5 SCIENTIFIC HIGHLIGHT OF THE MONTH

Calculation of Dispersion Energies

John F. Dobson and Timothy Gould

Queensland Micro and Nano Technology Centre

Griffith University,

Kessels Rd., Nathan, Queensland 4111, AUSTRALIA.

j.dobson@griffith.edu.au

1 Introduction

"Dispersion forces" [1], [2] are generally understood in the solid-state physics community to be that part of part of the non-covalent van der Waals (vdW) interaction that cannot be attributed to any permanent electric mono-or multipoles. (In the chemistry community, the whole of the non-chemically-bonded interaction is often termed the "van der Waals" (vdW) interaction, but in the the physics community this term is usually reserved for the outer dispersion component as defined above. A useful categorization of the many components of the total force is given in [3] from a perturbation theory standpoint). The ubiquitous dispersion forces occur wherever polarizable electron clouds are present, and are typically weaker than ionic and covalent bonding forces, but are of longer range than the latter, decaying algebraically rather than exponentially with separation. They are important in protein interactions, in rare-gas chemistry and in soft condensed matter generally. They are especially important, for example, in the cohesion and self-assembly of graphenic nanostructures including nanotubes and planar graphene-based systems, which have attracted strong recent interest in the condensed matter community. Much work has been done on the vdW interaction in the two extremes of (i) small molecules (via high-level quantum chemical methods such as coupled cluster (CCSD(T)) [4] or Symmetry adapted Perturbation theory (SAPT) [3]) and (ii) well-separated macroscopic objects (via Lifshitz theory and its extensions, for example [5], [6], [2]). However the study of vdW interactions between solids and nanostructures down to intimate contact, where dispersion competes with other forces, is still an area of active research. The selective adhesion of graphene to various metal substrates is an example of a delicate phenomenon where vdW forces are important but where a successful fully quantitative theory seems still to be lacking. This paper will outline the development of simple and more complex theories to account

for these phenomena within the electromagnetically non-retarded regime, as defined in the following paragraph. The website [http://www.cecam.org/workshop-2-411.html] of a recent CECAM workshop will give the flavour of some relatively recent work in this area.

vdW forces are a special case of the more general electromagnetically retarded interaction between matter, an interaction that is properly treated by regarding both the matter and the electromagnetic field as dynamical quantum systems. When the distance D between the interacting bodies is sufficiently small, the light transit time $\tau_{light} = D/c$ is small compared to the response time τ_{matter} of the charges in the matter, and then we can neglect the retardation of the electromagnetic field. This is sometimes designated the "vdW regime", and here one can treat the electromagnetic field as a non-retarded scalar classical Coulomb field, that serves merely to induce correlations between the charge fluctuations within the interacting bodies. The emphasis is then focussed on the dynamics of the interacting matter - the electronic many-body problem. This is the approach that will mainly be pursued below.

It is worthwhile, however, to consider briefly the opposite limit where retardation is important, and here the dispersion-type forces are often termed Casimir forces [7]. In this "Casimir regime" the response of the matter is often treated approximately via a spatially local dielectric function $\varepsilon(\omega)$ confined within sharp spatial boundaries representing the edges of the matter. The dispersion interaction is then often regarded as being due to the separation-dependence of the zero-point and/or thermal energy of the normal electromagnetic field modes. These modes are calculated from the classical Maxwell equations in the presence of chunks of matter characterized only by their macroscopic permittivity $\varepsilon(\omega)$. The two viewpoints are united by the very successful Lifshitz theory [5], [6], applied originally to the interaction between bulk samples with parallel planar faces, and quickly extended to other geometries in various approximate ways [1], [8], [9]. In recent years the Lifshitz type of approach has been applied, without approximation, to more general geometries such as spheres, cylinders, thin plates etc, but always with the caveat that the spatial scales must be long compared with the scale of the microscopic structure of the matter, so that only the long-wavelength response of the matter to e.m. fields is invoked [10], [11].

In fact the term "Casimir effect" has recently come to have a wider meaning, covering the dependence on geometry (shape, size or separation) of the total zero-point or thermal free energy of any kind of field in confined geometry. Apart from the electromagnetic Casimir forces described above, examples of this approach include (i) the effect of elastic wave fluctuations on the thermodynamics behavior of finite and/or curved elastic membranes (ii) the interaction between nuclei or nucleons in a Fermi sea of quarks, where the zero point kinetic energy of the free quark field carries the basic effect. Some flavor of the possibilities of this field-fluctuation approach can be obtained by visiting the website of a recent Kavli Institute for Theoretical Physics workshop entitled "Fluctuate 08": [http://www.kitp.ucsb.edu/directory/all/fluctuate08].

For the remainder of the present paper we will work in the electromagnetically non-retarded (non-Casimir) limit, which often means in practice that we can treat interacting systems at separations from about a micron down to full overlap of electronic clouds.

2 Simple models of the vdW interaction between small systems

It is worthwhile to consider first a very simple picture of the vdW interaction between two neutral spherical atoms at separation $R >> b$ where b is an atomic size. (For more detail see e.g. [12] , [13], [14] .) The Hartree field of a neutral spherical atom decays exponentially with distance, and so the Hartree energy cannot explain the algebraic decay of the vdW interaction.

2.1 Coupled-fluctuation picture

However the quantal zero-point motions of the electrons (or thermal motions where significant) can cause a temporary fluctuating dipole moment d_2 to arise on atom #2. The nonretarded Coulomb interaction energy between this dipole, and another dipole of order $\alpha_1 d_2 R^{-3}$ that it induces on atom #1, has a nonzero average value that can be estimated [12] , [13] as

$$E = - < \left(\alpha_1 d_2 R^{-3}\right)\left(-R^{-3}d_2\right) > \approx -C_6 R^{-6}, \quad C_6 = K\hbar\omega_0\alpha_1\alpha_2. \tag{1}$$

Here α_1 and α_2 are the dipolar polarizabilities of the atoms and ω_0 is a characteristic frequency (level spacing) of an atom. The coefficient C_6 for this geometry has been obtained using a harmonic oscillator analogy to estimate $< d_2^2 > = K\alpha_2\hbar\omega_0$ and this contains a dimensionless constant K, that is not easily specifiable from the above qualitative argument.

2.2 Model based on the static correlation hole: failure of LDA/GGA at large separations

The spontaneous dipole d_2 invoked above would be implied *if* we had found an electron at a position $\vec{r}'$ on one side of atom #2. The induced dipolar distortion on atom #1 then represents a very distant part of the correlation hole density $n_2(\vec{r}, \vec{r}'|)$ [15] due to discovery of the electron at $\vec{r}'$. The shape of this hole is entirely determined by the shape of atom #1, and is thus quite unlike the long-ranged part of the xc hole present in a uniform electron gas of density $n(\vec{r})$. It is therefore unsurprising that the local density approximation (LDA) misses the long-ranged tail of the vdW interaction. In fact, the LDA and the GGAs can only obtain the vdW tail via the distortion of the density of each atom. This distortion is predicted by these theories to decay exponentially with separation of the two atoms, thus ruling out the correct algebraic decay of the energy. The situation with GGA is less clear when the densities of the interacting fragments overlap. If the principal attractive correlation energy contribution comes from electrons near the overlap

region, then treating this region as part of a weakly nonuniform gas might be reasonable. In keeping with this, various different GGAs can give qualitatively reasonable results for vdW systems such as rare-gas dimers. The results are neither consistent nor reliable, however [16], [17], [18], [19], though surprisingly good results *near the energy minimum* are obtained [20], [21] with Hartree-Fock exchange plus the Wilson-Levy functional. Some discussion is given in [12].

2.3   Model based on small distortions of the ground state density

Instead of considering the energy directly for two atoms separated by distance R , Feynman [22] and Allen and Tozer [23] considered the small separation-dependent changes $\delta n(\vec{r}:R)$ in the groundstate density $n(\vec{r})$ of each atom, caused by the Coulomb interaction V_{12} between atoms. The Coulomb field acting at the nucleus of each atom created by $\delta n(\vec{r}:R)$ as source, leads to a force which was identified as the vdW force, in the distant limit. One can then obtain the correct result $\vec{F} = -\nabla_R(-C_6R^{-6})$ in the widely-separated limit, in agreement with (1). Such a result emerges, for example, if $\delta n(\vec{r};R)$ is calculated from a many-electron wavefunction correct to *second* order in V_{12}, involving a double summation with two energy denominators. (The *first*-order wavefunction perturbation makes zero contribution to $\delta n(\vec{r}:R)$.) By contrast, looking at the total *energy* to second order in V_{12} one already obtains the dispersion interaction with only a single summation and one energy denominator, a substantially easier task of the same order as obtaining the *first-order* perturbed wavefunction. From here on we restrict attention to approaches based directly on the energy.

2.4   Coupled-plasmon model

Another simple way to obtain the R^{-6} interaction is to regard the coupled fluctuating dipoles invoked above as forming a coupled plasmon mode of the two systems [13]. One solves coupled equations for the time-dependent density distortions on the two systems, leading to two normal modes (in- and out-of-phase plasmons) of free vibration of the electrons. The R dependence of the sum of the zero-point plasmon energies $\sum_i \hbar\omega_i/2$ gives an energy of form $-C_6R^{-6}$, in qualitative agreement with the coupled-fluctuation approach described above for the case of two small separated systems (see, e.g., [24], [1], [13]). A strength of the coupled-plasmon approach is that it is not perturbative, and is equally valid for large or small systems, even for metallic cases where zero energy denominators could render perturbation theory suspect. The coupled-plasmon theory is linked to the correlation-hole approach by the fluctuation-dissipation theorem to be discussed starting from Sect. 5 below.

2.5 Perturbation theory picture assuming no overlap

The factor R^{-6} in (1) can be understood as arising from *two* actions of the dipolar field, each proportional to R^{-3}, suggesting that this simplest approach relates to *second*-order perturbation theory in the inter-system Coulomb interaction . Indeed the application of standard 2nd order Rayleigh-Schrodinger perturbation theory, regarding the electrons of one system as distinguishable from those of the other and treating the inter-atom coulomb potential V as a perturbation, yields the formula

$$E_{AB}^{(2)} = -\frac{\hbar}{2\pi} \int_0^\infty du \int d\vec{r}_1 d\vec{r}_1{}' d\vec{r}_2 d\vec{r}_2' V(\vec{r}_1 - \vec{r}_2)\chi_A(\vec{r}_1, \vec{r}_1{}', iu)V(\vec{r}_2 - \vec{r}_1)\,\chi_B(\vec{r}_2, \vec{r}_2{}', iu) \tag{2}$$

where V is the bare electron-electron Coulomb potential and $\chi_A(\vec{r}_1, \vec{r}_1{}', \omega)\exp(-i\omega t)$ is the linear electron number density response at position $\vec{r}$ to an external potential perturbation of form $\delta V(\vec{x}) = \delta(\vec{x} - \vec{r}')\exp(-i\omega t)$: see (e.g.) [25], or [26]. χ_A is usually termed the electron density-density reponse of system A (or just the density response), and the expression (2) is sometimes known as the "(generalized) Casimir Polder formula". It is derived in a different fashion in Sect. 6.1 below.

By expanding the Coulomb potential in a multipole series around the centres of A and B, one obtains to lowest order a result of the form (1) with

$$C_6 = \frac{\hbar}{2\pi} \sum_{jk\ell m=1}^3 \int_0^\infty A_{jk}^{(A)}(iu)t_{j\ell}(\hat{R})t_{km}(\hat{R})A_{\ell m}^{(B)}(iu)du, \qquad t_{j\ell}(\hat{R}) = \hat{R}_j\hat{R}_\ell - 3\delta_{j\ell} \ . \tag{3}$$

(See e.g. [12]). Here $\vec{R}$ is the vector joining the centers of A and B, $\hat{R} = \vec{R}/\left|\vec{R}\right|$ and

$$A_{j\ell}^{(A)} = \int x_j x_\ell' \chi_A(\vec{x}, \vec{x}', iu)d\vec{x}d\vec{x}'$$

is the is the dipolar polarizability tensor of species A. $\vec{x}$ is the position of an electron relative to the center of A. For two isotropic systems $A_{jk}^{(A)} = \delta_{jk}A^{(A)}$ and similarly for $A_{jk}^{(B)}$. This leads to the possibly more familiar expression

$$E^{(2)} = -C_6 R^{-6}, \quad C_6 = \frac{3\hbar}{\pi} \int_0^\infty A^{(A)}(iu)A^{(B)}(iu)du \ . \tag{4}$$

Using (3) or (4) one reduces the calculation of the asymptotic vdW interaction between fragments to the calculation of the (imaginary) frequency-dependent dipolar polarizability A of each fragment. This is a surprisingly demanding task. It can be done accurately with high-level quantum chemical approaches, but even relatively sophisticated treatments like RPA or ALDA obtain accuracies only of order 10-20% for small atoms and molecules, where orbital self-interaction is an issue.

If the multipole expansion of the Coulomb potential in the Casimir-Polder formula (2) is taken to higher order, additional terms of form $C_8 R^{-8}$, and higher powers, are added to

the leading $-C_6 R^{-6}$ term. There are also mixed induction-dispersion terms in general. A good and very detailed enumeration of the possible terms is given in [3].

2.6 vdW and higher-order perturbation theory

For non-overlapping electronic systems one can go further within perturbation theory with respect to the inter-system Coulomb interactions V_{ij}. In third order one finds an interaction between three separated systems, which cannot be expressed as the pairwise sum of R^{-6} terms such as (1). At large separations for spherical systems the leading (dipolar) contribution to this third-order term has the Axilrod-Teller form $E^{\text{vdW},(3)} \approx C_9 R_{12}^{-3} R_{23}^{-3} R_{13}^{-3}$, (see e.g. [27]) where C_9 contains some angular dependence. There are also corrections to the pair interaction (2) from perturbation orders beyond 2 [3].

2.7 Perturbation theory including overlap: Symmetry Adapted Perturbation Theory

When the electron clouds of two systems 1 and 2 are allowed to overlap, the electrons in 1 and 2 can no longer be treated as indistinguishable, and Eq (2) is inapplicable. A perturbative approach in this case requires Symmetry Adapted Perturbation Theory (SAPT) [3]. In SAPT the antisymmetry of the many-electron wavefunction is imposed upon perturbation theory via a projection operator technique. This approach has been developed to a very high level of sophistication (including judicious use of Time Dependent Density Functional Theory to ease parts of the calculation) [28]. SAPT probably represents the current state of the art for the van der Waals interaction between pairs of molecules up to medium size. So far it seems not to be feasible for solids and large nanostructures, so it will not be considered further here.

3 The simplest models for vdW energetics of larger systems

3.1 Simple pairwise addition of $C_6 R^{-6}$ for well-separated macroscopic bodies

The simplest approach to the vdW interaction between many-atom systems, including solids, is to add energy contributions of form $-C_{6(ij)} R_{ij}^{-6}$ between each pair (i, j) of atoms. There is a large early literature of calculations of this kind for macroscopic solids with an empirical C_6 value. Often one replaces sums over atoms by continous integration using volume elements that may each contain many atoms. In this way one easily obtains analytic dependence on the separation D for macroscopic objects of each well-defined shape (thick slab, thin slab, sphere, cylinder etc). [1], [13], [8]. See also the right-hand column of Figure 1 below, for a few specific cases.

3.2 Pairwise addition with empirical short-range repulsion

If the interacting bodies can come into close contact, the attractive $-C_6R^{-6}$ interation must be attenuated (damped, saturated) at short range and replaced by a Pauli repulsion term. In empirical pairwise theories the short-ranged part is often of form $+C_{12}R^{-12}$ (Lennard-Jones potential) or $+B\exp(-CR)$. Since the polarizability A (see (3)) of an atom in a molecule or solid is usually quite different from that of the isolated atom, all coefficients C_6, C_{12} or B are often determined empirically. Two examples are the "universal graphitic potentials" [29], [30]. Such models have been used extensively to model interactions between carbon nanotubes, graphene sheets, bucky balls etc: see (e.g.) [31]. Similar terms are included in force fields (e.g. CHARMM) used for biochemical modelling.

3.3 Pairwise addition as a dispersion energy correction to LDA

Perhaps because of the availability of high-level quantum chemical methods, the simple pairwise approach seems to have been pursued much later for finite molecular systems than for other appplication areas. Wu and Yang [32] introduced a pair interaction of form $\sum_{ij} f_d^{ij}(R_{ij})C_6^{(ij)}R_{ij}^{-6}$ to be added to the Local Density Functional (LDA) energy, which of course already contains the Pauli repulsion. The coefficients C_6 were optimized by fitting a set of accurate molecular energies. They turned out to be surprisingly, though not perfectly, transferrable. This general approach is now often called "DFT+D" or DFT-D" and has been furthered by Grimme and others [33], [34]. In the last approach, transferability is improved by counting the number of effective bonds in which an atom participates, then using this to modify the atomic C_6 coefficients. Another approach [35] starts from accurate quantum chemical data for the vdW C_6 coefficients of free atom pairs. The vdW interaction is then modified to account for Pauli compression effects of nearby atoms on the atomic polarizabilities, using the effective volume of each atom in its molecular environment, according to a standard molecular space partitioning scheme.

4 Effects beyond pairwise additivity

As already indicated in Sect 2.5 above, perturbation theory naturally produces triplet and higher contributions to the dispersion energy, beyond pairwise interaction of atoms or spatial elements. For small weakly polarizable systems such as rare gas atoms, these terms are relatively small but can be significant, along with R^{-8} and higher terms, at shorter range as in rare gas crystals [36].

Stronger effects, not describable by a small number of triplet and higher perturbation terms, have been discovered in polarizable, highly anisotropic systems. Kim et al [37] studied chains of non-contacting polarizable SiO spheres in various geometric arrangements. They obtained the vdW interaction from the zero-point energy of coupled plasmons within a polarizable point-dipole model similar to that in [13] and found major

discrepancies compared with pair-summation. These discrepancies were not significantly improved by adding just triplet terms. Martyna et al. have applied a somewhat related model of coupled oscillators to solid xenon [38]. The multiple-coupled dipole approach has been popular in the past [13] and can be used [39] to derive the nonretarded Lifshitz interaction - see Sect 6.1 below.

Other formalisms have yielded equally large discrepancies for semiconducting linear hydrogen chains [40], [41]. The beyond-pairwise effects can be understood in terms of the screening of the coulomb interaction that couples fluctuations on two atoms, due to polarization of the electon clouds on other atoms . The non-additive effects are strong when the systems are very anisotropic (e.g. chains or thin films) and highly polarizable. An extreme case of a polarizable system is a metal, especialy in low dimensions (wires, sheets, graphene) where internal coulomb screening is less effective. For such cases it has been shown [42], [43], [44] that one can even obtain an exponent p in the asymptotic vdW power law $E \approx -CD^{-p}$ that differs from that predicted by $\sum C_6 \ R^{-6}$ theories. (See Figure 1 below).

5 The adiabatic connection - fluctuation dissipation (ACFD) approach to groundstate correlation energy

While coupled point polarizable dipole models are sensible and exhibit the required non-pairwise–additive vdW behavior, in general one needs a more general approach that allows for overlap and a detailed description of metals. This leads one to seek more fundamental approaches. The electronic Diffusion Monte Carlo (DMC) approach has been applied to a few simple nanostructures [45] [46], but it is very hard to ensure convergence of DMC in such systems, because of the need for a very big sample cell in order to capture long-ranged vdW correlations. In what follows we therefore concentrate mainly on approaches to the electronic correlation energy based on the Adiabatic Connection Formula and the Fluctuation Dissipation Theorem (ACDF approach) of which the simplest example is the (direct) Random Phase Approximation (dRPA) correlation energy to be described in the next Section.

The vdW energy is part of the electronic correlation energy in the groundstate of the total many-electron system. An exact formal expression for this groundstate correlation energy is the ACFD formula

$$E_c = -\frac{1}{2} \int_0^\infty du \int_0^1 d\lambda \int_0^\infty \frac{\hbar}{\pi} du \int d\vec{r} d\vec{r}' V(\vec{r}, \vec{r}') \left(\chi_\lambda(\vec{r}, \vec{r}', iu) - \chi_0(\vec{r}, \vec{r}', iu) \right) . \quad (5)$$

Here we have defined a "λ-system" in which the bare inter-electron coulomb interaction $V(\vec{r}, \vec{r}') \equiv e^2 |\vec{r} - \vec{r}'|^{-1}$ has been replaced by $\lambda V(\vec{r}, \vec{r}')$ while a λ-dependent static external potential is applied in order to keep the groundstate density constant at the true ($\lambda = 1$) value while λ is varied. χ_λ is the electronic density response of the λ-system, defined in general such that the linearized density perturbation of the λ-system under an external

potential $\delta V^{ext}(\vec{r}) \exp(-i\omega t)$ is

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

In (5) the integration over imaginary frequency u implements the Fluctuation–Dissipation theorem [47], [48], [14]: as such it constructs the correlated groundstate pair density $n_{2\lambda}(\vec{r}, \vec{r}')$ using the density response as input. The expression (5) is thus of the form of an electrostatic energy, except for the λ integration, which implements the Adiabatic Connection formula [49], [15]. The λ integration is based on the Feynman-Hellman theorem, and physically it re-introduces the zero-point *kinetic* energy of correlation, otherwise missed in an electrostatic energy type of integral. A particularly clear explanation of the Adiabatic Connnection is given in Gunnarsson and Lundqvist [15] starting from their Eq (28), with their "g" representing our "λ". A complete pedagogic derivation of (5) in the present context, including a first principles derivation of the appropriate version of the FD theorem, is given in [14].

Expressions based on (5) can be obtained for the exchange-correlation energy

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

and the exact exchange energy

$$E_x = -\frac{1}{2} \int_0^\infty du \int_0^1 d\lambda \left[\int_0^\infty \frac{\hbar}{\pi} du \chi_0(\vec{r}, \vec{r}', iu) + n(\vec{r})\delta(\vec{r} - \vec{r}') \right]$$

The latter reproduces the "DFT exact exchange", namely the Hartree-Fock expression for the exchange energy, but with Kohn-Sham orbitals in place of Hartree-Fock orbitals. An explicit constructive proof of this statement is given in [14].

6 The (direct) RPA for the correlation energy

Eq (5) is a purely formal expression giving the correlation energy in terms of the response function χ, and it is not immediately clear how sophisticated an approximation to χ is required in order to obtain useful accuracy in E_c. In fact it turns out that no explicit correlation physics is needed in χ_λ in order to obtain a non-zero correlation energy from (5). Indeed a very simple time-dependent Hartree approximation for χ_λ, namely

$$\chi_\lambda^{dRPA} = \chi_0 + \chi_0 \lambda V \chi_\lambda^{dRPA}, \tag{6}$$

produces the well-known Random Phase approximation for the correlation energy, first introduced long ago for the special case of the homogeneous electron gas. The correlation energy includes the mutual energy of coupled fluctuations of the density about the ground-state, fluctuations whose average value in the groundstate is zero so that they cannot contribute any extra energy in the static Hartree approximation. However when an explicit

density disturbance (with non-zero ensemble average) is introduced by a time-dependent external field, this can interact with disturbances elsewhere even at the (time-dependent) Hartree level. The Fluctuation Dissipation Theorem relates such interactions in the non-equilibrium driven system to the interactions between spontaneous fluctuations around the non-driven groundstate.

For the dRPA case the λ integration in (5) can be carried out analytically using the following formal operator identity in $(\vec{r}, \vec{r}')$ space: $\partial_\lambda \ln(1 - \lambda\chi_0 V) = (1 - \lambda\chi_0 V)^{-1} \chi_0 V = \chi_\lambda^{dRPA} V$ in which products are to be interpreted as spatial convolutions:

$$
\begin{aligned}
E_c^{dRPA} &= -\frac{1}{2} \int_0^\infty \frac{\hbar}{\pi} du \int d\vec{r} \, [\ln(1 - V\chi_0) + (V\chi_0)]_{\vec{r}\vec{r}} && (7) \\
&= -\frac{\hbar}{2\pi} \int_0^\infty du \, Tr \left[\ln(1 - V\chi_0) + (V\chi_0) \right] && (8) \\
&= -\frac{\hbar}{2\pi} \int_0^\infty du \, Tr \left[\ln(1 - V^{1/2}\chi_0 V^{1/2}) + \left(V^{1/2}\chi_0 V^{1/2} \right) \right] && (9)
\end{aligned}
$$

where the properties of the trace operation have been used in the last line to introduce a hermitian operator $V^{1/2}\chi_0 V^{1/2}$ which is convenient especially when diagonalization methods are used to evaluate the correlation energy.

While the dRPA correlation energy was calculated for the homogeneous electron gas many decades ago (see e.g. [50]), its practical evaluation in more complex systems including periodic systems is often numerically costly, and has only been carried out quite recently [51], [52], [53], [54], [55], [56], [57], [58], [59]. When used as a post-functional starting from PBE orbitals, it has proved to give a very good description of the lattice constants and elastic constants of many crystals [58] including most of the van der Waals bound rare gas crystals [60] (except He where self-interaction issues are arguably dominant - see the next Section). Atomization energies in the dRPA are good but slightly worse than those from a groundstate PBE calculation, which again may be related to self-interaction issues. Some methods have also been given to increase the numerical efficiency of dRPA and exact exchange calculations in solids [57].

For finite molecular systems the correlation energy in the dRPA and the related RPAx (see below) have been implemented in an efficient way, via methods and codes originally designed for molecular time-dependent Hartree-Fock calculations (see [55] and references therein) . On the formal side Furche [55] proved that

$$
E_c^{dRPA} = \frac{\hbar}{2} \sum_n \left(\Omega_n - \Omega_n^D \right)
$$

where Ω_n is an eigenfrequency of the RPA equation (6) and Ω_n^D is the same quantity to linear order in the Coulomb coupling strength λ. In fact the notion of using the separation-dependent part of the sum of zero point energies $\hbar\Omega/2$ of collective modes to obtain vdW energies is quite an old one ([1], [13]). For the macroscopic collective-mode-only models used in these old calculations one can show that this is correct (see e.g. [61]), but the Furche result is more general. For some discussion of the sum of zero

point energies see also Sec. 5 of [61] where it is pointed out that the asymptotic vdW interaction of undoped graphene planes is dominated by single-particle-type modes so that the older collective mode zero-point energy model is not sufficient.

Within formal perturbation theory, the dRPA is represented in Feynman energy diagrams by a sum of rings of open bubbles (where each open bubble represents χ_0). The dRPA and many other variants of the RPA idea can also be expressed as doubles ring diagrams in the Coupled Cluster approach.

6.1 Lifshitz-like vdW energy formula for non-overlapping systems, and its relation to RPA

The Lifshitz theory [5], [6] was the mainstay of macroscopic vdW calculations for many years. One can use a modified form of the ACFD to derive a slight generalization of the macroscopic Lifshitz formula [62] that renders it suitable for noncontacting nanosystems as well as the thick parallel slabs for which it was originally intended.

Consider 2 separated systems "1" and "2" separated by a variable distance D and with Coulomb interaction split into inter- and intra system interactions

$$V_{11} + V_{22} + \mu(U_{12} + U_{21}) \equiv V_{11} + V_{22} + \mu V_{12}$$

We assume no overlap so the systms lie in separated regions "S_1" and "S_2" of space. Then $U_{12}(\vec{r}_1, \vec{r}_2) = e^2 |\vec{r}_1 - \vec{r}_2|$ when both $\vec{r}_1 \in S_1$ and $\vec{r}_2 \in S_2$ but U_{12} is zero otherwise. Similarly for U_{21} while V_{11}, V_{22} only connect points inside the same system, Then $V_{12} \equiv U_{12} + U_{21} = 0$ if $\vec{r}_1$ and $\vec{r}_2$ lie in the same subsystem.

We start from two systems with no intersystem interaction ($\mu = 0$), but with full Coulomb interactions inside each subsystem. The energy in this situation is the same as for $D \to \infty$. That is

$$E(D \to \infty) = E(D, \mu = 0)$$

Then the D-dependent part of the energy is

$$
\begin{aligned}
E^{cross} &\equiv E(D, \mu = 1) - E(D \to \infty) = E(D, \mu = 1) - E(D, \mu = 0) \\
&= \int_0^1 \frac{dE(D, \mu)}{d\mu} d\mu = \frac{1}{2} \int \rho(D, \mu, r, \vec{r}') V_{12}(\vec{r}, \vec{r}') d\vec{r} d\vec{r}'
\end{aligned}
$$

where $\rho(D, \mu, r, \vec{r}')$ is the electronic pair distribution for slabs at distance D and interaction $V_{11} + V_{22} + \mu V_{12}$: the Feynman-Hellmann theorem was used in the last step.

By the Fluctuation Dissipation theorem this is related to the density response function

$$\frac{dE(D, \mu)}{d\mu} = \frac{1}{2} \int \left[-\frac{\hbar}{\pi} \int_0^\infty \chi(D, \mu, \vec{r}, \vec{r}', \omega = iu) du - n_0(\vec{r})\delta(\vec{r} - \vec{r}') + n_0(\vec{r})n_0(\vec{r}') \right] V_{12}(\vec{r}, \vec{r}') d\vec{r} d\vec{r}'$$

where χ is the density-density response of the fully interacting system. The direct Hartree cross energy (the last term) is not part of the vdW energy, and so will be ignored (see also [63]). The self-term with the delta function gives zero when folded with V_{12}. Thus

the cross energy is entirely due to correlation (because the in-principle-included exchange part is zero in this non-overlapped regime) and is given by

$$E^{cross}(D) = -\frac{\hbar}{2\pi} \int_0^\infty du \int_0^1 d\mu \int_0^\infty \chi(D, \mu, \vec{r}, \vec{r}', \omega = iu) V_{12}(\vec{r}, \vec{r}') d\vec{r} d\vec{r}'$$

$$= -\frac{\hbar}{2\pi} \int_0^\infty du \int_0^1 d\mu \int_0^\infty \left(\chi_{12}(D, \mu, \vec{r}, \vec{r}', \omega = iu) V_{12}(\vec{r}, \vec{r}') + [1 \leftrightarrows 2] \right) d\vec{r} d\vec{r}'$$

where χ_{12} (unlike χ_{012}) is NOT zero because of the coulomb interaction between the slabs. We now make the RPA assumption for the interaction between the slabs. This is the essential Lifshitz approximation - see the ring diagrams in [6]. Then $\chi_{21} = \delta n_2/\delta V_1$ can be found from the linear mean field equations in the presence of time dependent external potentials $\delta V_1, \delta V_2$ acting separately on the two systems. This gives

$$\chi_{21} = \left(1 - \mu^2 \chi_{22} V_{21} \chi_{11} V_{12}\right)^{-1} \mu \chi_{22} V_{21} \chi_{11}$$

and similarly for χ_{12}. Then the vdW interaction is

$$E^{cross}(D) = -\frac{\hbar}{2\pi} \int_0^\infty du \int_0^1 d\mu \int_0^\infty \chi_{12}(D, \mu, \vec{r}, \vec{r}', \omega = iu) V_{12}(\vec{r}, \vec{r}') d\vec{r} d\vec{r}' + \{12 \to 21\}$$

$$= -\frac{\hbar}{2\pi} \int_0^\infty du \int d\vec{r} \int_0^1 d\mu \frac{d}{d\mu} \ln \left(1 - \mu^2 \chi_{11} V_{12} \chi_{22} V_{21}\right)_{\vec{r}\vec{r}}$$

$$= \frac{\hbar}{2\pi} \int_0^\infty du \, Tr \ln \left(1 - \chi_{11} V_{12} \chi_{22} V_{21}\right) \tag{10}$$

where in general the "ln" is an operator log over the $(\vec{r}, \vec{r}')$ space. Also, χ_{11} and χ_{22} are for $D \to \infty$ - i.e. for the isolated subsystems but with full-strength e-e-interactions within each subsystem. Using the operator idensity $Tr \ln \hat{O} = \ln Det \hat{O}$ one can see that (10) is related to the interaction in the general Casimir scattering theory, Eq (5.16) of [10].

(10) is also valid within the dRPA. A more direct proof of (10) from the full RPA-adiabatic connection formalism, switching on all interactions together, can be constructed by diagrammatic means: a version for a specific case is given in ref. [62]. We will show presently that Eq (10) reduces to the non-retarded Lifshitz formula [5] for macroscopic slab systems. (See Eq (12) below). In general, because (10) is closely related to the Lifshitz approach, we expect that it will lead to the same asymptotic vdW power laws as Lifshitz in the electromagnetically nonretarded limit.

To obtain the nonretarded Lifshitz result we note that, from charge conservation and from insensivity to a spatially uniform applied potential [64], the "direct" responses $\bar{\chi}_{11}$ and $\bar{\chi}_{22}$ can be written in terms of a (generally nonlocal) polarizability $\alpha = (\varepsilon - 1)/4\pi$,

$$\bar{\chi}_{11} = \sum_{\mu\nu=1}^3 \frac{\partial^2}{\partial r_\mu \partial r'_\nu} \alpha_{11\mu\nu}(\vec{r}, \vec{r}', \omega). \tag{11}$$

For insulators (and for 3D metals with a finite plasma frequency $\omega_P(q \to 0)$), a remans finite as both $q \to 0$ and $\omega \to 0$. For two thick slabs of matter in vacuo with parallel surfaces separated by D, the standard non-retarded limit of the Lifshitz formula is

reproduced from (10) by approximatiing α_{11} and $\alpha_{2,2}$ via a macroscopic local dielectric functions ε_1, ε_2:,

$$\alpha_{11\mu\nu} = \delta(\vec{r} - \vec{r}')\frac{\varepsilon_1(\omega) - 1}{4\pi}\theta(\vec{r})\delta_{\mu\mu}$$

and similarly for α_{22}. Here θ restricts $\vec{r}$ and $\vec{r}'$ to lie within the slabs and $\varepsilon(\omega)$ is a local spatially constant dielectric function of each slab. After some algebra for fields varying as $\exp(i\vec{q}_{||}\vec{r})$ parallel to the slab surfaces, we obtain χ_{ii} from $\bar{\chi}_{ii}$ via the screening relation $\chi = \bar{\chi} + \bar{\chi}V\chi$, and we then reduce (10) to

$$E^{cross} = \frac{\hbar}{32\pi^2 D^2}\int_0^\infty du \int_0^\infty dx x^2 \left(\frac{\varepsilon_1(iu) + 1}{\varepsilon_1(iu) - 1}\frac{\varepsilon_2(iu) + 1}{\varepsilon_2(iu) - 1}e^x - 1\right)^{-1}, \quad x = 2q_{||}D \quad (12)$$

which upon differentiation yields the nonretarded Lifshitz force result given in Eq 3.1 of [5].

An expansion of the logarithm in (10) to lowest order in V_{12} also reproduces the generalized Casimir Polder formula (2), so (10) can also be regarded as is a generalization of (2). At the RPA level, higher terms in the expansion of the logarithm in (8) produce vdW interactions between theree or more centres (Axilrod-Teller and higher terms) [65]. One might think the perturbative form (2) always becomes asymptotic to (10) at sufficently large separation between two subsystems so that the perturbation V_{12} is "small". This is not in fact the case when the interacting systems have an infinitely large area as in sheets or slabs. The reason is that as $D \to \infty$ the interaction is dominated by excitations with a small wavenumber $q_{||} = O(D^{-1}) \to 0$ parallel to the surface, and the coulomb interaction between such excitations goes as $\exp(-q_{||}D)q_{||}^{-1}$ which is never small since $q_{||}D = O(1)$. For thick parallel plates this can give a discrepancy of up to around 20% between the Lifshitz result (10) and the generalized Casimir-Polder formula (2), a point already noticed by Lifshitz [5]. A discussion of this discrepancy for other geometries is given in Sec. 4 of [61].

In (10) no approximation has yet been made for the internally-interacting responses χ_{11}, χ_{22} of the isolated fragments. If these are approximated with the dRPA then (10) gives a useful form of the dRPA correlation energy, suitable for nonoverlapping systems.

6.2   Unusual asymptotic vdW power laws from dRPA

The dRPA correlation energy can sometimes be evaluated analytically for widely-separated nanostructures ($D \to \infty$) because then only the long-wavelength ($q \approx D^{-1} \to 0$) limit of the response χ_0 is needed. This long-wavelength form can be taken as $\chi_0(\vec{q}, \omega = iu) \approx -n_0q^2/mu^2$ for metals, $-n_0q^2m^{-1}(u^2 + \omega_0^2)^{-1}$ for insulators and (see [66], [67], [63]) $\chi_0(q_{||}, \omega = iu) = \frac{1}{4}\hbar^{-1}q_{||}^2(u^2 + v_0^2q_{||}^2)^{-1/2}$ for graphene. When these bare responses are applied to the dRPA for non-overlapping structures distant D, one can show [42], [43], [68], [69], [59], [70] that the asymptotic form of the vdW interaction is sometimes qualitatively different in dRPA from the predictions of pairwise additive theories where $E = \sum_{ij} C_{6ij}R_{ij}^{-6}$. In particular the exponent p in the form $E^{vdW} = -CD^{-p}$ can be different as summarized in Fig. 1.
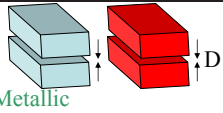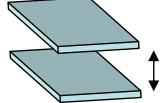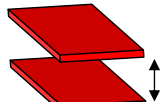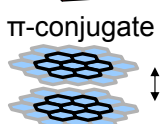
System	Present Theory [ref.]	Conv. Theory ($\sum D^{-6}$)
Metallic	$E^{\text{vdW}} \propto D^{-2}$	$E^{\text{vdW}} \propto D^{-2}$
	$E^{\text{vdW}} \propto D^{-\frac{5}{2}}$	$E^{\text{vdW}} \propto D^{-4}$
	$E^{\text{vdW}} \propto D^{-4}$	$E^{\text{vdW}} \propto D^{-4}$
π-conjugate	$E^{\text{vdW}} \propto D^{-3}$	$E^{\text{vdW}} \propto D^{-4}$
	$E^{\text{vdW}} \propto D^{-2}(\log \frac{D}{D_0})^{-\frac{3}{2}}$	$E^{\text{vdW}} \propto D^{-5}$
	$E^{\text{vdW}} \propto D^{-5}$	$E^{\text{vdW}} \propto D^{-5}$

Figure 1: Asymptotic vdW energy formulae for thick and thin slabs, and for parallel wires, pictured in the left column. Red indicates an insulator, blue a conductor, purple a semimetal (graphene). Right column: Predicted energy from pairwise additive theories. Middle column: Predicted energy from RPA [43]. For further cases of unusual powers see Refs. [44], [69], [70].

This can occur when all of the following are satisfied: (i) each system is macroscopic in at least one dimension so that electron density fluctuations of arebitrarily long wavelength ($q \to 0$) are possible; (ii) each system is small in at least one other space dimension, so that intra-system Coulomb screening of the charge fluctuations is incomplete; and (iii) the systems have a zero homo-lumo gap, as in 2D or 1D metals or graphene. The unusual power laws arise from the coupling of long-wavelength excitations that involve the coherent motions of electrons on many atoms, quite different from the pairwise physics. Significant differences in vdW interaction have also been predicted between metals and semiconductors in the non-asymptotic limit [71]. When condition (iii) is not satisfied but the gap is small, as in highly polarizable systems, then the asymptotic power exponent p in the form $E^{vdW} = -CD^{-p}$ will not be anomalous, but nevertheless non-pairwise additivity makes the coefficient C differ strongly from the prediction of $\sum C_6 R^{-6}$ theory. The unusual power exponents p predicted by dRPA (Fig. 1, second column) have been verified by electron Diffusion Monte Carlo calculations [46] for the case of parallel linear conductors. In the case of planar conductors these DMC calculations only partly confirmed the analytic dRPA result [68], but in this case there is a possibility that the simulation cell did not have a large enough area to capture the very long-wavelength fluctuations/correlations involved in the large-D vdW interaction. For the case of graphite a full numerical dRPA calculation of the layer binding energy $E(D)$ has recently been performed [59]. This calculation was able to confirm the presence of the predicted anomalous D^{-3} contribution at the largest D values ($\approx 3\,nm$) where the numerics were still feasible, but also showed that the D^{-3} contribution from the gapless electronic $\pi_z \to \pi_z^*$ transitions was still essentially negligible at this separation, compared with the much larger vdW energy from the gapped transitions involving "majority" Bloch bands other than the π_z bands. A similar consideration applies to observation of the anomalous asymptotic $-CD^{-2}(\ln D)^{-3/2}$ energy predicted [42], [43] for parallel metallic carbon nanotubes (though the unusual energy contribution may be more dominant for nanowires made of metallic atoms). Nevertheless at suffciently large separation D the anomalous metallic term will dominate, and it will be interesting to see whether sensitive modern force detection techniques such as atomic Force Microscopy are able to measure these anolamous forces directly. In terms of general modelling of solids and nanostructures, however, the wrong magnitude of the vdW interaction at short to intermediate distances because of non-pairwise-additivity effects is probably more important than the power law at asymptotic separations.

7   Diseases of dRPA

Despite the good success of the dRPA for many solids, with inclusion of vdW effects as just described, this theory has some very serious shortcomings in general, and it is important to use it only in circumstances where these are not significant or where they can be easily corrected.

7.1 Over-correlation by dRPA

Firstly, the depth of the short-ranged part of the electronic correlation hole is seriously over-estimated in dRPA, resulting in overestimation of the magnitude of the absolute correlation energy. This was apparent already in early work on the homogeneous electron gas. Fortunately, one is most often interested in energy *differences* $\Delta E_c = E_c(\{\vec{R}_j\}) - E_c(\{\vec{R}'_j\})$ between different arrangements of the same set of nuclei, with positions $\vec{R}_j$ in one configuration and $\vec{R}_j{}'$ in the other configuration. Here the incorrect short-ranged part of the hole is much less important as it is likely to be very similar in the two nuclear configurations and hence largely cancels in ΔE_c, provided that the nuclei are not moved too close to one another. Indeed Perdew and co-workers [72] noted that dRPA tends to overestimate $|E_c|$ per electron by a constant amount, so that "isoelectronic" energy differences (those with $N_{electrons}$ held constant) are relatively well described. Since the short-ranged hole is described much better in LDA/GGA, Perdew and collaborators also proposed in the same paper a theory correcting the RPA correlation energy for short-ranged effects by using LDA data

$$E_c^{RPA+} = E_c^{dRPA} + \int \left(\varepsilon_c^{\text{hom}}(n(\vec{r})) - \varepsilon_c^{\text{hom},dRPA}(n(\vec{r}))\right) n(\vec{r})d\vec{r}\,.$$

Here $\varepsilon_c(n)$ is the correlation energy per electron in the homogeneous electron gas of density n. More sophisticated versions termed "RPA+" based on gradient functionals were also derived [73]. Note that all of the sucessful dRPA calculations for solids by Harl et al., [58] were for isoelectronoic energy differences.

A different approach to the short-ranged diseases of dRPA is that of *range separation*, originally introduced by Savin and Stoll for molecular problems [74], [75]. This involves splitting the bare Coulomb interaction into short ranged and long ranged parts, with different many-body treatments applied to the two parts - e.g. dRPA for the long ranged part and LDA for the short ranged part. This has been tried recently as a correction to the dRPA with some success [76], but the approach probably deserves wider application for RPA as it also lessens the computational load associated with reproduction of the coulomb cusp in the pair function

7.2 Spurious electron self-interaction and dRPA

In a one-electron electron system the bare density response χ_0 is the exact response, and the correlation energy should be zero. However the time-dependent Hartree equation (6) contains a non-zero self-interaction term, the second mean-field term on the right side, which correponds in this case to an electron avoidiing itself. As a result the dRPA contains an incorrect self-correlation energy for a one-electron system. Bacause of the r^{-1} dependence of the Coulomb energy, this can be a very serious error for orbitals that are highly localized (having small radius r), as in the He atom for example. Partly as a result of this, dRPA starting from LDA or GGA orbitals gives an extremely bad account of the

binding energy curve of small dimers [77], [78]. Some improvement can be obtained by using starting orbitals and/or KS potential that incorporate groundstate self-interaction correction, since the correponding effective potential includes the correct $-e^2/r$ tail and reduces the polarizability of the outer orbitals compared with the incorrect high values obtained from the LDA potential. The problem of singles contributions, related to a non-self-consistent choice of starting orbitals, is also a significant issue [79].

The best-justified method to correct the self-interaction in dRPA is to go to higher members of the RPA class of theories. For example the "RPAx" energy comes from replacing (6) by the antisymmetrized Hartree Fock version of the mean field, and this entails the response of the 1-electron density matrix rather than just the density. This is implemented in a number of molecular packages, and it does improve the binding energy curves of small dimers where self interaction correction (SIC) is an issue [77], [76] . RPAx does have some problems and instabilities of its own, however, and is computatinally demanding in solids.

Another systematic way to improve dRPA is to add, to the dRPA ring energy diagrams, a sum of higher terms in the form of the Second Order Screened Exchange (SOSEX) diagram [80]. This exactly cancels the one-electron self-correlation term in the dRPA. It also makes a significant further improvement to the already good dRPA results for the energetics of solids [80] and gives excellent lattice spacings. Unfortunely it adds significantly to the already large computational cost of dRPA energy calculations for solids.

Another possible improvement to dRPA is the use of the Inhomogeneous Singwi-Tosi-Land-Sjolander (ISTLS) correlation theory [81], [82], [83], which not only cures the one-electron self-interaction problem but may improve the "many-electron self interaction" properties disciussed by Perdew and coworkers [84]and byYang and coworkers [78], related to the need for a linear dependence on any fractional orbital occupation numbers. Of couse ISTLS is also computationally very costly.

The success of the dRPA energetics for crystals with diffuse outer orbitals such as the π-clouds of graphene systems [59], or crystals of the larger rare-gas atoms [60], reflects the unimportance of orbital self-interaction for such diffuse orbitals. Significantly, the bonding of the He crystal with its tightly bound atomic orbitals was described much less well by dRPA than the higher rare-gas crystals [60].

8 Approximations to microscopic energy expressions for vdW energetics

A number of approaches have been proposed to obtain efficient vdW energy functionals by approximating microscopic energy expressions. Racpewicz and Ashcroft [27] and Andersson, Langreth and Lundqvist [85] postulated a nonlocal density based approximation for well-separated pairs of systems via indirect arguments. Dobson and Dinte [64] showed that this expression could be derived directly from the generalized Casimir Polder pertur-

bation theory (Eq (2) above) , via a local conserving density-based approximation to the density response χ. More complex theories have recently been proposed with this type of approach as a starting point [86], [87].

It is also possible to approximate *non-perturbative* ACFD energy expressions using only the groundstate electron density $n(\vec{r})$ as input. An early attempt in this direction was the functional of Dobson and Wang [88]. This approximated χ_0 by the double space gradient of a density-based approximation to the polarizabillity, followed by RPA screening without further appoximation. This approach reproduced the RPA cohesion energy of a pair of metal slabs right down to contact with overlap of electron clouds. Unfortunately the functional is not very efficient numerically and needs explicit cutoffs to describe insulators, and so far it has not been pursued further.

8.1 vdW-DF

By far the best-known functional of the "approximated ACFD" type is the "vdW-DF" of Dion et al [89], [90], [91]. A complete self-contained derivation of this functional seems to be lacking in the literature, but an attempt will be made here to list some features of the reasoning. The starting point is the exact ACFD, Eq (5). From this starting point the vdW-DF provides a nonlocal correction E_c^{nl} to the LDA correlation energy of a nonuniform system . The method is not limited to the RPA, but it is approximate, and five distinct approximations/assumptions appear to have been made in obtaining it:

Approximation (i) The method notes that the quantity $\varepsilon(\vec{r}, \vec{r}', \omega)$ defined in electrodynamics is equal to the screening function $1 - \bar{\chi} * V$ for the special case of the uniform gas. Here $\bar{\chi}$ denotes the "direct" response function relating the electron density to the total classical electrodynamic potential. The ACFD then assumes that plugging ε into the ACFD, instead of the exact $\chi_\lambda = (1 - \bar{\chi}_\lambda * V)^{-1} \bar{\chi}_\lambda$, results in the LDA correlation energy. The nonlocal correction to the LDA would then be given by

$$E_c^{nl} = \frac{1}{2} \int \frac{d\lambda}{\lambda} \int_0^\infty \frac{\hbar}{\pi} du Tr \left[(1 - \bar{\chi}_\lambda * \lambda V)^{-1} \bar{\chi}_l V_\lambda - \varepsilon_\lambda^{-1} (\varepsilon_\lambda - 1) \right]$$

where the dependence on $(\vec{r}, \vec{r}', \omega = iu)$ is suppressed for brevity, products are space convolutions and the Trace operation is $TrF = \int F(\vec{r}, \vec{r}) d\vec{r}$. The subtracted term is not exactly the LDA, so this amounts to the first approximation.

Approximation (ii) The "full potential approximation", explicitly introduced in vdW-DF, assumes that the λ integration in the ACFD can be done analytically to give an operator logarithm:

$$E_c^{nl} = \frac{\hbar}{2\pi} \int_0^\infty du Tr \ln \left[\varepsilon^{-1} (1 - \bar{\chi}_\lambda * \lambda V) \right] \tag{13}$$

This is exactly true in the dRPA where $\bar{\chi}_\lambda = \chi_0$ independent of λ, but it constitutes an approximation in other formalisms.

Approximation (iii) Since $\bar{\chi} = \nabla(\varepsilon - 1)\nabla / 4\pi$ exactly in general (see e.g. [64]), the nonlocal correlation energy correction (13) can be expressed in terms of ε alone. The logarithm

in (13) represents the solution of the time-dependent Hartree-coulomb screening problem. In vdW-DF, this screening problem is solved approximately by expanding the logarithm to second order in the quantity $(\varepsilon^{-1} - 1)$, termed "S" in [89], (but not exactly equal to to the dynamic structure factor despite the similarity to a common notation). This gives

$$E_c^{nl} = \frac{\hbar}{4\pi} \int_0^\infty Tr \left(S^2 - \left(\frac{\vec{\nabla} S . \vec{\nabla} V}{4\pi e^2} \right)^2 \right) du \ . \tag{14}$$

Here once again all products represent convolutions in position space.

Approximation (iv) Finally a modified plasmon pole type of approximation is made for S and substituted into (14), yielding after some algebra a functional of form

$$E_c^{nl} = \int n(\vec{r}) n(\vec{r}') \ \phi(\vec{r}, n(\vec{r}), \nabla n(\vec{r}) : \vec{r}', n(\vec{r}'), \nabla n(\vec{r}')) \ d\vec{r} d\vec{r}' \tag{15}$$

where $\phi \sim |\vec{r} - \vec{r}'|^{-6}$ as $|\vec{r} - \vec{r}'| \to \infty$. The dependence on gradients is built into the modification to the simple plasmon pole approximation, and the physics of this is based on many years of success by Langreth and co-workers with the development of gradient density functionals.

Approximation (v) In order to implement the functional in practice, it must be combined with a suitable approximation for the exchange energy E_x^0. Tests on a number of systems showed that neither LDA exchange nor exact DFT exchange produced results of useful accuracy. However it was found that the revPBE exchange functional was suitable, and some physical reasons were advanced for this choice. This is very crucial to the behavior of the functional for vdW-bound systems near to their equiilibrium binding separation D_0.

8.2 Features of vdW-DF

The vdW-DF turns out to be a numerically efficient approach with some very good general features. It has the $-\sum C_6 R^{-6}$ form at for well separated systems and hence never fails to produce a vdW interaction where required. A very strong feature is the natural saturation of the function ϕ at short distances (see Eq (15) above), without the need for any empirical input, in contrast to more empirical pairwise summation approaches. vdW-DF gives sensible results for a wide range of van der Waals bonded systems from rare gas dimers to solids and surfaces, often giving good vdW energies but sometimes significantly over-estimating D_0 [92], [93], [94]. Significant improvements have recently been made in its numerical implementation (e.g. [95], [96] and its speed is now quite competitive with more empirical pairwise-additive theories. Attention has also been focussed on improving the generalized plasmon pole approximation ("approximation (iv)" described above). Vydrov and van Voorhis [97], [98] took a frankly empirical approach and modified approximation (iv) so as to improve the predicted C_6 for atom dimers. The original authors [99] also suggested improvements to aspects (iv) and (v). Overall the method is robust and continues to be used for a variety of systems [100].

There are however a number of further aspects (approximations (i)-(iii) listed above) that could probably be improved. For example, as a result of approximating the logarithm as in Approximation (iii) above, the theory ends up having a pairwise additive form, with $\sum_{ij} C_{ij} R^{-6}$ behavior at large separations (compare Sect 4 above). This $\sum_{ij} C_{ij} R^{-6}$ long-ranged behavior means that the asymptotic vdW interaction for metallic systems will have the same exponent as for insulators in any geometry, contrary to known properties of thin metal or graphene sheets or metallic wires: see Sect 6.2 above. While the unusual behavior of such low-dimensional zero-gap systems at large distances is interesting, the force there is small and this alone would not constitute a serious disadvantage of the theory for practical binding calculations [59]. However the same pairwise property means that one might need to be careful about this functional for polarizable, highly anisotropic systems even in the non-asymptotic region of electron cloud overlap (see for example [37], [71], [41]). One should probably not be surprised that the theory appears not give a satisfactory account of the selective binding of graphene to specific metal surfaces [94], for example.

8.3 New directions for ACFD-based vdW functionals

It is tempting to try to go beyond the dRPA by using the ACFD (Eq (5)) but replacing the time dependent Hartree equation (6) of dRPA by the exact equation of linear Time Dependent Density Functional Theory (TDDFT) [101]:

$$\chi_\lambda = \chi_0 + \chi_0 \left(\lambda V + f_{xc\lambda} \right) \chi_\lambda \,. \tag{16}$$

If the usual Adiabatic Local Density Approximation (ALDA) is used for the dynamic exchange-correlation kernel f_{xc}, the ACFD energy from (16) is typically not improved over dRPA, because the ACFD energy samples all frequencies, not just low frequencies for which the ALDA is suited. Instead of this dRPA+ALDA approach, an ACFD energy formalism has been tried, with use of an "energy optimized" local exchange correlation kernel f_{xc} designed to improve the short ranged hole properties, and fitted to the xc energy of the homogeneous gas [102], [103]. This approach improved the energy over RPA for jellium spheres [104] and in fact it did better than the RPA+ approach described above in Sec 7.1. Other than this it has received little testing. The xc kernel $f_{xc}[n](\vec{r}, \vec{r}')$ used in these theories was local or semi-local in r and $\vec{r}'$ and had a similarly local functional dependence on the groundstate density $n(\vec{r}'')$. However it has become clear that any beyond-dRPA theory of van der Waals interactions requires f_{xc} to have a highly nonlocal functional dependence on $n(\vec{r}'')$ A limited discussion of this is given in [14], and work is proceeding on a possible implementation of this idea.

Even the simplest of the full many-body theories, the dRPA, is very costly numerically. For example a recent implementation [59] of dRPA for the binding energy curve $E(D)$ of graphite as a function of the layer spacing D using an efficient periodic code was near the limit of present numerical capabilities despite the small size (4 atoms) of the unit cell of graphite. This was partly because of the need to sample k space finely near the

Dirac points in the Brillouin zone - see e.g. [63]. dRPA-based modelling of technologically interesting graphenic nanostructures, such as graphene bound on various metals, would seem to be presently out of reach because large crystal unit cells are required. Pairwise additive theories including vdW-DF are not a priori reliable because of the highly anisotropic, highly polarizable nature of the systems involved. (see Sect 4). Thus a highly non-additive nonlocal but numerically efficient theory is required. One current approach to this problem is to keep a full solution of the time dependent Hartree screening problem (Eq (6)), corresponding to retention of the full logarithm in (8) or (13), without use of a second order expansion, thus avoiding restriction to pairwise additive physics. Instead one approximates the independent-electron response function $\chi_0(\vec{r}, \vec{r}', iu)$. A very recent development [105] is the use of the new Continuum Mechanics (CM) formalism of Tokatly, Vignale and co-workers [106] , [107] to calculate χ_0. CM is a hydrodynamic-style theory with the remarkable property that it gives the exact response χ_0 of one-electron and two electron systems at all frequencies, and for general many-electron systems at high frequencies. It satisfies the f-sum rule and various other exact constraints such as the Harmonic Potential Theorem [108]. Ref [105] develops this approach into a general-geometry non-pairwise theory that has good vdW properties both for insulators and for a simple metal test model. Work is proceeding on formal properties of the CM-based correlation theory, and on its numerical implementation for realistic geometries.

9   Summary

Macroscopic (Lifshitz) and few-atom (quantum chemical) approaches to dispersion forces have long been available. In recent years here has been much progress in the first-principles microscopic description of dispersion forces in solids and larger nanostructures, right down to microscopic contact separations. Modellers can now choose from a variety of computationally tractable semi-empirical pairwise-additive theories of these phenomena, as well as the pairwise additive vdW-DF theory. These are adequate for medium-accuracy calculations in the electromagnetically non-retarded limit, with the possible exception of systems that are simultaneously highly anisotropic and highly polarizable. An improvement for such cases can be obtained with models evaluating the zero point energy of self-consistent dynamical collective polarization modes, in arrays of localized polarizable dipoles. For a full decription of such cases however, including a detailed account of low-dimensional, low-gap systems one probably needs the computationally expensive full many body approaches, which are now available in packages such as VASP and ABINIT. These start with the simplest direct Random Phase Approximation (dRPA). Recent additions such as RPAx and dRPA+SOSEX can improve numbers but are even more costly. Currently these approaches are not feasible for large nanostructures in realistic, technologically interesting geometries. Work is continuing to remedy this situation.

References

[1] J. Mahanty and B. W. Ninham, *Dispersion Forces* (Academic Press, London, 1976).

[2] R. French, V. A. Parsegian, and R. P. et al., Rev. Mod. Phys. **82**, 1887 (2010).

[3] B. Jeziorski, R. Moszynski, and K. Szalewicz, Chem. Rev. **94**, 1887 (1994).

[4] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Mc Graw Hill, New York, 1989).

[5] E. M. Lifshitz, Soviet Physics JETP **2**, 73 (1956).

[6] I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, Adv. Phys. **10**, 165 (1961).

[7] S. Lamoureux, Rep. Prog. Phys. **68**, 201 (2005).

[8] V. A. Parsegian, *van der Waals Forces: a handbook for biologists, chemists, engineers, and physicists* (Cambridge University Press, Cambridge, 2006).

[9] R. F. Rajter *et al.*, Phys. rev. B **76**, 045417 (2007).

[10] S. J. Rahi *et al.*, Phys. Rev. D **80**, 085021 (2009).

[11] N. Graham *et al.*, Phys. Rev. D **83**, 125007 (2011).

[12] J. F. Dobson *et al.*, Australian J. Chem. **54**, 513 (2001).

[13] D. Langbein, *Theory of Van der Waals Attraction, Springer Tracts in Modern Physics* (Springer-Verlag, Berlin, 1974).

[14] J. F. Dobson, in *Fundamentals of Time dependent Density Functional Theory (Springer Lecture Notes in Physics V. 837), Lecture Notes in Physics*, edited by M. Marques *et al.* (Springer-Verlag, Berlin, 2011), Chap. 22.

[15] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[16] J. M. Perez-Jorda and A. D. Becke, Chem. Phys. Lett. **233**, 134 (1995).

[17] Y. Zhang, W. Pan, and W. Yang, J. Chem. Phys. **107**, 7921 (1997).

[18] D. C. Patton and M. R. Pederson, Phys. Rev. A **56**, R2495 (1997).

[19] D. C. Patton, D. V. Porezag, and M. R. Pederson, Phys. Rev. B **55**, 7454 (1997).

[20] J. M. Perez-Jorda, E. San-Fabian, and A. J. Perez-Jimenez, J. Chem. Phys. **110**, 1916 (1999).

[21] T. R. Walsh, Phys. Chem. Chem. Phys. **7**, 443 (2005).

[22] R. P. Feynman, Phys. Rev. **56**, 340 (1939).

[23] M. J. Allen and D. J. Tozer, J. Chem. Phys. **117**, 11113 (2002).

[24] J. F. Dobson *et al.*, Int. J. Quantum Chem. **101**, 579 (2005).

[25] H. C. Longuet-Higgins, Discussions of the Faraday Society **40**, 7 (1965).

[26] E. Zaremba and W. Kohn, Phys. Rev. B **13**, 2270 (1976).

[27] K. Rapcewicz and N. W. Ashcroft, Phys. Rev. B **44**, 4032 (1991).

[28] A. Hesselmann, G. Jansen, and M. Schutz, J. Am. Chem. Soc. **128**, 11730 (2006).

[29] J. X. Lu and W. H. Marlow, Phys. Rev. Lett. **74**, 1724 (1995).

[30] L. A. Girifalco, M. Hodak, and R. S. Lee, Phys. Rev. B **62**, 13104 (2000).

[31] T. A. Hilder and J. M. Hill, Phys. Rev. B **75**, 125415 (2007).

[32] Q. Wu and W. Yang, J. Chem. Phys. **116**, 515 (2002).

[33] J. Antony and S. Grimme, Phys. Chem. Chem. Phys. **8**, 5287 (2006).

[34] J. Antony, S. Grimme, S. Ehrlich, and H. Krieg, J. Chem. Phys. **132**, 154104 (2010).

[35] A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. **102**, 073005 (2009).

[36] P. Schwerdtfeger and A. Hermann, Phys. Rev. B **80**, 064106 (2009).

[37] H. Y. Kim *et al.*, J. Chem. Phys. **124**, 074504 (2006).

[38] A. Jones *et al.*, Phys. Rev. B **79**, 14411980 (2009).

[39] B. R. A. Nijboer and M. J. Renne, Chem. Phys. Lett. **2**, 35 (1968).

[40] R.-F. Liu and J. G. A. J. F. Dobson, J. Chem. Phys **134**, 114106 (2011).

[41] A. J. Misquitta, J. Spencer, A. J. Stone, and A. Alavi, Phys. Rev. B **82**, 075312 (2010).

[42] D. B. Chang, R. L. Coper, J. E. Drummond, and A. C. Young, Phys. Letts. **17A**, 311 (1971).

[43] J. F. Dobson, A. White, and A. Rubio, Phys. Rev. Lett. **96**, 073201 (2006).

[44] J. F. Dobson, T. Gould, and I. Klich, Phys. Rev. A **80**, 012506 (2009).

[45] L. Spanu, S. Sorella, and G. Galli, Phys. Rev. Lett. **103**, 196401 (2009).

[46] N. D. Drummond and R. J. Needs, Phys. Rev. Lett. **99**, 166401 (2007).

[47] H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951).

[48] L. D. Landau and E. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Massachusetts, 1969).

[49] D. C. Langreth and J. P. Perdew, Sol. State Commun. **17**, 1425 (1978).

[50] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer Verlag, Berlin, 1990).

[51] M. Fuchs and X. Gonze, Bull. Am. Phys. Soc. **46**, 1080 (2001).

[52] F. Furche, Phys. Rev. B **64**, 195120 (2002).

[53] T. Miyake *et al.*, Phys. Rev. B **66**, 245103 (2001).

[54] A. Marini, P. Garcia-Gonzalez, and A. Rubio, Phys. Rev. Lett. **96**, 136404 .

[55] F. Furche, J. Chem. Phys **129**, 114105 .

[56] D. Lu, Y. Li, D. Rocca, and G. Galli, Phys. Rev. Lett. **102**, 206411 (2009).

[57] H.-V. Nguyen and S. de Gironcoli1, Phys. Rev. B **79**, 205114 (2009).

[58] J. Harl and G. Kresse, Phys. Rev. Lett. **103**, 056401 (2009).

[59] S. Lebegue *et al.*, Phys. Rev. Lett. **105**, 196401 (2010).

[60] J. Harl and G. Kresse, Phys. Rev. B **77**, 045136 (2008).

[61] J. F. Dobson, J. Comp. Theoret. Nanosci. **6**, 960 (2009).

[62] V. Despoja, M. Sunjic, and L. Marusic, Phys. Rev. B **75**, 045422 (2007).

[63] J. F. Dobson, Surf. Sci. **605**, 960 (2011).

[64] J. F. Dobson and B. P. Dinte, Phys. Rev. Lett. **76**, 1780 (1996).

[65] D. Lu, H.-V. Nguyen, and G. Galli, J. Chem. Phys. **133**, 154110 (2010).

[66] K. W. K. Shung, Phys. Rev. B **34**, 979 (1986).

[67] A. H. Castro Neto *et al.*, Rev. Mod. Phys. **81**, 109 (2009).

[68] B. E. Sernelius and P. Björk, Phys. Rev. B **57**, 6592 (1998).

[69] T. Gould, K. Simpkins, and J. F. Dobson, Phys. Rev. B **77**, 165134 (2008).

[70] T. Gould, E. M. Gray, and J. F. Dobson, Phys. Rev. B **79**, 113402 (2009).

[71] A. White and J. F. Dobson, Phys. Rev. B **77**, 075436 (2008).

[72] S. Kurth and J. P. Perdew, Phys. Rev. B **59**, 10461 (1999).

[73] Z. Yan, J. P. Perdew, and S. Kurth, Phys. Rev. B **61**, 16430 (2000).

[74] H. Stoll and A. Savin, in *Density Functional Methods in Physics*, edited by R. Dreizler and J. da Providencia (Plenum, New York, 1985), p. 177.

[75] T. Leininger, H. Stoll, H.-J. Werner, and A. Savin, Chem. Phys. Lett. **275**, 151 (1997).

[76] J. Toulouse *et al.*, J. Chem. Phys. **135**, 084119 (2011).

[77] J. Toulouse *et al.*, Phys. Rev. Lett. **102**, 096404 (2009).

[78] A. J. Cohen, P. Mori-Sanchez, and W. Yang, J. Chem. Phys. **126**, 191109 (2007).

[79] X. G. Ren, A. Tkatchenko, P. Rinke, and M. Scheffler, Phys. Rev. Lett. **106**, 153003 (2011).

[80] A. Gruneis *et al.*, J. Chem. Phys **131**, 154115 (2009).

[81] J. F. Dobson, J. Wang, and T. Gould, Phys. Rev. B **66**, 081108R (2002).

[82] L. A. Constantin *et al.*, Phys. Rev. Lett. **100**, 036401 .

[83] L. A. Constantin, J. P. Perdew, and J. M. Pitarke, Phys. Rev. Lett. **101**, 016406 (2008).

[84] A. Ruzsinszky *et al.*, J. Chem. Phys. **126**, 104102 (2007).

[85] Y. Andersson, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. **76**, 102 (1996).

[86] T. Sato and H. Nakai, J. Chem. Phys. **131**, 224104 (2009).

[87] H.-V. Nguyen and S. de Gironcoli, Phys. Rev. B **79**, 115105 (2009).

[88] J. F. Dobson and J. Wang, Phys. Rev. Lett. **82**, 2123 (1999).

[89] M. Dion *et al.*, Phys. Rev. Lett. **92**, 246401 (2004).

[90] D. C. Langreth *et al.*, Int. J. Quantum Chem. **101**, 599 (2005).

[91] D. C. Langreth *et al.*, J. Phys. Condens. Matter **21**, 084203 (2009).

[92] E. Ziambaras, J. Kleis, E. Schrder, and P. Hyldgaard, Phys. Rev. B **76**, 155425 (2007).

[93] K. Berland and P. Hyldgaard, J. Chem. Phys. **132**, 134705 (2010).

[94] M. Vanin *et al.*, Phys. Rev. B **81**, 081408 (2010).

[95] G. Roman-Perez and J. M. Soler, Phys. Rev. Lett. **103**, 096102 (2009).

[96] A. Gulans, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **79**, 201105 (2009).

[97] O. A. Vydrov and T. V. Voorhis, Phys. Rev. Lett. **103**, 063004 (2009).

[98] O. A. Vydrov and T. V. Voorhis, J. Chem. Phys. **130**, 104105 (2009).

[99] K. Lee *et al.*, Phys. Rev. B **82**, 081101 (2010).

[100] N. Nijem, P. Thissen, and Y. Y. et al., J. Am. Chem. Soc. **133**, 12849 (2011).

[101] E. K. U. Gross and W. Kohn, Phys. Rev. Lett. **55**, 2850 (1985).

[102] J. F. Dobson and J. Wang, Phys. Rev. B **62**, 10038 (2000).

[103] J. Jung, P. Garcia-Gonzalez, J. F. Dobson, and R. W. Godby, Phys. Rev. B **70**, 205107 (2004).

[104] P. Garcia-Gonzalez, J. J. Fernandez, A. Marini, and A. Rubio, J. Phys. Chem. A **111**, 12458 (2007).

[105] T. Gould and J. F. Dobson, ArXiv 1106:0327 V4 (2011).

[106] J. Tao, X. Gao, G. Vignale, and I. V. Tokatly, Phys. Rev. Lett. **103**, 086401 (2009).

[107] X. Gao, J. Tao, G. Vignale, and I. V. Tokatly, Phys. Rev. B **81**, 195106 (2010).

[108] J. F. Dobson, Phys. Rev. Lett. **73**, 2244 (1994).