

# **Material point method simulation of enhanced penetrant diffusion in nanoparticle-polymer composite membranes**

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## **Abstract**

We have utilized 2D material point method (MPM) to study the influence of nanoparticles on the diffusivity of penetrants in model polymer membranes comprised of impenetrable spherical nanoparticles dispersed in a matrix with uniform penetrant solubility and diffusivity. The polymer membrane near the surface of a nanoparticle exhibits enhanced penetrant diffusion relative to that of the bulk polymer. In our model this region of enhanced diffusion is treated as a “skin” with a penetrant diffusion coefficient 100 times that of the bulk matrix. For a given skin thickness the penetrant diffusion in the composite membrane was found to increase exponentially with increasing area fraction of nanoparticles both above and below the percolation threshold. We found the total area fraction of particles + enhanced matrix (skin) to be a valid scaling variable for the effective diffusion coefficient of the nanoparticle-polymer composite membranes for the entire range of skin thickness and nanoparticle loadings investigated.

## **Introduction**

Polymers are widely used as membranes for hydrogen recovery, gas separation, dehydration of natural gas streams, filtration, polymeric electrolyte membranes for use in fuel cells and as ion-exchange membranes as well as for insulators and packaging materials [1]. Permeation in dense membranes occurs via a penetrant diffusion mechanism with permeability being a product of diffusion and solubility of the penetrant [2]. Experiments show that the addition of 10-30 wt% of nanosized fumed silica to a number of high-permeability polymers increases small penetrant permeation by up to an order of magnitude [3-7]. Normally, the addition of low-permeability fillers (such as silica) reduces penetrant diffusion simply by volume-fraction effects. It is believed that the anomalous behavior observed for nanosized particles is associated with the greater specific interfacial area for the same level of loading compared to conventional (i.e., micron-sized or larger) filler particles. The specific interfacial area (interfacial area/unit volume of composite) created when a given volume fraction of spherical particles is added to a polymer matrix scales inversely with the radius of the particles. Hence, while the addition of micron-sized particles to high-permeability membranes results primarily in an (unfavorable) volume effect, addition of nanoparticles can create orders of magnitude greater specific interfacial area than the addition of the same volume fraction of conventional particles, resulting in increased permeability due to the presence of particle-polymer interfaces. This makes the addition of nanoparticles a promising approach to controlling the permeability of polymer membranes, since the polymer structure and dynamics have a great influence on small penetrant diffusion.

Because nano-sized silica is known to leave penetrant solubility unchanged for filler concentrations up to 40-50 wt% [5], the observed permeation increase upon addition of nano-sized silica must be due to increased diffusion of the penetrants. It has been suggested [3] that the addition of impenetrable nanoparticles disrupts polymer chain packing adjacent to the filler surface leading to an increase in free volume for the interfacial polymer, which is consistent with positron annihilation lifetime spectroscopy [6] and  $^{129}\text{Xe}$  NMR spectroscopy [7] observations on these high permeability

nanocomposite membranes. The increase in accessible free volume leads to faster penetrant diffusion through the interfacial polymer layers. Coalescence of interfacial layers with high permeation, due to nanoparticle clustering, may result in the formation of long, high permeability, preferred pathways for penetrant diffusion. Indeed, silica nanoparticle TEM images [3] indicate formation of irregularly shape clusters with a wide distribution supporting the model for the formation of preferred pathways. Finally, enhancement in penetrant diffusion was found to monotonically increase with increasing filler surface area at a constant filler volume fraction [3], further supporting the claim that the amount and properties of the interfacial polymer are key factors determining the magnitude of diffusion enhancement upon addition of filler to polymer membranes.

The lack of fundamental understanding of the influence of nanoparticle fillers on penetrant diffusion in polymers is a major hurdle to rational design of nanoparticle-polymer composite (NPPC) membranes. Factors that are likely to be important in determining penetrant permeability in NPPC membranes include the nature of the polymer-surface interaction, nanoparticle shape, the specific nanoparticle surface area, the interaction of nanoparticles in a given polymer matrix and the size and shape of aggregates formed due to these interactions. In order to facilitate progress in the design of high-performance NPPC membranes we have utilized the material point method (MPM) to study the fundamental mechanisms of the nanofiller enhanced penetrant diffusion in membranes. As described below, we have focused our efforts on understanding three factors that we think are the most crucial for understanding of penetrant transport in NPPC membranes: the nanoparticle loading level, interaction of the nanoparticles and the distance from the particle surface over which the matrix material is perturbed (i.e., exhibits increased penetrant diffusion).

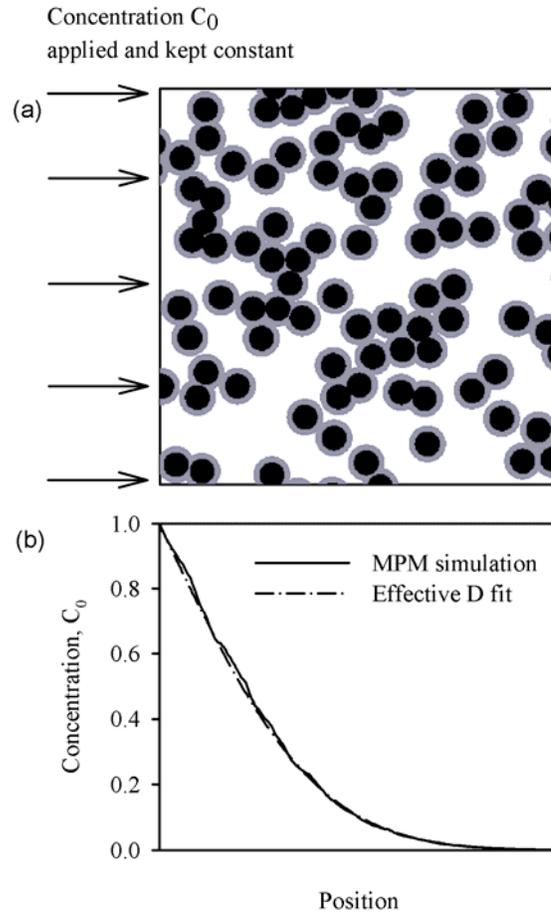
Penetrant diffusion in heterogeneous media can be conveniently studied using numerical methods, such as finite element method (FEM) [8] and the recently developed MPM (see below). Unlike theoretical solutions which based on assumptions about the geometric arrangements and size distributions of the different phases, numerical modeling can explicitly explore the shape, size and distribution effects of the inclusions on the effective properties of the composites. Thus, the links between the microscopic properties of the different phases and the macroscopic behavior of the composites can be studied, and the mechanisms of material property control can be obtained. The properties of the composites thus can be tailored according to these mechanisms.

Our basic assumption, supported by the experimental data described above, is that the polymer membrane near the surface of a nanoparticle exhibits enhanced penetrant diffusion relative to that of the bulk polymer. In our model this region of enhanced diffusion is treated as a “skin” on the nanoparticles which themselves are considered to be impenetrable and are heterogeneously distributed in the polymer matrix. In our study, we use MPM to study the diffusivity of the three-phase (nanoparticle, skin, bulk polymer) nanoparticle-polymer composites. In MPM [9-12] a material is discretized into a collection of material points. As the dynamic analysis proceeds, the solution is tracked on the material points by updating all required properties (position, velocity, concentration, etc.) at each material point. At each time step, the material point information is extrapolated to a background grid that serves as a computational scratch pad for solving the governing continuum equations. For the diffusion problem of interest here, the governing continuum equation is Fick’s second law

$$\frac{\partial C(x, y, t)}{\partial t} = \vec{\nabla} \cdot [D(x, y) \vec{\nabla} C(x, y)] \quad (1)$$

in 2D form, where  $C$  is the concentration of the diffusion substance,  $t$  is time,  $D(x, y)$  is the position dependent diffusion coefficient that differs for particle, bulk matrix and interface (skin) phases, and  $x$  and  $y$  are the space coordinates. Once the equations are solved for the current time step, the grid-based solution is used to update all material point properties.

There are two major advantages for using MPM over FEM method in simulations of diffusion in nanocomposite membranes: a) unlike mesh generation required for FEM, digitization of materials into material points is an easily-automated process; b) a simplicity of implementing position-dependent material properties to account for the expected variation of the penetrant diffusion coefficient in a membrane. These advantages proved very valuable in the previous MPM simulations of viscoelastic properties of highly filled composites [13] and polymer nanocomposites with distance dependent polymer properties [14]. In our simulations, the 2D MPM code [15] has been utilized. We choose 2D MPM code over 3D code is to reduce the complexity of the problem and to save the computational time. The simulation results can easily be extended to 3D cases.



**Figure 1.** Illustration of the MPM method used to determine the effective diffusion coefficient of the heterogeneous nanoparticle-polymer composite membrane. (a) The structure of a three-phase heterogeneous membrane and the application of the concentration boundary condition. (b) The concentration profile averaged over  $y$  direction from MPM simulation after time  $t$  and the fit with effective diffusion coefficient (Eq. (2)).

## Material Point Method (MPM) Simulation Methodology

### *Determination of penetrant diffusion in a composite medium*

Our primary method for utilizing MPM to determine the penetrant diffusion coefficient in a complex multi-phase medium is illustrated in Fig. 1. Here a finite concentration of the penetrant  $C_0$  is applied and kept constant at one boundary and the time evolution of the penetrant concentration profile

is solved for using MPM. An effective diffusion coefficient for the medium is then obtained from fitting to the concentration profile obtained by solving Eq. (1). Fig. 1(b) shows the concentration profile averaged over the  $y$  dimension from MPM simulations in a heterogeneous membrane shown in Fig. 1(a). An effective (homogenized) diffusion coefficient in  $x$  direction for the medium is obtained from fitting the MPM profile to the analytical solution for a homogeneous semi-infinite medium [16]

$$C(x,t) = C_0 \operatorname{erfc} \frac{x}{2\sqrt{D_e t}}, \quad (2)$$

where  $x$  is the distance from the boundary,  $t$  is time and  $D_e$  is the effective (homogenized) diffusion constant for the composite membrane. The time  $t$  is chosen to be long enough such that the profile is well-developed but sufficiently short such that the penetrant concentration at the  $x = L$  boundary is negligible, assuring the applicability of Eq. (2). The ability of Eq. (2) to represent the penetrant concentration profiles for the heterogeneous medium shown in Fig. 1(a) is illustrated in Fig. 1(b).

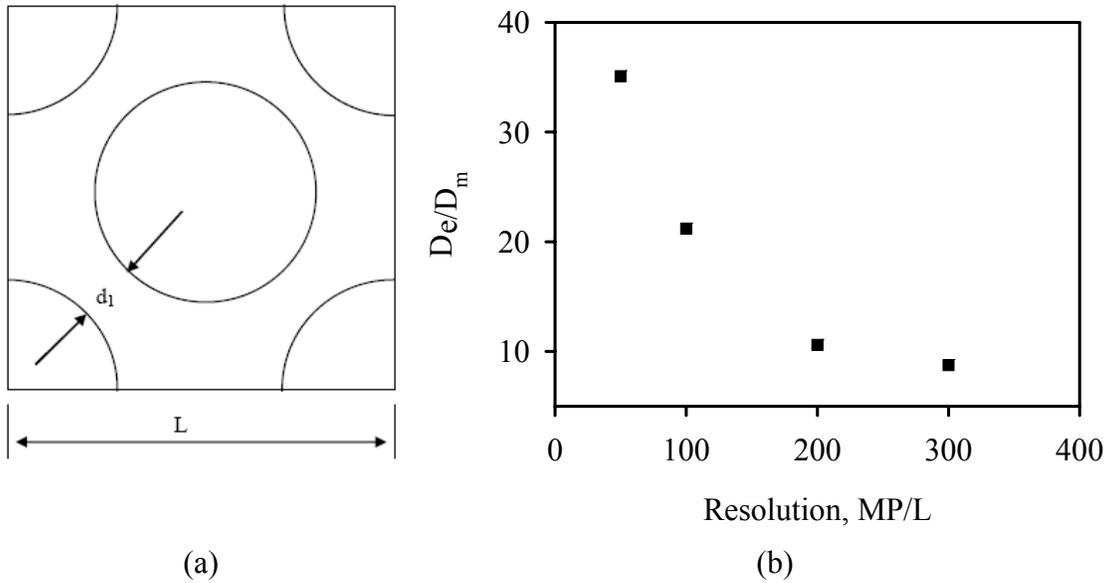


Figure 2. MPM spatial resolution effect to the effective diffusion coefficient. (a) Illustration of the simple periodic 2D particle/matrix composite. (b) Effective diffusion coefficient for the periodic composite as a function of resolution.

### ***Influence of MPM spatial resolution***

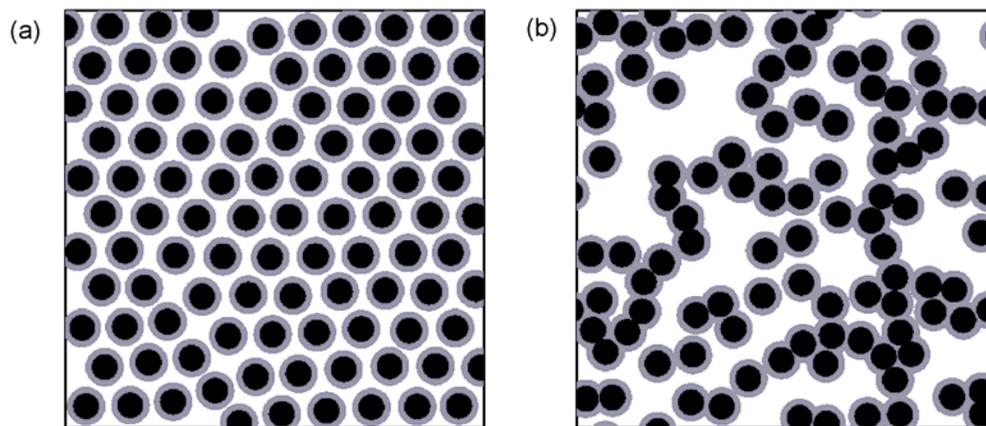
Our experience in predicting the viscoelastic properties of particle/matrix composites with disparate properties between particles and the matrix indicates that the spatial resolution of the MPM representation of the composite dramatically influences the description of the particle/matrix interface and consequently the predicted composite response[13]. We performed a series of simulations on a periodic model system consisting of two particles in a periodic square cell, illustrated in Fig. 2(a), in order to study the effect of MPM spatial resolution on the effective diffusion coefficient of particle/matrix composite. The relationship between the diffusion coefficients of the particle and the matrix is  $D_p/D_m=100$ . The distance between the particles  $d_1$  is such that for 50 MP/L resolution, where  $L$  is the size of the cell, there is only one material point (MP) between the particles. We varied overall resolution from 50 to 300 MP/L, i.e., from 1 to 6 MPs between the particles. The effective diffusion coefficient of the composite as a function of resolution is shown in Fig. 2(b). As resolution increases the effective diffusion coefficient decreases due to improved representation of the interface between

the particle and the matrix. However, for resolution greater than 200 MP/L (4 MPs between particles), there is almost no change in effective diffusion coefficient upon further increase in the resolution. Considering the balance between the simulation expense and accuracy, 4 MPs between particles appears to be a good compromise for spatial resolution.

We have to point out that the accuracy of the interfacial description depends on the disparity (or the contrast) between properties of the phases. The larger the disparity the higher the resolution should be to obtain the same accuracy [13]. The above resolution conclusion (4 MPs between particles) is for our systems of study. If the contrast between the diffusion coefficients  $D_p/D_m$  changes the resolution need to be changed to achieve a set accuracy.

### ***Generation of representative three-phase nanoparticle-polymer composite membranes***

As discussed above, it is believed that the enhancement of the diffusivity in NPPC membranes is primarily the consequence of high penetrant diffusivity in the matrix near the nanoparticle surface, i.e., in the interfacial polymer. The question arises as to the thickness of this interfacial regime, or phase, i.e., the distance from the particle surface over which the polymer properties are perturbed in a manner (e.g., increased free volume) such that penetrant diffusivity is enhanced. Since enhanced diffusion is seen only for nanosized fillers, it is immediately clear that the effects of the particle-polymer interface on polymer properties is limited to a few 10s of nanometers at most, and is more likely on the scale of 10 nanometers or less. For a given area fraction of particles, configuration of particles and penetrant diffusivity for the three phases (particle, skin, and matrix), the solution of Eq. (1) depends only upon the ratio of the skin thickness to the particle size. In other words, we would obtain the same solution for 1 micron diameter particles with a 100 nm skin as we would for the same configuration of 10 nm diameter particles with a 1 nm skin. We have studied the effective composite properties as a function of  $\gamma$  (skin thickness/particle diameter) for  $0.075 \leq \gamma \leq 0.25$ . With a skin thickness of  $\approx 5$  nm, this corresponds to (nano)particle diameters in the range  $20 \text{ nm} \leq D_p \leq 70 \text{ nm}$ .

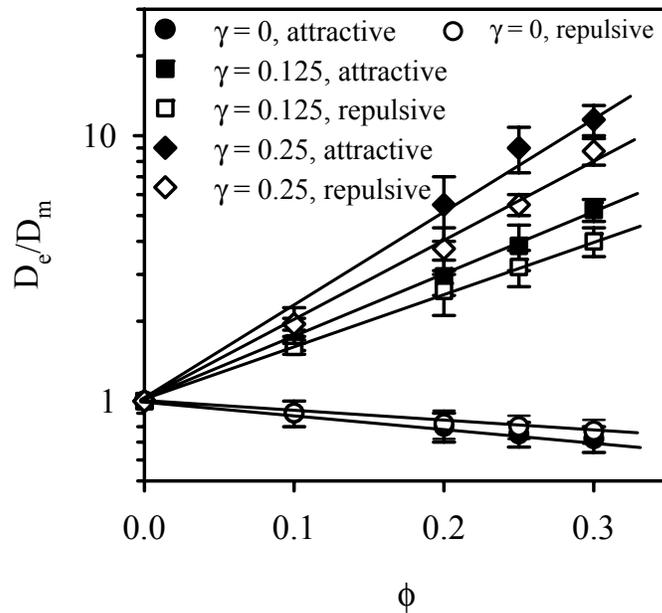


**Figure 3.** Representative configurations of repulsive and attractive nanoparticles for  $\phi = 0.30$  and  $\gamma = 0.25$ . (a) Repulsive nanoparticles. (b) Attractive nanoparticles.

Structures for our 2D NPPC membranes were generated using Monte-Carlo method with LJ potential between the particles. Periodic boundary conditions were applied during the generation of the structures. The well-depth of the LJ potential was adjusted to control the extent of the attractive interaction between nanoparticles. For configurations of attractive particles the skins from different particles were allowed to overlap resulting in clustered configurations such as shown in Fig. 3(b). For

systems with repulsive nanoparticle-nanoparticle interactions the distance between the particles was increased whenever overlap of skins occurred during generation to remove skin-skin contact, resulting in fully dispersed configurations such as shown in Fig. 3(a). For the NPPC membranes with repulsive (fully dispersed) particles the MP resolution was set such that there are at least 4 MPs in and between the skins. For the attractive (clustered) structures formed by there were also at least 4 MPs in the skins. Due to the large heterogeneity of the nanocomposite structures, several independent (at least 4) structures were generated using the Monte Carlo method described above for each membrane (particle area fraction,  $\gamma$ , and attractive vs. repulsive particles). The effective diffusion coefficients and the simulation errors for the composites were obtained by averaging the diffusion coefficients obtained for the various independent configurations of a given membrane.

In our model the nanoparticles were impenetrable while the interfacial skin had a penetrant diffusion coefficient  $D_s = 100 D_m$ , where the latter was the penetrant diffusion coefficient of the bulk matrix material. We chose  $D_s = 100 D_m$  for two reasons. One was that this choice yielded similar effective diffusion coefficient increase as the experimental results. Another reason was to reduce the simulation time. Our simulations showed that larger  $D_s$  will not further increase the effective diffusion coefficient much, especially for the well dispersed structures, but will significantly increase the simulation time due to the corresponding decrease of the time step.

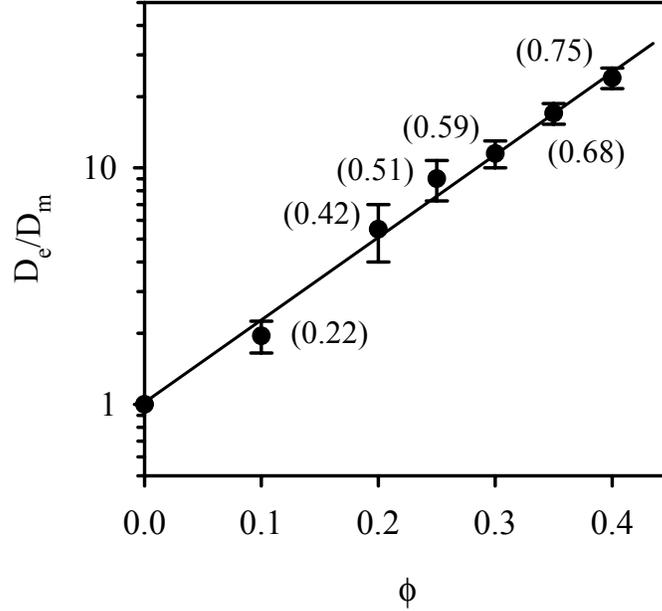


**Figure 4.** Effective diffusion coefficient of the nanoparticle-polymer composite membrane as a function of the particle area fraction for various skin thicknesses. The solid lines are exponential fits to the data. The error bars are obtained from the largest deviation of the various independent configurations for a given membrane.

### Simulation Results and Discussion

The effective diffusion coefficient of the nanoparticle-polymer composite membranes is shown as a function of the particle area fraction  $\phi$  in Fig. 4 for several skin thicknesses. For the NPPC membranes without a regime (skin) of enhanced diffusion (i.e.,  $\gamma = 0$ ), the effective diffusion coefficient of the membrane decreases with  $\phi$  since the impenetrable particles act as obstacles to

penetrant diffusion. For membranes loaded with nanoparticles exhibiting enhanced interfacial diffusion, the effective diffusion coefficient of the membrane increases exponentially with  $\phi$  for both attractive and repulsive nanoparticle configurations. We also observe that for the NPPC membranes loaded with attractive nanoparticles the effective diffusion coefficient increases more rapidly with particle loading than for membranes loaded with repulsive particles. The effective diffusion coefficient of the NPPC membrane also depends on the thickness of the enhance diffusion skin with thicker skins leading to larger effective diffusion coefficients.



**Figure 5.** Effective diffusion coefficient of the nanoparticle-polymer composite membrane as a function of the particle area fraction for  $\gamma = 0.25$  for attractive nanoparticles. The effective area of the nanoparticles, given as the area of the nanoparticles plus the skin, which determines percolation, is also marked on the figure. The solid line is an exponential fit to the data. The error bars are obtained from the largest deviation of the various independent configurations for a given membrane.

In order to study the influence of nanoparticle percolation on the effective diffusion coefficient of the composite membrane, we further increased the loading of attractive nanoparticles to levels much higher than the percolation threshold ( $< 53\%$  from Ref. [17]) for  $\gamma = 0.25$  for the clustering nanoparticle system. The effective diffusion coefficient for the NPPC membranes is shown in Fig. 5 as a function of  $\phi$ . The exponential relationship between the effective diffusion coefficient and  $\phi$  appears to hold continuously through the percolation threshold. The exponential relationship can be explained by the Agari and Uno model [18] that considers the connection of the particles and the formation of the particle chains even above the percolation threshold.

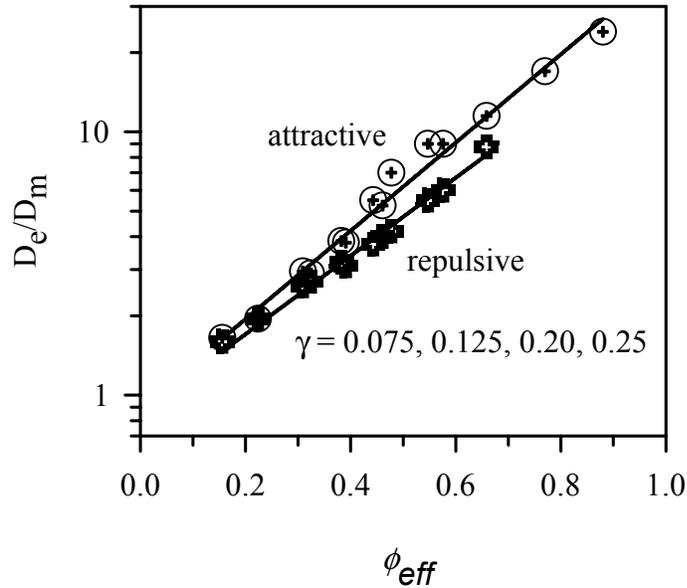
In Fig. 6 the effective diffusion coefficient is plotted for all NPPC membranes as a function of the “effective” area fraction  $\phi_{eff}$  of nanoparticles. Here,  $\phi_{eff}$  includes not only the area of the impenetrable nanoparticles but also the area of the skins, with the relationship

$$\phi_{eff} = \phi(1 + 2\gamma)^2 \quad (5)$$

The effective diffusion coefficient shows exponential dependence on  $\phi_{eff}$  for both attractive and repulsive nanoparticles. Thus we have

$$\log \frac{D_e}{D_m} = \kappa \phi_{eff} + c = \kappa \phi (1 + 2\gamma)^2 + c \quad (6)$$

where  $\kappa$  and  $c$  depend on the morphology (clustered vs. disperse) and  $D_s/D_m$  but not the level of particle loading or the skin thickness. This expression is consistent with our previous discussion of Fig. 4 in that the effective diffusion coefficient increases exponentially with the increase of the particle area fraction for a given skin thickness.



**Figure 6.** Effective diffusion coefficient of the nanoparticle-polymer composite membranes as a function of effective particle area. Solid lines are exponential fits to the data.

## Conclusions

We have utilized the MPM in studying the nanoparticle enhanced diffusion in high permeability polymer membranes. An additional skin around the nanoparticle is explicitly added to represent the free volume at the matrix and nanoparticle interface. The skin thickness and the morphology of the nanoparticles are varied to understand the penetrant transport in the polymer nanocomposite. Simulation results show linear logarithmic dependence between the effective diffusion coefficient and the effective area fraction of nanoparticle plus skin, which can be explained by the Agari-Uno model, and also agrees with the experimental measurements [4]. The percolation of the nanoparticles (skins) does not break the linear logarithmic relation.

## Acknowledgement

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