Ab initio vibrational properties of defected and disordered systems

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The recent advances in scanning tunneling electron microscopy (STEM) instrumentation, bringing the energy resolution of electron energy loss spectroscopy down to the sub-10 meV regime while maintaining atomic resolution, has opened a new field of research focused on the local investigation of atomic vibrations in systems, ranging from interfaces [1] to point [2] or extended defects [3]. Given the intrinsically long-range nature of vibrational modes, the proper modelisation of these newly available experimental results involves structures with a very large number of atoms, making the direct use of the available first-principles approaches rather impractical. Indeed, ab-initio description of phonon scattering from defects, even of the most elementary kind (point defects such as vacancies or substitutional defects) is sporadic, if not entirely lacking. This situation can be overcome starting from the observation that the change of the interatomic force constants (IFCs) induced by a structural or chemical defect is, in most of the cases, very well localised. This idea is at the core of the approach that we implemented in [2]: first, the IFCs of a relatively small system (hundreds of atoms) are calculated fully ab-initio (density functional theory); then, these IFCs are assembled with those of the "undefected" crystal to build the dynamical matrix of a more realistic system (several thousands of atoms). This strategy preserves the accuracy of ab initio techniques providing a direct access to the delocalised nature of the vibrational modes. In [2], this approach allowed us to determine the quasi-localised nature of the vibrations of a Si substitutional defect in graphene and explain STEM observations.The same approach can be used to study even more complex systems, such as the interface between an hexagonal SiC substrate and a few-layer-thick epitaxially-grown graphene (a system considered nowadays of technological interest [4]). In particular, I will present a detailed study of the vibrations occurring in the first graphitic layer (buffer layer) which is directly interacting with the silicon-terminated surface of the substrate, showing that, with about a quarter of carbon atoms covalently bound to the substrate, the buffer layer can be considered as a prototypical model for local chemical and structural disorder in graphene. Calculations will be used to interprete very recent atomic-resolution EELS obtained at the SuperSTEM Daresbury (group of Q.Ramasse). The evocation of disorder will then be an opportunity to discuss the results we have recently obtained on acoustic phonon branches of ice VII [5]. This high-pressure phase of ice indeed displays a

complete proton disorder while retaining a quasi-bcc oxygen sublattice. Due to its specific atomic structure, ice VII provides a very pedagogical example where the X-ray (or, equivalently, the energy loss) scattering cross-section naturally unfolds the phonon dispersion of this disordered system.

[1] R. Qi et al., *Nature* **599**, 599 (2021).
[2] F. S. Hage et al., *Science* **367**, 1124 (2020).
[3] X. Yan et al., *Nature* **589**, 65 (2021).
[4] J. Zhao et al., *Nature* **625**, 60 (2024).
[5] G. Radtke et al., *Phys. Rev. Lett.* **132**, 056102 (2024).