STRANGE Van Der Waals POWER LAWS FROM NONLOCAL RESPONSE

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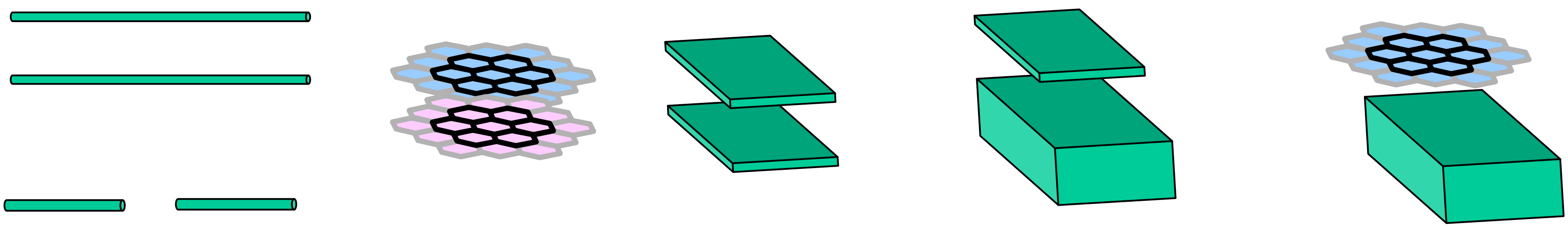
Failures of common van der Waals theories in the asymptotic (widely-spaced) limit: some surprising force laws for anisotropic low-D, zero-electronic-gap systems



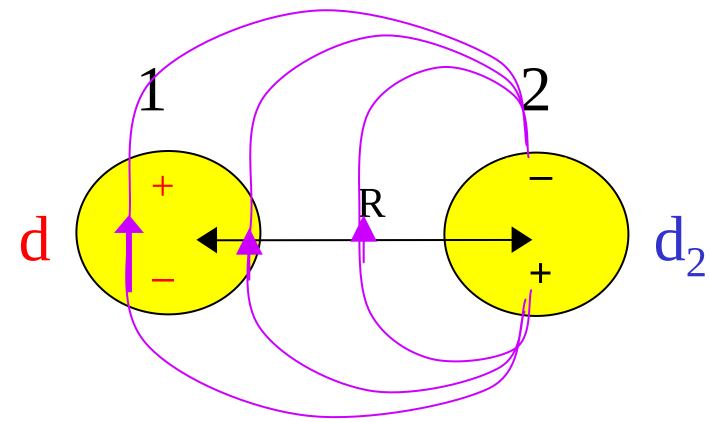
Failures of common theories for condensed limit (not widely spaced)?

Conclusion: need new functionals for soft-matter energetics

JFD et al, Phys Rev Lett 96, 073201 (2006), cond-mat/0502422

vdW betw. spherical atoms: matter fluctuation approach

Random zero-point (or thermal) dipole d on #1 initiates the process



Field on #2: $F_2 = -\dfrac{d}{R^3}$

Field Induces dipole on #2: $d_2 = -\alpha_2 \dfrac{d}{R^3}$

d_2 generates back-field on #1: $F_1 = -\dfrac{d_2}{R^3} = \dfrac{d\alpha_2}{R^6}$

Energy of F_1 with original dipole: $E \propto -F_1 d = -\dfrac{d^2 \alpha_2}{R^6}$

Time-averaged energy $\langle E \rangle = -\dfrac{\langle d^2 \rangle \alpha_2}{R^6} \approx -\dfrac{(\alpha_1 \hbar \omega_0)\alpha_2}{R^6}$ by *SHO* model

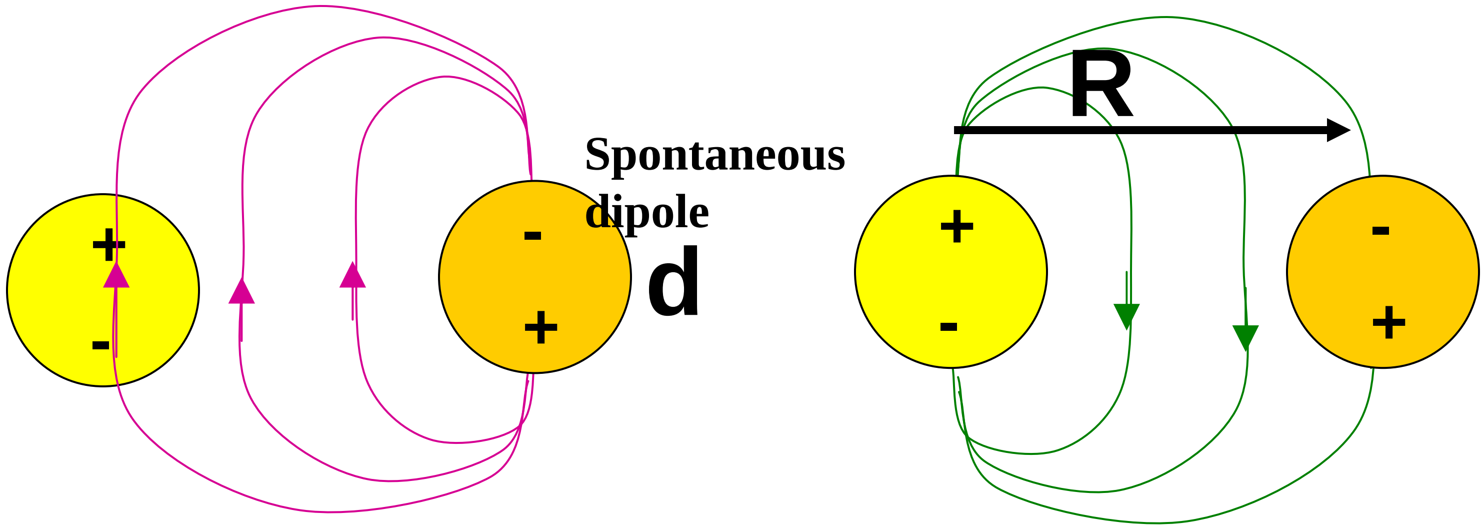
More accurate: $E = -C_6 R^{-6}, \quad C_6 = \dfrac{3\hbar}{\pi} \displaystyle\int_0^\infty \alpha_1(iu)\alpha_2(iu)\,du$

From 2^{nd} order Pertn th.

Incl. ZP KE

This form isotropic only

ORIGIN OF DISTANT VDW (DISPERSION) FORCE



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

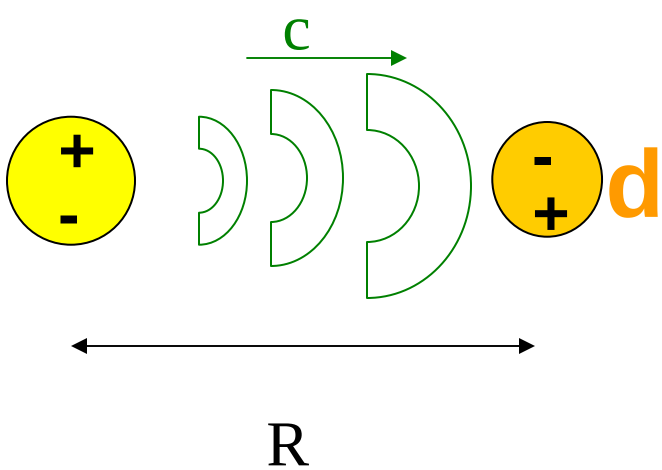
A correlation effect, highly nonlocal so LDA & GGA FAIL

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

Or via theory of response (polarisability, coupled plasmons)

Weak but ubiquitous - additional to covalent, ionic bonds

Electromagnetic retardation



Above treatments assumed instantaneous Coulomb interaction. In fact there is a delay $\tau_{light} \approx R/c$

If $\tau_{light} >> \tau_{el\ resp}$, then the original random dipole has decayed by the time a return signal arrives, resulting in a smaller attractive energy.

End result is to replace ω in previous results by $1/\tau_{light}$ so that

$$E^{\text{retarded regime}} \approx -\frac{\alpha_1 \alpha_2 \hbar c}{R^7}$$

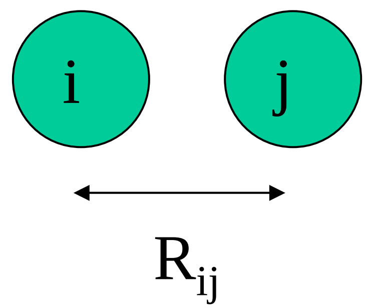
Condition for this to occur:

$R >> c\tau_{el\ resp} \approx (3.10^8)(2\pi.10^{-15}) \approx 2.10^{-6}$ m

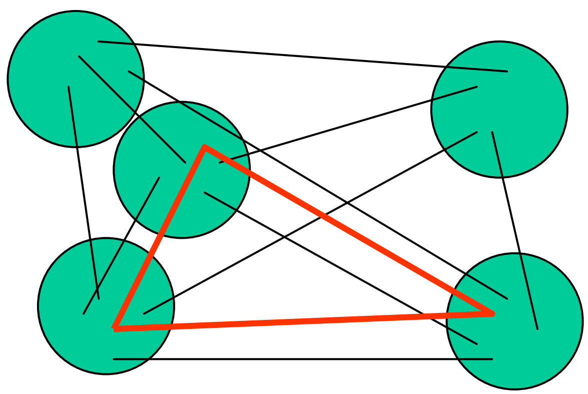
Treat non-retarded case from here on

Retarded case generally known as "Casimir effect": can get from e.m. ZP energy.

Conventional view: "universality" of asymptotic vdW



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



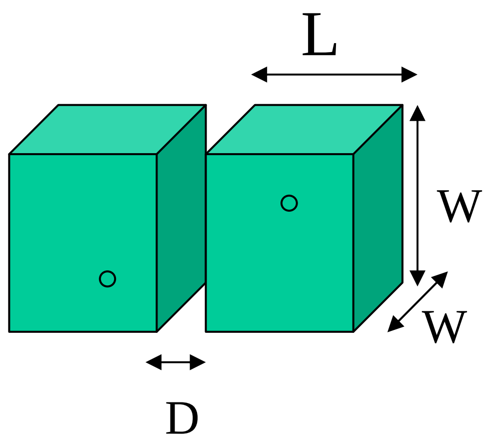
"Then total E_{vdW} is the sum of pairwise contributions

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

"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 <u>qualitative</u> difference."

Standard vdW theories for macroscopic systems (non-overlapping)



Thick slabs, L, W >>D

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

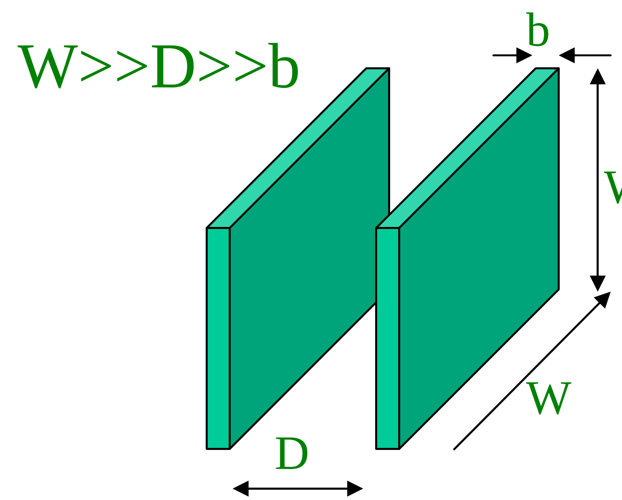
$$E/A \propto -A^{-1}\int_{V_1} d^3 r_1 \int_{V_2} d^3 r_2 r_{12}^{-6} = -CD^{-2}$$

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

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

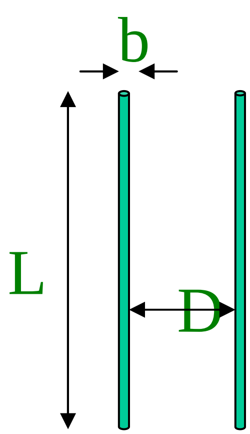
Most present functionals similarly give D^{-2} for this geometry ✔

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



ΣR^{-6} gives

$$E/A \propto -A^{-1}\int_{S2} d^2 r_1 \int_{S1} d^2 r_2 r_{12}^{-6} = -C\color{blue}{D}^{-4}$$



L>>D>>b

ΣR^{-6} gives

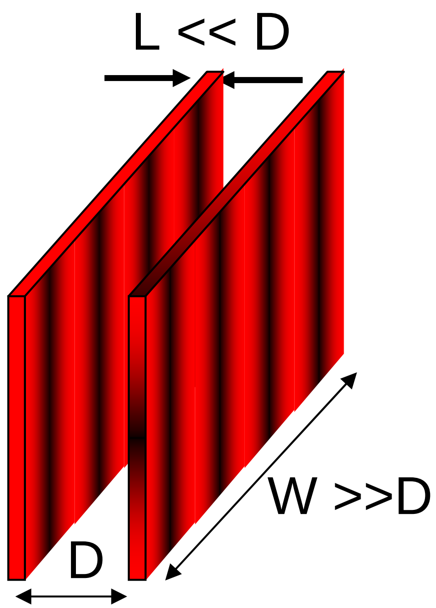
$$E/L \propto -\int_{2} dx_2 r_{12}^{-6} = -C\color{blue}{D}^{-5}$$

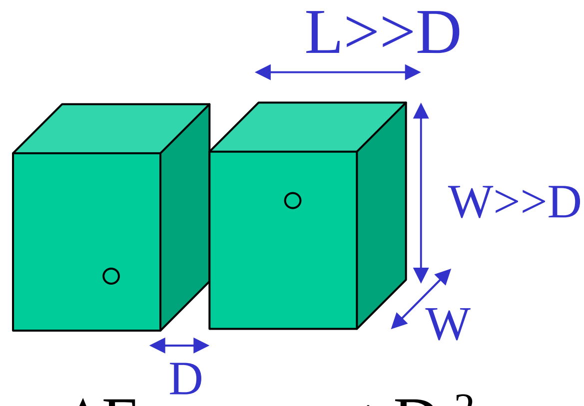
Different powers of D emerge, but these results are **"universal"** : i.e. they come from adding pairwise R^{-6} contributions.

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

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

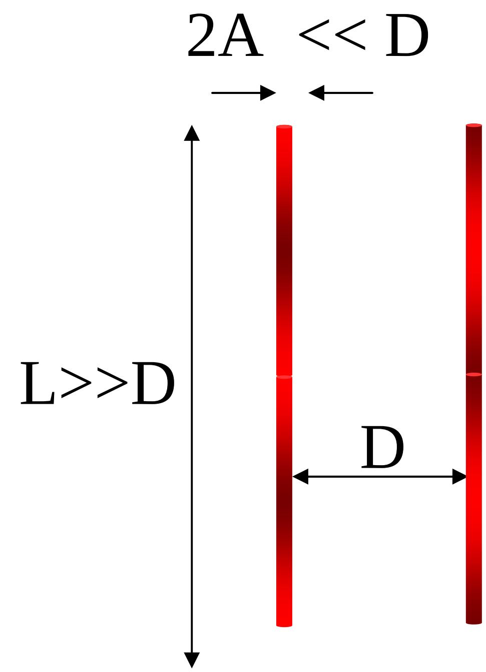
J. F. Dobson, A. White and A. Rubio, Phys. Rev. Lett. 96, 073201, Feb 2006





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

(metallic or insulating)



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

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

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

What causes the strange power laws $E=-CD^{-p}$?

Spatial Nonlocality of the response of the matter (electrons) to fluctuating electric fields

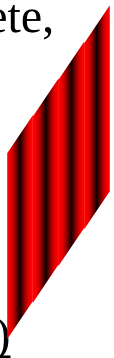
A: Strange power laws at "large" separations D (but still not in the regime of E.M. retardation)

The examples here come from the anomalously large response of charge fluctuations (e.g. plasmons) that have a very long wavelength ($q \approx D^{-1} \to 0$) and low frequency. The nonlocality means that dielectric function $\varepsilon(q,\omega)$ depends on q, when $q \to 0$.
(ie. ε is $\varepsilon(\underline{r},\underline{r}',\omega)$ in position space, NOT $\propto \delta(\underline{r}-\underline{r}')$)

In metals, one might think that electrons respond nonlocally: but in 3D there is essentially complete screening of external fields, which cancels this out. In fact for a 3D metal

$\varepsilon(q,\omega)=1-V(q)\chi_0(q,\omega) = 1 - [4\pi e^2/q^2][n_0 q^2/m\omega^2] = 1 - \omega_P^2/\omega^2$, INDEP OF q (spatially local).

However in LOWER-DIMENSIONAL metallic structures, Coulomb screening is incomplete, and the dielectric function can be q-dependent at small q and ω
e.g. for a 2DEG, $\varepsilon(q_{||},\omega)=1-V_{2D}(q_{||})\chi_0(q_{||},\omega) = 1- [2\pi e^2/q_{||}][n_{2D}q_{||}2/m\omega^2] = 1- \omega_{2D}(q_{||})^2/\omega^2$,
$\omega_{2D}(q_{||}) = [2\pi n_{2D} m^{-1} q_{||}]^{1/2}$



B: Strange power laws at "small" separations (but electron clouds not yet overlapped)

This can occur when separation D $\approx$ (char electronic length λ) e.g. λ_{Debye} for e-h plasma (semic.)

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 ($q \to 0$) 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)

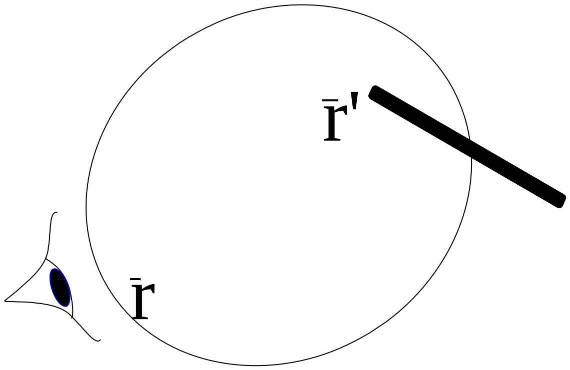
$\Rightarrow$ **Highly anisotropic soft near-metallic** matter
e.g. conducting nanotubes
layered graphitic systems, intercalates etc.)

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

JFD et al, PRL **96**, 073201 (2006), cond-mat/0502422, Surf Sci **601**, 5667 (2007)
IJQC **101**, 579 (2005), PRB 77, 075436 ('08); 165134 (08), cond-mat/0809.0736

Electronic response functions in TDDFT

(exact but looks like mean-field theory)



Density-density response function χ_λ

$$\delta n(\vec{r})\exp(-i\omega t) = \int \chi_\lambda(\vec{r},\vec{r}\,',\omega)\,\delta V(\vec{r}\,')\exp(-i\omega t)\,d\vec{r}\,'$$

Bare Resp $\chi_{KS} \equiv \chi_{\lambda=0}$ to ext field (one-body physics)

Bare Response to int field

$$\chi_\lambda(\vec{r},\vec{r}\,',\omega) = \chi_{KS}(\vec{r},\vec{r}\,',\omega) + \int \chi_{KS}(\vec{r},\vec{r}\,'',\omega) \times \int \left(\frac{\lambda e^2}{\left|\vec{r}\,''-\vec{r}\,'''\right|} + \cancel{f_{xc\lambda}(\vec{r},\vec{r}\,',\omega)} \right) \chi_\lambda(\vec{r}\,''',\vec{r}\,',\omega)\,d\vec{r}\,'''\,d\vec{r}\,''.$$

$$\chi_\lambda = \chi_0 + \chi_0 W_\lambda \chi_\lambda$$

$\Rightarrow$ **RPA,TDH**

Eff. Internal field **(beyond-RPA MB physics)**

EXACT ADIABATIC CONNECTION-FDT APPROACH FOR CORRELATION ENERGY (INCL VDW)

$$E_{xc} = \frac{1}{2}\int_0^1 d\lambda \int d^3r\, d^3r' \frac{e^2}{|\vec{r}-\vec{r}\,'|}\left\{< \delta\hat{n}(\vec{r})\delta\hat{n}(\vec{r}\,') >_\lambda - n(\vec{r})\delta(\vec{r}-\vec{r}\,')\right\}$$

$\downarrow$

Zero-tempFluct-dissipation thm

$\downarrow$

$$\boxed{E_{xc} = \frac{1}{2}\int_0^1 d\lambda \int d^3r\, d^3r' \frac{e^2}{|\vec{r}-\vec{r}\,'|}\left\{[-\frac{\hbar}{\pi}\int_0^\infty \chi_\lambda(\vec{r},\vec{r}\,',\omega = iu)du] - n(\vec{r})\delta(\vec{r}-\vec{r}\,')\right\}}$$

ACF-FDT (exact)

$$E_{x} = \frac{1}{2}\int_0^1 d\lambda \int d^3r\, d^3r' \frac{e^2}{|\vec{r}-\vec{r}\,'|}\left\{[-\frac{\hbar}{\pi}\int_0^\infty \chi_{KS}(\vec{r},\vec{r}\,',\omega = iu)du] - n(\vec{r})\delta(\vec{r}-\vec{r}\,')\right\}$$

Insert expr. for χ_{KS} from $\{\phi_i\}$ $\Rightarrow$ $E_x = E^{HF}(\{\phi_i\})$

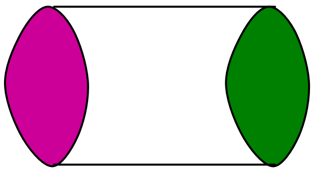
Our E_{xc} contains EXACT DFT EXCHANGE (hence covalent bonds)

Can show χ_{RPA} gives asy $-C_6R^{-6}$ result for vdW betw small systs.

ACF/FDT STARTING WITH χ_{KS} CONTAIN ALL THE BASIC CHEMICAL AND PHYSICAL FORCES - II

$$E_C = \frac{1}{2}\int_0^1 d\lambda \int d^3r\, d^3r' \frac{-e^2}{|\vec{r}-\vec{r}\,'|}\frac{\hbar}{\pi}\int_0^\infty \left[\chi_\lambda(\vec{r},\vec{r}\,',\omega=iu) - \chi_{KS}(\vec{r},\vec{r}\,',\omega=iu)\right]du$$

RPA $\Rightarrow$ vdW (Casimir-Polder):



E.g. for isolated spherical systems in the dipolar approx,

$$\chi_\lambda = \chi_\lambda^{RPA} \Rightarrow E^{(2)} = -\frac{3\hbar}{\pi R^6}\int_0^\infty A_a^{RPA}(iu)\; A_b^{RPA}(iu)du$$

This is the exact result from perturbation theory except $A \rightarrow A^{RPA}$

Result does not appear to be true for RPA+<u>approx</u> f_{xc}!

JFD pp 121-142 in 'Topics in condensed matter physics', Ed. M.P. Das, (Nova, NY 1994, ISBN 1560721804.) (Hard to get: reproduced in **cond-mat/0311371**)

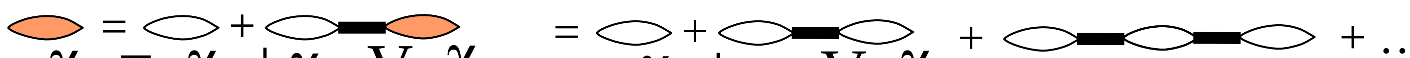
CORRELATION ENERGY VIA RPA-LIKE SCHEMES

•Want electronic groundstate energies of extended systems,

•with "seamless" treatment of all forces incl. vdW, at any separation

•**<u>RPA</u>** is a <u>response-based</u> energy scheme: gets covalent, electrostatic bonds and does not rely on non-overlap condition

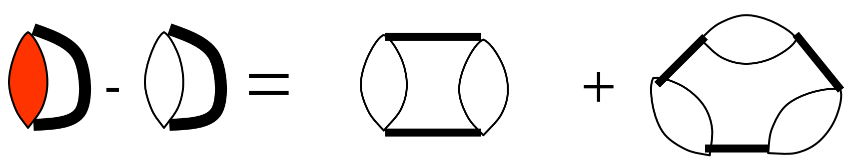
$$\chi_\lambda^{RPA} = \varepsilon_{RPA}^{-1}\chi_0 = (1 - V_\lambda \chi_0)^{-1}\chi_0$$



$$\chi_\lambda = \chi_0 + \chi_0 V_\lambda \chi_\lambda = \chi_0 + \chi_0 V_\lambda \chi_0 + \ldots$$

$$E_{c,RPA} = \frac{\hbar}{2\pi}\int_0^1 \frac{d\lambda}{\lambda}\int_0^\infty du\, Tr\left(V_\lambda * (\chi^{RPA}{}_\lambda - \chi_0)\right) = \frac{\hbar}{2\pi}\int_0^1 d\lambda \int_0^\infty du\, Tr\left(\left(\varepsilon_{RPA,\lambda}{}^{-1} - 1\right)\chi_0\right)$$

$$= \frac{\hbar}{2\pi}\int_0^\infty du Tr \ln\left(1 - V_{\lambda=1}\chi_0\right) + \Delta \quad (\Delta \; indep \; of \; separation)$$

E^c_{RPA} =  + ... **<u>Infinite</u>** Sum of rings values of the products of the operators will not reduce to averages by pairs.

We now proceed as follows. In the perturbation series for the free energy (or for the Green function of the long wavelength photons) the particle operators appear only in combinations of the form

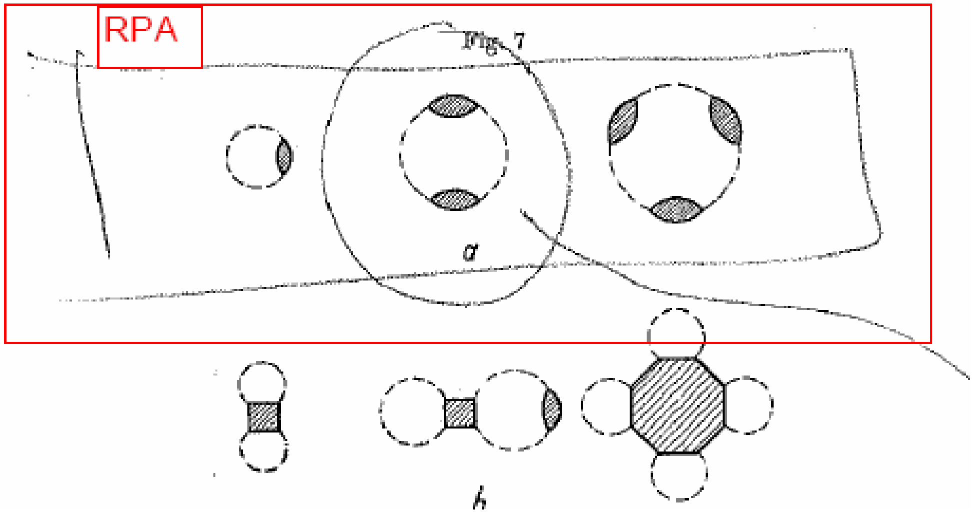
$$\langle T_\tau\{\bar\psi(\mathbf{r}_1,\tau_1)\psi(\mathbf{r}_1,\tau_1)\bar\psi(\mathbf{r}_2,\tau_2)\psi(\mathbf{r}_2,\tau_2)\}\rangle,$$
$$\langle T_\tau\{\bar\psi(\mathbf{r}_1,\tau_1)\psi(\mathbf{r}_1,\tau_1)\bar\psi(\mathbf{r}_2,\tau_2)\psi(\mathbf{r}_2,\tau_2)\bar\psi(\mathbf{r}_3,\tau_3)\psi(\mathbf{r}_3,\tau_3)\bar\psi(\mathbf{r}_4,\tau_4)\psi(\mathbf{r}_4,\tau_4)\}\rangle, \text{ etc.}$$

i.e. the number of operators under the averaging sign is always divisible by four, and the operators always appear in pairs of the type $\bar\psi(\mathbf{r},\tau)\psi(\mathbf{r},\tau)$. We subtract from the average value of the product of eight operators the quantity

$$\begin{aligned}&\langle T_\tau\{\bar\psi(\mathbf{r}_1,\tau_1)\psi(\mathbf{r}_1,\tau_1)\bar\psi(\mathbf{r}_2,\tau_2)\psi(\mathbf{r}_2,\tau_2)\}\rangle\langle T_\tau\{\bar\psi(\mathbf{r}_3,\tau_3)\psi(\mathbf{r}_3,\tau_3)\bar\psi(\mathbf{r}_4,\tau_4)\psi(\mathbf{r}_4,\tau_4)\}\rangle\\ &+\langle T_\tau\{\bar\psi(\mathbf{r}_1,\tau_1)\psi(\mathbf{r}_1,\tau_1)\bar\psi(\mathbf{r}_3,\tau_3)\psi(\mathbf{r}_3,\tau_3)\}\rangle\langle T_\tau\{\bar\psi(\mathbf{r}_2,\tau_2)\psi(\mathbf{r}_2,\tau_2)\bar\psi(\mathbf{r}_4,\tau_4)\psi(\mathbf{r}_4,\tau_4)\}\rangle\\ &+\langle T_\tau\{\bar\psi(\mathbf{r}_1,\tau_1)\psi(\mathbf{r}_1,\tau_1)\bar\psi(\mathbf{r}_4,\tau_4)\psi(\mathbf{r}_4,\tau_4)\}\rangle\langle T_\tau\{\bar\psi(\mathbf{r}_2,\tau_2)\psi(\mathbf{r}_2,\tau_2)\bar\psi(\mathbf{r}_3,\tau_3)\psi(\mathbf{r}_3,\tau_3)\}\rangle\end{aligned}$$

(i.e. that value which we would have obtained if the averaging had reduced only to all possible averages by fours of the above type), and we call this difference the irreducible quadrilateral, denoting it by a dashed square.

Fig. 7



Thus for the approximation $k_0 a \ll 1$ only diagrams of the form 7 (*a*) give a correction to the free energy. The corresponding expression for the free energy is

ACF/FDT contains plasmon zero-point energy

see e.g. JFD et al, IJQC **101,** 579-598 (2005)

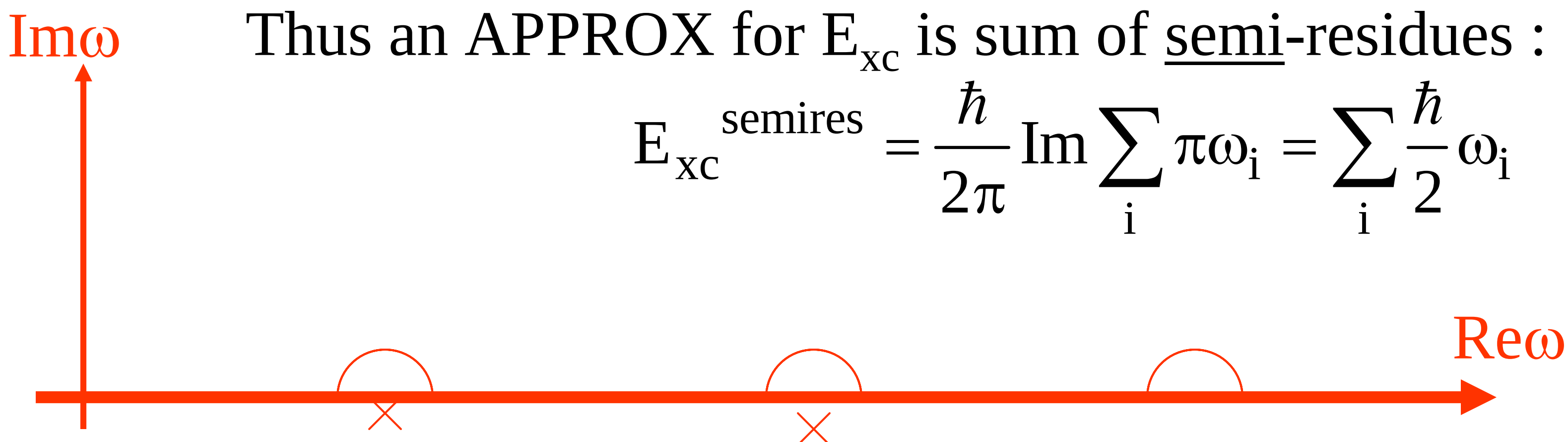
$$E_{xc}^{RPA} = \frac{-\hbar}{2\pi} \mathrm{Im} \int_0^\infty \mathrm{Tr}\left(\ln(1-\chi_0 * v_{coul})\right) d\omega + \Delta, \quad \Delta \text{ indep of } D.$$

$$= \frac{\hbar}{2\pi} \int_0^\infty \omega \frac{\partial a}{\partial \omega} a^{-1} d\omega \; + \Delta, \qquad a(\omega) = \mathrm{Det}(1-\chi_0 * v_{coul})$$

$a(\omega)$ has poles at plasmon frequencies ω_i where screening equation has free oscillation solutions. Residues of $\frac{\partial a}{\partial \omega} a^{-1}$ at these poles are 1.

Thus an APPROX for E_{xc} is sum of <u>semi</u>-residues :

$$E_{xc}^{semires} = \frac{\hbar}{2\pi} \mathrm{Im} \sum_i \pi \omega_i = \sum_i \frac{\hbar}{2} \omega_i$$



If χ_0 is exact or at least obeys time reversal invariance, $\exists$ better result $\Rightarrow$

RPA ENERGY AS SUM OF PLASMON ZERO POINT ENERGIES: I

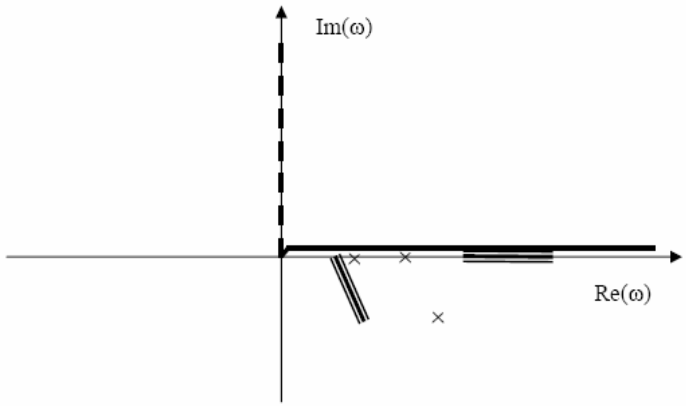


Fig. 5a: Deformation of original contour (▬ ▬ ▬) to just above positive real axis (▬▬▬). By causality, all singularities (e.g. poles × and cuts ═══) must lie on or below the real frequency axis.

JFD et al,
IJQC 101, 579 (2005)

JFD, J. Comp Th. Nanosc.
In press (Oct 08)

indep of separation

$$E_{xc}^{RPA} = \frac{-\hbar}{2\pi}\int_0^\infty d\omega\, Im\int_0^1 d\lambda\, Tr[(1-\lambda\chi_0 * v_{coul})^{-1} * \chi_0 * v_{coul}] + \Delta$$

$$= \frac{-\hbar}{2\pi} Im\int_0^\infty d\omega\, Tr[\ln(1-\chi_0 * v_{coul})] + \Delta.$$

λ integration done analytically

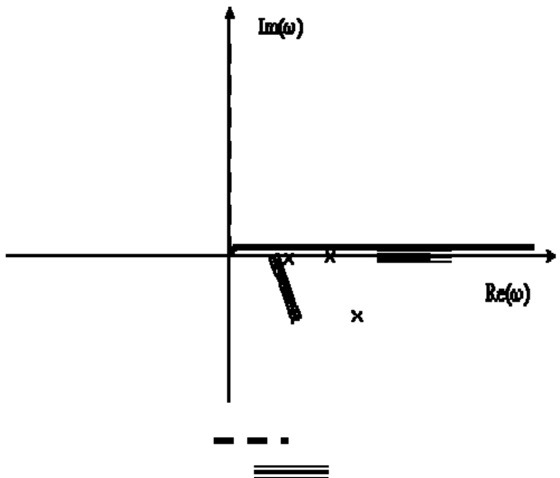
$$E_{xc}^{RPA} = \frac{+\hbar}{2\pi} Im\left(\int_0^\infty \left(\omega\frac{\partial}{\partial\omega}\right) Tr\ln\left((1-\chi_0 * v_{coul})\right)d\omega\right) + \Delta$$

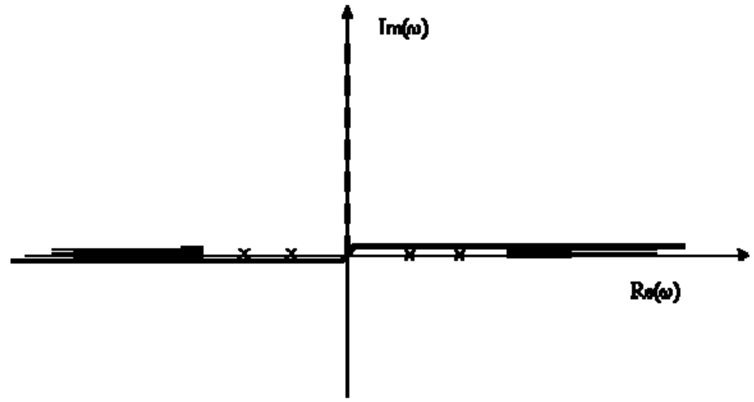
by parts in ω integration

$$= \frac{\hbar}{2\pi} Im\int_0^\infty d\omega\left(\omega\frac{\partial}{\partial\omega}\right)\ln Det\left((1-\chi_0 * v_{coul})\right) + \Delta$$

$$= \frac{\hbar}{2\pi} Im\int_0^\infty \omega\frac{\partial a}{\partial\omega}a^{-1}d\omega + \Delta, \quad a \equiv Det(1-\chi_0 * v_{coul})$$

RPA ENERGY AS THE SUM OF COUPLED PLASMON ENERGIES: II





If * **$\chi(-\omega) = \chi(\omega)$,** contour can be reflected about the origin, giving

$$E^{RPA} = \frac{1}{2}\frac{\hbar}{2\pi}\,\mathrm{Im}\int_{-\infty}^{\infty} \omega \frac{\partial a}{\partial \omega} a^{-1} d\omega + \Delta, \quad a = Det(1-\chi V)$$

In general, the function $f(\omega) = \omega\, a(\omega)^{-1}\, da(\omega)/d\omega$ behaves near its poles ω_i where $a(\omega) \approx a_i\,(\omega-\omega_i)^{-1}$ as

$$f(\omega) = \omega a^{-1}\frac{da}{d\omega} \sim \omega_i a_i^{-1}(\omega-\omega_i)\frac{-a_i}{(\omega-\omega_i)^2} \sim \frac{-\omega_i}{\omega-\omega_i}$$

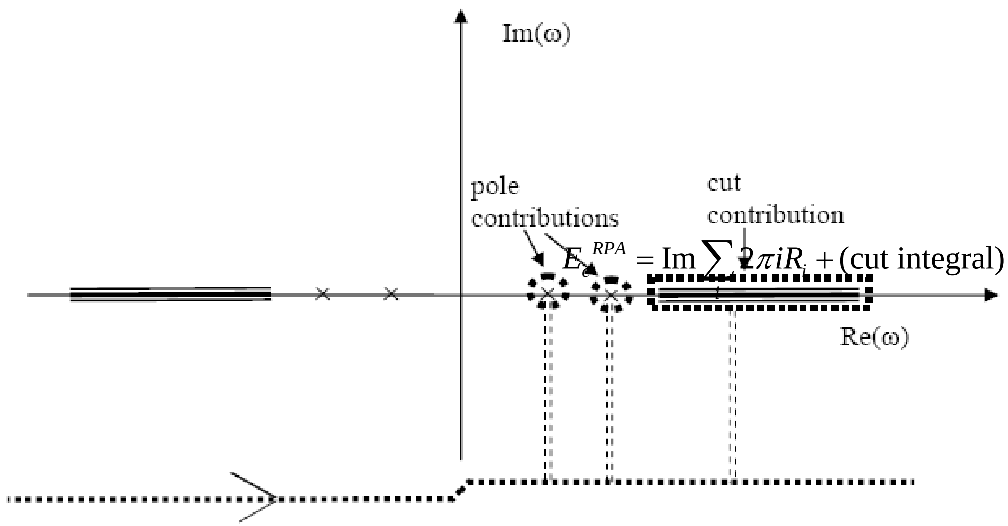
Thus the residues of $f(\omega)$ at $\omega = \omega_i$ are **$R_i = -\omega_i$,**

* This will not be the case for models containing phenomenological damping.

RPA ENERGY AS THE SUM OF COUPLED PLASMON ENERGIES: III

J. F. Dobson , J. Comp Th. Nanosc., in press at Oct 2008

$$E^{RPA} = \frac{1}{2}\frac{\hbar}{2\pi}\,\mathrm{Im}\int_{-\infty}^{\infty}\omega\frac{\partial a}{\partial\omega}a^{-1}d\omega + \Delta, \quad a = Det(1-\chi V)$$



By moving contour to Im(ω) → -∞, we collect (clockwise) pole contributions BUT ALSO IN GENERAL, CUT INTEGRALS

$$E_c^{RPA} = \frac{\hbar}{4\pi}\mathrm{Im}\sum_i(-2\pi i)R_i + (\text{cut integrals}) + \Delta$$

$$= \sum_i \frac{\hbar\omega_i}{2} + (\text{cut integrals}) + \Delta$$

RPA ENERGY AS THE SUM OF COUPLED PLASMON ENERGIES: IV

Following applies even to infinite systems provided the model for density-density response χ obeys full time reversal invariance, $\chi(-\omega) = \chi(\omega)$

$$E_{xc}^{RPA} = \sum_i \frac{\hbar\omega_i}{2} + \text{(cut integrals)} + \Delta$$

Sum of plasmon zero point energies

Cut term can be important in mesoscopic systems – e.g. cut gives the whole answer for vdW attraction in bi-graphene

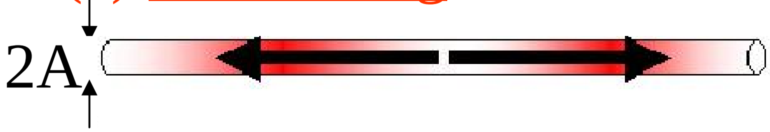
Independent of separation D, as $D \rightarrow \infty$

For finite systems Furche (preprint) has shown that sum of excitation zero-point energies gives E^{RPA} exactly. The cuts above come from the **continuum** excitations (continuous line of poles).

Nanotube attraction I: single wire/tube

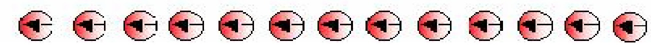
$\lambda = 2\pi/q$

(a) Conducting



$$\frac{\delta n}{\delta V^{tot}} \equiv \chi_0(q,\omega) = n_{1D} q^2 (m\omega^2)^{-1}$$

(b) semiconducting



$$\chi_0(q,\omega) = n_{1D} q^2 (m(\omega^2 - \omega_0{}^2))^{-1}$$

RPA equ.: $\delta n(q,\omega) = \chi_0(q,\omega)\left(\delta V^{ext} + W_{01D}(q)\delta n(q,\omega)\right)$

$$\frac{\delta n}{\delta V^{ext}} = \chi^{RPA} = \frac{\chi_0(q,\omega)}{1 - W_{01D}(q)\chi_0(q,\omega)}, \qquad W_{01D}(q) = 2e^2\left|\ln(qA)\right|$$

Plasmon freqs are zeros of $\varepsilon^{RPA} = 1 - W_{01D}\,\chi_0 = 1 - (\text{const})q^2|\ln(qb)|/\omega^2$

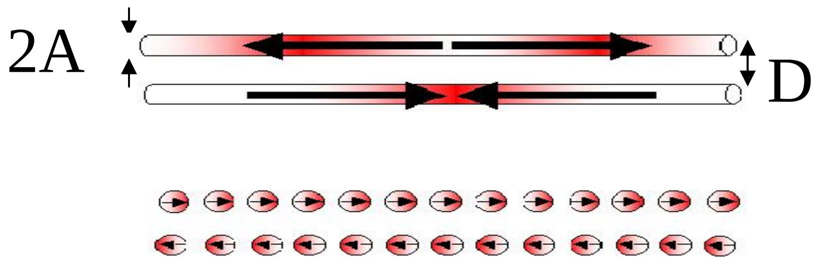
$$c.f. \quad \varepsilon^{3D} = 1 - \frac{4\pi e^2}{q^2}\frac{q^2}{m\omega^2} = 1 - \frac{\omega_{P3D}{}^2}{\omega^2} \quad \textit{indep of } q \;\therefore\; \textit{spatially local}$$

$$\omega^{RPA} = \omega_{1D}(q) \equiv q\sqrt{2n_{1D}e^2m^{-1}\ln(b^{-1}q^{-1})} \qquad \omega^{RPA} = \sqrt{\omega_{1D}{}^2 + \omega_0{}^2}$$

quasi-acoustic plasmon

optical plasmon

Nanotube attraction II: 2 parl'l tubes (D >> A)



Tube-tube coulomb int.

$$W_D(q) = \int_{-\infty}^{\infty} \exp(iqx) \frac{dxe^2}{\sqrt{x^2 + |D|^2}} = 2e^2 K_0(qD)$$

RPA Eq of motion for electron density pert^ns:

$$\delta n_1 = \chi_0(q,\omega)(W_0(q)\delta n_1 + W_D(q)\delta n_2)$$

$$\delta n_2 = \chi_0(q,\omega)(W_D(q)\delta n_1 + W_0(q)\delta n_2)$$

Coupled plasmon frequencies

$$\omega_\pm(q) = \sqrt{\omega_0{}^2 + q^2 m^{-1} n_0 (W(q) \pm W_D(q))}$$

vdW energy in RPA

$$\frac{1}{L} E^{vdW}(D) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\hbar}{2} \left(\omega_+(q) + \omega_-(q) - 2\omega_{wire}(q) \right) dq$$

Insulating case

$$\frac{E}{L} \approx \int_0^\infty - \frac{\left(2m^{-1} n_{1D} e^2 q^2 K_0(qD)\right)^2}{4\omega_0{}^{3/2}} dq = -\left(\frac{\left(2m^{-1} n_{1D} e^2\right)^2}{\omega_0{}^{3/2}} \int_0^\infty y^4 K_0{}^2(y) dy \right) \frac{1}{D^5}$$

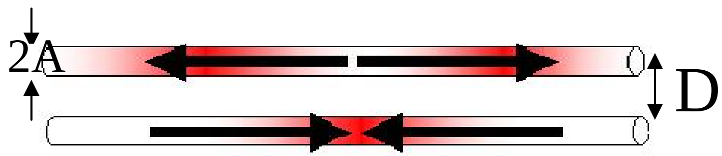
Nanotube attraction III: conducting case (ω_0=0)

vdW energy in RPA $$\frac{1}{L}E^{\mathrm{vdW}}(D)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\frac{\hbar}{2}\left(\omega_+(q)+\omega_-(q)-2\omega_{\mathrm{wire}}(q)\right)dq$$

$$\frac{E}{L}=\frac{\hbar\sqrt{2e^2n_{1D}/m}}{4\pi}\int_{-\infty}^{+\infty}|q|\left(\sqrt{\tilde V(q,0)+\tilde V(q,D)}+\sqrt{\tilde V(q,0)-\tilde V(q,D)}-2\sqrt{\tilde V(q,0)}\right)dq$$

where $\tilde V(q,0)=(2e^2)^{-1}V_0(q)=-\ln(A|q|)\ \ for\ \ |Aq|<<1$

$\tilde V(q,D)=(2e^2)^{-1}V_D(q)=K_0(qD)$



D>>A

Use $\sqrt{a+x}+\sqrt{a-x}-2\sqrt{a}\approx-\frac{x^2}{4a^{3/2}},\quad |x|<<a$

$$4\pi\hbar^{-1}(2e^2n_{1D}/m)^{-1/2}\frac{E}{L}=2\int_0^\infty q\left(-\frac{K_0{}^2(qD)}{4|\ln(Aq)|^{3/2}}\right)dq=-\frac{1}{2D^2}\int_0^\infty xK_0{}^2(x)\left(\ln(xD/A)\right)^{-3/2}dx$$

$$\approx-\frac{\left(\ln(\bar{x}D/A)\right)^{-3/2}}{2D^2}\int_0^\infty xK_0{}^2(x)dx=-\frac{\left(\ln(\bar{x}D/A)\right)^{-3/2}}{4D^2}$$

$$\bar{x}=\exp\left(\int_0^\infty xK_0{}^2(x)(-\ln x)dx\ \Big/\ \int_0^\infty xK_0{}^2(x)dx\right)=2.3_9$$

ISSUES FOR NANOTUBE ATTRACTION

Luttinger liquid? Maybe, but $q\to 0$ collective modes (1D plasmons) are same as in RPA (Li, Das Sarma PRB 1992). Drummond & Needs verified present theory using Diffusion Monte Carlo – PRL PRL **99,** 166401 (2007)

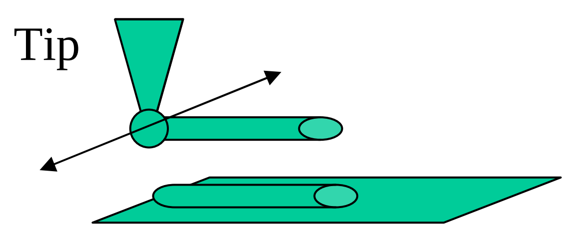
Retardation important?

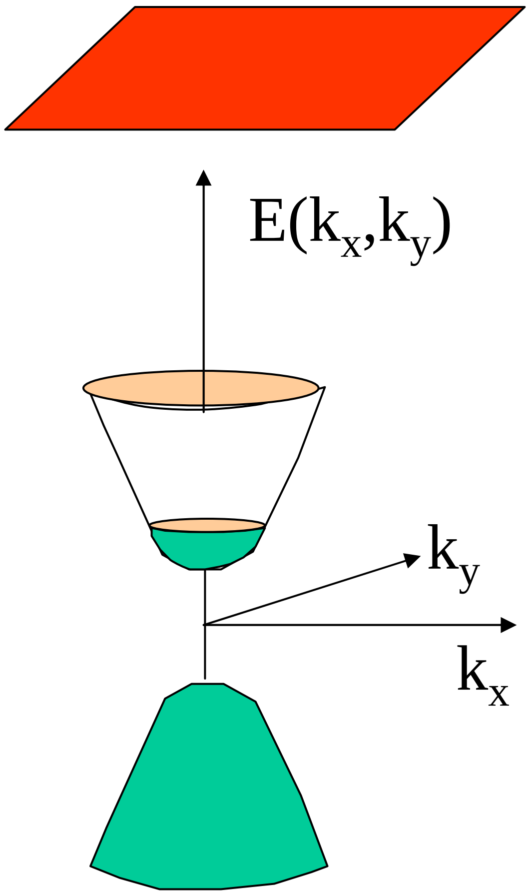
Only if $$2\pi/\omega_{1Dplasmon}(q=D^{-1}) = T_{plasmon} < T_{electromag} \equiv D/c$$

$$\sqrt{\ln(\frac{D}{b})} > 2\pi\frac{c}{v_{1D}}, \qquad \frac{D}{b} > \exp(4\pi^2\frac{c^2}{v_{1D}^2}) \approx e^{9.10^3} \; for\,(5,5)$$

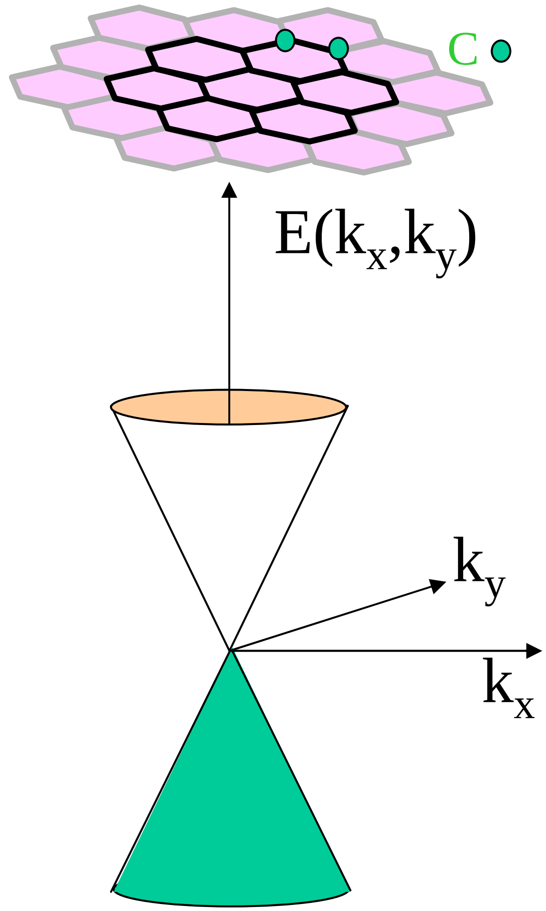
Still observable at large D where $F_{plasmon} >> F_{\Sigma R^{-6}}$?

For two (5,5) conducting nanotubes length 1 μ at D = 24A, estimate $F_{plasmon} > 10F_{\Sigma R^{-6}}$ and $F_{plasmon}$ = 10 pN.

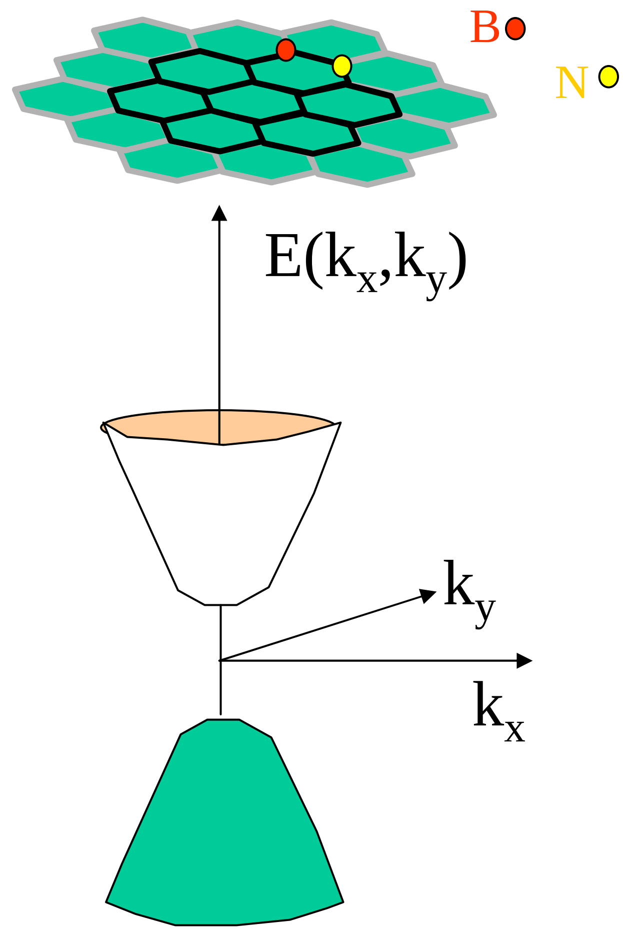




Bandstructure of metal (e.g. e⁻ doped BN plane)



Bandstructure of single graphene plane (semimetal)



Bandstructure of single BN plane (semiconductor)

$$\boxed{\overline{\chi}_0(\vec{q}, iu) \approx \frac{-q^2 n_0}{m^* u^2}}$$

$\alpha = \chi_0 q^{-2}$ diverges if $u \to 0$

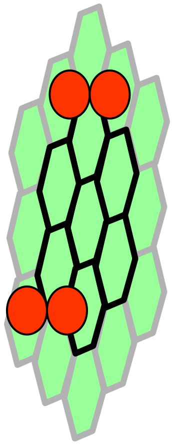
$$\boxed{\overline{\chi}_0(\vec{q}, iu) \approx \frac{-q^2}{2\hbar\sqrt{v_0^2 q^2 + u^2}}}$$

$\alpha = \chi_0 q^{-2}$ diverges if BOTH $q, u \to 0$

$$\boxed{\overline{\chi}_0(\vec{q}, iu) \approx \frac{-q^2}{m^*(u^2 + \omega_0^2)}}$$

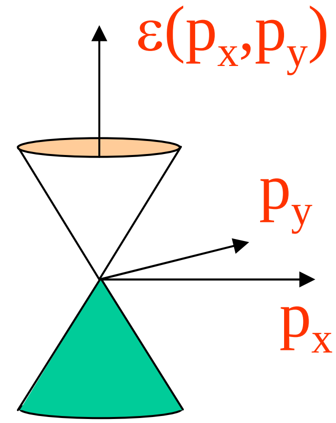
$\alpha = \chi_0 q^{-2}$ not divergent

T=0K graphene sheets (sketch)



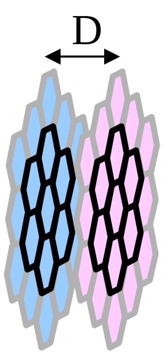
$u_{\pi z}(\underline{x},z)$

Single sheet has no free carriers. No plasmons exist at low q and real frequency.



∴ For vdW use or RPA corrl^n energy

$$E^{vdW}=\frac{\hbar}{2\pi}\int_0^\infty du\int_0^\infty 2\pi q_{\|}dq_{\|}\ln\left(1-\left[\frac{2\pi e^2}{q_{\|}}e^{-q_{\|}D}\frac{q_{\|}}{v_0\left(\sqrt{1+\left(\frac{u}{v_0 q_{\|}}\right)^2}+\frac{\pi e^2}{\hbar v_0}\right)}\right]^2\right)$$



Integrand depends on u only via u/v_0q. Remaining q dep is via $q_{\|}$ D. Scaling argument then shows

$$\boxed{E^{vdW}/A = -(\text{const})\,\hbar\, v_0\, D^{-3}}$$

JFD et al PRL 2006

2 insulating monolayers give D^{-4} , 2 2DEGS give $D^{-2.5}$

CO-AXIAL "POINTING" WIRES / NANOTUBES

JFD and Angela white, PRB **77**, 075436 (2008)

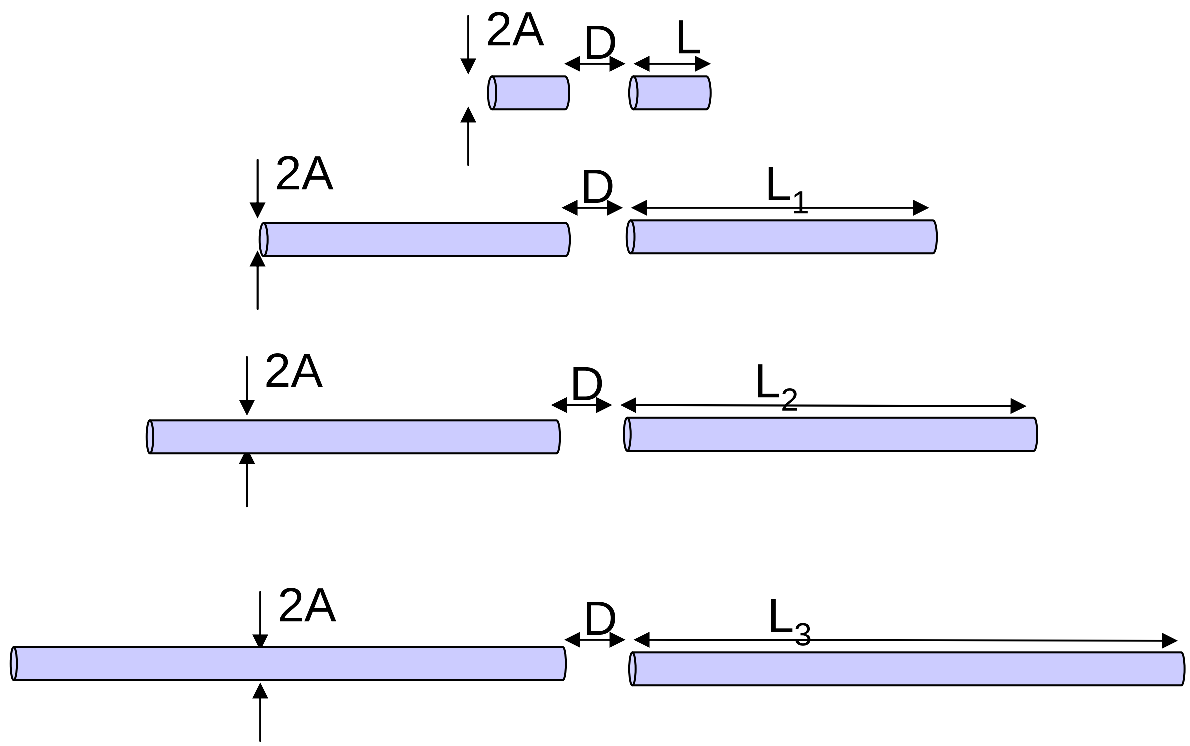
Calculation by <u>summing zero-pt energies of coupled RPA plasmons</u> (not pert^n)

Metallic case has enhanced forces c/w insulating case

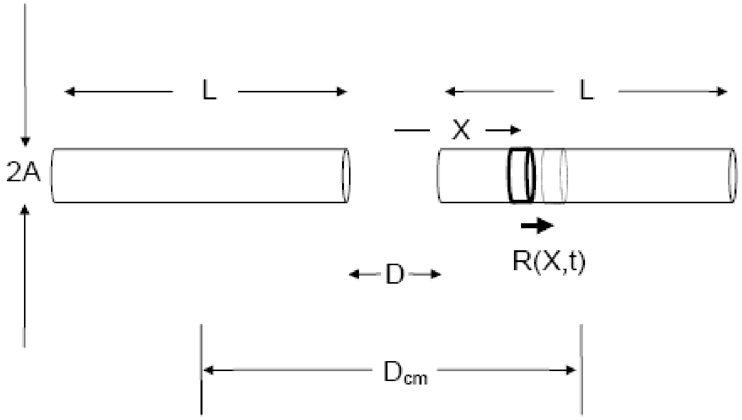
New finding: True even at small separations

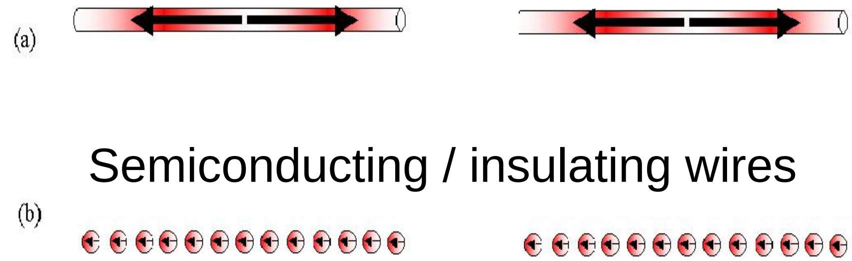
(non-asymptotic but no e$^-$cloud overlap yet)

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





Field due to electrons

Pinning to mimic insulator

Electron degeneracy pressure

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

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

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

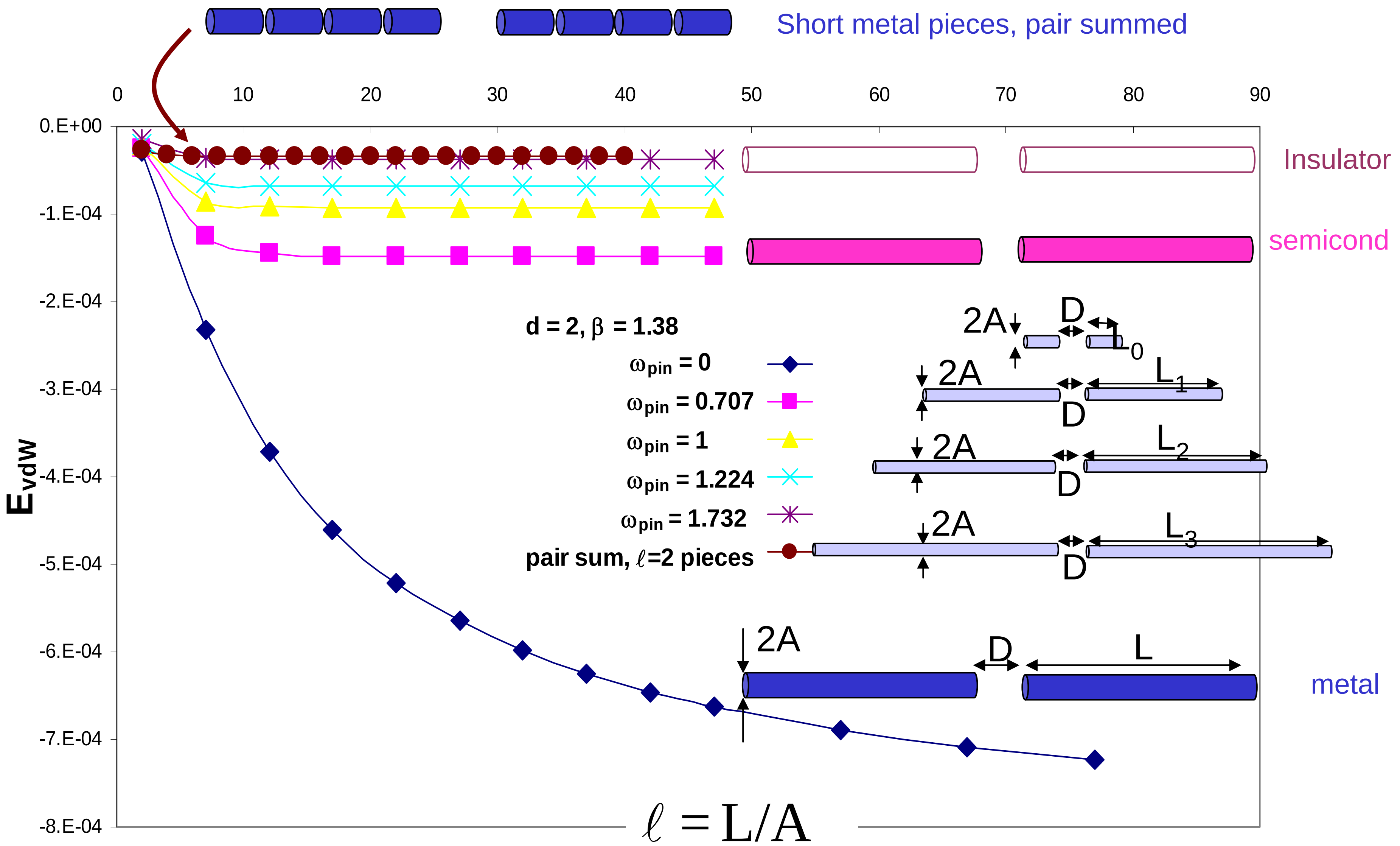
$$\tilde{\phi}(X) = \frac{e^2}{\sqrt{X^2 + A^2}}$$

Coulomb smeared for finite wire width

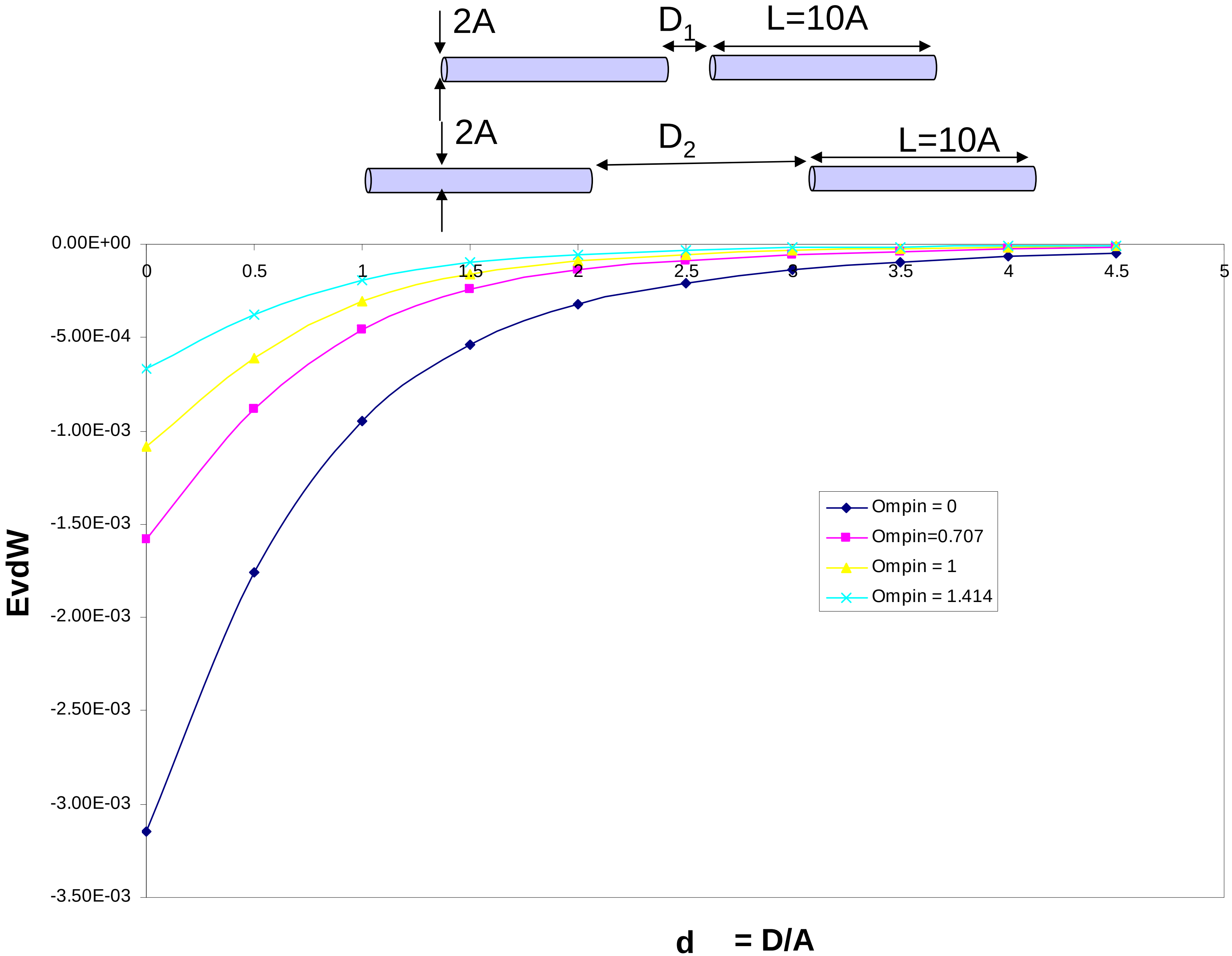
$$E^{disp} = \Sigma_i\left(\frac{\hbar\Omega_i(D)}{2} - \frac{\hbar\Omega_i(D\to\infty)}{2}\right)$$

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

versus wire length ℓ = L / A



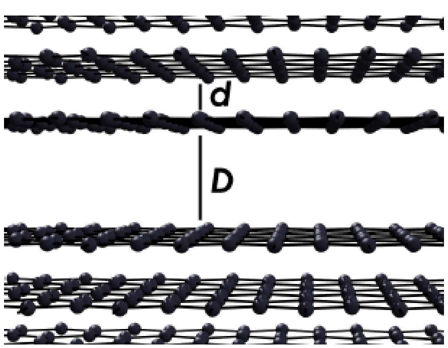
New ZPP dispersion energy saturates naturally at zero separation



COLLECTED RESULTS FOR PLANAR GEOMETRY

TABLE I. ASYMPTOTIC DISPERSION ENERGY OF PARALLEL STRUCTURES

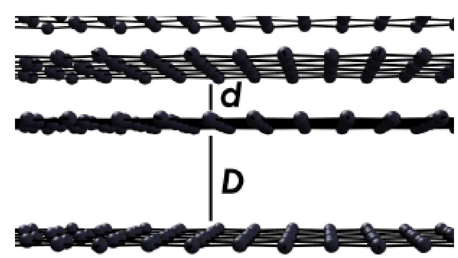
System	*Present prediction*[(a)]	*Standard prediction*
Two 1D metals [2]	$-D^{-2}(\ln(KD))^{-3/2}$	$-D^{-5}$
Two 1D nonmetals [2]	$-D^{-5}$	$-D^{-5}$
Two 2D metals [10,4,2]	$-D^{-5/2}$	$-D^{-4}$
Two π-conjugated graphene layers [2]	$-D^{-3}$ (at T=0K)	$-D^{-4}$
1 metallic, 1 π-layer [2]	$-D^{-3}\ln(D/D_0)$	$-D^{-4}$
2D insulators [2,11]	$-D^{-4}$	$-D^{-4}$
Two *thick* metals or insulators [4,6]	$-D^{-2}$	$-D^{-2}$
2D metal and thick metal (b)	$-D^{-5/2}$	D^{-3}
Graphene (T=0K) and thick metal (b)	$-D^{-3}\ln(D/D_1)$	D^{-3}



cleavage

	Graphite	Metal	Insulator
Stretching	D^{-3}	$D^{-5/2}$	D^{-4}
Cleavage	D^{-2}	D^{-2}	D^{-2}
Exfoliation	$\log(\frac{D}{D_0})D^{-3}$	$D^{-5/2}$	D^{-3}
Atom-bulk	D^{-3}	D^{-3}	D^{-3}

arXiv/cond-mat/0809.0736



exfoliation

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 ($q \to 0$) 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. conducting nanotubes
layered graphitic systems, intercalates etc.)

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

JFD et al, PRL **96**, 073201 (2006), cond-mat/0502422, Surf Sci **601**, 5667 (2007)
IJQC **101**, 579 (2005), PRB 77, 075436 ('08); 165134 (08), cond-mat/0809.0736

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RC1 "Theory of Cohesive Forces in Layered and Striated Nanostructures: Some Surprises", John F. Dobson, Proceedings of the 2006 International Conference on Nanoscience and Nanotechnology, Brisbane, July 2006, ISBN 1-4244-0453-3, .IEEE Cat No. 06EX1411C, Causal Productions

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