chemistry meets topology

what oxidation numbers are all about

Stefano Baroni

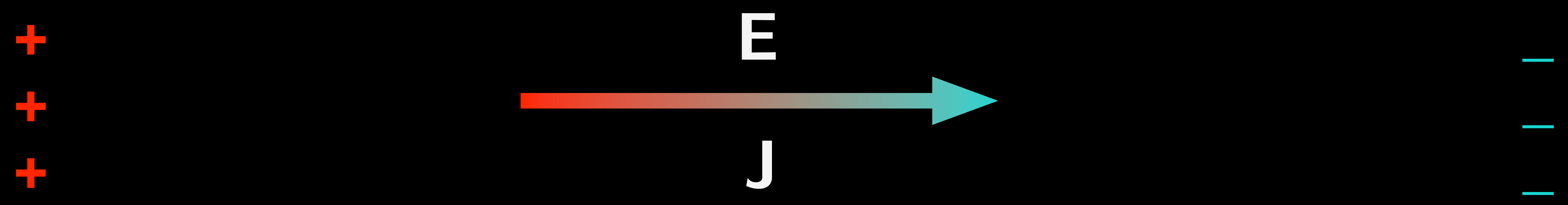
Scuola Internazionale Superiore di Studi Avanzati

Trieste — Italy

talk given at the workshop on *Physics & Topology*, Rome, January 29-31, 2024

a prequel

$$\mathbf{J} = \sigma \mathbf{E}$$



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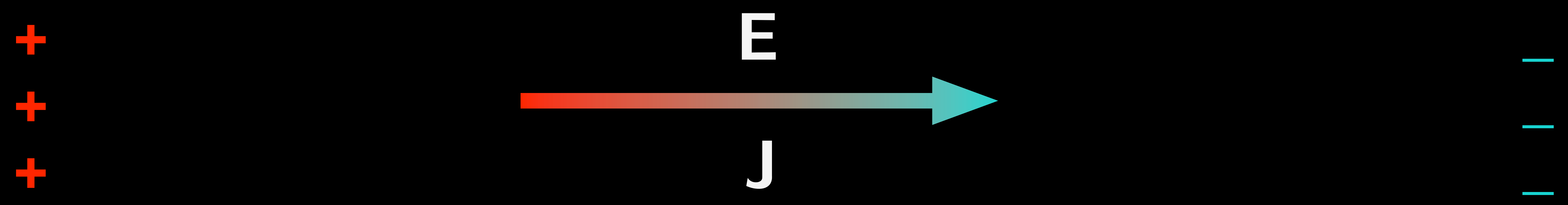

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$$\sigma = \frac{\Omega}{3k_B T}\int_0^\infty \langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle dt$$

+ E −
+ J −
+ −

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$$= \frac{\Omega}{3k_BT}\lim_{t\to\infty}\frac{1}{2t}\left\langle \left| \int_0^t \mathbf{J}(t')dt' \right|^2 \right\rangle$$

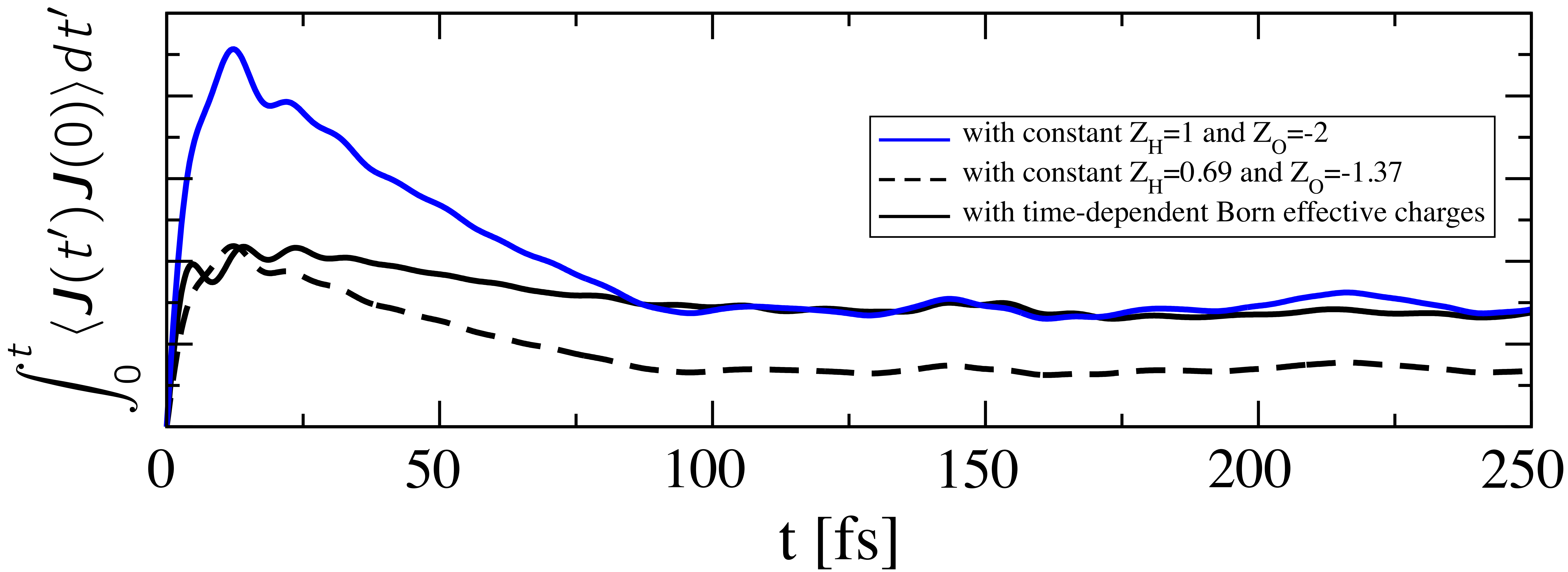
keep in mind!

a conundrum in transport theory

PRL **107,** 185901 (2011) PHYSICAL REVIEW LETTERS week ending 28 OCTOBER 2011

Dynamical Screening and Ionic Conductivity in Water from *Ab Initio* Simulations

Martin French,[1] Sebastien Hamel,[2] and Ronald Redmer[1]



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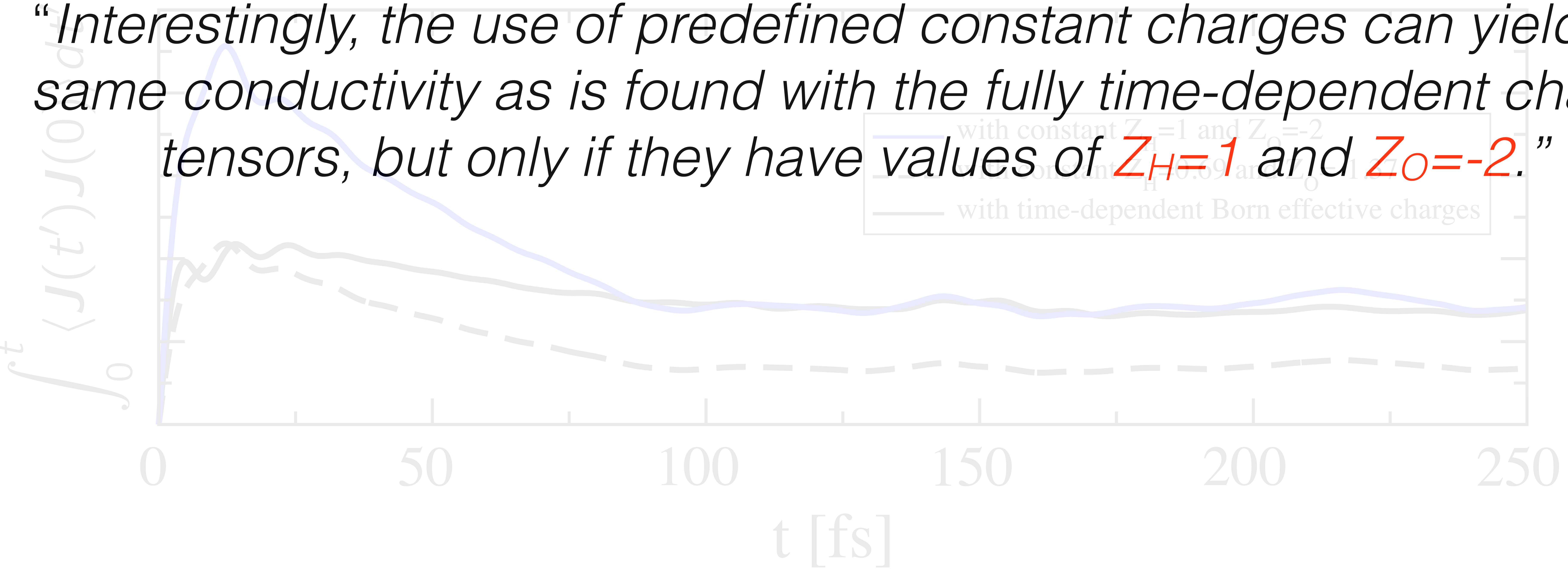

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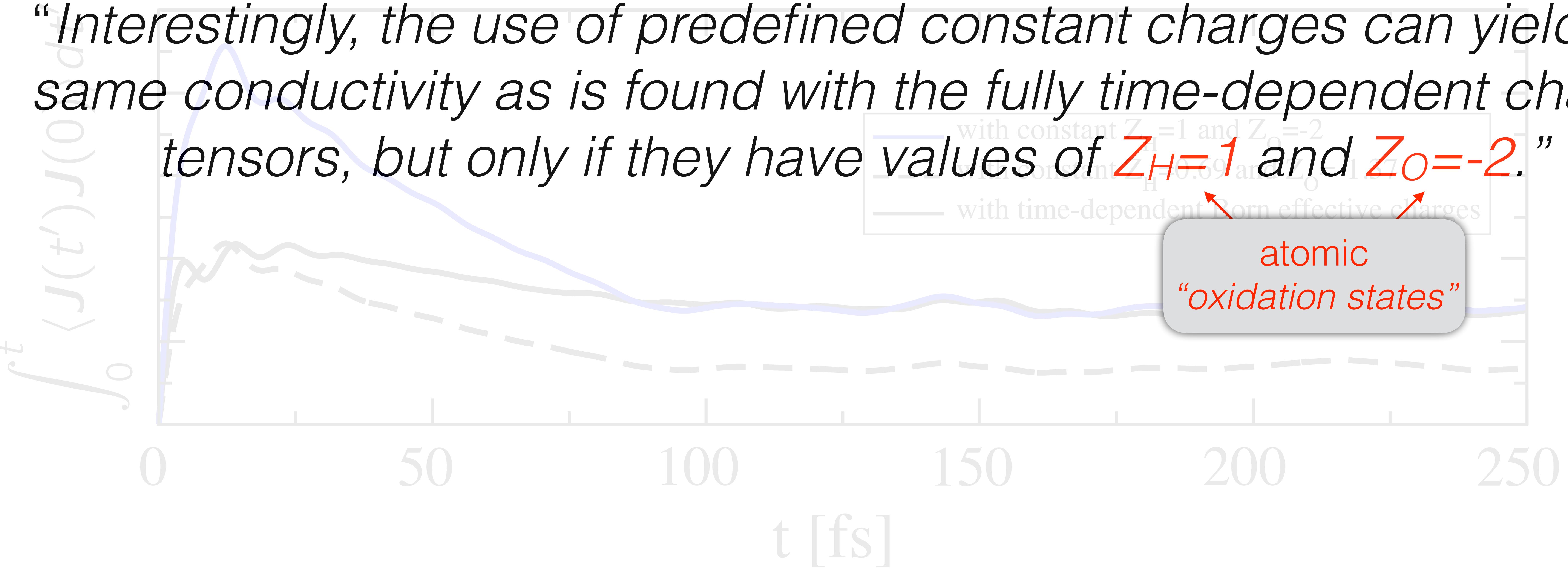

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atomic *"oxidation states"*

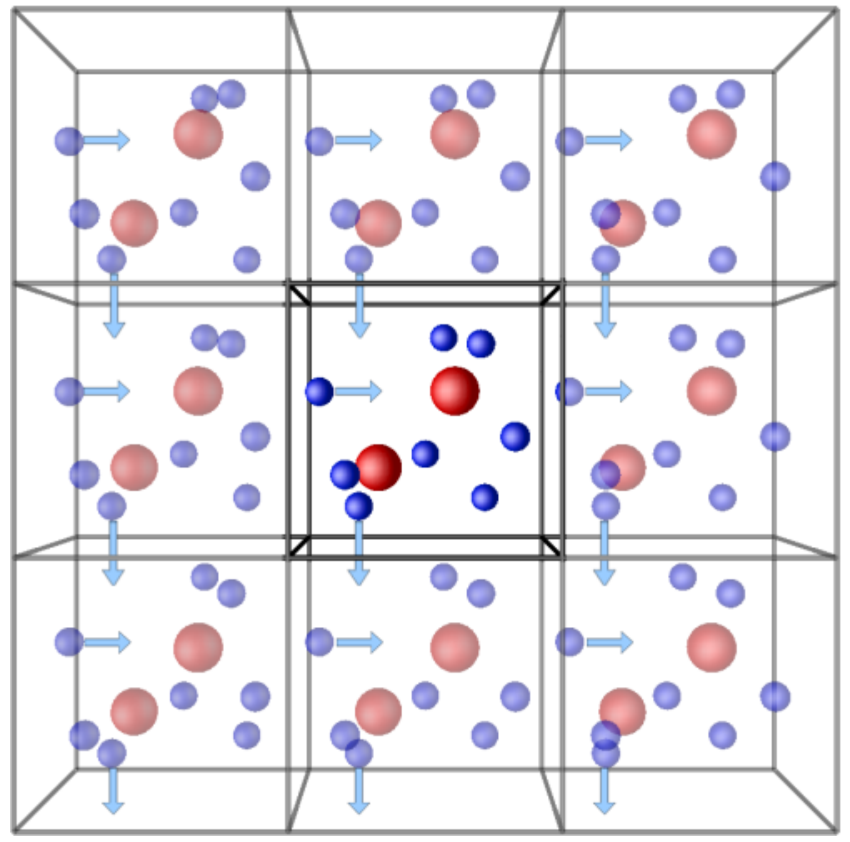
… but what are oxidation states, in the first place?

the oxidation state of an atom is the charge of this atom after ionic approximation of its heteronuclear bonds

https://doi.org/10.1351/goldbook.O04365

quantisation of adiabatic particle transport

classical PBC



$$V(x+L) = V(x)$$

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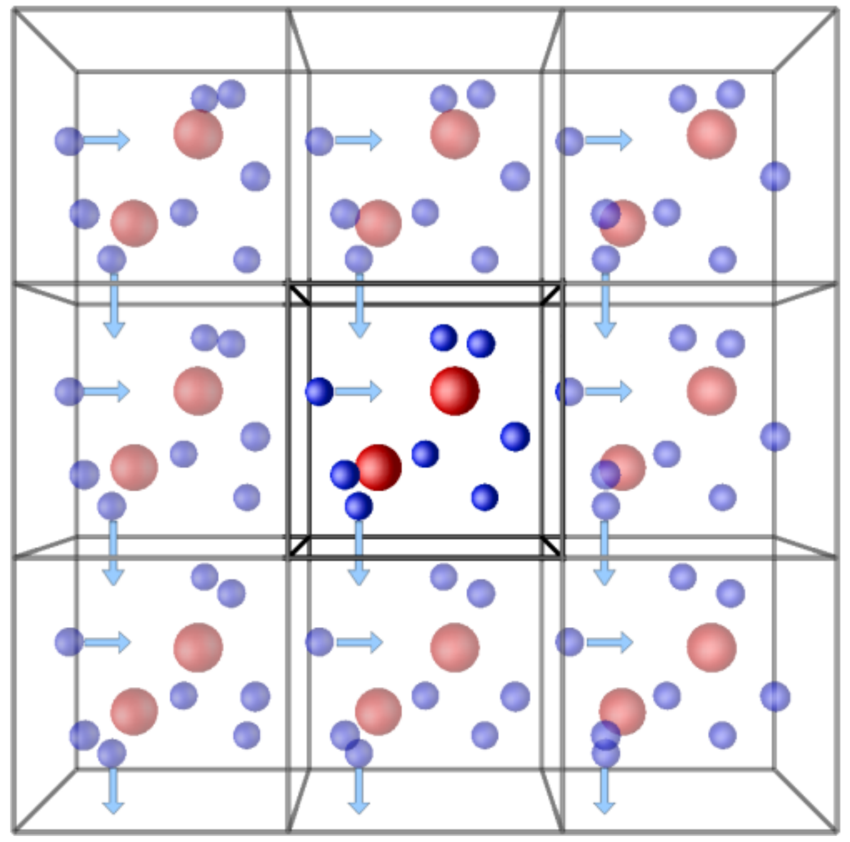

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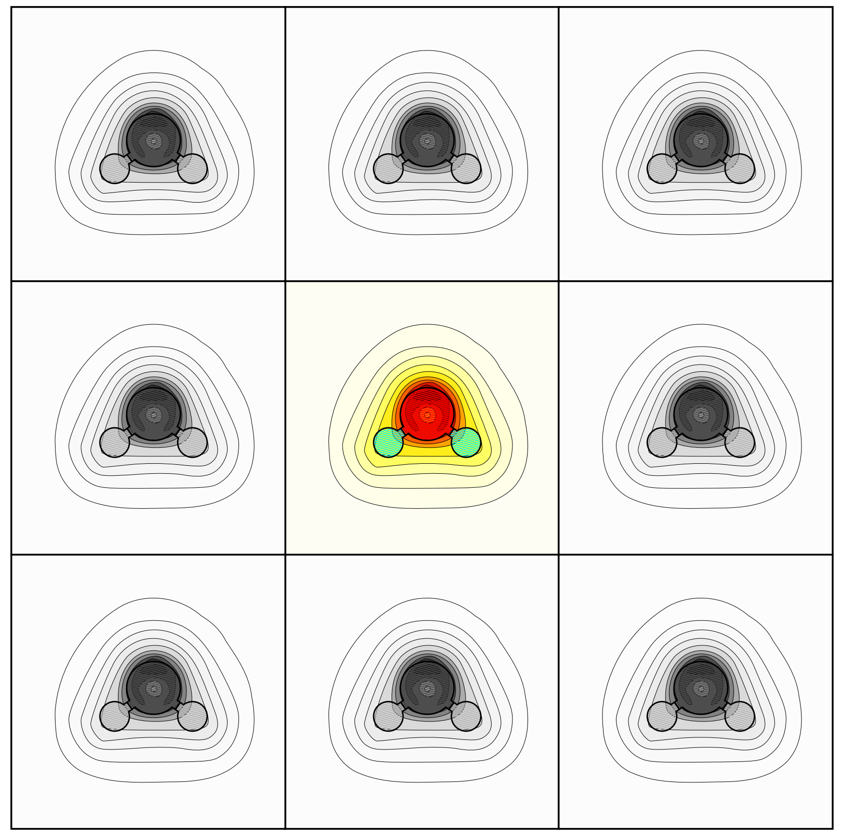

$$\psi(x+L) = \psi(x)$$

quantisation of adiabatic particle transport

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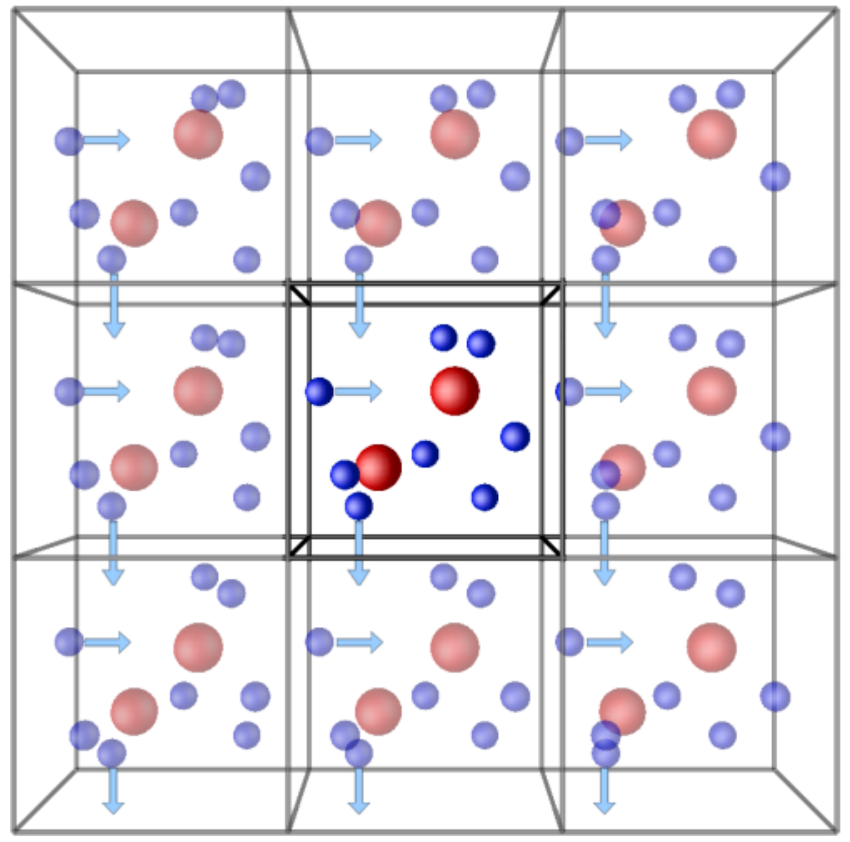

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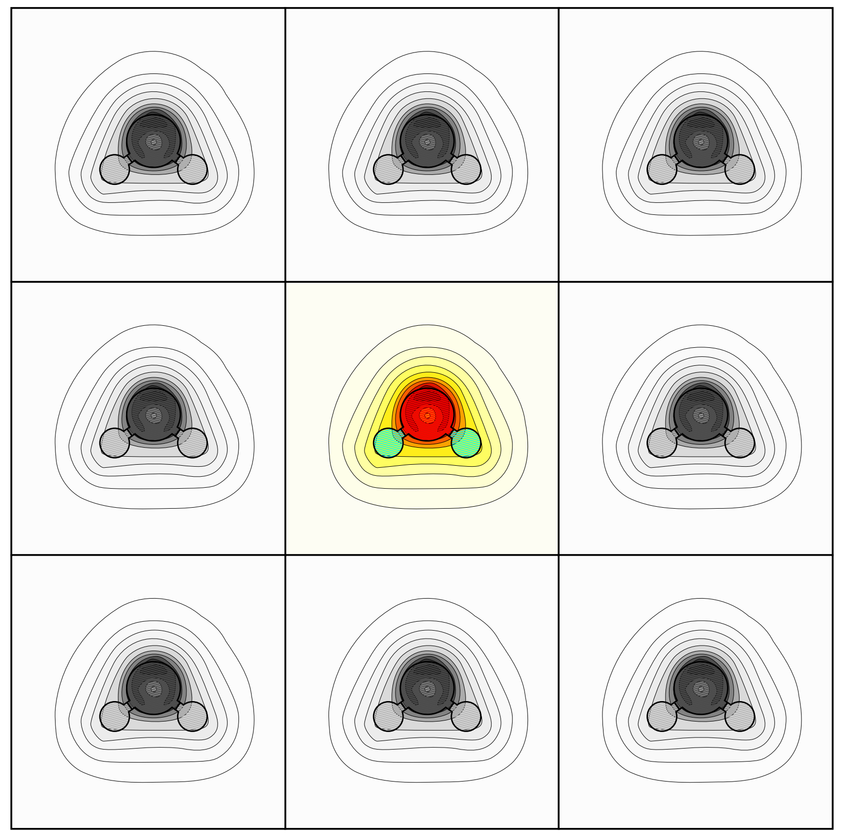
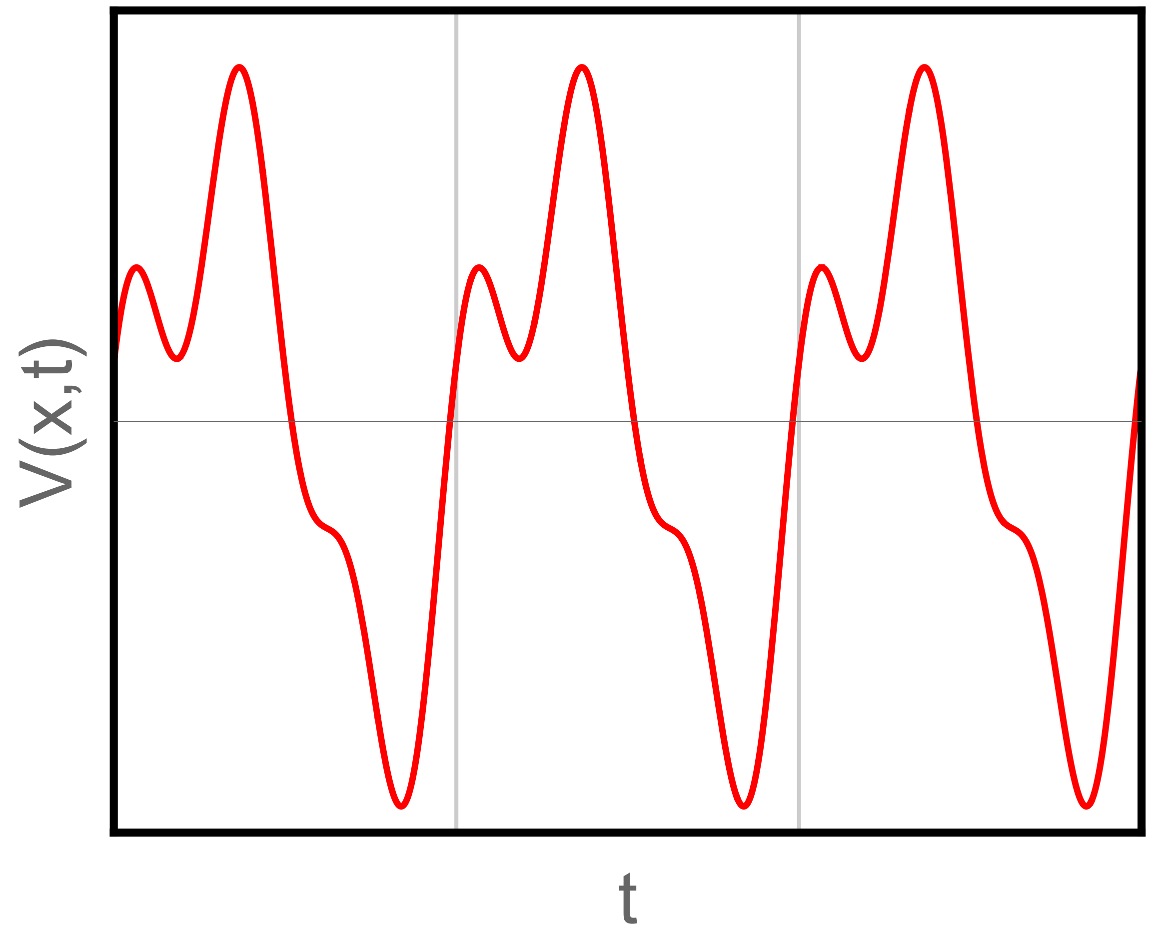


$\psi(x+L) = \psi(x)$

time periodicity

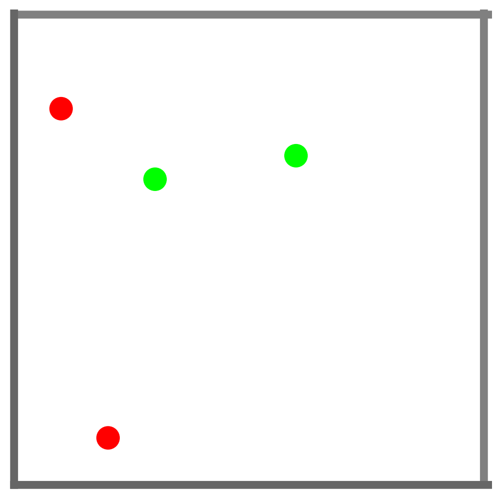


$V(x,t+T) = V(x,t)$

$$\frac{L^{d-1}}{e}\int_0^T J_\alpha(t)dt = Q_\alpha \in \mathbb{Z}$$

D.J. Thouless, *Quantization of particle transport*, Phys. Rev. B **27**, 2083 (1983)

what are oxydation states, in the first place?



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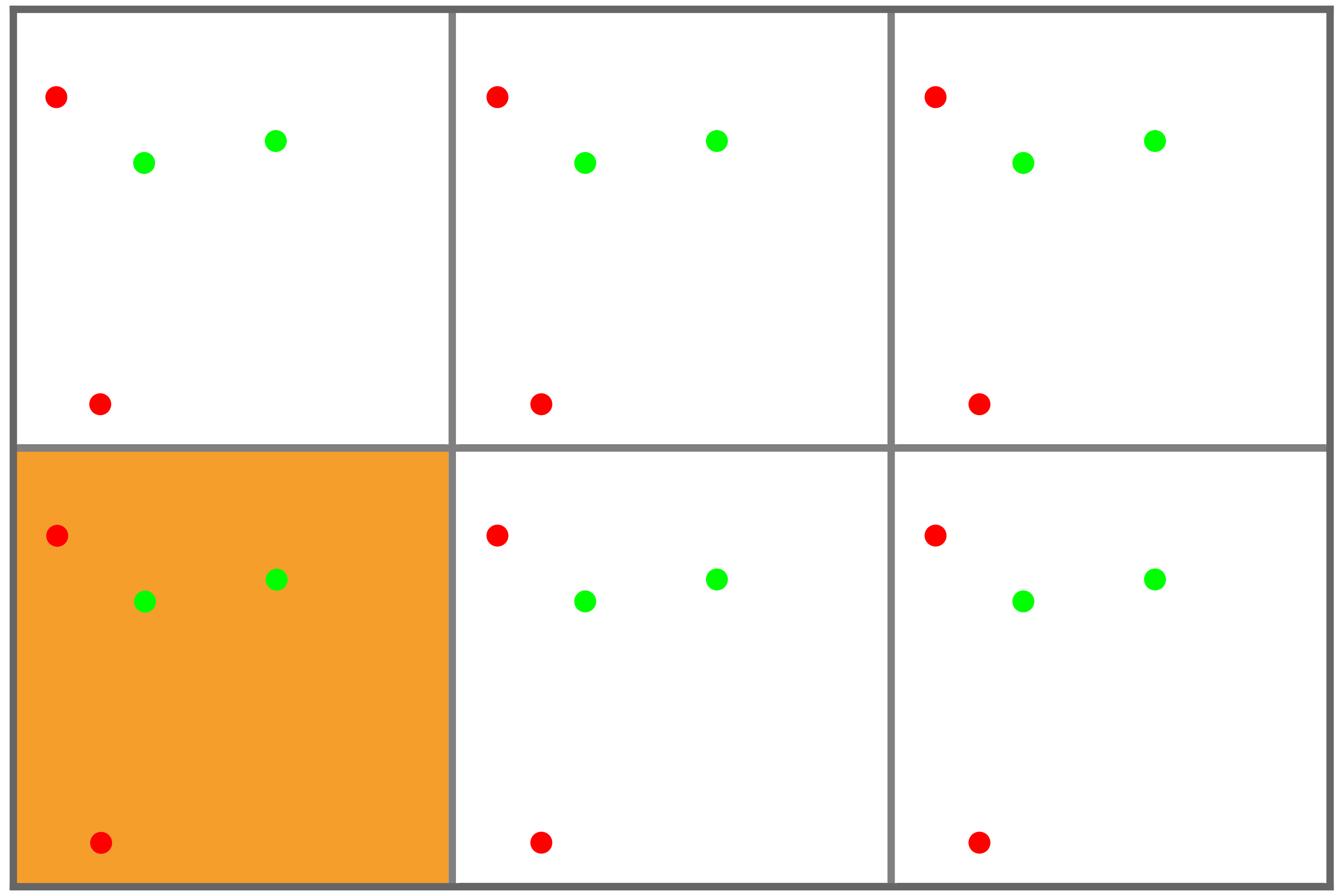
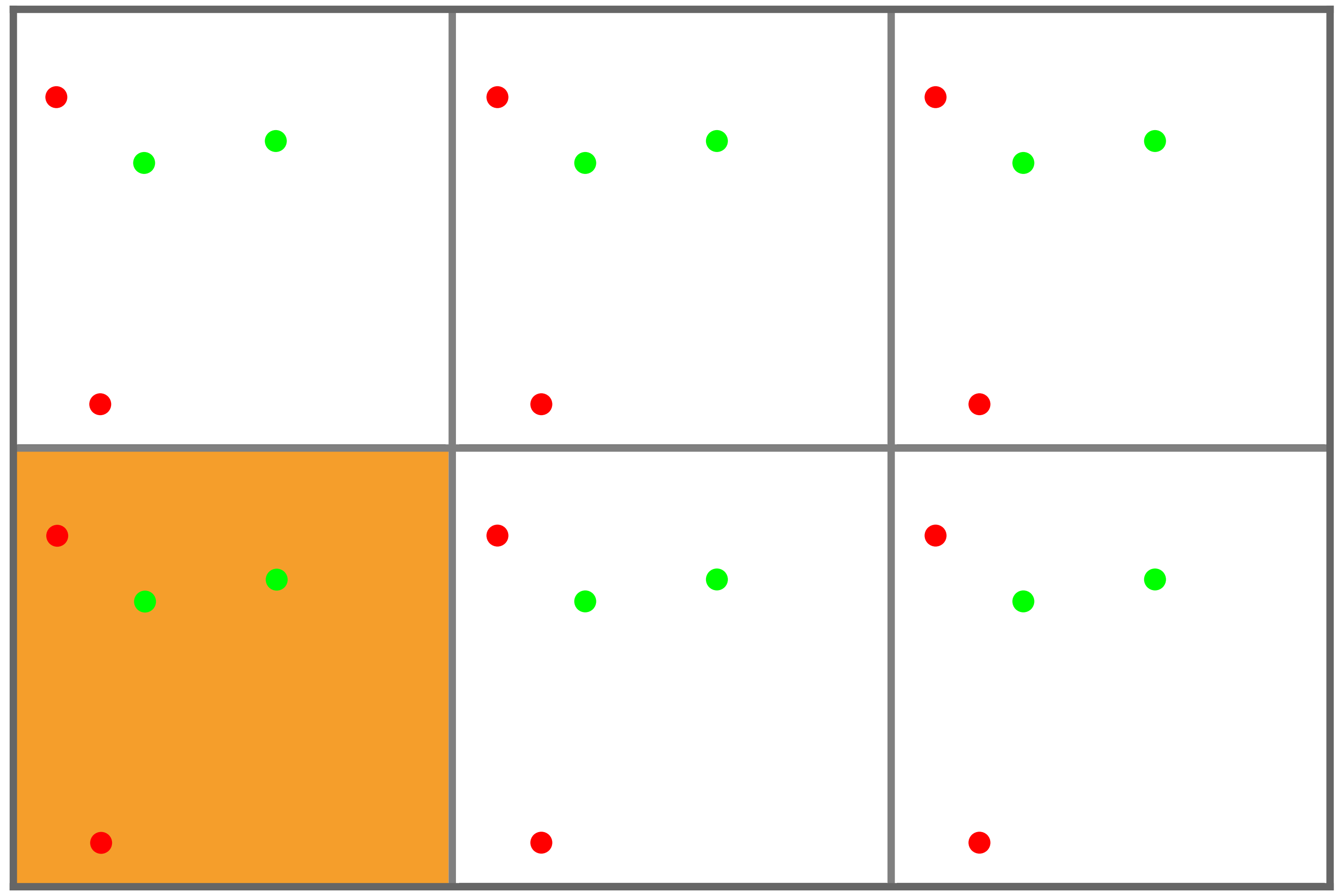
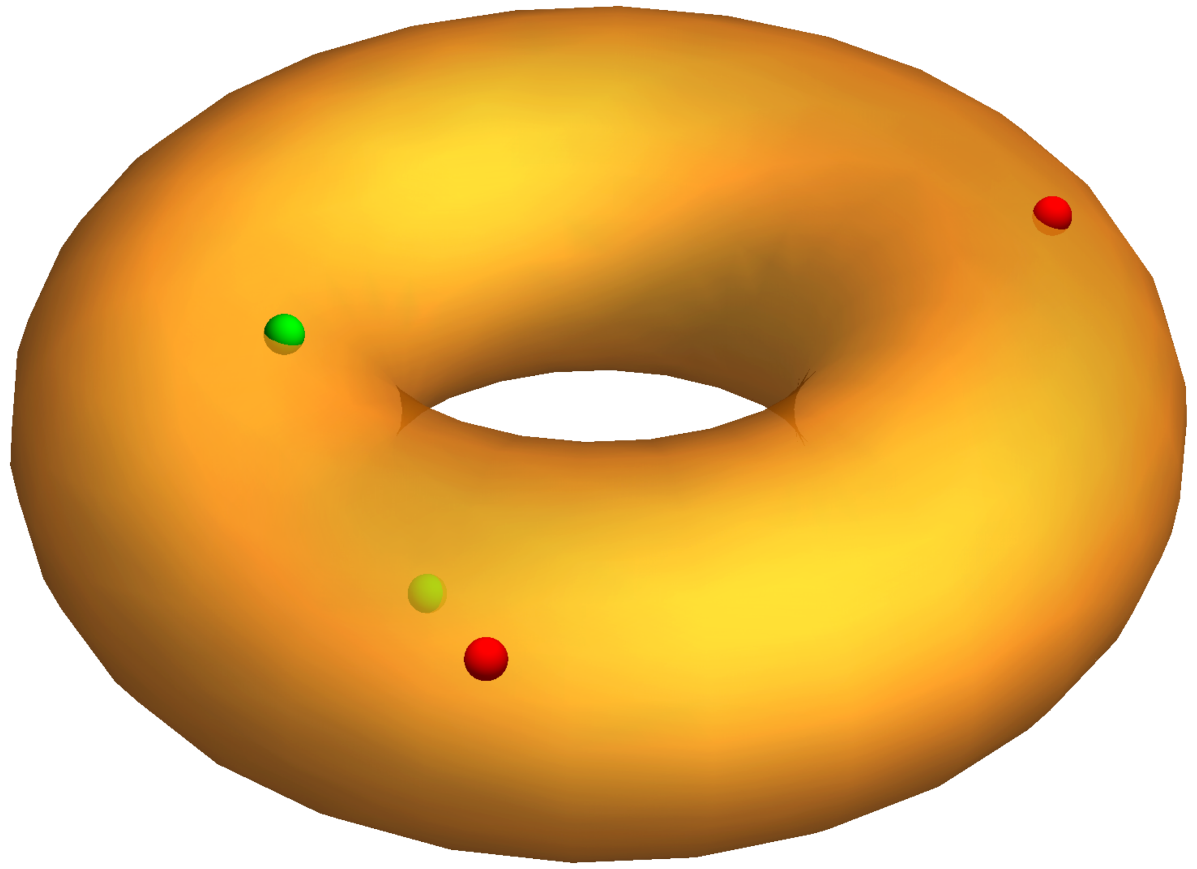


what are oxydation states, in the first place?

$$[0, L]^{3N} \xrightarrow{\text{PBC}} \mathbb{T}^{3N}$$





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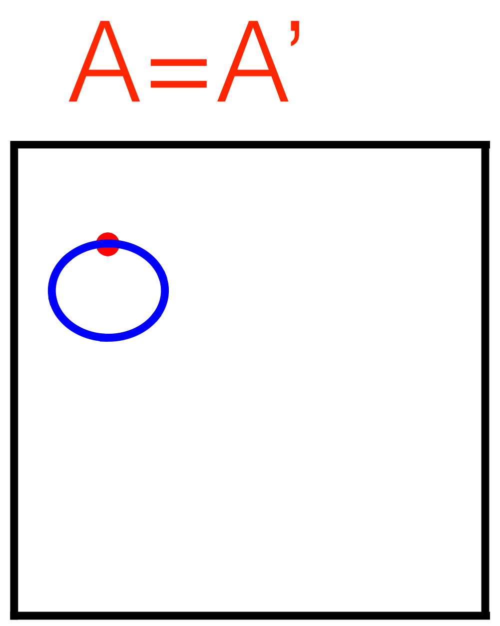

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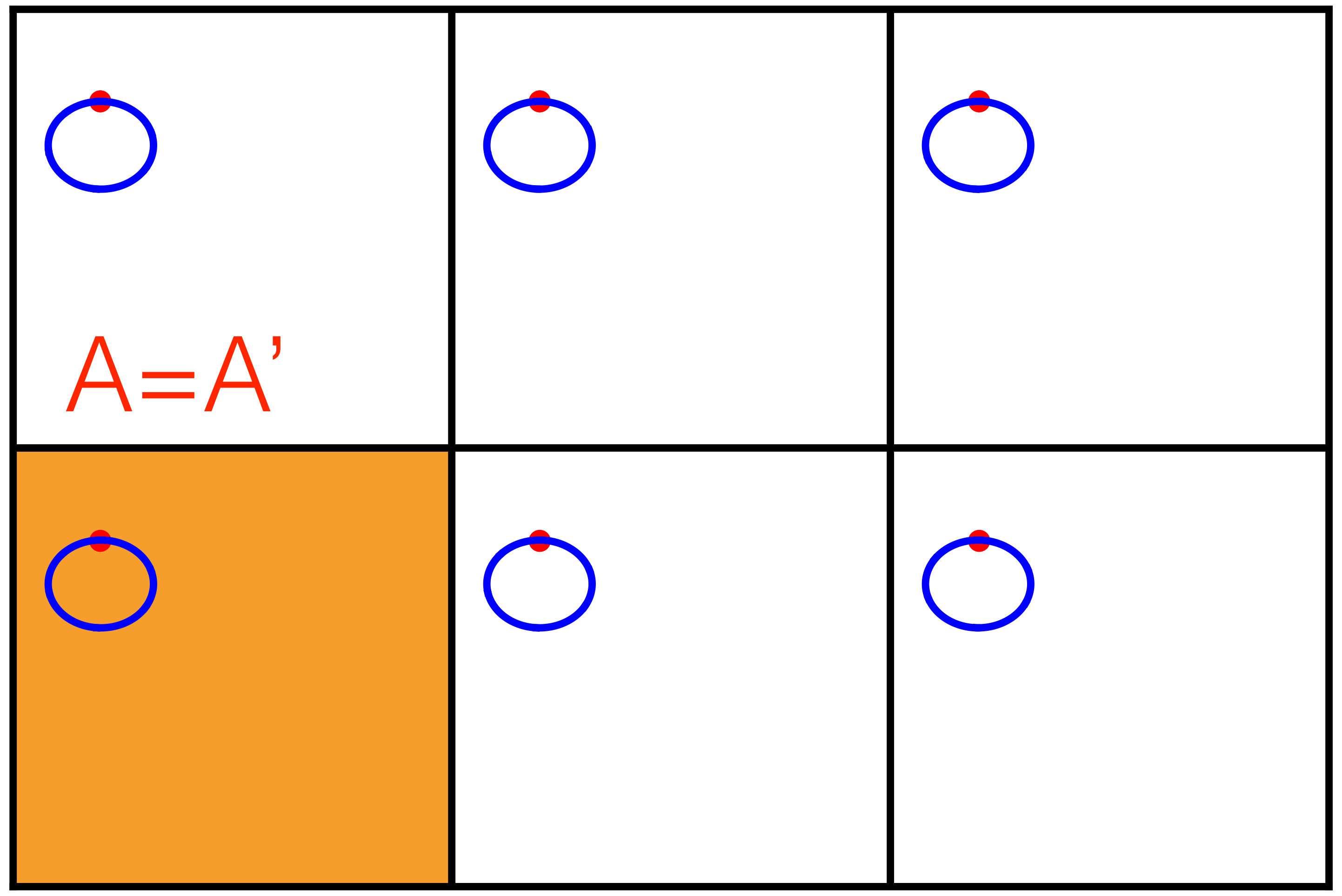

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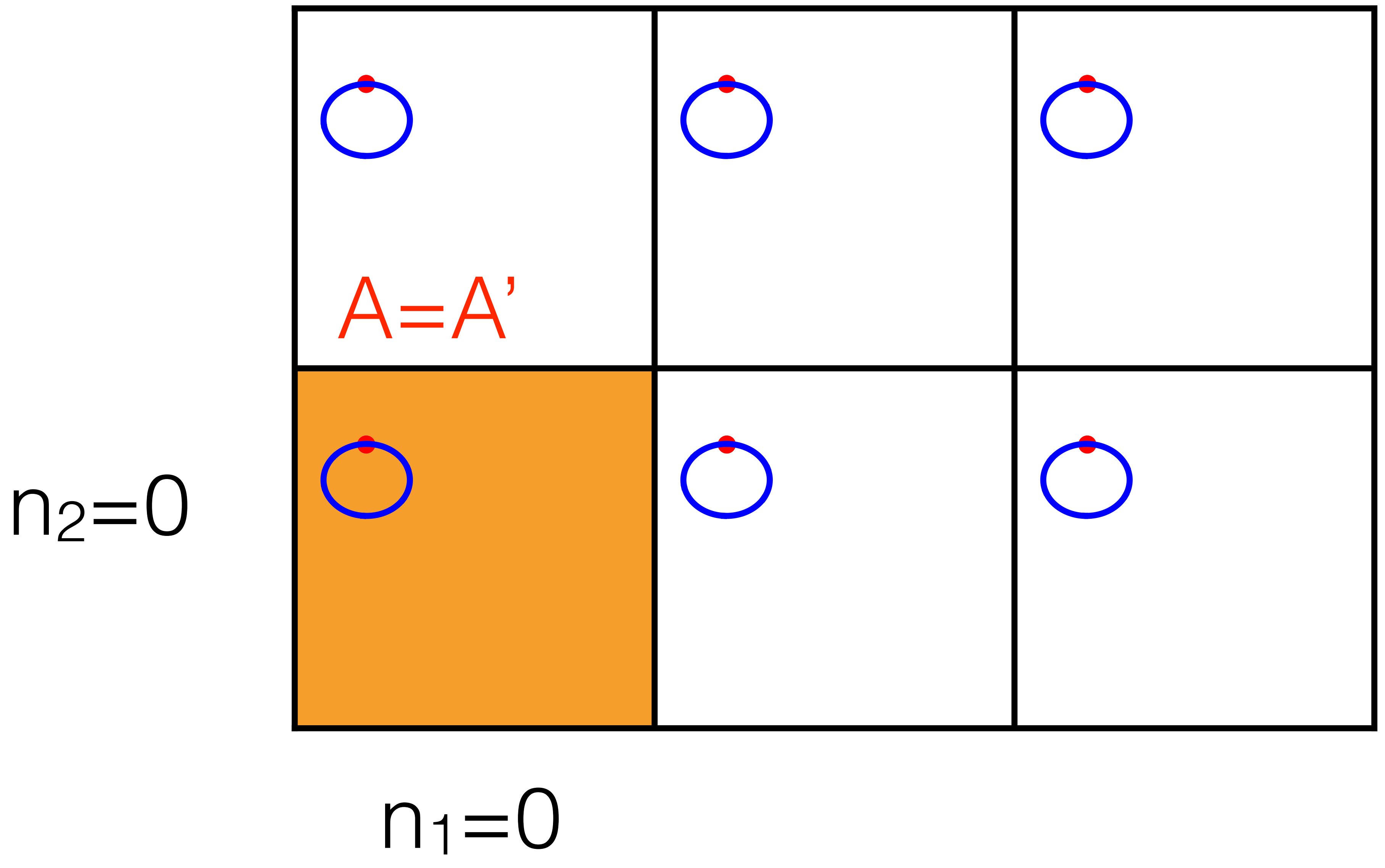

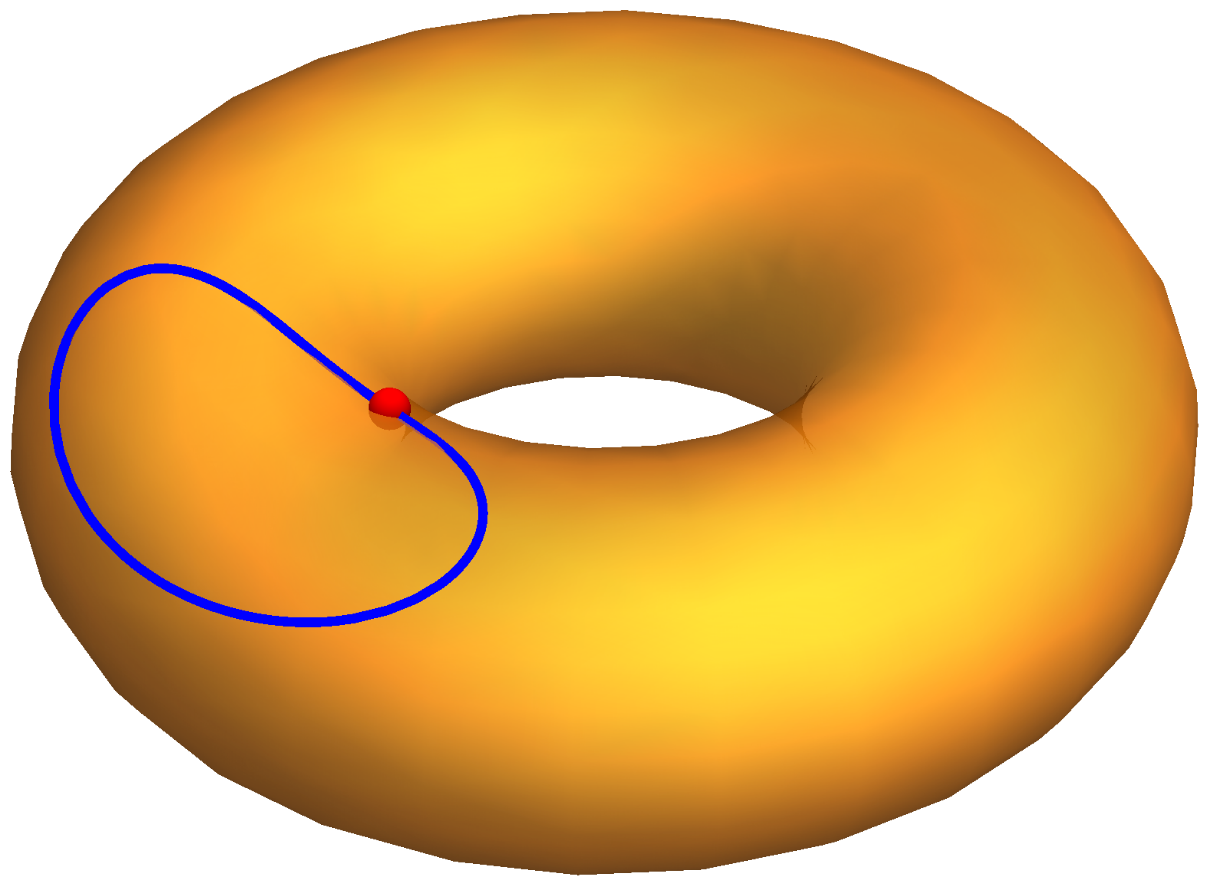

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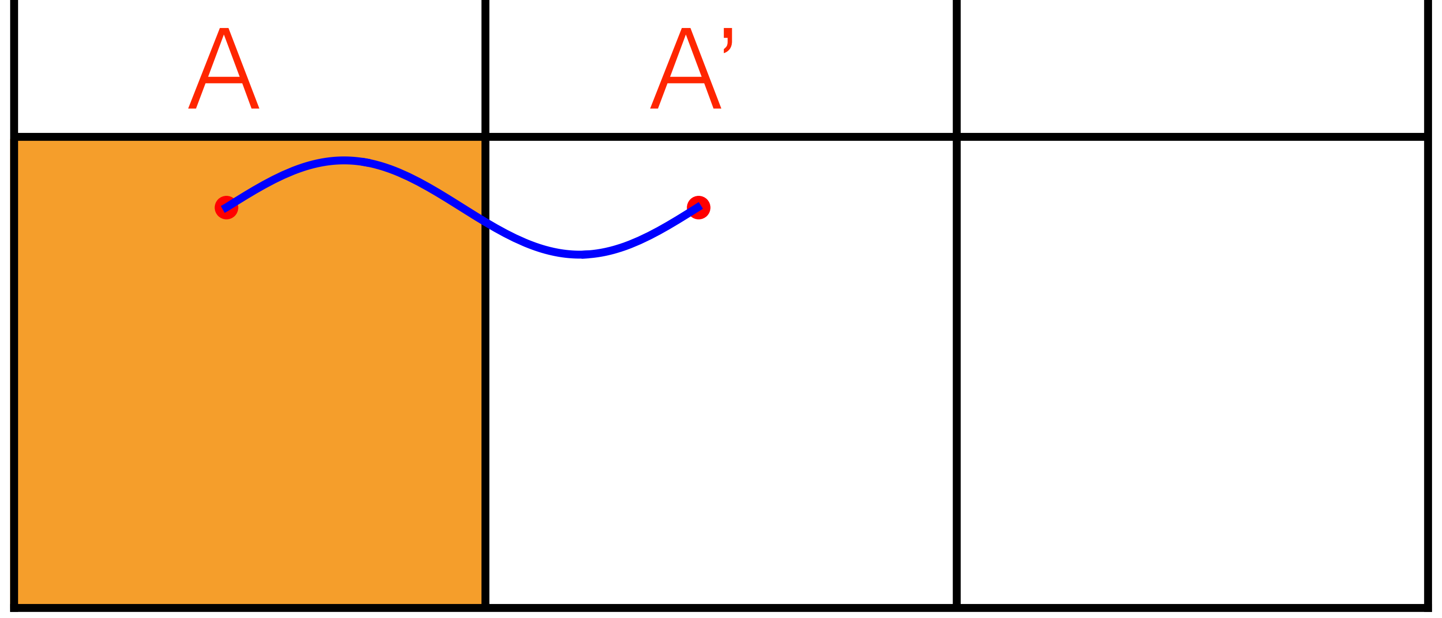

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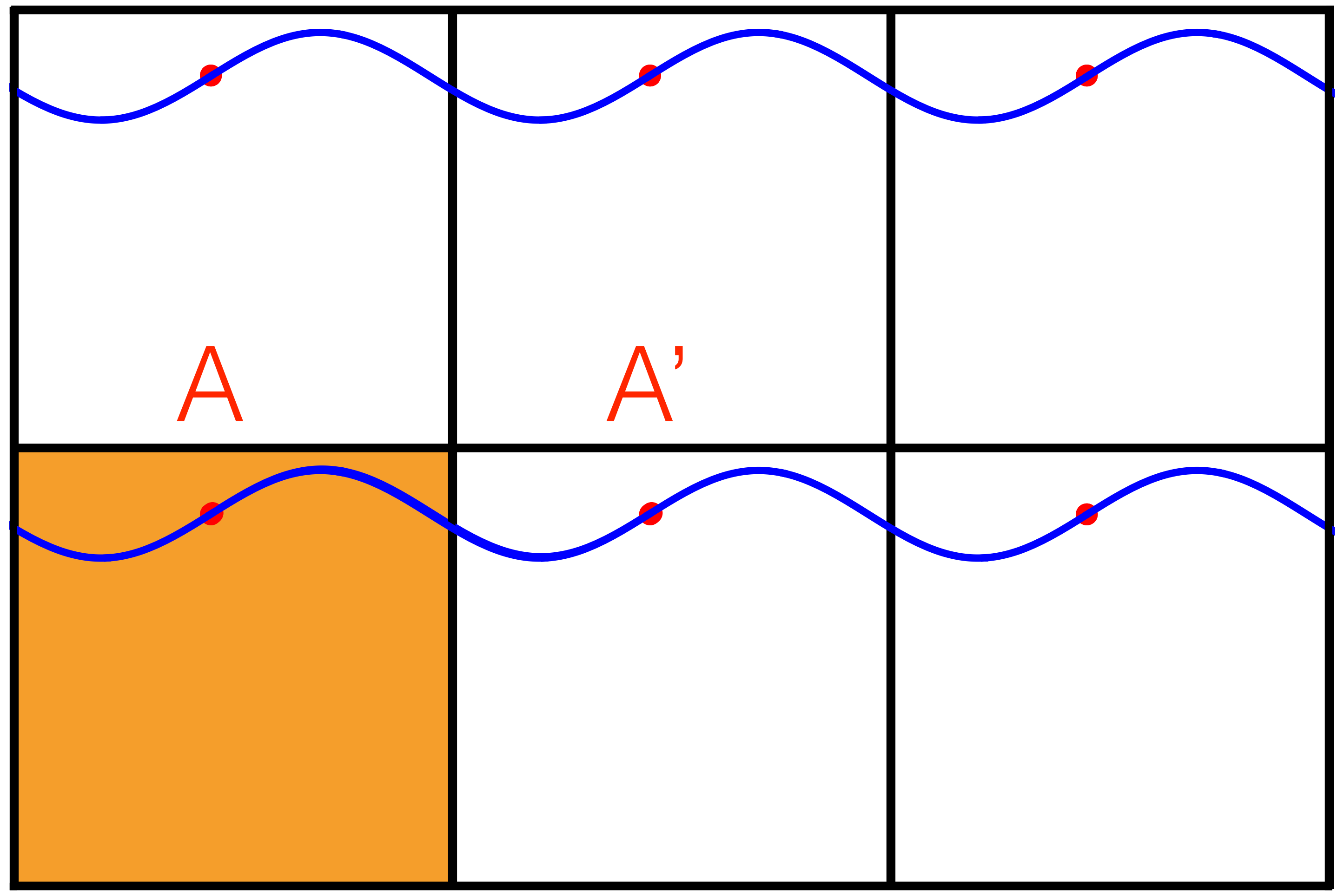

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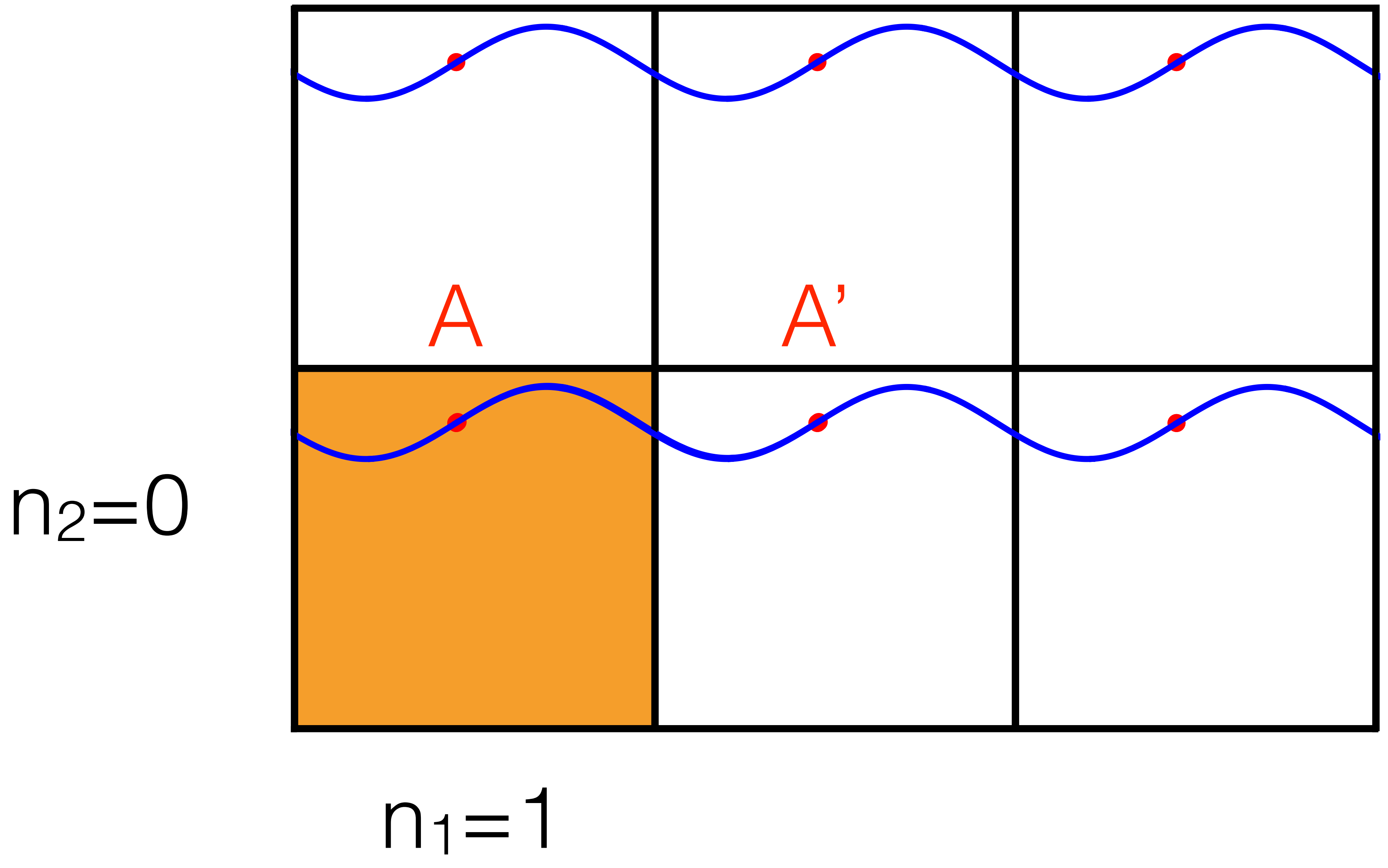

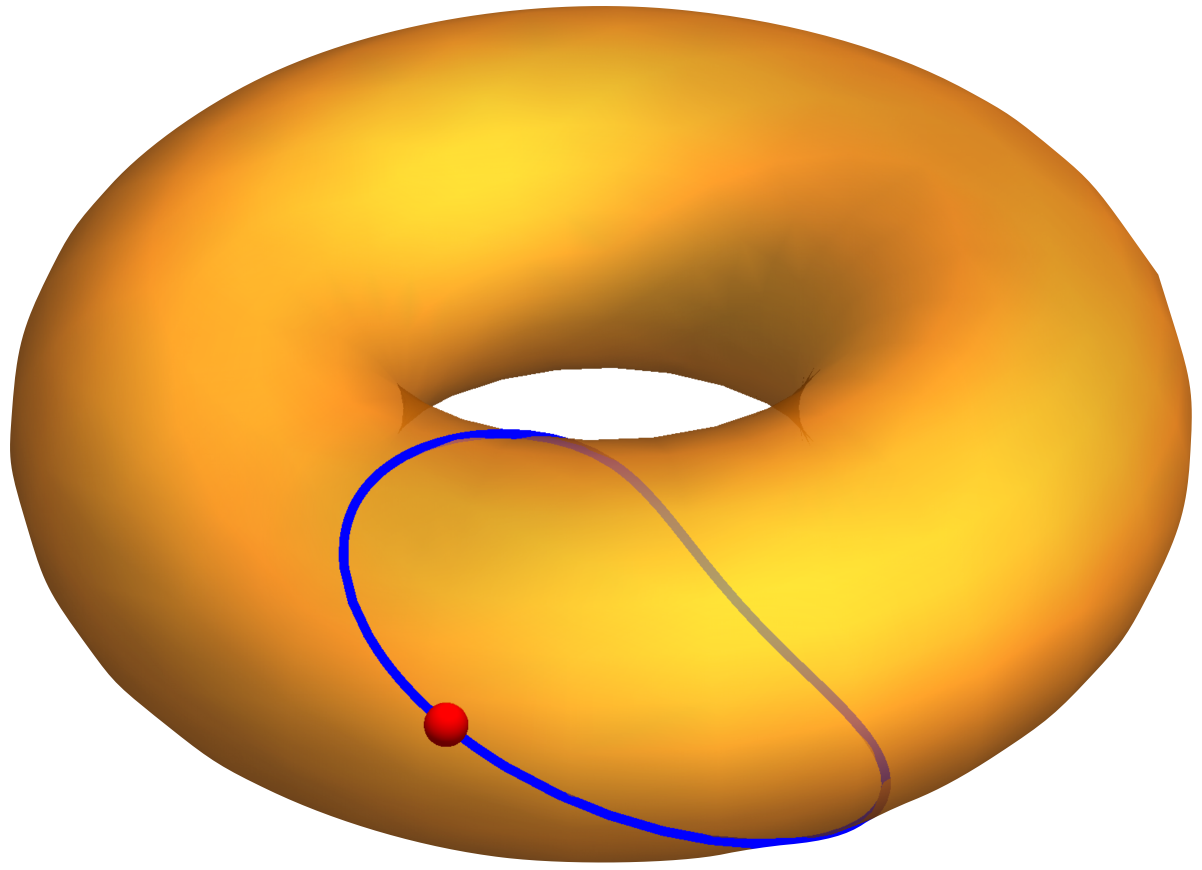

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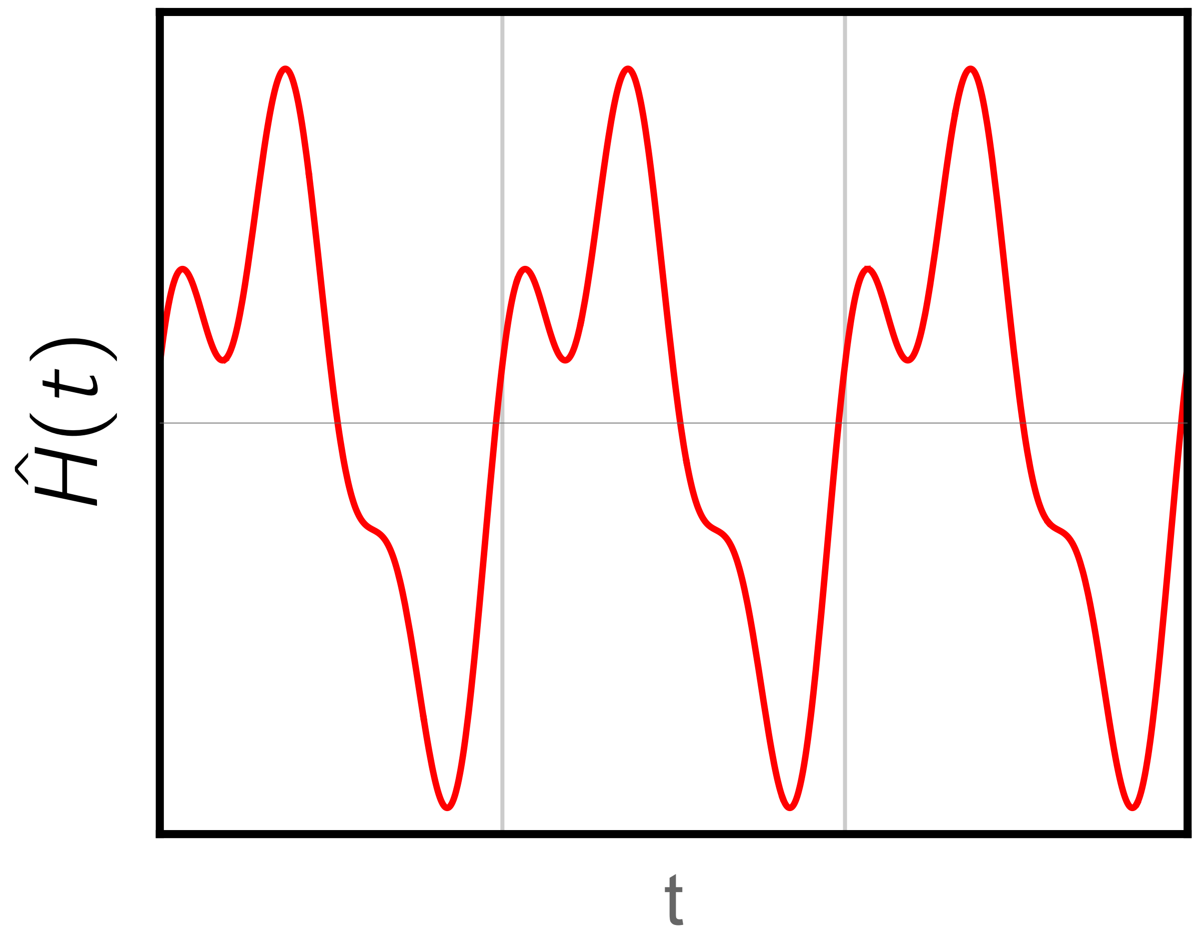
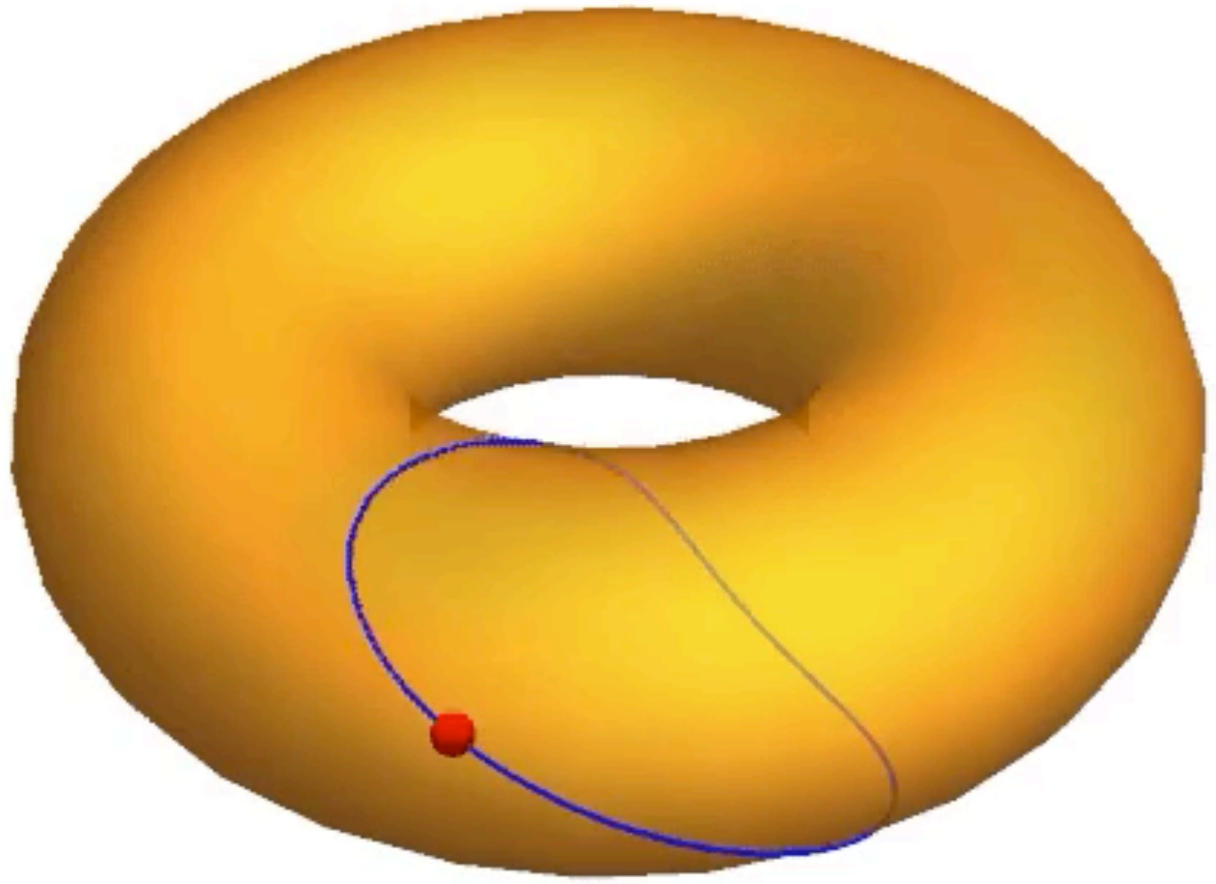


$$\hat{H}(t+T) = \hat{H}(t)$$



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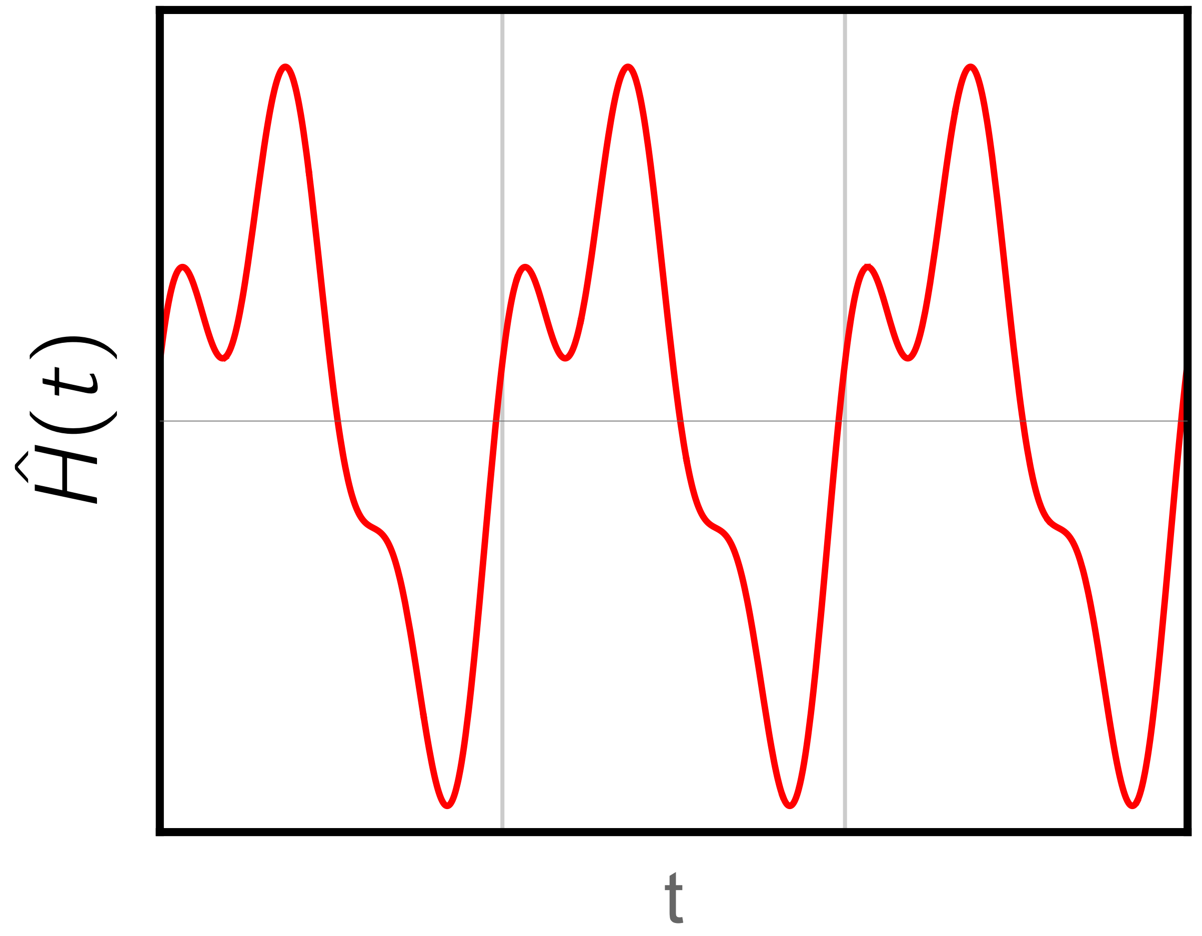

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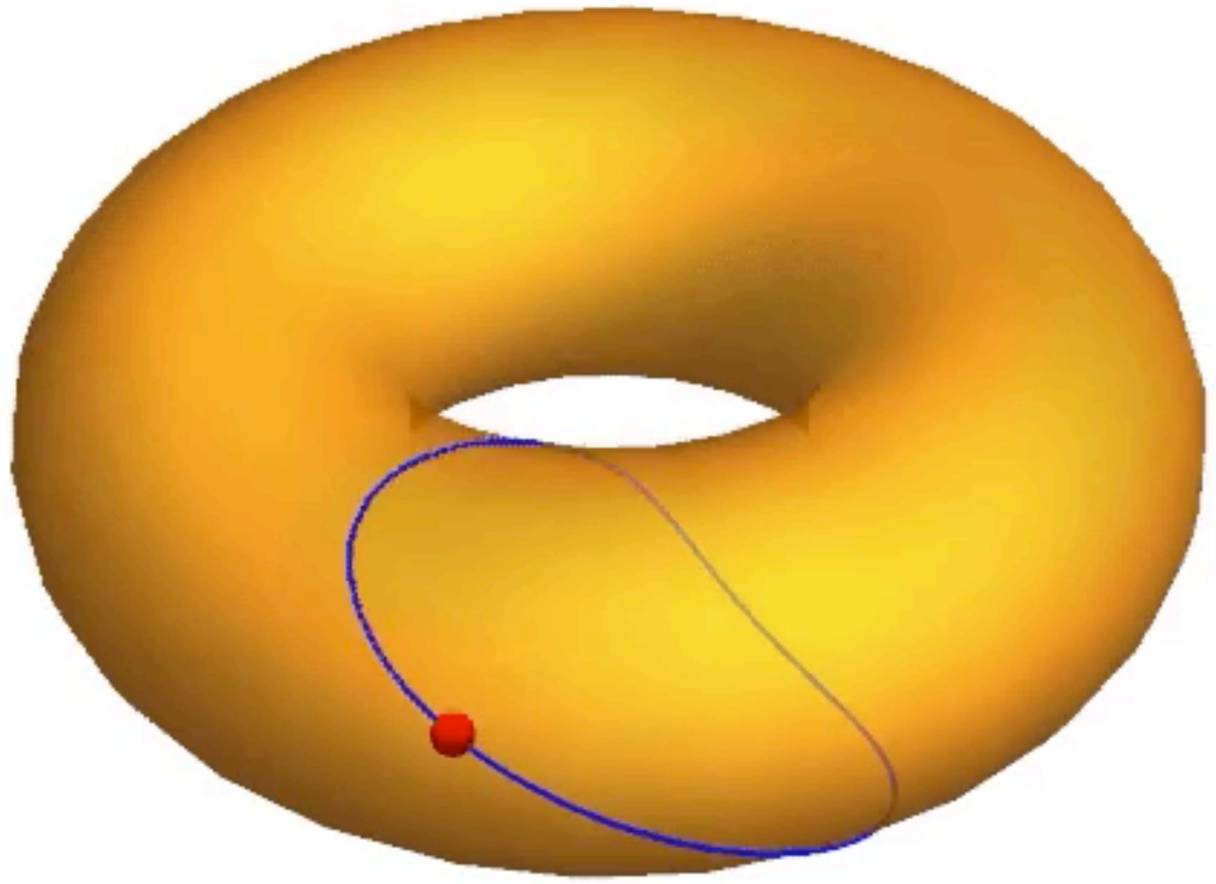

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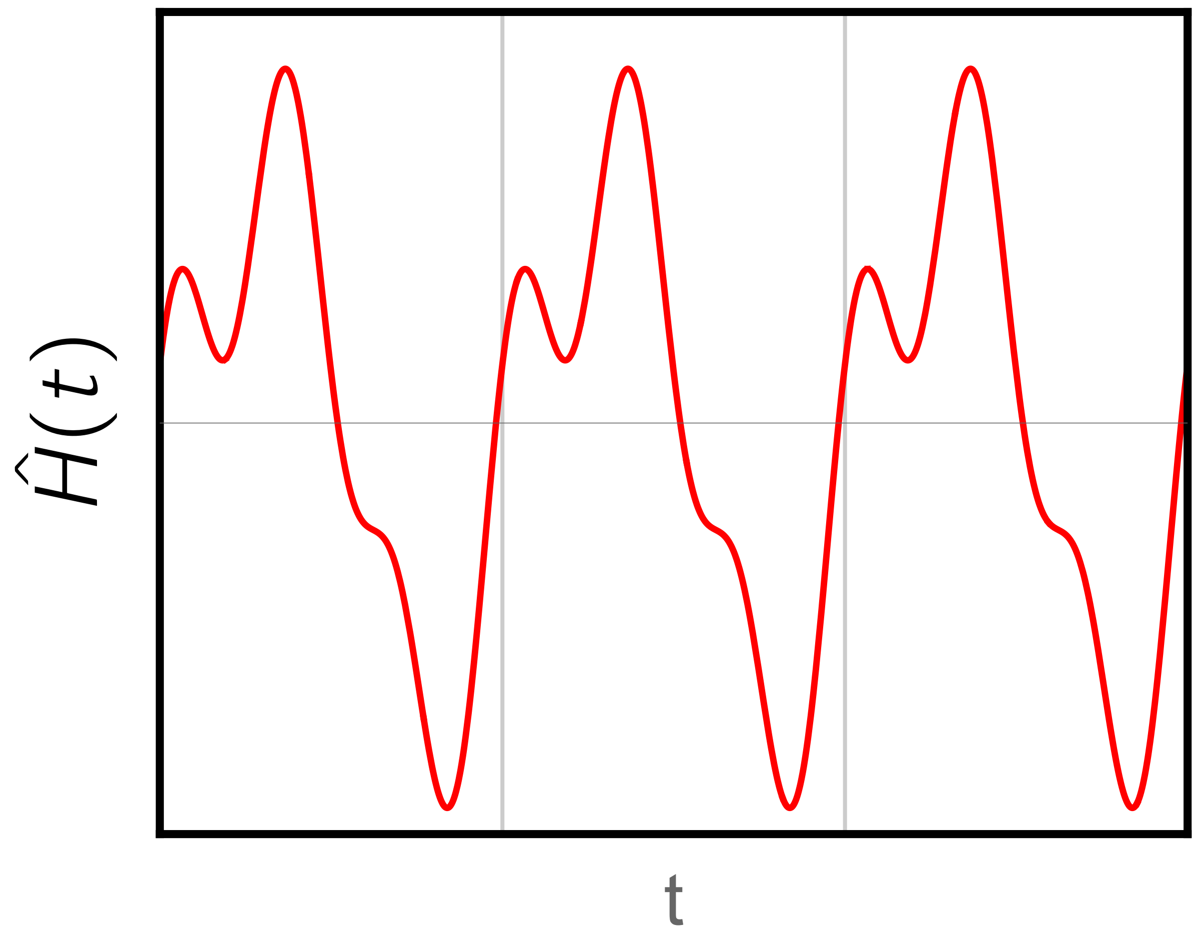

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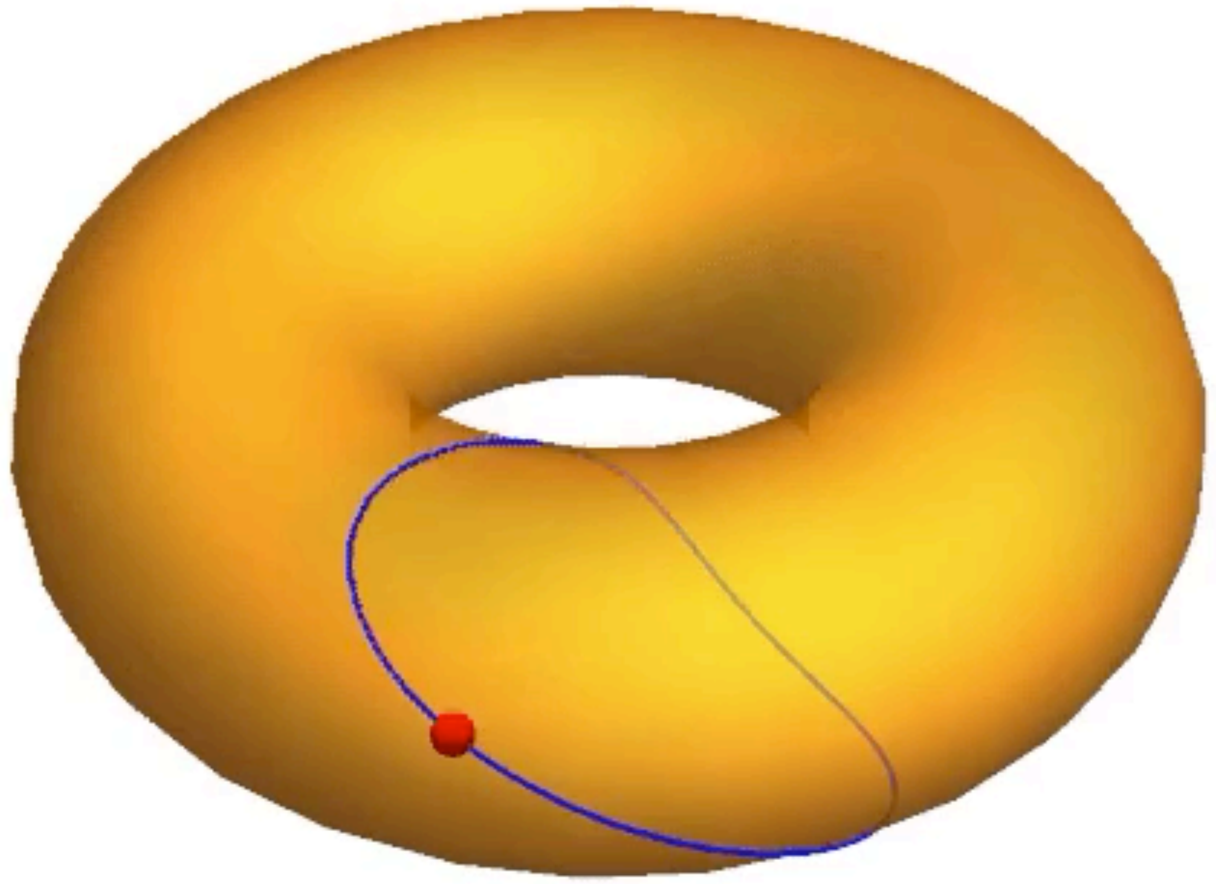

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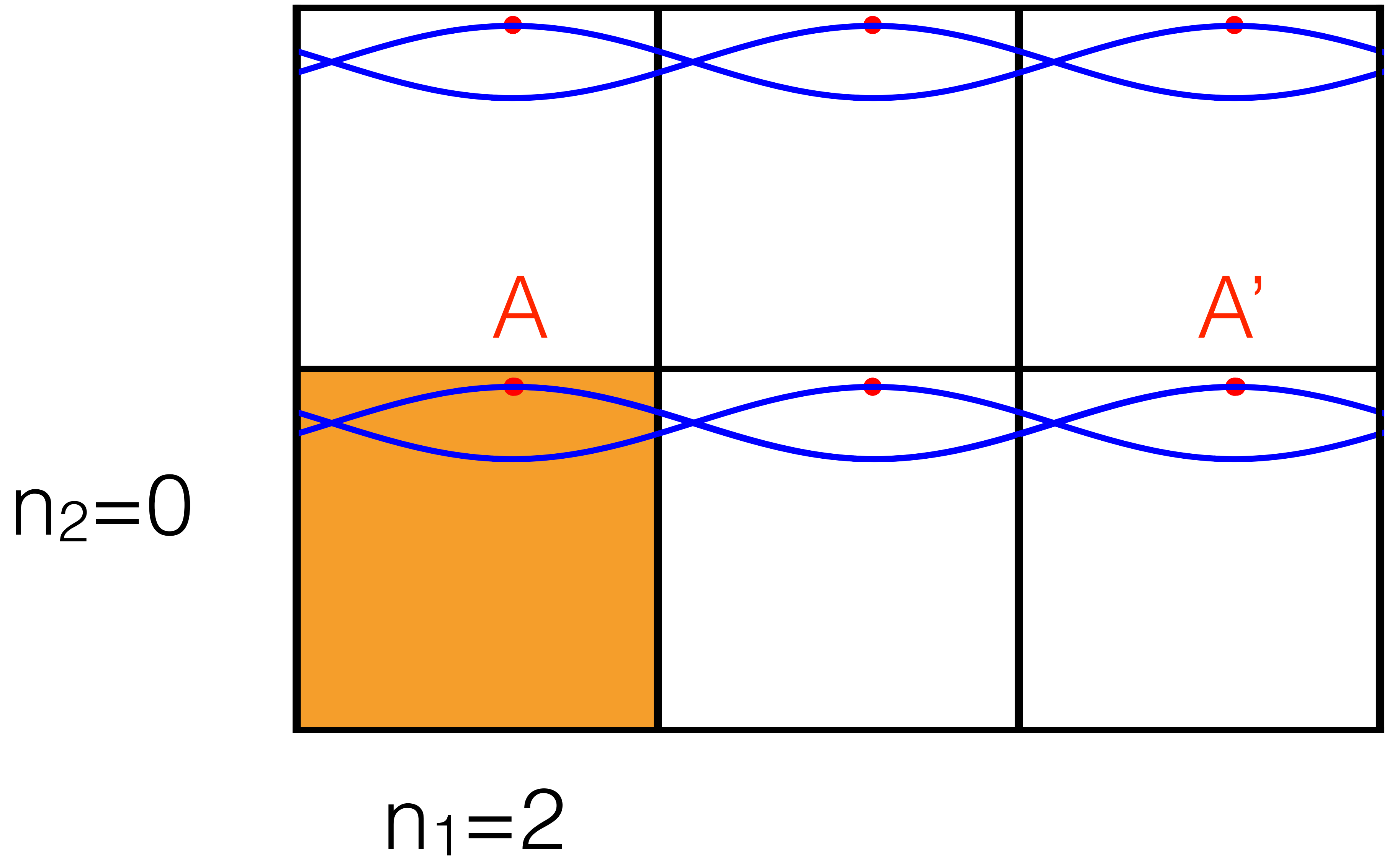

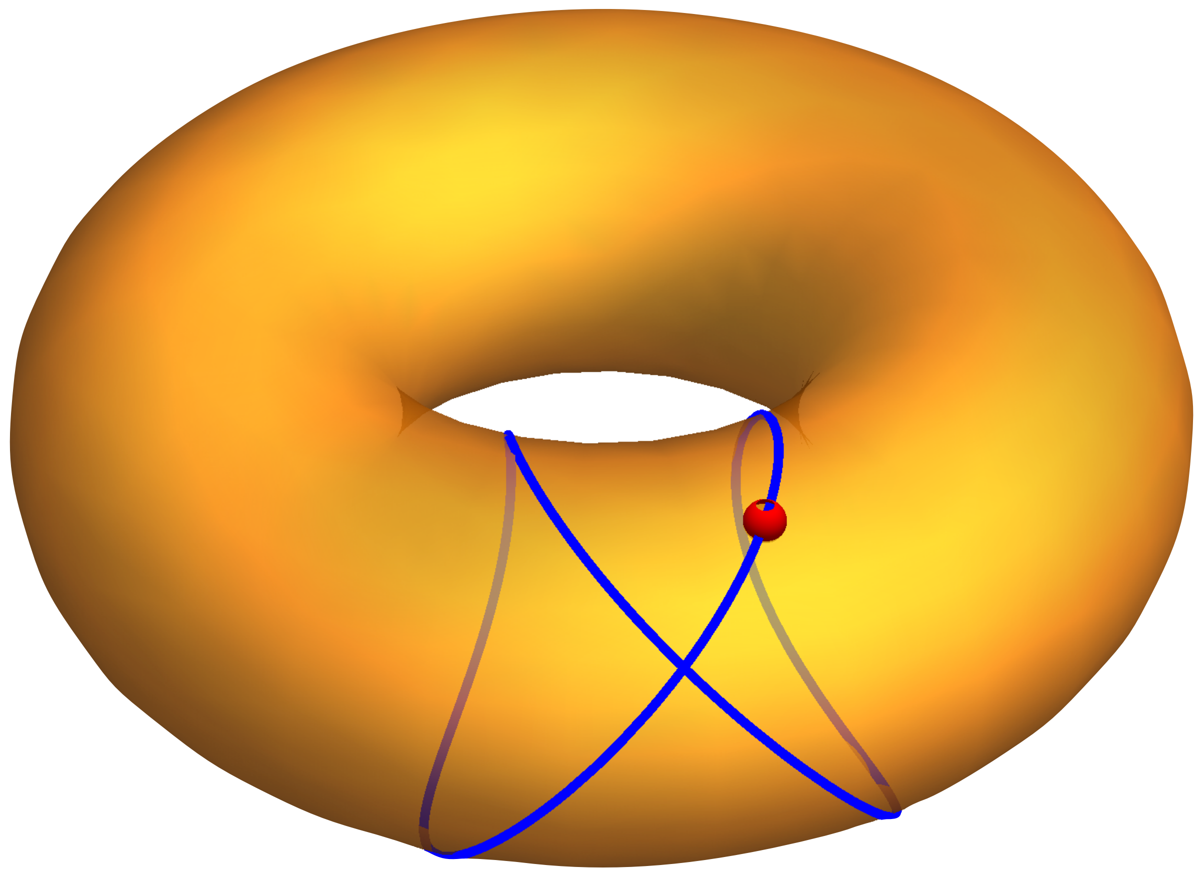

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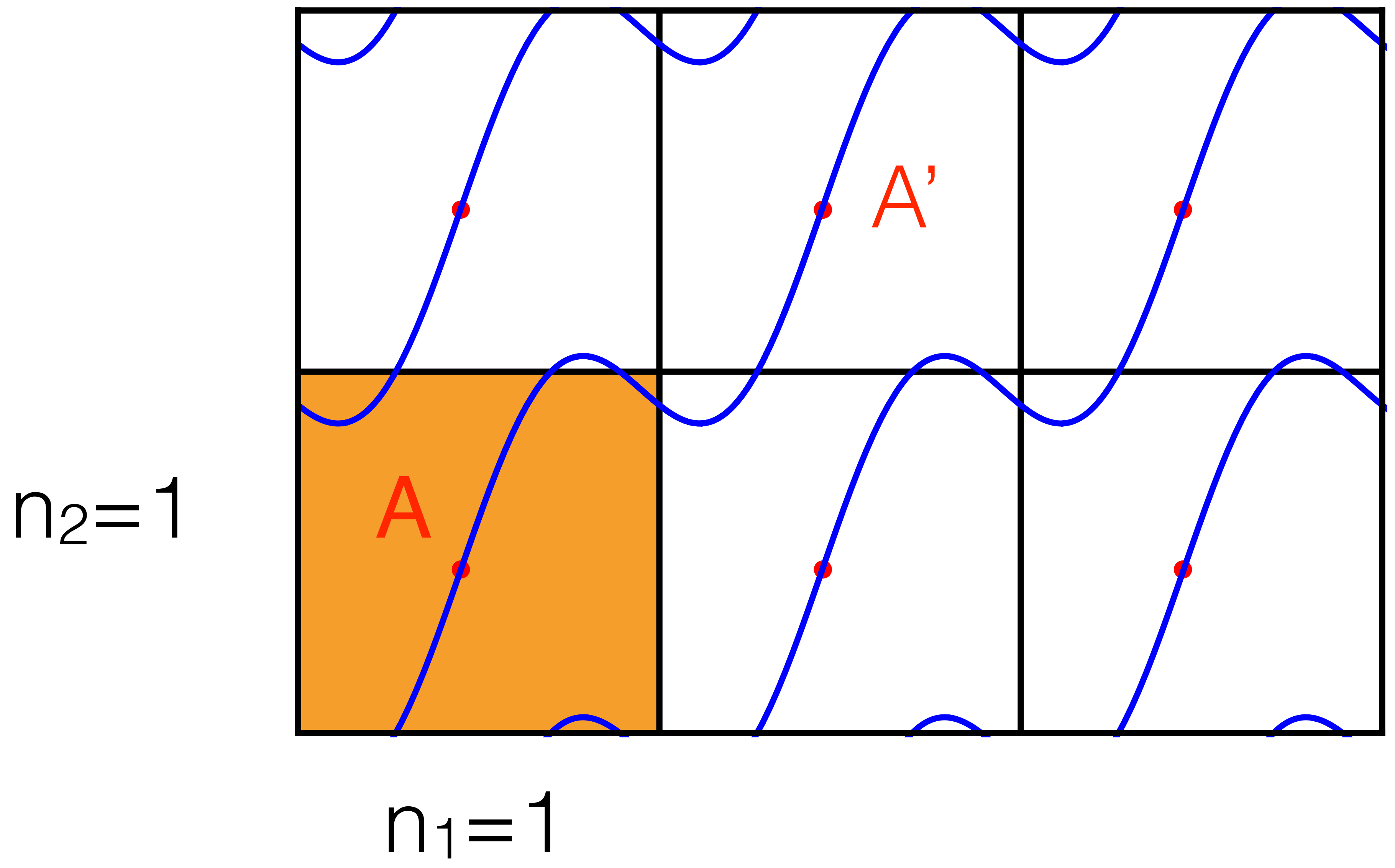

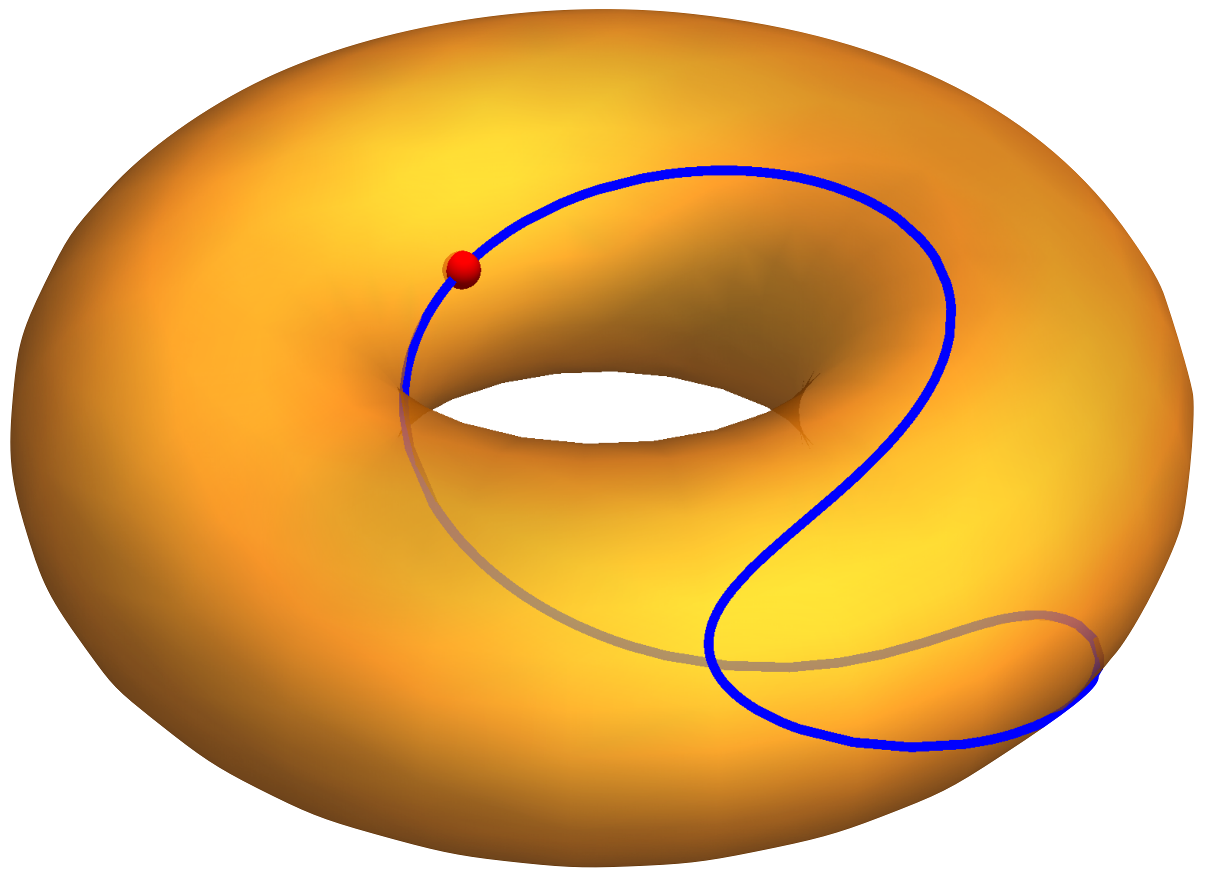

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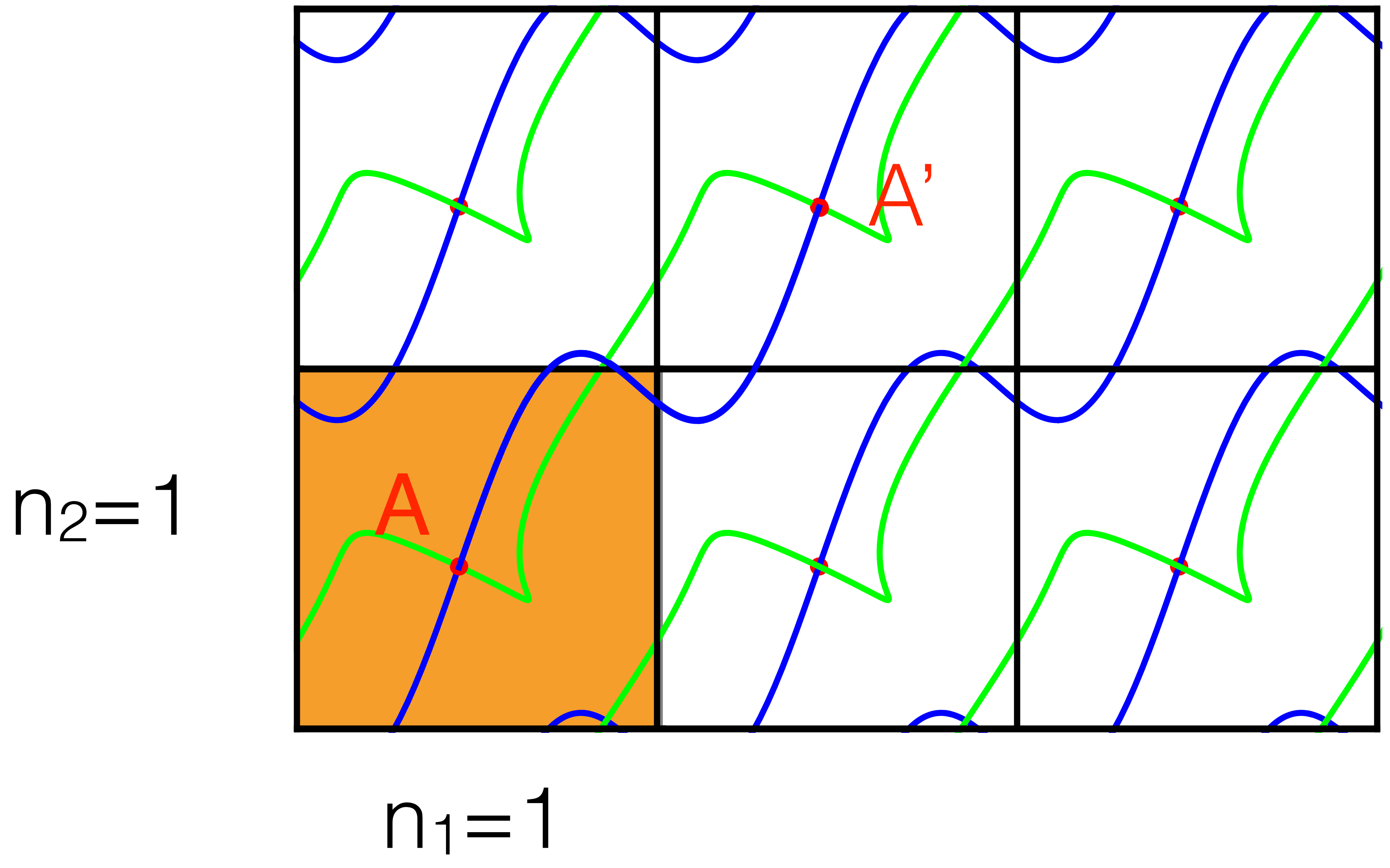

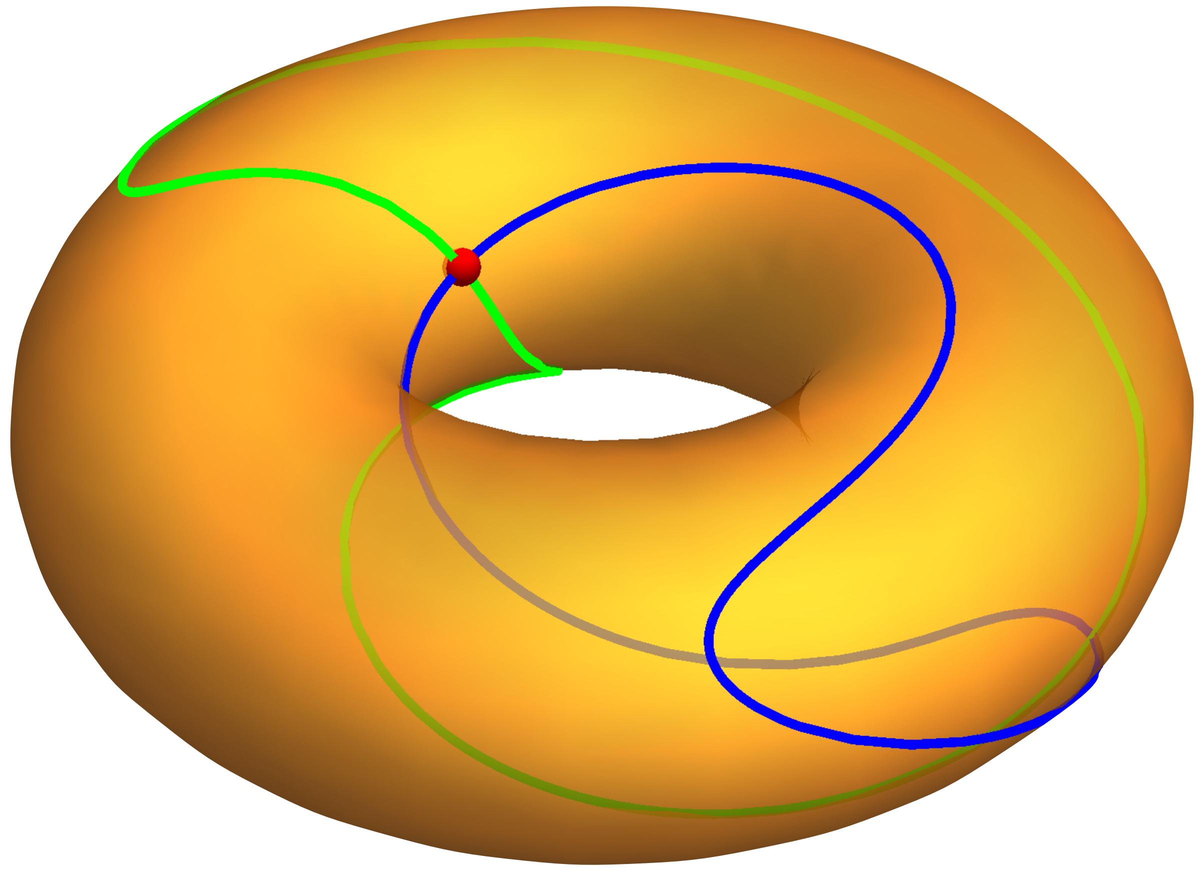

$$\color{blue}{Q_\alpha(AA')} = \color{green}{Q_\alpha(AA')} = Q_\alpha[n_1 = 1, n_2 = 1]$$

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atomic oxidation state

MA PER SEGUIR VIRTUTE E CANOSCENZA

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→

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atomic oxidation state

… they are topological invariants!

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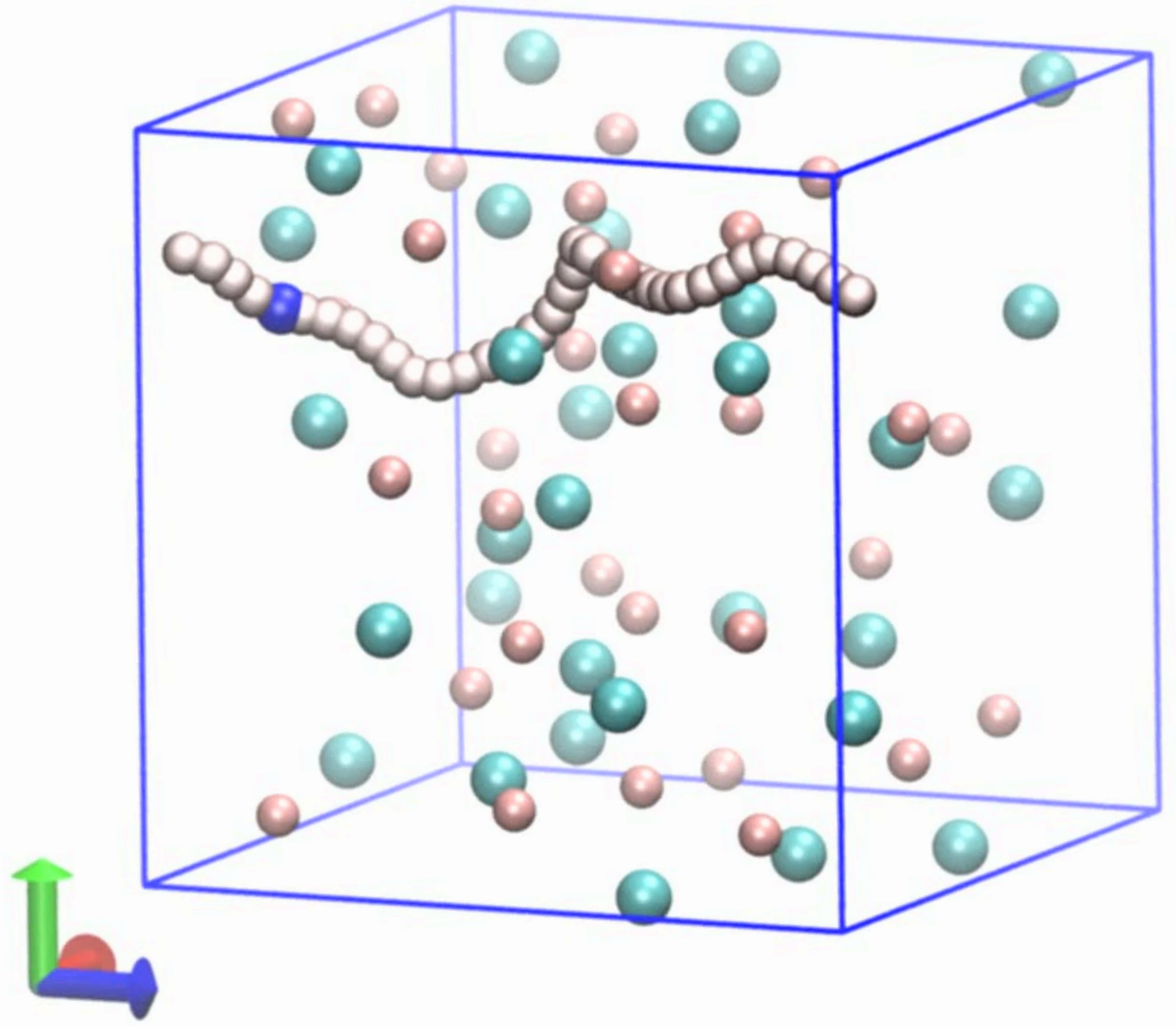
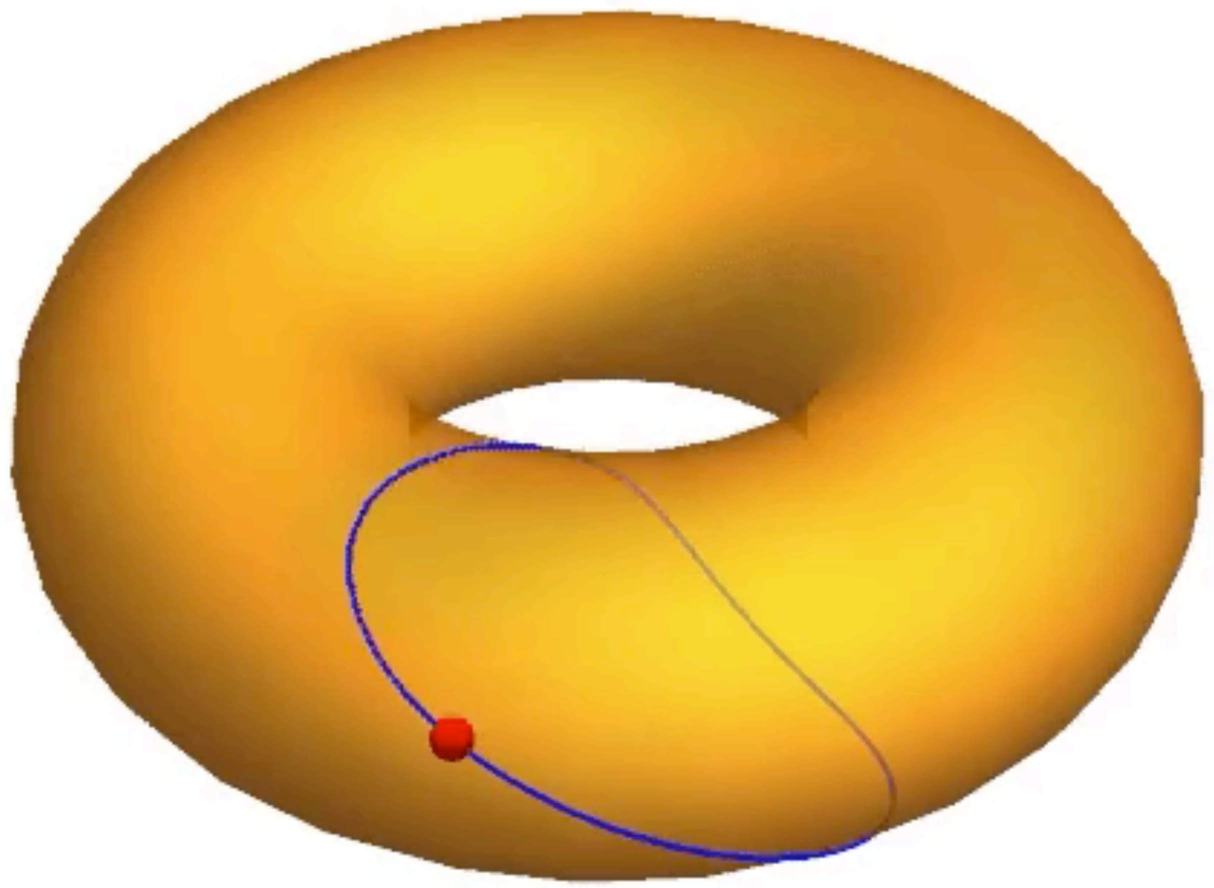
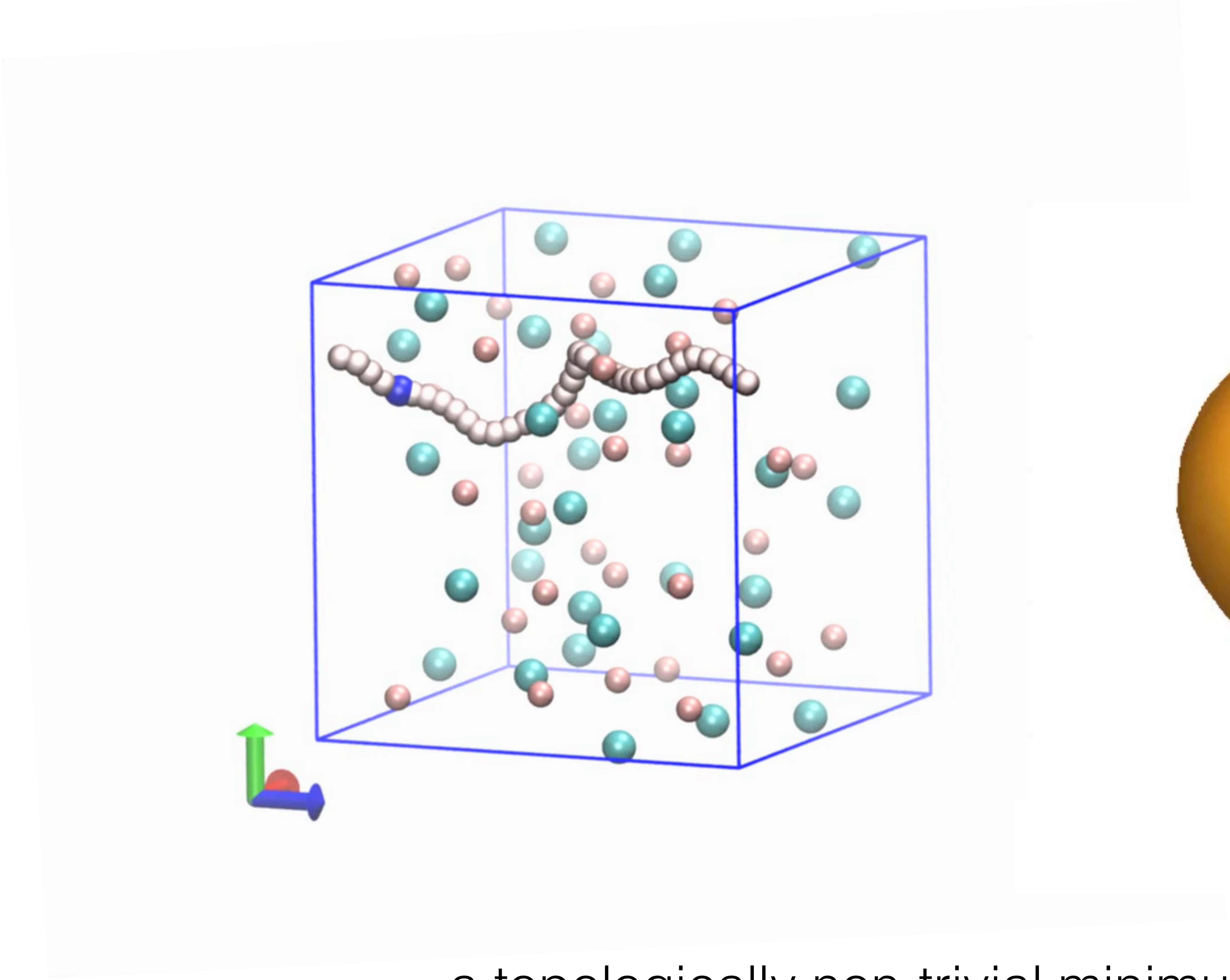
a numerical experiment on molten KCl

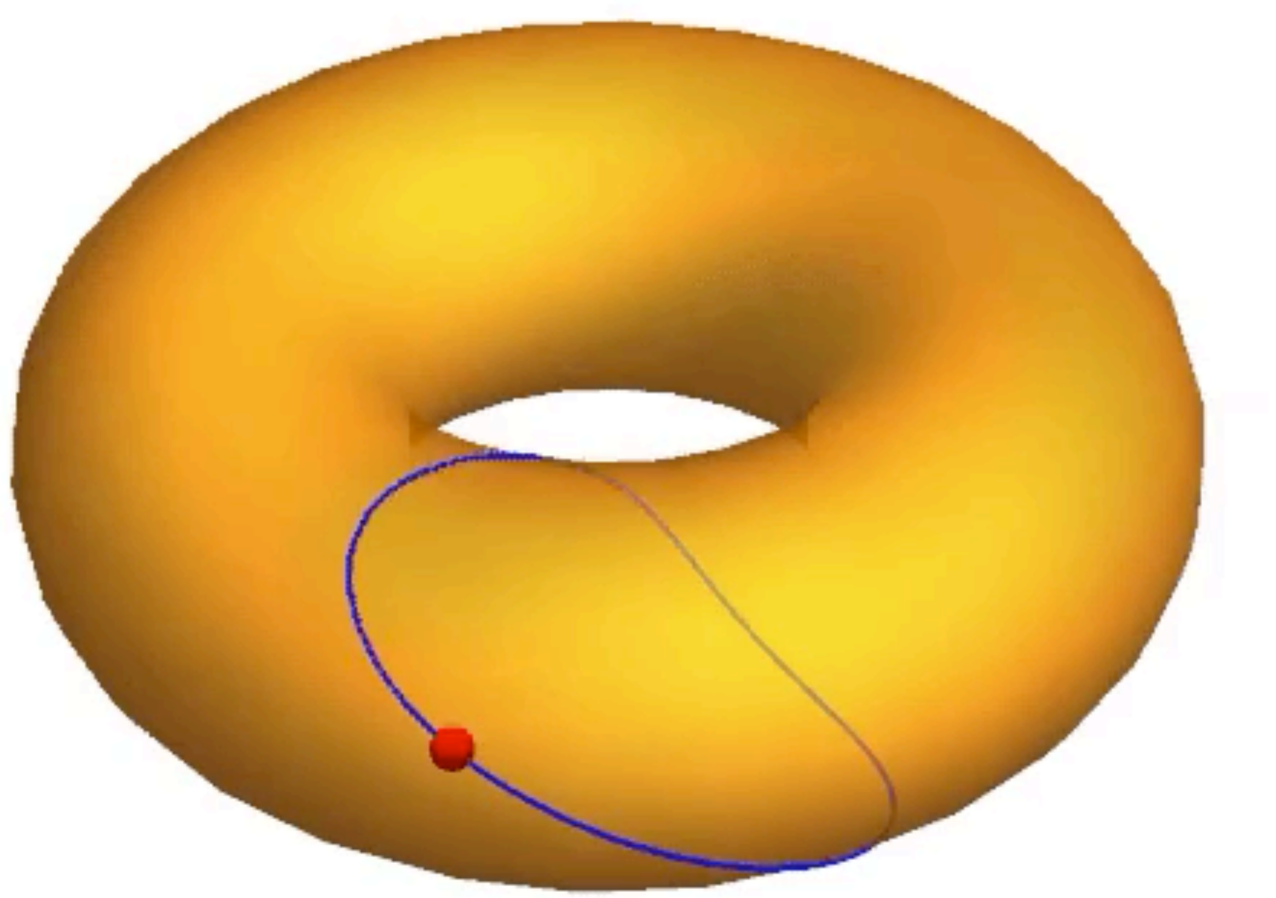




a topologically non-trivial minimum-energy path
connecting two identical configurations of a ionic melt

a numerical experiment on molten KCl





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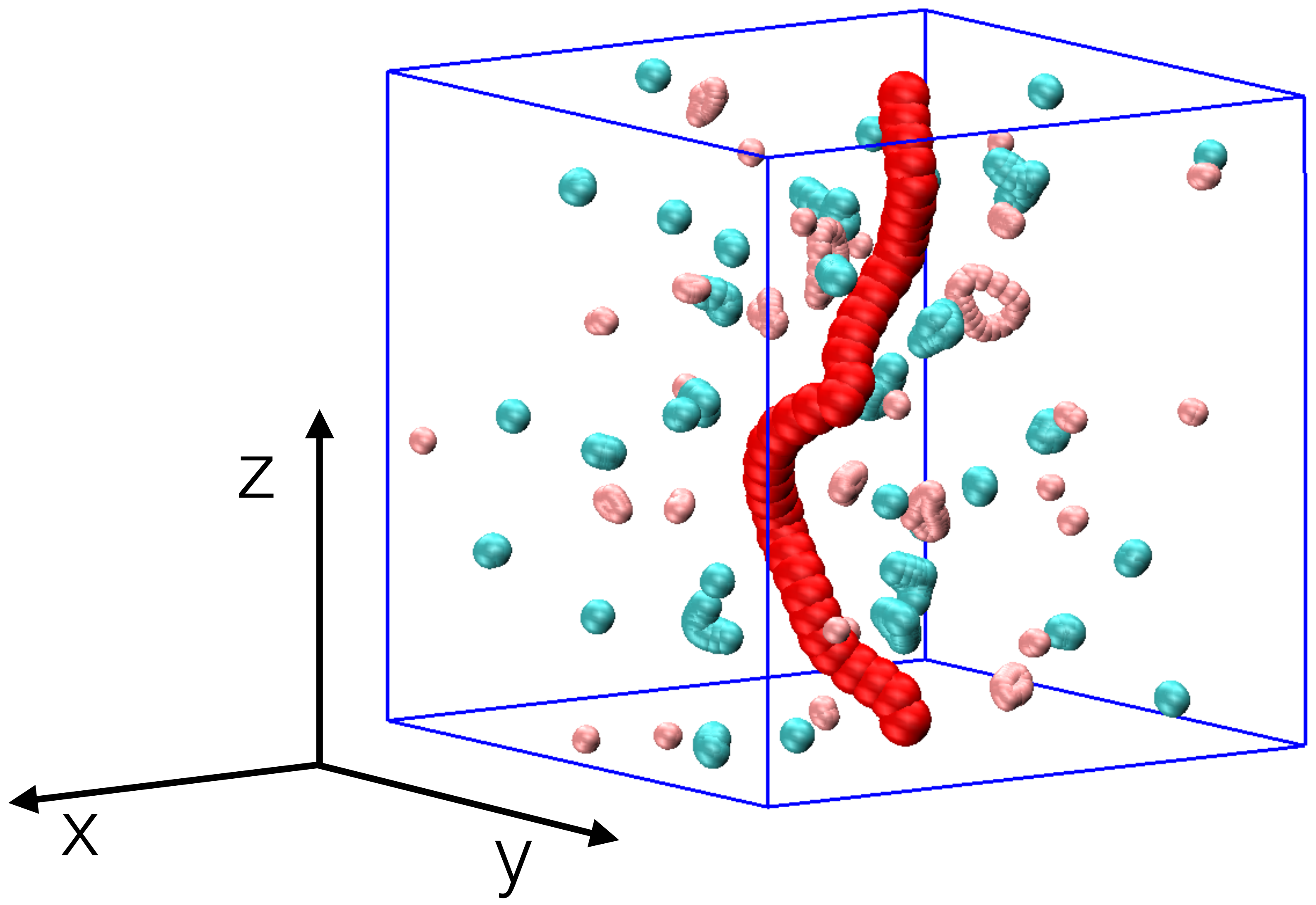

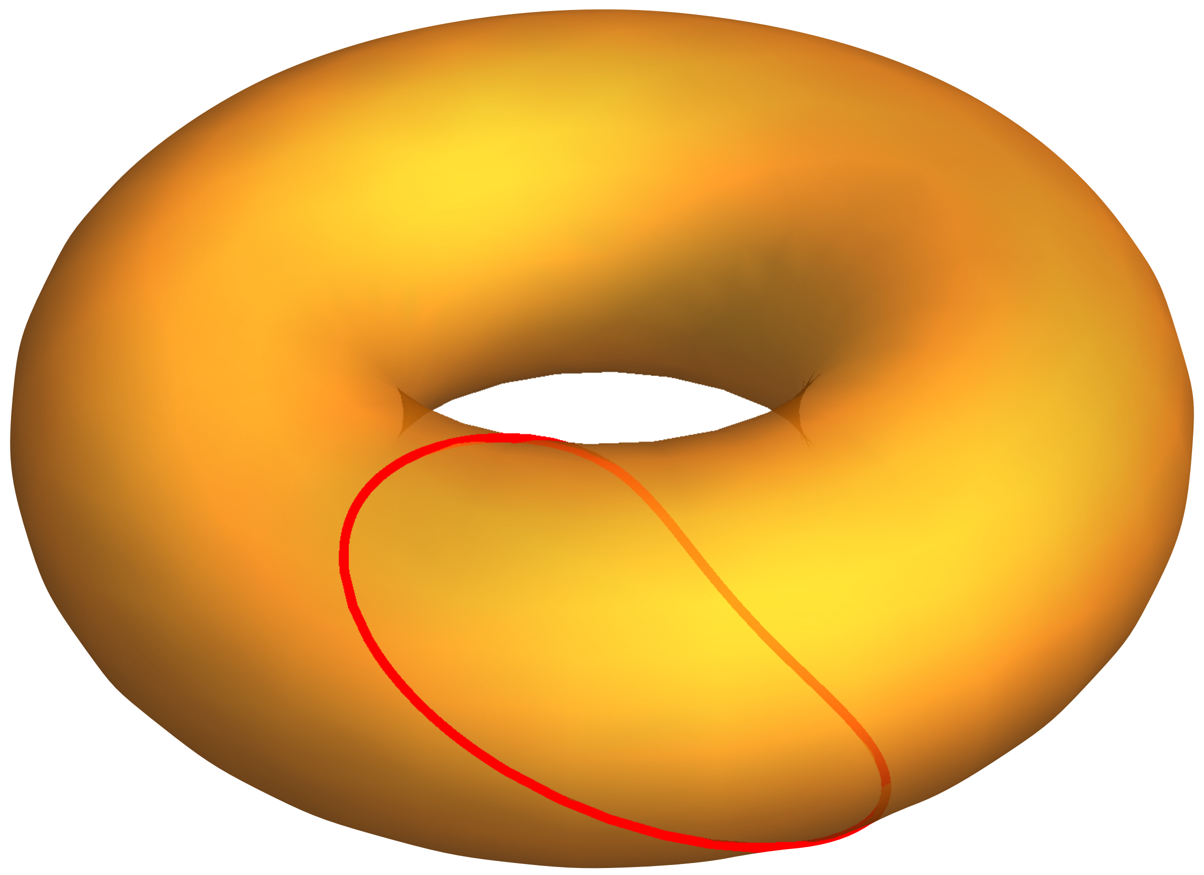

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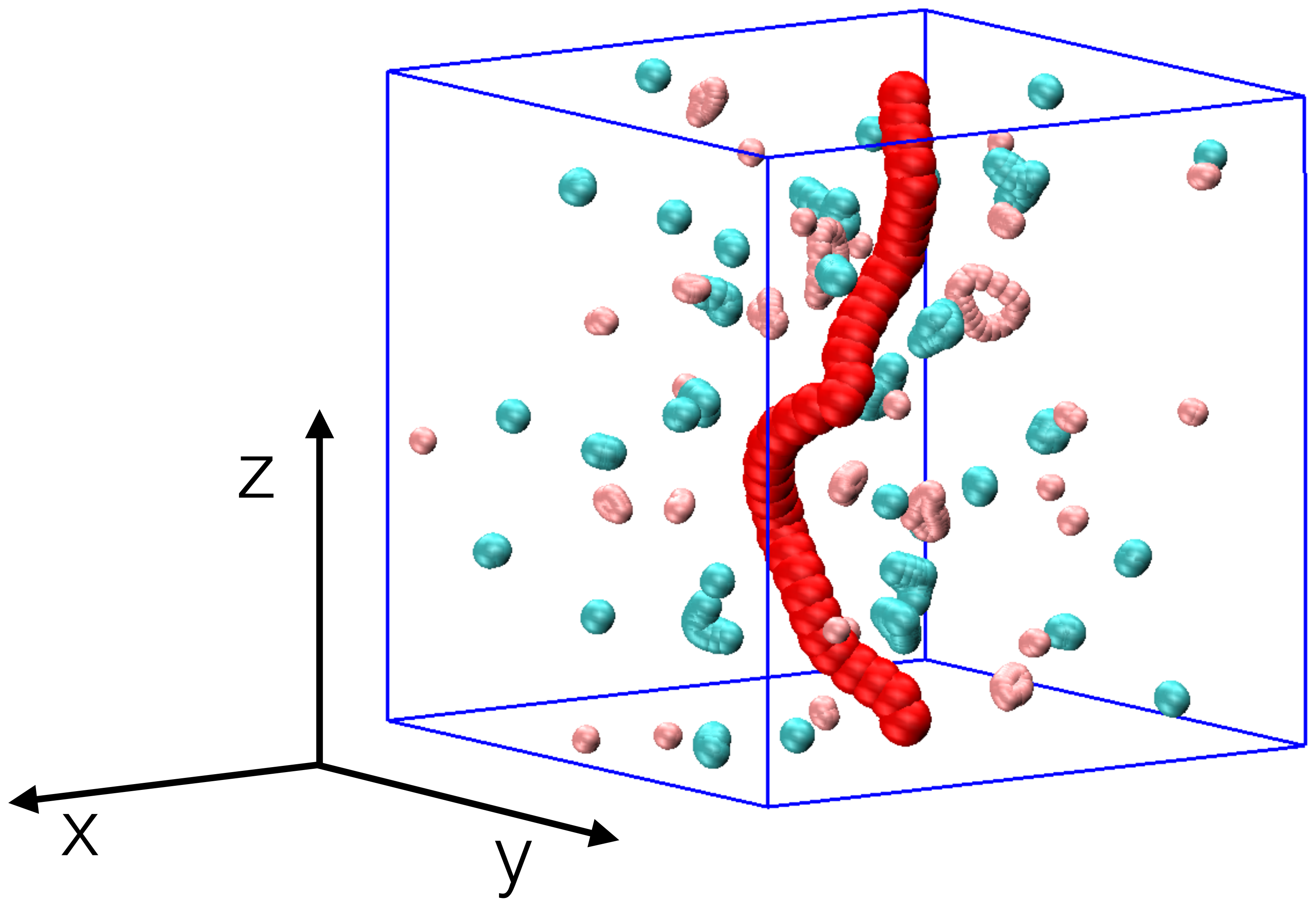

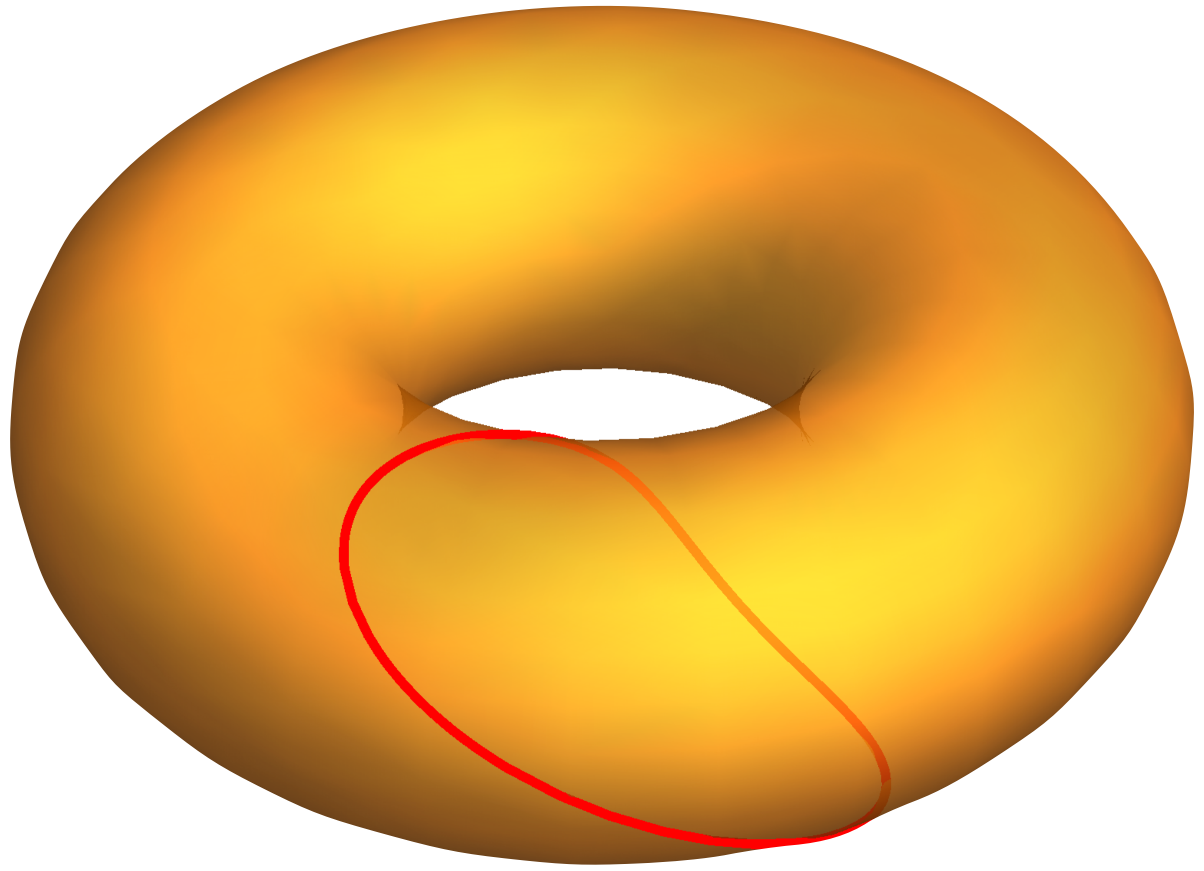

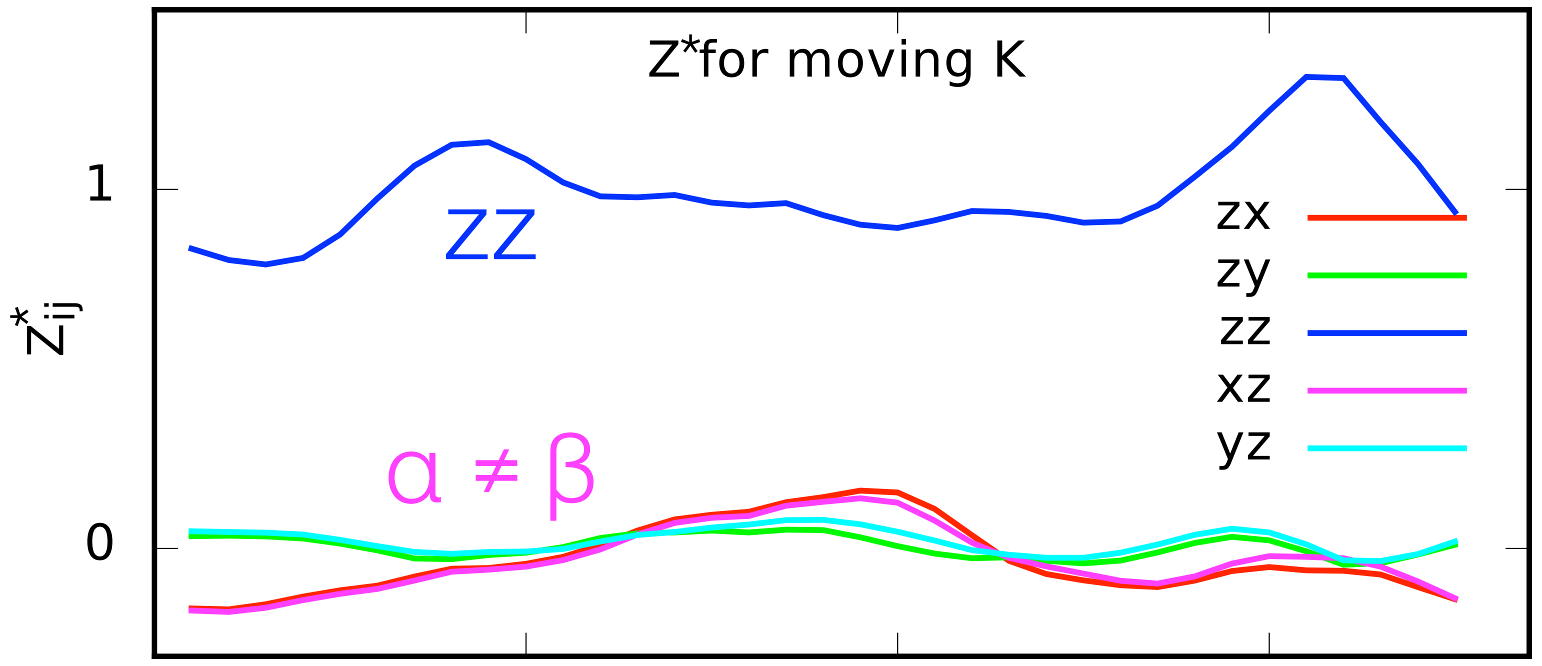

effective charge

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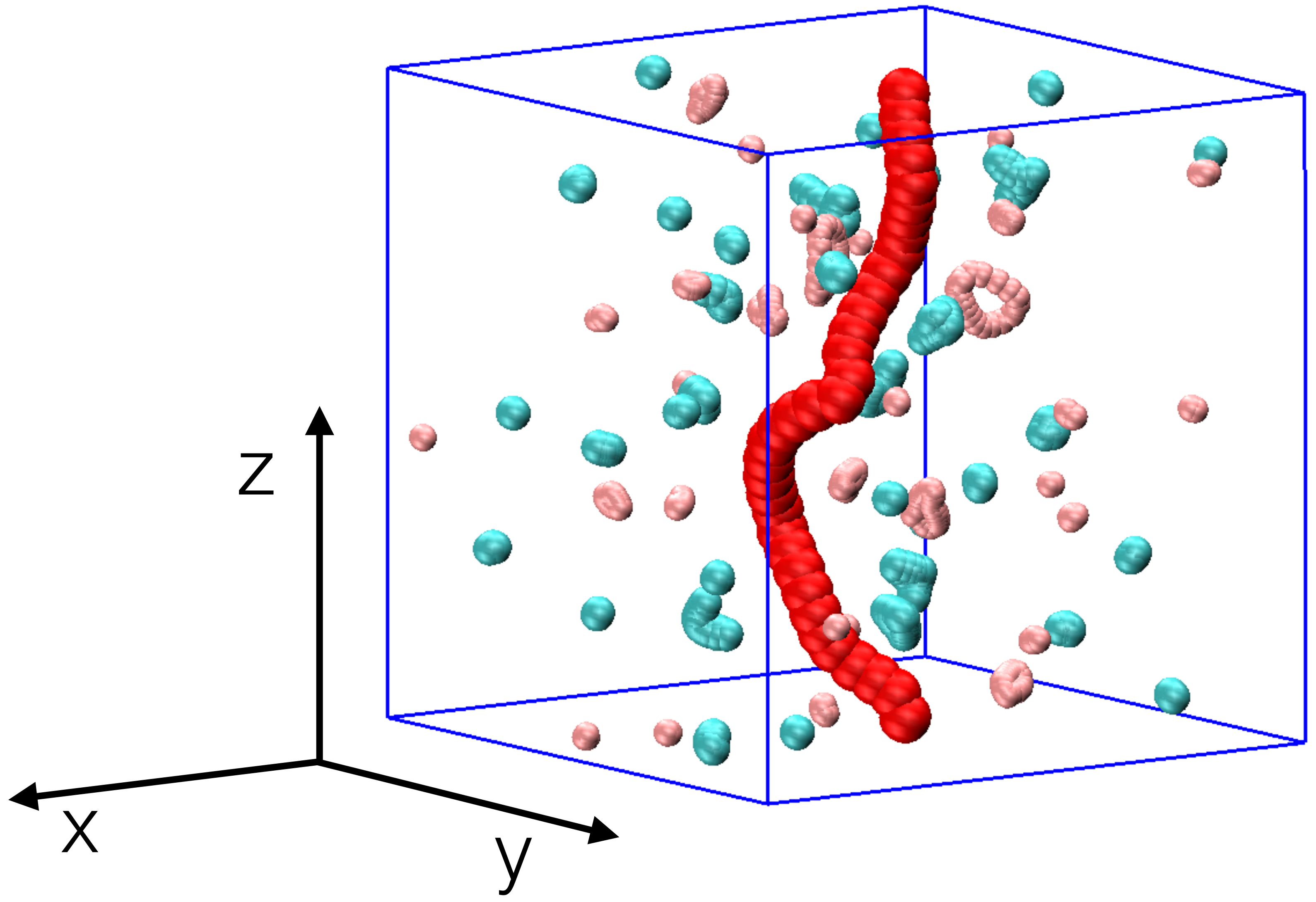

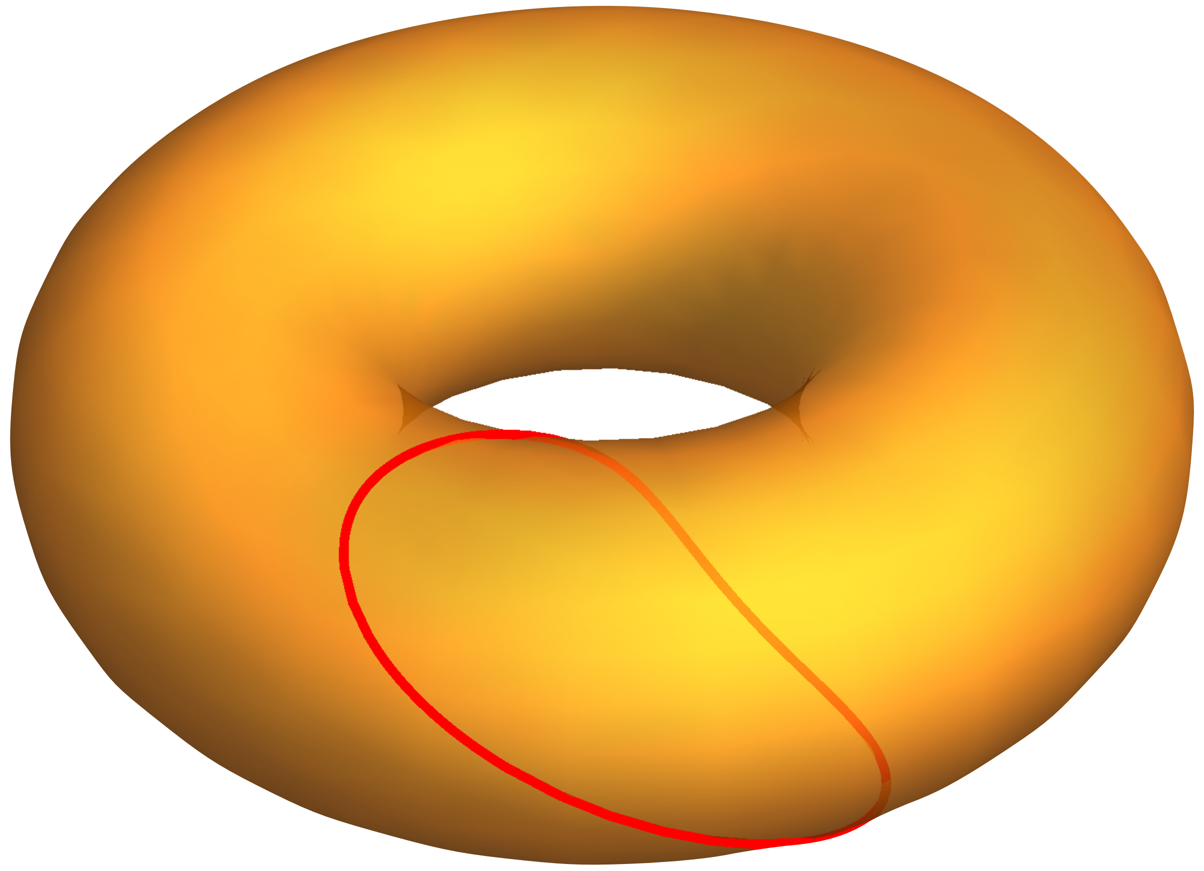

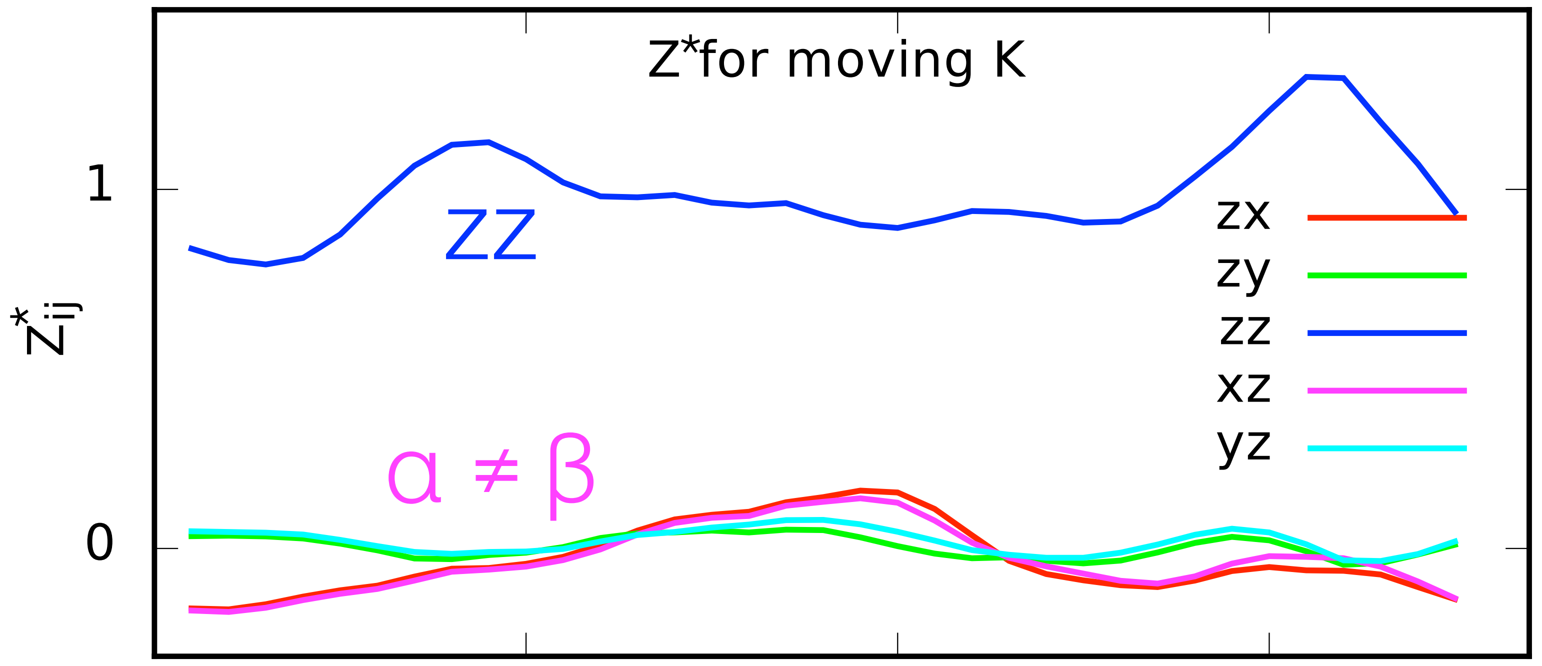

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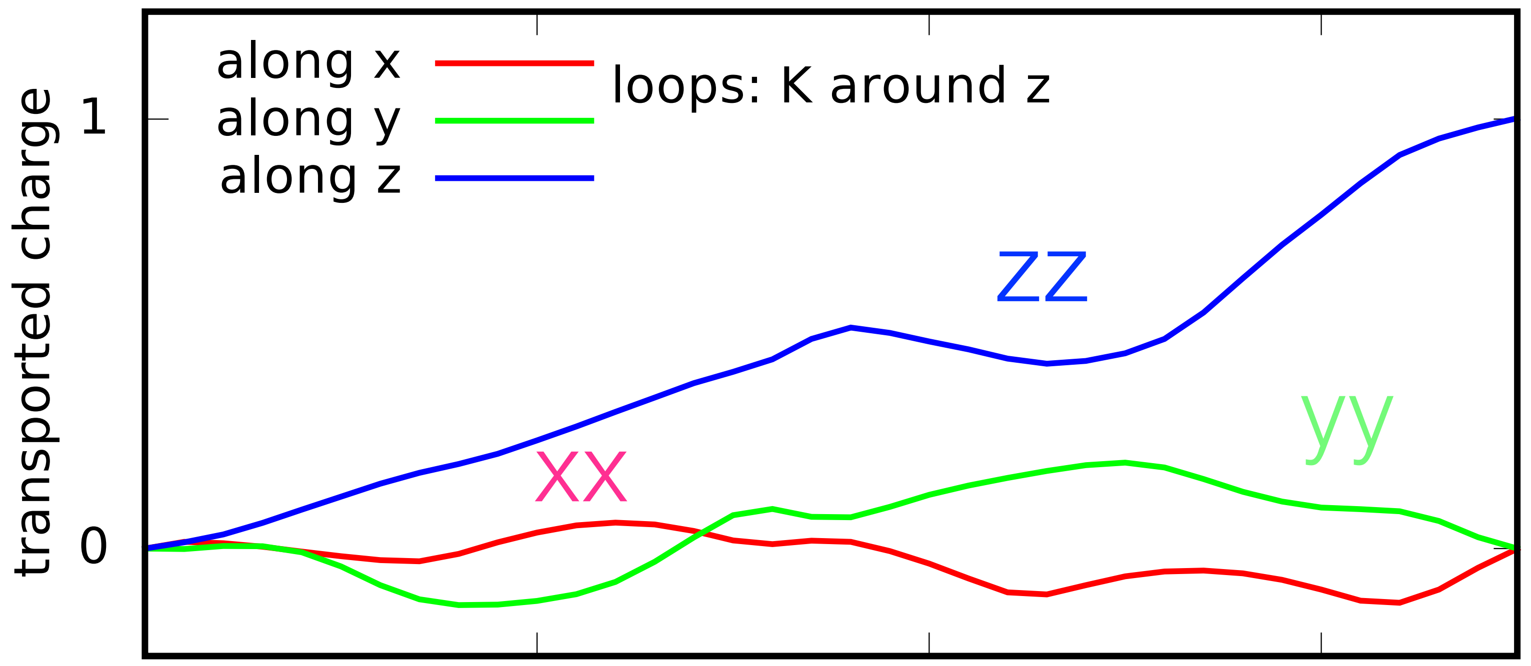

topological charge

Q_x = =-0.000(6); Q_y = 0.000(2); Q_z = 1.00(18)

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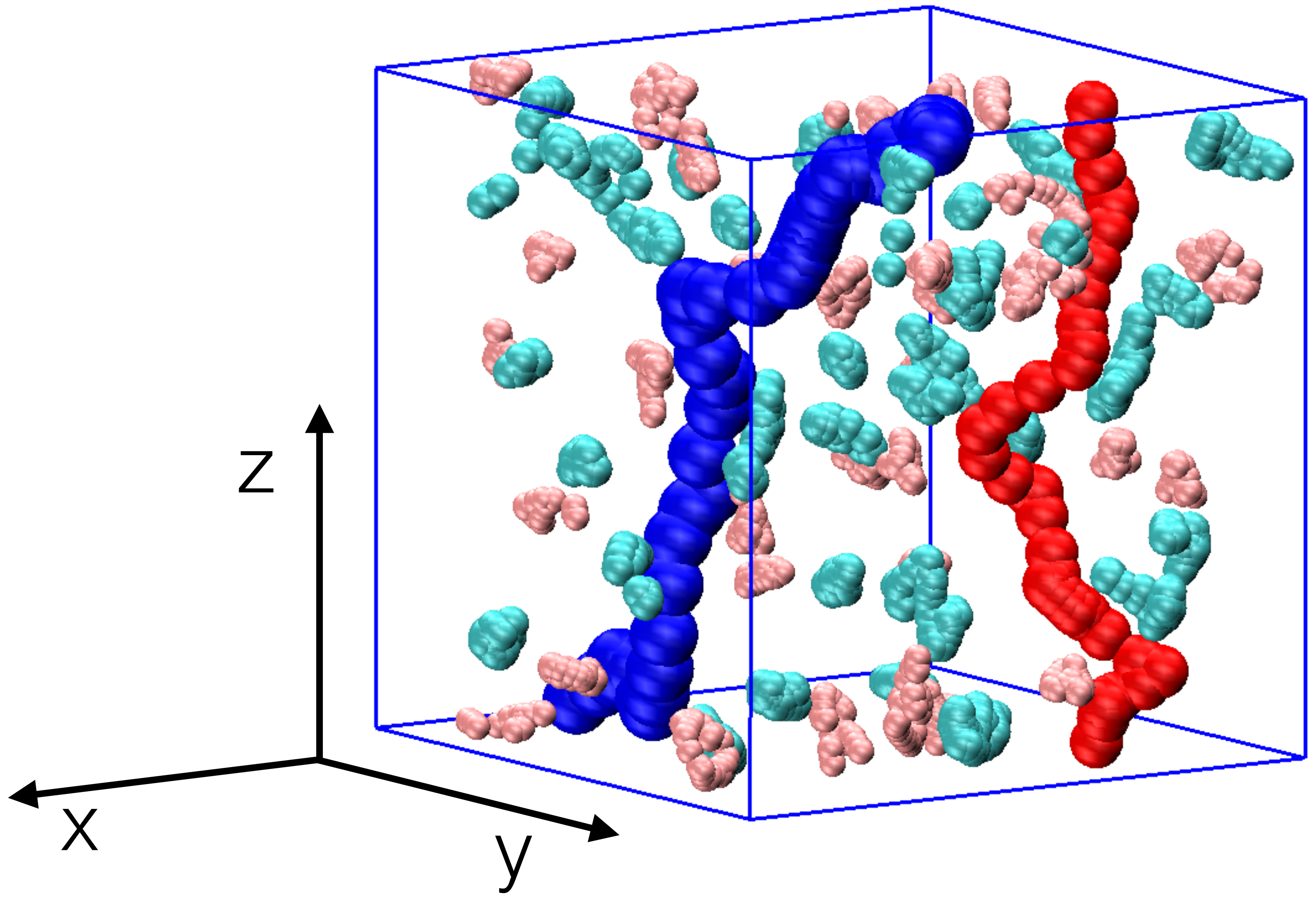
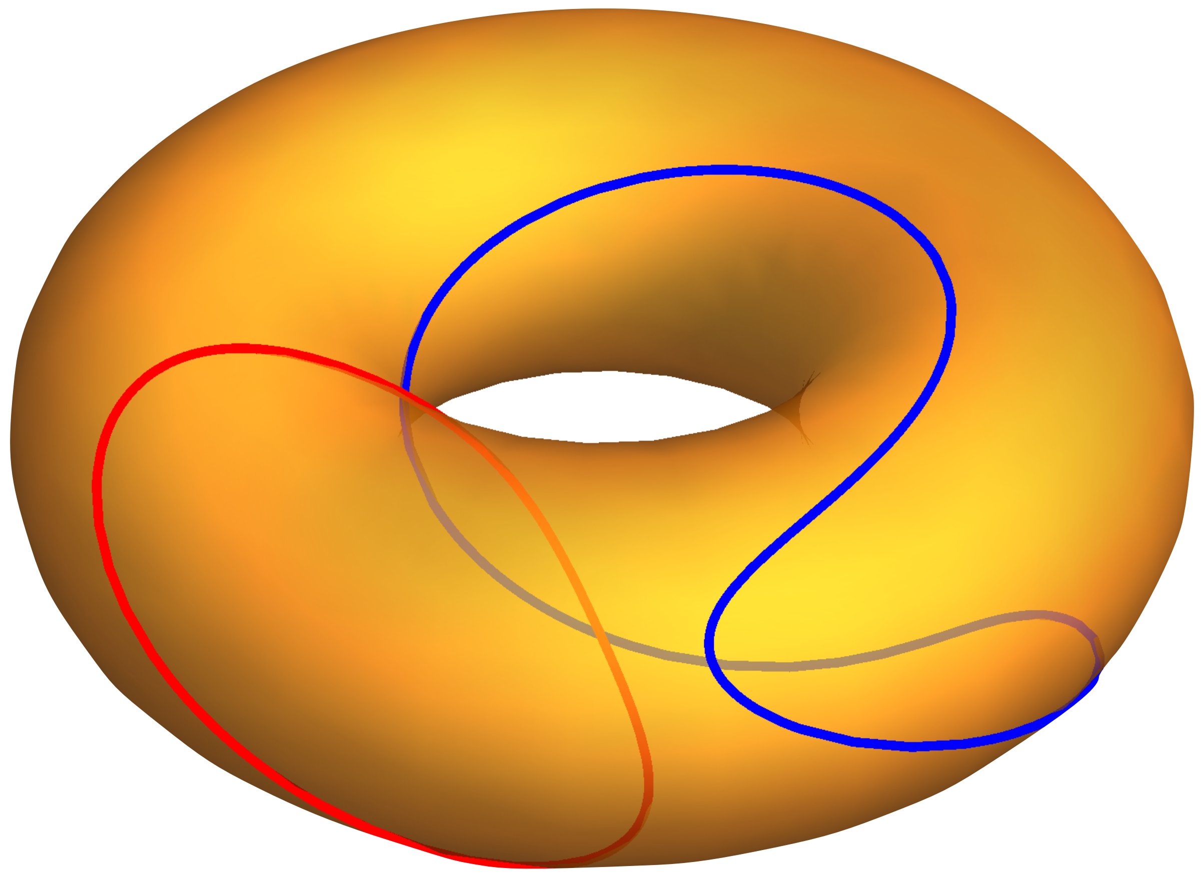
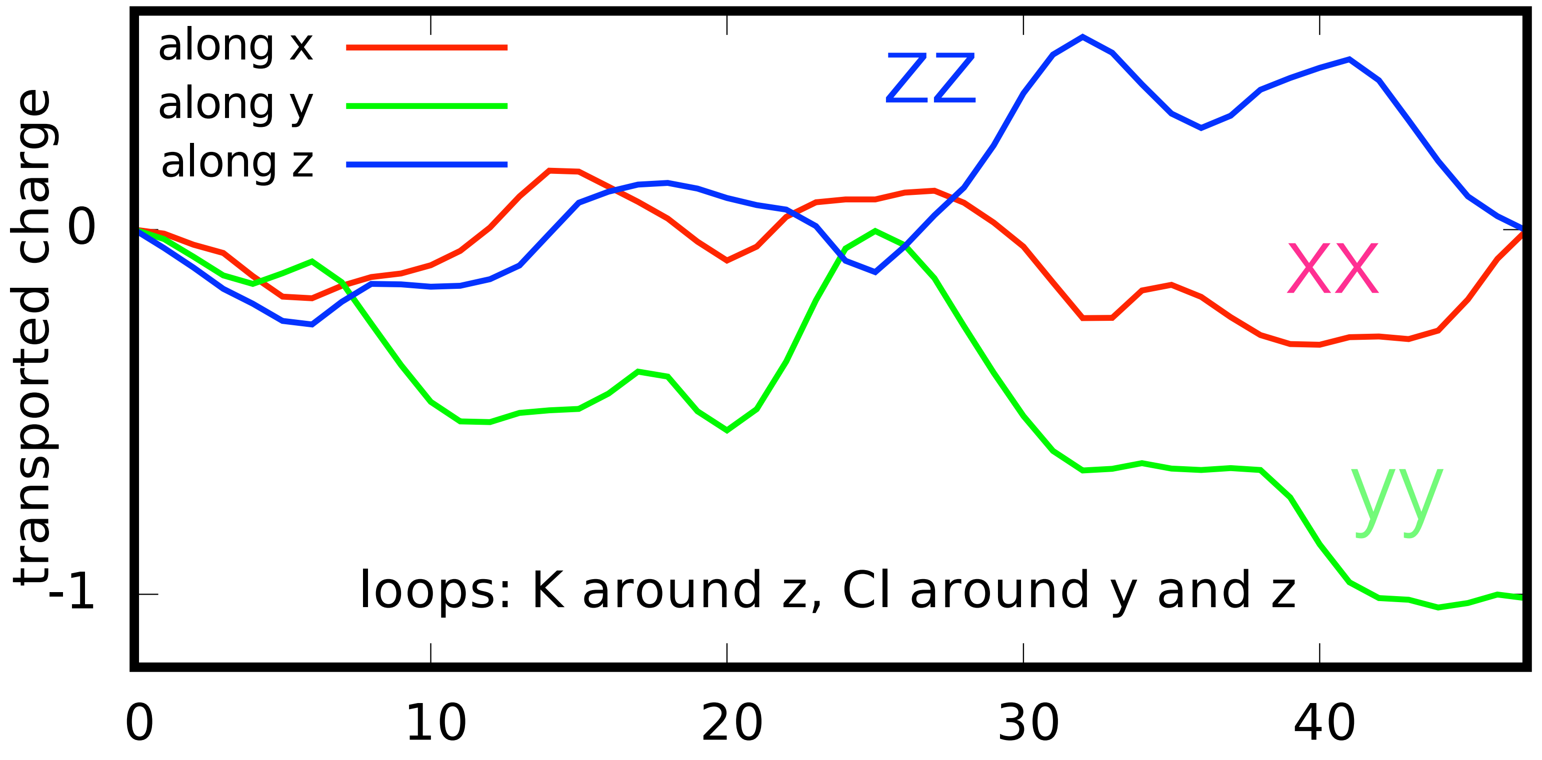




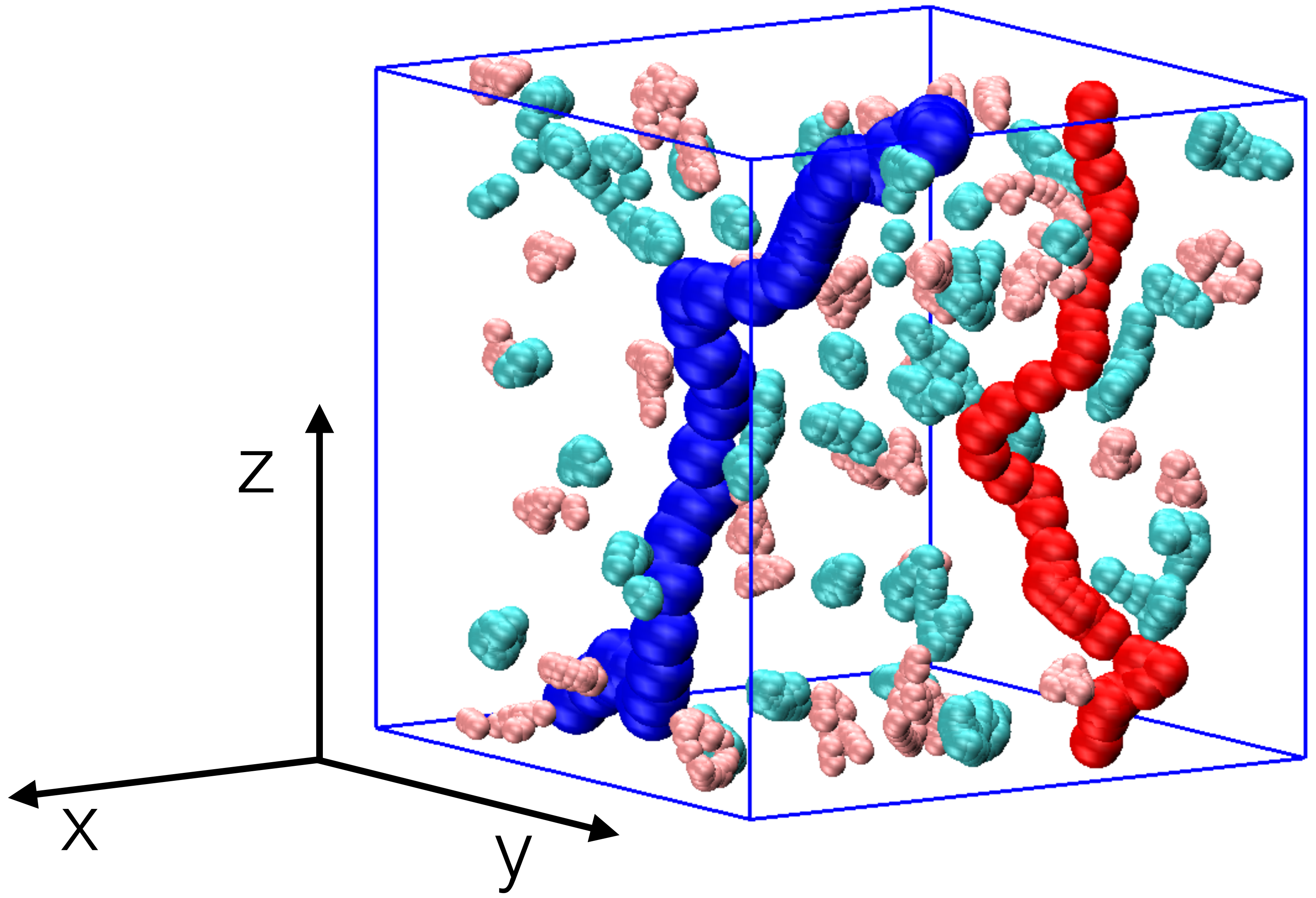
$Q_z[Cl]=-1$ $Q_y[Cl]=-1$

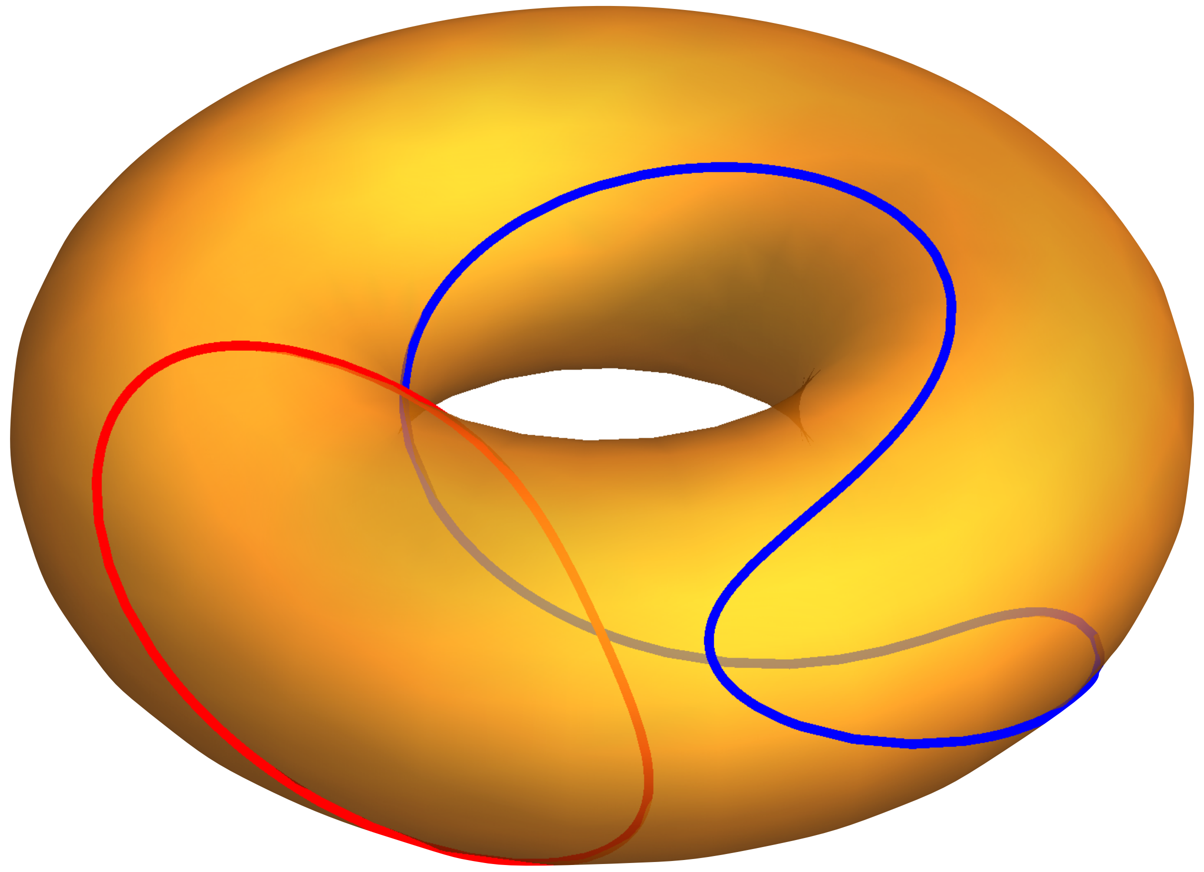
$Q_z[K] = 1$ $Q_z[K] = 0$



the charges transported by K and Cl
around z cancel exactly

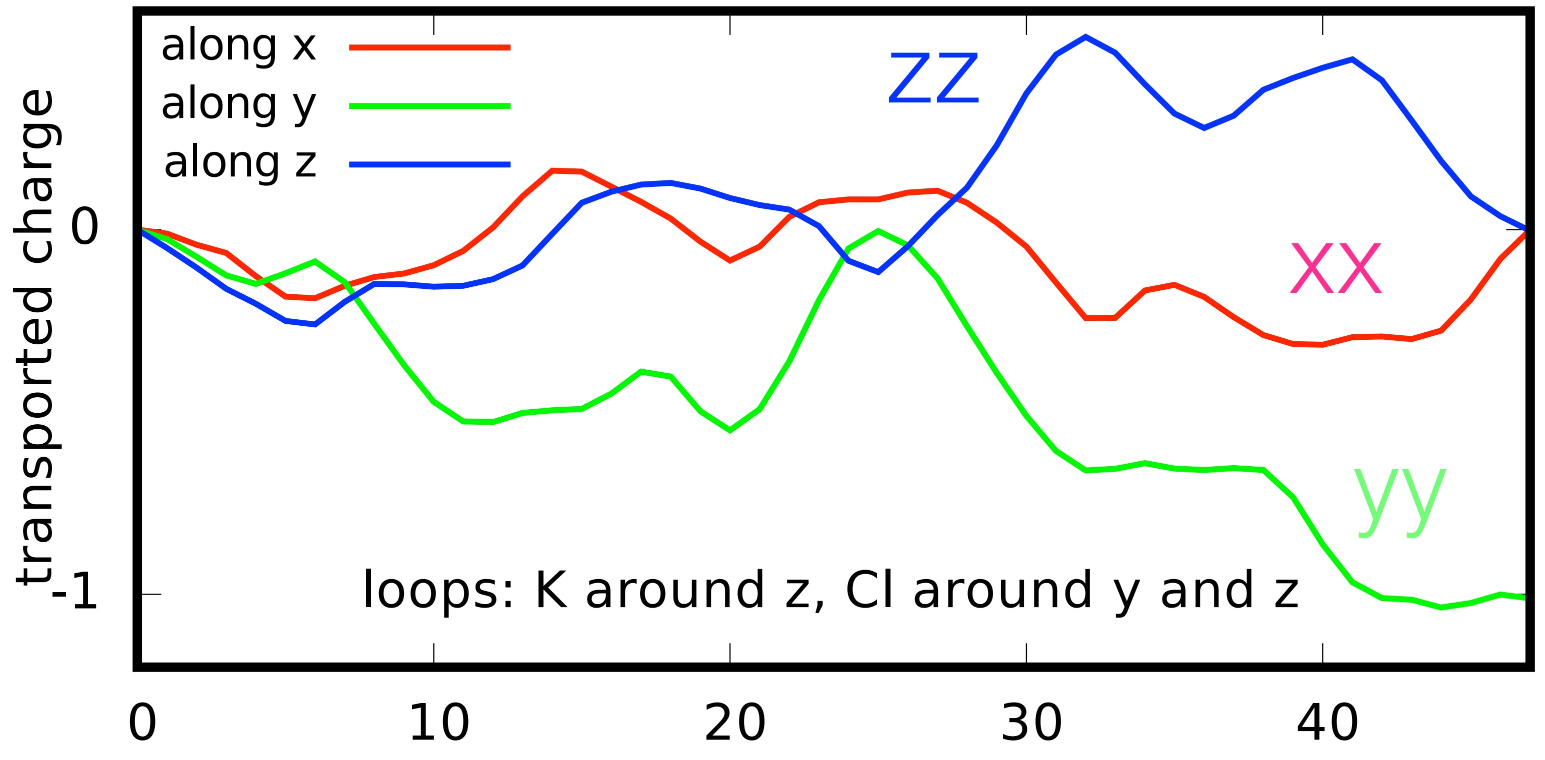
a numerical experiment on molten KCl





$Q_z[\mathrm{Cl}]=-1 \quad Q_y[\mathrm{Cl}]=-1$

$Q_z[\mathrm{K}] = 1 \quad Q_z[\mathrm{K}] = 0$



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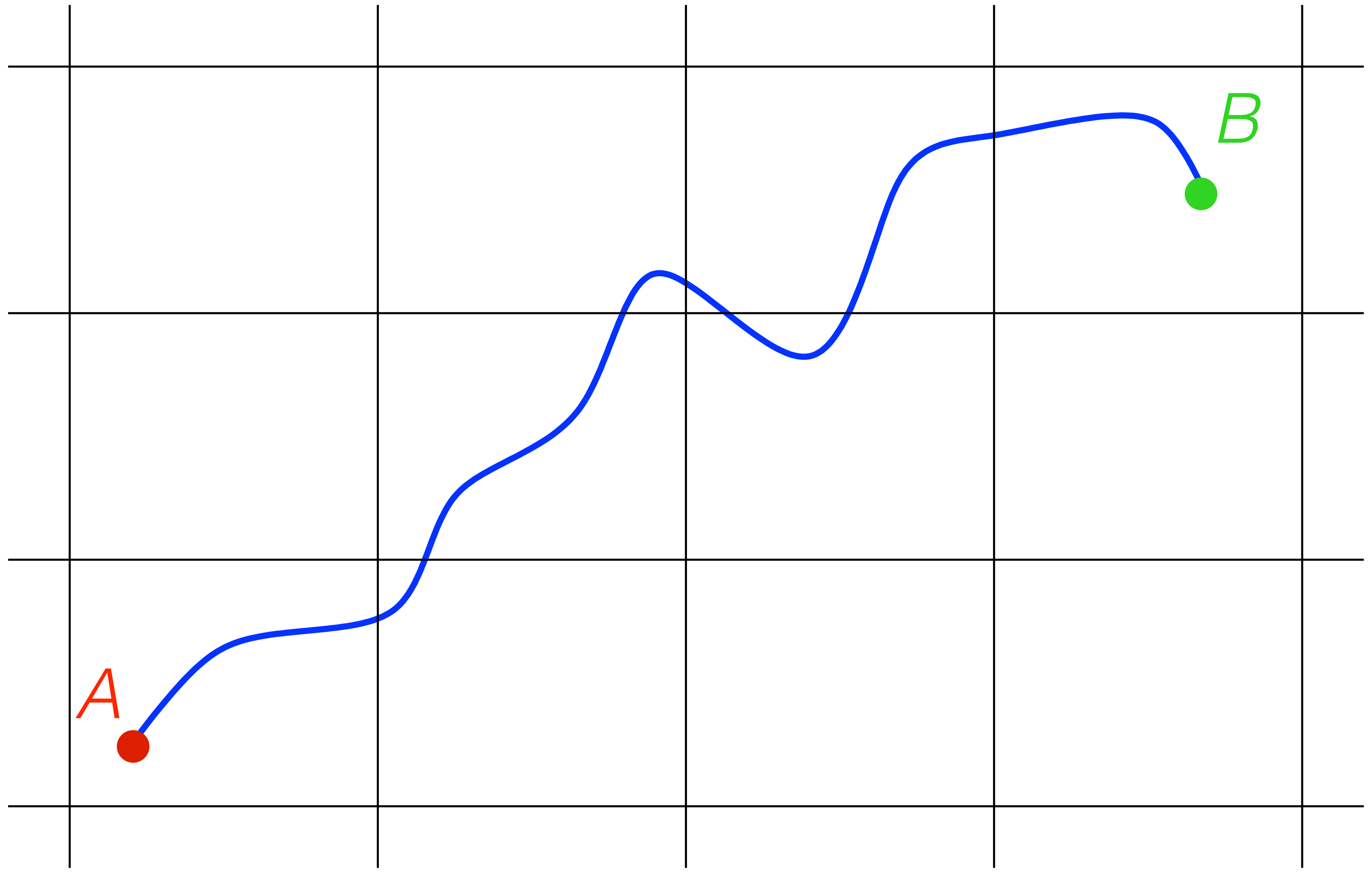
gauge invariance of charge transport

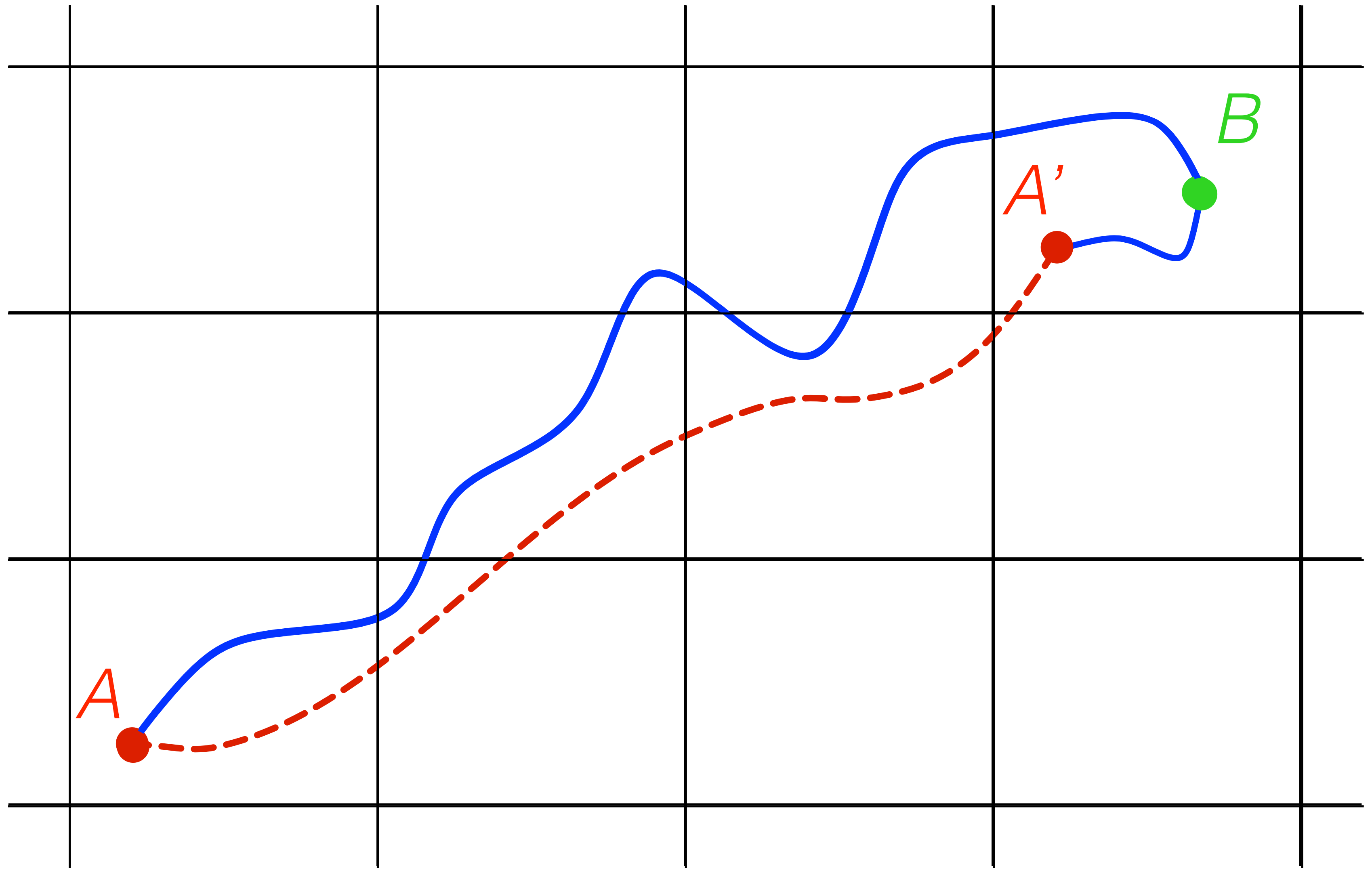


$$\sigma \propto \lim_{t\to\infty} \frac{1}{2t} \mathrm{var}\left[\mu_{AB}(t)\right]$$

$$\mu_{AB}(t) = \int_0^t J(t')dt'$$

gauge invariance of charge transport

$$\hat{H}(B) \neq \hat{H}(A)$$
$$\hat{H}(A') = \hat{H}(A)$$



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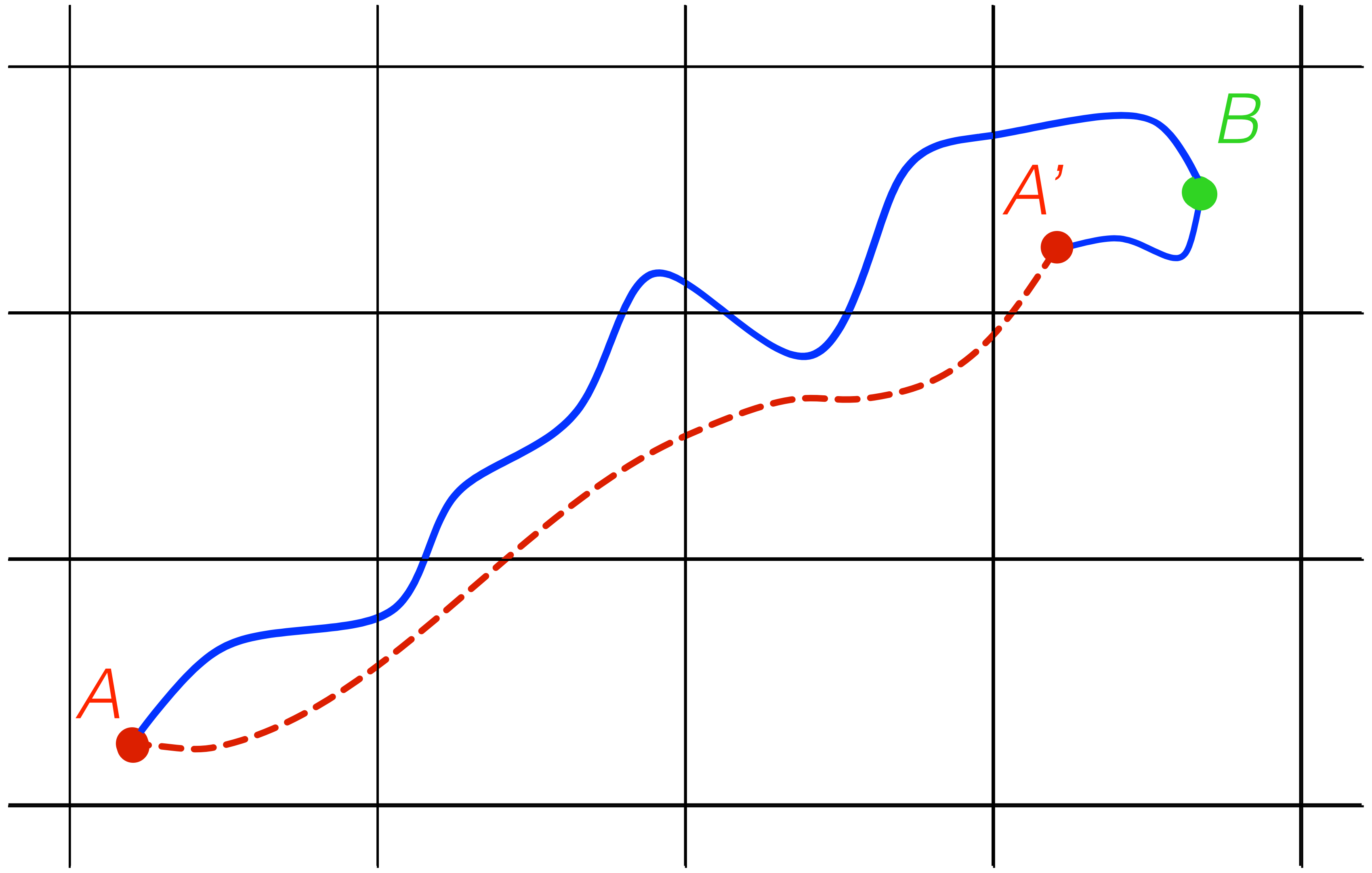

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$$= \mu_{AA'} + \mu_{A'B}$$

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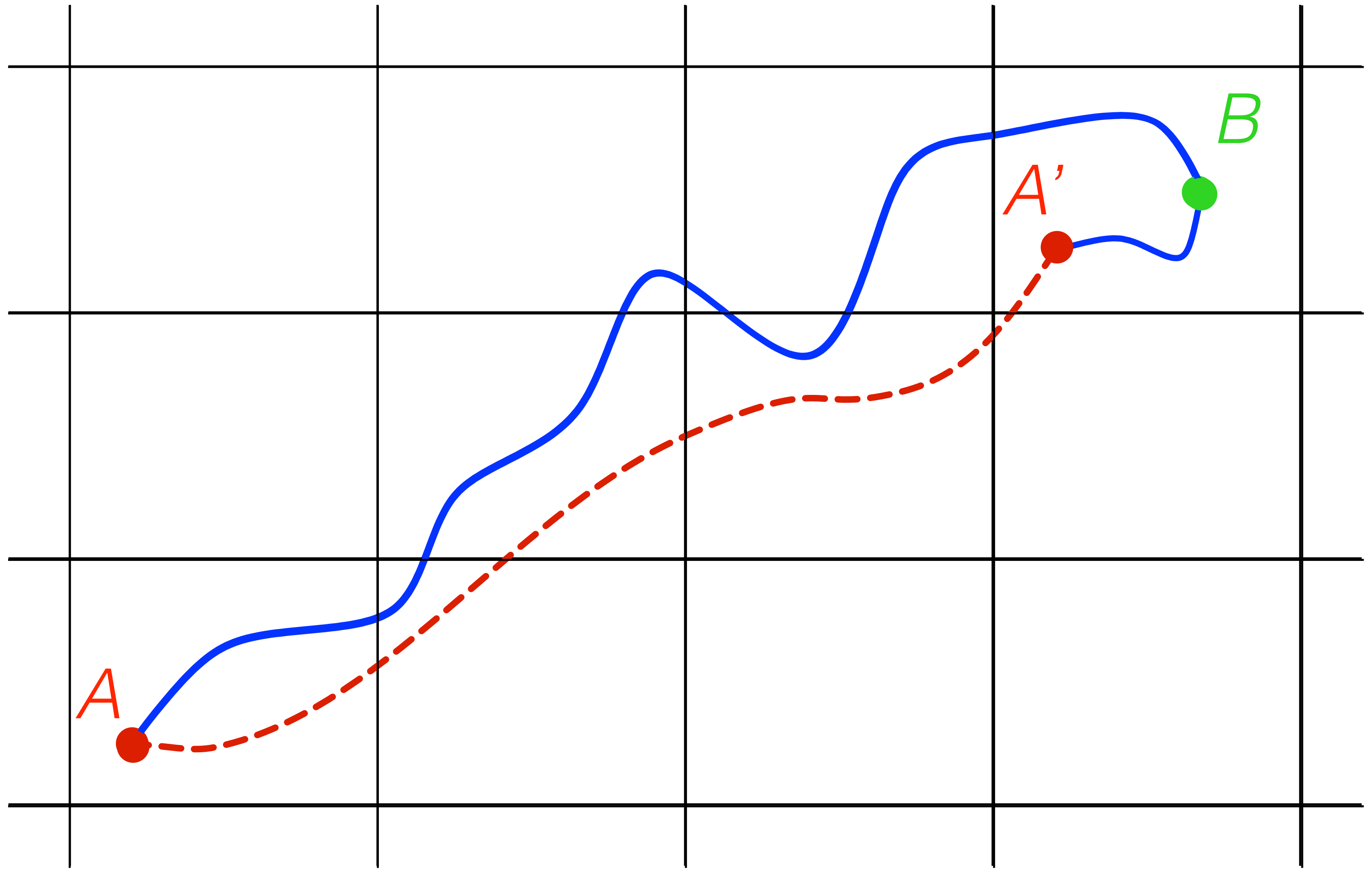

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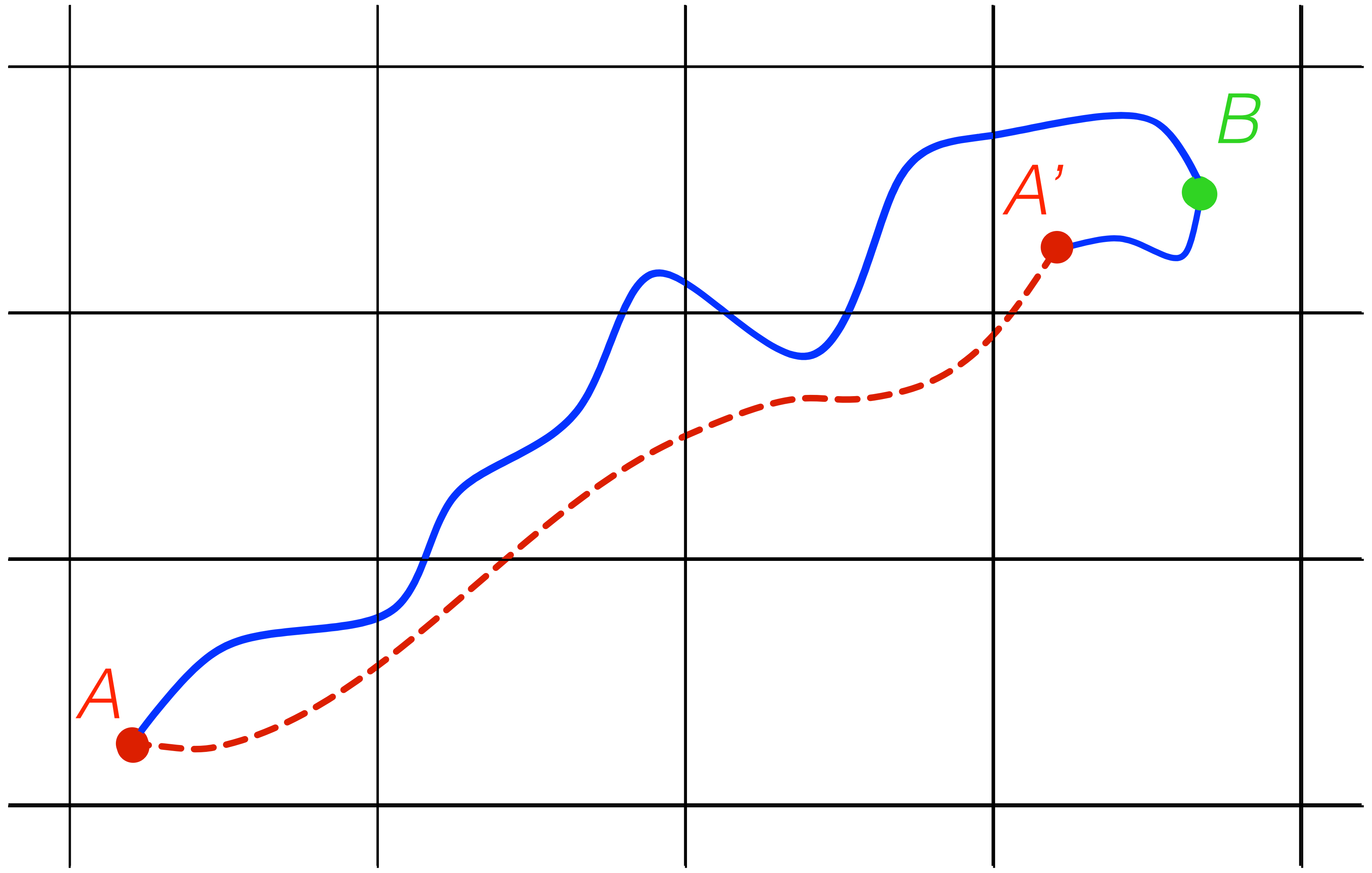

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$$J_\alpha = \sum_{i\beta} Z^*_{i\alpha\beta} v_{i\beta}$$

$$J'_\alpha = \sum_i q_{S(i)} v_{i\alpha}$$

$$\mu_{AB}(t) = \mu_{AA'} + \mathcal{O}(1)$$
$$= \mu'_{AA'} + \mathcal{O}(1) \quad \text{(Thouless)}$$

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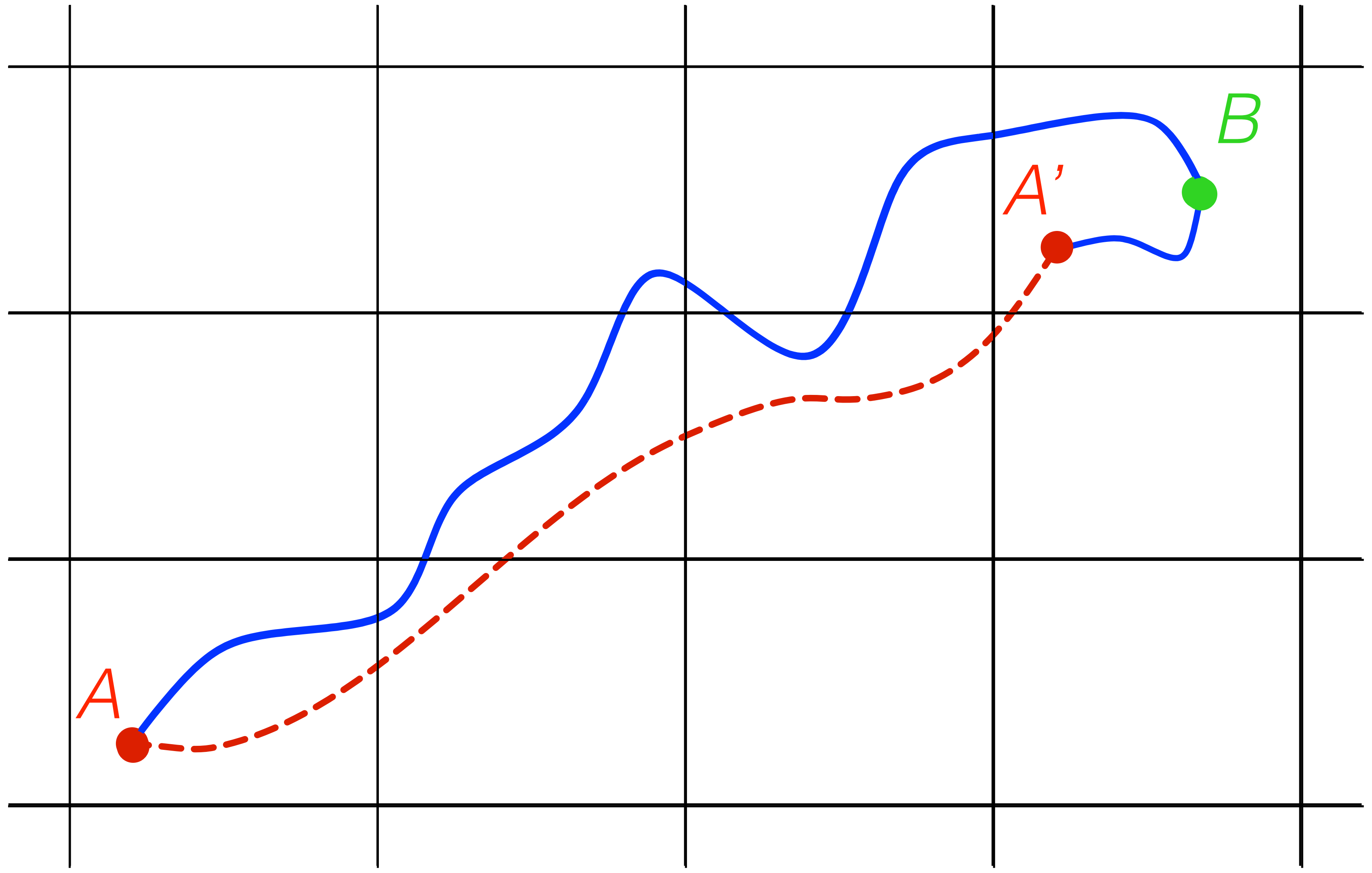

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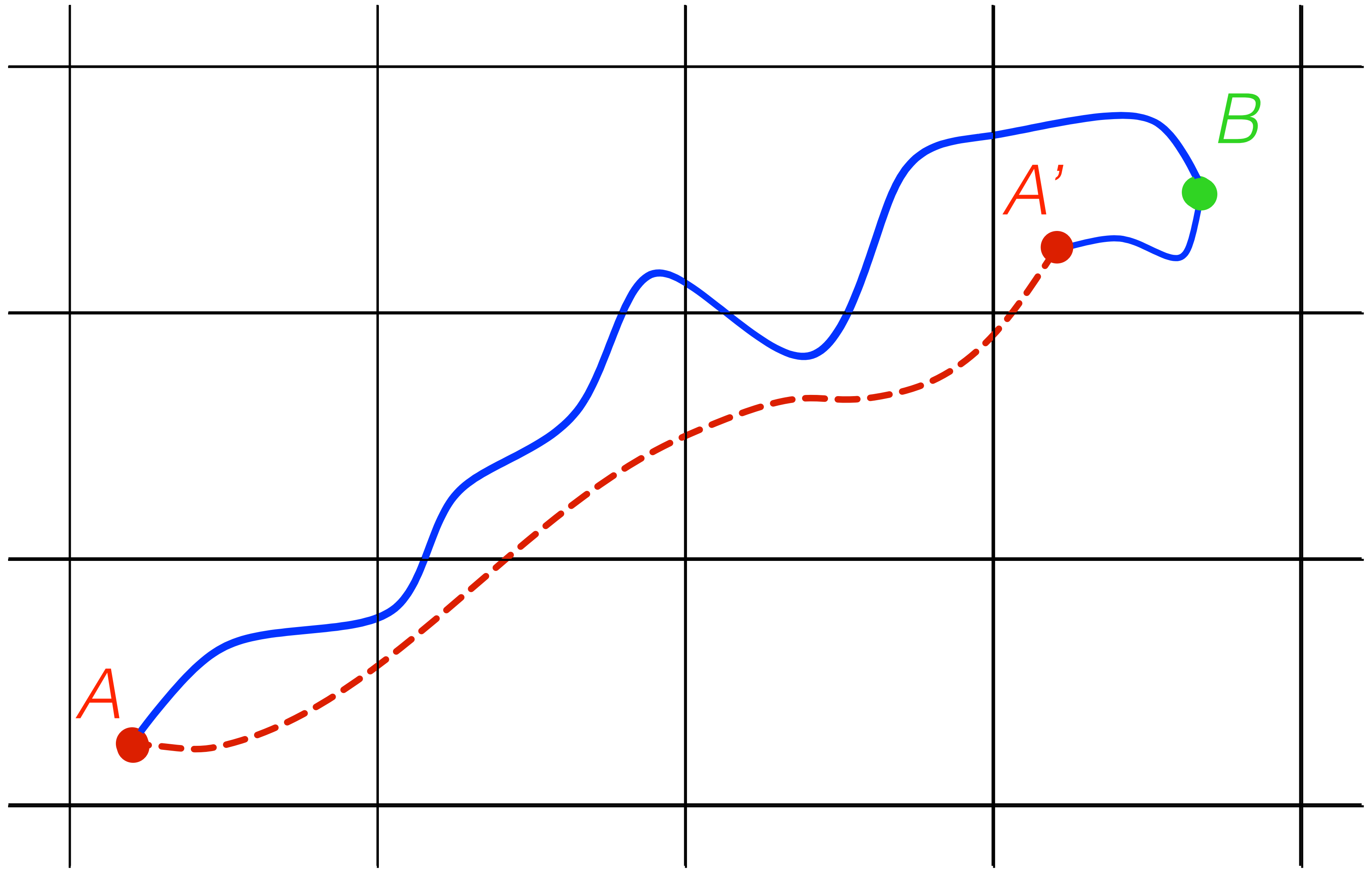

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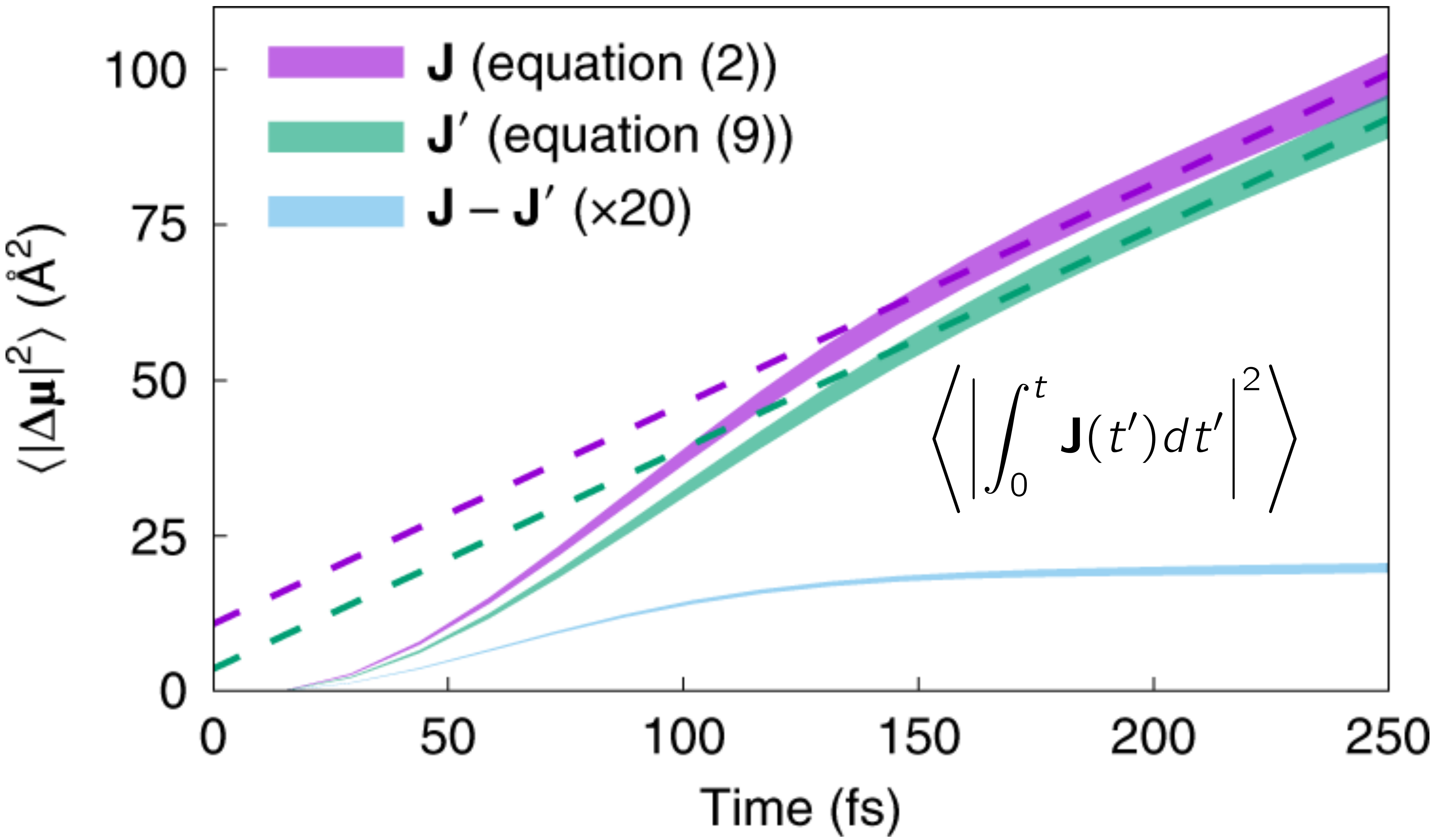
$$\sigma = \sigma'$$

currents from atomic oxidation numbers

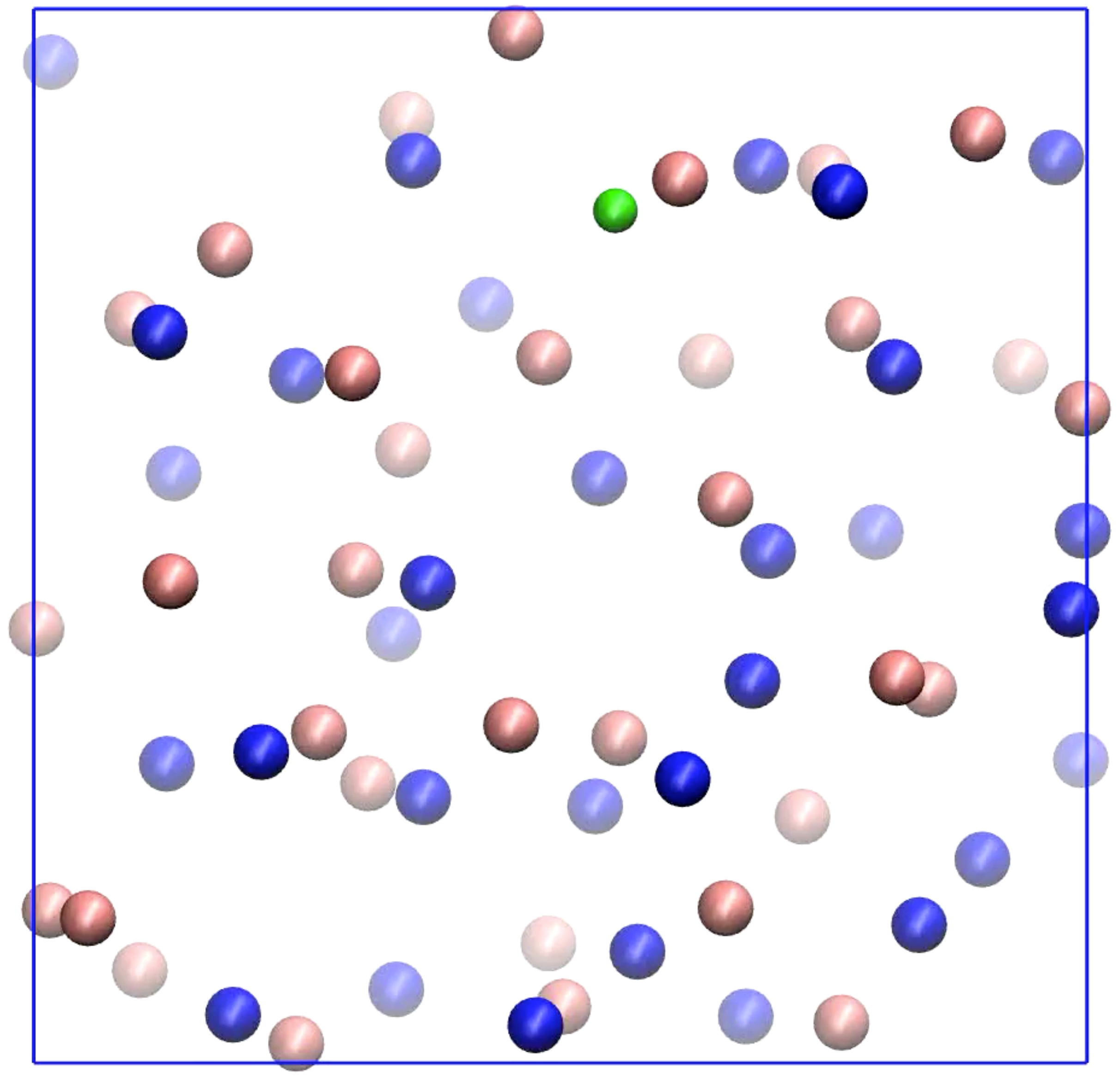
$$(2) \qquad J_\alpha = \sum_{i\beta} Z^*_{i\alpha\beta} v_{i\beta}$$

$$(9) \qquad J'_\alpha = \sum_{i} q_{S(i)} v_{i\alpha}$$



non-stoichiometric melts

$K_x(KCl)_{1-x}$



$K_{33}Cl_{31}$

$x \approx 0.06$

non-stoichiometric melts

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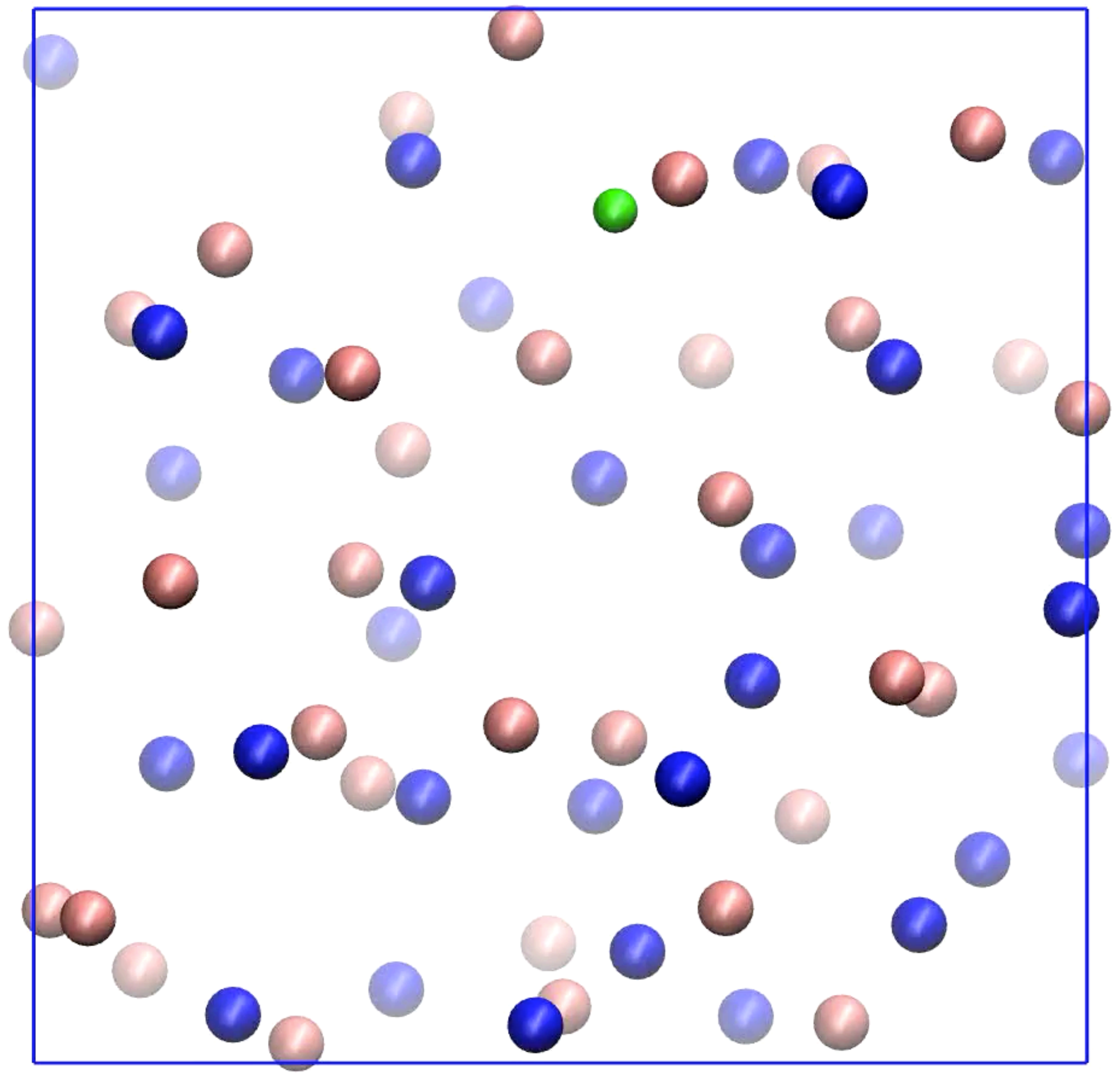

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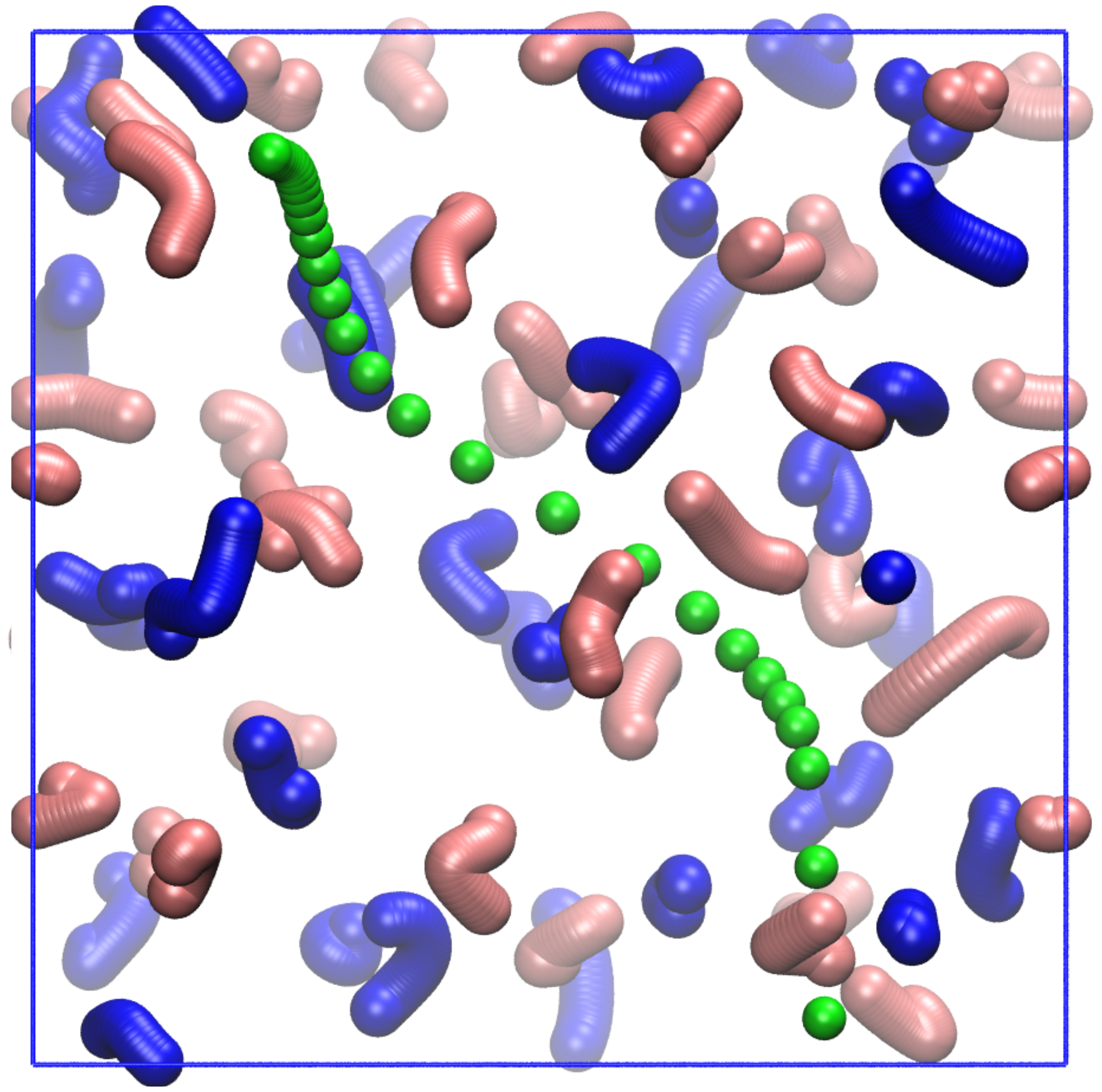

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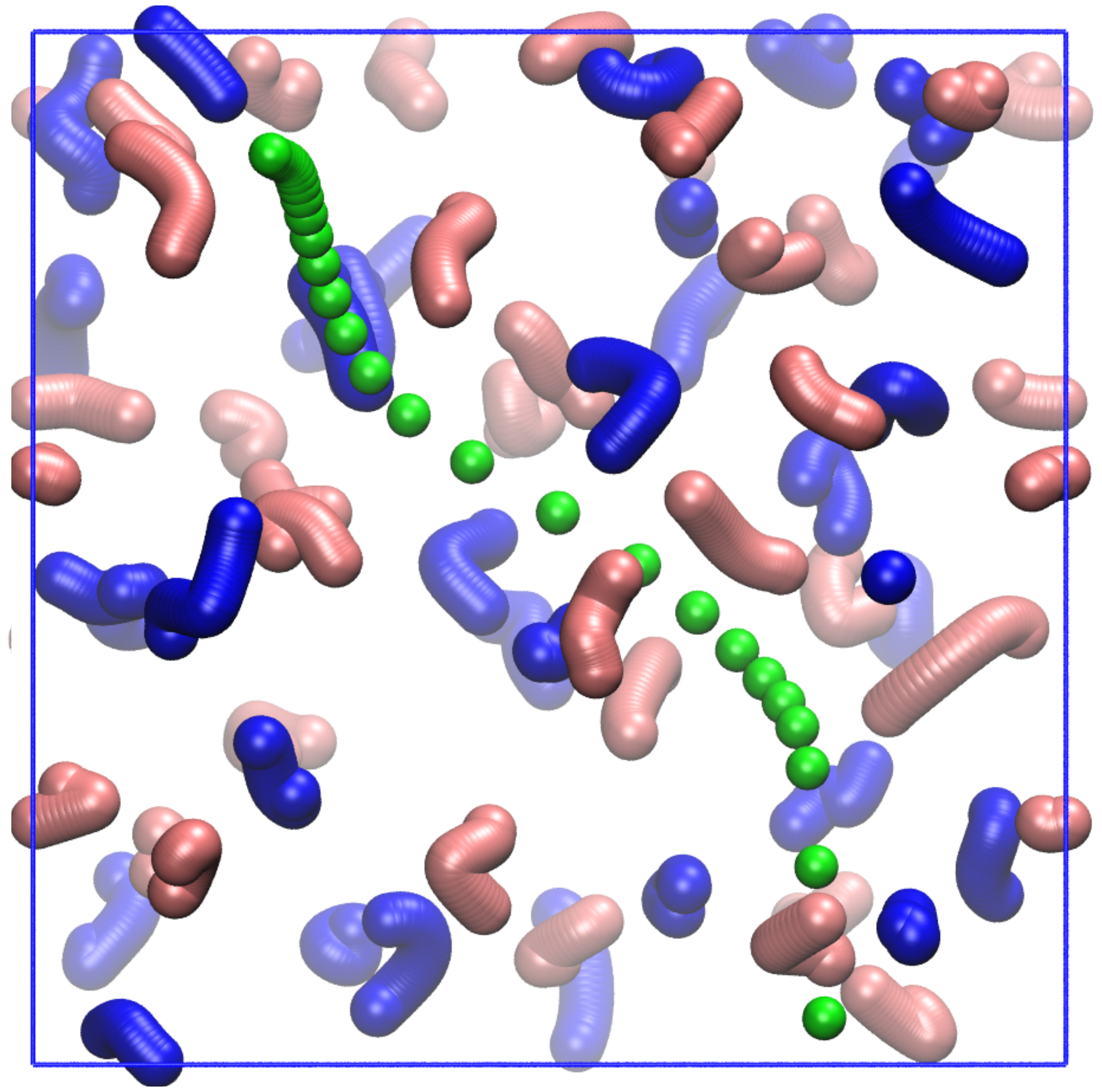

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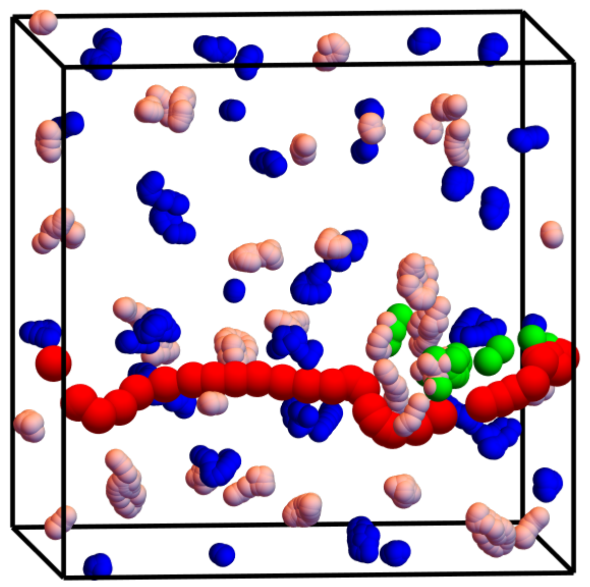

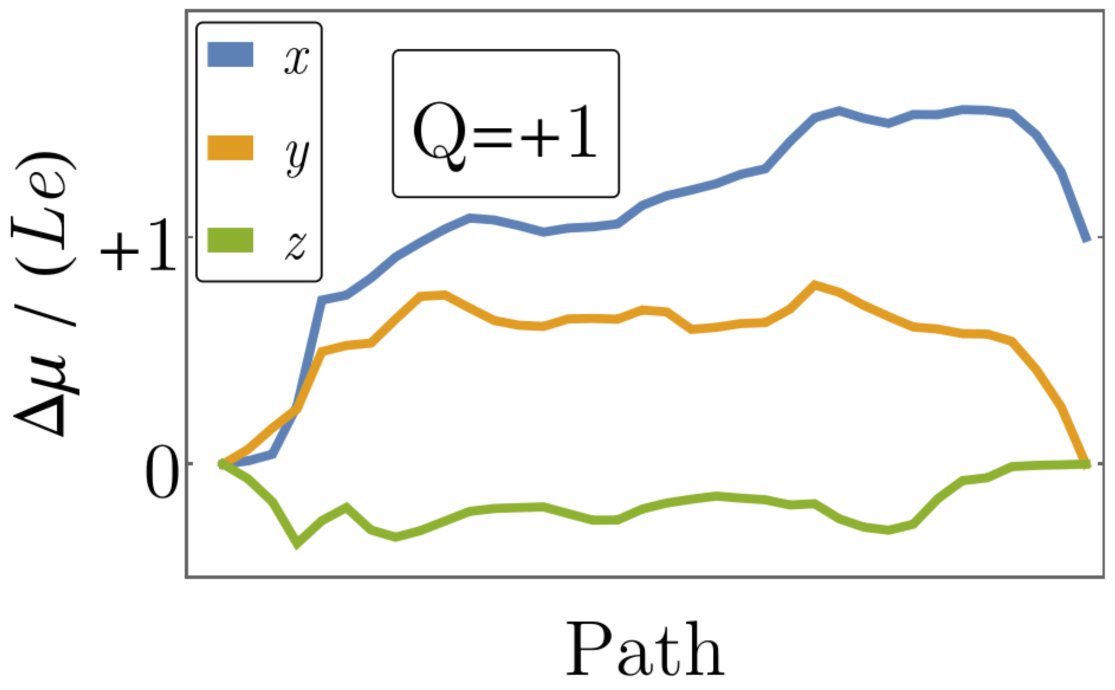

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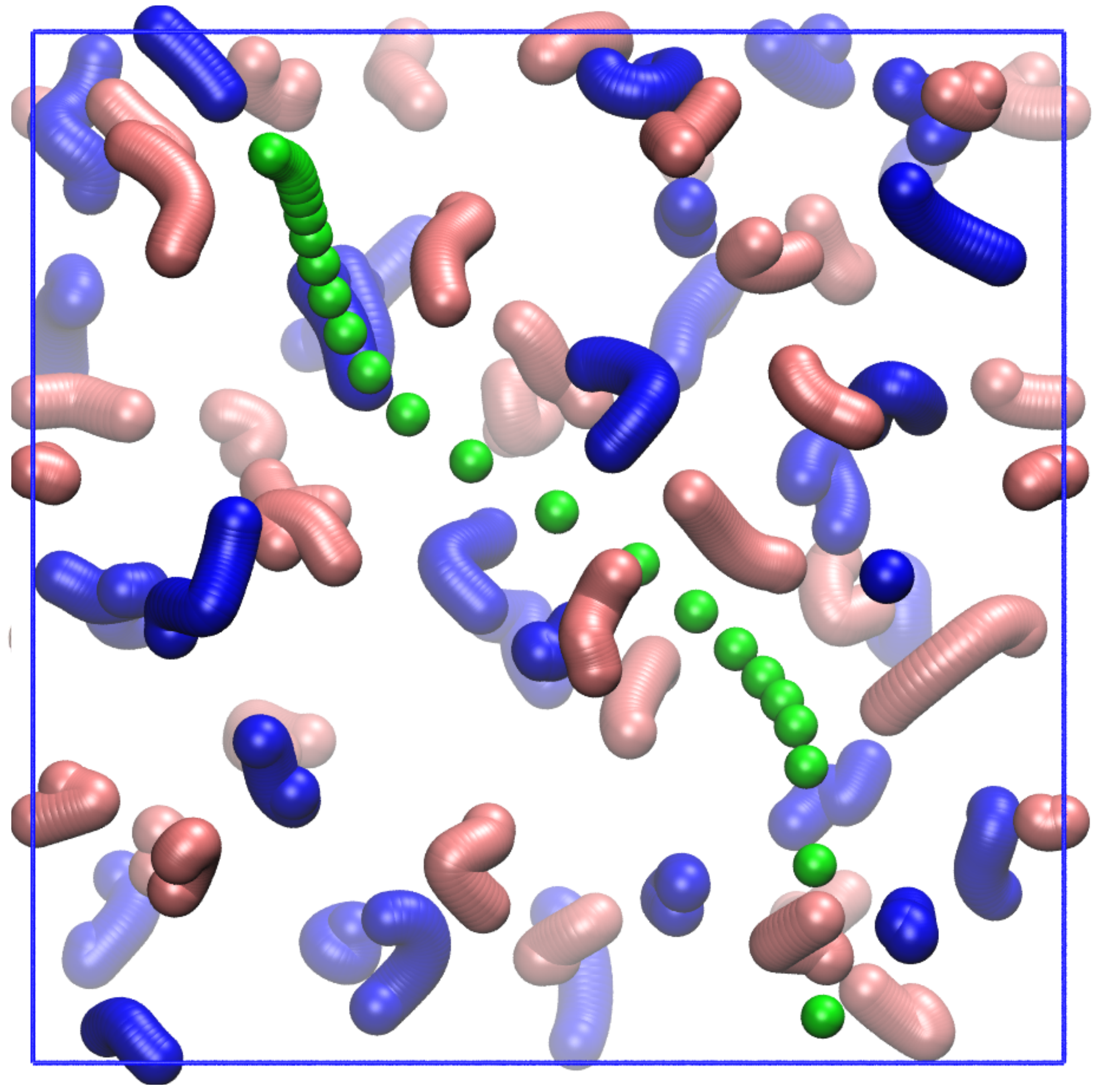

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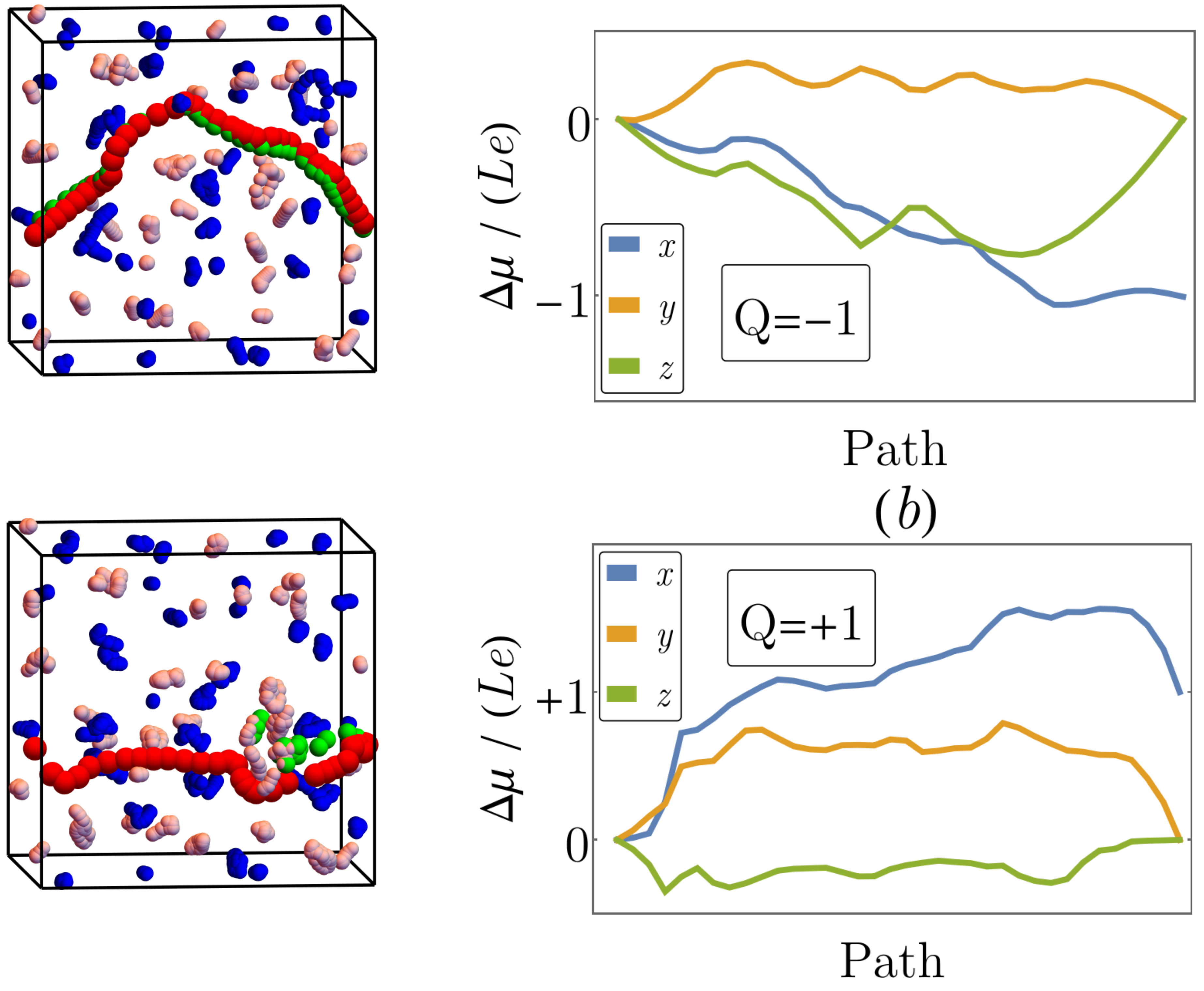
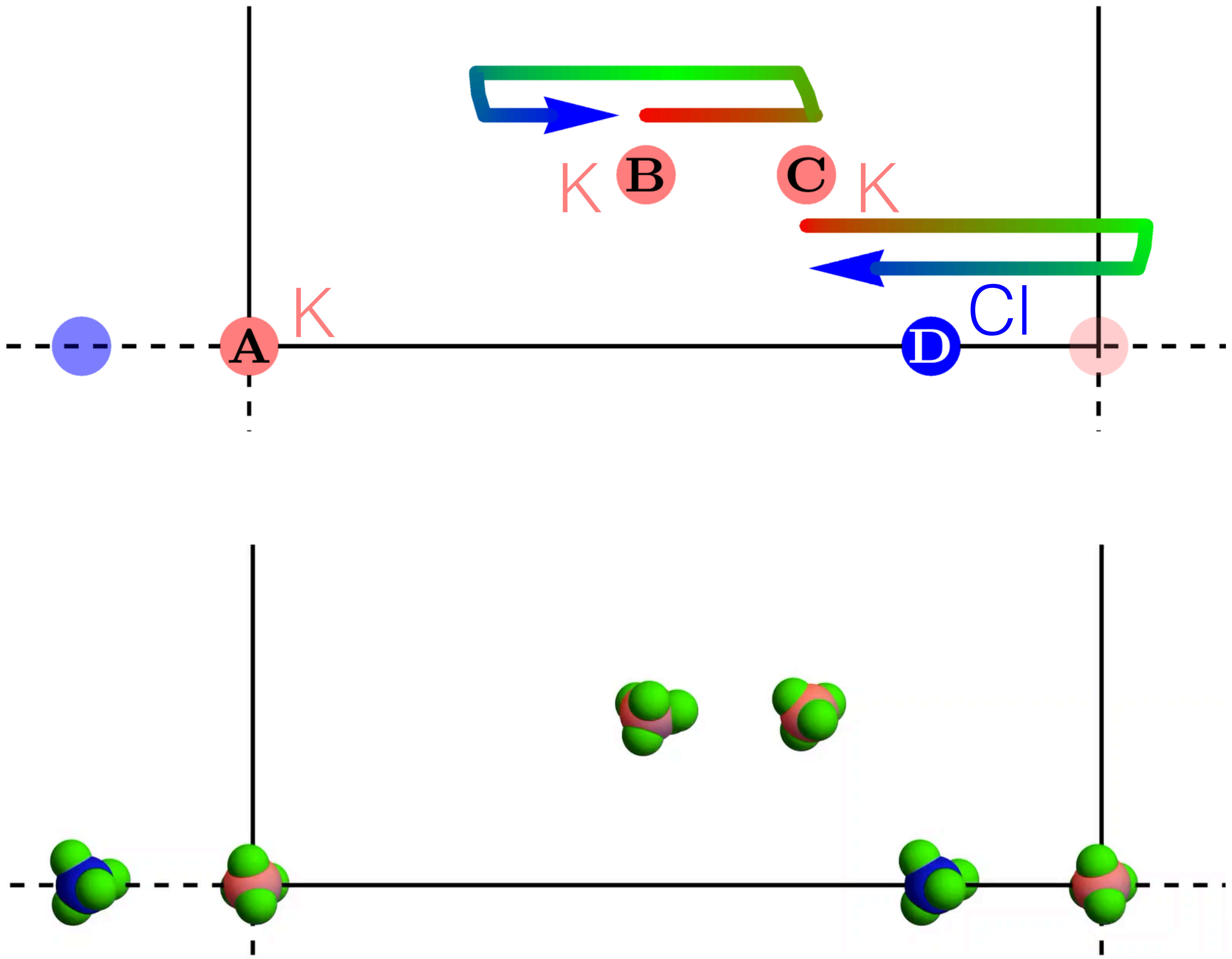
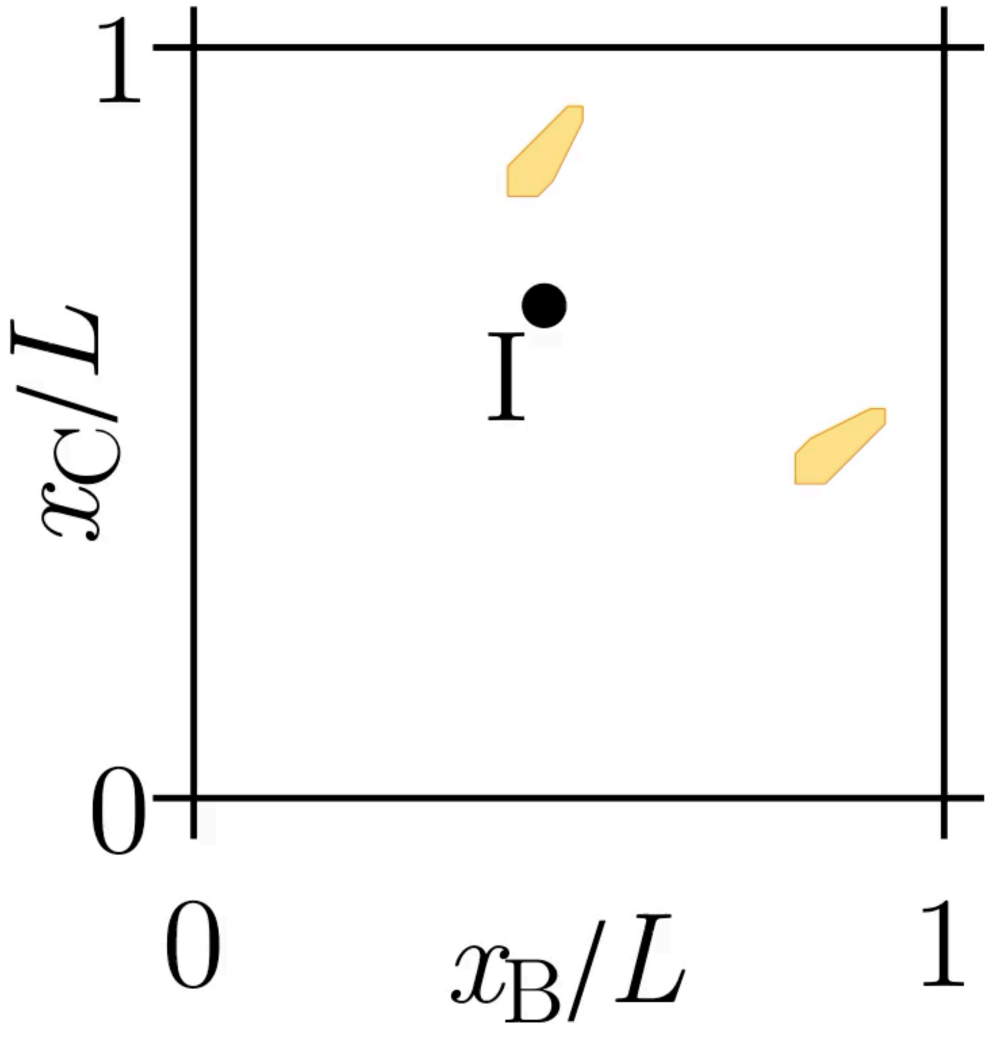


non-trivial particle transport





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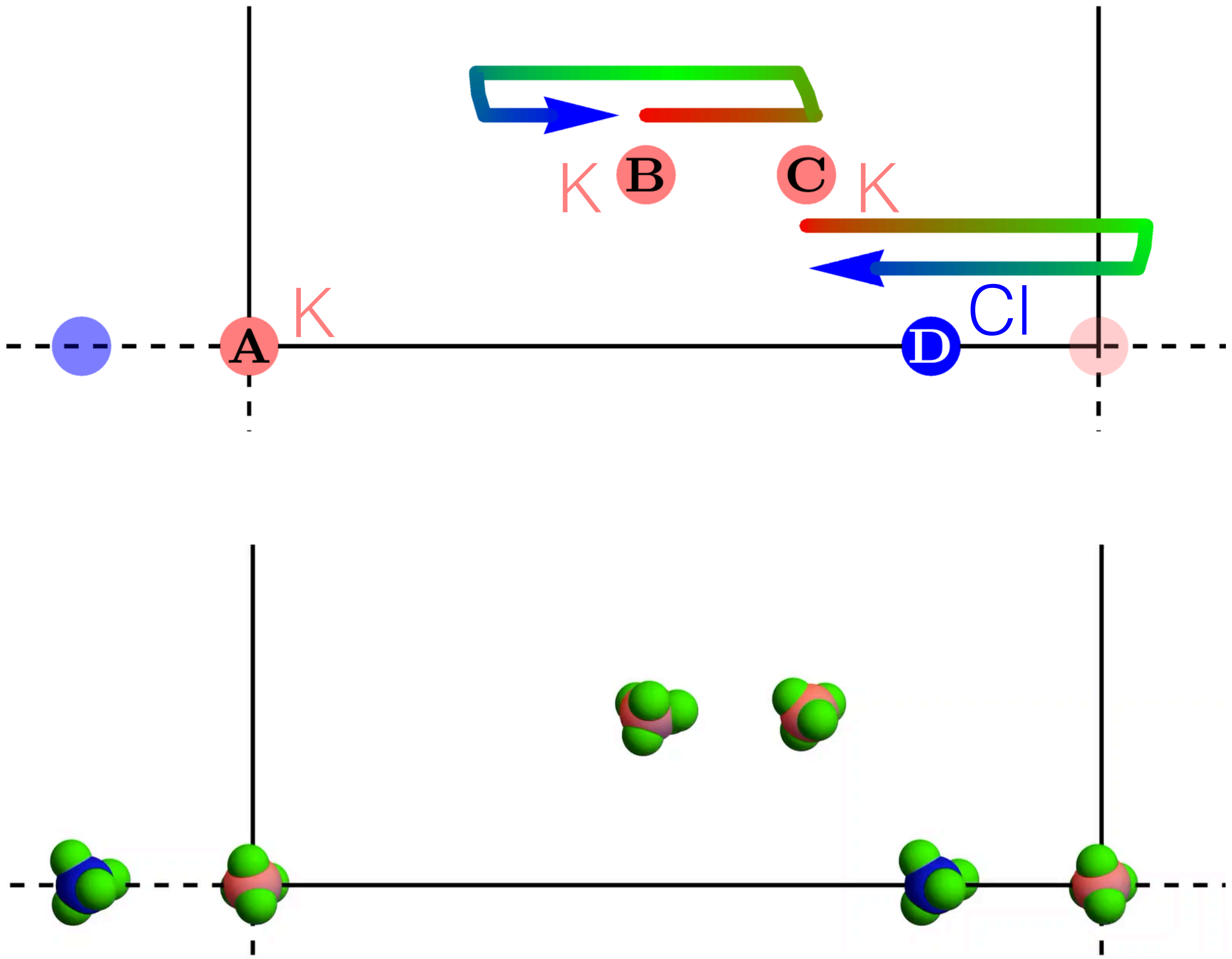

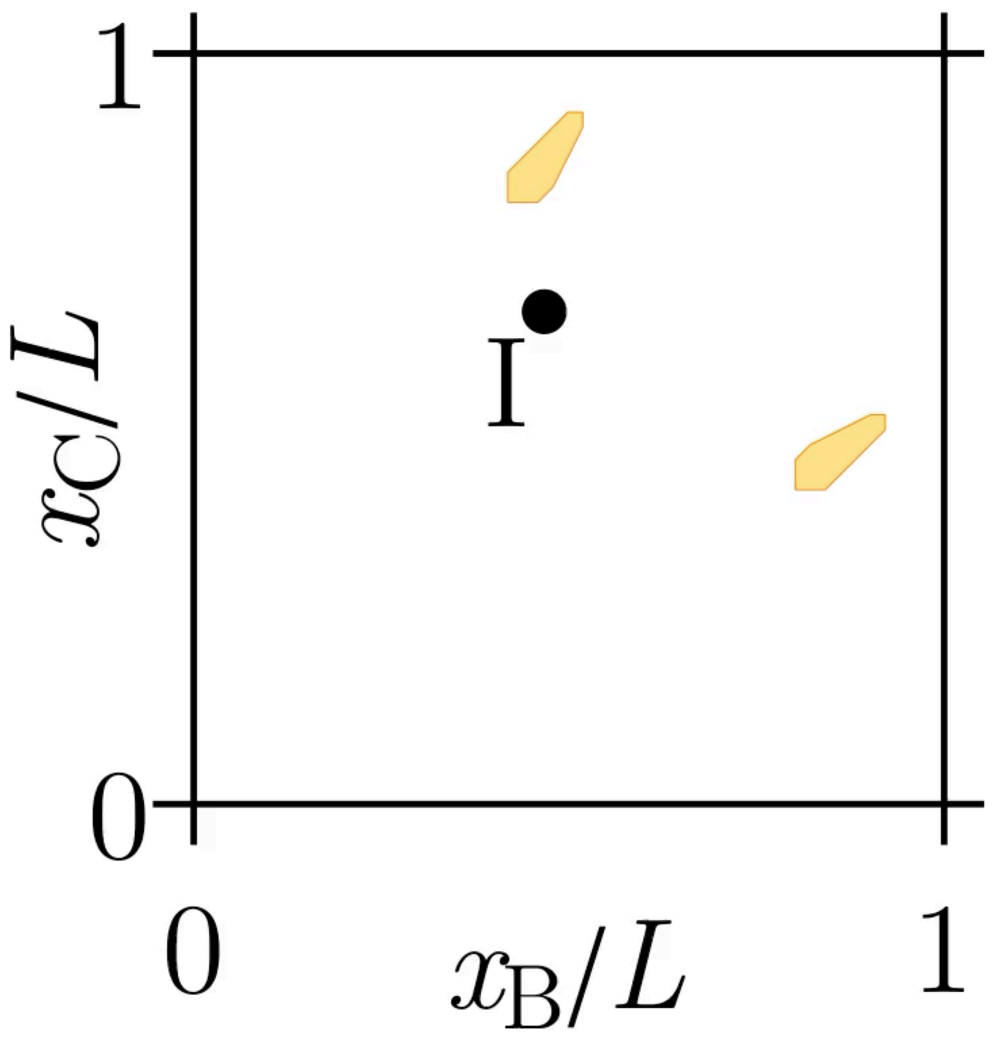

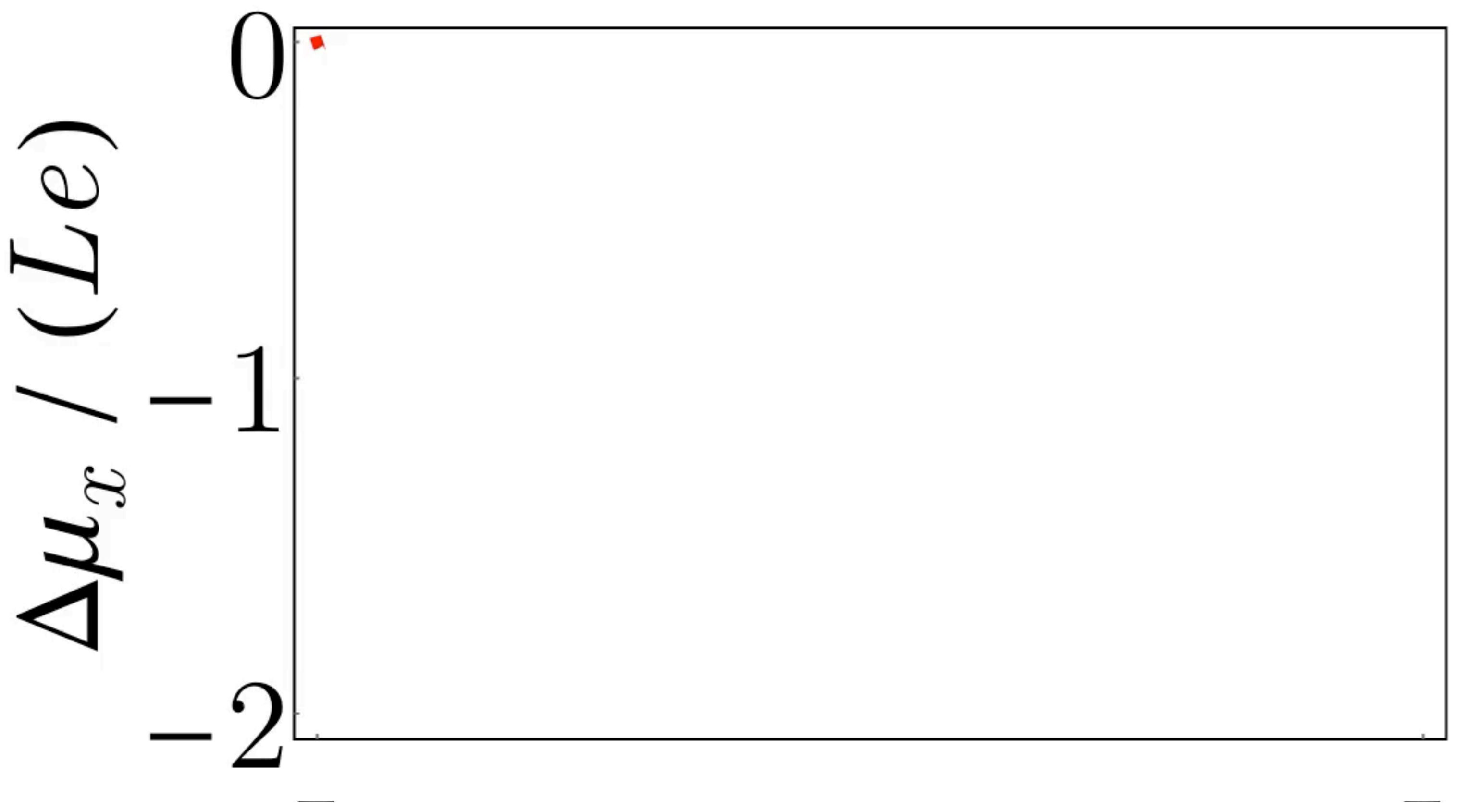

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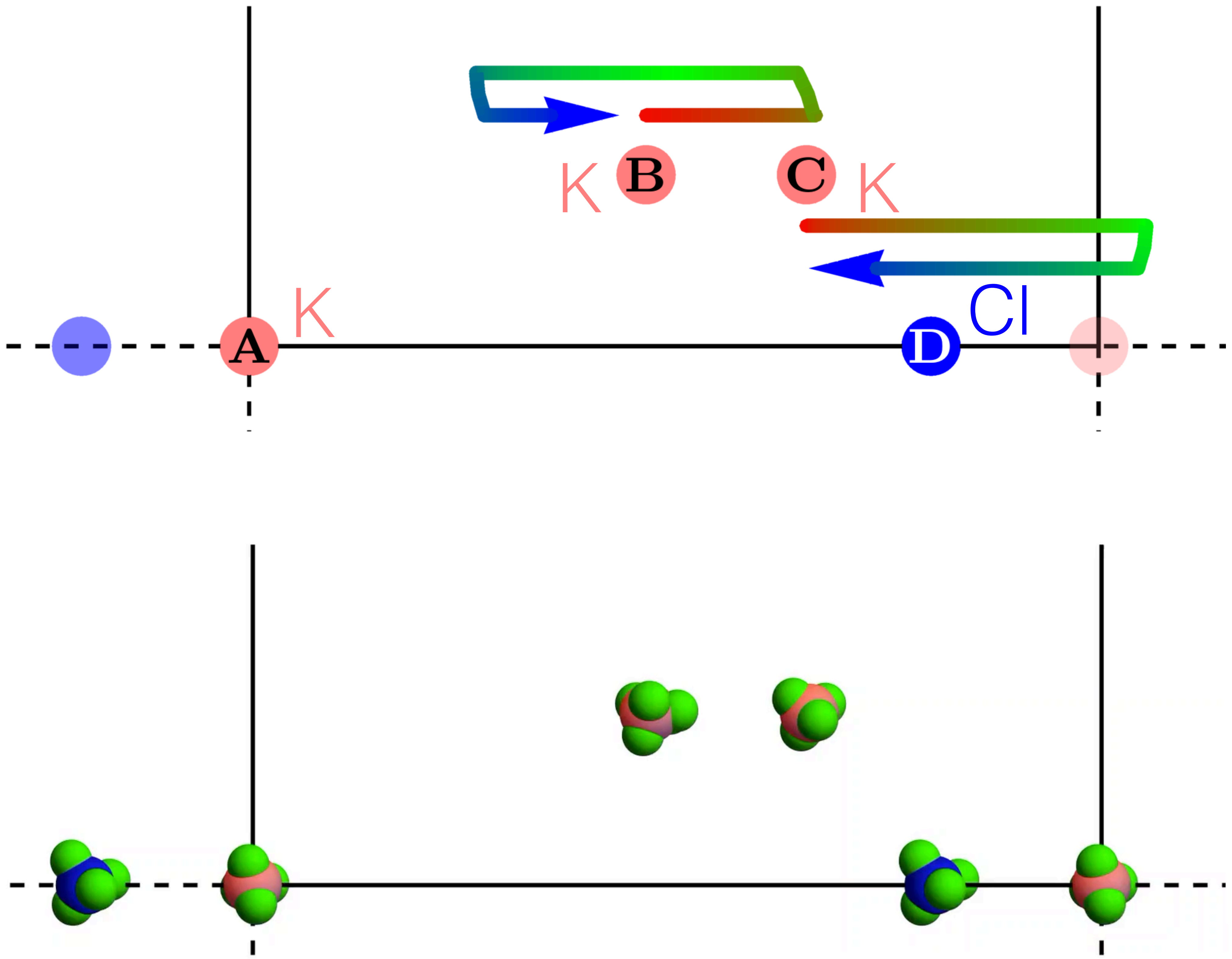
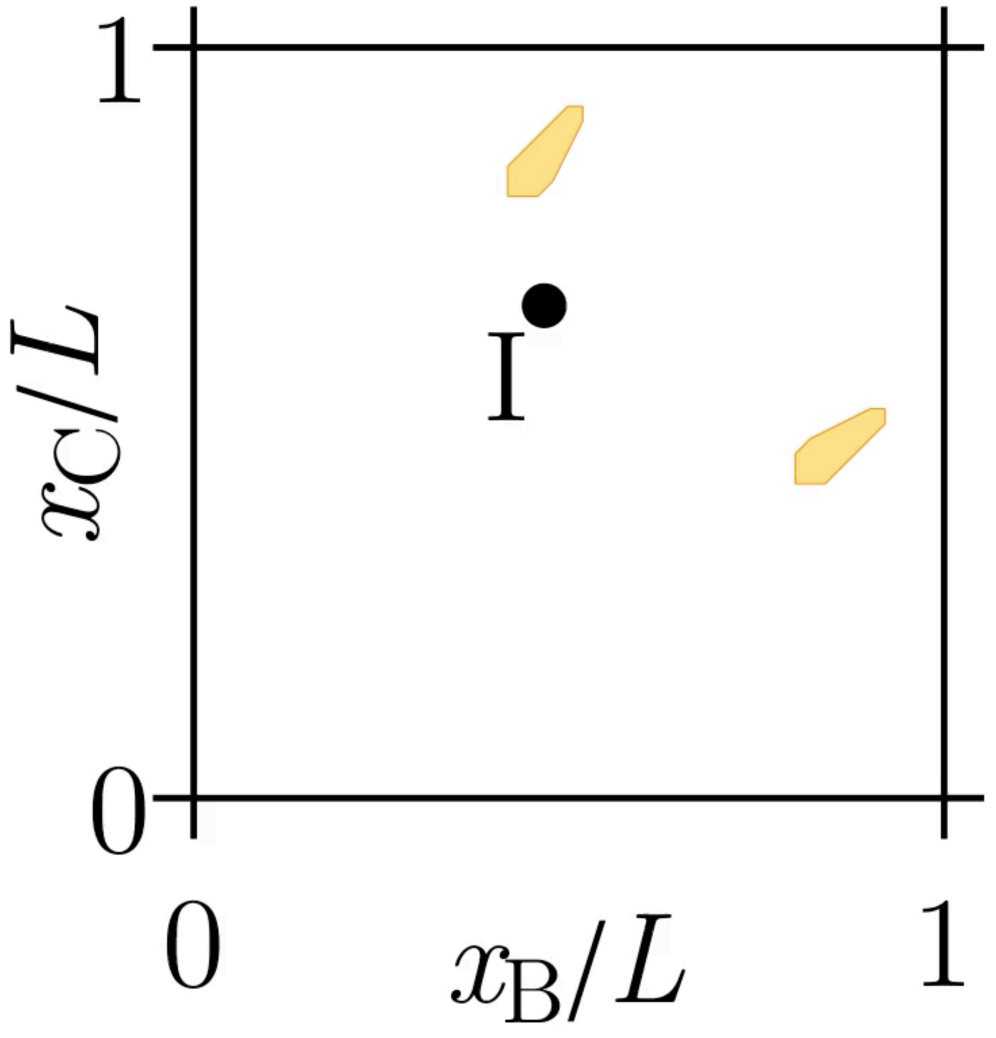
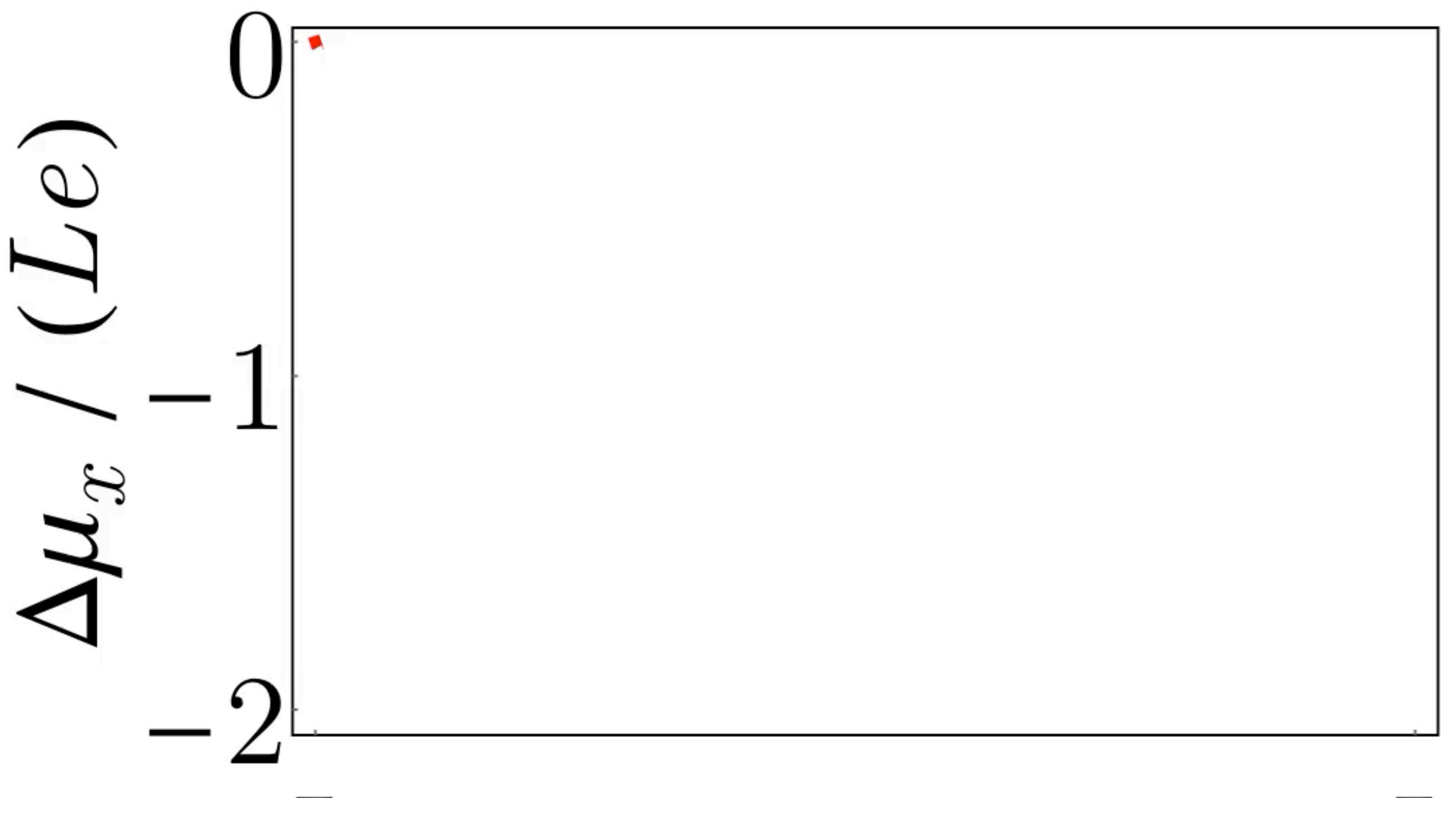
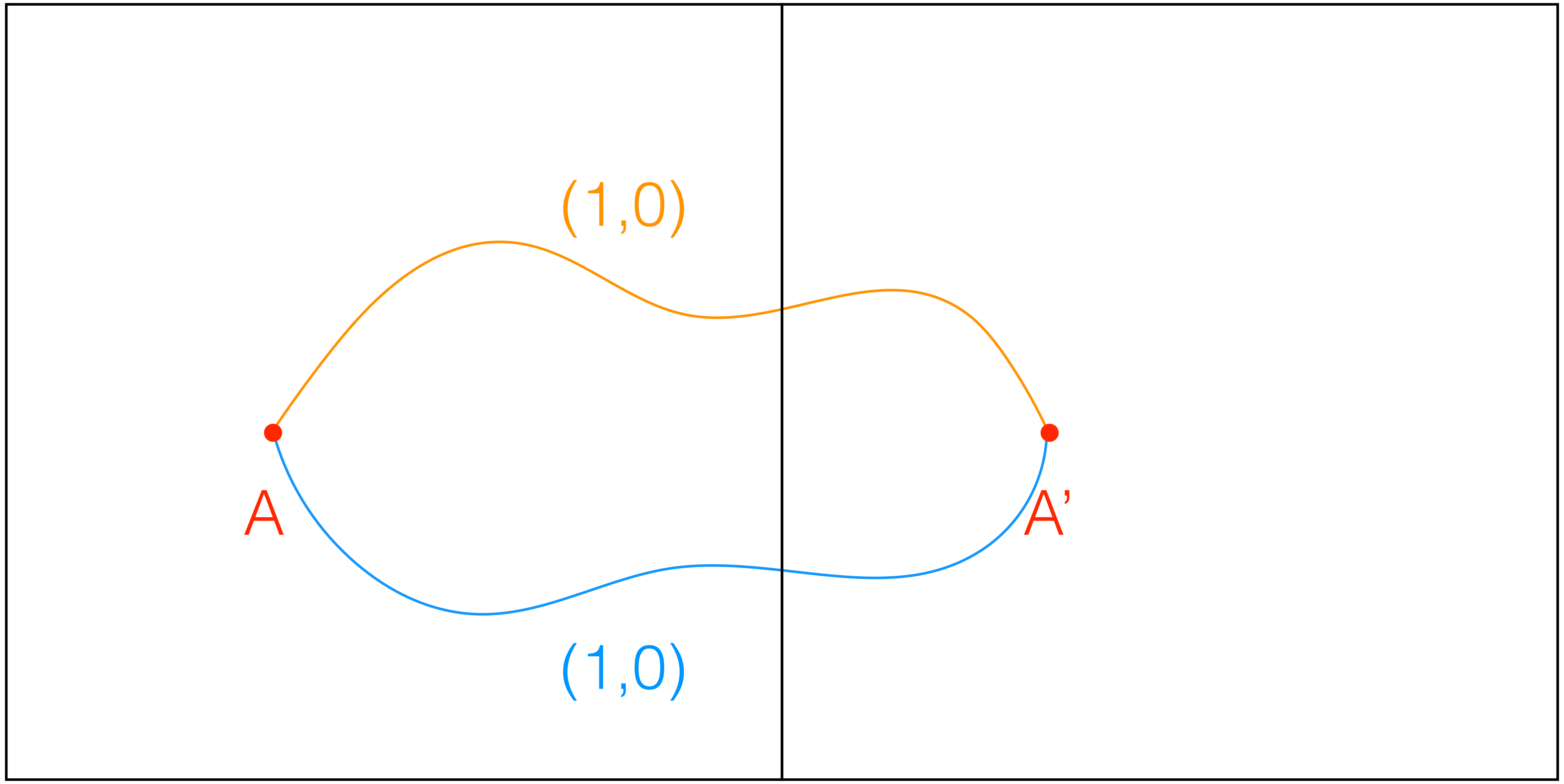




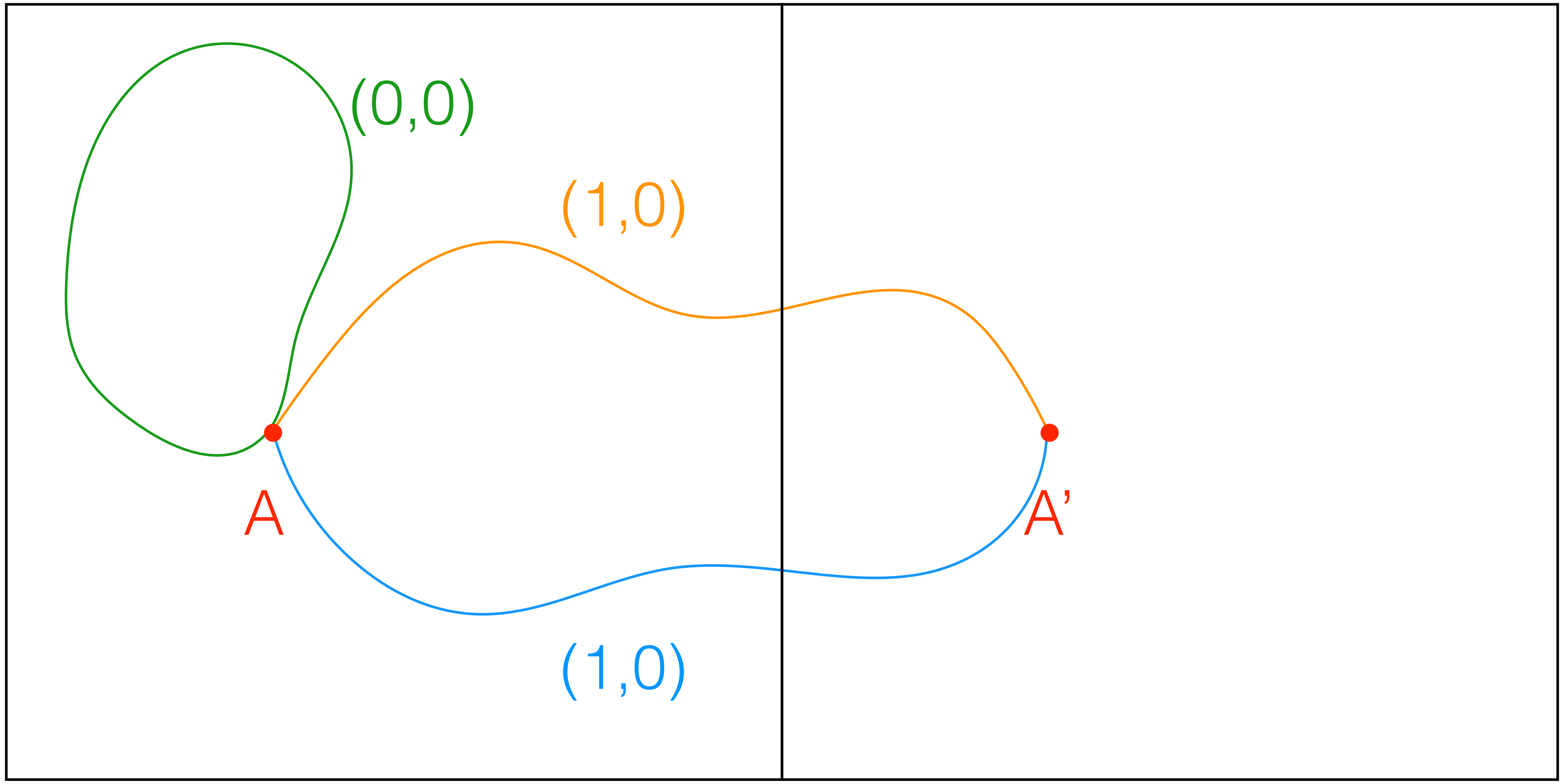


breach of strong adiabaticity



$$\mu = \mu^*$$

breach of strong adiabaticity



$$\mu = \mu^*$$
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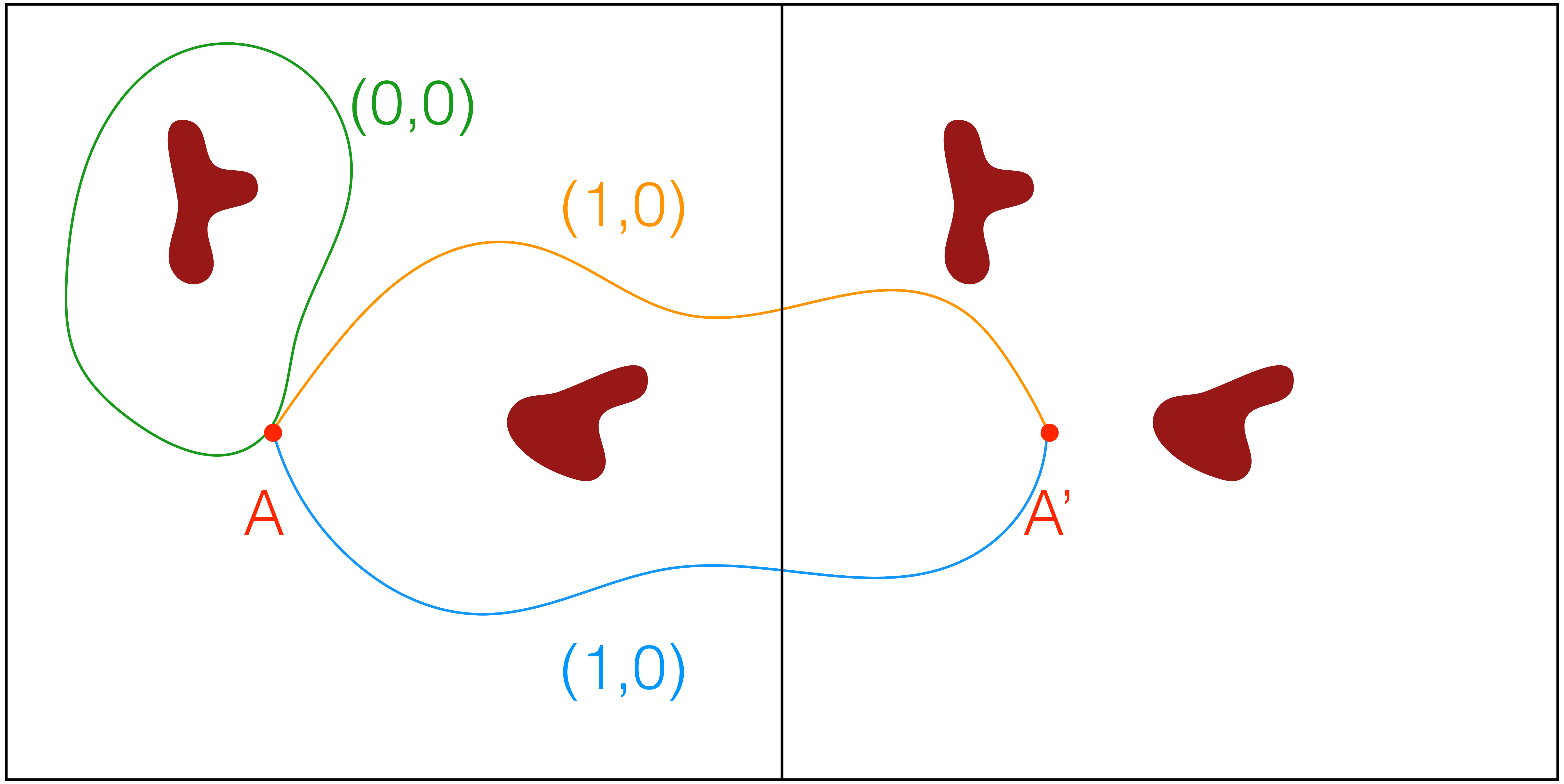
breach of strong adiabaticity



$$\mu \neq \mu^*$$
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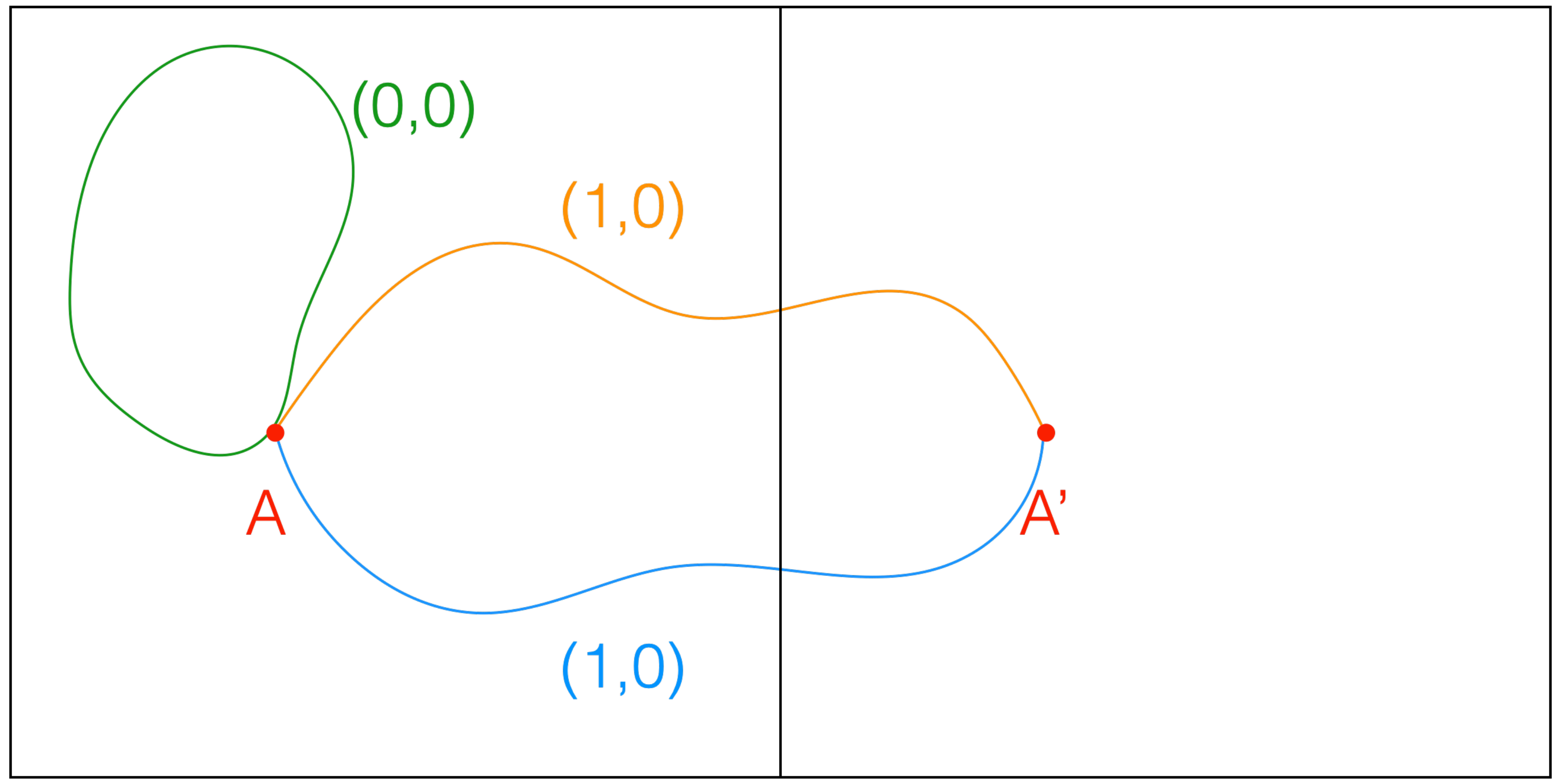
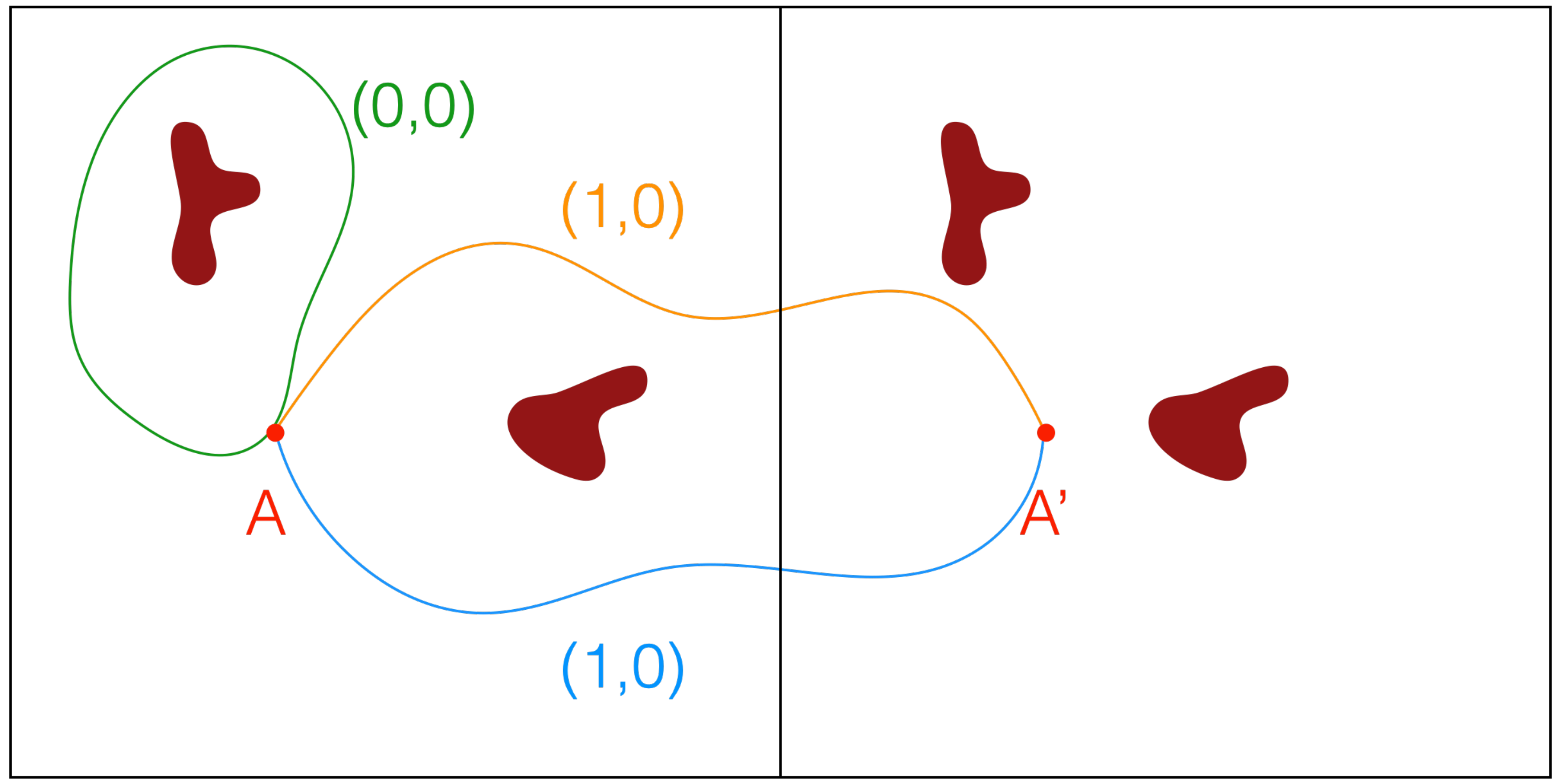
strongly adiabatic transport



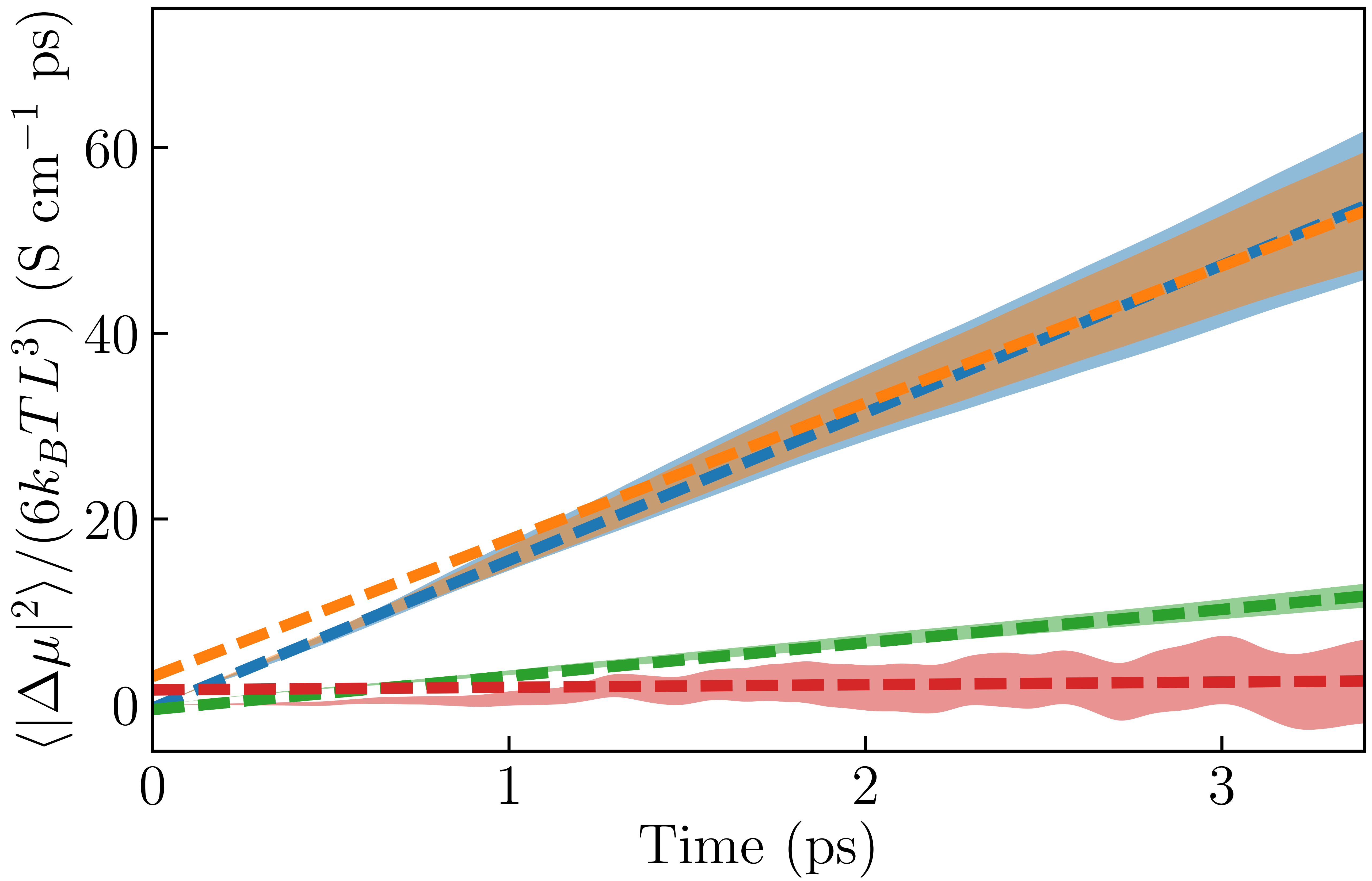
$\mu = \mu^*$
$\mu = 0$

weakly adiabatic transport



$\mu \neq \mu^*$
$\mu \neq 0$

not trivial weakly adiabatic conductivity



$$\Delta\boldsymbol{\mu} = e\int_0^t \mathbf{J}(t')dt'$$

$$J_\alpha(t) = \sum_{i\beta} Z^*_{i\alpha\beta}(t)v_{i\beta}(t)$$

$$J_\alpha(t) = \sum_i q_{S(i)}v_{i\alpha}(t) - 2v^{lp}_\alpha(t)$$

cross term

conclusions

- topological quantisation of adiabatic charge transport allows for a rigorous definition of the atomic oxidation states;
- gauge invariance and quantisation of charge transport make the electric conductivity of stoichiometry electrolytes depend on the formal oxidation numbers of the ionic species, via the Green-Kubo formula;
- breach of strong adiabaticity in non-stoichiometric electrolytes triggers an anomalous transport regime, intermediate between metallic and ionic, whereby charge may be transported without any concurrent mass displacement.

thanks to:

Federico Grasselli

Paolo Pegolo

now both @EPFL

nature physics ARTICLES
PUBLISHED ONLINE: 19 OCTOBER 2015 | DOI: 10.1038/NPHYS3509

Microscopic theory and quantum simulation of atomic heat transport

Aris Marcolongo[1], Paolo Umari[2] and Stefano Baroni[1*]

nature physics ARTICLES
https://doi.org/10.1038/s41567-019-0562-0

Topological quantization and gauge invariance of charge transport in liquid insulators

Federico Grasselli[1] and Stefano Baroni[1,2*]

PHYSICAL REVIEW X

Oxidation States, Thouless' Pumps, and Nontrivial Ionic Transport in Nonstoichiometric Electrolytes

Paolo Pegolo, Federico Grasselli, and Stefano Baroni
Phys. Rev. X **10**, 041031 – Published 12 November 2020

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Topology, Oxidation States, and Charge Transport in Ionic Conductors

Paolo Pegolo, Stefano Baroni, Federico Grasselli

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