A **small polaron hopping** *model for the multi-phonon-assisted transport along DNA molecules, in the presence of disorder*

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outline

- Experiments (3 slides)
- System Characteristics (3 slides)
- Model (… slides)

λ phage DNA

$\sigma = \sigma(T)$ at high / low T

Interpretation

Low-T:
ionic conduction
(counterions)
but
cannot account for high-T

High-T:
carrier excitations
across single-particle gaps
or
T-driven hopping
Alternatively
phonon-assisted
polaron hopping

Experiment 1
Tran et al, Phys. Rev. Lett. 85 (2000) 1564

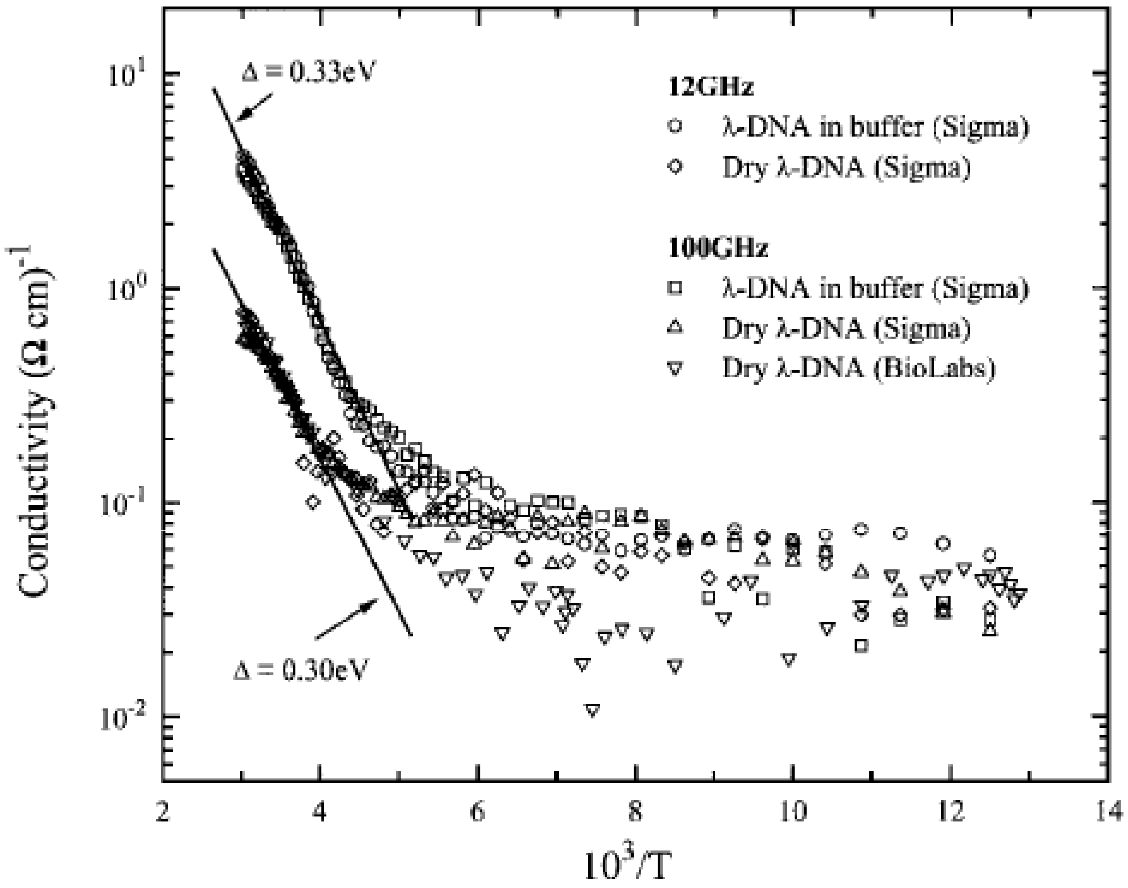


FIG. 2. Conductivity of dry λ-DNA and λ-DNA in buffer versus inverse temperature as measured at 12 and at 100 GHz. The magnitude of the conductivity was determined at 12 GHz, and the 100 GHz data were normalized to the 12 GHz results at room temperature. The full lines are Eq. (2) with Δ values as given in the figure and σ_0 values as given in the text.

poly(dA)-poly(dT),
poly(dG)-poly(dC)

I-V(T) i.e. G = G(T)
at high / low *T*

Interpretation

a *small* polaron hopping model

poly(dA)–poly(dT):
hopping distance
~ 16.8 Å (5 *base pairs*)

poly(dG)–poly(dC):
hopping distance
~ 25 Å (7 *base pairs*!)

Interpret Tran *et al*?
not quite convincing

other possible mechanisms?

$I \sim b\, V$
fitting parameter *b*
(with unclear *T*-dependence)

Experiment 2
Yoo et al, Phys. Rev. Lett. 87 (2001) 198102

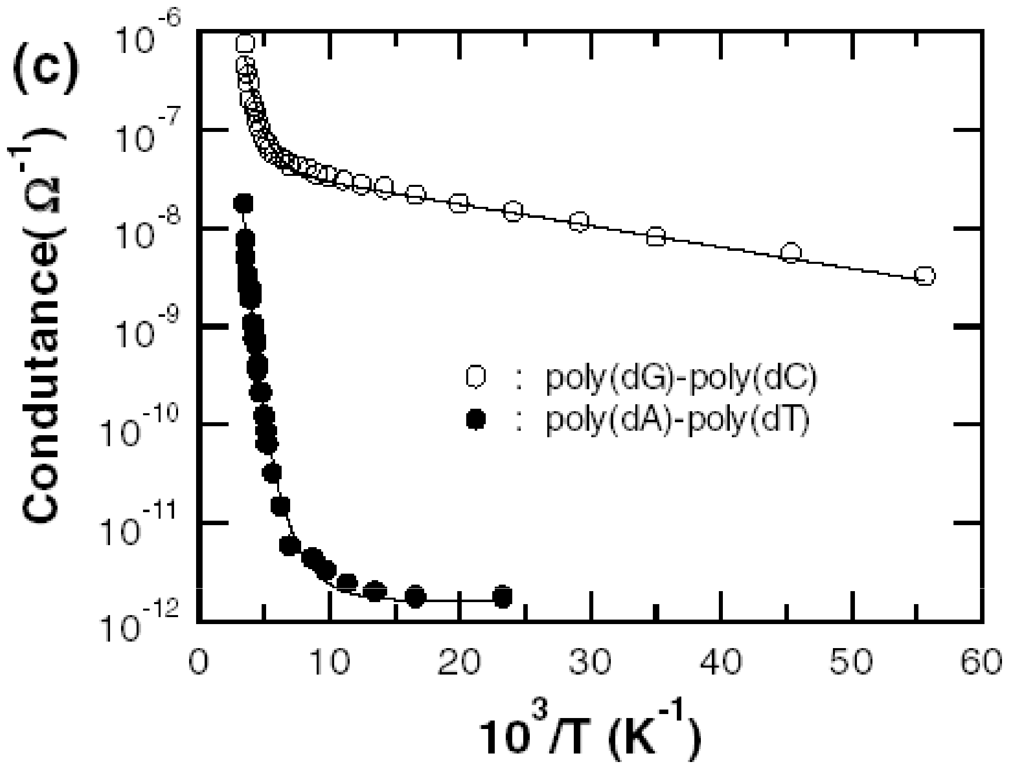


FIG. 2. (a) The *I*-*V* curves measured at various temperatures on poly(dA)-poly(dT) trapped between two metal electrodes. In the inset, the *I*-*V* curves are plotted in the logarithm scales. (b) *I* versus $\sinh(0.68V)\exp(-E_a/k_BT)$ at various temperatures, where E_a is assumed to be 0.18 eV, as determined from (c). (c) Conductance versus inverse temperature for poly(dA)-poly(dT) (●) and poly(dG)-poly(dC) (○), where the conductance at $V = 0$ was numerically calculated from the *I*-*V* curve. The solid curves are the calculated ones using $\sigma = \sigma_o \exp(-E_a/k_BT)$ with $E_a(T)$ given by Eq. (2). See the text for details.

native wet-spun
calf thymus Li-DNA

$\sigma = \sigma(T)$ at high T

Interpretation:

activated Arrhenius law + constant

$$\sigma = \sigma_0 \exp[-U / k_B T] + B$$

or

variable range hopping + constant

$$\sigma = \sigma_0 \exp[-(T_0 / T)^{1/2}] + B$$

Experiment 3
Kutnjak et al, Phys. Rev. Lett. 90 (2003) 098101

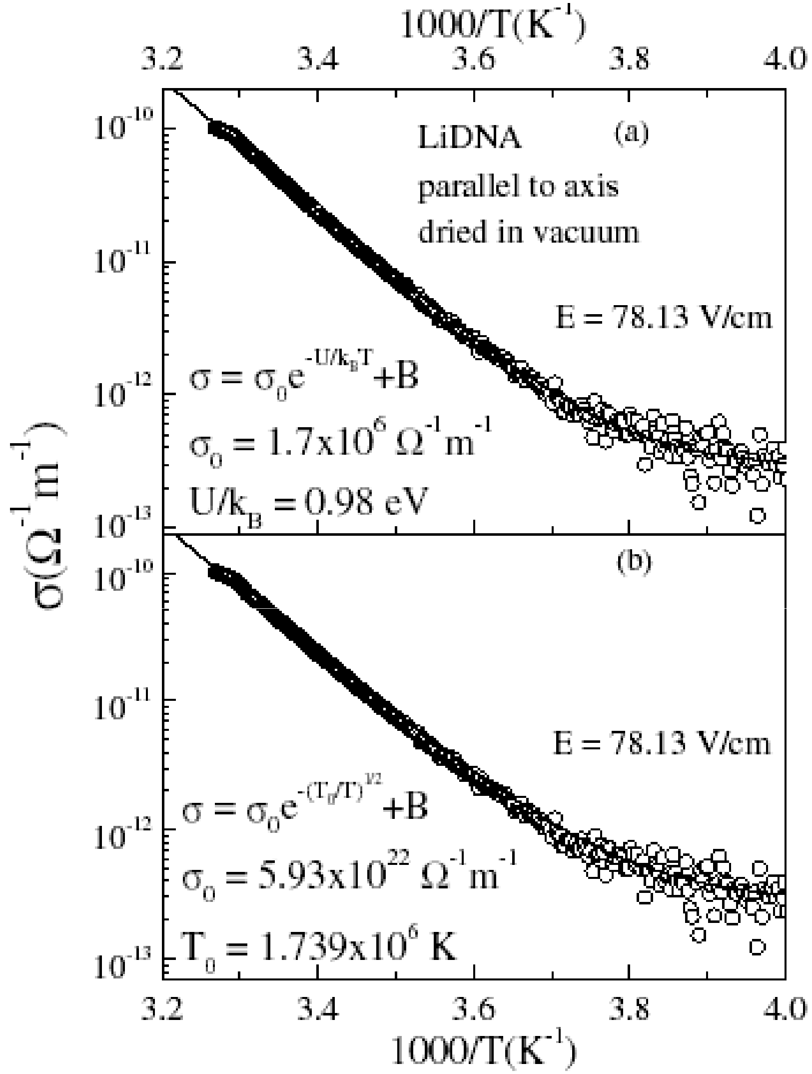
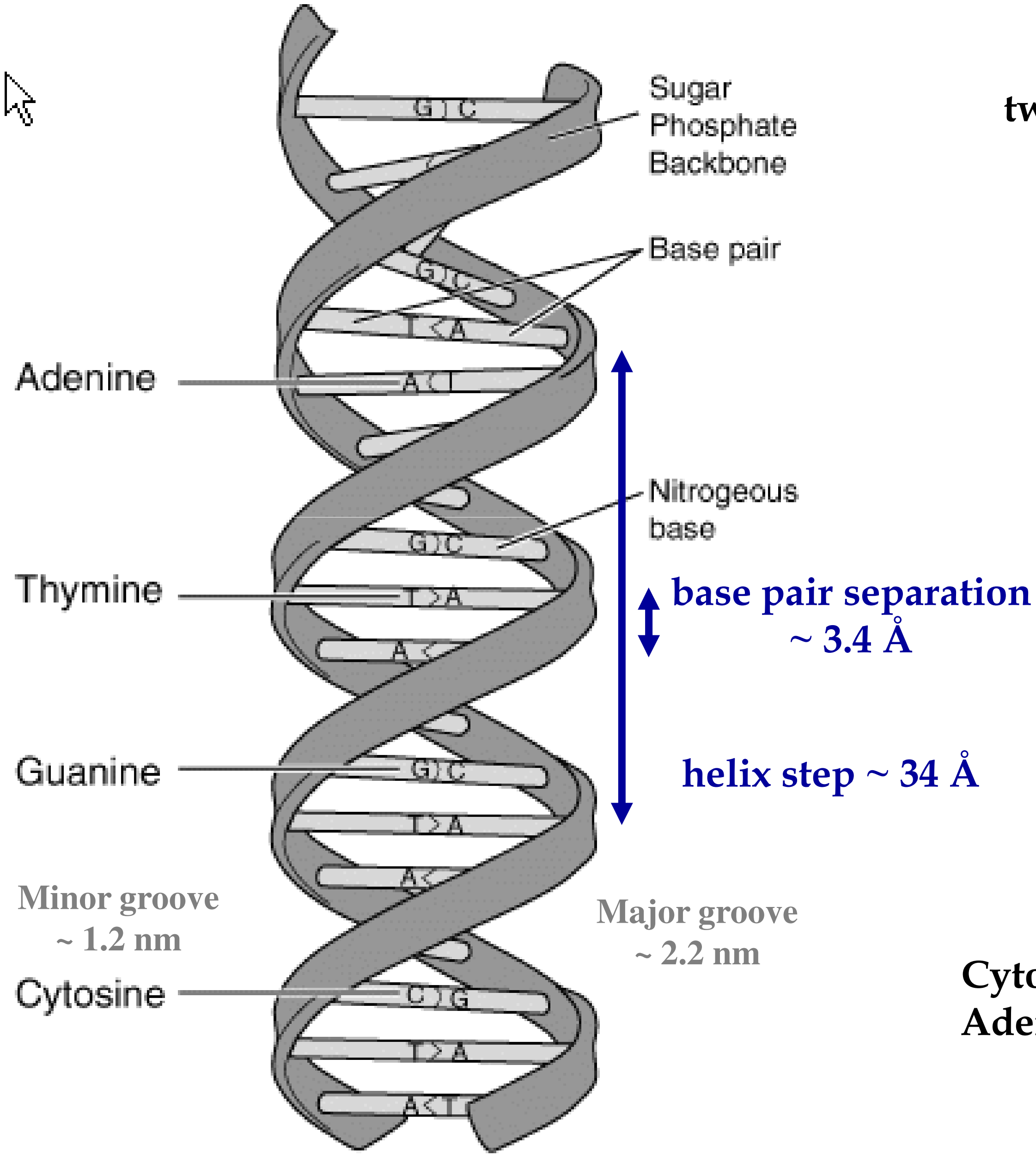


FIG. 3. Temperature dependence of the electric conductivity measured on dried Li-DNA. Shown are fits to an Arrhenius ansatz (a) and to the ansatz describing the variable range hopping (b). Here the electric field was applied parallel to the sample orientational axis.

… we have to take into account the system characteristics …

(1) deoxyribose nucleic acid



DNA double helix

two helices =
two polynucleotide strands

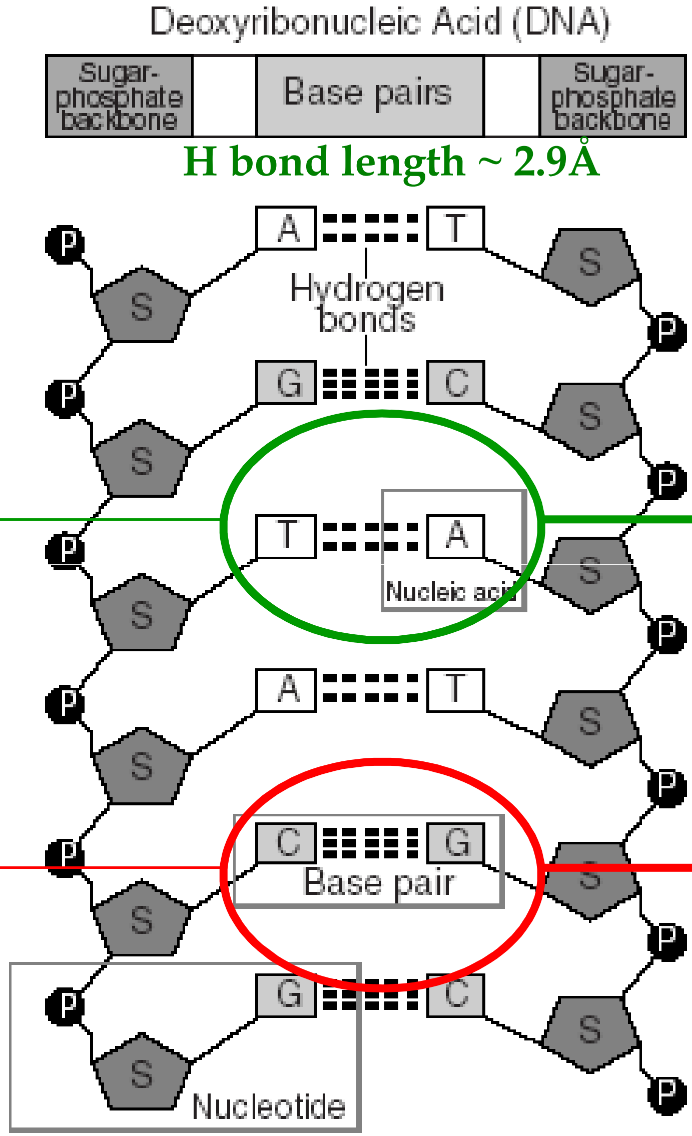
nucleotide =
phosphate +
sugar +
base (A, T, C, G)

→ 4 nucleotides

4 bases
Adenine (A)
Thymine (T)
Cytosine (C)
Guanine (G)

base pairs:
Cytosine <3 H bonds> Guanine
Adenine <2 H bonds> Thymine

(2) deoxyribose nucleic acid



Vibrating (phonons) ← → site j

Vibrating (phonons) ← → site i

"random"(non-periodic) base sequence

(disorder one)

base pair separation (i,i+1) ~ 3.4 Å

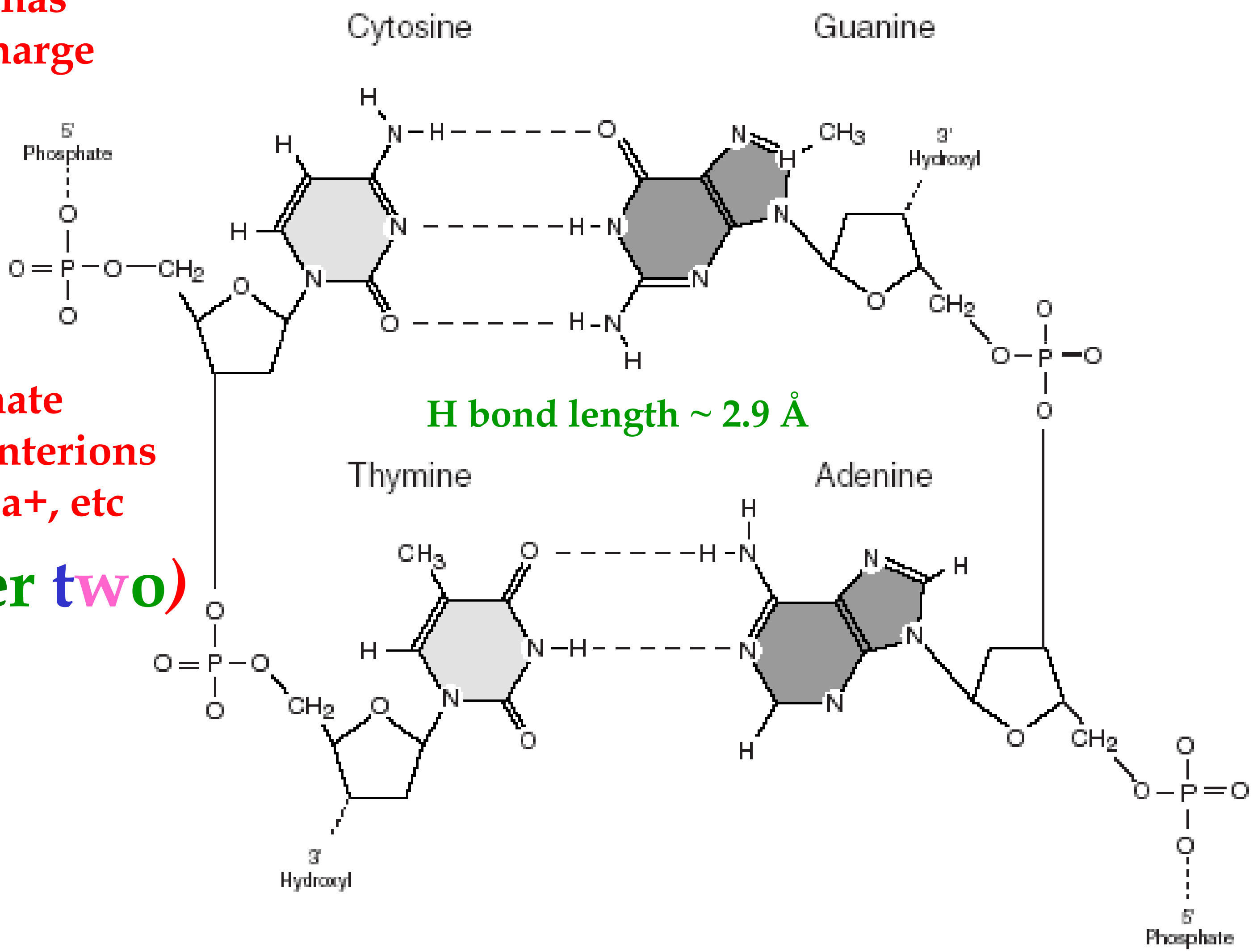
(helix step ~ 34 Å)

(3) deoxyribose nucleic acid

diameter ~ 20 Å

base end to end separation ~ 10.7 Å

Phosphate has
a negative charge



H bond length ~ 2.9 Å

Phosphate
attracts counterions
e.g. K+, Na+, etc

(disorder two)

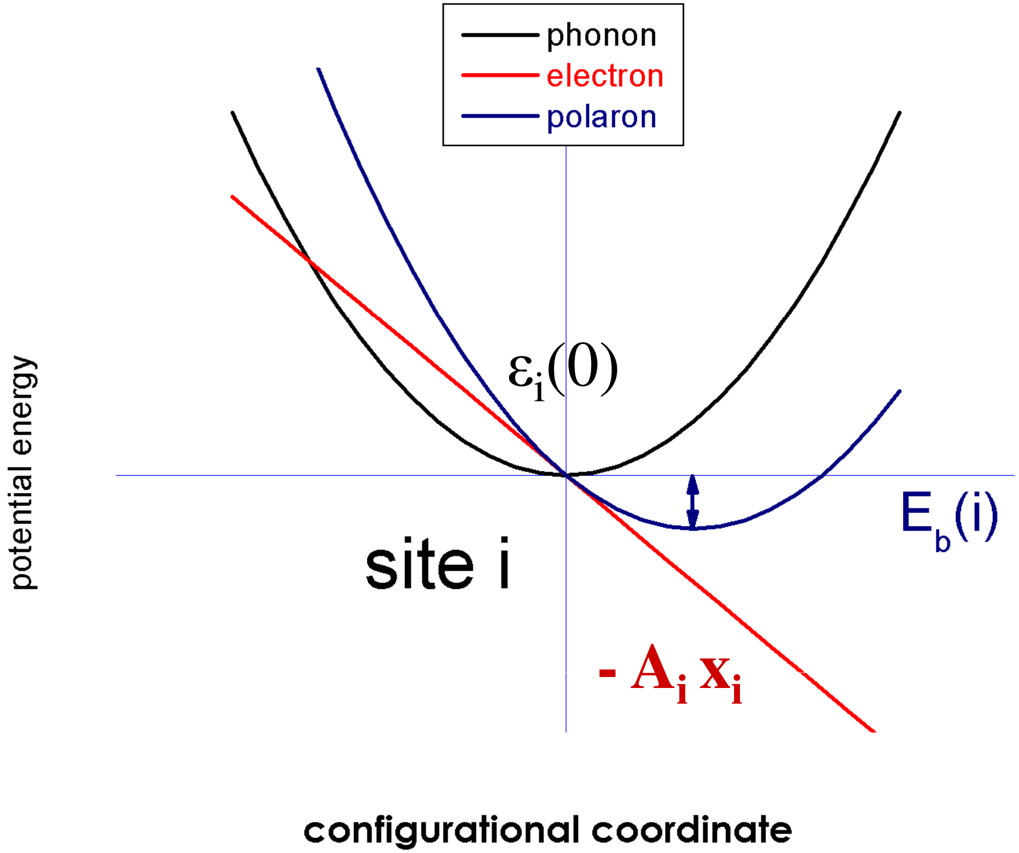
Polaron

1. Phonon (parabolic … + nearest neighbors)

2. Electron (linear interaction)

1, 2 comparable magnitude

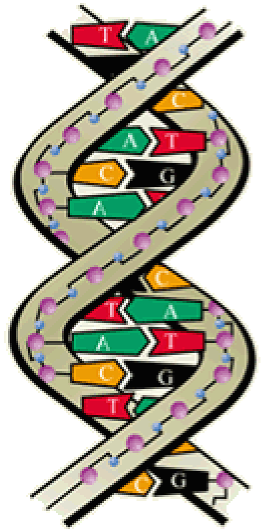
3. Polaron formation (Eb(i))



MCM (Molecular Crystal Model) 1D ordered all i equivalent
T. Holstein, Ann. Phys. NY **8** (1959) 343

GMCM (Generalized Molecular Crystal Model) 3D disordered
G. P. Triberis and L. R. Friedman, J. Phys. C: Solid State Phys. **14** (1981) 4631 high-*T*
G. P. Triberis, J. Non-Cryst. Solids **74** (1985) 1 low-*T*

What is the character of our system? What must the model take into account?



(1) **Molecular wire (quasi one dimensional character).**
Each base pair can be considered as a molecular site.

(2) **It is plausible that the carriers are**
small (wavefunction extent)
polarons (phonon + electron).
Phonon (parabola + nearest neighbors).

(3) **Disorder (random base sequence, counterions)**

(4) **multi-phonon assisted polaron hopping**
few-phonon assisted hopping

→ analytical expressions for
$\sigma = \sigma\ (T)$
$r_{\mathrm{m}} = r_{\mathrm{m}}(T)$

i) GMCM
ii) Percolation

Successful high-T (all experiments above) — fitting $\sigma = \sigma(T)$, reasonable $r_m = r_m(T)$

UnSuccessful low-T (all experiments above) — **ionic conductivity?** **sth else?**

equilibrium transition probability $$W_{ij}^0 = [n_i^0(1-n_i^0)]^{1/2}[n_j^0(1-n_j^0)]^{1/2}(\gamma_{ij}\gamma_{ji})^{1/2}$$

equilibrium occupation probability (n_i^0)

intrinsic transition rate ($\gamma_{ij}\gamma_{ji}$)

The analytical expressions

high-T (multi-phonon-assisted) ← W_{ij}^{0h} depends on E_i and E_j

≠

low-T (few-phonon-assisted) ← $W_{ij}^{0\ell}$ depends on E_i or E_j

transport problem transformed to equivalent network of impedances

V. Ambegaokar, B. I. Halperin and J. S. Langer, Phys. Rev. B **4** (1971) 2612

$$Z_{ij} = [(q^2/k_B T)(W_{ij}^0)]^{-1}$$

⇓

percolation condition high-T

≠

percolation condition low-T

⟹

conductivity high-T

≠

conductivity low-T

Conductivity

high-T

$$\sigma^{\mathrm{h}} = \sigma_0^{\mathrm{h}} \exp[-(T_0^{\mathrm{h}})^{2/3} T^{-2/3}]$$

$$\ln \sigma^h = \ln \sigma_0^h - \left(\frac{T_0^h}{T}\right)^{2/3}$$

$$r_{\mathrm{m}}^{\mathrm{h}} = \alpha^{-1} (T_0^{\mathrm{h}})^{2/3} T^{-2/3} / 2$$

low-T

$$\sigma^{l} = \sigma_0^{l} \exp[-(T_0^{l})^{1/2} T^{-1/2}]$$

$$\ln \sigma^l = \ln \sigma_0^l - \left(\frac{T_0^l}{T}\right)^{1/2}$$

$$r_{\mathrm{m}}^{l} = \alpha^{-1} (T_0^{l})^{1/2} T^{-1/2} / 2$$

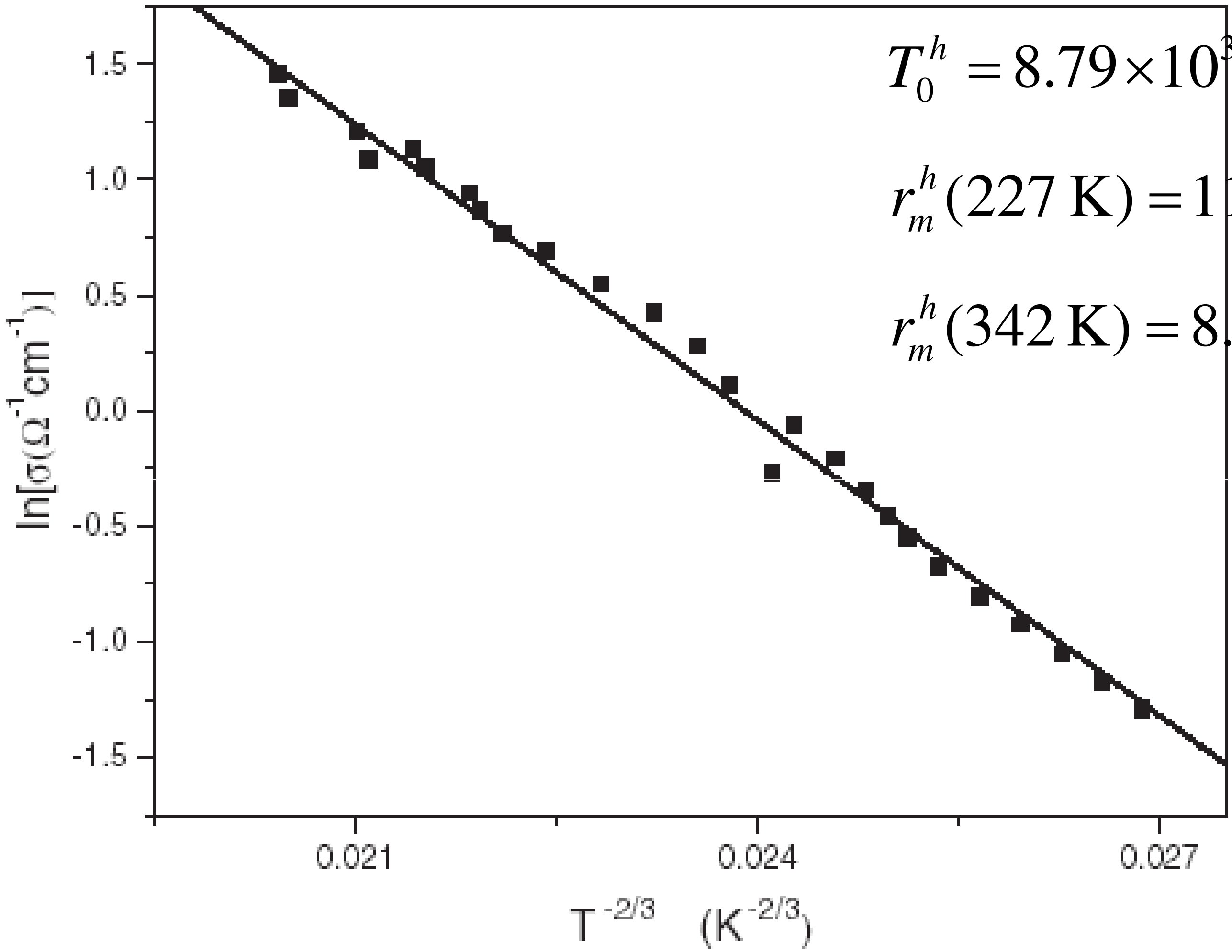
$$\sigma = \sigma_0 \exp(-2r_{\mathrm{m}}/\alpha^{-1})$$

$$T_0^{\mathrm{h}} = 27^{1/2} N_{\mathrm{s}}^{1/2} \alpha^{1/2} / N_0 k_{\mathrm{B}}$$

$$T_0^{l} = (4\alpha / N_0 k_{\mathrm{B}})$$

High-*T* Tran et al

G. P. Triberis, C. Simserides and V. C. Karavolas,
J. Phys.: Condens. Matter **17** (2005) 2681–2690



$$T_0^h = 8.79\times10^3 \text{ K}$$

$$r_m^h(227\text{ K}) = 11.4 \text{ Å} \ (\sim 3 \text{ base pairs})$$

$$r_m^h(342\text{ K}) = 8.7 \text{ Å} \ (\sim 2 \text{ base pairs})$$

Figure 1. ln σ versus $T^{-2/3}$ plot of the Tran *et al* [18] (12 GHz) (λ-DNA) data for the high temperature (227–342 K) region.

High-*T* Yoo et al

G. P. Triberis, C. Simserides and V. C. Karavolas,
J. Phys.: Condens. Matter **17** (2005) 2681–2690

$$T_0^h = 1.45 \times 10^4 \text{ K}$$

$$r_m^h(178 \text{ K}) = 18.8 \text{ Å} \ (\sim 5 \text{ base pairs})$$

$$r_m^h(306 \text{ K}) = 13 \text{ Å} \ (\sim 4 \text{ base pairs})$$

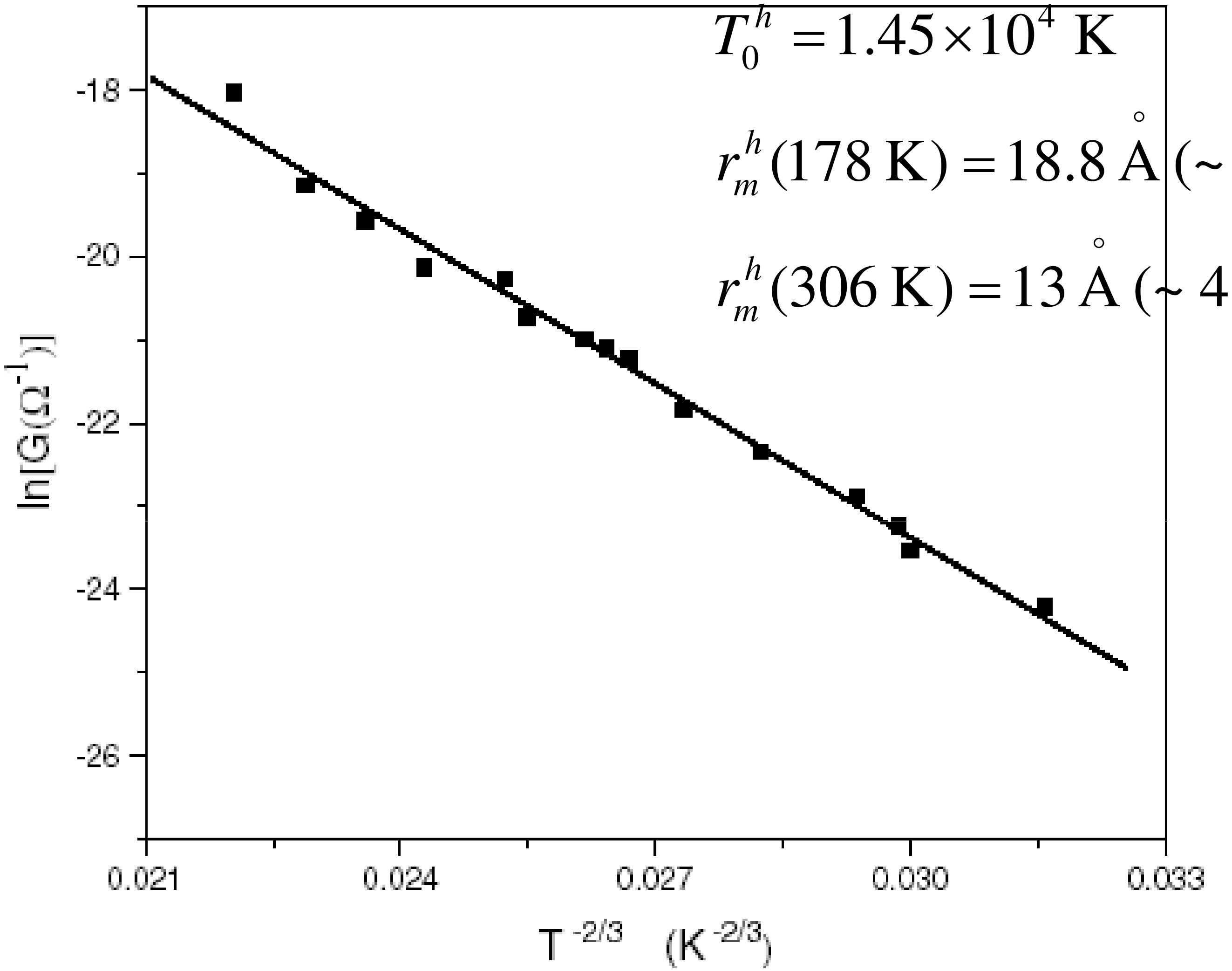


Figure 2. ln G versus $T^{-2/3}$ plot of the Yoo *et al* [24] poly(dA)–poly(dT) DNA data for the high temperature (178–306 K) region.

Percolation condition

high-T

$$\frac{R_{ij}}{r_m^h} + \frac{E_i}{E_m^h} + \frac{E_j}{E_m^h} \leqslant 1$$

r_m^h → max hopping distance

E_m^h → max site energy

r (spatial dimension) = 1
ε (number of energies) = 2

low-T

$$\frac{R_{ij}}{r_m^l} + \frac{E}{E_m^l} \leqslant 1$$

r_m^l → max hopping distance

E_m^l → max site energy

r (spatial dimension) = 1
ε (number of energies) = 1

Conductivity "Law" $$T^{-\frac{\varepsilon}{\varepsilon+r}}$$

ε = number of energies in the percolation condition
r = spatial dimensions

3D	high-T	$T^{-2/5}$	Triberis and Friedman
3D	low-T	$T^{-1/4}$	Mott
2D	low-T	$T^{-1/3}$	Pollak
1D	high-T	$T^{-2/3}$	here
1D	low-T	$T^{-1/2}$	here and in accordance with variable range hopping for localized states Pollak, Lee, Serota et al

Synopsis - Conclusion

Acknowledgments

Frank Angenstein
(Leibniz Institute for Neurobiology, Magdeburg, Germany)

Georgia Thodi
(DUTh, Molecular Biology and Genetics Department, Alexandroupolis, Greece)

End.

Thank you.

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Acrobat Document

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