Reply to "Comment on 'Raman spectra of misoriented bilayer graphene' "

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In their Comment, Ni *et al.* show new data as supporting their hypothesis, i.e., the two-dimensional band blueshift between graphene and misoriented bilayer is caused by a reduction in the Fermi velocity. In the first part of our reply, we will demonstrate that the exhibited data, which typically shows a constant blueshift for various excitation energies are in contradiction with a change in Fermi velocity. In the second part we will explain how charge transfer from the substrate that affects the phonon-dispersion curve can account for the observed discrepancies and how this hypothesis is supported by experimental observations.

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We start by showing that a reduction in Fermi velocity will necessarily induce a slope in blueshift curve versus excitation energy. Figure 1(a) sketches the band structure of graphene (black) and a hypothetical structure with a reduced Fermi velocity (red). Now let us calculate the excitation energy required to get an identical Raman shift (i.e., for identical phonons represented by horizontal arrow). This will indeed give a blueshifted Raman curve, as excitation energies will be different for a given phonon [Fig. 1(b)]. To compare with the Comment[1] figure, we plot in Fig. 1(c) the difference (subtraction of these two curves). Note that as both electronic dispersion curves from Fig. 1(a) goes through zero, the Raman-shift difference has to pass through the origin (a zero-energy excitation will produce identical Raman shift in both case).

On the plot that represents the difference between the graphene and misoriented bilayer two-dimensional (2D) Raman shift versus excitation energy, a reduction in the Fermi velocity will necessarily give an affine curve ($y=ax$) with a positive slope. Note that this demonstration is valid for any given phonon distribution.

Now that this point is clarified, let us turn to data analysis. We will take their validity for granted and discuss their physical meaning. The data presented in the Comment[1] come from three different groups in the world. The data from Ni *et al.*[1] come from four different samples. Some of them can indeed, thanks to error bar, support their hypothesis (although extrapolating from two close points is not very precise and a zero slope is also possible). Note however that sample labeled 2, which contains three measured points (thus the most precise data set available from the Ni *et al.*[1,2] group, as the other samples have only two points measured), contradict the author's own hypothesis as the blueshift is typically constant and there is no way this plot can be extrapolated to zero. The data they extracted from Gupta and Eklund[3] poster span over almost 0.6 eV and contains 5 points (although the original data contains 6 points and span over almost 1 eV, see Ref. 3) and shows a constant blueshift, which is clearly in contradiction with the Ni *et al.*[2] interpretation. Our result (three data points over 0.6 eV range[4]) is also in contradiction with a Fermi-velocity reduction, as we observe a negative slope.

In any case, there is a possible straightforward explanation of the plots reported in the Comment.[1] This effect has actually already been observed in graphene itself.[5] A change in doping (through electrostatic gating or accidental charge transfer from the substrate) will shift the 2D peak (as well as *G* peak) because changing the electronic densities changes the bonding strength and modifies the phonon-dispersion curves. As the phonon-dispersion curve is not a straight line with a constant slope that is simply rigidly shifted, a change in its shape could affect the 2D Raman shift in various ways, depending on the charge-transfer amount.

According to our original hypothesis,[4] the observed blueshift originates from a change in phonon-dispersion curve. As phonon-dispersion curve is sensitive to substrate charge transfer, then different substrate doping in different groups would lead to the divergence reported in the Comment.[1]

Recall now that a single graphene sheet is more sensitive to doping than a bilayer simply because of a shielding effect. If our hypothesis is correct, then data on graphene should exhibit more dispersion for various group or substrate than

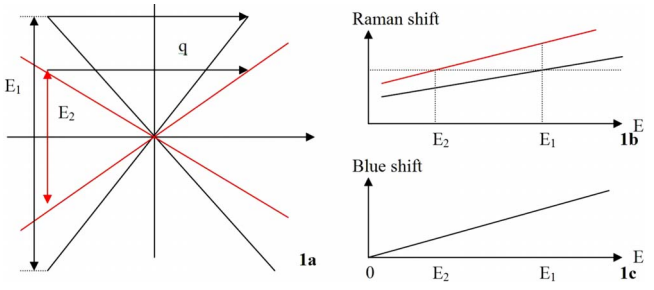

FIG. 1. (Color online) Consequences of Fermi velocity reduction on the Raman spectra and blueshift curves. (a) shows two linear model band structures with the red one having a lower Fermi velocity than the black one. (b) shows that for a given phonon, the red band structure will indeed give a blueshifted Raman spectra (red line) compared to the other one (black line). Finally, (c) plot the difference of the two Raman shift (referred to as blueshift in the Comment[1]). As for a zero-energy excitation, the two phonons have to be equal [see (a)], the blueshift curve has to pass through the origin. (b) shows that its slope has to be positive.

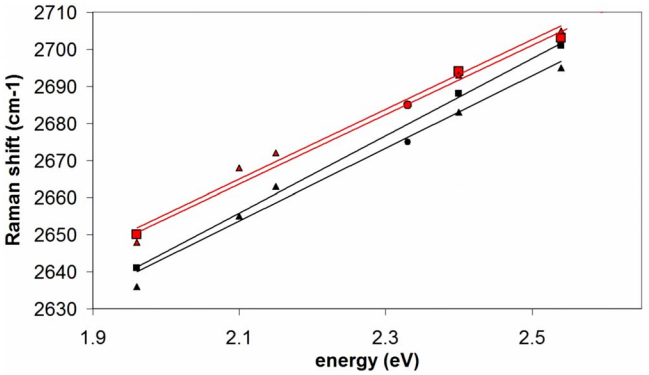

FIG. 2. (Color online) Measured Raman shift on graphene (black) and a misoriented bilayer (red) from Gupta and Ecklund (triangles), Ni (circles), and Poncharal (squares). Only one complete set of data (graphene and bilayer) was available from Ni *et al.*[2] For the other samples presented in the Comment, we cannot extract this information. The figure clearly shows that the agreement is rather good on misoriented bilayer, but there are divergences on graphene. A fact that support a modification of phonon-dispersion curve (see text).

data reported on bilayer as the accidental doping effect will be weakest on bilayer than on graphene.

To test this hypothesis, we have plotted in Fig. 2 the 2D Raman shift of graphene and misoriented bilayer (not only their difference) from Ni, Gupta and Eklund, and Poncharal. As it can be seen, for misoriented bilayers, the agreement is rather good between the three groups, the disagreement comes from measurements on graphene (a fact that was concealed in the original Ni *et al.* Comment[1] figure because they plot the difference between graphene and bilayers).

As we did not know the doping level and nature of the silicon used in the wafers of Gupta and Eklund[3] and of Ni *et al.*[1,2] group, we cannot go further in our analysis.

To summarize, single graphene layers shows slightly different phonon-dispersion curves due to accidental substrate charge transfer, which explain the discrepancies on 2D Raman shift of graphene (see Ref. 5 for more detail). Adding a second layer (misoriented or not) changes the phonon-dispersion curve as we claim. This change magnitude depending on the initial state of the system, the blueshift might be different from sample to sample.

To conclude, all the reported data (from Ni, Gupta and Eklund, or Poncharal), although presenting some apparent discrepancies, show that (i) the Raman dispersion curve of misoriented graphene bilayer is not identical to graphene dispersion curve; (ii) a reduction in Fermi velocity is contradicted by the majority of the reported measurements (even some of Ni *et al.*[1] data); and (iii) a change in phonon-dispersion curve can explain the reported effect and observed differences among the various groups.

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