topological quantisation and gauge invariance of charge transport in liquid insulators

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Trieste — Italy

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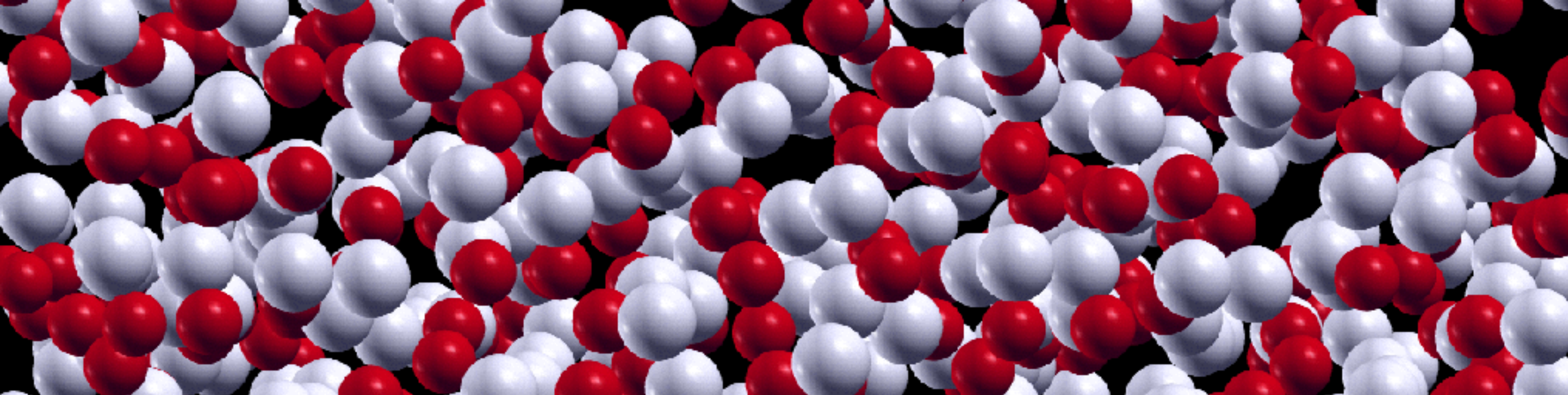

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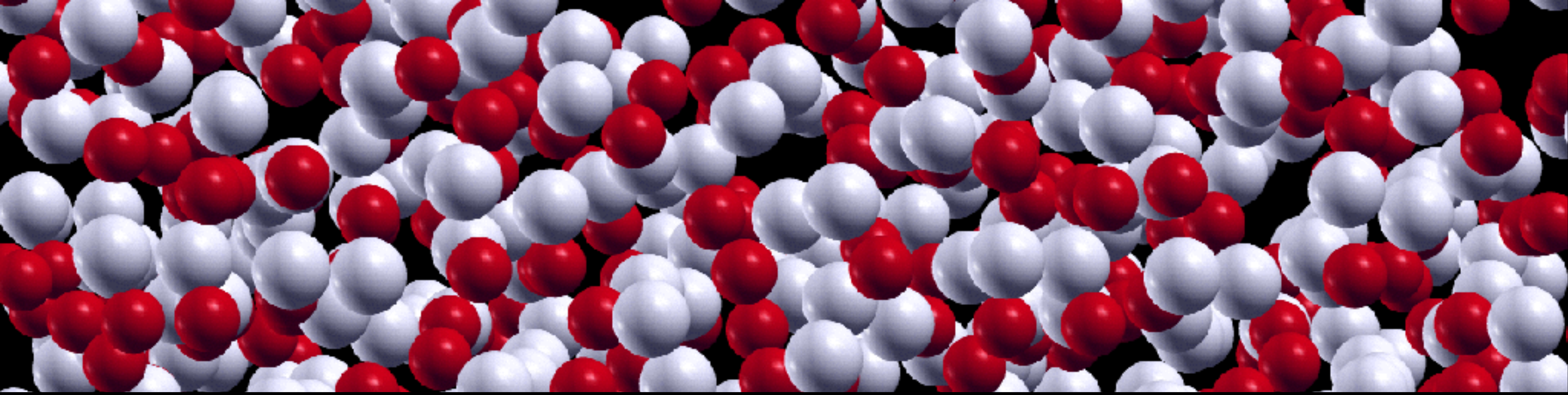

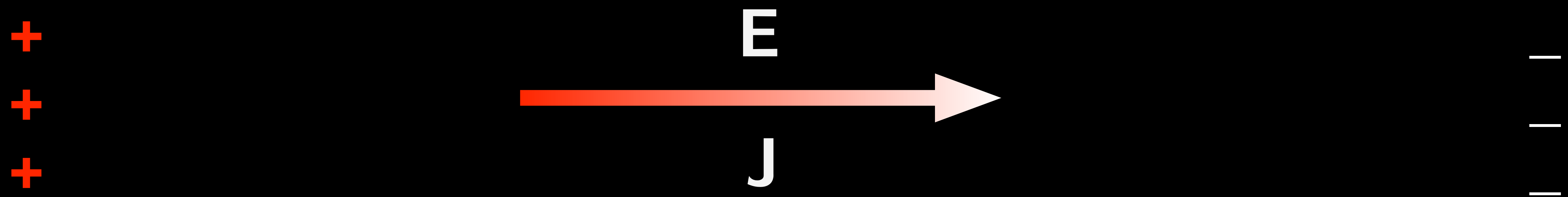

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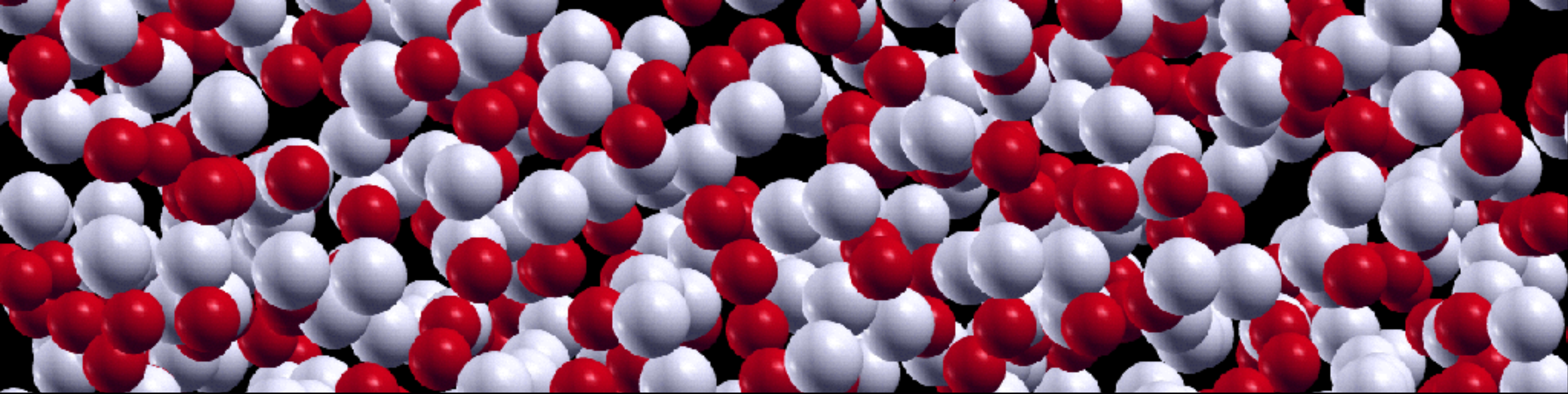
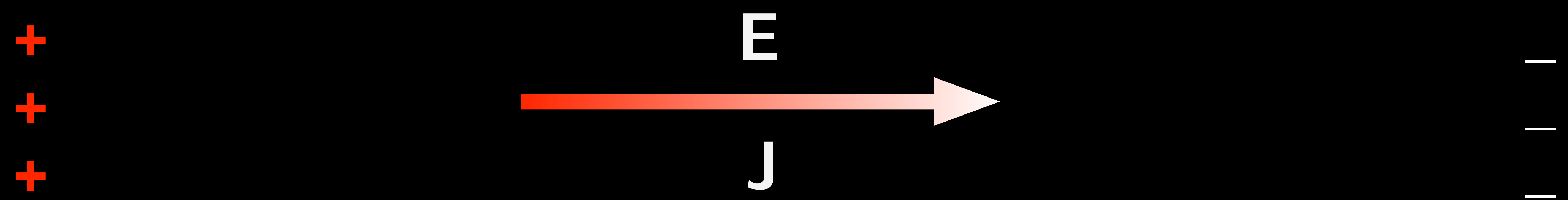
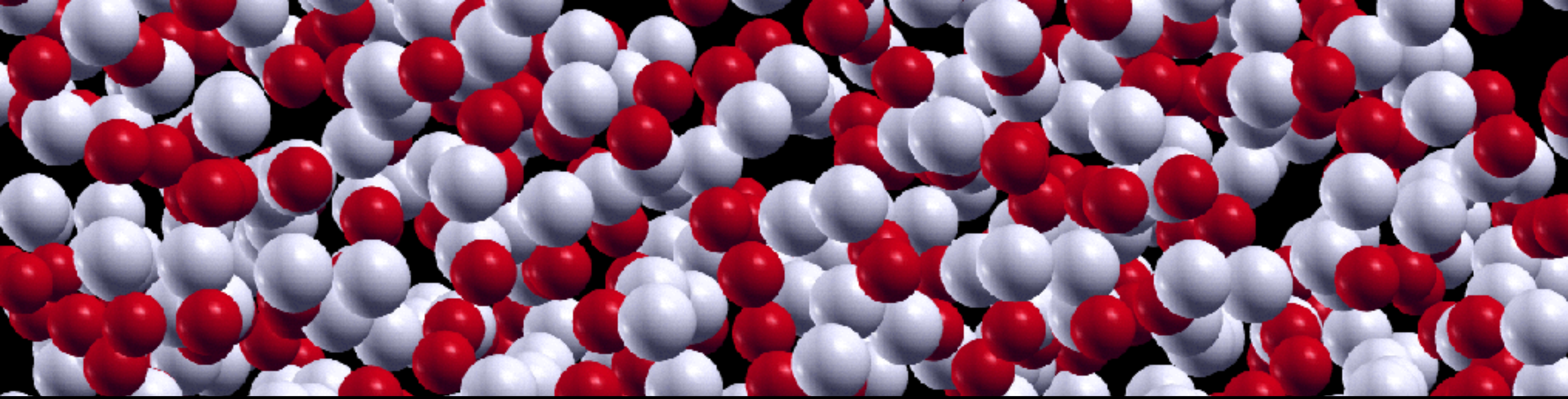
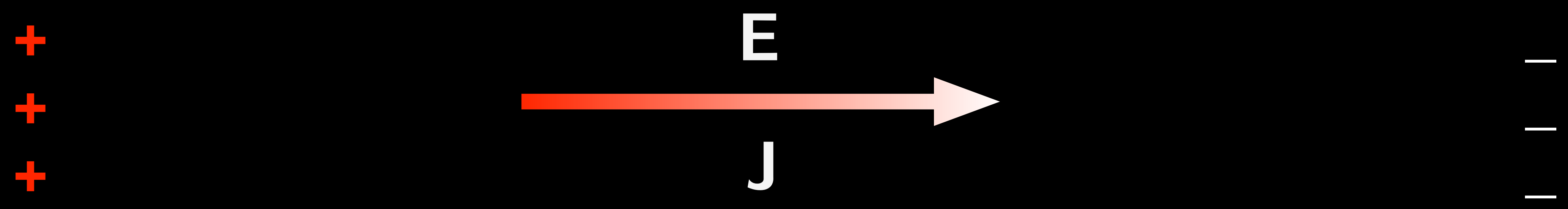




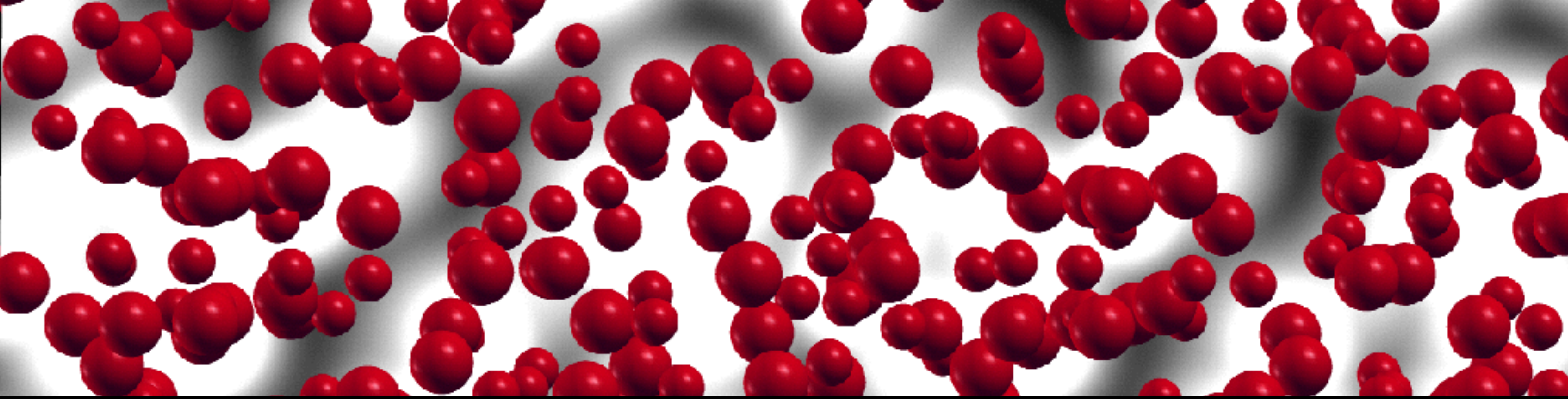
$$\mathbf{J} = \sigma \mathbf{E}$$





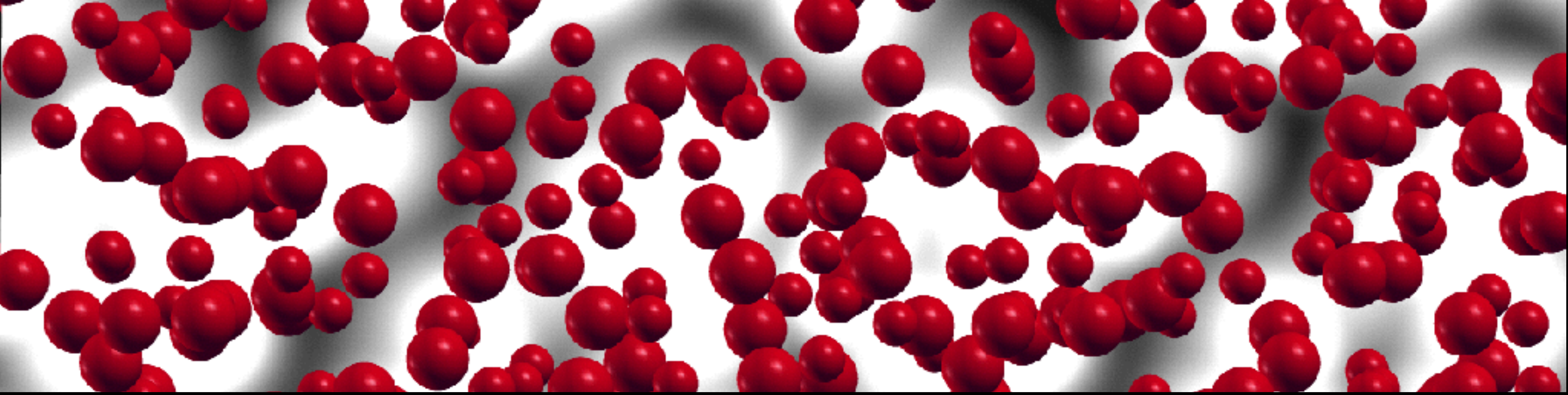
$$\mathbf{J} = \sigma \mathbf{E}$$

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



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

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



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

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

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

the Green-Kubo theory of transport

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

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

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

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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

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

the Green-Kubo theory of transport

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A = energy

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

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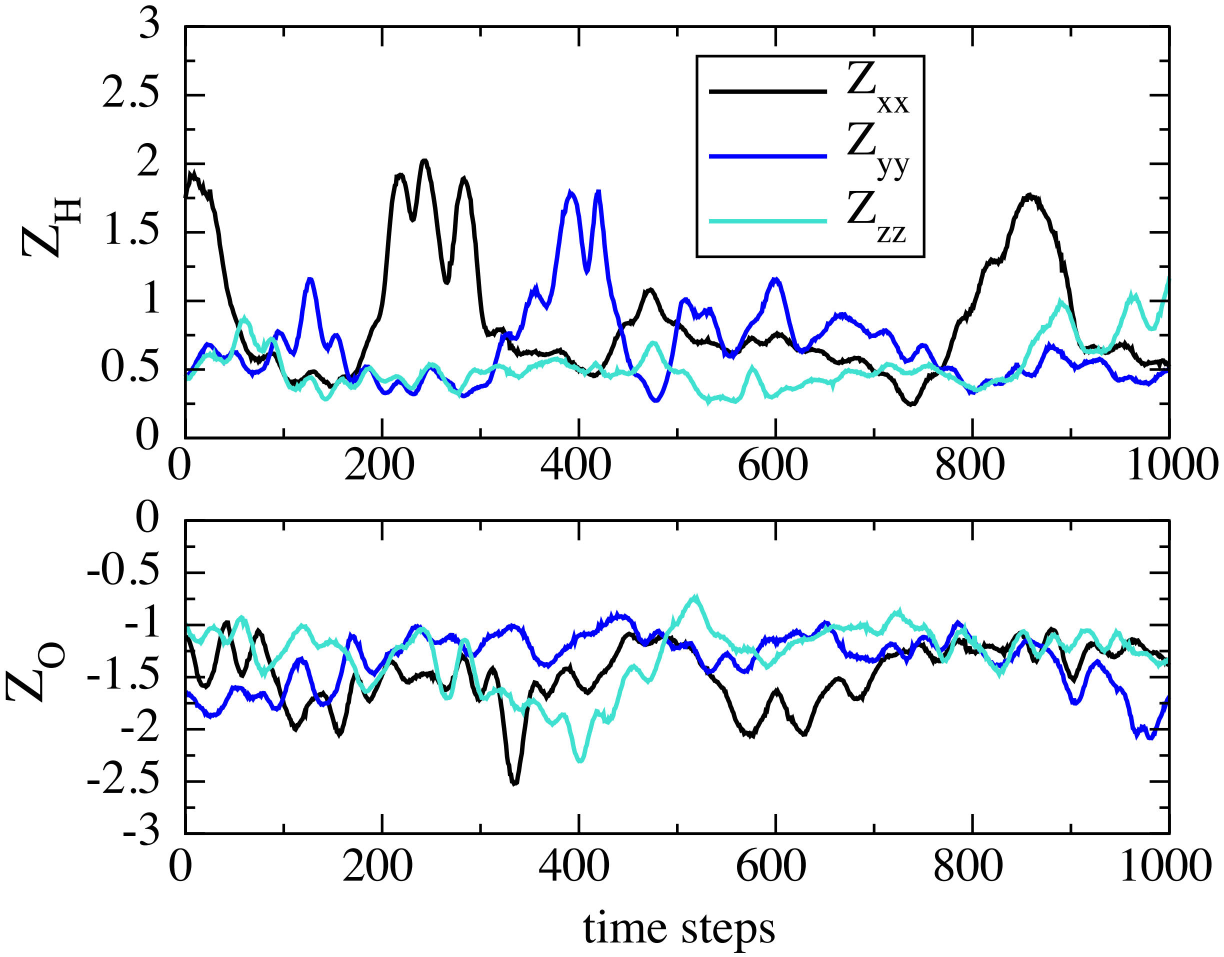
Q = charge

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

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

the conundrum

H_2O



the conundrum

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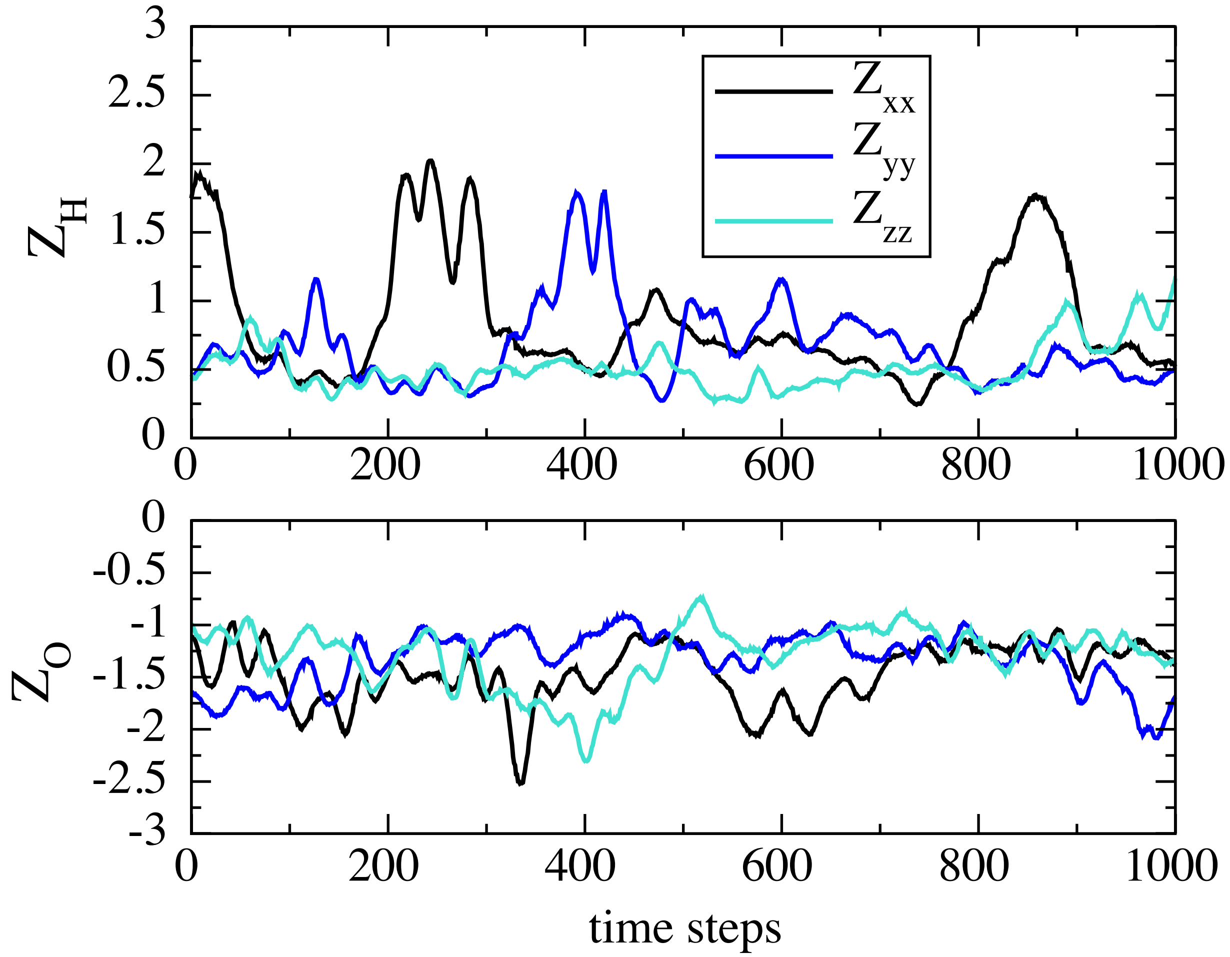

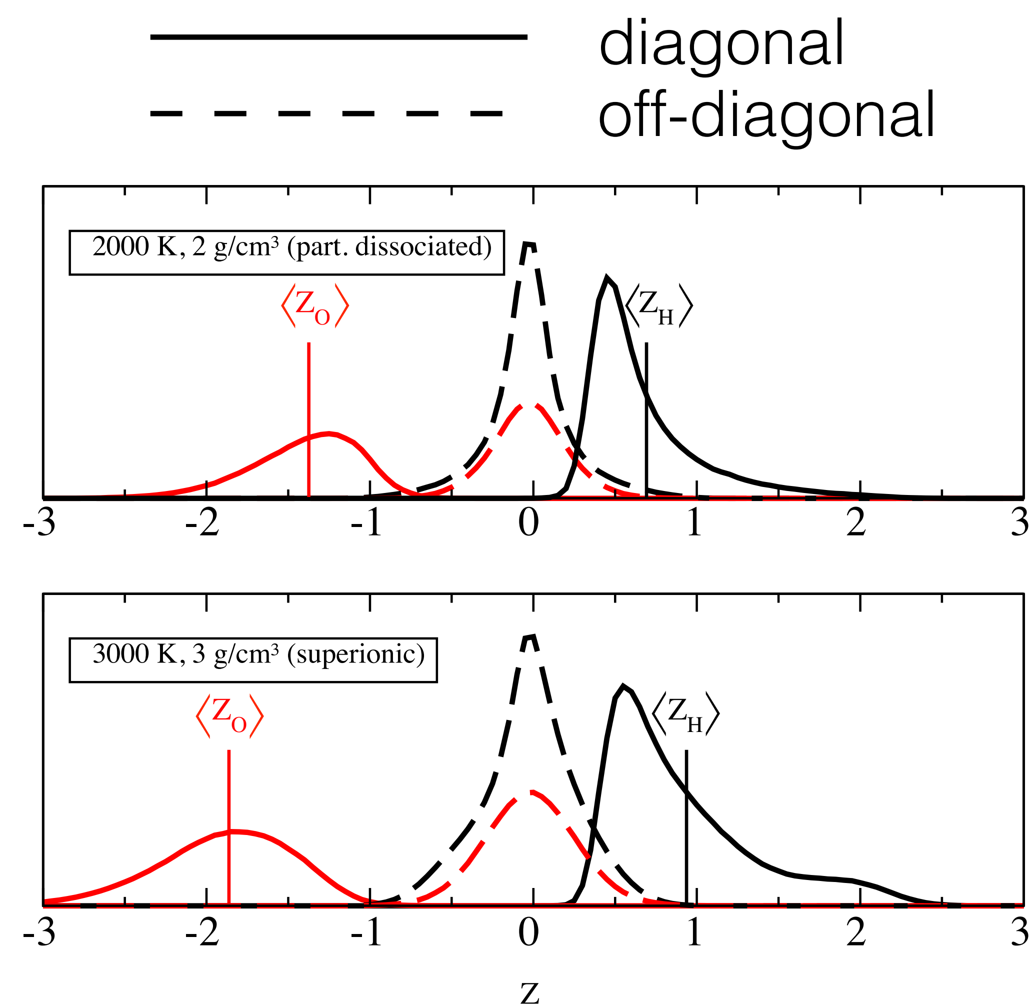

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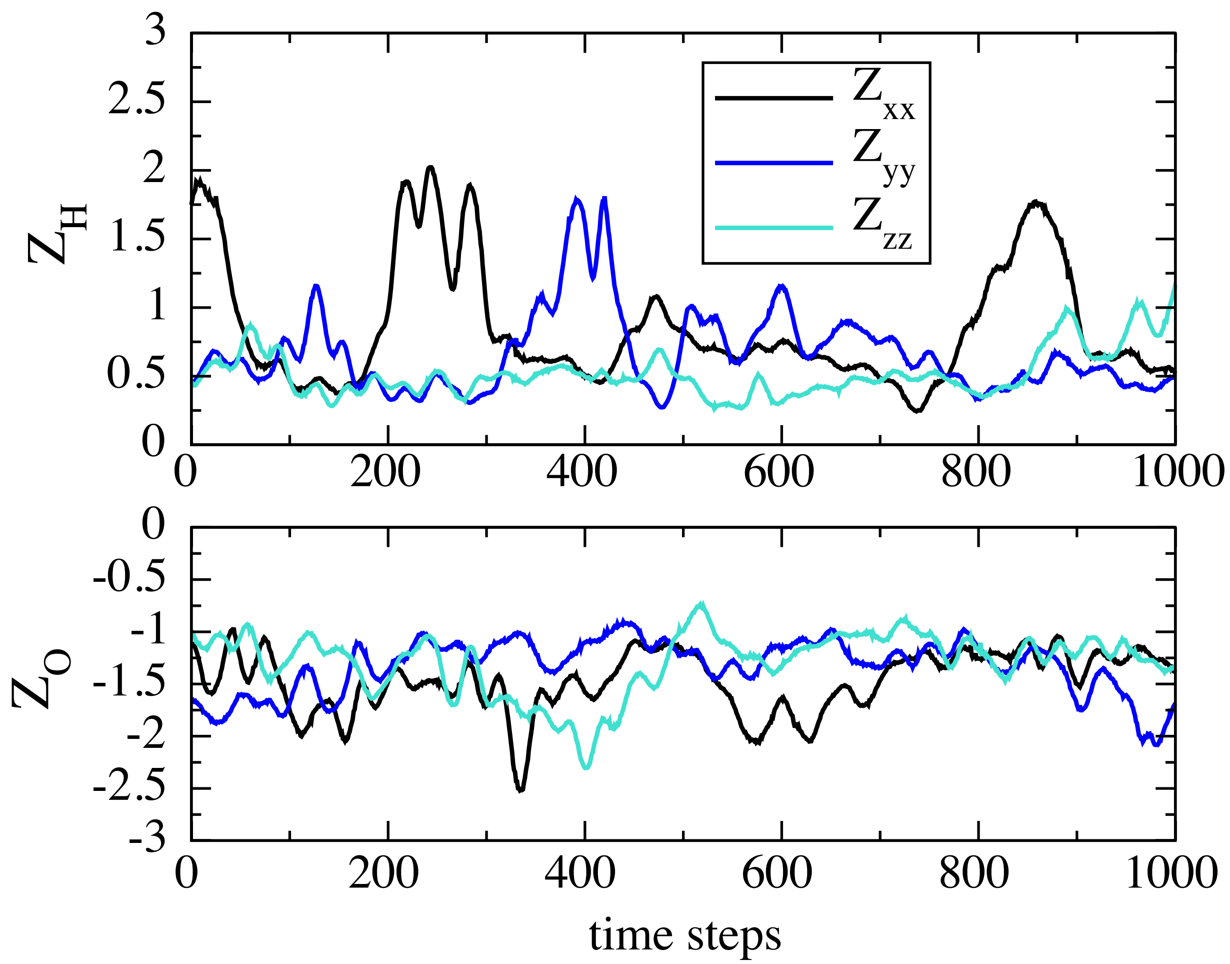
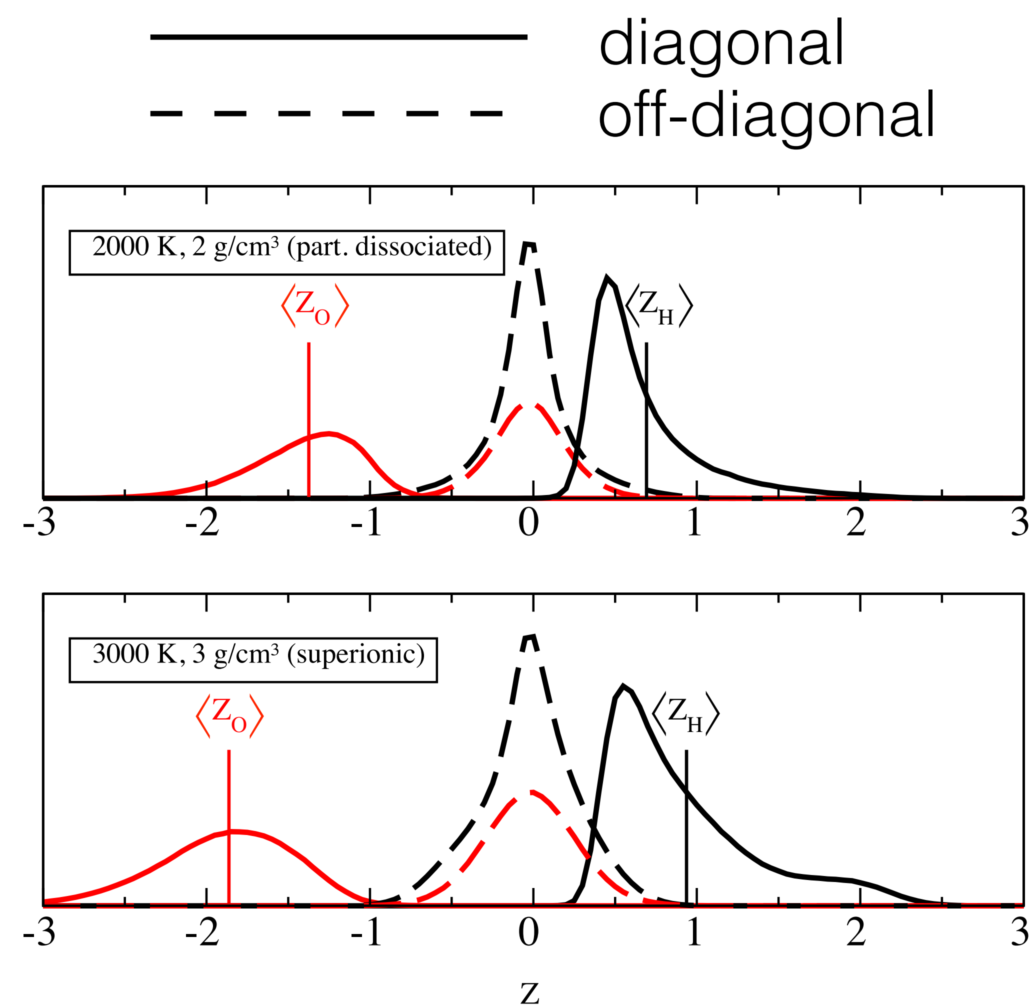
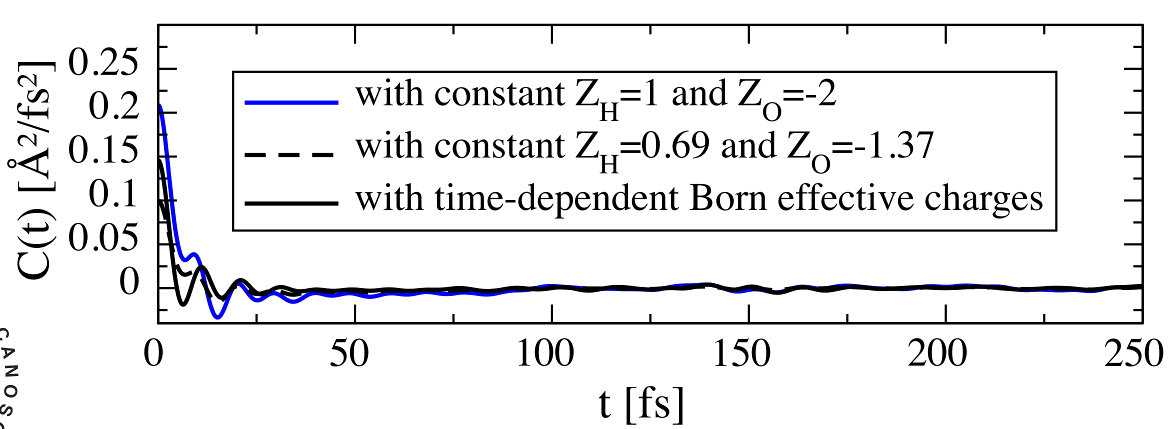




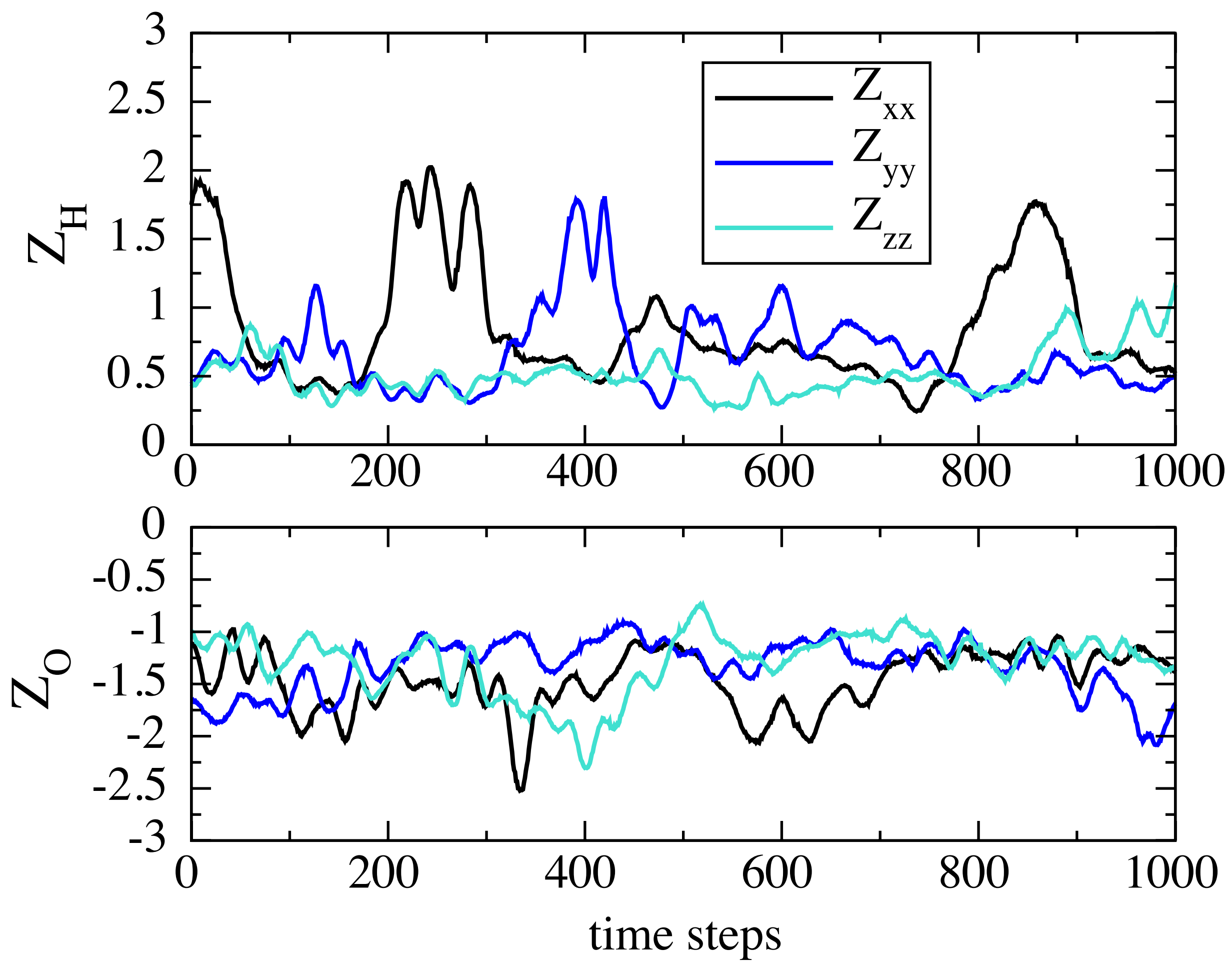


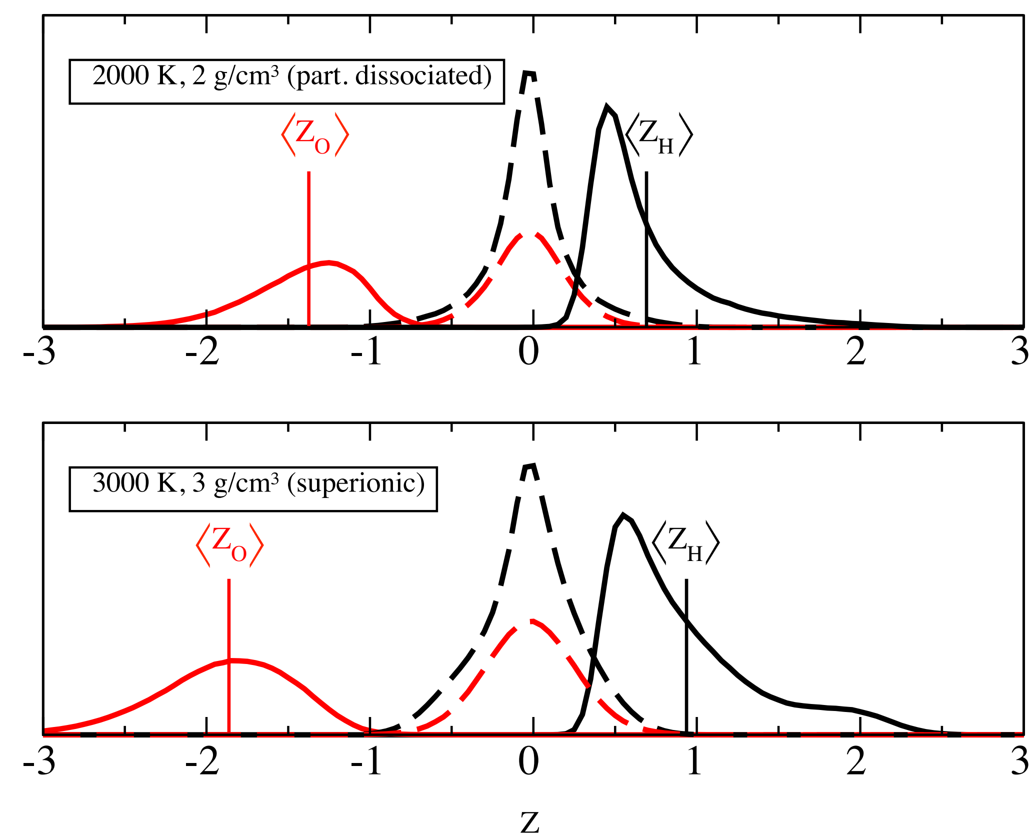
the conundrum

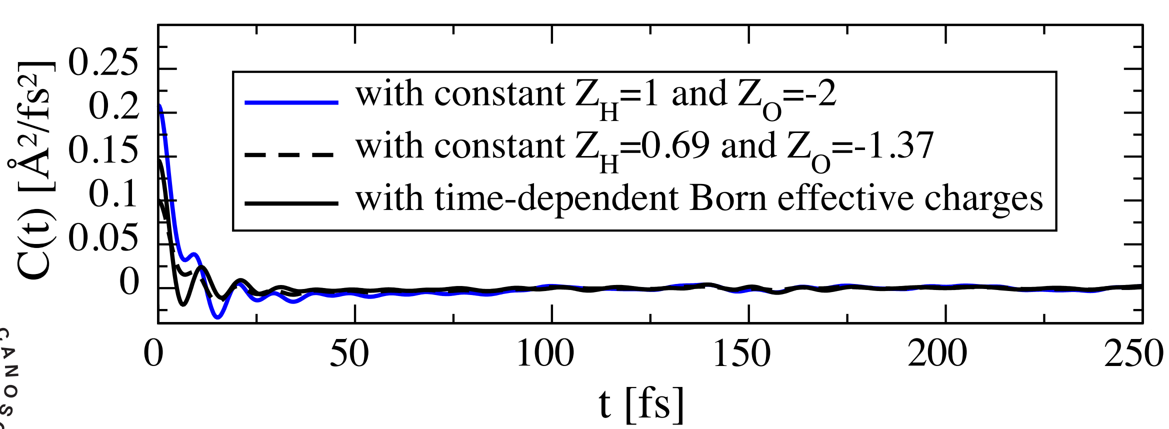
PRL **107,** 185901 (2011) PHYSICAL REVIEW LETTERS week ending 28 OCTOBER 2011

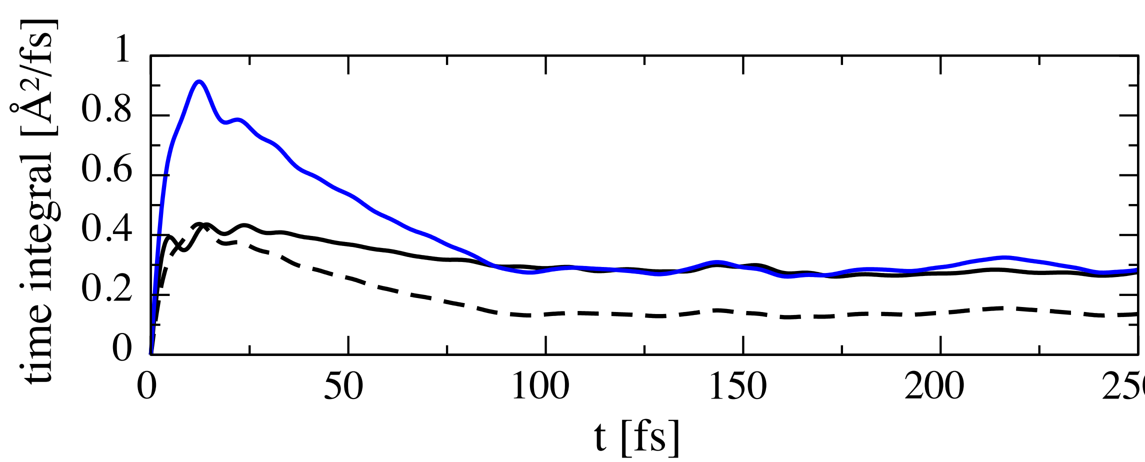
Dynamical Screening and Ionic Conductivity in Water from *Ab Initio* Simulations

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









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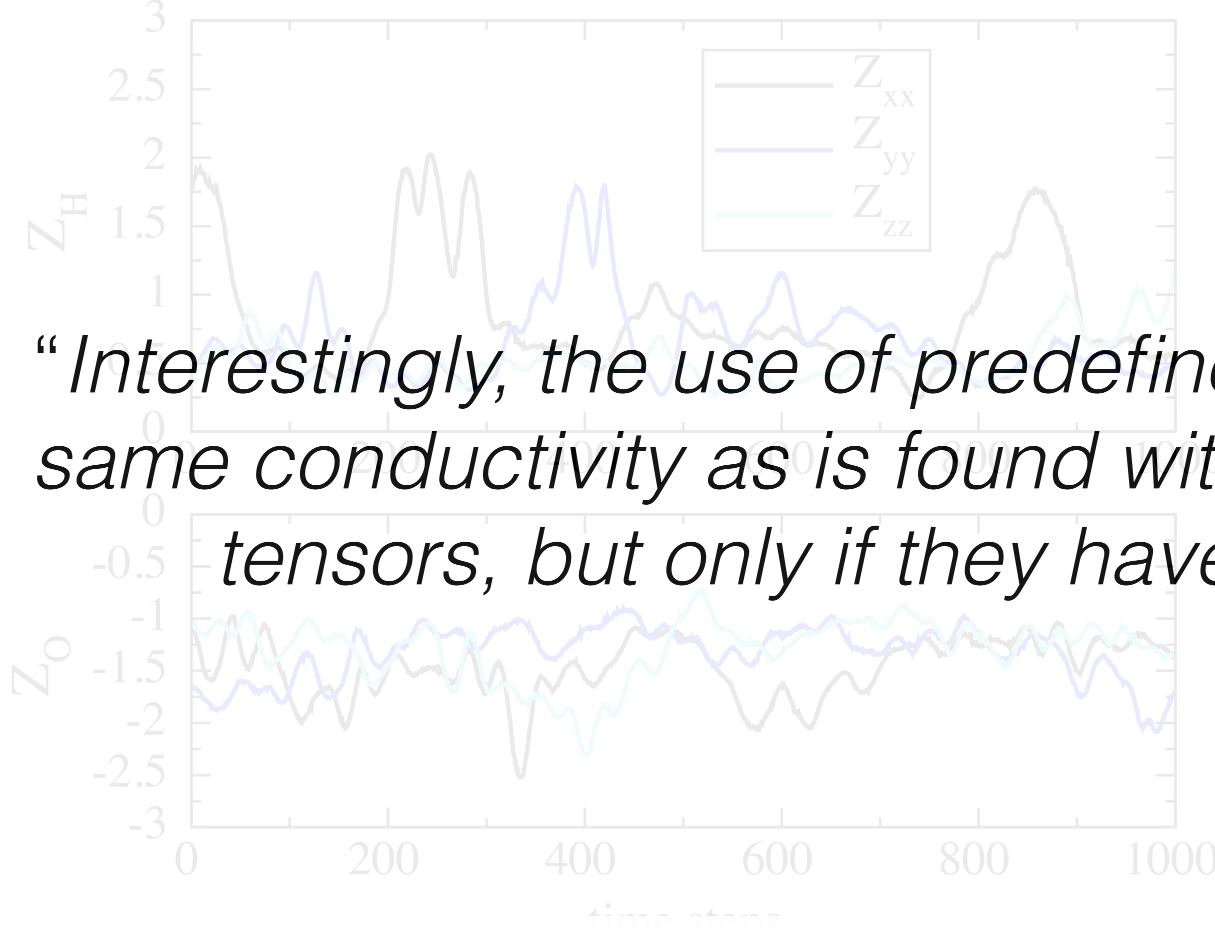
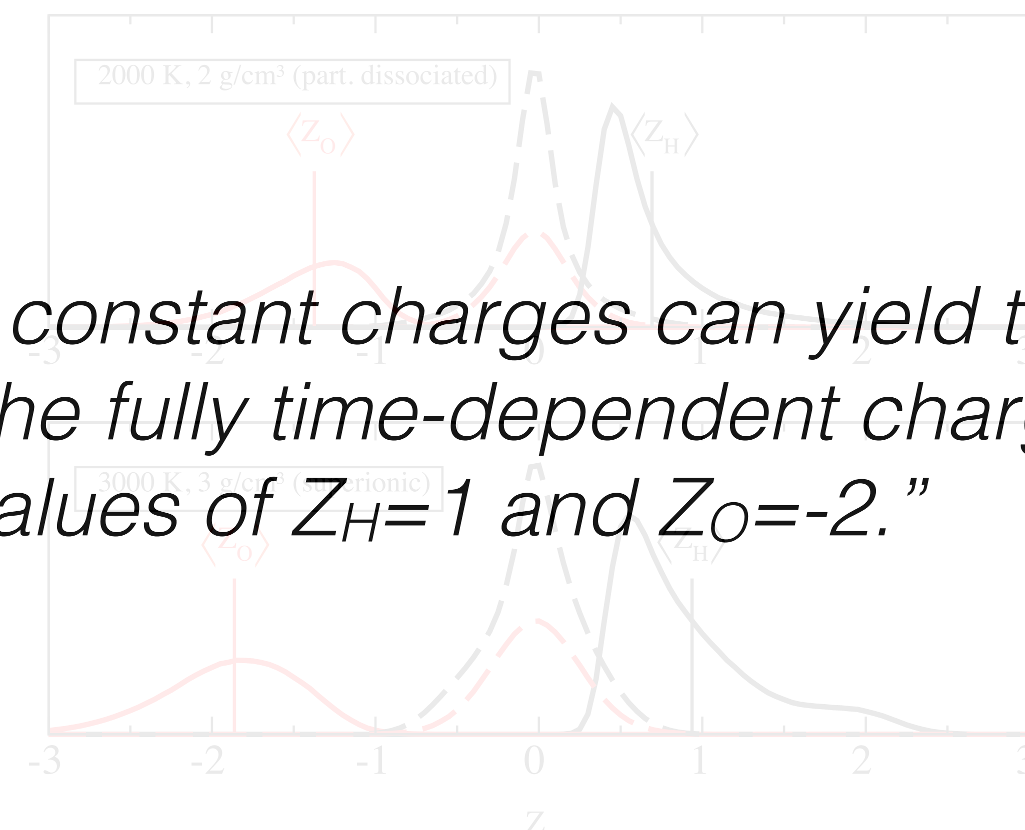
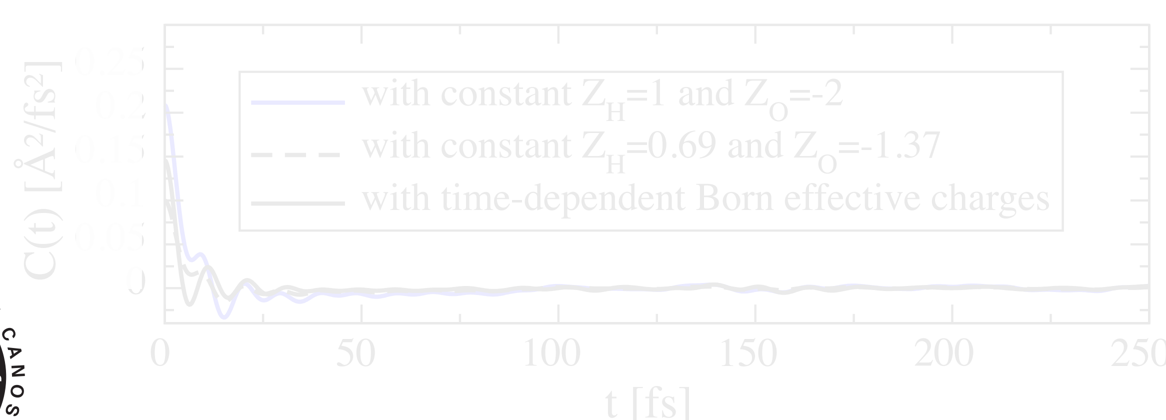




“*Interestingly, the use of predefined constant charges can yield the same conductivity as is found with the fully time-dependent charge tensors, but only if they have values of Z_H=1 and Z_O=-2.*”



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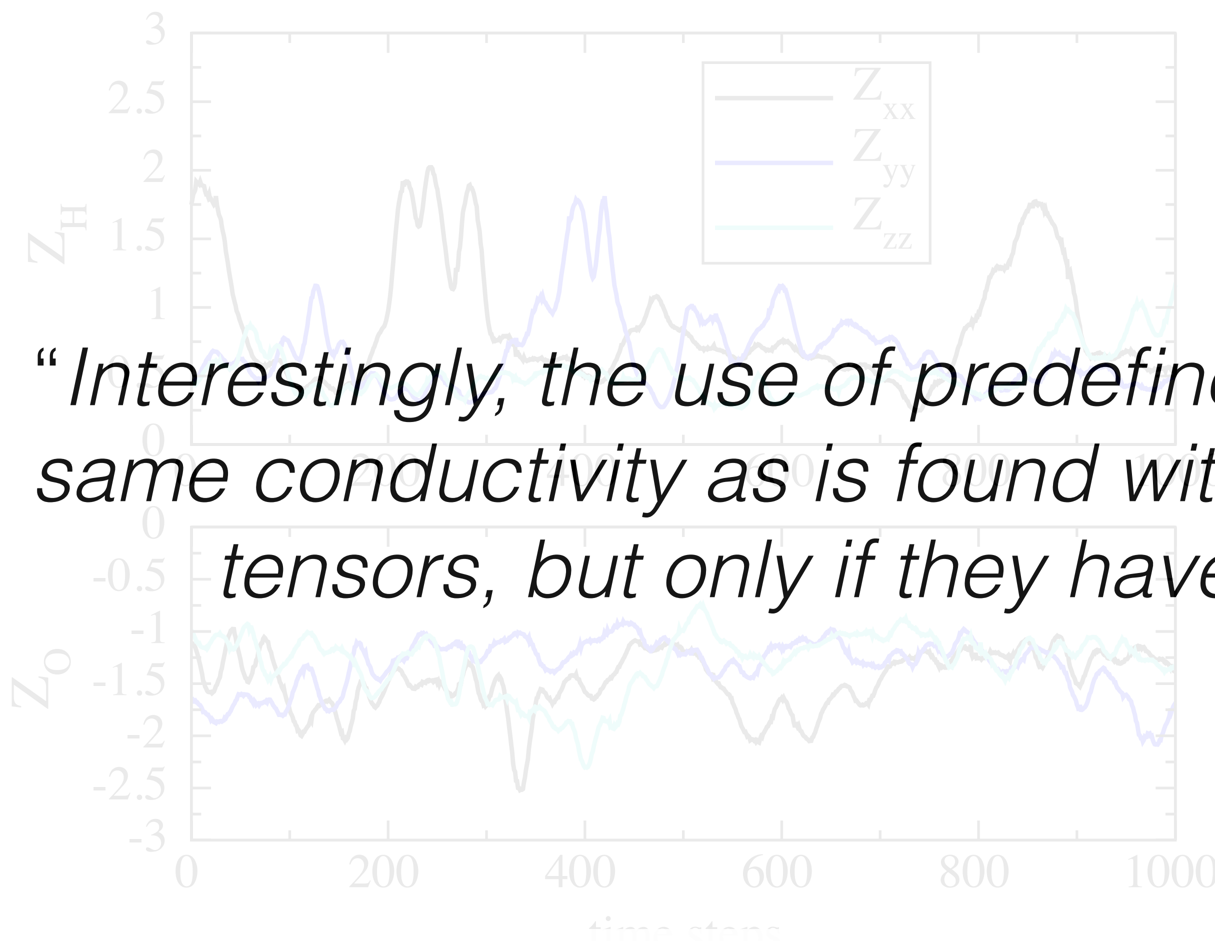

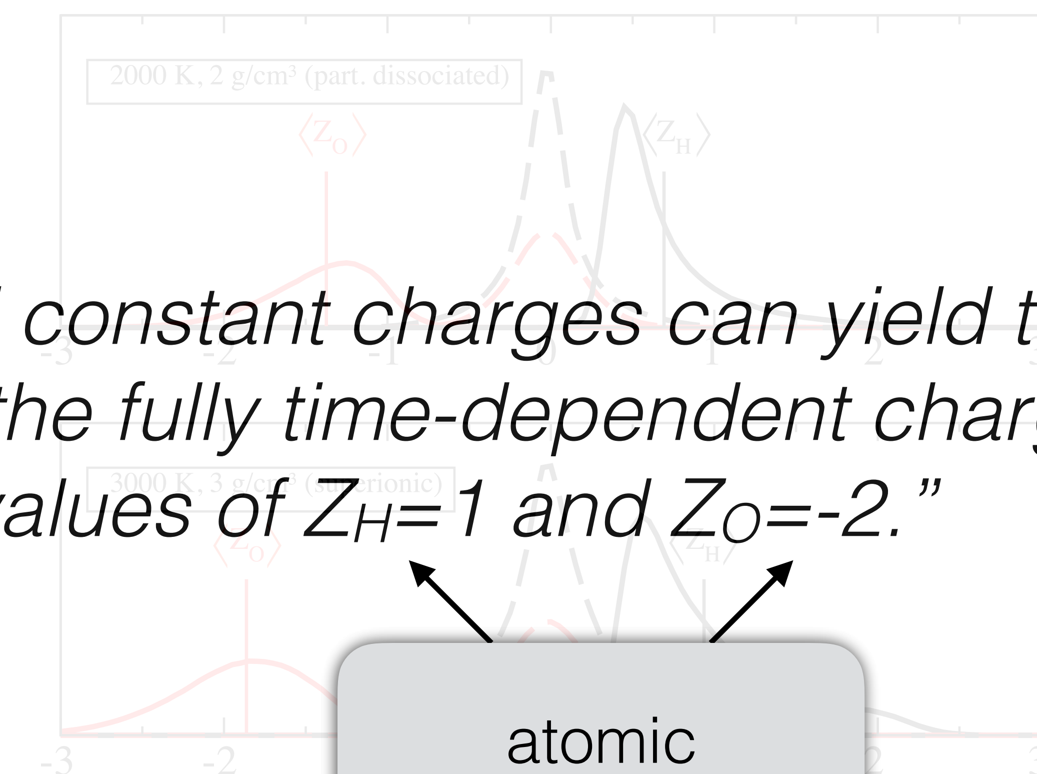

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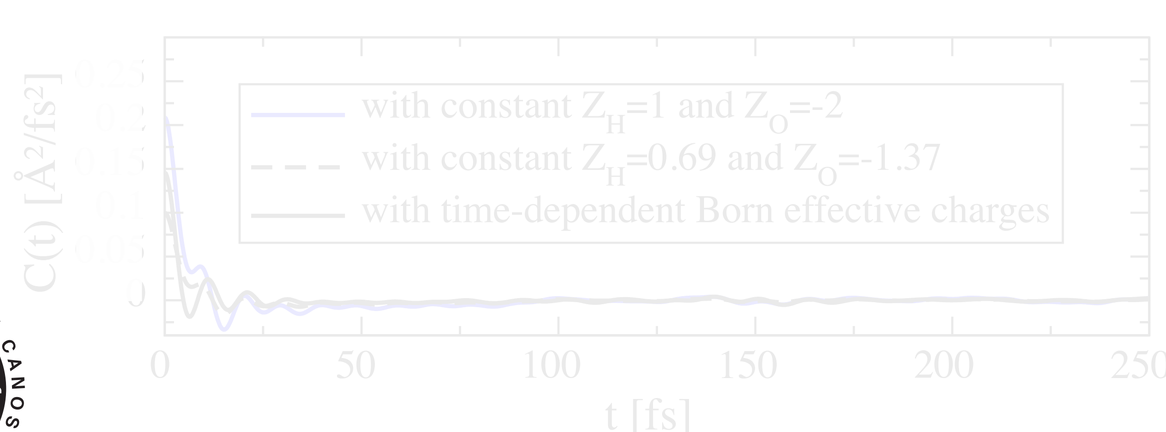
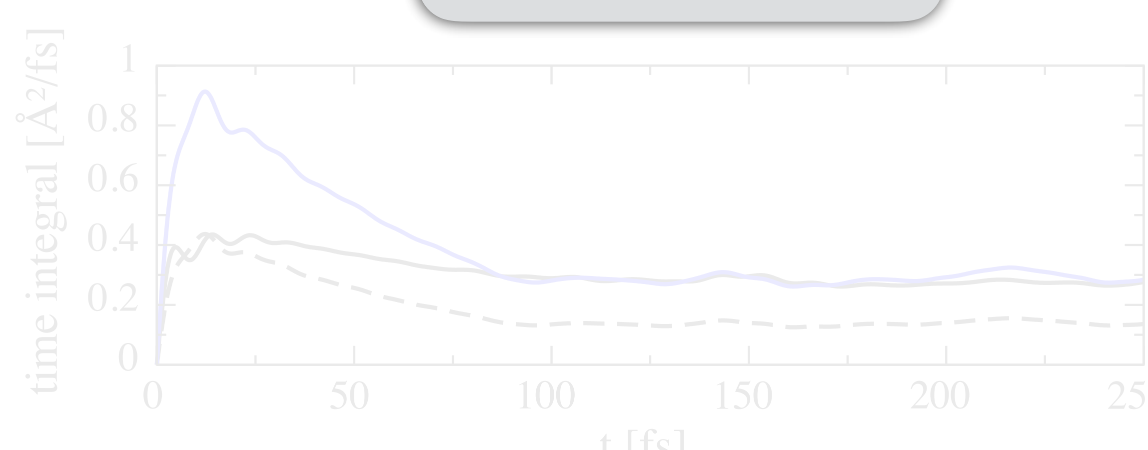
atomic
“oxidation states”





how come?

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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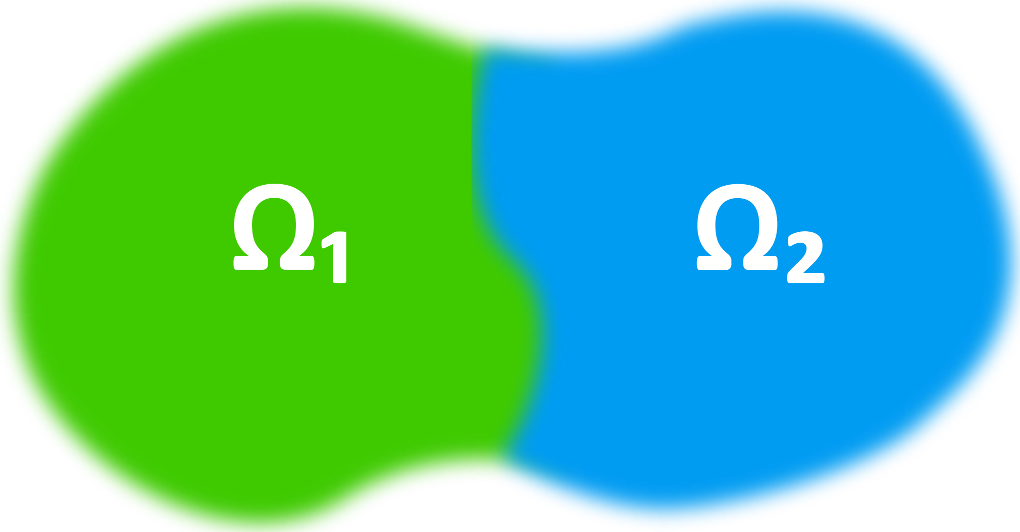
Helfand (1960)

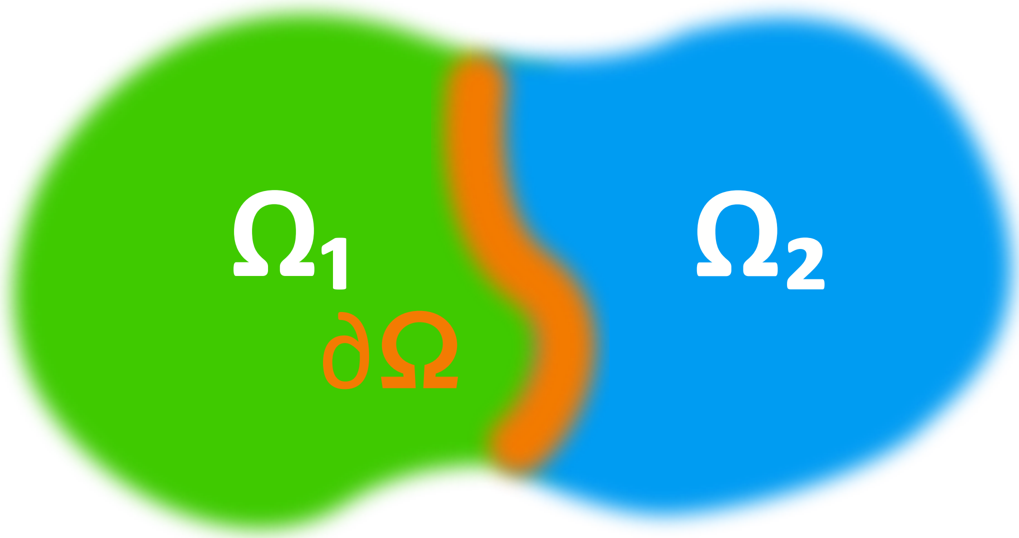
$$\left\langle \left| \int_0^t J(t') dt' \right|^2 \right\rangle \approx 2t \underbrace{\int_0^\infty \langle J(t) J(0) \rangle dt}_{\frac{k_B T}{\Omega} \lambda}$$

gauge transformation of conserved currents



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

gauge transformation of conserved currents



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

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

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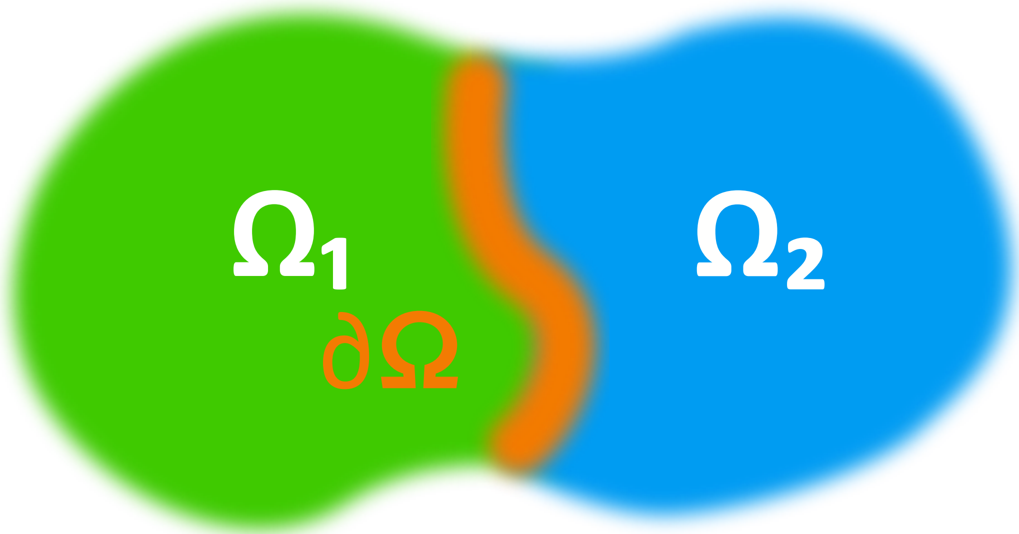

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extensivity

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

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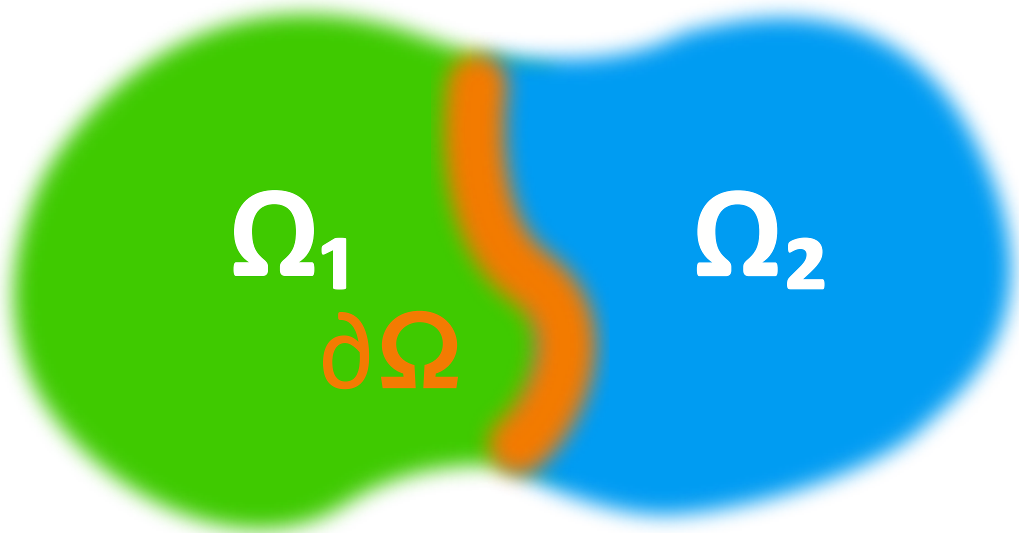

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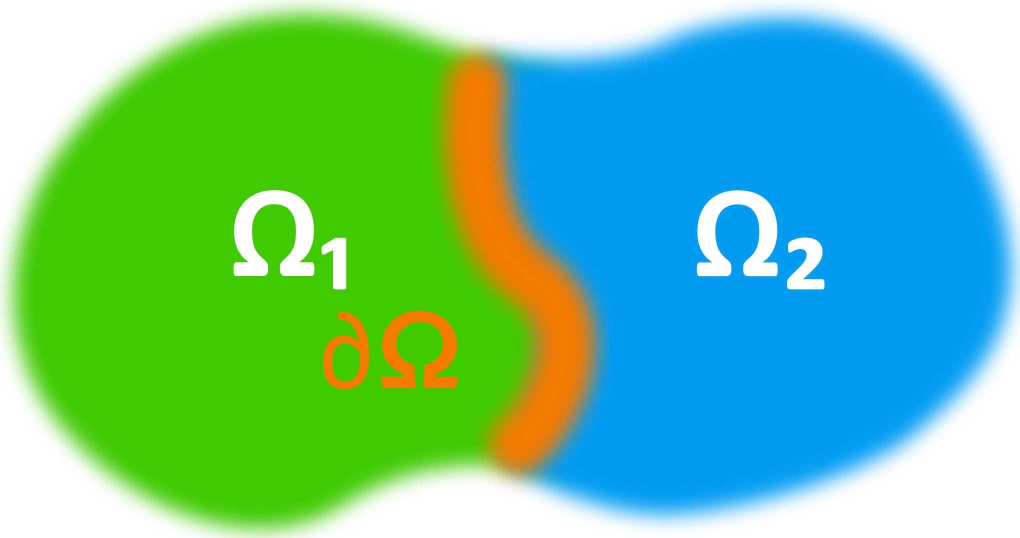

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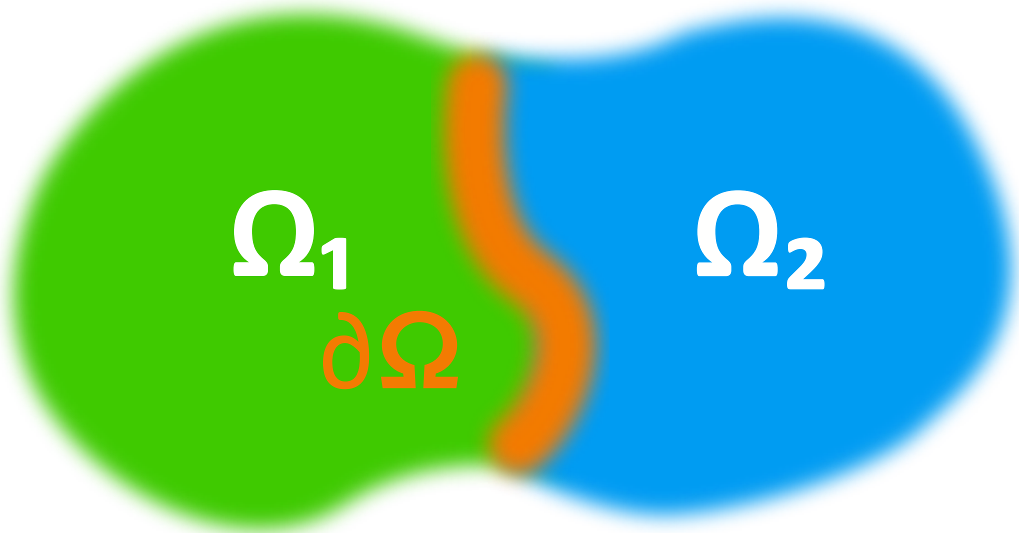
gauge invariance $\mathcal{E}'[\Omega] = \mathcal{E}[\Omega] + \mathcal{O}[\partial\Omega]$

gauge transformation of conserved currents



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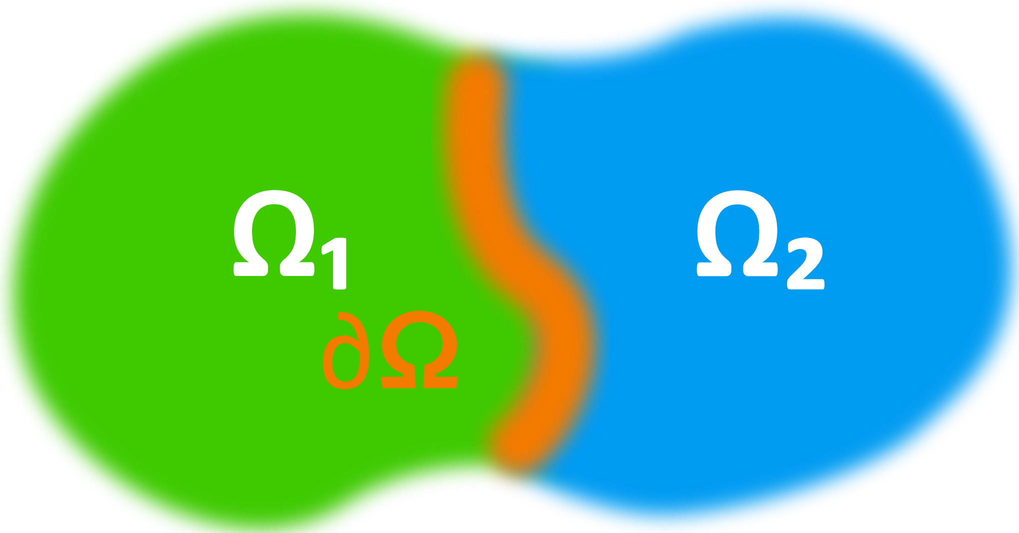
gauge transformation of conserved currents



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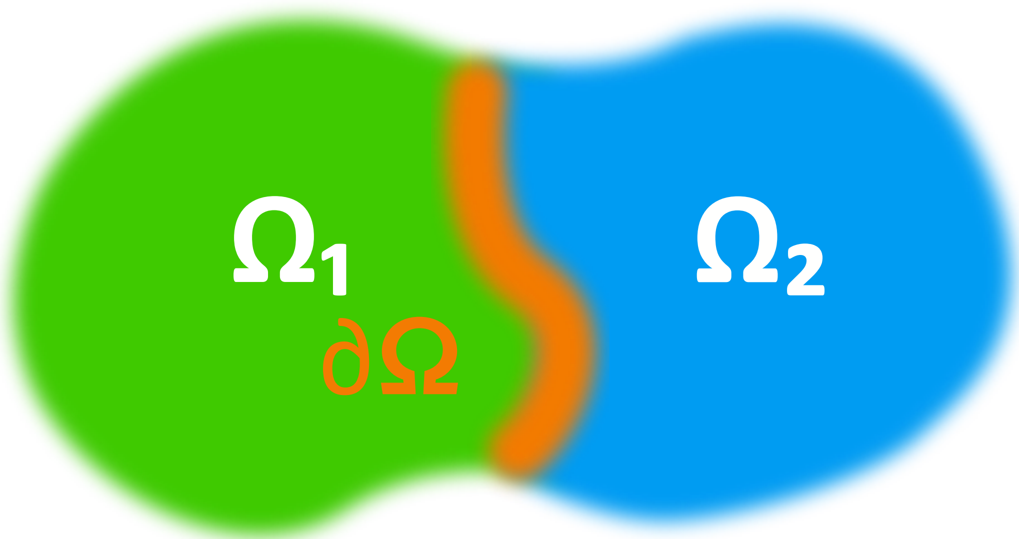

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gauge invariance $\quad \mathcal{E}'[\Omega] = \mathcal{E}[\Omega] + \mathcal{O}[\partial\Omega]$

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gauge invariance of transport coefficients

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

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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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$$\lambda' = \lambda$$

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gauge invariance of transport coefficients

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

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

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

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

$$D'(t) = D(t) + P(t) - P(0)$$

$$\lambda' = \lambda$$

$$\mathrm{var}\left[D'(t)\right] = \underbrace{\mathrm{var}\left[D(t)\right]}_{\mathcal{O}(t)} + \underbrace{\mathrm{var}\left[\Delta P(t)\right] + 2\mathrm{cov}\left[D(t)\cdot \Delta P(t)\right]}_{\mathcal{O}(t^{\frac{1}{2}})}$$

gauge invariance of heat transport

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

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Thermal Conductivity of Periclase (MgO) from First Principles

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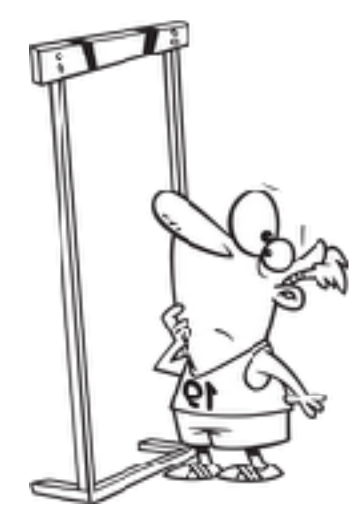
Bijaya B. Karki‡
Department of Computer Science, Louisiana State University, Baton Rouge, Louisiana 70803, USA
and Department of Geology and Geophysics, Louisiana State University, Baton Rouge, Louisiana 70803, USA

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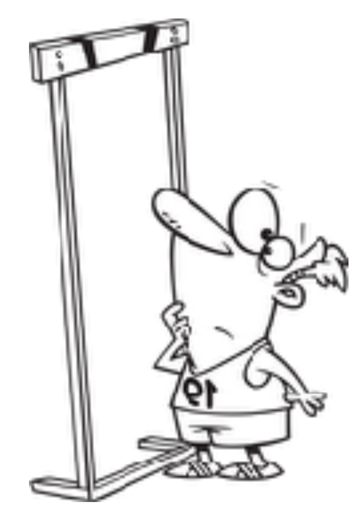
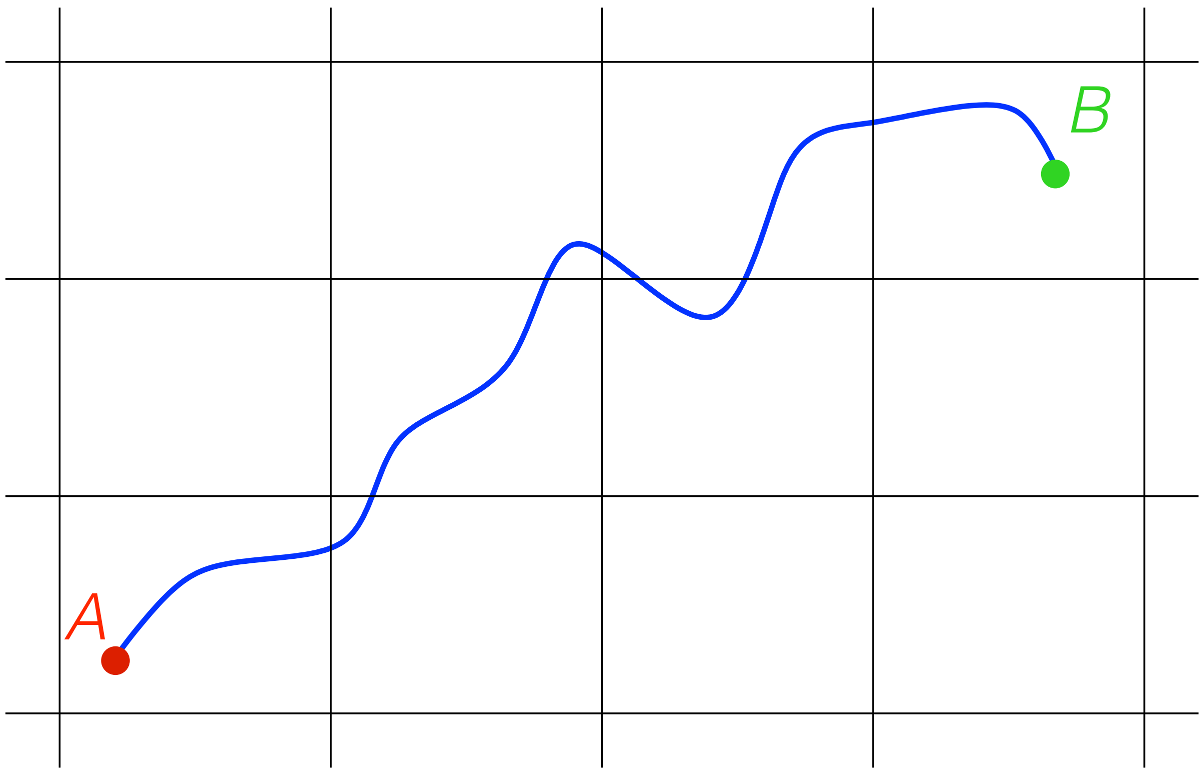
sensitive to the form of the potential. The widely used Green-Kubo relation [14] does not serve our purposes, because in first-principles calculations it is impossible to uniquely decompose the total energy into individual contributions from each atom.



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.

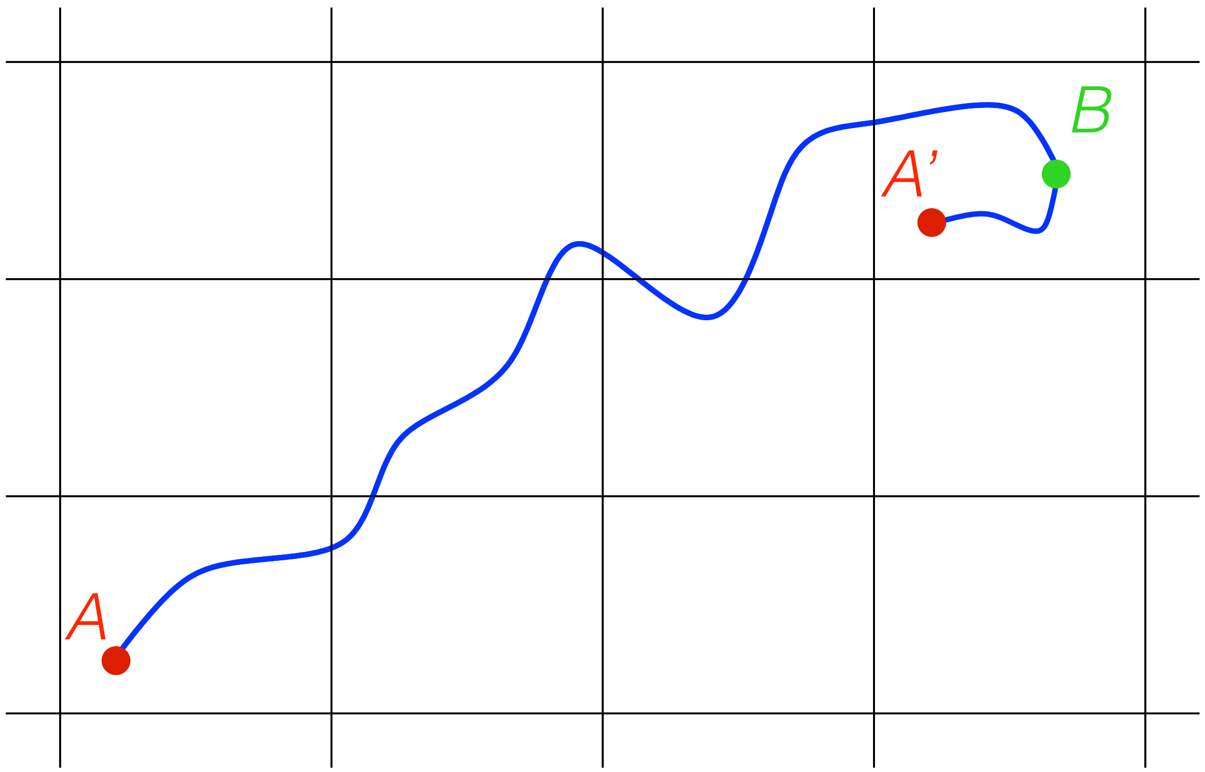
gauge invariance of charge transport



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

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

gauge invariance of charge transport



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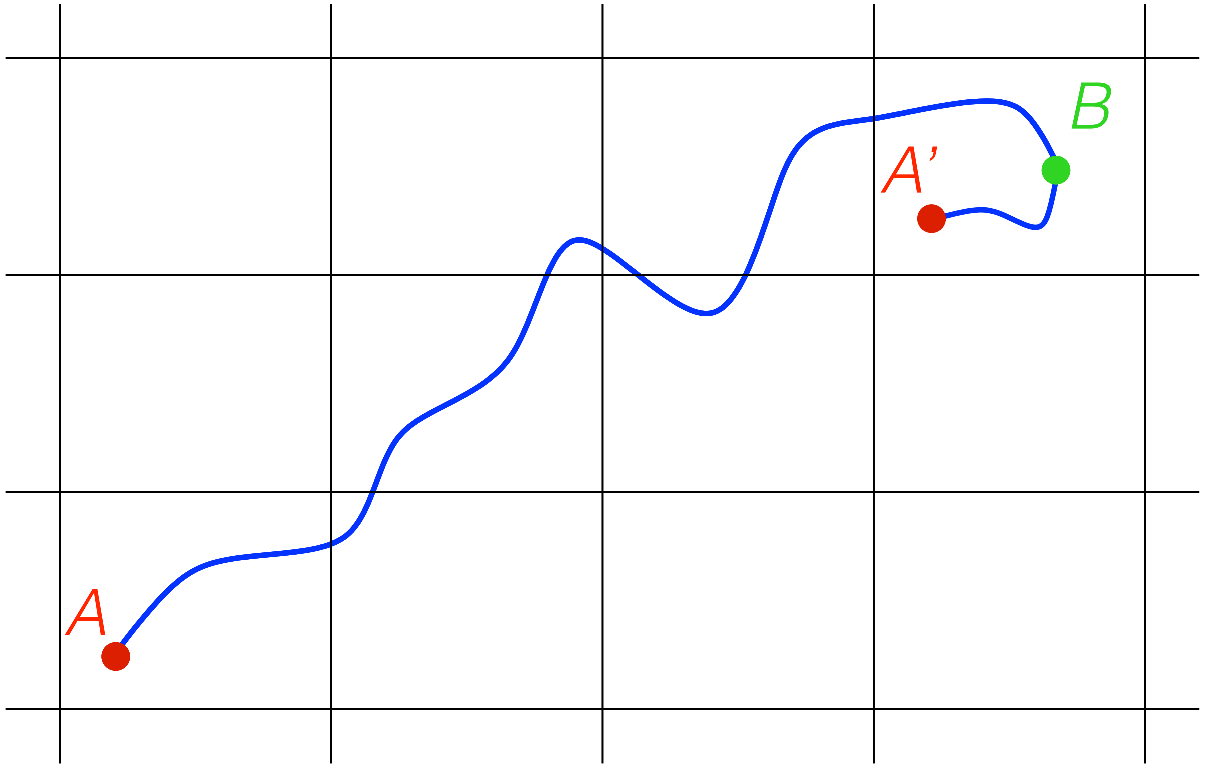

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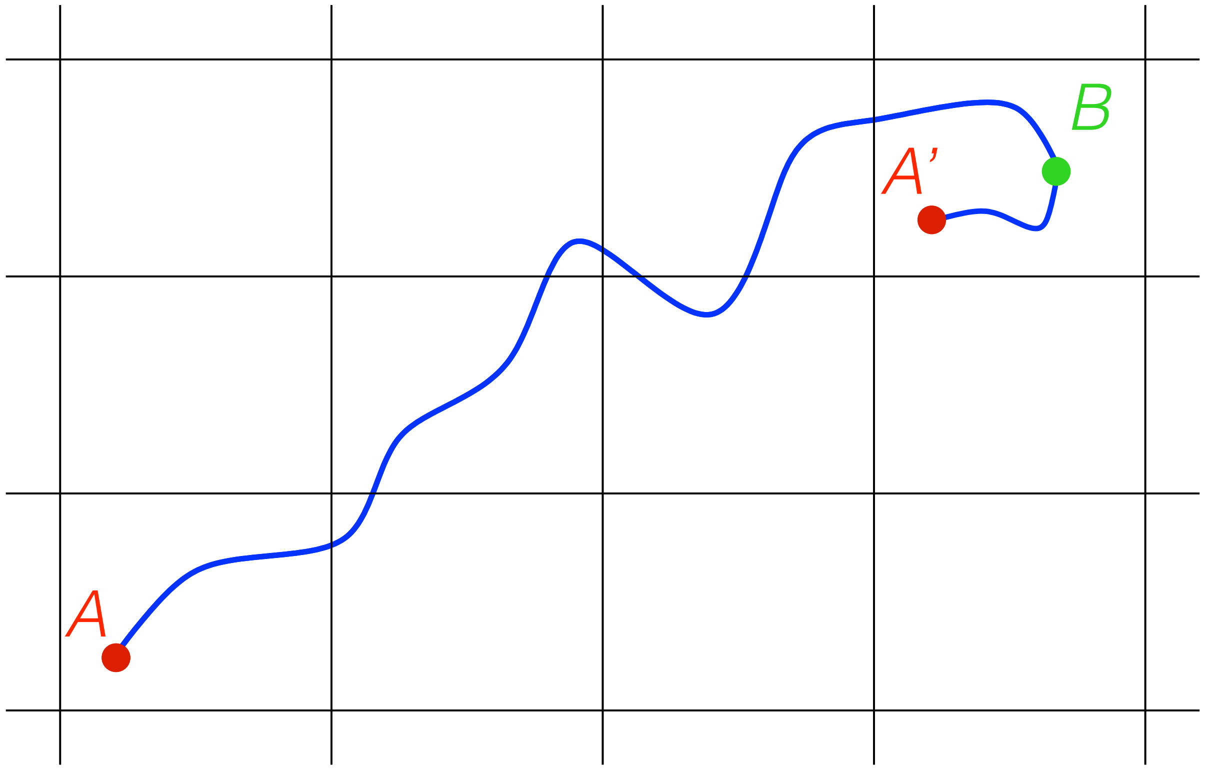
$$\mathrm{var}[\mu_{AB}] = \mathrm{var}[\mu_{AA'}] + \underbrace{\mathrm{var}[\mu_{A'B}]}_{bounded} + 2\mathrm{cov}[\mu_{AA'} \cdot \mu_{A'B}]$$

gauge invariance of charge transport



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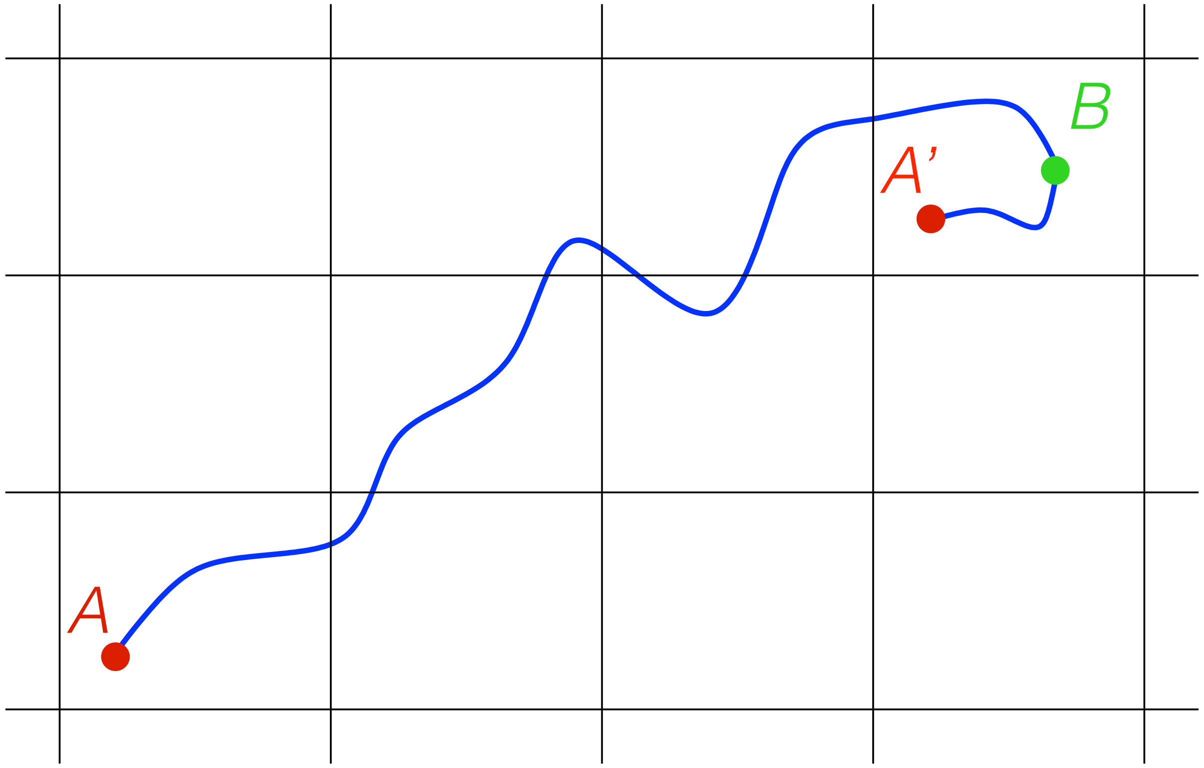
Thouless' quantisation of particle transport



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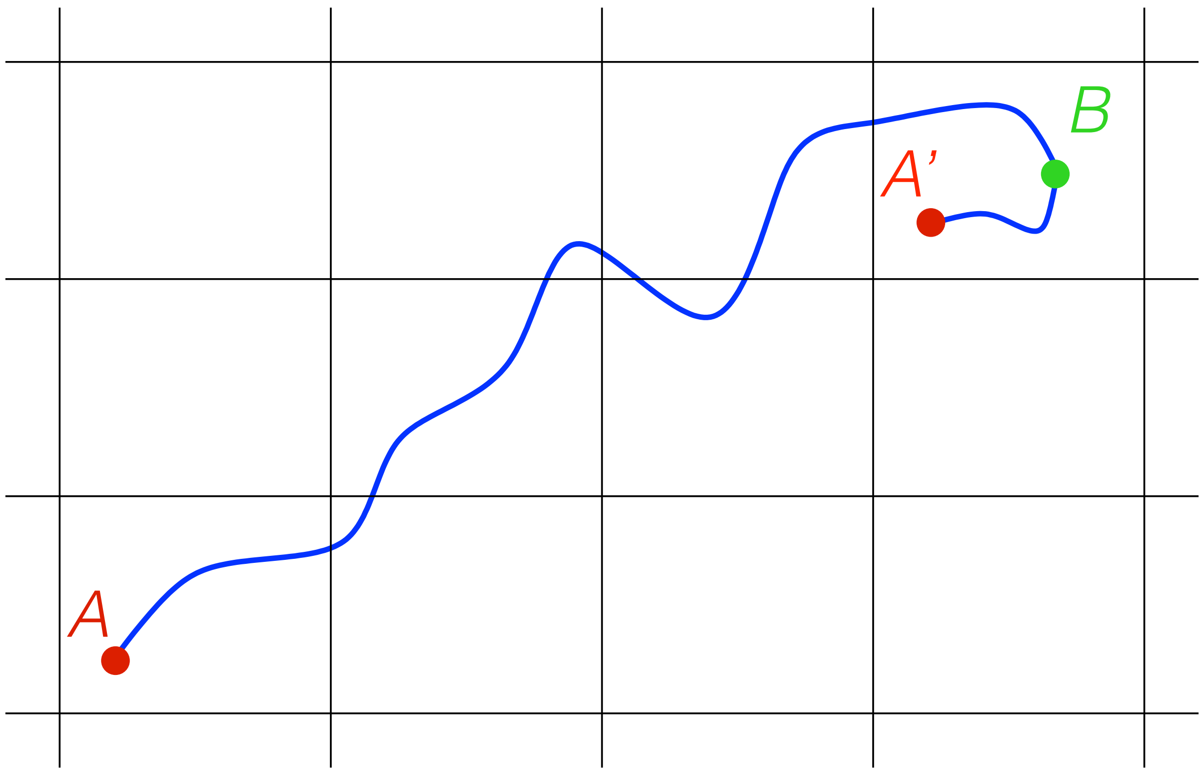


$$\sigma \propto \lim_{t\to\infty} \frac{1}{2t} \langle |\mu_{AA'}|^2 \rangle$$

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

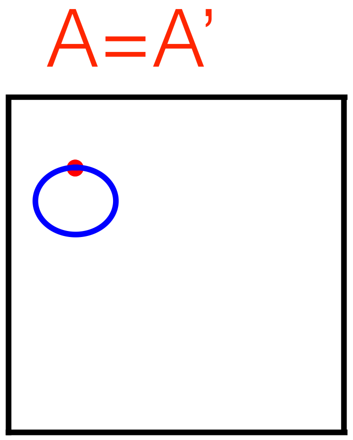
$$\hat{H}(A') = \hat{H}(A)$$

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

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

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

topological invariants



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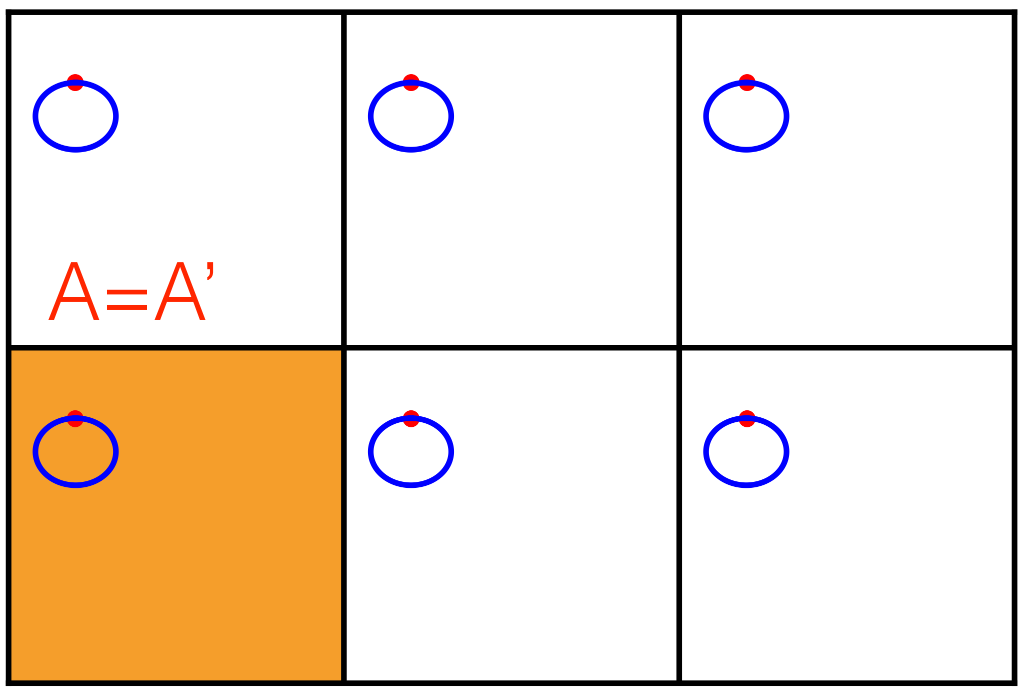

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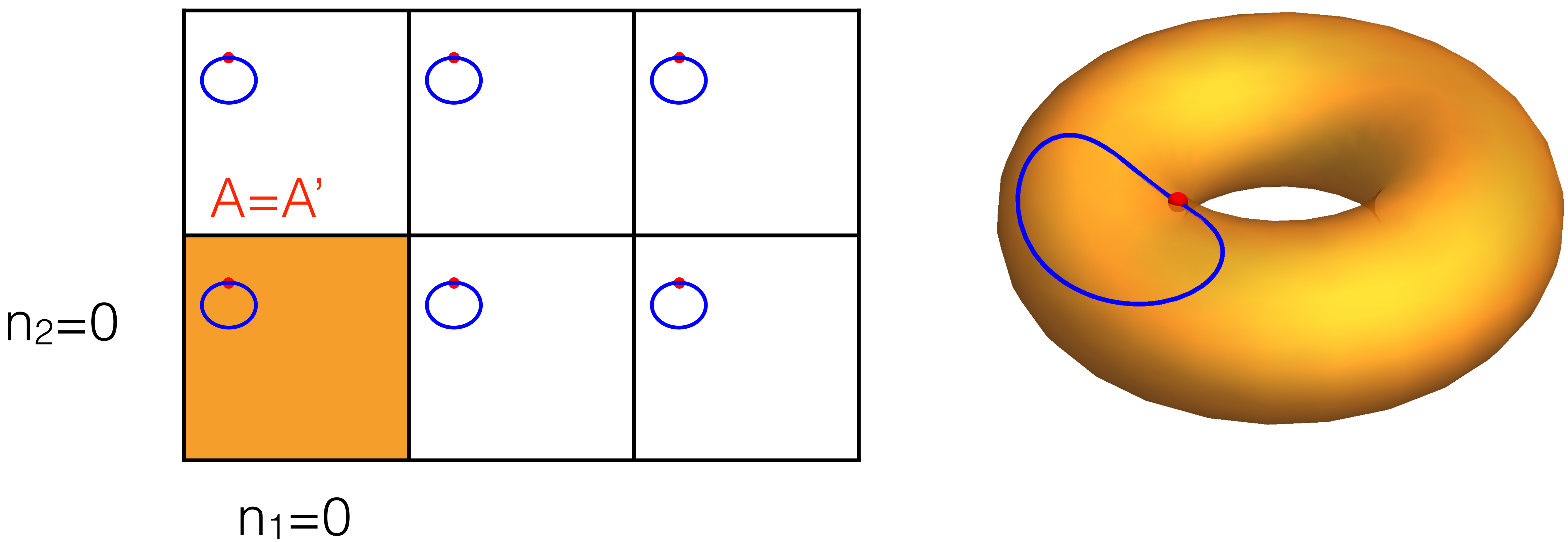

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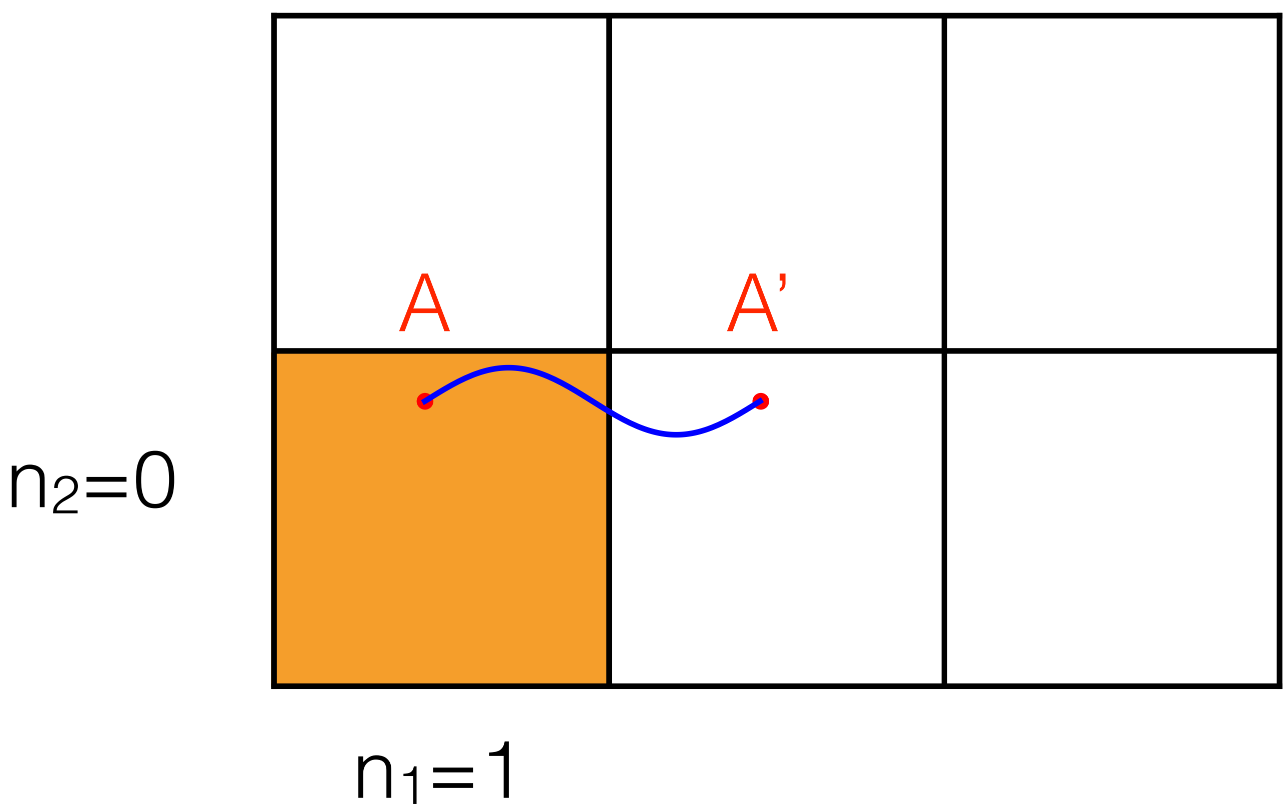

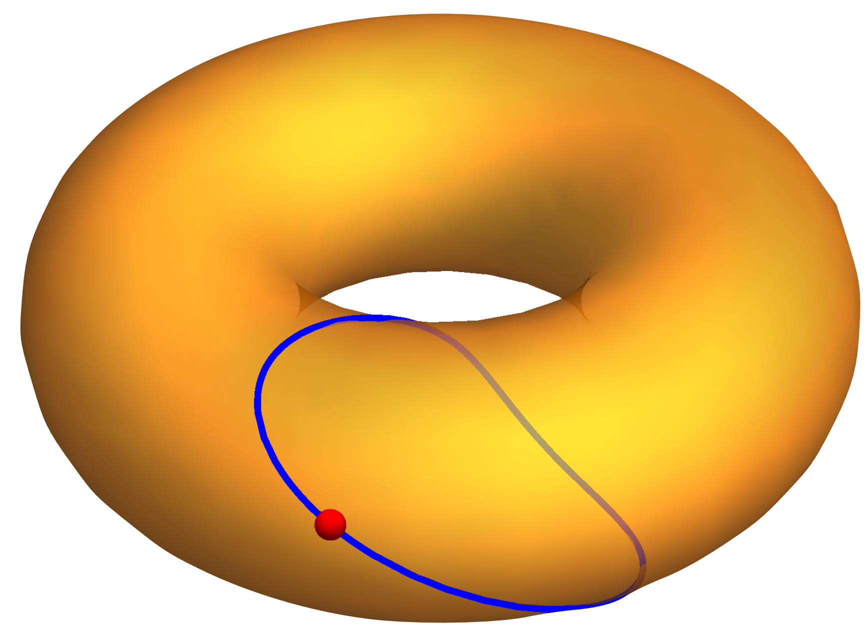

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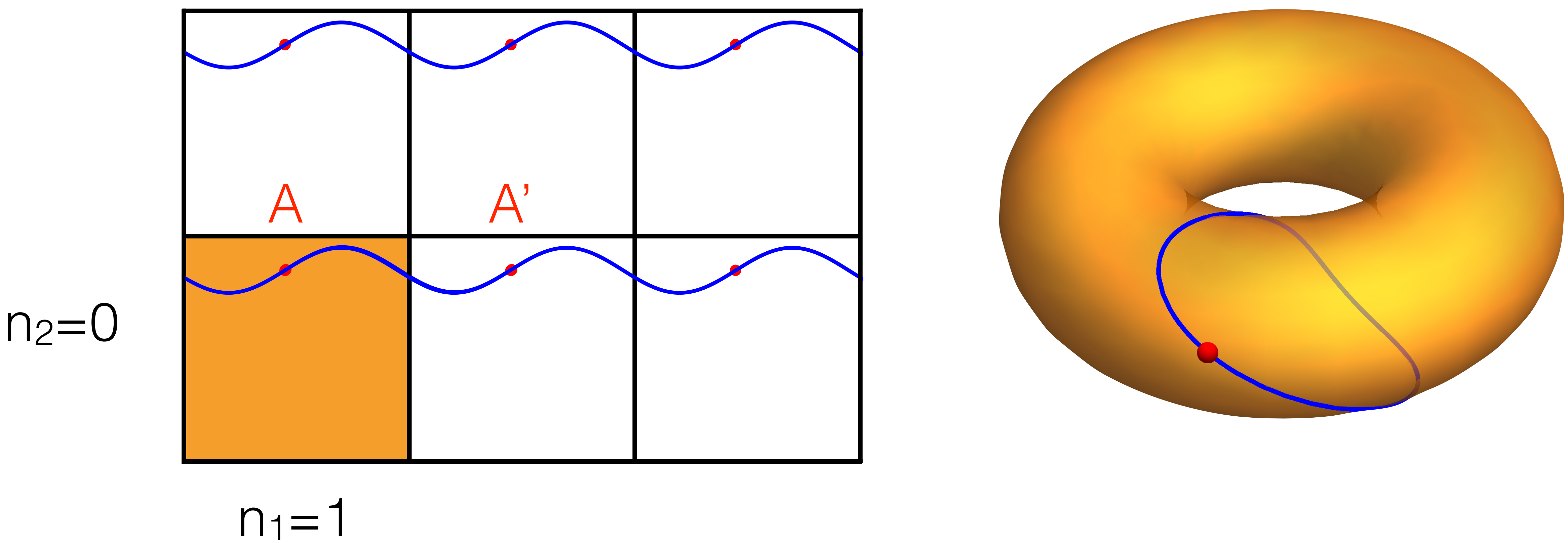

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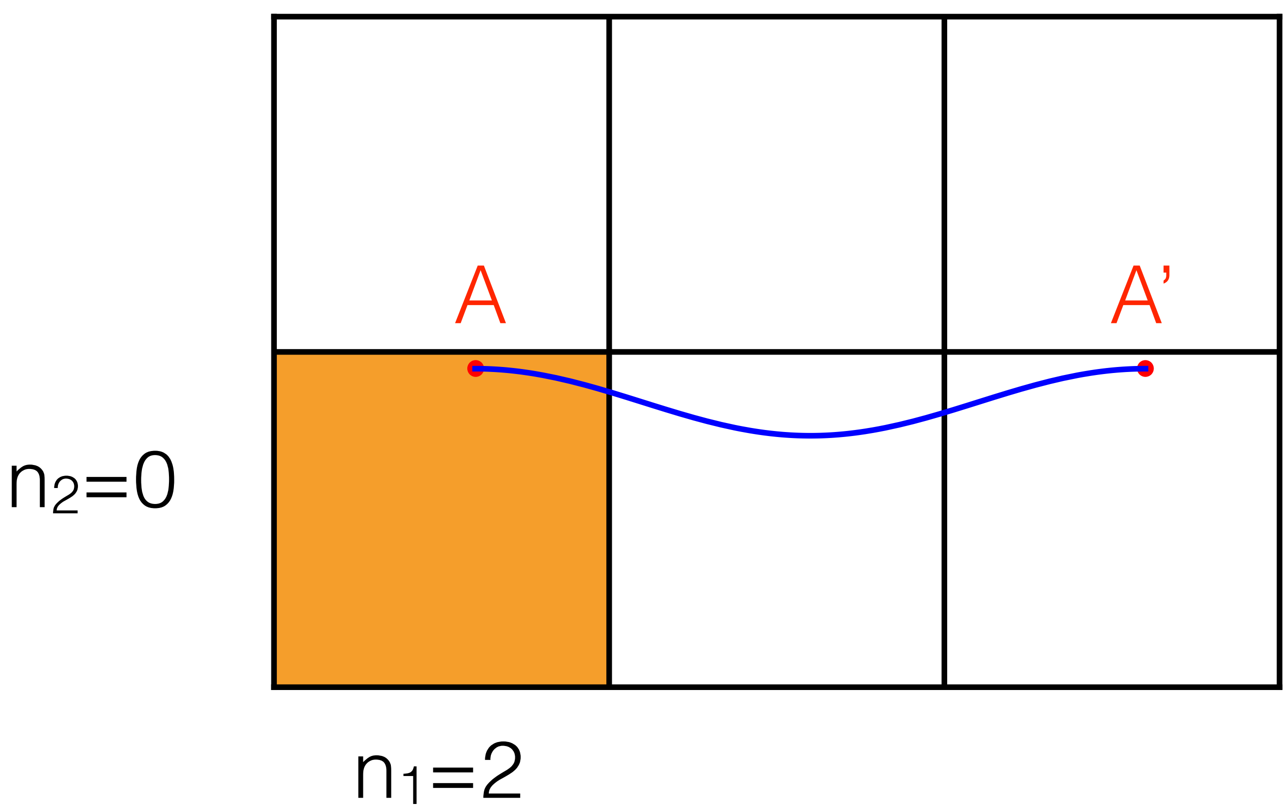

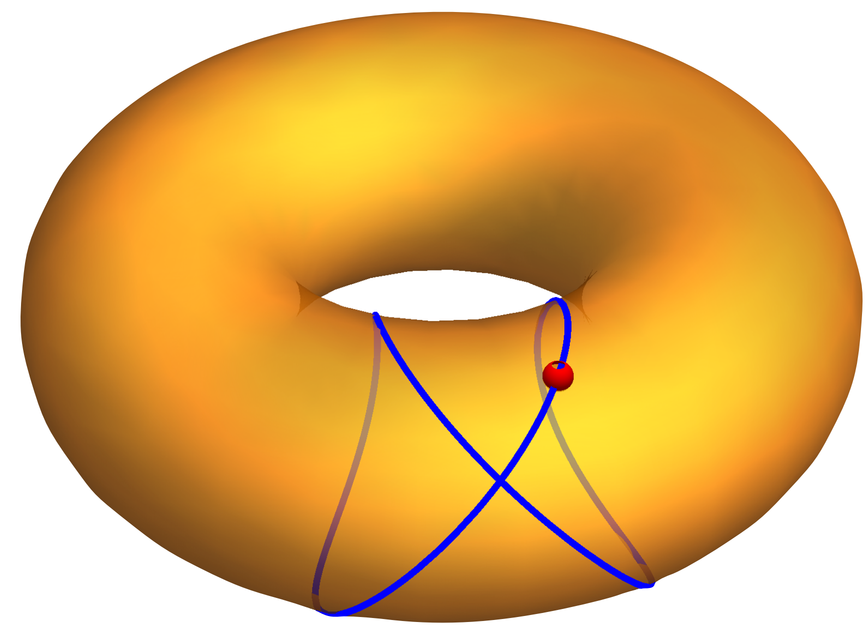

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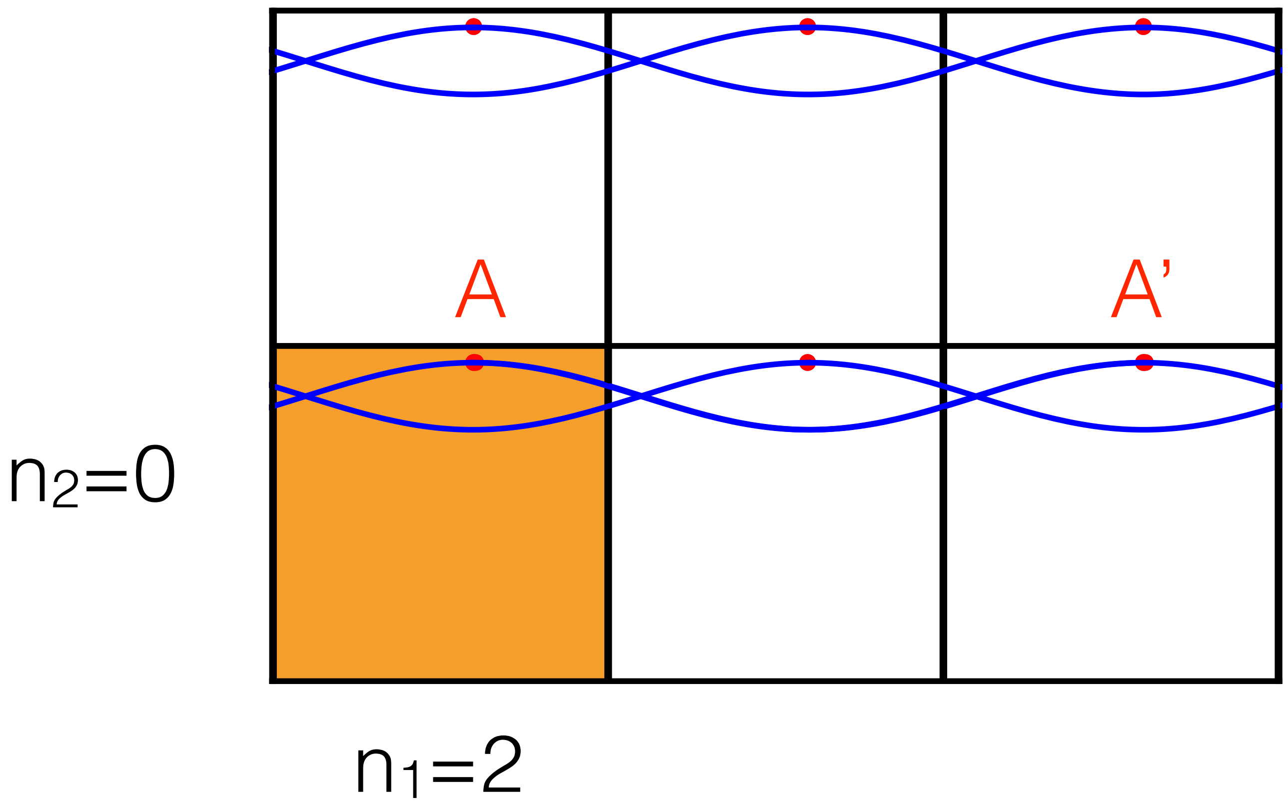

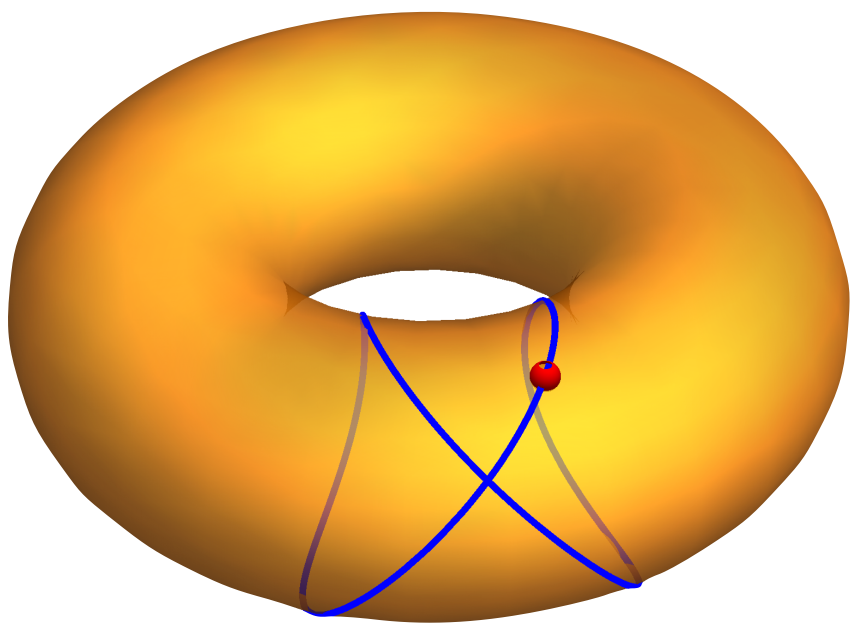

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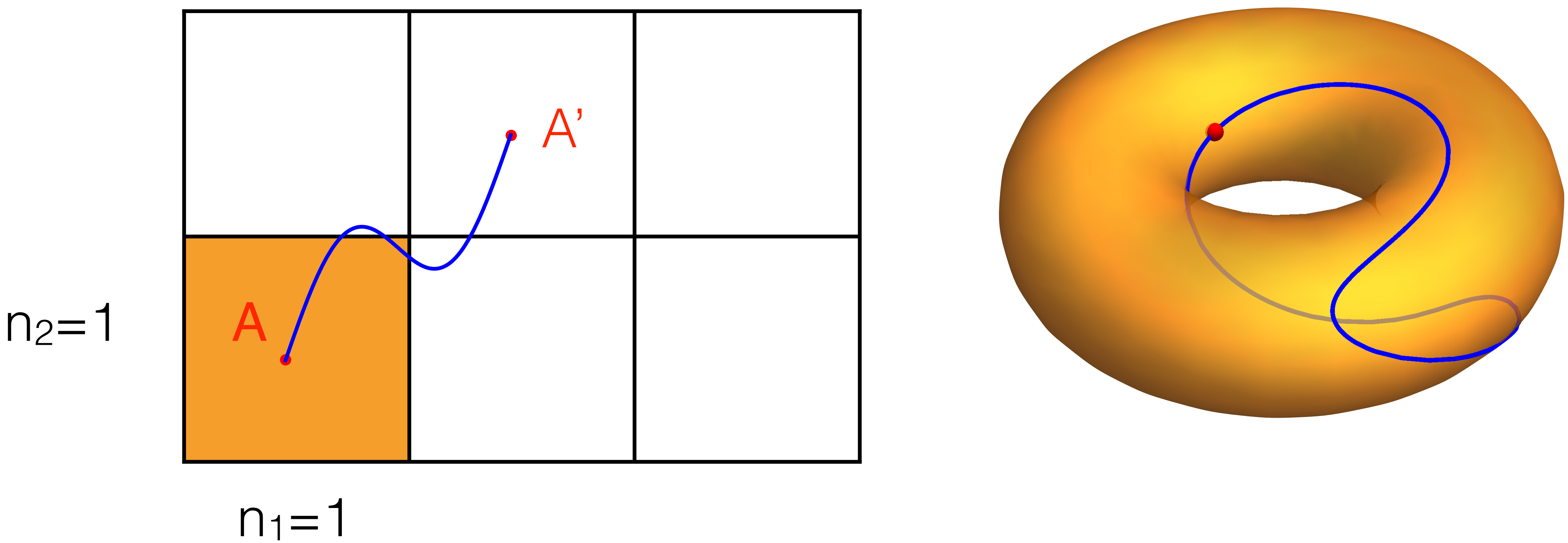

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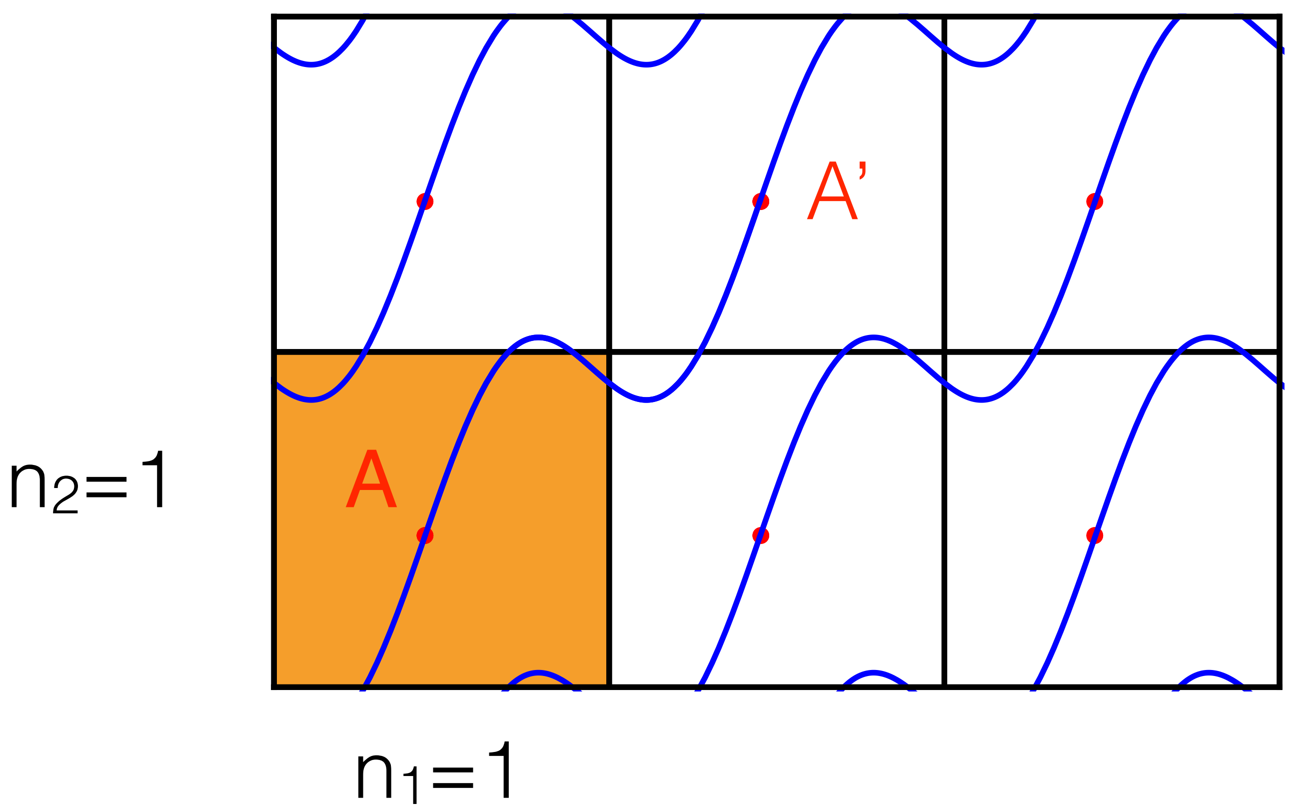

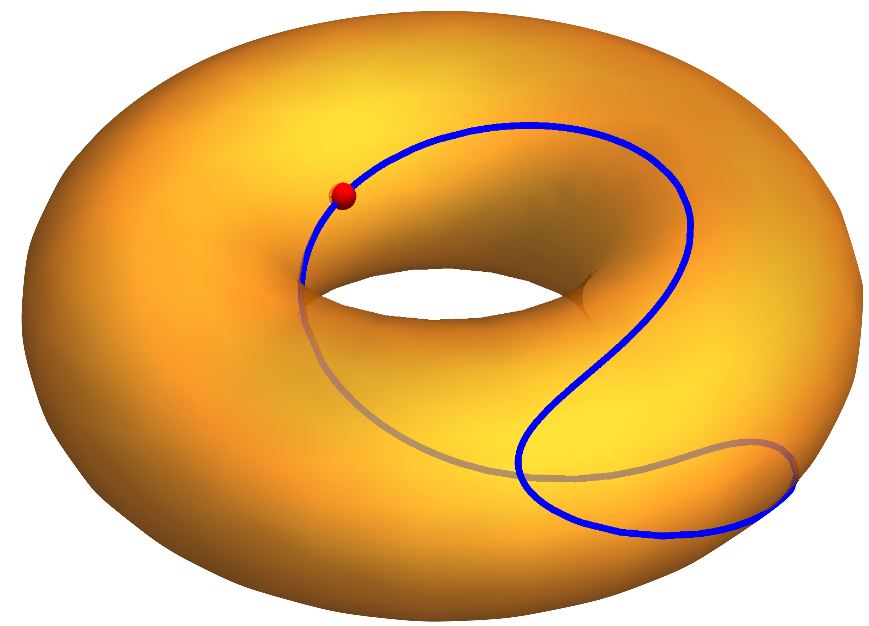

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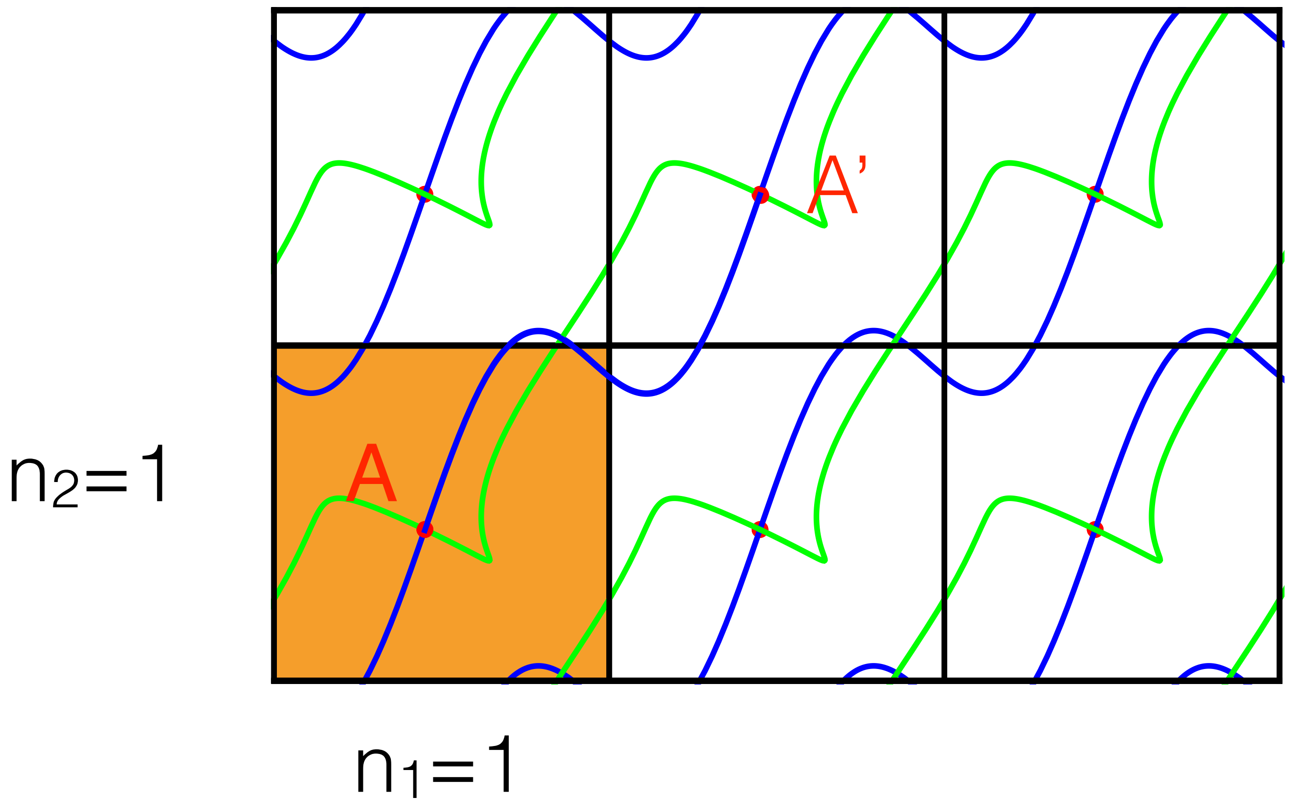
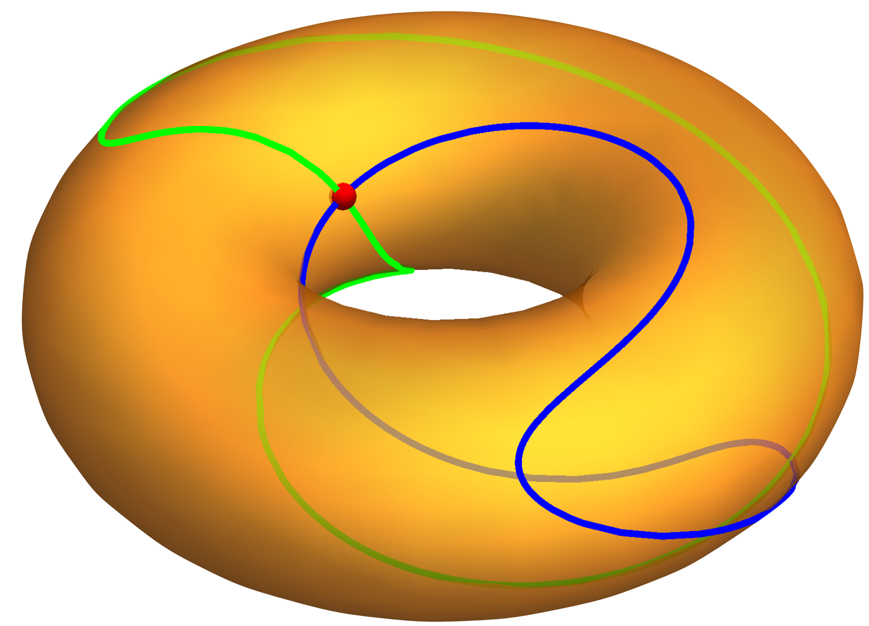
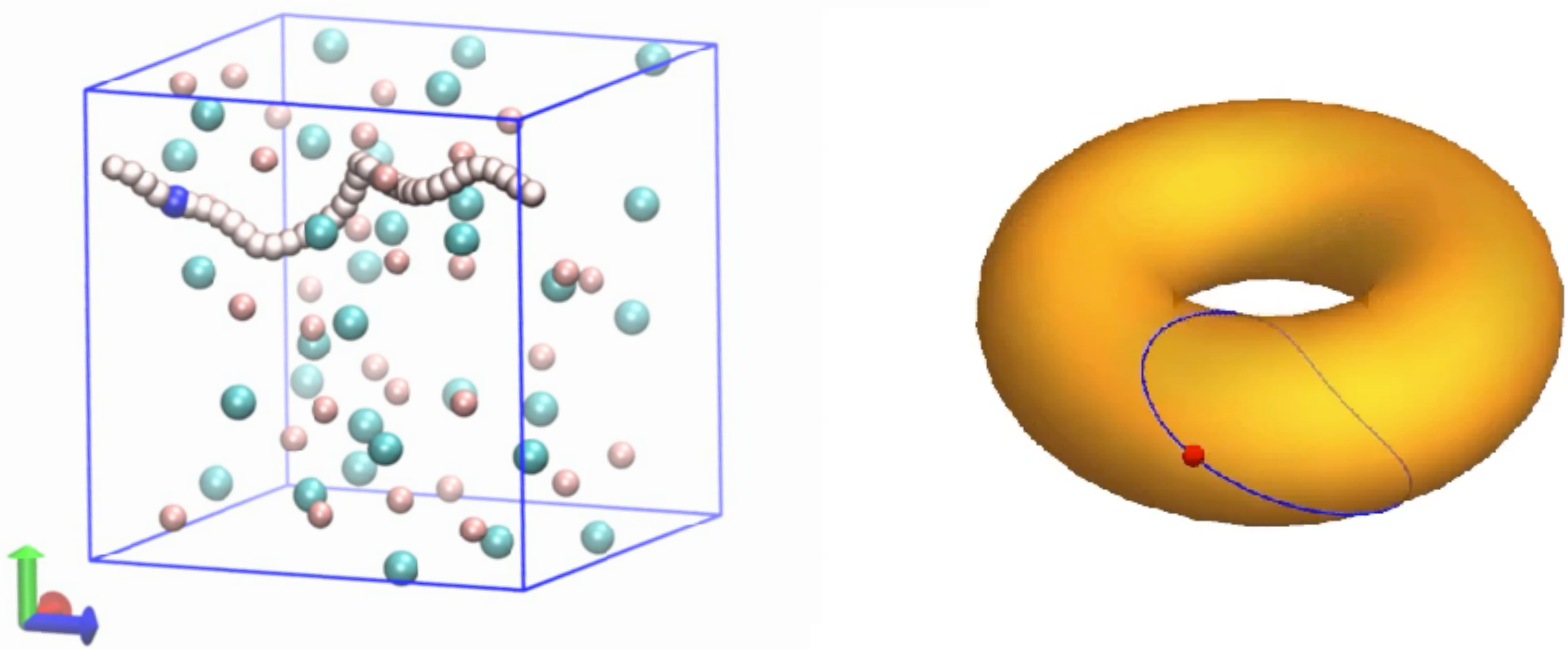




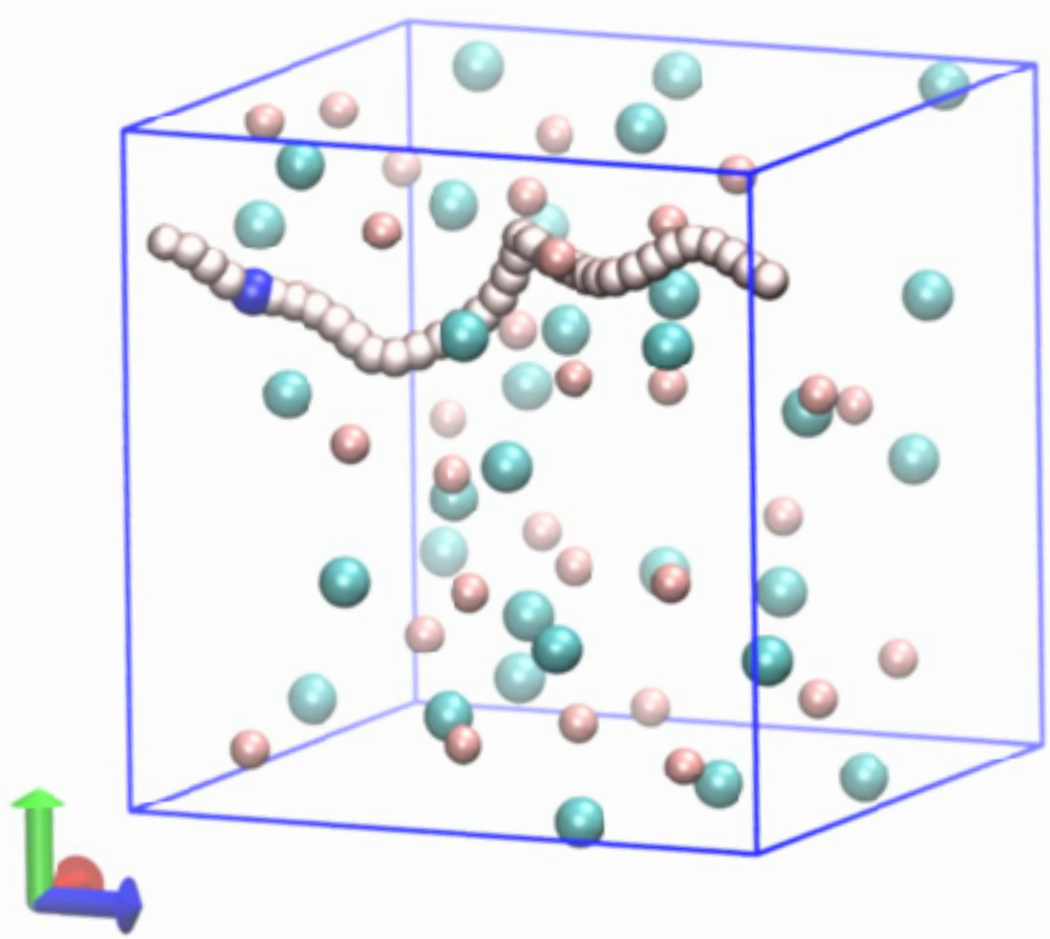
$$Q(AA') = Q(AA') = Q[n_1 = 1, n_2 = 1]$$

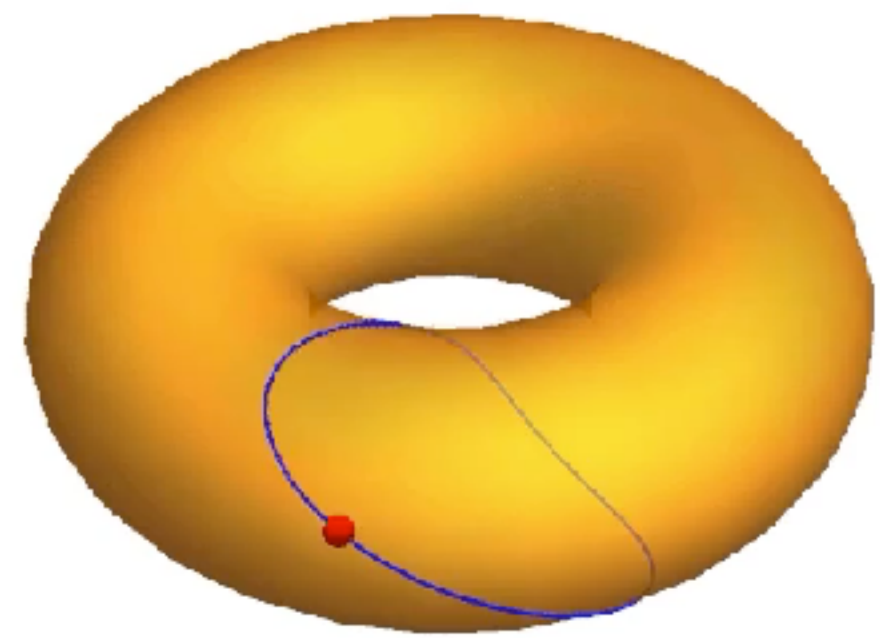
a numerical experiment on molten KCl



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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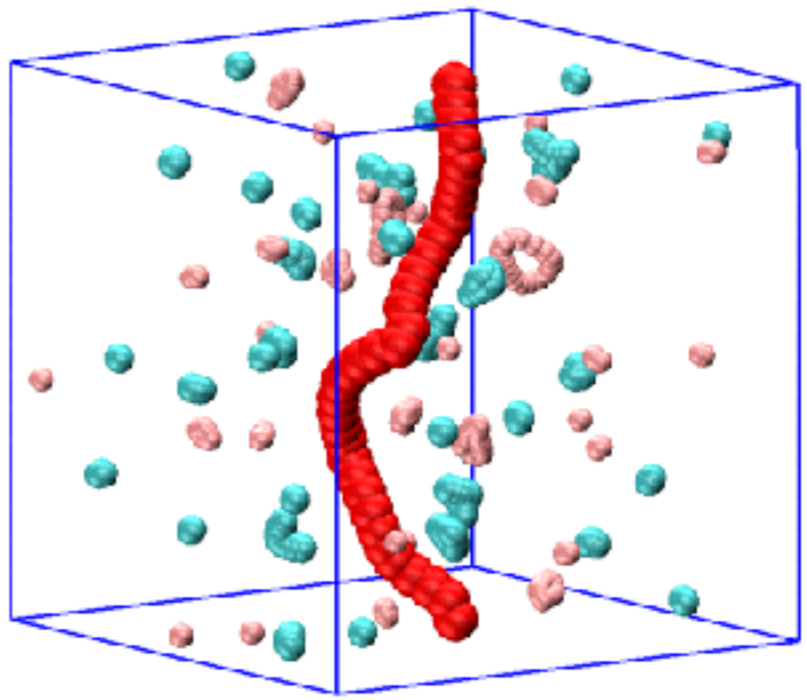

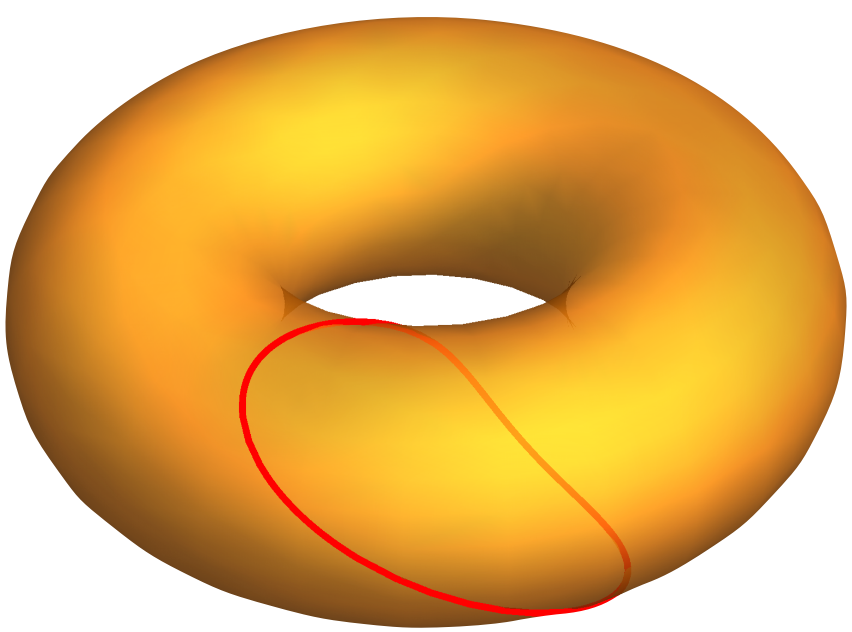

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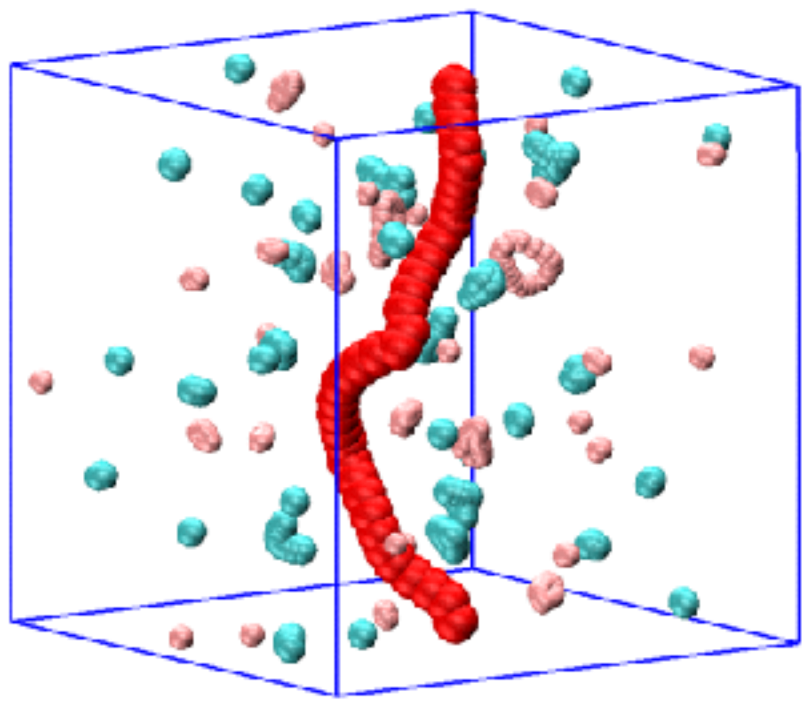

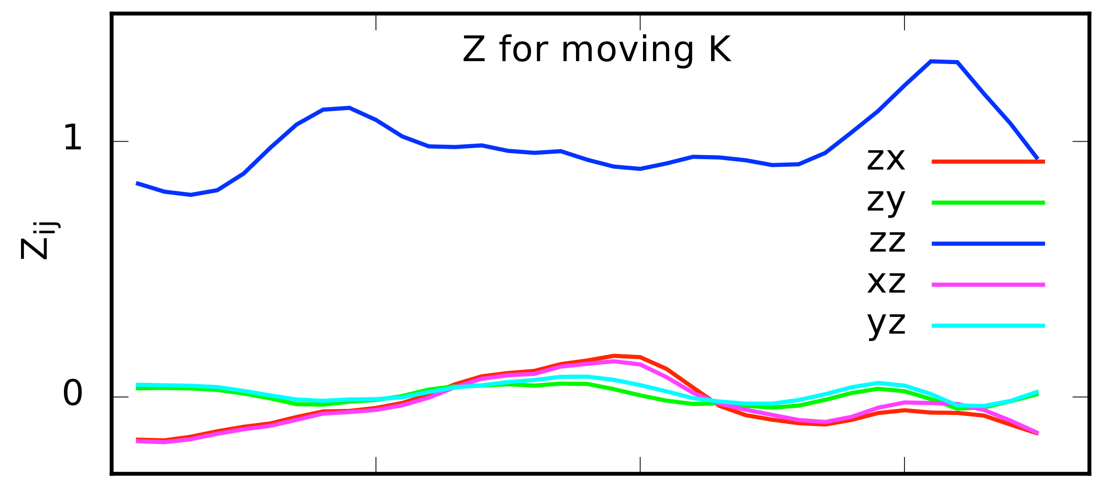

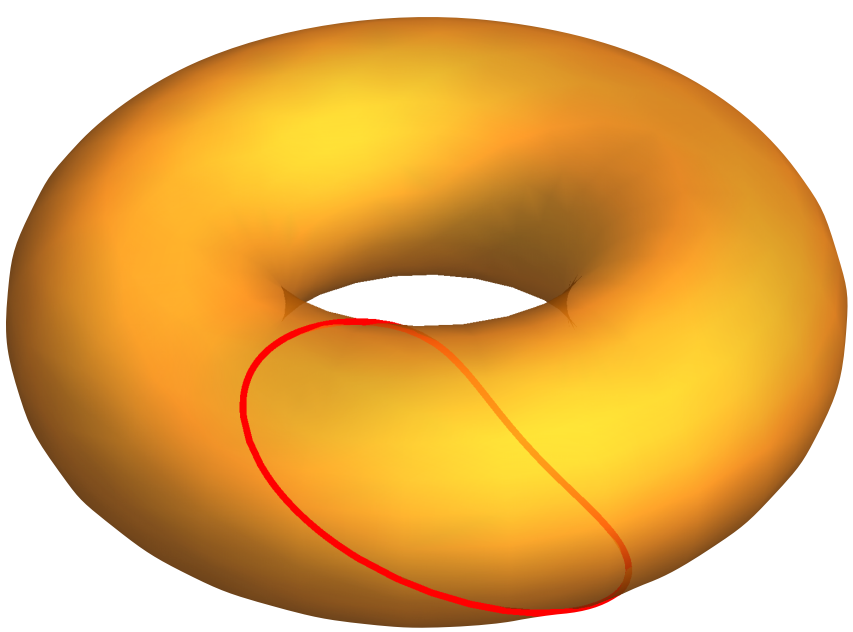

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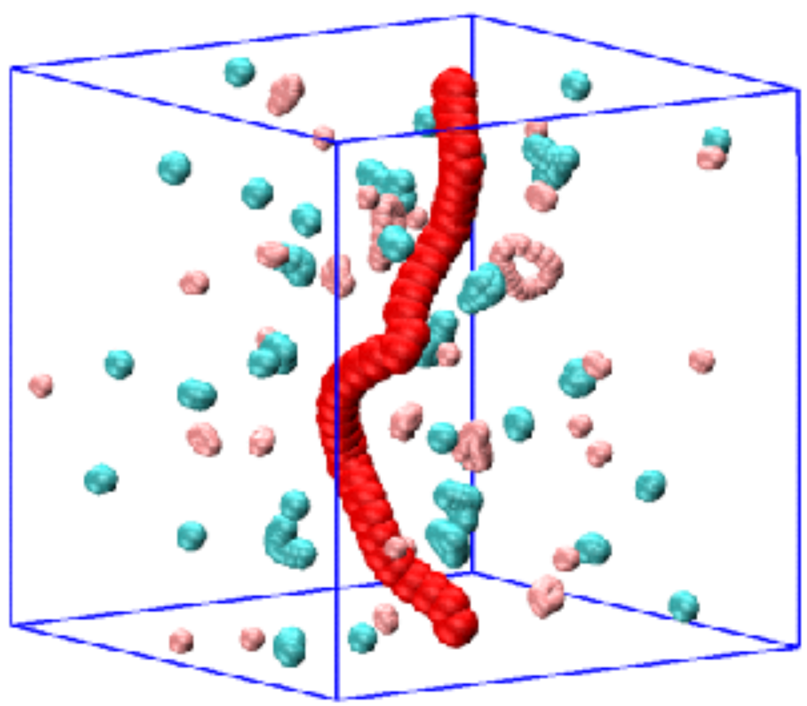
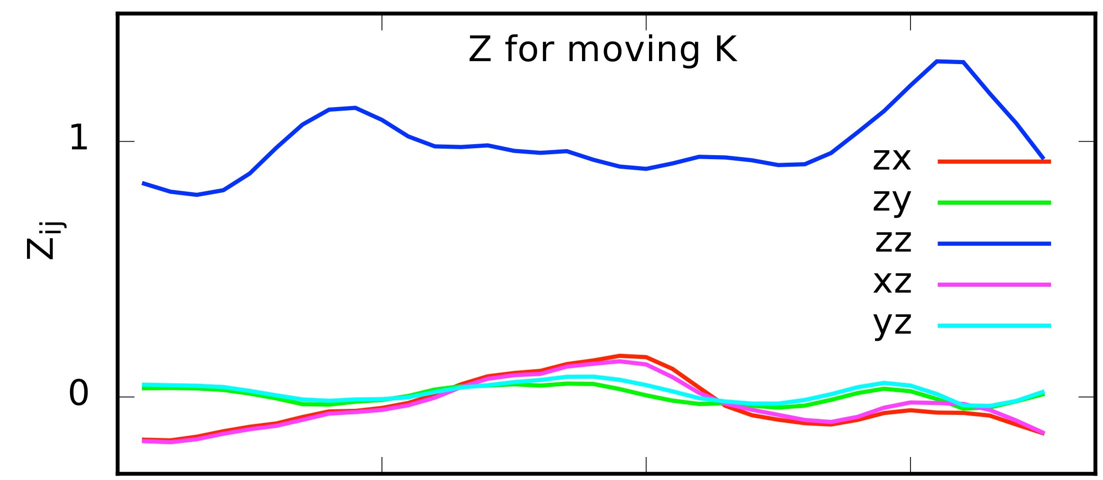
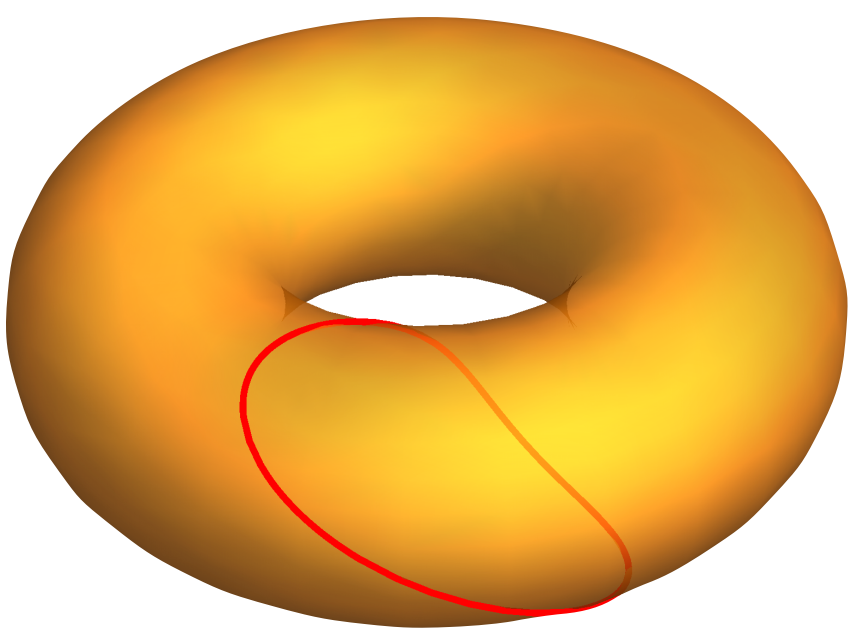
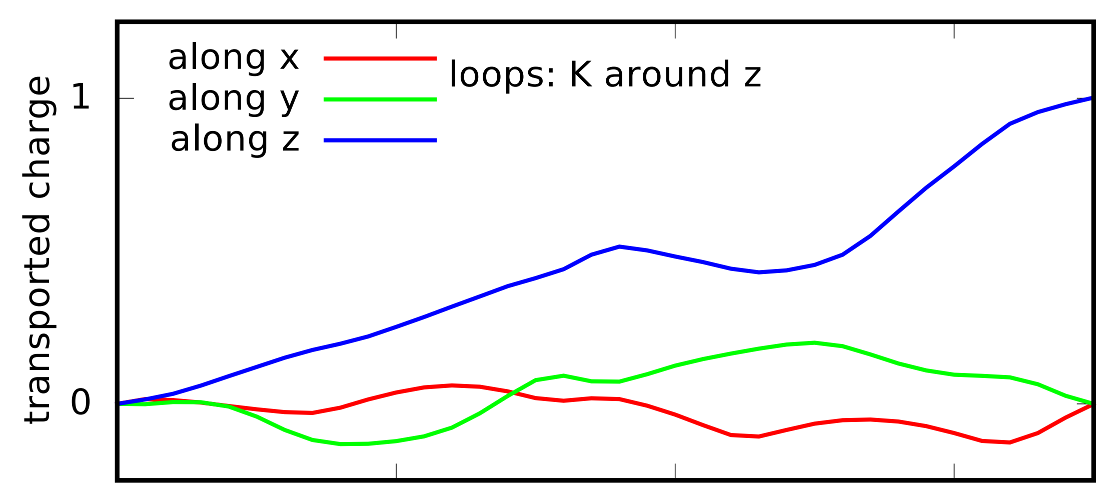


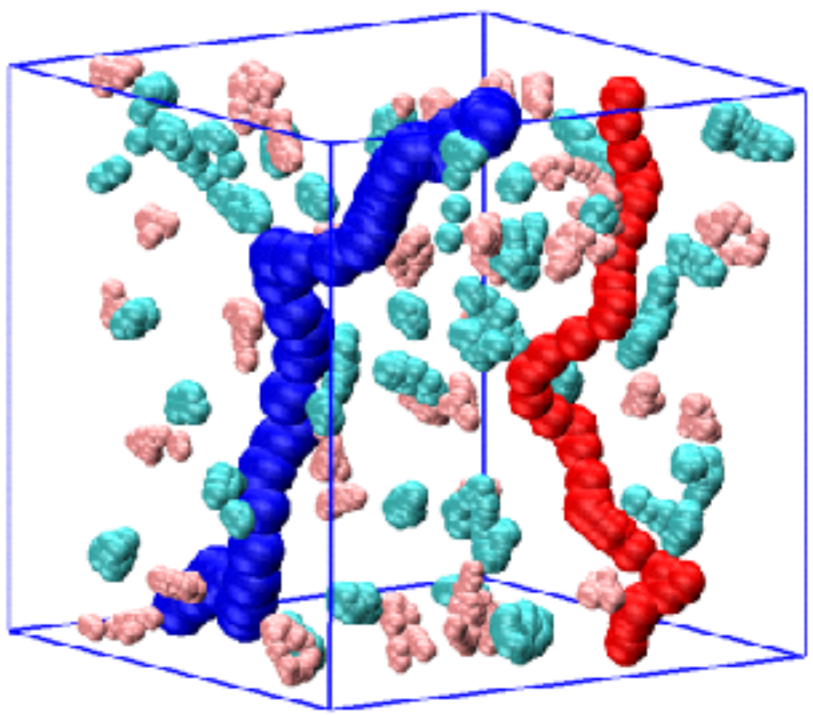






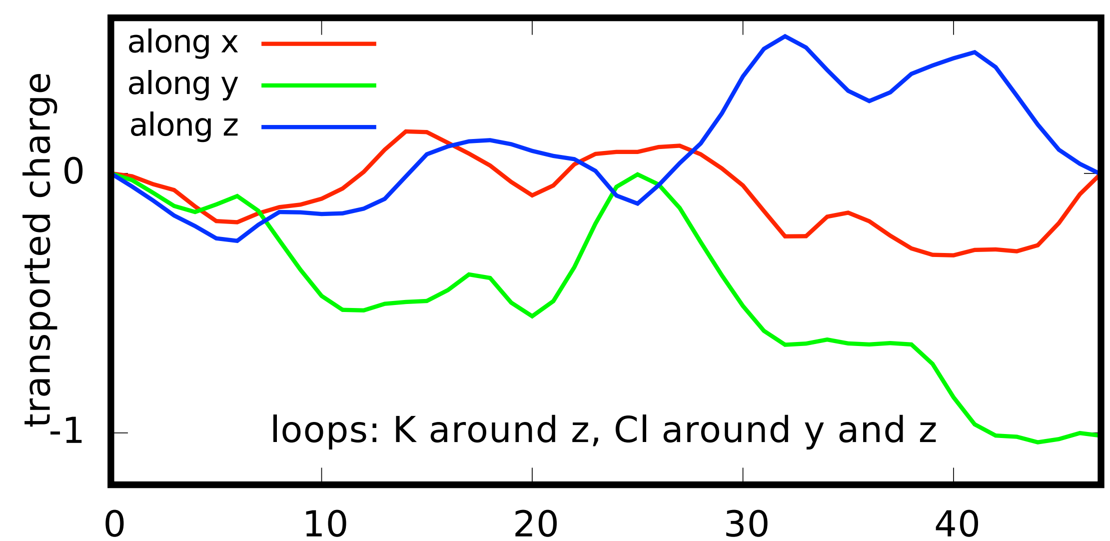
qx = =-0.000(6); qy = 0.000(2); qz = 1.00(18)

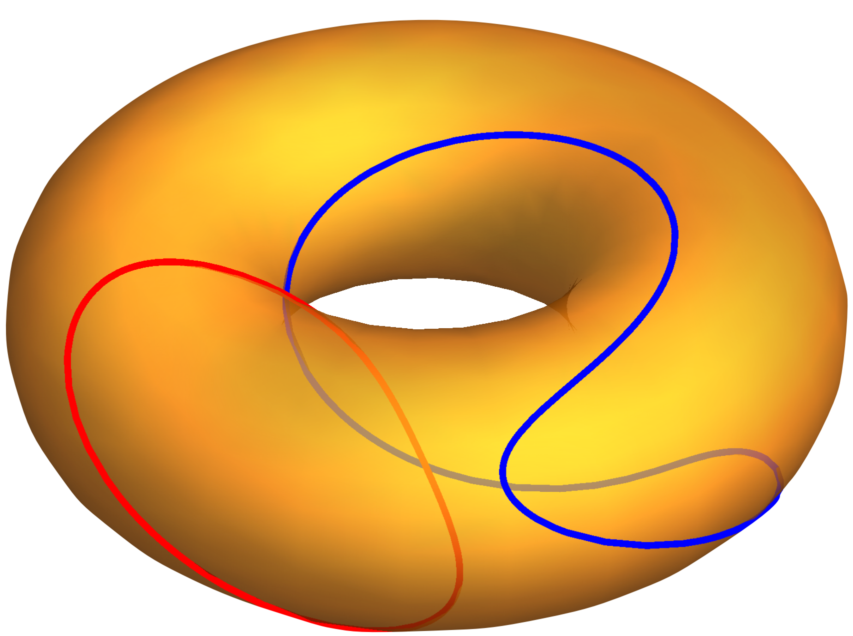
a numerical experiment on molten KCl



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

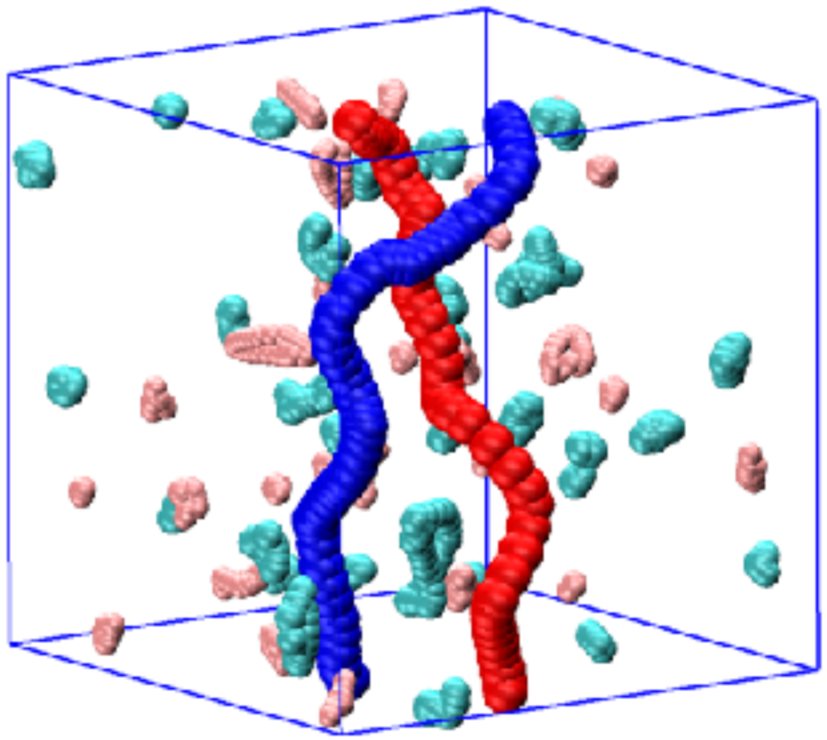
$Q_z[K] = 1$ $Q_z[K] = 0$

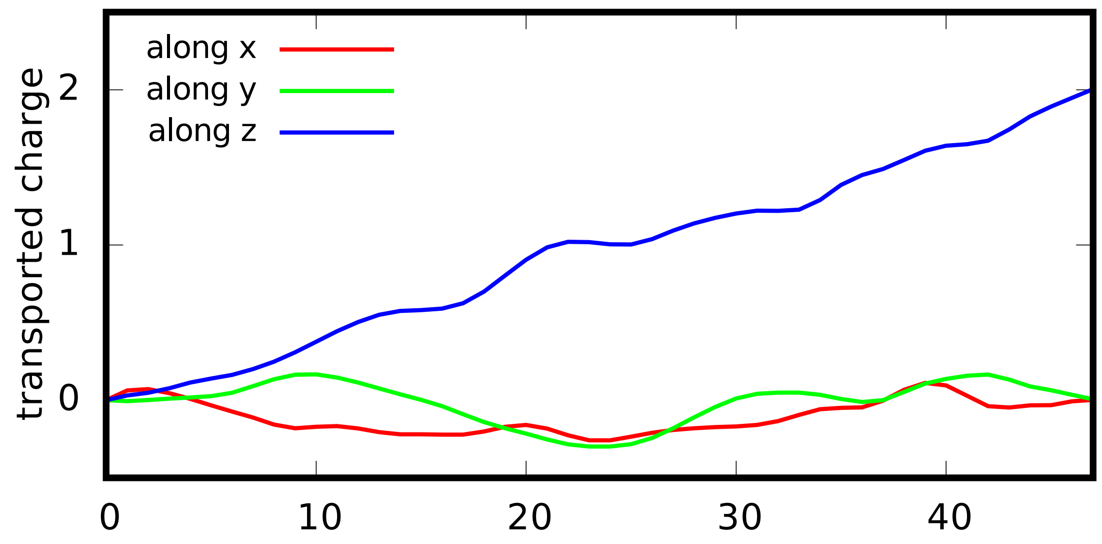


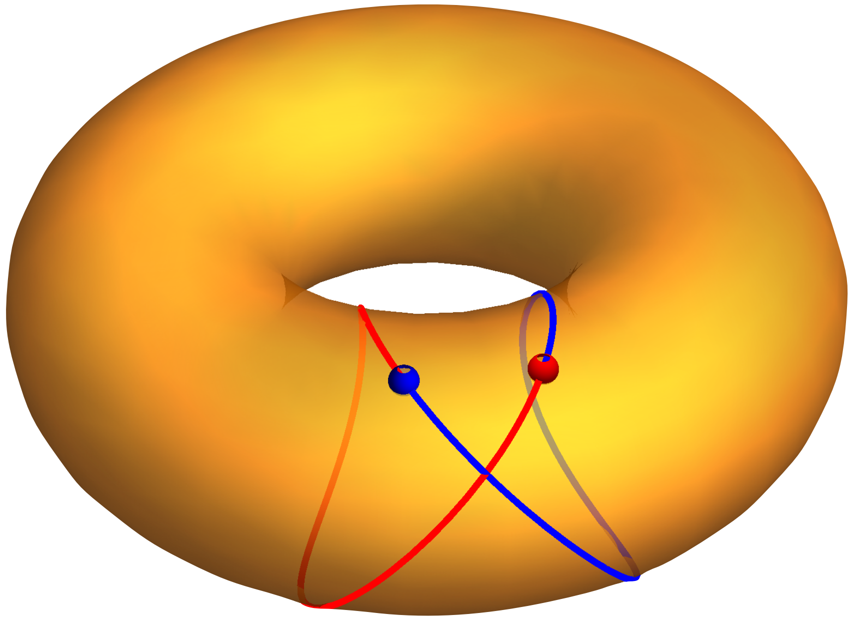


the charges transported by K and Cl around z cancel exactly

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

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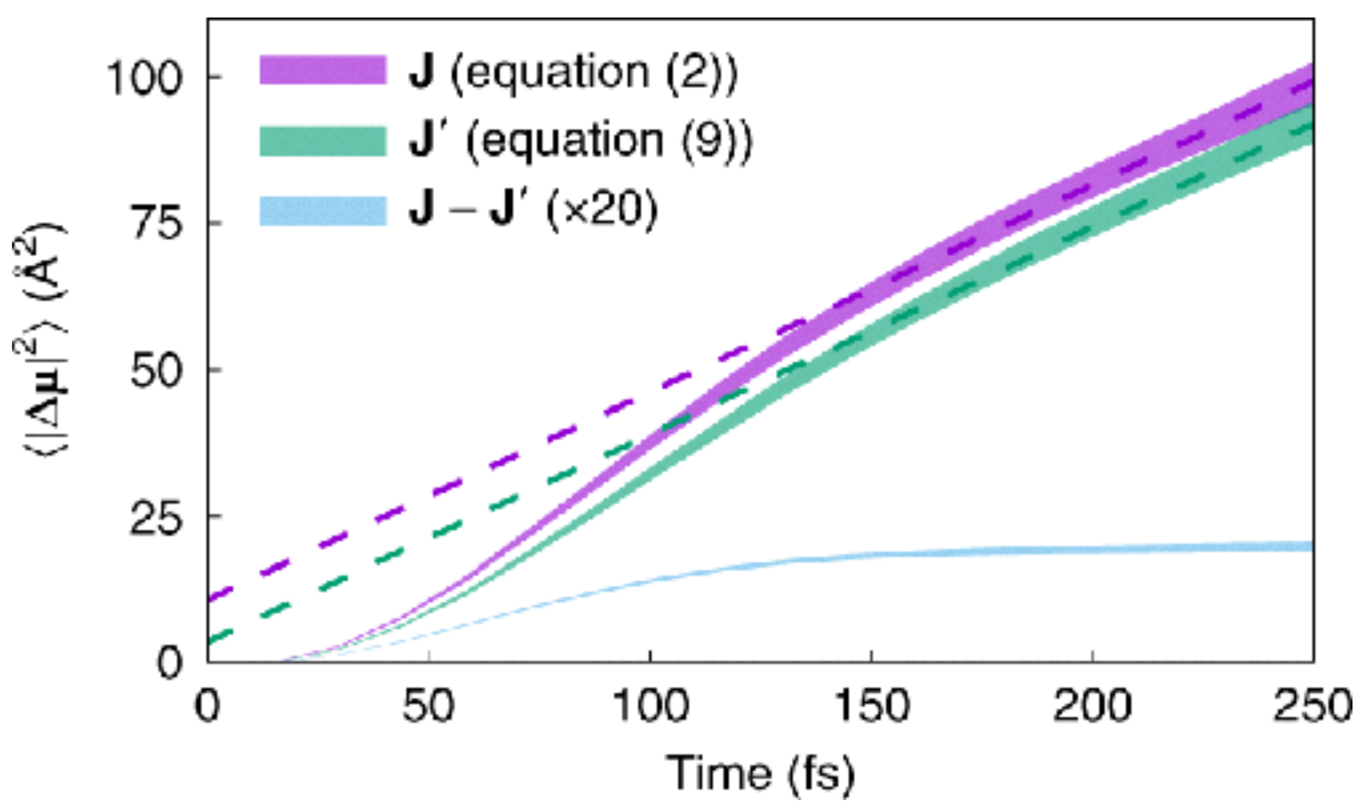
$$q_{i\alpha\beta} = q_{S(i)}\delta_{\alpha\beta}$$

atomic oxidation state

currents from atomic oxidation numbers

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

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



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

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- topological quantization of charge transport allows one to give a rigorous definition of the atomic oxidation states;
- gauge invariance and topological quantization 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.

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]*

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]*

Federico Grasselli
SISSA

Aris Marcolongo
SISSA, now @IBM Zürich

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