

Transport in nanostructures at the level of single electrons

Collaborators:

Thomas Ihn

Andrea Hofmann

Ville Maisi

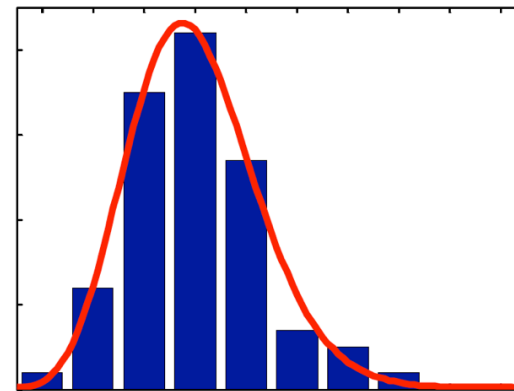
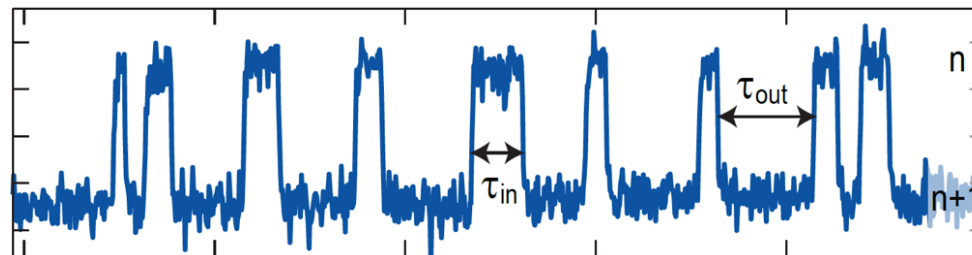
Bruno Küng

Simon Gustavsson

Roland Schleser

Martin Sgrist

Klaus Ensslin



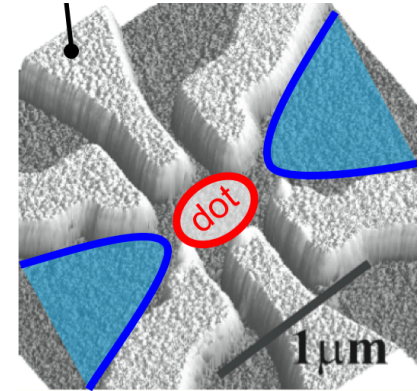
Wafers:

Werner Wegscheider

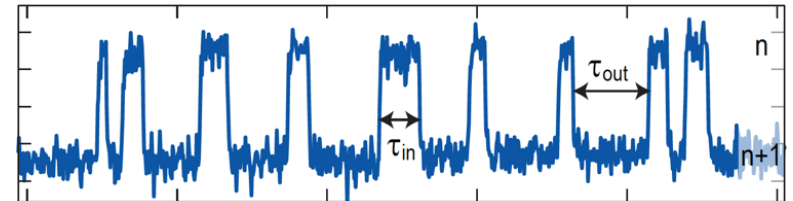
Christian Reichl

Our (tentative) program

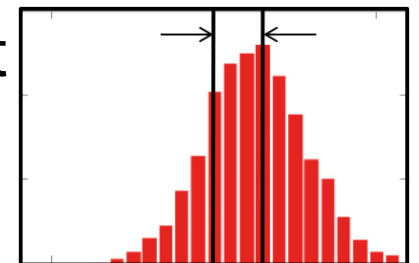
I. Handling single electrons



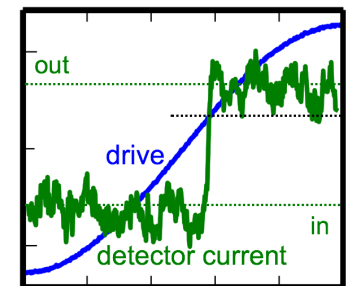
II. Single electrons in real time



III. Thermodynamic aspects of electron transport



IV. Non-equilibrium thermodynamics at the level of single electrons



Part I

Handling single electrons

Which groundbreaking paper of physics
was published 91 years ago?

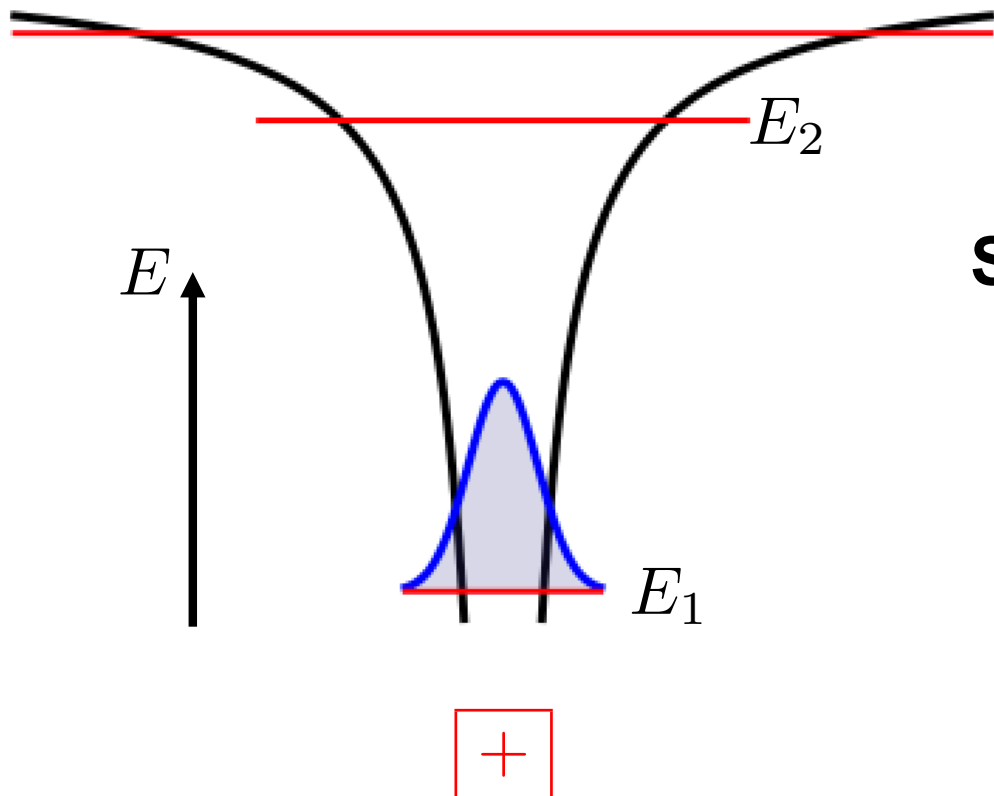
The hydrogen atom

E. Schrödinger, Phys. Rev. **28**, 1049 (1926).
Quantized energy levels in the hydrogen atom

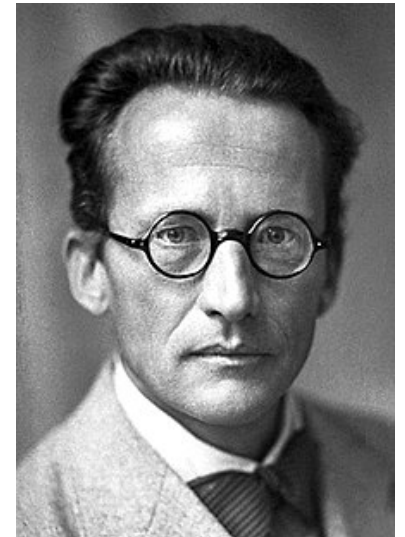


$$E_n = -\frac{E_{\text{Ry}}}{n^2}, \quad n = 1, 2, 3 \dots$$

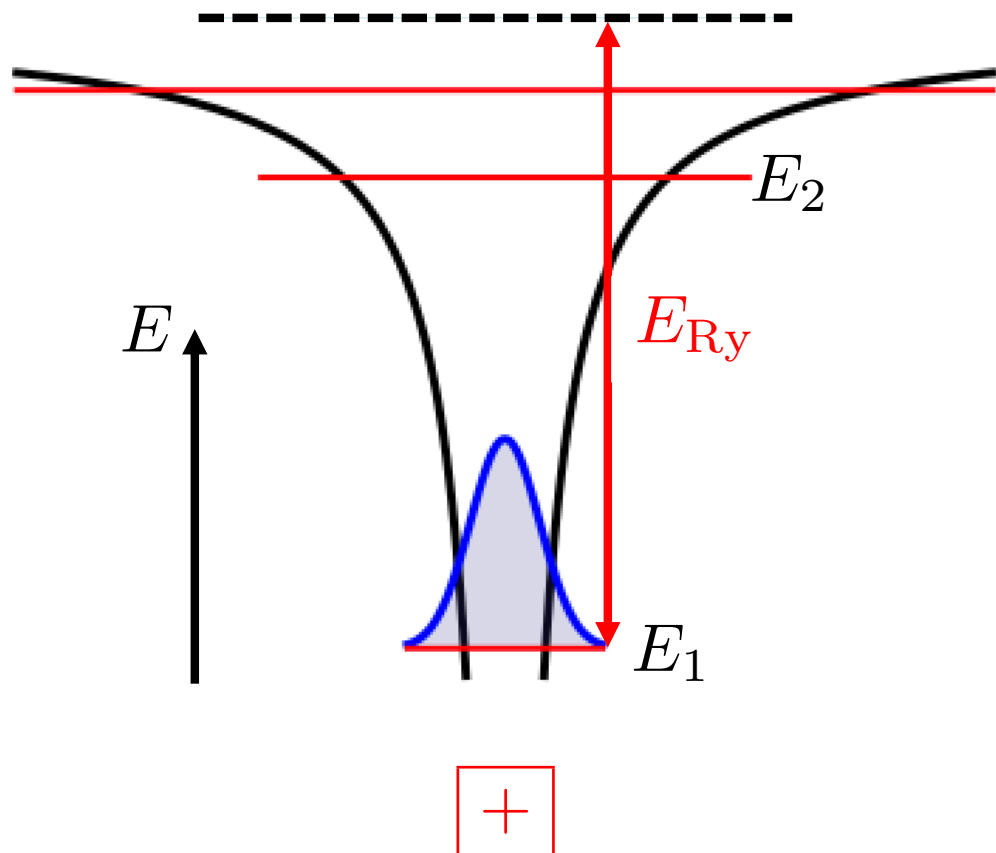
Single-particle level spectrum



The hydrogen atom



E. Schrödinger, Phys. Rev. **28**, 1049 (1926).
Quantized energy levels in the hydrogen atom



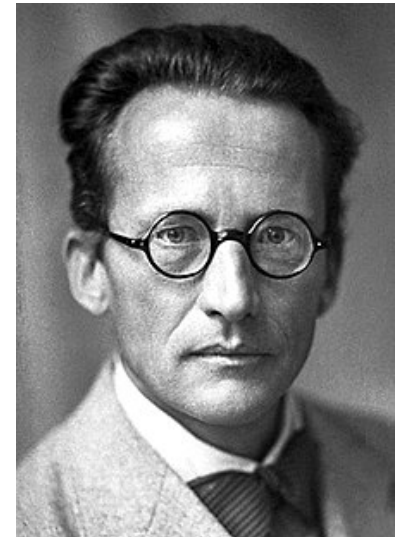
$$E_n = -\frac{E_{\text{Ry}}}{n^2}, \quad n = 1, 2, 3 \dots$$

$$E_{\text{Ry}} = \frac{2m}{\hbar^2} \left(\frac{e^2}{8\pi\epsilon_0} \right)^2$$

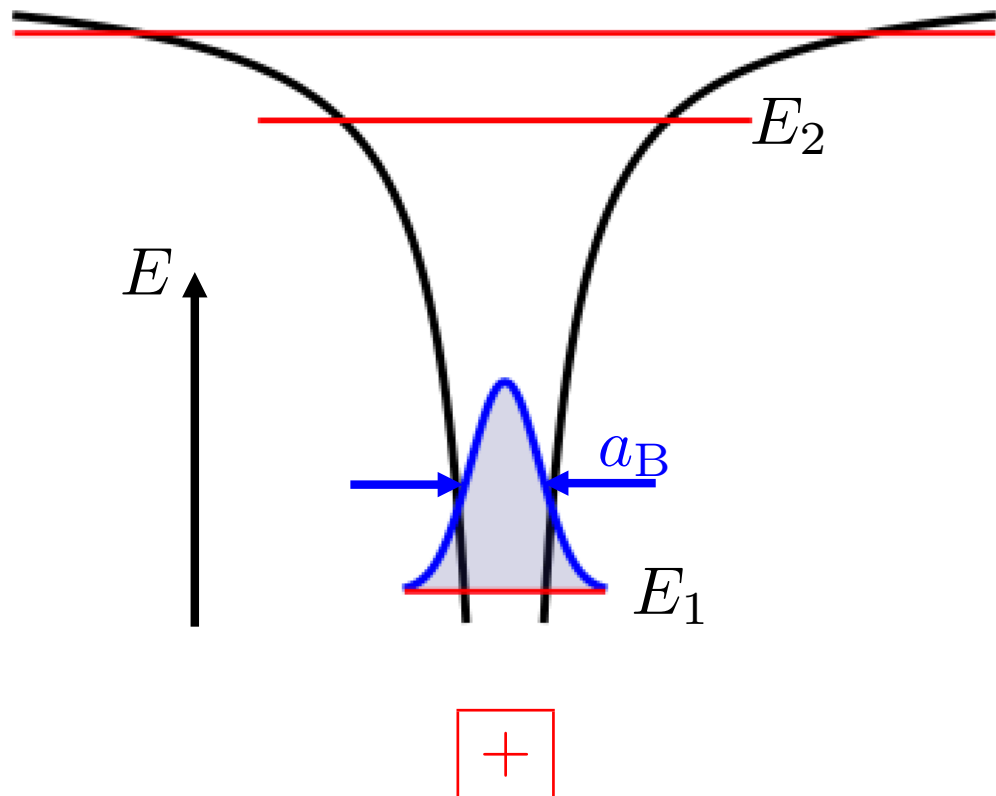
Atoms: 13.6 eV

GaAs: 6 meV

The hydrogen atom



E. Schrödinger, Phys. Rev. **28**, 1049 (1926).
Quantized energy levels in the hydrogen atom



$$E_n = -\frac{E_{\text{Ry}}}{n^2}, \quad n = 1, 2, 3 \dots$$

$$a_B = \frac{\hbar^2}{2m} \left(\frac{8\pi\epsilon_0}{e^2} \right)$$

Atoms: 0.53 Å

GaAs: 10 nm

Lessons from the hydrogen problem

Binding energy scales like $E_{\text{Ry}}^* \propto \frac{m^*}{\epsilon^2}$

Size scales like $a_{\text{B}}^* \propto \frac{\epsilon}{m^*}$

Technology sets a lower limit on size.

Materials with small m^* and large ϵ are advantageous.

The price is a smaller energy scale.

 Low-temperature experiments with nanostructures

Pauli's exclusion principle

Wolfgang Pauli:

- 1923 Privatdozent at the University of Hamburg
- Spring 1925: General formulation of the exclusion principle

W. Pauli, Z. Physik **31**, 765 (1925)

- Nobel Prize in Physics 1945



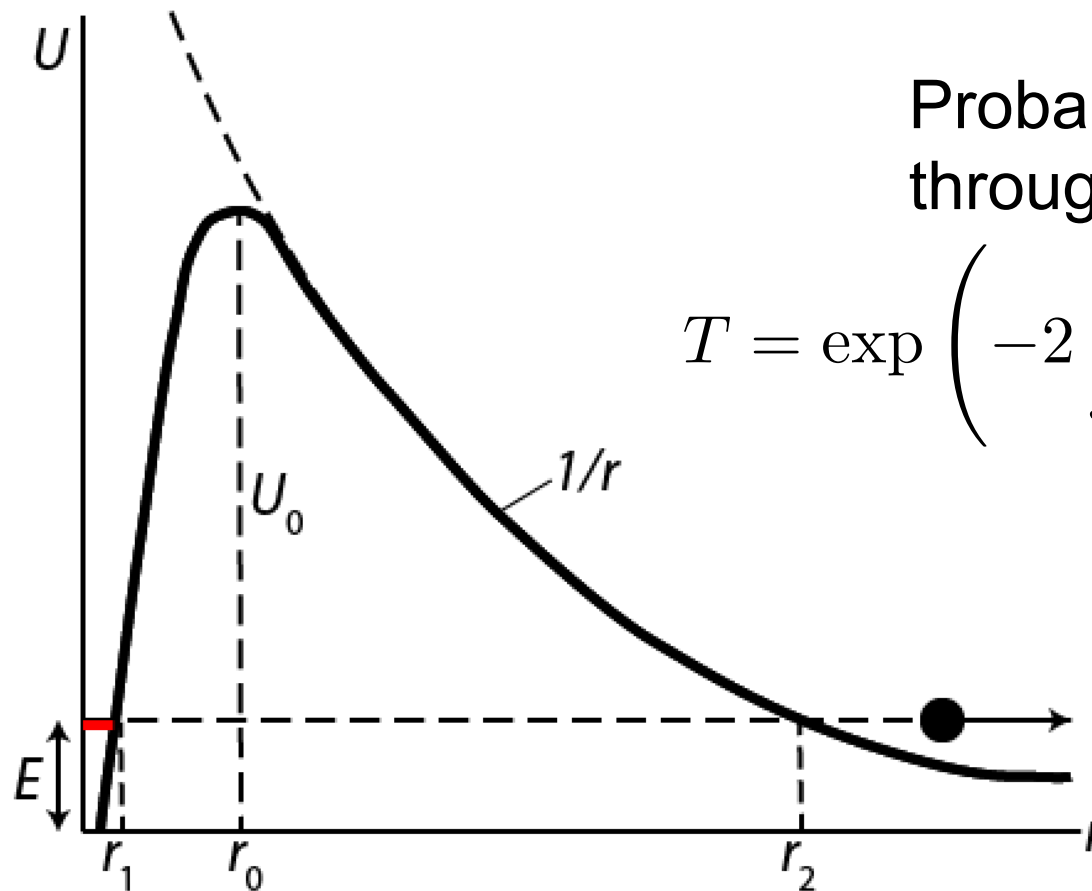
each level can be occupied with one spin-up electron and one spin-down electron

Could the fathers of quantum theory
envision tunneling from discrete levels?

Tunneling from discrete levels

G. Gamov, Z. Phys. **51**, 204 (1928).

α -decay described by tunneling from quantized levels



Probability of transmission
through barrier:

$$T = \exp \left(-2 \int_{x_1}^{x_2} \sqrt{\frac{2m[U(x) - E]}{\hbar^2}} dx \right)$$

Statistical properties of tunneling decays

Processes with constant (in time) tunneling rate Γ .

Tunneling probability (at any time): Γdt

Statistical properties of tunneling decays

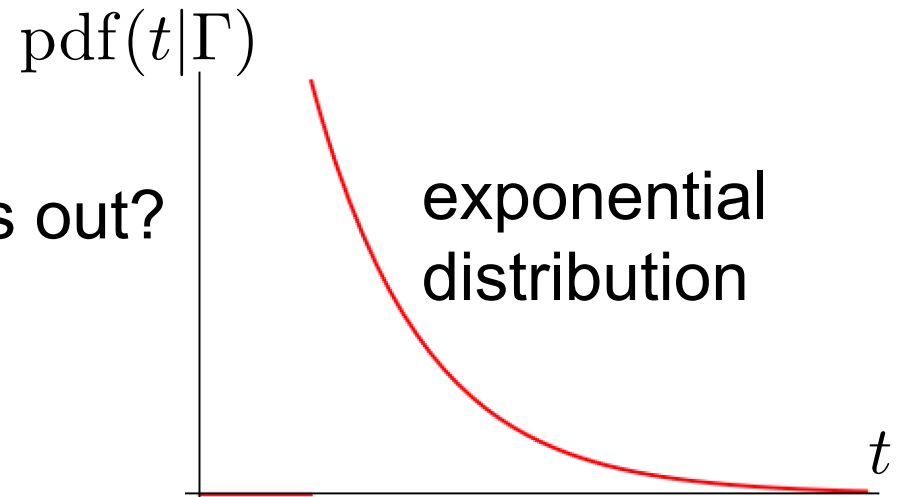
Processes with constant (in time) tunneling rate Γ .

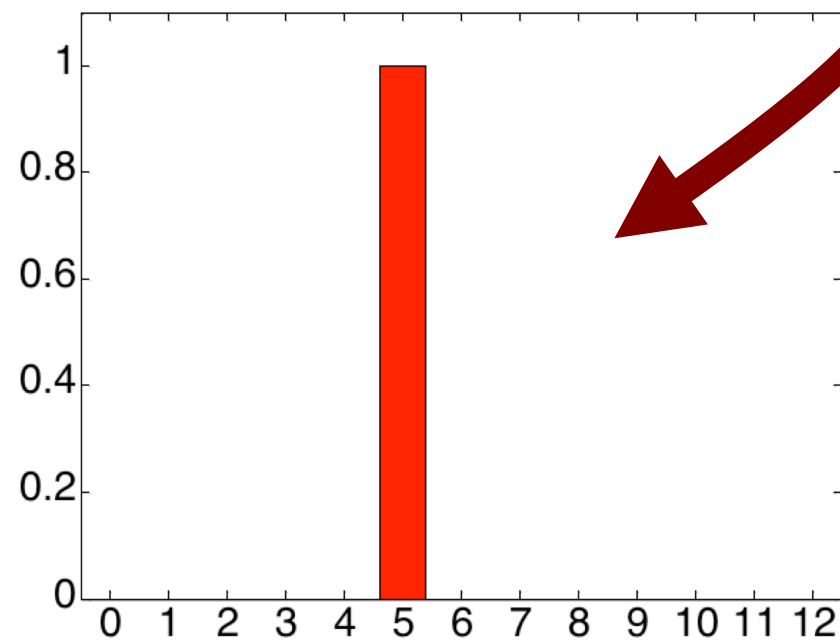
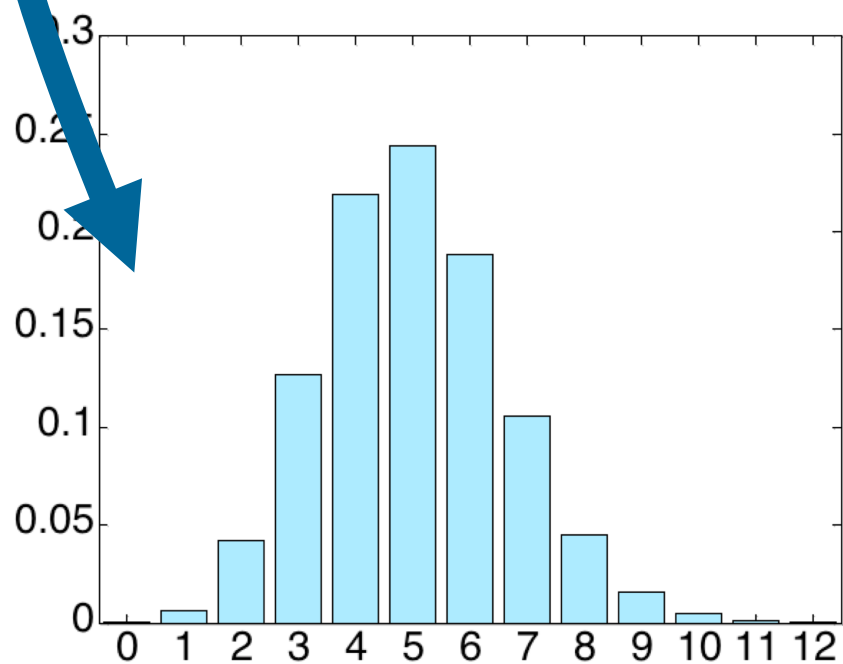
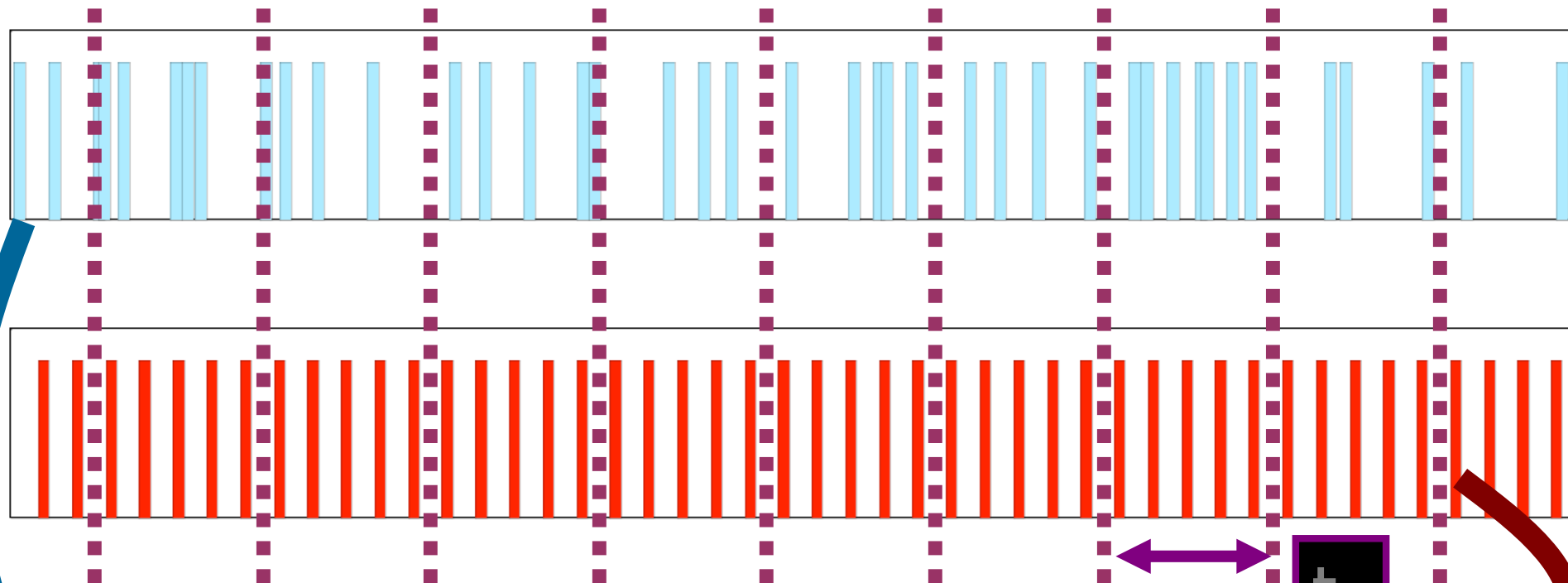
Tunneling probability (at any time): Γdt

Waiting time statistics:

$$\text{prob}(t|\Gamma) = e^{-\Gamma t} \Gamma dt$$

Place a particle in a quantum level
How long does it take until it tunnels out?





Statistical properties of tunneling decays

Processes with constant (in time) tunneling rate Γ .

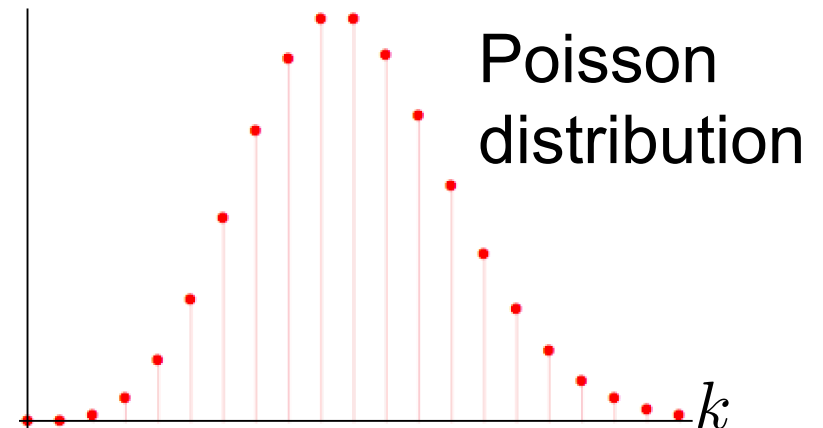
Tunneling probability (at any time): Γdt

Full counting statistics:

$$\text{prob}(k|\Gamma, \Delta t) = \frac{(\Gamma \Delta t)^k}{k!} e^{-\Gamma \Delta t}$$

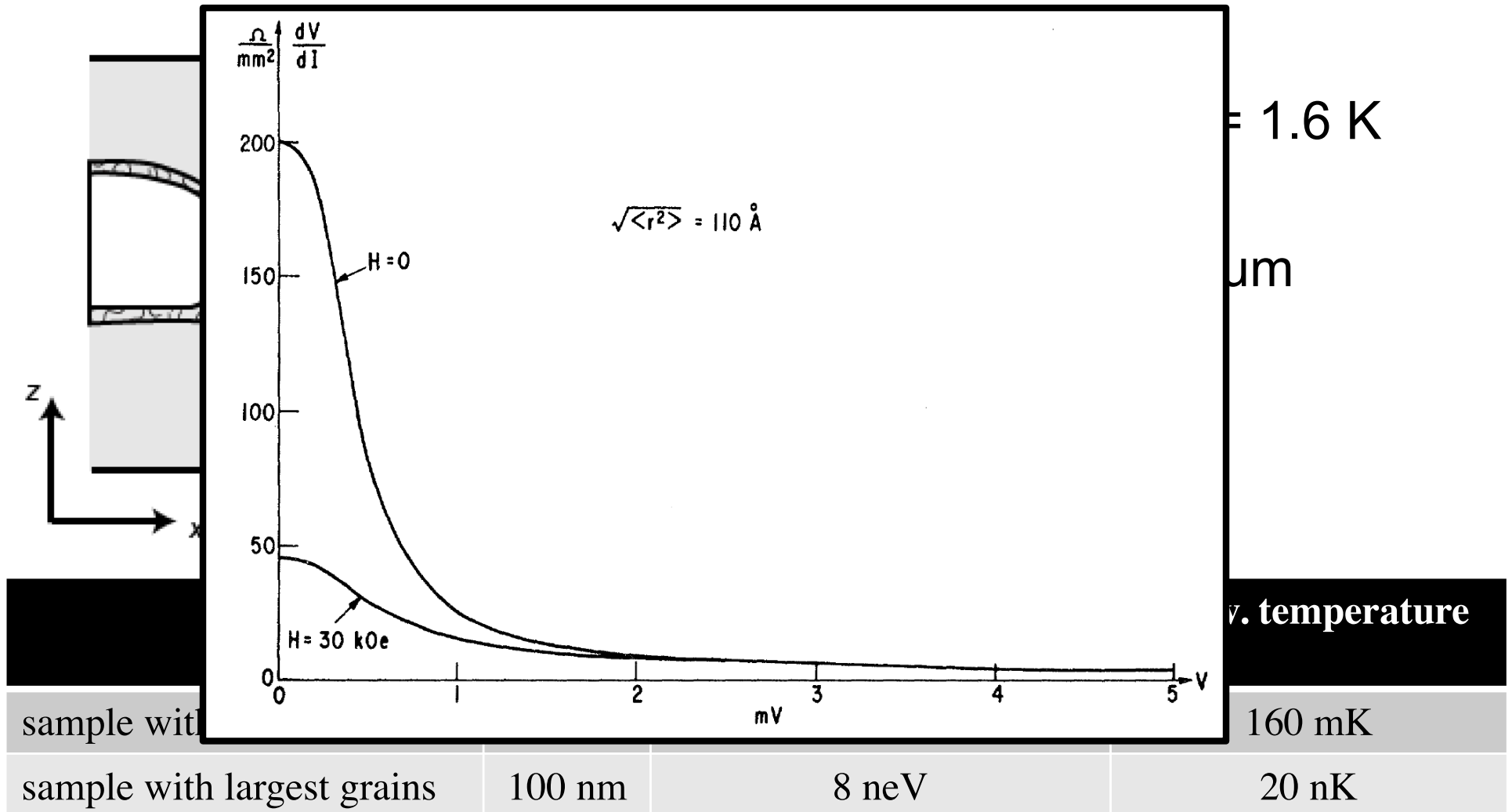
Take a large ensemble of systems that can decay starting from time 0. What is the probability that k of them have decayed within time Δt ?

$\text{prob}(k|\Gamma, \Delta t)$



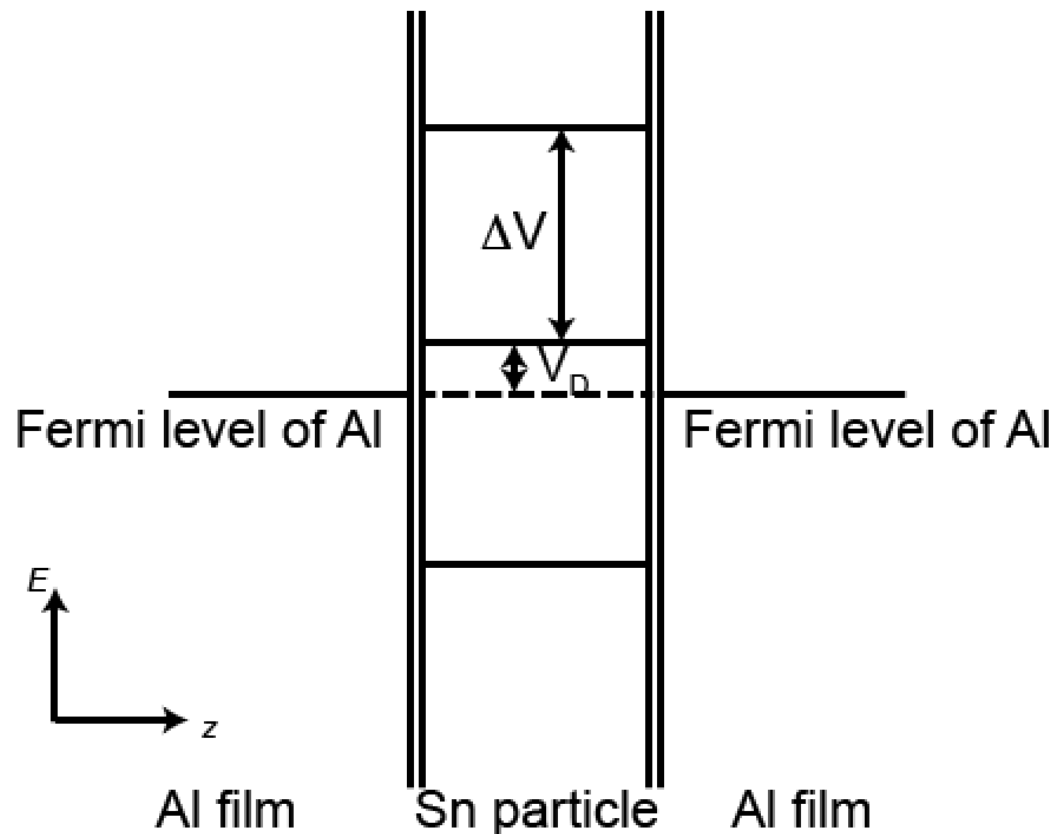
Electron tunneling through small grains of tin

Giaever and Zeller, Phys. Rev. Lett. **20**, 1504 (1968)



Coulomb gap in tunneling

Giaever and Zeller, Phys. Rev. Lett. **20**, 1504 (1968)



Charging a capacitor:

$$\Delta Q = C \Delta V$$

$$C = 4\pi\epsilon\epsilon_0 r \quad (\text{Sphere})$$

Charging a single electron:

$$\Delta V = \frac{e}{C} = \frac{e}{4\pi\epsilon\epsilon_0 r}$$

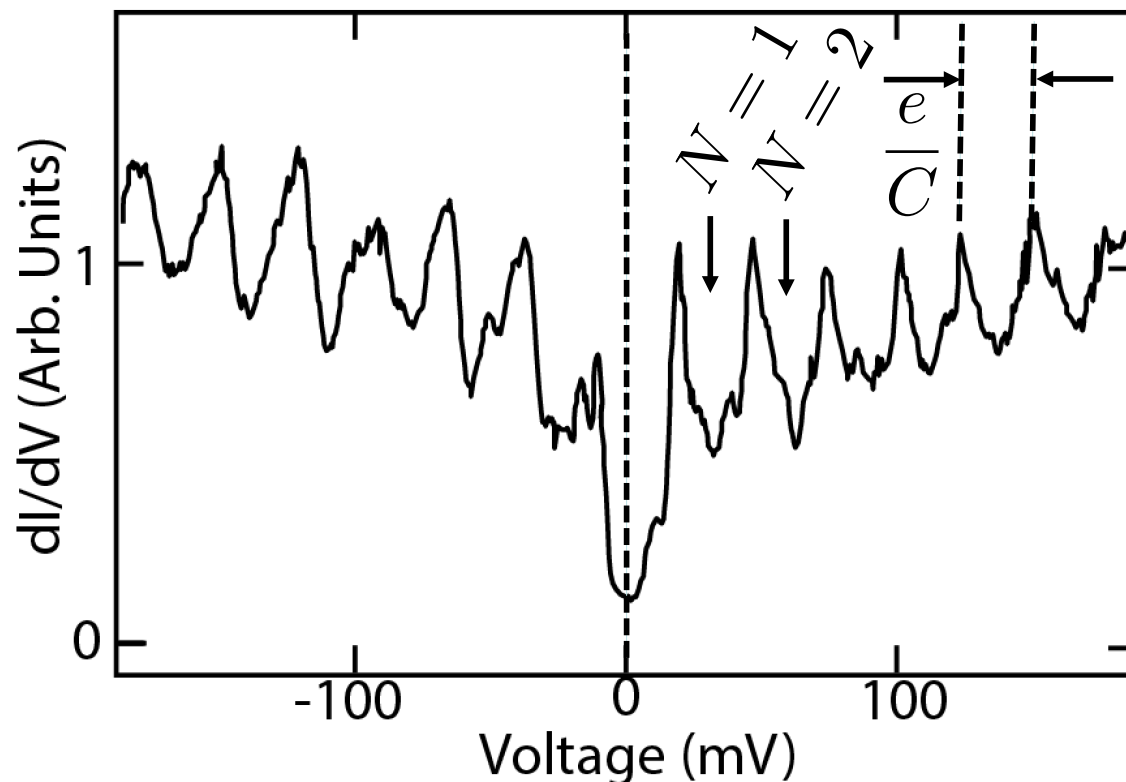
Grains: 1–10 mV

Atoms: 10 V

Coulomb staircase

Barner and Ruggiero, Phys. Rev. Lett. **59**, 807 (1987)

Addition spectrum (classical)



Silver grains 7.5 nm

aluminium oxide
tunneling barriers

$$E(N) = \frac{Q^2}{2C} = \frac{e^2 N^2}{2C}$$

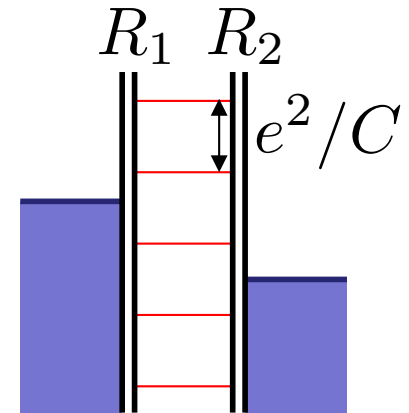
$$\Delta V(N) = \frac{e}{C} \left(N + \frac{1}{2} \right)$$

Single-electron tunneling current

Barner and Ruggiero, Phys. Rev. Lett. **59**, 807 (1987)

charging time of grain: $\tau_1 = R_1 C$

discharging time of grain: $\tau_2 = R_2 C$



Total single-electron tunneling time through one level:

$$\tau = (R_1 + R_2)C = RC$$

Single-electron tunneling current through one level:

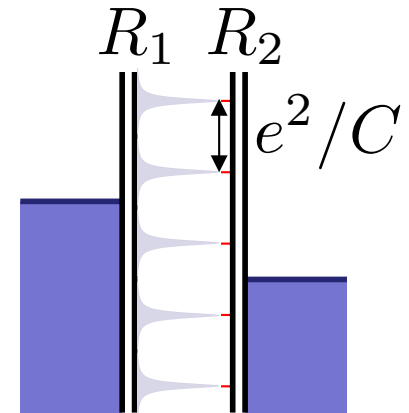
$$I = \frac{e}{\tau} = \frac{e}{RC}$$

How big is a tunneling resistance?

Condition on the tunneling resistance:
time-energy uncertainty

lifetime broadening of grain level:

$$\Delta E_{\tau} = \frac{h}{R_1 C} + \frac{h}{R_2 C} = \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \frac{h}{C}$$



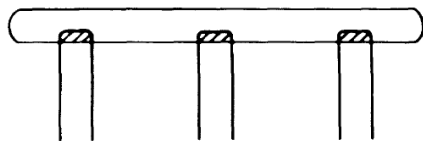
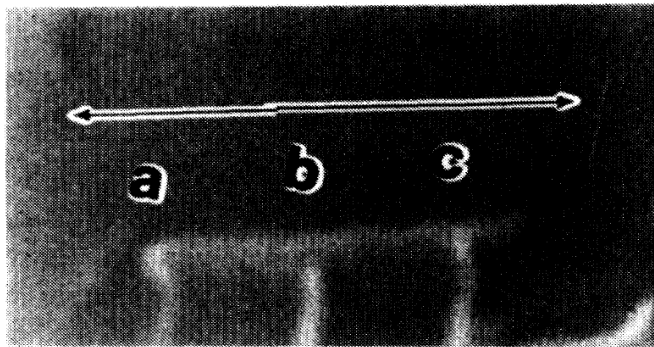
Resolving charging energy is possible, if

$$\Delta E_{\tau} \ll \frac{e^2}{C} \Rightarrow \frac{1}{R_1} + \frac{1}{R_2} \ll \frac{e^2}{h} = \frac{1}{25.8 \text{ k}\Omega}$$

Progress in nanolithography

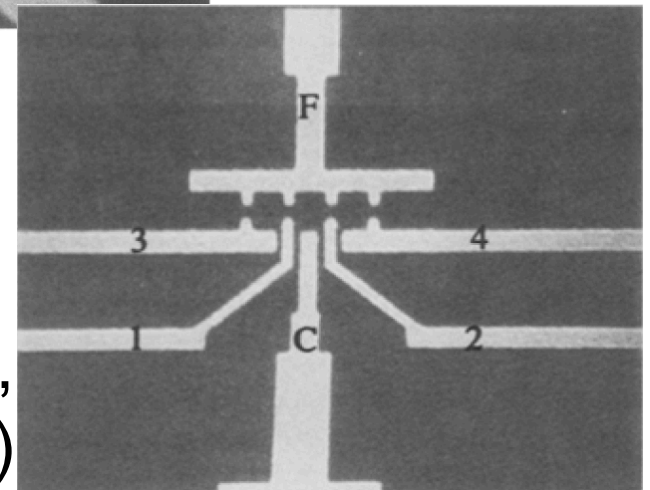
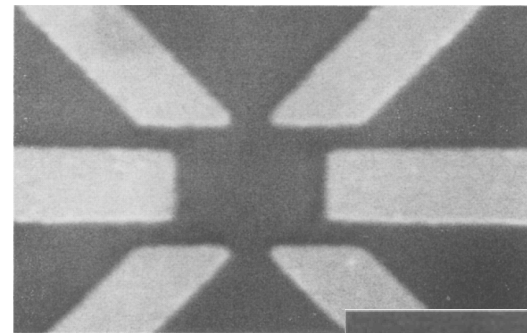
Lateral Metal Single-Electron Transistor (SET)

Fulton and Dolan,
Phys. Rev. Lett. **59**, 109 (1987)



Lateral Semiconductor Quantum Dot

Staring *et al*,
Physica B **175**, 226 (1991)



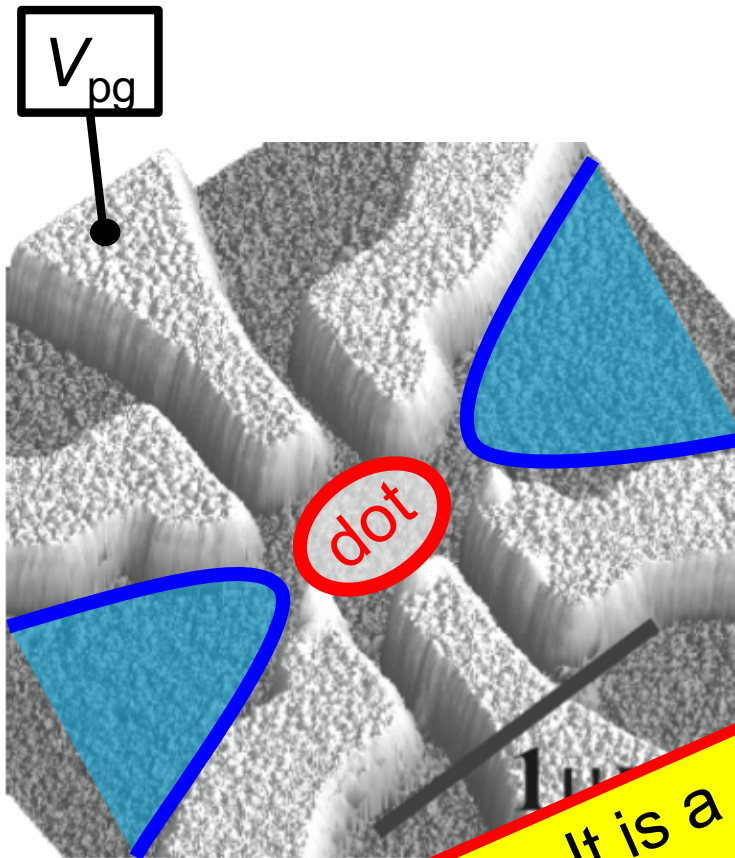
Kouwenhoven *et al*,
Z. Phys. B **85**, 367 (1991)

Atoms vs. quantum dots

	Atom	Quantum dot
Confinement	r^1 , strong, rigid hard to tune	r^2 , soft, parabolic tunable
Symmetry	perfect, given by nature	never perfect, hard to achieve
Electrical addressing	hard to achieve	well suitable tunable coupling
Optical addressing	well suitable	well suitable
Coupling to	thermal photons, ...	photons, phonons, other electrons

Both systems give access to single electron/spin manipulation

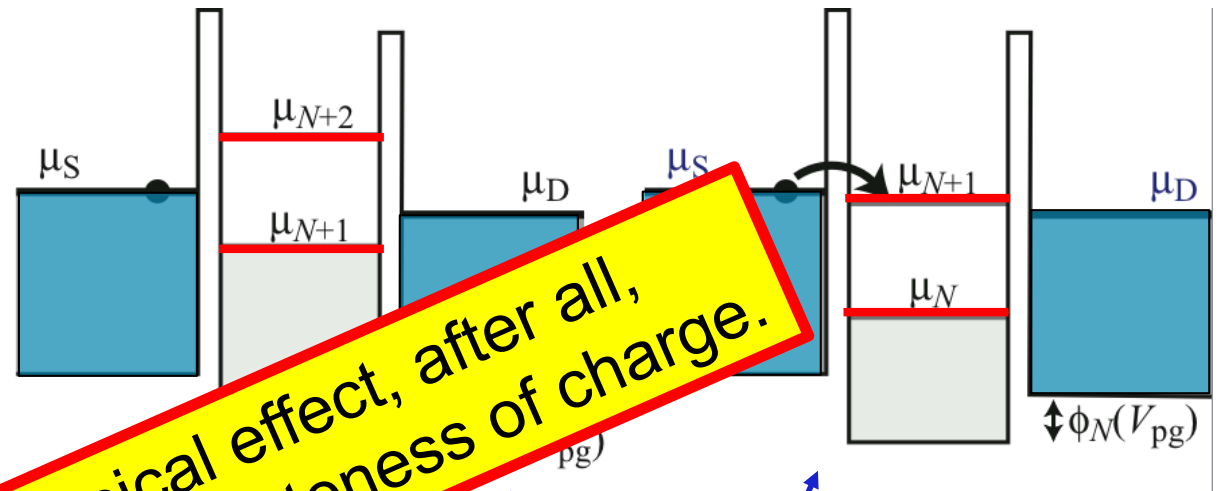
Coulomb blockade



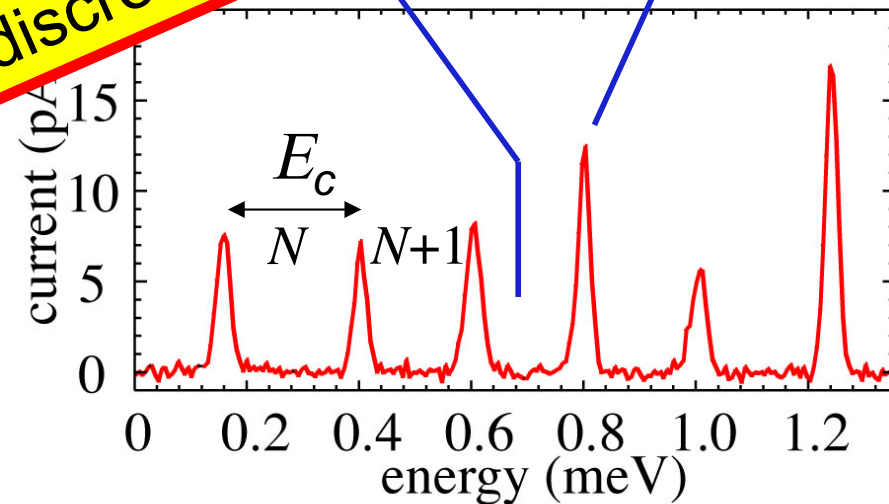
2D-electron gas
on the surface

Coulomb
blockade

Resonant
transport



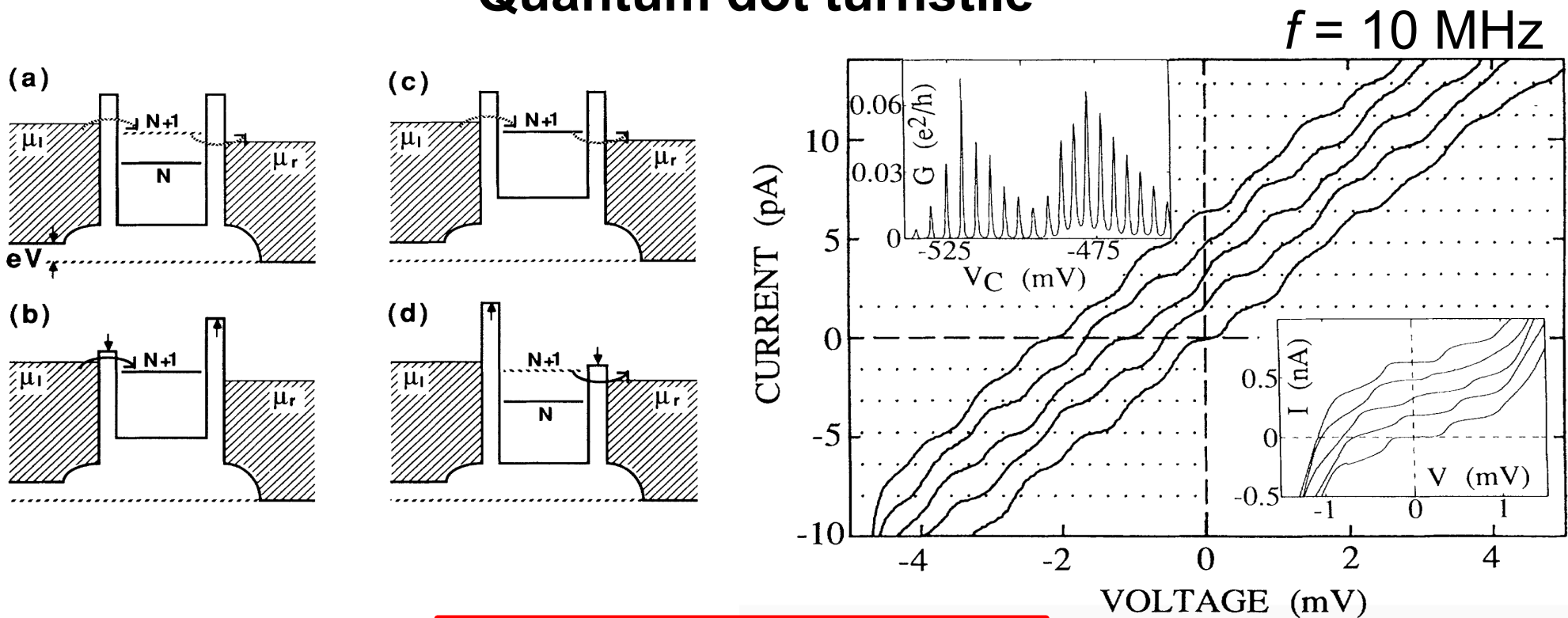
It is a classical effect, after all,
based on the discreteness of charge.



How do we know it is single electrons?

Kouwenhoven *et al*, Phys. Rev. Lett. **67**, 1626 (1991)

Quantum dot turnstile

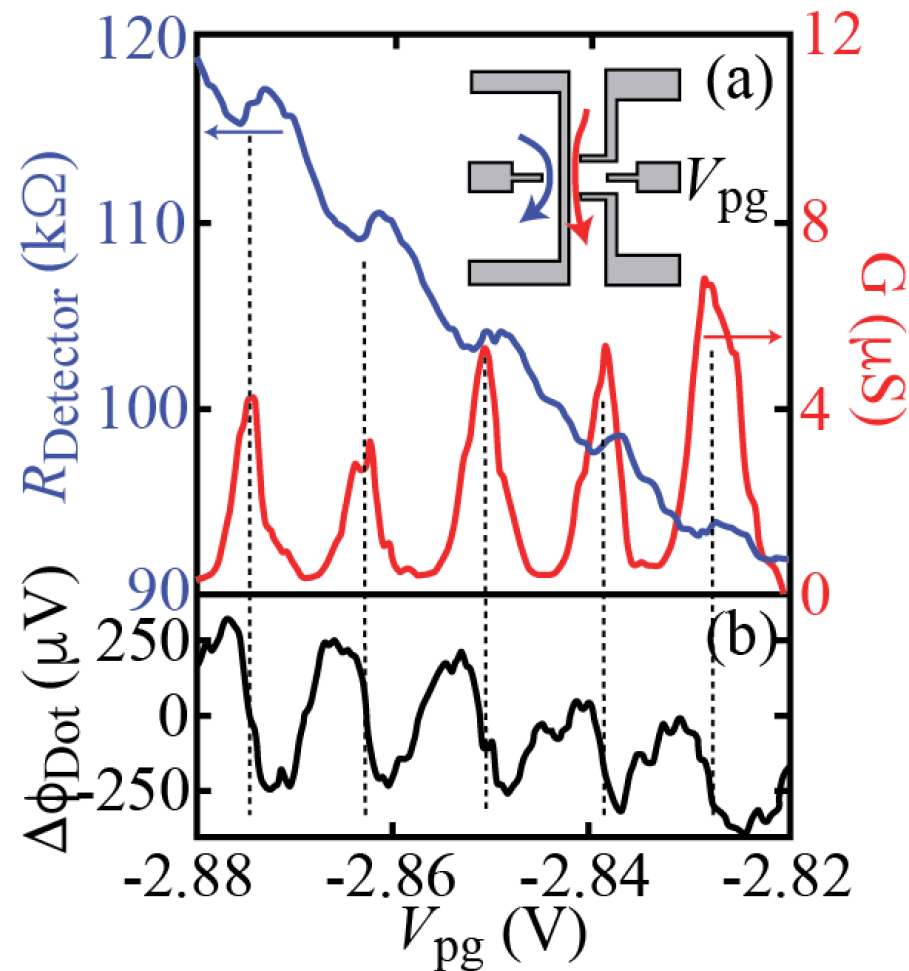


$$I = nef, \quad n = 1, 2, 3 \dots$$

How do we know it is single electrons?

Field *et al*, Phys. Rev. Lett. **70**, 1311 (1993)

Single-electron charge detection



Part II

Single electrons in real time

Single-electron switching in MOSFETs

1/ f and random telegraph noise in silicon metal-oxide-semiconductor field-effect transistors

M. J. Uren, D. J. Day,^{a)} and M. J. Kirton

Royal Signals and Radar Establishment, Great Malvern, Worcestershire, United Kingdom

(Received 30 May 1985; accepted for publication 17 September 1985)

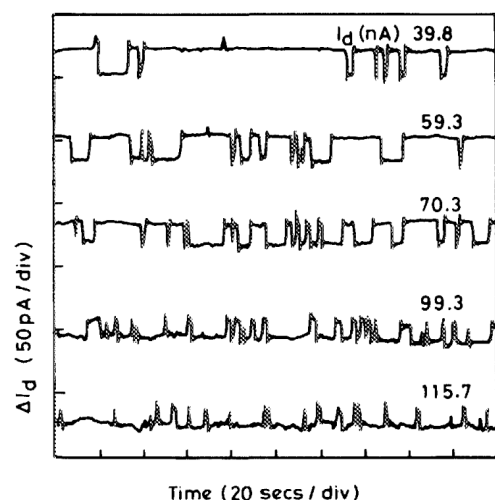


FIG. 2. Random telegraph signals. Change in current vs time measured at the indicated currents. Active area is $0.4 \mu\text{m}^2$, $V_g = 4 \text{ mV}$, $T = 293 \text{ K}$.

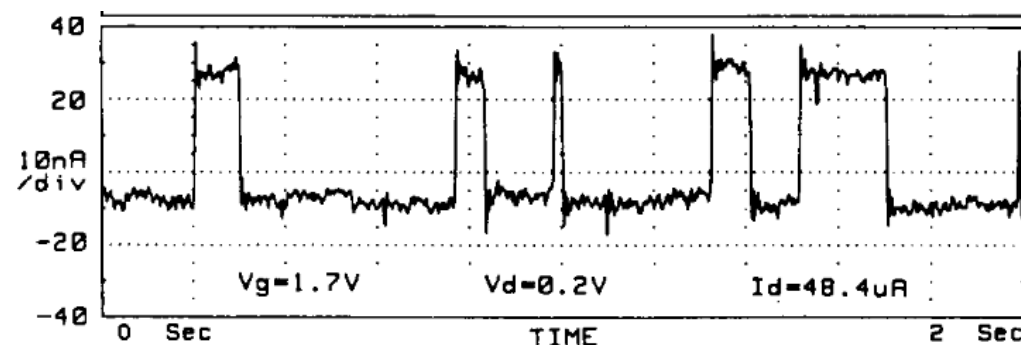


Fig. 1. The fluctuations of drain current at different gate voltages for a deep-submicrometer MOSFET ($W_{eff} = 1.2 \mu\text{m}$, $L_{eff} = 0.35 \mu\text{m}$, $T_{ox} = 8.6 \text{ nm}$).

Random Telegraph Noise of Deep-Submicrometer MOSFET's

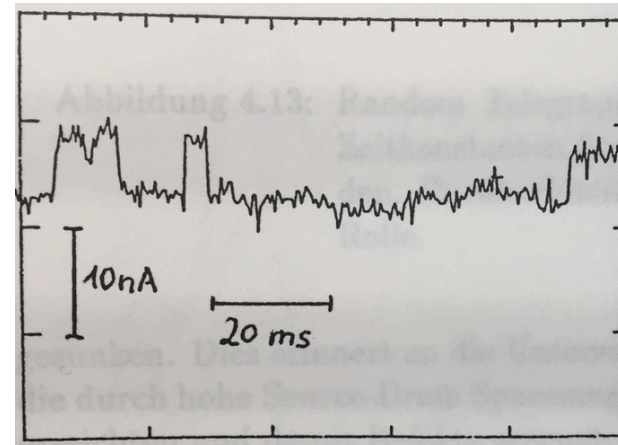
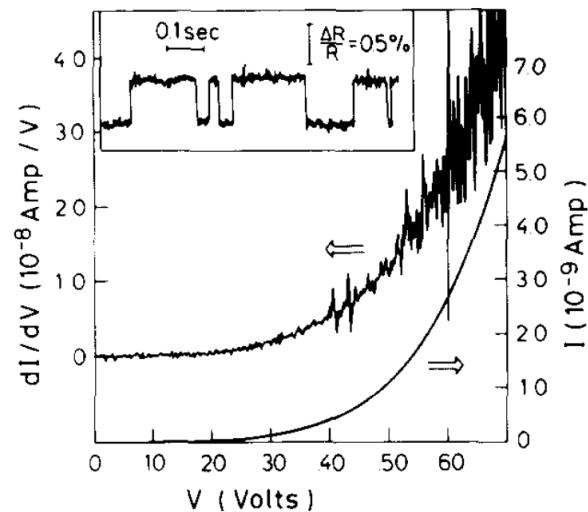
K.K. HUNG, P. K. KO, CHENMING HU, SENIOR MEMBER, IEEE, AND
YIU CHUNG CHENG, MEMBER, IEEE

Single-electron switching in amorphous barriers

RANDOM TELEGRAPHIC NOISE IN LARGE AREA $a\text{-Si:H}/a\text{-Si}_{1-x}\text{N}_x\text{:H}$ DOUBLE BARRIER STRUCTURES

Roberto ARCE^a, Lothar LEY^b, and Martin HUNDHAUSEN^b

Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-7000 Stuttgart 80, Federal Republic of Germany



Journal of Non-Crystalline Solids 137&138 (1991) 523-526
North-Holland

JOURNAL OF
NON-CRYSTALLINE SOLIDS

CURRENT FLUCTUATIONS IN THIN $a\text{-SiC:H}$ FILMS

Th. Ihn, A.K. Savchenko*, M.E. Raikh, R. Schwarz

Technische Universität München, Physikdepartment E16, James-Franck-Straße, W-8046 Garching, Federal Republic of Germany

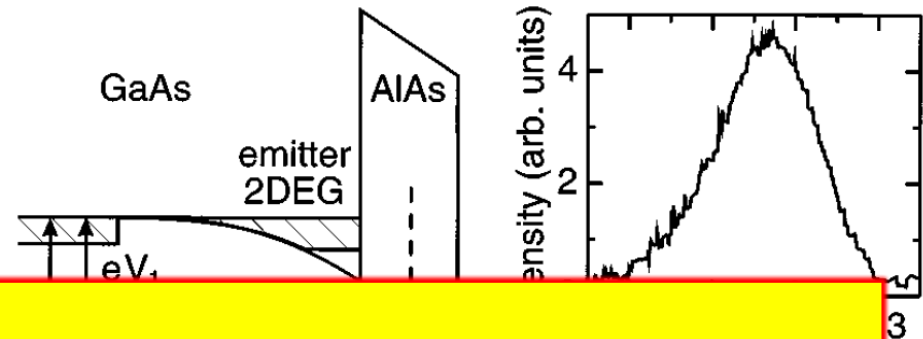
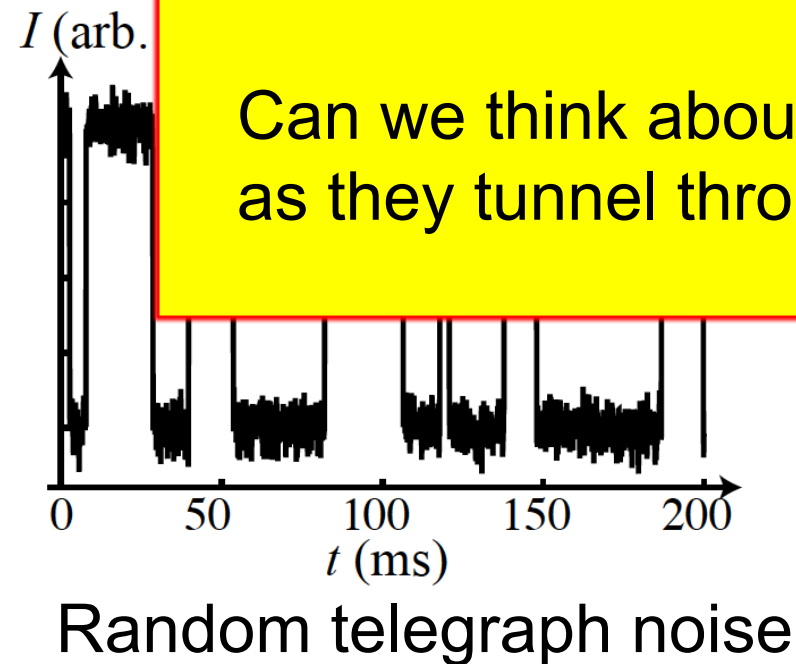
A physicist's dream

Tunneling through InAs quantum dots

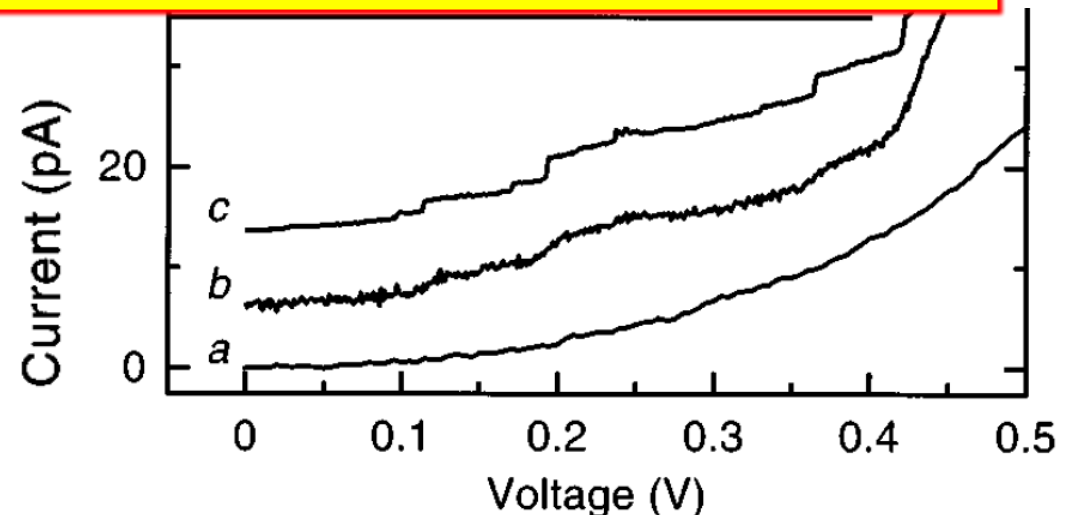
I.E. Itskevich, TI *et al*, Phys. Rev. B **54**, 16401 (1996).

Current fluctuations in thin a-Si:H films

TI *et al*, J Non-Crystalline Solids **137**, 523 (1991).



Can we think about a way to watch single electrons as they tunnel through quantum dots in real time?



Historic work

VOLUME 73, NUMBER 2

PHYSICAL REVIEW LETTERS

11 JULY 1994

Time-Resolved Tunneling of Single Electrons between Landau Levels in a Quantum Dot

N. C. van der Vaart, M. P. de Ruyter van Steveninck, L. P. Kouwenhoven,*

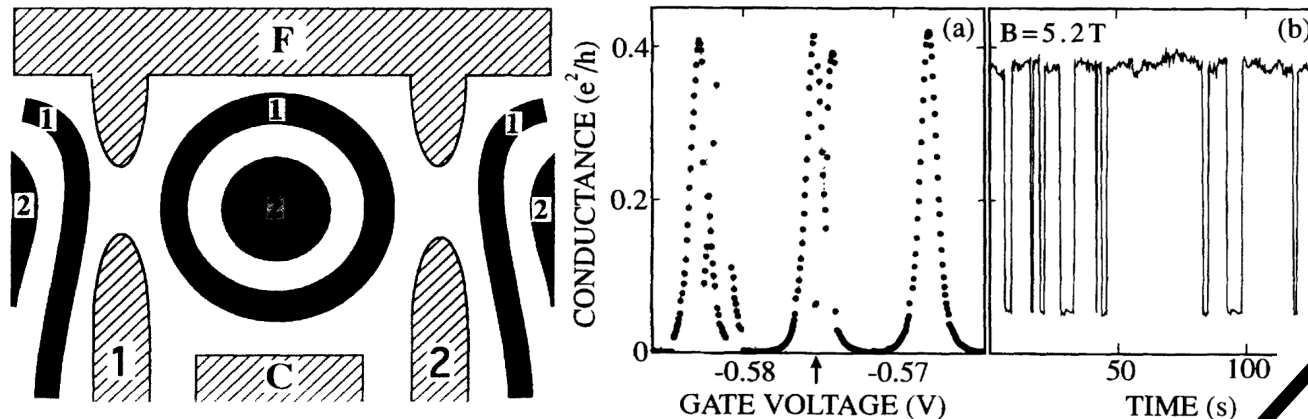
A. T. Johnson,[†] Y. V. Nazarov, and C. J. P. M. Harmans

Department of Applied Physics, Delft University of Technology, P.O. Box 5046, 2600 GA Delft, The Netherlands

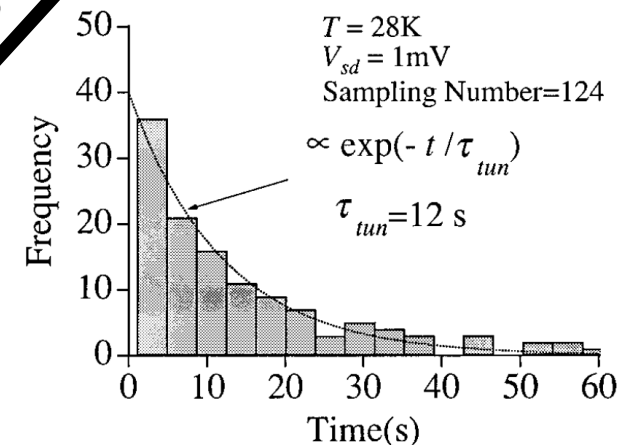
C. T. Foxon[‡]

Philips Research Laboratories, Redhill, Surrey RH15HA, United Kingdom

(Received 21 March 1994)



Waiting time distribution



Time-resolved measurement of single-electron tunneling in a Si single-electron transistor with satellite Si islands

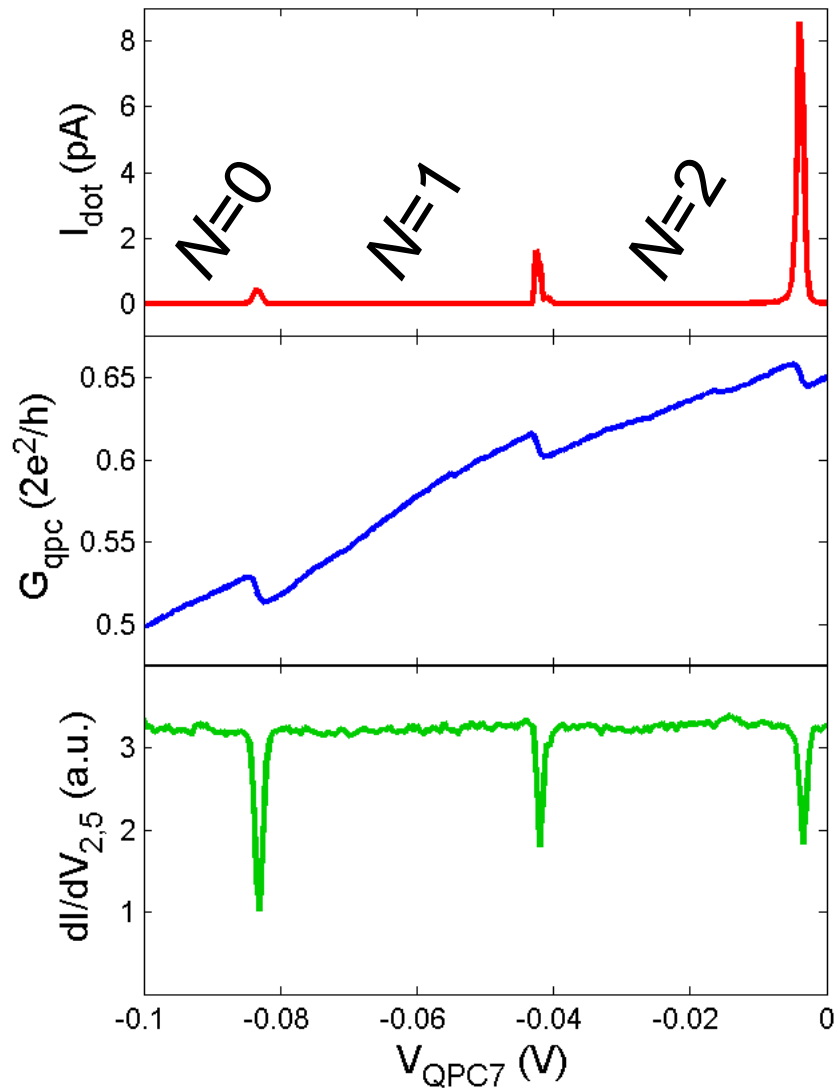
A. Fujiwara,^{a)} Y. Takahashi, K. Murase, and M. Tabe^{b)}

NTT LSI Laboratories, 3-1 Morinosato Wakamiya, Atsugi, Kanagawa 243-01, Japan

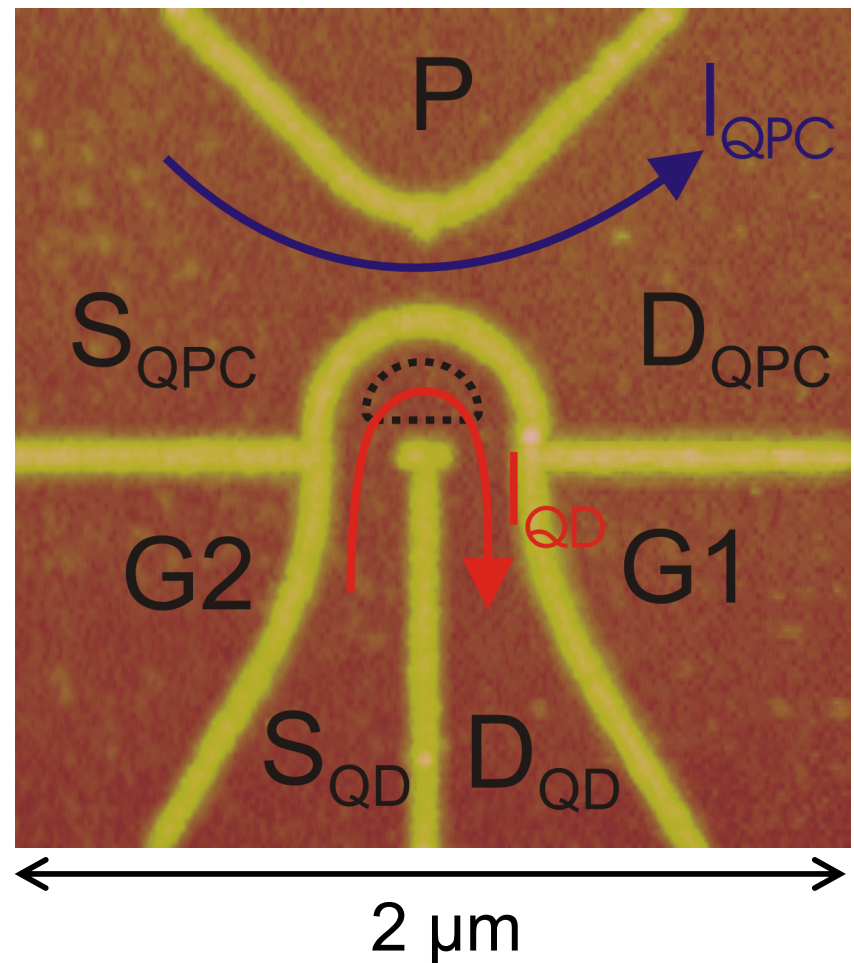
(Received 1 June 1995; accepted for publication 5 September 1995)

Can we see the first electron?

Schleser *et al*, Appl. Phys. Lett. **85**, 2005 (2004)



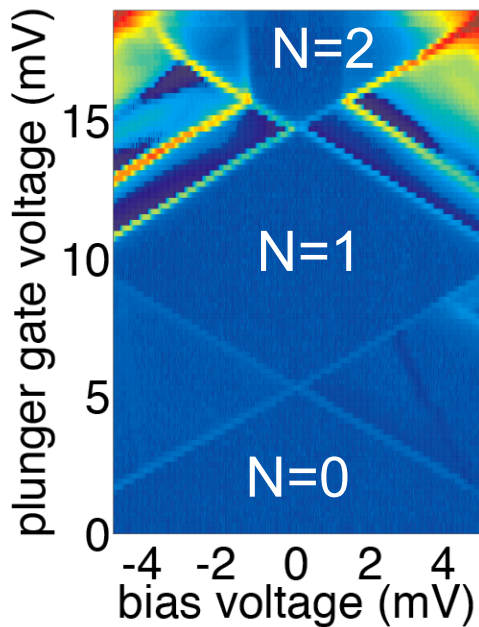
Semicircular quantum dot



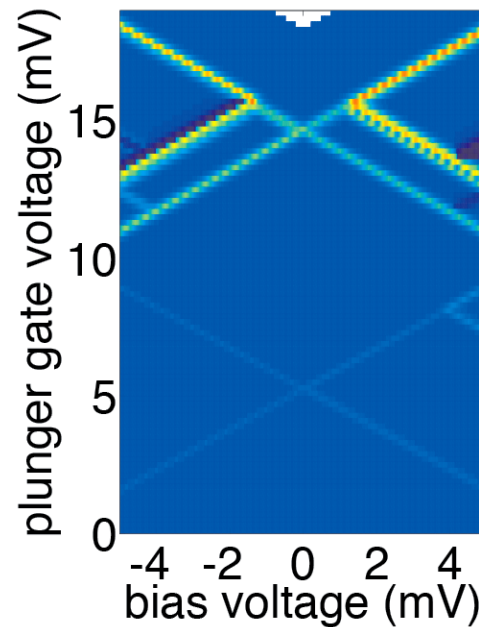
Quantum mechanics reappears!

Differential conductance

Experiment

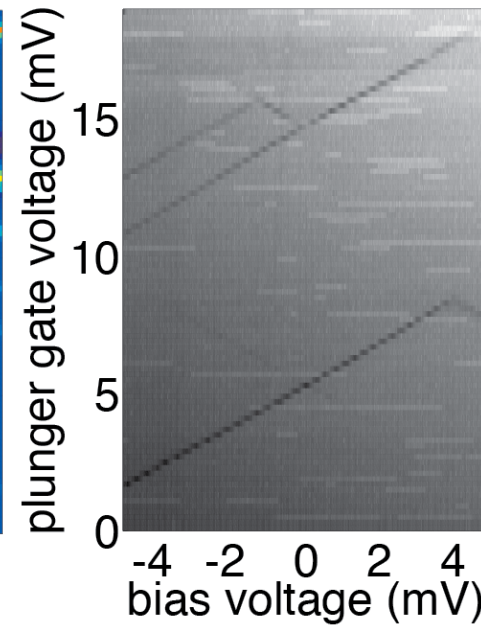


Simulation

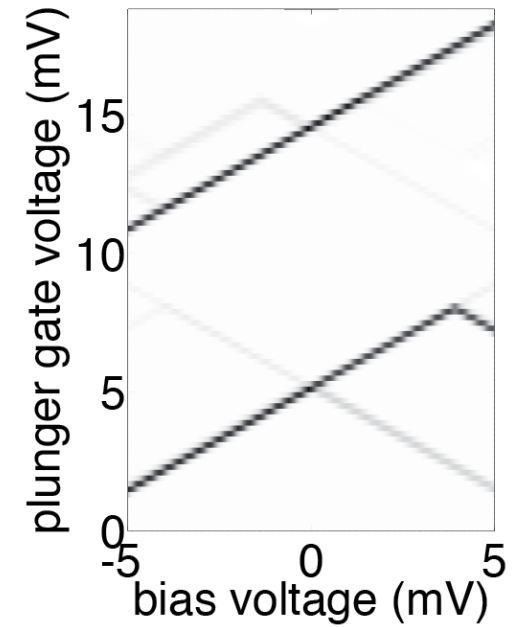


Differential charge

Experiment



Simulation

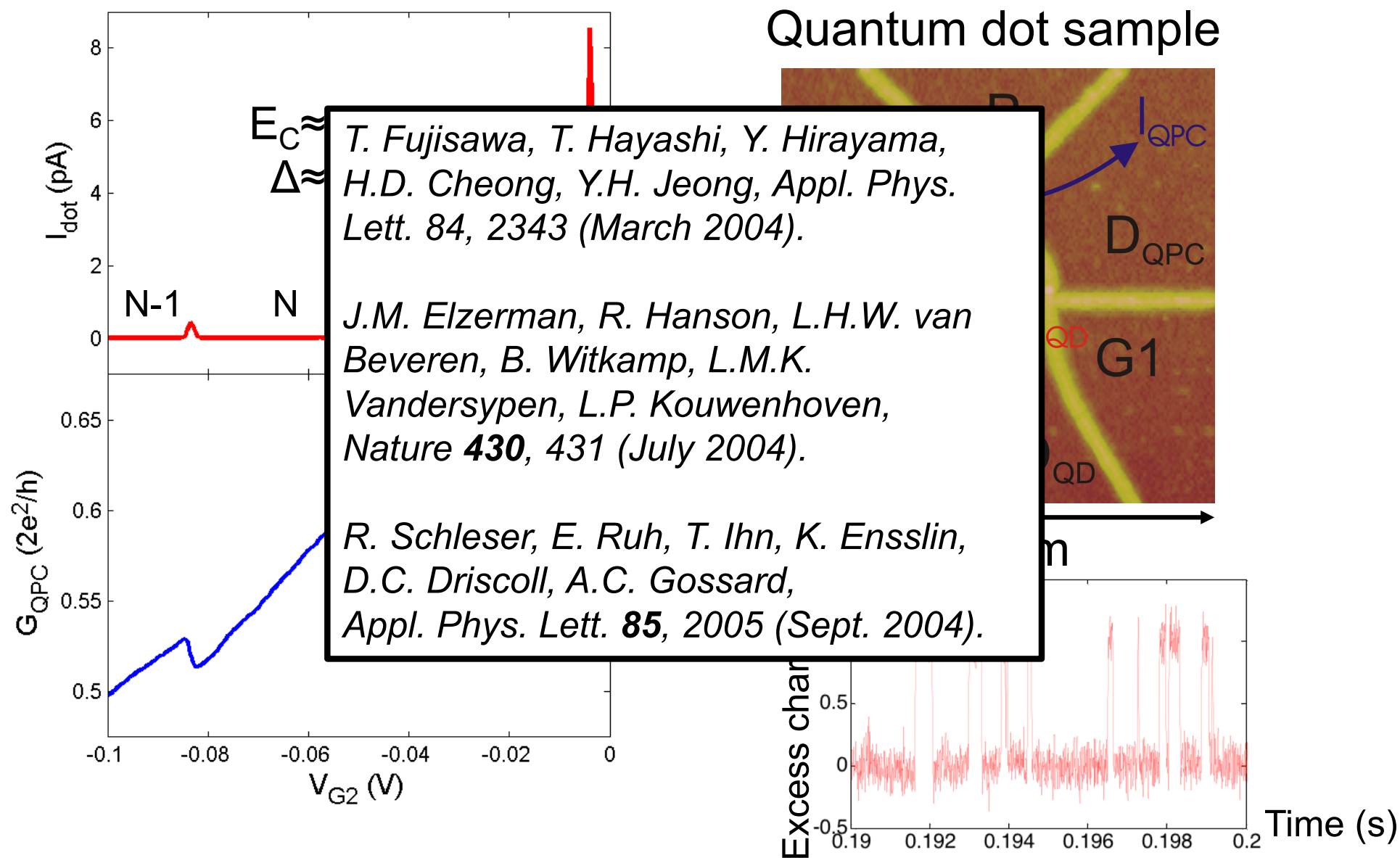


Martin Sigrist, PhD-thesis ETH (2005)

simulation rate equations: C.W. Beenakker, Phys. Rev. B **44**, 1646 (1991)

Single-electron tunneling in real time

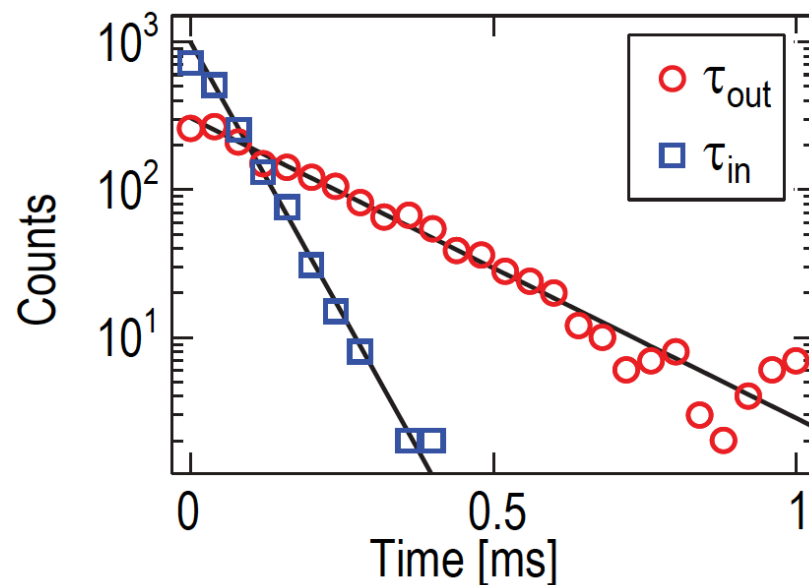
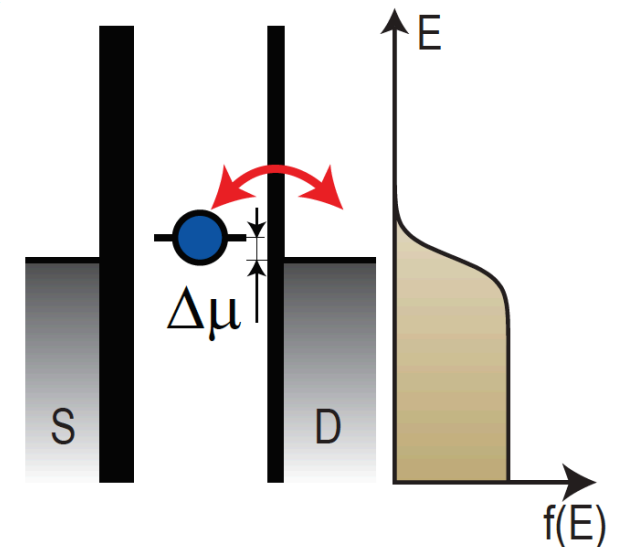
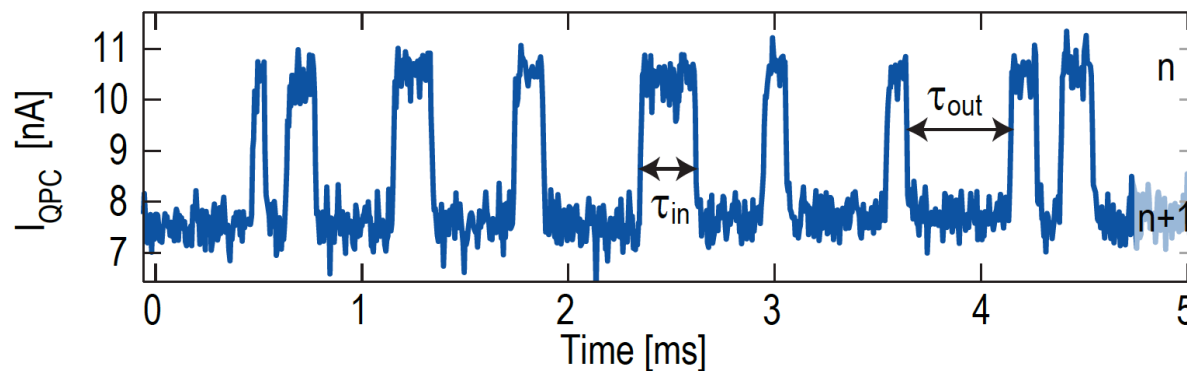
Schleser *et al*, Appl. Phys. Lett. **85**, 2005 (2004)



Waiting-time statistics for tunneling through a single barrier

Schleser *et al*, Appl. Phys. Lett. **85**, 2005 (2004)

S. Gustavsson, PhD-thesis ETH (2008)



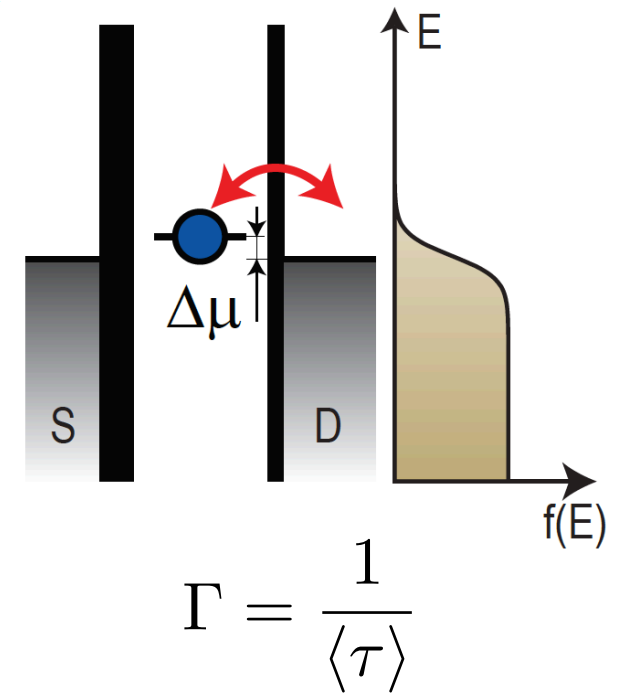
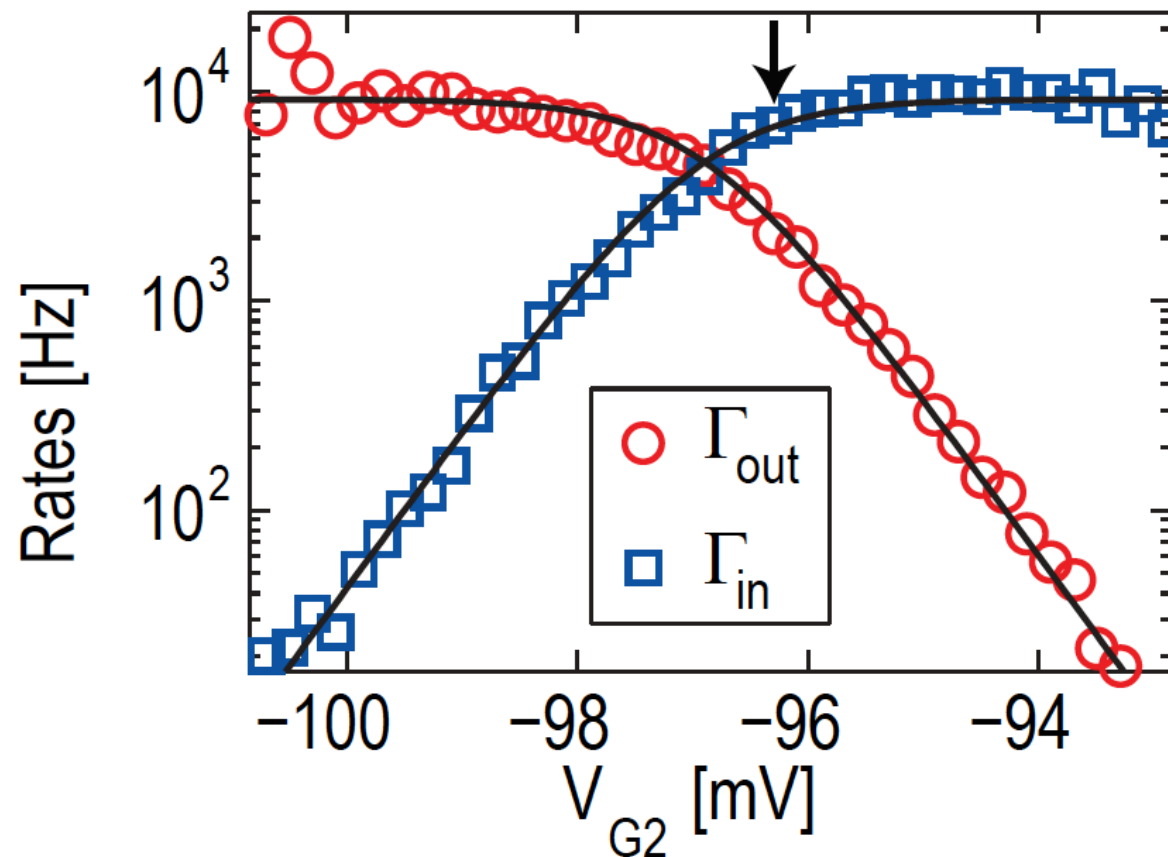
$\text{pdf}(\tau|\Gamma) = \Gamma e^{-\Gamma\tau}$
exponential distribution

$$\langle \tau \rangle = \int_0^\infty d\tau \tau \text{pdf}(\tau|\Gamma) = \frac{1}{\Gamma}$$

Tunneling through a single barrier

Schleser *et al*, Appl. Phys. Lett. **85**, 2005 (2004)

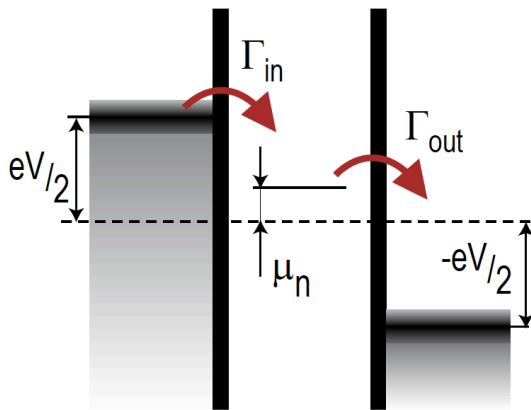
Simon Gustavsson, PhD-thesis ETH (2008)



$$\begin{aligned}\Gamma_{\text{in}} &= \gamma f(E) \\ \Gamma_{\text{out}} &= \gamma [1 - f(E)]\end{aligned}$$

Measuring current electron by electron

Gustavsson *et al*, Phys. Rev. Lett. **96**, 076605 (2006)

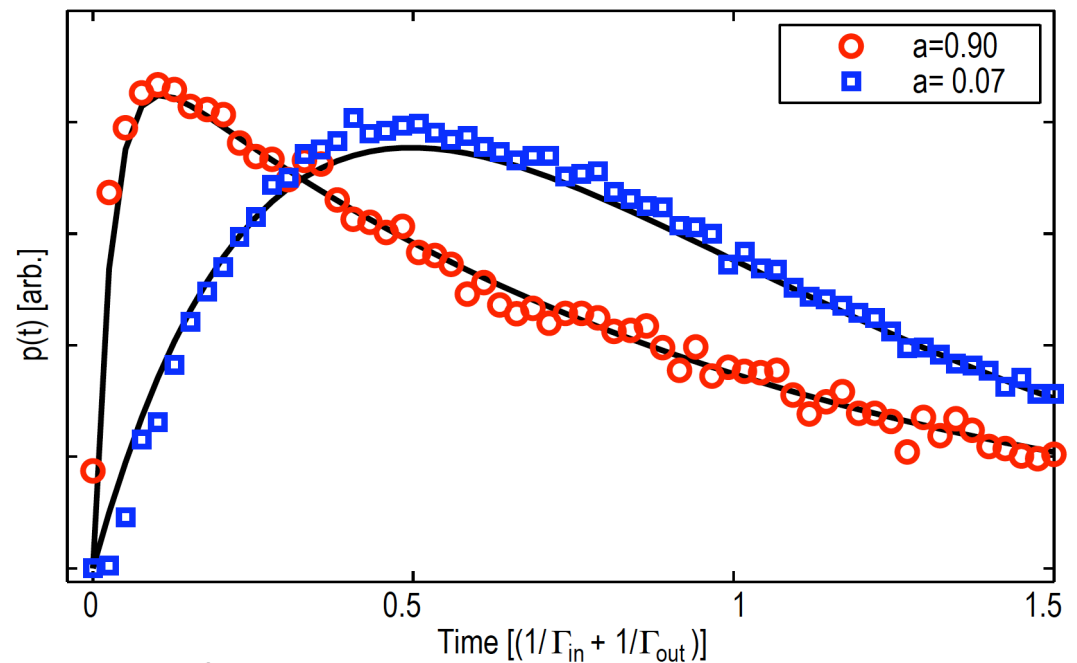


Waiting time between
successive tunneling-in
events

$$p(t)dt = \int_0^t e^{-\Gamma_{\text{out}}t'} \Gamma_{\text{out}} dt' e^{-\Gamma_{\text{in}}(t-t')} \Gamma_{\text{in}} dt$$

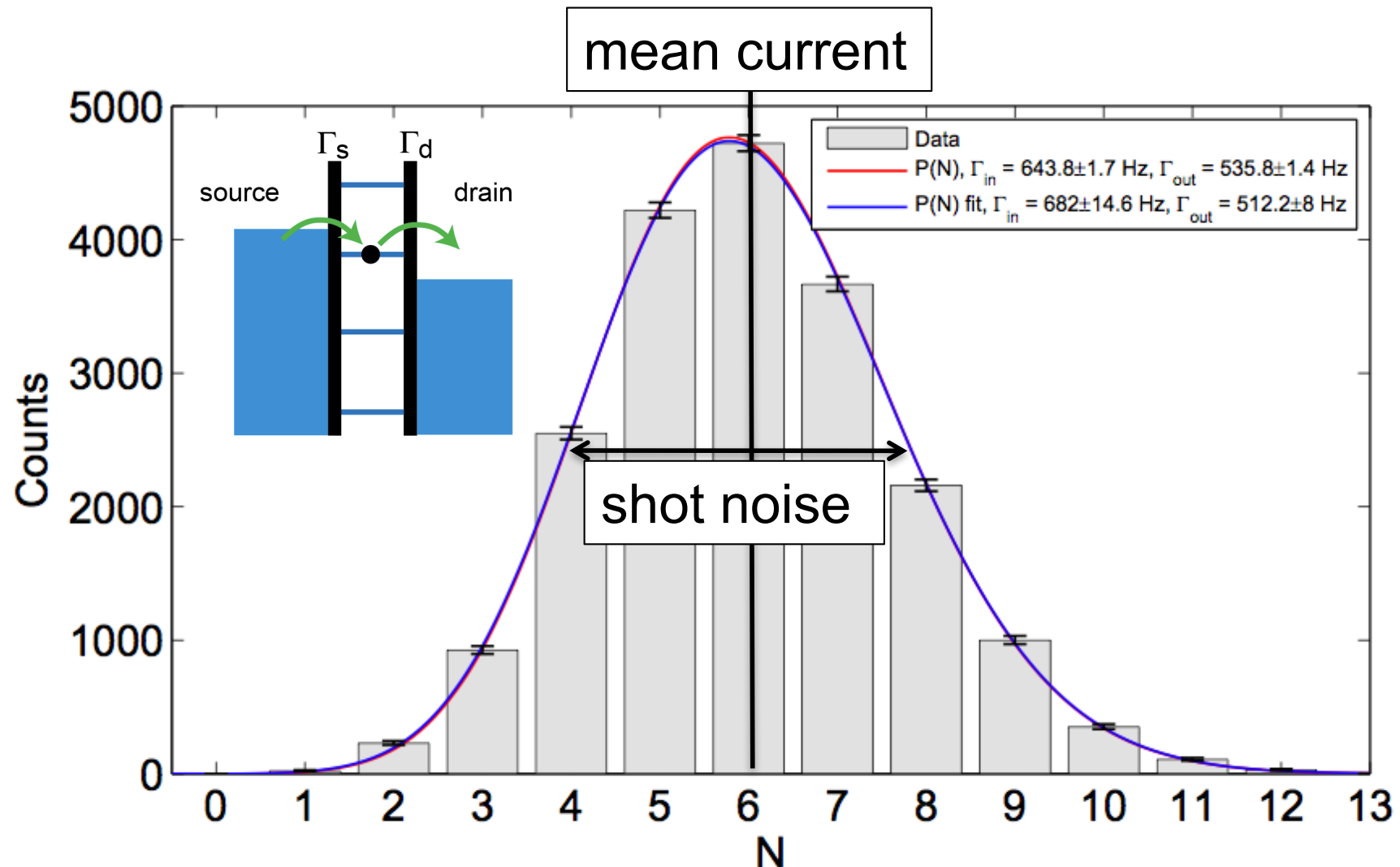
$$= \Gamma_{\text{in}} \Gamma_{\text{out}} \frac{e^{-\Gamma_{\text{out}}t} - e^{-\Gamma_{\text{in}}t}}{\Gamma_{\text{in}} - \Gamma_{\text{out}}} dt$$

Waiting time statistics



$$a = \frac{\Gamma_{\text{in}} - \Gamma_{\text{out}}}{\Gamma_{\text{in}} + \Gamma_{\text{out}}}$$

Full counting statistics of the current



Measurement by Simon Gustavsson: PRL **96**, 076605 (2006)

Theory: Bagrets and Nazarov, PRB **67**, 085316 (2003);

see also: C. Fricke *et al*, PRB **76**, 155307 (2007)

Single particle interference

Each photon then interferes only with itself.

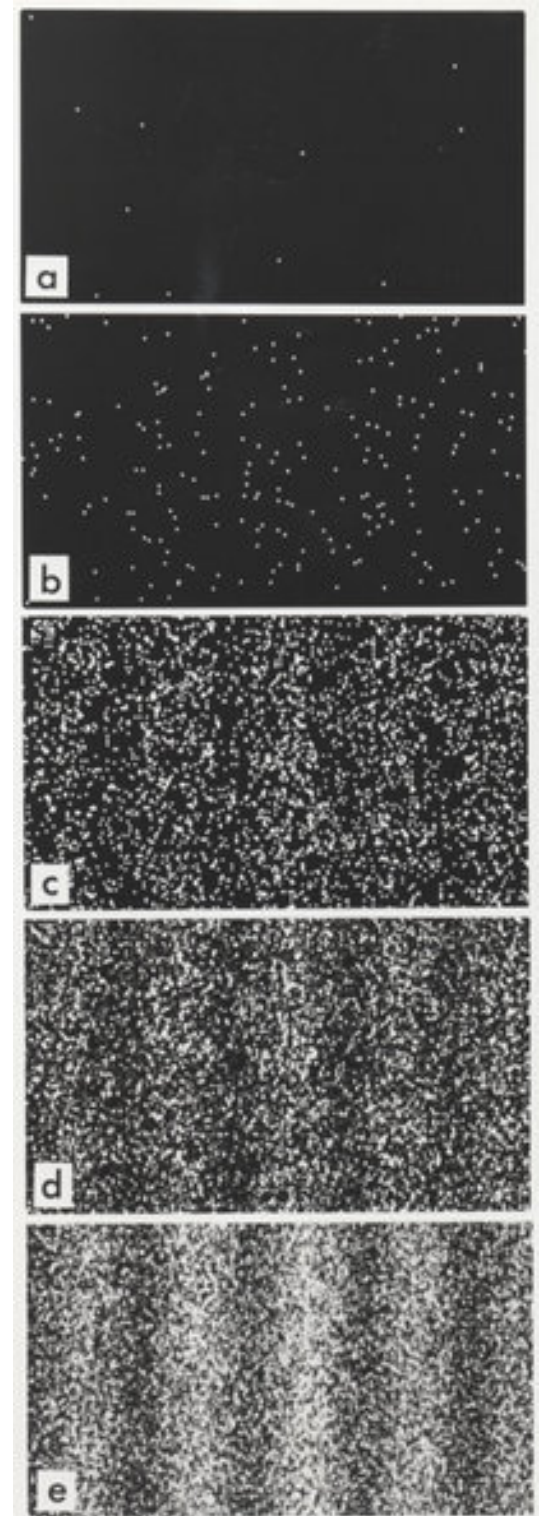
Paul Dirac,

The Principles of Quantum Mechanics, 4th ed., OUP

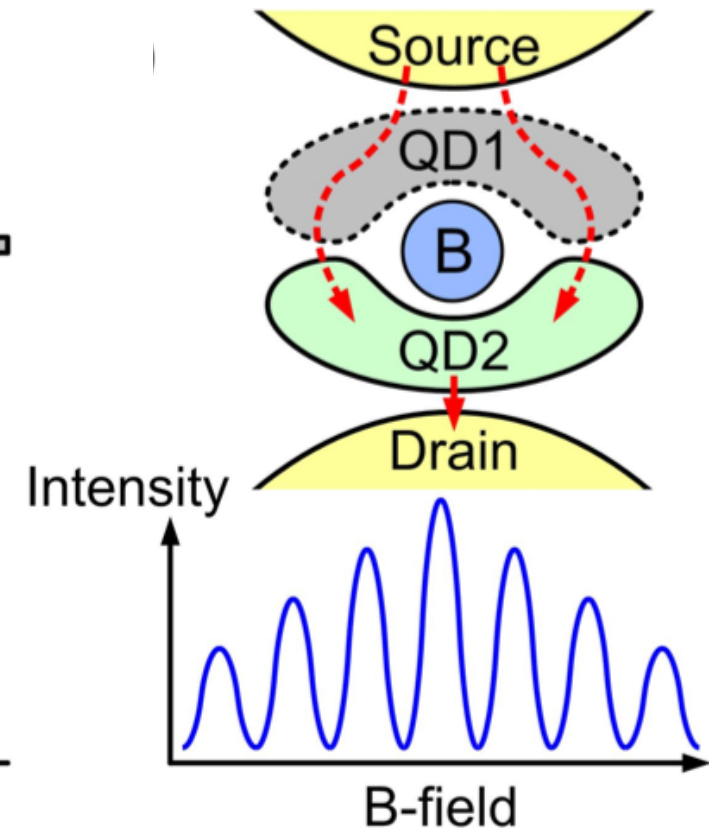
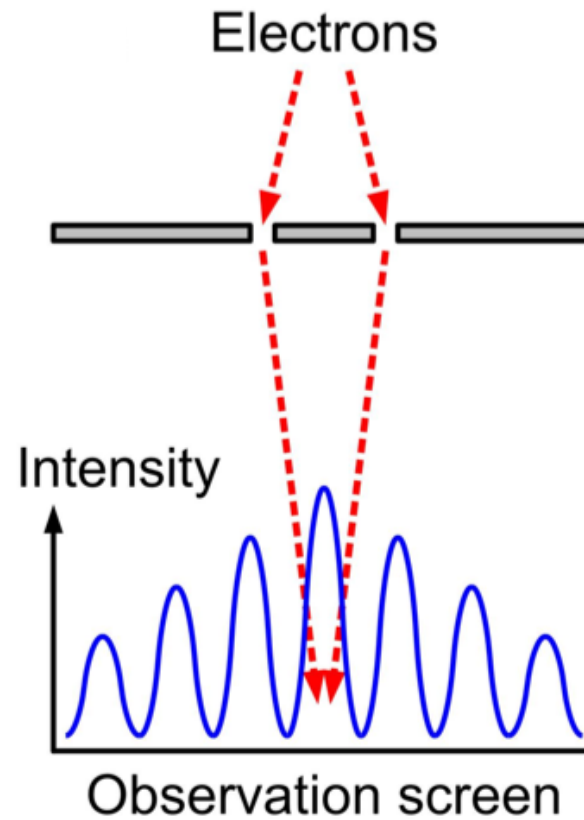
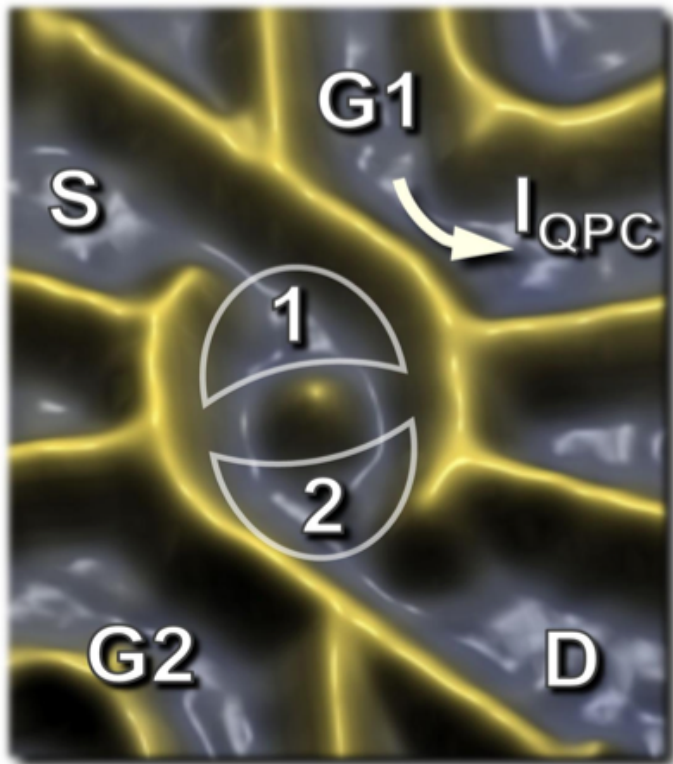
Experiment with single electrons

A. Tonomura et al.,

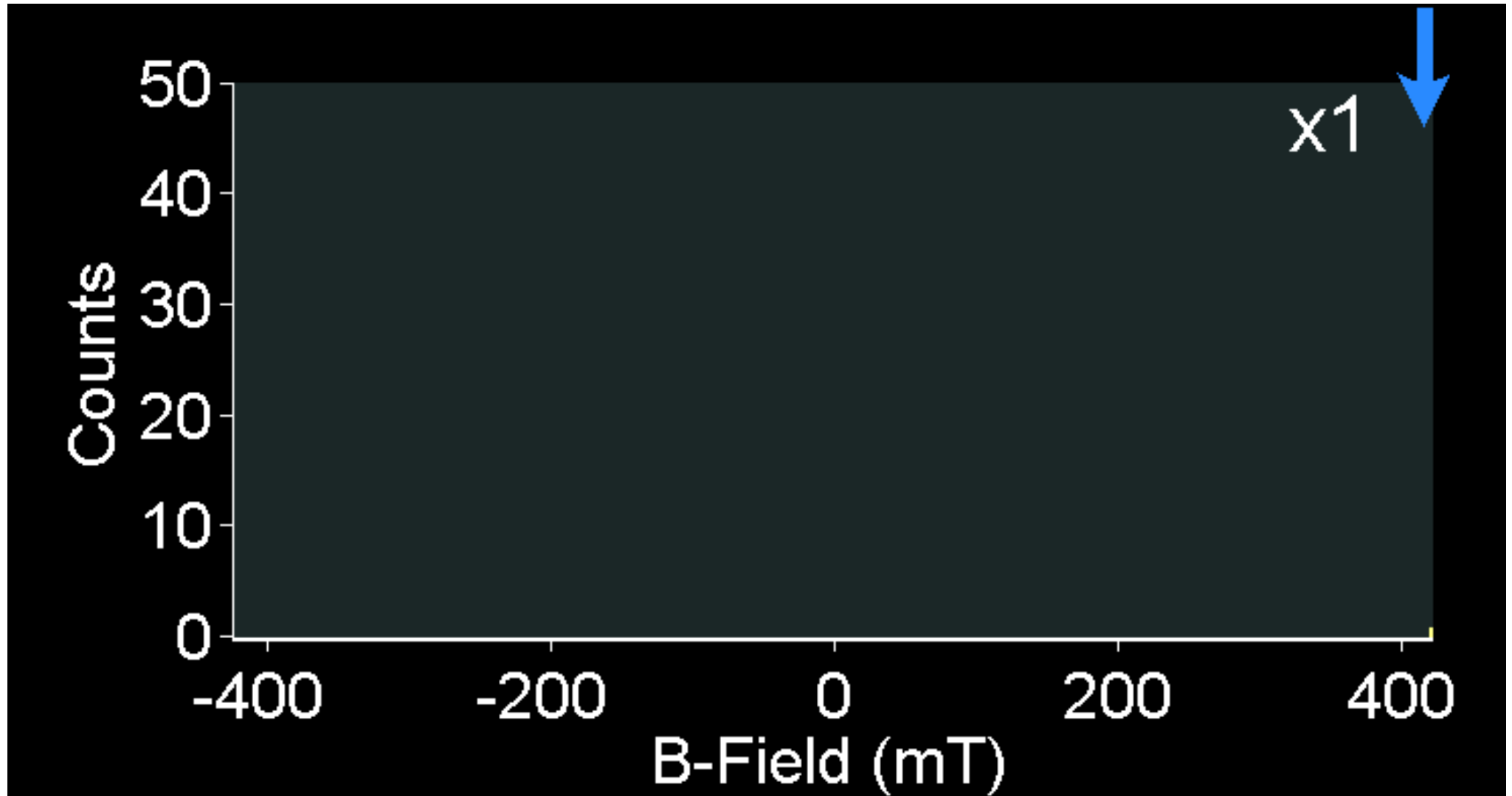
American Journal of Physics **57**, 117-120 (1989)



The setup



Building up an interference pattern



Conclusion

Here is the miracle:

QD extends over $100 \times 100 \times 10 \text{ nm}$
= $200 \times 200 \times 20 = 8 \times 10^5$ unit cells
= 6.4×10^6 atoms

They have 2.56×10^7 *valence* electrons
or 5×10^8 electrons in total.

**We are able to control and observe a single one
of them and its quantum properties in real time!**

Part III

Thermodynamic aspects of electron transport

A wealth of counting experiments

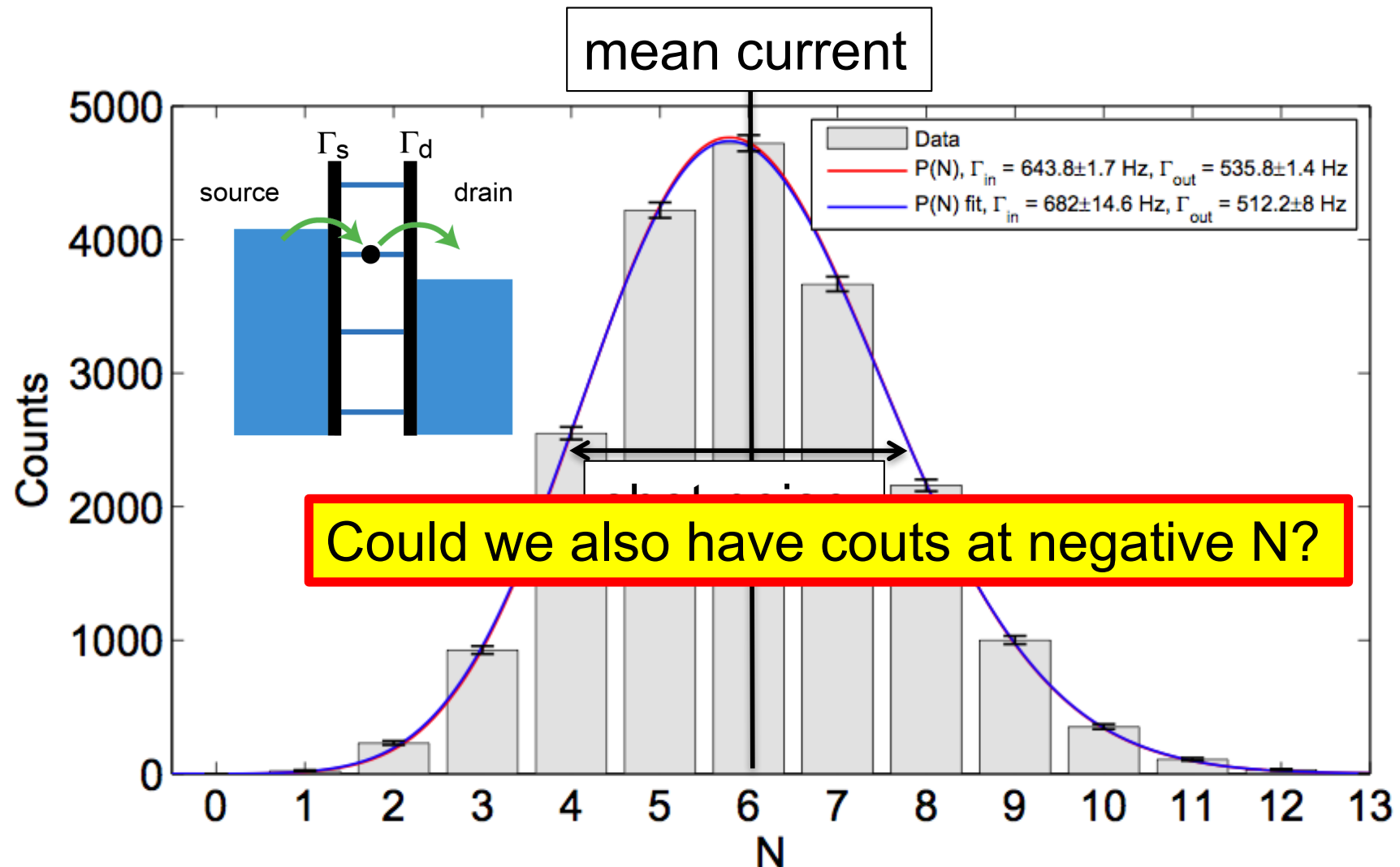
S. Gustavsson *et al*, Surf. Sci. Rep. **64**, 191 (2009).

T. Ihn *et al*, Solid State Commun. **149**, 1419 (2009).

...

- Shot noise and super-poissonian noise
- excited state spectroscopy
- single-electron interference
- co-tunneling in counting
- photon detection
- detector back-action
- charge detection in graphene and InAs nanowires
- radio-frequency read-out
- irreversibility and tunneling
- fluctuation theorems, Jarzinski relation
- the arrow of time
- measurement of degeneracies
- spin-blockade and spin-orbit interaction

Full counting statistics of the current

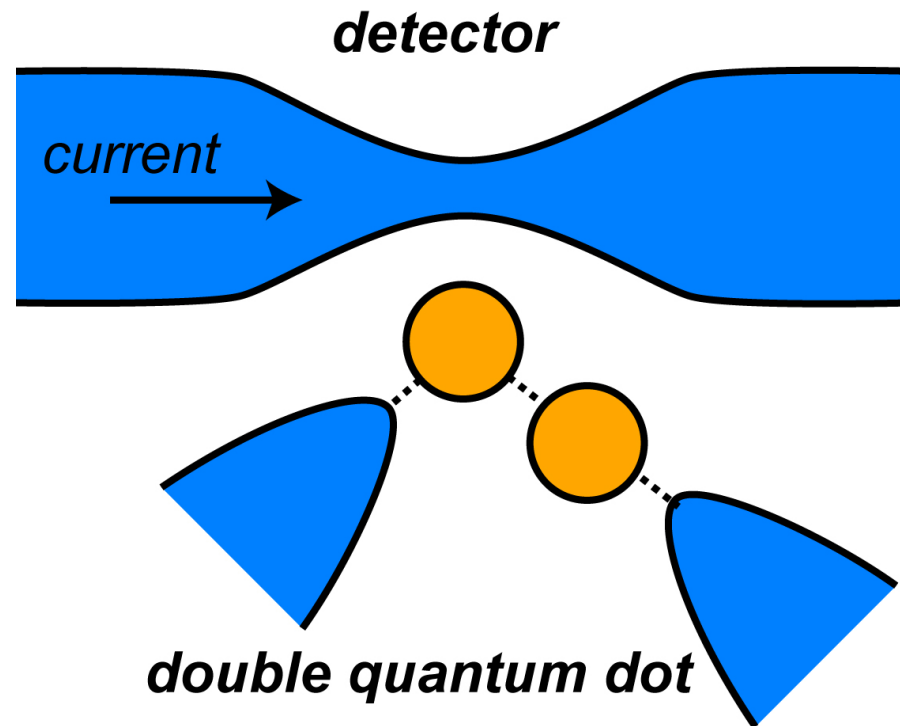


Measurement by Simon Gustavsson: PRL **96**, 076605 (2006)

Theory: Bagrets and Nazarov, PRB **67**, 085316 (2003);

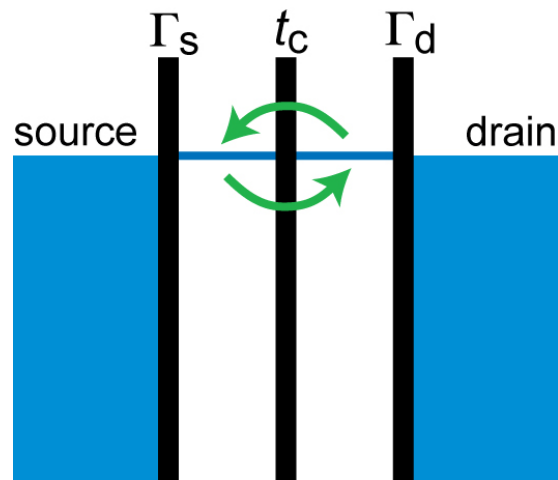
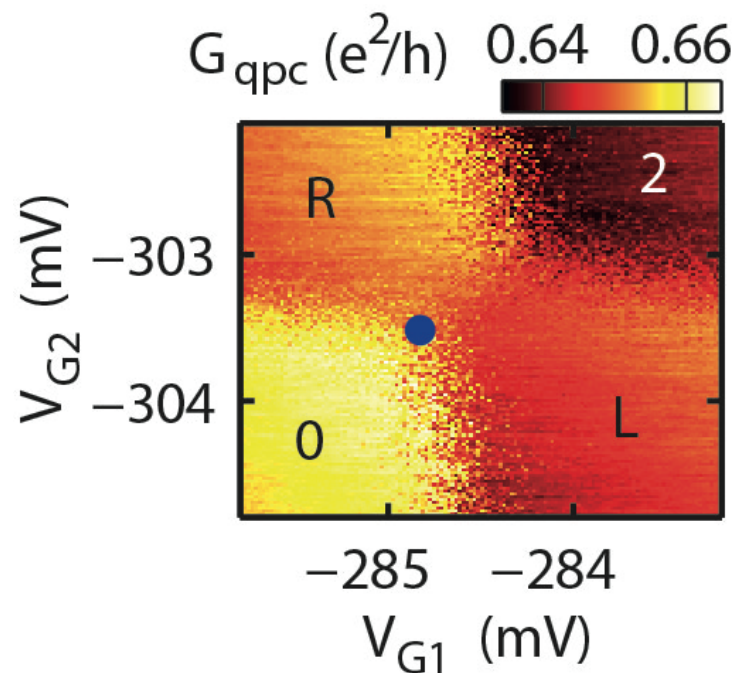
see also: C. Fricke *et al*, PRB **76**, 155307 (2007)

Charge detection in double quantum dots: the concept

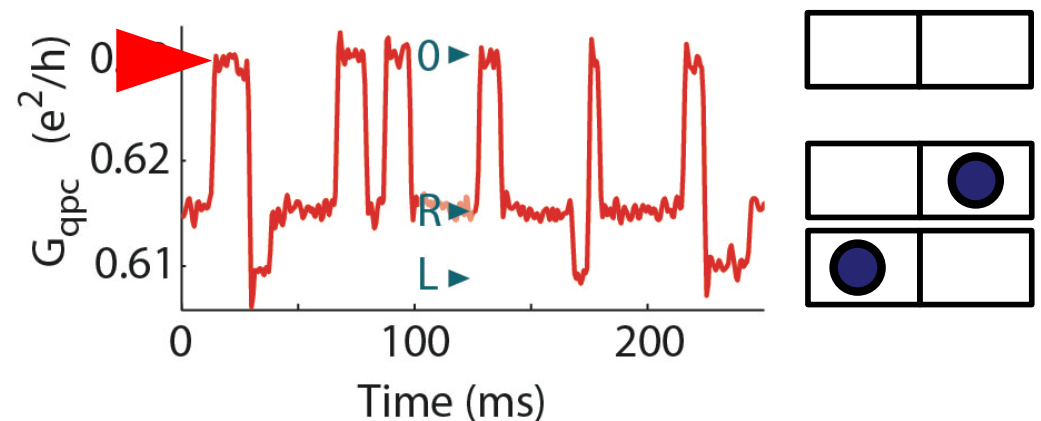
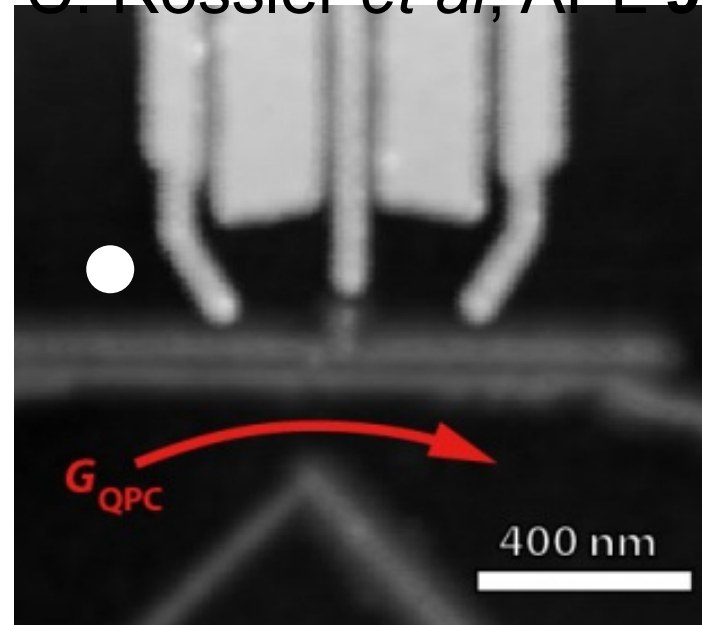


quantum point contact detector
detects the position of electrons inside the DQD structure

Charge detection in double quantum dots: an implementation

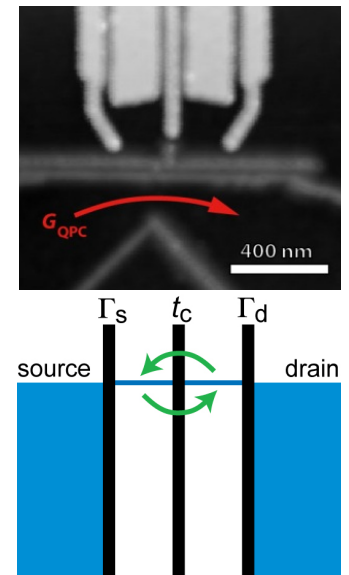
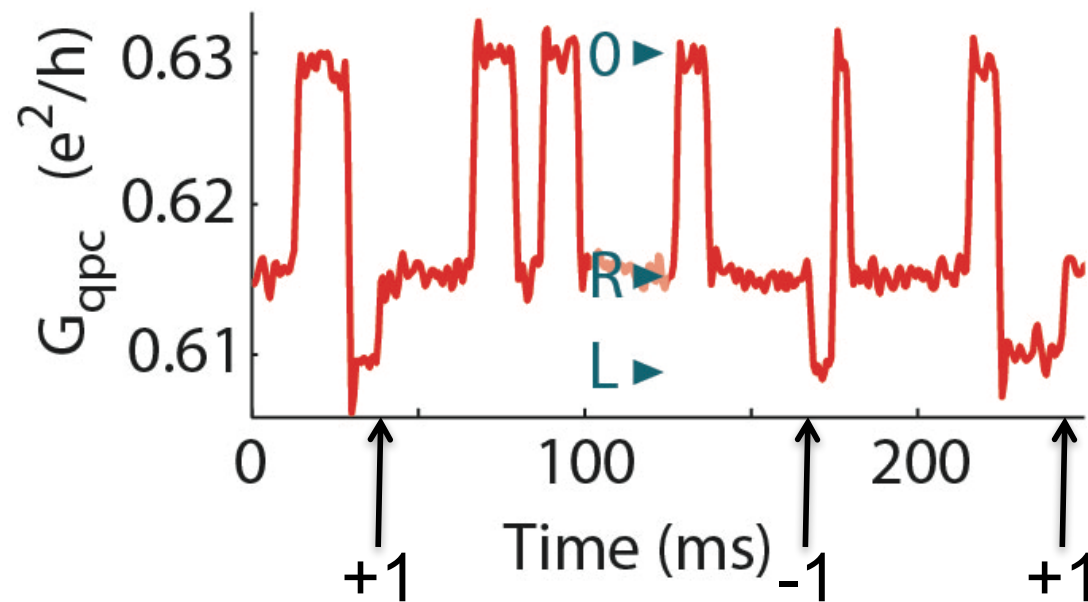


C. Rössler *et al*, APL **97**, 152109



see also: T. Fujisawa *et al*, Science **3**

How and what we count



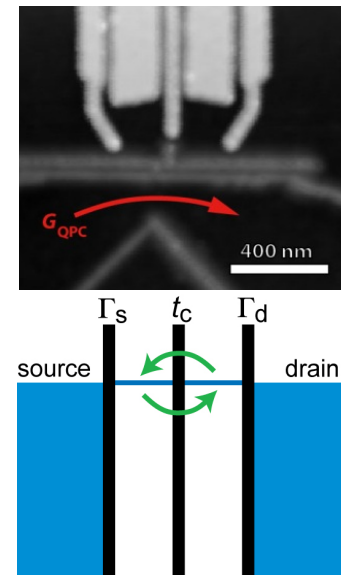
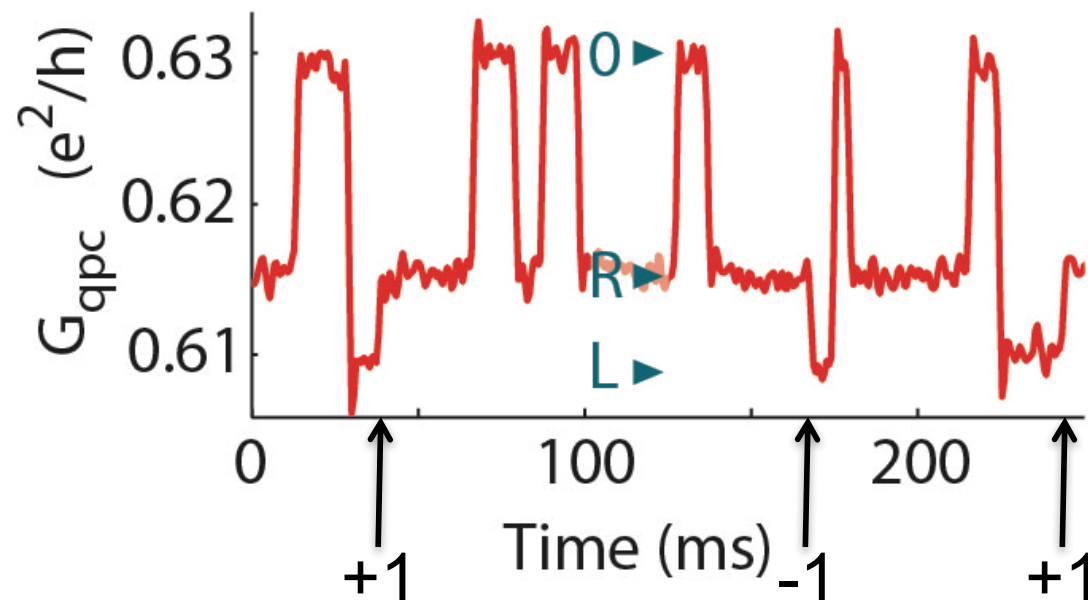
Count:

Transition from left to right dot: +1

Transition from right to left dot: -1

Sum of Counts per time interval: Full counting statistics

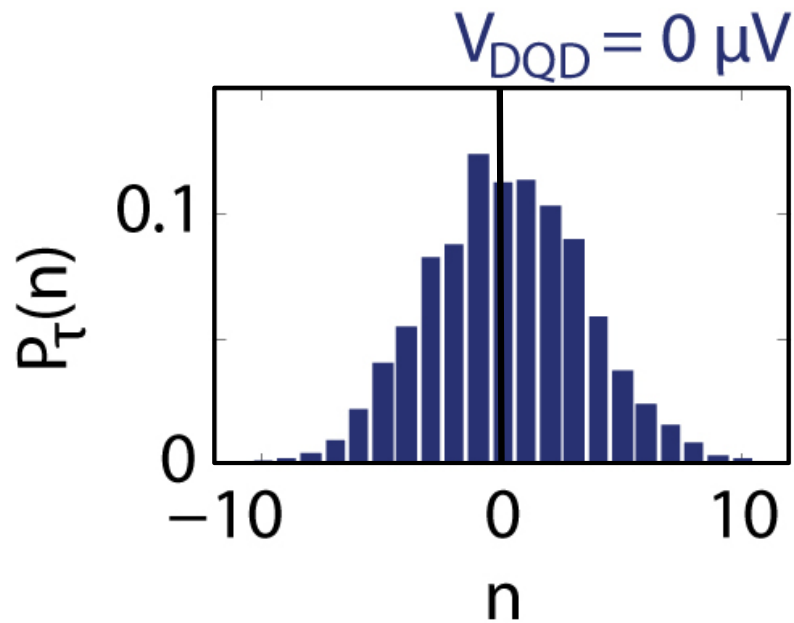
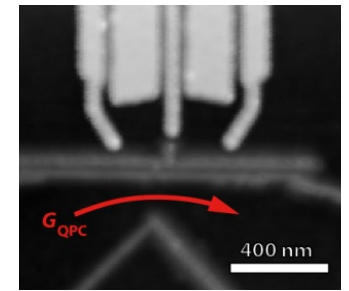
How and what we count



$$\frac{d}{dt} \begin{pmatrix} p_0 \\ p_1 \\ p_2 \end{pmatrix} = \begin{pmatrix} -(W_{10} + W_{20}) & W_{01} & W_{02} \\ W_{10} & -(W_{01} + W_{21}) & W_{12}e^{-i\chi} \\ W_{20} & W_{21}e^{i\chi} & -(W_{02} + W_{12}) \end{pmatrix} \begin{pmatrix} p_0 \\ p_1 \\ p_2 \end{pmatrix}$$

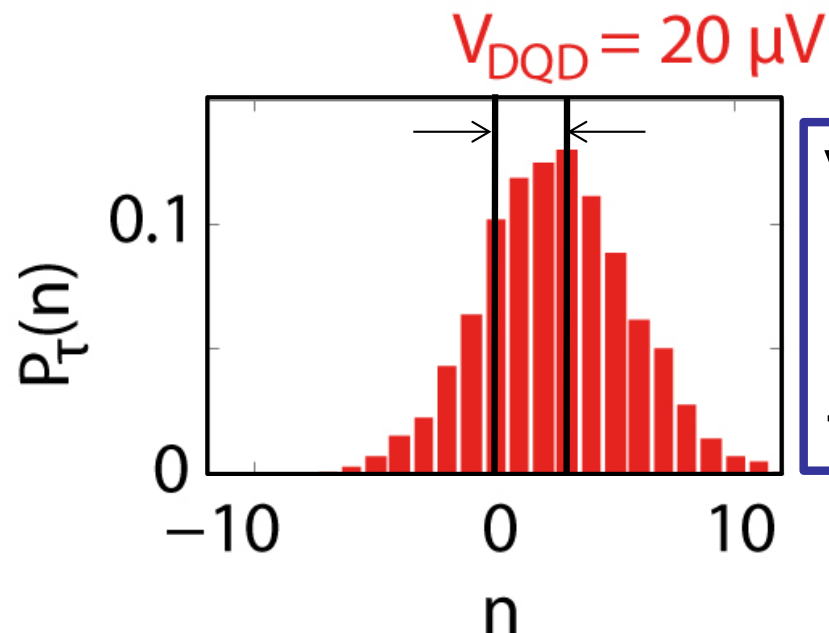
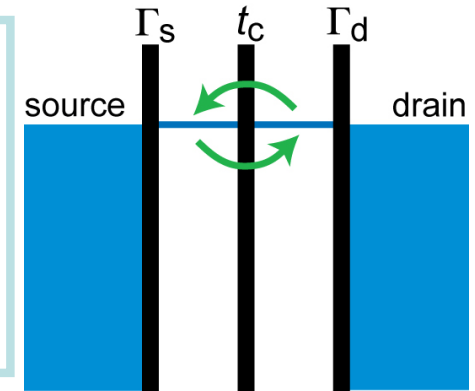
Allows **bi-directional counting**
Direct access to full counting statistics of the current

Full counting statistics of the current



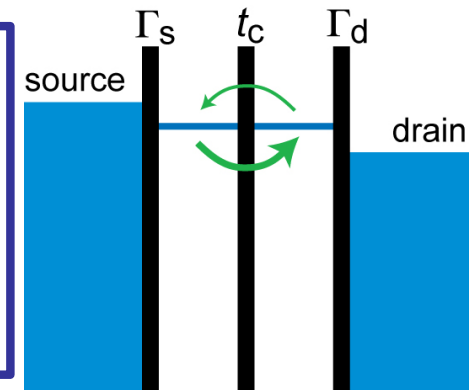
$V_{\text{DQD}} = 0 \mu\text{V}$
→ no net charge flow

$$\langle n \rangle = 0.09 \pm 0.09$$



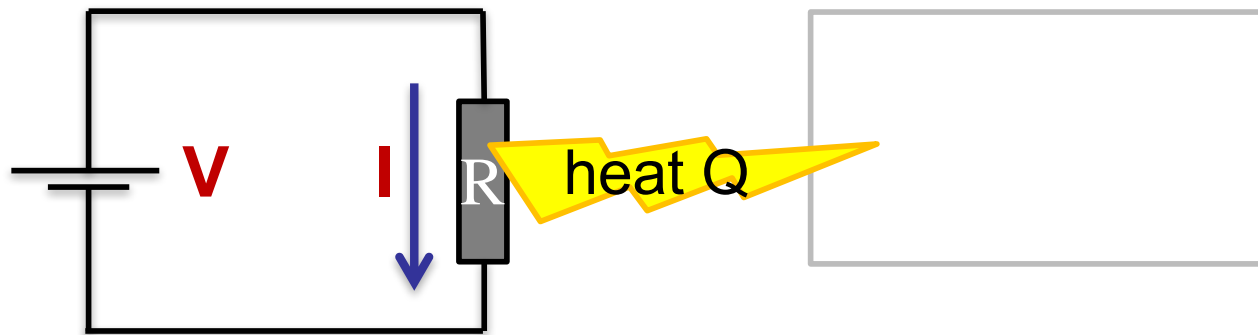
$V_{\text{DQD}} = 20 \mu\text{V}$
→ finite charge flow

$$\langle n \rangle = 2.39 \pm 0.09$$



Thermodynamics of electron transport

Dissipative current: Macroscopically irreversible process



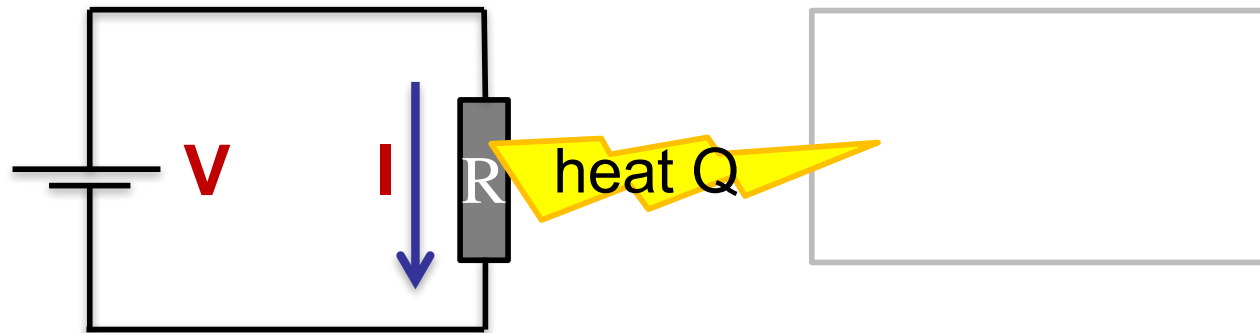
Non-equilibrium physics

2nd law of thermodynamics: $\Delta S = \Delta Q/T > 0$

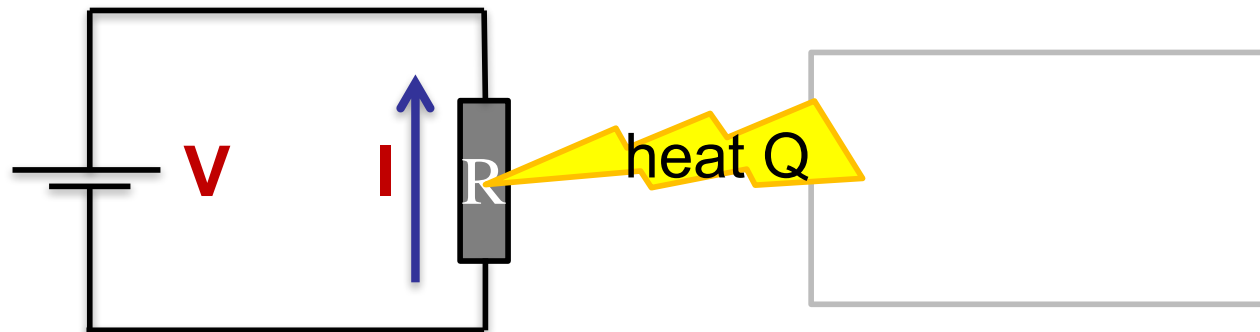
A macroscopic number of elementary processes average (large system or time scale) and give a net entropy increase

Taking a microscopic view

Reverse processes are not forbidden!



$$P_{\tau}(\Delta S > 0)$$



$$P_{\tau}(\Delta S < 0)$$

The second law can be violated on short time-scales τ and/or in small systems

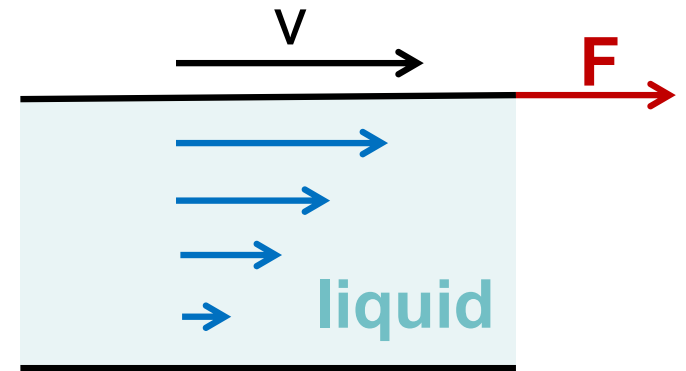
Entropy production $\Delta S = \Delta Q/T$

ΔS is a **fluctuating variable**, probability $P_{\tau}(\Delta S)$

The fluctuation theorem

Quantitative statement about $P_\tau(\Delta S)$

$$\frac{P_\tau(\Delta S)}{P_\tau(-\Delta S)} = e^{\Delta S/k_B}$$



*D.J. Evans, E.G.D. Cohen, G.P. Morriss, PRL **71**, 2401 (1993).*

$$p_{S \rightarrow D}(\epsilon) = \mathcal{T} f_S(\epsilon) [1 - f_D(\epsilon)]$$

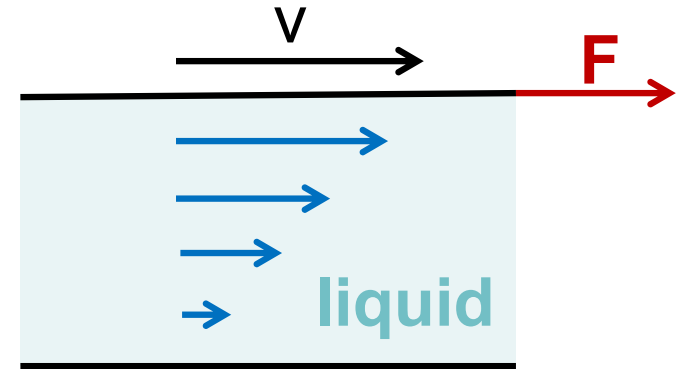
$$p_{S \leftarrow D}(\epsilon) = \mathcal{T} f_D(\epsilon) [1 - f_S(\epsilon)]$$

$$\begin{aligned} \frac{p_{S \rightarrow D}(\epsilon)}{p_{S \leftarrow D}(\epsilon)} &= \frac{f_S(\epsilon)}{1 - f_S(\epsilon)} \frac{1 - f_D(\epsilon)}{f_D(\epsilon)} \\ &= \exp \left(\frac{\epsilon - \mu_D}{k_B T_D} - \frac{\epsilon - \mu_S}{k_B T_S} \right) = \exp(\Delta S) \end{aligned}$$

The fluctuation theorem

Quantitative statement about $P_\tau(\Delta S)$

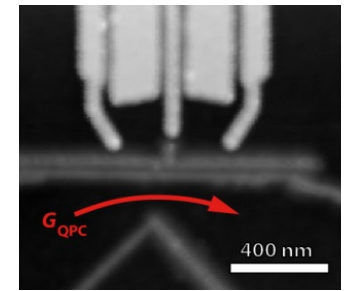
$$\frac{P_\tau(\Delta S)}{P_\tau(-\Delta S)} = e^{\Delta S/k_B}$$



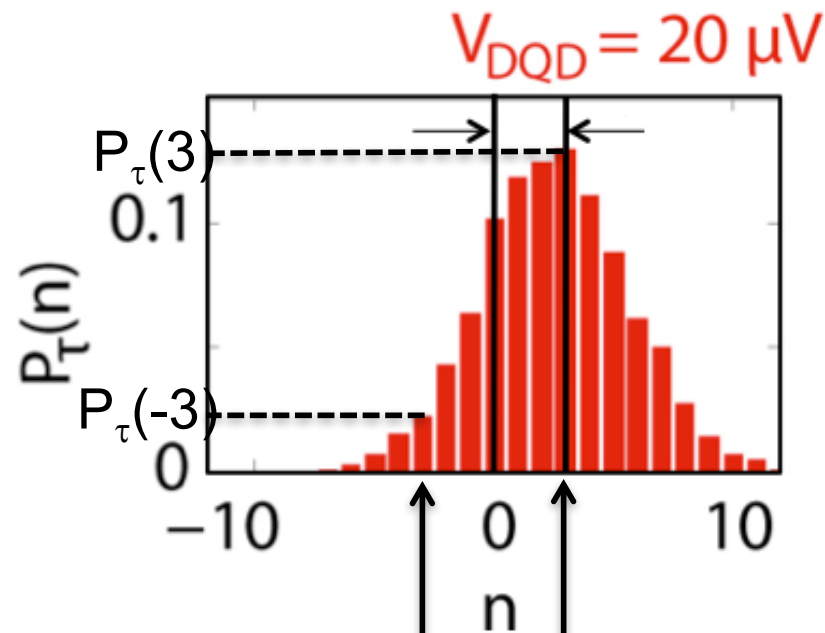
D.J. Evans, E.G.D. Cohen, G.P. Morriss, PRL 71, 2401 (1993).

Fluctuation theorem...

...and full counting statistics



$$\frac{P_{\tau}(\Delta S)}{P_{\tau}(-\Delta S)} = \exp\left(\frac{\Delta S}{k_B}\right) \Rightarrow \frac{P_{\tau}(n)}{P_{\tau}(-n)} = \exp\left(\frac{neV}{k_B T}\right)$$



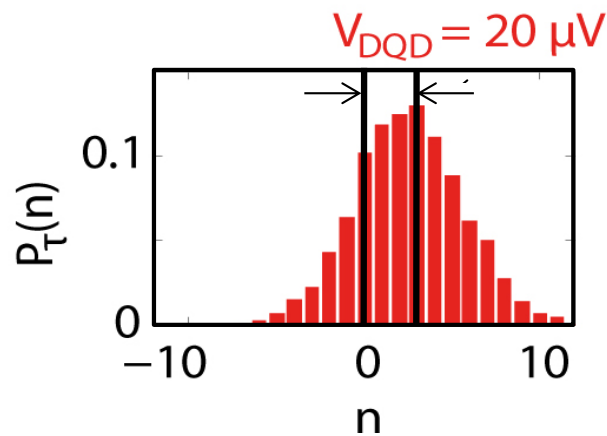
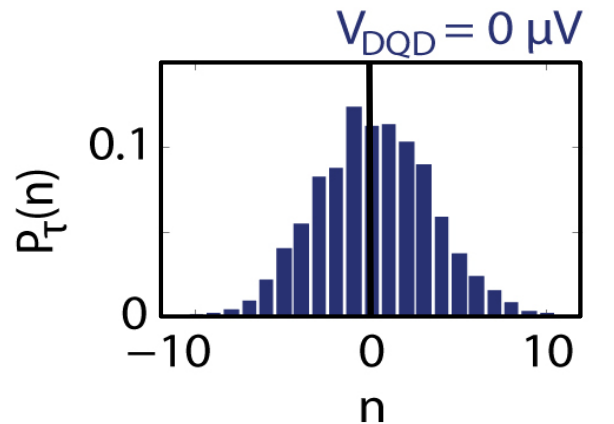
Example: -3 +3

n: number of charges
transferred from source to
drain

see also: Y. Utsumi *et al*, PRB **81**,

Experimental test...

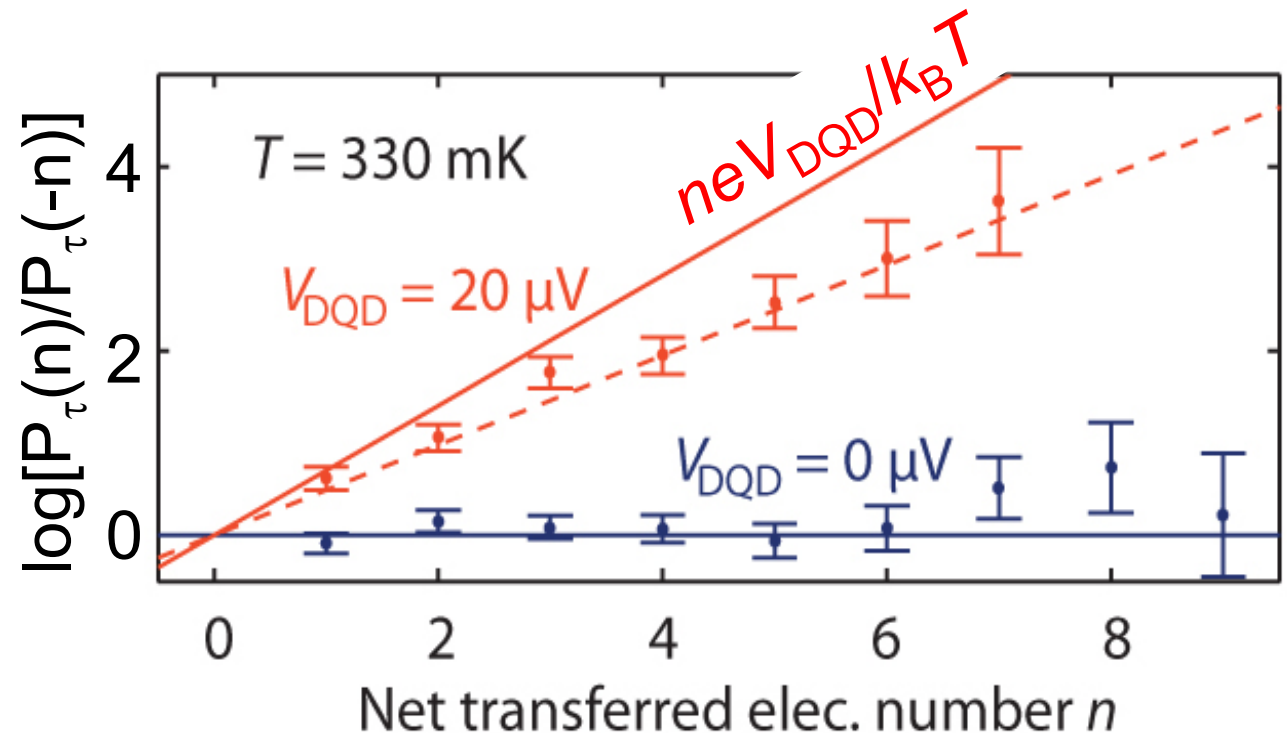
...of the fluctuation theorem



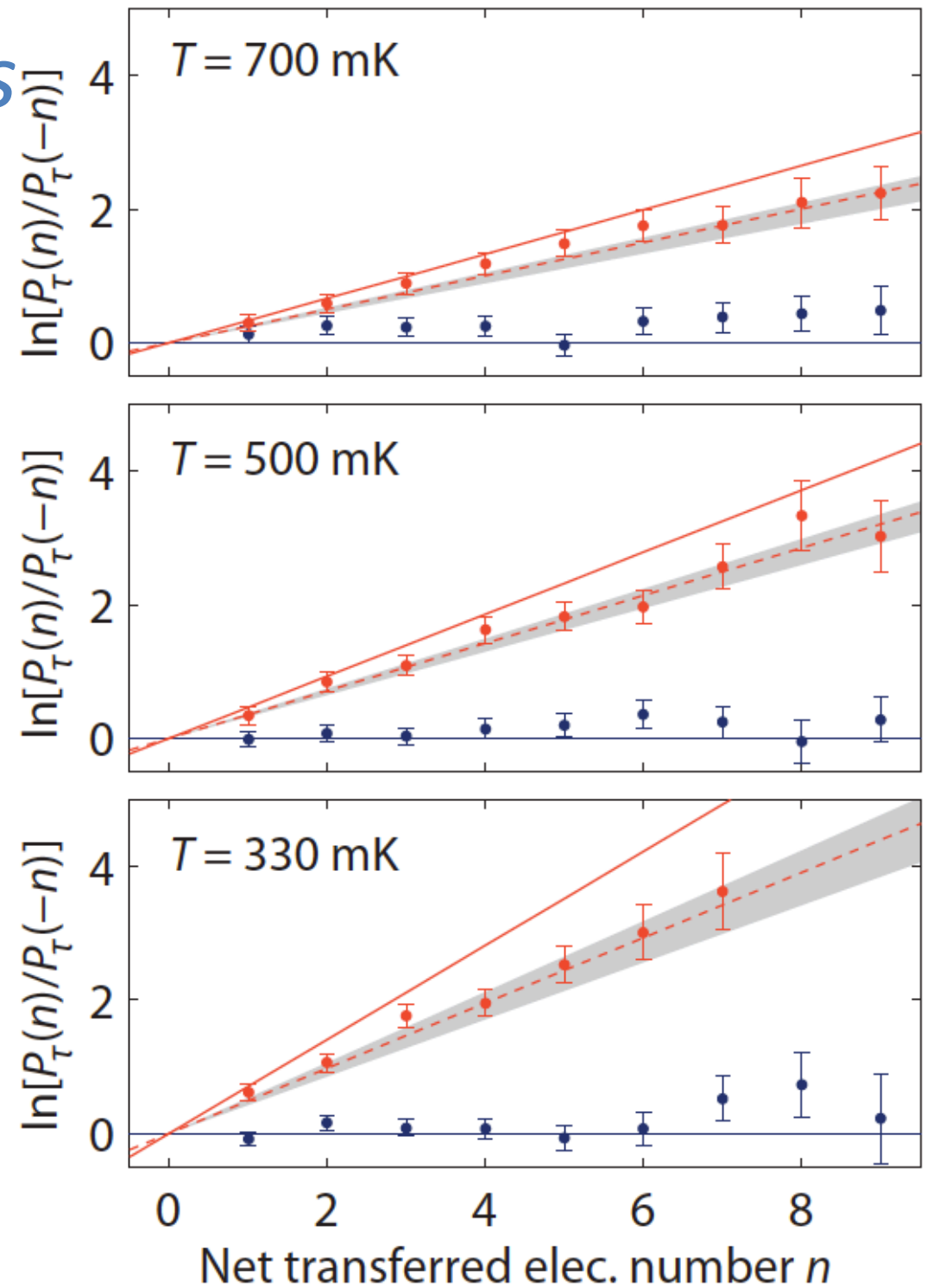
after finite
bandwidth
correction:
dashed line

$$\frac{P_\tau(n)}{P_\tau(-n)} = \exp\left(\frac{neV_{\text{DQD}}}{k_B T}\right)$$

B. Küng et al, PRX 2, 011001 (2012).



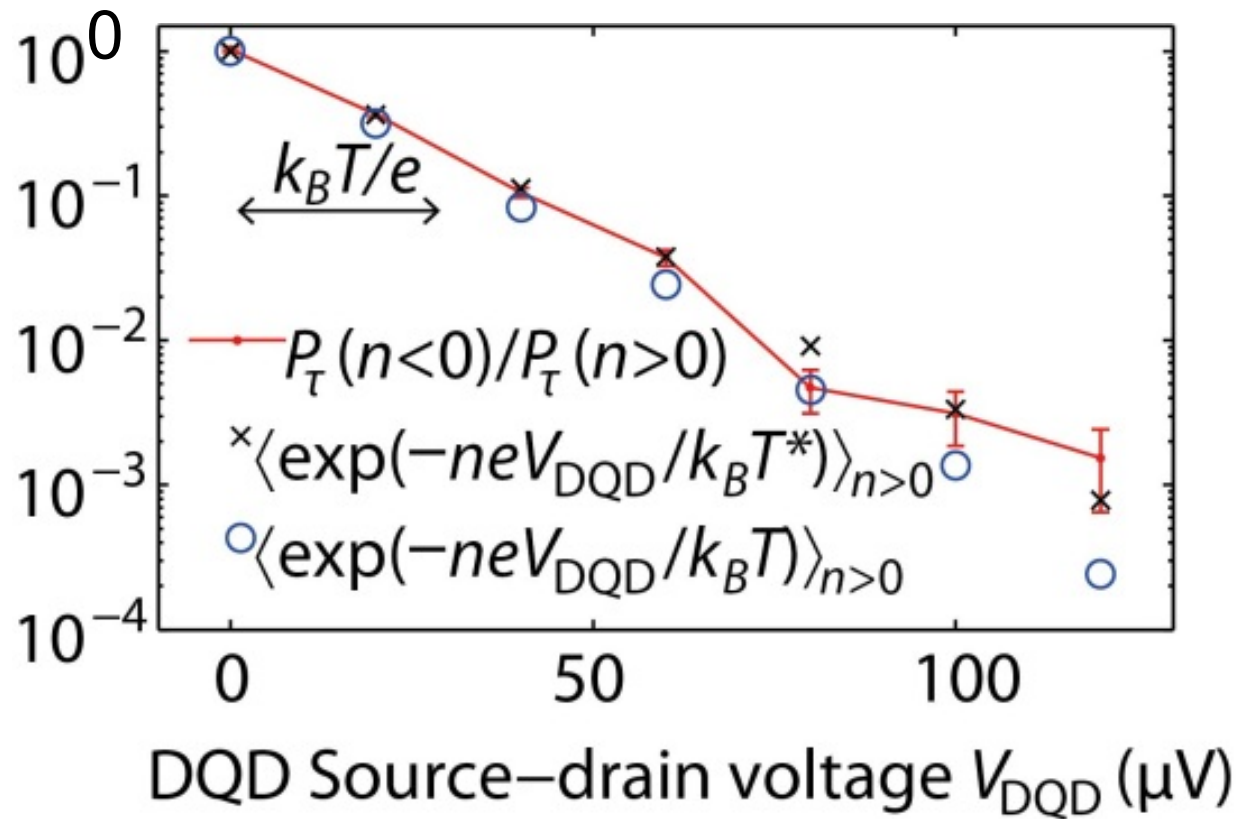
Higher temperatures



→ fluctuation theorem holds

Higher source–drain bias voltage

$$\frac{P_\tau(n)}{P_\tau(-n)} = \exp\left(\frac{neV_{\text{DQD}}}{k_B T}\right) \Rightarrow \frac{P_\tau(n < 0)}{P_\tau(n > 0)} = \frac{\sum_{n>0} P_\tau(n) \exp\left(\frac{-neV_{\text{DQD}}}{k_B T}\right)}{\sum_{n>0} P_\tau(n)}$$

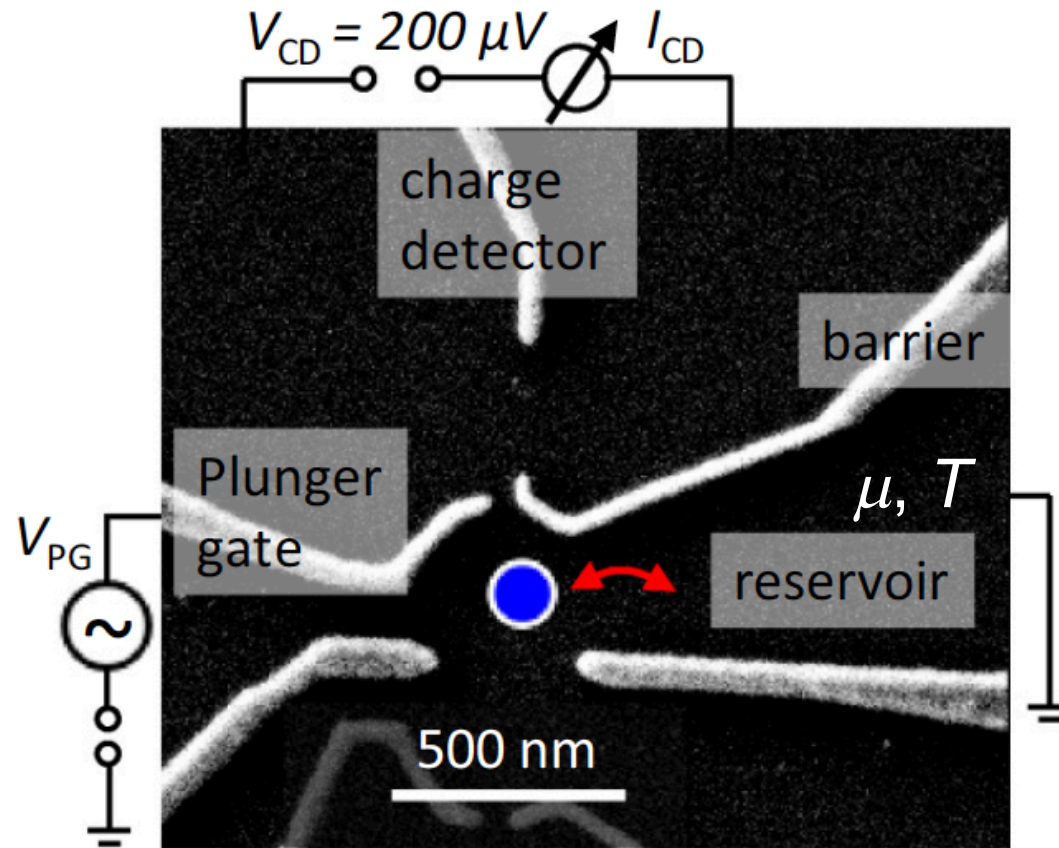


Plot integrated FT
(smaller error)

Part IV

*Non-equilibrium thermodynamics
at the level of single electrons*

Quantum dot thermodynamics



sample based
on GaAs 2DEG

State variables: μ , T , V_{PG}

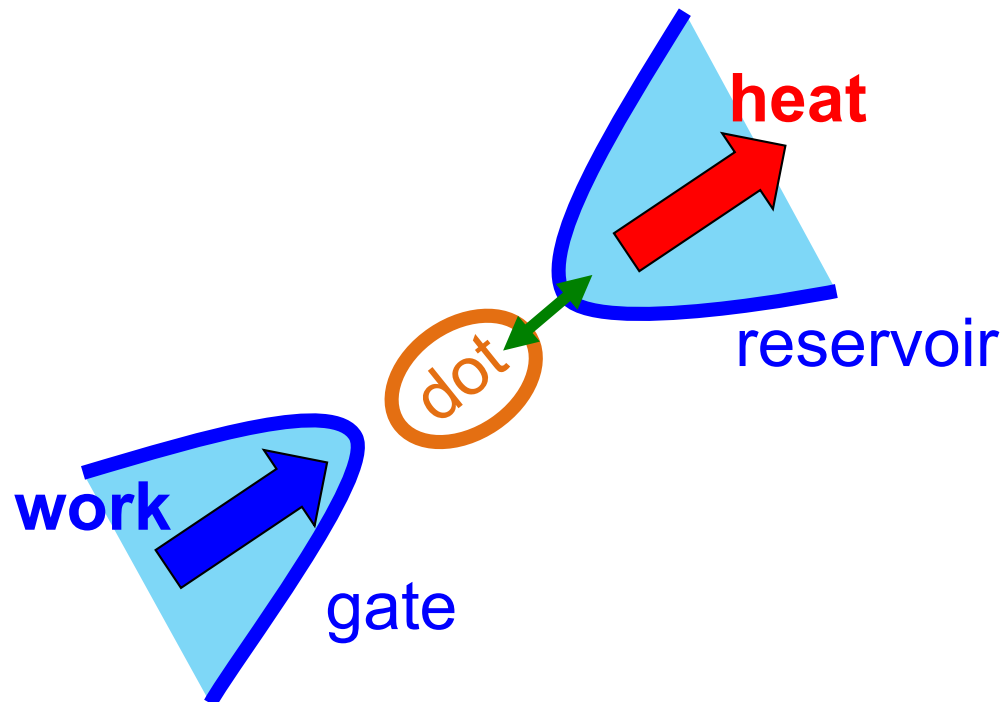
Thermodynamic process

Elementary thermodynamic process:

State A
 $V_G^{(1)}, T, E_F$



State B
 $V_G^{(2)}, T, E_F$



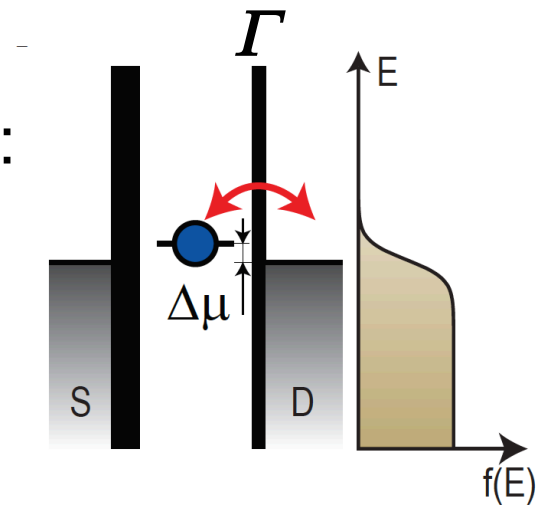
here:
work performed
on single electron

heat generated
by single electron

Non-equilibrium thermodynamics

Reversible processes:
system always close to equilibrium with reservoir

Quantum dot equilibration time:
tunneling rate Γ
fully tunable



Processes fast on the scale of Γ :

**Drive quantum dot far from
thermodynamic equilibrium with reservoir**

Jarzynski equality

Repeatedly drive a system that is in contact with a heat reservoir from initial equilibrium state to final non-equilibrium state

Statistical variable:
Work performed
on the system

Free energy difference
between initial and final
states in equilibrium

$$\left\langle \exp \left(-\frac{\Delta W}{k_B T} \right) \right\rangle = \exp \left(-\frac{\Delta F}{k_B T} \right)$$

Ensemble
average

Reservoir temperature

C. Jarzynski, PRL **78**, 2690 (1997)

Related work:

J. Liphardt et al, Science **296**, 5574 1832-1835 (2002)

O.P Saira et al., PRL. **109**, 180601 (2012)

Shuoming An et al, Nature Physics **11**, 193–199 (2015)

T. B. Batalhao et al., PRL **113**, 140601 (2014)

Thermodynamics of small numbers

Thermodynamic (statistical) fluctuations irrelevant due to

- ensemble averaging (macroscopic system)
- time averaging (small bandwidth observation)

$$\frac{\Delta W}{W_{\text{tot}}} \propto \frac{1}{\sqrt{N}}$$

Particle number
or number of repetitions
or of tunneling events

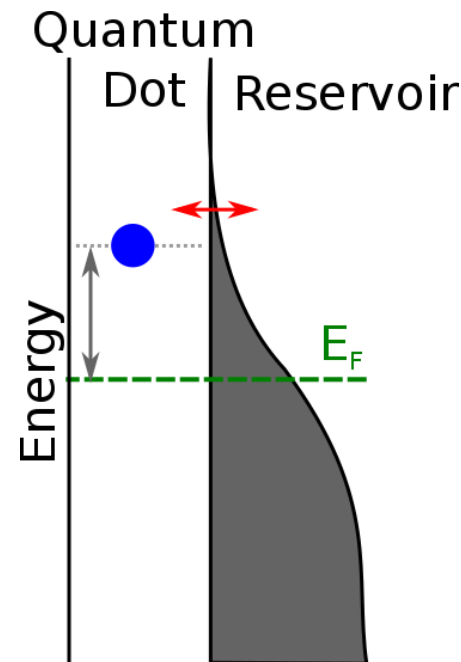
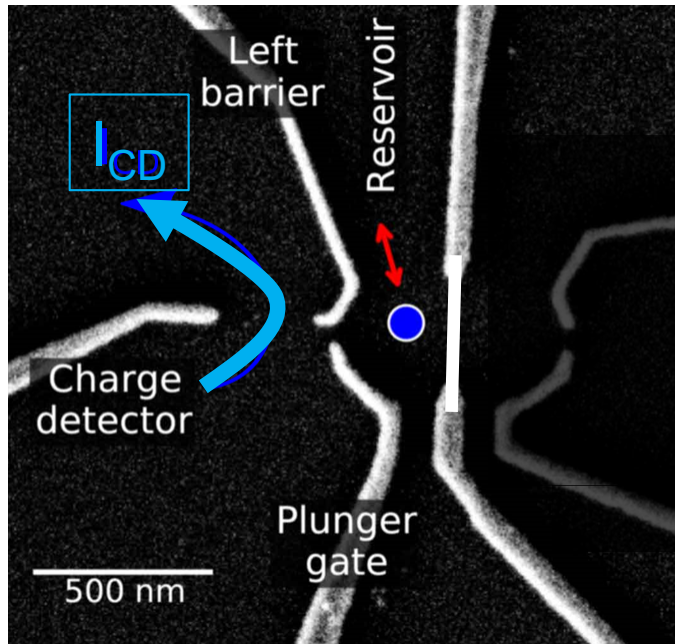
$$W_{\text{tot}} = \sum_{j=1}^N W_i$$

$$\Delta W^2 = \sum_{j=1}^N (W_i - \langle W_i \rangle)^2$$

What happens, if $N \rightarrow 1$?

Fluctuations become very relevant!

Calibration at equilibrium



Electron tunneling between the quantum dot and the reservoir

Tunneling rates:

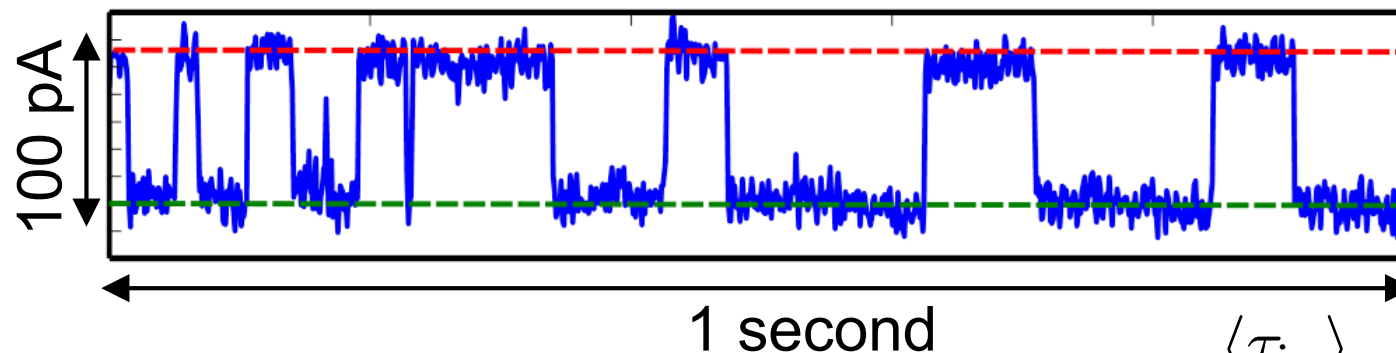
$$\Gamma_{\text{in,out}} = \frac{1}{\langle \tau_{\text{in,out}} \rangle}$$

out

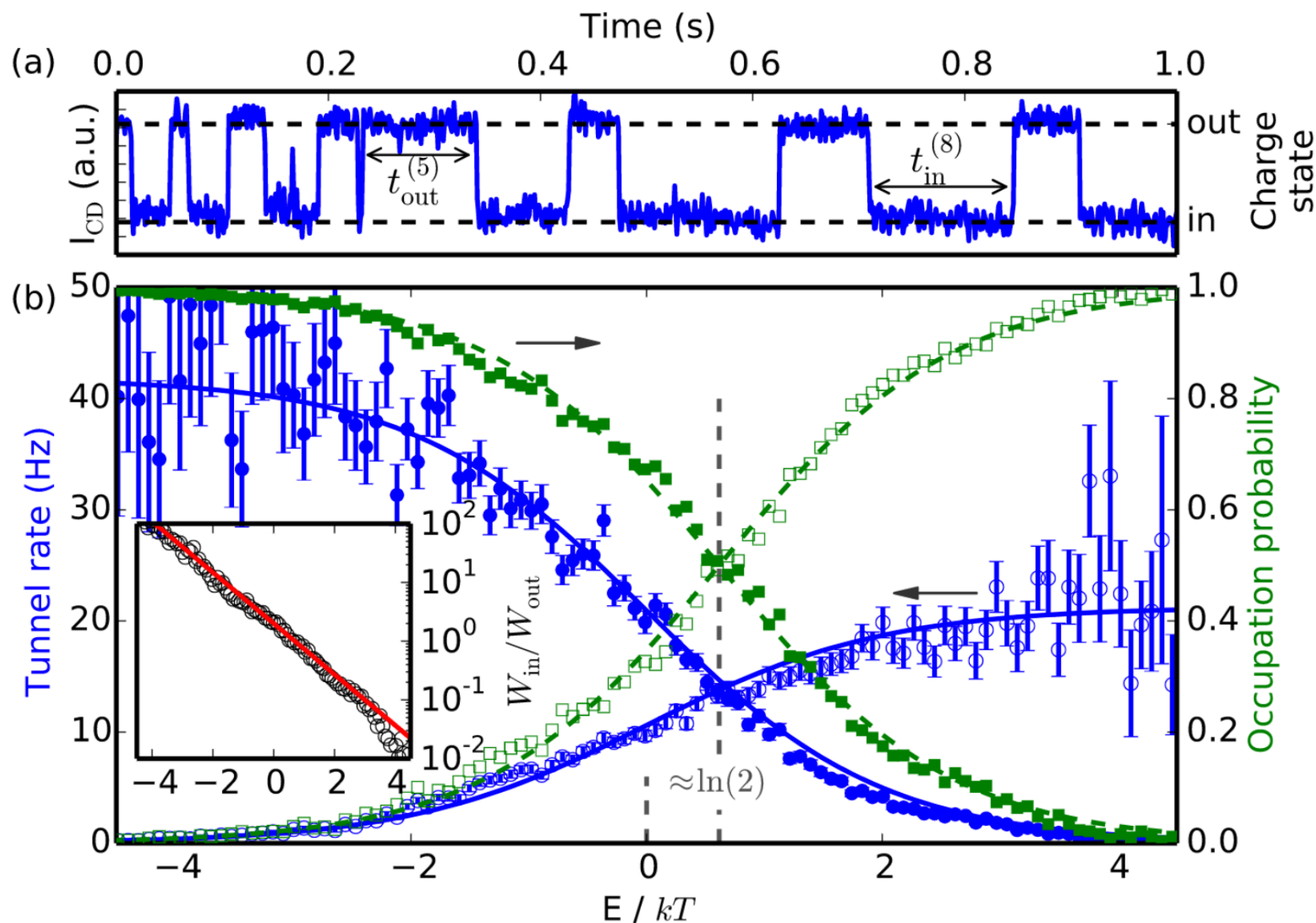
in

Temperature:

$$\frac{\langle \tau_{\text{in}} \rangle}{\langle \tau_{\text{out}} \rangle} = \exp \left(-\frac{E - E_F}{k_B T} \right)$$



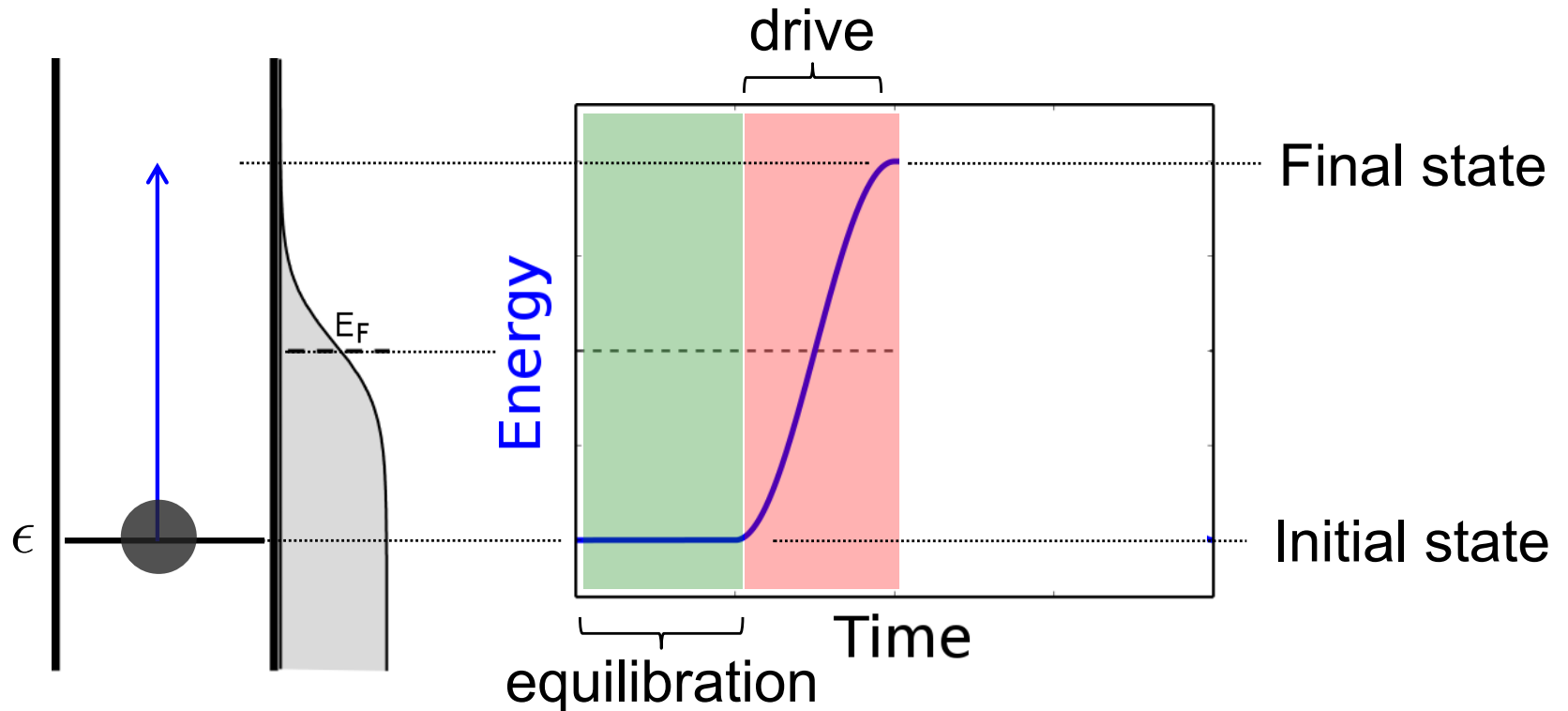
Calibration at equilibrium



Jarzynski equality

$$\underbrace{\left\langle \exp \left(-\frac{\Delta W}{k_B T} \right) \right\rangle}_{\text{Measurement}} = \underbrace{\exp \left(-\frac{\Delta F}{k_B T} \right)}_{\text{Theory}}$$

$$E(t) = E_F - A \cos(2\pi f t) \quad \text{for } 0 \leq t \leq 1/2f$$

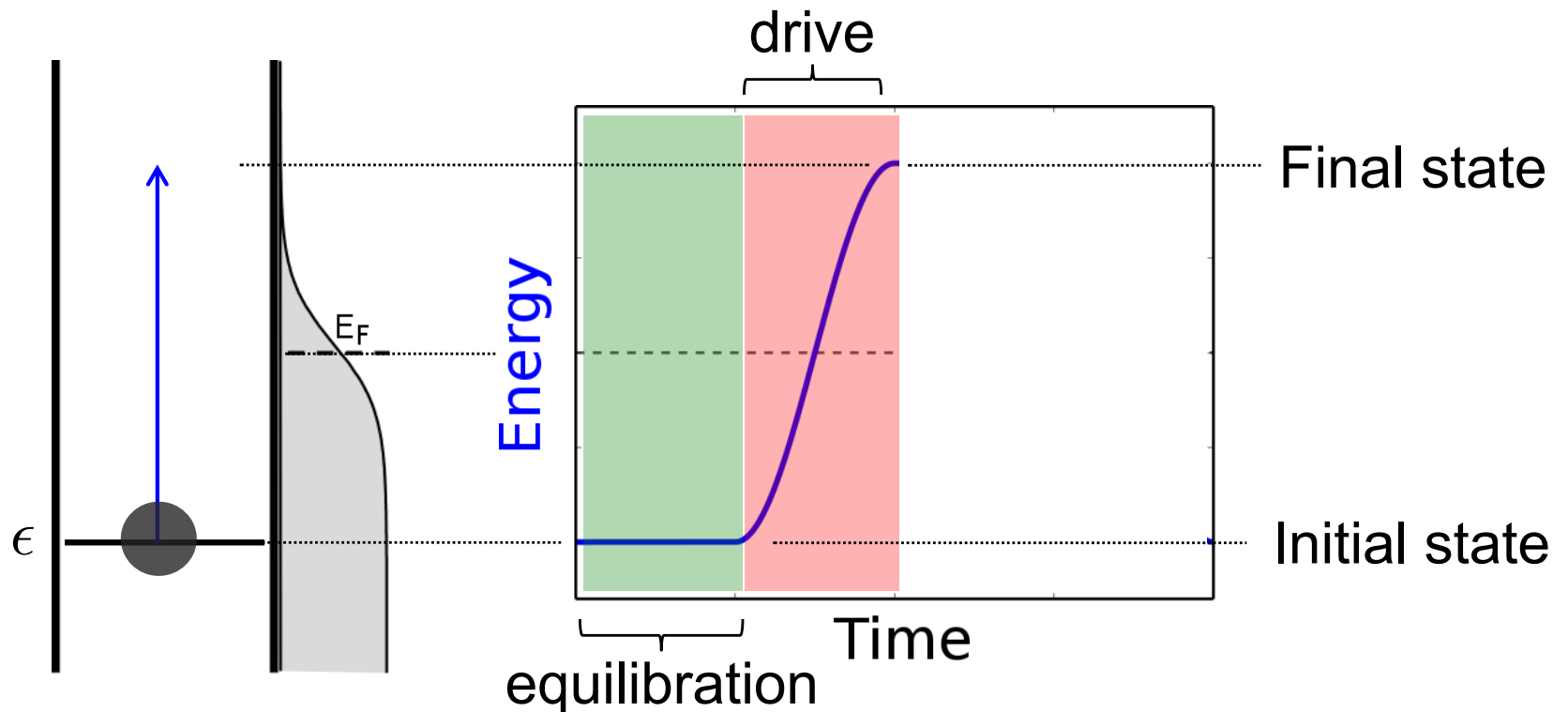


Jarzynsky equality

$$\underbrace{\left\langle \exp \left(-\frac{\Delta W}{k_B T} \right) \right\rangle}_{\text{Measurement}} = \underbrace{\exp \left(-\frac{\Delta F}{k_B T} \right)}_{\text{Theory}}$$

- measure ΔW during driving
- repeat the measurement 20'000 times

$$E(t) = E_F - A \cos(2\pi f t) \quad \text{for } 0 \leq t \leq 1/2f$$



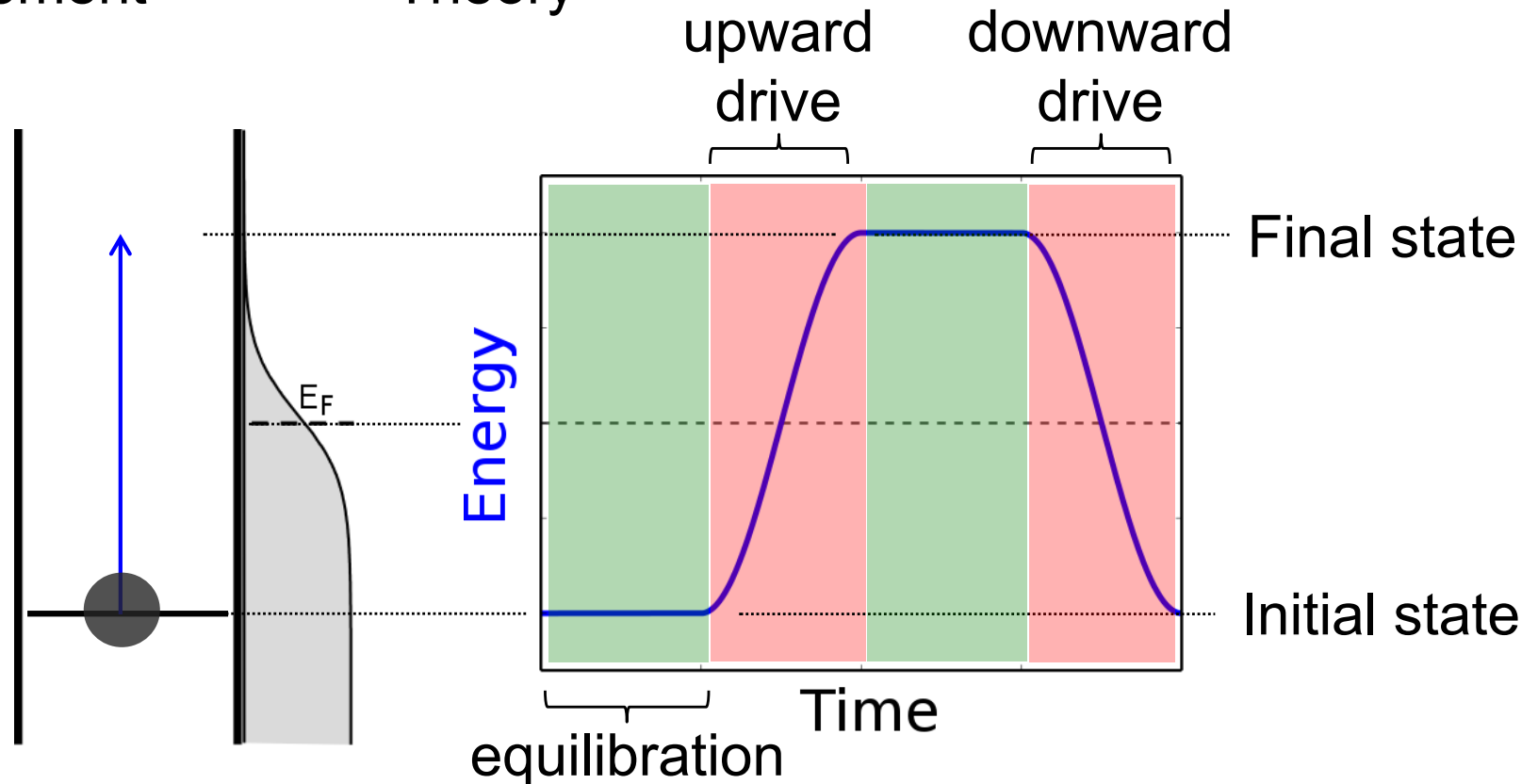
Jarzynsky equality

$$\underbrace{\left\langle \exp \left(-\frac{\Delta W}{k_B T} \right) \right\rangle}_{\text{Measurement}} = \underbrace{\exp \left(-\frac{\Delta F}{k_B T} \right)}_{\text{Theory}}$$

- measure ΔW during driving
- repeat the measurement 20'000 times

Measurement

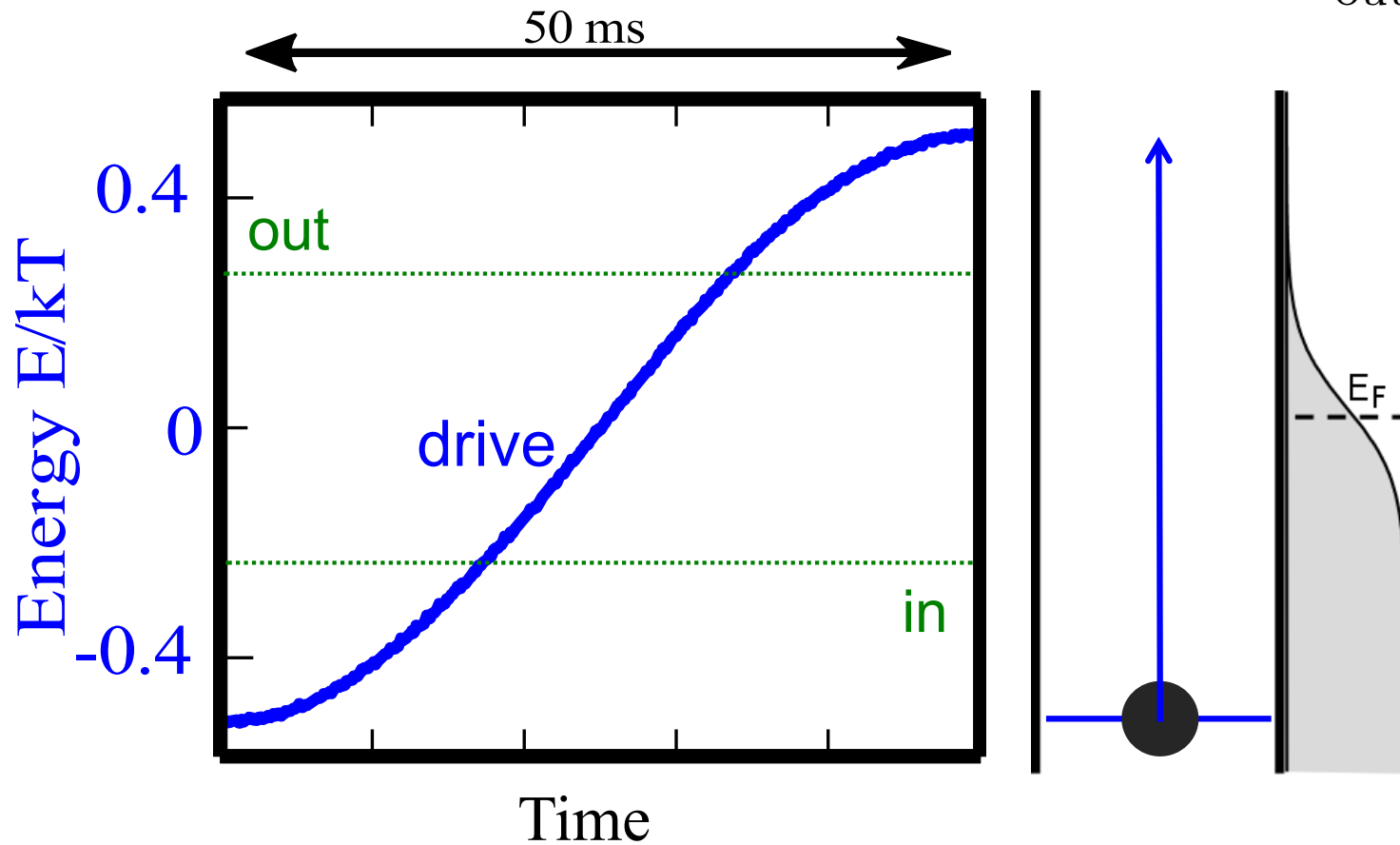
Theory



Upward drive

$$E(t) = E_F - A \cos(2\pi f t) \quad \text{for } 0 \leq t \leq 1/2f$$

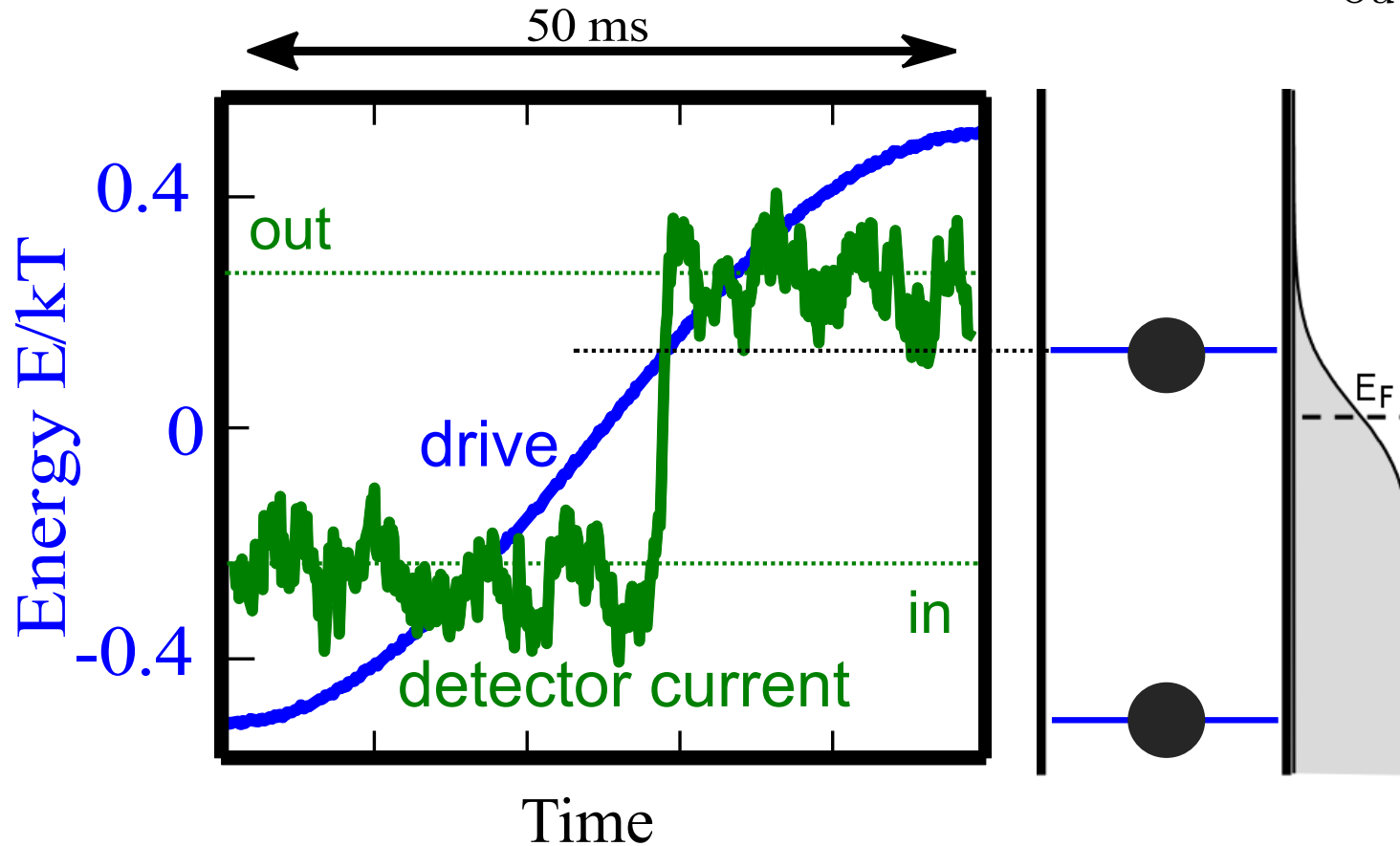
$\Gamma_{\text{in}} = 42 \text{ Hz}$
 $\Gamma_{\text{out}} = 21 \text{ Hz}$



Upward drive

$$E(t) = E_F - A \cos(2\pi f t) \quad \text{for } 0 \leq t \leq 1/2f$$

$\Gamma_{\text{in}} = 42 \text{ Hz}$
 $\Gamma_{\text{out}} = 21 \text{ Hz}$

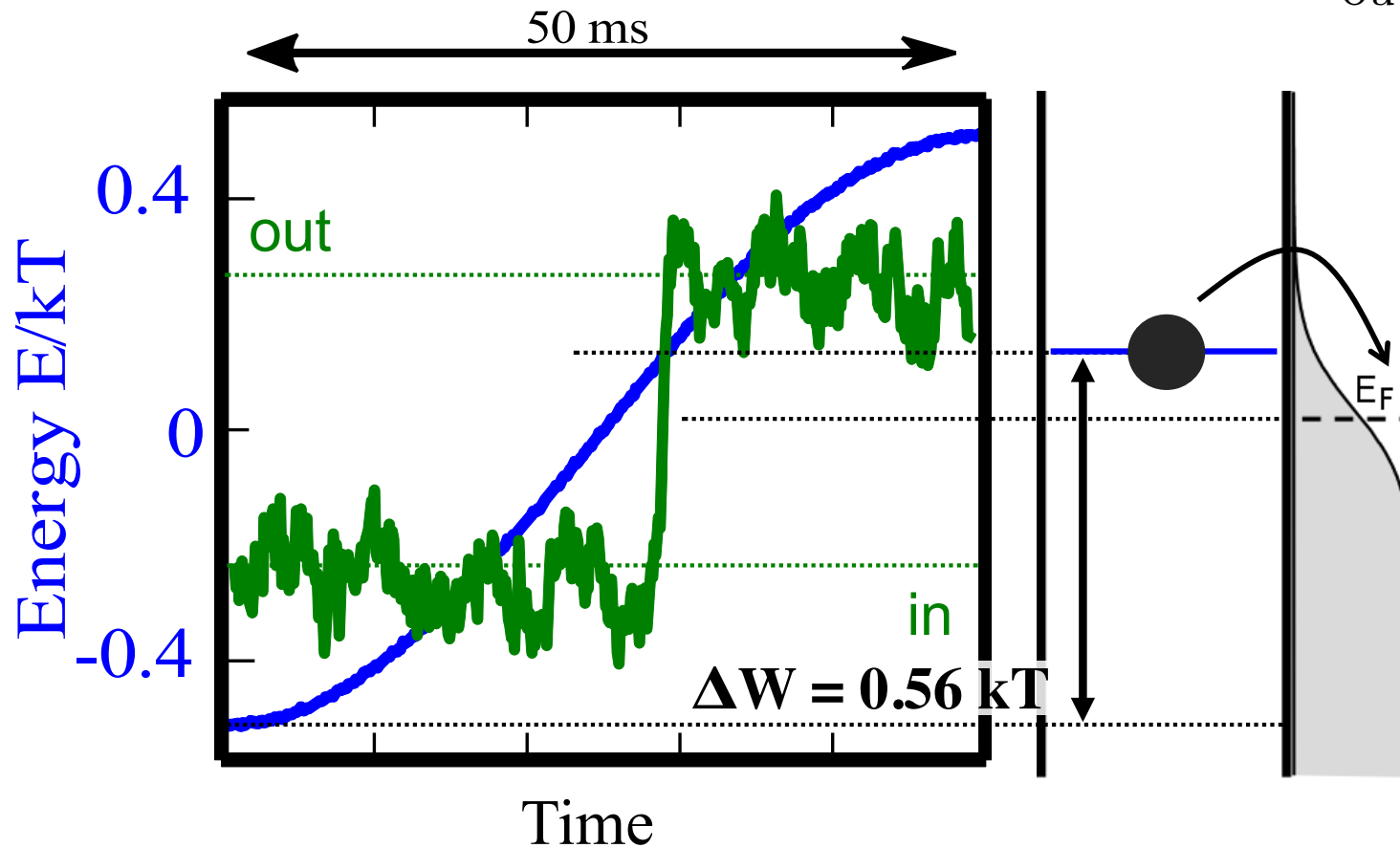


Upward drive

$$E(t) = E_F - A \cos(2\pi f t) \quad \text{for } 0 \leq t \leq 1/2f$$

$$\Gamma_{\text{in}} = 42 \text{ Hz}$$

$$\Gamma_{\text{out}} = 21 \text{ Hz}$$

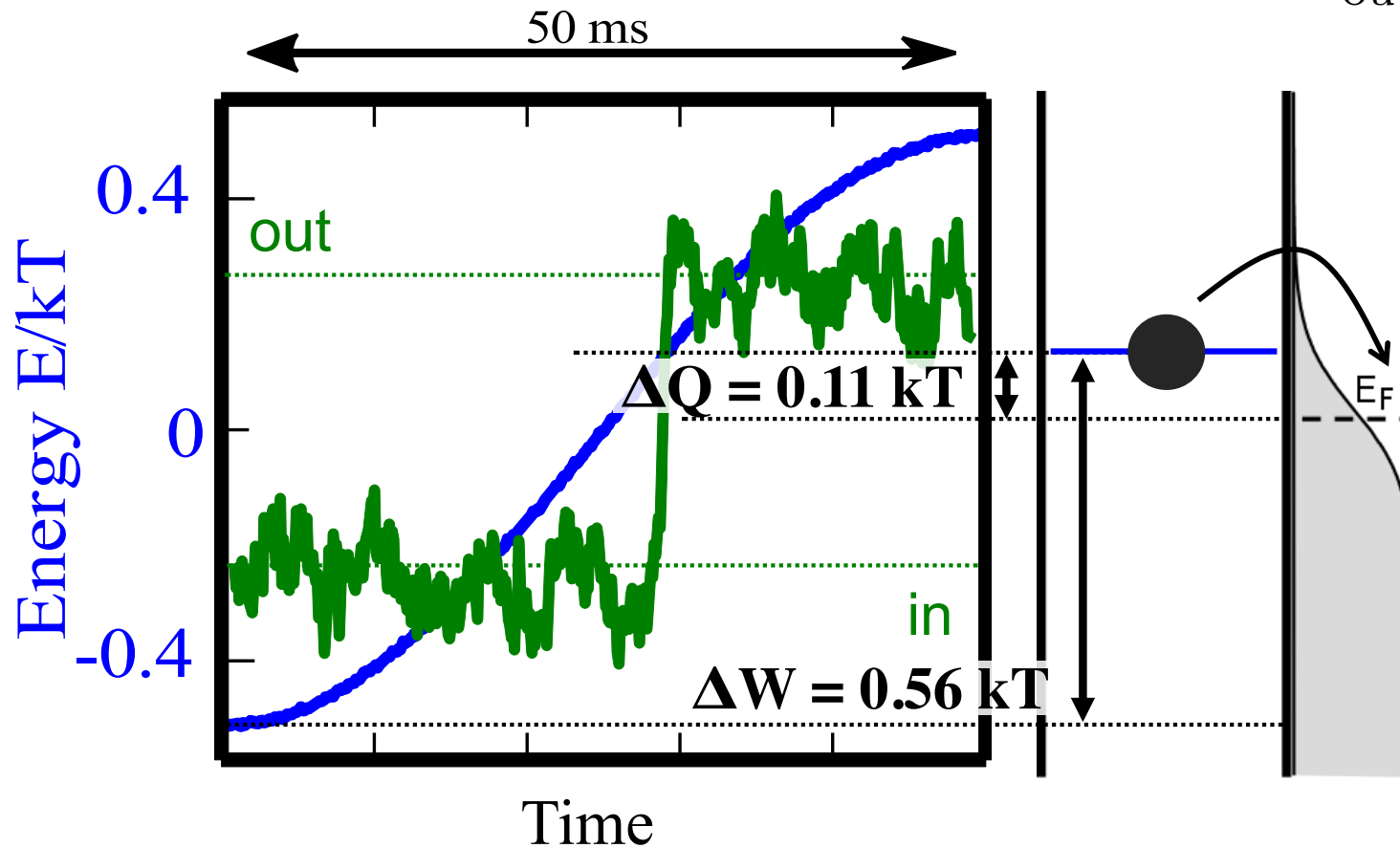


Upward drive

$$\Gamma_{\text{in}} = 42 \text{ Hz}$$

$$\Gamma_{\text{out}} = 21 \text{ Hz}$$

$$E(t) = E_{\text{F}} - A \cos(2\pi f t) \quad \text{for } 0 \leq t \leq 1/2f$$



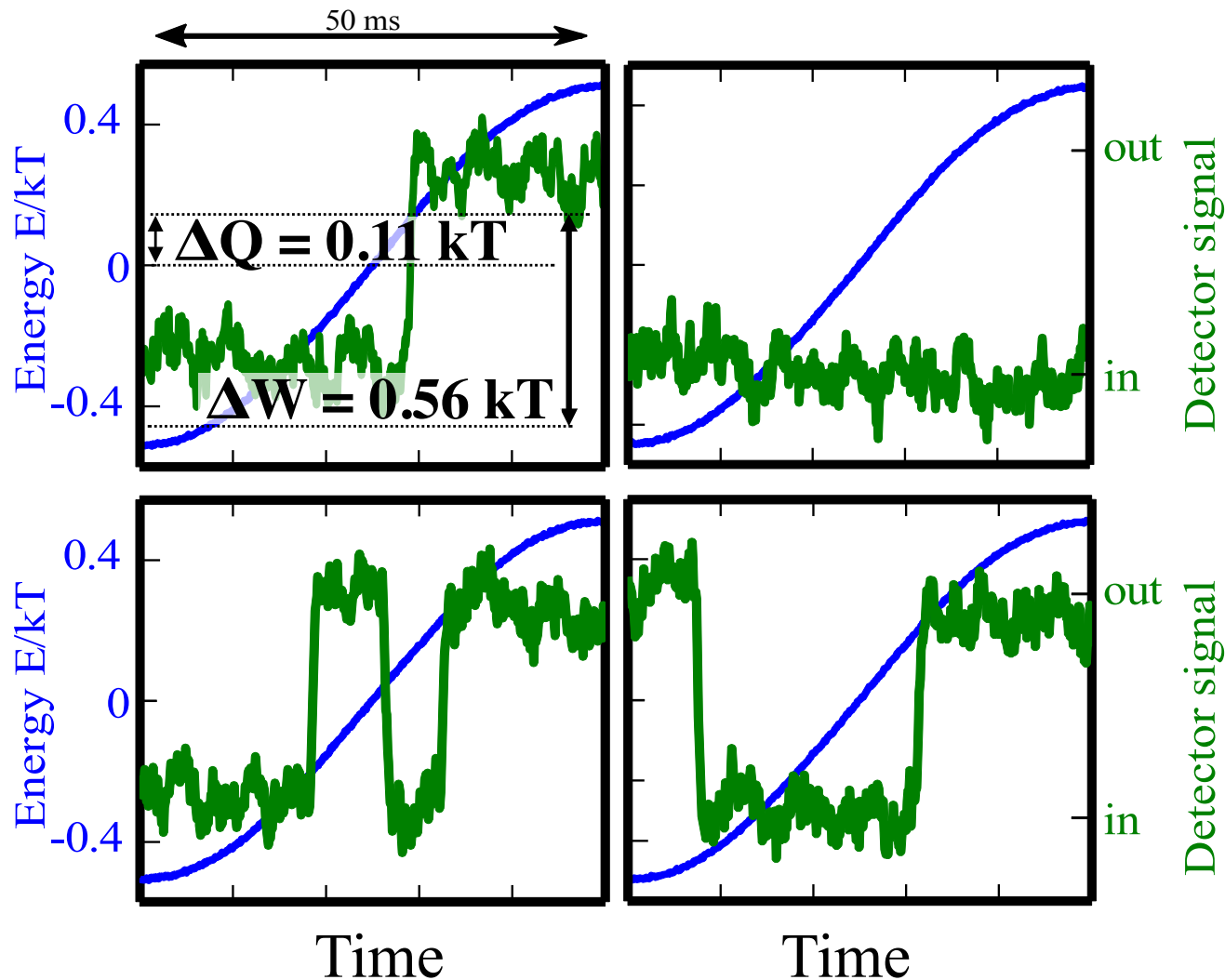
An ensemble of repetitions

$$\Gamma_{\text{in}} = 42 \text{ Hz}$$

$$\Gamma_{\text{out}} = 21 \text{ Hz}$$

~ 20'000 repetitions

Examples:

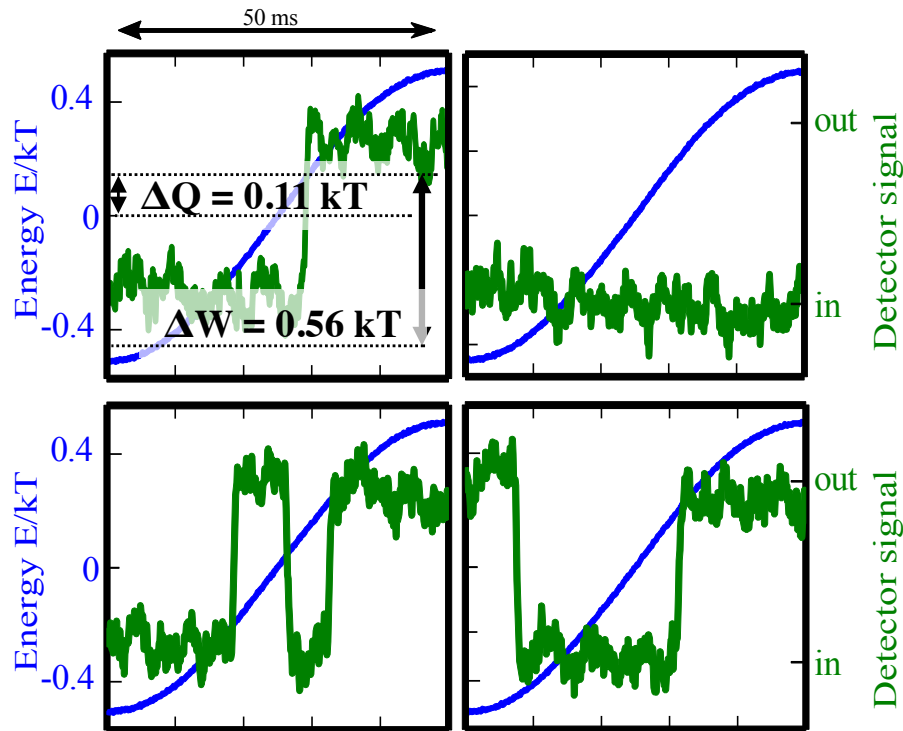


An ensemble of repetitions

$$\Gamma_{\text{in}} = 42 \text{ Hz}$$

$$\Gamma_{\text{out}} = 21 \text{ Hz}$$

~ 20'000 repetitions

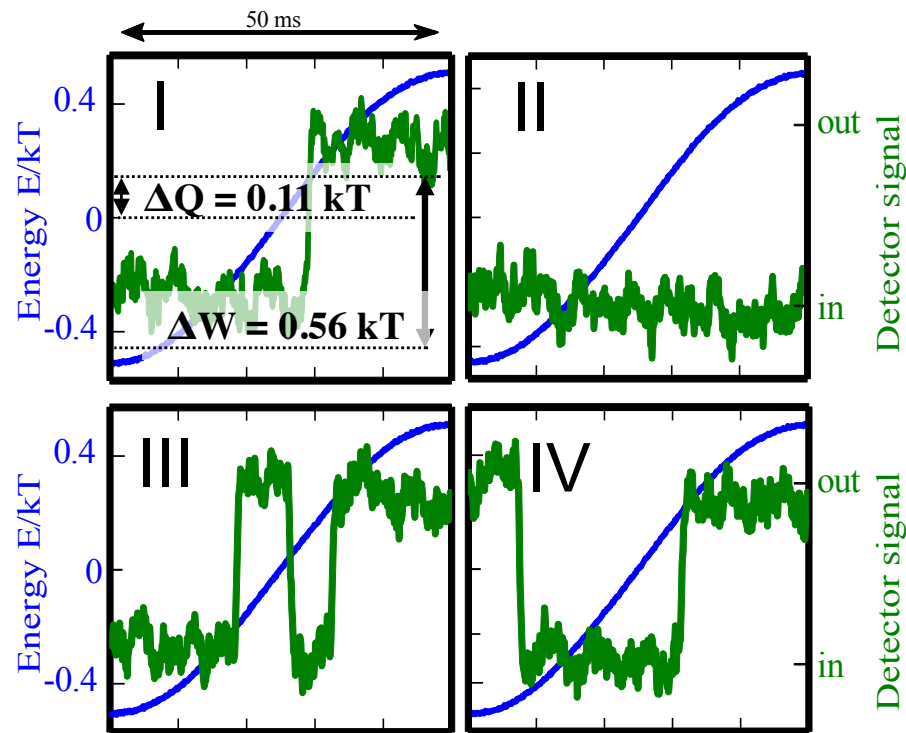


measured

$$\left\langle \exp\left(-\frac{\Delta W}{kT}\right) \right\rangle = \exp\left(-\frac{\Delta F}{kT}\right)$$

known from characterization

An ensemble of repetitions



~ 20'000 repetitions

equilibrium
thermodynamics

measured

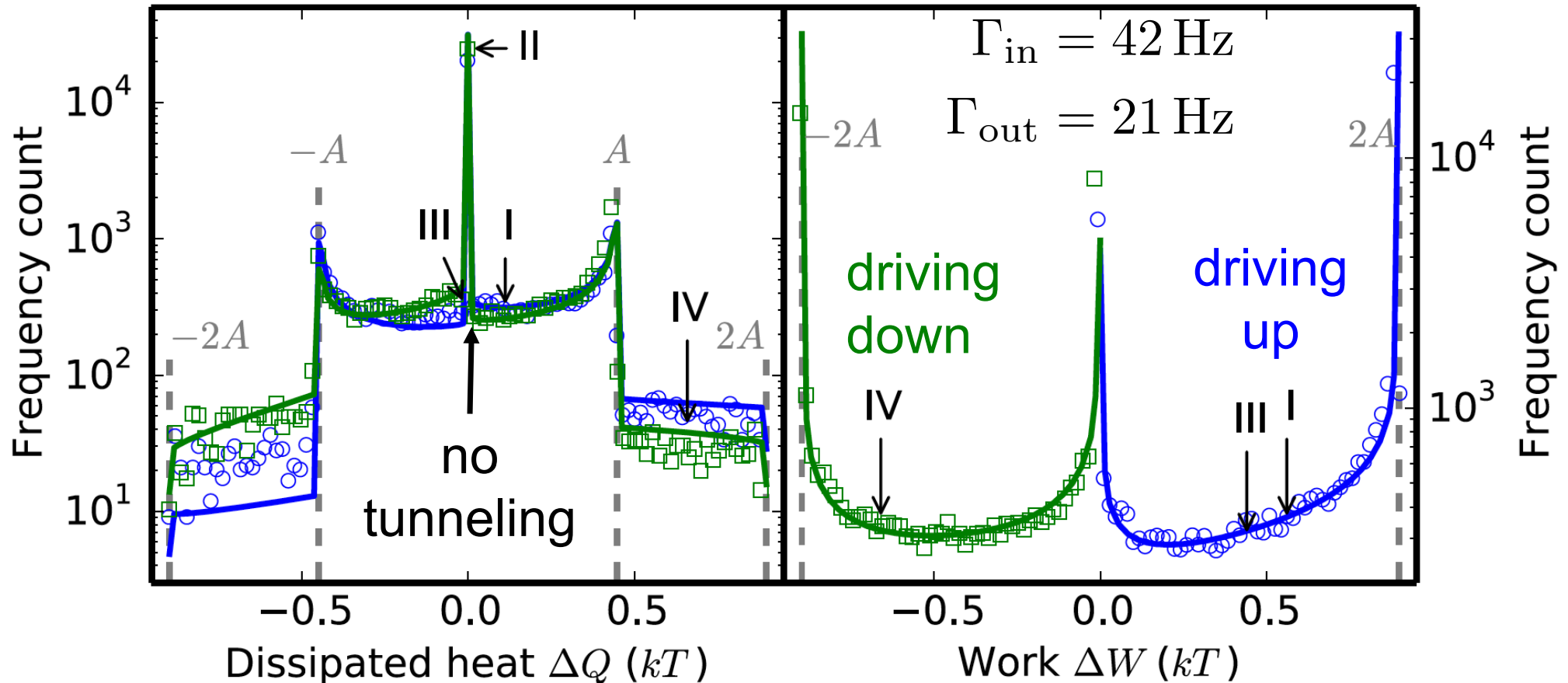
$$\Delta F = kT \ln \left(\frac{Z_0}{Z_1} \right)$$

$$\left\langle \exp \left(- \frac{\Delta W}{kT} \right) \right\rangle = \exp \left(- \frac{\Delta F}{kT} \right)$$

known from
characterization

Extracted distribution functions

$$f = 10 \text{ Hz}, \quad A = 0.45kT$$

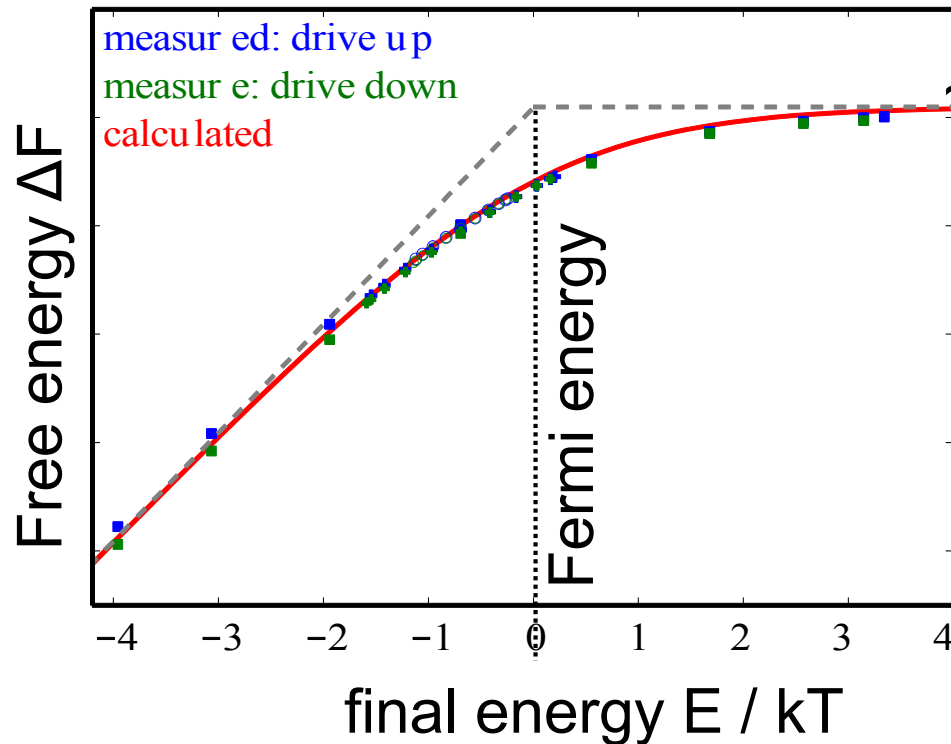


Distributions are far from gaussian => far from equilibrium
Solid lines: from rate equation model

A. Hofmann *et al*, PRB **93**, 035425 (2016).

An ensemble of repetitions

here: all measurements start at the same initial state



20'000 repetitions

equilibrium thermodynamics

$$\Delta F = kT \ln \left(\frac{Z_0}{Z_1} \right)$$

measured

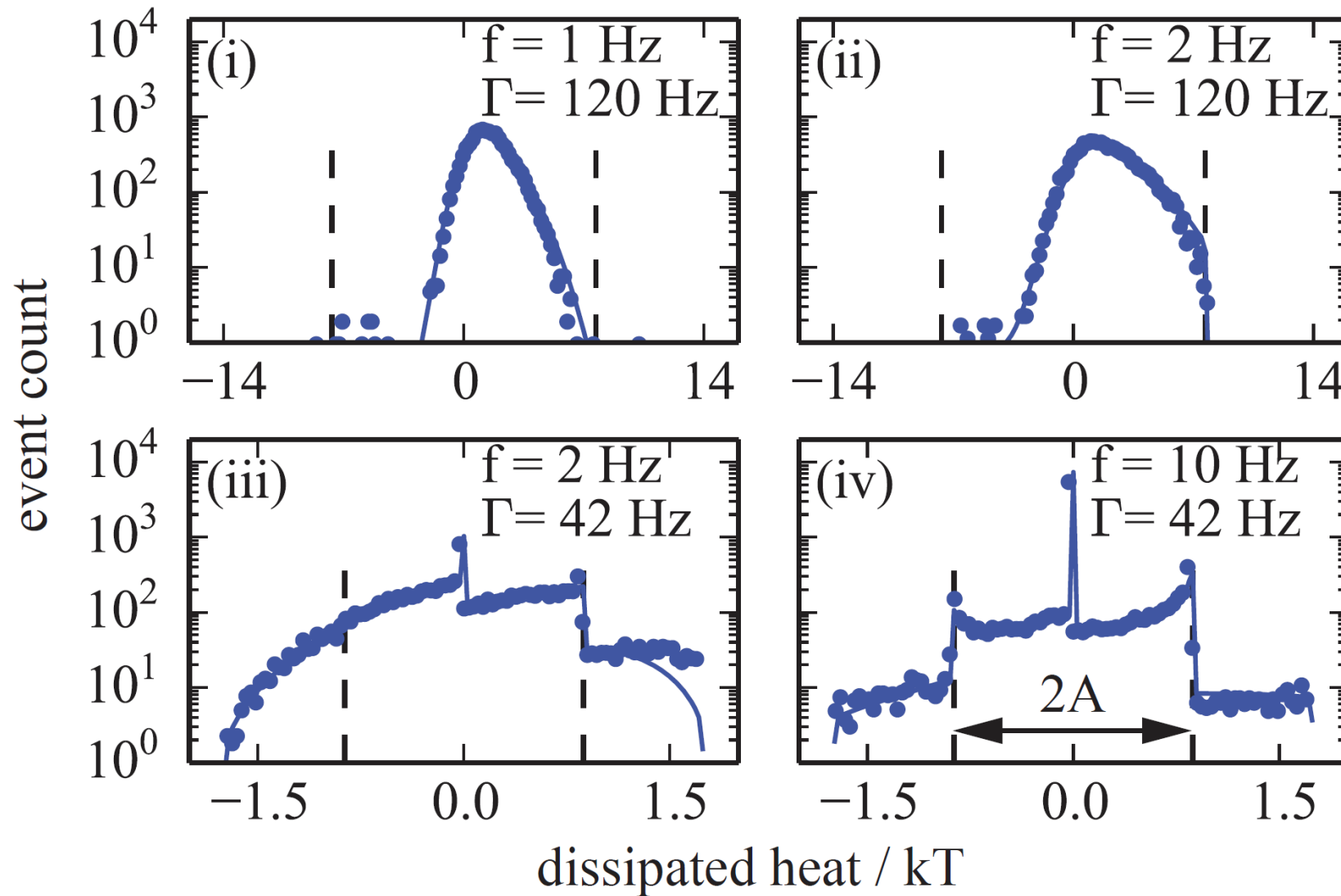
$$\left\langle \exp \left(- \frac{\Delta W}{kT} \right) \right\rangle = \exp \left(- \frac{\Delta F}{kT} \right)$$

known from characterization

$$Z(E) = 1 + 2e^{-E/kT}$$

A. Hofmann *et al*, PRB **93**, 035425 (2016).

From equilibrium to non-equilibrium



The arrow of time



Arthur Stanley
Eddington,
British Astronomer
1927

Microscopic laws of physics are
invariant under time-reversal

Thermodynamics:
as time progresses $\Delta S \geq 0$

Measuring ΔS allows us
to infer the direction of time

The arrow of time

For a given ΔF we have two sets:

- 20'000 realizations driving up (forward in time)
- 20'000 realizations driving down (backward in time)

We pick one of the realizations randomly.

Can we tell the set, from which the measurement was taken?

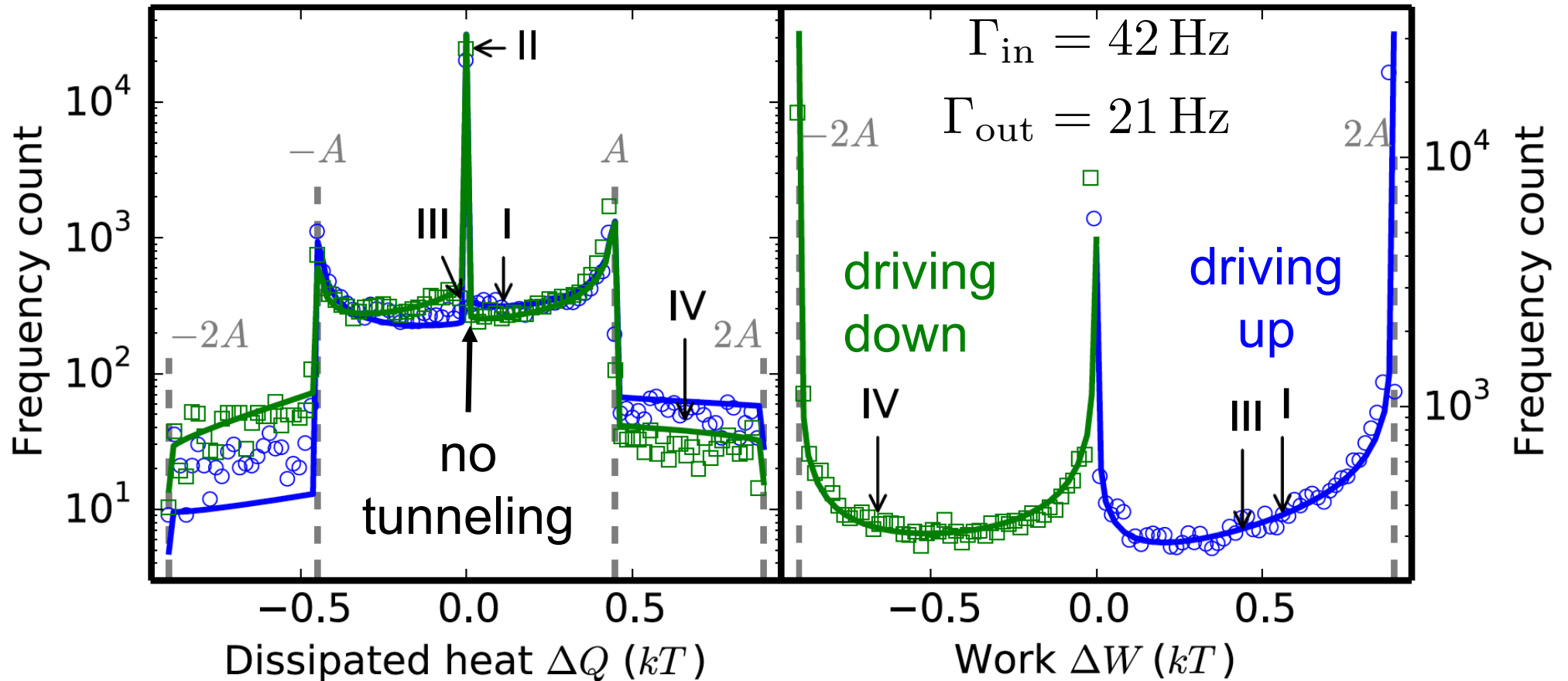
Key for the answer:

for a reversible process: $\Delta W - \Delta F = 0$

far from equilibrium: $\Delta W - \Delta F > 0$
(if forward in time)

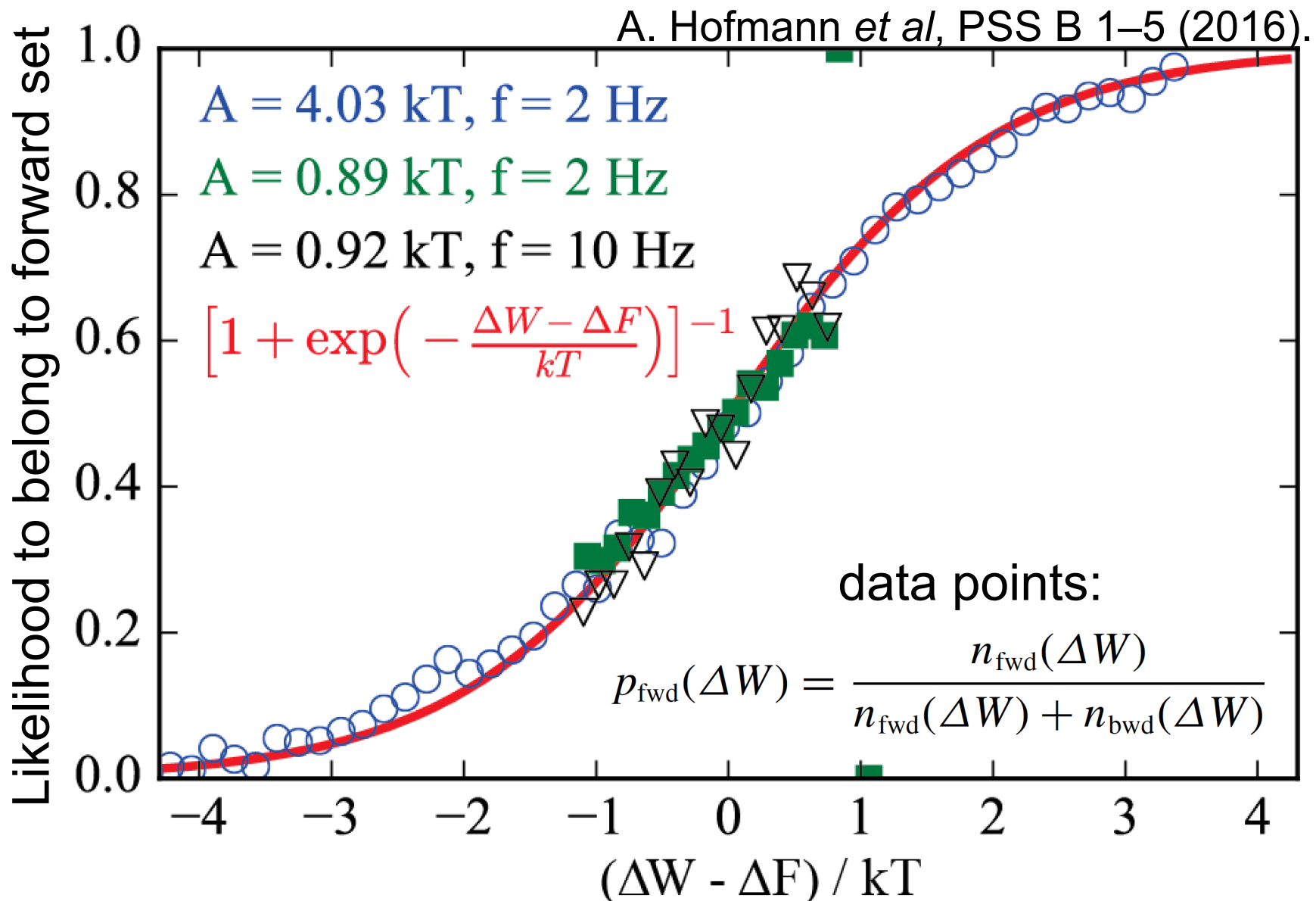
Extracted distribution functions

$$f = 10 \text{ Hz}, \quad A = 0.45kT$$



Distributions are not symmetric => “direction of time”

The arrow of time



Theory: Shirts *et al*, PRL **91**, 140601 (2003);
 Maragakis *et al*, J. Chem. Phys. **129**, 024102 (2008).