

Transition state theory for solvated reactions beyond recrossing-free dividing surfaces

Fabio Revuelta

Grupo de Sistemas Complejos
Universidad Politécnica de Madrid
Instituto de Ciencias Matemáticas

BRITS16, Dresden, 9th September 2016

PHYSICAL REVIEW E **93**, 062304 (2016)

Transition state theory for solvated reactions **beyond** ~~recrossing-free dividing surfaces~~

F. Revuelta,^{1,2} Thomas Bartsch,³ P. L. Garcia-Muller,⁴ Rigoberto Hernandez,⁵ R. M. Benito,¹ and F. Borondo^{2,6}

¹*Grupo de Sistemas Complejos, Escuela Técnica Superior de Ingeniería Agronómica, Alimentaria y de Biosistemas, Universidad Politécnica de Madrid, Avda. Complutense s/n 28040 Madrid, Spain*

²*Instituto de Ciencias Matemáticas (ICMAT), Cantoblanco, 28049 Madrid, Spain*

³*Department of Mathematical Sciences, Loughborough University, Loughborough LE11 3TU, United Kingdom*

⁴*Centro de Investigaciones Energéticas Medioambientales y Tecnológicas, Avda. Complutense 40, 28040 Madrid, Spain*

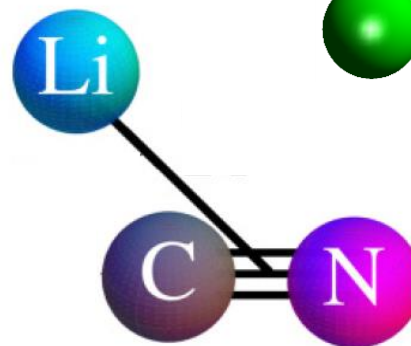
⁵*Center for Computational Molecular Sciences and Technology, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0430, USA*

⁶*Departamento de Química, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain*

(Received 19 August 2015; revised manuscript received 27 January 2016; published 6 June 2016)

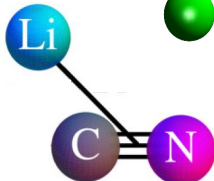
Motivation

Rate calculations are
computationally very
demanding



Motivation

**Transition
State
Theory**



An hourglass with orange sand falling from the top bulb to the bottom bulb. The top bulb is labeled 'Reactants', the narrow neck is labeled 'Transition State (bottleneck @ energetic barrier)', and the bottom bulb is labeled 'Products'.

Reactants

**Transition State
(bottleneck @
energetic barrier)**

Products

An hourglass with orange sand. The top bulb is labeled 'Reactants', the narrow neck is labeled 'Transition State (bottleneck @ energetic barrier)', and the bottom bulb is labeled 'Products'. A yellow line points to the neck, labeled 'Dividing surface'. Text on the left asks 'PROBLEM Recrossing-free????' and text on the right asks 'GOAL Can we avoid it????'.

Reactants

**Transition State
(bottleneck @
energetic barrier)**

**Dividing
surface**

PROBLEM

Recrossing-free????

GOAL

Can we avoid it????

Products

A close-up photograph of an hourglass with orange-brown sand falling from the top bulb to the bottom bulb. Two cinnamon sticks are positioned diagonally across the background, one on the left and one on the right, framing the hourglass. The lighting is warm, highlighting the texture of the sand and the wood of the sticks.

Outline

1. System and model under study

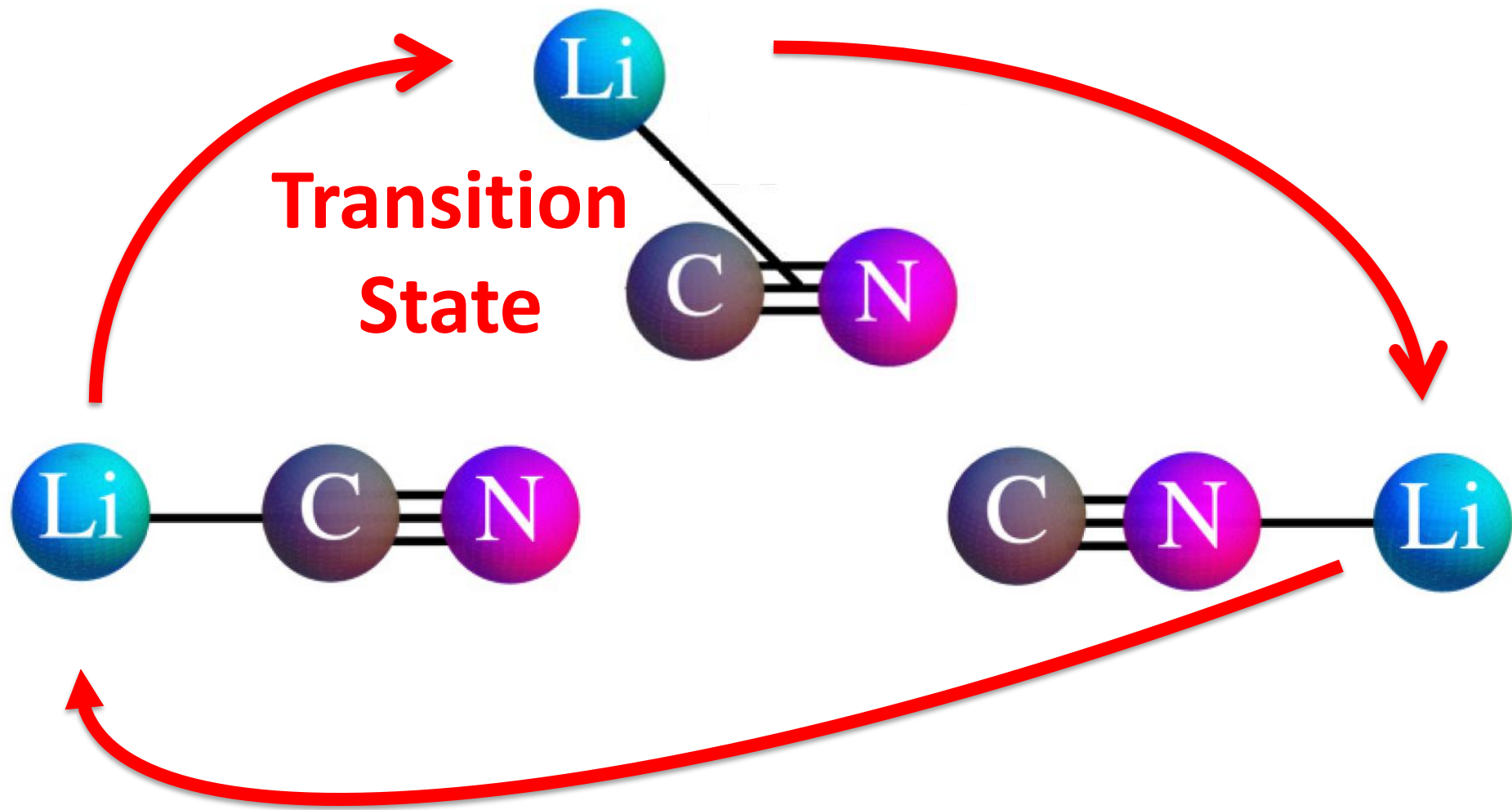
2. A recrossing-free dividing surface?

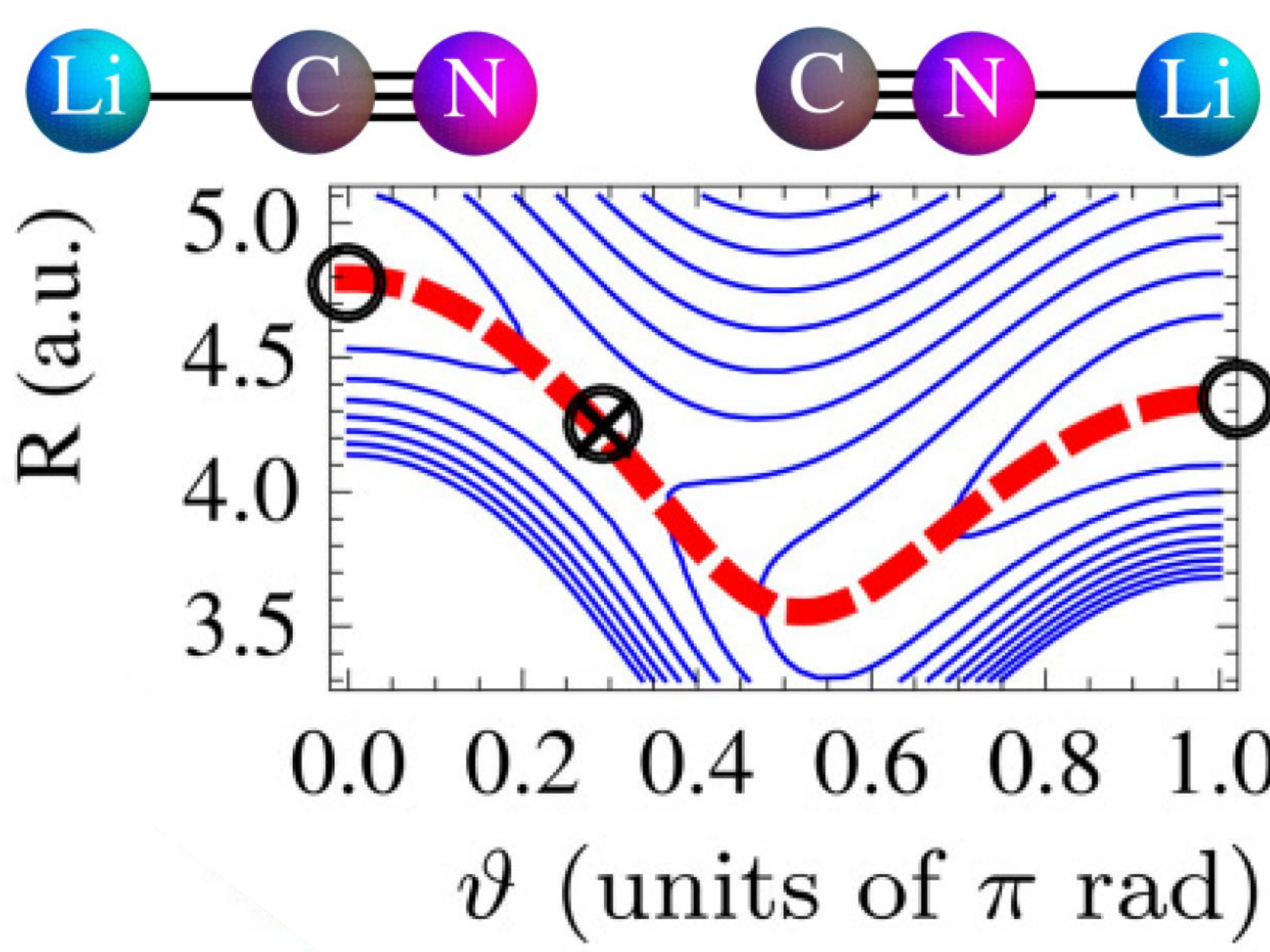
3. Results

4. Conclusions

System

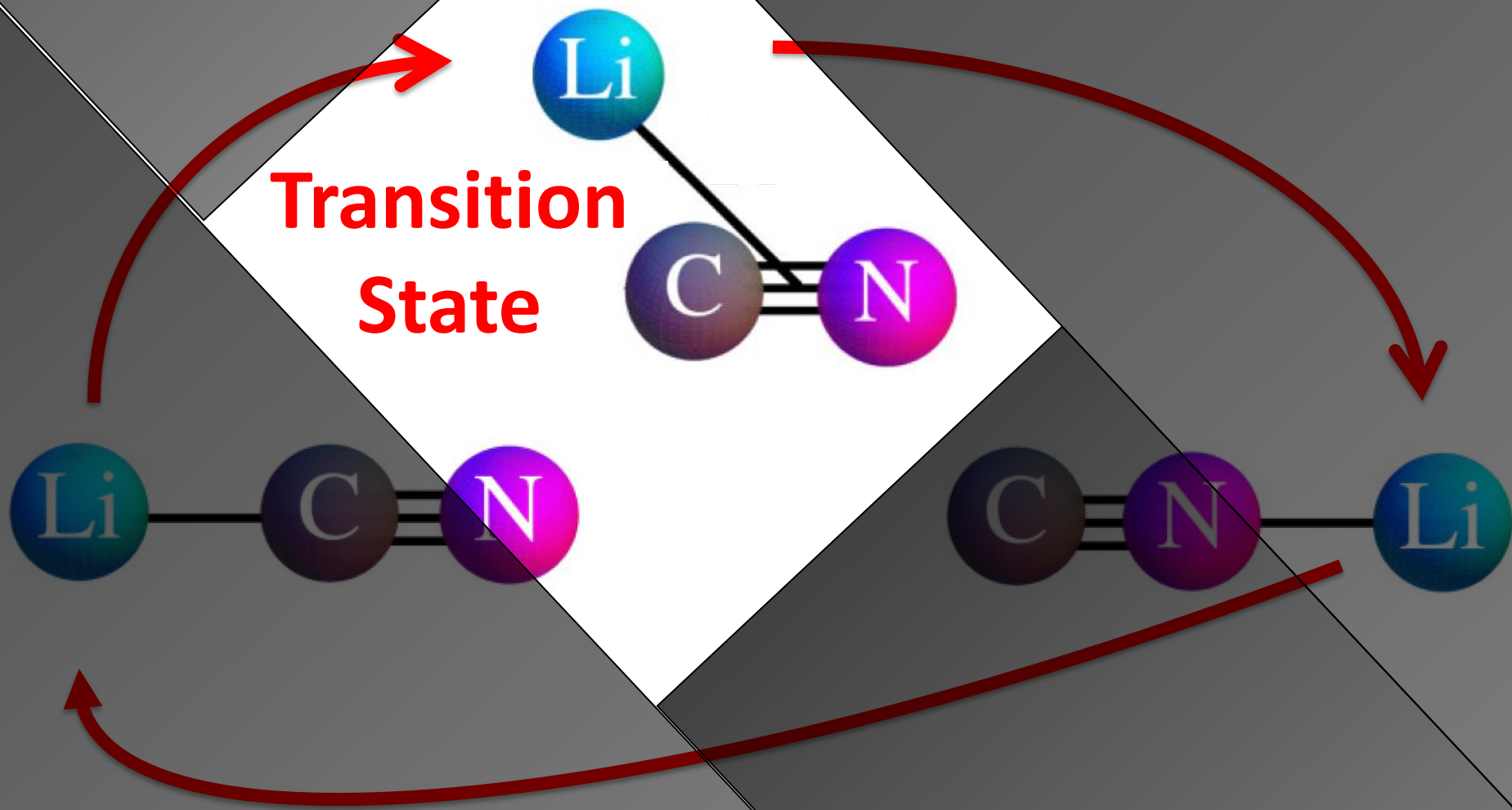
LiCN/LiCN isomerizing reaction





System

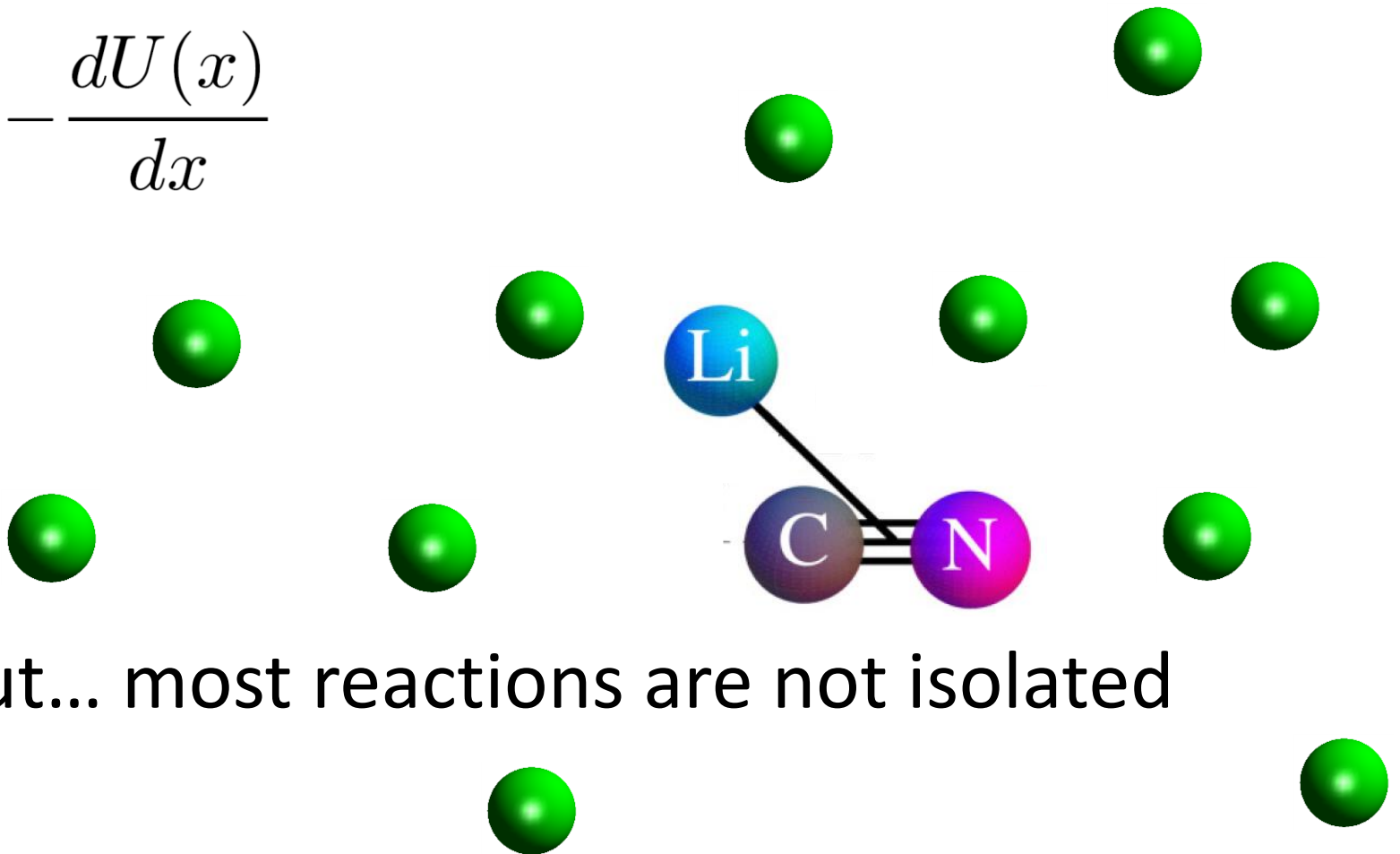
LiCN/LiCN isomerizing reaction



Model

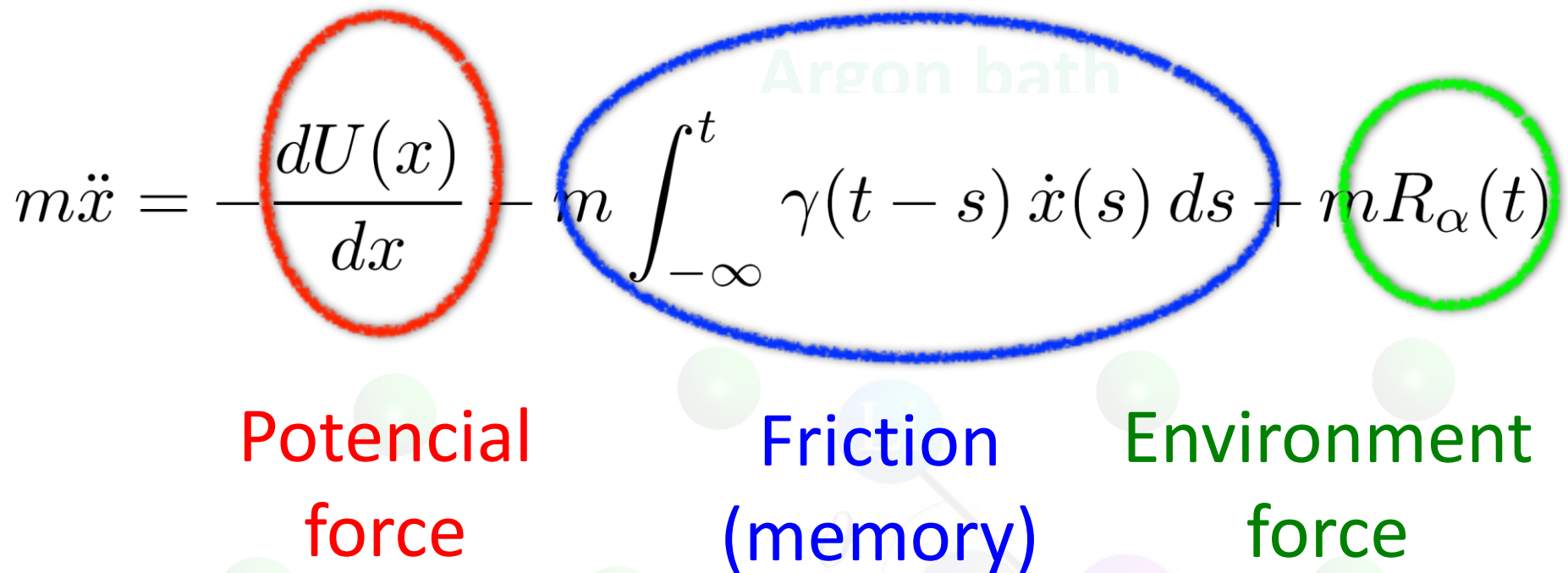
$$m\ddot{x} = -\frac{dU(x)}{dx}$$

Argon bath



But... most reactions are not isolated

Model: Generalized Langevin Equation



The diagram shows the Generalized Langevin Equation with three terms highlighted by colored ovals: a red oval around the potential force term, a blue oval around the friction (memory) term, and a green oval around the environment force term. The text 'Argon bath' is written in light green above the friction term. Below the equation, the three terms are labeled in matching colors: 'Potencial force' (red), 'Friction (memory)' (blue), and 'Environment force' (green). The background features a faint illustration of a particle in a fluid bath.

$$m\ddot{x} = -\frac{dU(x)}{dx} - m \int_{-\infty}^t \gamma(t-s) \dot{x}(s) ds + mR_{\alpha}(t)$$

Potencial force Friction (memory) Environment force

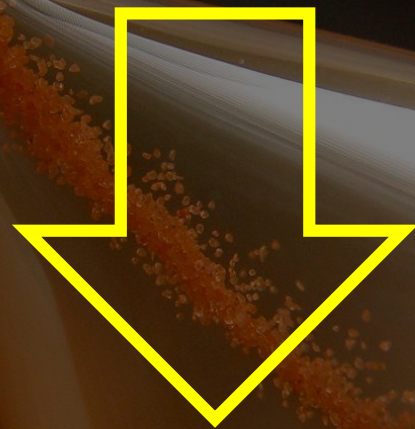
$$\langle R_{\alpha}(t) R_{\alpha}(0) \rangle = \frac{k_{\text{B}} T}{m} \gamma(t) = \frac{k_{\text{B}} T}{m} \frac{\gamma_0}{\tau} e^{-t/\tau}$$

An hourglass with orange-brown sand is the central focus, with two cinnamon sticks positioned diagonally on either side. The background is dark and moody.

Outline

1. System and model under study
2. A recrossing-free dividing surface?
3. Results
4. Conclusions

**A recrossing-free
dividing surface?**

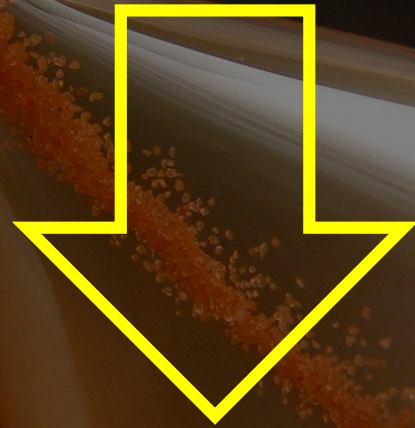


**TS
trajectory
(*T. Bartsh*)**

**Separatrices
(invariant manifolds)**

The background of the slide is a close-up, artistic photograph of an hourglass. The hourglass is tilted, and fine, golden-brown sand is captured in mid-fall, creating a dynamic, blurred trail from the upper bulb to the lower bulb. The lighting is dramatic, with strong highlights and deep shadows, emphasizing the texture of the sand and the glass of the hourglass.

Configuration space



Phase space

(Waalkens, Jaffé, Bartsch)

Method

1. Make a **Taylor expansion** of the potential around the saddle point @ energetic barrier (transition state)
2. Add a new **variable** to account for the memory effects in the bath
3. Compute the **TS trajectory**
4. Identify the **structures** that **separate** reactive from nonreactive trajectories.

Method (solution of GLE)

$$m\ddot{x} = -\frac{dU(x)}{dx} - m \int_{-\infty}^t \gamma(t-s) \dot{x}(s) ds + mR_\alpha(t)$$

1. Substitute the effect of the **memory** with a **new variable** (*Martens, Ferrari...*)

$$\zeta = - \int_{-\infty}^t \gamma(t-s) \dot{x}(s) ds$$

Method

Then, the equations of motion read...

$$\dot{x} = v$$

$$\dot{v} = -\frac{1}{m} \frac{dU(x)}{dx} + \zeta$$

$$\dot{\zeta} = -\frac{\gamma_0}{\tau} v - \frac{1}{\tau} \zeta + \xi_\alpha(t)$$

**White
noise!**

$$\langle \xi_\alpha(t) \xi_\alpha(s) \rangle_\alpha = \frac{2k_B T \gamma_0}{m\tau^2} \delta(t - s)$$

Method

2. Change to **diagonal coordinates**

$$(\lambda_i - \lambda_j)(\lambda_i - \lambda_k) z_i = (\lambda_j \lambda_k + \omega_b^2)x - (\lambda_j + \lambda_k)v + \zeta$$

where the equations of motion read...

$$\dot{z}_i = \lambda_i z_i + K_i f(x) + \frac{1}{F_i} \xi_\alpha(t)$$

Method

3. Change to **diagonal coordinates**

$$\Delta z_i(t) = z_i(t) - z_i^{\ddagger}(t)$$

$$z_i^{\ddagger}(t) = \frac{1}{F_i} S[\lambda_i, \xi_\alpha; t] \quad \begin{matrix} \text{TS} \\ \text{trajectory} \end{matrix}$$

$$S_{t'}[\mu, g; t] = \begin{cases} - \int_t^\infty g(t') \exp(\mu(t - t')) dt' & : \operatorname{Re} \mu > 0, \\ + \int_{-\infty}^t g(t') \exp(\mu(t - t')) dt' & : \operatorname{Re} \mu < 0. \end{cases}$$

Method

The equations of motion in diagonal coordinates

$$\Delta \dot{z}_i = \lambda_i \Delta z_i + \cancel{K_i f(x)}$$

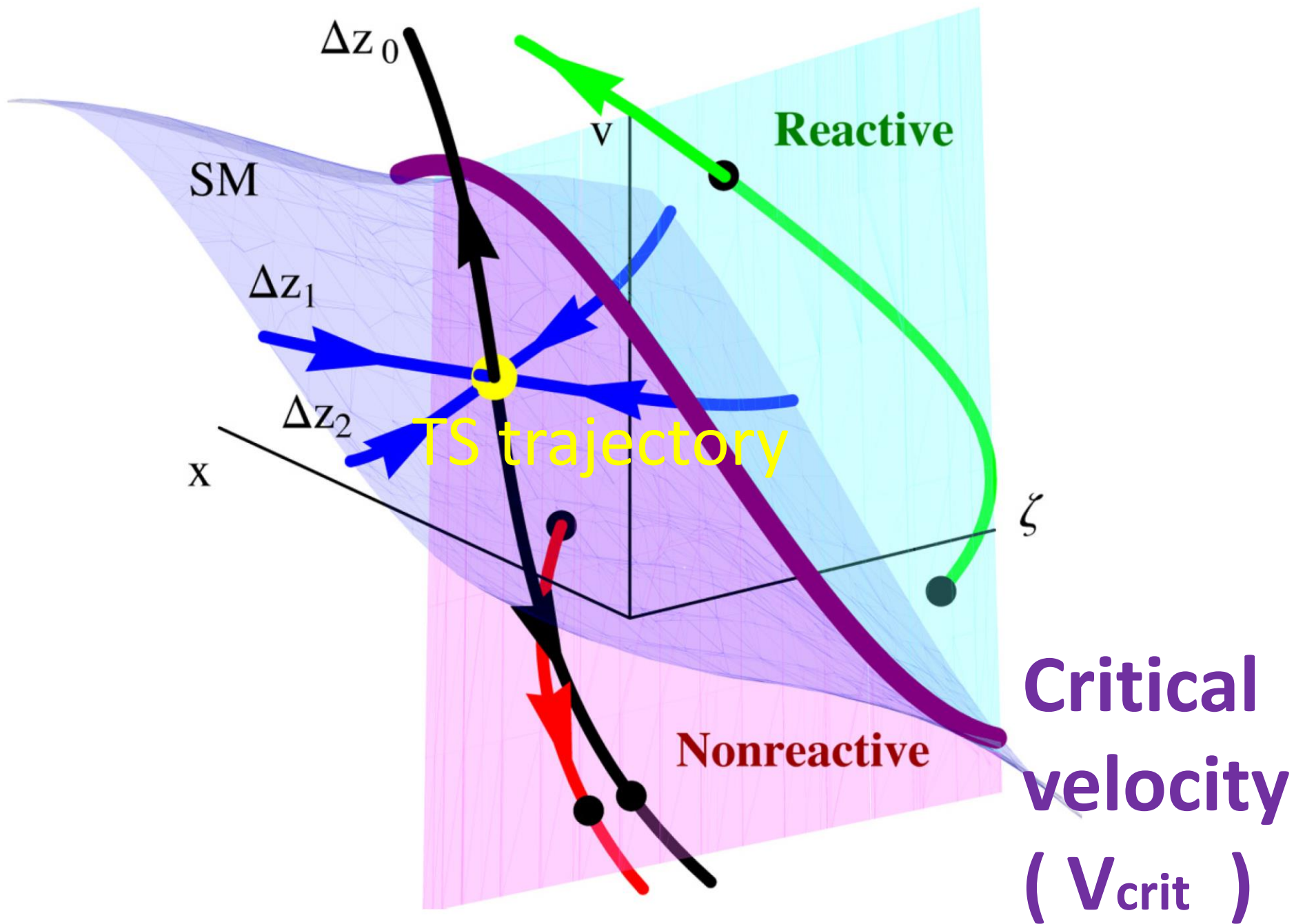
$$\Delta z_j(t) = \Delta z_j(0) e^{\lambda_j t}$$

Method

The equations of motion in diagonal coordinates

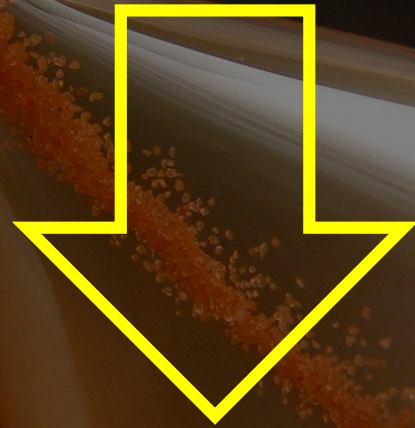
$$\Delta \dot{z}_i = \lambda_i \Delta z_i + K_i f(x)$$

$$\Delta z_j(t) = \Delta z_j(0) e^{\lambda_j t} + \text{h.c.t.}$$



The background of the slide is a close-up, artistic photograph of an hourglass. The hourglass is made of clear glass and is filled with a fine, golden-brown sand. The sand is captured in mid-fall, creating a dynamic, blurred trail as it moves from the upper bulb to the lower bulb. The lighting is soft, highlighting the texture of the sand and the smooth curves of the glass. The overall tone is warm and contemplative, symbolizing the passage of time and the flow of information or concepts.

Configuration space



Phase space

(Waalkens, Jaffé, Bartsch)

A close-up photograph of an hourglass with orange-brown sand falling from the top bulb to the bottom bulb. Two cinnamon sticks are positioned diagonally across the frame, one on the left and one on the right, framing the hourglass. The background is dark and out of focus.

Outline

1. System and model under study
2. A recrossing-free dividing surface?
3. Results
4. Conclusions

Results

- Using **invariant manifolds**, we can identify **reactive trajectories** uniquely.
- We have obtained **explicit anharmonic corrections** to **Grote-Hynes** expression (also in potentials with several dof!).

Transmission factor

$$\kappa = \frac{k_{\text{exact}}}{k_{\text{TST}}} = \left\langle e^{-mV^{\ddagger 2}/2k_{\text{B}}T} \right\rangle_{\alpha, \zeta}$$

$$\kappa = \kappa^{(0)} + \varepsilon \kappa^{(1)} + \varepsilon^2 \kappa^{(2)} + \dots$$

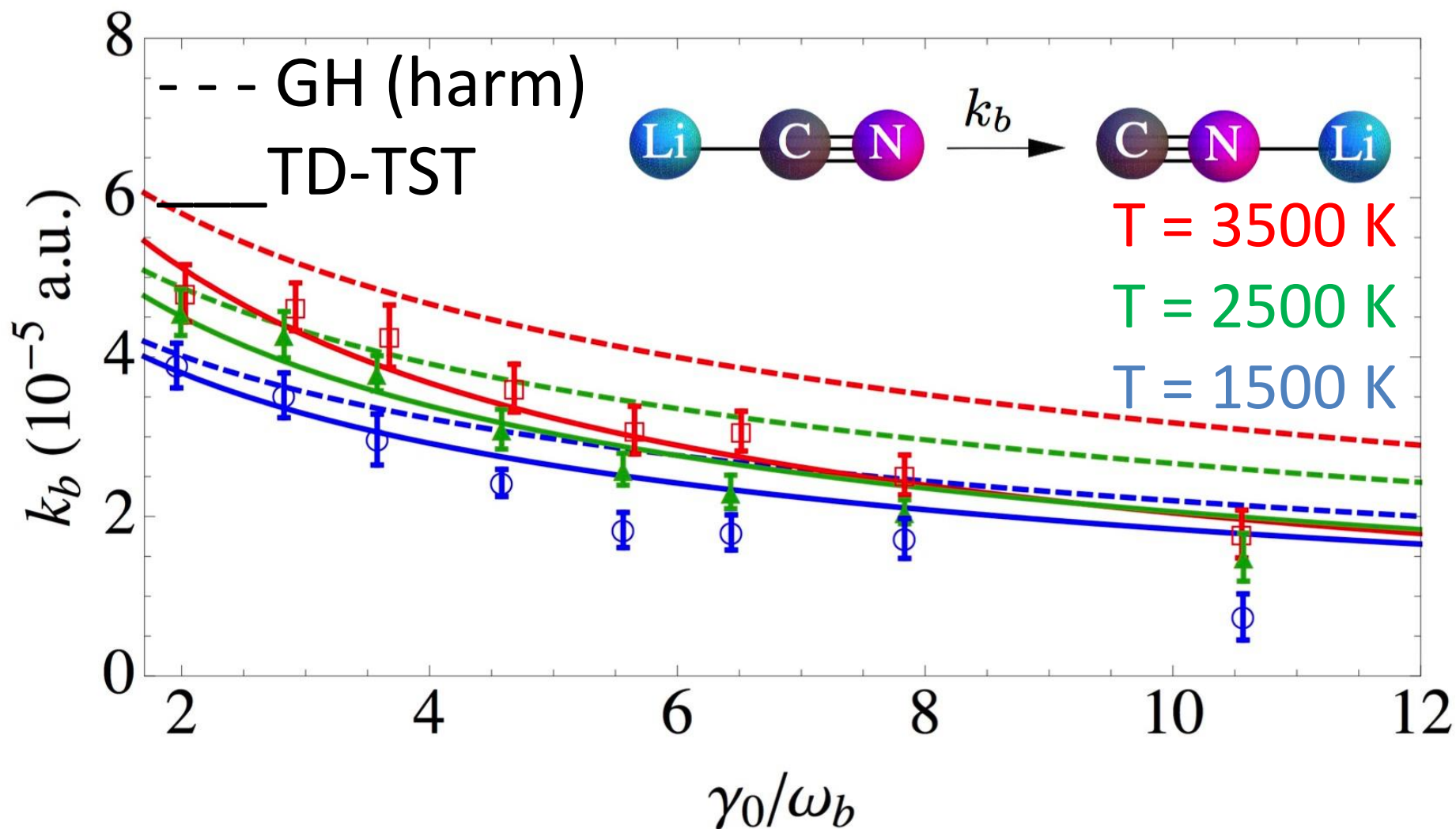
Transmission factor

$$\kappa = \kappa^{(0)} + \cancel{\varepsilon \kappa^{(1)}} + \varepsilon^2 \kappa^{(2)} + \dots$$

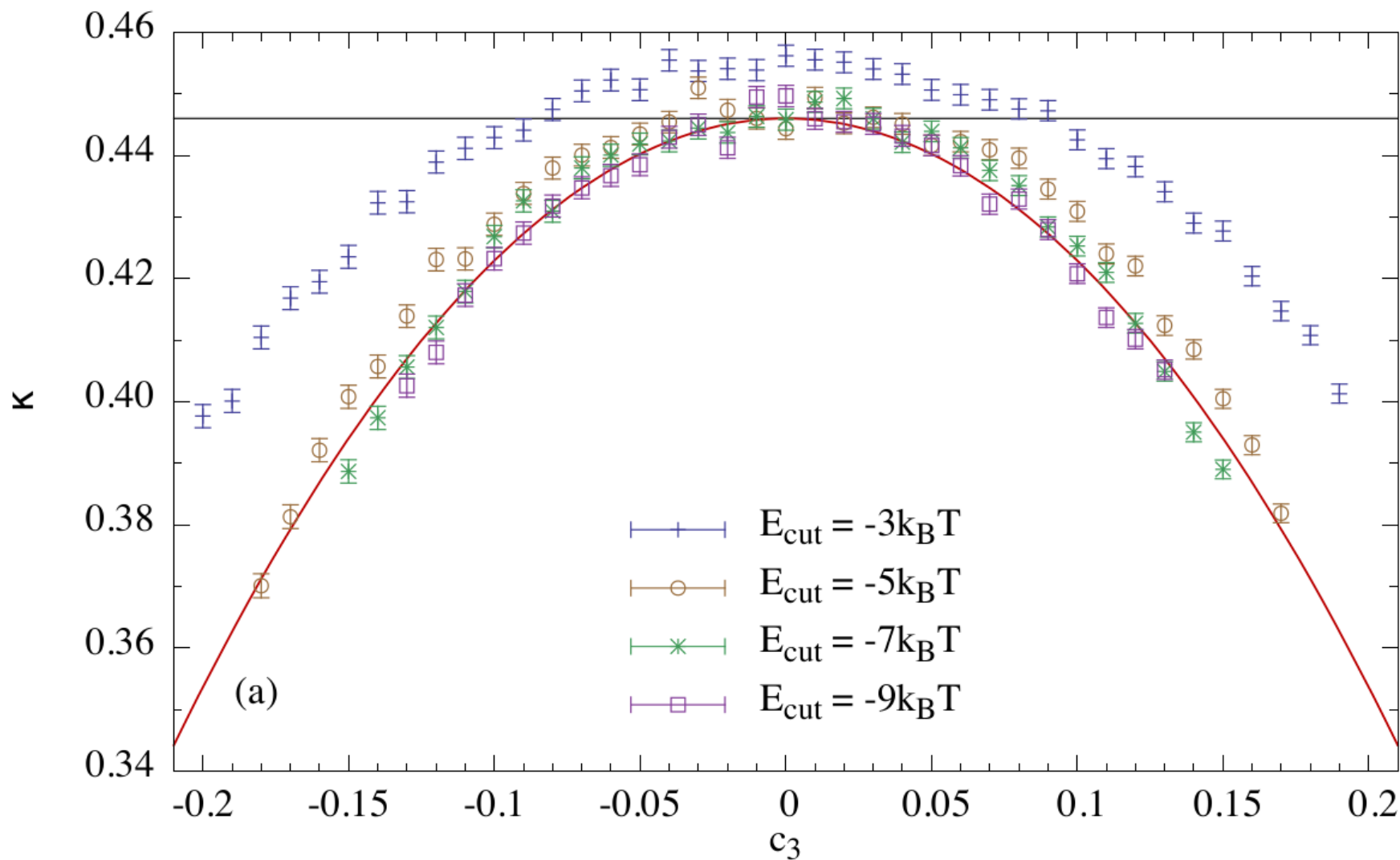
$$\kappa^{(0)} = \frac{\lambda_0}{\omega_b} \quad \textbf{Grote-Hynes expression} \\ \text{(harmonic limit)}$$

$$\begin{aligned} \kappa^{(2)} = & -\frac{c_3^2 k_B T}{6m\omega_b^6} \frac{\mu (\mu^2 - 1)^2}{(\mu^2 + \nu^2) [\mu^4 + 2\mu^2 (\nu^2 - 2) + 4\nu^2] [\mu^4 + \mu^2 (\nu^2 - 1) + \nu^2]^2 [4\mu^4 + \mu^2 (2\nu^2 - 1) + \nu^2]} \times \\ & \left[2 (10\mu^4 + 41\mu^2 + 10) \nu^{10} + (110\mu^4 + 329\mu^2 - 12) \mu^2 \nu^8 + 2 (115\mu^4 + 197\mu^2 - 28) \mu^4 \nu^6 + \right. \\ & \quad \left. 2 (115\mu^4 + 22\mu^2 + 8) \mu^6 \nu^4 + 2 (55\mu^4 - 94\mu^2 + 6) \mu^8 \nu^2 + 5 (4\mu^4 - 17\mu^2 + 4) \mu^{10} \right] \\ & - \frac{3 c_4 k_B T}{4m \omega_b^4} \frac{\mu (\mu^2 - 1)^2 (\mu^2 + \nu^2)^2}{[\mu^4 + \mu^2 (\nu^2 - 1) + \nu^2]^2} \end{aligned}$$

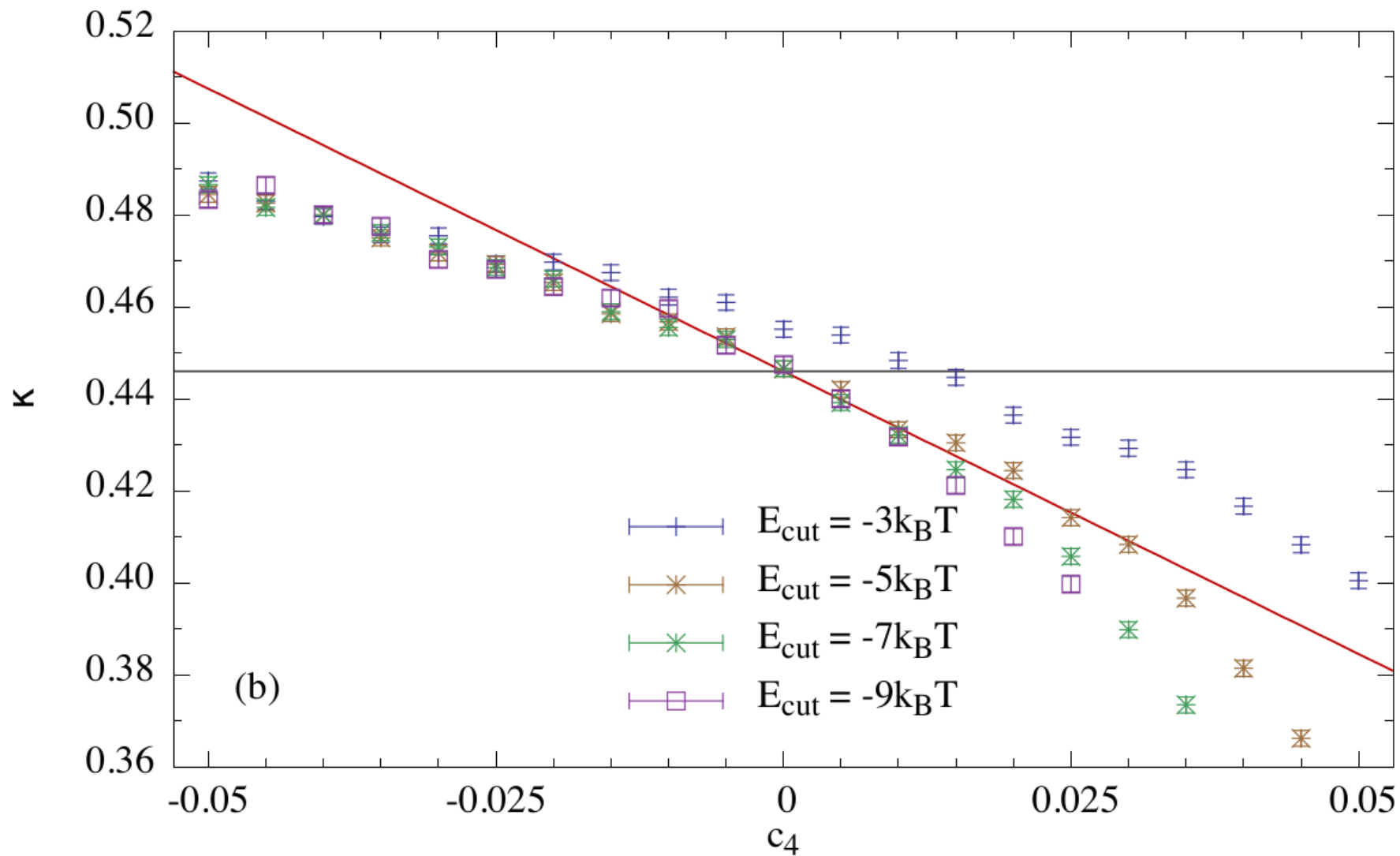
LiCN \rightarrow LiCN reaction rates



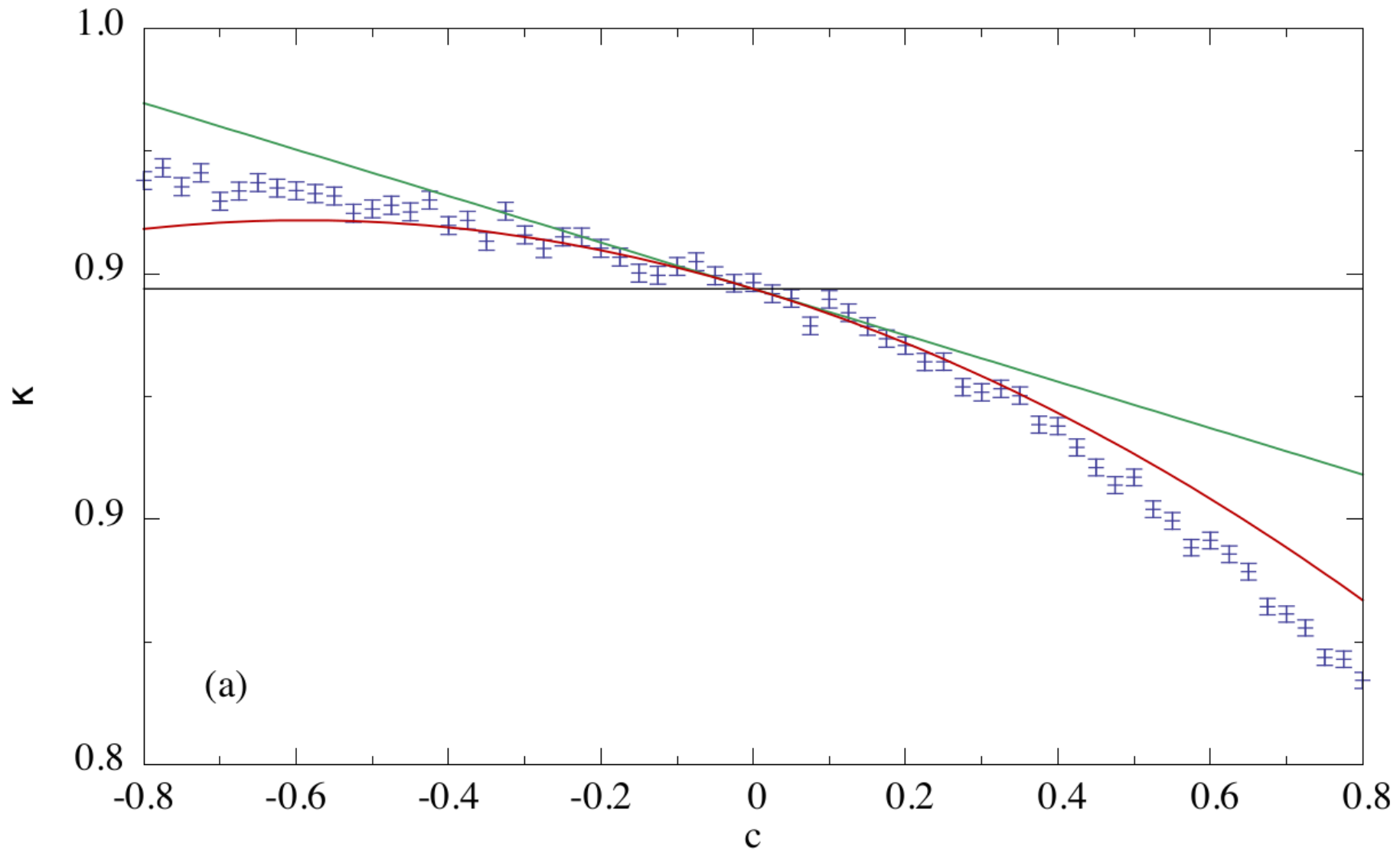
Cubic potential



Quartic potential



Potential with 2 dof



A close-up photograph of an hourglass with orange-brown sand falling from the top bulb to the bottom bulb. Two cinnamon sticks are positioned diagonally across the frame, one on the left and one on the right, framing the hourglass. The background is dark and out of focus.

Outline

1. System and model under study
2. A recrossing-free dividing surface?
3. Results
4. Conclusions

Conclusions

Conclusion

The **geometry** of the
phase space provides valuable
information of **reactivity**
(with a laser, white noise,
colored noise...)