How to define Newton trajectories for mechano-chemistry

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This manuscript was compiled on March 21, 2024

Catch bonds | Newton trajectories | Potential energy surface

We congratulate C.O.Barkan and R.F.Bruinsma (1) for adapting potential energy surfaces (PES) for selectins (Fig. 1). This letter concerns mathematical inaccuracies. One treats the mechanochemical potential

$$V_f(\mathbf{x}) = V(\mathbf{x}) - f\, l \cdot \mathbf{x} \qquad [1]$$

$V(.)$ is the PES, l is the direction of an external force, f its magnitude. The stationary points $\mathbf{x_c}$ of the PES move under the force. Barkan and Bruinsma develop with (2) a differential equation

$$\frac{d\mathbf{x}_c}{df} = H^{-1}(\mathbf{x}_c)\, l\ , \qquad [2]$$

$H^{-1}(\mathbf{x})$ is the inverse Hessian of $V(\mathbf{x})$. We argue that use of Eq. [2] should be avoided because on a path from a minimum to a saddle points (SP) it is $Det(H) > 0$ in the minimum and negative in the SP. So there is always a point on the path where $Det(H)$=0 and where Eq.[2] becomes singular because the inverse matrix is used. This problem was solved by Branin (3). The better equation is with (4)

$$\frac{d\mathbf{x}_c}{dt} = Det(H)\ H^{-1}(\mathbf{x}_c)\, grad(\mathbf{x}_c)\ . \qquad [3]$$

$grad(\mathbf{x})$ is the gradient of $V(\mathbf{x})$. So the right one desingularized Eq.[3] is made worse into an equation with a singularity [2]. The solutions of Branins Eq.[3] are called Newton trajectories (NT), for more than a third of a century (4–6).

Singularities of [2] are artificial. They do not generate a force-induced switch (1). Every solution of Eq. [3] to different directions l connects a minimum with an SP and crosses the curve where $Det(H) = 0$ applies (green) called bond breaking point (7–9).

What is the field for NTs? In Fig. 1 we draw a family of NTs (blue). They follow the **gradient field** of the PES of Eq. [3], however not the field [2] with l=(1,1). The 'flow' image in Fig. 1D in (1) uses Eq. [2]. This picture is misleading for the idea of NTs. The arrow field in this Fig. 1D asserts a general meaning of the vectors of Eq. [2] in the full configuration space. This is not correct. In Fig. 1 we insert a trajectory of Eq. [2] (magenta) with start in the magenta point, with l=(1,1). It is not an NT because it does not cross a stationary state, $\mathbf{x_c}$. The magenta curve demonstrates well the circular character of the field [2], however, it has nothing to do with the solution of our problem: the movement of stationary points of the PES under an external force. The direction l=(1,1) only applies to the bold NT of Fig. 1. Apart from this NT this direction is of no interest. Drawing a vector field like in Fig. 1D of (1) is possible, but its solution curves are useless for our problem. NTs are not 'elliptic' like claimed in (1).

NTs can have turning points (blue dots). One could use the first appearance of a TP as an indication of a possible switch from slip- to catch-bond character, see the magenta dot. NTs without a TP on their energy profile are slip bonds (6), however, a TP is not sufficient for catch bonding, see an extreme counterexample (4). So the l-switch points and switch-lines in (1) are not well justified (10).

NTs offer tools for the investigation of reaction path models. We request the use of Branins Eq.[3] for the treatment of mechano-chemistry.

Materials and Methods

We used Mathematica 13.3.1.0 for Linux x86(64-bit).

ACKNOWLEDGMENTS. Financial support: Spanish Ministerio de Economía y Competitividad (PID2019-109518GB-I00); Spanish Structures of Excellence María de Maeztu program (CEX2021-001202-M); Agència de Gestió d'Ajuts Univeristaris i de Recerca of Generalitat de Catalunya (Projecte:2021 SGR 00354).

W.Q. designed research; W.Q. and J.M.B. wrote the letter. We declare no competing interest.

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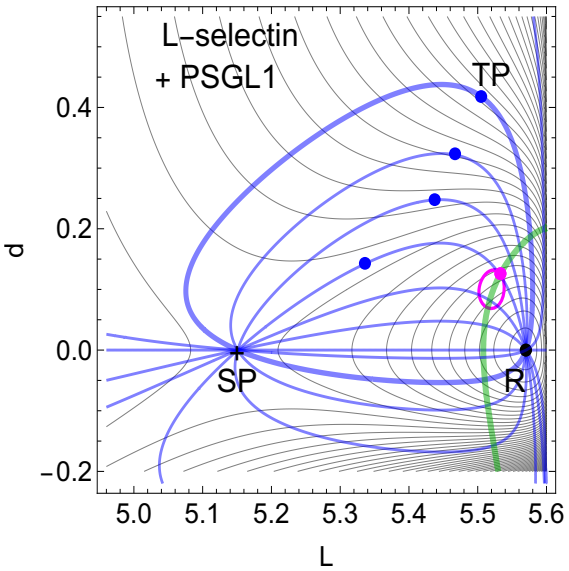

Fig. 1. PES of L-selectin (1) with x=(L, d) [nm], and NTs. R: minimum, thin black: level lines, thick blue: NT to direction (1,1), blue: other NTs, green: Det(H)=0 line, TPs: blue dots, magenta squiggle: trajectory to [2] through magenta dot.

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