Theory of first encounters in complex media

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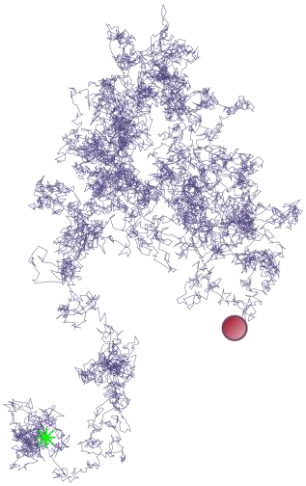

The first passage time is the time that a random walker, such as a diffusing molecule, needs to find a target for the first time (see figure showing an example of random trajectory joining a star source point and a round target point). Its determination is a key issue of random walk theory, with applications in contexts as varied as biophysics, finance or reactivity, because reactants unavoidably have to meet at least once before reacting. It is now well established that the transport step can qualitatively and quantitatively modify reaction kinetics. It is clear that contact kinetics depends on transport properties of the surrounding medium, both at large scales (which determine the frequency at which a random walker visits the neighborhood of the target) and at small scales (which set the probability of actual contact). However, it is generally difficult to take into account this complexity in the theoretical calculation of encounter kinetics. In this domain, we have recently solved a key step by introducing a new theory of first encounters that take into account memory effects (coming from interactions with other degrees of freedom) on first contact times [1,3].

In this thesis project, we will rely on these results, which at the current stage are relatively formal, to *explore different aspects of complexity on first encounter statistics in realistic systems.* More specifically, we will

(1) *Study the case of first encounters in viscoelastic media*. In this kind of fluids, the viscosity depends on the excitation frequency. In temporal space, this means that the friction on a tracer beads has a memory component, which complicates the description of first contact times. Here we will adapt our approach to predict the distribution of first encounters, as a function of the viscoelastic properties of the medium and of the local intrinsic reactivity.

(2) In a second time, we will study the case that the complexity comes from the structure of a macromolecule to which the reactant is attached. We will consider the example of the rare folding events of a fluctuating stiff rod (which is the standard model for DNA). In particular we will try to determine the regimes for which reaction is transport controlled. A possible application of such calculation is the understanding of a recent experiment that challenges the validity of DNA models (but which neglects transport aspects) [4]. As an extension, we will develop an analytical theory for imperfect rare events in systems with a large number of degrees of freedom, and identify transition paths times in such systems.

(3) Finally, another aspect of the thesis work will consist in suggesting experiments on first passage times in complex media that could be performed in the laboratory using complex polymer fluids (collaboration H Kellay) or optical traps (collaboration Y Louyer).

Profile: During the thesis, the student will mainly develop *analytical theoretical methods* that will be completed by *numerical (stochastic) simulations*. We are looking for a motivated student, with a solid background in physics, especially in statistical/theoretical physics. A specific knowledge of stochastic process is preferable, but not absolutely required (apart from Brownian motion). Mathematical rigor will be necessary to complete the thesis. If you are interested by this project, please send a CV, a motivation letter and the transcript of marks of your Master. Recommendation Letters and informal inquiries are welcome.

References

[1] T. Guérin, N. Levernier, O. Bénichou, R. Voituriez, Mean first-passage times of non-Markovian random walkers in confinement, *Nature*, **534**, 356-359 (2016)

[2] N Levernier, M Dolgushev, O Bénichou, R Voituriez, T Guérin, Survival probability of stochastic processes beyond persistence exponents, *Nature communications* **10** (1), 2990 (2019)

[3] T. Guérin, O. Bénichou, and R. Voituriez, Non Markovian polymer reaction kinetics, *Nature Chemistry*, **4**, 568-573 (2012)

[4] R Vafabakhsh, T Ha, Extreme bendability of DNA less than 100 base pairs long revealed by single-molecule cyclization, *Science*, **337**, 6098 1097 (2012)