topology, oxidation states, and charge transport in ionic conductors

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serious answers to four silly questions

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- how come the conductivity of (stoichiometric) electrolytes is correctly predicted when real-valued, time-dependent, tensor Born effective charges are replaced with integer-valued, time-independent, scalar atomic oxidation states?

serious answers to four silly questions

- how come the electric conductivity of molecular non-ionic fluids vanishes, when the current fluctuations that determine it, do not?
- how come the conductivity of (stoichiometric) electrolytes is correctly predicted when real-valued, time-dependent, tensor Born effective charges are replaced with integer-valued, time-independent, scalar atomic oxidation states?
- what are oxidation states, in the first place?

serious answers to four silly questions

- how come the electric conductivity of molecular non-ionic fluids vanishes, when the current fluctuations that determine it, do not?
- how come the conductivity of (stoichiometric) electrolytes is correctly predicted when real-valued, time-dependent, tensor Born effective charges are replaced with integer-valued, time-independent, scalar atomic oxidation states?
- what are oxidation states, in the first place?
- to start with: how come the heat conductivity is well defined, when the energy current that determines it, is not?

linear-response theory of transport

$$\boldsymbol{J} = \lambda \boldsymbol{F}$$

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charge transport

$$\boldsymbol{J}_{\mathcal{Q}} = \sum_{I} q_I \boldsymbol{V}_I$$

$$\boldsymbol{F}_{\mathcal{Q}} = -\nabla\phi$$

$\lambda =$ electric conductivity

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energy transport

$$\boldsymbol{J}_{\mathcal{E}} = \sum_I e_I \boldsymbol{V}_I + \frac{1}{2} \sum_{I \neq J} (\boldsymbol{V}_I \cdot \boldsymbol{F}_{IJ})(\boldsymbol{R}_I - \boldsymbol{R}_J)$$

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$$\lambda \propto \int_0^\infty \langle \boldsymbol{J}(t) \boldsymbol{J}(0) \rangle dt$$

Green-Kubo

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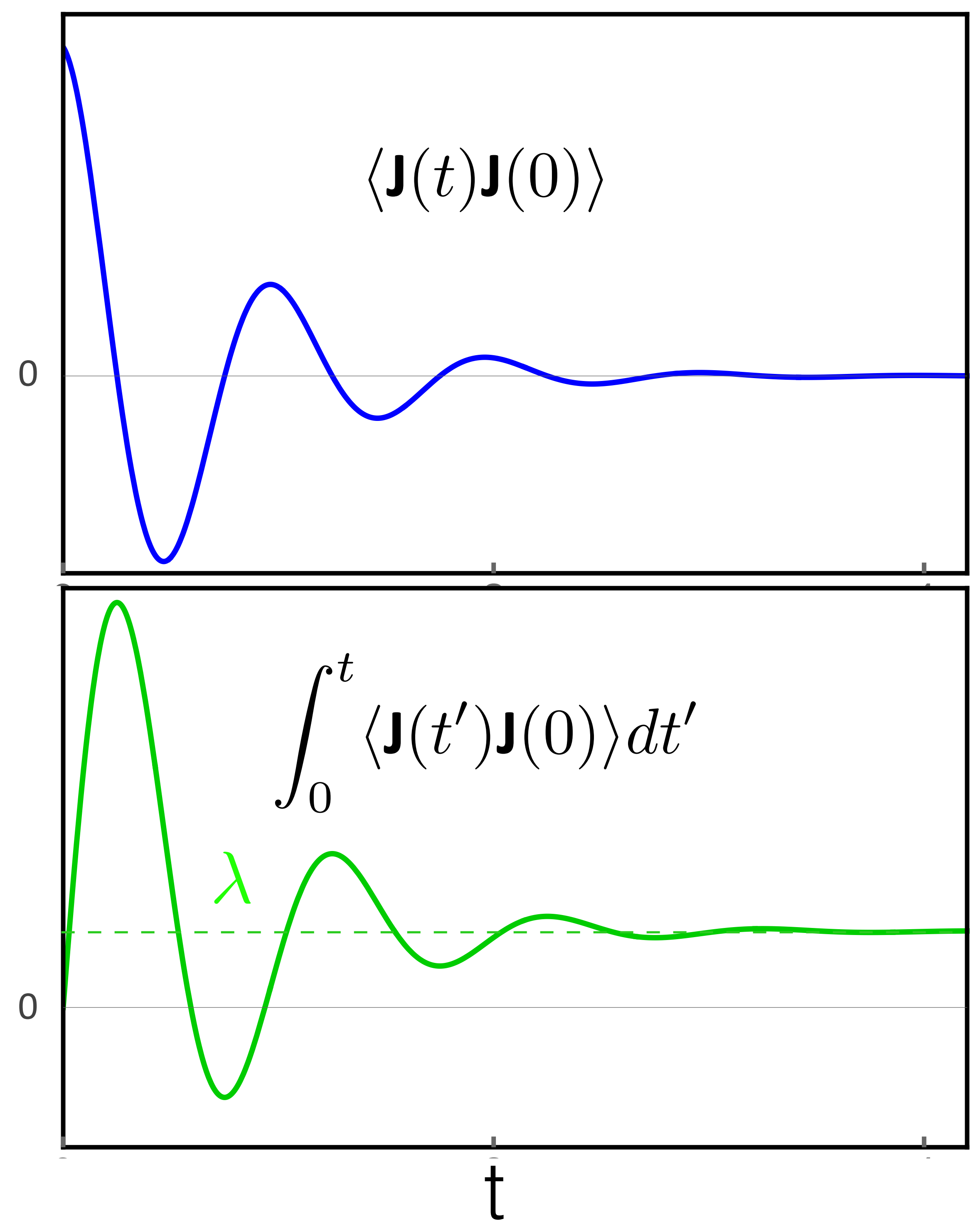

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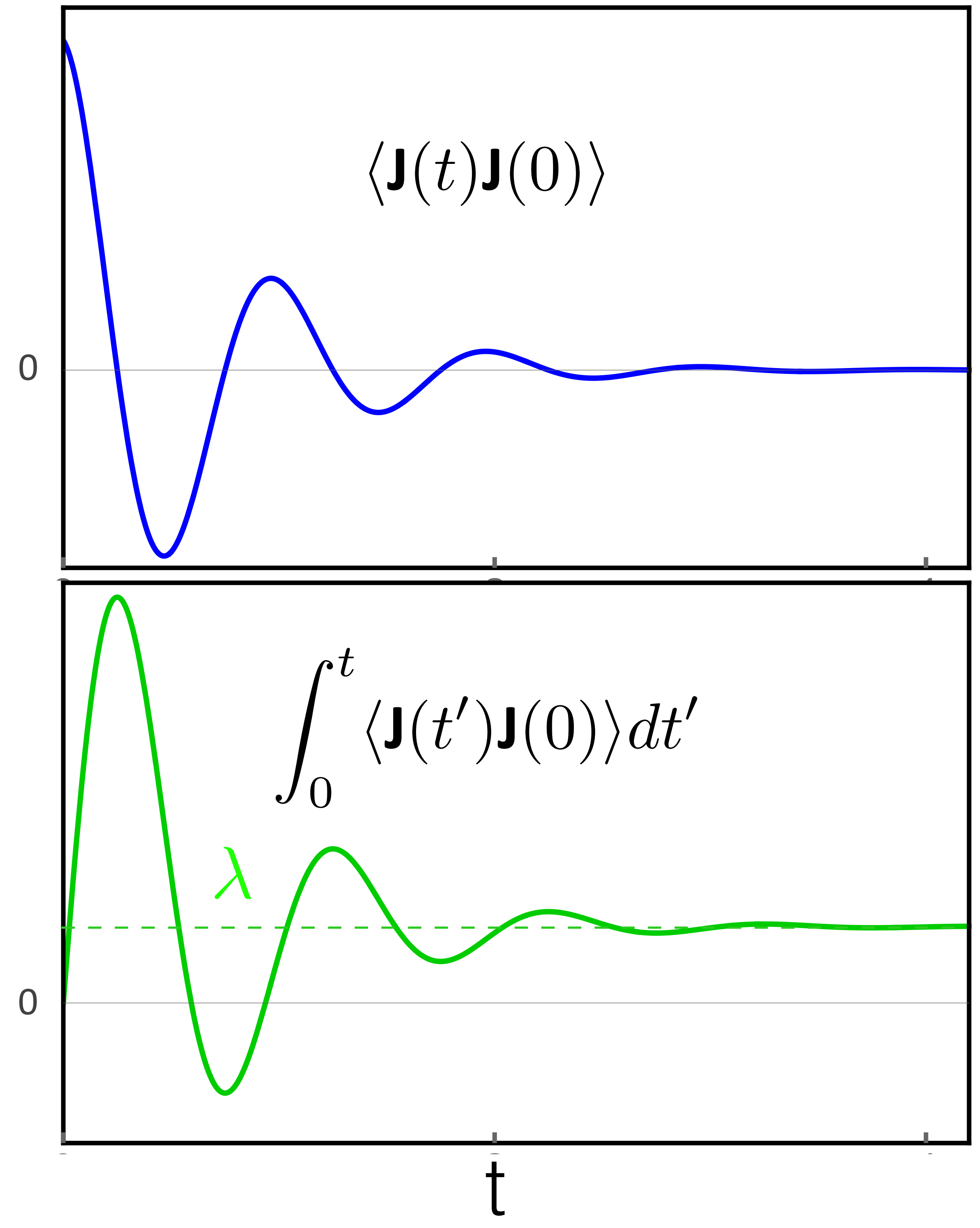
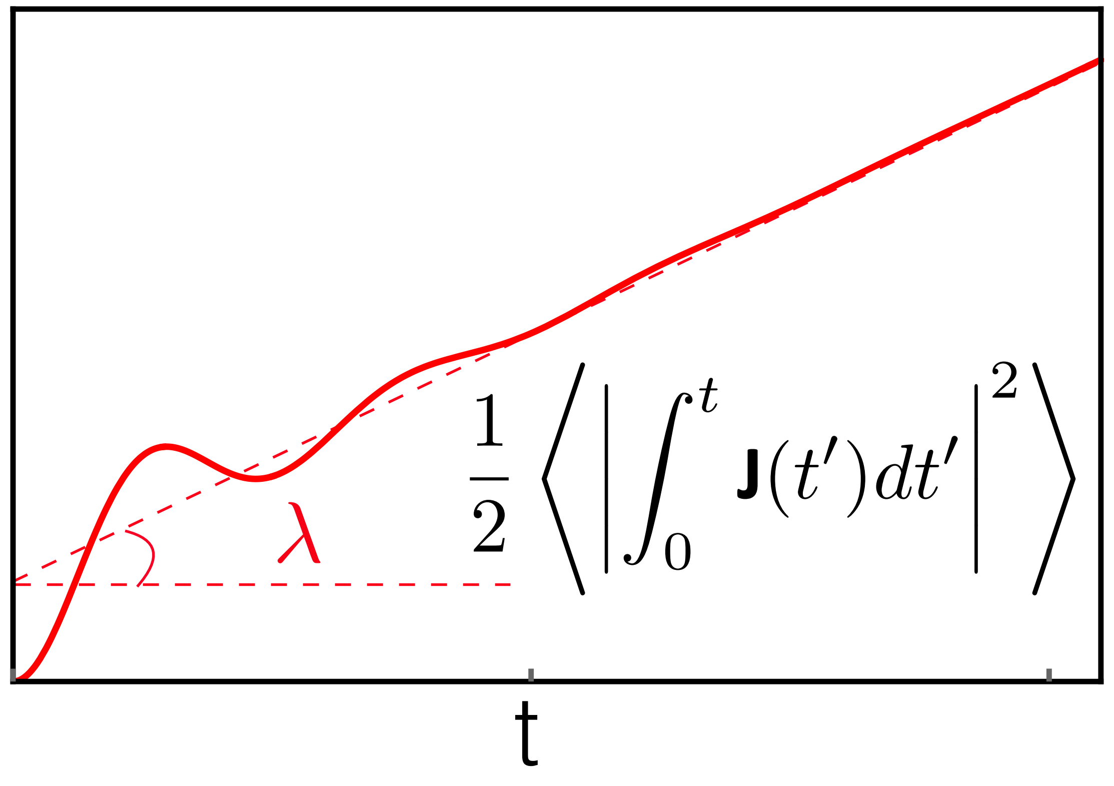
Einstein-Helfand

$$\lambda \propto \lim_{t\to\infty} \frac{1}{2t} \mathrm{var}\left[\int_0^t \boldsymbol{J}(t')dt'\right]$$





a prequel:
heat transport

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classical and quantum adiabatic heat transport

$$J_{\mathcal{E}} = \sum_I e_I \boldsymbol{V}_I + \frac{1}{2}\sum_{I\neq J}(\boldsymbol{V}_I \cdot \boldsymbol{F}_{IJ})(\boldsymbol{R}_I - \boldsymbol{R}_J)$$

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Thermal Conductivity of Periclase (MgO) from First Principles

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sensitive to the form of the potential. The widely used Green-Kubo relation [14] does not serve our purposes, because in first-principles calculations it is impossible to uniquely decompose the total energy into individual contributions from each atom.

classical and quantum adiabatic heat transport

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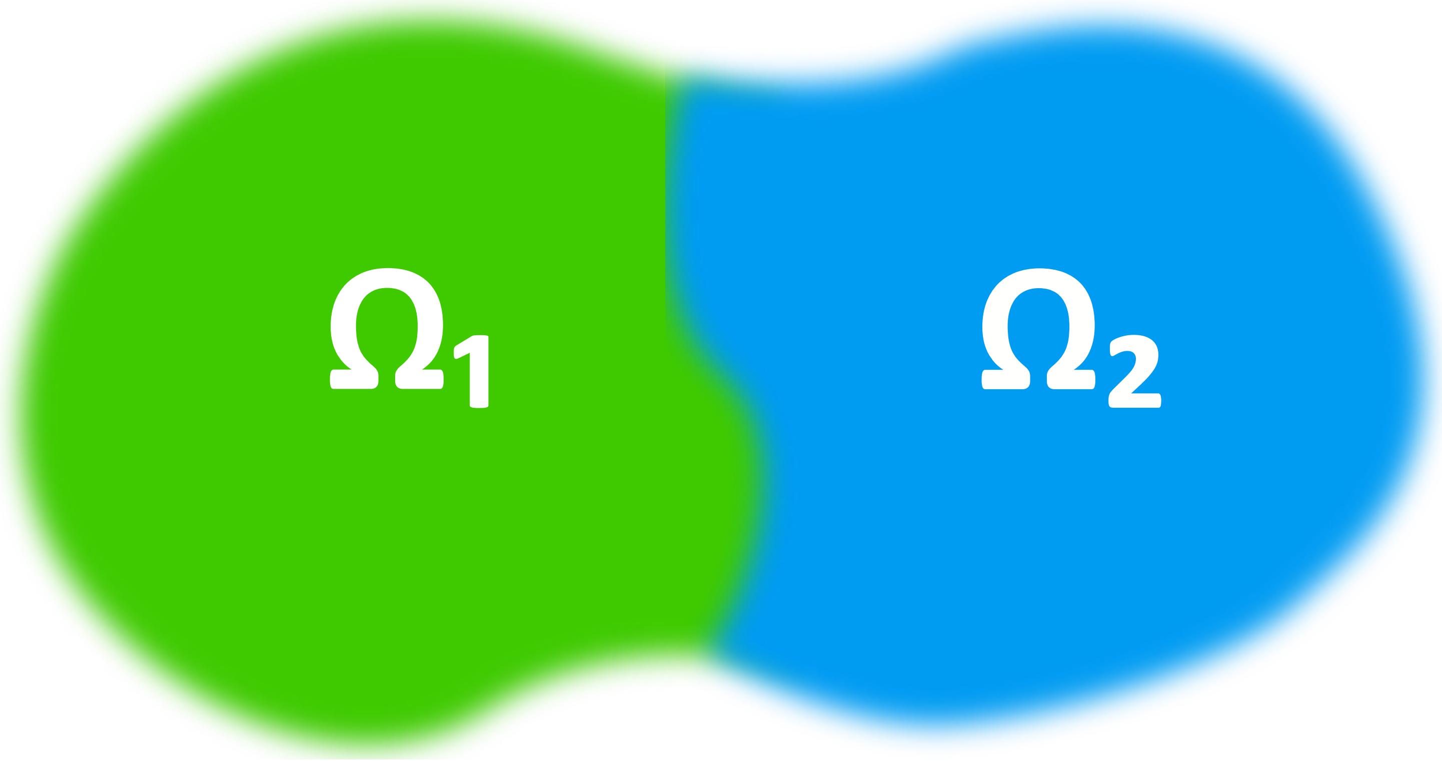
how come?

how come?

how is it that a formally exact theory of
the electronic ground state cannot predict
all measurable adiabatic properties?

gauge invariance of transport coefficients

energy is extensive



$$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2]$$

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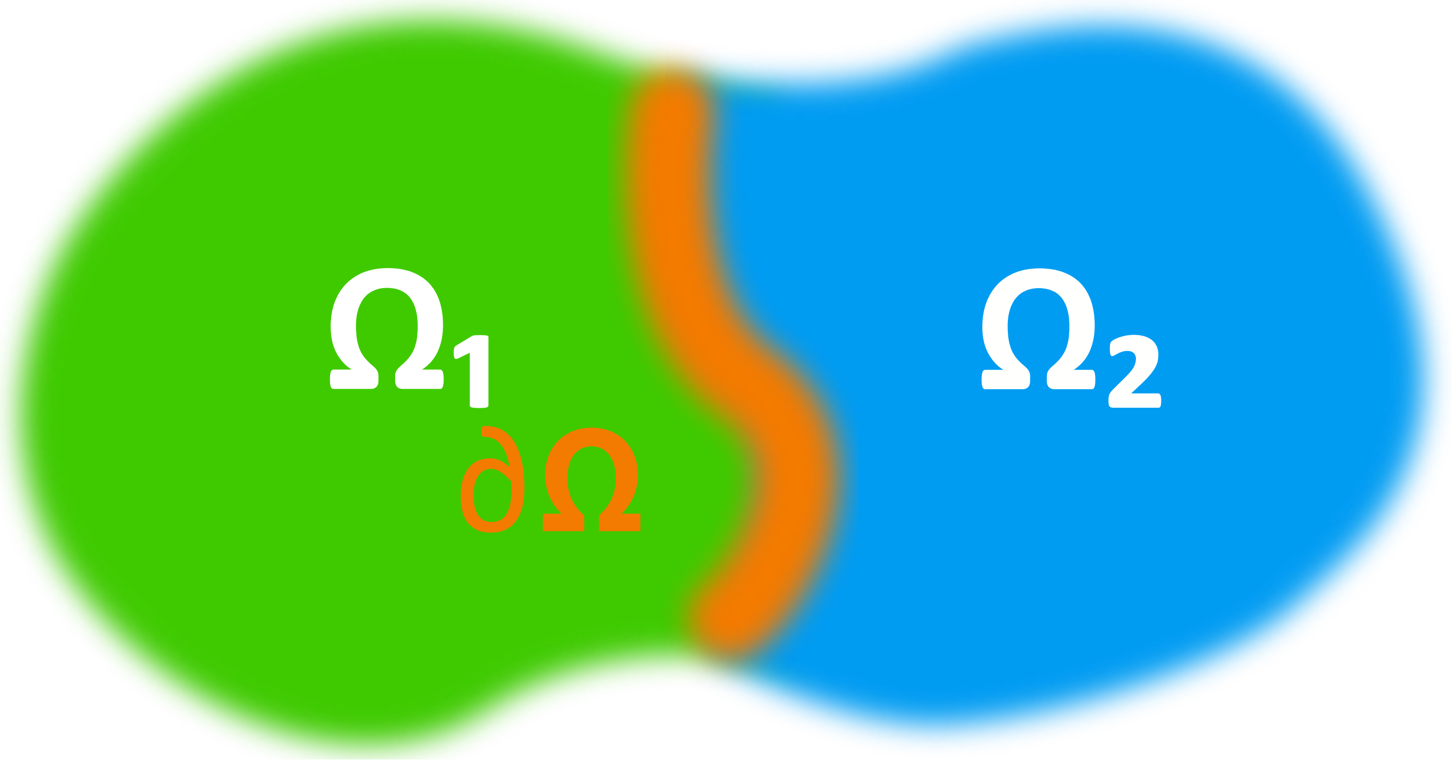

$$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial\Omega]$$

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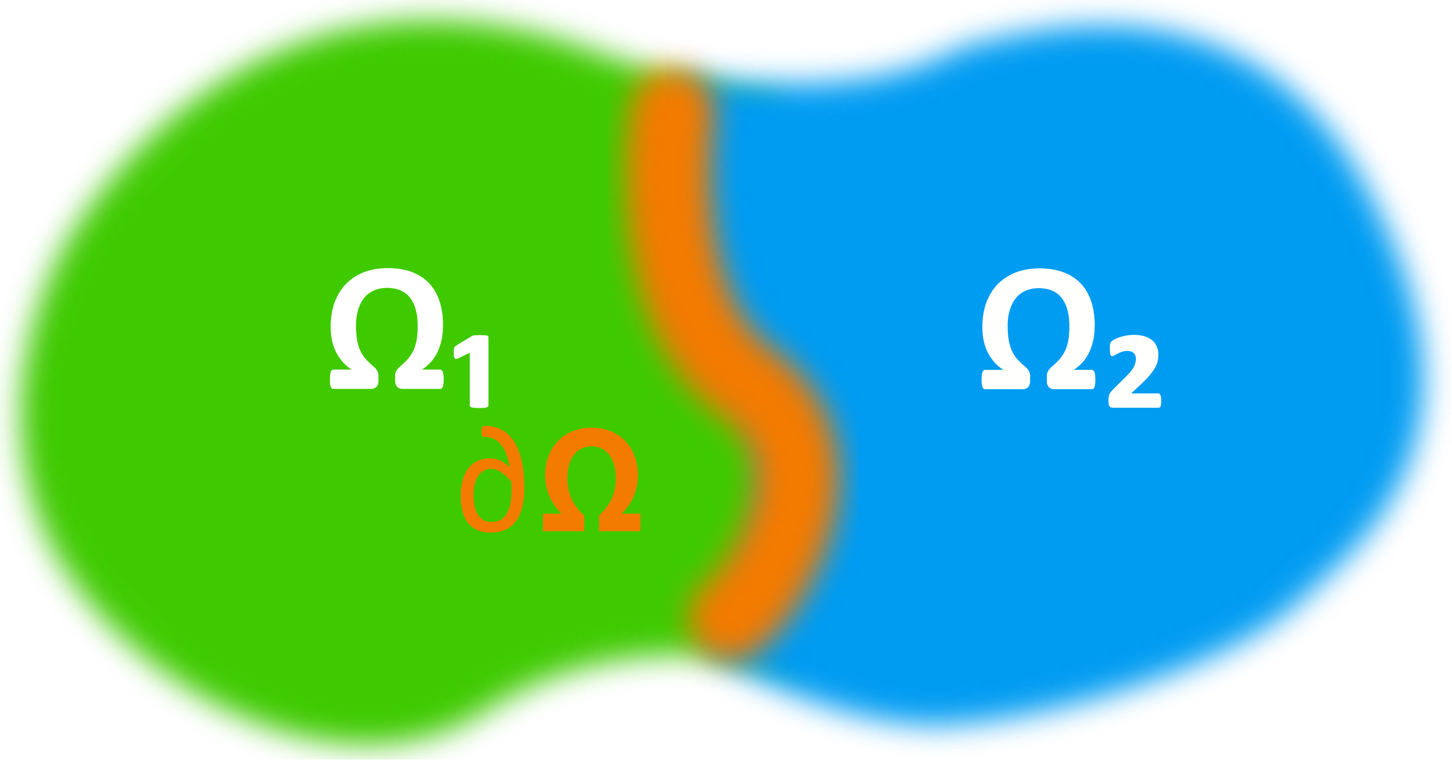

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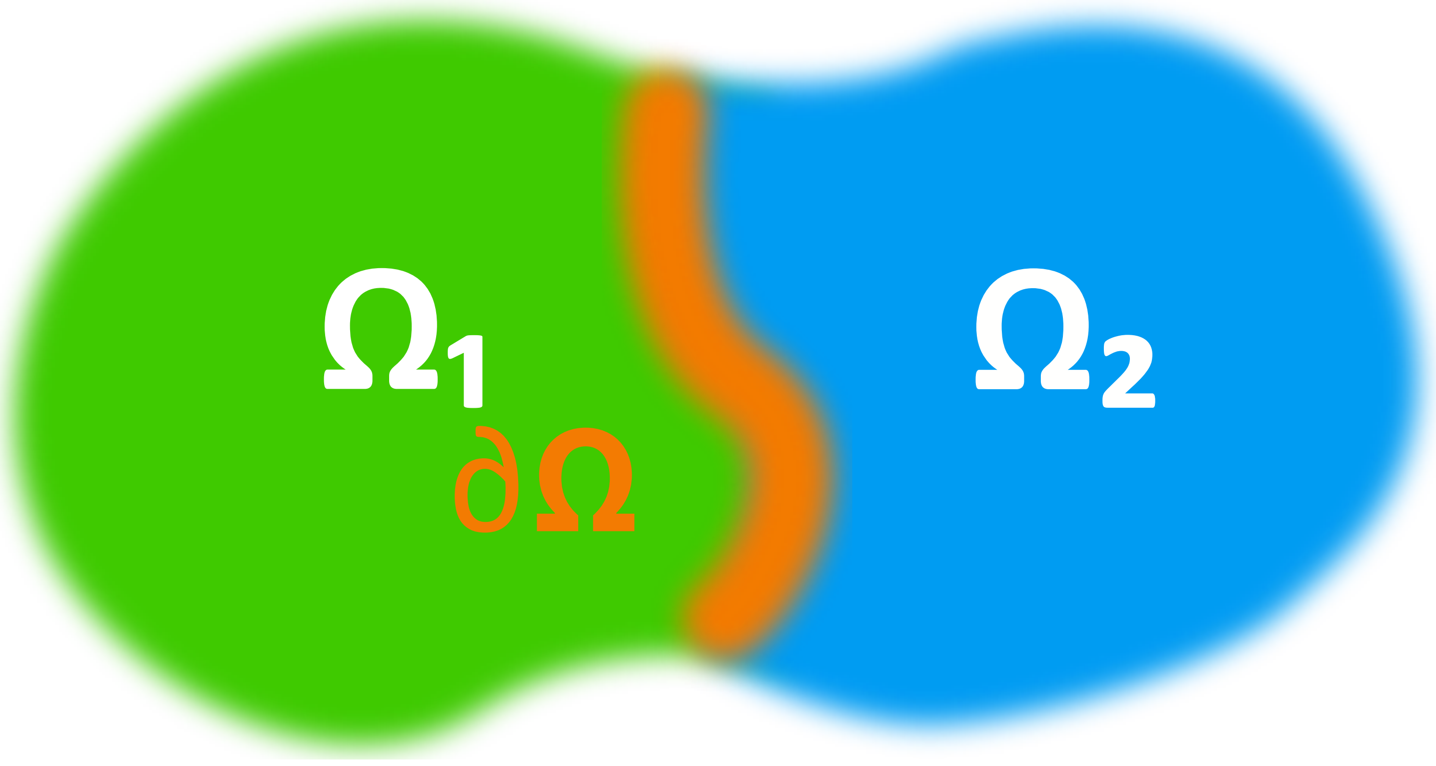

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thermodynamic invariance

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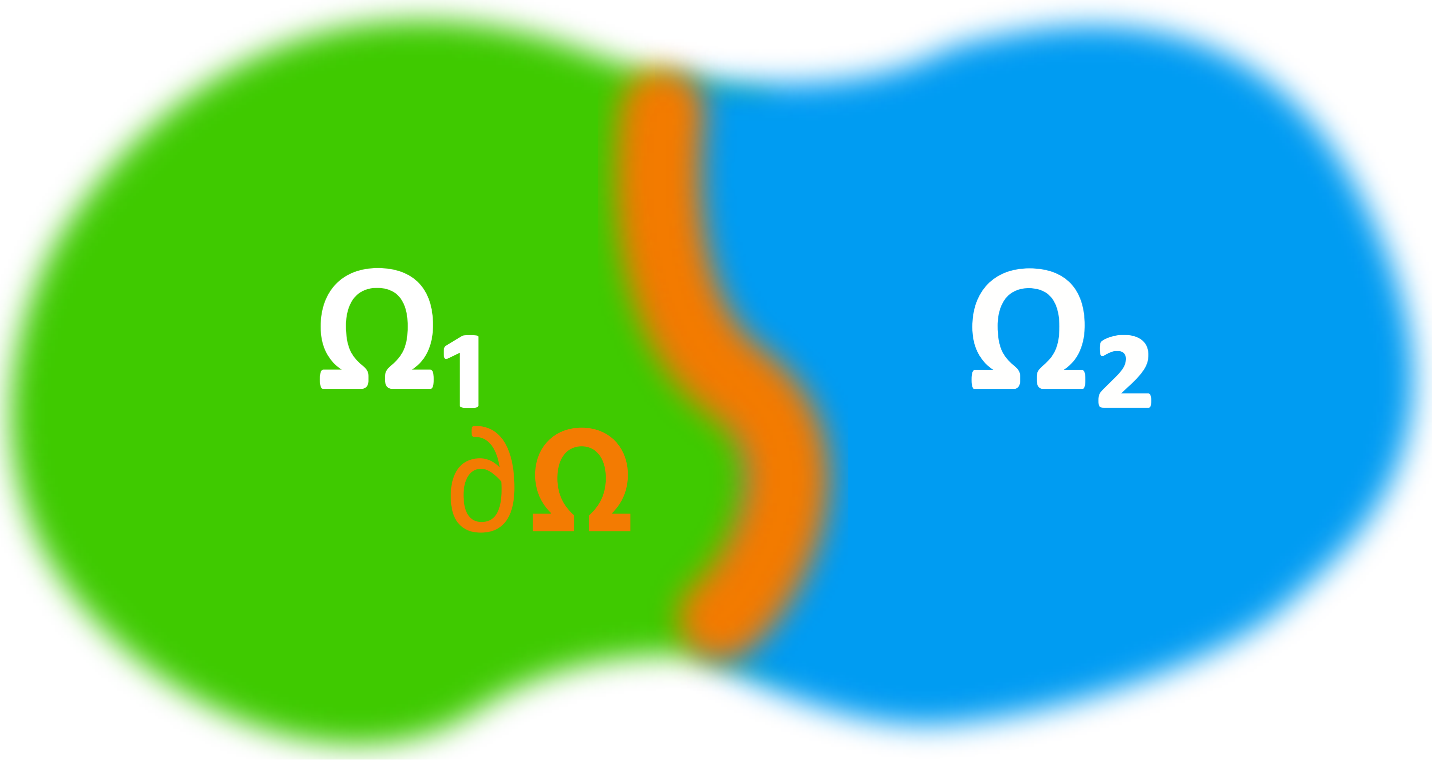

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gauge invariance

$$e'(\mathbf{r}) = e(\mathbf{r}) - \nabla \cdot \mathbf{p}(\mathbf{r})$$

gauge invariance of transport coefficients

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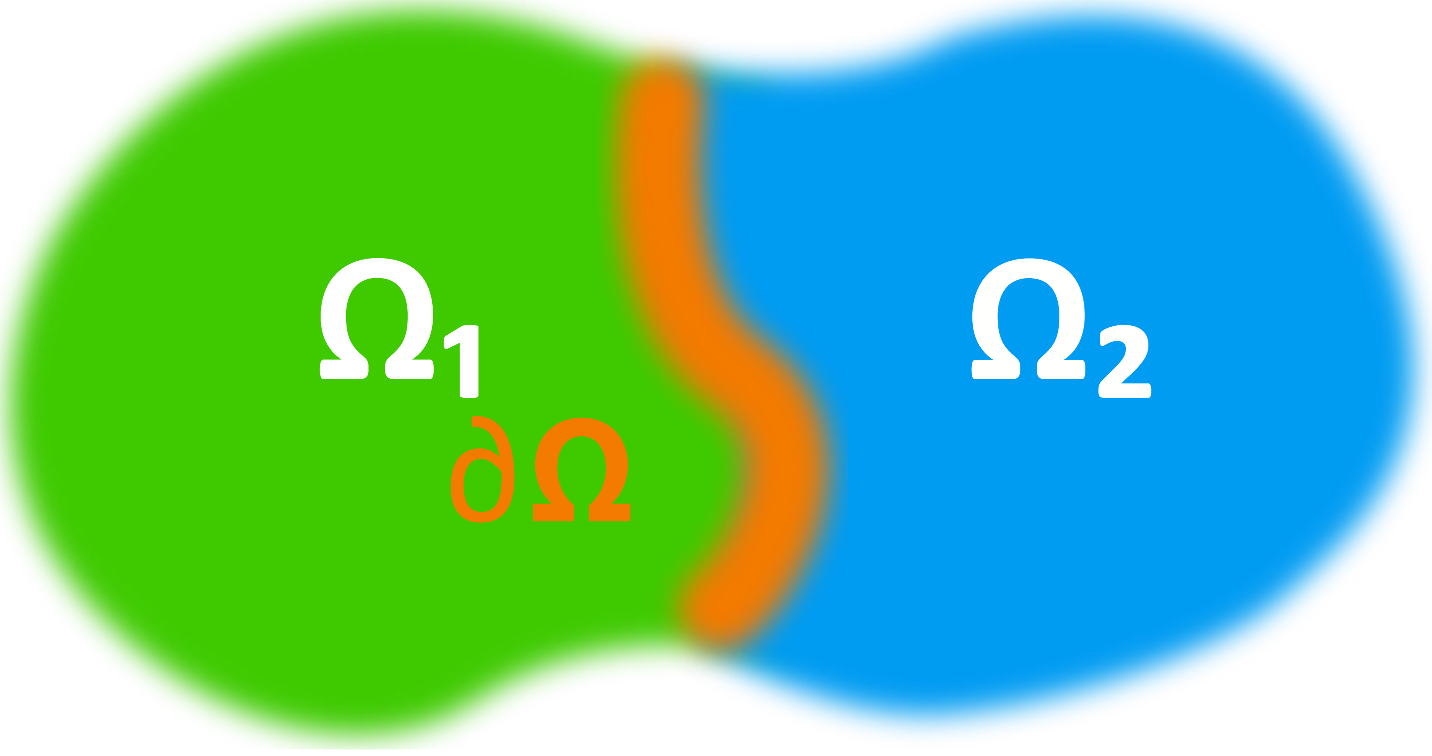

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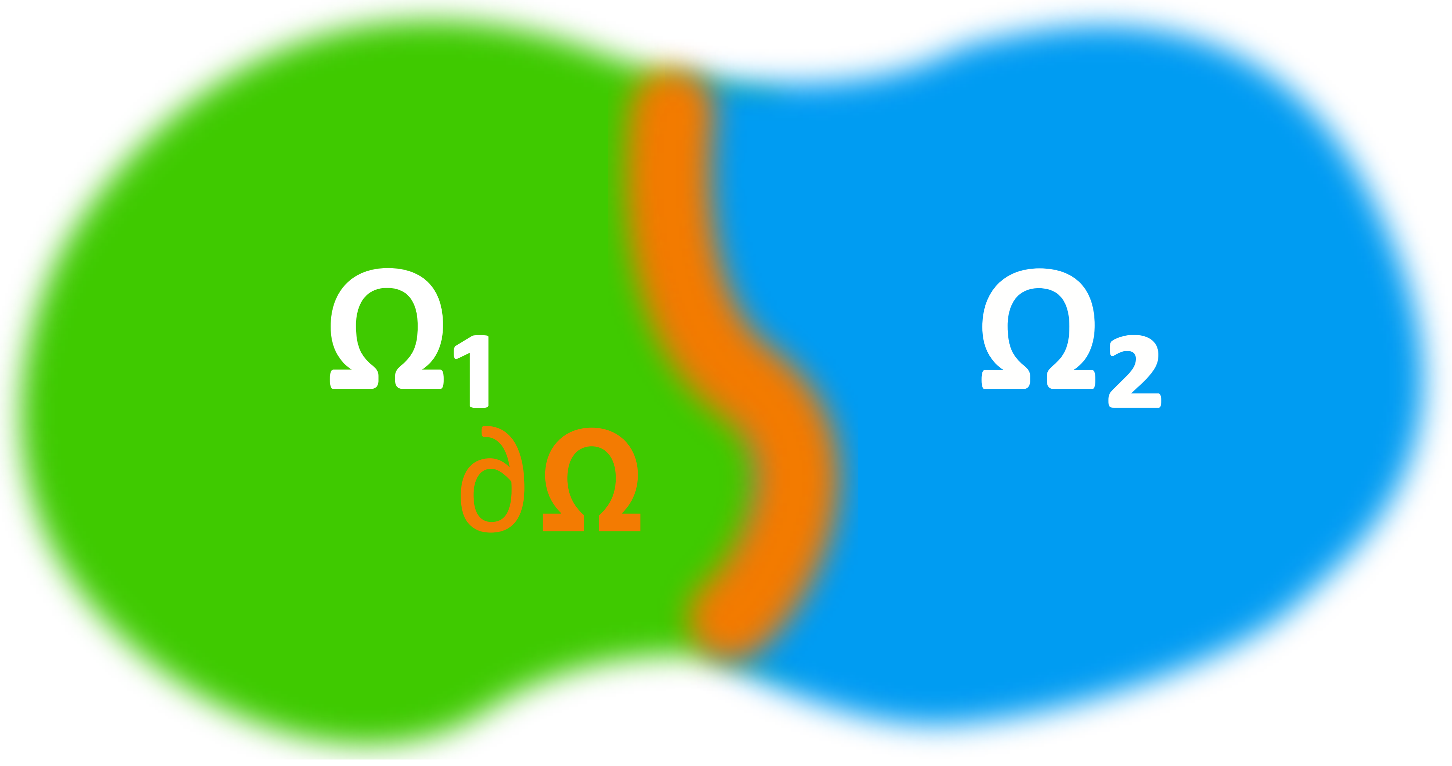
energy is conserved

$$\dot{e}(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t)$$

gauge invariance of transport coefficients

energy is extensive



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$$\mathbf{j}'(\mathbf{r}, t) = \mathbf{j}(\mathbf{r}, t) + \dot{\mathbf{p}}(\mathbf{r}, t)$$

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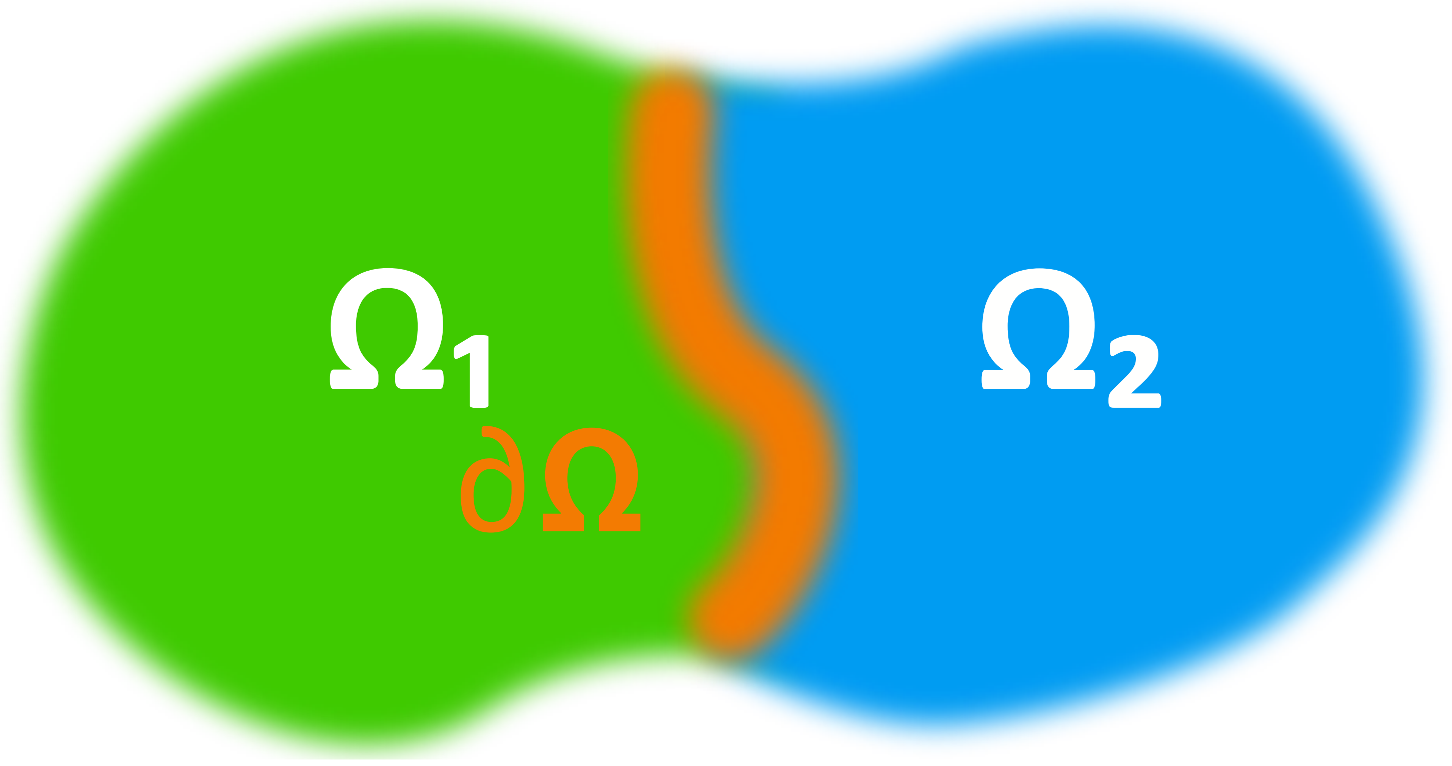

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$$\mathcal{E}[\Omega] = \int_\Omega e(\mathbf{r})d\mathbf{r}$$

$$\mathbf{J}(t) = \frac{1}{\Omega}\int \mathbf{j}(\mathbf{r},t)d\mathbf{r}$$

$$\mathbf{P}(t) = \frac{1}{\Omega}\int \mathbf{p}(\mathbf{r},t)d\mathbf{r}$$

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$$\mathrm{var}\left[\mathbf{D}'(t)\right] = \mathrm{var}\left[\mathbf{D}(t)\right] + \mathrm{var}\left[\Delta\mathbf{P}(t)\right] + 2\mathrm{cov}\left[\mathbf{D}(t)\cdot\Delta\mathbf{P}(t)\right]$$

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gauge invariance of transport coefficients

any two conserved densities that differ by the divergence of a (bounded) vector field are physically equivalent

the corresponding conserved fluxes differ by a total time derivative, and the transport coefficients coincide

nature physics

ARTICLES

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Microscopic theory and quantum simulation of atomic heat transport

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

gauge invariance of heat transport

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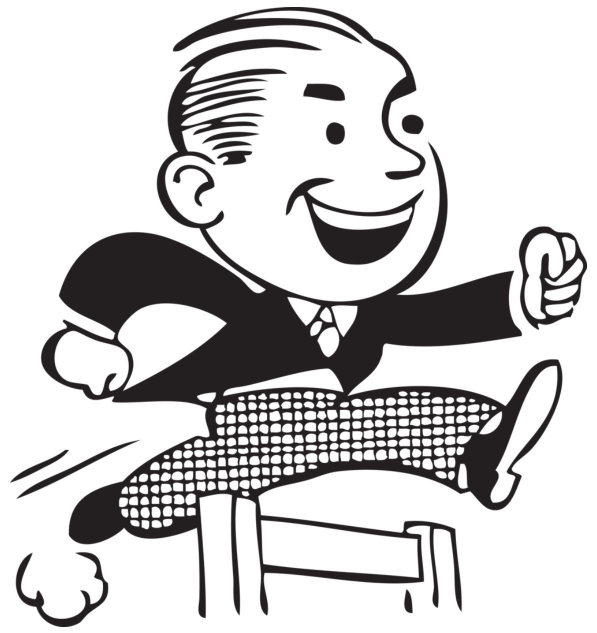
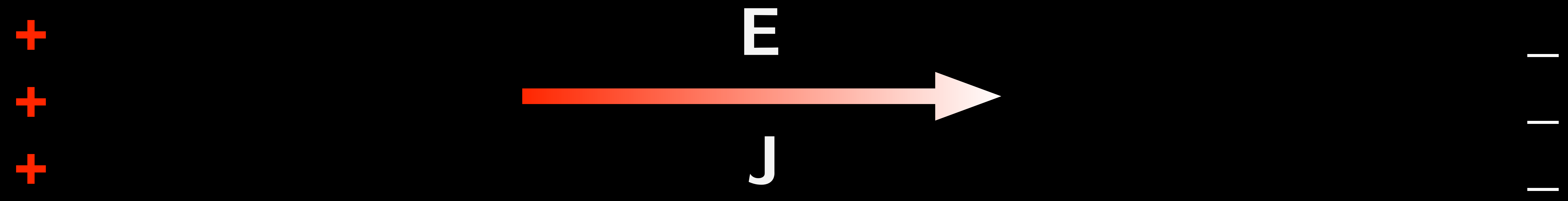
sensitive to the form of the potential. The widely used Green-Kubo relation [14] does not serve our purposes, because in first-principles calculations it is impossible to uniquely decompose the total energy into individual contributions from each atom.

solution:
choose *any* local representation of the energy that integrates to the correct value and whose correlations decay at large distance — the conductivity computed from the resulting current will be *independent* of the chosen representation.



ionic transport



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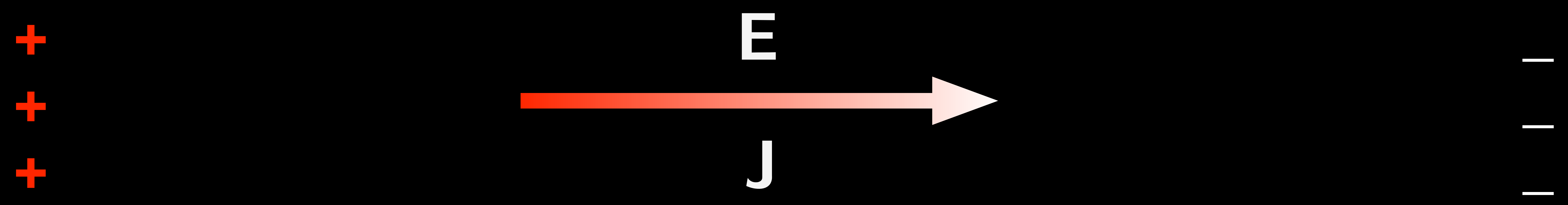

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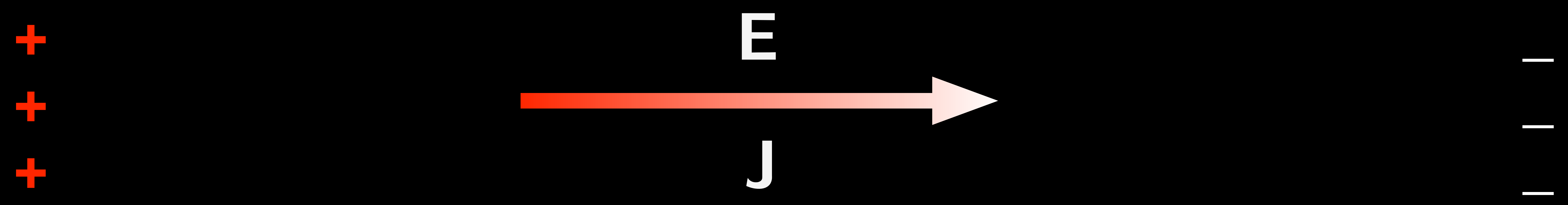

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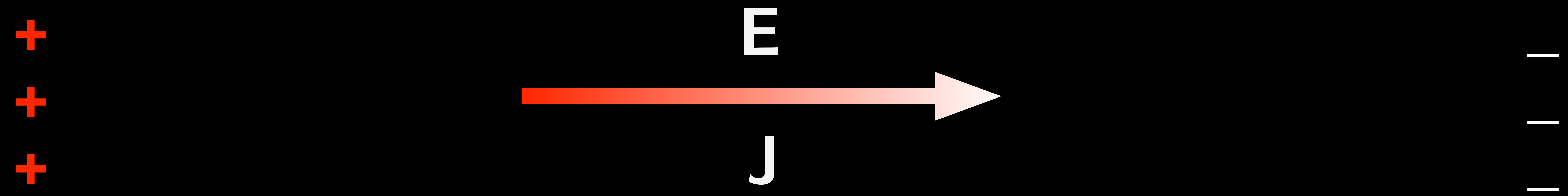
$$\begin{aligned}\mathbf{J} &= \frac{1}{\Omega}\dot{\boldsymbol{\mu}} \\ &= \frac{1}{\Omega}\sum_i \mathbf{Z}_i^* \cdot \mathbf{v}_i\end{aligned}$$

$$Z^*_{i\alpha\beta} = \frac{\partial \mu_\alpha}{\partial u_{i\beta}}$$



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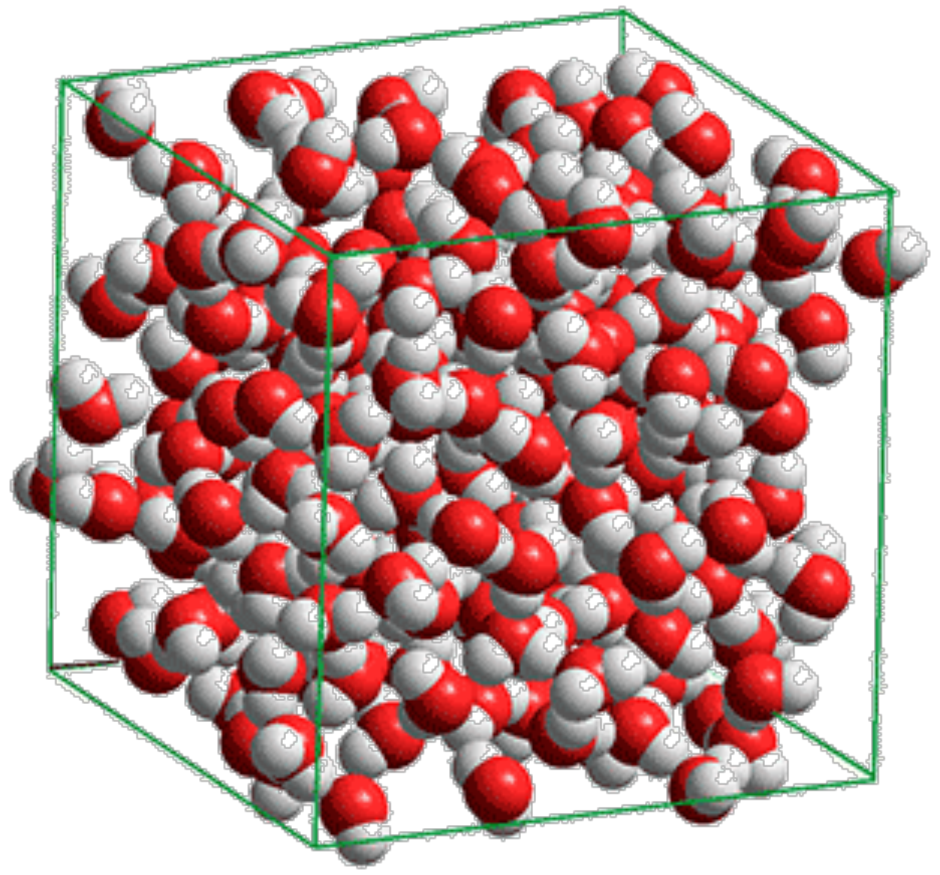
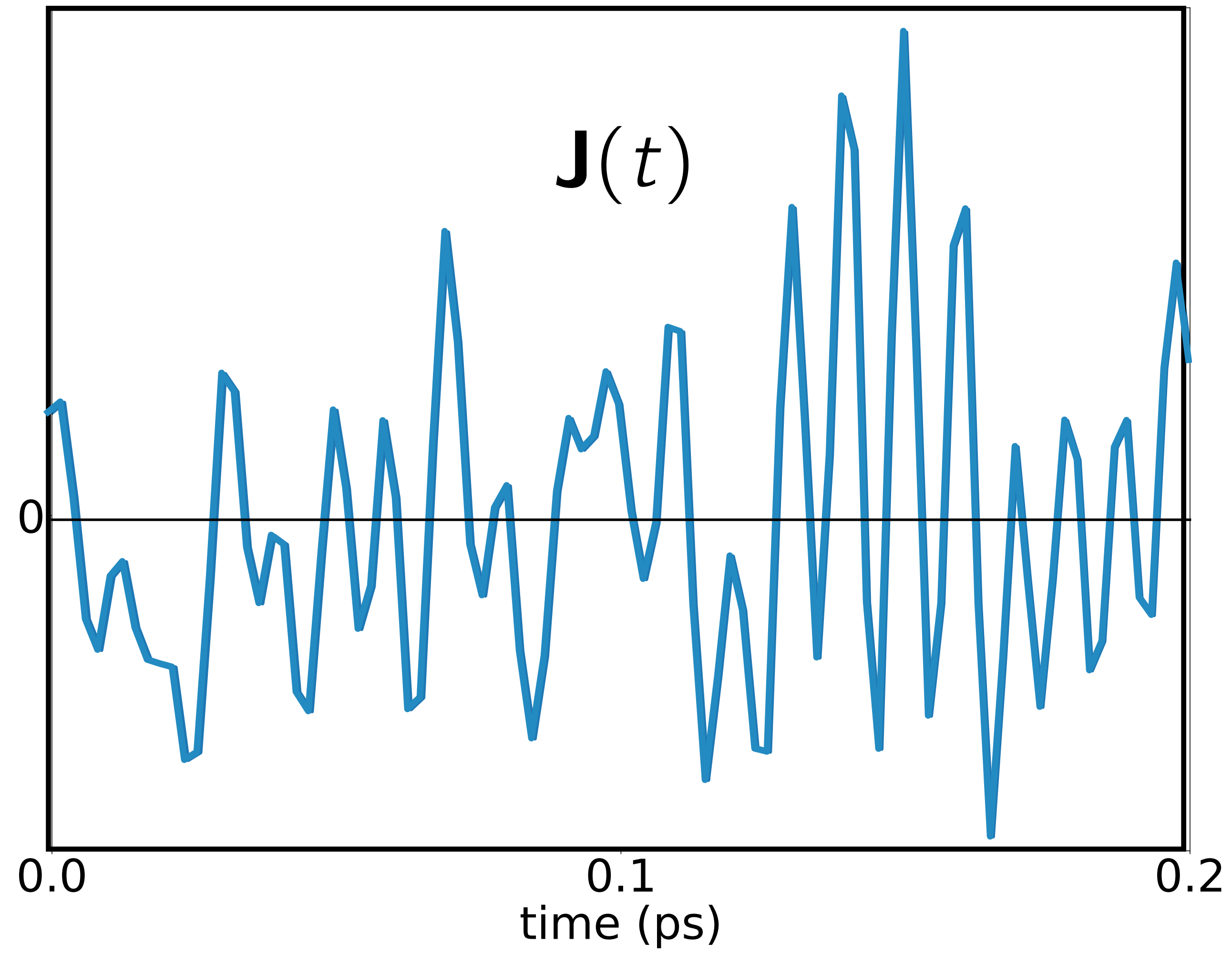
the conundrum

molecular H_2O





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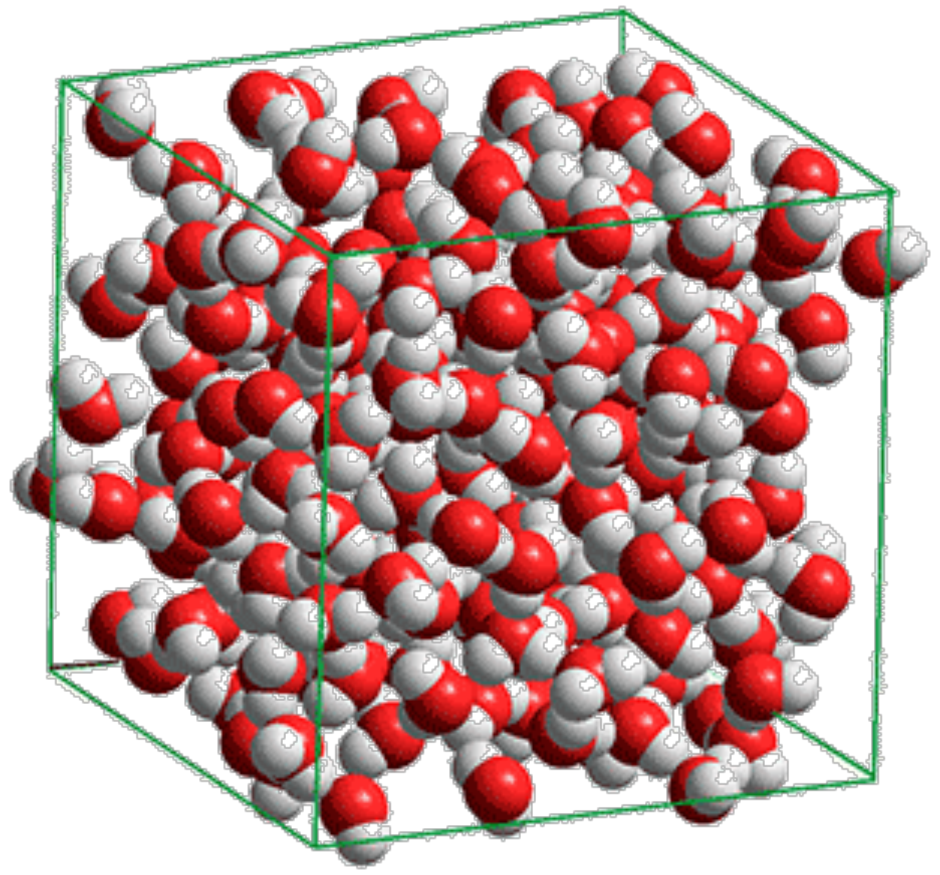

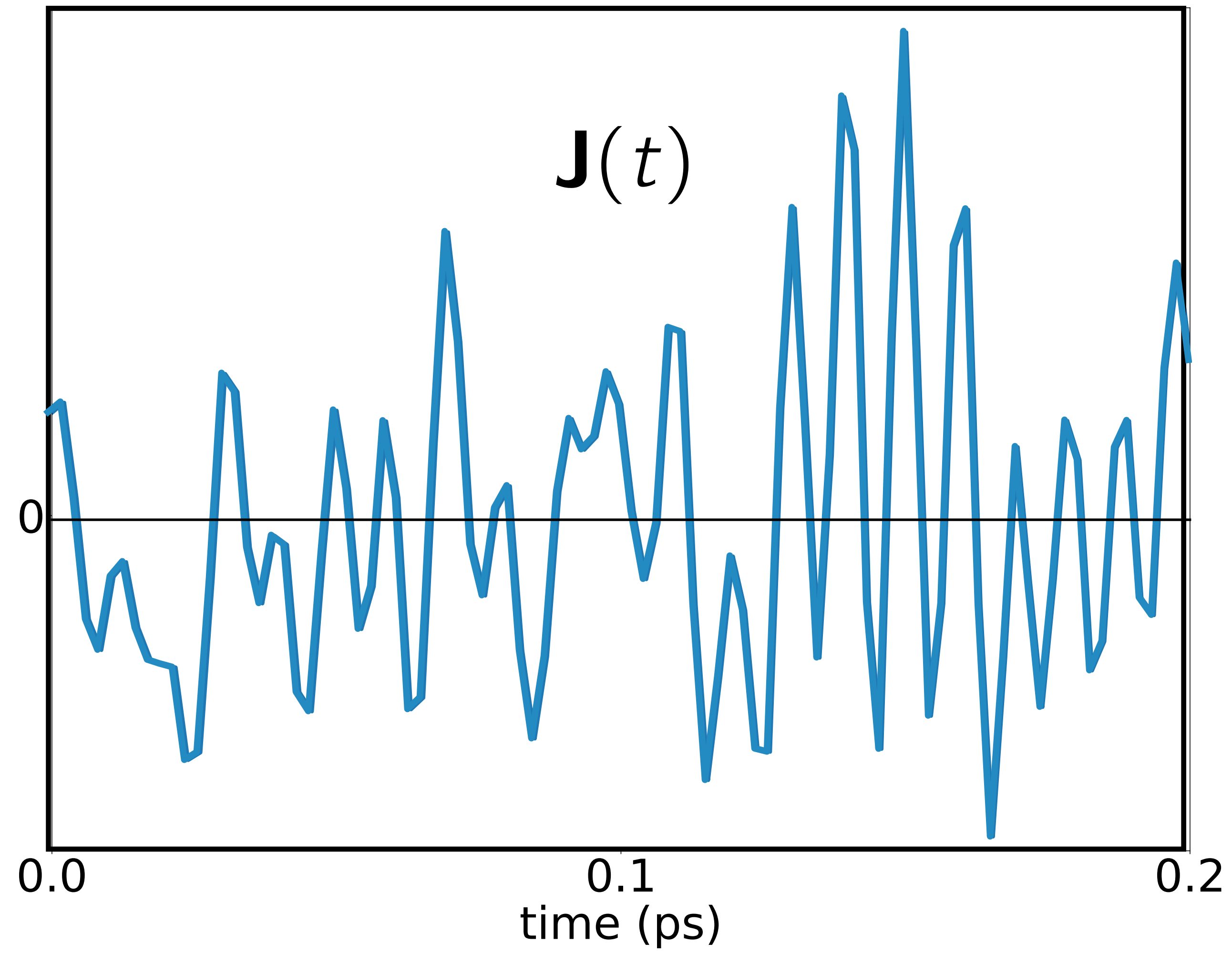

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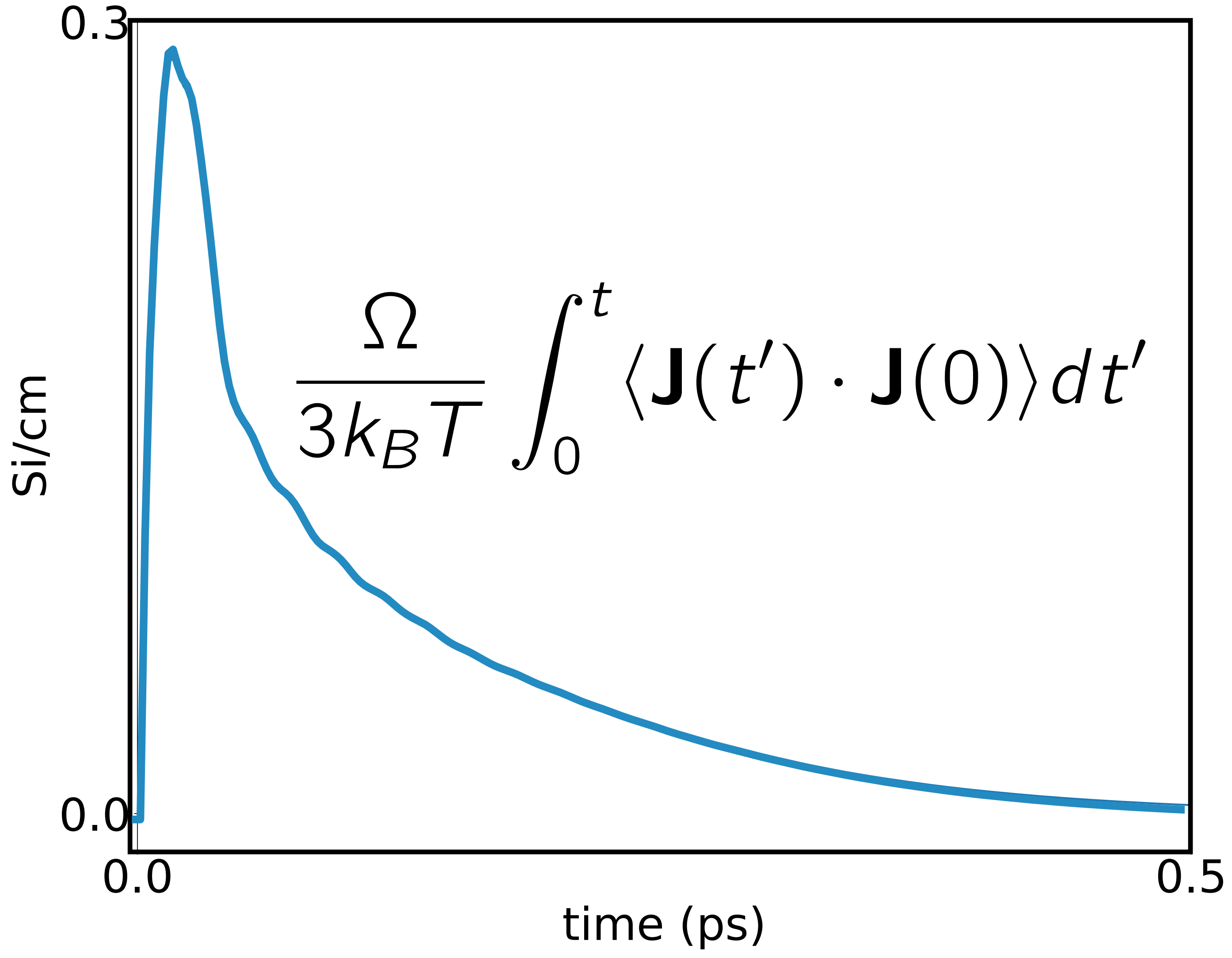

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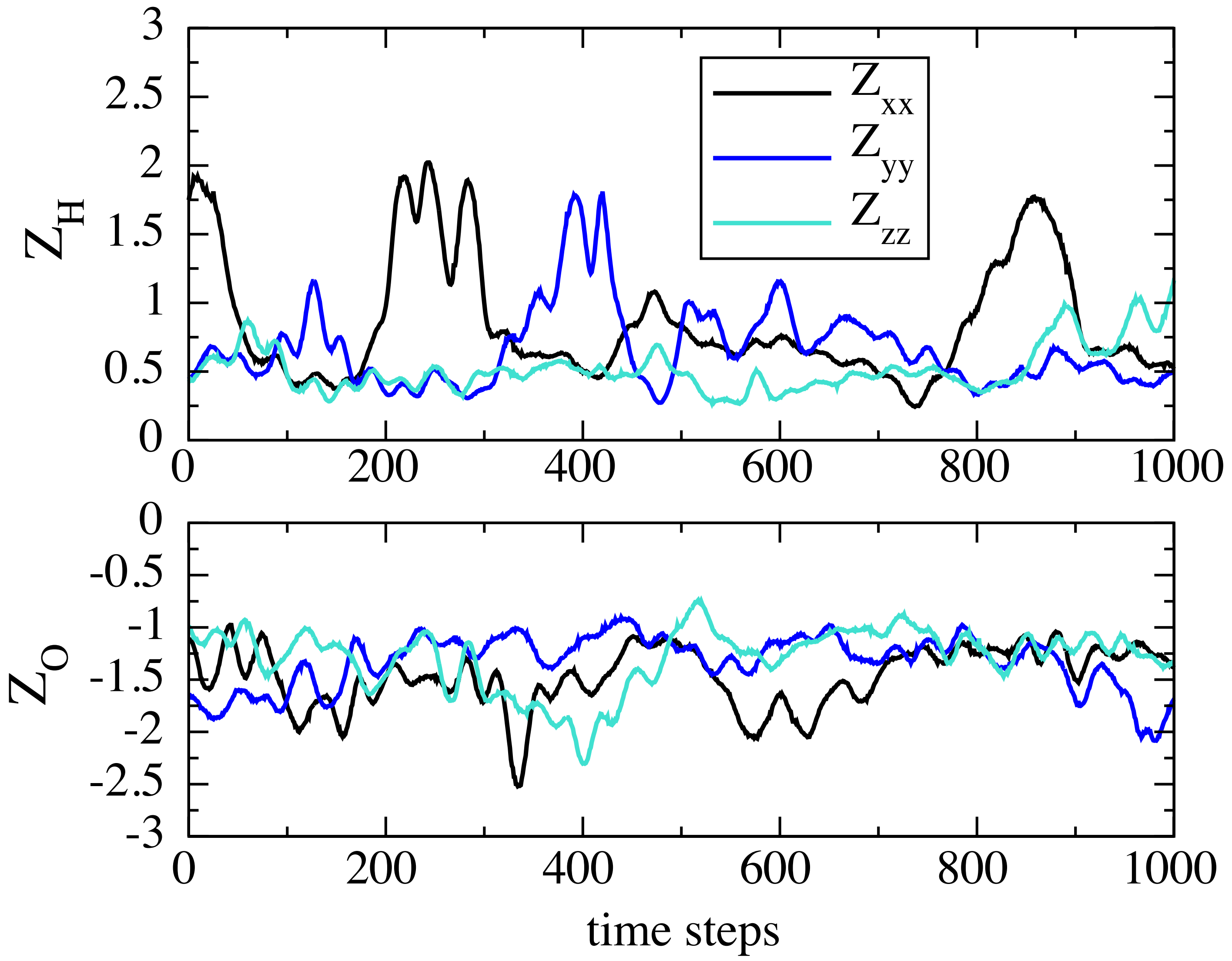
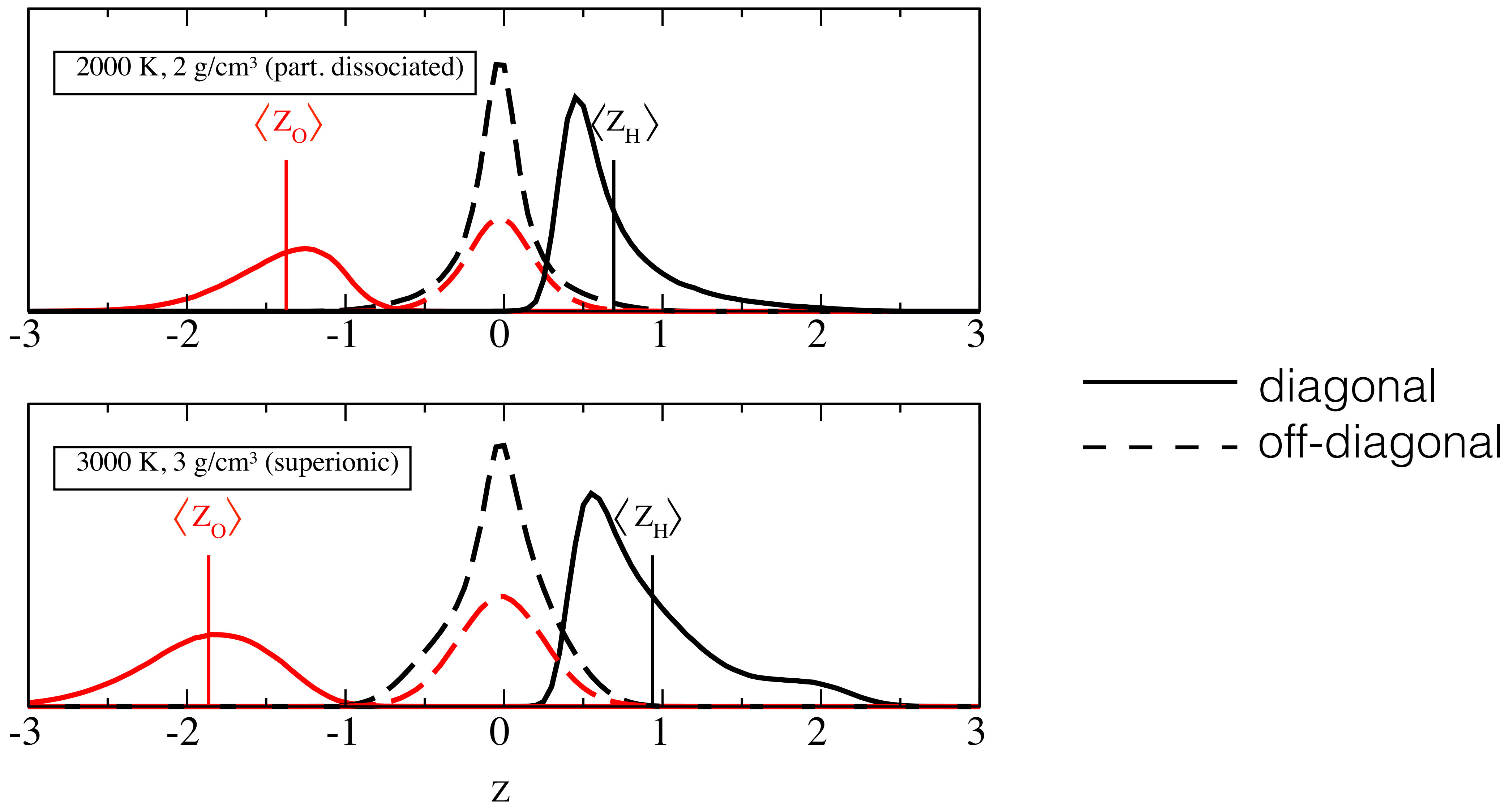
the conundrum

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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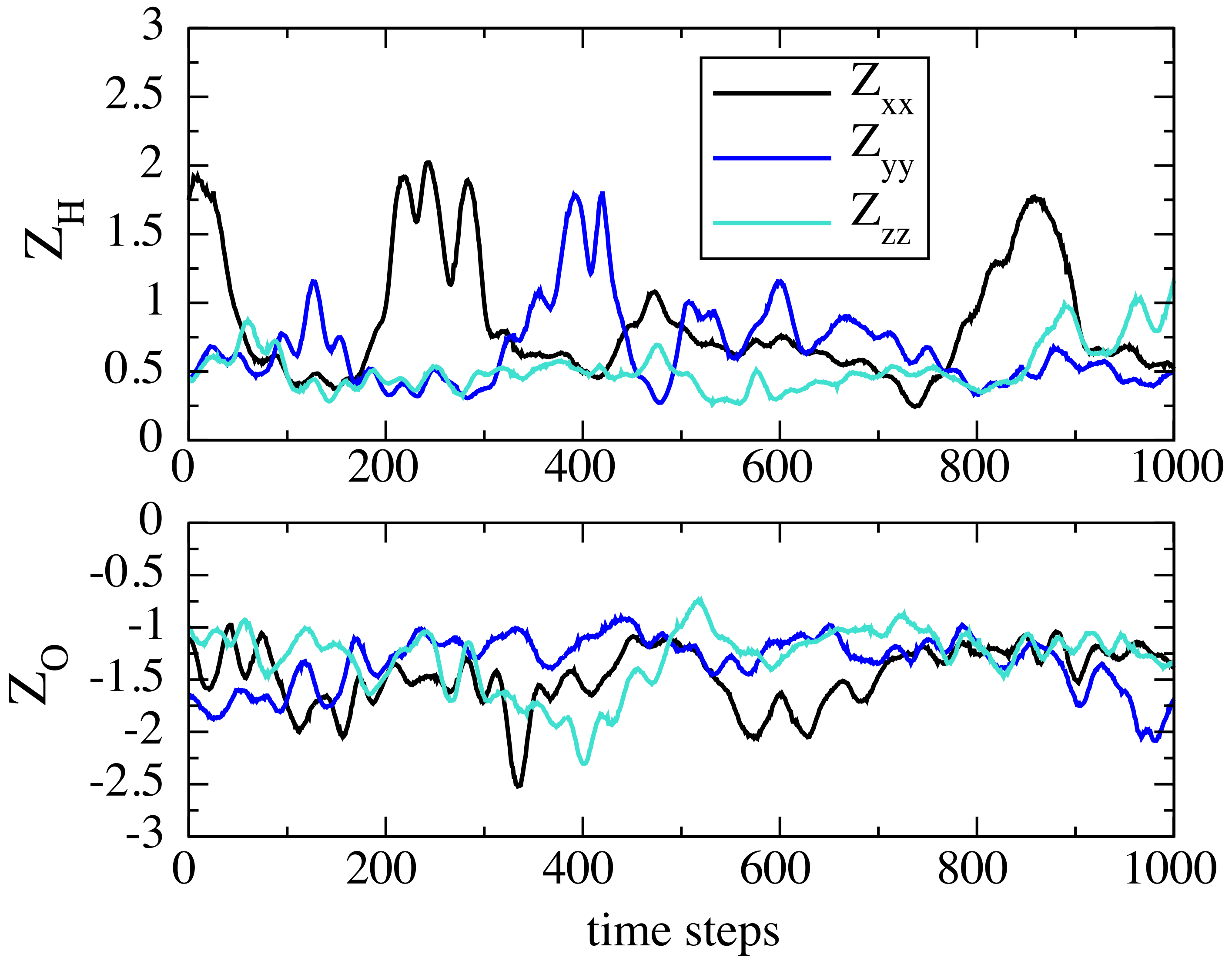

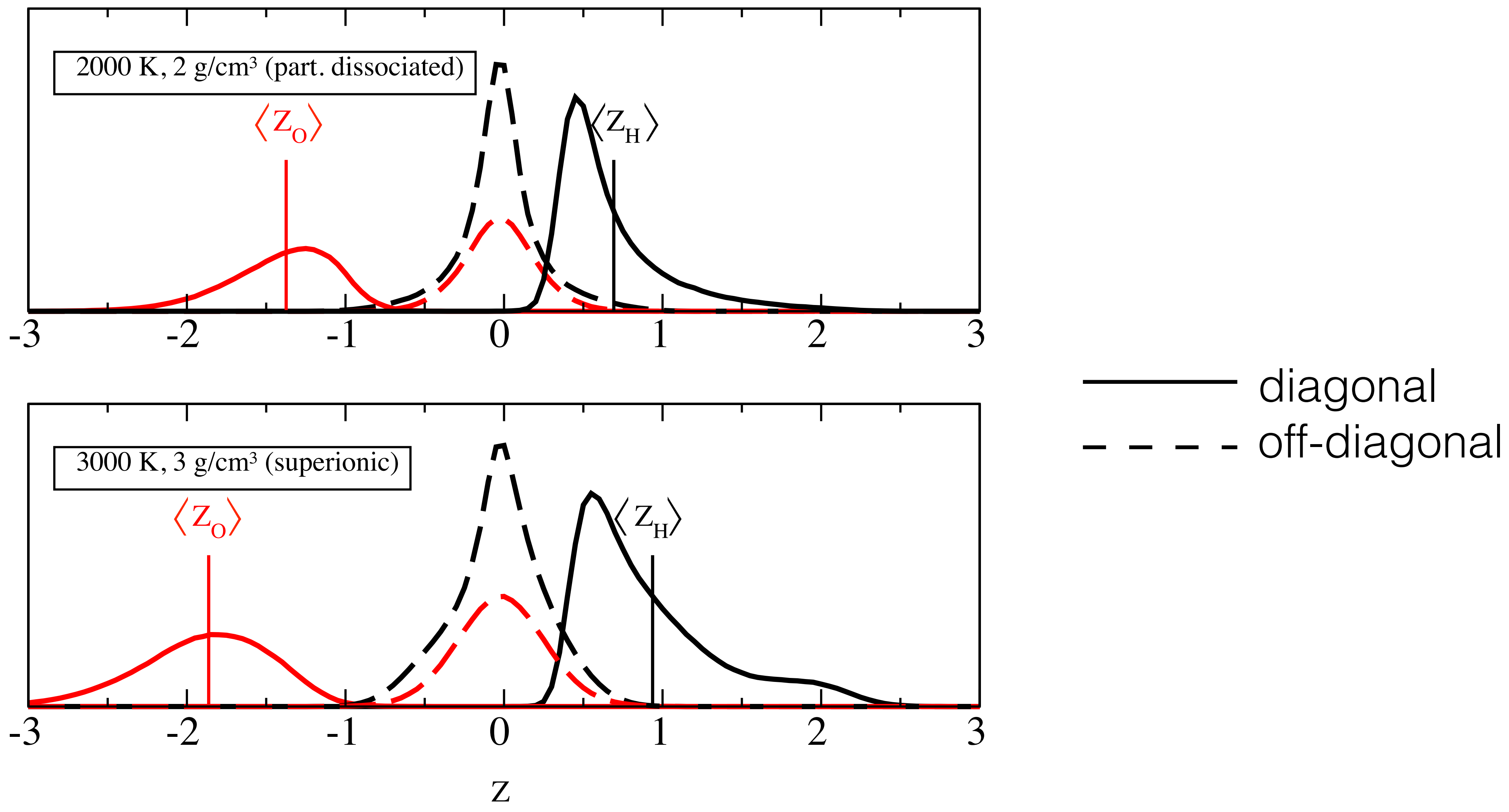

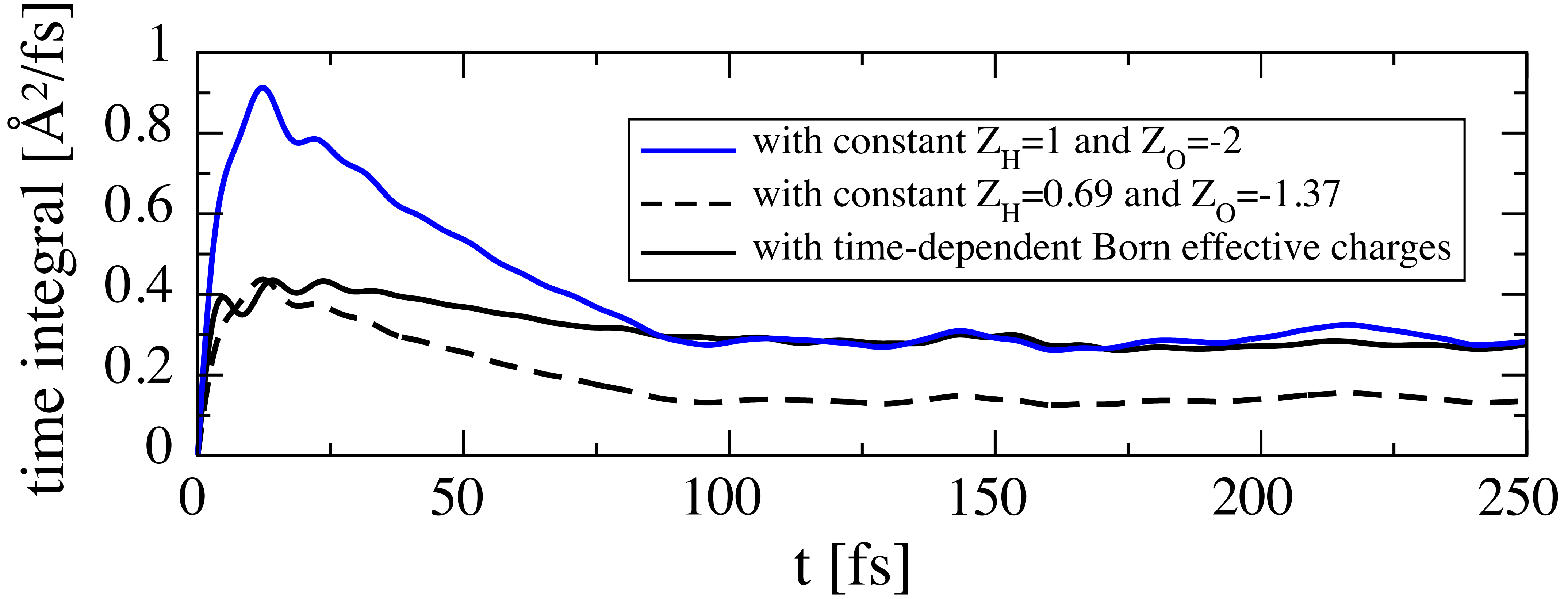

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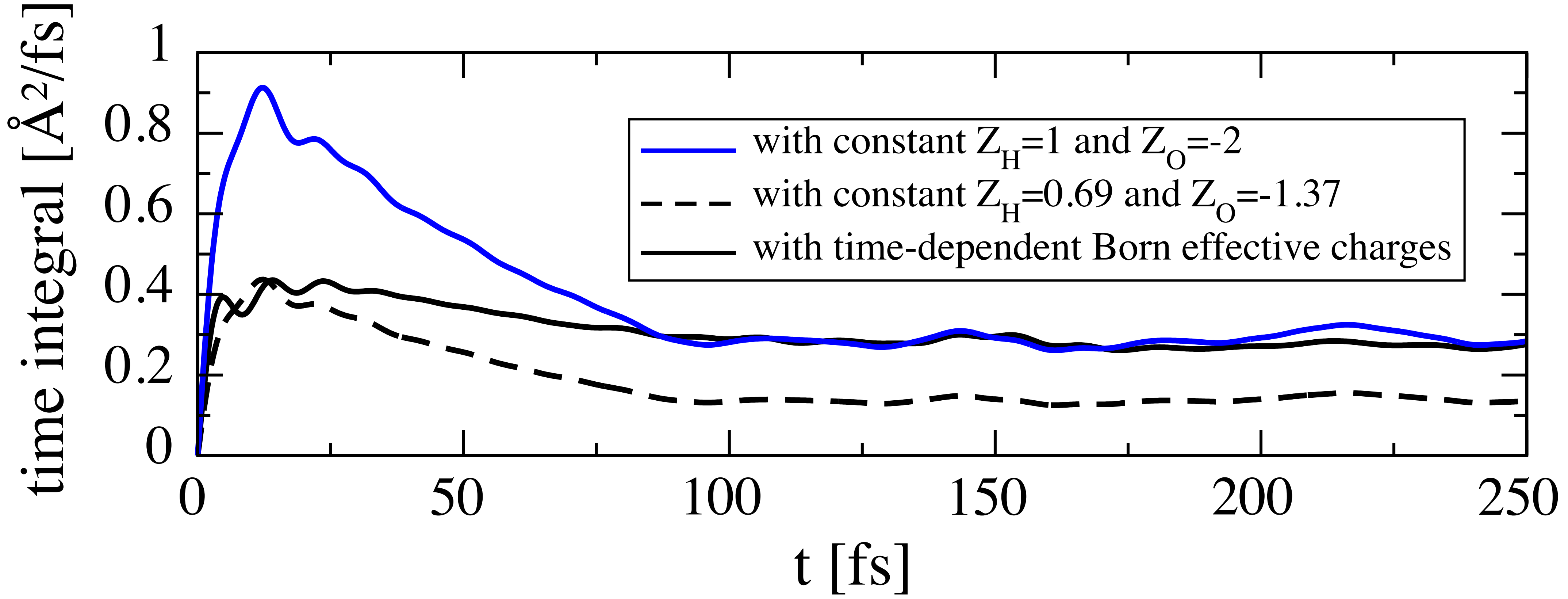

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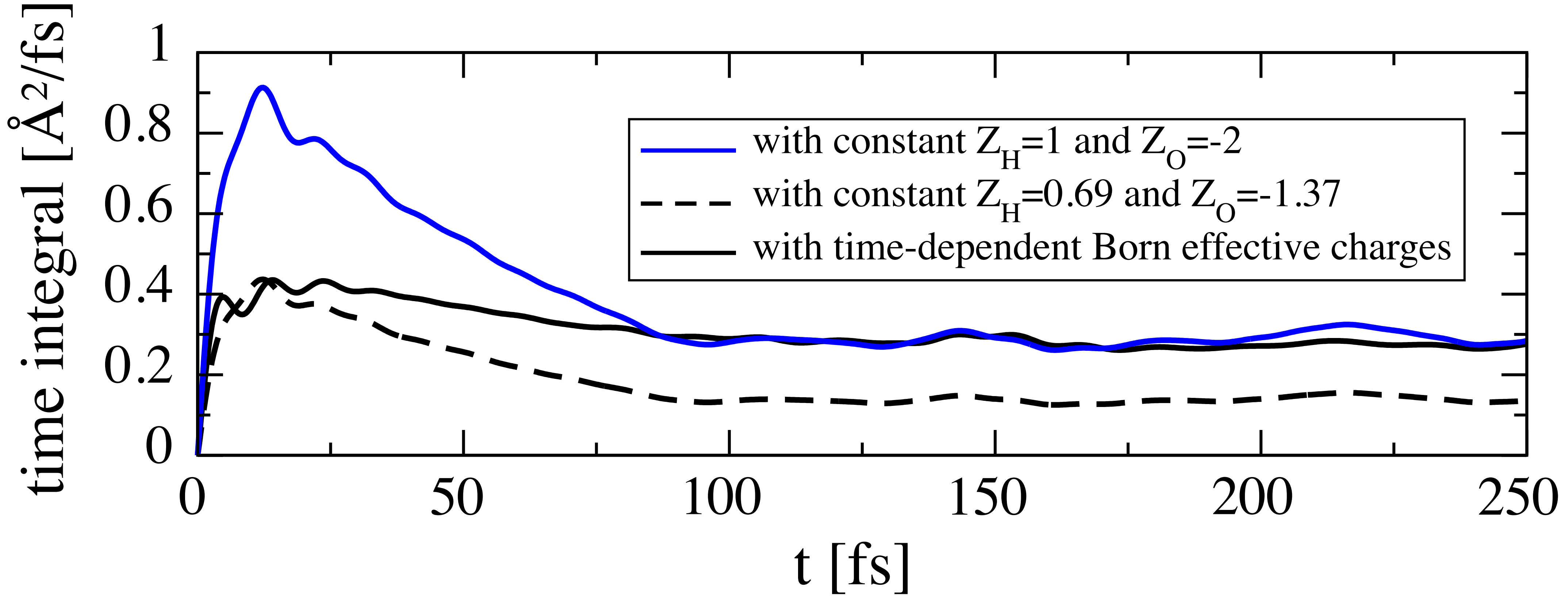
atomic *"oxidation states"*



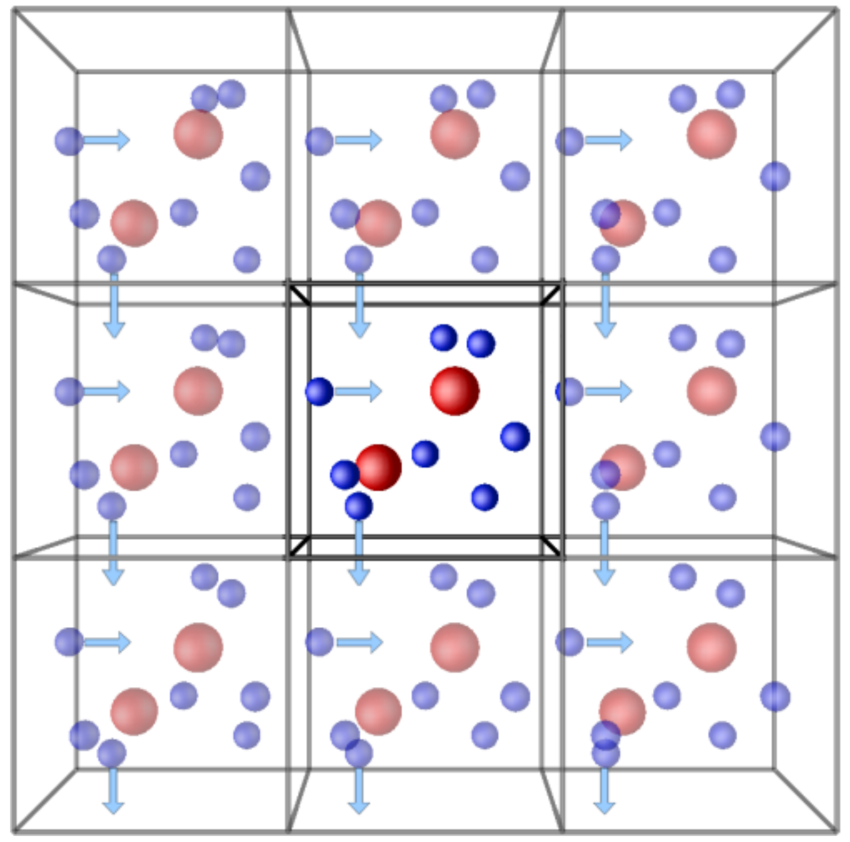
$$\int_0^t \langle \boldsymbol{J}(t')\boldsymbol{J}(0)\rangle dt'$$

how come?

and what are oxidation states, in the first place?

quantisation of adiabatic particle transport

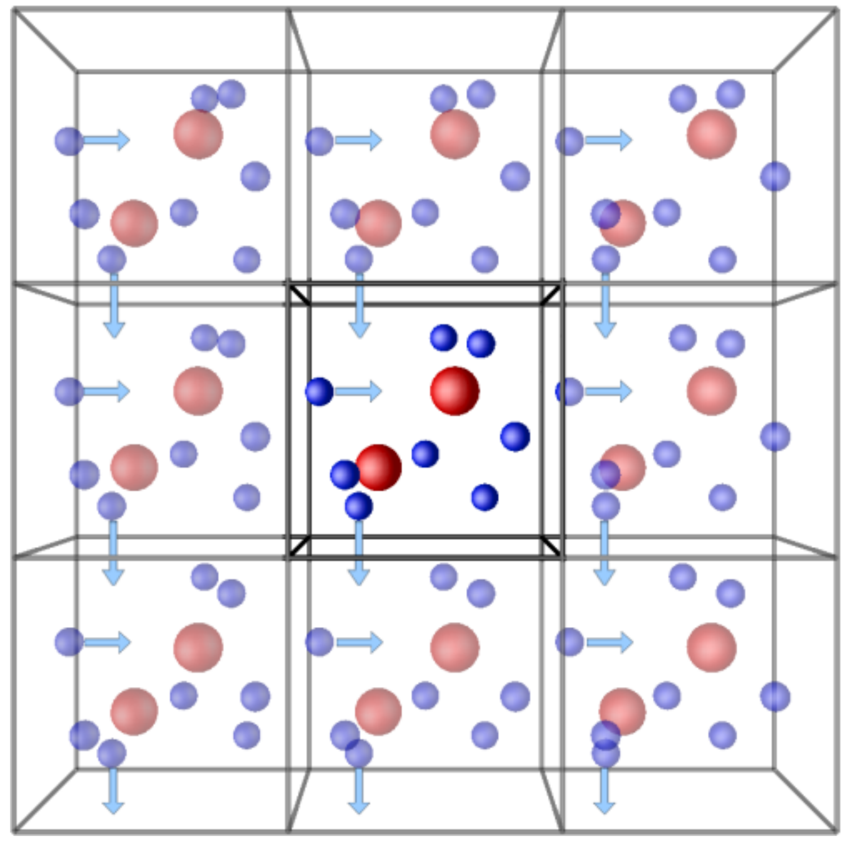
classical PBC



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

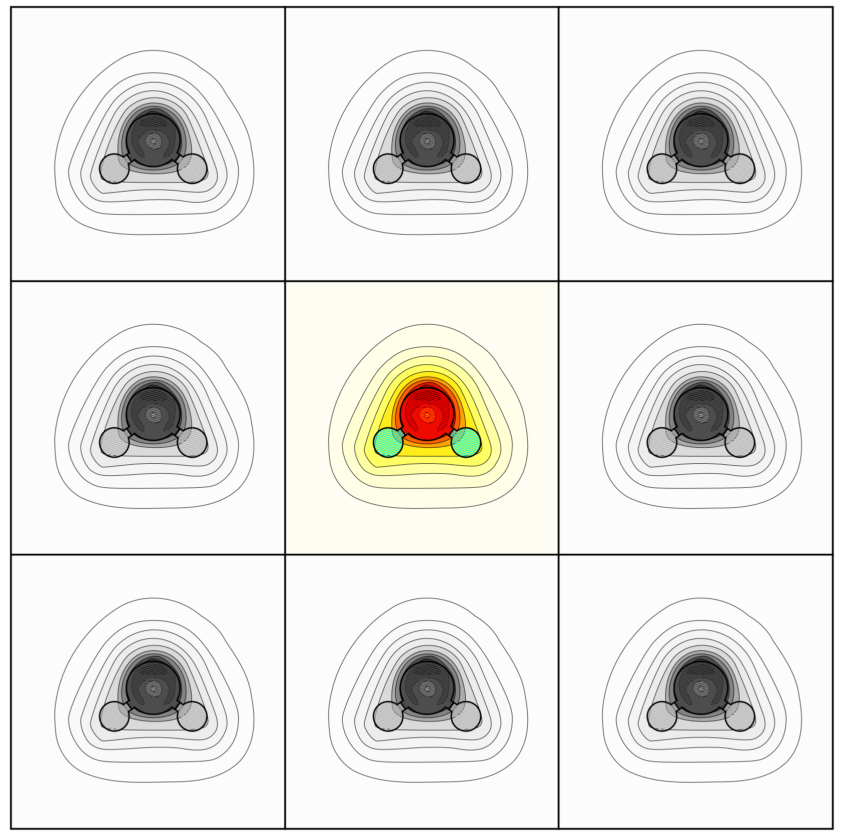
quantisation of adiabatic particle transport

classical PBC



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

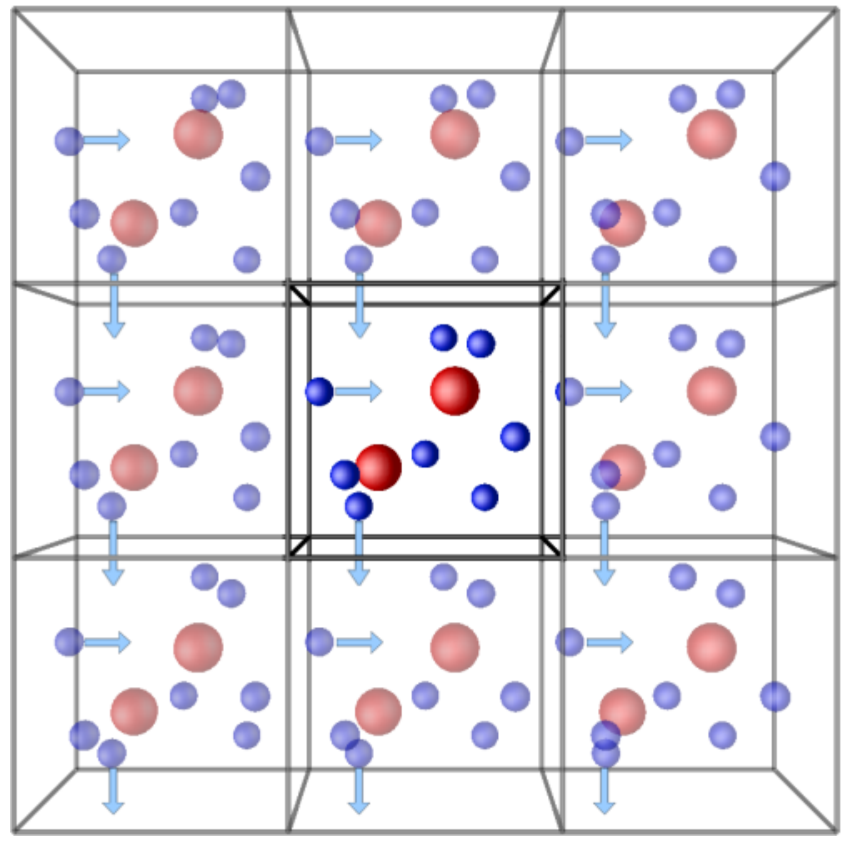
quantum PBC



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

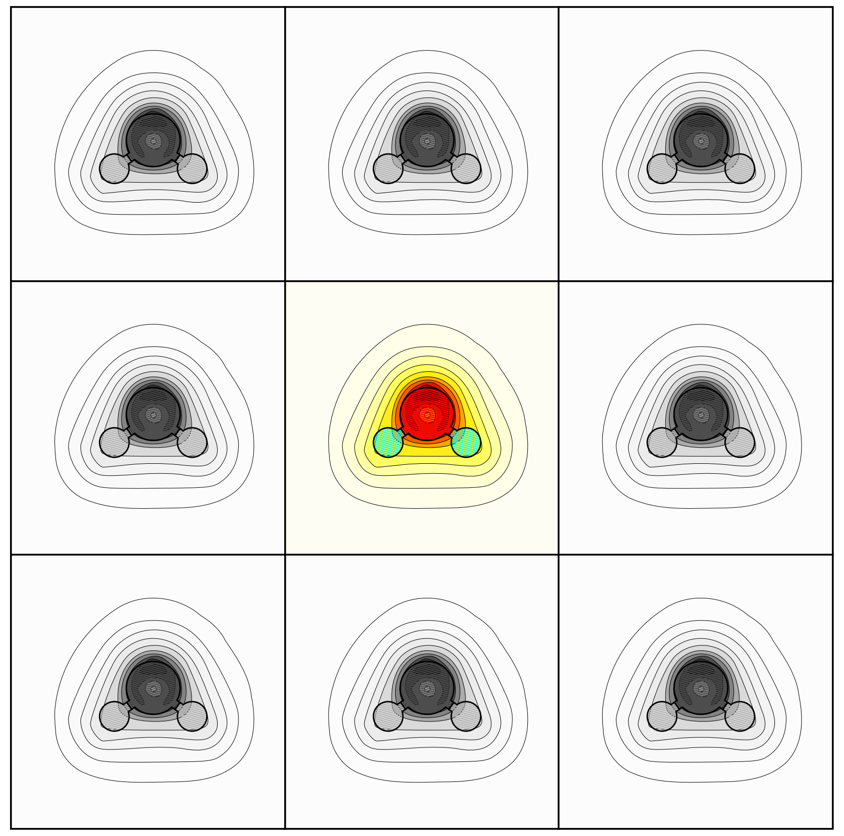
quantisation of adiabatic particle transport

classical PBC



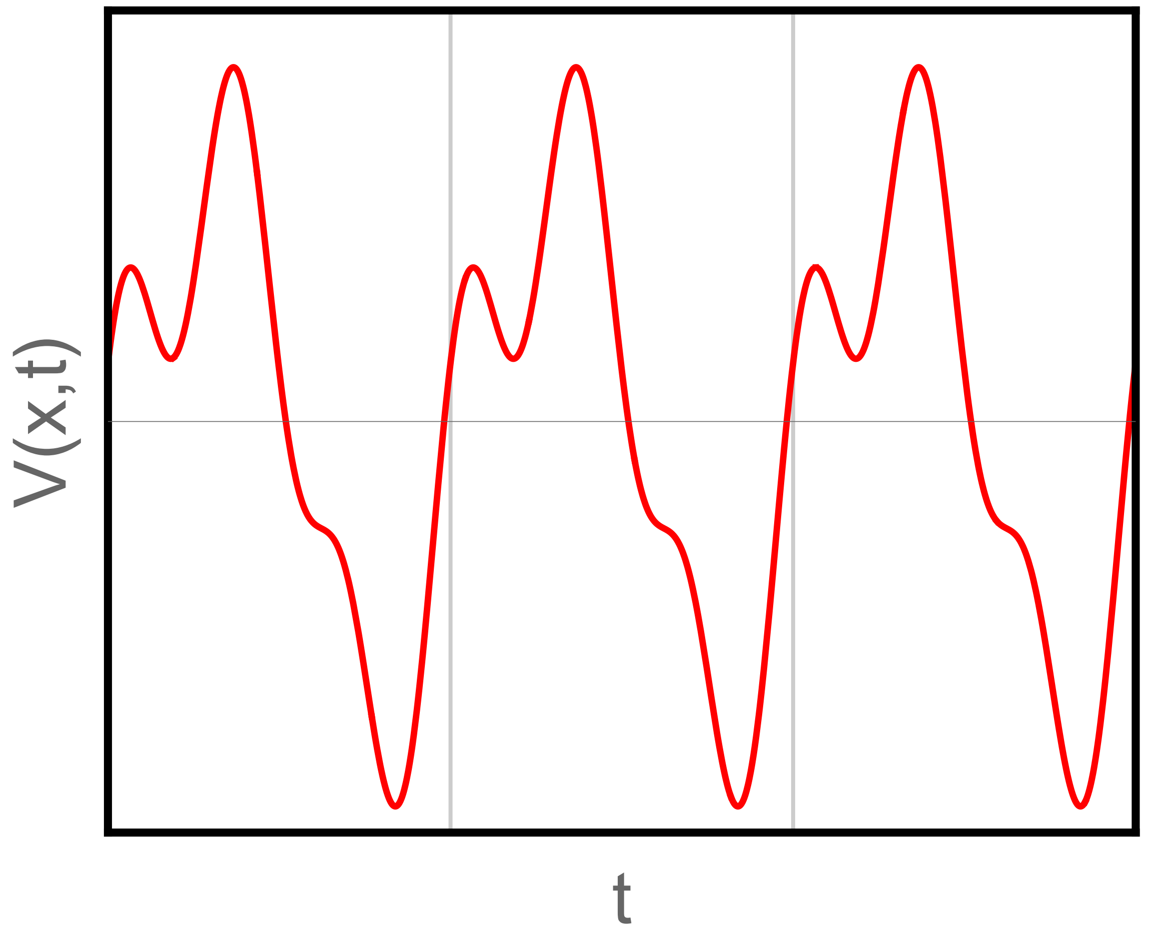
$V(x+L) = V(x)$

quantum PBC



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

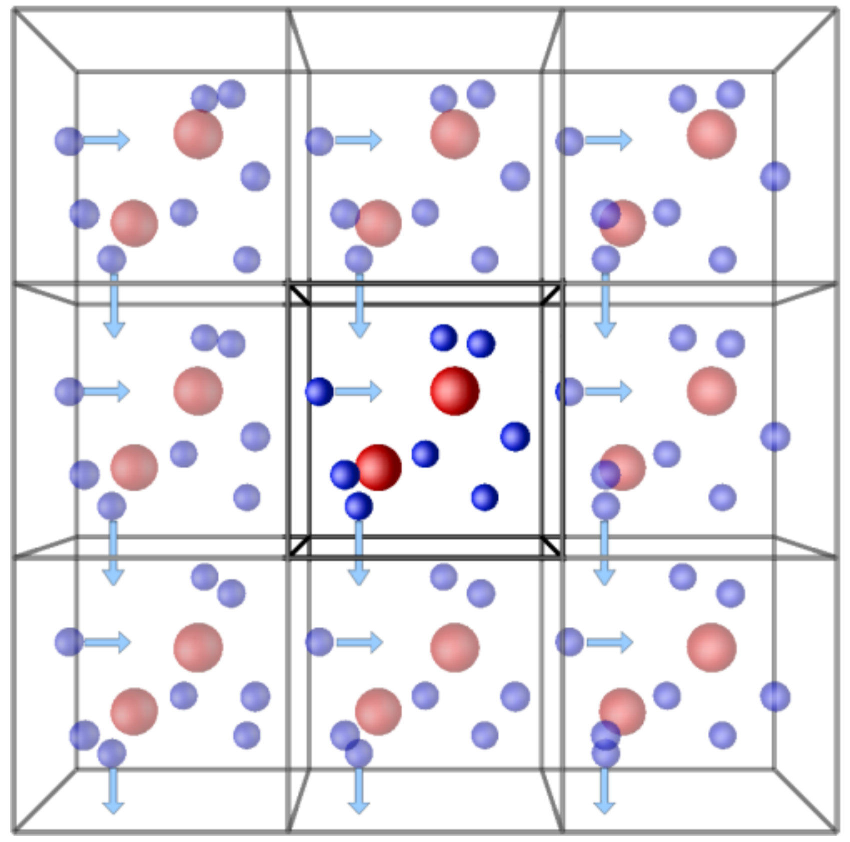
time periodicity



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

quantisation of adiabatic particle transport

classical PBC



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

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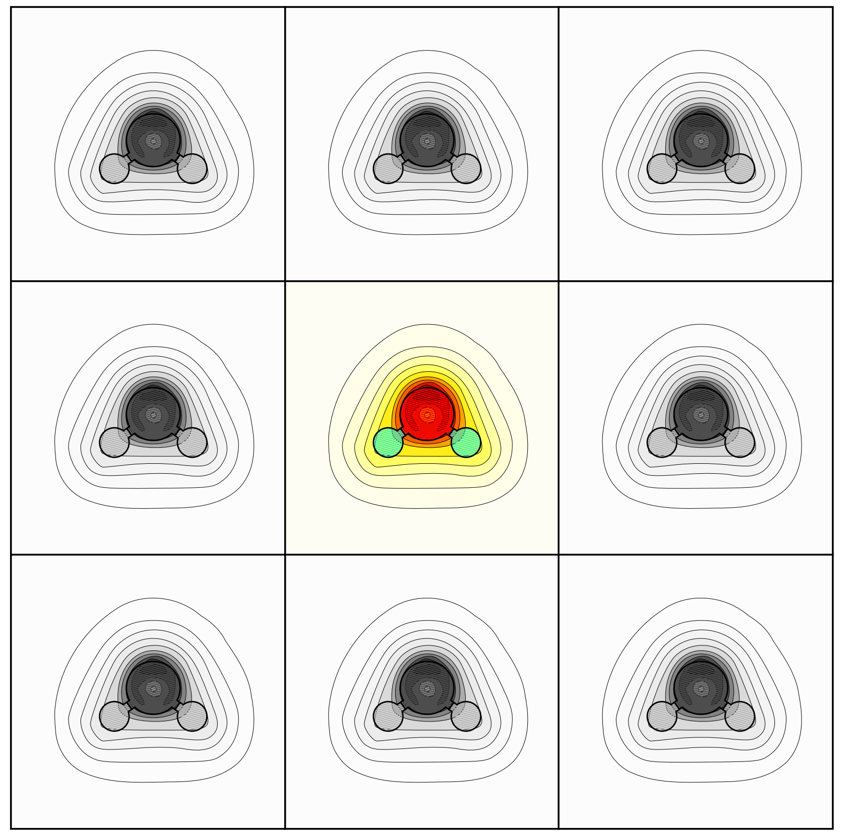
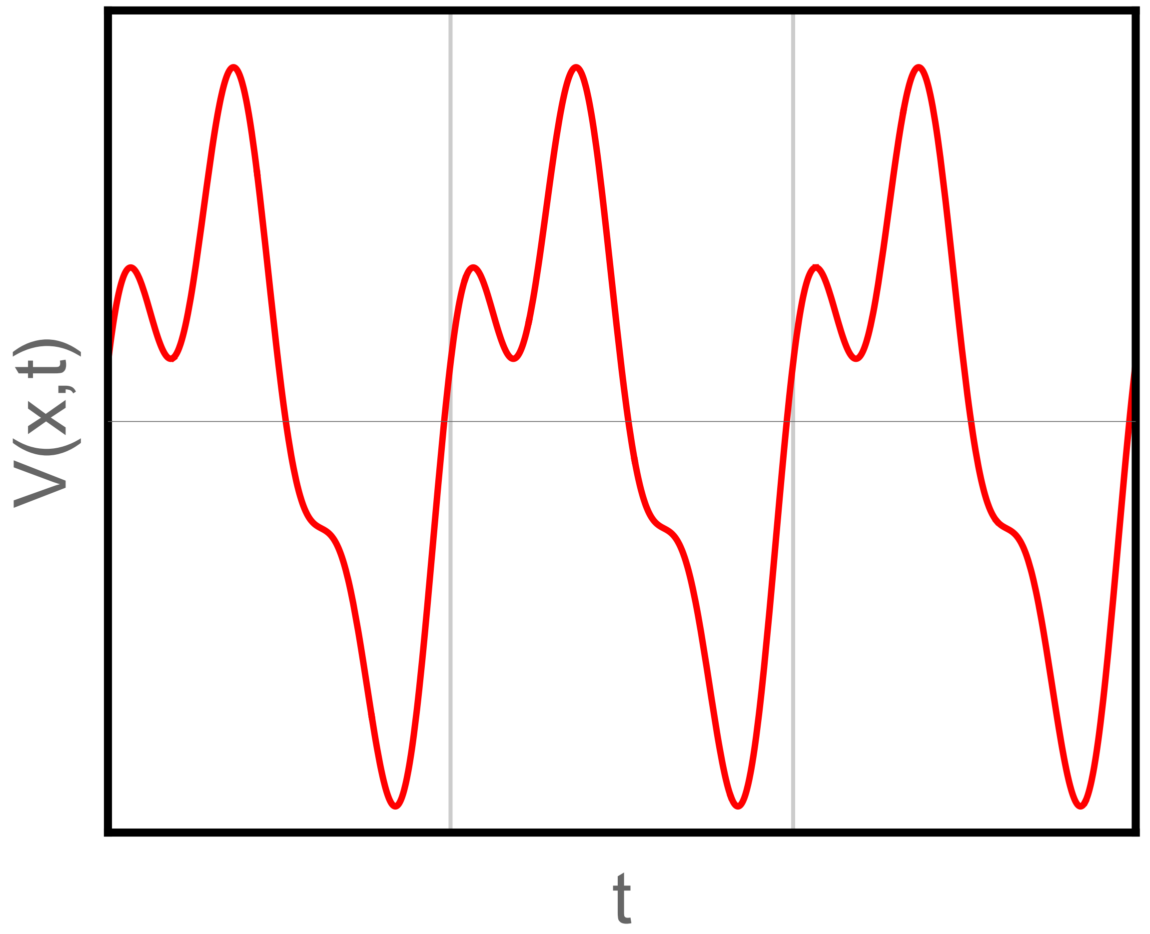


$$\psi(x+L) = \psi(x)$$

time periodicity



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

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

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

quantisation of adiabatic particle transport

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

$$J_\alpha(t) = \frac{e}{L^3}\sum_s Q_s V_{s\alpha}(t) + \frac{e}{2\pi L^2}\frac{d}{dt}\mathrm{Im}\log \overbrace{\langle\Psi(t)|e^{i\frac{2\pi X_\alpha}{L}}|\Psi(t)\rangle}^{\gamma(t)}$$

R. Resta, Phys. Rev. Lett. **80**, 1800 (1998)

quantisation of adiabatic particle transport

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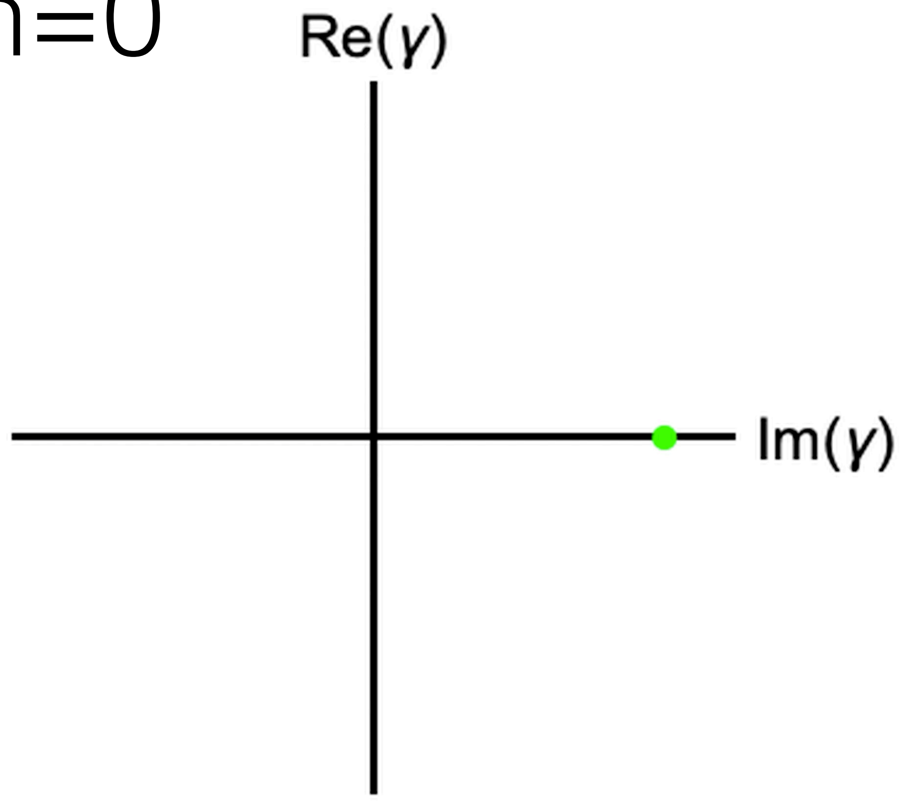
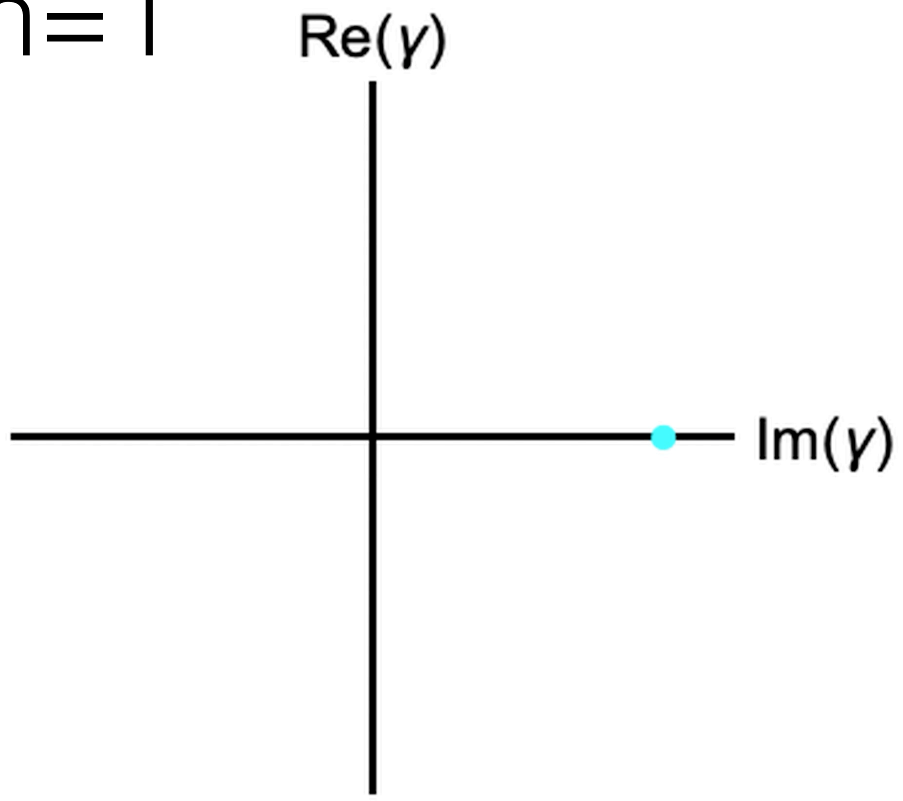
R. Resta, Phys. Rev. Lett. **80**, 1800 (1998)

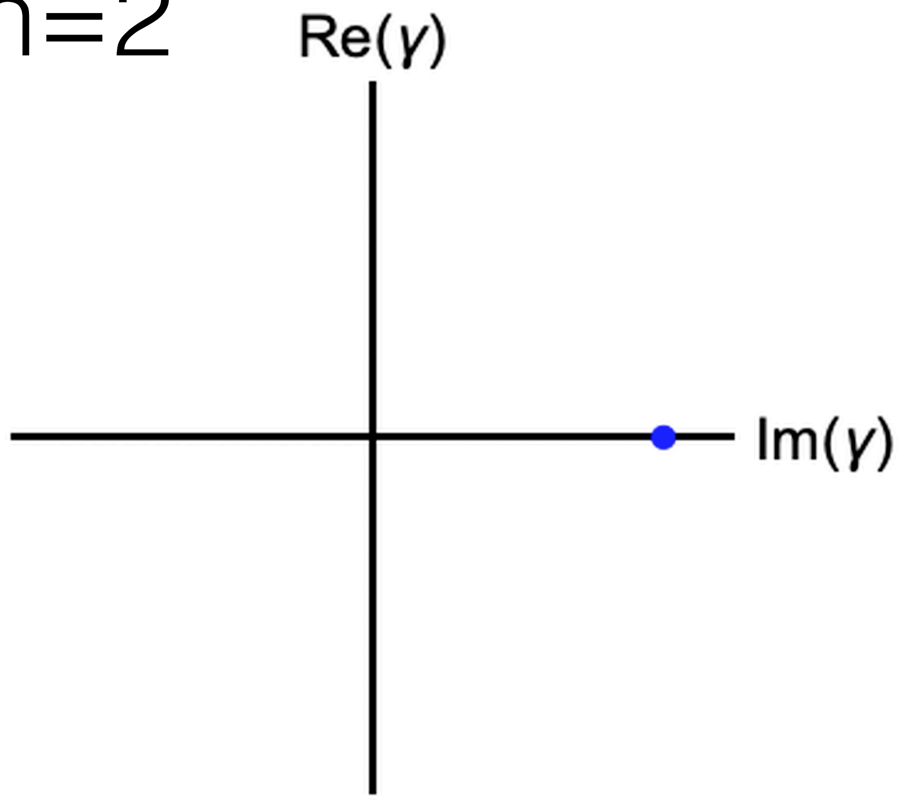
n=0



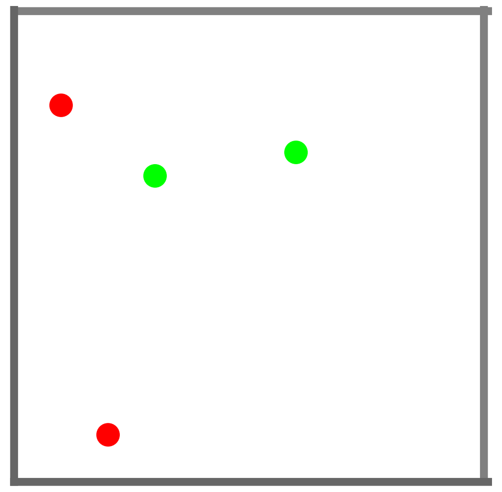
n=1



n=2



what are oxidation states, in the first place?



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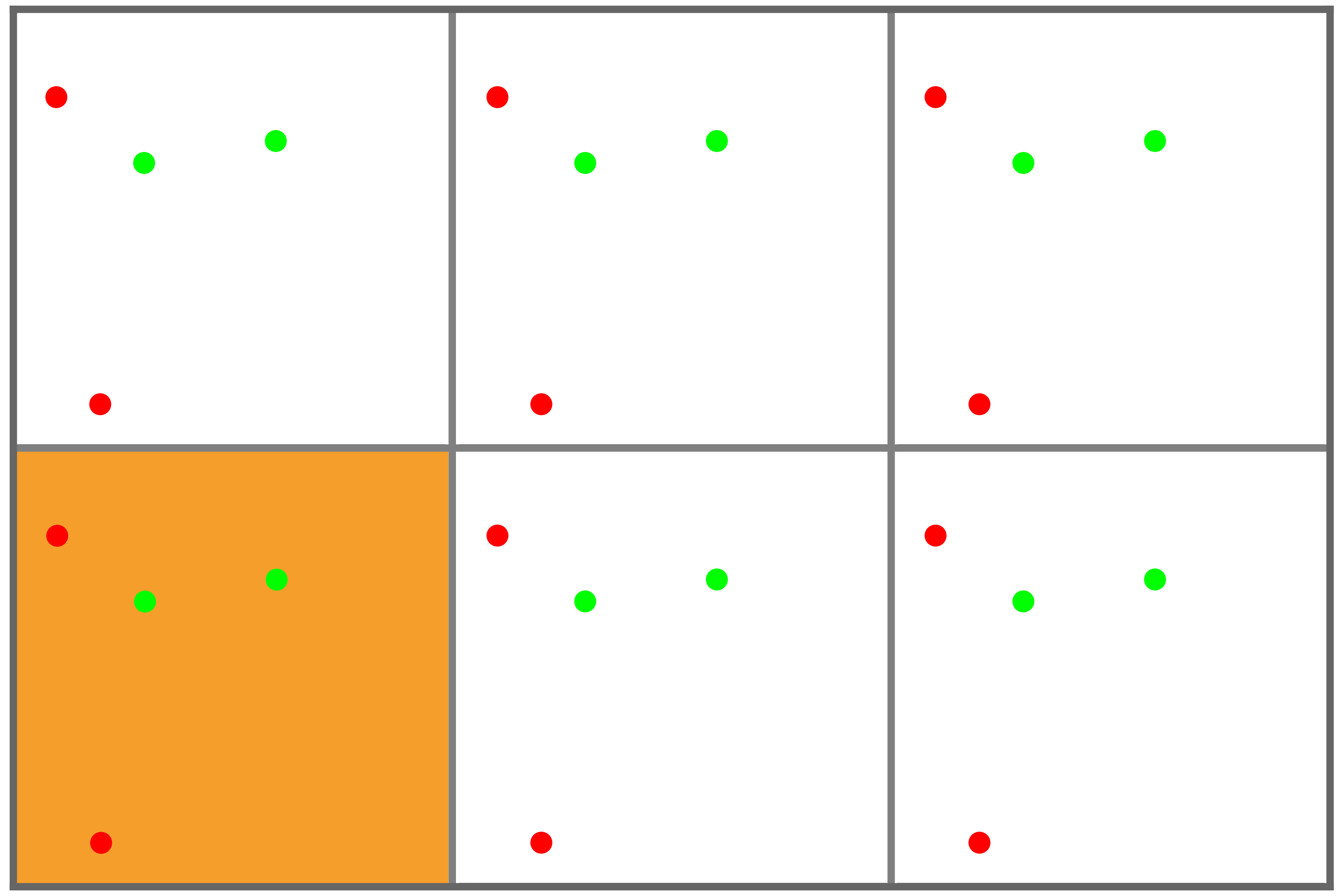
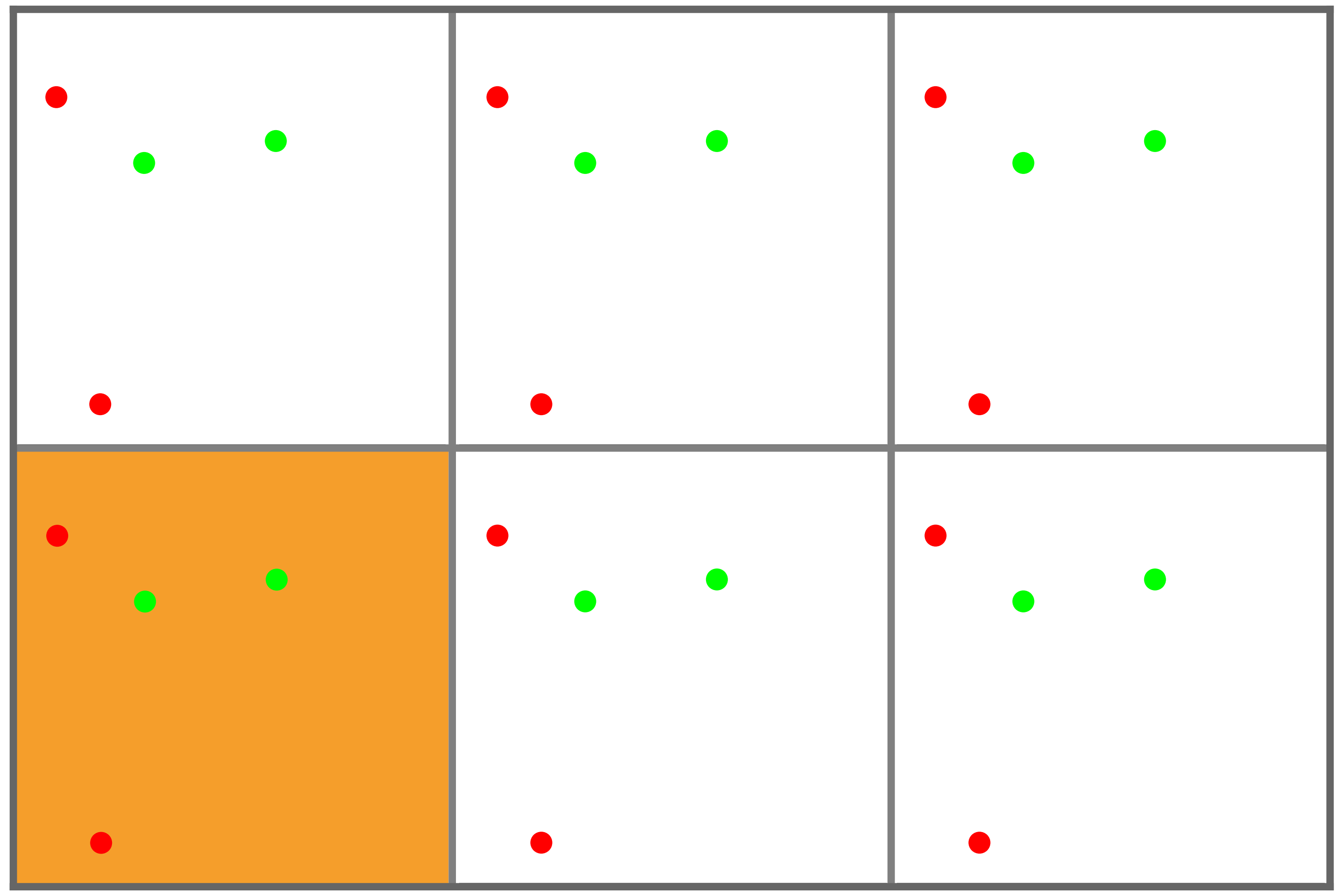
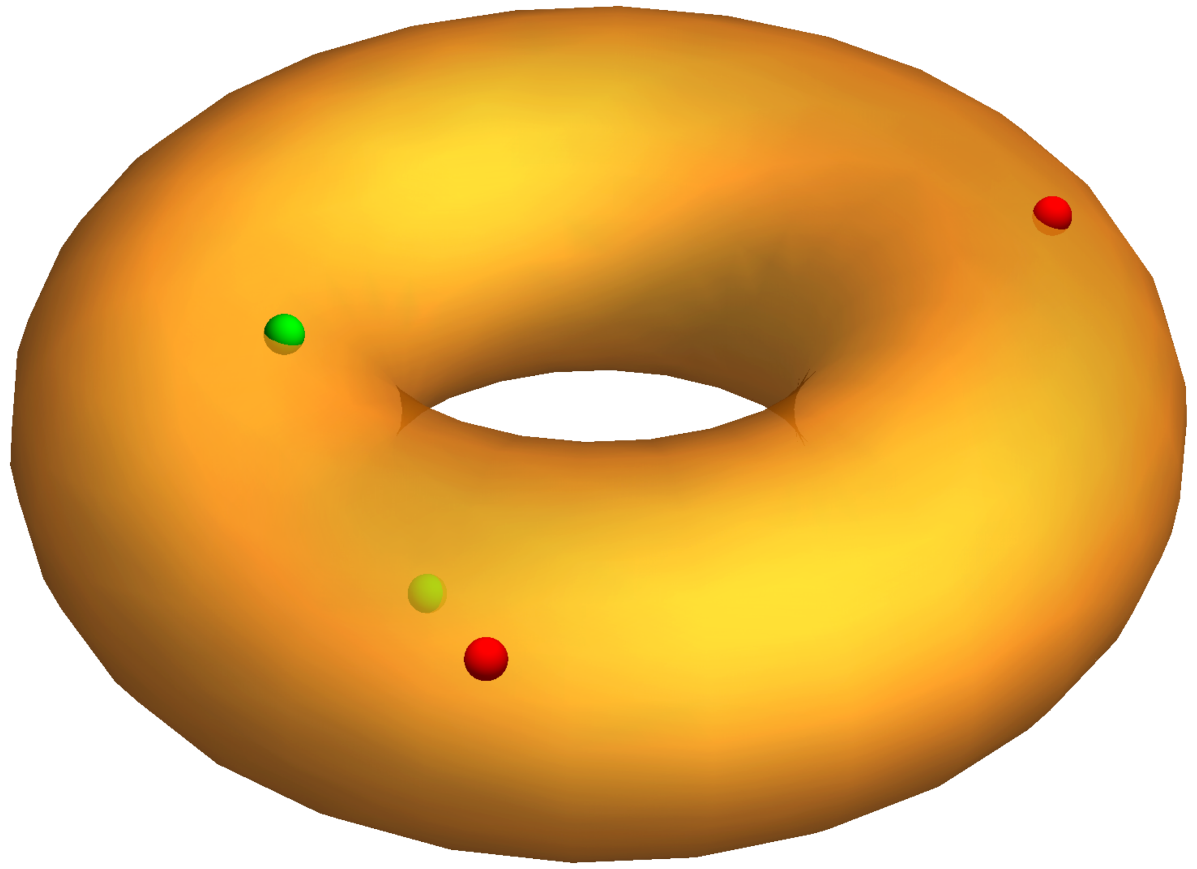


what are oxidation states, in the first place?

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





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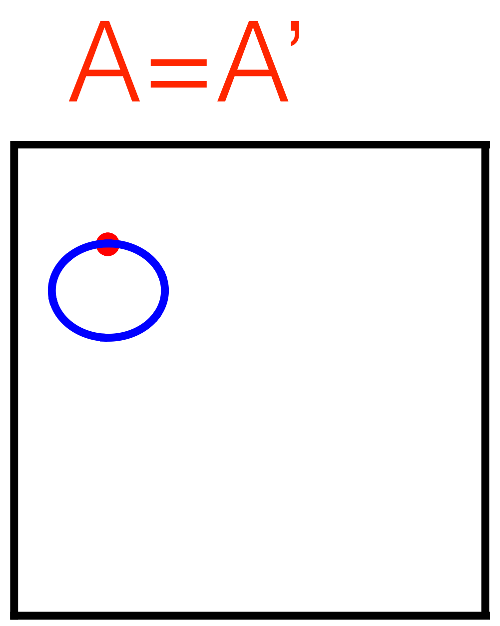

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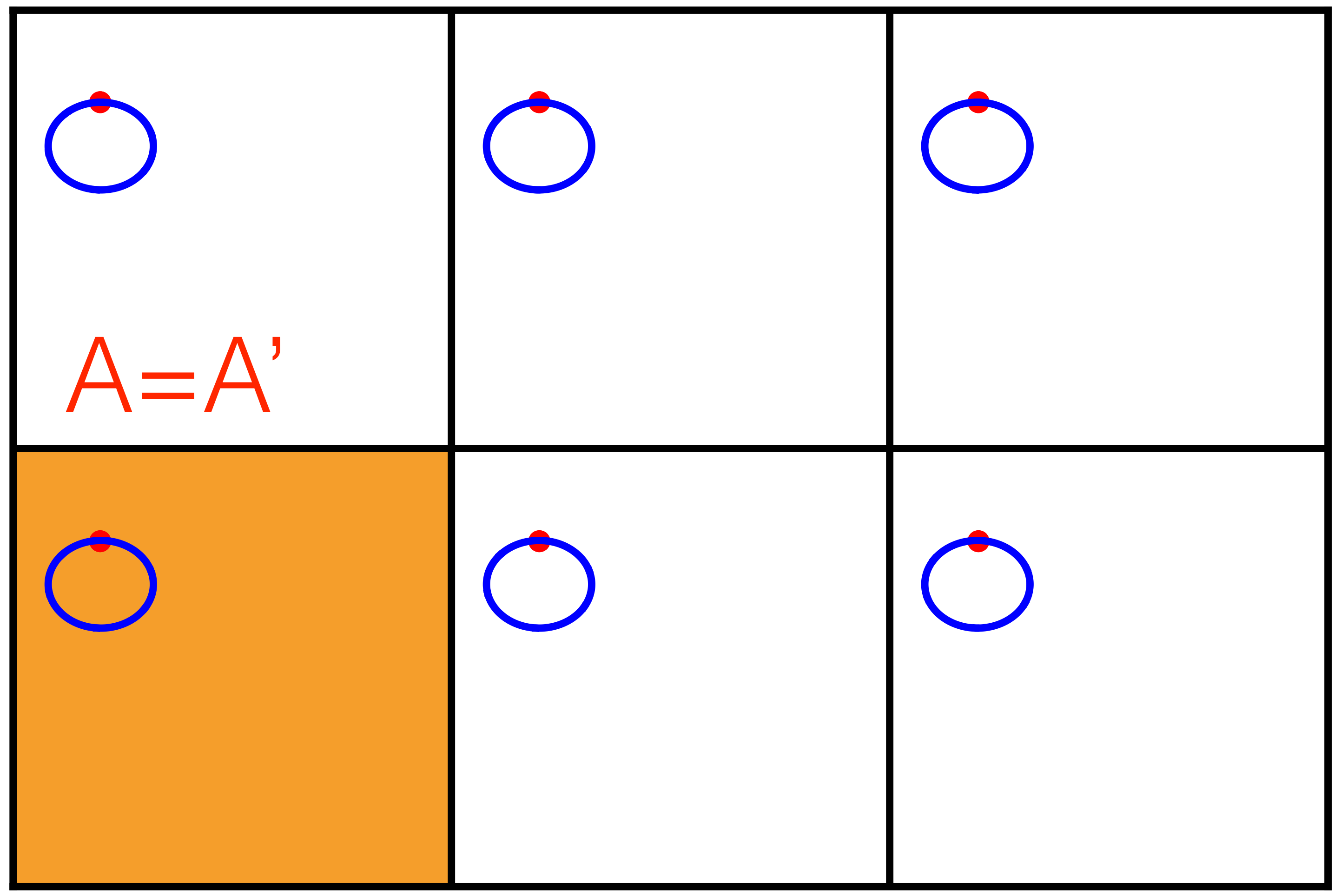

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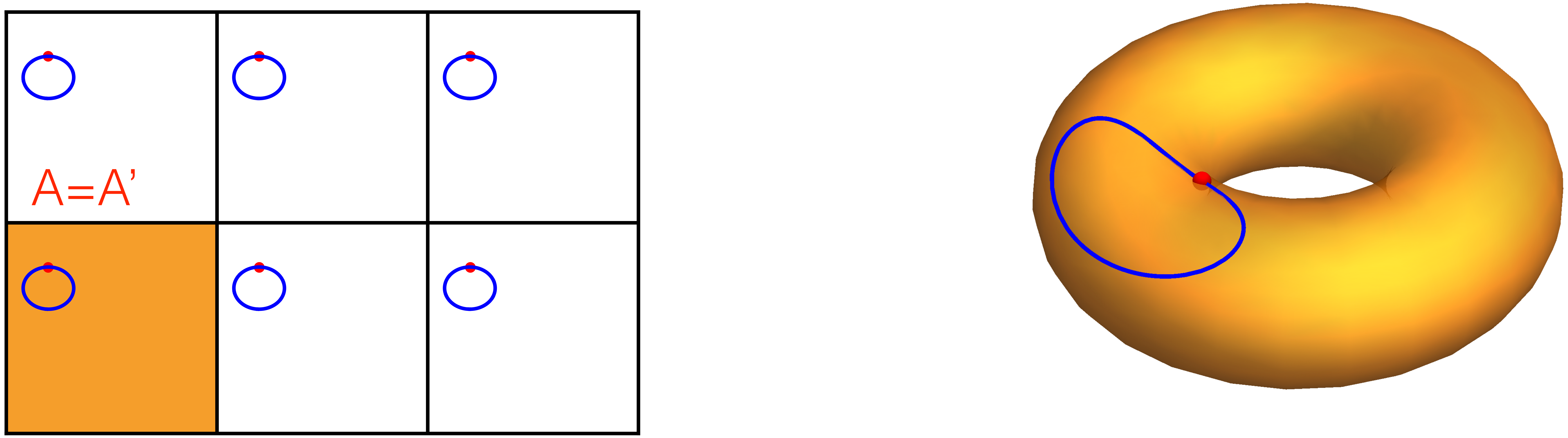

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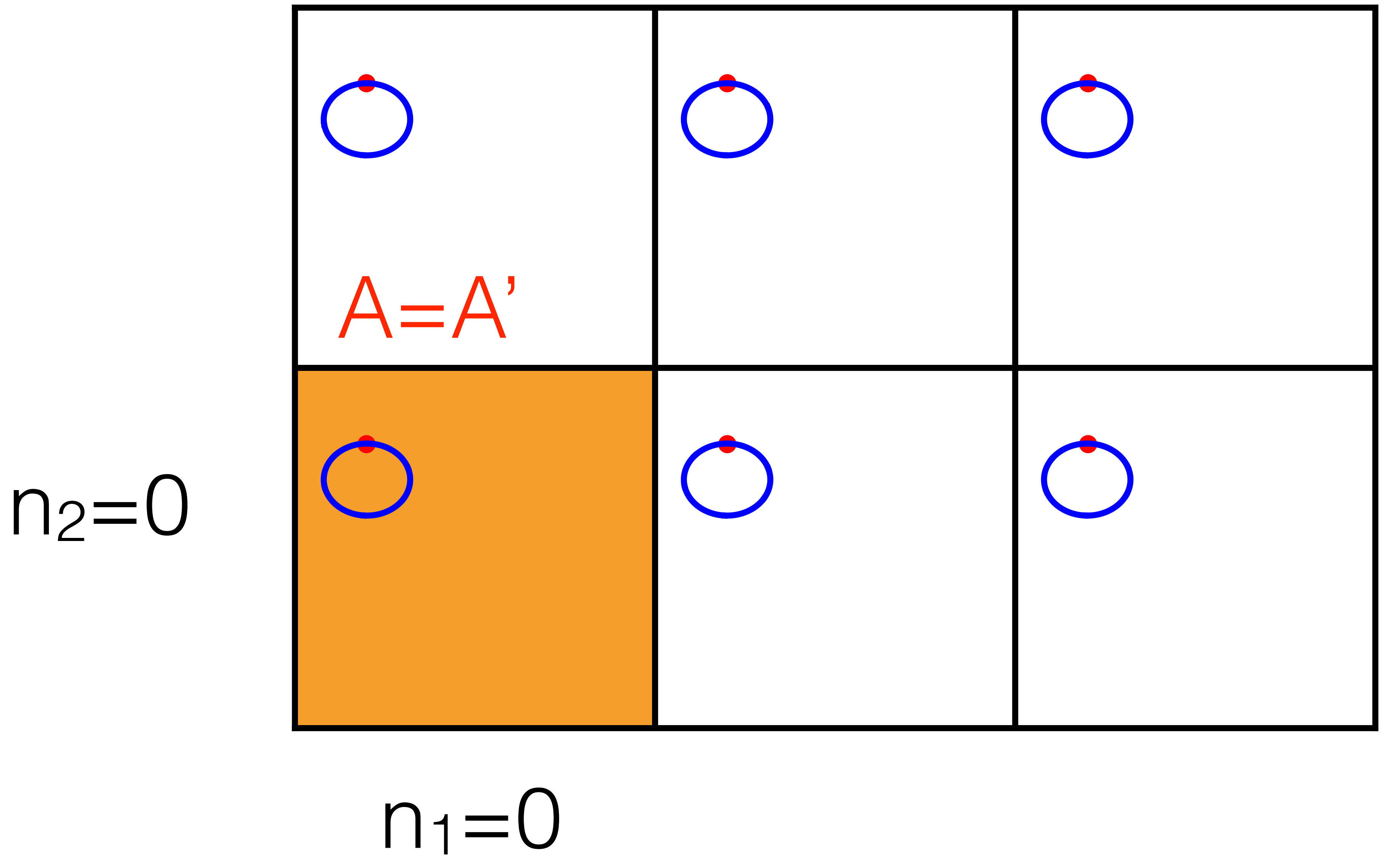

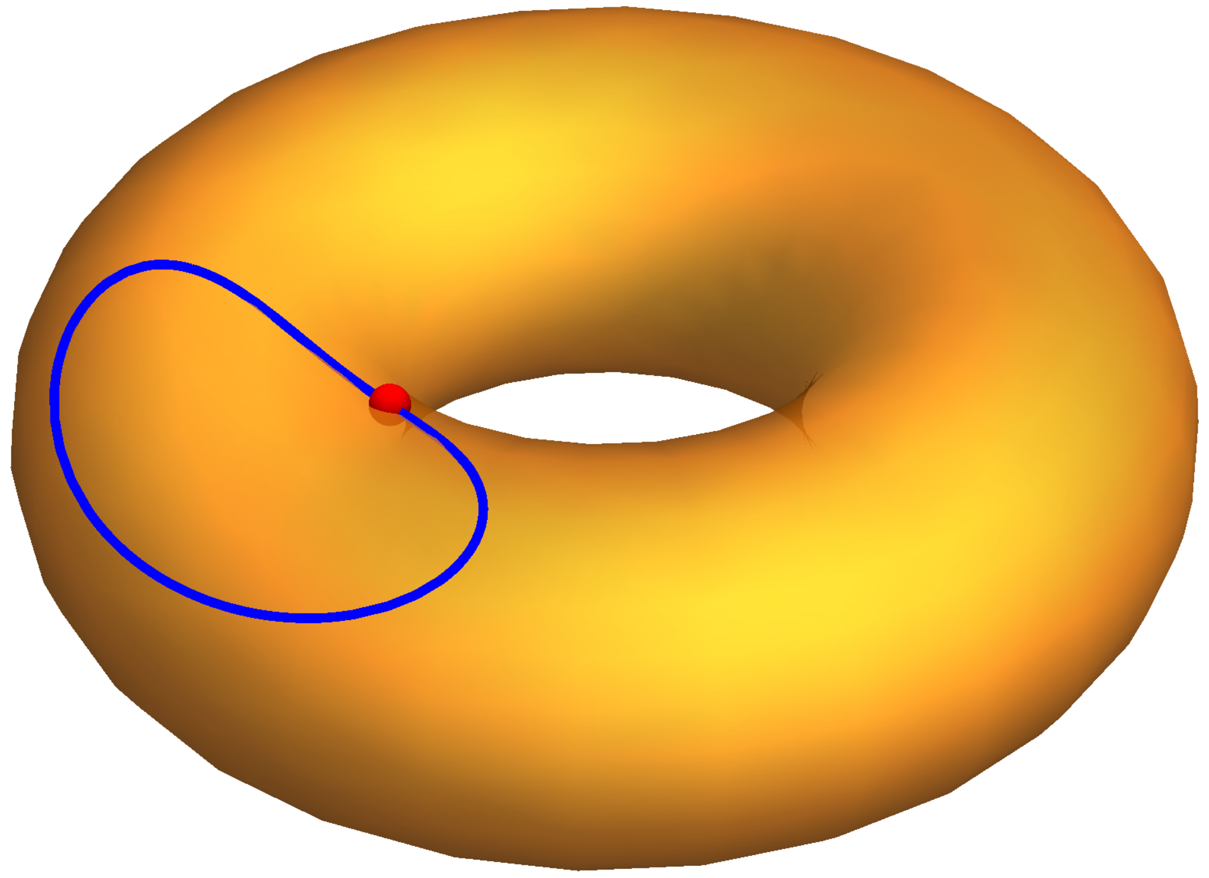

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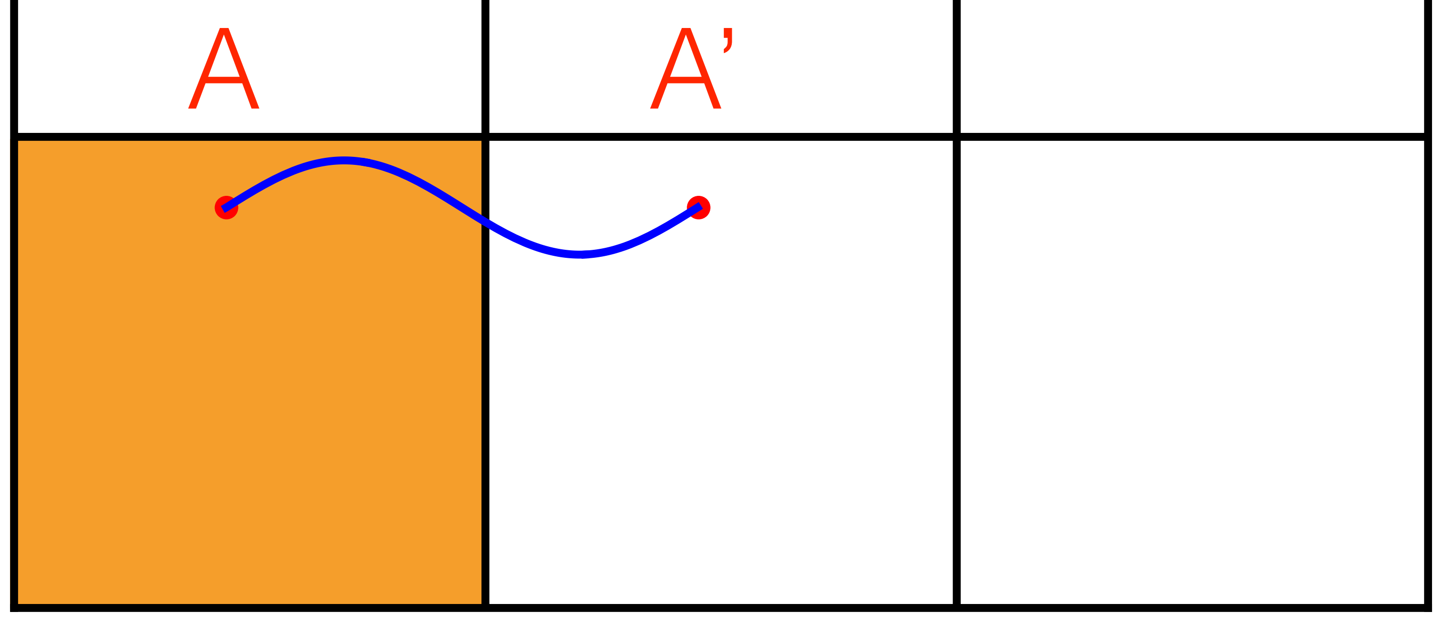

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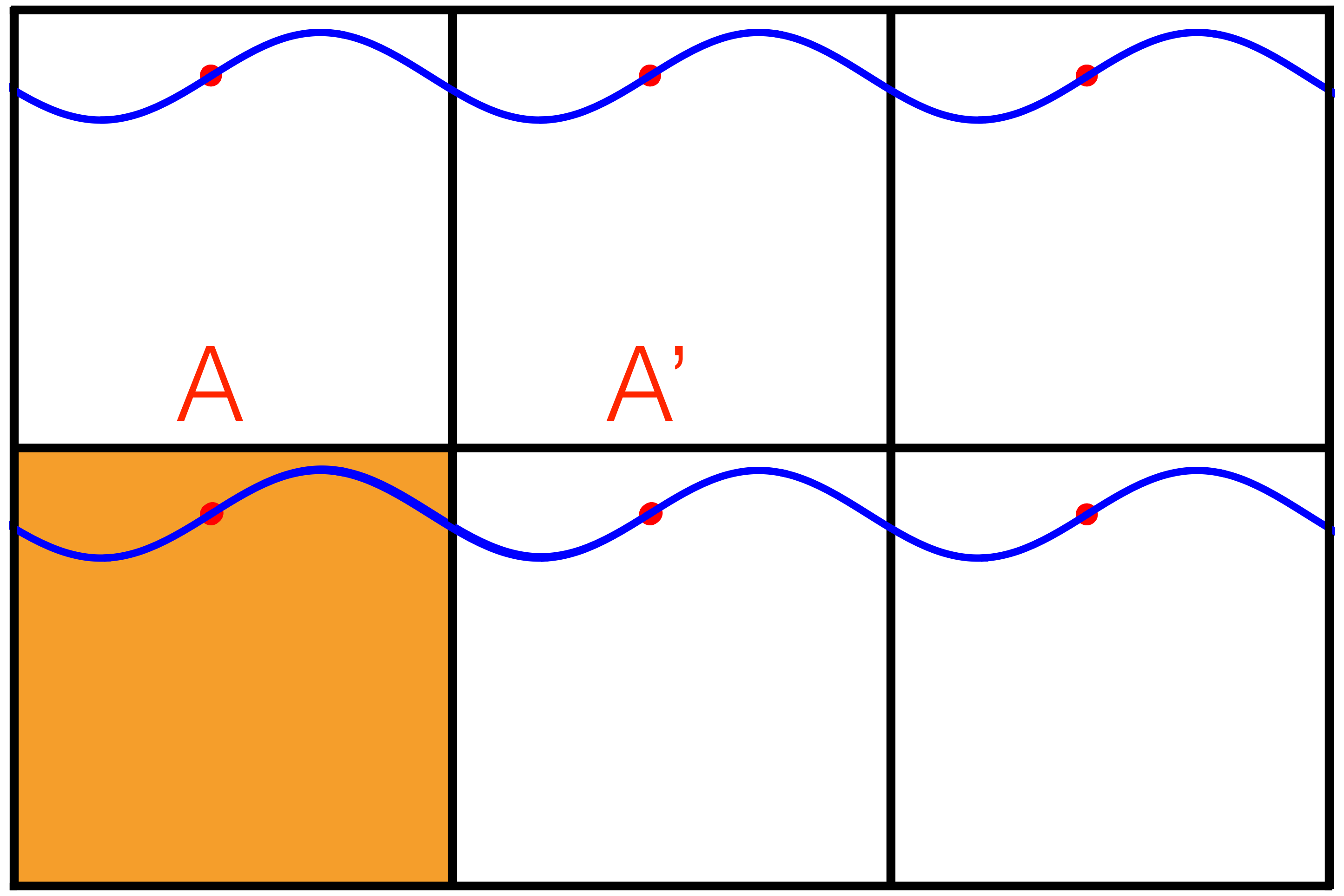

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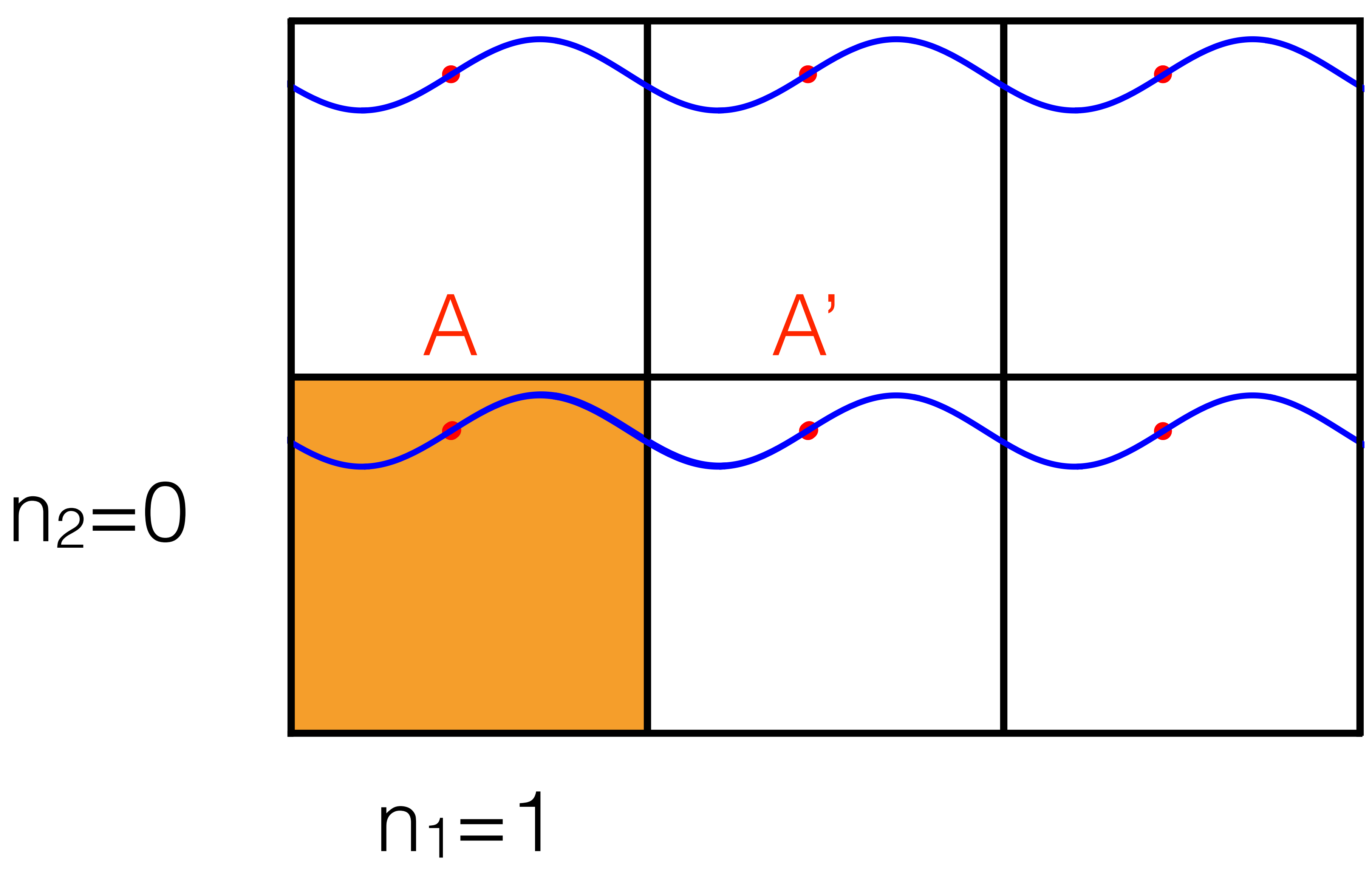

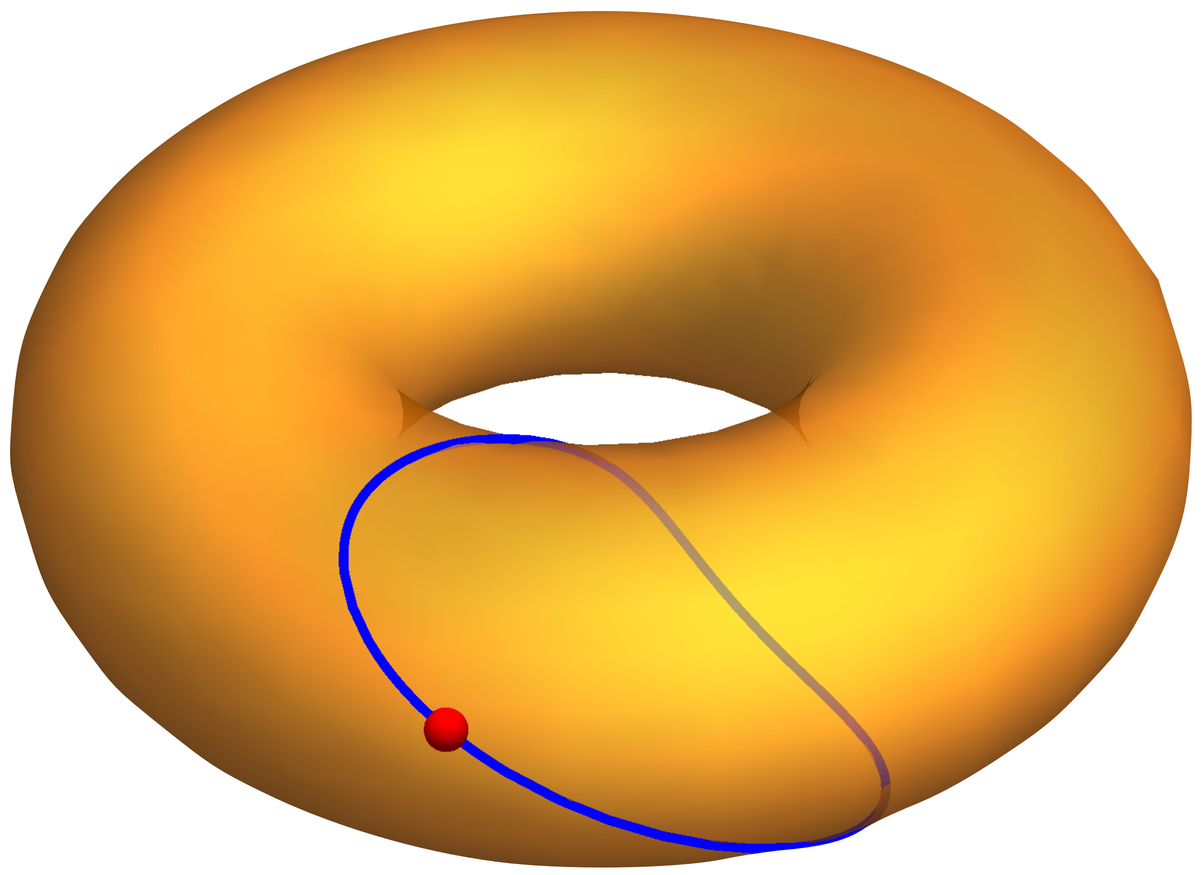

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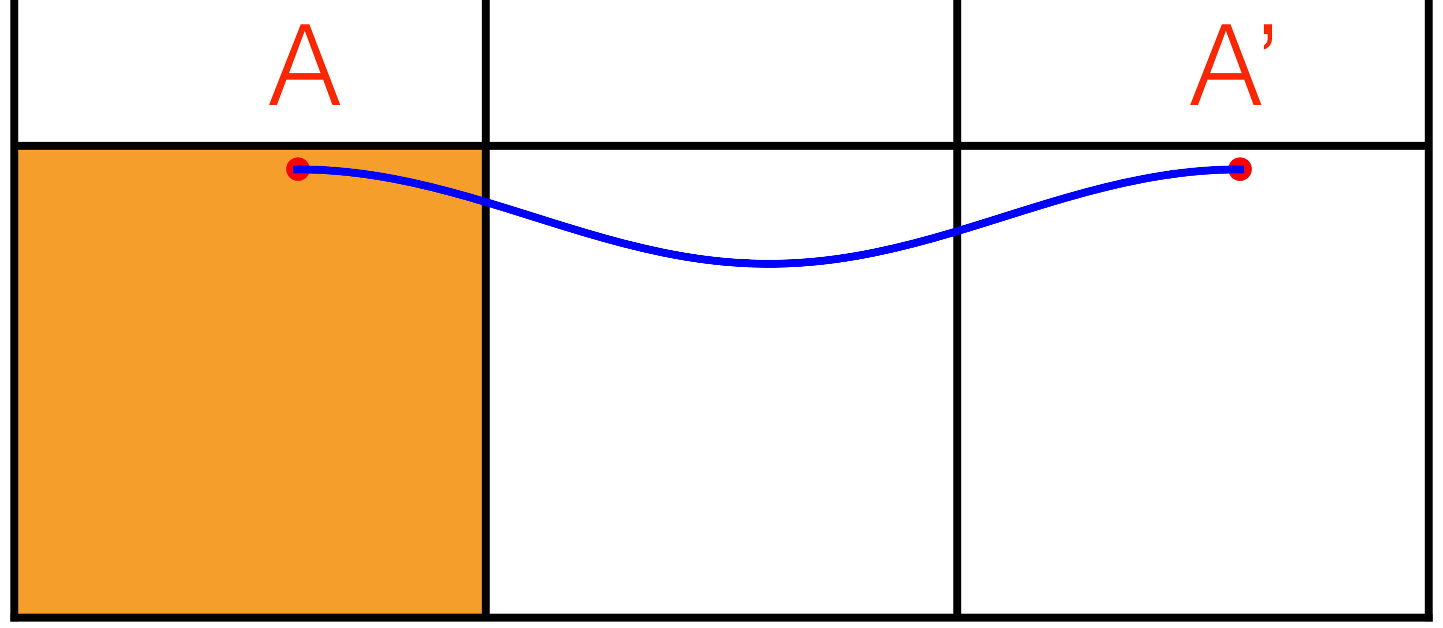

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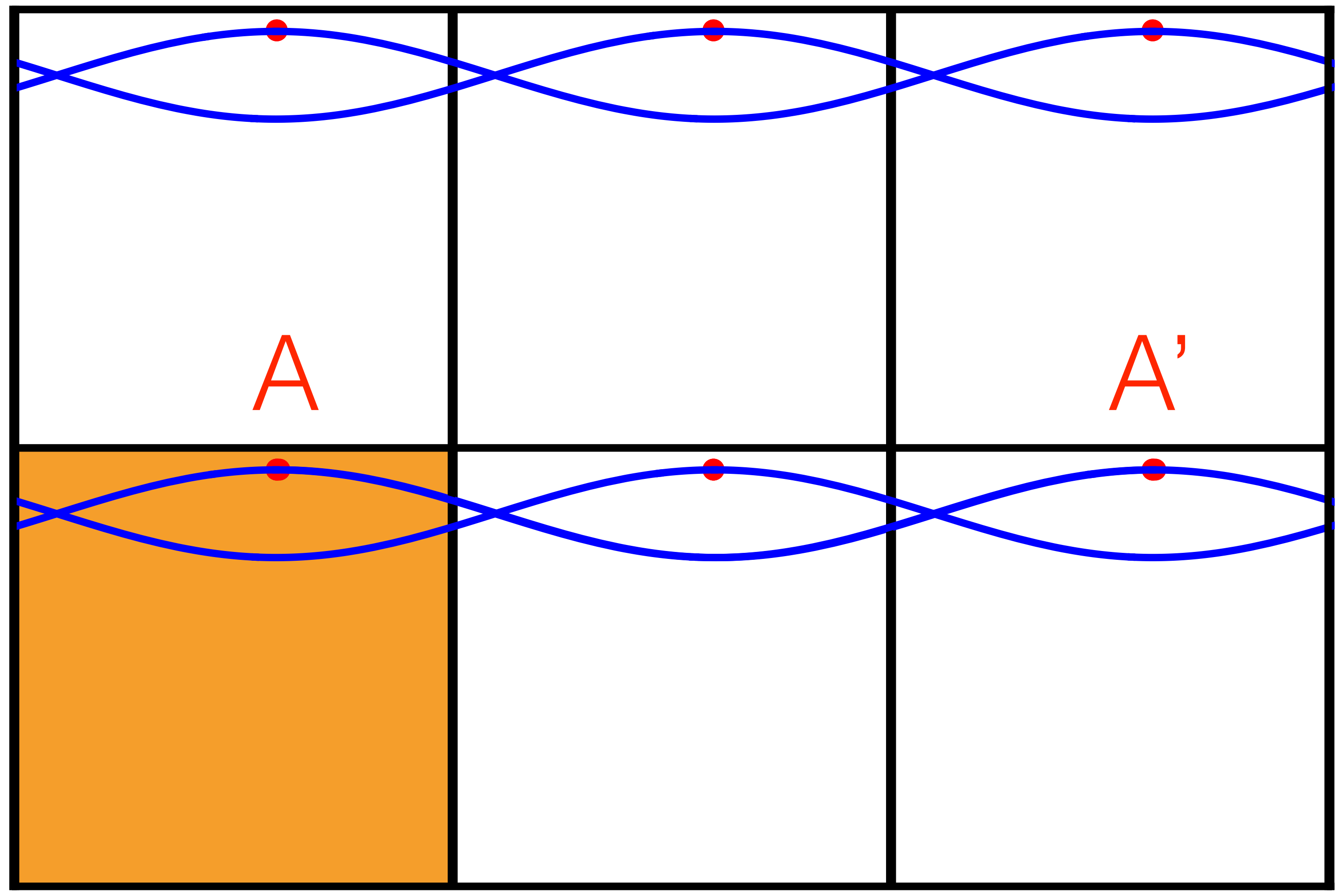

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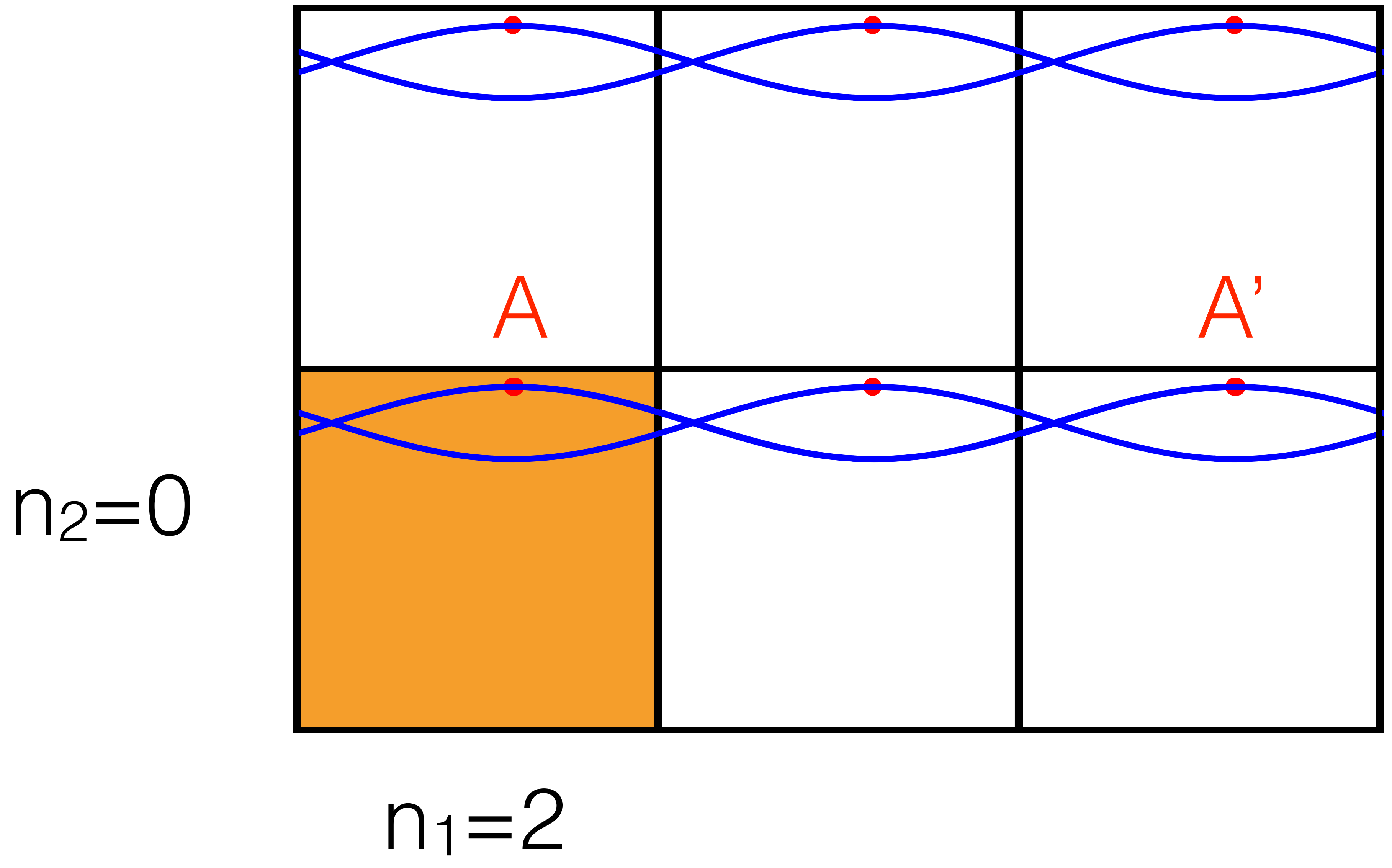

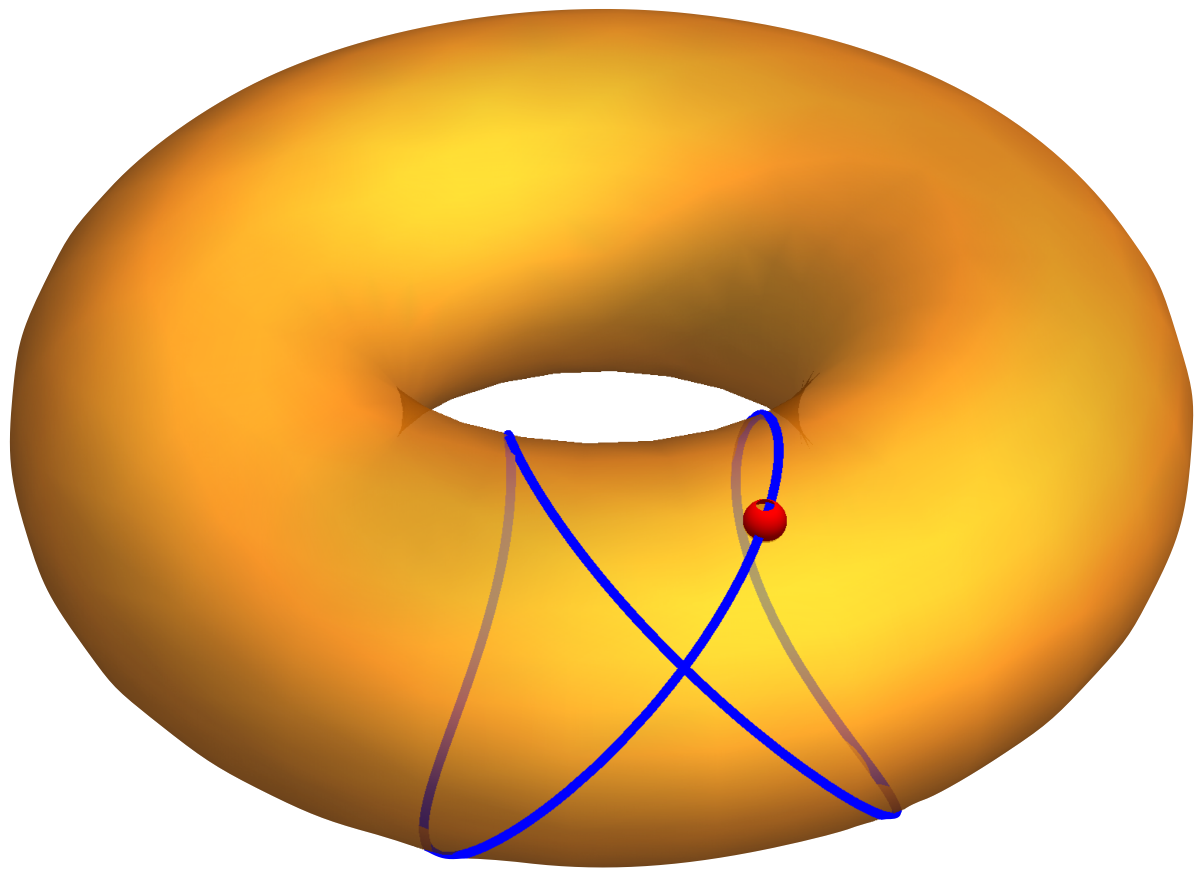

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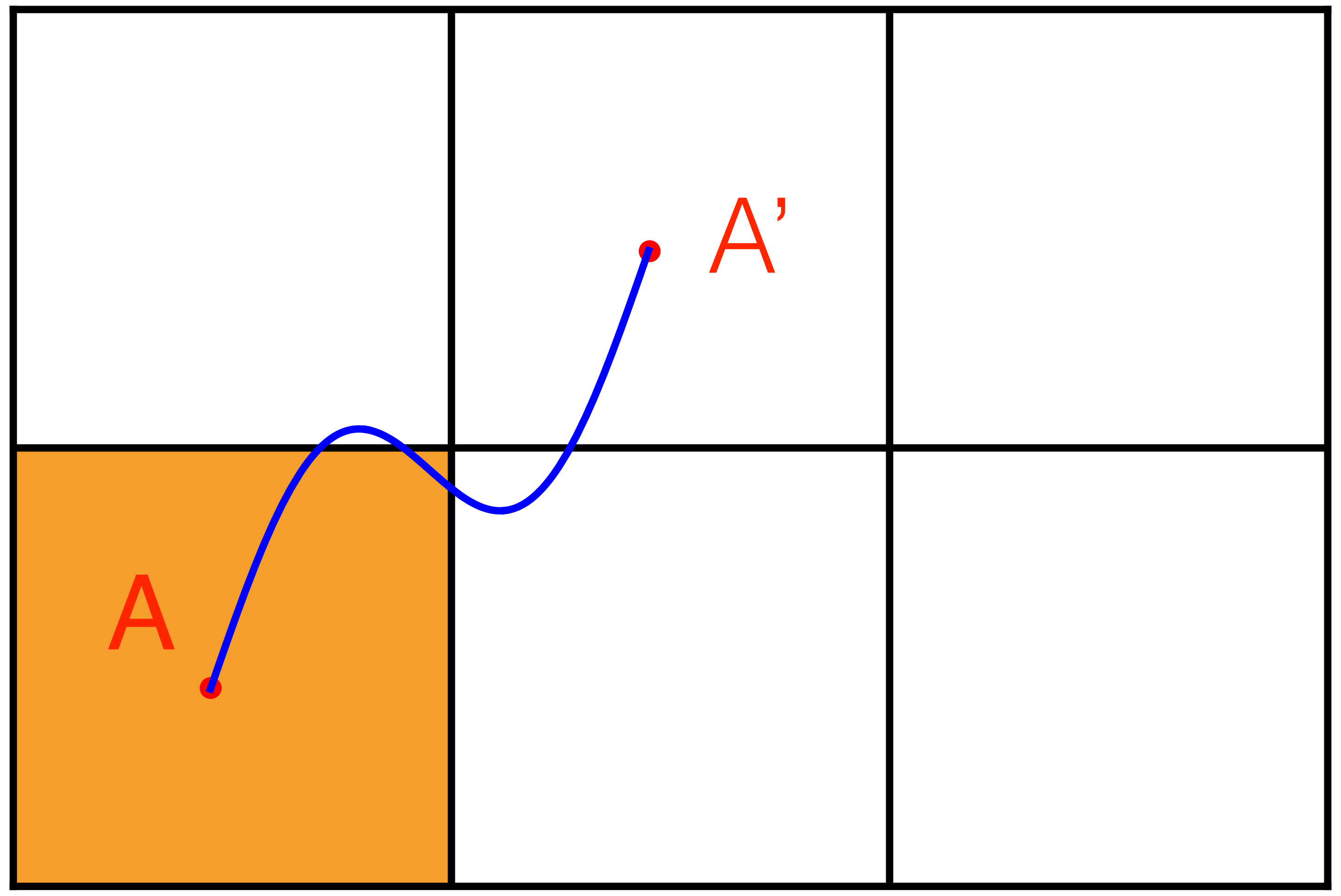

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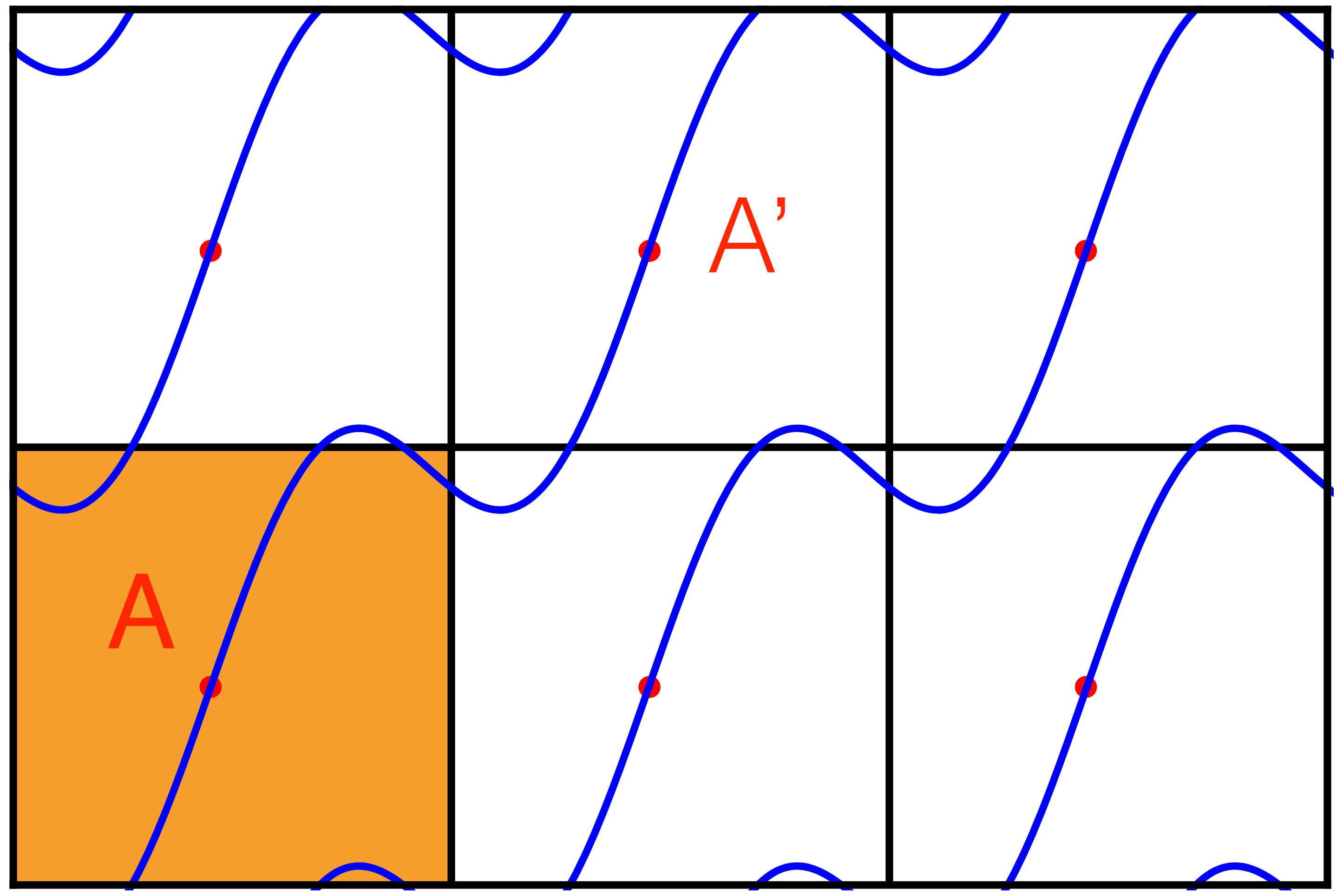

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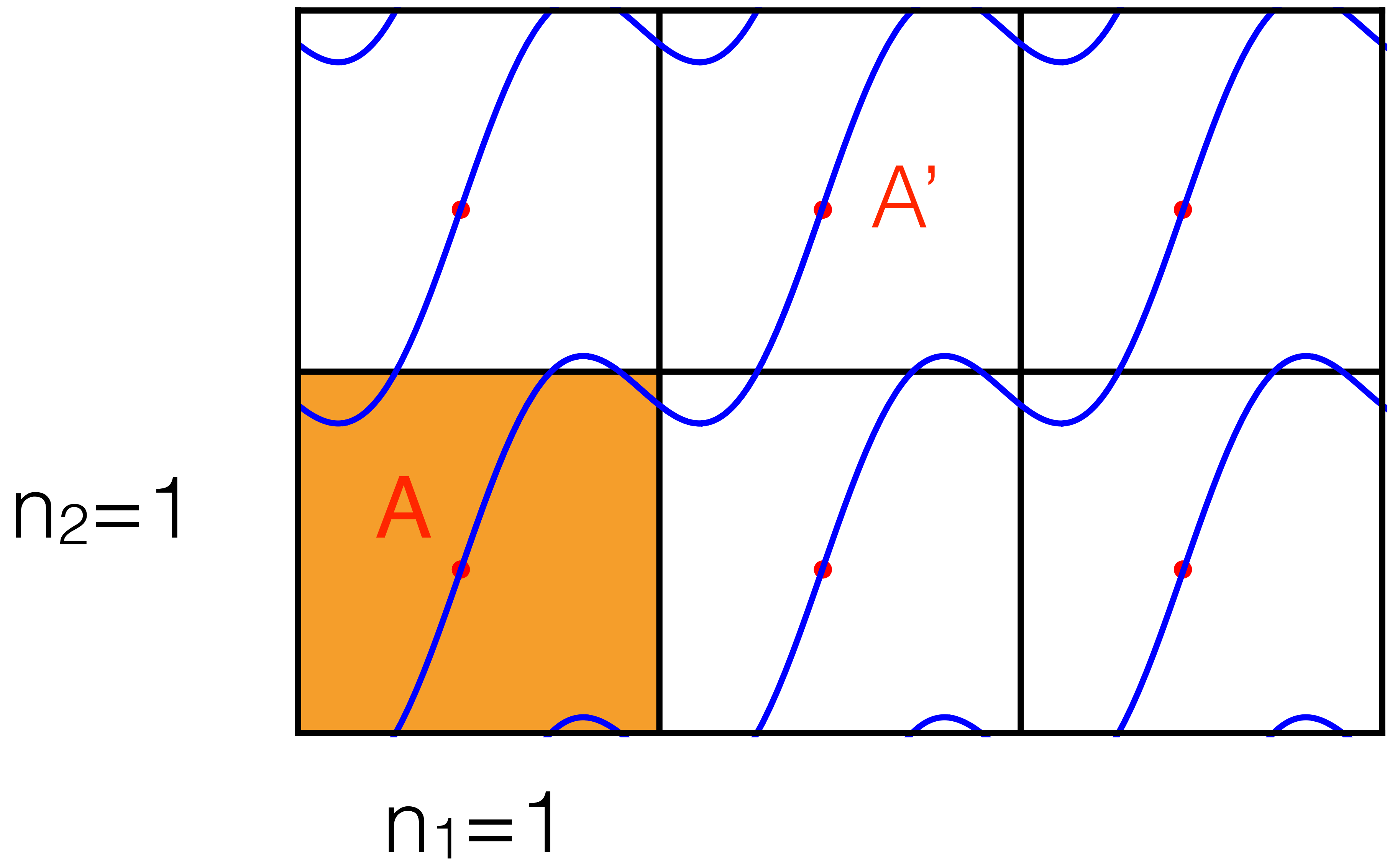

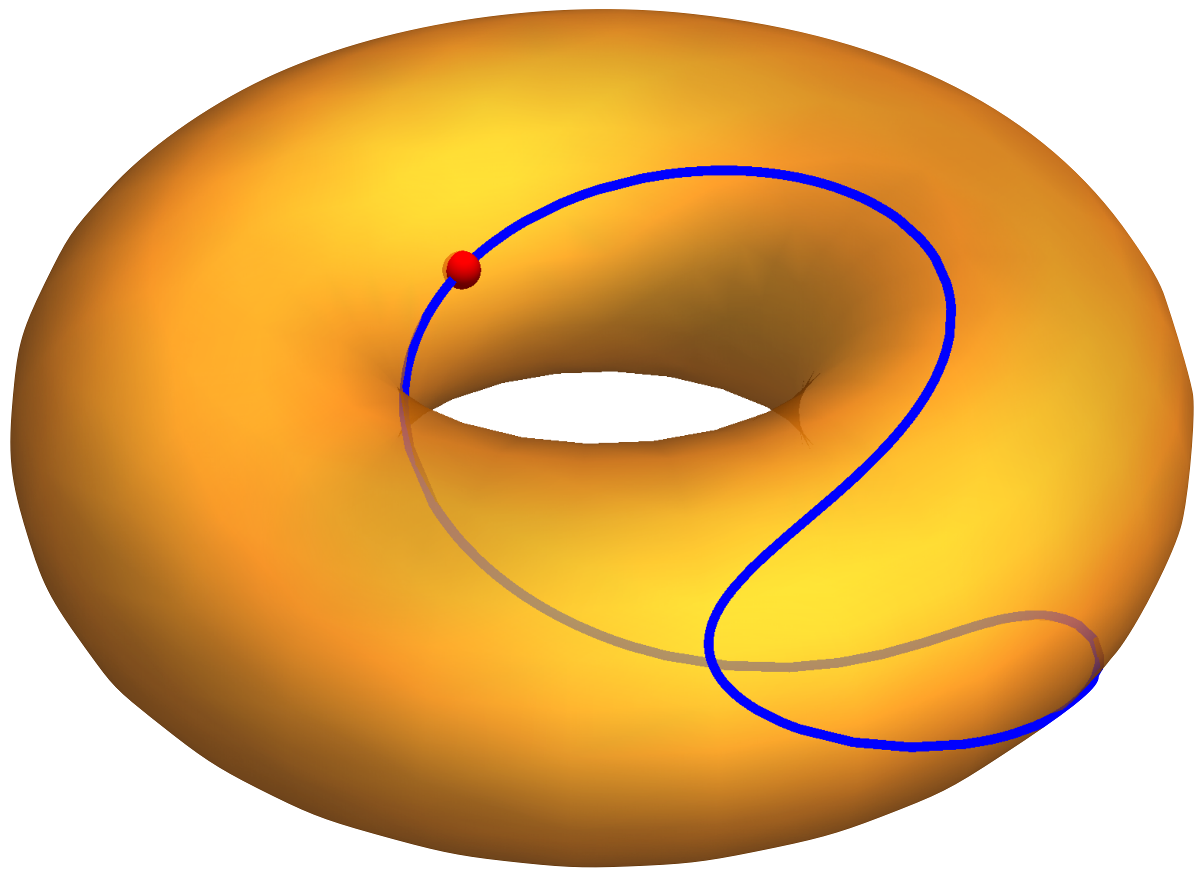

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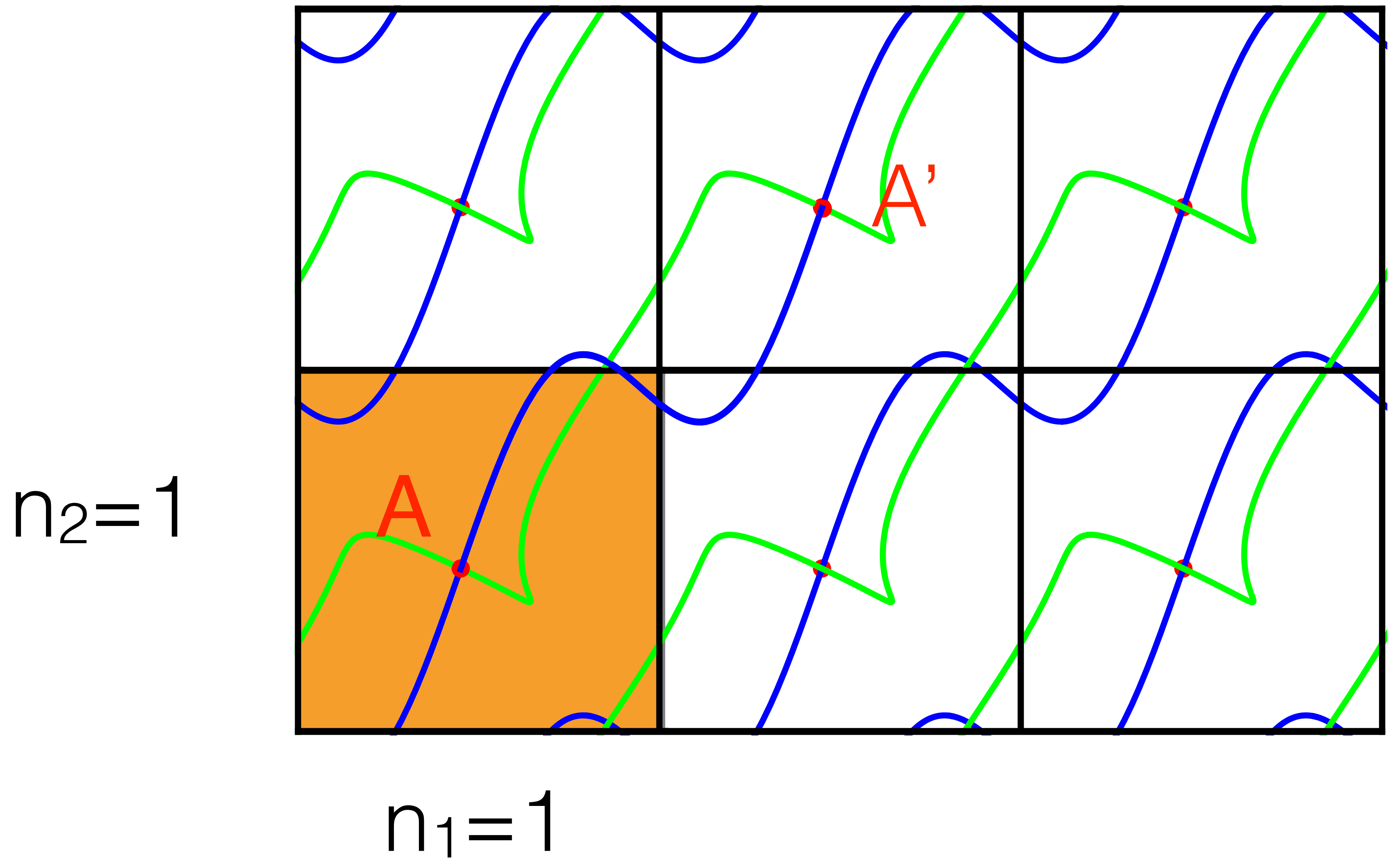

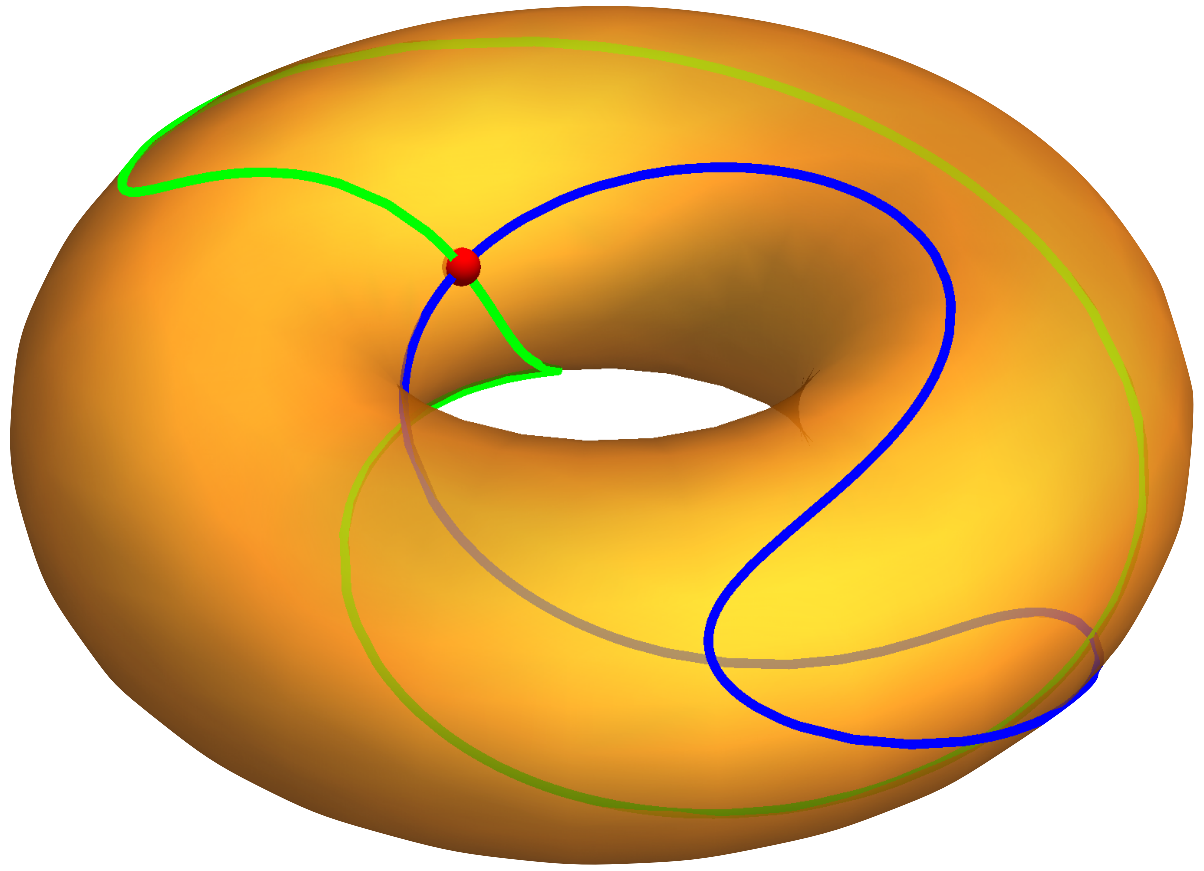

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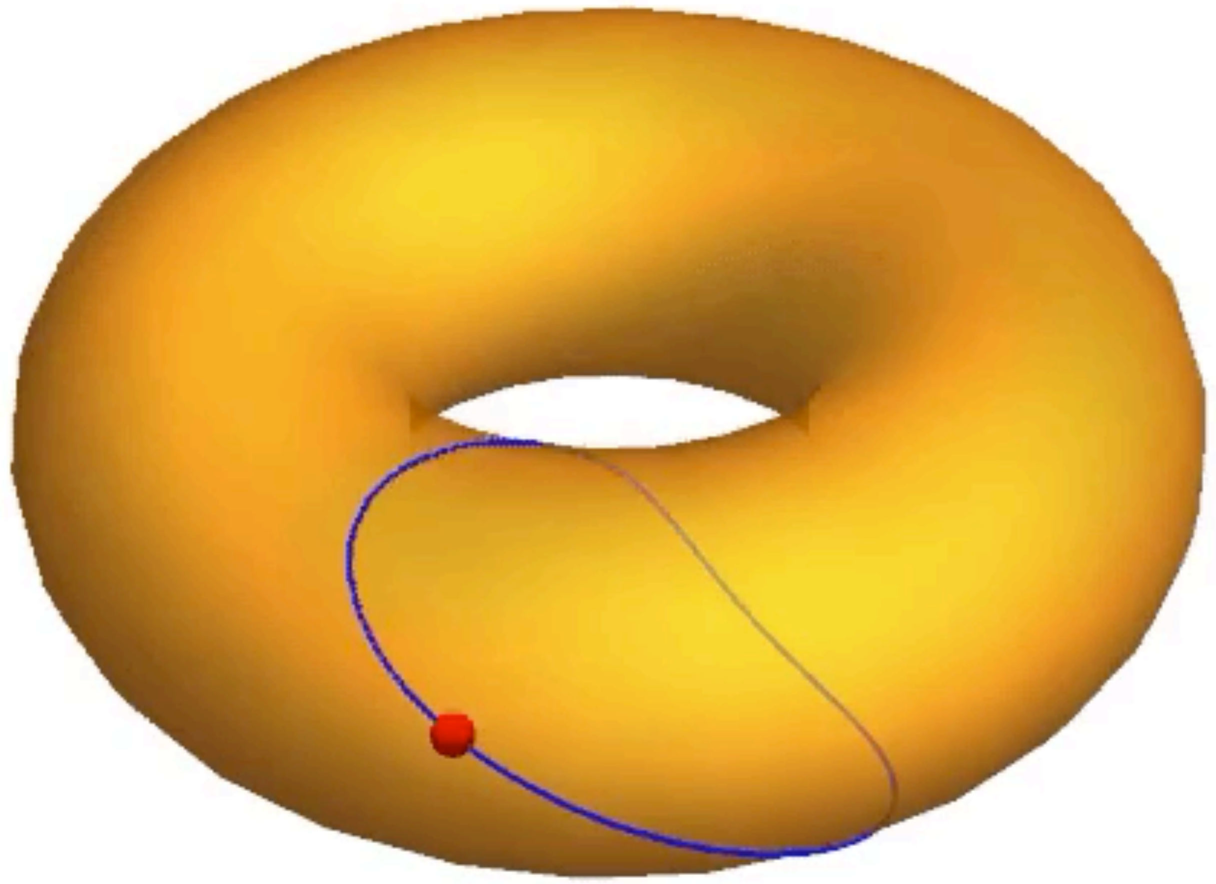

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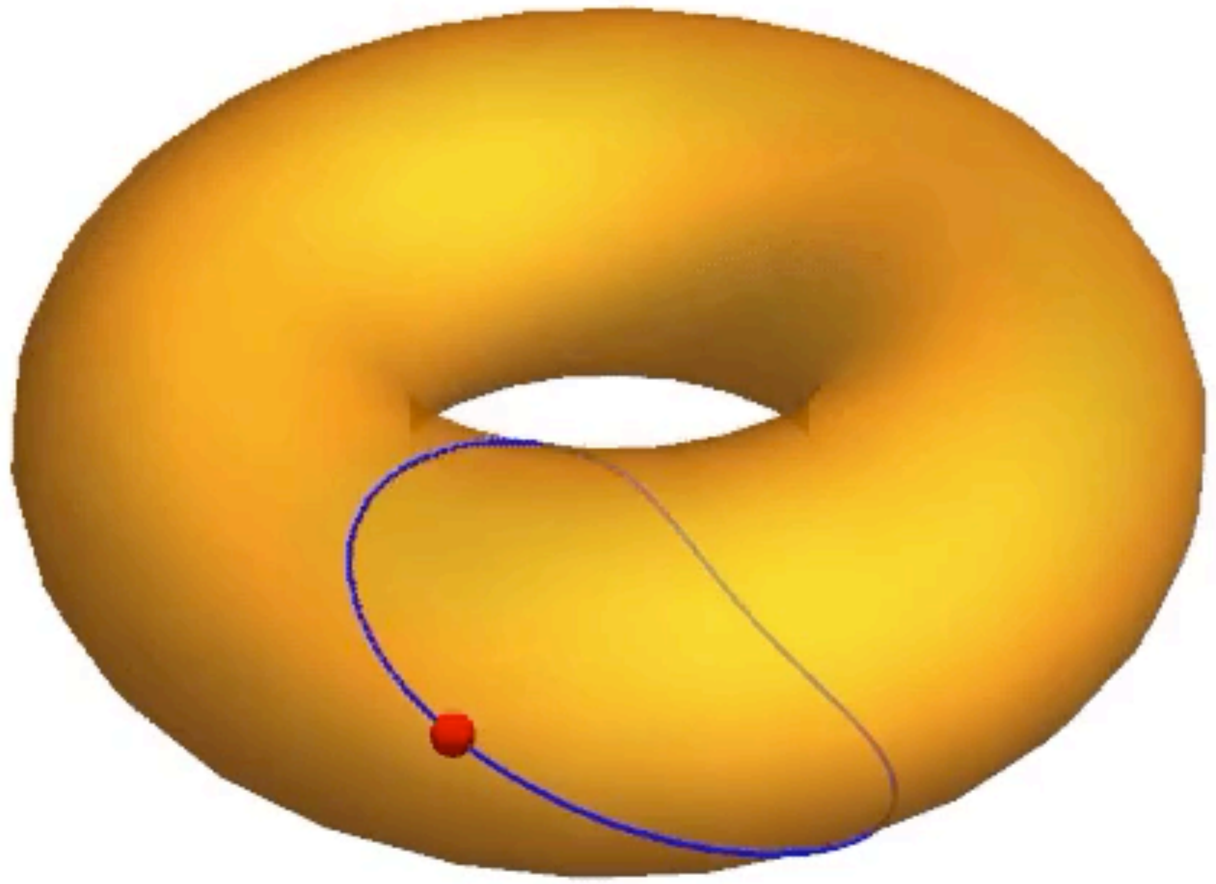

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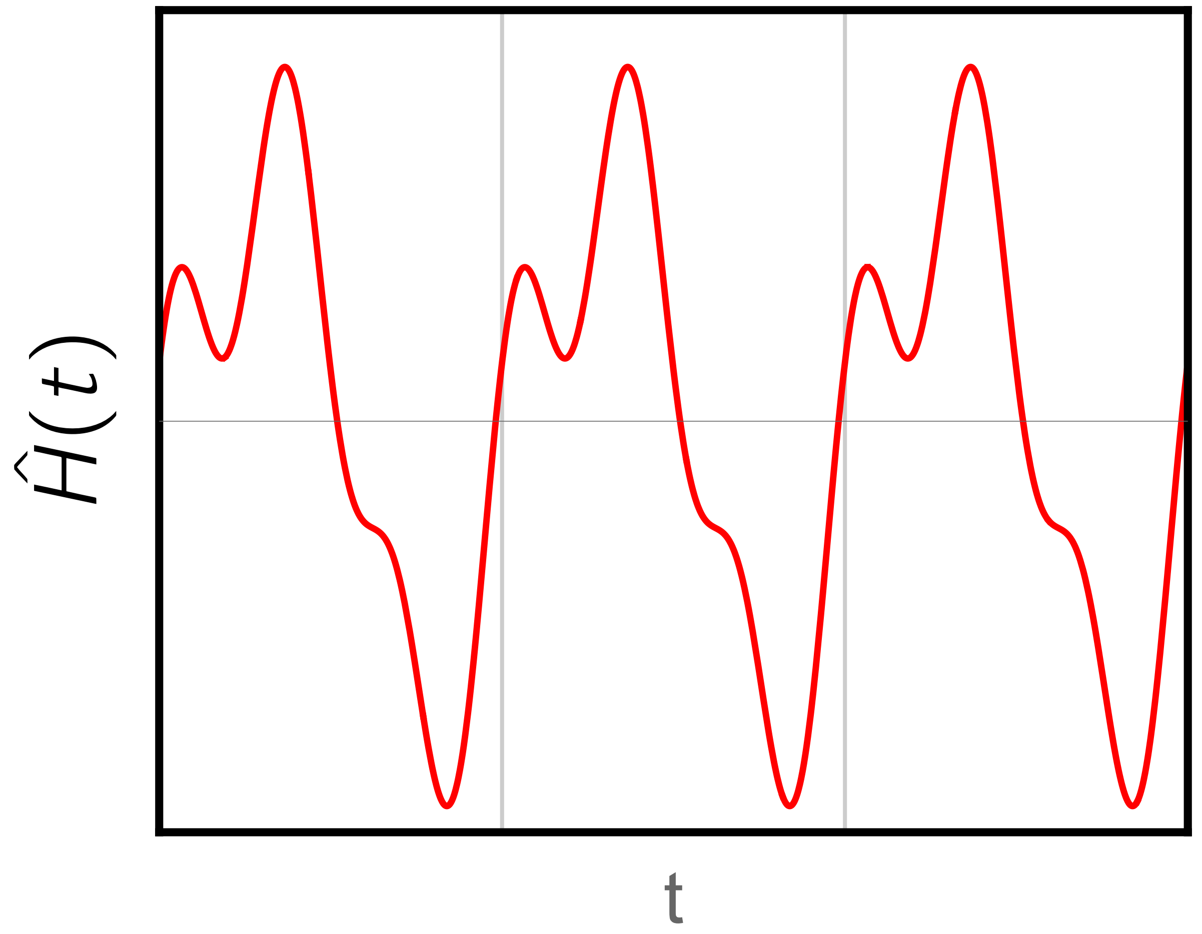
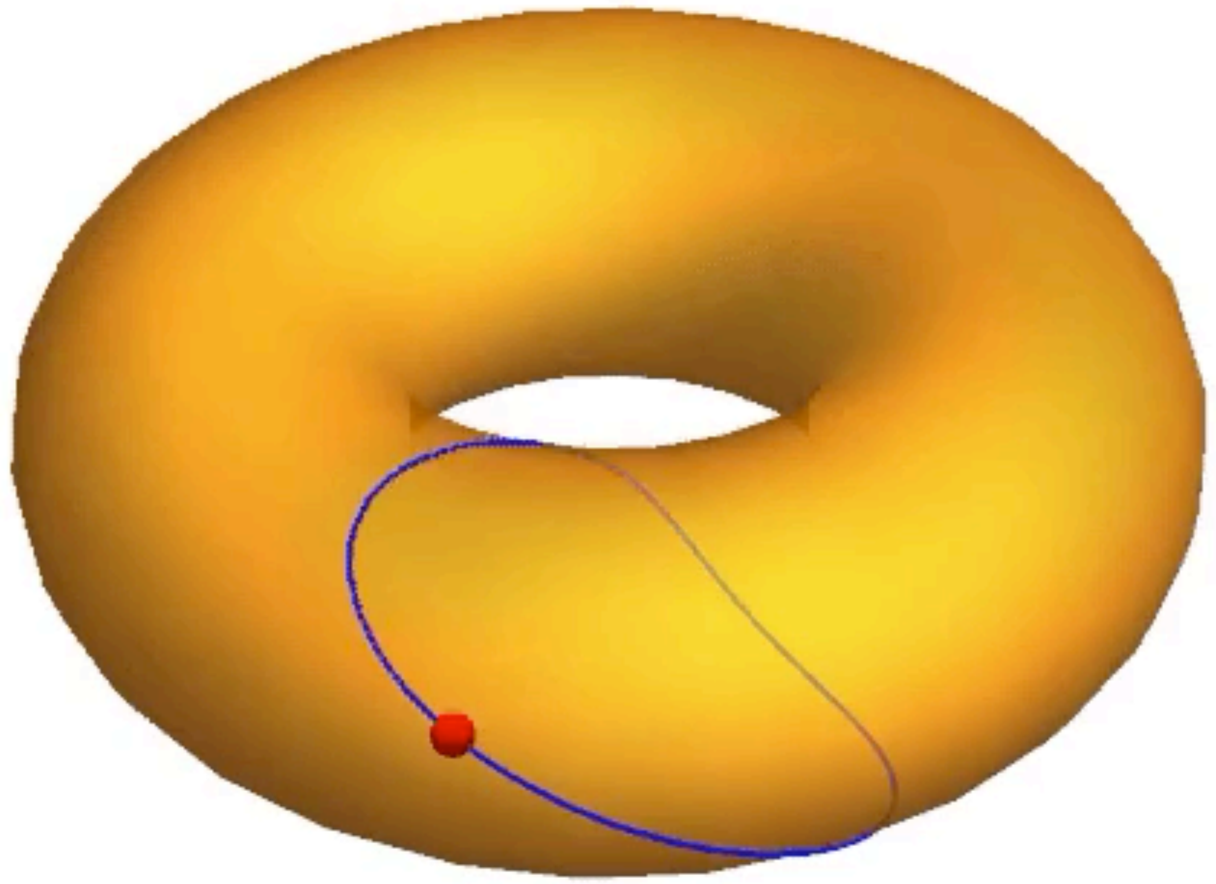


$$\hat{H}(t+T) = \hat{H}(t)$$



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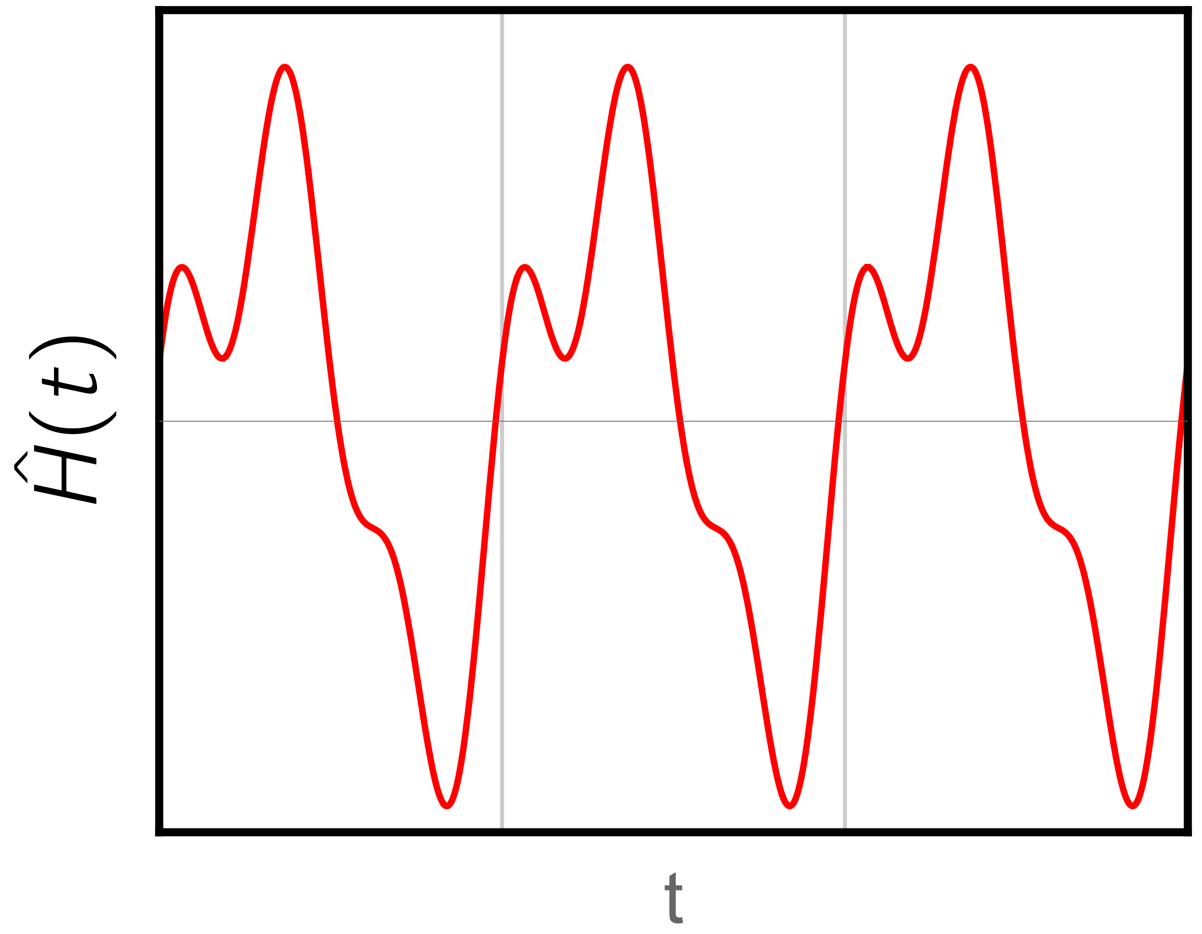

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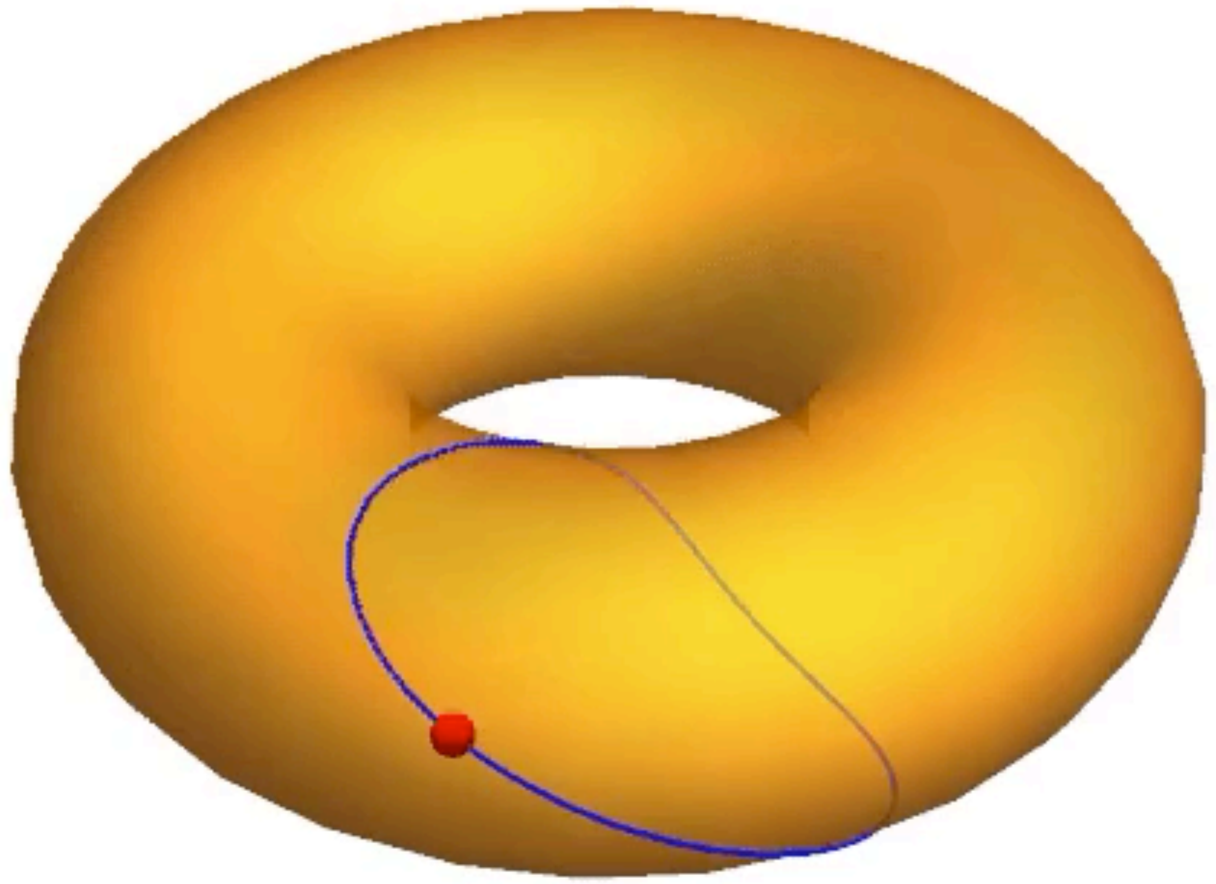
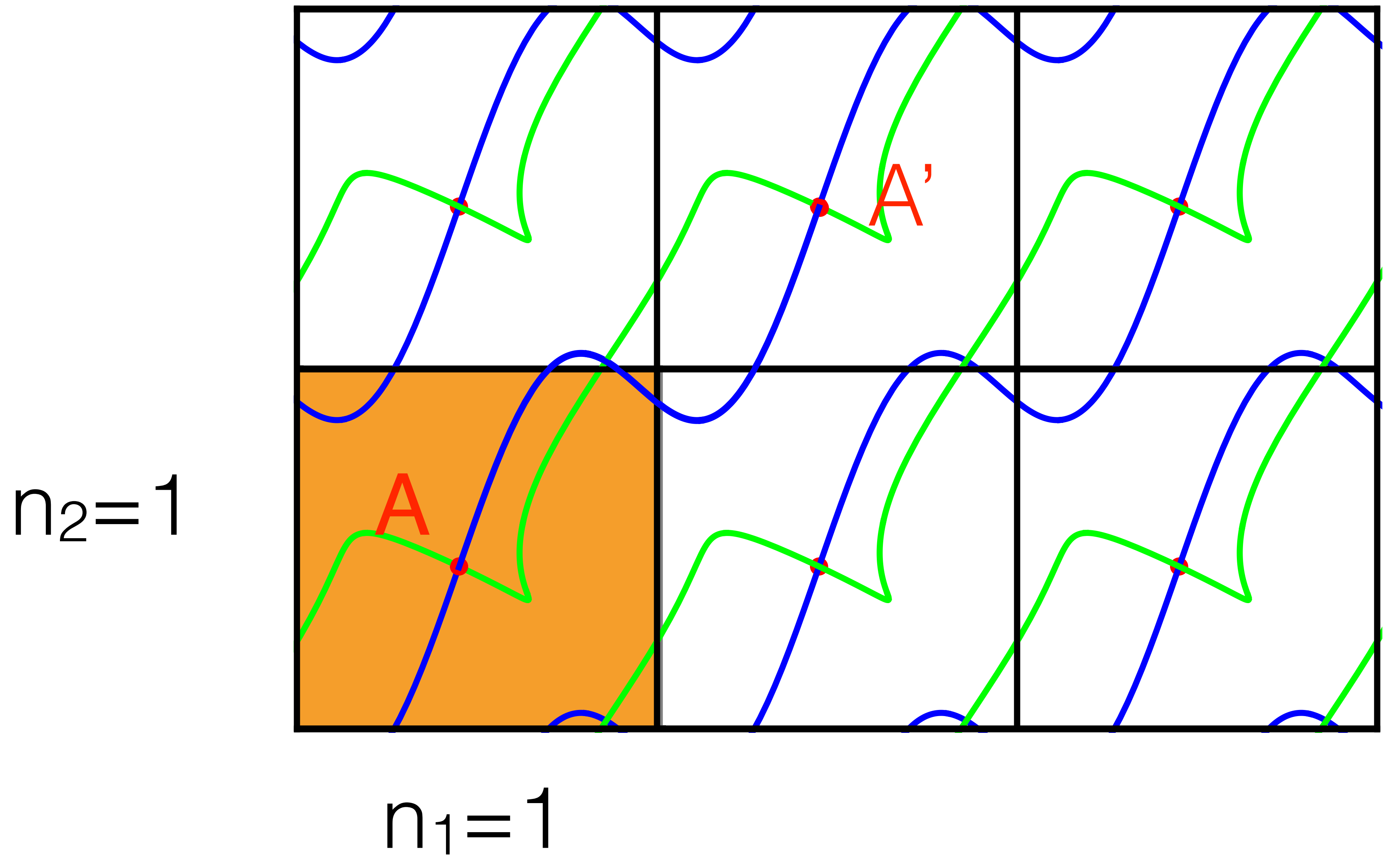
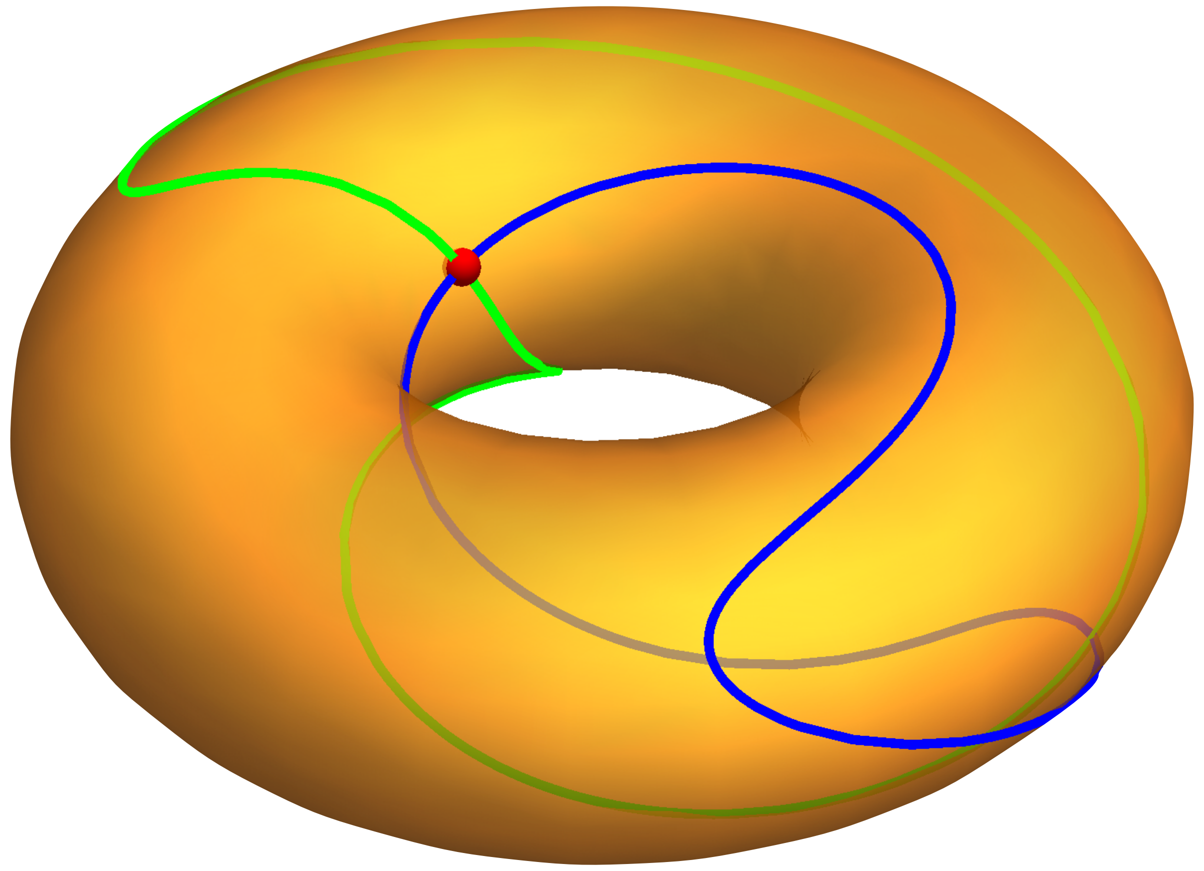


$$\frac{L^2}{e}\int_0^T J_\alpha(t)dt = \frac{1}{Le}\int d\mu_\alpha[X] = Q_\alpha \in \mathbb{Z}$$

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

what are oxidation states, in the first place?





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

what are oxidation states, in the first place?

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

what are oxidation states, in the first place?

$$
\begin{aligned}
Q_\alpha[\mathcal{C}] &= \frac{1}{\ell}\mu_\alpha[\mathcal{C}] \\
&= Q_\alpha(n_{1x}, n_{1y}, n_{1z}, \cdots n_{Nz})
\end{aligned}
$$

what are oxidation states, in the first place?

$$Q_\alpha[\mathcal{C}] = \frac{1}{\ell}\mu_\alpha[\mathcal{C}]$$
$$= Q_\alpha(n_{1x}, n_{1y}, n_{1z}, \cdots n_{Nz})$$

$$Q_\alpha[\mathcal{C}_1 \circ \mathcal{C}_2] = Q_\alpha[\mathcal{C}_1] + Q_\alpha[\mathcal{C}_2]$$

what are oxidation states, in the first place?

$$Q_\alpha[\mathcal{C}] = \frac{1}{\ell}\mu_\alpha[\mathcal{C}]$$
$$= Q_\alpha(n_{1x}, n_{1y}, n_{1z}, \cdots n_{Nz})$$

$$Q_\alpha[\mathcal{C}_1 \circ \mathcal{C}_2] = Q_\alpha[\mathcal{C}_1] + Q_\alpha[\mathcal{C}_2]$$

$$Q_\alpha(n_{1x}, n_{1y}, n_{1z}, \cdots n_{Nz}) = \sum_{i\beta} q_{i\alpha\beta} n_{i\beta}$$

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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*);

- Any two like atoms can be swapped without closing the gap

what are oxidation states, in the first place?

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$$Q_\alpha(n_{1x}, n_{1y}, n_{1z}, \cdots n_{Nz}) = \sum_{i\beta} q_{i\alpha\beta} n_{i\beta}$$

- All loops can be shrunk to a point without closing the gap (*strong adiabaticity*);
- Any two like atoms can be swapped without closing the gap

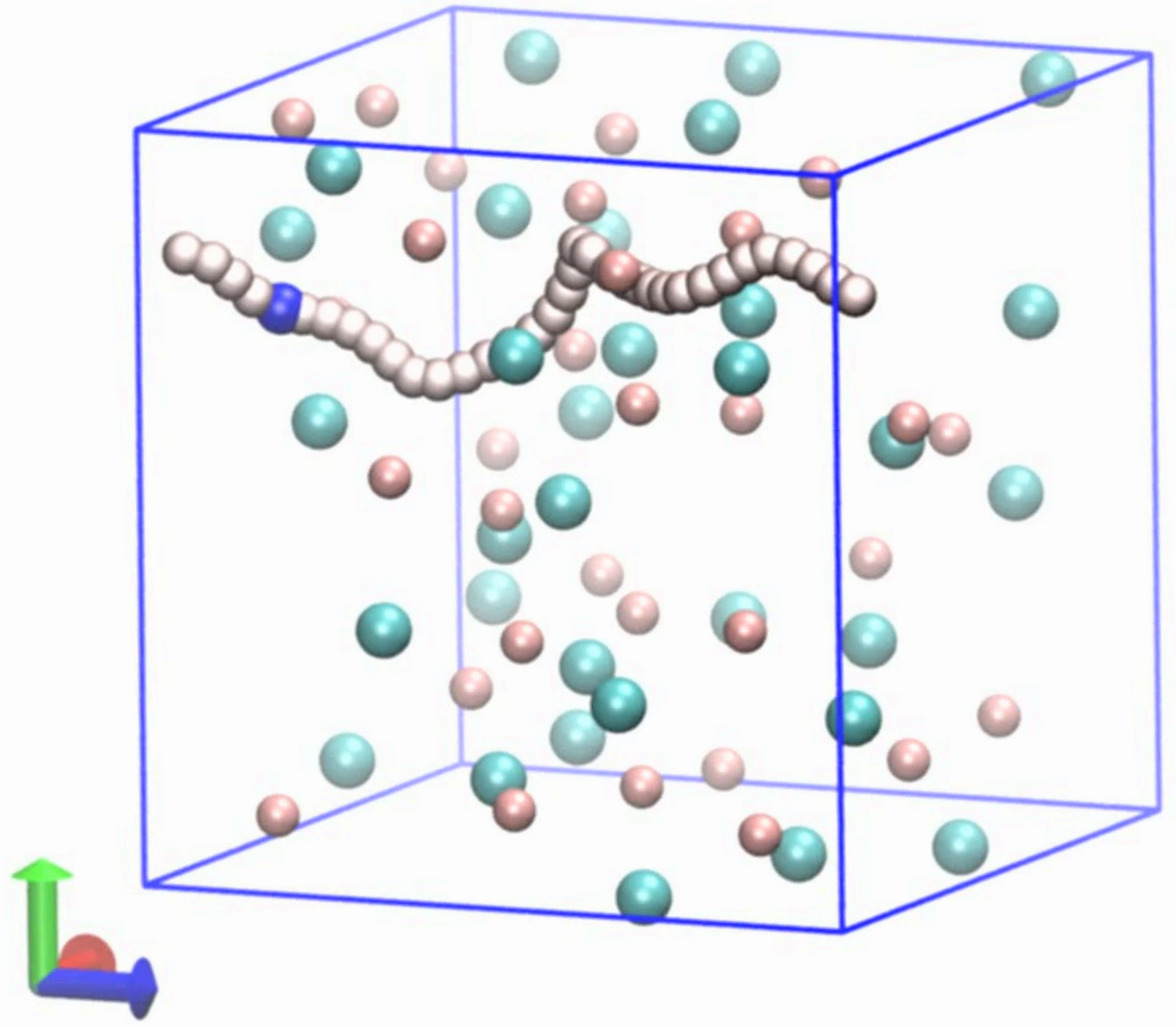
→

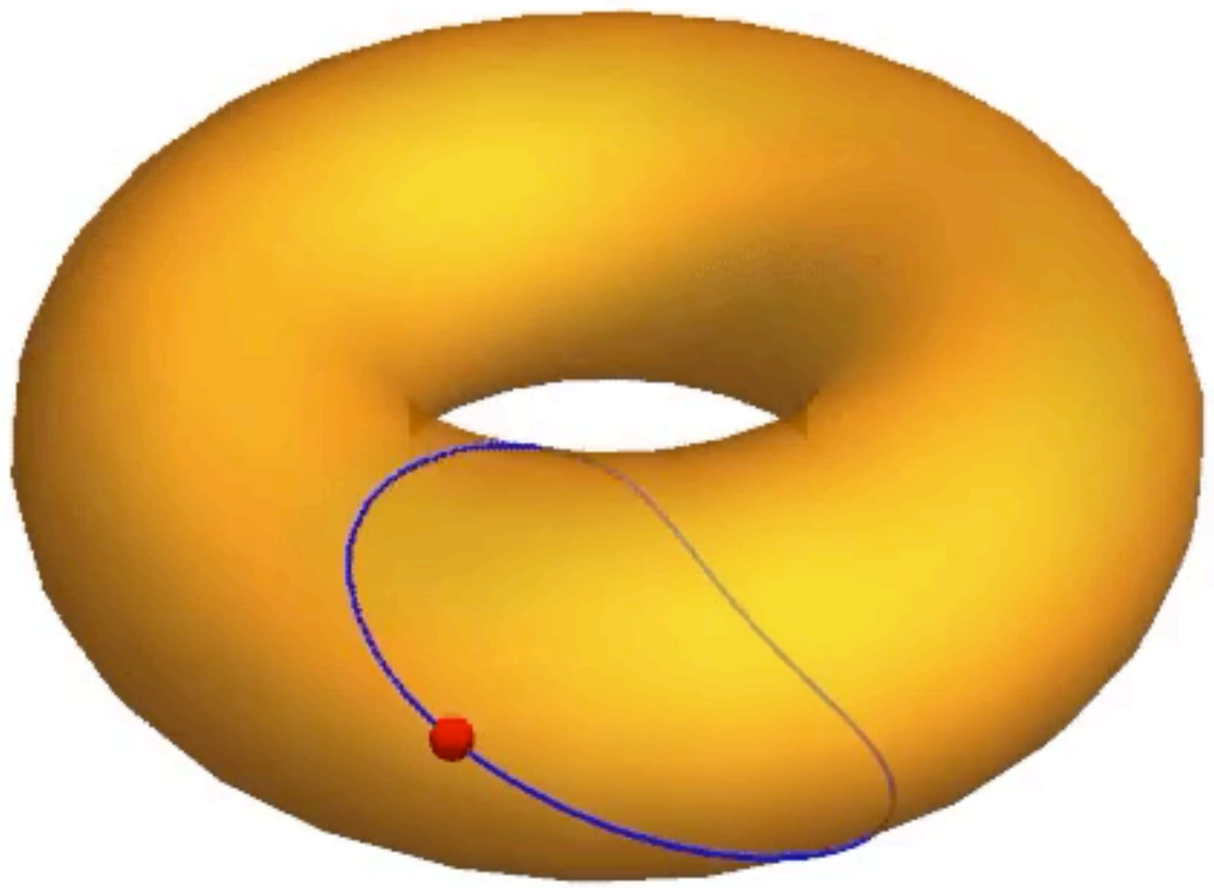
$$q_{i\alpha\beta} = q_{S(i)}\delta_{\alpha\beta}$$

atomic oxidation state

… they are topological invariants!

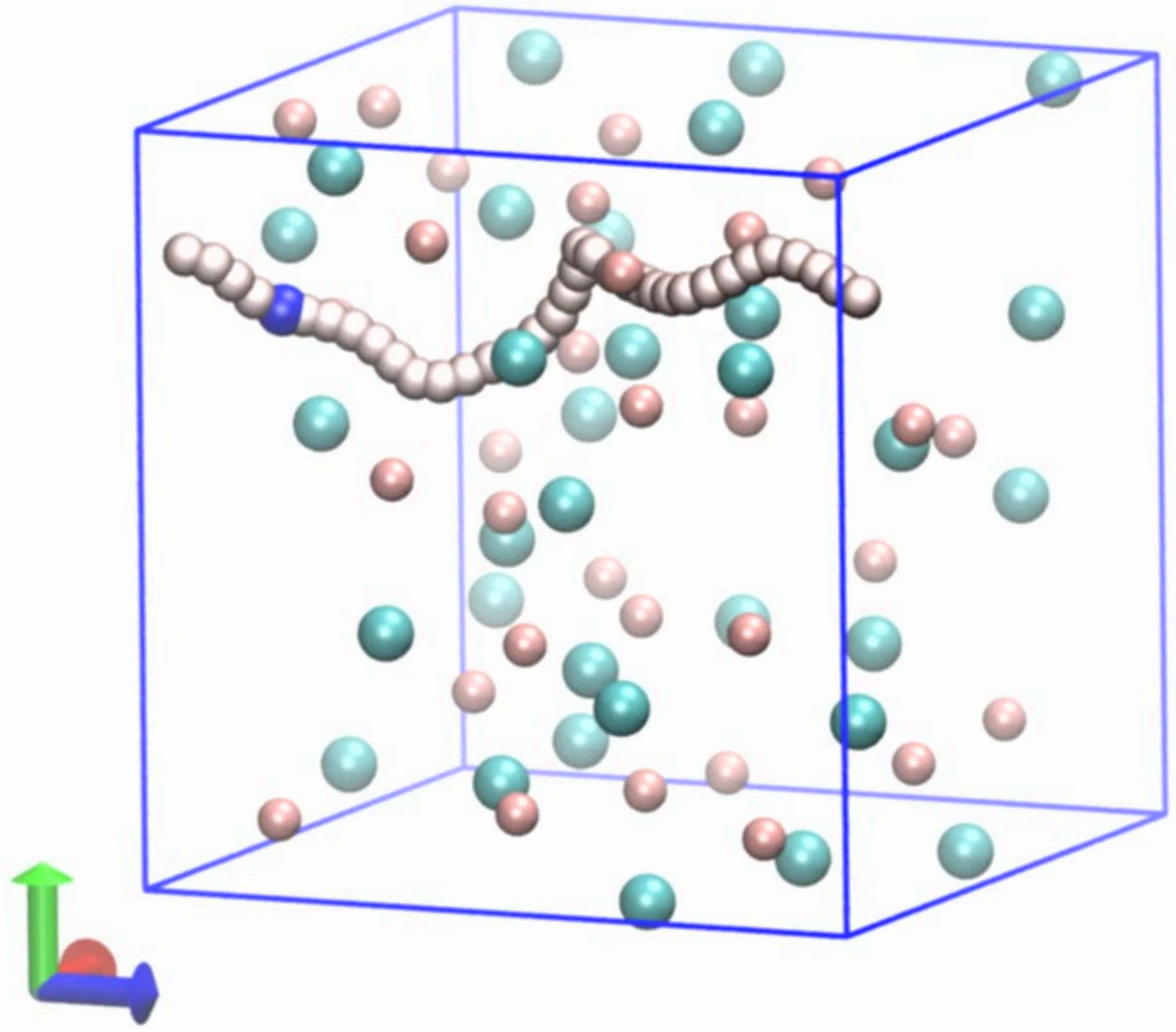
a numerical experiment on molten KCl

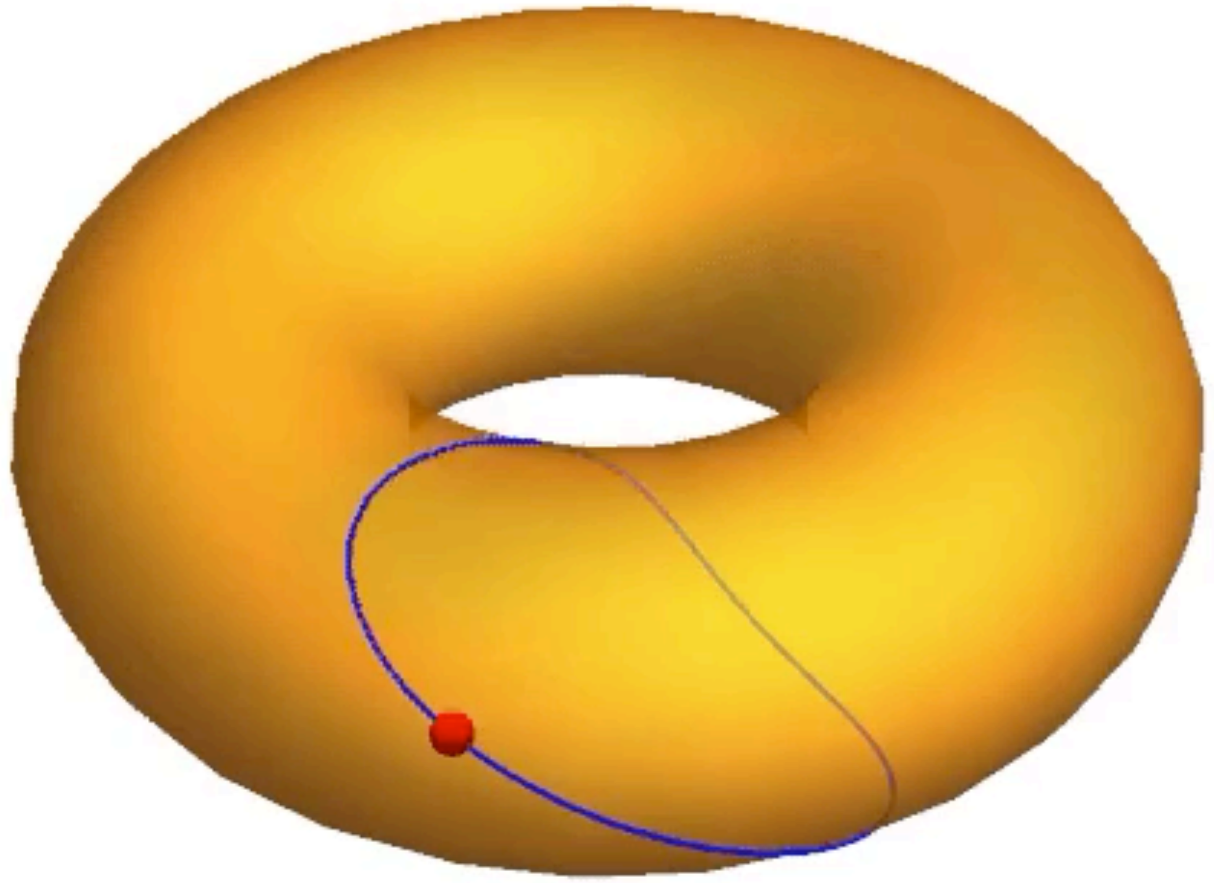




a topologically non-trivial minimum-energy path
connecting two identical configurations of a ionic melt

a numerical experiment on molten KCl





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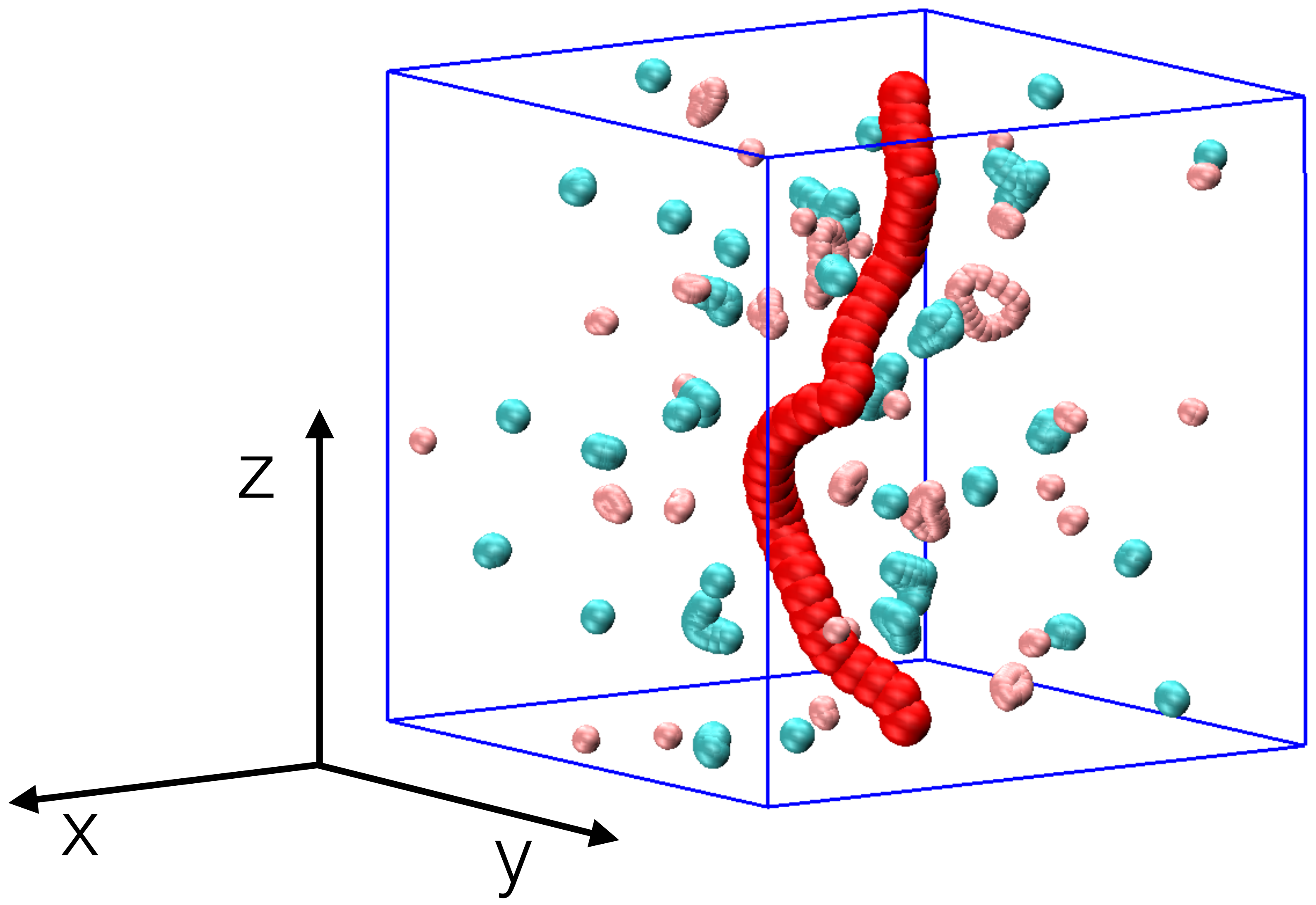
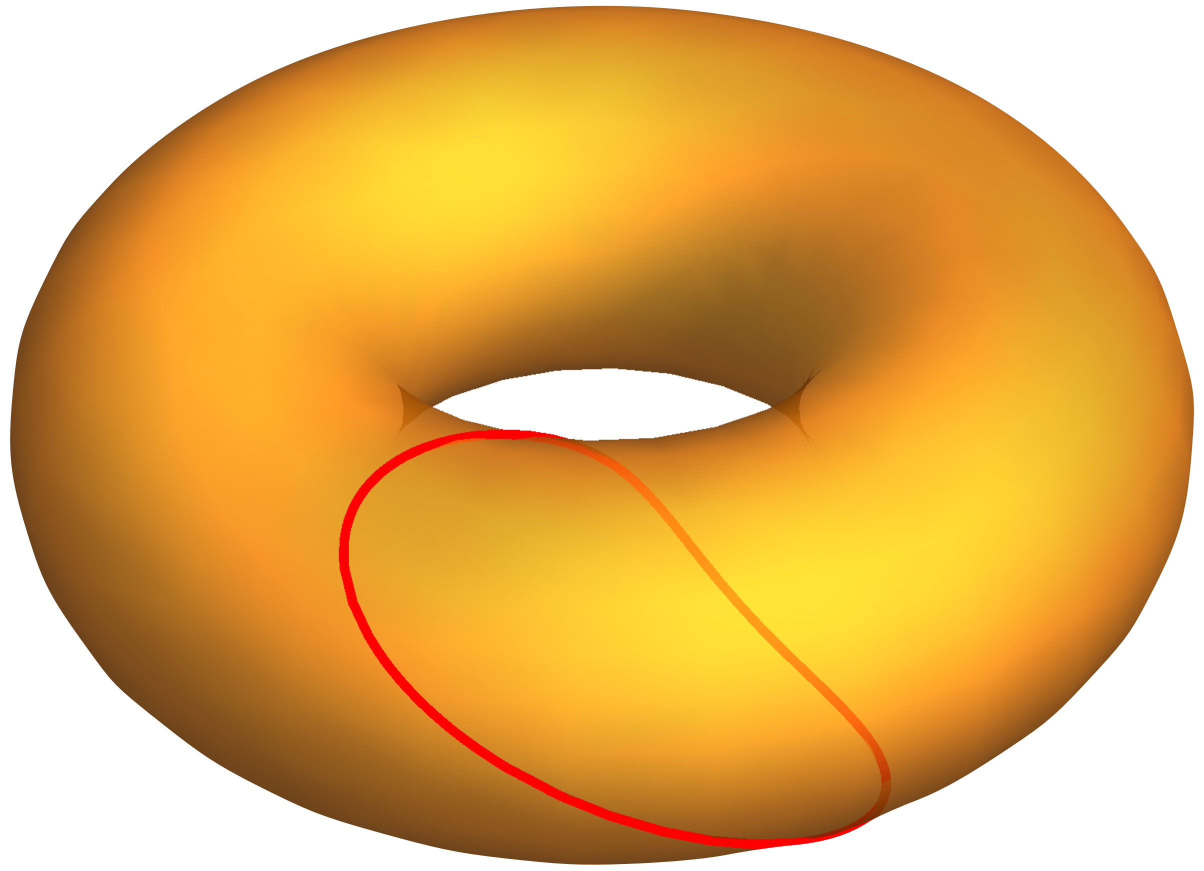
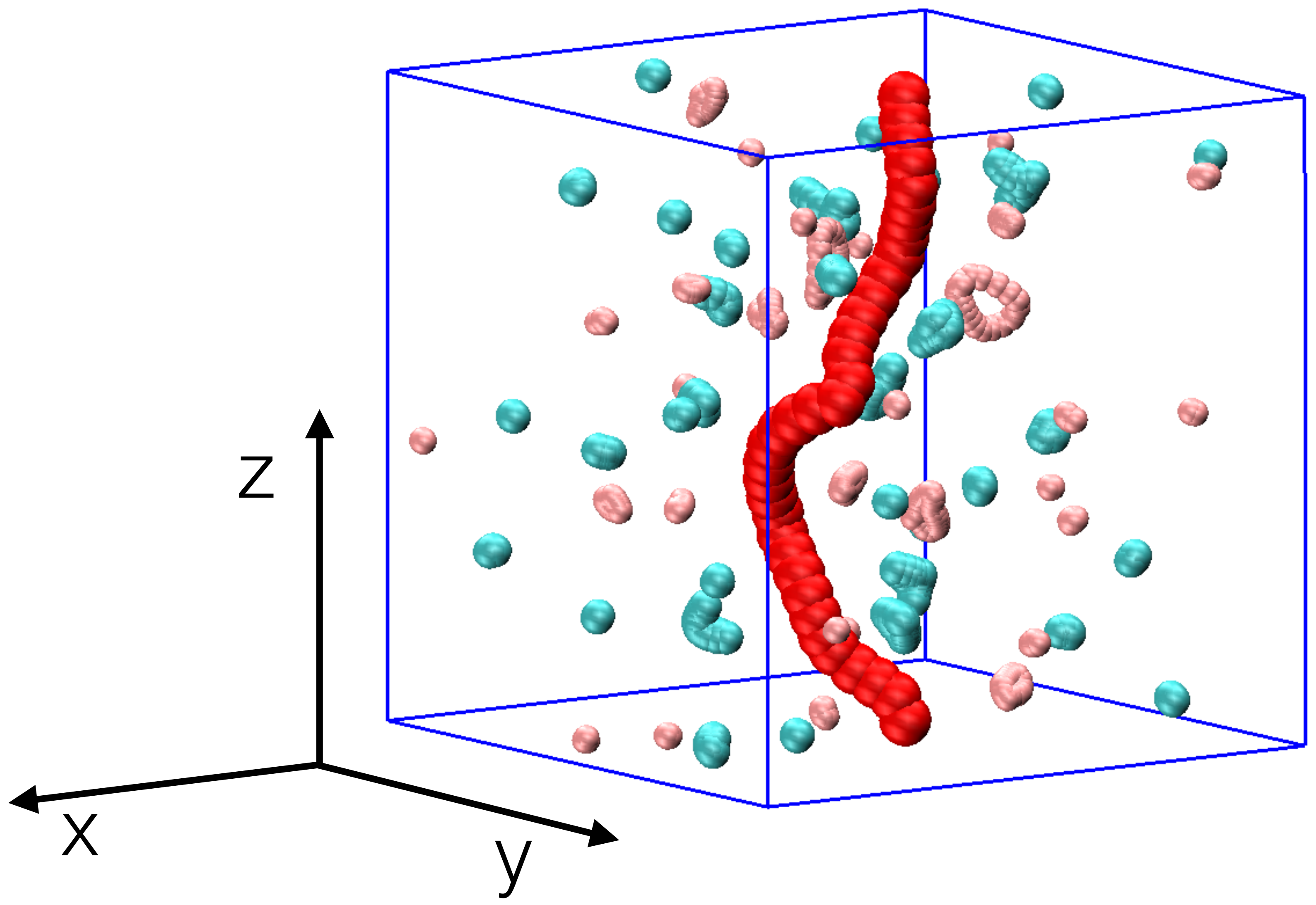
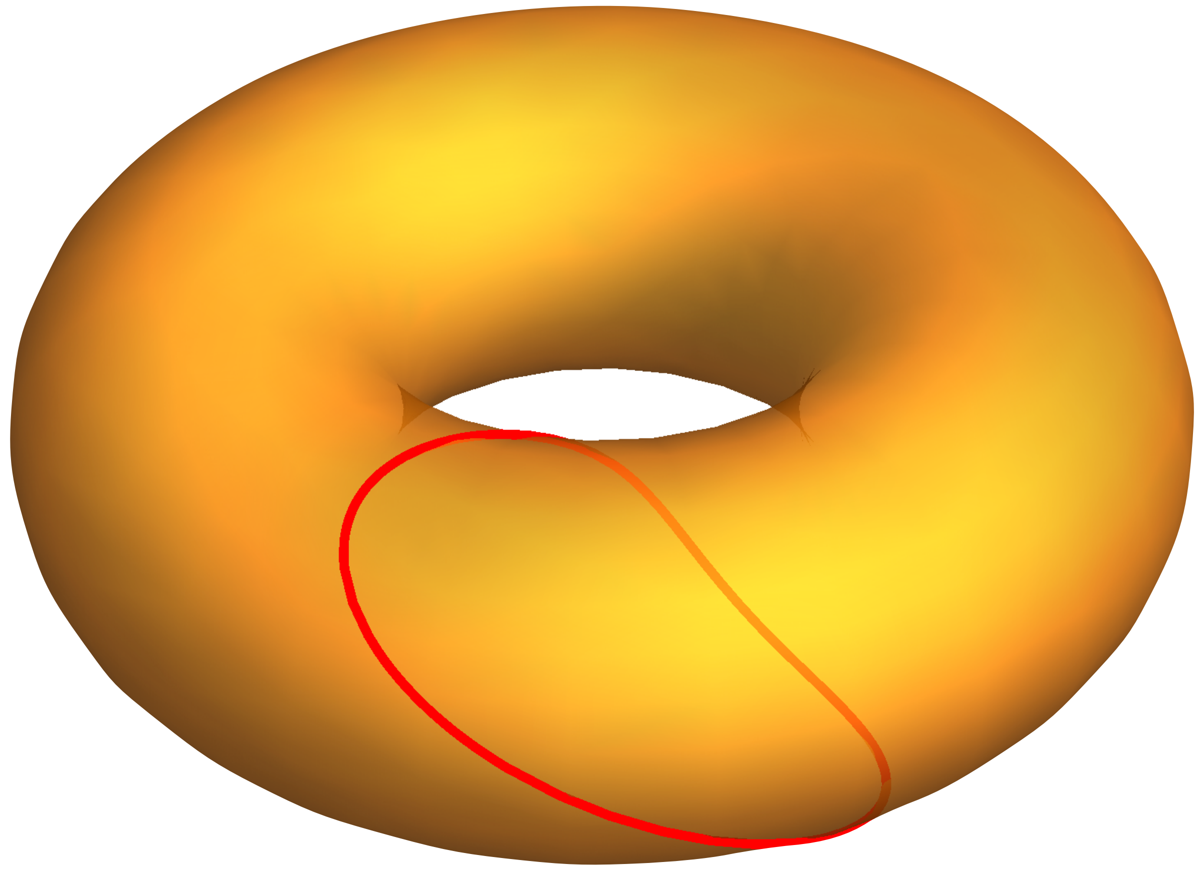
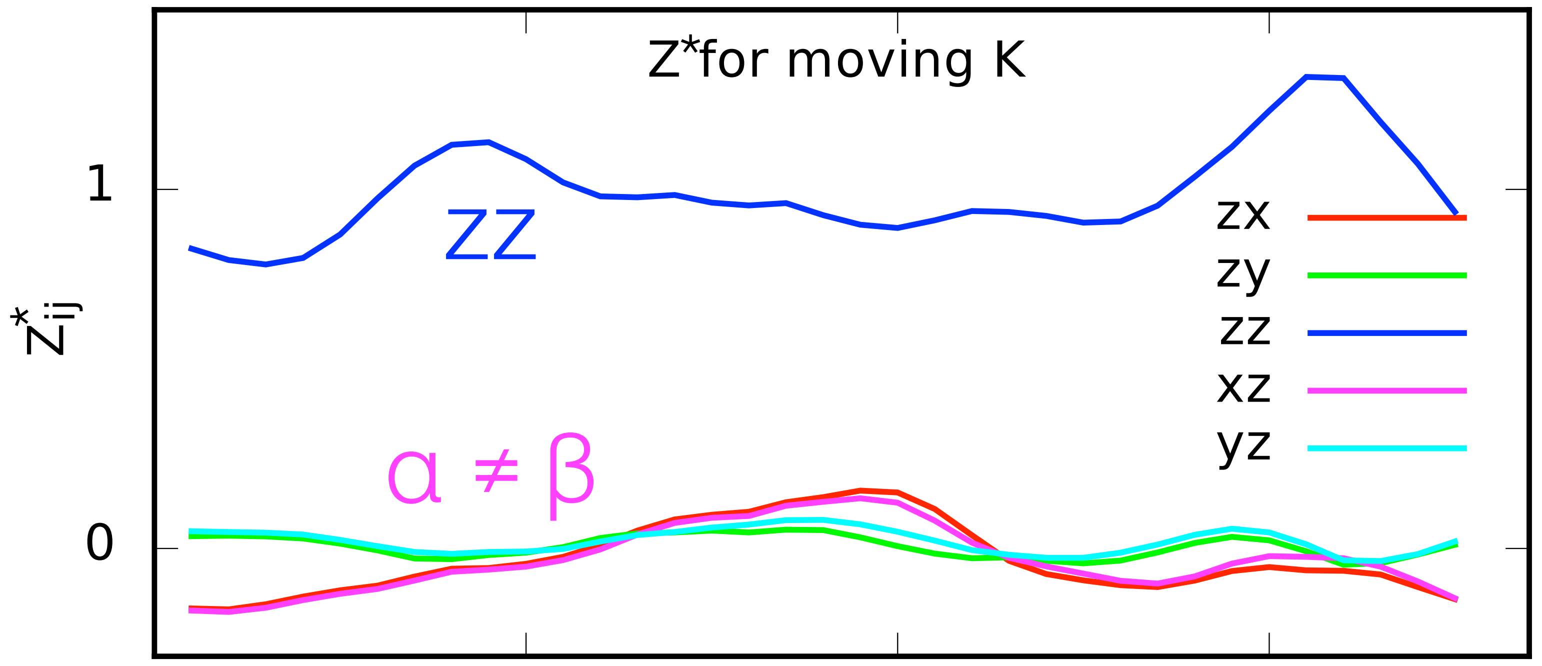




a numerical experiment on molten KCl

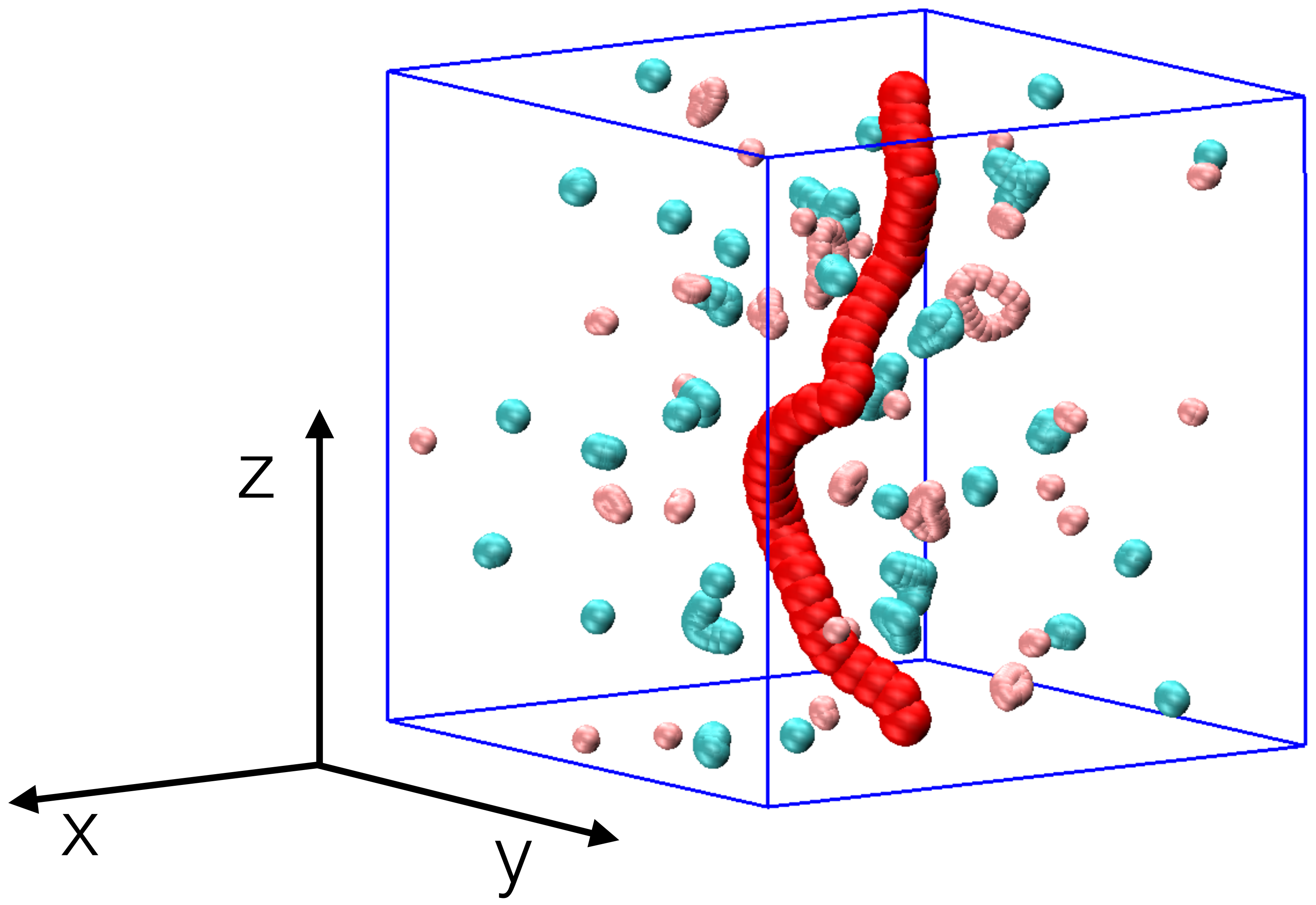


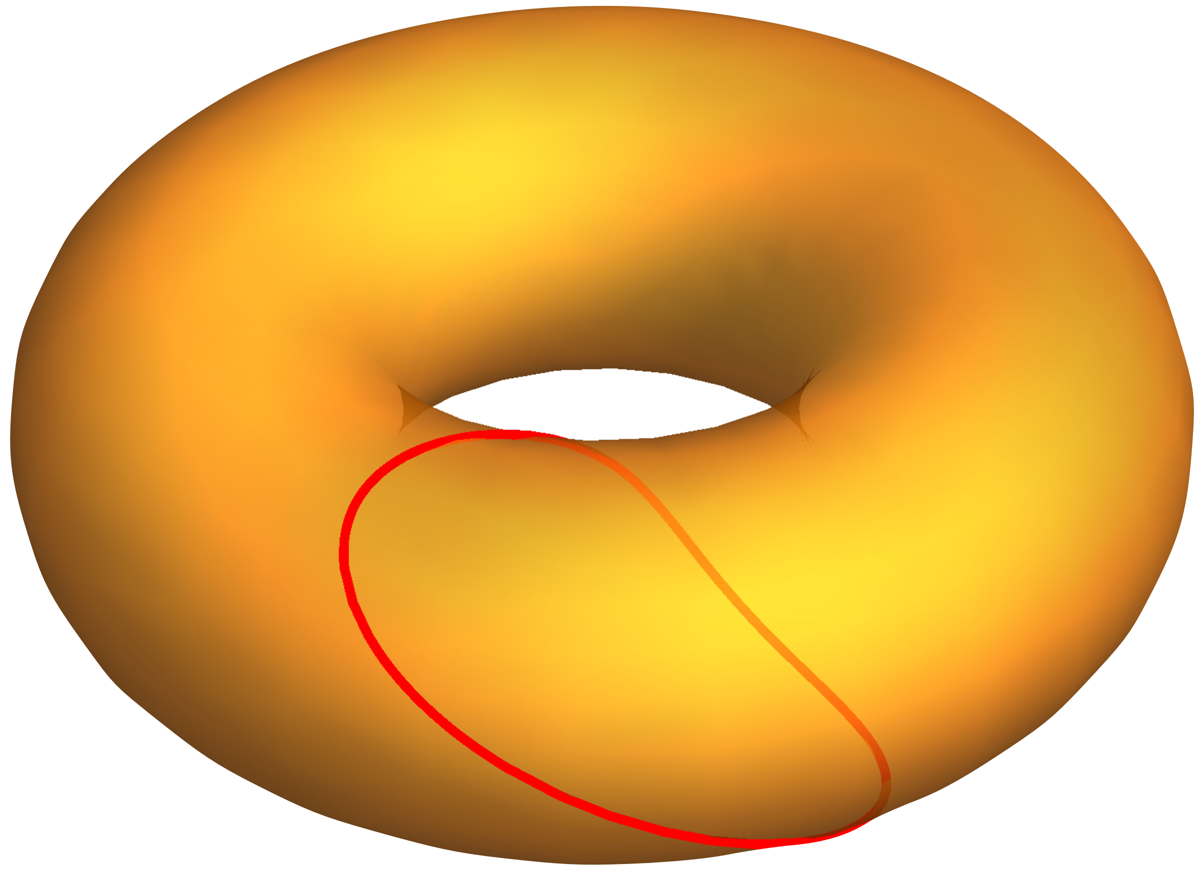


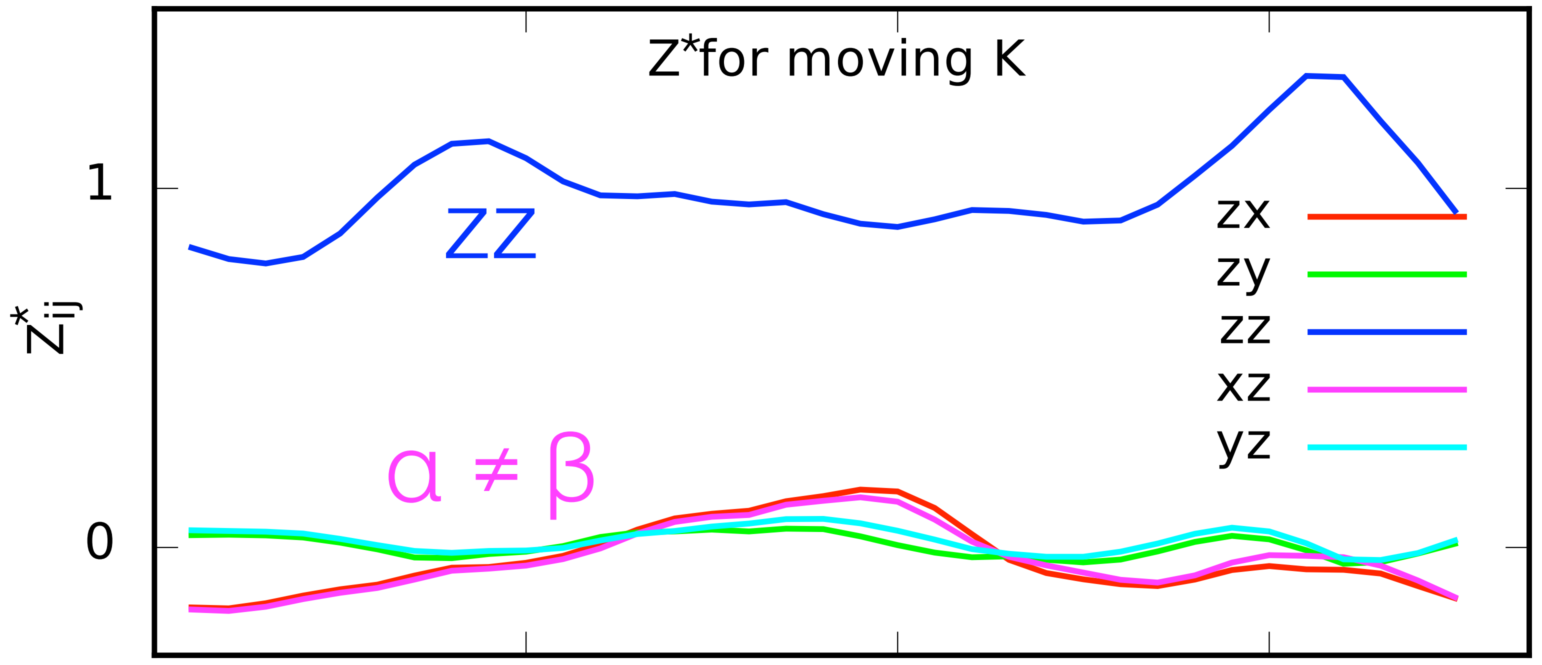


effective charge

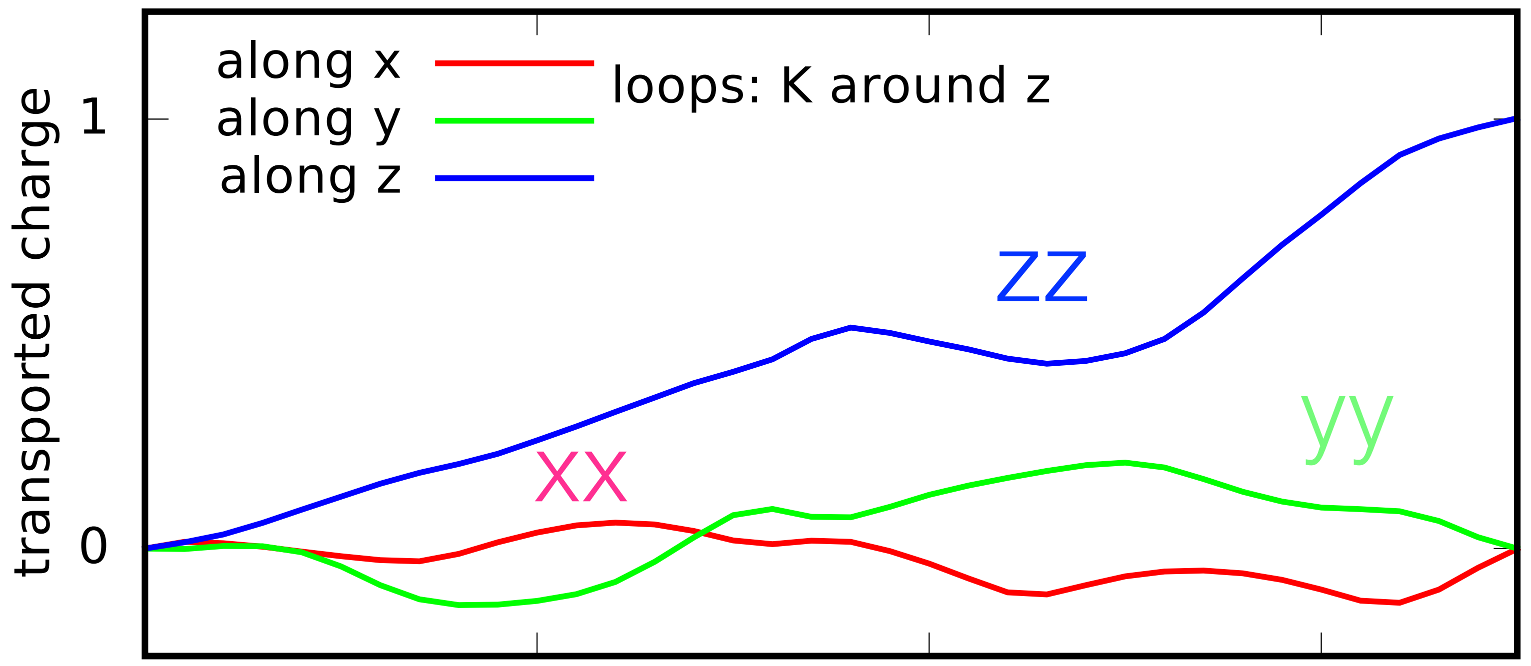
a numerical experiment on molten KCl







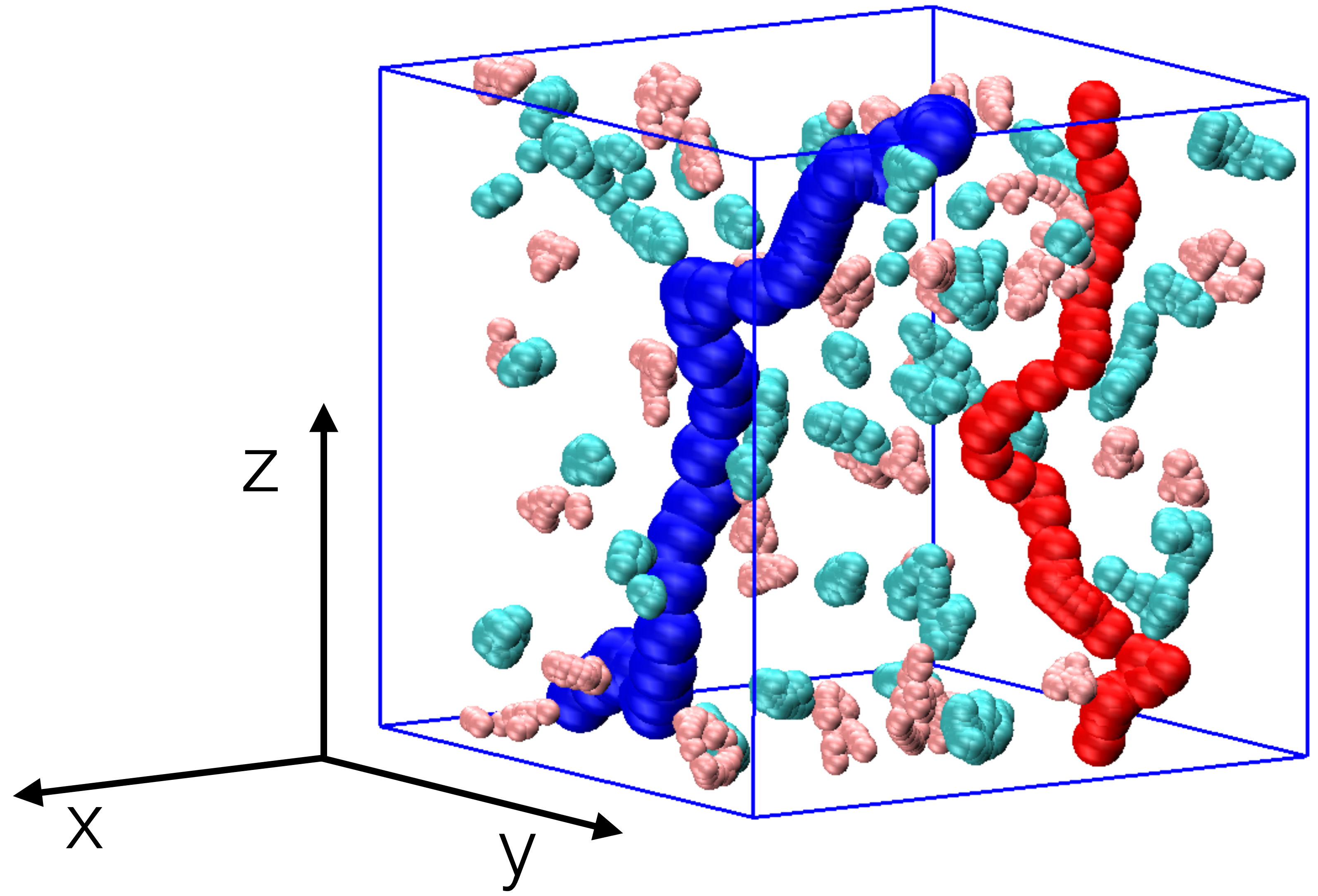
effective charge

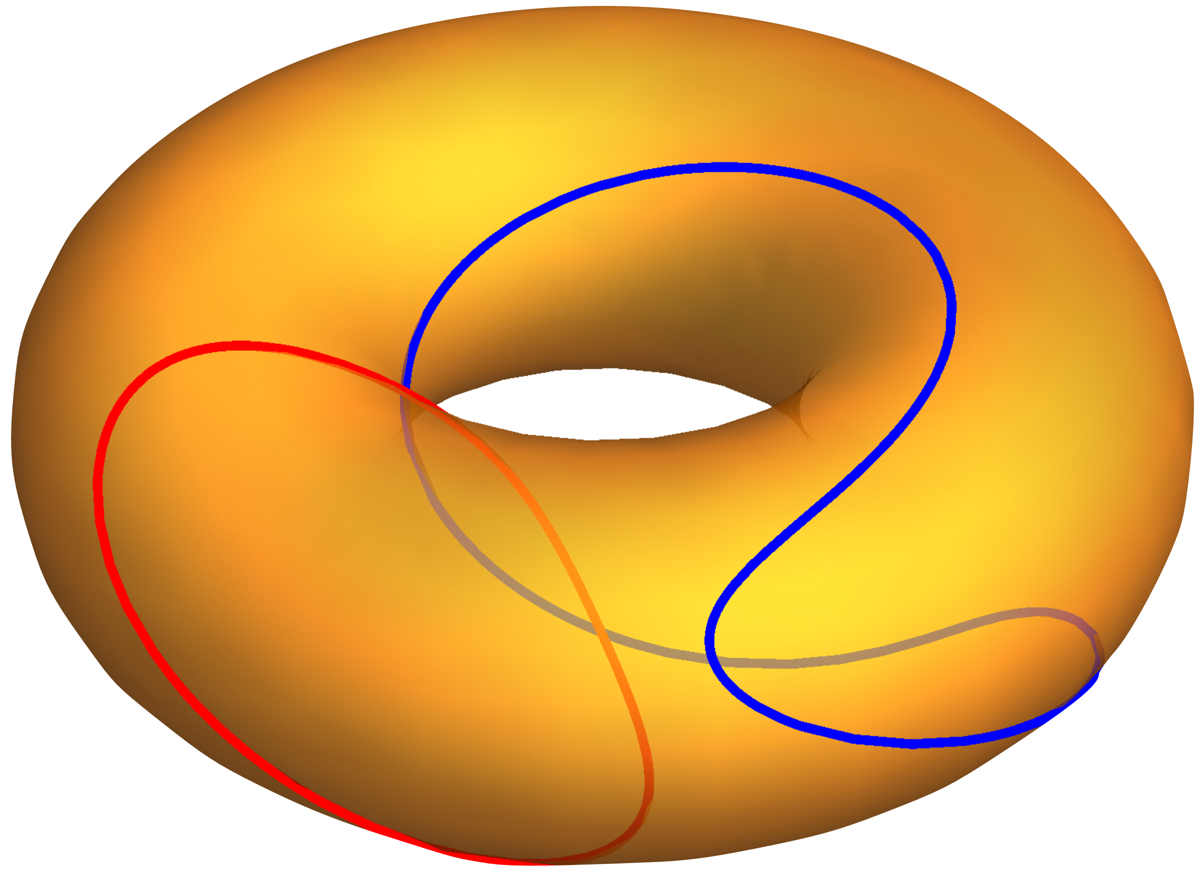


topological charge

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

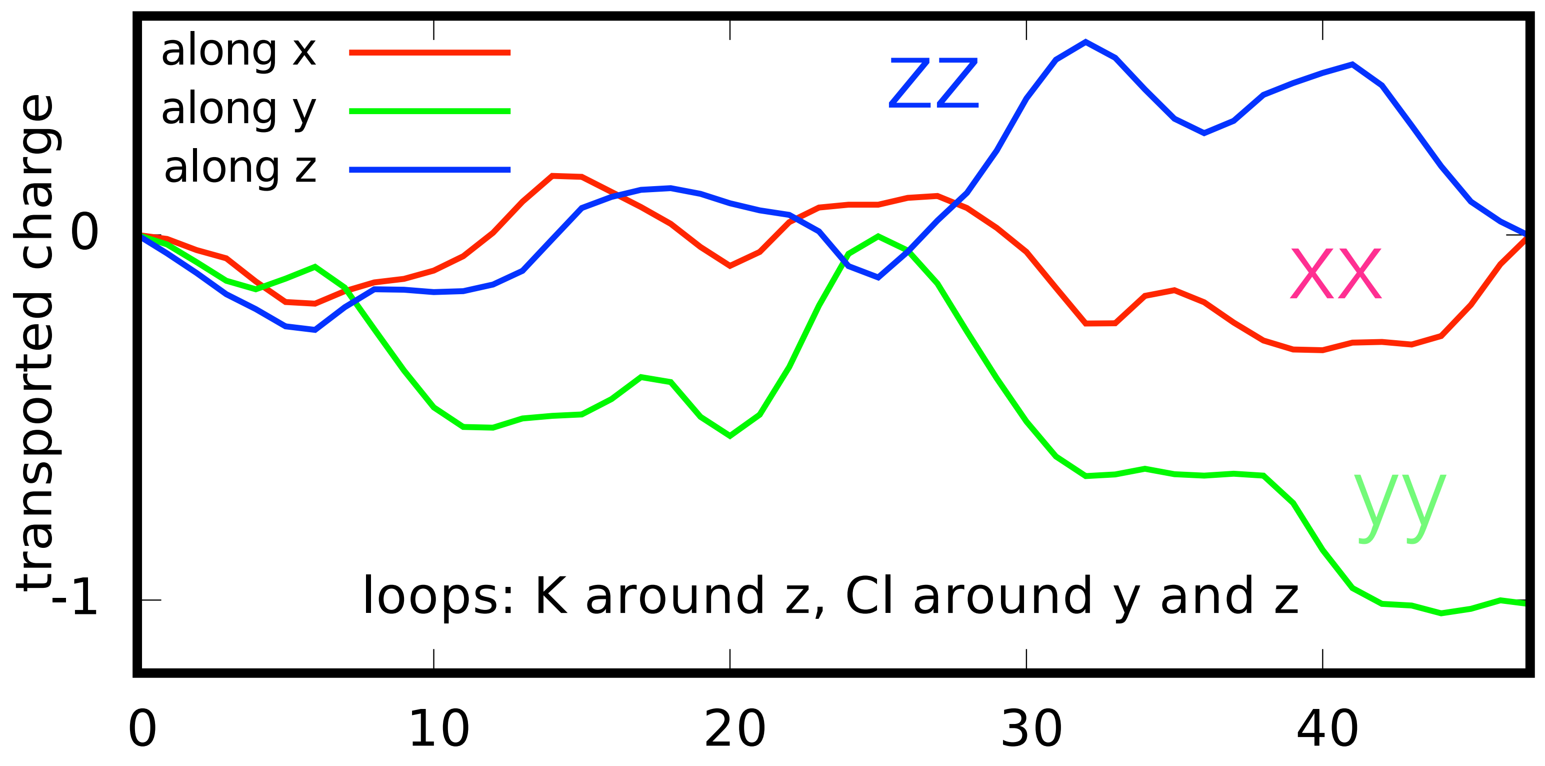
a numerical experiment on molten KCl





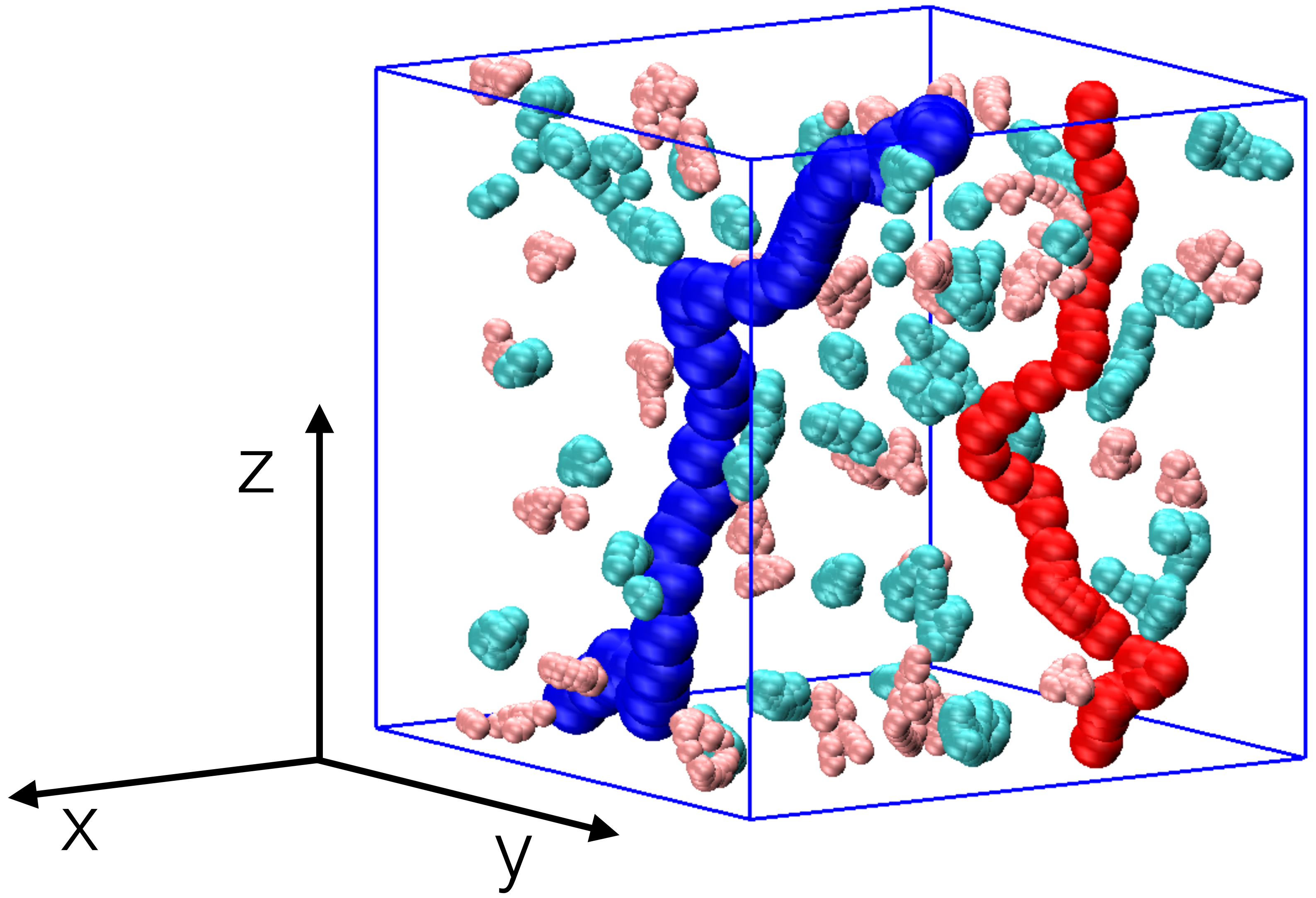
$Q_z[\text{Cl}]=-1 \quad Q_y[\text{Cl}]=-1$

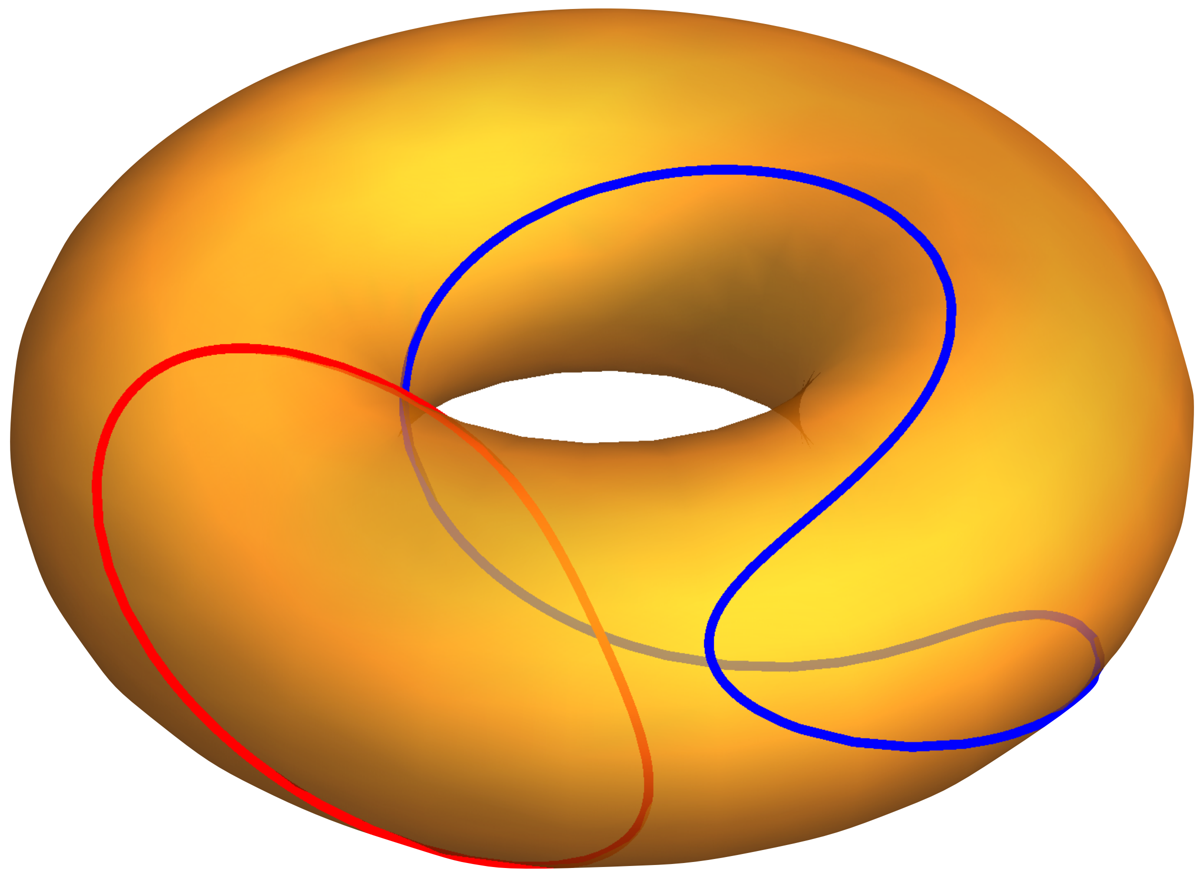
$Q_z[\text{K}] = 1 \quad Q_z[\text{K}] = 0$



the charges transported by K and Cl
around z cancel exactly

a numerical experiment on molten KCl





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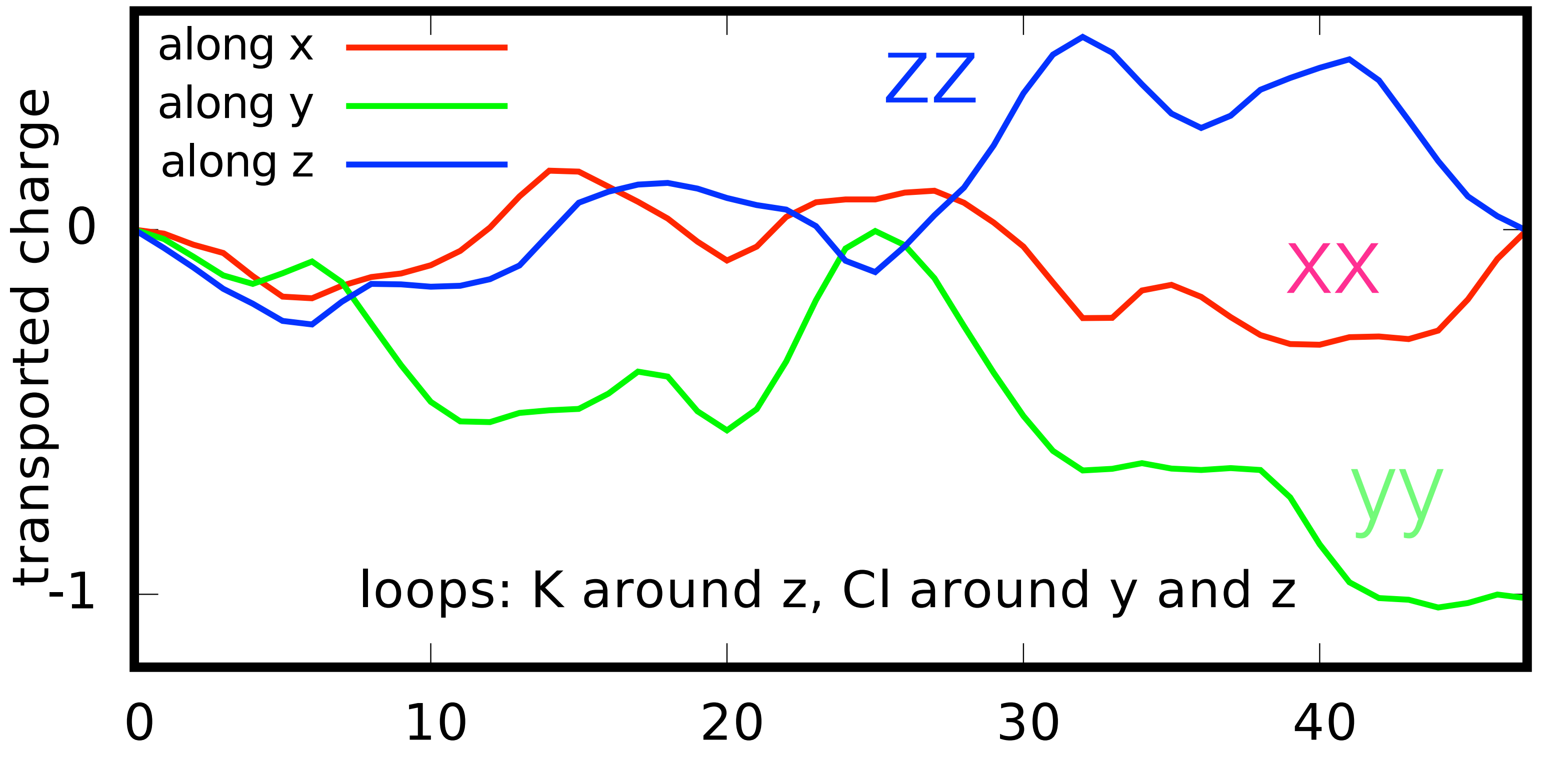

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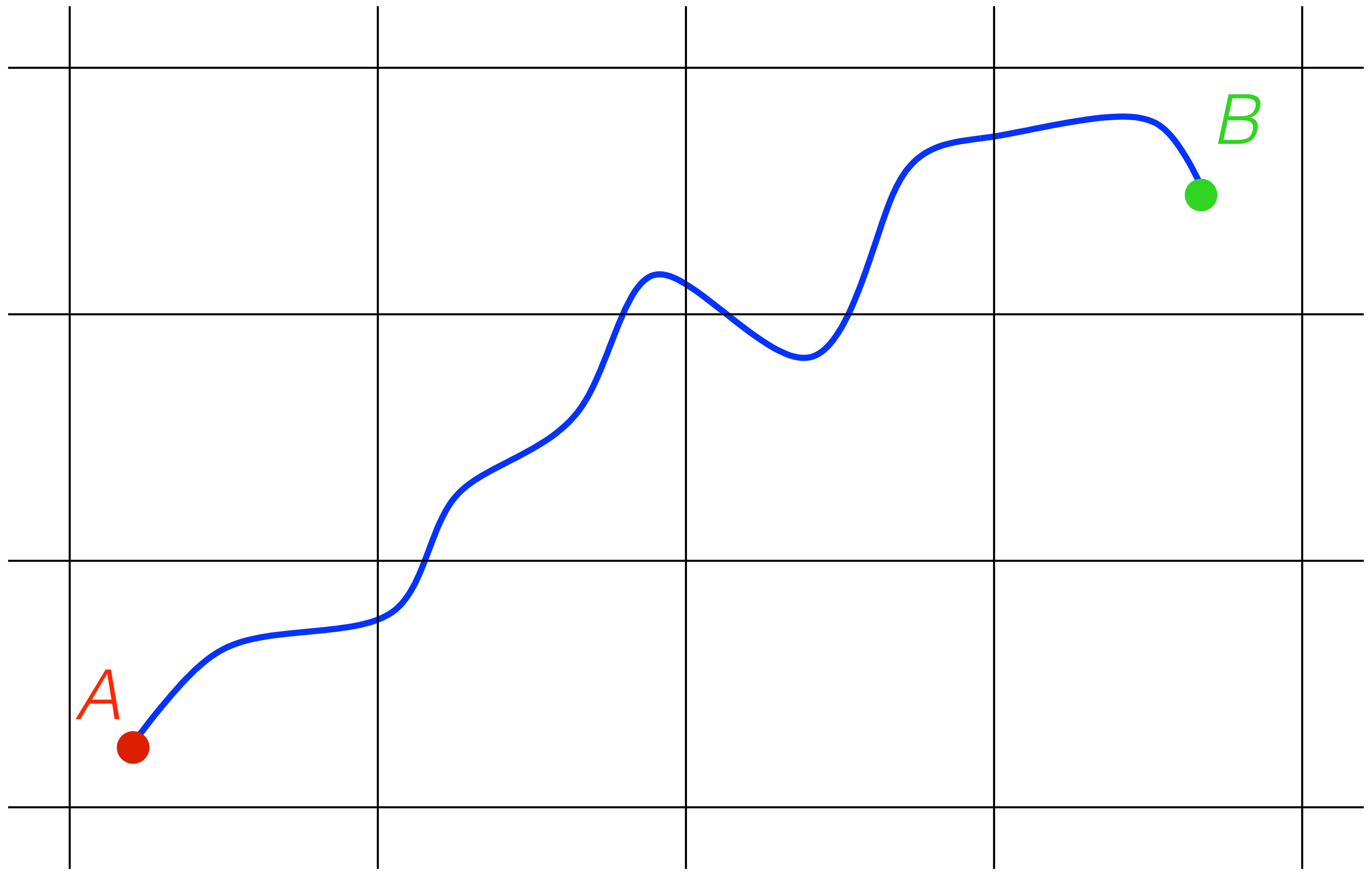
gauge invariance of charge transport



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

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

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

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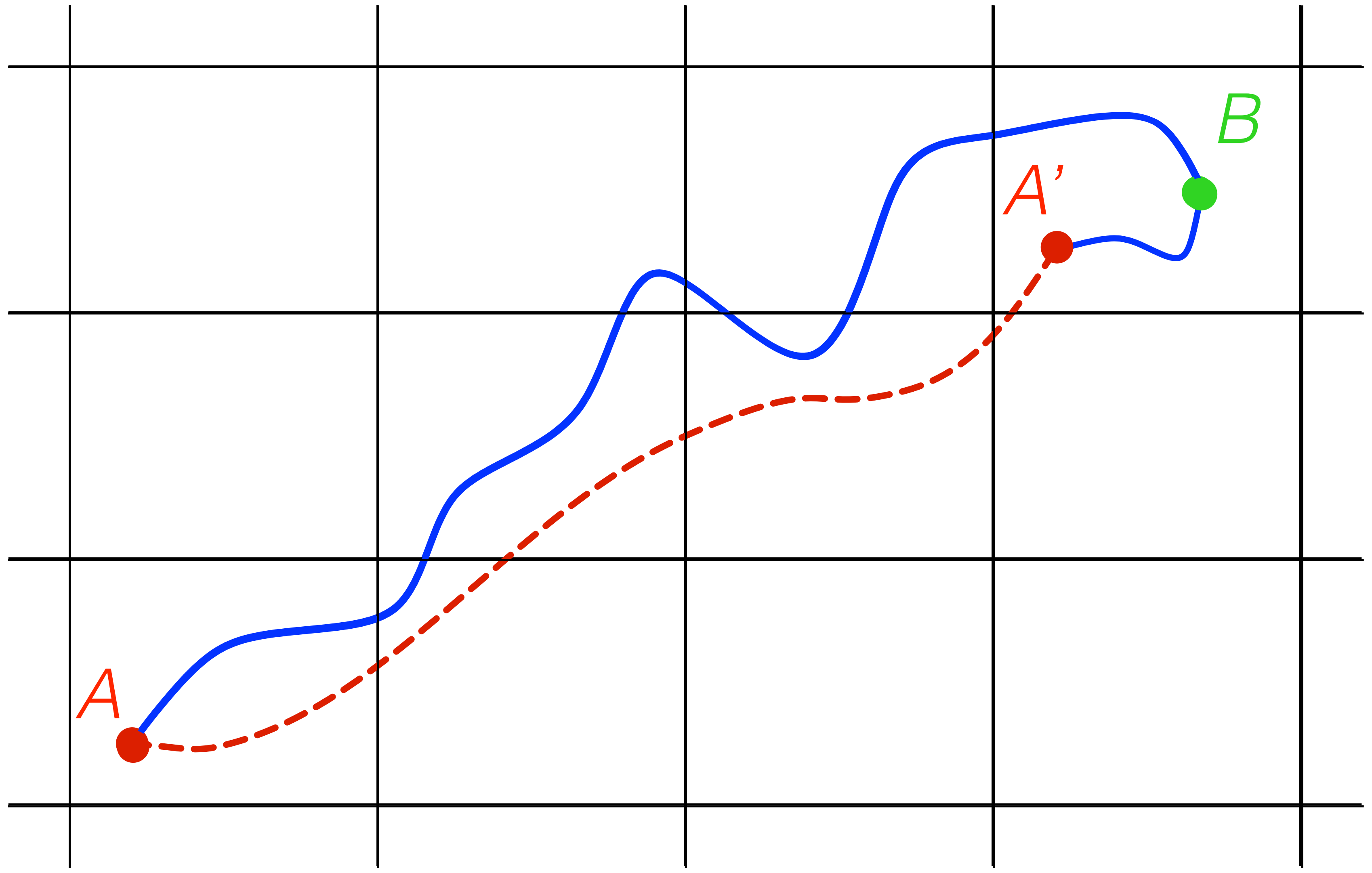

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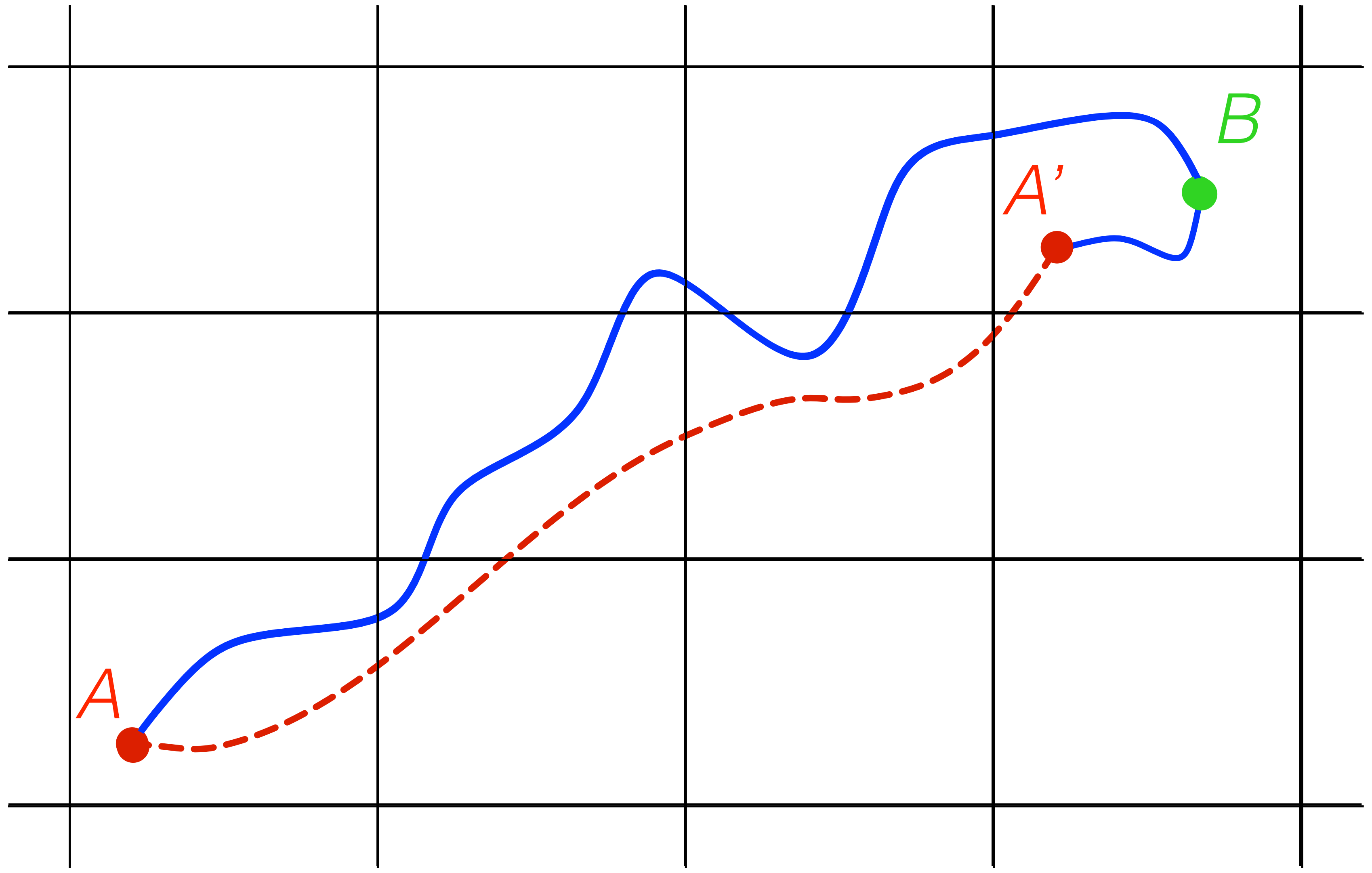

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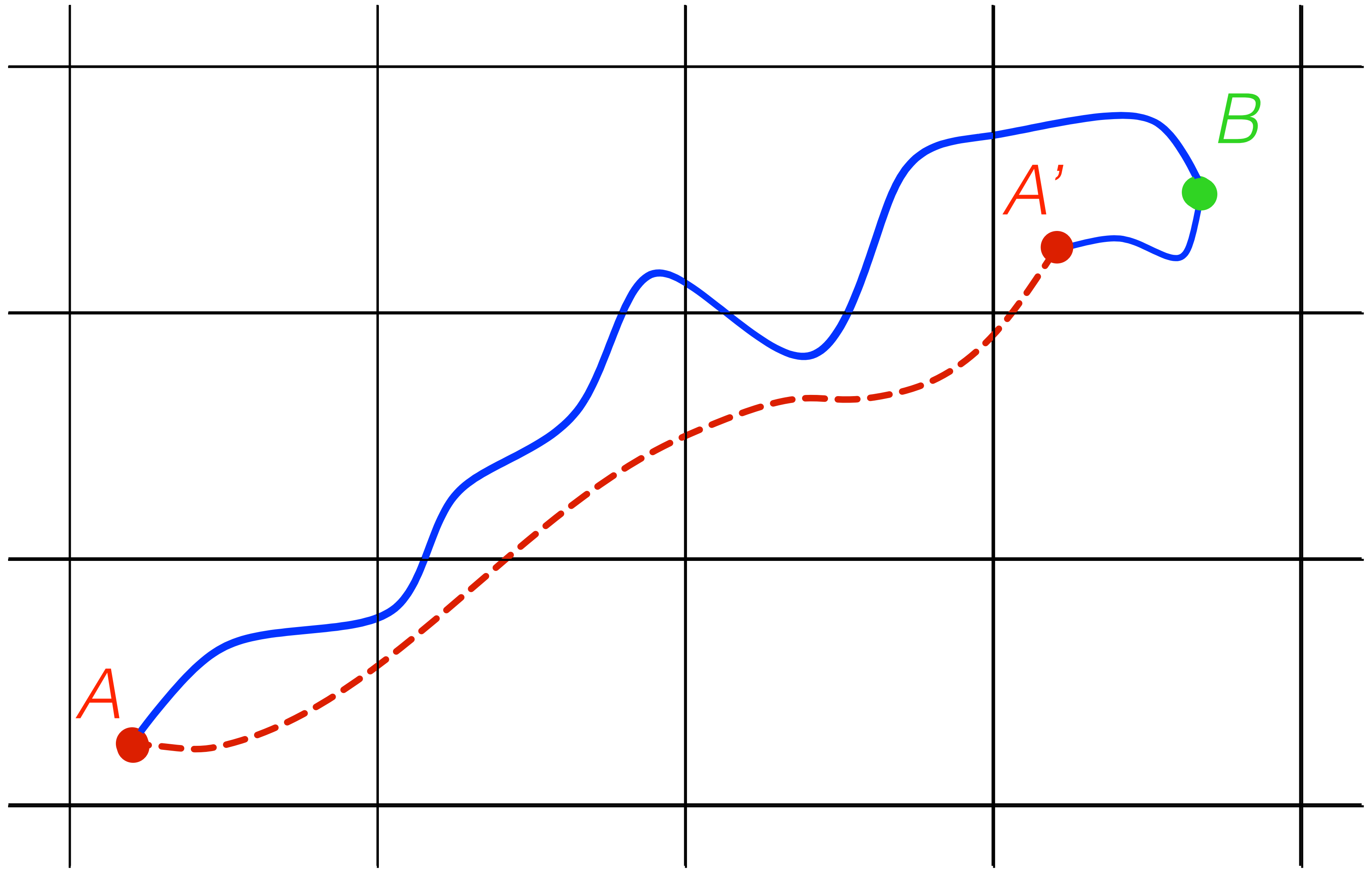

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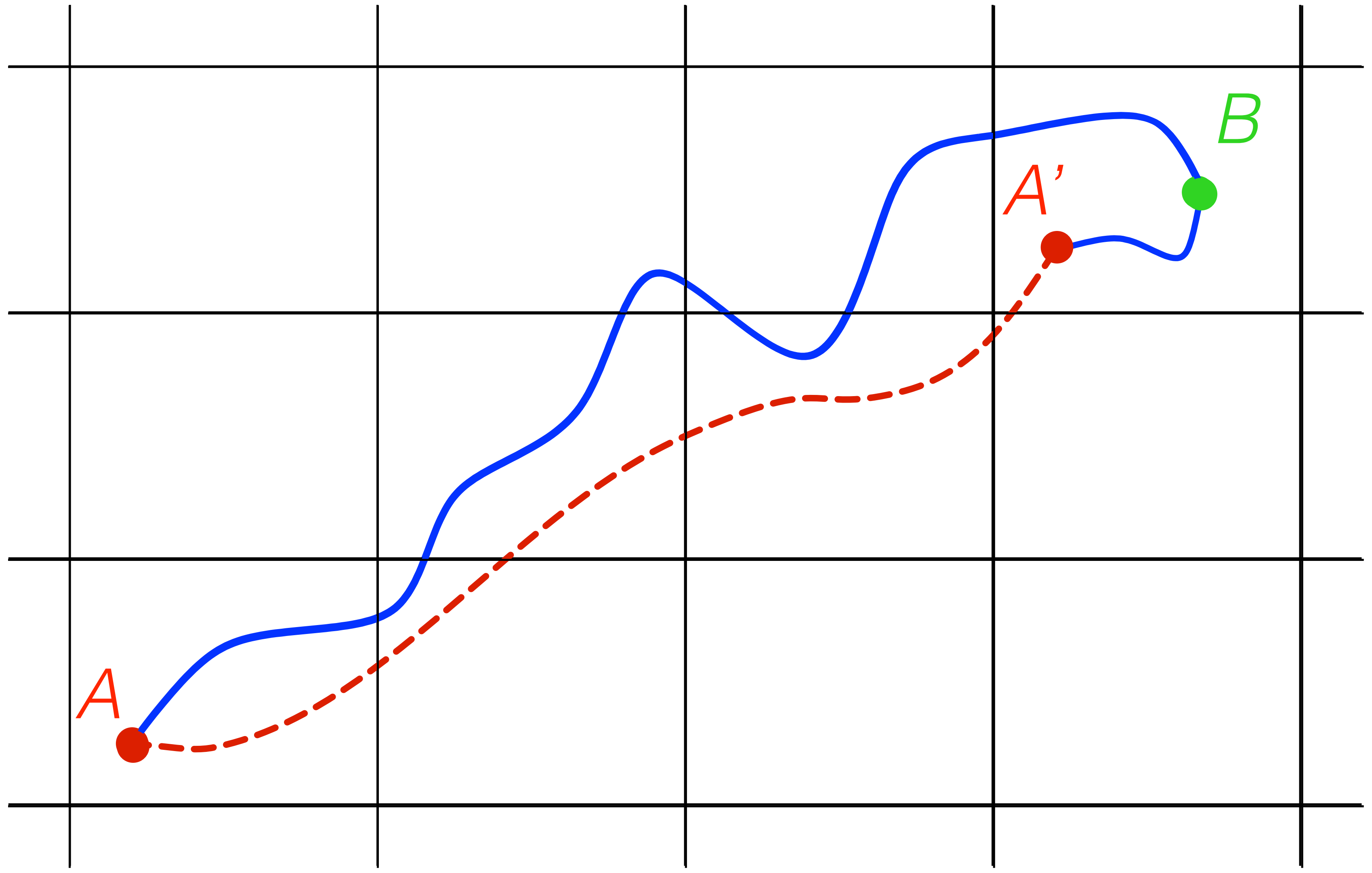

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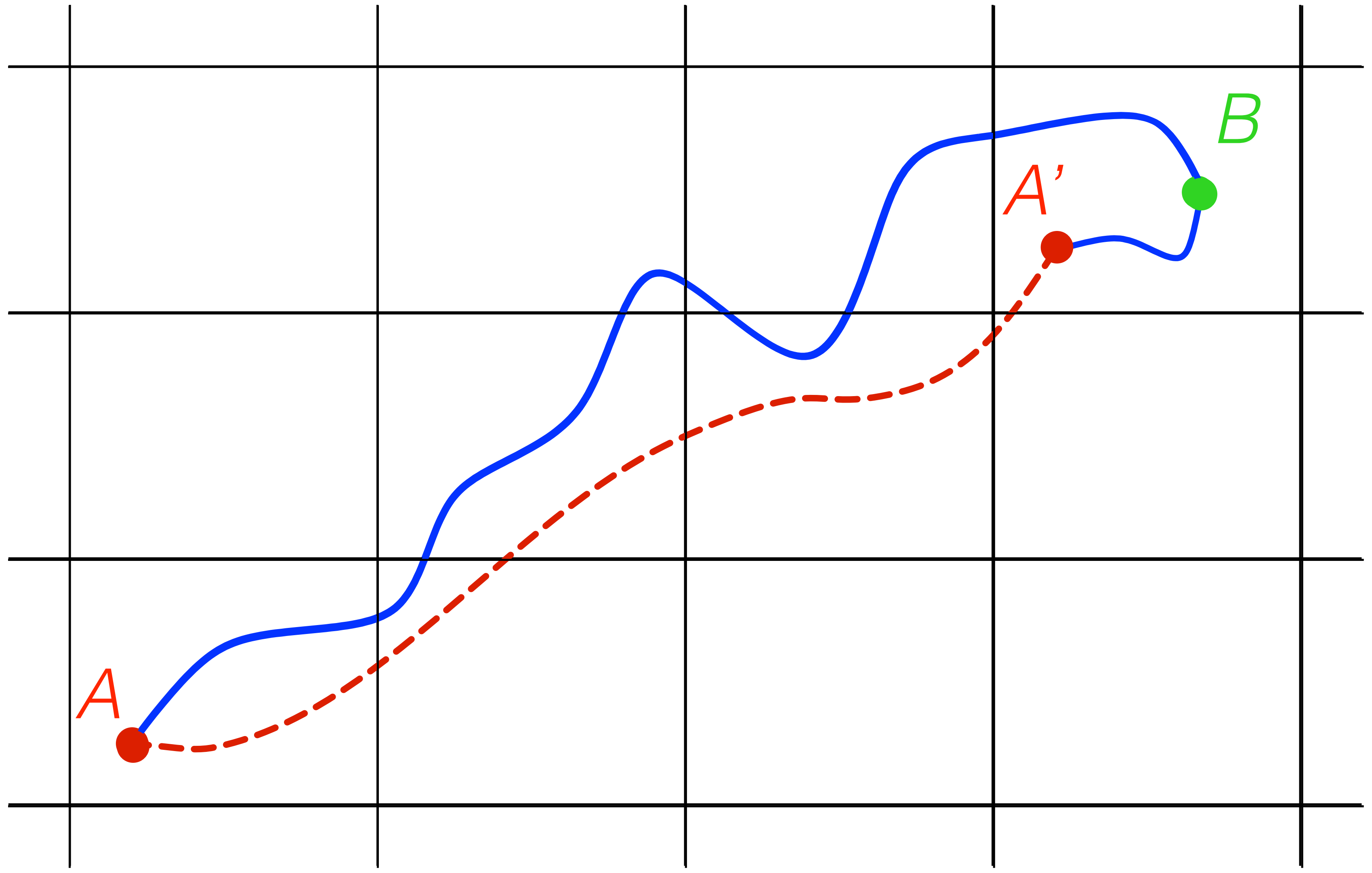

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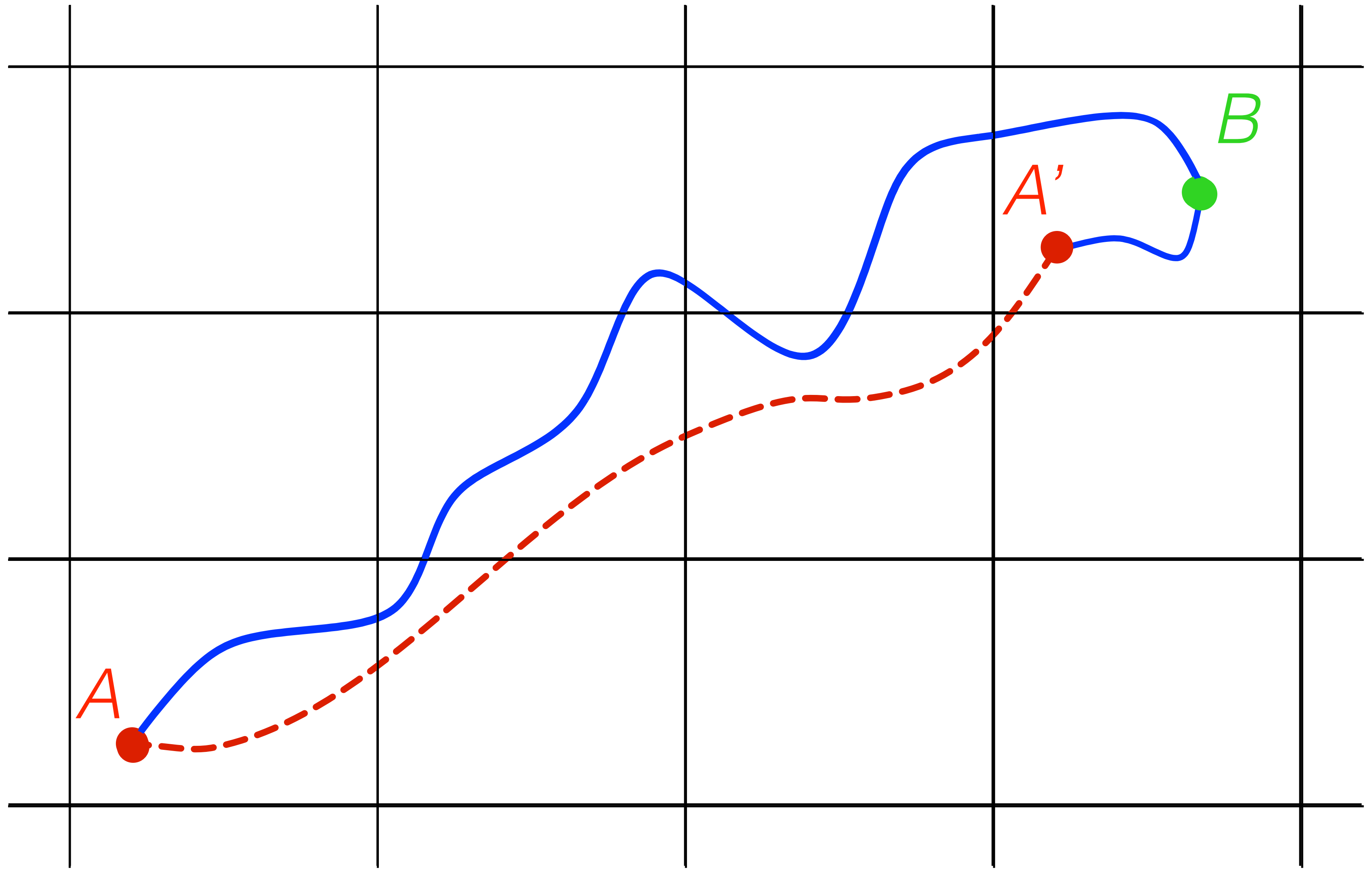

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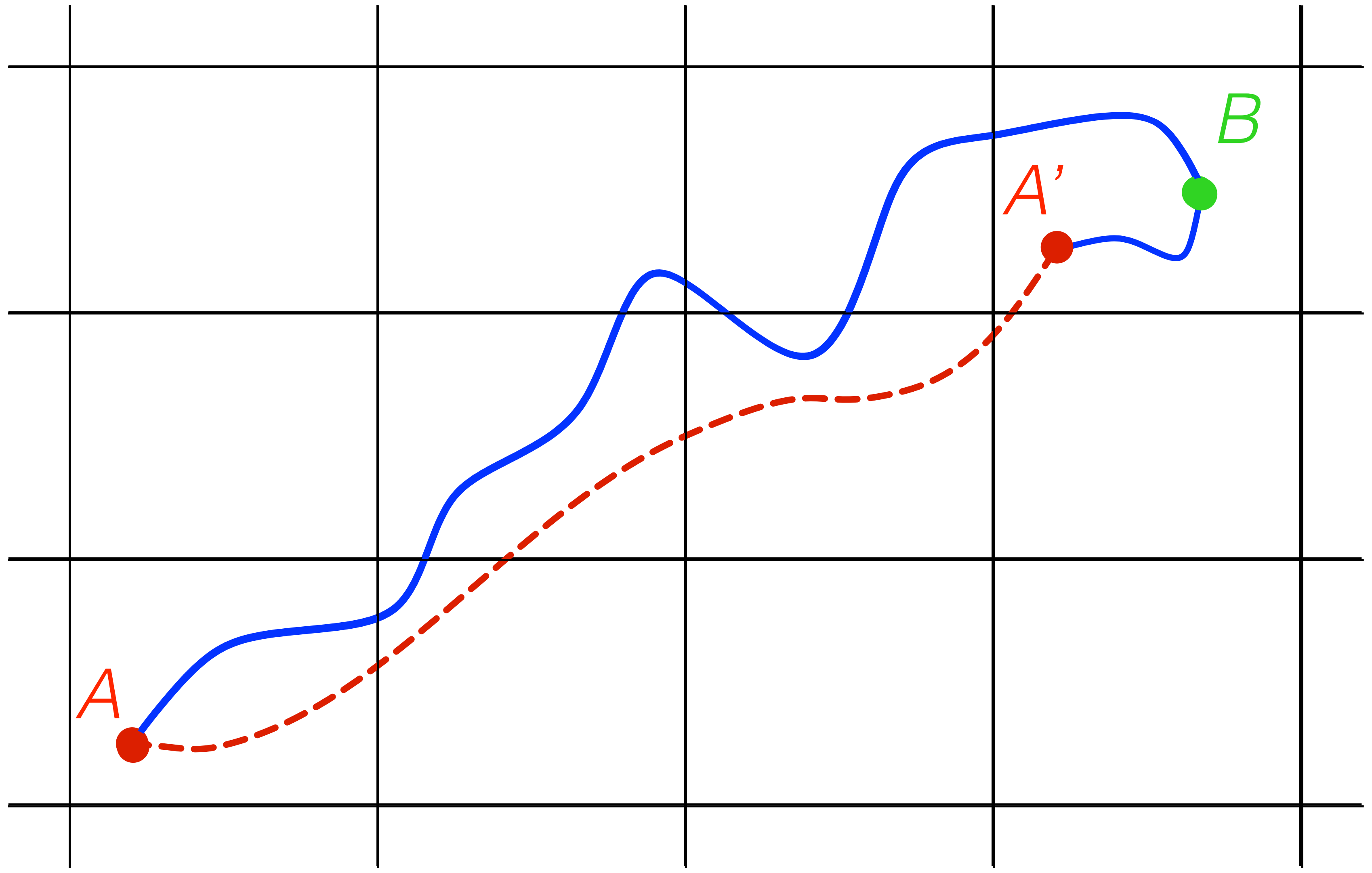

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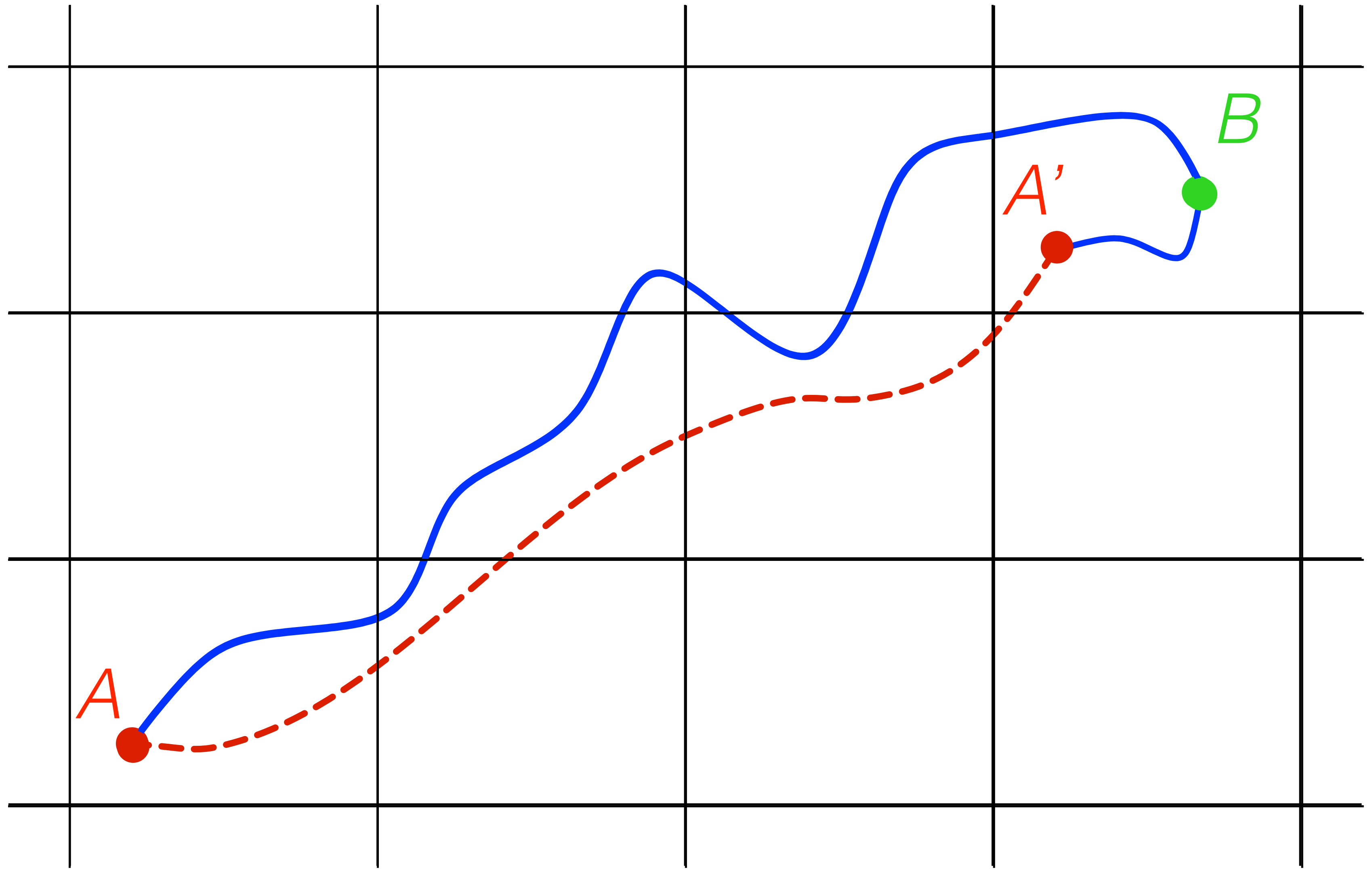

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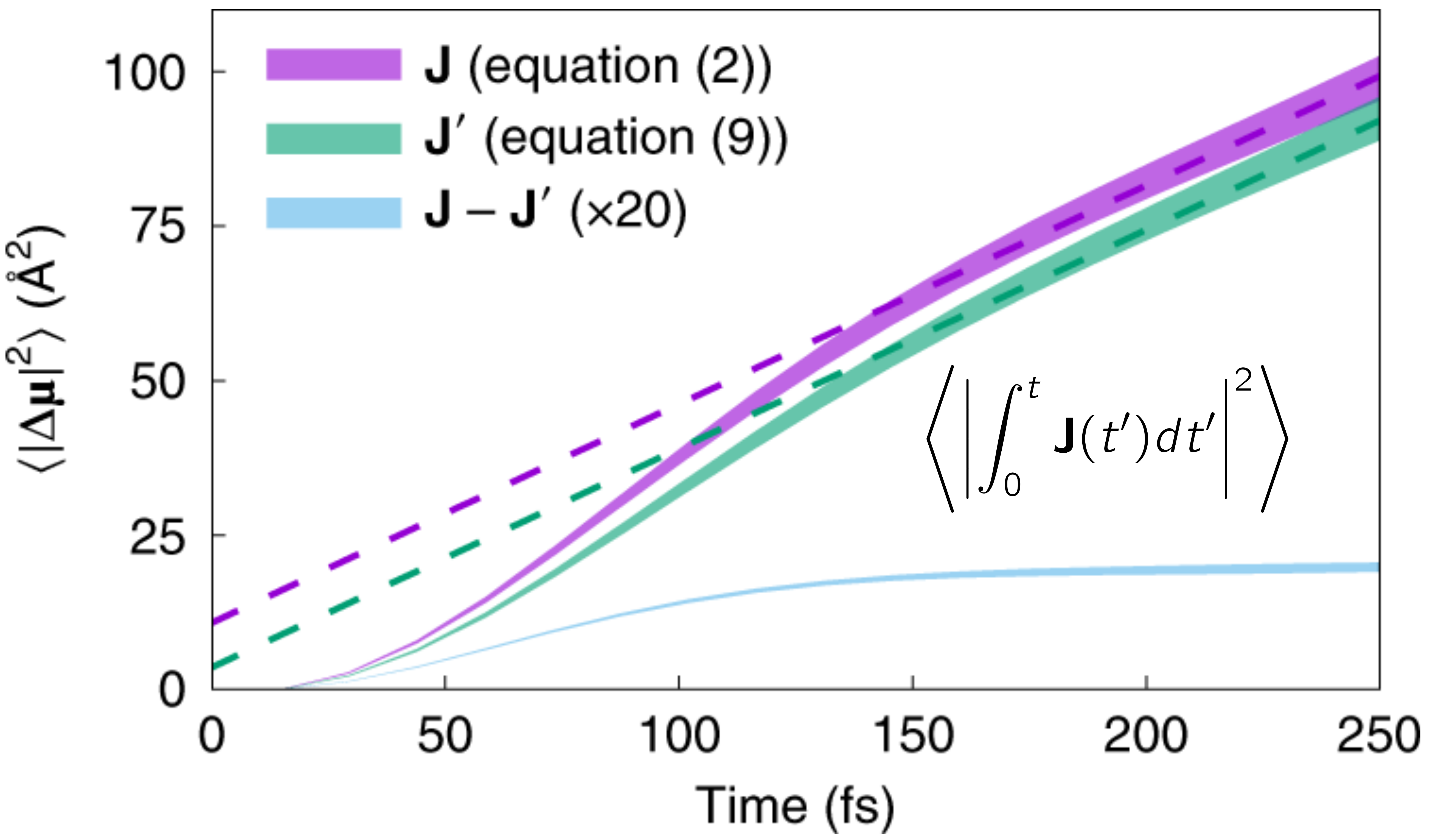
$$\sigma = \sigma'$$

currents from atomic oxidation numbers

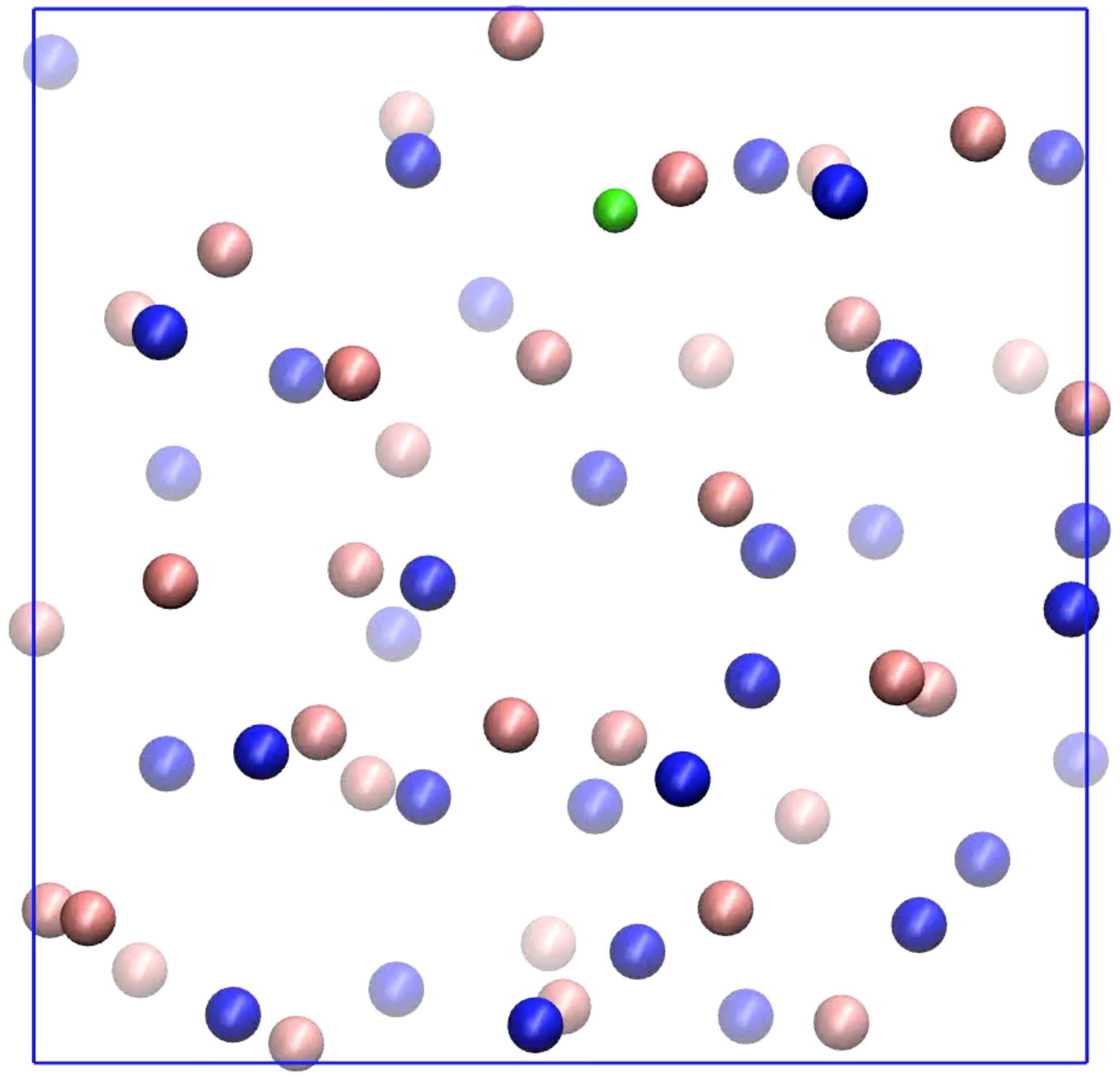
(2) $$J_\alpha = \sum_{i\beta} Z^*_{i\alpha\beta} v_{i\beta}$$

(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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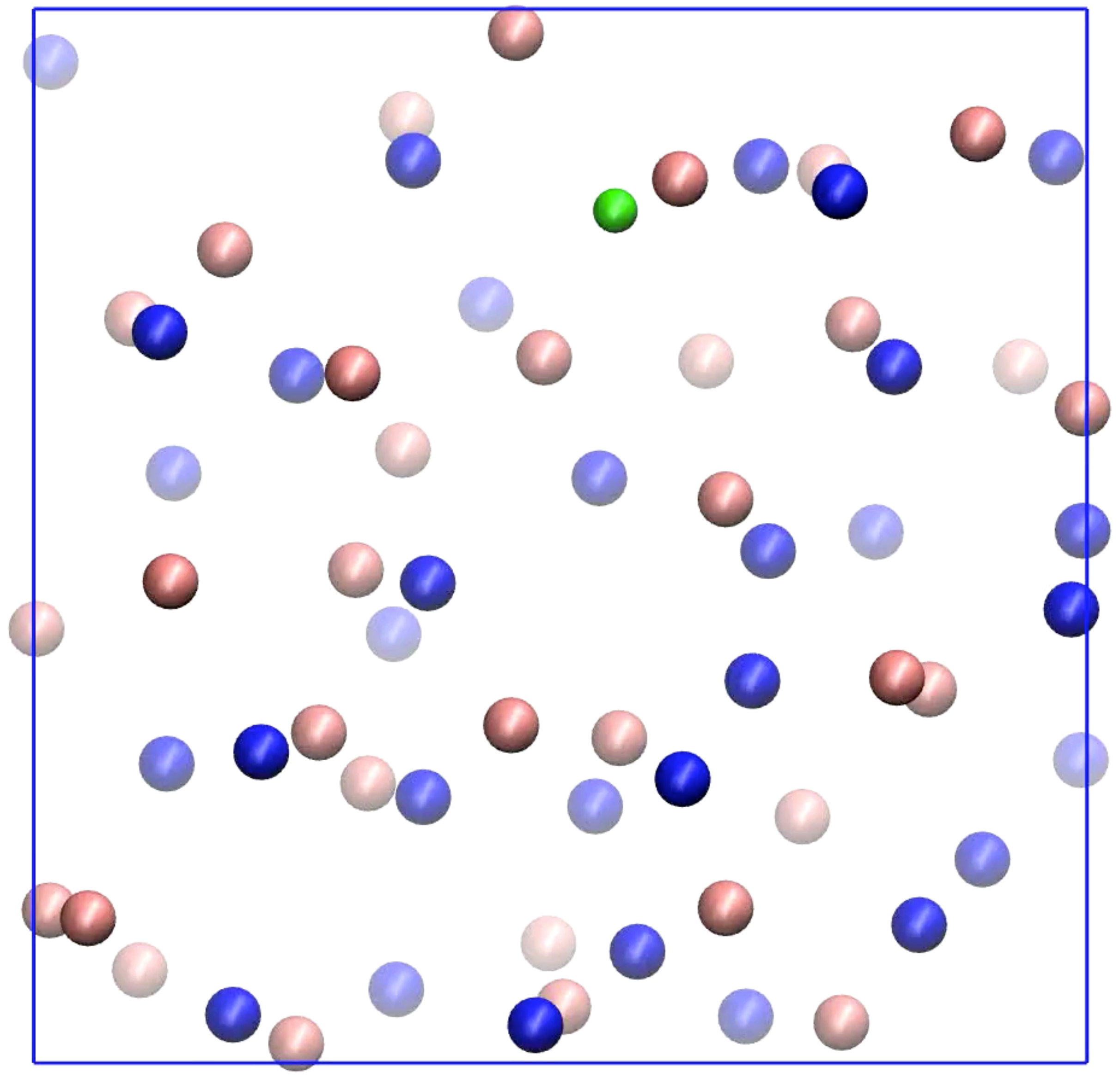

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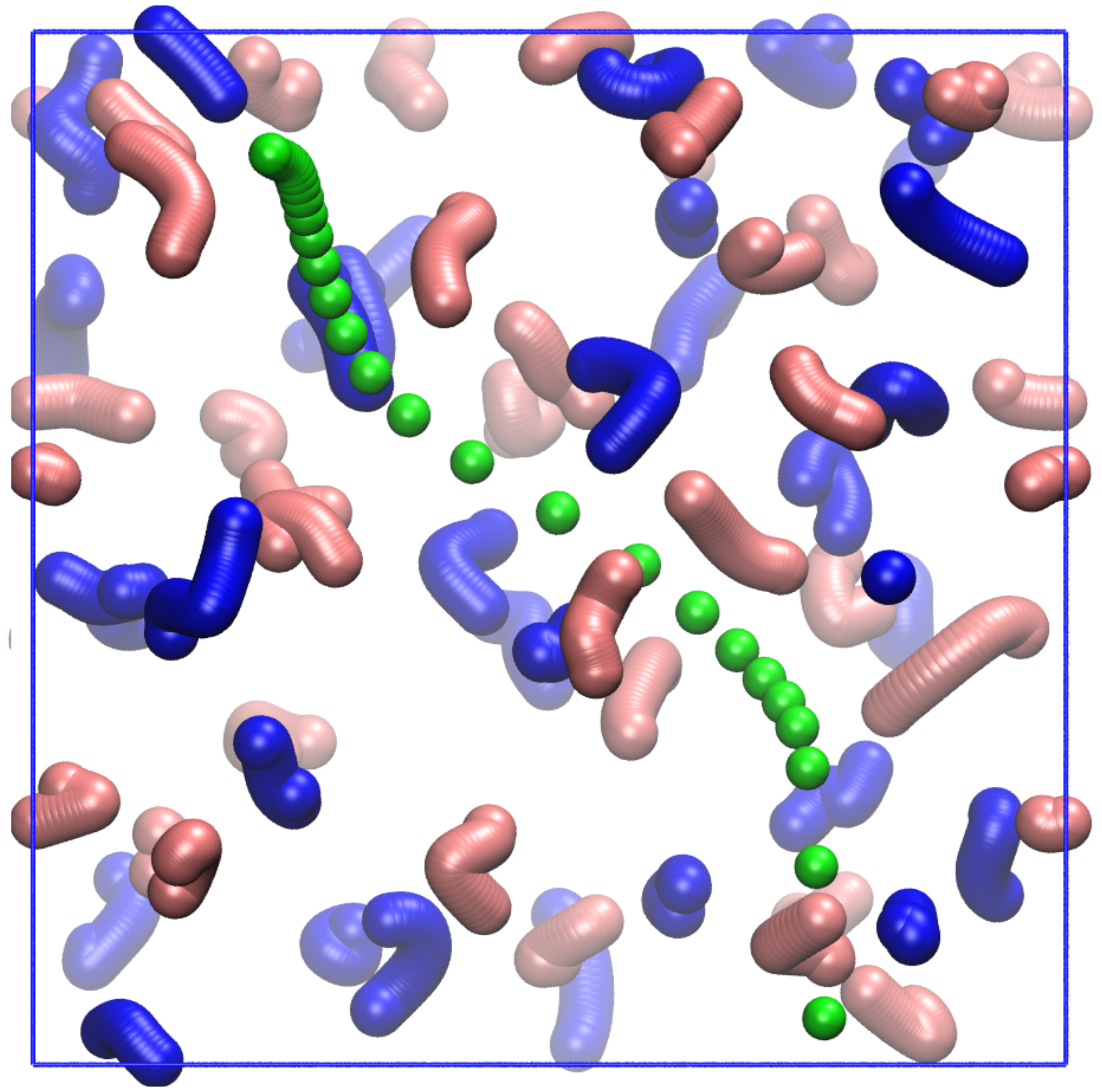

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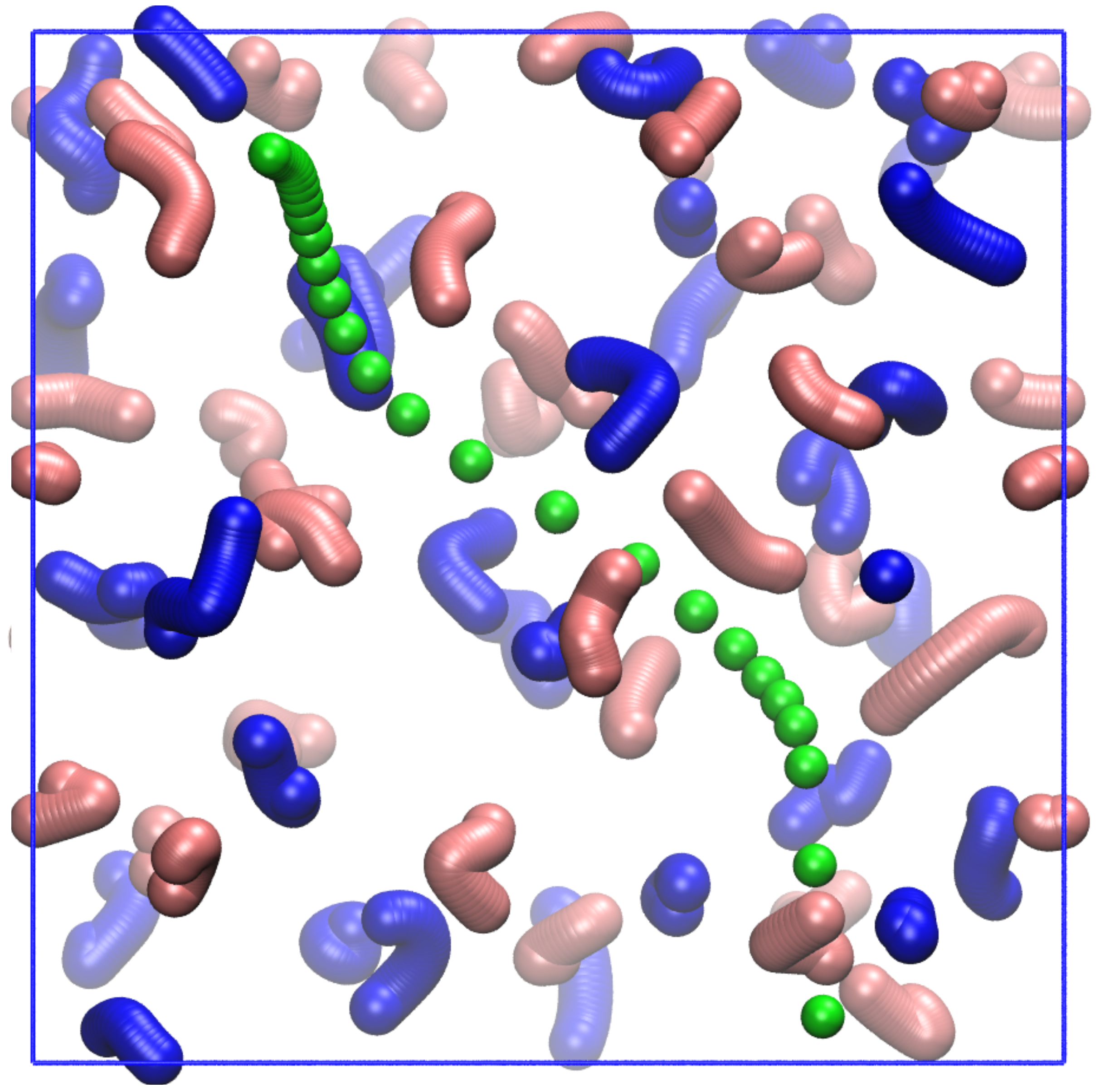

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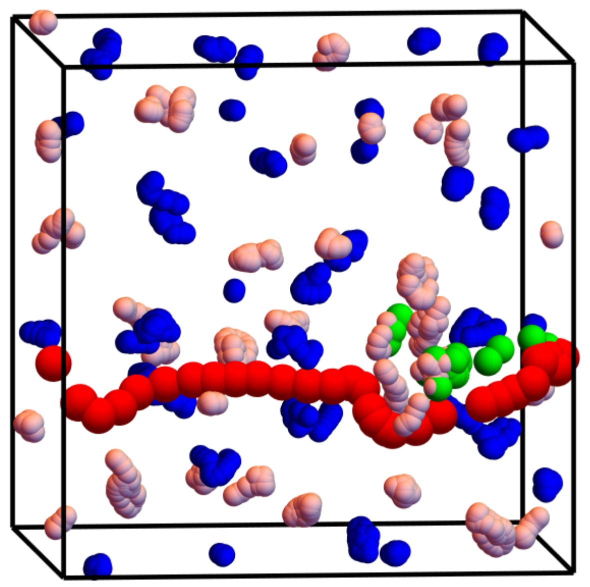

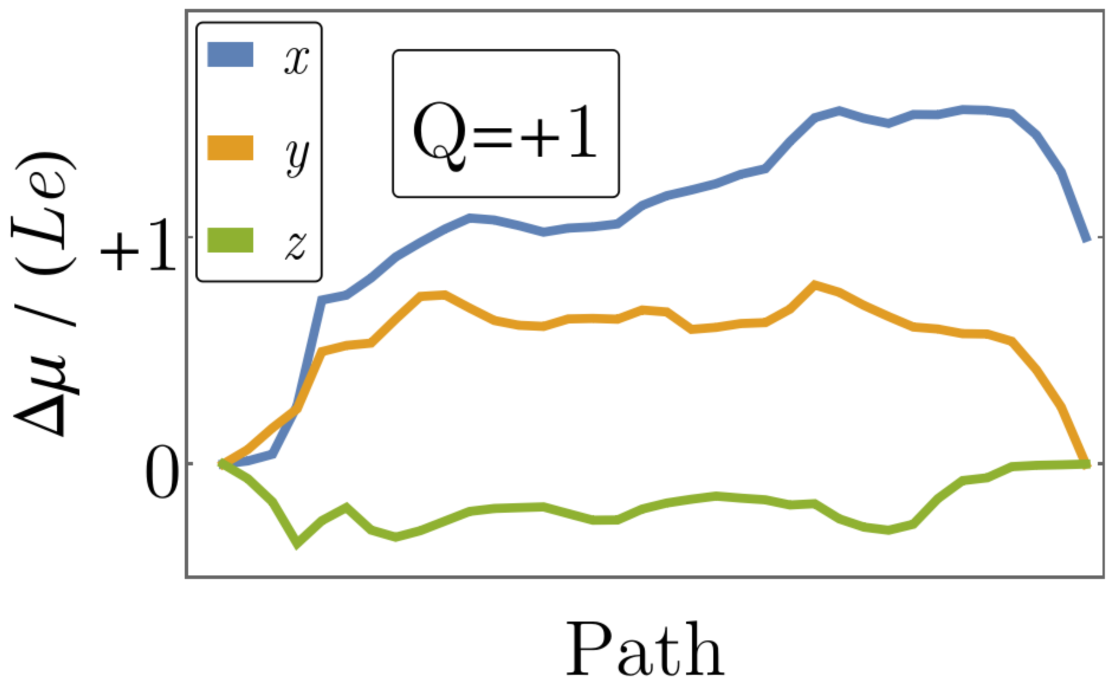

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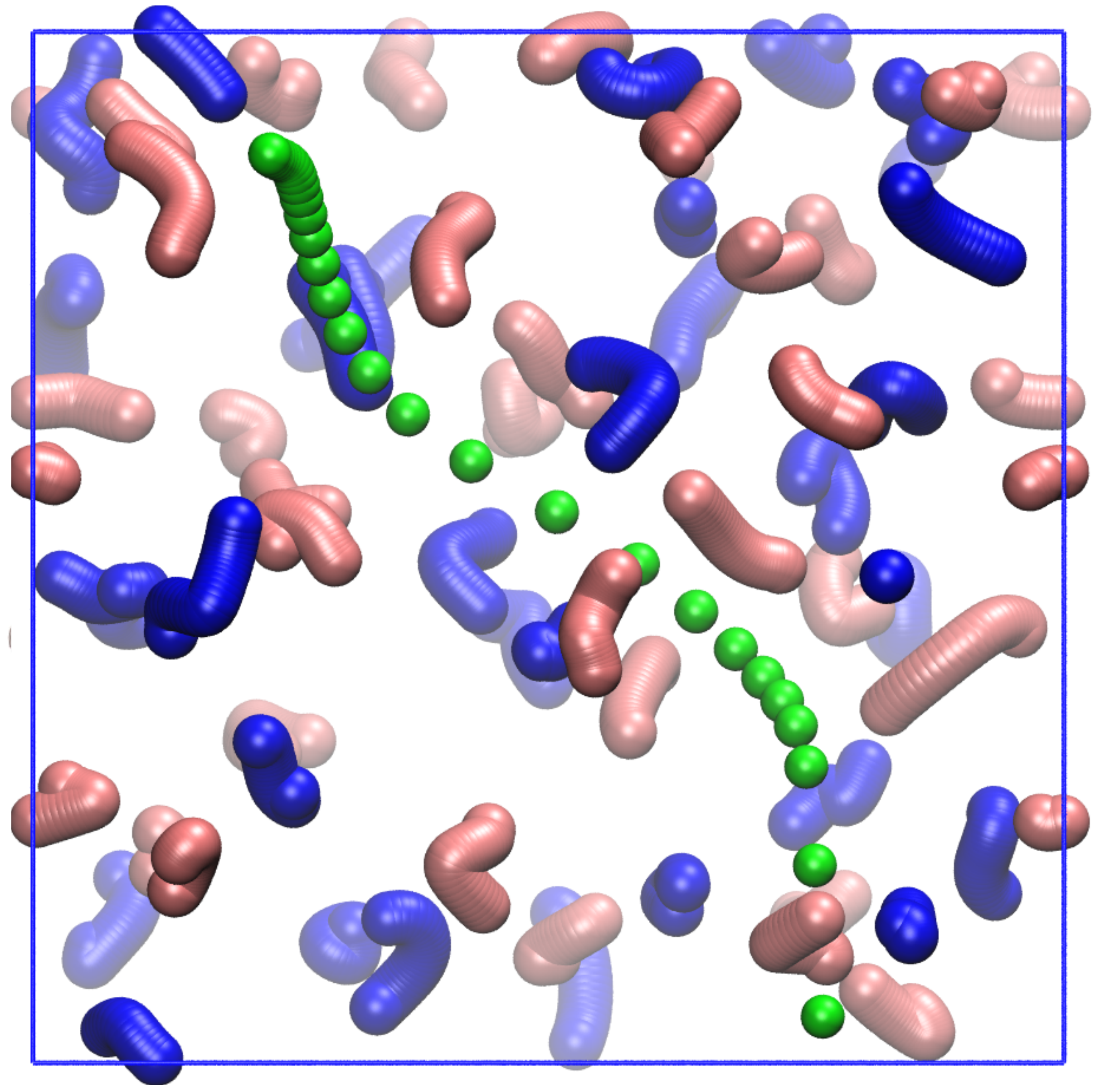

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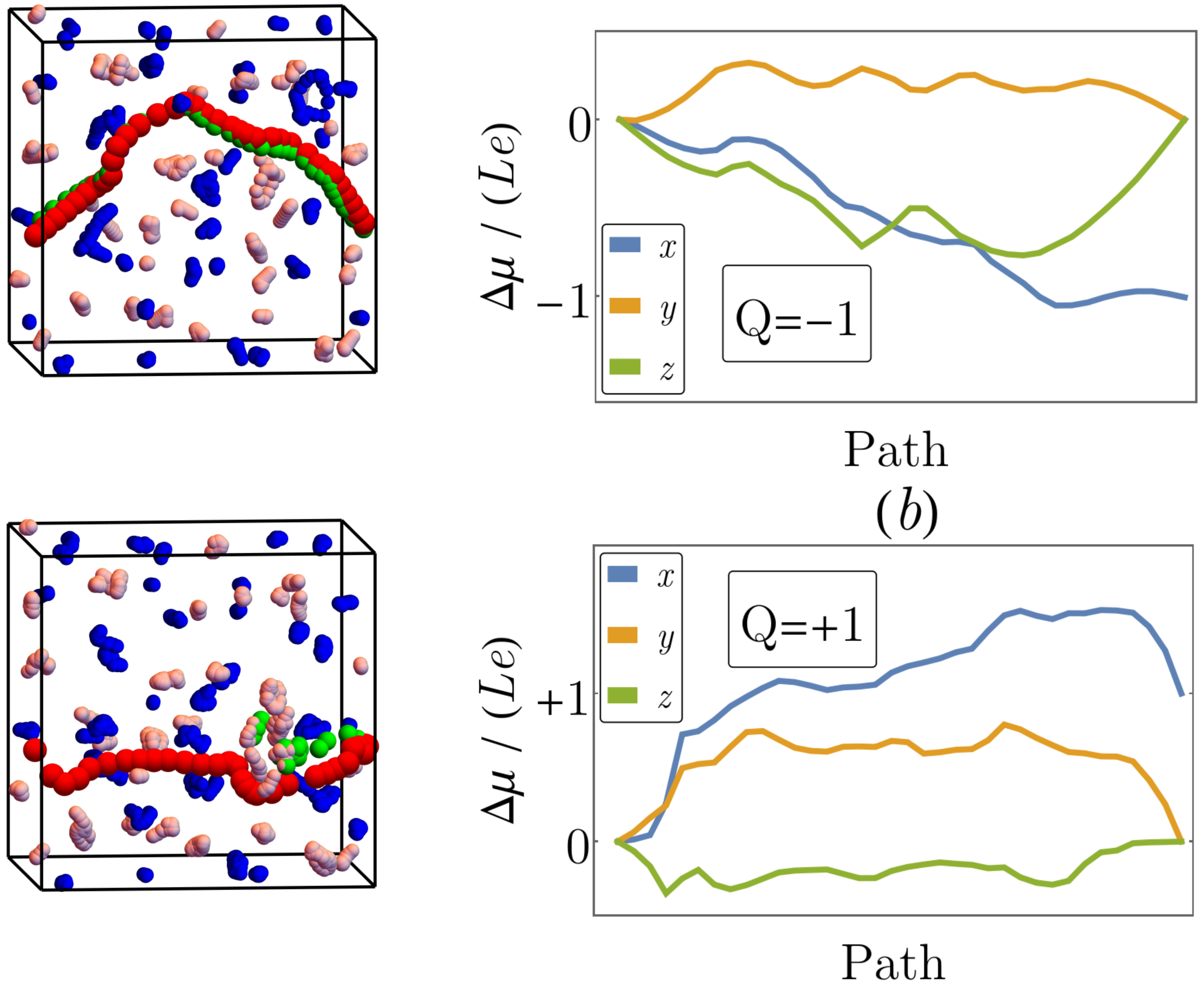
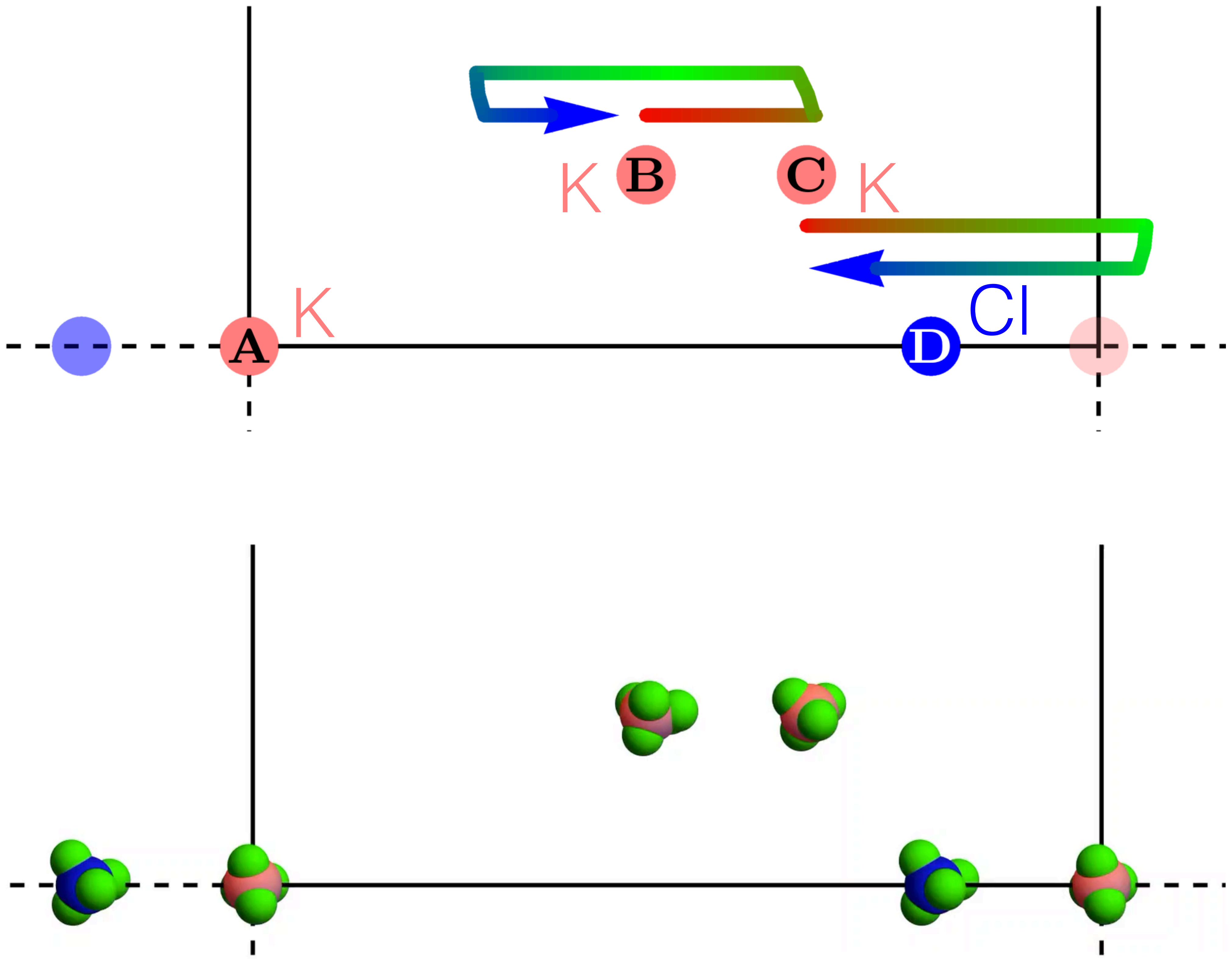
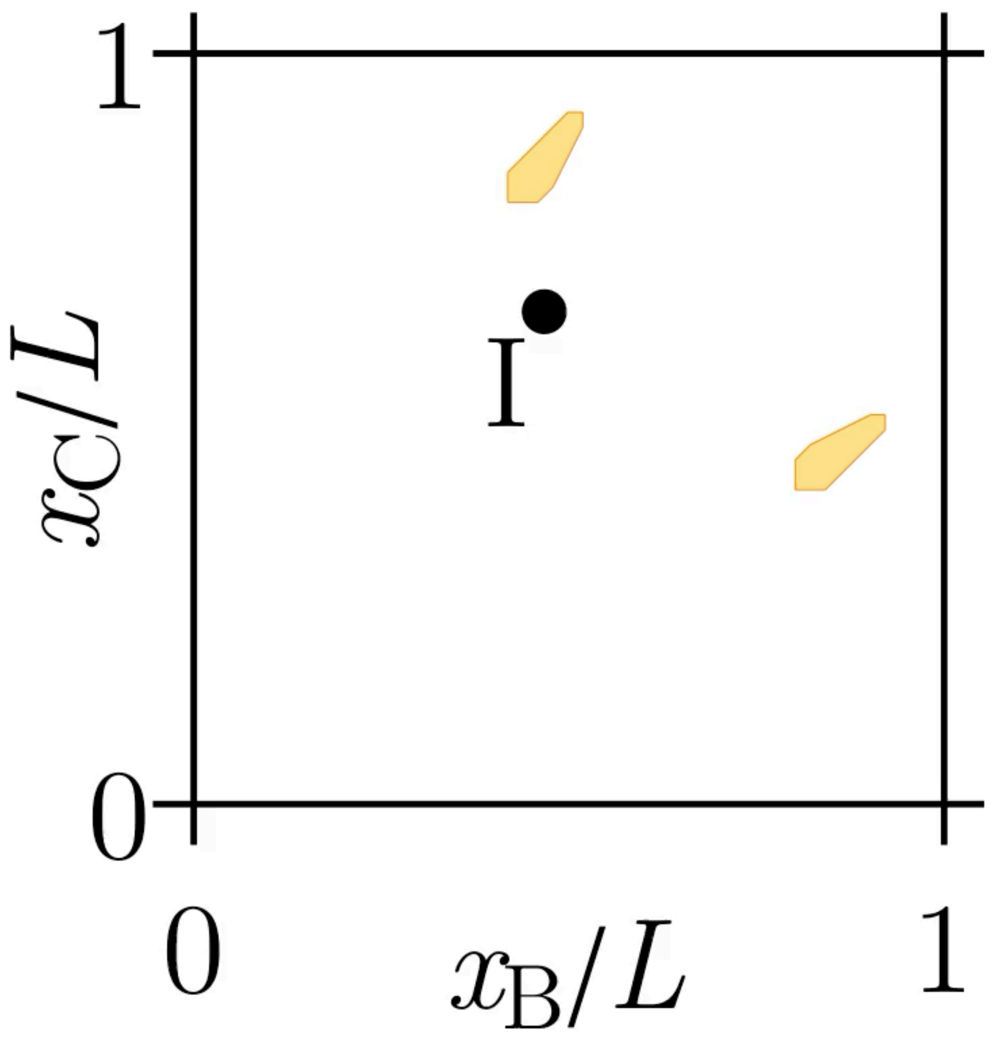
x≈0.06



non-trivial particle transport





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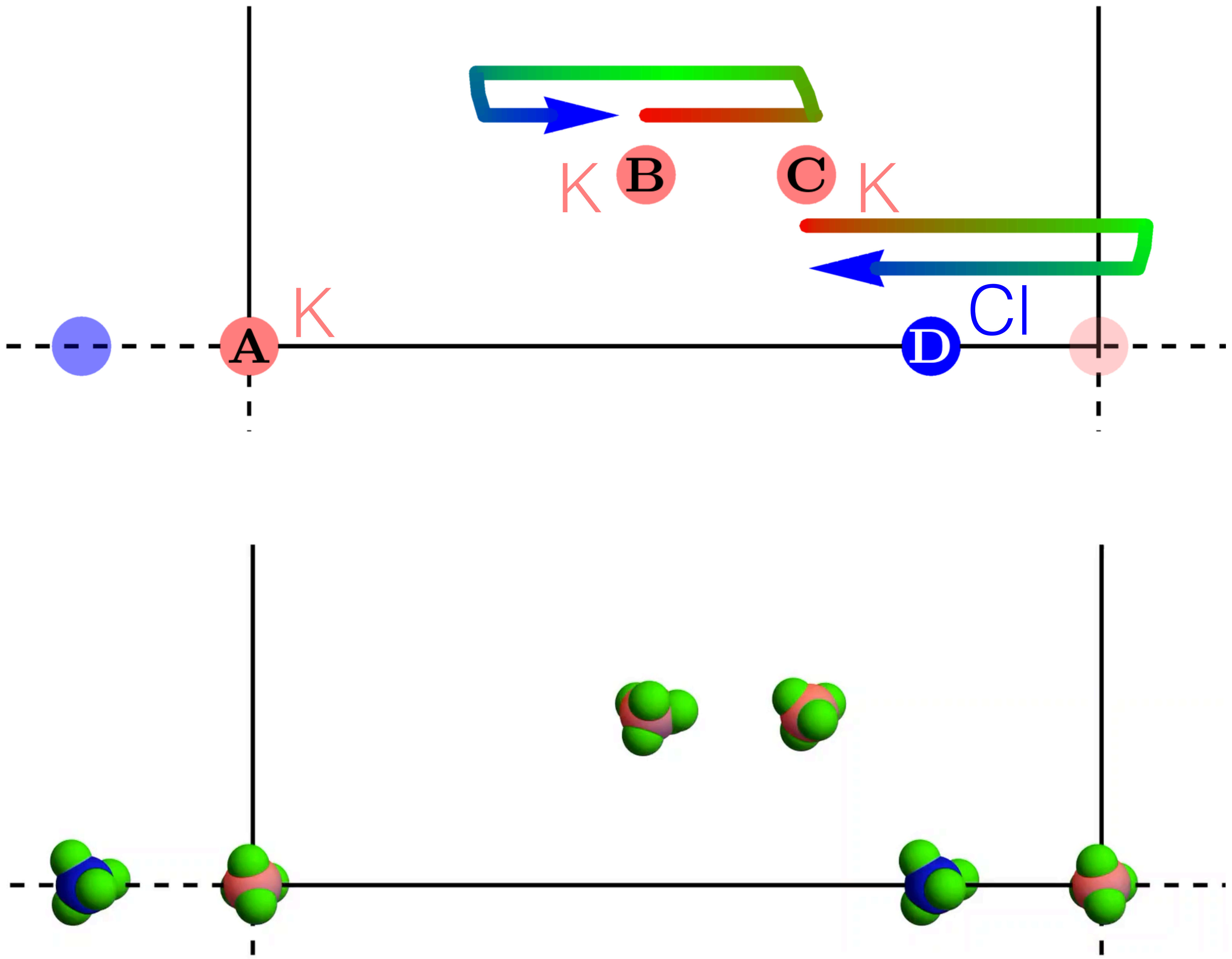

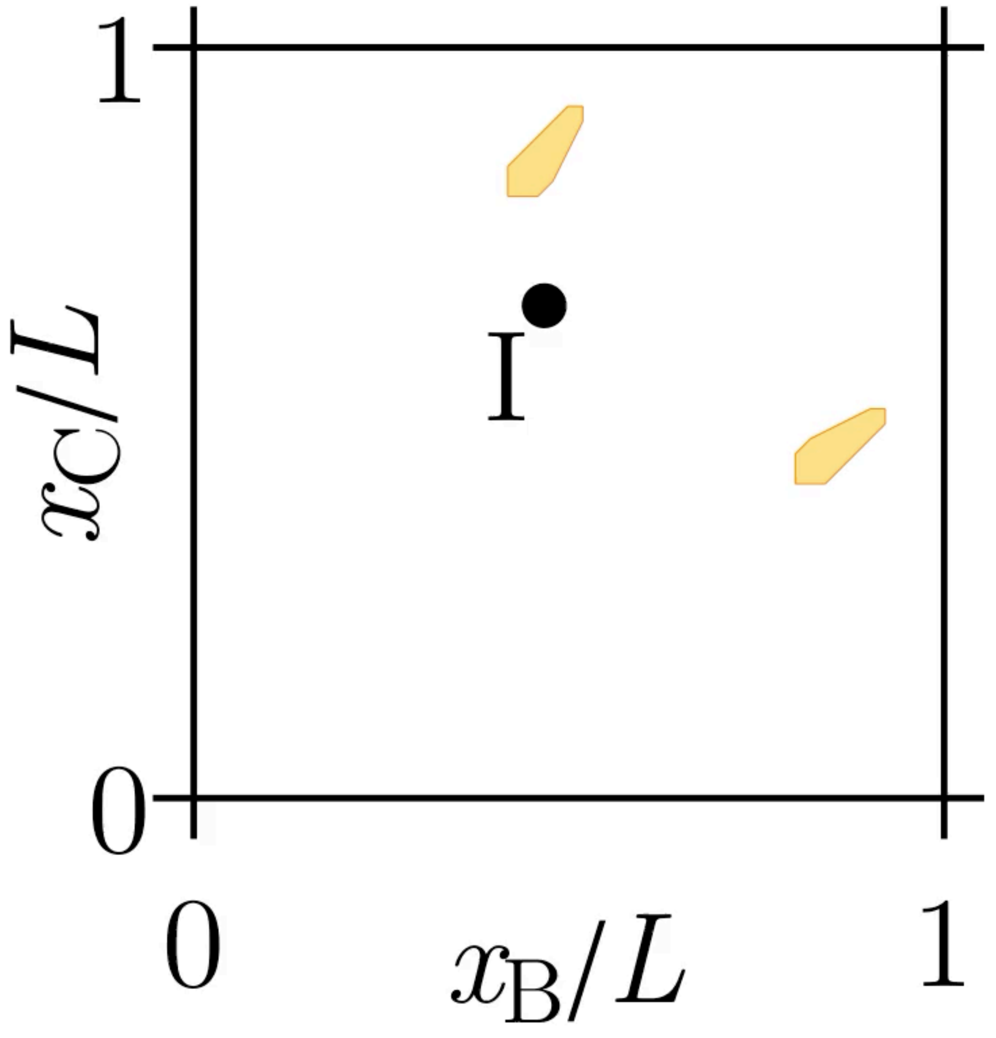

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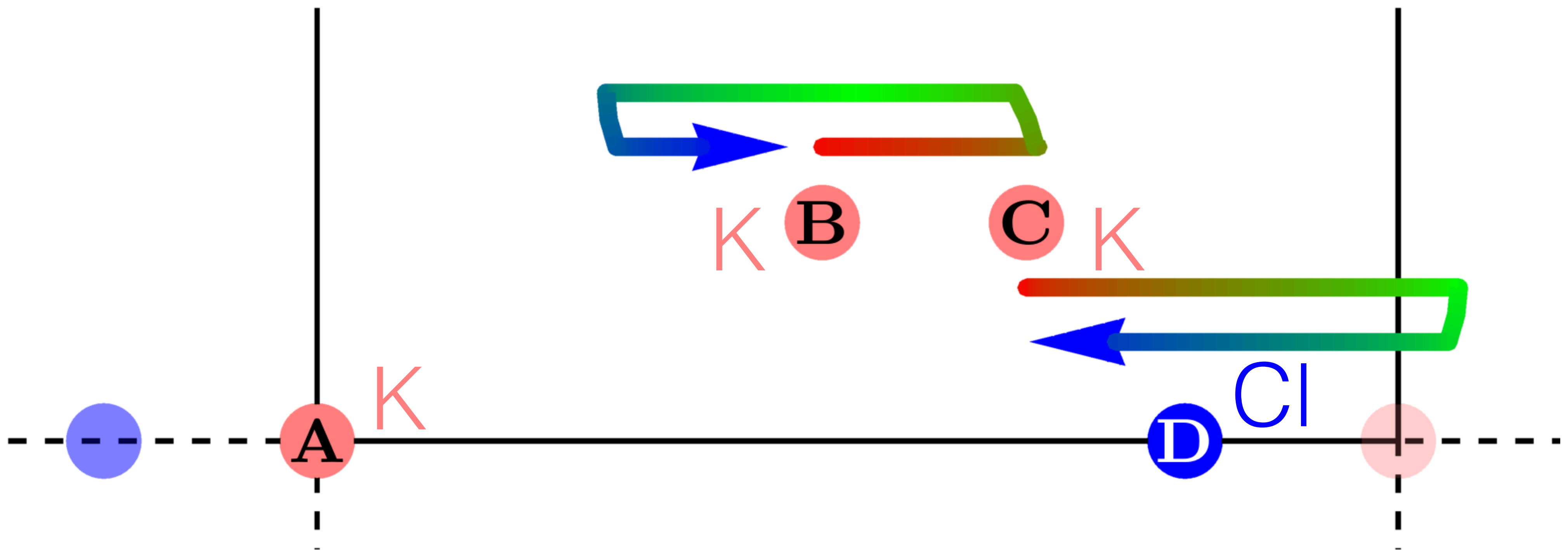
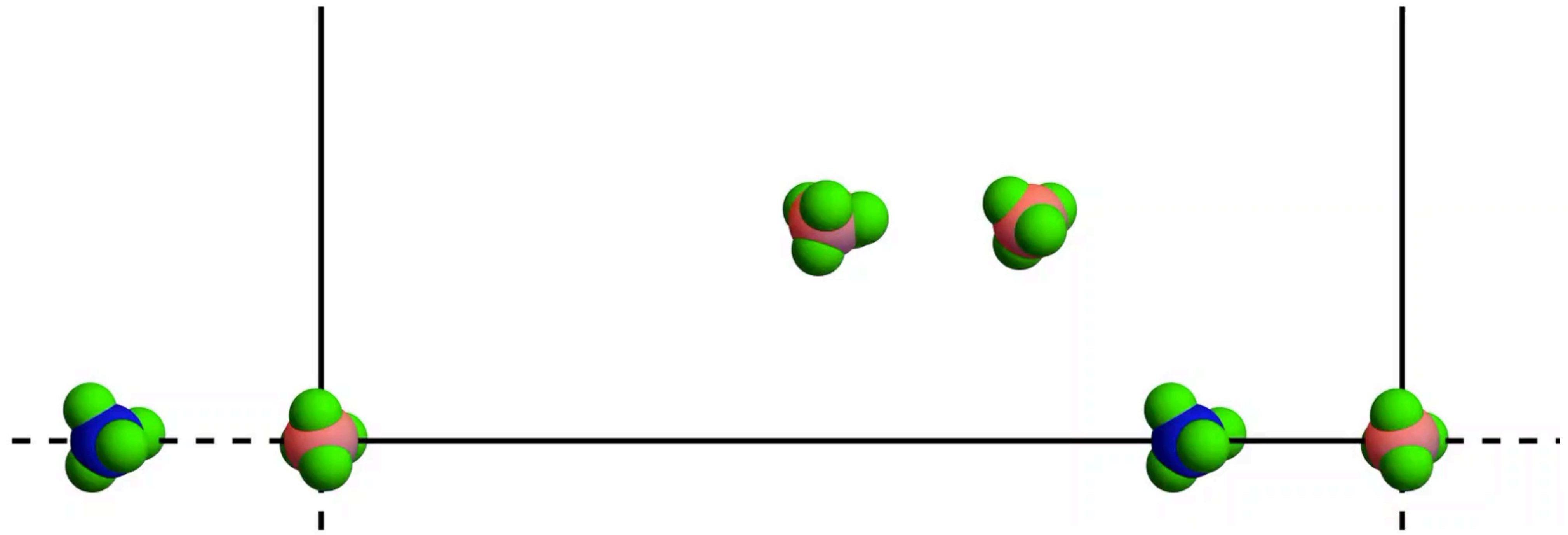
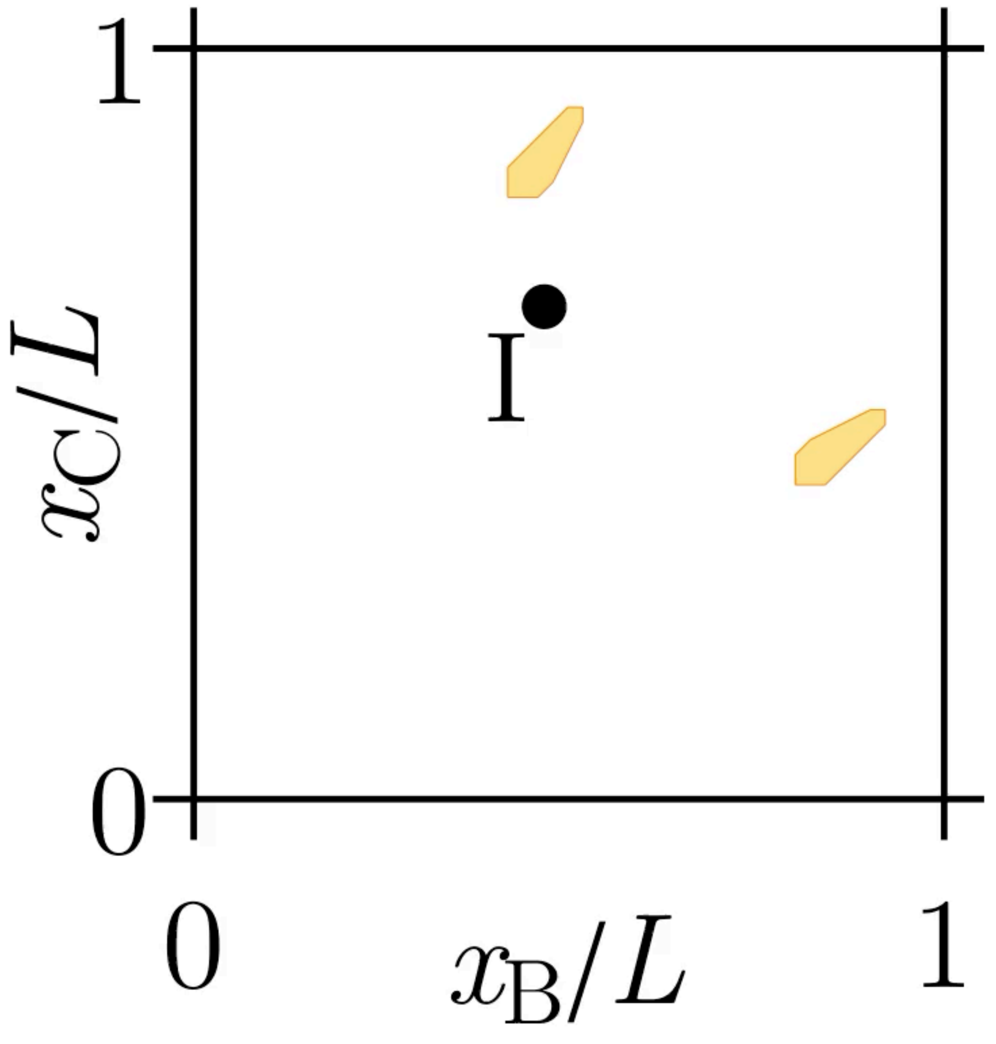
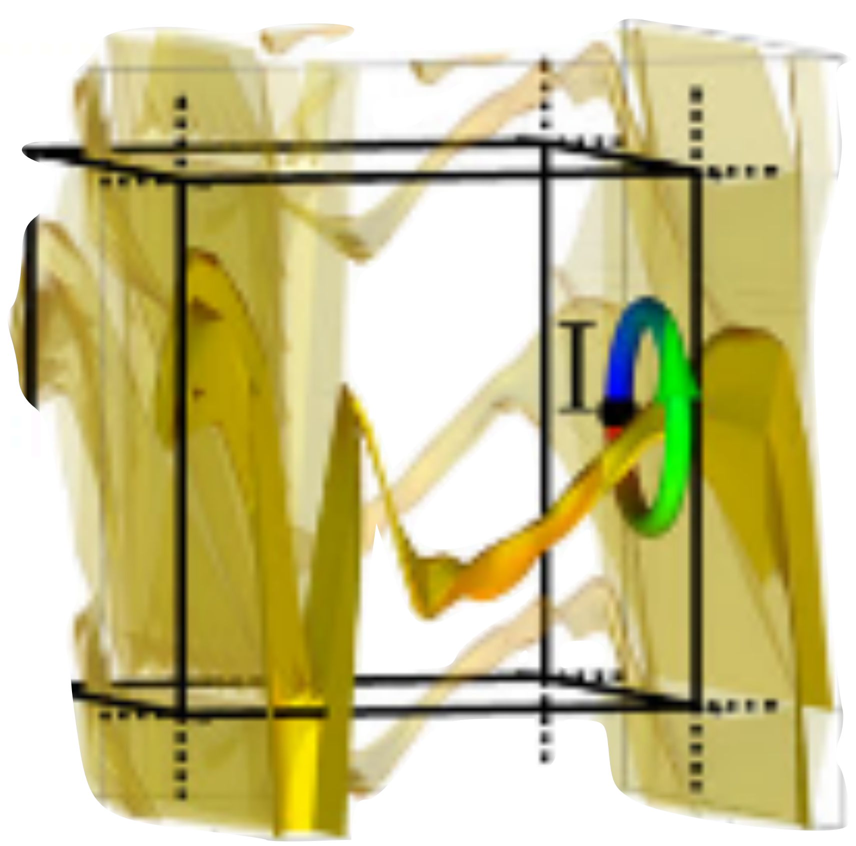
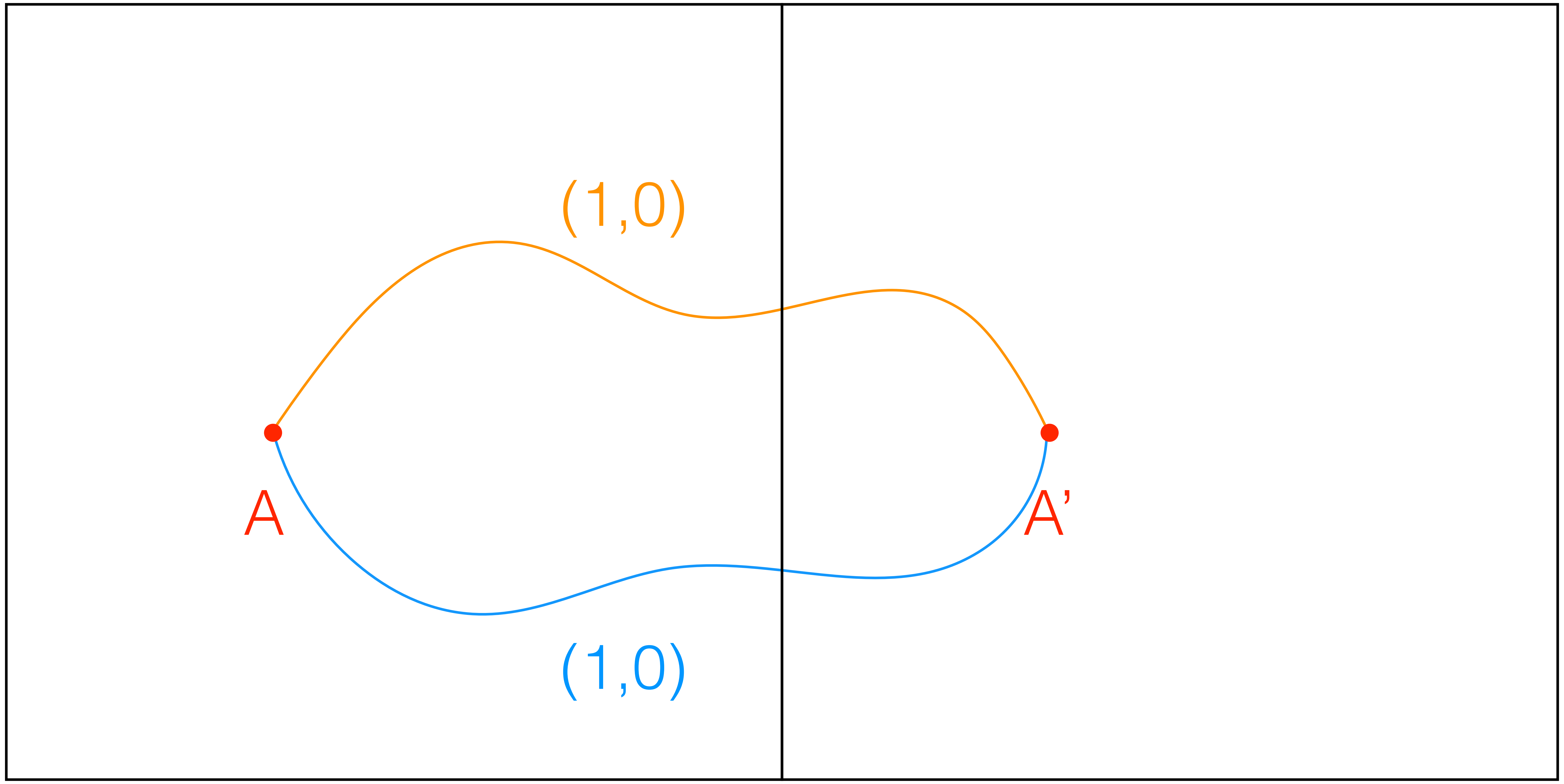








breach of strong adiabaticity



$$\mu = \mu^*$$

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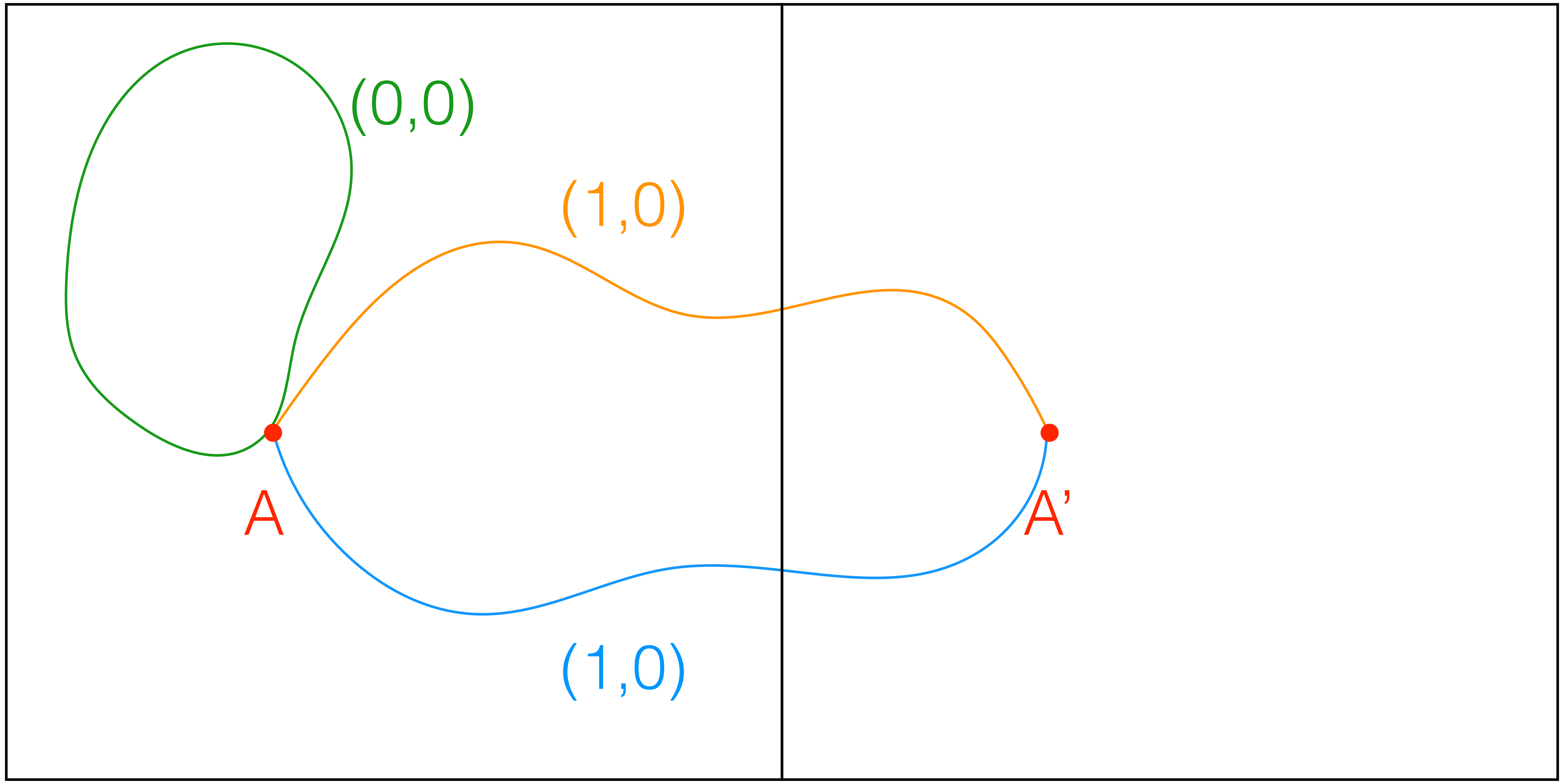

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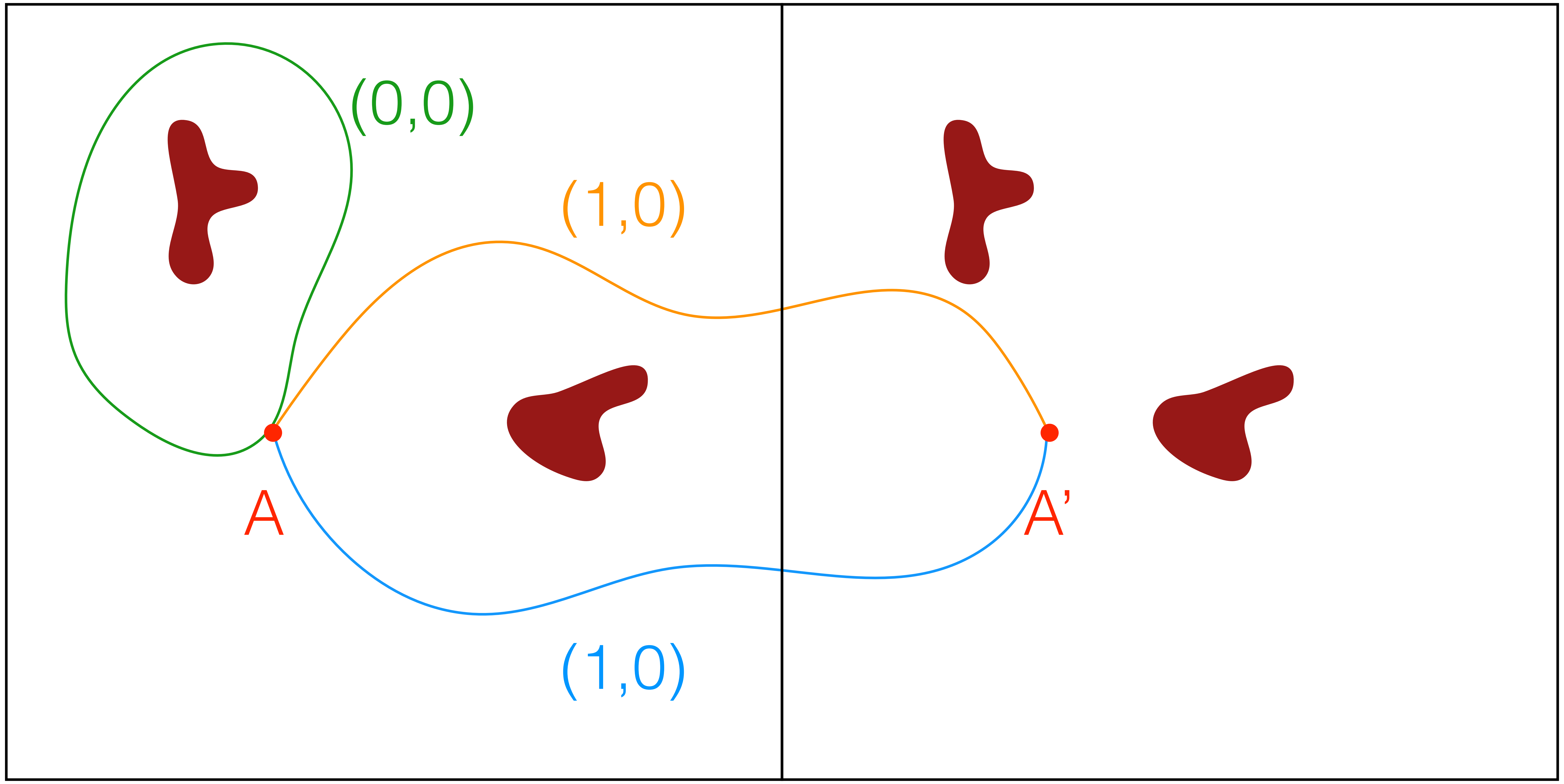

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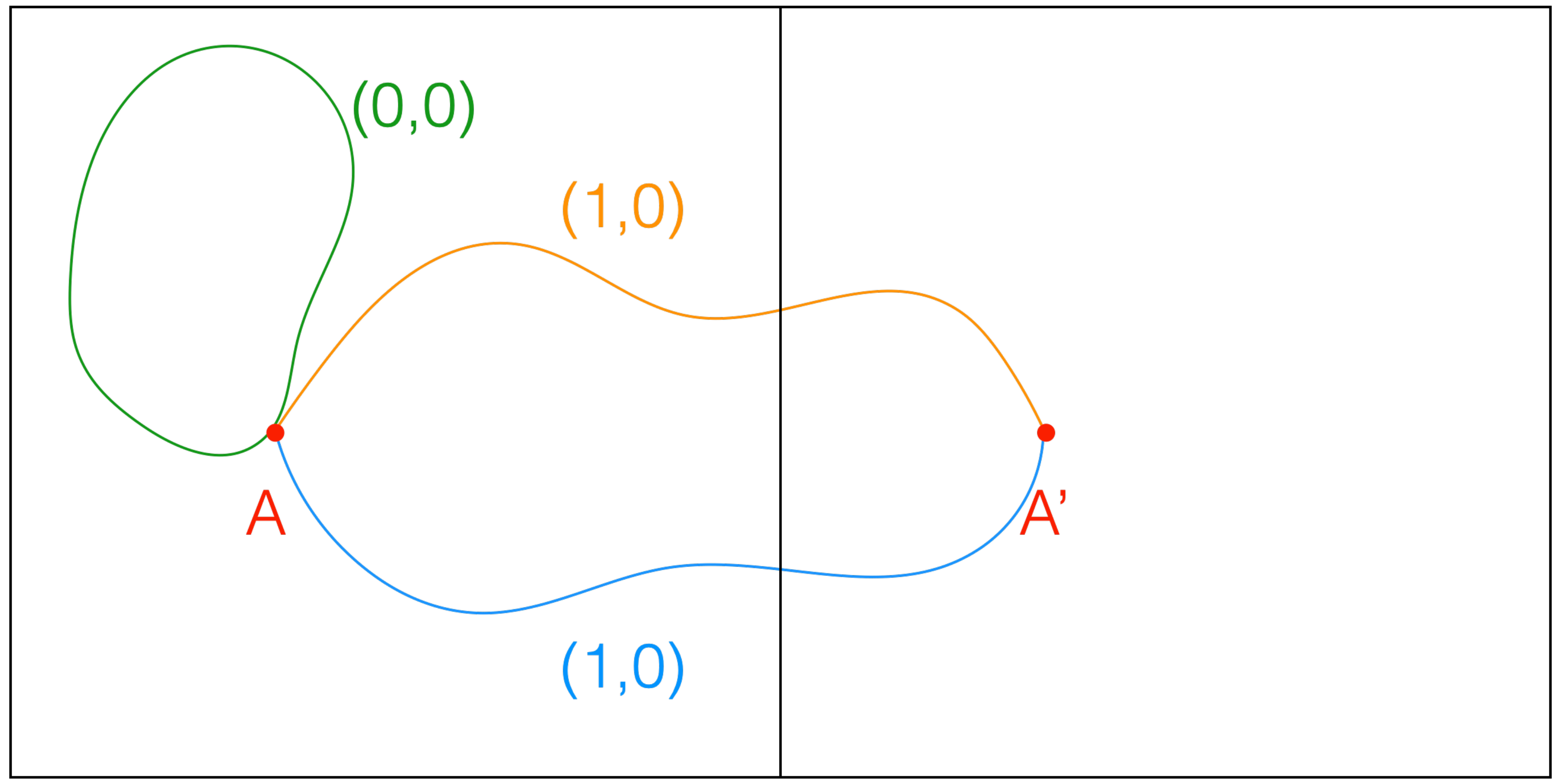
strongly adiabatic transport



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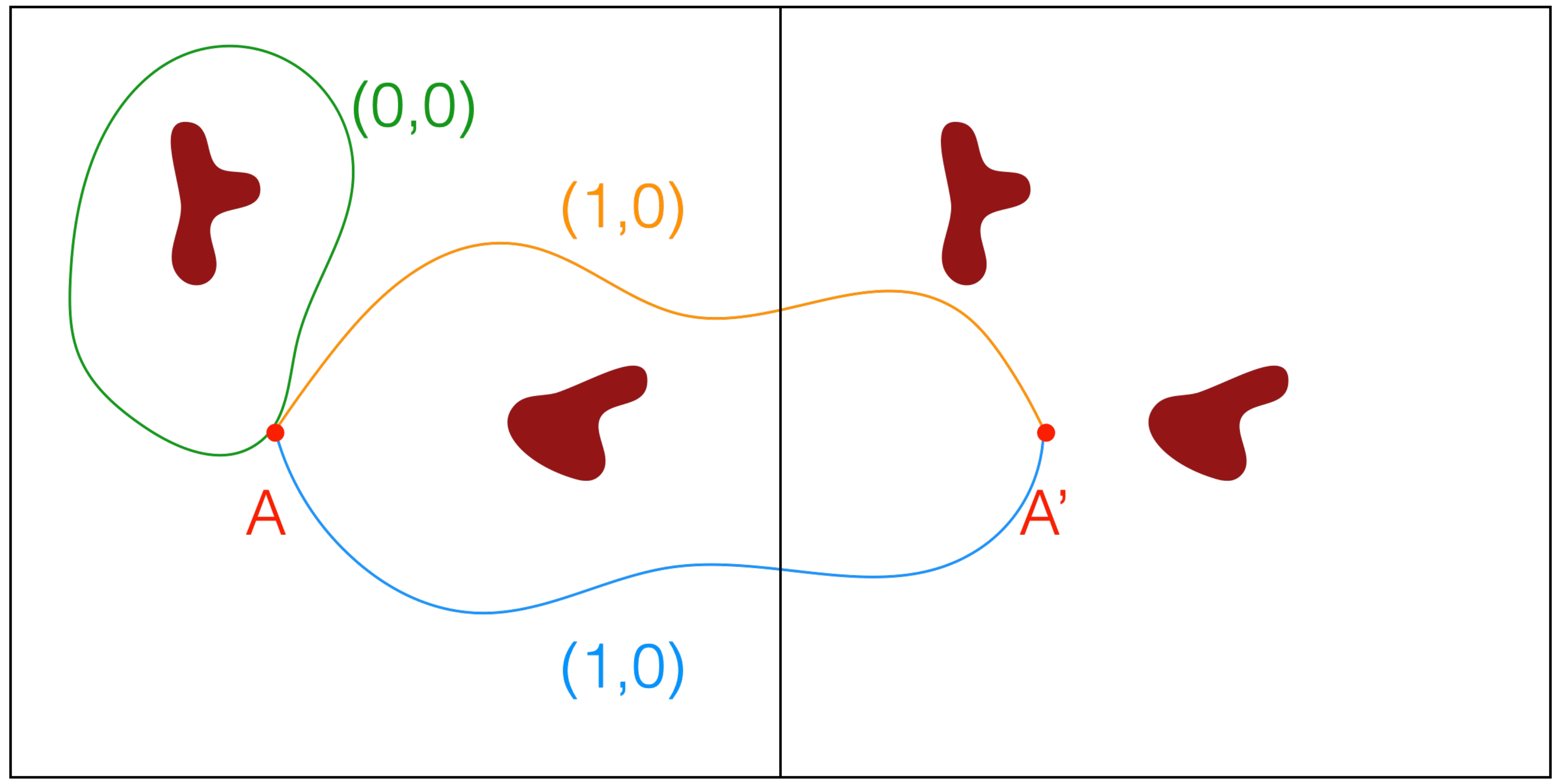
weakly adiabatic transport



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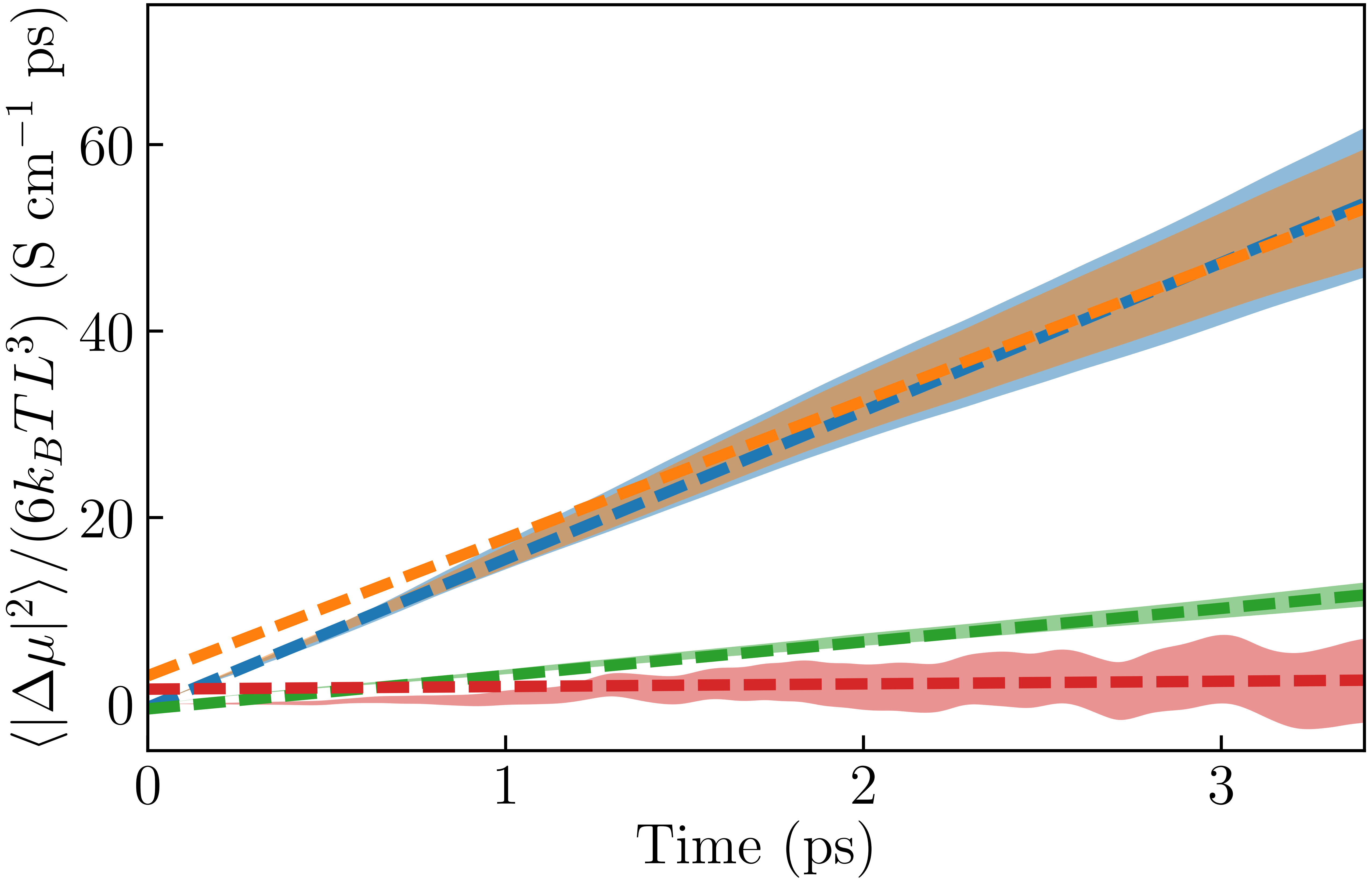
not trivial weakly adiabatic conductivity



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

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cross term

conclusions

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conclusions

- heat conductivity is a well defined, measurable property, iwhile the energy flux from which it can be computed from the Green-Kubo formula is not, because of a general *gauge invariance* principle stemming from energy additivity and conservation;

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- 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

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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