews their recent work on a reaction rate theory that is able to generalize the Arrhenius behaviour to low temperatures and to distributions of molecular states which do not follow Boltzmann statistics [42,43]. Different applications are given, from transport phenomena to quantum-mechanical tunnelling and to reactions that are strongly hindered.

Phase-space theory is the starting point of the contribution by Hervieux and co-workers [44]. In this article, the authors present a derivation of a four-component Wigner equation for a system composed of spin-1/2 fermions including the Zeeman effect and spin–orbit coupling. Through coupling with hydrodynamic equations, they show how this approach can be applied to condensed-phase systems or nano-objects.

To correctly use theories and perform simulations, the definition of molecular geometries is crucial. This is easy for relatively small molecules, while it becomes more difficult when molecules are flexible or for relatively large clusters. In the contribution by Marques and co-workers [45], an approach is presented based on an evolutionary algorithm to find minimum energy structures [46], applied here to an aggregation of solvent molecules, aggregates and micro-solvation of ions.

(b) Reactivity in the gas phase

Gas-phase reactivity provided historically the largest number of examples of non-statistical and non-equilibrium behaviours in chemical reactivity. This is for at least two reasons: (i) theory
and chemical dynamics simulations in the gas phase are easier to carry out, in terms of formal developments (for theory) and computation power (for simulations), and (ii) in the gas phase, due to the absence of a bath, which retains the excess energy, the molecular systems are not quickly thermalized and fast (non-equilibrium) processes are intrinsically easier.

Here, we have collected examples of systems in which different aspects of gas-phase reactivity are investigated, and in particular different mechanisms of unimolecular fragmentation. In the paper by Bowman and co-workers [47], the unimolecular fragmentation of H2CO is discussed using a newly parametrized PES. Particular emphasis is placed on the roaming mechanism observed previously by the same group [48], which is now enhanced with the new PES. Roaming is a particular mechanism of unimolecular dissociation that is not well described by TST and an IRC. To what extent this mechanism, typical for this kind of reaction, can be extended to other chemical reactions should be something of interest to investigate, not only for gas-phase reactions.

Another kind of reactivity, which cannot be described by TST, is given in the contribution by Yáñez and co-workers [49]. They give an overview of their recent work [50–52] in which they show that, to correctly understand collision-induced dissociation obtained in mass spectrometry experiments, it is necessary to go beyond the description of dissociation pathways only by minima and TSs. In particular, two non-statistical effects are reported: (i) the so-called shattering mechanism dealing with high-energy fragments, observed experimentally and which cannot be deduced only from the inspection of the PES, and (ii) the dynamics after the TS which do not follow the minimum energy path, such that a single TS leads to more than one mechanism. As remarked in the meeting by Prof. Yáñez, this study should show to the community of electronic structure theory that the information on the minima and TSs is only a first step to understanding chemical reactivity and that the dynamical effect can be crucial.

Another example of gas-phase reactivity is given in the contribution by Simon and co-workers [53]. They studied the decomposition of a particularly interesting class of molecules, the polycyclic aromatic hydrocarbons, which are relevant in astrophysics and astrochemistry. A problem in chemical dynamics is the level of theory employed in the electronic Hamiltonian. They show that tight-binding density functional theory (DFT) compares well with DFT, while the former is computationally much faster than the latter, giving access to more statistically grounded information. In their case, in which the energy is initially equally partitioned through all the internal modes, the decay is exponential and rate constants are extracted, similar to what Hase and co-workers have shown for other large molecules [54].

(c) Reactivity in the condensed phase and at interfaces

Chemical reactivity in the condensed phase is a more complex problem, as the environment can play different roles. TST sometimes works, but the ability of the solvent to equilibrate rapidly with the reactive system for exothermic reactions should be considered. In particular, viscosity and more general solvation dynamics are accounted for in the theories by Kramers [55] or Grote & Hynes [56]. Atomistic simulations are rather difficult since, if using an implicit solvation, local effects and friction (static or dynamic) are often not considered. While some authors have designed simulations in which the solvent dynamics is considered through a collective solvent coordinate [57–59] (as within a Langevin dynamics formalism) this is not a standard approach because the properties of the solvent coordinate are different for each system. Using an explicit description of solvent molecules makes the calculations ‘heavy’ in terms of computer power, limiting the statistical sampling. This is why often only the thermodynamics of the process is considered via, for example, umbrella sampling or related methods to calculate the free energy profiles [60–62]. Reaction dynamics in solution should, in principle, more closely follow the minimum energy path than in the gas phase, as the solvent is able to take the excess energy, keeping the trajectory in the vicinity of this ideal path. This is exactly why the solvent relaxation time is involved in determining the actual trajectory that a reactive path follows. Recently, some post-TS dynamics was performed in the liquid phase, pointing out the appearance of dynamical
effects [63–67]. The dynamics after the TS can be fast enough such that the solvent does not have
time to rearrange and equilibrate according to the solute motion.

In this issue, an example of how dealing with reactions in the condensed phase, where multiple
coordinates are involved, is given by Glowacki and co-workers [68]. In particular, they show how
by using an empirical valence bond approach, correctly calibrated to accurate quantum chemical
calculations, it is possible to study reactions at a gas–surface interface. Of particular interest is
the discussion of the energy transfer needed to make the reaction occur: energy dissipation from
the surface to hotspots is fast but a fraction of the dissociation reaction occurs before thermal
equilibrium, resulting in a non-equilibrium phenomenon.

(d) Excited states reactivity

Reactions occurring in excited electronic states are also examples in which the dynamics
often proceeds far from the minimum energy path and non-equilibrium phenomena often
observed [69–74]. These dynamics may have different origins, but an important issue is that
excited state potential energy barriers are often very small or non-existent, such that the system
reacts much before statistical equilibration of the original ground state nuclear wave-packet. In
this themed issue, we report a contribution by González and co-workers [75] on the complexity
of excited state dynamics. One particular problem which may arise is the need for accurate
potential energy surfaces for both the ground and excited electronic states. Dynamics in the
excited states is often characterized by motion on different adiabatic surfaces, which are coupled
in particular regions. These regions are even more difficult to treat and thus many developments
are present in the literature [76–82]. The González group gives an example of deactivation of
5-bromouracil after UV excitation by using their own development of surface-hopping dynamics
to deal with intersystem crossing regions, which are found from multi-reference wave function
calculations [83,84].

Another important point in excited electronic state reaction dynamics is the energy distribution
of products. To determine whether or not it is statistical, experimental determination is
fundamental. In the contribution by Bañares and co-workers [85], CH₃I photo-dissociation is
studied by non-resonant multi-photon ionization (NRMPI). Comparison with quantum dynamics
was able to provide the sensitivity of the NRMPI approach.

3. Conclusion

The topics we have briefly summarized in this Introduction are fully described and discussed in
the articles gathered in this themed issue. In the CECAM workshop related to the present themed
issue, extensive and fruitful discussions between all the participants added important value to
the presentation of these (and other) topics. Unfortunately, it is not possible to report all these
discussions, but here we can underline two of the main important issues:

(1) A first topic, which is important to correctly characterize dynamics, is the problem of
zero point energy (ZPE). Classical molecular dynamics follows Newtonian trajectories
and thus ZPE is not necessarily conserved. This can be crucial for the possibility of energy
leakage to occur: for example, when a high-frequency mode leaks its ZPE and this energy
is transferred to a low-frequency mode, sometimes resulting in unphysical reactivity; or
obtaining reaction products without the ZPE. Often the approach used is to discard such
trajectories, but this reduces the statistics, increasing the computational effort needed to
have converged results. In addition, it may be inaccurate to simply discard trajectories.
More theoretical and algorithmic developments in this direction are surely important.

(2) A second aspect is more related to the understanding, in terms of ‘simple’ pictures,
of reactions occurring on multi-dimensional PESs. Normally, the reaction is thought to
proceed on an idealized one-dimensional coordinate (the so-called reaction coordinate).
New properties can arise, for example, when moving to a two-dimensional surface.
For example, when a reaction is described on such a two-dimensional surface, it is possible to have two saddle points without any minimum in between (something not possible on a one-dimensional surface). Now, molecular systems proceed on 3N-6 hyper-surfaces: how can we conceive them? Is it always possible to reduce these problems to one- or two-dimensional problems? Can we see new phenomena that depend on such high dimensionality and that we cannot even conceive from standard one- or two-dimensional descriptions? This should be an issue to address for the future and, as was nicely commented on by Prof. B. Carpenter during the discussion, we will need a ‘Picasso’ to be able to conceive a ‘cubist’ molecular picture.

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Competing interests. The authors declare that they have no competing interests.

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References


