From exhaustive simulations to key principles in DNA nanoelectronics

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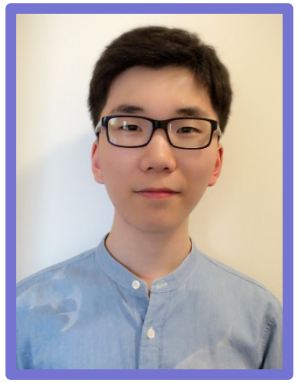

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(grad)

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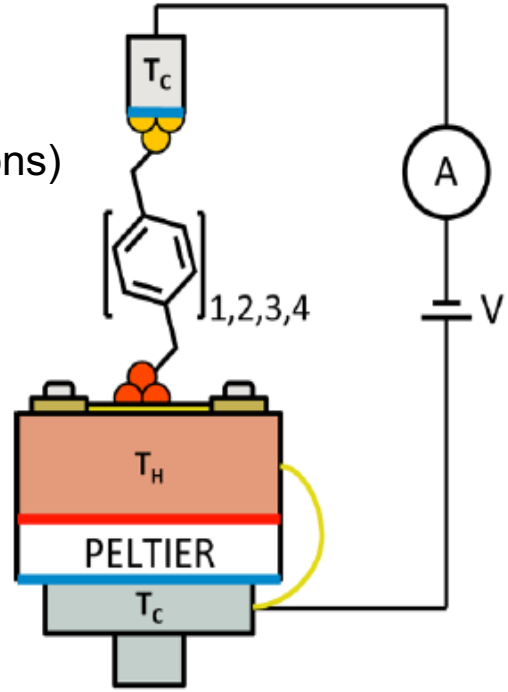
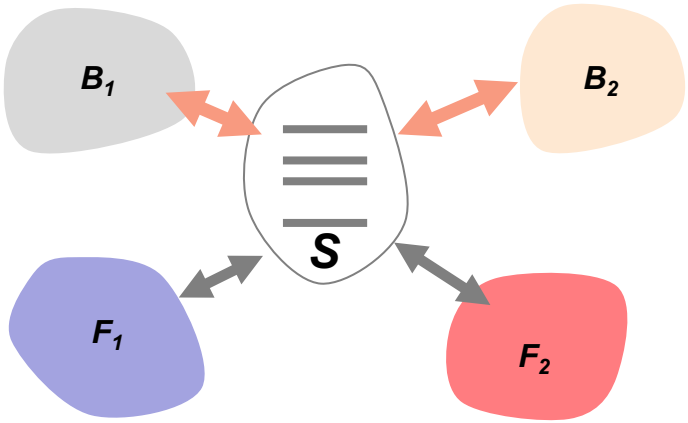
Challenge:

Dynamics of open quantum systems
many-body effects, out of equilibrium,
multiple reservoirs (electrodes, phonons)



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

Model:



Method:

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

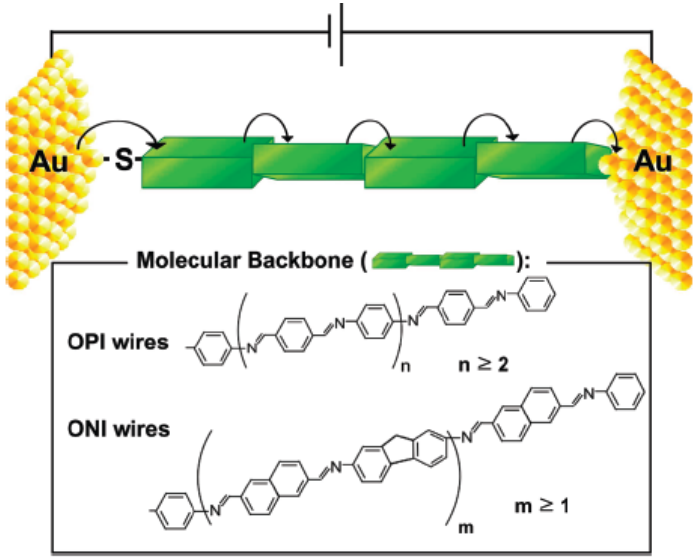
→Perturbative approaches
(QME, NEGF)

→Semiclassical, mixed q-c, hybrid

→Phenomenological tools
(fluctuation of parameters, Büttiker's probes)

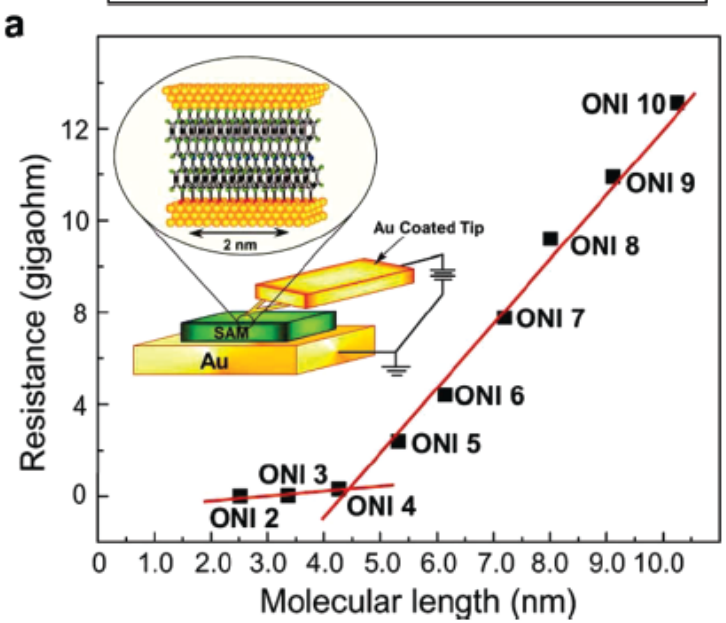
$$\rho_S(t)$$
$$\langle I_e(t)\rangle, \langle I_Q(t)\rangle$$
$$\langle I(t)I(\tau)\rangle$$
$$\eta = W/Q$$

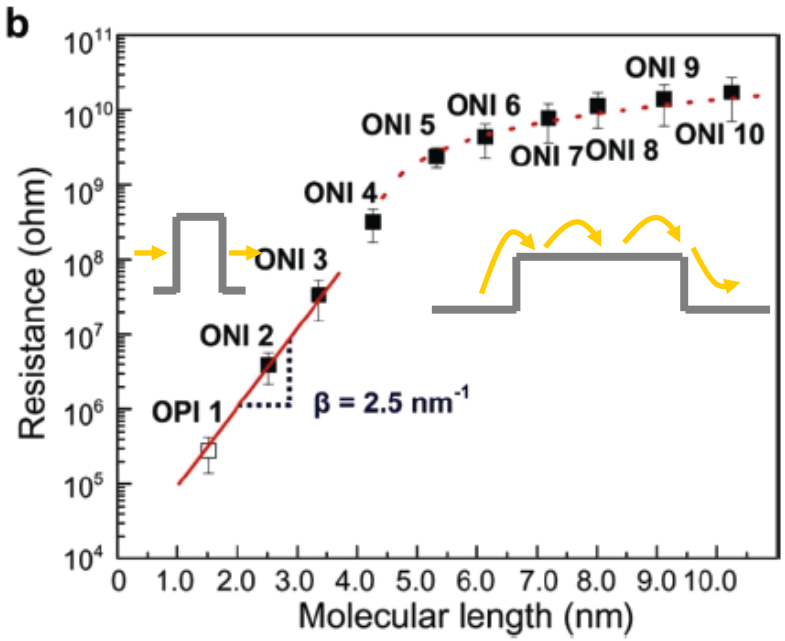
Charge transport mechanisms: Tunneling? Hopping? Intermediate?



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

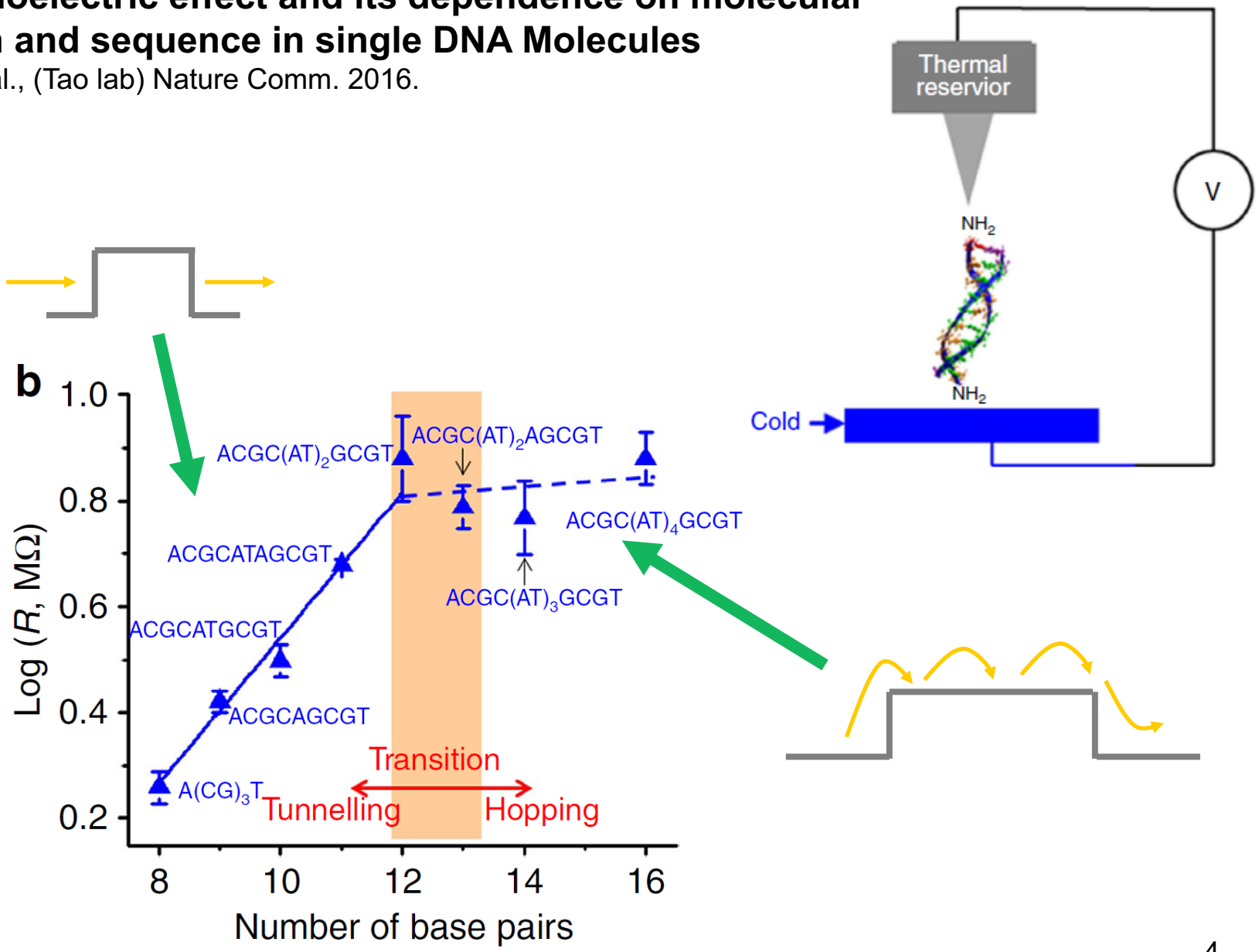
S. H. Choi et al (Frisbie lab) JACS 132, 4358 (2010)





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

Y. Li et al., (Tao lab) Nature Comm. 2016.



Objectives:

Goal: Develop a theoretical/computational tool that can capture transport behavior in such (relatively long) molecules.
Take into account environmental effects, electron-vibration interaction, solvent effects

Mechanisms:
- tunneling, hopping, ballistic motion (resonant transmission)

length, temperature, and energetic dependence.

Results should be meaningful:
- experiments
- other methods (quantum master equations, Green's function, stochastic SE)

Other requirements:
- weak-to-strong metal-molecule coupling
- quantum coherent limit to be included exactly (Landauer formula)
- low-to-high bias simulations, low-to-high temperature
- large scale simulations
- Fundamental understanding over the role of incoherent effects (Ohm's law, diode effect, thermopower)

Büttiker's probes in molecular electronics

Outline

1. **Introduction**
   30+ years with Büttiker's probes (1986)

2. **Charge transport in organic molecules**
   - linear response
   - high voltage results
   - applications: diodes

3. **Electronic conduction of DNA**
   - intermediate coherent-incoherent behavior
   - thermopower
   - exhaustive simulations

4. **Vibrational heat transfer**

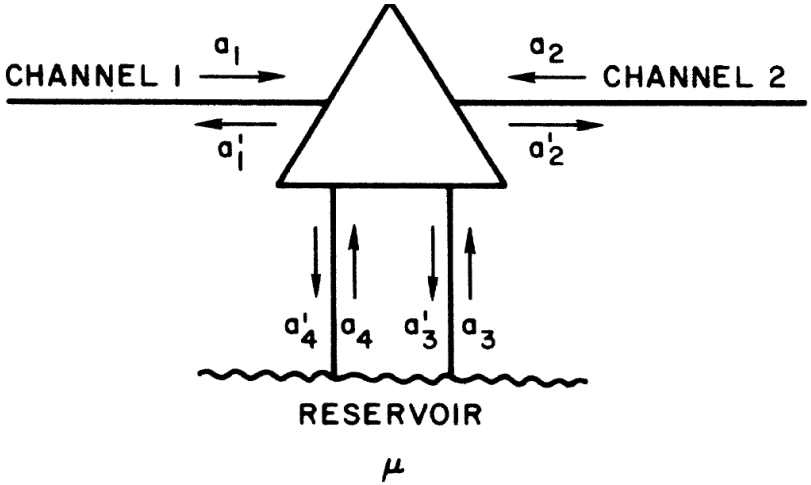
5. **Outlook**

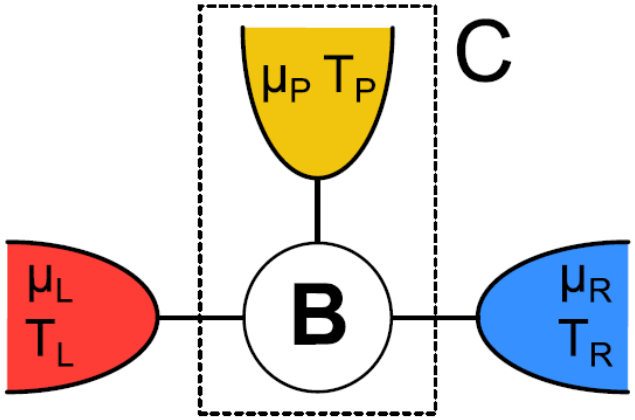
PHYSICAL REVIEW B VOLUME 33, NUMBER 5 1 MARCH 1986

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)

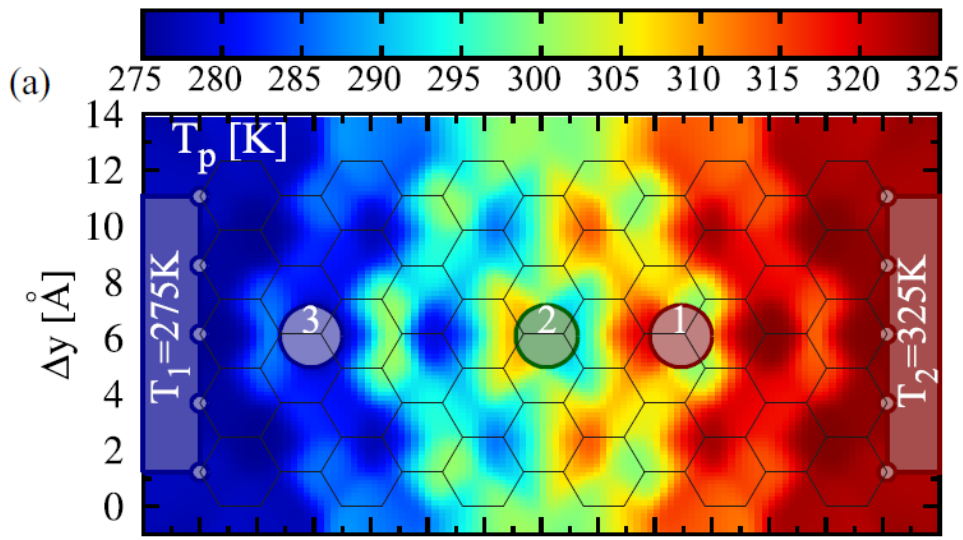
Landauer's approach which yields the resistance of an obstacle in an otherwise perfect wire due to elastic scattering at the obstacle is augmented by including localized inelastic scatterers within the sample. The inelastic scatterers invoked consist of an electron reservoir coupled via a lead to the 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.





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).



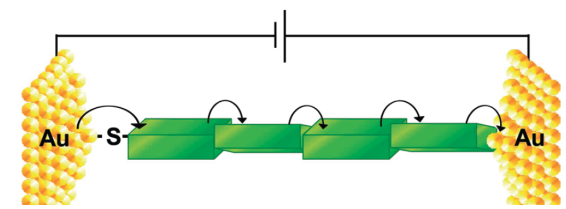
Local temperature of out-of-equilibrium quantum electron systems

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

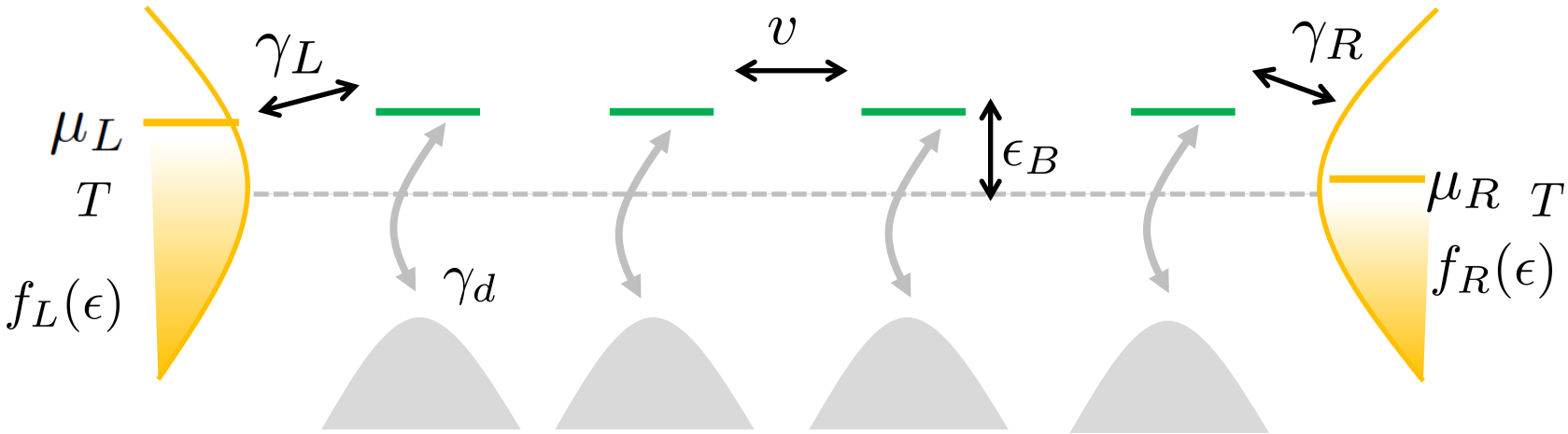
Molecular junction with Buttiker's probes

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

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



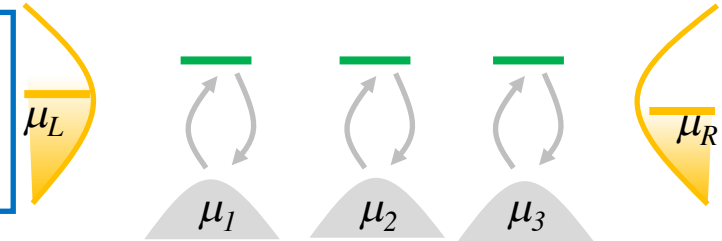
S. H. Choi et al JACS 132, 4358 (2010)



Probe condition: $I_n = 0; \quad n = 1-4$

Voltage probe: Incoherent **inelastic** scattering

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



Linear Response

Probe condition: $I_n = 0$

Linear equation for μ_n, probe chemical potentials $\mathbf{M}\mu = \mathbf{v}$

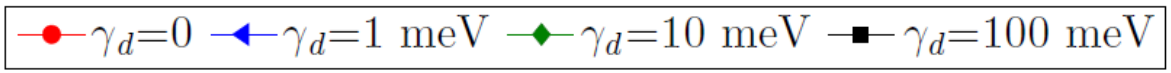
$$\mu_n \sum_\alpha \int_{-\infty}^{\infty} \left(-\frac{\partial f_{eq}}{\partial \epsilon}\right) \mathcal{T}_{n,\alpha}(\epsilon) d\epsilon - \sum_{n'} \mu_{n'} \int_{-\infty}^{\infty} \left(-\frac{\partial f_{eq}}{\partial \epsilon}\right) \mathcal{T}_{n,n'}(\epsilon) d\epsilon$$

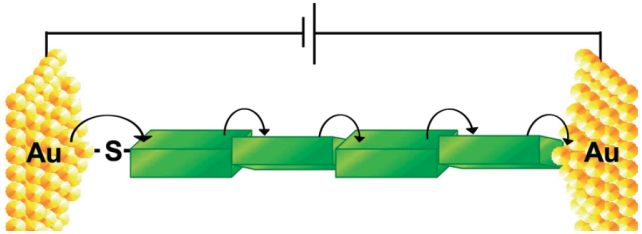
$$= \int_{-\infty}^{\infty} d\epsilon \left(-\frac{\partial f_{eq}}{\partial \epsilon}\right) \left[\mathcal{T}_{n,L}(\epsilon)\mu_L + \mathcal{T}_{n,R}(\epsilon)\mu_R\right].$$

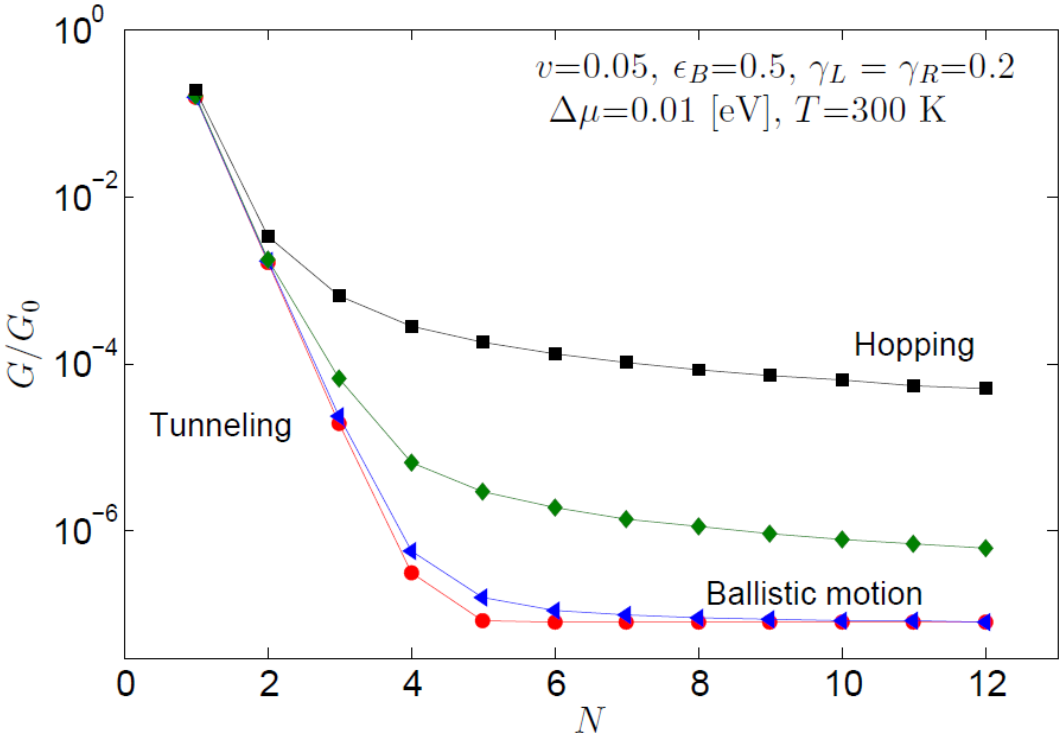
$$I_L = \frac{e}{2\pi\hbar}\sum_\alpha \int_{-\infty}^{\infty} \mathcal{T}_{L,\alpha}(\epsilon)\left[f_L(\epsilon) - f_\alpha(\epsilon)\right] d\epsilon$$

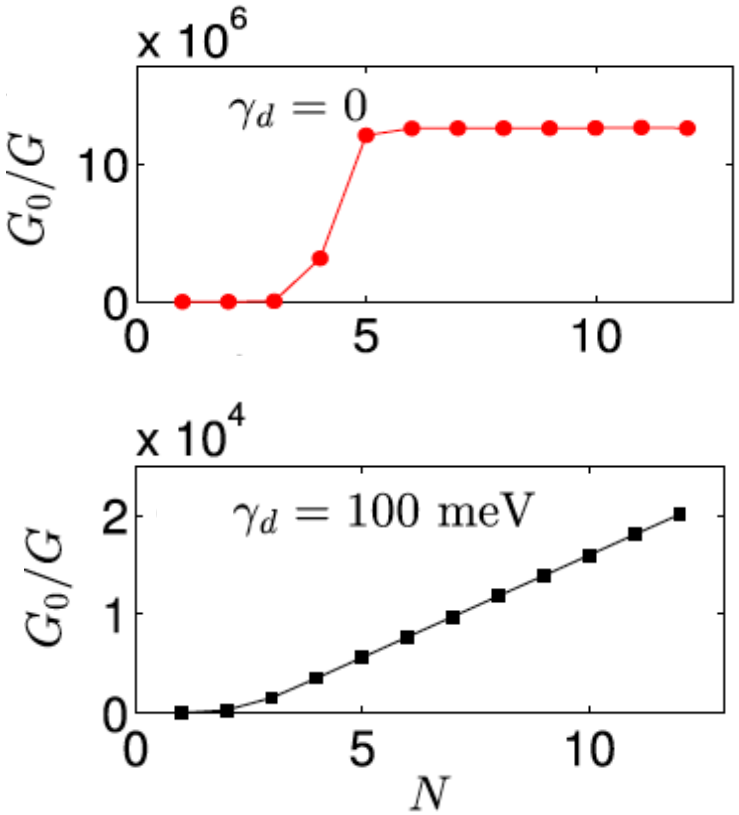
Low temperature → Pastawski formula $\mathcal{T}_{eff} = \mathcal{T}_{L,R} + \sum_{i,j} \mathcal{T}_{R,i} W^{-1}_{i,j} \mathcal{T}_{j,L}$

Length dependence





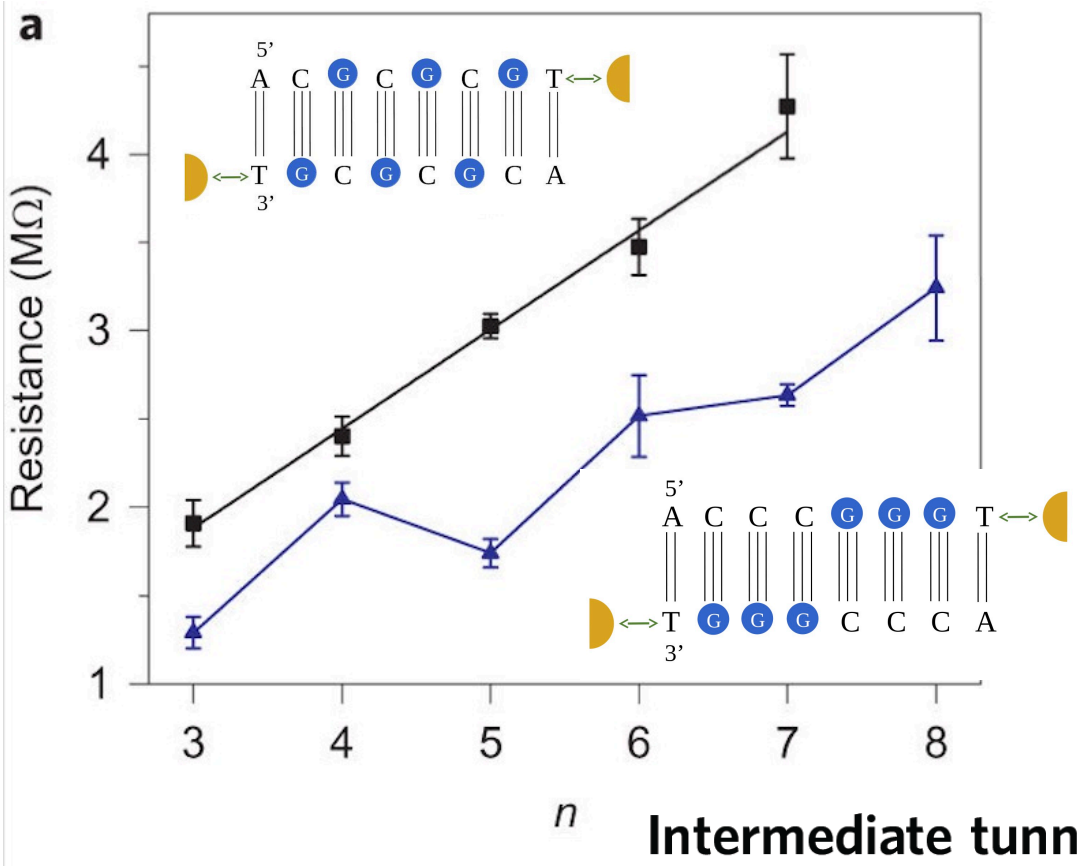


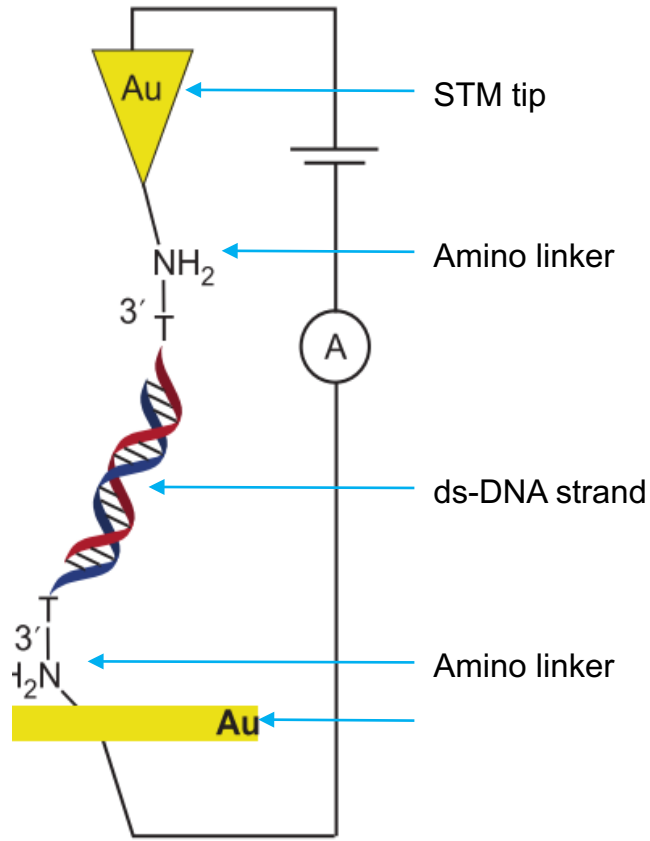


….. Finite voltage, diode operation, structured environment, thermoelectric properties,...

M. Kilgour, DS, JCP 143, 024111 (2015), JCP **144**, 124107 (2016), JPC C **119**, 25291 (2016),
R. Korol, M. Kilgour, DS, JCP **145**, 224702 (2016), H. Kim, DS, JCP **147**, 054 104 (2017).

Charge transport in DNA





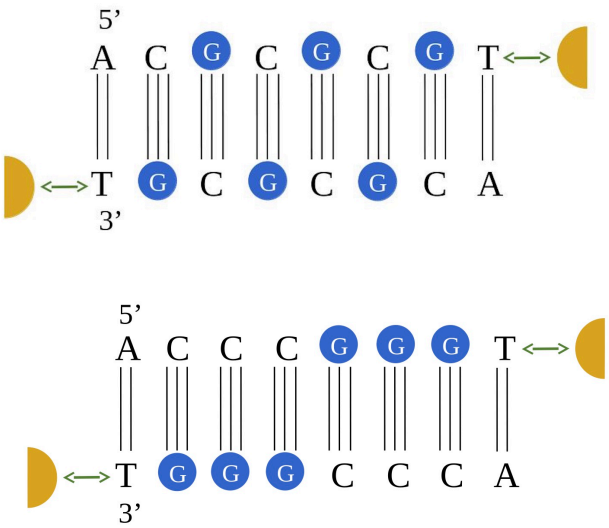
Intermediate tunnelling–hopping regime in DNA charge transport

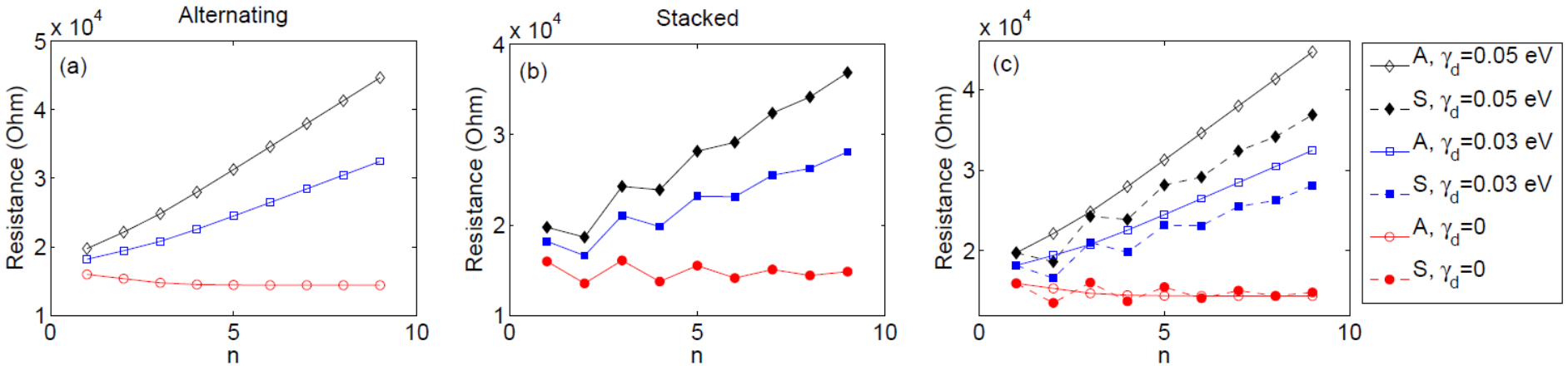
Limin Xiang[1,2], Julio L. Palma[1,2], Christopher Bruot[1], Vladimiro Mujica[2], Mark A. Ratner[3] and Nongjian Tao[1,4]*

Nature Chemistry 7 221 (2015)

Charge transport in DNA

- Intermediate coherent-incoherent behavior
  (H. Kim, M. Kilgour and DS, JPCC 119, 25291 **2016**)
- Thermopower
  (R. Korol, M. Kilgour and DS, JCP 145, 224702 **2016**)
- Exhaustive simulations
  (R. Korol and DS, JPCC 122, 4206 **2018**
  R. Korol, M. Kilgour, DS, Comp. Phys. Comm. 224, 396 **2018**)



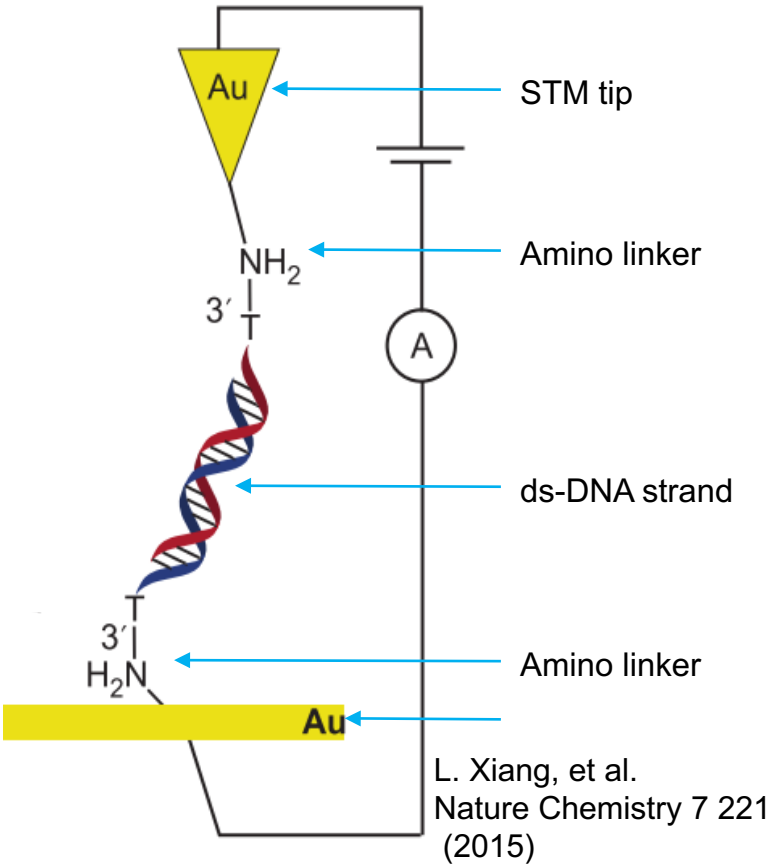


H. Kim, M. Kilgour, DS. JPC C **119**, 25291 (2016)

Electrical conduction of DNA

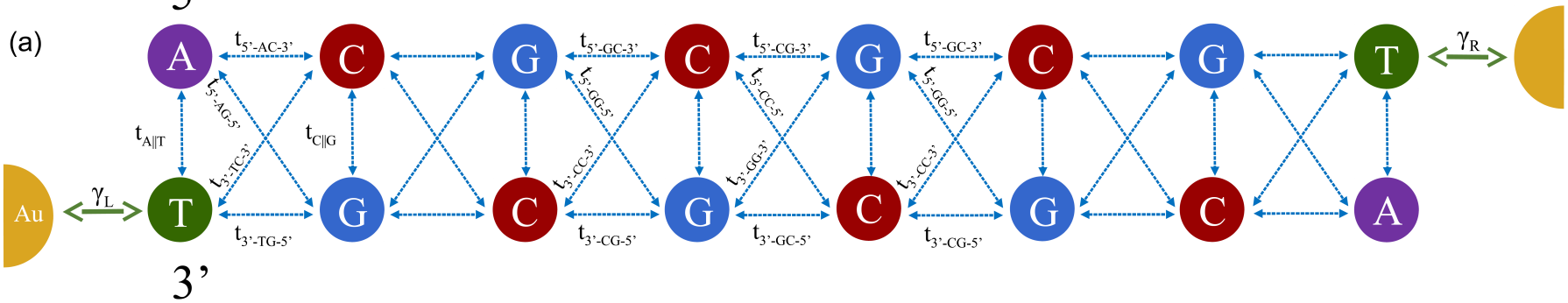
ϵ_G	ϵ_A	ϵ_C	ϵ_T	$t_{G\|\|C}$	$t_{A\|\|T}$
8.178	8.631	9.722	9.464	-0.055	-0.047

K. Senthilkumar, F. C. Grozema, C. F. Guerra, F. M. Bickelhaupt, F. D. Lewis, Y. A. Berlin, M. A. Ratner, and L. D. A. Siebbeles, J. Am. Chem. Soc. 127, 14894 (2005).



L. Xiang, et al. Nature Chemistry 7 221 (2015)

Alternating Sequence: 5'-A(CG)$_3$T-3'



Tight binding model:

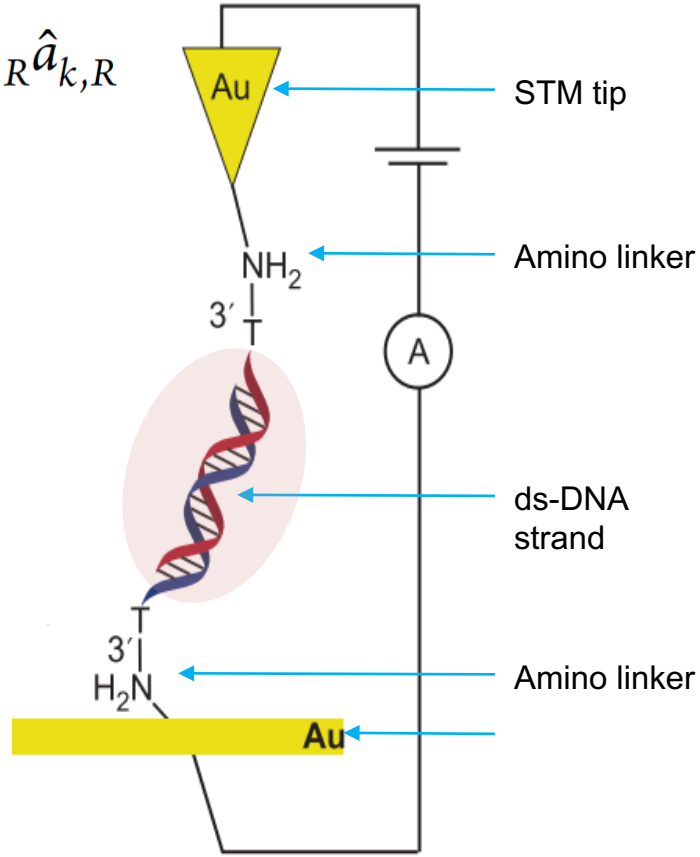
$$\hat{H}_L = \sum_k \epsilon_{k,L} \hat{a}^\dagger_{k,L} \hat{a}_{k,L}, \qquad \hat{H}_R = \sum_k \epsilon_{k,R} \hat{a}^\dagger_{k,R} \hat{a}_{k,R}$$

$$\hat{H}_M = \sum_{j=1}^{n} \Big[\sum_{s=1,2} \epsilon_{j,s} \hat{c}^\dagger_{j,s} \hat{c}_{j,s} + \sum_{s \neq s'=1,2} t_{j,ss'} \hat{c}^\dagger_{j,s} \hat{c}_{j,s'}$$

$$+ \sum_{s,s'=1,2} t_{j,j+1,ss'} (\hat{c}^\dagger_{j,s} \hat{c}_{j+1,s'} + \text{h.c.}) \Big]$$

$$\hat{V}_L = \sum_k g_{k,L} \hat{a}^\dagger_{k,L} \hat{c}_{j=1,s=1} + \text{h.c.}$$

$$\hat{V}_R = \sum_k g_{k,R} \hat{a}^\dagger_{k,R} \hat{c}_{j=n,s=2} + \text{h.c.}$$



+ Buttiker's probes on every site to account for environmental effects

Simplifications, approximations

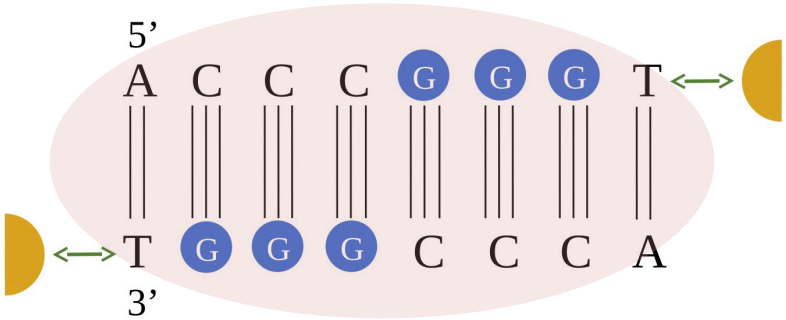
o Electronic Hamiltonian: Each base is represented by a single site, fixed parameterization.

o Environment: Nuclear dynamics is not explicitly included, only the resulting effects.
We encapsulate scattering effects of conducting charge carriers from different sources (low- and high-frequency phonon modes, static and dynamical fluctuations) into a single, constant parameter that dictates decoherence and energy relaxation.

o Contact: Realistic molecule-electrode contact is missing.

o Fermi energy: Set at the energy of the G base

o Fluctuations: missing→ use probes



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Article
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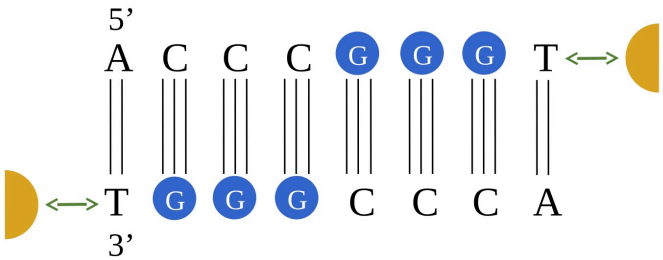
From Exhaustive Simulations to Key Principles in DNA Nanoelectronics

Roman Korol and Dvira Segal*



DNA as an electronic material

- mechanisms (tunneling, hopping, ballistic transmission, 'flickering resonance',…)
- identify and predict poor/good conductors
- general rules: content, structure, coupling strength, flexibility/rigidity, temperature, contact

How many?!

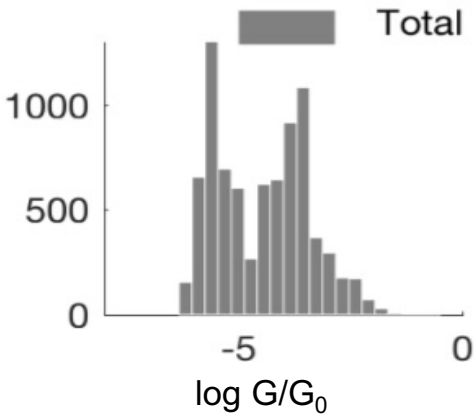
Odd n: $4^n/2$

Even n: $(4^n-4^{n/2})/2+4^{n/2}$

For n=3,4,..8,

distinct sequences:

32, 136, 512, 2080, 8192, 32896



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From Exhaustive Simulations to Key Principles in DNA Nanoelectronics

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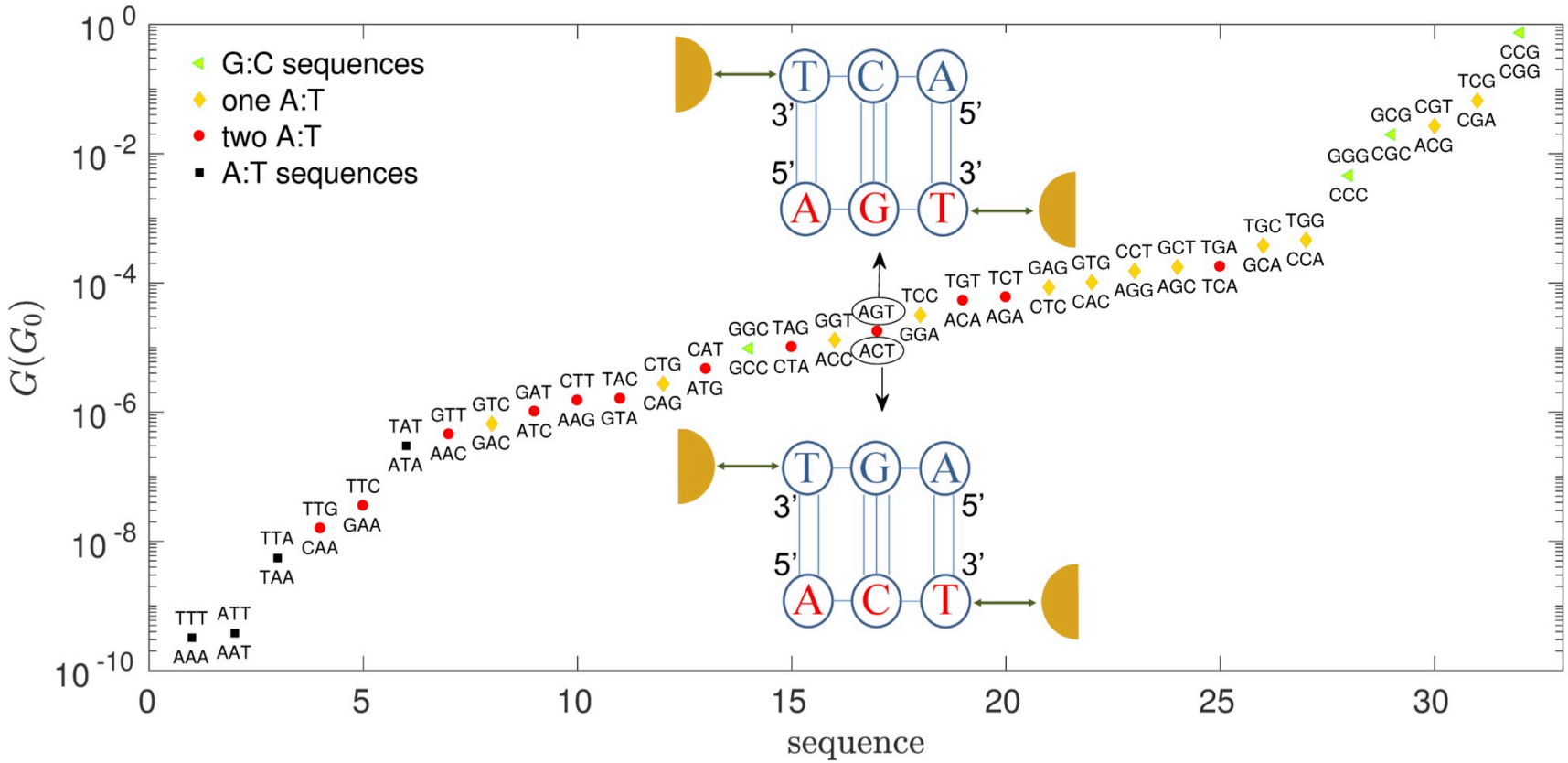
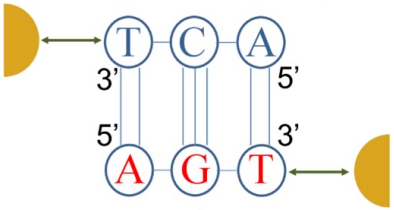
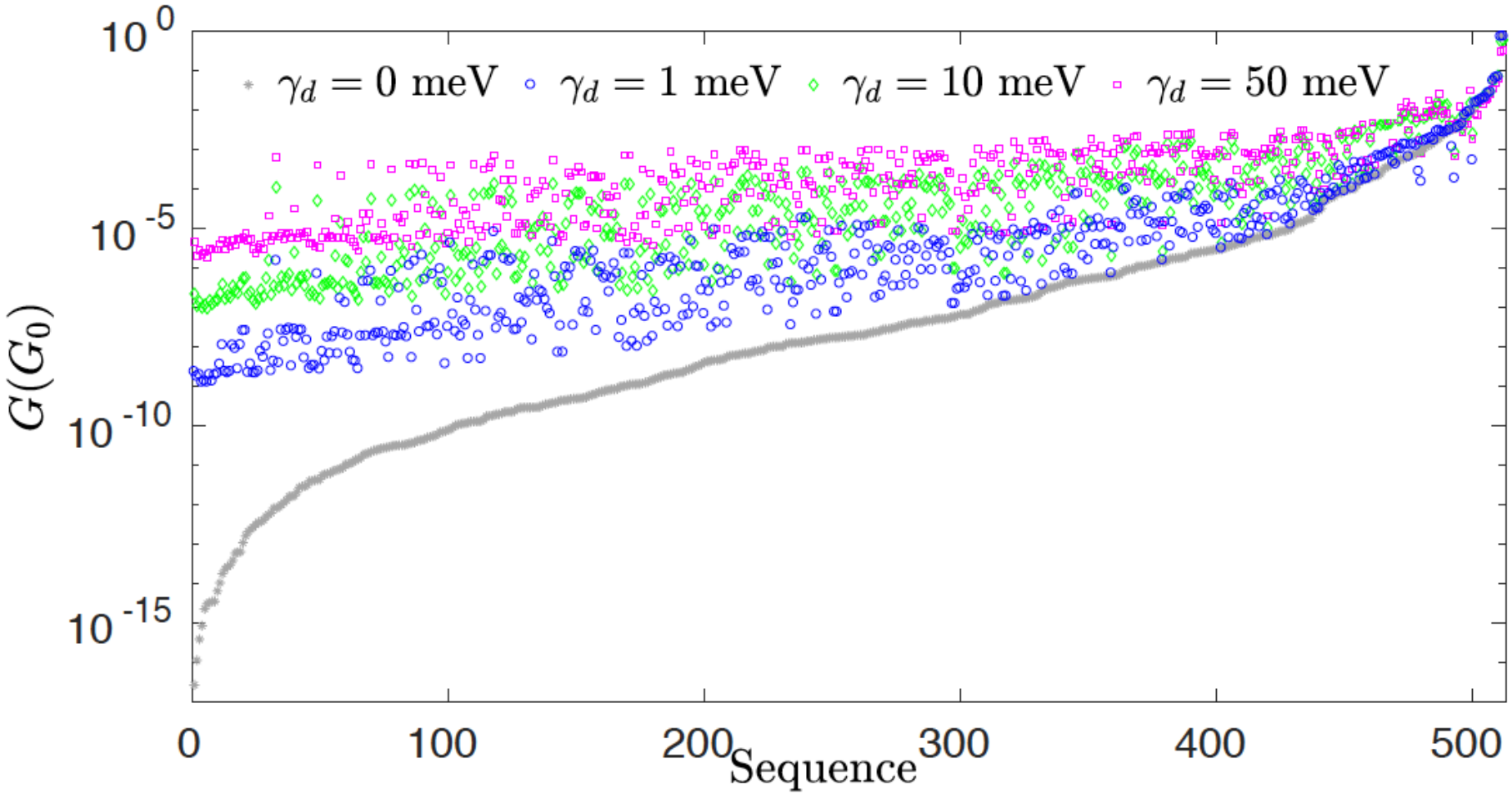


poor, $G < 10^{-11}\ G_0$	weak-moderate, $10^{-8} < G < 10^{-3}\ G_0$	good-excellent, $G > 10^{-2}\ G_0$
ATTTAAA (10^{-21})	ATGGGCA (5×10^{-7})	CCCCGGA (0.010)
AAAAAAA (10^{-20})	CGCATGC (10^{-6})	CACCCGG(0.015)
AATGAAA (10^{-18})	ACGATGG(10^{-6})	CCCCGAG (0.060)
CCTAAAA (10^{-16})	CTCGCGA (10^{-5})	CGGGGGA (0.064)
CAACAAT (10^{-15})	ACGCGGC (10^{-5})	CCGGGGG (0.70)
AAGAATA (10^{-14})	CTCCGTG (10^{-4})	CGGGGGG (0.75)

[a]Conductance is reported for a frozen molecule, $\gamma_d = 0$ at $T_{el} = 5$ K.

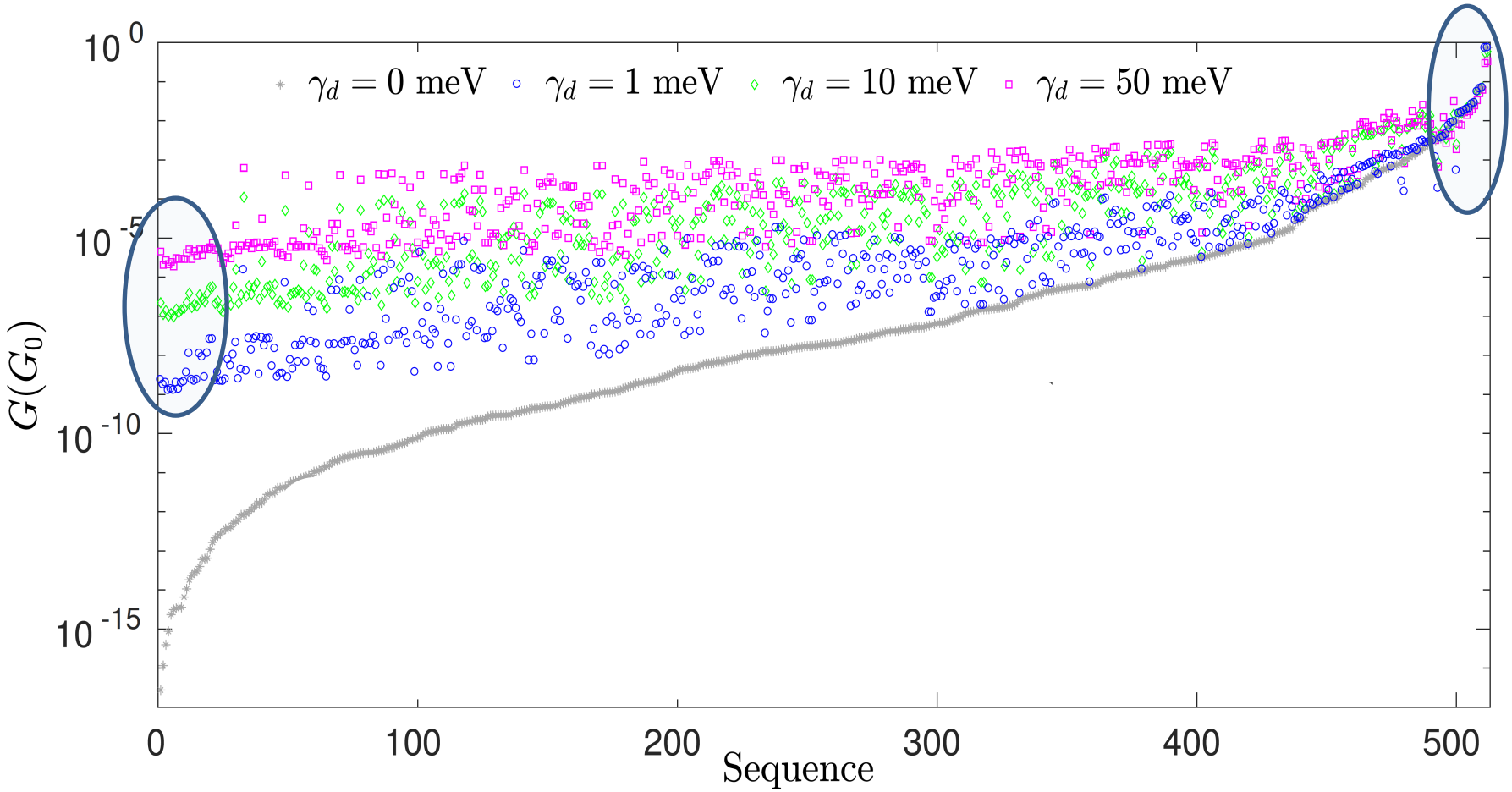


Transport mechanisms?



1 meV → 4 ps

Transport mechanisms?

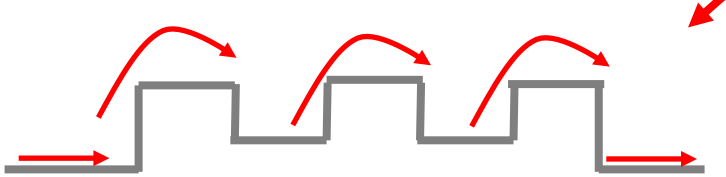


Good conductor: molecular wires
Poor conductors: Tunneling to hopping
Intermediate conductors: ???

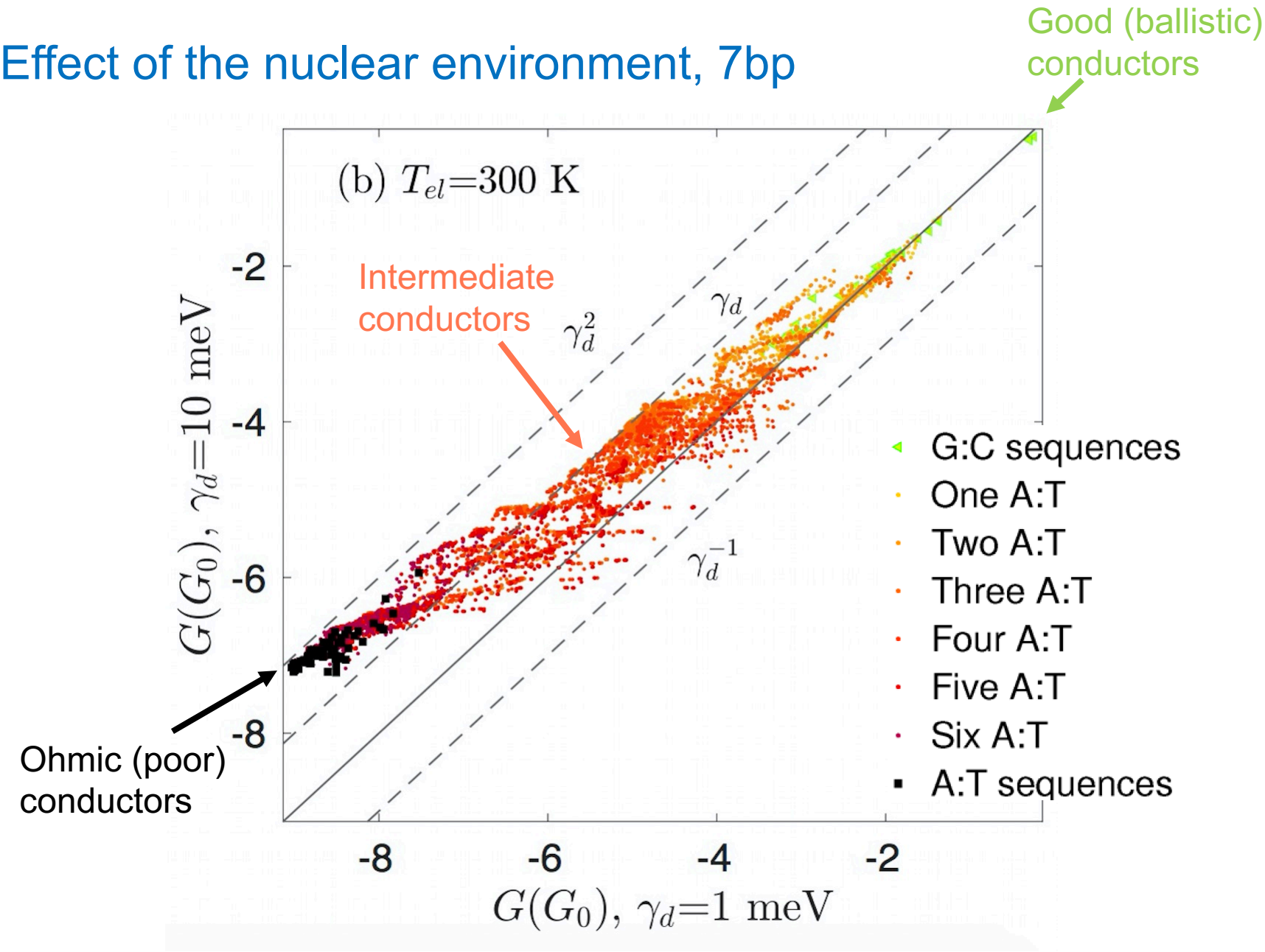
Composition-structure

Table 3. Role of the Structure (Clustering) on DNA Conductance, T_{el} = 300 K and $\gamma_{L,R}$ = 50 meV

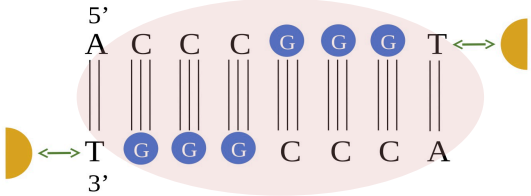
sequence 5′ to 3′	no. of A:T bp	log G/G_0			A:T block?
		γ_d = 0 meV	γ_d = 10 meV	γ_d = 30 meV	
AATGCGC	3	−8.0	−6.0	−5.3	yes
ACAGTCG	3	−8.0	−4.1	−3.7	no
AAATCGG	4	−8.0	−6.5	−5.7	yes
ACAGTGT	4	−8.0	−3.8	−3.4	no
AAAAAGG	5	−11.6	−7.0	−6.1	yes
AACAGTA	5	−11.6	−4.3	−4.1	no



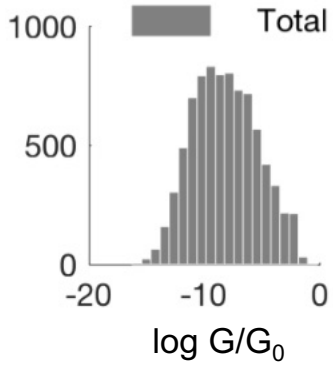
Effect of the nuclear environment, 7bp



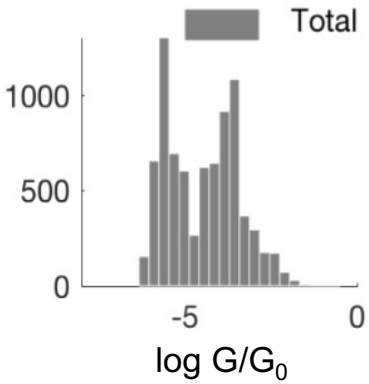
Composition-structure, 7bp

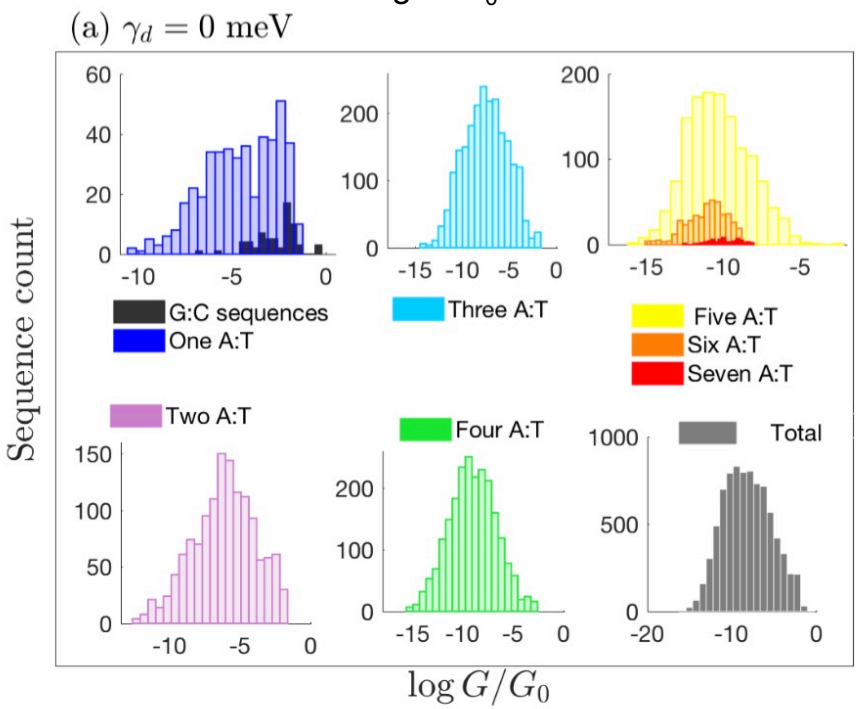


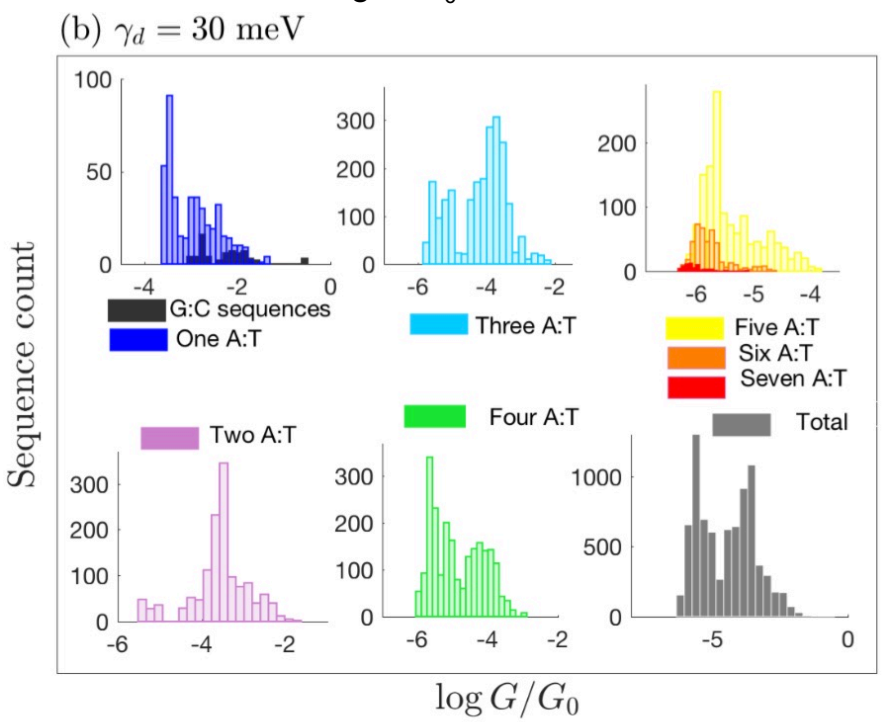
rigid structures



flexible structures

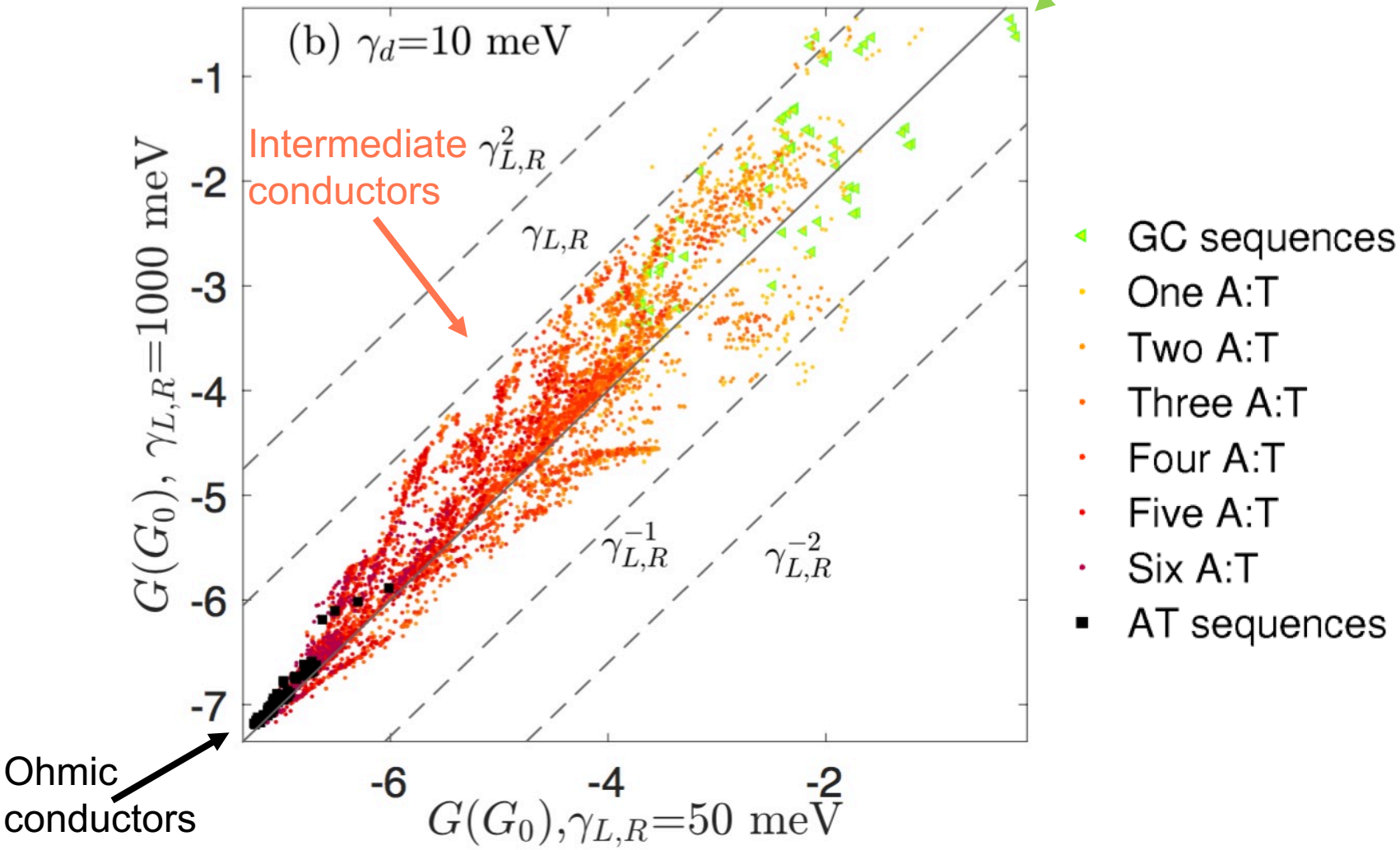






Metal contact

Good (ballistic) conductors



Ohmic conductors

R. Korol, DS, JPCC, 122 4206 (2018)

Dependence on the gateway states

Modelling charge transport in DNA

1. Frozen DNA: Tight binding Hamiltonian + Landauer formula – **rigid structures**

2. Many-body Physics: Tight binding Hamiltonian + selected modes; Green's function (Cuniberti) – **expensive, model system**

3. MD+QM/MM (Kubar, Elstner, Cuniberti)
   Molecular dynamics simulations to sample configurations, calculation of parameters on the fly, include the interaction with DNA backbone, counterions and water using a QM/MM scheme – **Very expensive**

4. Effective treatments: Solution of time dependent Schrodindger Equation: coarse grained Hamiltonain with fluctuations of parameters. (Beratan) – **Infinite temperature, violation of detailed balance**

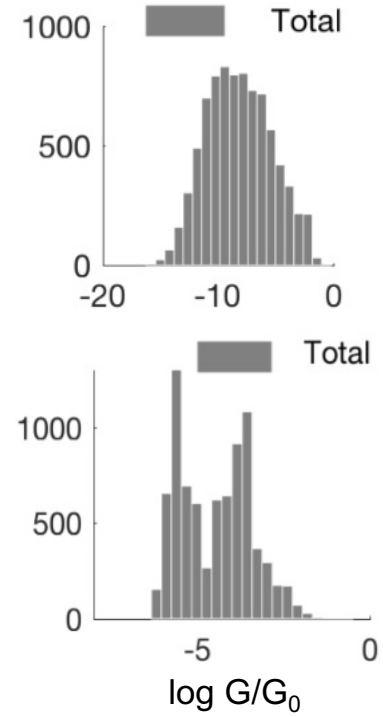
Table 1. Correlation Properties of Static Noise, White Noise, Temporal Noise, and Spatial-Temporal Noise[a]

	autocorrelation	spatial correlation
static	$\langle \delta\varepsilon_i(0)\ \delta\varepsilon_i(t)\ \rangle = \sigma_i^2$	$\langle \delta\varepsilon_i(0)\ \delta\varepsilon_j(t)\ \rangle = \text{Const.}$
white	$\langle \delta\varepsilon_i(0)\ \delta\varepsilon_i(t)\ \rangle = \delta(t)$	$\langle \delta\varepsilon_i(0)\ \delta\varepsilon_j(t)\ \rangle = 0$
temporal	$\langle \delta\varepsilon_i(0)\ \delta\varepsilon_i(t)\ \rangle = \sigma_i^2 e^{(-t/\tau)}$	$\langle \delta\varepsilon_i(0)\ \delta\varepsilon_j(t)\ \rangle = 0$
spatial-tempo	$\langle \delta\varepsilon_i(0)\ \delta\varepsilon_i(t)\ \rangle = \sigma_i^2 e^{(-t/\tau)}$	$\langle \delta\varepsilon_i(0)\ \delta\varepsilon_j(t)\ \rangle = \alpha_{ij}\sigma_i\sigma_j e^{(-t/\tau)}$ $\alpha_{ij} = \exp(-\lvert i-j\rvert/d)$

	mean (eV)	standard deviation (eV)	correlation lifetime (fs)
site energy	see Figure 7	0.15	200
V(Sa-A)	0.005	0.06	2000
V(A-A)	0.046	0.05	2000
V(A-Sd)	0.02	0.07	2000

C. Liu, D. Beratan, P. Zhang, JPCB 120 3624 (2016)

What did we learn about DNA?...



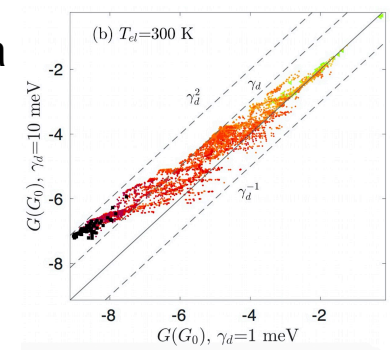
I) Mostly, DNA is a poor electronic conductor

II) The conductance of a **rigid** molecule **cannot** serve as a proxy for the conductance of a **flexible** molecule. Sequences that comparably conduct when frozen differ by up to 2 orders of magnitude when the environment is allowed to influence.

III) Both **composition** (content) and the **structure** (order) are important. DNA with an island of A:T bps shows a lower conductance compared to the case with dispersed A:T units.

IV) Gateway states largely affect the conductance of a rigid structure.

V) The majority of DNA molecules with 3-10 base pairs conduct via a **mixed** quantum classical (coherent-incoherent) mechanism. Only few special sequences were classified as tunneling barriers, ohmic conductors or ballistic molecular wires.

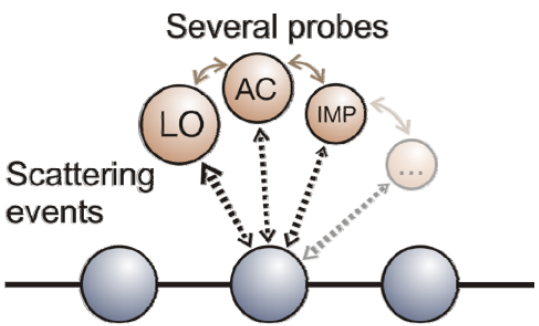


Outlook

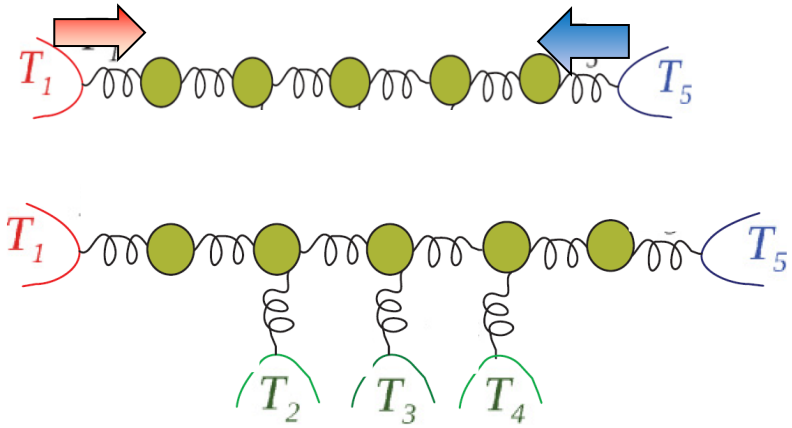
microscopic mechanisms + analytical results + extensive simulations

Future directions:

1. simulation of large scale systems: monolayers, devices
2. capture the nature of the scatterer
3. carefully compare to other methods
4. fluctuations, disorder
5. Vibrational heat transfer – capture phonon-phonon scattering



P. Greck et al IEEE 2010



Method: M. Kilgour, DS, JCP **143**, 024111 (2015)
JCP **144**, 124107 (2016), JPC C **119**, 25291 (2016).

DNA: R. Korol, M. Kilgour, DS, JCP **145**, 224702 (2016)
H. Kim, M. Kilgour, DS, JPCC **120**, 23591 (2016)
R. Korol, DS JPCC **122,** 4296 (2018).

Open-source code:
R. Korol, M. Kilgour, DS, Comp. Phys. Comm. **224**, 396 (2018).

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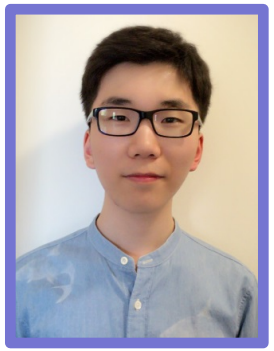

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- Salil Bedkihal (Exeter)
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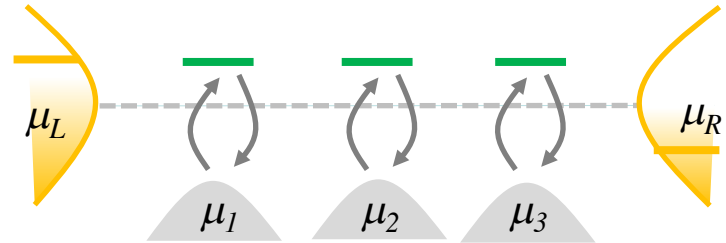
Voltage probe: Incoherent **inelastic** scattering

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



Far-from-equilibrium

Probe condition $I_n = 0$

Nonlinear equation for μ_n, probe chemical potentials!

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

Use Newton Raphson method to get the roots

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

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