

Intrinsic Superconductivity in graphene ?

Electron-phonon mechanisms
(Raman scattering)

Pure Coulomb mechanisms



Antonio H. Castro Neto



“Dynamics and Relaxation in Complex Quantum and Classical Systems and Nanostructures” – Max Planck Institute, Dresden, September 2006

Collaborators:

Francisco Guinea (ICMM, Spain)

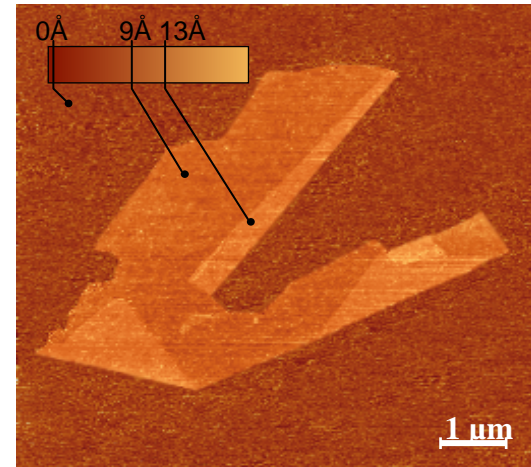
Johan Nilsson (BU, USA)

Vitor Pereira (Univ. Porto, Portugal)

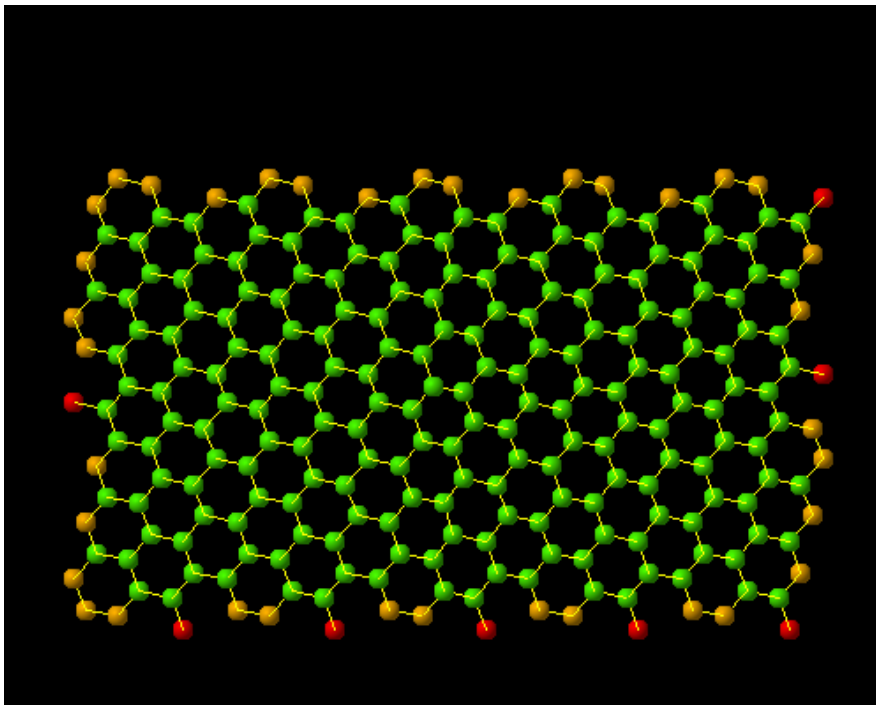
Nuno Peres (Univ. Minho, Portugal)

Bruno Uchoa (BU, USA)

Joao L. dos Santos (Univ. Porto, Portugal)



Novoselov et al, *Science* 306, 666 (2004)



cond-mat/0608543

cond-mat/0608515

cond-mat/0607343

Phys. Rev. B 73, 245426 (2006)

cond-mat/0604106

Phys. Rev. B 73, 241403 (2006)

Phys. Rev. B 73, 195411 (2006)

Phys. Rev. B 73, 214418 (2006)

Phys. Rev. B 73, 125411 (2006)

Phys. Rev. Lett. 96, 036801 (2006)

Phys. Rev. B 72, 174406 (2005)

Annals of Physics 321, 1559 (2006).

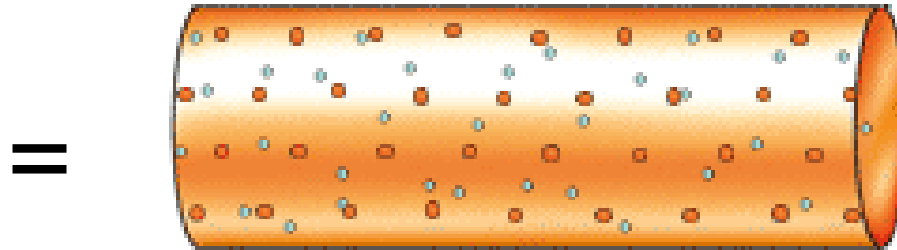
“The theoretical oriented scientist cannot be envied, because nature, i.e. the experiment, is a relentless and not very friendly judge of his work. In the best case scenario it only says ”maybe“ to a theory, but never ”yes“ and in most cases ”no“. If an experiment agrees with theory it means ”perhaps“ for the latter. If it does not agree it means ”no“. Almost any theory will experience a ”no“ at one point in time — most theories very soon after they have been developed.”

— **Albert Einstein**, Theoretische Bemerkungen zur Supraleitung der Metalle
[[Einstein, 1922](#)].

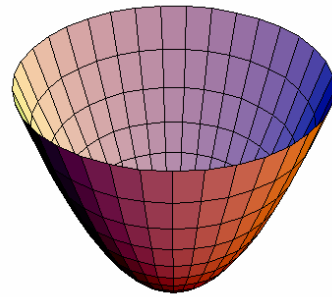
A Personal Note



Free non-relativistic electrons in a box



$$H = \frac{p^2}{2m}$$



← Ignorance is dumped here !

LATTICE



Felix Bloch

Paul Drude



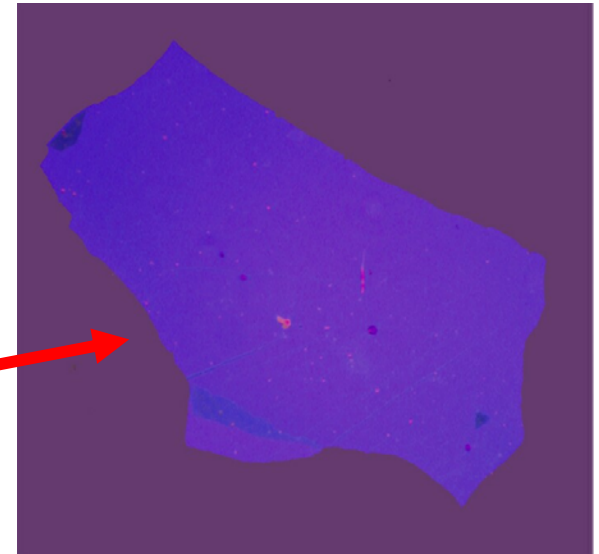
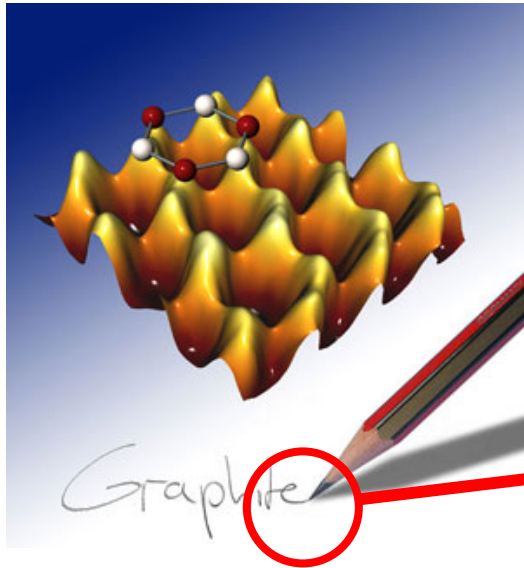
Arnold Sommerfeld



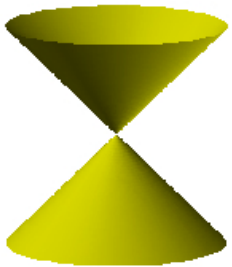
INTERACTIONS



Lev Landau



Novoselov et al, Science 306, 666 (2004)



$$H = vp \begin{pmatrix} 0 & e^{i\varphi(p)} \\ e^{-i\varphi(p)} & 0 \end{pmatrix}$$



Paul Dirac

Free relativistic electrons
in a box

DISORDER
INTERACTIONS

Ignorance is dumped here !

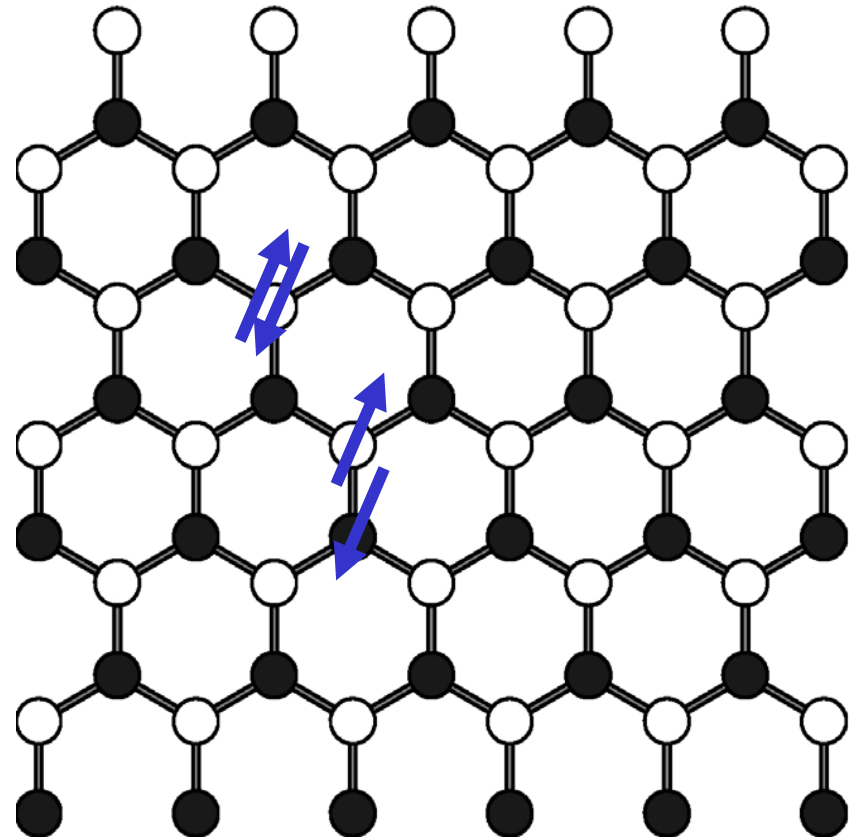
What would be the effective theory for superconductivity in graphene ?

$$\begin{aligned}
 H_{ef}^g = & -t \sum_{\sigma} \sum_{\langle ij \rangle} a_{i\sigma}^{\dagger} b_{j\sigma} + h.c. - \mu \sum_{i\sigma} [a_{i\sigma}^{\dagger} a_{i\sigma} + b_{i\sigma}^{\dagger} b_{i\sigma}] \\
 & + \frac{g_0}{2} \sum_{i\sigma} [a_{i\sigma}^{\dagger} a_{i\sigma} a_{i-\sigma}^{\dagger} a_{i-\sigma} + b_{i\sigma}^{\dagger} b_{i\sigma} b_{i-\sigma}^{\dagger} b_{i-\sigma}] \\
 & + g_1 \sum_{\langle ij \rangle} \sum_{\sigma\sigma'} a_{i\sigma}^{\dagger} a_{i\sigma} b_{j\sigma'}^{\dagger} b_{j\sigma'} ,
 \end{aligned}$$

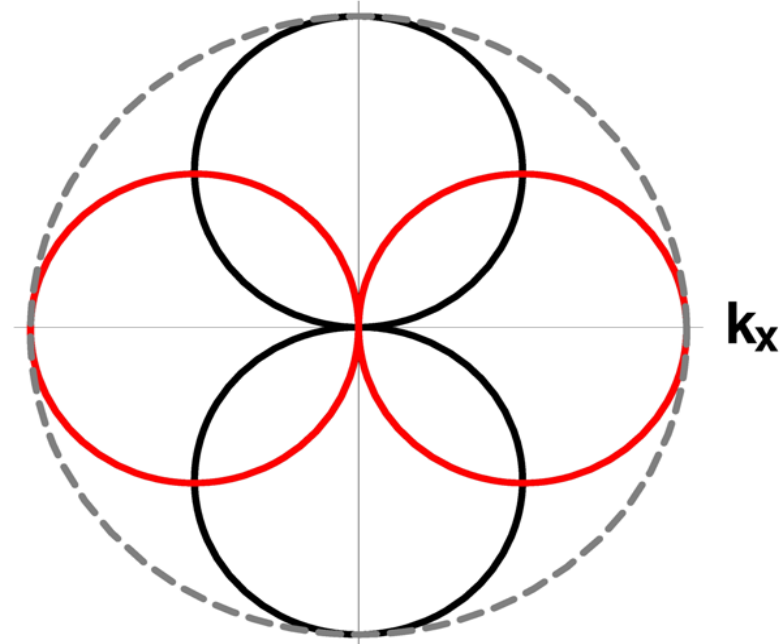
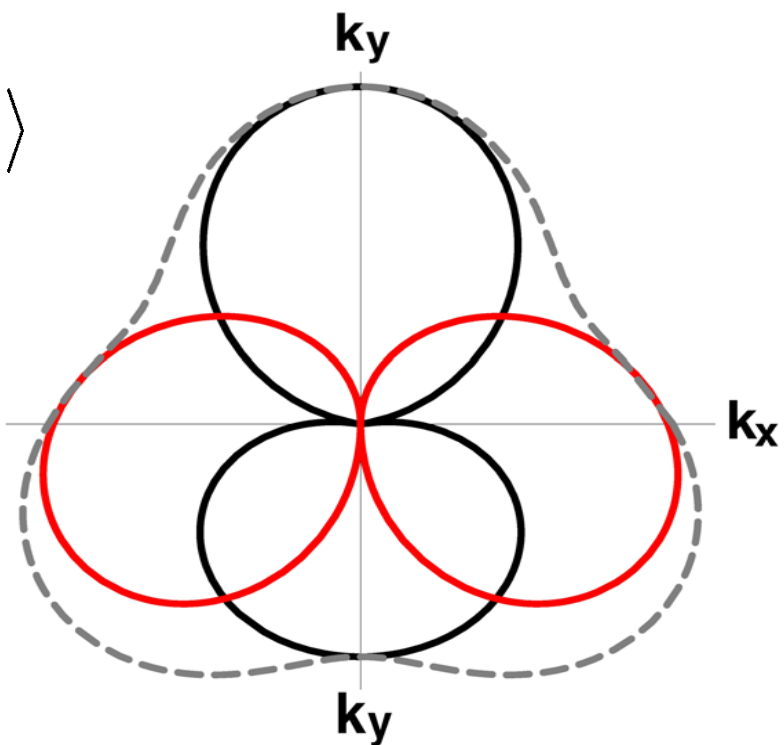
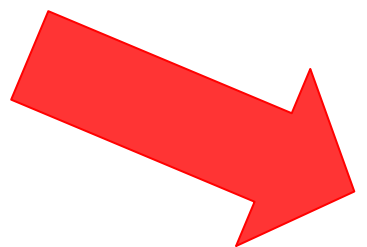
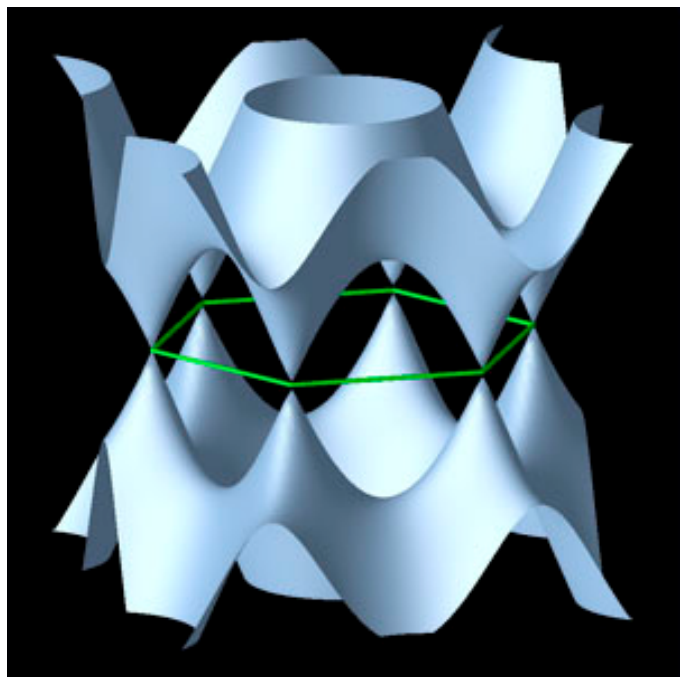
$$\Delta_{1,ij} = \langle a_{i\downarrow} b_{j\uparrow} - a_{i\uparrow} b_{j\downarrow} \rangle$$

~~p-wave~~
p-wave

$$\Psi = \psi_{S=0} \otimes \psi_{L=1} \otimes \psi_{A-B}$$



$$\Delta_{1,ij} = \langle a_{i\downarrow} b_{j\uparrow} - a_{i\uparrow} b_{j\downarrow} \rangle$$



Dirac Fermion pairing

AHCN, Phys. Rev. Lett. 86, 4382 (2001)

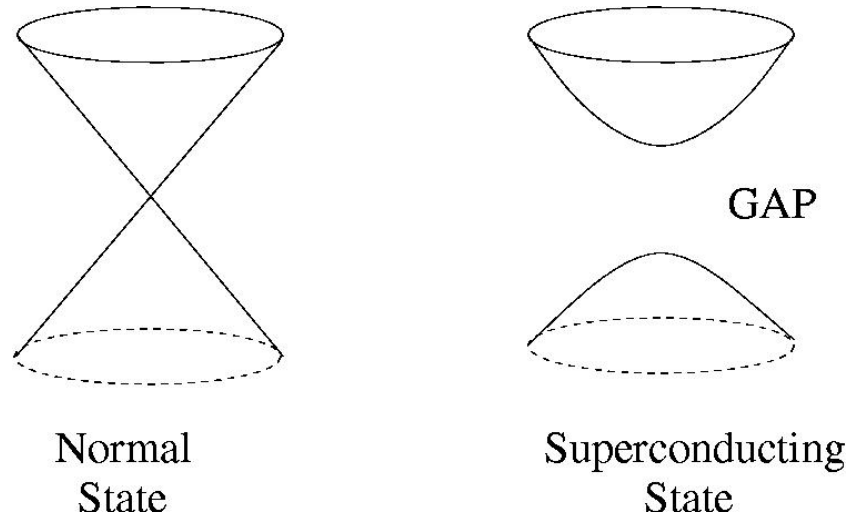
B.Uchoa, AHCN, G. Cabrera, Phys.Rev.B 69, 144512 (2004)

B.Uchoa, G. Cabrera, AHCN, Phys.Rev.B 71, 184509 (2005)

$$H_D = \sum_{i,\mathbf{k},\sigma} \Psi_{i,\sigma}^\dagger(\mathbf{k}) [\nu_F k_{\perp,i} \sigma^z + \nu_0 k_{\parallel,i} \sigma^x] \Psi_{i,\sigma}(\mathbf{k})$$

$$H_P = \sum_{\mathbf{k},a,b} [\sigma_{a,b}^y \Delta_s \psi_{a,\uparrow}^\dagger(\mathbf{k}) \psi_{b,\downarrow}^\dagger(-\mathbf{k}) + \text{H.c.}]$$

$$\Delta_s = -g \sum_{\mathbf{k},a,b} \sigma_{a,b}^y \langle \psi_{a,\uparrow}(\mathbf{k}) \psi_{b,\downarrow}(-\mathbf{k}) \rangle$$



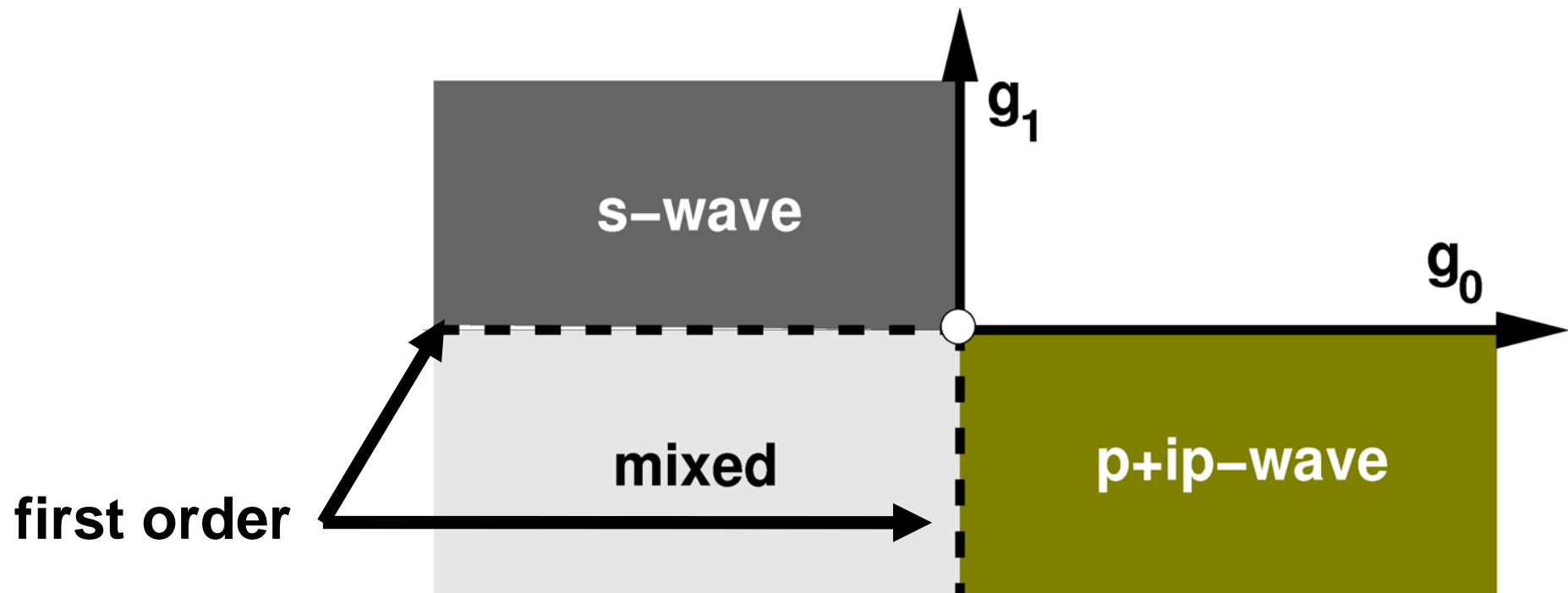
$$|\Delta_s(T, g)| = 2T \cosh^{-1}[\cosh[2\pi v_F v_0 / (Tg_c)] \times e^{-(2\pi v_F v_0 / Tg)}]$$

and $g_c = 4\pi^{3/2} \sqrt{v_F v_0} / \Lambda$. At $T = 0$ we have

$$|\Delta_s(0, g)| = 4\pi v_F v_0 (1/g_c - 1/g),$$

The quantum theory is critical

$$\frac{T_c}{\mu} = \frac{2\gamma}{\pi} e^{\Lambda(1-g_c/g_0)\mu^{-1}-1}$$



Electron-phonon coupling

$$\mathcal{H}_{E-P} = \frac{\partial t_0}{\partial l} \sum_{\mathbf{k}, \mathbf{q}} c_{A\mathbf{k}}^\dagger c_{B\mathbf{k}+\mathbf{q}} \left\{ x_{A\mathbf{q}} \left[1 - \frac{e^{i(\mathbf{k}+\mathbf{q})\mathbf{a}}}{2} - \frac{e^{i(\mathbf{k}+\mathbf{q})\mathbf{b}}}{2} \right] - x_{B\mathbf{q}} \left[1 - \frac{e^{i\mathbf{k}\mathbf{a}}}{2} - \frac{e^{i\mathbf{k}\mathbf{b}}}{2} \right] + \right. \\ \left. + y_{A\mathbf{q}} \left[\frac{\sqrt{3}}{2} e^{i(\mathbf{k}+\mathbf{q})\mathbf{a}} - \frac{\sqrt{3}}{2} e^{i(\mathbf{k}+\mathbf{q})\mathbf{b}} \right] - y_{B\mathbf{q}} \left[\frac{\sqrt{3}}{2} e^{i\mathbf{k}\mathbf{a}} - \frac{\sqrt{3}}{2} e^{i\mathbf{k}\mathbf{b}} \right] \right\} + \text{h.c.}$$

$$\frac{\partial t_0}{\partial l} = \alpha \approx 1.4 \text{ eV}\text{\AA}^{-1} \quad \begin{pmatrix} x_{A\mathbf{q}} \\ y_{A\mathbf{q}} \\ x_{B\mathbf{q}} \\ y_{B\mathbf{q}} \end{pmatrix} \equiv \frac{1}{\sqrt{2M_C\omega_{\mathbf{q}}}} (b_{\mathbf{q}}^\dagger + b_{-\mathbf{q}}) \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix}$$

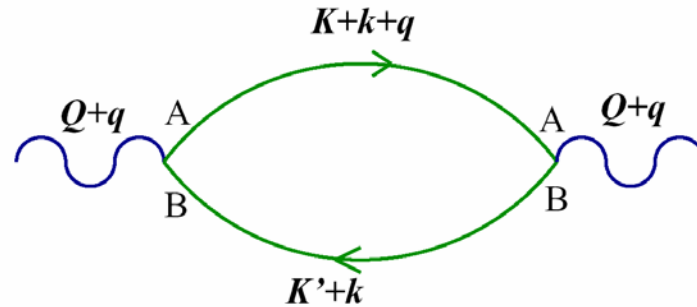
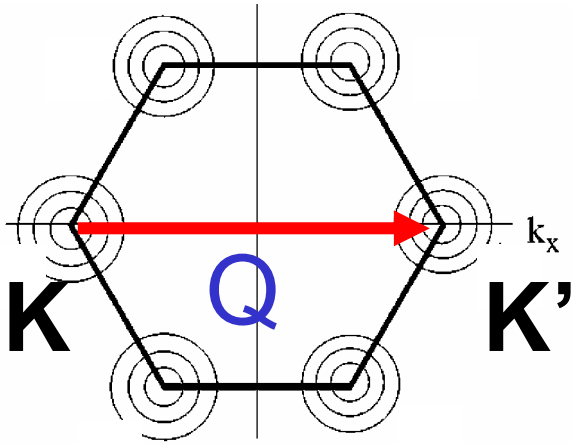
$$\lambda = \left(\frac{dt}{dl} \right)^2 \langle x^2 \rangle \frac{N(E_F)}{\omega_0}$$

$$N_{2D}(E_F) \propto \frac{1}{W}$$

Weak coupling

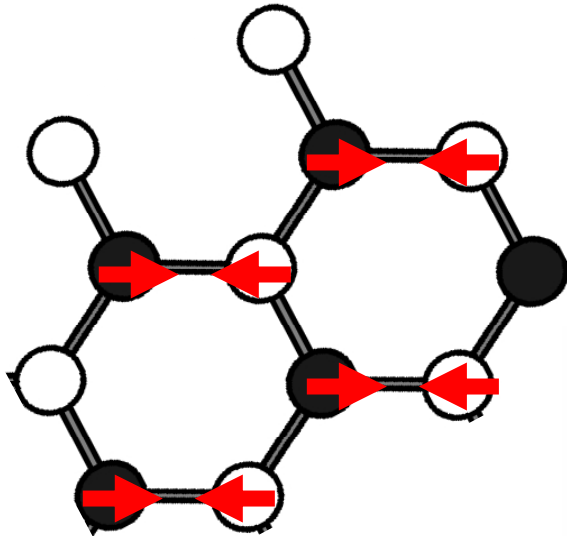
$$N_g(E_F) \propto \frac{E_F}{v_F^2 / a^2} \propto \frac{E_F}{W^2}$$

$$\mathcal{H}_{\mathbf{Q}} \equiv \frac{3\alpha}{2} \sum_{\mathbf{k}} c_{A\mathbf{K}}^{\dagger} c_{B\mathbf{K}'+\mathbf{k}} (x_{A\mathbf{Q}} - x_{B\mathbf{Q}} + iy_{A\mathbf{Q}} + iy_{B\mathbf{Q}}) + \text{h.c.},$$



$$\delta\omega_{\mathbf{Q}} = -\frac{9\sqrt{3}}{2\pi} \left(\frac{\partial t_0}{\partial l} \right)^2 \frac{k_{\text{F}} a}{M_C \omega_{\mathbf{Q}} t_0}$$

$$\delta\omega_{\mathbf{Q}} (\text{eV}) \approx -2.92 \times 10^{-10} \sqrt{n(\text{cm}^{-2})}$$

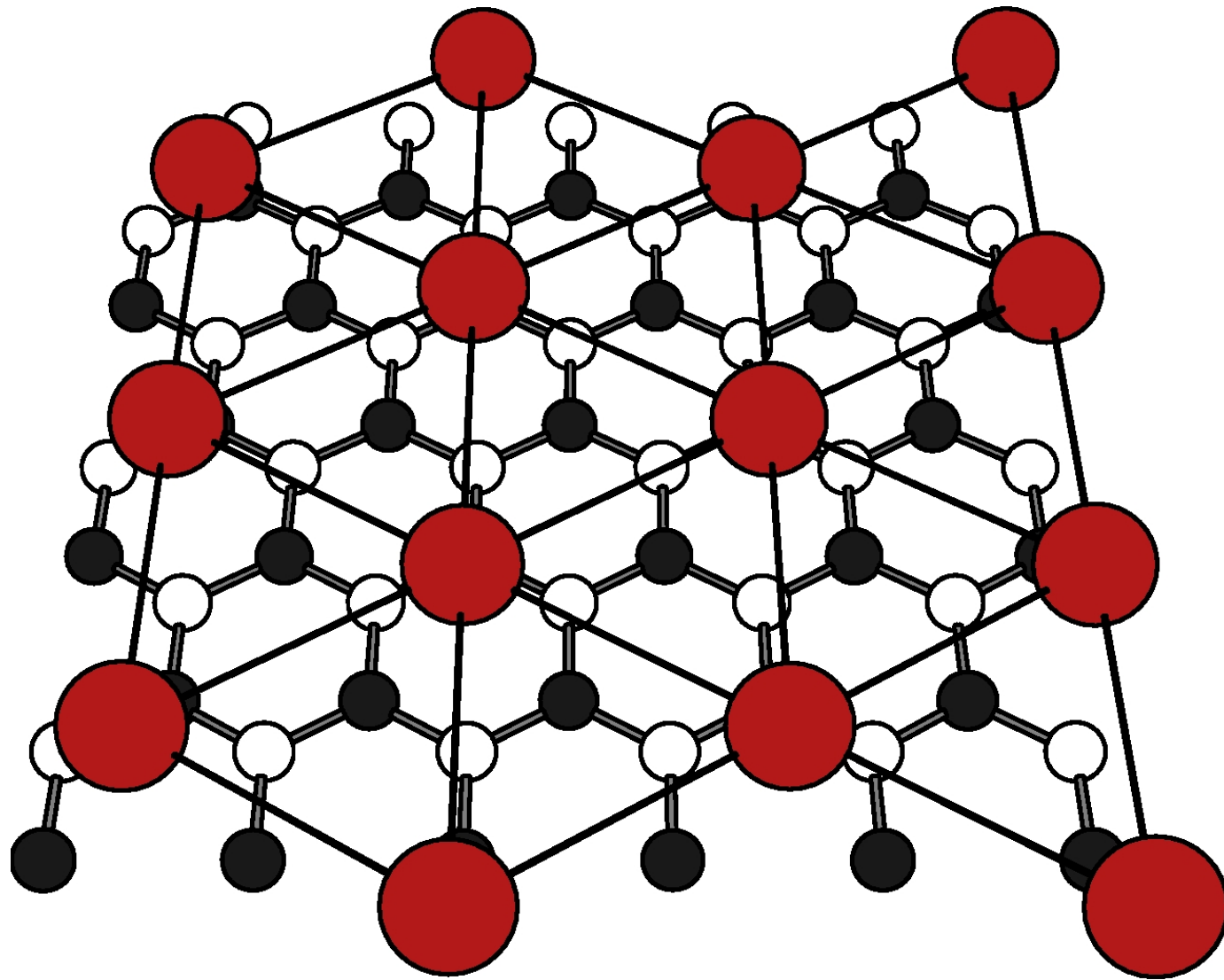


A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, et al., cond-mat/0606284.

A. Gupta, G. Chen, P. Joshi, S. Tadigadapa, and P. C. Eklund, cond-mat/0606593.

D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold, and L. Wirtz, cond-mat/0607562.

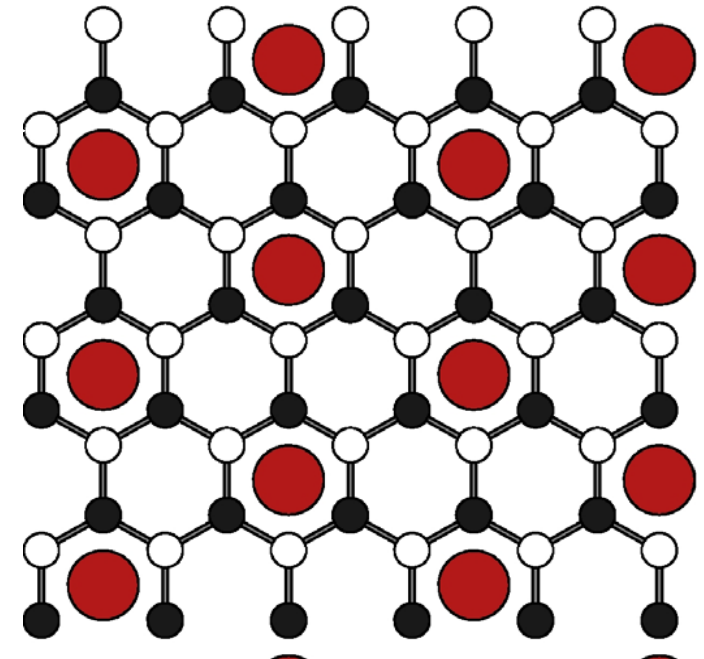
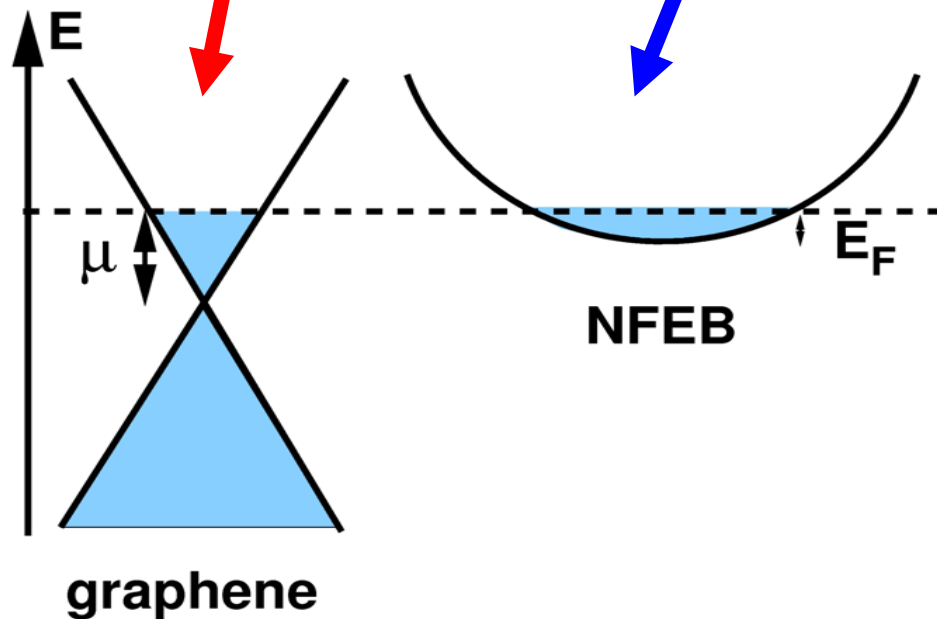
A proposal



The idea: start with the non-interacting problem

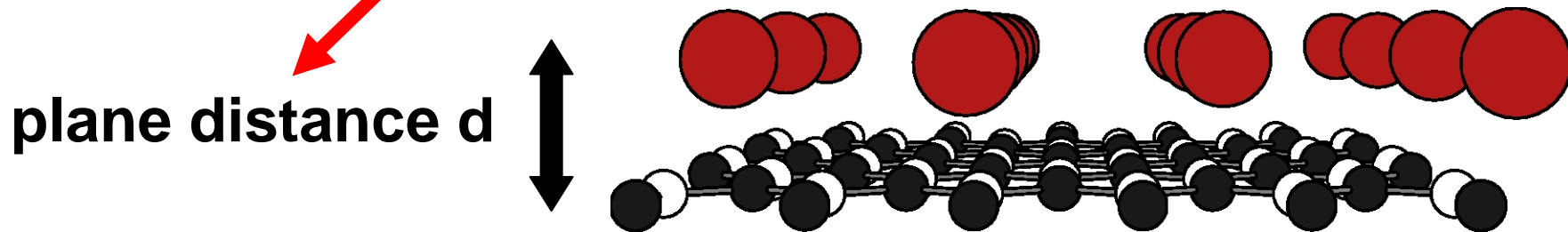
$$H_t = -t \sum_{\langle ij \rangle} \sum_{\sigma=\uparrow\downarrow} (a_{i,\sigma}^\dagger b_{j,\sigma} + h.c.) - \mu_0 \sum_i \hat{n}_{g,i}$$

$$H_{NFEB} = \sum_{\sigma,\mathbf{k}} \epsilon_{\mathbf{k}} f_{\mathbf{k}\sigma}^\dagger f_{\mathbf{k}\sigma}$$



And add Coulomb interactions

$$H_I = \sum_{ij} V(\mathbf{x}_i - \mathbf{x}_j) \hat{n}_f(\mathbf{x}_i) \hat{n}_f(\mathbf{x}_j) + \sum_{ij} V(\mathbf{R}_i - \mathbf{R}_j) \hat{n}_{g,i} \hat{n}_{g,j} \\ + 2 \sum_{ij} V(\mathbf{x}_i - \mathbf{R}_j) \hat{n}_f(\mathbf{x}_i) \hat{n}_{g,j} .$$

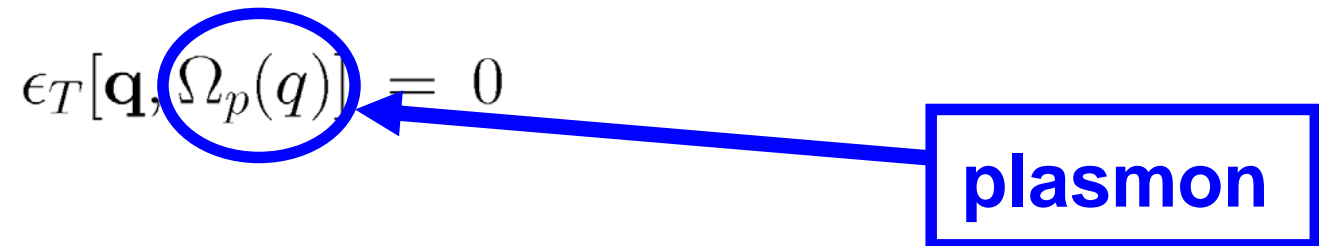


All interactions are repulsive !

Graphene Effective Interaction (RPA)

$$V_{ef,\mathbf{k}}^g(\omega) = \frac{V_{0,\mathbf{k}}}{\epsilon_T(\mathbf{k}, \omega)} \left[1 - (V_{\mathbf{k}} - V_{d,\mathbf{k}}) \chi_m^0(\mathbf{k}, \omega) \right]$$

The interaction can be strongly attractive close to the zeros of the dielectric function

$$\epsilon_T[\mathbf{q}, \Omega_p(q)] = 0$$


plasmon

where electrons resonate with
plasmons !

Fröhlich, H.
J. Phys. C **1**, 544-548 (1968)

Dielectric function

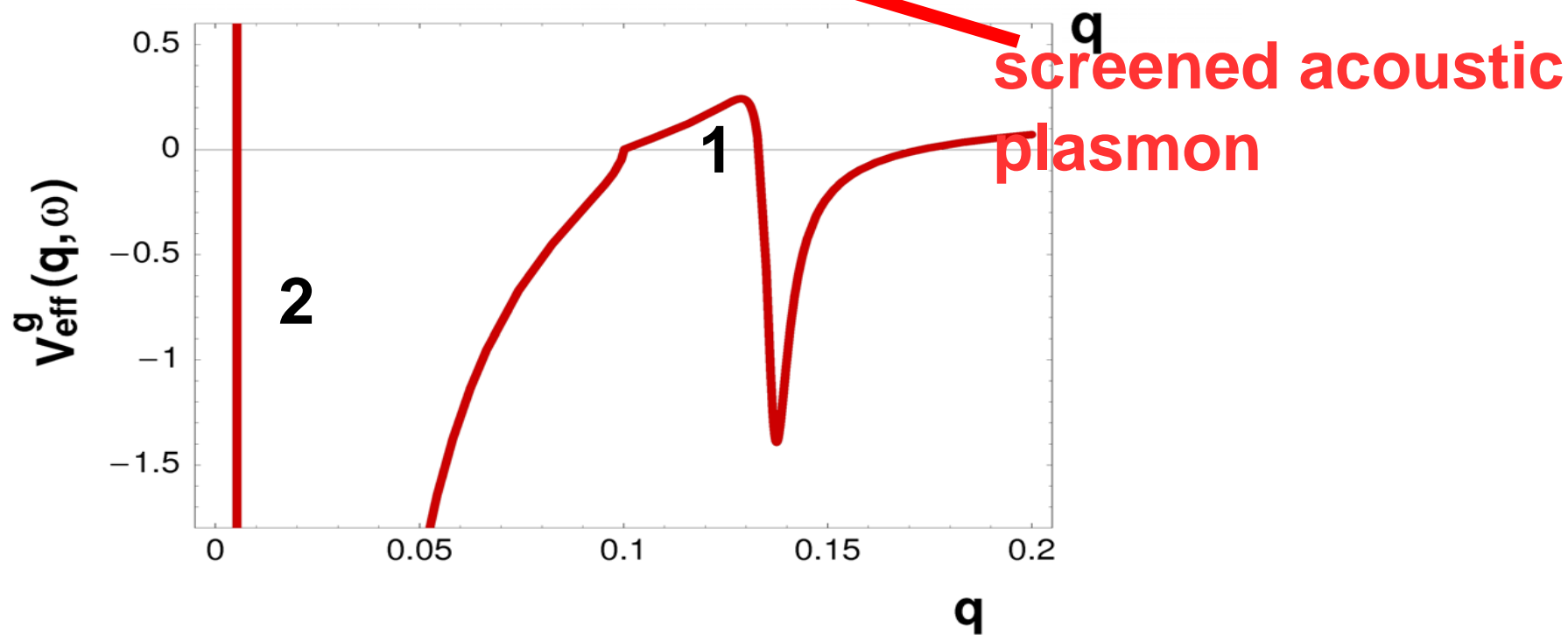
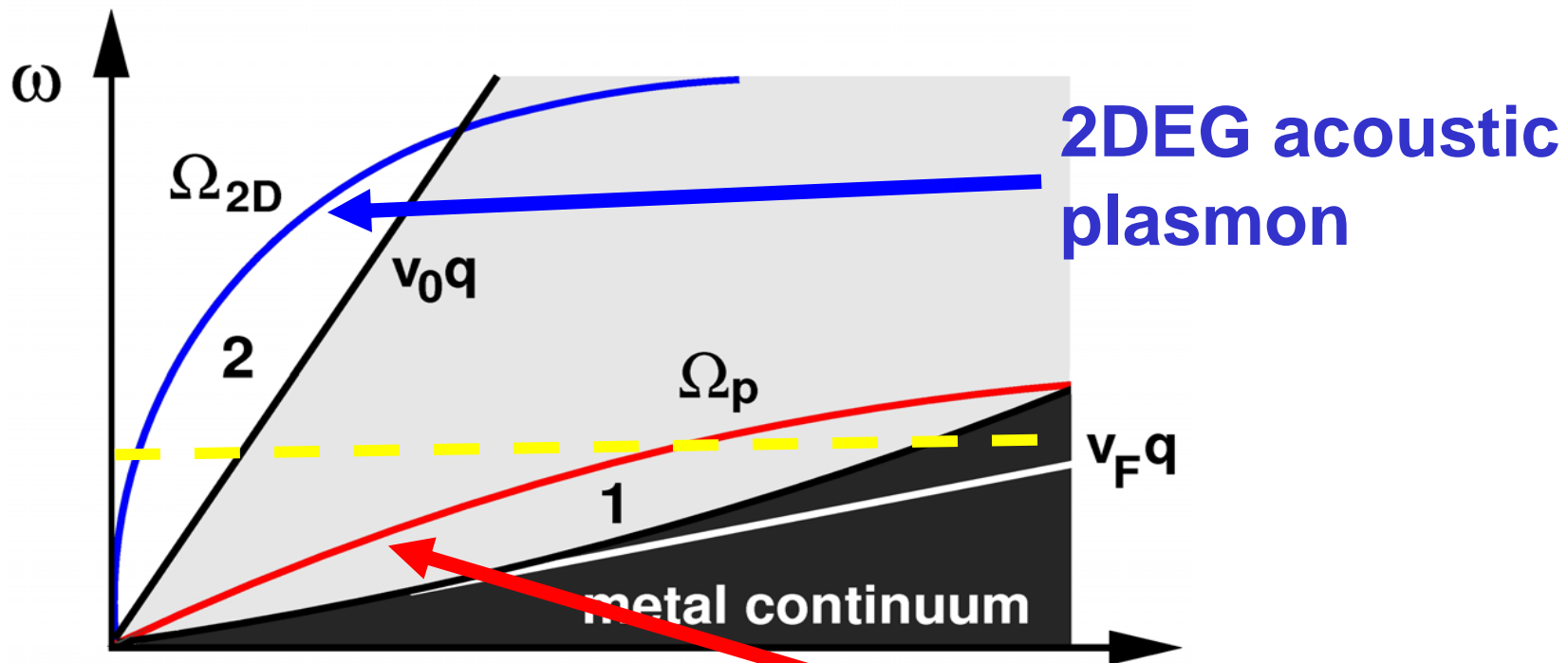
$$\epsilon_T(\mathbf{k}, \omega) = 1 - V_{0,k} [\Pi_g^0(\mathbf{k}, \omega) + \Pi_m^0(\mathbf{k}, \omega)] + [V_{0,\mathbf{k}}^2 - V_{d,\mathbf{k}}^2] \chi_m^0(\mathbf{k}, \omega) \chi_g^0(\mathbf{k}, \omega)$$

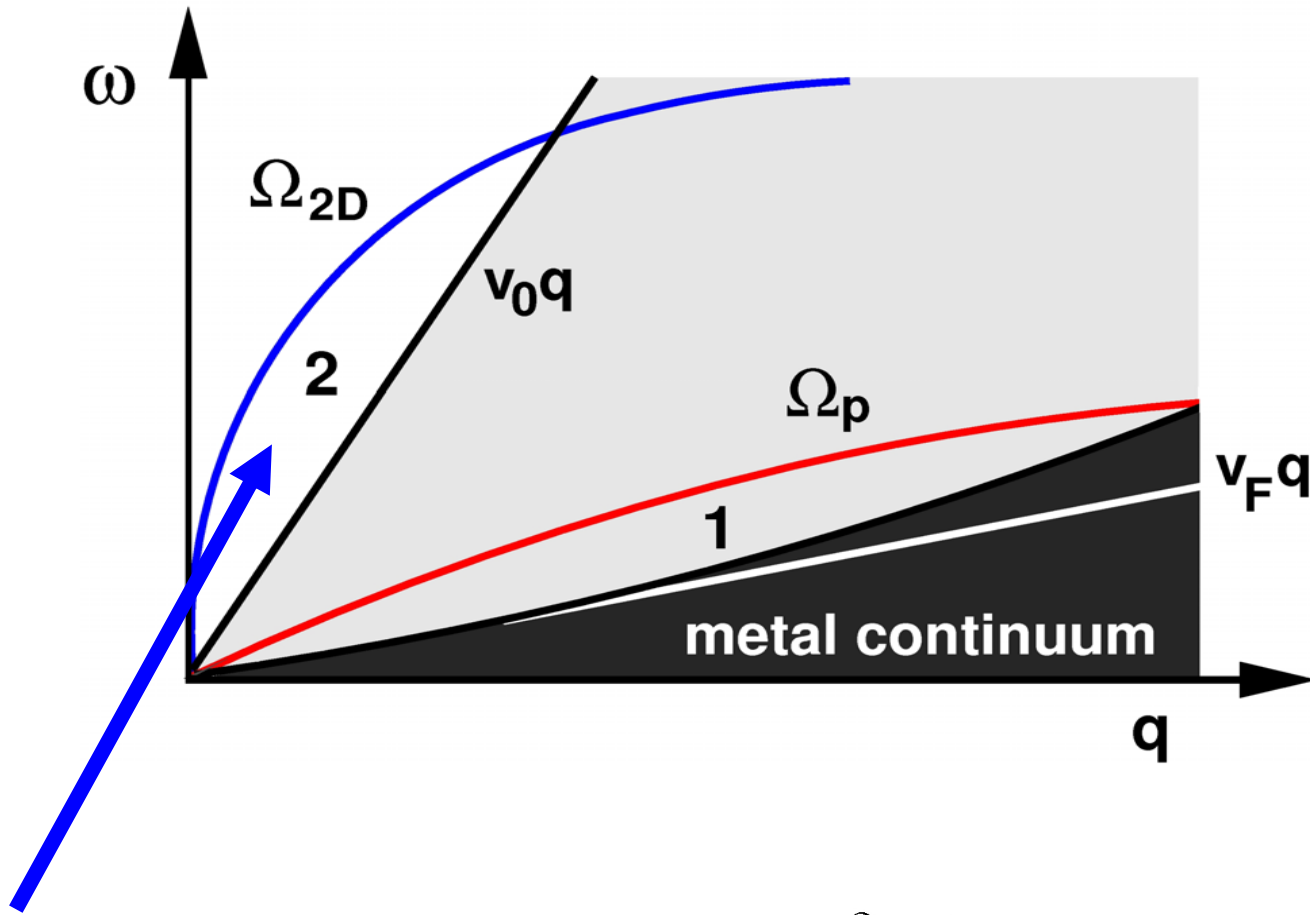
where $V_{d,q} = \frac{2\pi e^2}{\epsilon_0 q} e^{-qd}$ **2D Coulomb interaction**

$$\Pi_g^0(q, \omega) = -(2\mu/\pi v_0^2) \left[1 - \omega / \sqrt{\omega^2 - v_0^2 q^2} \right]$$

$$V_{0,q} \Pi_m^0(q, \omega) = \Omega_m^2 / \omega^2$$

$$\Omega_m(q) = e \sqrt{2E_F q / \epsilon_0}$$

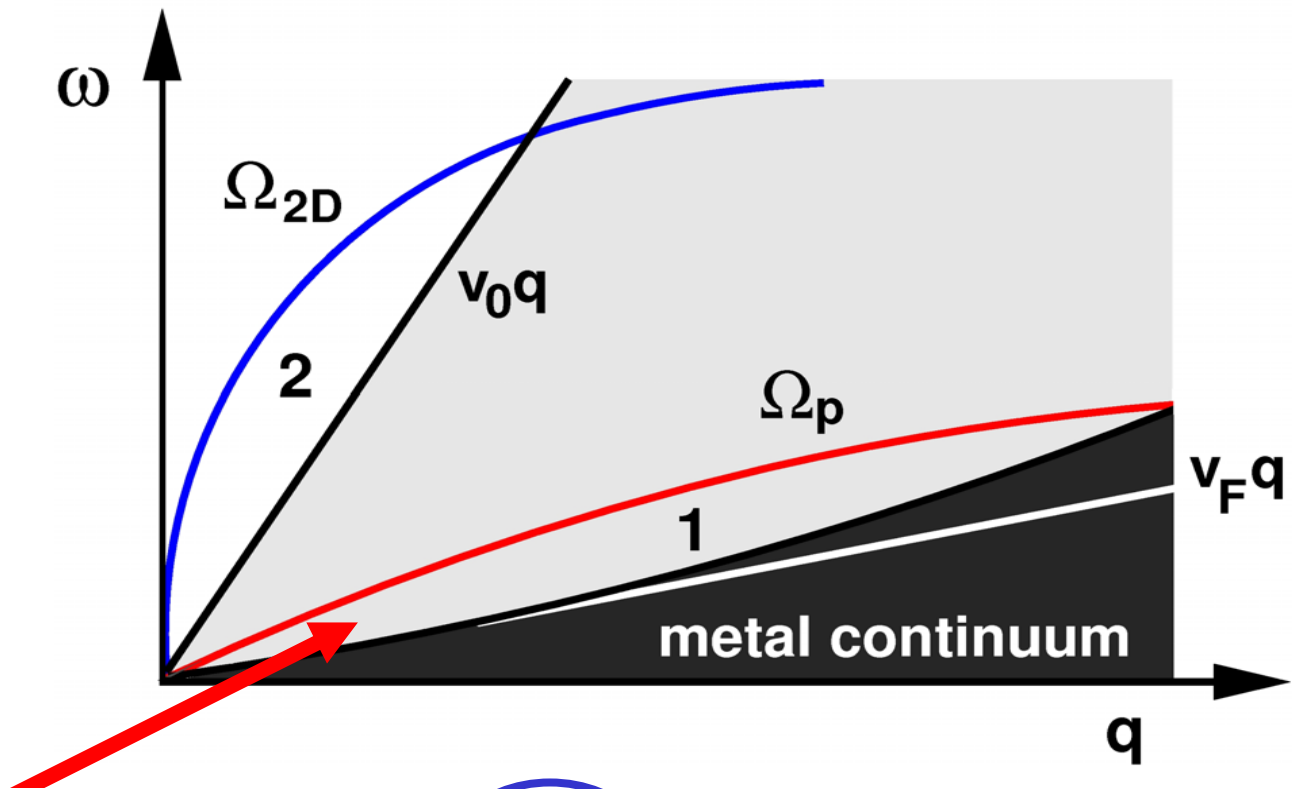




$$V_{ef}^g(q, \omega \gg v_0 q) = V_q \left[\frac{\Omega_{2D}^2(q)}{\omega^2 - \Omega_{2D}^2(q)} + 1 \right]$$

$$\Omega_{2D}(q) = e\sqrt{2(E_F + \mu)q/\epsilon_0}$$

2DEG plasmon



$$V_{ef}^g(q, \omega \ll v_0q) = \frac{V_q}{\epsilon_g(q, 0)} \left[\frac{\Omega_p^2(q)}{\omega^2 - \Omega_p^2(q)} + 1 \right]$$

$$\Omega_p(q) \rightarrow \sqrt{E_F^*/(2\mu)} v_0q \quad \leftarrow \text{screened acoustic plasmon}$$

The screened mode will exist if it is not overdamped by the electronic particle-hole continuum:

$$E_F \ll \frac{\epsilon_0 v_0}{4\alpha_g d} \sim 0.9 \text{ eV}$$

If x is the fraction of electrons per metallic atom that migrates to graphene in the compound, $\mathbf{C}_m \mathbf{A}_n$

this condition is equivalent to

$$x \ll 0.12(m/n)$$



Superconductivity is favored for a sufficiently diluted coverage of the metal (large n) !

Carbon Superconductivity

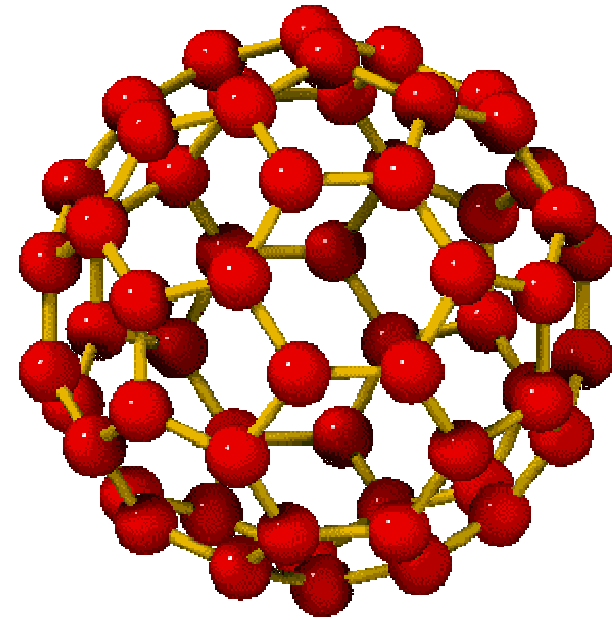
Fullerenes

C_{60} is an insulator but

$C_{60}K_3$ is a superconductor (18 K)

Hebard *et al.*, Nature 352, 223 (1991)

but $C_{60}K_4$ is an insulator indicating that
superconductivity happens with metal dilution



C_{60} buckyball

Intercalated Graphite

	IA																0	
1	1 H																	2 He
2	3 Li	4 Be										5 B	6 C	7 N	8 O	9 F	10 Ne	
3	11 Na	12 Mg										13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	+Ac	104 Rf	105 Ha	106	107	108	109	110								

C₂Li (1.9 K)

C₈K (0.5 K)

C₆Ca (11.5 K)

C₆Yb (6.5 K)

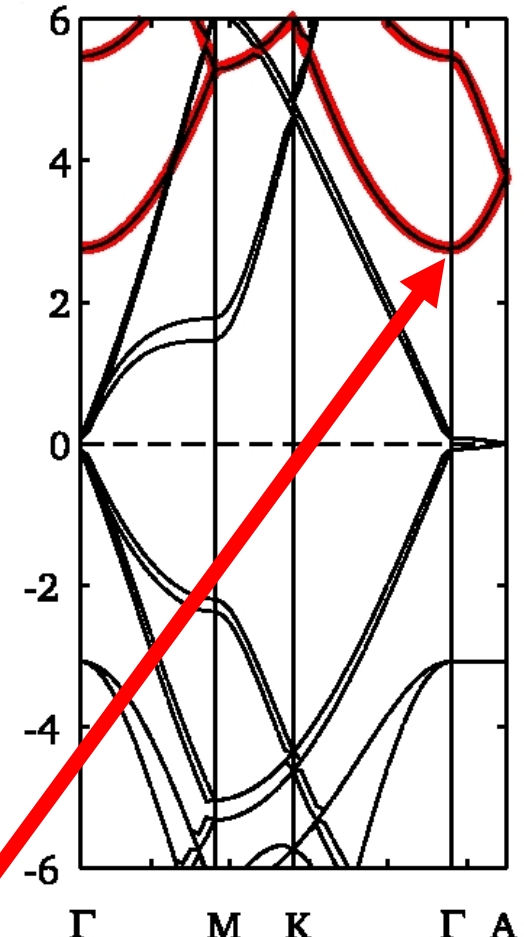
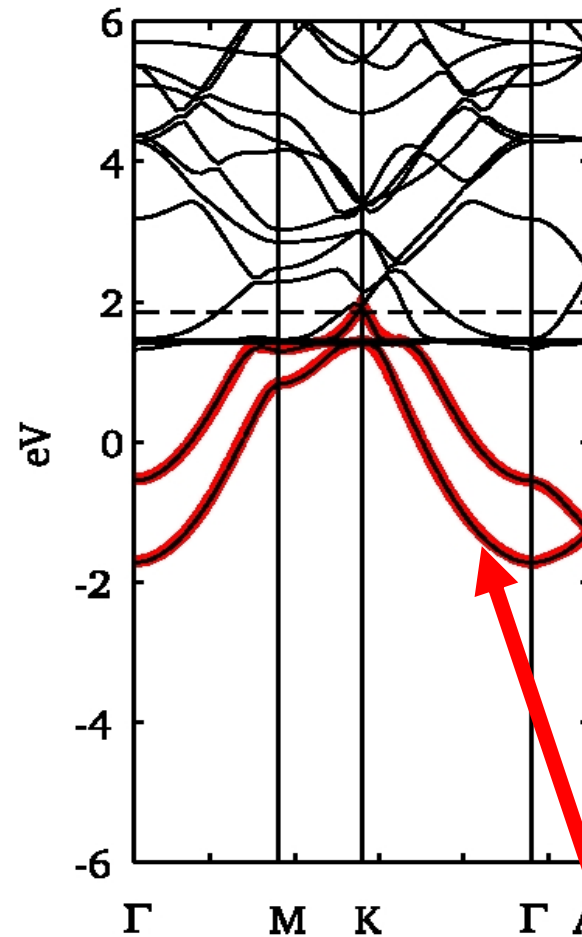
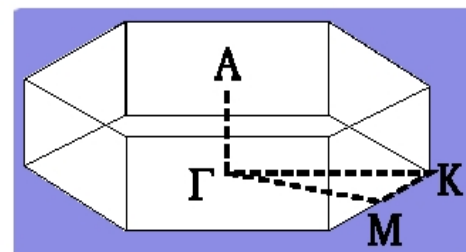
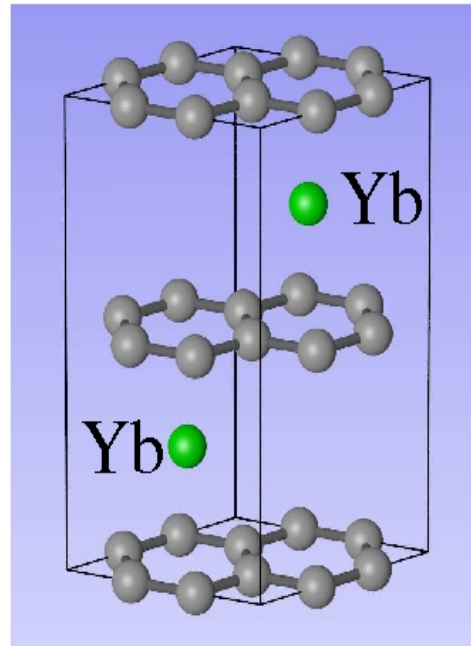
* Lanthanide Series
+ Actinide Series

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Graphite intercalated compounds (GIC)

Yb

Graphite



Czanyi *et al.*, Nat. Phys. 1, 42 (2005)

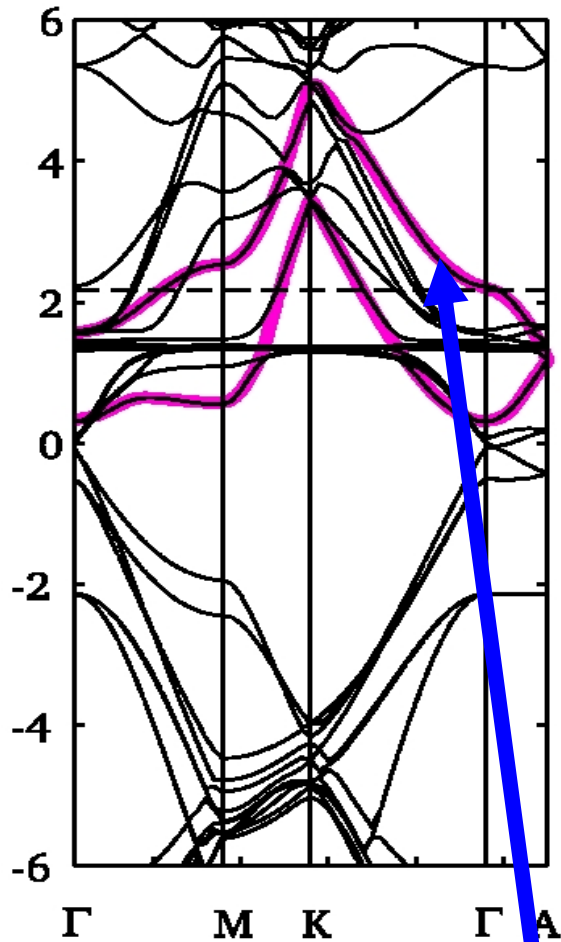
NFE

Graphite intercalated compounds (GIC)

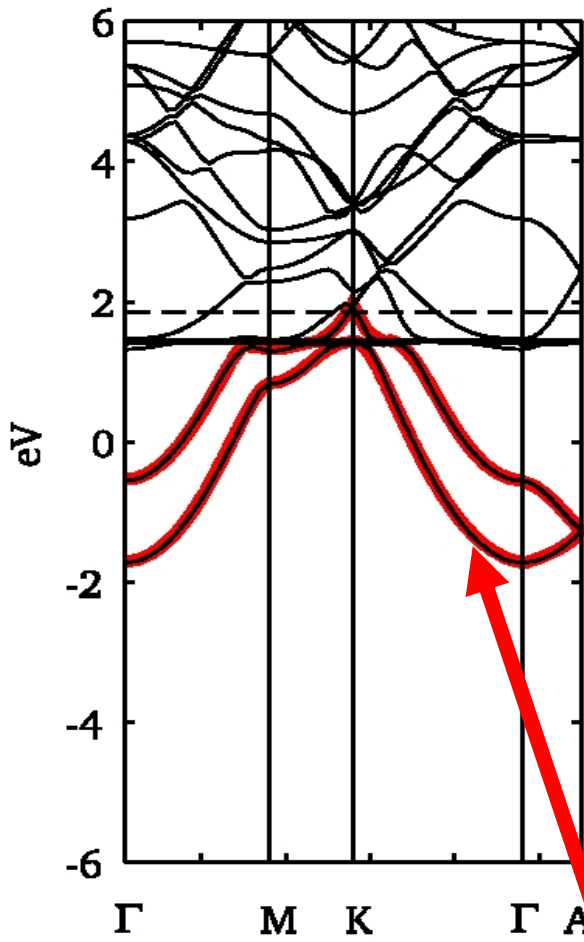
C₆Yb

Yb

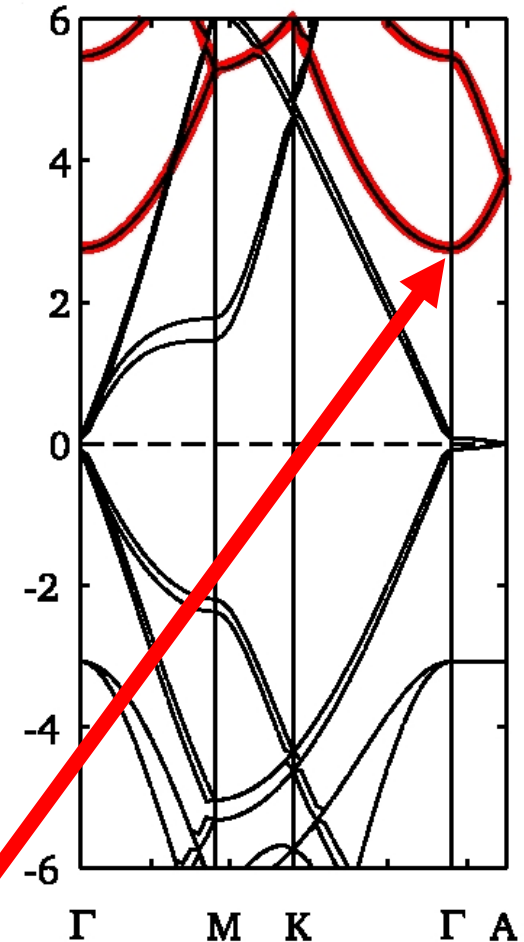
Graphite



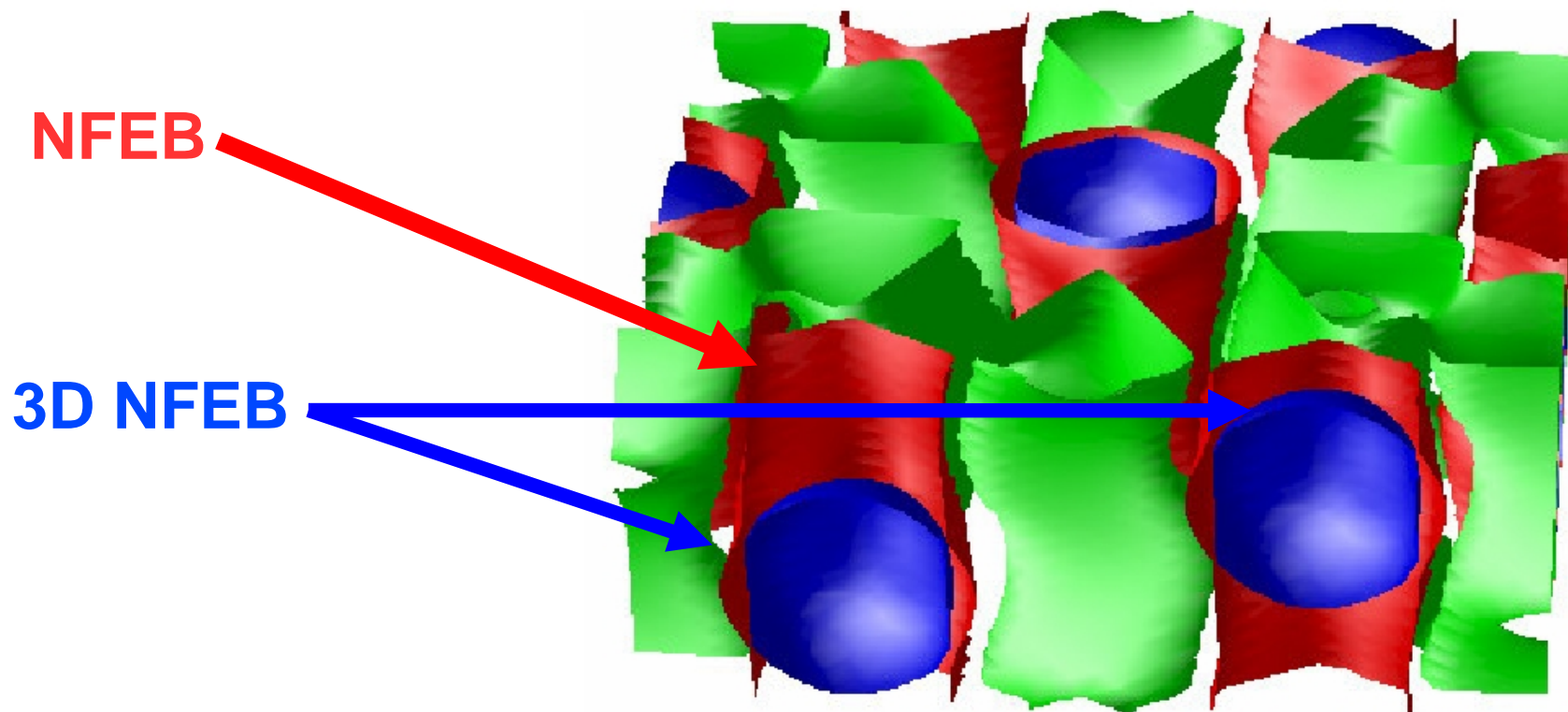
3D NFEB



NFEB

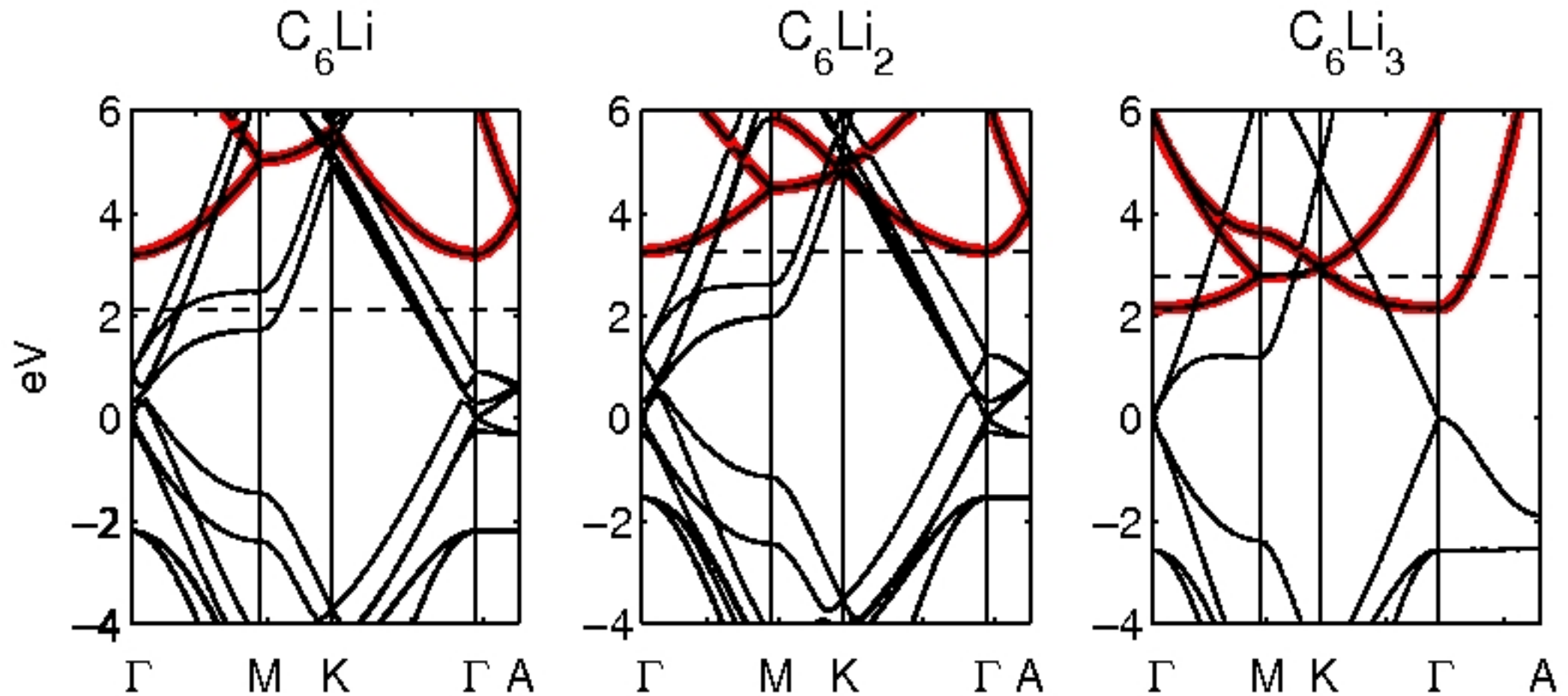


Graphite intercalated compounds (GIC)



Fermi surface

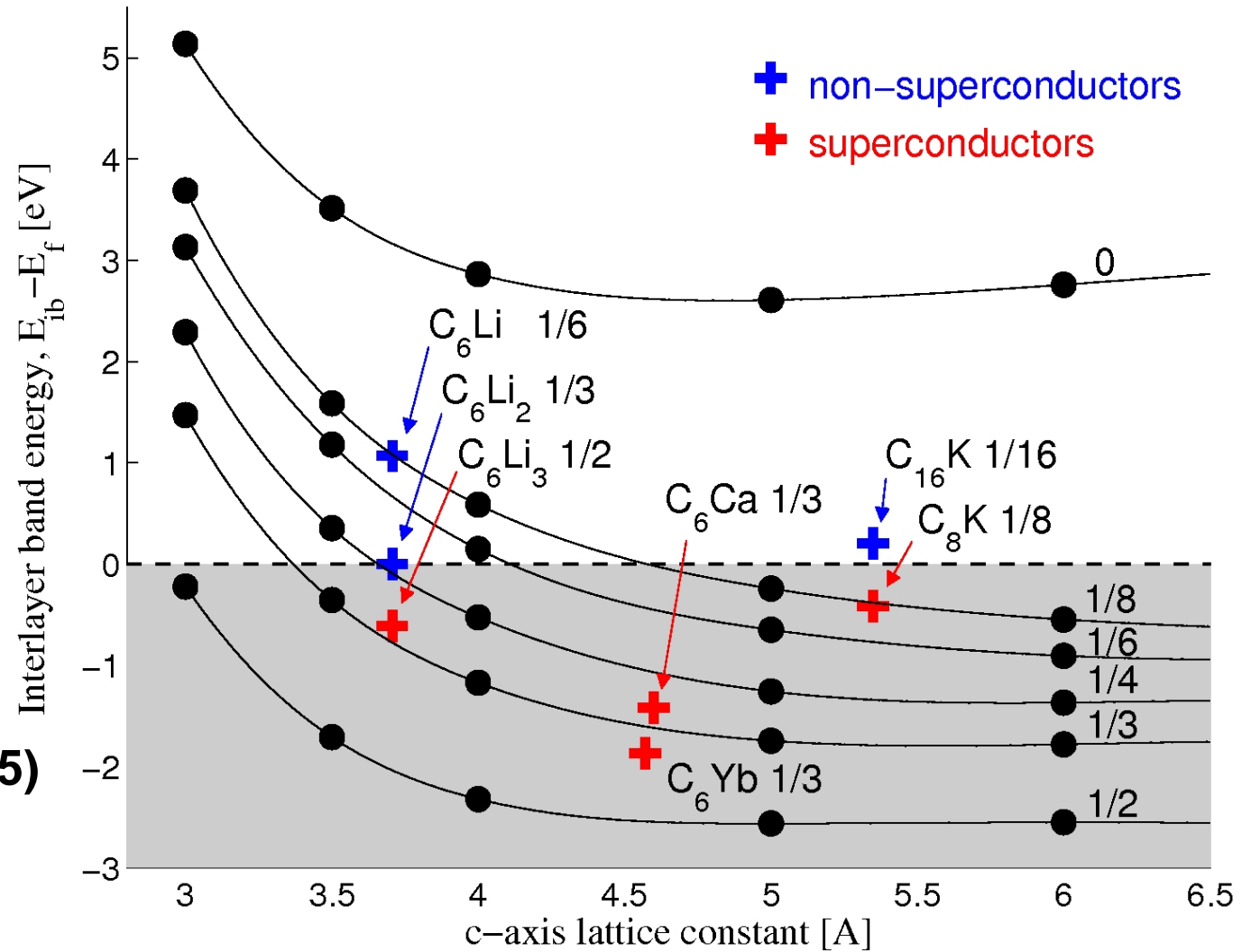
Graphite intercalated compounds (GIC)



NFEB FS?	No	No	Yes
SC?	No	No	Yes

Graphite intercalated compounds (GIC)

Czanyi *et al.*,
 Nat. Phys. 1, 42 (2005)



2 band model model superconductivity?

Conclusions

We showed that superconductivity is possible in graphene using a purely electronic mechanism

A reliable estimation of T_c requires the inclusion of retardation in the interaction (strong coupling theory)

Graphene has a new superconducting phase with $p+ip$ wave pairing in the singlet channel.