

Supplementary Materials: Exploring potential energy surfaces to reach saddle points above convex regions

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The supplementary materials contain 3 files: 2 videos and one gnuplot file.

Video 1: Exploration_from_min.mp4 This video has been added to help understanding how Fig. 3 of the main text has been created. Starting from the black minimum, 200 explorations of the 2D PES are performed. To start each of them, an initial vector $\mathbf{V}_{\text{rinit}}$ is used until escaping the starting convex region, for which the boundaries are indicated by the blue lines. The 200 vectors are chosen to be equally distributed along the two dimensions, which forms a circle. For each search, the small black dots indicate the positions at which the forces have been calculated. They can be seen as the path used by ARTn to reach the saddle point. At the end of each search, these points are reset and a line indicating the initial $\mathbf{V}_{\text{rinit}}$ direction is colored with the same color as for the reached saddle point. The red color indicates directions where no saddle point has been reached due to a perpetual cycling. The blue lines indicate the inflection hyperplanes, *i.e.* where the lowest eigenvalue is zero.

The three cases of Fig. 3 are shown on the video, to show the best solution to escape the convex region: in the first case $\mathbf{V}_{\text{CR}}=\mathbf{V}_{\text{min}}$, in the second case $\mathbf{V}_{\text{CR}}=\mathbf{V}_{\text{rinit}}$, and in the third case $\mathbf{V}_{\text{CR}}=\mathbf{V}_{\text{rinit}}+\mathbf{V}_{\text{rnew}}$. The $\mathbf{V}_{\text{CR}}=\mathbf{V}_{\text{rnew}}$ case is not shown as it gives the same kind of results as $\mathbf{V}_{\text{CR}}=\mathbf{V}_{\text{rinit}}+\mathbf{V}_{\text{rnew}}$, but with a bigger number of force evaluations. The difference between the three cases can be seen when the path goes through a convex region that is not the starting one.

Video 2: Solve_cycling.mp4 This video is an illustration of the cycling problem on the 2D PES shown in Fig. 7b of the main text. It corresponds to one particular ARTn search for which the trajectory has a cycling behavior.

The video is divided into two parts. In the first part, the cycling behavior that occurs when $\mathbf{V}_{\text{CR}}=\mathbf{V}_{\text{rinit}}$ is shown. It corresponds to one of the searches initiated by the $\mathbf{V}_{\text{rinit}}$ that is colored red in the Video 1. In the second part, the solution using $\mathbf{V}_{\text{CR}}=\mathbf{V}_{\text{rinit}}+\mathbf{V}_{\text{rnew}}$ is shown. The blue arrow corresponds to the starting direction $\mathbf{V}_{\text{rinit}}$. The white arrow corresponds to

the new random direction \mathbf{V}_{rnew} . The black arrow $\mathbf{V}_{\text{rinit}}+\mathbf{V}_{\text{rnew}}$ is the sum used to push the system into the positive curvature region. The red arrow is the eigenvector of the lowest Hessian eigenvalue \mathbf{V}_{min} . It is used when the lowest curvature is negative. The green arrow is the relaxation direction, orthogonal to the push vector. On the right side there are, respectively: the number of ARTn iterations (step), the total energy with respect to the minimum, (DE) the total force (F), with components that are parallel (Fpar) and orthogonal (Fperp) to the pushing vector, the lowest eigenvalue (λ_{min}), the number of orthogonal relaxation (Perp relax) and the vector used to push the system (\mathbf{V}_{min} , $\mathbf{V}_{\text{rinit}}$, or $\mathbf{V}_{\text{rinit}}+\mathbf{V}_{\text{rnew}}$). Each black dot corresponds to a force calculation. To avoid having too many black dots on the screen, only the 10 last ones are represented, whereas the previous ones are set to gray.

gnuplot file: artn.gnu This program permits to create the Figs. 1c, 3 and 9 of the main article by simply running "gnuplot artn.gnu". It is divided in 3 main parts. The first part (lines 1 to 150) defines the PES, its derivatives, and how it is plotted. Other portions of the PES can be plotted if the corresponding lines are uncommented, and different PES can be plotted by modifying the parameters of the predefined functions. The second part (lines 152 to 266) permits to show the different features of the PES: inflection hyperplane, valleys, ridges, perpendicular hyperplane, the minimum and the saddle points. Other properties can be printed if the corresponding lines are uncommented, as the eigenvector field, and force field. These properties are obtained by scanning 40000 points of the plotted PES, as described in the main text, partitioning the x and y dimensions into 200 points each. The third part (lines 270 to the end) is the ARTn algorithm done in many initial $\mathbf{V}_{\text{rinit}}$ directions. To obtain Fig. 3a, \mathbf{V}_{CR} must be modified to \mathbf{V}_{min} by uncommenting lines 365 and 366. To obtain Fig. 3b, the α parameter (line 280) must be set to 0. To see the progressive path used by ARTn in each search, the intermediate "replot" lines 386 and 437 must be uncommented.