Thermal van der Waals Interaction between Graphene Layers

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The van de Waals interaction between two graphene sheets is studied at finite temperatures. Graphene’s thermal length ($\xi_T = h\nu/k_BT$) controls the force versus distance ($z$) as a crossover from the zero temperature results for $z \ll \xi_T$, to a linear-in-temperature, universal regime for $z \gg \xi_T$. The large separation regime is shown to be a consequence of the classical behavior of graphene’s plasmons at finite temperature. Retardation effects are largely irrelevant, both in the zero and finite temperature regimes. Thermal effects should be noticeable in the van de Waals interaction already for distances of tens of nanometers at room temperature.

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I. INTRODUCTION

Graphene, the single layer honeycomb lattice of carbon atoms that forms graphite, has been realized experimentally in recent times. Its electronic properties characterized by a linear dispersion around Fermi points, fixed by charge neutrality (massless Dirac fermions with velocity $v \sim 10^6 \text{ m/s}$), have long attracted theoretical interest. But it is the present experimental accessibility, including Fermi level tuning by gate voltages, what has unleashed an explosion of activity, fueled in part by the prospects of tailoring its electronic (and perhaps magnetic) properties in the nanoscale.

More traditional areas like the van der Waals (vdW) interaction have also benefited from the present interest. Although graphite is often characterized as a vdW stack of graphene layers, fundamental aspects such as the asymptotic behavior of the vdW interaction between two graphene layers, have been unveiled only recently by Dobson et al., and shown not to conform to the naive sum of $R^{-6}$ contributions. Taking as reference the progress in accurate measurements of vdW interactions in general, the expected increase in availability of graphene, and its unique conceptual place as neither a metal nor a dielectric, the study of graphene’s vdW interaction seems worth of further considerations.

In this paper I consider the vdW interactions between two graphene layers at finite temperature ($T$). Graphene, being a critical system at zero $T$, lacks any characteristic length scale. Temperature provides such scale, the thermal length: $\xi_T = h\nu/k_BT$. We will show that the thermal length controls the vdW interaction between planes in the form of a crossover. For separations between the two layers ($z$) smaller than the thermal length, $z \lesssim \xi_T$, the zero-$T$ result ($f$) for the force prevails, $f \propto 1/z^2$. But for separations larger than the thermal length, $z \gtrsim \xi_T$, the force crosses over to a linear-in-$T$ material parameters independent, universal regime, $f \propto T/z^3$, that constitutes the genuine asymptotic large-separation interaction between two graphene sheets at finite $T$.

The linear-in-$T$ regime will be shown to reflect the classical nature of graphene’s low lying excitations at finite $T$: plasmons. As shown by Vafek, these plasmons are the charge fluctuations of thermally generated carriers (electrons and holes). Therefore, they are present only at finite $T$ and with energy scale tied to $T$, so that long-wavelength plasmons always behave classically. As such, this thermal regime will be shown to be present event for the instantaneous (non-retarded) Coulomb interaction. This should be contrasted with the usual linear-in-$T$, thermal limit of the vdW interactions between any material that sets in for distances larger than the thermal length of the field, $\lambda_T = h\nu/k_BT$. The explicit appearance of the light velocity $c$ in this generic case, is a manifestation of the classical population of the relevant electromagnetic modes. But not in graphene, where the existence of this regime even without retardation $c \to \infty$, and with the role of $c$ taken by $v$ in setting the range, shows it to be a consequence of the classical dynamics of matter. As a corollary, the inclusion of field’s dynamics (retardation) will be proven to be largely irrelevant both at zero and finite $T$. This is another aspect where graphene separates from ordinary dielectrics and metals, where retardation always matters for large enough separations. The relevance of the thermal length ($\xi_T$) (as opposed to $\lambda_T$) places graphene in an unique position for the experimental observation of thermal effects in the vdW interaction. For instance, at room temperature, the thermal regime should begin to be observable for distances $z \gtrsim \xi_T \sim 26 \text{ nm}$. In contrast, the onset of thermal effects linked to the classicality of the field (the situation for good metal and dielectrics, see section [V]) would require much larger distances at room temperature: $z \gtrsim \lambda_T \sim 300 \xi_T$.

Concerning the experimental situation, a word of caution is required. Throughout this paper, graphene is modeled as the usual set of Dirac fermions, known to provide an excellent description of the low energy physics (even up to $\sim 2 \text{ eV}$ in light absorption experiments). Nevertheless, the vdW calculation is incomplete for real graphene, where more electrons and bands contribute to the vdW force, particularly at short distances. These additional terms are estimated from published ab initio results in appendix [B] and shown not to compete with the low energy contribution already for distances of the
order of nanometers.

The paper is organized as follows. In section II, the formalism is presented and the results at zero $T$ recovered. Finite $T$ is considered in section III, the force versus scaled distance $(z/\xi_T)$ distance is computed numerically and its asymptotic behavior explained in terms of classical plasmons. Full retardation is included in section IV, where its contribution is shown to be quantitatively irrelevant for graphene’s parameters. Section V summarizes graphene’s vdW results, contrasting them with the known behavior of ideal dielectrics and metals. Appendix A calculates graphene’s transverse-response contribution to the vdW force, to show that it never competes with the longitudinal response considered in the body of the paper. Appendix B addresses real graphene, estimating the contributions to the vdW force beyond that of Dirac fermions considered here.

II. FORMALISM. ZERO TEMPERATURE RESULTS

Let us first present our non-retarded formalism recovering the zero-$T$ results. Consider two graphene layers perpendicular to the $z$-axis and separated by a distance $z$. Ignoring (for the moment) retardation effects, the mutual force per area can be written as:

$$ f = \int \frac{d^2 q}{(2\pi)^2} f_c(q,z) < \rho^{(1)}_q \rho^{(2)}_q >, \quad (1) $$

with Coulomb coupling between density fluctuations $\rho^{(1)}_q$ and $\rho^{(2)}_q$ given by $v_c(q,z) = e^2 \exp(-q|z|)/(2\epsilon_0 q)$ (elementary charge $e$ and vacuum permittivity $\epsilon_0$, SI units), and Coulomb force $f_c(q,z) = -\partial_z v_c(q,z)$.

Evaluating the thermal average to all orders in the mutual interaction, we can write:

$$ f = \frac{1}{2\pi^2} \int d^2 q \frac{f_c(q,z)}{\beta^{-1}} \cdot \sum_{\omega_n} \chi^{(1)}_{\rho \rho}(q,i\omega_n) W_c(q,i\omega_n,z) \chi^{(2)}_{\rho \rho}(q,i\omega_n), \quad (2) $$

with $\beta^{-1} = k_BT$, Matsubara densities $\hbar \omega_n = 2\pi n k_BT$, and the multiple-scattering-corrected interaction between planes given by:

$$ W_c(q,\omega, z) = \frac{v_c(q,z)}{1 - v_c(q,z)^2 \chi^{(1)}_{\rho \rho}(q,\omega) \chi^{(2)}_{\rho \rho}(q,\omega)}, \quad (3) $$

where $\chi^{(1)}_{\rho \rho} = \chi^{(2)}_{\rho \rho}$ is the charge-charge Green’s function of an isolated graphene layer, which can be written as:

$$ \chi^{(0)}_{\rho \rho}(q,\omega) = \frac{\chi^{(0)}_{\rho \rho}(q,\omega)}{1 - v_c(q,z=0)\chi^{(0)}_{\rho \rho}(q,\omega)}, \quad (4) $$

with $\chi^{(0)}_{\rho \rho}(q,\omega)$ as the polarization of an isolated graphene (proper polarization in diagrammatic sense). Before proceeding to the evaluation of $f$, let us remark that this formula is entirely equivalent to the (non-retarded version of) Lifshitz treatment, as can be seen by evaluating the field’s stress tensor in the presence of the (here non-local) material’s response. If we knew the exact polarization of a single graphene (including its crucial $q$-dependence), the only remaining approximation in (2) (and in Lifshitz’s approach) would amount to the neglect of proper polarization diagrams connecting both planes: local field corrections to the dielectric response, safely ignored for large separations. The diagrammatic description of the vdW calculation is presented in Fig. 1.

Throughout this paper, we will take as the proper polarization the non-interacting value, what amounts to the standard RPA for Eq. (1). It is given by:

$$ \chi^{(0)}_{\rho \rho} = N \sum_{\sigma, \sigma'} \int \frac{d^2 k}{(2\pi)^2} \frac{\delta \sigma' \delta k}{\hbar} n_f(E_k^\sigma) - n_f(E_{k+q}^\sigma), \quad (5) $$

with $N=2\times2$ fermion species, $n_f = \frac{1}{2} + \frac{\sigma' k^2 + k q}{2(N k q)}$, $n_f$ is the Fermi factor and $E_k^\sigma = \sigma \hbar vk$. If we use the zero-$T$ value\textsuperscript{17,18} for $\chi^{(0)}$:

$$ \chi^{(0)}(q,\omega) = -\frac{N}{16\hbar v} \frac{q^2}{\sqrt{q^2 - \omega^2}} \omega^2, \quad (6) $$

in Eq. (4), with the Matsubara sum becoming an integral $i\omega_n \rightarrow i\eta$, the resulting expression for $f$ is:

$$ f = -\frac{1}{2\pi} \int_0^\infty dq \frac{\hbar}{\pi} \int_0^\infty d\eta \cdot \exp(-2q|z|) \left( 1 + \frac{16}{N\pi \sqrt{1 + \eta^2/(vq)^2}} \right) \exp(-2q|z|), \quad (7) $$

![FIG. 1: Template diagram for the computation of the vdW force, as in Eqs. 2 and B. Bubbles: isolated graphene’s response (charge or current). Thin wavy lines: Coulomb interaction (or photon propagator). Thick wavy lines: multiple-scattering-corrected interaction (or photon propagator) between graphene’s layers as in Eq. 3. Zig-zag line represents force ($f_z$): distance derivative of the interaction line (or photon propagator).](image-url)
where \( \alpha = e^2/(2\epsilon_0 \hbar v) \) is a dimensionless measure of the effect of interactions in graphene, with value \( \alpha \sim 13.6 \).

Expression (7) can be shown to be entirely equivalent to the treatment of Dobson et al.\(^5\), leading to the following quantitative value for the force per area between graphene layers:

\[
f = -\frac{A}{z^2}, \quad A \sim 0.40 \text{ eV Å}.
\] (8)

Notice that other choices for the proper polarization complying with the scaling \( \chi^{(0)} \propto f(\omega/\epsilon q) \), such as the excitonic response of ref.\(^{19}\), would produce the same \( z^{-4} \) power law, although with different prefactor.

### III. Finite Temperature Results

Let's consider now a finite temperature still for non-retarded interactions. Although no simple analytical expression is known for \( \chi^{(0)} \) at finite \( T \) (see, though, ref.\(^{24}\), its scaling behavior\(^4\) is best described measuring lengths in units of \( \xi_T = h\epsilon/k_B T \), and energy in terms of \( k_B T \). Indeed, for the force calculation, matter and field appear in the dimensionless combination:

\[
v_c(q, z) \chi^{(0)}(q, \omega) = \alpha \exp(-q|z|) \tilde{\chi}(q \xi_T, \hbar \omega/k_B T),
\] (9)

where \( \tilde{\chi}(q \xi_T, \hbar \omega/k_B T) \) is a dimensionless function. It is clear that the force, Eq. (2), will depend on distance and temperature only through the combination \( z/\xi_T \), with the following scaling form:

\[
f(z, T) = \frac{k_B T}{\xi_T^2} \tilde{f}(z/\xi_T)
\] (10)

Therefore, knowledge of the dimensionless function \( \tilde{f}(z/\xi_T) \) provides all information for the vDW interaction at finite \( T \) and arbitrary distances in the scaling regime. We have evaluated numerically the force (Eqs. (3), (11) and (2)) with results plotted in Fig. 2. As expected, graphene’s thermal length marks a crossover between two regimes: the zero-\( T \) limit\(^5\) for \( z/\xi_T \ll 1 \) previously analyzed\(^2\), and the genuine large-distance regime at finite temperature for \( z/\xi_T \gg 1 \), that we now consider.

As discussed by Vafek\(^{11}\), the most important feature of the charge-charge response (1) at finite \( T \), is the emergence of plasmons. These appear as the zeros of the denominator of Eq. (1) and, in the long wavelength limit, the plasmon frequency is given by\(^{11,21}\):

\[
\frac{\hbar \omega_p(q)}{k_B T} = \sqrt{\frac{\ln 2}{2\pi \pi N} q \xi_T}, \quad q \xi_T \ll 1
\] (11)

Although plasmons possess an imaginary part \( \gamma(q) \), meaning that they decay into the electron-hole continuum\(^{11}\), they become very long-lived excitations for long wavelengths: \( \gamma(q)/\omega_p(q) \to 0 \) for \( q \xi_T \to 0 \).

Being the density fluctuations of thermally excited carriers, plasmons owe their existence and energy scale to temperature. In this respect, they differ from plasmons of ordinary 2d metals, already present and contributing\(^5\) to the vDW force at zero \( T \). Furthermore, the spectral power of the charge-charge response for \( \hbar q < \hbar \omega \lesssim k_B T \) and \( q \xi_T \ll 1 \) is dominated by the plasmon mode. Therefore, a single-pole approach for the response suffices for the plasmon contribution to \( \chi \) at finite \( T \), with the explicit form:

\[
\chi(q, \omega) = \frac{1}{v_c(q, z = 0)} \frac{\omega_p(q)^2}{\omega^2 - \omega_p(q)^2}
\] (12)

This response is valid for \( q \xi_T \ll 1 \) and \( \hbar \omega \lesssim k_B T \). Its use in Eq. (2) provides the wanted large-distance behavior of the vDW force at finite \( T \). The evaluation is best performed trading Matsubara sums for real frequency integration in Eq. (2):

\[
f = -\frac{1}{2\pi} \int_0^\infty q^2 dq \frac{\hbar}{\pi} \int_0^\infty d\omega \coth(\beta \hbar \omega/2) \cdot \left[ \frac{\exp(-2q|z|)}{(\omega_p(q)^2 - 1)^2 - \exp(-2q|z|)} \right]
\] (13)

leading to the following central result:

\[
f = -\frac{\zeta(3) k_B T}{8\pi z^3}, \quad z \gg \xi_T,
\] (14)

with the Riemann’s zeta function, \( \zeta(3) = 1.20205\ldots \). Eq. (14) is the large-distance asymptotic behavior for the force per area of two graphene sheets at finite temperature. The numerical solution does indeed merge with this analytical limit for \( z \gg \xi_T \), as seen in Fig. 2.

The result of Eq. (14) is truly remarkable: all material and electrical parameters have disappeared, leaving the temperature as the only surviving energy scale.
As remarked in the introduction, an identical formula describes the force between two metallic plates at finite temperature, for distances larger than the thermal length of the electromagnetic field, \( z \gg \lambda_T = \hbar c/k_B T \). This is the limit where the thermal population of the relevant electromagnetic modes becomes classical. But, in spite of the similarity, we cannot make an obvious connection with our result: our treatment has been obtained for the instantaneous, non-retarded Coulomb interaction, therefore there is no field dynamics, no field modes, and the issue of classicality for the field is out of place. Setting \( c = \infty \) in \( \lambda_T \) renders meaningless the would-be range for that classical limit. Yet, our regime of Eq. (14) for the instantaneous interaction appears for \( z \gtrsim \xi_T = \hbar v/k_B T \).

Nevertheless, the fact that \( v \) takes the role of \( c \) in setting the range for our non-retarded calculation prompts for the existence of a classical interpretation, but now for the only dynamical entity so far considered: matter. Plasmons, by the very fact that their existence and scale are tied to temperature, behave classically at long wavelengths:

\[
\frac{\hbar \omega_0(q)}{k_B T} \to 0, \quad q \xi_T \ll 1,
\]

and this suggests that there must be more transparent ways of getting such a simple result as Eq. (14). As reassurance that our reasoning is well founded, we will now recover Eq. (14) invoking only elementary classical concepts. Let’s consider graphene’s charge fluctuations as classical objects at temperature \( T \). The classical limit means that we can ignore kinetic energies and rely only on the potential (electrostatic) energy to account for the thermal population of these fluctuations. This electrostatic energy is:

\[
U_{el} = \sum_q v_e(q, z) \rho_q^+(1) \rho_q^-(2) + \frac{1}{2} v_e(q, 0) (\rho_q^+(1) a^+(2) + \rho_q^-(1) a^-(2))
\]

\[
= \sum_q \sum_{\sigma=\pm} \frac{1}{2} v_e(q, z) \rho_q^{(\sigma)} \rho_q^{(-\sigma)}
\]

where we have diagonalized the quadratic form with the normal modes: \( \rho_q^{(\pm)} = (1/\sqrt{2}) (\rho^{(1)}_q \pm \rho^{(2)}_q) \), with \( v_\pm(q, z) = v_e(q, 0) \pm v_e(q, z) \). The equipartition theorem allows us to write the thermal population of modes as < \( \rho^{(\pm)}_q \) > = \( k_B T/v_\pm(q, z) \). Expressing \( \rho^{(1,2)}_q \) in terms of \( \rho^{(\pm)}_q \), the thermal average of Eq. (11) can be obtained with the result of Eq. (14). This fully supports our interpretation that it is the classical population of thermal plasmons what leads to the vdW force.

Preparing for the discussion of retardation in the next section, it is worth noticing that the expression of Eq. (14) amounts to selecting the \( \omega_n = 0 \) term in the frequency sum of Eq. (2). Indeed, this is expected for a classical limit, but notice that the reason for such behavior is entirely due to the matter response \( \chi \) and, again, has nothing to do with the interacting field which, considered so far instantaneous, therefore shows no frequency dependence.

### IV. RETARDATION

Now we address the issue of the electromagnetic field dynamics, to show that the inclusion of retardation hardly affects the previous results. Following ref. [10], retardation effects are best handled in a gauge where only the vector potential \( A \) exists. The coupling matter-field is of the form \( \propto j \cdot A \), where the current lays in graphene’s planes, and can be decomposed into (in-plane) longitudinal and transverse components that are not mixed by the photon field. Let’s consider the longitudinal current responsible for charge fluctuations. It is straightforward to show that retardation can be included in the previous formalism with the following correspondences in Eqs. (2) and (3):

\[
\chi_{\rho\rho}(q, \omega) \rightarrow \chi_{\rhojl}(q, \omega)
\]

\[
v_e(q, z) \rightarrow D_l(q, \omega, z)
\]

\[
f_e(q, z) \rightarrow -\partial_\mu D_l(q, \omega, z)
\]

where \( D_l(q, \omega, z) \) is the (part of the) photon propagator that couples to in-plane longitudinal currents, with expression:

\[
D_l(q, \omega, z) = \frac{\epsilon^2 \eta \exp(-q'|z|)}{2 \epsilon_0 \omega^2},
\]

and \( q' = \sqrt{q^2 - \omega^2/c^2} \). \( \chi_{\rhojl} \) is the longitudinal current-current response, related by particle conservation to the charge-charge response by \( q^2 \chi_{\rhojl}(q, \omega) = \omega^2 \chi_{\rho\rho}(q, \omega) \). It can be checked that setting the light velocity \( c \to \infty \) in the above expressions, the non-retarded expression for the force is recovered. Again, as in the non-retarded case, this formalism for the force can be shown to be exactly equivalent to Lifshitz’s when applied to the longitudinal response.

Let’s consider the results for zero temperature first. Carrying out the prescription of Eq. (17) and trading \( q \) for \( q' \), the following expression is obtained for the vdW force due to longitudinal currents, including retardation:

\[
f = -\frac{1}{2 \pi} \int_0^{\infty} d\eta \int_0^{\infty} d\eta' \frac{\hbar}{\pi} \int_0^{\infty} d\eta'' \left( \exp(-2q'|\eta|) \cdot \frac{\exp(-2q'|\eta|)}{(1 + \frac{16}{N_\pi} \sqrt{1 + \eta^2/(v_{eff} q')^2})^2} - \exp(-2q'|\eta|) \right)
\]

where \( v_{eff} = v^2 - c^2 \). Comparing Eqs. (19) and (7) one sees that only two formal changes appear with respect to the zero-\( T \), non-retarded calculation. First, there is a renormalization of graphene’s velocity in the square root of Eq. (6), \( v \to v/\sqrt{1 - v^2/c^2} \), quantitatively irrelevant. Second, the integration over imaginary frequency acquires an upper limit, whose physical interpretation corresponds to the removal of the electromagnetic field modes that, for each space scale, are slower than matter. This is the dominant effect of retardation but, the integrand decaying as \( \sim \eta^{-2} \), it amounts to a meager
But for graphene, restricting to $n = 0$ adds nothing to the non-retarded result for Eq. (14). Indeed, such result is equivalent to selecting $n = 0$ in the matter response, although in that case this restriction was forced upon us by the classical behavior of matter’s plasmons while the field remained instantaneous. In other words, for the vdW interaction in graphene, there is no difference between classical matter + instantaneous field and classical field. We have computed the force with the numerically evaluated, finite-$T$ response of Eq. (19) and the retarded interaction, with results that would be hardly distinguishable from the non-retarded curve shown in FIG. 2.

A further contribution to the vdW force exists from the coupling of the field to transverse currents. In fact, for good dielectrics and metals and in the region where retardation is important, transverse and longitudinal current fluctuations contribute similarly to the vdW force, as discussed in section IV. But not for graphene: in appendix A this transverse contribution is calculated and shown to be, at best, of the order of $v/c$ times smaller than the longitudinal part, a result consistent with the absence of a retarded regime for the longitudinal part.

V. SUMMARY: Graphene vs Dielectric and Metal

Here we summarize graphene’s results for the vdW interaction and, to gain a better perspective, compare them with the standard prototypes of metals and dielectrics. The basic results for graphene, Eq. (8) and Eq. (14) are collected here:

$$f \propto -\hbar v z^{-4}, \quad z \ll \xi_T$$

$$f = -\frac{C_s}{8k_B T} \frac{\hbar}{c} z^{-3}, \quad z \gg \xi_T$$

We have seen that a single length, graphene’s thermal length: $\xi_T = \hbar v / k_B T$, controls the vdW force, which exhibits a crossover from the zero-$T$ results of Dobson et al. to a finite-$T$, universal regime. The latter has been understood as arising form the existence of classical plasmons: charge fluctuations of thermally generated carriers whose existence and energy scale are tied to temperature. These results, originally obtained for the longitudinal (charge) response with instantaneous Coulomb coupling, have been shown to survive virtually unaffected when retardation is included. In addition, the transverse contribution is shown in appendix A to never compete with the longitudinal one. Finally, we have emphasized that the temperature dependence of the vdW interaction in graphene reflects basically a property of matter, as opposed to the corresponding thermal regime of the archetypal metals and dielectrics that are described in the following subsections.

A. Graphene vs Dielectric

To make a meaningful comparison, we consider a two-dimensional insulator, with characteristic frequency (gap) and length scale of atomic dimensions: $\hbar \omega_0 \sim eV$ and $a_0 \sim A$. We assume low temperatures, so that the matter response is well approximated by the zero-$T$ response (room temperature is low temperature for an eV...
the mode magnetic modes with finite Matsubara frequencies leaves the short-ranged nature of the coupling due the electro- discussed) and Eq. (21) clearly exhibits that, for graphene, neither retardation nor transverse currents (see appendix A) do matter quantitatively, what explains the absence in graphene of a retarded regime like region II of a dielectric.

FIG. 4: Left panel: light-cone \((\omega = cq)\) versus dynamics of a dielectric of typical frequency \(\omega_0\), illustrating the three vdw regimes encountered with increasing distance at finite temperature (Eq. 21). Right panel: As in left panel but for a typical 2d metal, with dynamics characterized by plasmons (Eq. 22).

gap). In this situation, three regimes can be considered in the vDW force as a function of separation, corresponding to the \(q\) regions schematically shown in the left panel of Fig. 1:

\[
I : \quad f \propto -\hbar \omega_0 a_0^2 z^{-5}, \quad z \lesssim z_{\text{ret}}^{(\text{die})}
\]

\[
II : \quad f \propto -\hbar c a_0^2 z^{-6}, \quad z_{\text{ret}}^{(\text{die})} \lesssim z \lesssim \lambda_T
\]

\[
III : \quad f \propto -\hbar k_B T a_0^2 z^{-5}, \quad z \gtrsim \lambda_T
\]

where the characteristic distance for the onset of retarded effects is \(z_{\text{ret}}^{(\text{die})} = c/\omega_0\), with the field’s thermal length as before: \(\lambda_T = \hbar c/\hbar k_B T\). Notice that Fig. 1 and Eq. 21 are schematic: transitions between regimes are in the form of crossovers, and the very existence of a regime (particularly II), and its associated power law, assumes well separated values of \(z_{\text{ret}}^{(\text{die})}\) and \(\lambda_T\).

Regime I corresponds to the sum of \(R^{-6}\) contributions expected from a dielectric, where longitudinal (charge) fluctuations, instantaneously coupled, dominate the force. In region II, matter is quicker than field, and retardation matters, implying and additional power with distance. Here both longitudinal and transverse currents contribute similarly to the vDW force. Finally, a thermal regime (III) appears for distances beyond \(\lambda_T\), at which the short-ranged nature of the coupling due the electromagnetic modes with finite Matsubara frequencies leaves the mode \(\omega_n = 0\) as the sole contribution to the vDW force. Notice that the \(T\) dependence of the vDW force in this thermal regime is not due any \(T\)-dependence in the matter response, which remains that of zero-\(T\) for the low temperatures considered, as explained before.

The comparison of Eq. 20 (and accompanying discussion) and Eq. 21 clearly exhibits that, for graphene, it is a difference in the dominant matter response what changes the vDW force at finite \(T\) for distances above the \((T\)-dependent) thermal length, \(\xi_T\). For shorter distances, the zero-\(T\) response dominates while at larger distances, the coupling of classical charge fluctuations of thermally excited carriers dominates.
regime would require simultaneously $\omega_p^{(\text{graphene})}(q) \gg cq$ and $\hbar \omega_p^{(\text{graphene})} \gg k_B T$, something impossible for graphene’s temperature-tied plasmons (see Eq. [1]). The quantitative irrelevance of the transverse response for the vdW force in graphene, explained in the appendix [A] is also consistent with the absence of this Casimir regime (transverse currents are responsible of half the Casimir result in the 2d metal).

Finally, thermal effects do appear in regime III, where the result for metals is quantitatively identical to that of graphene, Eq. [14]. But there are profound differences in the reasons that lead to the same expression in both systems. In the 2d metal, the matter response remains that of zero-$T$, but temperature forces to select the $i\omega_n = 0$ term as the only electromagnetic mode that is not short-ranged. Therefore, although the result itself, Eq. (22) III), cannot exhibit the dynamics of the field, the explicit appearance of the light velocity $c$ in its range of applicability ($z \gtrsim \lambda_T = \hbar c/k_B T$) does reveal its origin. In contrast, graphene’s finite-$T$ behavior Eq. [13] (obtained for the instantaneous Coulomb coupling), has been shown to arise from the classical plasmonic response of matter, as explained before. Therefore the range of applicability of the thermal regime in graphene ($z \gtrsim \xi_T = \hbar c/k_B T$) does not contain the light velocity (infinite for non-retarded calculation), but a matter property: Dirac fermion’s velocity ($v$).

Let us close mentioning that there has recently been much interest in the issue of finite-$T$ vdW interactions in poor metals and its relation to non locality in the metal’s response.[24-27]. Graphene may well provide a natural ground for these concerns as a system exhibiting both a zero-$T$, dispersive-response, result and a classical linear-in-$T$ regime, but at much shorter distances than would otherwise be required for the classicality of the electromagnetic field: at room temperature, $\xi_T \sim 26$ nm for graphene versus $\lambda_T \sim 300 \xi_T$ for typical metals and dielectrics.

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APPENDIX A: TRANSVERSE CURRENTS CONTRIBUTION

Here we present the calculation of the force due to the (in-plane) transverse currents, to show that it never competes with the longitudinal part. As in section [IV] the force per area can be obtained with the following correspondence in Eqs. (2) and (3):

\[ \chi_{pp}(q, \omega) \to \chi_{ji,ji}(q, \omega) \]
\[ v_c(q, z) \to D_t(q, \omega, z) \]
\[ f_c(q, z) \to -\partial_z D_t(q, \omega, z) \]

where $D_t(q, \omega, z)$ is the (part of the) photon propagator that couples to in-plane transverse currents, with expression:

\[ D_t(q, \omega, z) = -\frac{e^2 \exp(-q|z|)}{2 \epsilon_0 q' c^2}, \]

and $q' = \sqrt{q^2 - \omega^2/c^2}$. $\chi_{ji,ji}$ is the transverse current-current response of an isolated graphene layer, with RPA expression given by:

\[ \chi_{ji,ji}(q, \omega) = \frac{\chi_{ji}(0)(q, \omega)}{1 - D_t(q, \omega, z = 0)\chi_{ji}(0)(q, \omega)}. \]

where the zero-$T$, non-interacting response is given by

\[ \chi_{ji}(0) = \frac{N v}{16 \hbar} \sqrt{q^2 - \omega^2/v^2}. \]

For graphene parameters, ($c \sim 300 \text{ v}$), it is straightforward to see that the RPA treatment is unnecessary for the response, therefore we take $\chi_{ji,ji} \sim \chi_{ji}(0)$. Trading $q$ for $q'$, with the Matsubara sum becoming an integral $\omega_n \to i\eta$, the resulting expression for the force $f_t$ is:

\[ f_t = -\frac{1}{2\pi} \int_0^\infty q^2 dq' \exp(-2q'|z|) \frac{\hbar}{\pi} \int_0^{q'} dq'' \left( \frac{iv}{v_{eff}^2} \right)^2 \left( 1 + \left( \frac{q_0^2}{v_{eff}^2} \right) \right) \]

\[ \times \left( \frac{N \alpha v^2}{16 c^2} \right)^2 \left( 1 + \left( \frac{q_0^2}{v_{eff}^2} \right) \right) \]

where, as in the main text, $v_{eff}^2 = v^2 - c^2$, and $\alpha = e^2/(2\epsilon_0 hv)$. Ignoring the meager renormalization implied by $v_{eff}$, and to lowest order in $v/c$, the following closed expression for the force is obtained:

\[ f_t = -\frac{(N \alpha)^2 v h v}{2 \pi^2 \Omega^2} \frac{1}{z^4} \]

Although the dependence with distance of Eq. (A6) is the same as that of the longitudinal contribution, Eq. (8) the salient feature is the ratio $v/c$ in the coefficient. Indeed, explicit comparison of Eq. (A6) and Eq. (8) leads to:

\[ f_t \sim 1.23 \frac{v}{c} f \sim 4.1 \times 10^{-3} f \]

Therefore, the neglect of the transverse contribution is fully justified. Even more, our result (Eq. (A7)) can be seen as a bound for the transverse force over an extended range of distances. The reason is that the transverse contribution here calculated uses the scaling form
for graphene’s response, Eq. \(A4\) but this response grows unbounded with (imaginary) frequency. Real graphene lives in a lattice and, therefore, we expect this response to saturate beyond a cut-off of the order of \(\hbar \omega_0 \sim eV\) (the standard diamagnetic local limit). This implies that our zero-\(T\) calculation \(A6\) should apply for distances \(z \gtrsim c/\omega_0\), while for shorter distances, the saturation of matter response must imply even lower (cut-off dependent) forces from the transverse response.

Finally, we consider the transverse contribution at finite \(T\). It suffices to notice that the zero-\(T\) result \(A5\) is dominated by the matter response at (imaginary) frequencies close to the light cone: \(\eta \sim c q\). At such high frequencies, temperature hardly affects the matter response, and the zero-\(T\) transverse contribution holds for distances up to \(z \gtrsim \lambda_T\) \((\lambda_T = h c / k_B T)\). Beyond such distances, as usual, only the \(\omega_n = 0\) term survives in the frequency sum (Eq. \(2\)) as the long-range interaction between graphene’s layers. Then, using the long-wavelength, finite-\(T\) result for the static transverse response:

\[
\chi_{ij}^{(0)}(q, i \omega_n = 0) = \frac{N}{24 \pi^3} \frac{(v_f q)^2}{k_B T} \frac{v}{c^2} \frac{1}{z^3}, \quad z \gtrsim \lambda_T
\]

we end up with the following expression for the large-distance, transverse contribution to the force per area between graphene’s layers at finite temperatures:

\[
f_t = -\frac{(N \alpha \xi T)^2 k_B T}{135 \pi^3} \frac{v^4}{c^4} \frac{1}{z^6}, \quad z \gtrsim \lambda_T
\]

This force replaces the zero-\(T\) expression \(A9\) for distances \(z \gtrsim \lambda_T\). Quantitatively, it is utterly small when compared with the corresponding finite-\(T\) longitudinal contribution (Eq. \(13\)). This completes our justification for the neglect of the transverse contribution in the body of the paper, both at zero and finite temperatures.

**APPENDIX B: REAL GRAPHENE VERSUS DIRAC FERMIONS**

The success of the Dirac fermion approach to explain the experimentally observed electronic properties of graphene leaves little doubt about its correctness for describing the low energy physics, including room temperature and above. The long distance behavior of the vdW interaction cannot be an exception: qualitative features such as the asymptotic power law of Eq. \(8\), are linked to the linear dispersion of Dirac fermions and its associated gapless excitations, as first shown by Dobson \textit{et al.}\(13\). On the contrary, \textit{sum of} \(R^{-6}\) treatments would lead to an incorrect \(1/z^5\) dielectric law for the force.

Nevertheless, the presence of further electrons (and states) besides those of Dirac cones makes our calculation quantitatively incomplete as far as \textit{real} graphene is concerned. These electron-hole excitations being gapped, their contribution to the vdW interactions is not expected to change the obtained asymptotic behavior. Nevertheless, estimating the size of this neglected contribution is important to assess the range of validity of our results.

Explicit calculation of these contributions is well beyond the scope of this work, but a fair estimation of its size can be obtained from published results\(13\). Such an estimation can be restricted to zero \(T\) because: i) the missing contribution corresponds to gapped excitations above \(\sim 2\) eV, hardly affected at any reasonable finite \(T\), ii) our results at finite \(T\), Fig. \(2\), are always greater than those at zero \(T\). Therefore, if the missing contributions do not compete with the asymptotic regime at zero \(T\), they will not at finite \(T\).

In ref. \textit{13}, an \textit{ab initio} calculation of the vdW interaction in graphene-like systems is performed. Not intended for large distances, the low energy physics in ref. \textit{13} is only approximated, leading to an effective long-distance interaction between carbon atoms of the traditional dielectric form: \(1/R^6\). Nevertheless, ref. \textit{13} includes electrons beyond the lowest \(sp\) band, and high energy excitations (up to tens on eV)\(12\), providing a quantitative estimate of the missing contributions. The attractive energy between two atoms in different graphene sheets separated by \(R\) is obtained there\(13\) as \(C_6/R^6\), with \(C_6 \approx 13.8\) eV \(\AA^6\), and around 50 percent of this contribution is reported as coming from excitations beyond the lowest \(sp\) band\(13\). From these numbers, one obtains an estimate of \(f = -D_6/z^5\), with \(D_6 \approx 6.3\) eV \(\AA^2\), for the force per area coming from the neglected terms. This contribution becomes comparable to that of Eq. \(8\) only at separations between graphene layers of the order of 1.5 nm, a rather short distance for a vdW scenario, just a few times graphite interlayer distance. Beyond this distance, the different power law makes the asymptotic contribution of Eq. \(8\) dominant (see also ref. \textit{28}). For instance, at a distance \(z \approx 27\) nm, corresponding to graphene’s thermal length a room \(T\), the asymptotic contribution here obtained (Fig. \textit{2}) is around 20 times the estimate from the ignored terms. At a separation of \(z \sim 100\) nm (graphene’s thermal length at liquid-nitrogen \(T\)), the force calculated in this work, would surpass the missing contributions \(\sim 80\) times. All this indicates that restricting to the low energy physics not only provides the large distance asymptotic behavior of the vdW interaction but also the \textit{quantitatively dominant} contribution for \textit{real graphene} for separation beyond a few nanometers.
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