The effects of nanoparticle shape and orientation on the low frequency dielectric properties of nanocomposites

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1. Motivation

. Dielectric properties of nanocomposites depend on the shape and orientation of nanoparticles.

. Nanocomposites consisting of metallic nanoparticles in organic hosts are promising for production of metamaterials from transformation optics to high energy density storage materials.

. A confusion regarding the effects of nanoparticles orientation exists in the literature.

. The goal of this work was to clarify the influence of shape and orientation of nanoparticles on the bulk dielectric properties.
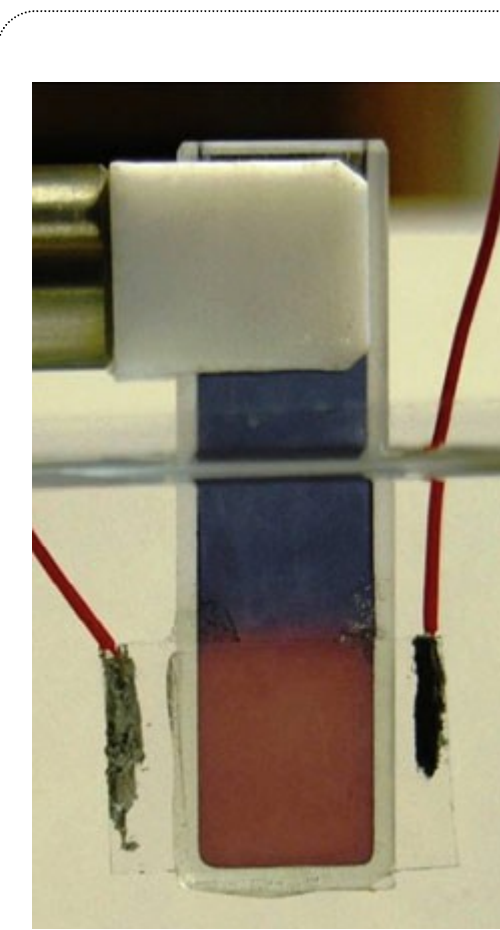
2. Experiments

. Investigated material - polystyrene coated Au nanorods (Au NR) suspended in toluene.

. Optical and dielectric properties of NR suspensions depend on the orientation of particles.
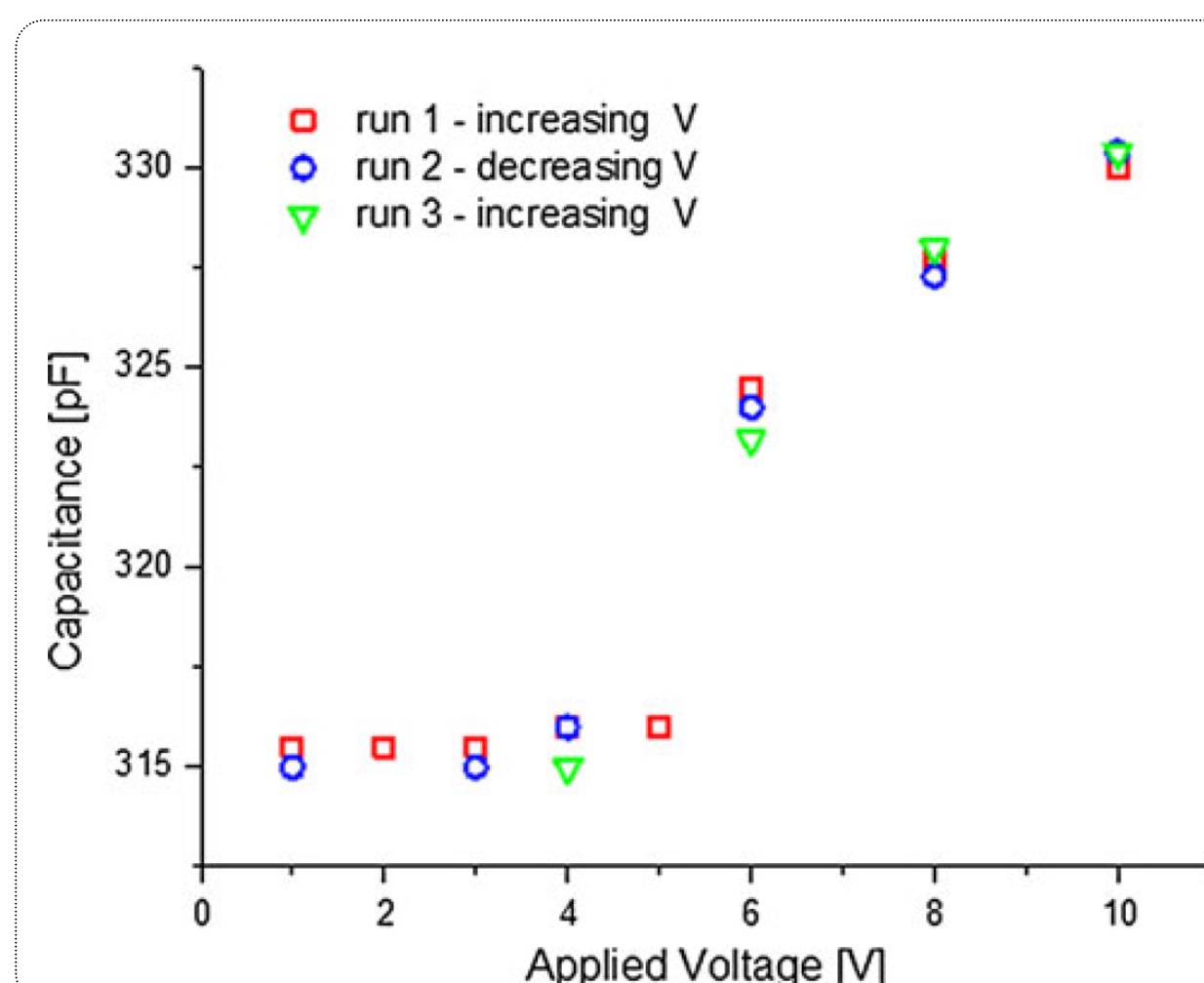
Optical absorbance measurements
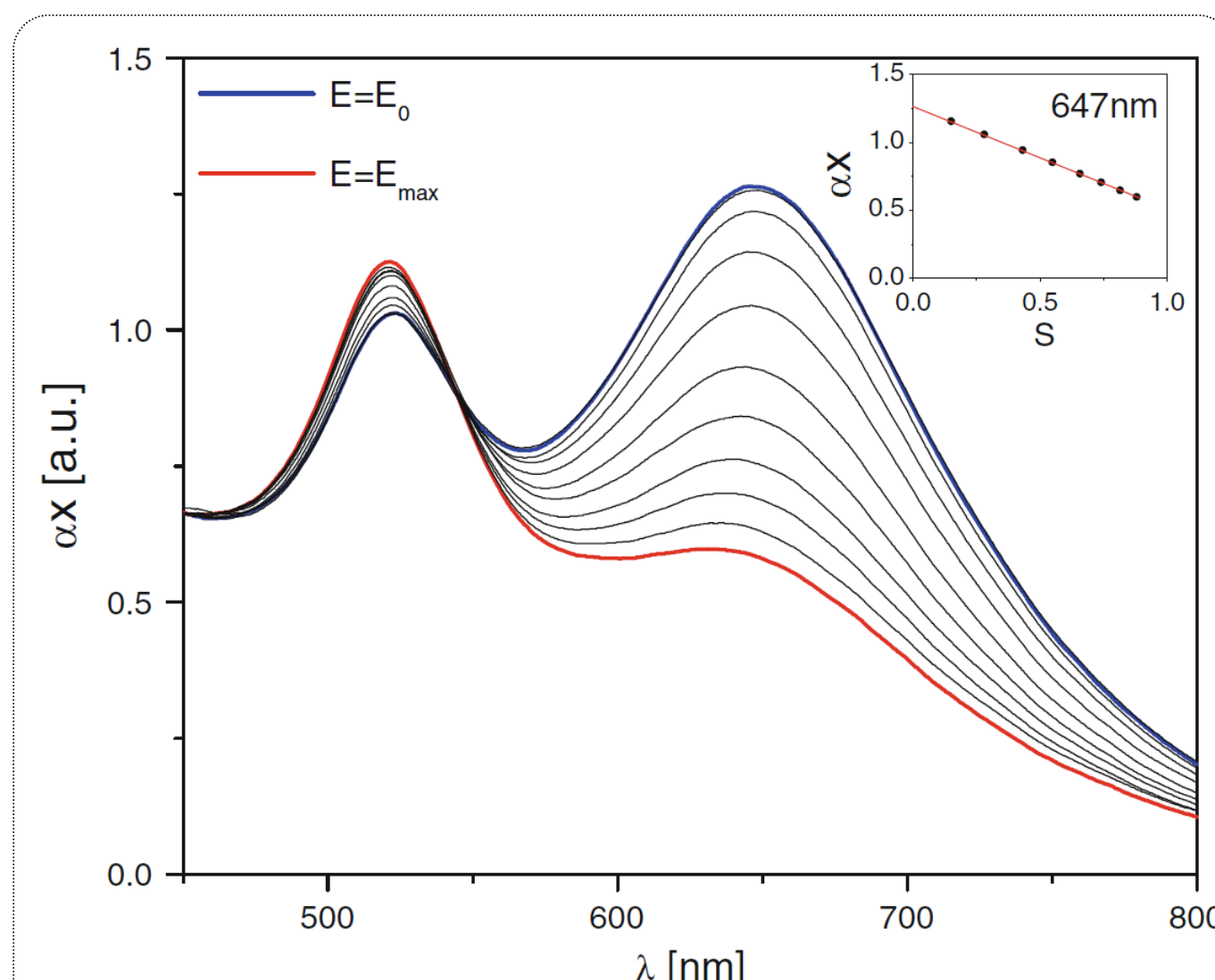
Absorbance of Au NRs, dispersed in toluene, for various applied fields. The inset shows absorbance vs. the order parameter S.

Au NRs in toluene (field applied perpendicular to the page).

Capacitance Measurements

Capacitance of polystyrene coated Au NR suspension in a glass cell. Capacitance increases as the NRs are aligned by the field.

Experimental results

. Au NRs align along the electric field.

. Effective dielectric constant increases with the applied field.

3. Dielectric Theory

. Considered is a dilute suspension of metallic spheroids in uniform dielectric host.

. Average permittivity of suspension:

$$\boldsymbol{\varepsilon}_{eff} = \varepsilon_{hl}\mathbf{I} + \varphi\langle\boldsymbol{\alpha}\rangle/v_o$$

ε_{hl} is the permittivity of the host, $\langle\boldsymbol{\alpha}\rangle$ is the average excess polarizability of a spheroid, v_0 is the particle volume and φ is the volume fraction of particles [1].
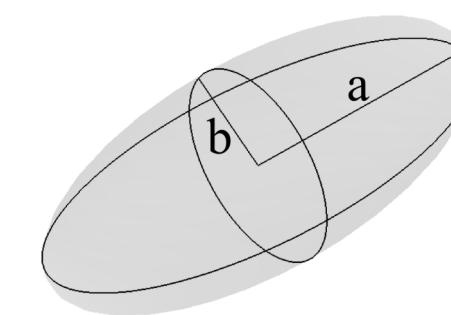
$$\boldsymbol{\alpha} = \varepsilon_o\varepsilon_h\frac{4}{3}\pi ab^2\left[\alpha_\parallel\hat{\mathbf{l}}\hat{\mathbf{l}} + \alpha_\perp(\hat{\mathbf{l}} - \hat{\mathbf{l}}\hat{\mathbf{l}})\right]$$

$$\alpha_\parallel = \frac{(\varepsilon_i - \varepsilon_h)}{\varepsilon_h + L_a(\varepsilon_i - \varepsilon_h)}$$

$$\alpha_\perp = \frac{(\varepsilon_i - \varepsilon_h)}{\varepsilon_h + \frac{1}{2}(1 - L_a)(\varepsilon_i - \varepsilon_h)}$$

Depolarizing factor:

$$L_a = \frac{a}{2b}\int_0^\infty \frac{\mathrm{d}x}{(x + (\frac{a}{b})^2)^{3/2}(x+1)}$$

Orientational order parameter: $S = \left\langle\frac{1}{2}(3(\hat{\mathbf{l}}\cdot\hat{\mathbf{N}})^2 - 1)\right\rangle$

The average dielectric permittivity of the metallic spheroid suspension:

$$\varepsilon_\parallel = \varepsilon_h\left\{1 + \frac{\varphi}{L_a(1-L_a)}\left[(\frac{1}{3}+L_a) + 2(\frac{1}{3}-L_a)S\right]\right\}$$

$$\varepsilon_\perp = \varepsilon_h\left\{1 + \frac{\varphi}{L_a(1-L_a)}\left[(\frac{1}{3}+L_a) - (\frac{1}{3}-L_a)S\right]\right\}$$

For rod-like particles, $\varepsilon_\parallel$ increases with:
- the particle volume fraction
- the aspect ratio
- the degree of orientational order S

4. Numerical Simulations

Capacitance Matrix

. One approach to calculate the dielectric properties of composites is through the capacitance matrix.

. For an assembly of M conductors in a uniform dielectric, the relation between charge and electric potential can be written as: $\mathbf{Q} = \mathbf{CV}$

$\mathbf{Q}$ and $\mathbf{V}$ are vectors representing charges and potentials of corresponding conductors, $\mathbf{C}$ is the capacitance matrix.

. The capacitance between conductors j and k:

$$C_{jk} = \frac{1}{(B_{jj} + B_{kk}) - (B_{jk} + B_{kj})}$$

$$\mathbf{B} = \mathbf{C}^{-1}$$

Simulated System

. Parallel plate capacitor with metallic particles.

. Capacitance between the two plates is calculated form the capacitance matrix, computed with FastCap [2] software
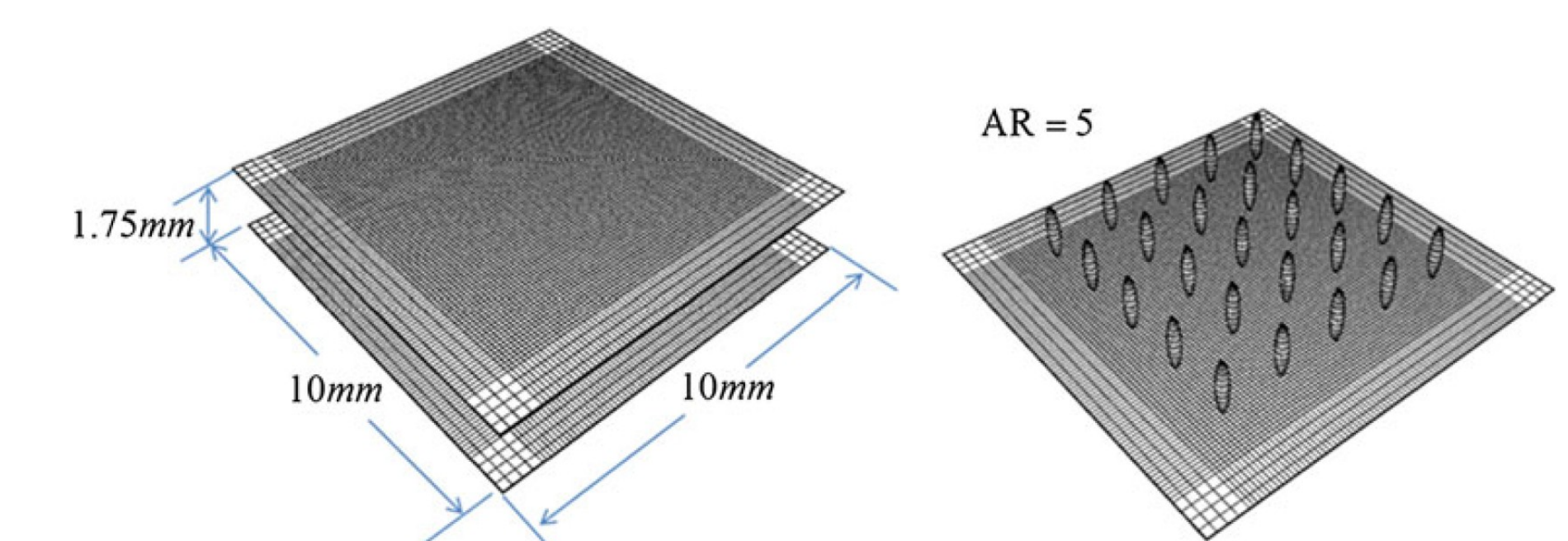
Parallel plate capacitor with aligned metallic particles. AR is the aspect ratio. The plates are 10x10 mm², separated by a 1.75 mm gap. 25 particles, with individual particle volume the same as a sphere with radius 0.25 mm, were placed between the plates. The orientation and the aspect ratio of the particles were varied.
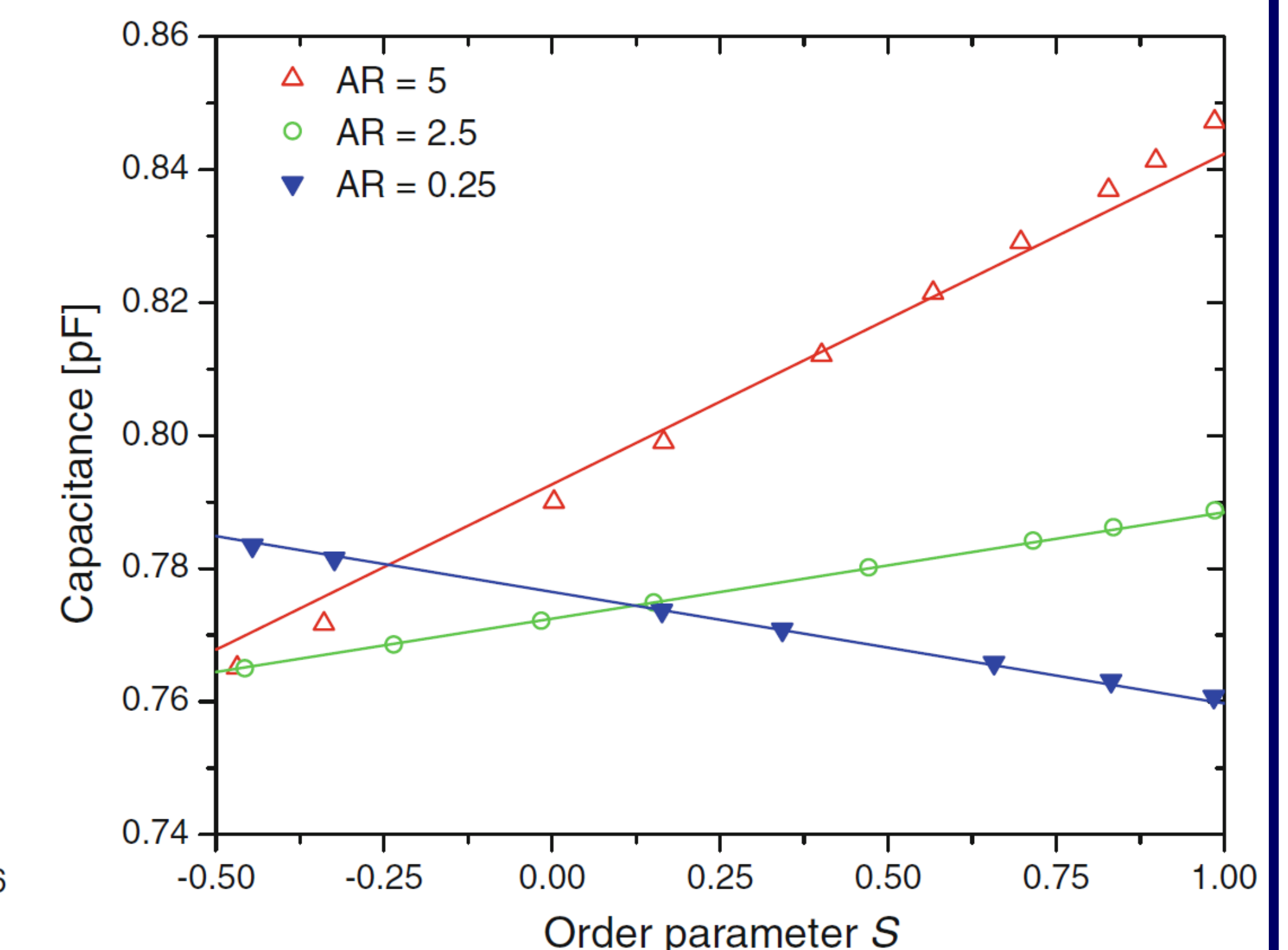
Results of Numerical & Analytical Calculations

Capacitance vs. Aspect Ratio of Particles

Capacitance vs. Order Parameter
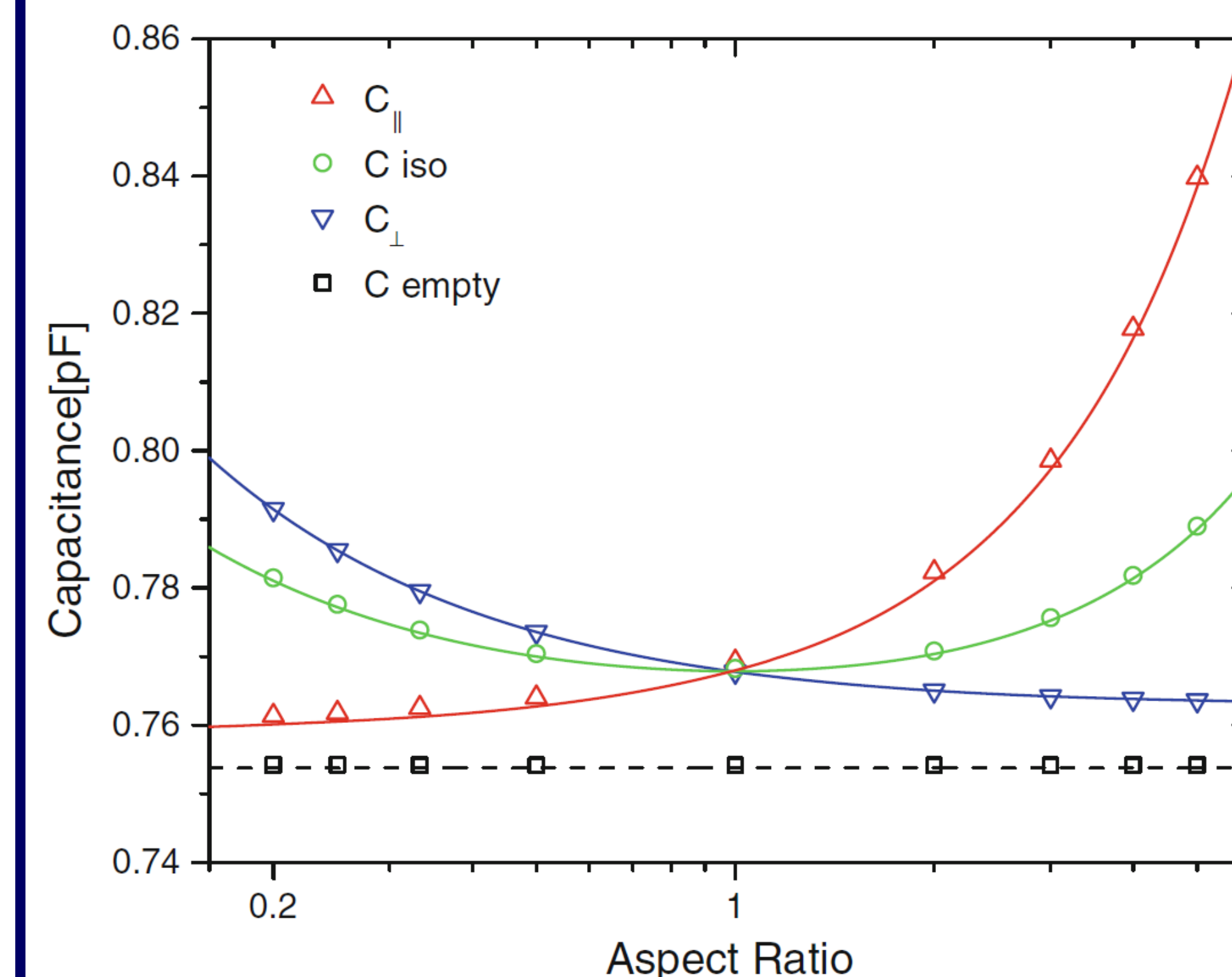
Capacitance as function of aspect ratio for aligned metallic particles and as function of orientational order . The symbols show numerical results, the solid lines theory. C$_\parallel$ and C$_\perp$ are the capacitances where the alignment direction is parallel and perpendicular to the field; C$_{iso}$ is the capacitance when there is no alignment and the sample is isotropic. AR is the aspect ratio

5. Conclusions

. Theory, experiments, simulations all indicate consistently that in the limit of low densities, the dielectric constant for a system of rod-like particles increases if the particles align along the field direction

. In the low density regime, well below the percolation threshold, the simple analytic results are in good agreement with simulations, and, in one instance, with experimental observations [3]. They may therefore serve as a useful guide to the estimation of the static dielectric properties of nanocomposites consisting of metallic nanoparticles having ellipsoidal shape.

References
[1] X. Zheng, J. Fontana, M. Pevnyi, M. Ignatenko, S. Wang, R. Vaia, and P. Palffy-Muhoray, *The effects of nanoparticle shape and orientation on the low frequency dielectric properties of nanocomposites*, J. Mater. Sci. **47**, 4914 (2012).
[2] K. Nabors and J. White, *FastCap: A Multipole Accelerated 3-D Capacitance Extraction Program*, IEEE Transactions on Computer-Aided Design. **10**, 11, 1447 (1991).
[3] J. Fontana, *PhD Thesis*, Chemical Physics Interdisciplinary Program. Kent State University, Kent, OH (2010)