Orientational randomness and its influence on the barrier properties of flake-filled composite films

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Abstract
This direct numerical study investigated the effect of orientational randomness on the barrier properties of flake-filled composites. Over 2500 simulations have been conducted in two-dimensional, doubly periodic unit cells, each containing 500 individual flake cross-sections which, besides being spatially random, assume random orientations within an interval \([-\varepsilon, +\varepsilon]\) \((0 \leq \varepsilon \leq \pi/2)\). We consider long flake systems (aspect ratio \(\alpha = 50, 100, \text{ and } 1000\)) from the dilute (\(\varepsilon < 1\)) to the concentrated (\(\varepsilon = 15\)) regime, where \(\psi\) is the flake volume fraction. At each \(\varepsilon\) and \(\alpha\), several realizations are generated. At each of those, the steady-state diffusion equation is solved, the mass flux across a boundary normal to the diffusion direction is computed and an effective diffusivity \(D_{\text{eff}}\) calculated from Fick’s Law. The computational results for \(D_{\text{eff}}\) are analyzed and the effects of \(\varepsilon\) and \(\alpha\) are quantified. These differ in the dilute \((\alpha < 1)\) and in the concentrated regimes \((1 < \alpha \psi < 15)\). In the dilute regime, the barrier improvement factor is a linear function of \(\varepsilon\) and a power function of \(\alpha\), with the exponent \((0.97)\) independent of orientation. In concentrated systems, we find that for aligned flakes or flakes showing small deviations from perfect alignment, the barrier improvement factor approaches the quadratic dependence on \(\alpha\) predicted by theory. However, the power exponent is found to decrease as \(\varepsilon\) increases, from 1.71 in the aligned system \((\varepsilon = 0)\) to \(\sim 0.9\) in the fully random system \((\varepsilon = \pi/2)\). We propose a scaling which incorporates the effects of both \(\alpha\) and \(\varepsilon\) on the barrier improvement factor, resulting in a master curve for all \(\alpha\) and \(\varepsilon\). Our results suggest that the anticipated barrier property
improvement may not be realized if the flake orientations exhibit a significant scatter around the desired direction.

**Keywords**
Barrier properties, composite films, diffusion, flakes, platelets

**Introduction**
Flake-filled polymeric composites, incorporating mica, glass, or metallic flakes, offer significant processing and property advantages, such as high dimensional stability and low warpage in molding, uniform in-plane mechanical properties and superior mechanical performance for two-dimensional loading, corrosion protection, sound insulation as well as appearance and color control.\(^1\)–\(^4\) Flake-filled polymeric composites also find uses as barrier materials in food packaging, where the objective is to hinder the oxygen, CO\(_2\), or other vapor diffusion to and from a container\(^5\)\(^6\) while maintaining all the formability and design advantages afforded by plastic materials. One additional advantage is that the geometries in which such barrier property improvement is to be realized are very similar to those in which the mechanical superiority of flake-filled systems is also evident, such as in plates, shells, cylinders, pipes, etc.; therefore, barrier improvement can be combined with good mechanical performance. Besides micron-sized flakes of inorganic materials such as mica, nano-scale platelets of clay minerals such as hectorite, saponite, and montmorillonite and more recently graphene-oxide platelets of aspect ratios well over 1000 have been used for this purpose.\(^7\) It has been demonstrated that incorporating such fillers aligned perpendicular to the macroscopic diffusion direction can be very effective in increasing barrier properties by providing a tortuous diffusion path for the diffusing species. When the flakes are randomly placed and well aligned, the predicted barrier efficiency improvement ranges from being \(\sim(\alpha\varphi)\) in dilute systems, where \(\alpha\) is the aspect ratio and \(\varphi\) the flake volume fraction, to being \(\sim(\alpha\varphi)^2\) in more concentrated dispersions.\(^6\)\(^8\)\(^9\) Considering the usually large flake aspect ratio, significant barrier property improvement can be achieved by adding a small amount of filler. Computational and experimental studies are in agreement with these predictions.\(^10\)–\(^18\)

While earlier works quantified the difference in barrier properties between aligned and random systems, there is limited understanding on how intermediate orientation states as well as random deviations from a predominant orientation might affect barrier properties. This is a significant shortcoming, especially for flake composites manufactured from the melt state through polymer processing operations.\(^19\)\(^20\) In such operations (extrusion,
compression or injection molding, thermoforming and others) flake orientation is achieved as flakes tend to orient along the prevailing flow field – either in the main flow direction with shear flow or transverse to it with extensional flow. Special care is therefore needed in designing polymer processing equipment for a desired flake orientation, and even then, it is possible that, when it comes to “on-site” use, not all flakes will be oriented perpendicular to the macroscopic diffusion direction. Even when the final average orientation is the desired one, not all flakes end up oriented in the desired direction, but instead have a distribution of orientations. The way this misalignment affects barrier properties is not well understood. This paper’s objective is to address this issue.

**Computational**

We carry out steady-state diffusion computations in doubly periodic representative volume elements (RVEs) containing up to 500 individual flake cross-sections. These are added in the domain sequentially, using a random sequential addition (RSA) procedure. Specifically, at each flake placement attempt, three random numbers are used to assign the flake center coordinates and its orientation angle. The latter is allowed to be uniformly distributed in the interval \([-\epsilon, +\epsilon]\). If \(\epsilon = 0\), all flakes are oriented normal to the macroscopic diffusion direction. If \(\epsilon = \pi/2\) flakes are allowed to assume completely random orientations. Intermediate states are formed for \(0 < \epsilon < \pi/2\). If, after placement, no overlap with other flakes is detected, the process continues with the next flake, until the desired number of flakes has been placed, or, until no flake has been placed after 50,000 attempts; the latter number signals an abortive case. High aspect ratio flakes were considered with \((\alpha)\) equal to 50, 100, and 1000. While flakes with \((\alpha)\) in excess of 1000 can be associated with nanocomposites, it is known that melt processing severely degrades flake size in traditional as well as nano-flake composites. In that case, our predictions concerning the BIF can be viewed as an upper bound, and composites with substantially lower flake aspect ratios would exhibit lower BIFs.

In order to enable subsequent computational domain meshing, a minimum allowable flake separation \((\delta)\) is imposed; we used \(\delta = 2t\) where \((t)\) is the flake thickness. In a rectangular unit cell with dimensions \((H)\) (in the bulk diffusion direction) and \((L)\) containing \((N)\) flakes of dimensions \((t, l)\) with \(\alpha = l/t\), the flake area fraction is \(\varphi = Nt^2/LH\) and each flake length is \(l = \sqrt{LH\alpha \varphi / N}\). In multi-particle simulations, using doubly periodic RVEs is essential when dealing with elongated particles in order to eliminate artifacts of oriented (or, depleted) layers which appear adjacent to cell boundaries. Figure 1 shows unit cells obtained for various values of \((\epsilon)\) with flakes extended outside the RVE limits to highlight the doubly periodic geometry.
The boundary conditions are cyclic on the right and left boundaries, namely $C_{\text{left}}(0,y) = C_{\text{right}}(L,y)$. On the top and bottom boundaries, fixed concentration values are prescribed. On each flake surface, we impose $\partial C / \partial n = 0$, indicating that the flakes are impermeable. It is known that in practical flake-filled composite applications, surfactants or surface modifiers are often used to facilitate flake dispersion in the polymer matrix and this could create irregular interfaces between the flakes and the matrix. We would expect our results to be valid for such systems also, as long as the flakes remain impermeable and as long as the matrix/flake proportions are not affected, that is, as long as no substantial inter-phase regions are formed. At each ($\varepsilon$) and ($\alpha \varphi$), we generate $\sim 10$ different realizations. The computational meshes are created.
by the mesh generating program Salome™ through an automated procedure developed in-house and each contain \( \sim 10^6 \) triangular elements. Figure 2 shows examples.

These meshes are used by OpenFoam™ to solve the steady-state diffusion equation \( \nabla^2 C = 0 \), \( C \) being the solute concentration, and obtain the distribution of \( C \) in the domain of interest. An isotropic matrix material assumption is also made. Figures 3 and 4 show typical concentration distributions, in which flake distributions corresponding to large \((\alpha \varphi)\) can also be seen. It is clear that, in the presence of orientational randomness, the macroscopically one-dimensional distribution of \((\alpha \varphi)\) typical of dilute systems becomes progressively two-dimensional as \((\alpha \varphi)\) increases. This is at the heart of the observed variation in \( D_{\text{eff}} \), as will be discussed in the following section. The solution also supplies the value of \((\partial C/\partial n)\) at each point on the upper (or lower) boundary. Thus, the mass flux along this boundary can be calculated as \( J = -D_0 \int_0^L \left(\frac{\partial C}{\partial n}\right) \text{d}x \), where \( n \) is the outward unit vector and \( L \) is the width of the unit cell. Because of impermeable flakes crossing boundaries, which results in sudden local changes of the flux, care must be taken in performing this integration. In this work, we used adaptive intervals and only accepted values of the integral when these were convergent with refinement. Equating this flux with the one obtained from Fick’s law in a macroscopic equivalent cell (whose diffusivity is \( D_{\text{eff}} \)), we obtain \( D_{\text{eff}} = \frac{H D_0}{\Delta C L} \int_0^L \left(\frac{\partial C}{\partial n}\right) \text{d}x \) where \( \Delta C \) is the macroscopically imposed concentration difference and \( D_0 \) the diffusivity of the matrix material. These effective diffusivities will be presented and discussed for various values of \((\epsilon)\), \((\alpha)\), and \((\varphi)\) in the following sections.

**Figure 2.** Computational mesh details. \((\alpha)\) is the flake aspect ratio and \((\varphi)\) the flake volume fraction.
We examined how the number of flakes included in the RVE affected the computed $D_{\text{eff}}$. Due to the doubly periodic nature of our RVEs, a convergent value is achieved with a relatively small (~100) number of flakes; however, we chose to work with $N=500$ to allow the systems to form inter-flake arrangements closer to what might be encountered in reality (e.g. Figures 3 and 4) and whose existence will be reflected in the computed effective diffusivities. In addition, and since the flake length to the characteristic length ratio of the

**Figure 3.** Concentration distribution in samples with $\varepsilon = \pi/4$. The number of flakes is $N=500$. Flakes assume random orientations in the interval $[-\varepsilon, +\varepsilon]$. ($\alpha$) is the flake aspect ratio and ($\varphi$) the flake volume fraction.

**Figure 4.** Concentration distribution in randomly oriented samples ($\varepsilon = \pi/2$). $N=500$. Flakes assume random orientations in the interval $[-\varepsilon, +\varepsilon]$. ($\alpha$) is the flake aspect ratio and ($\varphi$) the flake volume fraction.
unit cell is $l/\sqrt{LH} = \sqrt{\alpha \phi / N}$, it is evident that a larger ($N$) will help keep that ratio at acceptable levels; for $\alpha \phi = 15$ and $N = 500$ that ratio is 0.17, which we deem acceptable, given that our unit cells are doubly periodic.

One note on the actual orientation statistics of the generated geometries is in order. While at lower concentrations, the target random distribution of orientation angles is readily achieved, this is not a given at high $\alpha \phi$, as seen in Figures 3 and 4. Besides checking the orientation angle frequency distribution (the cumulative distribution would be a straight line for uniformly distributed orientation angles), we also evaluated a more formal orientation metric, namely the flow orientation strength ($f$) defined as

$$f = 1 - 4 \det(A)$$

where

\[
\begin{array}{|c|c|}
\hline
(A) & = & \text{the orientation tensor whose components are defined as} \\
A_{ij} = \langle p_i p_j \rangle & \text{and brackets} \langle \cdot \rangle \text{indicate ensemble averaging} \\
& & \text{over the entire flake population} \\
p & = & \text{the orientation vector of each flake cross-section}^{21} \\
\hline
\end{array}
\]

For a random orientation, we expect that $f = 0$. For the two-dimensional cross-sections considered in this study, $p_1 = \sin \theta$, $p_2 = \cos \theta$, and the tensor $A$ is

$$A = \begin{bmatrix} \langle \sin^2 \theta \rangle & \langle \sin \theta \cos \theta \rangle \\ \langle \sin \theta \cos \theta \rangle & \langle \cos^2 \theta \rangle \end{bmatrix}$$

It is straightforward to compute the orientation parameter in our computational samples ($f$), since the orientation vectors $p$ of all flakes are directly available. For $\alpha \phi = 10$, in a set of 10 realizations, we find that the average orientation parameter is $f_{av}(\alpha \phi = 10) = 0.00961 \pm 0.0051$ (at the 95% confidence level). At the more extreme value of $\alpha \phi = 20$ (at which we have not reported results for $\varepsilon = \pi/2$), we find that $f_{av}(\alpha \phi = 20) = 0.028 \pm 0.02$. For $\alpha \phi = 1$, it is $f_{av}(\alpha \phi = 1) = 0.00907 \pm 0.0037$. For comparison, a calculation of ($f$) in which 500 angles ($\theta_i$) were simply picked using a random number generator (without eliminating overlaps and thus without creating the structures of Figure 4) gave $f \sim 0.00202$. In conclusion, for randomly oriented systems ($\varepsilon = \pi/2$), there is a gradual deviation of the orientation parameter ($f$) from zero, as well as an increase of the corresponding standard deviation with increasing ($\alpha \phi$) but only at very high ($\alpha \phi$). For ($\alpha \phi$) at which we report results, the related statistics confirm that we are still safe in what would be considered “random” regime.
One final computational issue arising in fully aligned high ($\alpha \varphi$) systems is the fact that flakes may end up placed very close to the upper/lower RVE boundary and due to their large length and parallel orientation effectively “screen” a large portion of it. This can result in high scatter in the predicted $D_{\text{eff}}$ values, something that is not expected from the physics of the problem. The generated meshes can also be severely distorted in that region and this is significant, since subsequent flux calculation requires differentiating the concentration profile across that line. This was resolved by setting, for aligned systems only, a minimum flake separation from the upper/lower boundaries equal to 20 times the flake thickness and by finely meshing these regions.

**Results and discussion**

In the following, we present the results of a comprehensive computational study of diffusion across doubly periodic unit cells, each containing 500 randomly placed impermeable flakes of rectangular cross-section. Complete randomness corresponds to $\varepsilon = \pi/2$, while more narrow distributions are obtained for $\varepsilon < \pi/2$. This is a situation of relevance to flake composites manufactured from the melt state (or through other liquid-based processing routes), where a flow-induced average orientation is typically accompanied by random variations around that average orientation.

Figure 5 plots the barrier improvement factor ($BIF = D_0/D_{\text{eff}}$) versus the maximum misalignment angle ($\varepsilon$) for all computational results. It is evident that, for the ($\varepsilon$) and ($\alpha \varphi$) studied, the computed BIF’s vary over five orders of magnitude; this indicates that further data analysis is justified. Figure 6 presents $D_0/D_{\text{eff}}$ versus ($\alpha \varphi$). One observes that the flake aspect ratio appears to have very little effect on $D_{\text{eff}}$ for the ($\alpha$) studied. Earlier studies$^{15}$ show that, in the dilute limit, aspect ratios higher than 50 at constant ($\alpha \varphi$) do not noticeably change the diffusion coefficient, which approaches a plateau value. Our data suggest that this conclusion can be extended at least into the semi-concentrated regime.

Obviously, the key observation concerning the data in Figure 6 is that the effective diffusivity at each ($\varepsilon$) appears to be a power function of ($\alpha \varphi$), namely

$$D_{\text{eff}} = \frac{D_0}{1 + m(\alpha \varphi)^n}$$  \hspace{1cm} (1)

in which the power exponent ($n$) seems to not remain constant at the higher ($\alpha \varphi$). For this reason, the following data analysis will be carried out separately for the dilute regime ($\alpha \varphi \leq 1$) and the more concentrated systems – ($\alpha \varphi$) up to 15.
Figure 5. Computed barrier improvement factor (BIF) versus angle. All results (2552 data points) corresponding to $\alpha = 50, 100, 1000$, misalignment angles $(0 < \varepsilon < \pi/2)$ and $\alpha \phi$ as indicated. Flakes assume random orientations in the interval $[-\varepsilon, +\varepsilon]$. $(\alpha)$ is the flake aspect ratio and $(\phi)$ the flake volume fraction.

Figure 6. $D_{\text{eff}}/D_0$ versus $\alpha \phi$. All computational results (2552 data points) corresponding to $\alpha = 50, 100, 1000$, all misalignment angles $0 \leq \varepsilon \leq \pi/2$ and $0.005 \leq \alpha \phi \leq 15$. Aligned flakes form the lower edge of the data envelope, while randomly oriented systems with $\varepsilon = \pi/2$ the upper edge. Flakes assume random orientations in the interval $[-\varepsilon, +\varepsilon]$. $(\alpha)$ is the flake aspect ratio and $(\phi)$ the flake volume fraction.
Dilute systems \((0.005 \leq \alpha\phi \leq 1)\)

Figure 7 plots \(\ln(BIF-1)\) versus \(\ln(\alpha\phi)\) for \(\alpha\phi \leq 1\) and selected \((\varepsilon)\) along with the best-fit lines. All lines are parallel to one another suggesting that the exponent \((n)\) in equation (1) is not a function of \((\varepsilon)\). The mean for \((n)\) is 1.07, its standard deviation 0.00923 and the 95% confidence interval is \(\pm 4 \cdot 10^{-4}\).

Equation (1) is an excellent fit to the computational data at all \((\varepsilon)\), with a correlation coefficient greater than 99% in all cases. Further data analysis suggests that both parameters \((m)\) and \((n)\) are very weakly dependent on \((\alpha)\). We find that \((m)\) varies linearly with \((\varepsilon)\) between 0 and \(\pi/2\) (99.5% correlation), with slope \(-0.317\) and intercept 1.021, while \((n)\) is practically constant and averaging 1.07 – as evidenced by the lines in Figure 7 being parallel to each other. If these are taken into account, equation (1) can be written in terms of the \(BIF\) as

\[
\frac{BIF - 1}{1.021 - 0.317\varepsilon} = (\alpha\phi)^{1.07}
\]

Equation (2) suggests a scaling of the computational data in the dilute regime for all states of misalignment. Statistical analysis of the results in

\[\text{Figure 7.} \quad \text{Computational results for the barrier improvement factor (BIF) versus } \ln(\alpha\phi) \text{ in the dilute regime at selected misalignment angles (\(\varepsilon\)). Flakes assume random orientations in the interval } [-\varepsilon, +\varepsilon]. \quad \alpha \text{ is the flake aspect ratio and } \phi \text{ the flake volume fraction.}\]
light of equation (2) shows that at the 95% confidence level, it is

\[
\frac{BIF - 1}{(1.021 - 0.317\varepsilon) \cdot (\alpha\phi)^{1.07}} = 1.004 \pm 0.0034
\] (3)

Figure 8 plots the computational results as suggested by equation (2). The scatter observed at all \((\alpha\phi)\) and for all orientation states \((0 \leq \varepsilon \leq \pi/2)\) is substantially reduced. Figure 8 also shows the model predictions of Lape et al.\textsuperscript{8} according to which the BIF is given by \(BIF = \frac{D_{0}}{D_{\text{eff}}} = \frac{1 + (\alpha\phi/3)^2}{1 - \phi}\); in this case, for \((\alpha)\) and \((\alpha\phi)\) comparable to those used in our computations, we can safely set \(1 - \phi \sim 1\) in which case the model of Lape et al.\textsuperscript{8} is a quadratic polynomial in \((\alpha\phi)\) and in the dilute regime, the linear term dominates.

The linear relationship \(F(\varepsilon) = 1.021 - 0.317\varepsilon\) was derived from analyzing the computational data. In addition, we have examined the use and performance of functions of the form \(S(\varepsilon) = A\cos^2\varepsilon + B\sin^2\varepsilon\) to describe the misalignment effect on diffusivity. This functional form can be inferred by closely inspecting Figure 5 in the dilute regime, and this inference also appears in the orientation distribution function of Yang et al.\textsuperscript{23} used to describe flake orientation in composite coatings. We fitted our data with a function of the

![Figure 8](image.png)

**Figure 8.** Computed barrier improvement factor (BIF) versus \(\alpha\varepsilon\) in the dilute regime, plotted as suggested by equation (2), where \(F(\varepsilon) = 1.021 - 0.317\varepsilon\), with \((\varepsilon)\) in rad. The broken line are the predictions of Lape et al.\textsuperscript{8} for the quantity \((BIF-1)\); these correspond to a fully aligned composite \((\varepsilon = 0)\). Flakes assume random orientations in the interval \([-\varepsilon, +\varepsilon]\). \((\alpha)\) is the flake aspect ratio and \((\phi)\) the flake volume fraction.
form $S(\varepsilon)$ and found the best-fit parameters to be $A = 1.01$ and $B = 0.53$. The original data can therefore also be reduced to a master expression of the form

$$\frac{BIF - 1}{1.01 \cos^2 \varepsilon + 0.53 \sin^2 \varepsilon} \cdot (\alpha \phi)^{1.07} = 0.9984 \pm 0.0033$$  \hspace{1cm} (4)$$

The two expressions, equations (3) and (4) are practically equivalent and this can be understood by observing that the scaling function $F(\varepsilon)$ is essentially a linear approximation of $S(\varepsilon)$. Equation (4) allows us to compare our computations and model predictions to experimental evidence, namely that for small misalignment angles ($\theta$), it is $D_{eff}(\theta=0) \approx \cos^2 \theta$, in which $\theta = 0$ corresponds to a composite with flakes fully aligned normal to the diffusion direction. The above statement implies that $BIF \approx \frac{\cos^2 \theta}{D_{aligned}}$ and, since in the dilute regime $1/D_{aligned} \sim \alpha \phi$, we deduce that per experimental evidence $BIF \sim (\alpha \phi) \cos^2 \theta$ for small ($\theta$). From equation (4), one easily sees that for small angles ($\sin \varepsilon \sim 0$) our computations and model predict that $BIF \sim (\alpha \phi)^{1.07} \cos^2 \varepsilon$, which agrees with the above experimental observation – if the “misalignment angle $\theta$” in the previous expression is directly related to ($\varepsilon$) of our work. Without additional information, it is logical to consider that to be the case; however, for that reason, we treat this agreement as “qualitative.”

**Concentrated systems ($2 \leq \alpha \phi \leq 15$)**

Similar to Figure 7, Figure 9 plots the computed BIF versus $\ln(\alpha \phi)$ in the concentrated regime. It is evident from these as well as from additional results at all other ($\varepsilon$) values that the exponent of the power law equation (1) is now a strong function of the misalignment angle ($\varepsilon$). We find that it can be approximated as $n(\varepsilon) = 1.632 - 0.575(\varepsilon)$, with the angle ($\varepsilon$) expressed in rad. The correlation coefficient of that fit is $-0.972$. On the other side, ($\varepsilon$) and ($m$) were not correlated (correlation coefficient 0.07) and ($m$) is therefore approximated by its average value $m = 0.793 \pm 0.006$ (95% confidence level).

A correlation between BIF and ($\alpha \phi, \varepsilon$) in the concentrated regime could therefore be

$$\frac{1}{(1.632 - 0.575 \cdot \varepsilon)} \ln \left( \frac{BIF - 1}{0.793} \right) = \ln(\alpha \phi)$$  \hspace{1cm} (5)$$

If this were to hold, the BIF data plotted versus ($\alpha \phi$) in the manner suggested by equation (5) would fall on a straight line with unit slope. Figure 10 shows that this is indeed the case, with the slope of the best-fit line being
1.046. The correlation coefficient of \[ \frac{1.632 - 0.575 \cdot \varepsilon}{\ln(BIF-1)/0.793} \] versus \( \ln(\alpha \varphi) \) is 0.973. There is still scatter around that line; however, this is anticipated for such dense systems and we note the significant reduction in scatter as compared to the raw data; in that case, the correlation between \( \ln(BIF-1) \) and \( \ln(\alpha \varphi) \) is 0.743.

Statistical analysis of the results in light of equation (5) above shows that at the 95% confidence level, it is

\[
\frac{\ln(\alpha \varphi) \cdot (1.632 - 0.575 \cdot \varepsilon)}{\ln(BIF-1)/0.793} = 1.0464 \pm 0.0197
\]

It is interesting to see the complete picture, over all \( \varepsilon \) and \( \alpha \varphi \) studied (Figure 11). In the vertical axis, the raw data, presented as \( \ln(BIF-1) \), are shifted upwards by five units so as to be clearly discernible from the scaled data, which are presented as

\[
DATA = \ln[(BIF - 1)/F(\varepsilon)] \quad \text{for} \quad \alpha \varphi \leq 1
\]
and

$$DATA = \frac{\ln[(BIF - 1)/0.793]}{1.632 - 0.575\varepsilon} \quad \text{for} \quad \alpha\phi > 1 \quad (7b)$$

The scaled data, for all (\(\alpha\varphi\)), can be described as a linear function of \(\ln(\alpha\varphi)\) with slope 1.05 and intercept \(-0.07\) (correlation 0.999).

One final note on how the data behaves for perfect alignment (\(\varepsilon = 0\)) and complete randomness (\(\varepsilon = \pi/2\)). Figure 12 shows the BIF predictions from the data-derived models in this study, namely equation (2) for \(\alpha\phi \leq 1\) and equation (5) for \(\alpha\phi > 1\). Also, shown in Figure 12 are the model predictions of Lape et al.\(^8\) for aligned flakes and Liu et al.,\(^24\) in which \(BIF \approx (1 + 2\alpha\phi/3\pi)^2\) for randomly oriented flakes. For the aligned systems, it is clear that the Lape et al.\(^8\) model agrees with our data very well and into the concentrated regime, approaching a quadratic rise with (\(\alpha\varphi\)). However, the randomly oriented composite is very different. While up to \(\alpha\varphi \sim 2\), its BIF follows the same trend with the oriented data, namely \(BIF - 1 \sim (\alpha\varphi)^{1.07}\), and is in good
agreement with the Liu et al.\textsuperscript{24} model up to $\alpha \varphi \sim 2$. In the concentrated regime, the BIF rate of rise with ($\alpha \varphi$) drops and the BIF appears to be trending towards a plateau value.

The implication of these results is significant. While the BIF of the aligned flake composite shows a near-parabolic increase with ($\alpha \varphi$), as would be expected from theory,\textsuperscript{8,9} randomly oriented composites deviate from that behavior and, instead, achieve BIF values which seem to plateau for increasing ($\alpha \varphi$) at a fraction of the BIF of the corresponding aligned composite. A similar result is implicit in the work of Lusti et al.\textsuperscript{15} While these authors did not elaborate on the matter, they presented computational results for 3D randomly placed and oriented systems of disks, in the dilute and semi-dilute regimes, in terms of the parameter $\chi = (D_0 - D_{\text{random}})/(D_0 - D_{\text{aligned}})$, and proposed a polynomial form for ($\chi$) which best described their data, namely $\chi = -0.0082(\alpha \varphi)^2 + 0.0879(\alpha \varphi) + 0.4157$. While that polynomial is strictly limited to the ($\alpha \varphi$) in which data were obtained ($\alpha \varphi < 7$), it shows that the BIF of a randomly oriented flake system will grow slower with ($\alpha \varphi$) in the semi-dilute regime than the BIF of a fully aligned system. Figure 13 plots our computational results for the $(\text{BIF})_{\text{random}}/(\text{BIF})_{\text{aligned}}$.
ratio. We also plot the same ratio, when the \( (\text{BIF})_{\text{random}} \) is computed from the polynomial \( \chi(\alpha\varphi) \) proposed in Lusti et al.\(^{15} \) and the \( \text{BIF}_{\text{aligned}} \) is the same as the one computed in our study. Also, we plot the same ratio as \( (1 + 2\alpha\varphi / 3\pi)^2 / (1 + \alpha\varphi / \lambda)^2 \) in which the nominator corresponds to Liu et al.\(^{24} \) for randomly oriented flakes and the denominator corresponds to Lape et al.\(^{8} \) for an aligned composite. There is a qualitative agreement between the latter and our computational results up to intermediate \( (\alpha\varphi) \) (ratio dropping with increasing \( (\alpha\varphi) \)) and also a quantitative agreement up to \( \alpha\varphi \sim 2 \). At higher \( (\alpha\varphi) \) values, however, the ratio \( (1 + 2\alpha\varphi / 3\pi)^2 / (1 + \alpha\varphi / \lambda)^2 \) is predicted to approach a plateau, indicating the same (terminal) rate of increase for the \( \text{BIF}_{\text{random}} \) as for the \( \text{BIF}_{\text{aligned}} \) – for very concentrated, or very long flake systems. In this respect, these predictions differ from our results as well as from Lusti et al.\(^{15} \) This point certainly merits further investigation; however, our work in this direction is complicated by the ordering that naturally occurs in high \( (\alpha\varphi) \) systems of long flakes and the resulting progressive loss in orientational randomness. It is quite possible that randomly oriented systems at extreme \( (\alpha\varphi) \) simply do not exist. We are currently researching this topic.

Figure 12. Predictions of equations (2) and (5) for the barrier improvement factor (BIF) of a flake composite in two cases; aligned flakes (o) and randomly oriented flakes (+). The predictions of Lape et al.\(^{8} \) corresponding to an aligned and those of Liu et al.\(^{24} \) corresponding to a randomly oriented composite are also shown. \( (\alpha) \) is the flake aspect ratio and \( (\varphi) \) the flake volume fraction.
Conclusions

We have presented the results of a computational study in flake-filled composites aimed at elucidating the effect of deviations from perfect alignment on their barrier properties. These deviations take the form of uniformly distributed random variations in orientation angle ($\theta$) within the envelope $[-\varepsilon, +\varepsilon]$ in systems in which the average orientation is always perpendicular to the diffusion direction. The computed results for $D_{eff}$ are analyzed and the effect of $(\varepsilon)$ is decoupled from $(\alpha \varphi)$ to a satisfactory degree. These dependencies differ in the dilute $(\alpha \varphi \leq 1)$ and in the concentrated regimes $(1 < \alpha \varphi \leq 15)$. In the dilute regime, the BIF is a power function of $(\alpha \varphi)$, with the exponent $(\sim 1.07)$ being independent of the extent of orientational randomness, a finding that is in line with existing theories. The effect of misalignment is found to be described by a linear function of the maximum misalignment angle $(\varepsilon)$. A scaling is proposed by which we derive a simple explicit BIF model which incorporates both, $(\alpha \varphi)$ and $(\varepsilon)$. Through the proposed scaling, the data collapse on a line and the correlation coefficient is 0.996. We note that the proposed scaling is in agreement with experimental evidence. In the concentrated case $(\alpha \varphi > 1)$, we find that the power exponent is a function of the

Figure 13. Ratio of the barrier improvement factor (BIF) of a randomly oriented composite divided by the BIF of an aligned flake composite as a function of $(\alpha \varphi)$, where $(\alpha)$ is the aspect ratio of the flake and $(\varphi)$ its volume fraction. Computational results are shown as points (o). Also, shown are the ratio predictions based on earlier studies.15,8,24
maximum misalignment angle ($\varepsilon$). For aligned systems ($\varepsilon = 0$) or systems showing small deviations from perfect alignment, we find that the BIF approaches the quadratic dependence on ($\varphi \varphi$) predicted by theory. However, the power exponent is reduced progressively as the deviation from perfect alignment increases, from 1.71 in the aligned system to $\sim 0.9$ in the fully random one. A scaling is also proposed here by which all data fall on a line of slope 1.04 with a correlation coefficient 0.973. This suggests that the theoretically anticipated improvement in barrier properties may not be realized if the flake orientations exhibit a significant scatter around the desired direction, regardless of the average fiber orientation, which may well be perpendicular to the bulk diffusion direction. Finally, we investigated the $(\text{BIF})_{\text{random}}/(\text{BIF})_{\text{aligned}}$ ratio; our computational results show this ratio decreases as ($\varphi \varphi$) increases into the semi-concentrated regime, in line with earlier findings. 15

Declaration of Conflicting Interests
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