Challenges in the modelling of plasma-surface interactions

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This contribution briefly addresses some current challenges in the modelling of plasma-surface interactions. Different types of models focus on different time and length scales and have specific challenges of their own. From the shorter to the longer scales, these formulations include atomic level simulations, kinetic Monte Carlo algorithms (KMC) and deterministic descriptions. The biggest challenge, however, resides perhaps on how to include the detailed information of atomic scale simulations into reliable and effective models that can be easily incorporated in simulations of realistic systems. A key role can be played by the KMC methods, currently under expansion, as their intermediate degree sophistication places them in a perfect position to help bridging this gap.

1. Statement of the problem

Modeling of plasma-surface interactions is a multi-scale problem. At the lowest level lies the detailed atomic-scale description of the elementary acts of adsorption, desorption, diffusion, and reactions on the surface. Despite the huge progress in recent years on the computation of potential energy surfaces from density functional theory and their use in classical molecular dynamics (MD), there is still a substantial discrepancy in the time and length scales of what is practically feasible in terms of calculation time at the atomic level and the time and length scales involved in a real system [1]. Another challenge to MD calculations is to accurately account for excited states, electromagnetic fields, charged particles and photons.

At the next, mesoscopic, level, plasma-surface interactions can be modelled using stochastic kinetic Monte Carlo (KMC) algorithms [2]. KMC algorithms do not solve explicitly the master equation for a given system, but instead numerically simulate the underlying Markov process. Efficient algorithms describing NO and O_2 recombination in silica were recently presented [2], opening the door for a significant development of this approach. However, these models lack a truly predictive power, as they need as input the energy barriers for each elementary step and other physical parameters.

The KMC approach can be further coarse-grained to derive models adopting a deterministic description (DD), where surface kinetics is formulated in terms of fractional coverages of different types of adsorption sites, simulated by a system of reaction-rate differential equations. The main advantage of this mesoscopic approach is its simplicity and computational efficiency, which allows the straightforward coupling to gas phase chemistry in reactor-scale simulations and in computational fluid dynamics. However, compared to KMC, it does not account for spatial correlations and cannot handle easily probabilities that depend on the local configuration of the system, characterize fluctuations and relies on additional assumptions regarding the treatment of physisorbed species [2]. The incorporation of a description of surface modification under plasma exposure is another critical step for further development of both KMC and DD models.

To bridge the gap between the sophistication of MD and the effectiveness of the DD remains perhaps the biggest challenge of all. In this context, KMC simulations play a central role: on the one hand, they can incorporate the information coming from ab initio simulations regarding binding energies, energy barriers and dynamic surface modifications; on the other hand, they can be used to validate and benchmark DD models and the underlying approximations [2]. A combination of KMC and ab-initio calculations was already used for predictive modeling of real catalytic systems [3], but the application of this combined approach with generality remains another important challenge. A description of KMC methods and examples of application will be given at the conference.

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2. References

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