

Chemical reaction paths in classical potentials

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Abstract

Chemical reaction dynamics are usually tackled within the framework of Quantum Mechanics which can be computationally demanding. Here we suggest to use the energy-dependent Hamilton-Jacobi description with a classical reactive force field to obtain the most probable path. This may enable to calculate the reaction rate.

Reaction rates are an important characteristic of molecular processes and determine their speed. The chemical reaction rate is usually governed by the free energy barriers encountered during the reaction. The reaction dynamics can be analyzed by QM calculations [1] which can be computationally demanding. When the reaction time is shorter than the time period simulated by the classical molecular simulation, one can observe its dynamics by performing classical simulations with reactive force fields [2]. However, when the reaction is slower than the simulation time, the reaction typically does not occur during the simulation and therefore its dynamics cannot be determined by performing a standard simulation.

It has been suggested in a study on protein folding to switch from the time-dependent Newtonian description to the energy-dependent Hamilton-Jacobi (HJ) description in order to obtain the most probable path in protein folding, given the initial and final configurations. The HJ formulation considers intervals of fixed displacements rather than fixed time length and thus avoids the long times needed to cross high energy barriers [3, 4]. Here we suggest to use this technique to propagate the system from the reactants to the products of a chemical reaction (assuming the reaction occurs) using reactive force fields such as ReaxFF [2, 5]. The path obtained has a dominant contribution in the calculation of the path integral $p(\mathbf{x}_1, t_1 | \mathbf{x}_2, t_2)$ (see Ref. [4]).

If the reaction is known as a function of time it may be used to approximate the probability of the reaction

$$p(\mathbf{x}_1, t_1 | \mathbf{x}_2, t_2) = e^{-(U(\mathbf{x}_f) - U(\mathbf{x}_i))/2k_B T} \int_{\mathbf{x}_i}^{\mathbf{x}_f} \mathcal{D}x(\tau) e^{-S_{\text{eff}}[x]/2D}$$

$$\approx a e^{-(U(\mathbf{x}_f) - U(\mathbf{x}_i))/2k_B T} e^{-S_{\text{eff}}[x_{\text{prob}}]/2D},$$

where x_{prob} denotes the path as a function of time obtained in the simulation and a is a constant. By approximating the probability of the reaction we may estimate the reaction rate.

We assume in the analysis above that there is one dominant path in the chemical reaction. For a general treatment one should take into account all the dominant paths. We aim at demonstrating and further assessing this exploratory study in our future project.

References

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