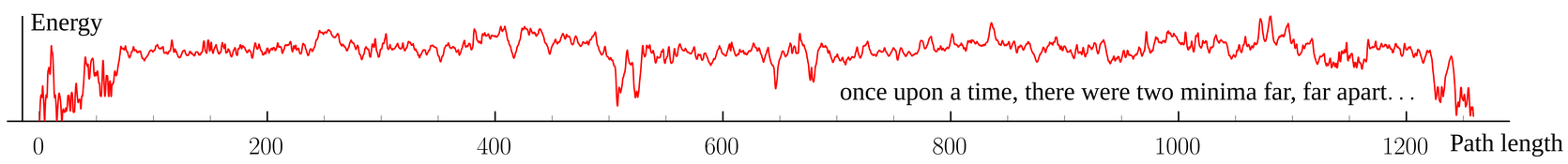
Finding Rearrangement Pathways

Semen A Trygubenko†, Tetyana V Bogdan# and David J Wales*

University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW, UK



The above is the energy profile for an example rearrangement of 75-atom Lennard-Jones cluster. The pathway was automatically generated using one of the connection algorithms developed by Wales group. It contains 482 intermediate minima.

Introduction

The potential energy surface (PES) governs the observed structure, dynamics and thermodynamics of any molecular system. It is often possible to gain new insight into these properties by expressing them in terms of stationary points of the PES, i.e. points where the gradient of the potential vanishes.[1]

The most important stationary points are minima and the transition states that connect them. Here we define a minimum as a stationary point where the Hessian, the second derivative matrix, has no negative eigenvalues, while a transition state is a stationary point with precisely one such eigenvalue.

The number of stationary points on the PES generally scales exponentially with system size,[1] which necessitates an appropriate sampling strategy of some sort for larger systems. In particular, to analyse dynamical properties a database of local minima and the transition states that connect them is usually constructed, which generally involves extensive use of single-ended and double-ended transition state searching techniques (see Refs. 1, 2 and references therein). The most successful single- and double-ended methods currently appear to be based upon hybrid eigenvector-following and the nudged elastic band approach, respectively.[1]

Any path connecting two minima on PES can be broken down into elementary rearrangements, each of which involves a single transition state. The corresponding mechanism can be analyzed in detail by calculating the two unique steepest-descent paths that lead downhill from the transition state.

Objective

The objective of this presentation is to introduce our methods for finding rearrangement pathways. We also describe several interesting properties of the rearrangement pathways, which may aid new algorithms development and design.

Doubly nudged elastic bands

Our ‘doubly nudged elastic band’ approach builds upon earlier work due to Henkelman and Jónsson and Czerminski and Elber. In our algorithm, a portion of the spring gradient perpendicular to the path is retained, overall rotation and translation of images are not removed, and the quasi-Newton L-BFGS method is used for minimization.[2]

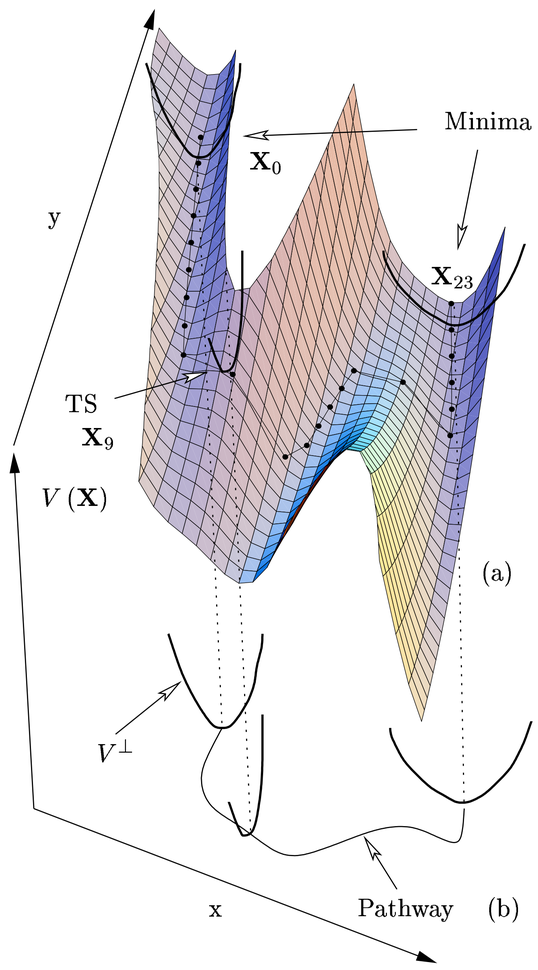


Figure 1: Graphical representation of the nudged elastic band approach. (a) The optimised nudged elastic band for a two-dimensional model surface. The band contains 21 images and connects two minima $\mathbf{X}_0$ and $\mathbf{X}_{23}$. Image $\mathbf{X}_9$ has the highest energy and might therefore be used to estimate transition state properties or as a starting guess for further refinement. (b) ‘Nudging’: the NEB depicted in (a) is projected onto the xy plane and feels only the perpendicular component of the true gradient from the effective potential $V^\perp$.

Connection algorithm

For minima separated by increasing distances in configuration space, the pathways that connect them are likely to involve more and more elementary steps, and are not unique. A new algorithm for locating multi-step pathways in such cases has recently been proposed.[1,2] According to this algorithm, consecutive DNEB runs aim to build up a connected path by progressively filling in connections between the endpoints or intermediate minima to which they are connected.

This is an advantageous strategy because the linear interpolation guesses usually become better as the separation decreases, and therefore fewer optimisation steps are required. Working with sections of a long path one at a time is beneficial because it allows the algorithm to increase the resolution only where it is needed.

Integrated path length and barrier height

Catastrophe theory establishes a quantitative connection between the potential energy barrier ΔV, the integrated path length Δs and the lowest vibrational frequency λ for a steepest-descent path linking a minimum and a transition state.[1,3] For short paths $\Delta V \propto (\Delta s)^2$, where the proportionality constant is a function of λ.

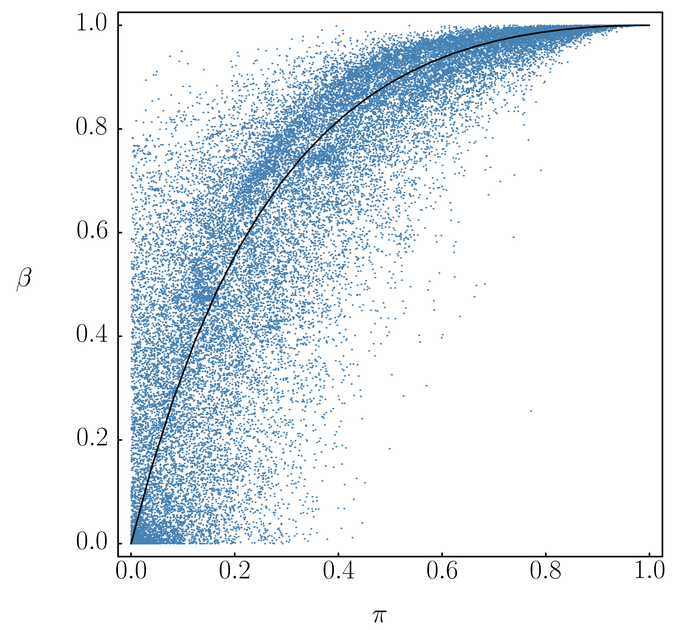


Figure 2: Barrier asymmetry index β as a function of integrated path length asymmetry index π.[2] The scatter plot shown is for an LJ_{75} pathway database. The parametric curve derived assuming quadratic dependence of barrier height on the integrated path length is also shown.

Cooperativity, localization and barrier height

For both clusters and bulk material cooperative rearrangements usually have significantly lower barriers than uncooperative ones, irrespective of the degree of localization.[4]

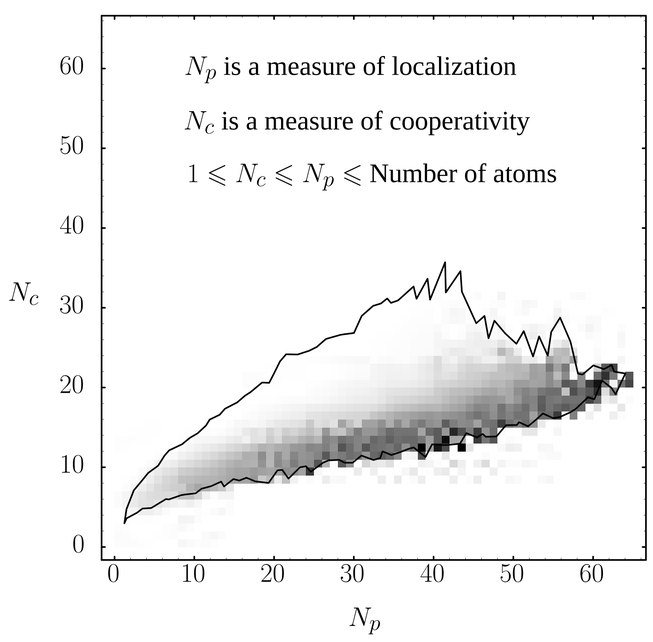


Figure 3: Average barrier as a function of N_p and N_c calculated for LJ_{75} pathway database. The darkest shading corresponds to the highest barriers. Outlying points are connected to illustrate the boundaries of the data area.

Sampling for stationary points

Stationary point databases constructed using random perturbations followed by quenching are likely to be biased towards uncooperative rearrangements.[4]

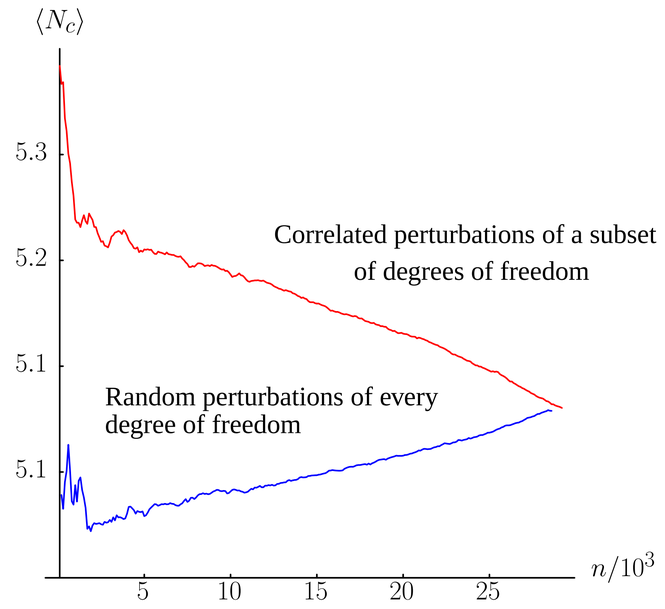


Figure 4: The average value of N_c for LJ_{13} pathway databases as new paths are added. 6-atom correlated perturbations (red curve) and random perturbations of every degree of freedom (blue curve) were used to produce starting points for refinement by eigenvector-following. Average values were calculated every time 100 new pathways were added.

Highlights

Extensive tests show that the DNEB/L-BFGS combination provides a significant performance improvement over previous implementations.[2]

Finding pathways in high-dimensional systems can become a challenging task. Some difficulties have been attributed to instabilities and inefficiencies in transition state searching algorithms, as well as the existence of very different barrier and path length scales.[2,4]

Catastrophe theory predicts quadratic dependence of an energy functional on the order parameter in the vicinity of structural or phase change.[3]

Uncooperative rearrangement pathways are usually harder to characterize using double-ended transition state searching algorithms since linear interpolation produces a poor initial guess.[4]

It is possible to influence the degree of localization of the pathways found using single-ended transition state searching algorithms.[4]

†E-mail: sat39|at|cam.ac.uk
WWW: http://www-wales.ch.cam.ac.uk/∼sat39/
#E-mail: tvb20|at|cam.ac.uk
WWW: http://www-wales.ch.cam.ac.uk/∼tvb20/
*E-mail: dw34|at|cam.ac.uk
WWW: http://www-wales.ch.cam.ac.uk/

References

[1] David J. Wales. *Energy Landscapes: Applications to Clusters, Biomolecules and Glasses*. Cambridge University, Cambridge, 2003.

[2] S. A. Trygubenko and David J. Wales. A doubly nudged elastic band method for finding transition states. *J. Chem. Phys.* , 120:2082–2094, 2004.

[3] T. V. Bogdan and David J. Wales. New results for phase transitions from catastrophe theory. *J. Chem. Phys.* , 120:11090–11099, 2004.

[4] Semen A. Trygubenko and David J. Wales. Analysis of cooperativity and localization for atomic rearrangements. *J. Chem. Phys.* , 121(14):6689–6697, 2