

Supplementary Materials for

Wavelike Charge Density Fluctuations and van der Waals Interactions at the Nanoscale

Alberto Ambrosetti,^{1,2} Nicola Ferri,¹ Robert A. DiStasio Jr.,^{3*} Alexandre Tkatchenko^{1,4*}

¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195, Berlin, Germany

²Dipartimento di Fisica e Astronomia, Università degli Studi di Padova, 35131, Padova, Italy

³Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA

⁴Physics and Materials Science Research Unit, University of Luxembourg, L-1511 Luxembourg

*correspondence to: distasio@cornell.edu (R.D.) alexandre.tkatchenko@uni.lu (A.T.)

This PDF file includes:

Theoretical Methods

Supplementary Text

Tables S1 to S3

Theoretical Methods

The Tight Binding Model

In this work, all tight binding (TB) calculations were performed on one-dimensional (1D) periodic chains consisting of atoms located on a regular lattice characterized by a spacing d . In agreement with the work of Misquitta et al. (23), the corresponding TB model Hamiltonian is given as:

$$\hat{H}_{\text{TB}} = \sum_i (\beta_1 a_{2i}^\dagger a_{2i-1} + \beta_2 a_{2i+1}^\dagger a_{2i} + \text{H.C.}), \quad (\text{S1})$$

in which a_i^\dagger and a_i represent the creation and annihilation operators for an electron at site i , respectively, and the free parameters β_1 and β_2 account for alternate nearest-neighbor bond strengths. This model Hamiltonian provides an effective description of systems like H_2 chains or π -conjugated polyenes, for instance.

The TB model defined above cannot predict a van der Waals (vdW) interaction between parallel 1D chains, as only nearest-neighbor interactions are taken into account in the Hamiltonian (cf. Eq. S1). To address this issue when considering two parallel chains A and B , we make use of the following second-order perturbative formula:

$$E_{\text{vdW}, \text{AB}}^{\text{LR}} \approx \sum_{i \in A, j \in B} \sum_{a \in A, b \in B} \frac{|\langle ij | r_{12}^{-1} | ab \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (\text{S2})$$

in which the indices i, j (a, b) represent occupied (virtual) independent-particle orbitals, ϵ_p is the p -th single-particle energy, and r_{12} is the distance between the two points located on the two different chains.

Notably, the single chain TB model can be diagonalized analytically in reciprocal space, leading to the following energy bands:

$$\epsilon(k) = \pm |\beta_1 e^{ikd} + \beta_2 e^{-ikd}|. \quad (\text{S3})$$

From this equation, it is clear that the β_1 and β_2 parameters provide one with the ability to describe the following qualitatively different limits: (i) for $\beta_1 \neq 0$ and $\beta_2 = 0$, one has two flat bands and a corresponding gap of $2\beta_1$, indicative of the insulating character of the chain, and (ii) for $\beta_1 = \beta_2$, no gap is present and the system becomes metallic at half-filling.

The computation of $E_{\text{vdW}, \text{AB}}^{\text{LR}}$ in Eq. S2 was performed using localized atomic orbitals according to the prescription defined by Misquitta et al. (23). Clearly, the TB model permits a straightforward control of the single chain eigenstates and the corresponding interwire vdW interaction.

These eigenstates are used in Eq. S2, which accounts for the metallic or insulating character of the system; as a result, the two limiting power laws of D^{-5} (insulating) and D^{-2} (metallic) are recovered, which is in qualitative agreement with the coupled fluctuating dipole model (CFDM) utilized within the many-body dispersion (MBD) framework (25, 29, 34, 35). Interestingly, the power law exponents for intermediate cases (with $0 < \beta_2/\beta_1 < 1$) vary and reach the D^{-5} limit at large D , which is also consistent with the reported MBD results.

The Coupled Fluctuating Dipole Model

Within the coupled fluctuating dipole model (CFDM), the many-body vdW or dispersion energy is computed via diagonalization of an effective Hamiltonian (cf. Eq. 2) which describes the coupling between localized atomic response functions, obtained from mapping the N atomic susceptibilities onto a set of N atom-centered quantum harmonic oscillators (QHO). The resulting Hamiltonian, which includes the dipole-dipole interaction between QHOs, is quadratic in the dipole-displacement variables and can be efficiently diagonalized with an $O(N^3)$ associated computational cost.

Diagonalization of this Hamiltonian yields a set of $3N$ eigenvalues $\bar{\omega}_i^2$, and the total vdW energy is then computed (25, 29) as

$$E_{\text{vdW}}^{\text{LR}} = \frac{1}{2} \sum_{i=1}^{3N} \bar{\omega}_i - \frac{3}{2} \sum_{j=1}^N \omega_j, \quad (\text{S4})$$

in which ω_j is the characteristic frequency of the j -th atom.

The dipole-dipole interaction tensor employed in the present calculations is derived from the interoscillator Coulomb interaction

$$v(|\mathbf{r}_1 - \mathbf{r}_2|) = \frac{\text{erf}[|\mathbf{r}_1 - \mathbf{r}_2|/\sigma_{1,2}]}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (\text{S5})$$

Here \mathbf{r}_j are the Cartesian coordinates of atom j and the parameter $\sigma_{1,2} = \sqrt{\sigma_1^2 + \sigma_2^2}$ controls the Coulomb interaction attenuation scale determined by charge overlap (assuming a Gaussian charge distribution on each QHO). The parameter σ_j determines the Gaussian width of the j -th QHO charge distribution, and is defined as $\sigma_j = (\sqrt{2/9\pi}\alpha_j)^{1/3}$, where α_j is the static atomic dipole polarizability. These polarizabilities reflect the chemical environment of a given atom according to the Tkatchenko-Scheffler approach (12), in which the free-atom reference polarizabilities are rescaled proportionally to the corresponding atomic Hirshfeld volume.

Numerical Computation of Power Law Exponents

Power law exponents provide an effective measure of the decay rate of the vdW interaction energy with respect to the distance between two objects. In the simplest case of two atoms A and B separated by a relatively large distance D_{AB} , a reasonable approximation to the interatomic vdW interaction energy can be obtained from the asymptotic pairwise expression derived from second-order perturbation theory:

$$E_{\text{vdW},AB}^{\text{LR}(2)} \propto C_{6,AB} D_{AB}^{-6}. \quad (\text{S6})$$

Here the vdW interaction energy is clearly characterized by a unique power law exponent which is independent of D_{AB} . By taking the logarithm of both sides of Eq. S6, this exponent can be straightforwardly computed as the slope of $\ln |E_{\text{vdW},AB}^{\text{LR}(2)}|$ with respect to $\ln D_{AB}$.

For the case of two arbitrary fragments A and B in which the vdW interaction energy $E_{\text{vdW},AB}$ cannot be expressed by a single exponent, a generalization of the above procedure should be followed. Since power law exponents are related to the slope on the logarithmic scale, a natural extension of the above procedure consists in taking the derivative of $\ln |E_{\text{vdW},AB}|$ with respect to $\ln D_{AB}$. Throughout the present manuscript, power law exponents P_{exp} at a given interfragment distance D are thus defined as

$$P_{\text{exp}}(D) = \left. \frac{\partial \ln |E_{\text{vdW},AB}(D_{AB})|}{\partial \ln D_{AB}} \right|_{D_{AB}=D}. \quad (\text{S7})$$

Supplementary Text

Comments on the Tight Binding Response Function

At this point, we have analyzed the marked differences that exist between the conducting and insulating cases within the framework of the TB model—differences which are primarily due to the nature of the corresponding wave functions. To provide a more comprehensive understanding of the problem, we consider here the TB single-chain response function,

$$\chi(x, x', \omega) = \sum_{i,j} (f_i - f_j) \frac{\phi_i^*(x) \phi_j^*(x') \phi_j(x) \phi_i(x')}{\epsilon_i - \epsilon_j + i\omega}, \quad (\text{S8})$$

where ϕ_j is the j -th single-particle eigenstate of the TB Hamiltonian, ϵ_j the corresponding eigenenergy, and f_j the Fermi occupation number. Given the periodicity of the system, the j -th eigenstate

of the Hamiltonian in Eq. S1 can be written in Bloch form, i.e., $\phi_j(x) = e^{ik_j x} u_j(x)$, where $u_j(x)$ is a function with a period that is equal to the unit cell length.

Considering the metallic limit, in which $\beta_1 = \beta_2 = \beta$, all sites become equivalent and the eigenstates of the Hamiltonian in Eq. S1 can be expressed as:

$$\epsilon(k) = 2\beta \cos(kd), \quad (\text{S9})$$

with $k \in [-\pi/d, \pi/d]$ (since the unit cell can be reduced in this case to a single atom). Substituting this expression into Eq. S8 yields:

$$\chi(x, x', \omega) = \sum_{i,j} (f_i - f_j) \frac{u_i^*(x) u_j^*(x') u_j(x) u_i(x') e^{i(k_j - k_i)(x - x')}}{-4 \sin\left(\frac{d(k_i + k_j)}{2}\right) \sin\left(\frac{d(k_i - k_j)}{2}\right) + i\omega}. \quad (\text{S10})$$

As a consequence of the metallic dispersion, the above response function is intrinsically non-local. Moreover, at small values of $(k_i + k_j)/2$ and $(k_i - k_j)/2$, the quantity $\epsilon_i - \epsilon_j$ is approximately equivalent to the free-particle case considered by Dobson et al. (21). A collection of uncorrelated single-atom polarizabilities therefore necessarily provides an incorrect description of the metallic limit.

In contrast, a strongly localized response function emerges in the insulating limit, in which $\beta_1 = \beta$ and $\beta_2 = 0$. In this case, the system can essentially be described as a collection of isolated dimers. Here one is therefore faced with a set of independent two-particle systems, each characterized by two energy levels: $\epsilon_{\pm} = \pm\beta$. The corresponding eigenstates are bonding and anti-bonding wave functions, obtained as linear combinations of the atomic orbitals, $\psi_A(x)$ and $\psi_B(x)$, i.e., $\phi_{\pm}(x) = \frac{1}{\sqrt{2}}(\psi_A(x) \pm \psi_B(x))$. In this case, there is no k -dependence of the energy eigenvalues, as confirmed by Eq. S3 as well. Moreover, both the bonding and anti-bonding wave functions are strongly localized, since the atomic orbitals are expected to be exponentially decaying functions. The response function can thus be written as a product of the independent two-atom contributions, with each vanishing at $|x - x'| > d$. Given the absence of intrachain dispersion correlations within the TB model, atomic dimers hence act at large interchain distances as a collection of independent oscillators, which is in stark contrast to the metallic limit.

Comments on the Coupled Fluctuating Dipole Model

While the TB model leads to a set of uncorrelated diatomic response functions in the insulating limit, the inclusion of intrachain correlation effects, as provided by the MBD framework, intro-

duces a collective nature into the dipole fluctuations. This of course is the physical motivation underlying the unconventional power laws examined in this work. In practice, although the CFDM is based on a set of localized QHOs, the intrachain correlation is still responsible for the emergence of a non-trivial k -dependent energy dispersion of the collective dipolar fluctuation modes. Moreover, we also observed that the small gap present in the MBD energy eigenvalue spectrum (cf. Fig. 1A) does not prevent this model from predicting strongly delocalized intrachain response functions. In fact, the eigenstates of the MBD Hamiltonian do not represent single-electron orbitals, but should be viewed instead as collective dipolar fluctuation modes. Hence, the k -dispersion in Fig. 1A is a clear indication of the non-locality of the system response.

Ensuring Numerical Convergence

Given the collective nature of the relevant single-chain dipolar fluctuations, convergence issues are of particular relevance in this context. Regarding the TB model, a dense k -point sampling is necessary, especially at large interchain distances, in order to resolve the Brillouin zone with sufficient enough detail. For this reason, we utilized a mesh of 1024 k -points to achieve convergence for the selected interwire separations. For the MBD model, a reciprocal-space algorithm was also adopted and the convergence was carefully checked with respect to the number of k -points. In particular, a regular mesh of 4000 k -points was used in all 1D periodic calculations. In 2D periodic systems, a 360×360 k -point mesh was adopted at all interlayer distances. In both the 1D and 2D cases, we found convergence of the collective dipolar fluctuation spectrum (concerning both the energetic gap and slope of the dispersion), and found no detectable modifications of the power law exponents by further increasing the number of k -points at the considered interfragment separations.

Table S1. Interwire interaction energies per C atom $\Delta E_{\text{vdW}}^{\text{LR}}$ (in Hartrees) and power law exponents P_{exp} for two parallel 1D carbyne-like atomic wires as a function of the interwire separation D (in nanometers) and several values of the interatomic C–C distance $d_{\text{C-C}}$ ranging from 1.2 Å (the C–C bond length in acetylene) to 3.0 Å computed using the MBD model. The data in this table were obtained by setting the Hirshfeld volume ratio to 0.97 for each C atom and sampling the Brillouin zone with a regular mesh of 4000 points in the direction of the longitudinal chain axes.

D	$d_{\text{C-C}}=1.2 \text{ \AA}$		$d_{\text{C-C}}=1.4 \text{ \AA}$		$d_{\text{C-C}}=2.0 \text{ \AA}$	
	$\Delta E_{\text{vdW}}^{\text{LR}}$	P_{exp}	$\Delta E_{\text{vdW}}^{\text{LR}}$	P_{exp}	$\Delta E_{\text{vdW}}^{\text{LR}}$	P_{exp}
0.46	4.79E-4	-3.94	4.50E-4	-4.15	2.74E-4	-4.80
0.50	3.49E-4	-3.81	3.21E-4	-4.05	1.85E-4	-4.76
0.60	1.80E-4	-3.63	1.57E-4	-3.92	7.80E-5	-4.72
0.70	1.06E-4	-3.45	8.76E-4	-3.79	3.78E-5	-4.70
0.80	6.78E-5	-3.32	5.34E-5	-3.71	2.02E-5	-4.69
1.00	3.32E-5	-3.20	2.36E-5	-3.65	7.10E-6	-4.69
1.20	1.88E-5	-3.10	1.22E-5	-3.62	3.01E-6	-4.71
1.50	9.54E-6	-3.05	5.45E-6	-3.62	1.05E-6	-4.74
2.00	4.00E-6	-3.02	1.90E-6	-3.67	2.64E-7	-4.78
2.50	2.03E-6	-3.04	8.19E-7	-3.76	8.99E-8	-4.83
3.00	1.16E-6	-3.10	4.05E-7	-3.88	3.71E-8	-4.86
4.00	4.66E-7	-3.21	1.29E-7	-4.05	9.07E-9	-4.90
6.00	1.21E-7	-3.42	2.37E-8	-4.29	1.23E-9	-4.93
8.00	4.41E-8	-3.60	6.70E-9	-4.46	2.94E-10	-4.96
10.00	1.94E-8	-3.75	2.44E-9	-4.57	9.70E-11	-4.97
15.00	3.99E-9	-4.04	3.69E-10	-4.74	1.28E-11	-4.98
20.00	1.21E-9	-4.24	9.31E-11	-4.82	3.06E-12	-4.99

Table S2. Interlayer interaction energies per unit cell $\Delta E_{\text{vdW}}^{\text{LR}}$ (in Hartrees) and power law exponents P_{exp} for two parallel 2D graphenic layers and MoS₂ as a function of the interlayer separation D (in nanometers) computed using the MBD model. To investigate the behavior of these power laws in highly polarizable 2D materials, several values of α_{C}^0 were considered for the graphenic layers, ranging from 12 bohr³ (the static atomic dipole polarizability of a C atom) to 50 bohr³. The data in this table were obtained by setting the Hirshfeld volume ratio to 0.87 for C, 1.03 for Mo, and 0.99 for S and sampling the 2D Brillouin zone with a regular mesh of 360×360 points. The decreases in the interlayer interaction energies occurring at short distances for the highly polarizable graphenic structures are due to charge overlap effects, as parameterized through Eq. S5.

D	Graphene						MoS ₂	
	$\alpha_{\text{C}}=12 \text{ bohr}^3$		$\alpha_{\text{C}}=20 \text{ bohr}^3$		$\alpha_{\text{C}}=50 \text{ bohr}^3$			
	$\Delta E_{\text{vdW}}^{\text{LR}}$	P_{exp}	$\Delta E_{\text{vdW}}^{\text{LR}}$	P_{exp}	$\Delta E_{\text{vdW}}^{\text{LR}}$	P_{exp}	$\Delta E_{\text{vdW}}^{\text{LR}}$	P_{exp}
0.60	3.59E-4	-3.67	2.43E-4	-3.67	1.01E-4	-4.08	1.24E-2	-6.73
0.70	2.07E-4	-3.58	1.41E-4	-3.52	5.66E-4	-3.74	3.97E-3	-7.42
0.80	1.29E-4	-3.52	8.96E-5	-3.42	3.53E-5	-3.53	1.76E-3	-6.10
1.00	5.95E-5	-3.47	4.26E-5	-3.33	1.68E-5	-3.34	5.73E-4	-5.02
1.20	3.18E-5	-3.44	2.35E-5	-3.26	9.38E-6	-3.18	2.60E-4	-4.33
1.50	1.48E-5	-3.43	1.15E-5	-3.21	4.74E-6	-3.06	1.08E-4	-3.92
1.80	7.89E-6	-3.44	6.43E-6	-3.19	2.76E-6	-2.97	5.57E-5	-3.65
2.00	5.49E-6	-3.45	4.60E-6	-3.18	2.03E-6	-2.92	3.85E-5	-3.51
3.00	1.34E-6	-3.50	1.27E-6	-3.20	6.39E-7	-2.81	9.96E-6	-3.24
4.00	4.86E-7	-3.55	5.02E-7	-3.23	2.87E-7	-2.76	4.00E-6	-3.13
5.00	2.19E-7	-3.59	2.43E-7	-3.27	1.56E-7	-2.74	2.01E-6	-3.07
6.50	8.45E-8	-3.65	1.02E-7	-3.32	7.62E-8	-2.72	9.02E-7	-3.03
8.00	3.94E-8	-3.68	5.10E-8	-3.37	4.34E-8	-2.71	4.82E-7	-3.01
9.50	2.09E-8	-3.71	2.85E-8	-3.41	2.73E-8	-2.70	2.88E-7	-3.00

Table S3. Interaction energies $\Delta E_{\text{vdW}}^{\text{LR}}$ (in Hartrees) and power law exponents P_{exp} for two parallel (3, 3) carbon nanotubes and a carbyne-wire–protein nanostructure as a function of the respective center-of-mass separations D (in nanometers) computed using the MBD model. Both the nanotubes and the wire have finite lengths (with 500 and 3000 unit cell replicas, respectively). The data in this table were obtained by setting $d_{\text{C-C}}$ to 1.200 Å in the chain and 1.421 Å in the nanotubes and the Hirshfeld volume ratio to 0.90 for the C atoms in the nanotubes, 0.97 for the C atoms in the wire, and 0.75 for all atoms in the 1MC5 protein.

D	nanotube-nanotube		wire-protein	
	$\Delta E_{\text{vdW}}^{\text{LR}}$	P_{exp}	$\Delta E_{\text{vdW}}^{\text{LR}}$	P_{exp}
1.40	5.07E-2	-5.13	1.55E-4	-1.82
1.80	1.46E-2	-4.86	6.52E-5	-2.04
2.20	5.58E-3	-4.77	4.49E-5	-2.22
2.60	2.53E-3	-4.75	3.19E-5	-2.38
3.00	1.28E-3	-4.73	2.33E-5	-2.52
3.40	7.10E-4	-4.73	1.74E-5	-2.64
3.80	4.19E-4	-4.74	1.51E-5	-2.72
4.20	2.60E-4	-4.76	1.02E-5	-2.84
4.60	1.69E-4	-4.77	7.99E-6	-2.93
5.00	1.13E-4	-4.78	5.99E-6	-3.02
5.50	7.16E-5	-4.80	4.57E-6	-3.11
6.00	4.71E-5	-4.82	2.78E-6	-3.22
7.00	2.23E-5	-4.84	1.78E-6	-3.36
8.00	1.16E-5	-4.87	1.18E-6	-3.48
9.00	6.54E-6	-4.89	8.09E-7	-3.58