PCCP

ROYAL SOCIETY OF CHEMISTRY

EDITORIAL

View Article Online
View Journal | View Issue

Cite this: *Phys. Chem. Chem. Phys.*, 2022, **24**, 28660

New perspectives on molecular simulation of chemistry and physics in external electric fields

Peter G. Kusalik,[a] Maria E. Gracheva,[b] Sason Shaik[c] and Niall J. English*[d]

DOI: 10.1039/d2cp90209e

rsc.li/pccp

The importance and topicality of external electric fields in our environment is increasing continuously, owing, in no small part, to the growth of wireless communication systems, together with rising interest in medical, environmental and industrial applications. Given that non-equilibrium molecular simulations in external electric fields offer a mechanistic perspective into such phenomena, they have become an essential tool in recent decades for developing our understanding of how external electric fields manipulate a systems' behaviour.

The first non-equilibrium molecular simulations, involving constant forces acting on Lennard-Jones particles featuring de-facto nominal, proxy 'charges', were carried out in the 1970s, whilst the first such simulations in external electric fields on molecular fluids (*i.e.*, involving field-induced torques) were conducted over 40 years ago. Indeed, the application of such external fields to empirical force-fields has multiplied greatly in activity in the past decade or so – to the point that the ability to apply external electric fields, at least in some fashion (perhaps in a static sense), has become a 'near-staple' of community software packages.

This themed issue highlights some important trends in external electric fields in molecular simulation. Most fundamentally, and thought-provokingly, Kathmann (https://doi.org/10.1039/D1CP03571A) has probed with insight and acuity the very underlying nature of *intrinsic* electric fields and potentials within condensed phases – providing the very physico-chemical context for how the external fields that other contributors explore couple to influence condensed-matter system behavior. Marracino *et al.* (https://doi.org/10.1039/D1CP04466D) have studied the details of the non-linear response of such systems to such external electric fields, underscoring the importance of external-field amplitude and non-equilibrium statistical mechanics. Based on such fundamental frameworks of field physics and statistical mechanics, Futera and English (https://doi.org/10.1039/D1CP04165G) have considered how equilibrium-state crystal dielectric properties are perturbed by oscillating fields, whilst Vanzo *et al.* (https://doi.org/10.1039/D1CP04220C) have probed electrowetting transition at surfaces and the influence of external-field polarity thereon. Very importantly, Wells *et al.* (https://doi.org/10.1039/D1CP03965B), Daivis *et al.* (https://doi.org/10.1039/D1CP04139H) and Choudhary *et al.* (https://doi.org/10.1039/D1CP04589J) have thoughtfully probed how molecular transport and diffusivity is affected by external fields, in terms of mechanistic details of field coupling therewith and momentum transfer thereto – which is of key technological importance. Of course, perhaps no area is more important than biological systems for exposing the dramatic effects of external-fields, and Noble *et al.* (https://doi.org/10.1039/D1CP05510K) have discussed and critiqued masterfully this rich "playground" – including the important and topical matter of field-manipulated chemical reactivity. Taking up this latter theme, Siddiqui and Dubey (https://doi.org/10.1039/D1CP03978D) have studied the intrinsic, or local, electric field as (literally) a reaction coordinate – also linking to Kathmann's exposé (https://doi.org/10.1039/D1CP03571A) of the importance of local electric fields in our thinking and understanding in general on fields in physics, chemistry and biology. Continuing this area of electric fields and chemical reactivity, Cassone *et al.* (https://doi.org/10.1039/D1CP04202E) have examined thoughtfully field-affected proton transfer, whilst Pei *et al.* (https://doi.org/10.1039/D1CP04444C) have clarified electrostatic effects on carbene catalysis where, once again, local fields are important.

Arguably the most pressing and exciting development in the past decade or so,

[a] *Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta T2N 1N4, Canada*
[b] *Department of Physics, Clarkson University, 8 Clarkson Ave., Potsdam, NY 13699, USA*
[c] *Institute of Chemistry, The Hebrew University of Jerusalem, Givat Ram Campus, Jerusalem 91904, Israel*
[d] *School of Chemical and Bioprocess Engineering, University College Dublin, Belfield, Dublin 4, Ireland. E-mail: niall.english@ucd.ie*

especially since the 2011 CECAM workshop on external electric fields,[1] has been the emergence of detailed studies of chemical reactivity in such fields. Indeed, this area has, in large part, served as motivation for the recent well-received Royal Society of Chemistry book on the topic of external electric fields in chemistry.[2] Although this area of enquiry is still in its relative infancy, the demonstration that energy barriers and activation energies are altered by both static and alternating electric fields is of interest and importance. This applies not only in the case of rearrangement of covalent bonds *per se*, but also in the case of wider diffusion- and mass-transfer-limited reactions. More broadly, there have been substantial algorithmic improvements in the handling of structural rearrangements in molecular systems – biological and otherwise, as well as an emergence of understanding in how external electric fields manipulate the covering of protein coronas, or cloaks, on nanoparticles.

A further important area, and opportunity, that has been less fulfilled, lies in how external electric fields, whether time-dependent or not, can be incorporated into enhanced-sampling approaches. This represents a rich new area for development – and this is particularly the case for electronic-structure approaches (*e.g.*, density-functional theory and tight-binding density-functional theory) with biased Hamiltonians that will allow for field effects on thermalised chemical reactions to be studied carefully, as well as associated reaction-energy barriers and activation energies.

In terms of future directions, the development of machine-learning approaches for higher-quality atomistic potentials, incorporating many-body and polarisability effects implicitly, can be fitted and tuned using high-quality electronic-structure simulations, and the prospect of combining external fields with electronic-structure calculations for the fitting of (field-adjusted, 'polarisation-aware') accurate machine-learning potentials is exciting – indeed intoxicating! This will allow for non-equilibrium molecular simulations to become an even more powerful predictive molecular-design tool for the control of external electric fields on many phenomena – including chemical reactivity, mass transfer and phase-change dynamics. In effect, this will liberate and unleash the true potential of high-accuracy quantum mechanics in external electric fields – 'democratising' its practice on modern high-performance computing systems most probably decades before quantum computing will allow this for full quantum accuracy.

References

1 CECAM Flagship Workshop on Molecular Simulation in External Electric and Electromagnetic Fields, 19-21 May 2011, University College Dublin; programme at: **https://www.cecam.org/workshop-details/783**.

2 *Effects of Electric Fields on Structure and Reactivity - New Horizons in Chemistry*, ed. S. Shaik and T. Stuyver, Royal Society of Chemistry, 2021, pp. 428, DOI: **10.1039/9781839163043**.