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Topical Review

Phonon dynamics of graphene on metals

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Abstract

The study of surface phonon dispersion curves is motivated by the quest for a detailed understanding of the forces between the atoms at the surface and in the bulk. In the case of graphene, additional motivation comes from the fact that thermal conductivity is dominated by contributions from acoustic phonons, while optical phonon properties are essential to understand Raman spectra. In this article, we review recent progress made in the experimental determination of phonon dispersion curves of graphene grown on several single-crystal metal surfaces. The two main experimental techniques usually employed are high-resolution electron energy loss spectroscopy (HREELS) and inelastic helium atom scattering (HAS). The different dispersion branches provide a detailed insight into the graphene–substrate interaction. Softening of optical modes and signatures of the substrate’s Rayleigh wave are observed for strong graphene–substrate interactions, while acoustic phonon modes resemble those of free-standing graphene for weakly interacting systems. The latter allows determining the bending rigidity and the graphene–substrate coupling strength. A comparison between theory and experiment is discussed for several illustrative examples. Perspectives for future experiments are discussed.

Keywords: phonons, graphene, surface dynamics

(Some figures may appear in colour only in the online journal)

1. Introduction

The isolation of single layer free-standing graphene (Gr) in 2004 opened the door to the experimental study of several unique physical properties, such as an extremely high carrier mobility, high thermal conductivity and a superior mechanical flexibility [1–7]. To a large extent, the renewed interest in Gr grown on metal surfaces comes from the current rise of research on free-standing Gr. It can be even said that the study of Gr/metal systems has become an important field of Gr research itself. Graphene-passivated metal surfaces are used in a variety of applications [8–11]. The strength of the Gr-metal interaction is one of the key parameters that can be determined from surface phonon dispersion curves. Further motivation comes from practical applications, since the so-called flexural phonon mode dominates the low-temperature dependence of resistivity in single layer and bilayer Gr [12–19], whereas acoustic phonons are responsible for the heat transport in Gr near room temperature [20, 21].

Phonon dispersion curves are extremely sensitive to interatomic forces of adsorbed layers, including the interaction between adlayer and substrate atoms. The system formed by Gr on metal surfaces provides a good example of how small changes in the strength of the Gr-substrate interaction modify...
the corresponding phonon dispersion curves. Thus, phonon spectra may provide valuable information on the bonding of Gr with the substrate as well as on the electron–phonon coupling [22]. The phonon spectrum allows to quantify subtle properties like the Gr–metal bond strength, the bending rigidity and Kohn anomalies, which are especially difficult to get for weakly interacting systems like the ones formed by Gr on Cu(1 1 1), Ir(1 1 1) and Pt(1 1 1). Moreover, phonon dispersion curves provide an excellent scenario to test the performance of current state-of-the-art calculations. We remind for instance that a recent study has shown that van der Waals DFT calculations are still unable to predict the right binding distance in systems with strong binding, like Gr on Ni, Co and Pd [23]. As far as we know, a full theoretical description of the phonon spectra for Gr bounded to a metal substrate is still lacking. Information on surface phonon modes might be relevant for the field of Gr plasmonics [24], since plasmon–phonon coupling [25–27] has been recently observed for Gr/ metal interfaces [28].

The two main experimental techniques usually employed to measure phonon dispersion spectra are high-resolution electron energy loss spectroscopy (HREELS) and inelastic helium atom scattering (HAS). HAS offers a better resolution in the acoustic phonons region (up to ∼50 meV), whereas HREELS measurements extend up to about 500 meV and are thus better suited to study optical phonons. Raman spectroscopy can be considered the standard technique used to characterize Gr layers. In particular, measuring of the so-called D and G peaks allows a clear identification of a single layer, from a bilayer or a few more layers of Gr [29–33]. However, the Raman signal is suppressed in systems with a strong Gr–metal interaction, like Gr/Ru(0001) and Gr/Ni(1 1 1). The strong hybridization of the carbon π bands with the orbitals from the substrate leads to a large energy difference between the π bands of Gr, and the resonance condition is lost [34]. In such cases, phonon dispersion curves are especially important to learn about the Gr-substrate dynamics.

First HREELS investigations of the phonon dispersion of supported Gr were performed by Oshima and coworkers [35–37] and by the Rieder group [38–40] in the 1990s. These studies were focused on Gr grown on transition metal carbides and Ni(1 1 1) single-crystal surfaces, and showed already that a great deal of information can be obtained from phonon dispersion curves. The Gr/Ni(1 1 1) system, for instance, is characterized by graphite-like phonon modes, softened due to a strong Gr–Ni interaction [37, 39]. This softening is removed after intercalation of Ag, Cu or Au underneath the Gr layer, rendering surface phonon dispersion curves which are very similar to those of graphite [38, 40, 41]. This provided the first evidence that quasi-free standing Gr can be prepared on Ni(1 1 1).

The focus of this review is on experimental determinations of phonon dispersion curves for Gr on metallic substrates, which are usually measured using HREELS and HAS. Comparison with calculations will be discussed for several systems. We start addressing strongly interacting systems and move on to weakly interacting ones. All results are presented using meV as energy unit.

Figure 1. Correlation of Gr–metal separation with the energy of the d-band center of the transition metal. A transition from ‘weak’ to ‘strong’ interaction occurs at a d-band center position ∼2 eV below the Fermi-level. Adapted with permission from [52]. © (2014) Royal Society of Chemistry.

2. Graphene on metals

2.1. Structural properties

There exist excellent review articles of Gr on transition metals. Two reviews have been published in 1997 by Oshima and Nagashima [42] and Rull et al [43]. More recent work has been reviewed by Winterlin and Bouquet [44], Batzill [45], Bonaccorso et al [46], Tetlow et al [47] and Dedkov and Voloshina [48]. The reader is referred to these articles to learn further details on the experimental methods used (e.g. CVD, C segregation, etc) to get epitaxial growth of Gr on different metallic substrates. In what follows, we provide a brief overview of the structural properties of these systems, which is going to be helpful to understand the phonon dispersion results discussed throughout this article.

Generally speaking, Gr–metal interfaces can be classified considering two main aspects: (i) lattice mismatch, and (ii) strength of the Gr–metal interaction. On Ni(1 1 1) and Co(0001) the lattice mismatch between Gr and substrate lattice constants is less than 2%, which allows Gr to form (1 × 1) structures by slightly stretching or quenching the C–C bonds. In contrast, Gr on, e.g. Ir(1 1 1), Pt(1 1 1), Rh(1 1 1) and Ru(0001) exhibits a lattice mismatch of ∼10%, which leads to the formation of Moiré superlattices. Usually, it is possible to find growth conditions such that Gr forms one domain, which is aligned with the main symmetry direction of the metal substrate. This is the case for Gr on Ru, Rh, Re and Ir. However, for most growth conditions on weakly interacting metals, such as Cu and Pt, different rotational domains are observed [44, 45]. The Moiré superstructure is often used as a template for the growth of two-dimensional molecular networks [49].

From the view point of the interaction, Gr–metal interfaces can be divided into strongly and weakly interacting systems [45, 50, 51]. One measure of the interaction strength is the Gr–metal separation. Figure 1 shows a plot of the Gr-substrate distance as a function of the binding energy of the d-band center relative to Fermi energy for different metals. It is clear that essentially two separations are observed: a value close to 2.1 Å for strongly interacting metals and a separation of 3.3 Å
for weakly interacting metals, which is close to the $c$-axis spacing in graphite. Figure 1 also shows that the transition from strongly to weakly interacting transition metals occurs at a d-band center binding energy of $\sim 2\text{eV}$ [45].

2.2. Phonon dispersion in graphite

We start with a brief description of the phonon dispersion of graphite, since the results presented below for Gr/metal systems will be compared with these dispersion curves. Graphene is a monolayer of sp$^2$ hybridized carbon atoms arranged in a honeycomb network with the nearest neighbour distance of 1.42 Å [5]. The honeycomb structure is a 2D-hexagonal lattice with a unit cell containing two carbon atoms and a lattice constant $a = 2.463\text{Å}$ (measured for graphite by x-ray diffraction [53]). With two atoms in the unit cell, Gr has six phonon branches: three are acoustic (A) and three are optic (O) phonon branches. The in-plane phonon modes are classified as longitudinal ($L$) or transverse ($T$) according to the direction of the nearest carbon–carbon atoms. Longitudinal (transverse) modes refer to vibrations parallel (perpendicular) to C–C directions, i.e. $\Gamma M$ ($\Gamma K$). The six phonon branches are named as follows: out-of-plane acoustic (ZA) and out-of-plane optical (ZO) phonons, whereby the Z indicates that the displacement vector is along the $Z$ axis; transverse acoustic (TA), transverse optical (TO), longitudinal acoustic (LA) and longitudinal optical (LO) phonons, which correspond to vibrations within the Gr plane [32, 33]. This notation is summarized in table 1.

Figure 2 shows the phonon dispersion curves in graphite measured by HREELS [54, 55], inelastic x-ray scattering [53] and inelastic neutron scattering [56], compared to DFT calculations for Gr from [57, 58]. In general, very good agreement is found with this and other calculations, although some discrepancies appear with the phonon frequencies predicted at the $\Gamma$, $K$ or $\bar{M}$ points of the Brillouin zone [58, 59]. For a comparison between phonon frequencies at the high-symmetry points obtained both from theory and experiment see [20]. These calculations also show the overall similarity of the graphite phonon spectrum with the six phonon branches of Gr. The only significant difference appears at low energies, near the $\Gamma$ point, where the weak interplane interactions in graphite lead to a splitting of the ZA mode. As it will become apparent throughout this review, the value of ZA at $\Gamma$ provides a way to quantify the strength of the Gr-substrate interaction. The LO and TO modes are degenerate at the $\Gamma$ point, and are Raman active. Moreover, the D-band and $G'$-band measured in Raman spectroscopy are related to phonon modes in the vicinity of the $K$ point [32, 33].

The Gr/metal interface might be a result of chemisorption as on Ni and Ru, where the electronic structure results from hybridization of the $\sigma$ and metal $d$ orbitals, or weak adsorption as in Cu, Ag and Pt, where the characteristic electronic structure of Gr remains almost intact. Due to the large difference between intralayer and interlayer forces of C atoms, the physical properties of adsorbed Gr layers are very anisotropic. This allows to interpret the changes of the phonon dispersion in Gr/metal systems in terms of changes in the in-plane or out-of-plane bonds.

2.3. Kohn anomalies

The coupling of phonons with the electronic excitation spectrum of a solid may lead to the appearance of phonon anomalies. This mechanism, called Kohn anomaly [60], is one of the key signatures of electron–phonon coupling and corresponds to the breakdown of the adiabatic separation of ionic and electronic degrees of freedom. In general, atomic vibrations are partially screened by electronic states. In a metal this screening can change rapidly for vibrations associated to certain $\mathbf{q}$ points of the Brillouin zone, which is determined by the shape of the Fermi surface. The consequent softening of some phonon modes is called Kohn anomaly [60], which at metal surfaces has been reported for a variety of systems [61]. Note that in particular, this means that it is not possible to derive the phonon branches at $\Gamma$ and $K$ by using a force constant approach. Kohn anomalies may occur only for wave vectors $\mathbf{q}$ such that there are two electronic states $\mathbf{k}_1$ and $\mathbf{k}_2 = \mathbf{k}_1 + \mathbf{q}$ on the Fermi surface [60]. The Fermi surface of pristine Gr consists of two equivalent points at $\mathbf{K}$ and $\mathbf{K}'$ which reflect the tips of the Dirac cones. Since $\mathbf{K}' = 2\mathbf{K}$, these are connected by the vector $\mathbf{K}$. Thus, Kohn anomalies are expected at $\Gamma$ and $K$ [22, 62]. In graphite, two Kohn anomalies are present in the phonon dispersion of the highest optical phonon at $\Gamma$ (LO mode) and at $\bar{K}$ (TO mode) [22, 57].

Table 1. Description of phonon modes in graphene.

<table>
<thead>
<tr>
<th>Label</th>
<th>Character</th>
<th>Polarization</th>
<th>Bending</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZA</td>
<td>Acoustic</td>
<td>Sagittal vertical (SV)</td>
<td>Out-of-plane</td>
</tr>
<tr>
<td>ZO</td>
<td>Optical</td>
<td>Shear horizontal (SH)</td>
<td>In-plane</td>
</tr>
<tr>
<td>TA</td>
<td>Acoustic</td>
<td>Longitudinal (L)</td>
<td>In-plane</td>
</tr>
<tr>
<td>TO</td>
<td>Optical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LA</td>
<td>Acoustic</td>
<td>Longitudinal (L)</td>
<td>In-plane</td>
</tr>
<tr>
<td>LO</td>
<td>Optical</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. Phonon dispersion of graphite from HREELS (red dots, [54, 55]), inelastic x-ray scattering (green dots, [53]) and inelastic neutron scattering (open circles, [56]). DFT calculations for Gr are shown by gray-dashed lines [57] and solid lines [58].
2.4. Heat transport and acoustic phonons

A detailed account of acoustic phonon transport in Gr can be found in a recent review article by Nika and Balandin [20]. The thermal conductivity of bulk graphite at room temperature is \(~2000\text{ W m}^{-1}\text{ K}^{-1}\). The corresponding value for free-standing Gr is known to be much higher, reaching 4000–5000 W m\(^{-1}\) K\(^{-1}\) at 300 K [6, 63–69]. However, a strong decrease of thermal conductivity is observed as soon as Gr is placed in contact with a substrate. For instance, for Gr deposited on a SiO\(_2\) substrate, heat conductivity is reduced to 600 W m\(^{-1}\) K\(^{-1}\) at 300 K [6]. This reduced value is due to phonons leaking across the Gr-support interface and strong interface-scattering of flexural modes [70]. However, the relative contributions of the different acoustic phonon modes to the thermal conductivity of Gr is still an open question. From the theory side, this problem has been addressed by several groups. It turned out that the results reported depend strongly on the specifics of the phonon dispersion used in the calculations, and therefore vary in a wide range. A detailed description of these approaches can be found in the articles by Nika and Balandin [20] and Sadeghi et al [21]. We present here a brief summary, in order to illustrate the current state-of-the-art.

Ong and Pop [71] used molecular dynamics (MD) simulations and continuum modeling to examine the thermal transport of Gr on SiO\(_2\). They concluded that coupling to the substrate reduces the thermal conductivity of supported Gr by an order of magnitude, due to damping of the flexural ZA phonons. A surprising result of this study is that increasing the strength of the Gr-substrate interaction enhances the effective thermal conductivity along supported Gr. This was attributed to coupling of the Gr ZA modes to the substrate Rayleigh waves, which linearizes the phonon dispersion, increasing the group velocity and therefore the thermal flux. These results are in line with the ones reported for free-standing Gr by Lindsay et al [72]. Using an exact numerical solution to the phonon Boltzmann transport equation, they have shown that flexural ZA phonons provide the dominant contribution to the lattice thermal conductivity of suspended Gr. A very different conclusion has been drawn by Qiu and Ruan [73, 74]. By performing MD simulations combined with phonon spectral analysis, these authors concluded that the reduction of thermal conductivity in supported Gr is actually due to stronger scattering of all phonon modes rather than only to the ZA mode in the presence of the substrate. These few examples make it clear that more work is needed in order to establish the relative contributions of the ZA, LA and TA modes to the thermal conductivity of supported Gr. From the experimental side, it could be very helpful to get more acoustic phonons measurements for Gr grown on different substrates, like the ones discussed in sections 4.4 and 4.5 for Gr/Cu(1 1 1) and Gr/Ir(1 1 1), respectively.

3. Experiment

3.1. Experimental techniques for phonon measurements

The two main experimental techniques usually employed to measure surface phonon dispersion curves are high-resolution electron energy loss spectroscopy (HREELS) and inelastic helium atom scattering (HAS). HAS offers a better resolution in the acoustic phonons region (up to \(~50\text{ meV}\), whereas HREELS measurements extend up to about 500 meV and are thus more convenient to study optical phonons. In addition, Raman scattering is used to measure the frequency of optical phonons at \(\Gamma\) and \(K\) points [32, 33]. In both HAS and HREELS experiments a monochromatic beam of particles with energy \(E_i\) impinges on a solid surface and scatters off with an energy \(E_f = E_i + E_q\), where \(E_q\) is the energy of the elementary excitation at the surface. The latter includes phonons, adsorbate’s modes, electronic transitions or surface plasmons. For a detailed overview of the HAS technique see [75, 76]; review articles on HREELS can be found in [77–80].

In the usual HAS experiment, the angle between incident and final beams \(\theta_{SD} = \theta_i + \theta_f\) is fixed (usually, \(\theta_{SD} = 90^\circ\)) and the sample is rotated [81, 82]. The He beam is produced in a nozzle source, then chopped into short pulses and scattered from the target surface. The total flight time of the atoms from chopper to detector is measured and from a set of such time-of-flight spectra for different angles \(\theta_i\) and \(\theta_f\) a dispersion curve is obtained. This allows exciting phonons even beyond the first surface Brillouin zone by choosing the proper incident conditions. Typical incident energies used for phonon measurements in HAS lie in the range between 10–100 meV. In HREELS experiments, phonons are measured by rotating the detector (i.e. varying \(\theta_f\)) while keeping the sample at a fixed \(\theta_i\) for a given incident energy \(E_i\). Electrons can lose energy at the surface via dipole scattering, which is used for studying the vibrational modes of adsorbed molecules, and through impact scattering, which is the relevant mechanism for phonon dispersion measurements. In this regime, electrons with high incident energies penetrate the surface to undergo short-range interactions with the ions of the first few layers on the substrate, and scatter off after exchanging energy and momentum with the surface lattice vibrations. HREELS measurements of surface phonon dispersion curves are usually performed at incident energies between 5–100 eV [78, 80, 83].

Both HAS and HREELS offer a similar high-resolution of 0.5 meV. However, the region below \(\sim 10\text{ meV}\) is usually difficult to access by HREELS. In contrast, the upper limit of the phonon energy detectable by HAS is given by ca. 80% of the incident energy, which in practice means that the limit is at \(~60\text{ meV}\). Thus, HAS is better suited for exploring the acoustic phonons region. The recent development of spin-echo \(^3\)He atom spectroscopy allows measurements from 10 meV down to the center of the Brillouin zone with a stunning resolution of 20 meV [84, 85]. The HAS and HREELS kinematics are very similar, except that He atoms carry enough momentum to allow also for Umklapp scattering processes involving the exchange of surface reciprocal lattice vectors \(G\); this can happen also in HREELS but typically at incident energies above 20 eV. In addition, since for electrons in HREELS \(E_q \ll E_i\), the corresponding scan curves are much simpler than those of He atoms in HAS. HAS scan curves allow measuring peaks at different \(\Delta K\) even for the same incident conditions [75, 76], whereas in HREELS experiments,
parallel momentum transfer is essentially fixed by the choice of incident and final angles.

One important difference between HAS and HREELS is that, while electrons in the impact regime are scattered from the high electron density at ion cores, thermal energy He atoms interact with the surface at a very low electron density ($\sim 10^{-4}$ a.u.), 3–4 Å above the surface atoms [86, 87]. Thus, He atoms can excite surface phonons only through the modulation of the surface electron density produced by atom displacements, i.e. through the electron–phonon interaction [88]. The range of the e–p interaction determines how deep a sub-surface atomic displacement can be detected by HAS. This is the case for small momentum transfer, where the out-of-plane mode of sub-surface layers can be easily measured by HAS (*quantum sonar effect*).

3.1.1 Selection rules. In surface scattering experiments, in-plane (out-of-plane) scattering is defined when the scattered beam momentum $k_i$ is inside (outside) the sagittal plane defined by the incident beam momentum $k_i$ and the normal to the surface. Selection rules apply only for in-plane scattering when the sagittal plane along a high symmetry direction coincides with a mirror plane of the surface. In this case, the excitation of an odd parity phonon is forbidden. This is because the wavefunctions of the initial and final states of the projectile are even with respect to the mirror plane reflection. However, the odd modes become visible along the same direction if the mirror plane of the sample is tilted with respect to the scattering plane [89, 90]. Misalignment from the high symmetry directions as well as the existence of domains with random orientations will render selection rules inactive. The violation of selection rules also occurs due to lowered crystalline quality which breaks the translational symmetry and thus can be interpreted as a signal of the disorder in the sample [91]. Finally, the interaction with a substrate also can break or reduce the symmetry of a Gr layer and thus reduce or even remove all selection rules [89]. A good example of the later is the Gr/Ni(1 1 1) system described in section 4.2.

4. Results

4.1. Graphene on transition metal carbides

Transition metal carbides are widely used for cutting tools, magnetic storage and many other applications [92]. Especially interesting are the metallic compounds TiC, ZrC, HfC and TaC, which are extremely hard, have very high melting points and even high conductivities. Early work by Aizawa et al has shown that high-quality Gr can be grown on carbides with rock salt structure, like the (1 1 1) and (0 0 1) surfaces of TaC, TiC and HfC(1 1 1) [35, 36]. The corresponding phonon structures have been measured by HREELS. Figure 3 shows the results reported for Gr/TaC(0 0 1) and Gr/TaC(1 1 1). On TaC(1 1 1), TiC(1 1 1) and HfC(1 1 1), the LA mode was found to be similar to that measured on graphite, whereas the LO and ZO modes were softened by 15 meV and ca. 30–40 meV, respectively. An additional low-energy branch was observed, which was attributed to the Rayleigh mode of the substrate.

![Figure 3. Phonon dispersion relations of Gr/TaC(0 0 1) and Gr/TaC(1 1 1) along ΓM measured by Aizawa et al [35] (red dots). Open circles indicate data points reported for graphite [54, 56]. DFT calculations for Gr [58] are shown by solid lines. The TA mode is forbidden due to symmetry selection rules [89]. The TO mode is forbidden along ΓM.](image)

The ZA mode was found to start from 34 meV at the Γ point for both TaC(1 1 1) and HfC(1 1 1). The phonon spectra were analyzed with a force-constant model, which revealed that the force constants related to vertical motion in the monolayer graphite are very much softened. This softening was interpreted as due to a selective softening of the $\pi$ bond, as result of charge transfer from the substrate into the Gr overlayer. For TaC(0 0 1), the observed dispersion of the ZA and ZO modes and the Gr lattice constant come very close to the graphite ones, which points to the formation of quasi-freestanding Gr [35, 36]. Similar trends have been observed on the (1 1 1) and (0 0 1) surfaces of NbC [93] and ZrC [94].

4.2. Graphene on Ni(1 1 1)

4.2.1. Phonon dispersion curves. The Gr/Ni(1 1 1) system is a benchmark example of a strongly interacting system. It allows to understand how changes in the strength of the Gr-substrate interaction modify the corresponding phonon dispersion curves. In addition, and owing to a misfit of less than 2%, Gr forms a ($1 \times 1$) structure on Ni(1 1 1) [95]. The adsorption structure of Gr on Ni(1 1 1) has been firstly proposed by Gamo et al based on LEED I–V curves [95]. According to this model, one C atom sits on top of a Ni atom, and the second C atom occupies a hollow site. This model has been confirmed by more recent ion scattering measurements [96] and DFT calculations [97, 98]. Thus, Gr/Ni(1 1 1) provides an excellent scenario to test state-of-the-art calculations of surface phonon dispersion curves. Gr–Ni interfaces have been recently reviewed by Dahal and Batzill [52]. Although Gr passivates...
the Ni(1 1 1) surface, a recent HREELS and STM study has shown that non-dissociative chemisorption of CO occurs on Gr/Ni(1 1 1) below \(\sim 225 \, \text{K} \) [99].

A recent HAS study has revealed that a sharper He specular peak is observed for the graphene-covered substrate [100]. This can be explained by looking into the different shapes of the background measured from the bare and Gr covered Ni(1 1 1). The form of the background is determined by inelastic single- and multi-phonon scattering as well as by diffuse elastic scattering by surface defects [101–103]. Thus, these results suggest that the Gr layer on Ni(1 1 1) reduces elastic scattering from step edges.

The phonon dispersion of Gr/Ni(1 1 1) has been measured by HREELS in the groups of Oshima (\(\Gamma M\) direction) [37] and Rieder (\(\Gamma K\) direction) [39]. These results are summarized in figure 4. Recent low-energy data measured by HAS are also included [100]. The most relevant features are the softening of the LO, TO and ZO modes. In addition, there is a pronounced splitting of the ZA and ZO modes of 13 meV at \(K\). These values are reproduced by calculations, although overestimated by ca. 40% [34]. A more careful analysis reveals the suppression of the Kohn anomaly present in graphite [22, 57] at \(K\) (TO mode) and perhaps also at \(\Gamma\) (LO mode), although some evidence for the anomaly at \(\Gamma\) is still visible in the HREELS data measured along \(\Gamma K\) [39]. In both ZA and ZO modes, carbon atoms vibrate vertically. These two modes deviate considerably from the ones of graphite. In the LA and LO modes, carbon atoms vibrate parallel to the surface, and the influence of the interaction with the substrate is smaller than for the ZO and ZA modes. Therefore, the overlayer can be identified as a graphite-like layer from these longitudinal modes, especially from the LA, which has a characteristic large dispersion. The softening of the ZO bond is a consequence of the chemical interaction, i.e. hybridization of the metal d-band with Gr \(\pi\)-bands, a suggestion made by Oshima et al [37, 42, 104] and confirmed by recent DFT calculations [34, 105]. The work by Allard and Wirtz [34] showed that the observed softening of the LO and TO modes is essentially due to a stretching of the C–C bond by 1.5%. The lifting of the ZO and ZA degeneracy at \(K\) is a consequence of the symmetry reduction of adsorbed Gr, which results from the occupation of alternating on top and hollow sites when forming a \((1 \times 1)\) structure on Ni(1 1 1) [34]. An important result from these calculations is the suppression of both Kohn anomalies (TO mode at \(K\) and LO mode at \(\Gamma\)) in Gr/Ni(1 1 1) as a consequence of the change of the electronic structure as compared to freestanding Gr. The hybridization of nickel d-electrons with Gr causes a downshift of the \(\pi\)-bands and opening of a gap. This annihilates electron–phonon coupling almost completely [34]. The calculations even show the ‘washing out’ of the Kohn anomaly by decreasing the Gr–Ni distance. Since there is some discrepancy for the LO mode between these calculations and the HREELS data measured along \(\Gamma K\), it would be interesting to perform additional studies on this system.

The most pronounced feature in the low-energy data measured with HAS is the presence of essentially the same Rayleigh wave (RW) on both clean Ni(1 1 1) and Gr/Ni(1 1 1) surfaces [100, 106]. Since the He-phonon interaction is directly related to the electron–phonon coupling strength [107], considering the strong C–Ni bonding, it is not surprising to detect the RW mode of the metallic substrate as has been the case also for Gr/Ru(0001) [108]. This finding provides an explanation for the high He-specular reflectivity (ca. 20%) of Gr/Ni(1 1 1), suggesting its use as inert focusing mirror in scanning He atom microscopy [109, 110]. The major difference between Gr/Ni(1 1 1) and graphene concerns the ZA branch, which does not go to zero for \(Q_\parallel \rightarrow 0\) due to the symmetry breaking induced by the Gr–Ni interplanar force constants. Extrapolation of the data along the two symmetry directions, considering also previously reported HREELS data [37, 39], gives an energy of \(\sim 20\) meV for the ZA mode at \(\Gamma\). This is close to the 16 meV reported for Gr/Ru(0001) [108], but is much lower than the 30 meV obtained in a DFT study [34]. As mentioned above, these calculations provide a good description of the optical phonon branches, including the softening of the ZO mode. From the overestimation of the ZAZO gap at \(\Gamma\) and \(K\), Allard and Wirtz [34] concluded that their DFT calculations might be overestimating the adsorption strength of Gr on the Ni substrate. The lower energy observed with HAS for the ZA mode at the \(\Gamma\) point confirms this view [100].

### 4.2.2. Ag, Cu and Au intercalation.

The Gr layer can be decoupled from the Ni(1 1 1) substrate by intercalating weakly interacting metals like Ag, Cu and Au. The first clear evidence of the formation of quasi-freestanding Gr was reported...
by Shikin et al after intercalation of Cu and Ag [38, 40]. By measuring the phonon spectra using HREELS, these authors showed that the softening of the LO, TO and ZO modes observed for Gr/Ni(1 1 1) is removed after intercalation of Ag or Cu underneath the Gr layer, rendering graphite-like surface phonon modes [38, 40]. This can be fully appreciated in figure 5, which shows the phonon spectra of Gr/Cu/Ni(1 1 1) and Gr/Ag/Ni(1 1 1) measured along the $\Gamma K$ direction. Similar results have been obtained along $\Gamma M$ [111]. Especially for Gr/Ag/Ni(1 1 1), the modes observed are almost identical to the ones expected for free-standing Gr (solid lines in figure 5). Note that even the ZO/ZA gap at the $K$ point, clearly visible in Gr/Ni(1 1 1), has disappeared. The Kohn anomaly of the LO mode at $\Gamma$ is clearly observed in both systems.

Calculations of the surface phonon dispersion based on the force constant model proposed by Aizawa et al [35] revealed that the force constants for the Gr/Cu and Gr/Ag interfaces are comparable to those reported for pristine graphite [112]. A similar behaviour has been observed after Au intercalation [41]. We mention for completeness that the stiffening of some phonon modes up to values of pristine graphite has been also observed after (partial) intercalation of C$_{60}$ [113]. Some stiffening of the ZA mode and softening of the LO mode were observed after intercalation of Yb in Gr/Ni(1 1 1) [39].

4.3. Graphene on Ru(0001)

4.3.1. Phonon dispersion curves. A HAS study of the low-energy phonon dynamics of Gr grown on Ru(0001) has been reported by Maccariello et al [108]. This system is especially interesting, since it is an excellent candidate to be used as a focusing mirror in scanning He atom microscopy [109, 110, 114, 115]. A very high surface reflectivity to He atoms (23%) has been reported [8, 116], which is surprising for a layer made of C atoms [117–121]. The phonon dispersion curves provide an explanation for this behaviour. Figure 6 shows the data points corresponding to the surface phonon dispersion curves along the $\Gamma M$ direction for Gr/Ru(0001) (red circles) and for the clean Ru(0001) surface (black circles). For comparison, the Gr modes reported in a DFT study [58] are also shown (black solid lines). The data for the clean Ru(0001) surface include the Rayleigh wave (RW) and the longitudinal resonance (LR) mode, which is characteristic to all metal surfaces.

The two steeper acoustic phonon branches observed with HAS, attributed to polarizations parallel to the surface and referred to as the longitudinal acoustic (LA) and shear-horizontal (SH or S7) surface modes, reproduce very well those originally measured with HAS for graphite (0001) surface along the same direction (not shown) [122]. This means that the interaction of Gr with the Ru substrate, despite the periodic corrugation of the Gr sheet, leaves practically unchanged the in-plane interactions. It should be noted that the S7 branch is too soft with respect to the SH branch known for the (0001) surface of graphite [122], so that the attribution to the SH branch remains questionable. More work is needed to clarify the possible electronic origin of this mode. The major difference between supported Gr and graphite concerns the graphite acoustic branch S1, which corresponds to the acoustic ZA branch in free-standing Gr, but does not go...
to zero for $Q_{||} \rightarrow 0$ due to the Gr–Ru interplanar force constants. However, for $Q_{||} \rightarrow M$, the data points approach the corresponding ZA branch of free-standing Gr, as expected for the growing, finally overwhelming importance of Gr in-plane force constants. The nature of the dispersionless mode M is clarified in next section.

The lowest observed acoustic branch vanishing for $Q_{||} \rightarrow 0$, corresponding to the RW mode is almost identical to the one measured on the clean Ru(0001) substrate. This is a quite surprising result, since Gr is completely covering the surface. DFT calculations [108] show that this is due to the strong C–Ru bonding and to the ability of HAS to detect subsurface phonons at short wavelengths, due to the induced surface-charge density oscillations. A calculation of the surface charge density oscillation (SCDO) induced by the Ru RW displacement at $Q = M$, keeping the Gr overlayer rigid, shows a modulation of the surface charge density profile for $1 \times 10^{-3}$ a.u. which is quite distant from the turning point profile sampled by He atoms. Therefore, the observed inelastic scattering intensity from Ru RW up to the zone boundary has been attributed to the quantum-sonar effect. This conclusion does not mean, however, that at large wavevectors the Gr layer does not mean, however, that at large wavevectors the Gr layer remains at rest, as assumed in the SCDO calculation: the Gr layer oscillates with the underlying Ru surface, as expected from the strong bonding to the substrate [123]. The Gr overlayer induces a mass-loading effect, which leads to a softening of the Ru(0001) RW branch at short wavelengths. At the zone boundary the addition of 24 carbon masses to 11 Ru masses yields a clean-to-covered ratio of the RW energies of $(1399/1111)^{1/2} = 1.12$, in agreement with the experimental data extrapolated to the M point.

These results provide an explanation for the surprisingly high reflectivity for neutral He and H$_2$ beams reported for the Gr/Ru(0001) surface [116]. Being the mass of the incoming He atoms and the C atoms on the Gr layer of similar order of magnitude, momentum transfer in the scattering process is expected to be very efficient, which should lead to the observation of a very low reflectivity, i.e. to a large Debye–Waller exponent. This is in contrast with the experimental observation of a reflectivity $\sim 23\%$ of the incoming intensity for He beams [116]. The removal of the (quasi-)parabolic dispersion of the ZA mode in Gr and its replacement with the linearly dispersed RW almost identical to that present on clean Ru(0001) finally solves the riddle, and shows that it arises as the result of a strong C–Ru interaction. It also suggests that systems with a similar strong C–substrate interaction could also behave as excellent mirrors for He atoms, as recently reported for Gr/Ni(1 1 1) [100].

4.3.2. Cu intercalation. The nature of the low-energy dispersionless mode observed in Gr/Ru(0001) (M mode in figure 6) has been clarified by intercalation of Cu below the Gr monolayer, which decouples it from the Ru substrate and changes substantially the out-of-plane, flexural phonon dispersion of epitaxial Gr [124]. HAS and STM data reveal that an ordered Gr layer covers the Cu–integrated surface, and that the Moiré superstructure is identical to the one of Gr/Ru(0001). Two representative Cu–integrated coverages have been investigated: Gr/Cu(0.4ML)/Ru and Gr/Cu(0.7ML)/Ru. A summary of these results is shown in figure 7. The dispersive branches characteristic of Gr/Ru(0001) (including the Rayleigh wave) are no longer detectable on the Gr/Cu(0.7ML)/Ru(0001) surface (blue dots in figure 7). The absence of a Rayleigh wave on a well-ordered surface is a quite unusual result that points to a drastic weakening of the bonding interaction with the substrate produced by the intercalation of Cu. Similar weakening of the coupling of Gr to the substrate has been reported for Cu and Ag intercalation on Gr/Ni(1 1 1) [38, 40] (see section 4.2.2).

The nanostructured nature of Gr/Ru(0001) and Cu–intercalated Gr/Ru(0001) resides behind the low-energy dispersionless mode detected in the TOF spectra [124]. The self-organized array of hills and valleys, with a lateral periodicity of 0.30 nm might be thought as a sort of flat ‘bubble wrap’ foil made of a periodic arrangement of nanodomes anchored to the substrate and independent of each other. These vibrating nanodomes lead to the appearance of the low-energy dispersionless mode. It is well-known that the strength of the C–Ru interaction varies strongly within the Moiré unit cell of Gr/Ru(0001) [125, 126]. In the valley site there is a strong bond between C and Ru atoms with a C–Ru distance of 0.214 nm, whereas in the hill site the interaction is

![Figure 7. Energy dispersion of the low-energy inelastic HAS data from Gr/Ru(0001) (red), Gr/Cu(0.4ML)/Ru (green) and Gr/Cu(0.7ML)/Ru (blue). The dark regions mark the energy ranges obtained from the model calculations for each system. Adapted with permission from [124]. © (2015) American Chemical Society.](image-url)
much weaker and the C–Ru distance is 0.30 nm [126]. Thus, it can be assumed that the nanodome is rigidly anchored to the substrate on the valley sites. The natural frequency of a dome has been estimated with a simplified structure by using the shallow shell theory; for a detailed description of the model used see [124]. The values obtained are shown as dark regions in figure 7. In spite of the simplicity of the model, it provides a satisfactory description of the data. This is a very interesting result, since it shows that inelastic HAS is suitable to determine localized low-energy vibrations of structures in the nanometer range, even if they are distributed over areas of the order of several square micrometers. The natural frequencies of the nanodomés are determined by the material and size of the nano-structures. The latter depends, in turn, on the interactions between the Gr layer and the substrate, i.e. of the intercalated element. In addition, the resolution of the technique allows determining changes in the vibrational frequencies of ~1 meV.

4.4. Graphene on Cu(1 1 1)

A HAS study of the structure and the acoustic phonon modes of Gr grown by CVD on Cu(1 1 1)/Al2O3 and on a peel-off epitaxial Cu(1 1 1) foil has been reported by Al Taleb et al [127]. The Gr lattice constant obtained from the He-diffraction spectra is \( a = (2.44 \pm 0.02) \text{ Å} \). Within experimental error, this value was found to be independent of surface temperature in the range between 110–500 K. This result is in quantitative agreement with calculations for free standing Gr [128]. The observation of a temperature independent Gr lattice constant in contact with a thermally expanding copper substrate is striking evidence of the weak Gr–Cu interaction [127].

4.4.1. Phonon dispersion curves. Figure 8 shows the phonon dispersion curves for Gr/Cu(1 1 1)/Al2O3 (black dots) and Gr on Cu(1 1 1) foil measured along the ΓM direction. Phonon dispersion curves for free standing Gr calculated from first principles [58] are also shown as dashed lines. Comparison to these calculations allows to assign most of the observed phonons as flexural phonons, more specifically perpendicular acoustic (ZA) phonon modes. Surprisingly, no data points were detected for the longitudinal acoustic (LA) and transverse acoustic (TA) modes. The latter would be anyway forbidden for planar scattering in the ΓM direction [89], but the LA mode should be present (in fact, it has been clearly detected on the graphite (0 0 1) surface with HAS [122]). For doped Gr, Guinea et al [129] have shown that the low screening of Gr leads to a significant stiffening of the LA mode; this could make its detection more difficult. First principles phonon calculations of a Gr/Cu interface predict a few meV shift of the ZA mode near the Γ point, which is a direct measure of the strength of the Gr–Cu interaction [130]. This shift is clearly seen at \( \omega_0 \sim 6 \text{ meV} \) in figure 8. A similar feature is observed at \( \omega \sim 12 \text{ meV} \), which is very likely an overtone of \( \omega_0 \).

An unshifted dispersion curve is also observed, which resembles the ZA mode of free-standing Gr [58]. This has been assigned to regions of the Gr sample where the interaction with the substrate is reduced, possibly due to nanoripples or to the existence of defects on the Cu substrate, which makes Gr domains behave as quasi free-standing. This could also come from the Rayleigh wave of the underlying Cu(1 1 1) substrate, since at this wavevector the penetration depth of He atoms is large enough to sample it [131]. Interestingly enough, the data points for the ZA mode follow a parabolic dispersion only at phonon wave vectors near the center of the Brillouin zone. Above 10 meV, a quasi-linear behaviour is observed, in agreement with recent calculations for bilayer Gr [132].

4.4.2. Graphene-Cu coupling strength. The dispersion curves can be used to derive more fundamental quantities like the Gr–Cu coupling strength, \( g \), and the free standing bending rigidity [133], \( \kappa \), following the model developed in [134]. For free-standing Gr, the dispersion of the acoustic perpendicular ZA mode is given by [135]:

\[
\omega_{ZA}^2(\Delta k) = \frac{\kappa}{\rho_{2D}} \Delta k^2,
\]

where \( \rho = 7.6 \times 10^{-8} \text{ g cm}^{-2} \) is the two-dimensional mass density of Gr. Coupling Gr to a substrate will introduce a gap at a frequency \( \omega_0 \) at the Γ point, whereby the dispersion relation is now given by:

\[
\omega_{ZA}^{\text{coupled}}(\Delta k) = \sqrt{\frac{\kappa}{\rho_{2D}}} \Delta k^2 + \omega_0^2,
\]

where \( \omega_0 = \sqrt{\frac{g}{\rho_{2D}}} \) and \( g \) is the coupling strength between Gr and substrate [134]. Therefore, from a fit to the

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**Figure 8.** Experimentally derived surface phonons for Gr/Cu(1 1 1)/Al2O3 (black dots) and Gr on Cu(1 1 1) foil (red dots) measured along the ΓM direction shown with DFT calculations for free standing Gr [58] (dashed curves). Error bars are shown for some data points. Red curve is a fit to the experimental data using equation (2). Reproduced with permission from [127]. © (2015) Elsevier.
experimental data using equation (2) it is possible to determine both $g$ and $\kappa$. The best–fit (red curve in figure 8) leads to $g = (5.7 \pm 0.4) \times 10^{19}$ N m$^{-3}$ and $\kappa = (1.30 \pm 0.15)$ eV for the Gr–Cu interaction. The derived $g$ value is 2–3 times smaller than that reported for Gr/SiO$_2$ interfaces [136], whereas $\kappa$ is consistent with DFT calculations that predict $\kappa = 1.20$–1.61 eV [133]. These results help to elucidate the current debate on the relative contributions of different acoustic phonon modes to the thermal conductivity of Gr [20], as outlined in section 2.4. In effect, the observed ZA dispersion for Gr/Cu is very similar to the one expected for free-standing Gr. The complete absence of data points from the LA mode suggests that this mode might be also involved in heat conduction in Gr.

4.5. Graphene on Ir(1 1 1)

4.5.1. Kohn anomalies. A very good example of how phonon spectra unveil subtle aspects of electron–phonon coupling, electron correlations, and the Gr-metal interaction is provided by the Gr/Ir(1 1 1) system. The dispersions of acoustical and optical phonon modes along the two high-symmetry directions of the surface Brillouin zone have been measured using HREELS by Endlich et al [137]. Owing to the weak Gr–Ir interaction [138], the measured dispersion curves were found to be very similar to those of free-standing Gr and graphite. However, there are subtle deviations, which allow getting new insights into the Gr-substrate interaction.

Kohn anomalies of the highest optical phonon modes LO and TO were observed at $\Gamma$ and $K$, respectively. This observation was interpreted in terms of a decrease of the electron–phonon interaction due to screening of Gr electron correlations by the metal electron gas. Figure 9 shows a closeup view of the phonon dispersion of the LO mode around $\Gamma$ (a) and of the TO mode around $K$ (b), both depicted as blue dots [137]. For comparison, inelastic x-ray data for graphite around $\Gamma$ [57] and $K$ [139] are shown as squares. Black dashed lines correspond to results of LDA calculations for Gr/Ir(1 1 1). Calculated dispersion curves for graphite and pristine Gr have been added as light gray and gray dashed lines, respectively [139, 140]. Around the $\Gamma$ point, all data sets exhibit good agreement, indicating that the Kohn anomaly of the LO mode persists in Gr/Ir(1 1 1). In particular, the experimental dispersion of this mode is very well reproduced by LDA–DFT calculations, which neglect the long-range character of the electron–electron interaction. Therefore, it can be concluded that for the LO phonon of Gr/Ir(1 1 1), correlation effects play a minor role, which is consistent with calculations from the LO phonon of graphite and pristine Gr [140].

A very different situation is observed for the TO phonon dispersion close to $K$. Compared with the graphite data (squares), the indentation of the TO mode around $K$ (b), both depicted as blue dots [137]. For comparison, inelastic x-ray data for graphite around $\Gamma$ [57] and around $K$ [139] are shown as squares. Black dashed lines correspond to results of LDA calculations for Gr/Ir(1 1 1). Calculated dispersion curves for graphite and pristine Gr have been added as light gray and gray dashed lines, respectively [139, 140]. Around the $\Gamma$ point, all data sets exhibit good agreement, indicating that the Kohn anomaly of the LO mode persists in Gr/Ir(1 1 1). In particular, the experimental dispersion of this mode is very well reproduced by LDA–DFT calculations, which neglect the long-range character of the electron–electron interaction. Therefore, it can be concluded that for the TO phonon of Gr/Ir(1 1 1), correlation effects play a minor role, which is consistent with calculations from the LO phonon of graphite and pristine Gr [140].
for pristine Gr and for Gr/Ir(1 1 1), Endlich et al. [137] demonstrate that electron correlations in Gr are reduced by the screening of the Ir(1 1 1) electronic system. This screening efficiently damps correlation effects that are not described by DFT calculations.

4.5.2. Graphene–Ir interaction. The presence of the Kohn anomalies at Γ and K already suggests a weak Gr–Ir coupling. A direct measure of the strength of the Gr–Ir interaction is provided by the non-zero energy of the ZA mode at Γ. The data points are shown in figure 10(a). Good agreement with the data is obtained by DFT calculations within LDA (upper black dashed line) and GGA approximations (lower black dashed line) to the exchange-correlation functional [141]. This is in contrast with the behaviour of the ZA phonon dispersion of free-standing Gr, which is expected to vanish at zero wave vector (gray dashed line). At Γ the ZA phonon energy of Gr on Ir(1 1 1) is ~6 meV. In a simple harmonic oscillator model for the C vibrations [35] the observed ZA phonon energy can be translated into a spring constant, \( K \approx 2.2 \text{ N m}^{-1} \), with \( m \) the mass of a C atom and \( \omega \) the angular frequency of the ZA phonon at Γ [141]. The spring constant can be taken as a rough estimate of the interaction between Gr and the metal surface. It is about a factor 18 lower than the one obtained for Gr on Ni(1 1 1) [34] and about a factor 4 lower than the spring constant for the interlayer coupling in graphite [59]. Applying the model discussed in section 4.4.2, we obtain \( g = (7.4 \pm 0.4) \times 10^{19} \text{ N m}^{-3} \) for the Gr–Ir interaction. This is ~30% larger than for the Gr–Cu system.

The ZO phonon dispersion around Γ is likewise affected by the interaction of Gr and Ir(1 1 1). As shown in figure 10(b), the experimental data points (blue dots) for Gr/Ir(1 1 1) are downshifted with respect to the calculated ZO dispersion of pristine Gr (gray dashed line) and Gr/Ir(1 1 1) (black dashed lines). The downshift of the ZO phonon mode at Γ can be explained in terms of the Gr–Ir interaction. DFT calculations show that bonding of Gr to Ir(1 1 1) is due to the van der Waals interaction, with a weak hybridization of carbon \( p_z \) orbitals with Ir \( d \) orbitals at C atoms sitting on top of Ir atoms [142]. Due to this hybridization, charge is transferred from C to Ir atoms, which leads to a weakening of \( \pi \) bonds between adjacent carbon atoms on the Gr layer [35]. Since the ZO mode involves the out-of-phase perpendicular oscillations of nearest-neighbor C atoms, a lowering of the ZO phonon energy at Γ is expected, as observed in experiment. These results are in line with the ones reported for Gr/Ni(1 1 1), where a charge transfer of 0.21 e per C atom [143] leads to a softening of the ZO phonon at Γ by ~23 meV compared to free-standing Gr [37, 39]. In the case of Gr/Ir(1 1 1), a charge transfer of 0.01 e [142] leads to a softening of the ZO phonon energy at Γ of ~5 meV, which is similar to the energy downshift observed from graphite [53].

A still unsolved issue on this system is the origin of the observed gap at the \( K \) point of the ZA, ZO and LA, LO modes [141]. The energy difference between the ZA and ZO phonon branches is 9 meV, while LA and LO phonon energies differ at \( K \) by 8 meV. These gaps are too large to be attributed to sample misalignment [141]. Calculations for Gr/Ir(1 1 1) are not able to reproduce this splitting [137]. However, in these calculations the Gr layer was assumed to be commensurate with the Ir(1 1 1) lattice, i.e. the Moiré superstructure was not considered. The different adsorption sites occupied by the C atoms may change the symmetries of ZA, ZO and LA, LO phonons at \( K \), lifting their degeneracy, which may result in the appearance of an energy splitting [141]. Thus, it remains as a challenge to perform state-of-the-art DFT calculations of Gr/Ir(1 1 1) including the Moiré superstructure, in order to see if they are able to reproduce the experimentally observed energy splitting for transverse as well as for longitudinal phonons at the \( K \) point.

Figure 10. Experimental dispersion data (dots) of (a) the ZA and (b) the ZO phonon of Gr/Ir(1 1 1) around the Γ point. Black dashed lines represent results of DFT calculations within LDA (upper curve in (a)) and GGA approximations (lower curve in (a)) to the exchange-correlation functional. In (b) both approximations nearly coincide. The gray dashed line shows calculations for free-standing Gr [59]. Reproduced with permission from [141]. © (2014) Wiley.
The Moiré pattern can also be considered as an electronic superlattice, whereby Gr electrons are subject to an additional potential with the Moiré periodicity. This superperiodic potential gives rise to Dirac cone replicas and the opening of minigaps in the band structure [138, 144]. In principle, a Moiré superstructure could also induce a replica of Gr phonon branches. A clear signature of this replica has been observed for the ZA and ZO modes of Gr/Ir(1 1 1) along $\Gamma M$ and $\Gamma K$ by Endlich et al [141]. Using a linear chain model of C atoms coupled to a rigid substrate, they showed that phonon replica occur at wave vectors that reflect the periodicity of the supercell when a periodic variation of C–C and C-substrate interactions is imposed.

4.6. Graphene on Pt(1 1 1)

The phonon dispersion relations of Gr/Pt(1 1 1) have been measured by HREELS along $\Gamma M$ [93] and $\Gamma K$ [145]. These phonon spectra were found to be very similar to the ones reported for pristine graphite, which proves the weak Gr–Pt interaction. This is also revealed by the thermal attenuation of the He-specular peak, which resembles that observed from graphite [146]. However, some deviations occur in the phonon dispersion curves. At the $\Gamma$ point, the degeneracy of the ZA and ZO phonons is lifted by $\sim 20$ meV. Although the presence of a ZA/ZO gap is expected due to the symmetry reduction in supported Gr [34], the value reported for Gr/Pt(1 1 1) is too large for a weakly interacting system, and requires a more convincing explanation. This situation is similar to the one discussed above for Gr/Ir(1 1 1). It is worth reminding that the lattice mismatch in Gr/Pt(1 1 1) is accommodated by Moiré structures with different rotational domains [44, 45, 47].

4.6.1. Kohn anomalies. The two Kohn anomalies present in graphite at $\Gamma$ (LO mode) and $K$ (TO mode) [22] are also observed in Gr/Pt(1 1 1) [147]. In a more recent HREELS study of the phonon dynamics of this system, the Kohn anomaly for the LO phonon has been observed at finite momentum $q \sim 2k_F$ from $\Gamma$ [148]. Surprisingly, a Kohn anomaly has been also observed at the same momentum for the out-of-plane ZO optical phonon. This is the first direct evidence of the coupling of an optical ZO mode with Dirac electrons. The results are summarized in figure 11. It is apparent the existence of a clear cusp at the same momentum $q_c \sim 0.13 \text{ Å}^{-1}$ for both LO and ZO modes. This suggests that both cusps are Kohn anomalies at $q = 2k_F$. The Fermi wave vector $k_F$ has been estimated from previous work, obtaining $2k_F \sim (0.10 \pm 0.05) \text{ Å}^{-1}$, in very good agreement with the experimental results. The solid lines in figure 11 are fits to the data using a simple model, which allows estimating the electron–phonon couplings [148]. The best–fit curves correspond to electron–phonon coupling parameters $\lambda_{LO} = 0.029$ and $\lambda_{ZO} = 0.087$. Especially remarkable is the large value obtained for the coupling of the ZO mode.

As discussed in the previous section, the LO and TO Kohn anomalies have been observed in Gr/Ir(1 1 1) [137]. It is interesting to consider if the anomaly of the ZO mode could be also observed in this system. According to ARPES results [138], $2k_F \sim 0.03 \text{ Å}^{-1}$ for Gr/Ir(1 1 1). This is too close to the $\Gamma$ point, making detection of the corresponding ZO Kohn anomaly more difficult. However, if the ZO electron–phonon coupling is large enough, it should be possible to observe this anomaly also in Gr/Ir(1 1 1).

4.6.2. Elastic properties. We mention for completeness another useful application of phonon dispersion curves. One of the most promising technological applications of Gr is its use as a membrane, owing to the unique combination of both flexibility and mechanical strength. A good knowledge of the elastic properties of Gr is needed in order to implement any practical application in nanodevices. Under certain conditions, continuous–medium elasticity theory can be applied to get relevant parameters like the Youngs modulus and the Poissons ratio [149, 150]. AFM nanoindentation is the most used technique to determine these values experimentally [3, 151]. However, the average elastic properties and the interatomic force constants of Gr can be also evaluated by analyzing the phonon dispersion curves. This approach has been applied by Politano et al [152] to determine the elastic properties of quasi-freestanding Gr grown on Pt(1 1 1). Based on the phonon spectra determined by HREELS, they obtained values of 0.19 for the Poissons ratio and 342 N m$^{-1}$ for the Youngs modulus, which are in excellent agreement with available data for a free-standing Gr membrane [153].

**Figure 11.** Phonon dispersions for Gr/Pt(1 1 1) close to the $\Gamma$ point, showing cusps around $q_c \sim 0.13 \text{ Å}^{-1}$. (a) Dispersion of the LO phonon. (b) Dispersion of the ZO phonon. Calculations are shown by solid lines. (c) Representative spectra used to produce (b). The frequencies are marked with a dashed line. Reproduced with permission from [148]. © (2015) American Physical Society.
5. General trends

Most relevant phonon energies at the high-symmetry points of the Brillouin zone for Gr/metal systems are summarized in tables 2–4. Table 2 includes the values $\Delta_{ZO}$ and $\Delta_{LO}$, which correspond to deviations from the corresponding ZO and LO energies measured for graphite. Tables 3 and 4 present $Z_{gap}$ and $L_{gap}$, which are the values of the gap between ZO–$ZA$ and LO–$LA$ at the M and K points, respectively.

We start by discussing the main trends observed in the acoustic phonon dispersion curves. For strong Gr-metal interaction, the most pronounced feature is the hybridization of the ZA mode with the Rayleigh wave (RW) of the substrate \cite{134}. This leads to the appearance of the substrate’s RW in the phonon spectra, as observed for Gr grown on the (1 1 1) surfaces of TaC, TiC and HfC \cite{35, 36}, Gr/Ni(1 1 1) \cite{100} and Gr/Ru(0001) \cite{108}. These results explain the surprisingly high reflectivity for He atoms reported for Gr/Ru(0001) \cite{8, 116} and Gr/Ni(1 1 1) \cite{100}. The removal of the (quasi)-parabolic dispersion of the ZA mode in Gr and its replacement with the linearly dispersed RW of the substrate shows that it is just a consequence of a strong C-metal interaction. Coupling to the substrate leads to splitting of the ZA mode, i.e. it does not go to zero for $Q \rightarrow 0$. The energy $\omega_{ZA}$ at the $\Gamma$ point is a direct measure of the Gr–substrate bond strength. Large values correspond to strongly interacting systems; $39$ meV has been reported for Gr/ZrC(1 1 1) \cite{94}, $34$ meV for both TaC(1 1 1) and HfC(1 1 1) \cite{35, 36}, $20$ meV for Gr/Ni(1 1 1) \cite{100} and $16$ meV for Gr/Ru(0001) \cite{108}. On the other hand, lower values are observed for weak Gr-metal interactions; $\omega_{ZA} \sim 6$ meV has been measured for both Gr/Ir(1 1 1) \cite{141} and Gr/Cu(1 1 1) \cite{127}. Surprisingly, these energies are much lower than

\begin{table}[h]
\centering
\caption{Energies (in meV) of ZA, ZO and LO phonons at the $\Gamma$ point for different Gr/metal systems.}
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
System & ZA & ZO & $\Delta_{ZO}$ & LO & $\Delta_{LO}$ & Tool & References \\
\hline
Graphene & 0 & 111 & -3 & 196.6 & 1.4 & LDA & \cite{58} \\
& 0 & 110.7 & -2.7 & 198 & 0 & LDA & \cite{59} \\
& 0 & 109.6 & -1.6 & 194.6 & 3.4 & GGA & \cite{59} \\
& 0 & 109.2 & -1.2 & 192.7 & 5.3 & GGA & \cite{154} \\
Graphite & 108 & 0 & 198 & 0 & HREELS & \cite{54} \\
& 9 & 107 & 1 & 197.7 & 0.3 & HREELS & \cite{55} \\
& 12.5 & 107.6 & 0.4 & 196 & 2 & IXS & \cite{53} \\
& 0 & 101 & 7 & 194 & 4 & LDA & \cite{53} \\
& 15.3 & & & 194.3 & 3.7 & IXS & \cite{57} \\
& & & & 196 & 2 & LDA & \cite{57} \\
ZrC(1 1 1) & 39 & 90 & 18 & 187 & 11 & HREELS & \cite{94} \\
TiC(1 1 1) & 36 & 88 & 20 & 191 & 7 & HREELS & \cite{35} \\
HfC(1 1 1) & 34 & 85 & 23 & 187 & 11 & HREELS & \cite{35} \\
TaC(1 1 1) & 33 & 82 & 26 & 186 & 12 & HREELS & \cite{35} \\
NbC(1 1 1) & 32 & 85 & 23 & 185 & 13 & HREELS & \cite{93} \\
Gr/Ru(0001) & 16 & & & & & HAS & \cite{108} \\
& 27 & 73 & 35 & 180 & 18 & HREELS & \cite{155} \\
Gr/Ni(0 0 1) & 16 & 88 & 20 & 180 & 18 & HREELS & \cite{37} \\
Gr/Ni(1 1 1) & 16 & 88 & 20 & 188 & 10 & HREELS & \cite{37} \\
& 88 & 20 & 188 & 10 & HREELS & \cite{38} \\
& 20 & & & & & HAS & \cite{100} \\
Gr/YbNi(1 1 1) & 29 & 91 & 17 & 184 & 14 & LDA & \cite{34} \\
Gr/Pt(1 1 1) & 6.5 & 104 & 4 & 197 & 1 & HREELS & \cite{114, 141} \\
& 5.7/7.1 & 108 & 0 & 197 & 1 & GGA/LDA & \cite{114, 141} \\
Gr/Cu(1 1 1) & 5.7 & & & & & HAS & \cite{127} \\
Gr/CuNi(1 1 1) & 3 & 108 & 0 & 189 & 9 & LDA & \cite{130} \\
Gr/CuNi(1 1 1) & 103 & 5 & 195 & 3 & HREELS & \cite{39} \\
& 105 & 3 & 200 & -2 & HREELS & \cite{111} \\
Gr/Au/Ni(1 1 1) & 106 & 2 & 196 & 2 & HREELS & \cite{111} \\
& 106 & 2 & 199 & -1 & HREELS & \cite{112} \\
Gr/Ag/Ni(1 1 1) & 106 & 2 & 199 & -1 & HREELS & \cite{94} \\
Gr/Al(1 1 1) & 106 & 2 & 199 & -1 & HREELS & \cite{94} \\
Gr/ZrC(0 0 1) & 106 & 2 & 199 & -1 & HREELS & \cite{94} \\
Gr/BeC(0 0 1) & 106 & 2 & 199 & -1 & HREELS & \cite{94} \\
Gr/TaC(0 0 1) & 106 & 2 & 199 & -1 & HREELS & \cite{35} \\
\hline
\end{tabular}
\end{table}

Note: $\Delta_{ZO}$ and $\Delta_{LO}$ indicate deviations from the corresponding ZO and LO graphite values measured with HREELS by Oshima et al \cite{54}. 


the ones reported for graphite: 12.5 meV has been determined from x-ray scattering [53], and 15.3 meV from neutron scattering [56]. Further work is needed to clarify this issue.

Concerning the optical branches, the most relevant feature observed for systems with a strong Gr-metal interaction is a pronounced softening of the LO, TO and ZO modes throughout

<table>
<thead>
<tr>
<th>System</th>
<th>ZA</th>
<th>ZO</th>
<th>Zgap</th>
<th>LA</th>
<th>LO</th>
<th>Lgap</th>
<th>Tool</th>
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<td>[58]</td>
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<td>LDA</td>
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<td>GGA</td>
<td>[59]</td>
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<td>LDA</td>
<td>[57]</td>
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</table>

Note: Zgap and Lgap are the values of the gap between ZO–ZA and LO–LA, respectively.

<table>
<thead>
<tr>
<th>System</th>
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<th>ZO</th>
<th>Zgap</th>
<th>LA</th>
<th>LO</th>
<th>Lgap</th>
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<td>HfC(1 1 1)</td>
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<td>147</td>
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<td>16</td>
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<td>[35]</td>
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<td>TaC(1 1 1)</td>
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<td>58</td>
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<td>[35]</td>
</tr>
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<td>61</td>
<td>8</td>
<td>146</td>
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<td>[93]</td>
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<td>156.5</td>
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<td>[59]</td>
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<td>19</td>
<td>146</td>
<td>163</td>
<td>17</td>
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<td>[37]</td>
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<td>16</td>
<td>146</td>
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<td>LDA</td>
<td>[34]</td>
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<td>Gr/Pt(1 1 1)</td>
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<td>158</td>
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<td>[93]</td>
</tr>
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<td>Gr/Ir(1 1 1)</td>
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<td>159</td>
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<td></td>
</tr>
<tr>
<td>Gr/Cu(1 1 1)</td>
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<td>166</td>
<td>169</td>
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<td>155</td>
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<td>20</td>
<td>160</td>
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<td>[94]</td>
</tr>
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<td>Gr/NbC(0 0 1)</td>
<td>51</td>
<td>78</td>
<td>27</td>
<td>160</td>
<td></td>
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<td>[93]</td>
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<td>Gr/TaC(0 0 1)</td>
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<td>27</td>
<td>160</td>
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<td></td>
<td></td>
<td>[35]</td>
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</tbody>
</table>

Note: Zgap and Lgap are the values of the gap between ZO–ZA and LO–LA, respectively.

Table 4. Energies (in meV) of ZA, ZO, LA and LO phonons at the K point for different Gr/metal systems.

<table>
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<tr>
<th>System</th>
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<th>ZO</th>
<th>Zgap</th>
<th>LA</th>
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<td>150.4</td>
<td>0</td>
<td>GGA</td>
<td>[154]</td>
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<tr>
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<td>9.8</td>
<td>158</td>
<td>158</td>
<td>0</td>
<td>HREELS</td>
<td>[59]</td>
</tr>
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<td>66.4</td>
<td></td>
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<td>149.5</td>
<td>149.5</td>
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<td>151.3</td>
<td>0</td>
<td>LDA</td>
<td>[57]</td>
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<tr>
<td>Gr/Ru(0001)</td>
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<td></td>
<td>139</td>
<td>149</td>
<td>10</td>
<td>HREELS</td>
<td>[59]</td>
</tr>
<tr>
<td>Gr/Ni(1 1 1)</td>
<td>47</td>
<td>60</td>
<td>13</td>
<td>141</td>
<td>168</td>
<td>27</td>
<td>HREELS</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>64</td>
<td>18</td>
<td>138</td>
<td>138</td>
<td>0</td>
<td>LDA</td>
<td>[34]</td>
</tr>
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<td>Gr/YbNi(1 1 1)</td>
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<td></td>
<td></td>
<td>141</td>
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<td></td>
<td></td>
<td>[39]</td>
</tr>
<tr>
<td>Gr/Pt(1 1 1)</td>
<td>59</td>
<td>68</td>
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<td>150</td>
<td>158</td>
<td>8</td>
<td>HREELS</td>
<td>[137, 141]</td>
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<tr>
<td>Gr/Ir(1 1 1)</td>
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<td>0.5</td>
<td>153</td>
<td>153</td>
<td>0</td>
<td>LDA</td>
<td>[137, 141]</td>
</tr>
<tr>
<td>Gr/Cu(1 1 1)</td>
<td>62.4</td>
<td>62.7</td>
<td>0.3</td>
<td>154</td>
<td>154</td>
<td>0</td>
<td>LDA</td>
<td>[130]</td>
</tr>
<tr>
<td>Gr/AuNi(1 1 1)</td>
<td>60</td>
<td>74</td>
<td>14</td>
<td>159</td>
<td>173</td>
<td>14</td>
<td>HREELS</td>
<td>[39]</td>
</tr>
<tr>
<td>Gr/AgNi(1 1 1)</td>
<td>69</td>
<td>69</td>
<td>0</td>
<td>153</td>
<td></td>
<td></td>
<td></td>
<td>[112]</td>
</tr>
</tbody>
</table>
the entire Brillouin zone. Softening of the ZO mode at the Γ point amounts 20 meV for Gr/Ni(1 1 1) [35, 38, 39] and 35 meV for Gr/Ru(0001) [153] and ca. 25 meV for Gr on TaC(1 1 1), TiC(1 1 1) and HfC(1 1 1) [35, 36]. In addition, for Gr/Ni(1 1 1) there is a splitting of the ZA and ZO modes of 16 meV and 13 meV at M and K, respectively. These values are reproduced by calculations, although they are overestimated [34].

Since in both ZA and ZO modes carbon atoms vibrate vertically, they are expected to be most affected in cases of strong Gr-substrate interaction. This is confirmed by data reported for Gr/Ni(1 1 1) [35, 38, 100] and Gr/Ru(0001) [108, 155], which show that ZA and ZO modes deviate considerably from the ones of graphite. The softening of the ZO bond is a consequence of the strong interaction, i.e. hybridization of the metal d-band with Gr π-bands, a suggestion advanced by Oshima et al. [37, 42, 104] and confirmed by recent DFT calculations [34]. In the LA and LO modes, in contrast, carbon atoms vibrate parallel to the surface and the influence of the Gr-substrate interaction is much smaller. Therefore, a signature for the existence of a graphite-like overlayer is provided by the observation of these two modes, especially from the LA mode, which has a characteristic large dispersion. This is nicely illustrated by several examples discussed above for both strongly and weakly interacting Gr-metal systems. The strength of this interaction leaves its mark on the two Kohn anomalies present in graphite at Γ (LO mode) and K (TO mode) [22, 57]. The two anomalies are clearly observed in Gr/Ir(1 1 1) [137] and Gr/Pt(1 1 1) [147], while the LO anomaly is visible after intercalation of Cu, Ag and Au in Gr/Ni(1 1 1) [38, 40, 111].

6. Conclusions

We have reviewed recent experimental and theoretical work on phonon dynamics of Gr/metal systems. The results reported for Gr/Cu(1 1 1), Gr/Ir(1 1 1) and Gr/Pt(1 1 1) demonstrate that, in spite of the weak Gr-metal interaction, clear signatures are observed in the Gr phonon dispersion curves. This allows determining the Gr-metal bond strength as well as the bending rigidity, a piece of information difficult to get with other experimental techniques. These parameters, together with the full dispersion curves, provide an excellent scenario to test the performance of current DFT calculations. Improved accuracy to describe these features is crucial to understand issues relevant for applications, like the thermal conductivity of supported Gr. More work is needed to clarify whether the main contribution to heat transport is due to the in-plane TA and LA phonons or to the flexuralZA mode. This is an additional motivation to perform acoustic phonon measurements of supported Gr, like the ones reported for Gr/Cu(1 1 1) [100] and Gr/Ir(1 1 1) [137, 141]. Knowledge gained from these investigations is expected to be useful for studies on related areas of research, as for instance Gr-like two-dimensional materials [156–159].

Acknowledgments

We are indebted to G Benedek for insightful comments and suggestions. This work has been supported in part by the European Union, FP7: Theme NMP.2012.1.4-3 Grant no. 309672.

References

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