Van der Waals forces in graphitic nanostructures

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QMC in the Apuan Alps IV
Vallico Sotto, 28th July 2008
History

Johannes Diderik van der Waals (1837-1923):
→ Postulation of intermolecular attraction in gases and liquids

Fritz London:
→ Unified treatment of “dispersion forces” in noble gases
  [Eisenschitz und London, Z. Physik 60, 491 (1930)]

Henk Casimir and Dirk Polder
→ Proposed force between metal plates in vacuum
  “The Influence of Retardation on the London-van der Waals Forces”
  [Phys. Rev. 73, 360 (1948)]
Definitions of terms

**Inter-molecular forces**: anything except covalent or ionic bonds

A) dipole-dipole force (two permanent dipoles)  
   [more general: multipole forces]

B) hydrogen bond

C) induced dipole force (permanent dipole/induced dipole)

D) dispersion forces (instantaneous dipole-dipole force)

**London force**  
→ synonym for “dispersion force” (sometimes including induced dipole force)

**van der Waals force**  
→ synonym for “intermolecular force”  
   (sometimes synonym for dispersion force)

**Casimir force**  
→ dispersion force between solids (continuum theory)
Dispersion force between atoms

⇒ long-distance correlations between electron positions within unpolar atom

\[ E_{\text{disp}}^{AB} \approx -\frac{3\alpha^A \alpha^B I_A I_B}{4(I_A + I_B)} R^{-6} \]

\( \alpha^A, \alpha^B \) polarizability

\( I_A, I_B \) ionization potential

\( R \) interatomic distance

obtained via QM-multipole expansion [Eisenschitz und London, Z. Phys. 60, 491 (1930)]
Casimir force

Macroscopic bulk description of force between polarizable media.

- depends on dynamic polarizability and geometry of media
- not additive (!)
- in case of metal bodies in vacuum
  ⇒ elegant computation via vacuum energy of intermediate space
- always attractive for symmetric combination of media
  (e.g. metal-vacuum-metal, air-liquid-air, etc.)
- reduced with increasing temperature
- reduced by relativistic retardation important for longer distances
intralayer bond length: \( d_{CC} = 1.4196 \, \text{Å} \)
atomization energy: \( E_{at} = 7.374 \, \text{eV/atom} \)
intralayer isotrop. elastic constant: \( C_{11} + C_{22} = 1240 \, \text{GPa} \)
interlayer distance: \( d_{interlayer} = 3.335 \, \text{Å} \)
exfoliation energy: \( E_{ex} = 35...52 \, \text{meV/atom} \)
interlayer elastic constant: \( C_{33} = 36.5 \, \text{GPa} \)
## Theoretical attempts on interlayer energetics

<table>
<thead>
<tr>
<th>Method</th>
<th>Method Details</th>
<th>(d_{\text{interlayer}}) (Å)</th>
<th>(E_{\text{ex}}) (meV/atom)</th>
<th>(C_{33}) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brennan (1952)</td>
<td>LCAO + vdW exp. input</td>
<td>exp. input</td>
<td>11 / 172</td>
<td>39 / 11</td>
</tr>
<tr>
<td>Girifalco (1956)</td>
<td>lattice summation</td>
<td>5.6</td>
<td>110</td>
<td></td>
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<tr>
<td>DiVincenzo (1983)</td>
<td>DFT + Thomas Fermi</td>
<td>5.6</td>
<td>110</td>
<td></td>
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<tr>
<td>Yin (1984)</td>
<td>DFT-LDA</td>
<td>7.05 ± 0.7</td>
<td>~ 13.6</td>
<td>54 ± 20</td>
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<tr>
<td>Jansen (1987)</td>
<td>all elec. augmented PW</td>
<td>6.83 ± 0.06</td>
<td>56 ± 9</td>
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</tr>
<tr>
<td>Schabel (1992)</td>
<td>DFT-LDA</td>
<td>6.72</td>
<td>24</td>
<td>24.3</td>
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<tr>
<td>Charlier (1994)</td>
<td>DFT-LDA</td>
<td>6.60</td>
<td>20</td>
<td></td>
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<tr>
<td>Telling (2003)</td>
<td>DFT-LDA</td>
<td>6.70</td>
<td>35</td>
<td></td>
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<tr>
<td>Rydberg (2003)</td>
<td>layered DFT-vdW</td>
<td>7.52</td>
<td>24</td>
<td>13</td>
</tr>
<tr>
<td>Zhechkov (2005)</td>
<td>DFTB + a posteriori vdW</td>
<td>6.76</td>
<td>38.5</td>
<td></td>
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<tr>
<td>Mounet (2005)</td>
<td>GGA (at exp. lattice const.)</td>
<td>exp. input</td>
<td>45</td>
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<tr>
<td>Donchev (2006)</td>
<td>QMPFF</td>
<td>6.972</td>
<td>54.9</td>
<td>40.6</td>
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<tr>
<td>Ortmann (2006)</td>
<td>GGA + semiemp. vdW</td>
<td>6.69</td>
<td>83.5</td>
<td>41.7</td>
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<tr>
<td>Ziambaras (2007)</td>
<td>general DFT-vdW</td>
<td>7.18</td>
<td>53</td>
<td>27</td>
</tr>
<tr>
<td>Hasegawa (2007)</td>
<td>DFT + semiemp. corr.</td>
<td>exp. input</td>
<td>60.4</td>
<td>exp. input</td>
</tr>
<tr>
<td>Gould (2008)</td>
<td>LDA/GGA + semiemp. corr.</td>
<td>exp. input</td>
<td>62.4 / 59.7</td>
<td>exp. input</td>
</tr>
</tbody>
</table>
Correlation between experiment and theory

exfoliation energy:  
42 meV/atom [Girifalco 1952: wetting by organic liquids]  
$\sim$ 20 meV/atom $\rightarrow$ various incorrect conversions  
35 meV/atom [Benedict 1998: collapse of nanotubes]  
52 meV/atom [Zacharia 2004: polyaromatic hydrocarbons]
$\pi$-conjugated electronic structure of graphene

in-plane $sp^2$-orbitals
→ strong $\sigma$-bonds

remaining $pz$-orbitals
→ semi-metallic $\pi$-bands

$\pi$-band structure of graphene:
Dispersion forces for thin layers

<table>
<thead>
<tr>
<th>System</th>
<th>Present</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D metals\textsuperscript{a}</td>
<td>(-D^{-2}(\ln(KD))^{-3/2})</td>
<td>(-D^{-5})</td>
</tr>
<tr>
<td>1D insulators [9]</td>
<td>(-D^{-5})</td>
<td>(-D^{-5})</td>
</tr>
<tr>
<td>2D metals [10,11]</td>
<td>(-D^{-5/2})</td>
<td>(-D^{-4})</td>
</tr>
<tr>
<td>(\pi)-conjugated layers\textsuperscript{a}</td>
<td>(-D^{-3})</td>
<td>(-D^{-4})</td>
</tr>
<tr>
<td>1 metallic, 1 (\pi) layer\textsuperscript{a}</td>
<td>(-D^{-3}\ln(D/D_0))</td>
<td>(-D^{-4})</td>
</tr>
<tr>
<td>2D insulators [6]</td>
<td>(-D^{-4})</td>
<td>(-D^{-4})</td>
</tr>
<tr>
<td>Thick metals or ins. [11]</td>
<td>(-D^{-2})</td>
<td>(-D^{-2})</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Denotes new derivations given here.

Graphite and QMC


• VMC with nonlocal pseudopotential
→ precision insufficient for vdW interactions


• VMC with inhomogeneous e-e-Jastrow term
→ no binding energy extracted
→ large number of parameters (3000 for 3x3x3 super cell)

Our approaches (work in progress!!)

vdW-tailored Jastrow term    DMC with finite-size corrections
The Jastrow-D-term

Inspired by classical dipole-dipole interaction:

\[ E = \frac{1}{4\pi\varepsilon_0 R^3} (d_A \cdot d_B - 3(d_A \cdot \mathbf{R})(d_B \cdot \mathbf{R})) \]

longitudial dipoles

attractive transverse dipoles
The Jastrow-D-term

Inspired by classical dipole-dipole interaction:

\[ E = \frac{1}{4\pi\varepsilon_0 R^3} (d_A \cdot d_B - 3(d_A \cdot R)(d_B \cdot R)) \]

Two independent D-terms:

\[
D_{\parallel} = \sum_{I < J} \sum_{i,j} (r_{Ii} \cdot R_{IJ})(r_{Jj} \cdot R_{IJ}) f_{||}^{IJ}(r_{Ii}, r_{Jj})
\]

\[
D_{\perp} = \sum_{I < J} \sum_{i,j} \left[ (r_{Ii} \cdot r_{Jj})R_{IJ}^2 - (r_{Ii} \cdot R_{IJ})(r_{Jj} \cdot R_{IJ}) \right] f_{\perp}^{IJ}(r_{Ii}, r_{Jj})
\]

\(f_{\parallel}^{IJ}\) and \(f_{\perp}^{IJ}\): scalar functions with cutoff, analogous to \(U\) term

\(\rightarrow\) optimized independently for each pair of atoms (reduced by symmetry)

\(\Rightarrow\) implemented, but yet to be tested ...
Graphite interlayer binding with CASINO

- CASTEP wave function (plane-wave $\rightarrow$ blip)
- using pseudo-potentials $\Rightarrow$ 4 electrons per C atom
- primitive cell containing two graphene layers with two atoms each
  $\Rightarrow$ 16 electrons per primitive cell
- starting out with 3x3x1 simulation cell
  $\Rightarrow$ 144 electrons in simulation cell
- Jastrow terms: $U$, $\chi$, $F$
  $\rightarrow N_u = N_\chi = 6$, $N_{f-ee} = N_{f-eN} = 2$
  $\rightarrow$ fixed cutoffs $L_u = 4$ a.u., $L_\chi = 3$ a.u., $L_f = 2$ a.u.
  $\rightarrow$ varmin-linjas optimization
DMC time-step and CPU cost analysis

→ 64 nodes á 100 configs
→ 1000 time steps data collection
→ $5 \times 64 = 320$ CPU hours

→ correlation time: $\sim 2$ a.u.
→ using $\text{dtdmc}=0.01$
Twist averaging

18 twist angles according to special points in hexagonal 2D Brillouin zone

[Cunningham, Phys. Rev. B 10, 4988 (1974)]
Preliminary results

<table>
<thead>
<tr>
<th>super cell</th>
<th>$E_{ex}$ (meV/atom)</th>
<th>CPU hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 × 3 × 1</td>
<td>102 ± 6</td>
<td>2 × 1000</td>
</tr>
<tr>
<td>3 × 3 × 2</td>
<td>68 ± 5</td>
<td>2 × 5000</td>
</tr>
<tr>
<td>4 × 4 × 1</td>
<td>53 ± 4</td>
<td>2 × 5000</td>
</tr>
<tr>
<td>experiment</td>
<td>35...52</td>
<td></td>
</tr>
</tbody>
</table>

Next steps

- more careful Jastrow optimization
- finite size correction for kinetic energy
- Ewald ↔ MPC
- check error from finite k-grid in DFT
- localize blip wfn (not yet implemented for complex wfn)

→ larger systems and more smaller and intermediate system sizes
Acknowledgements

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