gauge invariance of heat and charge transport coefficients

in electronic insulators

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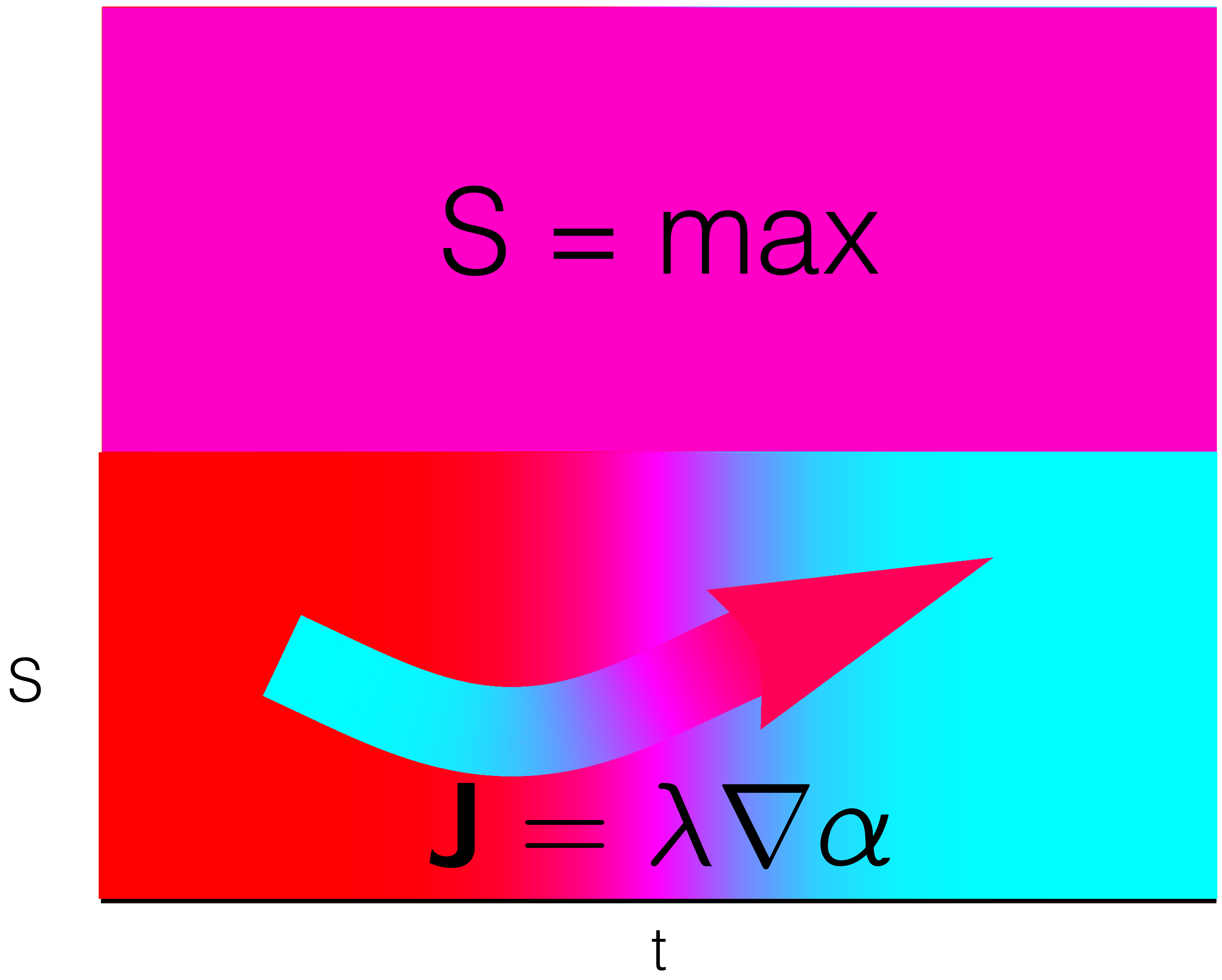
talk given at the March Meeting of the American Physical Society, March 2-6, 2020

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

conserved quantities (energy, charge, mass, …) in a macroscopic body flow from high- to low-density regions so as to maximise entropy



the linear-response theory of transport

$$\mathbf{J} = \lambda \nabla \alpha$$

energy transport

$$\alpha = \frac{1}{T}$$

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

charge transport

$$\alpha = \frac{\phi}{T}$$

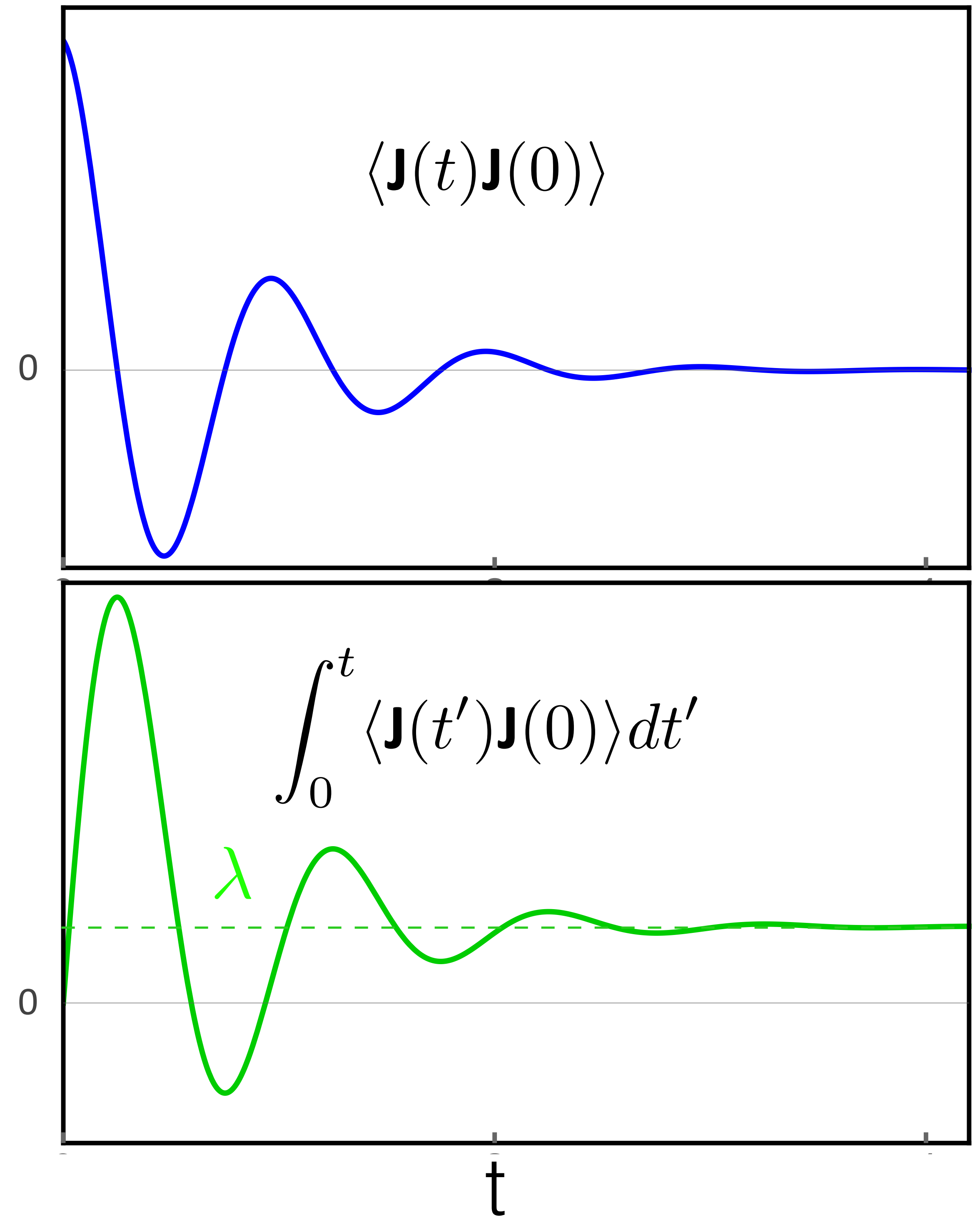
$$J_{\mathcal{E}} = -\sigma E$$

the linear-response theory of transport

$$\mathbf{J} = \lambda \nabla \alpha$$

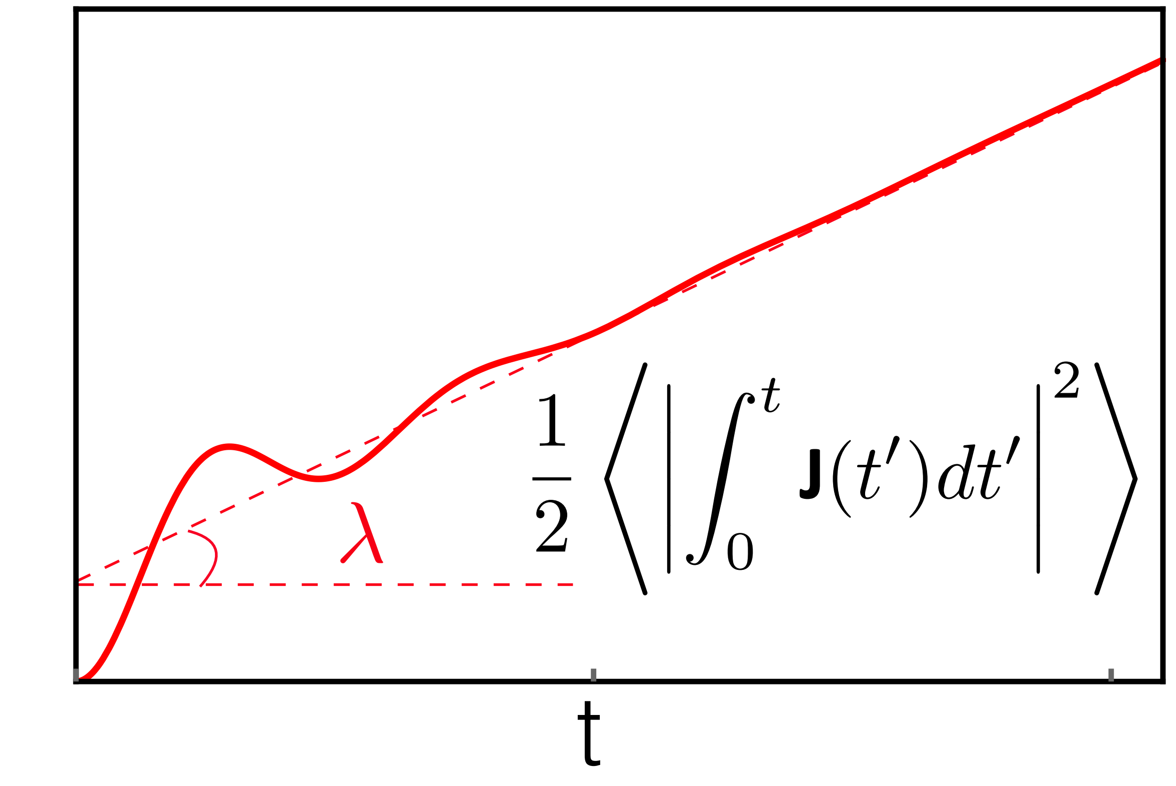
Green-Kubo

$$\lambda = \frac{\Omega}{k_B T} \underbrace{\int_0^\infty \langle J(t) J(0) \rangle dt}_{\langle J^2 \rangle \tau}$$



Einstein-Helfand

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



classical and quantum adiabatic heat transport

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

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

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Thermal Conductivity of Periclase (MgO) from First Principles

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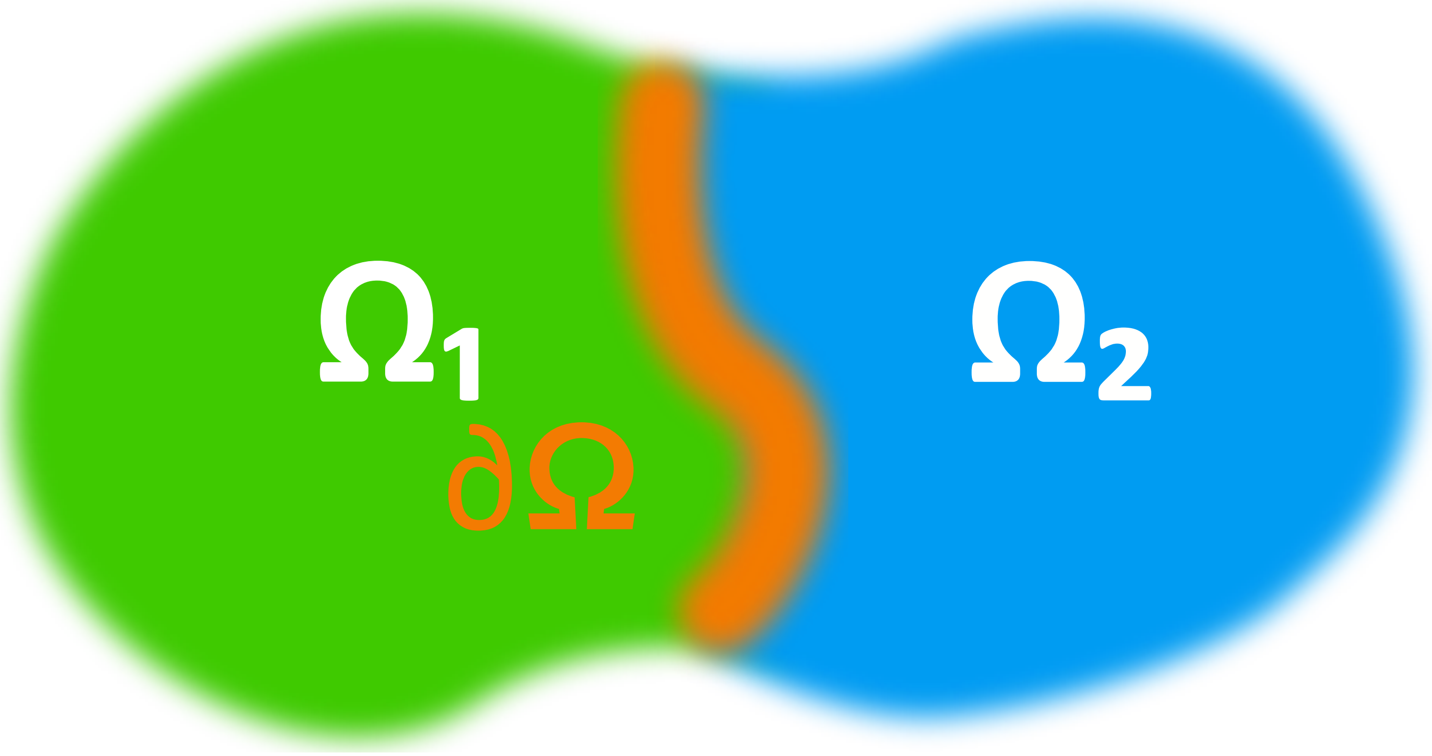
sensitive to the form of the potential. The widely used Green-Kubo relation [14] does not serve our purposes, because in first-principles calculations it is impossible to uniquely decompose the total energy into individual contributions from each atom.

how come?

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

gauge invariance of transport coefficients



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

extensivity

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

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

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

thermodynamic invariance

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

gauge invariance

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

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

$$\mathbf{J}'(t) = \mathbf{J}(t) + \dot{\mathbf{P}}(t)$$

conservation

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

gauge invariance of transport coefficients

$$\mathbf{J}'(t) = \mathbf{J}(t) + \dot{\mathbf{P}}(t)$$

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

$$\mathbf{D}'(t) = \mathbf{D}(t) + \mathbf{P}(t) - \mathbf{P}(0)$$

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

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

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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

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

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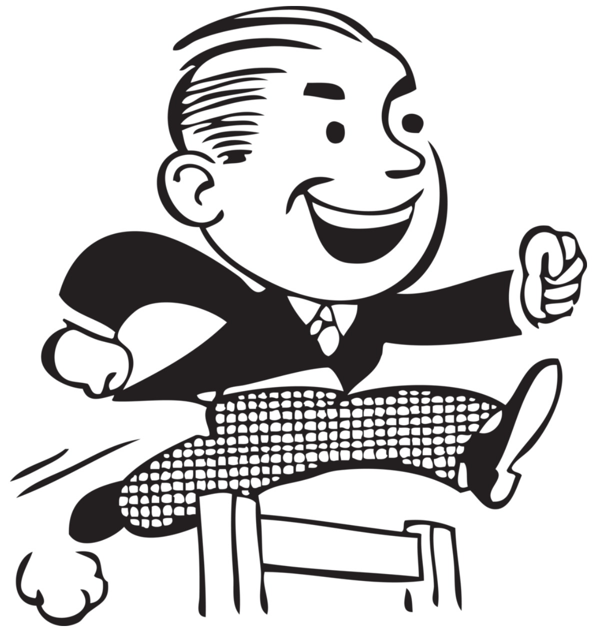
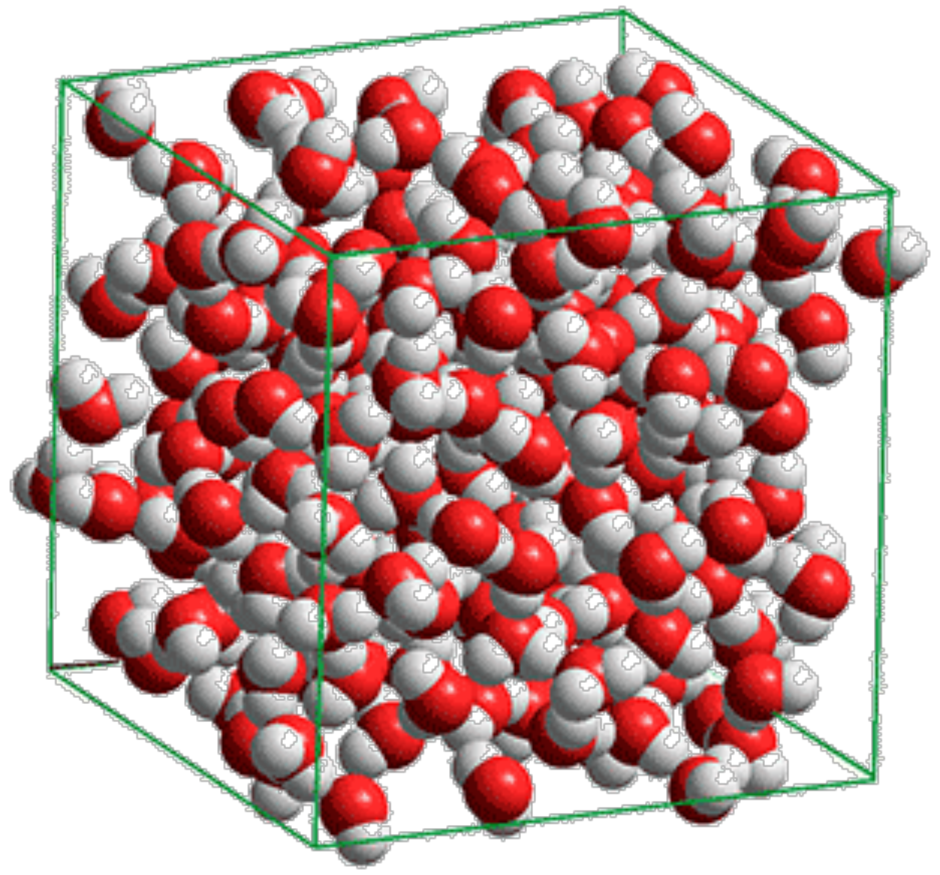
sensitive to the form of the potential. The widely used Green-Kubo relation [14] does not serve our purposes, because in first-principles calculations it is impossible to uniquely decompose the total energy into individual contributions from each atom.

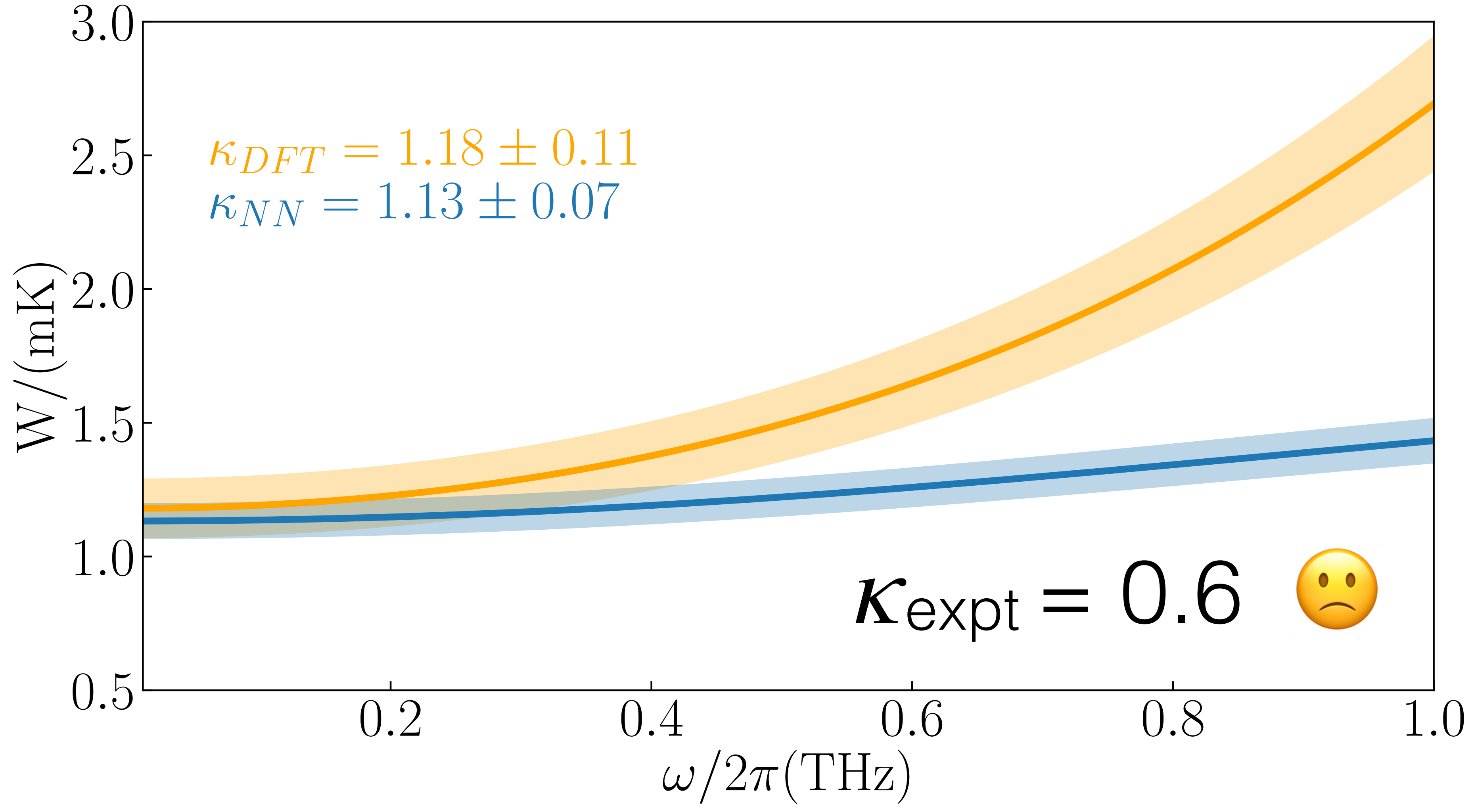
solution:

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.



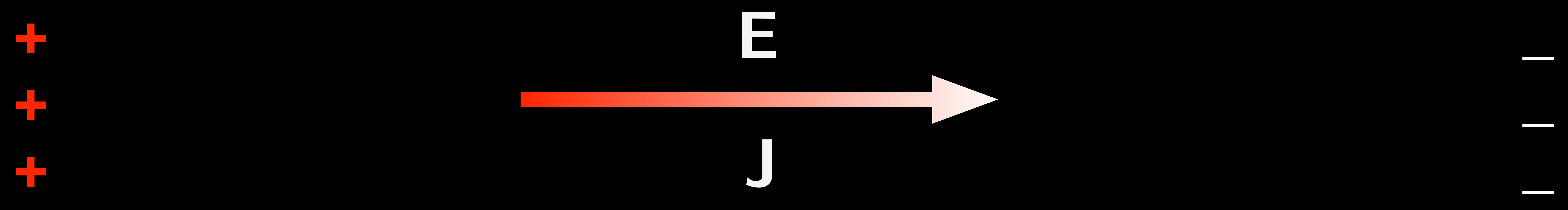
thermal conductivity of liquid water from DFT





ionic transport

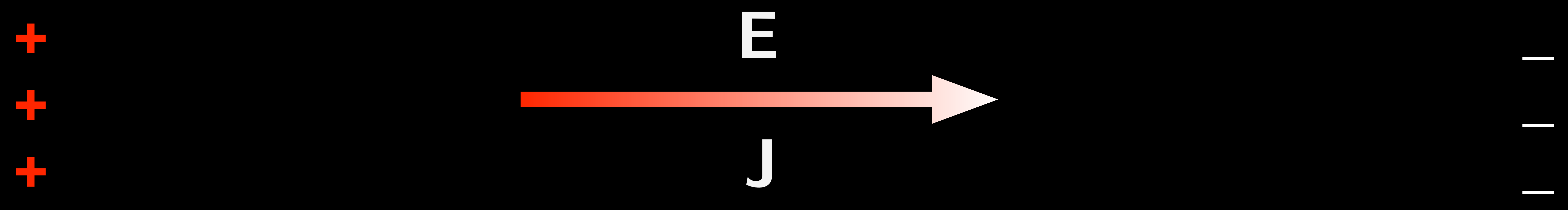
ionic transport



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

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

ionic transport



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

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

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

the conundrum

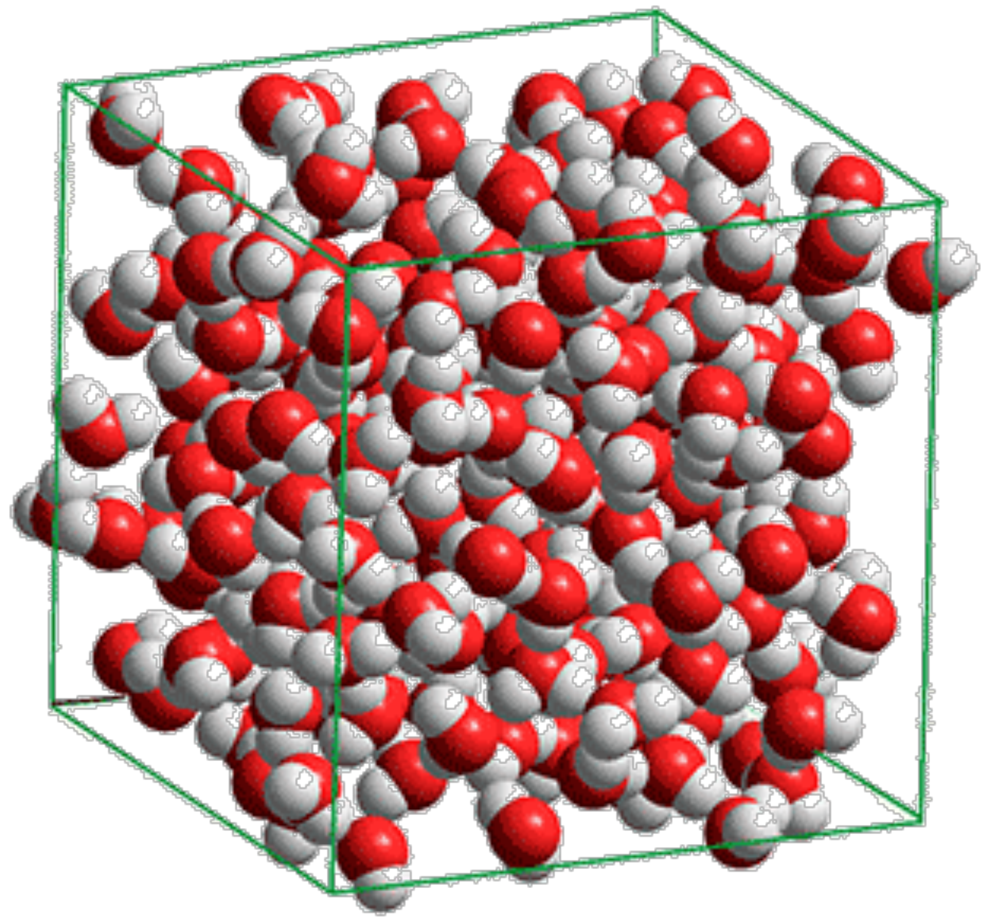
$$\mathbf{J} = \frac{1}{\Omega} \sum_i \mathbf{Z}_i^* \cdot \mathbf{v}_i$$

$$\neq 0$$

$$\sigma = \frac{\Omega}{6 k_B T} \lim_{t \to \infty} \frac{1}{t} \mathrm{var} \left[\int_0^t \mathbf{J}(t') dt' \right]$$

$$= 0 \quad ???$$

pure, undissociated
H_2O



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

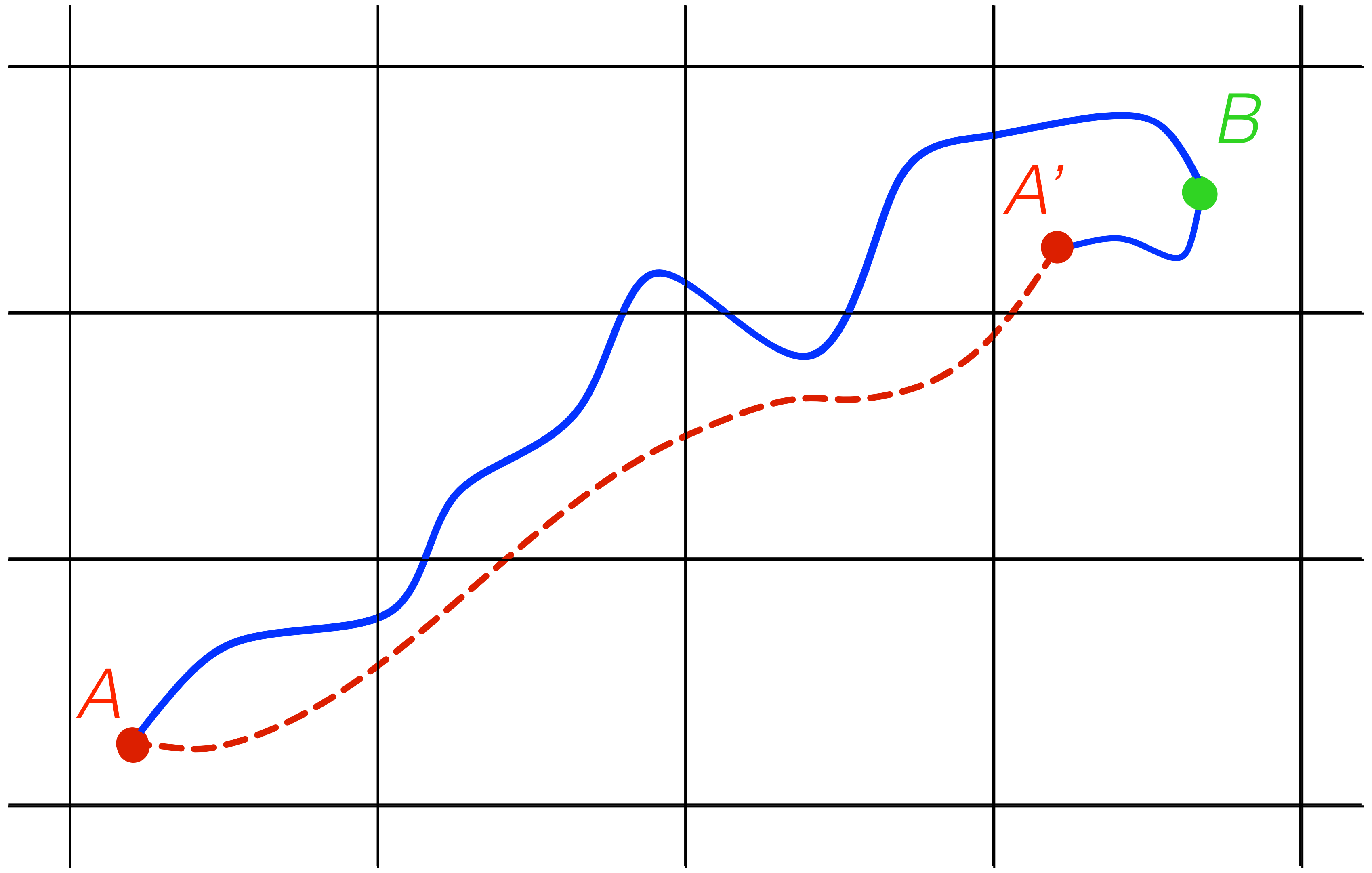
Martin French,[1] Sebastien Hamel,[2] and Ronald Redmer[1]

“*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?

gauge invariance of charge transport



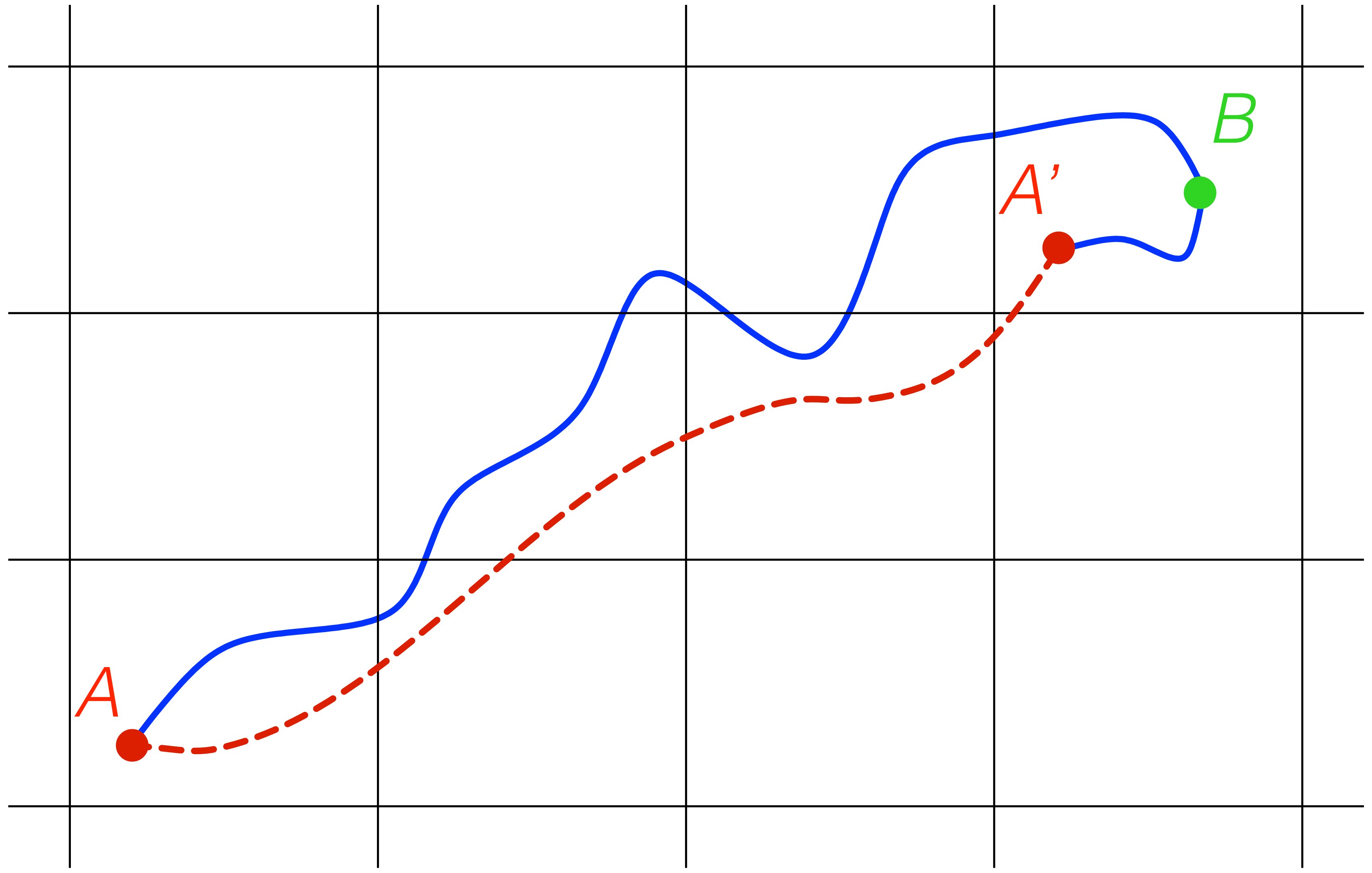
$$\sigma \propto \lim_{t\to\infty} \frac{1}{2t} \mathrm{var}\left[\mu_{AB}(t)\right]$$

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

$$\mathrm{var}\left[\mu_{AB}\right] = \underbrace{\mathrm{var}\left[\mu_{AA'}\right]}_{\mathcal{O}(t)} + \underbrace{\mathrm{var}\left[\mu_{A'B}\right]}_{\mathcal{O}(1)} + 2\,\underbrace{\mathrm{cov}\left[\mu_{AA'}\cdot\mu_{A'B}\right]}_{\mathcal{O}(t^{\frac{1}{2}})}$$

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

gauge invariance of charge transport



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

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

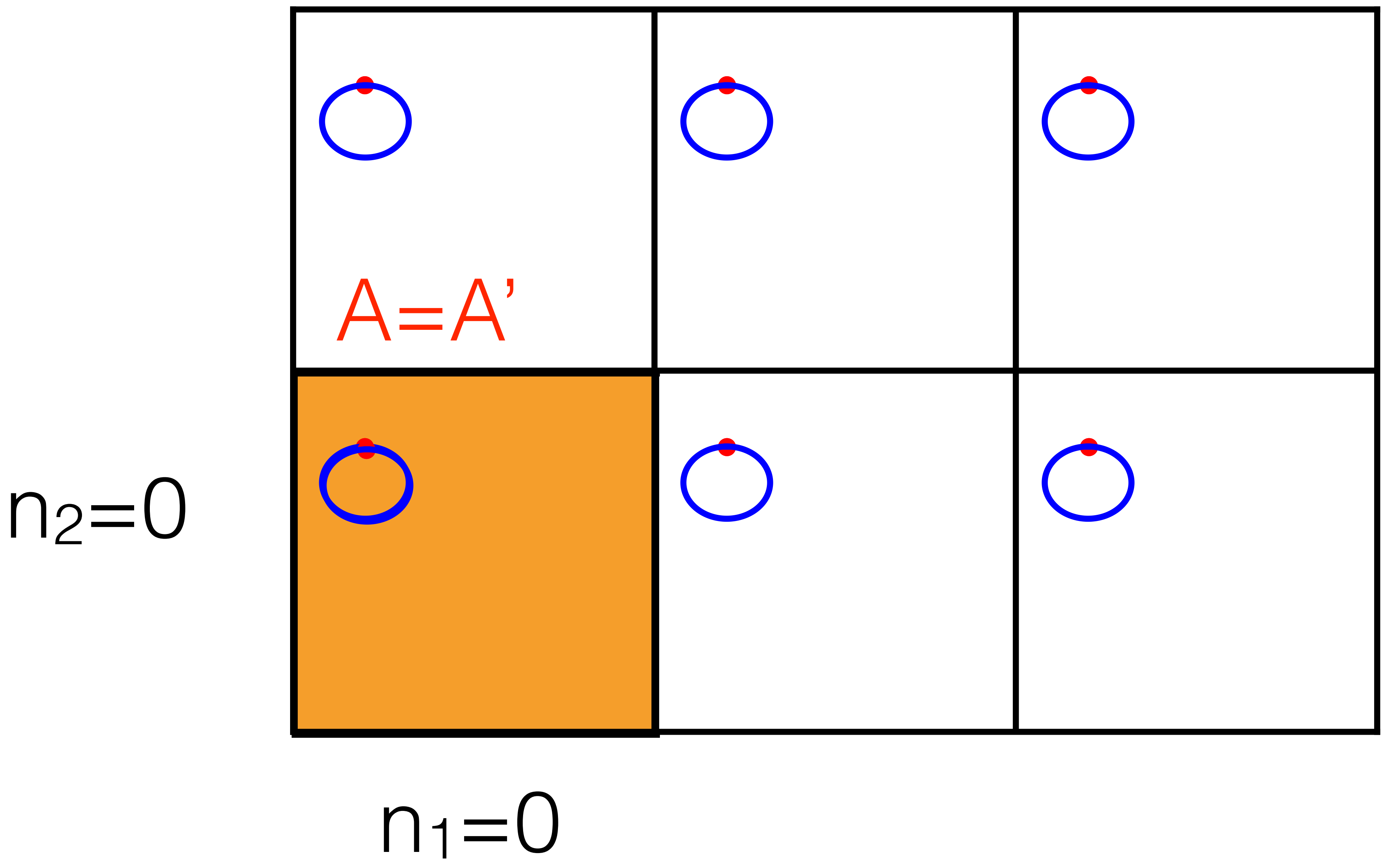
$$\hat{H}(A') = \hat{H}(A)$$

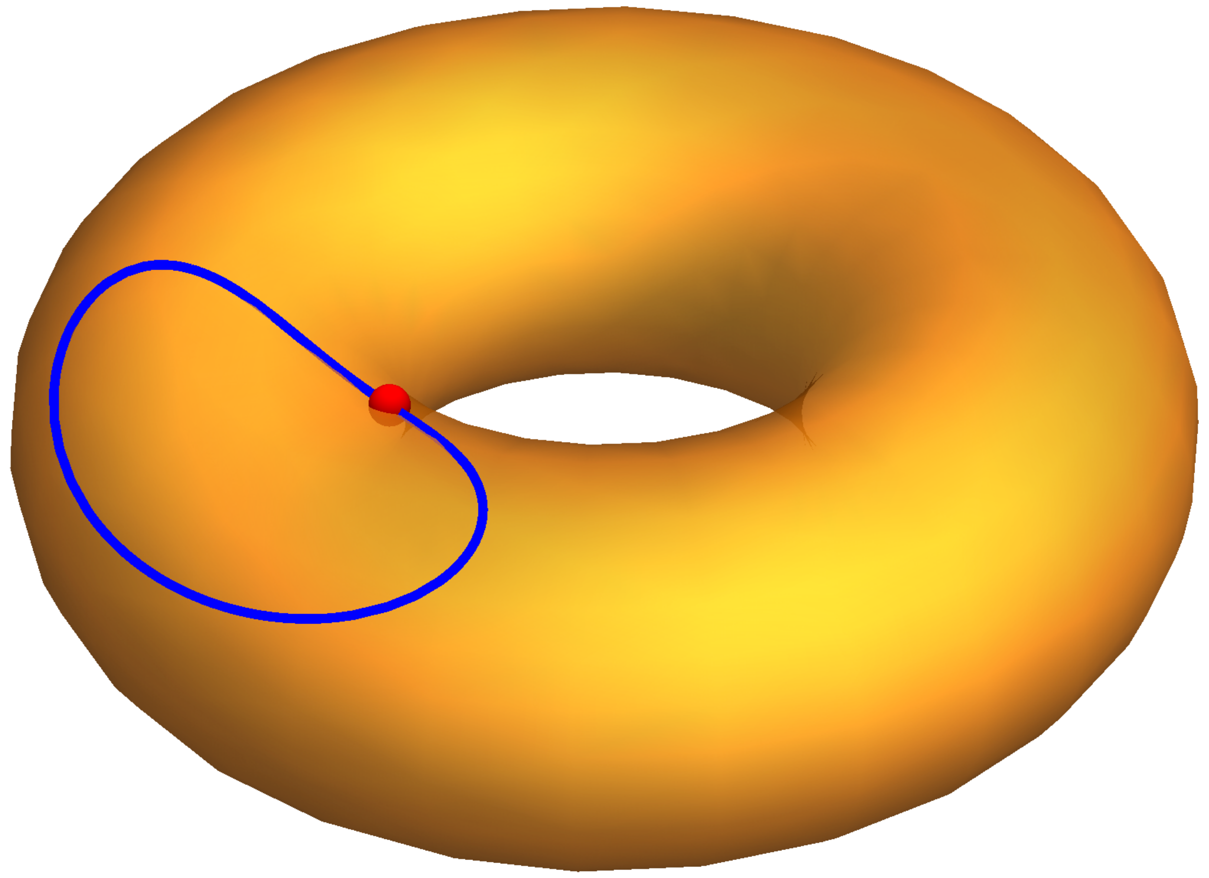
$$Q(AA') = \frac{1}{\ell} \int_A^{A'} d\mu(X)$$

$$\in \mathbb{Z}$$

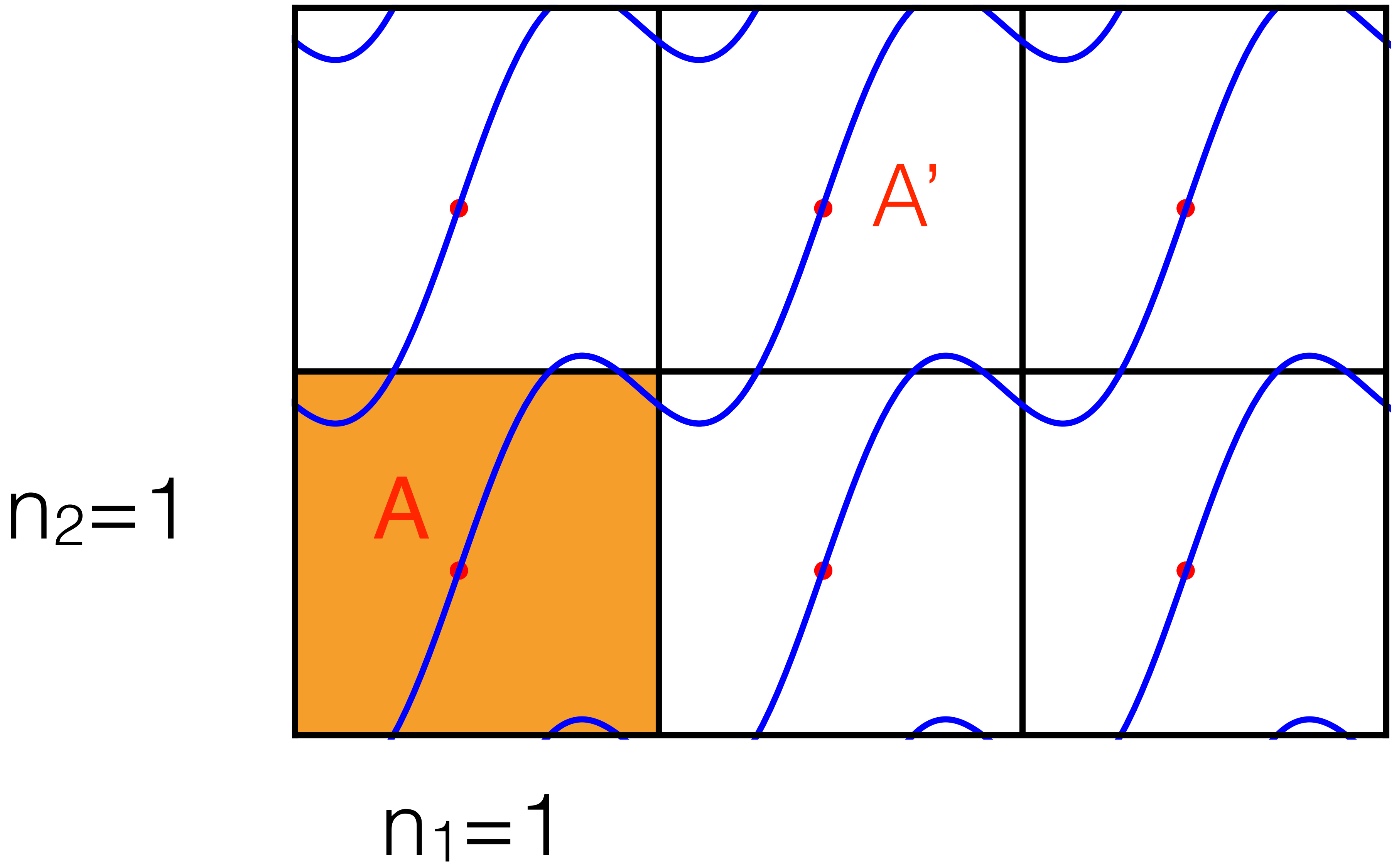
D.J. Thouless, *Quantization of particle transport*, Phys. Rev. B **27**, 2083 (1983)

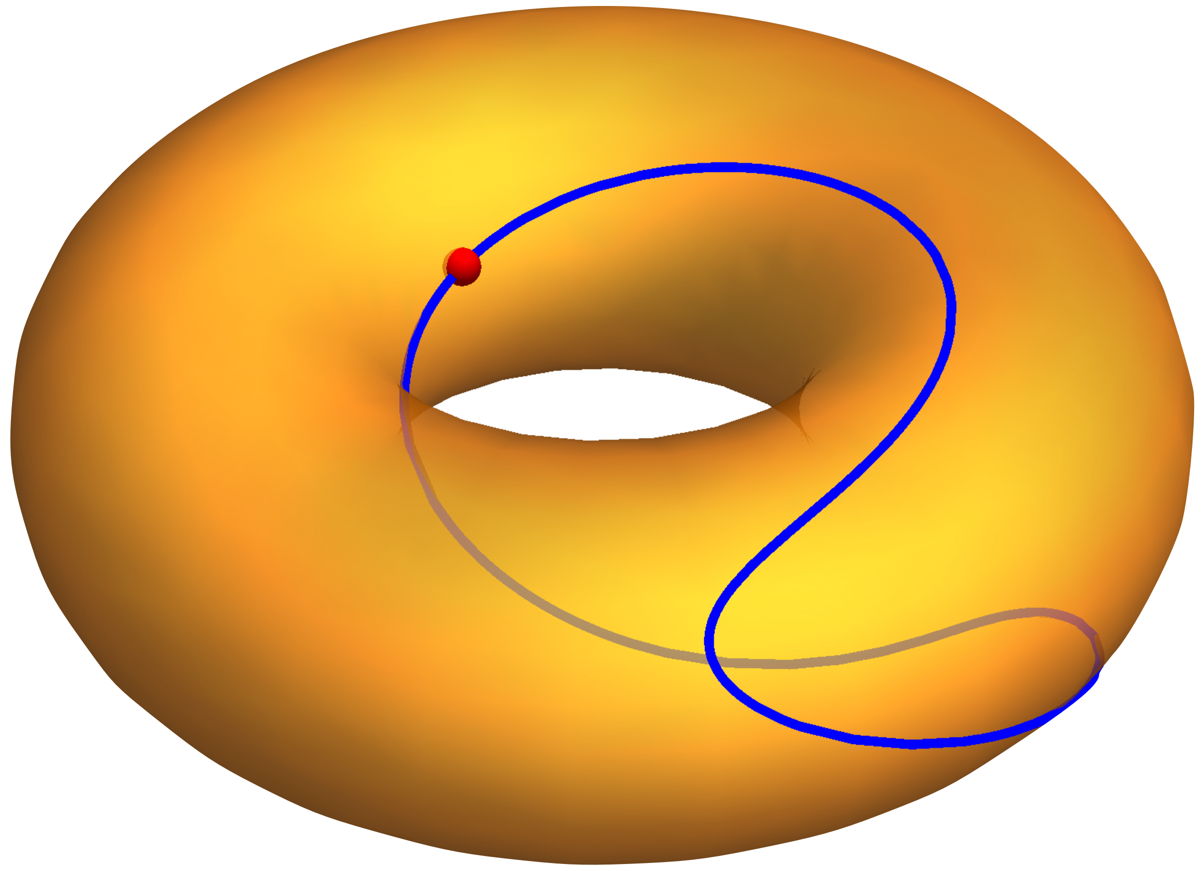
topological invariants



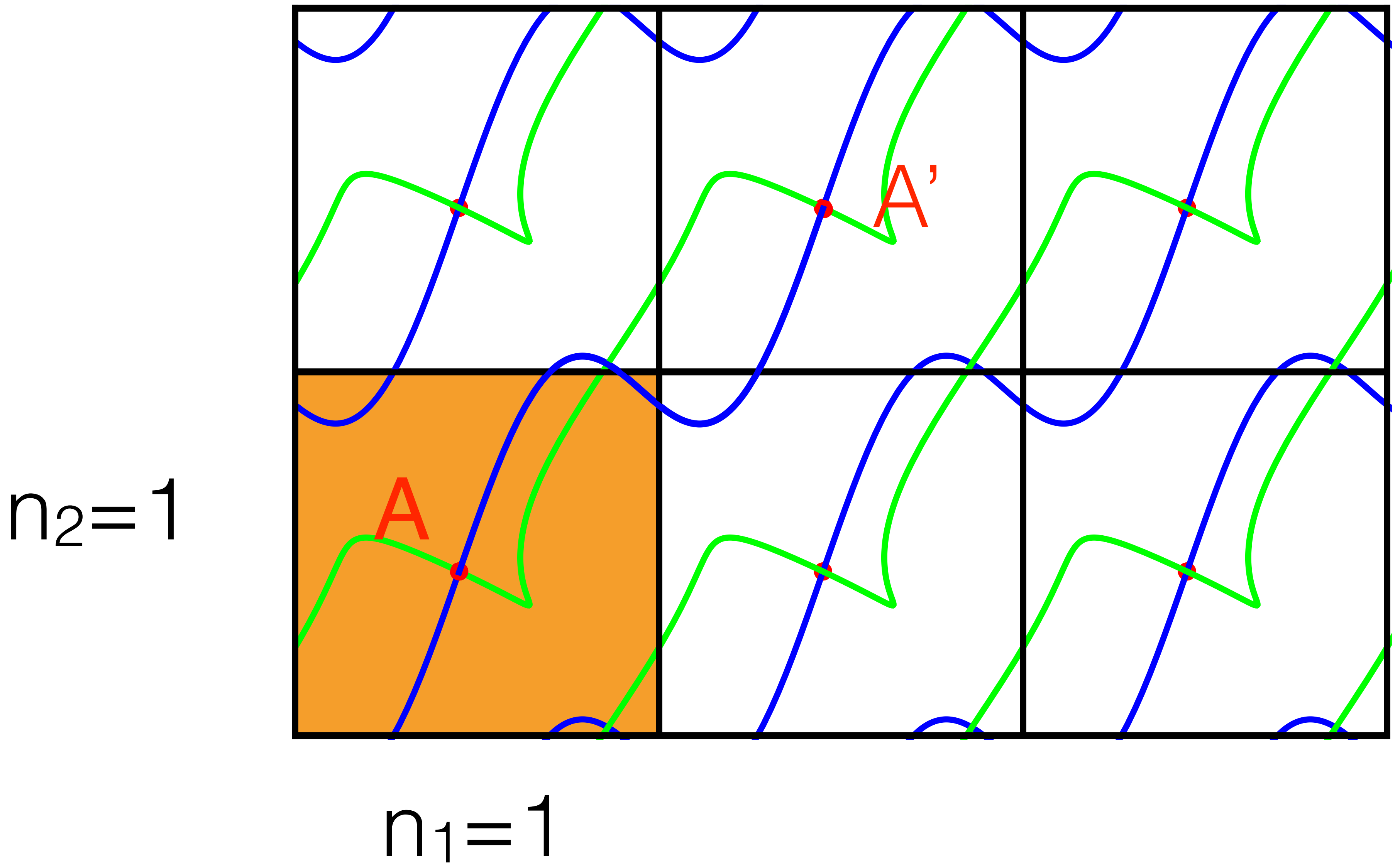


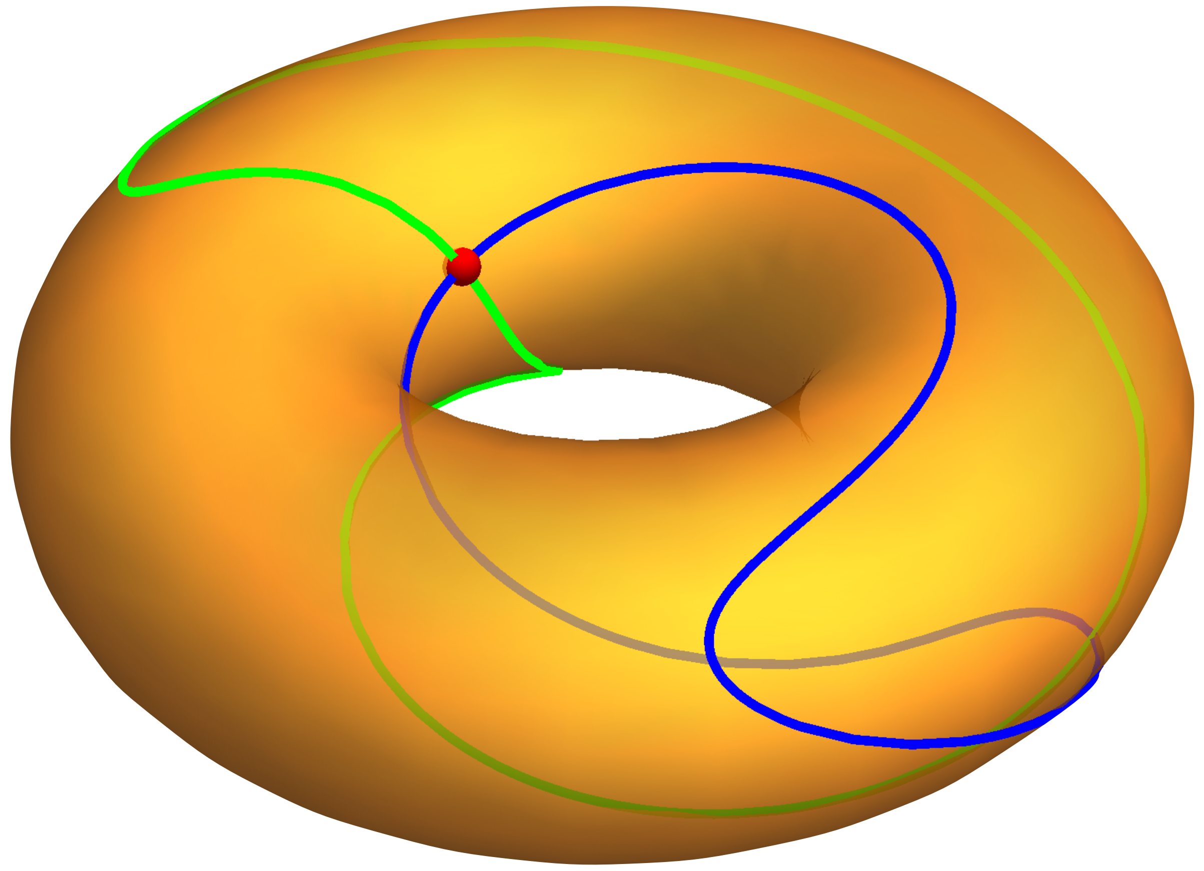
topological invariants





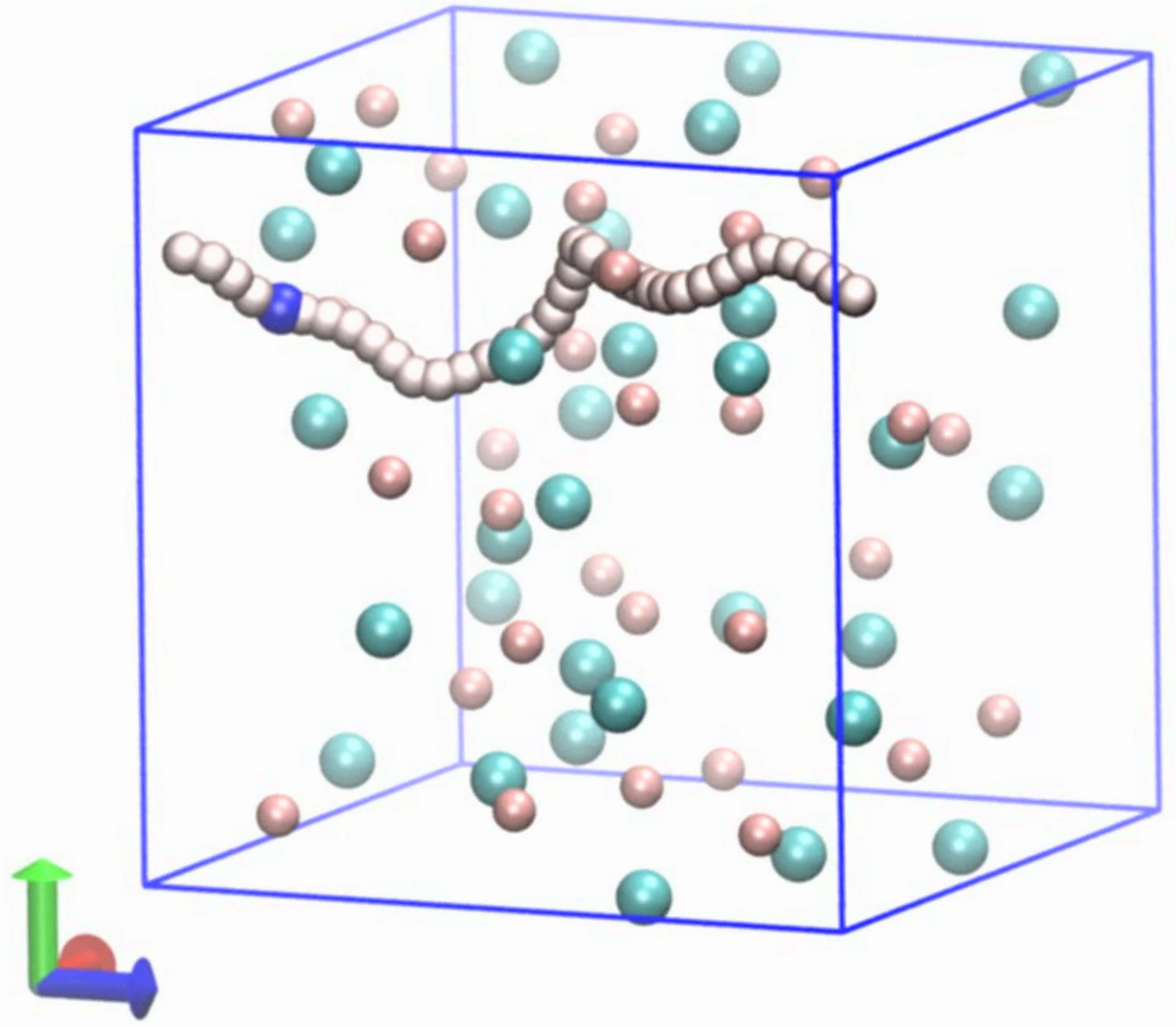
topological invariants

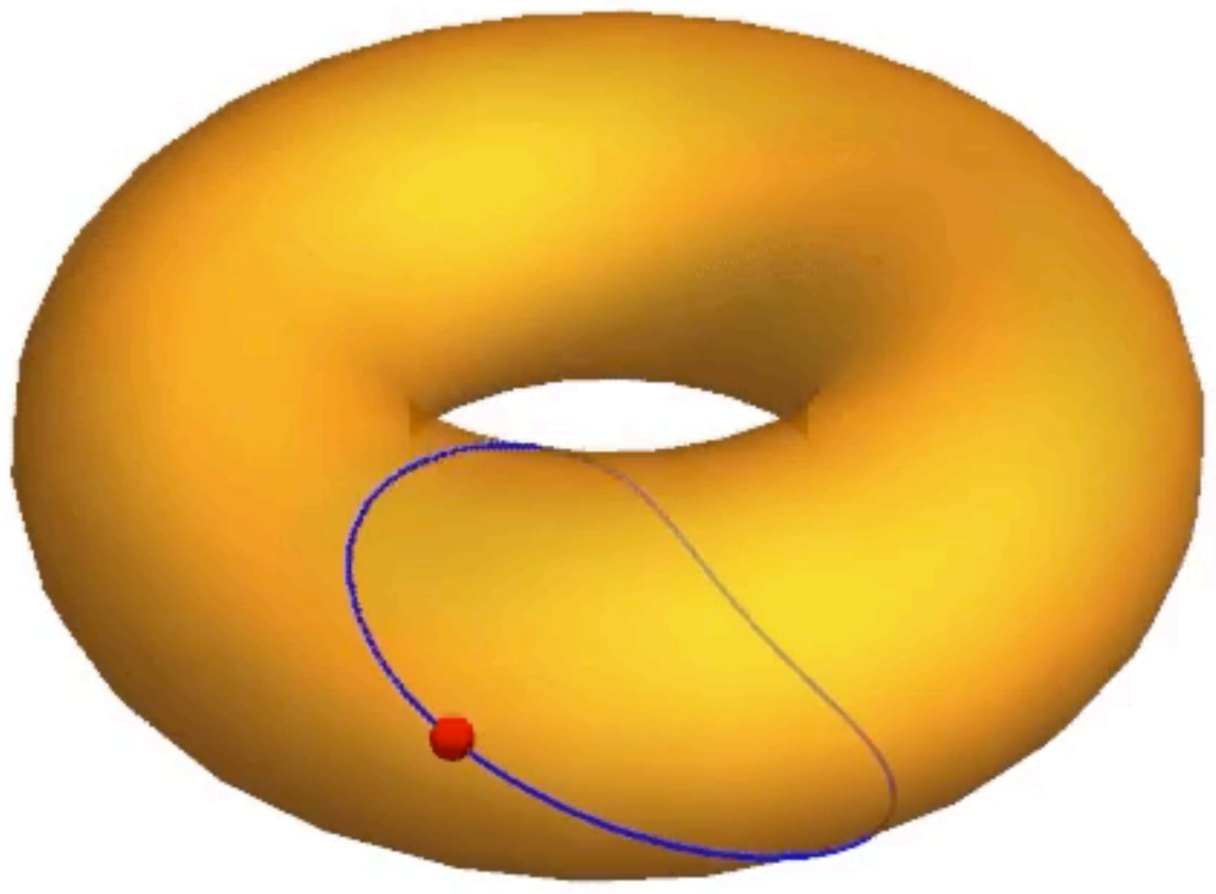




$$Q(AA') = Q(AA') = Q[n_1 = 1, n_2 = 1]$$

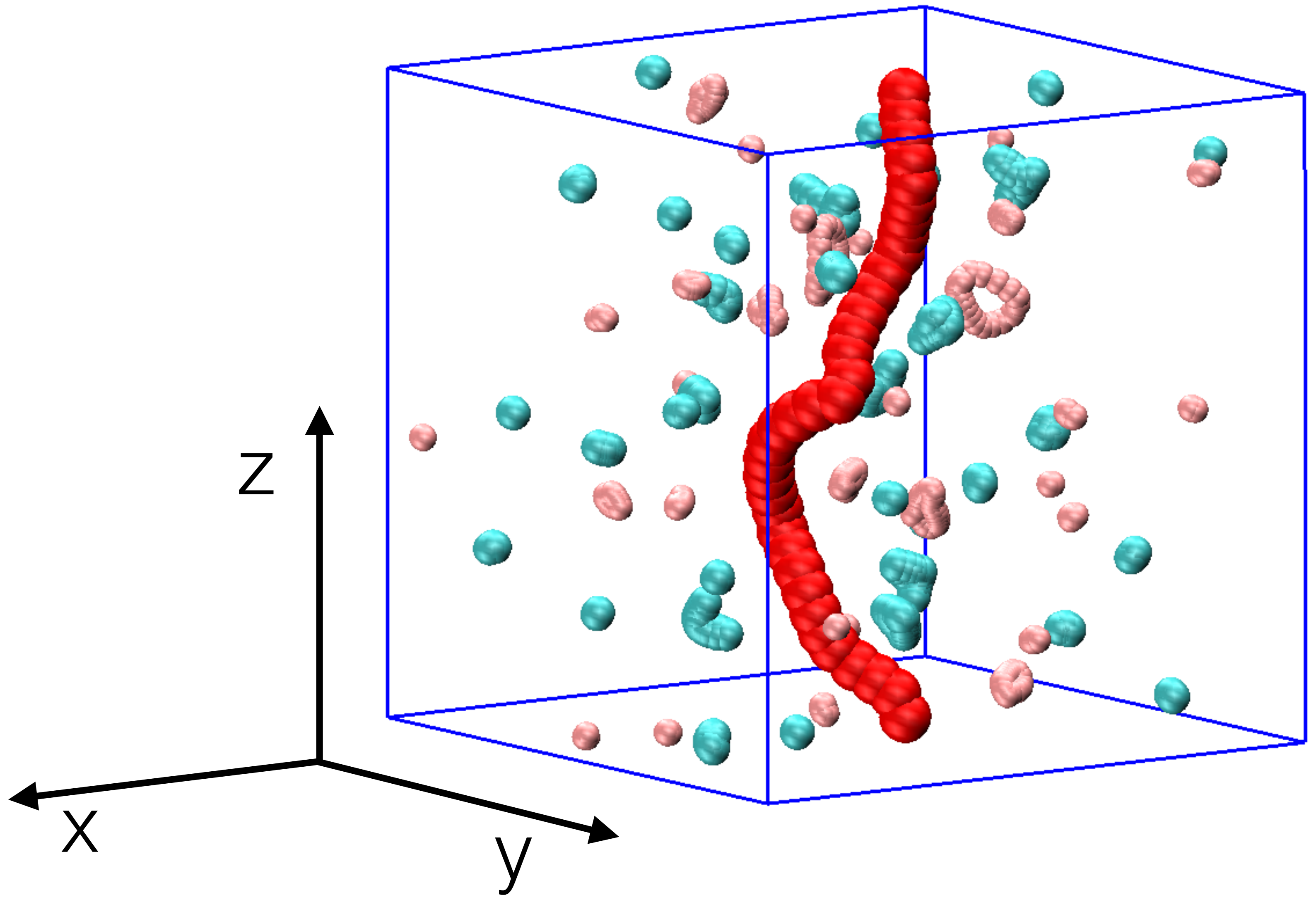
a numerical experiment on molten KCl

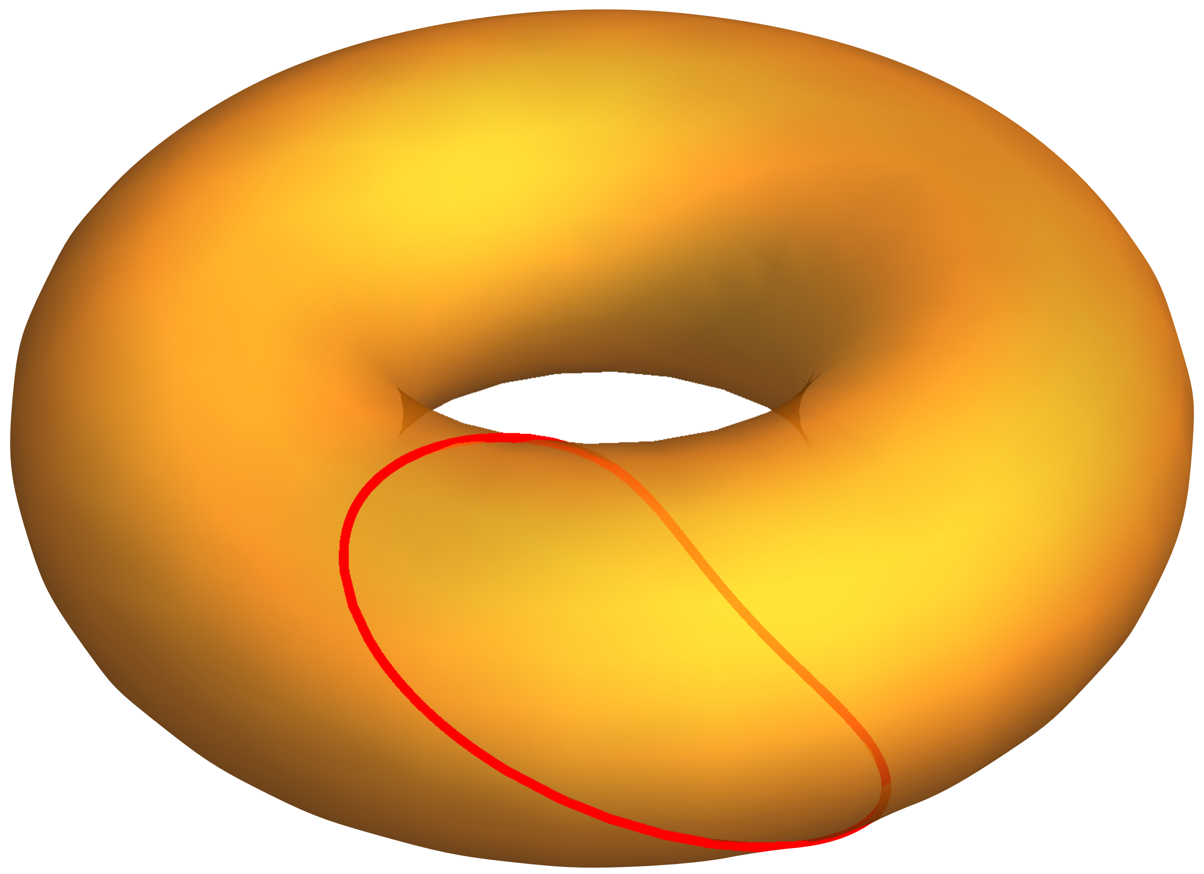


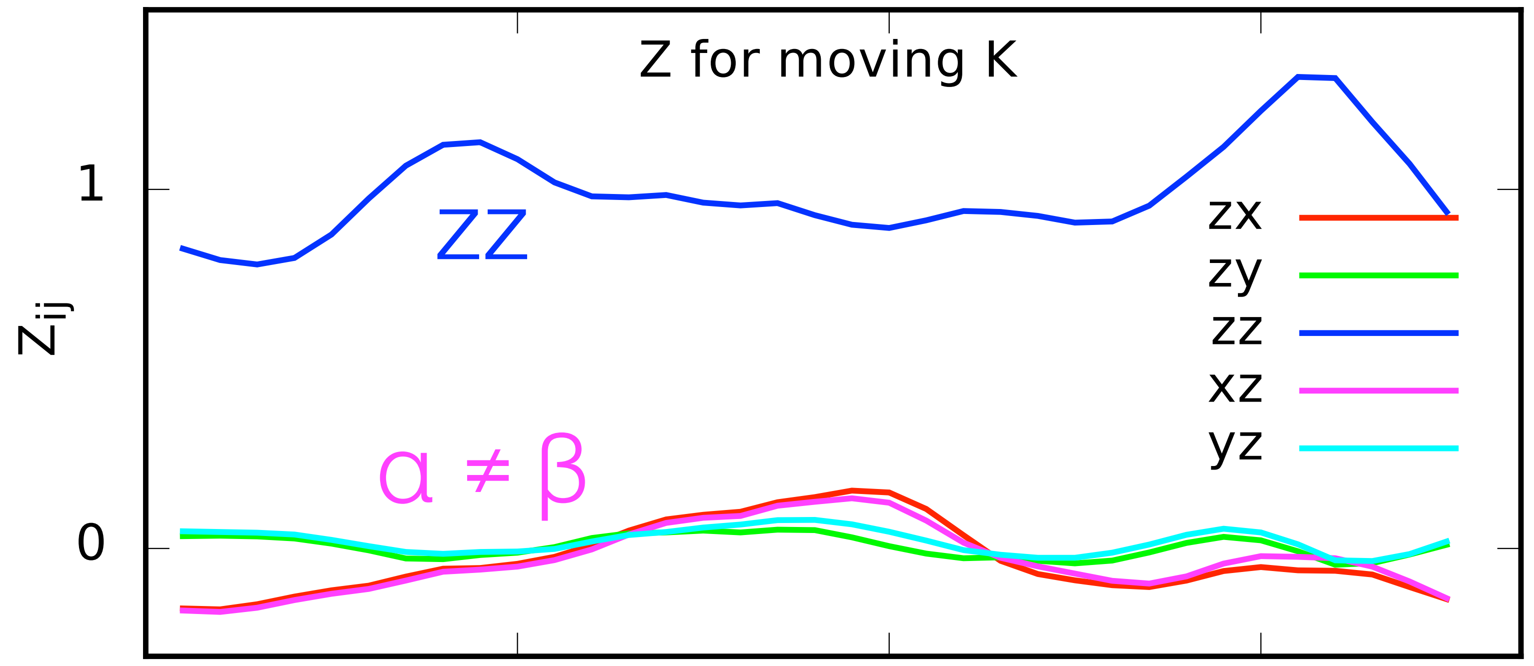


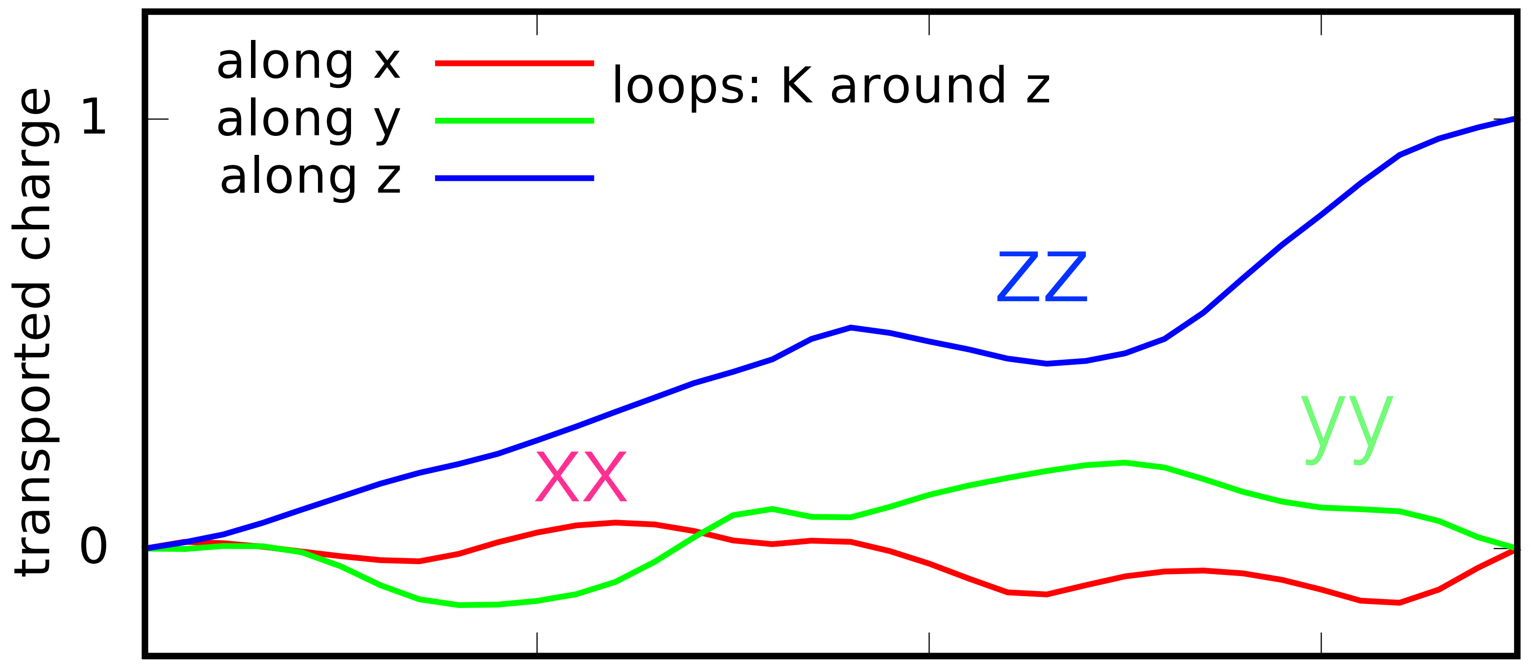
a topologically non-trivial minimum-energy path
connecting two identical configurations of a ionic fluid

a numerical experiment on molten KCl



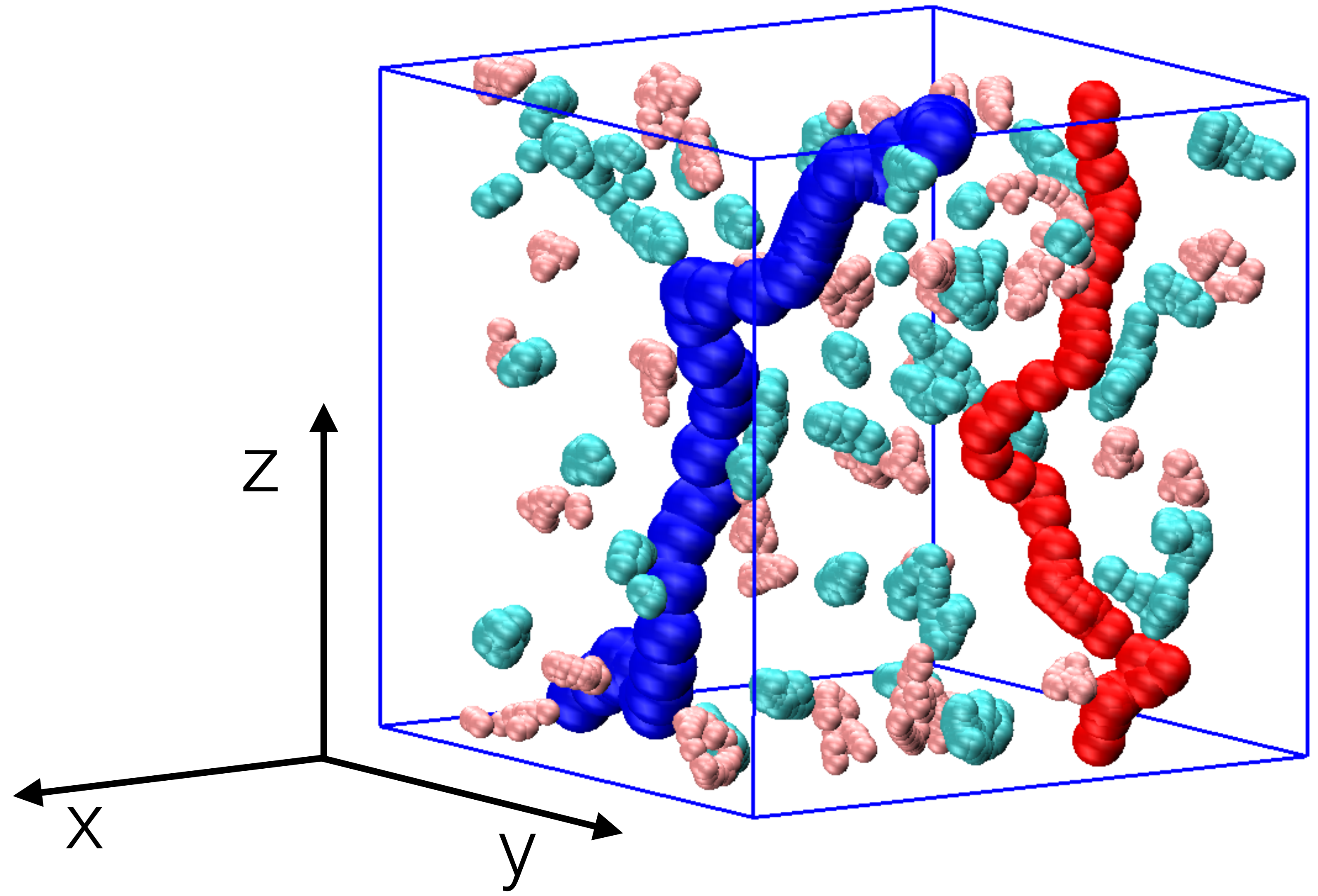


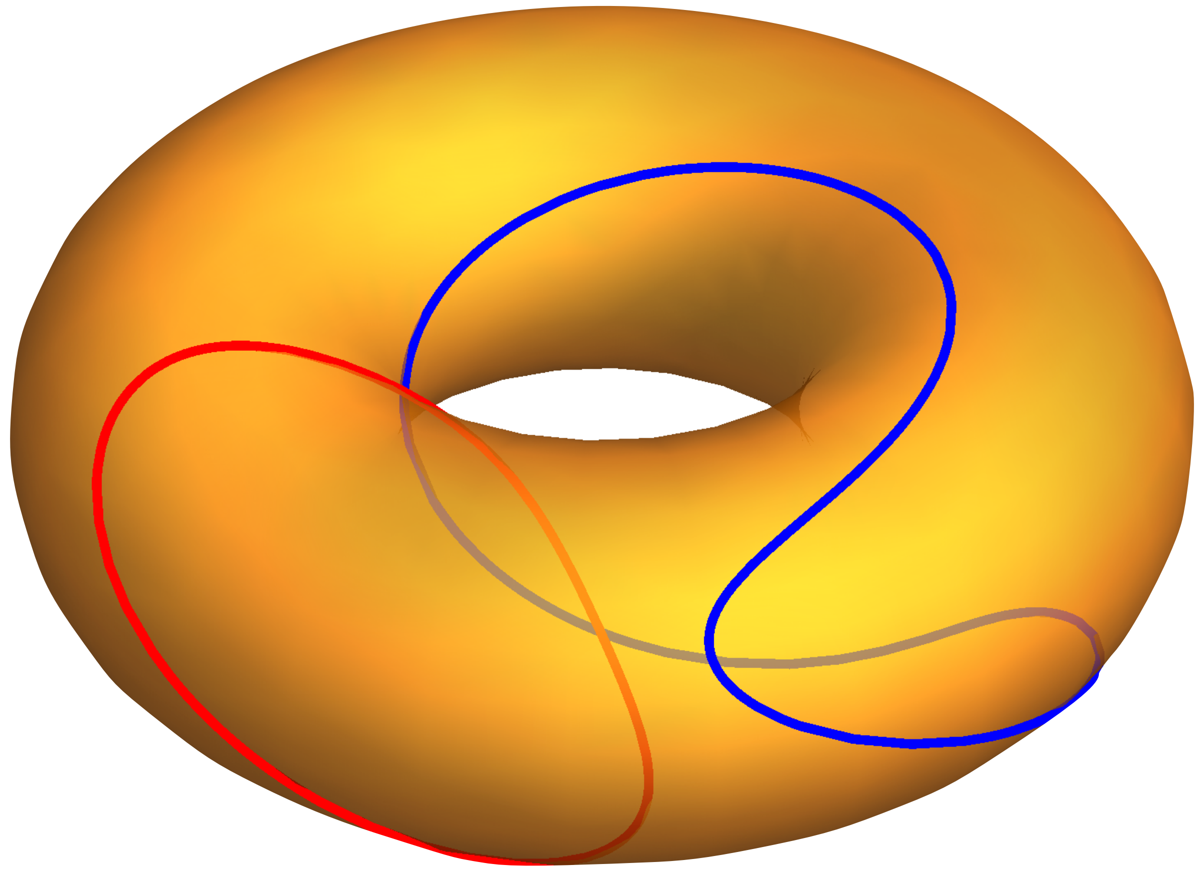




qx = =-0.000(6); qy = 0.000(2); qz = 1.00(18)

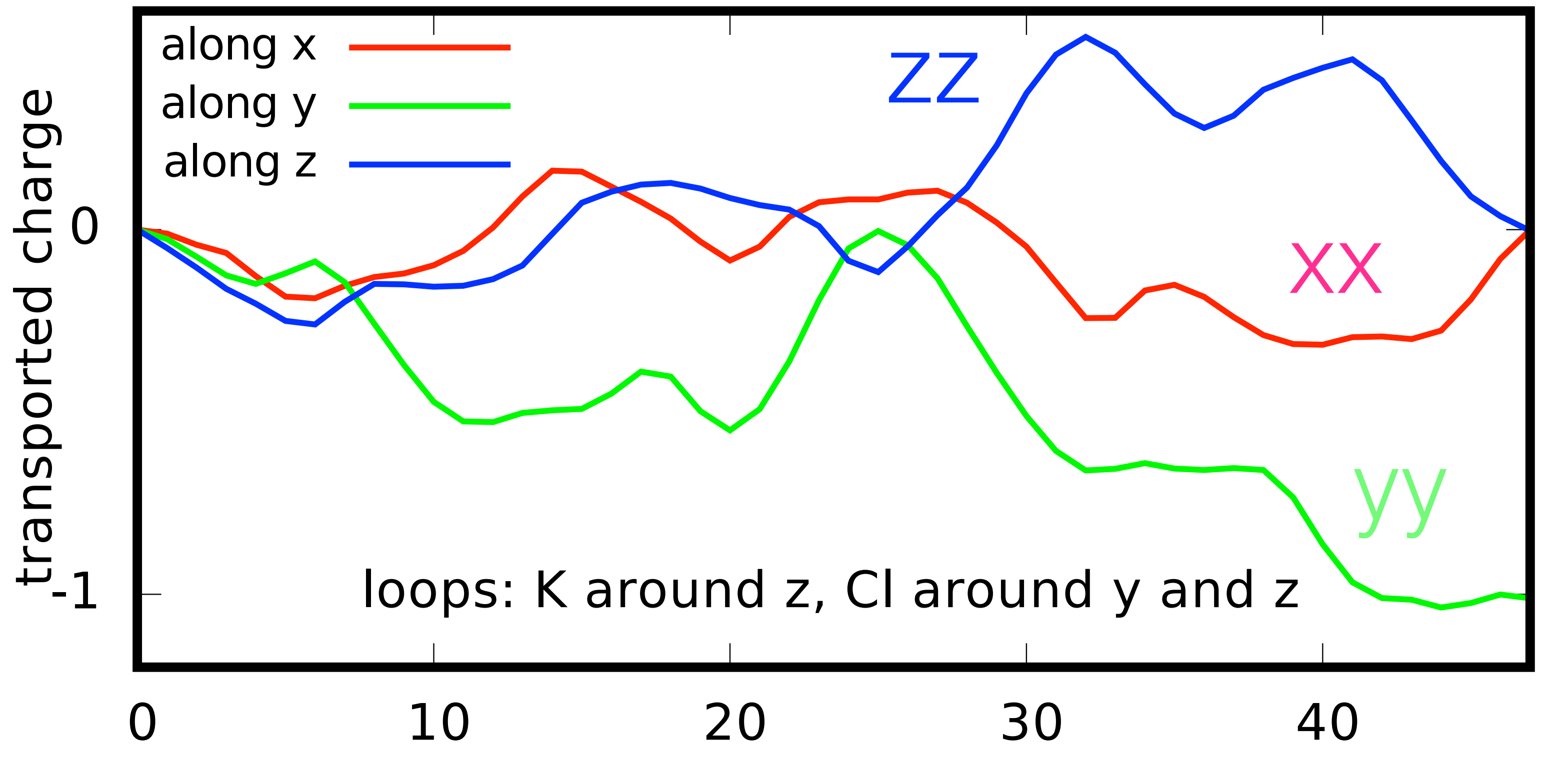
a numerical experiment on molten KCl





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

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



the charges transported by K and Cl
around z cancel exactly

atomic oxidation states

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

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

- 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

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

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

Leyla Isaeva[1], Giuseppe Barbalinardo[2], Davide Donadio[2] & Stefano Baroni[1,3]

these slides at http://talks.baroni.me