gauge invariance of heat and charge transport coefficients

in electronic insulators

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invited talk given at the 2021 (virtual) March Meeting of the American Physical Society, March 17, 2021


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Croatia
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Serbia
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Kosovo
Bulgaria
North Macedonia
Portugal
Spain
Albania
Tyrrhenian Sea
Greece
Gibraltar


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Italy
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Portugal
Albania
Spain
Greece
Tyrrhenian Sea
Gibraltar
Malta

serious answers to two silly questions

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- how come the heat conductivity is well defined, when the energy current that determines it, is not?

serious answers to two silly questions

- how come the heat conductivity is well defined, when the energy current that determines it, is not?
- how come the electric conductivity of non-ionic fluids vanishes, when the current fluctuations that determine it, do not?

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the 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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$$\lambda \propto \int_0^\infty \langle \boldsymbol{J}(t) \boldsymbol{J}(0) \rangle dt \qquad \text{Green-Kubo}$$

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Green-Kubo

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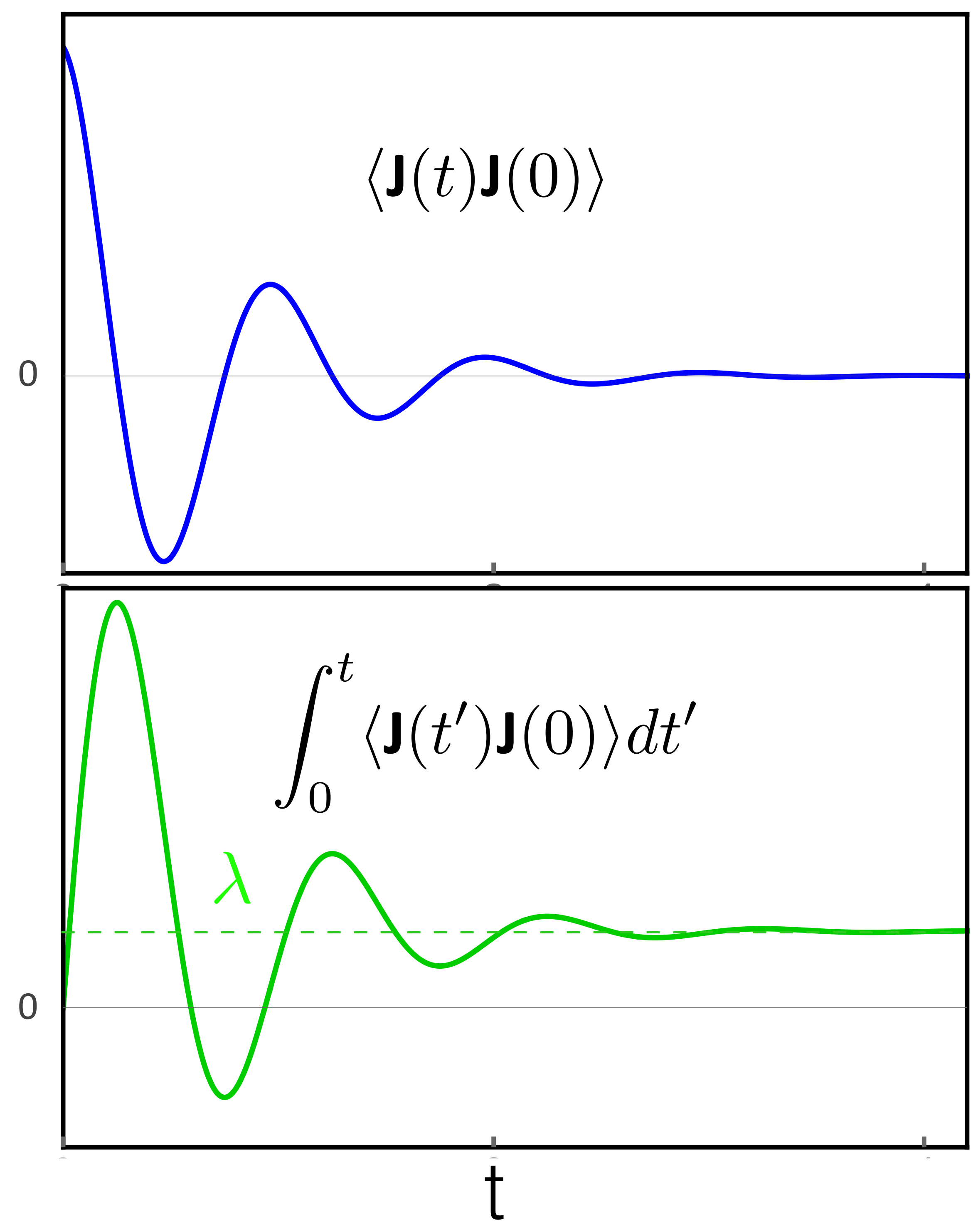

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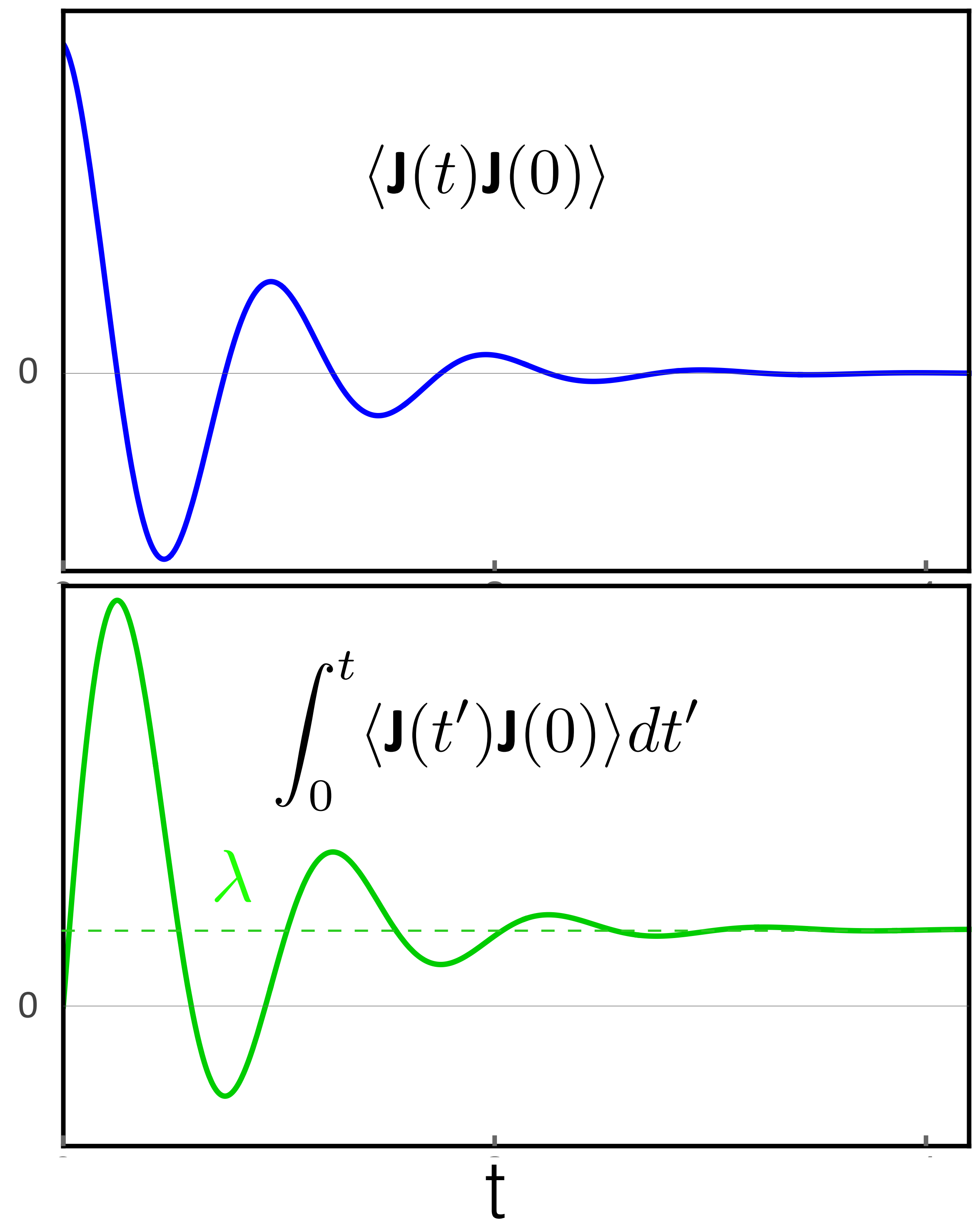
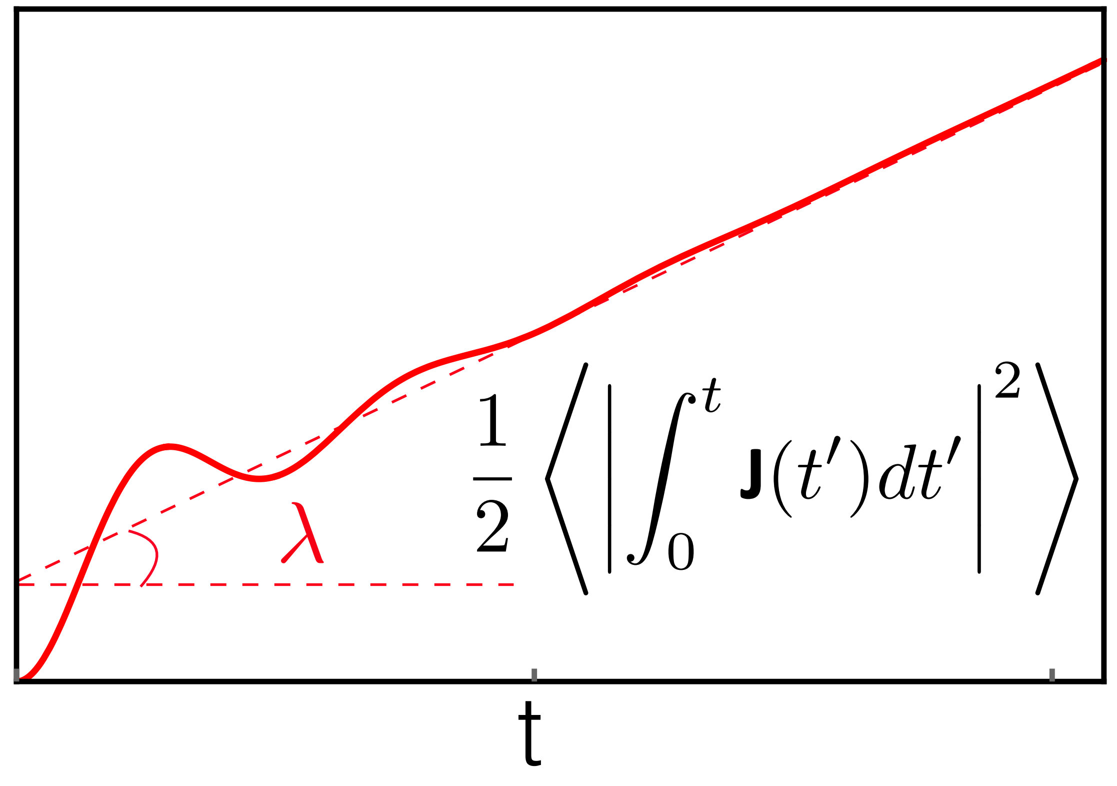
Einstein-Helfand

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





classical and quantum adiabatic heat transport

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

PRL **104**, 208501 (2010) PHYSICAL REVIEW LETTERS week ending 21 MAY 2010

Thermal Conductivity of Periclase (MgO) from First Principles

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Bijaya B. Karki‡

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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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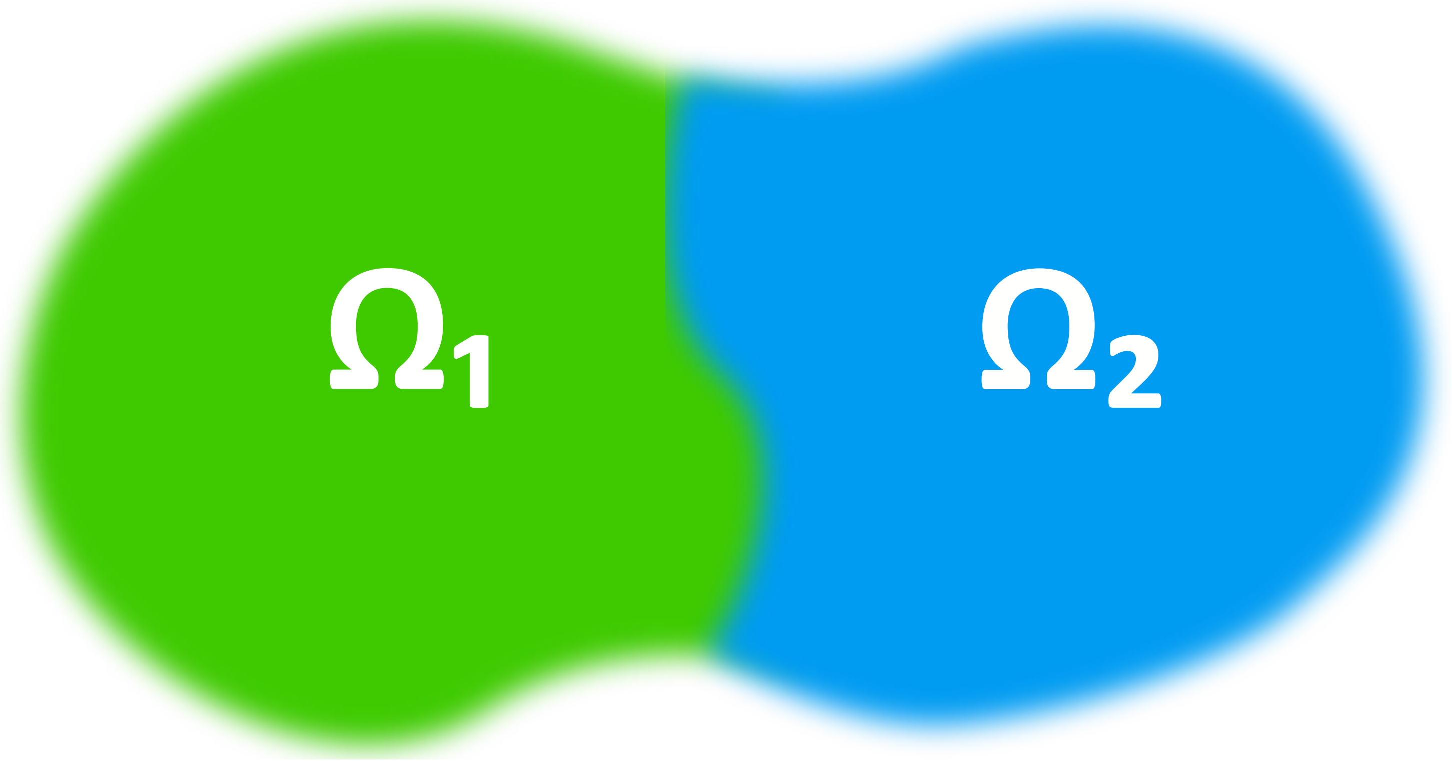
how come?

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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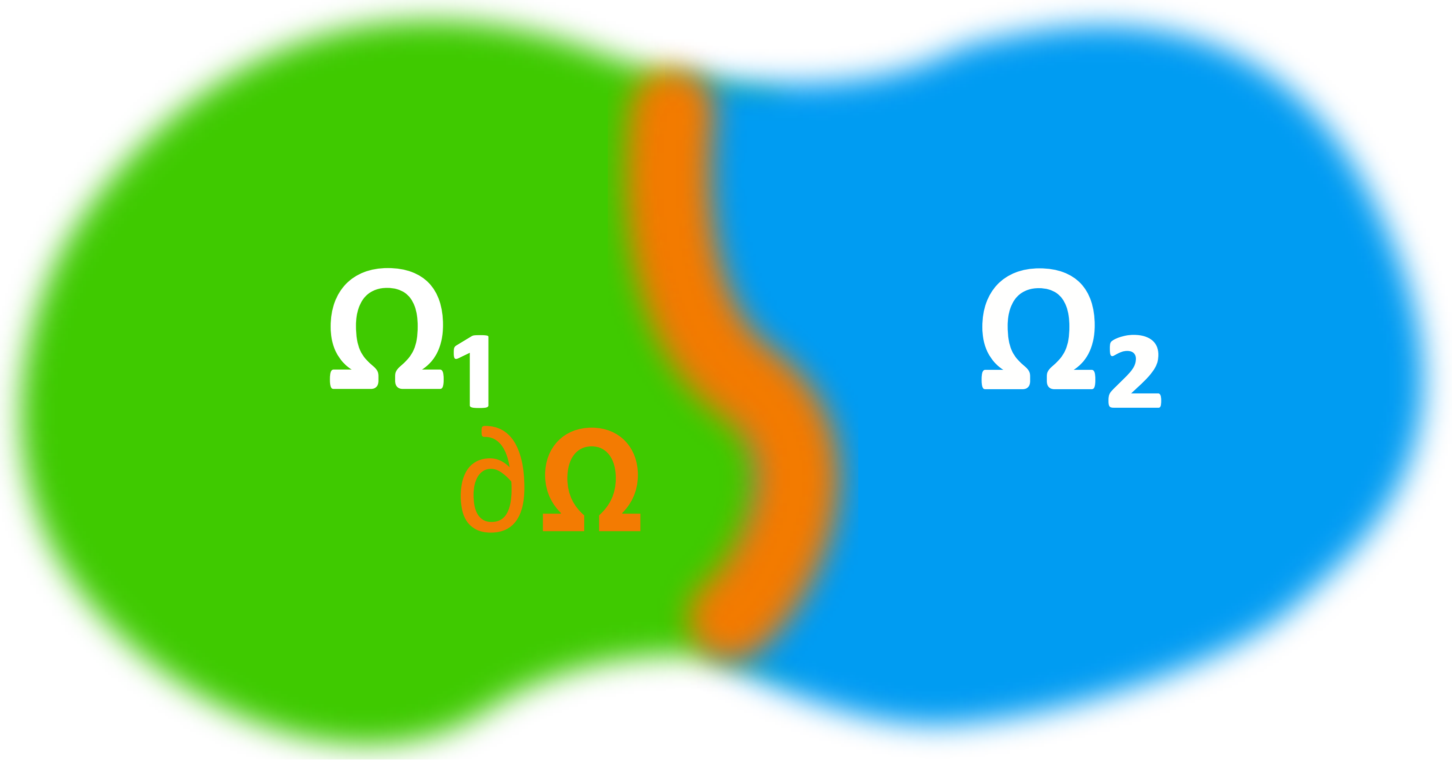

$$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial\Omega]$$

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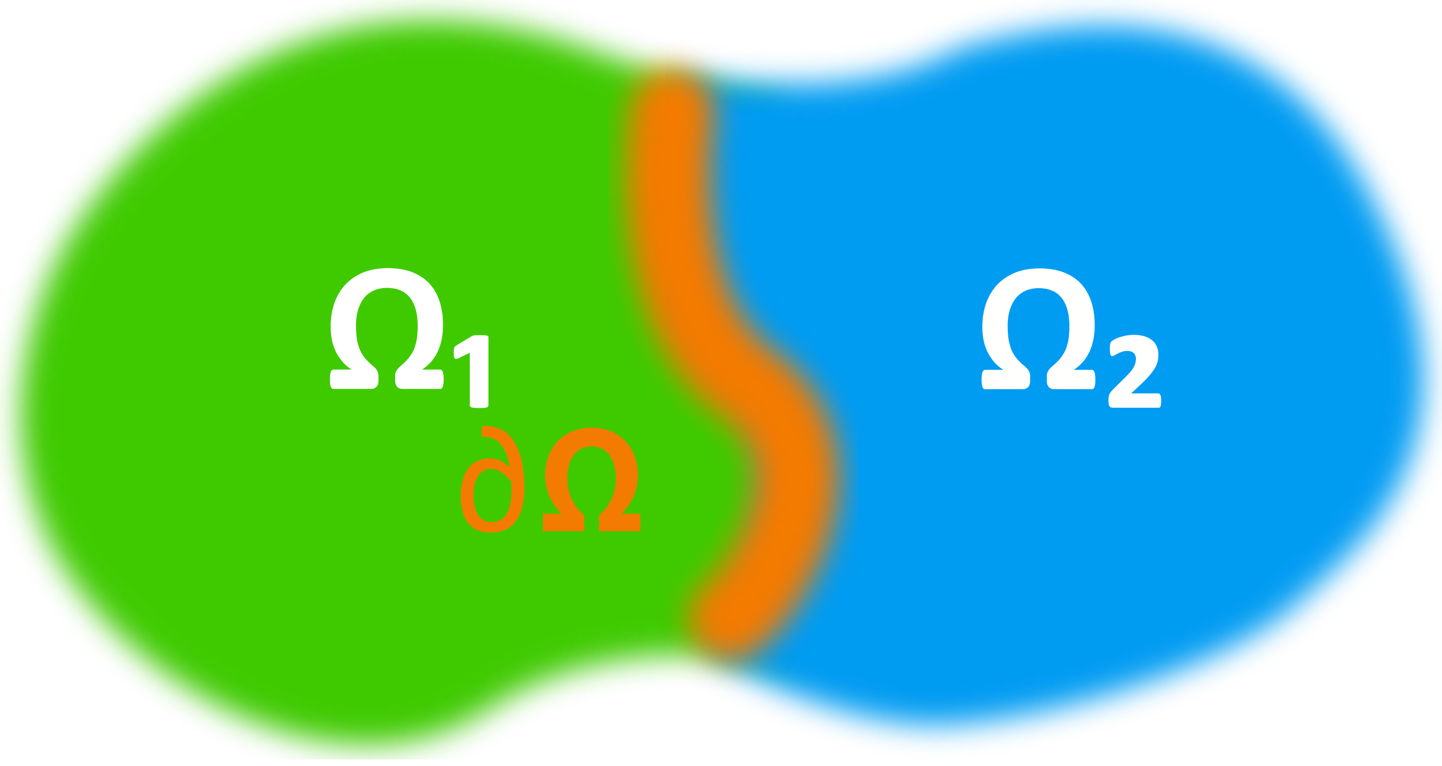

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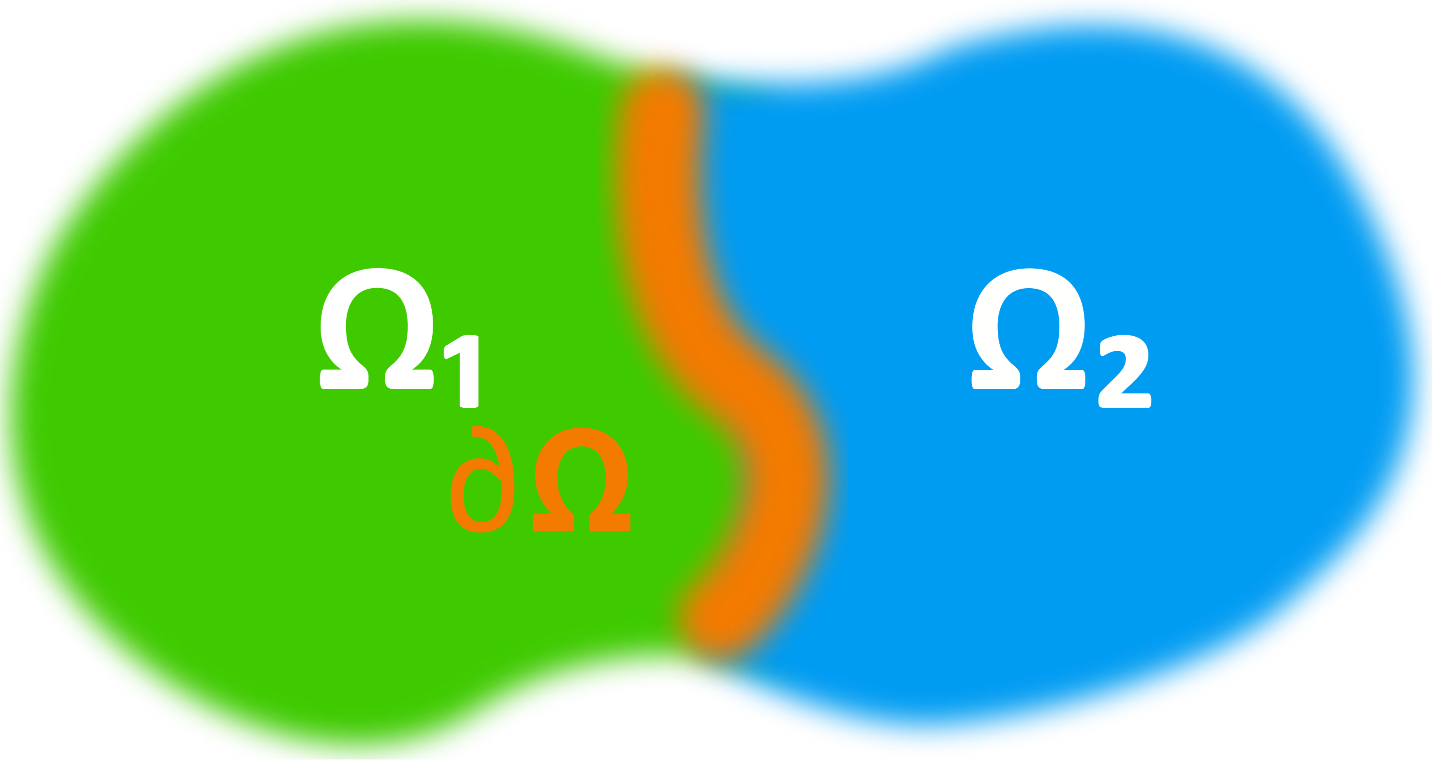

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thermodynamic invariance

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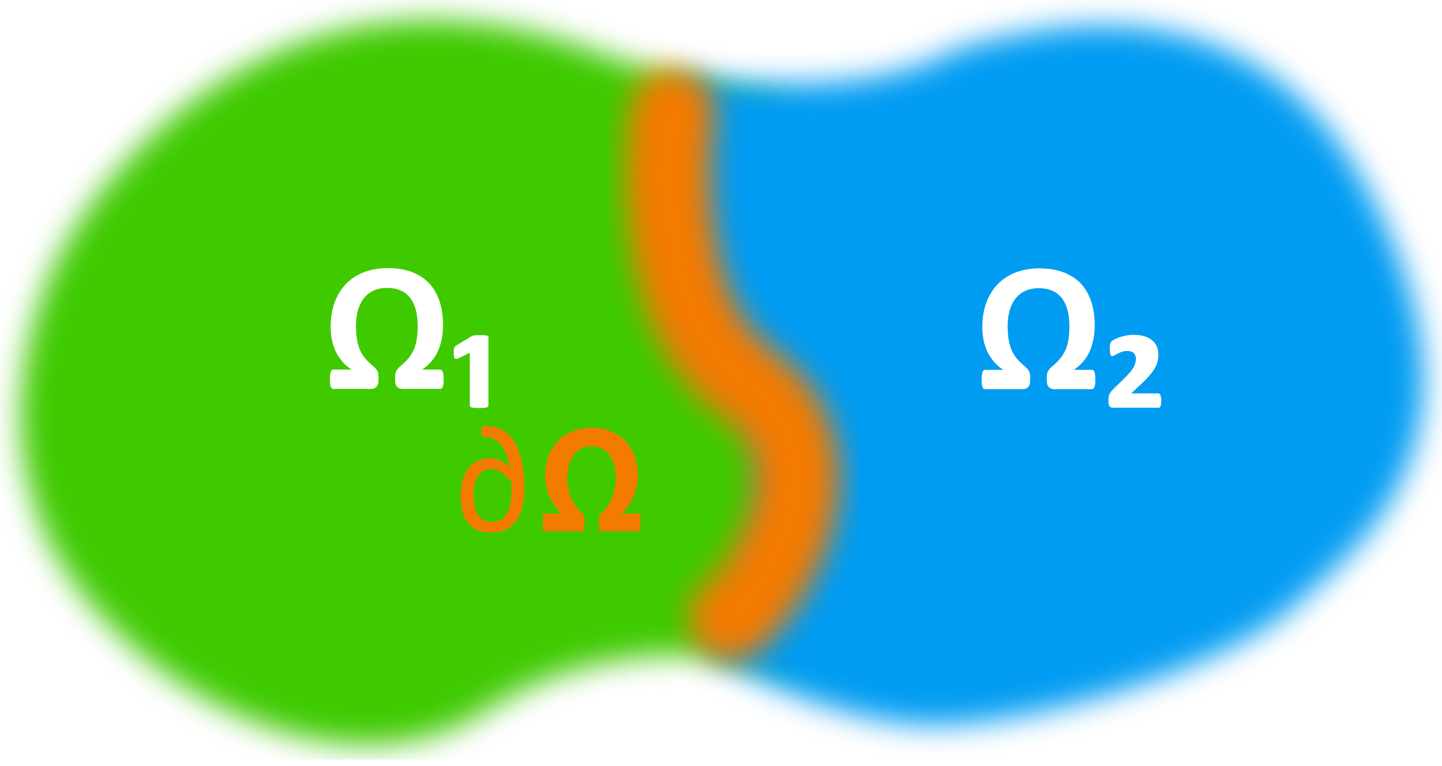
energy is extensive



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gauge invariance

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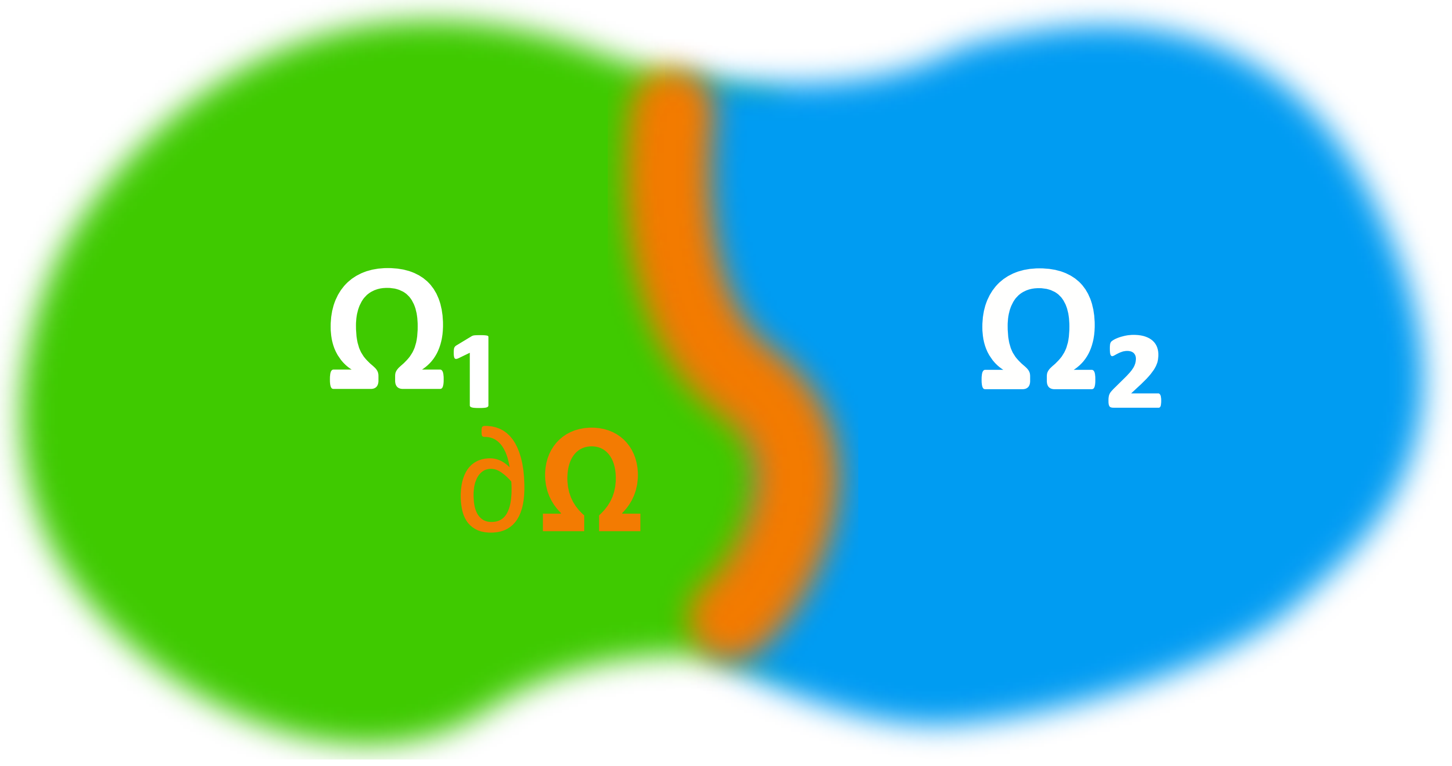

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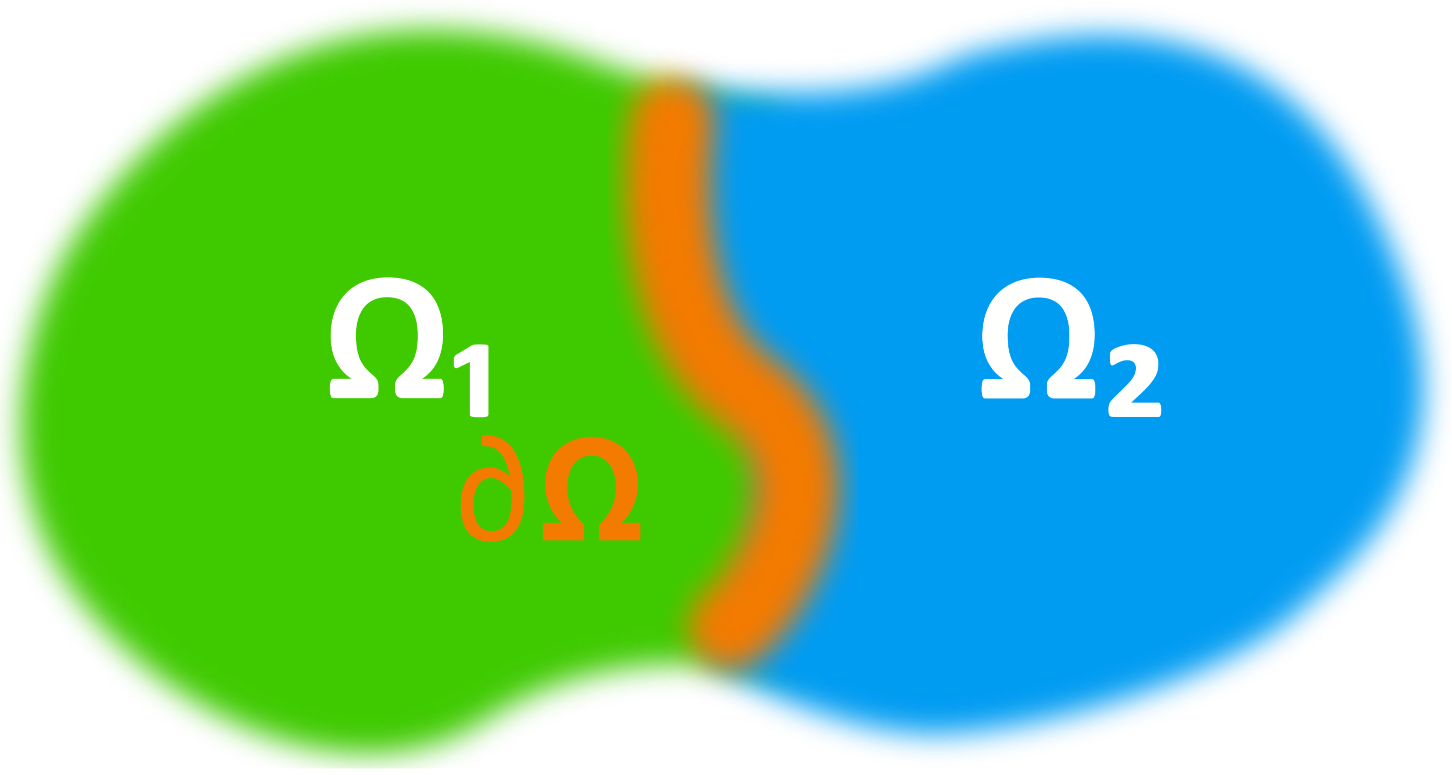
energy is conserved

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

gauge invariance of transport coefficients

energy is extensive



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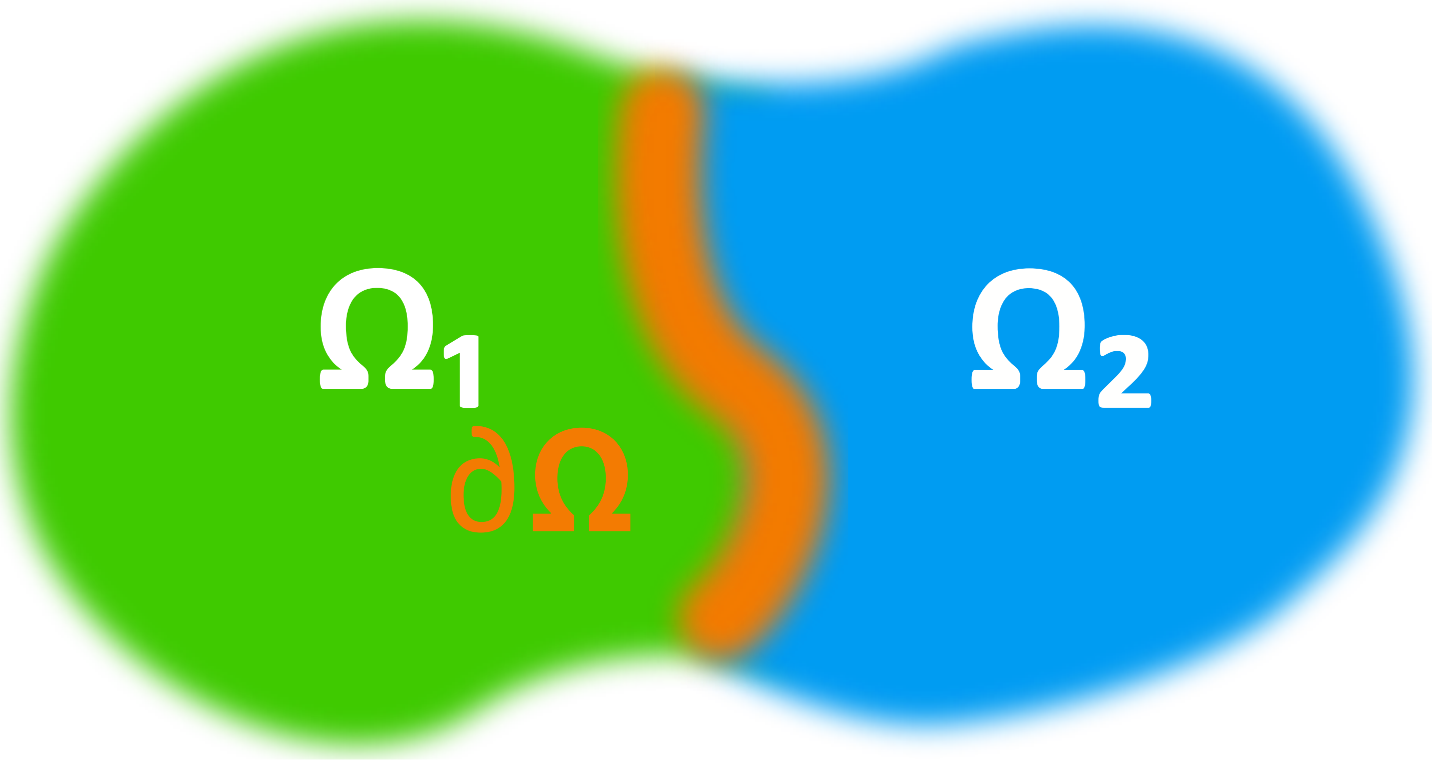

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$$\mathbf{J}(t) = \frac{1}{\Omega}\int \mathbf{j}(\mathbf{r},t)d\mathbf{r}$$

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

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$$\lambda \sim \frac{1}{2t}\mathrm{var}\left[\mathbf{D}(t)\right] \qquad \mathbf{D}(t) = \int_0^t \mathbf{J}(t')dt'$$

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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
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]*

gauge invariance of heat transport

PRL **104,** 208501 (2010) PHYSICAL REVIEW LETTERS week ending 21 MAY 2010

Thermal Conductivity of Periclase (MgO) from First Principles

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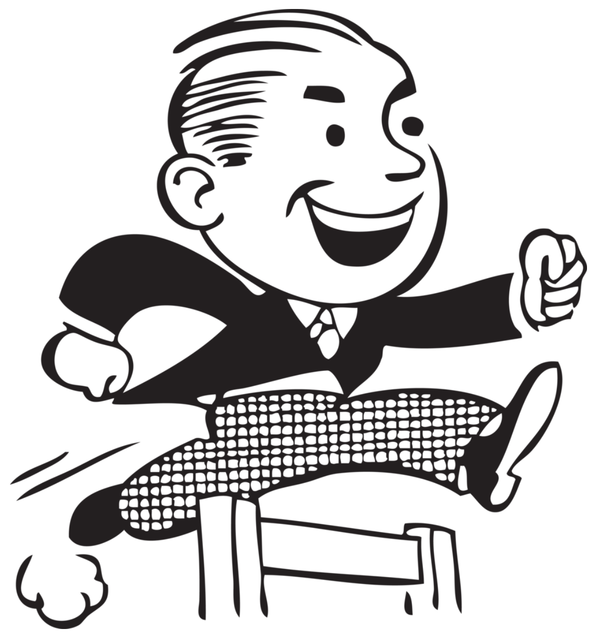
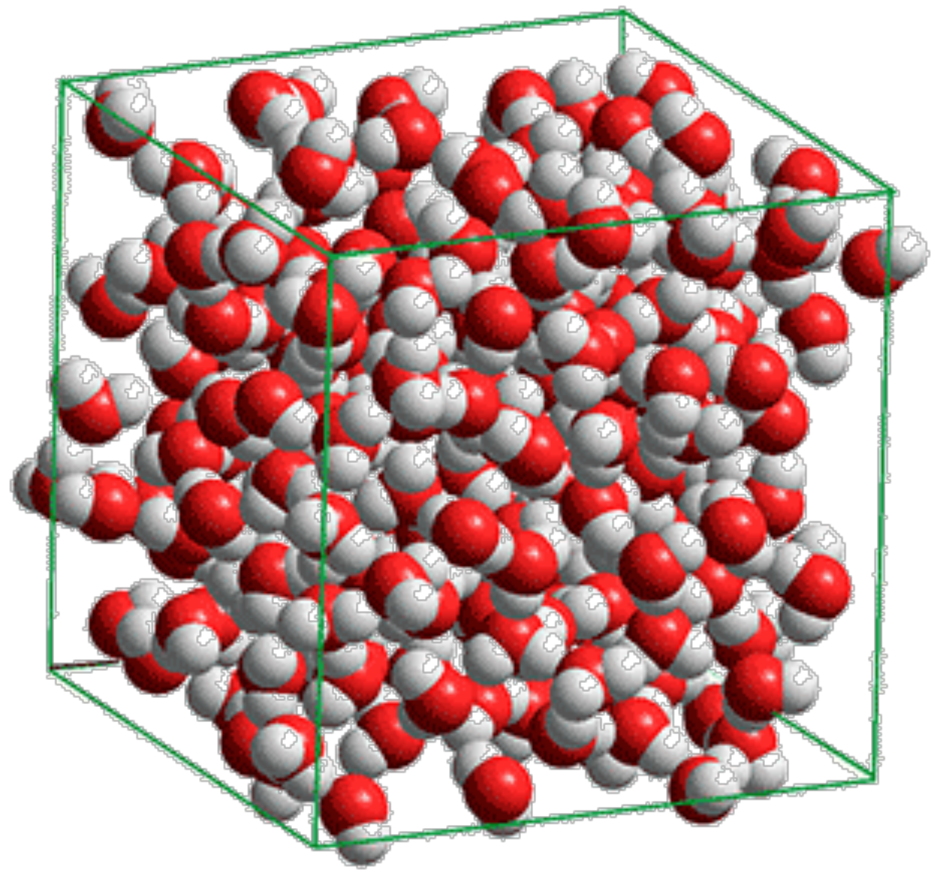
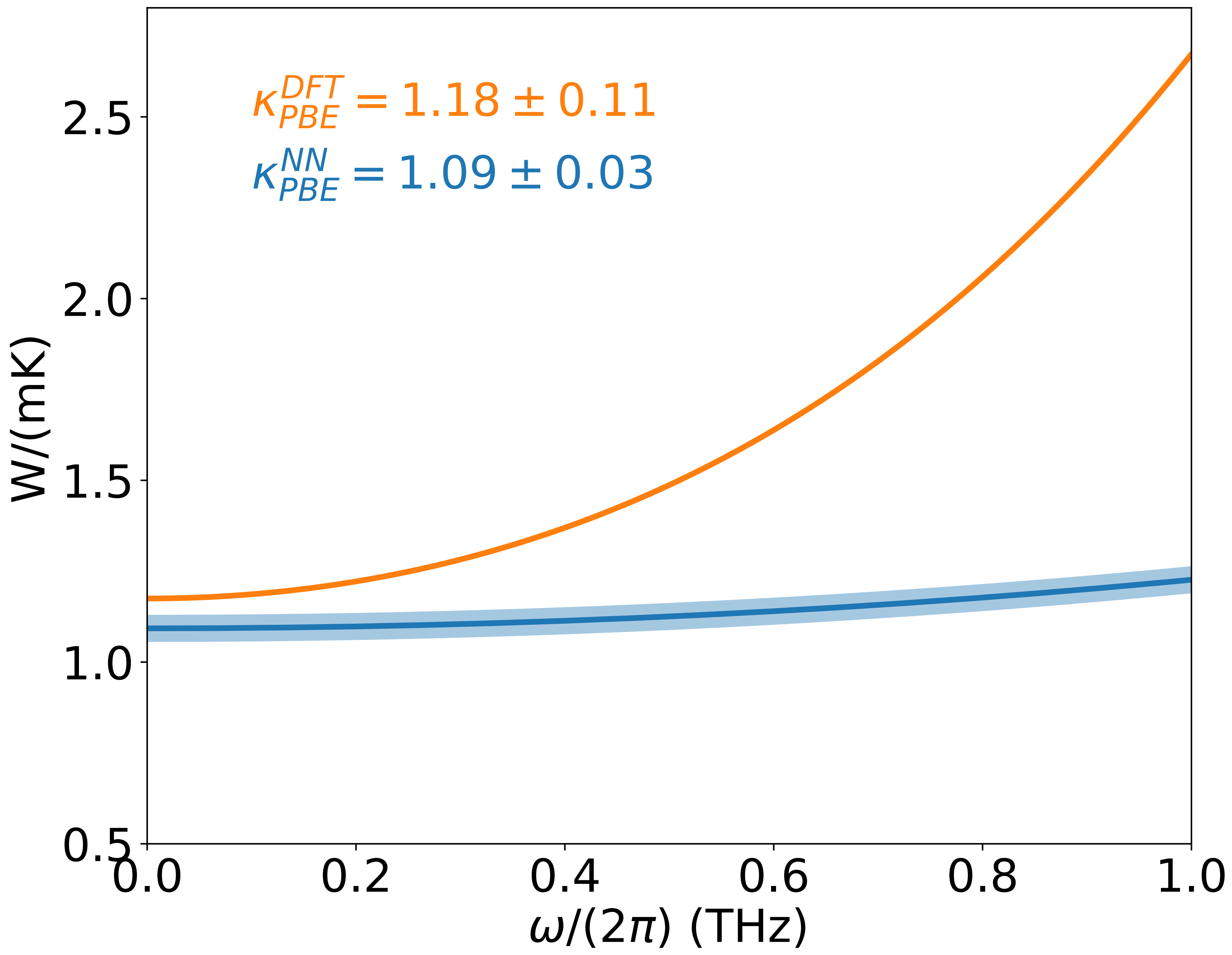
sensitive to the form of the potential. The widely used Green-Kubo relation [14] does not serve our purposes, because in first-principles calculations it is impossible to uniquely decompose the total energy into individual contributions from each atom.

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.



thermal conductivity of liquid water from DFT





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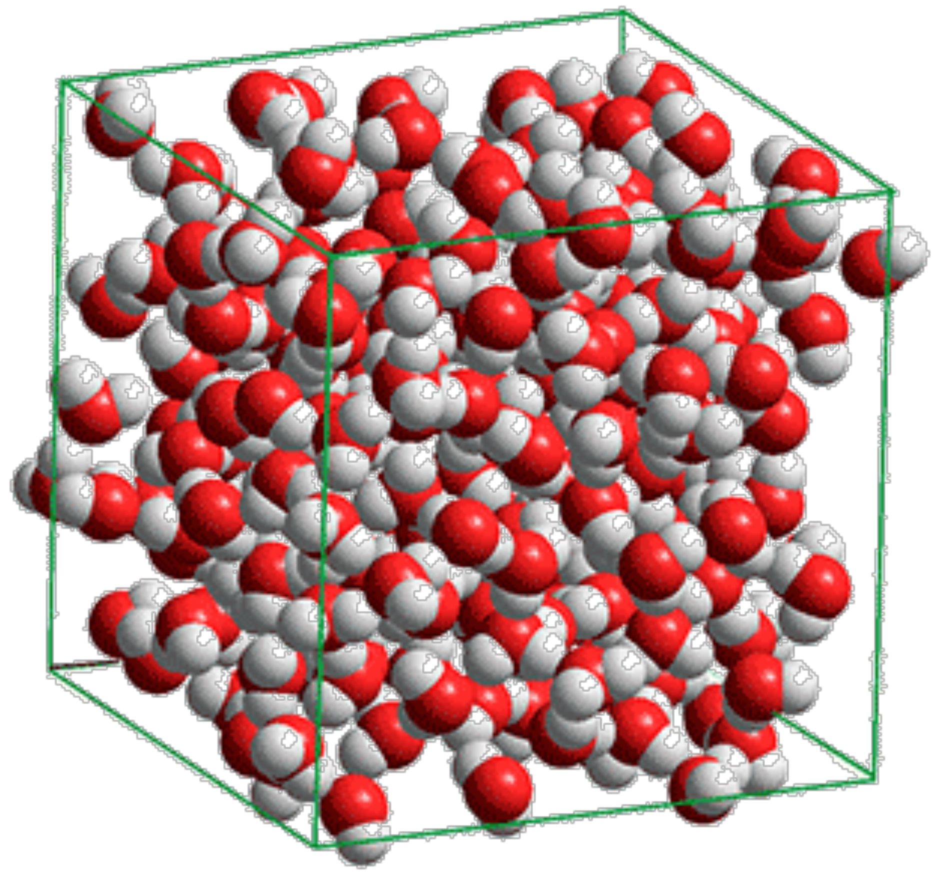

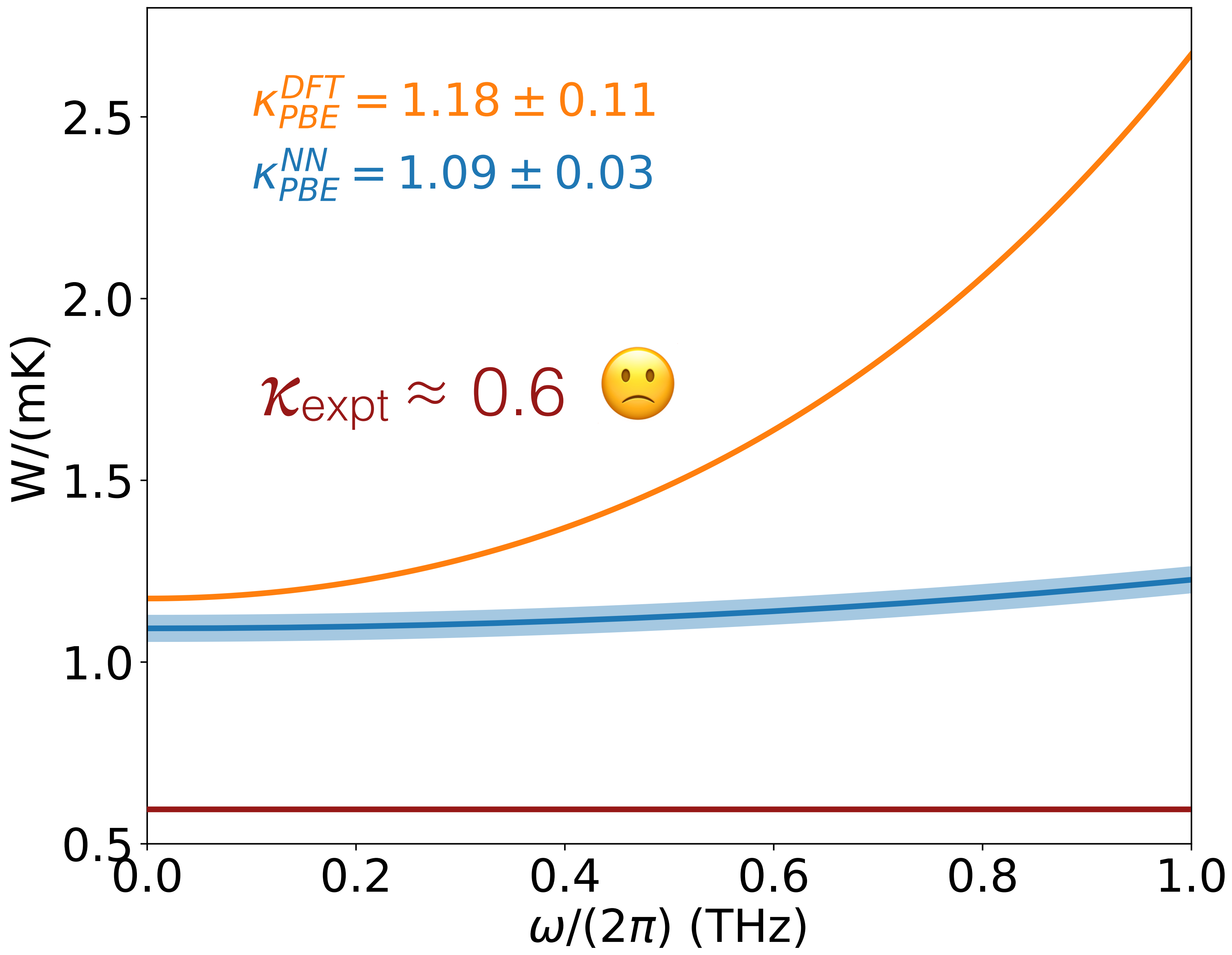

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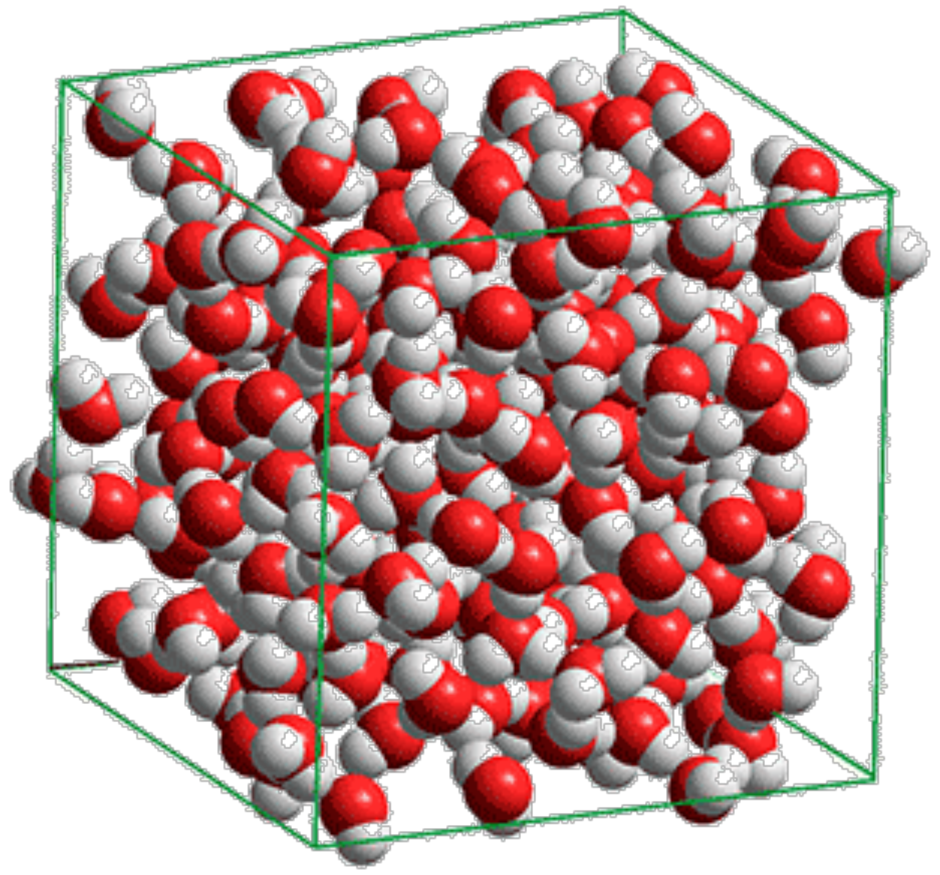

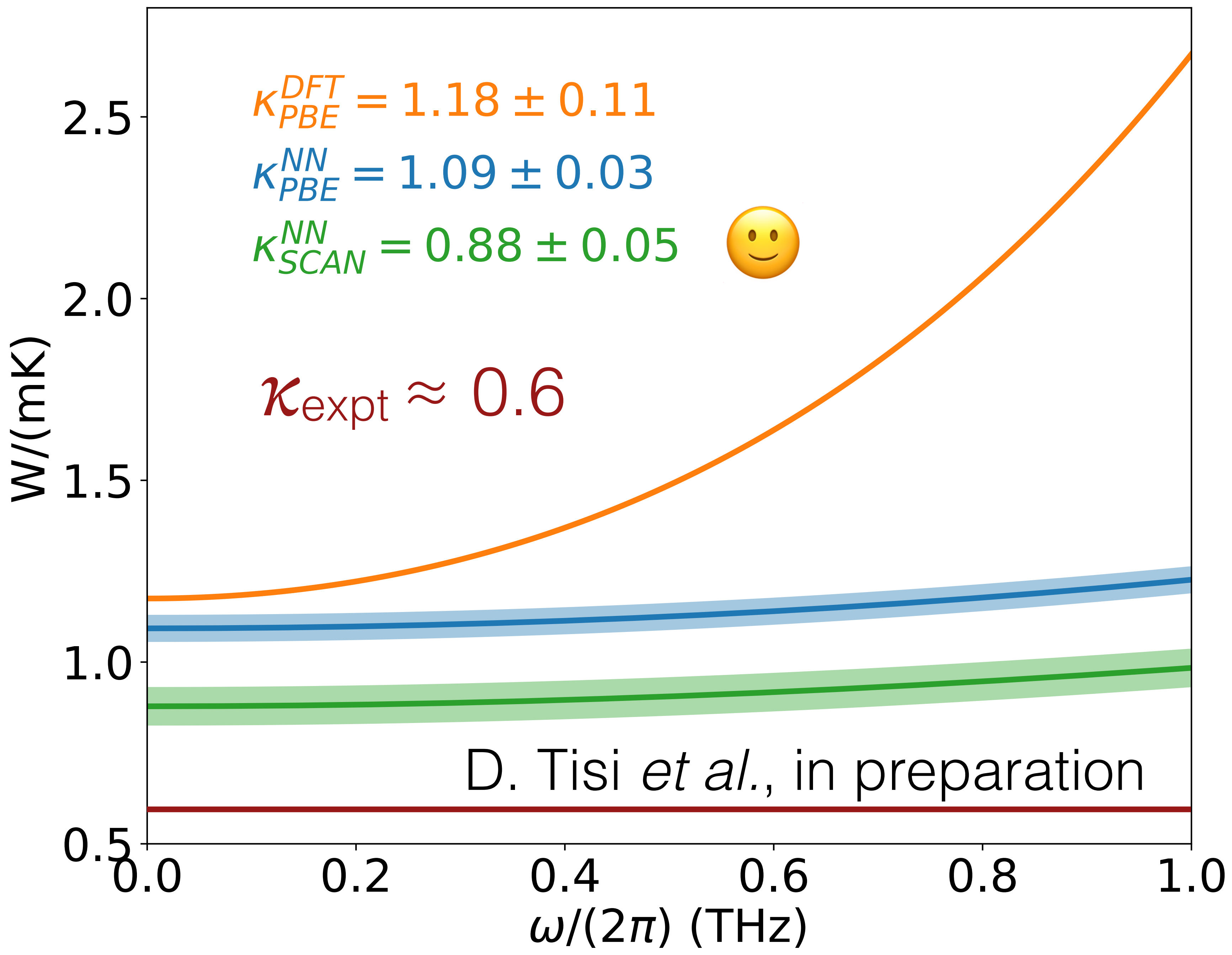

Monday, March 15, 2021
9:36AM - 9:48AM
Live

A20.00007: Heat transport in water from Deep Neural Network potentials
Davide Tisi, Linfeng Zhang, Roberto Car, Stefano Baroni

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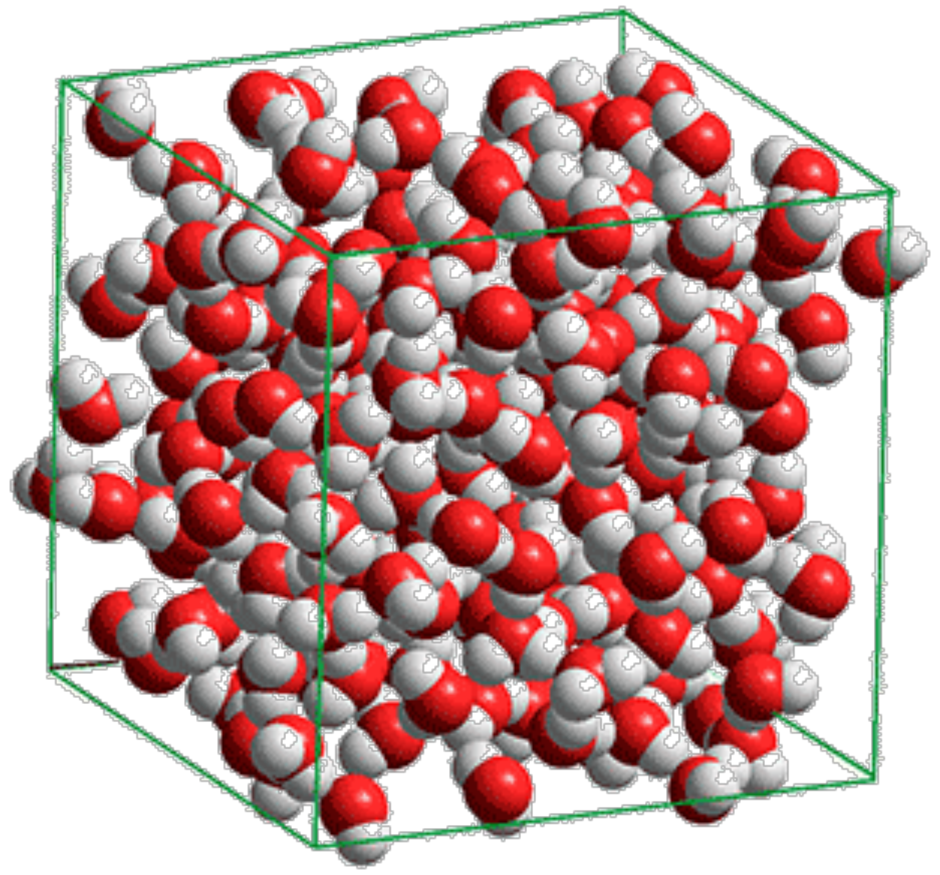

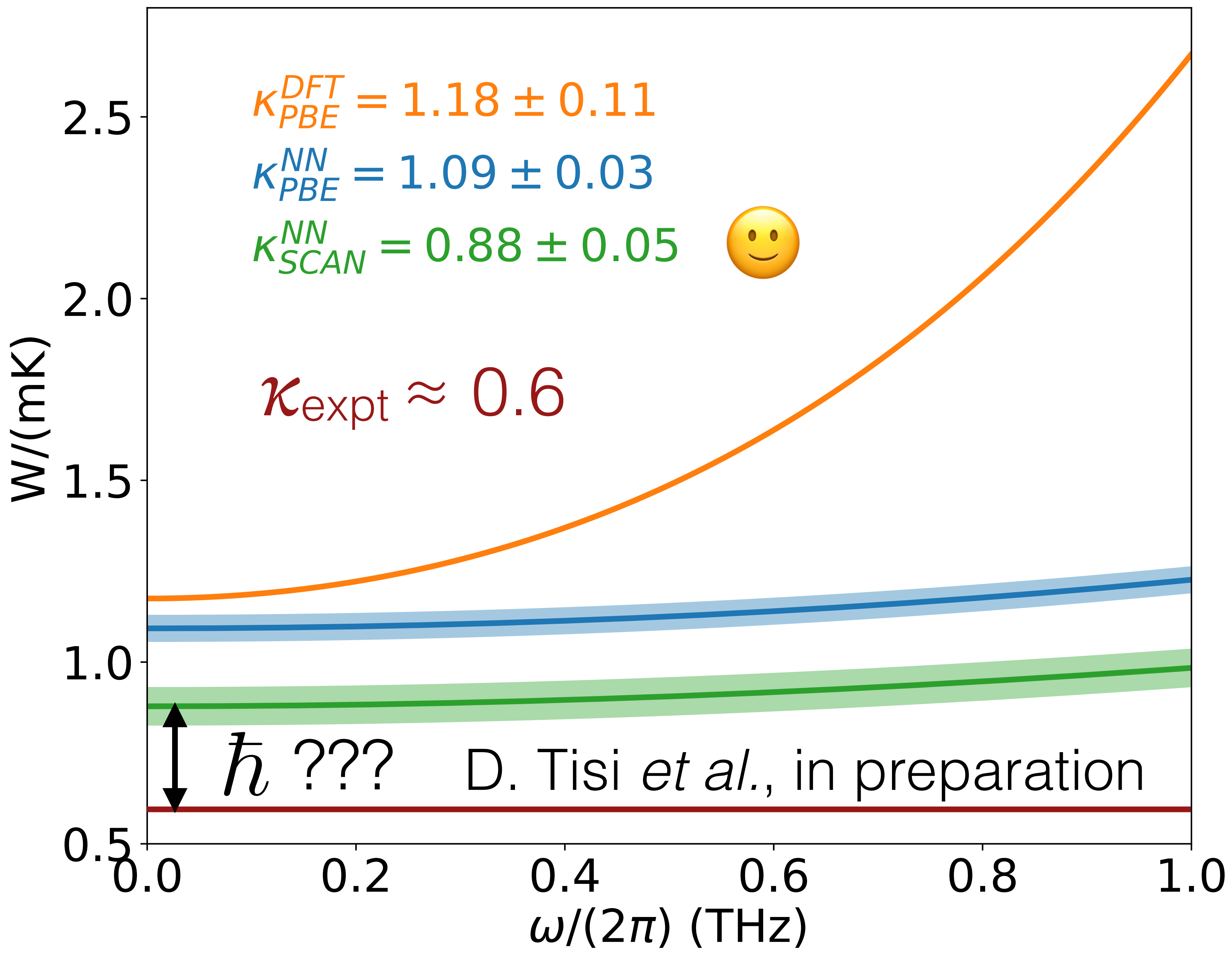

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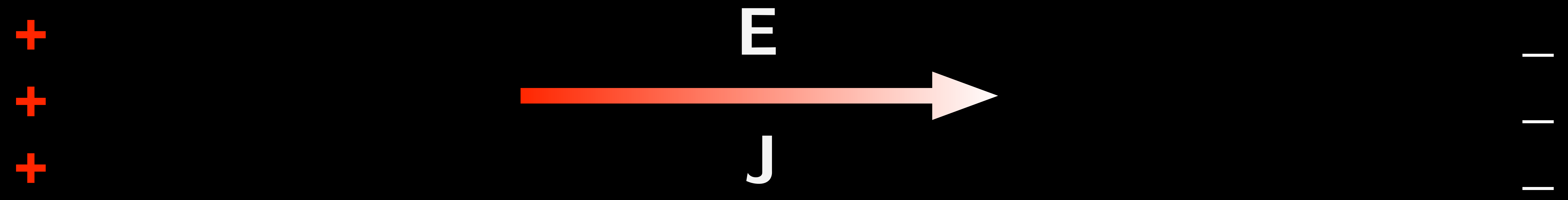
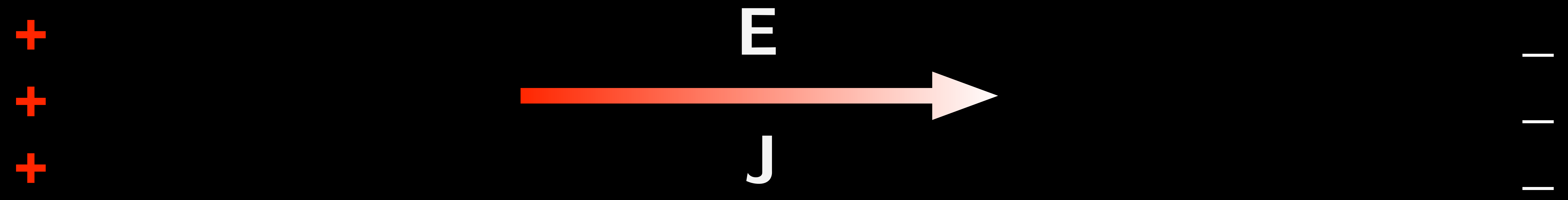
ionic transport

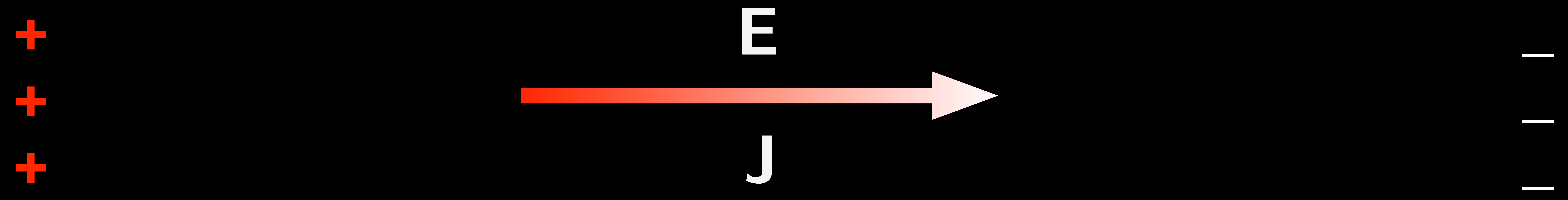


$$\mathbf{J} = \sigma \mathbf{E}$$



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

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



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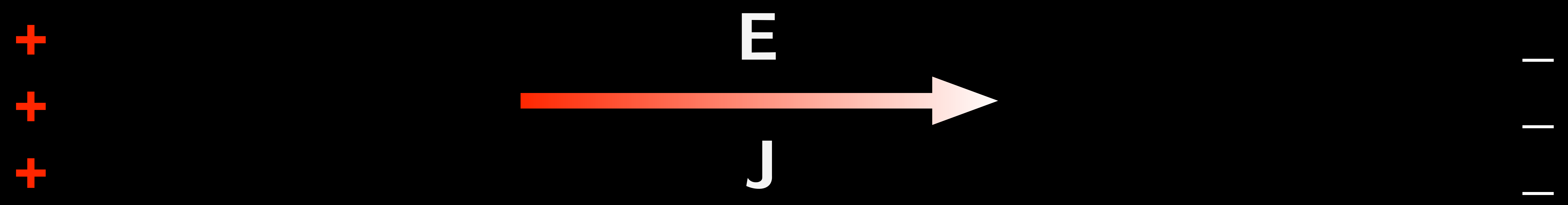

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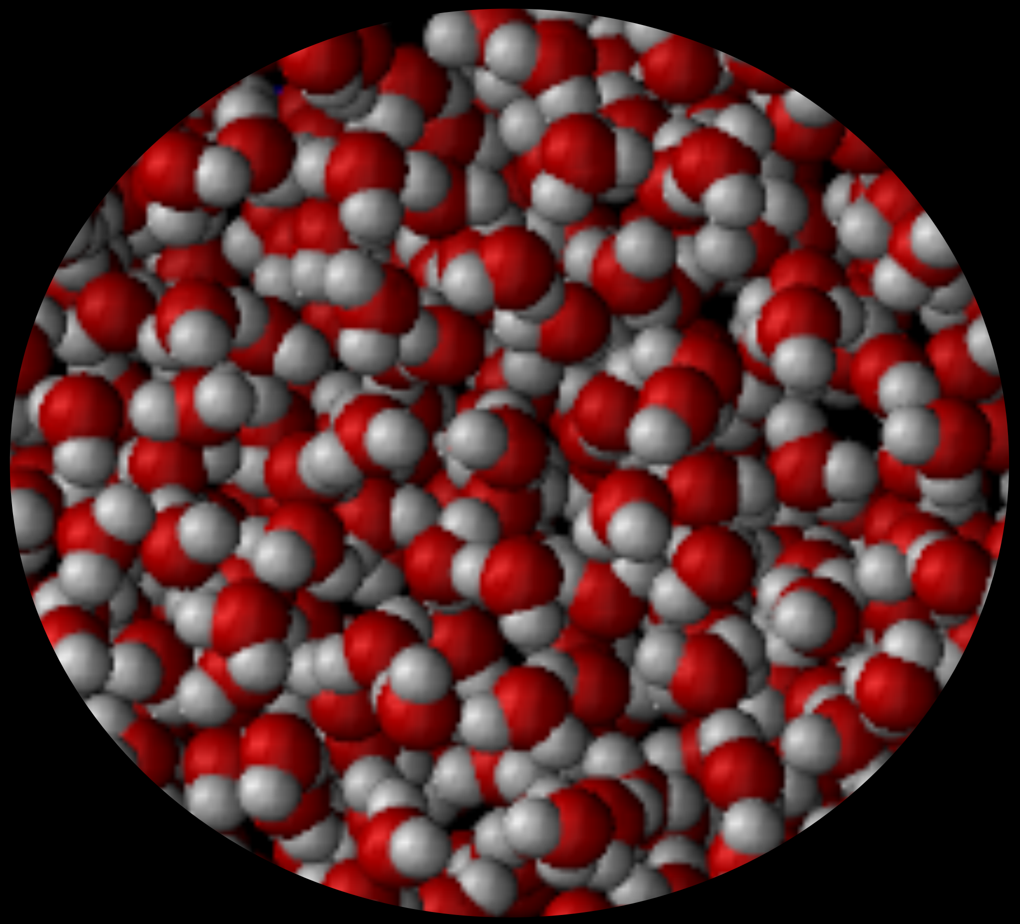
the conundrum



pure, undissociated
H_2O

$$\mathbf{J} = \frac{1}{\Omega}\sum_i \mathbf{Z}_i^* \cdot \mathbf{v}_i$$

$$\neq 0$$

$$\sigma = \frac{\Omega}{3k_BT}\left\langle |\mathbf{J}|^2 \right\rangle \times \tau_J$$

$$= 0$$

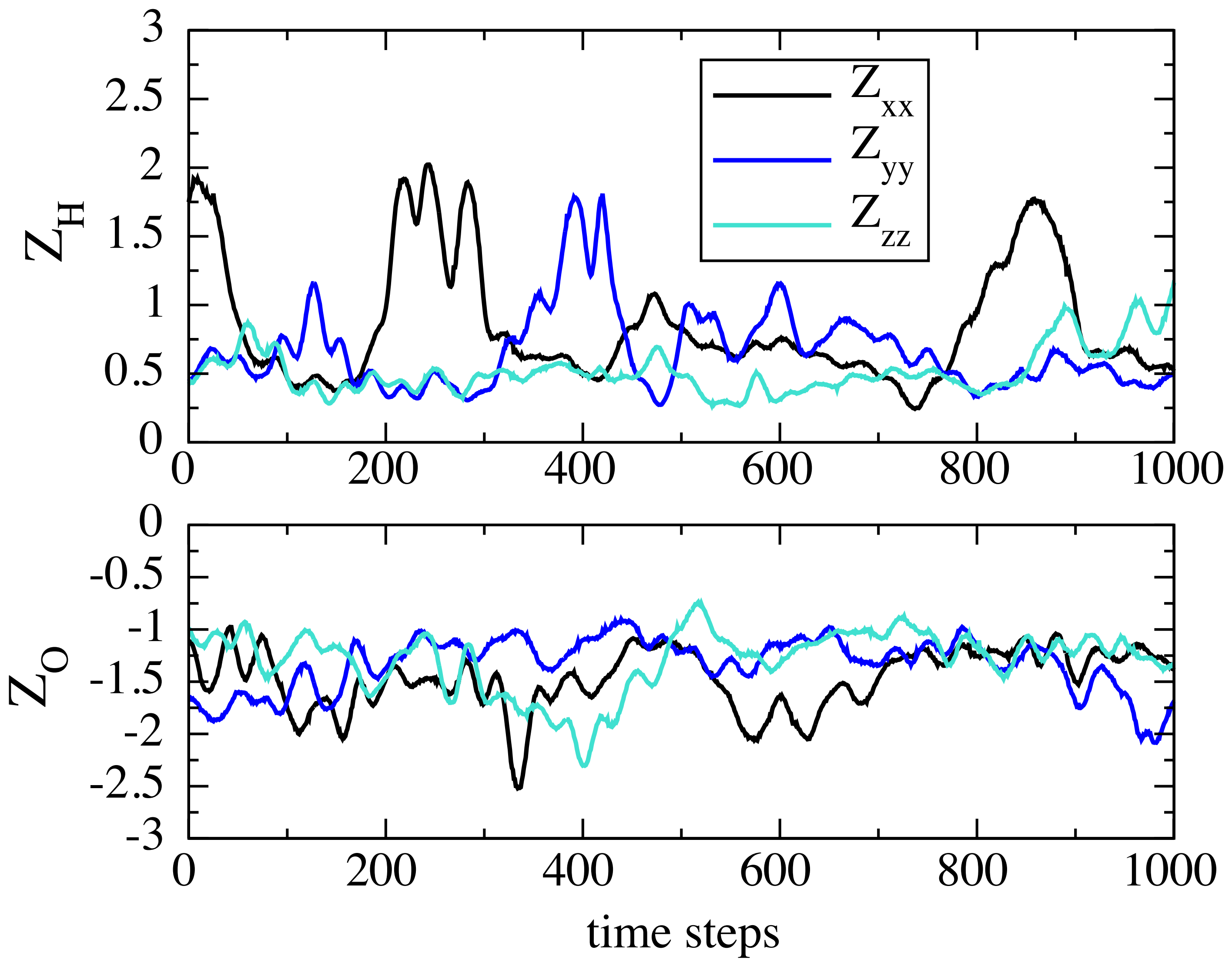
???

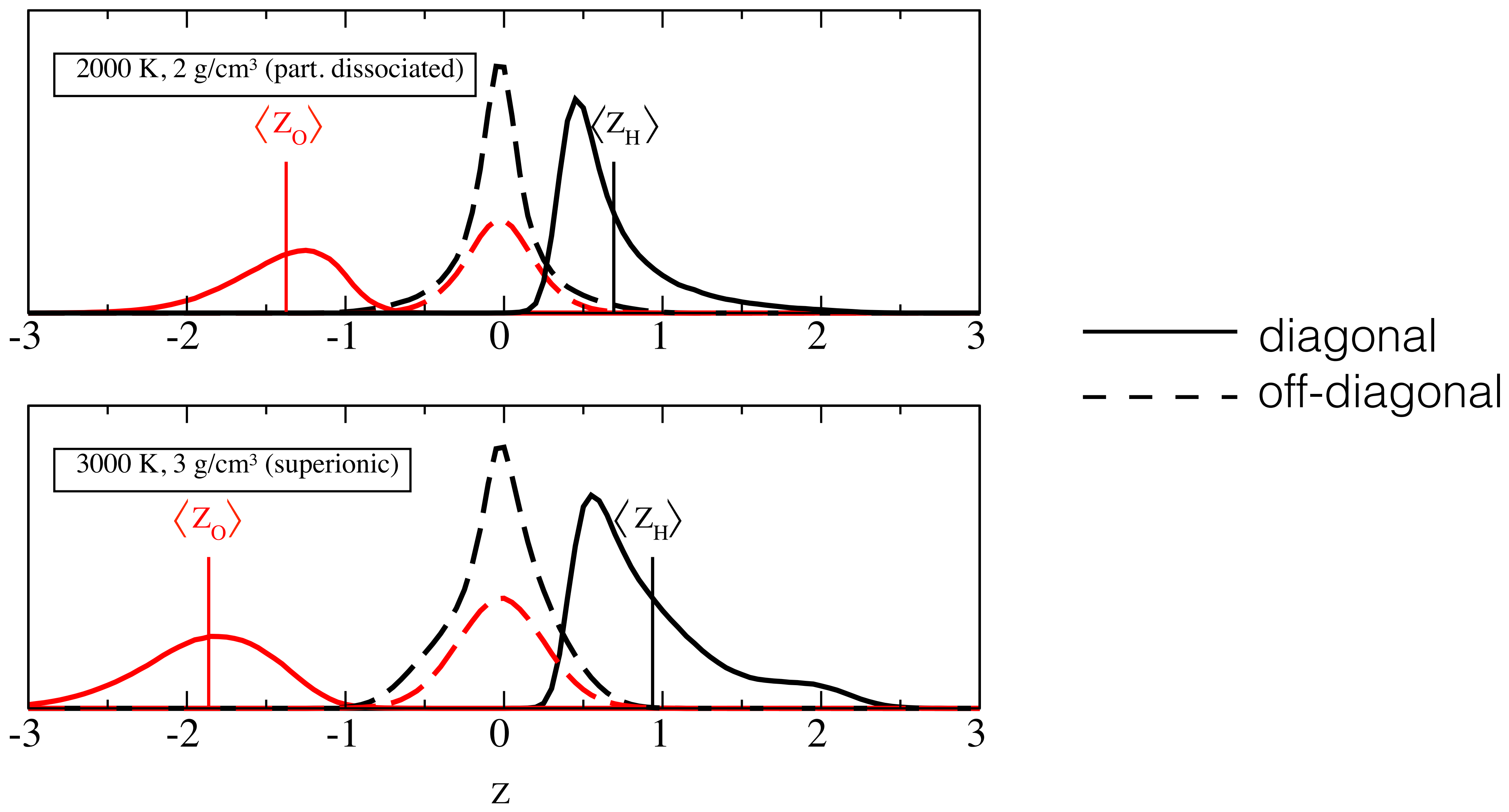
the conundrum

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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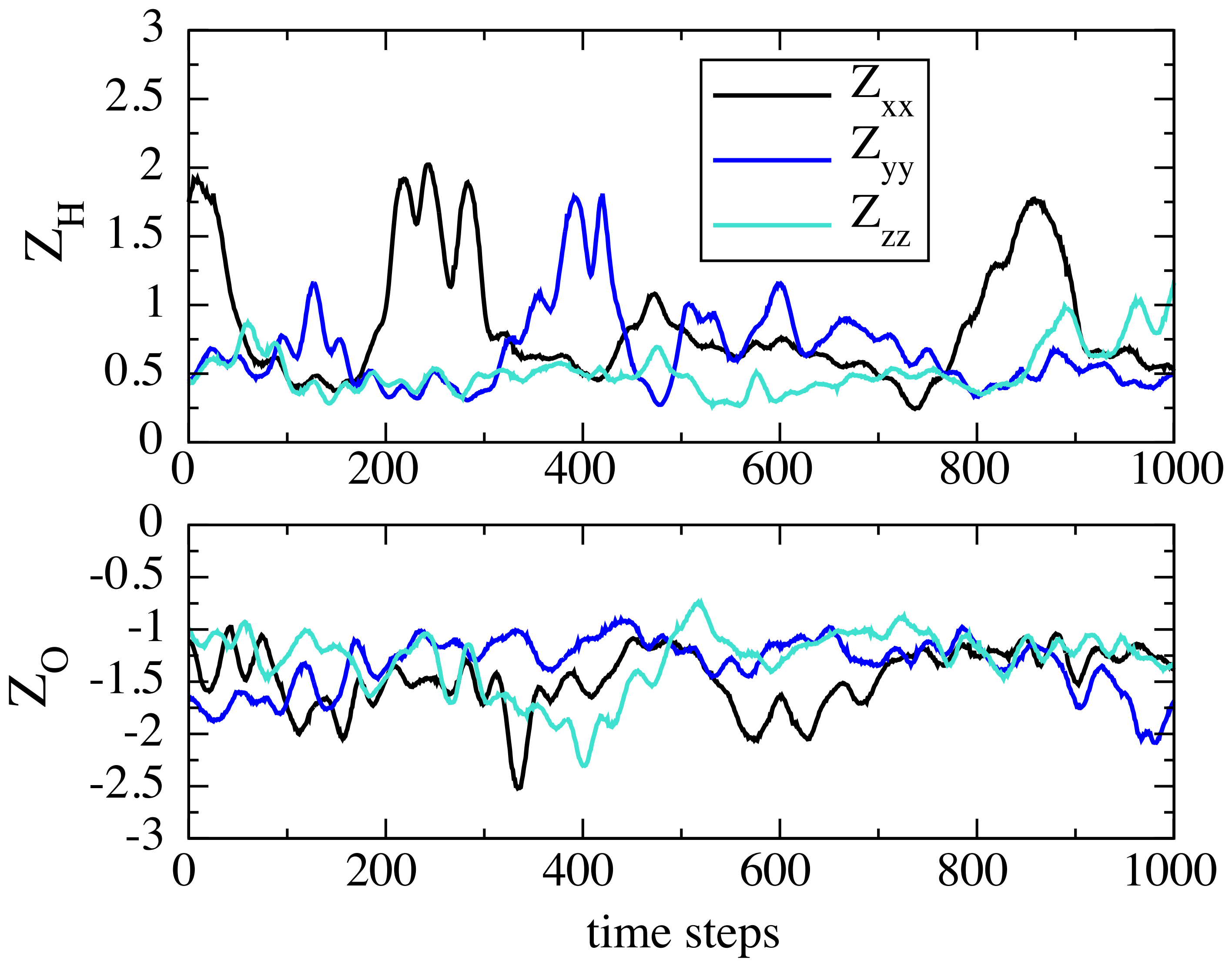
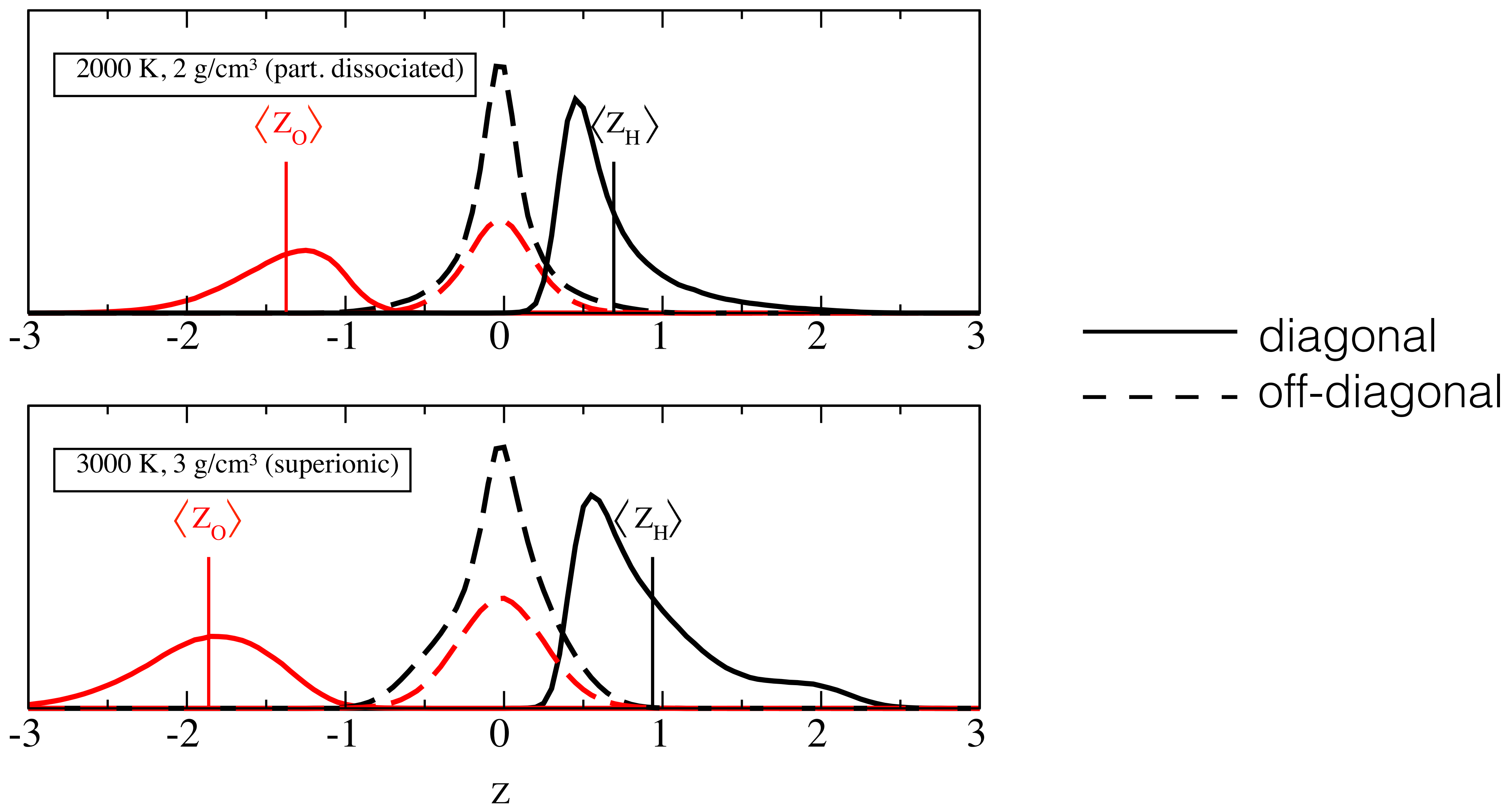
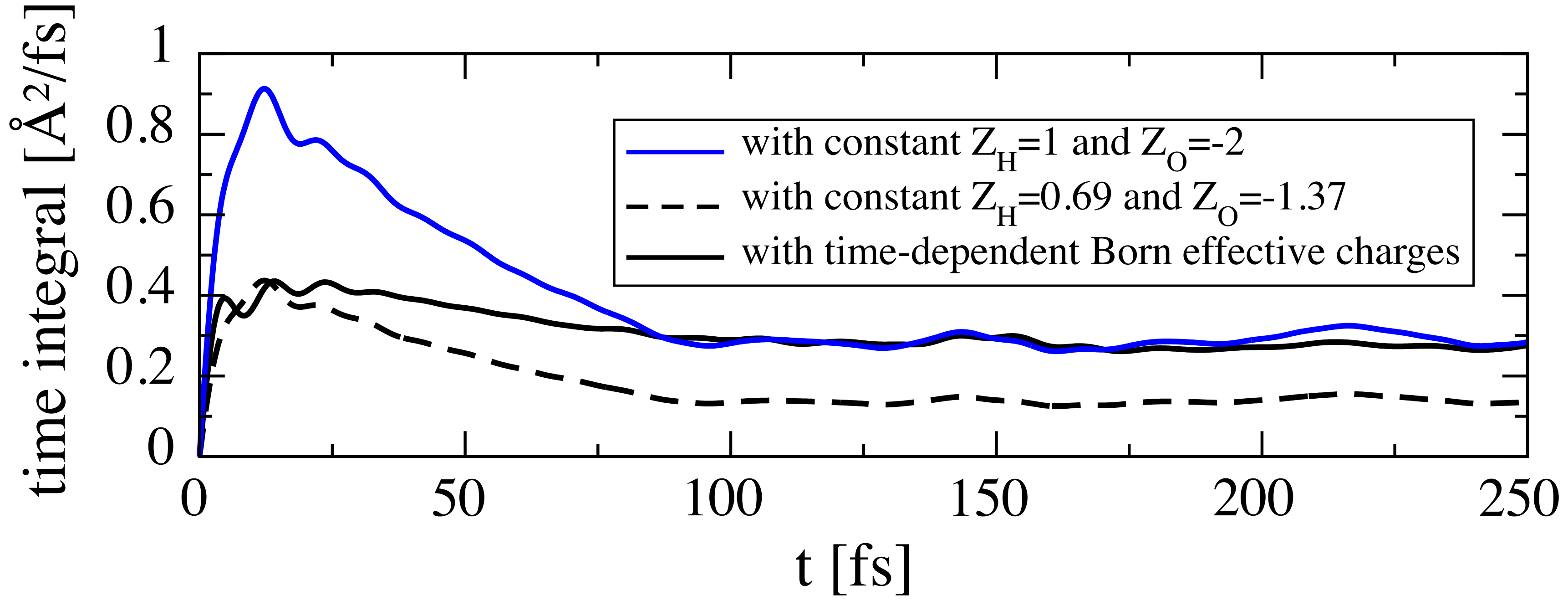
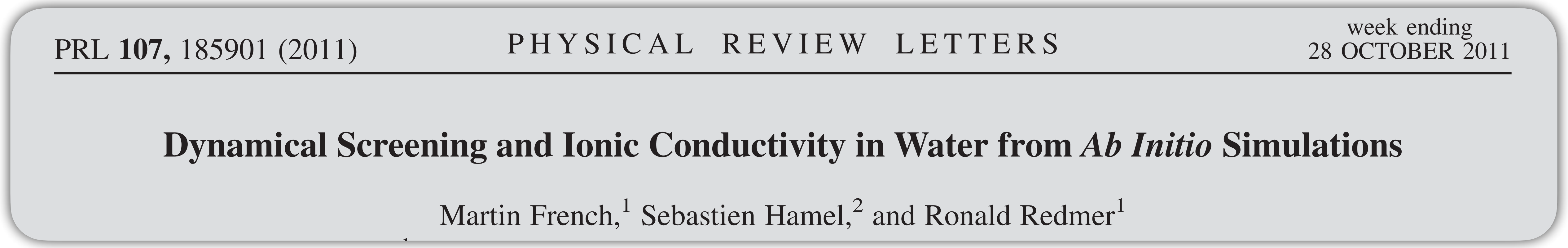






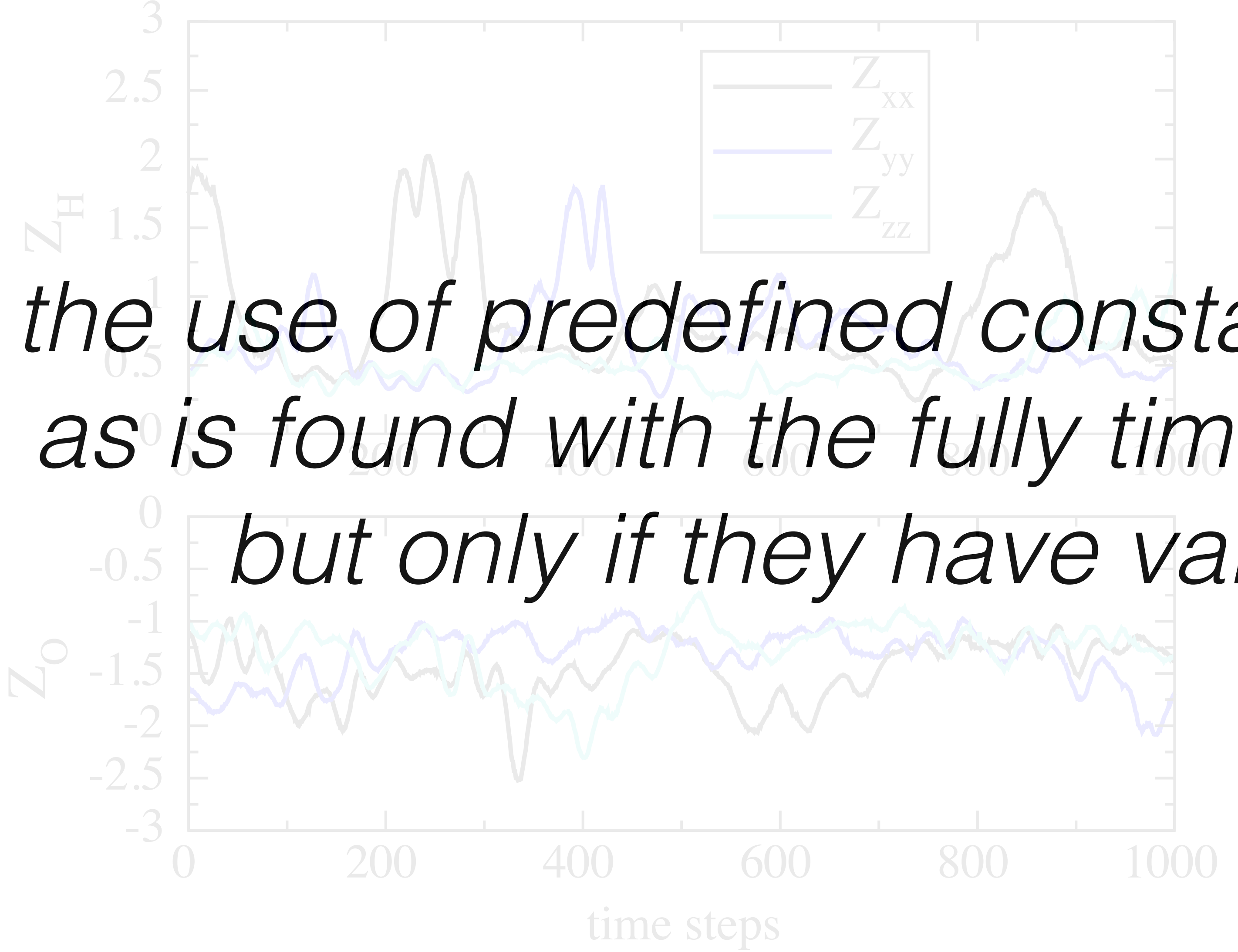
$$\int_0^t \langle \boldsymbol{J}(t')\boldsymbol{J}(0)\rangle dt'$$

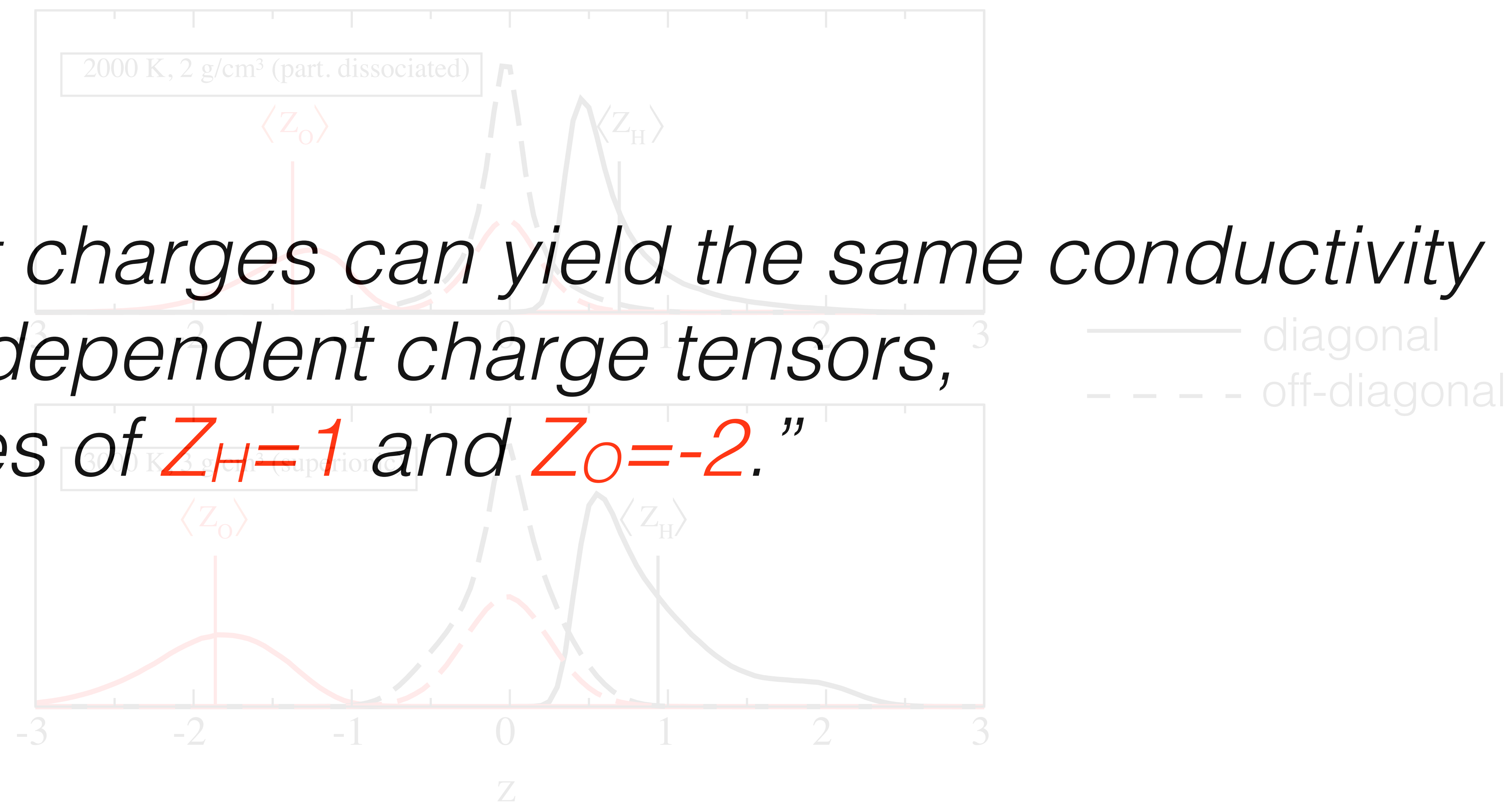
the conundrum


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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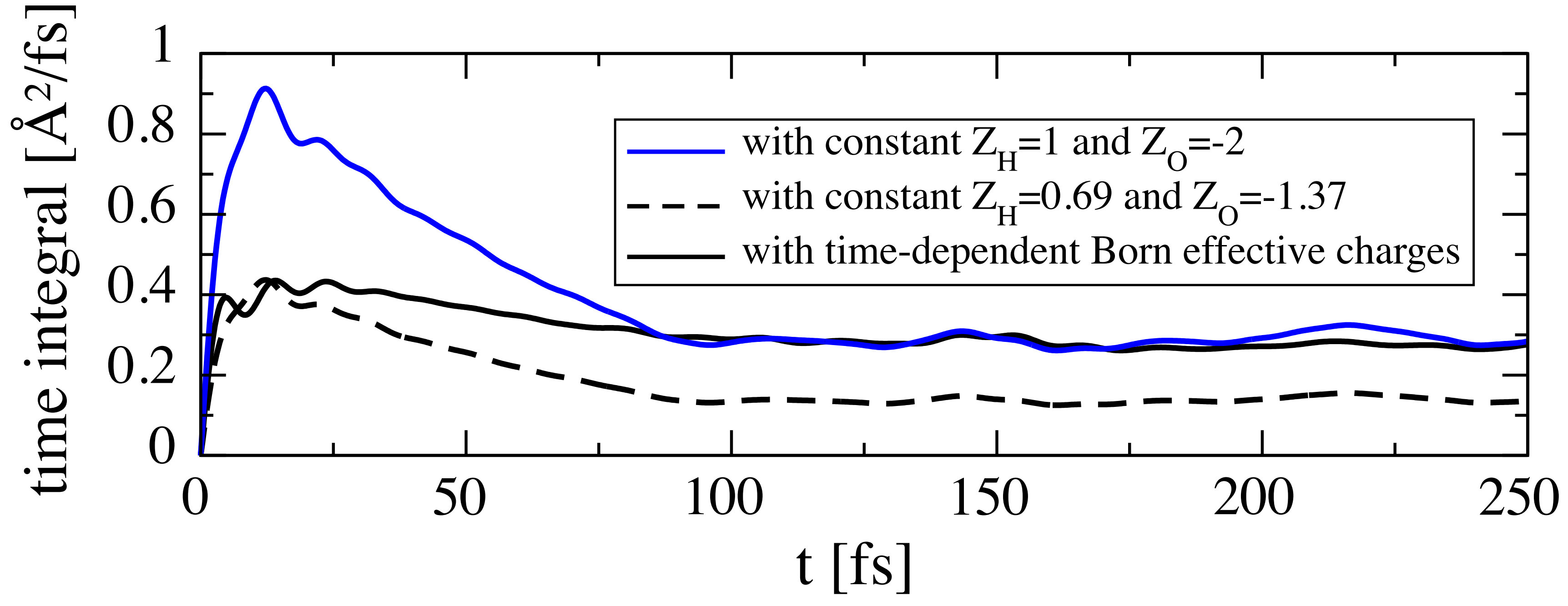

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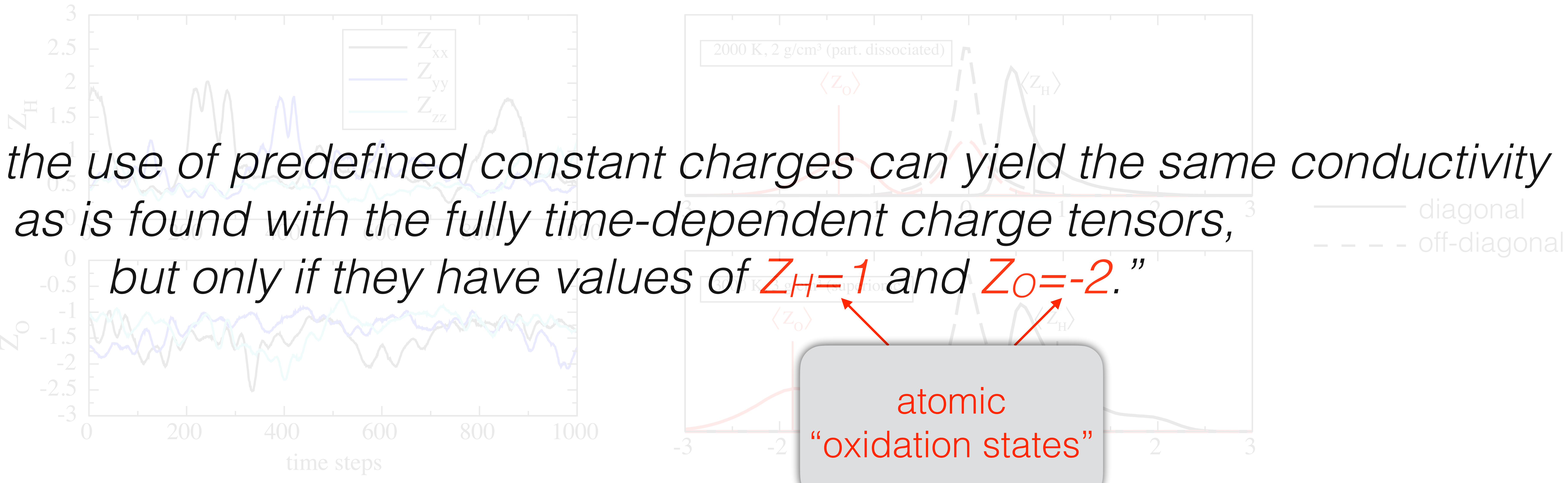

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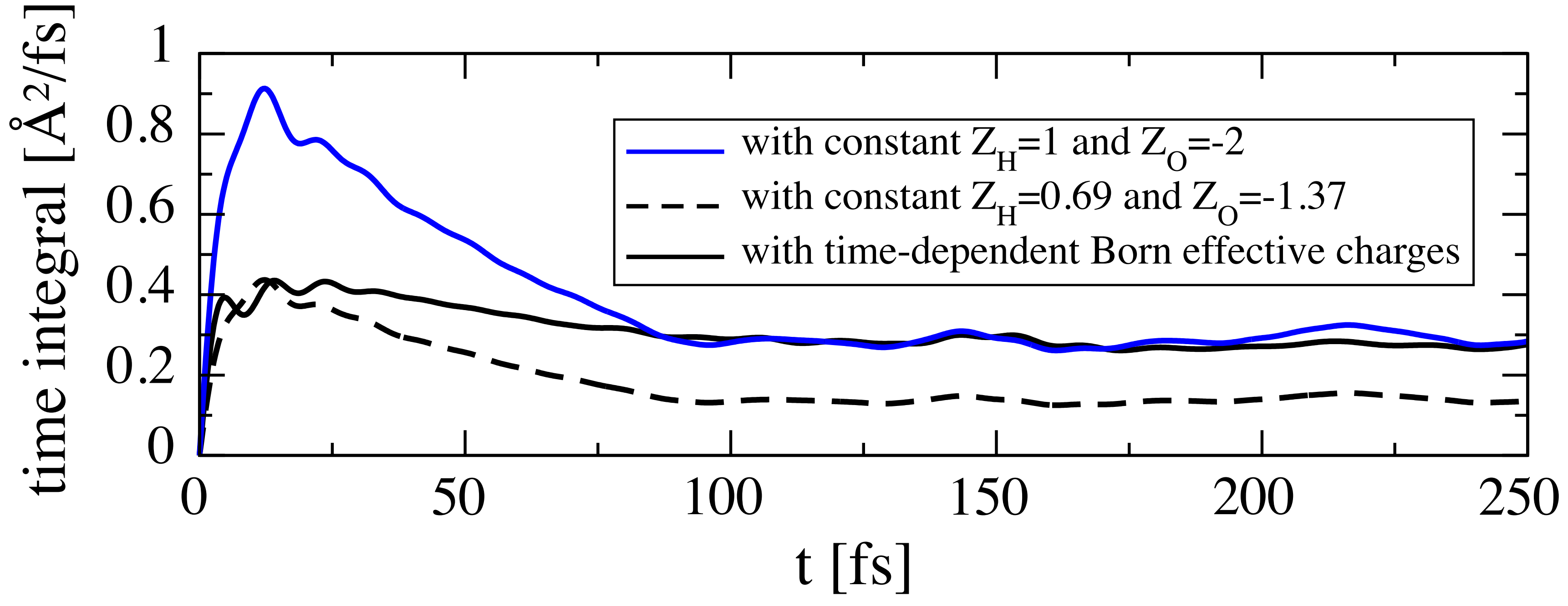
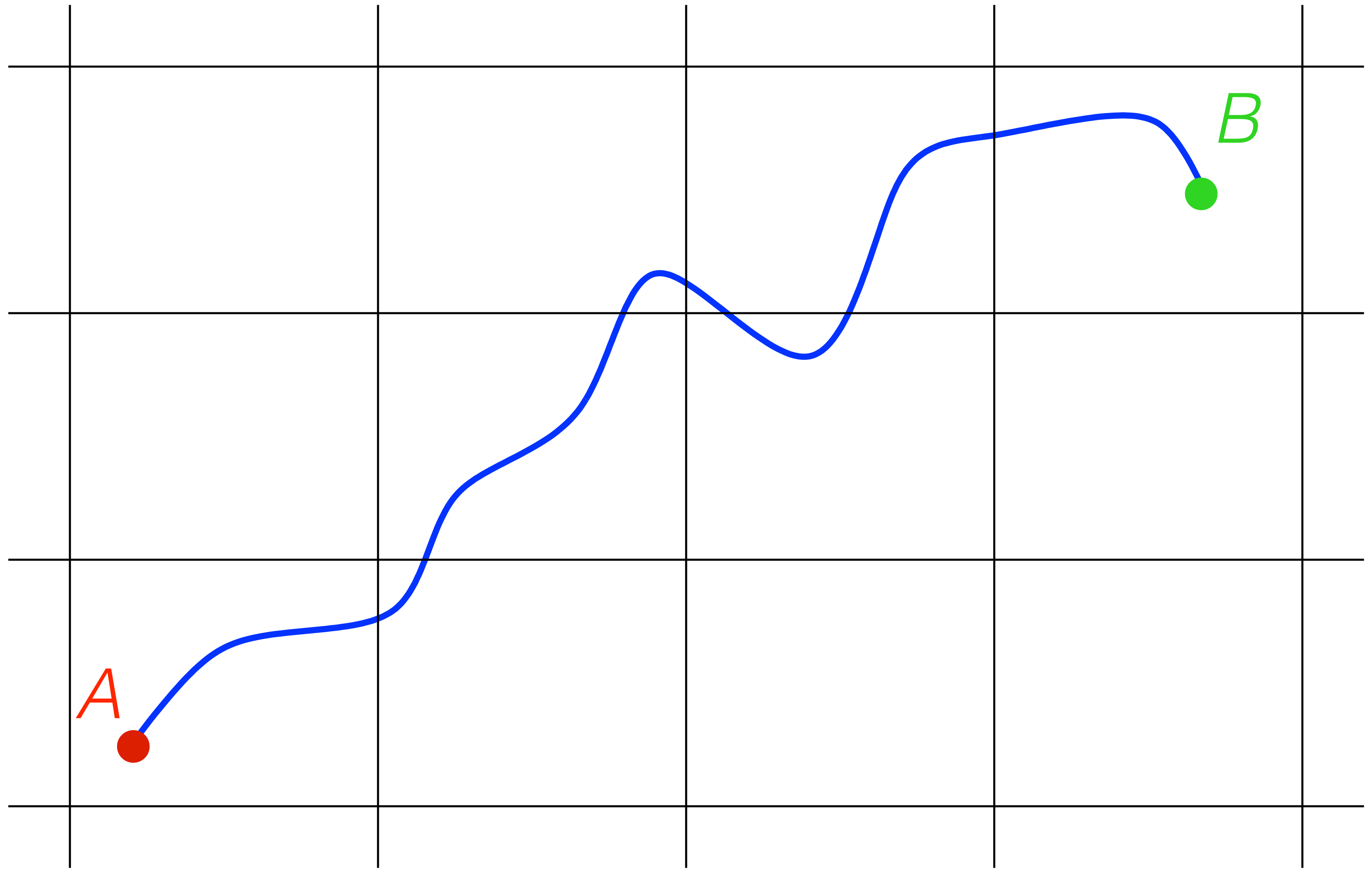
atomic "oxidation states"



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

how come?

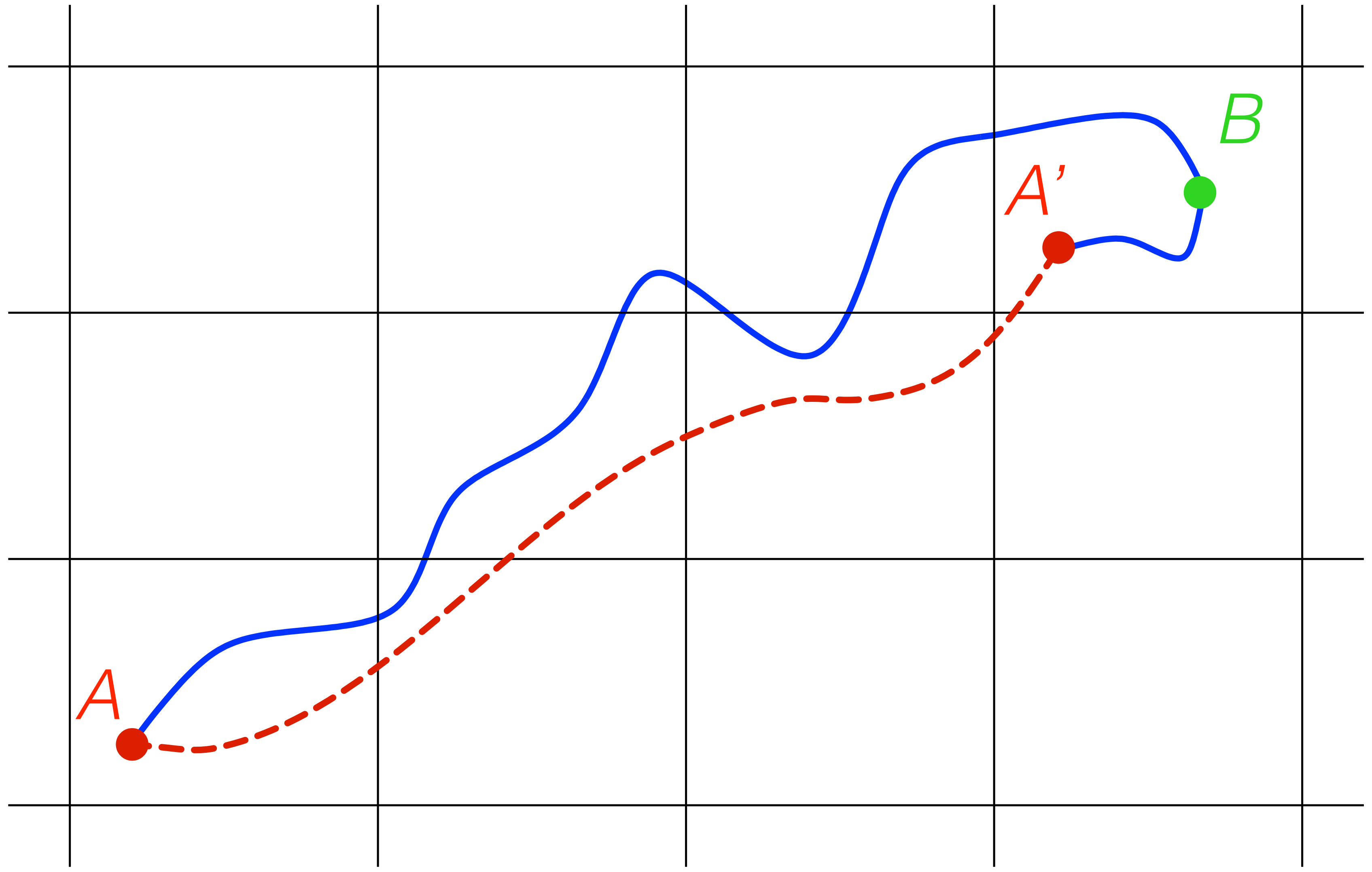
gauge invariance of charge transport



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

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

gauge invariance of charge transport



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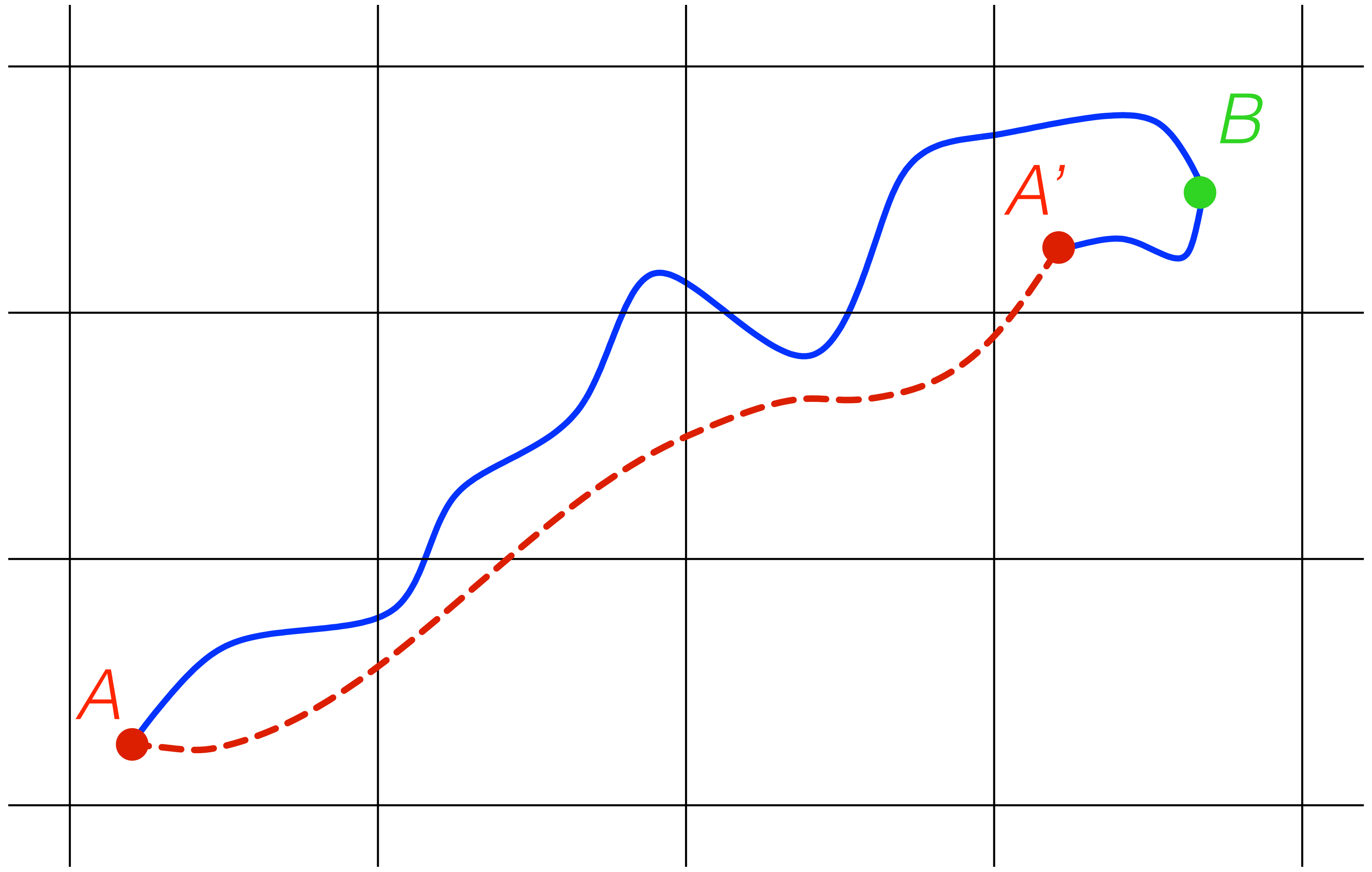

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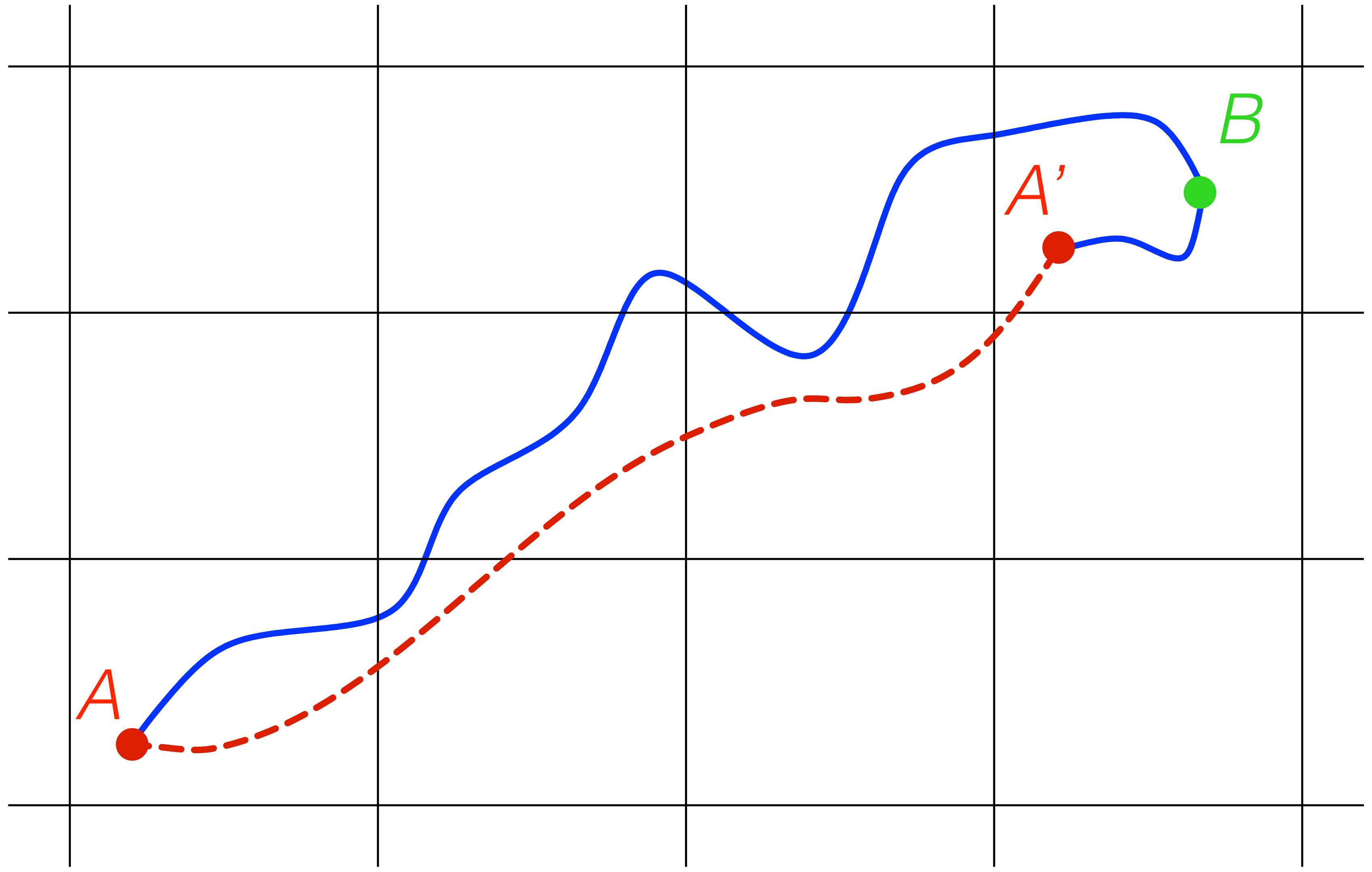
gauge invariance of charge transport



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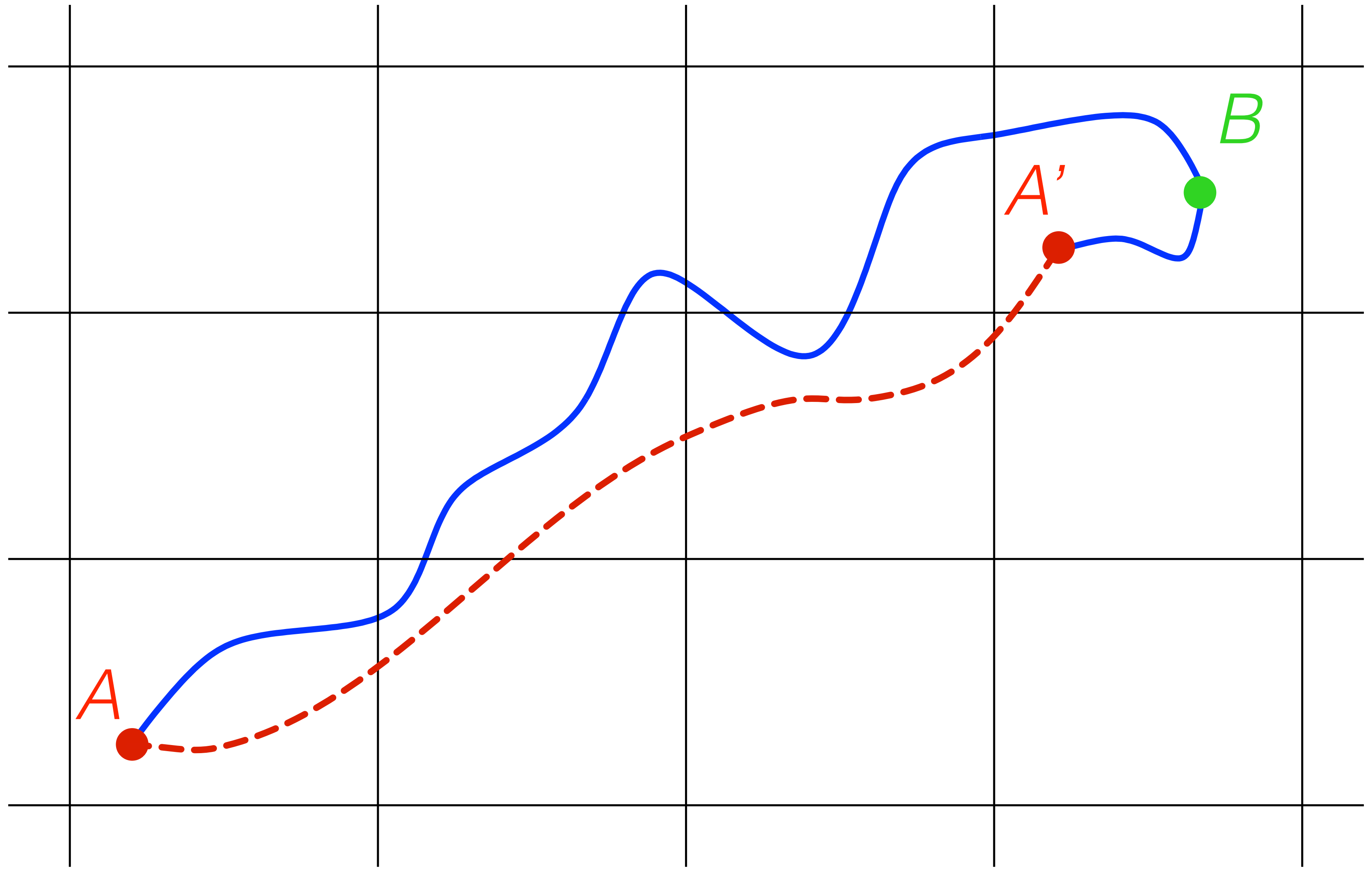

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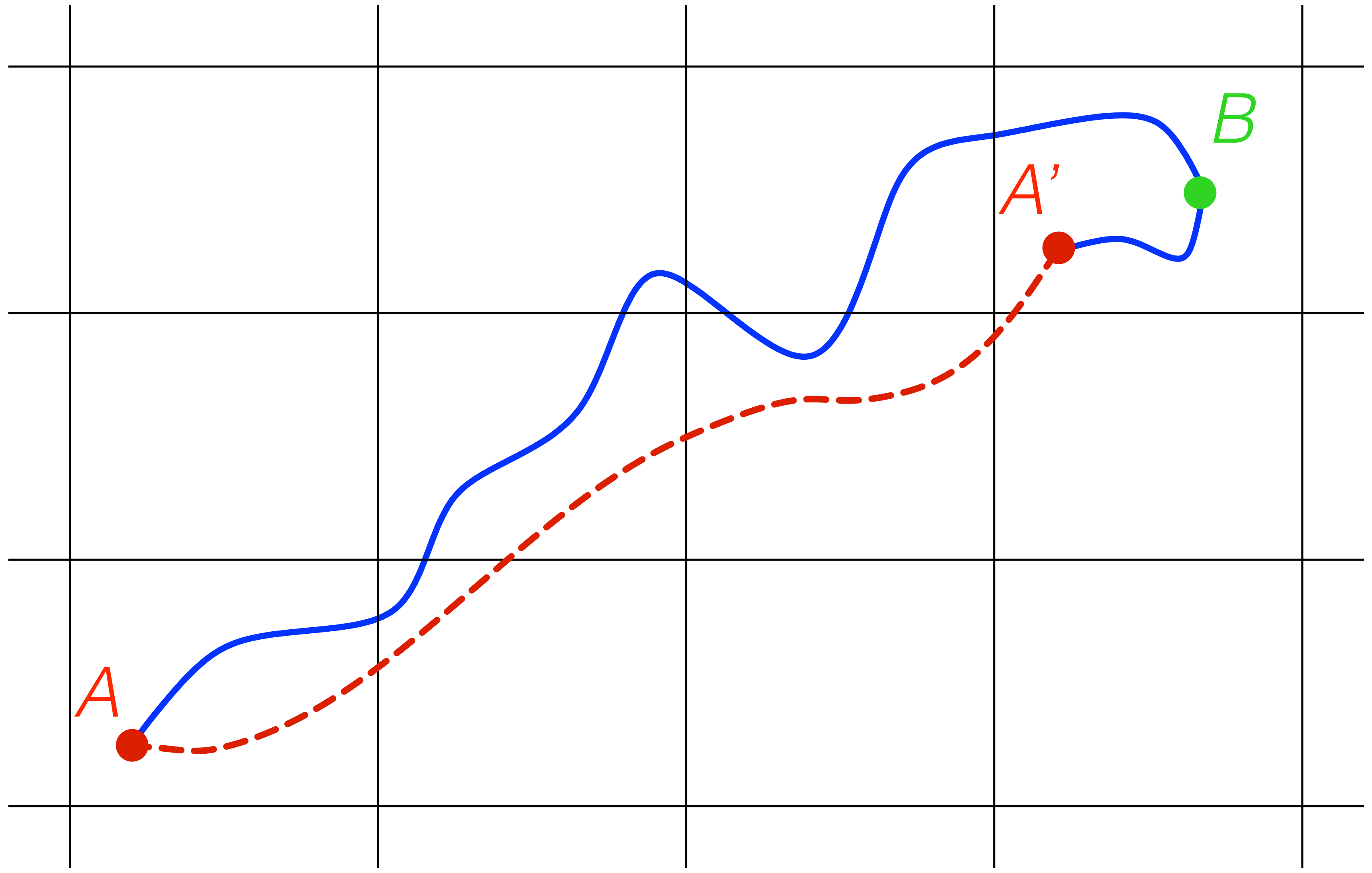
gauge invariance of charge transport



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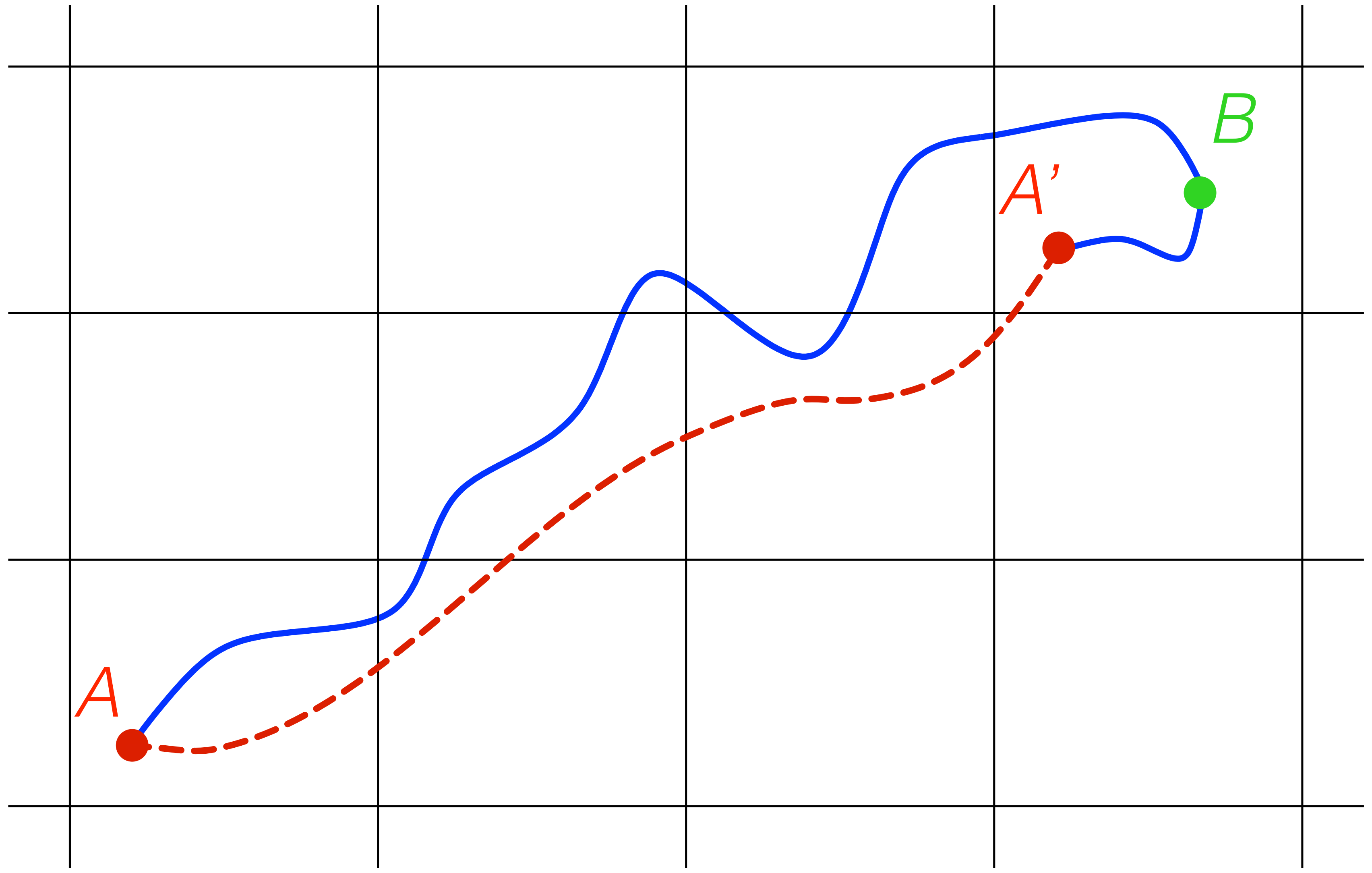

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$$\hat{H}(B) \neq \hat{H}(A)$$

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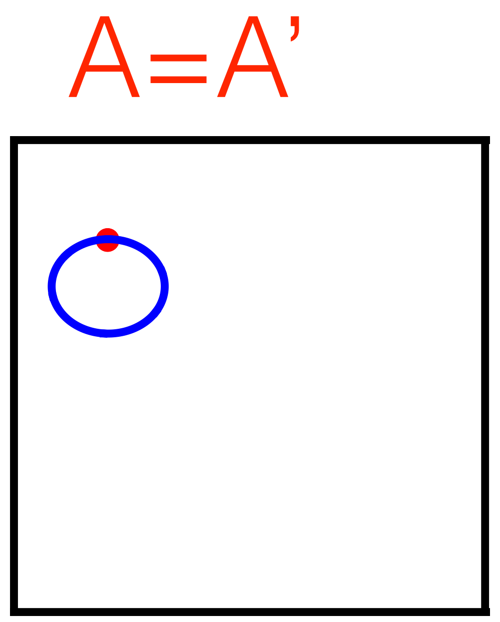
$$Q(AA') = \frac{1}{\ell} \int_A^{A'} d\mu(X)$$

$$\in \mathbb{Z}$$

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

topological invariants



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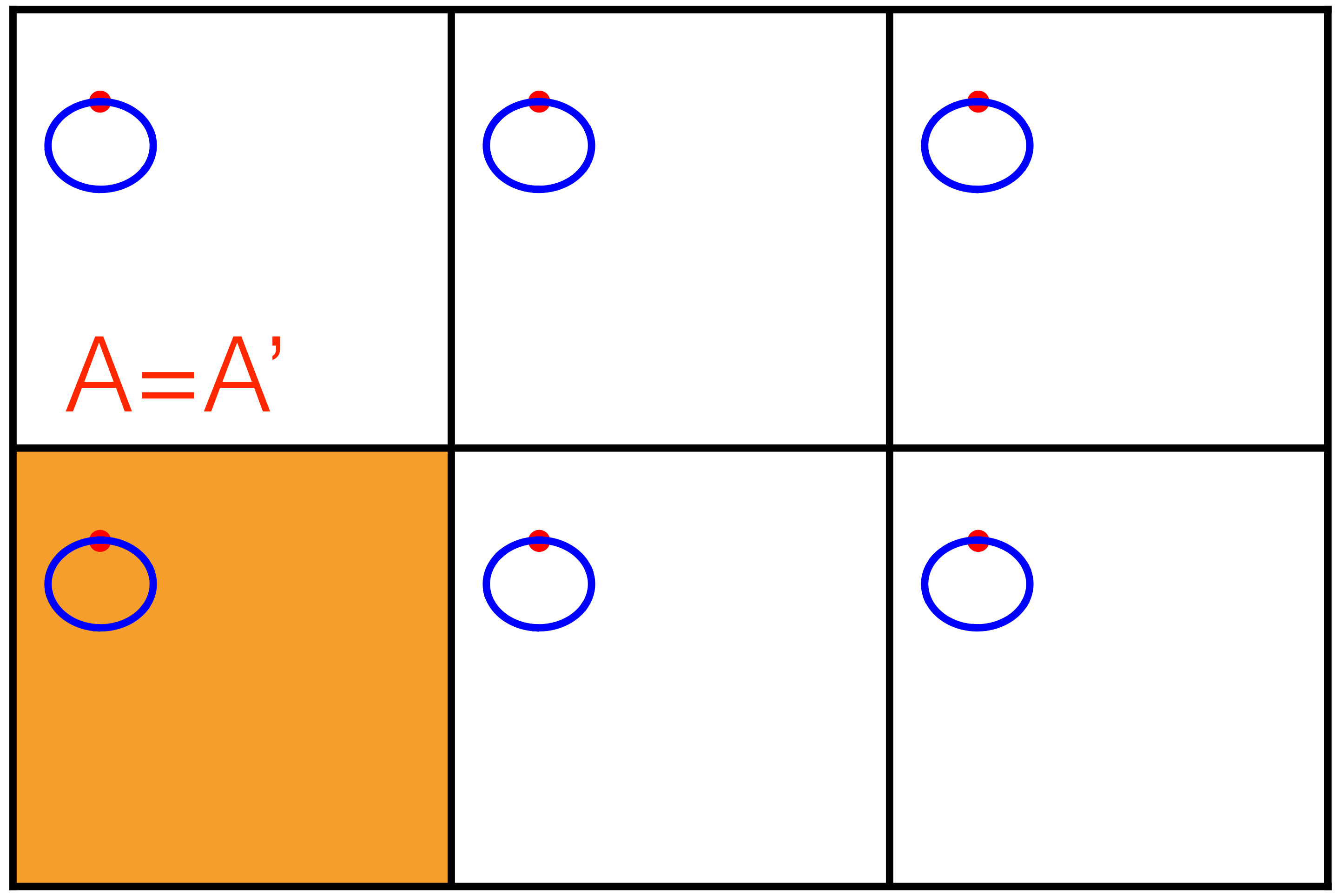

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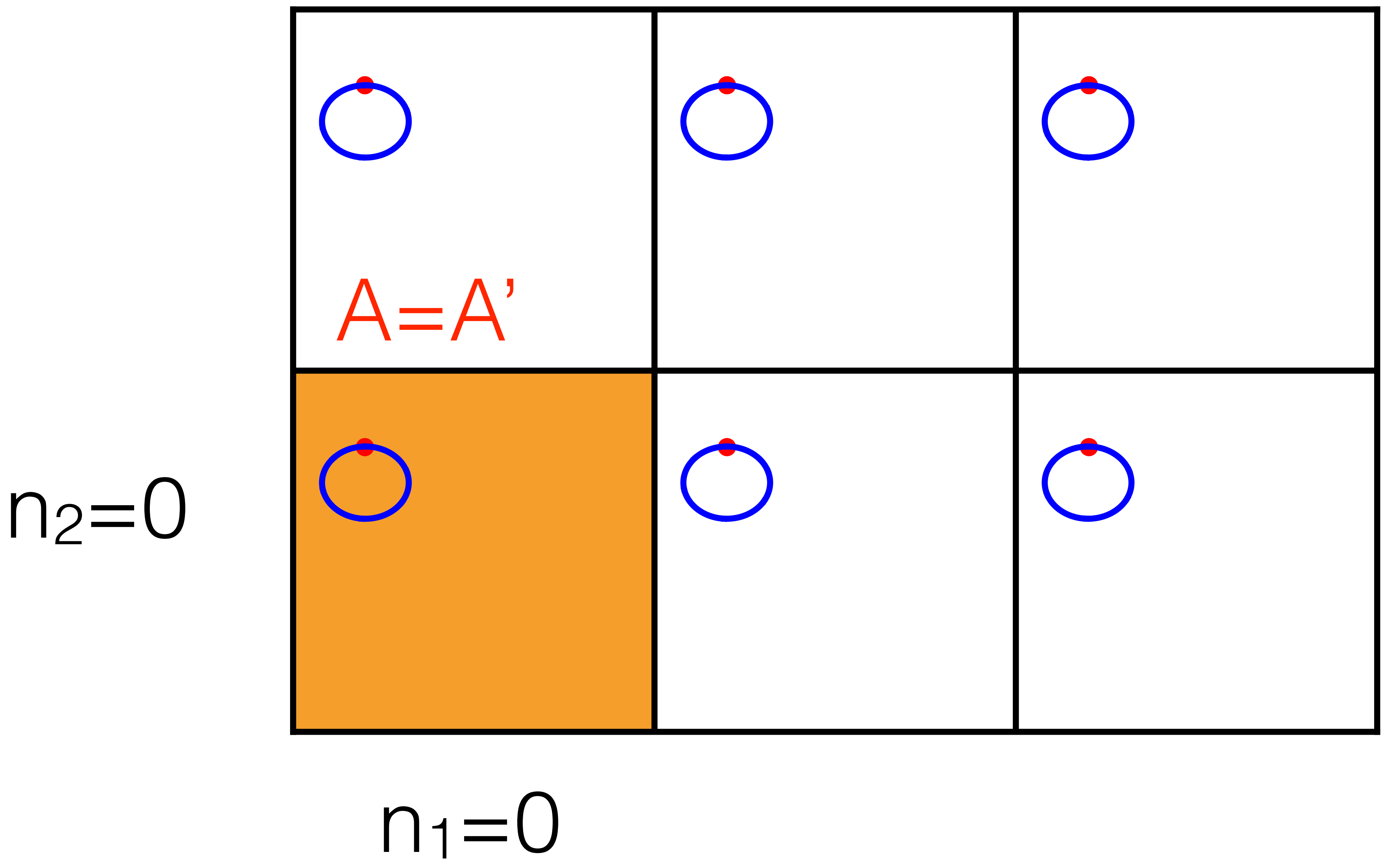

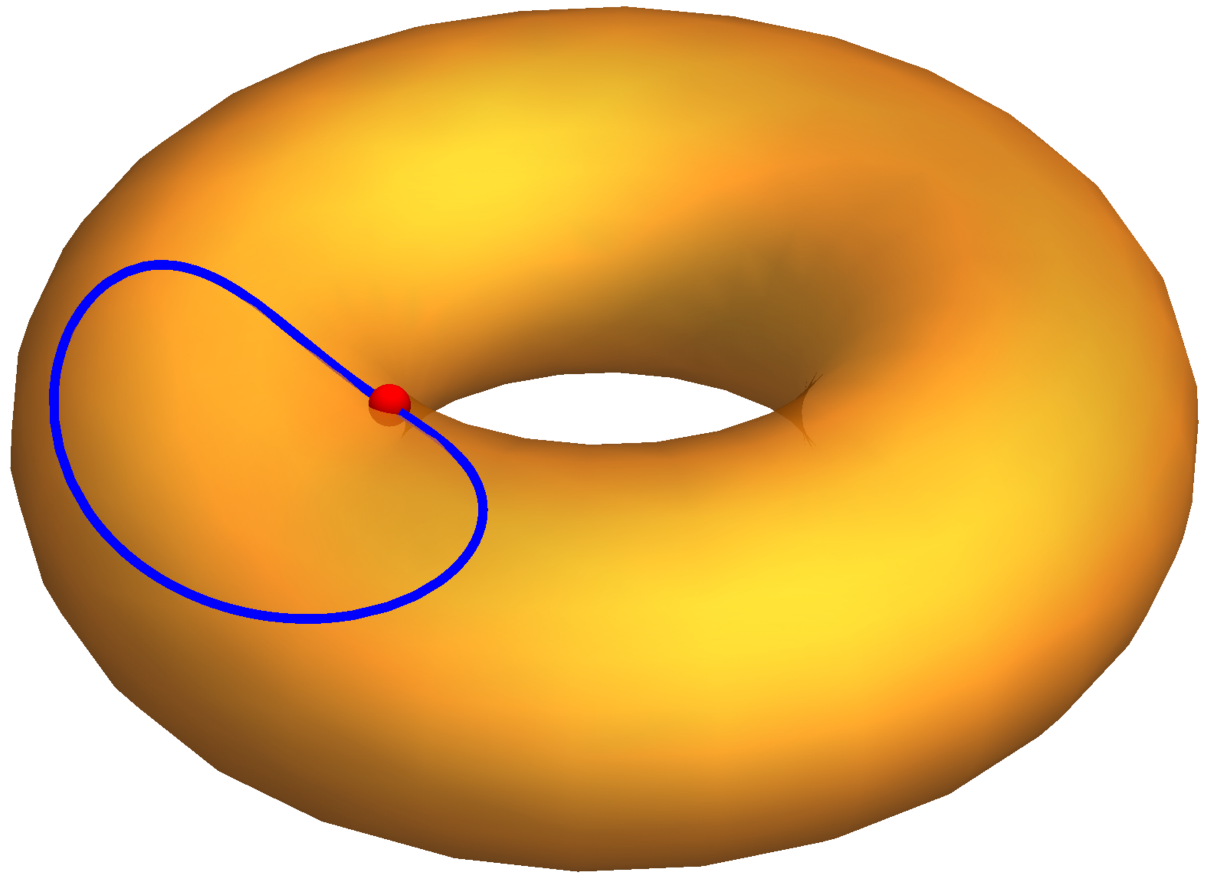

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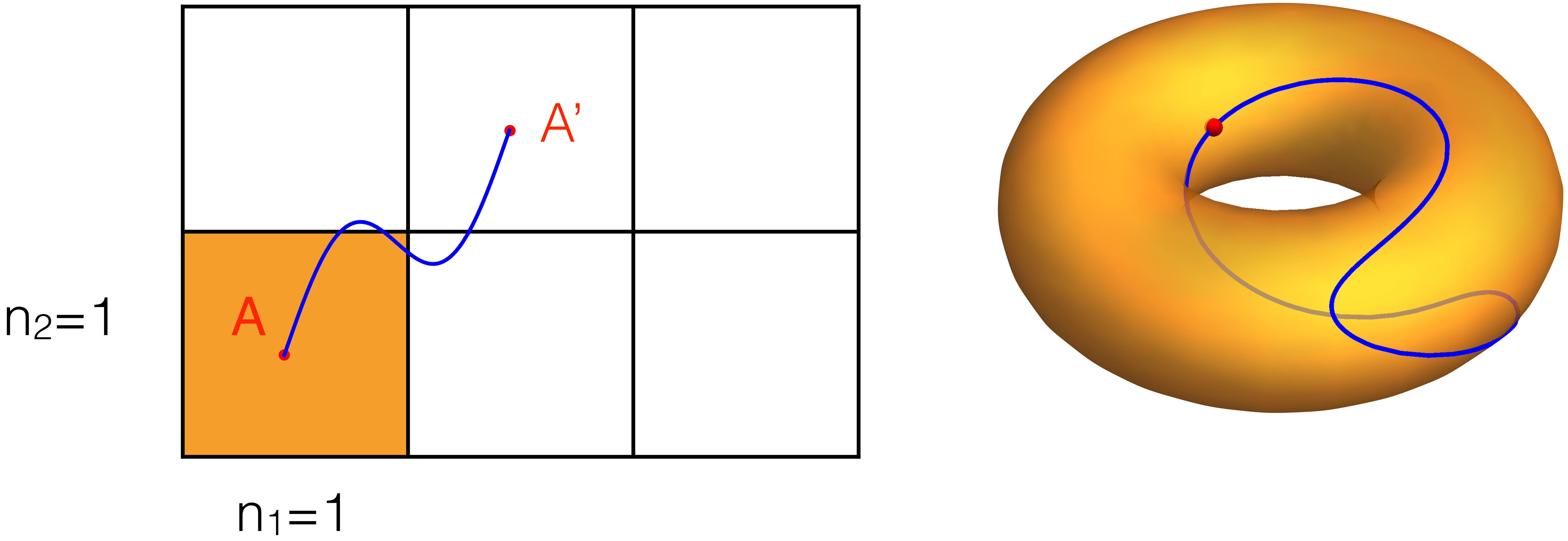

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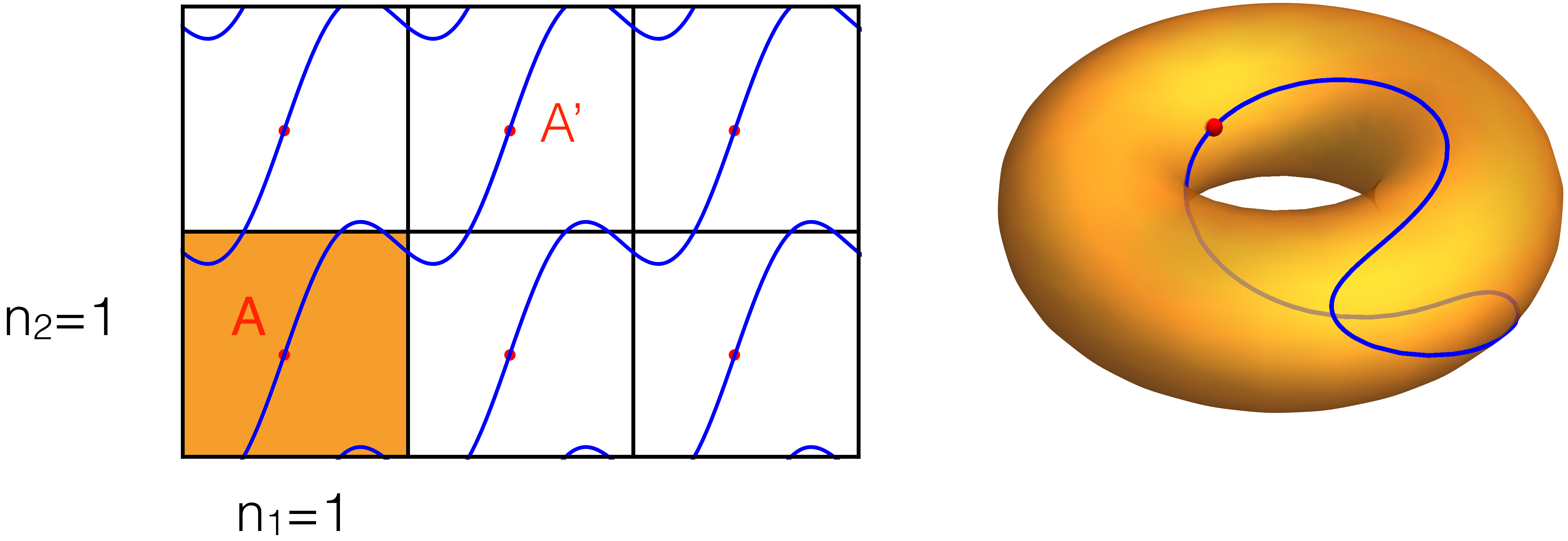

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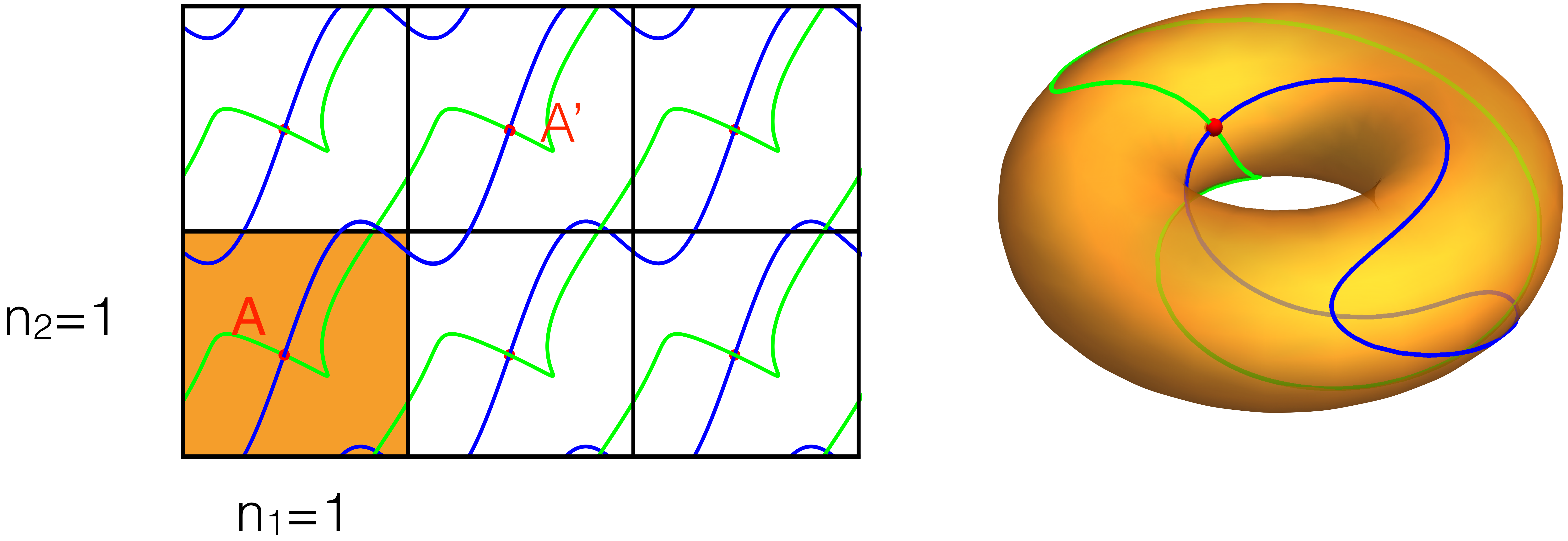

$$\color{blue}{Q(AA')} = \color{green}{Q(AA')} = Q[n_1 = 1, n_2 = 1]$$

atomic oxidation states

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

atomic oxidation states

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

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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

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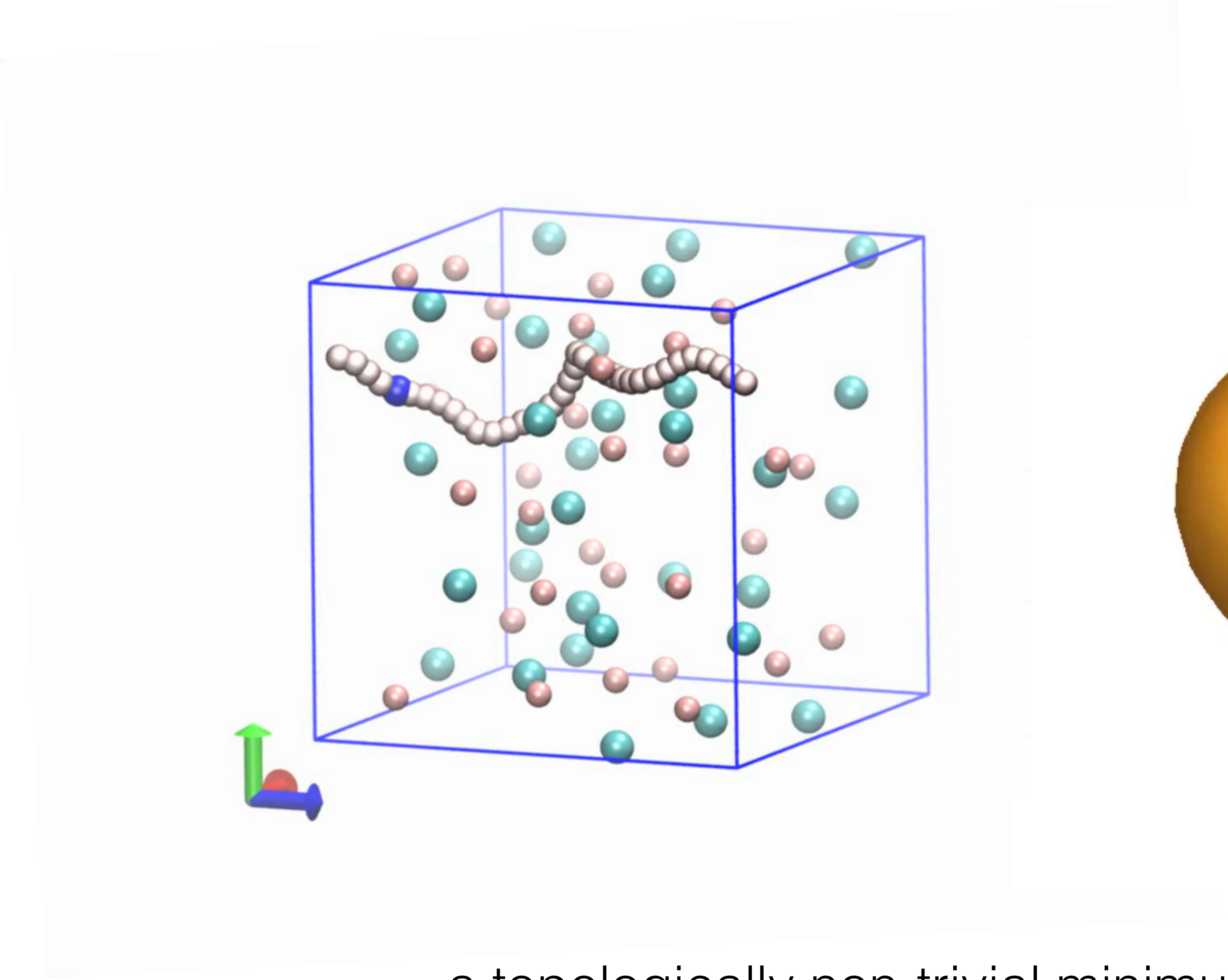
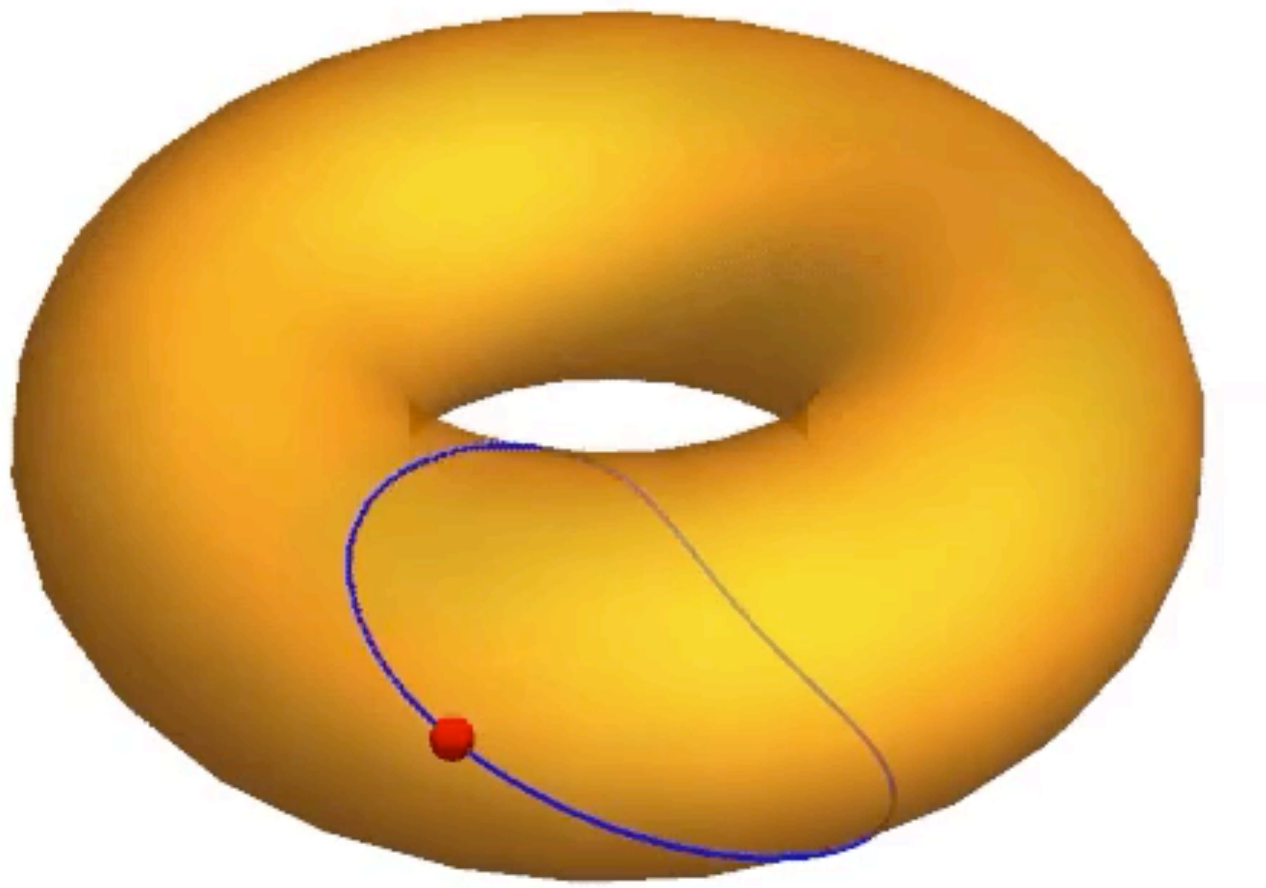
$$q_{i\alpha\beta} = q_{S(i)}\delta_{\alpha\beta}$$

atomic oxidation state

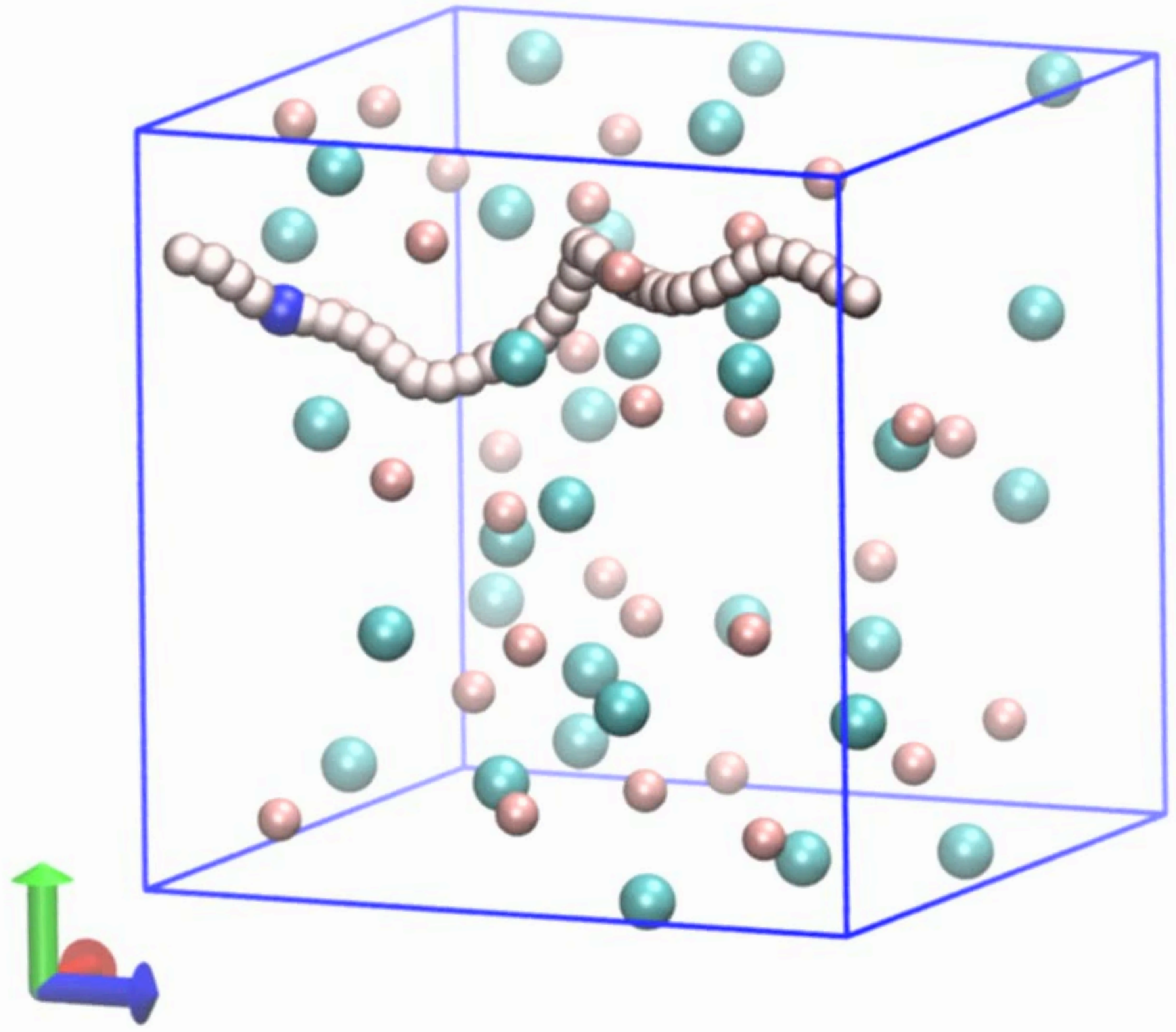
a numerical experiment on molten KCl

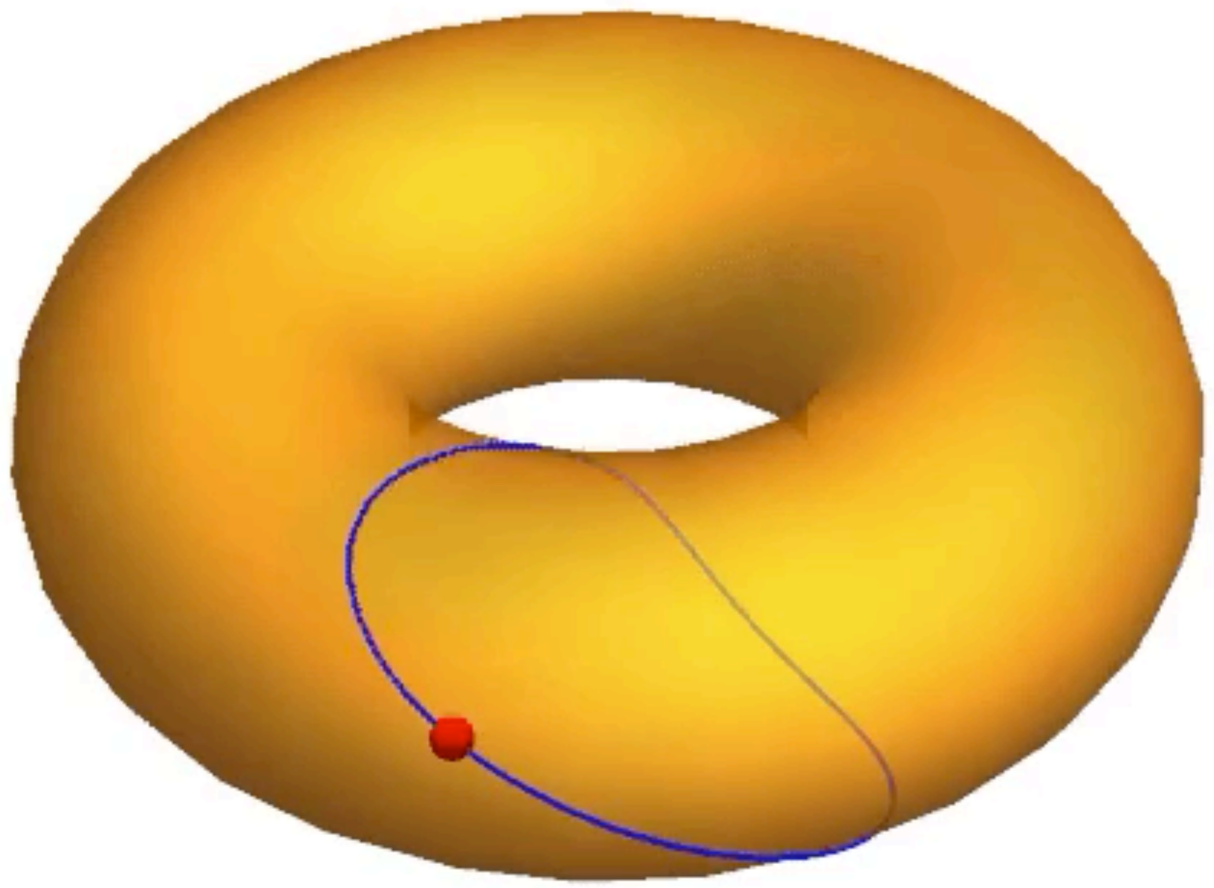




a topologically non-trivial minimum-energy path
connecting two identical configurations of a ionic fluid

a numerical experiment on molten KCl





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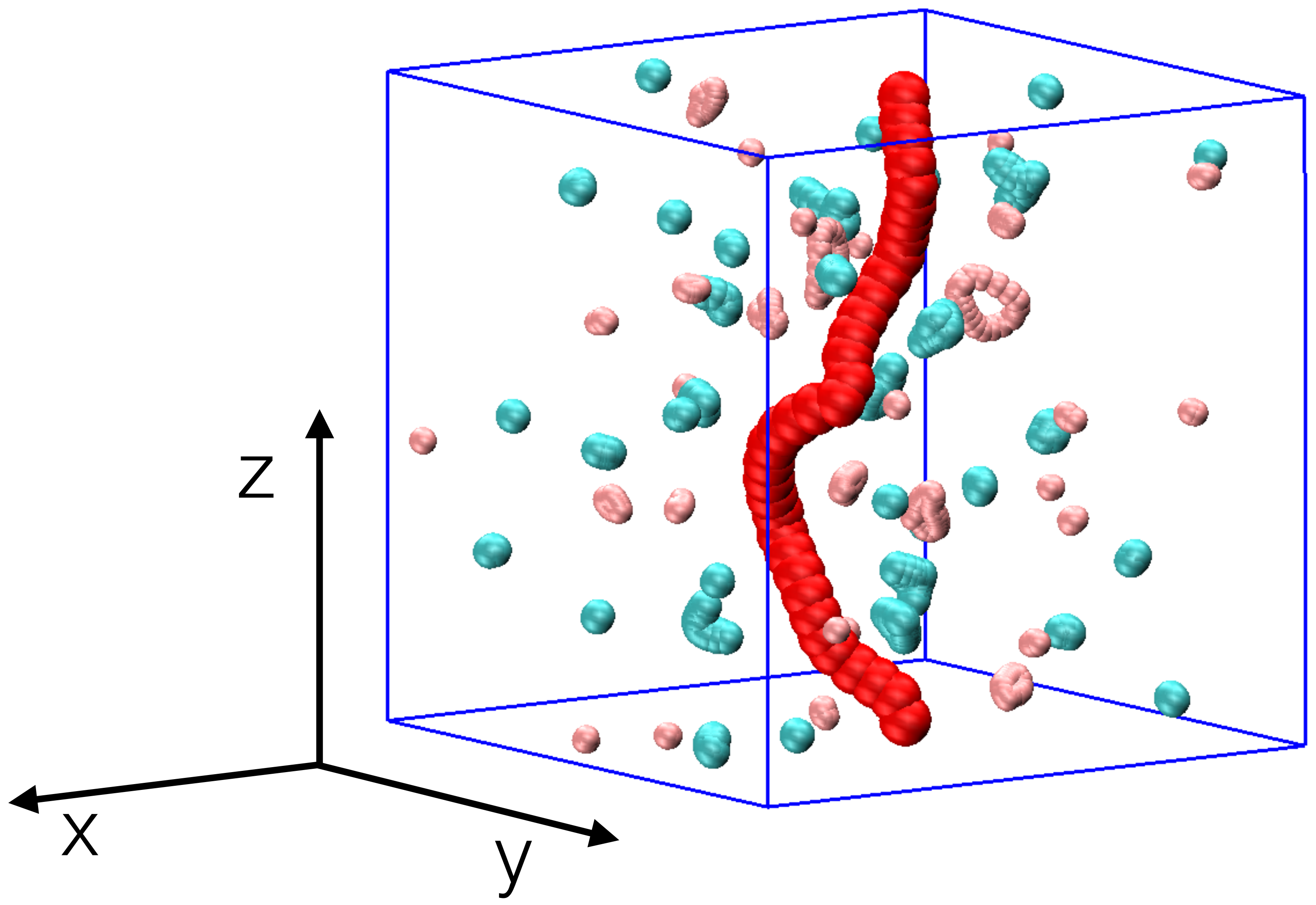

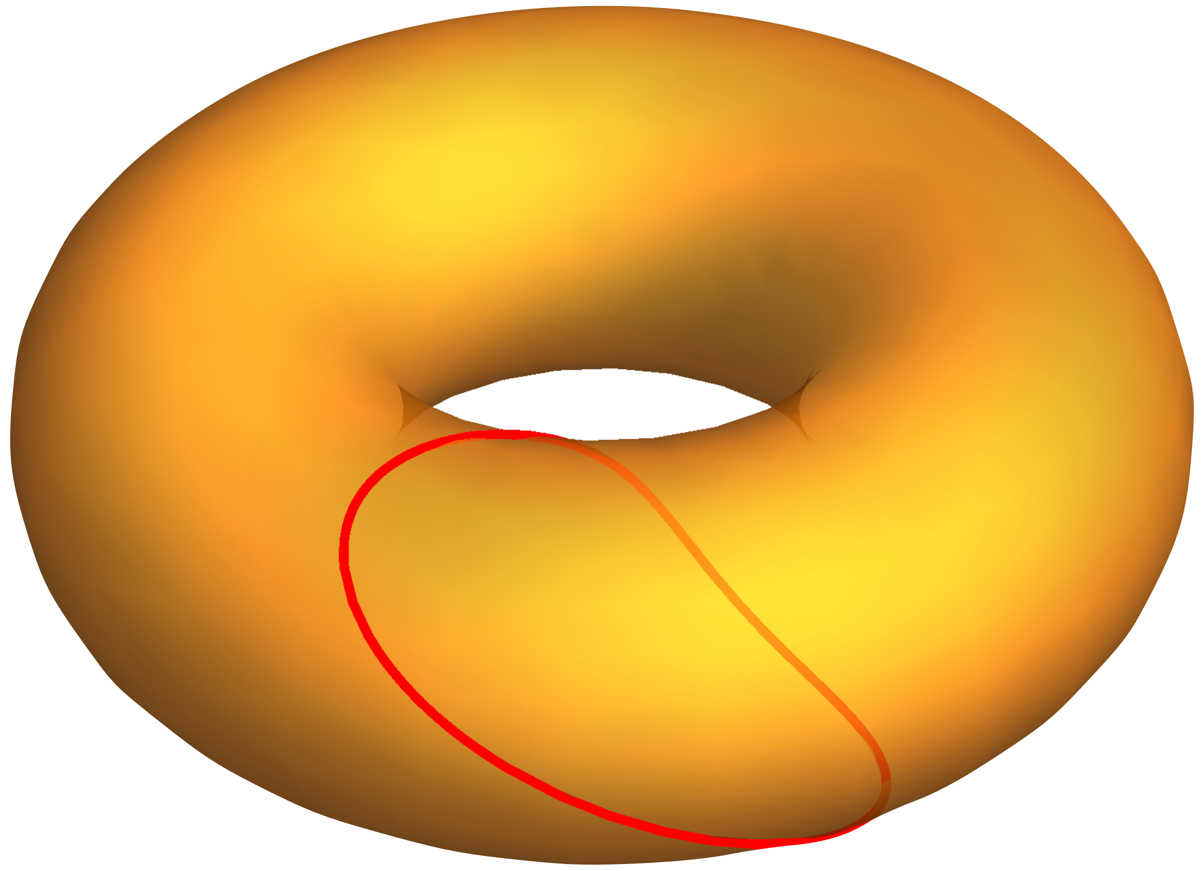

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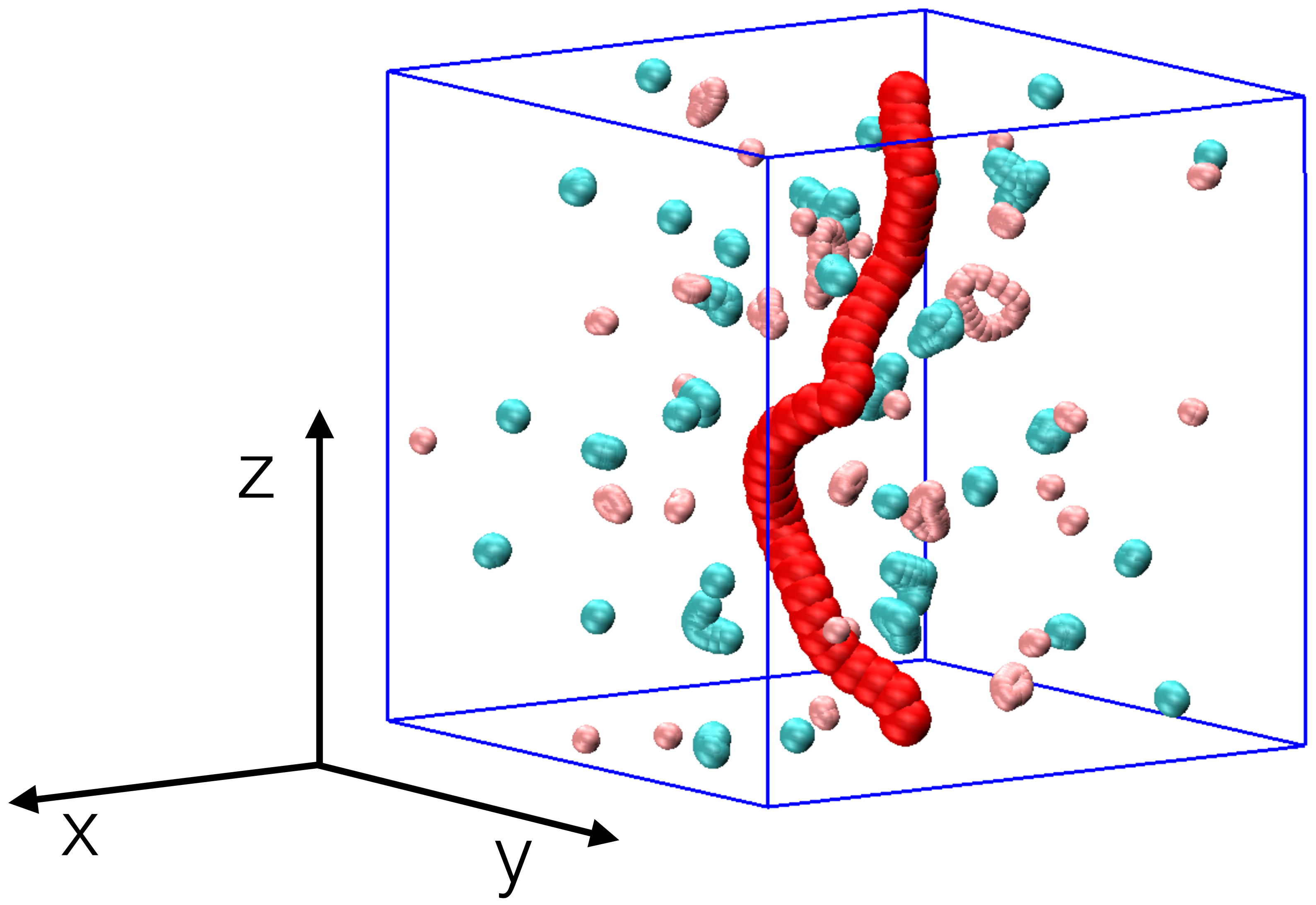
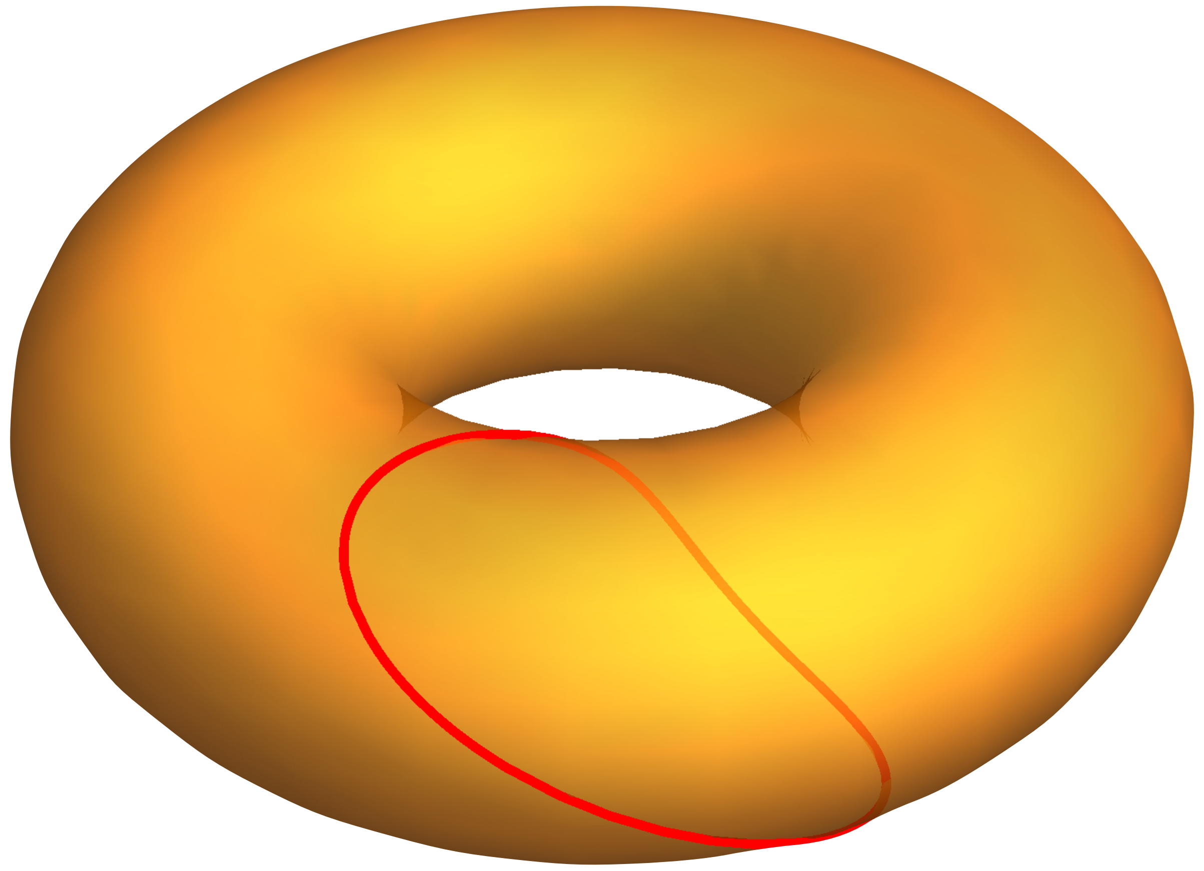
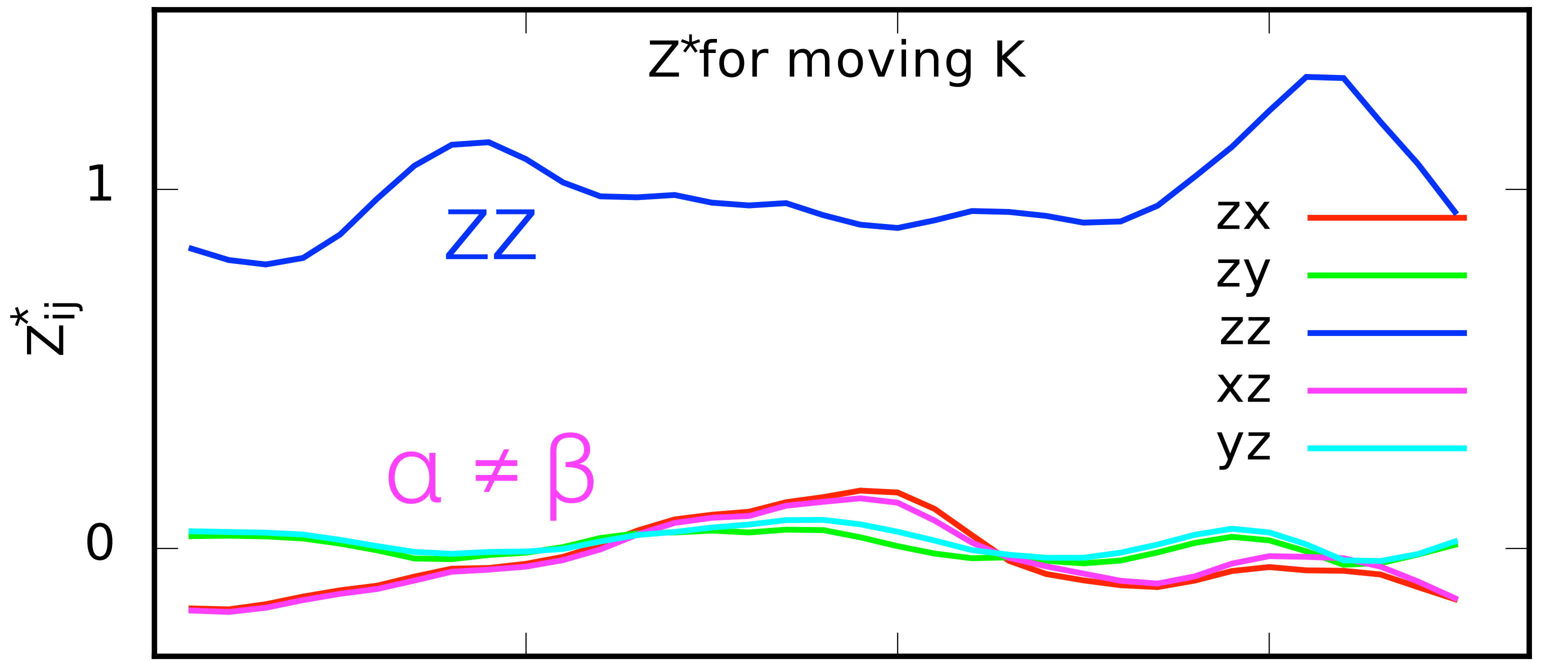
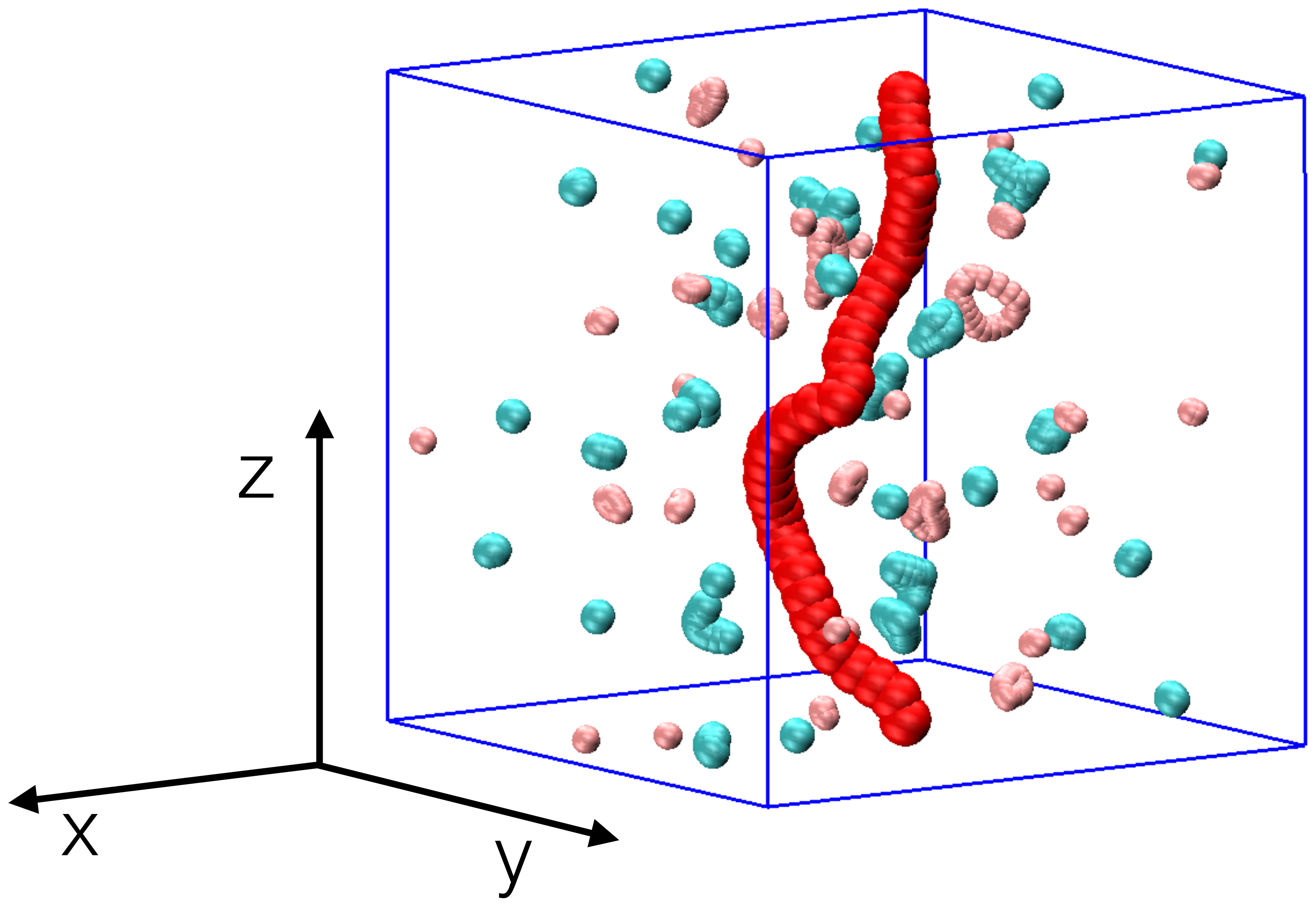


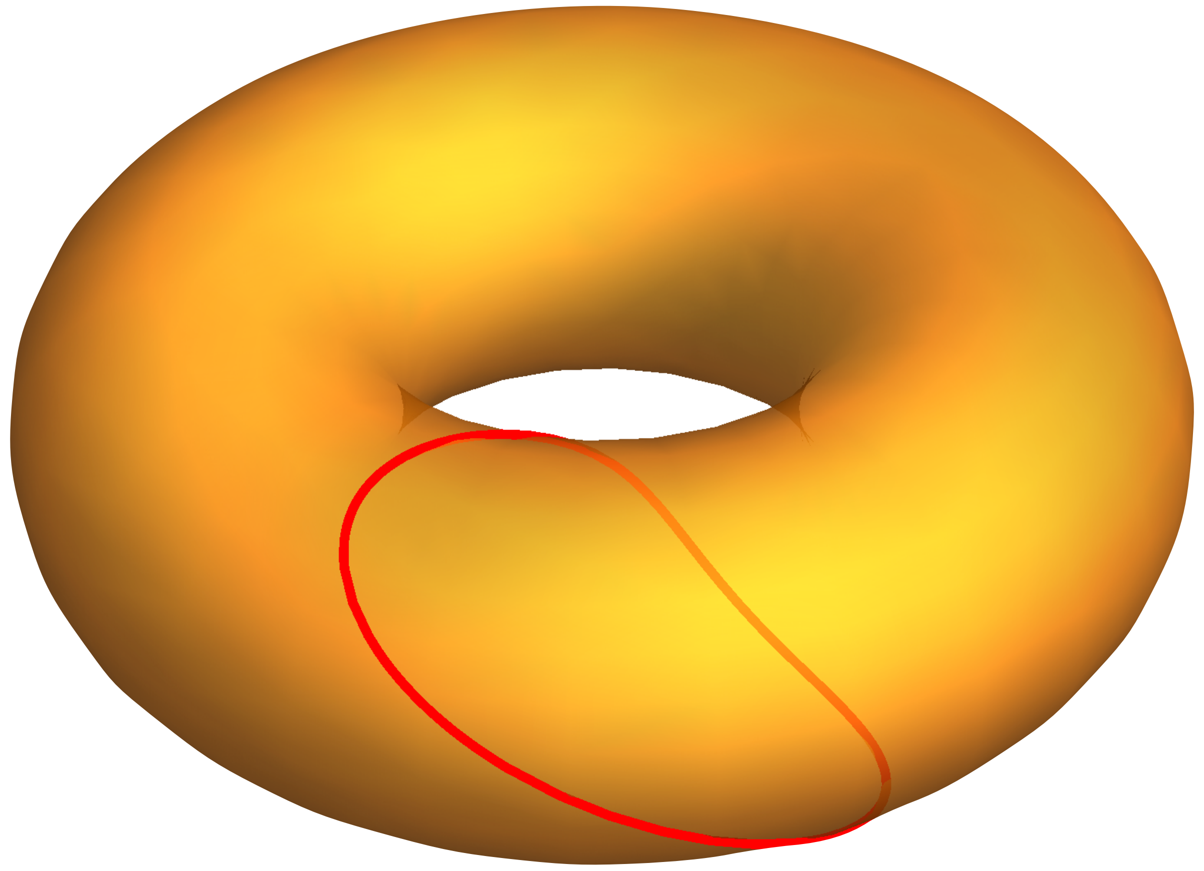


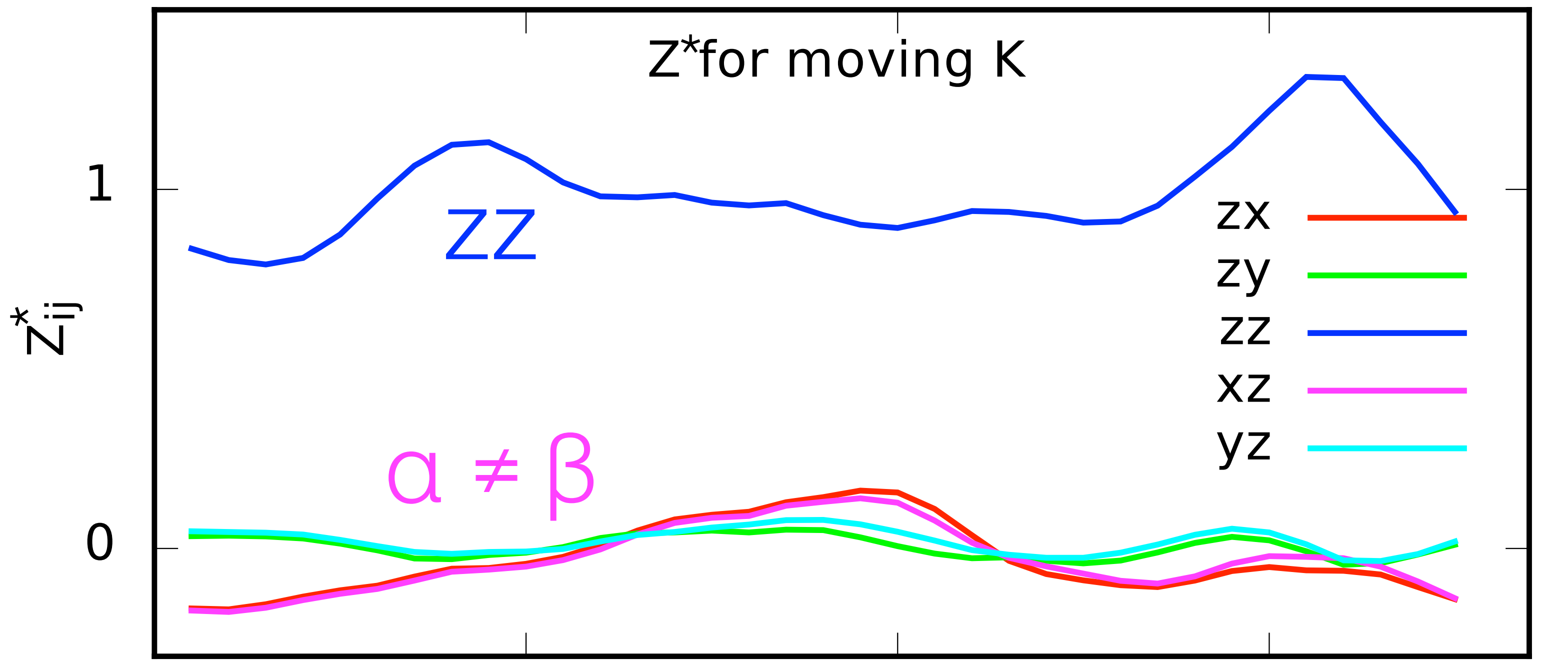


effective charge

a numerical experiment on molten KCl







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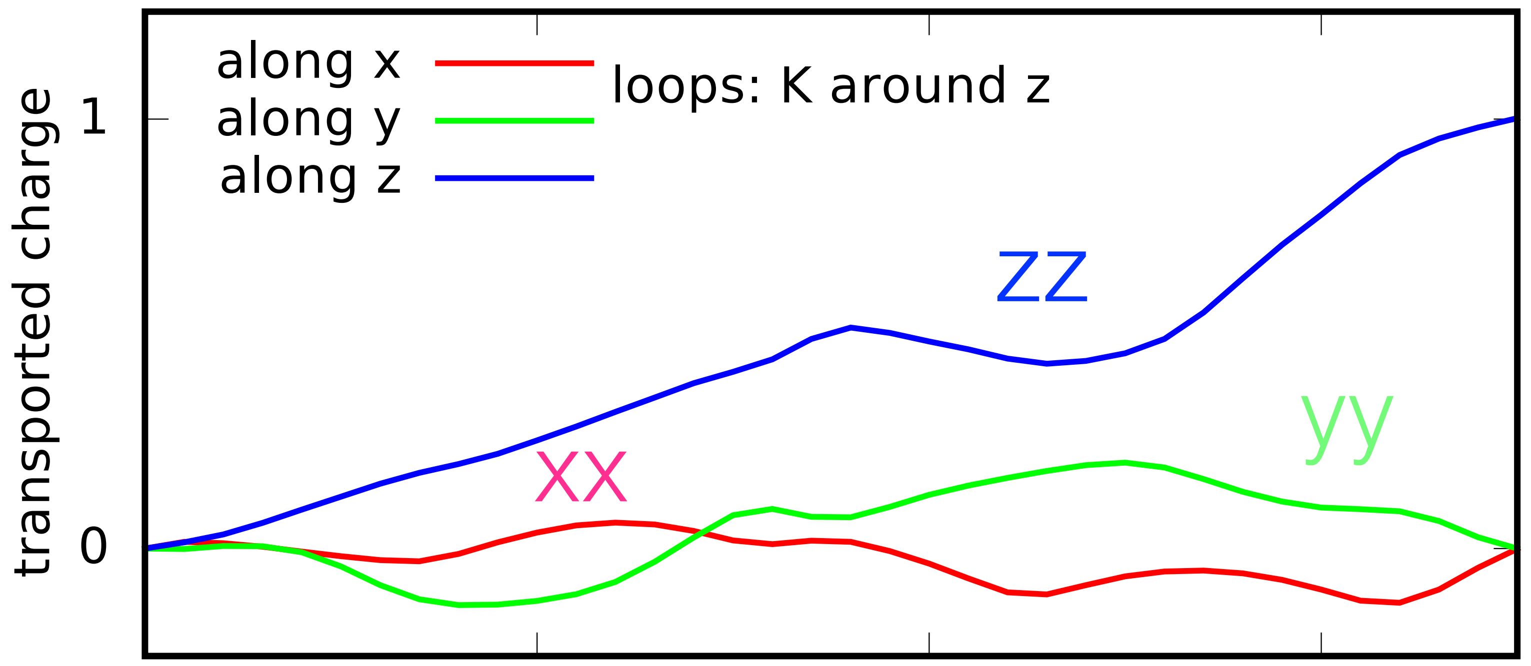
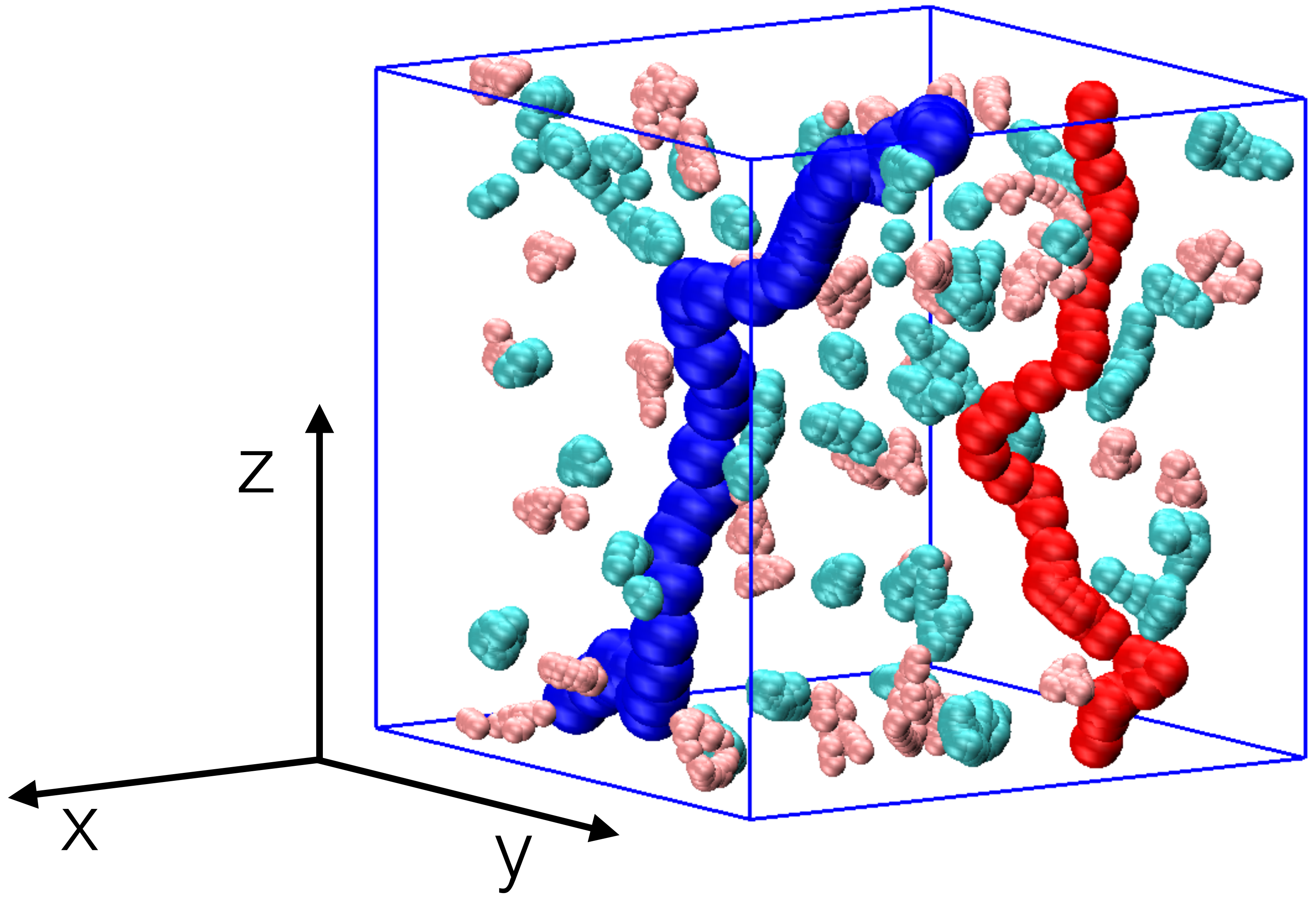
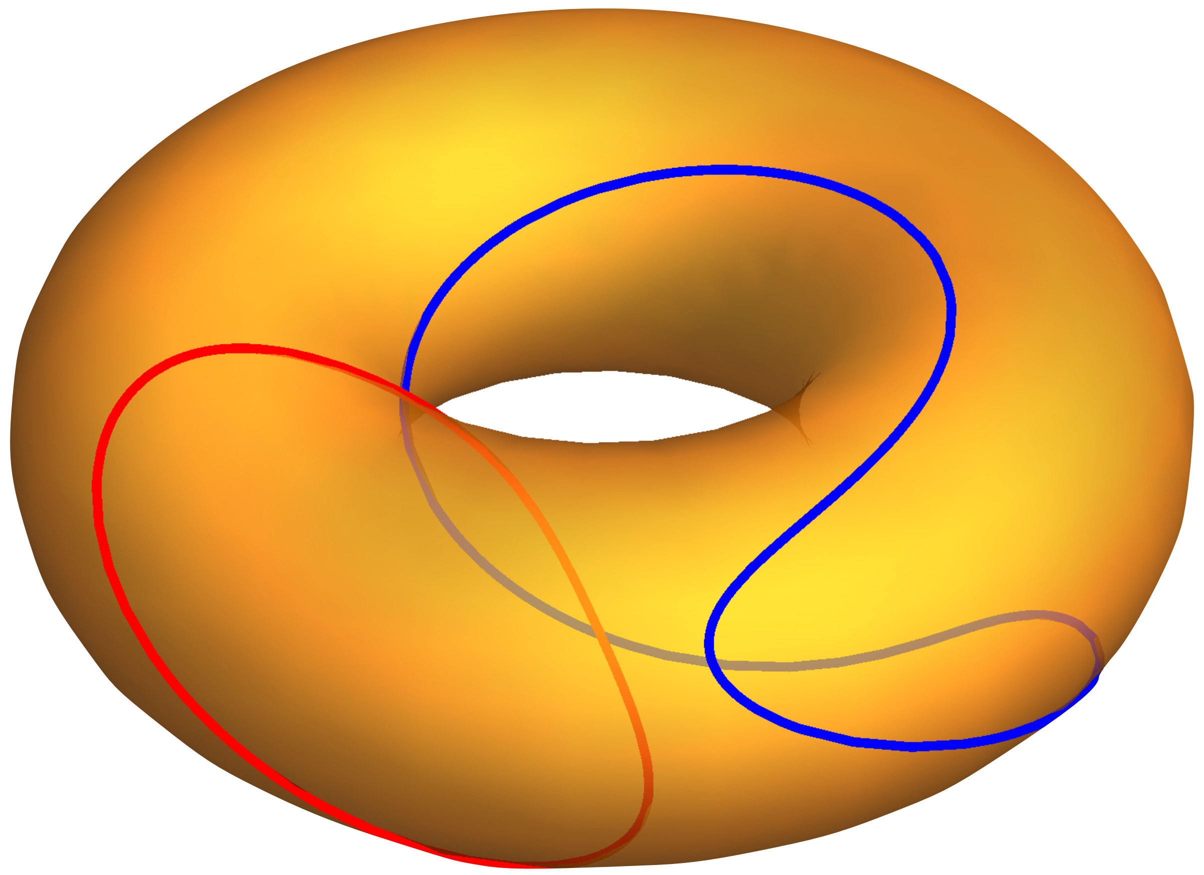


topological charge

qx = =-0.000(6); qy = 0.000(2); qz = 1.00(18)

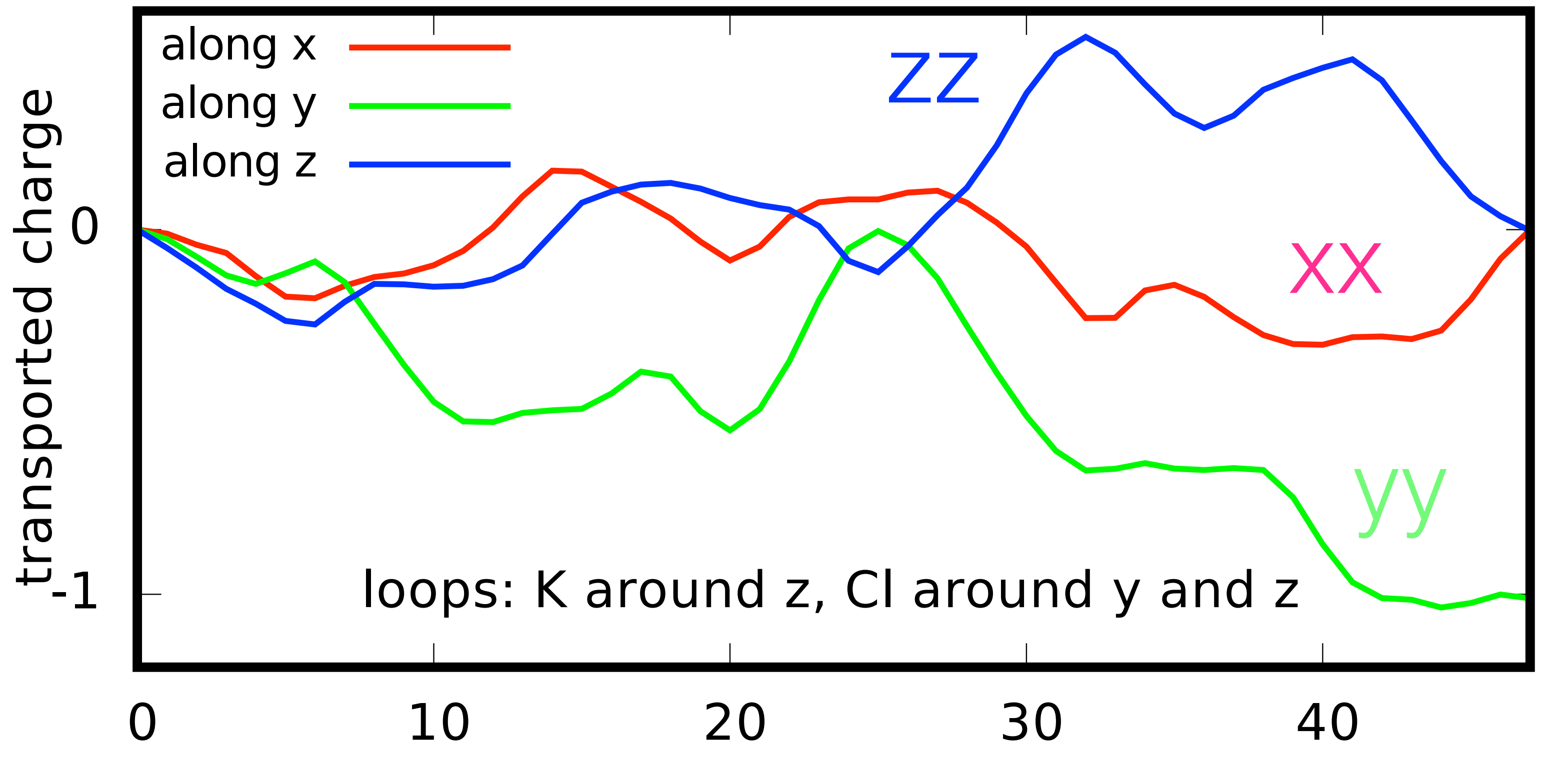
a numerical experiment on molten KCl





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

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



the charges transported by K and Cl
around z cancel exactly

currents from atomic oxidation numbers

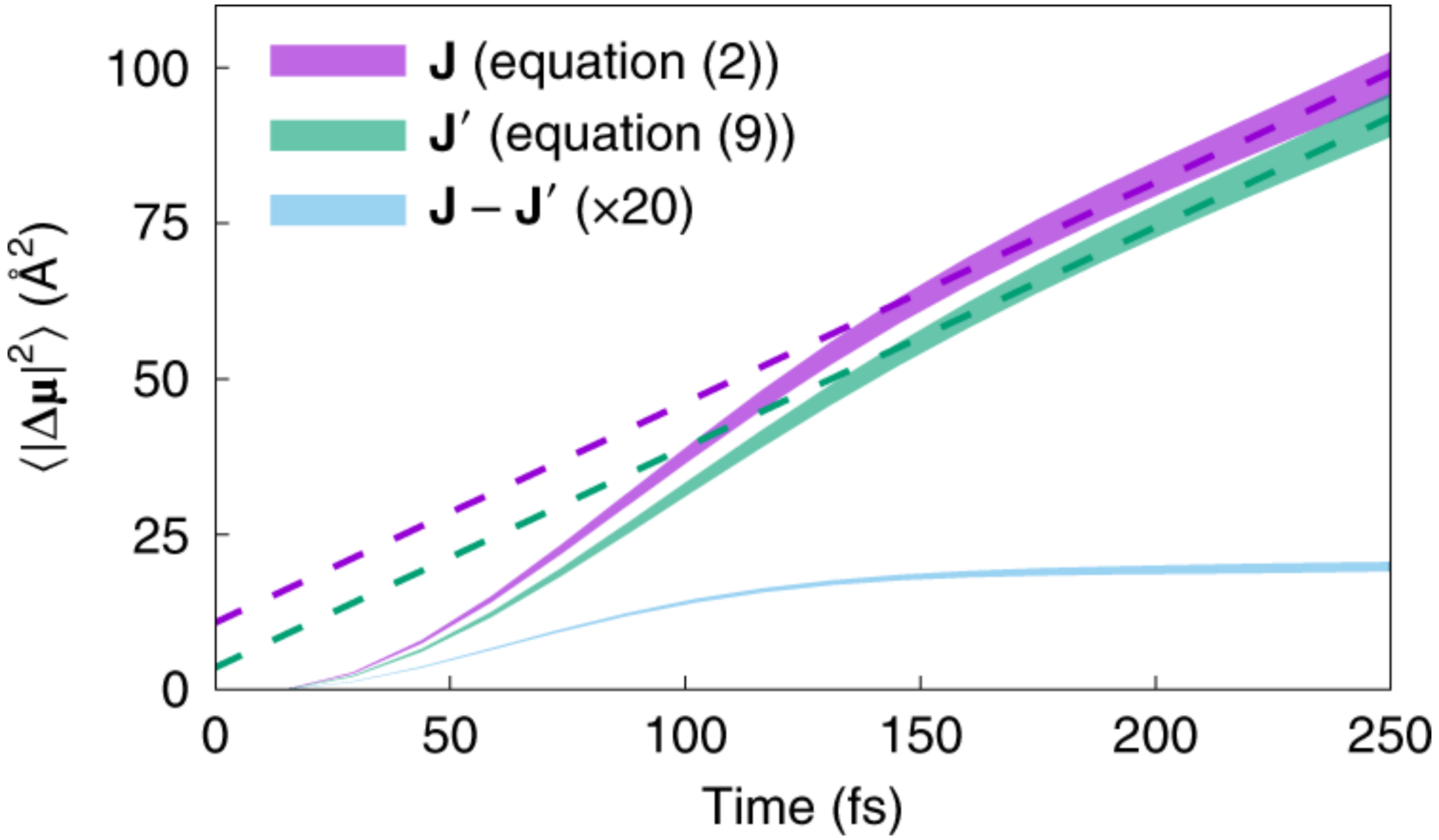
$$J_\alpha = \sum_{i\beta} Z^*_{i\alpha\beta} v_{i\beta} \qquad (2)$$

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

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

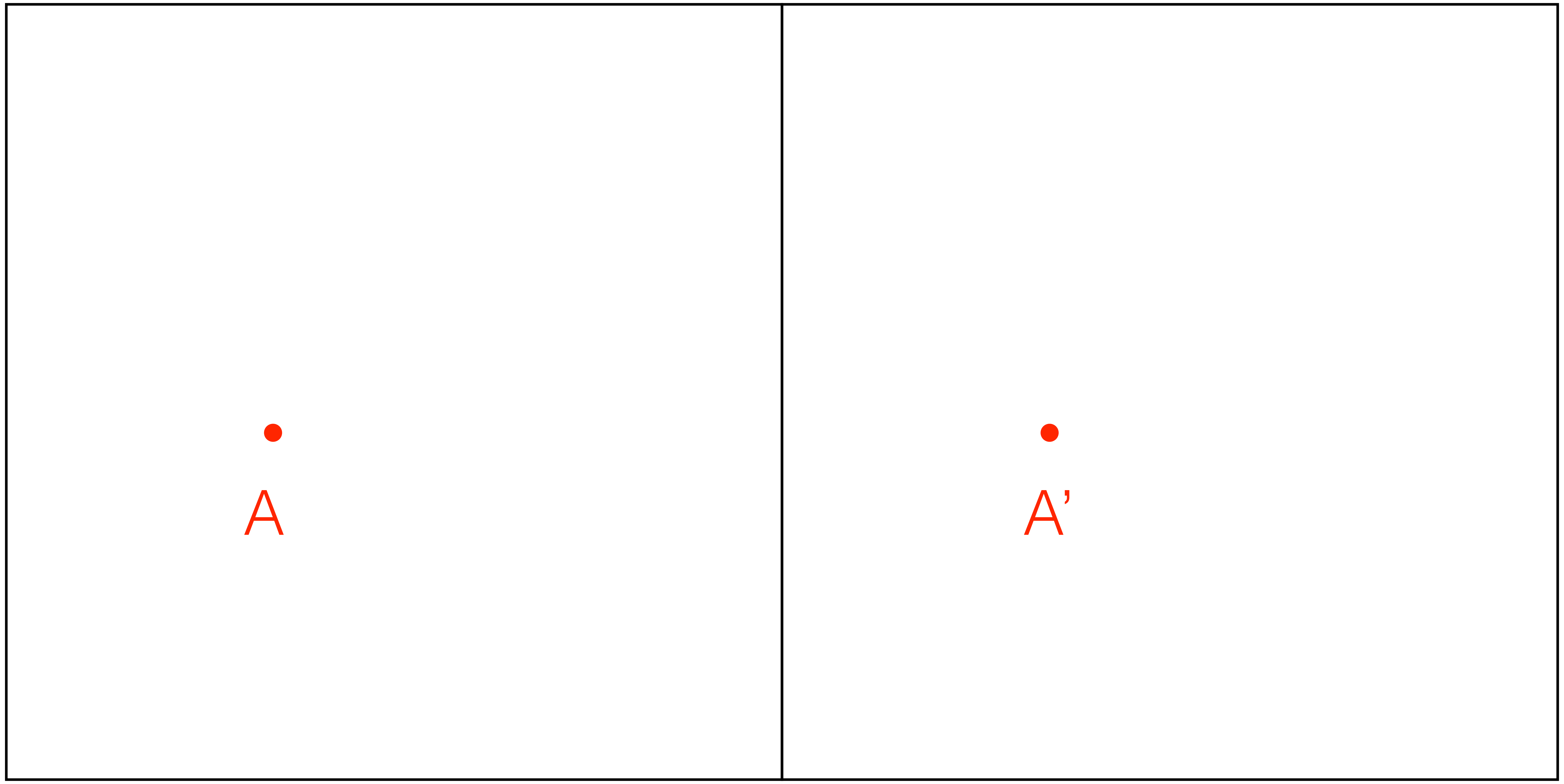
Topological quantization and gauge invariance of charge transport in liquid insulators

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



$$\left\langle \left| \int_0^t \mathbf{J}(t')dt' \right|^2 \right\rangle$$

breach of strong adiabaticity



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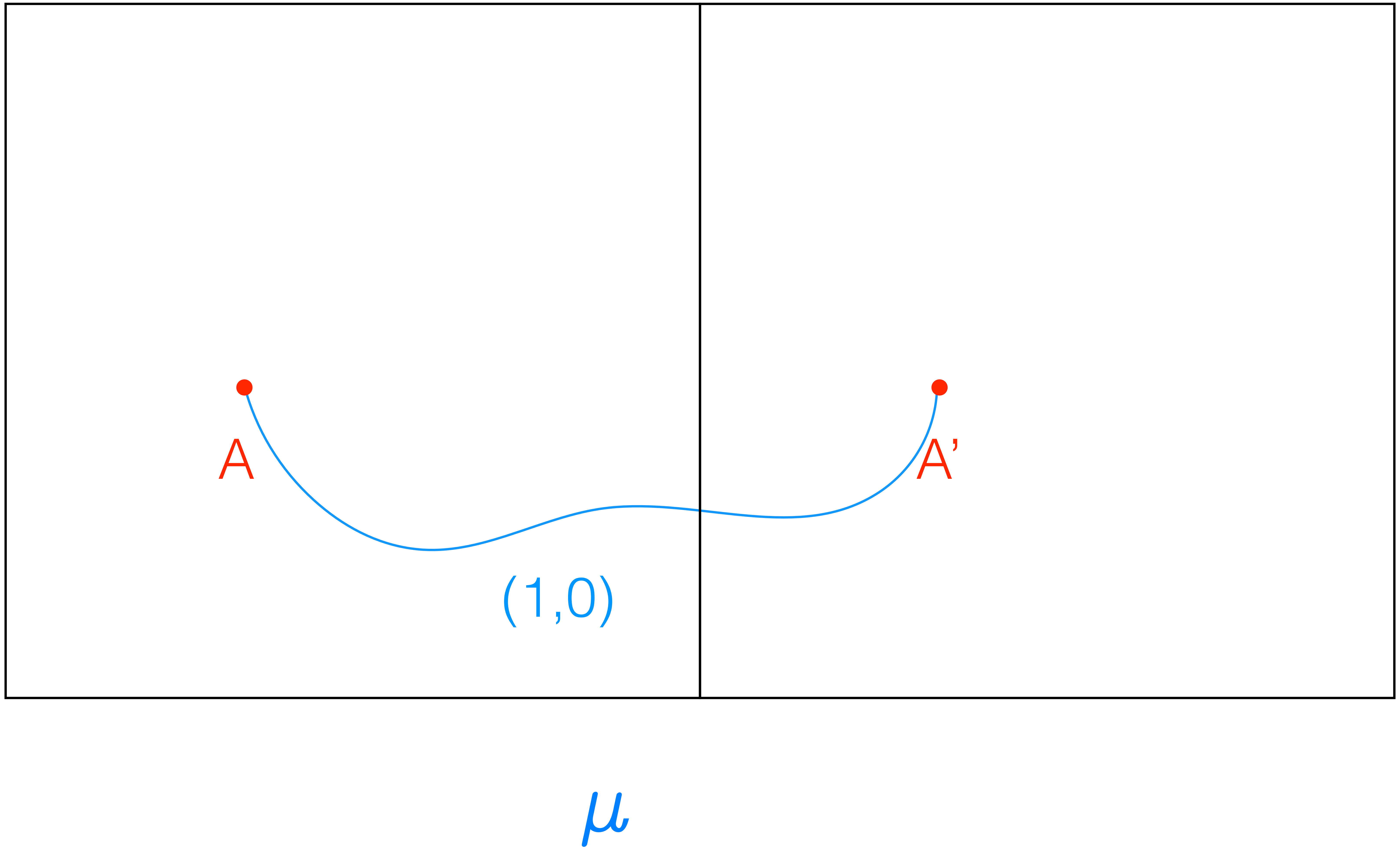

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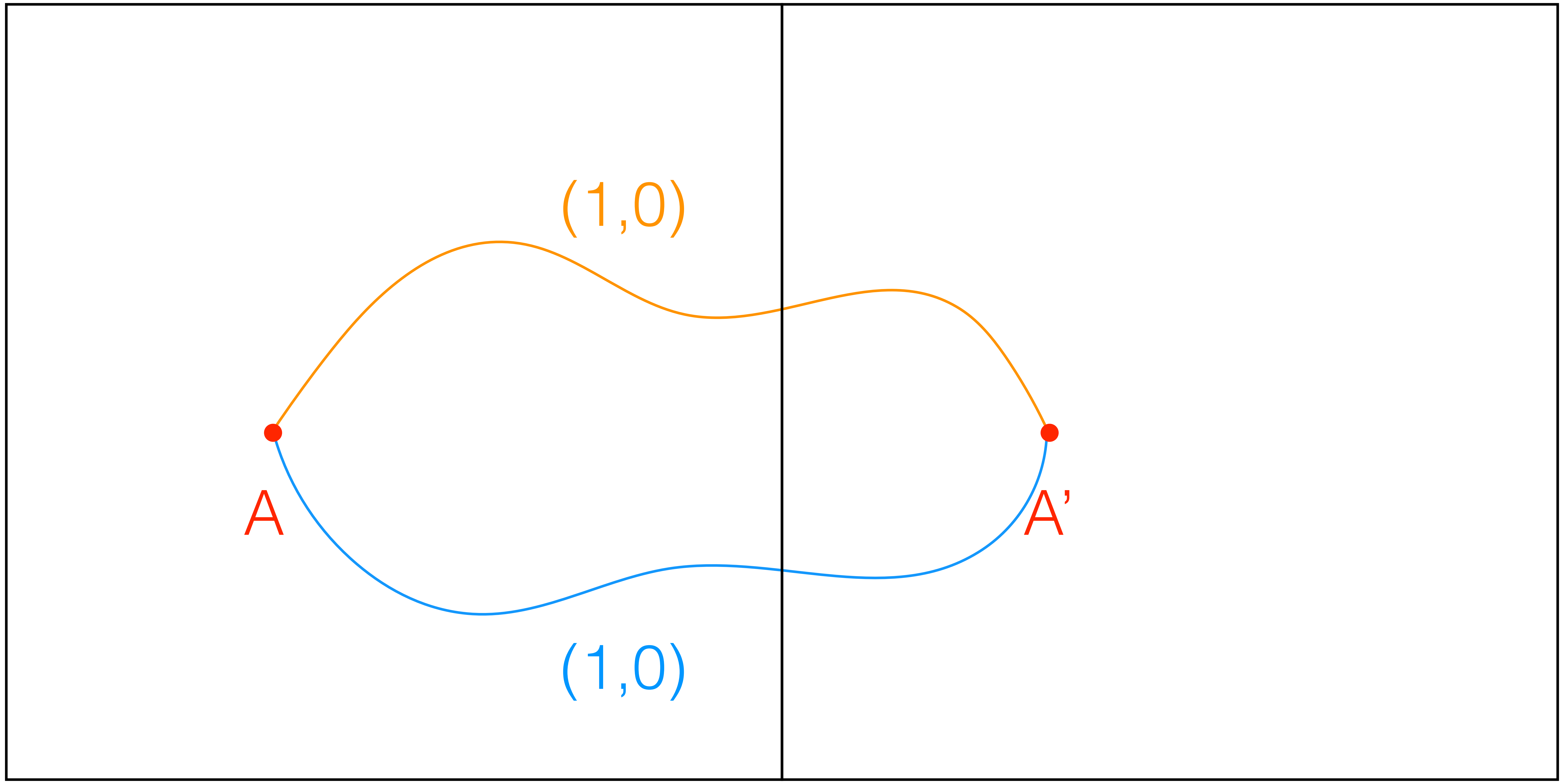
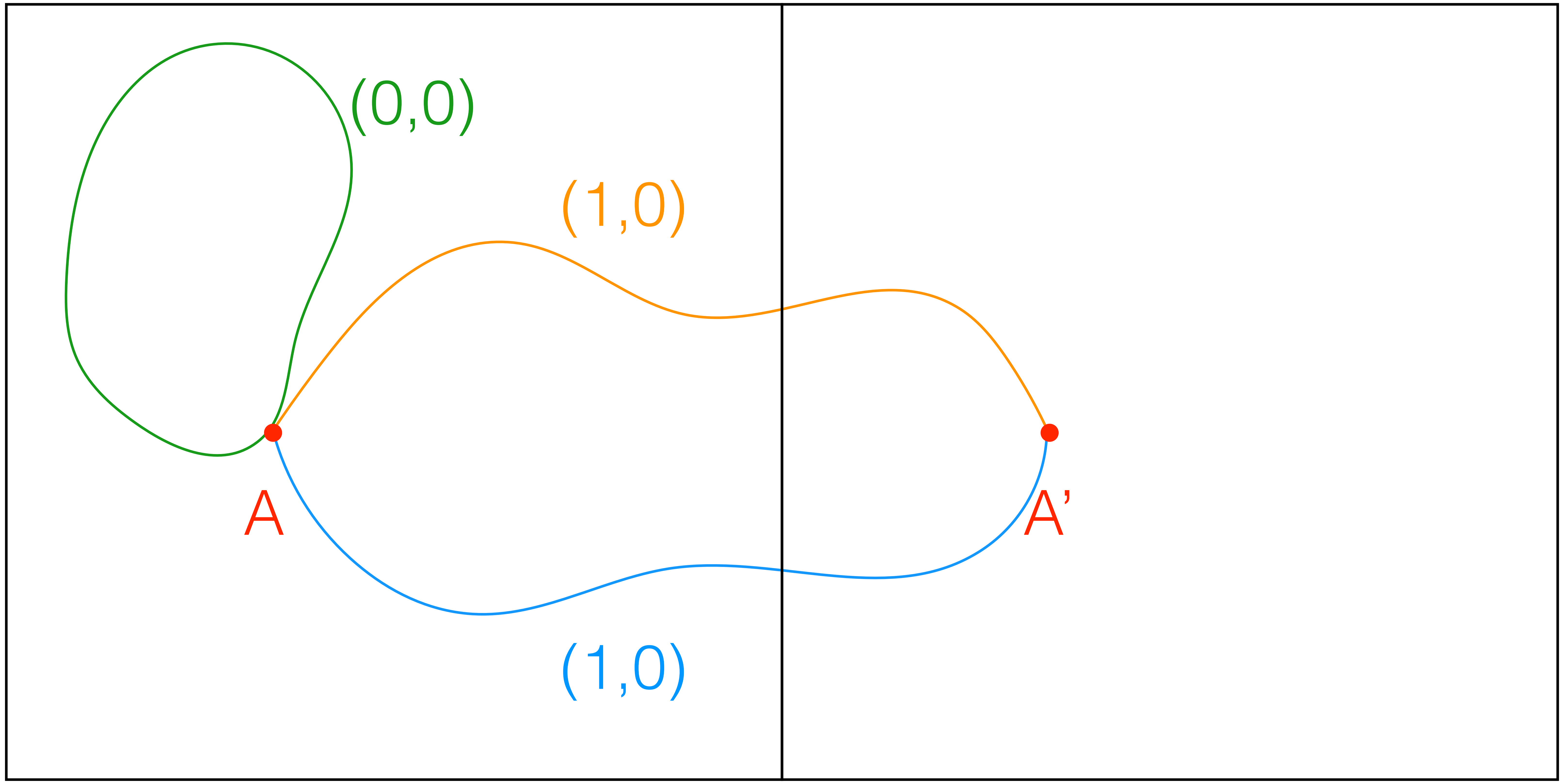


$$\mu = \mu^*$$

breach of strong adiabaticity



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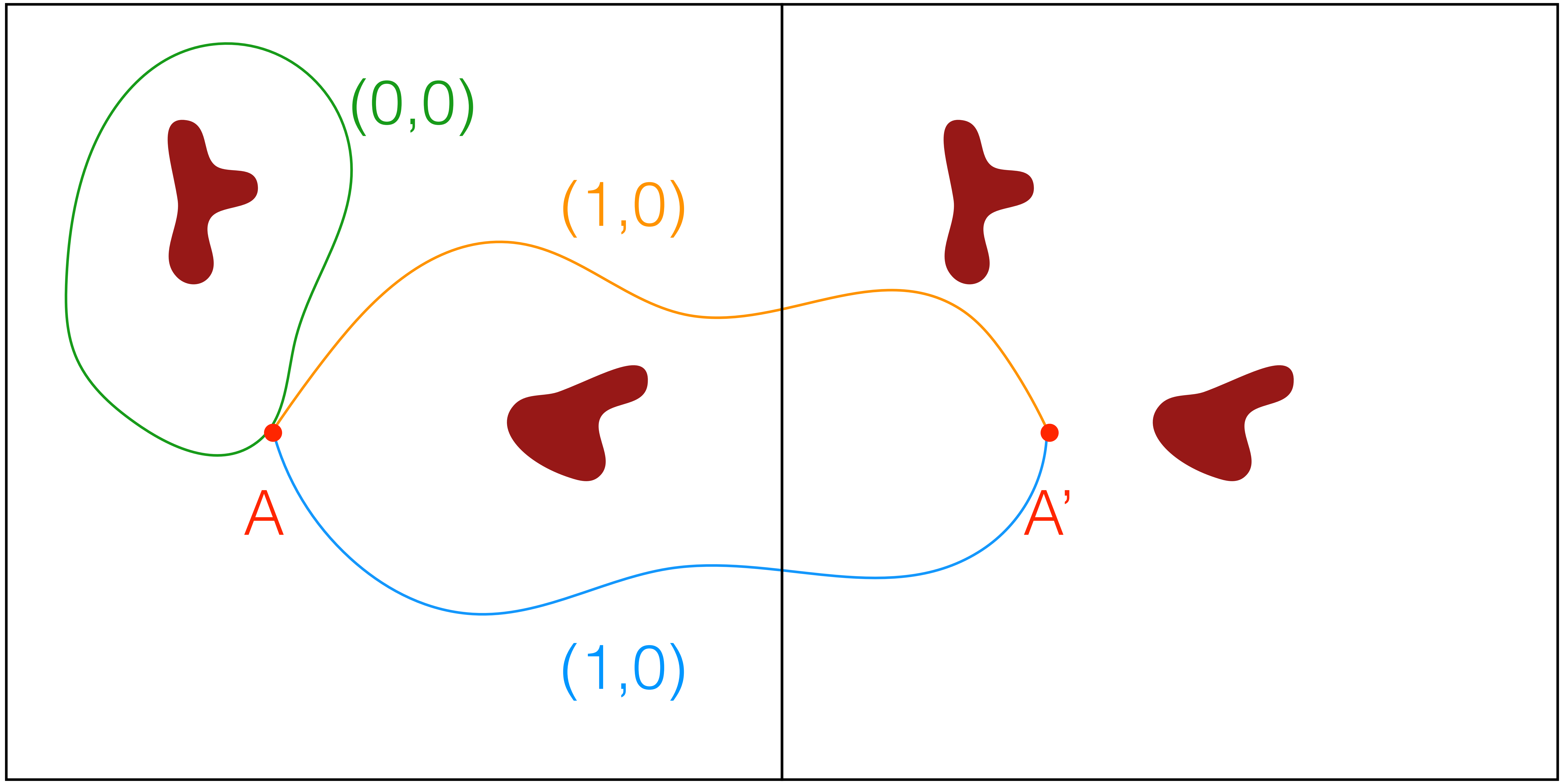

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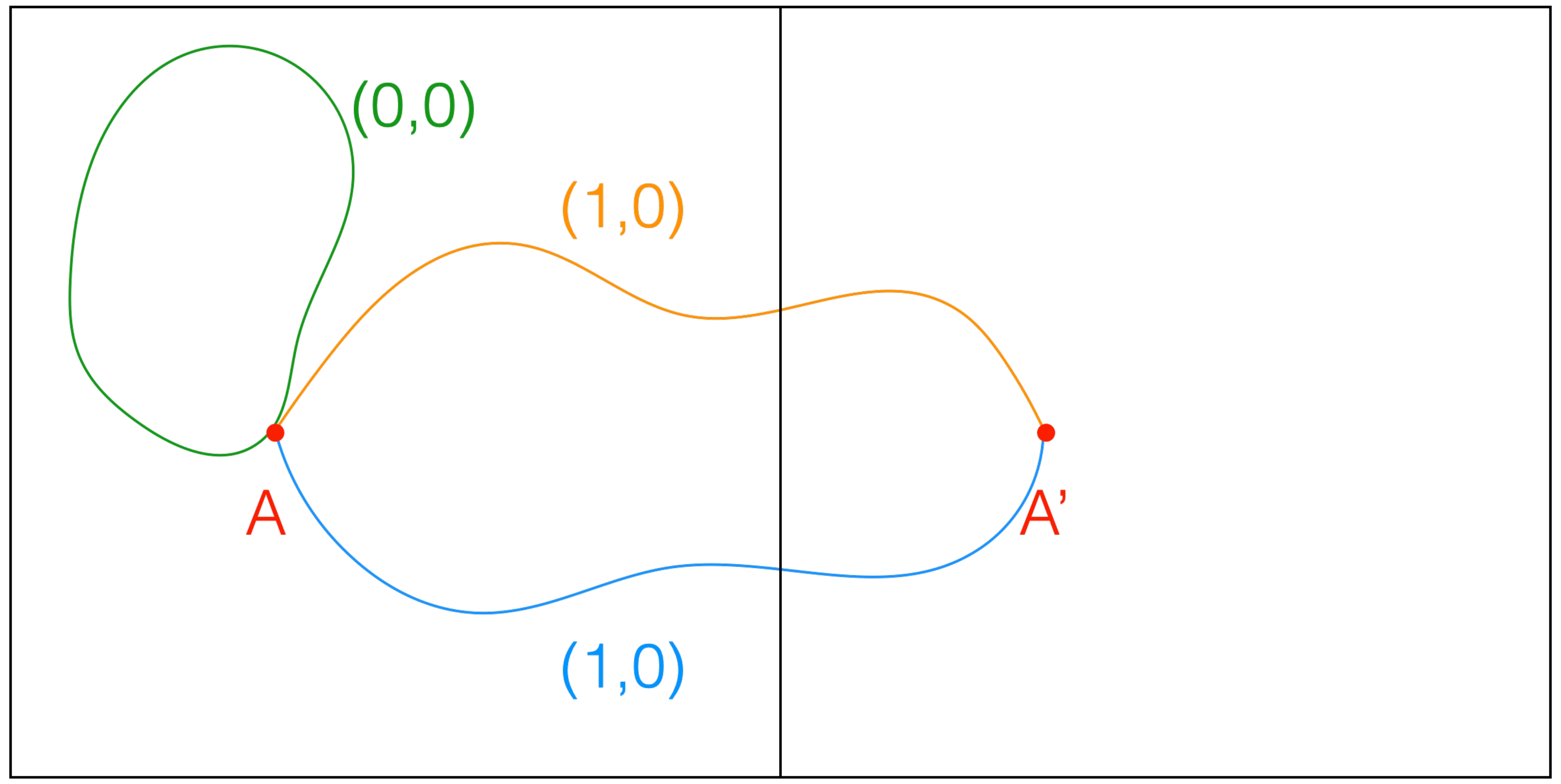
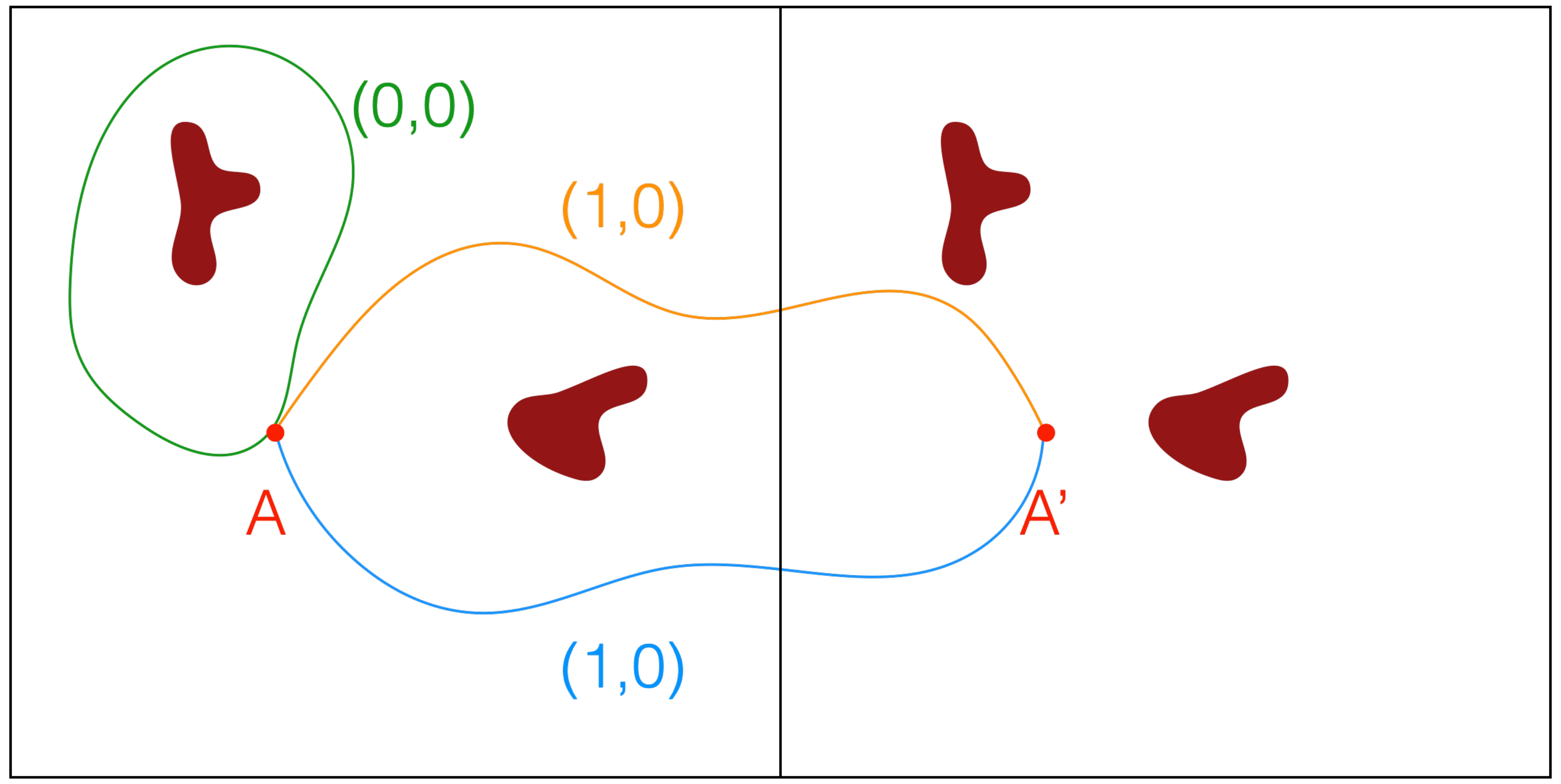
strongly adiabatic transport



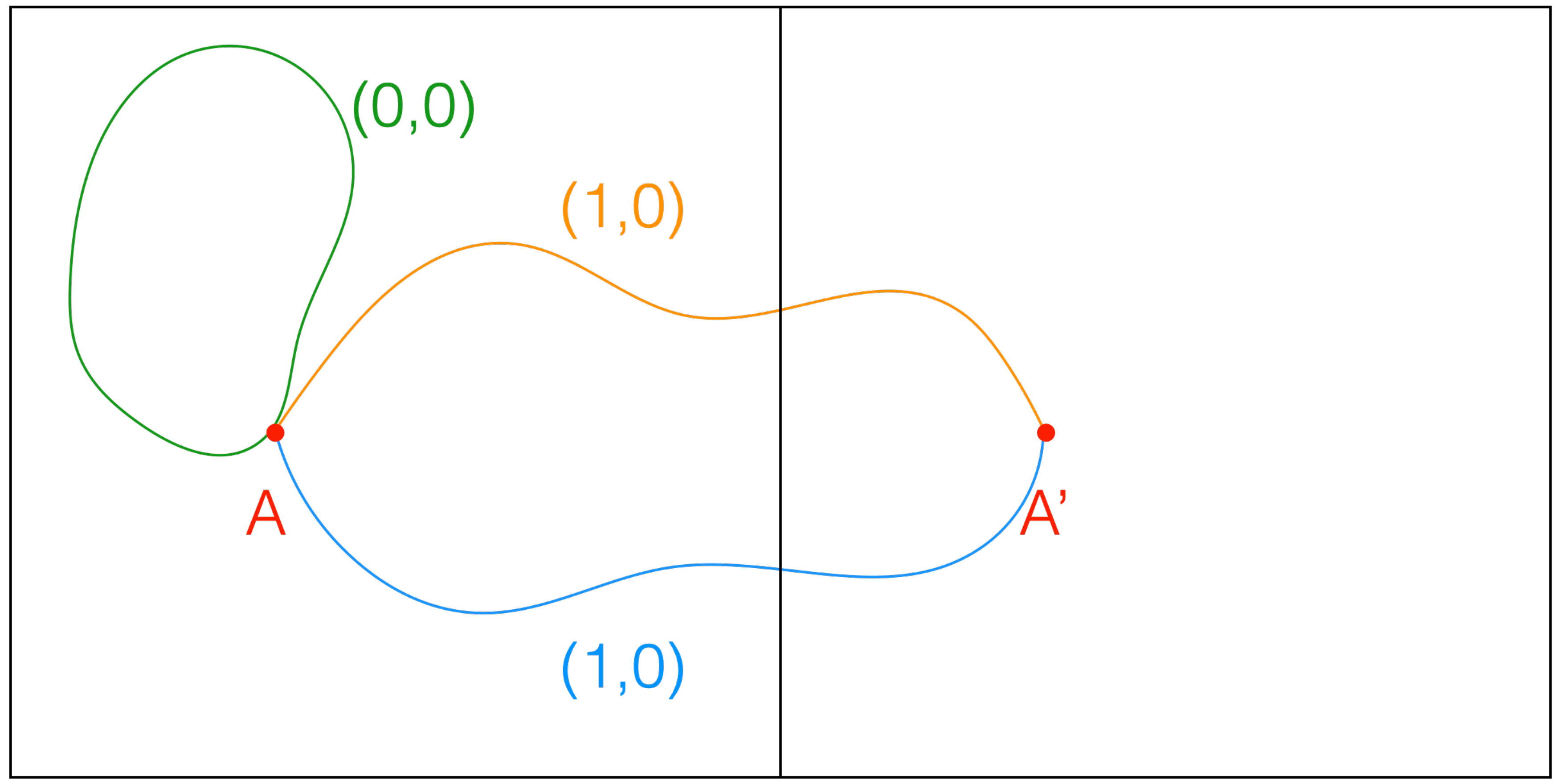
$$\mu = \mu^*$$
$$\mu = 0$$

weakly adiabatic transport



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

strongly adiabatic transport



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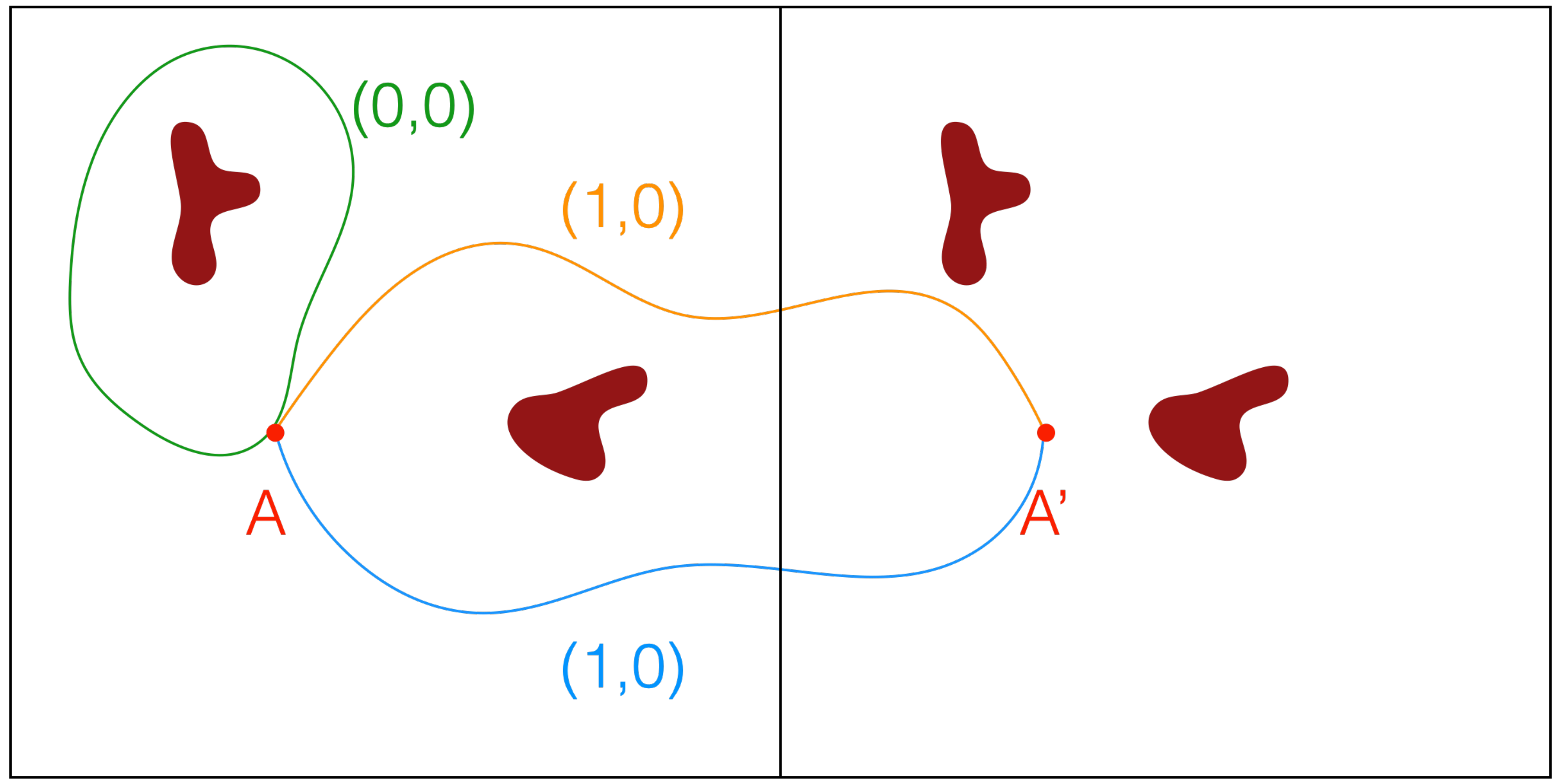
weakly adiabatic transport



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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

Wednesday, March 17, 2021
1:54PM - 2:06PM
Live

M20.00011: Oxidation states, Thouless' pumps, and nontrivial transport in nonstoichiometric electrolytes

Paolo Pegolo, Federico Grasselli, Stefano Baroni

conclusions

- conserved currents are intrinsically ill-defined at the atomic scale;
- conservation and extensiveness make transport coefficients independent of the specific microscopic representation of the conserved densities and currents;
- this *gauge invariance* of transport coefficients makes it possible to compute thermal transport coefficients from DFT using equilibrium AIMD and the Green-Kubo formalism;
- topological quantisation of charge transport allows one to give a rigorous definition of the atomic oxidation states;
- gauge invariance and topological quantisation of charge transport make the electric conductivity of stoichiometry ionic conductors depend on the formal oxidation numbers of the ionic species, via the Green-Kubo formula;
- surprises are to be expected in non-stoichiometric ionic conductors.

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thanks to:


Aris Marcolongo


Loris Ercole


Riccardo Bertossa


Leyla Isaeva


Giuseppe Barbalinardo


Davide Donadio


Federico Grasselli


Paolo Pegolo


Davide Tisi

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

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nature COMMUNICATIONS

ARTICLE
https://doi.org/10.1038/s41467-019-11572-4 OPEN

Modeling heat transport in crystals and glasses from a unified lattice-dynamical approach

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PHYSICAL REVIEW X

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

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Phys. Rev. X **10**, 041031 – Published 12 November 2020

conclusions

- conserved currents are intrinsically ill-defined at the atomic scale;
- conservation and extensiveness make transport coefficients independent of the specific microscopic representation of the conserved densities and currents;
- this *gauge invariance* of transport coefficients makes it possible to compute thermal transport coefficients from DFT using equilibrium AIMD and the Green-Kubo formalism;
- topological quantisation of charge transport allows one to give a rigorous definition of the atomic oxidation states;
- gauge invariance and topological quantisation of charge transport make the electric conductivity of stoichiometry ionic conductors depend on the formal oxidation numbers of the ionic species, via the Green-Kubo formula.
- surprises are to be expected in non-stoichiometric ionic conductors