

Many-body dispersion interactions between semiconducting wires

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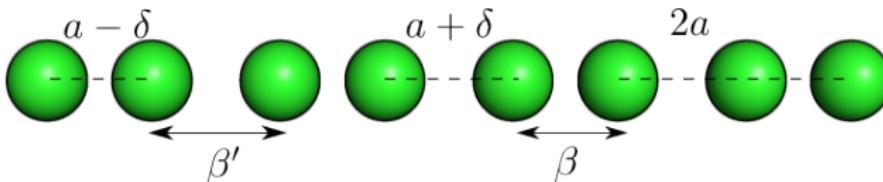
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Collaborators

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Hückel chains



- ▶ Interactions between two parallel infinite wires.
- ▶ Two-band Hamiltonian:

$$H = \sum_i^n (\beta a_{2i}^\dagger a_{2i-1} + \beta' a_{2i+1}^\dagger a_{2i} + h.c.) \quad (1)$$

- ▶ Models interactions between $(\text{H}_2)_n$ chains or π -conjugated polyenes.
- ▶ Band-gap is given by

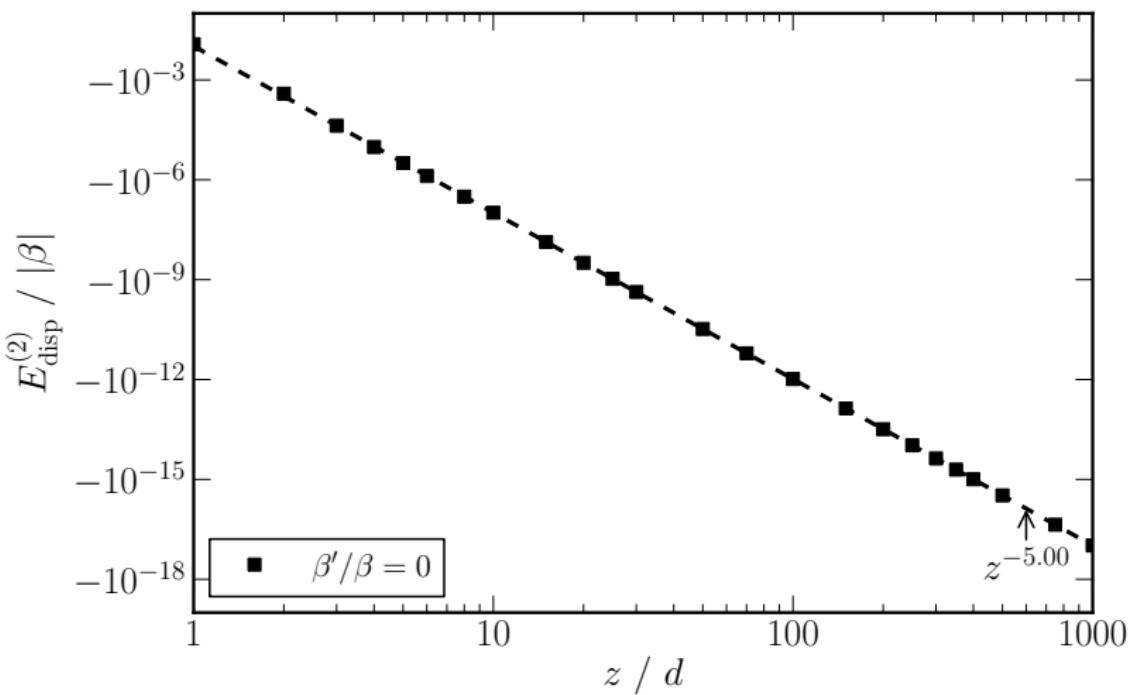
$$\Delta E_g = 2(\beta - \beta') \quad (2)$$

► Dispersion energy:

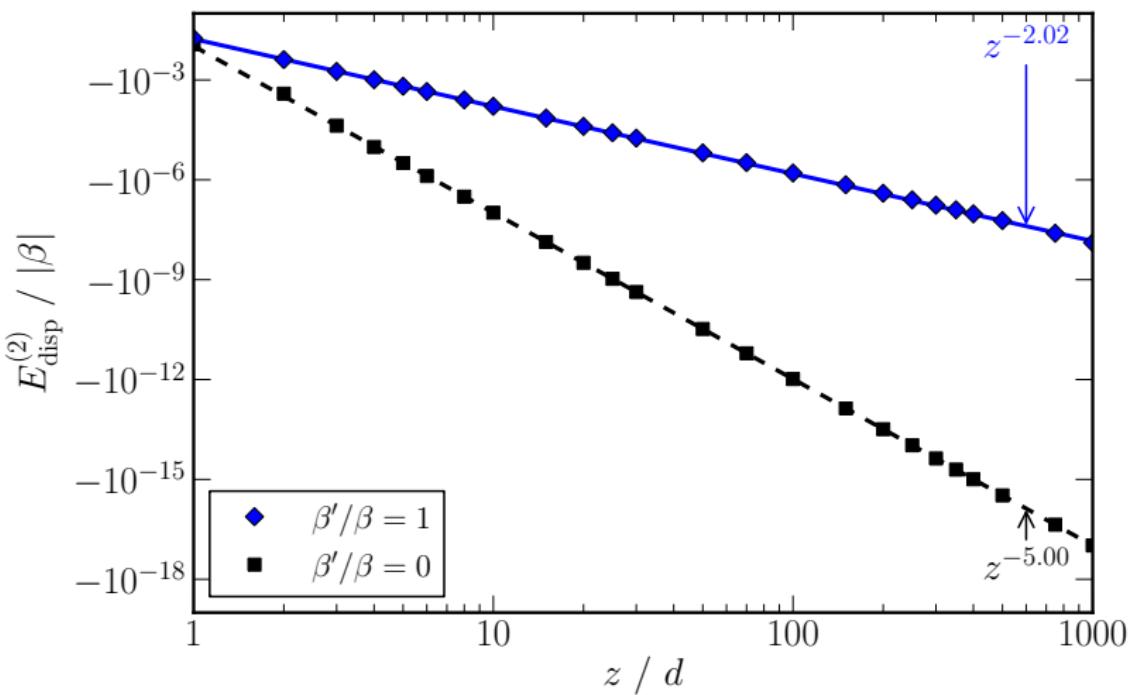
$$E_{\text{disp}}^{(2)} = \sum_{i \in A, j \in B} \sum_{a \in A, b \in B} \frac{|\langle ij | r_{12}^{-1} | ab \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}. \quad (3)$$

- Large finite-size effects: k -point sampling equivalent to a crystal cell with 16802 sites.

Infinite, parallel chains with gap: $\Delta E_g = 2\beta$



Infinite, parallel chains with gap: $\Delta E_g = 0$

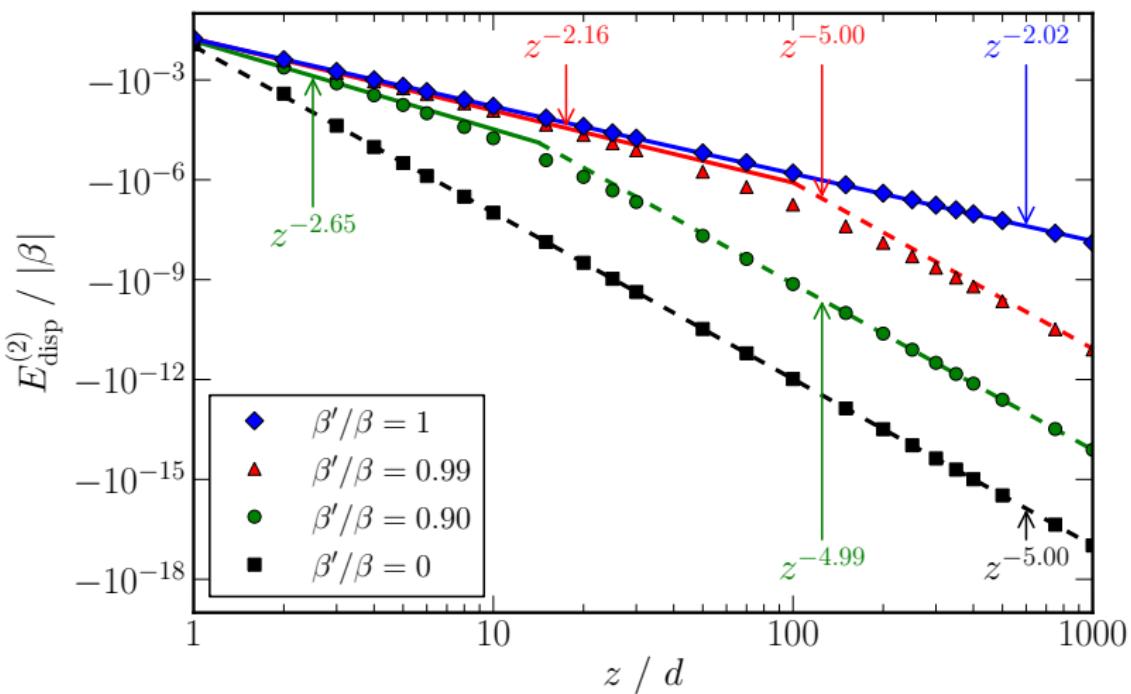


Dobson, White & Rubio, PRL **96**, (2006).

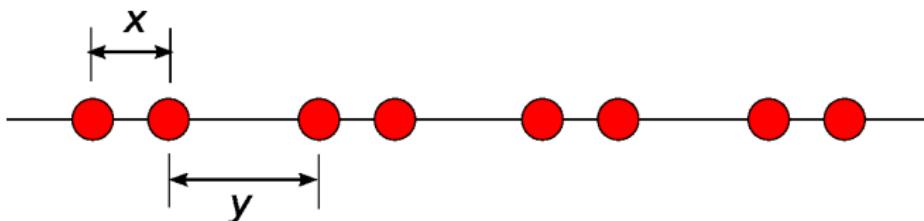
System	Metals	Insulators
1-D	$-R^{-2}(\ln(KR))^{-3/2}$	$-R^{-5}$
2-D	$-R^{-5/2}$	$-R^{-4}$

- ▶ Verified using DMC calculations on the 1-D and 2-D HEG by Drummond & Needs (PRL **99**, (2007)).
- ▶ 1-D result probably known much earlier: Coulson & Davies (Trans. Faraday Soc. 1952) and Longuet-Higgins & Salem (Proc. R. Soc. A. 1961). The latter studied the non-additivity of the dispersion energy.

Infinite, parallel chains with gap: $\Delta E_g = 2(\beta - \beta')$



SAPT(DFT) Interaction of $(\text{H}_2)_n$ chains using SAPT(DFT) (symmetry-adapted perturbation theory based on DFT).



- ▶ Finite chains: $n = 2, 4, 8, 16, 32$
- ▶ Control HOMO–LUMO gap using bond alternation. $\eta = y/x$.
- ▶ Gap goes from 10 eV (smallest chain) to 1 eV.

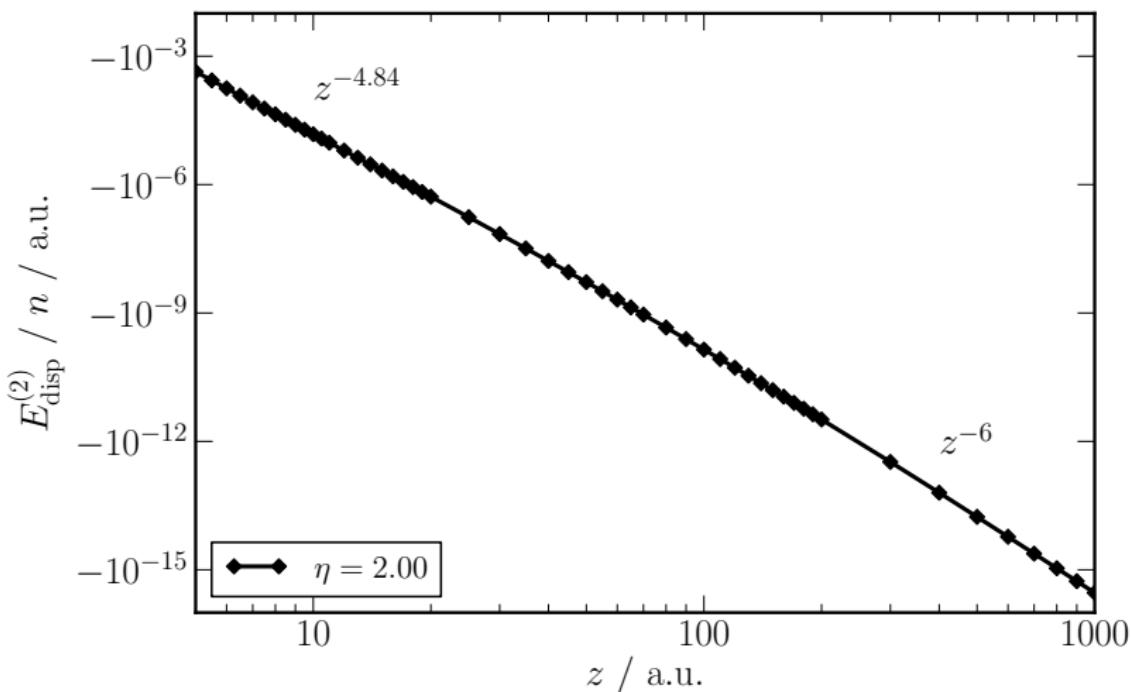
- ▶ SAPT(DFT) dispersion is calculated using the generalized Casimir-Polder expression (Longuet-Higgins (1965)):

$$E_{\text{disp}}^{(2)} = -\frac{1}{2\pi} \int_0^{\infty} dw \int \frac{\alpha_A(\mathbf{r}_1, \mathbf{r}'_1; iw)\alpha_B(\mathbf{r}_2, \mathbf{r}'_2; iw)}{|\mathbf{r}_1 - \mathbf{r}_2| |\mathbf{r}'_1 - \mathbf{r}'_2|} d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2$$

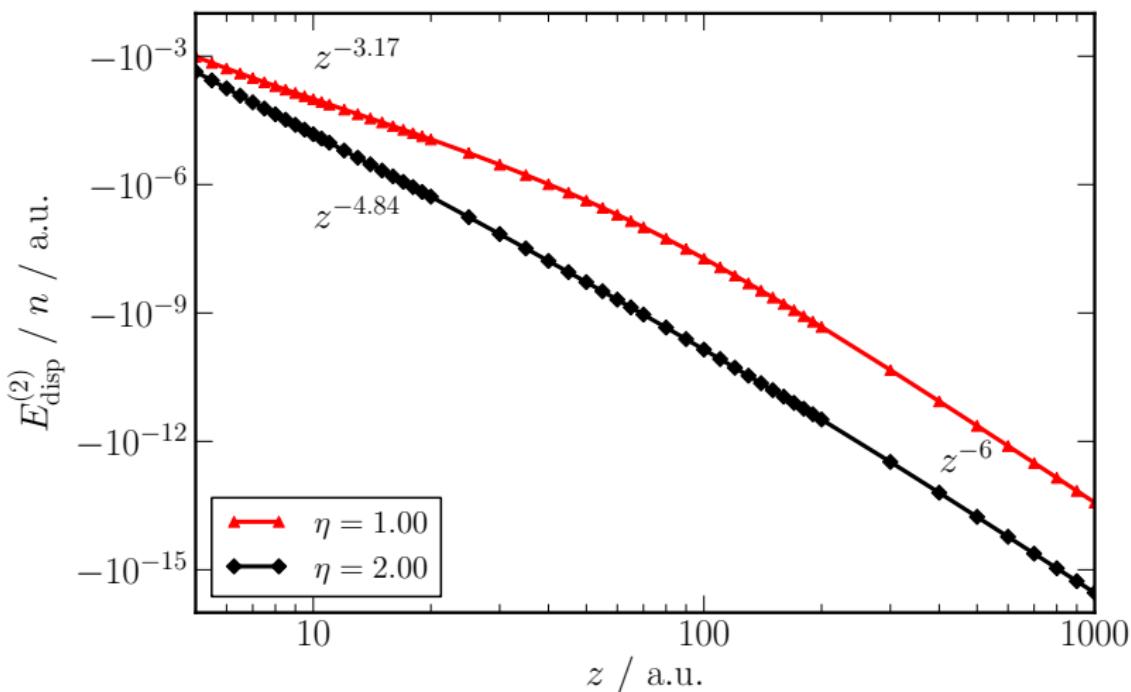
Where $\alpha(\mathbf{r}, \mathbf{r}'; \omega)$ is the frequency-dependent density susceptibility function (FDDS).

- ▶ Advantages of perturbation theory: separate out the dispersion from the long-range electrostatics.

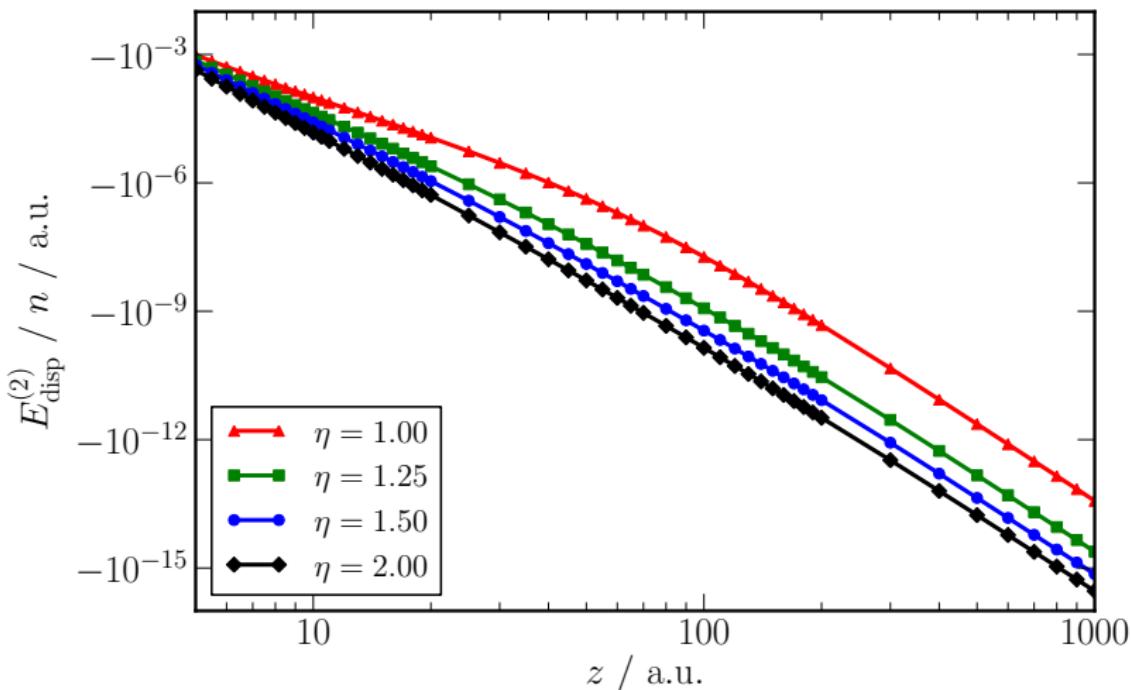
Bond alternation: $\eta = y/x = 2$, $E_g = 0.366$ a.u.



Bond alternation: $\eta = y/x = 1$, $E_g = 0.057$ a.u.



Bond alternation: $\eta = y/x$



- ▶ No single power law.
- ▶ Two regions (distances in a.u.):

$$z^{-6} : \text{for } z \gg L$$

$$z^{-x} : x < 5 \text{ for } 6 < z < 20.$$

The anomalous power law occurs at physically important separations.

- ▶ Enhanced dispersion: At $z = 40$ a.u. (roughly half chain length), two orders of magnitude between chains with $\eta = 1$ and $\eta = 2$.
- ▶ Enhancement orders of magnitude less than for the Hückel chains: importance of screening.

- ▶ Non-additivity of total polarizabilities can explain three order of magnitude enhancement at very long range. Longitudinal static polarizabilities for $(\text{H}_2)_{32}$ chains:

$$\frac{\alpha(\eta = 1.0)}{\alpha(\eta = 2.0)} = \frac{11589}{415} = 28 \quad (4)$$

Dispersion energy depends quadratically on the polarizability.

- ▶ But extrapolation to intermediate distances overestimates dispersion by orders of magnitude.
- ▶ Failure of additivity.
- ▶ Not damping or retardation.
- ▶ Severe finite-size effects...

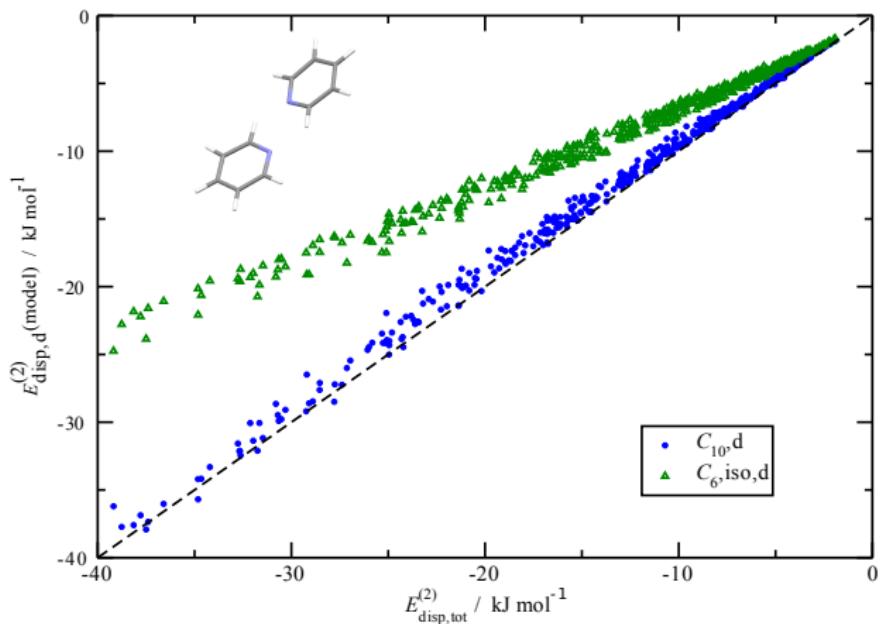
Multipole Expansion

- ▶ At the time, I had been working on very accurate multipole expansions for the dispersion energy using WSM method (available in the **CAMCASP** program):

$$E_{\text{disp}}^{(2)} = - \sum_{a,b} \left(\frac{C_6^{ab}}{R_{ab}^6} + \frac{C_7^{ab}}{R_{ab}^7} + \frac{C_8^{ab}}{R_{ab}^8} + \dots \right) \quad (5)$$

- ▶ Based on density-response functions calculated using linear-response TD-DFT.
- ▶ Consistent with SAPT(DFT) dispersion energies.
- ▶ Very accurate models. R.m.s. errors of 0.5 kJ mol^{-1} across large energy ranges (-40 to 0 kJ mol^{-1}).

Pyridine dimer: WSM dispersion models (damped).



Multipole Expansion

- ▶ For $z > 6$ a.u.: Density overlap is negligible. So multipole expansion should be valid.
- ▶ Usually we take this to mean that

$$E_{\text{disp}}^{(2)} = - \sum_{a,b} \frac{C_6^{ab}}{R_{ab}^6}. \quad (6)$$

- ▶ But this cannot yield an effective power law with exponent less than 5.
- ▶ Nor can the more general expression:

$$E_{\text{disp}}^{(2)} = - \sum_{a,b} \left(\frac{C_6^{ab}}{R_{ab}^6} + \frac{C_7^{ab}}{R_{ab}^7} + \frac{C_8^{ab}}{R_{ab}^8} + \dots \right) \quad (7)$$

where each coefficient is angular dependent.

- ▶ Longuet-Higgins (1965) expression for the dispersion energy:

$$E_{\text{disp}}^{(2)} = -\frac{1}{2\pi} \int_0^\infty dw \int \frac{\alpha_A(\mathbf{r}_1, \mathbf{r}'_1; iw)\alpha_B(\mathbf{r}_2, \mathbf{r}'_2; iw)}{|\mathbf{r}_1 - \mathbf{r}_2| |\mathbf{r}'_1 - \mathbf{r}'_2|} d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2$$

- ▶ Taylor expansion (systems separated by \mathcal{R}): Leading order term is usually written as the dipole-dipole interaction:

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = -\hat{\mu}_\alpha \frac{3R_\alpha R_\beta - R^2 \delta_{\alpha\beta}}{R^5} \hat{\mu}_\beta \quad (8)$$

But this is insufficient. It leads to the usual $-C_6R^{-6}$ form.

- ▶ Generalize:

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \hat{Q}_t^A T_{tu}^{AB} \hat{Q}_u^B \quad (9)$$

where $t = 00, 10, 11c, 11s, \dots$ label the rank of the multipole moment operators.

- ▶ A T-function of ranks l and l' behaves like $R^{-l-l'-1}$.
- ▶ Distribute: For extended systems use multiple centres:

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_a \sum_b \hat{Q}_t^a T_{tu}^{ab} \hat{Q}_u^b. \quad (10)$$

- ▶ Inserting this in the Longuet-Higgins expression gives:

$$E_{\text{disp}}^{(2)} = -\frac{1}{2\pi} \sum_{a,a'} \sum_{b,b'} T_{tu}^{ab} T_{t'u'}^{a'b'} \int_0^\infty \alpha_{tt'}^{aa'}(iw) \alpha_{uu'}^{bb'}(iw) dw \quad (11)$$

where the *non-local polarizabilities* are defined as

$$\alpha_{tt'}^{aa'}(\omega) = \iint \hat{Q}_t^a(\mathbf{r}) \alpha(\mathbf{r}, \mathbf{r}'; \omega) \hat{Q}_{t'}^{a'}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (12)$$

This is the correct multipole expansion for the dispersion. For details see Stone 'The Theory of Intermolecular Forces' (1996).

- ▶ To obtain the usual expansion we must *localize* the non-local polarizabilities. This is usually done by another multipole expansion, but there are other methods.
- ▶ The result is that only terms involving the same site remain.
- ▶ This is an approximation that assumes that

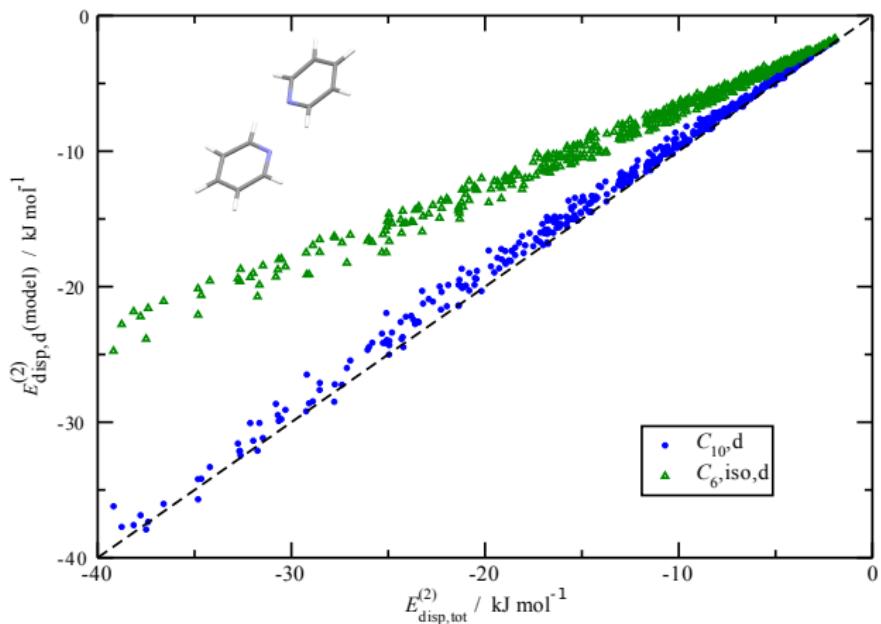
$$\alpha^{aa'} \sim e^{-\gamma|R_{aa'}|}, \quad (13)$$

where $\gamma \sim 1$.

- ▶ When this is true, the localization is valid and we get

$$\begin{aligned} E_{\text{disp}}^{(2)} &= -\frac{1}{2\pi} \sum_a \sum_b T_{tu}^{ab} T_{t'u'}^{ab} \int_0^\infty \alpha_{tt'}^a(iw) \alpha_{uu'}^b(iw) dw \\ &= - \sum_a \sum_b \left(\frac{C_6^{ab}}{R_{ab}^6} + \frac{C_7^{ab}}{R_{ab}^7} + \frac{C_8^{ab}}{R_{ab}^8} + \dots \right) \end{aligned}$$

Pyridine dimer: WSM dispersion models (damped).



What are the non-local polarizabilities?

- ▶ The lowest rank polarizability is $\alpha_{00,00}^{aa'}$.
- ▶ If V^a is the potential at site a , the change in charge at site a is given by

$$\Delta \hat{Q}_{00}^a = - \sum_{a'} \alpha_{00,00}^{aa'} (V^{a'} - V^a). \quad (14)$$

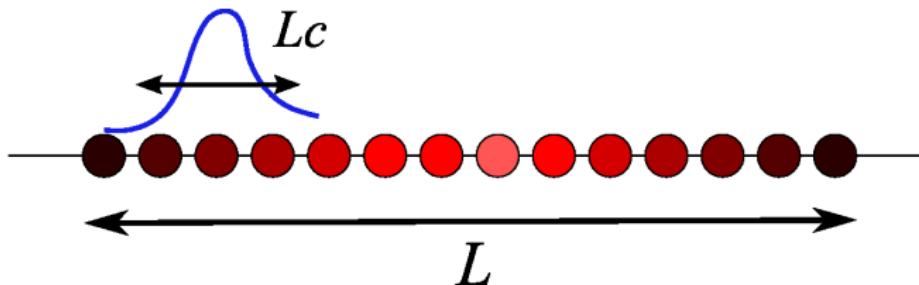
- ▶ Such terms describe the flow of charge in response to a potential. They are therefore termed *charge-flow* polarizabilities.
- ▶ These are the analogue of the low (zero) frequency plasmon modes.
- ▶ They contribute R^{-2} terms to the dispersion energy.

- ▶ Sum rule: Charge conservation requires that

$$\int \alpha(\mathbf{r}, \mathbf{r}'; \omega) d\mathbf{r}' = 0, \quad (15)$$

and this results in the charge-flow sum rule

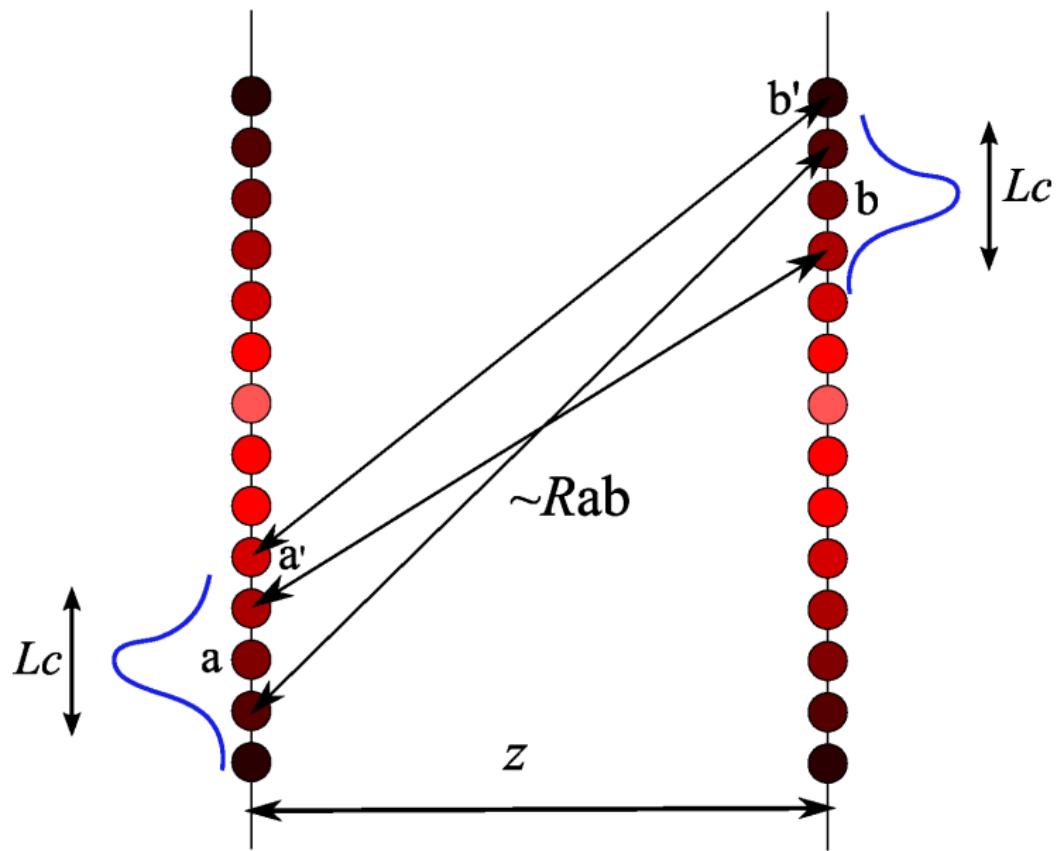
$$\sum_{a'} \alpha_{t,00}^{aa'} = 0. \quad (16)$$



Charge-flow contribution to the dispersion energy:

$$E_{\text{disp}}^{(2)}(00,00) = -\frac{1}{2\pi} \sum_{aa',bb'} \frac{1}{R_{ab}R_{a'b'}} \int_0^\infty \alpha_{00,00}^{aa'}(iw) \alpha_{00,00}^{bb'}(iw) dw \quad (17)$$

- ▶ $z \leq L_c$: Large R^{-2} contribution.
- ▶ $L_c \ll z < L$: Charge-fluctuations small compared to R_{ab} and only $R_{a'b'}$ close to R_{ab} contribute... (see fig)...



- ▶ $L_c \ll z < L$:

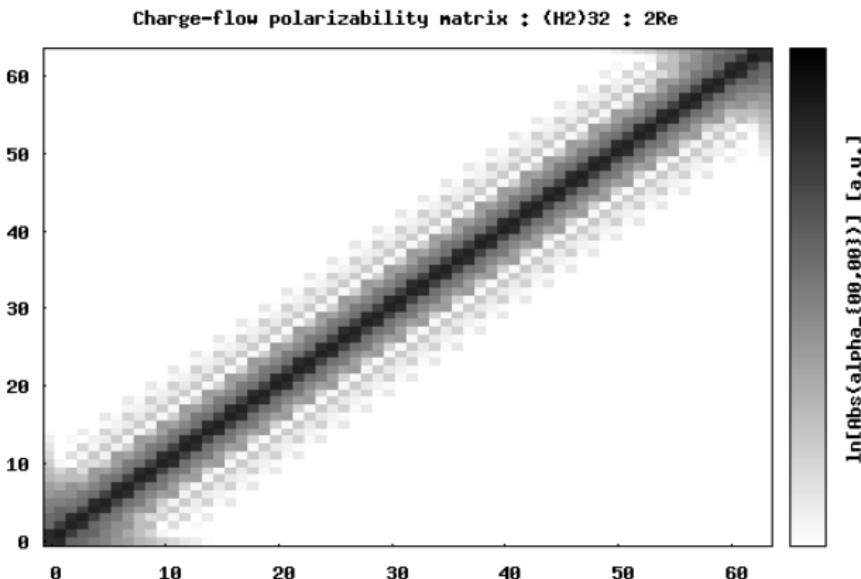
$$\begin{aligned}
 E_{\text{disp}}^{(2)}(00,00) &= -\frac{1}{2\pi} \sum_{aa',bb'} \frac{1}{R_{ab}R_{a'b'}} \int_0^\infty \alpha_{00,00}^{aa'}(iw) \alpha_{00,00}^{bb'}(iw) dw \\
 &\approx -\frac{1}{2\pi} \sum_{ab} \frac{1}{R_{ab}R_{ab}} \\
 &\quad \int_0^\infty \left(\sum_{a'} \alpha_{00,00}^{aa'}(iw) \right) \left(\sum_{b'} \alpha_{00,00}^{bb'}(iw) \right) dw \\
 &= 0
 \end{aligned} \tag{18}$$

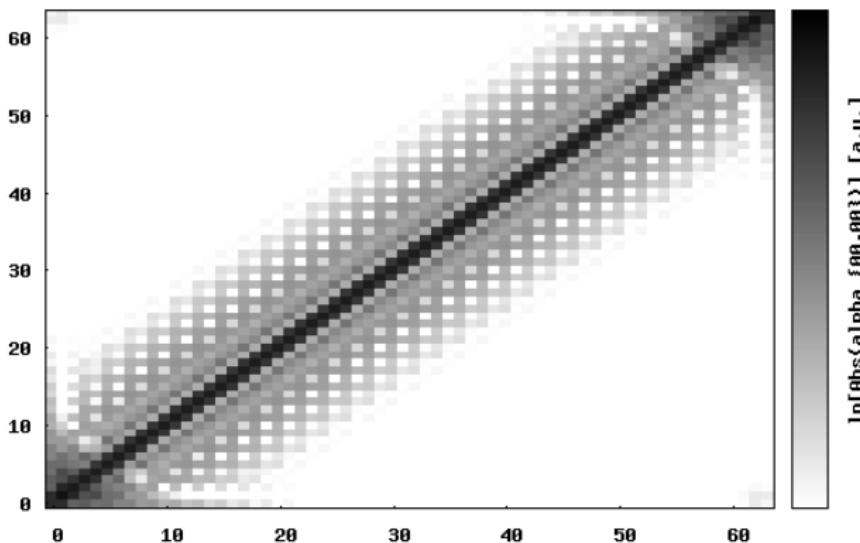
But higher-order terms are non-zero.

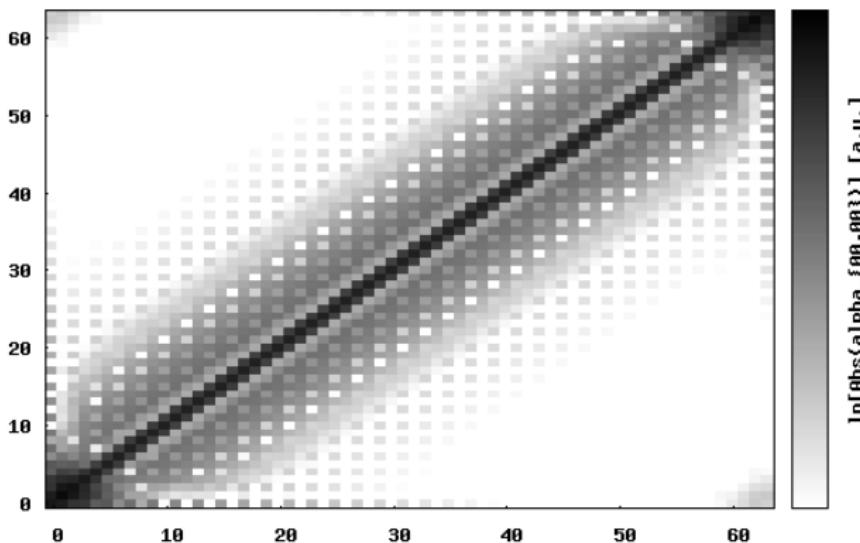
- ▶ $L \ll z$: In this limit both R_{ab} and $R_{a'b'}$ can be expanded in a multipole expansion about $\mathcal{R} = (0, 0, z)$:
 - ▶ $R_{ab}^{-1} = |\mathcal{R} - (\mathbf{r}_a - \mathbf{r}_b)|^{-1} = |\mathcal{R} - \mathbf{r}_{ab}|^{-1} \approx z^{-1} - \frac{1}{2} r_{ab}^2 z^{-3}$
 - ▶ Use sum-rule.

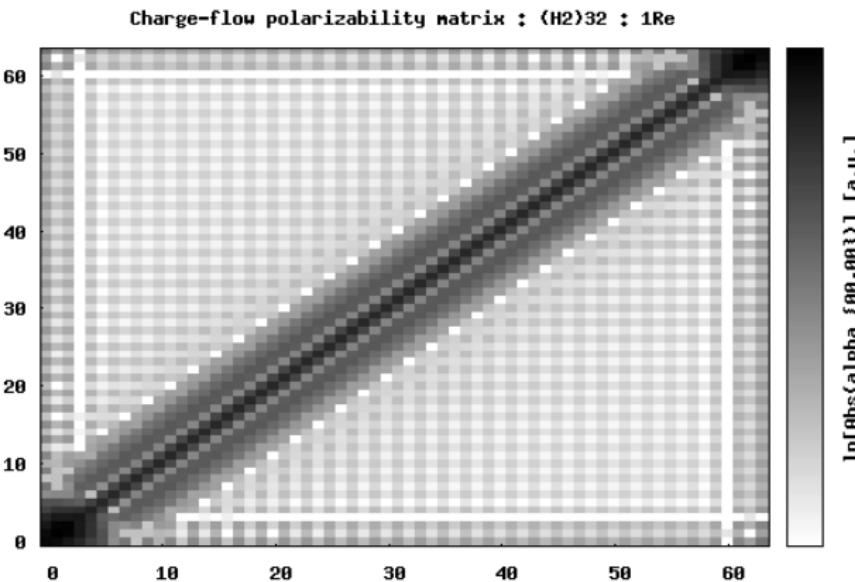
$$\begin{aligned}
 E_{\text{disp}}^{(2)}(00,00) &\approx -\frac{1}{2\pi} \frac{1}{4z^6} \sum_{aa'} \sum_{bb'} r_{ab}^2 r_{a'b'}^2 \\
 &\quad \times \int_0^\infty \alpha_{00,00}^{aa'}(iw) \alpha_{00,00}^{bb'}(iw) dw \\
 &\equiv -\frac{C_6(00,00)}{z^6}. \tag{19}
 \end{aligned}$$

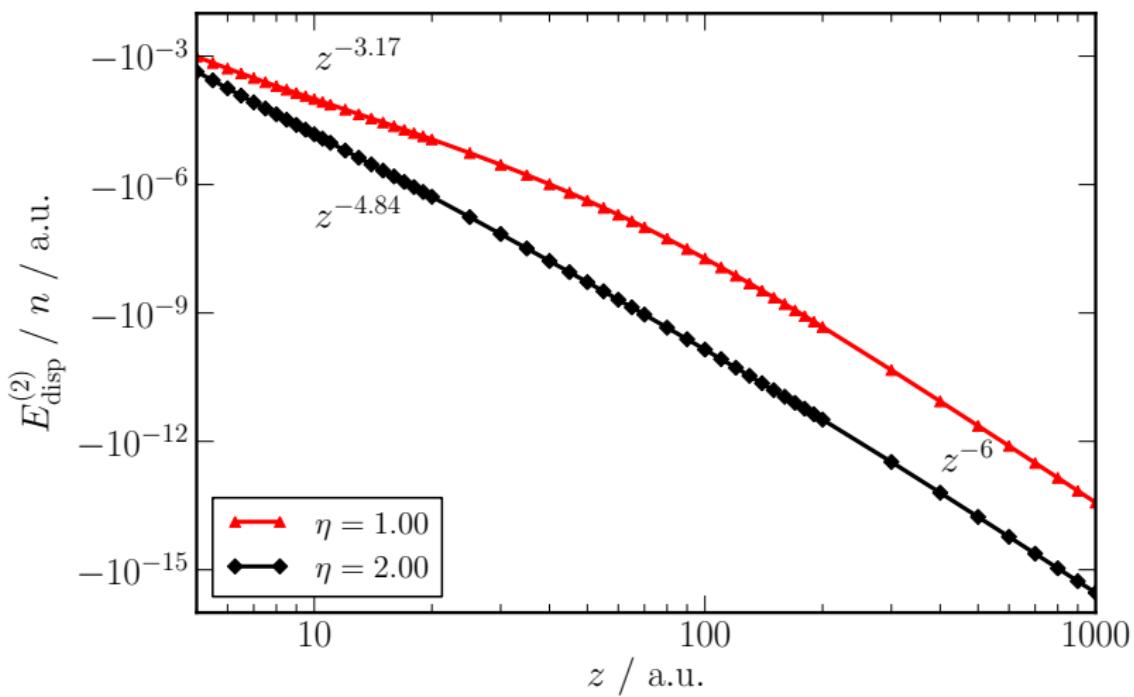
How do the charge-flow terms behave for the chains?

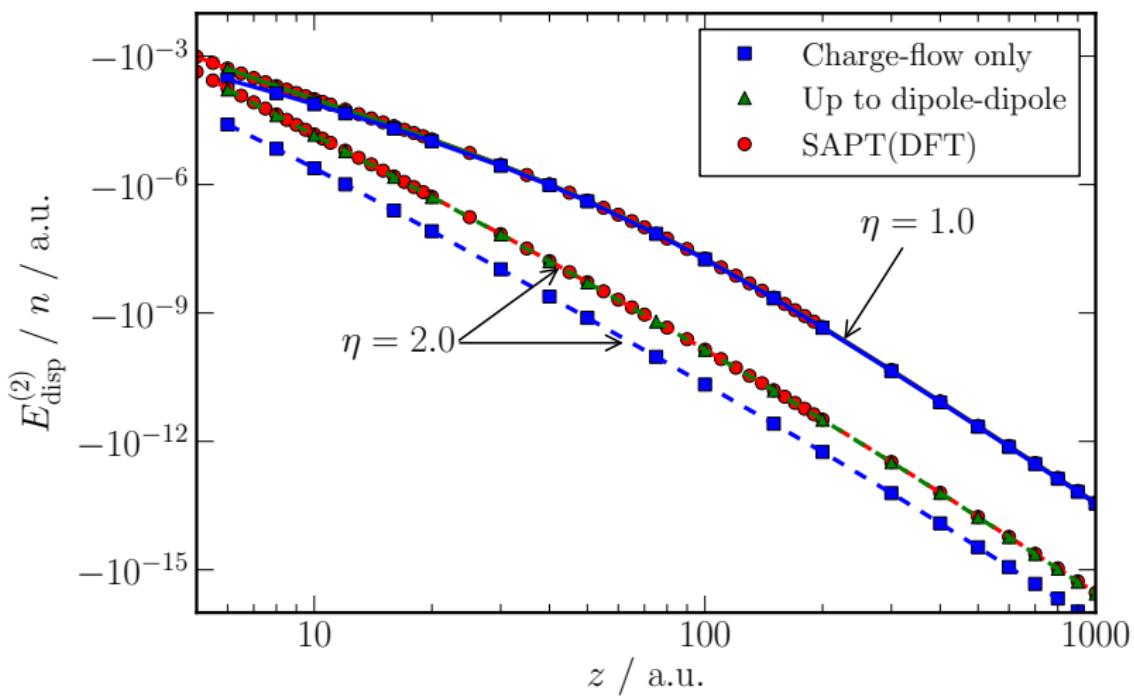


Charge-flow polarizability matrix : (H₂)₃₂ : 1.5Re

Charge-flow polarizability matrix : (H₂)₃₂ : 1,25Re







Angyan (2007,2009) has shown that the charge-flow polarizabilities are related to the XC-hole by relating the density autocorrelation function

$$S(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r})\delta(\mathbf{r} - r\hat{\mathbf{p}}) + \rho(\mathbf{r})h_{xc}(\mathbf{r}, \mathbf{r}') \quad (20)$$

to the FDDs using the Unsold approximation:

$$\alpha(\mathbf{r}, \mathbf{r}'; 0) = \frac{\pi}{\hbar\bar{\omega}} S(\mathbf{r}, \mathbf{r}'). \quad (21)$$

Therefore,

$$\begin{aligned} \alpha_{00,00}^{aa'} &= \int_{\Omega_a} \int_{\Omega_{a'}} \alpha(\mathbf{r}, \mathbf{r}'; 0) d\mathbf{r} d\mathbf{r}' \\ &= \frac{\pi}{\hbar\bar{\omega}} \left(N_a \delta_{aa'} + \int_{\Omega_a} \rho(\mathbf{r}) \int_{\Omega_{a'}} h_{xc}(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' \right) \end{aligned}$$

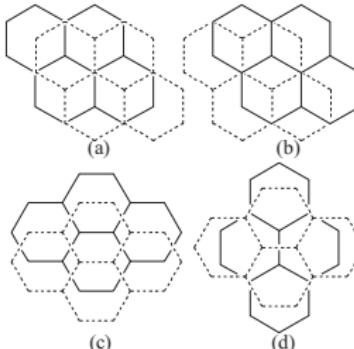
Analysis

- ▶ Failure of additivity (and the pair-wise $-C_6/R^6$ model) as the gap decreases and system length increases.
- ▶ Require explicit non-local terms. This non-locality is contained in the full density response function $\alpha(\mathbf{r}, \mathbf{r}'; \omega)$.
- ▶ The non-local charge-flow terms do two things: (1) change the power-law for the interaction, and (2) enhance the dispersion interaction.
- ▶ Is this really important? What about carbon systems...?
- ▶ What about 2-D systems like graphene?

PAHs: SAPT(DFT) Pair Potential

$$U_{ab} = \underbrace{G \exp \left[-\alpha_{ab} (R_{ab} - \rho_{ab}(\Omega_{ab})) \right]}_{\text{short-range}} - \underbrace{f_6(R_{ab}) \frac{C_{6,\text{iso}}}{R_{ab}^6}}_{\text{long-range}} + E_{\text{elst}}(\text{model})$$

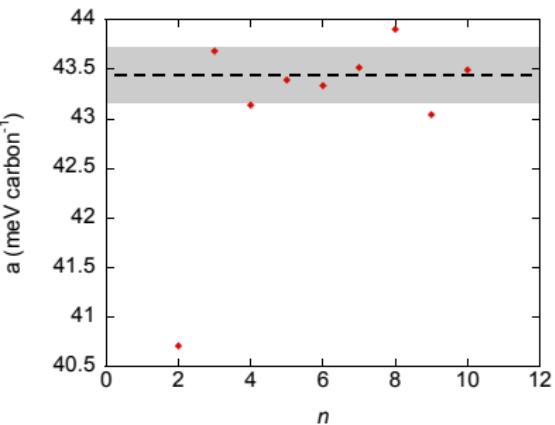
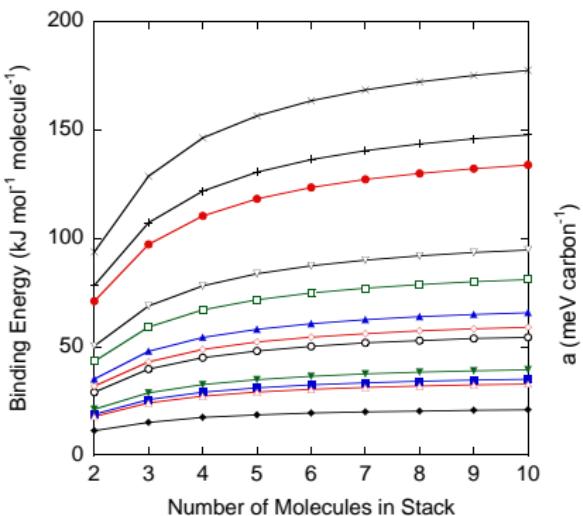
- ▶ Benzene dimer interaction energies (500 geometries).
- ▶ Larger PAH dimers: naphthalene, anthracene, pyrene.

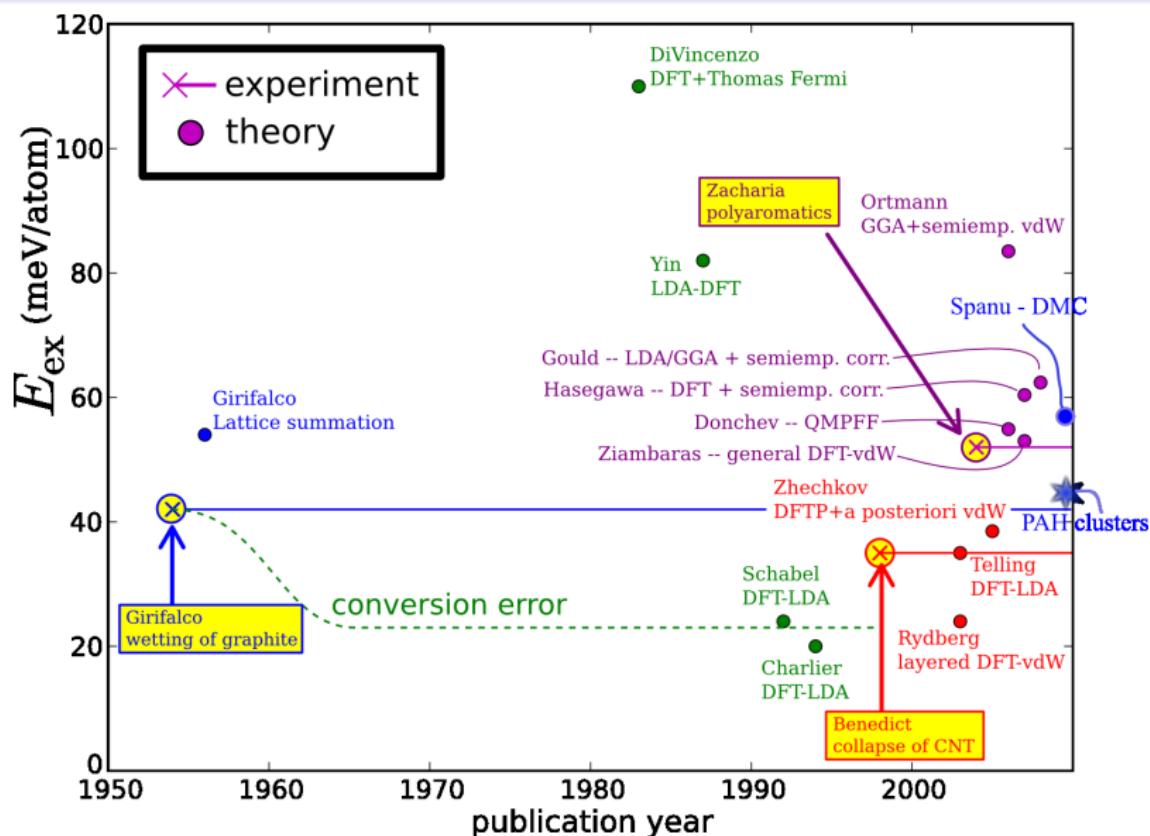


- ▶ Validated on coronene dimers (not included in the fit).

Graphene & graphite Estimate of *additive* exfoliation energy of graphite by extrapolation:

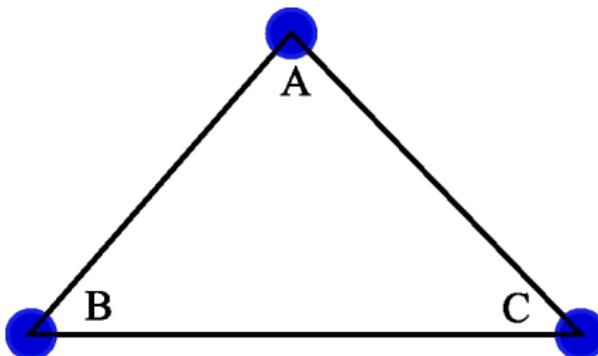
$$\frac{E_{\text{bind}}(m)}{m} = \frac{am}{b + m} \quad (22)$$





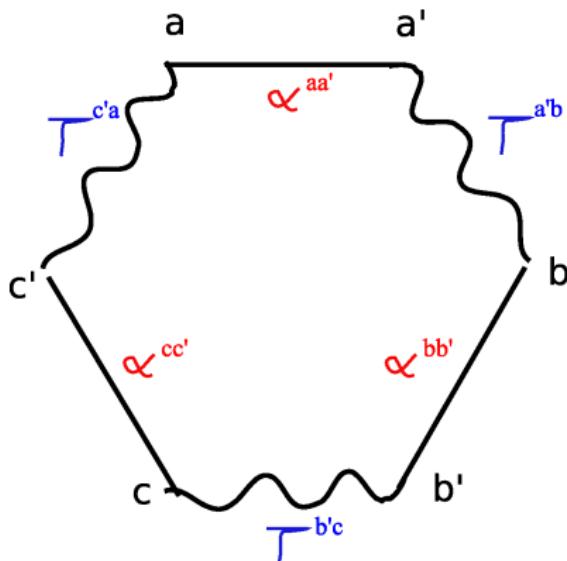
3-body dispersion For 3 atoms: Axilrod–Teller–Muto:

$$E_{\text{disp}}^{(2)}(3 - \text{body}) = C_9 \frac{1 + 3 \cos \hat{A} \cos \hat{B} \cos \hat{C}}{R_{AB}^3 R_{AC}^3 R_{BC}^3} \sim \frac{C_9}{R^9} \quad (23)$$

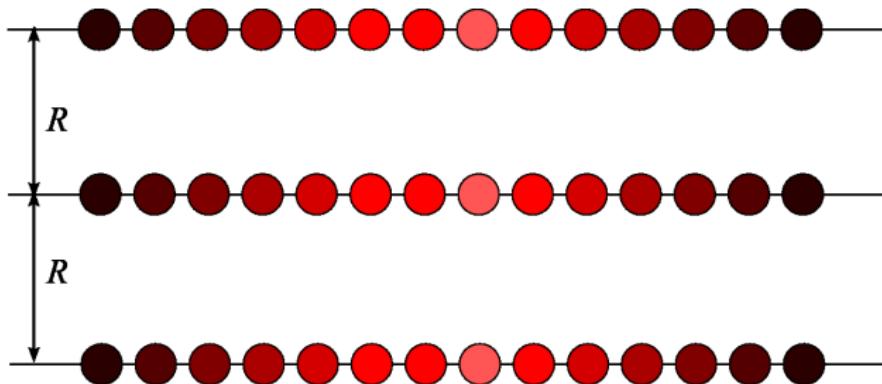


Generalization for non-local, anisotropic, polarizabilities based on expression given by Stogryn (1971):

$$E_{\text{disp}}^{\text{asym}}[3] = \frac{\hbar}{\pi} \int_0^\infty \alpha_{\alpha\beta}^{aa'}(i\omega) \alpha_{\gamma\delta}^{bb'}(i\omega) \alpha_{\epsilon\phi}^{cc'}(i\omega) d\omega T_{\gamma\beta}^{ba'} T_{\epsilon\delta}^{cb'} T_{\alpha\phi}^{ac'} \quad (24)$$

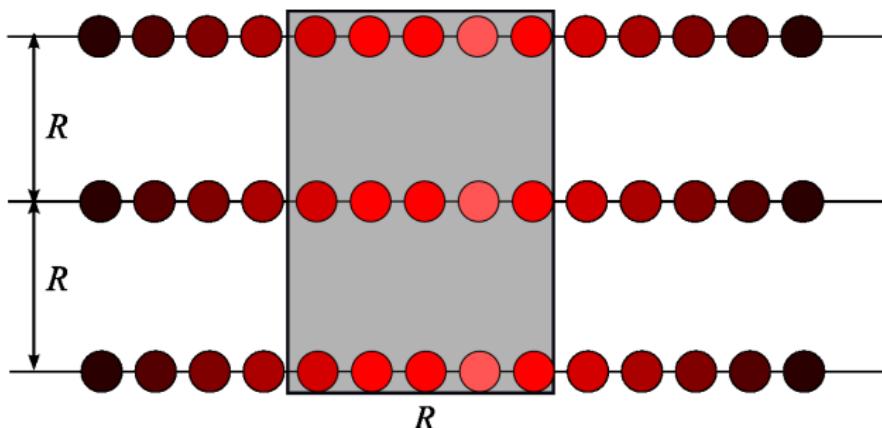


Infinite, parallel chains with finite gap



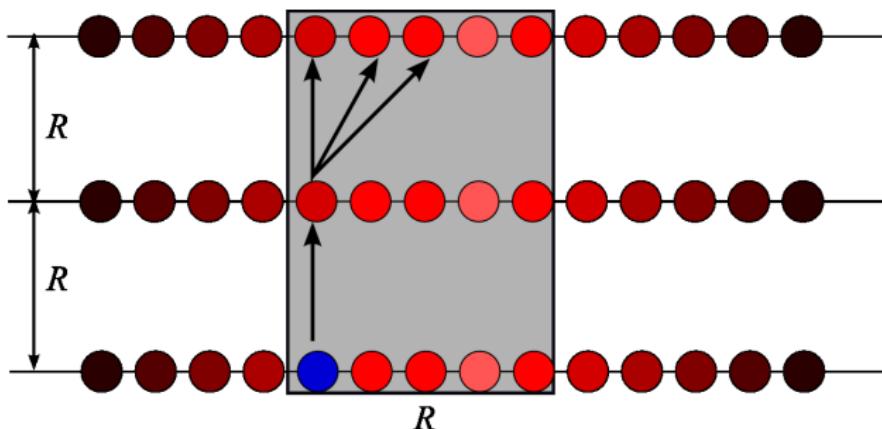
- ▶ Length scale: R

Infinite, parallel chains with finite gap



- ▶ Length scale: R
- ▶ Select section of order R .

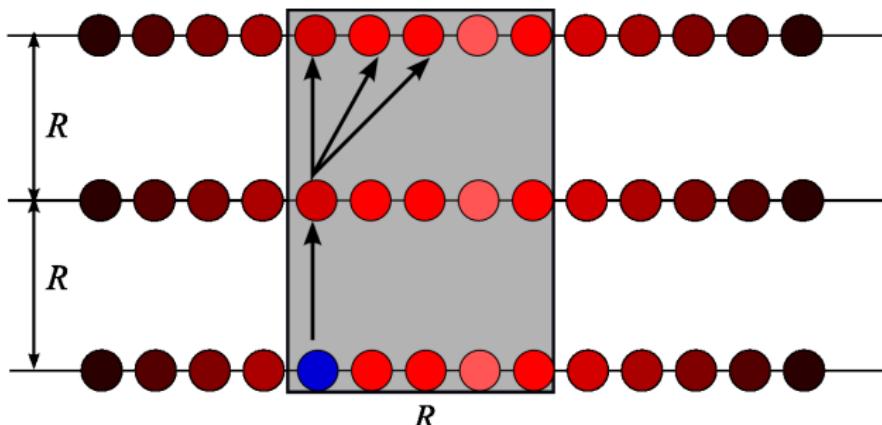
Infinite, parallel chains with finite gap



- ▶ Interaction of blue atom with others is:

$$\frac{C_9}{R^9} \times (R \times R) \quad (25)$$

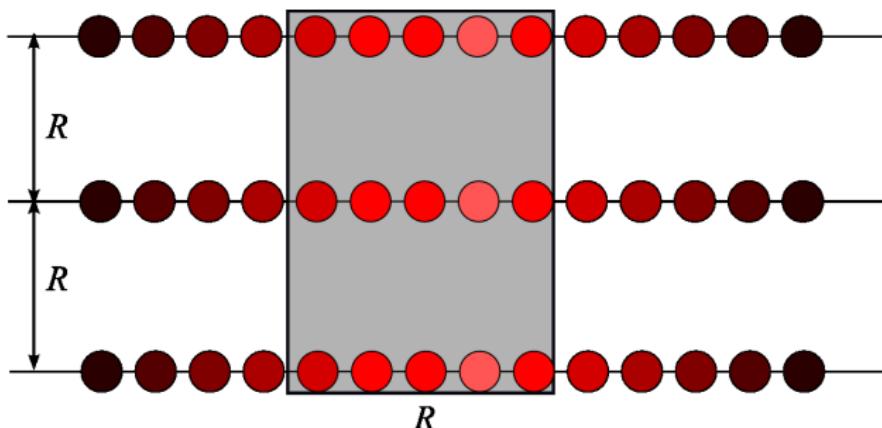
Infinite, parallel chains with finite gap



- ▶ But there are order R blue atoms, so interaction between the bits in the box is:

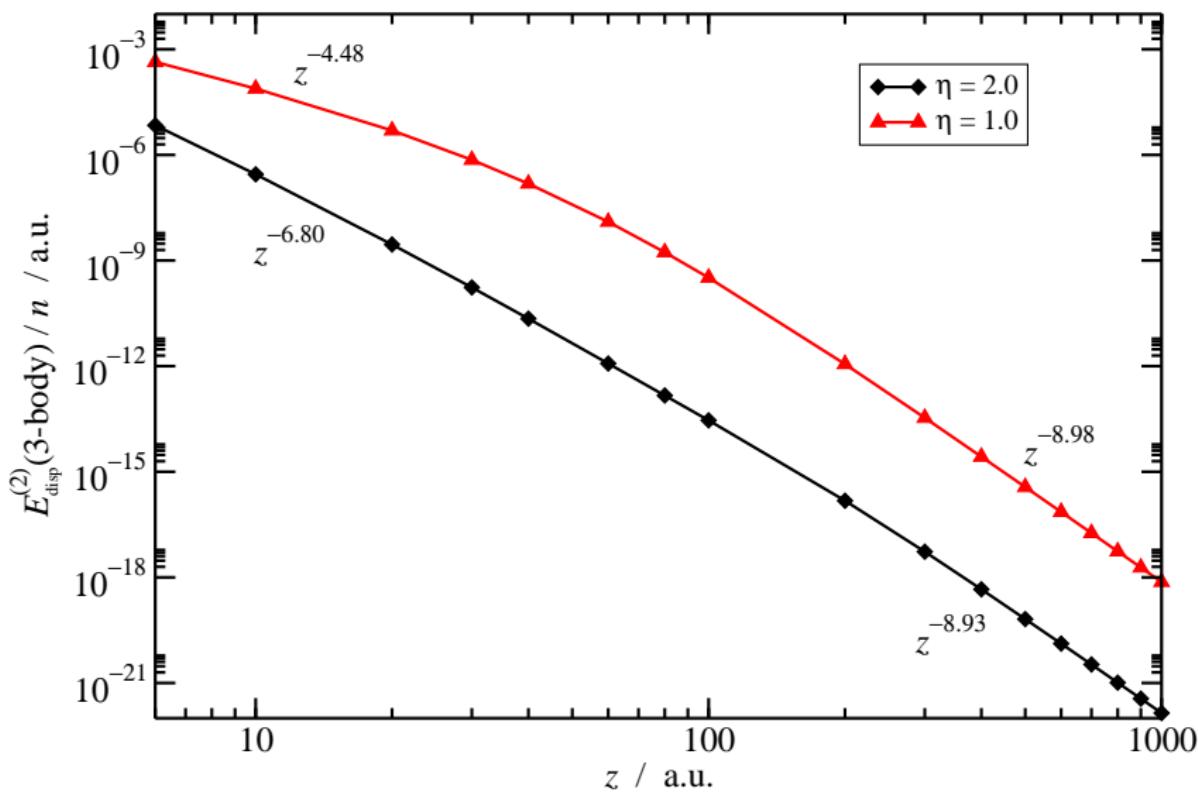
$$\frac{C_9}{R^9} \times (R \times R) \times R \quad (26)$$

Infinite, parallel chains with finite gap



- ▶ And interaction per unit length is:

$$\frac{C_9}{R^9} \times (R \times R) \times R/R = \frac{C_9}{R^7} \quad (27)$$



References

- ▶ A. J. Misquitta, J. Spencer, A. J. Stone and A. Alavi
“Dispersion interactions between semiconducting wires”, to appear in Phys. Rev. B (I hope!) (online at <http://arxiv.org/1005.1332>).
- ▶ All calculations were performed with the **CAMCASP** suite of programs. Download:
<http://www-stone.ch.cam.ac.uk/programs.html>.
- ▶ Non-local polarizabilities are calculated using the constrained density-fitting method described in AJM & Stone, J. Chem. Phys. **124**, 024111 (2006).
- ▶ The WSM method for local polarizability models is described in AJM, Stone and Price, J. Comput. Theor. Chem. **4**, 7 (2008), J. Comput. Theor. Chem. **4**, 19 (2008).
- ▶ Dispersion models in AJM & Stone, Mol. Phys. **106**, 1631 (2008).