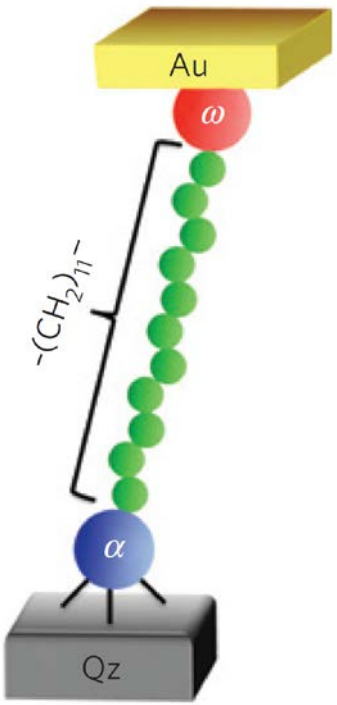
Büttiker's probe in molecular electronics: Applications to charge and heat transport

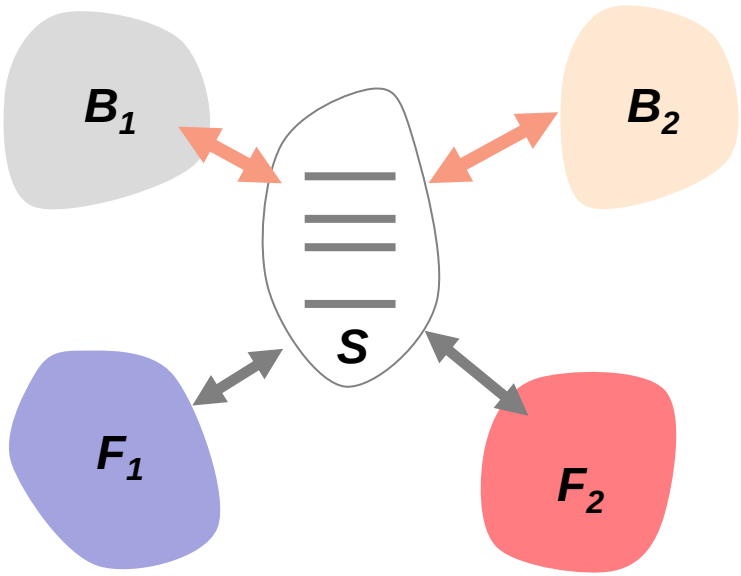
Dvira Segal
Department of Chemistry
University of Toronto

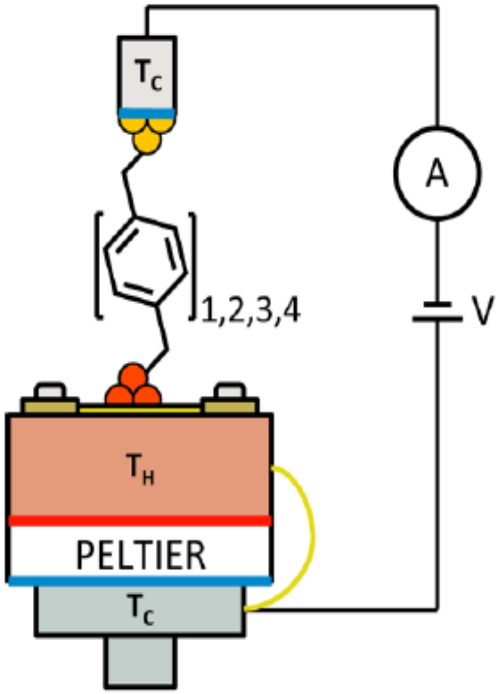
Michael Kilgour
(poster)

Büttiker's probe in molecular electronics: Applications to charge and heat transport



… D. Cahill, Nature Mat. 11 502 (2012)

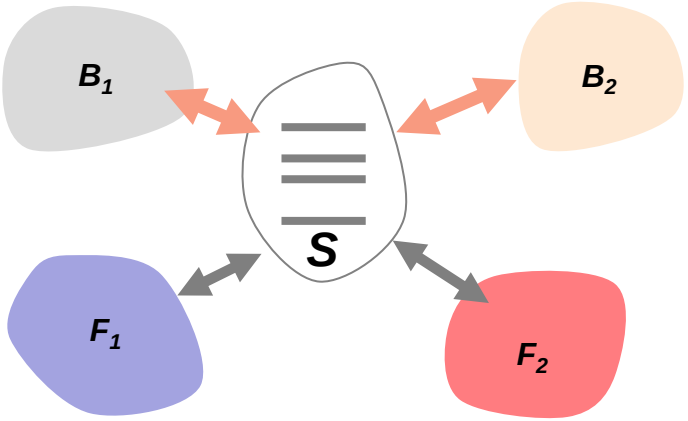




…, L. Venkataraman Nano Lett 13 2889 (2013)

Methods:

open, quantum,
many-body effects,
multiple reservoirs
out of equilibrium



Numerically exact methods (MC, Influence functional, MCTDH, HEOM)

Perturbative approaches (QME, NEGF)

Asymptotic approaches (bounds)

Phenomenological tools (Büttiker's probes)

Semiclassical, mixed q-c, hybrid

Outline

1. **Introduction**
   30 years with Büttiker's probes 1986-2016
…. 45 years of self-consistent reservoirs

2. **Charge transfer**
   - **o** Technical details: dephasing probe and voltage probe
   - **o** Linear response
   - **o** High voltage results
   - **o** Applications: diodes

3. Vibrational heat transfer
- **o** Simple examples
- **o** Large scale simulations

4. Outlook

VOLUME 32, NUMBER 3

Small normal-metal loop coupled to an electron reservoir

M. Büttiker
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
(Received 26 April 1985)

A conceptually simple approach is proposed to introduce dissipation into a normal-metal loop penetrated by a flux. The loop is coupled via a single current lead to an electron reservoir. Scattering processes in the loop are elastic. Inelastic processes occur only in the reservoir and are the source of dissipation. We investigate the effect of this reservoir on the persistent currents in the loop and the absorption of power in the presence of a sinusoidally modulated flux.

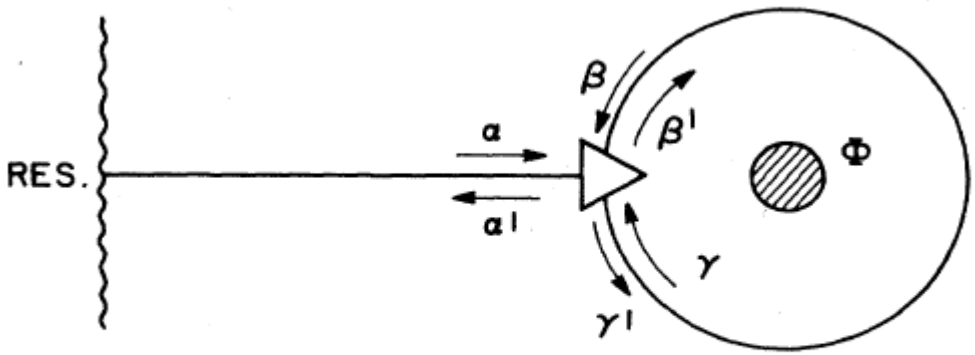


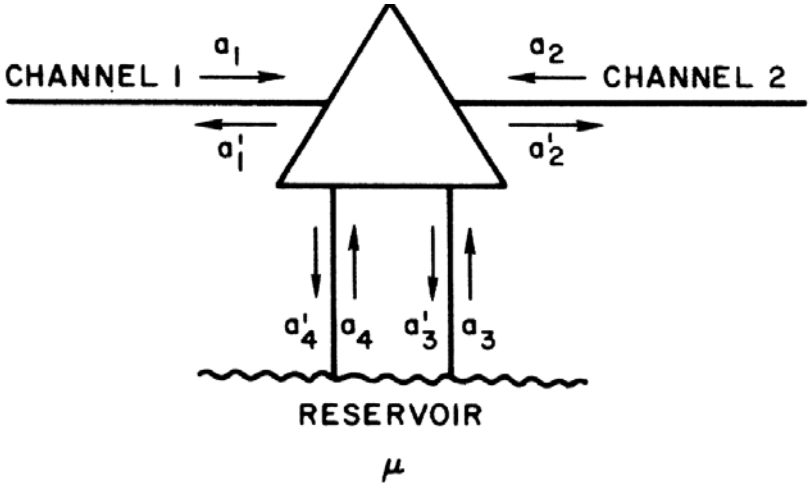
FIG. 1. Loop coupled via an ideal conductor to a dissipative electron reservoir.

PHYSICAL REVIEW B VOLUME 33, NUMBER 5 1 MARCH 1986

Role of quantum coherence in series resistors

M. Büttiker
IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
(Received 24 July 1985)

Landauer's approach which yields the resistance of an obstacle in an otherwise perfect wire due to elastic scattering at the obstacle is augmented by including localized inelastic scatterers within the sample. The inelastic scatterers invoked consist of an electron reservoir coupled via a lead to the wire. The key advantage of this method is that the effect of inelastic scattering can be studied by solving an elastic scattering problem. We investigate the resistance of a series of two (or more) obstacles and study the transition from completely coherent transmission through the sample to completely incoherent transmission. For a sample with a small transmission probability, increasing inelastic scattering decreases the resistance. At an intermediate value of inelastic scattering, the resistance reaches a minimum to increase again when inelastic scattering processes start to dominate the resistance.

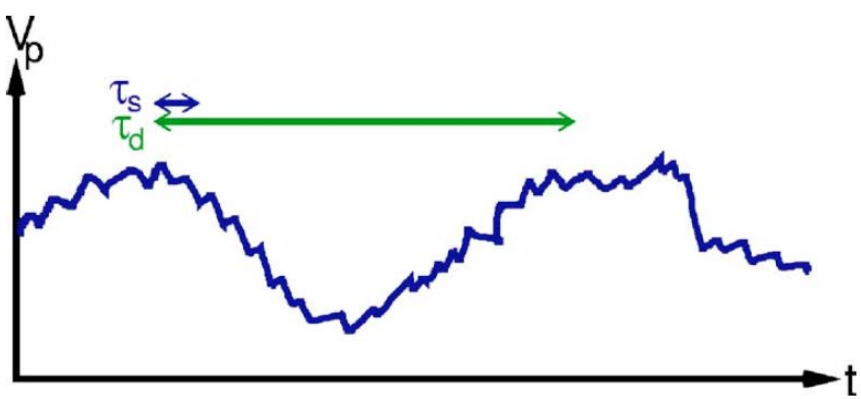


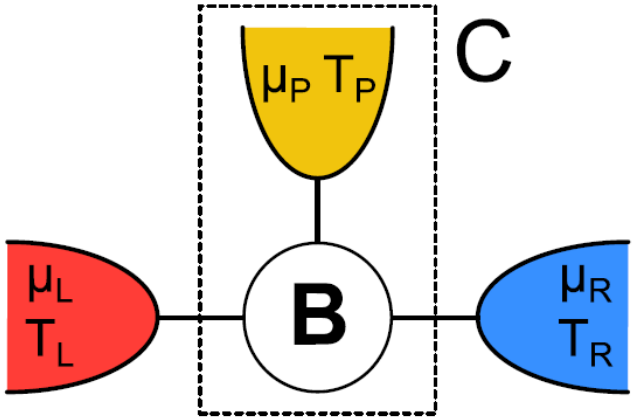
PHYSICAL REVIEW B **75**, 035340 (2007)

Voltage and dephasing probes in mesoscopic conductors: A study of full-counting statistics

Heidi Förster,[1] Peter Samuelsson,[2] Sebastian Pilgram,[3] and Markus Büttiker[1]
[1]*Départment de Physique Théorique, Université de Genève, CH-1211 Genève 4, Switzerland*
[2]*Department of Physics, University of Lund, Box 118, SE-22100, Sweden*
[3]*Theoretische Physik, ETH Zürich, CH-8093 Zürich, Switzerland*

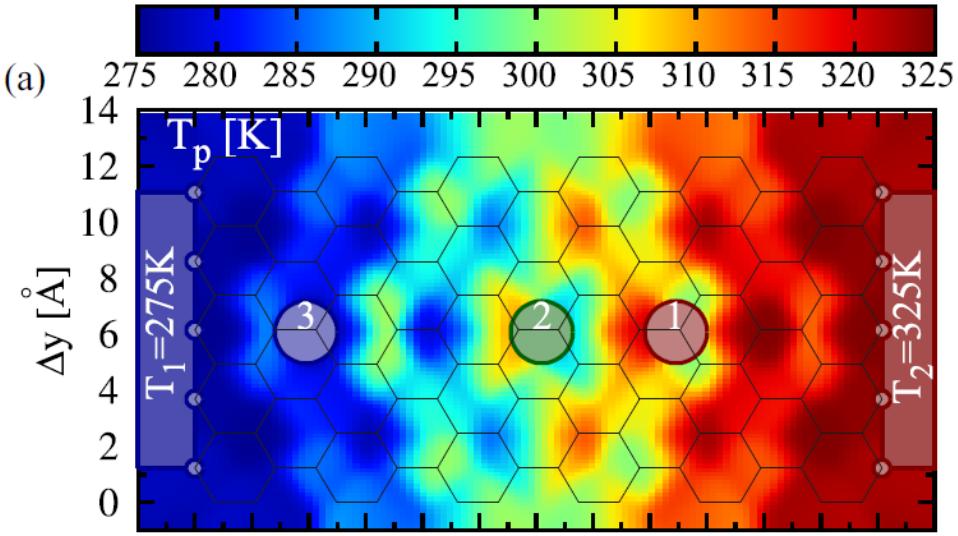
Voltage and dephasing probes introduce incoherent inelastic and incoherent quasielastic scattering into a coherent mesoscopic conductor. We discuss in detail the concepts of voltage and dephasing probes and develop a full-counting statistics approach to investigate their effect on the transport statistics. The formalism is applied to several experimentally relevant examples. A comparison of different probe models and with procedures like phase averaging over an appropriate phase distribution shows that there is a perfect equivalence between the models for the case of one single-channel probe. Interestingly, the appropriate phase-distribution function is found to be uniform. A uniform distribution is provided by a chaotic cavity with a long dwell time. The dwell time of a chaotic cavity plays a role similar to the charge response time of a voltage or dephasing probe. For mu ge and dephasing probes differs and the equiva-
ler





Strong bounds on Onsager coefficients and efficiency for three-terminal thermoelectric transport in a magnetic field

K. Brandner and U. Seifert, PRL **110**, 070603 (2013).



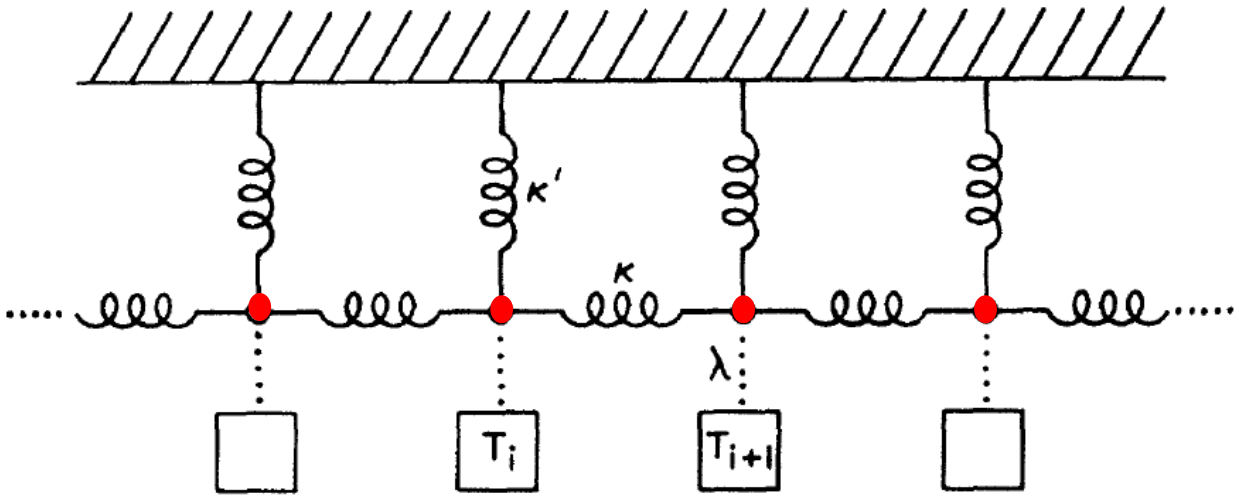
Local temperature of out-of-equilibrium quantum electron systems

J. Meair, J. P. Bergfield, C. A. Stafford, Ph Jacquod
PRB **90**, 035407 (2014)

Simulation of Nonharmonic Interactions in a Crystal by Self-Consistent Reservoirs*

M. Bolsterli, M. Rich, and W. M. Visscher
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544
(Received 13 November 1969)

Independent heat reservoirs are postulated to interact with the atoms in a harmonic system as a substitute for real nonharmonic forces. The temperature of each reservoir is determined by the condition that it exchange no energy with the system in the steady state. An explicit solution for the covariance matrix is obtained for the case of the linear chain. The thermal conductivity is finite and inversely proportional to the coupling to the reservoirs.



PRA **1,** 1086 (1970)

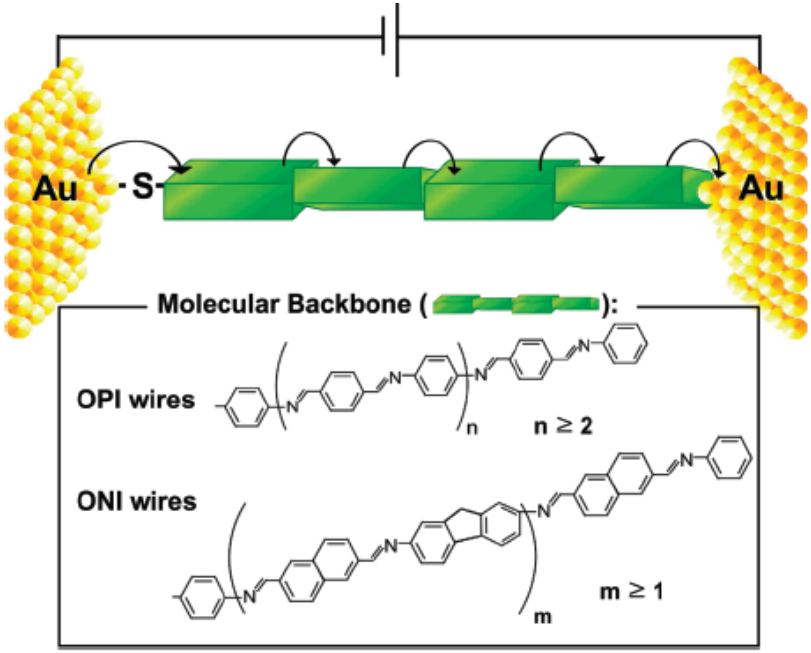
Büttiker's probes in molecular electronics

Goal: Mimic environmental effects, electron-vibration interaction effects (IETS signals?!...). Understand dephasing/voltage probe, low/high voltage.

Mechanisms:
o tunneling to hopping
o ballistic motion to hopping
length, temperature, and energetic dependence.

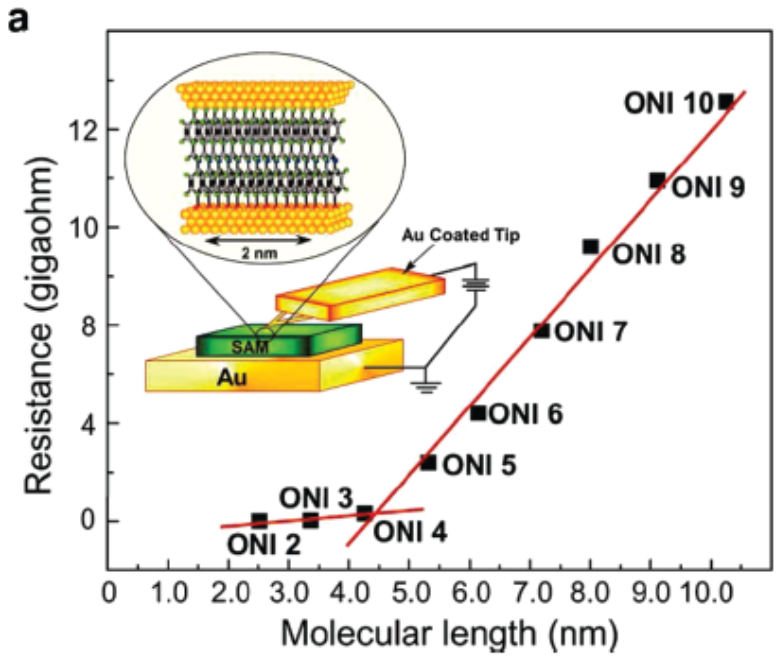
Results should be meaningful:
o experiments
o other methods (quantum master equations, GF)

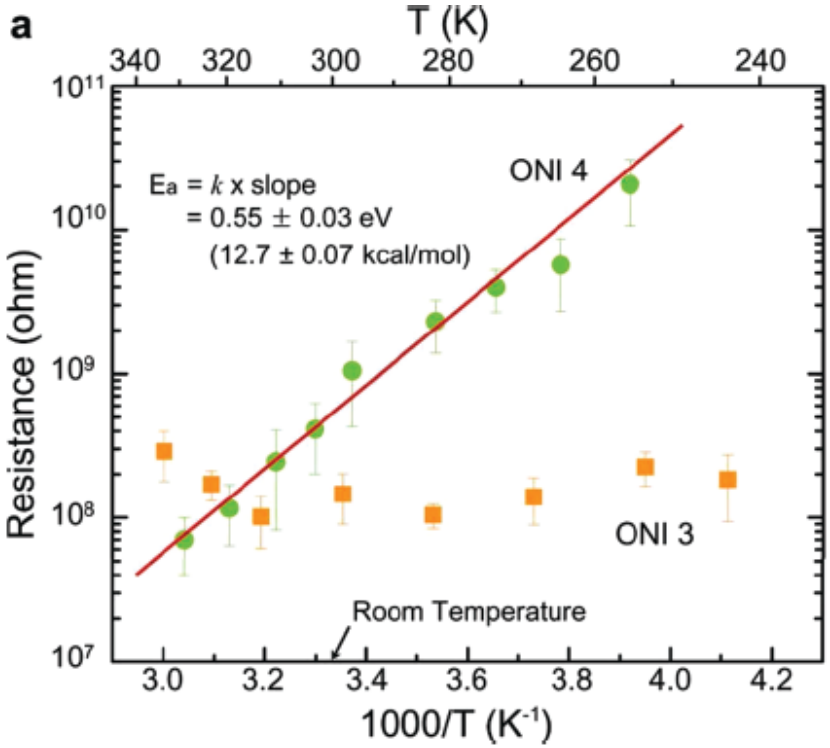
Advantages of the probe method:
o weak-to-strong metal-molecule coupling - elastic limit is included exactly
o low-to-high bias simulations, low-to-high temperature
o large scale simulations
o Fundamental understanding over the role of incoherent effects (Fourier's law, diode effect)

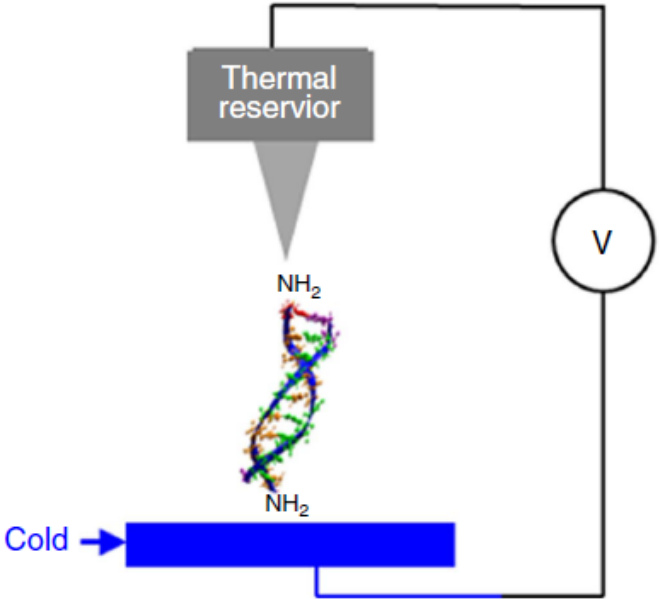


Transition from tunneling to hopping transport in long, conjugated Oligo-imine wires connected to metals

S. H. Choi et al (Frisbie lab) JACS 132 4358 (2010)



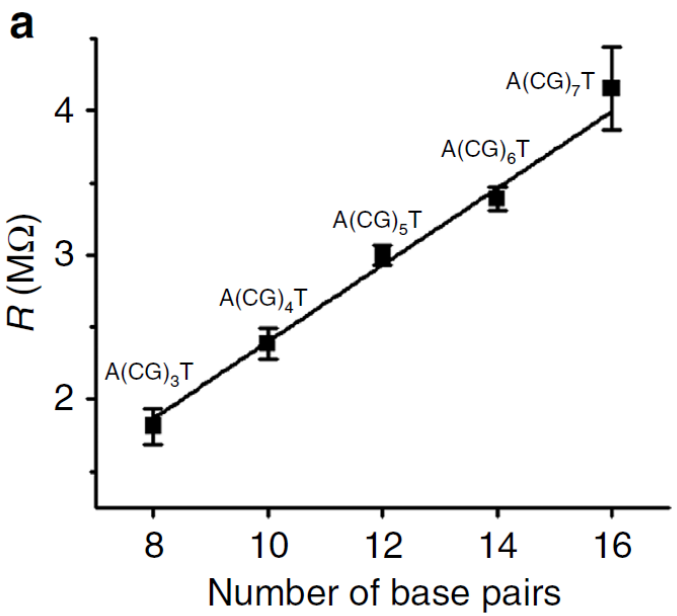


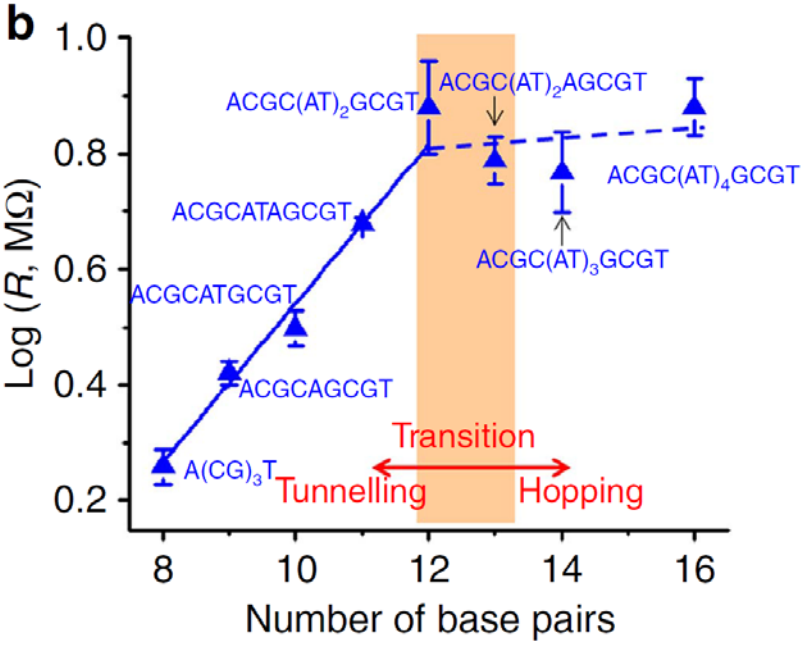


Thermoelectric effect and its dependence on molecular length and sequence in single DNA Molecules

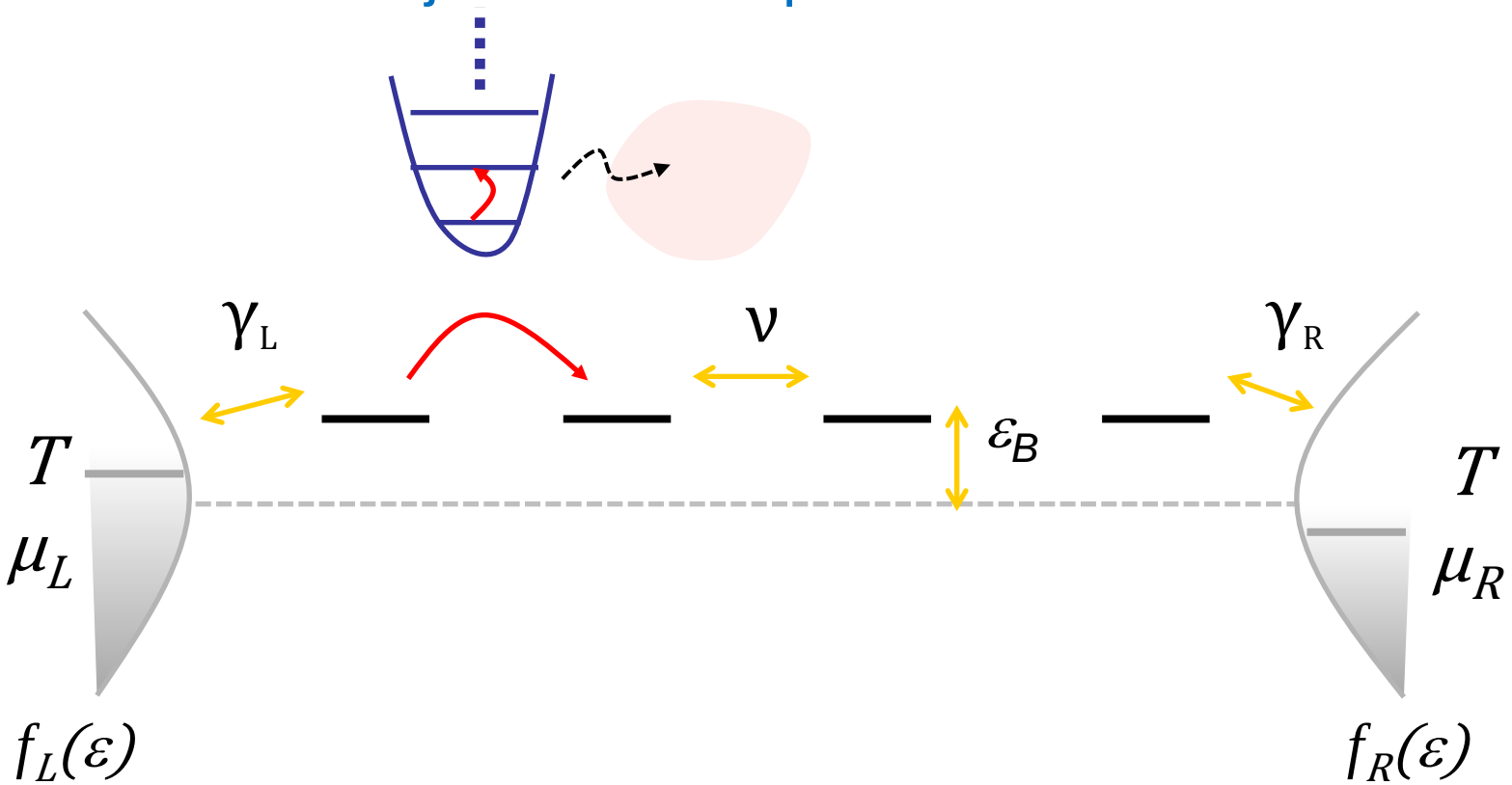
Y. Li et al., (Tao lab)

Nature Comm. 2016.

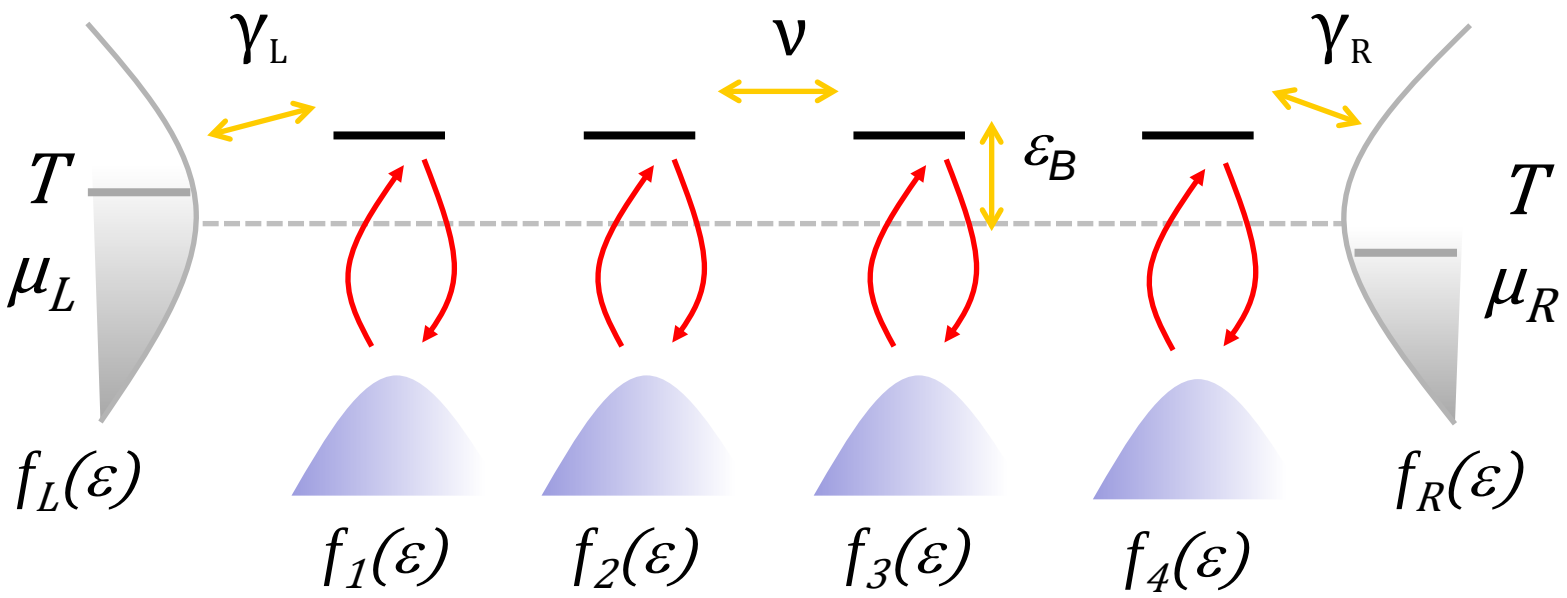




Molecular junction with probes

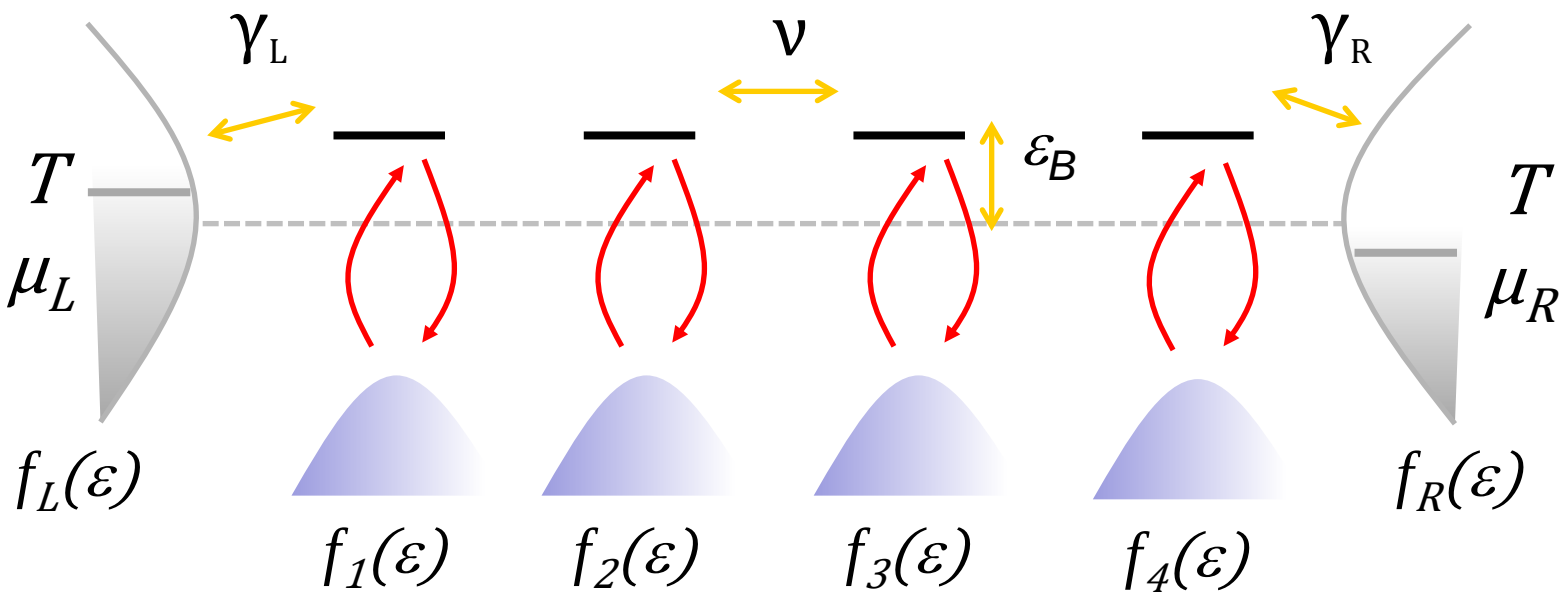


Molecular junction with probes



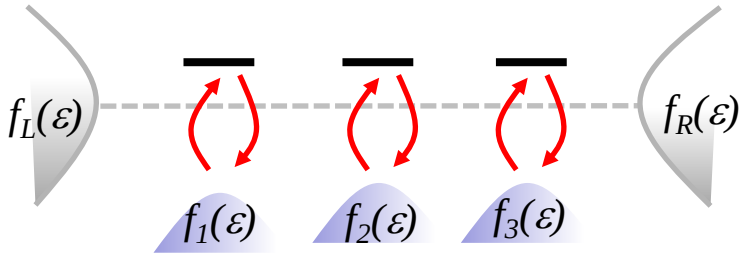
Molecular junction with probes

$$I_L = \frac{e}{2\pi\hbar} \sum_\alpha \int_{-\infty}^{\infty} \mathcal{T}_{L,\alpha}(\epsilon) \left[f_L(\epsilon) - f_\alpha(\epsilon) \right] d\epsilon$$



$$I_n = \frac{e}{2\pi\hbar} \sum_\alpha \int_{-\infty}^{\infty} \mathcal{T}_{n,\alpha}(\epsilon) \left[f_n(\epsilon) - f_\alpha(\epsilon) \right] d\epsilon$$

Dephasing probe: Incoherent **elastic** scattering



$$I_L = \frac{e}{2\pi\hbar}\sum_\alpha \int_{-\infty}^{\infty} \mathcal{T}_{L,\alpha}(\epsilon)\left[f_L(\epsilon) - f_\alpha(\epsilon)\right] d\epsilon$$

$$I_n = \frac{e}{2\pi\hbar}\sum_\alpha \int_{-\infty}^{\infty} \mathcal{T}_{n,\alpha}(\epsilon)\left[f_n(\epsilon) - f_\alpha(\epsilon)\right] d\epsilon$$

Probe condition: $i_n(\epsilon) = 0,$ $\quad I_n = \int d\epsilon\, i_n(\epsilon)$

Linear equation for $f_n(\varepsilon)$, probe distribution

$$\mathbf{M}(\epsilon)\mathbf{f}(\epsilon) = \mathbf{v}(\epsilon)$$

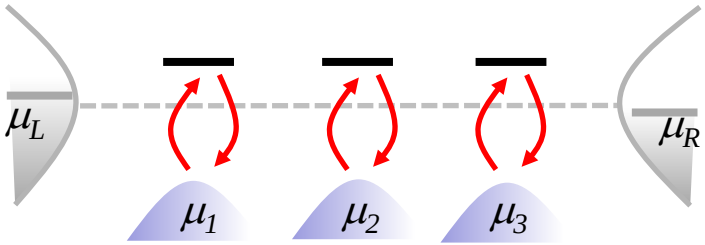
$$\mathbf{M}(\epsilon) = \begin{bmatrix} \sum_\alpha \mathcal{T}_{1,\alpha}(\epsilon) & -\mathcal{T}_{1,2}(\epsilon) & -\mathcal{T}_{1,3}(\epsilon) & -\mathcal{T}_{1,4}(\epsilon) & \dots \\ -\mathcal{T}_{2,1}(\epsilon) & \sum_\alpha \mathcal{T}_{2,\alpha}(\epsilon) & -\mathcal{T}_{2,3}(\epsilon) & -\mathcal{T}_{2,4}(\epsilon) & \dots \\ -\mathcal{T}_{3,1}(\epsilon) & -\mathcal{T}_{3,2}(\epsilon) & \sum_\alpha \mathcal{T}_{3,\alpha}(\epsilon) & -\mathcal{T}_{3,4}(\epsilon) & \dots \\ & & \dots & \dots & \dots \end{bmatrix}$$

$$\mathbf{v}_n(\epsilon) = \mathcal{T}_{n,L}(\epsilon) f_L(\epsilon) + \mathcal{T}_{n,R}(\epsilon) f_R(\epsilon)$$

Voltage probe: Incoherent **inelastic** scattering

$$I_n = \frac{e}{2\pi\hbar}\sum_\alpha \int_{-\infty}^{\infty} \mathcal{T}_{n,\alpha}(\epsilon)\left[f_n(\epsilon) - f_\alpha(\epsilon)\right] d\epsilon$$

Probe condition: $I_n = 0$



Linear Response:

Linear equation for μ_n, probe chemical potentials!

$$\mathbf{M}\mu = \mathbf{v}$$

$$\mu_n \sum_\alpha \int_{-\infty}^{\infty} \left(-\frac{\partial f_{eq}}{\partial \epsilon}\right) \mathcal{T}_{n,\alpha}(\epsilon) d\epsilon - \sum_{n'} \mu_{n'} \int_{-\infty}^{\infty} \left(-\frac{\partial f_{eq}}{\partial \epsilon}\right) \mathcal{T}_{n,n'}(\epsilon) d\epsilon$$

$$= \int_{-\infty}^{\infty} d\epsilon \left(-\frac{\partial f_{eq}}{\partial \epsilon}\right) \left[\mathcal{T}_{n,L}(\epsilon)\mu_L + \mathcal{T}_{n,R}(\epsilon)\mu_R\right].$$

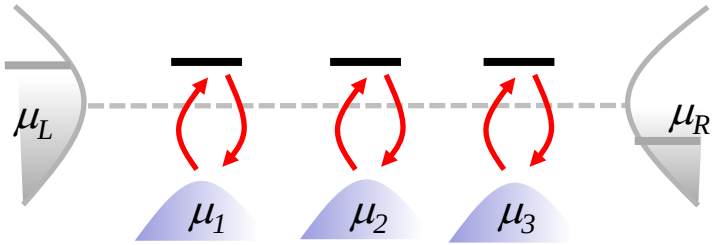
Low temperature → Pastawski formula

$$\mathcal{T}_{eff} = \mathcal{T}_{L,R} + \sum_{i,j} \mathcal{T}_{R,i} W^{-1}_{i,j} \mathcal{T}_{j,L}$$

Voltage probe: Incoherent **inelastic** scattering

$$I_n = \frac{e}{2\pi\hbar}\sum_\alpha \int_{-\infty}^{\infty} \mathcal{T}_{n,\alpha}(\epsilon)\left[f_n(\epsilon) - f_\alpha(\epsilon)\right] d\epsilon$$

Probe condition: $I_n = 0$



Far-from-equilibrium

Nonlinear equation for μ_n, probe chemical potentials!

$$\cancel{\mathbf{M}\mu = \mathbf{v}}$$

Use Newton Raphson method to get the roots

$$\begin{bmatrix} \mu_1^{k+1} \\ \mu_2^{k+1} \\ \mu_3^{k+1} \end{bmatrix} = \begin{bmatrix} \mu_1^{k} \\ \mu_2^{k} \\ \mu_3^{k} \end{bmatrix} - \begin{bmatrix} \frac{\partial I_1}{\partial \mu_1} & \frac{\partial I_1}{\partial \mu_2} & \frac{\partial I_1}{\partial \mu_3} \\ \frac{\partial I_2}{\partial \mu_1} & \frac{\partial I_2}{\partial \mu_2} & \frac{\partial I_2}{\partial \mu_3} \\ \frac{\partial I_3}{\partial \mu_1} & \frac{\partial I_3}{\partial \mu_2} & \frac{\partial I_3}{\partial \mu_3} \end{bmatrix}_k^{-1} \begin{bmatrix} I_1 \\ I_2 \\ I_3 \end{bmatrix}_k$$

$$\boxed{I_L = \frac{e}{2\pi\hbar}\sum_\alpha \int_{-\infty}^{\infty} \mathcal{T}_{L,\alpha}(\epsilon)\left[f_L(\epsilon) - f_\alpha(\epsilon)\right] d\epsilon}$$

Working Expressions

$$\mathcal{T}_{\alpha,\alpha'}(\epsilon) = \mathrm{Tr}[\hat{\Gamma}_{\alpha'}(\epsilon)\hat{G}^r(\epsilon)\hat{\Gamma}_{\alpha}(\epsilon)\hat{G}^a(\epsilon)]$$

$$\hat{G}^r(\epsilon) = [\epsilon\hat{I} - \hat{H}_M + \frac{i}{2}(\hat{\Gamma}_L + \hat{\Gamma}_R + \sum_n \hat{\Gamma}_n)]^{-1}$$

$$\hat{G}^a(\epsilon) = [\hat{G}^r(\epsilon)]^\dagger$$

… But probes do more than level broadening!

Tunneling, ballistic motion, hopping, and **crossover** between regions.

$$[\hat{\Gamma}_n]_{n,n} = \gamma_d,$$

$$[\hat{\Gamma}_L]_{1,1} = \gamma_L \quad [\hat{\Gamma}_R]_{N,N} = \gamma_R$$

$$\hat{H} = \hat{H}_M + \hat{H}_L + \hat{H}_R + \hat{H}_T + \hat{H}_P + \hat{V}_P$$

$$\hat{H}_M = \sum_{n=1}^{N} \epsilon_n \hat{c}_n^\dagger \hat{c}_n + \sum_{n=1}^{N-1} v_{n,n+1} \hat{c}_n^\dagger \hat{c}_{n+1} + h.c.$$

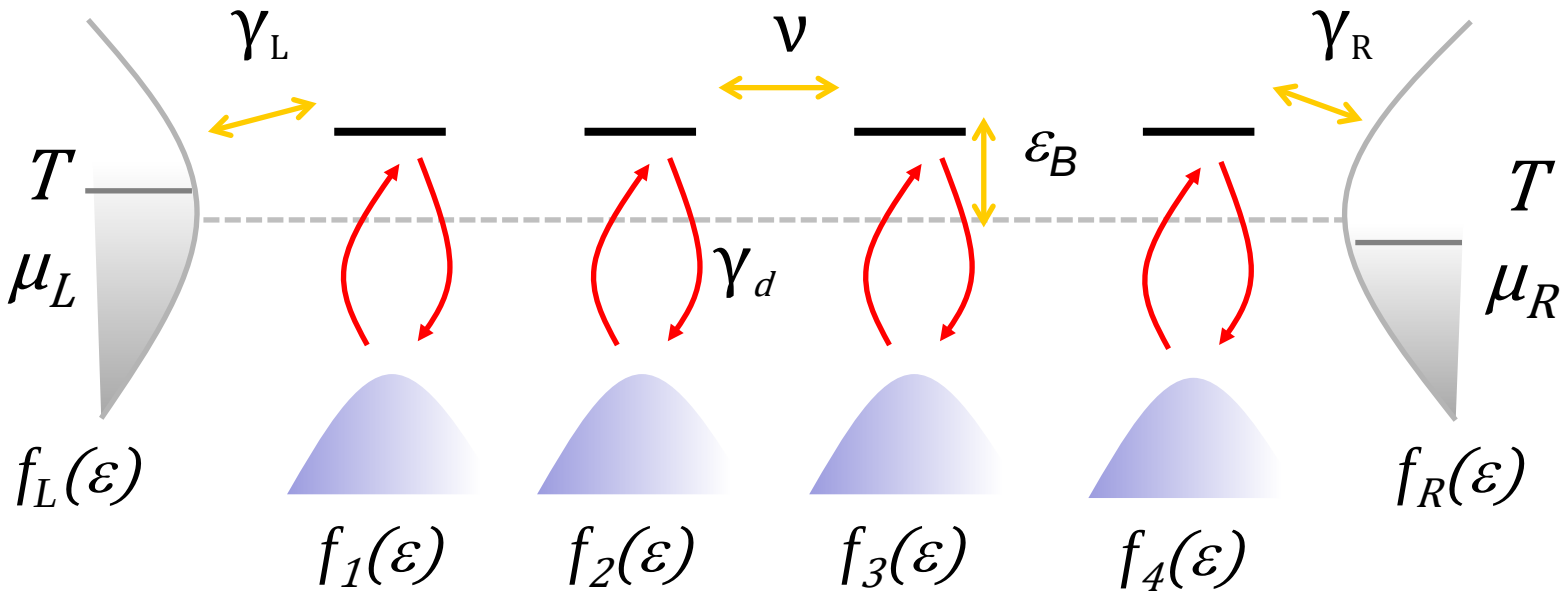
$$\hat{H}_T = \sum_k g_{L,k} \hat{a}_{L,k}^\dagger \hat{c}_1 + \sum_k g_{R,k} \hat{a}_{R,k}^\dagger \hat{c}_N + h.c.$$

$$\hat{H}_\nu = \sum_k \epsilon_{\nu,k} \hat{a}_{\nu,k}^\dagger \hat{a}_{\nu,k}, \quad \nu = L, R.$$

$$\hat{H}_P = \sum_{n=1}^{N} \sum_k \epsilon_{n,k} \hat{a}_{n,k}^\dagger \hat{a}_{n,k} \qquad \hat{V}_P = \sum_{n=1}^{N} \sum_k g_{n,k} \hat{a}_{n,k}^\dagger \hat{c}_n + h.c.$$

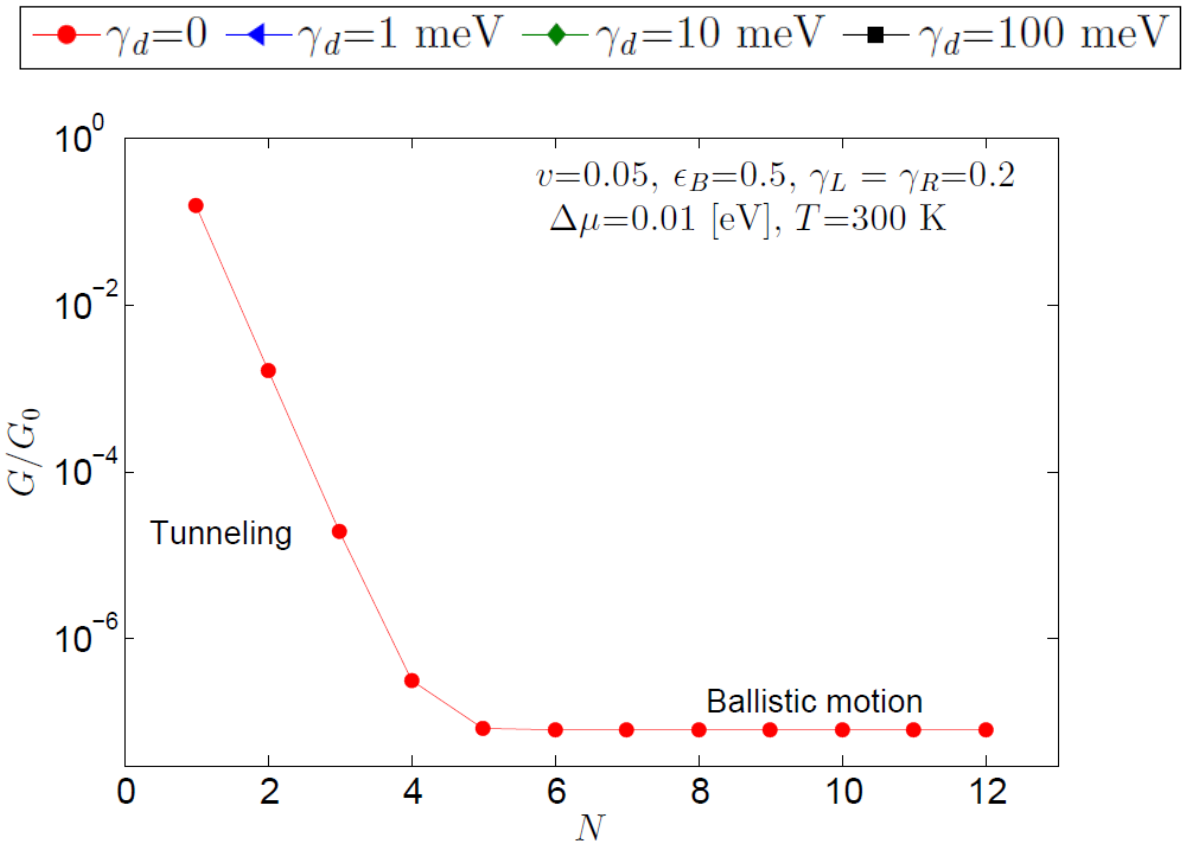
$$\gamma_\alpha(\epsilon) = 2\pi \sum_k |g_{\alpha,k}|^2 \delta(\epsilon - \epsilon_{\alpha,k})$$

Molecular junction with probes



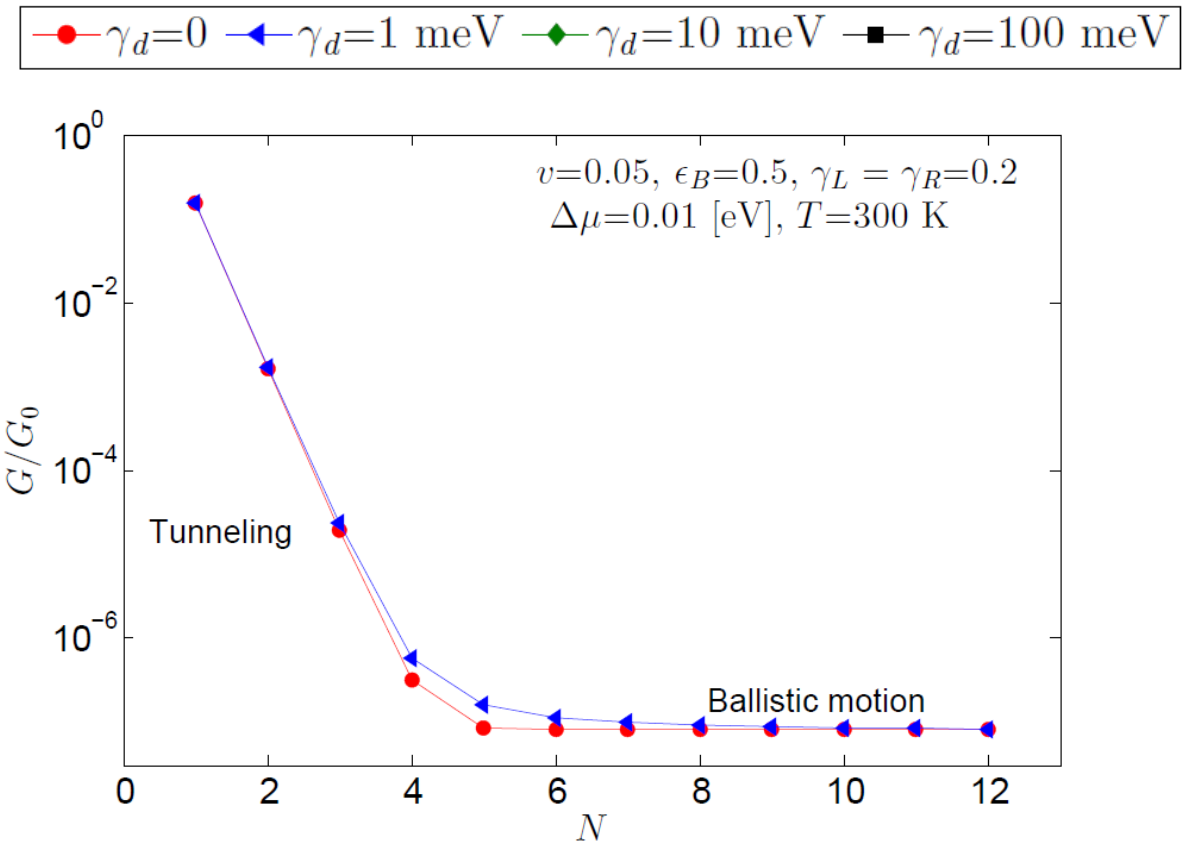
ε_B=0.5, ν= 0.05, $\gamma_{L,R}$=0.2 [eV]
Linear tilting of levels

Distance dependence



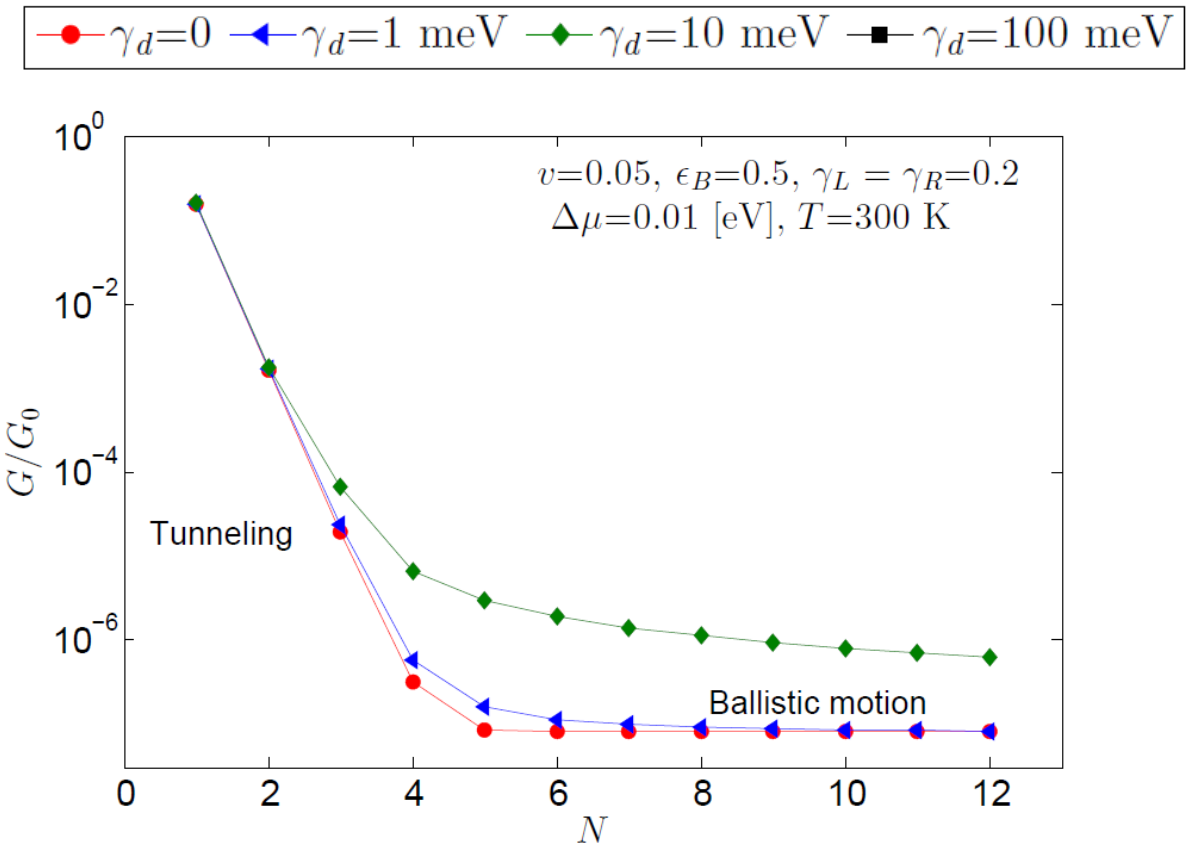
M. Kilgour and DS JCP 143, 024111 (2015)

Distance dependence



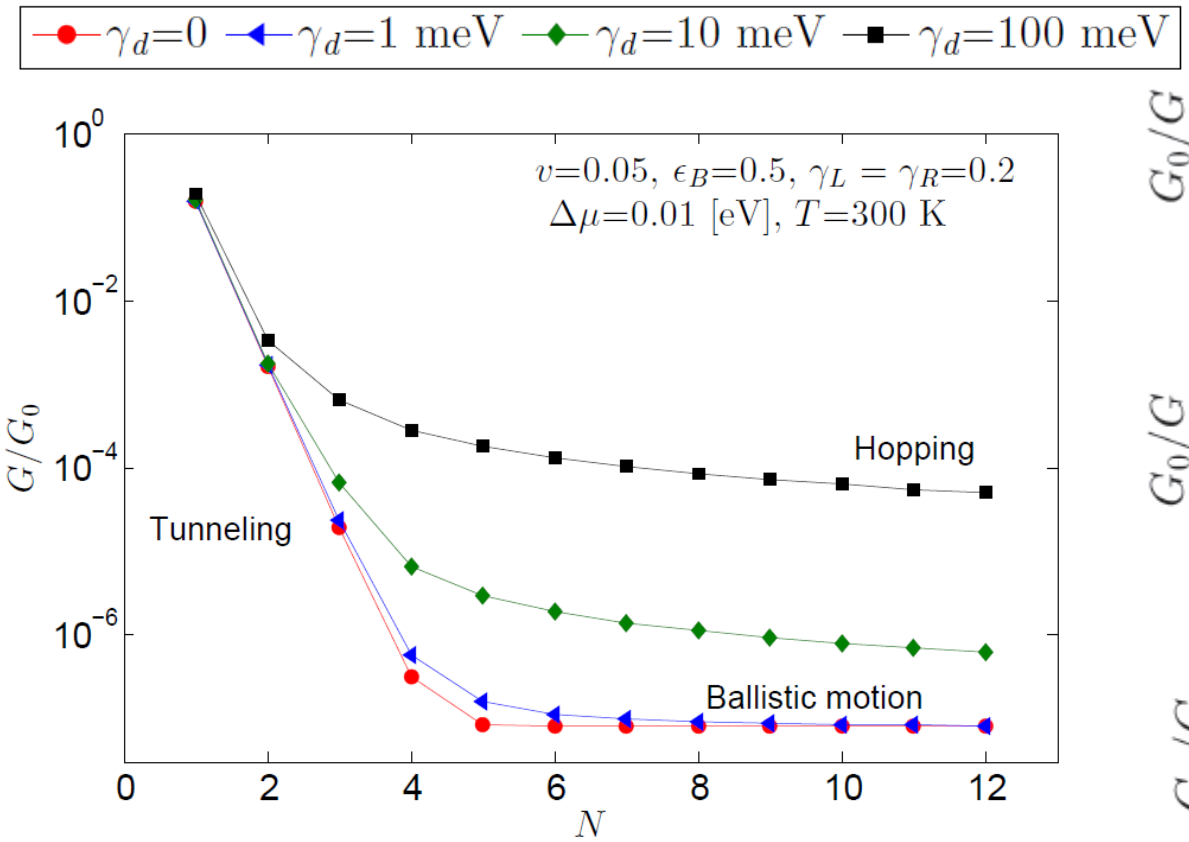
M. Kilgour and DS JCP 143, 024111 (2015)

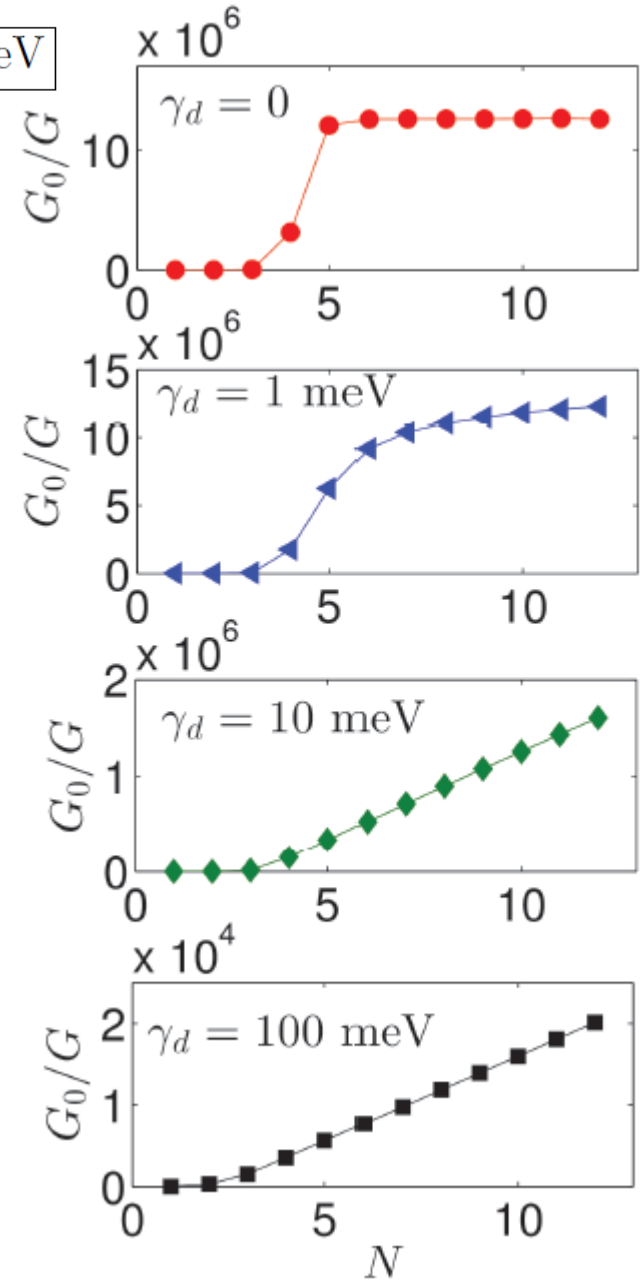
Distance dependence



M. Kilgour and DS JCP 143, 024111 (2015)

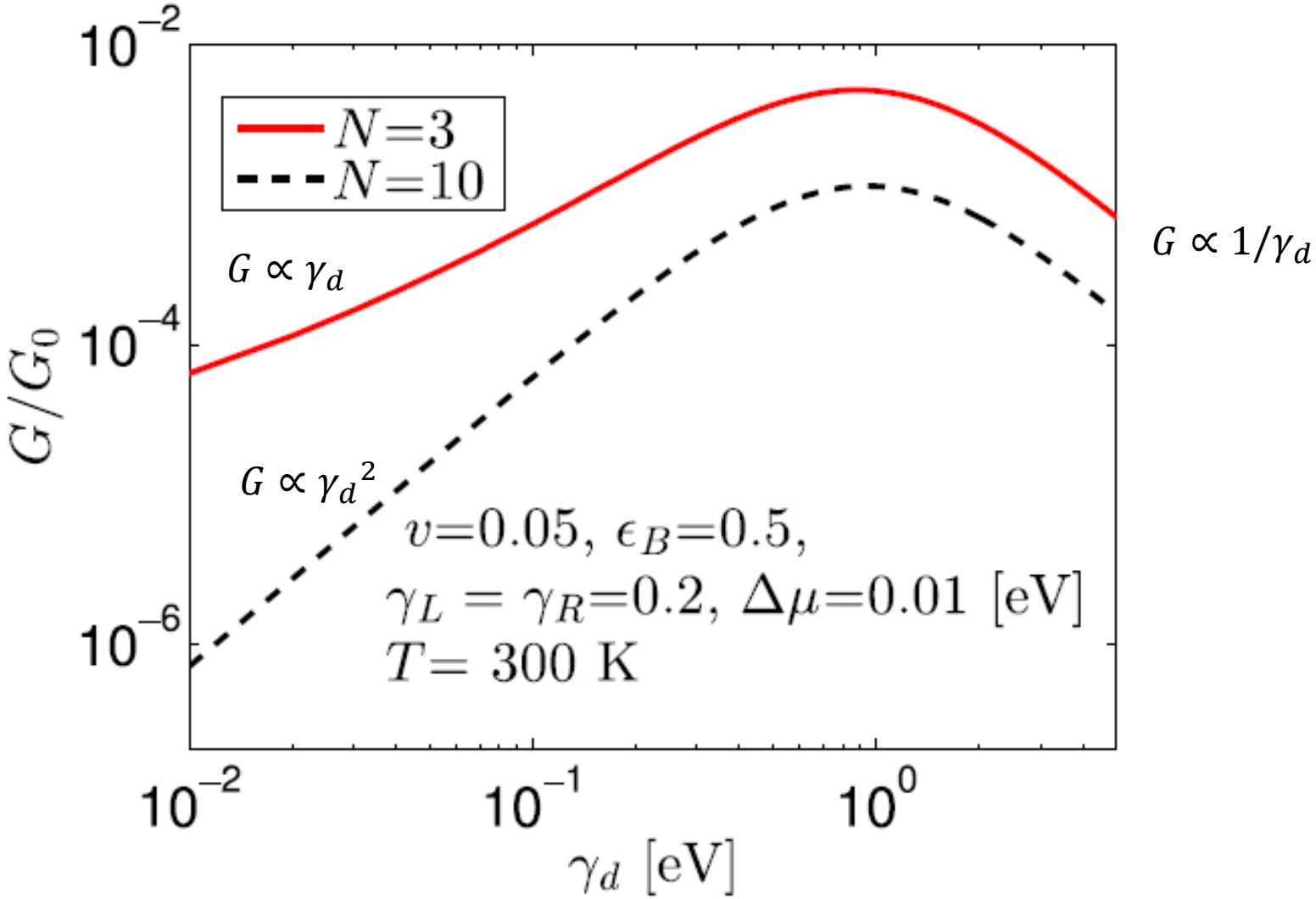
Distance dependence





M. Kilgour and DS JCP 143, 024111 (2015)

Kramer's like turnover

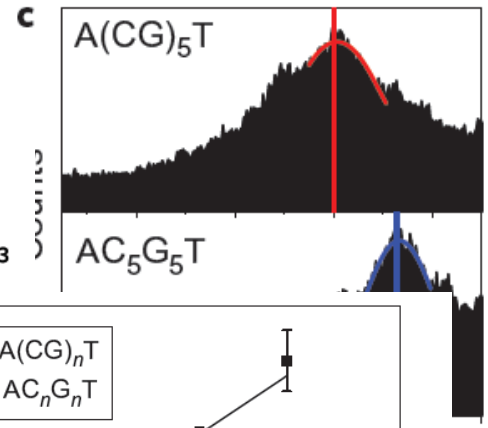


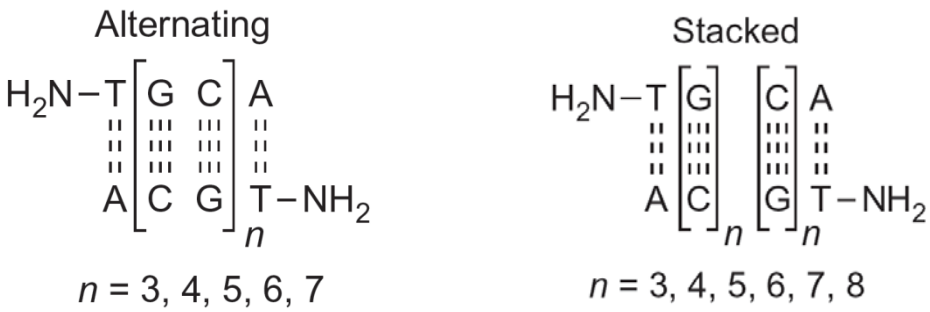
M. Kilgour and DS, JCP **143**, 024111 (2015)

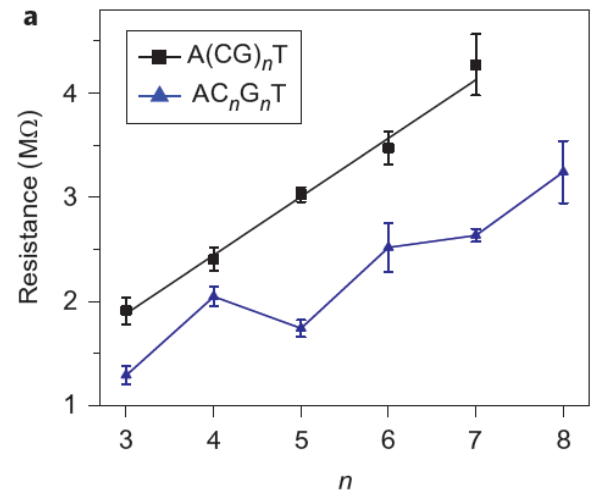
NATURE CHEMISTRY | VOL 7 | MARCH 2015 | www.nature.com/naturechemistry

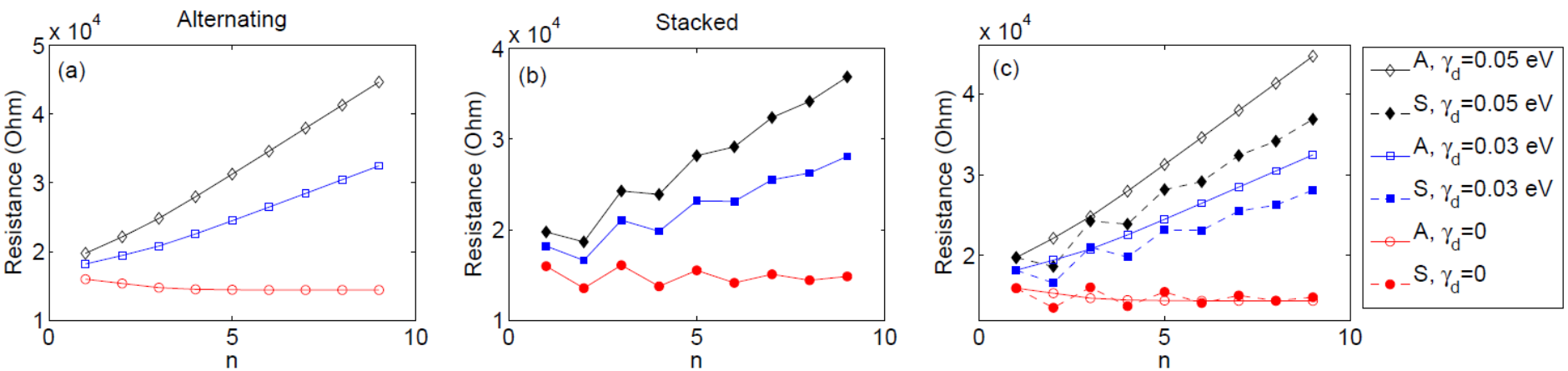
Intermediate tunnelling–hopping regime in DNA charge transport

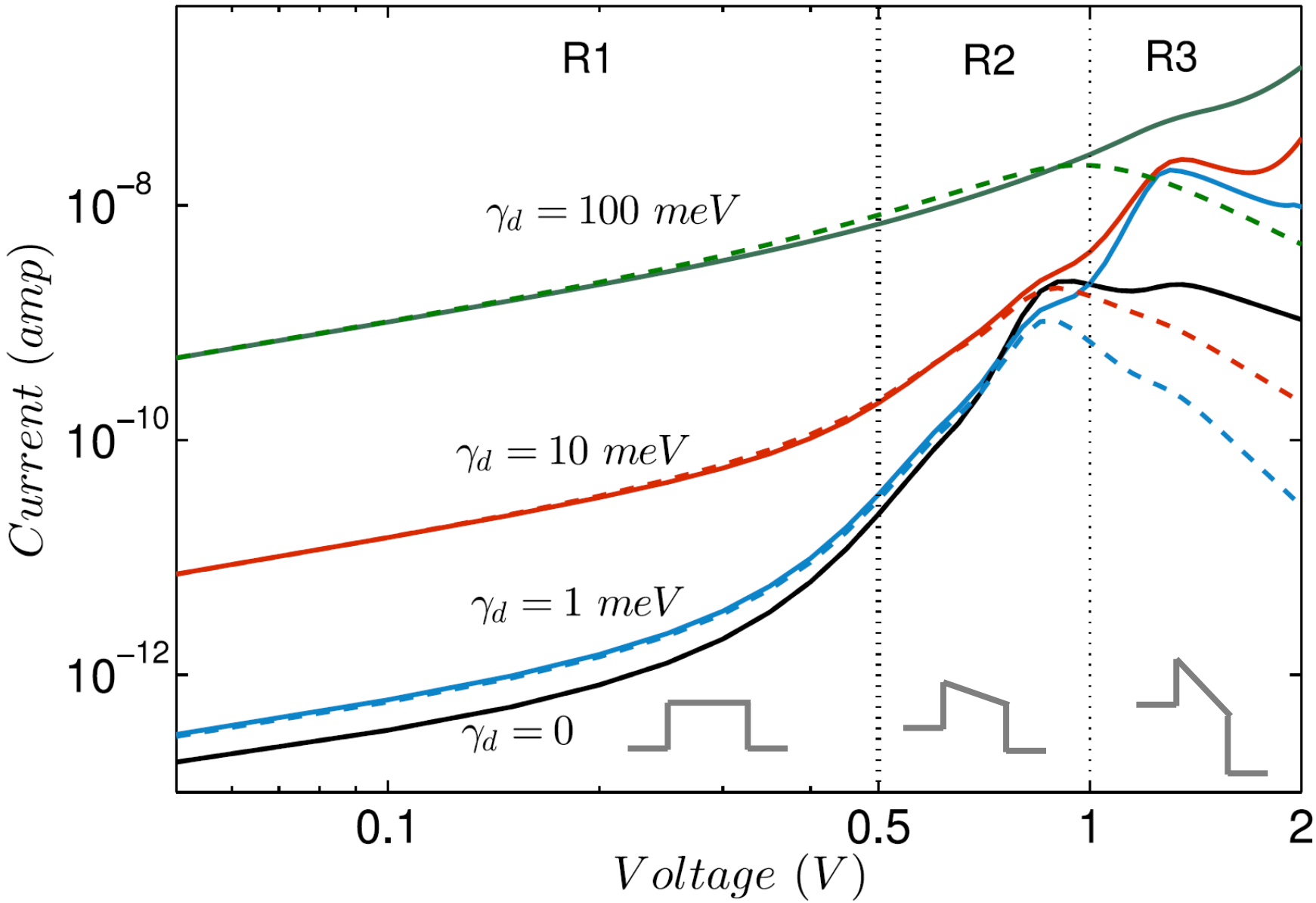
Limin Xiang[1,2], Julio L. Palma[1,2], Christopher Bruot[1], Vladimiro Mujica[2], Mark A. Ratner[3] and Nongjian Tao[1,4]*





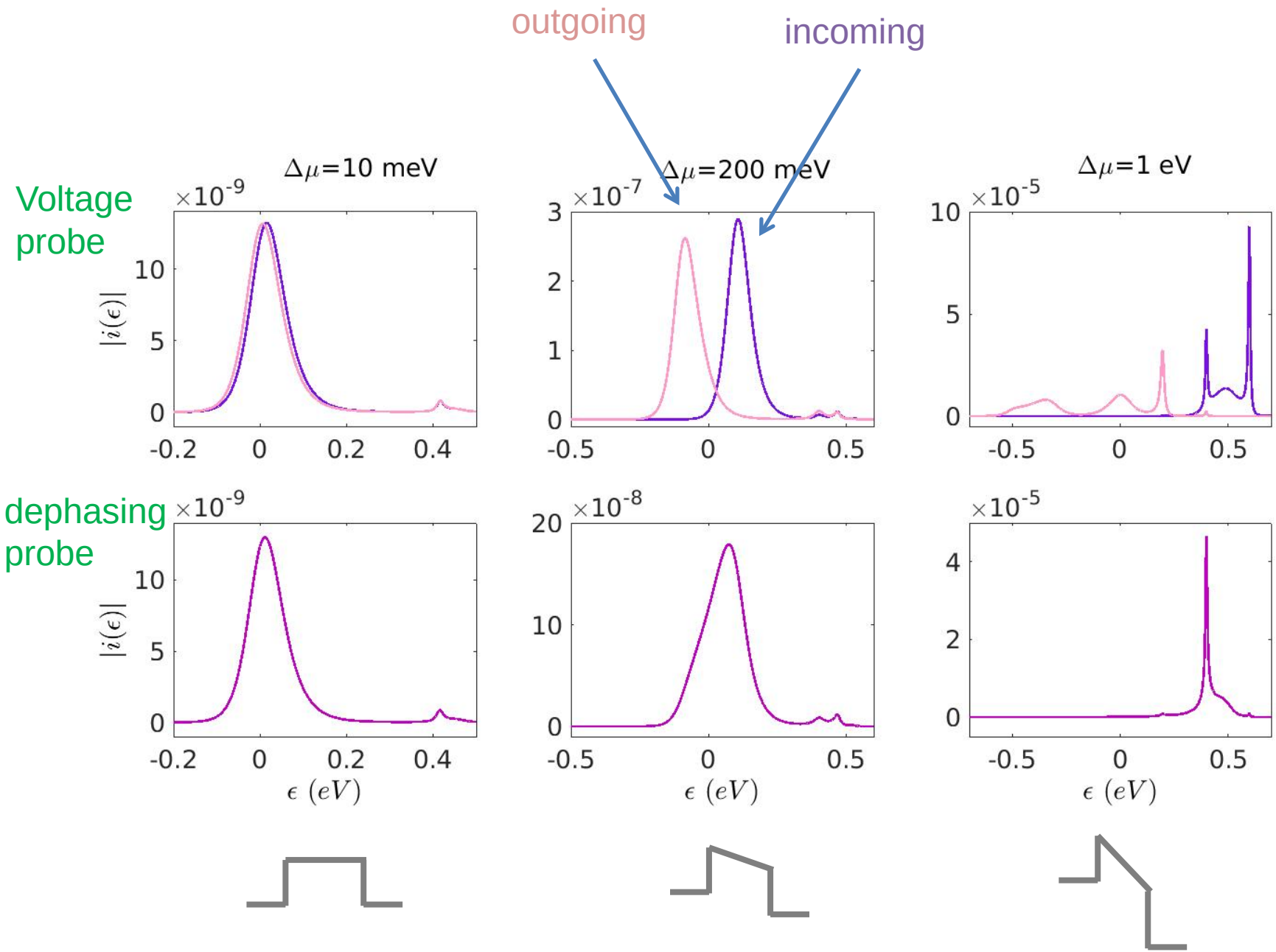






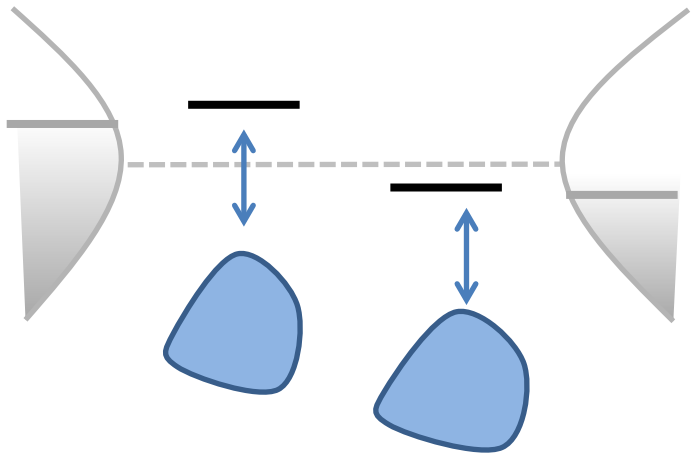
M. Kilgour and DS JCP **144**, 124107 (2016)

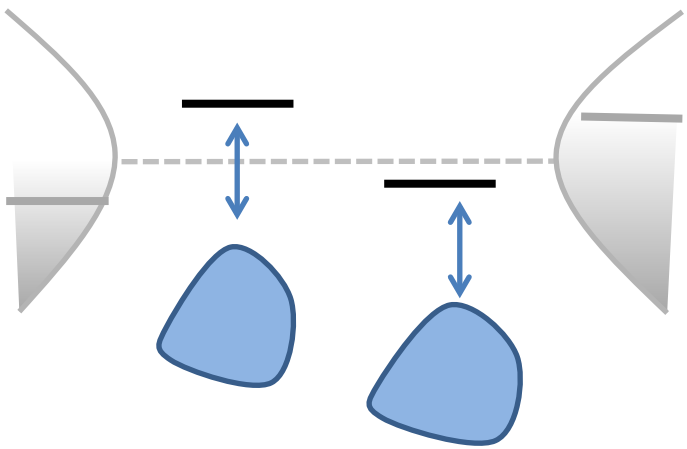
$$\epsilon_n = \epsilon_B + \frac{\Delta\mu}{2} - \frac{\Delta\mu(n-1)}{N-1}$$


outgoing
incoming
Voltage probe
dephasing probe
Δμ=10 meV
Δμ=200 meV
Δμ=1 eV
×10^-9
×10^-7
×10^-5
×10^-8
|i(ϵ)|
ϵ (eV)

Diode: Absence of rectification with dephasing probes

➔ Rectification with voltage probe – beyond linear response (Michael's poster)





$$i_L^+(\epsilon) = \mathcal{T}_{L,R}(\epsilon)[f_L(\epsilon) - f_R(\epsilon)] + \sum_n \mathcal{T}_{L,n}(\epsilon)[f_L(\epsilon) - f_n^+(\epsilon)]$$

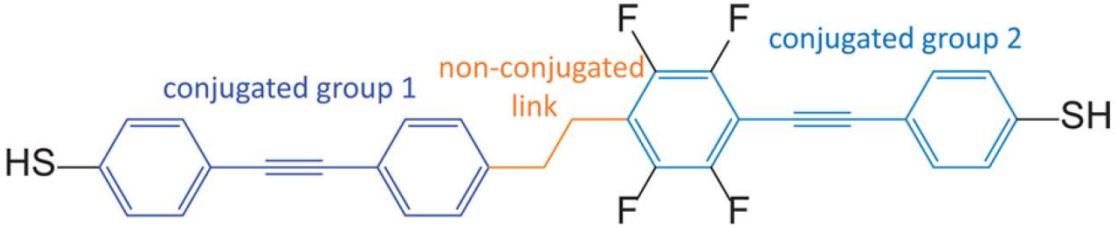
$$i_L^-(\epsilon) = \mathcal{T}_{L,R}(\epsilon)[f_R(\epsilon) - f_L(\epsilon)] + \sum_n \mathcal{T}_{L,n}(\epsilon)[f_R(\epsilon) - f_n^-(\epsilon)]$$

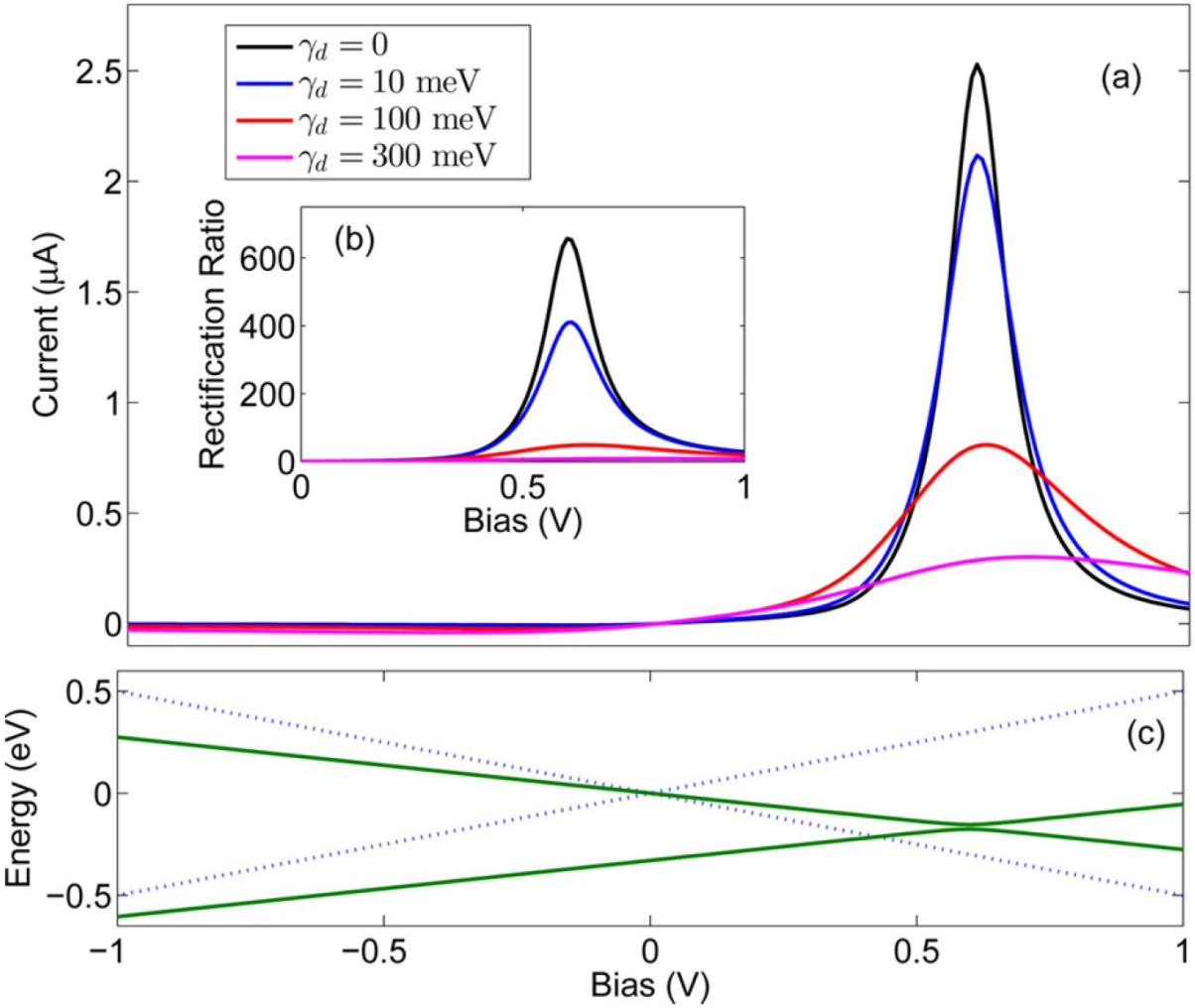
$$\Delta i(\epsilon) = \sum_n \mathcal{T}_{L,n}(\epsilon)[f_L(\epsilon) + f_R(\epsilon) - f_n^+(\epsilon) - f_n^-(\epsilon)]$$

$$= 0$$

from the dephasing probe condition

Tunneling Diodes





Tunneling diodes under environmental effects
M. Kilgour and DS
JPC C 119, 25291 (2016)

Summary:
Buttiker's probes in molecular electronics **charge transport**

1. Examine susceptibility of coherent phenomena to incoherent (elastic/inelastic) environmental scattering effects

- Cheap at low bias and at low T.

- Expensive high bias simulations: nonlinear function

2. Capture turnover between different transport mechanisms

M. Kilgour and DS, JCP **143**, 024111 (2015)

M. Kilgour and DS JPC C **119**, 25291 (2016)

M. Kilgour and DS JCP **144**, 124107 (2016)

NANO LETTERS

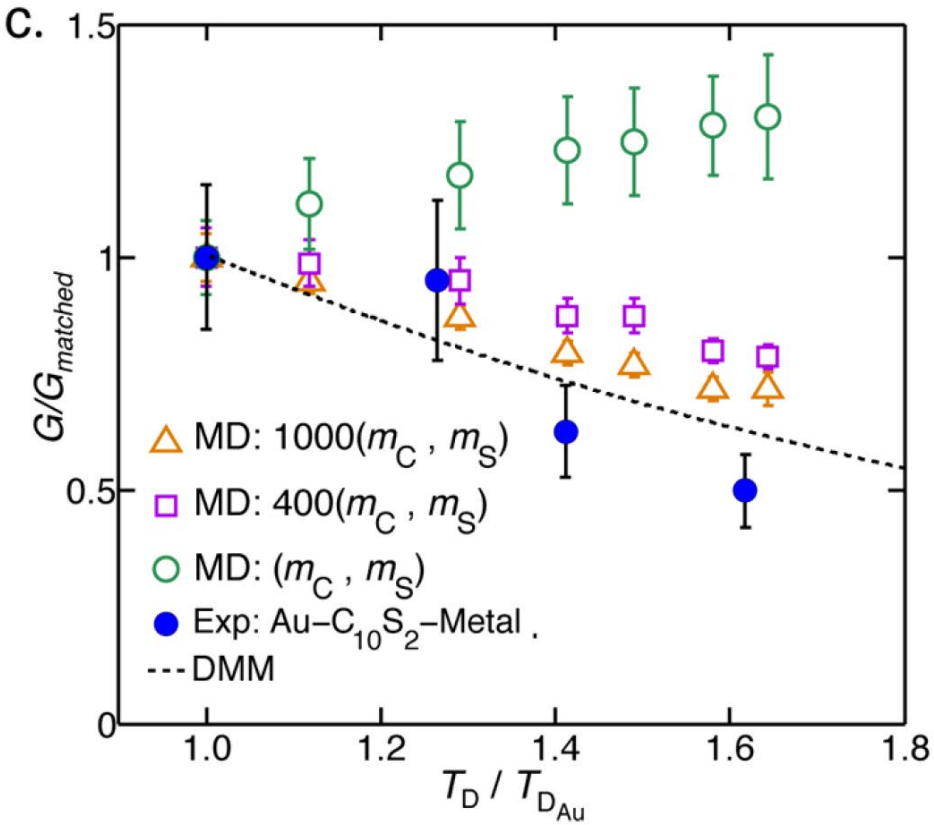
Nano Lett., 2015, 15 (5), pp 2985–2991

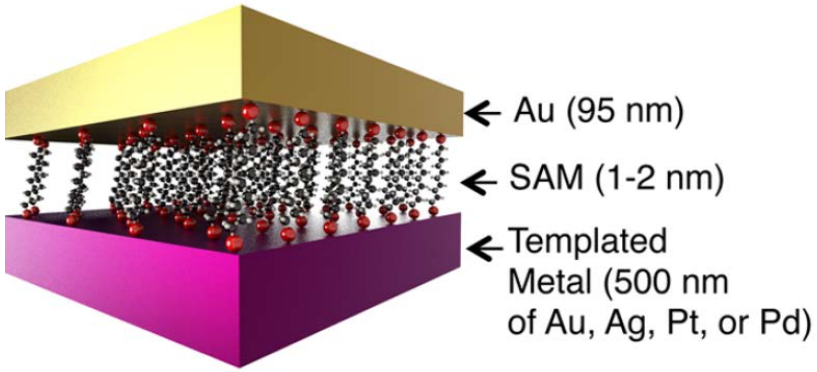
Letter

pubs.acs.org/NanoLett

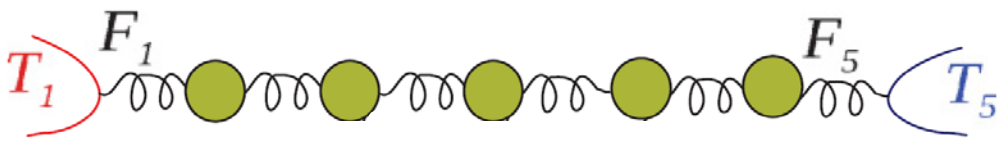
Vibrational Mismatch of Metal Leads Controls Thermal Conductance of Self-Assembled Monolayer Junctions

Shubhaditya Majumdar,[†] Jonatan A. Sierra-Suarez,[‡] Scott N. Schiffres,[†] Wee-Liat Ong,[†] C. Fred Higgs, III,[†,‡] Alan J. H. McGaughey,[†,§] and Jonathan A. Malen*[,†,§]



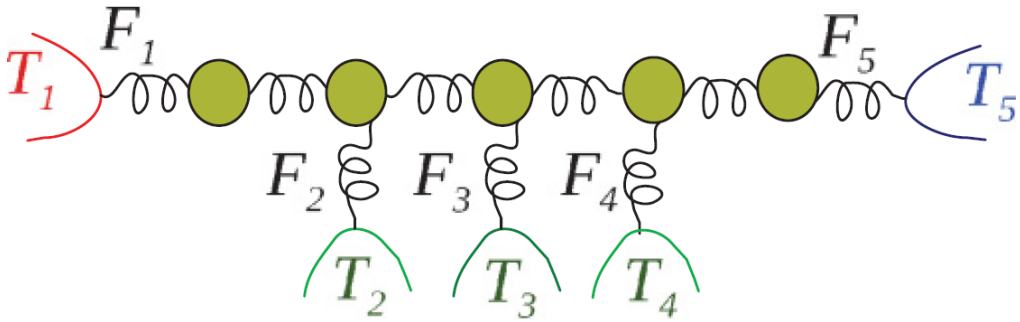


Methods for **quantum** heat transfer:



I. Landauer Formalism - harmonic force field

II. Phenomenology of anharmonic effects: self consistent reservoirs



III. Genuine anharmonic effects: Green's function, quantum master equation, Boltzmann's equation…

Simulation of Nonharmonic Interactions in a Crystal by Self-Consistent Reservoirs*

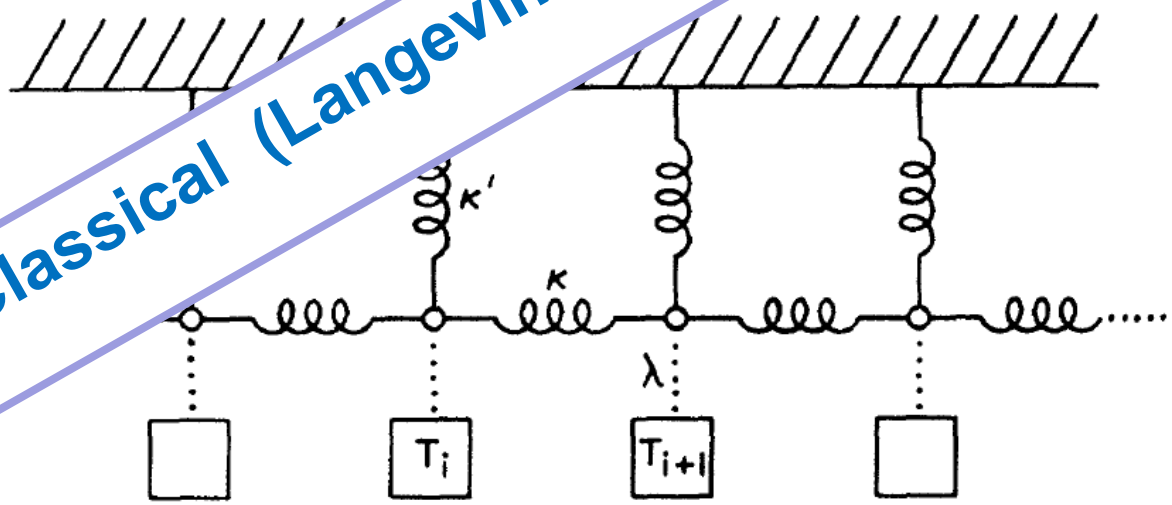
M. Bolsterli, M. Rich, and W. M. Visscher

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544

(Received 13 November 1969)

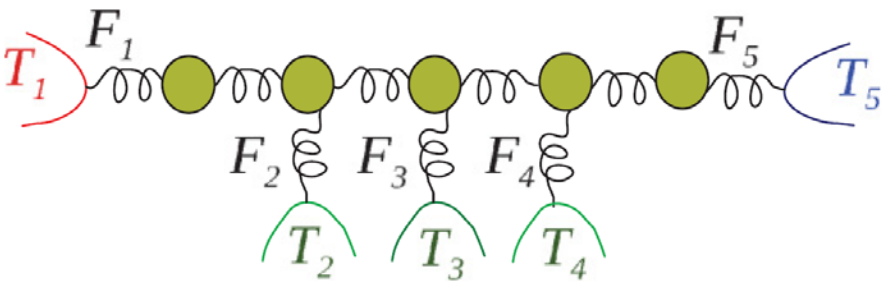
Independent heat reservoirs are postulated to interact with t ms in a harmonic system as a substitute for real nonharmonic forces. The tempe h reservoir is determined by the condition that it exchange no energy wi e steady state. An explicit solution for the covariance matrix is o e of the linear chain. The thermal conductivity is finite and inversel e coupling to the reservoirs.

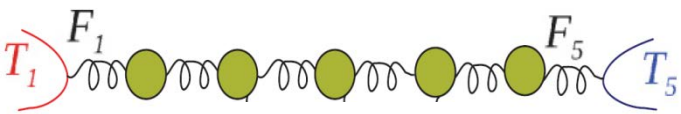
Classical (Langevin equation)



PRA **1,** 1086 (1970)

Anharmonicity: Phenomenological Approach





$$J_Q = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \hbar\omega \mathcal{T}(\omega)[n_L(\omega) - n_R(\omega)]$$

Harmonic model: simple, and… not so interesting…

Effective anharmonicity: overall energy is conserved, but not the number of quanta

$$M_l \ddot{X}_l = -(2X_l - X_{l-1} - X_{l+1}) - \gamma_l \dot{X}_l + \eta_l$$

$$\frac{1}{2}\langle \eta_l(\omega)\eta_m(\omega') + \eta_l(\omega')\eta_m(\omega)\rangle$$

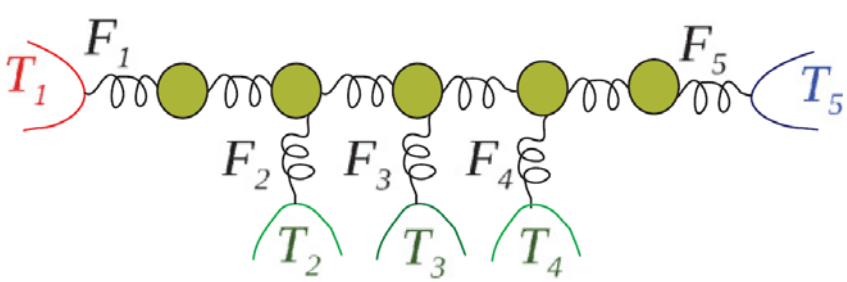
$$= \frac{\gamma_l \omega}{2\pi} \coth\left(\frac{\omega}{2T_l}\right)\delta(\omega+\omega')\delta_{l,m}$$

$$F_l = \sum_{m=1}^{N} \gamma_l \gamma_m \int_{-\infty}^{\infty} d\omega \omega^2 |[G(\omega)]_{l,m}|^2 \frac{\omega}{\pi} [n_B(\omega, T_l) - n_B(\omega, T_m)]$$

Solve for T_l: $F_l = 0, \quad l = 2,3,\ldots,N-1$ $\Rightarrow$ $T_2, T_3 \ldots T_{N-1}$

Heat current: $J = F_1 = -F_N$

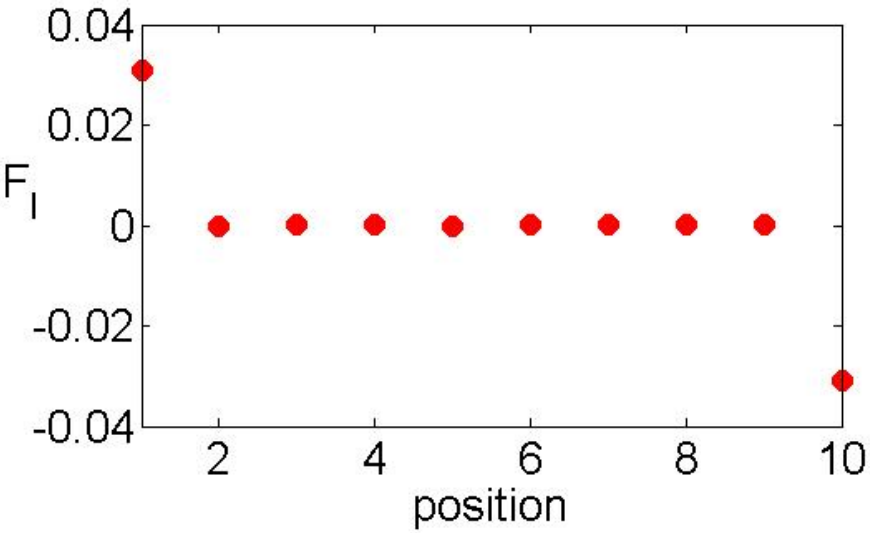
Here G is the inverse of a tridiagonal matrix with off diagonal elements equal to -1 and diagonal elements $2 - M_l\omega^2 - i\gamma_l\omega$



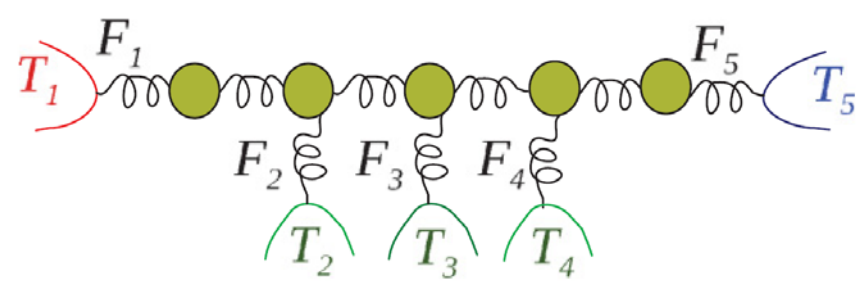
$$F_l = \sum_{m=1}^{N} \gamma_l \gamma_m \int_{-\infty}^{\infty} d\omega \omega^2 |[G(\omega)]_{l,m}|^2 \frac{\omega}{\pi} [n_B(\omega, T_l) - n_B(\omega, T_m)]$$

Solve for T_l: $F_l = 0, \quad l = 2,3,\ldots,N-1$ $\Rightarrow$ $T_2, T_3 \ \ldots T_{N-1}$

Heat current: $J = F_1 = -F_N$



atrix with off diagonal
ents $2 - M_l\omega^2 - i\gamma_l\omega$



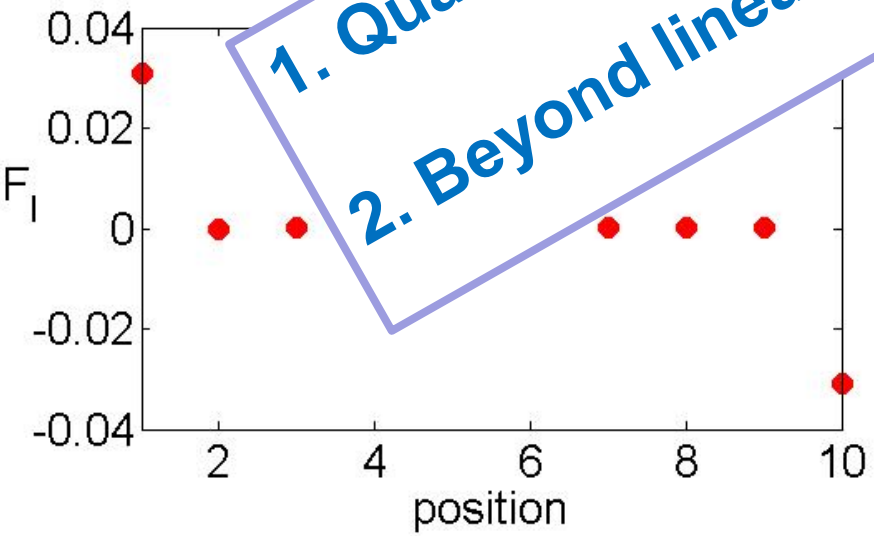
$$F_l = \sum_{m=1}^{N} \gamma_l \gamma_m \int_{-\infty}^{\infty} d\omega \omega^2 |[G(\omega)]_{l,m}|^2 \frac{\omega}{\pi} [n_B(\omega, T_l) - n_B(\omega, T_m)]$$

Solve for T_l: $F_l = 0, \quad l = 2,3$ $\Rightarrow$ $T_2, T_3 \ \ldots T_{N-1}$

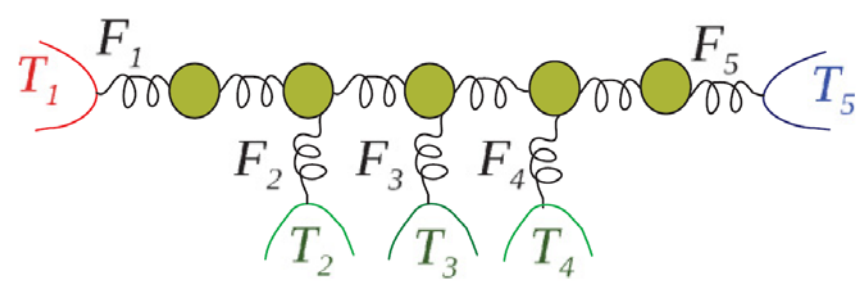
Heat current: $J =$

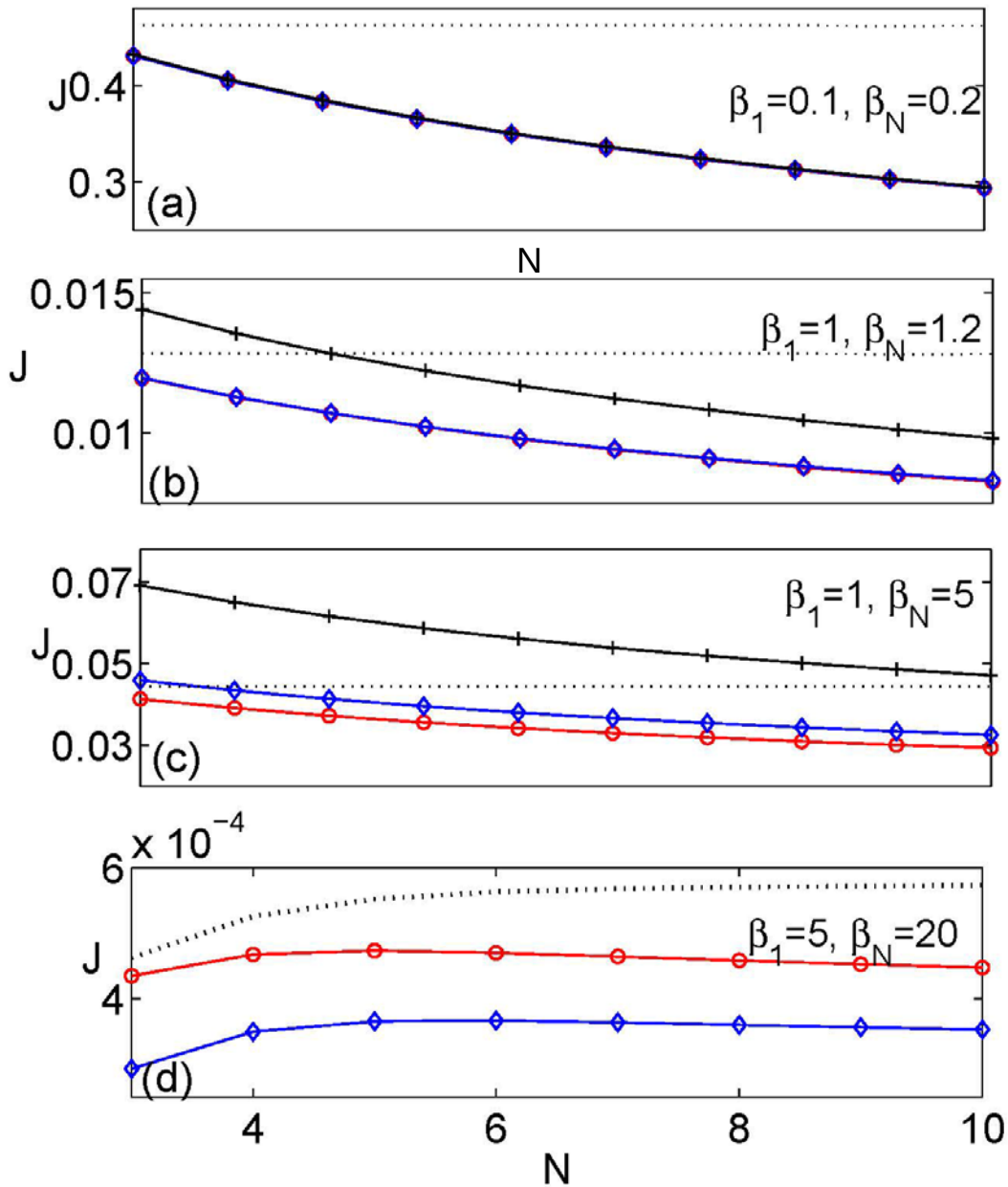
1. Quantum (Langevin equation)

2. Beyond linear response



atrix with off diagonal
nents $2 - M_l\omega^2 - i\gamma_l\omega$





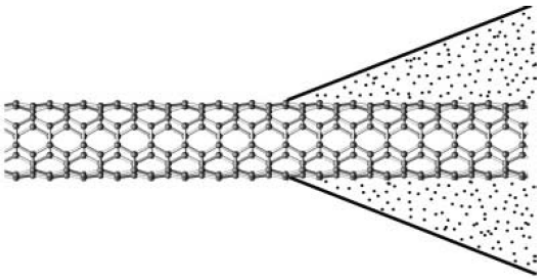
+ Classical
O Exact quantum
◊ Quantum linear response

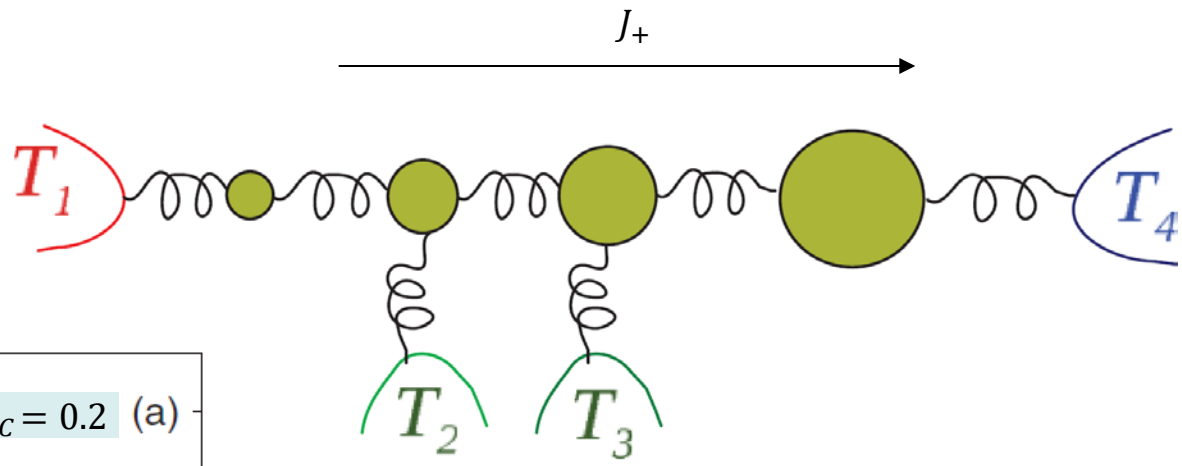
(dotted line: Exact quantum, no internal reservoirs)

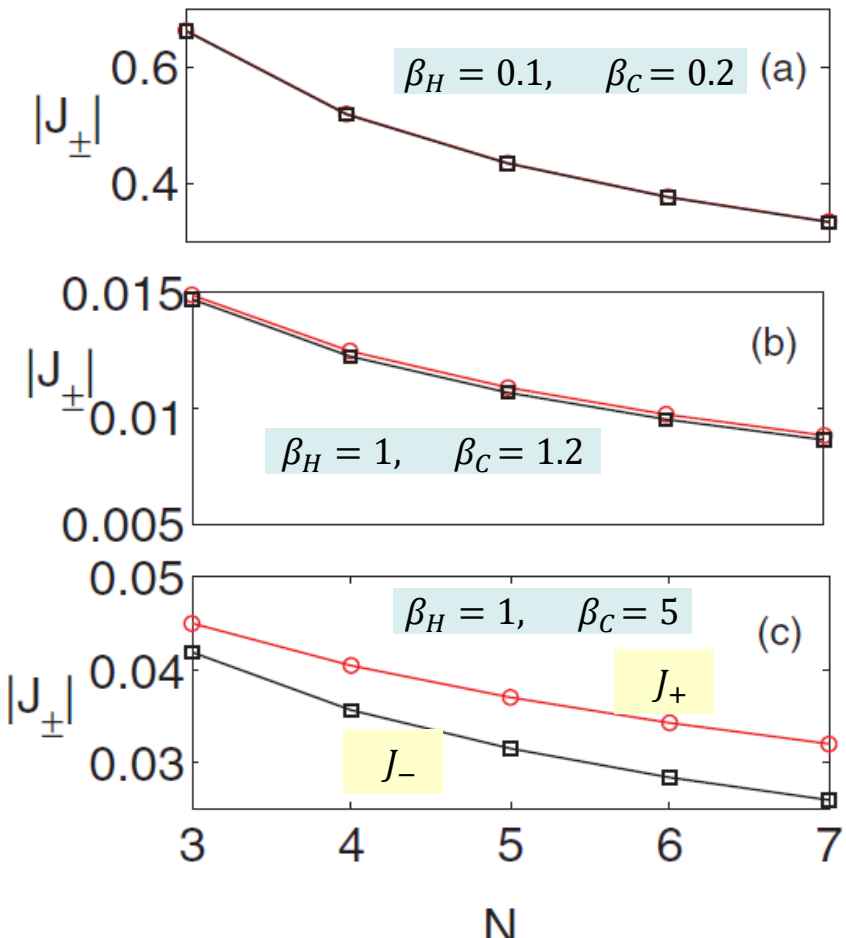
$M = 1, \quad \gamma = 0.2$

M. Bandyopadhyay and D. Segal
Phys. Rev. E 84, 011151 (2011)

Quantum heat diode







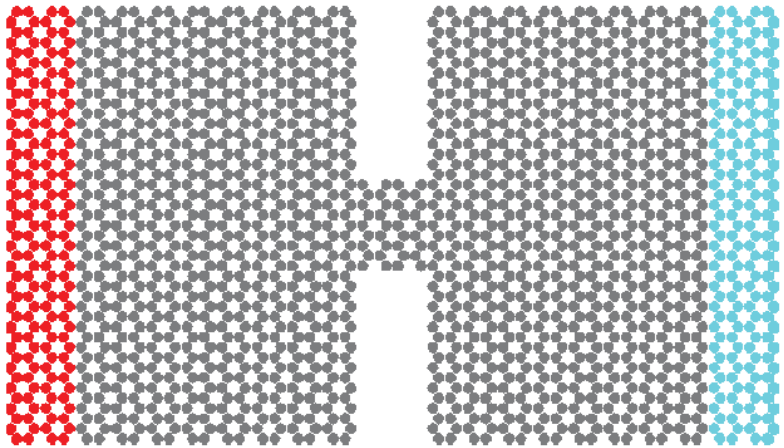
$\gamma = 0.2, \qquad M_n = 0.2 + (n-1)0.2$

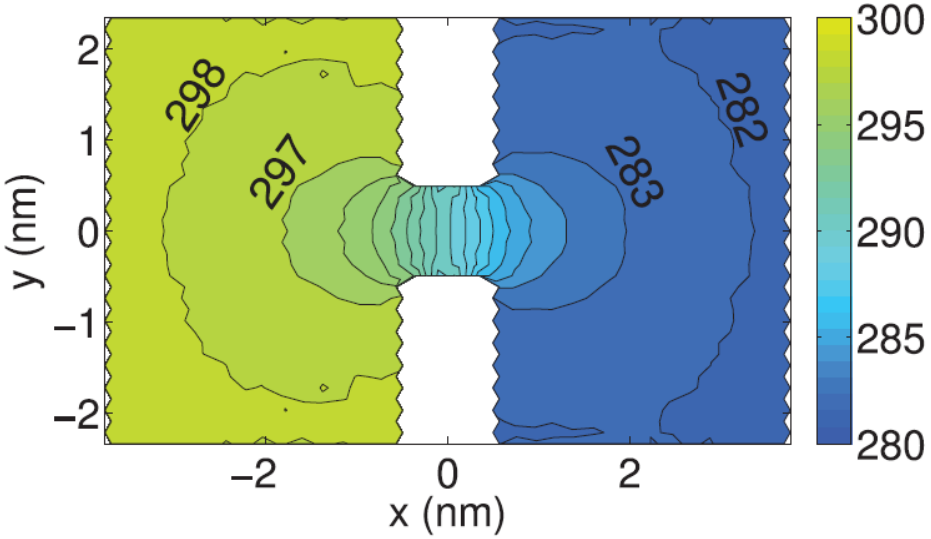
Quantum heat transfer in harmonic chains with self consistent reservoirs: Exact numerical simulations

M. Bandyopadhyay and DS

Phys. Rev. E 84, 011151 (2011)

Application: Self-consistent reservoirs





Thermal transport through two dimensional constrictions of graphene

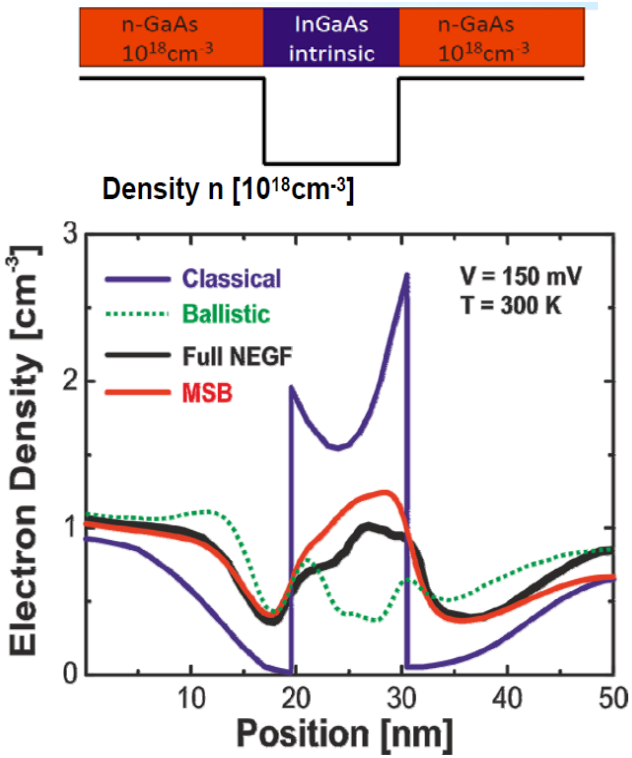
K. Saaskilahti, J. Oksanen, J. Tulkki PRE 88, 012128 (2013).

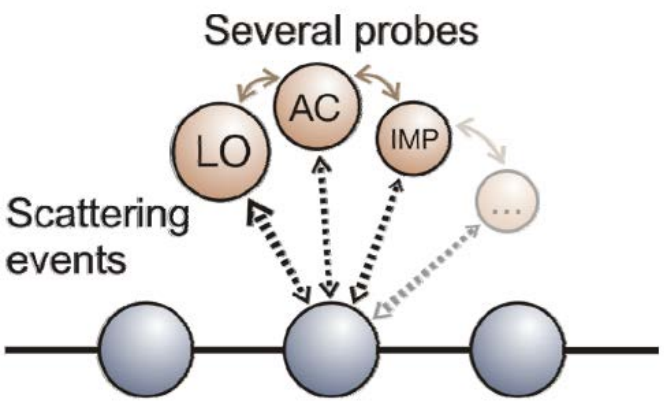
Conclusions-outlook

Large-scale + microscopic mechanisms + analytical results

Future directions:

1. simulation of large scale systems: monolayers, devices
2. capture the nature of the scatterer
3. carefully compare to other methods
4. dynamical effects





The noneq Green's functions method and descendants: Ways to avoid and to go
P. Greck et al IEEE 2010 Walter Schottky Institute

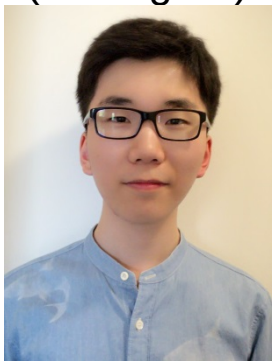
Canada Research Chair Program

NSERC CRSNG

People. Discovery. Innovation.

CQIQC

Hyehwang Kim
(undergrad)



Michael Kilgour
(grad)

Malay Bandyopadhyay
Pdoc→ IIT Bhubaneswar

Hava Friedman
(grad)

Bijay Kumar Agarwalla
(pdoc)