Kinetic Models

for Electronic transport

in Aperiodic Solids

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D. Spehner, *Contributions à la théorie du transport électronique, dissipatif dans les solides apériodiques*, Thèse, 13 mars 2000, Toulouse.

D. Spehner, J. Bellissard, *A Kinetic Model for Quantum Jumps* J. Stat. Phys., **104**, 525-572, (2001).

J. Bellissard, R. Rebolledo, D. Spehner, W. von Waldenfels, *The Quantum Flow of Electronic transport I: The finite volume case* `mp-arc` 02-212, (2002)

J. Bellissard, *Coherent and dissipative transport in aperiodic solids*, in *Dynamics of Dissipation*, P. Garbaczewski, R. Olkiewicz (Eds.). Lecture Notes in Physics, **597**, pp. 413-486, Springer (2002).

Content

1. Experimental Aspects

2. Master Equation and Green-Kubo formulæ

3. Kinetic models

I - Experimental Aspects

Few Mechanisms

1. For metals, $\sigma(\mathbf{T})$ increases as temperature decreases

$$\sigma(\mathbf{T}) \overset{T\downarrow 0}{\sim} \mathbf{T^{-2}}, \; \left(\textit{Fermi liquid theory}\right).$$

2. For a thermally activated process

$$\sigma(\mathbf{T}) \overset{T\downarrow 0}{\sim} \mathbf{e^{-\Delta/T}} \; \left(\textit{If a gap holds at Fermi level}\right).$$

3. For weakly disordered systems

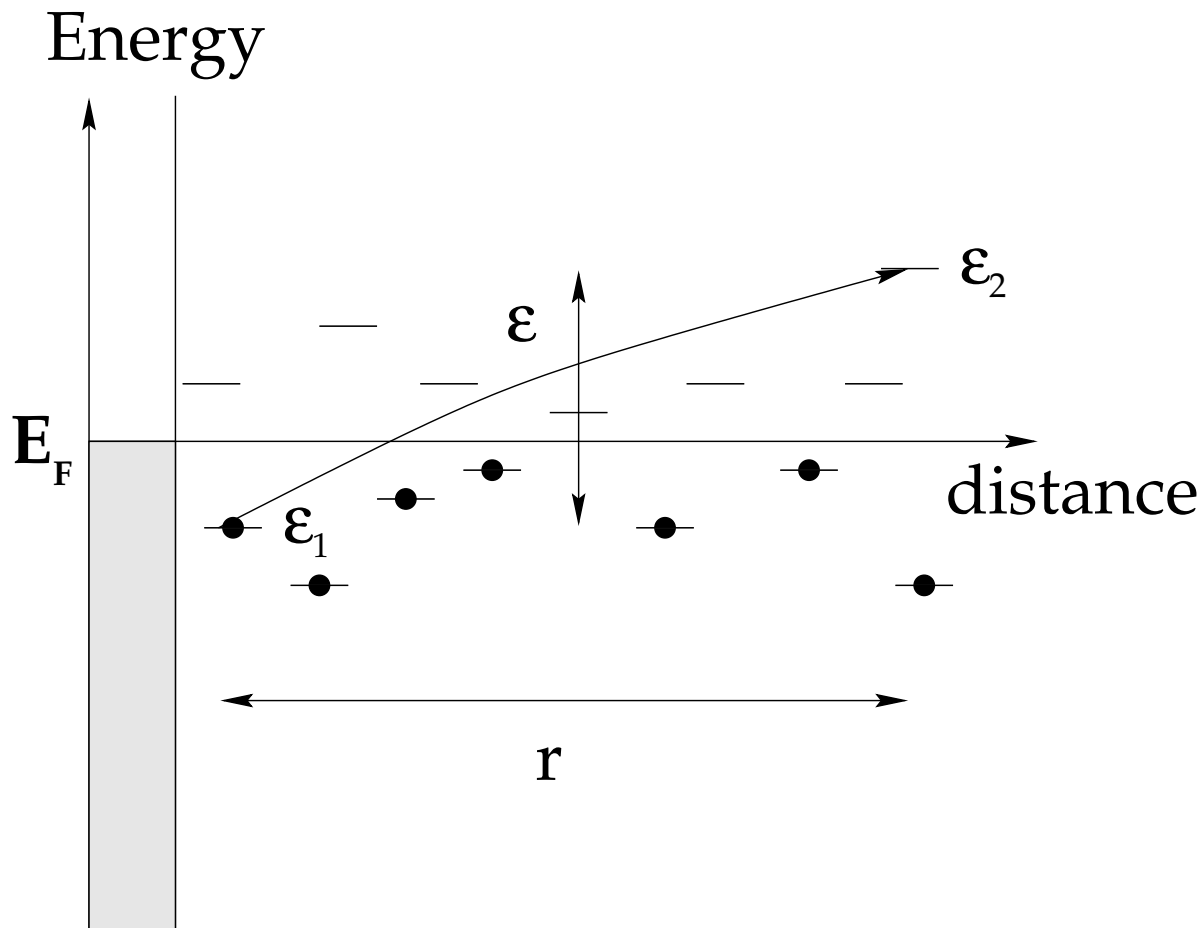$$\sigma(\mathbf{T}) \overset{T\downarrow 0}{\to} \sigma(\mathbf{0}) > \mathbf{0} \; \left(\textit{residual conductivity}\right).$$

4. For strongly disordered systems in $3D$ (Quantum Hall Effect)

$$\sigma(\mathbf{T}) \overset{T\downarrow 0}{\sim} \mathbf{e^{-(T_0/T)^{1/4}}} \; \left(\textit{variable range hopping}\right).$$

Mott's variable range hopping

N. F. MOTT, *J. Non-Crystal. Solids* **1**, 1 (1968).
& *Metal-Insulator Transitions* (Taylor and Francis, London, 1974).

B. SHKLOVSKII, A. L. EFFROS, *Electronic Properties of Doped Semiconductors,*
Springer-Verlag, Berlin, (1984).

- Strongly localized regime, dimension d

- Low electronic DOS, Low temperature

- Absorption-emission of a phonon of energy ε

$$Prob \propto e^{-\varepsilon/k_B T}$$

- Tunnelling probability at distance **r**

$$Prob \propto e^{-r/\xi}$$

- Density of state at Fermi level n_F,

$$\varepsilon\, n_F\, r^d \approx 1$$

- Optimizing, the conductivity satisfies

$$\sigma \propto e^{-(T_0/T)^{1/d+1}} \qquad \textbf{Mott's law}$$

- Optimal energy $\varepsilon_{opt} \sim T^{d/(d+1)} \gg T$
- Optimal distance $r_{opt} \sim 1/T^{1/(d+1)} \gg \xi$

Transport in Quasicrystals

Lectures on Quasicrystals,
F. Hippert & D. Gratias Eds., Editions de Physique, Les Ulis, (1994),

S. ROCHE, D. MAYOU AND G. TRAMBLY DE LAISSARDIÈRE,
Electronic transport properties of quasicrystals, J. Math. Phys., **38**, 1794-1822 (1997).

Quasicrystalline alloys

Metastable QC's: **AlMn**
*(Shechtman D., Blech I., Gratias D. & Cahn J., PRL **53**, 1951 (1984))*

$$\textbf{AlMnSi}$$
$$\textbf{AlMgT} \ (T = Ag, Cu, Zn)$$

Defective stable QC's: **AlLiCu** $\left(\textit{Sainfort-Dubost, (1986)}\right)$

GaMgZn $\left(\textit{Holzen et al., (1989)}\right)$

High quality QC's: **AlCuT** $(T = Fe, Ru, Os)$
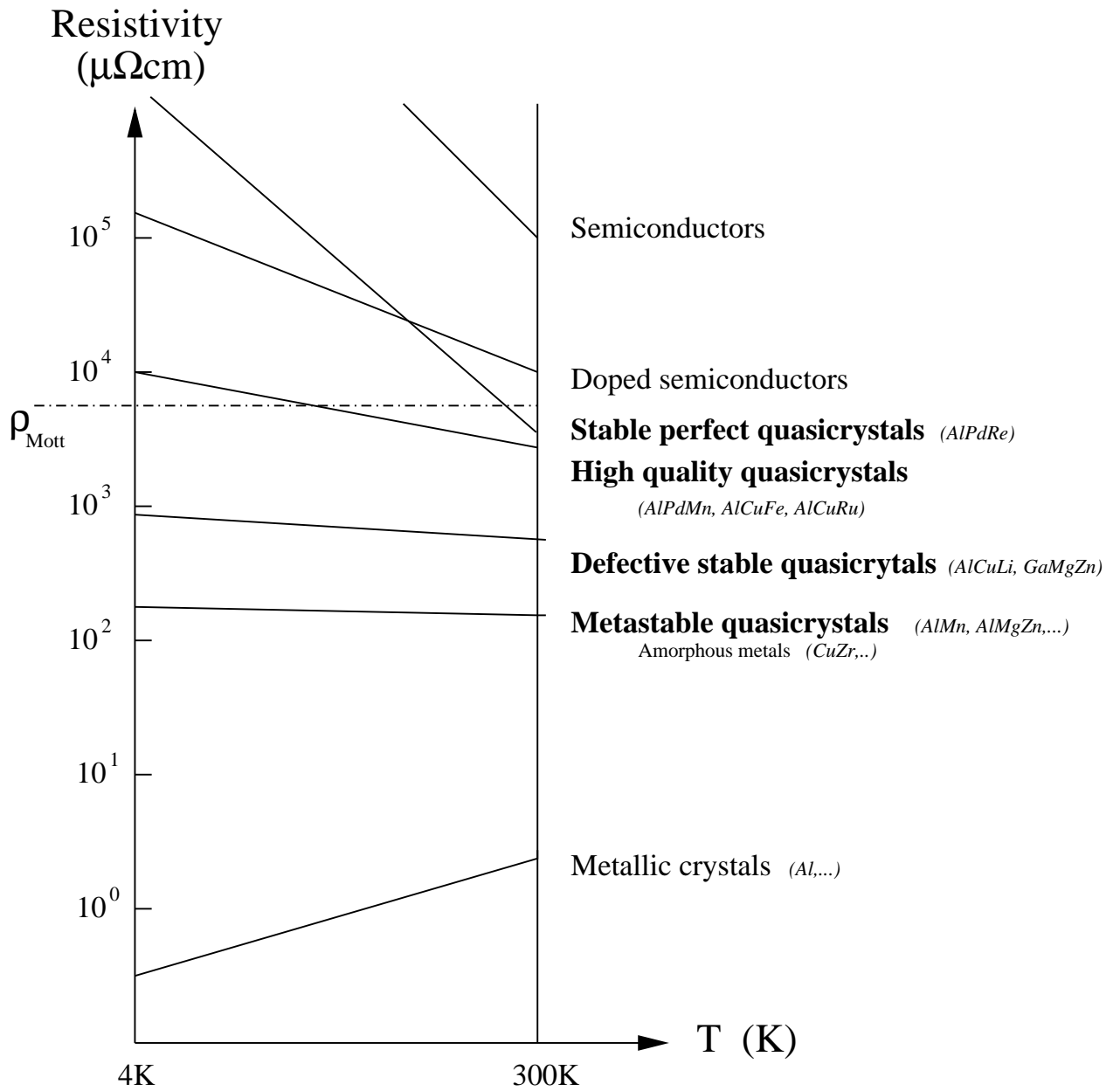
$\big($ *Hiraga, Zhang, Hirakoyashi, Inoue, (1988); Gurnan et al., Inoue et al., (1989);*

*Y. Calvayrac et al., (1990)* $\big)$

"Perfect" QC's: **AlPdMn**

AlPdRe

Resistivity (μΩcm) — vertical axis, **T (K)** — horizontal axis

10^5, 10^4, ρ_{Mott}, 10^3, 10^2, 10^1, 10^0

4K, 300K

Semiconductors

Doped semiconductors

Stable perfect quasicrystals *(AlPdRe)*

High quality quasicrystals
(AlPdMn, AlCuFe, AlCuRu)

Defective stable quasicrytals *(AlCuLi, GaMgZn)*

Metastable quasicrystals *(AlMn, AlMgZn,...)*
Amorphous metals *(CuZr,..)*

Metallic crystals *(Al,...)*

Typical values of the resistivity

$\Big($Taken from *C. Berger* in ref. *Lectures on Quasicrystals*$\Big)$
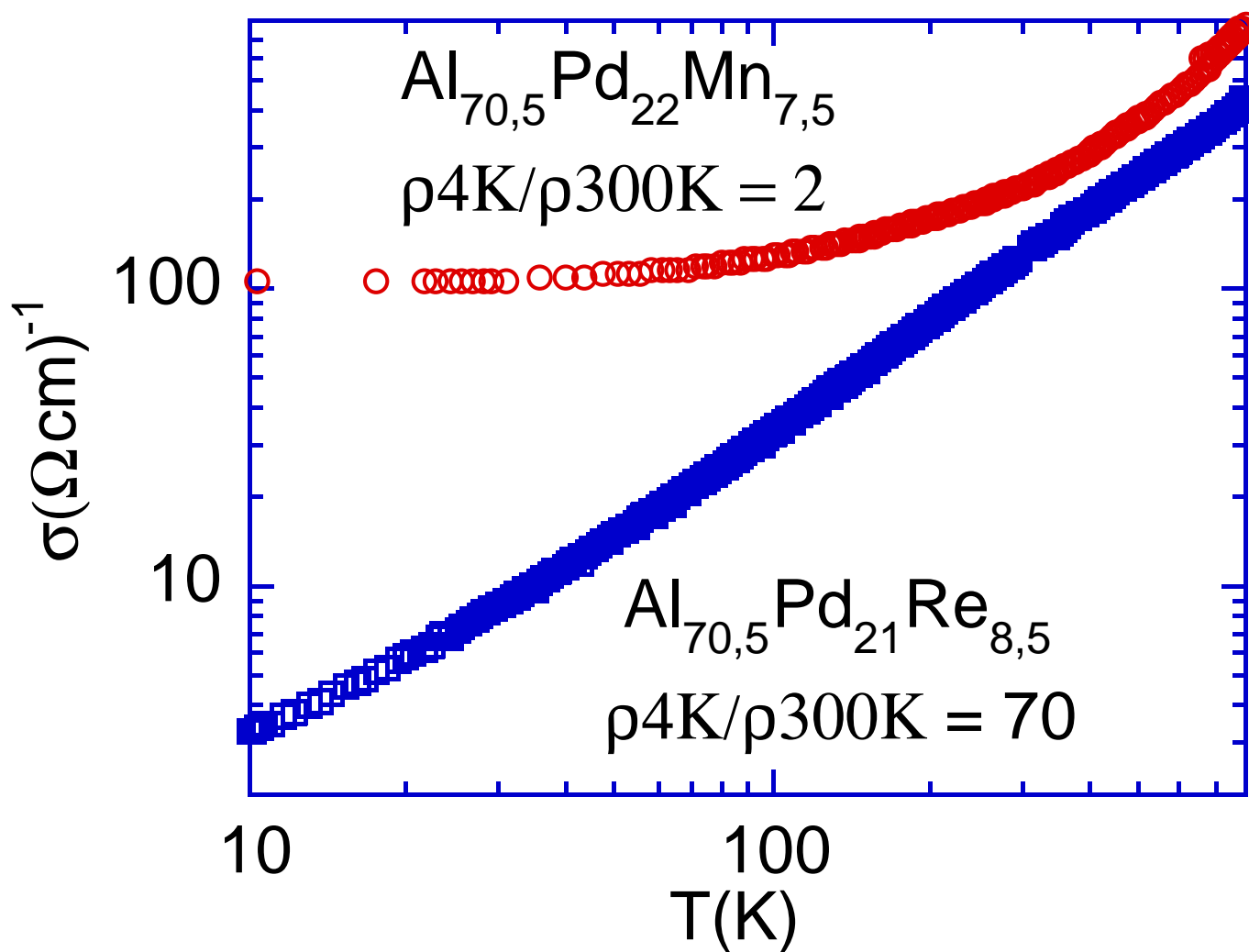
Comparison between conductivities of the two QC's

For Quasicrystals

1. *Al*, *Fe*, *Cu*, *Pd* are very good metals : why is the conductivity of quasicrystalline alloys so low ? Why is it decreasing ?

2. At high enough temperature

$$\sigma \propto T^{\gamma} \qquad 1 < \gamma < 1.5$$

There is a new mechanism here!

3. At low temperature for $\mathbf{Al_{70.5}Pd_{22}Mn_{7.5}}$,

$$\sigma \approx \sigma(0) > 0$$

4. At low temperature for $\mathbf{Al_{70.5}Pd_{21}Re_{8.5}}$,

$$\sigma \propto e^{-(T_0/T)^{1/4}} \qquad \text{C. BERGER } \textit{et al.} \text{ (1998)}$$

Disorder can be eliminated: recent samples impurity concentration lower than 10^{-6}.

II - Master Equation

Thermodynamics

1. The system is divided into cells of *mesoscopic size* in which a *local equilibrium* is established after a *mesoscopic time* $\delta t \ll$ measurement time. (*Local Equilibrium Approximation*)

2. On microscopic scale, a mesoscopic cell is an *infinite volume totally open* thermodynamical quantum system at *equilibrium* during a period of time δt with a time and cell dependent inverse temperature β. The Gibbs state is defined through

$$\hat{H}_{th} = \hat{H} - \mu\hat{N} - P\hat{V} + \cdots = \hat{H} + \sum_{\alpha=2}^{K} F_\alpha \hat{X}_\alpha$$

$\hat{H}$ = *cell Hamiltonian*, $\hat{X}_\alpha$ = other *conserved quantities*, F_α = *conjugate variables*.

$\left(\hat{N} \text{ is the particle number in the cell}, \hat{V} \text{ is the cell volume}, \textit{etc.}\right)$

3. $\beta, F_2, \cdots, F_K$ are macroscopically space and time dependent.

Mesoscopic Quantum Evolution

- *Observable algebra* $\mathcal{A} = \mathcal{A}_S \otimes \mathcal{A}_E$
  ($S =$ system, $E =$ environment).

- *Quantum evolution* $\eta_t \in \text{Aut}(\mathcal{A})$,
  $t \in \mathbb{R} \mapsto \eta_t(B) \in \mathcal{A}$ continuous $\forall B \in \mathcal{A}$.

- *Initial state* $\rho \otimes \rho_E$

- *System evolution*

$$\rho(\Phi_t(A)) \;=\; \rho_t(A) \;=\; \rho \otimes \rho_E\left(\eta_t(A \otimes \mathbf{1})\right)$$

  $\Phi_t : \mathcal{A}_S \mapsto \mathcal{A}_S$ is *completely positive*,
  $\Phi_t(\mathbf{1}) = \mathbf{1}$ and $t \mapsto \Phi_t(A) \in \mathcal{A}_S$ is continuous.

- *Markov approximation*: for δt mesoscopic

$$\Phi_{t+\delta t} \;\approx\; \Phi_t \circ \Phi_{\delta t} \;\approx\; \Phi_{\delta t} \circ \Phi_t$$

  Then
$$\frac{\delta \Phi_t}{\delta t} \;=\; \mathfrak{L} \circ \Phi_t \;=\; \Phi_t \circ \mathfrak{L}$$
  $\mathfrak{L}$ is the *Lindbladian*.

- *Dual evolution* $\Phi_t^\dagger(\rho) = \rho \circ \Phi_t$ giving rise to $\mathfrak{L}^\dagger$.

Theorem 1 (Lindblad '76) *If $\mathcal{A}_S = \mathcal{B}(\mathcal{H})$ and if Φ_t is pointwise norm continuous, there is a bounded selfadjoint operator H on $\mathcal{H}$ and a countable family of operators L_i such that*

$$\mathfrak{L}(A) \; = \; \imath[H, A] + \sum_i \left(L_i^\dagger A L_i - \frac{1}{2}\{L_i^\dagger L_i, A\} \right)$$

The first term of $\mathfrak{L}$ is the *coherent part* and corresponds to a usual Hamiltonian evolution.

The second one, denoted by $\mathfrak{D}(A)$ is the *dissipative* part and produces damping.

- *Stationary* states correspond to solutions of $\mathfrak{L}^\dagger \rho = 0$.

- *Equilibrium* states are stationary states with maximum entropy: the *KMS* states with respect to the *thermal dynamics* generated by

$$\hat{H}_{th} \; = \; \hat{H} + \sum_{\alpha=2}^{K} F_\alpha \hat{X}_\alpha$$

Derivation of Green-Kubo Formulæ

- In many cases there is a *position operator* acting on the Hilbert space of states and given by a commuting family $\vec{R} = (R_1, \cdots, R_d)$ of selfadjoint operators. They describe the position of particles in the system S.

- $\vec{R}$ generates a d-parameter group of automorphisms $\vec{k} \in \mathbb{R}^d \mapsto e^{\imath \vec{k} \cdot \vec{R}} A e^{-\imath \vec{k} \cdot \vec{R}}$ of the C^*-algebra $\mathcal{A}_S$. Thus $\vec{\nabla} = \imath[\vec{R}, \; \cdot \;]$ defines a $*$-derivation of $\mathcal{A}_S$.

- The *mesoscopic velocity* of the particles is given by

$$\vec{V} \; = \; \frac{d\vec{R}}{dt} \; = \; \mathfrak{L}(\vec{R}) \; = \; \vec{\nabla} H + \mathfrak{D}(\vec{R})$$

  The first part corresponds to the *coherent velocity* the other to the *dissipative one*.

- The current associated with $\hat{X}_\alpha$ is given by

$$\vec{J}_\alpha \; = \; \frac{1}{2}\{\vec{V}, \hat{X}_\alpha\} \; = \; \vec{J}_\alpha^{(coh)} + \vec{J}_\alpha^{(diss)}$$

- At time $t = 0$, S is at equilibrium

$$\Rightarrow \rho_{in} = \rho_{eq.} \qquad \mathfrak{L}^\dagger \rho_{eq.} = 0$$

- At $t > 0$, *forces* are switched on

$$\mathcal{E} = (\vec{\mathcal{E}}_1, \cdots, \vec{\mathcal{E}}_K) \quad \text{with} \quad \vec{\mathcal{E}}_\alpha = \vec{\nabla}(F_\alpha/T)$$

so that

$$\mathfrak{L}_\mathcal{E} = \mathfrak{L} + \sum_\alpha \vec{\mathcal{E}}_\alpha \vec{\mathfrak{L}}_\alpha + O(\mathcal{E}^2)$$

- Hence the current becomes

$$\vec{J}_\alpha^\mathcal{E} = \vec{J}_\alpha + \sum_\alpha \vec{\mathcal{E}}_\alpha \vec{\mathfrak{L}}_\alpha(\vec{R}) + O(\mathcal{E}^2)$$

- Then, if the forces are constant in time

$$\vec{j}_\alpha = \lim_{t\uparrow\infty} \int_0^t \frac{ds}{t} \rho_{eq.} \left(e^{s\mathfrak{L}_\mathcal{E}} \vec{J}_\alpha^\mathcal{E} \right)$$

$$= \lim_{\epsilon\downarrow 0} \int_0^\infty \epsilon dt\, e^{-t\epsilon} \rho_{eq.} \left(e^{t\mathfrak{L}_\mathcal{E}} \vec{J}_\alpha^\mathcal{E} \right)$$

$$= \lim_{\epsilon\downarrow 0} \rho_{eq.} \left(\frac{\epsilon}{\epsilon - \mathfrak{L}_\mathcal{E}} \vec{J}_\alpha^\mathcal{E} \right)$$

- Since $\mathfrak{L}^\dagger \rho_{eq.} = 0$, $\rho_{eq.} \left(\frac{\epsilon}{\epsilon - \mathfrak{L}} \vec{J}_\alpha \right) = 0$

- Thus

$$
\vec{j}_\alpha = \lim_{\epsilon \downarrow 0} \rho_{eq.} \left(\frac{\epsilon}{\epsilon - \mathfrak{L}_\mathcal{E}} \vec{J}_\alpha^\mathcal{E} - \frac{\epsilon}{\epsilon - \mathfrak{L}} \vec{J}_\alpha \right)
$$

$$
= \lim_{\epsilon \downarrow 0} \rho_{eq.} \left(\frac{\epsilon}{\epsilon - \mathfrak{L}} \sum_{\alpha'} \vec{\mathcal{E}}_{\alpha'} \cdot \vec{\mathfrak{L}}_{\alpha'} \frac{1}{\epsilon - \mathfrak{L}_\mathcal{E}} \ \vec{J}_\alpha \right)
$$

$$
+ \lim_{\epsilon \downarrow 0} \rho_{eq.} \left(\frac{\epsilon}{\epsilon - \mathfrak{L}} \sum_{\alpha'} \vec{\mathcal{E}}_{\alpha'} \cdot \vec{\mathfrak{L}}_{\alpha'}(\vec{R}) \right)
$$

$$
+ O(\mathcal{E}^2)
$$

- Since $\rho_{eq.} \circ \mathfrak{L} = 0$ this gives

$$
\vec{j}_\alpha = - \sum_{\alpha'} \vec{\mathcal{E}}_{\alpha'} \ \rho_{eq.} \left(\vec{\mathfrak{L}}_{\alpha'} \ \frac{1}{\mathfrak{L}} \ \vec{J}_\alpha + \vec{\mathfrak{L}}_{\alpha'}(\vec{R}) \right)
$$

$$
+ O(\mathcal{E}^2)
$$

- Hence the *Onsager cœfficients* are

$$
L_{\alpha,\alpha'} = -\rho_{eq.} \left(\vec{\mathfrak{L}}_{\alpha'} \ \frac{1}{\mathfrak{L}} \ \vec{J}_\alpha + \vec{\mathfrak{L}}_{\alpha'}(\vec{R}) \right)
$$

Validity of Green-Kubo Formulæ

The previous derivation is formal. Various conditions must be assumed.

- The explicit expressions for $\mathfrak{L}$ and the $\vec{\mathfrak{L}}_{\alpha'}$'s are *model dependent*.

- It is necessary to prove that $\mathfrak{L}_{\mathcal{E}}(\vec{R}) \in \mathcal{A}_S$.

- The *inverse* of $\mathfrak{L}$ is not *a priori* well defined.

However, the dissipative part $\mathfrak{D}$ is usually responsible for the existence of the inverse. This is because

$$\mathrm{Spec}(\imath[H,\cdot]) \subset \imath\mathbb{R}$$

while $\mathfrak{D}$ gives a *non zero real part* to eigenvalues.
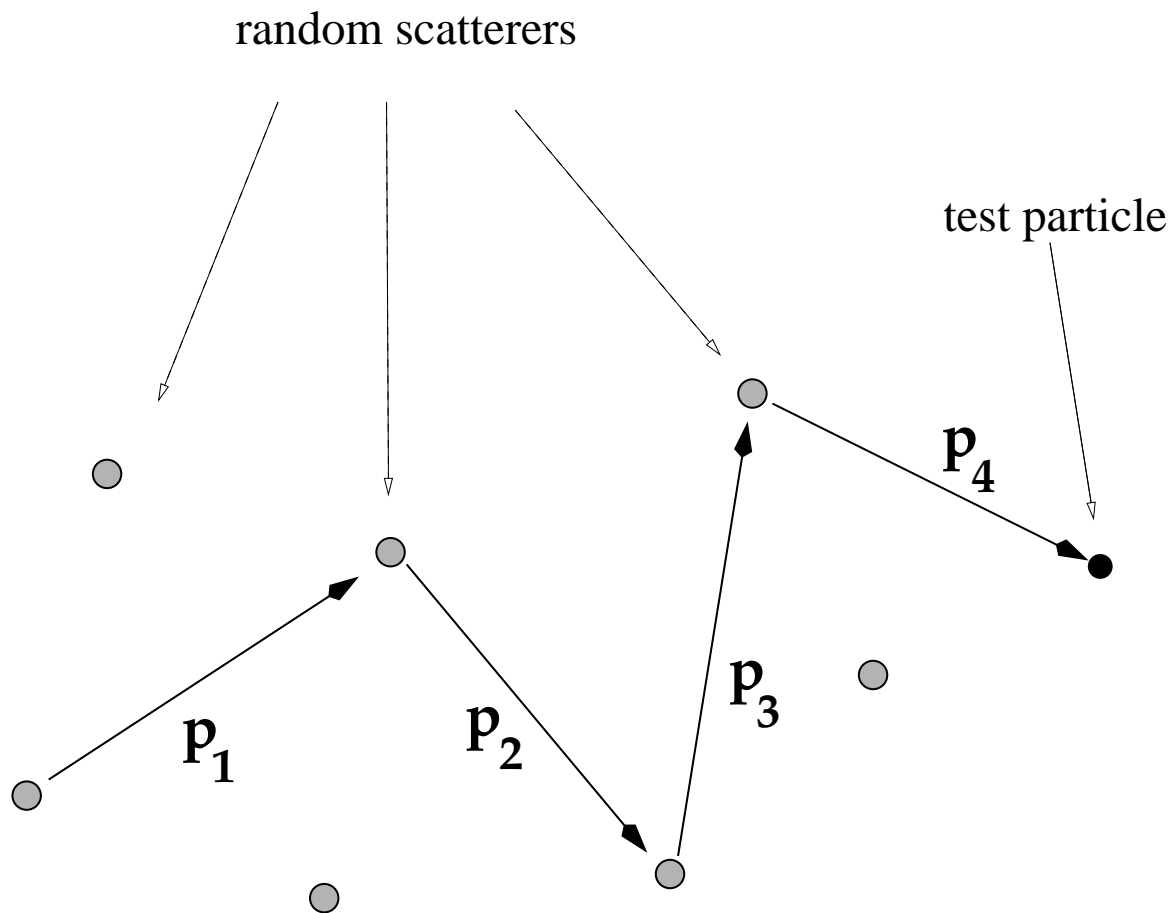In the *Relaxation Time Approximation*,

$$\mathfrak{D}(A) = A/\tau \quad \Rightarrow \quad \mathrm{Spec}\left(\imath[H,\cdot] + \frac{1}{\tau}\right) \subset \imath\mathbb{R} + \frac{1}{\tau}$$

where τ is the *relaxation time*.

III - Kinetic Models

The Drude Model

- Electrons in a metal are free classical particles of mass m_* and charge $-e$.

- Electron density is n.

1. Between two collisions, the electron motion is governed by Newton's law with external forces (*e.g.* electric field).

2. Collisions occur at random Poissonian times
   $$\cdots < t_{-1} < t_0 < \cdots < t_{n+1} < \cdots \quad \text{with}$$

   $$< t_{n+1} - t_n > = \tau_{rel}$$

   .

3. Right after each collision, the momentum p_n is updated randomly according to the Maxwell-Boltzman distribution at the temperature of the metal.

As a consequence

$$\sigma = \frac{e^2 n}{m_*} \, \tau_{rel} \qquad \textbf{Drude formula}$$

A Quantum Drude Model

1. Replace the classical motion by the quantum motion under investigation with Hamiltonian H.

2. Replace collisions by *quantum jumps* indexed by r at random Poissonian times

$$\cdots < t_{-1}^{(r)} < t_0^{(r)} < \cdots < t_{n+1}^{(r)} < \cdots$$

$$\langle t_{n+1}^{(r)} - t_n^{(r)} \rangle = \Gamma_r^{-1}$$

3. At collisions of type r the state ρ changes to $\mathcal{K}_r^\dagger(\rho)$. $\mathcal{K}_r^\dagger$ must be a *completely positive affine continuous* map from the state space into itself.

4. The *dissipation operator* is

$$\mathfrak{D}^\dagger(\rho) = \sum_r \Gamma_r \left(\rho - \mathcal{K}_r^\dagger(\rho)\right)$$

Γ_r and $\mathcal{K}_r^\dagger$ may depend on external forces.

Dissipative Evolution

The Liouville operator associated with $A = A^*$ is

$$\mathcal{L}_A = \frac{\imath}{\hbar}[A, \cdot]$$

The evolution of the state is given by

$$\rho(t) = \eta^\dagger_{t-t_n} \circ \mathcal{K}^\dagger_{r_n} \circ \eta^\dagger_{t_n-t_{n-1}} \circ \cdots \circ \mathcal{K}^\dagger_{r_1} \circ \eta^\dagger_{t_1}(\rho)$$

if

1. $t_0 \leq 0 < t_1 < \cdots < t_n \leq t < t_{n+1}$ are the collision times and $r_1, \cdots, r_n$ the corresponding quantum jumps.

2. $\eta^\dagger_t$ is the action on states of the quantum evolution associated with $H_{\vec{\mathcal{E}}} = H - q\vec{\mathcal{E}} \cdot \vec{R}$.

Theorem 2 *The time average evolution is given by the Lindbladian*

$$\mathfrak{L}^\dagger = -\mathcal{L}_H + \frac{q}{\hbar}\vec{\mathcal{E}} \cdot \vec{\nabla} - \mathfrak{D}^\dagger$$

The Relaxation Time Approximation

The RTA corresponds to a unique type of quantum jumps with $\Gamma = 1/\tau_{rel}$ and $\mathcal{K}^\dagger(\rho) = \rho_{eq.}$. Then

$$\frac{d\rho}{dt} = \frac{\imath}{\hbar}\,[H, \rho] - \frac{\rho - \rho_{eq.}}{\tau_{rel}}$$

The solution of this equation exists and converges exponentially fast to equilibrium.

Variable Range Hopping

1. The electrons are *independent fermions* and moving on a *random sublattice* L_ω of $\mathbb{Z}^d$.

2. $\mathbb{Z}^d$ acts on the *compact space* Ω indexing L so that $L_\omega + a = L_{\mathrm{T}^a \omega}$ for $a \in \mathbb{Z}^d$ and $\mathbb{P}$ is an *ergodic invariant* probability on Ω.

3. Given $\omega \in \Omega$ a quantum jump occurs between any pair $r = (x \to y) \in L_\omega^{\times 2}$. Then

$$\mathcal{K}^\dagger_{x \to y}(\rho) = (\mathbf{1} + K_{x \to y})\rho(\mathbf{1} + K^*_{x \to y})$$

$$K_{x \to y} = |y\rangle\langle x| - |x\rangle\langle x|$$

4. The one-electron Hamiltonian is

$$H_{\vec{\mathcal{E}}, \omega} = \sum_{x \in L_\omega} \left(V_\omega(x) - q\vec{\mathcal{E}} \cdot \vec{x} \right) |x\rangle\langle x|$$

(*strong localization limit*).

5. The potential $V_\omega(x)$ is created by the charges of ionic impurities and depends upon the *occupation number* n_x by electrons ($n_x = 1$) or holes ($n_x = 0$) at each sites of L_ω. At equilibrium, V and n are determined uniquely.

6. The Mott argument suggests

$$\Gamma_{x \to y}(\omega) = \Gamma_0 \, e^{-(V_\omega(y) - V_\omega(x) + q\vec{\mathcal{E}} \cdot (x-y))/k_B T}$$
$$\dots e^{-|x-y|/\xi} \, (1 - n_y) n_x$$

7. The Algebra $\mathcal{A}_S$ is generated by covariant operators with matrix elements

$$\langle x | A_\omega | y \rangle = A(\mathrm{T}^{-x} \omega, y - x)$$

with $(\omega, x) \in \Omega \times \mathbb{Z}^d \mapsto A(\omega, x) \in \mathbb{C}$ continuous with compact support contained in the subset with $x \in L_\omega$.

Theorem 3 *The previous model defined unambiguously a Lindbladian acting on $\mathcal{A}_S$.*

J. BELLISSARD, Lecture Notes in Physics, **597**, 413-486, (2003).

Theorem 4 *The instantaneous Hamiltonian dynamics with external noise at infinite volume is well defined, almost surely non unitary. It becomes unitary if the noise is included in the Hilbert space of states. The corresponding averaged evolution is described by the previous Lindbladian.*

D. SPEHNER, J. BELLISSARD, J. Stat. Phys., **104**, 525-572, (2001).

This model gives an equivalent version of the Miller & Abrahams random resistor network approach to this problem. See:

D. SPEHNER, Ph.D. Thesis, Toulouse, 13 March 2000.

Quantum Noise Models

1. Electrons are treated in *second quantization*, and in a *finite volume*.

2. The time dependent noise is produced by *bosons* (quantum Poissonian noise) mimicking the effect of *phonons* (environment).
   They produce *random electron jumps*.

3. The quantum evolution is *unitary* if the environment is included.

4. The average over the environment gives a Lindbladian $\mathfrak{L}_Q$.

5. If a *detailed balance condition* is imposed to the jump probabilities, $\mathfrak{L}_Q$ admits a unique equilibrium state that is the usual Gibbs state.

6. The previous analysis leading to Kubo's formula applies.

Conclusion

1. Various mechanisms of conductivity observed in a-periodic solids (semiconductors or quasicrystals at low temperature) leads to consider again transport theory for such systems.

2. Linear response theory requires *a coarse-graining* of the microscopic theory to define the current that is measured macroscopically. This leads to the *local equilibrium approximation* (LEA), to entropy creation by constant return to local equilibrium and to the validity of linear response.

3. The *Master equation* describes the dynamics within the LEA, provided the Markov approximation is valid on time scales of the order of the relaxation time to local equilibrium.

4. The Master Equation leads to the *Green-Kubo* formula for Onsager (transport) cœfficients.

5. Kinetic models are usually proposed to mimick the effect of the *environment* (Phonons, *etc.*)