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Supplementary Information

Understanding anisotropic transport in self-assembled membranes and maximizing ionic conductivity by microstructure alignment

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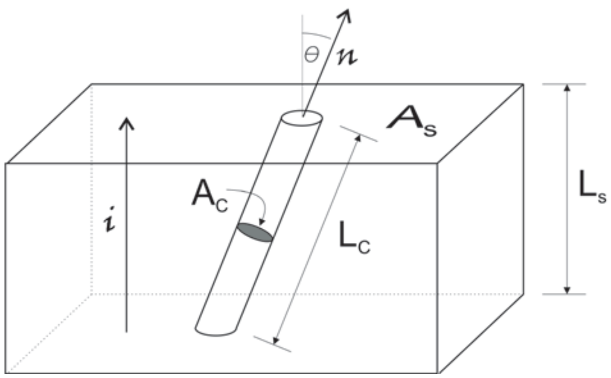
Derivation of conductivity of composite media composed of anisotropic elements of cylindrical and lamellar morphology

In our derivation we start from the definition of conductivity (σ_S) of the rectangular slab composed of conductive cylindrical or lamellar elements with isotropic conductivity (σ_C and σ_L, respectively) embedded in a non-conductive matrix (Eqns. 1.1 and 2.1). For simplicity, there is only one cylinder and one lamella depicted on the schematics below, but in general there can be *n* elements intersecting the slab. By applying the parallel conduction law, the inverse of the overall resistance of the system is the inverse of resistance of each element times the number of the elements (Eqns. 1.2 and 2.2). We can further substitute the length of the conductive element with the length of the slab corrected by a proper function of the tilt angle θ (Eqn. 1.3 and 2.3). For consistency with general convention, followed in this manuscript, we have defined θ as an angle between the unique vector, or the director, of the anisotropic element and the measurement direction (apparent current flow direction). For cylinder the director is parallel to its axis while for lamella it coincides with its normal vector. Such convention, in our opinion, is more precise and profits in further derivation steps but nevertheless introduces two different functional forms in Eqns. 1.3 and 2.3. Eqns. 1.4 and 2.4 are obtained by substitution of the previous results into Eqns. 1.1 and 1.2, respectively. Simplicity of our approach consists in the "natural" emergence of the volume fractions of the conductive elements (Eqns. 1.5 and 2.5) in the course of the derivation. In particular, it circumvents somewhat troublesome constraint on the conservation of the volume fraction of the cylinders or the lamellae inside the slab when one tilts them. In the last step we substitute expressions from Eqns. 1.6 and 2.6 into Eqns. 1.4 and 2.4, respectively and obtain an angular dependence of the conductivity in these systems (Eqns. 1.7 and 2.7).

Our derivation does not define a lateral extension of the analyzed rectangular slab so we implicitly allow it to widen infinitely to accommodate for tilting of the anisotropic objects. In the system of finite size one expects a sharp drop of conductivity when the objects are tilted beyond an angle providing connectivity between the upper and lower electrodes. A model describing such situation for fiber conductivity was given by Weber and Kamal long with an excellent review of other models for conductivity of polymer-conductive fibers composites.[1]

The results obtained in Eqns. 1.7 and 2.7 can be used to calculate ensemble-average conductivities of polycrystalline samples composed of isomorphic grains with random spatial orientations of conductive domains. One of advantages of defining the tilt angle with respect to the unique axes of cylinders and lamellae is the same form of orientation probability distribution function for both systems i.e. sin(θ), normalized on [0, π /2] azimuthal angle interval (Eqns. 1.8 and 2.8). The azimuthal integrations (Eqns. 1.9 and 2.9) lead to the same values of conductivities of random polycrystalline cylindrical (Eqn. 1.10) and lamellar system (Eqn. 2.10), as discussed in the main article.

Conductive cylinders



$$\sigma_S = \frac{L_S}{A_S}\frac{1}{R_S} \quad \text{(Eqn. 1. 1)}$$

$$\frac{1}{R_S} = \frac{n_C}{R_C} = n_C\left(\frac{\sigma_C A_C}{L_C}\right) \quad \text{(Eqn. 1. 2)}$$

$$L_S = L_C \cos\theta \quad \text{(Eqn. 1. 3)}$$

$$\sigma_S = \frac{L_C \cos\theta}{A_S} n_C \left(\frac{\sigma_C A_C}{L_C}\right) = \sigma_C \cos\theta \left(\frac{n_C A_C}{A_S}\right) \quad \text{(Eqn. 1. 4)}$$

$$\varphi = \frac{volume\ of\ cylinders}{volume\ of\ system} = \frac{n_C A_C L_C}{A_S L_S} = \frac{n_C A_C}{A_S \cos\theta} \quad \text{(Eqn. 1. 5)}$$

$$\left(\frac{n_C A_C}{A_S}\right) = \varphi \cos\theta \quad \text{(Eqn. 1. 6)}$$

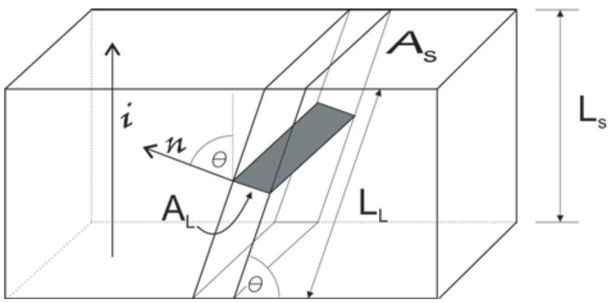
$$\rightarrow \boldsymbol{\sigma_S = \sigma_C\, \varphi \cos^2\theta} \quad \text{(Eqn. 1. 7)}$$

$$P(\theta) = \sin\theta \quad \text{(Eqn. 1. 8)}$$

$$\langle\sigma_S\rangle = \sigma_C\varphi \int_0^{\pi/2} \cos^2\theta \sin\theta \, d\theta \qquad \text{(Eqn. 1. 9)}$$

$$\rightarrow \boldsymbol{\langle\sigma_S\rangle = \frac{1}{3}\sigma_C\varphi} \qquad \text{Eqn. 1. 10)}$$

Conductive lamellae



$$\sigma_S = \frac{L_S}{A_S}\frac{1}{R_S} \qquad \text{(Eqn. 2. 1)}$$

$$\frac{1}{R_S} = \frac{n_C}{R_L} = n_L\left(\frac{\sigma_L A_L}{L_L}\right) \qquad \text{(Eqn. 2. 2)}$$

$$L_S = L_L \sin\theta \qquad \text{(Eqn. 2. 3)}$$

$$\sigma_S = \frac{L_L \sin\theta}{A_S} n_L \left(\frac{\sigma_L A_L}{L_L}\right) = \sigma_L \sin\theta \left(\frac{n_L A_L}{A_L}\right) \qquad \text{(Eqn. 2. 4)}$$

$$\varphi = \frac{volume\ of\ cylinders}{volume\ of\ system} = \frac{n_L A_L L_L}{A_S L_S} = \frac{n_L A_L}{A_S \sin\theta} \qquad \text{(Eqn. 2. 5)}$$

$$\left(\frac{n_L A_L}{A_S}\right) = \varphi \sin\theta \qquad \text{(Eqn. 2. 6)}$$

$$\rightarrow \boldsymbol{\sigma_S = \sigma_L \varphi \sin^2\theta} \qquad \text{(Eqn. 2. 7)}$$

$$\langle\sigma_S\rangle = \sigma_L\varphi \int_0^{\pi/2} \sin^3\theta \, d\theta \qquad \text{(Eqn. 2. 8)}$$

$$\rightarrow \boldsymbol{\langle\sigma_S\rangle = \frac{2}{3}\sigma_L\varphi} \qquad \text{(Eqn. 2. 9)}$$

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1. M. Weber and M. R. Kamal, *Polymer Composites*, 1997, **18**, 711–725.