Finding reaction paths and separatrices, a method based on Supersymmetic Quantum Mechanics.

Chemical systems often have a dynamics with well-separated timescales. For example, some polymers can be in a helix or a coil state. The dynamics within each one of these states is fast, essentially equilibrium and unremarkable, while the passage from one to another, which is what we are really interested in, may take a much longer time.

If chemistry is one day going to be practiced 'in the computer', then methods will be needed to sample directly the reaction currents, without having to wait for them to happen spontaneously. Thus, a considerable interest – as judged by the number of papers and congresses – has been devoted in recent years to this end, and a plethora of methods have emerged. None is entirely satisfactory, so there is room for progress.

In classical Hamiltonian dynamics there is an analogous situation, in which rare trajectories can be the ones that matter most. For example, planetary systems are very easily unstable. When a new system is observed, one usually assumes that it has been essentially the same for some time, and this implies fine-tuning of the observational data – small errors will make the system short-lived.

In the last few years I have been persuing, together with my thesis students S. Tanase-Nicola and J. Tailleur, a line of reseach originally inspired in supersymmetric quantum mechanics and its relation with Morse theory [1], to obtain practical methods to find such rare (but interesting) trajectories.

A. Supersymmetric quantum mechanics

Given a Langevin process, with or without inertia, one can express the evolution towards equilibrium of the probability by means of a Fokker-Planck or Kramers equation. For

[1] E. Witten, J. Di. Geom 17, 661 (1982).

example, in the overdamped case:

$$\begin{aligned} \frac{dP(\mathbf{x},t)}{dt} &= -H_{FP}P(\mathbf{x},t) \\ H_{FP} &= -\sum_{i}^{N}\frac{\partial}{\partial x_i}\left(T\frac{\partial}{\partial x_i}+\frac{\partial V}{\partial x_i}\right) \end{aligned} \tag{1}$$

The lowest (zero) eigenvalue of H_{FP} corresponds to the stationary measure, but *all low-lying eigenvalues* correspond to metastable states.

If we now supplement the space with N fermionic variables $(a_i^\dagger, a_i)$, and we define:

$$H_{SUSY} \equiv H_{FP} + \sum_{ij}\frac{\partial^2 V}{\partial x_i \partial x_j}a_i^\dagger a_j \tag{2}$$

we obtain the supersymmetric quantum mechanics, familiar from field theory though written in a different base. H_{SUSY} can be written as a perfect square $(Q+\bar{Q})^2$, where Q and $\bar{Q}$ are the (nilpotent) supersymmetric charges, which commute with H_{SUSY}.

The spectrum of H_{SUSY} can be classified according to the fermion number. It is quite simple to see that zero-fermion eigenvectors correspond to the Fokker-Planck process, those associated with low-lying eigenvalues are the metastable states. More interestingly, *one-fermion eigenvectors $\psi = \sum_i J_i(x)a_i^\dagger|- >$ with low eigenvalues encode the reaction current distributions $J_i(x)$ between states.* In general, k-fermion eigenvectors are k-forms peaked at the manifolds emanating downhill from states with k unstable directions. The spectrum is organised as in Fig. 1.

Up to here, we have paraphrased and generalised the work of Witten, followed by Helffer and Nier (In Ref. [57,60] without inertia, in [65] with inertia – apparently for the first time).

B. Two methods for finding reaction paths

The practical strategies we proposed are based on recalling that the dynamics in the zero-fermion sector (corresponding to the Fokker-Planck process) coverges to states, while the one in the one-fermion sector converges to reaction currents. *Just as we use a Langevin/Fokker-Planck process in practice to find states, we propose to use the process associated with one-fermion evolution to find directly the reaction currents.*

A first version is based on finding the 'Langevin-like' process that gives the dynamics of one-fermion wavefunctions. This consists of a series of walkers diffusing according to the

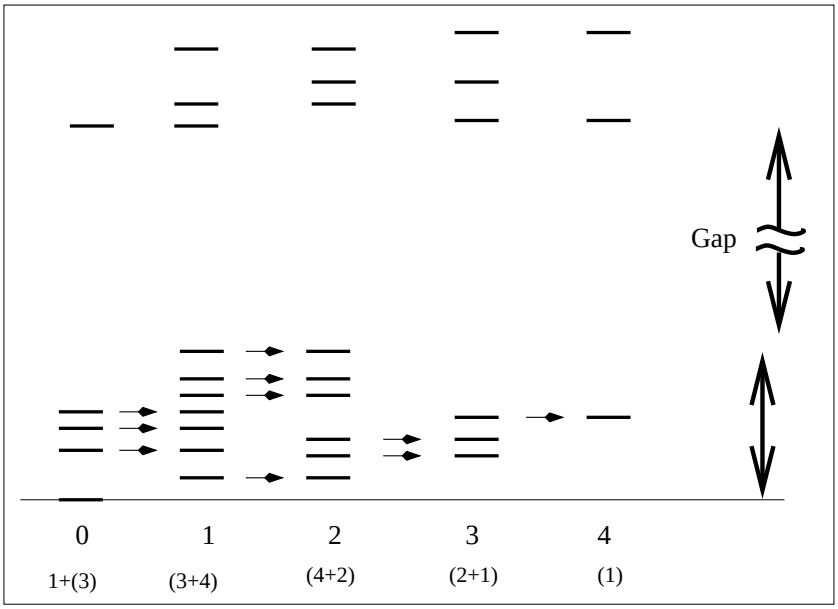

FIG. 1 The spectrum of supersymmetric quantum mechanics. The eigenvalues below the gap give the states and the transitions. The arrows indicate the action of the SUSY operator. Morse-theory relations can be read from this diagram, bearing in mind that eigenvectors 'below the gap' are related to unstable manifolds emanating from saddles.

ordinary Langevin process in the potential, but having a vector **u** attached to them evolving through:

$$\dot{u}_i = \sum_j \frac{\partial^2 V}{\partial x_i \partial x_j} u_j \tag{3}$$

The walkers are cloned or killed according to the rate of stretching of the vector **u** (see Fig. 2), which is normalised after each time interval. In Figure 3 we sketch how the walker

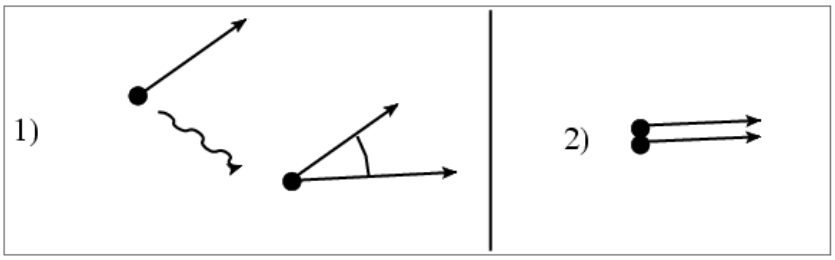

FIG. 2 The dynamics in the one-fermion sector consists of diffusion plus cloning proportional to the rate of expansion of the tangent vector.

density looks like, while Figure 4 shows the actual convergence of walkers to a reaction path:

notice that this is direct and involves no activations! Together with S. Tanase-Nicola and J.

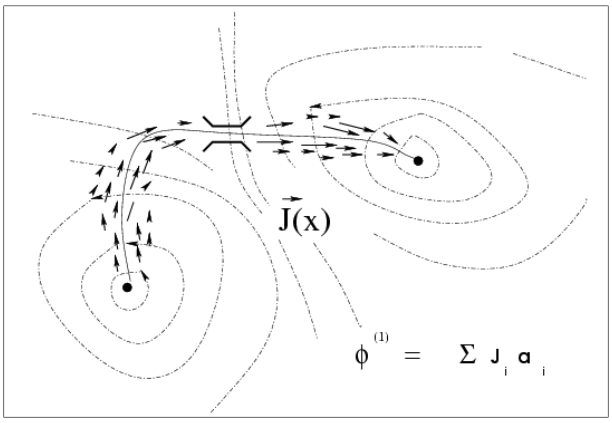

FIG. 3 One-fermion dynamics. Walkers converge to the reaction path. The coarse-graining of 'arrows' is the reaction current.

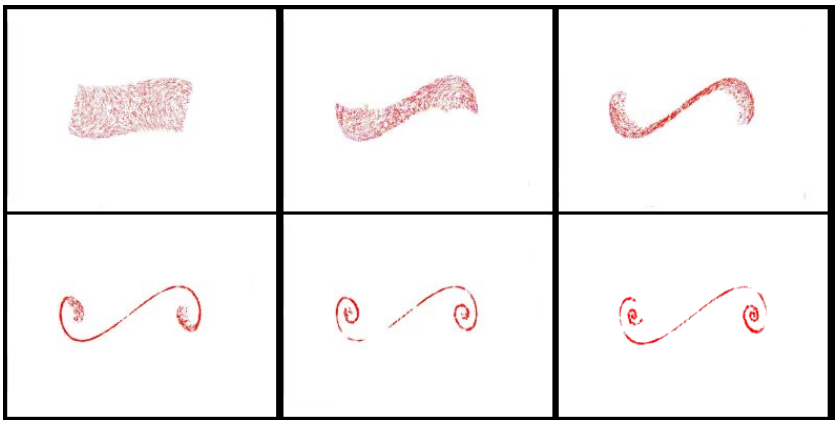

FIG. 4 A sequence showing the convergence of walkers to a transition path.

Tailleur, we have generalised this approach to the case with inertia, when the dynamics takes place in phase-space. For this we had to generalise Witten's approach to that case, a work that has arisen some interest in mathematicians [2]. At any rate, from the practical point of view, recently Mossa and Clementi [3] have applied the method to the helix-coil transition, with promising results (see Fig. 5).

[2] F. Herau, M. Hitrik, J. Sjoestrand, arXiv.org:math/0703684, M. Bismut, J. Amer. Math. Soc. 18(2005), 379

[3] A. Mossa, and C. Clementi, Physical Review E 75 046707 (2007)

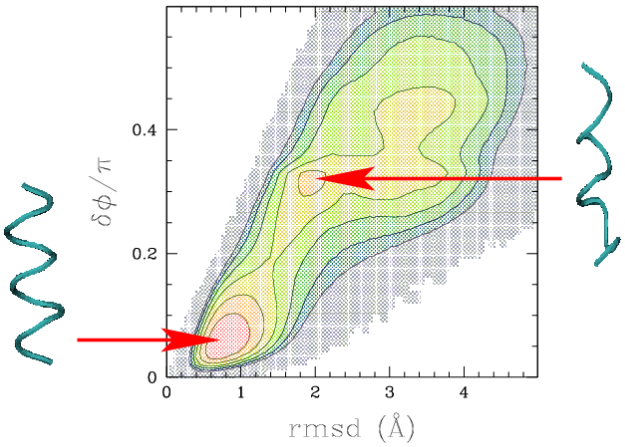

FIG. 5 The reaction path found by walkers in the helix-coil transition, taken from Mossa and Clementi. The phase-space has 72 degrees of freedom, of which only two are shown.

A second strategy for studying reactions is based on the so-called 'Transition Path Sampling' technique [4]. In this kind of approach, one samples over trajectories – essentially performing a numerical evaluation of a path integral. Now, if one adapts this method to work in the *one-fermion* subspace, one can show that this allows to retrieve the same information, but sampling mostly the barrier, rather than the metastable states. It turns out that the only modification one has to do is to weigh the trajectories with their ordinary (Onsager-Machlup) weight *plus the logarithm of their Lyapunov exponent*. Figure 6 shows what the typical trajectories look like: one sees that the sampling is concentrated on the barrier, to the point that fixing the extremes becomes even unneccessary.

[4] Bolhuis PG, Chandler D, Dellago C and Geissler PL, Annual Review of Physical Chemistry 53:291-318 (2002)

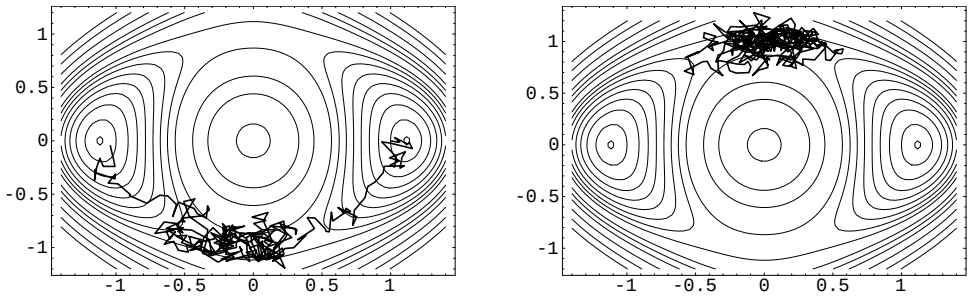

FIG. 6 Transition path sampling with Lyapunov weighting. Left: both ends of the reaction fixed. Right: no ends fixed, the trajectories find the saddle.

There is still a way to go to make a convincing ready-to-use program that can be applied for larger molecules. I intend to set up a collaboration with experts in the field of simulations, as this is the only way to make practical progress at this stage.

C. Rare trajectories in Hamiltonian systems

Together with J. Tailleur, we started the investigation [56,70] of a dynamics like the one in Fig. 2 in a pure Hamiltonian system. In fact, we actually generalised it, by multiplying the cloning rate by α one can show that one samples trajectories with an exponential weight $e^{\alpha\lambda}$ (with λ the Lyapunov exponent). This is the so-called *Thermodynamic Formalism* of trajectories [5], what we have done is a practical way to compute expectations. Setting α very negative, we select trajectories with small Lyapunov exponents: in Fig 7 we show how the tiny tori buried in a chaotic sea can be detected efficiently. This kind of situation arises, as mentioned above, in planetary systems.

On the opposite extreme, for $\alpha >> 1$ we can search for the most chaotic structures. Figure 8 shows the (very subtle) effect of a very weak chaotic perturbation on a separatrix.

The previous examples concern low-dimensional systems for which almost any method will work. Where the present method reveals its power is in a higher dimensional case. In Fig. 9 we set α negative to look for exceptionally low-Lyapunov trajectories for the Fermi-Pasta-Ulam chain: the program converges to a kink solution. We have also used α positive to detect 'chaotic breather' solutions. Note that the algorithm searches automatically the

[5] P. Grassberger, R. Badii and A. Politi, J. Stat. Phys 51, 135 (1988) 135; R Benzi, G Paladin, G Parisi and A Vulpiani, J. Phys. A:Math. Gen. 18 (1985) 2157-2165

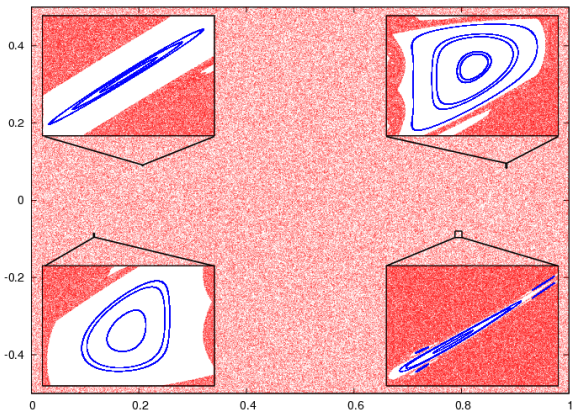

FIG. 7 Finding small tori (in the inset enlarged up to a hundred times) in a chaotic sea.

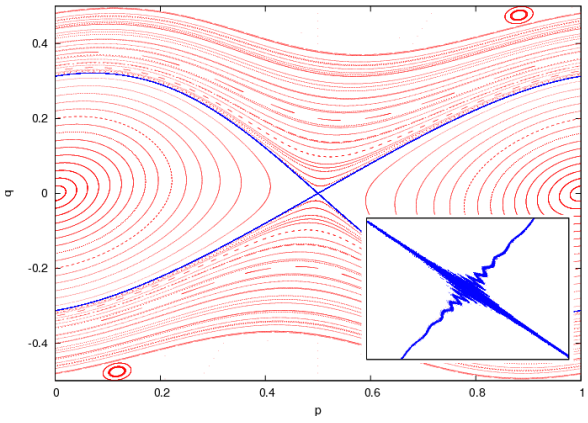

FIG. 8 The principal separatrix distorted by a very weak chaoticity. In dark blue: the walker distribution.

configurations, even when they are very unstable and rare. There is no need to choose carefully the initial conditions.

There are quite a few open perspectives, starting from finding solitons in biomolecules, where they may play an important role for transport, and in Bose-Einstein condensates. Also quite interesting would be to apply the algorithm in a problem of celestial mechanics: we have discussed this with the experts, and the conclusion is that it can only be done using as a basis an integrator already optimised by them.

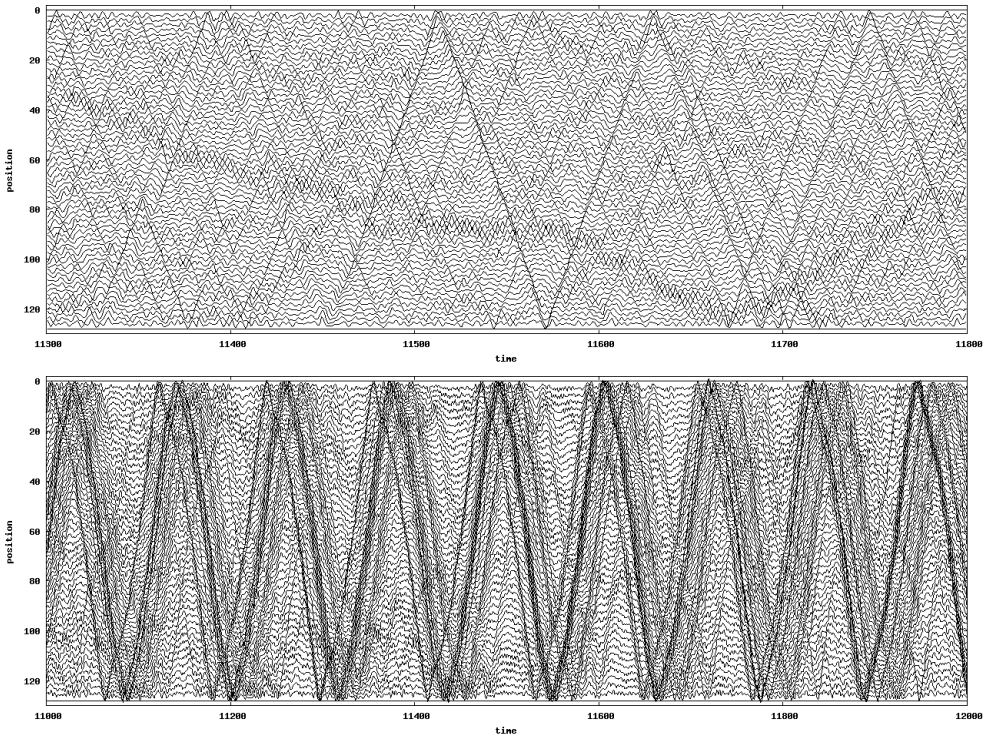

FIG. 9 Finding solitons. Top: an equilibrium trajectory of a Fermi-Pasta-Ulam chain. Bottom: same, but biased to have an exceptionally low Lyapunov exponent: the kink excitations are clearly visible.