Wave-like Nature of van der Waals Interactions in Polarizable Nanostructures

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Wavelike charge density fluctuations and van der Waals interactions at the nanoscale

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Recent experiments on noncovalent interactions at the nanoscale have challenged the basic assumptions of commonly used particle- or fragment-based models for describing van der Waals (vdW) or dispersion forces. We demonstrate that a qualitatively correct description of the vdW interactions between polarizable nanostructures over a wide range of finite distances can only be attained by accounting for the wavelike nature of charge density fluctuations. By considering a diverse set of materials and biological systems with markedly different dimensionalities, topologies, and polarizabilities, we find a visible enhancement in the nonlocality of the charge density response in the range of 10 to 20 nanometers. These collective wavelike fluctuations are responsible for the emergence of nontrivial modifications of the power laws that govern noncovalent interactions at the nanoscale.
Van der Waals: common understanding

**Pairwise methods** - currently the most popular vdW energy approach

\[
E_{vdW} = -f(R_{ij}) \sum_{i,j} \frac{C_{ij}^6}{R_{ij}^6} + \ldots
\]

- Simple, intuitive and computationally efficient
- Work well in small molecules

They strongly influence the current understanding of vdW effects:

- Well defined power law decay of vdW energy

\[\sim 1/R^6\]

\[\sim 1/R^5\]

\[\sim 1/R^4\]
Pairwise methods: limits

Pairwise methods rely on strong assumptions, i.e.:

I) ATOMIC LOCALIZATION OF CHARGE FLUCTUATIONS
II) ATOMS CORRELATE ONLY IN PAIRS

Pairwise methods could not describe:

I) Strongly delocalized fluctuations → might occur in metallic systems
   [J. Dobson, IJQC 114, 1157 (2014)]

II) Non-additive collective effects (3 body ATM, n-body, ... screening)
   [Ambrosetti, Alfe', DiStasio, Tkatchenko JPCL 5 849 (2014) ]
Pairwise methods: breakdown

If the basic hypotheses are not satisfied pairwise methods can fail:

- **Parallel metallic wires** [Dobson et al. PRL 96, 073201 (2006); Misquitta et al. PRB 82, 075312 (2010)]: interwire dispersion energy falls as

  \[ E_{vdW} \sim D^{-2} \text{ for vanishing gap} \]
  \[ E_{vdW} \sim D^{-5} \text{ for large gap} \]

  Delocalized electrons

  Localized electrons
Pairwise methods: breakdown

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dispersion energy falls as

\[
E_{vdW} \sim D^{-2} \text{ for vanishing gap} \quad E_{vdW} \sim D^{-5} \text{ for large gap}
\]

**Effect due to I) Strongly delocalized electronic fluctuations**

What if we consider **II) collective modes?**

Due to Many Body correlation → ubiquitous in principle
Collective modes – how to?

In **finite-gap** systems electrons are fairly **localized**

→ we rely on **atomic response** functions

- **Collective** modes = **correlated** fluctuations occurring in different atoms

- Can be described by **RPA** : coupling of localized atomic response functions
Collective modes – how to?

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**Efficient Approach: Coupled Quantum Harmonic Oscillators**

**Long been used** [Bade JCP 27 1280 (1957); probably even before!]

**Recently revised & applied** [Tkatchenko et al. PRL 108 236402 (2012); Martyna PRB 87 144103 (2013); Silvestrelli JCP 139 054106 (2013); ..... ]

\[
H_{MBD} = -\sum_{p}^{N} \frac{\nabla^{2} \xi_{p}}{2} + \sum_{p}^{N} \frac{\omega_{p}^{2} \xi_{p}^{2}}{2} + \sum_{p>q}^{N} \omega_{p} \omega_{q} \sqrt{\alpha_{p} \alpha_{q}} \xi_{p} T_{LR,pq} \xi_{q}
\]
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**Efficient Approach: Coupled Quantum Harmonic Oscillators**

\[ H_{MBD} = -\sum_{p}^{N} \frac{\nabla_{\xi_{p}}^{2}}{2} + \sum_{p}^{N} \frac{\omega_{p}^{2} \xi_{p}^{2}}{2} + \sum_{p>q}^{N} \omega_{p} \omega_{q} \sqrt{\alpha_{p} \alpha_{q}} \bar{\xi}_{p} T_{LR,pq} \bar{\xi}_{q} \]

**Static polarizability**

**Charge displacement**

**Dipole tensor**

**Effective RPA treatment of the vdW energy @ N^3 scaling**

The MBD Hamiltonian describes coupled dipole fluctuations.

Can be diagonalized exactly

Direct access to polarization eigenmodes (collective dipole oscillation modes)
Single Strained Carbon chain

MBD single chain eigenmodes: energy

- Uncoupled C atom modes
- Chain collective modes

2000 C atoms chain C-C distance 1.2 Å + PBC

- Appearance of low energy strongly collective polarization modes:

\[ \alpha(0) \bar{\omega}^2 = \text{Constant} \]

- high \( \alpha(0) \) and low \( \bar{\omega} \)
Single Strained Carbon chain

MBD single chain eigenmodes: energy

2000 C atoms chain C-C distance 1.2 Å + PBC

• Appearance of low energy strongly collective polarization modes:

\[ \alpha(0) \bar{\omega}^2 = \text{Constant} \]

Intra-wire MB effects cause dipole alignment

Macroscopic dipole waves along the wire

Low-energy eigenmodes: geometry

Uncoupled C atom modes

Chain collective modes

\[ N \text{ (eigenvalue number)} \]

\[ E \text{ (Ha)} \]

Dipole displacement

\[ \bar{\omega} \]

\[ \text{Å} \]
Parallel Carbon chains - energy

No more single-atom, but collective single-chain modes interacting

Asymptotic decay varies with $q$

\[
E_{c,12}^{LR(2)} = \frac{-\left(\alpha_C^0 \bar{\omega}_C^2\right)^2 L}{16\pi d_{C-C}^2} \int \frac{K_0^2(qD)q^4}{\bar{\omega}^3(q)} dq
\]
Parallel Carbon chains - energy

No more single-atom, but collective single-chain modes interacting

Asymptotic decay varies with $q$

RPA coupling of collective wave-like Modes

Macroscopic deviation from standard (pairwise) $R^{-5}$ power law in non-metallic systems.

Longer-ranged vdW interactions
Many Body effects controlled by \( \alpha^0 d_{CC}^{-3} \)

At large C-C distance: Degenerate modes → Localized response

At short C-C distance: Steep modes dispersion → Delocalized response

Collective modes dispersion

- 1.2 Å
- 1.4 Å
- 2.0 Å
- 3.0 Å
Many Body effects controlled by $\alpha^0 d_{C-C}^{-3}$

At large C-C distance: Degenerate modes → Localized response

At short C-C distance: Steep modes dispersion → Delocalized response

- Relation between modes dispersion and vdW asymptotics
- Exotic power laws related to the non-locality of the response
- Pairwise limit recovered only at large C-C distance (localized response)
Higher dimensionality reduces the range of correlation effects

However, complex power laws are found in realistic 2D systems as well:

- Importance of strain and atomic polarizability is preserved.
- The larger polarizability of MoS$_2$ gives larger power law deviations than graphene.

VdW interactions can be engineered through:
- Atomic species
- Dimensionality
- Strain
Conclusions

- Long-range correlation can induce **collective wave-like** charge fluctuation modes in low-dimensional finite-gap systems → **Strongly non-local response.**

- A **close relation** exists between **non-locality** of response and **power law** decay of vdW energy.

- Clear **limit of pairwise** methods: do not account for the actual normal modes of the system (generally collective).

- **Many body** treatment of long-range correlation needed to describe the **correct vdW asymptotics**.
Conclusions

- Long-range correlation can induce **collective wave-like** charge fluctuation modes in low-dimensional finite-gap systems → **Strongly non-local response**.

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Outlook

- Investigating vdW asymptotics in complex **biological** and **nanostructured** systems.

- **Engineering** vdW interactions by modifying geometry, polarizability and strain → possible control of **self-assembly** and biological processes.