Beaucage Research

-Quantification of nano-particle dispersion using SAXS/SANS

-Quantification of mesh size for percolated particles

-Correlation of hierarchical structure with dynamics

-Gibbs free energy for hierarchical growth as a basis for simulation

-Emergence/maturation/evolution of multi-hierarchical structures in complex systems

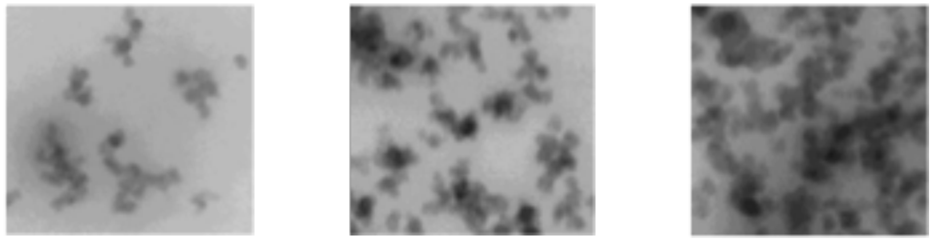
Paint/Inks

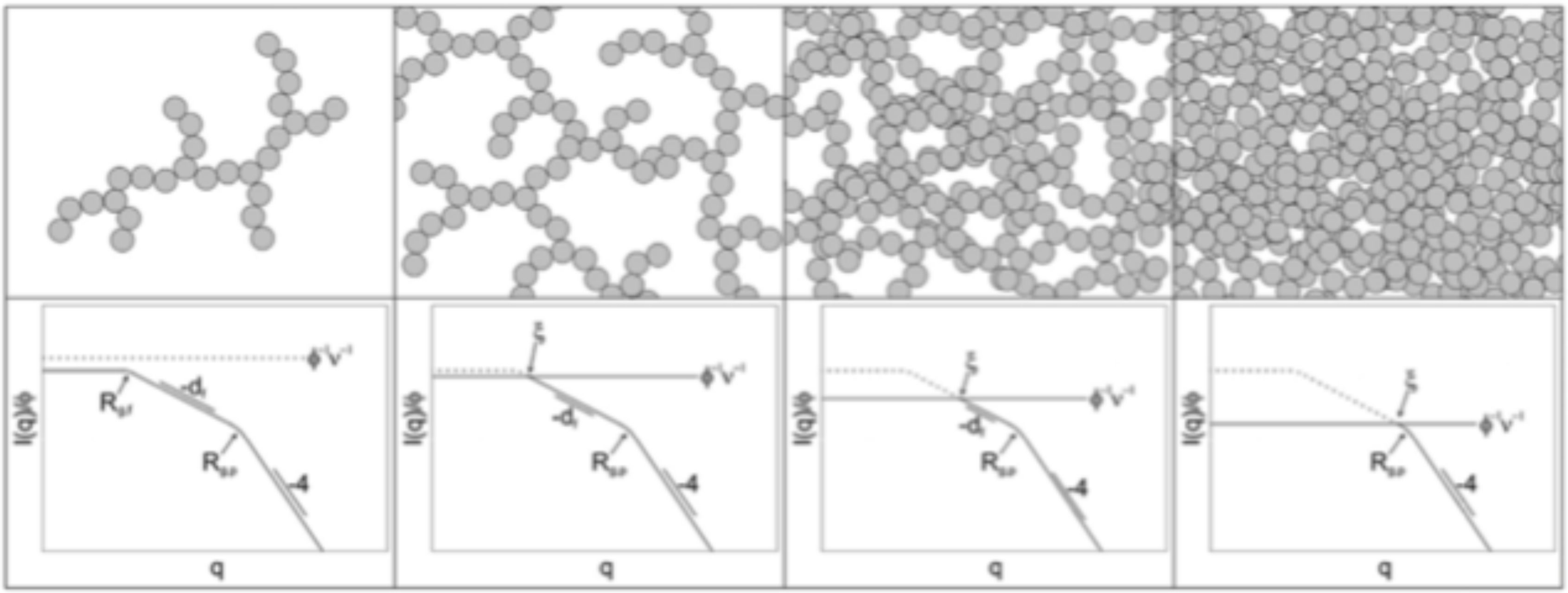
Reinforced elastomers

Ion conducting solid electrolytes

A Colloidal Model for Nanocomposite Dispersion.*

$$\frac{\phi}{I(q)} = \frac{\phi_0}{I_{\phi_0}(q)} + \nu\phi$$





*A pseudo-thermodynamic description of dispersion for nanocomposites Y. Jin, et al. *Polymer* 129 (2017) 32-43.**

Structural emergence in particle dispersions A. Mulderig, et al. *Langmuir* 33 (2017) 14029-37.

Thermodynamic stability of worm-like micelle solutions K. Vogtt, et al. *Soft Matter* 13 (2017) 6068-6078.

Worm-Like Micelles Display a Mesh Reminiscent of Polymers

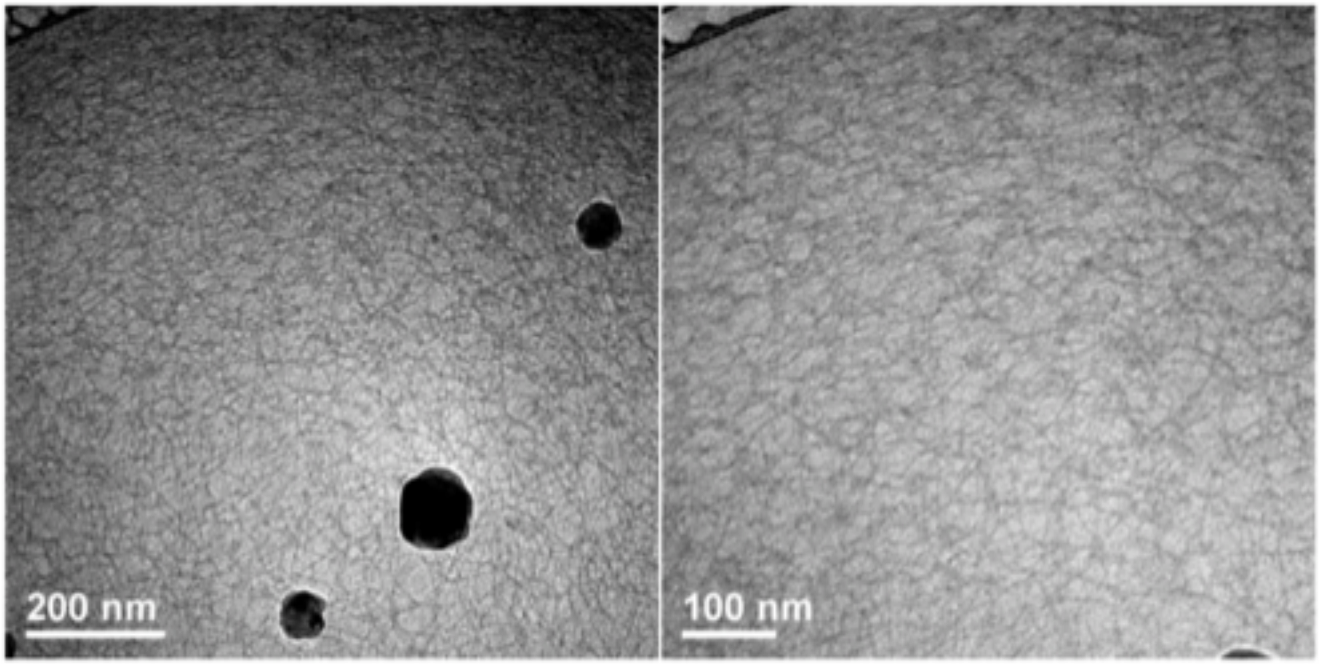


Fig. 13. Cryo-TEM images showing mesh size around tens of nanometers from sample with 3.72 wt.% MS 4.5 wt.% NaCl prepared at room temperature.

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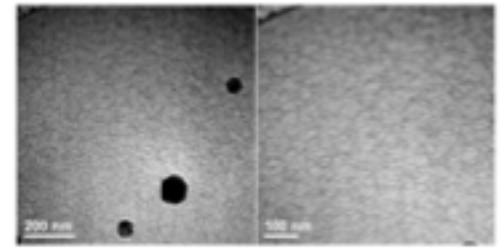


Fig. 13. Cryo-TEM images showing mesh size around tens of nanometers from sample with 3.72 wt.% MS 4.5 wt.% NaCl prepared at room temperature.

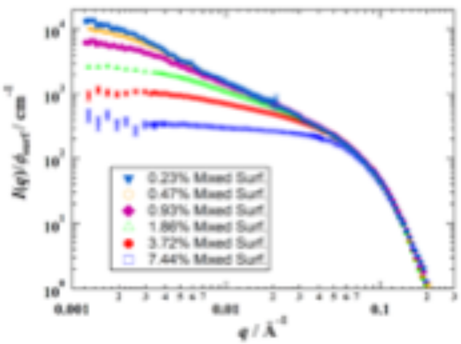


Fig. 2. Normalized scattering profiles of mixed surfactant samples at various concentrations in presence of 3 wt.% NaCl at 24.3 °C. Structural screening leads to a suppression of the low-q reduced intensity.

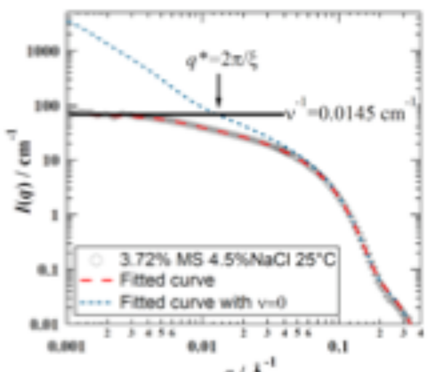


Fig. 3. Log-log plot of the scattering profile of 3.72 wt.% MS in the presence of 4.5 wt.% NaCl at 24.3°C. Determination of the structural screening parameter ν is demonstrated.

$$G''^2 = G_0^2/4 - (G' - G_0/2)^2$$

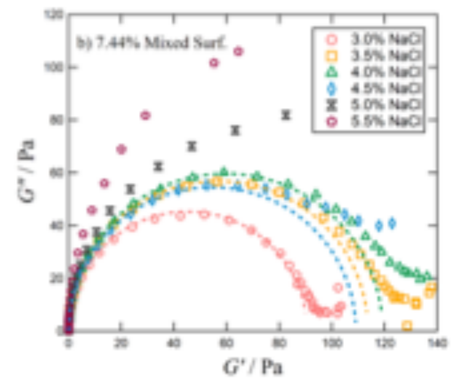


Fig. 11. Cole-Cole plots of the mixed surfactant samples at various salt concentrations. The plateau modulus of each sample was obtained by fits based on Maxwell's model[40] (dotted lines). (a) 3.72 wt.% MS, (b) 7.44 wt.% MS.

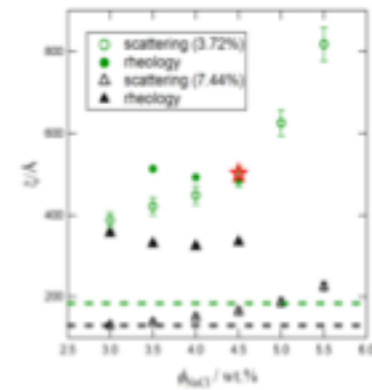
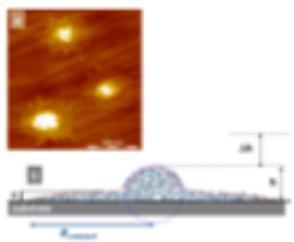


Fig. 14. Comparison of mesh size obtained through SANS, rheology (at 25 °C), Cryo-TEM (3.72 wt.% MS 4.5 wt.% NaCl, red star), and calculation based on eqn (2) (dotted lines). (color code: green: 3.72 wt.% MS; black: 7.44 wt.% MS)

Structural Screening to Quantify Dispersion

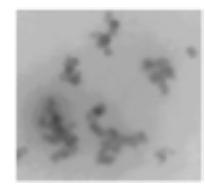
Compatibility	Incompatibility
Model Particles	Commercial Materials
Monodisperse	Polydisperse
Unaggregated	Aggregated
Enhanced compatibility	Incompatible

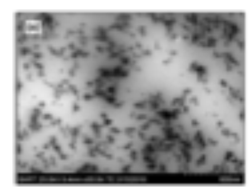
SMNPs and Microgels



Mourran A, Wu Y, Gumerov RA, Rudov AA, Potemkin II, Pich A, Möller M Langmuir 2016, 32, 723–730

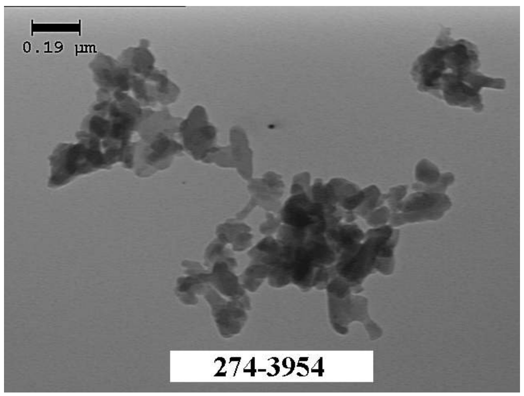
Kumar S, Jouault N, Benicewicz B, Neely T Macromolecules 2013, 46, 3199–3214





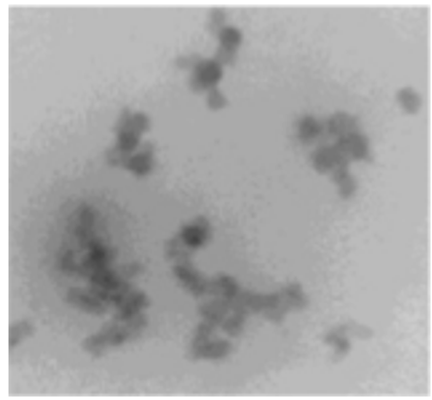
Among aggregated nanoparticles

Pigment + Surfactant

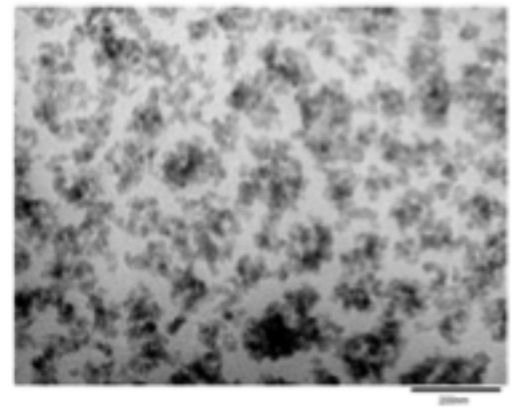


PY14 with Triton® X-100

Carbon Black



Silica



A colloidal approach for a compatible colloid:

e.g. inkjet ink: dispersed as pigment with surfactant

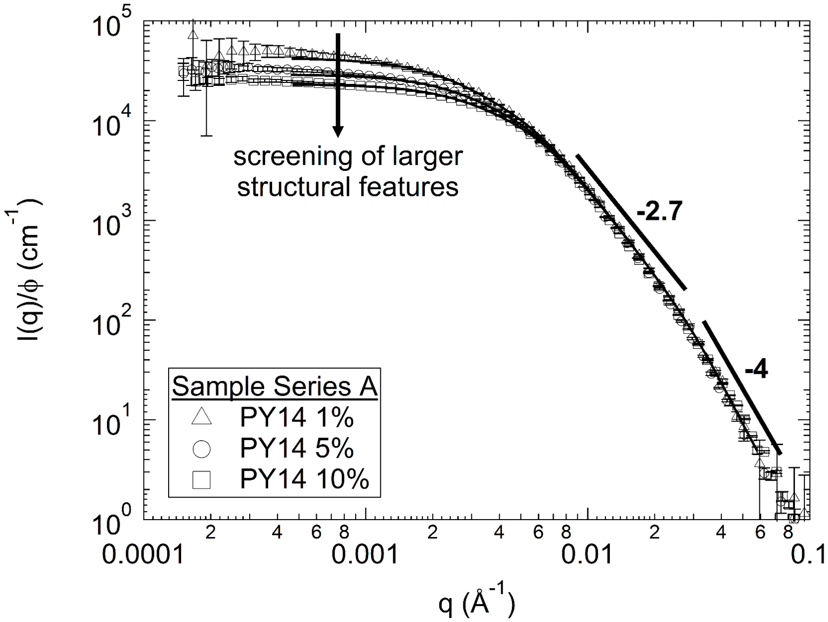
on drying *emergent structure can be a dual hierarchy*

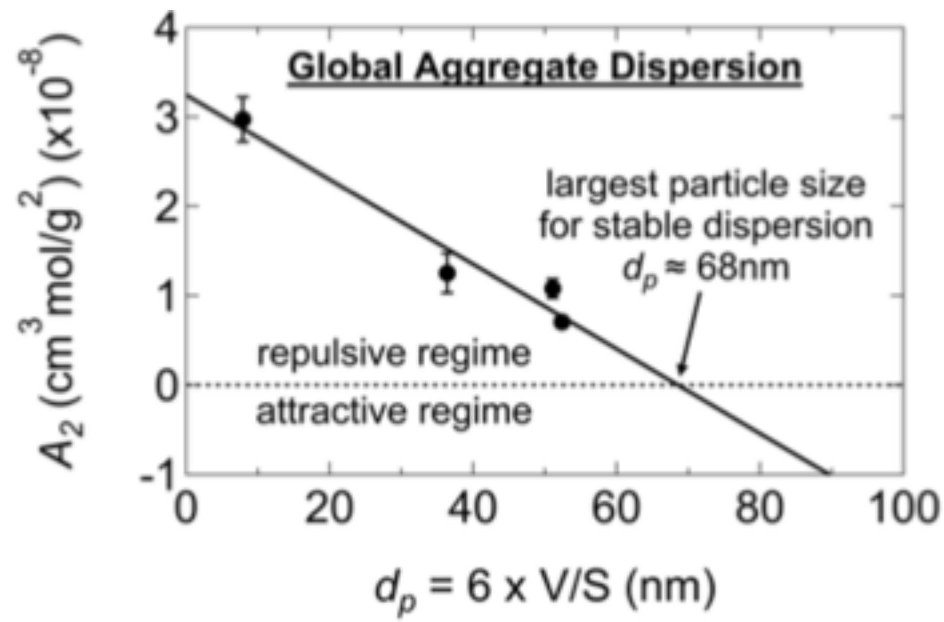
Incompatible complex system:

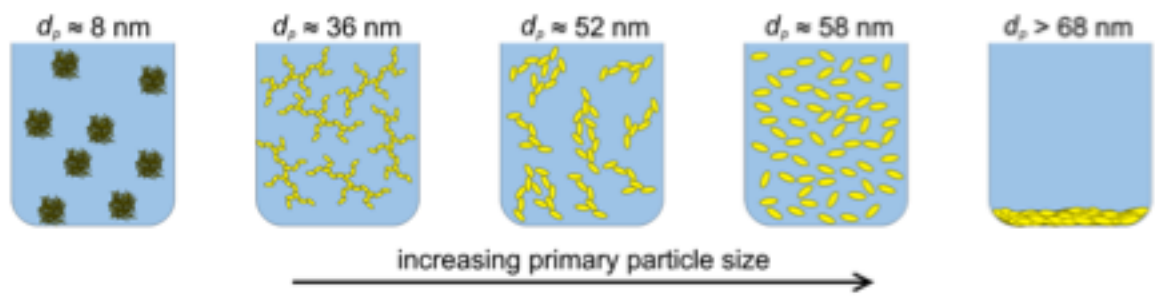
e.g. tires: carbon/silica with elastomer

similar emergent dual hierarchical networks

Structural Screening and Emergent Mesh Size

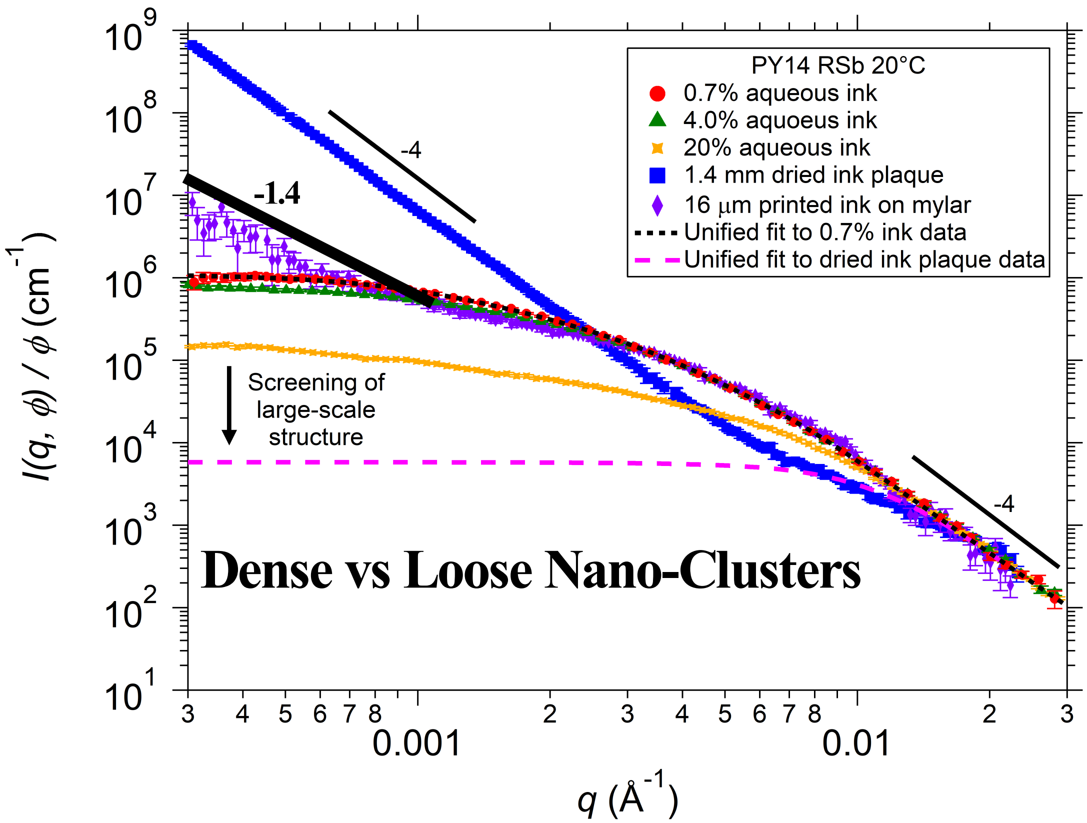


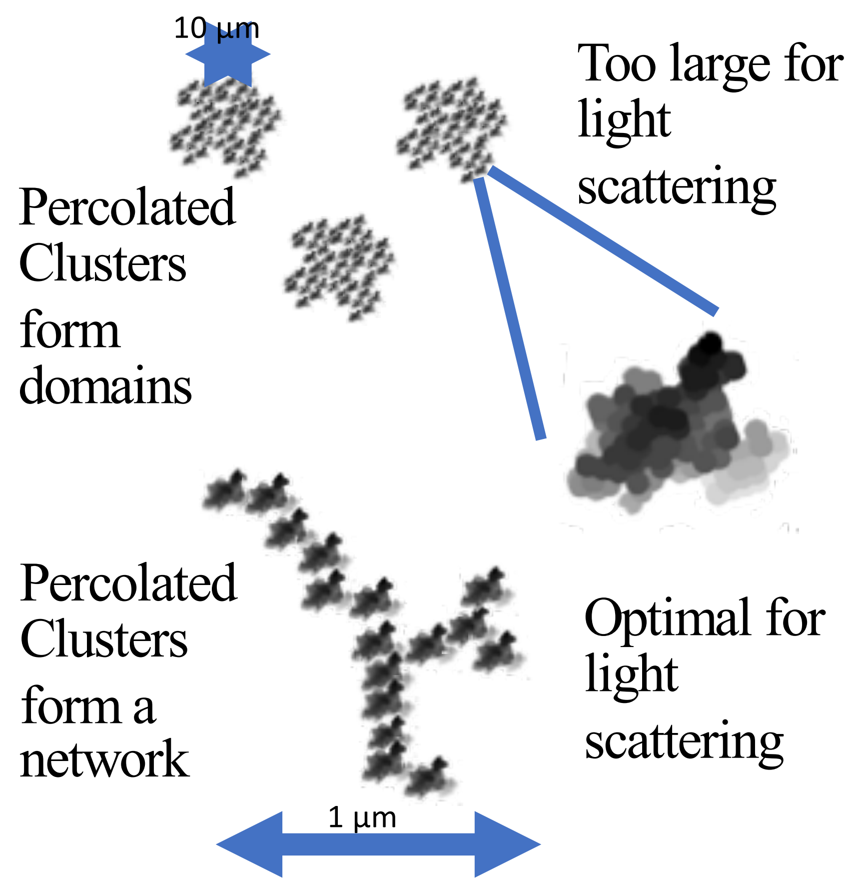




Structural emergence in particle dispersions A. Mulderig, et al. *Langmuir* 33 14029-37 (2017).

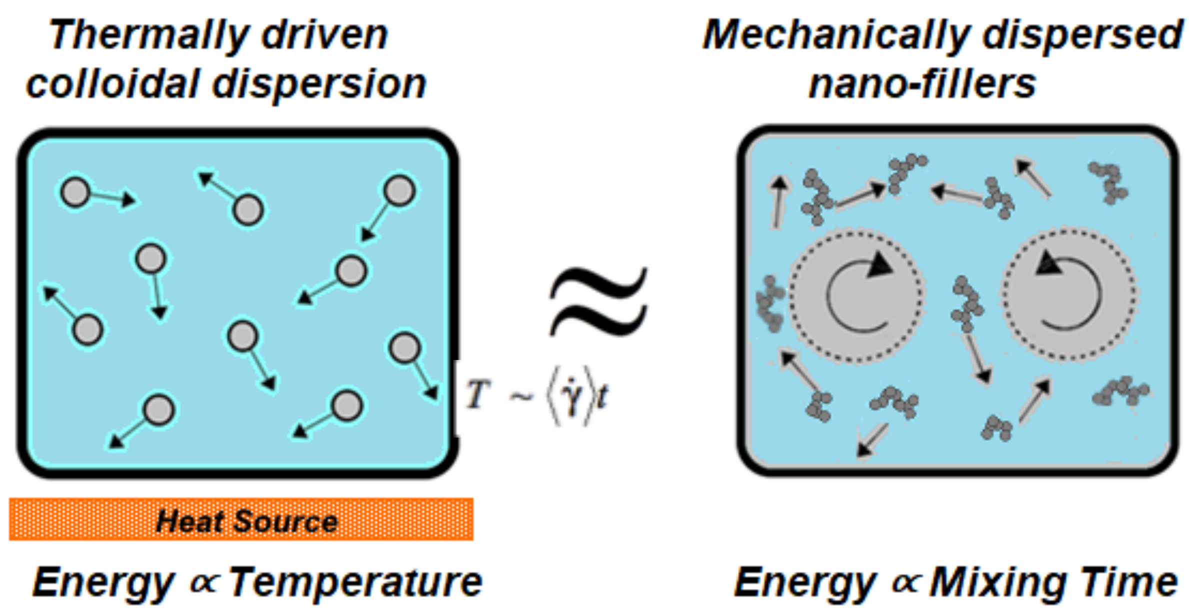
Dual Hierarchical Networks Emerge on Drying





Structural emergence in particle dispersions A. Mulderig, et al. *Langmuir* 33 14029-37 (2017).

Can this approach be applied to incompatible polymer nanocomposites?

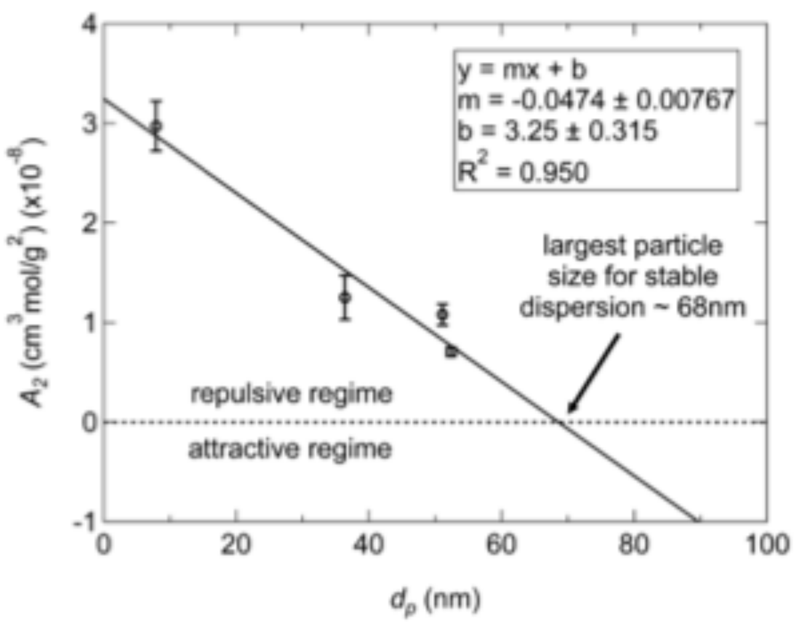


$$A_2(T) = \frac{N_A}{M^2}\left(b - \frac{a}{kT}\right)$$

$$A_2(t) = \frac{N_A}{M^2}\left(b^* - \frac{a^*}{t}\right)$$

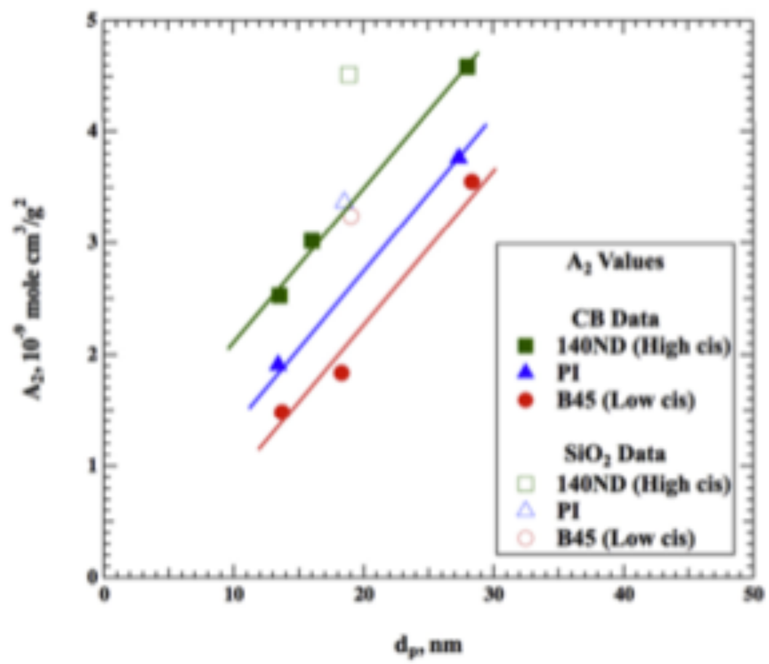
Nanoscale Dispersion (within clusters)

Compatible
Organic Pigment with Triton X100



Thermally driven nano-dispersion/Stokes drag coefficient

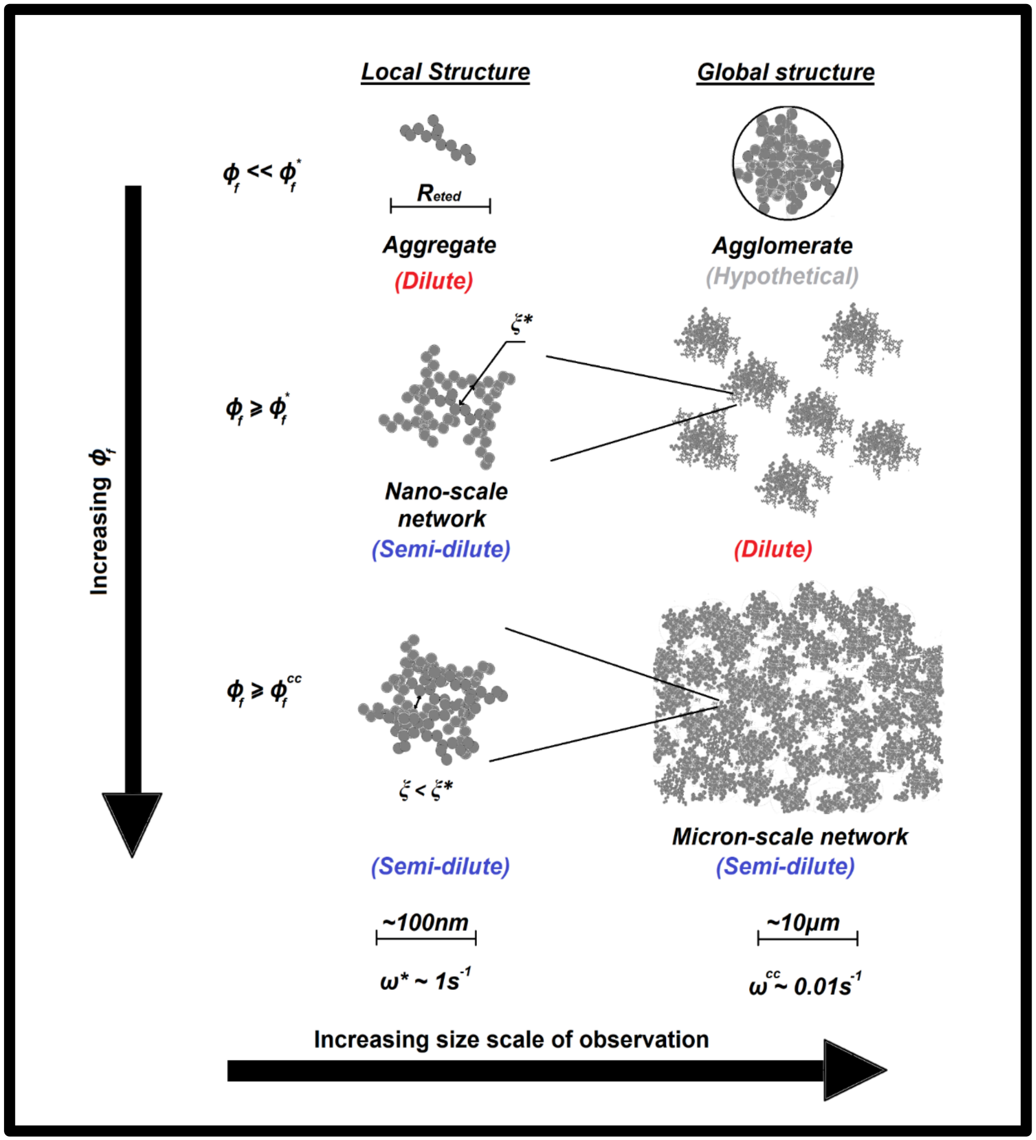
Incompatible
Carbon Black and Silica in Elastomer



Mechanically driven nano-dispersion/Lever arm

Mulderig A, et al. (2017) Structural emergence in particle dispersions *Langmuir* **33** 14029-37.
Jin Y, et al. (2017) A Pseudo-Thermodynamic Description of Dispersion for Nanocomposites. *Polymer* **129** 32–43.

Model



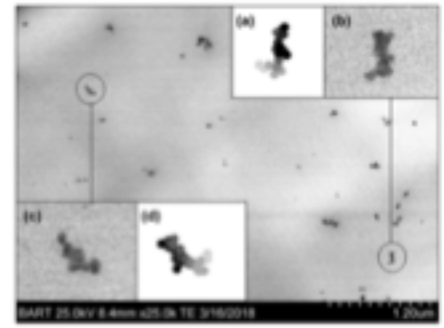
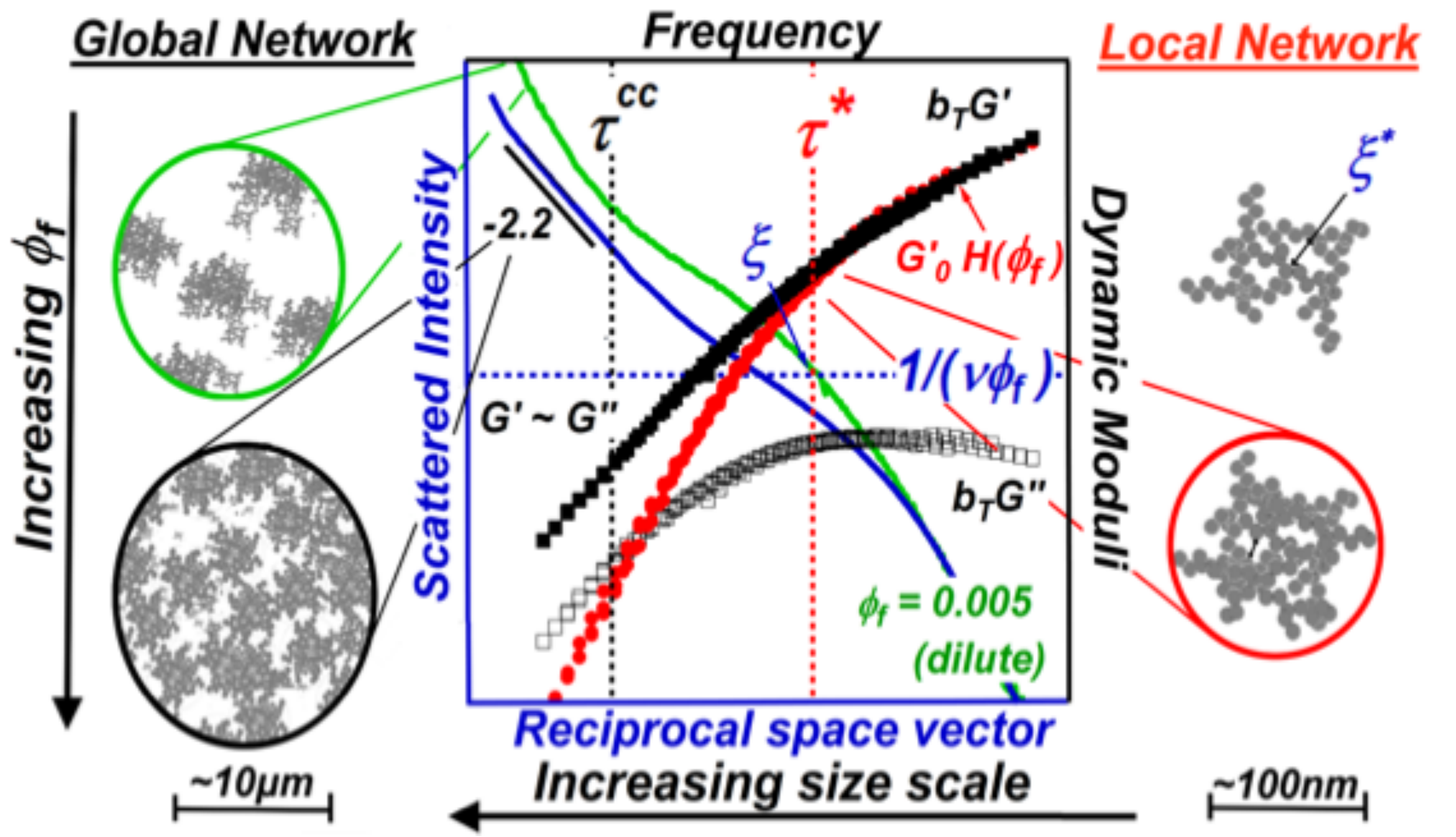


Figure 4. TEM micrograph for the dilute filler (ϕ_f = 0.005) with an average feature size (encircled) associated with the filler aggregate of 120 nm or about a tenth of the scale bar. The size is about the same as the aggregate size determined from USAXS in Figure 3; inset images (a) and (d) are simulated average aggregates obtained from the scattering fit parameters using the Mulderig et al. method.[14] These aggregates are similar to the aggregates in the inset images (b) and (c), respectively.

Overview



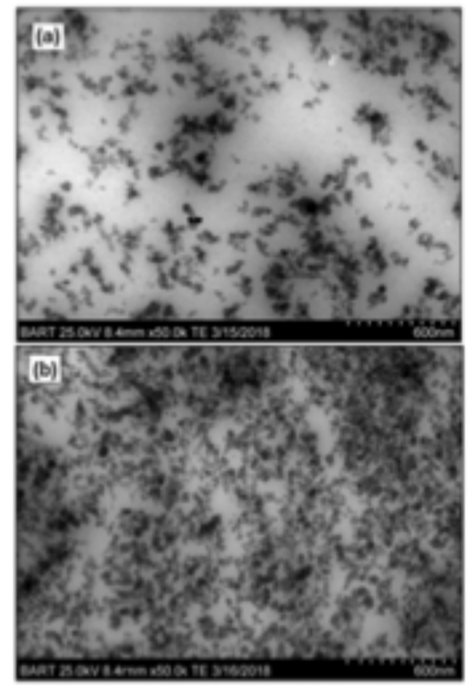
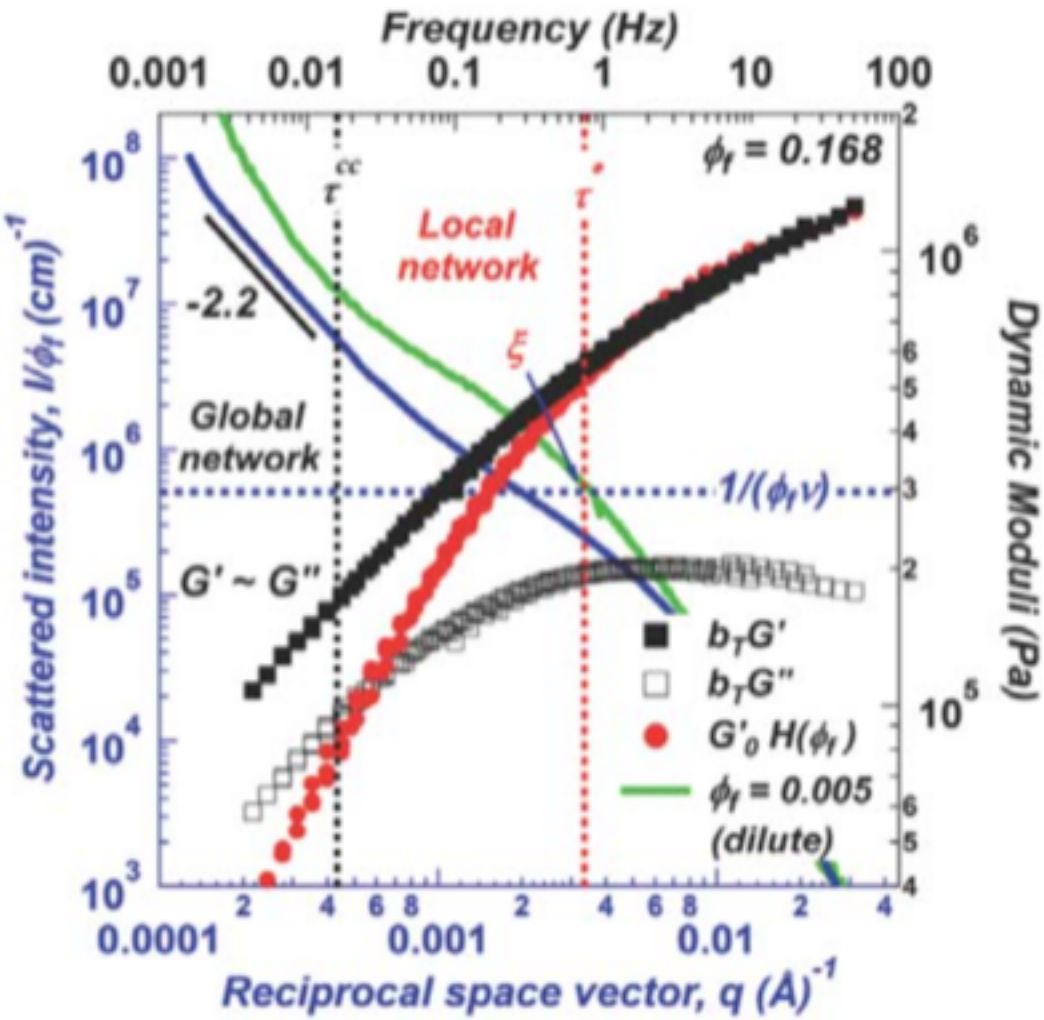
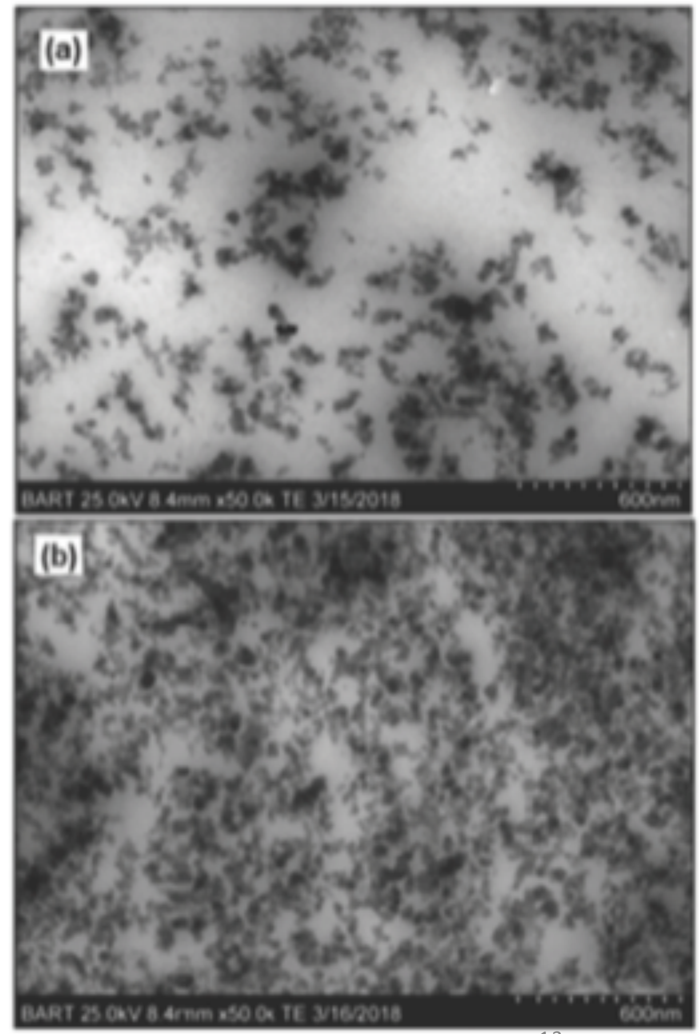


Figure 6. TEM micrographs for nanocomposites (a) ϕ_f = 0.077 with an average separation distance between the features ~300 nm or half the scale bar; and (b) ϕ_f = 0.168 with an average separation distance between the features ~180 nm or three-tenths the scale bar. The


Frequency (Hz)
0.001 0.01 0.1 1 10 100
ϕ_f = 0.168
Local network
-2.2
Global network
$1/(\phi_f \nu)$
G' ~ G''
τ^{cc}
τ^*
ξ
$b_T G'$
$b_T G''$
$G'_0 H(\phi_f)$
ϕ_f = 0.005 (dilute)
Scattered intensity, I/ϕ_f (cm)$^{-1}$
Dynamic Moduli (Pa)
0.0001 0.001 0.01
Reciprocal space vector, q (Å)$^{-1}$


(a)
BART 25.0kV 8.4mm x50.0k TE 3/15/2018 600nm
(b)
BART 25.0kV 8.4mm x50.0k TE 3/16/2018 600nm

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