Nonuniversality of the dispersion interaction: analytic benchmarks for van der Waals energy functionals

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We highlight the non-universality of the asymptotic behavior of dispersion forces, such that a sum of inverse sixth power contributions is often inadequate. We analytically evaluate the cross-correlation energy $E_{\text{xc}}$ between two $\pi$-conjugated layers separated by a large distance $D$, within the electromagnetically non-retarded Random Phase Approximation, via a tight-binding model. For two perfect semimetallic graphene sheets at $T=0K$ we find $E_{\text{xc}} \propto D^{-3}$, in contrast to the “insulating” $D^{-4}$ dependence predicted by currently accepted approximations. We also treat the case where one graphene layer is replaced by a thin metal, a model relevant to the exfoliation of graphite. Our general considerations also apply to nanotubes, nanowires and layered metals.

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Dispersion (van der Waals, vdW) interactions\textsuperscript{1,2} are especially significant in soft matter, though they coexist there with stronger covalent and metallic forces. It is known\textsuperscript{3,4,5,6,7} that all the relevant physics (in the electromagnetically non-retarded regime) is contained in microscopic generalizations of the Lifshitz\textsuperscript{8} approach: these use the fluctuation-dissipation theorem (FDT) to generate the electronic correlation energy, starting from a sufficiently accurate nonlocal electronic density-density response function $\chi$. They are “universal” in that they capture the vdW interaction in systems of any size, shape or composition, and “seamless” in that they work equally well at all separations of the sub-systems. Here we point out that many currently popular approaches do not share this universality: for example, the usual sum of asymptotic atom-atom contributions of form $-C_{6}R_{AB}^{-6}$ (see e.g.\textsuperscript{2}) is inappropriate in many anisotropic systems of great current interest, even in well-separated regimes.

To implement the FDT approach, $\chi$ can be usefully modelled, for example, by time-dependent density functional theory\textsuperscript{8} with its exchange-correlation kernel $f_{\text{xc}}$. The simplest case, $f_{\text{xc}}=0$, gives the Random Phase Approximation (RPA) correlation energy. While theories of this class have been applied successfully without further approximation to vdW interactions in simple systems such as small dimers\textsuperscript{9,11} or layered jellium\textsuperscript{3,11,12}, the numerics become formidable for soft systems of realistic complexity. There has been progress recently in creating more tractable theories\textsuperscript{11,13,14,15,16}. Based on these approaches, functionals have been proposed\textsuperscript{16} that are solely or principally density-based, that give sensible results for the energetics of compact systems and that have the typical asymptotic $1/R^{6}$ form

$$E \approx - \int f(n_{A},\nabla n_{A},n_{B},\nabla n_{B})r_{AB}^{-6}d\vec{r}_{A}d\vec{r}_{B} \quad (1)$$

for separated electron densities $n_{A} \equiv n_{A}(\vec{r}_{A}),n_{B} \equiv n_{B}(\vec{r}_{B})$. These seamless theories are promising for weakly bonded finite molecules and small clusters, giving a natural “saturation” of the $R^{-6}$ van der Waals energy contributions at shorter distances, a long-anticipated goal\textsuperscript{17}. Perturbation theory also supports\textsuperscript{11}.

It has therefore been widely supposed that (1) is the correct asymptotic form, and that only detailed applications remain to be analyzed. We show here that the situation is not so simple, at least for soft layered and strained structures. We motivate our general point by new results for the cohesion energetics of graphitic systems\textsuperscript{11,13}, a controversial\textsuperscript{15,20} and technologically relevant\textsuperscript{21,22,23} topic. Graphene sheets are highly polarizable, so vdW forces should be involved\textsuperscript{24}. Nevertheless, the electronic local density approximation (LDA) gives good equilibrium layer spacings\textsuperscript{25} and breathing phonon frequencies\textsuperscript{26} despite the complete lack of distant vdW forces in the LDA\textsuperscript{12,26}. However, for the depth $-\min_{D}E(D)$ of the binding energy curve of graphene sheets distant $D$, the LDA gives a value ($\approx 20mH/atom$) that is little more than half of the most accepted experimental values (35$mH/atom$ or more\textsuperscript{12,20}). Recent calculations\textsuperscript{12} found the LDA similarly underestimates the binding of a pair of thin parallel high-density jellium electron gases, another strongly anisotropic layered system that might (e.g.) represent alkali-intercalated graphite. For other layered jellium systems the LDA gave varying degrees of unsatisfactory behavior near equilibrium\textsuperscript{12}, related to the absence of vdW interactions in LDA. Nevertheless the LDA in fact performs much better than the common gradient functionals for these systems\textsuperscript{15,27}. Current opinion\textsuperscript{18} seems to be that LDA should be used near the equilibrium lattice configuration, and extended by fitting to a sum including...
atom-atom terms $-C_6 R_\Lambda^{-6}$ in order to treat “stretched” soft matter.

A known exception is the interaction energy $E$ of two thin metals at large separation $D$, for which $\sum_{ij} C_{ij} R_{ij}^{-6}$ predicts $E \propto -C_4 D^{-4}$, but the correct dependence (e.g. from RPA energetics) is $-C_5/2 D^{-5/2}$. We will show that this is not an isolated case. Qualitatively speaking, part of the reason for this difference is that conducting electrons can move long distances and are not confined to the vicinity of atoms, in contrast to the models that lead to $R^{-6}$ force laws. The low dimensionality is also important, leading to weak metallic screening and hence to gapless two-dimensional (2D) plasmons at low wavenumber. By contrast, thick metallic slabs have gapped surface plasmons and give a conventional attraction law, $E \approx -C/D^2$ whose form can be obtained by summing $R^{-6}$ atom-atom contributions.

What does this type of physics imply for the energetics of layered planar graphene-based systems? Firstly, an isolated graphene sheet is not a metal but a zero-gap insulator: the two-dimensional Bloch electron dispersion relation has a “conical” shape near the Fermi level, with a zero energy gap at the Fermi level but a zero density of states at the gap $[21]$. When the graphene layers are brought to their equilibrium separation to create graphite, the graphene bands overlap slightly at the Fermi level to create small pockets of electrons and holes. Thus the layers in equilibrium graphite are metallic, but this only involves a small fraction of the electrons. When the layers are separated (at zero electronic temperature) this overtly metallic character is lost, so that one cannot argue for a $-C_5/2 D^{-5/2}$ energetics at large layer separation $D$ and $T = 0K$. We show below, however, that the attraction energy between well-separated graphite planes at $T = 0K$ is of form $-C_3 D^{-3}$, closer to metallic $D^{-5/2}$ behavior than to insulating $D^{-4}$ behavior. This is a principal quantitative result of the present work, and it poses a significant asymptotic constraint on electromagnetically non-retarded van der Waals energy functionals. Fitted interactions including $\sum_{ij} C_{ij} R_{ij}^{-6}$ terms are, and seamless energy functionals proposed recently, for example, produce the insulating $D^{-4}$ behavior, and so do not conform to the new constraint. Neither do ground-state LDA calculations. We now give the details of our argument leading to this new $D^{-3}$ form of interaction.

All the new physics here comes from electrons close to the Fermi level: we can ignore the response of the tightly-bound covalent $sp^2$ electrons, whose finite energy gap ensures that they produce a conventional vdW attraction of insulator type (energy $\propto -D^{-4}$), negligible at large separations compared with the $D^{-3}$ vdW attraction that we shall find between the $\pi_z$ electrons of interest here. In the tight binding (TB) model, the valence and conduction $\pi_z$ Bloch orbitals and their energies $\varepsilon^{(v,c)}(\mathbf{k})$ are constructed via bonding and antibonding combinations of a single $\pi_z$ (Wannier) orbital $w(\mathbf{r}) = w(\mathbf{x} + z\hat{k})$. From Rayleigh-Schrödinger perturbation theory the zero-temperature density-density response $\chi_{K\Sigma}$ of independent $\pi_z$ electrons moving in the groundstate Kohn-Sham potential of a graphene layer is then of the form

$$\chi_{K\Sigma}(\mathbf{q}, \mathbf{G}, \mathbf{G}', z, z', \omega = iu) = SS^{*}\tilde{\chi}_0(\mathbf{q}, iu).$$  

Here $\mathbf{q}$ lies in the 2D Brillouin zone, $\mathbf{G}, \mathbf{G}'$ are 2D reciprocal lattice vectors, $z$ and $z'$ are positions measured in the direction perpendicular to the planes, $S = S(\mathbf{q} + \mathbf{G}, z)$, $S' = S(\mathbf{q} + \mathbf{G}', z')$ with $S(\mathbf{k}, z) = \int d^2xe^{ikz} w^*(\mathbf{x}) w(\mathbf{x} + z\hat{k})$, and the effective 2D response in (2) is an integral over the 2D Brillouin zone (BZ),

$$\tilde{\chi}_0(\mathbf{q}, iu) = -\int_{\mathcal{BZ}} \frac{|L(\mathbf{p}, \mathbf{p} + \mathbf{q})|^2}{(2\pi)^2} \frac{2\Delta \varepsilon d^2p}{\Delta \omega^2 + (hu)^2}. $$  

Here $\Delta \varepsilon = \varepsilon^{(v,c)}(\mathbf{p}) - \varepsilon^{(v,c)}(\mathbf{p} + \mathbf{q})$, and $L$ is an overlap integral evaluated below. $L$ approaches zero when $|\mathbf{q}| << |\mathbf{p}|$, by valence-conduction orbital orthogonality, so that, for $q << G$, the Brillouin zone integral is dominated by small $p$ values. (Here $\mathbf{p}$ is measured from a $K$ point in the Brillouin zone where the bands cross). For the small $q$ values required below, we can therefore use the linear band dispersion $\varepsilon^{(v,c)}(\mathbf{p}) = \mp hv_0 |\mathbf{p}|$. (We take the graphene velocity to be $v_0 = 5.7 \times 10^6 m/s$). In the same approximation the overlap element is $|L(\mathbf{p}, \mathbf{p}^{'})|^2 = 4 \sin^2(\frac{3\pi}{2G})$ where $\theta$ is the angle between $\mathbf{p}$ and $\mathbf{p}'$. Eq. (3) can be evaluated analytically (see e.g. [31]) by extending the $\mathbf{p}$ integration to all space, finite-BZ corrections vanishing as $q \to 0$:

$$\tilde{\chi}_0(\mathbf{q}, iu) \approx -\frac{q^2}{2h\sqrt{v_p^2q^2 + u^2}}. $$

The divergence of the polarizability $q^{-2}\tilde{\chi}_0$ at low $q$ and $u$, and the parallel dependence on $q$ and $u$, are crucial.

For two non-overlapping graphene sheets centered at $z = 0$ and $z = D$, the “bare” (Kohn-Sham) polarizability from (2) is then

$$\chi_0(\mathbf{q}, iu) = \chi_0(\mathbf{q}, iu) (S_0 S_0^{*} + S_D S_0^{*})$$

where $S_D = S(\mathbf{q} + \mathbf{G}, z - D)$ and $S_D' = S(\mathbf{q} + \mathbf{G}', z' - D)$. The interacting RPA density-density response function $\chi_\lambda(\mathbf{q}, \mathbf{G}, \mathbf{G}', z, z', \omega)$ satisfies the following screening equation, where stars represent both convolution in $(z, z')$ space and matrix multiplication in $(\mathbf{G}, \mathbf{G}')$ space:

$$\chi_\lambda = \chi_0 + \chi_0 * \lambda V^{\text{cond}} * \chi_\lambda. $$

Here $V^{\text{cond}} = 2\pi e^2 \exp(-|\mathbf{G} + \mathbf{G}'| |z - z'|)\delta_{\mathbf{GG}'} / (|\mathbf{G} + \mathbf{q}|)$. The factorizable $(z, z')$ and $(\mathbf{G}, \mathbf{G}')$ dependence in (6) arises because only a single $\pi_z$ orbital is involved in the TB description of the $\pi$-conjugated Bloch states. This leads to an analytic solution of (6), where $\chi_\lambda$
has intra-layer terms \( \tilde{\chi}_{111}, \tilde{\chi}_{222} \) similar to \( \delta \), and also inter-layer terms \( \chi_{122}, \chi_{212} \): 
\[ \chi_{122} = (1 - \tilde{\chi}_0 V_{11}) \tilde{\chi}_0 / \varepsilon, \quad \chi_{212} = \tilde{\chi}_{122} = 2 \chi_{12} = V_{12} \chi_{12}^2 / \varepsilon, \]
where
\[ \varepsilon(\mathbf{q}, iu) = (1 - \tilde{\chi}_0 (V_{11} + V_{12}))(1 - \tilde{\chi}_0 (V_{11} - V_{12})), \]
\[ V_{ij}(\mathbf{q}) = \sum_{\mathbf{G}} d\mathbf{z}'' d\mu'' S_i^\mu(\mathbf{q} + \mathbf{G}'', \mathbf{z}'' - \mathbf{z}_i) \times V^{\text{coul}}(\mathbf{q} + \mathbf{G}'', \mathbf{z}'' - \mathbf{z}_i) S_j^\mu(\mathbf{q} + \mathbf{G}'', \mathbf{z}'' - \mathbf{z}_j), \]
and with \( z_1 = 0, z_2 = D \).

The asymptotic vdW interaction between large objects is commonly found by summing the zero-point energies of the weakly-damped plasmons of the combined system, minus that of the isolated systems \( \delta \). For \( T = 0K \), however, the isolated graphene layers do not exhibit weakly damped plasmons at small surface-parallel wavevector \( q \). Therefore we need to go back to the more general and basic RPA correlation energy formulation, to which the sum-of-plasmon-energies approach is an approximation, valid only when plasmon poles near the real frequency axis dominate (see e.g. \( \delta \)). The adiabatic connection-FDT gives the “cross-correlation” energy of the present well-separated system as (see e.g. \( \delta \)):
\[ E_c^{cr} = \frac{-\hbar}{2\pi} \int_0^\infty d\lambda \int_0^1 d\mathbf{q} (J_c(\mathbf{q}, \mathbf{q}, \mathbf{q}, \mathbf{q})) , \]
\[ J_c(\mathbf{q}, \mathbf{q}, \mathbf{q}, \mathbf{q}) = \varepsilon^2 \int_0^\infty d\mu \int_{-\infty}^{\infty} dz dz' \exp(-q|z - z'|) \times \left( \chi_\mathbf{q}(\mathbf{q}, \mathbf{q}, \mathbf{q}, \mathbf{q}) - \chi_\mathbf{q}(\mathbf{q}, \mathbf{q}, \mathbf{q}, \mathbf{q}) \right) \]
where \( \chi_\mathbf{q} \) is the combined interacting response obtained above for two graphene planes separated by distance \( D \). In the cross correlation energy \( \delta \) for distant graphenes, only the \( \mathbf{G} = \mathbf{G}' + \mathbf{G}'' \) component of the response functions are required because the coulomb interaction between \( \mathbf{G} \neq \mathbf{0} \) fluctuations on the two layers is of order \( \exp(-q|\mathbf{G}|) = 0(\exp(-\pi D/a)) \). This is \( c << 1 \) when the layer separation \( D \) greatly exceeds the intraplanar spacing \( a \) between carbon atoms. \( \delta \) and \( \delta \) give
\[ J_{c,\text{RPA}}(\mathbf{q}, \mathbf{q}) = J_{c,\text{RPA}}(\mathbf{q}, \mathbf{q}, \mathbf{q}, \mathbf{q}), \]
\[ = \frac{q}{2\pi} \int_0^\infty du (2V_{11}(\mathbf{q}) \chi_{121}(\mathbf{q}, \mathbf{q}, \mathbf{q}, \mathbf{q})) + \] 
\[ + 2V_{11}(\mathbf{q}) \left( \chi_{111}(D, \mathbf{q}, \mathbf{q}, \mathbf{q}, \mathbf{q}) - \chi_{111}(\infty, \mathbf{q}, \mathbf{q}, \mathbf{q}, \mathbf{q}) \right) \]
where \( \chi_{111} \) and \( \chi_{222} \) are defined in \( \delta \). Because every term in an expansion of \( \delta \) in powers of the small quantity \( \chi_{222} \) is at least of order \( \chi_{222}^2 \), we deduce that the cross energy \( \delta \) for distant slabs \( D \rightarrow \infty \) is dominated by small parallel wavenumbers \( q \) of order \( D^{-1} << a^{-1} \). For \( D >> a \) we can therefore approximate \( \chi_{222} \), assuming that \( q \) is small compared with any \( |\mathbf{G}| \). In this limit \( \delta \) is dominated by the \( \mathbf{G}'' = \mathbf{0} \) terms, \( \chi_{111} \approx 2\pi e^2 / q, \chi_{222} \approx 2V_{11}(\mathbf{q}) \exp(-qD) \).

and \( \delta \) we then have \( J_c^2(\mathbf{q}, \mathbf{q}) = \frac{2}{\pi^2} F_\lambda(\mathbf{D}) \), where by substituting \( u = v_0 q \sinh x \) and defining the dimensionless constant \( c = \pi e^2 / \hbar v_0 = 12.145 \) for graphite we find 
\[ F_\lambda(\mathbf{y}) = -\int_\mathbf{y}^\infty c \left( \frac{c + \lambda bE_+ + E_+}{(c + \lambda bE_+)(c + \lambda bE_-)} - 1 \right) dx. \]
Here \( c = \cosh x \) and \( x_\pm = \pm \exp(-y) \). Then the interaction energy per unit area is (in Gaussian esu units)
\[ E_c^{cr} = \int_0^1 d\lambda E_c^{cr} = -Be^{2}D^{-3} \]
where \( B = (2\pi)^{-1} \int_0^\infty d\lambda \int_0^\infty y^2 F_\lambda(\mathbf{y}) dy = 2.0036 \times 10^{-2} \) is dimensionless and independent of \( D \).

Eq \( \delta \) is a principal result of the present work. It shows that the asymptotic van der Waals attraction energy, at \( T = 0K \), between parallel graphene planes distant \( D \), falls off like \( D^{-3} \). This is to be compared with \( D^{-5/2} \) for 2D metallic planes \( \delta \), and \( D^{-4} \) for planes of finite-gap 2D insulators: the \( D^{-4} \) law follows equally from a sum of atom-atom \( R^{-6} \) contributions or from the zero-point energy of gapped plasmons. Clearly the gapless graphene planes behave in this respect more like metals than insulators, despite the lack of undamped 2D plasmon modes on a graphene sheet. These examples illustrate the non-universality of the vdW functional as well as its nonlocality \( \delta \). Adding an exchange-correlation kernel \( f_{xc} \) to the calculation of the response function in eq. \( \delta \) would modify the coefficient in Eq \( \delta \) but not the \( D^{-3} \) power law dependence.

Another interesting case, possibly more accessible experimentally, is the interaction between a graphene layer and a weakly metallic 2D layer. This could represent, for example, the outer part of the energy curve for interaction between a layer being peeled off a solid graphite surface, and the last layer of the remaining solid, in an exfoliation experiment. Because of a weak overlap of orbitals in the \( z \) direction perpendicular to the graphene planes, each layer of the solid has small pockets of electrons and holes and can reasonably be modelled by a 2D electron gas in the present context.

We therefore applied the above RPA method to the non-overlapping interaction between an isolated graphene layer and a metallic graphite layer with Fermi energy \( \varepsilon_F = O(0.02 eV) \). For \( D >> D_0 \), the energy per unit area is (c.f. \( \delta \))
\[ E_c^{cr} \approx -Ce^{2}D^{-3} \ln(D/D_0). \]
Here \( C \) is a dimensionless constant. Like the case of two non-metallic graphene planes, the result \( \delta \) disagrees with standard theories.

In summary, our new calculations (see \( \delta, \delta, \delta, \delta \)) reinforce our main point that the asymptotic (large-\( D \)) dispersion energy is a highly non-universal function of
separation $D$ between non-overlapping subsystems. In particular we have highlighted the inadequacy, in this distant regime at least, of the usual sum of contributions of form $C_6 R^{-6}$ between pairs of atoms distant $R$, and therefore of various functionals that reduce to this asymptotic limit as $R \to \infty$. A finite sum of multipole, or triplet and higher terms will also not reproduce what we have discussed. This inadequacy seems to occur when the component systems are (i) metallic (or have a zero electronic Bloch bandgap), (ii) of large spatial extent in at least one dimension, so that long-wavelength (low-$q$) charge fluctuations are possible, and (iii) low-dimensional (of nanoscopic dimensions in another spatial direction), so that the electron-electron screening is reduced compared to 3D bulk metallic systems, leaving a divergent polarizability at low frequency and wavenumber. This physics is expected to be important in prediction of the cohesive energy of graphite, intercalated graphite, graphitic hydrogen storage systems, bundles of metallic nanotubes or nanowires, biomolecules and a large variety of weakly bound compounds (“soft matter”). Although it is only in the widely-separated regime that the relevant long-wavelength electronic response is dominant, these low wavenumbers are still likely to be relevant near the overlapped equilibrium configuration. We have discussed some partial evidence for this conclusion, from existing jellium layer calculations[17]. These used RPA-like nonlocal seamless microscopic theory that treats covalent, metallic and van der Waals effects on an equal footing. A similar level of theory is required for more realistic non-jellium models of soft matter, and this is leading to challenging numerical calculations[18]. Simplified versions[19] will probably have to take explicit account of large-scale geometry and/or nonlocal entities such as electronic bandgap. We note finally that our considerations might affect the analysis of some seminal experiments[20] concerning graphitic cohesion, because these relied at some point on theory involving a sum of $R^{-6}$ contributions.

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