Theory of liquid film growth and wetting instabilities on graphene

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We investigate wetting phenomena near graphene within the Dzyaloshinskii-Lifshitz-Pitaevskii theory for light gases of hydrogen, helium and nitrogen in three different geometries where graphene is either affixed to an insulating substrate, submerged or suspended. We find that the presence of graphene has a significant effect in all configurations. When placed on a substrate, the polarizability of graphene can increase the strength of the total van der Waals force by a factor of two near the surface, enhancing the propensity towards wetting. In a suspended geometry unique to two-dimensional materials where graphene is able to wet on only one side, liquid film growth becomes arrested at a critical thickness which may trigger surface instabilities and pattern formation analogous to spinodal dewetting. The existence of a mesoscopic critical film with a tunable thickness provides a platform for the study of a continuous wetting transition as well as engineering custom liquid coatings. These phenomena are robust to some mechanical deformations and are also universally present in doped graphene and other two-dimensional materials, such as monolayer dichalcogenides.

The wetting of an electrically neutral solid surface by a liquid is controlled by the relative size of attractive van der Waals interactions between molecules in the liquid and those between the liquid and substrate. For weak liquid-substrate interactions, the surface may undergo partial wetting manifest as the coexistence of distinct liquid droplets with an atomically thin layer of adsorbed molecules between them. In the opposite complete wetting regime, the liquid atoms are strongly attracted to the surface resulting in the formation of a macroscopically thick film in equilibrium with the vapor above it [1].

The growth and stability of this film beyond a few atomic layers is dominated by the long range tail of the van der Waals (vdW) interaction which can be thought of as creating an effective repulsion between the liquid-vapor and liquid-substrate boundaries [2,3]. For intermediate liquid-surface interactions it is possible that at a critical film thickness, $d_c$, (larger than any atomic length scale) this repulsion vanishes and wetting is arrested due to the lack of any energetic gain for molecules in the vapor to adsorb into the liquid – a scenario known as incomplete wetting [1,5,6].

While a phase transition between partial and complete wetting driven by temperature is generically first order (being controlled by short-distance details of the adsorption potential) a transition from incomplete to complete wetting can be continuous due to the presence of only long range vdW forces [8,9] (critical wetting). However, engineering substrates with weak interactions to observe incomplete wetting and any associated critical phenomena has been challenging, with experiments concentrating on quantum fluids at low temperatures [10,11] or liquid substrates such as alkynes on water at high temperature [12,13].

In this letter we report on the physics of wetting in the novel class of geometries depicted in Fig. 1 made possible by the ability to readily fabricate and manipulate atomically flat two-dimensional (2D) crystals such as graphene [15], transition-metal dichalcogenides [10] (e.g. MoS$_2$) and representatives of the 2D topological insulator family [17,20] (silicene and germanene). This includes graphene placed on a substrate, submerged in a liquid, or suspended with a vacuum underneath, realizable due to the impermeability of graphene to even small atoms [21,22].

We devise an extension of the Dzyaloshinskii-Lifshitz-Pitaevskii (DLP) theory [2,3] (the standard many-body approach used for accurate analysis of experiments [23,21]) to include the polarization of a 2D material in an anisotropic layered dielectric sandwich. The results indicate that light gases near suspended 2D materials are an ideal system to study and characterize critical wetting phenomena. Our main findings include: (I) the presence of graphene on a substrate can enhance liquid film growth consistent with studies of its “partial wetting transparency” to liquid water [25]. (II) This effect rapidly decreases with film thickness and occurs at nm scales as opposed to the μm distances where relativistic effects may become important [26]. (III) In the suspended geometry, the existence of vacuum beneath graphene causes incomplete wetting with a critical film thickness on the order of 3 to 50 nm that can be tuned through the dynamic polarizability of the adsorbant or the properties of the semimetal (e.g. strain). This phenomenon is universally present, and can be additionally controlled in doped graphene as well as in insulating dichalcogenides, thus spanning a wide range of 2D Dirac materials. (IV) The mesoscopic film may exhibit critical surface instabilities including pattern formation in analogy to spinodal decomposition [27,33]. Together these findings represent not only the introduction of a new platform for the study of wetting and associated critical phenomena, but hint at applications including the creation of tunable surface...
coating or drying mechanisms via electrostatic gating or mechanical manipulation.

The remainder of this paper is organized as follows: we review the DLP theory and show how it is modified by the insertion of a graphene sheet. We report quantitative results for wetting and film growth in the three configurations in Fig. 1. For the suspended geometry, we examine the spreading of droplets on the liquid surface and discuss the formation of long-wavelength surface instabilities. We conclude with a discussion of the experimental measurement of these effects. Accompanying supplemental materials (SM) provide information on the effects of temperature, different 2D materials and substrates, uniaxial strain and electronic doping.

The starting point is the calculation of the vdW energy \( U(d) \) of a charge neutral system composed of three substances (having dielectric functions \( \varepsilon_{1,2,3} \)) as shown in Fig. 1 with the atomically thin graphene layer, characterized by polarization \( \Pi \), inserted at the boundary between regions 2 and 3. \( U(d) \) represents the vdW interaction between the 1-2 and 2-3 material surface boundaries separated by distance \( d \). It is well-known that \( U(d) \) can be related to the momentum \( \mathbf{q} \) and frequency \( \omega \) dependent effective dielectric function \( \varepsilon_{\mathbf{q},\omega} \) which characterizes the screening of the interlayer Coulomb potential. \( U(d) = \frac{\hbar}{n}(2\pi)^{-3} \int d^2q \int_0^\infty d\omega \ln \varepsilon_{\mathbf{q},\omega} \), where \( n = N/V \) is the density of the liquid (material 2). It should be noted that for a single-material system (i.e. characterized by only one dielectric constant) this formula is simply the random phase approximation (RPA) correlation energy, while in the case of anisotropic layered structures it represents the fluctuation (vdW) energy. We set \( \hbar = 1 \) from now on.

The calculation of \( \varepsilon \) involves the electrostatics of a three layer system. For example, for the configurations of interest in Fig. 1 one obtains the following formula for the properly screened interlayer Coulomb potential \( U_{12} \) between 1 and 2: \( U_{12} = V_{12}/\varepsilon_g \), \( V_{12} = 8\pi e^2 \varepsilon_2/[qD(q)] \), where \( q = |\mathbf{q}| \) is the magnitude of the in-plane momentum,

\[
D(q) = (\varepsilon_1 + \varepsilon_2)(\varepsilon_2 + \varepsilon_3)e^{qd} + (\varepsilon_1 - \varepsilon_2)(\varepsilon_2 - \varepsilon_3)e^{-qd} \quad (1)
\]

and the effect of graphene is in the additional screening characterized by

\[
\varepsilon_g(\mathbf{q},\omega) = 1 - V_2(q)\Pi(\mathbf{q},i\omega). \quad (2)
\]

Here, \( V_2 \) is the Coulomb potential within the lower boundary plane

\[
V_2 = \frac{4\pi e^2}{qD(q)} \left[ (\varepsilon_1 + \varepsilon_2)e^{qd} + (\varepsilon_2 - \varepsilon_1)e^{-qd} \right]. \quad (3)
\]

The polarization of graphene \( \Pi(\mathbf{q},i\omega) \) is described in the SM. Then, keeping in mind that \( U_{12} \propto e^2 e^{-qd}/[q\varepsilon_{\mathbf{q},i\omega}] \), we obtain \( \varepsilon_{\mathbf{q},i\omega} = \varepsilon_g(\mathbf{q},i\omega)D(q)e^{-qd} \), and finally

\[
U(d) = \frac{1}{n(2\pi)^3} \int d^2q \int_0^\infty d\omega \ln [\varepsilon_g(\mathbf{q},i\omega)D(q)e^{-qd}]. \quad (4)
\]

It is instructive to simplify Eq. (4) in the limit \( (\varepsilon_2 - 1) \ll 1 \), which is satisfied with high accuracy for the low-density systems we have studied (such as He and other light elements). In this case, their vapor can be considered as vacuum \( (\varepsilon_1 = 1) \), and suppressing \( q \) and \( \omega \) dependence:

\[
U(d) \approx \frac{1}{n(2\pi)^3} \int d^2q \int_0^\infty d\omega (U_d + U_g), \quad (5)
\]

with dielectric:

\[
U_d = \frac{(\varepsilon_2 - 1)(\varepsilon_3 - \varepsilon_2)}{(\varepsilon_2 + 1)(\varepsilon_3 + \varepsilon_2)}e^{-2qd} \quad (6)
\]
The corresponding vdW force can be obtained from \( F(d) = -\partial U(d)/\partial d \) which has dimensions of energy due to the normalization factors chosen in Eq. (4).

When graphene is absent \( (U_g = 0) \), we recover the well known DLP theory expression \([3, 4, 39]\). In particular it describes the important property of vdW repulsion (a force per unit area known as the disjoining pressure) for \((\varepsilon_3 - \varepsilon_2) > 0\). We note that inserting graphene will always lead to repulsion as \( \Pi < 0 \). Eq. (7) can be used to describe the three main configurations: graphene on a substrate (characterized by \( \varepsilon_3 \)), submerged \((\varepsilon_3 = \varepsilon_2)\), and suspended graphene \((\varepsilon_3 = 1)\).

To calculate \( U_g \), we take the dielectric function of light elements to have a single oscillator form: \( \varepsilon_2(\omega) = 1 + C_A/[1 + (\omega/\omega_A)^2] \), where for \(^4\)He we use \( \omega_A = \omega_{\text{He}} \approx 27\text{ eV} \) and \( C_{\text{He}} = 0.054 \). Parameters for other materials are given in the SM \([34]\). The substrate dielectric function can typically be well fitted to the form \([40]\), \( \varepsilon_3(\omega) = 1 + C_{1R}/[1 + (\omega/\omega_{1R})^2] + C_{UV}/[1 + (\omega/\omega_{UV})^2] \). For example in the case of \( \text{SiO}_2 \) (quartz): \( \omega_{UV} \approx 13.37\text{ eV} \), \( \omega_{1R} \approx 0.138\text{ eV} \), and \( C_{1R} = 1.93 \), \( C_{UV} = 1.359 \). Other cases are studied in the SM \([34]\).

The final result can be conveniently written as:

\[
F(d) = \frac{\omega_A}{16\pi^2 \varepsilon_0^2} \frac{I(d)}{d^3} = \frac{\Gamma(d)}{d^3},
\]

where the dimensionless expression for \( I(d) \) is given in the SM \([34]\) and is used to calculate \( \Gamma(d) \). It is clear from Eqs. (5)–(7) that the dielectric part leads to a pure

1/d^3 dependence of the force \( (\Gamma(d) = \Gamma_0 \) as \( \varepsilon_1, 2, 3 \) do not depend on momentum). However, the graphene contribution has substantial momentum dependence (due to the polarization \( \Pi(q, \omega) \)), and causes a 1/d^3 law above some length-scale. The overall behavior has the scaling form (second term due to graphene):

\[
\Gamma(d) = \Gamma_0 + \frac{\Gamma_1}{d + L}.
\]

Fig. 2 shows how the insertion of graphene on a quartz substrate enhances the vdW repulsion between...
the substrate-liquid and liquid-gas interfaces for helium and nitrogen gas. Graphene introduces a substantial distance dependence to the force that is larger than that previously reported for graphite [26, 11]. While relativistic corrections can create crossovers in the distance dependence [26], they happen at larger micron-scales, while here we see a dominant, purely non-relativistic contribution. The long range tail of the vdW interaction, they can display textbook behavior [44] for an unstable system. The suspended film transition from stable ($d < d_c$) through a metastable region with $d = d_c$, where $\partial \Delta \mu / \partial d > 0$; and finally becomes unstable for $d > d_c$, $\partial \Delta \mu / \partial d < 0$. The values of the critical film thickness $d_c$ are found to be on the order of 3 to 30 nm and are reported in Table I.

We now concentrate on the properties and implications of the incomplete wetting scenario where a liquid film with thickness $d_c$ is absorbed on suspended graphene. As processes governing the further wetting (partial or complete) of the liquid surface are governed only by the long range tail of the vdW interaction, they can display a wealth of phenomena of both theoretical and experimental importance [11, 16, 17, 18, 19, 21, 22, 45–50]. We can formulate an important question regarding wetting of the liquid film via a calculation of the contact angle $\theta$ of droplets which can form its surface. As these droplets are “far” from the substrate, the short-range adsorption potential is irrelevant, opening up the possibility of universal and continuous critical behavior. The value of the contact angle is related to the area under the $\Delta \mu(d > d_c)$ curve [2]:

$$1 - \cos(\theta) = \frac{n}{\sigma_{l-v}} \int_{d_c}^{\infty} \Delta \mu(l) dl = -\frac{n}{\sigma_{l-v}} \int_{d_c}^{\infty} \frac{\Gamma(l)}{l^3} dl$$

(11)

where $\sigma_{l-v}$ is the liquid-vapor surface tension. Results are shown in Table I and we find small angles on the order of a degree that increase with the polarizability of the adsorbant vapor. The fact that $\theta > 0$ in all cases allows us to consider a remarkable analogy between surface film instabilities and the theory of spinodal decomposition [27, 33]. The characteristic pattern instability length scale is governed by the competition between destabilizing vdW forces and the stabilizing action of the surface tension. The wavelength $\lambda$ which corresponds to amplified surface fluctuations (which could ultimately cause “spinodal

| Atom | He | H$_2$ | N$_2$ |
|------|----|------|------|
| $d_c$ (Å) | 300 | 120  | 35   |
| $\theta$ (°) | 0.33 | 0.83 | 2.41 |

TABLE I. Critical film thickness and contact angles for three elements. The surface tensions were taken to be: $\sigma_{He} \approx 0.26$ mN/m, $T = 2.5$ K; $\sigma_{H_2} \approx 2$ mN/m, $T = 20$ K; $\sigma_{N_2} \approx 10$ mN/m, $T = 70$ K.

$\Delta \mu = \mu(d) - \mu(d = \infty)$, are determined by the usual equilibrium condition (where $P_0$ is the saturated vapor pressure) [23, 44]

$$\Delta \mu = -\frac{\Gamma(d)}{d^3} = T \ln \frac{P}{P_0} \leq P_0$$

(10)

Fig. 4 shows the resulting chemical potential for helium, hydrogen and nitrogen on suspended graphene which exhibits textbook behavior [44] for an unstable system. The suspended film transition from stable ($d < d_c$) through a metastable region with $d = d_c$, where $\partial \Delta \mu / \partial d > 0$; and finally becomes unstable for $d > d_c$, $\partial \Delta \mu / \partial d < 0$. The values of the critical film thickness $d_c$ are found to be on the order of 3 to 30 nm and are reported in Table I.

The vdW force in the submerged and suspended geometries that are unique to 2D materials can also be evaluated with the results shown in Fig. 3 for helium, hydrogen and nitrogen films. In all cases we compare with calculations from Cheng and Cole [26] for adsorption on graphite (dashed lines). For submerged graphene ($\varepsilon_3 = \varepsilon_2$, filled circles) $U_d = 0$ (see Eq. (6)) and $\Gamma(d)$ decays to zero, in stark contrast to the case of a graphene plated substrate. For suspended graphene ($\varepsilon_3 = 1$, squares), we observe a novel physical effect for all elements: there is a critical distance $d_c$ at which graphene’s (always positive) contribution becomes so weak it can no longer compensate the negative dielectric part and $\Gamma(d_c) = 0$. Such an effect is only possible for purely 2D materials that can be suspended without a supporting substrate - graphite [21, 12, 43] is the best (but not only) candidate in this family. For $d > d_c$, the liquid film growth stops under equilibrium conditions and the system becomes unstable. This is the incomplete wetting scenario discussed in the introduction. For $d < d_c$ the characteristic isotherms that determine the change of the chemical potential of the film (relative to bulk),
dewetting”) in the unstable region \((\partial \Delta \mu / \partial d < 0)\) is given by \((d \gg L)\)

\[
\lambda^2 \simeq -8\pi^2 \frac{\sigma_{l-v}}{n} \left( \frac{\Delta \mu}{\partial d} \right) \approx \frac{8\pi^2}{3} \frac{\sigma_{l-v} d^4}{n|\Gamma_0|} \tag{12}
\]

From Fig. 3 for example for H\(_2\) we can estimate \(|\Gamma_0| \sim 10^3 \text{KA}^3\), which yields \(\lambda \sim 10^{-4} - 10^5 \text{A}\) for \(d \approx 150 - 300 \text{Å}\).

In conclusion we have considered how the relatively weak van der Waals interactions between light atoms and graphene can substantially affect their wetting behavior when graphene is placed on a substrate, submerged in a liquid or suspended above vacuum. We find that placing graphene on a substrate enhances its propensity towards wetting during initial film growth which may have implications for its use as a conductive coating. For suspended graphene, the absence of any substrate material leads to an instability where film growth becomes arrested at a critical thickness. As the vapor pressure above this film is increased, droplets may form, driving surface fluctuations which can potentially have large amplitudes. It is significant that the critical film thickness \(d_c\) is dependent on mechanical deformations (e.g. uniaxial strain) in graphene, and is also universally present for other 2D materials, such as members of the group-VI dichalcogenides family (MoS\(_2\), WS\(_2\), MoSe\(_2\), etc.) [34]. Quite importantly, we also find that the instability occurs in doped graphene, within a wide range of experimentally accessible carrier densities [34]. Thus we conclude that this is a universal phenomenon in suspended 2D Dirac materials, ranging from insulating monolayer dichalcogenides to semi-metallic (undoped) and doped graphene. The exact value of \(d_c\) itself, which we find to be on the order of several hundred Angstroms, depends on material characteristics such as band gap, quasiparticle velocity, strain and doping level. Experimental confirmation of these effects would involve the measurement of adsorbed film thickness using standard quartz microbalance [10, 51] or interferometry [14] techniques. The ability to electronically or mechanically manipulate free-standing atomically flat substrates opens up the possibility of producing an exotic quantum wetting phase transition driven by a non-thermal control parameter.

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Supplementary material for “Theory of liquid film growth and wetting instabilities on graphene”

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In this supplement we provide additional information and details on the theory of Dzyaloshinskii-Lifshitz-Pitaevskii, the polarization function of graphene and the dielectric constants of the light gases and substrates studied in the main text. We provide complementary results for different substrates in general experimental use and present additional calculations on how the conclusions of the main text would be altered when placing the two-dimensional (2D) substrate under uniaxial strain or doping. Results for several transition-metal monolayer dichalcogenides (which exhibit energy gaps) are compared with graphene. We conclude with a technical discussion on the effects of temperature which can be safely neglected in the parameter regime of interest in the main text. In what follows, we adopt the units $\hbar = k_B = 1$.

Dzyaloshinskii-Lifshitz-Pitaevskii (DLP) theory

The DLP theory [S1, S2] is the standard many-body approach used to calculate the van der Waals forces in a substrate-liquid-vapor configuration and then relate the film thickness to pressure when analyzing experiments (Eq.(10)). Comparison with experiments on various materials [S3–S5] generally shows very good agreement, with deviations occurring in various circumstances typically attributable to presence of forces beyond long-range van der Waals (e.g. short-range forces), or the very complex nature of dielectric screening, etc. From a theoretical viewpoint DLP provides calculation of the van der Waals effective force between the two boundaries (“disjoining pressure”). It treats the dielectrics as effective homogeneous media with certain frequency-dependent dielectric functions, which themselves could be hard to calculate but are fairly well-known for standard materials after many years of comparison with experiment. The polarization loops within DLP theory are basically re-summed self-consistently in close analogy with the RPA (random phase approximation), which is the standard way to include self-consistent screening. It should also be noted that examination of different theoretical aspects of DLP theory [S1, S6, S7] shows that the approach used in the main text of the paper (based on the calculation of the effective dielectric function) is equivalent to other approaches, such as those based on determining electromagnetic fluctuations via photon Green’s functions in a medium and the van der Waals stress tensor.

Graphene Polarization and Gas Parameters

The dynamical polarization of graphene at zero chemical potential (charge neutrality point), on the imaginary frequency axis, has the form [S8]:

$$\Pi(q, i\omega) = -\frac{1}{4} \frac{|q|^2}{v^2|q|^2 + \omega^2},$$

(S1)

where $v = 6.6$ eV Å is the velocity of the Dirac quasiparticles.

The parameters of the three light gases (medium 2) discussed in the main text are as follows (see e.g. [S9, S10]). For Helium the dynamical dielectric constant is

$$\varepsilon_2(i\omega) = 1 + 4\pi n_{He} \alpha(i\omega), \quad \alpha(i\omega) = \frac{\alpha_{He}}{1 + (\omega/\omega_{He})^2},$$

(S2)

where the density $n_{He} = 2.12 \times 10^{-2}$ Å$^{-3}$, the static polarizability $\alpha_{He} = 1.38$ a.u., and the characteristic oscillator frequency $\omega_{He} = 27.2$ eV. The atomic unit of polarizability is defined as 1 a.u. = 0.148 Å$^3$.

For Nitrogen and Hydrogen, which have densities comparable to Helium but significantly larger polarizabilities, more accurate formulas based on the Clausius-Mossotti relation are typically used:

$$\varepsilon_2(i\omega) = 1 + \frac{4\pi n_A \alpha(i\omega)}{1 - \frac{4}{3} n_A \alpha(i\omega)}, \quad A = N_2, H_2,$$

(S3)

The dynamical polarizability is defined as in Eq. (S2). For $H_2$ the parameters are: $n_{H_2} = 2.04 \times 10^{-2}$ Å$^{-3}$, $\alpha_{H_2} = 5.44$ a.u., $\omega_{H_2} = 14.09$ eV. For $N_2$: $n_{N_2} = 1.73 \times 10^{-2}$ Å$^{-3}$, $\alpha_{N_2} = 11.74$ a.u., $\omega_{N_2} = 19.32$ eV.
A convenient expression for the dimensionless quantity $I(d)$ appearing in Eq. (8) is

$$I(d) = \int_0^\infty \int_0^\infty dy dx \frac{1}{x^2} e^{-\frac{\varepsilon_2(y)}{\varepsilon_2(y) + \varepsilon_3(y)}} \times$$

$$\left\{ \varepsilon_3(y) - \varepsilon_2(y) + \frac{4gx\varepsilon_2(y)}{[\varepsilon_2(y) + \varepsilon_3(y)] \sqrt{x^2 + y^2} [\Omega(d)]^2 + 2gx} \right\}, \quad (S4)$$

where $\Omega(d) = 2\omega_A d/v$ and $x = 2qd$. Since $\varepsilon_2(i\omega)$ is a function of the frequency ratio, $\varepsilon_2(i\omega/\omega_A)$, we define $y = \omega/\omega_A$ and use the notation $\varepsilon_2(i\omega/\omega_A) \rightarrow \varepsilon_2(y)$. In the substrate dielectric function $\varepsilon_3$, see below, this leads to the rescaling $\varepsilon_3(y) = 1 + \frac{C_{IR}}{1 + (\omega/\omega_{IR})^2} + \frac{C_{UV}}{1 + (\omega/\omega_{UV})^2}$. The dimensionless coupling $g = (\pi/2)(e^2/v) \approx (\pi/2)(2.2)$ characterizes the Coulomb interaction strength in graphene in vacuum.

### Substrate Effects

It is instructive to investigate the effect of different substrates (medium 3) on wetting. Many dielectric substrates are accurately described by the formula $[S11]$

$$\varepsilon_3(i\omega) = 1 + \frac{C_{IR}}{1 + (\omega/\omega_{IR})^2} + \frac{C_{UV}}{1 + (\omega/\omega_{UV})^2}. \quad (S5)$$

As an example, we have performed calculations for 6H-SiC, see Fig. S1, to be compared with our results in Fig. 2 of the main text (for a SiO$_2$ substrate). While the magnitude of the van der Waals force shows significant variations between substrates, the overall distance dependence, and crossover length scale remains comparable.

![FIG. S1. Van der Waals force contribution $\Gamma(d)$ for a 6H-SiC substrate with parameters $C_{IR} = 3.67$, $\omega_{IR} = 0.1$ eV, $C_{UV} = 5.53$, $\omega_{UV} = 7.39$ eV [S11]. This can be compared with that of a SiO$_2$ substrate plotted as Fig. 2 of the main text.](image)

Another important quantity which characterizes the van der Waals force is the length scale $L$ defined in Eq. (9) which sets the crossover from $1/d^3$ to $1/d^4$ behavior. Due to the Dirac fermion motion in graphene (i.e. the strong momentum dependence of graphene’s polarization) the force crosses over to a stronger power law at distances beyond $L$. In Fig. S2 we present a general analysis of the substrate dependence of $L$, for He. Due to helium’s large atomic frequency $\omega_{He} \approx 27$ eV, it is easy to see that only the ultraviolet (UV) part in Eq. (S5) provides an important contribution to the relevant integral, while the infrared (IR) part is irrelevant. Our results can be used to characterize a variety of substrates [S11], beyond the two main ones studied in this work. It is important to notice that $L$ remains fairly small (several Å) for practically all available substrates.

### Influence of Uniaxial Strain in Graphene

The existence of two-dimensional (2D) materials such as graphene opens up the attractive possibility to manipulate van der Waals forces by mechanical manipulation of the substrate – strain. This is due to the strong influence of
strain on the electronic motion and consequently substantial change in graphene’s polarization \([S12, S13]\). The case of uniaxial strain is the most straightforward to analyze, in which case graphene’s polarization is

\[
\Pi(q, i\omega) = -\frac{1}{4v_xv_y} \frac{v_x^2q_x^2 + v_y^2q_y^2}{\sqrt{v_x^2q_x^2 + v_y^2q_y^2 + \omega^2}}.
\] (S6)

Here we assume strain is in the \(y\) (armchair) direction leading to decrease of the electron velocity \(v_y\) in that direction (while the velocity in the perpendicular \((x)\) direction remains practically unchanged). It is convenient to introduce the ratio \(v_\perp = v_y/v_x < 1\) which reflects the strain (relative increase in lattice spacing); this ratio is perturbatively proportional to strain for small values but exhibits non-linear behavior for larger deformations \([S12, S13]\). For example \(v_\perp = 0.2\) corresponds to 34% strain, \(v_\perp = 0.4\) corresponds to 25% strain, and \(v_\perp = 0.75\) corresponds to 10% strain.

Figure S3 quantifies the effects of strain. Due to the increase of the graphene polarization Eq. (S6), the van der Waals interaction increases and thus strain promotes wetting. While at present such strong strain is difficult to achieve...
in graphene, mechanical deformations are also expected to be present in a variety of 2D materials \[S14\], and thus the general tendencies described here could be important in a variety of physical situations.

As a consequence of the enhanced van der Waals interaction with strain, the tendency towards film growth is enhanced. In particular, while in the suspended geometry (suspended graphene with no supporting substrate) films can grow only up to a finite thickness \(d_c\), the value of \(d_c\) increases with strain as illustrated in Fig. S3 (right). This effect is quite weak for small strain and becomes significant as strain grows. In addition we find substantial dependence on the type of atom (the effect is strongest for helium).

2D Materials: Insulating Dichalcogenides and Doped Graphene

FIG. S4. Variation of the van der Waals force \(\Gamma(d)\) in the case of He in the suspended geometry: MoS\(_2\) compared to doped and undoped graphene. The result shows significant decrease of the maximum film thickness \(d_c\) (from 300\(\AA\) to \(\approx 180\AA\)), caused by the suppression of the force due to the presence of the large electronic gap \(\Delta\) in MoS\(_2\). A representative (quite substantial) doping value is also shown to illustrate the tendency with doping. The shown value of \(\varepsilon_F\) corresponds to graphene carrier density \(n_e \approx 7 \times 10^{12}\) cm\(^{-2}\), well above the lowest-possible density that can be achieved in suspended graphene \((\approx 10^{9-10}\) cm\(^{-2}\)). More detailed variation with density appears on the next figure.

FIG. S5. Left: Variation of the van der Waals force \(\Gamma(d)\) in the case of He in the suspended geometry, for doped graphene. The densities corresponding to the shown Fermi energies are: \(n_e \approx 8 \times 10^9, 10^{11}, 7 \times 10^{12}, 2 \times 10^{13}\) cm\(^{-2}\). For smaller densities \((\varepsilon_F < 40\) meV\) the results are indistinguishable from the undoped situation. The Fermi energy is related to the density via \(\varepsilon_F = v \sqrt{n_e}\). The overall effect of doping is quite small and becomes noticeable for higher densities only. The general tendency is an increase of \(d_c\) due to the increased polarization of doped graphene (inset). Right: Comparison of various members of the dichalcogenides family, showing remarkably similar behavior. The material parameters, \(\Delta - \) gap, \(v - \) velocity, \(g = (\pi/2)e^2/v\) - Coulomb interaction, are: WS\(_2\): \(\Delta = 1.79\) eV, \(v = 4.38\) eV \(\AA\), \(g = 5.16\); WSe\(_2\): \(\Delta = 1.6\) eV, \(v = 3.94\) eV \(\AA\), \(g = 5.74\); MoS\(_2\): \(\Delta = 1.66\) eV, \(v = 3.51\) eV \(\AA\), \(g = 6.44\); MoSe\(_2\): \(\Delta = 1.47\) eV, \(v = 3.11\) eV \(\AA\), \(g = 7.26\).
Dichalcogenides. While graphene provides the most well studied example of a 2D material, it is important to assess the applicability of our results to other 2D compounds. Numerous 2D materials have been discovered, forming groups suitable for designing so-called van der Waals heterostructures [S15]. In particular the group-VI dichalcogenides [S16] include e.g. MoS$_2$, WS$_2$, MoSe$_2$, etc., which exhibit a significant electronic gap $\Delta$ of order 1 eV, as well as a small spin-orbital interaction. For the purpose of van der Waals calculations, the most significant modification (compared to graphene) to be taken into account is the presence of the gap, while the spin-orbital component can be neglected. The polarization function in this case is [S17]

$$\Pi(q, i\omega) = -\frac{|q|^2}{\pi} \left[ \frac{m}{q^2} + \frac{1}{2q} \left( 1 - \frac{4m^2}{q^2} \right) \tan^{-1} \left( \frac{\tilde{q}}{2m} \right) \right], \quad \tilde{q} \equiv \sqrt{\nu^2 |q|^2 + \omega^2}, \quad m = \Delta/2,$$

where $m$ is the Dirac mass (half of electronic gap). For example for MoS$_2$ $\Delta = 1.66$ eV, and other materials have similar parameters [S16]. Neglecting the small spin-orbit interaction can result in several percent error but our main conclusions will remain intact. We assume materials are in their insulating phases, i.e. the Fermi energy is in the gap.

We consider the wetting instability in the suspended geometry, as was done for graphene in the main text (Figure 3). The main effect of the gap is the suppression of the van der Waals force. Consequently this causes a significant enhancement of the instability (film growth arrested at smaller thickness $d = d_c$) as shown in Fig. S4 for MoS$_2$, to be compared with results for graphene in Figure 3 of the main text. Results for other dichalcogenides are similar and summarized in Fig. S5 (right). Therefore the critical wetting instability is present in the four main members of the dichalcogenides family, with very similar values of the critical film thickness $d_c$.

Doped Graphene. It is also important to investigate the effect of finite carrier concentration $n_e$ in graphene, when the Fermi energy $\varepsilon_F$ is shifted away from the Dirac (charge neutrality) point, and compare with results for undoped graphene ($\varepsilon_F = 0$). Experimentally, in suspended graphene samples [S18, S19], the carrier density can be very small $n_e < 10^{10}$ cm$^{-2}$, and thus a close proximity to the Dirac point can be achieved, with $\varepsilon_F \sim 10$ meV.

We use the well-known polarization for doped graphene [S20]

$$\Pi(q, i\omega) = -\frac{q^2}{4\sqrt{\omega^2 + v^2 q^2}} - \frac{2\varepsilon_F}{\pi v^2} + \frac{q^2}{2\pi \sqrt{\omega^2 + v^2 q^2}} \Re \left[ \arcsin \left( \frac{2\varepsilon_F + i\omega}{vq} \right) + \left( \frac{2\varepsilon_F + i\omega}{vq} \right) \sqrt{1 - \left( \frac{2\varepsilon_F + i\omega}{vq} \right)^2} \right]$$

and our results are summarized in Fig. S5 (left). It is clear that at small densities the results for doped and undoped graphene are practically identical. Significant modification of $d_c$ starts appearing only in the regime $\varepsilon_F > 100$ meV, which corresponds to substantial density $n_e \gtrsim 10^{12}$ cm$^{-2}$. It is natural that the instability tends to become suppressed with doping (i.e. $d_c$ tends to increase) since the polarization of graphene in the metallic regime increases. However we can confidently conclude that in the low-density regime, easily achievable in suspended graphene samples, our results discussed in the main body of the paper remain practically unchanged. In addition, the critical wetting instability also remains fully present in strongly-doped suspended graphene (Fig. S5 (left)).

Overall we conclude that the instability in the suspended geometry, with $d_c$ within several hundred Angstroms, is present in all three main 2D Dirac material groups: (insulating) dichalcogenides, semi-metallic (undoped) graphene, and doped graphene. Figure S4 summarizes the main tendencies exhibited by representatives of those groups, namely an increase of the critical film thickness as systems transition from insulating to metallic behavior.

Effect of Temperature

The instability in the suspended graphene geometry is essentially a zero temperature phenomenon, since we work in the temperature range where the light elements we consider form a liquid (e.g. $T \approx 2K$ for He, and somewhat higher $T \approx 20K$ for H$_2$). In fact we can readily see that the effect of temperature at the distances involved in any of our geometries (up to several hundred Angstroms) is negligible. Indeed, the basic expressions Eqs. (6–7) of the main text have the following form, which we now write in the finite temperature formalism, introducing the Matsubara frequencies $\omega_m$ (the prime means that the zero frequency term should be divided by two)

$$T \sum_m \left( f_1(i\omega_m) + f_2(i\omega_m) \frac{e^{2\Pi(q, i\omega_m)}}{q} \right), \quad \omega_m = 2\pi m T.$$

Here we have written explicitly only the frequency sums, not showing the momentum integrations (weighted by the exponential factors $e^{-2\Pi(d)}$). The function $f_1(i\omega_m) \sim |\varepsilon_2(i\omega_m) - 1|^2$ in the suspended geometry ($\varepsilon_3 = 1$), while
In the second term, involving graphene, we have $f_2(i\omega_m) \sim [\varepsilon_2(i\omega_m) - 1]$, proportional to the atomic polarizability. There exist other combinations of substrate dielectric screening factors within these two functions but we do not write them explicitly since it is easy to see that their existence is harmless and does not change the arguments that follow.

In the first term, since the dielectric function enters via the frequency ratio $\omega_m/\omega_A$ (Eq. (S2)), i.e. the combination $T/\omega_A \ll 1$, it is evident that the sum transforms into the zero temperature frequency integration. Recall that $\omega_A \sim 10^7$ eV.

In the second term, the characteristic momentum is of order $q = q^* \sim 1/d$ (which is the momentum where the integral over $q$ accumulates due to the presence of the exponential factor). Taking into account that $I$ has the form Eq. (S1) it is clear that as long as $T \ll v/d$, the sum is essentially at zero temperature. One should keep in mind that: (I) This condition is satisfied up to distances of several hundred Angstroms, e.g. $v/d \approx 150$K at $d = 500 \AA$, and the ratio increases at smaller distances, (II) the polarization itself has a finite $T$ contribution, i.e. is of the form $\Pi(q, i\omega_m) + \Pi_I(q, i\omega_m)$, where $\Pi_I(q, i\omega_m)$ can be found explicitly [S21]. Calculations that take into account the full temperature dependence of the polarization confirm the above estimates and show that indeed the corrections are small and certainly negligible up to several hundred $\AA$.

To summarize, our main conclusions, especially concerning the instability leading to finite film thickness $d_c \lesssim 400 \AA$ as shown in Figures 3-4 of the main text, remain valid at finite (but small) temperatures which is the regime of interest for liquid phases of light elements. At larger distances, finite temperature as well as relativistic corrections will gradually become more pronounced.

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