van der Waals interactions (long-ranged e^- correlations) in Nanostructures

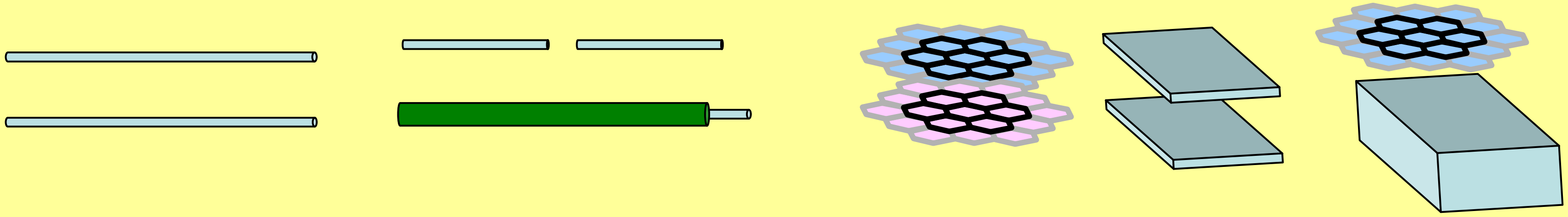
John Dobson,
Nanoscale Science & Tech. Centre, Griffith University, Qld, Australia

Acknowledgments: Ken Simpkins, Angela White, Angel Rubio, Tim Gould

Donostia International Physics Center, Ecole Polytechnique

Failures of common van der Waals theories in the asymptotic (widely-spaced) limit.

Gives surprising force laws for some low-dimensional, zero-electronic-gap systems

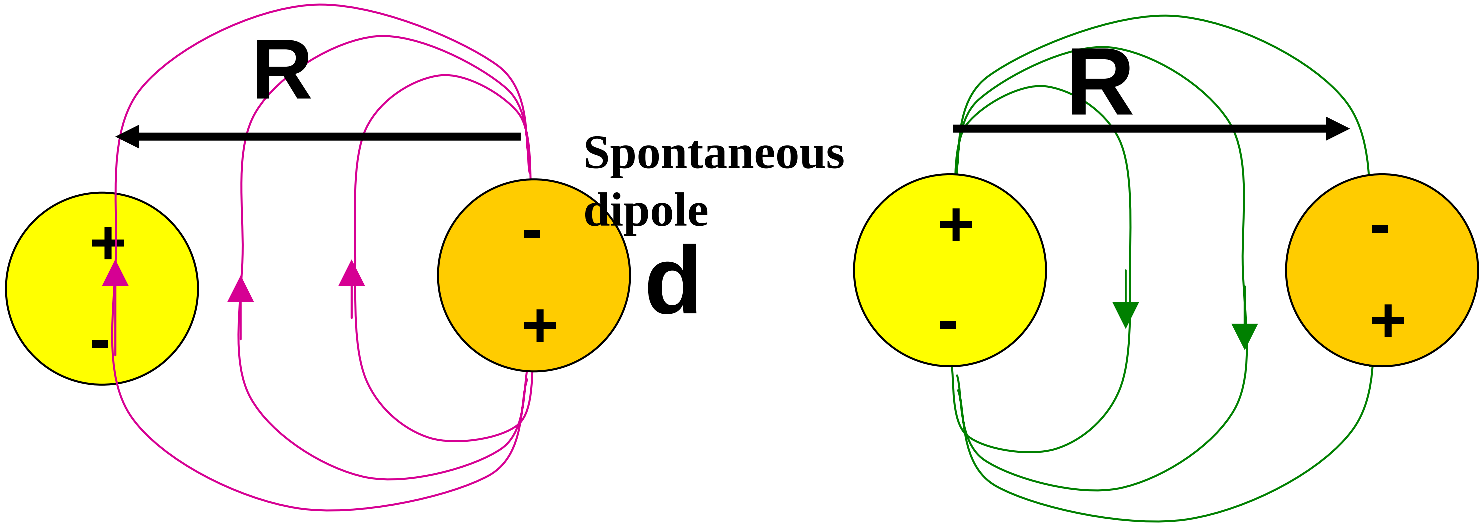


Failures of common theories for condensed limit (not widely spaced)?

Conclusion: may need new functionals for soft-matter energetics

JFD et al, PRL 96, 073201 (2006), cond-mat/0502422, /0609624
JFD, Surface Science, in press. http://dx.doi.org/10.1016/j.susc.2007.06.041

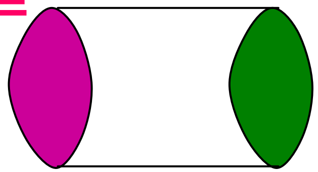
ORIGIN OF DISTANT VDW (DISPERSION) FORCE



$$E^{(2)} = -\left\langle \alpha_2 \frac{d}{R^3}\frac{1}{R^3}d \right\rangle \approx -\frac{\alpha_2\alpha_1\hbar\omega_0}{R^6}$$

A correlation effect, highly nonlocal so LDA & GGA FAIL

Occurs already in 2nd order pert^n theory for the energy

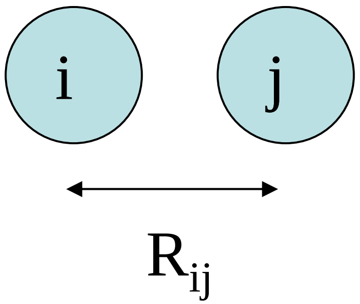


RPA E_c contains this term: understand via ZPE of coupled plasmons

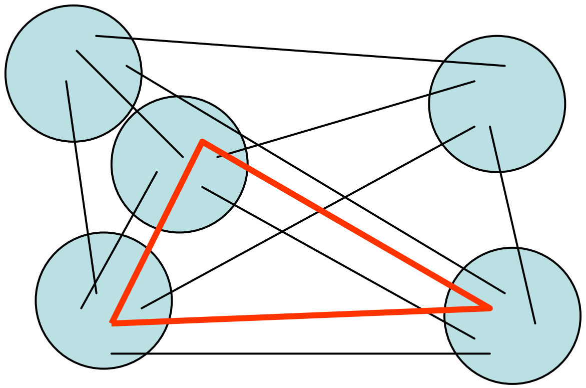
see also JFD+ IJQC 101, 579 (2005), cond-mat/0311371 (JFD, Mahanty Festschrift 1994)

Weak but ubiquitous - additional to covalent, ionic bonds

Conventional view: “universality” of asymptotic vdW



“Take vdW as given between atoms or sub-units: $E_{ij} \approx -C_6^{(ij)} R_{ij}^{-6}$, $R_{ij} \to \infty$.”



“Then total E_{vdW} is the sum of pairwise contributions

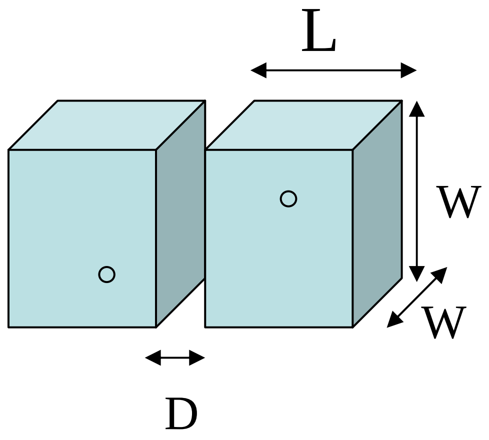
$$E_{vdW} = -\sum_{i,j:\ i \neq j} C_6^{(ij)} R_{ij}^{-6} \text{"}$$

“Triplet and higher terms – e..g.

$$E_{vdW}^{(3)} = -\sum_{i,j,k} C_9^{(ijk)} R_{ij}^{-3} R_{jk}^{-3} R_{ik}^{-3}$$

do not make a qualitative difference.”

Standard vdW theories for macroscopic systems (non-overlapping)



Thick slabs, L, W >>D

ΣR^{-6} (see Mahanty & Ninham book) gives

$$E/A \propto -A^{-1}\int_{V_1} d^3r_1 \int_{V_2} d^3r_2\, r_{12}^{-6} = -CD^{-2}$$

Lifshitz theory: (JETP 2, 73 (1956)) uses a random field method and assumes a local dielectric function

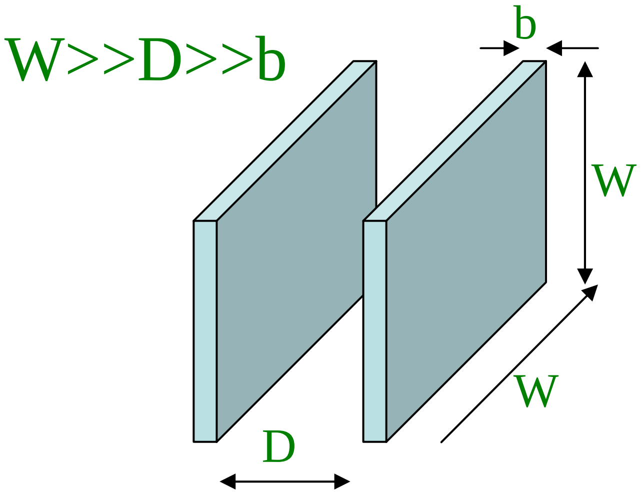
$$\frac{E}{A} \approx -K\hbar D^{-2}\int_0^{\infty}\int_0^{\infty} \frac{x^2}{\frac{\varepsilon_1(iu)+1}{\varepsilon_1(iu)-1}\frac{\varepsilon_2(iu)+1}{\varepsilon_2(iu)-1}e^{-x}-1}\,dx\,du$$

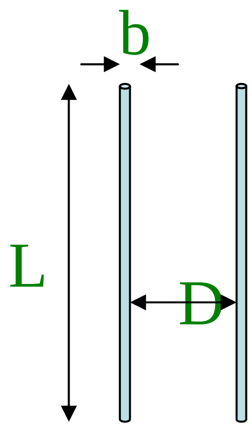
Most present functionals similarly give D^{-2} for this geometry ✓

More simple standard results for macroscopic systems: nanoscopically thin slabs, wires

ΣR^{-6} gives

$$E/A \propto -A^{-1}\int_{S2} d^2 r_1 \int_{S1} d^2 r_2\, r_{12}^{-6} = -CD^{-4}$$





L>>D>>b

ΣR^{-6} gives

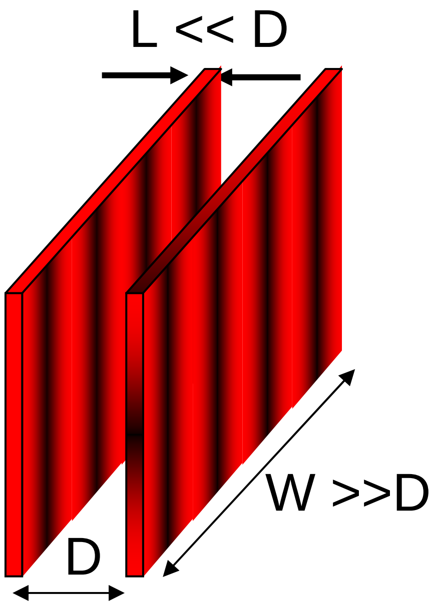
$$E/L \propto -\int_2 dx_2\, r_{12}^{-6} = -CD^{-5}$$

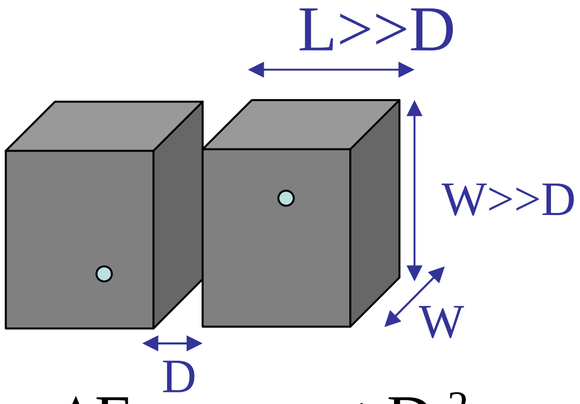
Different powers of D emerge, but these results are **"universal"** :
i.e.   they come from adding pairwise R^{-6} contributions.

Most new functionals agree with this, and indeed some are constructed to give ΣR^{-6}, but actually ΣR^{-6} is WRONG for metallic cases above.

Distant vdW interaction from coupled-plasmon ZPE / RPA - preview

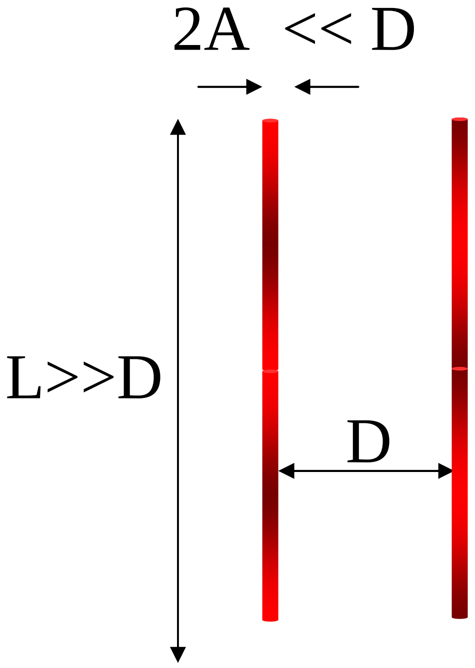
J. F. Dobson, A. White and A. Rubio, Phys. Rev. Lett. 96, 073201, 2006





$\Delta E_c \sim \text{const } D^{-2}$

(metallic or insulating)



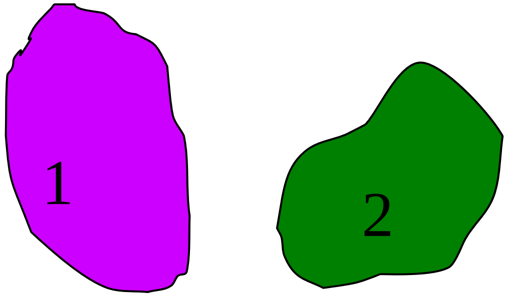
$$\Delta E_c \sim \begin{cases} -AD^{-5/2} & \text{conducting} \\ -BD^{-4} & \text{insulating} \\ -CD^{-3} & \text{pi} - \text{conj (graphene)} \end{cases}$$

$$\Delta E_c \sim \begin{cases} -KD^{-2}[\ln(D/A)]^{-3/2} & \text{metallic} \\ -CD^{-5} & \text{insulating} \end{cases}$$

- Insulators, **3D** metals: $\Sigma C_6 R^{-6}$ gives qualitatively OK results, but
- $\Sigma \mathbf{C_6 R^{-6}}$ can be very wrong for anisotropic **nano**conductors where electrons can move large distances leading to large polarizations, **poorly screened because low-Dim**

A unified way to derive unusual vdW power laws: W_{12} perturbation theory (NOT MP2)

$$E^{(2)} = \sum_{a,b} \frac{\left|\langle ab | W_{12} | 00 \rangle\right|^2}{E_0^{(1)} + E_0^{(2)} - E_a^{(1)} - E_b^{(2)}}$$



$$E_{12}^{(2)} = -\frac{\hbar}{2\pi} \int d^3r_1 d^3r_{1'} d^3r_2 d^3r_{2'} \frac{e^2}{r_{12}} \frac{e^2}{r'_{12}}$$

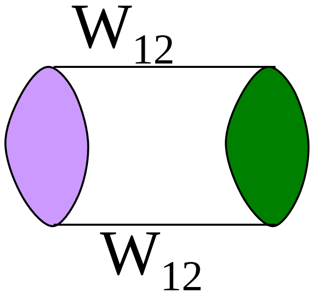
$$\times \int_0^\infty \chi_2(\vec{r}_1, \vec{r}_1{}', iu)\, \chi_2(\vec{r}_2, \vec{r}_2{}', iu)\, du$$

Gen. nonoverlapping

finite systems

nonlocal dens-dens resp of system 2 (incl W_{22} to all orders)

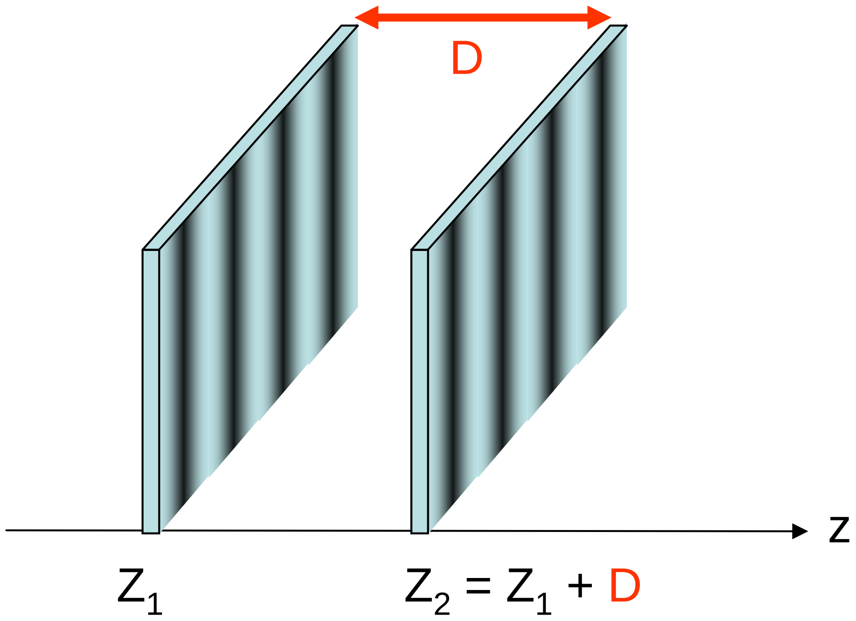
`H.C. Longuet-Higgins, Disc. Faraday Soc. 40, 7 (1965).`
`E. Zaremba and W. Kohn, P.R.B 13 2270 (1976).`



"ZK formula"

vdW Power law is correct but prefactor may be off for planar cases

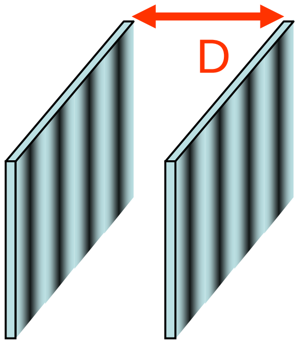
2ND ORDER DISPERSION INTERACTION FOR TWO PARALLEL PLANAR SYSTEMS



$$\chi_1(\vec{r},\vec{r}\,',iu)=\delta(z-Z_1)\delta(z'-Z_1)\frac{1}{(2\pi)^2}\int\overline{\chi}_1(q_\parallel,iu)\exp(i\vec{q}_\parallel.(\vec{r}_\parallel-\vec{r}_\parallel\,'))d^2q_\parallel$$

$$\frac{E^{(2)}(D)}{A}=\frac{-\hbar}{(2\pi)^3}\int_0^\infty 2\pi q_\parallel dq_\parallel\left(\frac{2\pi e^2\exp(-q_\parallel D)}{q_\parallel}\right)^2\int_0^\infty du\,\overline{\chi}_1(q_\parallel,iu)\overline{\chi}_2(q_\parallel,iu)$$

DISTANT 2ND ORDER DISPERSION INTERACTION : PLANAR METAL OR INSULATOR



$$\bar{\chi}_0(q,iu) = \frac{-n_{2D}q^2}{m_{eff}(u^2+\omega_0{}^2)} \qquad Bare$$

$V_{ee} = 2\pi e^2/q$

$$\bar{\chi}(q,iu) = \frac{-n_{2D}q^2}{m_{eff}(u^2+\omega_0{}^2+\omega^2{}_{2D}(q))} \qquad RPA-screened$$

Pinning frequency ω_0

(zero for metal)

$$\omega_{2D} = q^{1/2}\sqrt{2\pi n_{2D}e^2 m_{eff}{}^{-1}}$$ 2D plasma frequency

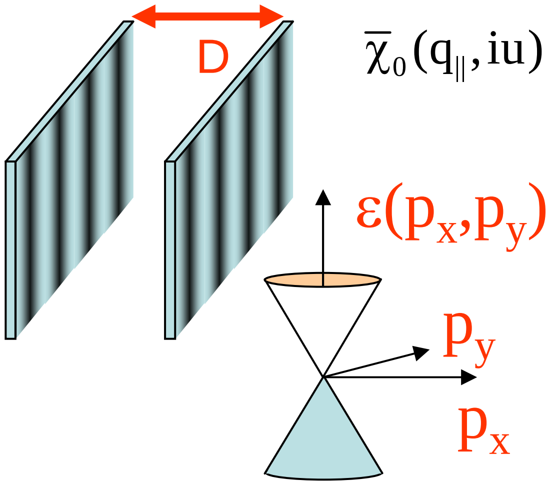
Insulating case, large separation: $q \sim D^{-1} \to 0$, $\omega_{2D} \ll \omega_0$

$$\frac{E^{(2)}}{A} = \frac{-\hbar}{(2\pi)^3}\int_0^\infty 2\pi q_\| dq_\| \left(\frac{2\pi e^2\exp(-q_\| D)}{q_\|}\right)^2 \int_0^\infty \left(\frac{n_{2D}q_\|{}^2}{m_{eff}(u^2+\omega_0{}^2)}\right)^2 du = -\frac{3}{16}\frac{\hbar\pi e^4 n_{2D}{}^2}{m_{eff}{}^2\omega_0{}^3}D^{-4}$$

Metallic case, $\omega_0 = 0$ (no pinning of electrons)

$$\frac{E^{(2)}}{A} = -\frac{\hbar}{16\pi}(\frac{2\pi n_{2D}e^2}{m_{eff}})^{1/2}\int_0^\infty q_\|{}^{3/2}e^{-2q_\| D}dq_\| = -1.17\times10^{-2}\hbar(\frac{2\pi n_{2D}e^2}{m_{eff}})^{1/2}D^{-5/2}$$

2ND ORDER DISPERSION INTERACTION: 2 GRAPHENE PLANES (T=0K)



Bandstructure of single graphene plane (semimetal)

$$\bar{\chi}_0(q_\parallel, iu) = \frac{-q_\parallel}{2\hbar v_0\sqrt{1+\left(\frac{u}{v_0 q_\parallel}\right)^2}} \qquad (q_\parallel \to 0)$$

= U

$c.f.$

$$\bar{\chi}_0 = -n_{2D} q_\parallel^{\,2} / m u^2 \quad (2D\ \ metal)$$

$$\bar{\chi}_0 = N_{02D} q_\parallel^{\,2} / m \omega_0^{\,2} \quad (2D\ insulator)$$

$$\bar{\chi} = \frac{-q_\parallel}{2\hbar v_0\sqrt{1+\left(\frac{u}{v_0 q_\parallel}\right)^2}\left(1+\frac{2\pi e^2}{q_\parallel}\frac{q_\parallel}{2\hbar v_0\sqrt{\ldots}}\right)}$$

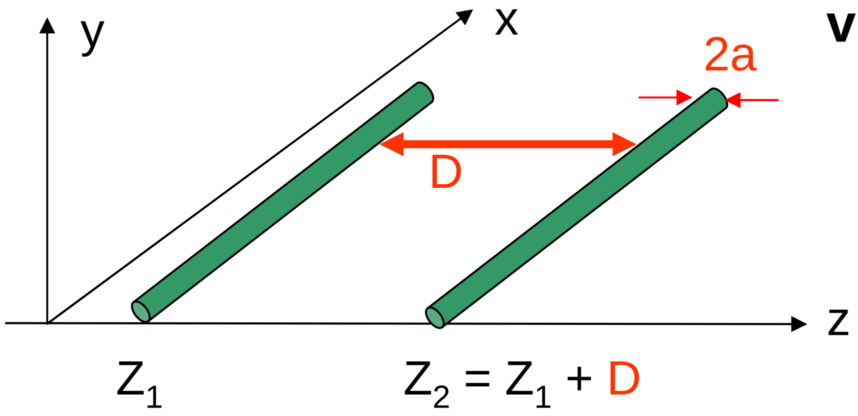
= x

$$\frac{E^{(2)}}{A} = \frac{-\hbar}{(2\pi)^3}\int_0^\infty 2\pi q_\parallel dq_\parallel \left(\frac{2\pi e^2 \exp(-q_\parallel D)}{q_\parallel}\right)^2 \left(\frac{q_\parallel}{2\hbar v_0}\right)^2 \int_0^\infty \frac{v_0 q_\parallel dU}{\left(\left(1+U^2\right)^{1/2}+\frac{\pi e^2}{\hbar v_0}\right)^2}$$

$$= -\frac{e^2}{D^3}\left(\frac{e^2}{\hbar v_0}\right)^{1/2}\int_0^\infty x^2 e^{-2x} dx \int_0^\infty \frac{dU}{\left(\left(1+U^2\right)^{1/2}+\frac{\pi e^2}{\hbar v_0}\right)^2} = -1.97\times 10^{-2} e^2 D^{-3}$$

c.f. D^{-4} from ΣR^{-6}

JFD, White, Rubio PRL 06



vdW interaction betw quasi-1D metals

(e.g. infinitely long metallic nanotubes)

$$V_{ee}(q) = -2e^2 \ln(qa) \quad \textit{on one wire},$$

$$V_{ee}(q) = 2e^2 K_0(qD) \quad \textit{between 2 wires}$$

$$\chi(\vec{r},\vec{r}\,',iu) = \delta^2(\vec{r}_\perp - Z\hat{x})\delta^2(\vec{r}_\perp\,' - Z\hat{z})\frac{1}{2\pi}\int_{-\infty}^{\infty}\bar{\chi}(q_\parallel, iu)\exp(i\vec{q}_\parallel(x-x')dq_\parallel$$

$$\delta n = q^2 N_{1D} m^{-1}\omega^{-2}(\delta V^{ext}(q) - 2e^2\ln(qa)\delta n), \quad (SelfCons\ RPA\ \ screening)$$

$$\chi_1 = \frac{\delta n(q)}{\delta V^{ext}(q)} = \frac{q^2 N_{1D}}{m(\omega^2 - \omega_{1D}{}^2(q))}, \qquad \omega_{1D} = \sqrt{2N_0 e^2 m^{-2}}\, q\sqrt{|\ln(qa)|}$$

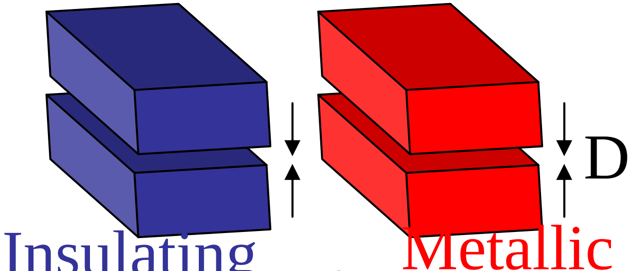
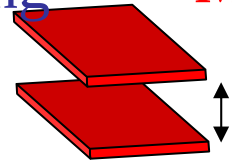
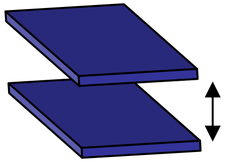
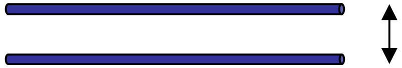
$$E^{(2)}/L = \frac{-\hbar}{(2\pi)^2}\int_{-\infty}^{\infty} dq_\parallel \left(2e^2 K_0(q_\parallel D)\right)^2 \int_0^\infty \left(\frac{N_{1D} q_\parallel{}^2}{m_{1D}(u^2+\omega_{1D})^2}\right)^2 du$$

$$E^{(2)}/L = -\frac{\hbar c_{1D}}{8\pi D^2}\int_0^\infty x K_0{}^2(x)\left|\ln(ax/D)\right|^{-3/2} dx \approx -\frac{\hbar c_{1D}}{16\pi D^2}\left|\ln(ax_0/D)\right|^{-3/2}$$

cf. D^{-5} in conv theories

Now verified by DMC (Drummond & Needs subm 07)

ASYMPTOTICS $D \rightarrow \infty$

	Present theory Coupled plasmon, RPA Dobson et al PRL 2006	Conv. theories ΣR^{-6}, "vdW-DF"
	$E \propto -D^{-2}$	$E \propto -D^{-2}$
	**$E \propto -D^{-5/2}$**	$E \propto -D^{-4}$
	$E \propto -D^{-4}$	$E \propto -D^{-4}$
	**$E \propto -D^{-3}$**	$E \propto -D^{-4}$
	**$E \propto -D^{-2} (\ln D/b)^{-3/2}$**	$E \propto -D^{-5}$
	$E \propto -D^{-5}$	$E \propto -D^{-5}$
		

CO-AXIAL “POINTING” WIRES / NANOTUBES

JFD and Angela white, PRB subm.

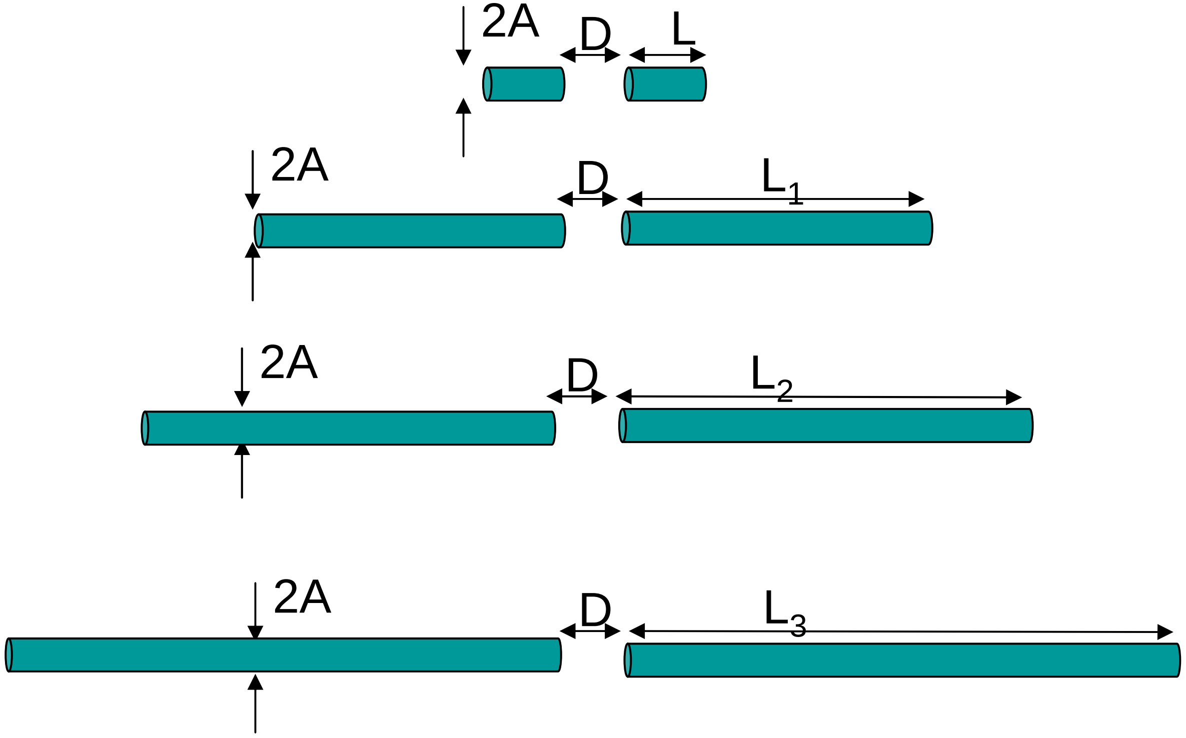
Calculation by summing zero-pt energies of coupled RPA plasmons (not pert^n)

Metallic case has enhanced forces c/w insulating case

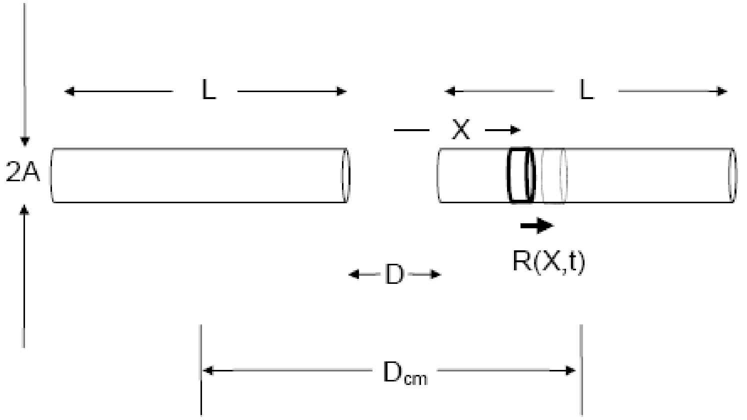
New finding: True even at small separations

(non-asymptotic but no e$^-$cloud overlap yet)

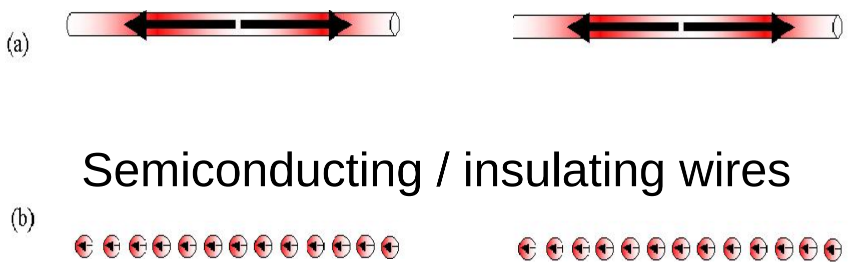
Theory gives finite E_{vdW} at D = 0 – i.e. it saturates



Method: Numerical sum-of-zero point energies $\hbar\Omega_i/2$ of coupled plasmons



Metallic wires



Semiconducting / insulating wires

Field due to electrons

Pinning to mimic insulator

Electron degeneracy pressure

$$-M\Omega^2 R(X) = -\frac{\partial}{\partial X}\Phi(X) - M\Omega_{pin}{}^2 R(X) - MB^2\frac{\partial^2 R}{\partial X^2}$$

$$\Phi(X) = \left(\int_{-L-D/2}^{-D/2} + \int_{D/2}^{L+D/2}\right)\tilde{\phi}(X - X')\delta n(X') \qquad (RPA!!)$$

$$\delta n(X') = -\frac{\partial}{\partial X}(n_0(X)R(X))$$

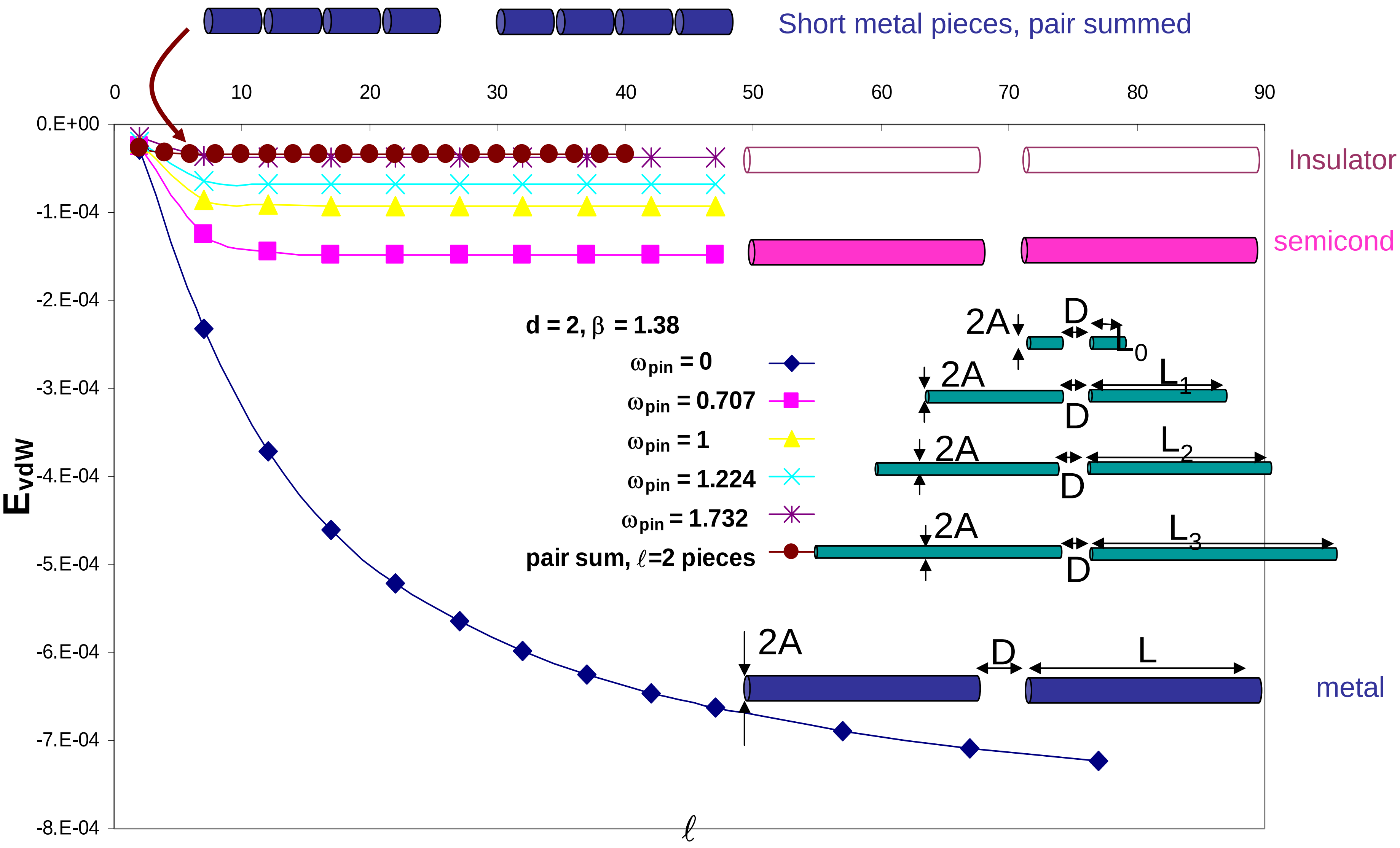
$$\tilde{\phi}(X) = \frac{e^2}{\sqrt{X^2 + A^2}}$$

Coulomb smeared for finite wire width

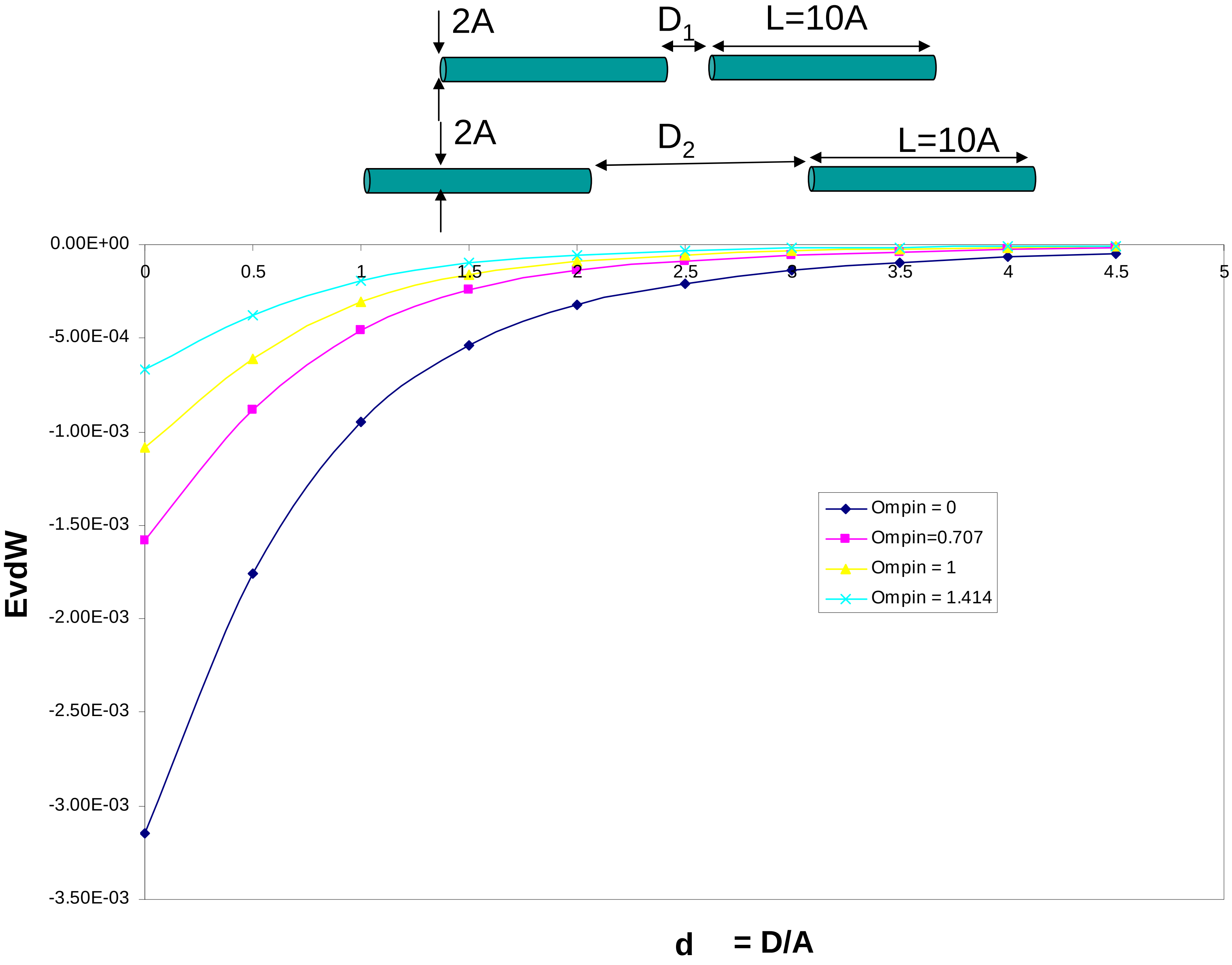
$$E^{disp} = \Sigma_i\left(\frac{\hbar\Omega_i(D)}{2} - \frac{\hbar\Omega_i(D\to\infty)}{2}\right)$$

vdW energy for fixed separation d = D / A = 2

versus wire length ℓ = L / A



New ZPP dispersion energy saturates naturally at zero separation



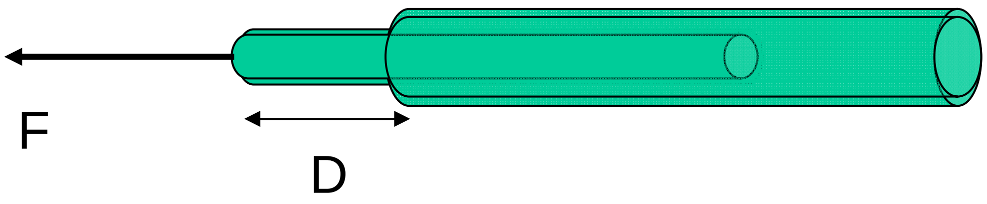
REALISTIC GEOMETRY, ELECTRON CLOUD OVERLAP?

Can’t use perturbation theory, can’t distinguish e^-s on the two subsystems

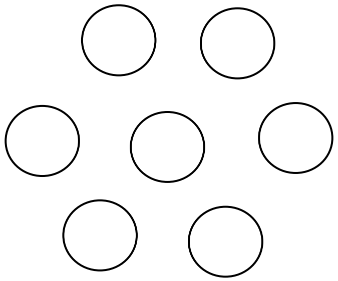
FULL E$_{correlation}$ (IN RPA OR HIGHER MBT) FOR TRUE GEOMETRY?

Problem: no-one has yet converged E_c^{RPA} for graphitics!

SUPER-NONLOCAL CORRECTION TO MORE CONVENTIONAL DFT+ ΣR^{-6} THEORY?



telescope tubes



tube bundles /
arrays

$$E = E_{\text{combined}}(\text{true geometry, LDA} + \Sigma R^{-6})$$

$$+ E(\text{simple geom, plasmon}) - E(\text{simple geom, } \Sigma R^{-6})$$

When is E_{vdW} NOT $\approx \Sigma C_{ij} R_{ij}^{-6}$ for large R_{ij}?

(i) System is **large** in at least one direction, so that long-wavelength fluctuations ($q \rightarrow 0$) are possible

(ii) System is **metallic** or has **zero electronic gap**, so bare polarizability $q^{-2}\chi_0$ becomes large at low ω and q

(iii) System is **nanoscopic** in at least one dimension, so that coulomb screening is incomplete and does not destroy the divergence of the polarizability $q^{-2}\chi_0$ at low ω and q. (ε is nonlocal)

$\Rightarrow$ **Highly anisotropic soft near-metallic** matter

e.g. parallel nanotube arrays

layered graphitic systems, intercalates etc.)

Where free plasmons are present, they will be gapless ($\omega(q) \rightarrow 0$ as $q \rightarrow 0$)

JFD et al, PRL **96**, 073201 (2006), cond-mat/0502422, Surf Sci in press

IJQC **101**, 579 (2005), .ICONN conf (IEEE Cat No. 06EX1411C)