Vibrational nonequilibrium

in transport through single molecules

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Felix von Oppen

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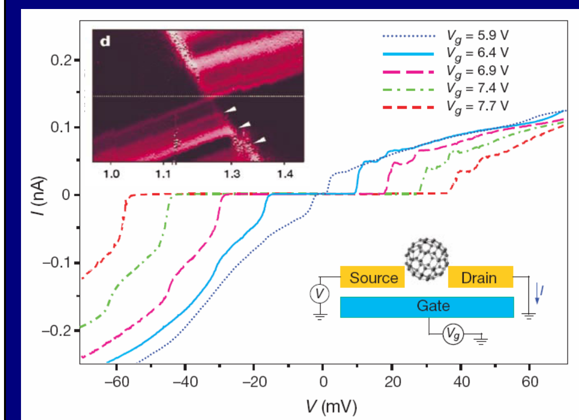
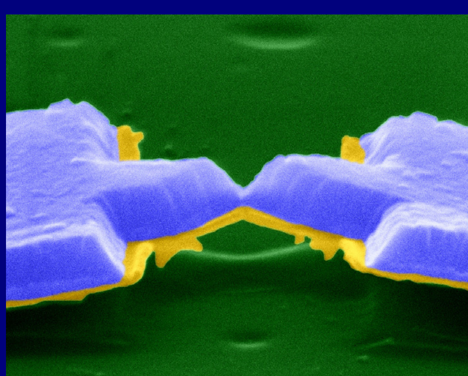
Experiments: Examples

Nanomechanical oscillations in a single-C_{60} transistor

Hongkun Park*‡§, Jiwoong Park†, Andrew K. L. Lim*, Erik H. Anderson‡, A. Paul Alivisatos*‡ & Paul L. McEuen†‡

NATURE | VOL 407 | 7 SEPTEMBER 2000

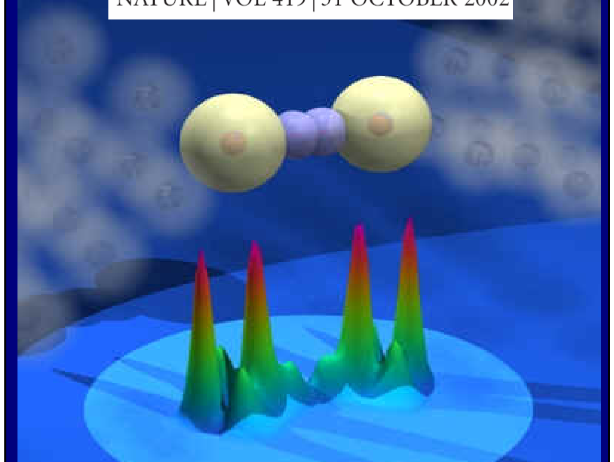


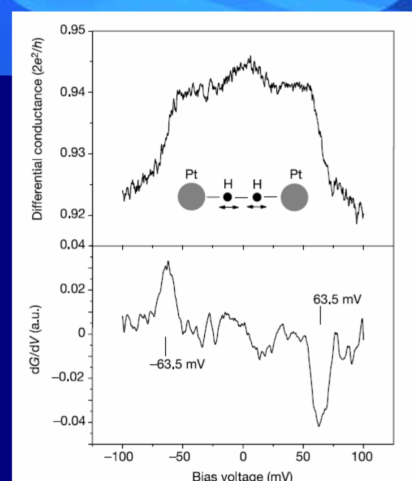


Measurement of the conductance of a hydrogen molecule

R. H. M. Smit*, Y. Noat*†, C. Untiedt*, N. D. Lang‡, M. C. van Hemert§ & J. M. van Ruitenbeek*

NATURE | VOL 419 | 31 OCTOBER 2002

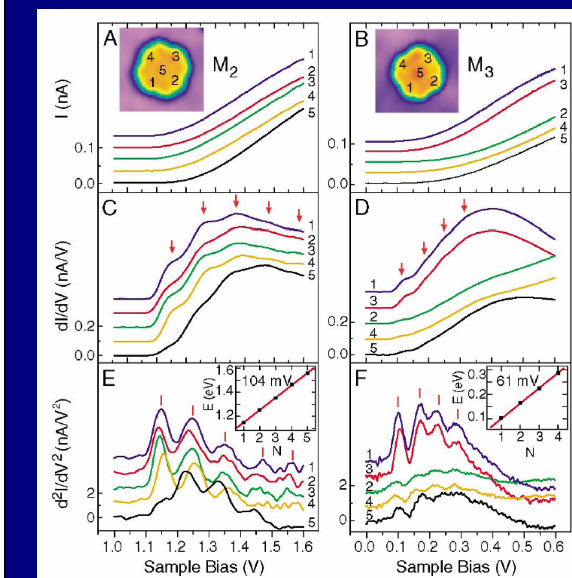


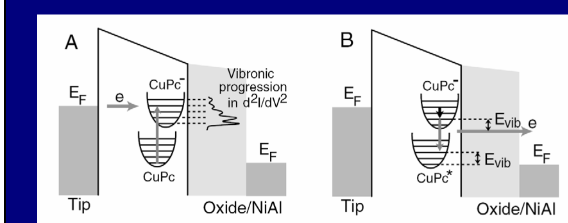


Vibronic States in Single Molecule Electron Transport

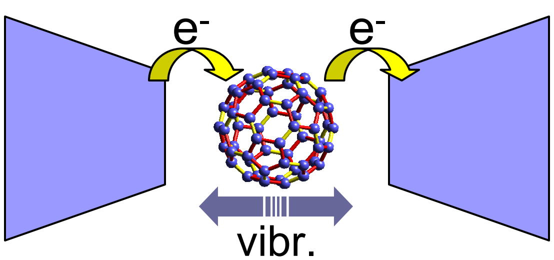
X. H. Qiu, G. V. Nazin, and W. Ho*

Phys. Rev. Lett. **92** (2004) 201602



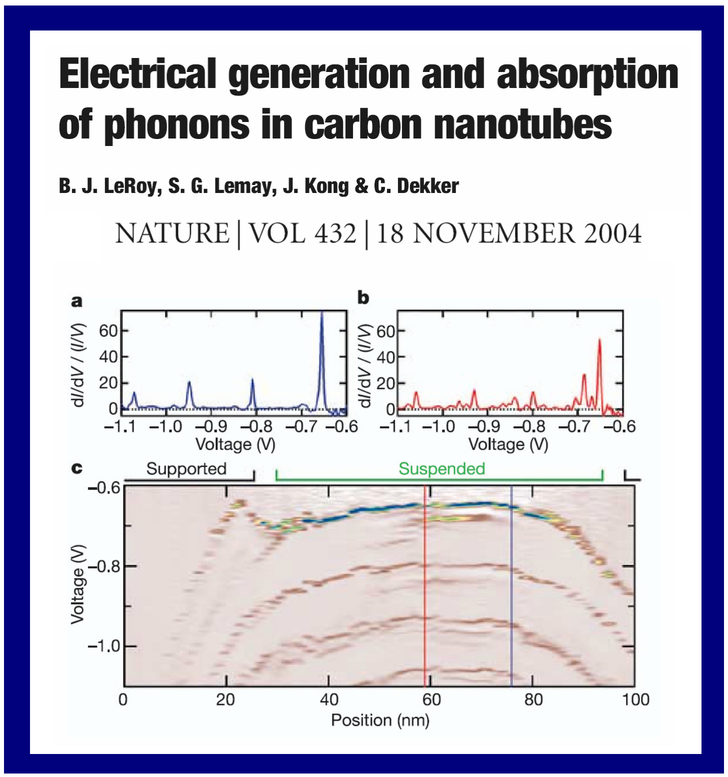


Vibrational nonequilibrium



Rate of electron transfer: **I/e**

$$I = \begin{cases} 1\text{nA} & \longrightarrow \quad 10 \text{ electrons/ns} \\ 1\mu\text{A} & \longrightarrow \quad 10 \text{ electrons/ps} \end{cases}$$



Experiments:

- Vibrational relaxation time: τ as large as 10ns

interesting regime discussed in this talk:

Molecular vibrations do not relax to ground state between subsequent tunneling electrons

$$\frac{I}{e} \gg \frac{1}{\tau}$$

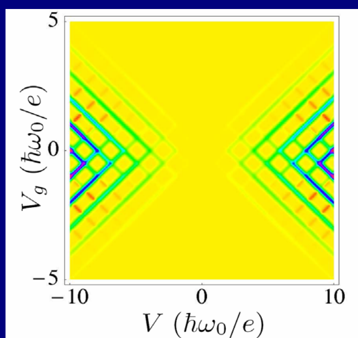
extreme case: quantum shuttles

A. Donarini and A.-P. Jauho *et al.*, e.g. cond-mat/0411190 (2004)

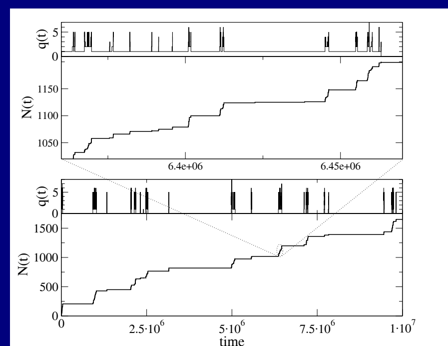
Outline

- Introduction
  - Transport through single molecules
  - Model
- Our results
  - Strong electron-phonon coupling

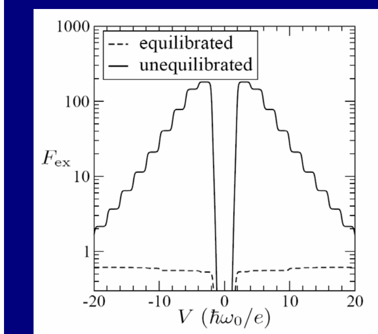
Strong electron-phonon interaction



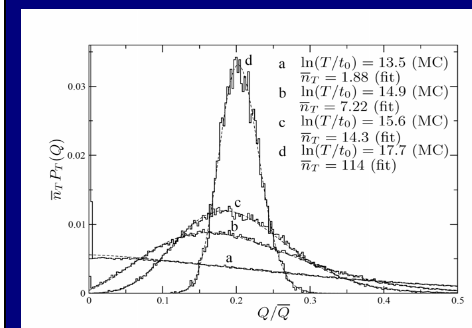
Franck-Condon blockade



self-similar avalanche transport



giant current noise



analytical full counting statistics

with Felix von Oppen
cond-mat/0409667
(accepted for publication in Phys. Rev. Lett.)

with Misha Raikh
& Felix von Oppen
cond-mat/0501065

Outline

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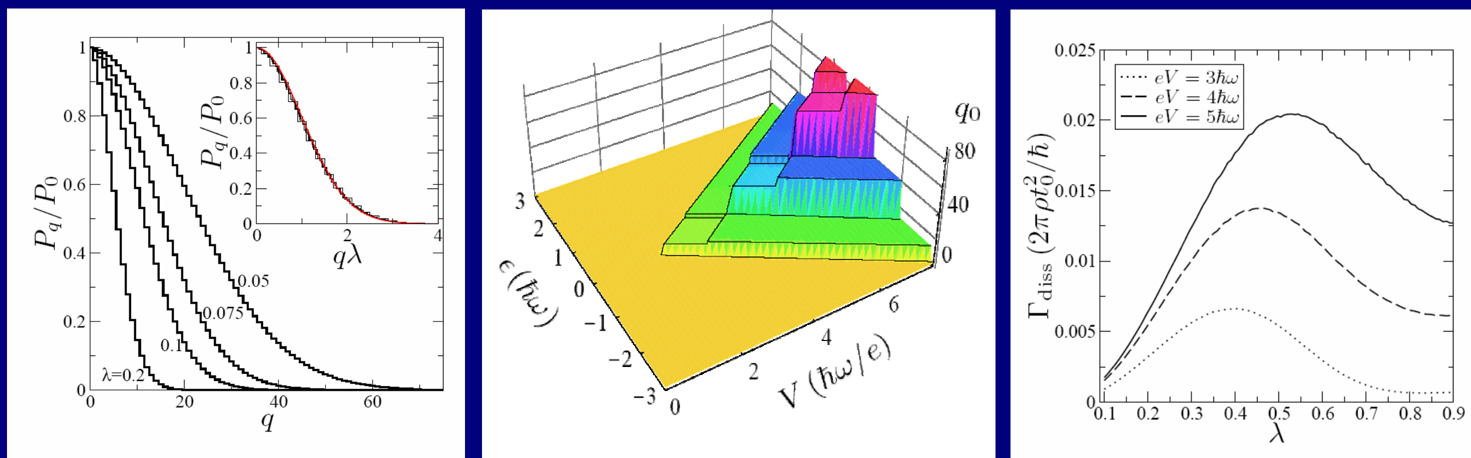
  - Strong electron-phonon coupling
  - Weak electron-phonon coupling

Weak electron-phonon interaction



broad phonon distributions *scaling behavior* *dissociation rates*

with Matthias Semmelhack, Felix von Oppen & Abraham Nitzan

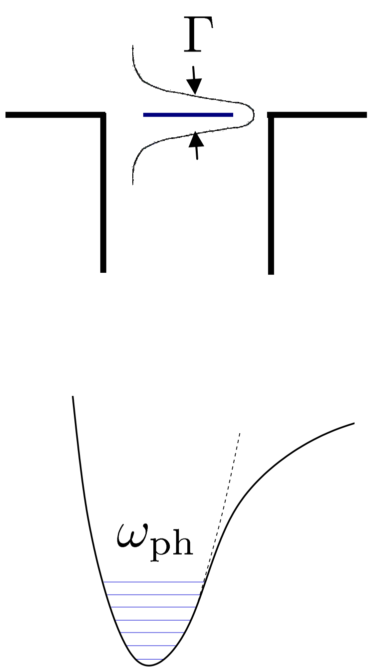
cond-mat/0504095

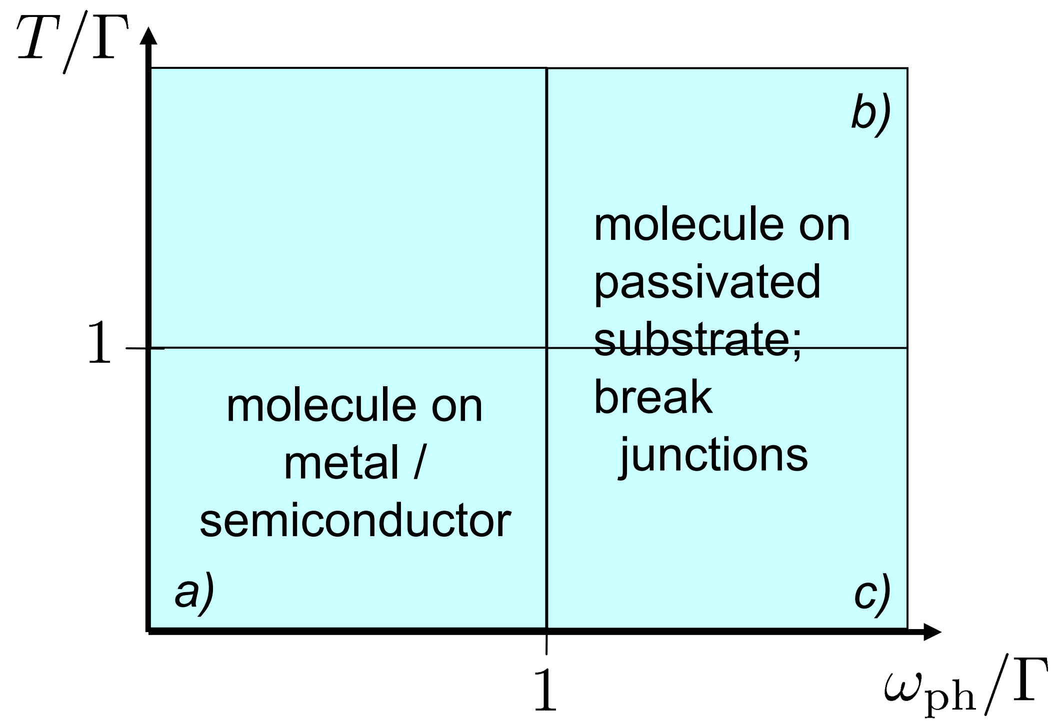
Outline

- Introduction
  - Transport through single molecules
  - Model
- Our results
  - Strong electron-phonon coupling
  - Weak electron-phonon coupling
  - Thermopower of a single molecule

    J. Koch, F. v. Oppen, Y. Oreg, and Eran Sela,
    Phys. Rev. B **70** (2004), 195107

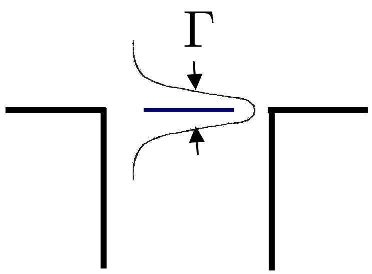
Transport regimes

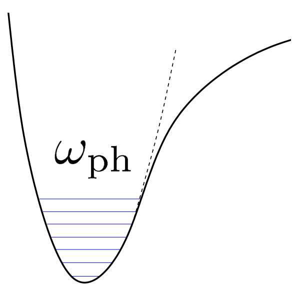


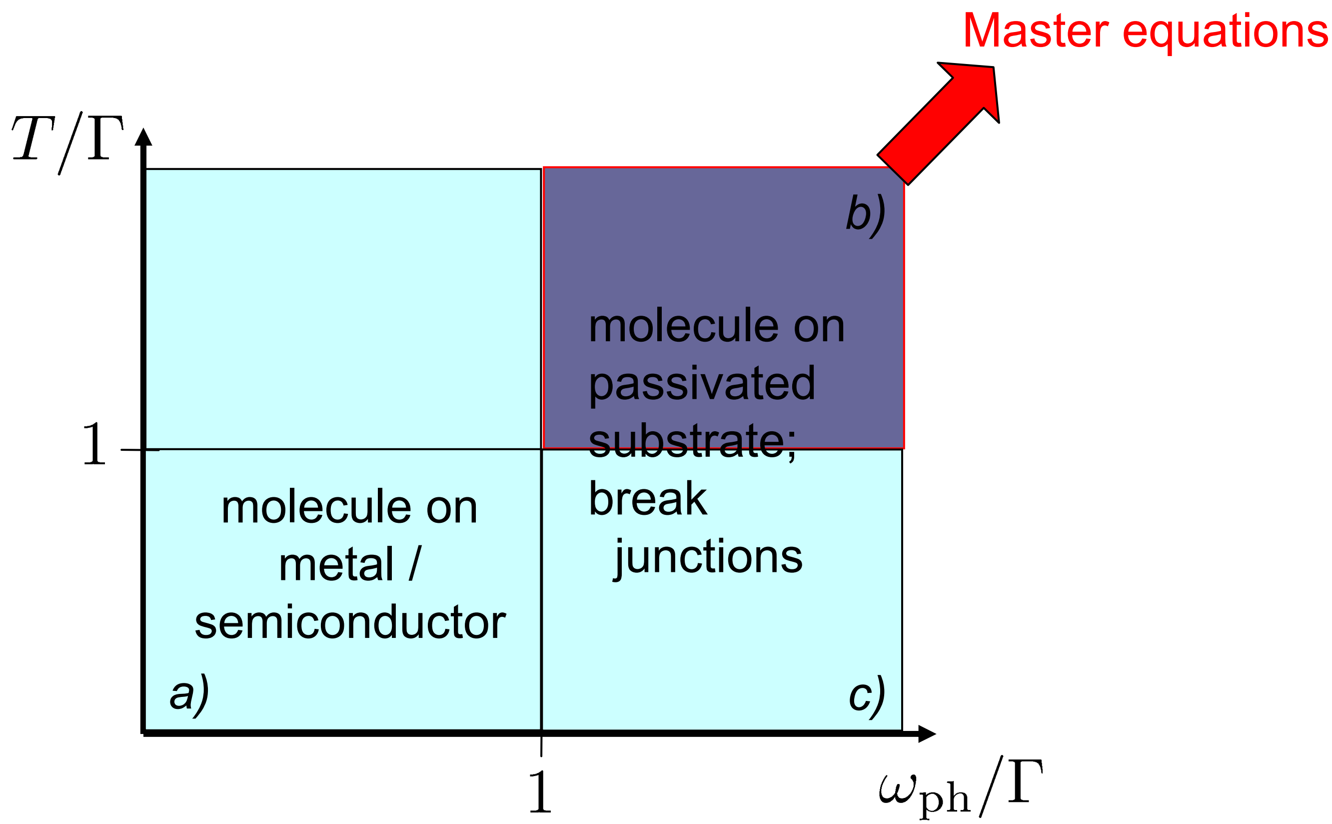


e.g.
a) Mitra et al., Phys. Rev. B **69** (2004) 245302 – Keldysh approach
b) Mitra et al., ibid.; Braig & Flensberg, Phys. Rev. B **68** (2003) 205324
c) Flensberg, Phys. Rev. B **68** (2003) 205323

Transport regimes







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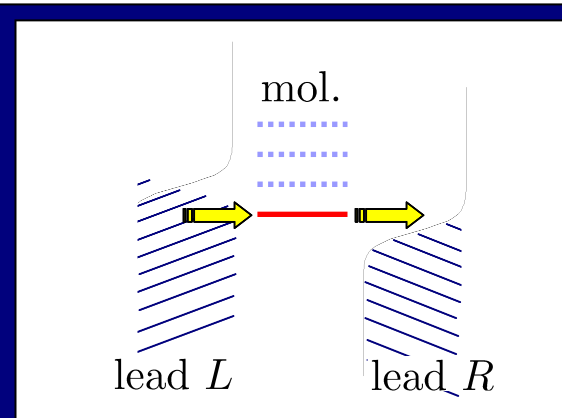
Model including electron-phonon coupling

(in Born-Oppenheimer approximation)

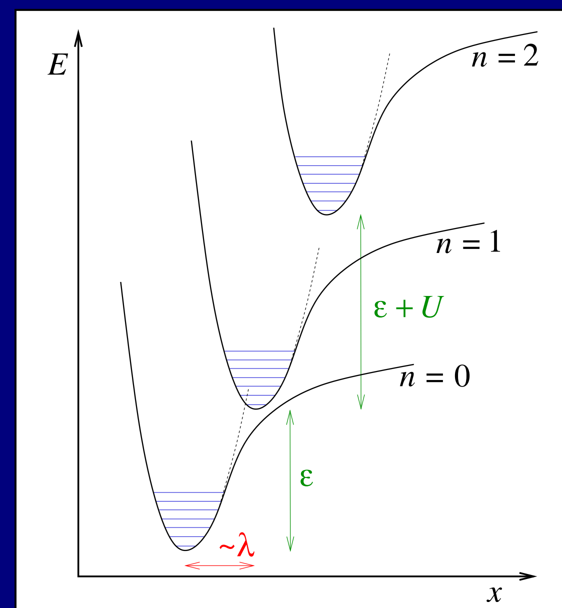


Hamiltonian:

$$H = H_{\mathrm{mol}} + H_{\mathrm{leads}} + H_{\mathrm{mix}}$$

where

$$\begin{aligned} H_{\mathrm{mol}} =& (\varepsilon - eV_g)n_d + \frac{U}{2} n_d(n_d - 1) \\ &+ \lambda \hbar\omega_{\mathrm{vib}}(b^\dagger + b)n_d + \hbar\omega_{\mathrm{vib}}(b^\dagger b + 1/2) \\ H_{\mathrm{leads}} =& \sum_{a=L,R} \sum_{\mathbf{p},\sigma} \epsilon_{\mathbf{p}} c^\dagger_{a\mathbf{p}\sigma} c_{a\mathbf{p}\sigma} \ , \\ H_{\mathrm{mix}} =& \sum_{a=L,R} \sum_{\mathbf{p},\,\sigma} \left(t_a c^\dagger_{a\mathbf{p}\sigma} d_\sigma + \mathrm{h.c.} \right) . \end{aligned}$$

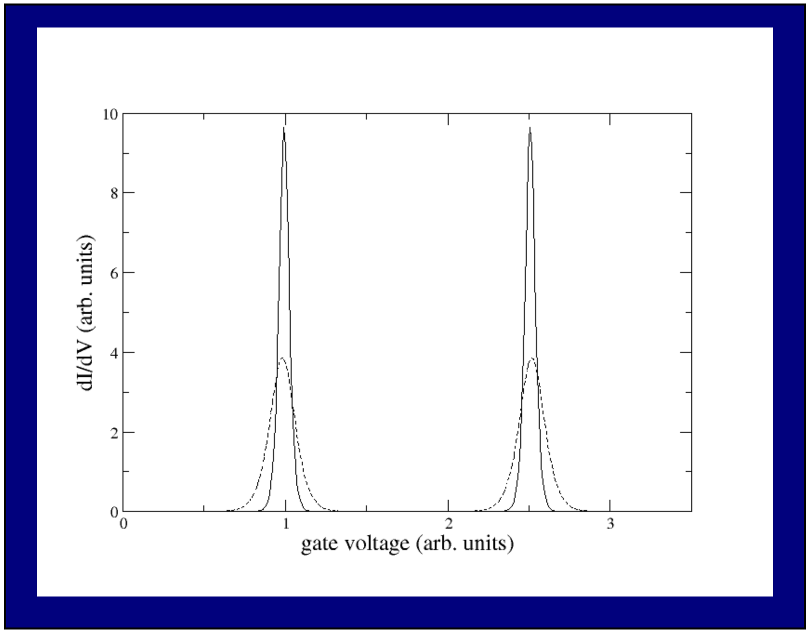


vibrations

Compare:
Works on phonon effects in resonant tunneling
Glazman, Shekhter: Sov. Phys. JETP **67** (1988) 163
Wingreen, Jacobsen, Wilkins: PRL **61** (1988) 1396

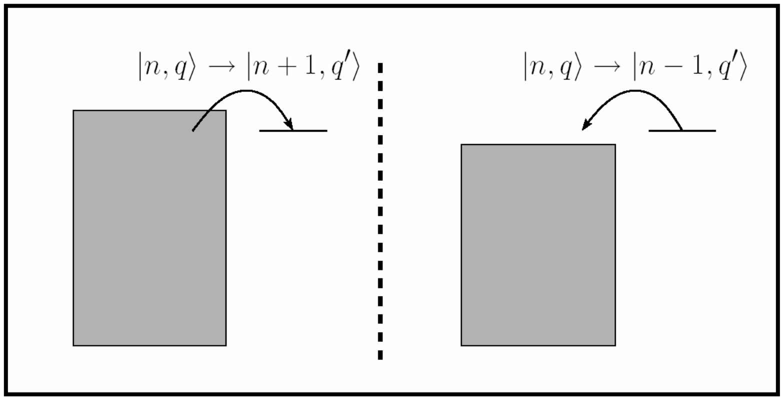
Basic processes

- Perturbation theory in molecule-lead coupling



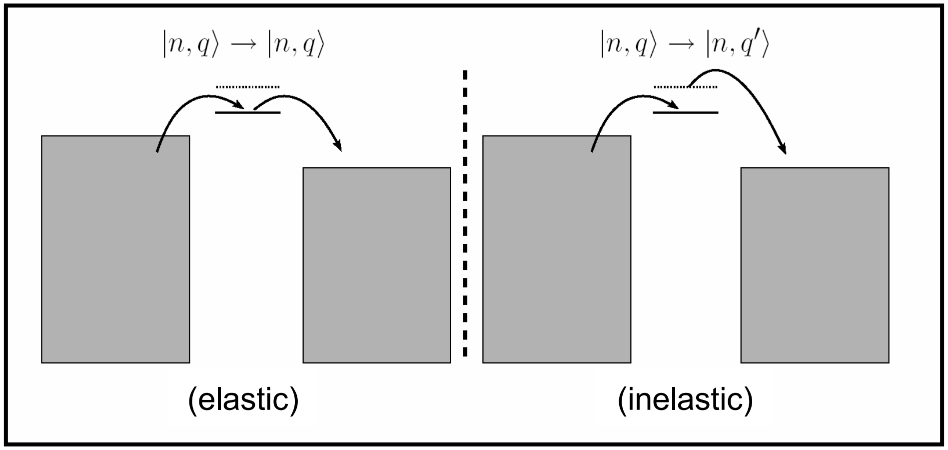
Lowest order

Sequential tunneling:



Next-leading order

Cotunneling:



- Eliminate electron-vibron coupling
  - Canonical transformation: $H' = e^{iS} H e^{-iS^\dagger}$ with $S = i\lambda(b - b^\dagger)n_d$

    Renormalizations: $\varepsilon' = \varepsilon - \lambda^2 \hbar\omega_0,\ U' = U - 2\lambda^2\hbar\omega_0$

    $$t'_a = e^{-\lambda(b^\dagger - b)} t_a$$

- Diagonalize transformed Hamiltonian (w/o tunneling)
  - Eigenstates $|n, q\rangle$ characterized by electron and phonon number

- Rate equations

$$\frac{dP_q^n}{dt} = \sum_{n',q'} \left[P_{q'}^{n'} W_{q'\to q}^{n'\to n} - P_q^n W_{q\to q'}^{n\to n'} \right] - \underbrace{\frac{1}{\tau}\left[P_q^n - P_q^{\mathrm{eq}} \sum_{q'} P_{q'}^n \right]}$$

phonon relaxation

- Current

$$I = \sum_{n,q,q'} P_q^n \left[W_{q\to q';\,L}^{n\to(n+1)} - W_{q\to q';\,L}^{n\to(n-1)} \right]$$

Transition rates

- **Total transition rates**
  - Sequential tunneling (e.g. $|\, n, q \,\rangle \rightarrow |\, n-1, q' \,\rangle$)

$$W_{q\rightarrow q'}^{n\rightarrow(n-1)} = \sum_{a=L,R} \left[1 - f_a\left(E_q^n - E_{q'}^{(n-1)}\right)\right] \Gamma_{q\rightarrow q';\,a}^{n\rightarrow(n-1)}.$$

occupation probabilities in the leads

- **Fermi's golden-rule**

$$\Gamma_{q\rightarrow q';\,a}^{n\rightarrow(n-1)} = s^{n\rightarrow(n-1)} \frac{2\pi}{\hbar} \rho\, |t_0|^2\, |\langle\, n-1, q' \,|\, H_{\mathrm{mix},a} \,|\, n, q \,\rangle|^2$$

$$= s^{n\rightarrow(n-1)} \frac{2\pi}{\hbar} \rho\, |t_0|^2\, |M_{q\rightarrow q';\,a}|^2$$

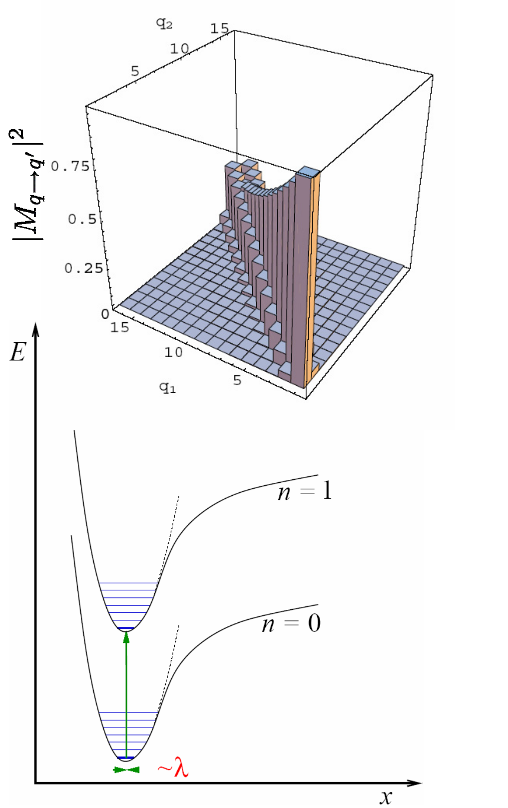
electronic contributions

phononic contributions:
Franck-Condon matrix elements

Franck-Condon matrix elements

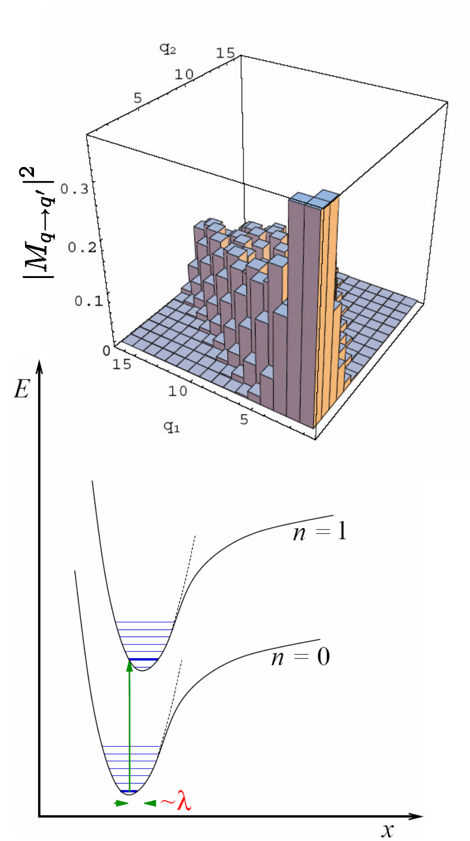
$$M_{q\to q'} = \langle\, q' \,|\, e^{-\lambda(b^\dagger - b)} \,|\, q \,\rangle = \int_{-\infty}^{\infty} dx\, \phi^*_{q'}(x)\phi_q(x - \sqrt{2}\lambda\ell_{\rm osc})$$

harmonic oscillator wavefunctions



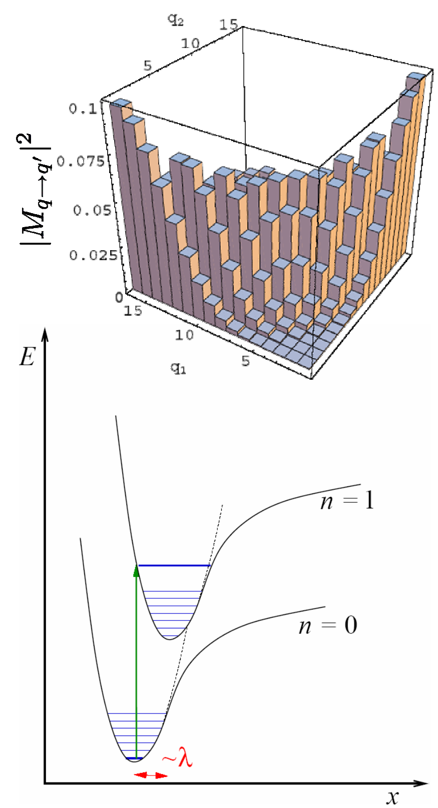
weak

$\lambda \ll 1$



intermediate

$\lambda \sim 1$

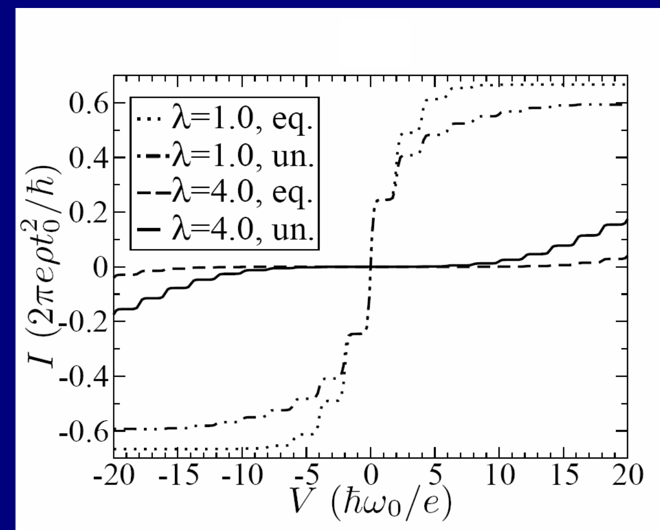


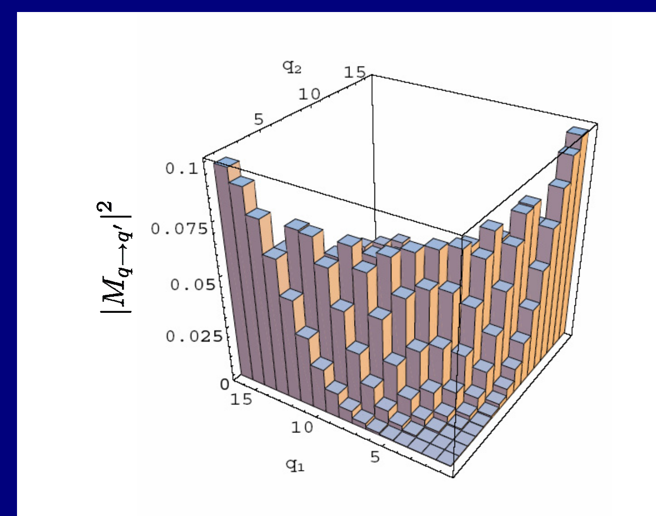
strong

$\lambda \gg 1$

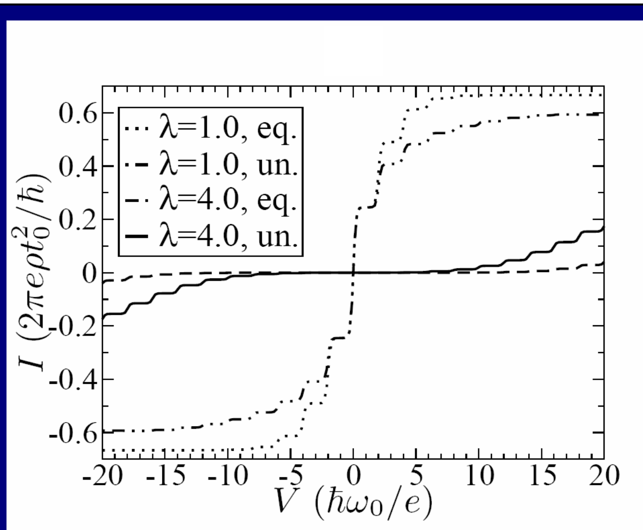
Strong electron-phonon coupling

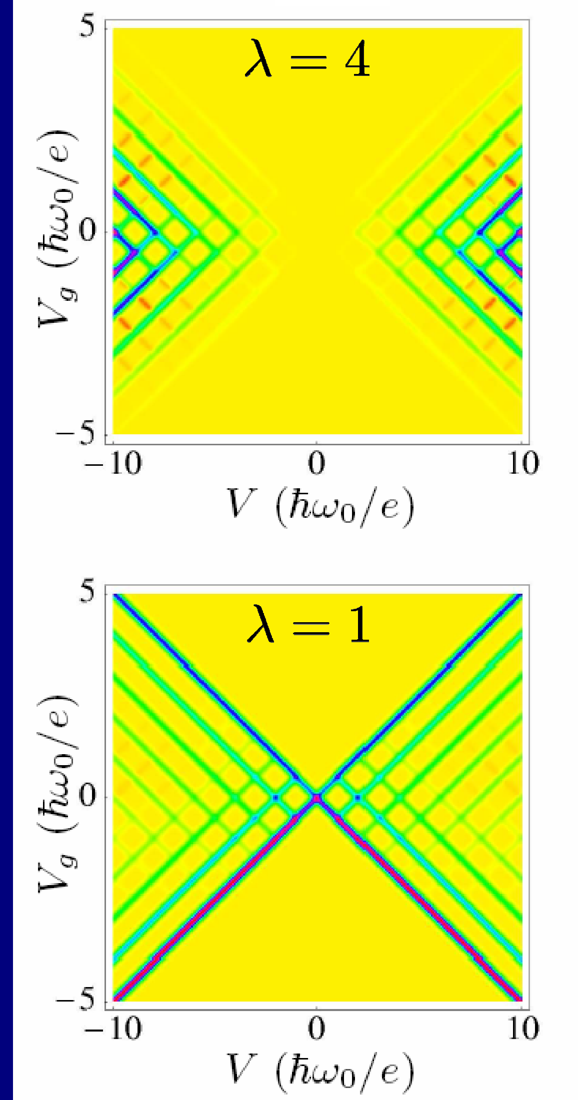
- Franck-Condon Blockade
  - Significant low-bias current suppression for strong coupling
    - Franck-Condon Blockade –
  - Blockaded bias range:
    $$eV \sim \lambda^2 \hbar\omega_0$$
  - Reason: Exponentially suppressed Franck-Condon matrix elements
  - Suppression is less strict for unequilibrated phonons





Franck-Condon blockade: Experimental fingerprints



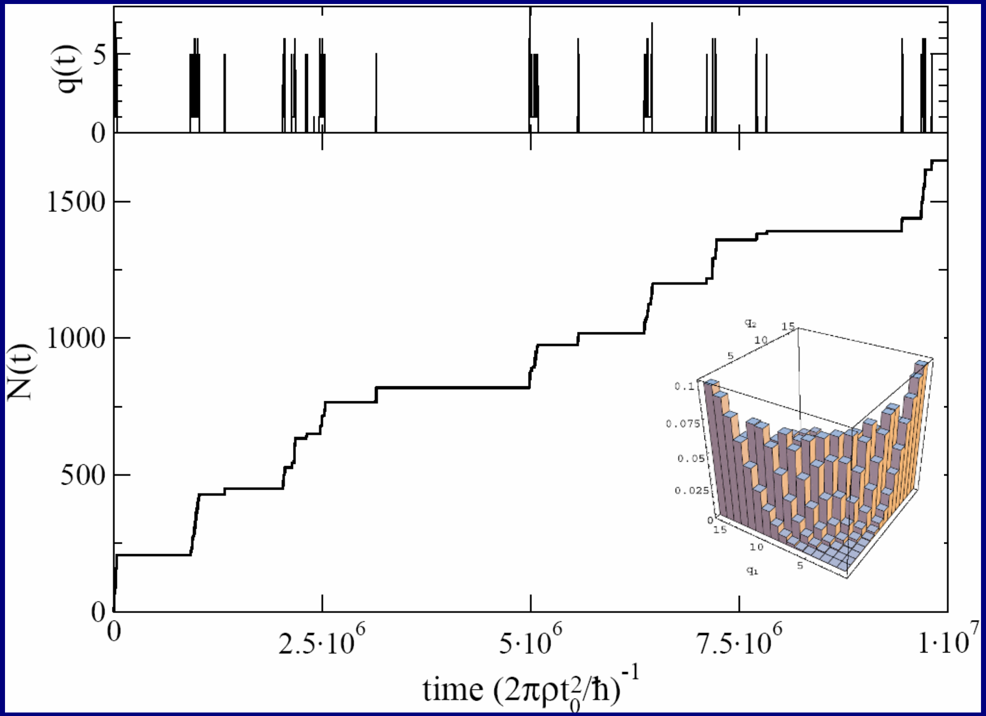


- Step height succession in IV
  - Increasing step heights in FCB regime
- FCB cannot be lifted by gate voltage
  - Extended blockaded region in dI/dV plots

Monte Carlo simulations

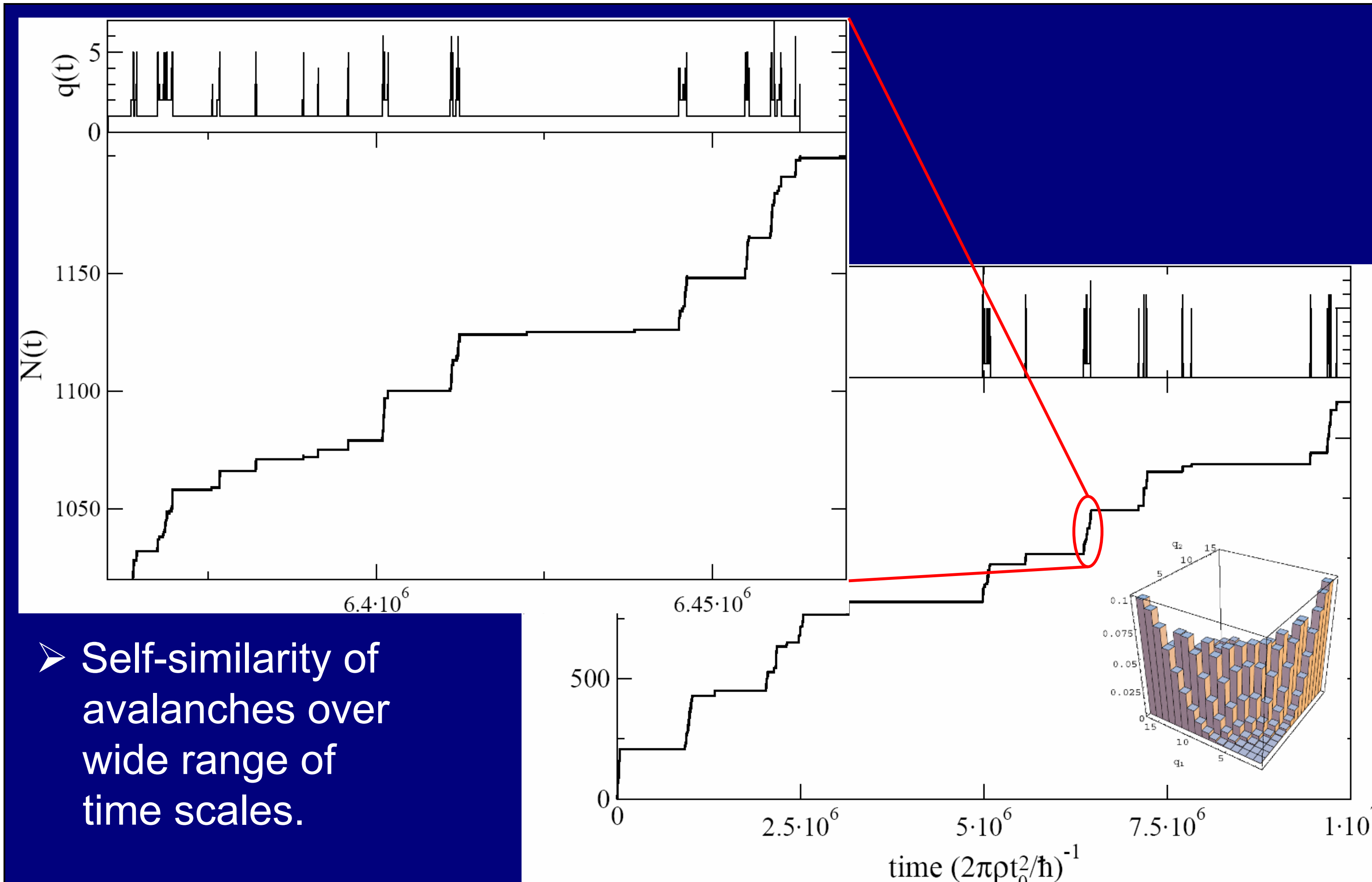
- Simulate tunneling events in time: **Strong e-ph coupling, nonequilibrium**

- Avalanche-like electron transport



Monte Carlo simulations

- Simulate tunneling events in time: **Strong e-ph coupling, nonequilibrium**



- Self-similarity of avalanches over wide range of time scales.

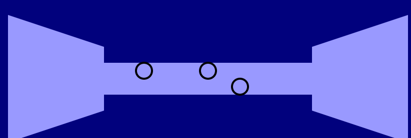
Shot noise

- Current noise: $$S(\omega) = 2\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle \delta I(t+t')\delta I(t')\rangle_{t'}$$
- Schottky (1918): $$S = 2e|I|$$
- Fano factor: $$S(\omega = 0) = 2e|I| \cdot F$$
- Noise contains information about
  - Charge of carriers
  - Type of conduction process

Noise in nanostructures: Examples

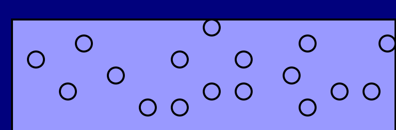
Single-channel wire

$$S = 2e|I|(1-T)$$



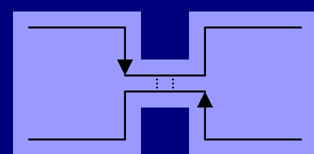
Diffusive many-channel wire

$$S = 2/3e|I|$$



FQHE $\nu = 1/3$

$$S = 2/3e|I_{\mathrm{bs}}|$$



Noise in transport through single molecules

- Current noise:

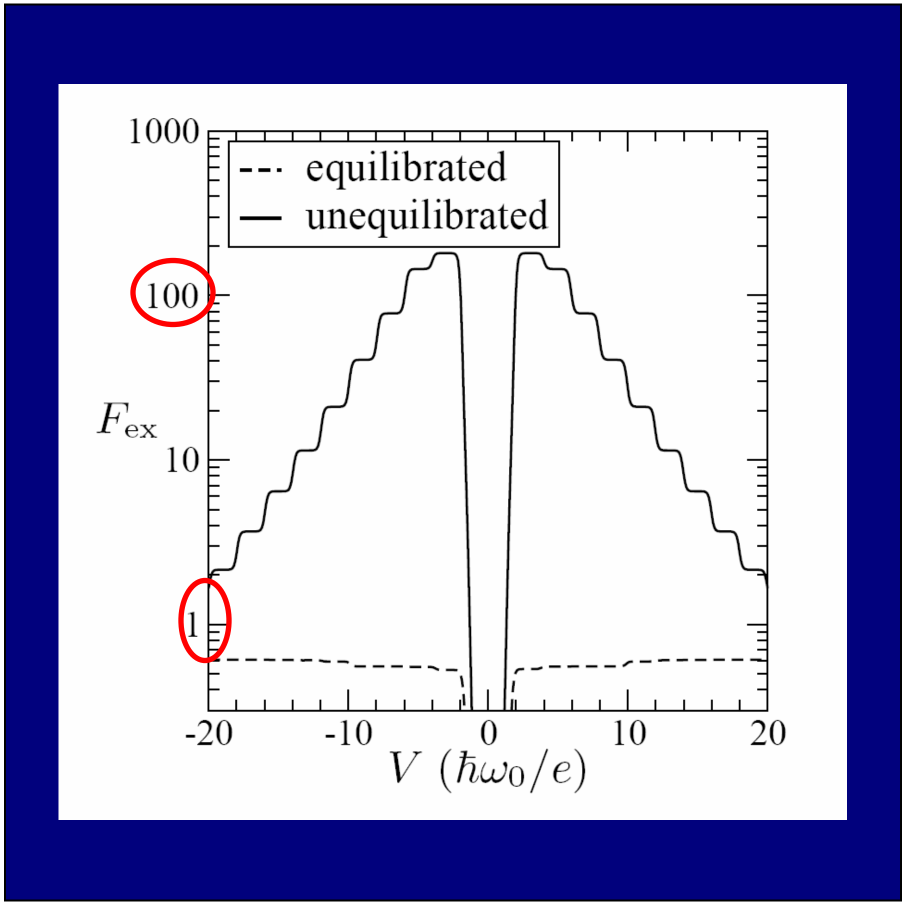
$$S(\omega) = 2\int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle \delta I(t+t')\delta I(t')\rangle_{t'}$$

- Fano factor: $S(\omega=0) = 2e|I| \cdot F$

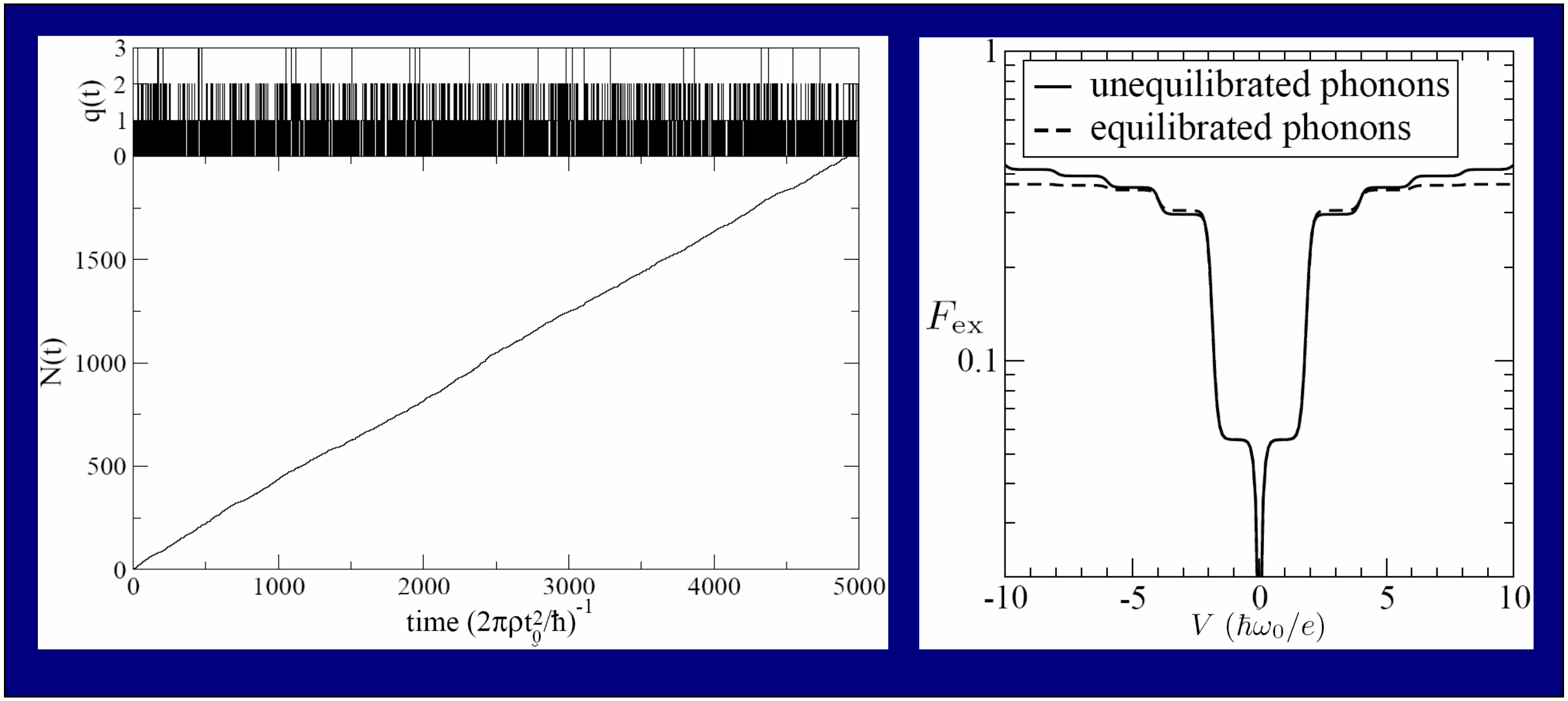
Computation: Use rate equations combined with Langevin approach
[Korotkov, Phys. Rev. B **49** (1994) 10381]

➢ Strong electron-phonon coupling and weak vibrational relaxation:

giant Fano factors F=10²..10³



Comparison: Intermediate electron-phonon coupling



- sub-Poissonian noise
- no avalanches

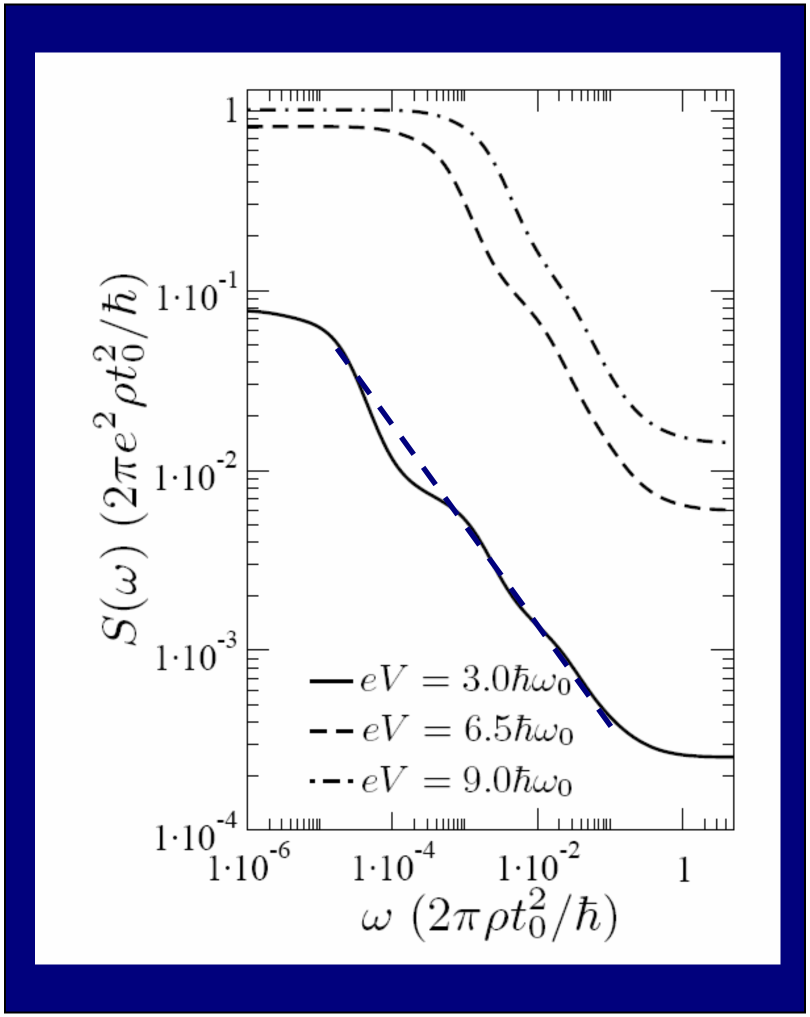
Noise power spectrum

- Approximate power-law behavior

$$S(\omega) \sim \omega^{-\alpha}, \qquad \alpha \approx 1/2$$

self-similarity of avalanches

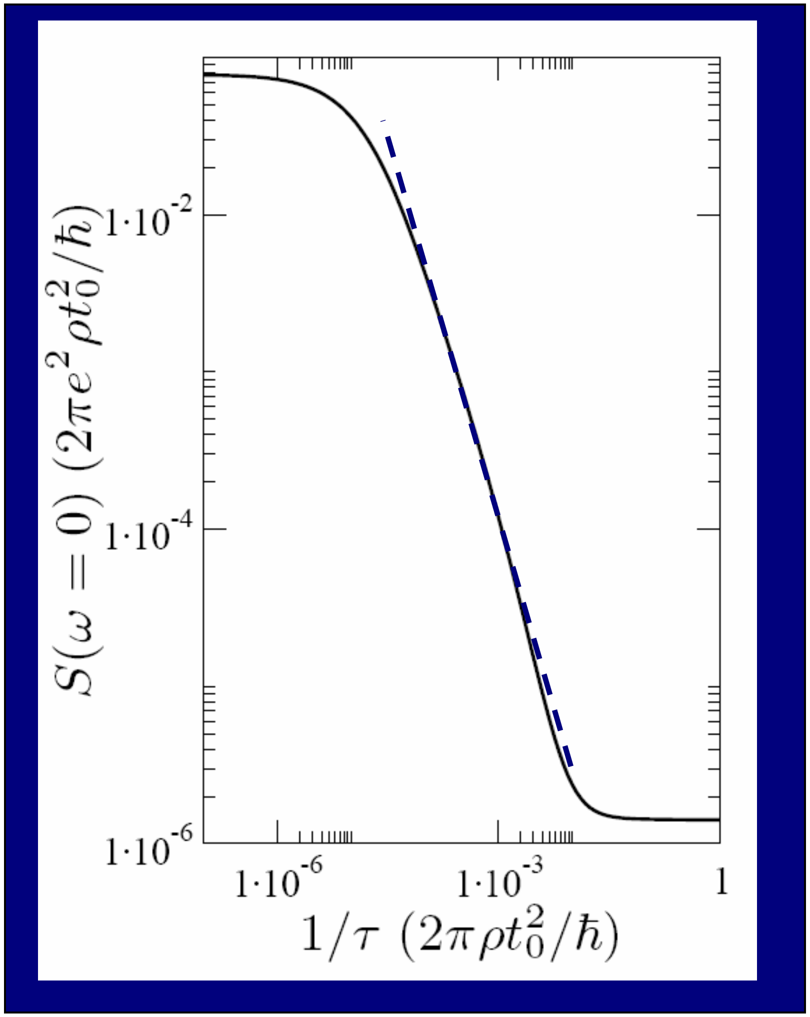
- Small oscillatory deviations from pure power law due to discreteness of the variable q



Dependence on vibrational relaxation rate

- Similar power-law behavior

$$S(\omega=0) \sim \tau^{\beta}, \qquad \beta \approx 2$$



➡ weak suppression of large Fano factors by vibrational relaxation

Analytical results

- Analytical results for current noise in low-frequency limit

$$F = \langle N_i \rangle \frac{\langle t_i^2 \rangle - \langle t_i \rangle^2}{\langle t_i \rangle^2} + \frac{\langle N_i^2 \rangle - \langle N_i \rangle^2}{\langle N_i \rangle} = 2\overline{N}^{(0)}$$

  - noise originates from fluctuations of waiting times and avalanche heights
  - Fano factor proportional to mean avalanche height

- Derivation of power-law exponents

$$S(\omega \simeq 1/\tau_{q+1}) = \frac{\overline{N}^{(q+1)}}{\overline{N}^{(q)}} S(\omega \simeq 1/\tau_q) \quad \textit{and} \quad \tau_q/(\overline{N}^{(q)})^2 \approx \text{const.} \Rightarrow S(\omega) \sim \omega^{-1/2}$$

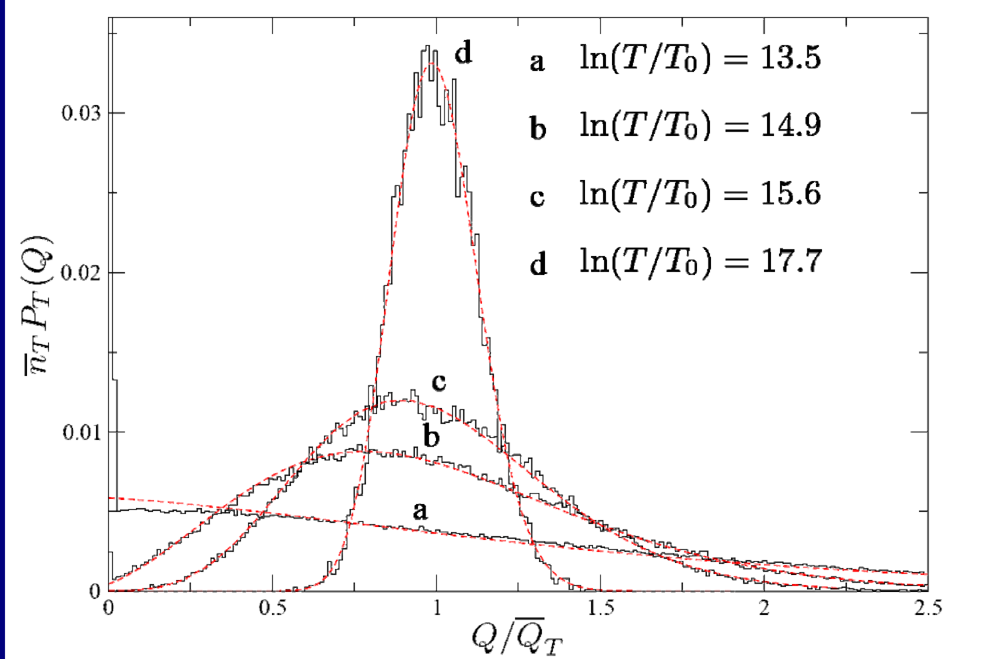
similar arguments for noise vs. relaxation time power-law

Full counting statistics

$$P_T(Q) = e^{-\overline{n}_T}\delta(Q) + e^{-\frac{Q}{\overline{N}^{(0)}} - \overline{n}_T}\sqrt{\frac{\overline{n}_T}{\overline{N}^{(0)}Q}}\, I_1\left(2\sqrt{\frac{\overline{n}_T Q}{\overline{N}^{(0)}}}\right)$$

$\overline{N}^{(0)}$: mean number of electrons per level-0 avalanche

$\overline{n}_T$: mean number of level-0 avalanches within time *T*



- strongly *non*-Gaussian (except for very long times)

Experimental realizations

■ Molecules

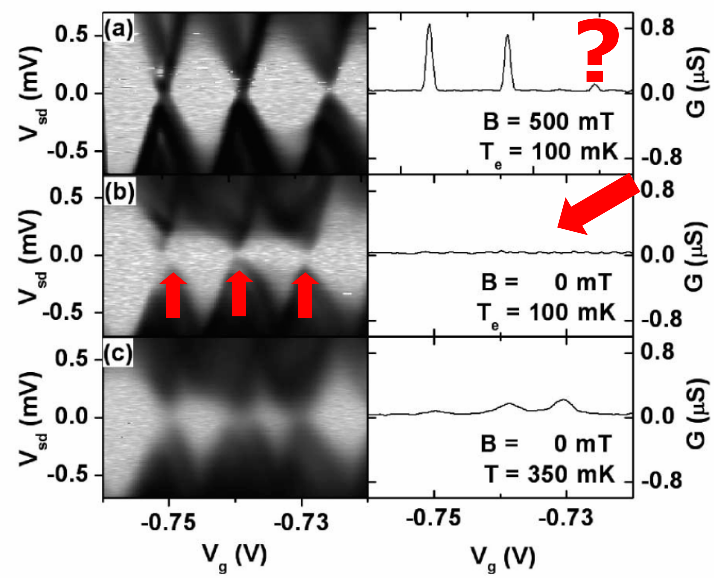
- Hydrogen molecule H_2
  $\lambda \simeq 1.8$
- Krypton molecule Kr_2
  $\lambda \simeq 5.4$
- Fluorine molecule F_2
  $\lambda \simeq 4.4$

using data from:
Huber, Herzberg: Molecular Spectra and Molecular Structure, vol. IV

■ Suspended quantum dots

Kotthaus group

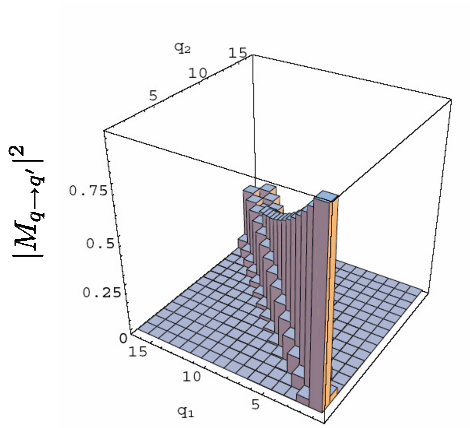
Phys. Rev. Lett. **92** (2004) 046804



Franck-Condon blockade ?

[Figure: van Ruitenbeek]

Weak electron-phonon interaction



$\lambda \ll 1$

- Asymptotics of FC matrix elements

$$|M_{q\to q'}|^2 \simeq \frac{Q!}{q!}\frac{\lambda^{2\Delta q}}{(\Delta q!)^2}$$

$$Q = \max\{q_1, q_2\}$$
$$q = \min\{q_1, q_2\}$$
$$\Delta q = Q - q$$

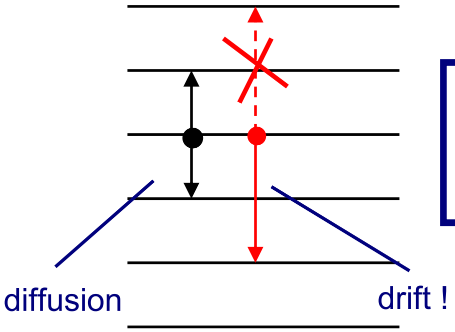
- Transitions: $q \to q \pm \Delta q$

$\Delta q = 0, 1$ dominate

- random walk in space of vibrational levels
- stationary phonon distribution ???
- slowdown of diffusion as $\lambda \to 0$

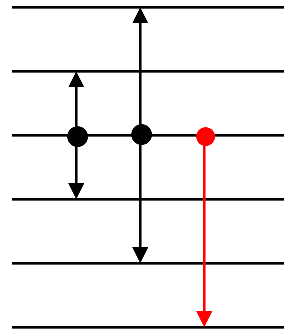
Phonon drift and scaling behavior

$2\hbar\omega < eV < 4\hbar\omega$



$q_0 \sim \frac{1}{\lambda}$

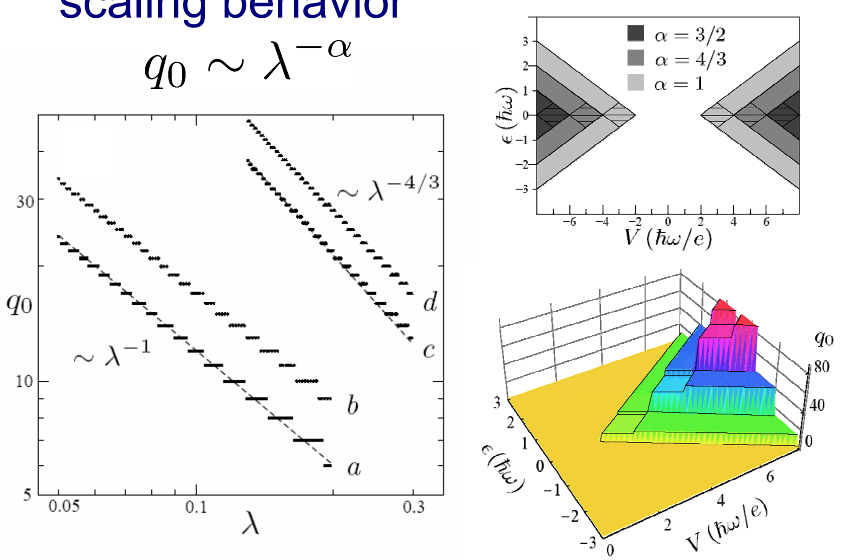
$4\hbar\omega < eV < 6\hbar\omega$



$q_0 \sim \frac{1}{\lambda^{4/3}}$

scaling behavior

$q_0 \sim \lambda^{-\alpha}$



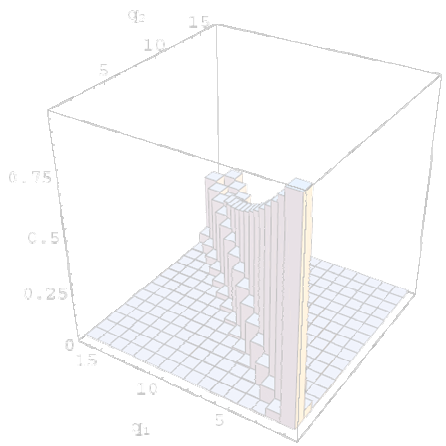
vibrational nonequilibrium grows stronger for *weaker* electron-phonon coupling

breakdown of perturbation theory

Fokker-Planck-equation

keeping leading order terms,
one obtains:

$$0 = \frac{1}{2}\frac{\partial^2}{\partial q^2}[D(q)P(q)] - \frac{\partial}{\partial q}[A(q)P(q)]$$



with $D(q) \sim q\lambda^2$ and $A(q) \sim \lambda^2 - c(q\lambda^2)^{\Delta q_m + 1}$

Solution:

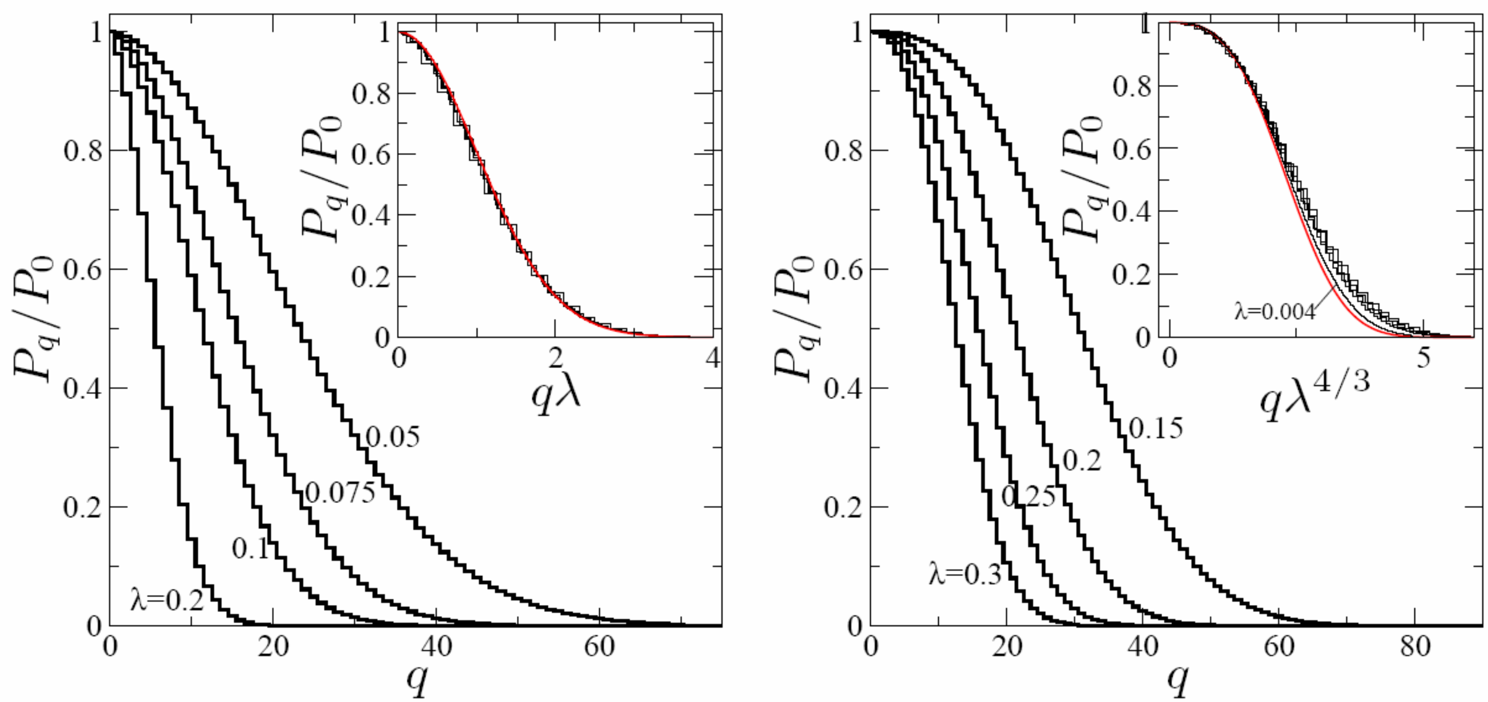
$$P(q) = \lambda^\alpha f(\lambda^\alpha q)$$

with

$$\alpha = \frac{2\Delta q_m}{\Delta q_m + 1}$$

$$f(x) \sim \exp\left[-x^{\Delta q_m + 1}/b\right]$$

Numerical confirmation

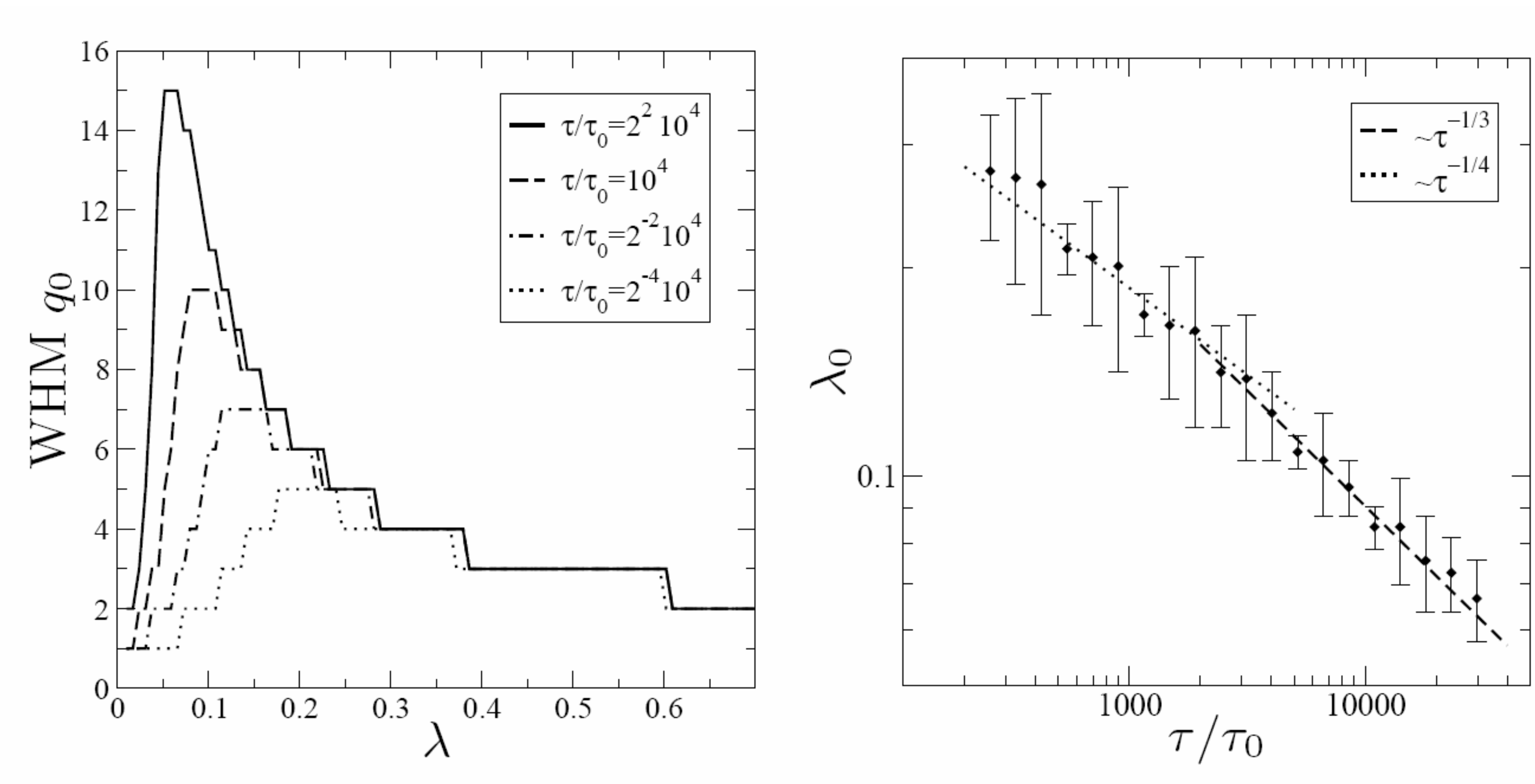


$eV = 3\hbar\omega$ $\qquad$ $eV = 5\hbar\omega$

Black: solution of rate equation for electron transport

Red: scaling solution of Fokker-Planck-equation

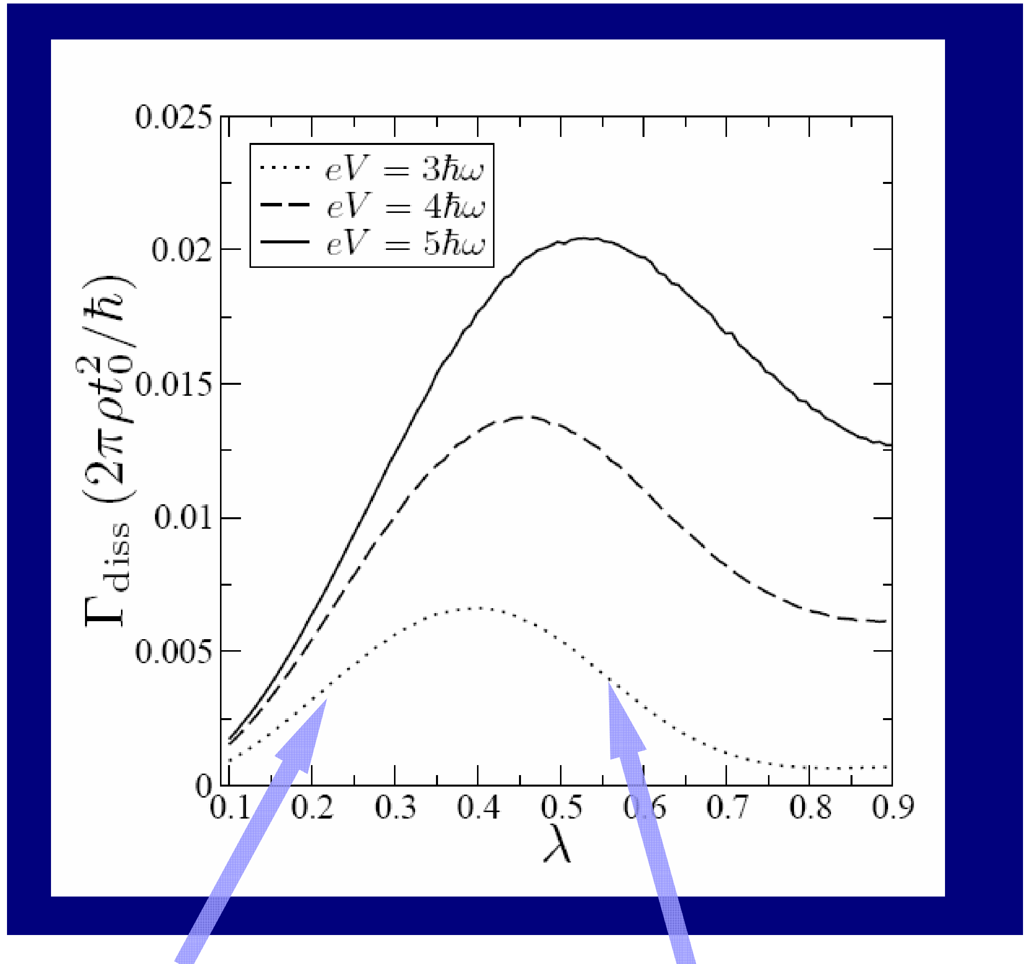
Effects of vibrational relaxation



- vibrational relaxation cuts off widening of phonon distributions below threshold λ_0

Dissociation rates

- describe potential surface by Morse potential
- Monte-Carlo simulation of rate equations with appropriately modified FC matrix elements
- measure time until electron enters vibrational continuum states



slow down of diffusion increasing width

with decreasing e-ph coupling

Conclusions

- relevance of current-induced nonequilibrium of nuclear motion
- strong electron-phonon interaction
  - Franck-Condon blockade
  - giant Fano factors for *non*equilibrated vibrational states
  - self-similar avalanche-like transport
- weak electron-phonon interaction
  - width of phonon distribution diverges for small coupling
  - analytical theory of phonon distribution from Fokker-Planck equation
  - consequences for current-induced dissociation

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