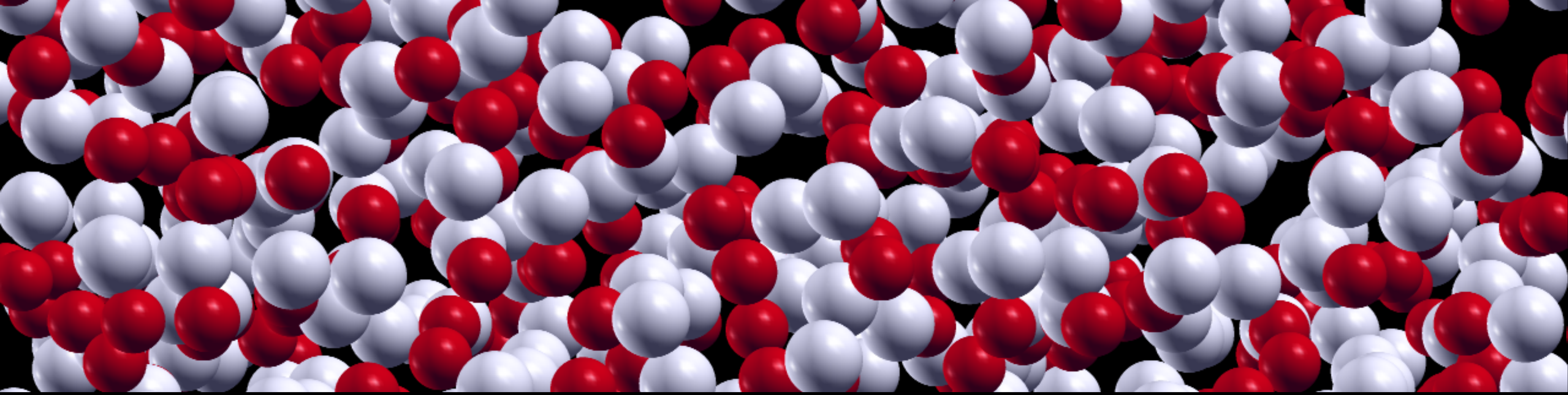
quantum topological effects in the transport properties of ionic conductors

Stefano Baroni
Scuola Internazionale Superiore di Studi Avanzati
Trieste — Italy

talk given at the Department of Chemistry, University of Cambridge, February 12, 2020



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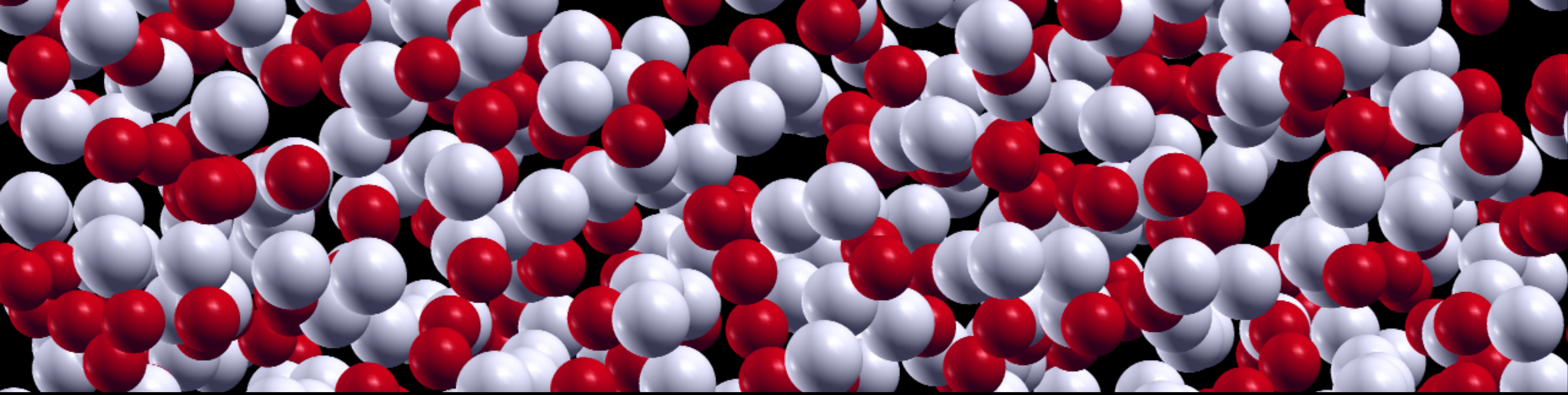
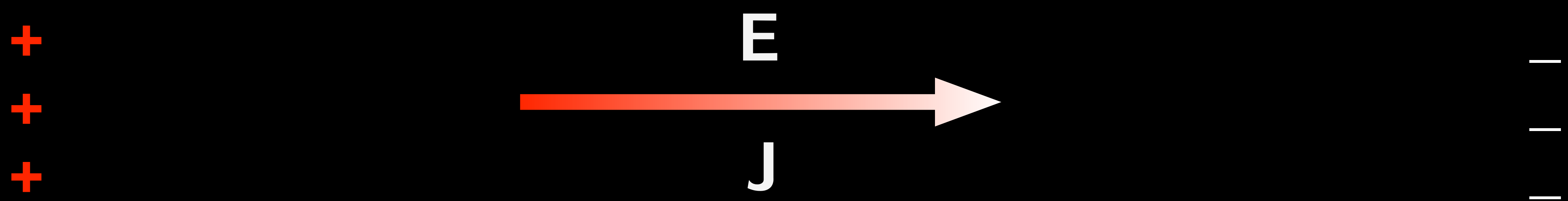
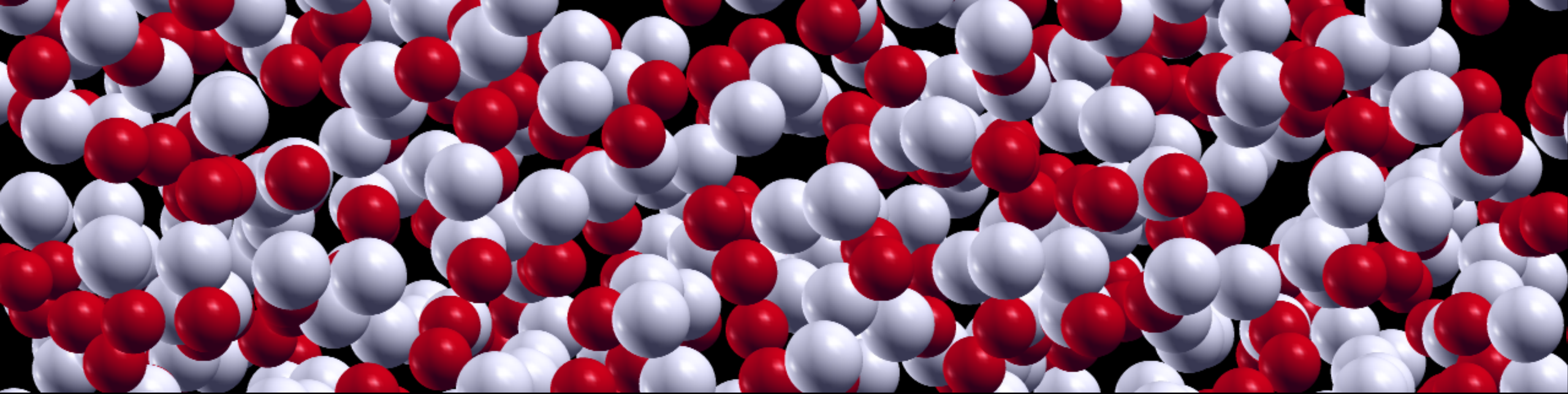
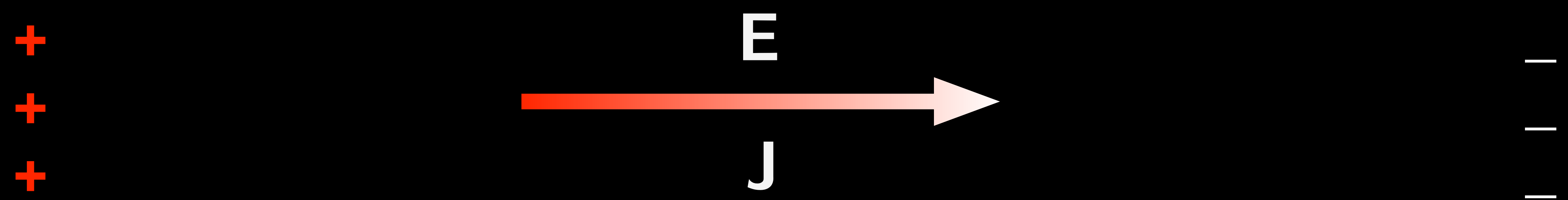




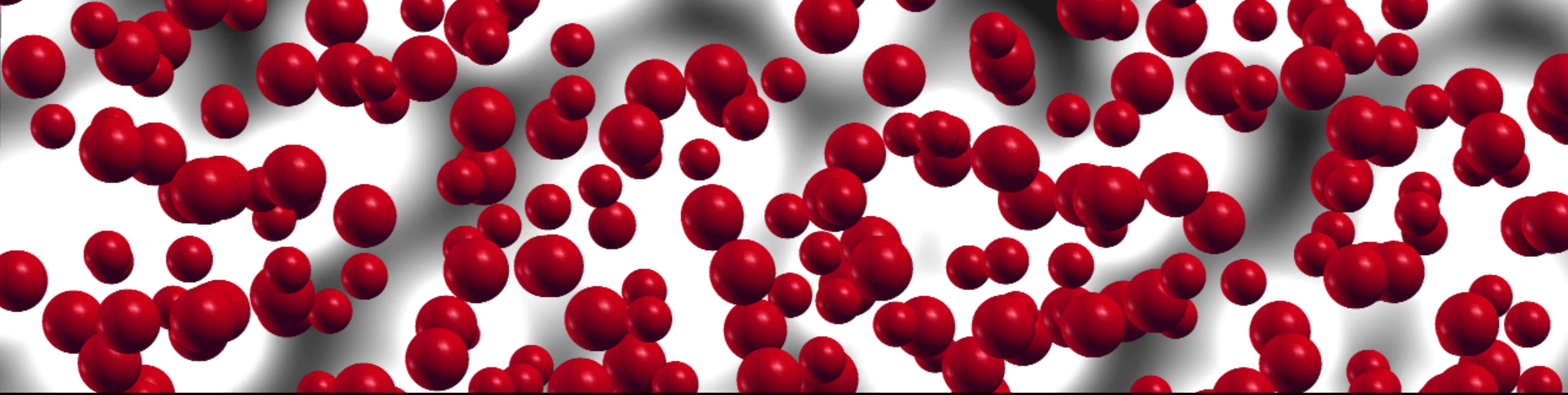
$$\mathbf{J} = \sigma \mathbf{E}$$





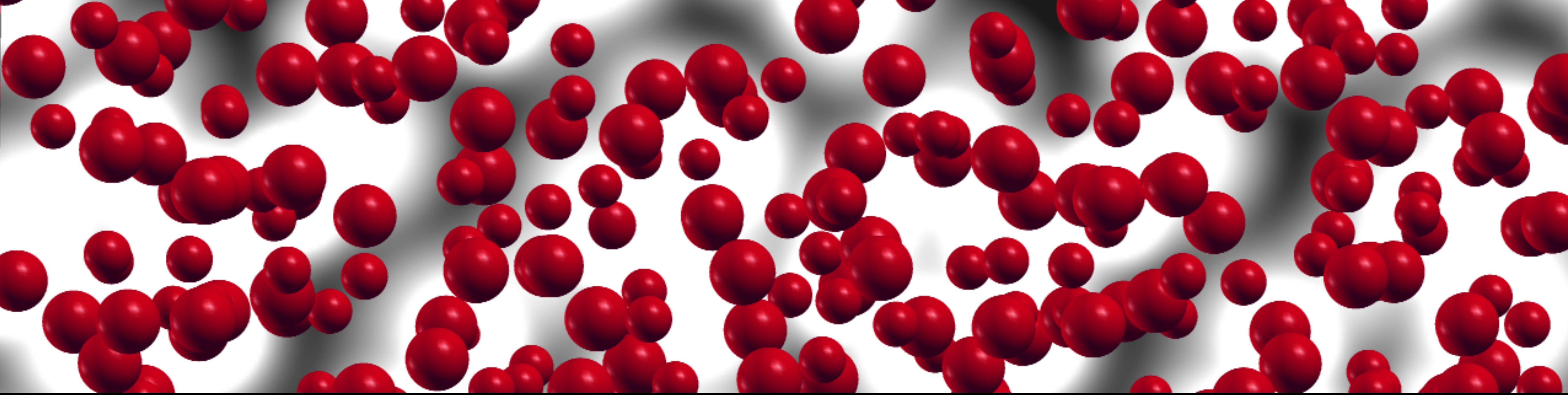
$$\mathbf{J} = \sigma \mathbf{E}$$

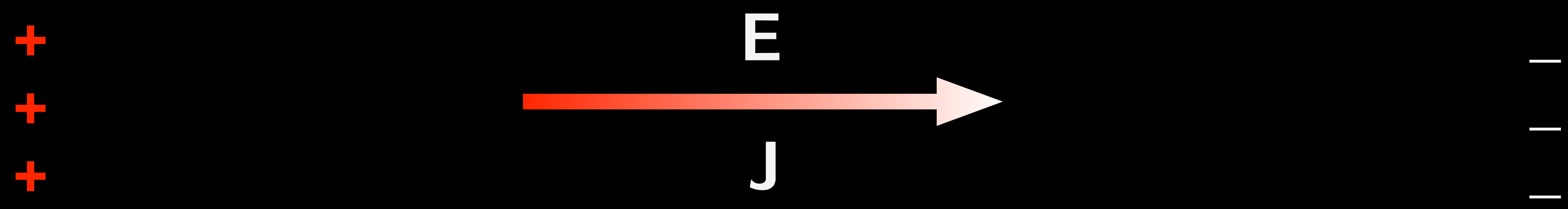
$$\mathbf{J} = \sum_i q_i \mathbf{v}_i$$



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

$$\mathbf{J} = ???$$





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

$$\mathbf{J} = \dot{\mathbf{P}} = \frac{1}{\Omega}\dot{\boldsymbol{\mu}}$$

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

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

the conundrum

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

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

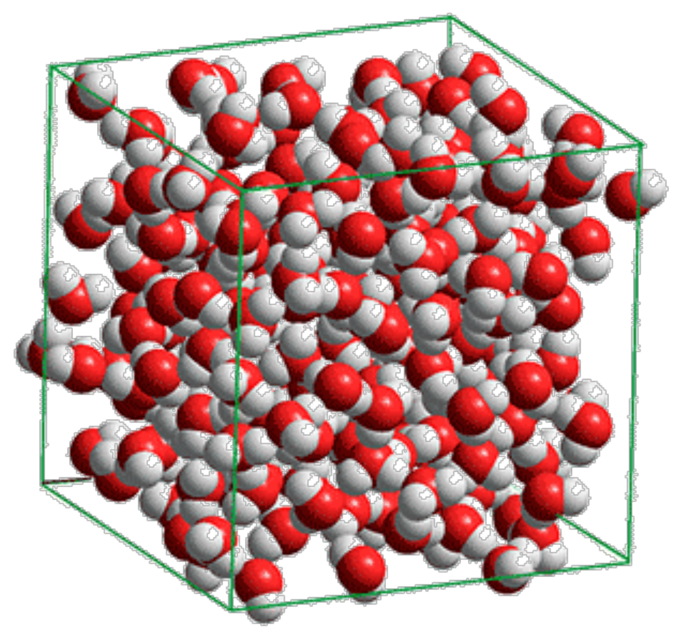
the conundrum

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

$$\neq 0$$

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

pure, undissociated
H_2O



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the conundrum

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$$= 0 \quad ???$$

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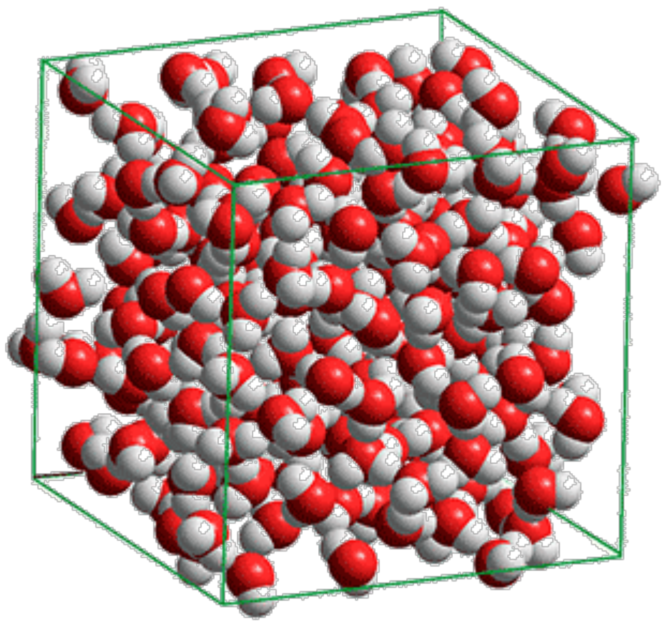
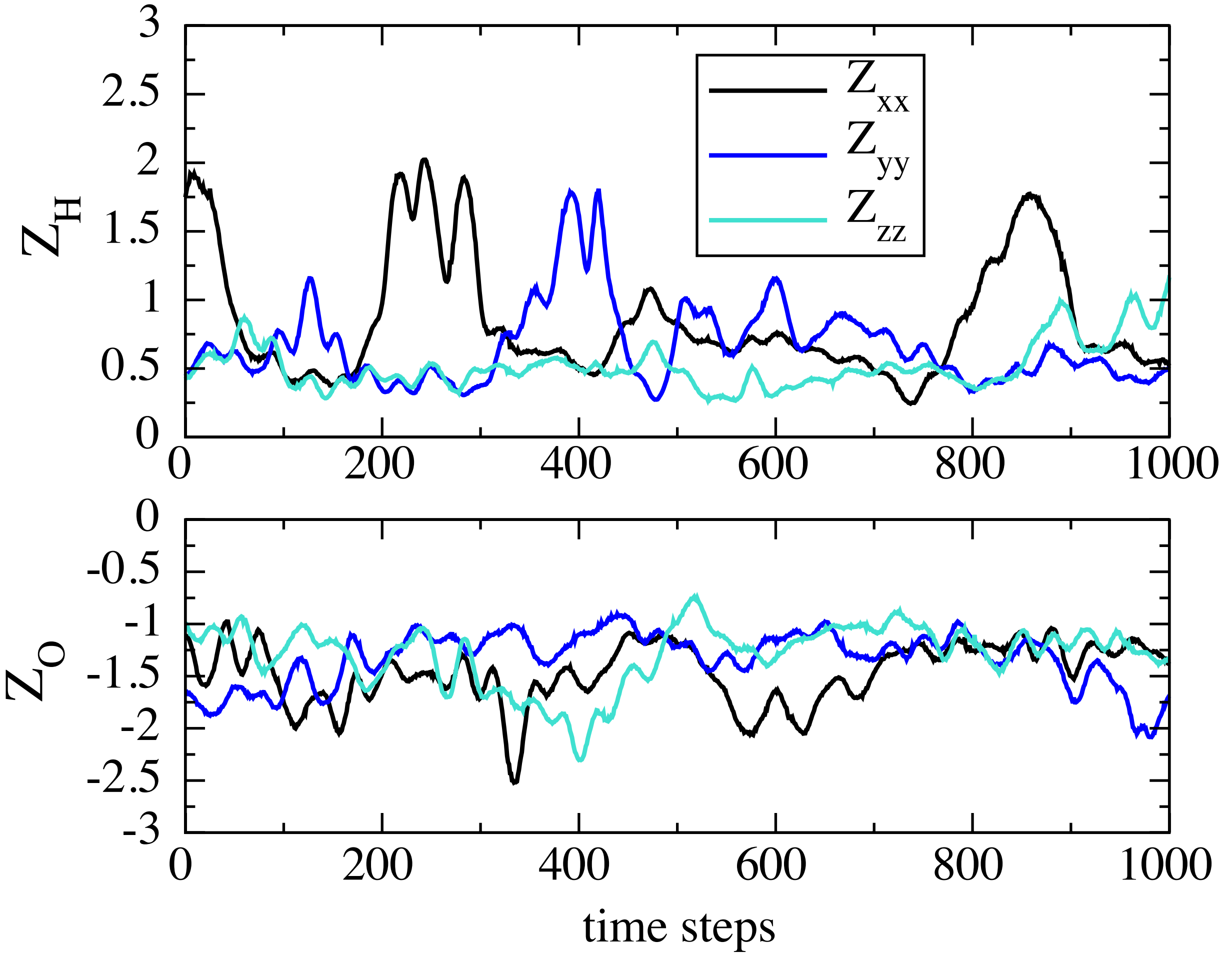


the conundrum

partially dissociated H_2O



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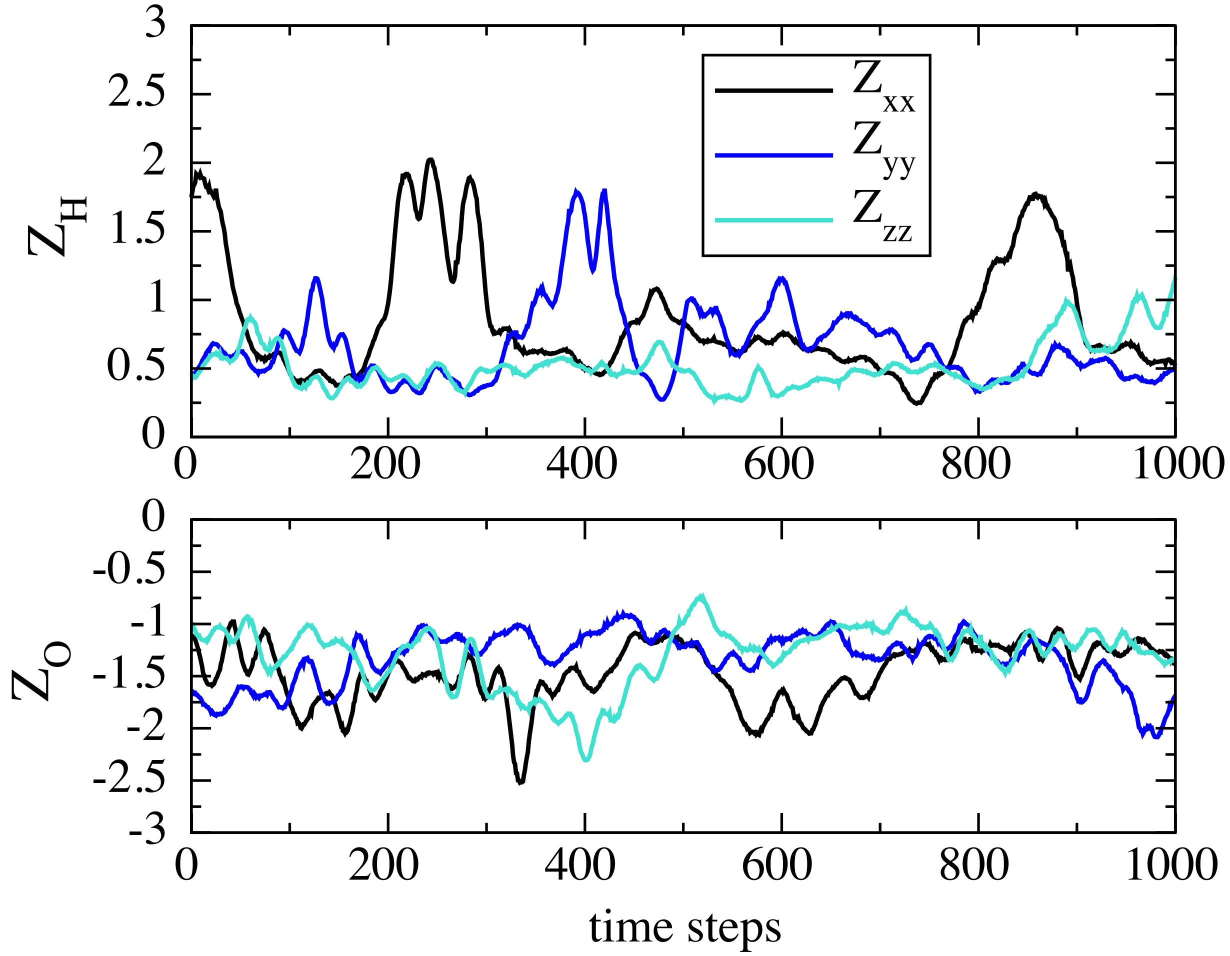

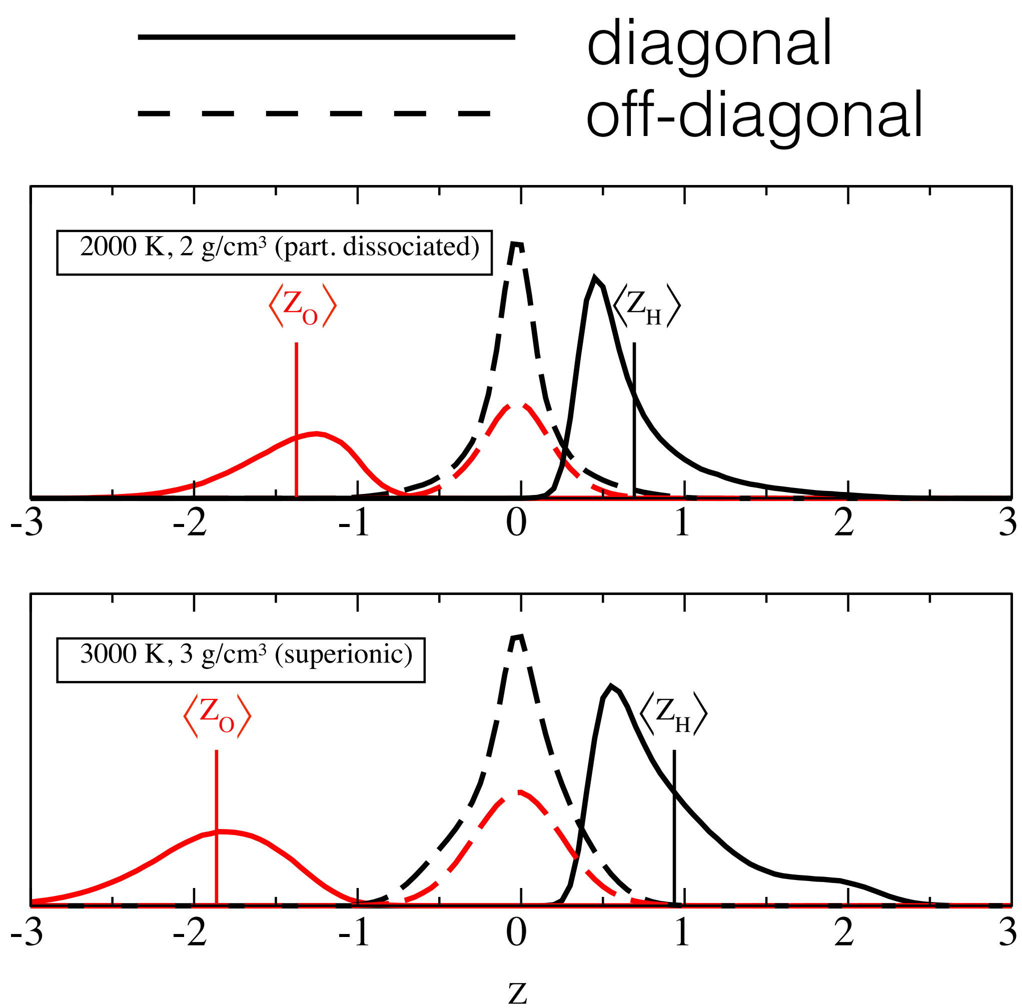

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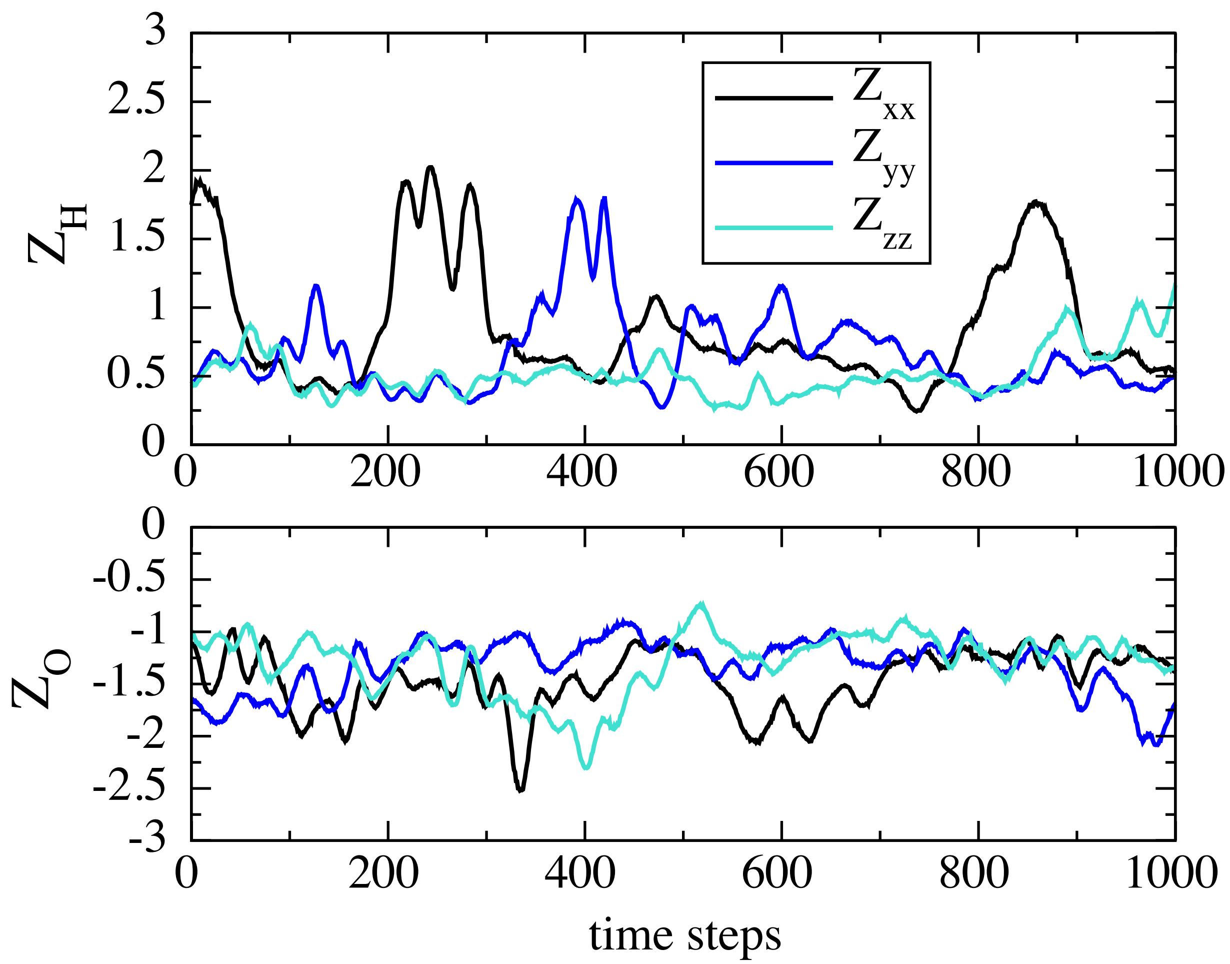
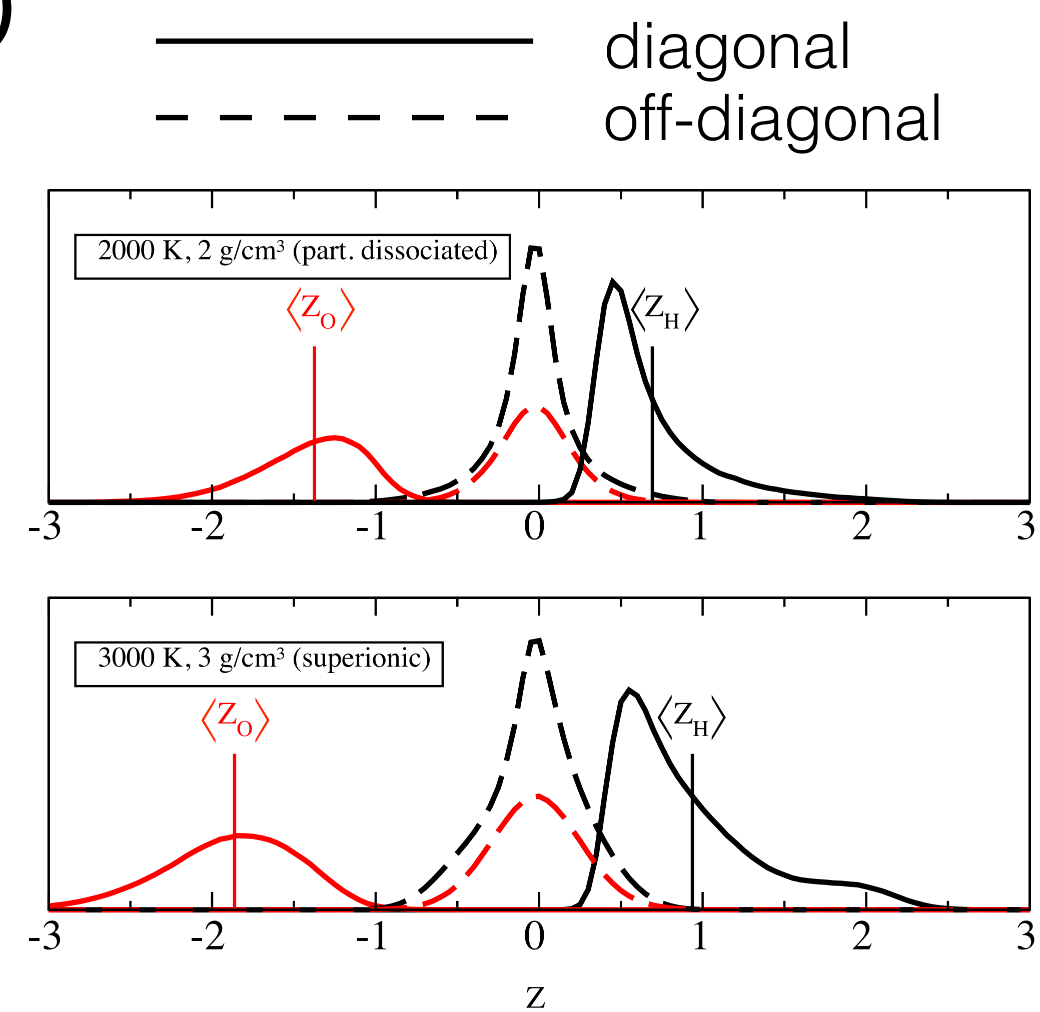
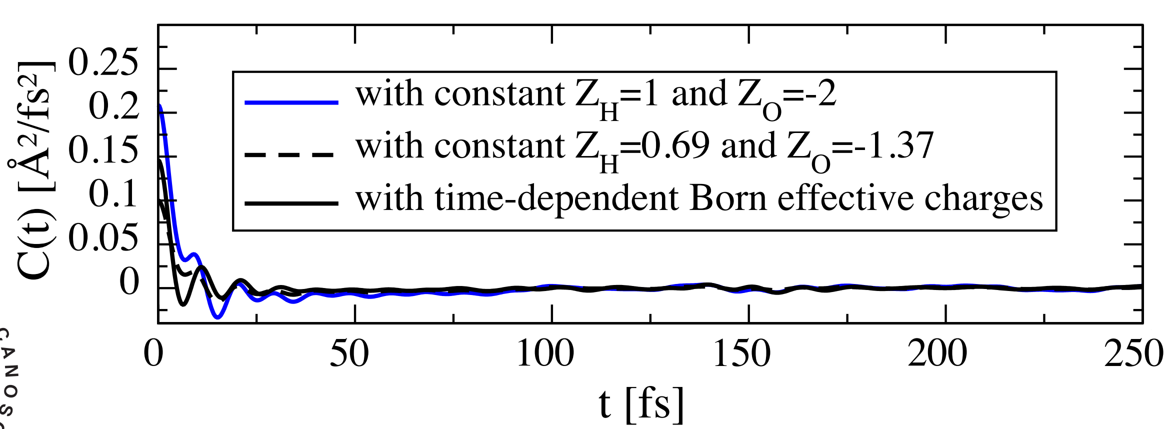




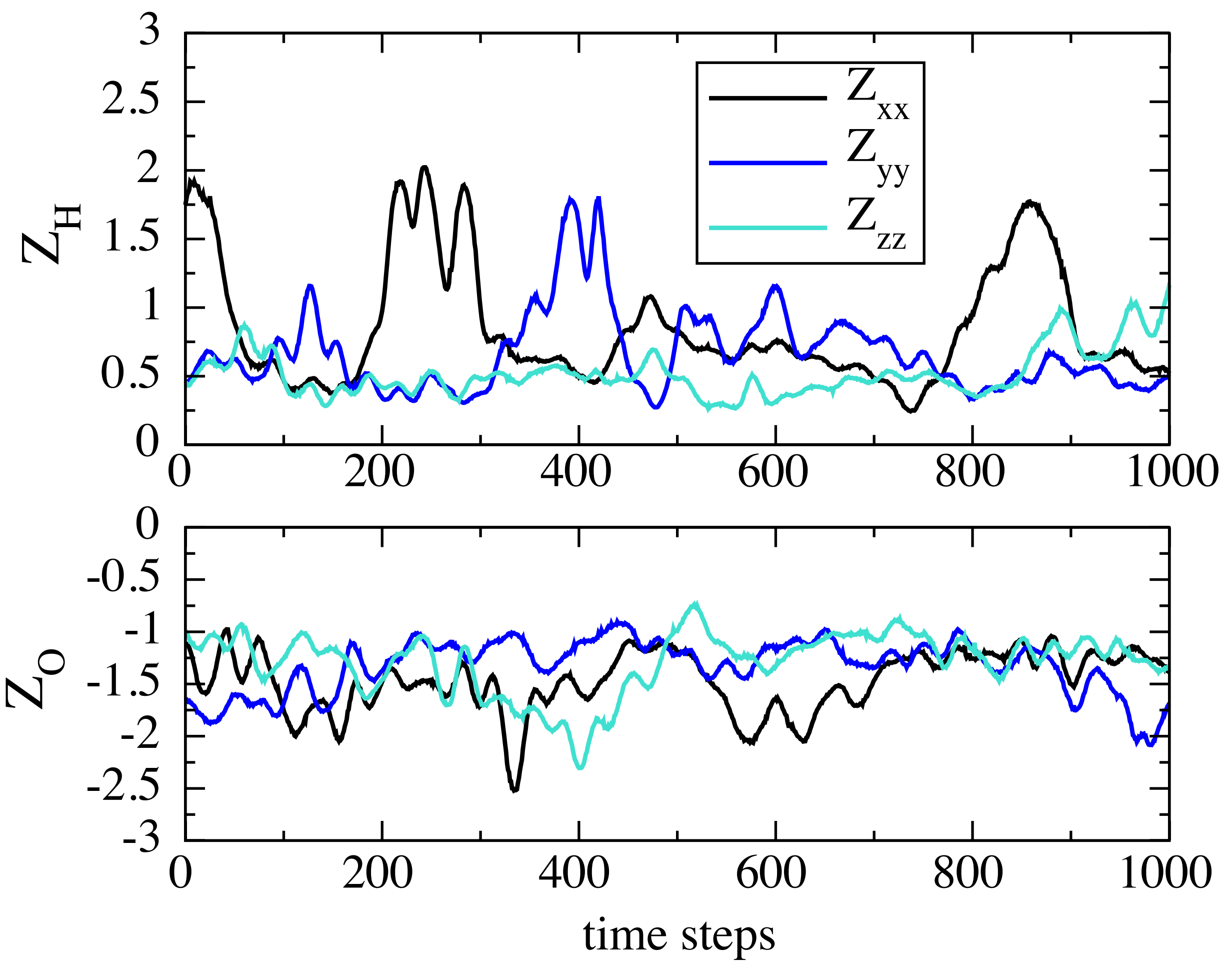


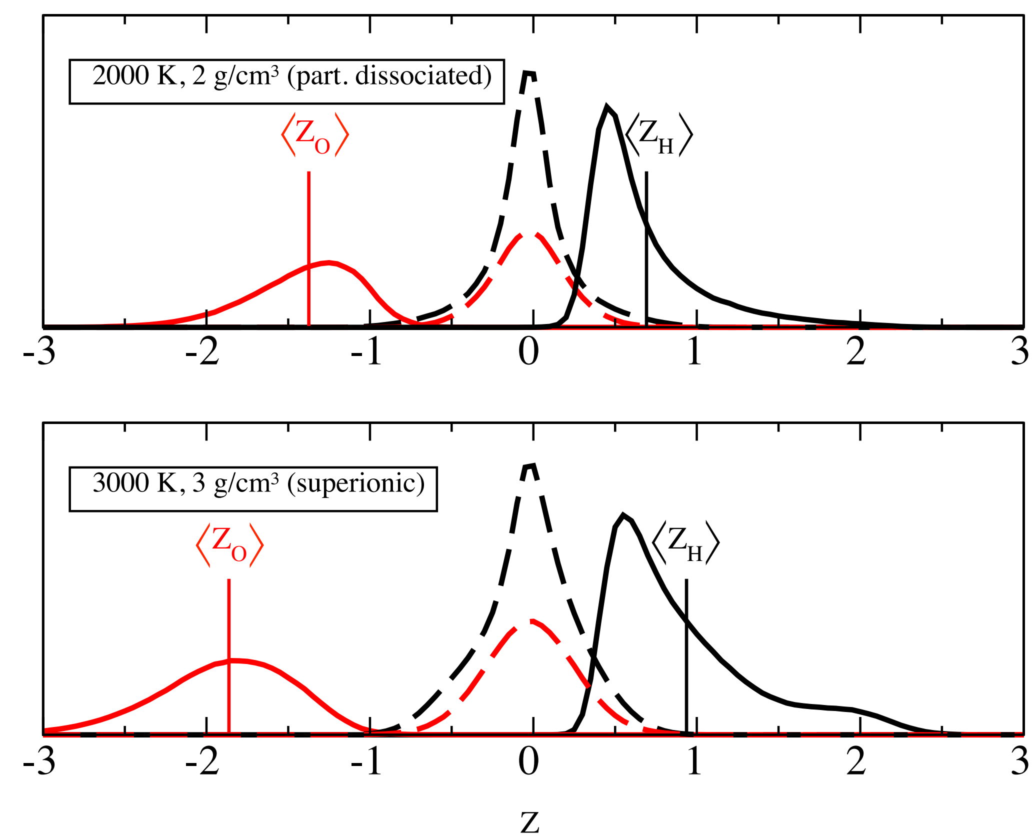
the conundrum

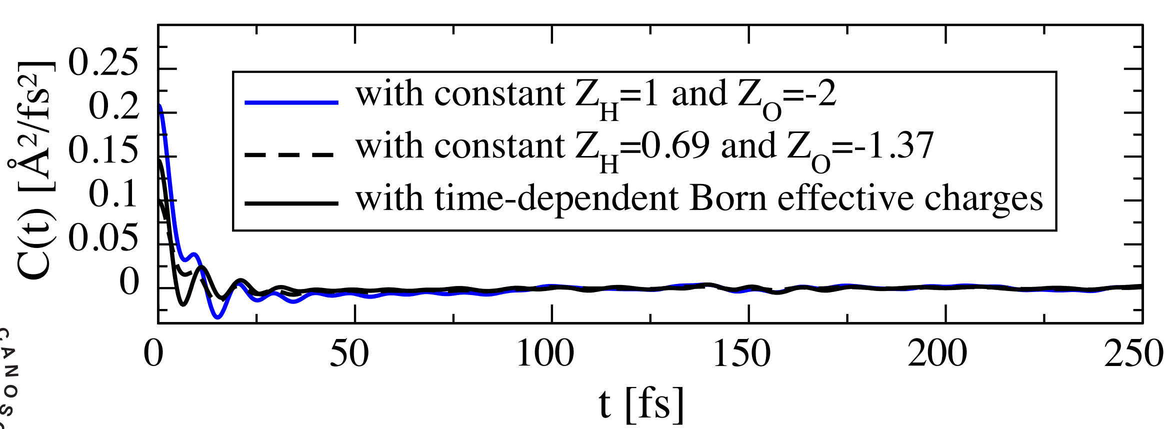
PRL **107,** 185901 (2011) PHYSICAL REVIEW LETTERS week ending 28 OCTOBER 2011

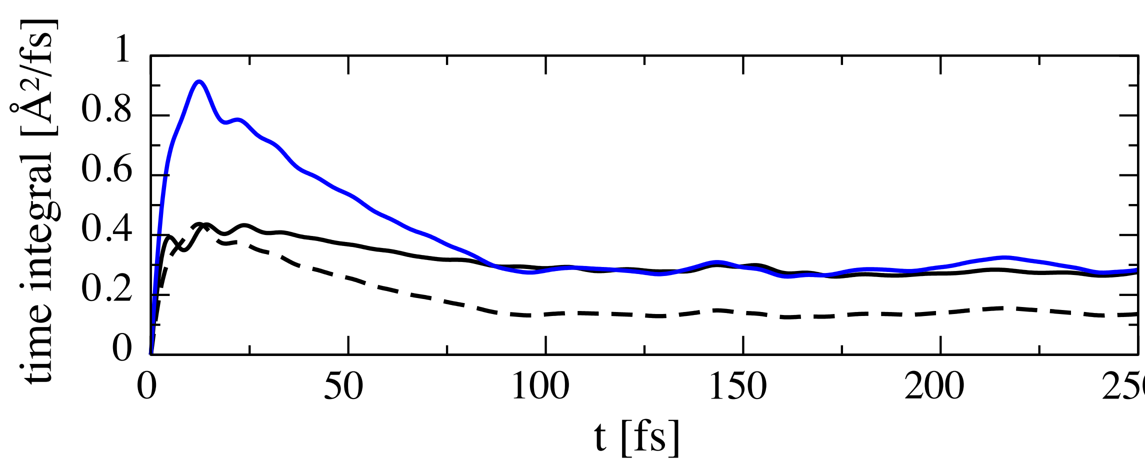
Dynamical Screening and Ionic Conductivity in Water from *Ab Initio* Simulations

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









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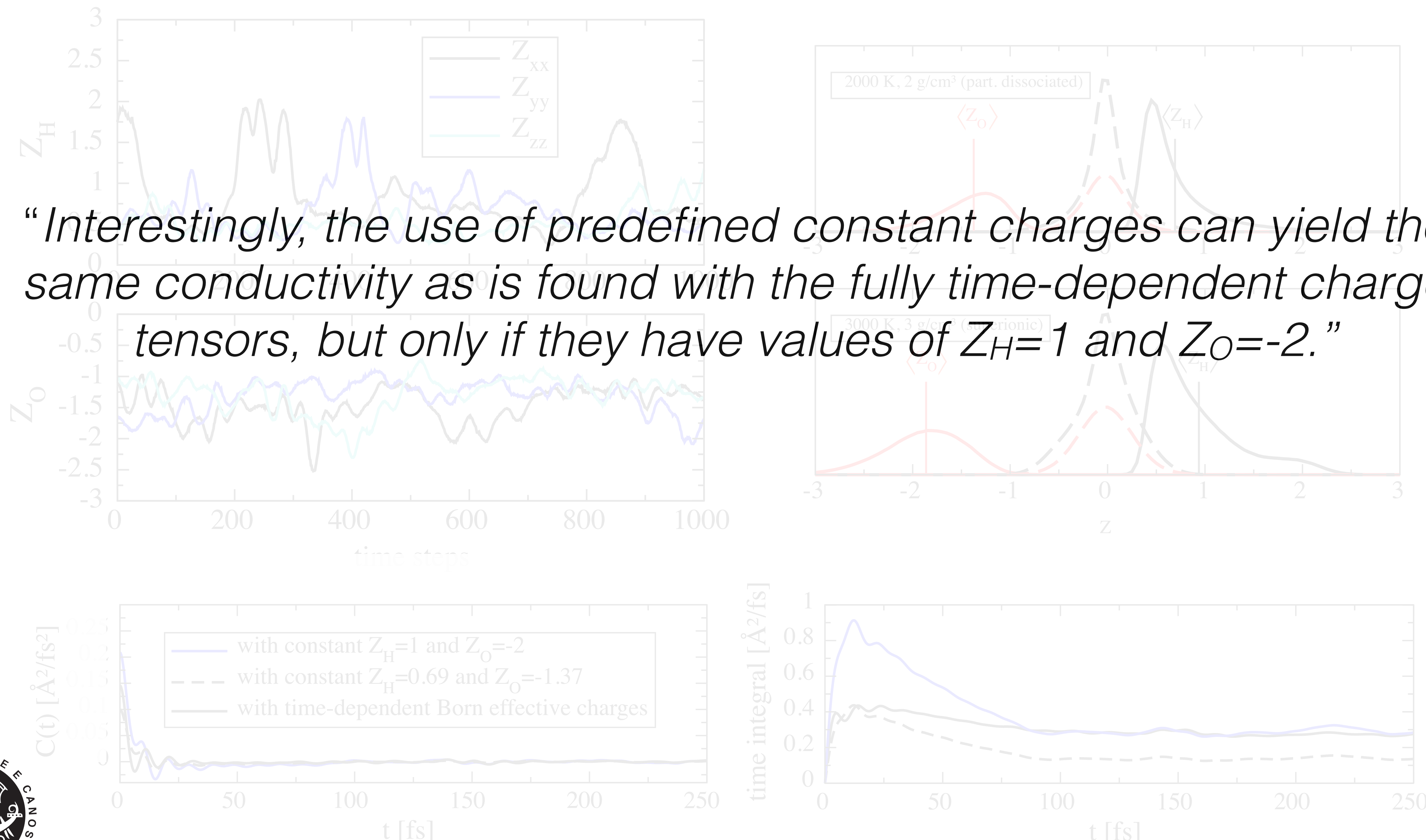

"Interestingly, the use of predefined constant charges can yield the same conductivity as is found with the fully time-dependent charge tensors, but only if they have values of Z_H=1 and Z_O=-2."

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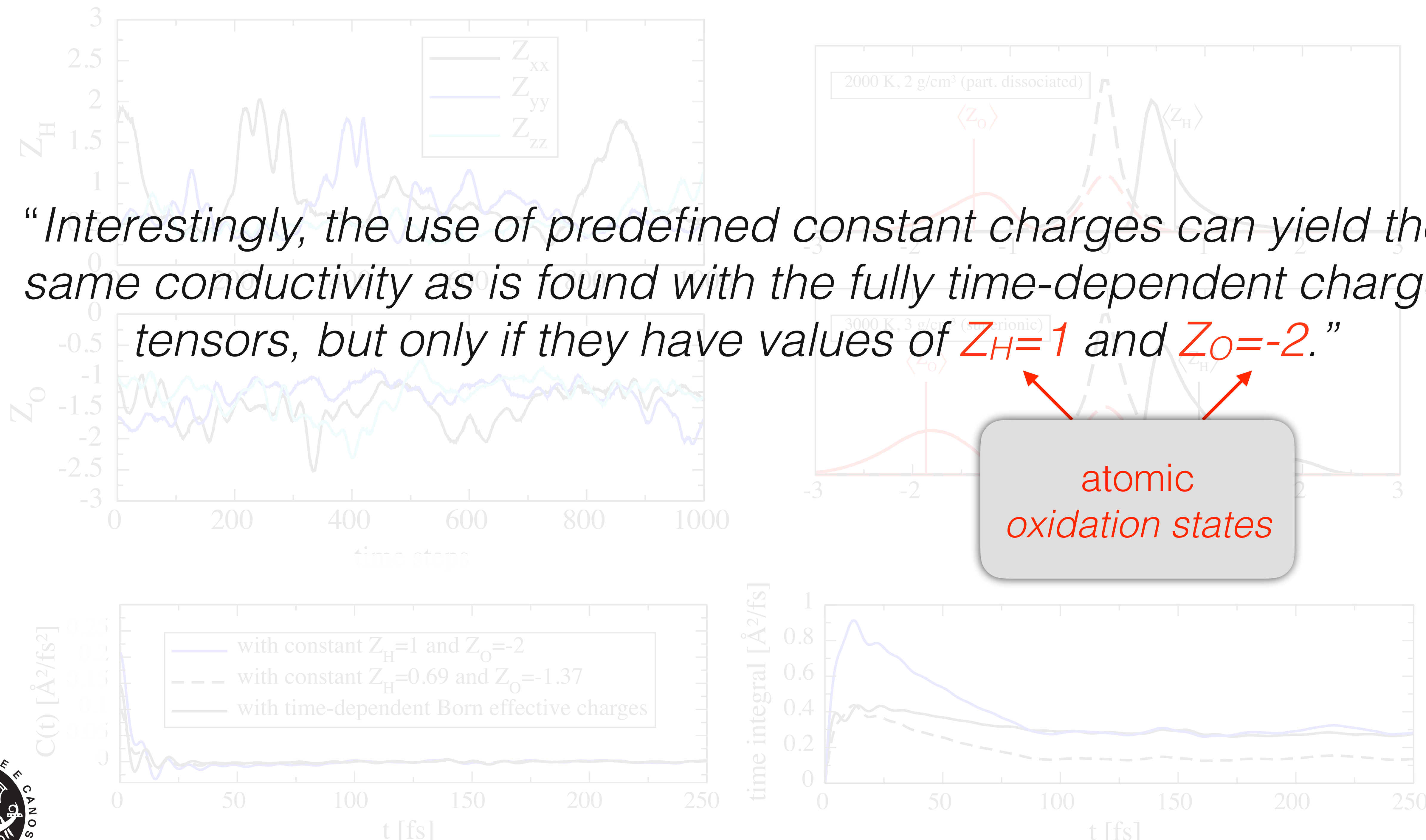

"Interestingly, the use of predefined constant charges can yield the same conductivity as is found with the fully time-dependent charge tensors, but only if they have values of $Z_H=1$ and $Z_O=-2$."

atomic *oxidation states*

how come?

the Green-Kubo theory of transport

A is extensive (energy, entropy, mass, …)

$$A = \int_{\Omega} a(\mathbf{r}) d\mathbf{r}$$

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the Green-Kubo theory of transport

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Linear response

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

$$\begin{cases} \mathbf{J} = \dfrac{1}{\Omega} \displaystyle\int_\Omega \mathbf{j}(\mathbf{r}) d\mathbf{r} \\ \mathbf{F} = \dfrac{1}{\Omega} \displaystyle\int_\Omega \nabla x(\mathbf{r}) d\mathbf{r} \\ x = \dfrac{\partial S}{\partial A} \end{cases}$$

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Green-Kubo

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the Green-Kubo theory of transport

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A = energy

$$J_\mathcal{E} = -\kappa \nabla T$$

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A = charge

$$J_{\mathcal{Q}} = \sigma E$$

$$\sigma = \frac{\Omega}{k_B T} \int_0^\infty \langle J_{\mathcal{Q}}(t) J_{\mathcal{Q}}(0) \rangle dt$$

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adiabatic heat transport

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

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$$-\frac{\partial e_I}{\partial \mathbf{R}_J}$$

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$$\mathbf{F}_{IJ} = -\frac{\partial e_I}{\partial \mathbf{R}_J}$$

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

Thermal Conductivity of Periclase (MgO) from First Principles

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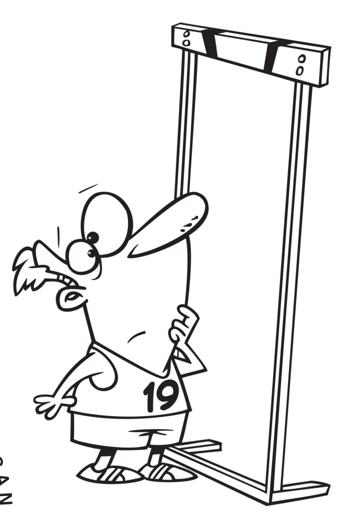
sensitive to the form of the potential. The widely used Green-Kubo relation [14] does not serve our purposes, because in first-principles calculations it is impossible to uniquely decompose the total energy into individual contributions from each atom.



the Einstein-Helfand relations

Einstein (1905)

$$\left\langle |x(t) - x(0)|^2 \right\rangle = \left\langle \left| \int_0^t v(t')dt' \right|^2 \right\rangle$$

$$\approx 2t \underbrace{\int_0^\infty \langle v(t)v(0)\rangle dt}_{D}$$

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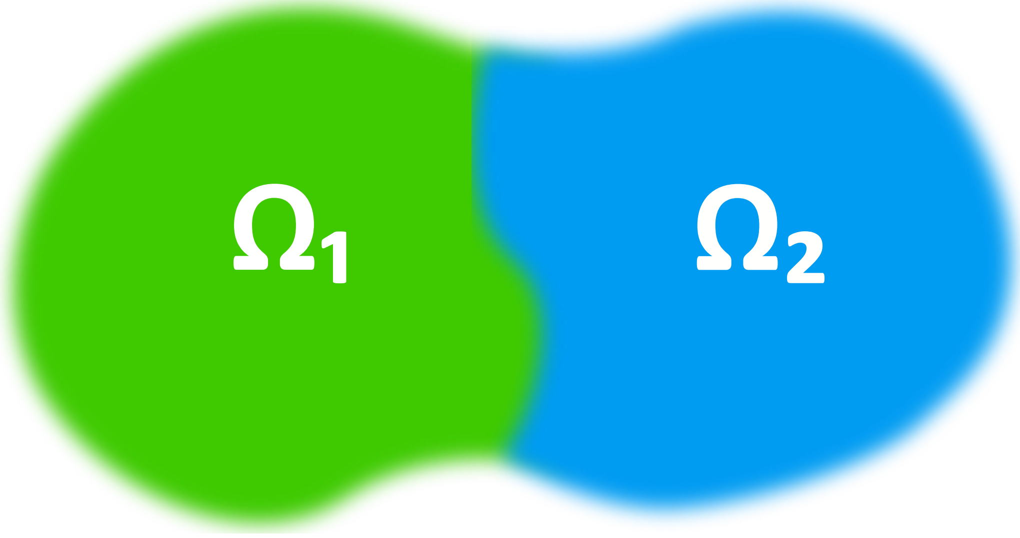
Helfand (1960)

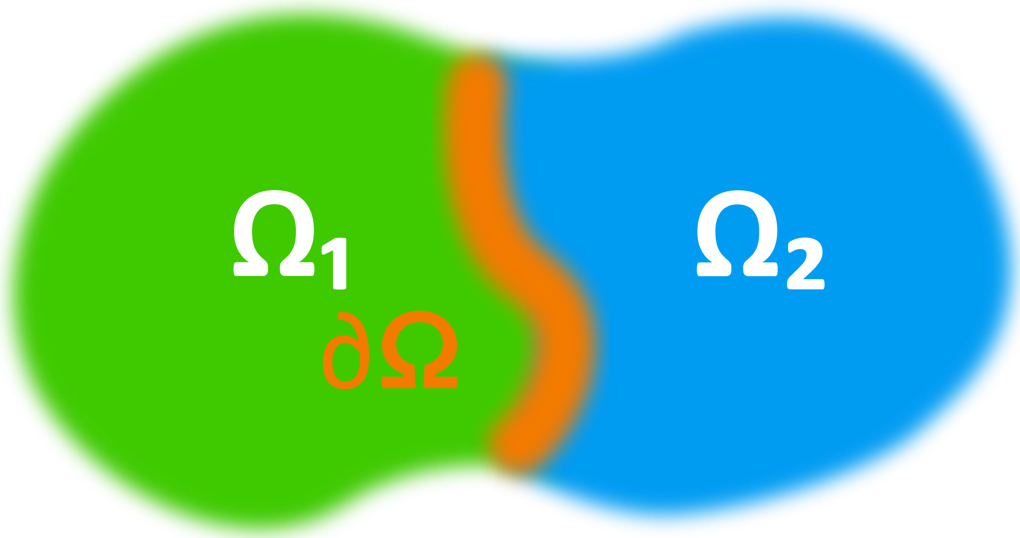
$$\left\langle \left| \int_0^t J(t')dt' \right|^2 \right\rangle \approx 2t \underbrace{\int_0^\infty \langle J(t)J(0)\rangle dt}_{\frac{k_B T}{\Omega}\lambda}$$

gauge invariance of transport coefficients



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

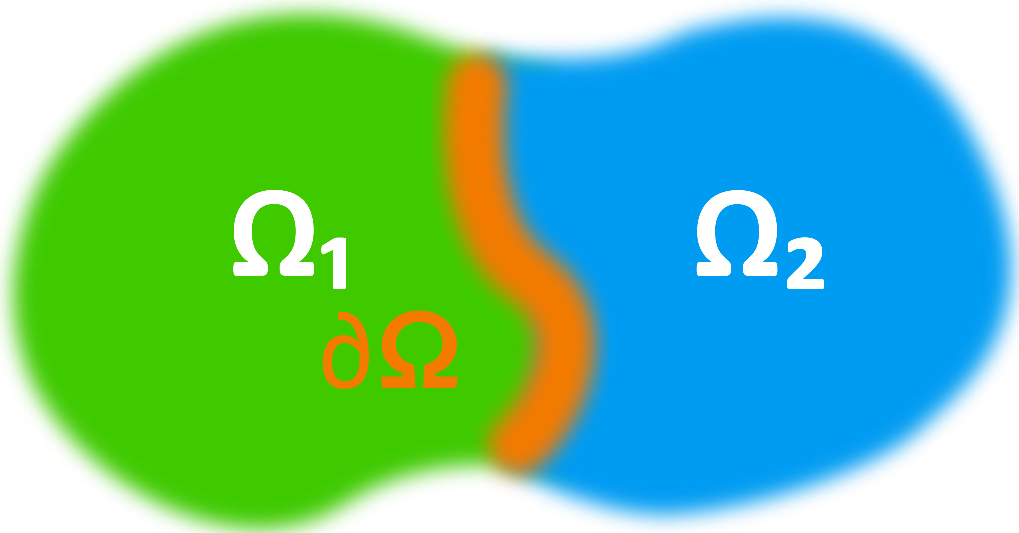
gauge invariance of transport coefficients



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

$$\stackrel{?}{=} \mathcal{E}[\Omega_1] + \mathcal{E}[\Omega_2]$$

gauge invariance of transport coefficients



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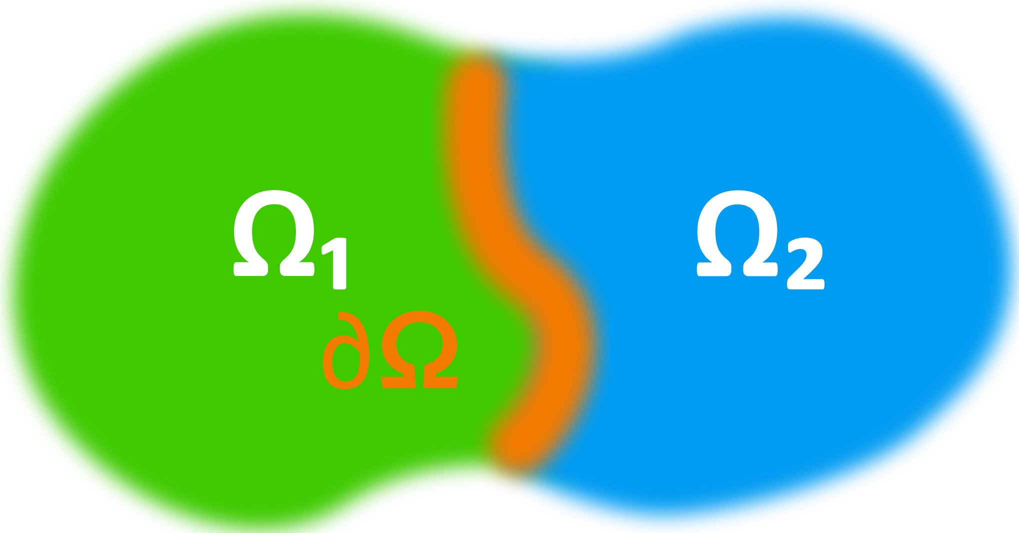
extensiveness

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

gauge invariance of transport coefficients



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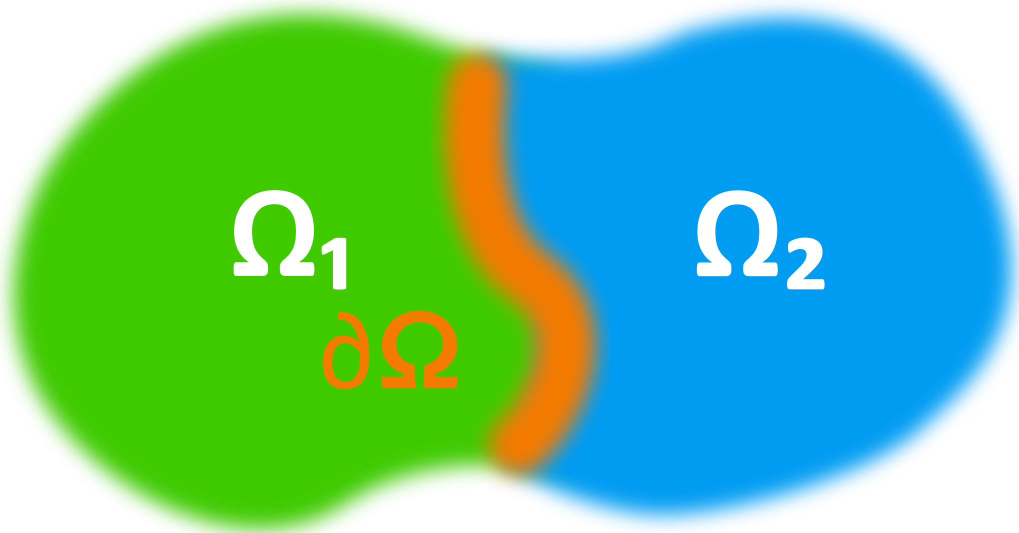

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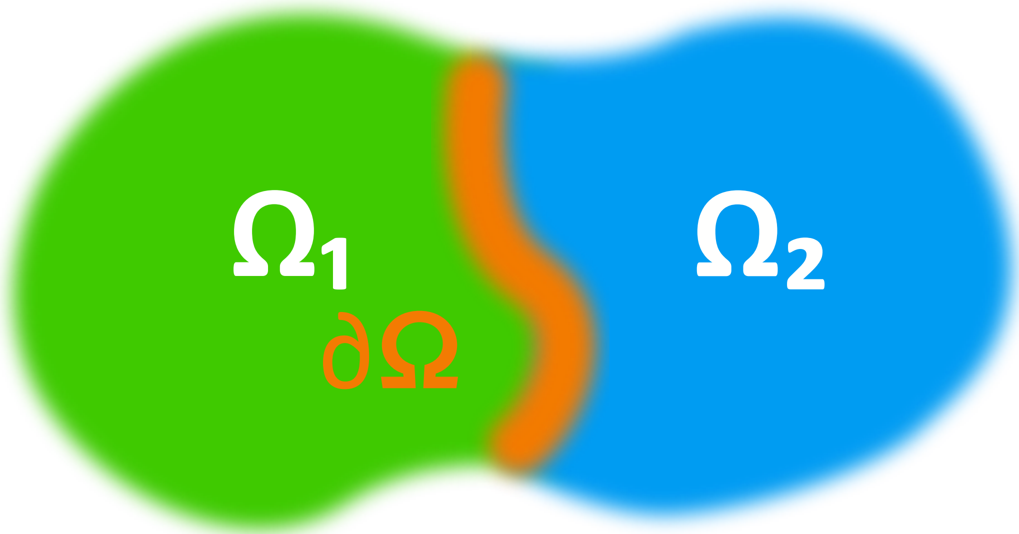
gauge invariance of transport coefficients



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gauge invariance

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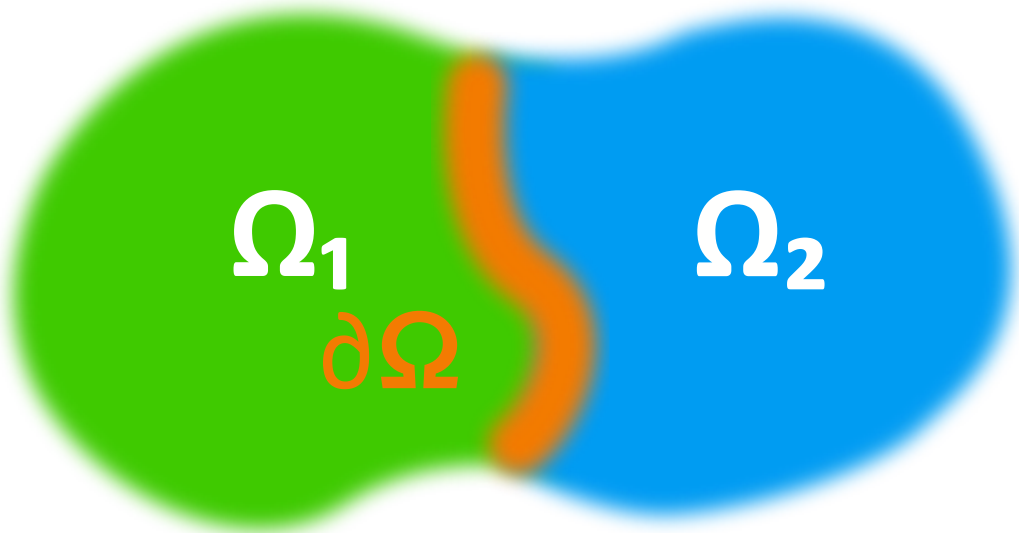
gauge invariance of transport coefficients



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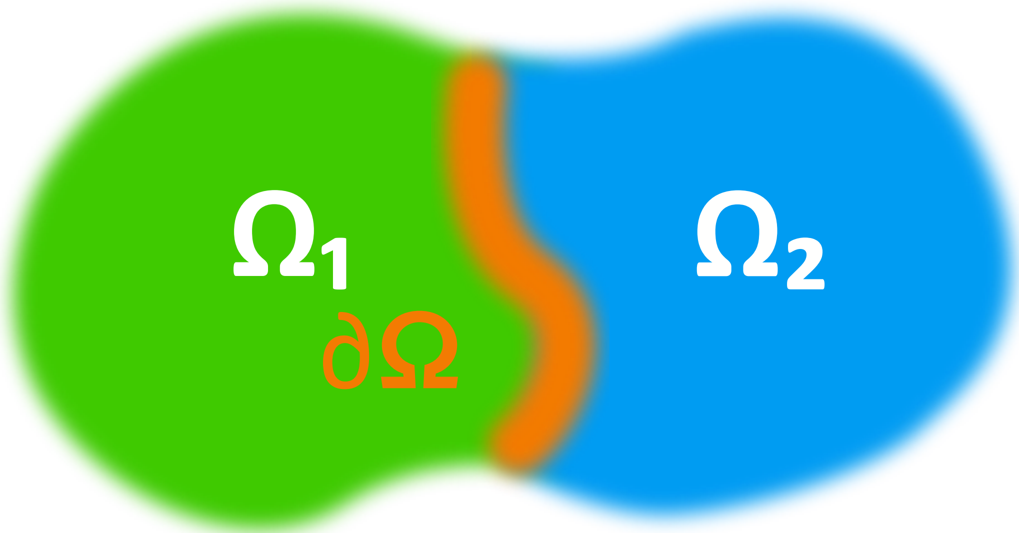
gauge invariance of transport coefficients



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gauge invariance of transport coefficients

$$J' = J + \dot{P}$$

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

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

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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

gauge invariance of heat transport

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and Department of Geology and Geophysics, Louisiana State University, Baton Rouge, Louisiana 70803, USA

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.

gauge invariance of heat transport

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

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

Thermal Conductivity of Periclase (MgO) from First Principles

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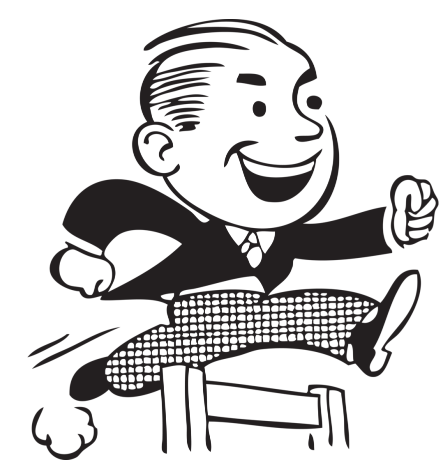
sensitive to the form of the potential. The widely used Green-Kubo relation [14] does not serve our purposes, because in first-principles calculations it is impossible to uniquely decompose the total energy into individual contributions from each atom.

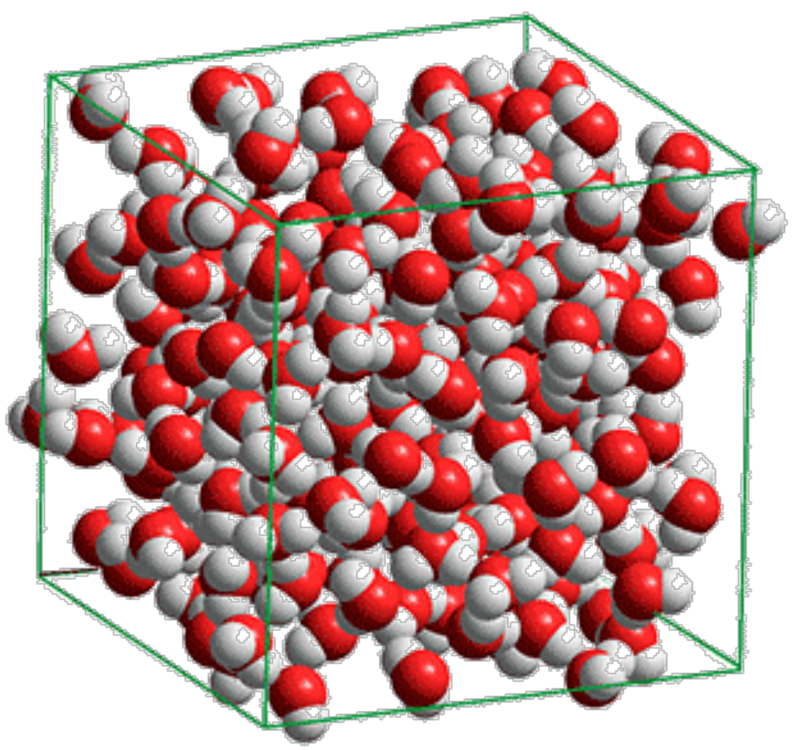
solution:

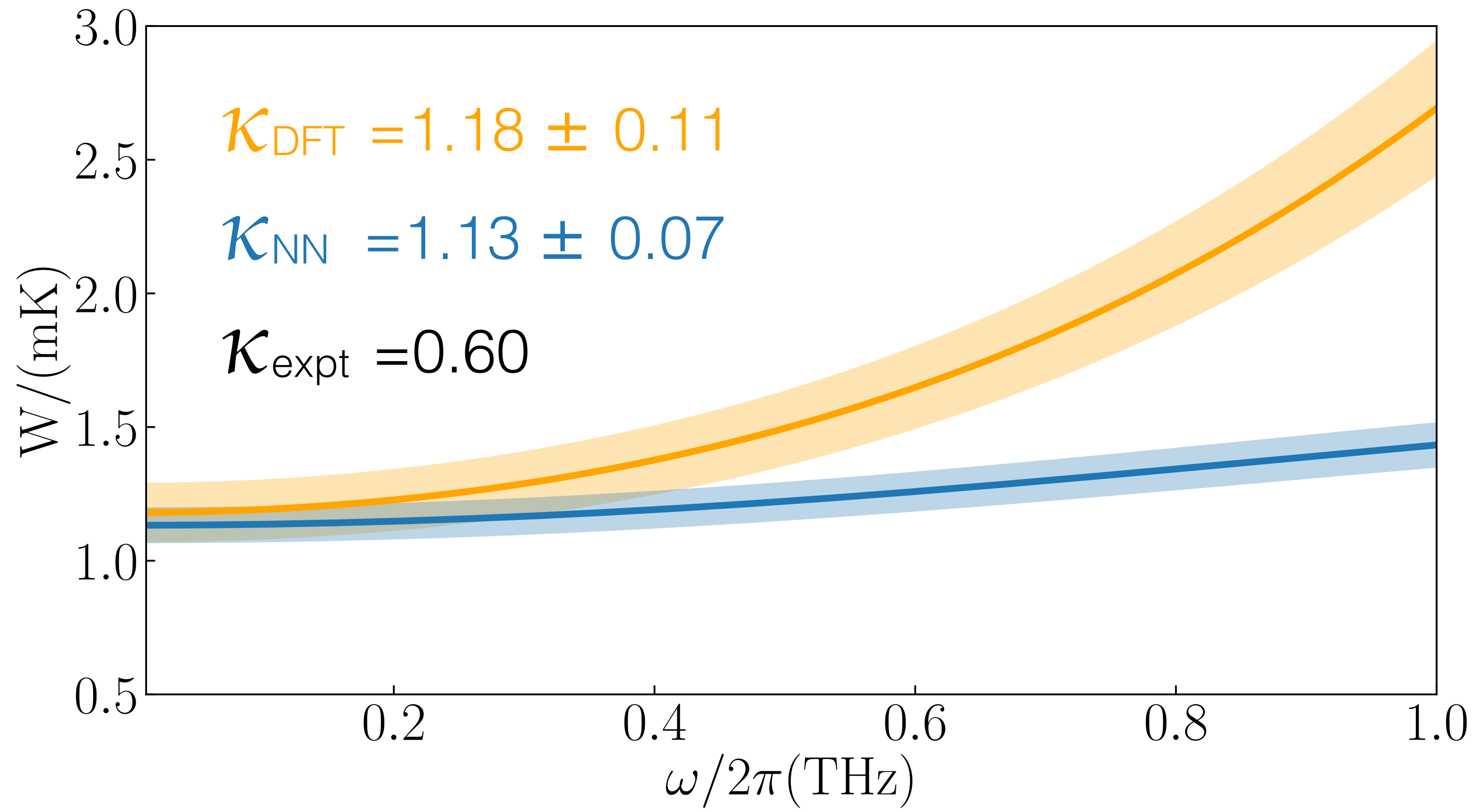
choose *any* local representation of the energy that integrates to the correct value and whose correlations decay at large distance — the conductivity computed from the resulting current will be *independent* of the representation.



thermal conductivity of liquid water from DFT

H_2O

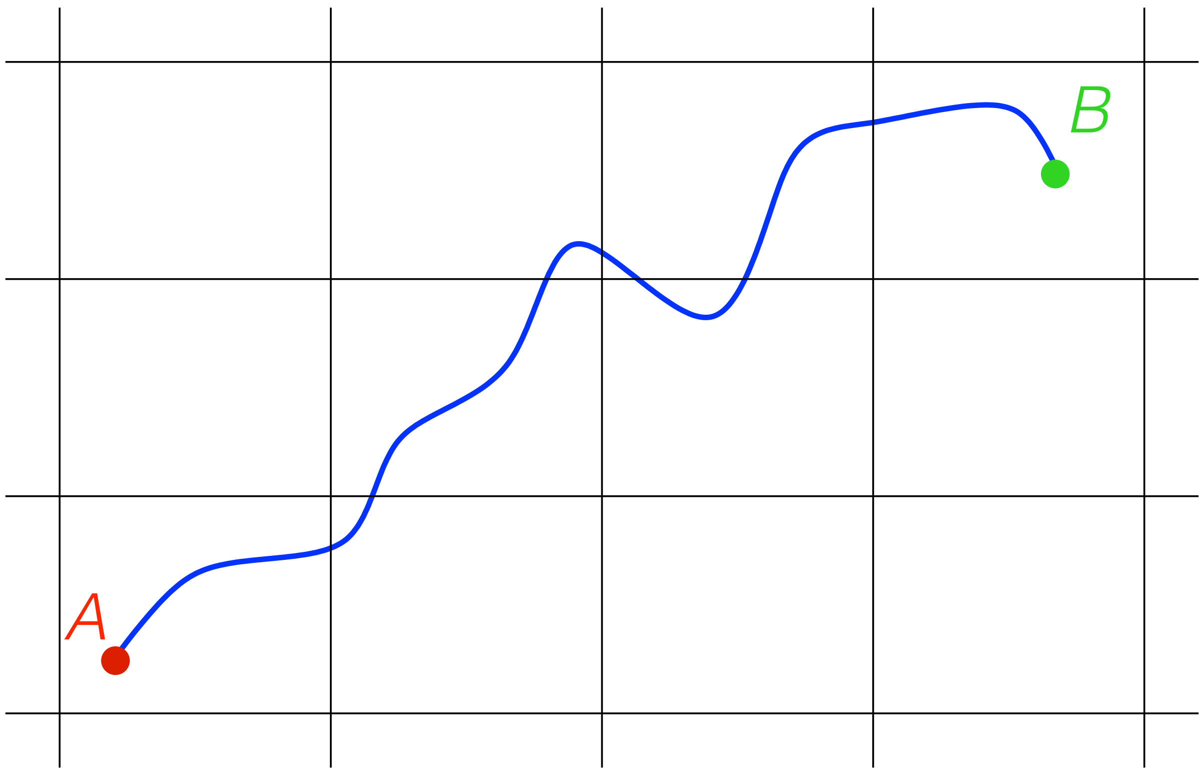




back to our business

electric conductivities can be computed from oxidation states, instead of from effective charges

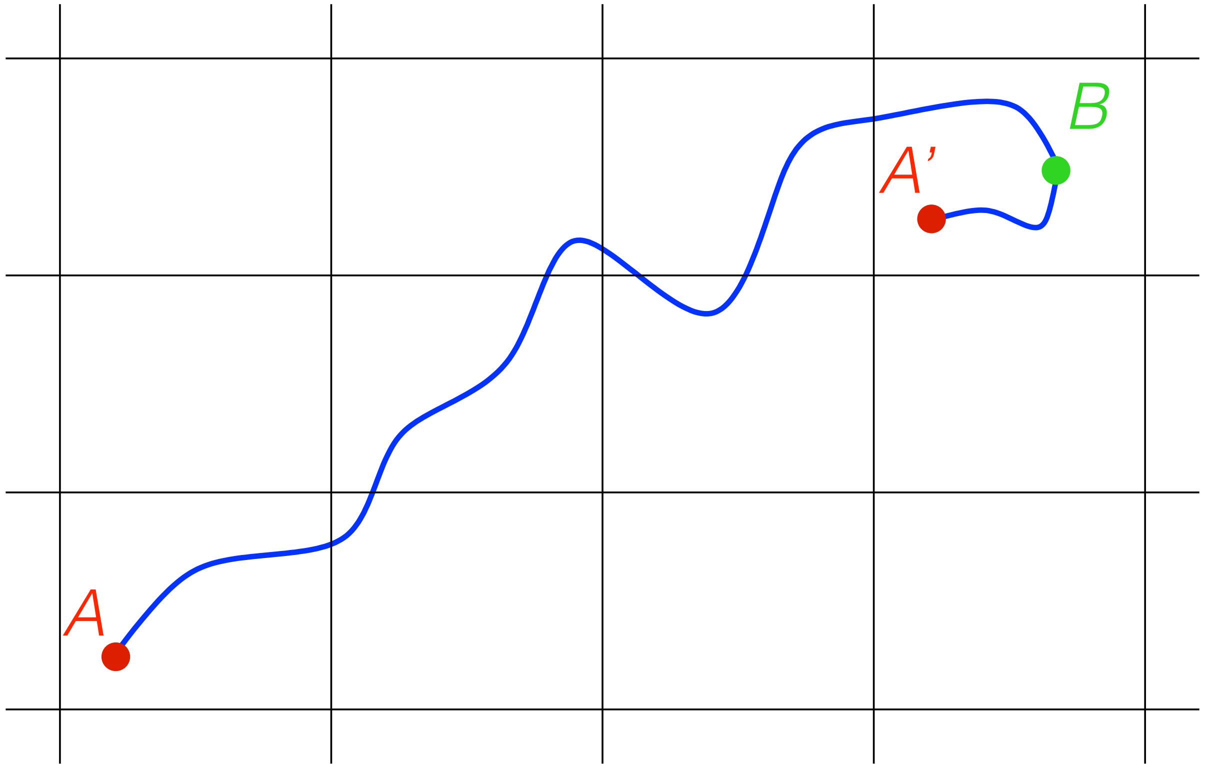
gauge invariance of charge transport



$$\sigma \propto \lim_{t\to\infty} \frac{1}{2t} \left\langle |\mu_{AB}|^2 \right\rangle$$

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

gauge invariance of charge transport



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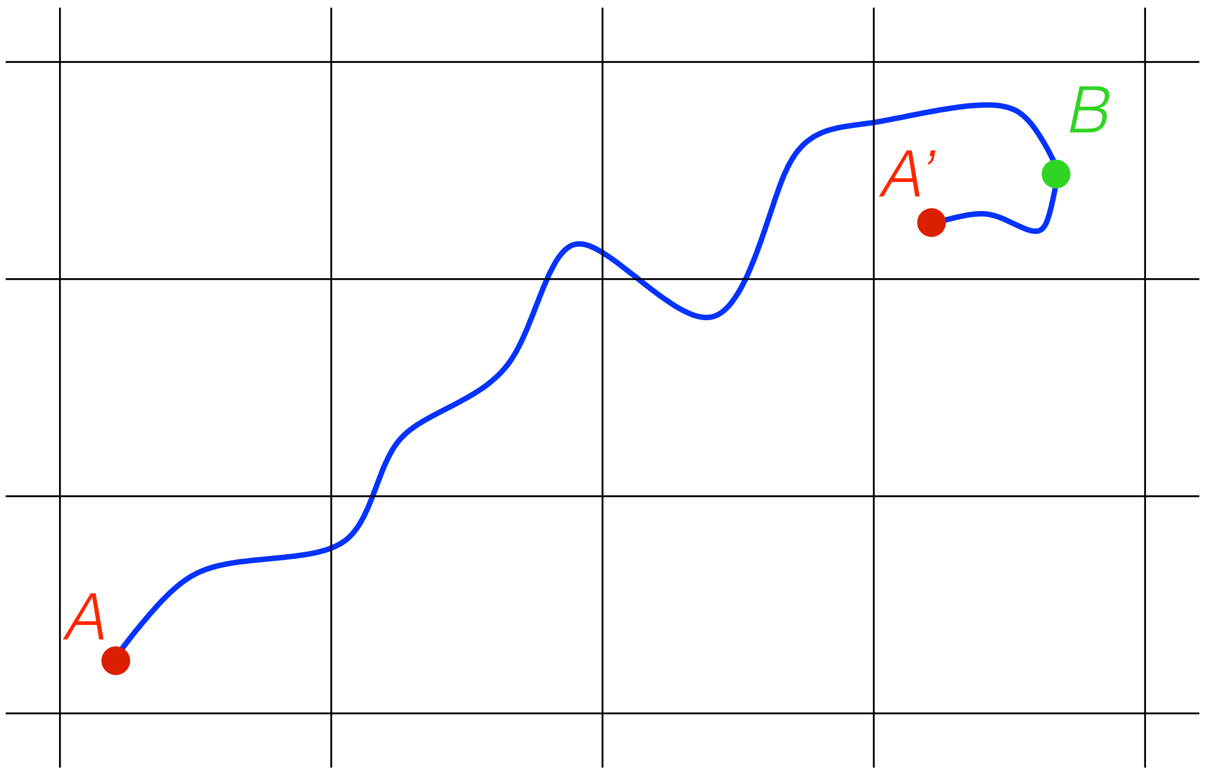
$$= \mu_{AA'} + \mu_{A'B}$$

gauge invariance of charge transport



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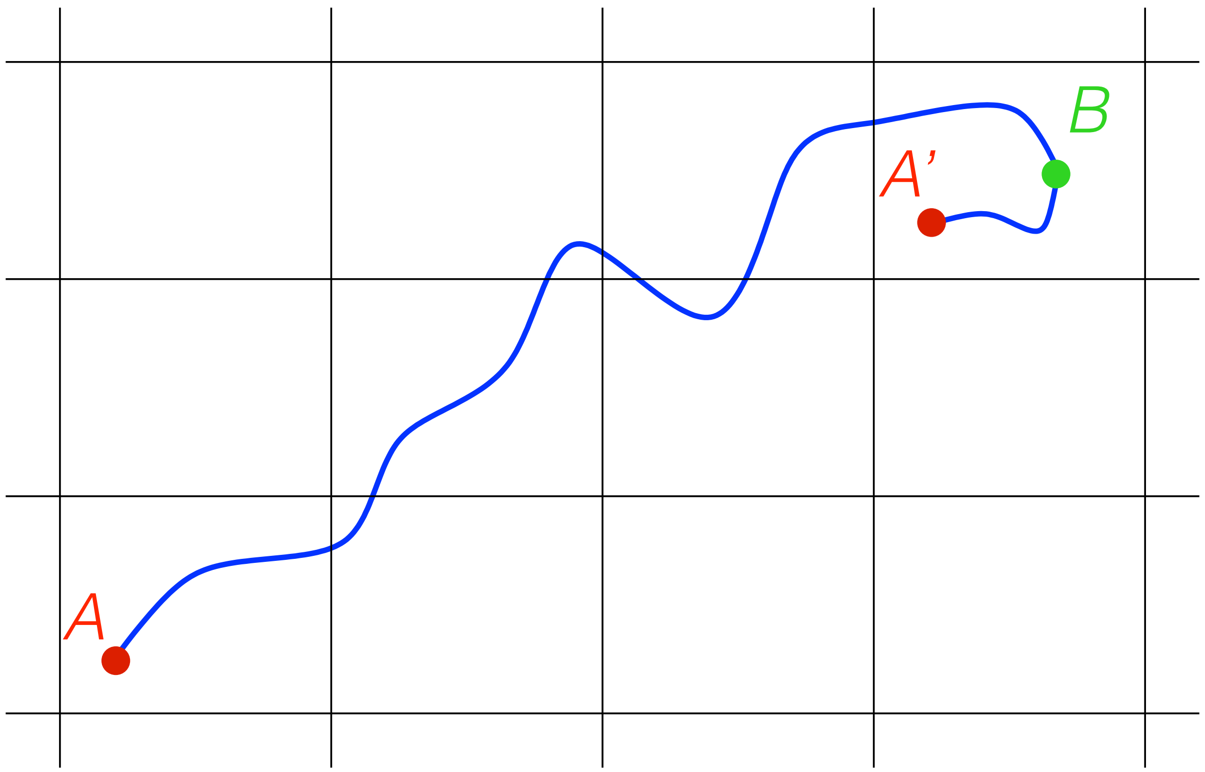
$$\mathrm{var}\left[\mu_{AB}\right] = \mathrm{var}\left[\mu_{AA'}\right] + \underbrace{\mathrm{var}\left[\mu_{A'B}\right]}_{bounded} + 2\mathrm{cov}\left[\mu_{AA'} \cdot \mu_{A'B}\right]$$

gauge invariance of charge transport



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$$\mathcal{O}(t) \qquad \mathcal{O}(1)$$

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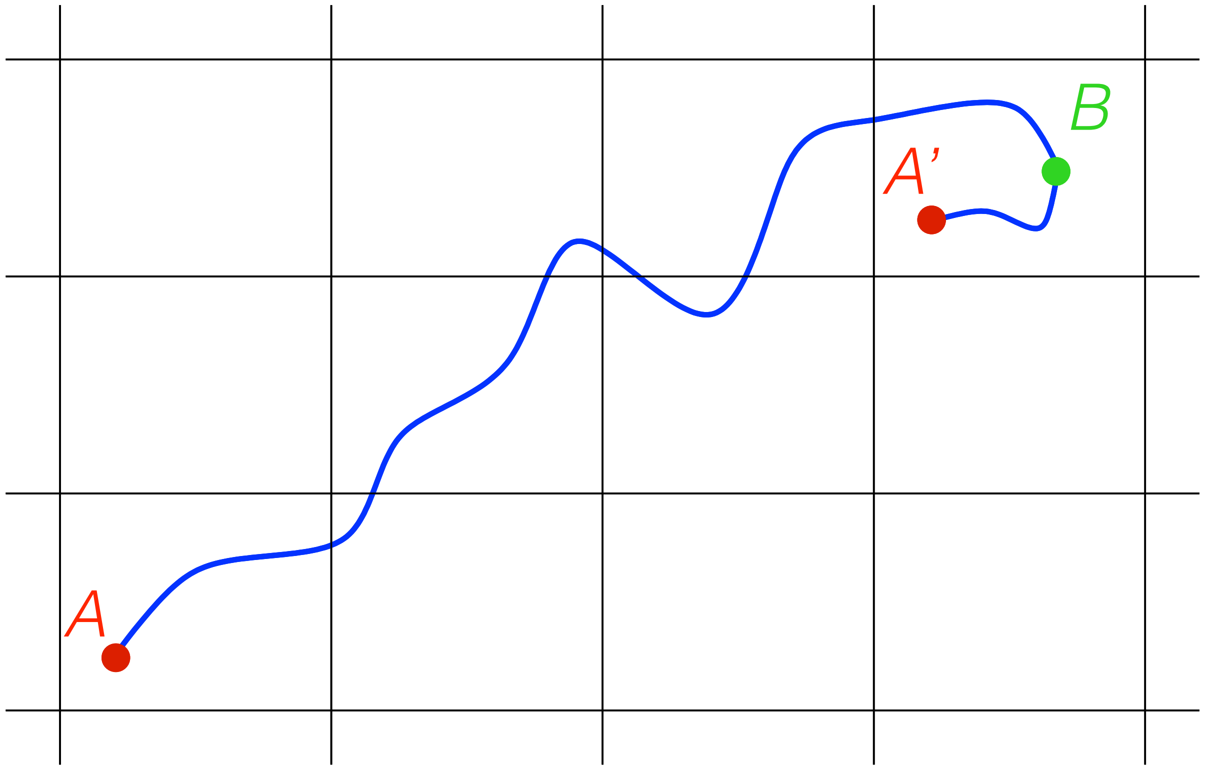
gauge invariance of charge transport



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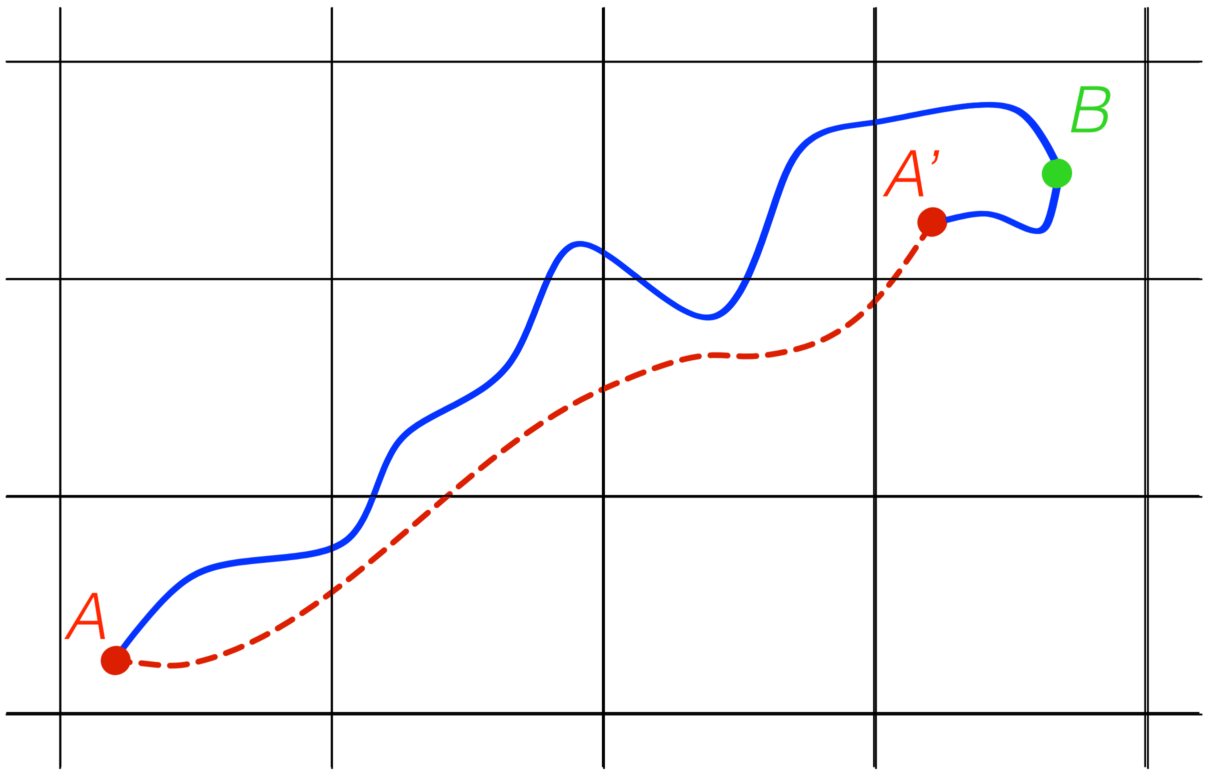
$$\hat{H}(B) \neq \hat{H}(A)$$

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

gauge invariance of charge transport



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

$$\mu_{AA'} = \int_A^{A'} d\mu(X)$$

$$= \ell Q(AA')$$

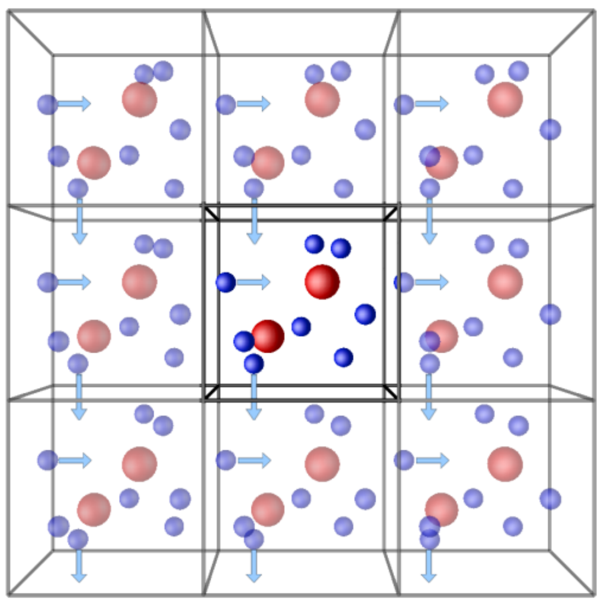
$$Q(AA') \in \mathbb{Z}$$

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

quantisation of adiabatic particle transport

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

classical PBC



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

quantisation of adiabatic particle transport

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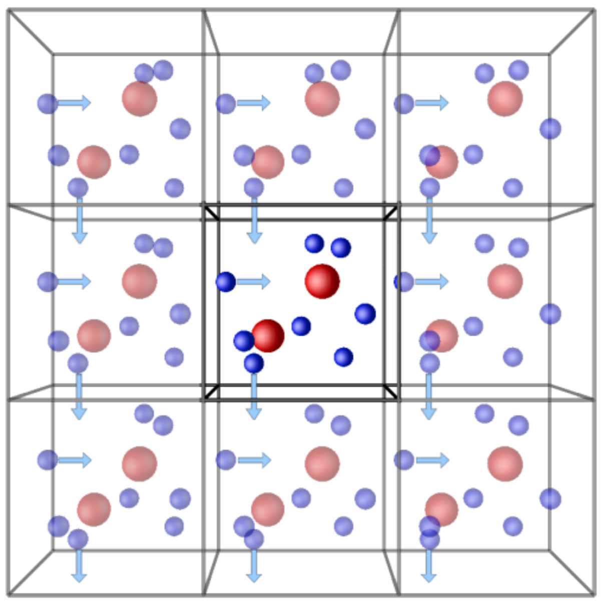

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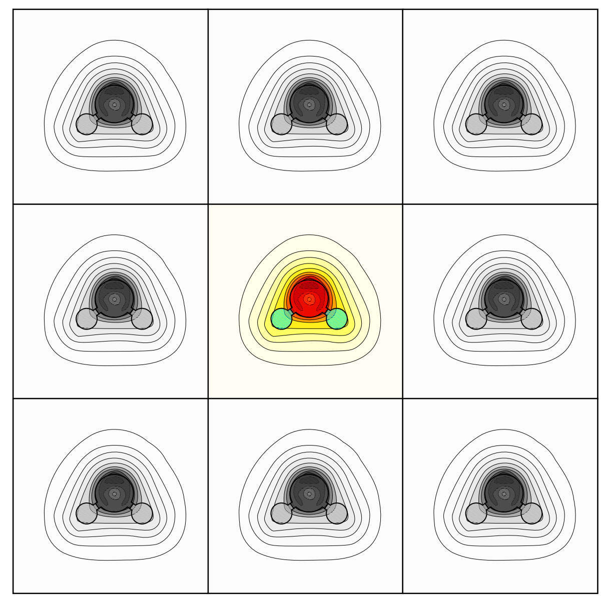
quantum PBC



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

quantisation of adiabatic particle transport

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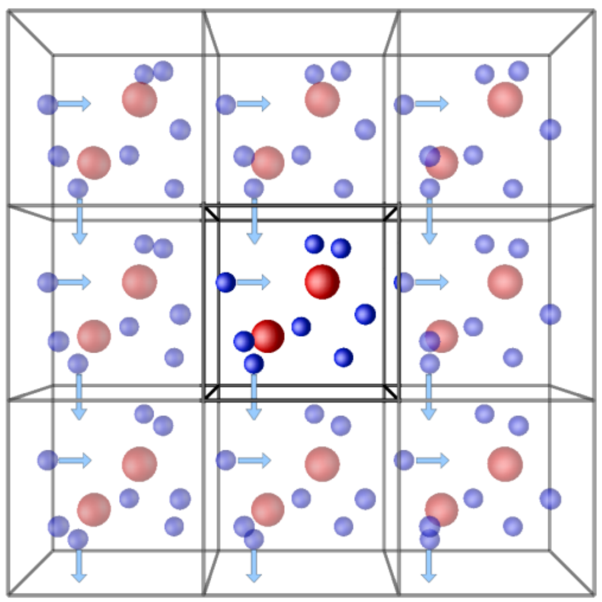

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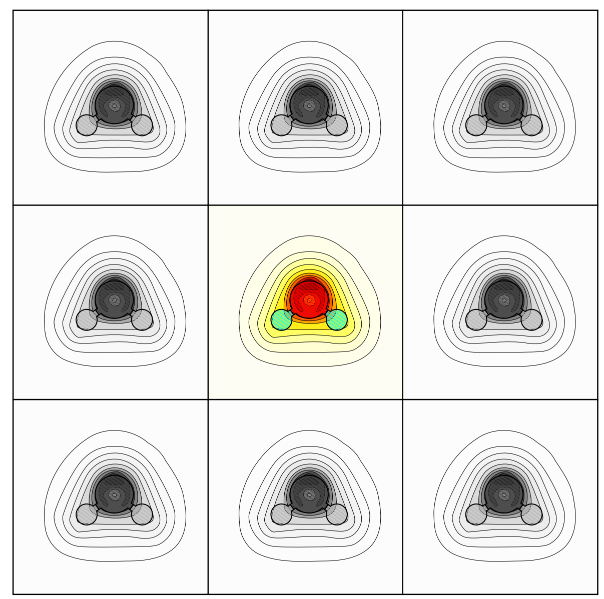
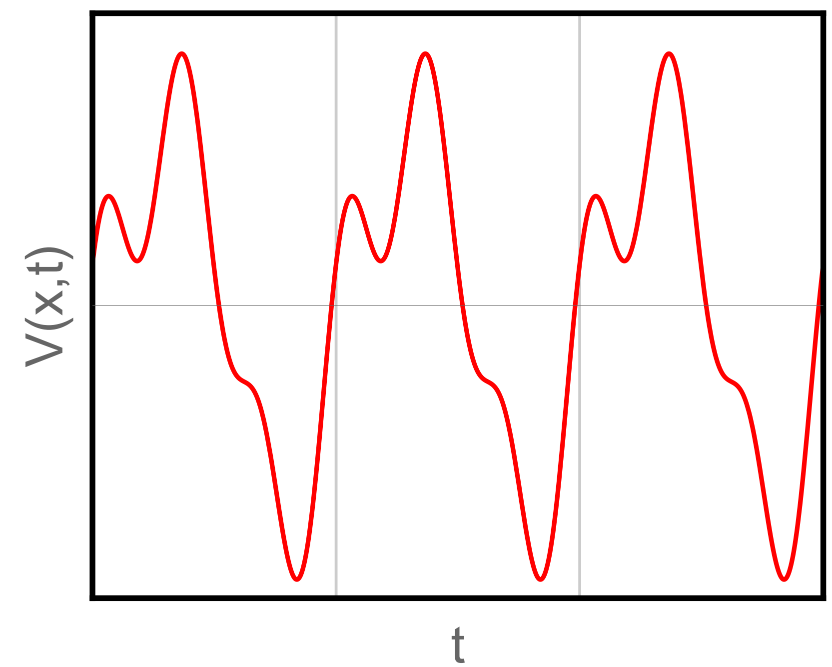


$$\psi(x+L) = \psi(x)$$

time periodicity

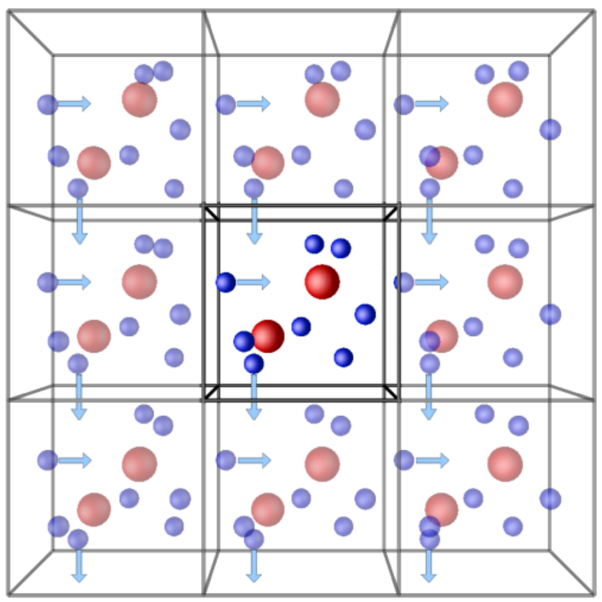


$$V(x, t+T) = V(x, t)$$

quantisation of adiabatic particle transport

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

classical PBC



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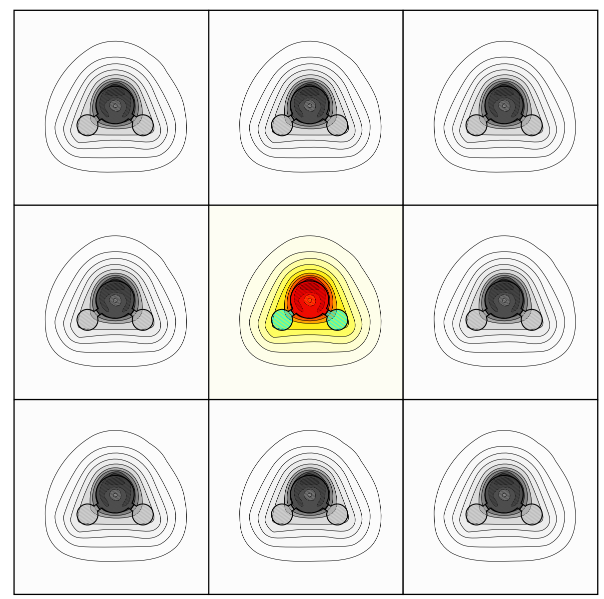
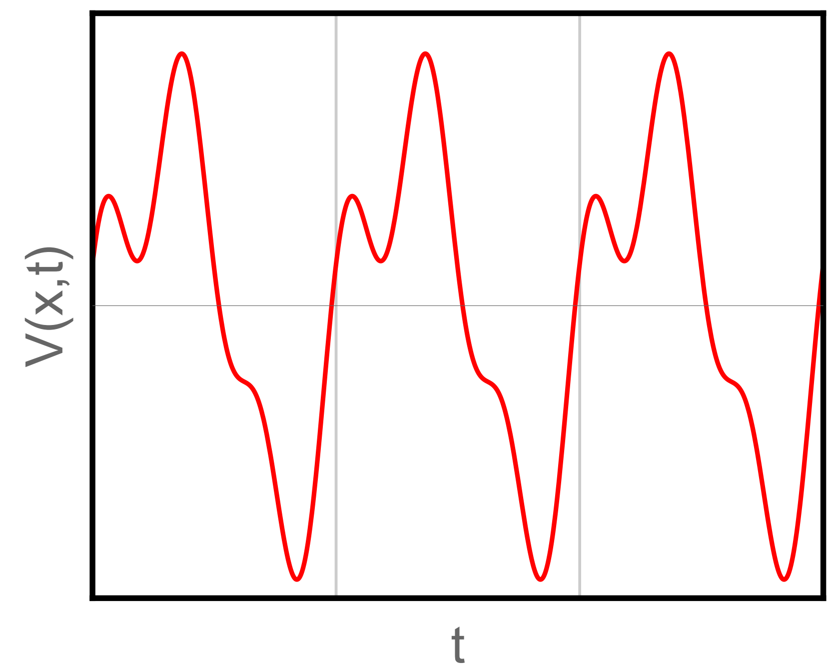


$$\psi(x+L) = \psi(x)$$

time periodicity



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

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

quantisation of adiabatic particle transport

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

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

quantisation of adiabatic particle transport

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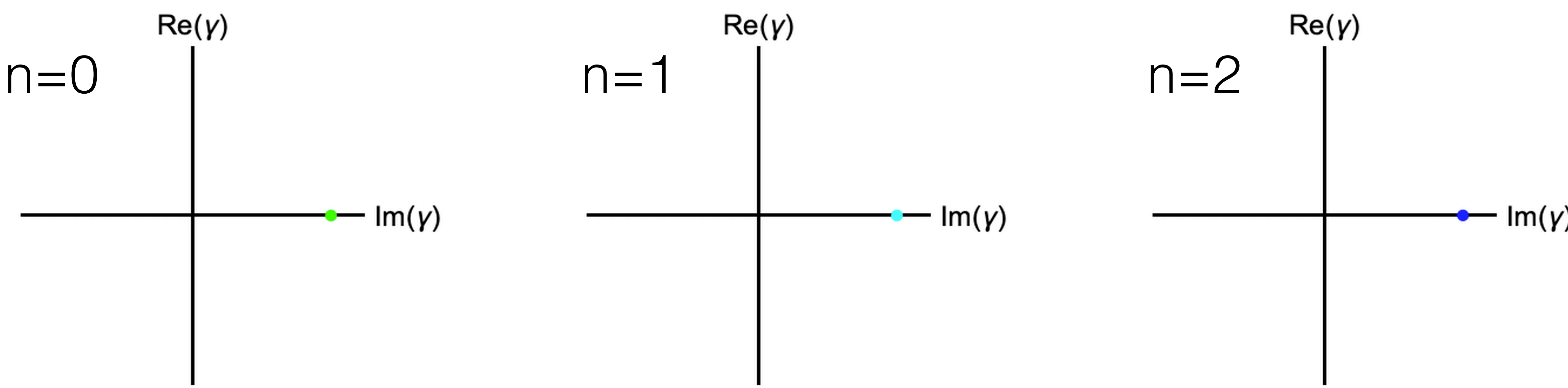

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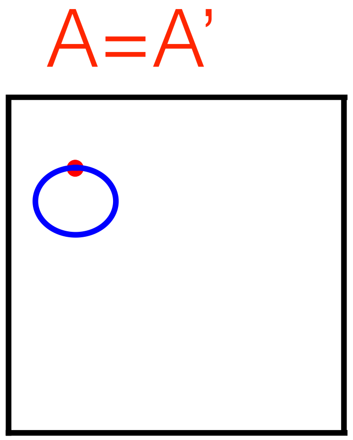
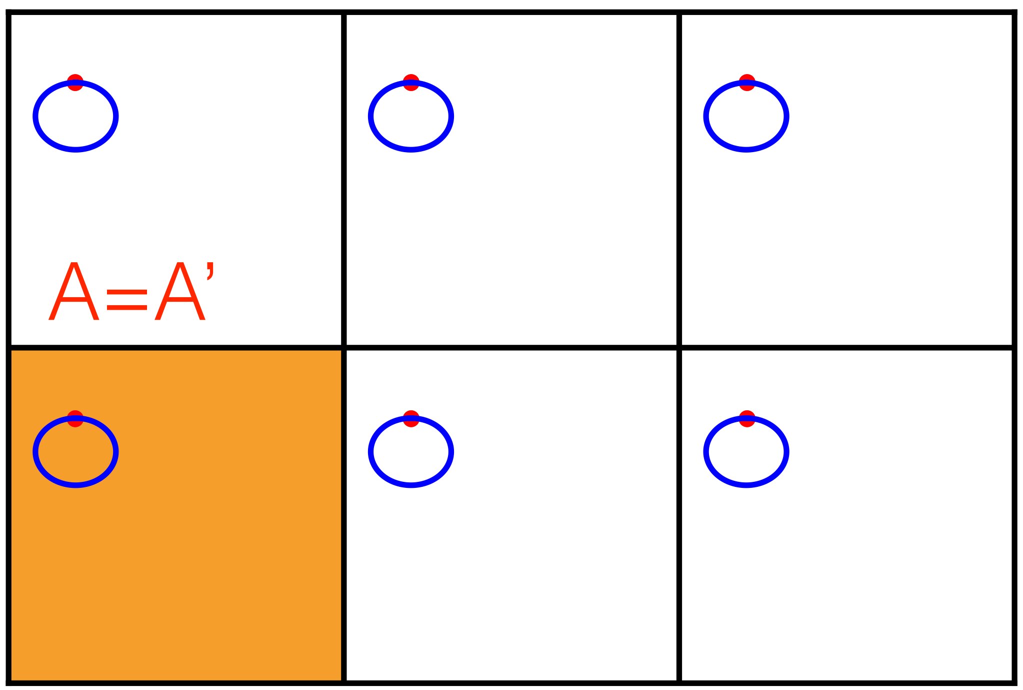
topological invariants



topological invariants



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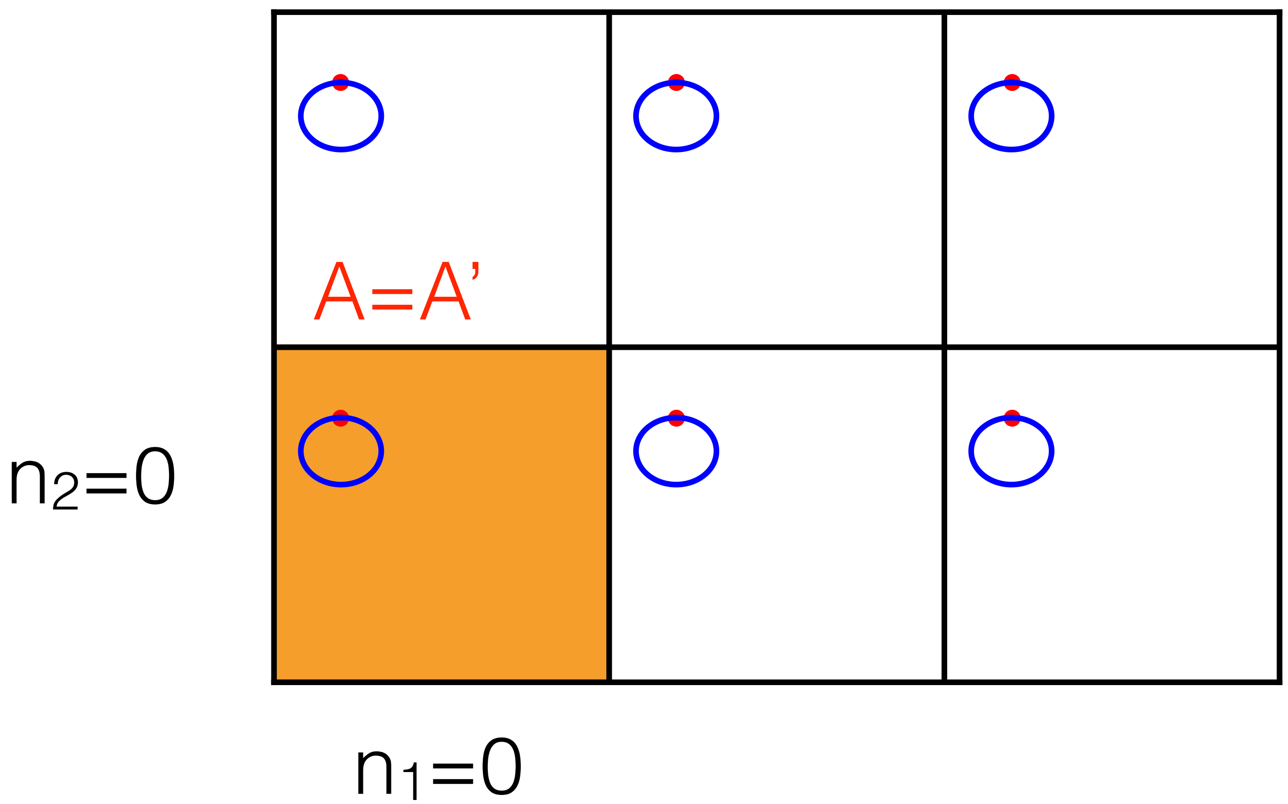

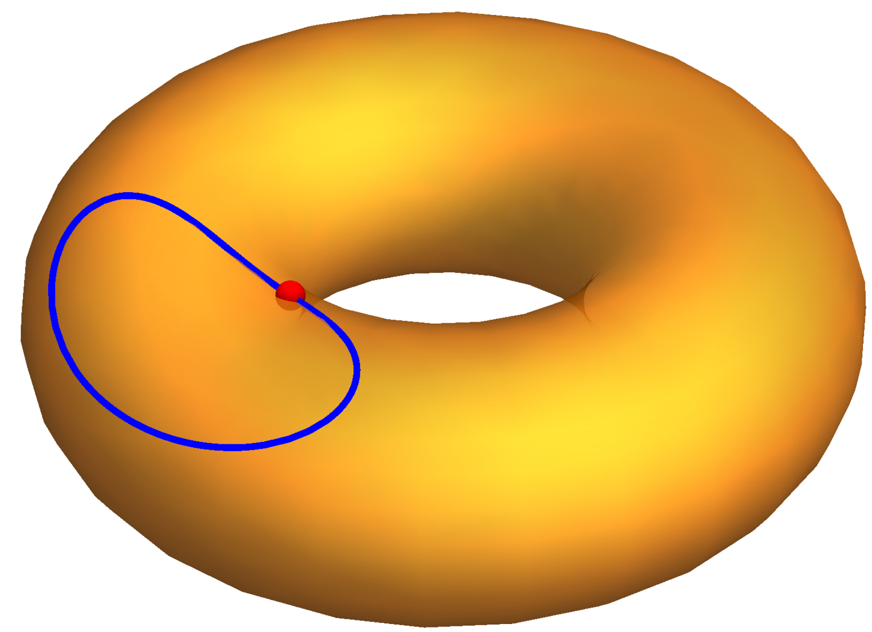

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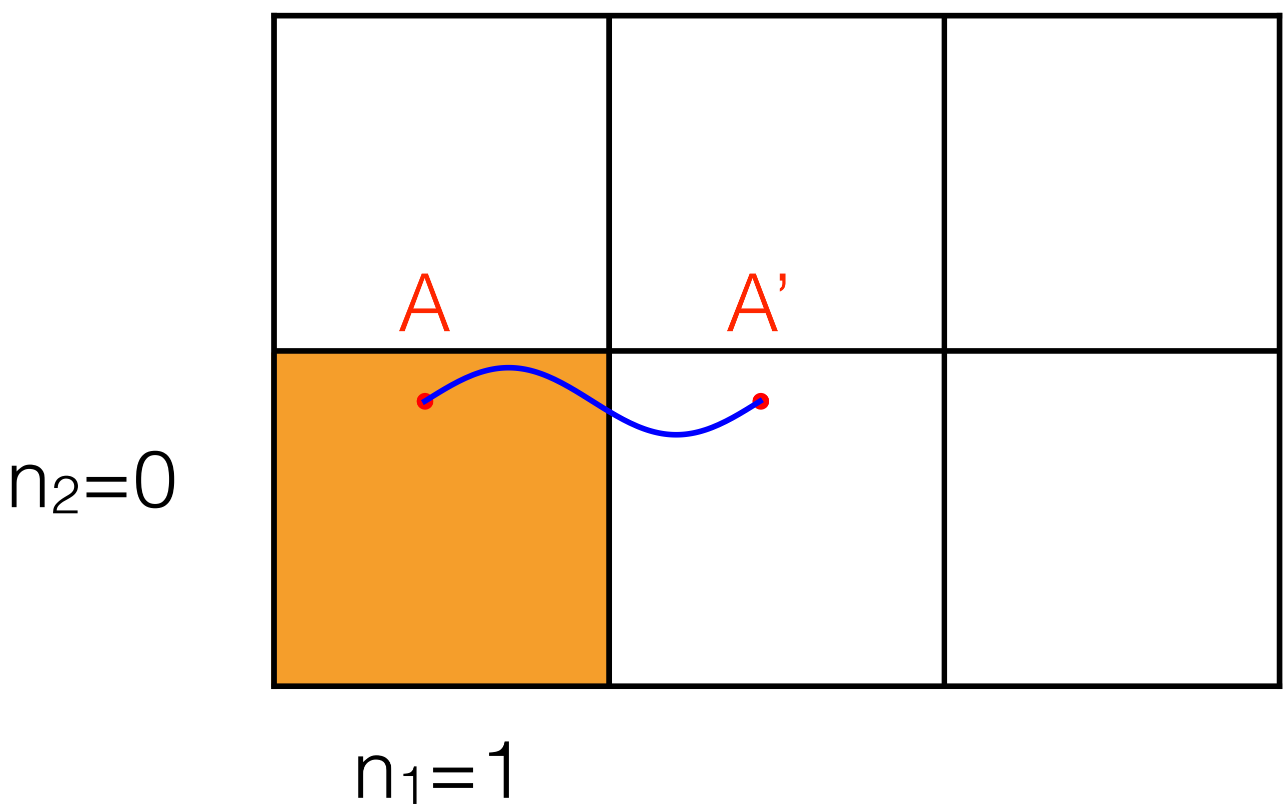

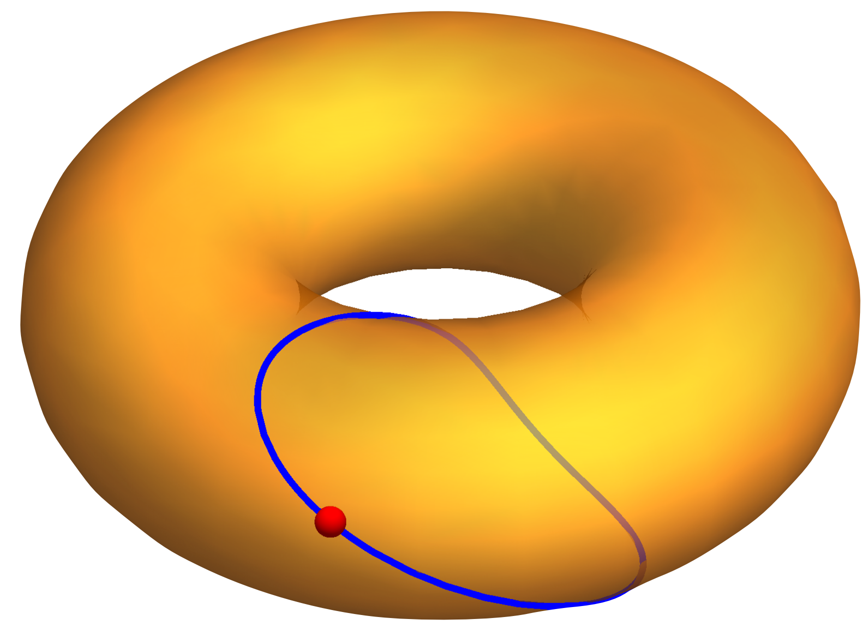

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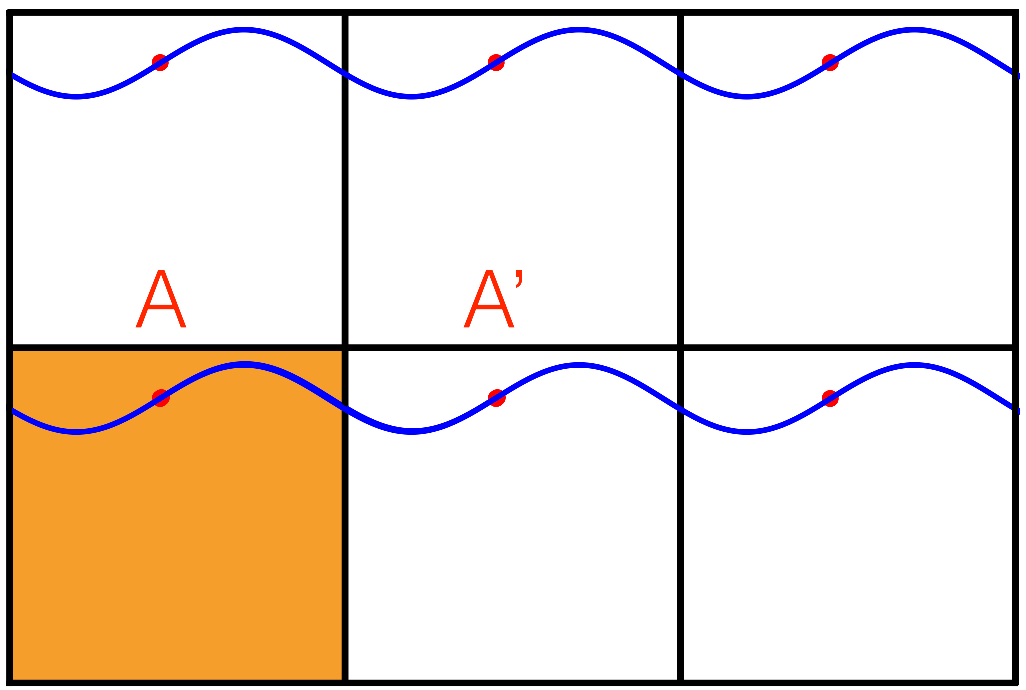
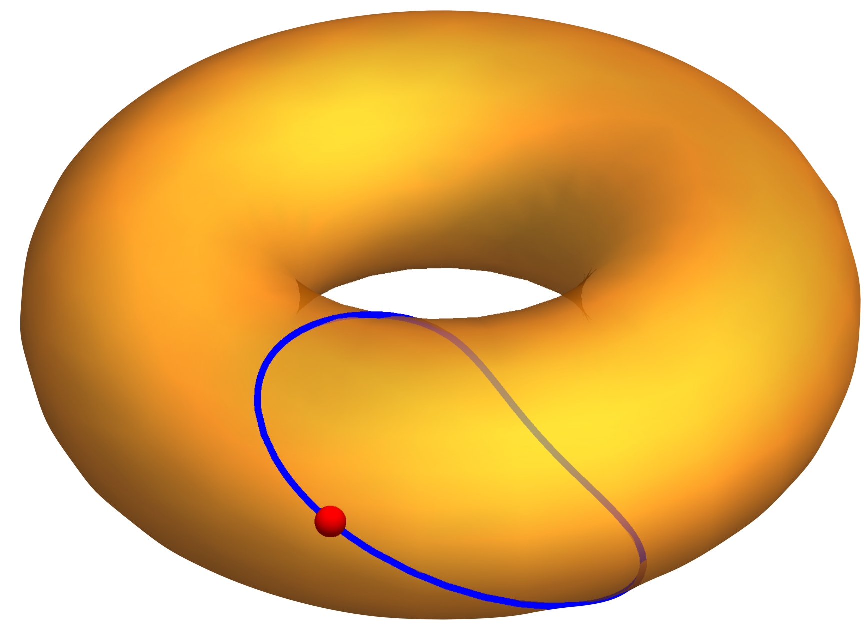


$n_2=0$

$n_1=1$



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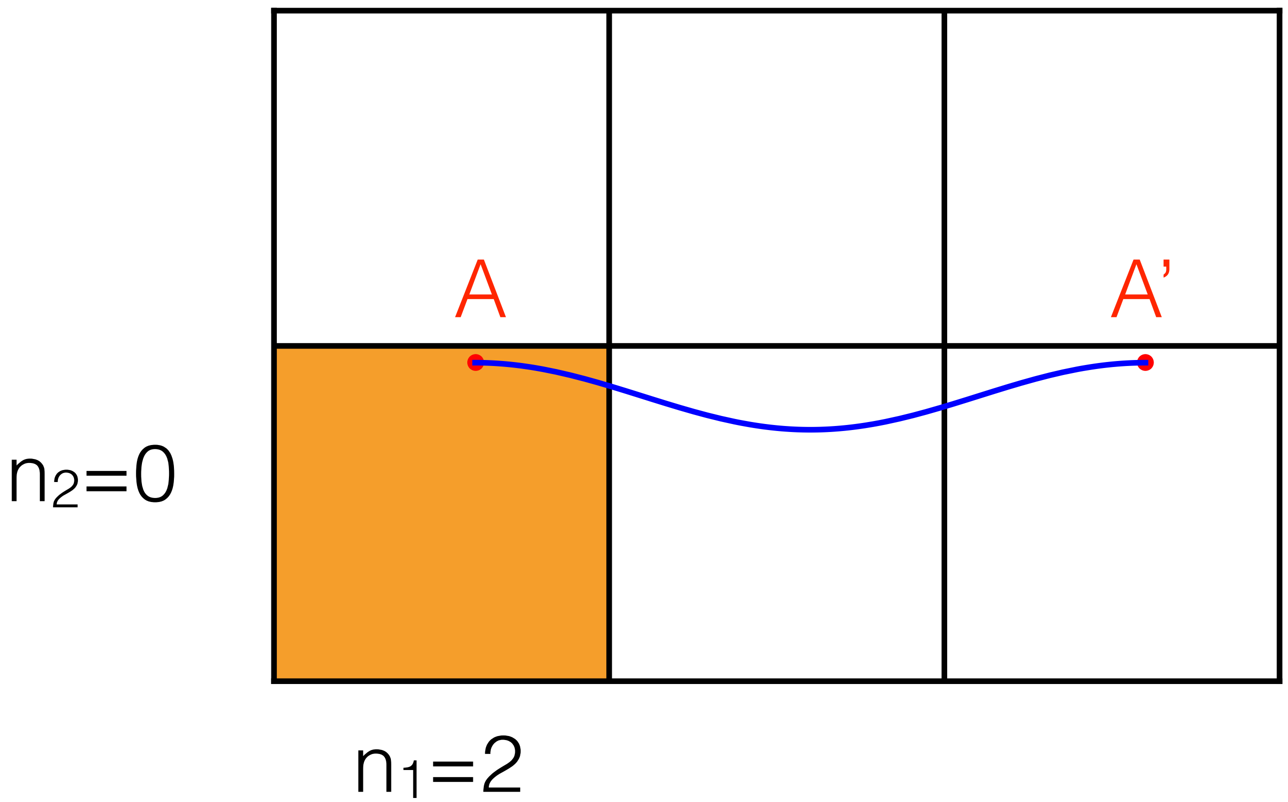

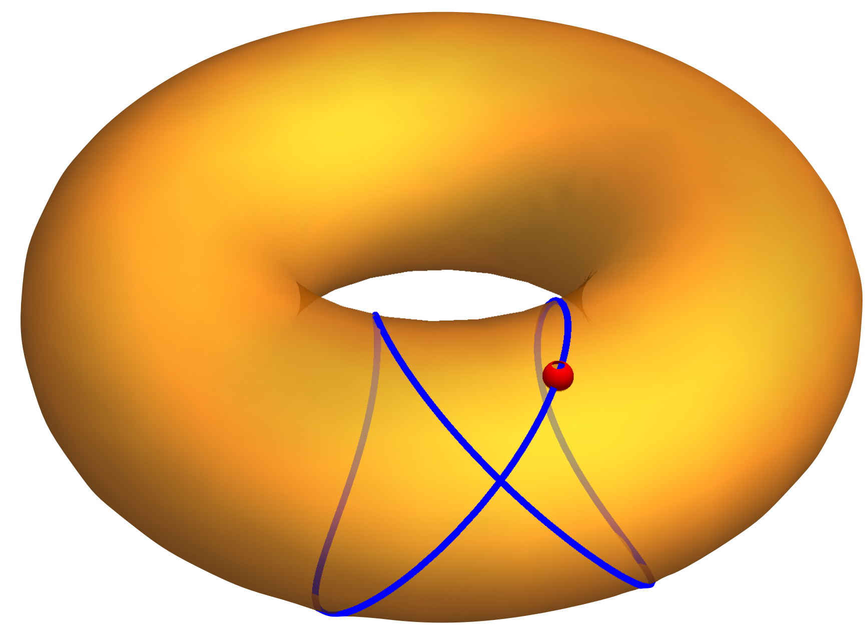

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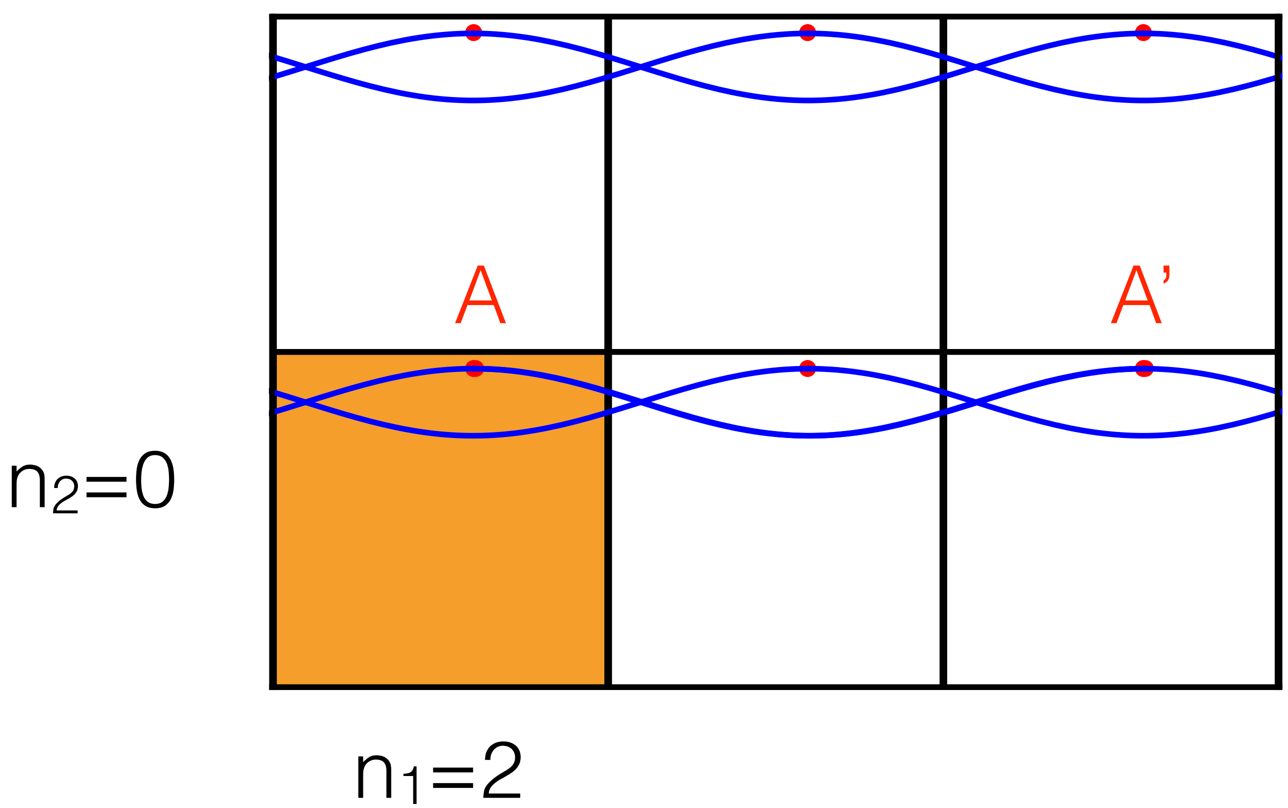

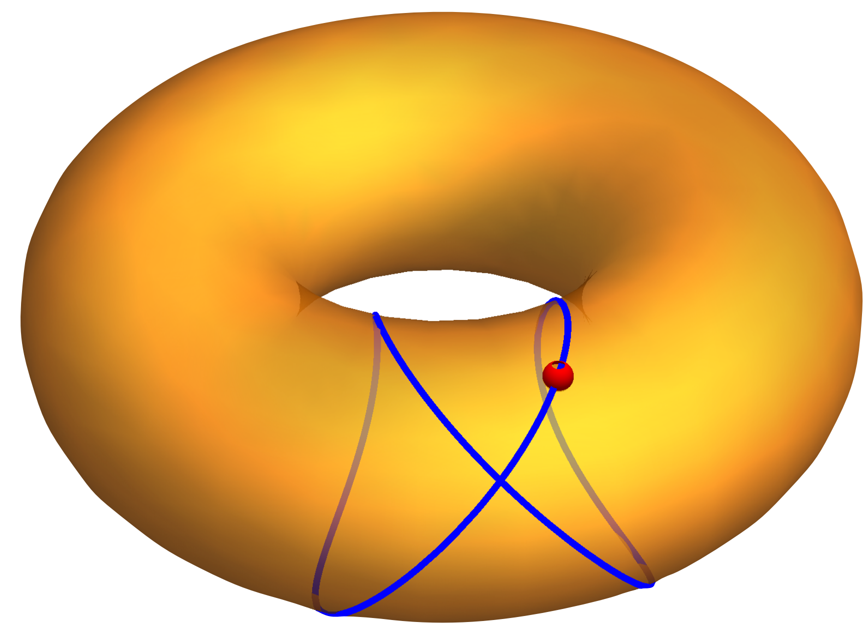

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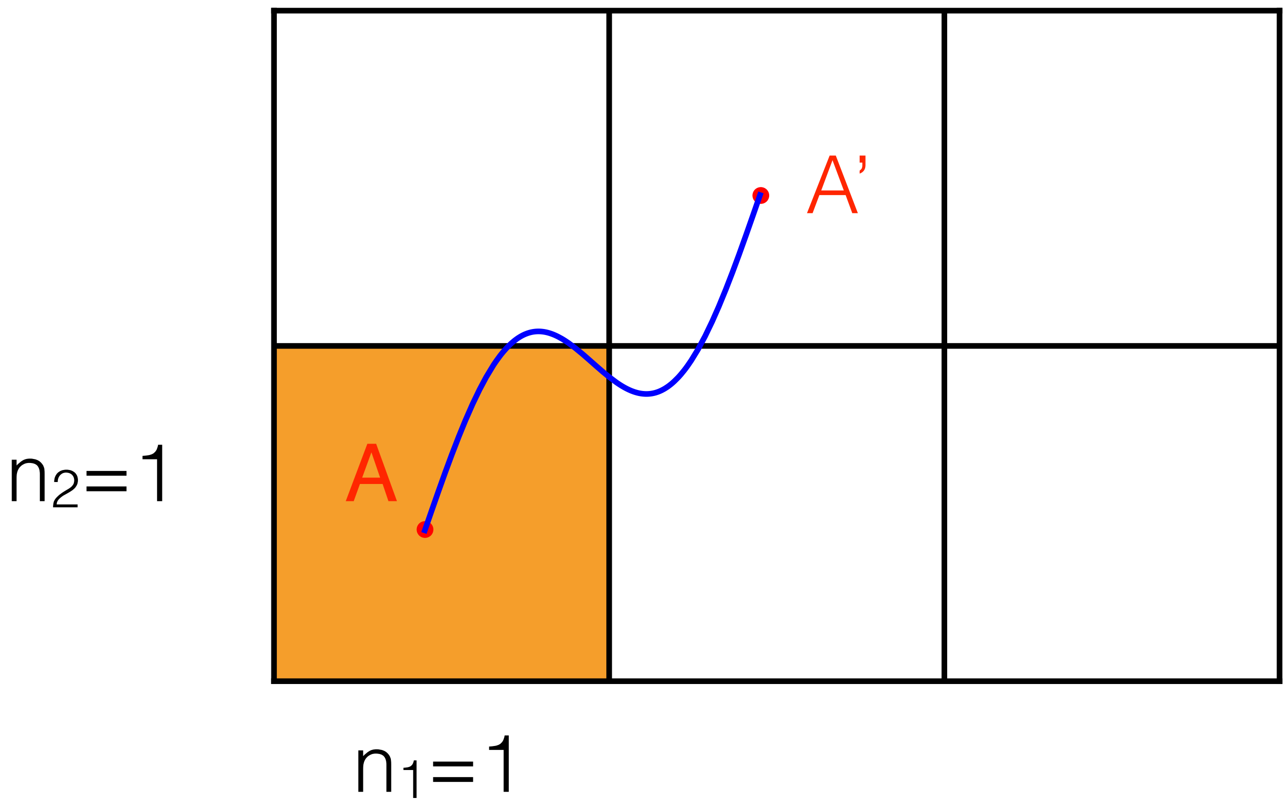

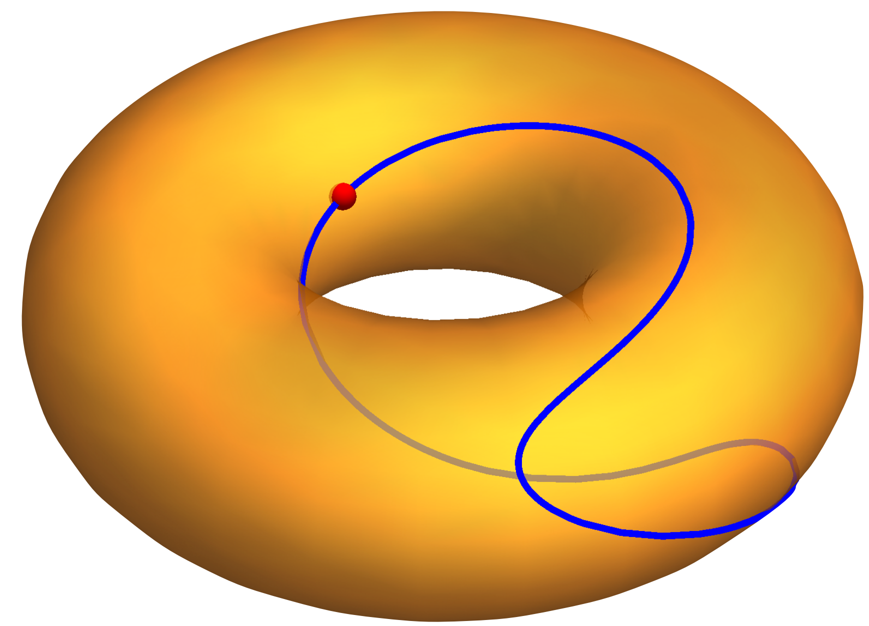

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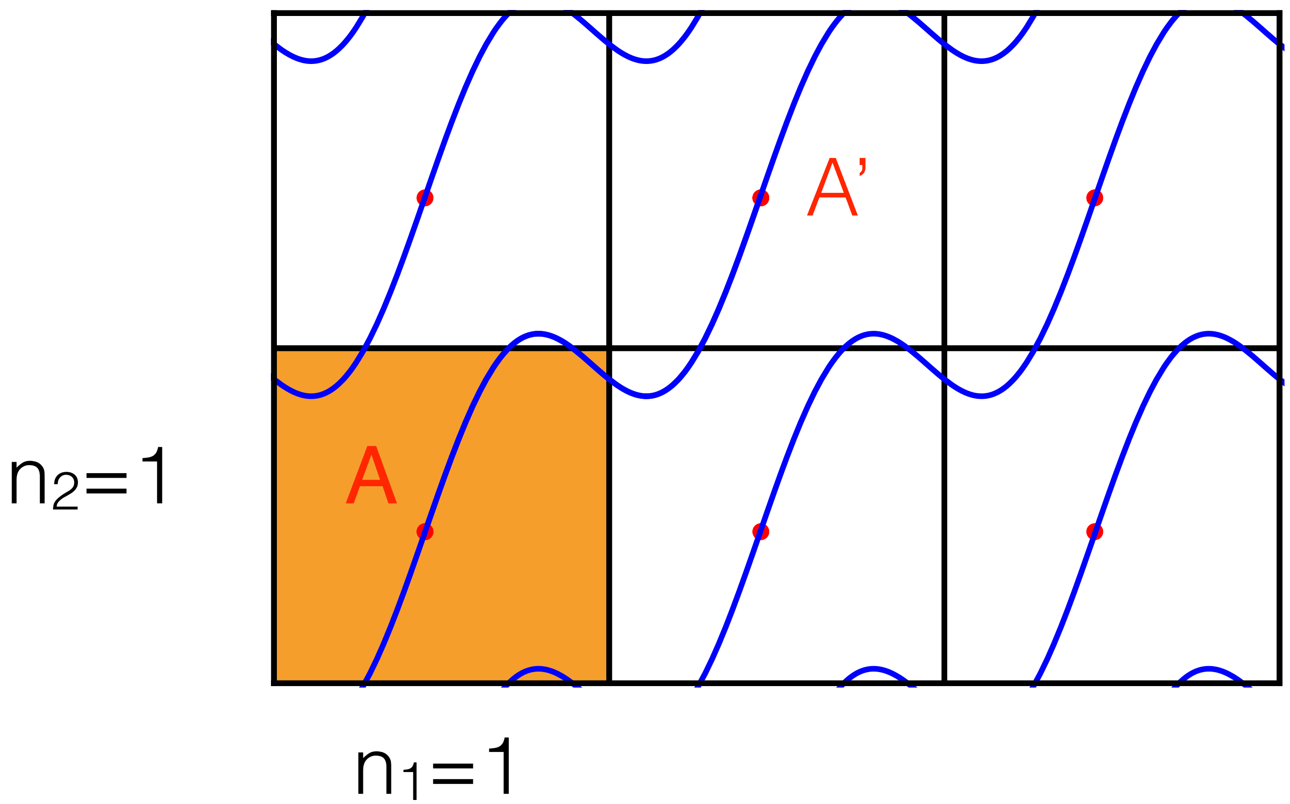

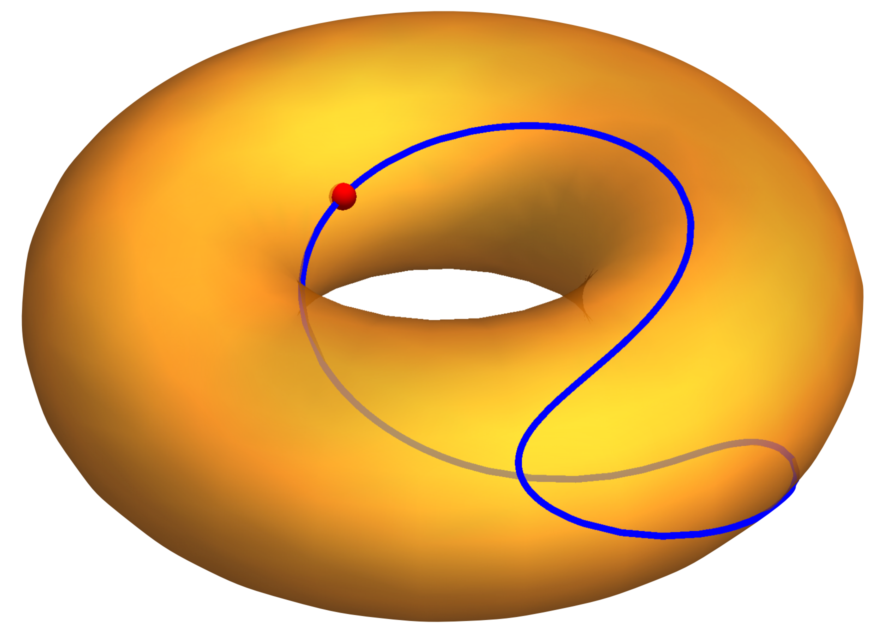

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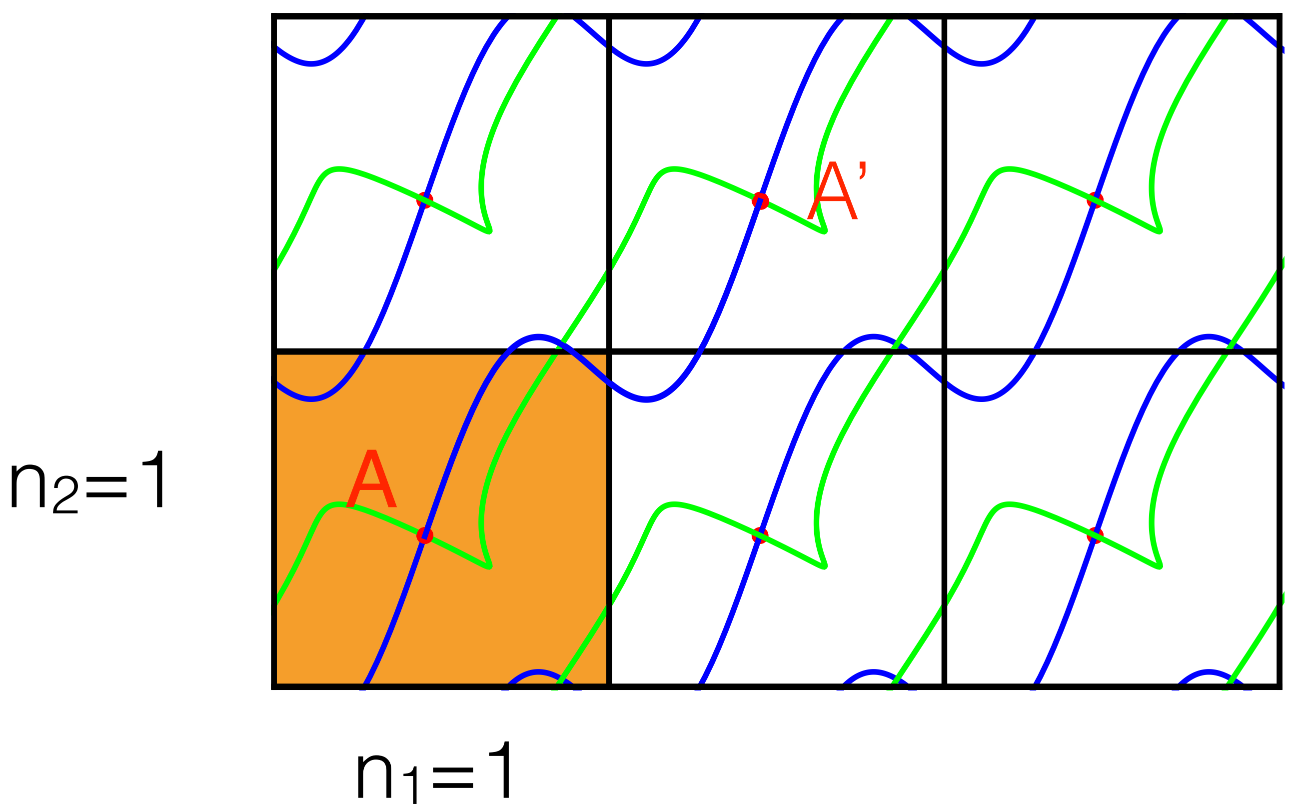
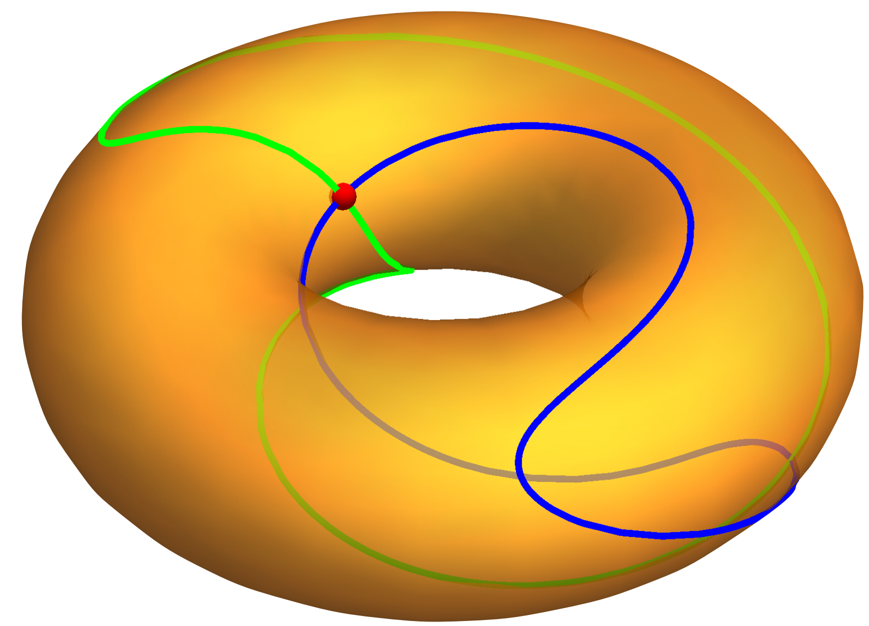
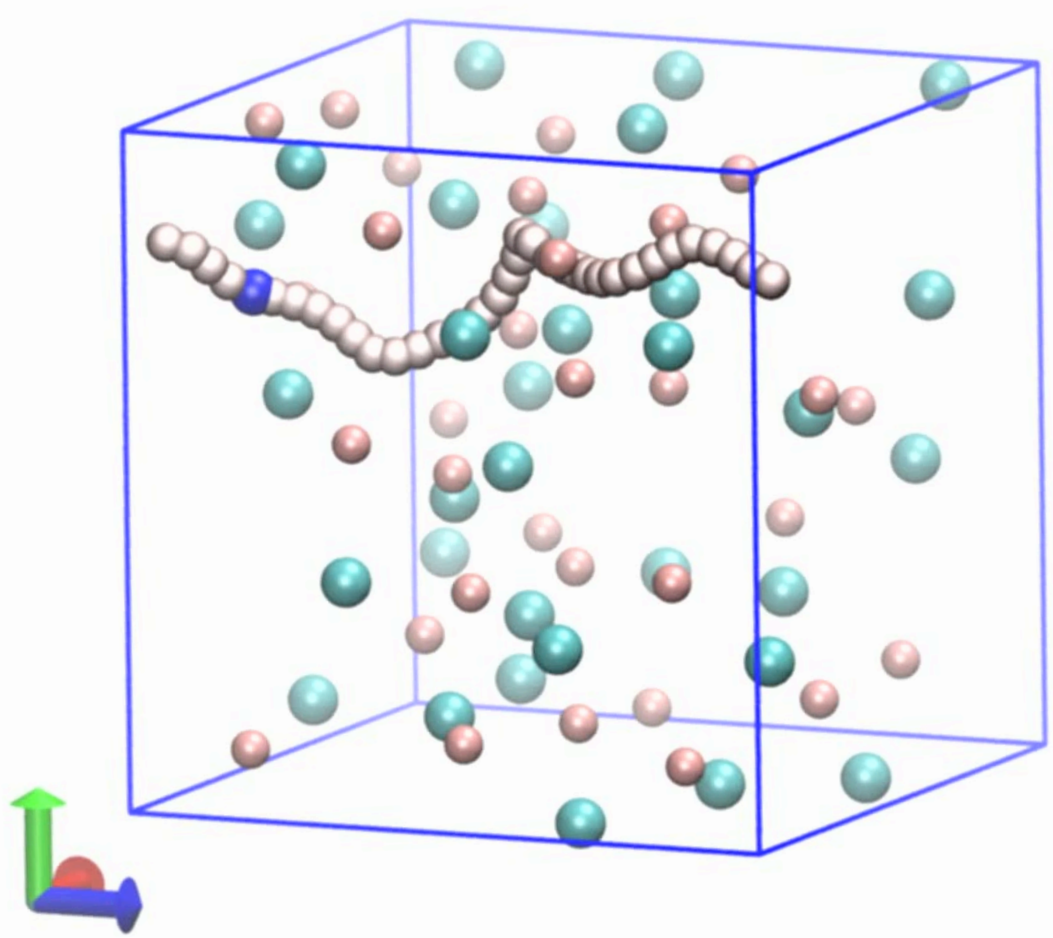
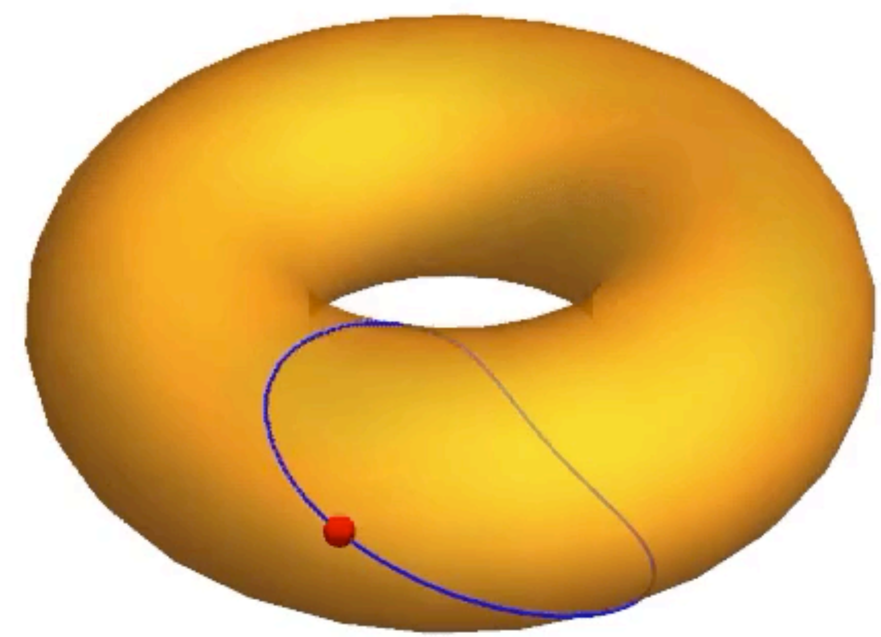




$$Q(AA') = Q(AA') = Q[n_1 = 1, n_2 = 1]$$

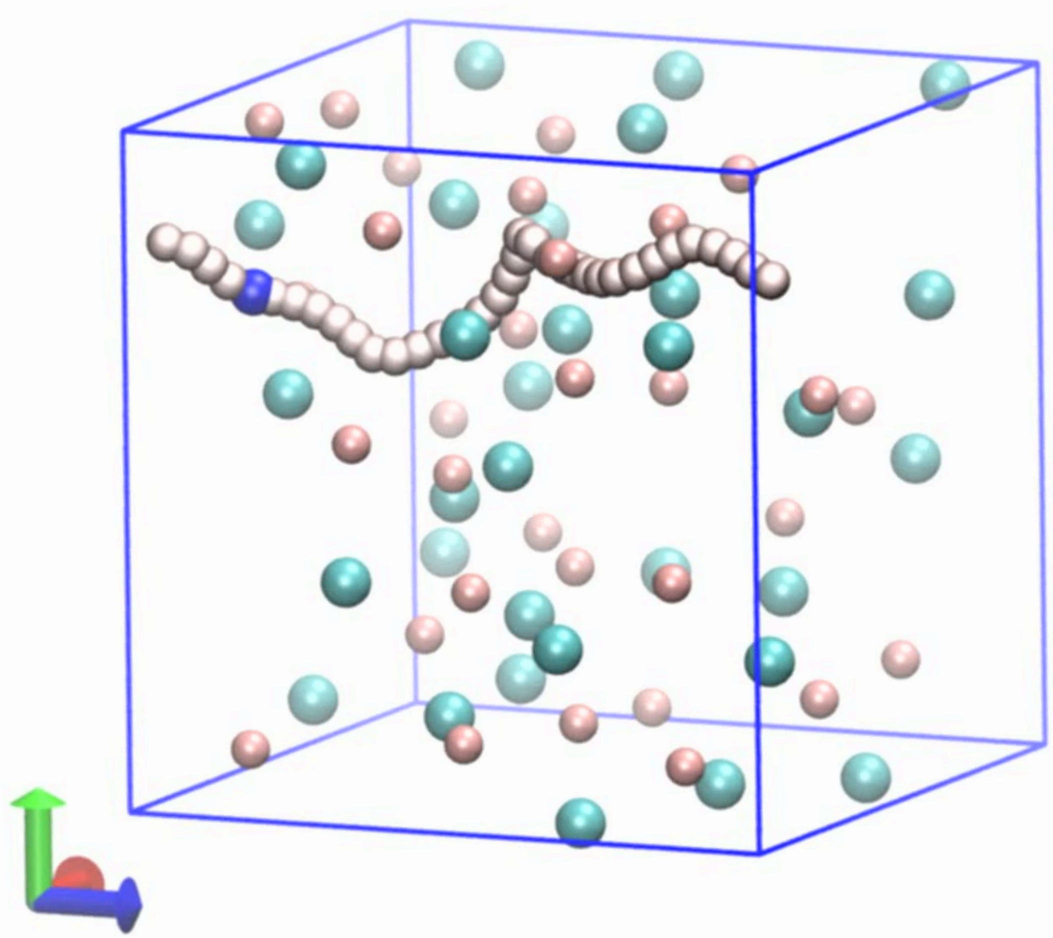
a numerical experiment on molten KCl

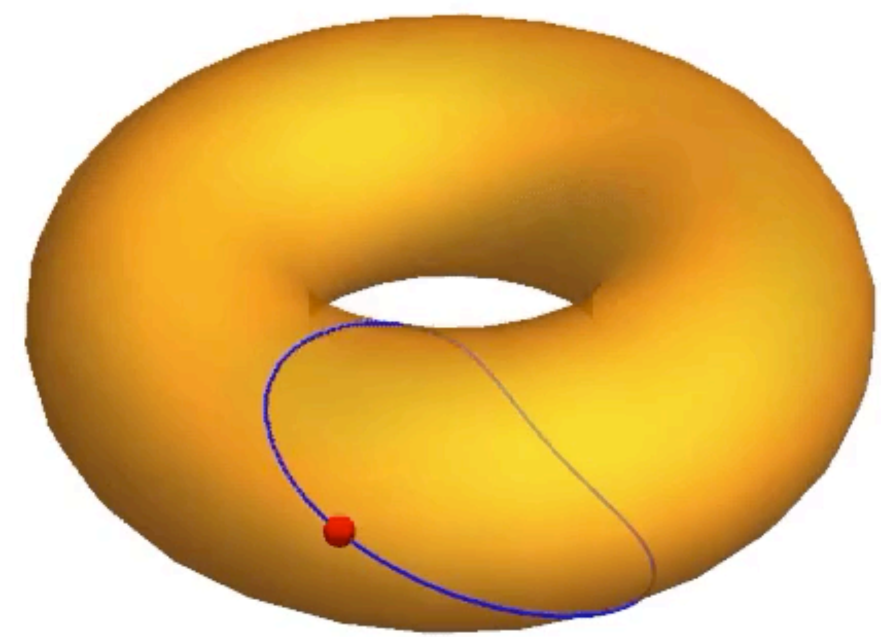




a topologically non-trivial minimum-energy path
connecting two identical configurations of a ionic fluid

a numerical experiment on molten KCl





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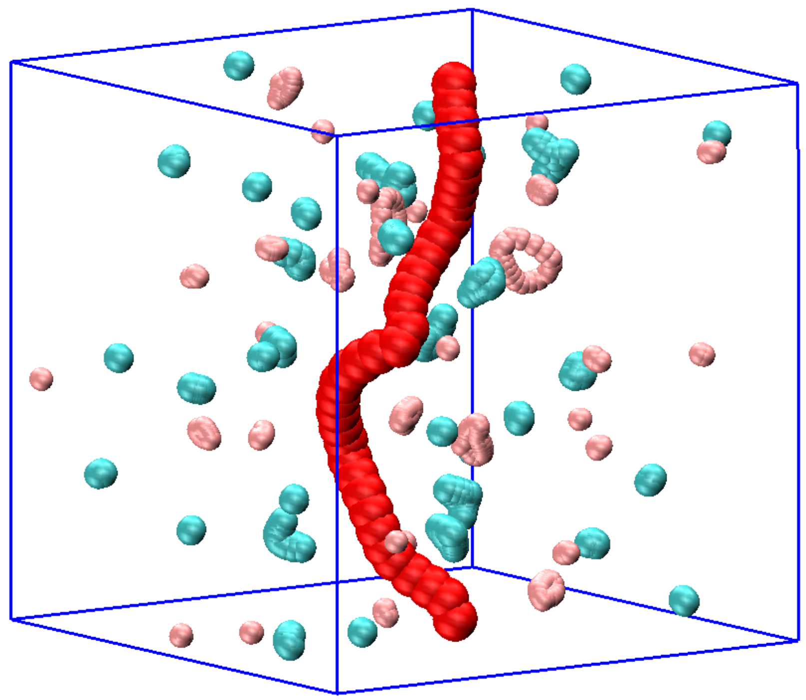

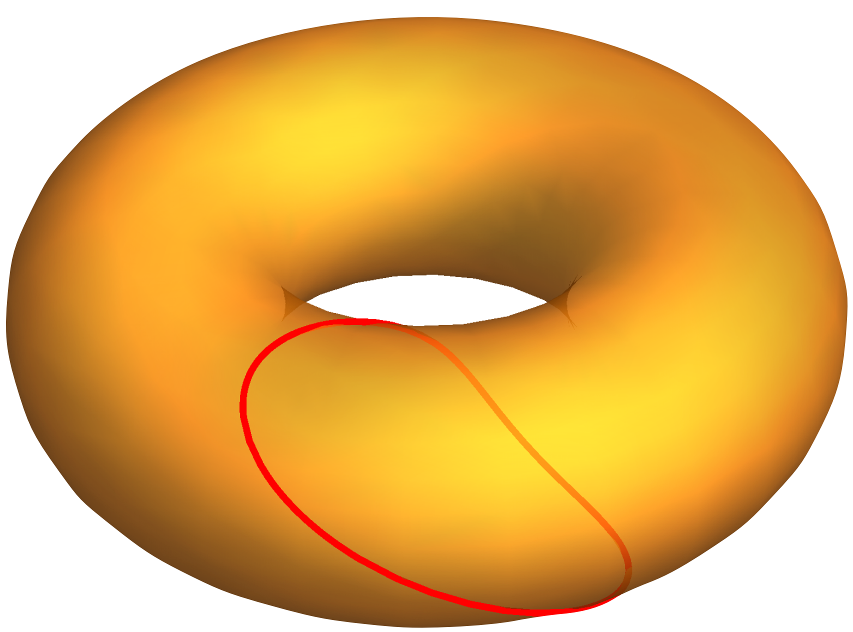

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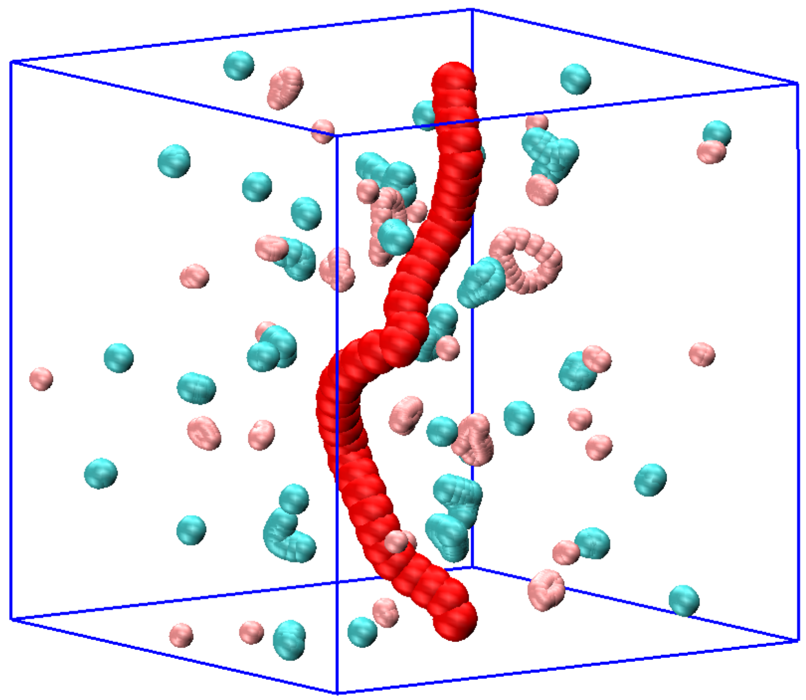

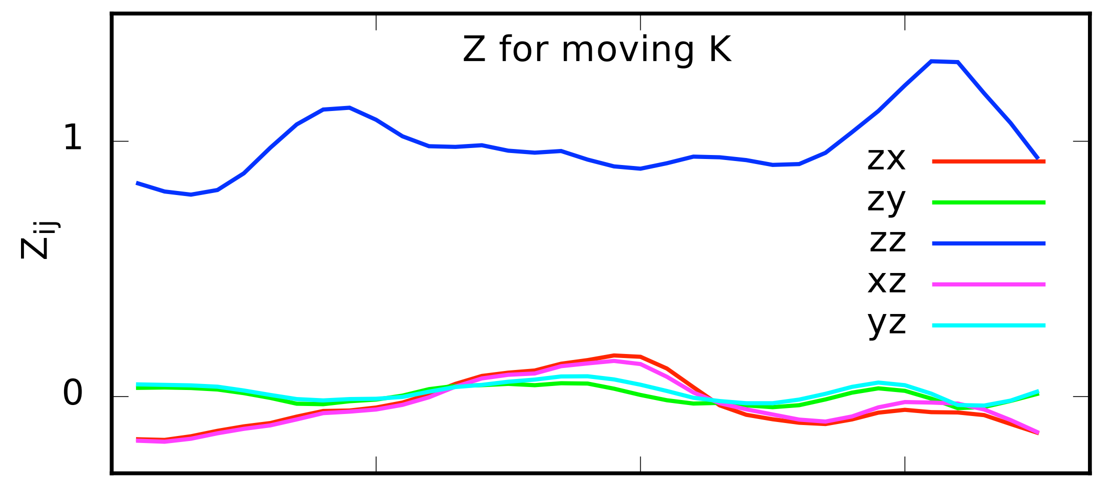

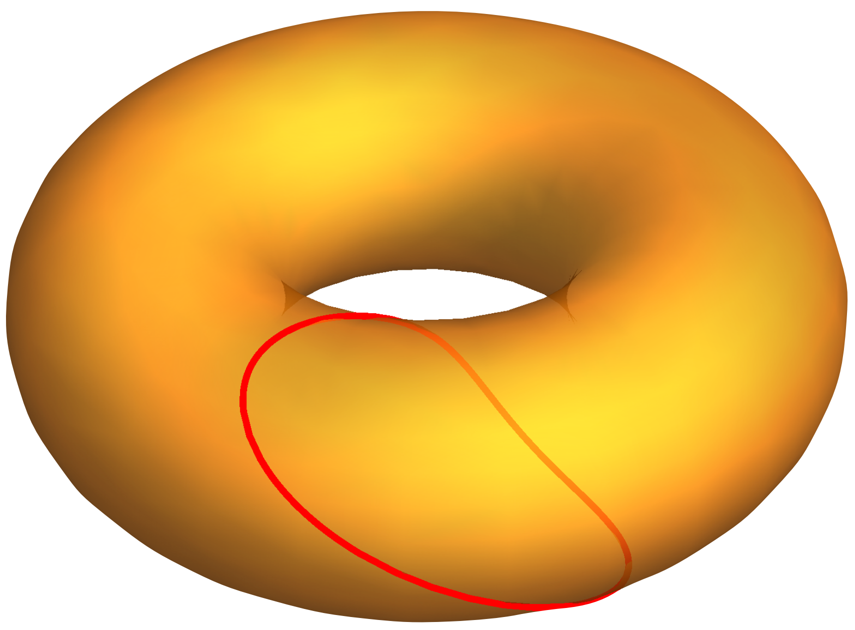

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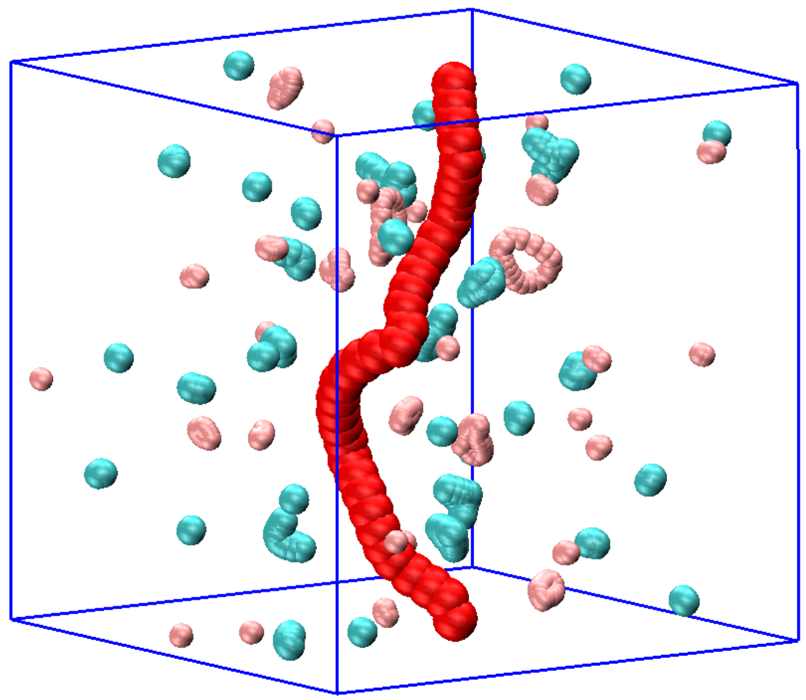
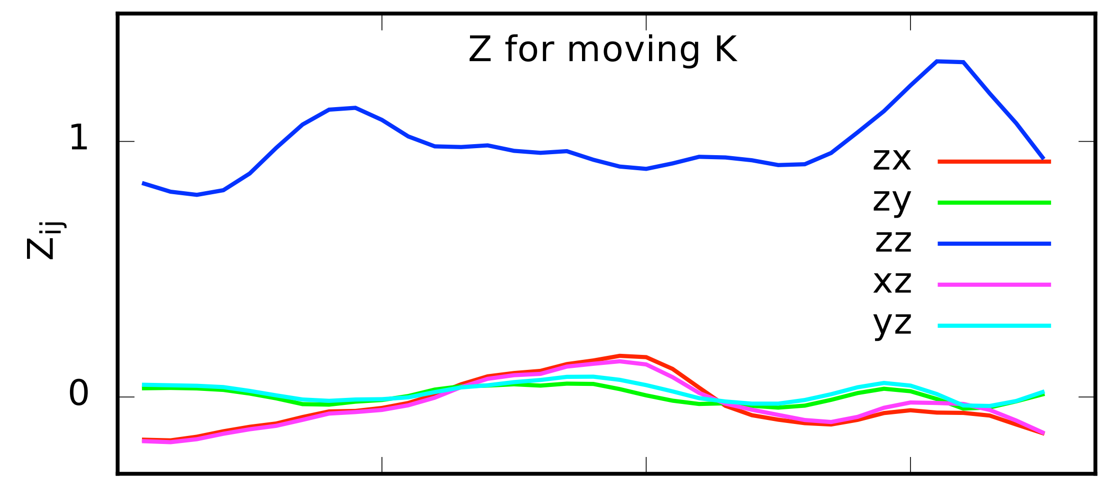
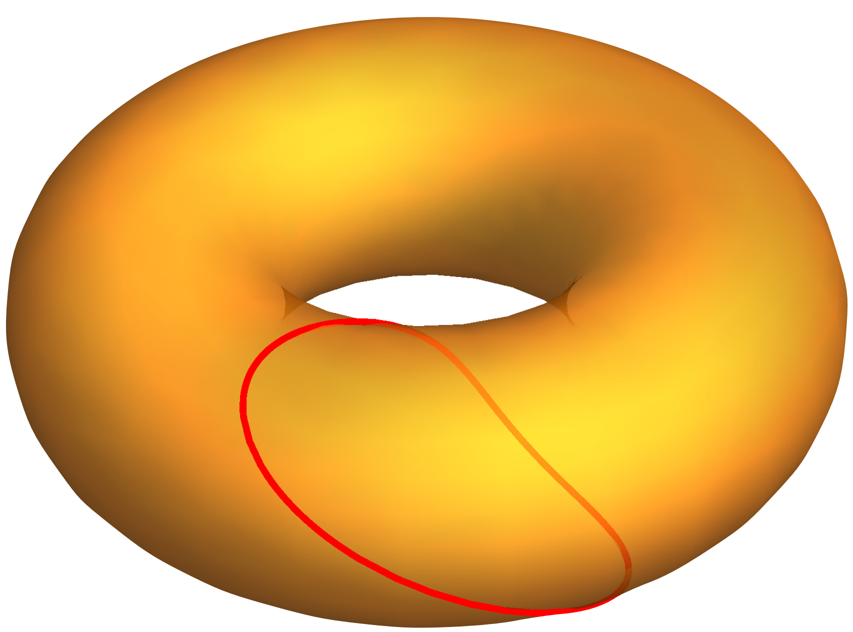
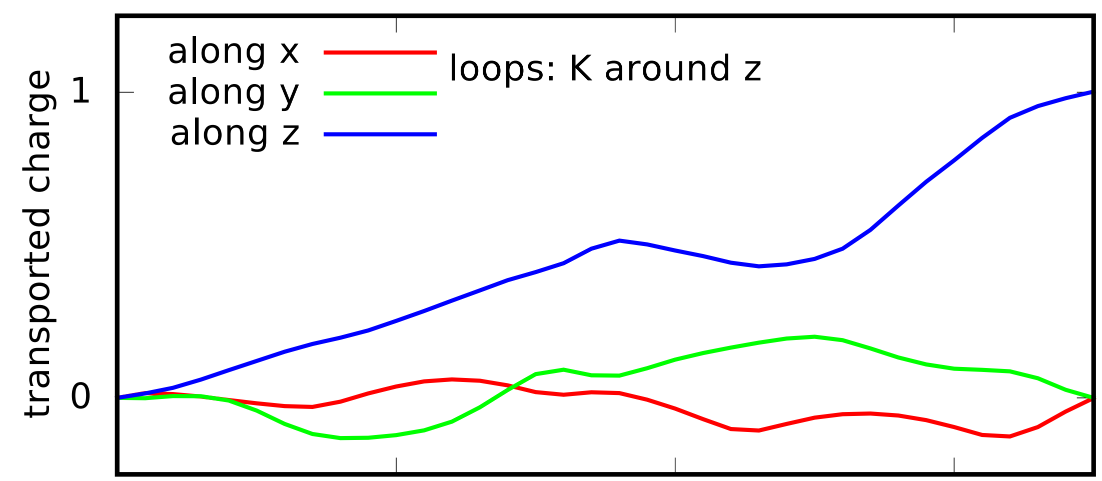


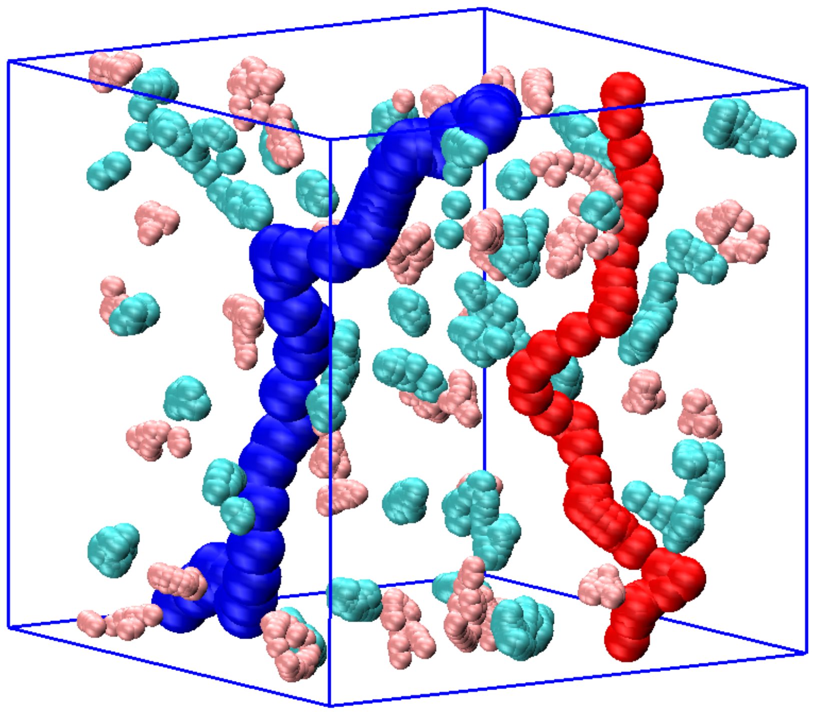






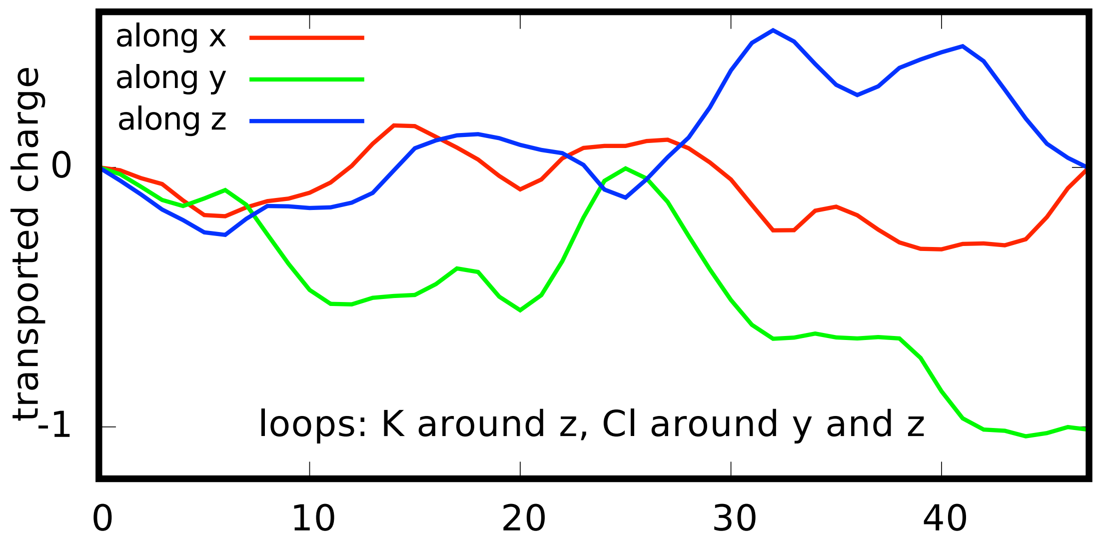
qx = =-0.000(6); qy = 0.000(2); qz = 1.00(18)

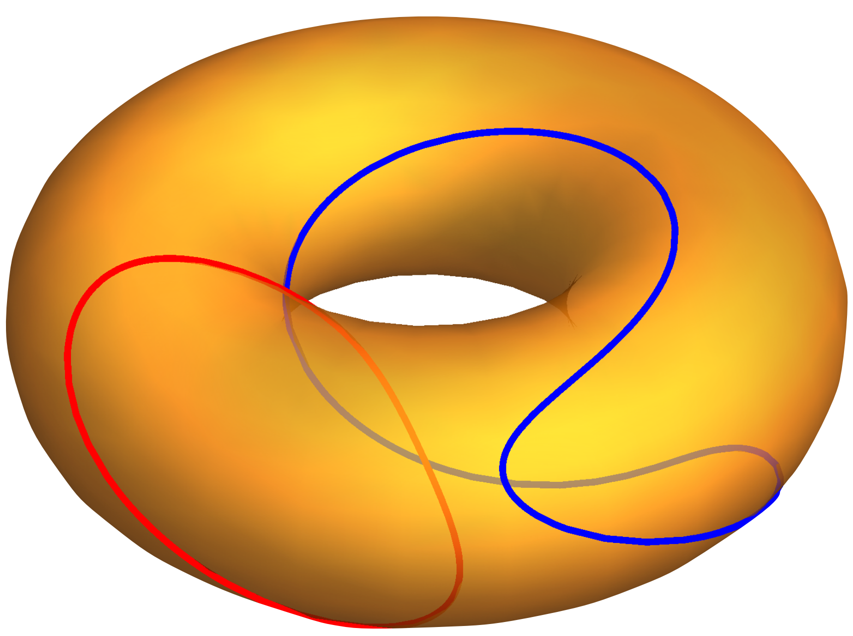
a numerical experiment on molten KCl



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

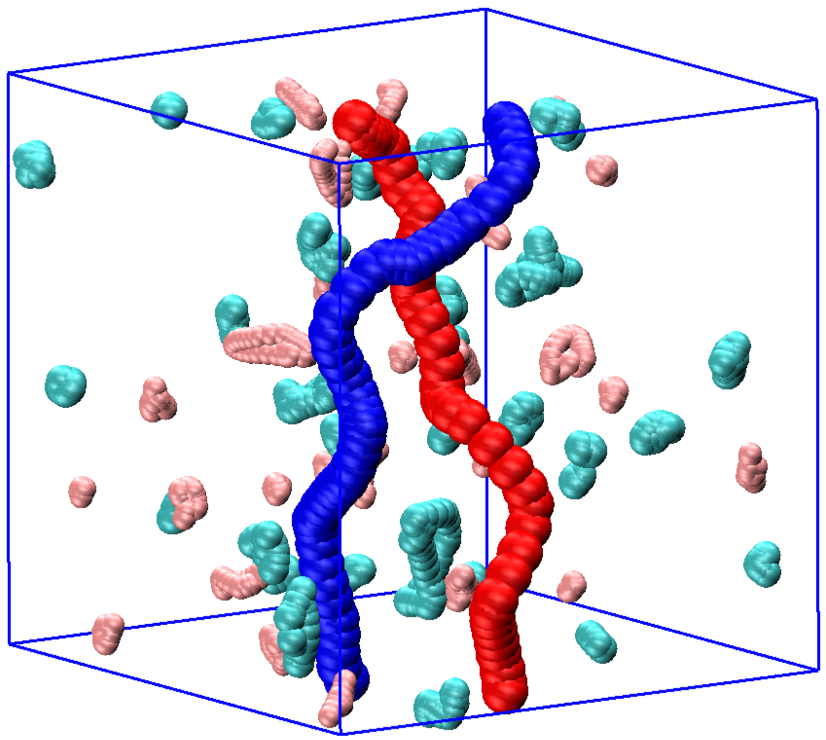
$Q_z[K] = 1$ $Q_z[K] = 0$

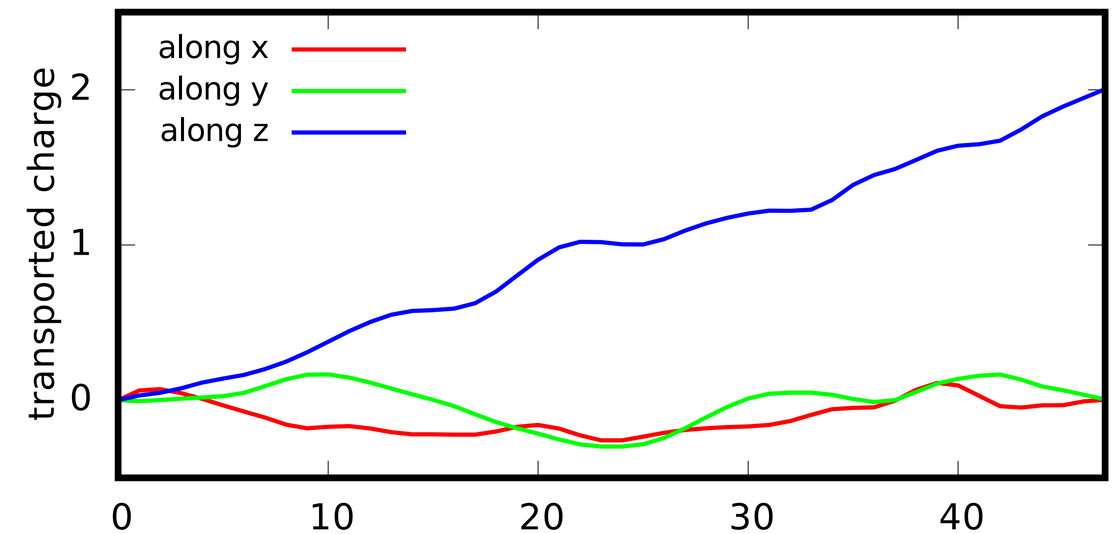


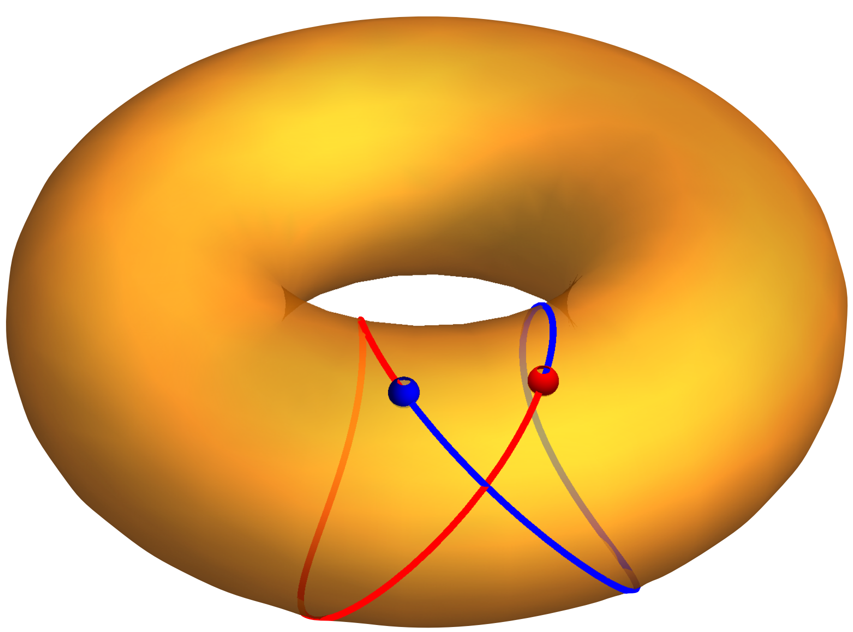


the charges transported by K and Cl around z cancel exactly

a numerical experiment on molten KCl







the exchange of two cations
transports a net charge equal to +2

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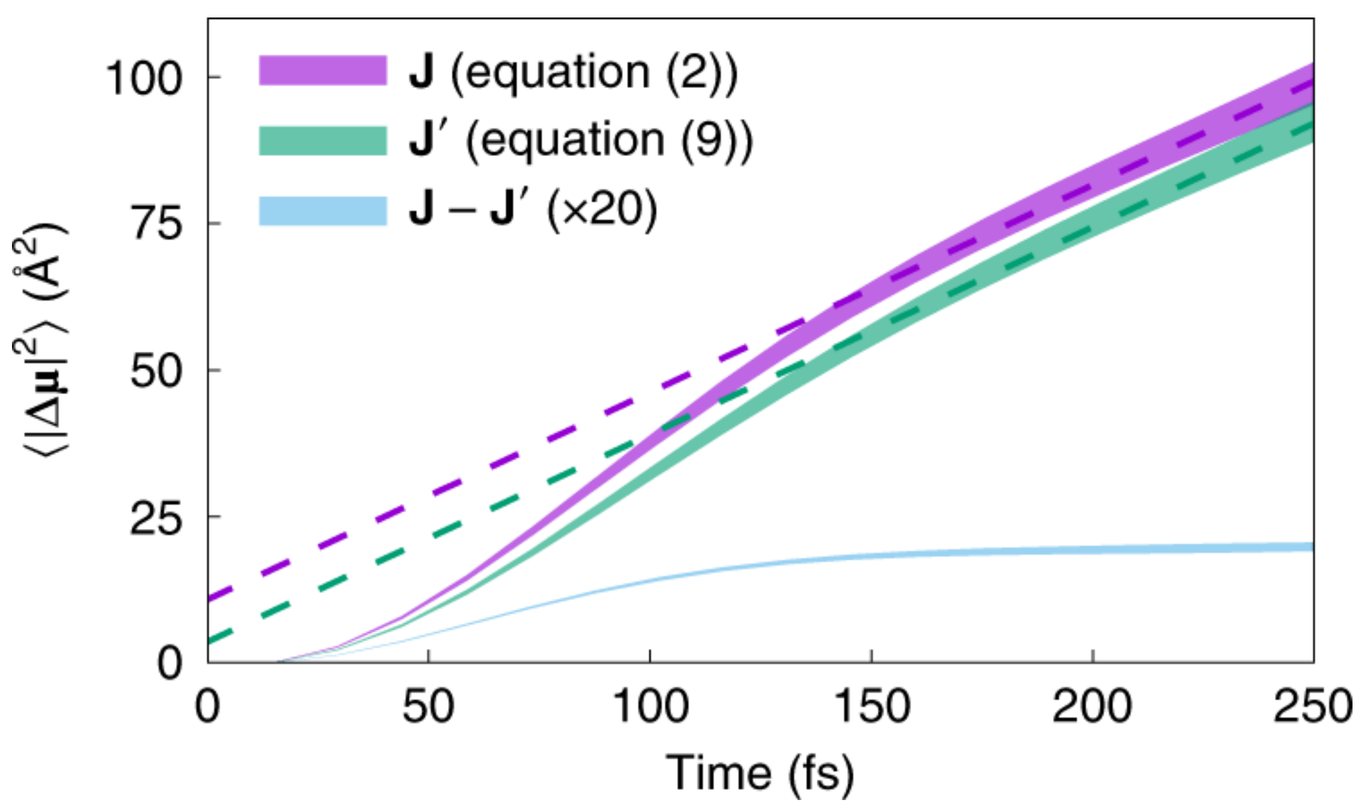
$$q_{i\alpha\beta} = q_{S(i)}\delta_{\alpha\beta}$$

atomic oxidation state

currents from atomic oxidation numbers

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

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



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

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- *gauge invariance* and *topological quantisation* of charge transport make the electric conductivity of ionic fluids depend on the formal oxidation numbers of the ionic species, via the Green-Kubo formula.

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Topological quantization and gauge invariance of charge transport in liquid insulators

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

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Microscopic theory and quantum simulation of atomic heat transport

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

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SISSA, now @IBM Zürich

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we are sorry to see you leaving …
… arrivederci!
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