# Transient fluctuation relations for particle transport

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# Outline

- Introduction: fluctuation relations
- Master equation with time-dependent rates
  - Applies in semiclassical regime, quantum input: rates
  - Current statistics & stochastic path integral
  - Quantum generalization
- Fluctuation relation for time-dependent voltage protocol
  - Must combine statistics for work and charge
  - Jarzynski relation
  - Cumulant relations for time-dependent transport
- Illustration: mesoscopic single-electron transistor with time-dependent voltage protocol

# Fluctuation relations

- Exact statements for nonequilibrium systems
  - Near equilibrium: recover fluctuation-dissipation theorem
  - Relate probability distribution of work, entropy production rate, steady-state current, etc., to distribution function under time-reversed force protocol
  - Very active field, first experimental tests available

*Marconi et al., Phys. Rep. 2008;*

*Esposito et al., Rev. Mod. Phys. 2009*

- Steady-state vs transient fluctuation relations
  - Transient: finite time interval, time-dependent force, initially: equilibrium distribution → Crooks relation & Jarzynski relation
  - Steady state: constant force, long time limit → Gallavotti-Cohen & Evan-Searles fluctuation relation

# Crooks relation

*Bochkov & Kuzovlev, JETP 1979*
*Crooks, PRE 1999*

for work *W* done by time-dependent external force $f_t$ in $t \in [-\tau, \tau]$ starting with equilibrium ensemble:

$$\frac{P_f(W)}{P_b(-W)} = e^{\beta(W-\Delta F)}$$

- Backward protocol: $\left(\hat{T}f\right)_t = f_{-t}$
- Free energy difference for equilibrium states with fixed forces $f_{\pm\tau}$
- Relation between probability distribution functions under forward vs backward protocol
- Work is stochastic quantity (initial equilibrium ensemble)
- Detailed balance condition (microreversibility)
- Classical and quantum versions exist

# Jarzynski relation

*Jarzynski, PRL 1997*

- Normalization of probability: $\int dW \; P_b(-W) = 1$

  Crooks implies Jarzynski relation

  $$\int dW \; P_f(W) \; e^{-\beta W} \equiv \left\langle e^{-\beta W} \right\rangle_f = e^{-\beta \Delta F}$$

  – Jensen inequality: $\langle W \rangle \geq \Delta F$ → second law of thermodynamics formulated as equality

  – Rare fluctuations „violating“ second law necessary

  – Free energy difference from nonequilibrium statistics

- When initial & final force identical: „sum rule“

  $$\left\langle e^{-\beta W} \right\rangle_f = 1$$

# Full counting statistics (FCS)

*Levitov, Lee & Lesovik, J. Math. Phys. 1996*

- Related question: statistics of „transferred charge“ Q during long „counting interval“ 2τ
  - Stationary current: $I = Q / 2\tau$
- Fluctuation relation for FCS?
  - Two-terminal setup, constant voltage bias V
  - Forward and backward protocol identical (B=0)
  - „Counting field“

$$P(Q) = \int d\chi \; e^{i\chi Q} Z(\chi)$$

$$Z(\chi) = \left\langle e^{-i\chi\hat{Q}} \right\rangle$$

# Fluctuation relation for current

*Bochkov & Kuzovlev, Physica A 1981;*
*Tobiska & Nazarov, PRB 2005;*
*Esposito et al., Rev. Mod. Phys. 2009*

FCS generating function obeys „Crooks“ symmetry relation

$$Z(\chi) = Z(-\chi + i\beta eV)$$

$$\frac{P(Q)}{P(-Q)} = e^{\beta VQ}$$

- Consequence: nonlinear coefficients $L_{k,l}$ describing response to voltage in order $V^l$ of cumulant $\langle\langle I^k \rangle\rangle$ obey hierarchy of relations
- FDT contained as special case: thermal noise = linear conductance · temperature $L_{2,0} = TL_{1,1}$

# Fluctuation relations for time-dependent voltage?

Current response to time-dependent external voltage protocol contains much more information than for DC case!

- Formulation of fluctuation relation?
- How to make use of it?
- Constraints on observable quantities due to such transient fluctuation relations?

# Functional probability

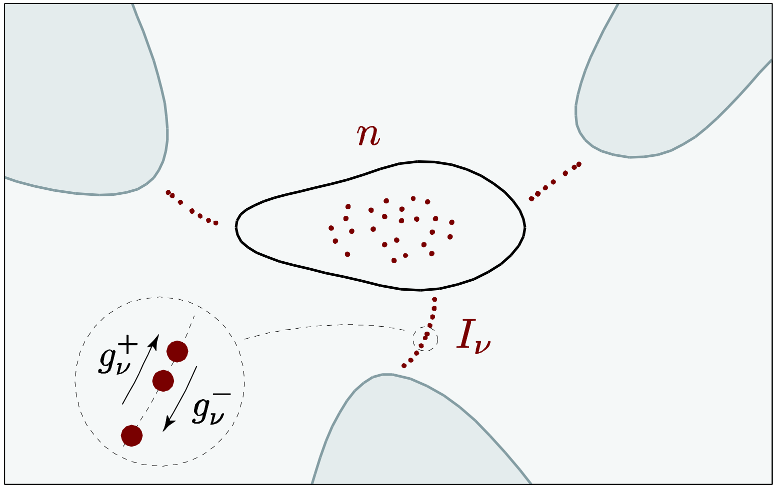
- Information about current statistics now stored in functional probability for time-dependent current profiles $P_{f,b}[I_{1,t},\ldots,I_{M,t}]$
  - M reservoirs connected to „system“, particle number conservation $\partial_t n_t + \sum_\nu I_{\nu,t} = 0$
  - Discreteness of particle exchange (integer „charge“ n): self-generated nonequilibrium shot noise
- Transport master equations
  - capture low-energy physics in many applications
  - assume (for now) classical long-time many-particle dynamics → stochastic path integral

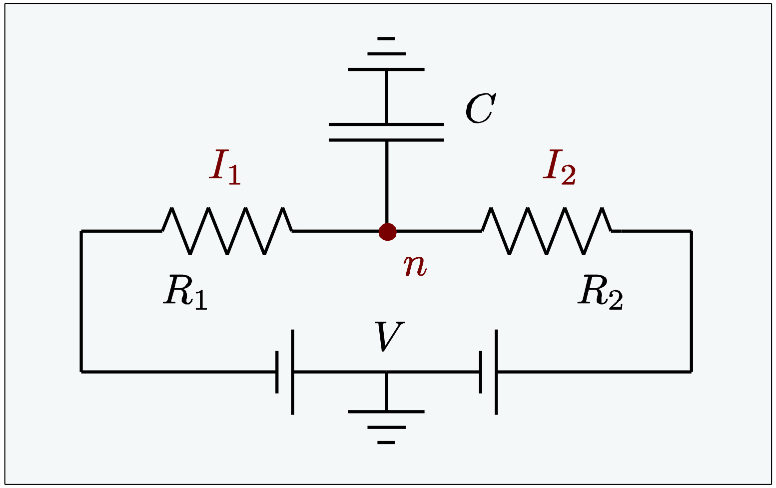
*Kubo et al., J. Stat. Phys 1973; Pilgram et al., PRL 2003*

# Schematic setup

Generic system exchanging particles with M reservoirs

Concrete example: electric RC circuit with time-dependent voltage (M=2)




Generalization to many system variables straightforward…

# Master equation

$$\partial_t P_t(n) = -\hat{H}_g P_t(n)$$

$$\hat{H}_g = \sum_{\nu,\pm} \left(1 - e^{\mp \hat{p}}\right) g^{\pm}_{\nu,t}(n)$$

Rates for flux into/out of the system via reservoir ν

lower/raise n by one unit

Detailed balance condition $$\frac{g^{+}_{\nu,t}}{g^{-}_{\nu,t}} = e^{-\beta(E_\nu(n+1) - E_\nu(n))}$$

cost function $$E_\nu(n) = U(n) - n f_{\nu,t}$$

Assume no driving force at start & end:

initial weight $$\rho(n_{-\tau}) \sim e^{-\beta U(n_{-\tau})}$$

# Applications

| system | n | U(n) | $f_{v,t}$ |
|---|---|---|---|
| electric circuits | charge | charging energy | bias voltage |
| molecular motors | mechanochemical state of motor protein | load potential | ATP concentration |
| chemical reaction networks | number of reaction partners | internal energy | chemostat concentrations |
| adaptive evolution | allele frequencies | log equilibrium distribution | fitness gradients |

# Stochastic path integral (SPI)

*Kubo et al., J. Stat. Phys. 1973*

Master equation formally identical to imaginary-time Schrödinger equation: path integral for „partition function“ $Z_f = \sum_n P_\tau(n) = 1$

$$Z_f = \int D(n,p)\ \rho(n_{-\tau})\ e^{-S(n,p)}$$

$$S = -\int_{-\tau}^{\tau} dt\left[p_t \dot{n}_t - H(n_t, p_t)\right]$$

- Auxiliary „momentum“ integrated over imaginary axis
- Information about discreteness encoded in $e^{\pm p}$ terms in Hamiltonian

# Counting fields

- To extract information, we need time-dependent counting fields (minimal coupling to vector potentials):

$$H(n,p,\chi)=\sum_{\nu,\pm}\left(1-e^{\pm(p-i\chi_\nu)}\right)g_\nu^{\pm}(n)$$

- Cumulants of currents:

$$\left\langle\left\langle I_{\nu_1,t_1} I_{\nu_2,t_2}\cdots\right\rangle\right\rangle=\frac{i\delta}{\delta\chi_{\nu_1,t_1}}\frac{i\delta}{\delta\chi_{\nu_2,t_2}}\cdots\ln Z_f[\chi=0]$$

$$\Leftrightarrow Z_f[\chi]=\left\langle e^{-i\sum_\nu\int dt\chi_\nu I_\nu}\right\rangle_f$$

# Generating functional as SPI

$$Z_f[\chi] = \int D(n,p)\rho(n_{-\tau})\; e^{-S(n,p,\chi)}$$

$$S(n,p,\chi) = -\int_{-\tau}^{\tau} dt\left(p_t\dot{n}_t - H(n_t,p_t,\chi_t)\right)$$

Functional probability distribution function for currents

$$P_f[I] = \int D\chi\; e^{i\sum_\nu \int dt \chi_\nu I_\nu} Z_f[\chi]$$

Backward functional is computed in the same way but for time-reversed protocol $\left(\hat{T}f_\nu\right)_t = f_{\nu,-t}$

# Transient fluctuation relations for currents

*Altland, De Martino, Egger & Narozhny, arXiv:1007.1826*

- SPI action has invariance property under time reversal
- This yields general fluctuation relation

$$Z_f[\chi_{\nu,t}] = Z_b[-\chi_{\nu,-t} + i\beta f_{\nu,-t}]$$

$$\Longrightarrow \quad P_f[I] \big/ P_b[-I] = \exp\left(-\beta \int_{-\tau}^{\tau} dt \sum_\nu f_{\nu,t} I_{\nu,t}\right)$$

  - For constant voltage: previous „FCS expressions“ are recovered
  - Same result follows under quantum mechanical Keldysh approach for mesoscopic quantum dot

# Connection to quantum theory

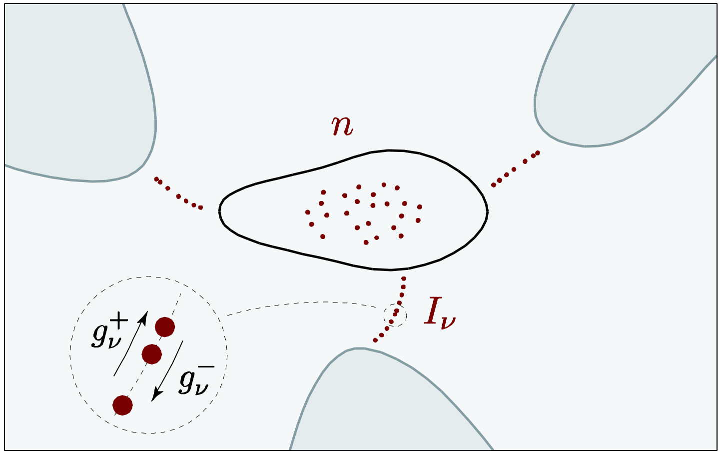
*Altland et al., arXiv:1007.1826*
*Campisi, Talkner & Hänggi, arXiv:1006.1542*

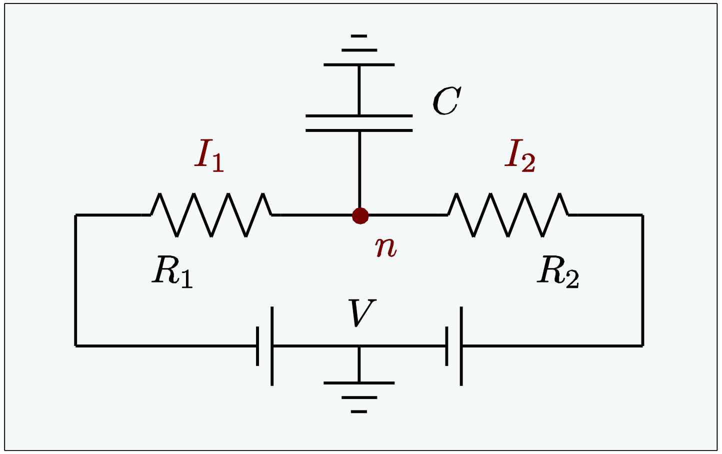
- Stochastic path integral follows from quantum Keldysh nonequilibrium approach for $\hbar \to 0$
  - Explicit derivation for Keldysh action of mesoscopic dots available
  - Quantum case can be studied from full Keldysh action
- Fully quantum case
  - Current operators do not commute for different times
  - Nonetheless the fluctuation relations stay valid!

# Implications?

- Functional probabilities contain excessive information (infinitely many degrees of freedom!)
  - Reduction to practically useful statements necessary
- Derived relations
  - Statistics of charge transport is linked to work
  - Jarzynski relation
  - Nonlinear Fourier coefficients
- Illustration for mesoscopic RC circuit

# Example: RC circuit




System: central capacitor, n: particle/charge number
M=2 reservoirs, symmetric barriers

internal energy: charging energy

$$U(n) = \frac{e^2}{2C}\left(n - n_g\right)^2$$

$$n_g = 1/2$$

driving force: time-dep. bias voltage

$$f_{\nu,t} = \pm \, eV_t / 2$$

# RC circuit: master equation

- Orthodox sequential tunneling regime: classical master equation with quantum rates

$$E_{\nu=1,2=\pm}(n) = U(n) \mp \frac{n}{2} eV_t$$

$$g^{\pm}_{\nu,t}(n) = \frac{1}{R} \frac{\pm \Delta E_{\nu}(n)}{e^{\pm \beta \Delta E_{\nu}(n)} - 1}$$

$$\Delta E_{\nu}(n) = E_{\nu}(n+1) - E_{\nu}(n)$$

- Numerical simulation of master equation for asymmetric voltage pulse

$$V_t = V_0 \frac{\gamma t}{t^2 + \gamma^2}$$

  – RC time scale: $\Omega^{-1} = \frac{RC}{2}$

# Generalized Crooks relation

- Consider statistics of transmitted charge and dissipated power $Q = \int_{-\tau}^{\tau} dt \; I_t$ $\qquad W = \int_{-\tau}^{\tau} dt \; I_t V_t$
  - constant voltage: $W = QV$
  - time-dependent voltage: there is no fluctuation relation for only $P(Q)$
- Consider joint probability for Q and W

# Time-dependent FCS fluctuation relation

- Joint probability $P_f(Q,W) = \langle \delta(Q - Q[I])\delta(W - W[I]) \rangle_f$

$$= \int \frac{d\chi_q d\chi_w}{(2\pi)^2} e^{i(\chi_q Q + \chi_w W)} Z_f[\chi_q + \chi_w V_t]$$

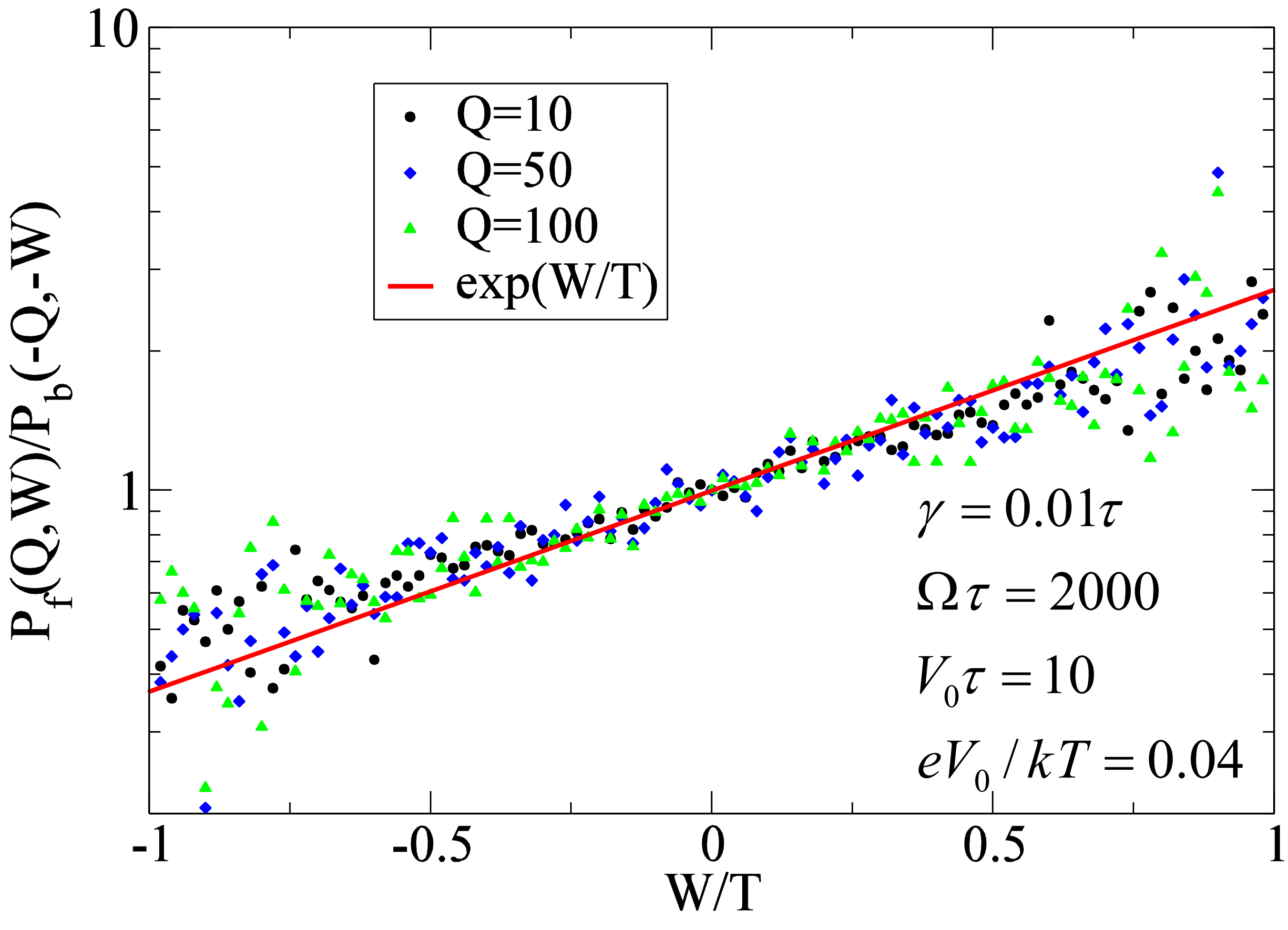
- Now insert fluctuation relation & integrate

**generalized Crooks relation**

$$P_f(Q,W) \Big/ P_b(-Q,-W) = \exp(\beta W)$$

  - integral over Q: Crooks relation for work statistics
  - In general no fluctuation relation for charge alone

# Numerical test: RC circuit



# Fluctuations around Jarzynski relation

*Altland, De Martino, Egger & Narozhny, arXiv:1005.4662*

$$\langle X \rangle = 1, X = e^{-\beta W}$$

- – Sum rule for exponentiated dissipated power
- – How big are fluctuations around unit value?
- – Useful „filter“ to detect nonequilibrium fluctuations?

- Consider variance as specific case
  - – Order-of-magnitude estimate for variance follows from stationary phase analysis of SPI

# Fluctuations: order of magnitude estimate

- Shot noise dominated regime $|eV| >> kT$

$$\langle X^2 \rangle \sim \exp\left[ 2\tau |\langle I \rangle| \exp\left( \frac{|eV|}{2kT} \right) \right]$$

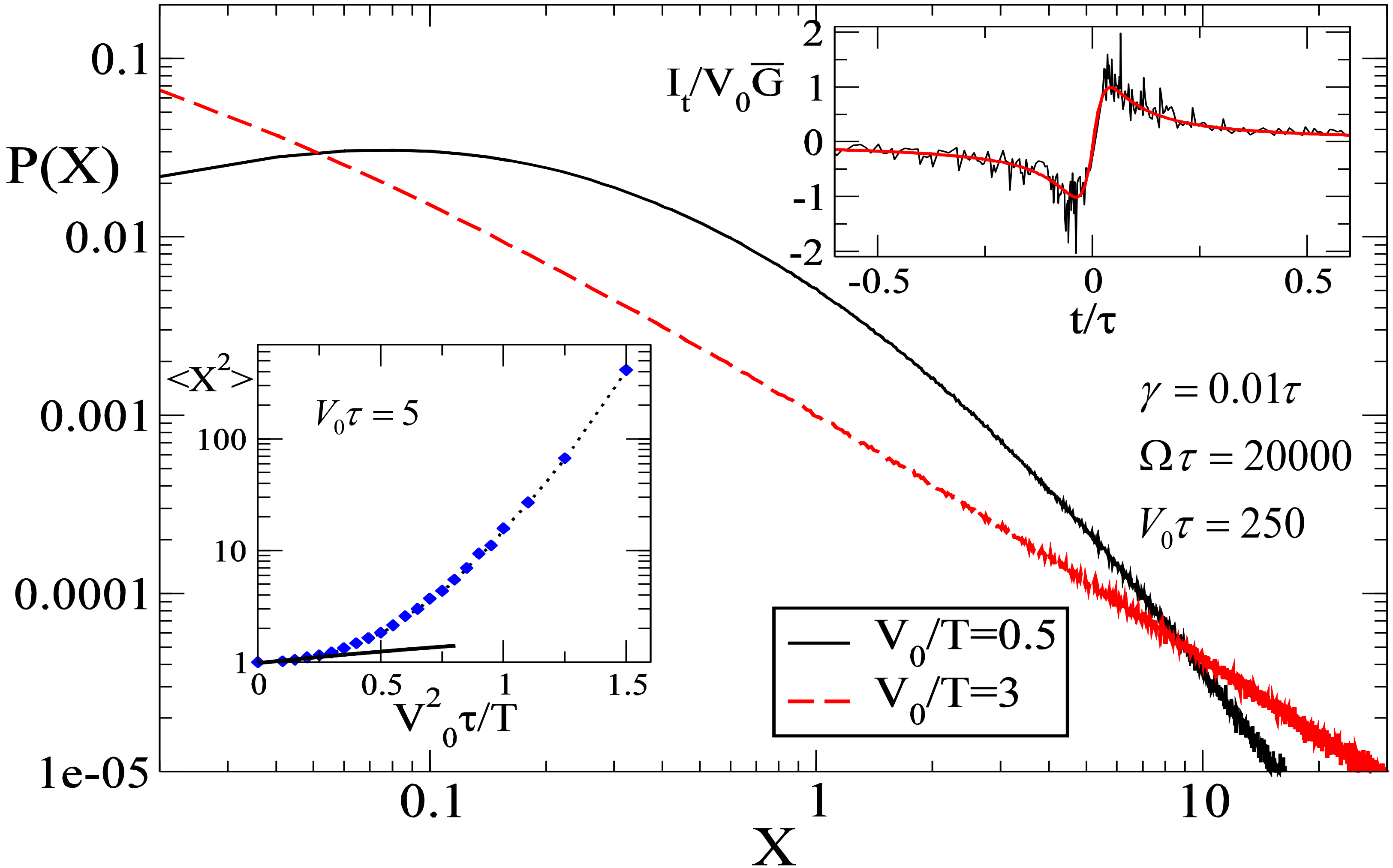
  – Fluctuations are astronomically large, Jarzynski relation then meaningless

- Thermal regime

$$\langle X^2 \rangle \sim \exp\left[ \tau \frac{(eV)^2}{kT} \frac{g_1 g_2}{g_1 + g_2} \right]$$

  – Fluctuations benign, unit average can be resolved

# Fluctuations in RC circuit



# Nonlinear coefficients

- Expand current cumulants in powers of voltage
  - Fourier expansion $I_t = \sum_j e^{i\pi jt/\tau} \widetilde{I}_j$
- Schematically:

$$\langle\langle \widetilde{I}_{j_1} \cdots \widetilde{I}_{j_k} \rangle\rangle = \sum_{l=0}^{\infty} \frac{1}{l!} \sum_{\{m\}} \widetilde{V}_{m_1} \cdots \widetilde{V}_{m_l} L_{k,l}(\{j;m\})$$

- Nonlinear expansion coefficient describe time-dependent response
- Fluctuation relation implies relations between different coefficients
- Here: two examples for general but time-symmetric voltage protocol

# Examples

- Lowest order: recover spectral representation of fluctuation dissipation theorem

$$TL_{1,1}(n_1;n_2)=L_{2,0}(n_1,n_2)$$

- Example for genuine nonequilibrium relation:

$$TL_{1,2}(n_1;n_2,n_3)=L_{2,1}(n_1,n_2;n_3)$$

  – Connect leading nonlinear current response to linear order in voltage for the current noise
- Benchmark criteria for time-dependent nonequilibrium transport

# Conclusions

- Fluctuation relations provide benchmark constraints for nonequilibrium transport
- Functional fluctuation relation allows to extract derived relations for transport under time-dependent forces
  - Generalized Crooks relation: connect charge and work statistics
  - Cross-relations connecting different nonlinear transport coefficients

**References: arXiv:1005.4662, arXiv:1007.1826**

# Transient fluctuation relations for currents

- Invariance relation

$$S_g[n,p,\chi] = S_{\hat{T}g}\left[\hat{T}n, \hat{T}(p-\beta\partial_n U), \hat{T}(\chi + i\beta f)\right] + \beta\{U(n_\tau) - U(n_{-\tau})\}$$

- This yields general fluctuation relation

$$Z_f[\chi] = \int D(n,p)\ \rho(n_{-\tau})\ e^{-S_{\hat{T}g}\left[n,p,\hat{T}(\chi+i\beta f)\right]} = Z_b\left[\hat{T}(\chi + i\beta f)\right]$$

$$\Longrightarrow \quad P_f[I] \Big/ P_b\left[\hat{T}I\right] = \exp\left(-\beta\int_{-\tau}^{\tau} dt \sum_{\nu=1}^{M} f_{\nu,t} I_{\nu,t}\right)$$

- For constant voltage: FCS expressions above are recovered