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Orientation of graphene nanosheets in suspension under an electric field: theoretical model and molecular dynamic simulations

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Abstract

Orientation regulation of nanoparticles in a suspension by an electric field is a powerful tool to tune its mechanical, thermal, optical, electrical properties etc. However, how molecular modification can affect the orientation of two-dimensional nanoparticles is still unclear. In this paper, the influence of molecular modification on the orientation of graphene nanosheets (GNS) in water was investigated through theoretical analyses and molecular dynamics (MD) simulations. Firstly, a new orientation angle model was proposed, which considers hydration effects, dipole moments and resistance torque. Then, MD simulations were conducted to investigate the effects of position, direction, type, and number of functional groups on the orientation of GNS. The trend observed in MD simulations is consistent with the proposed theoretical model. The results reveal that, under the combined influence of the dipole moment and hydration effects, the modification with hydrophilic functional groups can reduce the orientation angle from 21.31° to 8.34°, while the modification with hydrophobic functional groups increases it to 26.43°. Among the hydrophilic functional groups, orientation of hydroxylated GNS is the best. With an increase in the number of hydroxyl groups, orientation angle is decreased from 12.61° to 8.34°. This work can provide valuable guidance for the design of high-performance suspensions and composites, such as thermal smart materials with adjustable thermal conductivity and intelligent devices with tailored capabilities.

Supplementary material for this article is available online

Keywords: molecular modification, graphene nanosheet, rotational diffusion coefficient, orientation by electric field, molecular dynamics simulation

1. Introduction

Nanoparticle suspensions are composed of based fluid and nanoparticles, such as graphene [1, 2], carbon nanotubes [3], metal nanoparticles [4], metal oxide nanoparticles [5], and so

on. Low-dimensional nanoparticles are promising in improving the mechanical [6], thermal [7, 8], optical [9], electrical [10], and chemical properties [11] of the base fluid. For the physical parameter of thermal conductivity, the incorporation of nanoparticles can increase the thermal conductivity of fluid almost $1.78 \times [12]$, and nanoparticle suspensions have been widely used in heat transfer equipment [13], such as electronic cooling, solar thermal collectors, heat exchangers, automobile

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radiators, and thermal storage. However, the performance improvement of nanoparticle suspensions is not significant when nanoparticles distributed randomly. The critical challenge lies in how to improve the orientation of nanoparticles [14]. The orientation of nanoparticles can impact thermal conductivity [7, 14, 15], electrical conductivity [16], fracture toughness [17], and friction coefficient [18], among other properties [19–22]. Moreover, the directed assembly of nanoparticles is crucial for designing intelligent devices with tailored capabilities, such as selective sensing, lab-on-a-chip, optoelectronics, and controlled photonic bandgap.

There are various methods to achieve the orientation of nanoparticles, including mechanical stretching [23], electric field [24, 25], magnetic field [18, 26], and shear flow [27]. Among these methods, electric field is more straightforward, exhibits faster responsiveness, and consumes less energy. Currently, there are two physical mechanisms to explain the orientation of nanoparticles induced by an electric field: the torque induced by dipole moments and the hydration effects of polar water molecules. While experiments indicated that the main reason for oriented distribution is the dielectrophoretic force and the dielectrophoretic torque experienced by polarized nanoparticles [28, 29], molecular dynamics (MD) simulations also suggested that even non-polarizing nanoparticles without charge can orient themselves in water under a direct current (DC) electric field. This phenomenon can be attributed to hydration effects of polar water molecules [30, 31]. However, previous researches just considered the two mechanisms separately and did not establish a model to calculate the orientation angle.

Functional groups on the surface of nanoparticles can influence dipole moments and hydration effects, thereby affecting orientation. Ma *et al* [32] experimentally observed that oxidized multi-walled carbon nanotubes exhibited better dispersion and orientation compared to pristine multi-walled carbon nanotubes [33]. Mostafa and Banerjee [34] found that under an electric field, pristine carbon nanotubes exhibited the best orientation, followed by lateral functionalization, and then terminal functionalization. Lim *et al* [10] observed that both carboxyl-functionalized and amino-functionalized carbon nanofibers have similar orientation structures under an electric field. However, previous researches have discrepancies in conclusions regarding the influence of functional groups on orientation of nanoparticles.

In this study, we disclosed the influence of molecular modification on orientation of graphene nanosheets (GNS) in suspension under an electric field through theoretical analyses and MD simulations. The type of molecular modification includes hydrophilic groups (hydroxyl, carboxyl, and amino) and hydrophobic groups (methyl, and hydrogen). Firstly, an orientation angle model was proposed, which accounts for hydration effects, dipole moments and resistance torque. This model was verified through simulation results. Then, through MD simulations, the rotational diffusion coefficients, orientation angles, and orientation degrees of GNS in water were calculated, and the influence of position, direction, type, and number of functional groups on orientation of GNS in water under a DC electric field was analyzed.

2. Model

As shown in figure 1, the unit direction vectors (L, N), and W) are introduced. L is parallel to the long side of GNS, N is perpendicular to the plane of GNS, and W is parallel to the short side of GNS. The angle between the direction of electric filed **E** and **L** is denoted as φ_{L-E} , and the angle between the *E* and *N* is $\varphi_{\rm N-E}$. Given that the range 0°–90° and 180°– 90° are considered equivalent and to prevent two equivalent peaks in angular probability distribution, φ_{L-E} is defined over a range of 0°-90°. Kim and Shkel [35] elucidated the orientation mechanism of micro/nanoparticles in suspensions induced by electric field, and provided formulas for both electric field induced torque and viscous torque acting on particles. Mostafa and Banerjee [36] employed a continuum mechanics based model to predict the time required for orientation of carbon nanotubes. Referring to above analyses, we conduct a torque analysis on GNS under a DC electric field, and propose an orientation angle model that accounts for hydration effects, dipole moments and resistance torque.

2.1. Torque generated by hydration effects

Water molecules interact by hydrogen bonds among themselves. When GNS are introduced into water, a large number of hydrogen bonds are disrupted, leading to an increase in enthalpy. To maintain as many hydrogen bonds as possible, dipole moment vectors of water molecules in the first hydration layer predominantly orient parallel to the surface of GNS, which is called hydration effects. Under a DC electric field, dipole moments of water molecules not only orient towards the direction of electric field, but also parallel to the surface of GNS to maximize hydrogen bonds. As a result, GNS are compelled to orient their long side in the direction of electric field. The torque generated by hydration effects at equilibrium, denoted as M_w , can be approximated as,

$$M_{\rm W} = hE\sin\theta,\tag{1}$$

where *h* represents the hydrophilicity coefficient, *E* is the electric field strength, and θ is φ_{L-E} at equilibrium.

2.2. Torque generated by dipole moments

Functional groups are symmetrically distributed along the outer long edge of GNS, the dipole moment vector of GNS is denoted as μ . When all functional groups have the same direction, the dipole moment vector can be expressed as,

$$\boldsymbol{\mu} = n\boldsymbol{p},\tag{2}$$

where *n* represents the number of functional groups, and *p* denotes the dipole moment vector of a single functional group. Under an electric field, the torque of GNS caused by the dipole moment vector is given as [35],

$$M_{\mu} = \mu_{\parallel} \times E_{\perp} - \mu_{\perp} \times E_{\parallel}, \qquad (3)$$

where μ_{\parallel} and μ_{\perp} respectively denote the dipole moment along and perpendicular to L. E_{\parallel} (where $E_{\parallel} = E \cdot \cos\theta$) and E_{\perp} (where $E_{\perp} = E \cdot \sin \theta$) represent the electric field intensities along and perpendicular to L, respectively. Equation (3) can be expressed as,

$$M_{\mu} = \mu E \cos \alpha \sin \theta - \mu E \sin \alpha \cos \theta, \qquad (4)$$

where α is the angle between dipole moment vector μ and long side vector L. The orientation depends on α , because M_{μ} can be increased by reducing α . When functional groups are symmetrically added to the outer long edge of GNS, μ is parallel to L and $\alpha = 0$. The equation (4) can be simplified as,

$$M_{\mu} = \mu E \sin \theta. \tag{5}$$

2.3. Resistance torque

The Reynolds number of GNS in water is very small ($Re \leq 1$). The viscous torque in equilibrium is given by Stokes' law as [35],

$$M_{\rm f} = 3\eta K V {\rm curl}(v_{\infty}), \qquad (6)$$

where η represents the kinematic viscosity of water, *K* is the shape factor, *V* is the volume of nanoparticles, and v_{∞} is the velocity of the surrounding water. Electric field intensity will affect the velocity of water, thus influencing viscous torque.

2.4. Orientation angle model

Under the combined influence of hydration effects, dipole moments, and resistance torque, GNS rotate to an equilibrium state. Through torque analysis, the torque equilibrium equation in the equilibrium state can be obtained as follows,

$$M_{\rm W} + M_{\mu} - M_{\rm f} = 0. \tag{7}$$

From this, the expression for φ_{L-E} can be derived as,

$$\varphi_{\rm L-E} = \theta = \arcsin \frac{3\eta K V {\rm curl}(v_{\infty})}{(h+np)E}.$$
(8)

The equation (8) suggests that enhancing hydrophilicity, increasing dipole moment, raising electric field strength, and reducing resistance torque can all decrease φ_{L-E} , and thus improve orientation of GNS.

3. Method

3.1. Simulation details

The orientation of GNS in water is investigated using MD simulations. We have selected GNS suspended in water as a simulation system. Figure 1 displays a schematic of simulation system at the initial moment, with the water density set at 1000 kg m⁻³. Periodic boundary conditions are applied in the *x*, *y*, and *z* directions. Both velocity and angular velocity of



Figure 1. Schematic illustration of simulation system at the initial moment and unit direction vectors.

GNS are initialized to zero, and velocity of water molecules corresponds to Gaussian distribution at 300 K.

The potential energy model for water adopts the SPC/E [37] model. Long-range electrostatic interactions between water molecules are addressed with the particle-mesh Ewald method [38]. Bond length between oxygen and hydrogen atoms is constrained to 1.0 Å using the SHAKE algorithm [39], with H–O–H bond angle being 109.47°. GNS are set as rigid bodies to reduce computational time. Carbon atoms not bonded to functional groups are uncharged. Interatomic interactions encompass electrostatic forces and the Lennard–Jones potential components, described as,

$$\varphi\left(r\right) = \frac{q_i q_j}{r} + 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^6 \right],\tag{9}$$

where *r* is the distance between atoms *i* and *j* with charge q_i and q_j , and ε_{ij} and σ_{ij} are potential parameters which depend on the atomic type. The potential parameters for hydroxyl and carboxyl groups are sourced from OPLS-AA force field [40], while parameters for amino, methyl, and hydrogen are derived from CHARMM27 force field [41]. The potential parameters and charges are provided in Supporting Information. The cutoff radius is set to 1.2 nm [42].

The simulations are conducted using the LAMMPS software package [43]. The NPT ensemble is utilized during simulation [42]. Temperature regulation is achieved using the Nose–Hoover thermostat, setting the system temperature at T = 300 K. Pressure is controlled by Nose–Hoover barostat, with the system pressure set at P = 1 atm. The simulations use a timestep of 1 fs and run for a total of 8 ns [44]. The initial 1 ns serve to equilibrate the system, and data from the subsequent 7 ns are used for analysis.

3.2. Calculation of important physical quantities

The rotational diffusion coefficient [45] is used to quantitatively characterize the intensity of Brownian rotation at equilibrium. Increasing the hydrophilicity of GNS can weaken Brownian rotation, thereby reducing the rotational diffusion coefficient. Cao's group [42, 44, 46, 47] has developed a method to calculate the rotational diffusion coefficients and diffusion tensors of nanoparticles, finding that the rotational diffusion coefficient is negatively correlated with orientation degree. By recording the changes of u_k (where $u_1 = L$, $u_2 = N$, $u_3 = W$) over time *t*, angular displacement Δq can be approximately obtained using the following equation in a short time [48, 49],

$$\Delta q = \frac{1}{2} \sum_{k=1}^{3} \boldsymbol{u}_{k}(0) \times \boldsymbol{u}_{k}(t).$$
(10)

The rotational diffusion coefficients D_{r-L} , D_{r-N} and D_{r-W} are given as,

$$D_{\mathbf{r}-i} = \frac{1}{2} \frac{\langle \Delta q_i^2 \rangle}{\Delta t} \left(i = L, N, W \right), \tag{11}$$

where <...> represents ensemble averaging, and Δq_i denotes the angular displacement with direction vectors L, N or W as the rotation axes.

A DC electric field *E* is applied to the simulation system using the efield command, oriented along the *x*-axis. The voltage intensity range selected in this simulation is typical for targeted studies of nanoparticles [30, 50]. Although the experimental value of *E* is significantly lower than the simulation value, a larger value is required in MD to obtain more pronounced phenomena and reduce computational time. Orientation angle φ is obtained by ensemble averaging. The optimal orientation for GNS is when φ_{L-E} is 0° and φ_{N-E} is 90°. Orientation degree λ is determined using the orientation tensor [51],

$$\boldsymbol{T}_{ij} = \frac{3}{2N} \sum_{n=1}^{m} \left[\boldsymbol{l}_{i}^{(n)} \boldsymbol{l}_{j}^{(n)} - \frac{1}{3} \delta_{ij} \right],$$
(12)

where *m* represents the number of all instantaneous GNS, $l^{(n)}$ denotes the unit direction vector *L* or *N*, and the subscripts *i* and *j* are chosen from the *x*, *y* and *z* directions. The largest eigenvalue of the tensor corresponds to orientation degree λ . A higher value indicates better orientation, and GNS are considered fully oriented when $\lambda = 1$.

4. Results and discussion

Research has revealed that when a DC electric field is applied to the system, φ_{N-E} closely approaches to 90°. This suggests that the plane of GNS is parallel to the direction of electric field. Molecular modification has minimal influence on φ_{N-E} , while they significantly impact φ_{L-E} . This effect is correlated with the position, direction, type, and number of functional groups.

4.1. The influence of functional group position and direction

According to equation (4), when functional groups are symmetrically added to the outer long edge of GNS, dipole moment vector is parallel to long side vector of GNS. This distribution can result in a larger torque generated by dipole moments, thus exhibiting better orientation. Therefore, functional groups are modified on the outer long edge of GNS in this study.

The influence of position and direction of hydrophilic functional groups on orientation is investigated using hydroxyl groups as an example. The GNS are modified with four hydroxyl groups and have a length (L) of 3.267 nm and a width (W) of 0.738 nm, as illustrated in figures 2(a) and (b). The position parameter for functional groups is represented by $d_{\rm L} = 2d/L$, where d is the average distance from functional groups to the central line of long side of GNS. A smaller $d_{\rm L}$ value indicates that functional groups are closer to the center of GNS. Figures 2(c) and (d) depict the variations of λ and φ_{L-E} with respect to d_L . The position of hydroxyl groups has a minimal effect on λ_{N-E} , while it significantly affects λ_{L-E} . As hydroxyl groups approach the center of GNS, φ_{L-E} becomes smaller and λ_{L-E} increases, indicating better orientation. In the central region of GNS, water molecules are parallel to the plane of GNS. At the edge region of GNS, water molecules become disordered due to the influence of interactions with outer-edge water molecules. By introducing hydrophilic groups in the central region of GNS, hydration effects become stronger. In addition, the interactive forces between hydrophilic functional groups and water molecules contribute resistance torque on the rotation of GNS in water. As hydroxyl groups near the central region of GNS, the hydration effects strengthen and the resistance torque decreases. According to equation (8), h increases and $3\eta KV \text{curl}(v_{\infty})$ decreases, which lead to a decrease in φ_{L-E} . The total distance from functional groups to the central line plays a major role in orientation of GNS, rather than the distance between functional groups, as discussed in Supporting Information. When hydroxyl groups are directed in opposite direction, the dipole moment is zero, and GNS are subjected to hydration effects and resistance torque. When hydroxyl groups are directed in the same direction, GNS is influenced by a combination of hydration effects, dipole moments and resistance torque. Due to the influence of dipole moments, when hydroxyl groups have the same direction, they exhibit a smaller φ_{L-E} and a higher λ_{L-E} compared to when they are opposite.

4.2. The influence of functional group type and number

Different types of hydrophilic functional groups are added to the outer long edge of GNS with L = 1.988 nm and W = 0.738 nm. The hydrophilicity of functional groups is correlated with the number and strength of their hydrogen bonds. Among the hydrophilic functional groups studied in this paper, carboxyl group exhibits the strongest hydrophilicity, followed by hydroxyl group, and then amino group.



Figure 2. Hydroxyl groups directed in the (a) same and (b) opposite direction. Purple spheres represent carbon atoms, red spheres represent oxygen atoms, and white spheres represent hydrogen atoms. (c) Orientation degree λ and (d) orientation angle φ_{L-E} as a function of d_L .

Figure 3 presents how the rotational diffusion coefficient $(D_{\rm r} = D_{\rm r-L} + D_{\rm r-W} + D_{\rm r-N})$ of GNS varies with the number of functional groups. The rotational diffusion coefficient of the pristine GNS is 2.17×10^9 rad² s⁻¹, and hydrophilic functional groups can reduce the rotational diffusion coefficient of GNS. Given an equal number of functional groups, amino-functionalized GNS have the highest D_r , followed by hydroxyl-functionalized GNS, and then carboxylfunctionalized GNS. This indicates that D_r is negatively correlated to the hydrophilicity of the added functional groups. Moreover, D_r decreases with an increase in the number of hydrophilic functional groups. The presence of hydrophilic functional groups increases hydrogen bonds between water molecules and the surface of GNS, thereby enhancing the adhesive and electrostatic forces between GNS and water molecules. These interactive forces decelerate rotational Brownian motion of GNS. As the number of hydrophilic functional groups increases, the interaction force intensifies because of a rise in hydrogen bonds, resulting in a decrease in D_{r} .

As figure 4(a) depicts, GNS are functionalized by a pair of oppositely directional functional groups, yielding functionalized GNS with a dipole moment of zero. The functionalized GNS are primarily affected by hydration effects under an electric field. Figures 4(b) and (c) show both pristine GNS and functionalized GNS have φ_{N-E} around 90°, and λ_{N-E} is approximately 0.98. By modifying GNS with hydrophilic functional groups, the hydration effects are enhanced. Therefore, φ_{L-E} is reduced based on orientation angle model. Conversely, when GNS are modified with hydrophobic functional groups, the hydration effects weaken, resulting in an increase in φ_{L-E} and a decrease in λ_{L-E} . MD simulation results are consistent with the orientation angle model. When GNS are functionalized with an identical number of functional



Figure 3. Variation of the rotational diffusion coefficient D_r with respect to type and number of functional groups.

groups in the same position and have a dipole moment of zero, superior hydrophilicity of functional group results in a smaller D_r . Figure 4(d) demonstrates that λ_{L-E} has an inverse relationship with rotational diffusion coefficient D_r . The orientation behavior of GNS is fundamentally the combined effect of external fields and rotational Brownian motion when dipole moments are not considered. Reducing the rotational diffusion coefficient D_r can effectively enhance the orientation.

As illustrated in figure 5(a), the outer long edge of GNS is modified with functional groups directed in the same direction. Owing to the symmetrical distribution of functional groups, μ is parallel to *L*. Table 1 lists dipole moment values for different



Figure 4. (a) Schematic illustration of functionalized GNS with functional groups directed in opposite direction. Red spheres in GNS represent functional groups. Variation of (b) orientation angle and (c) orientation degree with type of functional groups. (d) Relationship between λ_{L-E} and D_r .

 Table 1. Dipole moment values of different functionalized GNS.

Types of GNS	GNS-COOH	GNS-OH	$GNS-NH_2$	GNS-CH ₃	GNS-H
Dipole moment μ (eÅ)	3.690	4.277	2.428	0.509	0.656

functionalized GNS. Figures 5(b) and (c) depict angular probability distribution of φ_{L-E} and φ_{N-E} for both pristine GNS and the GNS modified with hydrophilic functional groups. The modification with hydrophilic functional groups results in an increased peak value for φ_{L-E} , with a corresponding decrease in the angle at the peak. Both pristine GNS and functionalized GNS exhibit a pronounced orientation distribution near 90° for φ_{N-E} , with the hydrophilic functional group modification leading to an increased peak value and enhanced orientation.

Figures 6(a) and (b) depict the variation in φ_{L-E} and λ_{L-E} as a function of the number of functional groups. For pristine GNS, the value of φ_{L-E} is 21.31° and λ_{L-E} is quantified as 0.77. GNS modified with hydrophilic functional groups demonstrate superior orientation compared to pristine GNS. Among these, orientation of hydroxylated GNS is the most pronounced, primarily because the influence of dipole moments outweighs that of hydration effects. In contrast, GNS modified with hydrophobic functional groups display weakened hydration effects and lesser dipole moments. Their orientation is inferior to that of pristine GNS, and no clear trend is observed with an increase in the number of functional groups. Figures 6(c) and (d) illustrate angular probability distribution for GNS modified with varying numbers of hydroxyl groups. As shown in figure 6(c), the orientation distribution around 90° for φ_{N-E} is very prominent, and as the number of hydroxyl groups increases, the peak value amplifies, indicating enhanced orientation. Figure 6(d) reveals that with an increasing number of hydroxyl groups, the peak value of φ_{L-E} rises, the angular distribution range narrows, and the angle corresponding to the peak value gradually diminishes.

4.3. Orientation angle model of hydroxylated GNS

The position, direction, type, and number of functional groups can alter torque generated by hydration effects, dipole moments, and resistance. These changes influence φ_{L-E} of GNS according to the orientation angle model. The closer the functional group is to the center of GNS, the smaller the resistance torque, leading to better orientation. As the number of hydrophilic functional groups increases, dipole moment becomes larger and hydration effect strengthens, resulting in improved orientation. The simulation results are found to be qualitatively consistent with the orientation. Hence, we fit MD simulation data to the orientation angle model and derive an equation for predicting φ_{L-E} of hydroxylated GNS, which



Figure 5. Functionalized GNS modified with different types of functional groups. (a) Schematic illustration. Red spheres in GNS represent functional groups. Angular probability distribution of (b) φ_{L-E} and (c) φ_{N-E} .



Figure 6. Variation of (a) φ_{L-E} and (b) λ_{L-E} with the number of functional groups. Angular probability distribution of (c) φ_{N-E} and (d) φ_{L-E} for GNS modified with varying numbers of hydroxyl groups.

the hydroxyl groups are modified on the outer long edge of GNS in maximal number. The formula for φ_{L-E} is as follows,

$$\varphi_{\rm L-E} = \arcsin \frac{M_{\rm f0} + aE}{(h+np)E},\tag{13}$$

where the unit of *E* is V nm⁻¹, $M_{f0} = 0.0387$ eV, a = 0.516 eÅ, h = 2.4 eÅ. The number of hydroxyl groups is obtained from n = 2L/s, where s = 0.426 nm which is equal to three carbon–carbon bond lengths. As shown in figure 7, we obtain φ_{L-E} of hydroxylated GNS at different lengths, widths, and electric field strengths. The MD simulation results are in good agreement with the orientation angle model. The longer the GNS

is, the more hydroxyl groups that can be added, resulting in a larger dipole moment and consequently a smaller φ_{L-E} . The width has a minimal impact on orientation of hydroxylated GNS. Orientation of GNS increases with the enhancement of electric field strength.

For pristine GNS with L = 1.988 nm and W = 0.738 nm, φ_{L-E} value stands at 21.31°. Upon hydroxylation, φ_{L-E} decreases to 8.34°, while λ_{L-E} increases to approximately $1.25 \times$ that of pristine GNS. It is evident that modification with hydrophilic functional groups can significantly enhance orientation of GNS. This model provides guidance for orientation control of hydroxylated GNS under a DC electric field. In practical applications, the length of GNS is much larger than the scale simulated in this study. Hence, similar orientation results



Figure 7. φ_{L-E} of hydroxylated GNS with different lengths, widths, and electric field intensities.

as in the simulations can be observed using a much weaker electric field. The orientation angle model and MD simulations can explain the effects of molecular modification on the orientation of GNS in suspension. However, it is difficult to control the position of functional groups in the actual preparation of materials. Interactions between functional groups and aggregation may affect the orientation of GNS. Both the orientation angle model and MD simulations have not taken these factors into account.

5. Conclusion

In this study, we systematically investigated the influence of molecular modification on the orientation of GNS in water under a DC electric field using both theoretical analyses and MD simulation methods. Theoretically, we developed an orientation angle model, which takes into account hydration effects, dipole moments, and resistance torque. Based on the orientation angle model, we derived an equation to predict φ_{L-E} of hydroxylated GNS. MD simulations were employed to study the effects of position, direction, type, and number of functional groups on orientation of GNS. It was observed that the optimal position for molecular modification is on the outer long edge of GNS with all functional groups symmetrically distributed and directed in the same direction. Such an arrangement ensures that the dipole moment vector is parallel to the long side of GNS. It also found that hydrophilic functional groups enhance the dipole moment and hydrophilicity of GNS, thereby enhancing their orientation, whereas hydrophobic functional groups decrease orientation. Specifically, hydrophilic functional group modification can reduce the orientation angle φ_{L-E} from 21.31° to 8.34°, while hydrophobic modification increases it to 26.43°. As the number of hydrophilic functional groups increases, both the dipole moment and hydration effects intensify, leading to enhanced orientation of GNS. This work can give valuable insights for the orientation of nanoparticle suspensions and composites, offering guidance for the design of materials with tunable mechanical, thermal, optical and electrical performances.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

- [1] Sun C, Huang Y, Shen Q, Wang W, Pan W, Zong P A, Yang L, Xing Y and Wan C 2020 Sci. Adv. 6 eabb1338
- 2] Geim A K 2009 Science **324** 1530
- [3] Felicia L J and Philip J 2014 *Phys. Rev.* E **89** 022310
- [4] Sankar N, Mathew N and Sobhan C 2008 Int. Commun. Heat Mass Transfer 35 867
- [5] Chevalier J, Tillement O and Ayela F 2009 Phys. Rev. E 80 051403
- [6] Allaoui A, Bai S, Cheng H M and Bai J 2002 Compos. Sci. Technol. 62 1993
- [7] Zhang Z T, Dong R Y, Qiao D S and Cao B Y 2020 Nanotechnology 31 465403
- [8] Cardellini A, Fasano M, Bigdeli M B, Chiavazzo E and Asinari P 2016 J. Phys.: Condens. Matter 28 483003
- [9] Jing D, Sun L, Jin J, Thangamuthu M and Tang J 2020 J. Phys. D: Appl. Phys. 54 013001
- [10] Lim C S, Rodriguez A J, Guzman M E, Schaefer J D and Minaie B 2011 Carbon 49 1873
- [11] Venu H and Appavu P 2021 Int. J. Ambient Energy 42 1588
- [12] Mousavi S, Esmaeilzadeh F and Wang X 2019 J. Therm. Anal. Calorimetry 137 879
- [13] Okonkwo E C, Wole-Osho I, Almanassra I W, Abdullatif Y M and Al-Ansari T 2021 J. Therm. Anal. Calorimetry 145 2817
- [14] Wu S, Ladani R B, Zhang J, Bafekrpour E, Ghorbani K, Mouritz A P, Kinloch A J and Wang C H 2015 Carbon 94 607
- [15] Pan X, Jin H, Ku X, Guo Y and Fan J 2024 Phys. Chem. Chem. Phys. 26 2402
- [16] Xia X, Hao J, Wang Y, Zhong Z and Weng G J 2017 J. Phys.: Condens. Matter 29 205702
- [17] Ravindran A R, Ladani R B, Wu S, Kinloch A J, Wang C H and Mouritz A P 2018 Composites A 106 11
- [18] Solodov A N et al 2023 Diam. Relat. Mater. 138 110211
- [19] Verma A and Parashar A 2018 Comput. Mater. Sci. 143 15
- [20] Verma A and Parashar A 2018 Nanotechnology 29 115706
- [21] Setoodeh A, Badjian H and Jahromi H S 2017 J. Mol. Model. 23 2

- [22] Jahromi H S, Mehdipour F and Firoozi G 2021 Mapta J. Mech. Ind. Eng. 5 2517
- [23] Wang Q, Dai J, Li W, Wei Z and Jiang J 2008 Compos. Sci. Technol. 68 1644
- [24] Gao J, He Y and Gong X 2018 Results Phys. 9 493
- [25] Khamidullin T, Lounev I, Solodov A, Vakhitov I, Hashemi S A and Dimiev A M 2021 J. Phys. Chem. C 125 26823
- [26] Shah S A, Reeves D B, Ferguson R M, Weaver J B and Krishnan K M 2015 Phys. Rev. B 92 094438
- [27] Hobbie E K, Wang H, Kim H, Lin-Gibson S and Grulke E 2003 Phys. Fluids 15 1196
- [28] Oliveira L, Saini D, Gaillard J B, Podila R, Rao A M and Serkiz S M 2015 Carbon 93 32
- [29] Li J, Zhang Q, Peng N and Zhu Q 2005 Appl. Phys. Lett. 86 153116
- [30] Guo X, Su J and Guo H 2012 Soft Matter 8 1010
- [31] Daub C D, Bratko D, Ali T and Luzar A 2009 Phys. Rev. Lett. 103 207801
- [32] Ma C, Zhang W, Zhu Y, Ji L, Zhang R, Koratkar N and Liang J 2008 Carbon 46 706
- [33] Sengezer E C, Seidel G D and Bodnar R J 2015 *Polym. Compos.* **36** 1266
- [34] Mostafa M and Banerjee S 2014 J. Phys. Chem. C 118 11417
- [35] Kim G and Shkel Y M 2004 J. Mater. Res. 19 1164
- [36] Mostafa M and Banerjee S 2014 J. Appl. Phys. 115 244309

- [37] Song Y and Dai L L 2010 Mol. Simul. 36 560
- [38] Hickory R and Eastwood J 1988 Computer Simulation Using Particles (Taylor & Francis Group) (https://doi.org/10. 1201/9780367806934)
- [39] Ryckaert J P, Ciccotti G and Berendsen H J 1977 J. Comput. Phys. 23 327
- [40] Tang H, Liu D, Zhao Y, Yang X, Lu J and Cui F 2015 J. Phys. Chem. C 119 26712
- [41] Chen C et al 2020 Desalination **491** 114560
- [42] Dong R Y, Cao P, Cao G X, Hu G J and Cao B Y 2017 Acta Phys. Sin. 66 14702
- [43] Plimpton S 1995 J. Comput. Phys. 117 1
- [44] Zhang Z T, Zhao X and Cao B Y 2019 Sci. Rep. 9 18943
- [45] Heyes D, Nuevo M, Morales J and Branka A 1998 J. Phys.: Condens. Matter 10 10159
- [46] Dong R Y and Cao B Y 2014 Sci. Rep. 4 6120
- [47] Cao B Y and Dong R Y 2014 J. Chem. Phys. 140 034703
- [48] Kraft D J, Wittkowski R, Ten Hagen B, Edmond K V, Pine D J and Löwen H 2013 Phys. Rev. E 88 050301
- [49] Cichocki B, Ekiel-Jeżewska M L and Wajnryb E 2015 J. Chem. Phys. 142 214902
- [50] Dang H, Song D, Lin Z, An M, Ma W and Zhang X 2022 Int. J. Heat Mass Transfer 190 122751
- [51] Börzsönyi T, Szabó B, Törös G, Wegner S, Török J, Somfai E, Bien T and Stannarius R 2012 Phys. Rev. Lett. 108 228302