

Long-Range Repulsion Between Spatially Confined van der Waals Dimers

Mainak Sadhukhan and Alexandre Tkatchenko*

Physics and Materials Science Research Unit, University of Luxembourg, Luxembourg L-1511, Luxembourg
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It is an undisputed textbook fact that nonretarded van der Waals (vdW) interactions between isotropic dimers are attractive, regardless of the polarizability of the interacting systems or spatial dimensionality. The universality of vdW attraction is attributed to the dipolar coupling between fluctuating electron charge densities. Here, we demonstrate that the long-range interaction between *spatially confined* vdW dimers becomes repulsive when accounting for the full Coulomb interaction between charge fluctuations. Our analytic results are obtained by using the Coulomb potential as a perturbation over dipole-correlated states for two quantum harmonic oscillators embedded in spaces with reduced dimensionality; however, the long-range repulsion is expected to be a general phenomenon for spatially confined quantum systems. We suggest optical experiments to test our predictions, analyze their relevance in the context of intermolecular interactions in nanoscale environments, and rationalize the recent observation of anomalously strong screening of the lateral vdW interactions between aromatic hydrocarbons adsorbed on metal surfaces.

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Interactions induced by quantum-mechanical charge density fluctuations, such as van der Waals (vdW) and Casimir forces, are always present between objects with finite dimensions [1–4]. Such interactions are important not only for many fundamental phenomena throughout the fields of biology, chemistry, and physics but also for the design and performance of micro- and nano-structured devices. While Casimir forces can be both attractive or repulsive, depending on the nature of the fluctuations (quantum and/or thermal) and the spatial structure (topology and/or geometry) of the interacting systems [5–8], it is undisputed common wisdom that nonretarded vdW interactions between two objects *in vacuo* are inherently attractive [9–11]. The universality of vdW attraction is attributed to the ubiquitous zero-point energy lowering, induced by dipolar coupling between fluctuating electron charge densities [9,10].

However, many biological, chemical, and physical phenomena of importance in materials happen in spatially confined environments, as opposed to isotropic and homogeneous vacuum. The confinement can be artificially engineered by applying static or dynamic electromagnetic fields or arise as a result of the encapsulation of molecules in nanotubes, fullerenes, and/or by adsorption on polarizable surfaces. Moreover, in biological systems, proteins are typically confined in an inhomogeneous environment. We remark that even when such confinement entails tiny modification of the electron density (having no apparent effect on the electrostatics), it can visibly affect the interactions stemming from density fluctuations due to their long-range inhomogeneous nature.

Here, we demonstrate that the breaking of rotational and/or translational symmetry of 3D vacuum results in repulsive long-range interactions for vdW dimers.

The repulsive interaction stems from the full Coulomb coupling between charge density fluctuations and is a universal signature of constrained electric-field lines in 1D, 2D, or quasi-3D spaces. In fact, reported cases of long-range repulsion between physisorbed molecules abound in recent experimental literature [12–16]. The usual explanation attributes the repulsion to the charge transfer between the Fermi level of the metal surface and the molecular orbitals of the adsorbate [17] or the dominance of Pauli repulsion over a London-type dispersion interaction [18–20]. These explanations, however, do not apply to large molecules physisorbed on metallic surfaces. Our calculations suggest an alternative explanation for these and other experiments in nano-confined systems. In contrast to previously known cases of van der Waals repulsions, which are either mediated by another molecule (three-body Axilrod-Teller-Muto interaction [21]) or a dielectric medium [19], the present effect has a different distance dependence and it exists under arbitrary confinement.

We start our analysis by investigating a pair of coupled isotropic 3D Drude oscillators [22–24] (charge-separated overall-neutral quantum harmonic oscillators) in reduced spatial dimensions [see Fig. 1(a) and discussion below]. The Drude oscillators model the instantaneous quantum-mechanical electronic fluctuations (not the permanent deformations of the electron density), therefore being a model for electron correlation via the adiabatic connection fluctuation-dissipation theorem [25]. Consequently, the analysis of this work corresponds to dynamic electron correlation effects in confined environments. Despite being bosonic, Drude oscillators [22] provide a reliable and robust model of van der Waals interactions between valence electron densities [26–40]. For example, the

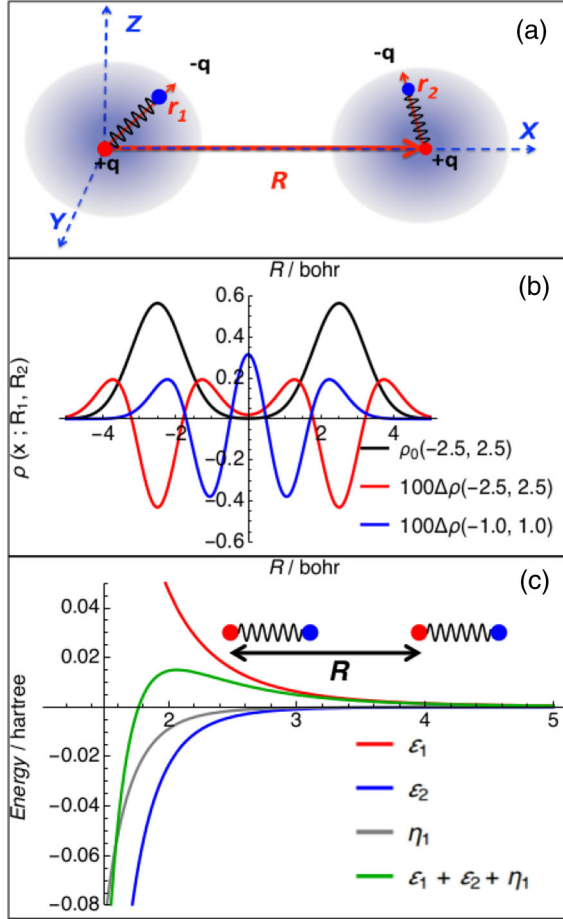


FIG. 1. (a) Drude oscillators embedded in the global reference frame (blue). (b) Probability density of uncoupled oscillators ρ_0 placed at ± 2.5 bohr (black), the difference density ($\Delta\rho = \rho_{\text{dip}} - \rho_0$) of dipole-correlated oscillators (red), and the $\Delta\rho$ for the pair of oscillators (blue) placed at ± 1 bohr. (c) Leading-order interaction terms of beyond-dipole perturbation expansion in 1D for $q = m = \omega = 1$ [See Eqs. (13)–(16) for the definition of ϵ_1 , ϵ_2 and η_1].

harmonic oscillator model, within the so-called many-body dispersion (MBD) framework, has been applied to accurately model vdW interactions in molecules, molecular crystals, solids with and without defects, surfaces, and nanostructured materials [31,41–45]. Here, we go beyond the MBD model by developing a perturbative analysis to study the effects of the full Coulomb interaction on the physically confined electric-field lines of the dipole-coupled Drude oscillators.

The developments in this article are based on the perturbation theory of Coulomb-coupled Drude oscillators developed by Jones *et al.* in Ref. [33]. We also develop and apply an alternative perturbation expansion, which takes coupled dipolar oscillators as a starting point.

Individual Drude oscillators follow the quantum mechanics of harmonic oscillators of frequency ω and mass μ . The full Coulomb potential between a pair of

Drude oscillators, each connected to charges $\pm q$ (using vacuum permittivity $\epsilon_0 = 1/4\pi$), is

$$V = q^2 \left(\frac{1}{|\mathbf{R}|} + \frac{1}{|\mathbf{R} - \mathbf{r}_1 + \mathbf{r}_2|} - \frac{1}{|\mathbf{R} - \mathbf{r}_1|} - \frac{1}{|\mathbf{R} + \mathbf{r}_2|} \right), \quad (1)$$

where \mathbf{R} , \mathbf{r}_1 , and \mathbf{r}_2 refer to the interoscillator separation vector and individual oscillator coordinates (positive charges are origins of individual oscillators' coordinates), respectively [see Fig. 1(a)]. The zero-distance limit for \mathbf{r}_1 and \mathbf{r}_2 , a presumably valid approximation at large \mathbf{R} , results in a widely used dipole-approximated potential

$$V_{\text{dip}} = \frac{q^2}{R^5} \{ R^2 \mathbf{r}_1 \cdot \mathbf{r}_2 - 3(\mathbf{r}_1 \cdot \mathbf{R})(\mathbf{r}_2 \cdot \mathbf{R}) \}, \quad (2)$$

which allows an exact solution of the coupled oscillator problem and leads to an interoscillator attraction, regardless of the oscillator parameters and dimensionality of space. A general 3D oscillator state $|\mathbf{n}\rangle$ (total quanta n) is the product of three independent 1D oscillators

$$\langle \zeta | \mathbf{n} \rangle = \frac{1}{\sqrt{2^{n_\zeta} n_\zeta!}} \left(\frac{\mu_\zeta \omega_\zeta}{\pi \hbar} \right)^{1/4} e^{-[\mu_\zeta \omega_\zeta \zeta^2 / 2\hbar]} H_{n_\zeta} \left(\sqrt{\frac{\mu_\zeta \omega_\zeta}{\hbar}} \zeta \right), \quad (3)$$

where $\zeta \in \{x, y, z\}$, $n = \sum_\zeta n_\zeta$, and H_{n_ζ} is a Hermite polynomial of order n_ζ . Therefore, any energy integral corresponding to Eq. (1) for a 3D Drude oscillator can be expressed as the product of three independent 1D integrals due to the identity

$$\frac{1}{r} = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-s^2 r^2} ds. \quad (4)$$

Now, we will consider the limiting case of confinement as complete quenching of oscillator motion in one or more directions, which is equivalent to negligible polarizations in those directions. A mathematical equivalent of fully quenched motion of one of the oscillator components (say Z) can be obtained via $n_z = 0$ and $\mu_z \rightarrow \infty$. Consequently, the 3D model transforms to an effective 2D model, following the identity $\delta(x) = \lim_{a \rightarrow \infty} (a/\sqrt{\pi}) e^{-a^2 x^2}$. Similarly, we can obtain an effective 1D model by completely confining two dimensions of the original 3D model. The resulting effective quasi-1D/2D potentials vary with the inverse of interoscillator distance (this will be called ‘‘Coulomb’’ potential henceforth) but do not satisfy the Laplace equation for the oscillator charges, unlike the original 3D model. Physically, the restricted motions confine the electric-field lines in a restricted region of space, which produces repulsion between the oscillators, as we will show below.

We start by analyzing the quantum mechanics of a full-Coulomb-coupled 1D oscillator dimer. Formally, a Taylor expansion of the interoscillator (with individual coordinates x_1 and x_2) 1D ‘‘Coulomb’’ potential is

$$V_{\text{int}} = \sum_{m=2}^{\infty} V_m = \frac{q^2}{R} \sum_{m=2}^{\infty} \sum_{k=1}^{m-1} \binom{m}{k} \frac{x_1^{m-k} (-x_2)^k}{R^m}. \quad (5)$$

Full-Coulomb-coupled oscillator states can be obtained by perturbing independent oscillator states with V_{int} , starting with dipole potential given by the $m = 2$ term in Eq. (5) (full-Coulomb perturbation) or perturbing the analytic dipole-coupled oscillator states [38] by V_{int} , starting from $m = 3$ of Eq. (5) (beyond-dipole perturbation expansion). While these two approaches are formally equivalent, in practice, the beyond-dipole expansion converges faster and allows novel insights into Coulomb-coupled oscillators (see Ref. [46]).

A system of two similar (mass μ and frequency ω) dipole-coupled 1D Drude oscillators is equivalent to two independent oscillators [22–24] in collective coordinates

$$a_1 = \frac{x_1 + x_2}{\sqrt{2}}, \quad (6)$$

$$a_2 = \frac{x_1 - x_2}{\sqrt{2}}, \quad (7)$$

with frequencies $\omega_1 = \omega/f_-$ and $\omega_2 = \omega/f_+$, respectively, where

$$f_{\pm} = \left(1 \pm \frac{2q^2}{\mu\omega^2 R^3}\right)^{-1/2}. \quad (8)$$

Figure 1(b) shows the anisotropic charge density that is created around free oscillator states due to dipole coupling, leading to emerging dipole moments. The consequent lowering of zero-point energy contains London attraction ($-C_6/R^6$) as the leading contribution but does not contain effects due to higher-order multipole moments [38]. We now employ beyond-dipole perturbation expansion on these dipole-coupled states as defined in the previous paragraph. Two leading-order perturbation terms correspond to $m = 3$ and 4 in Eq. (5), and when expressed in collective coordinates a_1 and a_2 [Eqs. (6) and (7)], they are

$$V_3 = \frac{-3q^2}{\sqrt{2}R^4} (a_1^2 a_2 - a_2^3) \quad (9)$$

and

$$V_4 = \frac{q^2}{2R^5} (7a_2^4 - a_1^4 - 6a_1^2 a_2^2), \quad (10)$$

respectively. The ground state of dipole-coupled oscillators has even symmetry with respect to a_1 and a_2 . Hence, the leading contribution to the first-order beyond-dipole perturbation theory comes from leading even-order potential in Eq. (5) (viz. V_4), yielding the first-order correction from fourth-order potential [Eq. (10)] (superscript and subscript on energy components indicate order of perturbation and order of potential, respectively)

$$E_4^{(1)} = \frac{3q^2}{8R^5} \left(\frac{\hbar}{\mu\omega}\right)^2 [7f_+^2 - f_-^2 - 2f_- f_+]. \quad (11)$$

Similar symmetry consideration yields the leading second-order perturbation correction from Eq. (9) (see Supplemental Material [47] for details):

$$E_3^{(2)} = -\frac{9q^4}{16\mu\omega^2 R^8} \left(\frac{\hbar}{\mu\omega}\right)^2 [3f_+^2 - f_+ f_-]^2. \quad (12)$$

The power series expansion of Eq. (11) in powers of R [using Eq. (8)] yields

$$E_4^{(1)} = \varepsilon_1 + \varepsilon_2 + \dots = 2\frac{\alpha_2 \hbar \omega}{R^5} - 8\frac{\alpha_2 \alpha_1 \hbar \omega}{R^8} + \dots \quad (13)$$

The appearance of quadrupole polarizability $\alpha_2 = \frac{3}{4}(q^2/\mu\omega^2)(\hbar/\mu\omega)$ in the leading repulsive term

$$\varepsilon_1 = 2\frac{\alpha_2 \hbar \omega}{R^5} \quad (14)$$

and the following attractive term

$$\varepsilon_2 = -8\frac{\alpha_2 \alpha_1 \hbar \omega}{R^8} \quad (15)$$

indicates that ε_1 corresponds to the mean-field energy of an instantaneous quadrupole in the field generated by fluctuations in another electronic fragment. A similar approach yields

$$\eta_1 = -3\frac{\alpha_2 \alpha_1 \hbar \omega}{R^8} \quad (16)$$

as the leading term of Eq. (12). Note that η_1 appears to share a similar origin with ε_2 ; i.e., both η_1 and ε_2 come from the interaction between the singly excited and the ground states of the noninteracting oscillator pair. Similar power laws could have also come from the first-order perturbation correction due to V_7 , which, however, vanishes identically. As expected, the cumulative effect of ε_1 , ε_2 , and η_1 remains repulsive [Fig. 1(c)] in the long range. The addition of the London dispersion $C_6 R^{-6}$ term does not alter the asymptotic repulsion. Note that the source of this repulsion is ε_1 , which is proportional to the quadrupole polarizability (linear in \hbar), unlike the case of isotropic and homogeneous vacuum (see Fig. 7 in Ref. [33]).

It is important to note that $E_4^{(1)}$, which originates from the fourth derivative of the V_{int} , vanishes identically in isotropic and homogeneous vacuum, unlike the aforementioned quasi-1D case. The analogous quantity in the full-3D case

$$\sum_{\alpha,\beta,\gamma,\delta} \frac{\partial^4}{\partial r_\alpha \partial r_\beta \partial r_\gamma \partial r_\delta} V_{\text{int}} \quad (17)$$

sums over four variables α , β , γ , and δ , each of which can have only 3 values, i.e., x , y , and z . As a result, all possible combinations of α , β , γ , and δ in Eq. (17) contain at least one repeated index, yielding

$$\sum_{\gamma,\delta} \frac{\partial^2}{\partial r_\gamma \partial r_\delta} \sum_{\alpha} \frac{\partial^2}{\partial r_\alpha \partial r_\alpha} V_{\text{int}}. \quad (18)$$

The second summation in Eq. (18) vanishes, resulting in the dipole potential as the correct asymptotic limit in the case of homogeneous and isotropic vacuum.

The extension of our analysis to two dimensions is straightforward. Similar to Eq. (5), the Laplace expansion of the Coulomb potential, followed by the power series expansion of the Legendre polynomial, yields the even parity terms of interoscillator interaction as

$$V^{(2p)} = \frac{4^p q^2}{R^{2p+1}} \sum_{t=0}^p \sum_{s=0}^{p-t} \binom{2p}{2t} \binom{\frac{2(p+t)-1}{2}}{2p} \binom{p-t}{s} \times [(\Delta x)^{2(p-s)} (\Delta y)^{2s} - x_2^{2(p-s)} y_2^{2s} - x_1^{2(p-s)} y_1^{2s}], \quad (19)$$

where $\Delta x = (x_1 - x_2)$, and $\Delta y = (y_1 - y_2)$, and $p \in \mathbb{Z}^+$. Aligning \mathbf{R} with the global X direction, i.e., along the line joining positive charges of two oscillators,

$$V^{(4)} = V_x^{(4)} + \frac{3}{4} V_y^{(4)} - \frac{3q^2}{2R^5} [7a_2^2 b_2^2 - 4a_1 b_1 a_2 b_2 - a_1^2 b_1^2 - a_1^2 b_2^2 - a_2^2 b_1^2] \quad (20)$$

is obtained as the fourth-order term in collective coordinates $a_1 = (1/\sqrt{2})(x_1 + x_2)$, $a_2 = (1/\sqrt{2})(x_1 - x_2)$, $b_1 = (1/\sqrt{2})(y_1 + y_2)$ and $b_2 = (1/\sqrt{2})(y_1 - y_2)$. The Y -directional component $V_y^{(4)} = (\tilde{q}^2/R^5)[6y_1^2 y_2^2 - 4(y_1^3 y_2 + y_2^3 y_1)]$ is expressed in terms of reduced charge $\tilde{q} = q/\sqrt{2}$ to retain the usual form of the dipole term. The third term in Eq. (20) is the coupling between X and Y components of the potential. The final expression shows that the leading contribution to the long-range energy

$$E_{2D,4}^{(1)} \approx \frac{3}{4} \epsilon_{1,y} = \frac{3}{2} \frac{\alpha_2^y \hbar \omega}{R^5} \quad (21)$$

arises out of the cancellation between the leading orders of the repulsive first and the attractive third term of Eq. (20). The resulting long-range repulsive energy, similar to the 1D example, is the mean-field energy of an instantaneous quadrupole and varies as R^{-5} . Curiously, the predominant effect comes from the orthogonal component (to the interoscillator axis, here, global X axis) of polarizability and may have nontrivial implications, for example, for molecules confined between layered materials [48].

Next, we extend our analysis to the quasi-3D case, which is relevant for modeling lateral interactions between molecules adsorbed on polarizable (metallic or semiconducting) surfaces. For molecules physisorbed on surfaces, the interaction potential follows the Poisson equation. Aligning the global XY plane with the surface (here, we assume perfect reflection and discuss the general case later) and X axis with \mathbf{R} , one realizes that the Z component of the oscillator experiences a half-oscillator potential

$$V(z) = \begin{cases} \infty & ; z \leq 0 \\ \frac{m\omega^2}{2} z^2 & ; z > 0 \end{cases} \quad (22)$$

The resulting oscillator state will be the product of usual X - and Y -directional 1D oscillators and the

$$\langle z | \mathbf{n} \rangle = N_{n_z} H_{2n_z+1} \left(\sqrt{\frac{m\omega}{\hbar}} z \right) e^{-m\omega z^2/2\hbar} \Theta(z), \quad (23)$$

with $N_{n_z} = [1/\sqrt{4^{n_z}(2n_z+1)!}] (m\omega/\pi\hbar)^{1/4}$, and $\Theta(z)$ is the step function, accounting for the absence of the oscillator wave function below the metal surface. The continuity of the wave function therefore demands a node on the surface, forcing the solution to be the odd subset of full quantum oscillator solutions.

Note that the long-range repulsive energies in quasi-1D [Eq. (11)] and quasi-2D confinement [Eq. (21)] are outcomes of first-order perturbation over dipolar-correlated states. The same quantity for a pair of asymmetric 3D oscillators exhibits long-range repulsion that varies as C_5/R^{-5} , with $C_5 = \frac{9}{4} (q^2/m\omega^2) (\hbar/m\omega) \hbar\omega$, providing a generalization of the 1D and 2D confined oscillator cases. Using the parameters of the methane molecule and Ar atom [33], we obtain an estimate of long-range intermolecular lateral potential (Fig. 2). As expected, the interaction is repulsive in the long range for both cases. Note that the model presented here assumes ideal confinement. For realistic surfaces, the effects of different adsorption heights, tunneling penetration of molecular electron density through the confining boundary, and the possibility of imperfect reflection all need to be considered. Moreover, the interaction is purely attractive in the absence of confinement. Therefore, we expect a crossover from attraction to repulsion, depending on the polarizability of the adsorbate molecule and the penetration depth of the adsorbent electron density having observable effects on the surface structure of the adsorbed molecules.

We would now like to examine the relevance of the present analyses in realistic experimental situations where long-range repulsions or a significant decrease in attractive van der Waals interaction in the presence of confinements

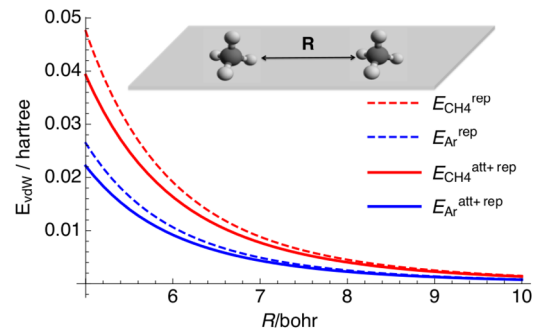


FIG. 2. Repulsive interaction E^{rep} (broken lines) and the sum of repulsion and London attraction (E^{att}) energy (solid lines) for argon and methane dimers on a perfectly reflecting surface.

have already been reported. To connect the presented 1D analysis to experimental findings, we note that it has been found that the flow rate of water through carbon nanotubes (CNTs) increases significantly with decreasing CNT diameter [49]. Classical molecular dynamics simulations [50] and density functional calculations (see Ref. [51] for a contemporary review) underestimate these effects by several orders of magnitude. The repulsion presented in this Letter, which is missing from classical force fields and density functional approximations, would introduce an intermolecular repulsion, which may rationalize a higher flow rate with increasing confinement. The 2D oscillator dimer example is related to a recent experiment [52] where a previously unknown ice structure has been discovered when water molecules are encapsulated between two graphene sheets, thereby suggesting peculiar intermolecular interaction between water molecules under quasi-2D confinement. In fact, a recent quantum Monte Carlo study [53] of stable square ice between graphene sheets shows that most dispersion-corrected DFT functionals overestimate the binding in the water layer. Finally, the long-range repulsion between a quasi-3D oscillator dimer presented here may provide an alternate interpretation of lateral repulsion between monolayer structures of hexabenzocoronene on Au(111), where a 90% screening of the lateral vdW interactions by the surface was suggested previously [12].

In summary, we have solved the problem of two oscillators coupled with a Coulomb potential under 1D, 2D, and quasi-3D confinement, utilizing a novel perturbation expansion based on Ref. [33] and correlated dipolar oscillator states. The breaking of spherical symmetry yields a long-range repulsive interaction, suggesting that this is a general phenomenon for confined dimers. Our findings can be extended to systems such as atoms in optical traps, molecules confined in nanopores, and molecules adsorbed on polarizable surfaces. While the presented analytic results are valid for vdW dimers, Coulomb-induced many-body effects in many-particle systems might turn out to be even more intricate and could be addressed by extending the developed perturbation expansion on top of the microscopic many-body dispersion Hamiltonian [30,54].

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*alexandre.tkatchenko@uni.lu

- [1] V. Parsegian, *Van der Waals Forces: A Handbook for Biologists, Chemists, Engineers, and Physicists* (Cambridge University Press, Cambridge, 2005).
 [2] G. L. Klimchitskaya, U. Mohideen, and V. M. Mostepanenko, *Rev. Mod. Phys.* **81**, 1827 (2009).

- [3] J. F. Dobson and T. Gould, *J. Phys. Condens. Matter* **24**, 073201 (2012).
 [4] L. M. Woods, D. A. R. Dalvit, A. Tkatchenko, P. Rodriguez-Lopez, A. W. Rodriguez, and R. Podgornik, *Rev. Mod. Phys.* **88**, 045003 (2016).
 [5] R. Zhao, J. Zhou, T. Koschny, E. N. Economou, and C. M. Soukoulis, *Phys. Rev. Lett.* **103**, 103602 (2009).
 [6] A. W. Rodriguez, F. Capasso, and S. G. Johnson, *Nat. Photonics* **5**, 211 (2011).
 [7] P. Rodriguez-Lopez and A. G. Grushin, *Phys. Rev. Lett.* **112**, 056804 (2014).
 [8] P. Jakubczyk, M. Napiórkowski, and T. Sęk, *Eur. Phys. Lett.* **113**, 30006 (2016).
 [9] D. Langbein, in *Springer Tracts in Modern Physics* (Springer Berlin Heidelberg, Berlin, Heidelberg, 1974), pp. 1–139.
 [10] A. Stone, *The Theory of Intermolecular Forces*, International Series of Monographs on Chemistry (Clarendon Press, Oxford, 1997).
 [11] I. Kaplan, *Intermolecular Interactions: Physical Picture, Computational Methods and Model Potentials*, Wiley Series in Theoretical Chemistry (Wiley, Chichester, 2006).
 [12] C. Wagner, D. Kasemann, C. Golnik, R. Forker, M. Esslinger, K. Müllen, and T. Fritz, *Phys. Rev. B* **81**, 035423 (2010).
 [13] C. Kleimann, B. Stadtmüller, S. Schröder, and C. Kumpf, *J. Phys. Chem. C* **118**, 1652 (2014).
 [14] X. J. Liu, Y. Wei, J. E. Reutt-Robey, and S. W. Robey, *J. Phys. Chem. C* **118**, 3523 (2014).
 [15] B. Stadtmüller, M. Willenbockel, S. Schröder, C. Kleimann, E. M. Reinisch, T. Ules, S. Soubatch, M. G. Ramsey, F. S. Tautz, and C. Kumpf, *Phys. Rev. B* **91**, 155433 (2015).
 [16] S. Thussing and P. Jakob, *J. Phys. Chem. C* **120**, 9904 (2016).
 [17] S. Simpson and E. Zurek, *J. Phys. Chem. C* **116**, 12636 (2012).
 [18] I. Kröger, B. Stadtmüller, C. Wagner, C. Weiss, R. Temirov, F. S. Tautz, and C. Kumpf, *J. Chem. Phys.* **135**, 234703 (2011).
 [19] R. F. Tabor, R. Manica, D. Y. C. Chan, F. Grieser, and R. R. Dagastine, *Phys. Rev. Lett.* **106**, 064501 (2011).
 [20] K. V. Shajesh and M. Schaden, *Phys. Rev. A* **85**, 012523 (2012).
 [21] B. M. Axilrod and E. Teller, *J. Chem. Phys.* **11**, 299 (1943).
 [22] W. L. Bade, *J. Chem. Phys.* **27**, 1280 (1957).
 [23] W. L. Bade and J. G. Kirkwood, *J. Chem. Phys.* **27**, 1284 (1957).
 [24] W. L. Bade, *J. Chem. Phys.* **28**, 282 (1958).
 [25] D. Langreth and J. Perdew, *Solid State Commun.* **17**, 1425 (1975).
 [26] F. Wang and K. D. Jordan, *J. Chem. Phys.* **114**, 10717 (2001).
 [27] T. Sommerfeld and K. D. Jordan, *J. Phys. Chem. A* **109**, 11531 (2005).
 [28] A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.* **102**, 073005 (2009).
 [29] A. Jones, A. Thompson, J. Crain, M. H. Müser, and G. J. Martyna, *Phys. Rev. B* **79**, 144119 (2009).
 [30] A. Tkatchenko, R. A. DiStasio Jr., R. Car, and M. Scheffler, *Phys. Rev. Lett.* **108**, 236402 (2012).

- [31] V. V. Gobre and A. Tkatchenko, *Nat. Commun.* **4**, 2341 (2013).
- [32] V. K. Voora, J. Ding, T. Sommerfeld, and K. D. Jordan, *J. Phys. Chem. B* **117**, 4365 (2013).
- [33] A. P. Jones, J. Crain, V. P. Sokhan, T. W. Whitfield, and G. J. Martyna, *Phys. Rev. B* **87**, 144103 (2013).
- [34] P. E. M. Lopes, J. Huang, J. Shim, Y. Luo, H. Li, B. Roux, and A. D. Mackerell, Jr., *J. Chem. Theory Comput.* **9**, 5430 (2013).
- [35] W. Liu, A. Tkatchenko, and M. Scheffler, *Acc. Chem. Res.* **47**, 3369 (2014).
- [36] A. Ambrosetti, D. Alfè, R. A. Distasio, Jr., and A. Tkatchenko, *J. Phys. Chem. Lett.* **5**, 849 (2014).
- [37] N. Ferri, R. A. DiStasio, Jr., A. Ambrosetti, R. Car, and A. Tkatchenko, *Phys. Rev. Lett.* **114**, 176802 (2015).
- [38] T. T. Odbadrakh, V. Voora, and K. D. Jordan, *Chem. Phys. Lett.* **630**, 76 (2015).
- [39] V. P. Sokhan, A. P. Jones, F. S. Cipcigan, J. Crain, and G. J. Martyna, *Proc. Natl. Acad. Sci. U.S.A.* **112**, 6341 (2015).
- [40] M. Sadhukhan and F. R. Manby, *Phys. Rev. B* **94**, 115106 (2016).
- [41] A. Tkatchenko, *Adv. Funct. Mater.* **25**, 2054 (2015).
- [42] A. M. Reilly and A. Tkatchenko, *Chem. Sci.* **6**, 3289 (2015).
- [43] R. J. Maurer, V. G. Ruiz, and A. Tkatchenko, *J. Chem. Phys.* **143**, 102808 (2015).
- [44] W. Gao and A. Tkatchenko, *Phys. Rev. Lett.* **114**, 096101 (2015).
- [45] W. Gao and A. Tkatchenko, *Phys. Rev. Lett.* **111**, 045501 (2013).
- [46] When using the full-Coulomb perturbation expansion, we obtain only single power law contribution from each term in Eq. (5), while in present formalism, we get an infinite number of terms with decreasing power of R for a given order of perturbation theory. We can interpret these terms as higher-order diagrams.
- [47] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.118.210402> for details of the derivation.
- [48] K. S. Vasu, E. Prestat, J. Abraham, J. Dix, R. J. Kashtiban, J. Beheshtian, J. Sloan, P. Carbone, M. Neek-Amal, S. J. Haigh, A. K. Geim, and R. R. Nair, *Nat. Commun.* **7**, 12168 (2016).
- [49] D. Mattia, H. Leese, and K. P. Lee, *J. Membr. Sci.* **475**, 266 (2015).
- [50] S. K. Kannam, B. D. Todd, J. S. Hansen, and P. J. Davis, *J. Chem. Phys.* **138**, 094701 (2013).
- [51] A. Striolo, A. Michaelides, and L. Joly, *Annu. Rev. Chem. Biomol. Eng.* **7**, 533 (2016).
- [52] G. Algara-Siller, O. Lehtinen, F. C. Wang, R. R. Nair, U. Kaiser, H. A. Wu, A. K. Geim, and I. V. Grigorieva, *Nature (London)* **519**, 443 (2015).
- [53] J. Chen, A. Zen, J. G. Brandenburg, D. Alfè, and A. Michaelides, *Phys. Rev. B* **94**, 220102 (2016).
- [54] R. A. Distasio, Jr., V. V. Gobre, and A. Tkatchenko, *J. Phys. Condens. Matter* **26**, 213202 (2014).