# Mobility and bulk electron-phonon interaction in two-dimensional materials

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Abstract—We present calculations of the phonon-limited mobility in intrinsic n-type monolayer graphene, silicene and MoS<sub>2</sub>. The material properties, including the electron-phonon interaction, are calculated from first principles. Unlike graphene, the carriers in silicene show strong interaction with the outof-plane modes. However, we find that graphene only has a slightly higher mobility compared to silicene. For  $MoS_2$  we obtain several orders of magnitude lower mobilities and in agreement with other recent theoretical results. The simulations illustrate the predictive capabilities of the newly implemented Boltzmann Transport Equation (BTE) solver in the Atomistix ToolKit (ATK) simulation tool.

## I. INTRODUCTION

Two-dimensional (2D) materials are promising candidates for future electronic devices [1], [2], [3]. Examples of three such materials are illustrated in Fig.1, showing a monolayer of graphene (A), its Silicon based counterpart, silicene (B), and  $MoS_2$  (C). In such systems two-dimensionality allows very precise control of the carrier density by a gate which enables tuning of the electron-phonon interaction[2]. Electron-phonon interaction in graphene has been studied previously[4], [5], [6], but with the recent advances in fabrication of other 2D materials, like the first demonstration of a silicene transistor[3], further studies of interaction phenomena in 2D materials are necessary.



Fig. 1. The monolayered two-dimensional systems that are considered are A) graphene, B) silicene and C)  $MoS_2.$ 

Density functional theory (DFT) and atomistic methods can be used to describe the electronic structure and electronphonon coupling in novel 2D materials where fitted deformation potential parameters are not available. In this paper, we present a detailed description of the implementation of the bulk electron-phonon coupling, and a Boltzmann Transport Equation (BTE) solver in the Atomistix ToolKit (ATK) simulation tool[7]. We apply atomistic simulations with ATK to study electron-phonon coupling in two-dimensional materials from first-principles. In addition, we perform calculations of the low field mobility and its dependence on carrier density and temperature to obtain a better understanding of transport in graphene, silicene and MoS<sub>2</sub>.

# II. METHODS

In the diffuse transport limit, dominated by phonon scattering, the mobility can be obtained by solving the semiclassical BTE for the electronic distribution function,  $f_{kn}$ :

$$\frac{\partial f_{\mathbf{k}n}}{\partial t} + \mathbf{v}_{\mathbf{k}n} \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}n} + \frac{\mathbf{F}}{\hbar} \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}n} = \left. \frac{\partial f_{\mathbf{k}n}}{\partial t} \right|_{coll} \tag{1}$$

Here  $\mathbf{k}$ , *n* labels the k-point and band index, respectively. The velocity is defined as  $\mathbf{v}_{\mathbf{k}n} = 1/\hbar \nabla_{\mathbf{k}} \varepsilon_{\mathbf{k}n}$  and  $\mathbf{F} = q(\mathbf{E}+\mathbf{v}\times\mathbf{B})$  gives the external force. The right hand side in eqn. 1 describes different sources of scattering and dissipation that drives the system towards steady state. In the case of a homogeneous system, zero magnetic field, and a time-independent electric field in the steady state limit, the BTE simplifies to:

$$\frac{q\mathbf{E}}{\hbar} \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}n} = \left. \frac{\partial f_{\mathbf{k}n}}{\partial t} \right|_{coll} \tag{2}$$

Assuming instantaneous, single collisions, which are independent of the driving force, the collision integral is defined as

$$\frac{\partial f_{\mathbf{k}n}}{\partial t}\Big|_{coll} = - \sum_{\mathbf{k}'n'} \left[ f_{\mathbf{k}n} \left( 1 - f_{\mathbf{k}'n'} \right) P_{\mathbf{k}\mathbf{k}'}^{nn'} - f_{\mathbf{k}'n'} \left( 1 - f_{\mathbf{k}n} \right) P_{\mathbf{k}'\mathbf{k}}^{n'n} \right]$$
(3)

The transition rate from a state  $|\mathbf{k}n\rangle$  to  $|\mathbf{k}'n'\rangle$  is obtained from Fermi's golden rule (FGR):

$$P_{\mathbf{k}\mathbf{k}'}^{\lambda nn'} = \frac{2\pi}{\hbar} |g_{\mathbf{k}\mathbf{k}'}^{\lambda nn'}|^2 \left[ n_{\mathbf{q}}^{\lambda} \delta\left(\epsilon_{\mathbf{k}'n'} - \epsilon_{\mathbf{k}n} - \hbar\omega_{\mathbf{q}\lambda}\right) \delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}} \right. \\ + \left. \left( n_{-\mathbf{q}}^{\lambda} + 1 \right) \delta\left(\epsilon_{\mathbf{k}'n'} - \epsilon_{\mathbf{k}n} + \hbar\omega_{-\mathbf{q}\lambda}\right) \delta_{\mathbf{k}',\mathbf{k}-\mathbf{q}} \right] (4)$$

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describing absorption (first term) and emission (last term) of a phonon. The last term includes spontaneous emission which remains at zero temperature. The total transition rate is given as  $P_{\mathbf{kk}'}^{nn'} = \sum_{\lambda} P_{\mathbf{kk}'}^{\lambda nn'}$ , where  $\lambda$  labels the phonon modes. We have implemented a supercell method to calculate the bulk electron-phonon interaction,  $g_{\mathbf{kk}'}^{\lambda nn'}$ , employing finite differences in a localized basis set. Defining a relaxation time,  $\tau_{\mathbf{k}n}$ , so that  $f_{\mathbf{k}n} = f_{\mathbf{k}n}^0 + q\mathbf{E} \cdot \mathbf{v}_{\mathbf{k}n} \tau_{\mathbf{k}n} \frac{\partial f_{\mathbf{k}n}^0}{\partial \epsilon_{\mathbf{k}n}}$ , we rewrite the linearized BTE in the relaxation time approximation[8], [9]:

$$\frac{1}{\tau_{\mathbf{k}n}} = \sum_{\mathbf{k}'n'} \frac{(1 - f_{\mathbf{k}'n'}^0)}{(1 - f_{\mathbf{k}n}^0)} \left(1 - \cos(\theta_{\mathbf{k}\mathbf{k}'})\right) P_{\mathbf{k}\mathbf{k}'}^{nn'}$$
(5)

Here  $f^0$  is the equilibrium Fermi distribution function and the scattering angle is given by  $\cos(\theta_{\mathbf{kk'}}) = \frac{\mathbf{v}_{\mathbf{k'n'}} \cdot \mathbf{v}_{\mathbf{kn}}}{|\mathbf{v}_{\mathbf{k'n'}}|| \cdot |\mathbf{v}_{\mathbf{kn}}|}$ . The velocities are obtained from perturbation theory to avoid finite difference errors from crossing bands. From the relaxation time we evaluate the low field electron mobility

$$\mu_e = -2q^2 \frac{\sum_{\mathbf{k}n} |\mathbf{v}_{\mathbf{k}n}|^2 \frac{\partial f_{\mathbf{k}n}^0}{\partial \epsilon_{\mathbf{k}n}} \tau_{\mathbf{k}n}}{\sum_{\mathbf{k}n} f_{\mathbf{k}n}^0} \tag{6}$$

where a factor of two accounts for the spin degeneracy.

### **III. SIMULATIONS AND RESULTS**

The simulations were performed using the ATK DFT code with the PBE-GGA functional for exchange-correlation for graphene and silicene, and LDA in the case of MoS<sub>2</sub>. In all cases we use a Double-Zeta-Polarized (DZP) basis-set. The real-space grid cutoff was 75 Ha. The geometries were relaxed until all forces were smaller than 0.001 eV/Å, and  $51 \times 51$  in-plane k-points were used in the electronic structure calculations. A vacuum gap of 30 Å was used in the direction normal to the material plane and Dirichlet boundary conditions was used in the Poisson equation for this direction. The bulk electron-phonon interaction and phonon dispersion was obtained from a  $11 \times 11$  supercell calculation in the case of graphene and a  $9 \times 9$  supercell for silicene and MoS<sub>2</sub>. The delta-functions in eqn. 4 were numerically represented by lorentzians with a broadening of 3 meV.

One obtains linear valence and conduction bands near the Dirac point, K, in both graphene and silicene, as shown by the band structures in Fig. 2A. Both materials have six phonon branches. The three acoustic modes will dominate the low temperature scattering where two modes have a linear q-dependence and the third out-of-plane acoustic (ZA) mode has a q<sup>2</sup>-dependence near the Brillouin zone center, see Fig. 2B. MoS<sub>2</sub> is found to be a direct-gap semiconductor with a band gap of  $1.89 \,\text{eV}$ , see Fig. 2C. The electron- and phonon bandstructures, in Fig. 2C-2D, are consistent with previous theoretical results[10].

We now turn to the calculated bulk electron-phonon coupling, as obtained from a basis of localized orbitals employing a supercell method and finite differences. In Fig. 3 we illustrate the bulk electron-phonon interaction obtained for the four modes coupling with electrons in graphene. The interaction is obtained around 300 meV from the Dirac *K*-point, and the



Fig. 2. Electron bandstructure of A) graphene and silicene and C)  $MoS_2$  and phonon dispersion of B) graphene and silicene and D)  $MoS_2$ .



Fig. 3. Bulk electron-phonon coupling in graphene for the four modes with nonzero coupling. The interaction is illustrated as a function of phonon q-vector at a k-point shifted 300 meV from the Dirac K-point towards the  $\Gamma$ -point. We refer the reader to [6] for a detailed discussion of the interpretation of the plots for the TA and LA modes. The scattering rate is obtained as an integral around a constant energy circle satisfying  $\varepsilon_{\mathbf{k}'} = \varepsilon_{\mathbf{k}} + \hbar\omega$ .

interaction with the acoustic modes seems slightly higher but with same symmetry as in previously published results[6]. Unlike graphene, the carriers in silicene display a strong interaction with the ZA mode[11], see Fig. 4. This is related to the buckling of the silicene sheet, where one basis atom is displaced approximately 0.44 Å out-of-plane hence breaking the planar symmetry.

In Fig. 5 we show the bulk electron-phonon interaction obtained for the five modes coupling with electrons in  $MoS_2$ . Unlike graphene and silicene, which are semimetals,  $MoS_2$ 





Fig. 4. Bulk electron-phonon coupling in silicene. Unlike graphene also the out-of-plane modes (ZA, ZO) couple significantly with electrons. The interaction is illustrated as a function of phonon **q**-vector at a **k**-point shifted from the Dirac K-point towards the  $\Gamma$ -point. The scattering rate is obtained as an integral around a constant energy circle satisfying  $\varepsilon_{\mathbf{k}'} = \varepsilon_{\mathbf{k}} + \hbar\omega$ . Previous studies have calculated the life-time of carriers in silicene[11].

is a semiconductor and the interaction is evaluated at the conduction band minimum, since only n-doping is relevant in MoS<sub>2</sub>. Again we find very anisotropic couplings where the symmetry compares well to previously published results[10]. We obtain a lower coupling for the homopolar mode, see Fig. 5D, but the coupling with the TA, LA and TO modes are of the same magnitude, Fig. 5A,B,C. Fig. 5E shows the Fröhlich interaction for the polar optical LO<sub>2</sub> mode. The Fröhlich interaction is difficult to converge with respect to supercell size. In the long-wavelength limit this element should diverge. We find that the peaks increase in magnitude and move toward  $|\mathbf{q}| \rightarrow 0$  if the supercell size is increased from  $9 \times 9$  to  $15 \times 15$ .

In Fig. 6 we illustrate the obtained carrier concentration and mobility<sup>1</sup> of graphene, silicene (A, B) and MoS<sub>2</sub> (C, D). We only include intervalley scattering in the present analysis. The electron-phonon coupling is evaluated for every k-point in a 100 × 100 q-mesh up to an energy-cutoff. The coupling, energies and velocities were subsequently interpolated to twice

Fig. 5. Bulk electron-phonon coupling in  $MoS_2$ . The interaction is illustrated as a function of phonon **q**-vector at the conduction band minimum K-point.

this q-space resolution before the BTE was solved. For the k-space we evaluate the scattering rate in the k-points that contribute, from a very dense  $1500 \times 1500$  Monkhort-Pack sampling of the first Brillouin zone, up to a given fermi-level/carrier-density.

The intrinsic mobilities calculated here shows that graphene can have a mobility close to  $10^5 \, \mathrm{cm}^2 / \mathrm{Vs}$  at  $100 \, \mathrm{K}$  and a carrier density of  $10^{12}$  cm<sup>-2</sup>. In addition, we find the mobility of silicene to be slightly lower than graphene but still very high. For MoS<sub>2</sub> our calculated mobility decreases from a value of  $2500 \,\mathrm{cm^2/Vs}$  at  $100 \,\mathrm{K}$  to approx  $500 \,\mathrm{cm^2/Vs}$  at 300 K. These results are in good agreement with published first principles simulations and experimental values[10], [12]. We note that the electron-phonon coupling as a function of q, as was shown for all materials for a single k-point, was evaluated at all k-points in the mobility calculations. Another approach that is often applied is to evaluate the scattering rate along a single k-line obtained from a  $|g_{\mathbf{k}\mathbf{k}'}^{\lambda nn'}|$  at a fixed k-point. This can be transformed to a generic energy-dependence which is used to evaluate the mobility. This approach however, neglects part of the anisotropy in the bulk electron-phonon coupling, which was included in the presented results.

<sup>&</sup>lt;sup>1</sup>The mobility calculations were carried out on a cluster of 128 CPUs (Intel Xeon E5-series) and took approximately 24 hours for each material. Most of the time was used for evaluating the bulk electron-phonon interaction in the **k**- and **q**-space, which however shows close to linear speedup.



Fig. 6. Carrier concentration as a function of Fermi-level for graphene and silicene (A) and  $MoS_2$  (C). The conduction band edge of  $MoS_2$  is at 0.95 eV. The mobility as a function of carrier density is also shown for graphene (B) and silicene (B, inset) and  $MoS_2$  (D).

### **IV. CONCLUSION**

In summary, we have presented a Boltzmann Transport Equation (BTE) solver implemented in the Atomistix ToolKit (ATK) simulation tool. The method allows for calculation of material properties, including the electron-phonon interaction, from first principles. We have applied the tool to calculate the phonon-limited mobility in intrinsic n-type monolayer graphene, silicene and  $MoS_2$ . Our results compares well to published theoretical results and experiments for  $MoS_2$  and graphene and extends previous theoretical calculations for silicene. The simulations provide an upper bound for the electron mobilities of the selected two-dimensional materials.

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