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Intrinsic Conductivity of Carbon Nanotubes and Graphene Sheets Having a Realistic Geometry^{*,†}

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Abstract

The addition of carbon nanotubes (CNTs) and graphene sheets (GSs) into polymeric materials can greatly enhance the conductivity and alter the electromagnetic response of the resulting nanocomposite material. The extent of these property modifications strongly depends on the structural parameters describing the CNTs and GSs, such as their shape and size, as well as their degree of particle dispersion within the polymeric matrix. To model these property modifications in the dilute particle regime, we determine the leading transport virial coefficients describing the conductivity of CNT and GS composites using a combination of molecular dynamics, path-integral, and finite-element calculations. This approach allows for the treatment of the general situation in which the ratio between the conductivity of the nanoparticles and the polymer matrix is arbitrary so that insulating, semi-conductive, and conductive particles can be treated within a unified framework. We first generate ensembles of CNTs and GSs in the form of self-avoiding worm-like cylinders and perfectly flat and random sheet polymeric structures by using molecular dynamics simulation to model the geometrical shapes of these complex-shaped carbonaceous nanoparticles. We then use path-integral and finite element methods to calculate the electric and magnetic polarizability tensors (α_E , α_M) of the CNT and GS nanoparticles. These properties determine the conductivity virial coefficient $[\sigma]$ in the conductive and insulating particle limits, which are required to estimate $[\sigma]$ in the general case in which the conductivity contrast between the nanoparticle and the polymer matrix is arbitrary. Finally, we propose approximate relationships for α_E and α_M that should be useful in materials design and characterization applications.

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I. INTRODUCTION

Allotropes of carbon such as carbon black [1–3], fullerenes [4, 5], carbon nanotubes (CNTs) [6–9], carbon fiber [10] and graphene sheets (GSs) [11–15] have long-standing interest as fillers to enhance the mechanical and electrical properties of polymeric materials. Current and potential applications of nanocomposites utilizing carbon-based nanoparticles exist in the optics, electronics, biotechnology, and aerospace fields [11, 12, 16, 17]. However, to fully take advantage of the special properties of these materials, it is necessary to have a better understanding of how the different structural parameters of these nanofillers, such as size and shape, as well as the degree of dispersion of these fillers in the polymer matrix, impact the properties of the resulting composite material. The present work centers on the dilute particle limit where particle dispersion is not an issue. This regime is also central to particle characterization, as in the case of polymer characterization [18, 19].

There have been many recent experimental studies of the electrical conductivity σ of polymer nanocomposites with CNT [7, 20–22] and GS [15] additives, as well as several reviews on this topic [6, 11, 16, 23–25]. Theoretical analyses of the conductivity of these materials treat the CNTs and GSs as idealized rods [22] and platelets, respectively, and this type of calculation assumes that the polymer matrix has a zero conductivity and that the onset of material conductivity is associated with the onset of geometrical percolation. We approach this problem differently, allowing the pure polymer medium to have a finite conductivity that becomes altered by the nanoparticle additives, even in the absence of geometrical percolation. We also treat the nanoparticle shape with much greater realism. Based on this more fundamental approach, initiated by Maxwell [26, 27] for spherical particle additives and extended by Fricke [28–30] for ellipsoidal particles, we calculate σ for these carbon-based composites. In particular, the change of electrical conductivity σ as well as the thermal conductivity [31–33] for a material containing arbitrarily shaped objects having a different conductivity σ_{particle} can be exactly described within continuum theory as a virial expansion in the particle concentrations [34],

$$\sigma/\sigma_{\text{matrix}} = 1 + [\sigma]\phi + O(\phi^2), \quad (1)$$

where $[\sigma]$ is the leading conductivity virial coefficient or “intrinsic conductivity” and ϕ is the volume fraction of the particles [35]. Since the pioneering work of Fricke [28–30], Eq. (1) has been used in a wide range of applications such as determining the volume fraction of white blood cells in blood, the fat content of milk and in a geological context where it is used in the estimation of the porosity of soil and rock formations. In those applications, the matrix fluid is generally complex, even without these inhomogeneities, so that the utility of Eq. (1) relies on impurity effects that largely cancel in the *ratio*, $\sigma/\sigma_{\text{matrix}}$. A similar philosophy has been applied recently to describe the viscosity of particle suspensions in the situation where the matrix is non-Newtonian [36]. We also note the successful application of Eq. (1) to describe the thermal conductivity of suspensions of multi-wall CNTs [37] and laponite suspensions [38], the nanoparticle types considered in the present work. Finally, Eq. (1) is also a basic starting point for any description of σ at higher particle concentration ϕ . Moreover, $[\sigma]$ is also basic input into effective medium theory [39] or any other continuum theory description of the conductivity of composites at non-dilute particle concentrations.

The electric polarizability tensor α_E and the magnetic polarizability tensor α_M arise in the determination of $[\sigma]$ for limiting values of the conductivity relative to the polymer matrix [34], as we discuss in Sections III and IV. This calculation is complicated by the fact that $[\sigma]$ depends on the property contrast, the ratio between the particle conductivity to that of the surrounding media, but Garboczi and Douglas [35] have shown that $[\sigma]$ for particles having any arbitrary shape and size can be expressed to an excellent approximation by the Padé approximant,

$$[\sigma(\Delta)] = \frac{[\sigma]_\infty (\Delta - 1)^2 + a (\Delta - 1)}{(\Delta - 1)^2 + ([\sigma]_\infty + a/d) (\Delta - 1) + a}, \quad (2)$$

where d is the spatial dimensionality and a is a particle shape-dependent constant,

$$a = \frac{[\sigma]_\infty - [\sigma]_0 + [\sigma]_\infty [\sigma]_0}{1 + (1 - 1/d) [\sigma]_0}. \quad (3)$$

Here, $[\sigma]_\infty$ and $[\sigma]_0$ are the limiting values of $[\sigma]$ as $\Delta \rightarrow \infty$ and $\Delta \rightarrow 0$, respectively, and these quantities only depend on α_E and α_M polarizability tensors. A complete determination of $[\sigma(\Delta)]$ in the case of arbitrary particle shape and property contrast then requires a knowledge of α_E and α_M . Although Eq. (2) greatly simplifies our calculations, the determination of $[\sigma]_\infty$ and $[\sigma]_0$ is still not an easy task. Despite their obvious practical importance, the quantities have been calculated for only a limited number of shapes because of the well-known difficulty of calculating these properties analytically. Even numerical finite element calculations for non-trivial shapes are minimally available and difficult to perform accurately [34]. The reliance on percolation modeling, and its implicit assumption that $\sigma_{\text{matrix}} = 0$, has led to a neglect of the determination of $[\sigma]$ in nanocomposites, although the determination of this quantity for other mixtures is actually rather common [34]. Information about $[\sigma]_0$ is particularly sparse, and the present work is the first study of these structures for objects having the complexity of CNTs and GSs.

Although peripheral to our main topic of calculating σ for composite materials, α_E and α_M arise in any consideration of the forces [40, 41] and torques acting when electromagnetic fields are applied to separate [42], align [43, 44] or manipulate nanoparticles [45–47]. Specifically, the force and torque exerted on the nanoparticle are directly determined by the polarizability tensor components [48]. The optical absorption properties of metal nanoparticles having different shapes and cluster geometries also depend on α_E [49, 50]. A better theoretical understanding of these polarizability tensors is thus highly relevant for manipulation of these nanoparticles and characterization of their optical properties. There are also electrodynamic relationships linking these polarizability tensors to hydrodynamic particle properties described by similar mathematics. Specifically, α_M of a conductive body mathematically equals (up to a proportionality constant) the hydrodynamic virtual mass tensor $\mathbf{M}$ [51] and α_E is related to the stress dipole created when shearing a suspension of particles [34]. The hydrodynamic–electrodynamic analogies are a source of useful information about $[\sigma]$ [34] that can be applied to test numerical methods for calculating $[\sigma]$.

Treating CNTs and GSs as rods and sheets, respectively, is clearly a rather crude model for nanoparticle additives, and we have thus made a concerted effort to calculate these tensors based on more physically realistic models of the CNTs and GSs. While our illustrative particle types have significant research interest, our computational methods apply to almost any type of particle that one might encounter, even nanoparticles with grafted polymer layers [52] or nanoparticles with protein or other complex adsorbed structures such as DNA-wrapped CNTs [53].

The CNTs are modeled as fixed radius three dimensional (3D) rod-like and worm-like tubes having different persistence lengths. We model the GSs as two-dimensional polymers [54] having different flexibilities and a finite thickness, where the lateral dimensions are larger than the thickness. A continuum approach is used to calculate the polarizability tensors of model CNTs and GSs whose structures are generated by MD. The justification for this continuum approach to evaluate the polarizability of these nanosized particles is based on studies demonstrating the close agreement between continuum analyses, *ab-initio* analyses and experimental measurements. For example, Paillet et al. [55] experimentally probed the charge distribution on individual CNTs and found that the distribution can be explained by classical electrostatics. As for *ab-initio* analysis, the Density Functional Theory (DFT) was found to agree well with the distribution calculated using electrostatic analysis under the assumption that all the atoms in the outer layer of the CNT are at a constant potential [56, 57]. This continuum approach accords with the traditional approach to polymers in solution and the success of this approach motivates its extension to CNTs and GS, which are likewise polymeric structures.

The paper is organized as follows. In section II, we describe the molecular model utilized to generate configurations of CNTs and GSs via MD. In Section III, we show the results for α_E calculations using the path-integral software ZENO [58] and the commercial finite-element package COMSOL[*] [59, 60] for the configurations generated by MD. In Section IV, we present the results for α_M calculated using COMSOL. In Section VI, we develop approximations to determine the components of α_E for the morphologies studied here. We conclude in Section VII.

II. MOLECULAR MODEL FOR CARBON NANOTUBES AND GRAPHENE SHEETS

In this section, we describe the coarse-grained model utilized to generate the CNT and GS geometrical structures. The main goal of using these molecular models is to reproduce the salient physical features of CNTs and GSs. This approach is validated by comparing the nanoparticle morphologies generated by our model with the ones observed by high resolution imaging (see Figure 1) and the motivation for our choice of interparticle potentials involved in our modeling is given in a previous paper [61]. Briefly, the potentials allow us to create representative configurations of CNTs and GSs. The same models that we use for CNTs and GSs have been successfully applied before to model duplex DNA [62] and DNA origami [52], where the parameters of the interaction potentials are chosen to take into

account the effects of hydration, polarizability, and charge condensation that are difficult to treat by atomistic modeling.

A. Carbon Nanotube Molecular Model

In this model, each CNT is represented by a number of beads (N) connected by springs (bead-spring model [63]). All the beads interact via a Weeks–Chandler–Andersen (WCA) potential,

$$U_{WCA}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \epsilon & \text{for } r \leq 2^{1/6} \sigma \\ 0 & \text{for } r > 2^{1/6} \sigma, \end{cases} \quad (4)$$

where r is the radial distance between the centers of two beads, and σ and ϵ are the length and energy Lennard–Jones parameters, respectively. Neighboring beads along the chain are connected via a finitely extensible, nonlinear elastic (FENE) anharmonic spring potential,

$$U_{FENE}(r) = -\frac{kR_0^2}{2} \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right], \quad (5)$$

with the bond strength $k = 30 \epsilon / \sigma^2$ and maximum bond extension $R_0 = 1.5 \sigma$.

Since we would like to mimic the geometrical properties of commercial CNTs, we relate $\sigma \approx 21$ nm to the diameter of multi-walled CNTs [64–66]. We consider an average density of $\rho_{\text{CNT}} = 1.726$ g/cm³ for the multi-walled CNTs [67], and we generate CNTs having lengths $L \approx (210, 420, 1500, 2100, 4200, \text{ or } 15000)$ nm. Additionally, neighboring connected beads along the CNT interact via a bending potential,

$$U_{\text{bend}}(\theta) = k_{\text{bend}} [1 - \cos(\theta)], \quad (6)$$

where k_{bend} is the bending constant for the CNTs, and θ is the angle formed by three consecutive beads. In this study, we consider $k_{\text{bend}} = 9 \epsilon, 40 \epsilon$ and 80ϵ , which provide CNT persistence lengths $l_p = (187 \pm 3.2)$ nm, (724 ± 4.2) nm and (1736 ± 5.6) nm, respectively. We present the methodology for the calculation of l_p in the supplemental information [68]. The variation of l_p on the experimental measurements has been attributed to different synthesis conditions, including variations in catalysis type, e.g., Ni, Co, Fe, catalysis concentration, and synthesis temperature [66]. Figure 1 (a) shows a representative CNT configuration obtained from our molecular model, and Figure 1 (c) shows a high-magnification scanning electron microscope image of multi-walled CNTs having an average diameter $d \approx 21$ nm and various lengths.

In a separate publication, we studied CNTs having a highly irregular “tumbleweed morphology”, as often found in commercial sources of this material [61], while the present paper focuses on the study of CNTs having a genuinely tube-like morphology in which the CNT can be described as worm-like cylinders [64]. The synthesis and size separation of this “better quality” material is currently rather time consuming and expensive, and this class of materials seems to be more suitable in applications where more regular structures are required (electronic and medical applications). Part of the complexity of CNT-based

materials is the high variability of the morphology of this class of carbon nanoparticle additives, depending on the synthesis conditions. This situation is similar to using carbon black as an additive.

B. Graphene Sheet Molecular Model

Each graphene sheet GS is modeled as an square array of N^2 beads whose steric repulsion is given by Eq. (4). A similar model has been studied extensively in reference. [54]. Here, we choose $\sigma \approx 1$ nm as the average experimental value reported for graphene thickness [13–15] (z -direction). We consider GSs having an unperturbed area of $A = (100, 400, 2500, 10000$ or $40000)$ nm² (xy -plane). In this molecular model, all the beads are connected by using FENE potentials such as Eq. (5) along the x - and y -directions (Figure 1) (b). Since we consider the GS to be elastically isotropic, we use an interaction potential similar to Eq. (7) in the x and y -directions, with either $k_{\text{bend-x}} = k_{\text{bend-y}} = 0.1 \text{ } \varepsilon$ or $10 \text{ } \varepsilon$. Additionally, we account for the shear stiffness of the GS by introducing a perpendicular potential,

$$U_{\text{perp}}(\gamma) = \frac{k_{\text{perp}}}{2} \left(\gamma - \frac{\pi}{2} \right)^2, \quad (7)$$

that depends on the angle γ formed by three neighboring beads on the GS; two beads on one direction, and the third one in the perpendicular direction. We chose $k_{\text{perp}} = 0, 1 \text{ } \varepsilon$ for the $k_{\text{bend-x}} = k_{\text{bend-y}} = 0.1 \text{ } \varepsilon$ case and $k_{\text{perp}} = 1 \text{ } \varepsilon$ for the $k_{\text{bend-x}} = k_{\text{bend-y}} = 10 \text{ } \varepsilon$, so we can generate flexible and semi-flexible GSs configurations. A representative GS configuration is shown in Figure 1 (b).

We integrate Newton's equation of motion for systems of CNT and GS nanoparticles formed by beads that interact via the aforementioned potentials using MD [69]. All simulations were performed in at fixed number of particles, volume and temperature (NVT ensemble). T is controlled by using the Nosé–Hoover thermostat [70, 71] and we chose for all our calculations $T = 1.0 \text{ } \varepsilon/k_B$, where k_B is the Boltzmann constant. We carry out our simulations for periods of time 10^7 time steps δt , where $\delta t = 0.006 \text{ } \sigma(m/\varepsilon)^{1/2}$, by using the Large-scale Atomic Molecular Massively Parallel Simulator (LAMMPS) [72]. We report the average property for each system resulting from 10^3 different configurations after it has reached thermal equilibrium. The uncertainty calculations from ZENO and COMSOL are detailed in the supplemental information [68]. We use Visual Molecular Dynamics VMD [73] to render representative configurations of the different systems. We fit and plot the data using the software GRACE [74], which uses the Levenberg–Marquardt fitting algorithm.

III. ELECTRIC POLARIZABILITY TENSOR α_E AND INTRINSIC CONDUCTIVITY $[\sigma]_\infty$ OF CONDUCTIVE PARTICLE ADDITIVES

A. Calculation of α_E using ZENO

We first compute the electric polarizability tensor α_E based on input CNT and GS configurations obtained from MD simulation. The determination of α_E results from solving Laplace's equation with Dirichlet boundary conditions. To do so, we use the software package ZENO [75, 76], which is based on a path-integration algorithm described briefly

below. More detailed information about the algorithm can be found in reference [77], and the idea underlying these calculations are described in a companion paper devoted to CNT materials [61]. In brief, ZENO exploits the relationship between the Laplacian operator and random walks, so that mathematical problems that are described by this operator can be solved using this type of probabilistic approach. This path-integration method has been validated for relatively simple objects having exact solutions to an uncertainty of about 1.5 % [76]. In this method, n random walks are executed starting from a uniform on the surface of a launch sphere of radius R enclosing the “probed” object (CNT or GS nanoparticle). Each of these random walks either hits the object and “dies” or returns to the launch sphere. If the latter happens, the walk either goes to infinity or it is relaunch to probe the particle again, base on a probabilistic consideration. Additionally, each walk is assigned three charges, one for each direction, x , y and z . These charges can be positive +1 or negative -1, and their sign in each direction, i.e., x , is chosen randomly from a uniform probability density distribution [76, 77]. Based on the statistics of the trajectories of these symbolically “charged” walks, we calculate the nine elements α_{Eij} of the electric polarizability tensor,

$$\alpha_E = \begin{pmatrix} \alpha_{Exx} & \alpha_{Exy} & \alpha_{Exz} \\ \alpha_{Eyx} & \alpha_{Eyy} & \alpha_{Eyz} \\ \alpha_{Ezx} & \alpha_{Ezy} & \alpha_{Ezz} \end{pmatrix}. \quad (8)$$

Rotating the particle allows α_E in Eq. (8) to be expressed in its diagonal form,

$$\alpha_E = \begin{pmatrix} \hat{\alpha}_{Exx} & 0 & 0 \\ 0 & \hat{\alpha}_{Eyy} & 0 \\ 0 & 0 & \hat{\alpha}_{Ezz} \end{pmatrix}, \quad (9)$$

where $\hat{\alpha}_{E_{ii}}$ are the eigenvalues of the tensor, and their corresponding eigenvectors define a base $\{\hat{x}; \hat{y}, \hat{z}\}$ that represents a preferable set of coordinates to describe the properties of the object. We next discuss an illustrative calculation of α_E for a CNT. Figure 2 shows an example CNT worm-like configuration represented in both set bases, in silver $\{x; y, z\}$ and blue $\{\hat{x}; \hat{y}, \hat{z}\}$, respectively. The $\alpha_{E_{ii}}$ components in $\{x; y, z\}$ for this illustrative structure are determined as,

$$\alpha_E = \begin{pmatrix} 1.793 & -0.609 & 0.331 \\ -0.609 & 2.562 & -2.114 \\ 0.331 & -2.114 & 2.119 \end{pmatrix} (nm)^3, \quad (10)$$

and for the rotated reference system (blue) in which α_E is diagonal we have,

$$\alpha_E = \begin{pmatrix} 0.197 & 0 & 0 \\ 0 & 1.650 & 0 \\ 0 & 0 & 4.628 \end{pmatrix} (nm)^3. \quad (11)$$

To arrive at uncertainty values for this example calculation, we have performed the ZENO path-integral calculations using 2×10^6 random walkers. The calculation of α_E was done in

4 min and 37 s on a desktop machine having a CPU running at 3.40 GHz and with 8 Gb in RAM memory for a representative CNT. We are interested in the average of the trace of the α_E tensor,

$$\langle \alpha_E \rangle = \frac{1}{3} \left(\hat{\alpha}_{E_{xx}} + \hat{\alpha}_{E_{yy}} + \hat{\alpha}_{E_{zz}} \right), \quad (12)$$

which is an invariant of α_E . The intrinsic conductivity $[\sigma]_\infty$ for *any shaped* nanoparticle, averaged over all directions, and having a volume V is defined as [75],

$$[\sigma]_\infty = \langle \alpha_E \rangle / V. \quad (13)$$

The calculation of α_E for conductive particles also enables a precise estimate of the leading transport coefficient $[\eta]$ for the shear viscosity of a suspension of rigid particles having the same shape [78]. To a leading approximation, $[\eta]$ is simply proportional to $[\sigma]_\infty$ for particles having any arbitrary shape i.e., $[\eta] \propto [\sigma]_\infty$, and the estimation of $[\eta]$ to within $\mathcal{O}(1\%)$ uncertainty can be obtained through the use of the components of the full polarizability tensor [75]. This numerical uncertainty is usually smaller than experimental uncertainties so that the relation between $[\eta]$ and $[\sigma]_\infty$ can be regarded as essentially “exact”. Measurements of $[\eta]$ are sparse for CNT and GS materials, but Shaffer and Windle [79] have estimated $[\eta] = (100 \text{ and } 48) \text{ cm}^3 \text{g}^{-1}$ or for CNT materials having an aspect ratio of about 110 and 37, respectively. Further measurements on better characterized materials would be valuable.

Both CNTs and GSs can be viewed as polymeric forms of matter and it is natural to treat $[\sigma]_\infty$, in Figure 3, using a mathematical description that is similar to the conventional description used for the value of $[\eta]$ for polymer solutions. In particular, $[\eta]$ for polymeric structures is often described empirically by a power-law in the particle mass M ,

$$[\eta] = k M^a, \quad (14)$$

where k is a structure dependence constant and a is a scaling exponent, conventionally termed the “Mark–Houwink exponent”. Given the near proportionality between $[\eta]$ and $[\sigma]_\infty$, we may describe $[\sigma]_\infty$ estimates for CNT and GS similarly,

$$[\sigma_{CNT}]_\infty = k_{CNT} L^a, \quad (15)$$

$$[\sigma_{GS}]_\infty = k_{GS} A^a, \quad (16)$$

since in this model the CNT length L and the GS area A are proportional to the nanoparticle mass [75]. Figure 3 shows $[\sigma]_\infty$ for CNTs having rigid rod-like or worm-like morphologies (upper panel) and for flat or flexible GSs (lower panel) as function of the nanoparticle size (length or area, respectively). Of course, we can convert L and A to mass in Eq. (15) and Eq. (16) so that $[\sigma]_\infty$ takes the form of Eq. (14). The symbols correspond to simulation results and the lines correspond to fits to Eq. (15) and Eq. (16), for CNTs and GSs, respectively. We find a monotonic increase of $[\sigma]_\infty$ with the CNT length or GS area, but the rate of increase depends strongly on the stiffness of the nanoparticle. For CNTs, this variation is greater than

for GSs, especially for the case of large tubes where the difference can be almost two orders of magnitude. The scaling exponents a in Eqs. (15)–(16) are reported for all sets of data as the slope of the fitting lines. In general, the CNT or GS “conformational” complexity can be measured by determining the exponent a . This method has been applied by Bauer et al. [80] to CNTs through measurements of $[\eta]$, which is essentially proportional to $[\sigma]_{\infty}$ [76].

Variations of the rod-thickness along the particle [76] and boundary shape of the sheet [75] (i.e., round, square, triangular, etc.) also influence the scaling relations in Eq. (15) and Eq. (16), mainly influencing the prefactor if these variations from circular cylinder or square sheet are not too extreme. All such variations in particle shape arising in practice can easily be treated using ZENO. In reference [54], $[\eta]$ was calculated for two-dimensional polymer sheets or membrane polymers as a function of M for a range of bending rigidity values, where the exponent a was found to vary over a range between 0.11 and 0.5 as the membrane stiffness was varied. The smaller exponent value corresponds to “crumpled” sheets, where mass scaling exponent for the radius of gyration is near 1/3. In addition, we previously investigated a model equivalent to our coarse-grained GS model to study DNA origami, another two-dimensional polymer structure [52, 81]. Exfoliated clay [6, 9], polymerized layers [82] and many other biological structures such the erythrocyte membrane [83] can also be modeled as a two-dimensional polymers.

B. Calculation of α_E using COMSOL

The generated CNTs and GSs were composed of slightly overlapping beads, which do not pose a challenge for the ZENO package. However, the finite-element method (FEM) of particles composed of overlapping spheres proved to be extremely difficult. The main challenges were that the overlapping regions, by the virtue of the bead-spring model, were tiny in comparison to the radius of the bead. Therefore, a fine mesh was required to mesh such tiny overlapping regions. The tetrahedral mesh had to then grow rapidly in size to represent thousands of beads used to model the CNTs and GSs. For the larger CNTs and GSs containing thousands of beads, respecting this geometry was extremely challenging without using a prohibitively large number of FEM tetrahedra in the meshing description of the object. Hence, an alternative simpler representation for the CNTs and the GSs was employed for the FEM analysis. This alternative representation had no significant impact on the calculated polarizability but greatly speeded up the computations. This was confirmed by comparing α_E calculated using the bead model with ZENO and using the simpler representation and the FEM analysis will be detailed in this subsection.

For the CNTs, the alternative FEM representation consisted of modeling the CNT as a swept tube that encloses the overlapping spheres from the bead-spring model, as shown in Figure 4. The meshing of the swept tube into FEM tetrahedra is more computationally efficient than the meshing of the overlapping spheres in the bead-spring model. To generate this tube, a spline line passing through the centers of the spheres was generated using COMSOL. The line was extrapolated at the beginning and the end of the line to account for the radius of the first and last sphere in the bead-spring model. A circle is drawn at the beginning of the extrapolated spline line such that its orientation is normal to the line at its beginning. The circle is swept along the line to generate the tube model of the CNT. As shown in Figure 4,

the tube tightly encloses the spheres of the bead–spring model. In addition to being more computationally efficient, the advantage of the swept tube in comparison to the bead–spring model is that it better resembles the true morphology of the CNTs. However, due to the structural differences between the swept tube and the bead–spring models it is anticipated that there would be some small differences between the polarizability calculated using ZENO and COMSOL for the shorter CNTs. In a separate paper, we model the more complicated branched network structures observed in many commercial CNT samples [61].

Similarly, for GSs the bead–spring model is converted to a “flake model” by first creating a plane that passes through the centers of the spheres in the bead–spring model. This plane is then extrapolated at its four edges by an amount equal to the radius of the spheres in the bead model. To give this plane a finite thickness, the normal vector at each point on the plane is calculated. Each point on the plane is then shifted in the direction of its normal by $+R$ to create the top plane and by $-R$ to create the bottom plane. The two planes, top and bottom, sandwich the beads in the beads–spring model as shown in Figure 5. The corresponding edges of the top and bottom plane are connected to create four sides, which create the flexible box or flake model of graphene shown in Figure 5. The outer surface of the flake is then meshed in STereoLithography (STL) format and imported to COMSOL.

Considering these mesh representations for CNTs and GSs, we compute α_E using the electrostatic module of the COMSOL package. Here, we solve Laplace's equation [84]

$$\nabla^2 \phi = 0, \quad (17)$$

where ϕ is the electrostatic potential. We set the CNTs and GSs to have a relative dielectric permittivity ϵ_i , immersed in an embedding medium with relative dielectric permittivity, ϵ_e . The matrix relative dielectric permittivity ϵ_e is set to unity in all the cases considered in this study. A static incident electric field, $\vec{E}_{inc}$, oriented in either the x , y , or z directions is then applied. Each field orientation will yield three elements or one row of the polarizability tensor. Consider, for example, the first step where the incident field will be oriented in the x –direction $\vec{E}_{inc} = E_0 \vec{\alpha}_x$. In the vicinity of the inclusion, the field will be perturbed, but far away from the inclusion the field should converge to the incident electric field, $E_0 \vec{\alpha}_x$. The magnitude of the incident electric field E_0 is set to unity in all the cases considered in this paper. Ideally, the inclusion should be embedded in an infinite domain to calculate the polarizability but due to limited computational resource the embedding medium is set to be a finite sphere much larger than the inclusion. The radius of the embedding sphere is increased until the calculated polarizability values converge. Typically, a sphere five times larger than the largest dimension of the inclusion is sufficient to achieve convergence. The boundary condition on the outer surface of this embedding sphere is that the field is equal to the incident field, $\vec{E}_{inc}$. Eq. (17) is then solved to yield the potential ϕ and the electric field E everywhere. The dipole moment $\vec{p}$ generated by the inclusion can be then calculated as follows [84]:

$$\begin{aligned}\vec{p} &= \int_V \vec{P} dV = (\epsilon_i - \epsilon_e) \epsilon_0 \int_V \vec{E}_i dV \\ &= \epsilon_0 \epsilon_e (\tau - 1) \int_V \vec{E}_i dV,\end{aligned}\quad (18)$$

where $\vec{p}$ is the polarization density, ϵ_0 is the permittivity of free space equal to 8.85×10^{-12} F/m, $\vec{E}_i$ is the electric field inside the inclusion, and $\tau = \epsilon_i/\epsilon_e$ is the relative contrast between the inclusion and the embedding medium. The integral in Eq. (18) is over the volume of the inclusion. Since the incident field is in the x -direction, the following three components of α_E can now be calculated [84],

$$\begin{aligned}\alpha_{E_{xx}} &= (\tau - 1) \int_V \vec{E}_{ix} dV \\ \alpha_{E_{xy}} &= (\tau - 1) \int_V \vec{E}_{iy} dV \\ \alpha_{E_{xz}} &= (\tau - 1) \int_V \vec{E}_{iz} dV,\end{aligned}\quad (19)$$

where E_{ix} , E_{iy} , and E_{iz} are the x , y , and z components, respectively, of the electric field inside the inclusion. For the electric polarizability, the limit $\tau \rightarrow \infty$ is needed, which implies a zero field E_i inside the inclusion. In this case, Eq. (19) becomes undetermined and, therefore, an alternative equivalent expression has to be employed to calculate the electric polarizability [85],

$$\begin{aligned}\alpha_{E_{xx}} &= \int_V x \left(\vec{E}_e \right) \cdot \hat{n} dS \\ \alpha_{E_{xy}} &= \int_V y \left(\vec{E}_e \right) \cdot \hat{n} dS \\ \alpha_{E_{xz}} &= \int_V z \left(\vec{E}_e \right) \cdot \hat{n} dS.\end{aligned}\quad (20)$$

Here, $\vec{E}_e$ is the field just outside the inclusion, $\hat{n}$ is the unit vector normal to the surface of the inclusion, and the integral in Eq. (20) is over the outer surface of the inclusion. In the COMSOL simulations, the outer surface of the inclusion will be set to a perfectly conducting boundary condition or *floating potential* which is equivalent to setting the relative dielectric permittivity of the inclusion $\epsilon_i = \infty$.

We repeat this process with an incident field in the y -direction to compute $\alpha_{E_{yx}}$, $\alpha_{E_{yy}}$, $\alpha_{E_{yz}}$ and in the z -direction to compute the $\alpha_{E_{zx}}$, $\alpha_{E_{zy}}$, and $\alpha_{E_{zz}}$ components. We use the fact that $\alpha_{E_{zx}}$ is a symmetric tensor i.e., $\alpha_{E_{ij}} = \alpha_{E_{ji}}$, to check the accuracy of the inclusion meshing. For these calculations, we consider CNTs having rigid rod configurations and worm-like CNTs having a persistence length $l_p = (1736 \pm 5.6)$ nm.

IV. MAGNETIC POLARIZABILITY TENSOR α_M AND INTRINSIC CONDUCTIVITY $[\sigma]_0$ OF INSULATING PARTICLE ADDITIVES

The calculation of the intrinsic conductivity in the case of insulating particles in a conductive matrix $[\sigma]_0$ is generally a much more difficult problem than calculating the intrinsic conductivity of conductive particles in an insulating matrix $[\sigma]_\infty$, because the former computation requires the determination of α_M rather than α_E , as indicated in Eq. (13). Very few analytic results are known for α_M , beyond those few shapes that can be

inferred from the exact relationship between $\alpha_{\mathbf{M}}$ and the hydrodynamic virtual mass tensor [34, 51]. $\alpha_{\mathbf{M}}$ is an extremely important quantity in understanding the dynamics of airplanes, submarines and other submersible vehicles, ships, projectiles, depth charges, the forces due to the waves on piles and drilling platforms, not to mention the drag force on accelerating bodies and the vibrational frequencies of objects within fluids [34]. Fortunately, a number of exact mathematical results for the hydrodynamic virtual mass have accumulated since the 1800's that are extremely useful for validating numerical calculations of $[\sigma]_0$ and for quantitatively understanding how $[\sigma]_0$ depends on shape. Many of these results are reviewed by Schiffer and Szeg [86] and in the well-known book by Pólya and Szeg [87]. These results were “transformed” from $\alpha_{\mathbf{M}}$ estimates into $[\sigma]_0$ estimates by Douglas and Garboczi [34], who also provide some finite-element calculations for $[\sigma]_0$ for a variety of shapes where no analytic results exist, an enterprise that has been extended below.

Another difficulty in determining $[\sigma]_0$ is that we currently have no method for calculating $\alpha_{\mathbf{M}}$ based on numerical path-integration, although methods for such Neumann boundary conditions are currently under development [88]. At present, we must then rely heavily on finite-element techniques. Below we present the calculations of $[\sigma]_0$ for CNTs and GSs based on the same nanoparticle models considered in the previous section. We next define $\alpha_{\mathbf{M}}$ and its relation to $[\sigma]_0$. For that purpose, we use COMSOL to compute the nine elements of the magnetic polarizability tensor $\alpha_{M_{ij}}$ by setting $\tau = 0$ in Eq. (19). This implies that the relative dielectric permittivity of the inclusion ϵ_i is set equal to 0, representing the case of adding perfect insulating nanoparticles into a conductive media. The average magnetic polarizability tensor is determined by,

$$\langle \alpha_{\mathbf{M}} \rangle = \frac{1}{3} \left(\hat{\alpha}_{M_{xx}} + \hat{\alpha}_{M_{yy}} + \hat{\alpha}_{M_{zz}} \right), \quad (21)$$

and, therefore, $[\sigma]_0$ for purely insulating particles having the shape of the CNTs and GSs nanoparticle is,

$$[\sigma]_0 = \langle \alpha_{\mathbf{M}} \rangle / V. \quad (22)$$

We have spent a considerable amount of effort in calculating $\alpha_{\mathbf{M}}$ and $[\sigma]_0$ because of the many applications of these quantities in material science and technology [34]. In particular, $\alpha_{\mathbf{M}}$ of worm-like cylinder CNTs and two-dimensional polymer structures such as GSs has apparently never been investigated before, and in this section we explore how $[\sigma]_0$ varies with the size and mesh of these structures. In Section VI, we develop approximate methods for estimating $[\sigma]_0$ since this property gives great insight into how to select the particle shape to create composite materials having insulating properties in terms of thermal conductivity, electrical conductivity, and gas permeability.

We find that the shape dependence of $[\sigma]_0$ is completely unlike the variation found for $[\sigma]_\infty$ and highly useful approximations emerge from our analysis that allow us to estimate $[\sigma]_0$ for nanoparticles having the geometry of CNTs and GSs. This is just the information we need (See Eq. (2)) to treat $[\sigma]$ and mathematically related properties of CNTs and GSs having arbitrary contrast property and conformational shape. We expect these approximate

relationships to have many applications in other materials science and technology fields, although we do not pursue these developments in the present paper.

In Figure 6 (a), we see that the variation of $[\sigma]_0$ with CNT tube length L is rather weak, its value ranging between that of a sphere $[\sigma(\text{sphere})]_0 = -3/2$ and a needle $[\sigma(\text{needle})]_0 = -5/3$. This result is not obvious since the worm-like cylinder CNTs have a fractal dimension, defined by the scaling of their radius of gyration with the CNT mass, in a range between 1 and 2. The “surface-like” quality of CNTs is apparently not reflected in $[\sigma]_0$, which has values appropriate for a slender body. This confirms the common observation that the addition of uncharged polymers to a solvent tends to have only a small effect on the diffusion coefficient of the solvent (e.g., polyethylene oxide in water or water in hydrogels) [89]. The solvation of aqueous polymers by water leads to a change of the effective volume fraction, and this has the effect of leading to a modest change in $[\sigma]_0$ on the virial associated with the water diffusion coefficient by a modest amount. This change on the intrinsic virial is often taken as a measure of the amount of hydration water in biological macromolecules [90]. In Section VI B, we develop approximations for $[\sigma]_0$ for CNTs and the α_{Mij} components that should be useful for slender polymeric objects such as CNTs. These estimates are based on the mathematical relationship between the hydrodynamic virtual mass and α_M and a physical interpretation of the hydrodynamic virtual mass involving the fluid volume swept through a interface by a moving particle.

We see that $[\sigma]_0$ for GSs varies with particle mass M in a quite different fashion from that of the CNTs. This relatively strong transition is difficult to understand given the sparse analytic results for $[\sigma]_0$ for non-trivial particle shapes such as those exhibited by the GSs. In Figure 6, we compare finite-element calculations for $[\sigma]_0$ in the case of ideal square GSs and “crumpled” GSs and, intriguingly, we find that these results track each other closely, although the crumpling does seem to modify the “effective area” of the platelet counterpart of the flat GSs. In both cases, $[\sigma]_0$ scales with the GS mass with an effective scaling exponent near 0.35, i.e., $[\sigma]_0 \sim M^{0.35} \sim A^{0.35}$, which is reminiscent of the scaling observed for the intrinsic viscosity $[\eta]$ of semi-flexible sheets [54, 81]. This scaling is also similar to the scaling for $[\sigma]_\infty$ for GSs described in Sect III, where we found the scaling exponent, 0.45. Evidently, this type of scaling relation, $[\sigma] \sim M^a$ provides a useful way of determining the mass of the GSs as in the case of polymer solution characterization. In Section VI C, we develop a useful approximation for $[\sigma]_0$ that is appropriate for GS structures.

V. INTRINSIC CONDUCTIVITY $[\sigma]$ FOR VARIABLE CONTRAST

As mentioned briefly in the introduction, if we know $[\sigma]_0$ and $[\sigma]_\infty$ for a given particle, we can estimate $[\sigma(\gamma)]$ for any ratio γ between the conductivity of the particle and the conductivity of the matrix by using a Padé expression, introduced by Douglas and Garboczi [35], described by Eq. (2). We next validate this relation by performing finite-element calculations of $[\sigma]$ for variable γ and comparing to this approximant.

Figure 7 (a) shows calculations for $[\sigma]$ as a function of γ for straight and worm-like CNTs having exactly the same length of 1050 nm. $[\sigma]$ is calculated using the Padé approximation in Eq. (2) and COMSOL. We find good agreement between the Padé approximation and

COMSOL, indicating the accuracy of the approximation even for complex shapes such as worm-like CNTs. By comparing the values for straight and worm-like CNTs, we found that for $\kappa \lesssim 10^2$, both shapes yielded similar value for $[\sigma]$. On the other hand, for $\kappa \gtrsim 10^2$, $[\sigma]$ for straight and worm-like CNTs differ significantly. Therefore, particle shape strongly influences $[\sigma]$ when κ takes values greater than 10^2 , which is typically the case for CNTs and GSs embedded in polymeric materials. Figure 7 (b) shows calculations of $[\sigma]$ as a function of κ for flat and flexible GSs, having an area of 10^4 nm^2 , implying that they also had approximately the same volume. Once more, we find very good agreement between the Padé approximation and the COMSOL calculations. In the low contrast range, $10^{-2} < \kappa < 10^2$, the difference between the intrinsic conductivity for flat and flexible GSs is marginal. This is anticipated since at $\kappa = 1$ the effect of the shape vanishes and $[\sigma]$ vanishes for all shapes. On the other hand, for contrast values, $\kappa < 10^{-2}$ or $\kappa > 10^2$, the shape of the GS has a large impact on $[\sigma]$.

VI. USEFUL APPROXIMATIONS FOR α_E AND α_M

In the design of composite materials, it is just as important to have an understanding of the general trends regarding how particle shape and property contrast affect composites properties as having precise numerical estimates. This situation is especially true given the tendency of nanoparticles to aggregate even at low particle concentration, a source of uncertainty in the modeling and variability in the ultimate properties of the nanocomposite material. In this section, we briefly describe some approximations that we have discovered in the course of our investigation that serve to give a physical insight into how particle shape and property contrast affect material properties. At the same time, we obtain useful estimates of the transport virial coefficients in situations where precise property properties are required.

Section VI A illustrates a curious relation that we have found between the components of α_E and the components of the radius of gyration tensor of the particle, R_g . Section VI B considers the shape dependence of α_M in the important case of CNT materials.

A. Approximation relation between α_E and R_g

The radius of gyration R_g is a standard measure of particle or polymer size, and this quantity is commonly encountered in the characterization of particles using light or neutron scattering [91]. From a mathematical standpoint, R_g is defined similarly to α_E in terms of the radius of gyration tensor R_g^2

$$R_g^2 = \begin{pmatrix} R_{gxx}^2 & R_{gxy}^2 & R_{gxz}^2 \\ R_{gyx}^2 & R_{gyy}^2 & R_{gyz}^2 \\ R_{gzx}^2 & R_{gzy}^2 & R_{gzz}^2 \end{pmatrix}. \quad (23)$$

where R_g^2 is determined from its trace as in the case of $[\sigma]_\infty$ (Eq. (12)),

$$\begin{aligned}
 R_g^2 &= \text{trace} \left(\mathbf{R}_g^2 \right) \\
 &= 3 \left\langle \mathbf{R}_g^2 \right\rangle \\
 &= (\Lambda_1 + \Lambda_2 + \Lambda_3),
 \end{aligned} \quad (24)$$

where Λ_i are the eigenvalues of $\mathbf{R}_g^2$ and $\Lambda_1 \geq \Lambda_2 \geq \Lambda_3$. The components of $\mathbf{R}_g^2$ are commonly used to characterize the particle shape through averages of $\mathbf{R}_g^2$ that are invariant under particle rotation. For example, a commonly used shape descriptor is κ^2 , called the relative shape anisotropy [92],

$$\kappa^2 = 1 - 3 \frac{\Lambda_1 \Lambda_2 + \Lambda_2 \Lambda_3 + \Lambda_1 \Lambda_3}{(\Lambda_1 + \Lambda_2 + \Lambda_3)^2}, \quad (25)$$

where $\kappa^2 = 1$ for linear particles and $\kappa^2 = 0$ for particles with spherical symmetry. The ratio Λ_3/Λ_1 constitutes another shape descriptor and the asphericity parameter b defines

$$b = \Lambda_1 - \frac{1}{2} (\Lambda_2 + \Lambda_3). \quad (26)$$

For a more detailed discussion of these and other shape descriptors for various polymeric structures, see reference. [93].

The electric polarizability tensor can be determined by optical measurements [94, 95] and its components can also be used to construct shape descriptors [96] such as the measurable quantity,

$$\kappa_e^2 = \frac{(\hat{\alpha}_{xx} - \langle \alpha_E \rangle)^2 + (\hat{\alpha}_{yy} - \langle \alpha_E \rangle)^2 + (\hat{\alpha}_{zz} - \langle \alpha_E \rangle)^2}{6 \langle \alpha_E \rangle}. \quad (27)$$

Given this parallelism between the definition of α_E and $\mathbf{R}_g^2$, it is natural to compare the components of these tensors to see if they imply similar information about particle shapes. Such a relation would be highly useful since the radius of gyration tensor and its shape-related invariants are not normally measurable. In Figure 8, we show that the components of the electric polarizability and the radius of gyration tensors are remarkably correlated with each other, so that the shape information between these quantities is indeed rather similar. The basis of these correspondence however, is obscure at present, and we note that α_E and $\mathbf{R}_g^2$ do not even have the same units. In the next section, we consider the relationship between α_M and $\mathbf{R}_g^2$, where we find that no strong correlation exists between tensors for CNT structures so that describing the CNTs as effective ellipsoids having the $\mathbf{R}_g$ of the particle is a poor approximation in the case of α_M . The shape dependence of α_M is evidently quite distinct from the shape dependence of α_E and $\mathbf{R}_g^2$ so that the correlation in Figure 8 is all the more striking.

B. Approximation of $\alpha_{\mathbf{M}}$ for CNTs and Other Polymeric Structures

The calculation of $\alpha_{\mathbf{M}}$ for complex objects such as worm-like CNTs and GS is laborious by finite element methods, and under these circumstances we seek an effective method for estimating this quantity that we can validate against existing computational results. We are also concerned with a better understanding of this fundamental shape function in connection with the use of this property in shape classification applications. Payne [97, 98] has shown, for axi-symmetric and *simply connected* general bodies of revolution, that the axial component of the magnetic polarizability tensor, termed $\alpha_{M_{xx}}$, is related to the transverse components of the electric polarizability tensor, termed $\alpha_{E_{yy}} = \alpha_{E_{zz}}$, by the relation,

$$\alpha_{M_{xx}} = -\frac{\alpha_{E_{yy}}}{2} = -\frac{\alpha_{E_{zz}}}{2}, \quad (28)$$

and this led to the introduction of the following approximations for the elements of the magnetic polarizability tensor for elongated bodies,

$$\alpha_{M_{xx}} = -\frac{\alpha_{E_{yy}}}{2} = -\frac{\alpha_{E_{zz}}}{2} \quad (29a)$$

$$\alpha_{M_{yy}} = \alpha_{M_{zz}} = 1 + \frac{s}{1+s}, \quad (29b)$$

where s is the aspect ratio of the elongated body.

We thought this approximation might be suitable for structures having the highly elongated shapes of CNTs, if we modeled these worm-like structures as “effective ellipsoids” of revolution whose largest and smallest R_g tensor components are equated to the CNT values. Unfortunately, this intuitively and theoretically well-motivated approximation completely failed to match the magnetic polarizability values calculated using finite element simulations. The largest mismatch was in the axial component, which was incorrectly approximated by more than a factor of 10. The reason for this mismatch is that the curvature of the worm-like CNTs creates semi-loops and these loops make $\alpha_{\mathbf{M}}$ behave more like $\alpha_{\mathbf{M}}$ of a torus, which does not obey Eq. (29) (a) [86, 99]. In particular, a torus does not obey Eq. (29) (a) since it has a cavity and, therefore, it is not a simply connected object, a condition required for the validity of Eq. (29) (a) [86, 99]. Therefore, we sought another approximation.

To understand how the elements of $\alpha_{\mathbf{M}}$ of worm-like CNTs depend on the shape of idealized models, we discovered an approximation inspired by a hydrodynamic analogy between the magnetic polarizability and hydrodynamic virtual mass of arbitrary-shaped bodies, quantities rigorously equivalent mathematically up to a constant factor, which by normal convention equals -1 .

The hydrodynamic virtual mass relates to the fluid motion “excited” in the surrounding medium about an accelerating particle [100–105], and this quantity is fundamental to the dynamics and drag characteristics of bodies such as ships, and submarines, and aircraft [100–105]. Recent studies have shown that the virtual mass tensor components M_{ij} can be

understood from a physical point of view as the amount of fluid that the particle carries with it through a phantom interface through which it passes, providing an intuitive physical picture of this fundamental shape-dependent property in terms of “swept volume” [100–105]. The Stokes hydrodynamic friction coefficient of particles undergoing Brownian motion can similarly be understood to an excellent approximation in terms of the volume swept out by a Brownian particle per unit time [106], a quantity exactly proportional to the electrostatic capacity C of the particle. We then explore this geometrical perspective of $\mathbf{M}$.

We implement this formally exact interpretation of the hydrodynamic virtual mass tensor $\mathbf{M}$, and then also the magnetic polarizability tensor $\alpha_{\mathbf{M}}$, in a highly simplified way in the present work in the case of CNTs. In particular, we simply assume that the volume of the fluid pulled through the imaginary interface in which the particle passes is proportional to the projected area of the particle, i.e., the particle “cross-section”. This simple approximation proved to be highly effective for estimating the magnetic polarizability tensor components as we now illustrate using a straight needle with an infinitesimally small radius and length L , shown in Figure 9. The needle is rotated with various angles β around the z -axis, and in each case, $\alpha_{\mathbf{M}}$ and $\mathbf{M}$, are calculated exactly. When the needle is aligned with the x -axis or when $\beta = 0$, the magnetic polarizability tensor can be expressed as follows:

$$\mathbf{M} = -\alpha_{\mathbf{M}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}. \quad (30)$$

If the needle is rotated with an angle β around the z -axis, the new $\alpha_{\mathbf{M}}$ and the new $\mathbf{M}$ can be calculated exactly through the use of rotation matrices as follows:

$$\mathbf{M} = -\alpha_{\mathbf{M}} = \begin{pmatrix} 1+\sin^2(\beta) & -\sin(\beta)\cos(\beta) & 0 \\ -\sin(\beta)\cos(\beta) & 1+\cos^2(\beta) & 0 \\ 0 & 0 & 2 \end{pmatrix}. \quad (31)$$

Moreover, the rotation with an angle β leads to a projected length on the yz -plane $P_x = L \sin(\beta)$, a projected length on the xz -plane $P_y = L \cos(\beta)$, and a projected length on the xy -plane $P_z = L$. Therefore, an exact expression for the diagonal components of $\alpha_{\mathbf{M}}$ and $\mathbf{M}$ of a straight needle at an arbitrary angle can be expressed as a function of the projected lengths as follows:

$$M_{xx} = -\alpha_{M_{xx}} = 1 + (P_x/L)^2 \quad (32a)$$

$$M_{yy} = -\alpha_{M_{yy}} = 1 + (P_y/L)^2 \quad (32b)$$

$$M_{zz} = -\alpha_{M_{zz}} = 1 + (P_z/L)^2. \quad (32c)$$

Figure 6 shows that the intrinsic conductivity for a perfectly insulating CNT, $[\sigma]_0$, varies within a very narrow range around $-5/3$ for all CNT sizes. This is anticipated since $[\sigma]_0$ for a

needle like structure approaches $-5/3$. The projected length approach in Eq. (32) provided a reasonable approximation for the elements of the diagonalized magnetic polarizability tensor of worm-like CNTs as shown in Figure 10. For each worm-like CNT considered, the diagonalized magnetic polarizability tensor elements are arranged such that $\alpha_{M_{xx}} > \alpha_{M_{yy}} > \alpha_{M_{zz}}$. The maximum difference between the approximations and the exact values in Eq. (32) for all the shapes considered was less than 10 %. The main advantage of the approximation in Eq. (32) is that it is much easier to calculate than the exact elements of α_M .

C. Approximation of α_M for GSs and Other Two-Dimensional Polymer Structures

Special shapes such as ellipsoids have equations that relate the elements of α_M with the elements of α_E . More specifically, the following relations connecting the elements of the diagonalized α_M and the diagonalized α_E are exact for a tri-axial ellipsoid:

$$\alpha_{M_{xx}} = - \frac{\alpha_{E_{yy}} \alpha_{E_{zz}}}{\alpha_{E_{yy}} + \alpha_{E_{zz}}} \quad (33a)$$

$$\alpha_{M_{yy}} = - \frac{\alpha_{E_{xx}} \alpha_{E_{zz}}}{\alpha_{E_{xx}} + \alpha_{E_{zz}}} \quad (33b)$$

$$\alpha_{M_{zz}} = - \frac{\alpha_{E_{xx}} \alpha_{E_{yy}}}{\alpha_{E_{xx}} + \alpha_{E_{yy}}} \quad (33c)$$

We tested the previous relations for GS of different sizes and, since the GSs considered in this work are simply connected, Eq. (33) provided a good approximation to the elements of α_M . For each GS considered, the diagonalized magnetic polarizability tensor elements are arranged such that $\alpha_{M_{xx}} > \alpha_{M_{yy}} > \alpha_{M_{zz}}$. Figure 11 (a) shows that Eq. (33) (a) is inaccurate for $\alpha_{M_{xx}}$ whereas Figure 11 (b) and (c) show that Eq. (33) (b) and (c) are relatively accurate for $\alpha_{M_{yy}}$ and $\alpha_{M_{zz}}$, respectively. The magnetic polarizability element $\alpha_{M_{xx}}$ is the one with the smallest magnitude. For a flat GS with zero thickness, this element $\alpha_{M_{xx}}$ will converge to unity [34, 106]. For the GS considered in this work, $\alpha_{M_{xx}}$ varies within a very narrow range, $1.15 < \alpha_{M_{xx}} < 1.32$, with an average value of 1.23. Using the approximation $\alpha_{M_{xx}} \approx 1.23$ and the approximations in Eq. (33) (b) and (c) for $\alpha_{M_{yy}}$ and $\alpha_{M_{zz}}$, respectively, $[\sigma]_0$ is calculated using Eq. (22) and plotted in Figure 11 (d). Very good agreement with the calculated COMSOL values is achieved by this approximation for all the GS sizes considered. The approximation $\alpha_{M_{xx}} \approx 1.23$ and Eq. (33) (b) and (c) provide a computationally efficient approximation to the intrinsic conductivity of an insulating GS $[\sigma]_0$ in terms of the elements of α_E .

VII. CONCLUSIONS

Adding nanoparticles such as carbon nanotubes (CNTs) and graphene sheets (GSs) to polymeric materials can alter the composite electromagnetic response (e.g, conductivity). Tracking these changes in properties from a theoretical point of view represents a scientific challenge, since these types of calculations usually involve the solution of differential

equations having complicated boundary conditions. In the past, the calculation of the composite properties has normally been restricted to rather idealized descriptions of particle shape for mathematical expediency (e.g., ellipsoids or spheres), which have limitations in terms of adequacy of physical description. To address this issue, we have obtained precise estimates of the electromagnetic properties of CNTs and GSs nanoparticles having realistic shapes by combining MD, path-integral calculations and finite-element methods. We started by calculating the electric α_E and magnetic α_M polarizability tensors, and we found simple relations among the elements of α_E and α_M for CNTs and GSs that simplify the determination of α_M . The calculations of these tensors enable the determination of the intrinsic conductivity $[\sigma]$ assuming perfectly conductive nanoparticles in a dielectric medium $[\sigma]_\infty$ and dielectric nanoparticles in conductive media $[\sigma]_0$. Knowing $[\sigma]_\infty$ and $[\sigma]_0$, we used a Padé approximant to accurately estimate $[\sigma]$ in the case where the ratio between the conductivity of the nanoparticles and the polymer matrix is arbitrary. Very few values of $[\sigma]_0$ were known previously, and most of the technical work underlying the present paper involved calculating $[\sigma]_0$ for model CNT and GS structures and learning to understand the shape variation of this quantity. Given the difficulty of these calculations, we also have developed effective approximations for $[\sigma]_0$ that should be useful in material characterization and design applications.

We found that the leading virial coefficient $[\sigma]_\infty$ for the conductivity of a polymer composite with conductive additives generally increase with nanoparticle size for both CNTs and GSs, where these changes strongly depend on nanoparticle shape, an effect especially presented for CNTs. In contrast, $[\sigma]_0$ depends weakly on the shape for CNTs, while for GSs it is sensitive to both shape and size. The effect of shape on $[\sigma]$ is also evident when we explore nanoparticles with different property contrast from the polymer matrix.

The virial coefficients for transport properties have applications apart from the property estimation and material design of nanocomposites. The measurement of the dilute suspension properties can be inverted to estimate the properties of the suspended particles as in the characterization of polymers by solution measurements. For example, the intrinsic viscosity $[\eta]$ measurement of polymer solutions is a standard means of estimating polymer mass M through the observed scaling of $[\eta]$ with M [81]. Similarly, we can envision measuring $[\sigma]$ and $[\eta]$ of CNTs and two-dimensional polymers [54, 81] such as GS and exfoliated and synthetic clay to determine the length and area of these polymers from their corresponding Mark-Houwink scaling exponent a . Ratios of such properties provide valuable information about topology and rigidity. Alternatively, we can use this type of measurement to determine the properties of the particle in comparison to the background matrix if we know the particle (e.g, conductivity) shape [107]. Finally, $[\sigma]$ is basic input information into the General Effective Medium (GEM) Theory [39], which allows for the estimation of the conductivity of composites beyond the dilute regime. This theory in combination with the determination of $[\sigma]_\infty$ can be used to determine the conductivity percolation threshold of particles having essentially arbitrary shape [61].

The properties of nanoparticles can be quite different from their bulk counterparts, and the estimation of nanoparticle properties is often a fundamental theoretical difficulty in material design. Intrinsic property measurements offer a method for addressing this problem

experimentally and should suggest that enhanced nanoparticle characterization is a necessary element for material design.

In order to better understand and predict the changes in conductivity in carbon–base nanocomposites, the nanoparticle shape and property contrast must be considered more carefully. The frequency dependence of the particle conductivity must also be considered, since the particles can be either conductive or insulating depending on applied frequency. In a subsequent paper, we will explore this frequency dependence and the resonant interaction with light that can arise at certain frequencies, which lead to plasmonic effects that depend strongly on particle shape.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Snapshot of a representative configuration obtained from simulations of: a) a multi-walled CNT with length $L \approx 4200$ nm and diameter $d = 21$ nm, b) a GS with area $A \approx 10^4$ nm², both generated via MD. c) A high-magnification scanning electron microscope image of multi-walled CNTs having an average diameter $d \approx 21$ nm and various lengths and d) a transmission electron microscope image of a GS obtained by exfoliating graphite.

Figure 2.

A CNT worm-like configuration represented in both set bases, in blue $\{x, y, z\}$ and silver $\{\hat{x}, \hat{y}, \hat{z}\}$, respectively

Figure 3.

The intrinsic conductivity $[\sigma]_{\infty}$ for: (upper panel) CNTs having rigid rod-like (black circles) or worm-like (blue triangles, green diamonds, and red squares) configurations, and (lower panel) for flat (black circles) or flexible GSs (green diamonds and red squares). The data are solid symbols and the solid lines represent fits to Eq. (15) and Eq. (16), respectively, and where the scaling exponent represents the slope of the line. The slope is related to the flexibility of the nanoparticle with smaller slopes for more flexible nanoparticles.

Figure 4. Bead-spring model and swept tube model for the CNT. In (a) the walls of the swept tube are made transparent to show the beads they enclose, whereas in (b) the walls of the swept tube are made opaque.

Figure 5.

A graphene sheet represented in a) as a collection of beads (400 beads), b) both the bead and STL mesh overlaid to show how close they overlap.

Figure 6.

Intrinsic conductivity $[\sigma]_0$ of insulating particles having the geometry of a) straight and worm-like CNTs, and b) straight and flexible GSs embedded in a perfectly conductive medium $[\sigma]_0$ as a function of CNT length and GS surface area. The virial coefficient $[\sigma]_0$ for the CNTs does not vary much and in all cases takes a value close to needle limit of $-5/3$ [35]. On the other hand, $(-[\sigma]_0)$ for GSs follows a non-trivial power-law increase with nanoparticle area.

Figure 7.

Intrinsic conductivity as a function of the ratio of the conductivity of the filler to the conductivity matrix for a) rod-like (black circles) and worm-like CNTs (red squares) and b) flat (black circles) and flexible (red squares) GSs. Knowing $[\sigma]_0$ and $[\sigma]_\infty$ for the filler, we can estimate $[\sigma(\Delta)]$ for any value of Δ using Eq. (2) (solid lines in both panels).

Figure 8.

Electric polarizability tensor components as a function of the radius of gyration tensor components for worm-like CNTs having different lengths and $l_p = (1736 \pm 5.6)$ nm. The tensor components have been normalized by the tensor trace.

Figure 9.
Illustration of a rotating needle used to clarify the relationship between the projected length and the elements of the magnetic polarizability tensor.

Figure 10.

Magnetic polarizability tensor elements $\alpha_{M_{xx}}$, $\alpha_{M_{yy}}$, $\alpha_{M_{zz}}$ and the intrinsic conductivity $[\sigma]_0$ of perfectly insulating CNTs calculated using COMSOL (in black) and approximated (in red) using the elements of the electric polarizability tensor, Eq. (32).

Figure 11.

Magnetic polarizability tensor elements $\alpha_{M_{xx}}$, $\alpha_{M_{yy}}$, $\alpha_{M_{zz}}$ and the intrinsic conductivity $[\sigma]_0$ of perfectly insulating GSs calculated using COMSOL (in black) and approximated (in red) using the elements of the electric polarizability tensor, Eq. (33). In estimating $[\sigma]_0$, we simply take $\alpha_{M_{xx}}$ to be a constant, $\alpha_{M_{xx}} = 1.23$.