Transient localisation: an unconventional transport mechanism in two-dimensional molecular crystals

Pavel Buividovich (speaker)

Work in collaboration with Johann Ostmeyer, Alessandro Troisi, Ben Hind

[ArXiv:2312.14914, 2411.17460, 2512.23560]

[J. Ostmeyer, T. Nematiaram, A. Troisi, PB Phys. Rev. Applied 22 (2024) L031004]

Physics of low-temperature spontaneously ordered states vs. real-time physics of hot plasma

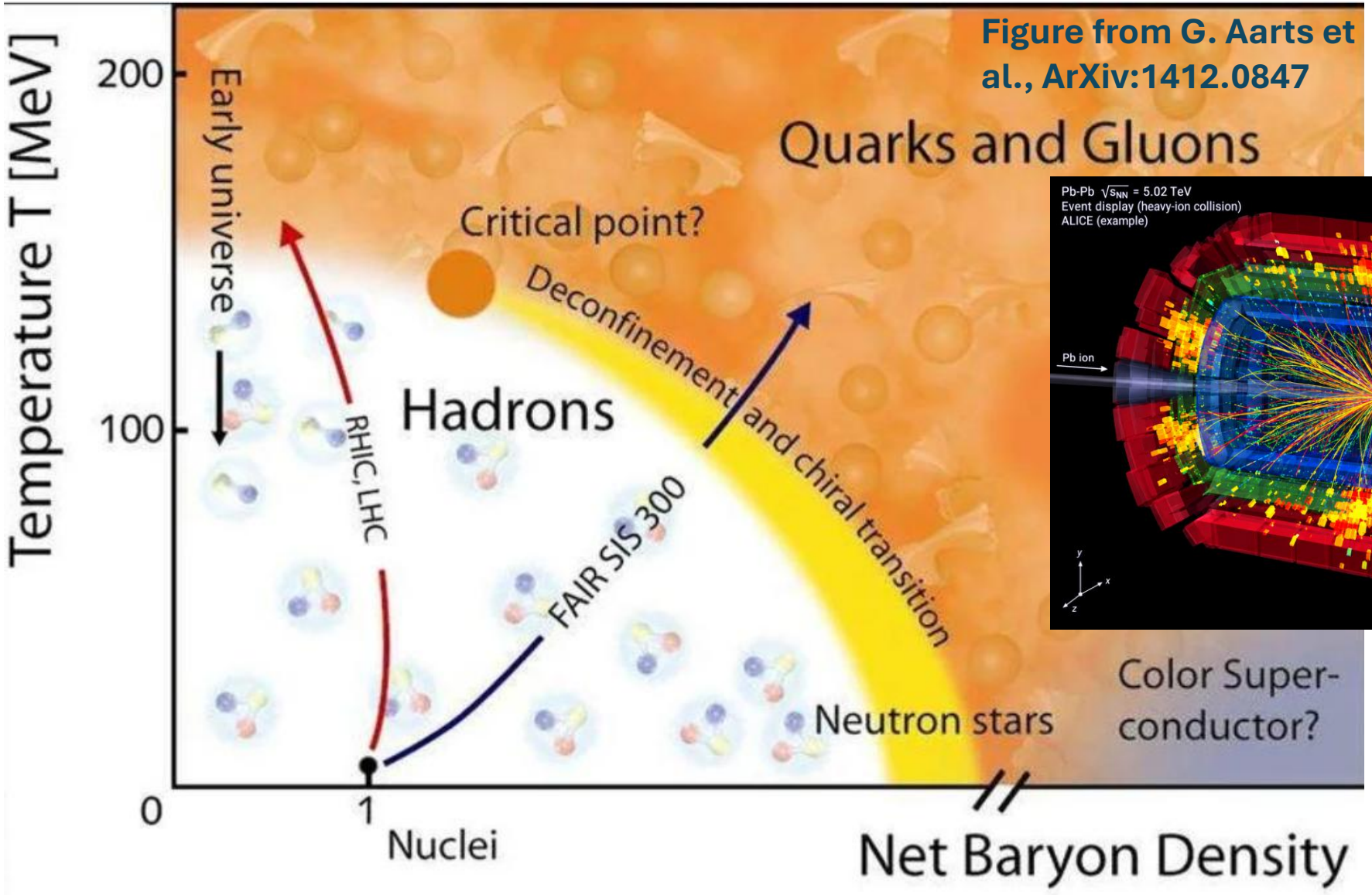
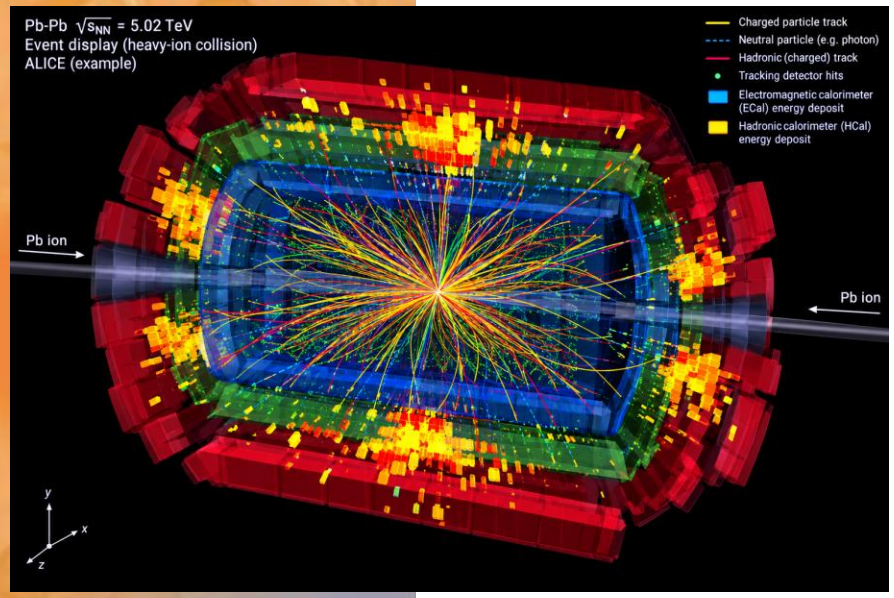
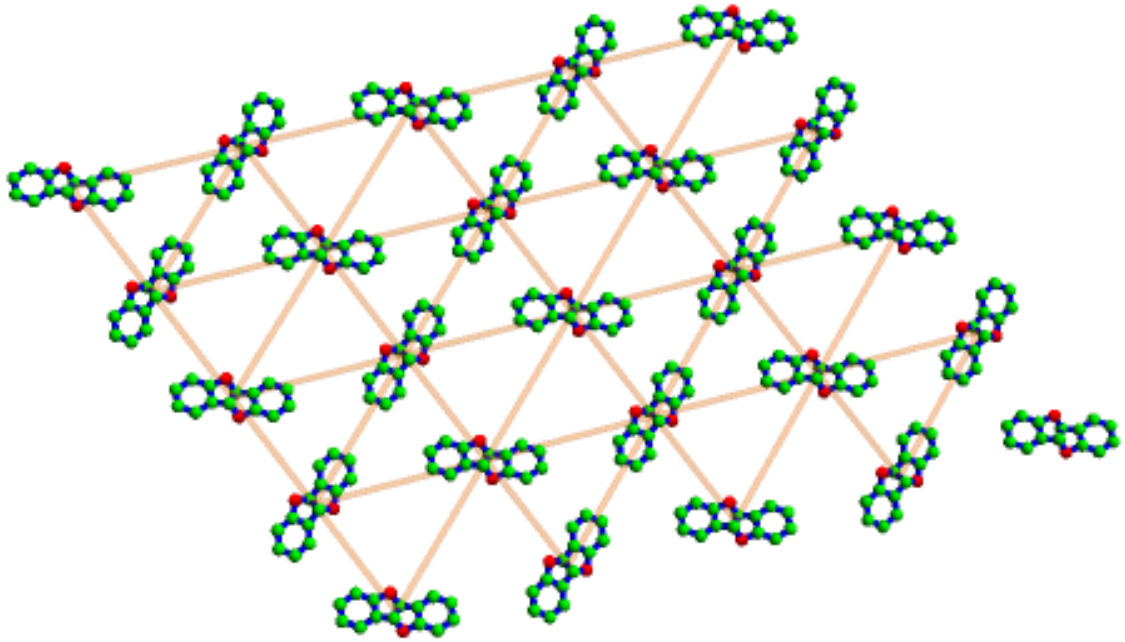


Figure from G. Aarts et al., ArXiv:1412.0847



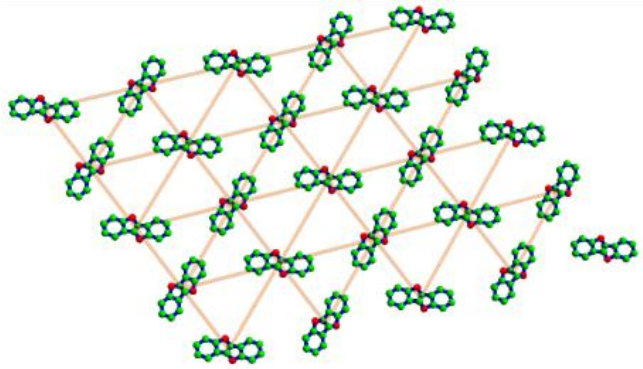
Organic molecular semiconductors
(pentacene, rubrene,…)

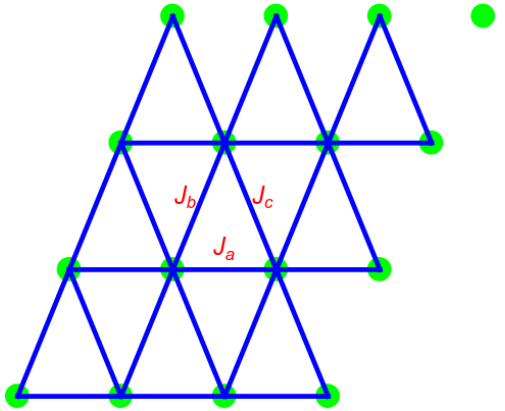
- Promising candidates for organic-based electronics/photovoltaics
- Large device area
- 3D printable
- Recyclable, soluble
- **Feature very interesting physics**



Goal: find compounds with high mobilities

Model description of electron-phonon interactions





Su–Schrieffer–Heeger (SSH) type Hamiltonian [Fratini et al., Nature Mat. 16, 998 (2017)]

reasonably good model description for **~4000 compounds**

$$\hat{H} = -\sum_{i,a,\sigma} J_a \left(1 - \lambda_a \hat{x}_{ia}\right)\left(\hat{c}^{\dagger}_{i,\sigma}\hat{c}_{i+a,\sigma} + \hat{c}^{\dagger}_{i+a,\sigma}\hat{c}_{i,\sigma}\right) - \mu\sum_{i,\sigma}\hat{c}^{\dagger}_{i,\sigma}\hat{c}_{i,\sigma} + \sum_{i,a}\left(\frac{1}{2m}\hat{p}^2_{ia} + \frac{m}{2}\omega_0^2\hat{x}^2_{ia}\right)$$

Multiple charge carriers interacting with lattice vibrations (phonons)

$$\hat{H} = \sum_{k,l,\sigma} \hat{c}^{\dagger}_{k,\sigma} h_{kl}\left(\hat{x}_{ia}\right)\hat{c}_{l,\sigma} + \hat{H}_B\left(\hat{p}_{ia}, \hat{x}_{ia}\right)$$

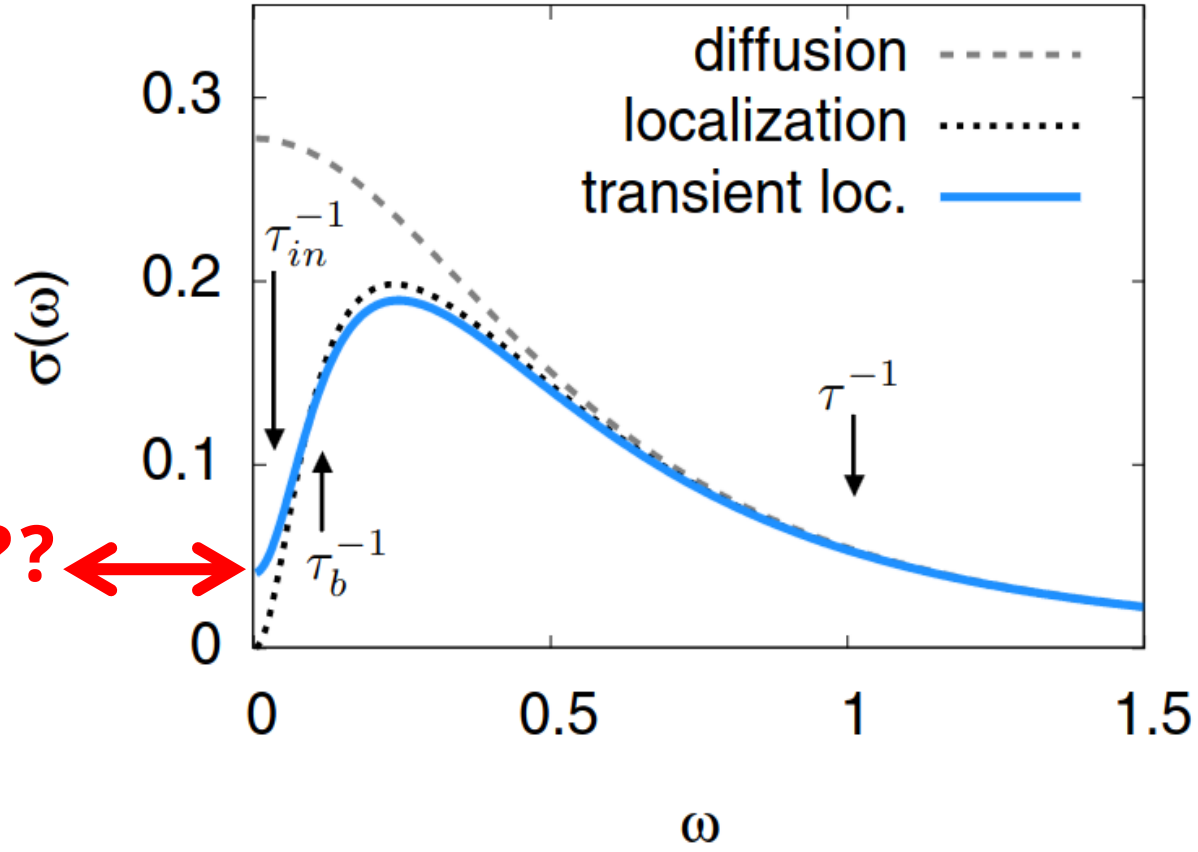
Hamiltonian not exactly solvable despite simplicity of interactions

Dynamical thermal disorder

- Typical phonon frequency ω_0~0.005 eV
- $\omega_0/T \sim 0.2$ – nearly classical (room temp. T~0.025 eV)
- Transfer integrals/hopping amplitudes J~0.1 eV
- Disorder modulation $\Delta J/J \sim 0.5$
- Strong dynamical disorder
- No intrinsic small parameter, neither hopping nor band theory work
- Charge carrier concentration: ~0.01 electrons/site

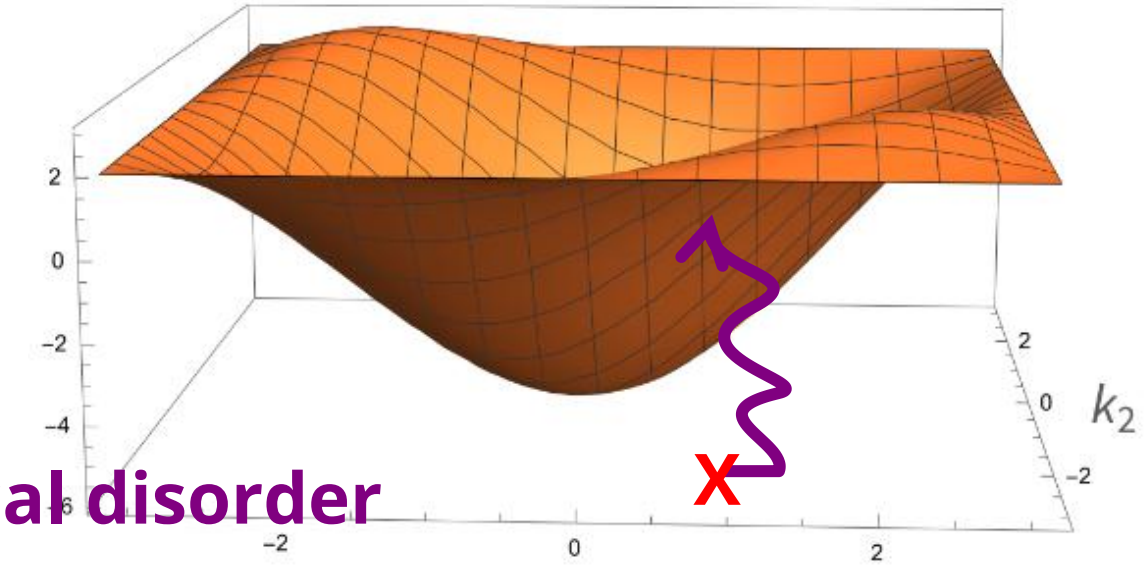
Transient localization and optical conductivity

Plot from [Fratini, Mayou, Ciuchi, Adv.Funct.Mater.26(2016)2292]



???

- "Free limit": no AC conductivity at all
- "Static phonons": no DC conductivity,
- Anderson localization (1D/2D)

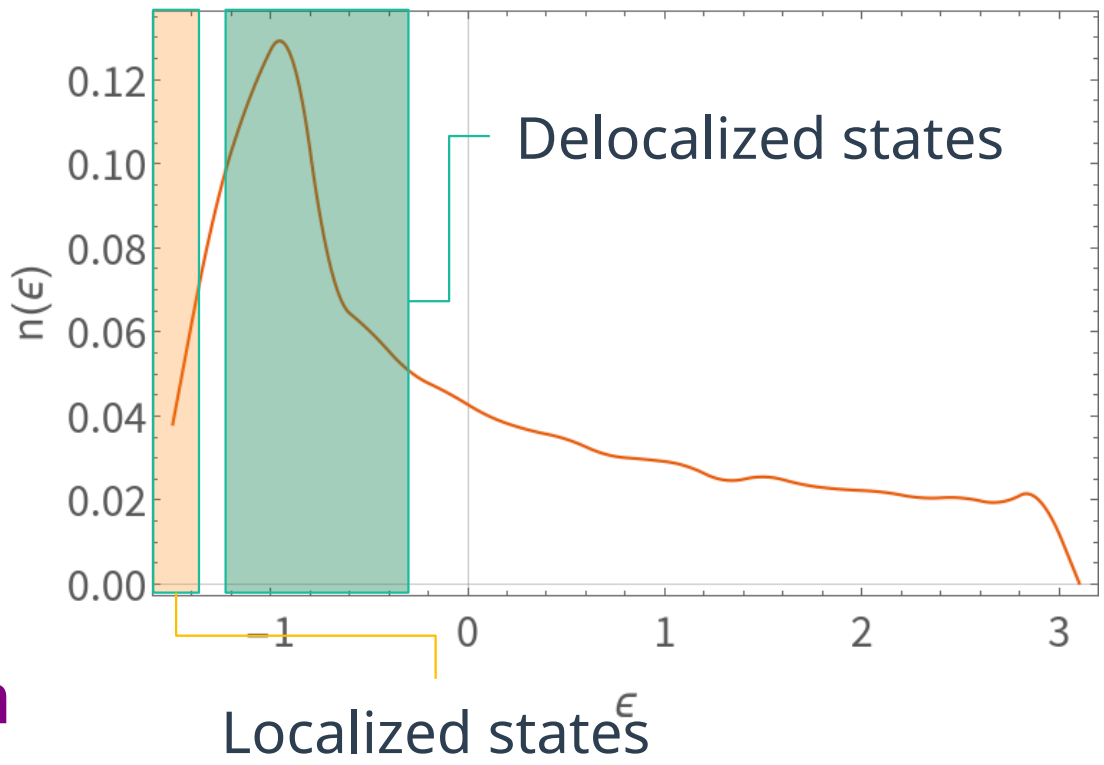


Charge transport driven by dynamical disorder

Transient localization scenario

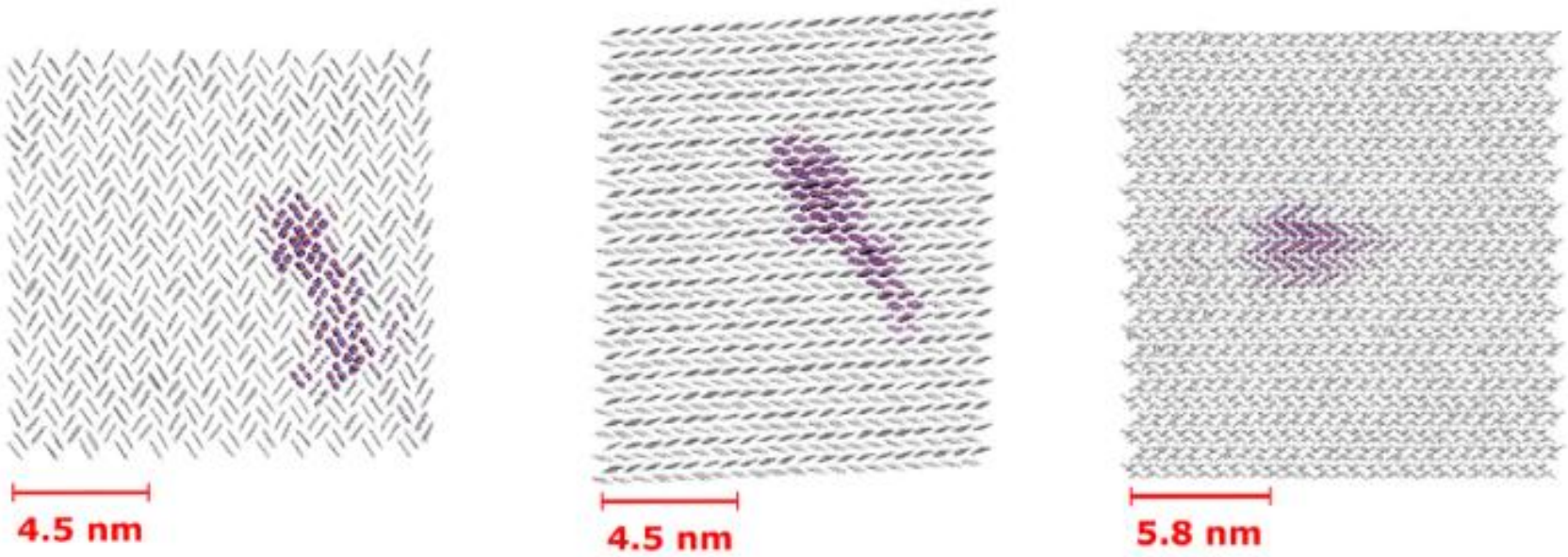
- Electronic states more delocalized towards the center of the band
- Only the lower/upper edge are populated (*<n>~0.01*)
- "Transient" excursions to the region of delocalized states due to dynamical disorder
- Localization of electronic wavefunctions: timescales shorter than $1/\omega_0$
- Phenomenological description: relaxation time [Fratini et al.,Adv.Funct.Mater.(2016)]

Schematic density of states



$$\epsilon_n \rightarrow \epsilon_n + i\,\tau_r^{-1}$$

Flickering polarons



From [S. Giannini et al., Adv. Theory Simul., 3: 2000093]

Quantum real-time polaron dynamics

- **Ehrenfest dynamics** (fermions fully quantum, bosons classical) [Troisi, Orlandi PRL 96 (2006) 086601] – artificial fermion over-heating
- **Surface hopping** (FOB-SH) [J. Spencer, F. Gajdos, J. Blumberger, J. Chem. Phys. 2016, 145, 064102] - still treats nuclei classically
- **MASH** [*J. Chem. Phys.* 159, 094115 (2023)]
- **Relaxation time approximation** [Fratini, Mayou, Ciuchi] – purely phenomenological
- **Quantum Monte-Carlo** (Worldline + DiagMC) in 1D [Mischenko et al., PRL 114 (2015) 146401]

Quantum Monte-Carlo: path integral

Imaginary (Euclidean) time

Time-ordered exponent

Single-particle Hamiltonian In the background of phonon fields

$$\mathcal{Z} = \int \mathcal{D}x_{ia}(\tau) \left[\det \left(I + \mathcal{T} \exp \left(- \int_0^\beta d\tau \, h(x_{ia}(\tau)) \right) \right) \right]^{N_\sigma} \times$$

Phonon field (nuclei displacements)

$$\times \exp \left(- \int_0^\beta d\tau \left(\frac{m}{2} \dot{x}_{ia}^2(\tau) + \frac{m\omega_0^2}{2} x_{ia}^2(\tau) \right) \right)$$

$$\mathcal{U}_E(\tau_1, \tau_2) := \mathcal{T} \exp \left(- \int_{\tau_1}^{\tau_2} d\tau \, h(x_{ia}(\tau)) \right)$$

Imaginary-time action of phonon fields

- **Integral over all phonon configurations in space + imaginary time**
- **Phonon (bosonic) part:** local, easy to calculate
- **Electron (fermionic) part:** nonlocal, determinant of large/ill-conditioned matrix, hard to calculate, **nonnegative for two spin components**

Physical observables – charge transport

Conceptually more difficult problem, as transport is NOT an equilibrium phenomenon

Electric current operator

$$\hat{\mathcal{J}}_a = -i \sum_{i,\sigma} J_a \left(1 - \lambda_a \hat{x}_{ia}\right) \left(\hat{c}^\dagger_{i,\sigma} \hat{c}_{i+a,\sigma} - \hat{c}^\dagger_{i+a,\sigma} \hat{c}_{i,\sigma}\right) = \sum_{k,l} \hat{c}^\dagger_k \left(\mathcal{J}_a\right)_{kl} \hat{c}_l$$

Single-particle current operator

Current-current correlators

$$G^E_{ab}(\tau) = \mathcal{Z}^{-1} \operatorname{Tr}\left(\hat{\mathcal{J}}_a e^{-\tau \hat{H}} \hat{\mathcal{J}}_b e^{-(\beta-\tau)\hat{H}}\right)$$

$$G^E_{ab}(\tau) = \mathcal{Z}^{-1} \int \mathcal{D}x_{ia}(\tau)\, \mathcal{W}_E\left[x_{ia}(\tau)\right] \operatorname{Tr}\left(\mathcal{J}_a \mathcal{G}(0,\tau)\, \mathcal{J}_a \mathcal{G}(\tau,\beta)\right)$$

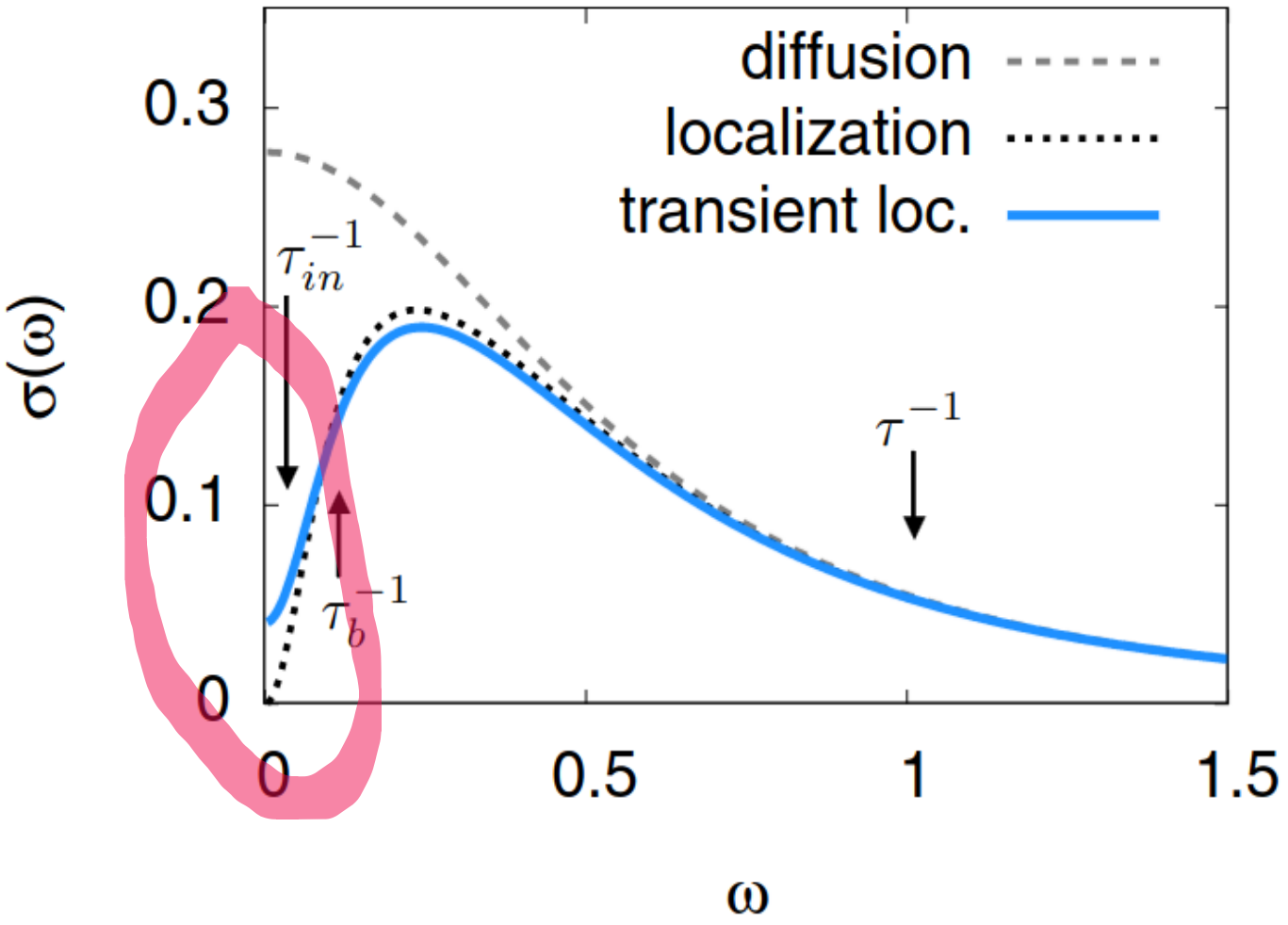
Fermionic Green's functions

$$\mathcal{G}(\tau_1,\tau_2) = \mathcal{U}_E(\tau_1,\tau_2) - \mathcal{U}_E(\tau_1,\beta)\,\mathcal{U}_E(\beta,0)\,\mathcal{U}_E(0,\tau_2) + \ldots \simeq$$
$$\simeq \frac{\mathcal{U}_E(\tau_1,\tau_2)}{I + \mathcal{U}_E(0,\beta)}$$

Green-Kubo relations for optical conductivity – numerically ill-defined problem

$$G^E_{ab}(\tau) = \hbar \int_0^{+\infty} \frac{dw}{2\pi} \frac{2w \cosh\left(w\left(\tau - \beta/2\right)\right)}{\sinh\left(\beta\, w/2\right)} \sigma(w)$$

Physical limit of low frequencies / long times



To resolve **transient localization**:

probe long times

t ≥ 1/w0 ≥ 1/(5 meV)

or low frequencies

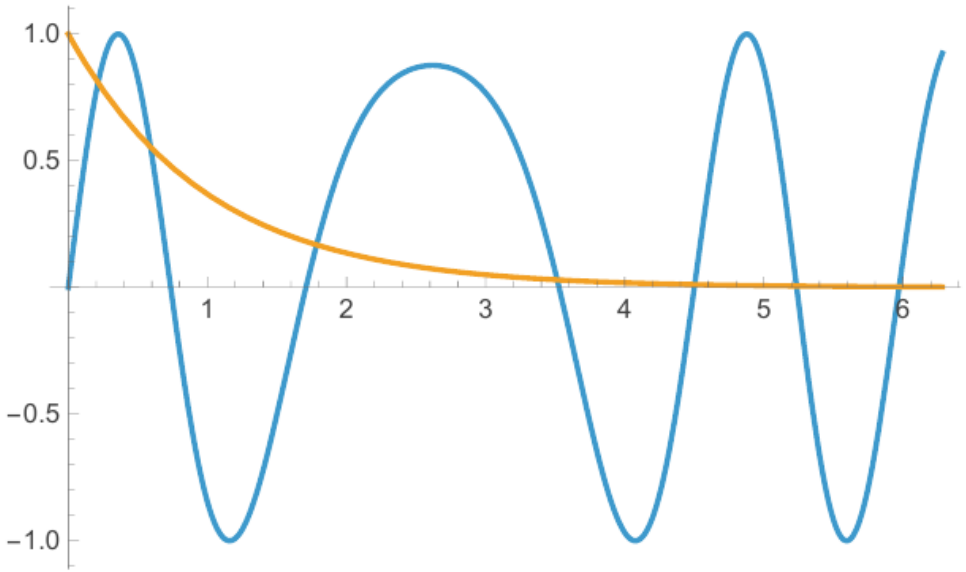
w ≤ w0 ≤ 5 meV

Physical observables – charge transport

- Fourier transform of imaginary-time correlators in terms of real-time correlators:
  (imaginary time is periodic => Matsubara frequencies)

$$G_E(w_k) = -\int_0^{+\infty} dt\, e^{-|w_k|\,t}\, G_R(t), \quad w_k = 2\pi k\, T, \quad k \in \mathbb{Z}.$$

- Imaginary-time data **exponentially insensitive** to real-time data at $t > \pi T$!
- Limited real frequency resolution $\Delta\omega \sim \pi T \sim 80\ meV$



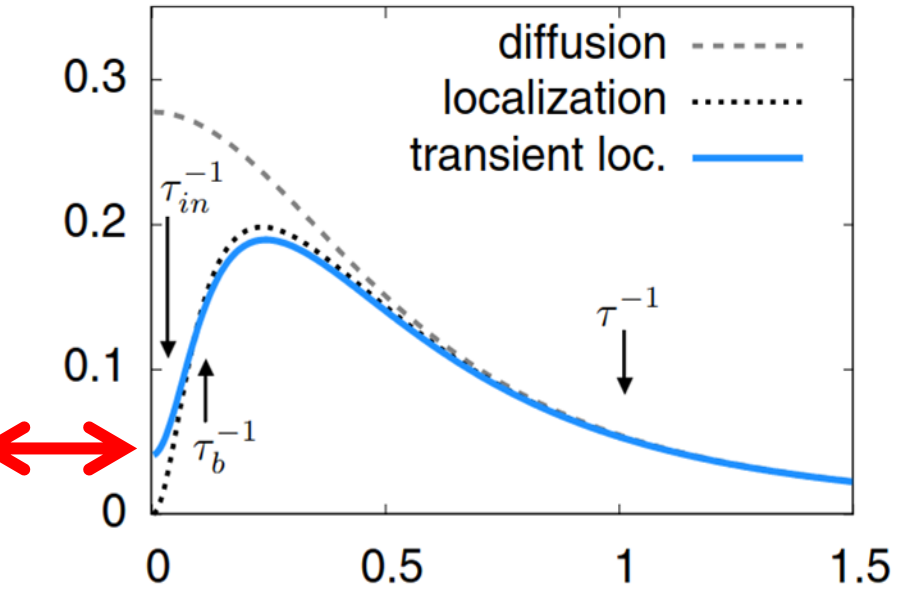
- No free lunch: **NP-hardness** of **quantum real-time evolution** returns in another disguise

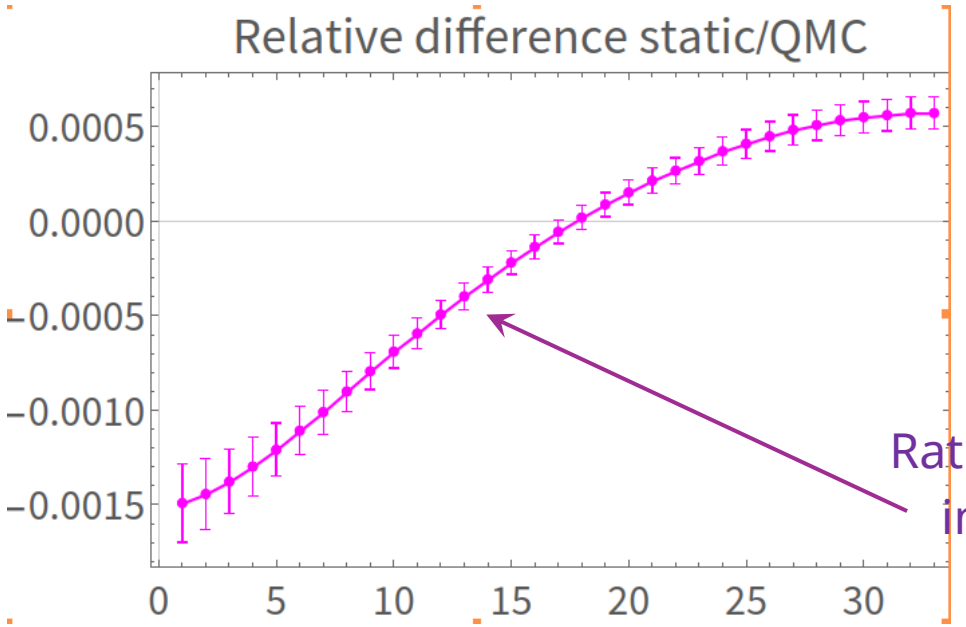
- **Still OK if frequency resolution not a bottleneck [ArXiv:1206.0619]**

Static approximation and beyond

- $w_0/T \sim 0.2$, path integral dominated by **static, τ-independent** phonon configurations (zero Matsubara frequencies)
- Reasonable approximation: **Quantum fermions** in **static boson background**
- **Spectral function exactly calculable** from single-particle Hamiltonian $h[x_{ia}]$ $(O(V^3))$
- **We know that static limit is not enough – do we see the difference with QMC?**

Plot from [Fratini, Mayou, Ciuchi, Adv.Funct.Mater.26(2016)2292]





Ratio of static to full imaginary-time correlators

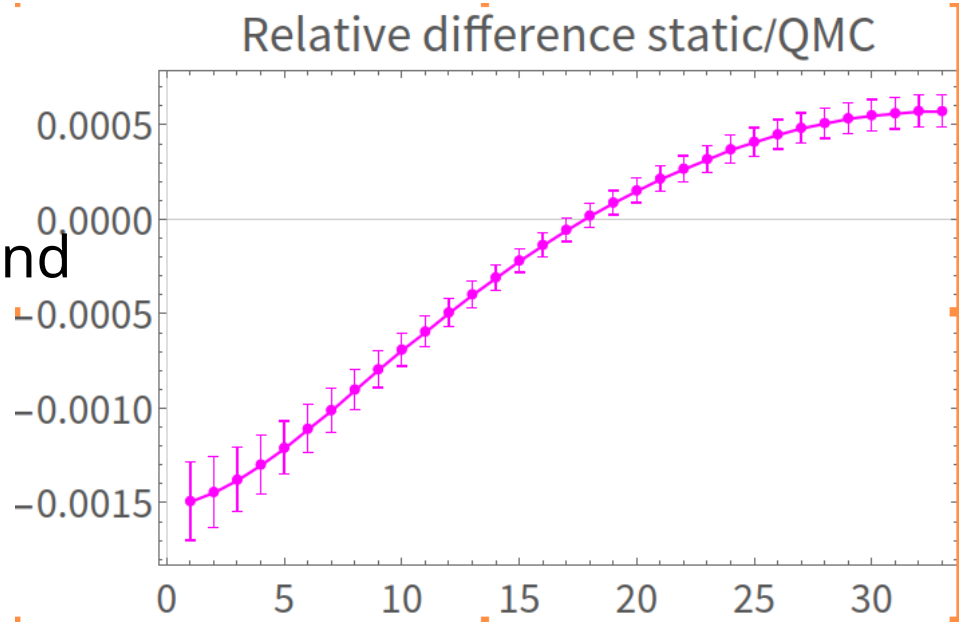
Contribution to $G_E(\tau)$

$$\sim \exp\left(-\frac{\pi T}{w}\right)$$

Static approximation and beyond

How to extract low-frequency/long-time behaviour from tiny corrections to static correlators?

- **Idea 1:** one-parameter fit with relaxation time – **failed miserably**
- **Idea 2:** Backus-Gilbert on the difference between full and static correlators – **fails** because the difference is not positive
- **Idea 3:** MaxEnt with static spectral function as prior – achieves very good fit to the full data with only small corrections spread out across all frequencies (so **fails miserably**)
- **Idea 4:** MaxEnt with smeared static spectral function, forced to modify low-frequency region – **not particularly stable**
- **Idea 5:** physics-inspired fits **(works reasonably well)**

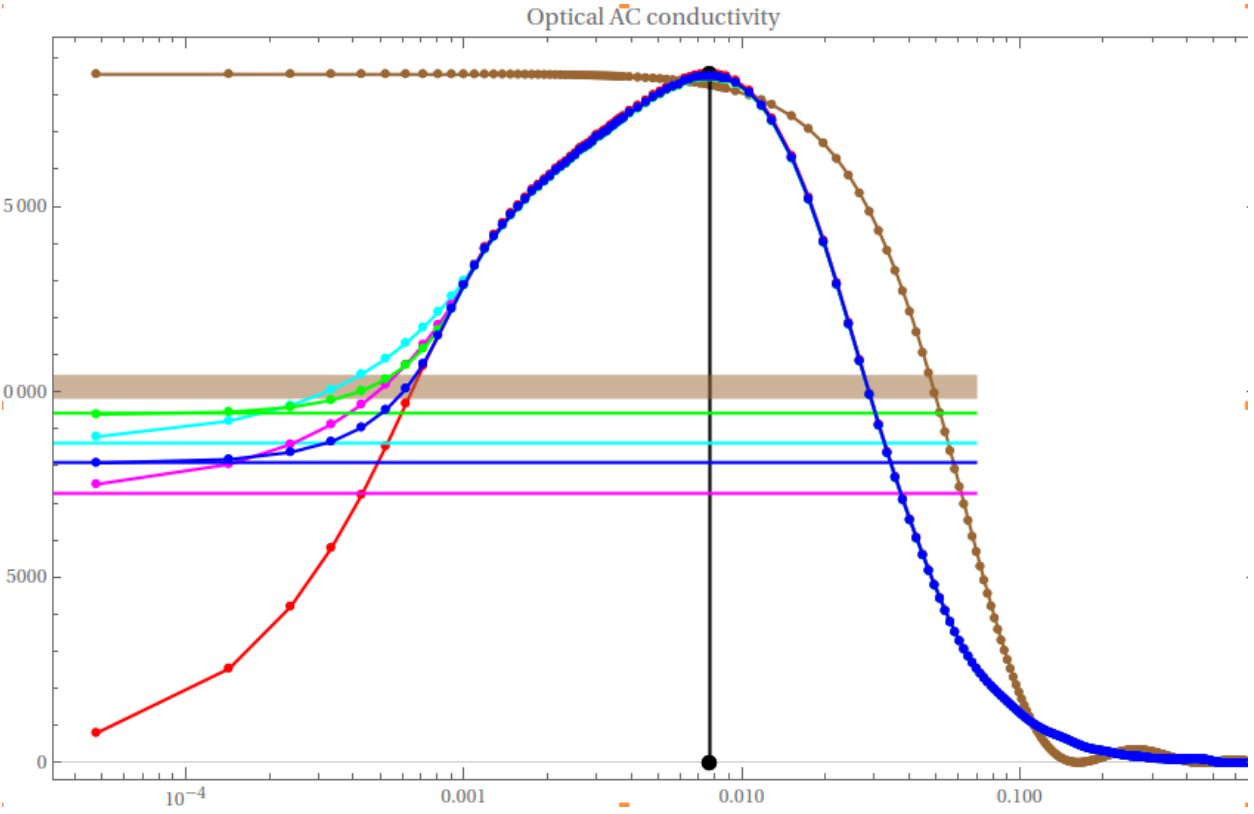


Euclidean data can also be used to test and verify quantum real-time approaches!

Extracting dynamical information from QMC data

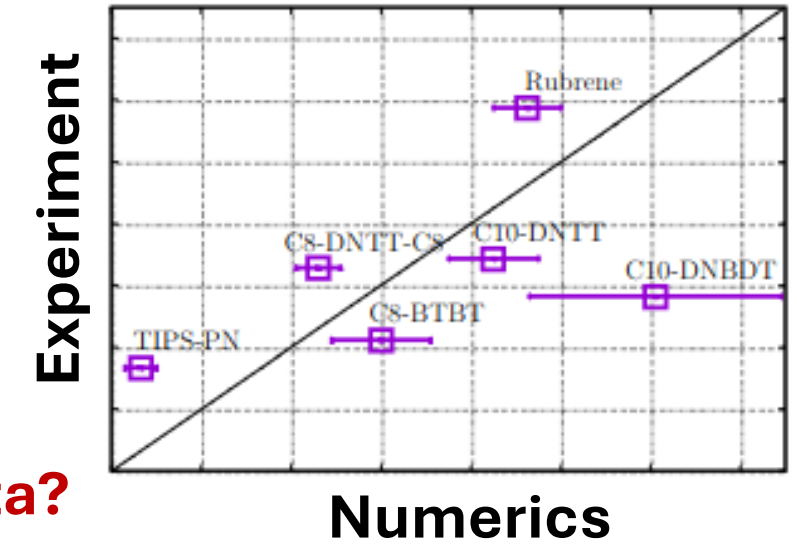
Physics-inspired fits of imaginary-time data:

- static at high frequencies
- transport at low frequencies



Precision just enough to start tackling the low-frequency region

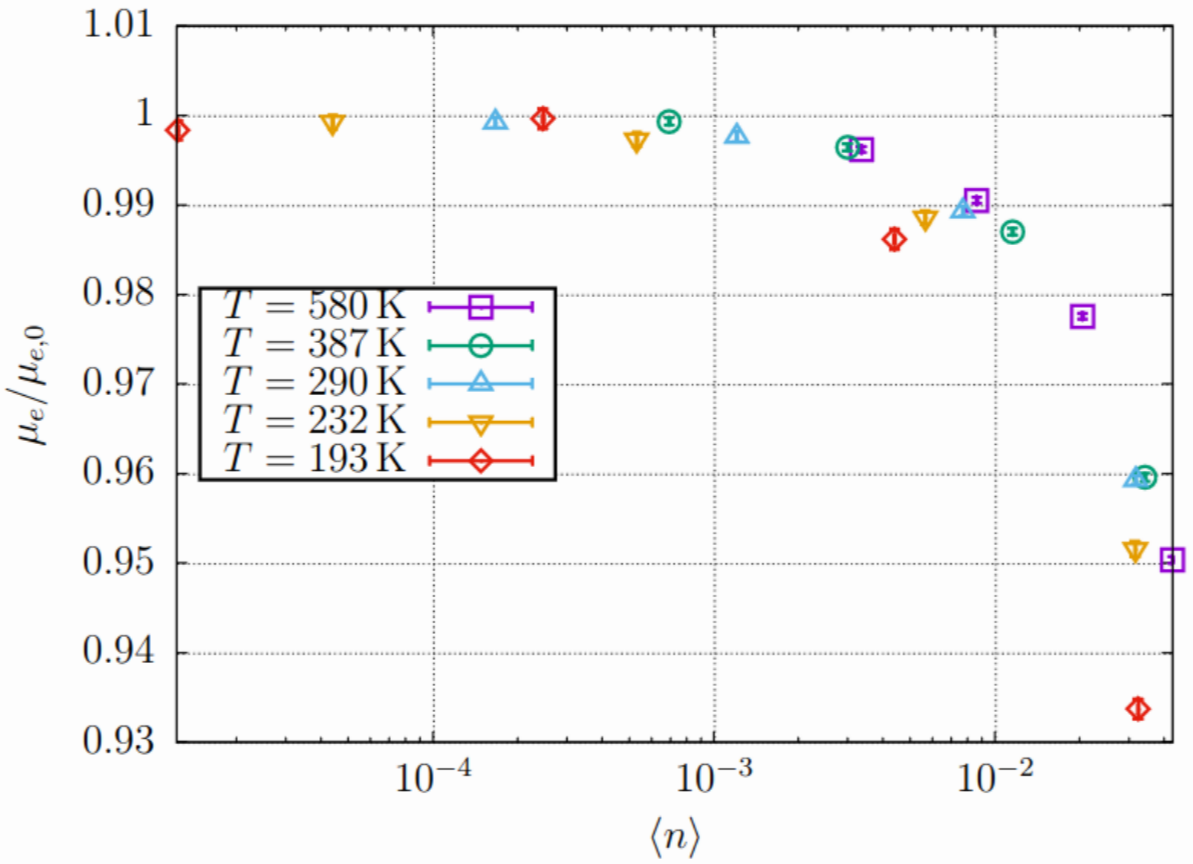
Good agreement with experimental data (often imprecise/controversial)



How do we get to sufficiently precise Euclidean data?

When can single-particle picture be trusted?

Mobility = conductivity / charge carrier concentration



[Characteristic parameters for OSs]

- Typical charge carrier concentration ***<n>~0.01*** (per unit cell) for most realistic compounds in transistor applications
- Characteristic localization length ***L~10***
- For ***<n>~0.01~1/L²,*** delocalized states start overlapping

Limit of low charge carrier densities

We send $\mu \to +\infty$

Carrier concentration $\langle n \rangle \sim e^{-\mu/T}$

$$\mathcal{U}_E(0,\beta) \sim e^{-\beta\mu}$$
$$[\det(I + \mathcal{U}_E(0,\beta))]^{N_\sigma} = 1 + O(e^{-\beta\mu})$$

Fermion determinant does not depend on phonons

Path integral weight becomes a Gaussian functional of $x_{ia}(\tau)$:

$$\mathcal{W}[x_{ia}(\tau)] = \exp\left(-\int_0^\beta d\tau \left(\frac{m}{2}\dot{x}_{ia}^2(\tau) + \frac{m\omega_0^2}{2}x_{ia}^2(\tau)\right)\right) + O(e^{-\beta\mu})$$

Multi-normal distribution =>
Can be sampled **without any autocorrelations**!

Current-current correlators saturated by single-particle states

$$G_{ab}^E(\tau) = \mathcal{Z}^{-1}\int \mathcal{D}x_{ia}(\tau)\,\mathcal{W}_E[x_{ia}(\tau)]\,\mathrm{Tr}\left(\mathcal{J}_a\mathcal{U}_E(0,\tau)\;\mathcal{J}_a\mathcal{U}_E(\tau,\beta)\right) + O(e^{-2\beta\mu})$$

$$\mathcal{U}_E(\tau_1,\tau_2) \sim e^{-(\tau_2-\tau_1)\mu}$$

Conductivity $\sigma \sim e^{-\mu/T}$ density $\langle n \rangle \sim e^{-\mu/T}$ → **mobility $\mu_e = \sigma/\langle n \rangle$ finite**

No more determinant calculations!

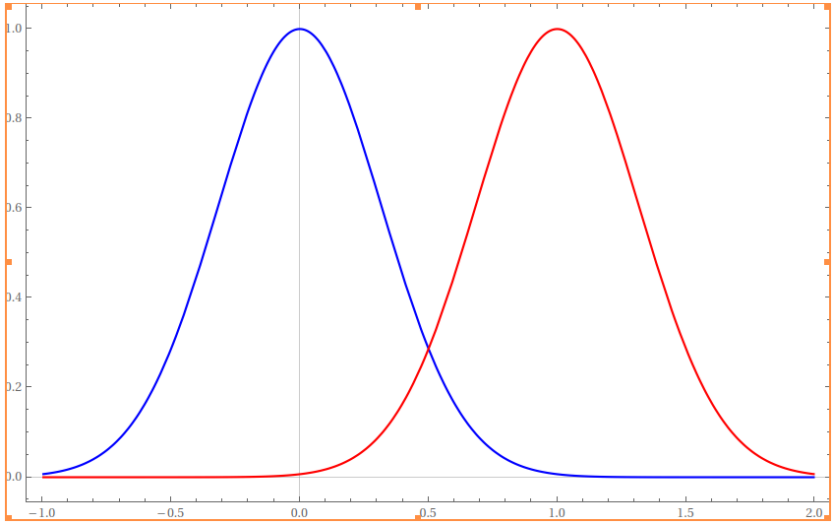
Noise reduction and log-normal distribution

$$G^E_{ab}(\tau) = \mathcal{Z}^{-1} \int \mathcal{D}x_{ia}(\tau)\, \mathcal{W}_E[x_{ia}(\tau)]\, \mathrm{Tr}\left(\mathcal{J}_a \mathcal{U}_E(0,\tau)\ \mathcal{J}_a \mathcal{U}_E(\tau,\beta)\right) + O\left(e^{-2\beta\mu}\right)$$

~Exp(-X²) *~Exp(-α X)*

$$P(x) \sim e^{-x^2/2}, \quad y = e^{\alpha x}$$

$$P(y) \sim y^{-1} \exp\left(-\frac{1}{2\alpha^2}\log^2(y)\right)$$



[Endres,Kaplan,Lee,Nicholson,ArXiv:1106.0073]

To reduce overlap, problem, a new flavour of HMC

$$G^E_{ab}(\tau) = \mathcal{Z}^{-1} \int \mathcal{D}x_{ia}(\tau)\, \mathcal{W}_E[x_{ia}(\tau)]\, \mathrm{Tr}\left(\mathcal{U}_E(0,\beta)\right) \frac{\mathrm{Tr}\left(\mathcal{J}_a \mathcal{U}_E(0,\tau)\ \mathcal{J}_b \mathcal{U}_E(\mathcal{U}_E(0,\tau))\right)}{\mathrm{Tr}\left(\mathcal{U}_E(0,\beta)\right)}$$

Observable

Hybrid Monte-Carlo for polaron problems

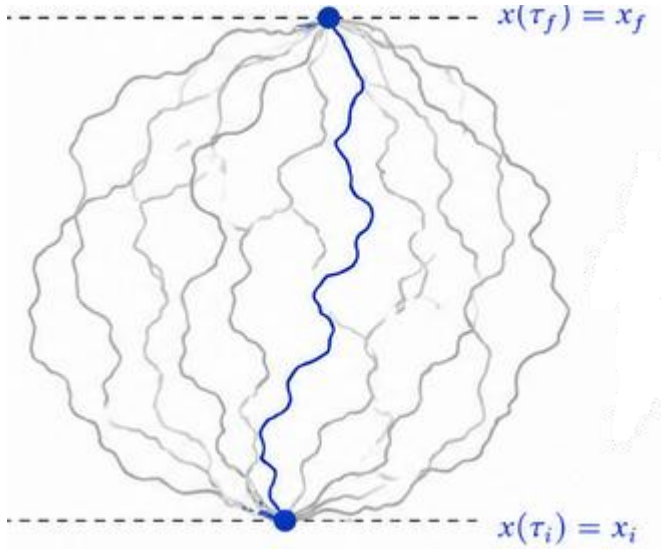
Sample phonon configurations with statistical weight

$$W\left[x_{ia}\left(\tau\right)\right] = \mathrm{Tr}\,\left(\mathcal{U}_E\left(0,\beta\right)\right) \times \exp\left(-\int_0^\beta d\tau \left(\frac{m}{2}\dot{x}_{ia}^2 + \frac{m w_0^2}{2} x_{ia}^2\right)\right)$$

$$\mathcal{U}_E\left(0,\beta\right) := \exp\left(-h\left(x_{ia}\left(\tau_1\right)\right)\Delta\tau\right)\exp\left(-h\left(x_{ia}\left(\tau_2\right)\right)\Delta\tau\right)\ldots\exp\left(-h\left(x_{ia}\left(\tau_N\right)\right)\Delta\tau\right)$$

- ***Tr(U_E(0,β))*** positive at sufficiently high temperatures
- Rare negative values can be treated by reweighting
- ***Tr(U_E(0,β))*** is a sum over **all charge carrier worldlines** in imaginary time

$$-\frac{\partial}{\partial x_{ia}\left(\tau\right)}\mathrm{Tr}\,\left(\mathcal{U}_E\left(0,\beta\right)\right) \sim \mathrm{Tr}\,\left(\mathcal{U}_E\left(0,\tau\right)\frac{\partial h}{\partial x_{ia}}\mathcal{U}_E\left(\tau,\beta\right)\right)$$



Force calculation for Molecular Dynamics considerably cheaper now, no inversions

Hybrid Monte-Carlo for polaron problems

Hilbert space structure now:

- States of a **single fermion** X **Fock spaces of all phonons**

Hamiltonian:

$$\hat{\mathcal{H}} = h\left[\hat{x}_{i,a}\right] \otimes \hat{I}_B + I_F \otimes \sum_{i,a} \left(\frac{\hat{p}_{i,a}^2}{2} + \frac{w_0^2 \hat{x}_{i,a}^2}{2} \right)$$

Conclusions

Unconventional application of HMC: polaron problems

Single charge carrier + bath of phonons

Collective phonon updates in HMC allow to consider large polarons which span many lattice cells

Physics somewhat similar to jet quenching in quark-gluon plasma

Completely first-principles, but imaginary-time results: ideal for validating phenomenological real-time approaches

Useful lessons for high-temperature QCD (and gauge theories in general)

Dimensional reduction (τ-independence) at high temperatures: allows to construct good approximations for the full spectral function

Scale separation: highly occupied, slow bosonic modes + fast fermions

Classical bosons + quantum fermions

Well-known “classical-statistical” approximation

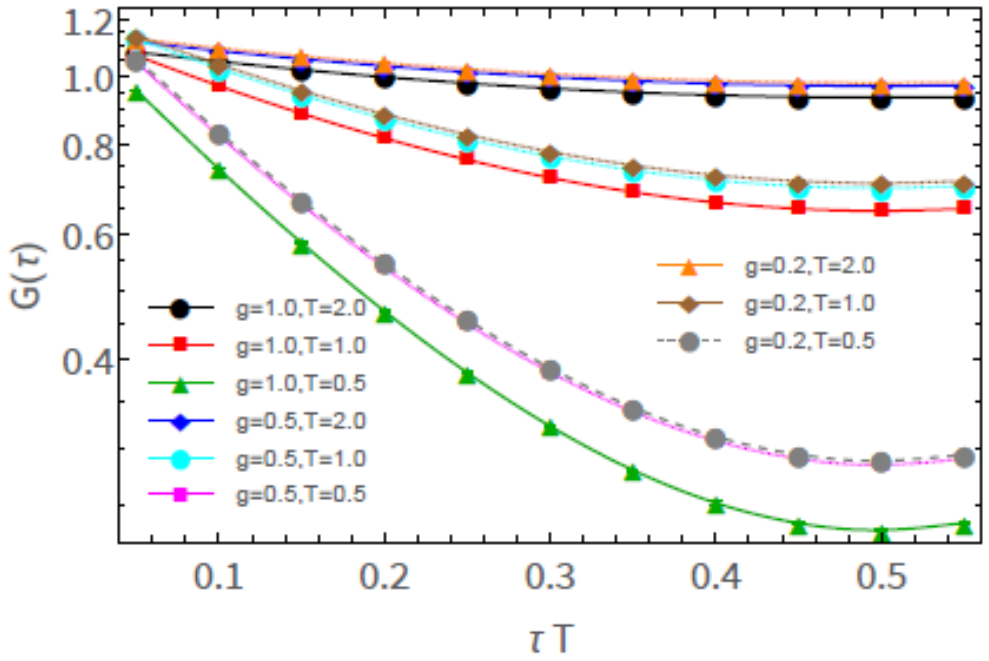
Toy model: $U(1)$ lattice gauge theory in $D = 1 + 1$

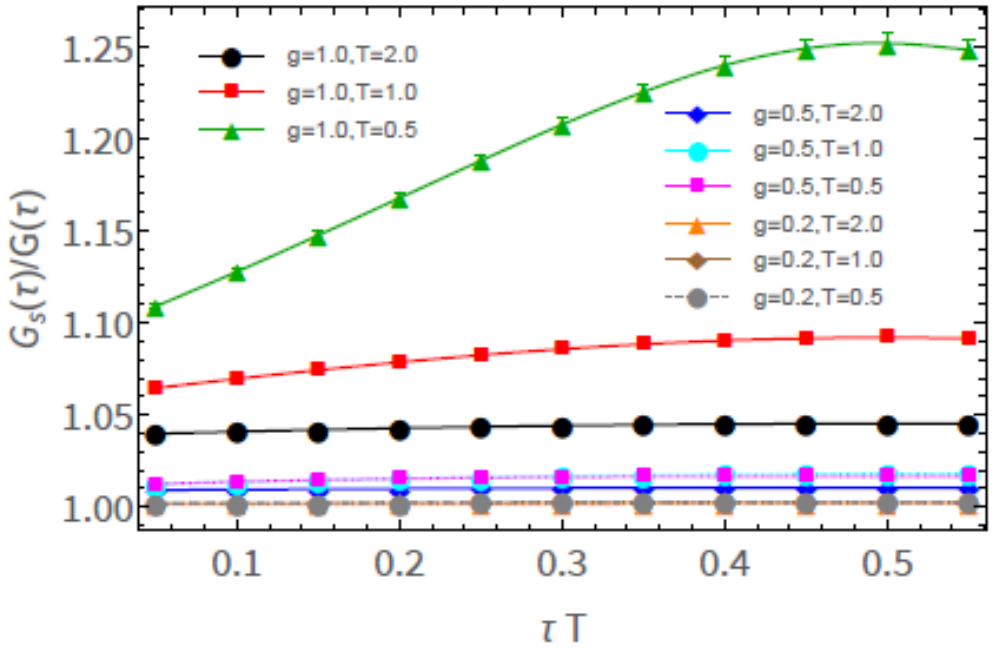
- $U(1)$ link variables $e^{i\hat{\theta}_x}$, electric fields $\hat{E}_x = -i\frac{\partial}{\partial\theta_x}$
- Two flavours of spinless fermions: $\left\{\hat{a}_x^\dagger, \hat{a}_y\right\} = \delta_{xy}$, $\left\{\hat{b}_x^\dagger, \hat{b}_y\right\} = \delta_{xy}$, opposite charges (no sign problem in QMC).

$$\hat{H} = \frac{g^2}{2}\sum_x \hat{E}_x^2 + \sum_x \kappa\left(\hat{a}_{x+1}^\dagger e^{-i\hat{\theta}_x}\hat{a}_x + \hat{a}_x^\dagger e^{+i\hat{\theta}_x}\hat{a}_{x+1}\right) + \sum_x \kappa\left(\hat{b}_{x+1}^\dagger e^{+i\hat{\theta}_x}\hat{b}_x + \hat{b}_x^\dagger e^{-i\hat{\theta}_x}\hat{b}_{x+1}\right) \tag{8}$$

- Solved by exact diagonalization (cutoff on $\hat{E}_x$ flux) $\Rightarrow$ Numerically exact results for $G(\tau)$, $S(w)$, compare with $G_s(\tau)$, $S_s(w)$

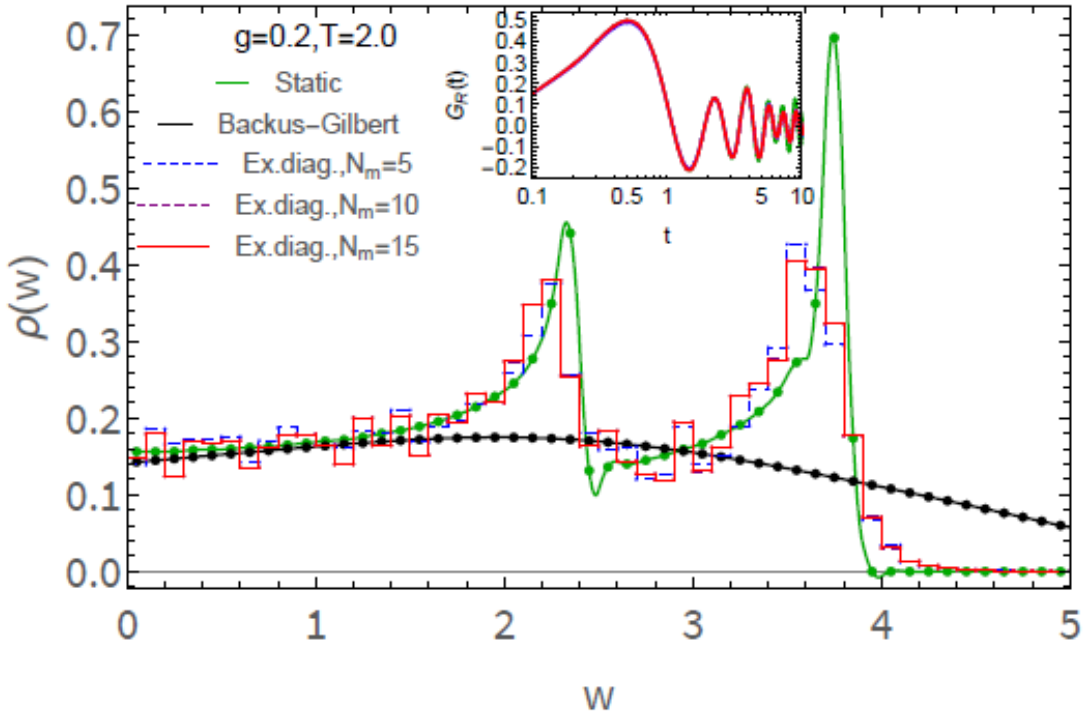
Euclidean correlators in the toy model, $\hat{O} = \hat{q}_x - \hat{q}_{x+1}$

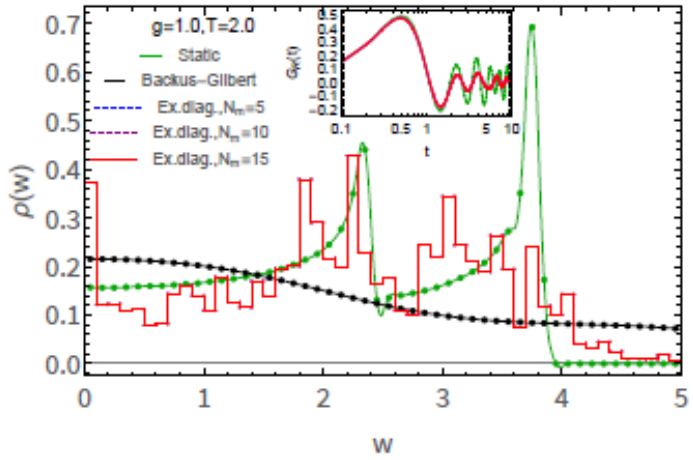


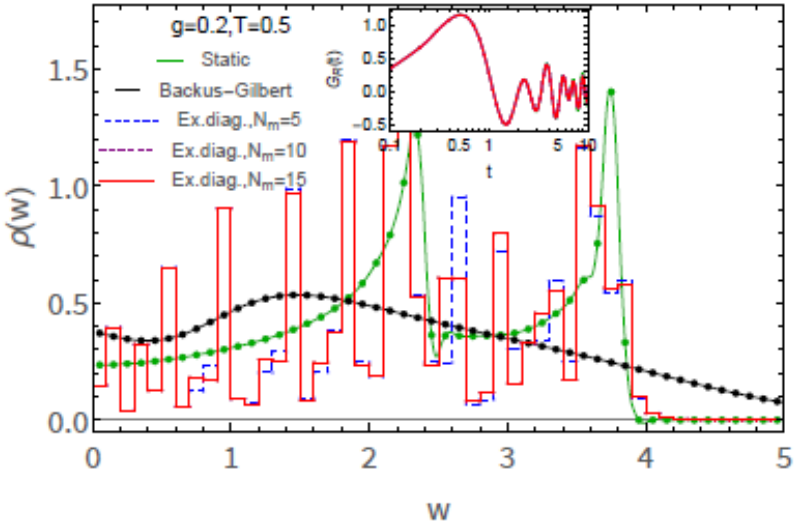


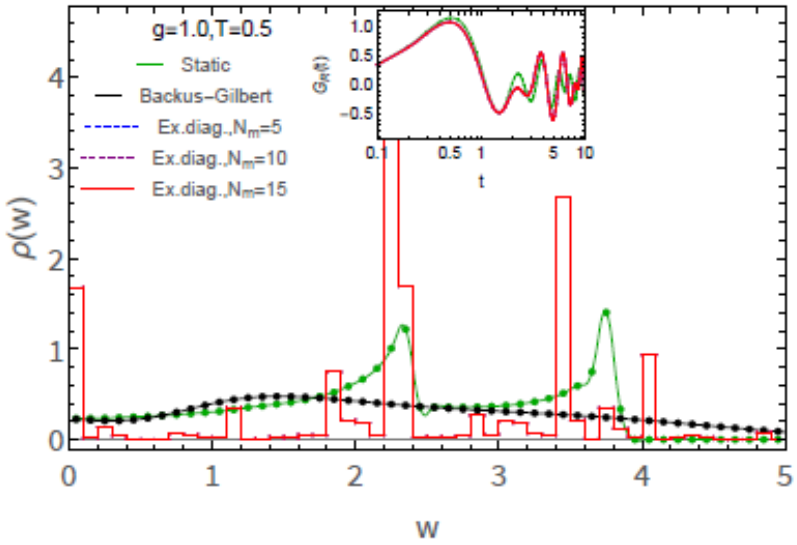
- $L = 5$ sites, $\kappa = 1$, flux cutoff between 5 and 10
- Static limit is a good description for $G(\tau)$ at small g, temperature dependence less pronounced
- $t \sim g^{-2}$ - characteristic timescale for gauge field dynamics
- Fermions are much faster - static limit justified!

Spectral function comparison, $\hat{O} = \hat{q}_x - \hat{q}_{x+1}$









Static spectral functions and CSFT approximation

CSFT equations of motion:

$$\partial_t \vec{A} = g^2 \, \vec{\mathcal{E}},$$

$$\partial_t \vec{\mathcal{E}} = -\mathrm{Tr}\left(\rho_F \vec{j}\right) + g^{-2} \, \vec{\nabla} \times \left(\vec{\nabla} \times \vec{A}\right),$$

$$\partial_t \rho_F = ih\left[\vec{A}\right] \rho_F - i\rho_F \, h\left[\vec{A}\right],$$

Initial conditions sampled from the Wigner transform of the density matrix

$$\rho_W\left[\vec{A}, \vec{\mathcal{E}}\right] = \int \mathcal{D}\vec{A}_q\left(\vec{x}\right) \rho\left[\vec{A} + \frac{\vec{A}_q}{2}, \vec{A} - \frac{\vec{A}_q}{2}\right] e^{i \int d^3\vec{x} \vec{A}_q(\vec{x}) \cdot \vec{\mathcal{E}}(\vec{x})}$$

Static spectral functions and CSFT approximation

Assume gauge modes are slow, evolve fermions only:

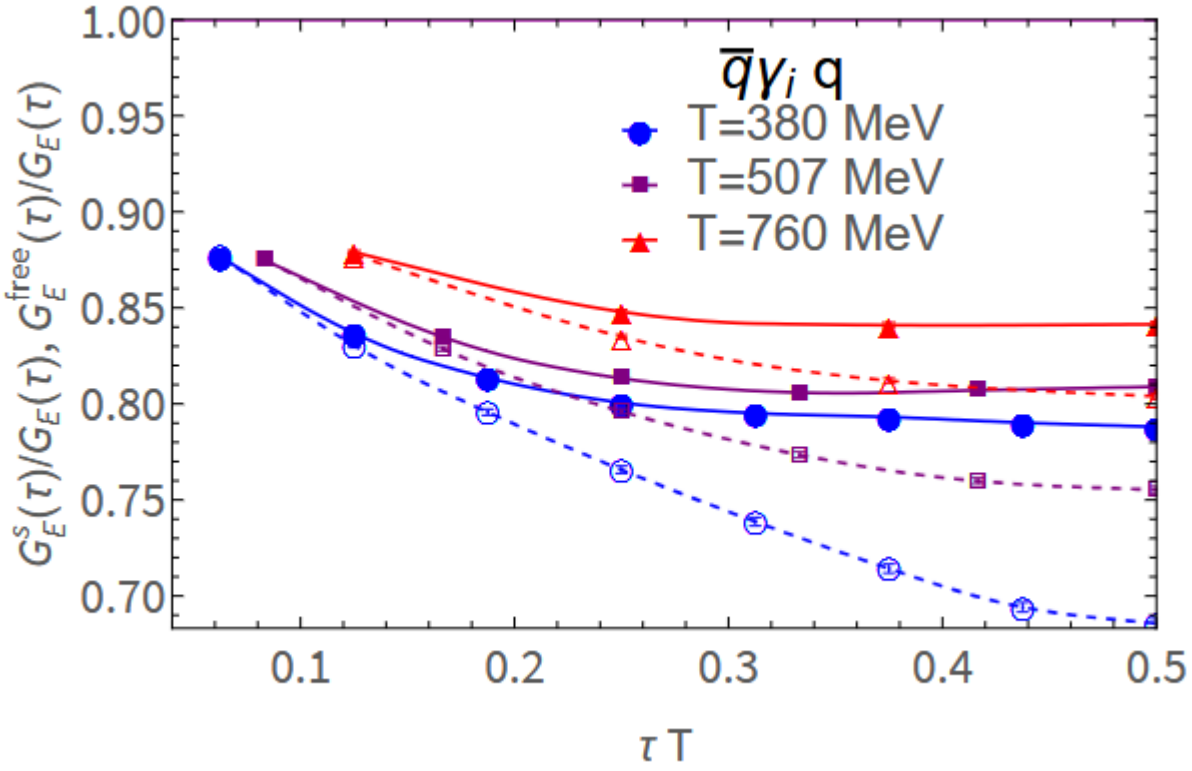
$$\partial_t \rho_F = i h\left[\vec{A}\right] \rho_F - i \rho_F \, h\left[\vec{A}\right]$$

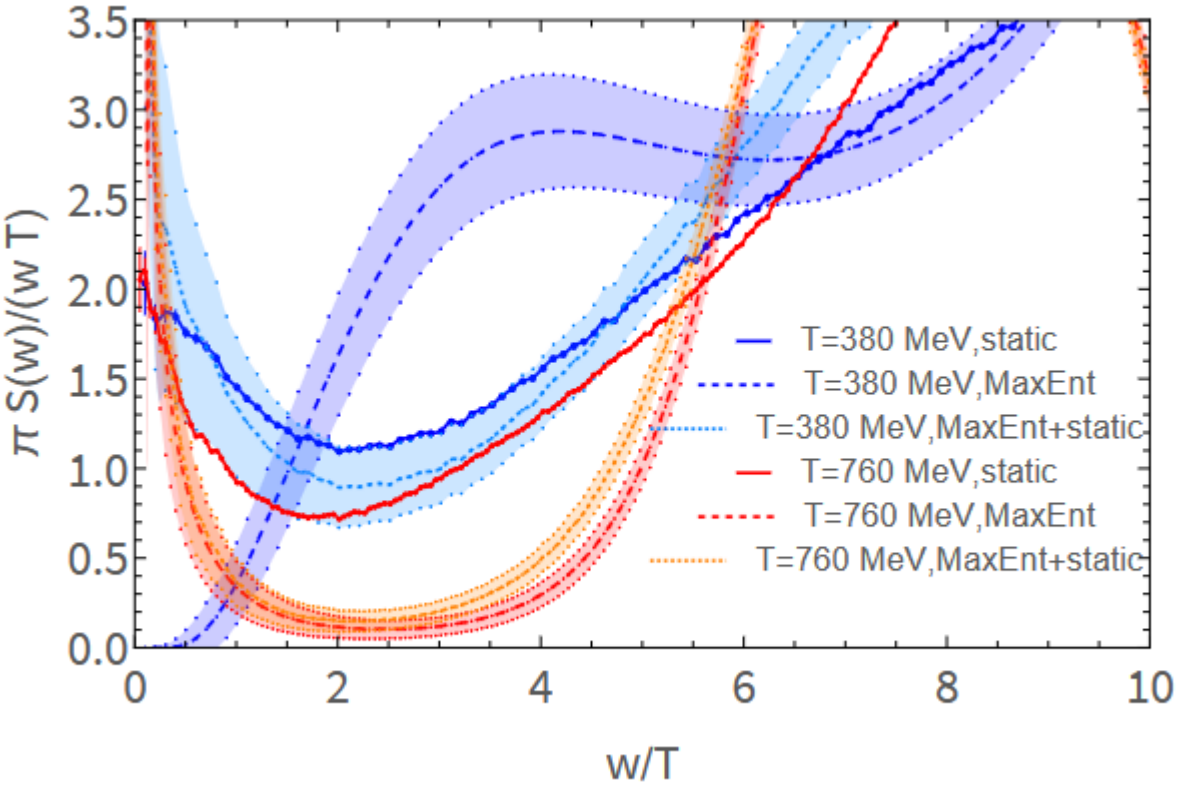
Initial conditions for A sampled from

$$\rho\left[\vec{A}\right] = \int \mathcal{D}\vec{\mathcal{E}}\, \rho\left[\vec{A}, \vec{\mathcal{E}}\right] = \langle \vec{A}| \, e^{-\beta \hat{H}} \, |\vec{A}\rangle$$

Distribution of gauge fields on a fixed Euclidean time slice

How good is static approximation in real QCD





- Static approximation better than the free quark limit
- Qualitatively different spectral functions if static limit used as prior

Parametrically improved frequency resolution?

At high temperatures, soft chromo-magnetic fields dominate the path integral

- Characteristic timescale for chromo-magnetic fields: $t_M^{-1} \sim g^2(T)\ T$
- Characteristic time-scale for chromo-electric fields: $t_E^{-1} \sim g(T)\ T$
- We assume static chromo-magnetic fields, neglect electric fields (assume screened)
- Frequency resolution $\sim g(T)\ T$ instead of $\sim \pi\ T$?