Permeability and conductivity of platelet-reinforced membranes and composites

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We present large scale simulations of the diffusion constant $D$ of a random composite consisting of aligned platelets with aspect ratio $a/b >> 1$ in a matrix (with diffusion constant $D_0$) and find that $D/D_0 = 1/(1 + c_1 x + c_2 x^2)$, where $x = av_f/b$ and $v_f$ is the platelet volume fraction. We demonstrate that for large aspect ratio platelets the pair term ($x^2$) dominates suggesting large property enhancements for these materials. However a small amount of face-to-face ordering of the platelets markedly degrades the efficiency of platelet reinforcement.

Thin reinforcing platelets can be extremely effective at improving the barrier and in-plane mechanical properties of composites and membranes. In particular there has been an explosion of interest in clay-reinforced thermoplastics, thermostets and rubbers, with target applications ranging from packaging to cars [1–5]. To achieve the theoretically promised enhancements requires well-aligned and well-dispersed clay platelets in these polymer matrices.

The traditional theory of composite reinforcement is based on single inclusion theories which form a basis for self-consistent or effective-medium approximations. However the effect of aligned reinforcing platelets is not correctly described by single inclusion models [6,7], except at very low inclusion concentrations, even though many publications assume this approximation. The correct variable to use in describing platelet reinforcement in the large aspect ratio limit is the product of the aspect ratio $(a/b)$ times the volume fraction $(v_f)$, $x = av_f/b$. Since the aspect ratio of clay platelets ranges from 100 – 2000, $x$ is typically not small as even a 1% inclusion volume fraction leads to large values of $x$. We calculate the diffusion constant in regimes where $x$ is not small and derive a simple form which represents the data well. We find that the quadratic term dominates (i.e. a term proportional to $x^2$) and its dominance is due to narrow necks between platelets which are not included in single inclusion theories.

However, chemically nano-dispersed clays tend to have face-to-face stacking, which leads to channels of matrix material through which diffusion is relatively easy. In a thermodynamic picture this corresponds to a phase separation of the material into platelet rich and platelet poor regions. We calculate the dependence of the diffusion constant on face-to-face alignment and show that the rule of mixtures works effectively. In clay-polymer materials deleterious platelet-poor channels are broken up by using extrusion or mechanical mixing. To date no-one has found a way to chemically modify the clays so that they prefer to arrange themselves in a more optimal (e.g. staggered) array. Nevertheless, theoretical studies suggest that nematic and staggered phases can be thermodynamically stable [11].

The leading order term in the reduction in permeability due to platelet reinforcement is familiar in the composites community, though in a different context. There it is well known that a number density of aligned cracks, $n = N/V$ ($N$ is the number of cracks and $V$ is the sample volume), reduces the conductivity of a material of initial conductivity $\sigma_0$ according to,

$$\sigma = \sigma_0 (1 - \pi a^2 n + \ldots)$$

for slits of length $2a$ in a homogeneous two-dimensional medium [1], and

$$\sigma = \sigma_0 (1 - \frac{8}{3} a^3 n + \ldots)$$

for penny shaped cracks of radius $a$ in a homogeneous three-dimensional medium [2]. The perpendicular (i.e. normal to the crack surface) conductivity of cracked solids $\sigma/\sigma_0$, the perpendicular permeability, $k/k_0$, of platelet-reinforced membranes and the perpendicular diffusion constant measured in platelet reinforced membranes, $D/D_0$, are related by, $\sigma/\sigma_0 = k/k_0 = D(1 - v_f)/D_0$. However the experimental results for the permeability of barrier films are presented as a function of inclusion volume fraction, $v_f$. This is derived simply from Eq. (1) and (2) by using $v_f = n v^*$, where $v^*$ is the volume of an inclusion. Thus for barrier membranes, the leading order behavior for aligned rectangular sticks in two dimensions ($v^* = 4ab$) is,

$$\frac{k}{k_0} = 1 - \frac{\pi}{4} \frac{av_f}{b} + \ldots$$

and for aligned penny-shaped platelets of radius $a$ and thickness $2b$, is,

$$\frac{k}{k_0} = 1 - \frac{4}{3\pi} \frac{av_f}{b} + \ldots$$

The importance of the variable $x = av_f/b$ is evident from these expressions. In the barrier film community the reduction in permeability due to platelets is approximated

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in a different way. There it is argued that for high aspect ratio platelets, the increased tortuosity of typical diffusion paths \(L_p/L_0\) gives the qualitatively correct reduction in the diffusion constant, i.e. \(D/D_0 \sim L_0/L_p\). The dependence of path tortuosity on inclusion volume fraction is given by \(L_p/L_0 = (1 + av_f/2b)\), where \(a/b\) is the platelet aspect ratio. Note that this is of the same form as an effective medium theory based on equations (3) and (4). However, as we now show this tortuosity argument is qualitatively incorrect for platelet reinforced materials and if done correctly leads to a quadratic (i.e. \(O((b/(av_f))^2)\)) reduction in the diffusivity in both two and three dimensions.

We use the resistor representation to calculate the effect of tortuous diffusion paths on the overall conductivity, permeability and diffusivity. Consider a composite composed of randomly centered, aligned, non-overlapping, insulating sticks or pennies placed in a matrix of conductivity \(\sigma_0\). We define the typical perpendicular distance between inclusions to be \(l\). The volume fraction is related to \(l\) via, \(v_f \approx 2b/(l + 2b) \approx 2b/l\) as the inclusion volume fractions that are observed for high-aspect ratio materials are typically less than 10%. A tortuous path through a random array of these aligned platelets is approximated by a series combination of resistors each of which has typical resistance,

\[
r_t \approx \frac{\rho_0 \sigma}{l a^{d-2}},
\]

where \(\rho_0 = 1/\sigma_0\). This resistance is calculated by considering a “neck” of matrix material between two adjacent inclusions. This resistor has typical length of order \(l\) and cross-section of order \(l^2\). This resistor has typical length of order \(l\) and cross-section of order \(l^2\).

The effective diffusion constant is then found by extracting the slope of a plot of \((\tau^2)\) versus \(t\). Our code for the “blind ant” method described above is very efficient, which enables simulations on very large lattices over long times. This is essential for the large aspect ratio composites discussed here. Note that \(k/k_0 = D(1 - v_f)/D_0\) due to the fact that random walkers cannot be placed on the zero permeability barriers. In experiments, the permeability is measured by placing the barrier in a pressure gradient, with pressure \(p\) of gas (e.g. Oxygen) on one side of the membrane and the other side maintained at very low pressure. The steady-state flux of gas, \(f\), through the membrane is measured and the permeability \(k = p/f\).

The diffusion constant is measured by tracking the tracer diffusion of tagged particles, for example using NMR.

A high precision test of Eq. (7) is presented in Fig. 2a for aligned sticks in two dimensions and Fig. 2b for aligned squares in three dimensions. We plot the quantity \((D_0/D - 1)/x\) which, if Eq. (7) is correct, should be linear, i.e. \((D_0/D - 1)/x = c_1 + c_2 x\). The data of Fig. 2 confirms this form remarkably well over the entire range of inclusion concentrations, even close to the dense packing limit. A linear fit to the data of Fig. 2 yields the coefficients to the quadratic term, \(c_2^d = 0.105 \pm 0.01\) (from Fig. 2a), and \(c_2^d = 0.050 \pm 0.005\) (from Fig. 2b). The leading order coefficient in the concentration expansion, \(c_1\), is quite poorly converged in two dimensions. From Fig. 2a, it is seen that this \(c_1^d\) is still decreasing even for large aspect ratio platelets. For the largest aspect ratios we studied its value is \(c_1^d(a/b = 250) = 0.46 \pm 0.01\). In three dimensions the convergence is much better and we find \(c_1^d = 0.44 \pm 0.03\). The theoretical values (from Eqs. (3) and (4))
are $c_{\text{dist}}^2 = \pi/4 = 0.785...$ and $c_{\text{penng}}^2 = 4/(3\pi) = 0.425...$ respectively. The numerical simulations are on lattices and so cannot be expected to be exactly the same as the continuum results (3) and (4). Nevertheless, it is clear that materials reinforced by well-dispersed platelets are not correctly described by effective medium theory based on a linear expansion in $x$, or the Nielsen formula ($D/D_0 = 1/(1+x/2)$) which is used in the diffusion community. An important consequence of this result is that the property enhancements which are theoretically possible from platelet reinforced materials, for example clay-polymer nanocomposites, are much larger than has previously been suggested or observed.

However the real morphology of, as synthesized, clay-polymer materials is illustrated in Fig. 3. The presence of channels of matrix material (light regions in Fig. 3a) and the strong face-to-face packing of the platelets is evident in Fig 3b. These materials do not provide the barrier performance promised by the result Eq. (7). The channels of matrix material act as a diffusion “short-circuit” so that the effective diffusion constant remains closer to that of the matrix material. In order to make the diffusion paths through the matrix material more tortuous, materials such as this are mixed in extruders or sheared in other ways in order to produce better platelet dispersion. The effect of various degrees of platelet phase separation on the diffusion constant is illustrated in Fig. 4. The platelets are initially in a perfectly staggered array and then one sublattice of the array is shifted by an amount $0 \leq s \leq a$ until the platelets are in a perfect face-to-face arrangement. The rule of mixtures works quite well for these phase separated systems (see Fig. 4), so that,

$$D(s) = \frac{s}{a} \frac{D(s=1)}{D_0} + (1 - \frac{s}{a}) \frac{D(s=0)}{D_0}. \quad (8)$$

Clearly even a small amount of phase separation (finite $s$) leads to a significantly increased diffusion, that is the first term in Eq. (8) dominates for $s > a/(c_2x^2) = b^2/(c_2v/a)$. In a very real sense, the larger the platelets are the more sensitive the system is to phase separation. For example if the reduction in diffusion constant promised by the formula (6) is 1000 fold, then any matrix channel, which is not highly tortuous, of size 1/1000 or larger will be deleterious for the composite performance. This means that platelet dispersion must be very good indeed to achieve the full performance enhancements promised by large aspect ratio platelets.

In summary, we have shown that the effective diffusion constant (as well as the conductivity and permeability) of platelet reinforced composites is not well described by single inclusion theories, even though almost all experimental studies in the literature use expressions which are based on this limit. This is good news, as it means that the theoretically possible property enhancements are quadratic in the volume fraction, rather than linear. This general result should also apply to many other transport and mechanical properties of well-dispersed platelet reinforced materials, and is due to the dominance of narrow necks in large aspect-ratio limit. However we also showed that face-to-face platelet ordering is extremely deleterious to the performance of these materials (see Fig. 4 and Eq. (8)), so that achieving the full enhancements promised by these materials remains a challenging synthesis problem.

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FIG. 1. Aligned square platelets randomly embedded in a three-dimensional cube. The aspect ratio $a/b = 25$, the boundary conditions are periodic in all directions.

FIG. 2. Tests of the form (7) of the text. A plot of $(D_0/D - 1)/x$ as a function of $x = av_f/b$, where $a/b$ is the platelet aspect ratio and $v_f$ their volume fraction. The solid lines are fits to the largest aspect ratio data. (a) Data for aligned slits randomly placed, without overlap, onto a square lattice. The simulations were carried out on square lattices of size $2048^2$, over $6 \times 10^4$ steps in the blind ant algorithm (see text) and averaged over 30,000 configurations. (b) Data for aligned squares (see Fig. 1) placed, without overlap, onto a cubic lattice. The simulations were carried out on cubic lattices of size $512^3$, over $5 \times 10^4$ steps in the blind ant algorithm (see text) and averaged over 20,000 configurations.
FIG. 3. Experimental platelet morphology at two length scales. (a) The upper figure shows that there is a phase separation into platelet rich and platelet poor regions. (b) The lower figure illustrates the face-to-face alignment of the platelets. The dark regions are clay, the light regions are the polymer (from ref. [14]).

FIG. 4. The effective diffusion constant as a function of face-to-face alignment of the platelets (of aspect ratio $a/b = 128$). The inset shows the geometry that was used for the calculations. Also included is the data for a random system with the same aspect ratio and it shows that the random system is similar to the perfectly staggered array of barriers, at least at the resolution of this plot. The three plots at intermediate $s$ (dots, small dashes and large dashes) are fits using the rule of mixtures (Eq. (8)).