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Green's function modeling of response of two-dimensional materials to point probes for scanning probe microscopy ☆

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ABSTRACT

A Green's function (GF) method is developed for interpreting scanning probe microscopy (SPM) measurements on new two-dimensional (2D) materials. GFs for the Laplace/Poisson equations are calculated by using a virtual source method for two separate cases of a finite material containing a rectangular defect and a hexagonal defect. The prescribed boundary values are reproduced almost exactly by the calculated GFs. It is suggested that the GF is not just a mathematical artefact but a basic physical characteristic of material systems, which can be measured directly by SPM for 2D solids. This should make SPM an even more powerful technique for characterization of 2D materials.

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1. Introduction

Since the advent of graphene [1], many new [2] two-dimensional (2D) materials have been synthesized and tested. These include silicene [3–6], germanene [3], stanene [7], phosphorene [8], geometrically-modified graphene [9,10], hexagonal boron nitride [11], and single-layer transition-metal dichalcogenides (i.e., MoS_2 [12], $MoSe_2$ [13], WS_2 [14], WSe_2 [15], and $PtSe_2$ [16]), which have received much attention in recent years. These new materials have the potential to revolutionize the materials industry due to their size and unique electronic, mechanical, thermal, and photonic properties [12,14,15,17,18] (for reviews and other references, see [19,20]). Because of their low dimensionality, small structural changes can significantly affect the transport and other physical properties of 2D materials [9,10]. It is therefore important to develop accurate and fast characterization techniques for these materials, supported by robust and computationally efficient mathematical models. Such techniques are needed to accelerate the industrial application of these materials.

Scanning tunneling microscopy (STM) is a scanning probe microscopy (SPM) technique that uses raster scanning and tunneling electrons to map out the nanoscale topography and electronic properties of conductive surfaces [21]. In addition to the conventional atomic force microscopy (AFM), SPM includes new powerful techniques such as scanning electrostatic microscopy (SESM) and scanning thermal microscopy (SThM). In a typical SPM experiment, one measures the response of the sample to a point probe or a distribution of point probes. Interestingly, that is exactly the mathematical definition of the Green's function – response to a point probe [22]. A Green's function (GF) based method is, therefore, the natural choice for modeling SPM experiments on 2D materials.

Normally GF is understood to be a mathematical technique that is used for solving operator equations. In fact, GF is more than that. An operator in physics represents a process of measurement. The GF corresponding to an operator is the inverse of that operator and gives the response [23] of the material to the measurement process represented by that operator. The GF is independent of the probe and, operating on the probe, it gives the result of that measurement. If, instead of calculating it through various mathematical steps and physical assumptions, the GF can be directly measured, it should prove to be a valuable tool for physical characterization as well as mathematical modeling of materials.

Here we suggest that the GF is a physical entity that contains all the information about the material as modeled by the corresponding operator equation. At least for a 2D material, the GF can be measured directly by SPM. The measurability of the GF is particularly useful because, in principle, it can be used for modeling other related characteristics of that material. This is an interesting

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example of an apparently mathematical artefact becoming a tool for experimental characterization of 2D materials.

Of course even for 3D materials, SPM yields response to a point force. However, SPM can directly measure the response only at the same surface at which the probe is applied. For ordinary 3D solids, the physical characteristics of a surface are, in general, different than the bulk of the material. Moreover, many other factors contribute to the surface response such as interlayer interactions, presence of randomly distributed point defects as well as topological and extended defects such as dislocations, stacking faults, etc. All these contributions make it very difficult to deconvolve the measured response to extract useful values of the GF. The availability of single layer 2D solids has now made it possible to actually measure the GF.

In this paper we describe a GF method for solving the Poisson equation, or its homogeneous part the Laplace equation, in 2D materials. The Poisson equation gives the distribution of the electric field or voltage in electrostatic experiments such as in SESM or the temperature field in SThM. The Poisson equation is a highly studied equation because of its wide range of applications. Its analytical solution is possible only for fairly simple geometries and infinite solids [24]. For any realistic geometry or for finite solids, one has to resort to partial or fully numerical techniques.

A major advantage of the GF method is that it is partly analytic. We start with an analytical form of the free-space GF for a perfect infinite solid and then impose suitable boundary and/or continuity conditions to simulate finite boundaries and defects. We use the virtual source (VS) method for satisfying the prescribed boundary conditions. The VS method is analogous to the virtual force method, which was used previously in elastostatics for planar boundaries [25–27]. In this paper, we have adopted this method to boundaries of arbitrary shapes. The test of the reliability of a solution of any boundary value problem is how well the boundary conditions are satisfied. We find that the calculated GF satisfies the boundary conditions almost exactly.

The material system that we consider in this paper is a perfectly flat 2D finite material containing a single rectangular or hexagonal defect of finite size. The VS method is very general and is applicable to material systems containing any number of defects. Further, the defects can be of arbitrary shapes and sizes. A defect may be an antidot or an inclusion of a different material as used for functionalization. An antidot in a 2D material is a hole, which corresponds to a void in a 3D material. Antidots [9,10,28] in graphene are of strong topical interest because they can be engineered to tune the electric and thermal characteristics of the material. Various designs and arrays of antidots and inclusions have been proposed in the literature for making efficient thermoelectric devices for energy harvesting and energy conversion [29]. For all such applications, we need to solve the Poisson/Laplace equation, which is the objective of the present paper.

2. Mathematical formulation

Perhaps the most common numerical technique used for solving the Poisson/Laplace equation is the finite element method (FEM). The FEM is an extremely versatile and powerful technique but computationally rather expensive. It requires inversion of $N_v \times N_v$ matrices where N_v is the number of all the points in the bulk of the material. It is necessary to solve the equation numerically at all the points in the solid even if the results are needed only in a small region, which is often the case.

An alternative to the FEM for linear problems is the boundary element method (BEM), which involves integrals only near the boundaries or discontinuities in the solid where the boundary conditions are prescribed [26]. The BEM requires inversion of $N_s \times N_s$ matrices where N_s is the number of points at the boundary (or surface in 3D systems). Since N_s is much smaller than N_v, the BEM requires inversion of matrices of much lower dimensions as compared to the FEM. However, it does not necessarily have a major advantage over the FEM in terms of computational efficiency. This is because the matrices to be inverted in the FEM are large but sparse, whereas in the BEM they are smaller but dense. Many other methods [25–27,30,31] for calculating the GF are available in the literature such as those based upon integral transforms, complex variables, Dyson's equation, etc. These methods are useful for specific geometries.

We use the GF method, which is intimately linked with the BEM. The BEM uses free-space GF as the starting solution and the Green's or the Gauss theorem with suitable interpolation functions to satisfy the prescribed boundary conditions. For an excellent discussion of the GF and its mathematical properties along with its applications to various materials systems of interest, see the recent monograph by Pan and Chen [32].

In our GF method, we obtain the final GF directly by using a suitable distribution of VSs. The final GF incorporates all the boundary conditions and gives the total response of the material system. Thus, it includes the effect of any defects such as surfaces, boundaries, and discontinuities associated with various defects in the material. The final GF is also called the defect GF in contrast to the free infinite space GF, which is called the perfect GF. In the interest of brevity in this paper, unless stated otherwise, GF will refer to the final GF.

The VS method is somewhat similar to the method of images [24] in electrostatics. The VSs are applied just outside the boundary of the solution domain. The boundary conditions are specified on a contour just inside the boundary. Thus, the contour at which the boundary conditions are prescribed is just inside the solution domain whereas the contour at which the VSs are applied, are just outside the solution domain. This ensures that the VSs give a solution of the homogeneous equation. Further, the differential separation between the loci of the VS and the boundary values avoids the characteristic singularity in the GF at a point where the source and the field points coincide.

The VS method is rapidly convergent and numerically stable. The main computational cost of our GF method is in the calculation of the VSs. However, the VSs are in modular form and can be stored for later use. This can reduce the subsequent computational cost. One computational advantage of our GF method is that we need to numerically solve the main equation only near the boundaries or the discontinuities. In the bulk of the solution domain, the solution is given in a semi-analytic form in terms of the GF and/or its derivatives and the VSs. The most important advantage of the GF method is, as mentioned before, that it gives the response of the material to a point electrostatic or thermal probe, which is directly measurable by SPM.

Fig. 1 shows the geometry of the 2D material that we model. We neglect the discrete atomistic structure of the material so our calculations are valid at length scales larger than the atomistic dimensions. This is consistent with the continuum approximation inherent in the Laplace/Poisson equation. This allows us to neglect the zig-zag structure of the edges and any ripples or unevenness at the surface. Thus, the treatment given here is applicable to graphene as well as other 2D materials beyond graphene.

We consider two separate types of defects – rectangular (Fig. 1(a)) and hexagonal (Fig. 1(b)). The shape of the host solid in both the cases is assumed to be a square. We choose a 2D Cartesian frame of reference. The coordinate axes are assumed to be parallel to the outer edges of the solid with the origin at the center as shown in Fig. 1. We denote the position vector of a point by $\boldsymbol{r}$ (written in bold) and its X and Y coordinates by the subscripts 1 and 2. Thus $r_1 = X$ and $r_2 = Y$. The magnitude of a vector $\boldsymbol{r}$ is de-