topological features of a quantum soup: electrons in broth, forty years on

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Trieste — Italy

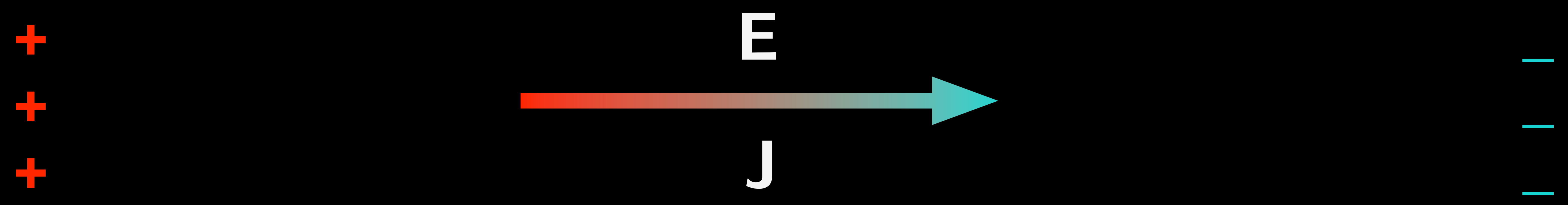
talk given at the *Annabella Selloni Retirement Symposium*, Princeton, June 12-13, 2025

ionic transport

nothing flows as simply as it appears

a prequel

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



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+ + +

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$\mathbf{J}$

− − −

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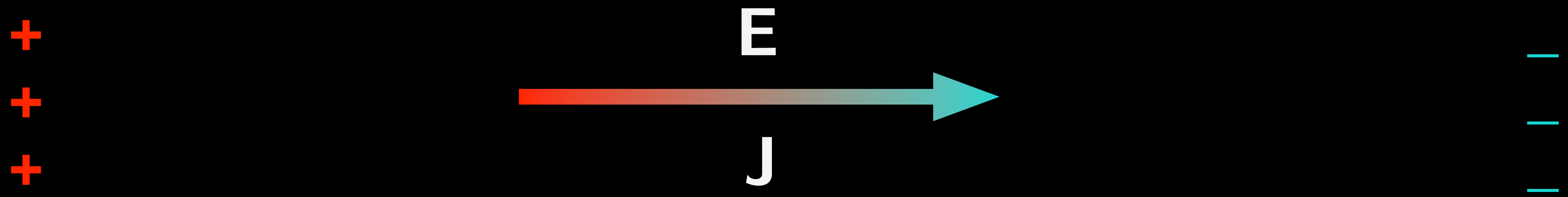

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keep in mind!

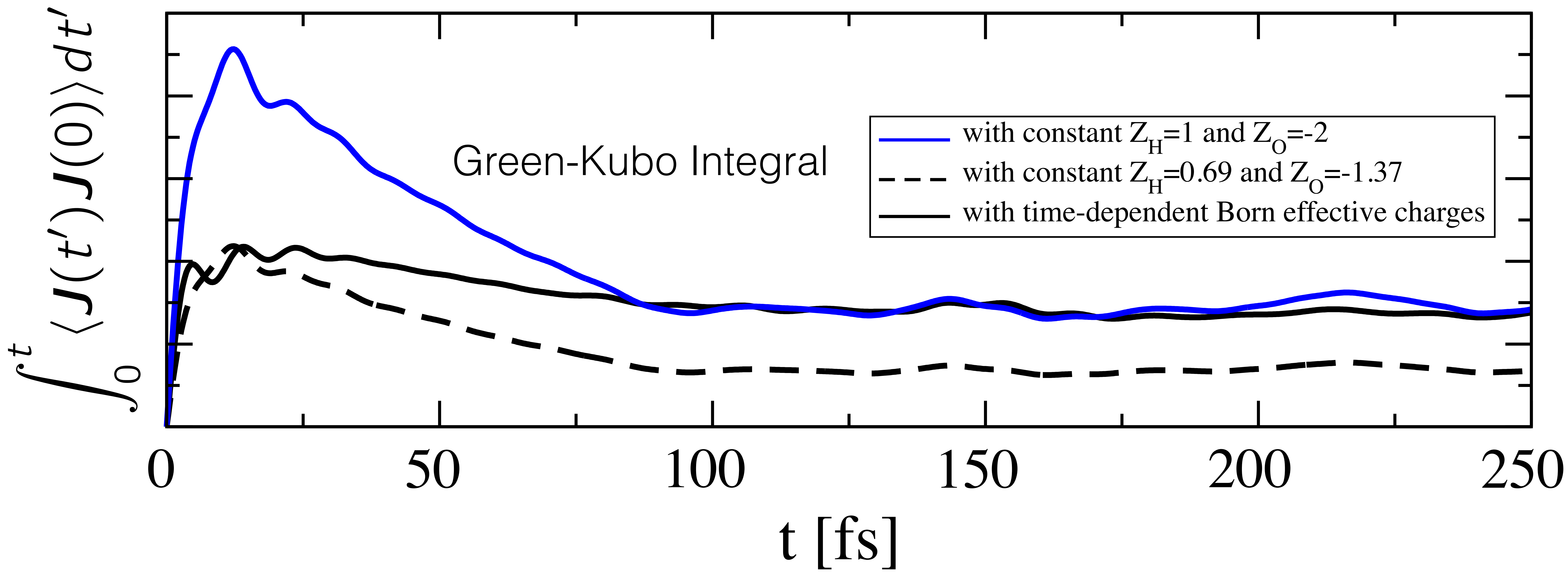
a conundrum in transport theory

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]

partially dissociated water



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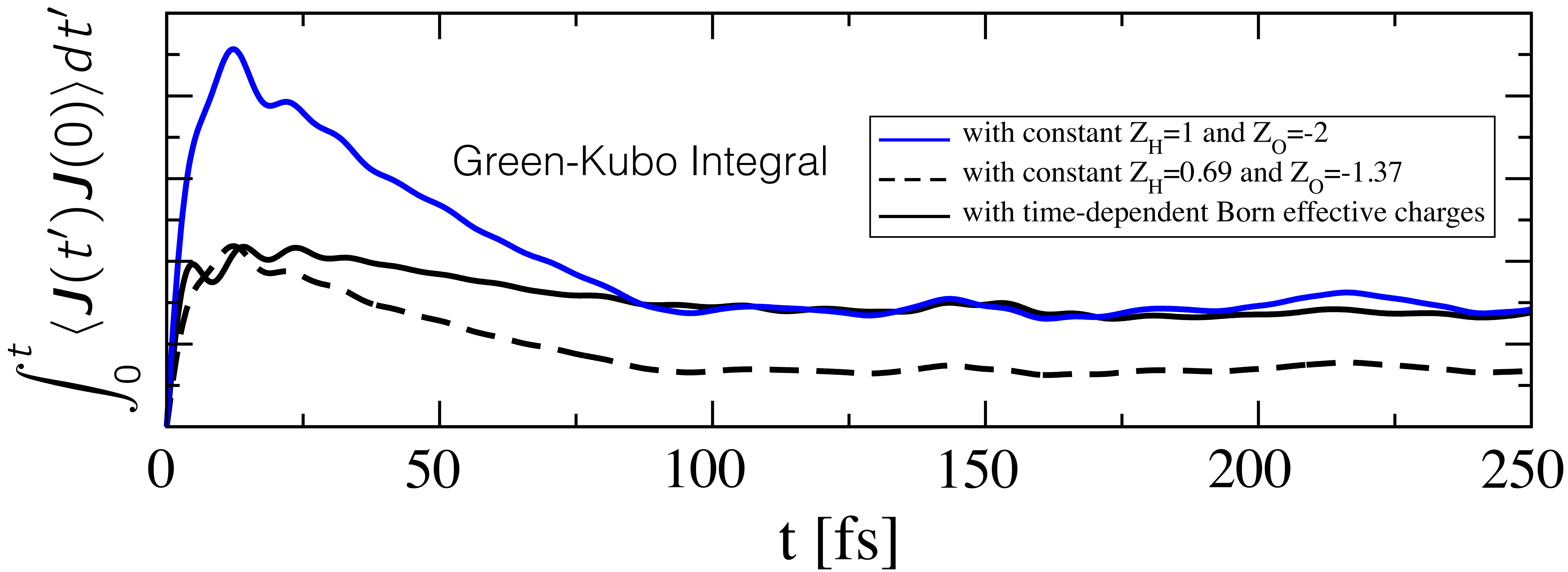

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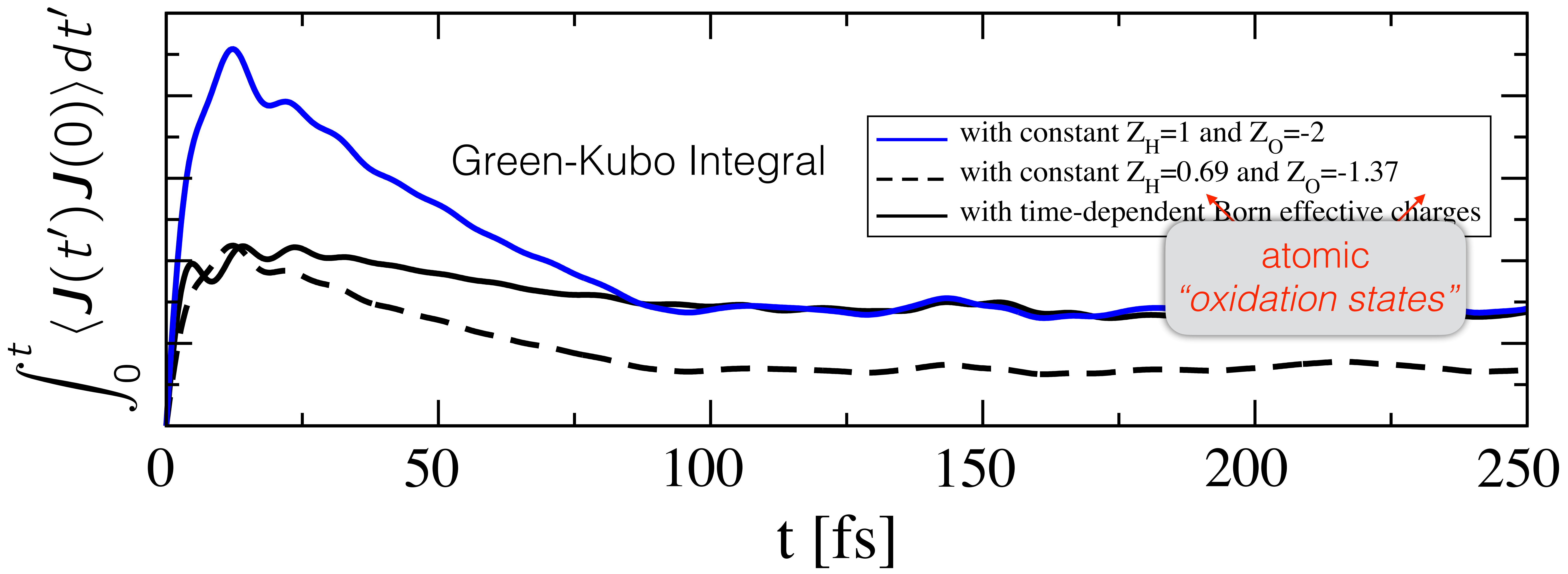

how come?

and what are oxidation states, in the first place?

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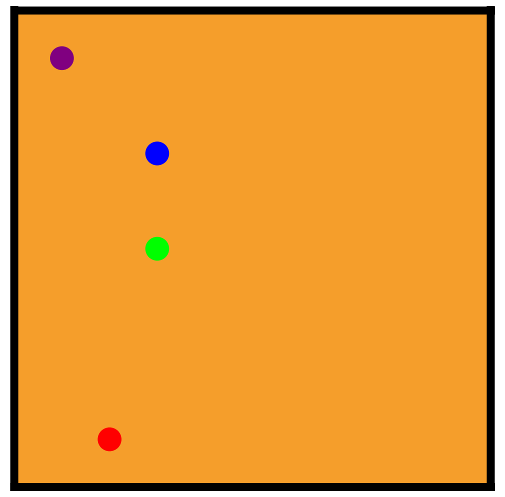
$[0, L]^{3N}$



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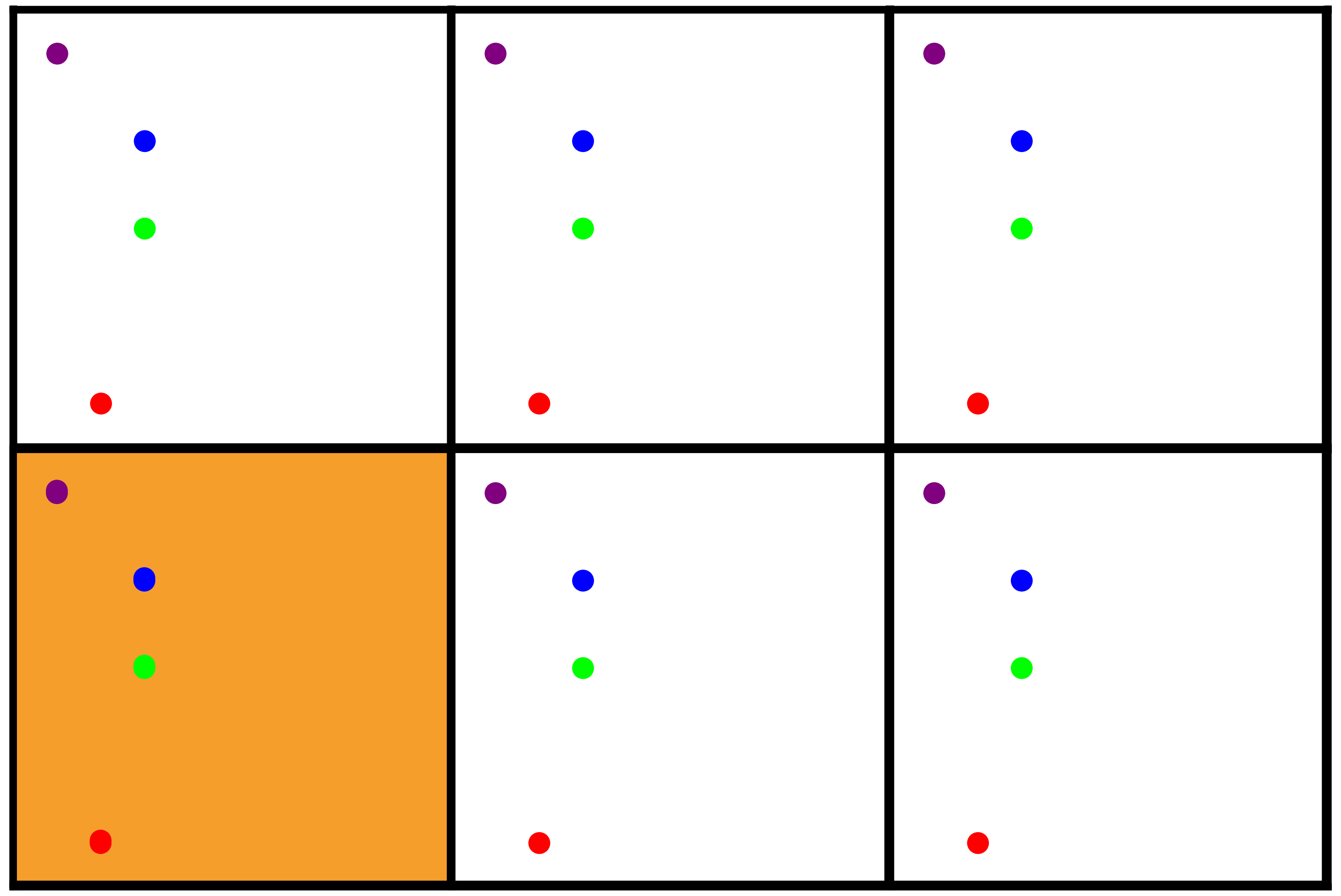
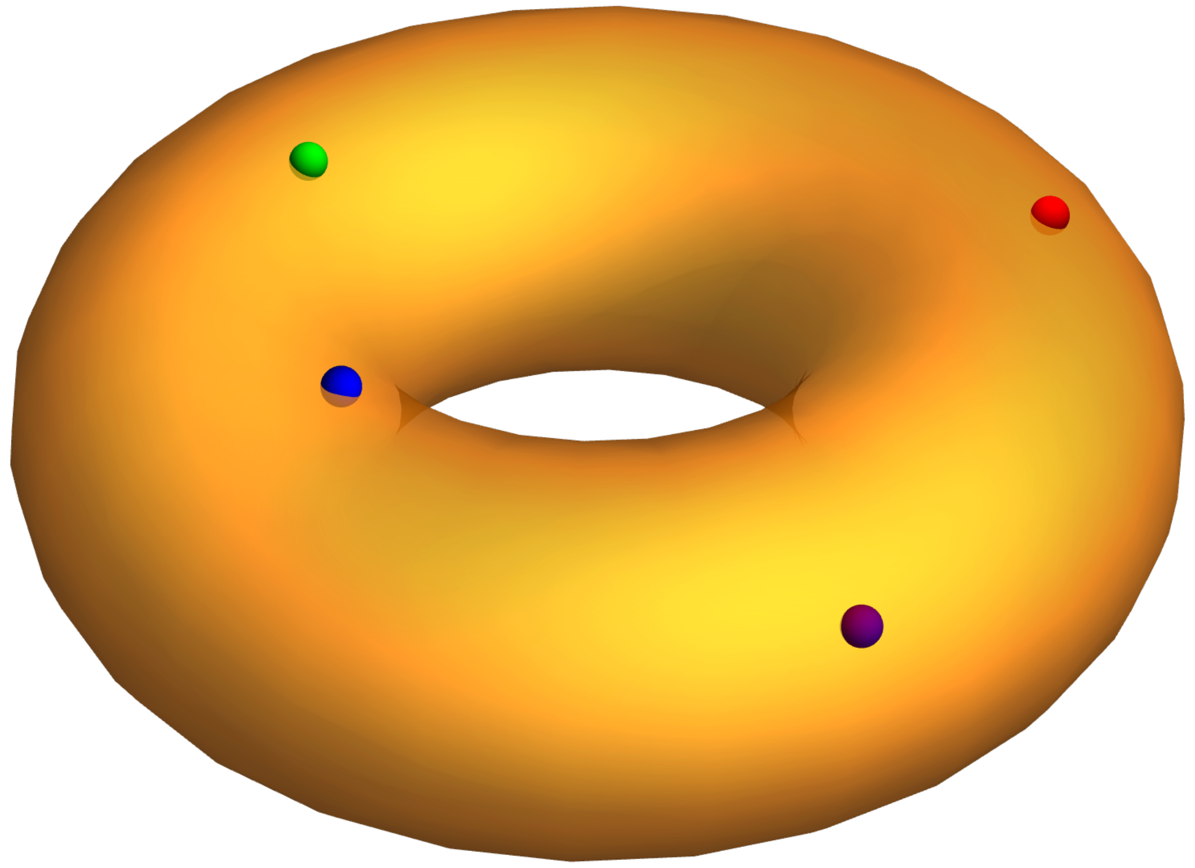


$\xrightarrow{\text{PBC}}$

$\mathbb{T}^{3N}$



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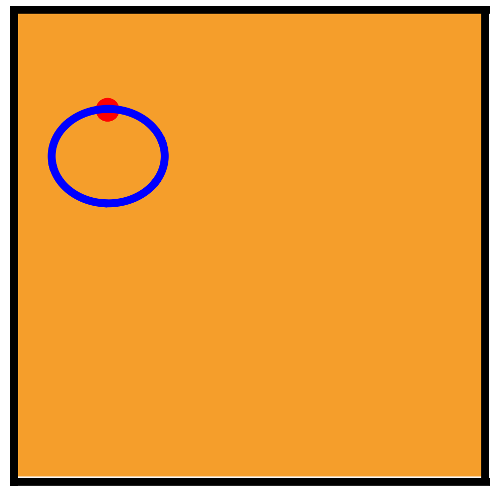
A=A'



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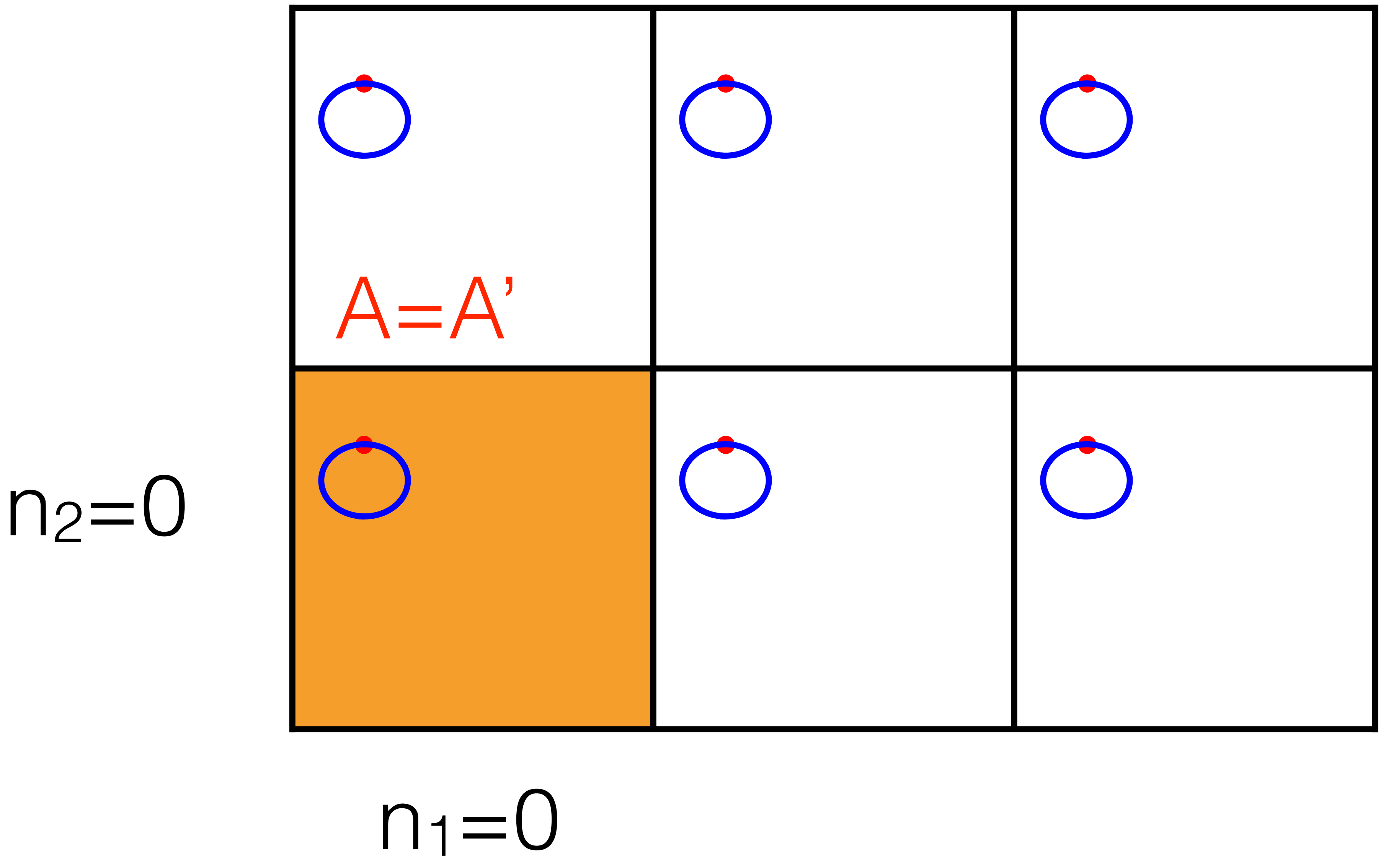

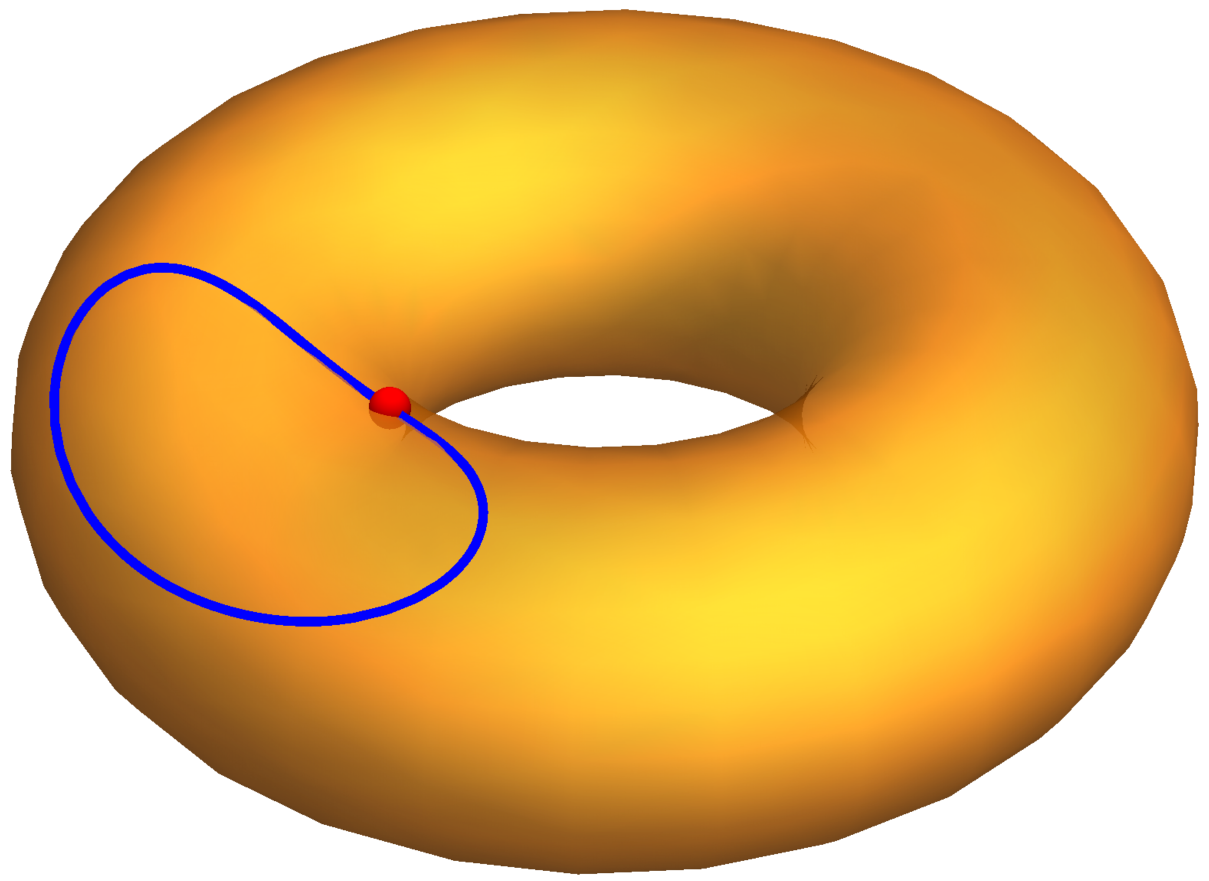

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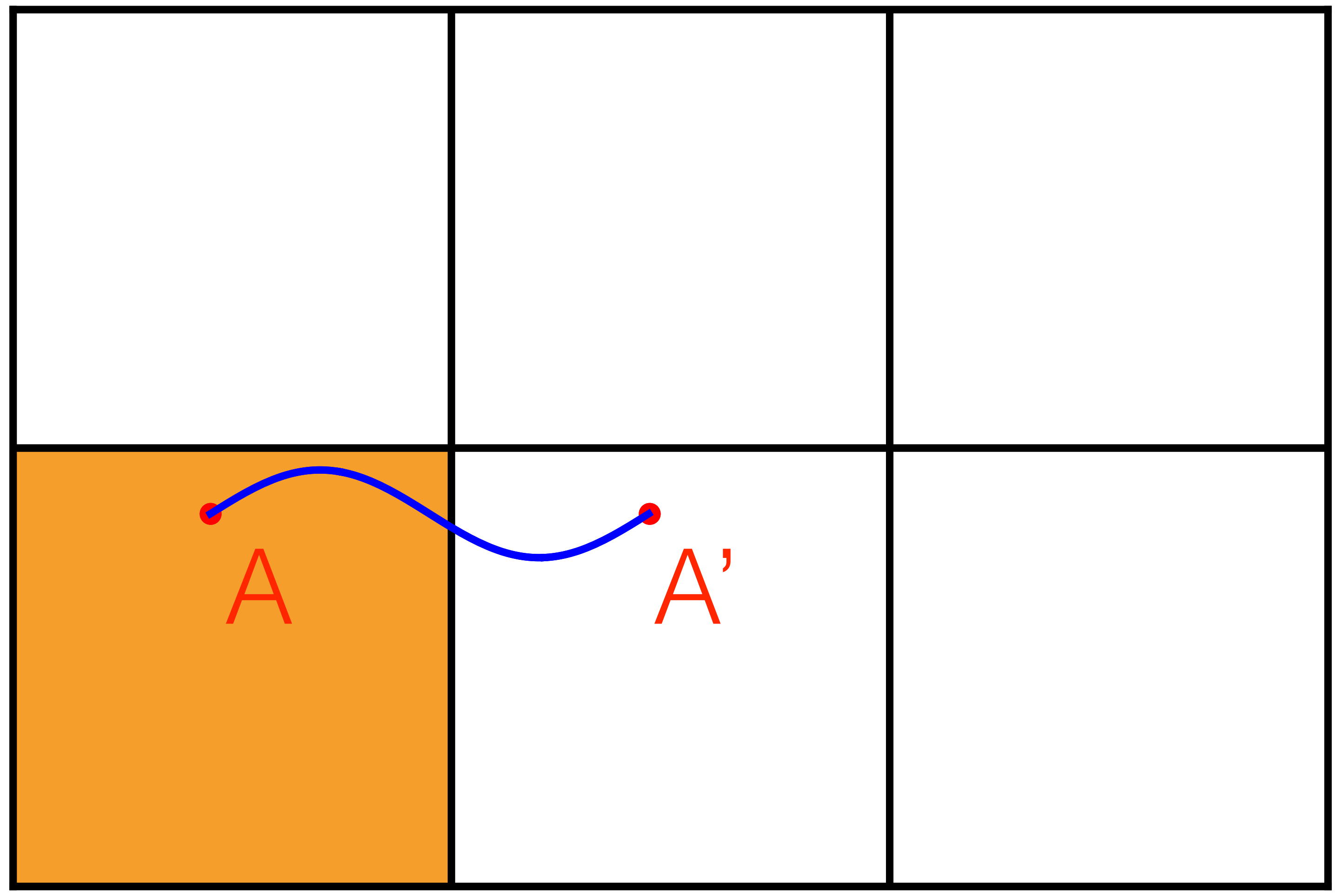

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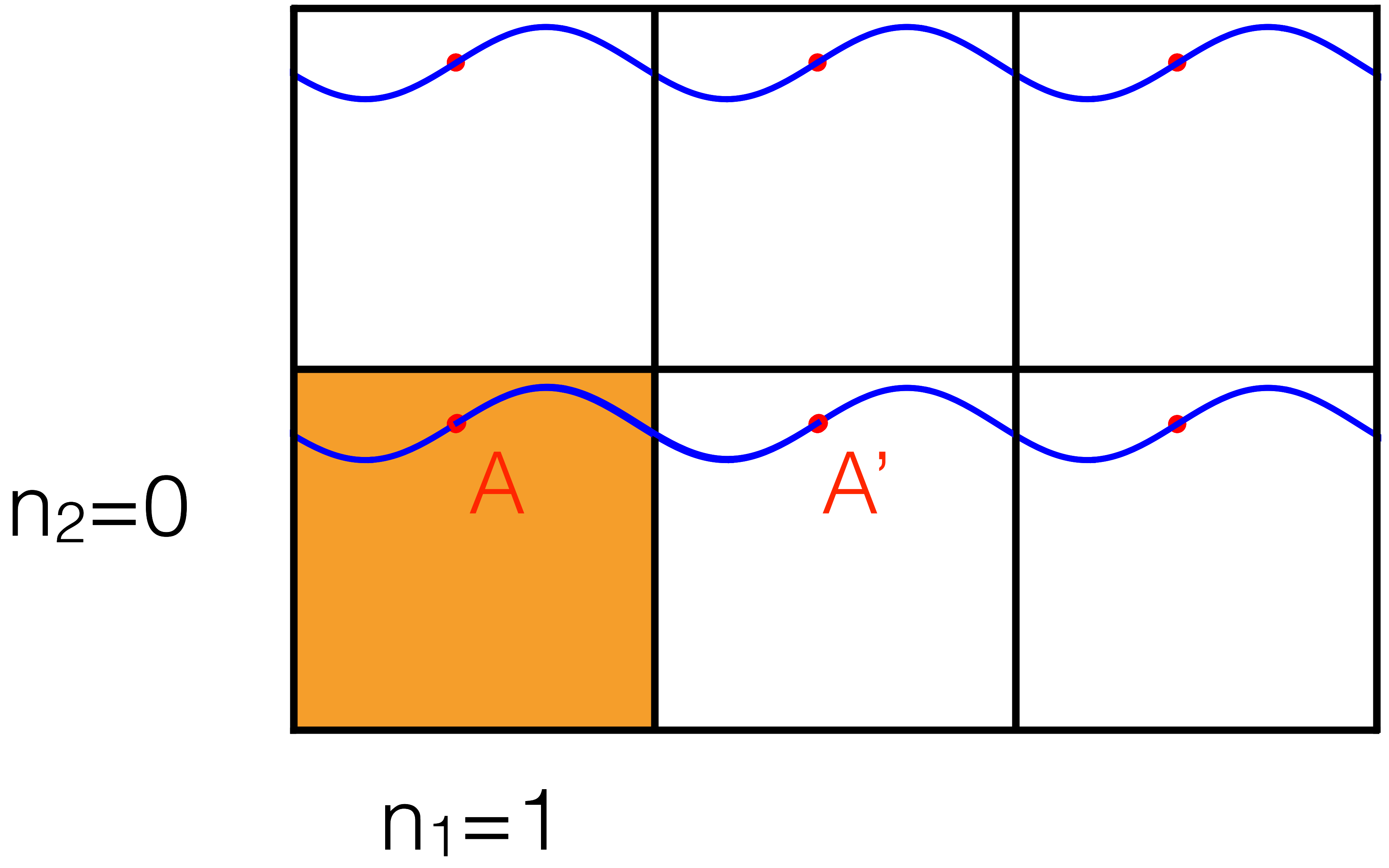

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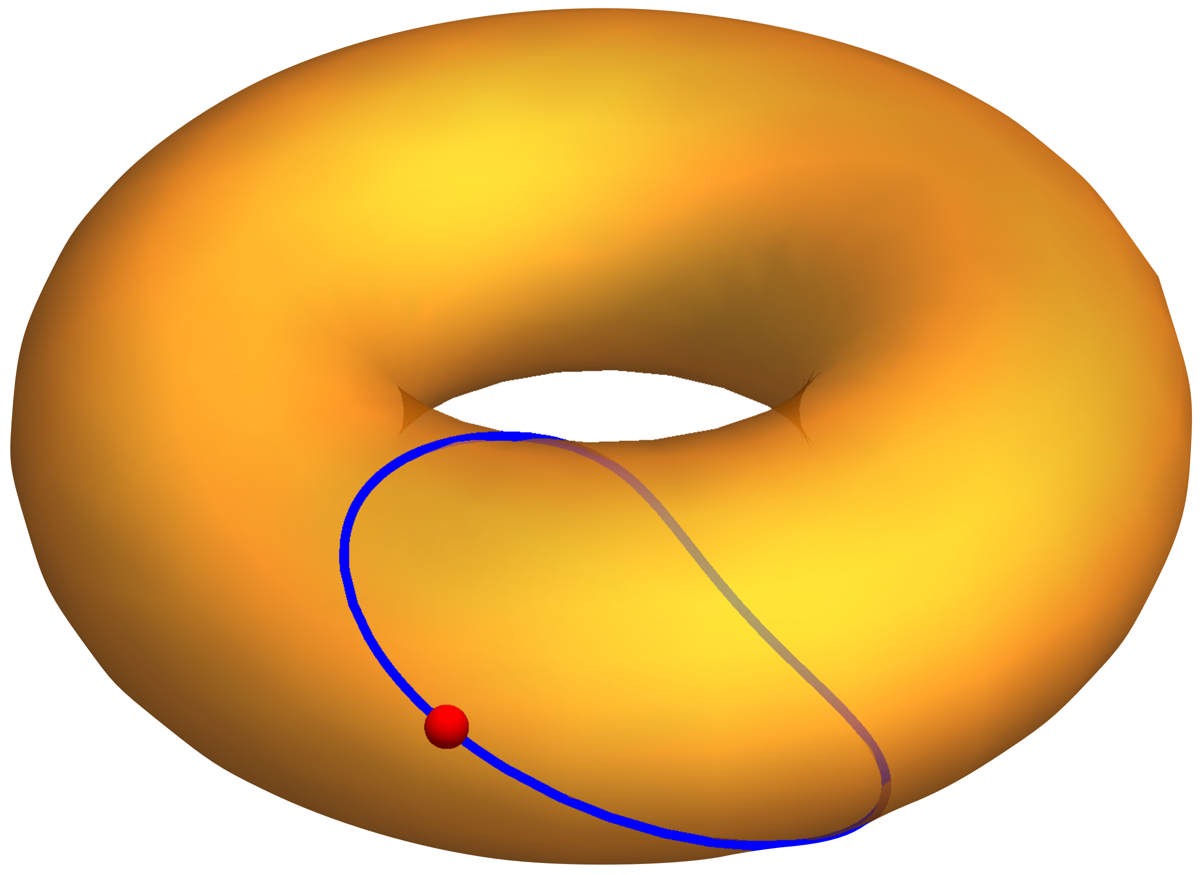

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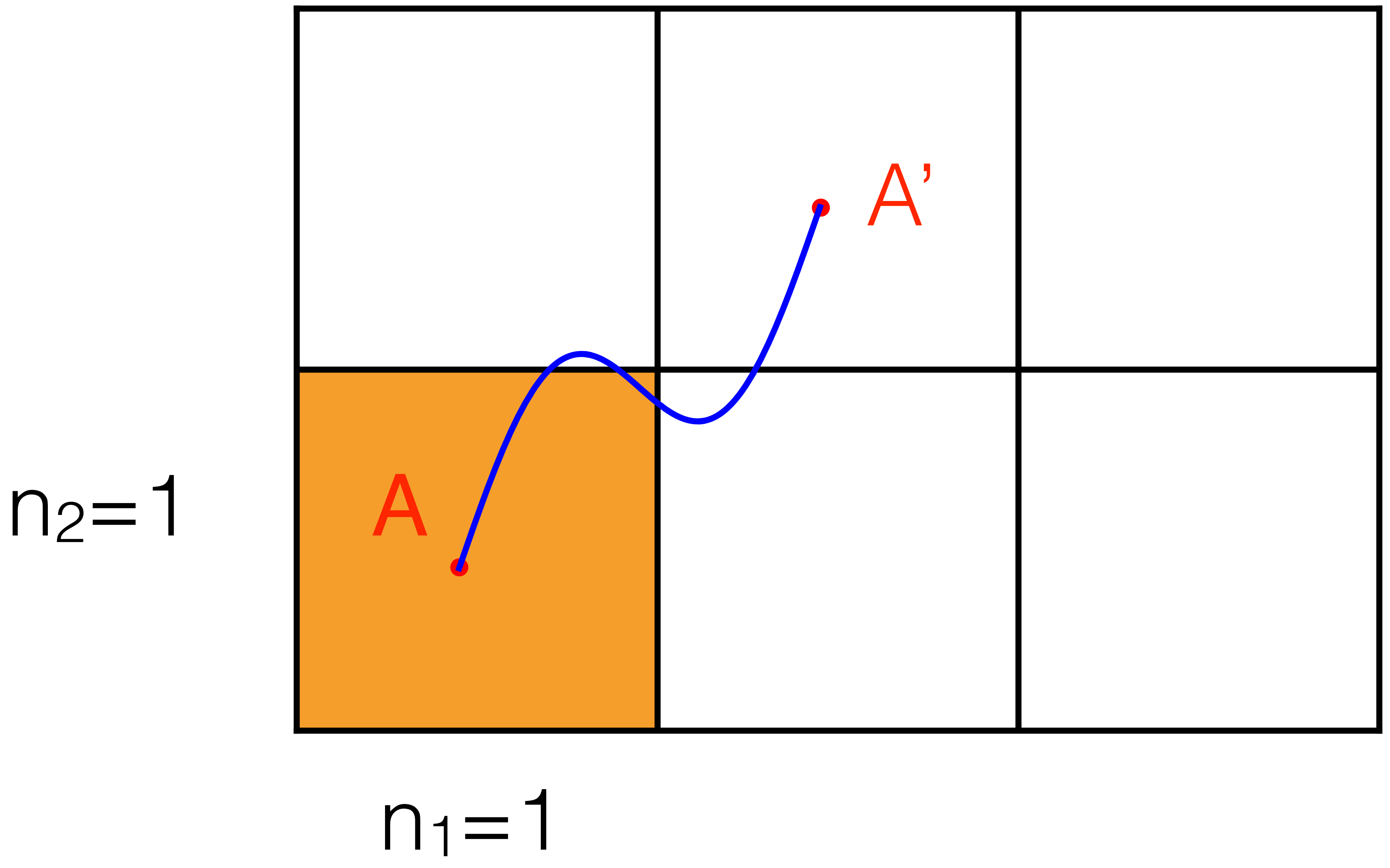

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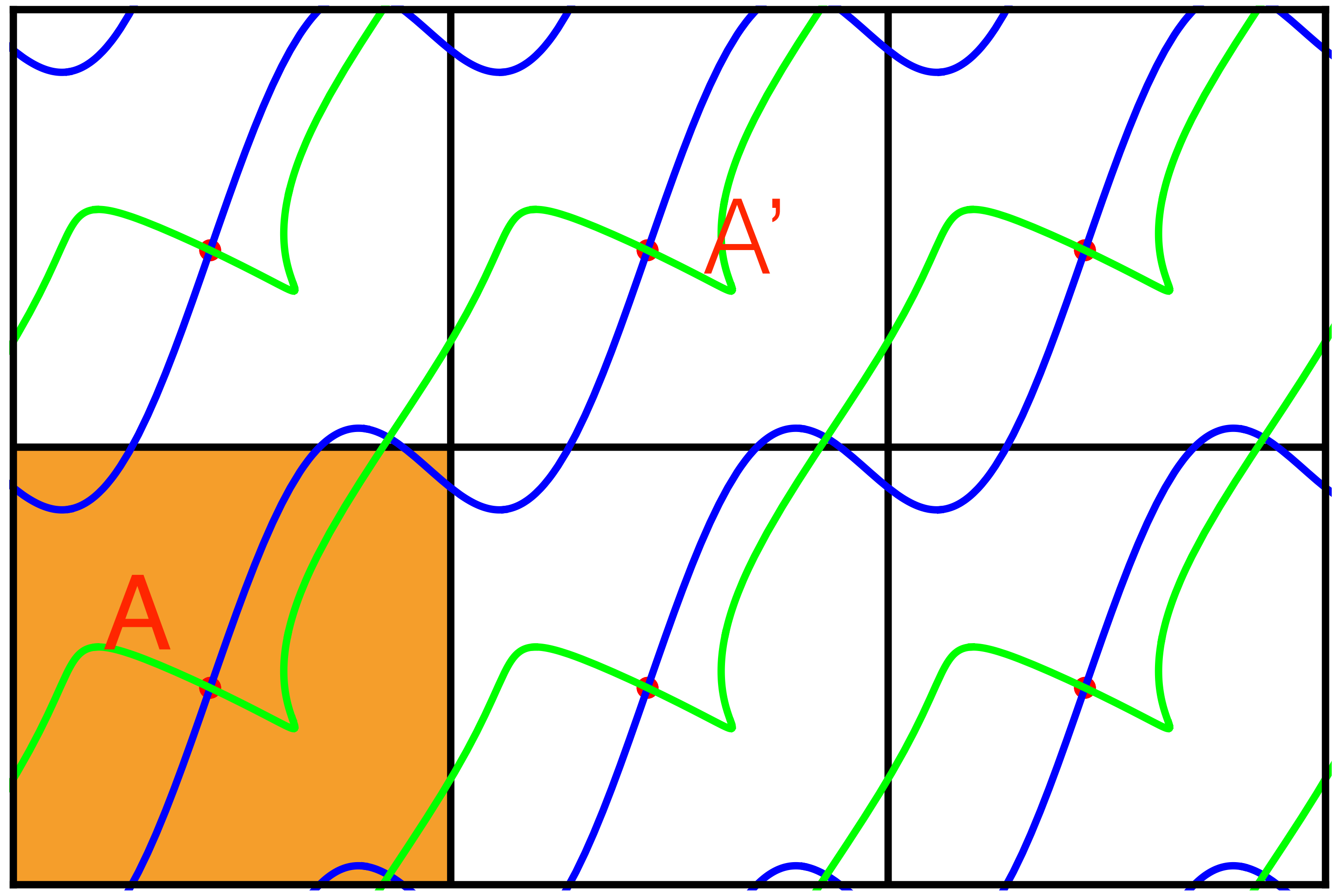
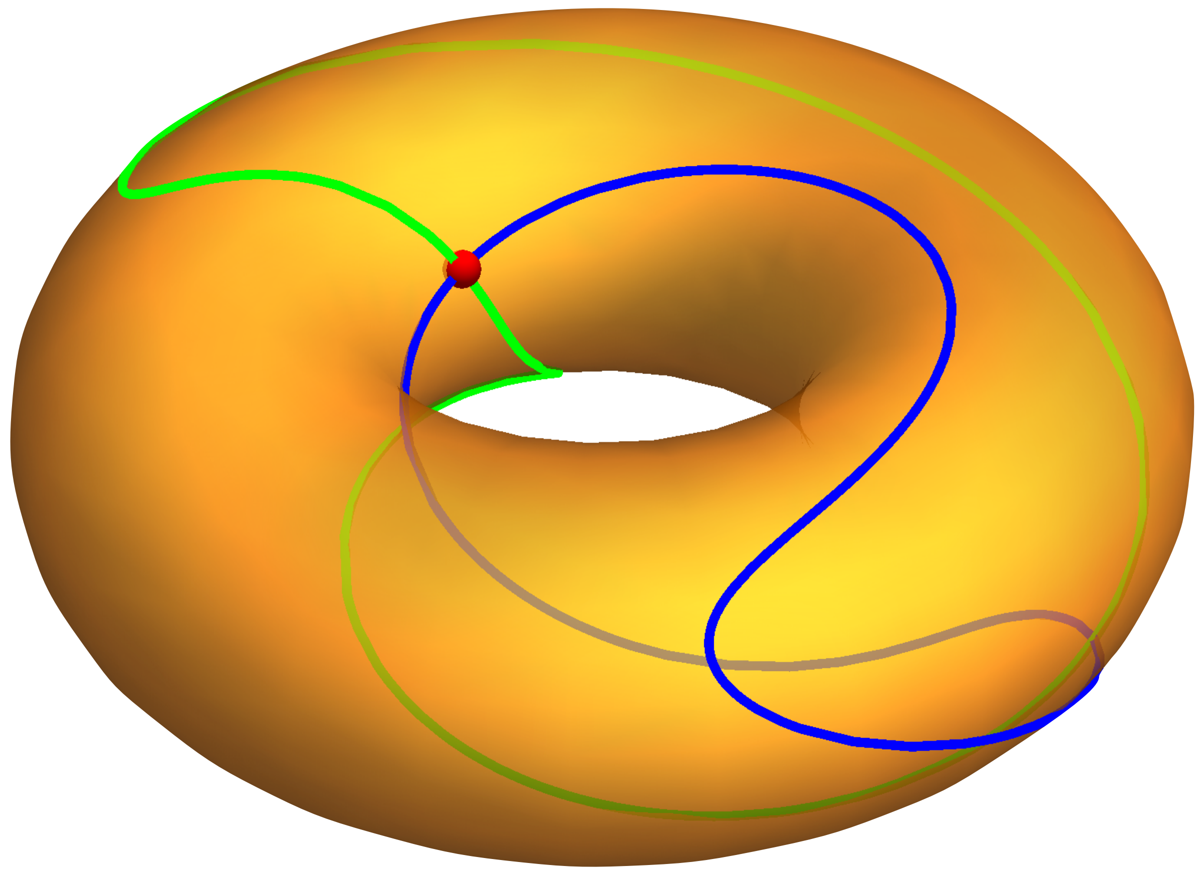


n_2=1

n_1=1

$\xrightarrow{\text{PBC}}$

$\mathbb{T}^{3N}$



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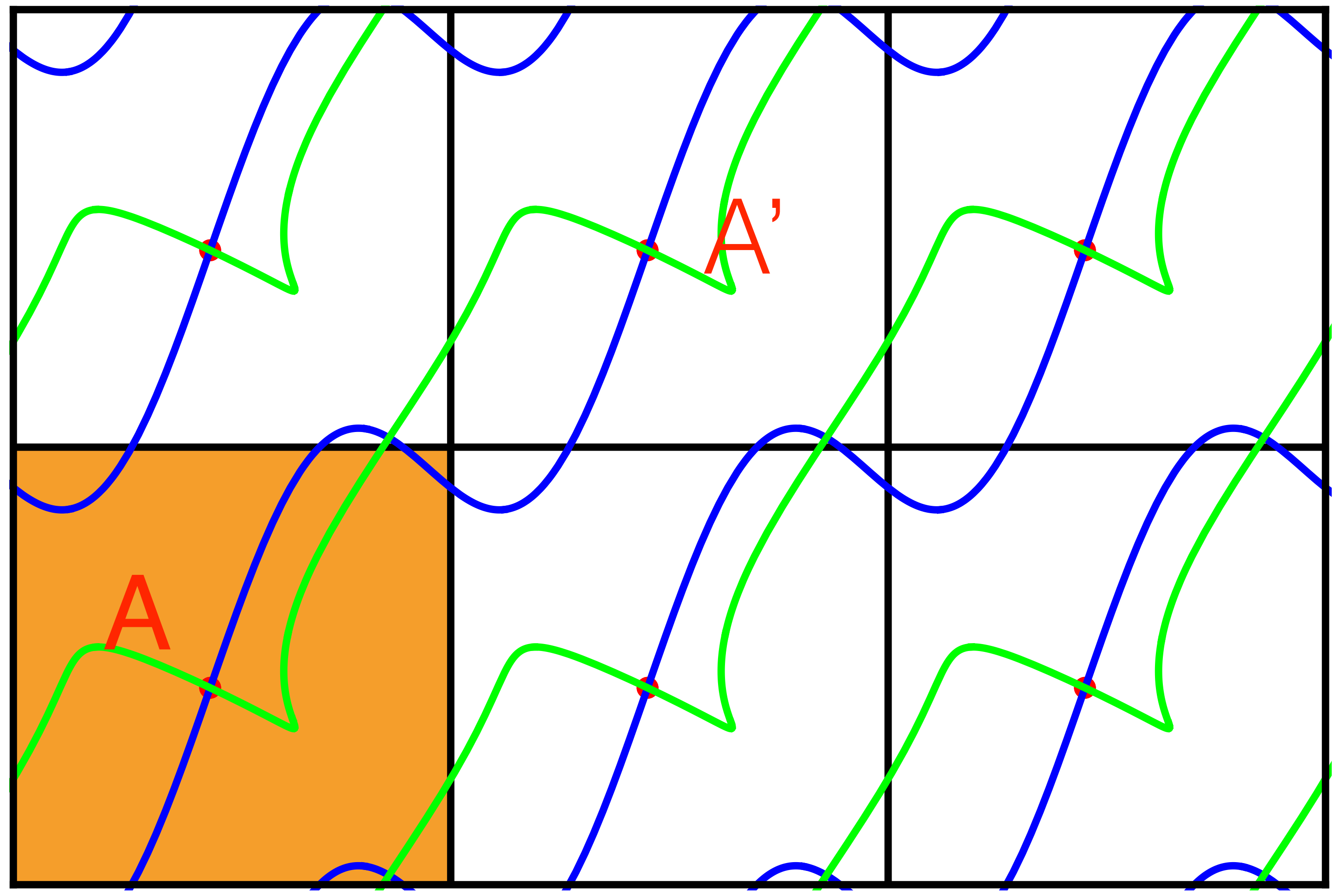

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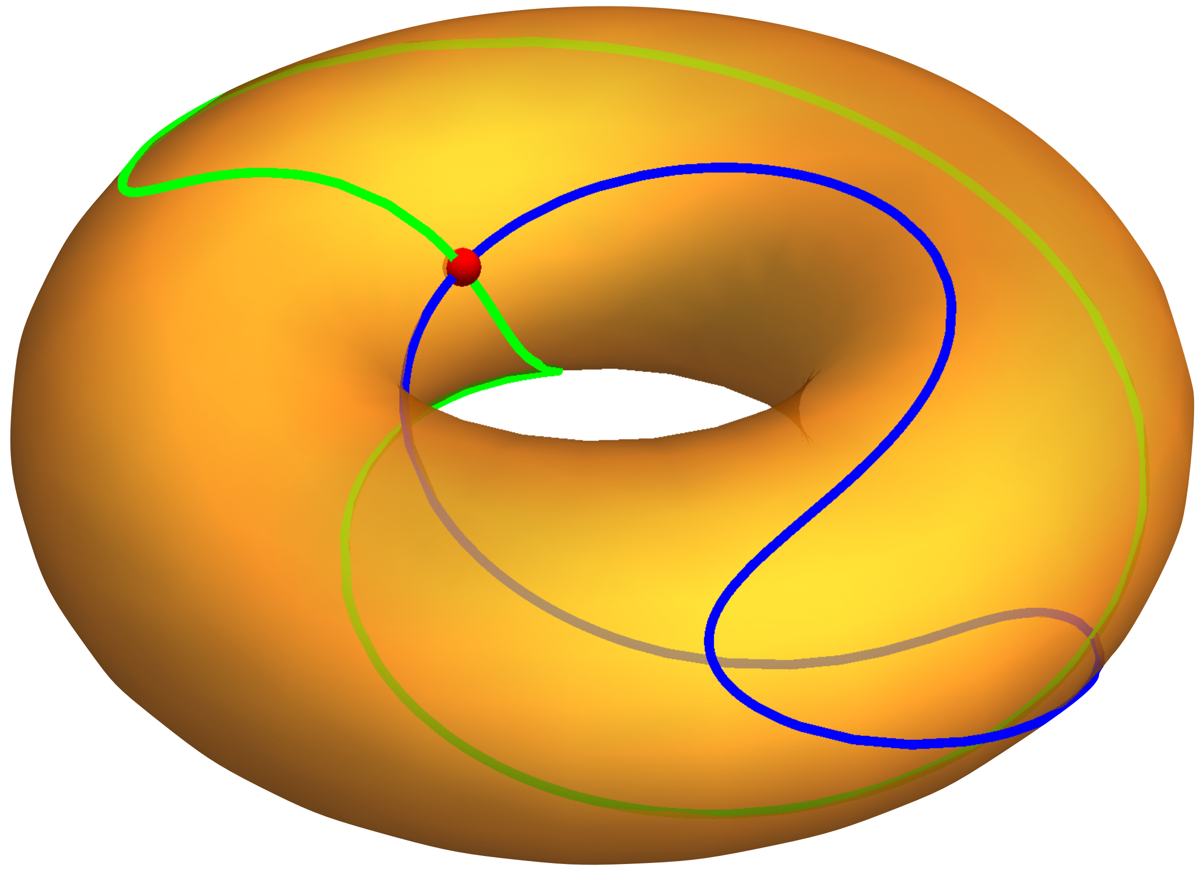

$$\frac{L^2}{e}\int_0^T J_\alpha(t)dt = \frac{1}{Le}\int d\mu_\alpha[X] = Q_\alpha \in \mathbb{Z}$$

D.J. Thouless, 1983
R.Resta, 1990s

$$Q_\alpha(AA') = Q_\alpha(AA') = Q_\alpha[n_1 = 1, n_2 = 1]$$

what are oxidation states, in the first place?

$$Q_\alpha[\mathcal{C}] = \frac{1}{\ell}\mu_\alpha[\mathcal{C}]$$

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- All loops can be shrunk to a point without closing the gap (*strong adiabaticity*);

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atomic oxidation state

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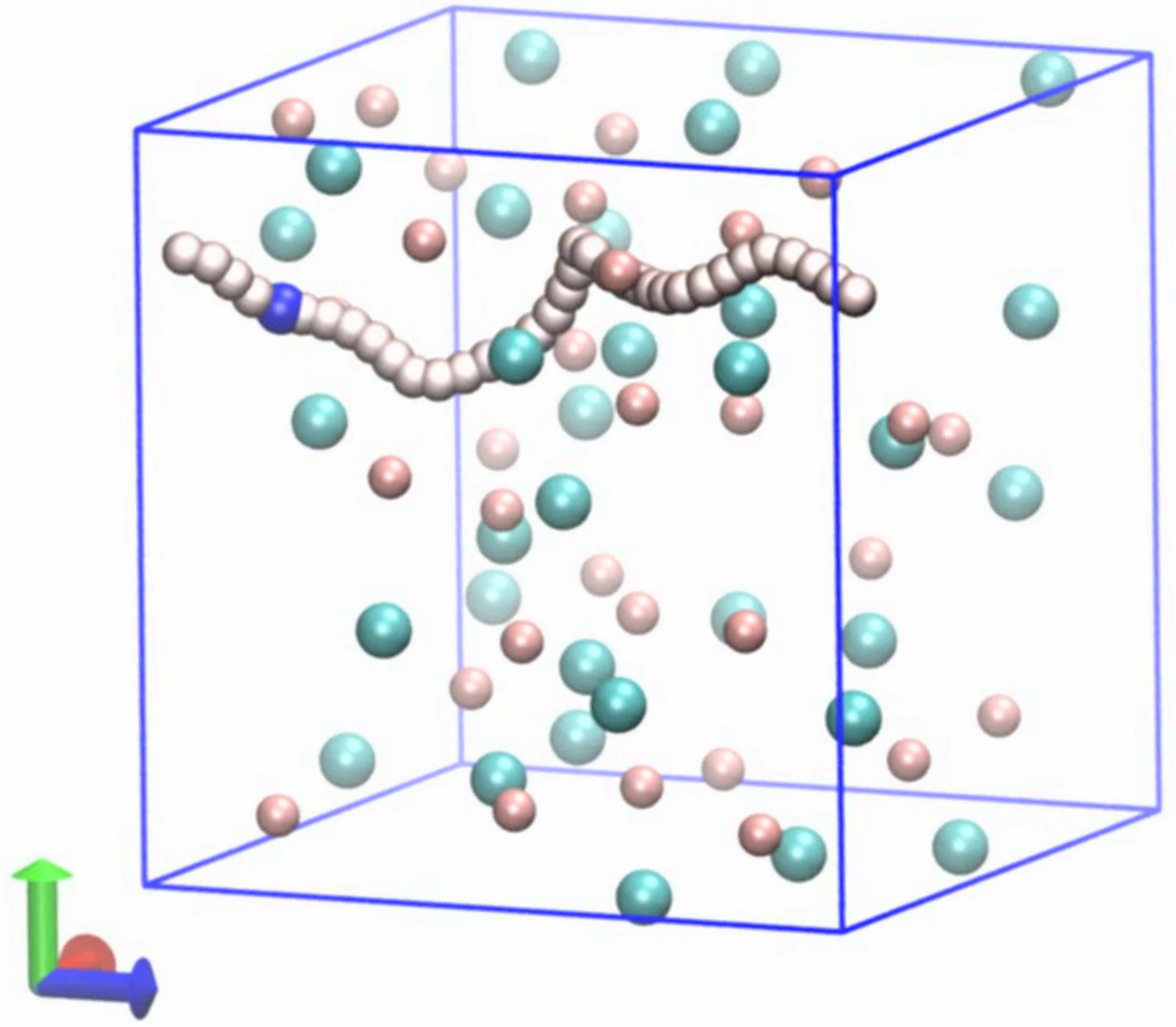
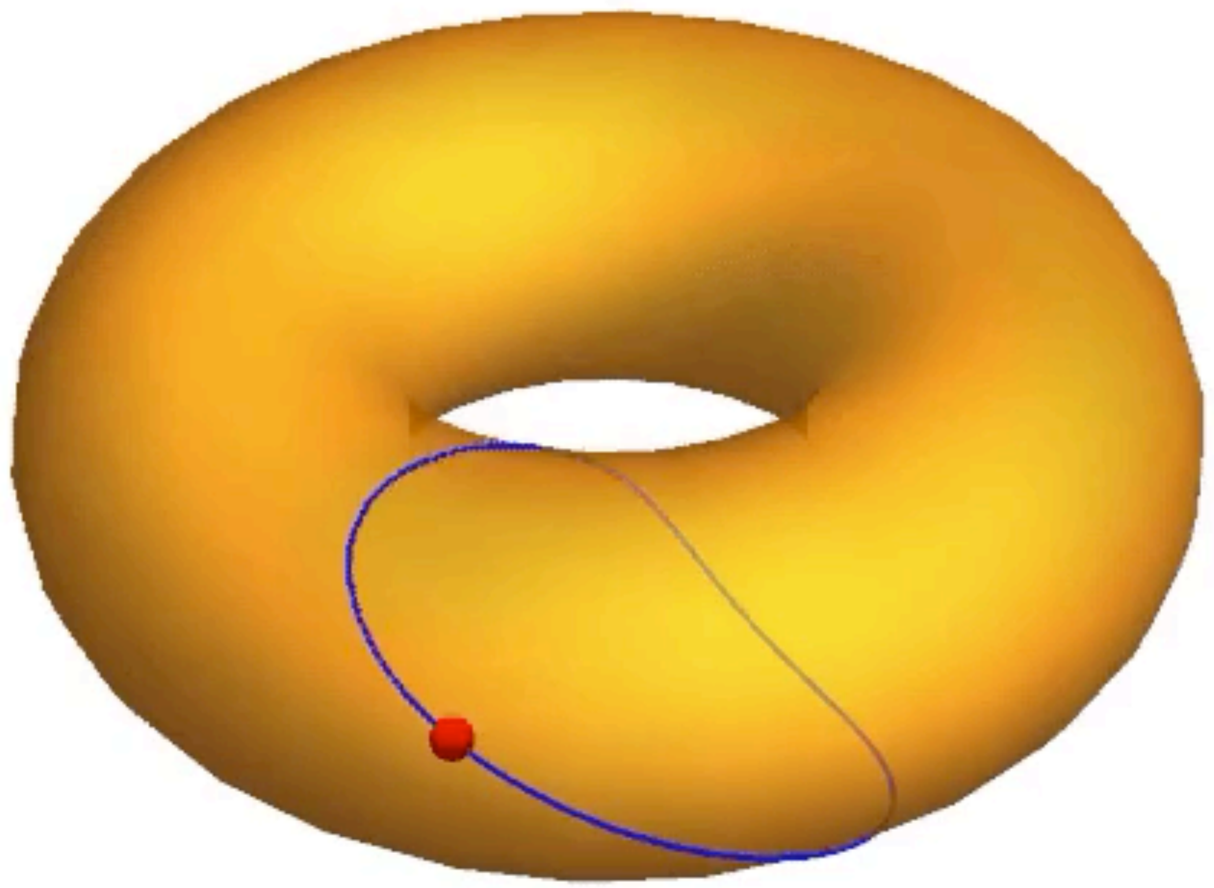
atomic oxidation state

… they are topological invariants!

a numerical experiment on molten KCl





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

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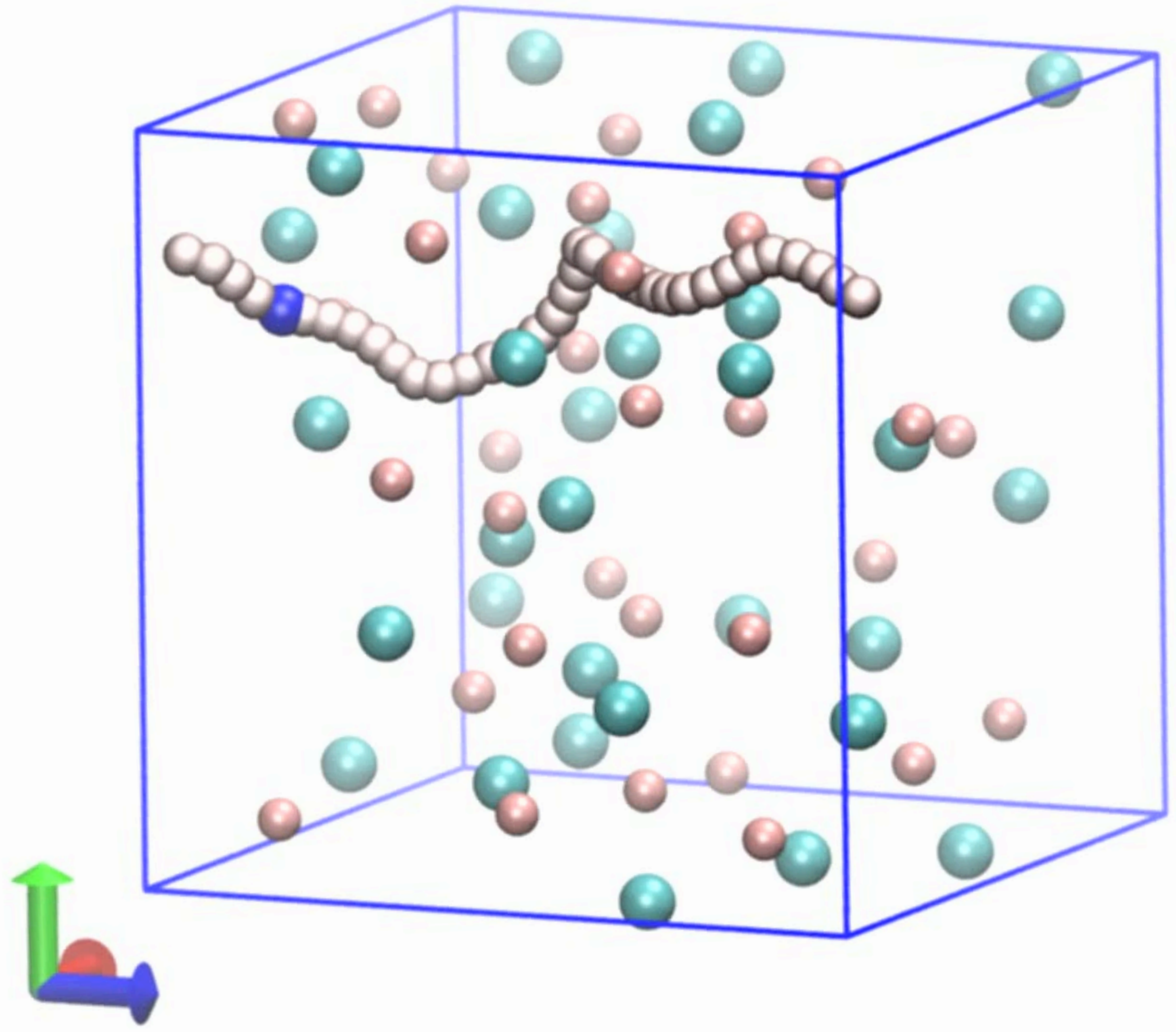

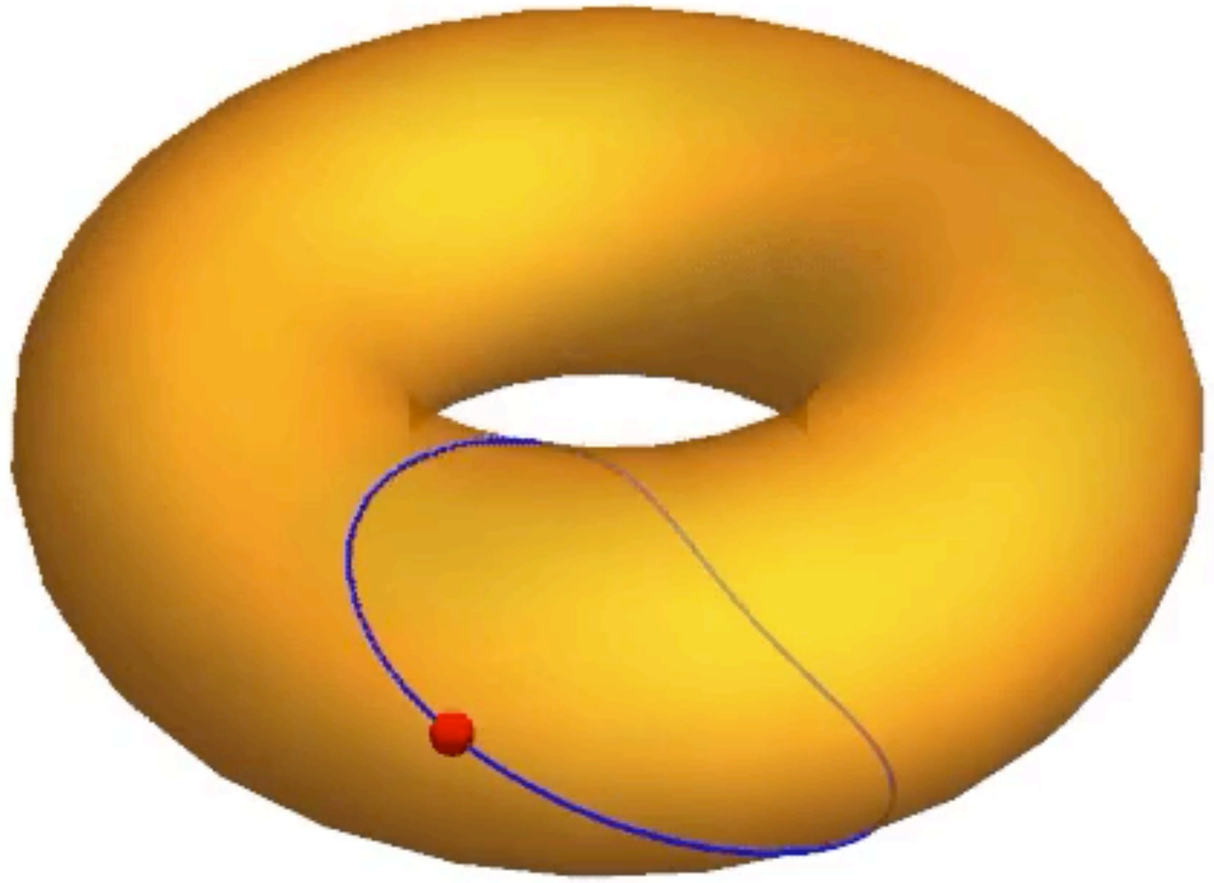

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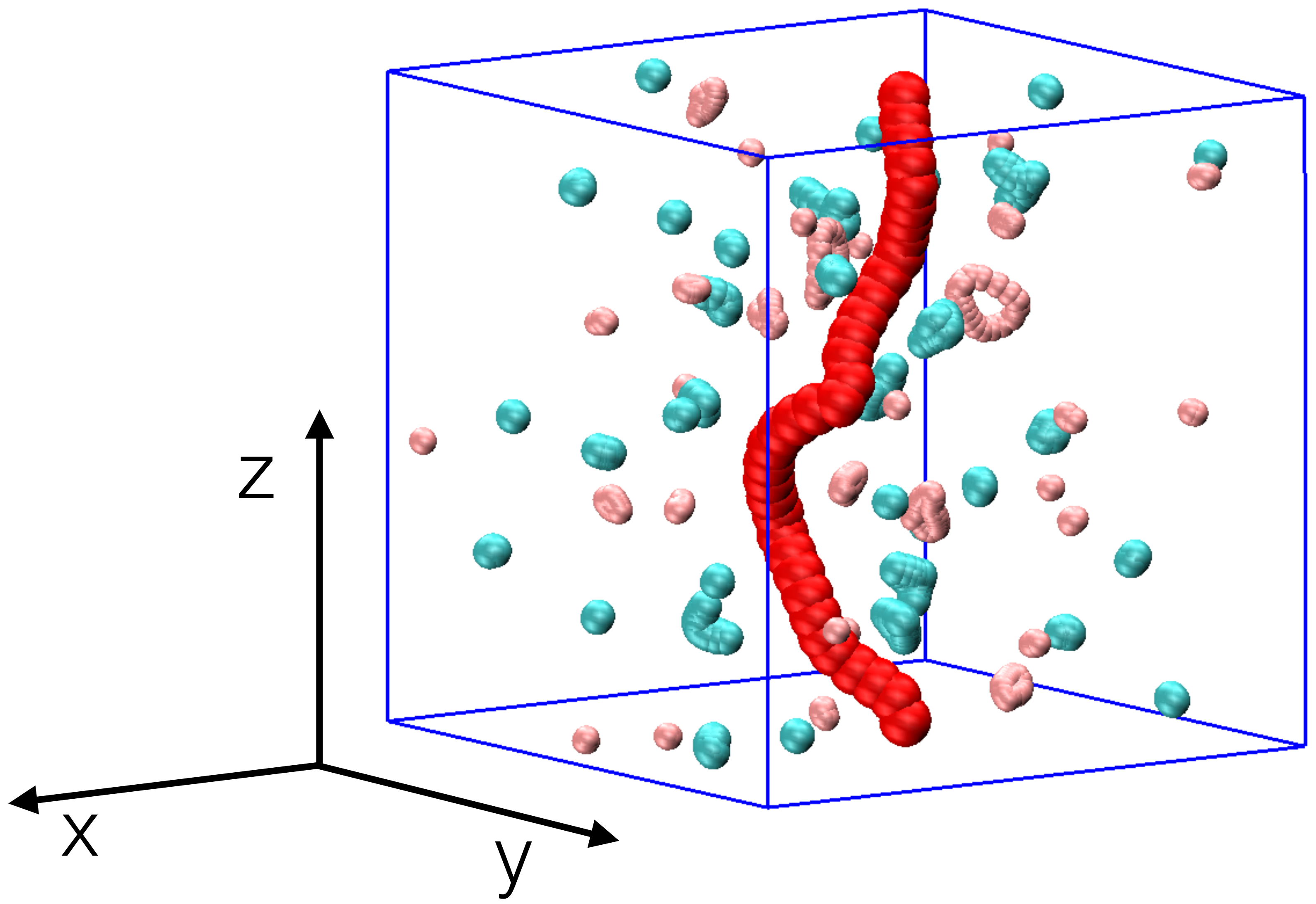

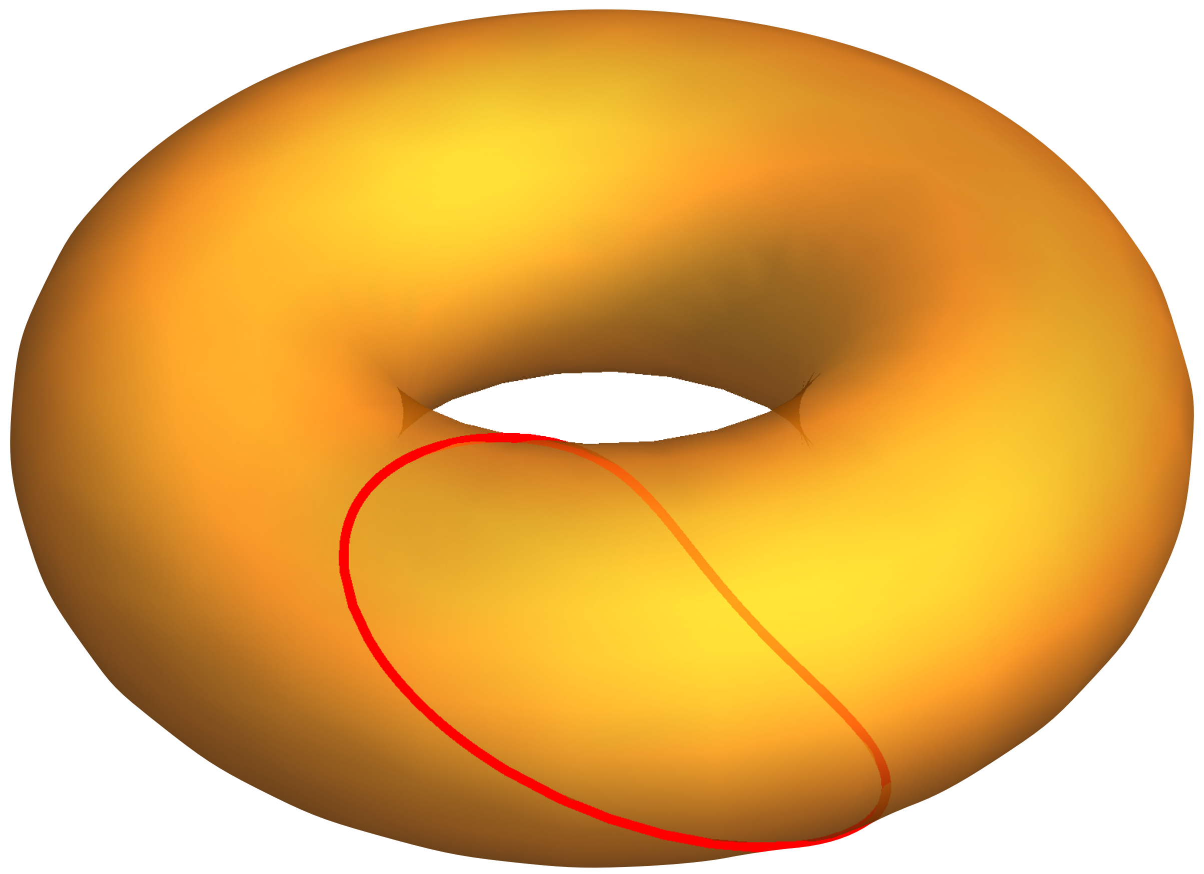

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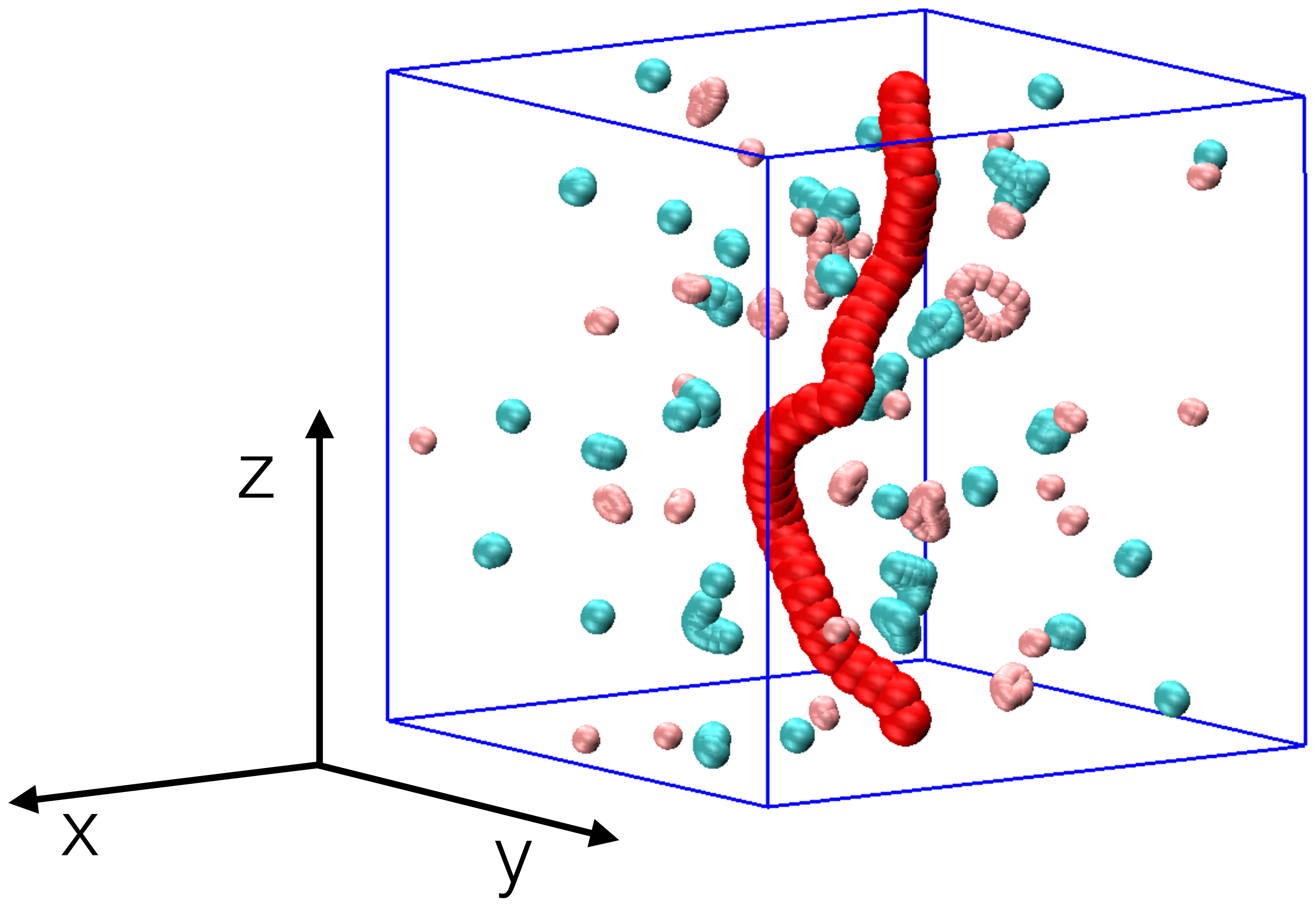

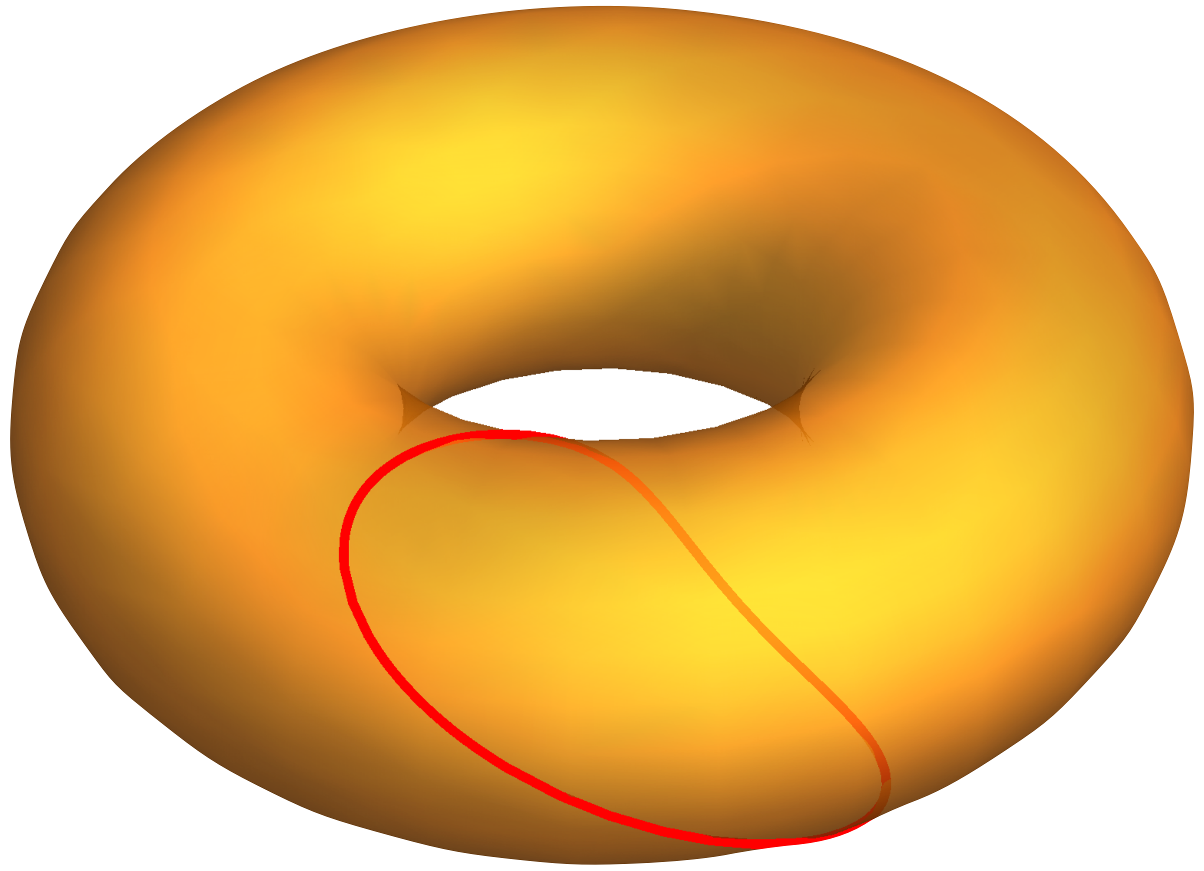

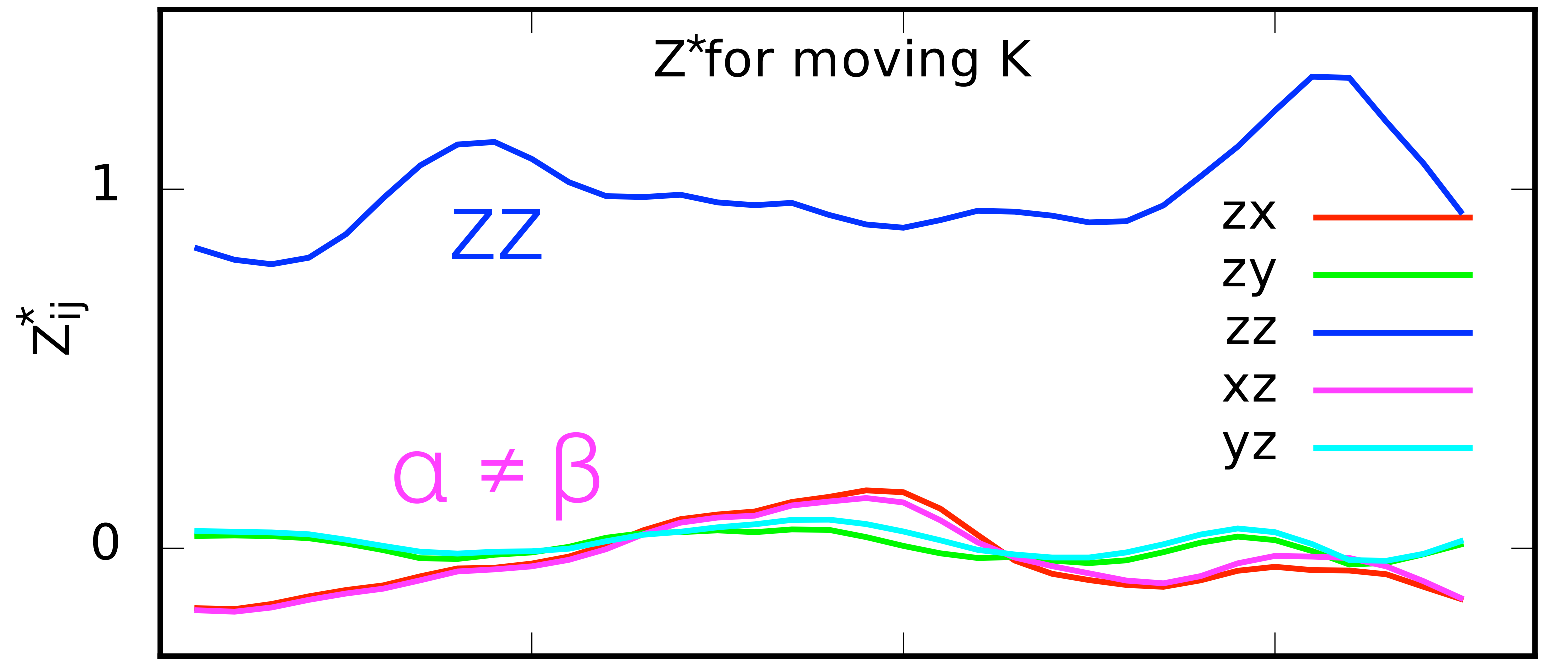

effective charge

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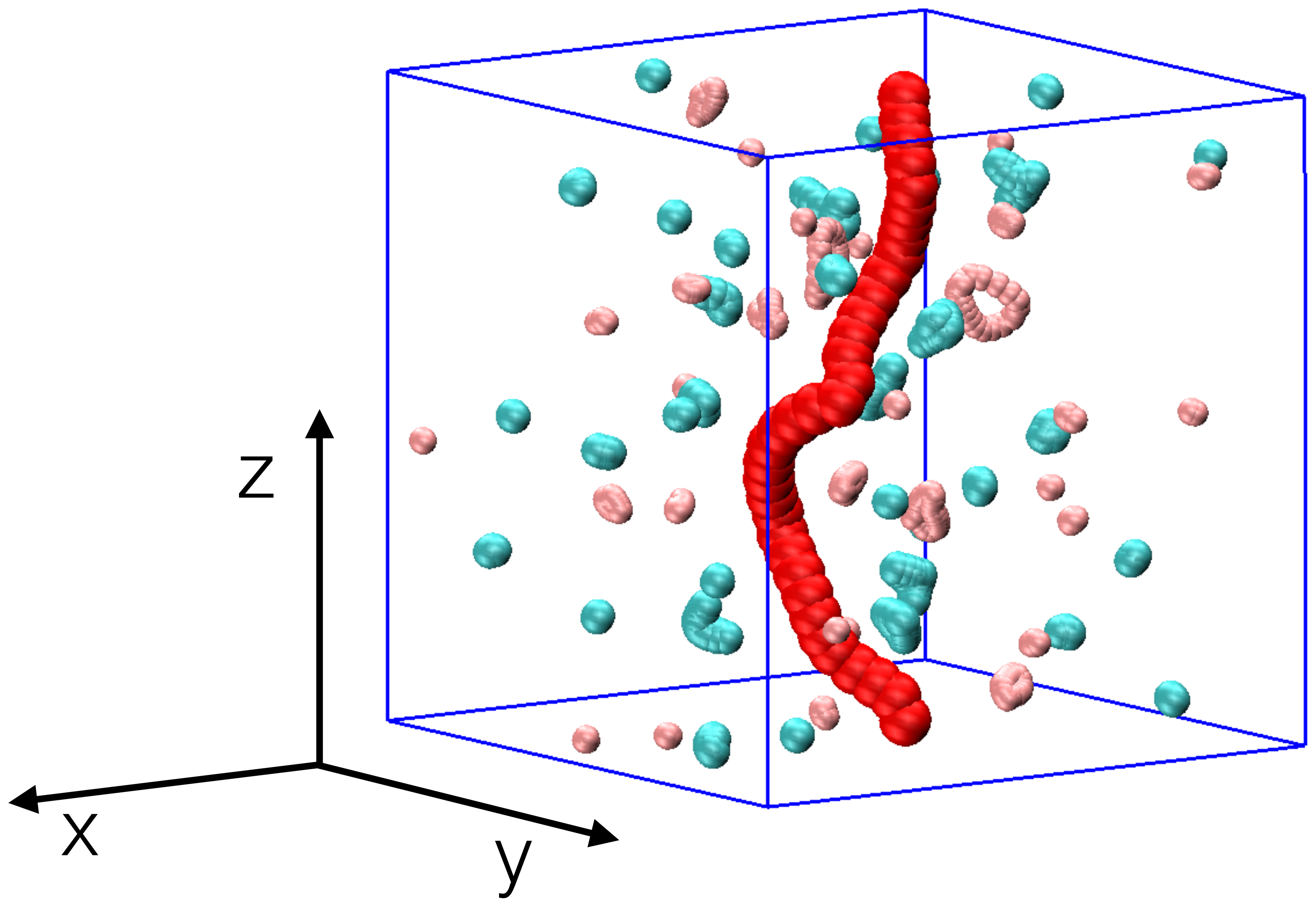

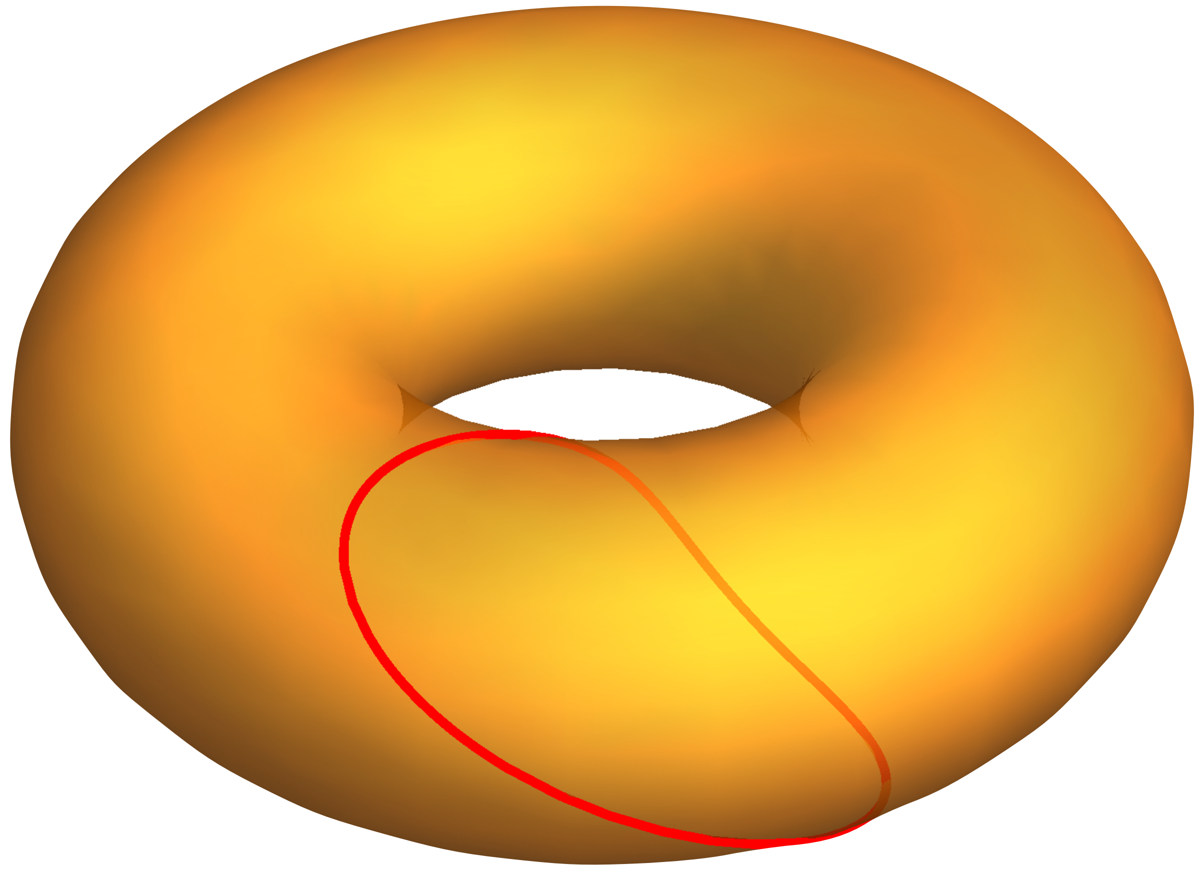

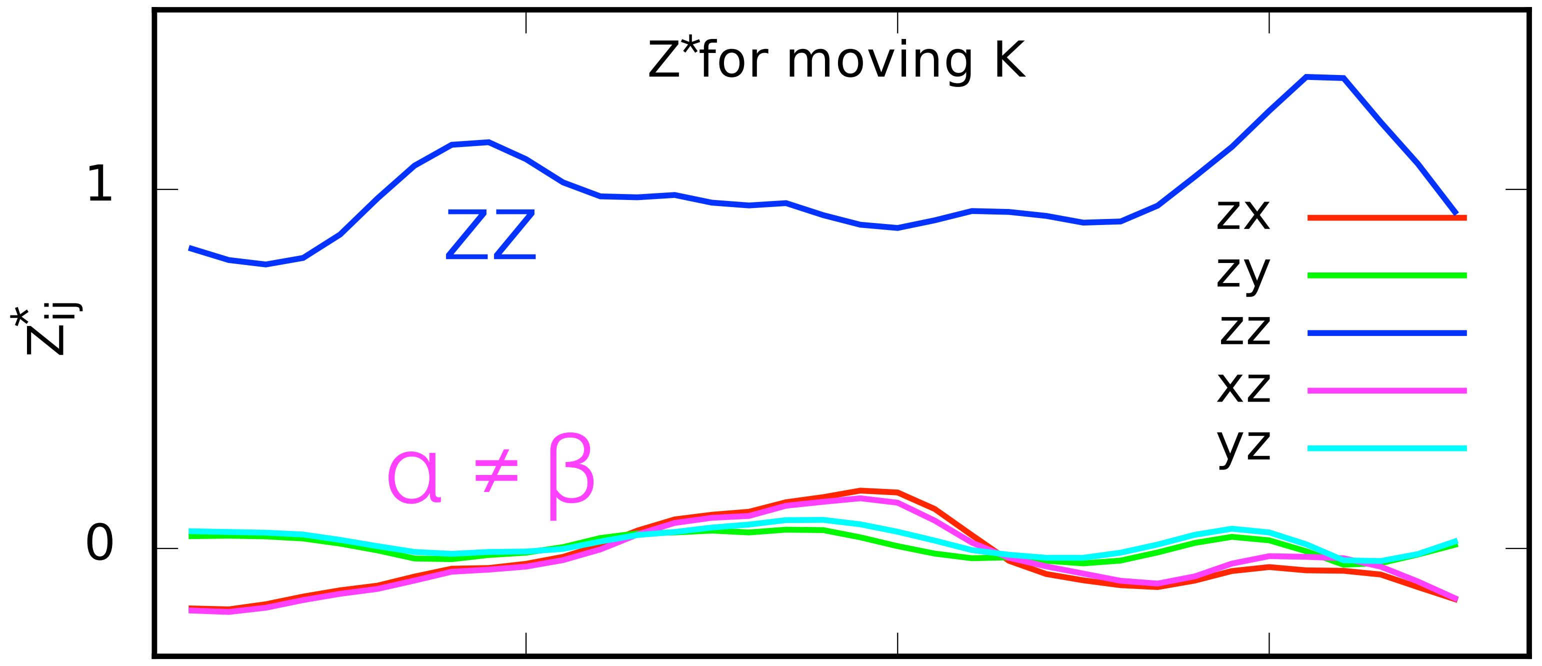

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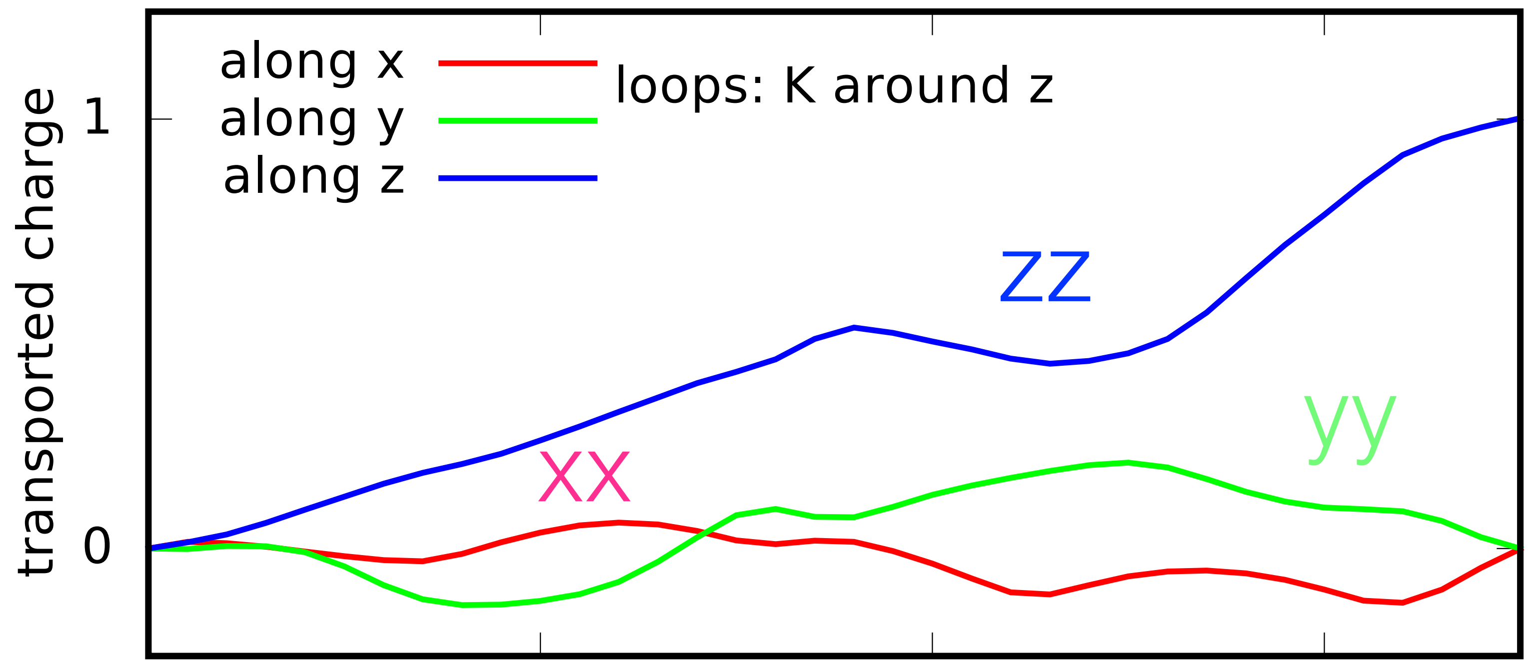

topological charge

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

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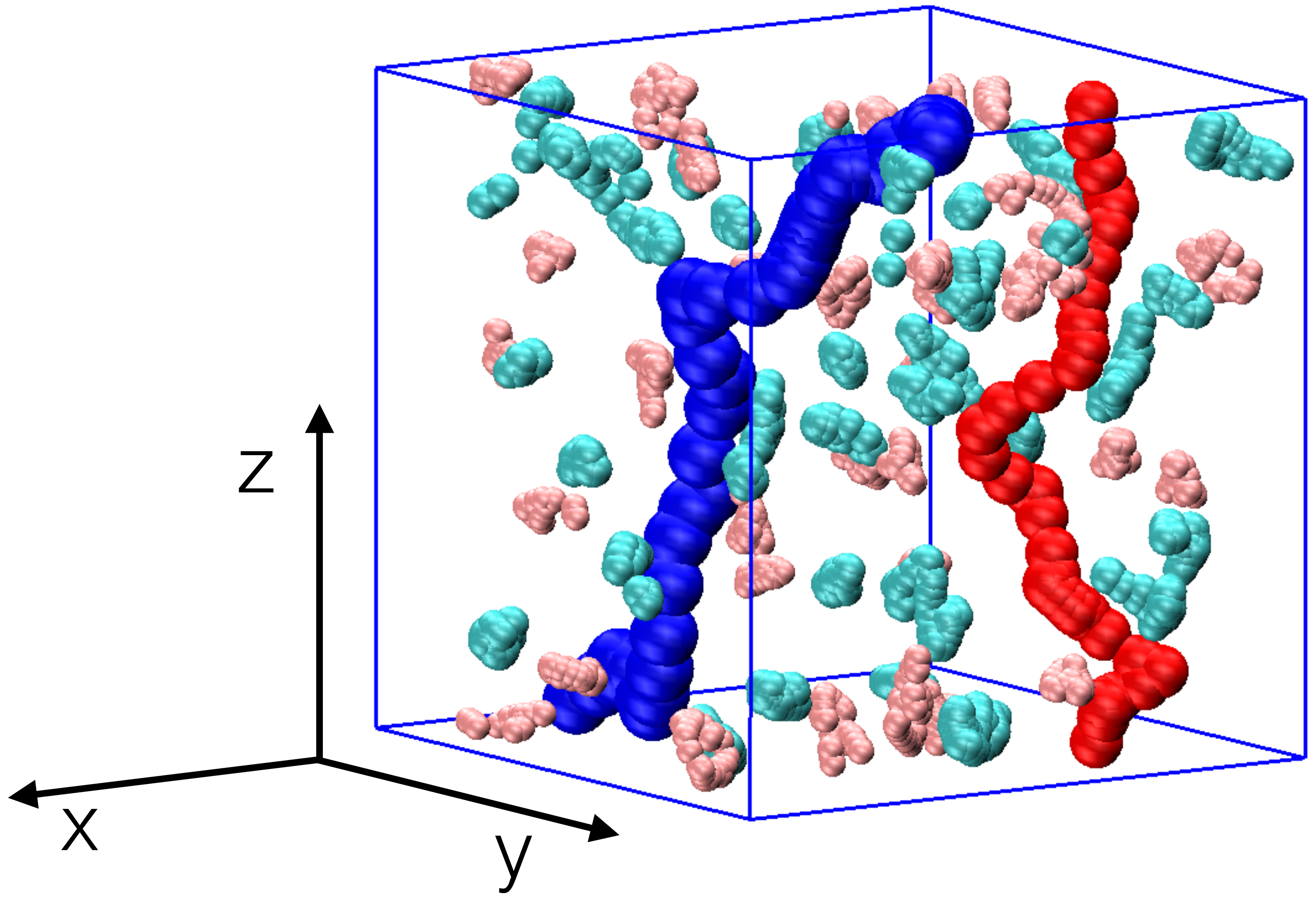
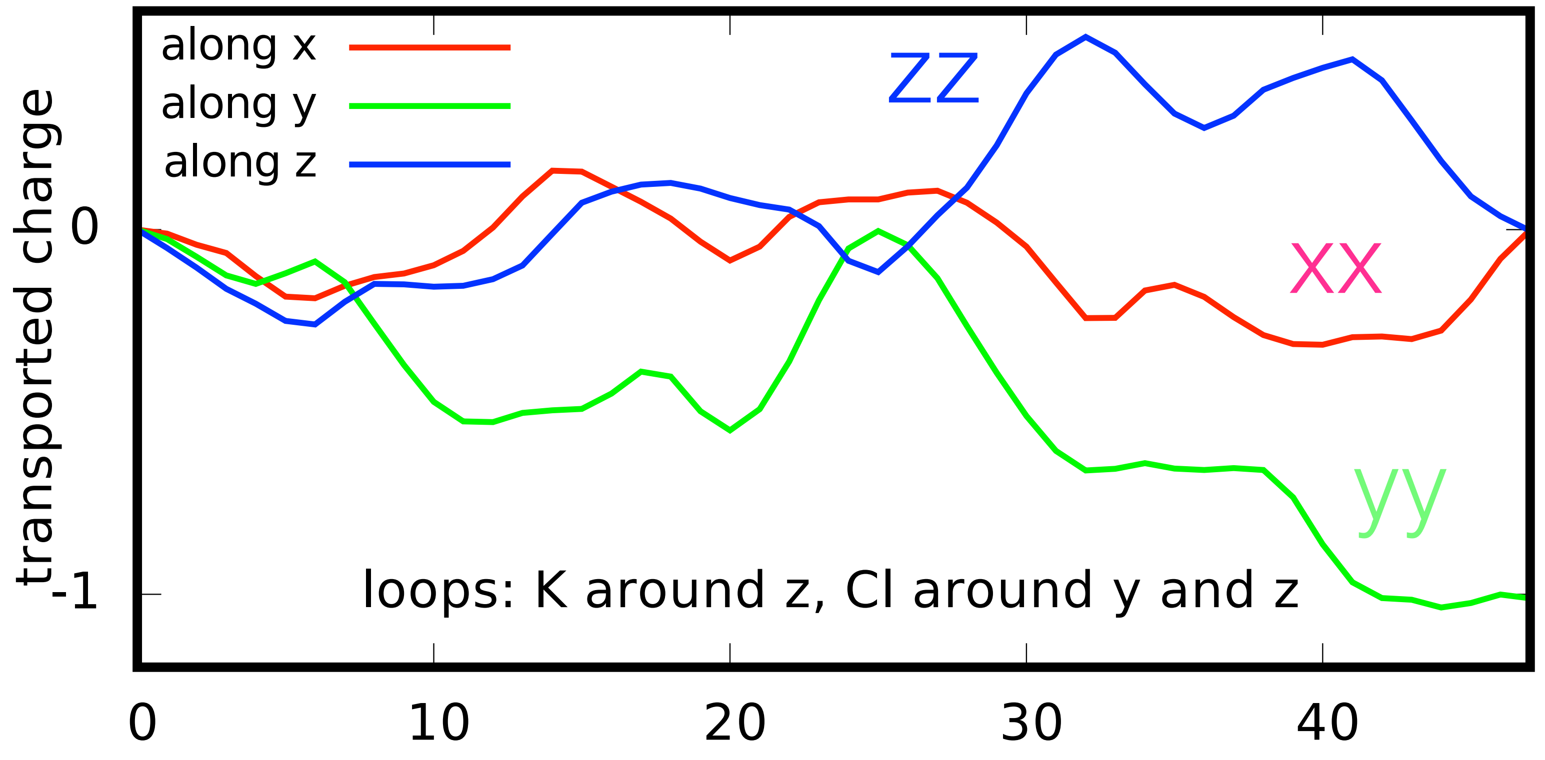
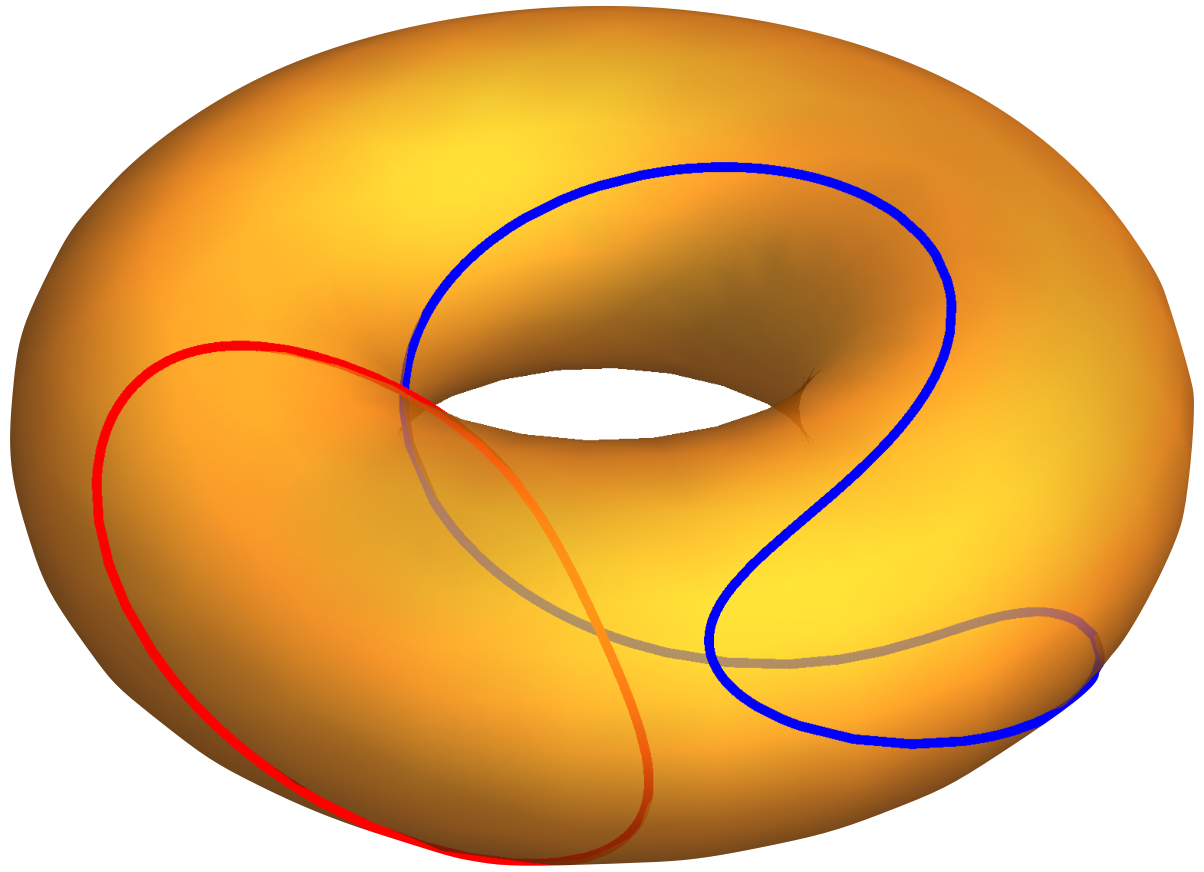


$Q_z[Cl]=-1 \quad Q_y[Cl]=-1$

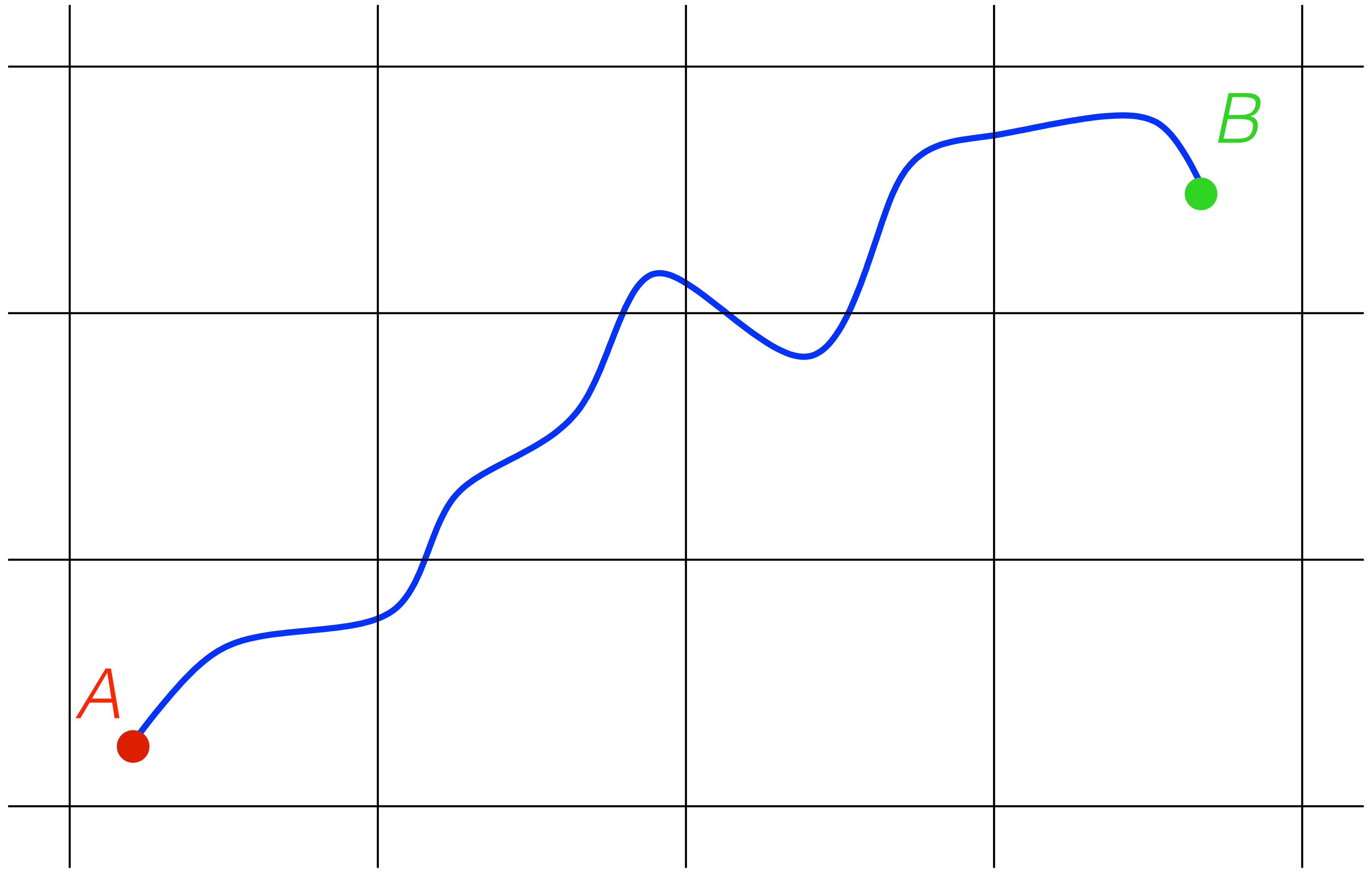
$Q_z[K] = 1 \quad Q_z[K] = 0$





the charges transported by K and Cl around z cancel exactly

gauge invariance of charge transport



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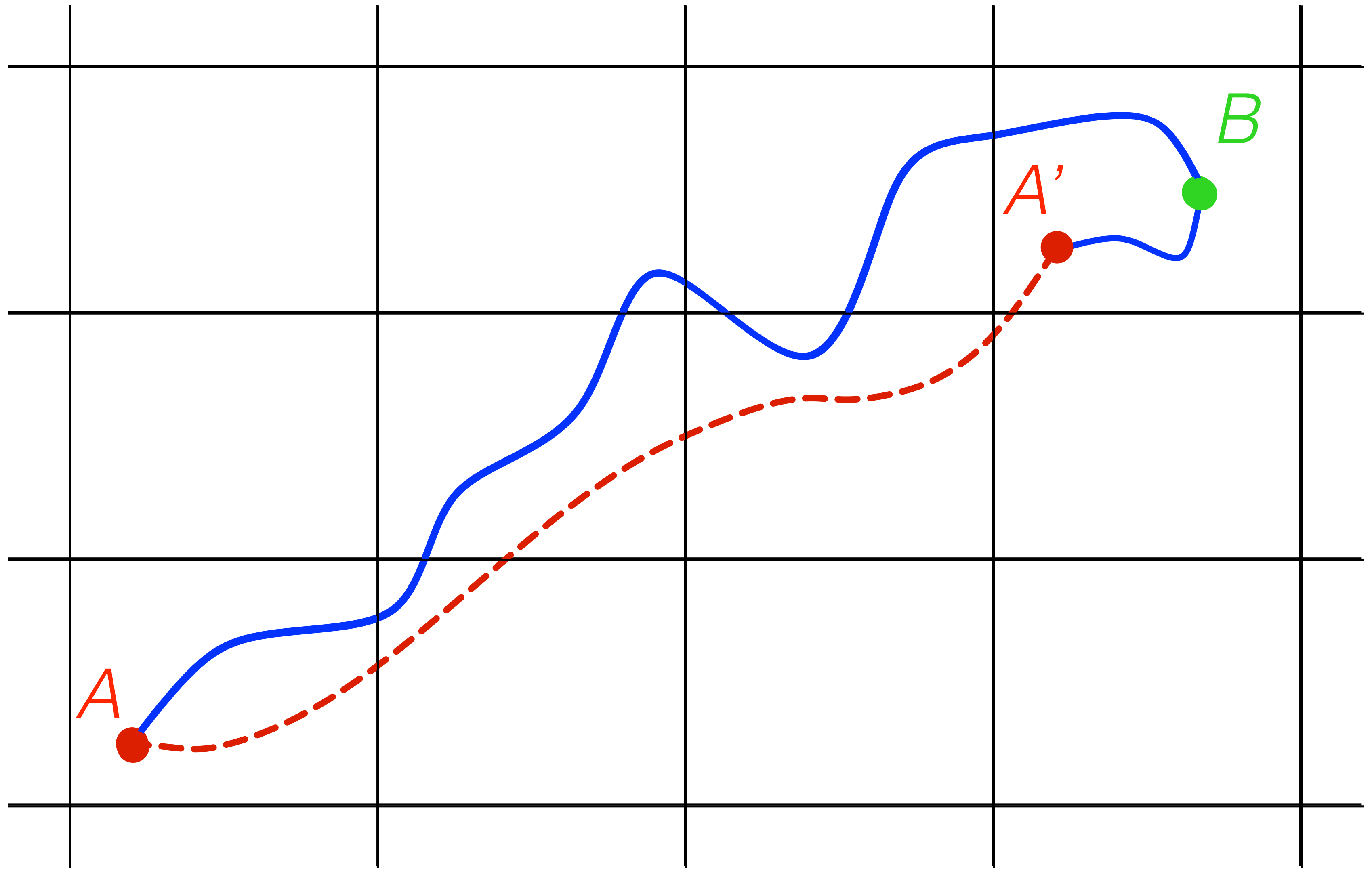

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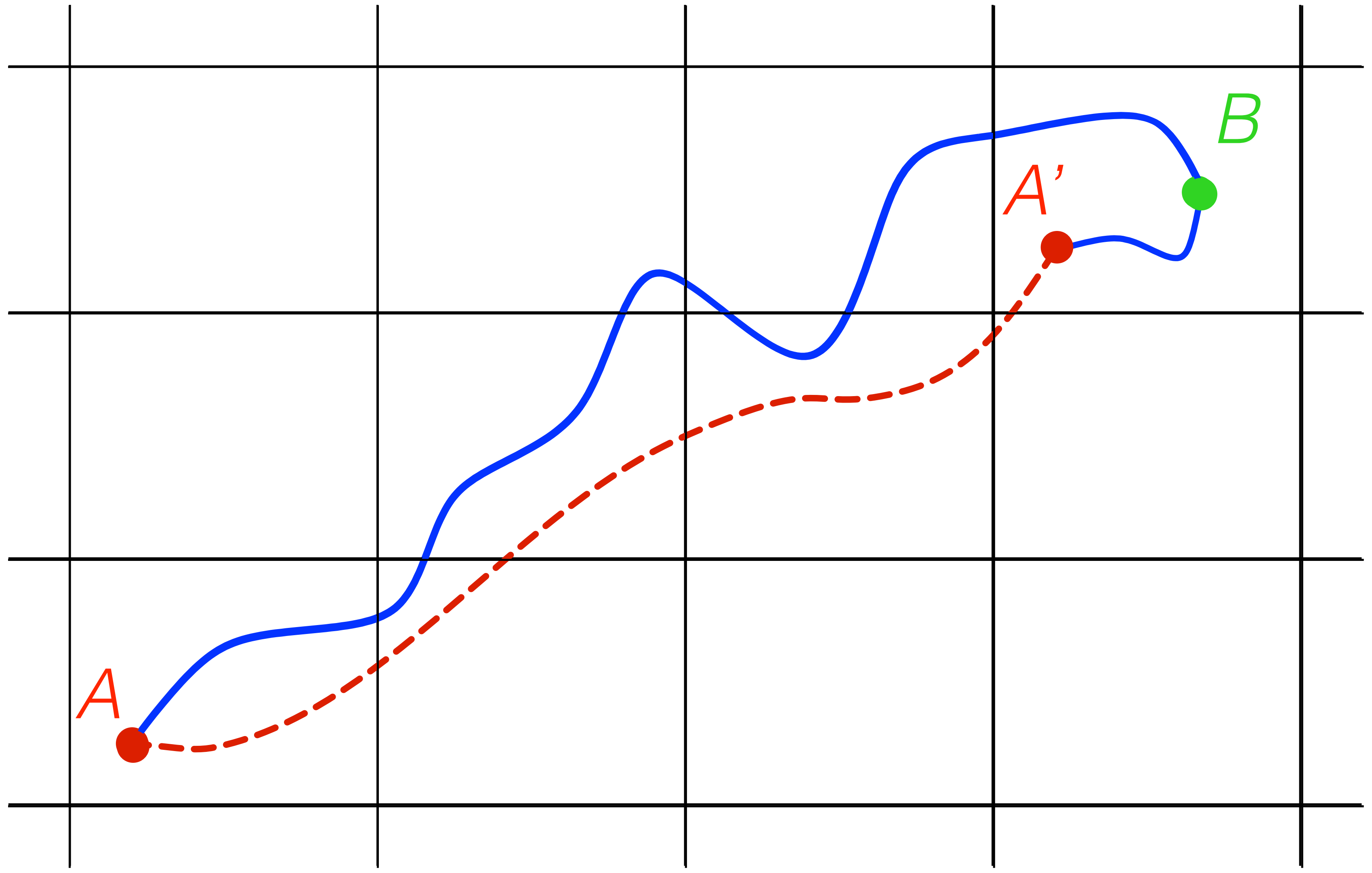

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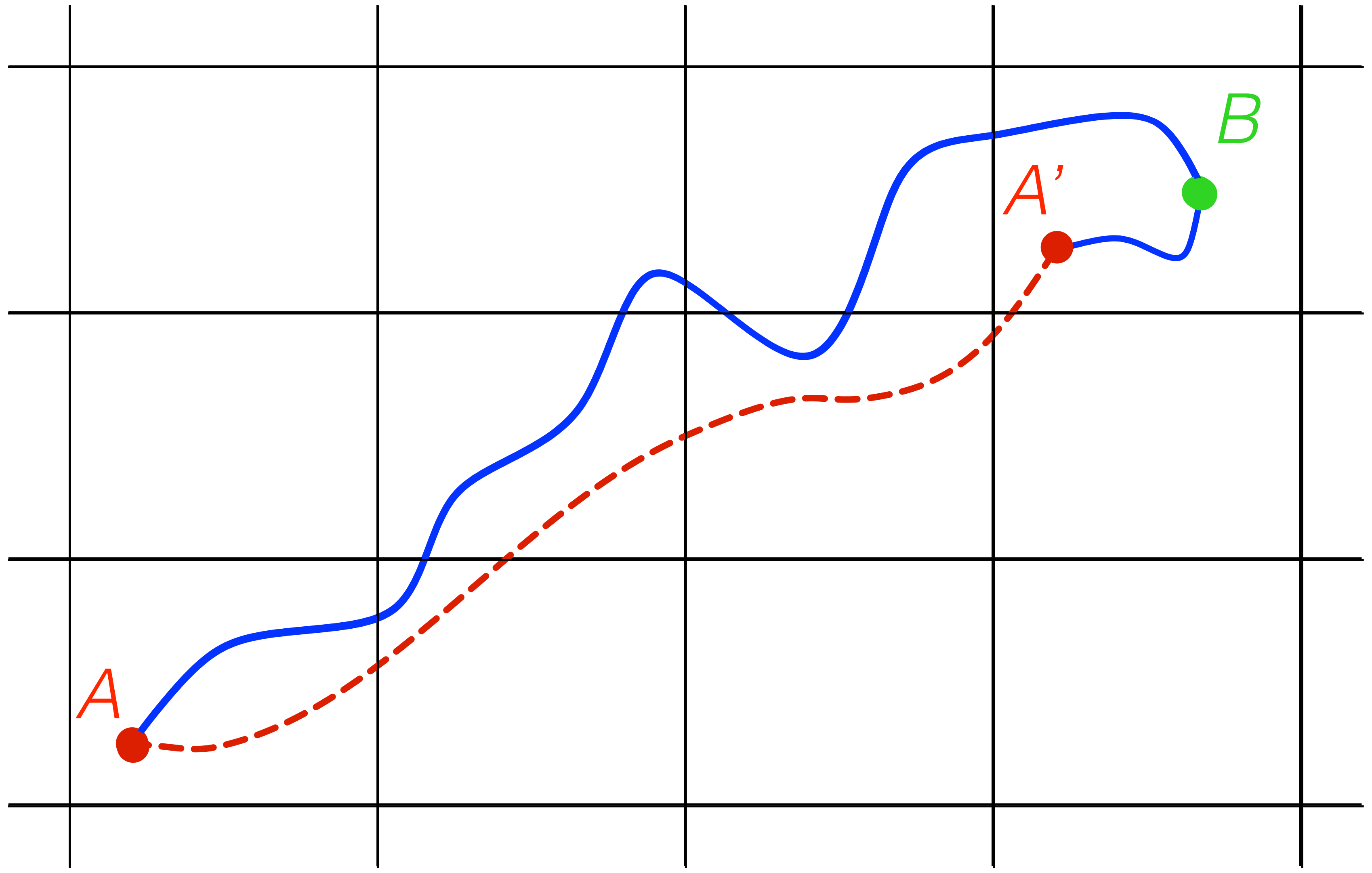

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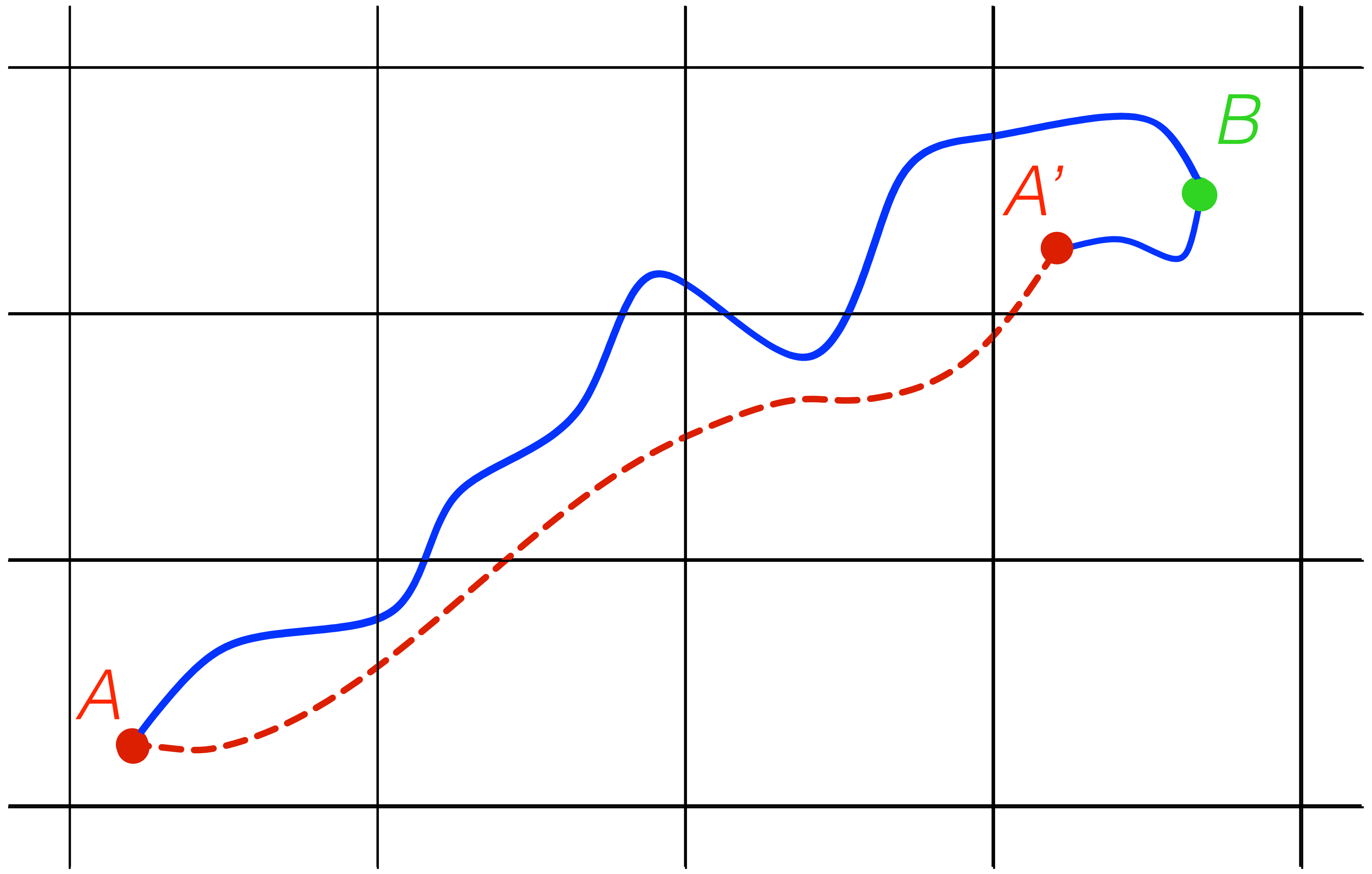

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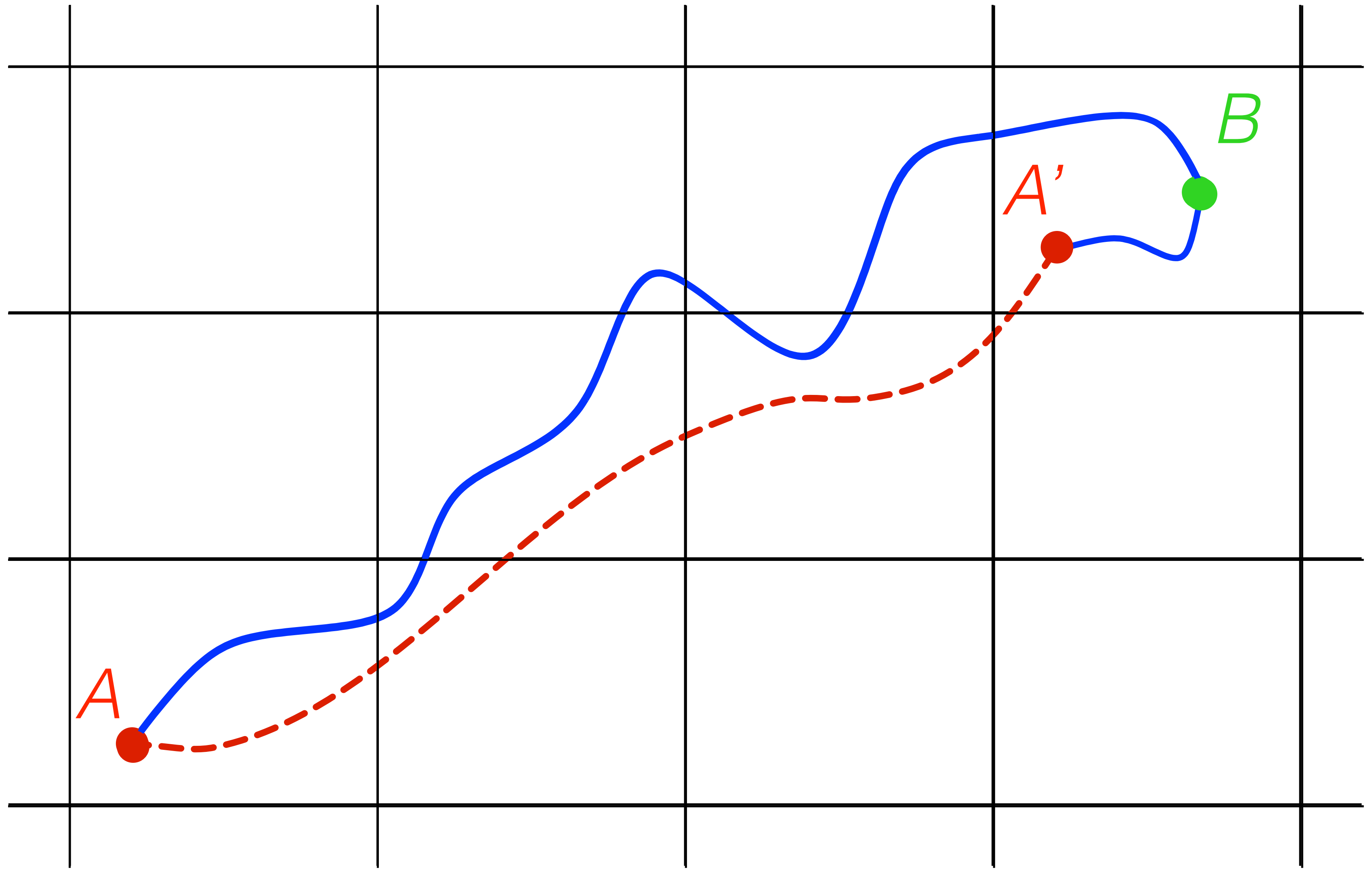

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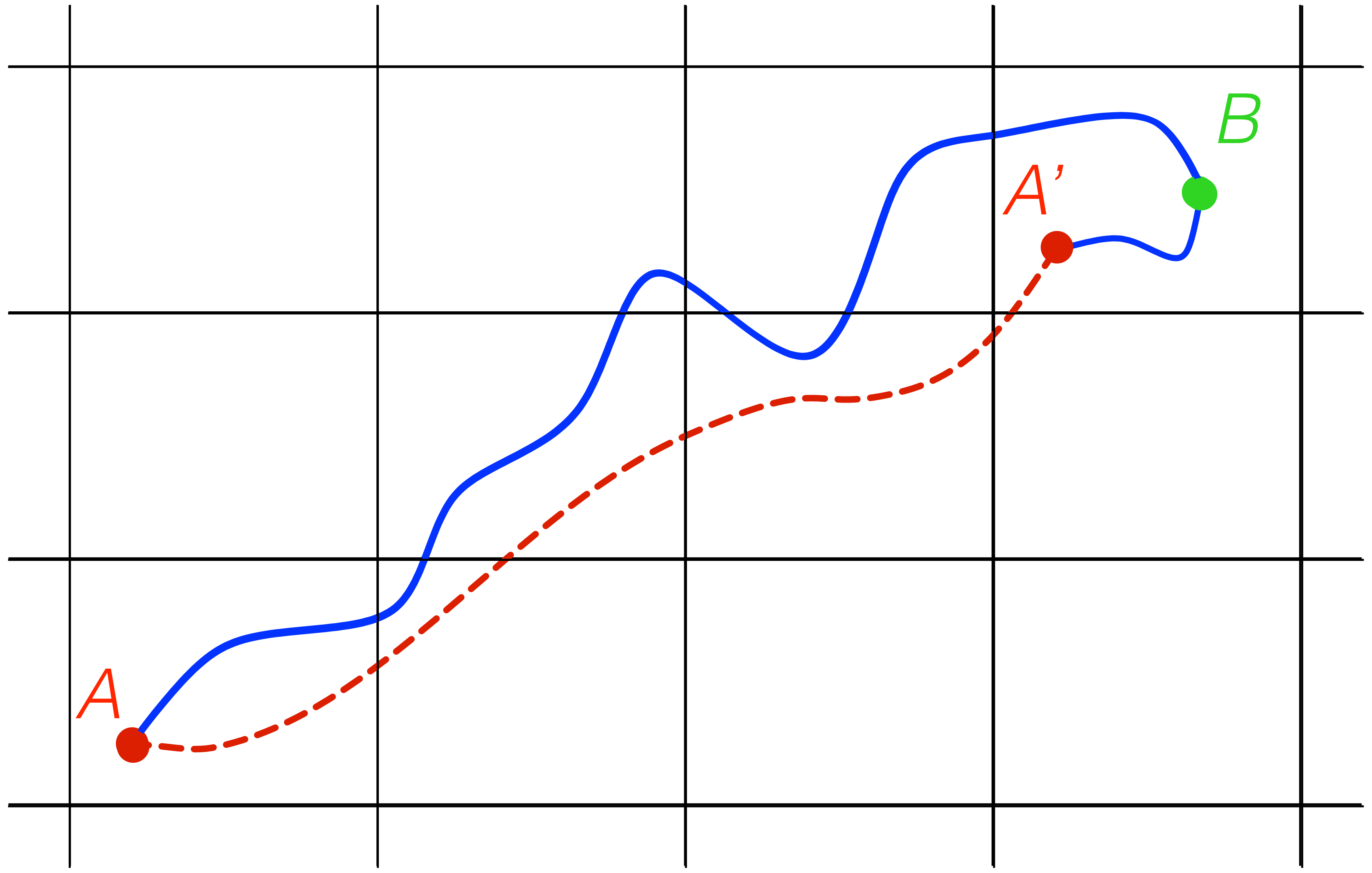

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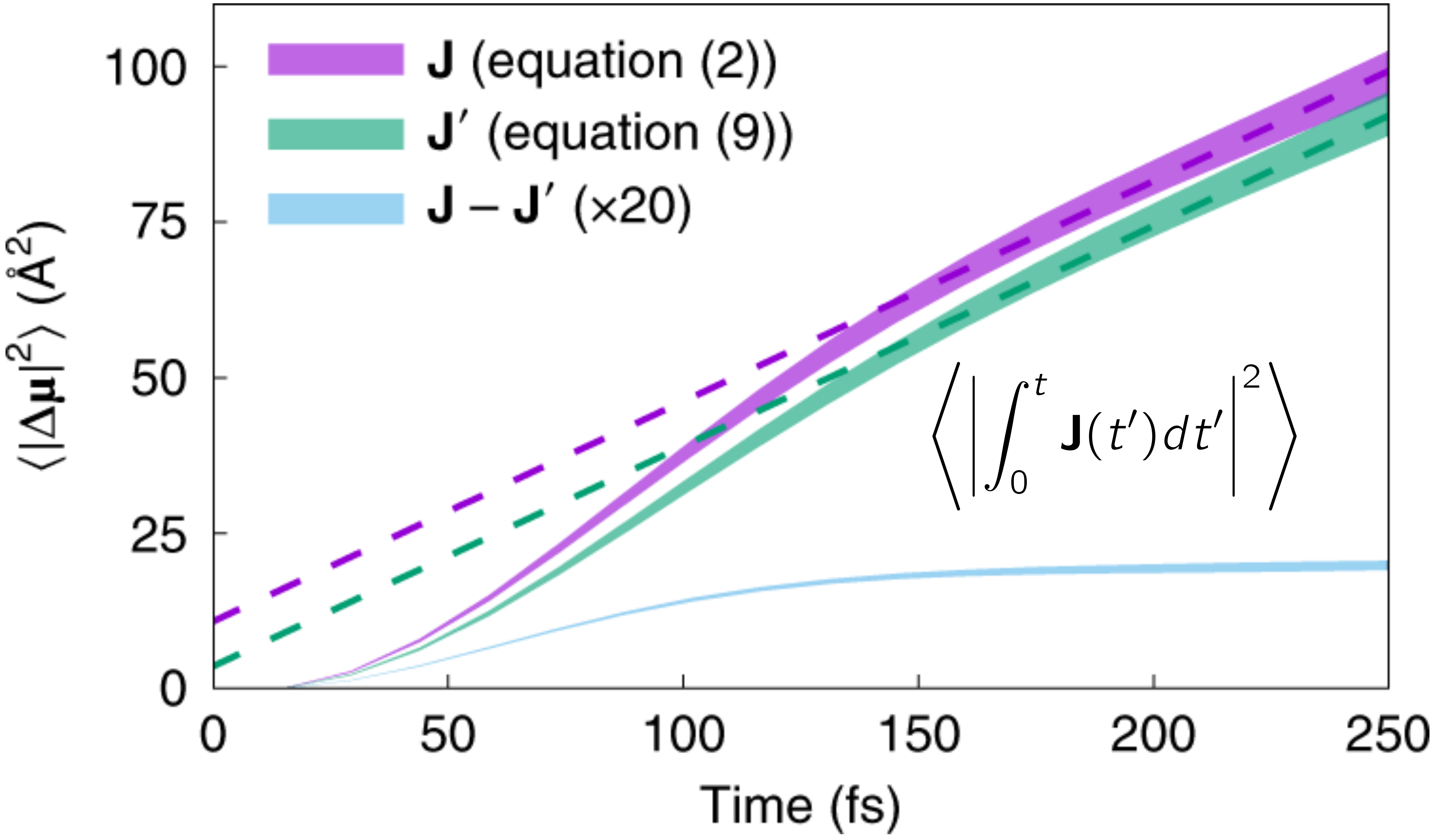
$$\boxed{\sigma = \sigma'}$$

currents from atomic oxidation numbers

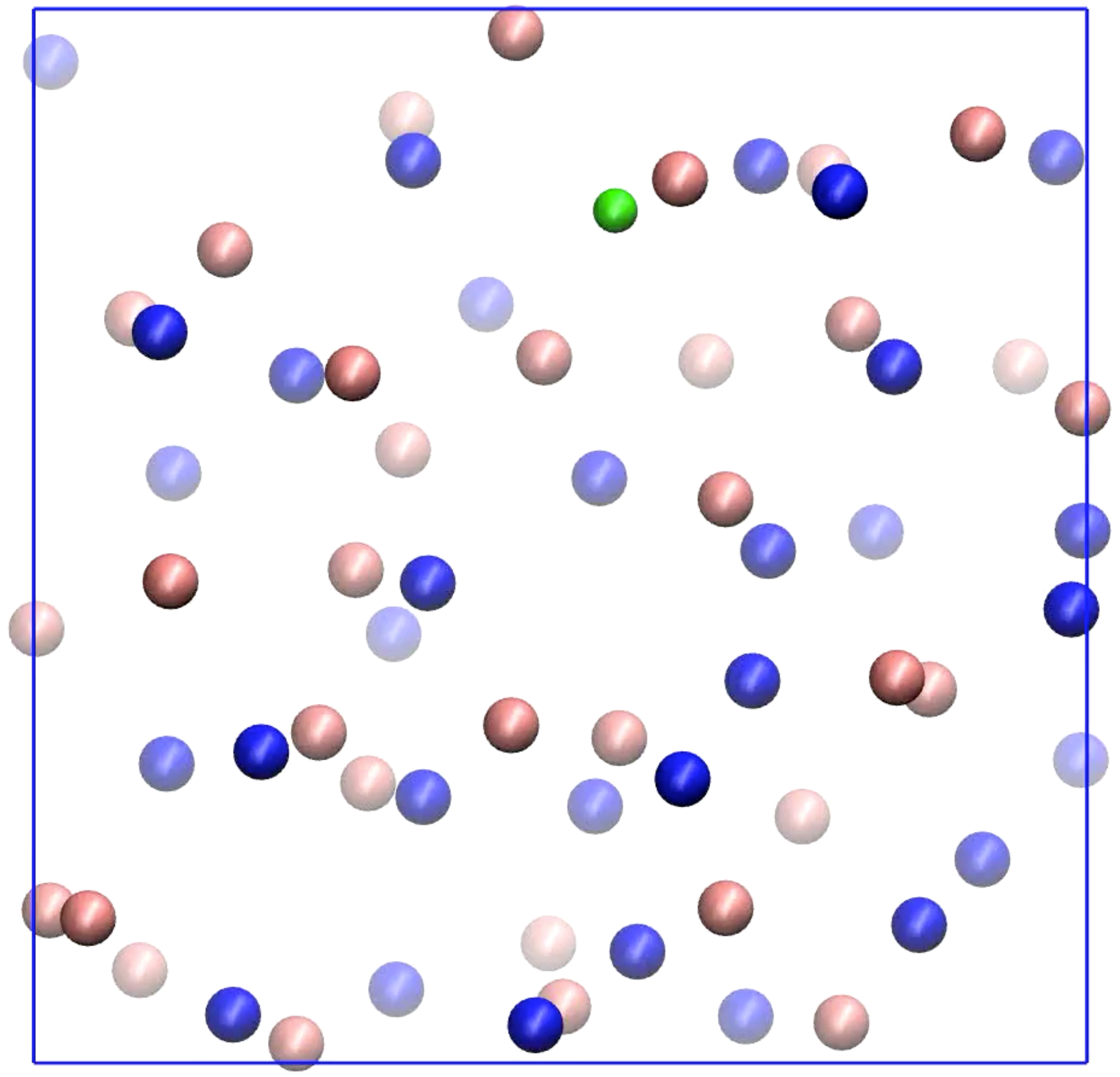
(2) $$J_\alpha = \sum_{i\beta} Z^*_{i\alpha\beta} v_{i\beta}$$

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



non-stoichiometric melts

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



$K_{33}Cl_{31}$

$x \approx 0.06$

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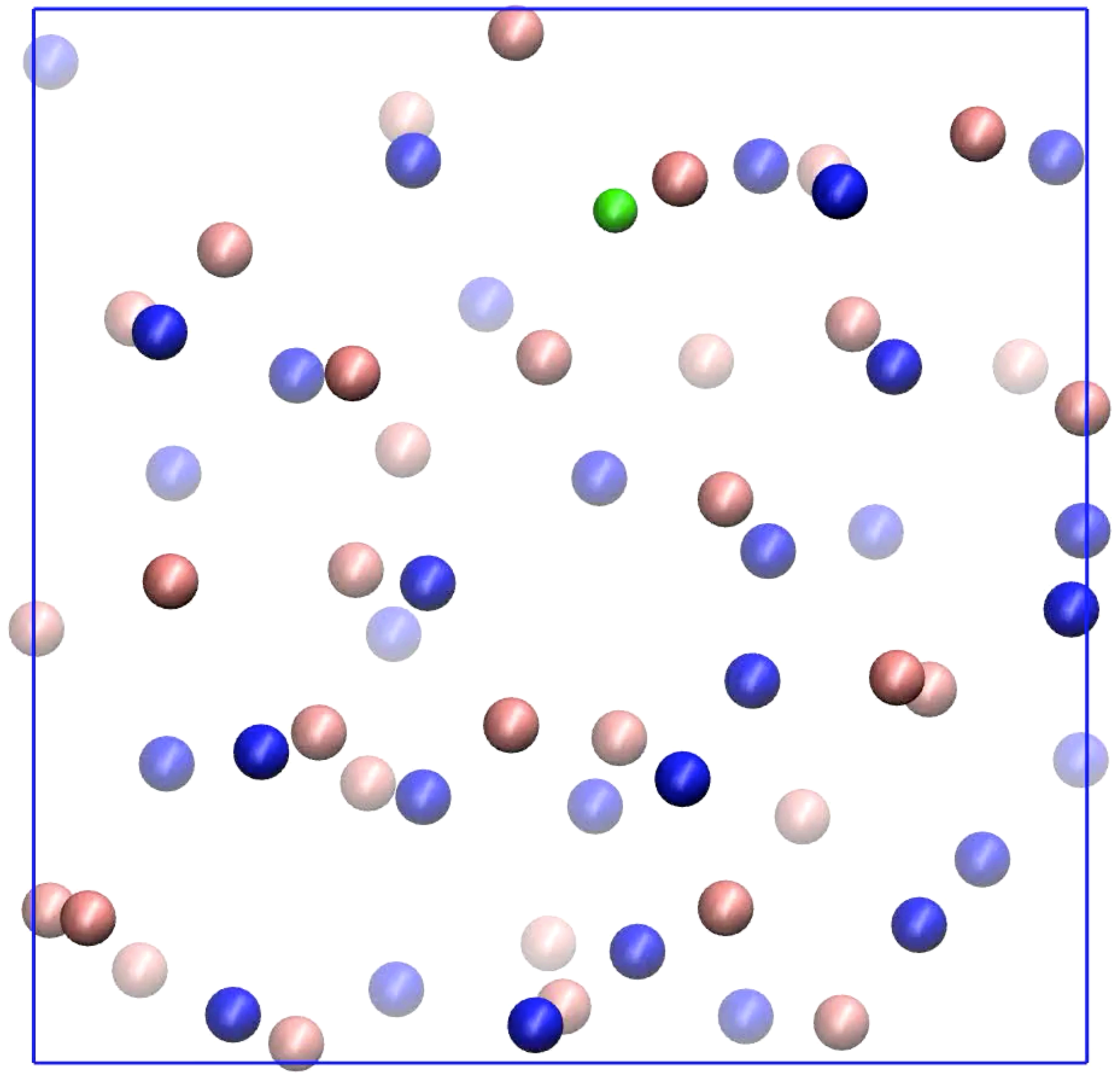

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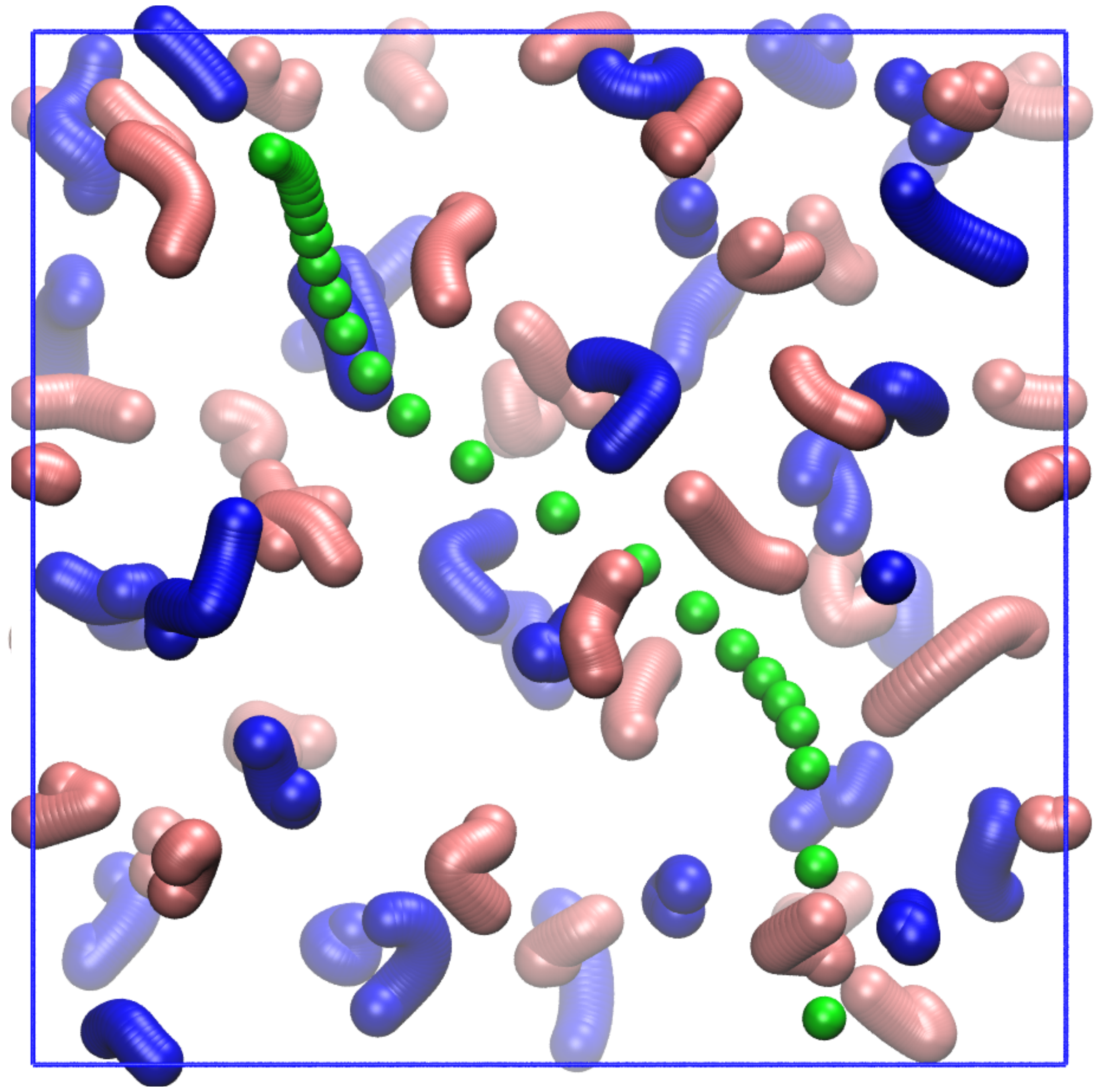

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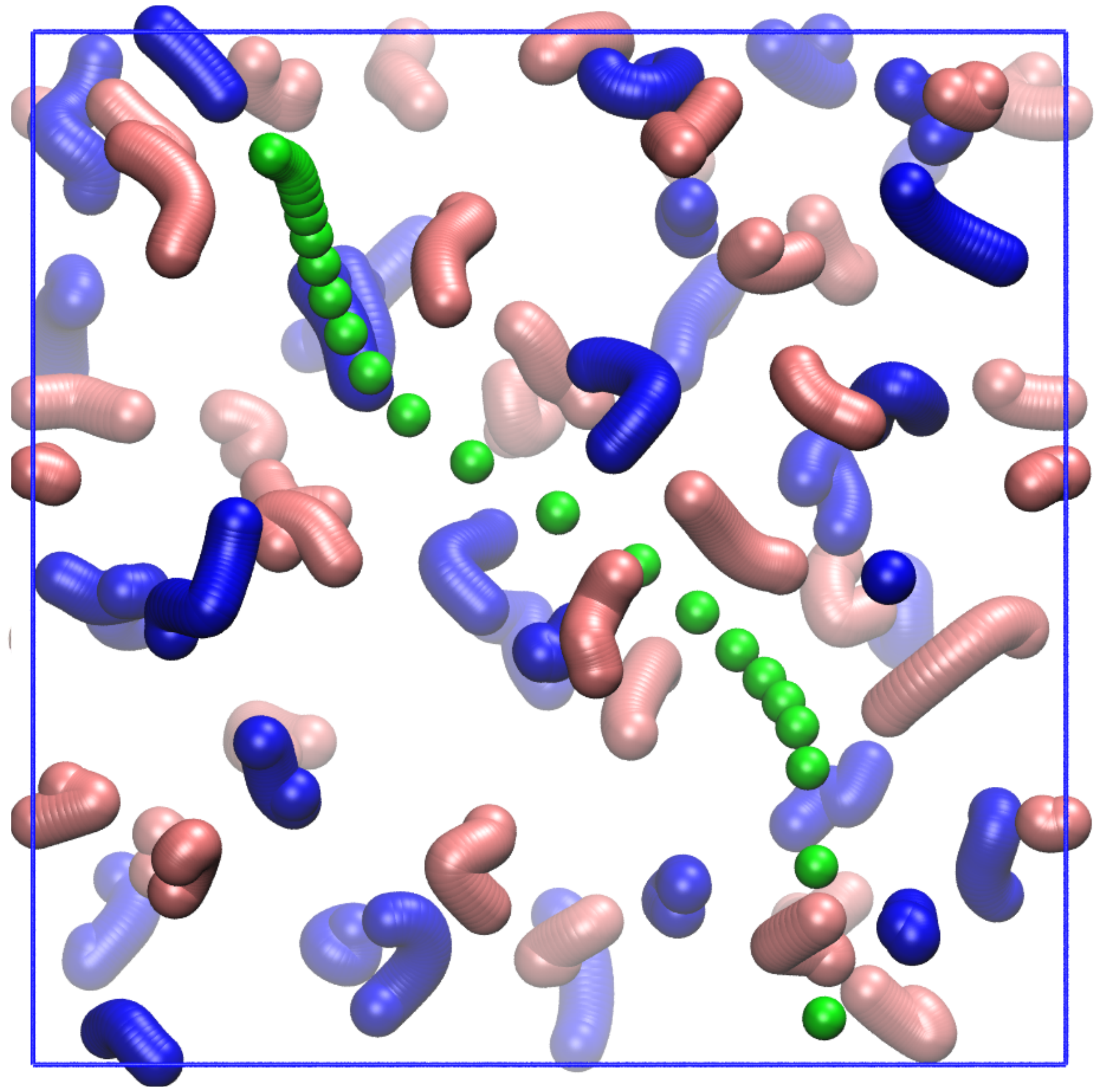

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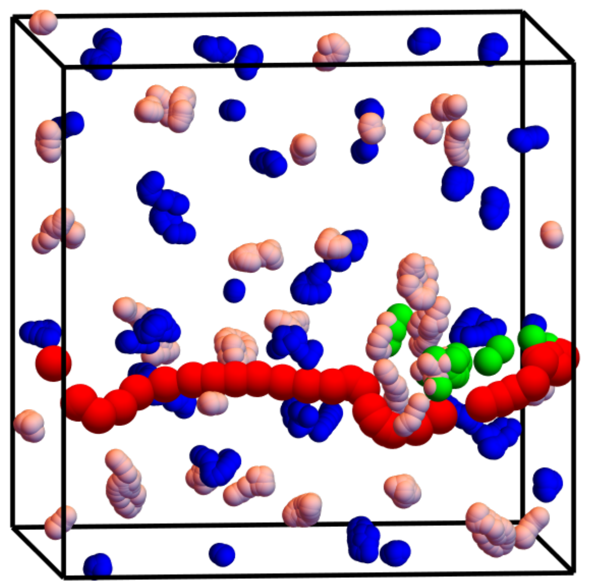

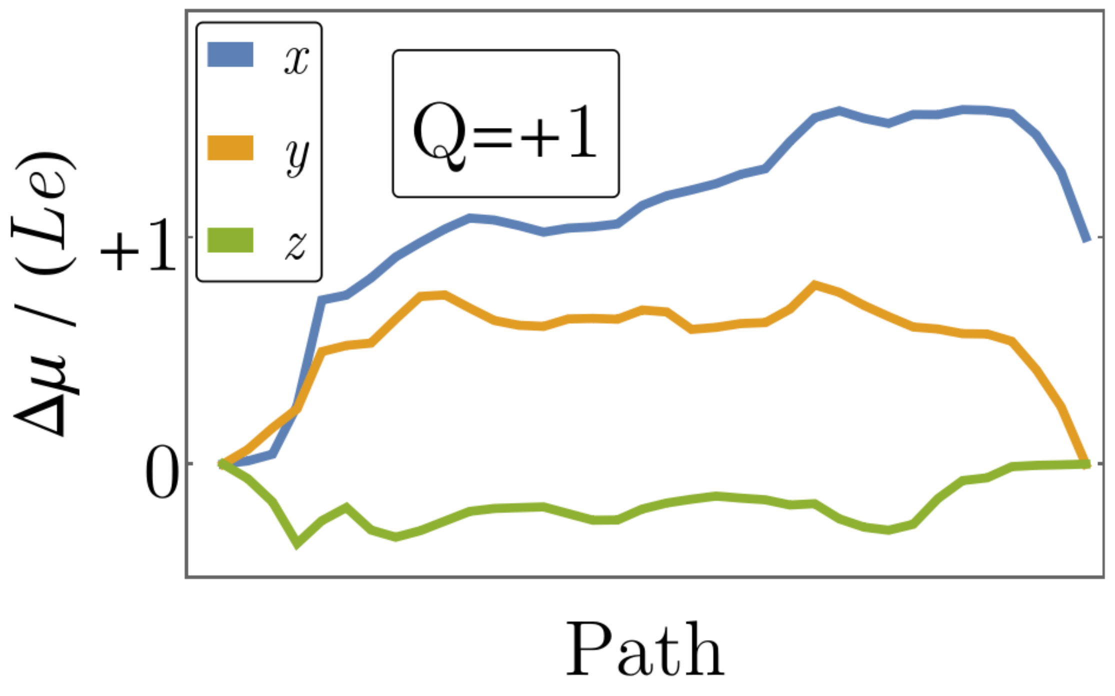

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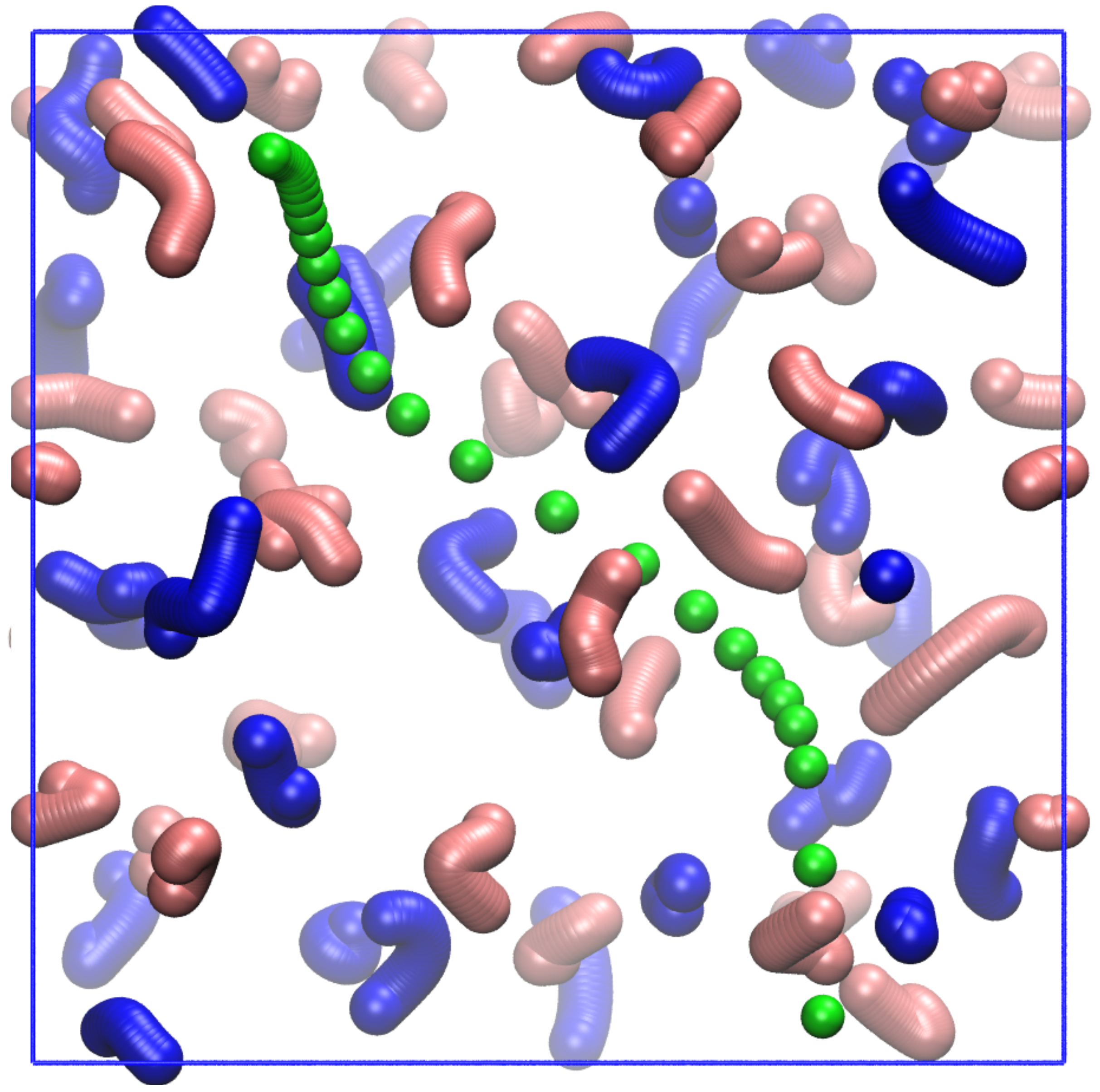

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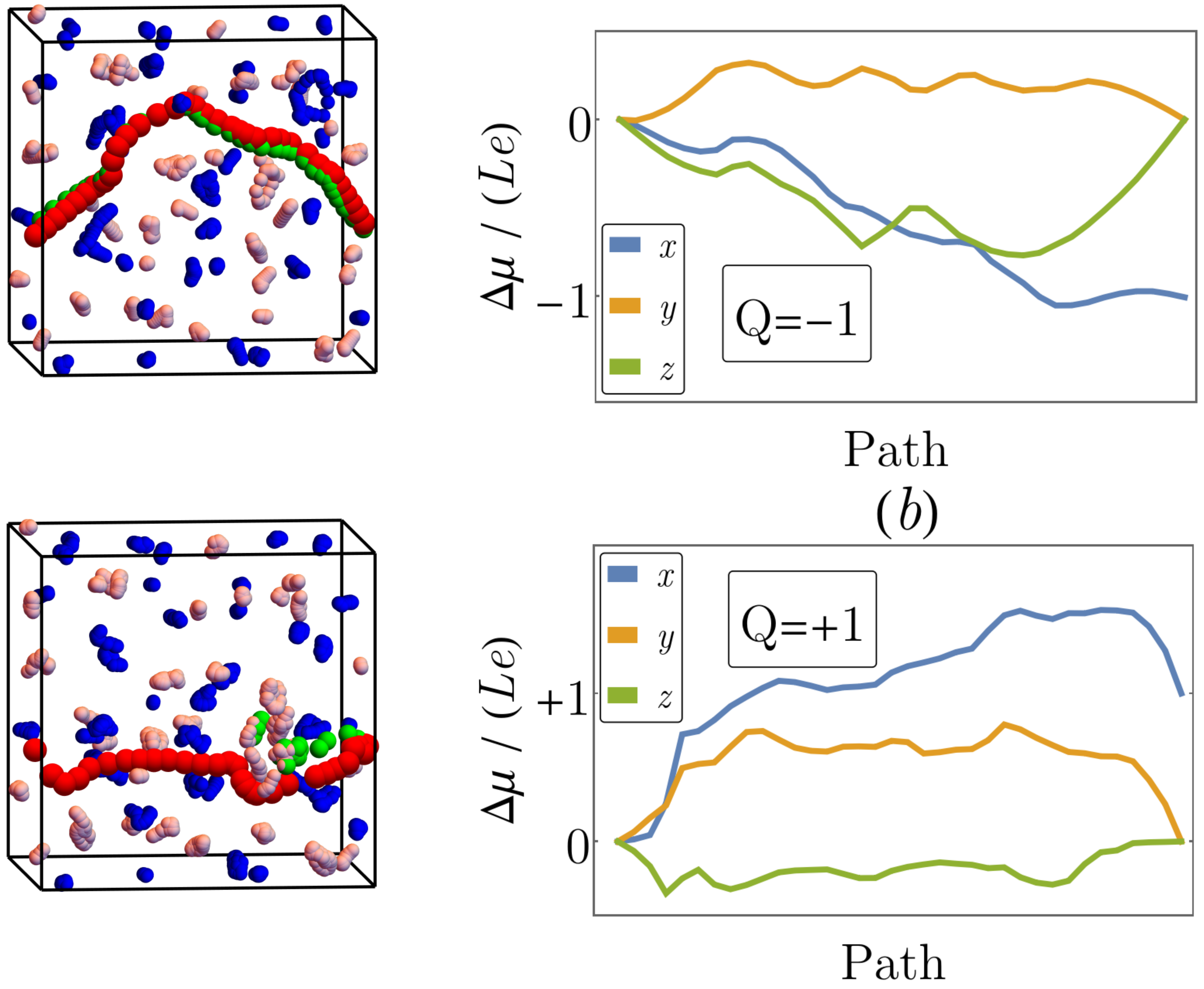
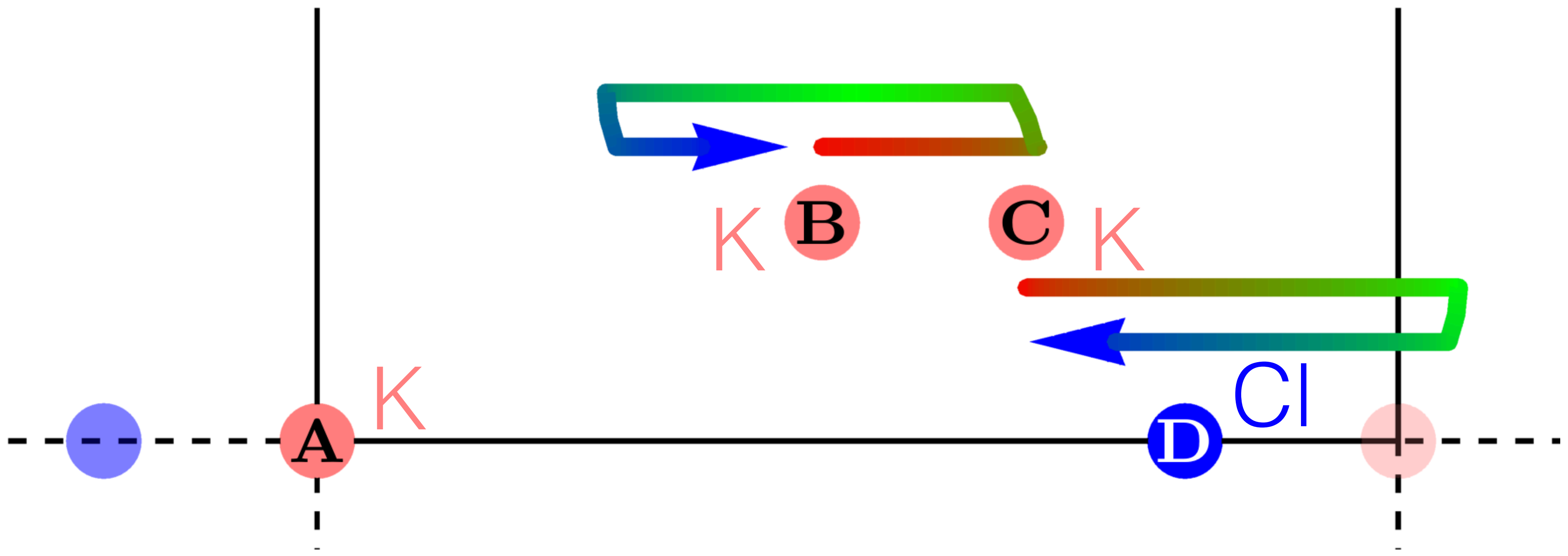
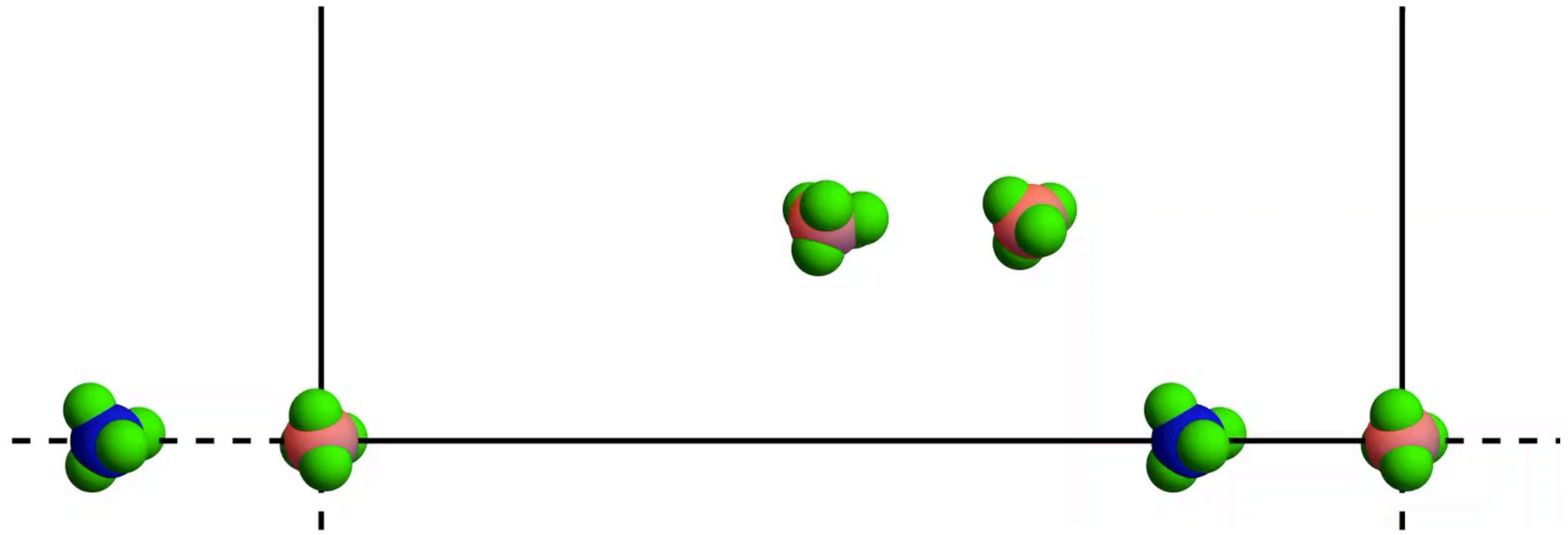
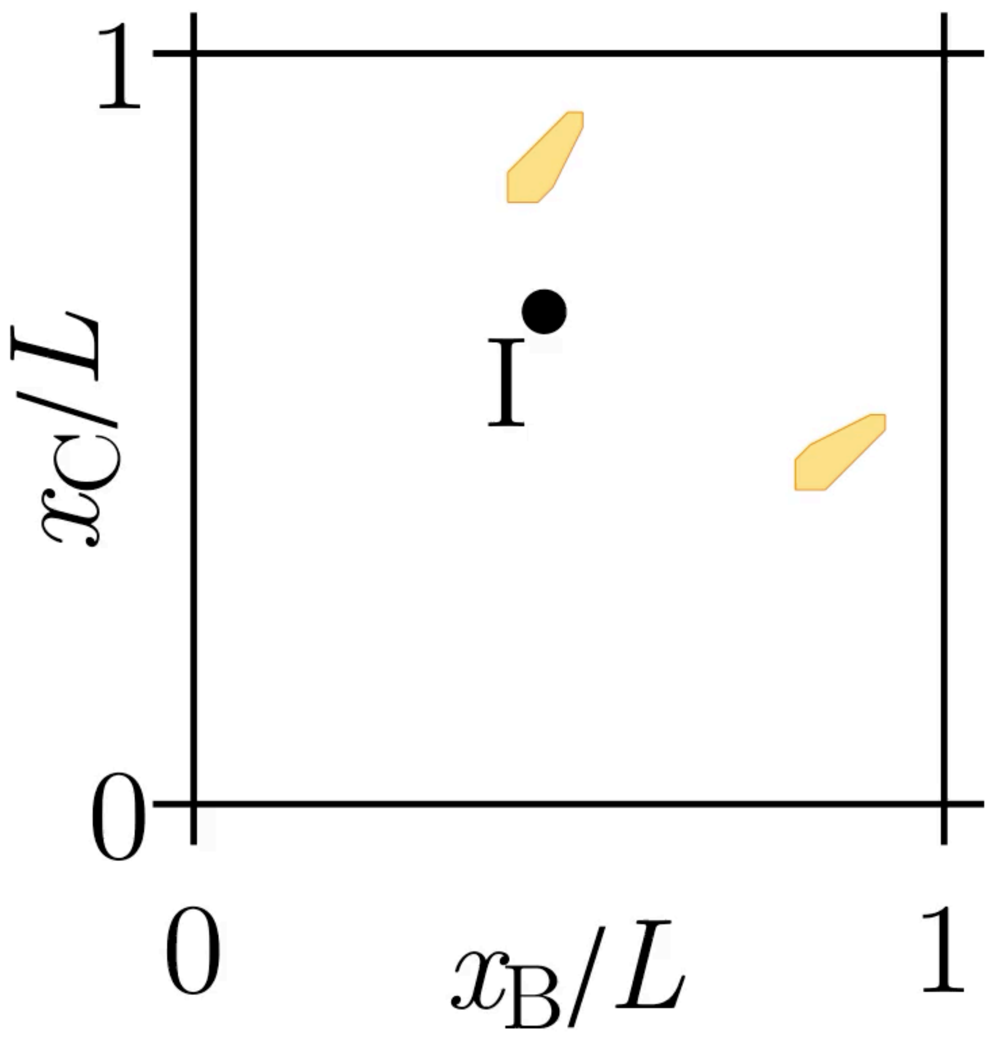


non-trivial particle transport







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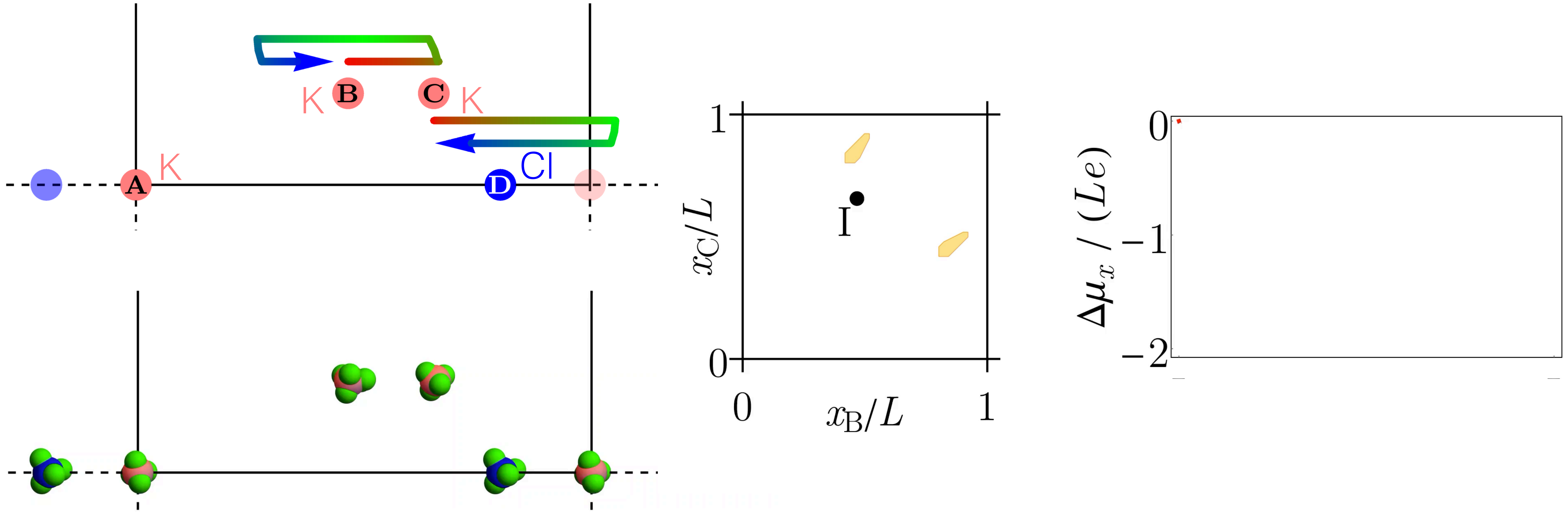

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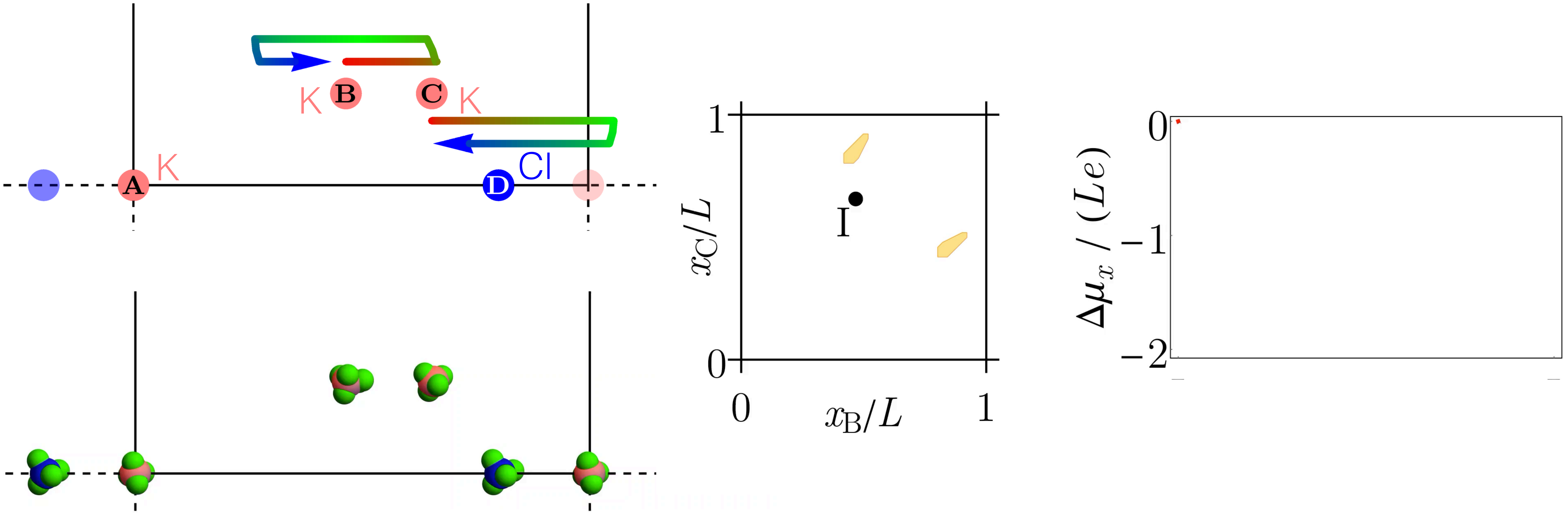
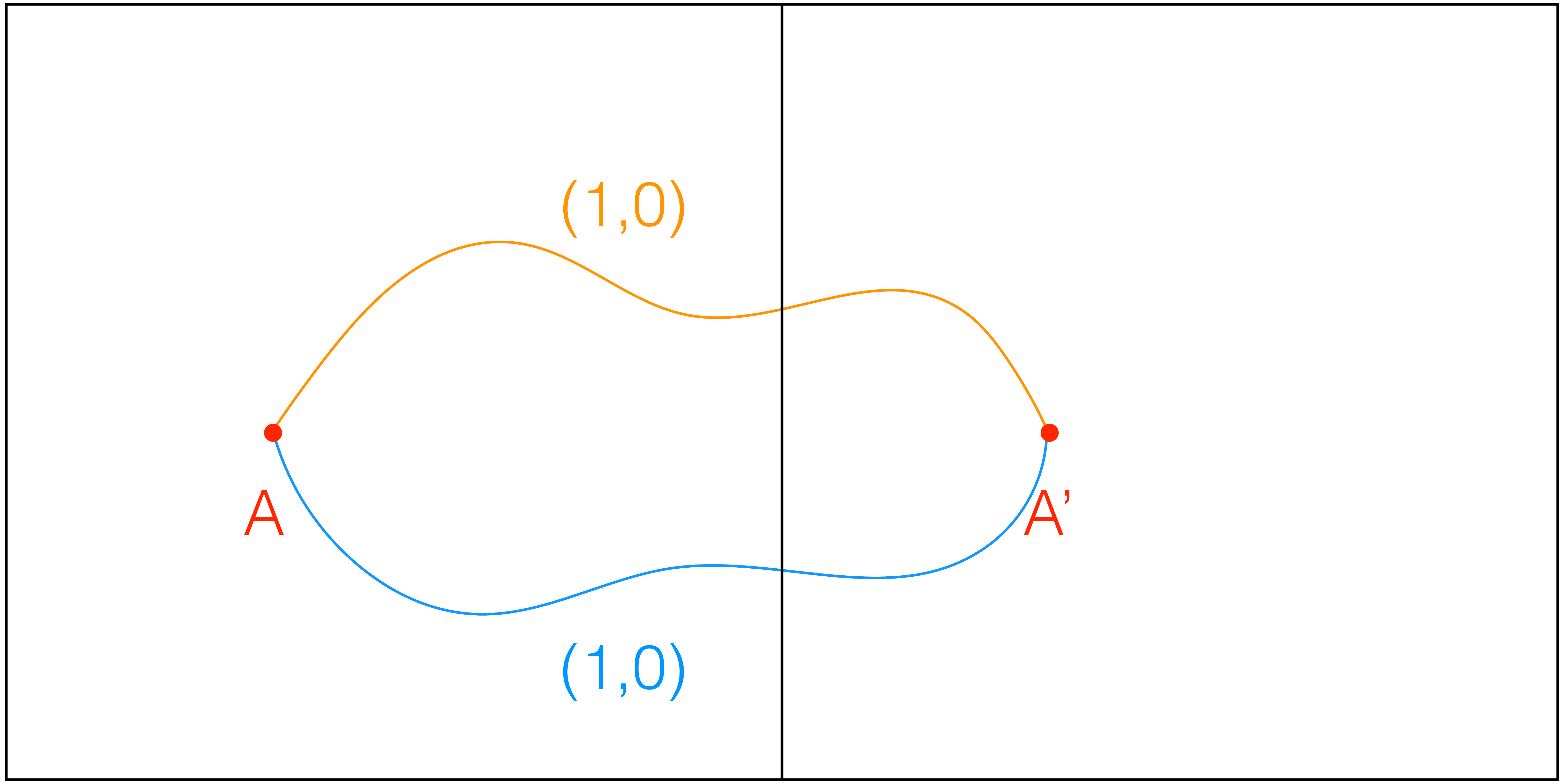


breach of strong adiabaticity



$$\mu = \mu^*$$

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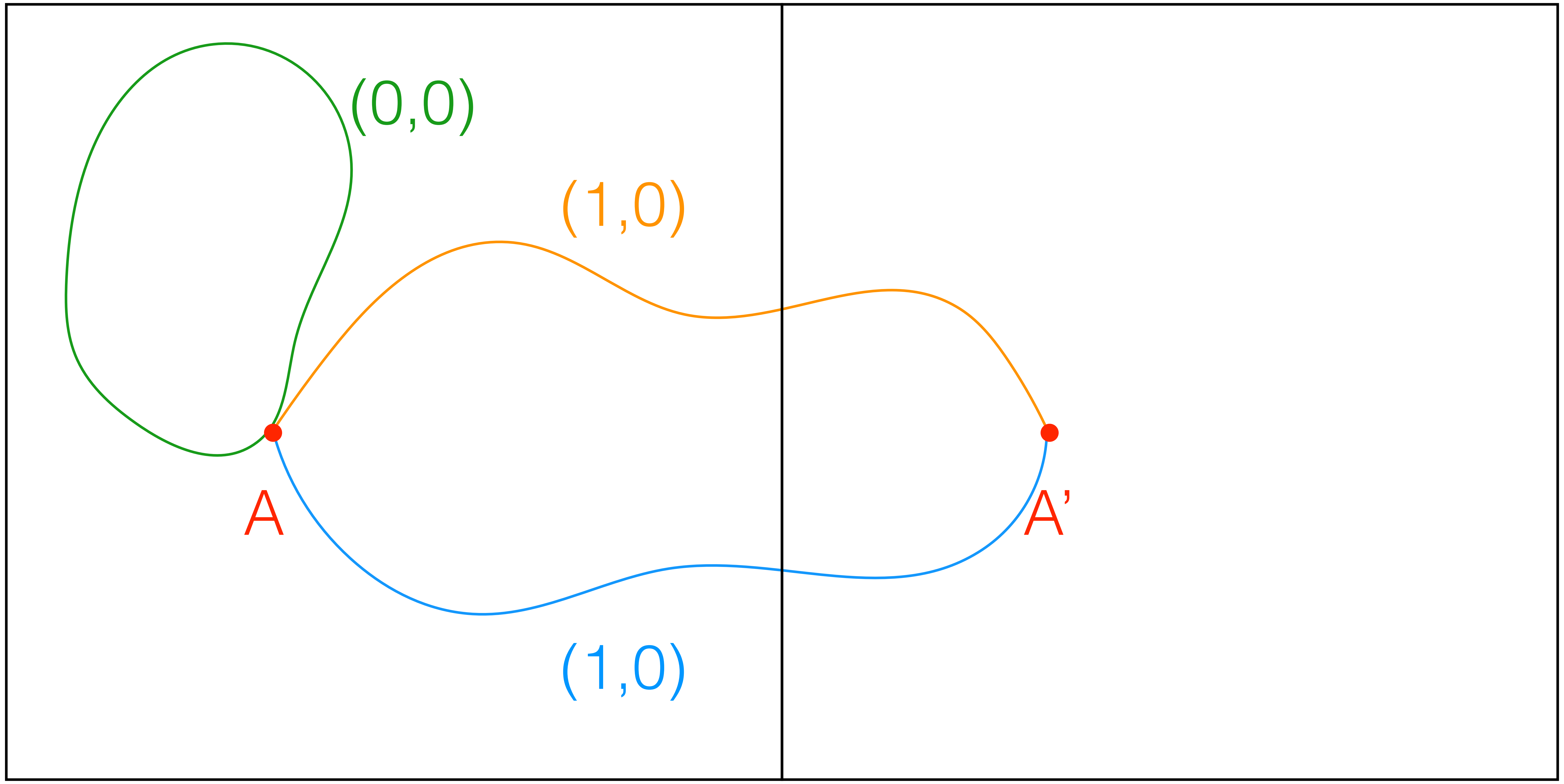

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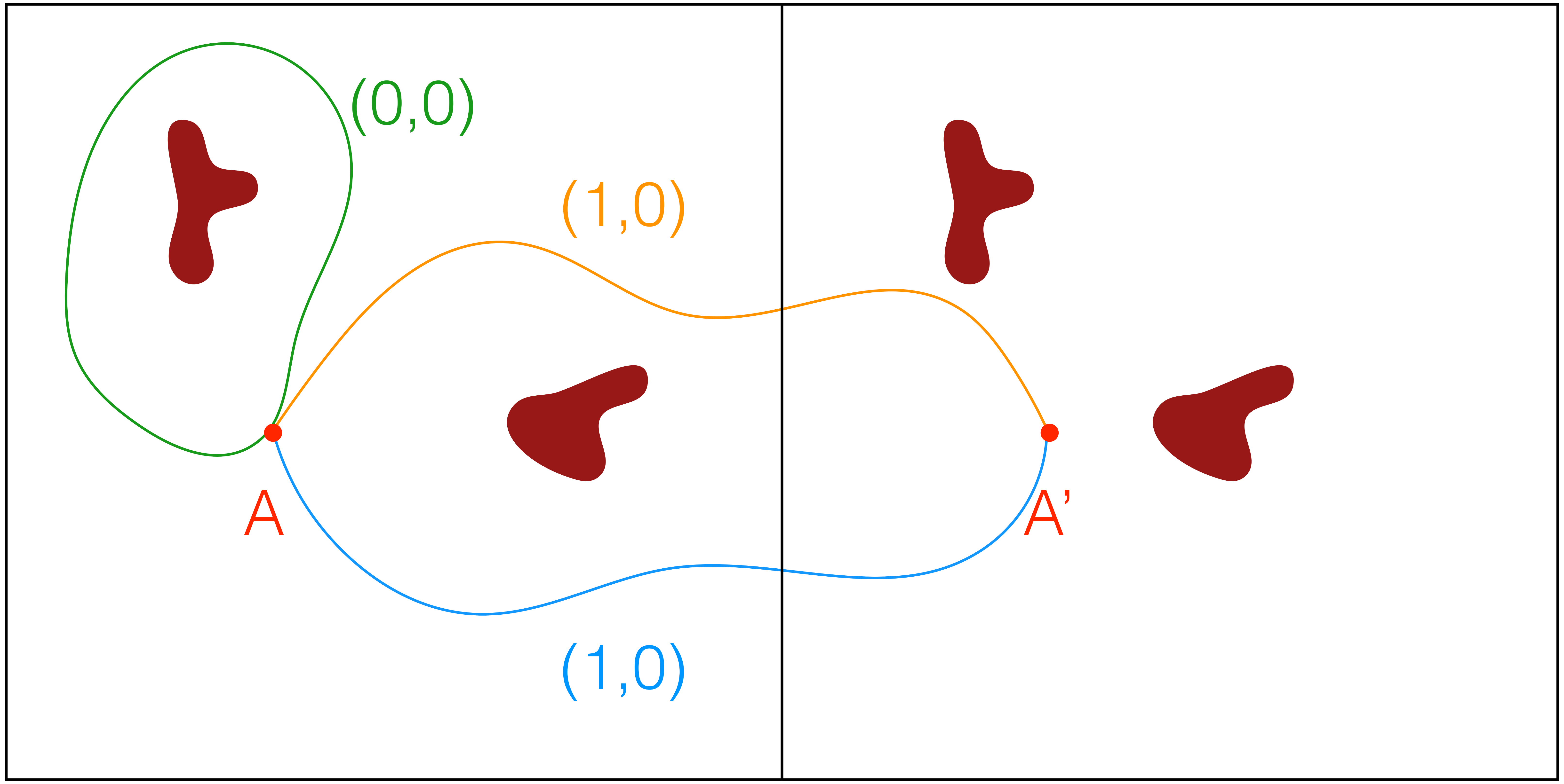
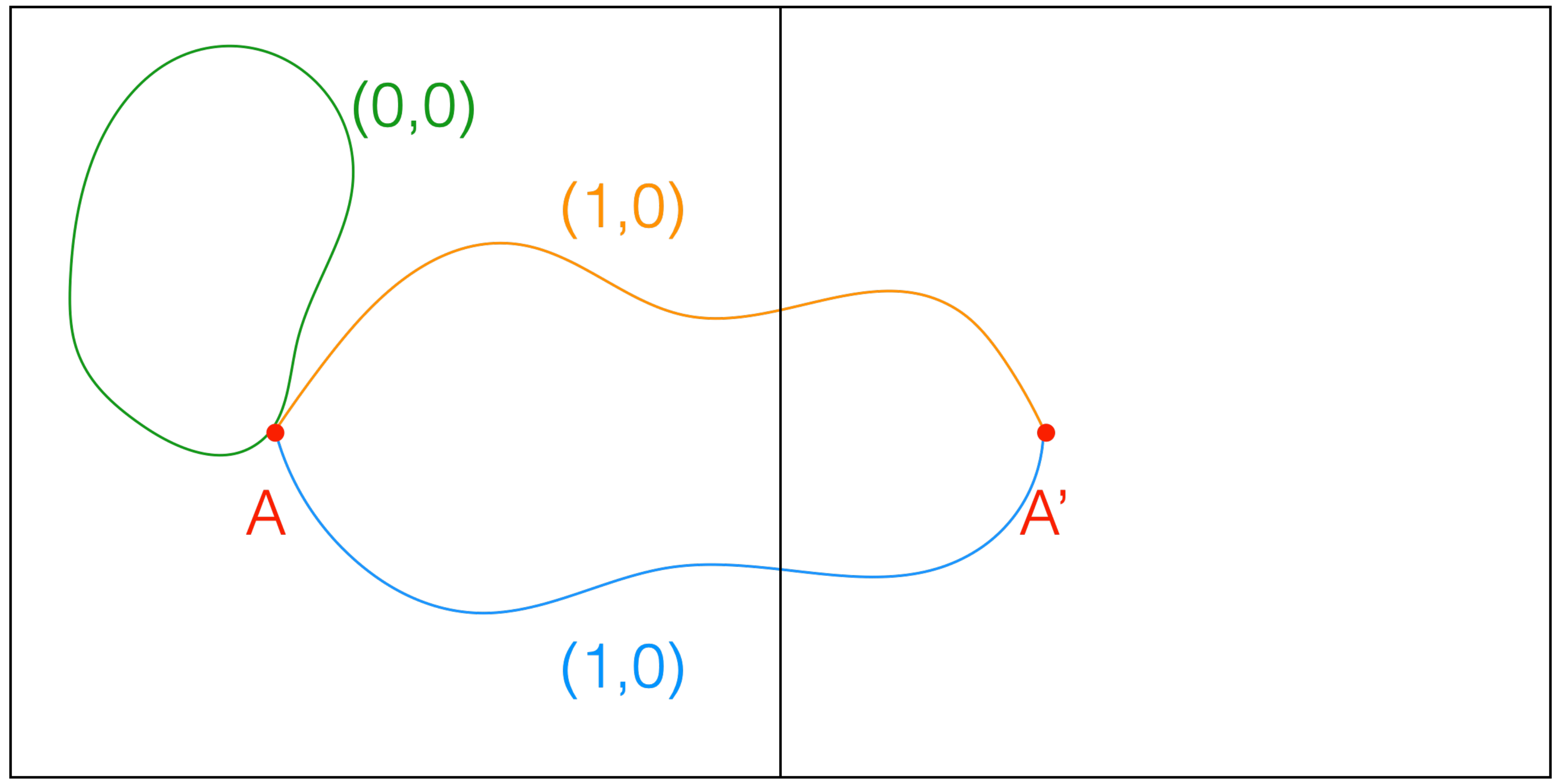


$$\mu \neq \mu^*$$

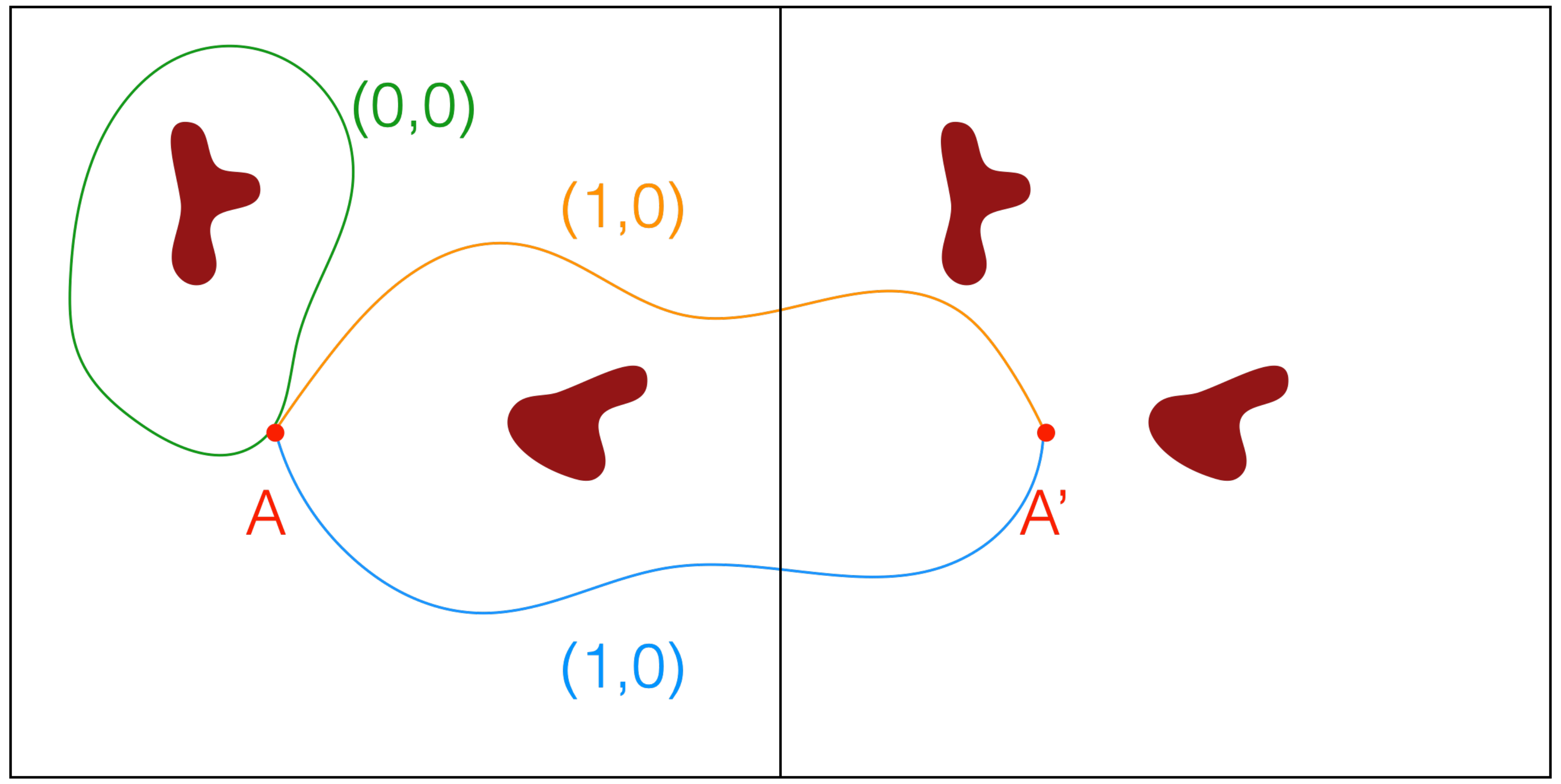
$$\mu \neq 0$$

strongly adiabatic transport



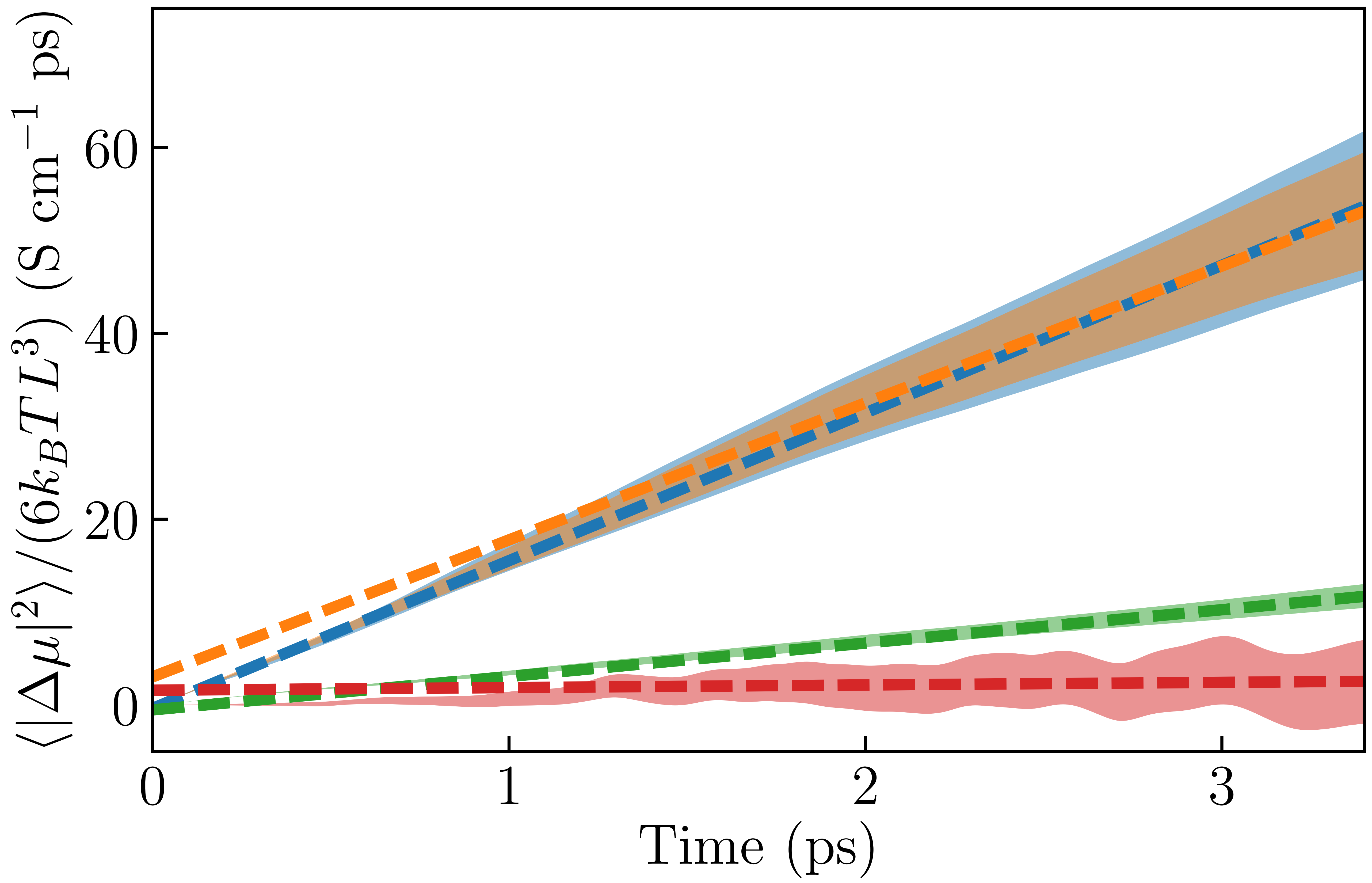
$$\mu = \mu^*$$
$$\mu = 0$$

weakly adiabatic transport



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

not trivial weakly adiabatic conductivity



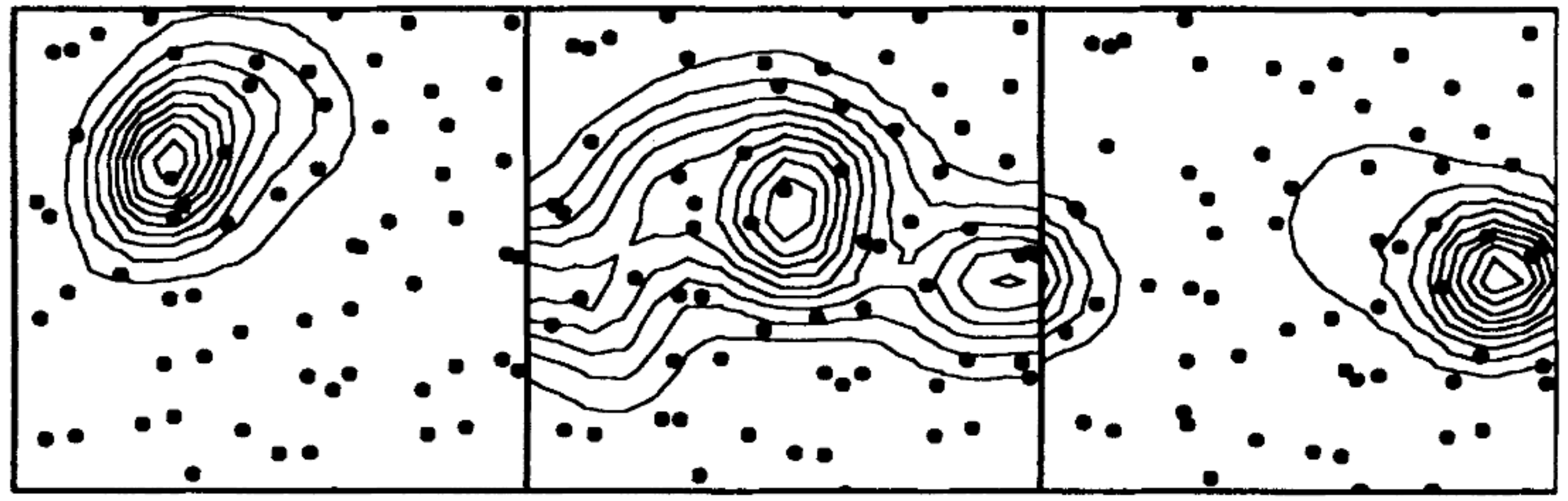
$$\Delta\boldsymbol{\mu} = e\int_0^t \mathbf{J}(t')dt'$$

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

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

cross term

effects of self-interactions



VOLUME 59, NUMBER 7 PHYSICAL REVIEW LETTERS 17 AUGUST 1987

Localization, Hopping, and Diffusion of Electrons in Molten Salts

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and

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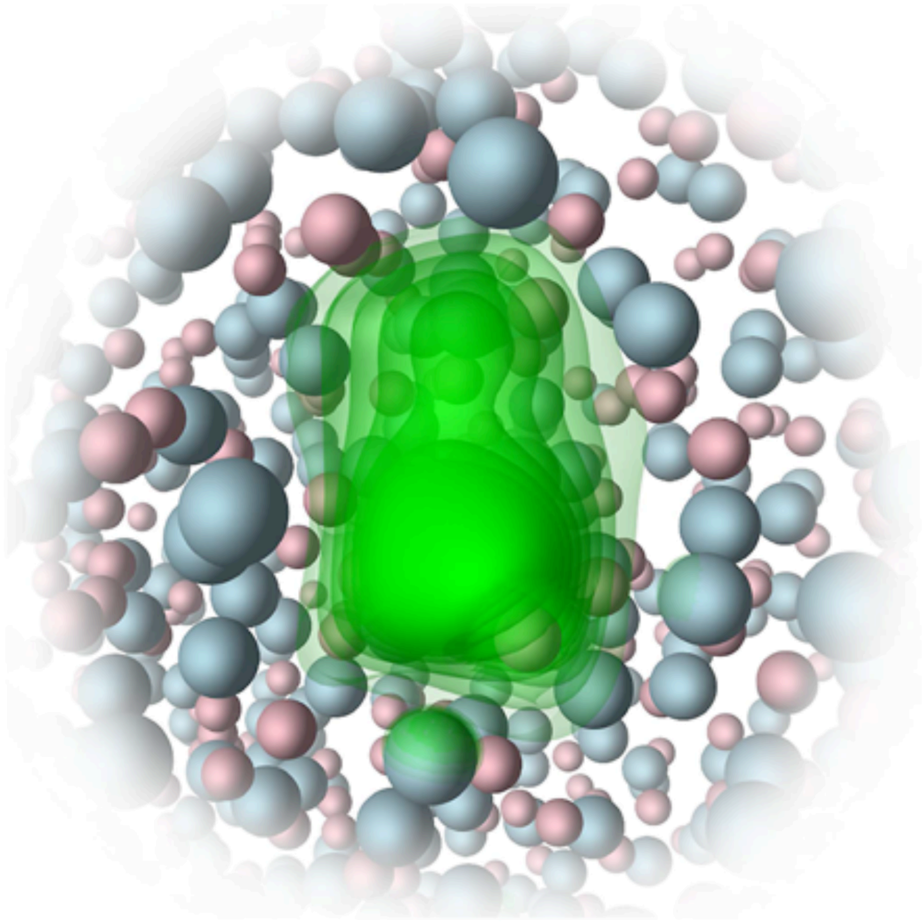
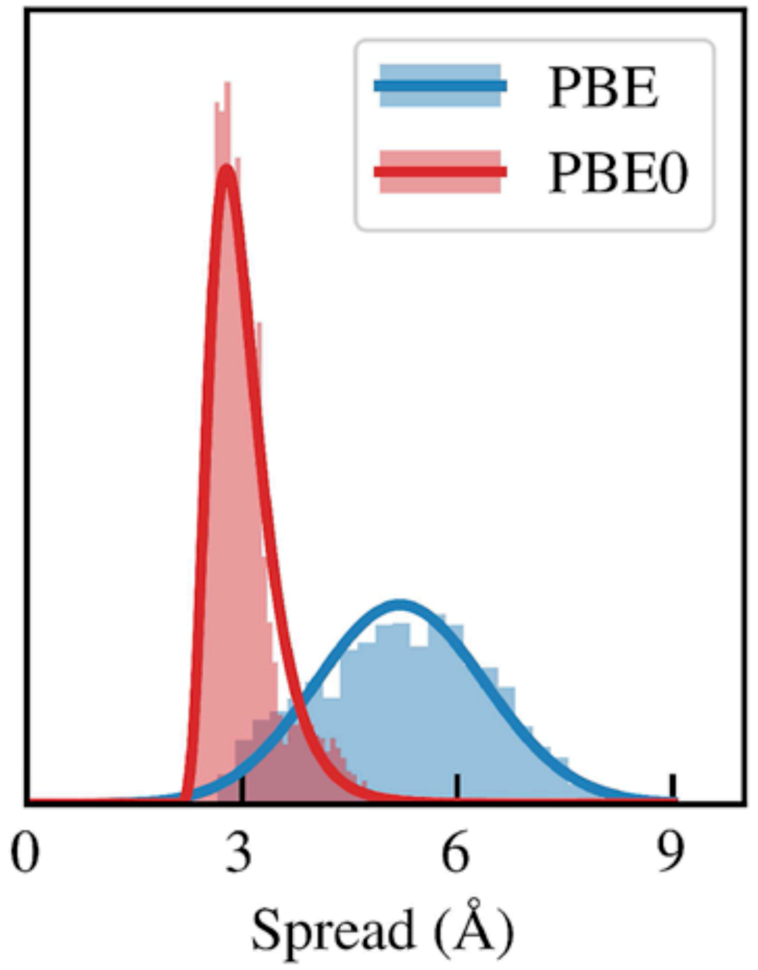
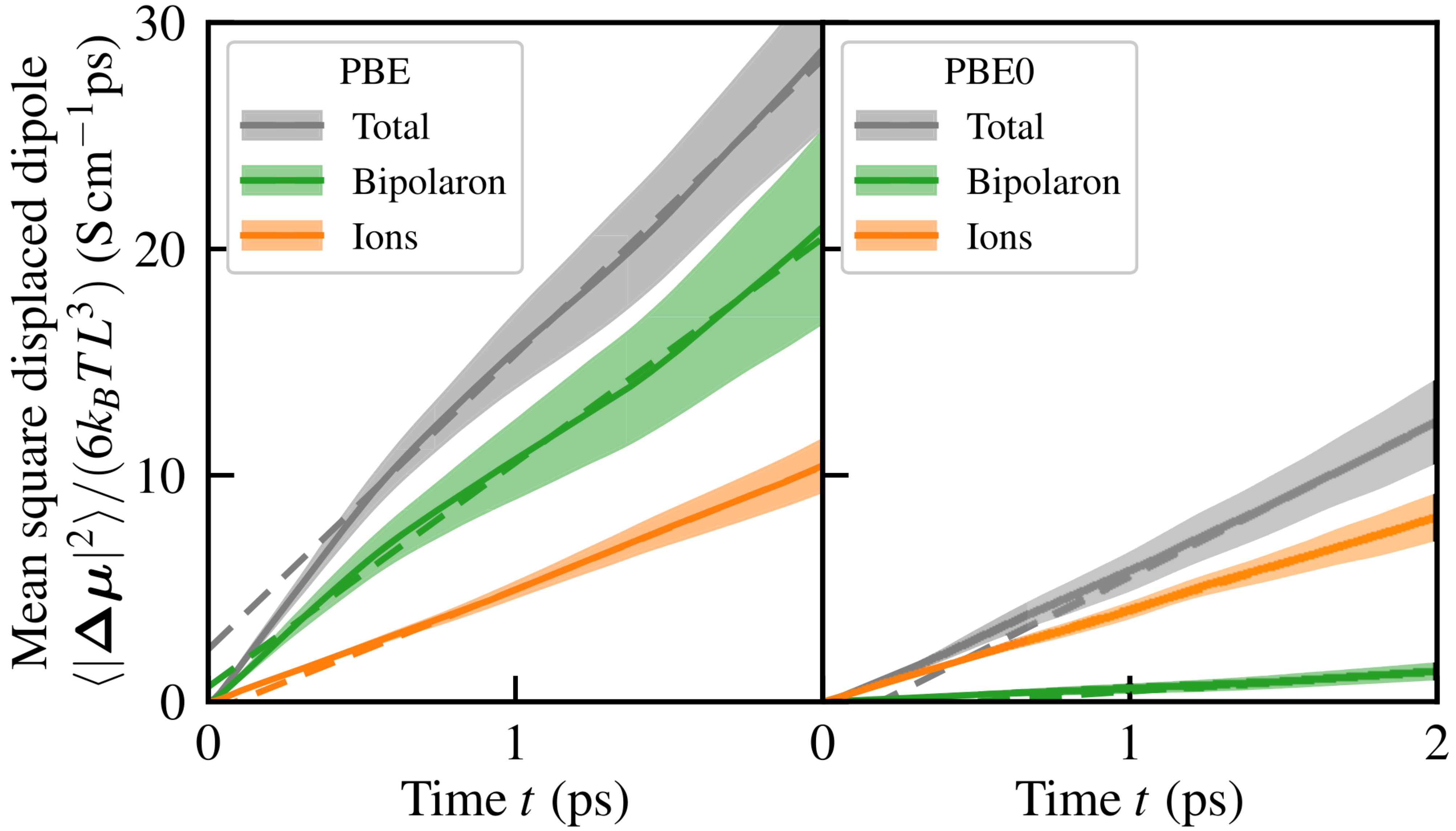
(Received 24 April 1986; revised manuscript received 3 April 1987)







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- the degree of electron localization in the ionic broth is strongly influenced by self-interaction effects, which are treated differently by various exchange-correlation functionals; the resulting electride contribution to the conductivity varies accordingly.

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as we used to be!

thanks to:

Federico Grasselli

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ARTICLES

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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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Paolo Pegolo, Stefano Baroni, Federico Grasselli

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Paolo Pegolo,[1,a)] Stefano Baroni,[1,2,b)] and Federico Grasselli[3,c)]

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