THE EFFECT OF SHAPE AND ORIENTATION ON THE BARRIER PROPERTIES OF FLAKE-FILLED COMPOSITES: A 3D APPROACH

Andreas Tsiantis[1] and T.D. Papathanasiou[*,1,2]

[1]Mechanical Engineering, University of Thessaly, Volos, Greece

[2]Chemical & Materials Engineering, Nazarbayev University, Astana, Kazakhstan

[*]athpapathan@uth.gr; athanasios.papathanasiou@nu.edu.kz

ABSTRACT

We carry out fully three-dimensional (3D) simulations in flake-filled composites with the objective of determining the effect of flake shape and orientation on their barrier properties. Our simulations are carried out in multi-particle unit cells, each containing up to 4,000 individual flakes. We represent the flakes as 2D rectangles of dimensions (l) and (w); this representation is suitable for very thin flakes, such as exfoliated nano-platelets of montmorillonite or graphene-oxide. We analyze the effect of flake shape on the effective diffusivity D_{eff} and find that square flakes offer the best barrier improvement. For constant flake area, the barrier properties are predicted to decrease as the diagonal and/or the aspect ratio of the flake increase. We also analyze the effect of flake misalignment with respect to the direction of macroscopic diffusion and find that, in a manner similar to what has been seen in 2D systems, the decrease in D_{eff} with flake loading and/or flake diameter is less severe as the degree of misalignment increases. Finally, fully 3D systems are compared to systems in which one flake dimension is progressively approaching the dimensions of the unit cell, thus rendering mass transport essentially two-dimensional. We find that in this case the predicted D_{eff} is lower than that of a system in which mass transfer is three-dimensional in nature.

1. INTRODUCTION

The topic of diffusion across flake filled systems has attracted some attention in recent years and several studies have been published [1-6]. This is because of the promise of flake-filled composites in general, and nano-composites in particular, as barrier materials. In such materials, the topology of the inter-flake space is characterized by a much higher tortuosity than that of particulate or fiber composites at comparable loadings. As a result, there is a promise for substantial improvement in barrier properties at very modest flake concentrations. According to available two-dimensional results [7-10] (strictly suitable for ribbon composites but taken as a conservative limit of an actual three-dimensional flake system), using perfectly aligned flakes of aspect ratio 300 at 1% volume fraction would increase the Barrier Improvement Factor (BIF, defined as D_0/D_{eff}, where D_0 and D_{eff} are, respectively, the diffusivities of the diffusing substance in the matrix material and in the composite) between 400 % and 550 %. The effect of deviation of flake orientation from perfect alignment and, in particular, the effect of orientational randomness on BIF have recently been studied by [8-10] and models have been proposed which are in excellent agreement with computational results in two-dimensional unit cells, each containing many thousands of individual flake cross-sections. However, all these results are strictly valid for ribbon composites and their relevance to three-dimensional reality is yet to be proven. It is fair to say that there has been no comprehensive study of three-dimensional diffusion in flake composites, which would cover a large range of the pertinent parameters. The effect of the shape of flake cross-section remains unclear as is the effect of mis-orientation. Finally, the relevance of existing and well-studied models for fully-aligned systems [7, 10-12] to three-dimensional reality is not proven. In this study we carry out a comprehensive computational study of diffusion in three-dimensional, multi-particle unit cells with the objective of giving answers to these questions.

2. COMPUTATIONAL

We carry out steady-state diffusion computations in three-dimensional unit cells using the open source software package OpenFoam. Each unit cell is a cube of length size (H) and contains N=4,000 individual flakes. To better approximate flakes relevant to nano-composites, in which the flake thickness is much smaller than the planar flake dimensions, we represent each flake as a two-dimensional rectangle of length (l) and width (w). Each flake is characterized by an aspect ratio (r), defined as $r=l/w$. The flakes are placed within the unit cell using a random sequential addition procedure, in which random numbers assign the centroid coordinates of each flake. In randomly-oriented configurations the orientation vectors are assigned random values and, based on these, the flakes are rotated at the X axis then the Y axis and finally at the Z axis. In the cases where the flakes are unidirectional, the rotation is applied only to the Z axis thus rotating the flakes perpendicular to the direction of diffusion. Example geometries are shown in Figure 1.

The equation solved is

$$\nabla^2 C = 0 \qquad [1]$$

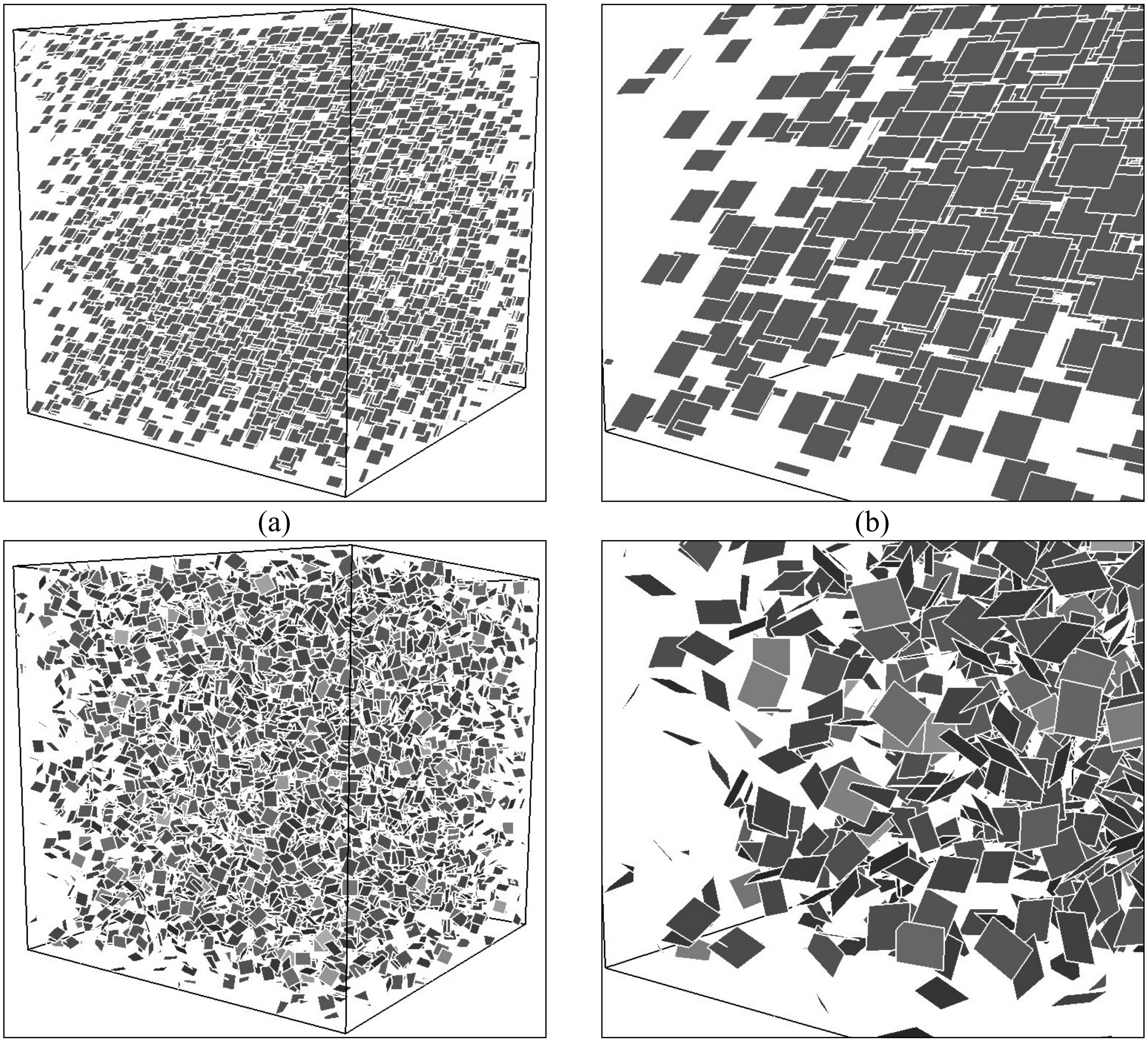
Subject to the following boundary conditions

(i) On the surface of each flake, an adiabatic condition is imposed ($\partial C/\partial \boldsymbol{n} = 0$), where (**n**) is the direction of the unit vector normal to the flake surface.

(ii) On the "top" and "bottom" surfaces of the unit cell, constant concentrations are applied, so that a macroscopic concentration difference ΔC is established across the unit cell. On the sides surfaces of the unit cell, cyclic boundary conditions are applied ($C_{left}=C_{right}$ and $C_{front}=C_{back}$.

Solution of Eq.(1) supplies the concentration (C) and the concentration gradient ($\partial C/\partial \boldsymbol{n}$) at each position of the domain. Figure 2 shows a representative concentration field as well as a representative distribution of mass flux on the top surface. Once the mass flux (Q) on the top surface is computed, an effective diffusivity (D_{eff}) can be determined from Fick's law as

$$D_{eff} = \frac{HD_0}{\Delta C \cdot D \cdot L} \int_0^D \int_0^L \left(\frac{\partial C}{\partial \mathbf{n}}\right) dx dy \qquad [2]$$



(a) (b) (c) (d)

Figure 1: Example geometries containing 4,000 randomly placed flakes. (a) unidirectional flakes, (b) detail of unidirectional flakes, (c) Flakes with random orientation, (d) Detail of randomly oriented system. Some flakes appear to be smaller; this is due to their intersection with the boundaries of the unit cell, as required by geometric periodicity.

3. RESULTS

In the following we will focus our attention on the analysis of computational results as they pertain to composites containing flakes of varying aspect ratio (*r*), aligned perpendicular to the direction of bulk diffusion and composites containing unidirectional flakes forming an angle (θ) with the direction of macroscopic diffusion. The flake aspect ratio ranges from 1 (square flakes) to 16 and the orientation angle (θ) from 0 to π/2. Example geometries are shown in Figure 3. We also study the case of ribbon composites, namely composites containing flakes with one dimension approaching the size of the containing unit cell. This allows us to evaluate the effect of the three-dimensional nature on mass transfer on the effective diffusivity of the composite. We have carried out simulations in over 2,000 individual geometries, each differing in terms of flake dimensions, flake placement and flake orientation, such as shown in Figures 1, 3 or 5. To the best of our knowledge, this is the largest such dataset that has appeared in the literature to-date.

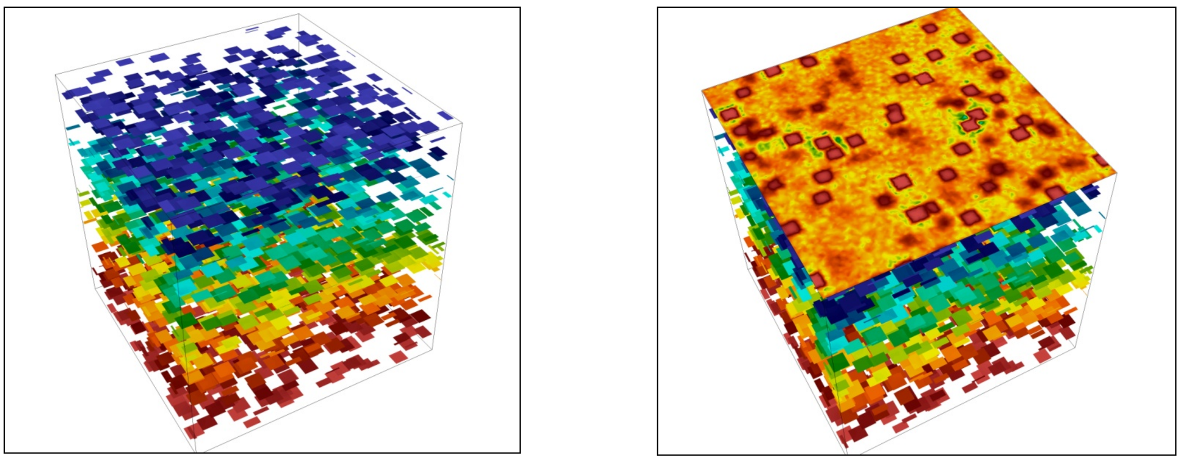
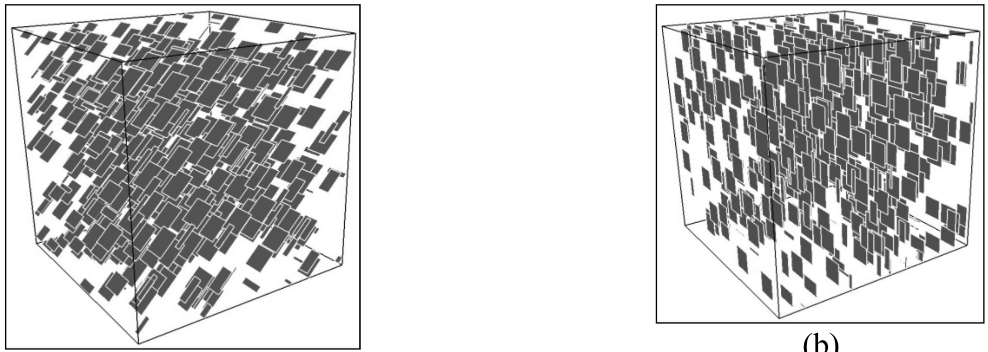


Figure 2: Example concentration fields in a 3D flake system containing randomly placed flakes oriented perpendicular to the direction of diffusion (left). The figure to the right shows the distribution of mass flux on the top surface. The position of the flakes below the surface can be inferred by variations in the mass flux.

3.1 The effects of flake misalignment and flake aspect ratio

In the following we focus our attention to systems in which the flakes show a uniform deviation from perfect alignment, expressed by the angle (θ) formed between the Z-axis (direction of macroscopic diffusion) and the plane of the flake. Example geometries are shown in Figure 3 and the computational results are summarized in Figure 4, illustrating the effect of flake shape and misorientation on the effective diffusivity (D_{eff}).



(a) (b)

Figure 3: 3D unidirectional flake configurations for (a) θ=45º and (b) θ=90º. The number of flakes has been reduced to 500 for clarity.

It is clear from Figure 4 that misalignment reduces the barrier factor (increases the effective diffusivity) compared to the fully aligned system with θ=0. This is in agreement with earlier results of 2D simulations [9]. It is also interesting that as the parameter $\beta = N\frac{lw}{H^2}\sqrt{l^2+w^2}$ increases, the effective diffusivity of a fully aligned composite will decrease monotonically, while D_{eff} of misaligned systems appears to approach a plateau value. It is noted that since in each of the graphs of Figure 4 the aspect ratio of the flakes is constant, increasing the parameter β is equivalent to increasing the flake width (w). As will be discussed in following section, this makes the system approach a 2D (ribbon) composite, which is characterized by a lower value of D_{eff} compared to a 3D system. In light of this, the behavior observed in Figure 4 is similar to what was observed in earlier 2D simulations [9,10] in terms of the dimensionless scaling parameter $N(l/H)^2$. It is noted that in all simulations, the results for (*r*) and (*1/r*) are identical.

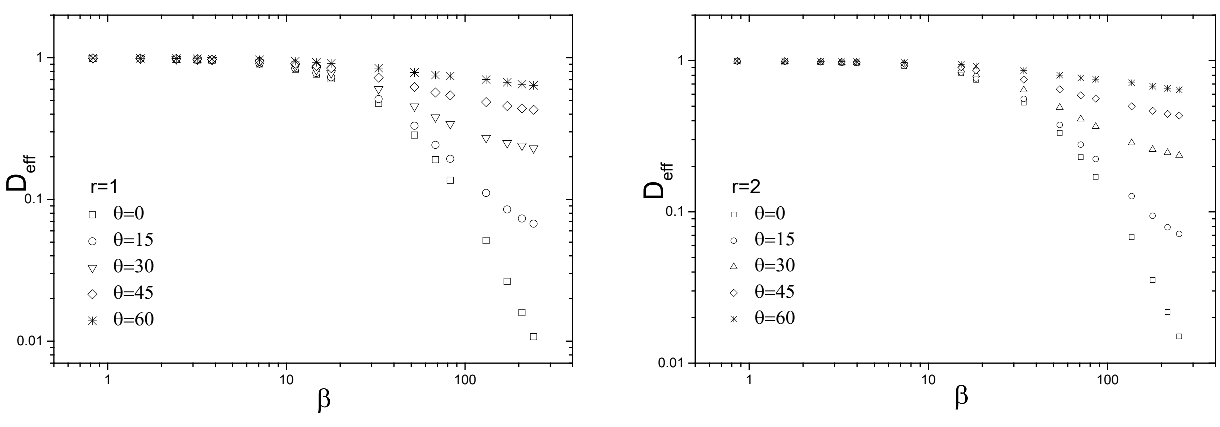
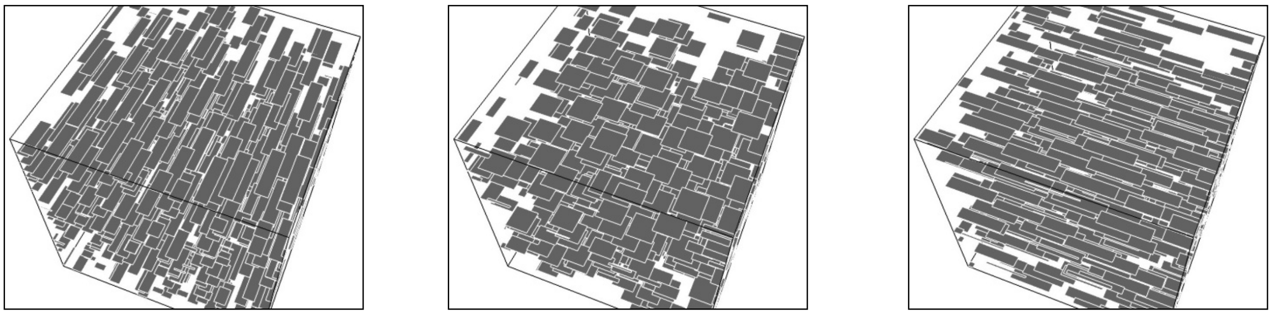


Figure 4: D_{eff} for square flakes *(r=1*, left) and rectangular flake (*r=2*, right) at various angles of mis-alignment with respect to the Z-axis (only averages are shown since the scatter is smaller than the point size).

In the following we investigate the effect of flake aspect ratio (*r=l/w*) on the effective diffusivity. Example geometries are shown in Figure 5.



(a) (b) (c)

Figure 5: 3D oriented flake configurations for various values of the flake aspect ratio at θ=0°. (a) *r=4*, (b) *r=1* (square flakes) and (c) *r=1/4*. Number of flakes has been reduced to 500 for clarity.

If we keep the area or the diagonal of the flakes constant and change the aspect ratio we can see the effect of *r* on D_{eff} . Since the values of D_{eff} do not change when (*l*) and (*w*) are interchanged, we also define the flake aspect ratio as $r^* = Max(l,w)/Min(l,w)$, so that it will always be $r^*>1$.

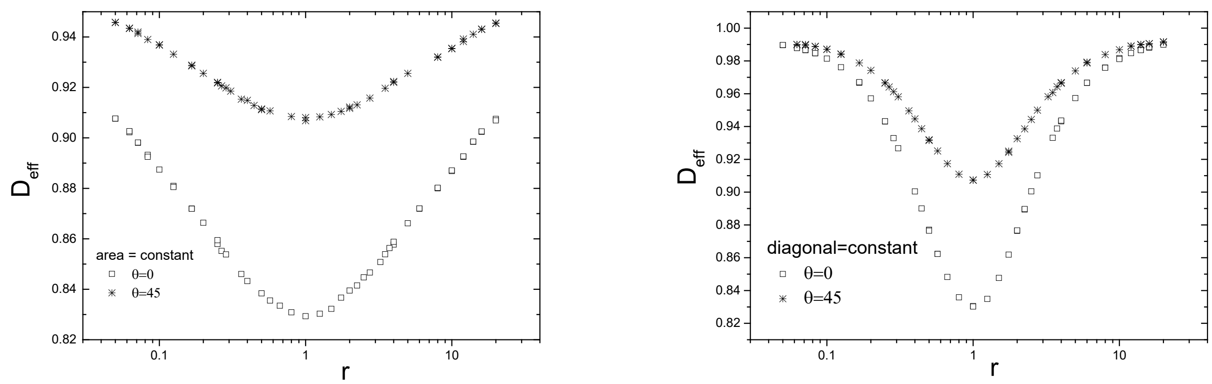


Figure 6. D_{eff} vs. (*r*) as other geometrical characteristics, namely flake area (left) and flake diagonal (right) remain constant. In both graphs, at *r=1* (square flakes) the flake length *l* corresponds to $N(l/H)^2=5$. N=4000

It is clear that maximum barrier effect is achieved by using square flakes (*r=1*). This is in agreement with the results of [1], where it was found that elongated ellipsoidal disks are less effective, for barrier purposes, than disks of circular profile. Elongated particles are less effective as barrier materials, since they provide shorter alternative diffusion paths around their small axis, than would rectangular inclusions. It is also interesting to note that as we deviate from the case of square flakes the effective diffusivities are the same if we interchange *l* and *w*. This is intuitively correct, since in 3D the axes perpendicular to the direction of macroscopic diffusion can be interchanged.

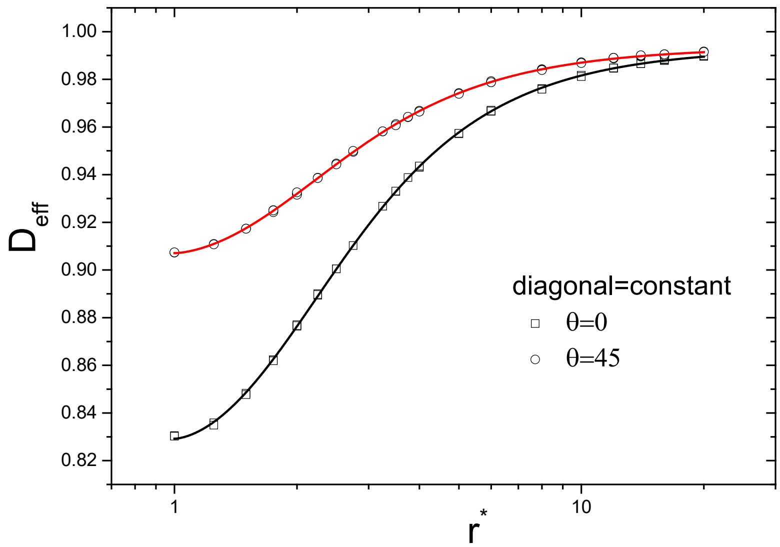


Figure 7. Computational results (points) and fit of D_{eff} vs. r^* to Eq.(3) (lines). The flake diagonal remains constant.

It can be seen that the predicted values for D_{eff} follow the sigmoidal model of Eq. (3) for the full range of r^*. The best fit parameters were K=2.46 and n=1.56, for the entire range of (r^*) and all misalignment angles (θ) that were examined.

$$\mathrm{D}_{\mathrm{eff}_{r^*}} = \mathrm{D}_{\mathrm{eff}_{r^*=1}} + \left(\mathrm{D}_{\mathrm{eff}_{r^*\to\infty}} - \mathrm{D}_{\mathrm{eff}_{r^*=1}}\right) \cdot \frac{(r^*-1)^n}{K-(r^*-1)^n} \qquad [3]$$

According to Eq.(3), the effective diffusivity (D_{eff}) of a flake composite containing flakes of aspect ratio (r^*) can be expressed in terms of the D_{eff} of the corresponding system containing square flakes (subscript $r^*=1$) and the D_{eff} of the corresponding ribbon composite ($r^*\to\infty$). Similar behavior is observed in the case of constant flake area.

3.2 Relation between two- and three-dimensional systems

In the following we explore relationships between diffusion in 2D and 3D flake composites. It is obvious that for any θ, as the width (w) of the flake increases (and thus the aspect ratio r^* increases) an initially 3D system approaches a two-dimensional one. This transition is illustrated in Figure 8.

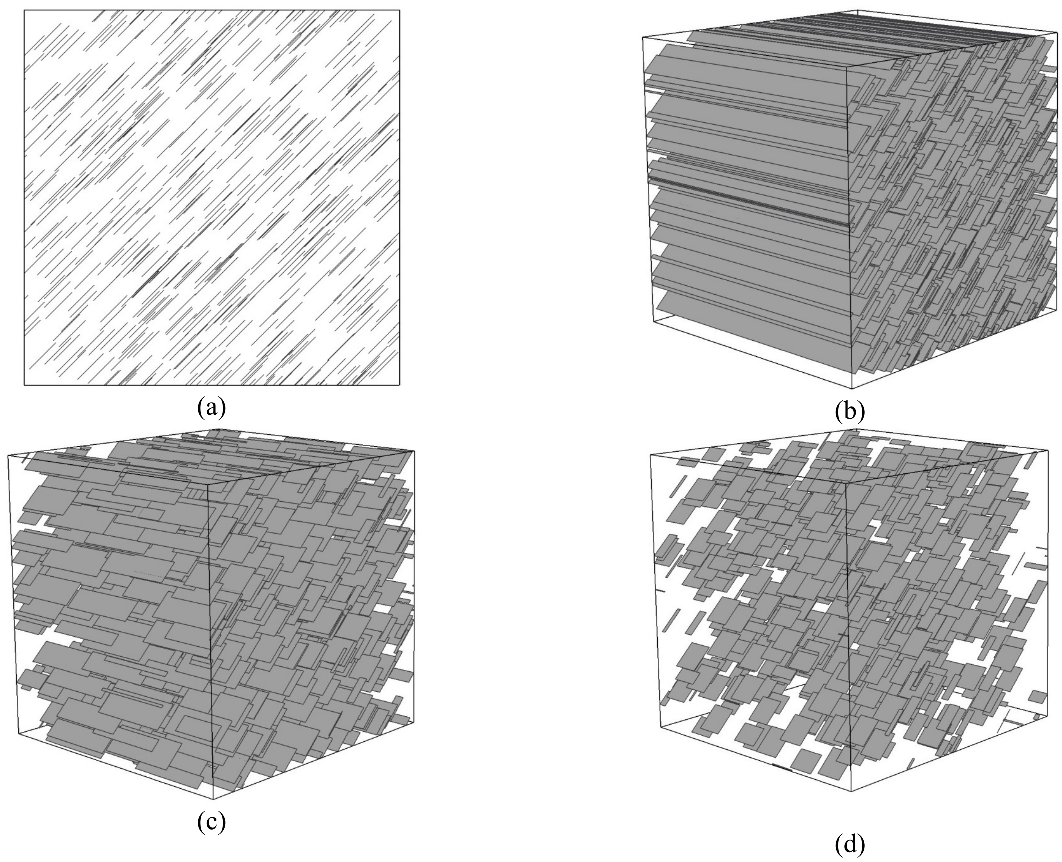
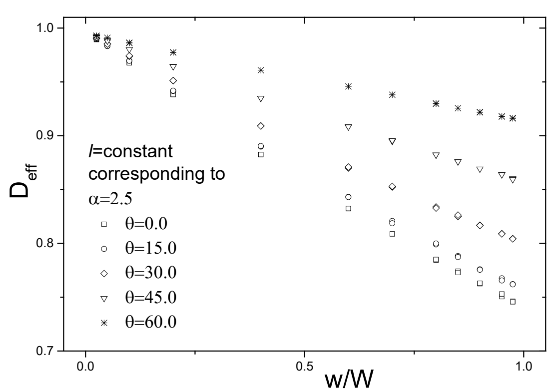


Figure 8: Sample geometries illustrating the transition from a 3D to a 2D system. (a) idealized 2D representation, (b) 3D equivalent geometry at w=D, corresponding to a ribbon composite (c) 3D geometry with *r*=3* and (d) 3D geometry with *r*=1*. Number of flakes has been reduced to N=500 for visual clarity.

Figure 9 summarizes the computational results for D_{eff} as *w* increases from *w=l* (*r*=1*) to *w=W* and a range of misalignment angles. It is clear that when the ratio *w/H* increases, the D_{eff} decreases. This is true at all levels of misalignment. Our results confirm the intuitive expectation that the barrier factor ($\sim 1/D_{eff}$) predicted by a 2D analysis will be higher, compared to what a fully 3D analysis might predict.



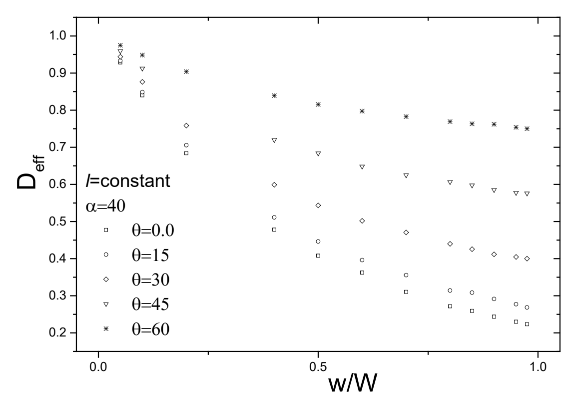


Figure 9: D_{eff} versus w/W as w increases from $w=l$ ($r^*=1$) to W (ribbon composite, Fig. 8(b)). Left for l that corresponds to $\alpha=2.5$ and right for an l that corresponds to $\alpha=40$. Unit cell is a cube ($L=H=W$). At the rightmost point of the graph we approach the 2D ribbon geometry. N=4,000. The parameter (α) is defined as $\alpha=N(l/H)^2$

4. CONCLUSIONS

We have investigated computationally three dimensional diffusion in model systems consisting of several thousands of randomly placed unidirectional flakes. Simulation results show that the biggest improvement in barrier properties if offered by flakes of square shape. As the flakes become elongated, their barrier effectiveness decreases. We propose an empirical model that captures the effect of flake aspect ratio on the effective diffusivity. The barrier factor is maximum when the flakes are aligned perpendicular to the direction of macroscopic diffusion (z-axis). When the flakes form an angle (θ) with the z-axis, the barrier factor is reduced. Finally, we study the behavior of the effective diffusivity of flake composites as the flake width increases to approach the width of the unit cell. In the limit of this transition we recover a 2D system (ribbon composite). Comparison of the D_{eff} of fully three-dimensional systems with that of ribbon composites shows that the latter are characterized by substantially lower effective diffusivity. Experimental verification of the presented results by comparison to measured transport rates in physical composite specimens containing flakes is not a trivial matter. One obvious difficulty is that the internal microstructure of a flake-filled specimen is, in general, unknown, in terms of placement (uniform vs. random), orientation and shape of the flakes. The advent of 3D printing is offering one possibility for the fabrication of test specimens with precisely defined microstructural characteristics. It is therefore conceivable that the results of simulations, such as those presented in this study, can be compared to actual mass (or heat) transfer experiments, once suitable (albeit artificial) physical models have been constructed. When dealing with actual, manufactured, flake composites, the only available miscrostructural information is based on micrographs of polished sections of the material, in which the flakes appear as "lines" of variable length and orientation. We are currently working on a methodology that will enable us to provide estimates of the (true) effective diffusion coefficient of such composites based only on 2D cross-sectional images. One additional difficulty, particularly relevant to nano-composites, is the fact that in such systems there are several additional factors coming into play, most notably a drastic modification of the matrix in the vicinity of the nano-flakes. In principle, such inter-phases, albeit of uncertain thermo-physical properties, can be included in a 3D model. In any event, simulations such as those presented in this work, provide a base-line against which physical experiments can be compared and the possible existence of additional operative mechanisms identified.

5. REFERENCES

1. Roding, M. Gaska, K. Kadar, R. Loren, N. "Computational Screening of Diffusive Transport in Nanoplatelet-Filled Composites: Use of Graphene To Enhance Polymer Barrier Properties", *ACS Appl. Nano Mater.* (2018): 160-167.
2. Tan, B. Thomas, NL. "A review of the water barrier properties of polymer/clay and polymer/graphene nanocomposites" *Journal of Membrane Science* 514 (2016): 595-612. https://doi.org/10.1016/j.memsci.2016.05.026

3. Zid, S. Zinet, M. Espuche, E. “Modeling Diffusion Mass Transport in Multiphase Polymer Systems for Gas Barrier Applications: A Review”, *Journal of Polymer Science Part B Polymer Physics* 56 (2018): 621-638. DOI: 10.1002/polb.24574

4. Greco, A. Maffezzoli, A. “Two-dimensional and three-dimensional simulation of diffusion in nanocomposite with arbitrarily oriented lamellae*.” J. Membrane Science* 442 (2013): 238-244. https://doi.org/10.1016/j.memsci.2013.04.038

5. Gusev, AA. Lusti, HR. “Rational design of nanocomposites for barrier applications.” *Adv. Mater.* 21 (2001): 1641-1643. https://doi.org/10.1002/1521-4095(200111)

6. Lusti, HR. Gusev, AA. Guseva, O. “The influence of platelet disorientation on the barrier properties of composites: A numerical study.” *Modelling Simul. Mater. Sci. Eng*. 12 (2004): 1201-1207.

7. Lape, NK. Nuxoll, EE. Cussler, EL. “Polydisperse Flakes in Barrier Films”, *J. Membrane Science* 236 (2004): 29-37. https://doi.org/10.1016/j.memsci.2003.12.026

8. Chen, X. Papathanasiou, TD. “Barrier properties of flake-filled membranes: Review and numerical evaluation.” *Journal of Plastic Film and Sheeting* 23 (2007): 319-346. https://doi.org/10.1177/8756087907088437

9. Tsiantis, A. Papathanasiou, TD. “The Barrier Properties of Flake-Filled Composites with Precise Control of Flake Orientation.” *Materials Sciences and Applications: Special Issue on Additive Manufacturing* 8 (2017): 234-246. DOI: 10.4236/msa.2017.83016

10. Tsiantis, A. Papathanasiou, TD. “A closed-form solution for the barrier properties of randomly-oriented high aspect ratio flake composites.” *Journal of Composite Materials*, in print, 2019, DOI: 10.1177/0021998318825295

11. Dondero, M. Tomba, JP. Cisilino, AP. “The effect of flake orientational order on the permeability of barrier membranes: numerical simulations and predictive models.” *J. Membrane Science* 514 (2016): 95–104. DOI: 10.1016/j.mem.sci.2016.04.064

12. Papathanasiou, TD. Tsiantis, A. “Orientational Randomness and its Influence on the Barrier Properties of Flake-Filled Composite Films*.” Journal of Plastic Film and Sheeting* 33 (2017): 438-456. DOI: 10.1177/8756087916682793