Hopping transport in disordered solids

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Outline of the talk

- Hopping transport
- Models for electron-phonon interactions
- Link with classical Markov processes
- Random walk in a random environment

Joint work with: J. Bellissard, A. Faggionato, H. Schulz-Baldes, R. Rebolledo

Outline of the talk

- Hopping transport

Anderson localization

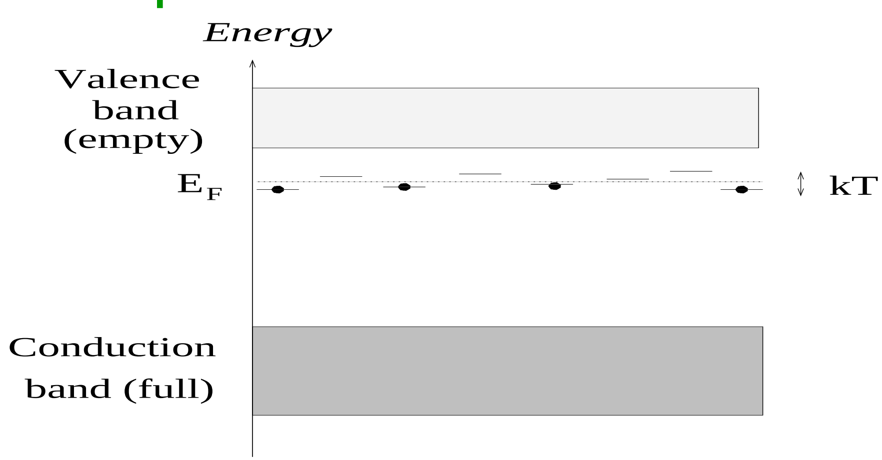
$H = -\Delta + V_\omega$ = electron Hamiltonian in a disordered solid.

- The low energy part of $\mathrm{spect}(H)$ is a.s. pure point,

$$H|\psi_i\rangle = E_i|\psi_i\rangle \quad , \quad E_i \in [-\Delta, \Delta]$$

  The eigenfunctions ψ_i are exponentially localized around random points $x_i \subset \mathbb{R}^d$.

- At low temperature $k_B T \ll \Delta$, the relevant states for transport are close to the Fermi level $E_F = 0$



$$H_e = P_{-[\Delta,\Delta]} H P_{-[\Delta,\Delta]}$$

$\mathrm{spect}(H_e)$ pure point (a.s.)

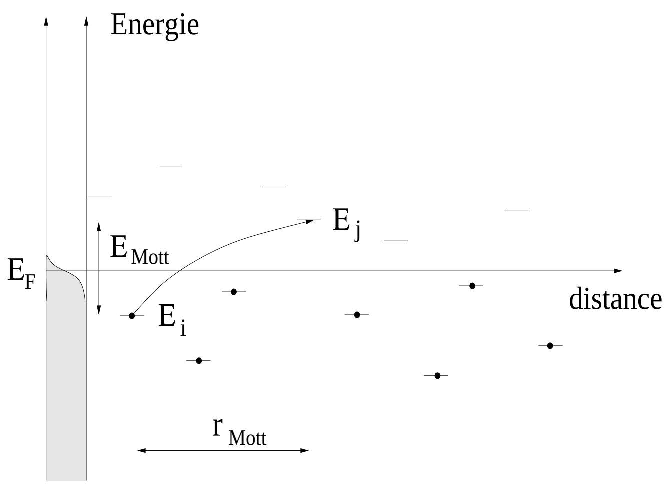
Coupling with phonons

- Apply to the solid a small constant electric field $\mathcal{E}$

  $$H_e \longrightarrow H_{e,\mathcal{E}} = H_e + \mathcal{E}X \quad , \qquad X = \text{position operator.}$$

  $\mathrm{spect}(H_{e,\mathcal{E}})$ a.c. with resonances $E_i(\mathcal{E})$ close to $\mathbb{R}$-axis.
  electons in perturbed states $\psi_i(\mathcal{E})$ remain localized
  $\hookrightarrow$ *no transport!*

- At temperature $T > 0$: coupling with phonons allows for electronic jumps between the localized states $\psi_i(\mathcal{E})$



$\hookrightarrow$ *hopping transport*

Conductivity σ_β

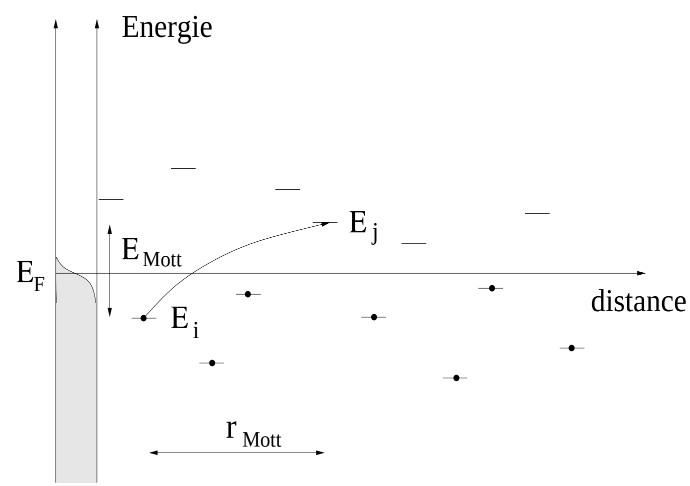
Let $|E_j - E_i| \gg k_B T$, $|x_i - x_j| \gg 1 =$ localization length.

Jump rate from ψ_i to ψ_j: $\gamma_{i\to j} \propto e^{-|x_i - x_j|}\, e^{-\beta \max\{E_j - E_i, 0\}}$

Effective jump rate *(Mean Field)*: $c_{i\to j} = \gamma_{i\to j} f_i (1 - f_j)$

$f_i = \left(e^{\beta(E_i - \mu)} + 1\right)^{-1} =$ mean $\sharp$ of electrons in ψ_i for $\mathcal{E} = 0$

$$\Rightarrow \quad c_{i\to j} \propto e^{-|x_i - x_j|} e^{-\beta(|E_i - E_j| + |E_i| + |E_j|)}$$



Optimal jumps for $|x_i - x_j| \sim r_{\text{Mott}}$
and $|E_i - E_j| \sim \epsilon_{\text{Mott}}$,

$$r_{\text{Mott}} = \text{const. } \beta^{1/(d+1)}$$

$$\epsilon_{\text{Mott}} = \text{const. } \beta^{-d/(d+1)}$$

(const. depends on DOS at E_F).

Mott law: $\sigma_\beta \sim \sigma_0 \exp\left\{-\text{const.}\beta^{\frac{1}{d+1}}\right\}$, $\beta \gg 1$ [Mott ' 68]

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Electron dynamics (exact)

- Electron Hamiltonian $\hat{H}_e = \sum_i E_i \, a_i^\dagger a_i$ (2^{nd} quantization)

  Electronic observables A_e belong to a CAR algebra $\mathcal{A}_e$ = C*-algebra generated by the creation op. $a_i^\dagger = a^\dagger(\psi_i)$.

- Electron-phonon interaction Hamiltonian (for N atoms):

$$\hat{H}_{e-ph} = \frac{\lambda}{\sqrt{N}} \sum_q \sqrt{\nu_q} \, \widehat{e^{iqX}} \left(b_q + b^\dagger_{-q} \right)$$

  $b_q^\dagger =$ creation op. of a longitudinal acoustic phonon with momentum q and frequency $\nu_q = c_s |q|$

  $\lambda =$ coupling constant.

- Assume the phonons are in state ω_{ph} at time $t = 0$ and are uncorrelated with the electrons

$$A_e(t) = \omega_{ph} \left(e^{it(\hat{H}_e + \hat{H}_{ph} + \hat{H}_{e-ph})} A_e \otimes 1_{ph} \, e^{-it(\hat{H}_e + \hat{H}_{ph} + \hat{H}_{e-ph})} \right).$$

Van Hove limit (weak coupling)

- Phonons = ∞ bath at equilibrium with inv. temperature β
  $\hookrightarrow$ initial state ω_{ph} = β-KMS state for free bosons.

- Van Hove limit: $\lambda \to 0\ ,\ t = \lambda^{-2}\tau \to \infty$ [Davies '74]

$$\|A_e(\lambda^{-2}\tau) - e^{\tau(\mathcal{L}_e + \mathcal{D})}(A_e)\| \to 0.$$

Liouvillian : $\mathcal{L}_e(A_e) = i\big[\hat{H}_e, A_e\big]$

$$\mathcal{D}(A_e) = \sum_{i \neq j} \gamma_{i \to j} \Big(a_i^\dagger a_j A_e\, a_j^\dagger a_i - \frac{1}{2}\Big\{ a_i^\dagger a_i\, a_j a_j^\dagger, A_e \Big\}\Big)$$

$=$ Lindblad generator

$\hookrightarrow$ commutes with $\mathcal{L}_e$

$a_i^\dagger, a_i$ $=$ creation & annihilation op. of an electron in state ψ_i

$\gamma_{i \to j}$ $=$ jump rate from ψ_i to ψ_j as given by Fermi golden rule.

When is weak coupling OK?

- Let $f, g \in L^2(\mathbb{R}^d, \mathrm{d}^3 q)$, $(H_{ph} f)(q) = \omega_q f(q)$

  $b(f) =$ annihilation op. of a phonon in state f.

  Phonon correlation time τ_c: If f, g are analytic in a strip around the $\mathbb{R}$-axis, the phonon correlation function

  $$\omega_{ph}\big(b^\dagger(f) b(e^{-i\tau H_{ph}} g)\big) = \langle f | e^{-i\tau H_{ph}} (e^{\beta H_{ph}} - 1)^{-1} g \rangle$$

  decreases exponentially to 0 as $\tau \to \infty$ with a rate $1/\tau_c$.

- The electron dynamics is well-approximated by the semigroup of *completely positive maps* $(e^{t(\mathcal{L}_e + \mathcal{D})})_{t \geq 0}$ if

  (1) $\tau_c \ll t \lesssim \lambda^{-2} \tau_c^{-1}$ (*Markov limit* + *perturbation theory*)

  (2) $\Delta E \gg \lambda^2 \tau_c$ with $\Delta E =$ smallest energy difference $|E_i - E_j|$ for relevant jumps (*adiabatic limit*).

  Here $\Delta E \sim \epsilon_{\text{Mott}}$, $\tau_c = \beta \quad \hookrightarrow \lambda \ll \beta^{-(2d+1)/(2d+2)}$.

Current density j

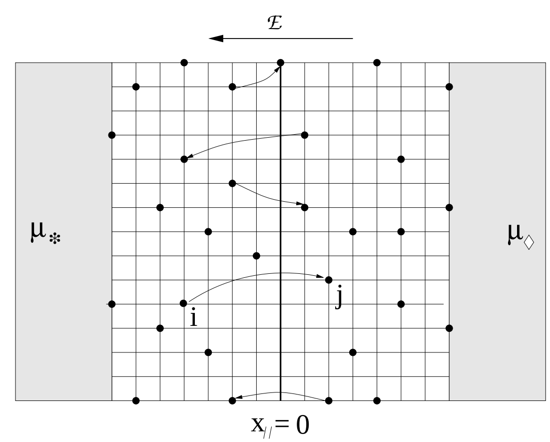
- Apply to the solid a small constant electric field $\mathcal{E}$

$$\mathcal{L}_e \quad \longrightarrow \quad \mathcal{L}_{e,\mathcal{E}} = i[\hat{H}_e + \mathcal{E}\hat{X}\ ,\ \cdot]$$

$$\mathcal{D} \quad \longrightarrow \quad \mathcal{D}_{\mathcal{E}} \qquad \text{depends on } \mathcal{E}.$$

$\hat{X} = \sum_i \langle \psi_i | X | \psi_j \rangle a_i^\dagger a_j$ = 2^{nd} quantized position op.

- Solid with **finite volume** Ω connected to **two reservoirs** with chemical potentials $\mu_* \neq \mu_\diamond$.



$\hookrightarrow$ Dynamics in van Hove limit: semigroup $(\Phi_{t,\mathcal{E}})_{t\geq 0}$ with generator

$$\mathcal{L}_{e,\mathcal{E}} + \mathcal{D}_{\mathcal{E}} + \text{electron exchanges with reservoirs}$$

- **Current density:** $j = \dfrac{1}{|\Omega|} \lim\limits_{t\to\infty} \varphi_{eq}\Big(\Phi_{t,\mathcal{E}}\, \underbrace{(\mathcal{L}_{e,\mathcal{E}} + \mathcal{D}_{\mathcal{E}})(\hat{X})}_{\text{velocity}}\Big).$

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Invariant commutative algebra

- Electron Hamiltonian $\hat{H}_e = \sum_{i \in I} E_i \, a_i^\dagger a_i$

  Eigenvectors in Fock space

$$|\eta\rangle = \prod_{i \in I} (a_i^\dagger)^{\eta_i} |0\rangle \ , \ \eta \in \{0,1\}^I$$

- The dissipative part $\mathcal{D}$ of the generator commutes with $\mathcal{L}_e = i[\hat{H}_e, \cdot]$ *(adiabatic approximation)*

  If (i) $\hat{H}_e$ has simple eigenvalues

  (ii) $e^{t(\mathcal{L}_e + \mathcal{D})}$ has a unique stationary state φ_∞ . Then

1. $\ker \mathcal{L}_e = \{\hat{H}_e\}' =$ commutative invariant algrebra for the semigroup $(e^{t(\mathcal{L}_e+\mathcal{D})})_{t \geq 0}$.
2. $\varphi_\infty\big(\mathcal{L}_e(A)\big) = 0$ for any $A \in \mathcal{A}_e$.

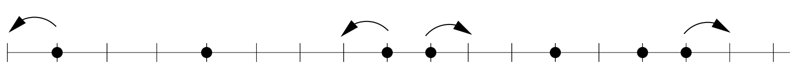
Decoherence

Thm : If (i) $\hat{H}_e$ has simple eigenvalues
(ii) $e^{t(\mathcal{L}_e+\mathcal{D})}$ has a unique stationary state φ_∞

1. $e^{t(\mathcal{L}_e+\mathcal{D})}\big|_{\{\hat{H}_e\}'}$ defines a Markov semigroup with generator

$$\begin{aligned}(\mathcal{L}_{\text{cl}}\, f)(\eta) &= \langle\eta|\mathcal{D}\Big(\textstyle\sum_{\eta'} f(\eta')|\eta'\rangle\langle\eta'|\Big)|\eta\rangle \\ &= \frac{d}{dt}\,\mathbb{E}_\eta\big(f(\eta_t)\big) \quad , \quad f \in C(\{0,1\}^I)\end{aligned}$$

2. The corresponding Markov process $(\eta_t)_{t\geq 0}$ is an exclusion process on $\{x_i\}$ with the jump rates $\gamma_{i\to j}$



$\mu_\infty =$ invariant measure.

3. For any state φ and any observable $A \in \mathcal{A}_e$,

$$\lim_{t\to\infty} \varphi\big(e^{t(\mathcal{L}_e+\mathcal{D})}A\big) = \int \langle\eta|A|\eta\rangle\, d\mu_\infty(\eta)\ .$$

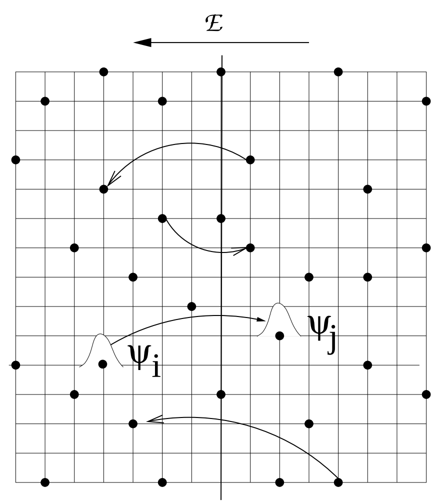
Classical current

Current density:

$$j = \frac{1}{|\Omega|} \lim_{t\to\infty} \varphi_{eq}\Big(\Phi_{t,\mathcal{E}}(\mathcal{L}_{e,\mathcal{E}} + \mathcal{D}_{\mathcal{E}})(\hat{X})\Big)$$

$$= \frac{1}{|\Omega|} \int \langle \eta | \mathcal{L}_{\mathrm{cl},\mathcal{E}}(\hat{X}_{\mathrm{diag},\mathcal{E}}) | \eta \rangle \, d\mu_{\infty,\mathcal{E}}(\eta)$$

$$\hat{X}_{\mathrm{diag},\mathcal{E}} = \sum_i \langle \psi_i(\mathcal{E}) | X | \psi_i(\mathcal{E}) \rangle a_i^\dagger(\mathcal{E}) a_i(\mathcal{E})$$



$$\hookrightarrow \; j_{\|} \propto \sum_{(x_i)_{\|}<0<(x_j)_{\|}} \Big(\gamma_{i\to j}\, \mu_\infty\big(\eta_i(1-\eta_j)\big) - (i \leftrightarrow j) \Big).$$

see [Miller & Abrahams ’ 60]

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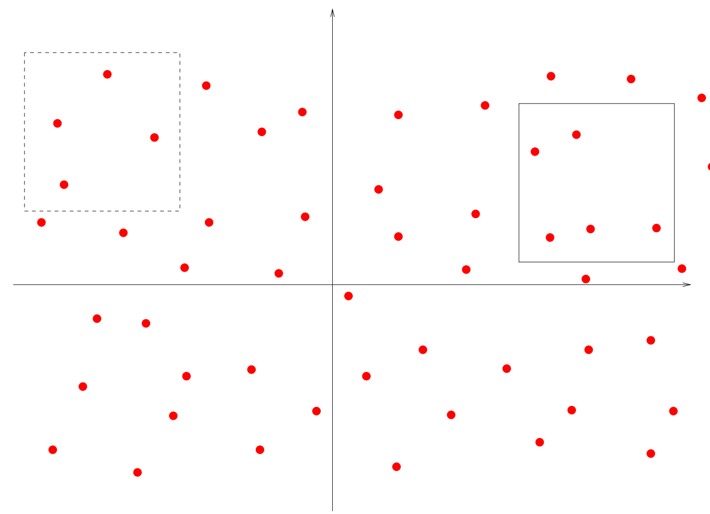
Random environment

- Let x_i be random distinct points in $\mathbb{R}^d$ with a stationary and mixing distribution $\hat{\mathcal{P}}$.



$$N_B = \sharp \text{ points in } B \subset \mathbb{R}^d \quad (B \text{ bounded Borel set})$$

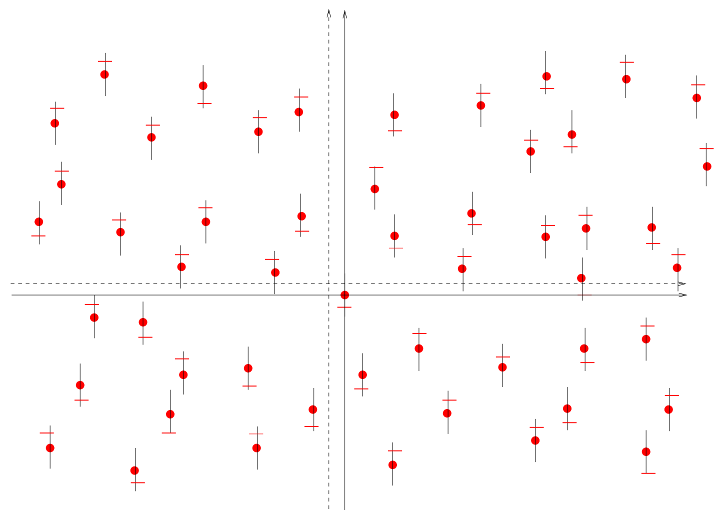
$$\mathbb{E}_{\hat{\mathcal{P}}}(N_B) = \rho|B| \,,\ \rho = \text{mean density},\ \rho < \infty.$$

- EX : (stationary) Poisson process
  (i) $\hat{\mathcal{P}}(N_B = n) = (\rho|B|)^n e^{-\rho|B|}/n!$
  (ii) the N_B are independent for disjoint B's.

Random environment (2)

- To each point x_i is associated a random energy $E_i \in [-1, 1]$.

  The E_i are independent and have all the distribution ν.



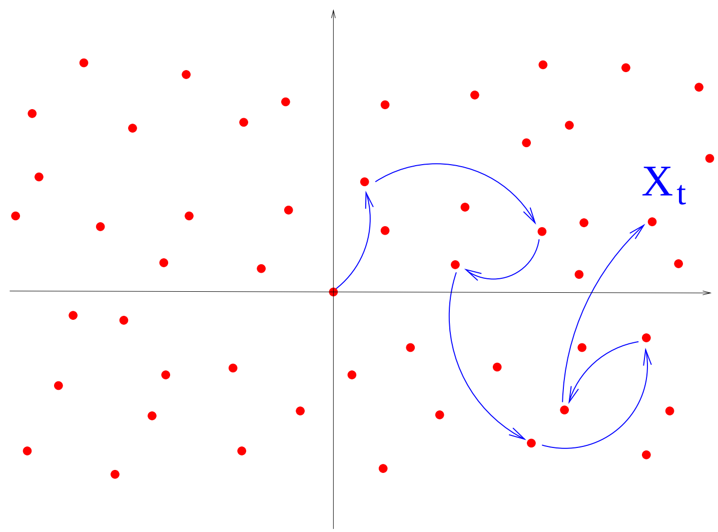
- Pick up (at random) a point among $\{x_i\}$ and choose it as the origin $\rightarrow$ new distribution = Palm distribution $\hat{\mathcal{P}}_0$

  EX : $\hat{\mathcal{P}} =$ stat. Poisson process $\rightarrow \hat{\mathcal{P}}_0$ is obtained by adding 1 (deterministic) point at $x = 0$.

Random walk

Configuration of the environment $\xi = \{x_i, E_i\}$.

A particle located at X_t at time t, starting from $X_0 = 0$, walks randomly on $\{x_i\}$:

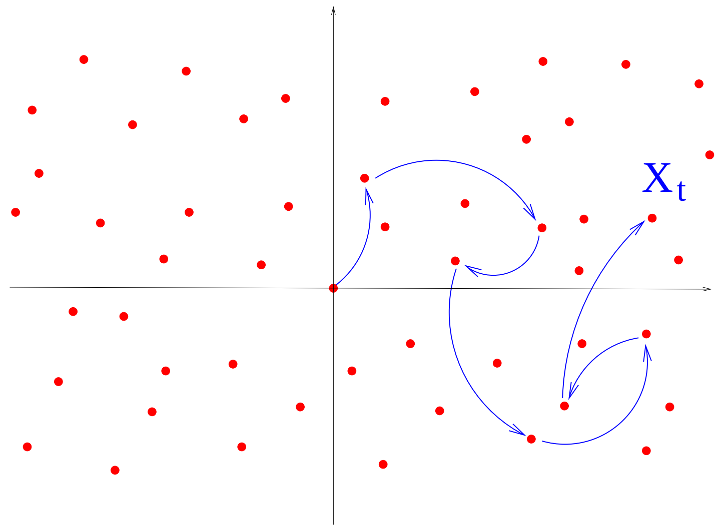


Jumps are possible between any pair of points (x_i, x_j), with the rate

$$c_{x_i \to x_j} = e^{-|x_i - x_j|} e^{-\beta(|E_i - E_j| + |E_i| + |E_j|)}$$

$\beta =$ inverse temperature.

Random walk (2)



For a given configuration $\xi = \{x_i, E_i\}$ of the environment, let $\mathbf{P}^\xi$ be the distribution of the Markov process $(X_t)_{t\geq 0}$.

$\forall\ x_i \neq x_j, \forall\ t, t_0 \geq 0,$

$$\mathbf{P}^\xi(X_{t_0+t} = x_j | X_{t_0} = x_i) = t\, c^\xi_{x_i \to x_j} + \mathcal{O}(t^2)\,.$$

No explosion if $\mathbb{E}_{\hat{\mathcal{P}}_0}(N_B^2) < \infty$.

Main results

Of interest here: diffusion constant

$$D_\beta = \lim_{t\to\infty} \frac{1}{t} \mathbb{E}_{\mathcal{P}_0}(\mathbb{E}_{\mathbf{P}^\xi}(X_t^2))$$

Thm 1 : in dimension $d \geq 2$,

(i) D_β exists and $D_\beta > 0$ (normal diffusion)

(ii) the process $Y_t = \varepsilon X_{t\varepsilon^{-2}}$ converges weakly in probability as $\varepsilon \to 0$ to a Brownian motion W_D.

Thm 2 : Let $d \geq 2$, energy distribution s.t. $\exists\; g_0 > 0, \exists\; \alpha \geq 0$,

$$\nu(|E_i| \leq E) \geq g_0\, E^{1+\alpha}\ .$$

Then

$$D_\beta \geq \; c\, \beta^{-\frac{(\alpha+1)(d-2)}{\alpha+1+d}} \exp\left\{ -\left(\frac{\beta}{\beta_0}\right)^{\frac{\alpha+1}{\alpha+1+d}} \right\}$$

($c, \beta_0 =$ constants independent of β).

Low temperature limit

Energy distribution for $E \to 0$:

$$\nu(|E_i| \le E) \sim g_0\, E^{1+\alpha}$$

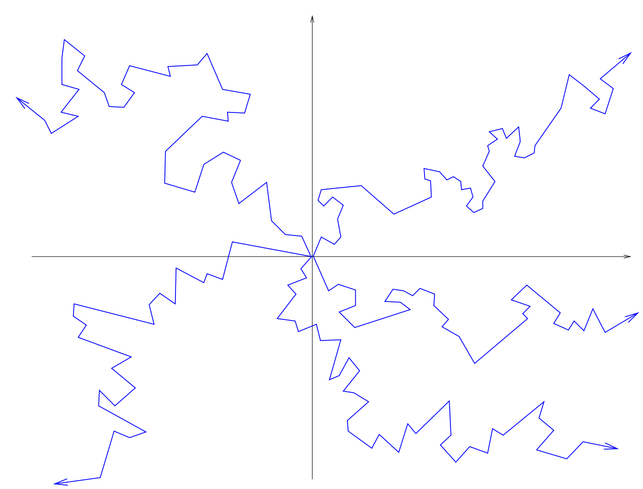
$$\Rightarrow \ln D_\beta \sim -\left(\frac{\beta}{\beta_0}\right)^{\frac{\alpha+1}{\alpha+1+d}}, \ \beta \uparrow \infty$$ [Mott '68]

(heuristic). [Ambegoakar, Halperin, Langer '71]

For $\beta \uparrow \infty$, the jump rates

$$c_{x_i \to x_j} = e^{-|x_i - x_j|} e^{-\beta(|E_i - E_j| + |E_i| + |E_j|)}$$

fluctuate widely with x_i, x_j



$\hookrightarrow$ the particle follows with high probability one of the optimal paths.