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1. Background

To study the phonon properties of an infinite or semi-infinite system, two approaches are widely used: Green's function (GF) approach and slab model approach. Take the surface phonon for example, surface resonance modes and surface isolated modes are two types of surfaces-related phonons. Green's function approach can be used to obtain the frequency information of both modes easily and accurately. The slab model with increasing thickness is a good method to identify the surface-isolated modes which keeps unchanged with thickness, but it is not able to gain information of surface resonance modes. The advantage of slab model is it can provide information of atomic displacements of phonons directly from eigenvectors.

In this manual, we provide the theory and instructions of the python code `GreensFunction.py`. This code is used to get the GF density of states (GF DOS) of phonons for a system bonded with

a semi-infinite lead at a specific wavevector. It also can be used to obtain GF DOS for a solid to study the surface projected phonon band of a solid.

2. Theory of Green's function approach

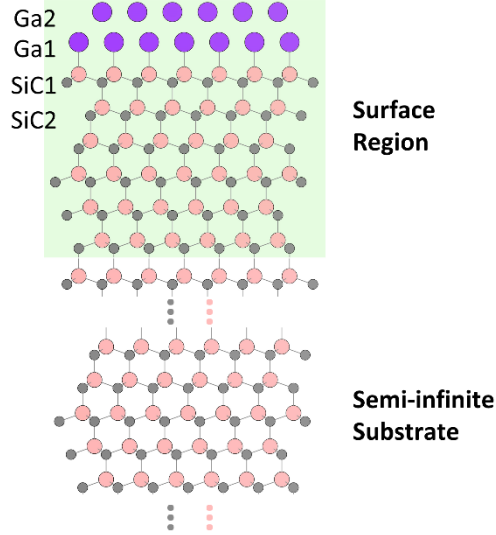


Figure 1. Atomic structure of 2D Ga/SiC semi-infinite system. The surface region used in the Green's function approach is indicated in green. The bottom is a semi-infinite SiC substrate.

The theoretical part is from the ref [1].

The Green's function \tilde{G} corresponding to the dynamical matrix of a system is given by

$$(\epsilon I - D)\tilde{G} = I, \quad (1)$$

where $\epsilon = (\omega + i\eta)^2$; η is a positive infinitesimal number 0^+ ; I is the identity matrix; D is the dynamical matrix; \tilde{G} is the Green's function matrix of the whole system which can be partitioned according to individual parts.

A 2D system (2D Ga) bonded with a semi-infinite substrate (SiC) is illustrated in **Figure 1**. Hence, the dynamical matrix in Equation (1) is a semi-infinite matrix. The Green's function \tilde{G} can be partitioned into submatrices as follows

$$\tilde{G} = \begin{bmatrix} G_S & G_{SB} \\ G_{BS} & G_B \end{bmatrix} = \begin{bmatrix} (\epsilon I_S - D_S) & d_{SB} \\ d_{SB}^\dagger & (\epsilon I_B - D_B) \end{bmatrix}^{-1}, \quad (2)$$

where the matrix $(\epsilon I_S - D_S)$ corresponds to the surface region; $(\epsilon I_B - D_B)$ is a semi-infinite matrix of the substrate; d_{SB} and d_{SB}^\dagger (\dagger represents conjugate transpose) are the coupling matrices

which take into account interactions between the surface region and the substrate. We include interactions between all atoms in the surface region. For the coupling matrices, the interactions between the nearest six layers of SiC, which is one unit of 6H-SiC in the bulk, are included. This is obtained by the density functional perturbation calculations (DFPT) of SiC bulk. To get interactions between the nearest 6L SiC, it is better to compute the dynamical matrix of a 1x1x2 SiC bulk and apply a truncation to the dynamical matrix.

The retarded Green's function of the surface region can be expressed explicitly as

$$G_S = (\epsilon I_s - D_S - \Sigma)^{-1}, \quad (3)$$

where $\Sigma = d_{SB} G d_{SB}^\dagger$ is the self-energy term. G is the so-called uncoupled Green's function of the substrate[2]. The self-energy Σ is calculated by an iterative procedure[3, 4] discussed below.

The self-energy term Σ in Equation (3) arises from couplings between the surface region and the bottom substrate. In other words, it corrects the finite boundary at one end of the isolated surface region to a semi-infinite boundary. The substrate can be treated as the semi-infinite stack of principle layers with nearest-neighbour interactions. Hence in 2D Ga/SiC systems, each principle layer contains one 6H-SiC unit and interactions between the nearest six SiC layers are considered.

Since the surface region contains one principle layer of SiC, the elements of d_{SB} are assumed to be zero for all elements that connect this principle layer (A) to other principle layers in the bulk that are not the nearest neighbour to A. So Σ can be obtained by

$$\Sigma = d_{SB,S0} G_{00} d_{SB,S0}^\dagger \quad (4)$$

where the subscript '0' refers to the first principle layer in the bulk. G_{00} is known as the surface Green's function[2] and is the first element in the uncoupled Green's function matrix G , given by

$$(\epsilon I_B - D_B)G = I, \quad (5)$$

where the submatrix D_B is the dynamical matrix of bulk SiC. To compute G_{00} , we introduce the calculation of uncoupled Green's function here[4].

As the semi-infinite substrate can be treated as a linear chain of principle layers, the Equation 5 leads to series of equations (the identity matrix after ϵ are omitted below)

$$\begin{aligned} (\epsilon - D_{00})G_{00} &= I + D_{01}G_{10} \\ (\epsilon - D_{00})G_{10} &= D_{01}^\dagger G_{00} + D_{01}G_{20} \\ &\dots \\ (\epsilon - D_{00})G_{n0} &= D_{01}^\dagger G_{n-1,0} + D_{01}G_{n+1,0}, \end{aligned} \quad (6)$$

where D_{nm} and G_{nm} are matrix elements of the dynamical and Green's function matrix, and there is $D_{00} = D_{nn}$ and $D_{01} = D_{n,n+1}$ for all n . Lopez-Sancho et al[3] have introduced the transfer matrices T and \bar{T} to describe the relationship between the Green's function of one individual principle layer and that of the preceding or following one. This is given by $G_{10} = TG_{00}$ and $G_{00} = \bar{T}G_{10}$. These transfer matrices can be obtained through an iterative procedure as

$$\begin{aligned} T &= t_0 + \tilde{t}_0 t_1 + \tilde{t}_0 \tilde{t}_1 t_2 + \cdots + \tilde{t}_0 \tilde{t}_1 \tilde{t}_2 \dots t_n \\ \bar{T} &= \tilde{t}_0 + t_0 \tilde{t}_1 + t_0 t_1 \tilde{t}_2 + \cdots t_0 t_1 t_2 \dots \tilde{t}_n, \end{aligned} \quad (7)$$

where t_i and \tilde{t}_i are given by the recursion formulas

$$\begin{aligned} t_i &= (I - t_{i-1} \tilde{t}_{i-1} - \tilde{t}_{i-1} t_{i-1})^{-1} t_{i-1}^2 \\ \tilde{t}_i &= (I - t_{i-1} \tilde{t}_{i-1} - \tilde{t}_{i-1} t_{i-1})^{-1} \tilde{t}_{i-1}^2, \end{aligned} \quad (8)$$

and the initial matrix

$$\begin{aligned} t_0 &= (\epsilon - D_{00})^{-1} D_{01}^\dagger \\ \tilde{t}_0 &= (\epsilon - D_{00})^{-1} D_{01}. \end{aligned} \quad (9)$$

The iterations should be enough to get converged transfer matrices or until $t_n, \tilde{t}_n \leq \delta$ where δ is small. From the first equation in Equation 6 set and the definition of T , we can get the surface Green's function

$$G_{00} = (\epsilon - D_{00} - D_{01}T)^{-1}. \quad (10)$$

Using equation 3 and 4, we can get the Green's function of the surface region.

The spectral function of the surface region is given by

$$A(\omega) = i(G_S - G_S^\dagger), \quad (11)$$

and the density-of-states (DOS) is given by

$$DOS(\omega) = \omega Tr(A(\omega))/\pi. \quad (12)$$

The DOS defined here is the GF-DOS in the main text. η is $1E^{-8}$ in our calculations.

In the case of a solid which is infinite on both side, the self-energy correction from both right and left leads are required. Hence the Green's function of a solid can be obtained by

$$G_{solid} = (\epsilon - D_{00} - D_{01}T - D_{01}^\dagger \bar{T}). \quad (13)$$

The surface-projected bulk phonon bands of a bulk system can be obtained by a series of Green's function density of states at in-plane wavevectors along high-symmetry paths using equation 12 and 13.

3. How to use the code?

3.1. Input files

| File name | Description |
|--------------------------|--|
| dyn_3Nx3N-bulk.dat | D_{00} (Equation 5) Dimension: NxN |
| dyn_3Nx3N-connection.dat | D_{01}^{\dagger} & d_{SB}^{\dagger} : Two matrices are same because the surface region includes a part of substrate as shown in Figure 1. (Equation 2 & 5) Dimension: NxN |
| dyn_3Rx3R-device.dat | D_S (Equation 2) Dimension: RxR |

3.2. Output files

| File name | Description (x-axis: frequency (cm^{-1})) |
|-------------|--|
| Dos.dat | $DOS(\omega)$ (Equation 12) |
| Spectra.dat | $A(\omega)$ (Equation 11) |

3.3. Input parameters

| Parameters | Description |
|--------------|-------------------------------------|
| n_atm | N |
| n_atm_device | R |
| omega | First frequency of DOS (unit: Ry) |
| omega_max | Upper limit of frequency (unit: Ry) |
| omega_step | Step size of frequency (unit: Ry) |

| | |
|----------|--|
| zero | Positive infinitesimal number (unit: Ry) |
| it_cycle | Iterative cycle. (Increase it to make sure the convergence of your result) |

3.4. GF DOS of the surface region

Prepare all inputfiles and the code in the same folder, then use the command below:

```
$ module load Python
$ module load numpy
$ python GreensFunction.py
```

3.5. GF DOS of a solid

Look into the code, then comment and uncomment some lines as instructed. (Line 162-179)

After that, use the code as that in 3.4.

3.6. Notes

- If you cannot run the code, try again after removing the comment lines on top.
- For off-gamma point, you need to provide dynamical matrix at the same q-point for all input files. And use the same code.
- Dynamical matrix(D) elements are computed from force constant matrix (FC) given by “.dyn” file of QuantumEspresso. $D_{pi,qj} = FC_{pi,qj} / \sqrt{M_p M_q}$, where p and q are indices of atoms, i and $j = x, y, z$. $FC_{pi,qj}$ is in the unit of Ry/Bohr.
- Please cite the paper J. Phys. Chem. Lett. 2022, 13, 18, 4015–4020 (Shear Modes in a 2D Polar Metal) if you use this code. And please cite the original papers about GF approach ref. 2-4.

4. References

- [1] He, W., M.T. Wetherington, K.A. Ulman, J.L. Gray, J.A. Robinson, and S.Y. Quek, *Shear Modes in a 2D Polar Metal*. J. Phys. Chem. Lett., 2022. **13**(18): p. 4015-4020.
- [2] Sadasivam, S., Y. Che, Z. Huang, L. Chen, S. Kumar, and T.S. Fisher, *The Atomistic Green's function Method for Interfacial Phonon Transport*. Annu. rev. heat transf., 2014. **17**: p. 89-145.
- [3] Sancho, M.P.L., J.M.L. Sancho, J.M.L. Sancho, and J. Rubio, *Highly Convergent Schemes for the Calculation of Bulk and Surface Green Functions*. J. Phys. F: Met. Phys., 1985. **15**(4): p. 851-858.
- [4] Nardelli, M.B., *Electronic Transport in Extended Systems: Application to Carbon Nanotubes*. Phys. Rev. B, 1999. **60**(11): p. 7828-7833.
- [5] Giannozzi, P., S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, and R.M. Wentzcovitch, *QUANTUM ESPRESSO: A Modular and Open-source Software Project for Quantum Simulations of Materials*. J. Condens. Matter Phys., 2009. **21**(39): p. 395502.