Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information for:

Decoupling Energetic Modifications to Diffusion from Free Volume in Polymer/Nanoparticle Composites

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Here we summarize an effective medium calculation by the method of Maxwell[1, 2] to determine the effective diffusivity for a composite of dilute, monodisperse spheres, D_ϕ, with a core/shell structure embedded at random in a matrix. The core has volume fraction ϕ_P, is impermeable and is of diameter d. The attached shell has thickness δ and volume fraction ϕ_δ (see Figure S1). The matrix-penetrant pair has (constant, bulk) diffusion coefficient D_B while the shell-penetrant pair has (constant) diffusion coefficient D_δ. The ratio of shell partition coefficient to matrix partition coefficient is K_δ/K_B. Below appears an effective partition coefficient for the composite, K_ϕ. From ref. [2] K_ϕ is defined according to what concentration is used in the Fick's first law flux for the composite. Using penetrant mass per unit total volume leads to

$$K_\phi = (1 - \phi_P - \phi_\delta)K_B + \phi_\delta K_\delta \qquad \text{(S1)}$$

where

$$\phi_\delta = \left[\left(1 + \frac{2\delta}{d}\right)^3 - 1\right]\phi_P \qquad \text{(S2)}$$

Denote by ψ and λ respectively, the steady concentration field in the matrix surrounding, and in the shell of, an isolated core/shell particle under a constant macroscopic concentration drop along one direction, say z. These each obey Laplace's equation, which is, for example

$$\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}\psi + \frac{\partial}{\partial \eta}(1-\eta^2)\frac{\partial}{\partial \eta}\psi = 0 \quad ; \eta = cos\theta \tag{S3}$$

for ψ, in a spherical coordinate system with the particle core centered on the origin and the associated z axis pointing along the direction of the macroscopic gradient (see Figure S1). The solutions sought for ψ and λ are finite for $\eta = \pm 1$ and obey the boundary conditions

$$\lim_{r\to\infty} \frac{\partial}{\partial r}\psi = G\eta \quad , \tag{S4}$$

$$\left.\frac{\partial}{\partial r}\psi\right|_{r = 0.5d + \delta} = \left.\frac{D_\delta}{D_B}\frac{\partial}{\partial r}\lambda\right|_{r = 0.5d + \delta} \quad , \tag{S5}$$

$$\left.\frac{K_\delta}{K_B}\psi\right|_{r = 0.5d + \delta} = \lambda|_{r = 0.5d + \delta} \quad , \tag{S6}$$

$$\left.\frac{\partial}{\partial r}\lambda\right|_{r = 0.5d} = 0 \quad . \tag{S7}$$

Eqns. S4-S7 express, respectively, that the far-field gradient match the imposed gradient G, that the normal components of the penetrant flux out from the shell and into the matrix match at the shell/matrix boundary, that the penetrant concentration partitions according to K_δ/K_B at the shell/matrix boundary, and that the core is impermeable. We seek eigen-function expansions ψ and λ in terms of the Legendre polynomials $\Phi_n(\eta)$ and so apply the transform

$$\begin{pmatrix}\Psi_n(r)\\ \Lambda_n(r)\end{pmatrix} \equiv \int_{-1}^{1} \Phi_n(\eta)\begin{pmatrix}\psi_n(r,\eta)\\ \lambda_n(r,\eta)\end{pmatrix} d\eta \quad ; n = 0,1,2,... \tag{S8}$$

giving the equidimensional equation for the $\Psi_n(r)$

$$\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\Psi_n(r) - n(n+1)\Psi_n(r) = 0 \tag{S9}$$

and an analogous equation for the $\Lambda_n(r)$. The homogeneous solutions are

$$\Psi_n(r) = A_n r^n + B_n r^{-(n+1)} \text{ and} \tag{S10}$$

$$\Lambda_n(r) = C_n r^n + D_n r^{-(n+1)}.$$

Applying the transform Eq. S8 to the boundary conditions Eqs. S4-S7 and using the results to resolve the constants in Eq. S10 leads to:

$$A_0 = \text{ arbitrary constant,} \tag{S11}$$

$$A_1 = \sqrt{\frac{2}{3}}G,$$

$$A_n = 0 \text{ for } n \geq 2,$$

$$B_0 = 0,$$

$$B_1 = \sqrt{\frac{2}{3}}G\left(\frac{d}{2}+\delta\right)^3\left[\frac{\left(1-\frac{D_\delta K_\delta}{D_B K_B}\right)+\left(\frac{1}{2}+\frac{D_\delta K_\delta}{D_B K_B}\right)\left(\frac{d}{d+2\delta}\right)^3}{\left(2+\frac{D_\delta K_\delta}{D_B K_B}\right)+\left(1-\frac{D_\delta K_\delta}{D_B K_B}\right)\left(\frac{d}{d+2\delta}\right)^3}\right],$$

$$B_n = 0 \text{ for } n \geq 2,$$

$$C_0 = \text{ arbitrary constant,}$$

$$C_1 = \sqrt{\frac{2}{3}}\frac{K_\delta}{K_B}G\left[\frac{3}{\left(2+\frac{D_\delta K_\delta}{D_B K_B}\right)+\left(1-\frac{D_\delta K_\delta}{D_B K_B}\right)\left(\frac{d}{d+2\delta}\right)^3}\right],$$

$$C_n = 0 \text{ for } n \geq 2,$$

$$D_0 = 0,$$

$$D_1 = \frac{1}{16}C_1 d^3,$$

$$D_n = 0 \text{ for } n \geq 2,$$

Consequently the concentration field in the matrix is

$$\psi_n(r,\eta) = c_\infty(r,\eta) + c_0(r,\eta) \tag{S12}$$

where $c_\infty(r,\eta)$ means the concentration field in the absence of the particle, i.e. the undisturbed field

$$c_\infty(r,\eta) = A + Gr\eta = A + r\cdot\nabla c_\infty(r) \tag{S13}$$

where A is an arbitrary constant, and $c_0(r,\eta)$ means the disturbance due to a single core-shell particle located at the origin

$$c_0(r,\eta) = \left(\frac{d}{2}+\delta\right)^3 \left[\frac{\left(1-\frac{D_\delta K_\delta}{D_B K_B}\right) + \left(\frac{1}{2}+\frac{D_\delta K_\delta}{D_B K_B}\right)\left(\frac{d}{d+2\delta}\right)^3}{\left(2+\frac{D_\delta K_\delta}{D_B K_B}\right) + \left(1-\frac{D_\delta K_\delta}{D_B K_B}\right)\left(\frac{d}{d+2\delta}\right)^3}\right] \frac{1}{r^3} r\cdot\nabla c_\infty(r) \tag{S14}$$

So, the far-field perturbation $c_0(r)$ from a single core-shell particle located at $r^{'}$ is

$$c_0(r) = \frac{d^3}{8}\beta\frac{r\cdot\nabla c_\infty}{|r-r^{'}|^3} \tag{S15}$$

with

$$\beta = \left(1+\frac{2\delta}{d}\right)^3 \left[\frac{\left(1-\frac{D_\delta K_\delta}{D_B K_B}\right) + \left(\frac{1}{2}+\frac{D_\delta K_\delta}{D_B K_B}\right)\left(\frac{d}{d+2\delta}\right)^3}{\left(2+\frac{D_\delta K_\delta}{D_B K_B}\right) + \left(1-\frac{D_\delta K_\delta}{D_B K_B}\right)\left(\frac{d}{d+2\delta}\right)^3}\right] \tag{S16}$$

Maxwell's effective medium method involves determining the far-field effect of a cluster of N particles confined in a spherical test volume of radius R centered on the origin. Superposition leads to

$$c_0(r) = \sum_V \frac{d^3}{8}\beta\frac{r\cdot\nabla c_\infty}{|r-r^{'}|^3} \simeq \phi_P R^3 \beta \frac{r\cdot\nabla c_\infty}{r^3}. \tag{S17}$$

This must match the far field disturbance by a sphere on the origin of radius R with effective properties D_ϕ and K_ϕ , namely[2]

$$c_0(r) = R^3 \beta_\phi \frac{r \cdot \nabla c_\infty}{r^3} \tag{S18}$$

with

$$\beta_\phi = \frac{D_B - D_\phi K_\phi}{2D_B + D_\phi K_\phi} \tag{S19}$$

Consequently

$$\phi_P \beta = \beta_\phi \tag{S20}$$

defines D_ϕ. Keep in mind that this calculation does NOT account for the interaction of particles in the test volume on the far field disturbance and so is strictly valid only in the dilute limit

$$\phi_P \left(1 + \frac{2\delta}{d}\right)^3 \ll 1 \tag{S21}$$

It is therefore convenient to express D_δ/D_B as a power series in ϕ_P. For the simple case $K_\delta/K_B = 1$ and $K_\phi = 1 - \phi_P$ using Taylor's expansion, this turns out to be

$$\frac{D_\phi}{D_B} \simeq 1 + (1 - 3\beta)\phi_P + O\left({\phi_P}^2\right). \tag{S22}$$

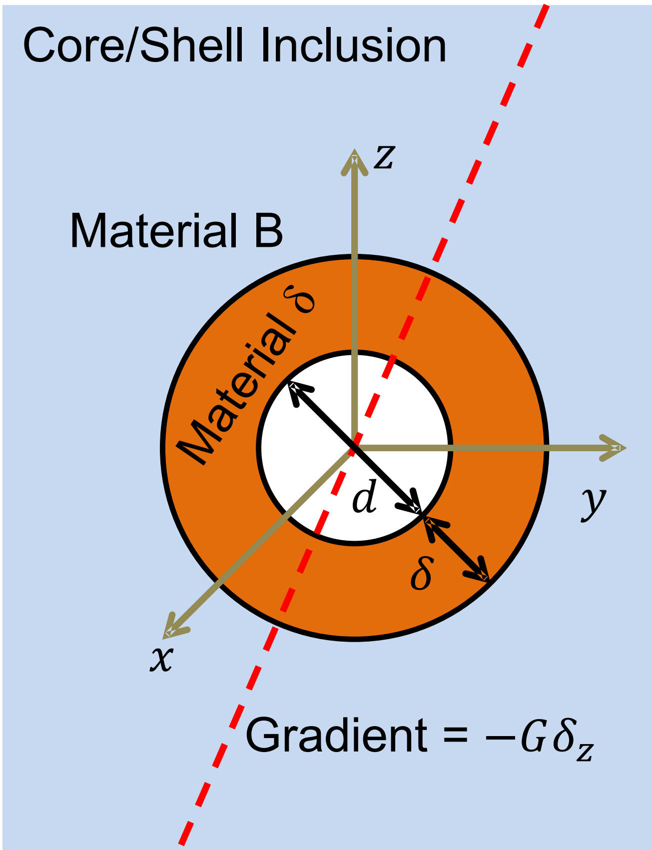

Figure S1. Coordinate system and geometry of system theoretically modeled above.

References

1. C. Maxwell, *Treatise on Electricity and Magnetism*, Oxford University Press, London, 1873.
2. W. M. Deen, *Analysis of Transport Phenomena*, Oxford University Press, New York, 1998.