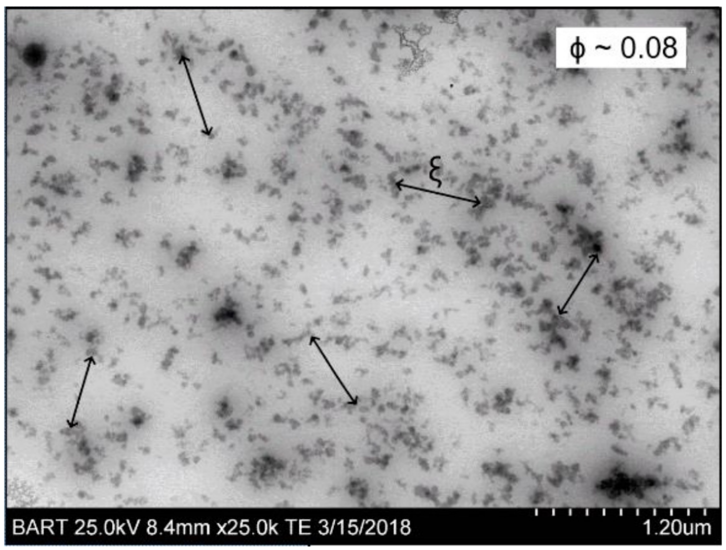
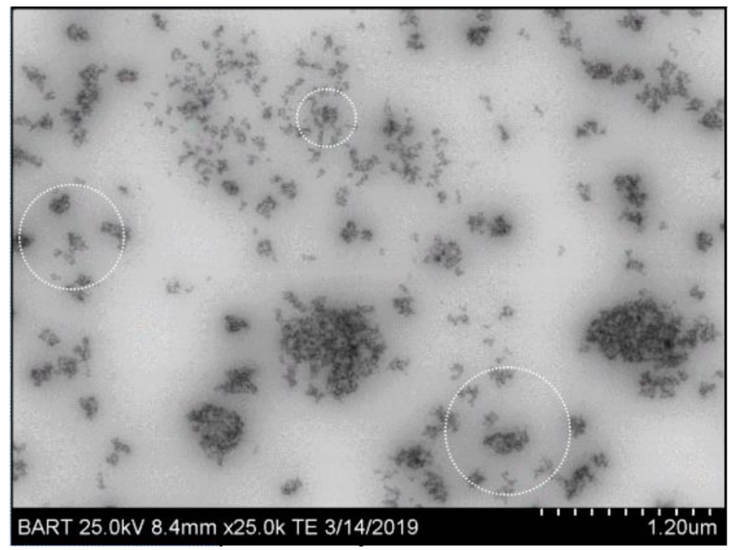
X-ray Scattering for CB and CB Nanocomposites

Greg Beaucage, Professor of Chemical and Materials Engineering
Department of Materials Science & Engineering, University of Cincinnati
beaucag@uc.edu; 513 373 3454

Kabir Rishi, PhD NIOSH/CDC Cincinnati Research Laboratory





X-ray Scattering for CB and CB Nanocomposites

-Overview of X-ray Scattering

-Nanocomposite Dispersion and Distribution
Carbon Black in Elastomers and other Polymers

Greg Beaucage, University of Cincinnati gbeaucage@gmail.com

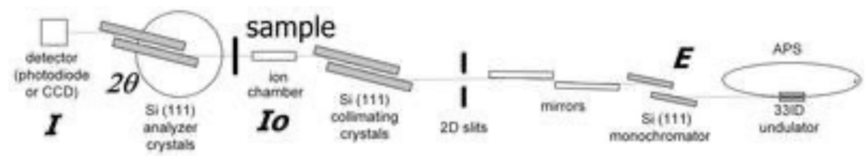
X-ray Scattering

2-D Narrow size range

Pinhole XRD/SAXS/(USAXS)

1-D 4+-orders of size

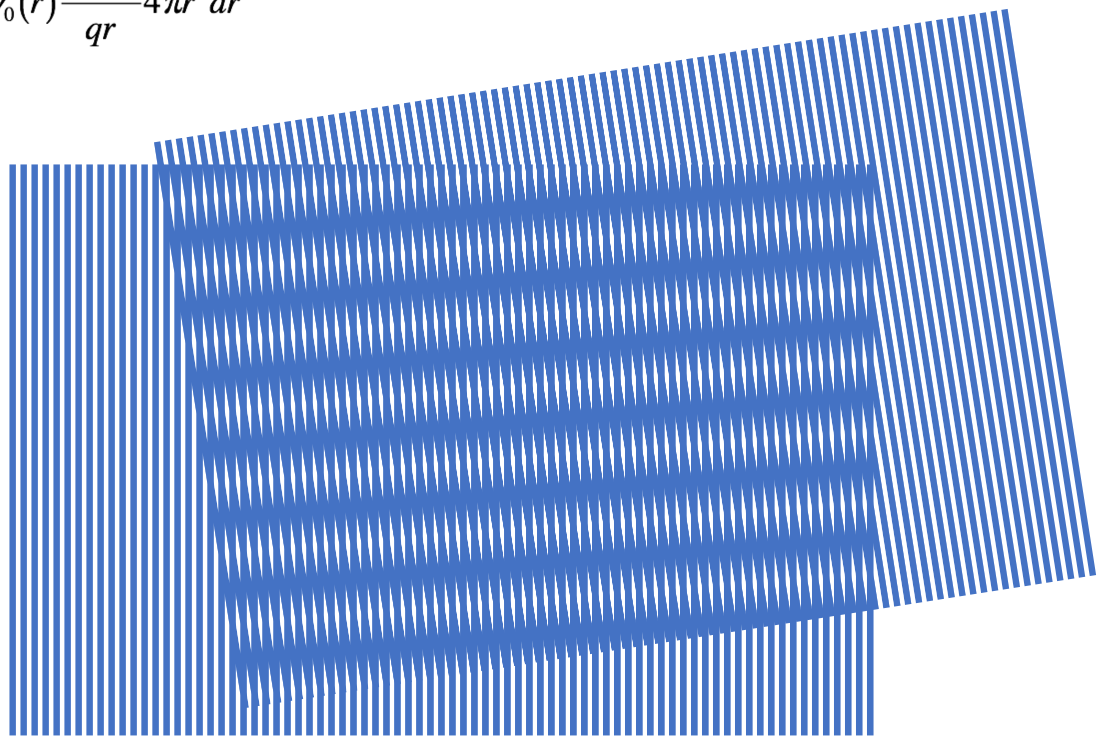
Bonse-Hart Camera USAXS



Consider the origin of the vector **r ~ 2π/q (Braggs Law)**

$$I(q) = \left\langle F^2(q) \right\rangle = V\rho_e^2 \int_0^\infty \gamma_0(r) \frac{\sin qr}{qr} 4\pi r^2 dr$$

q = 4π/λ sin(θ/2)



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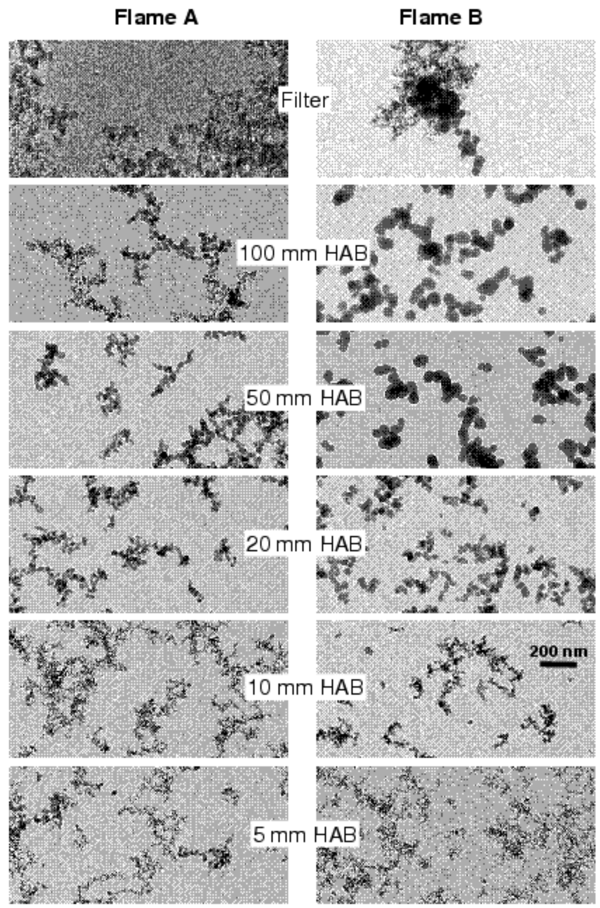
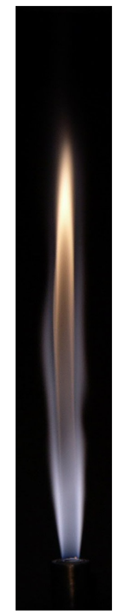
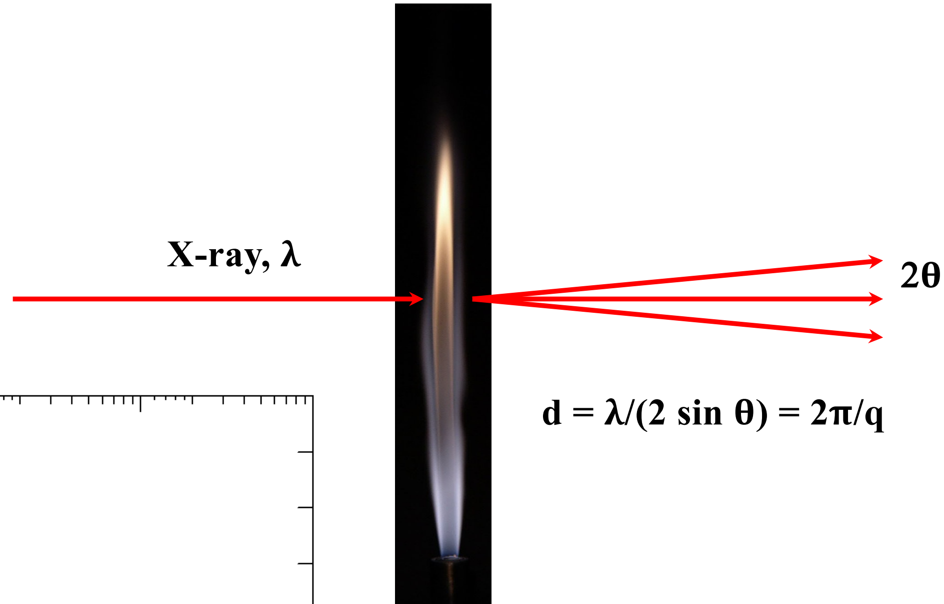
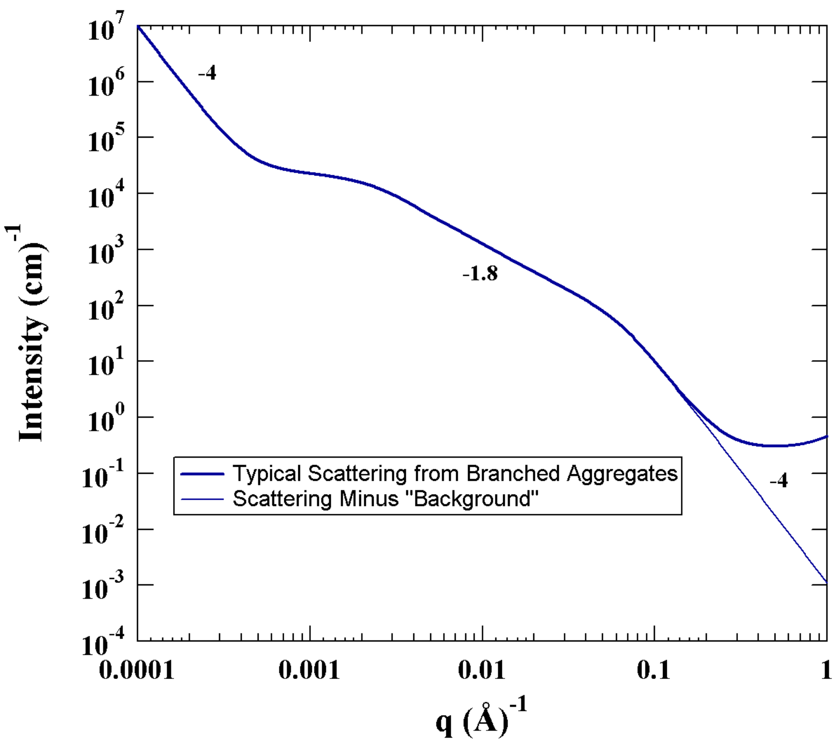




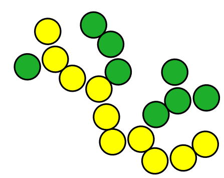
Kammler HK, Beaucage G, Kohls DJ, Agashe N. Ilavsky J
J Appl. Phys. 97(2005) (Article 054309).

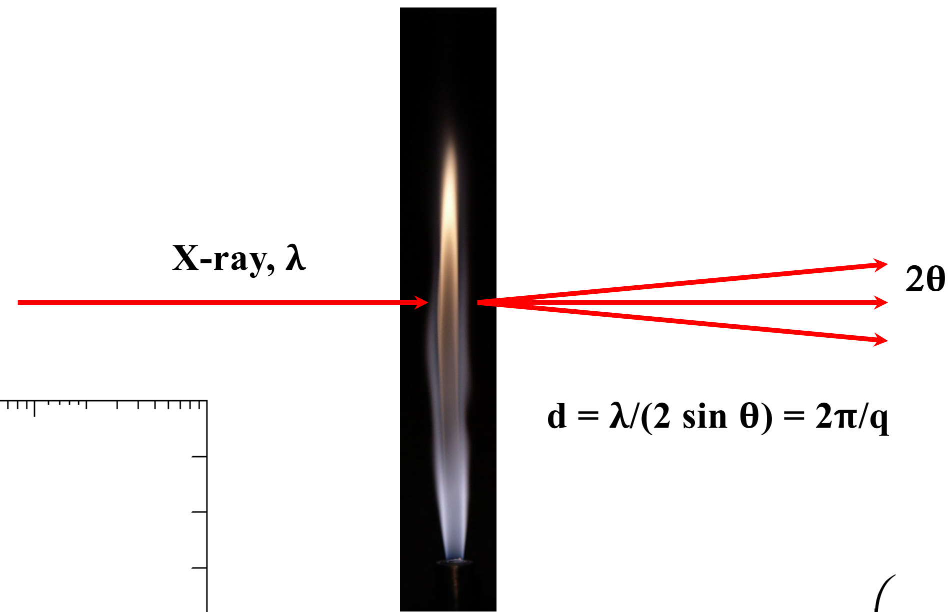


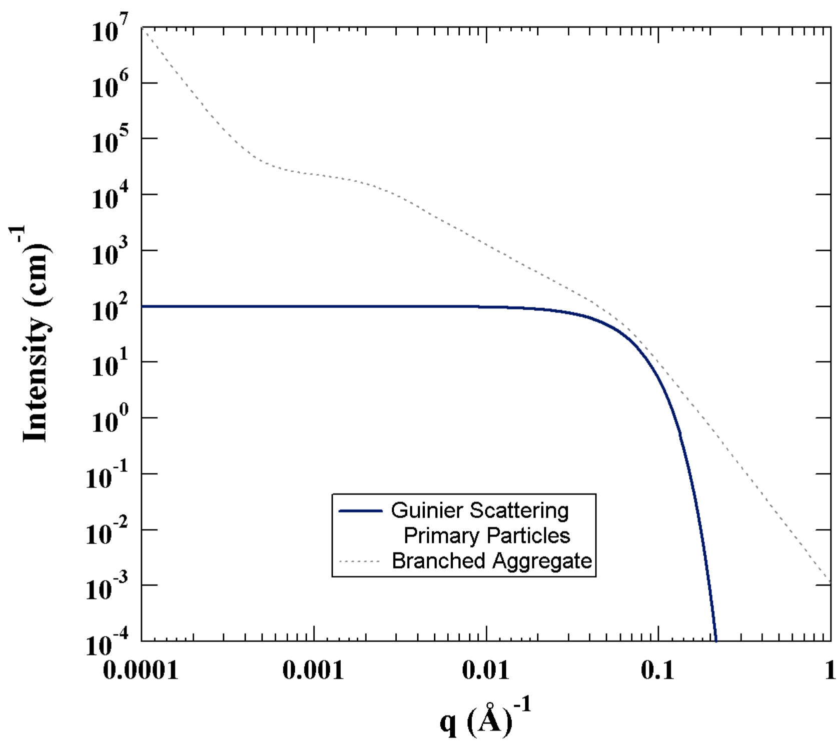
$$d = \lambda/(2\sin\theta) = 2\pi/q$$



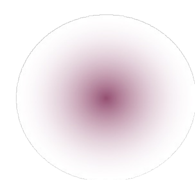
Branched Aggregates







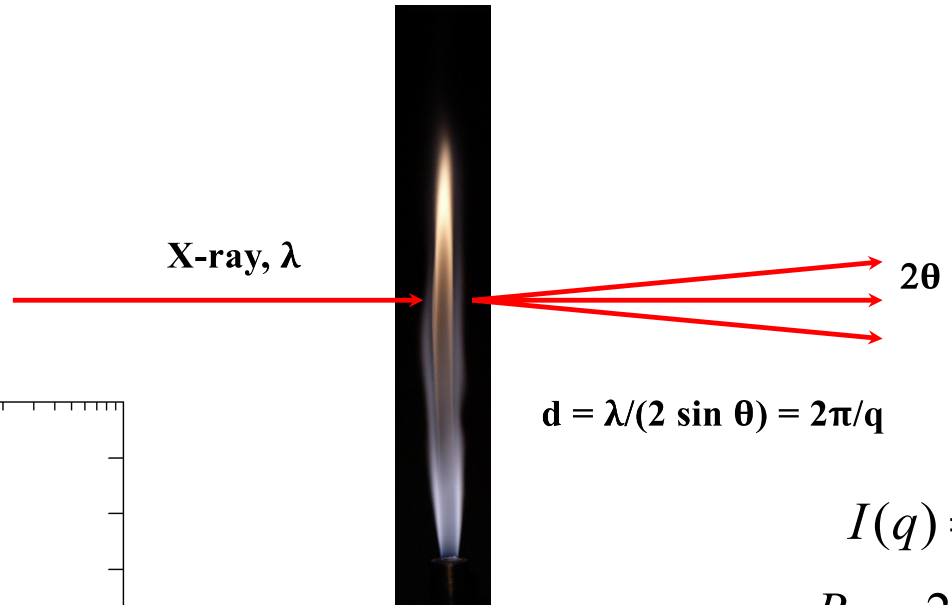
$$I(q) = G_1 \exp\left(\frac{-q^2\left\langle R_{g,1}^2\right\rangle}{3}\right)$$



$$G = N\rho_e^2\left\langle V^2\right\rangle \sim \left\langle \mathrm{R}^6\right\rangle$$

Guinier's Law

$$\left\langle R_g^2\right\rangle \sim \frac{\left\langle \mathrm{R}^8\right\rangle}{\left\langle \mathrm{R}^6\right\rangle}$$



d = λ/(2 sin θ) = 2π/q

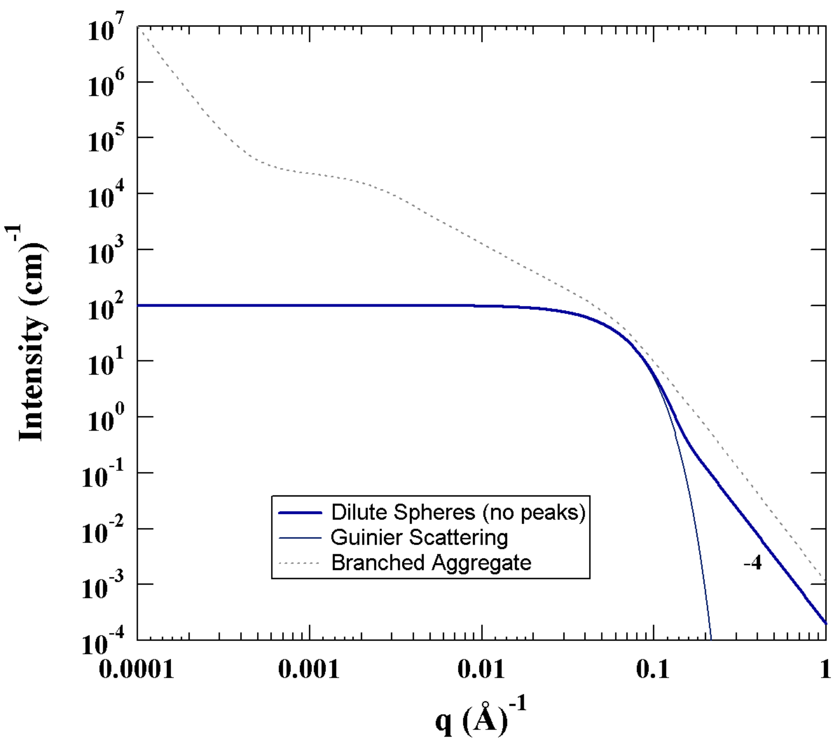
$$I(q) = B_P q^{-4}$$

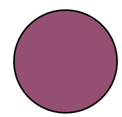
$$B_P = 2\pi N \rho_e^2 \langle S \rangle$$

$$\langle S \rangle \sim \langle R^2 \rangle$$

$$Q = \int q^2 I(q) dq = N \rho_e^2 \langle R^3 \rangle$$

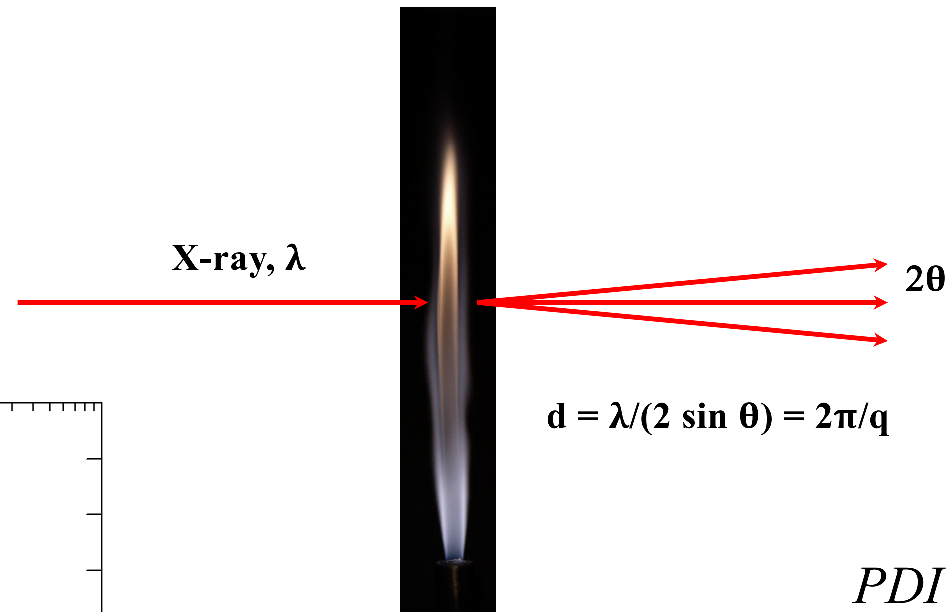
$$d_p = \frac{Q}{2\pi B_P} = \frac{\langle R^3 \rangle}{\langle R^2 \rangle}$$

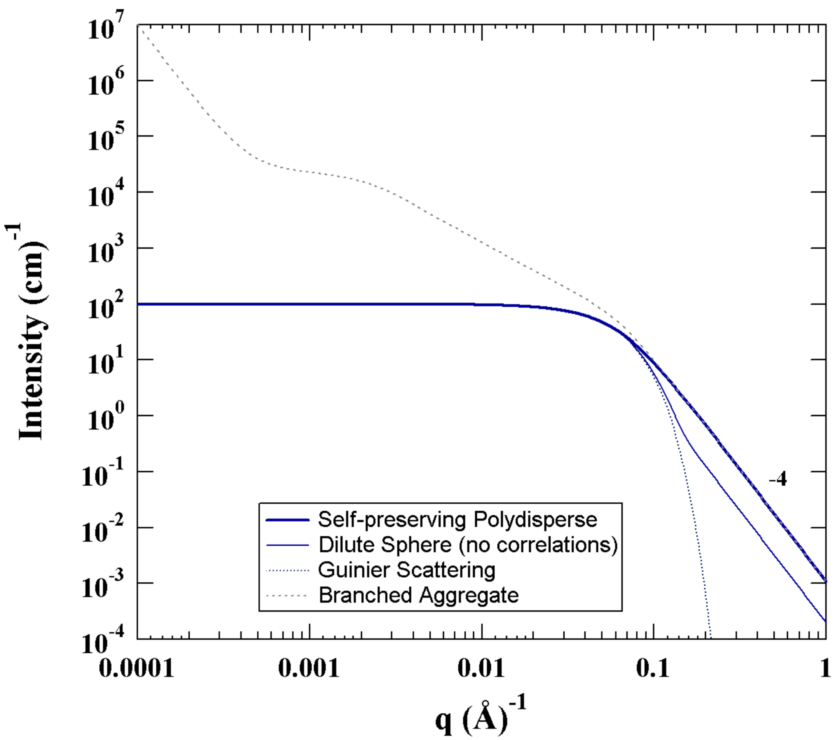




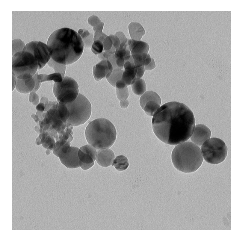
Guinier and Porod Scattering

Structure of Flame Made Silica Nanoparticles By Ultra-Small-Angle X-ray Scattering
Kammler/Beaucage Langmuir 2004 <u>20</u> 1915-1921





Polydispersity

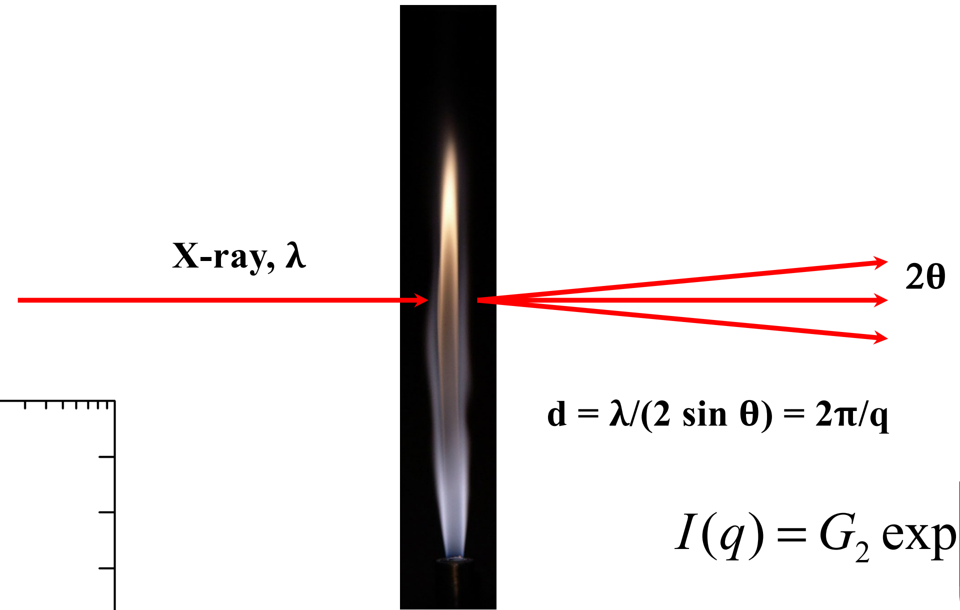


Particle size distributions from small-angle scattering using global scattering functions, Beaucage, Kammler, Pratsinis J. Appl. Cryst. 37 523-535 (2004).

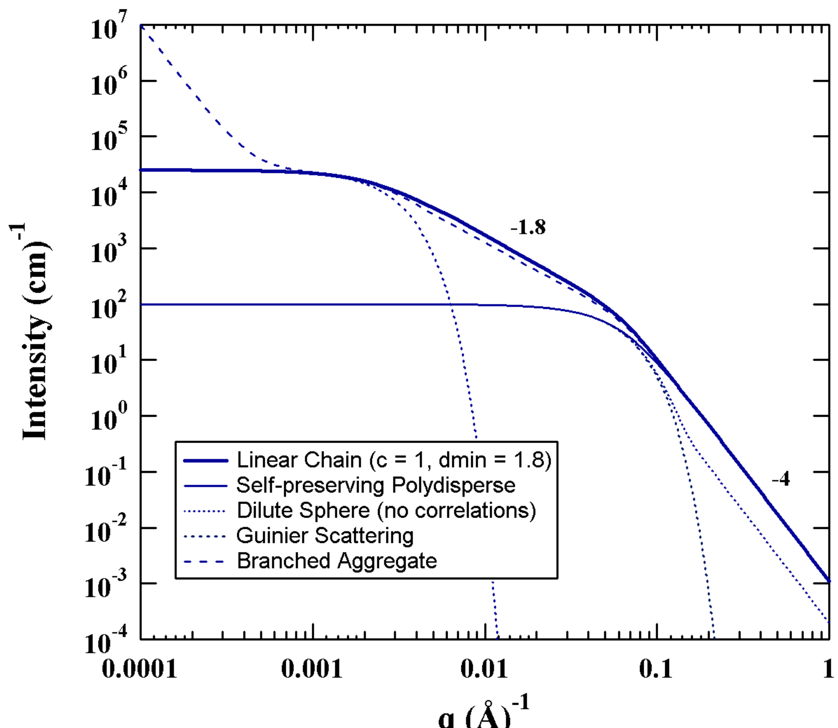
$$PDI = \frac{B_P R_g^4}{1.62G}$$

$$\sigma = \ln(\sigma_g) = \left[\frac{\ln(PDI)}{12}\right]^{1/2}$$

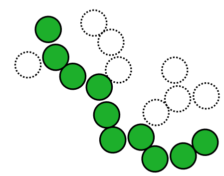
$$m = \left[\frac{5R_g^2}{3e^{14\sigma^2}}\right]^{1/2}$$



$$I(q) = G_2 \exp\left(\frac{-q^2 \langle R_{g,2}^2 \rangle}{3}\right)$$



Linear Aggregates

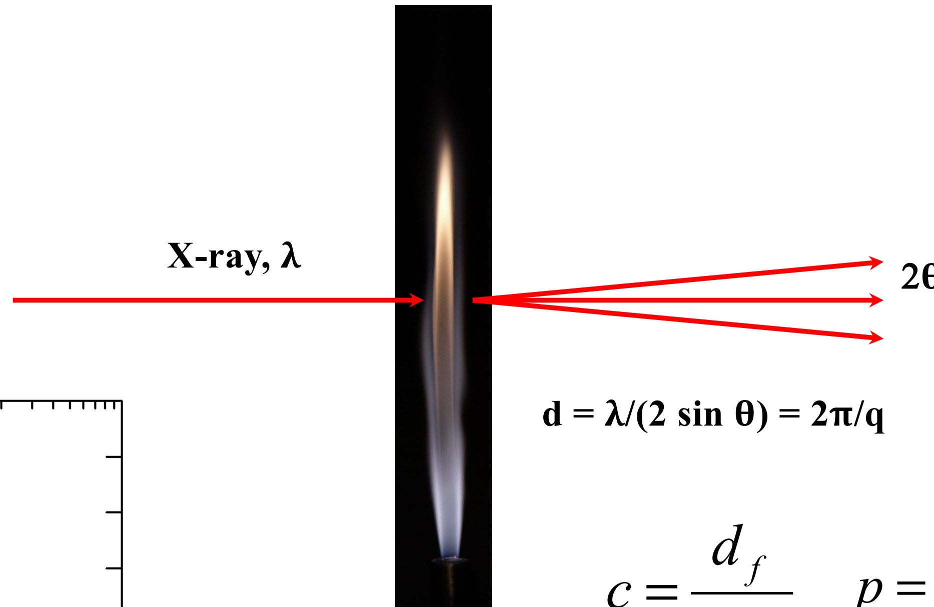


$$z = \frac{G_2}{G_1} = \left(\frac{R_2}{R_1}\right)^{d_f}$$

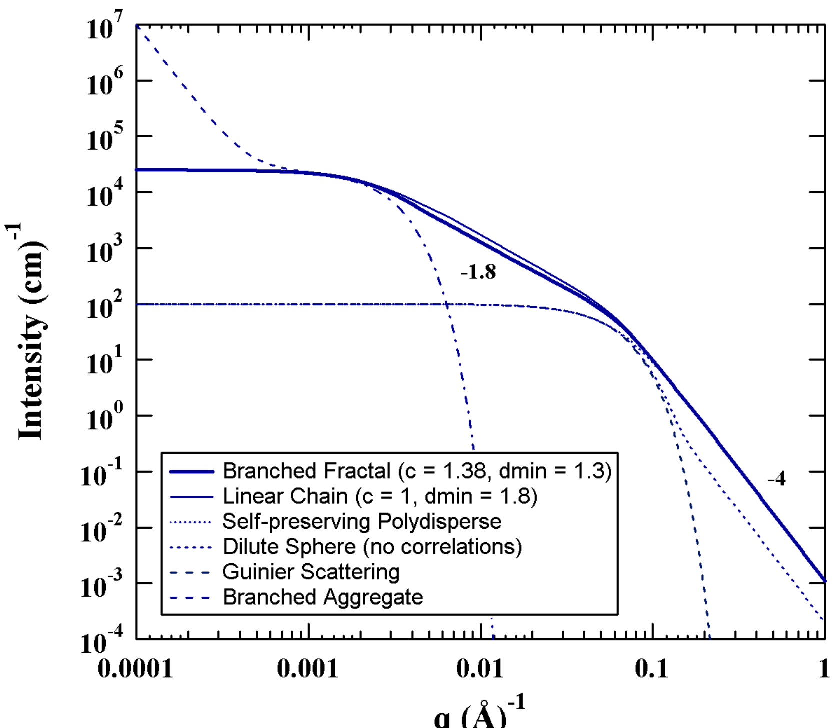
$$I(q) = B_f q^{-d_f}$$

Beaucage G, Small-angle Scattering from Polymeric Mass Fractals of Arbitrary Mass-Fractal Dimension, J. Appl. Cryst. 29 134-146 (1996).

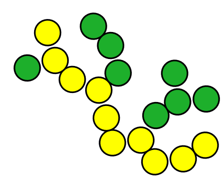
$$B_f = \frac{G_2 d_f}{R_{g,2}^{d_f}} \Gamma\left(d_f/2\right)$$



$$c = \frac{d_f}{d_{min}} \qquad p = \left(\frac{R_2}{R_1}\right)^{d_{min}} = z^{1/c}$$



Branched Aggregates

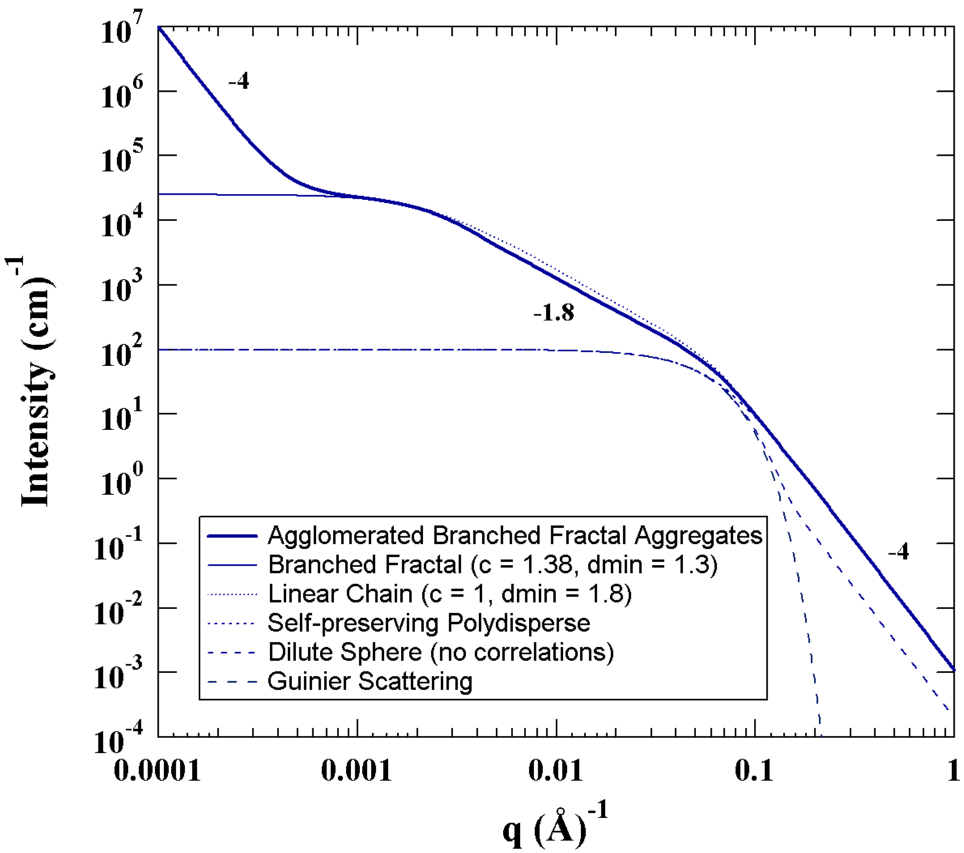


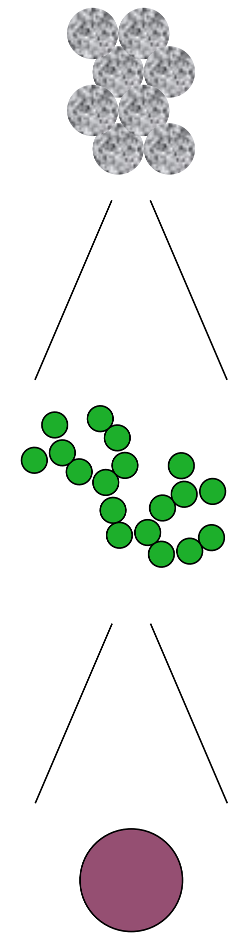
$$\phi_{Br} = 1 - \left(\frac{R_2}{R_1}\right)^{d_{min} - d_f}$$

Beaucage G, Determination of branch fraction and minimum dimension of fractal aggregates Phys. Rev. E 70 031401 (2004).

$$B_f = \frac{G_2 d_{min}}{R_{g,2}^{d_f}} \Gamma\left(d_f/2\right)$$

Large Scale (low-q) Agglomerates

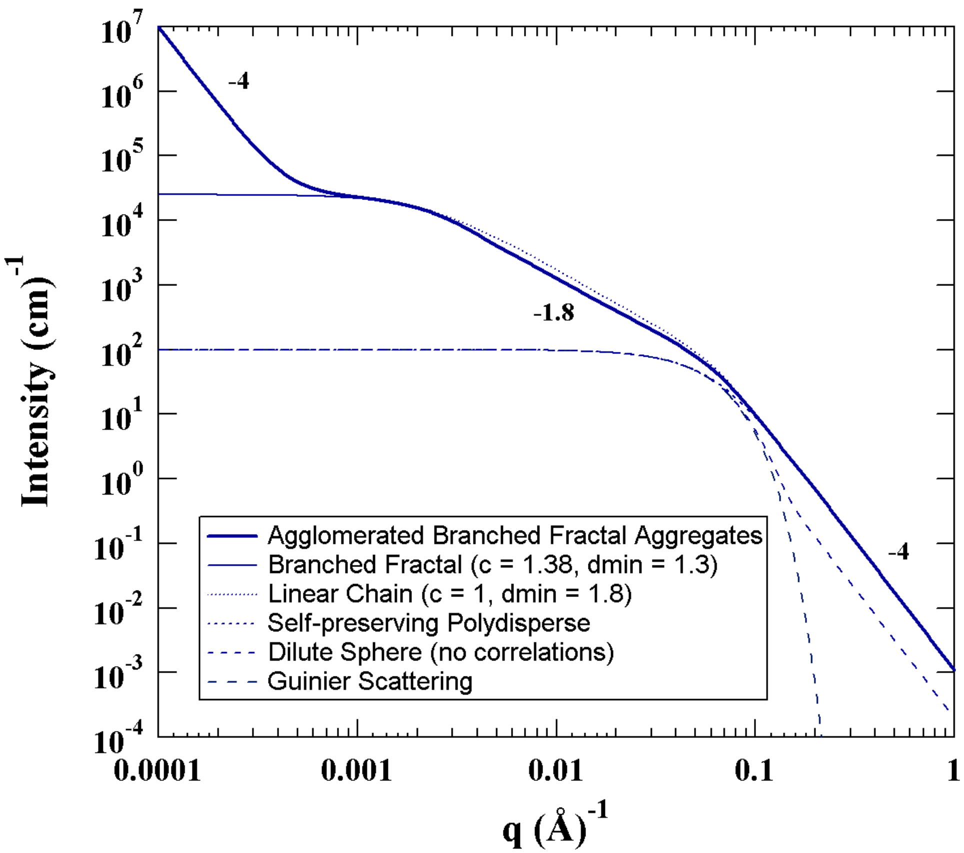


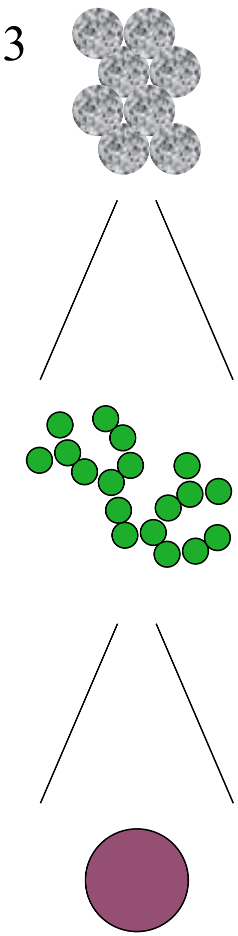


$$I(q) = B_P q^{-4}$$

Greg Beaucage, University of Cincinnati gbeaucage@gmail.com

Large Scale (low-q) Or a **network** if |slope| < 3





$$I(q) = B_P q^{-4}$$

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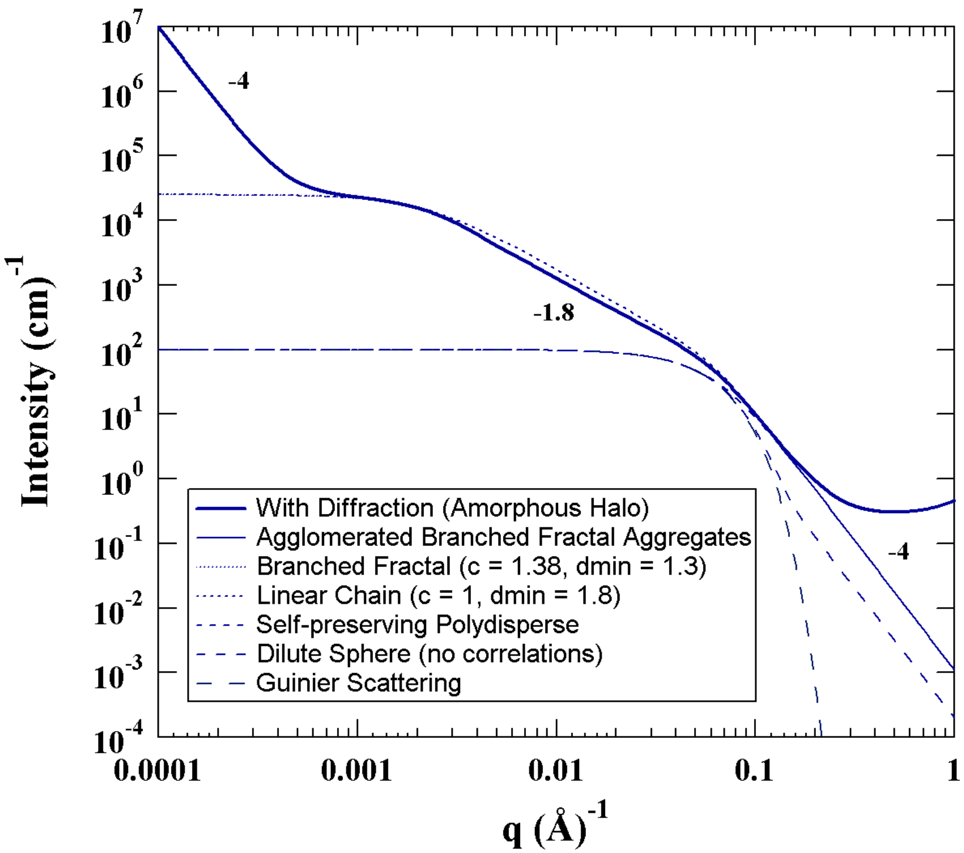
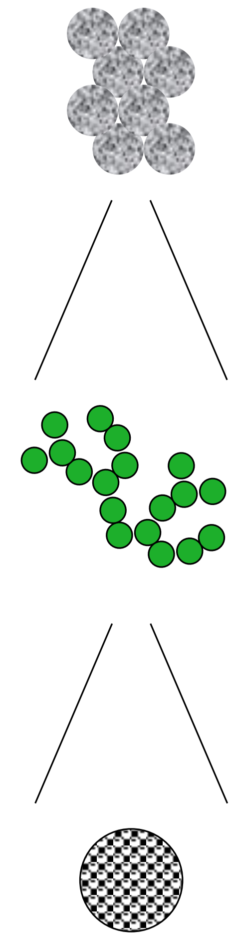
Small-scale Crystallographic Structure





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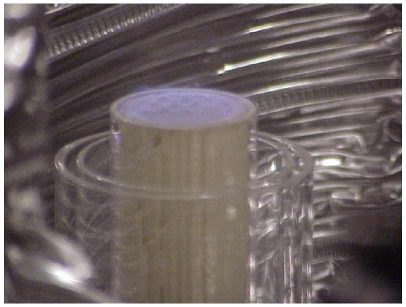
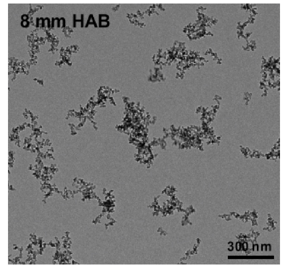
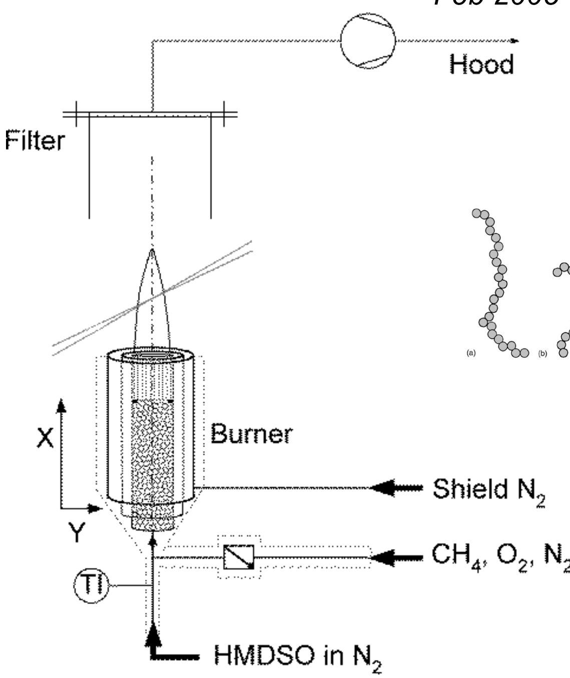
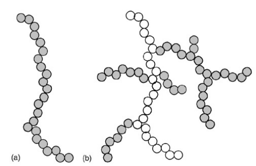


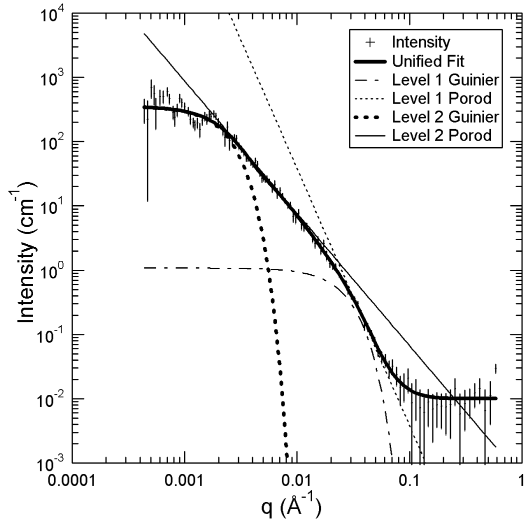


APS UNICAT
Silica Premixed Flames
J. Appl. Phys 97 054309
Feb 2005





Branched Aggregates



5mm LAT 16mm HAB
Typical Branched Aggregate
d_p = 5.7 nm
z = 350
c = 1.5, d_{min} = 1.4, d_f = 2.1
ϕ_{br} = 0.8

Beaucage G, *Determination of branch fraction and minimum dimension of fractal aggregates* Phys. Rev. E 70 031401 (2004).

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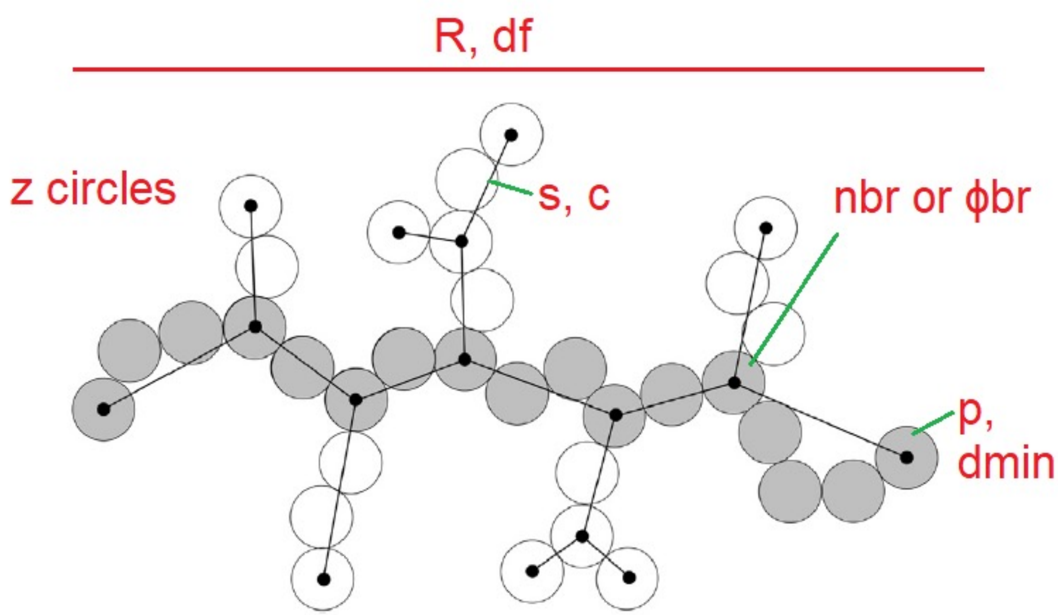
Descriptors

Aggregate size, R
Primary particle size, d_p
Degree of aggregation, z
Short-circuit path length, p
Connective path length, s
Fractal dimension, d_f
Tortuosity, d_{min}
Connectivity, c
Branch fraction, ϕ_{br}
Branch number, n_{br}



Beaucage, G. Determination of branch fraction and minimum dimension of mass-fractal aggregates. ***Physical Review E – Statistical, Nonlinear, and Soft Matter Physics* 2004**, 70, 031401-1–031401-10.
Rai, D., Beaucage, G., Jonah, E. O., Britton, D. T., Sukumaran, S., & Härting, M. Quantitative investigations of aggregate systems. ***J. Chem. Phys.* 2012**, 137, 044311–1–044311-6.
Ramachandran, R., Beaucage, G., Kulkarni, A. S., McFaddin, D., Merrick-Mack, J., & Galiatsatos, V. Branch content of metallocene polyethylene. ***Macromolecules* 2009**, 42, 4746–4750.

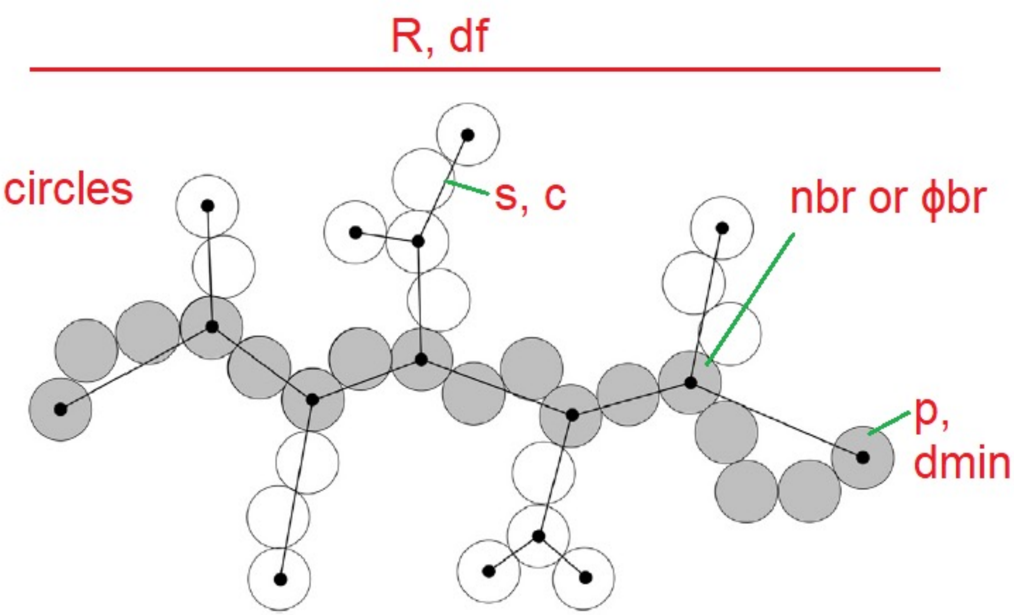
$d_f = c\ d_{min}$

Density impacted by topology and convolution

$z \geq p$ and s

Disk: $c = 2$, $d_{min} = 1$

Chain: $c = 1$, $d_{min} = 2$



Crumple paper: c fixed at 2; d_{min} increases from 1 to ≤ 1.5

Rip arms off an aggregate: d_{min} fixed; c decreases towards 1

Algorithm:

Input z and a sticking probability
Randomly grow aggregates
Compute the scattering parameters, p, R, n_{Br} etc.
Iterate by varying sticking probability until computed matches experimental

A. Mulderig, G. Beaucage, K. Vogtt, H. Jiang and V. Kuppa, Quantification of branching in fumed silica, **J. Aerosol Sci. 2017**, 109, 28–37.

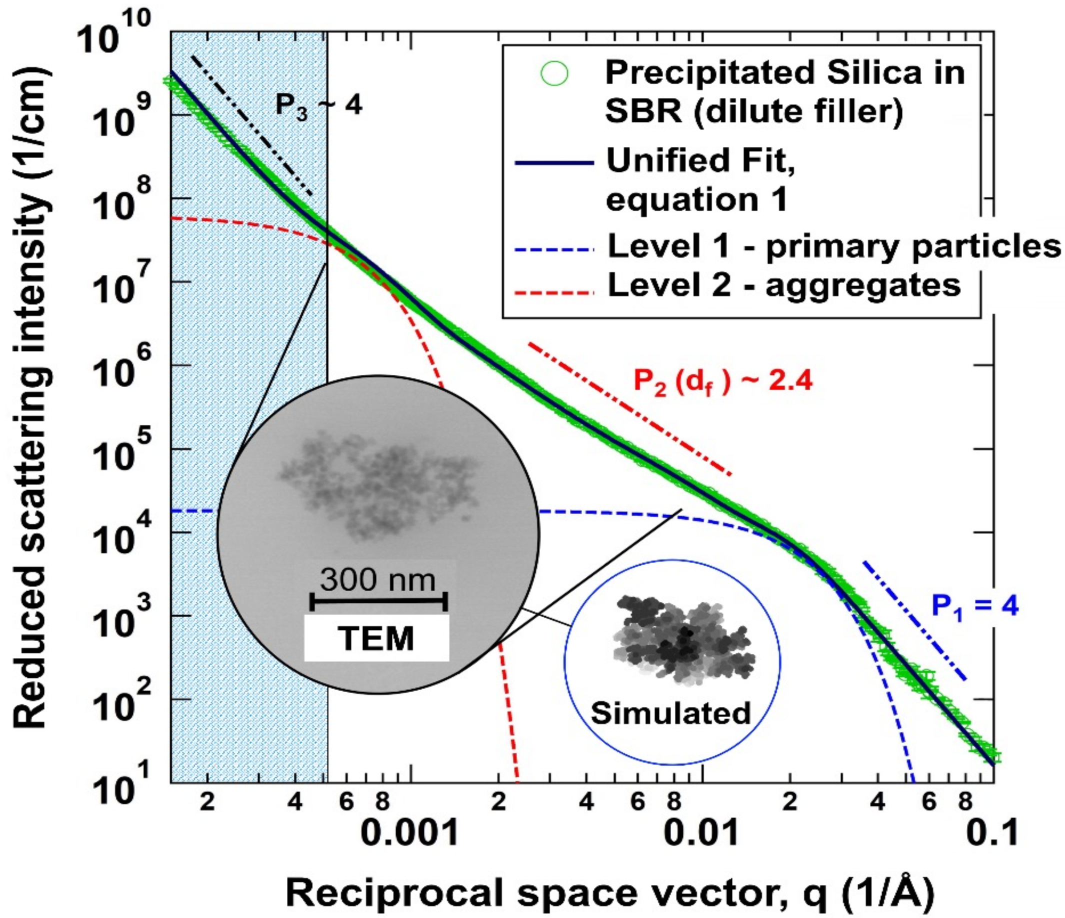
Experimental

Sample	A	B	C	D	E	F
R	19	19	26	24	37	91
d_p (nm)	36	21	17	14	12	10
C_p	1.54	1.53	1.51	1.50	1.52	1.51
z	157	177	483	567	819	6430
p	36	35	46	38	37	91
s	66	75	195	265	819	6430
d_{min}	1.21	1.20	1.17	1.14	1.00	1.00
c	1.41	1.46	1.62	1.75	1.86	1.95
d_f	1.70	1.75	1.90	1.98	1.86	1.95
n_{br} ($f = 3$)	19	23	68	106	409	3215
ϕ_{br}, %	77	80	91	93	95	99

Simulation

z	157	177	483	567	819	6430
Sticking probability	0.40	0.37	0.11	0.23	0.82	1.00
R	18	19	26	29	40	93
p	31	33	45	42	40	93
s	68	75	191	298	819	6430
d_{min}	1.2	1.2	1.17	1.11	1	1
c	1.47	1.48	1.62	1.7	1.82	1.93
d_f	1.76	1.75	1.9	1.89	1.82	1.93
n_{br}	21	26	68	121	409	3215
ϕ_{br}, %	80%	81%	91%	93%	95%	99%

A. Mulderig, G. Beaucage, K. Vogtt, H. Jiang and V. Kuppa, Quantification of branching in fumed silica, **J. Aerosol Sci. 2017**, 109, 28–37.



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A. Mulderig, G. Beaucage, K. Vogtt, H. Jiang and V. Kuppa, Quantification of branching in fumed silica, **J. Aerosol Sci. 2017**, 109, 28–37.

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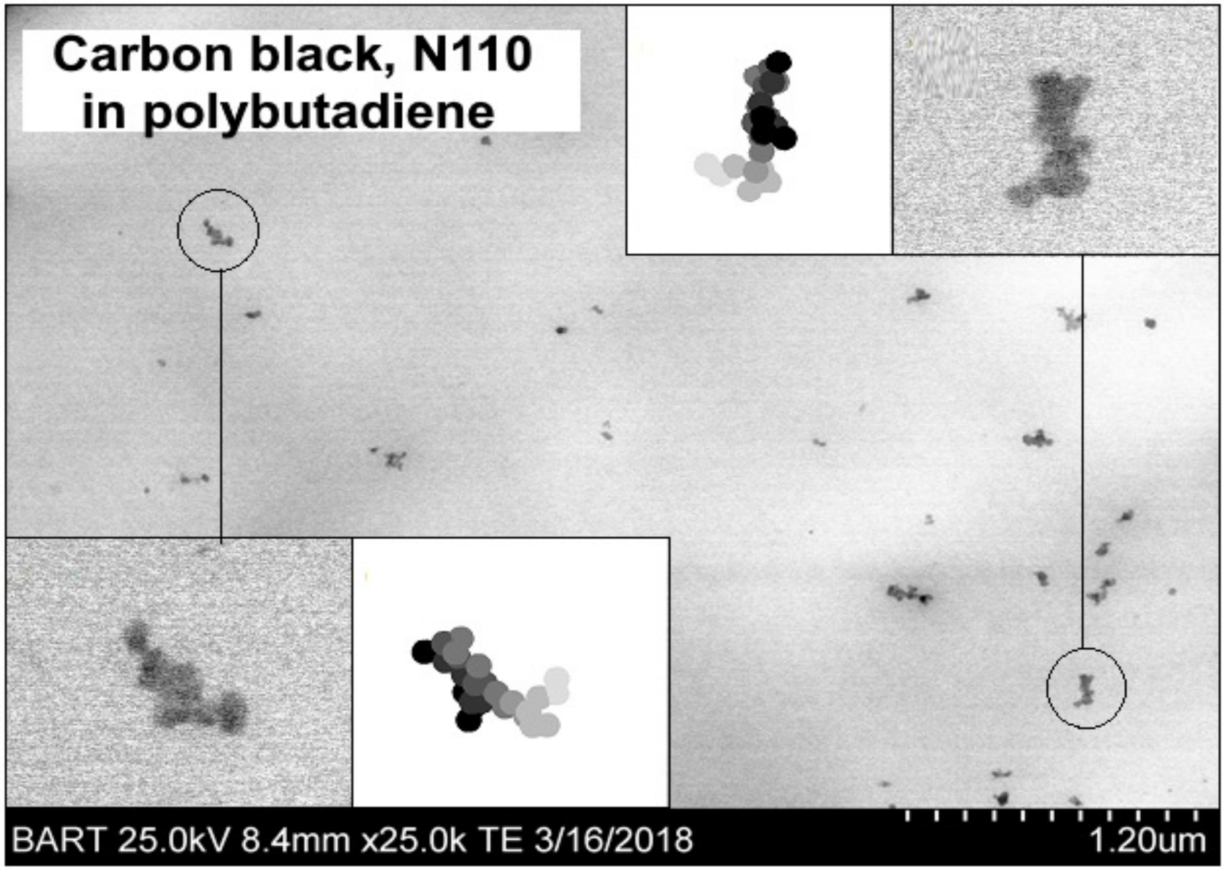

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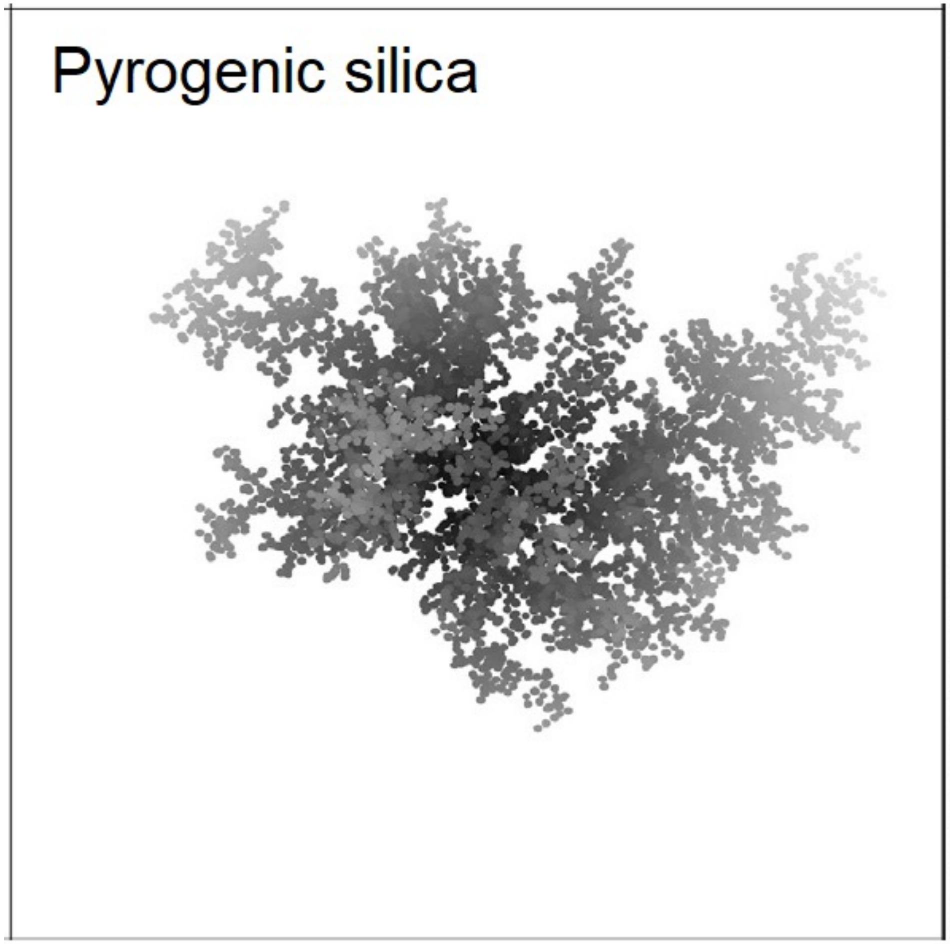
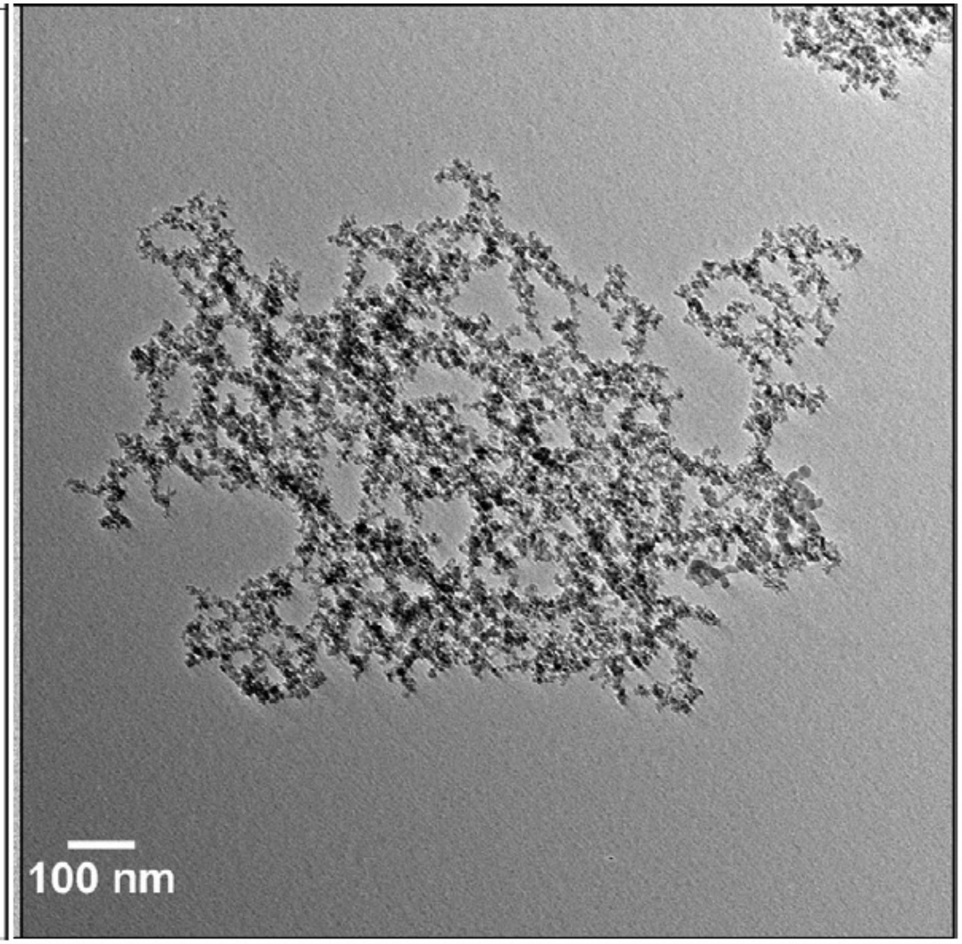
A. Mulderig, G. Beaucage, K. Vogtt, H. Jiang and V. Kuppa, Quantification of branching in fumed silica, J. Aerosol Sci. 2017, 109, 28–37.





A. Mulderig, G. Beaucage, K. Vogtt, H. Jiang and V. Kuppa, Quantification of branching in fumed silica, **J. Aerosol Sci. 2017**, 109, 28–37.

At concentrations above c^*

When concentration is greater than Mass of CB aggregate By Volume of aggregate

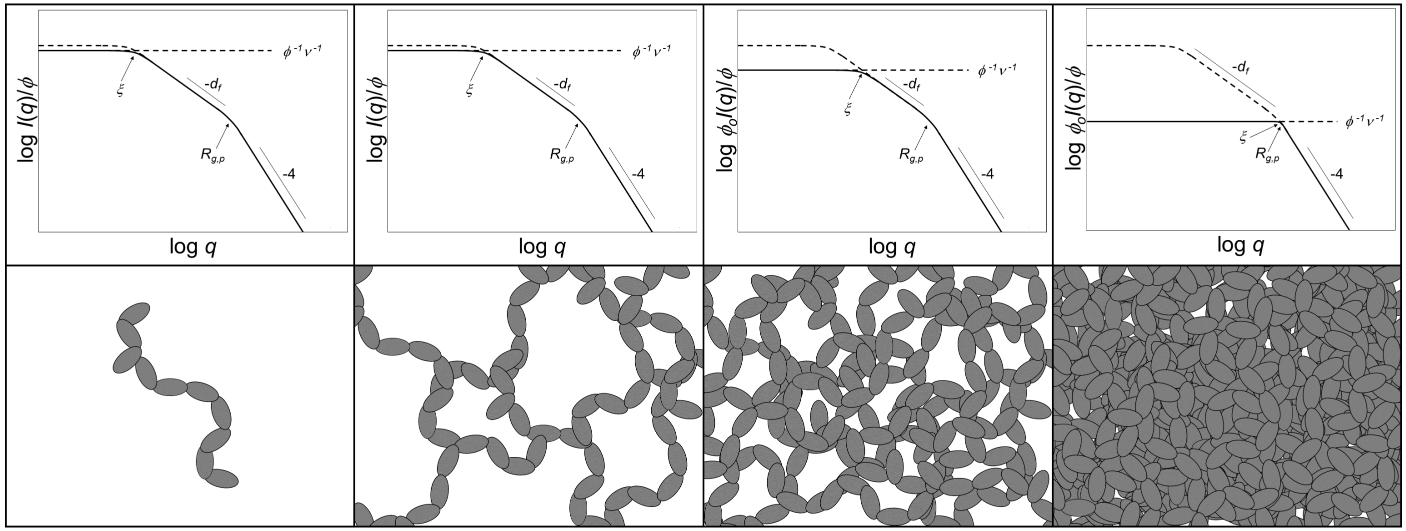
c^* = M/V of CB aggregate

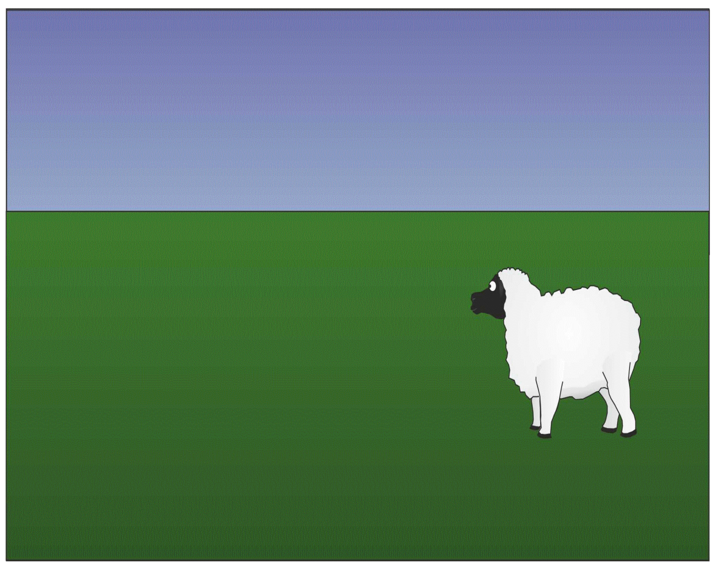
Then the aggregate can't be seen

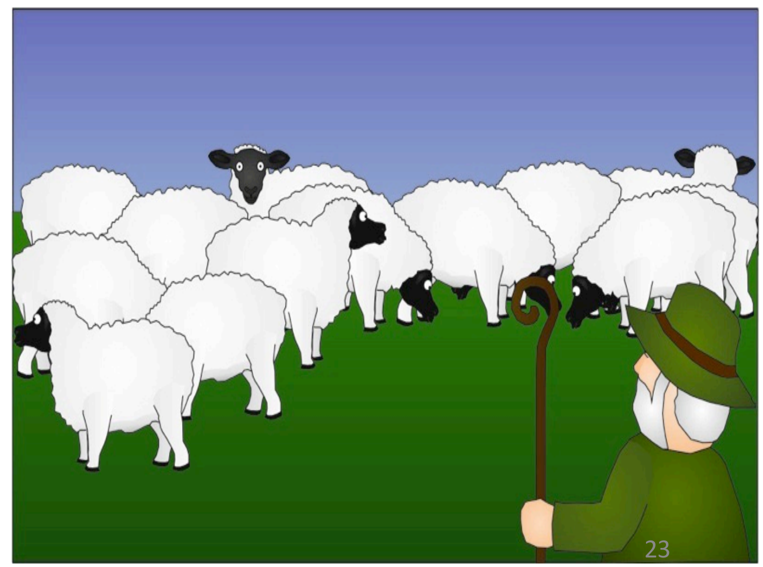
It is screened above a screening length, ξ

Below ξ we see the structure

Above ξ we see uniform contrast

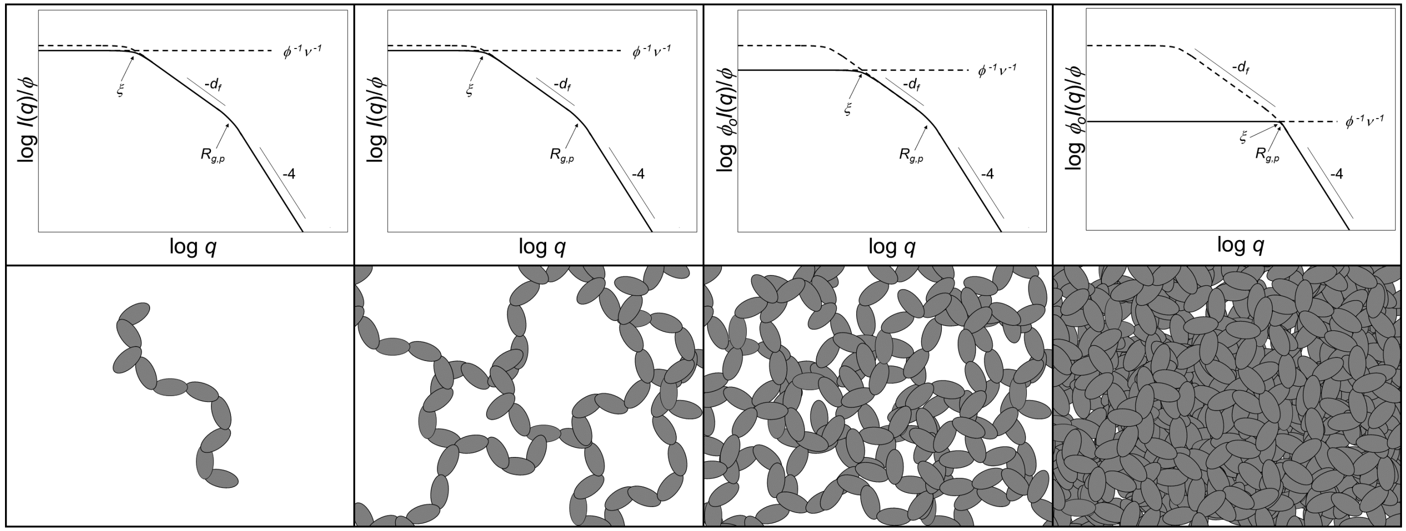






The RPA Equation

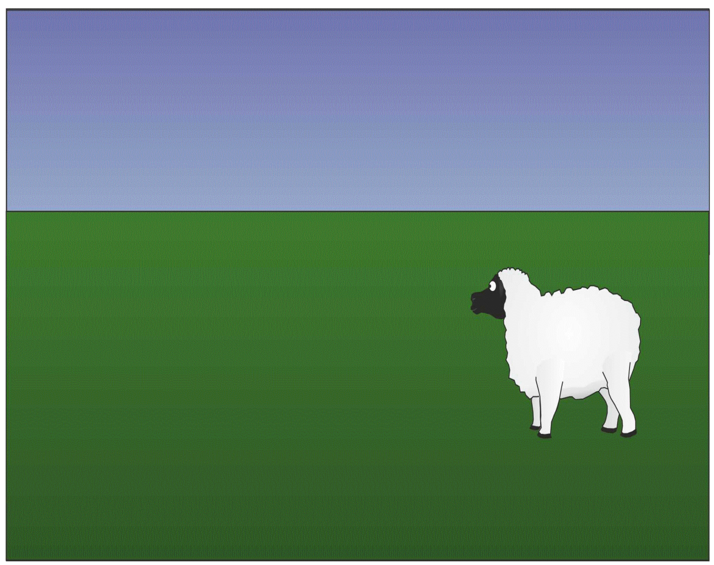
$$\frac{\phi}{I(q,\phi)} = \frac{\phi_0}{I(q,\phi_0)} + \phi\upsilon$$

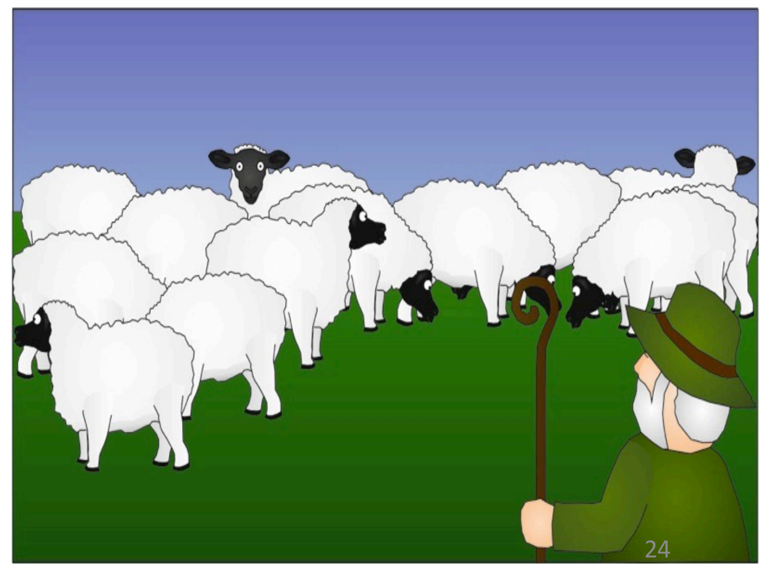


Reduced high-q intensity remains unchanged, Reduced low-q intensity is diminished with concentration increase

The q => 0 intercept is a measure of the strength of binary interactions (the Second Order Virial Coefficient)

This assumes no specific interactions. A mean field is considered.





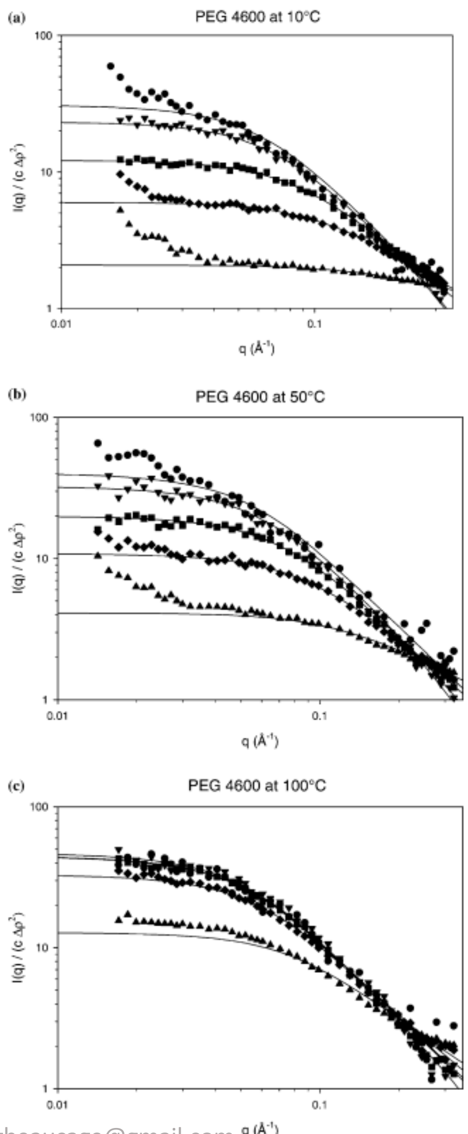
Van der Waals Model

$A_2 = b - a/T$

b = excluded volume

a = attractive interaction

$$\frac{\phi}{I(q,\phi)} = \frac{\phi_0}{I(q,\phi_0)} + k\phi A_2$$



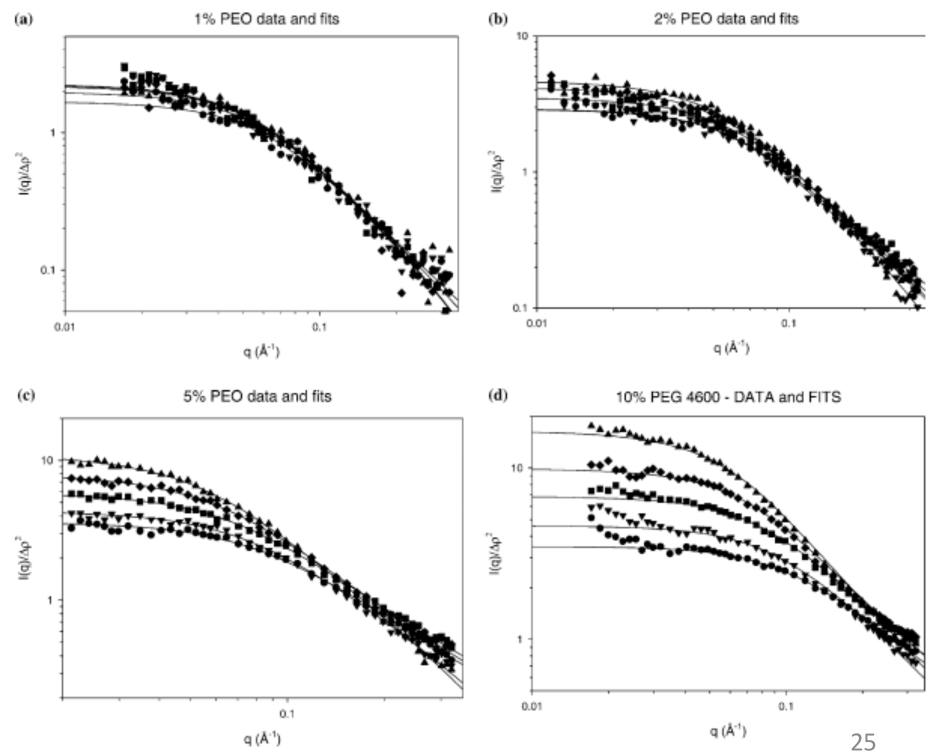
Progr Colloid Polym Sci (2005) 130: 70–78
DOI 10.1007/b107350
Published online: 3 June 2005

Jan Skov Pedersen
Cornelia Sommer

Temperature dependence of the virial coefficients and the chi parameter in semi-dilute solutions of PEG

Fig. 1 SAXS data with fits (curves) for PEG 4600 solutions at fixed temperature as a function of concentration. (a) 10°C (b) 50° C (c) 100° C. Signatures: 1 wt% circles, 2 wt% triangle down, 5 wt% square, 10 wt% diamond, 20 wt% triangle up. The data have been divided by the square of the excess electron density ($\Delta\rho$ was in units of e/Å^3) of the PEG chains in order to eliminate the influence in the plot of the change in contrast with temperature

Fig. 2 SAXS data with fits (curves) for PEG 4600 solutions at fixed concentration as a function of temperature. (a) 1 wt% (b) 2 wt% (c) 5 wt% (d) 10 wt%. Signatures: 20°C circles, 40°C triangles down, 60°C squares, 80°C diamonds and 100°C triangles. The data have been divided by the square of the excess electron density of the PEG chains in order to eliminate the influence in the plot of the change in contrast with temperature



Pedersen Sommer Paper 2005

Mean Field System

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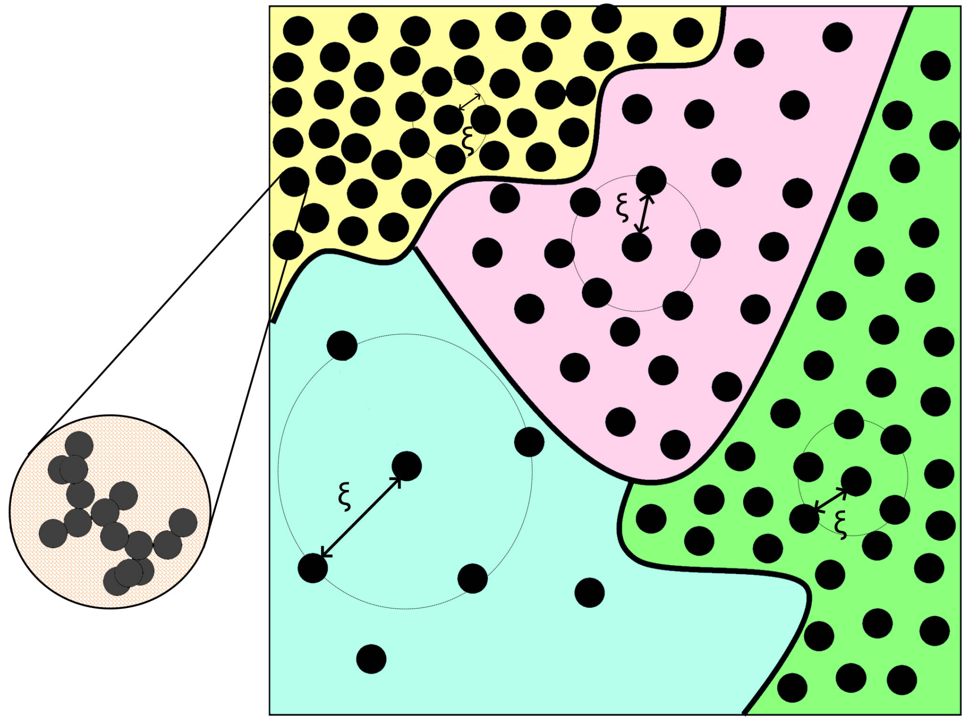
Specific Interaction System

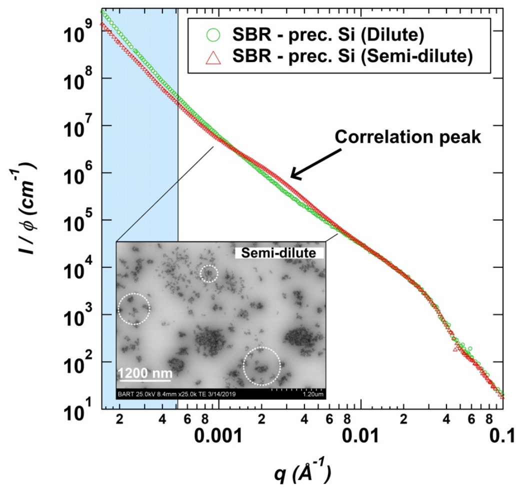


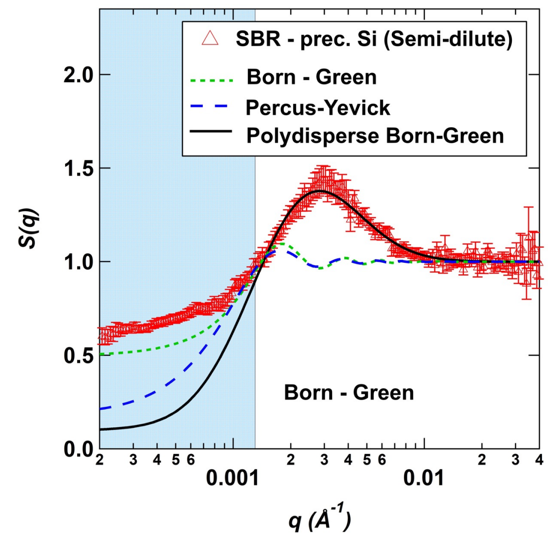
McGlasson, A.; Rishi, K.; Beaucage, G.; Chauby, M.; Kuppa, V.; Ilavsky, J.; Rackaitis, M. Quantification of Dispersion for Weakly and Strongly Correlated Nanofillers in Polymer Nanocomposites. ***Macromolecules*** 2020

For specific interactions we consider the structure factor S(q)

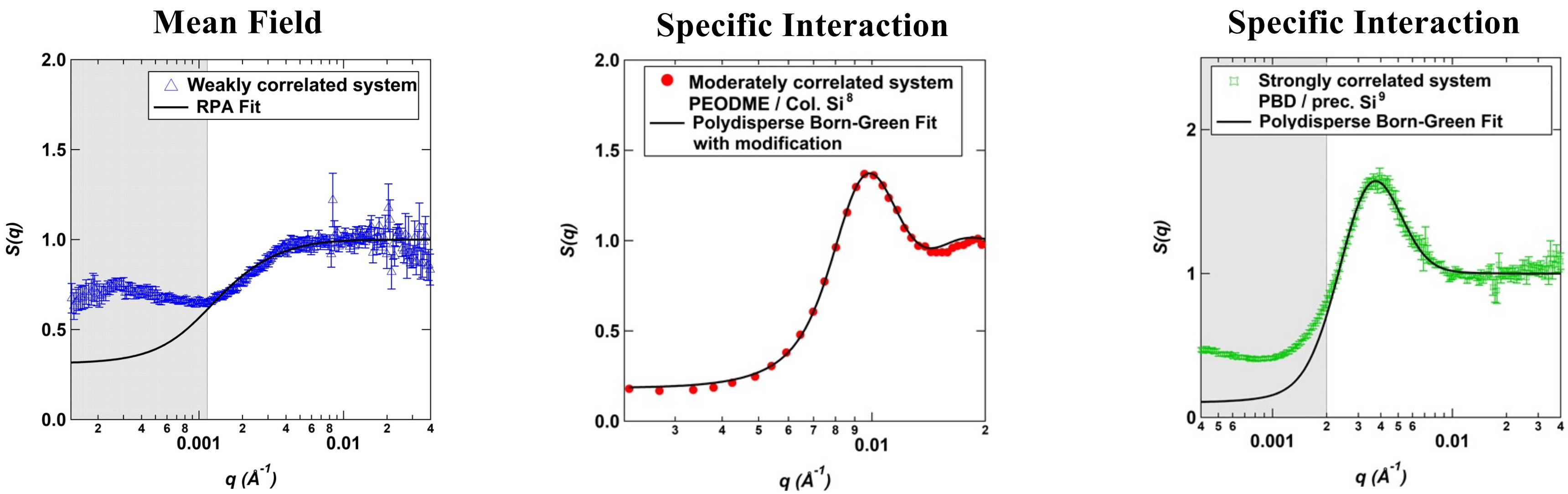
$I(q) = F^2(q)\, S(q)$

$S(q) = I(q)/\phi\, (\phi_0/I_0(q))$





Greg Beaucage, University of Cincinnati gbeaucage@gmail.com



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$$S_{RPA}(q) = \frac{1}{1 + \phi v(I_0(q, \phi_0)/\phi_0)}$$

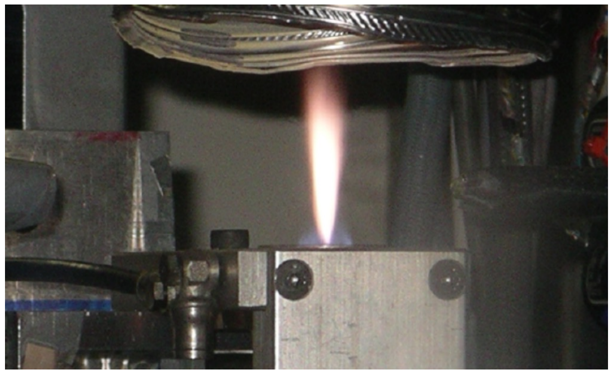
$$S_{PBG}(q, \xi) = \int_0^\infty P(\xi) \times \left[\frac{1}{1 + p\theta(q, \xi)}\right] d\xi$$

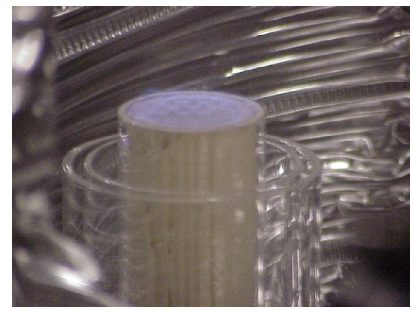
$$S_{PBG}(q, \xi) = \int_0^\infty P(\xi) \times \left[\frac{1}{1 + p\theta(q, \xi)}\right] d\xi$$

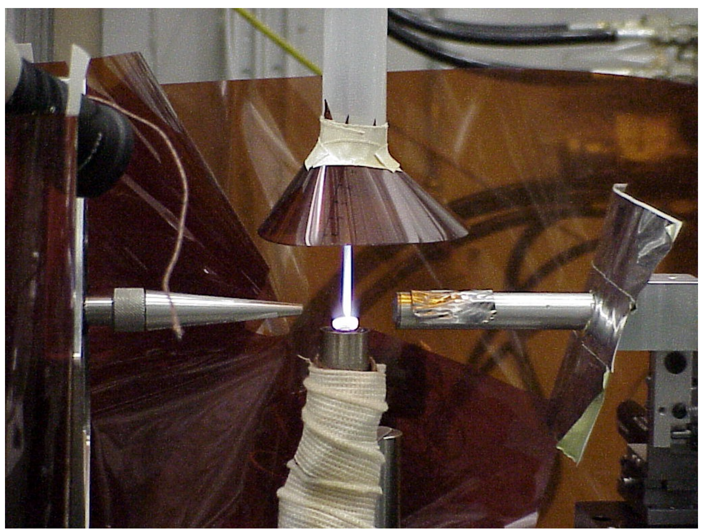
$$q_{mod} = q \times \exp\left\{\delta \frac{(q - q_{peak})}{q}\right\}$$

8 Data from Anderson, B. J. and Zukoski, C.F. Rheology and Microstructure of Polymer Nanocomposite Melts: Variation of Polymer Segment– Surface Interaction. ***Langmuir*** **2010**, 26, 8709–8720.

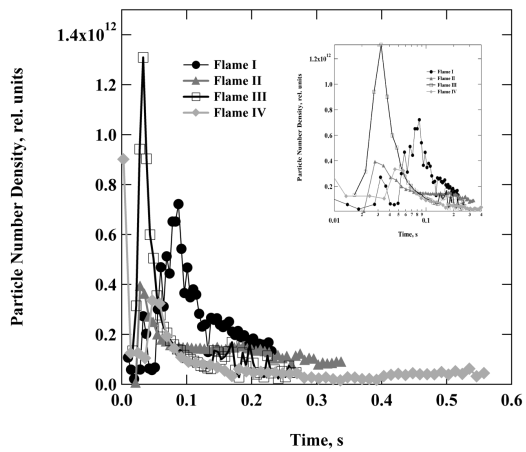
9 Data from Jin, Y.; Beaucage, G.; Vogtt, K.; Jiang, H.; Kuppa, V.; Kim, J.; Ilavsky, J.; Rackaitis, M.; Mulderig, A.; Rishi, K.; et al. A Pseudo- Thermodynamic Description of Dispersion for Nanocomposites. ***Polymer*** **2017**, 129, 32-43.

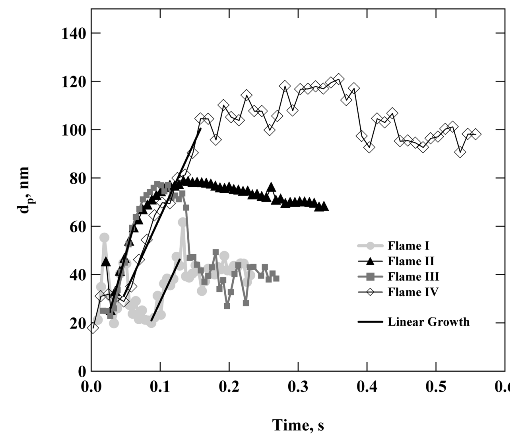


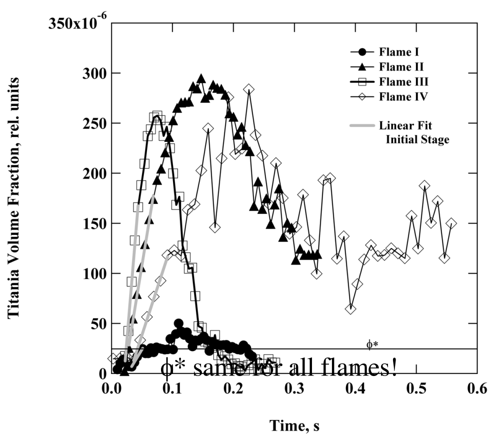


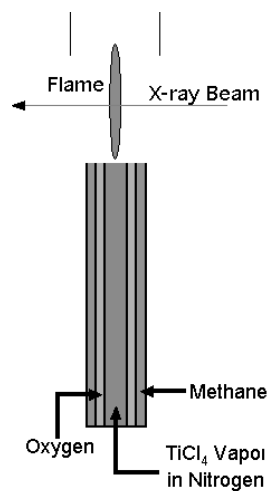


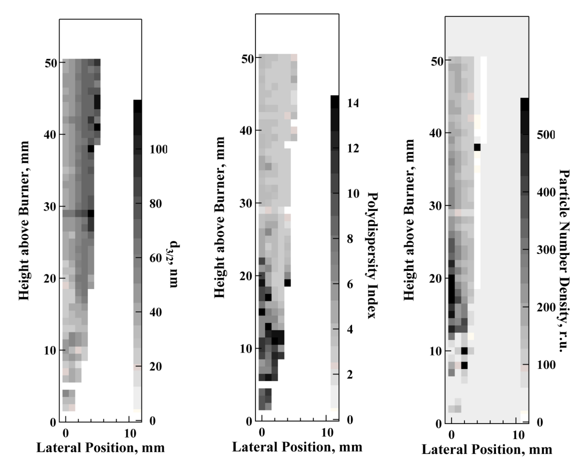
$TiCl_4$ Diffusion Flame Nucleation and Growth



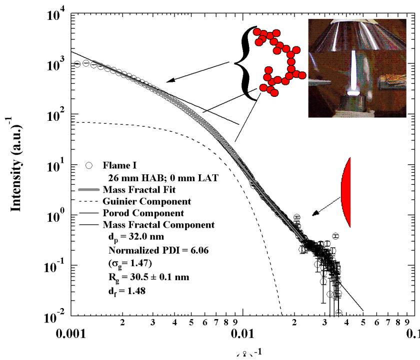


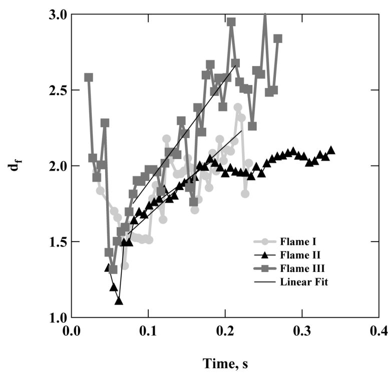


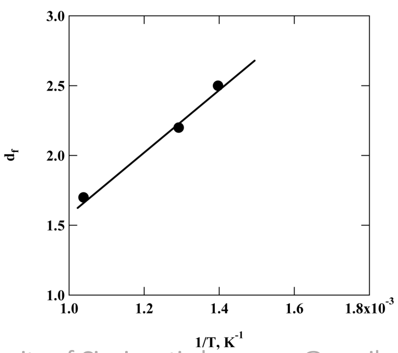




Greg Beaucage, University of Cincinnati gbeaucage@gmail.com



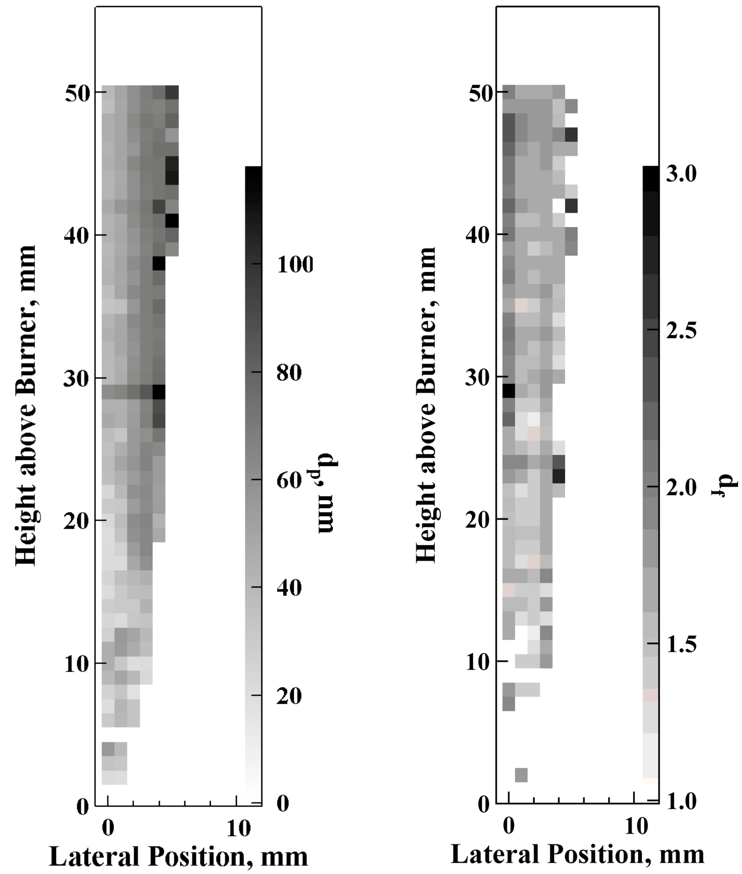




Activated growth for z

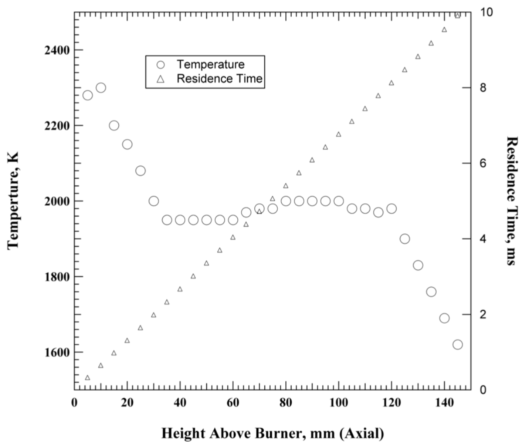
$$\ln(z) \sim d_f \ln\left(\frac{2R}{d_p}\right)$$

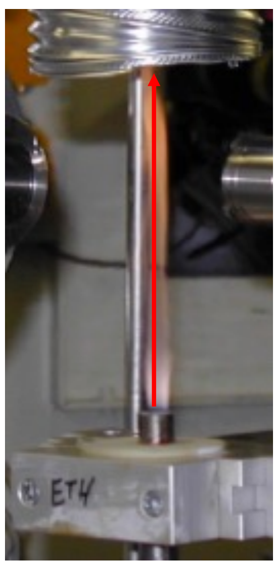
$$\sim \frac{-\Delta E}{kT}$$



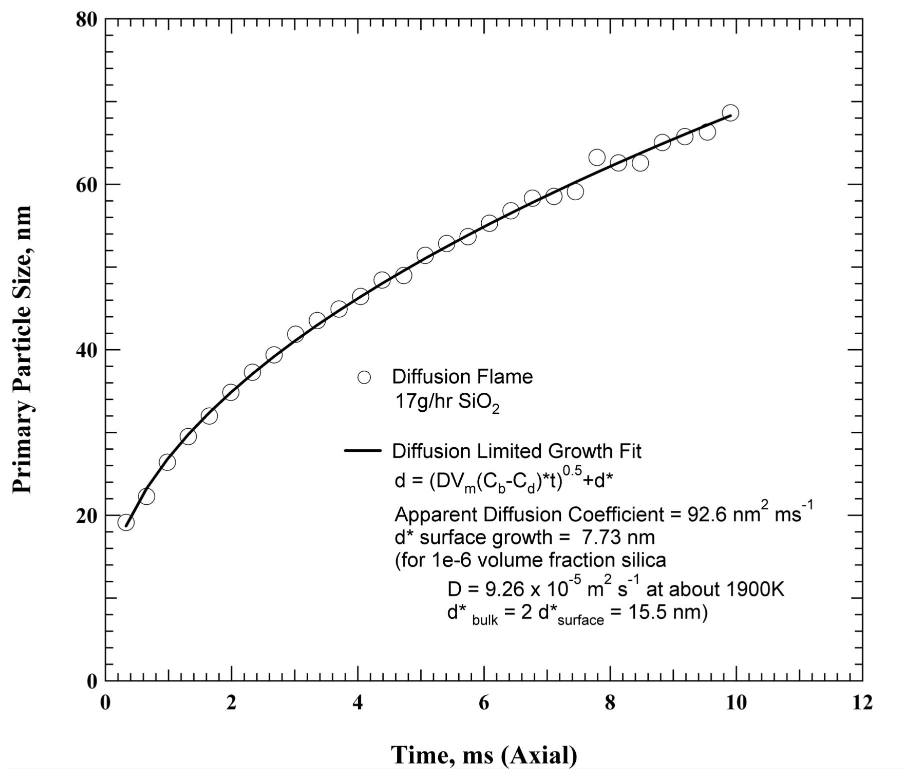
Titania Diffusion Flame from $TiCl_4$

Beaucage G, Agashe N, Kohls D, Londono D, Diemer B





Silica Diffusion Flame
Axial Particle Growth follows
Classic Diffusion Limited Surface Growth, $d \sim t^{1/2}$

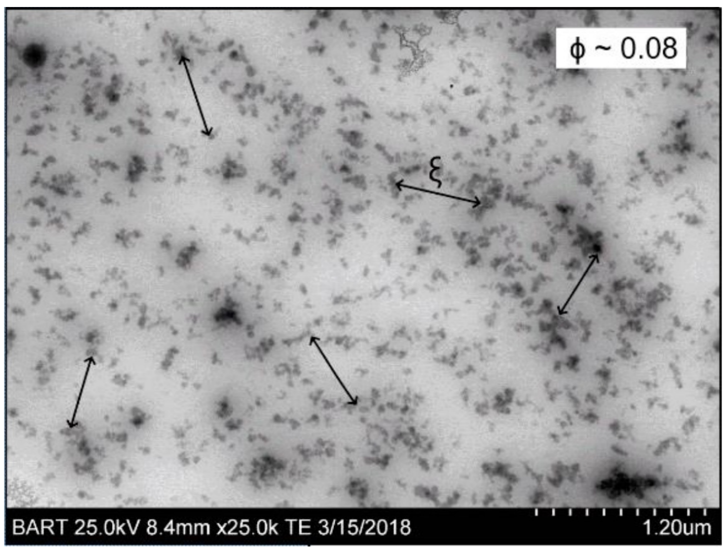


Greg Beaucage, University of Cincinnati gbeaucage@gmail.com

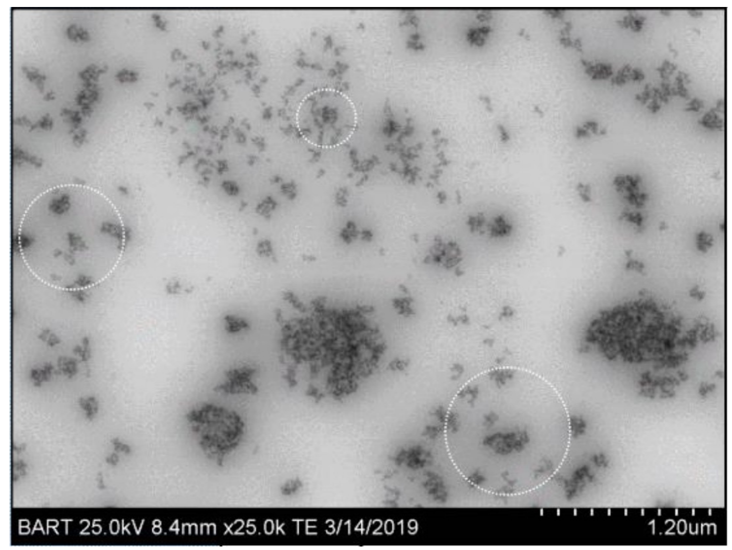
Nanoparticle Dispersion and Distribution in Nanocomposites

Kinetically mixed systems

Mean field



Specific interactions



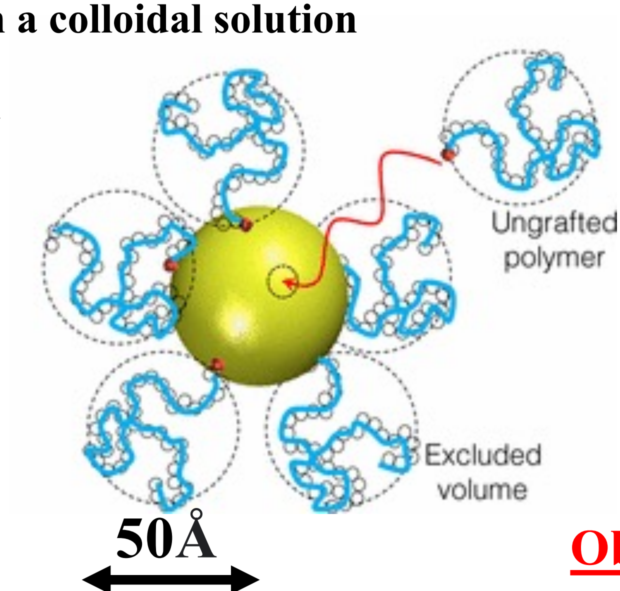
Clustering due to immiscibility

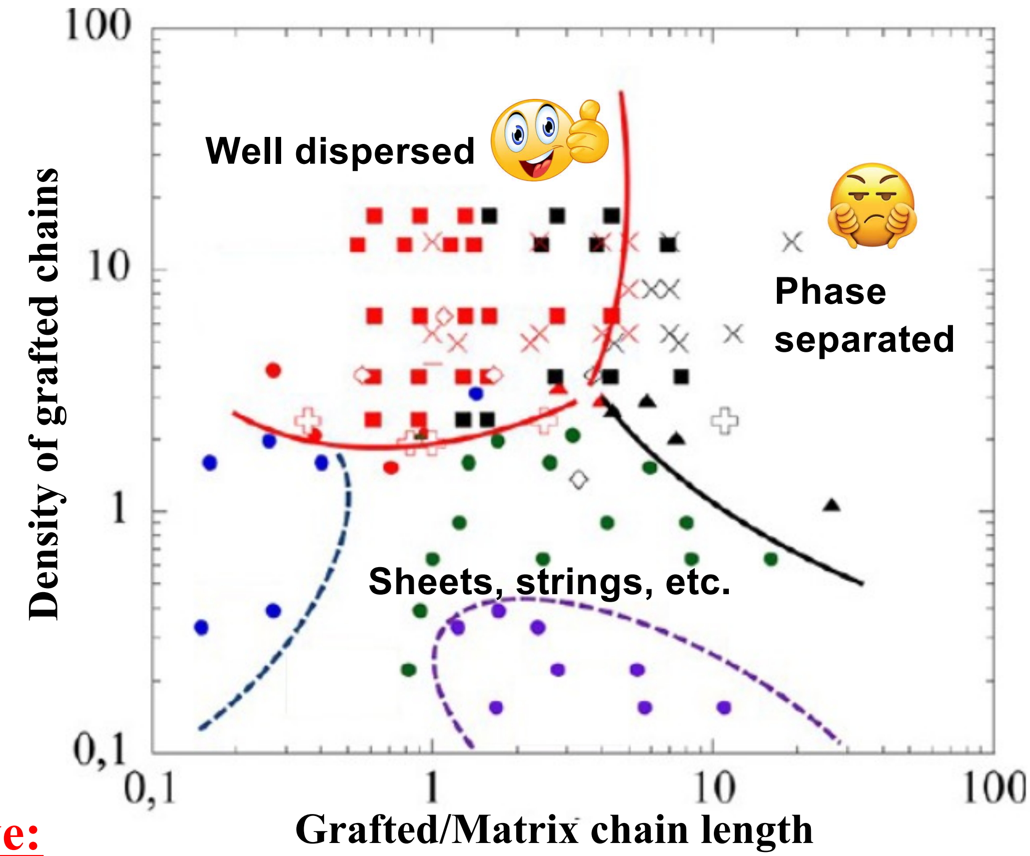
Greg Beaucage, University of Cincinnati gbeaucage@gmail.com

Current state-of-the-art academic nanocomposite

Monodisperse colloidal particles
Cast from a colloidal solution

Thermally
Dispersed





Objective:
Enhance miscibility

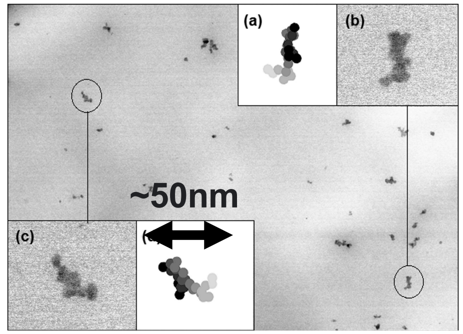
Kumar, S.K., Jouault, N., Benicewicz, B. and Neely, T., 2013. Nanocomposites with polymer grafted nanoparticles. *Macromolecules*, *46*(9), pp.3199-3214.
Kumar, S.K., Benicewicz, B.C., Vaia, R.A. and Winey, K.I., 2017. 50th anniversary perspective: are polymer nanocomposites practical for applications?. *Macromolecules*, *50*(3), pp.714-731.
Asai, M., Zhao, D. and Kumar, S.K., 2017. Role of grafting mechanism on the polymer coverage and self-assembly of hairy nanoparticles. *ACS Nano*, *11*(7), pp.7028-7035.

The original nanocomposite

Polydisperse aggregates

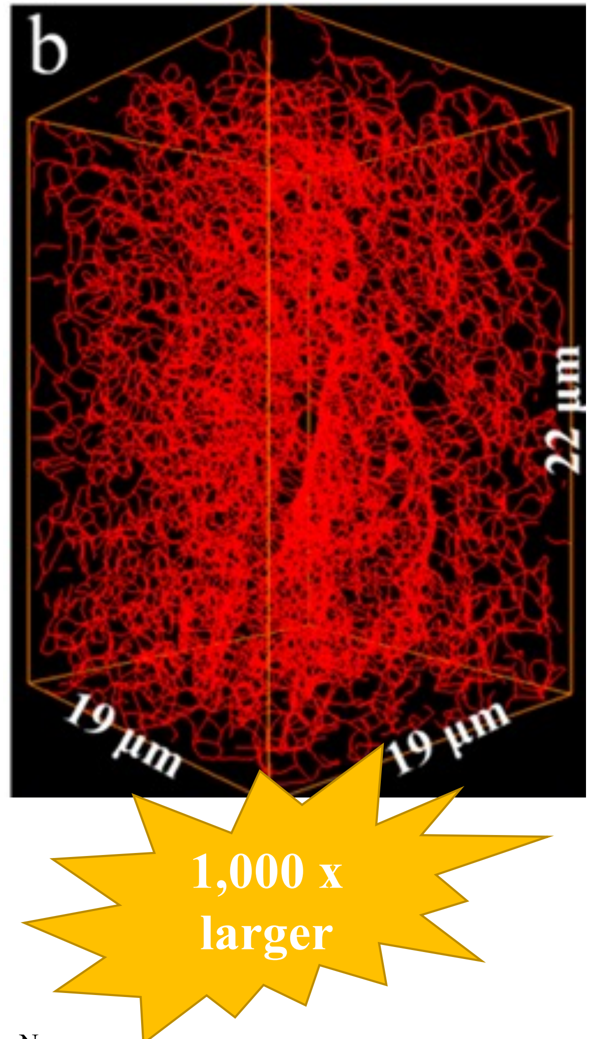
Melt state processed

Kinetically mixed **immiscible**



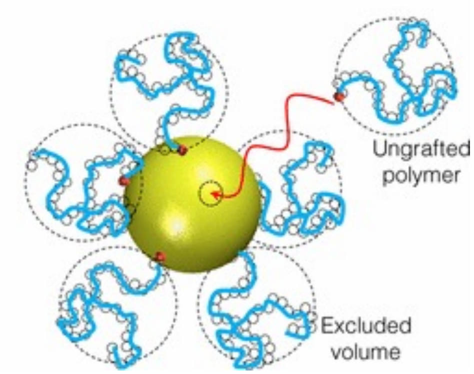
Objective:
Complex hierarchical structure
Tear resistance
Static charge dissipation

Why/how do added nanoparticles impact structures 100-1,000 times larger?



Song, L; Wang, Z; Tang, X.; Chen, L.; Chen, P.; Yuan, Q.; **Li, L.** Visualizing the Toughening Mechanism of Nanofiller with 3D X-ray Nano-CT: Stress-Induced Phase Separation of Silica Nanofiller and Silicone Polymer Double Networks Macromolecules 50 7249-7257 (2017).

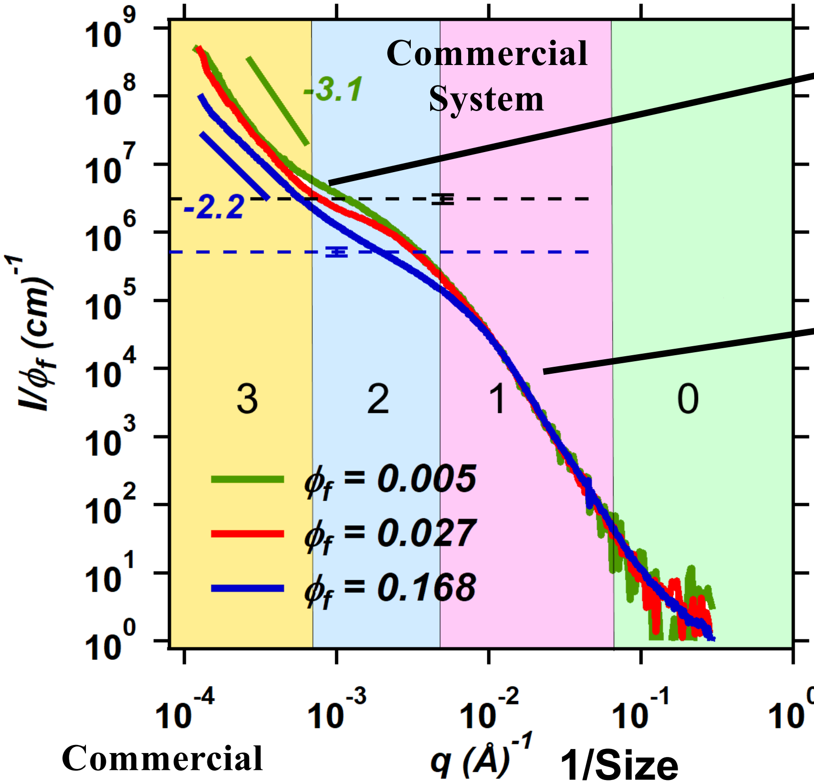
Simple Structure



50Å

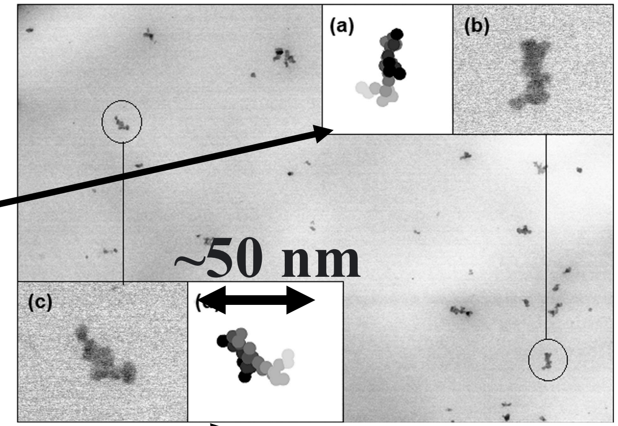
Academic State of the Art Model System

Multiscale Hierarchical Structures



Commercial System

1/Size



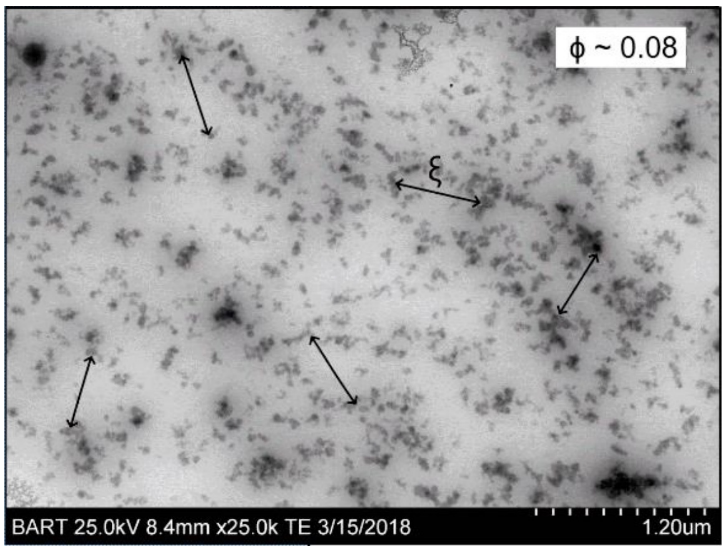
Aggregates of primary particles
Agglomerate due to immiscibility
Form macroscopic network
Controlled by mixing kinetics
And immiscibility

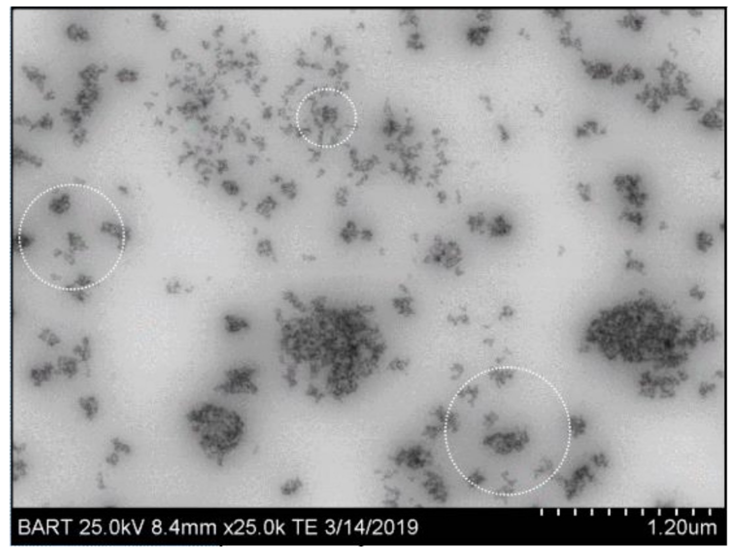
One size scale vs. multiple hierarchical size scales

Rishi, K., Beaucage, G., Kuppa, V., Mulderig, A., Narayanan, V., McGlasson, A., Rackaitis, M. and Ilavsky, J., 2018. Impact of an emergent hierarchical filler network on nanocomposite dynamics. *Macromolecules*, *51*(20), pp.7893-7904.
Mulderig, A., Beaucage, G., Vogtt, K., Jiang, H. and Kuppa, V., 2017. Quantification of branching in fumed silica. *Journal of Aerosol Science*, *109*, pp.28-37.

Dispersion/Distribution can have a size-scale dependence

Macroscopically disperse systems
might be clustered on the nanoscale



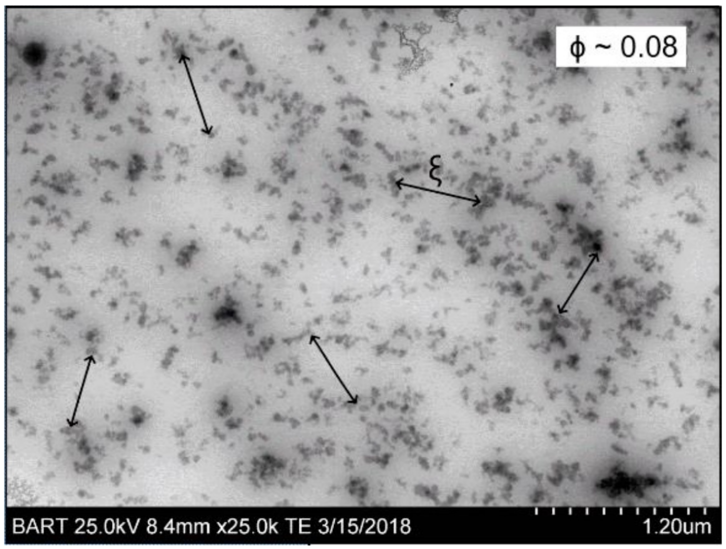


Clustering due to immiscibility

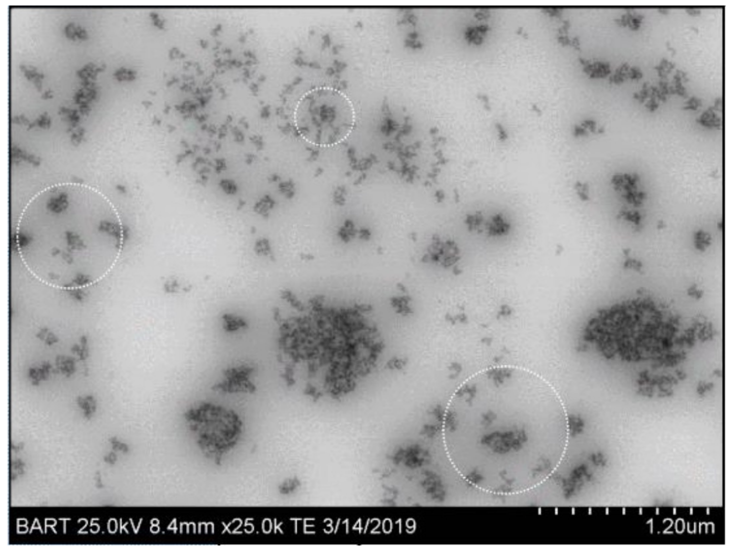
How can dispersion/distribution be quantified on the nano-scale?

Kinetically mixed systems

Mean field



Specific interactions

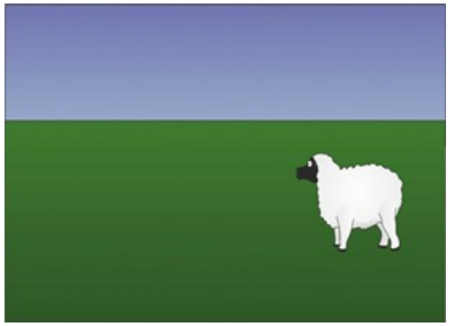


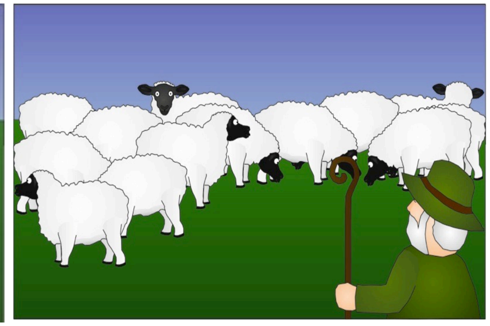
Clustering due to immiscibility

Greg Beaucage, University of Cincinnati gbeaucage@gmail.com

B_2 (or A_2) from scattering

B_2 "excluded volume" per aggregate



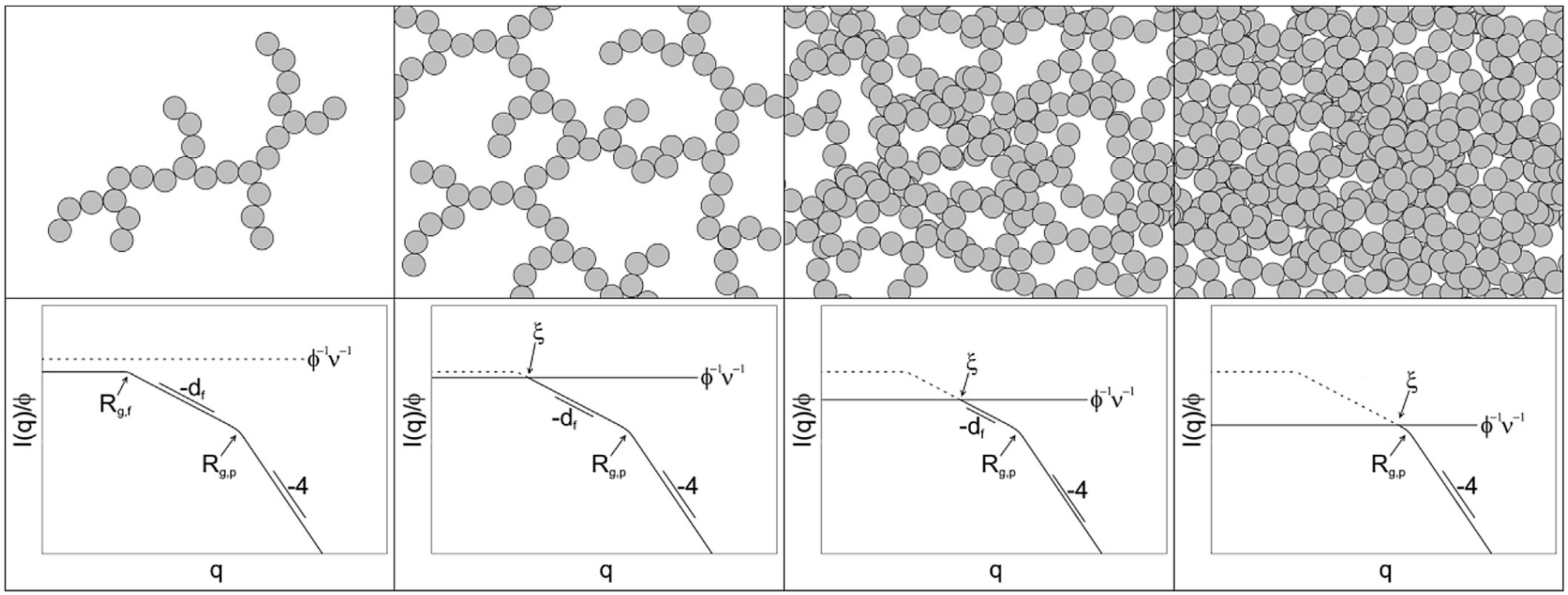


Quantitative measure of nano-dispersion

$$A_2 = \frac{\upsilon \langle \Delta\rho \rangle^2}{2N_A (\rho_f)^2}$$

$$B_2 = M^2 A_2 \big/ N_a$$

Correlation length, ξ



Pedersen, J. S.; Sommer, C. Temperature Dependence of the Virial Coefficients and the Chi Parameter in Semi-Dilute Solutions of PEG. In *Scattering Methods and the Properties of Polymer Materials*; Springer Berlin Heidelberg: Berlin, Heidelberg, 2005; pp 70–78.

Vogtt, K.; Beaucage, G.; Weaver, M.; Jiang, H. Thermodynamic Stability of Worm-like Micelle Solutions. *Soft Matter* 2017, *13* (36), 6068–6078.

Jin, Y.; Beaucage, G.; Vogtt, K.; Jiang, H.; Kuppa, V.; Kim, J.; Ilavsky, J.; Rackaitis, M.; Mulderig, A.; Rishi, K.; Narayanan, V. A Pseudo-Thermodynamic Description of Dispersion for Nanocomposites. *Polymer (Guildf).* 2017, *129*, 32–43.

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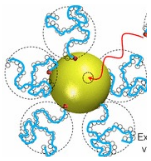
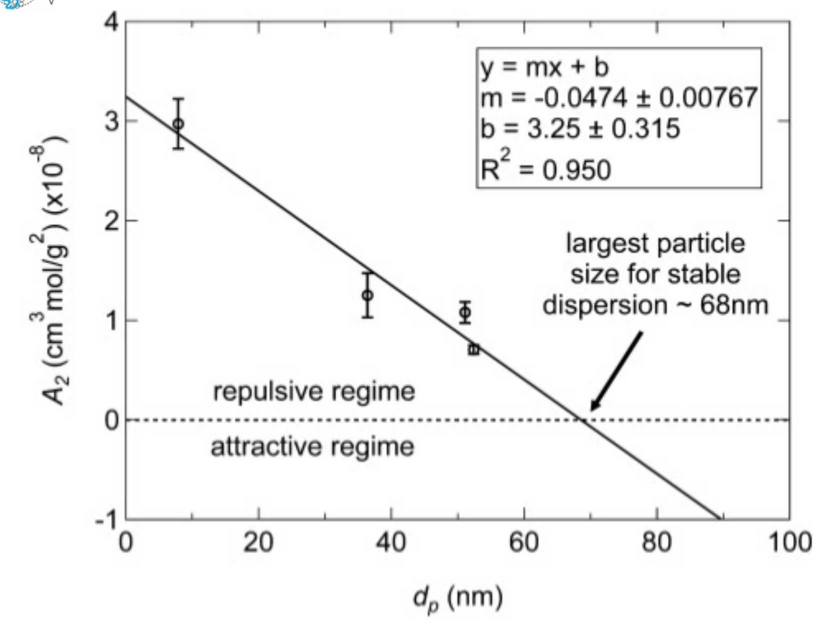
Thermal Distribution versus Kinetic Distribution



Miscible:

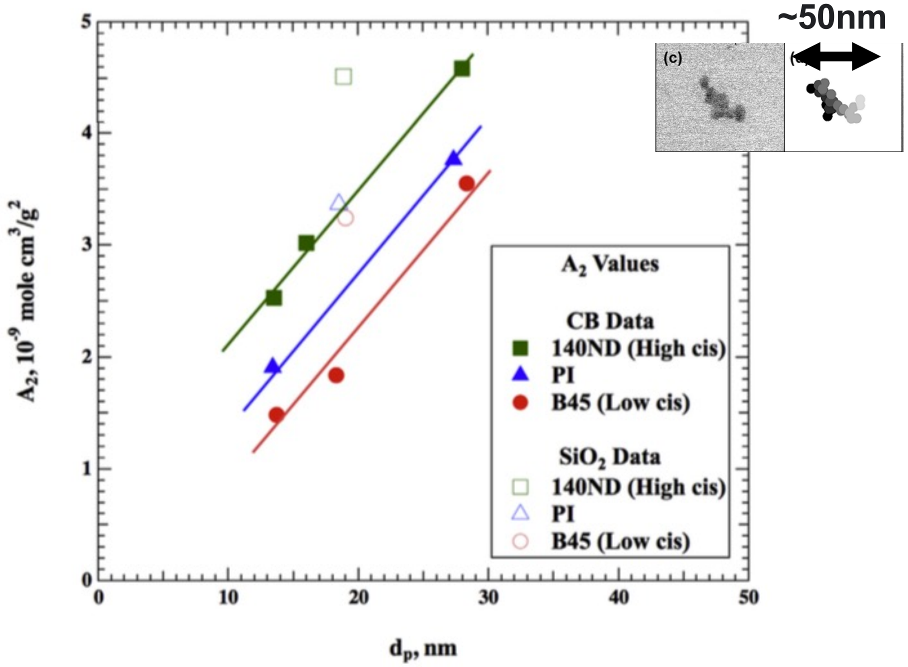
Organic Pigment with Triton X100



Thermally driven nano-dispersion (Stokes drag coefficient)

Immiscible:

Carbon Black and Silica in Elastomer



Mechanically driven nano-dispersion (Lever arm)

Mulderig, A.; Beaucage, G.; Vogtt, K.; Jiang, H.; Jin, Y.; Clapp, L.; Henderson, D. C. Structural Emergence in Particle Dispersions. *Langmuir* **2017**, *33* (49), 14029–14037.

Jin, Y.; Beaucage, G.; Vogtt, K.; Jiang, H.; Kuppa, V.; Kim, J.; Ilavsky, J.; Rackaitis, M.; Mulderig, A.; Rishi, K.; Narayanan, V. A Pseudo-Thermodynamic Description of Dispersion for Nanocomposites. *Polymer (Guildf)*. **2017**, *129*, 32–43.

van der Waals Analogy

a reflects the attractive energy of interaction between aggregates.

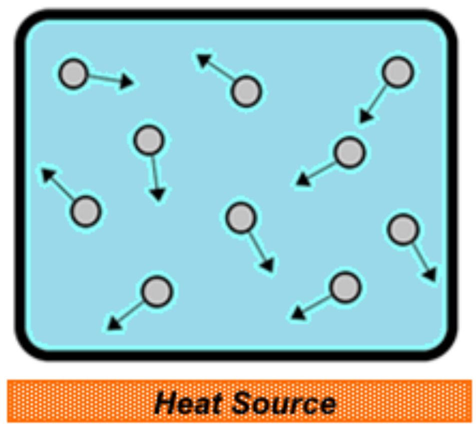
$$\Pi = \frac{kT}{(V+b)} - \frac{a}{V^2}$$

b is the excluded volume

a is the attractive enthalpic interaction leading to phase separation

$$\Pi = kT\left(\frac{1}{V} + \frac{B_2}{V^2} + \cdots\right)$$

Thermally driven colloidal dispersion

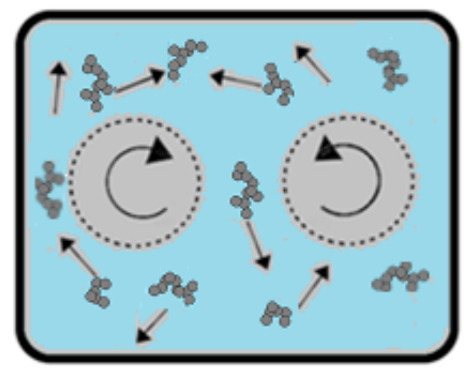


Energy ∝ Temperature

$$B_2(T) = b - \frac{a}{kT}$$

≈

Mechanically dispersed nano-fillers



Energy ∝ Mixing Time

$$B_2(t) = b^* - \frac{a^*}{\gamma}$$

$$\mathrm{B}_2(\mathrm{t}) = \frac{A_2(t)M^2}{N_A} = b^* - \frac{a^*}{t}$$

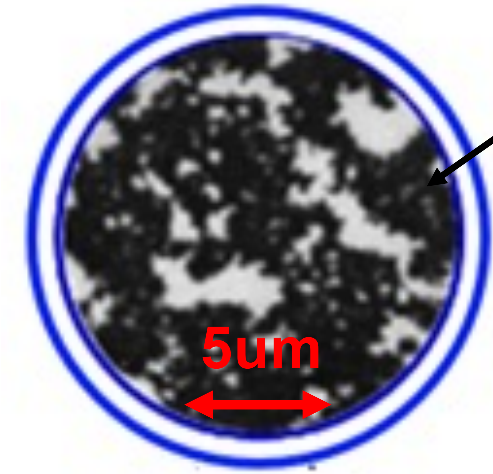
A_2 arrives from using mass concentration rather than molar or number concentration

Greg Beaucage, University of Cincinnati gbeaucage@gmail.com

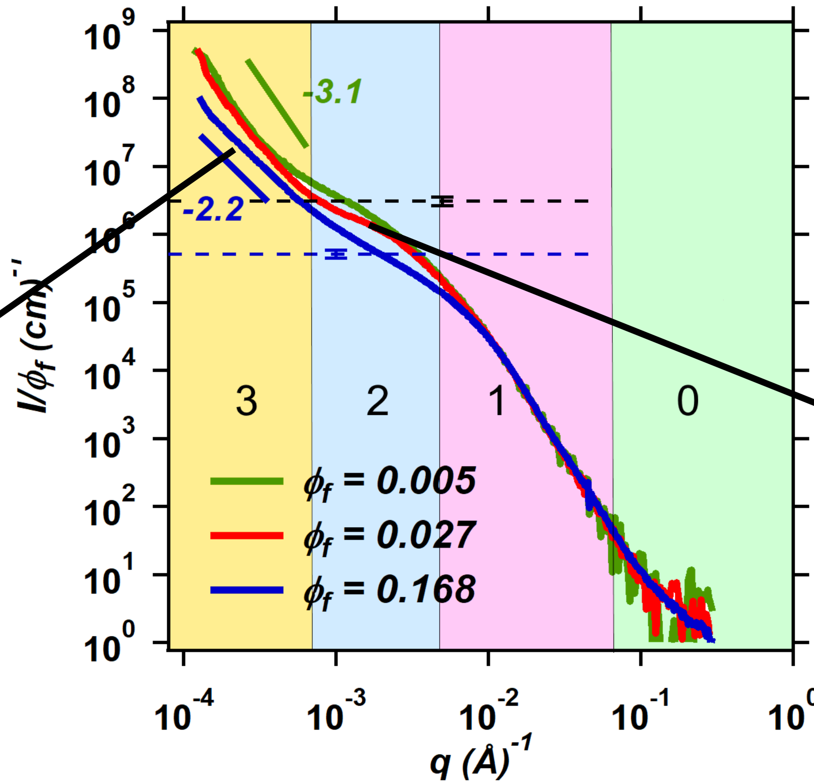
Multiscale Hierarchical Structures

Immiscibility forms clusters

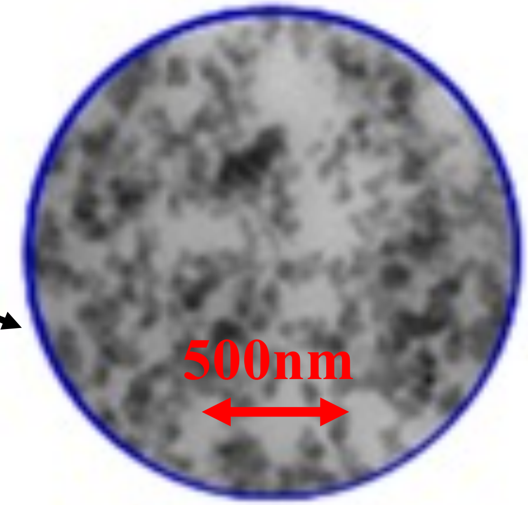
Bulk network



Size

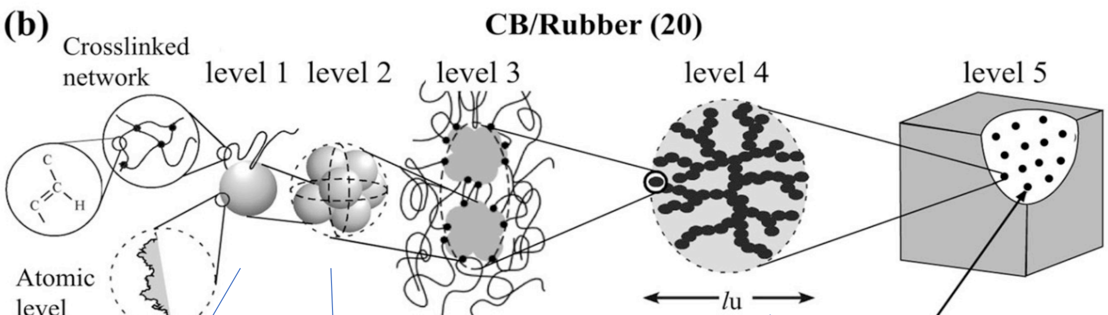


Local network



Rishi, K., Beaucage, G., Kuppa, V., Mulderig, A., Narayanan, V., McGlasson, A., Rackaitis, M. and Ilavsky, J., 2018. Impact of an emergent hierarchical filler network on nanocomposite dynamics. *Macromolecules*, *51*(20), pp.7893-7904.
Trappe, V. and Weitz, D.A., 2000. Scaling of the viscoelasticity of weakly attractive particles. *Physical review letters*, *85*(2), p.449.
Mulderig, A., Beaucage, G., Vogtt, K., Jiang, H. and Kuppa, V., 2017. Quantification of branching in fumed silica. *Journal of Aerosol Science*, *109*, pp.28-37.

Multiscale Hierarchical Structures

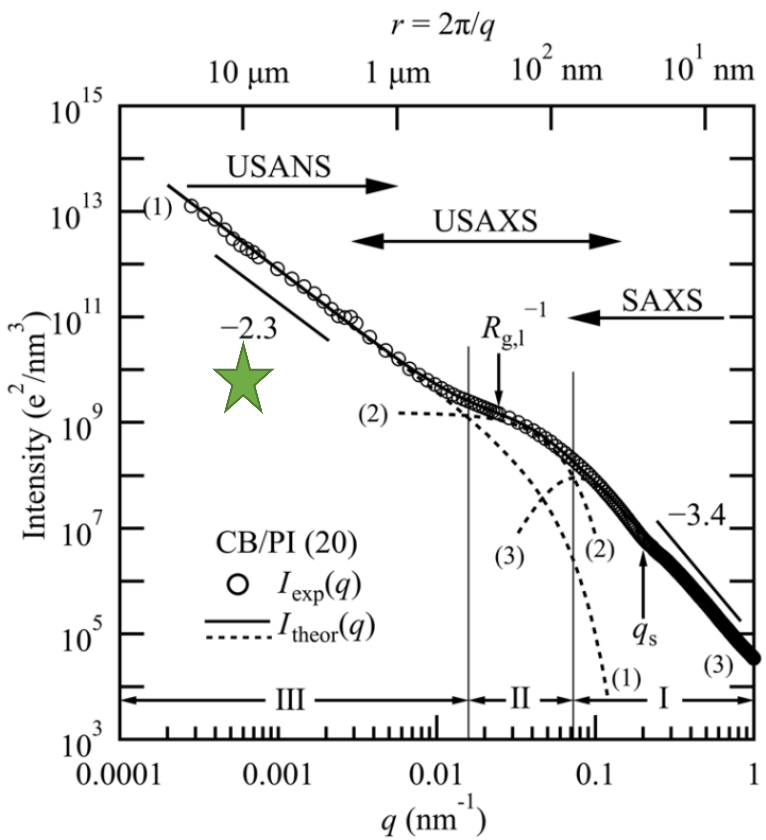


Primary Particles

Aggregates

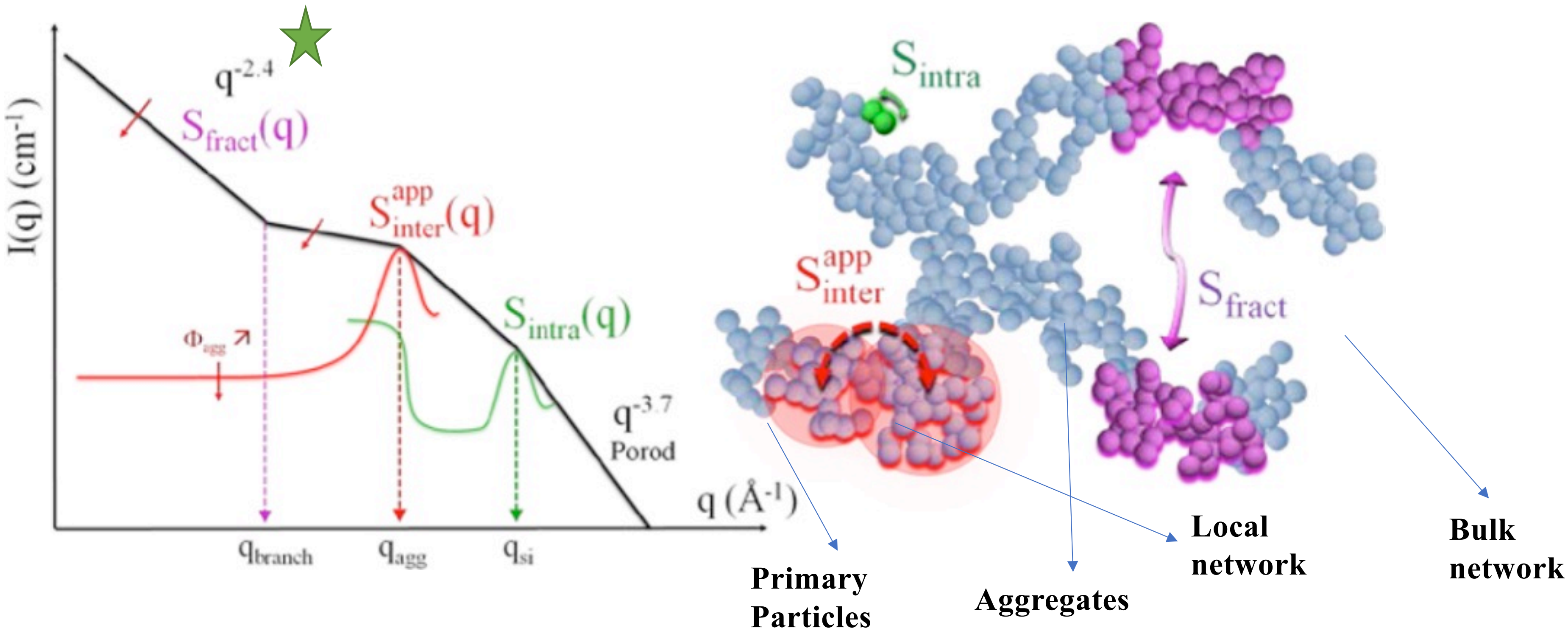
Local network

Bulk network



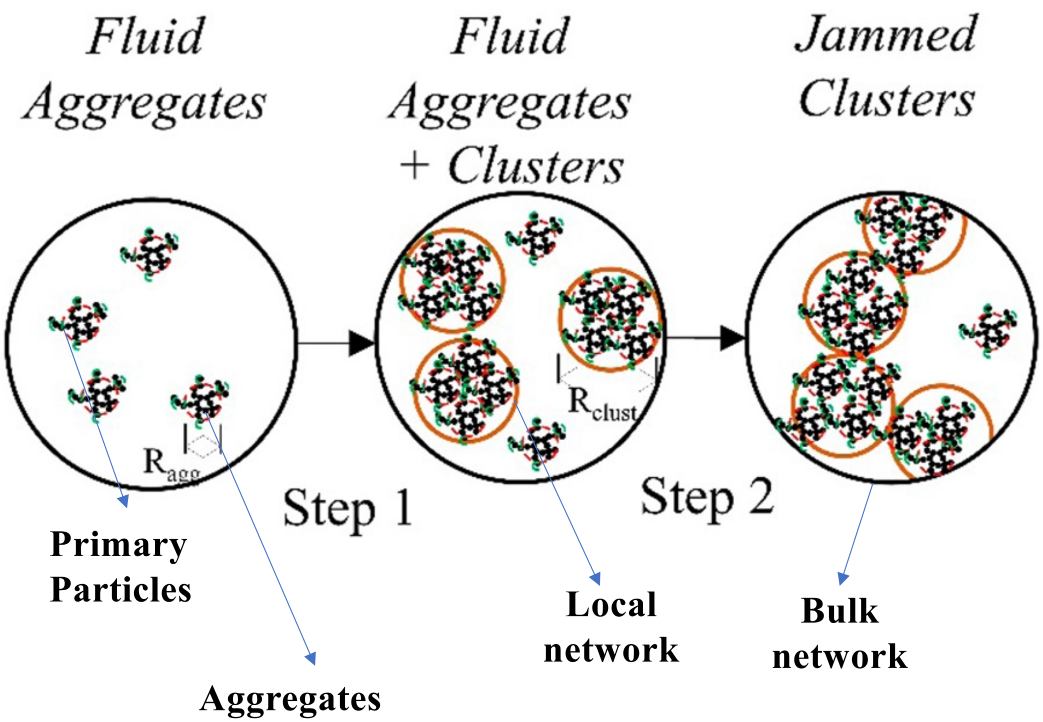
Hashimoto, T., Amino, N., Nishitsuji, S. and Takenaka, M., **2019**. Hierarchically self-organized filler particles in polymers: cascade evolution of dissipative structures to ordered structures. *Polymer Journal*, *51*(2), pp.109-130.

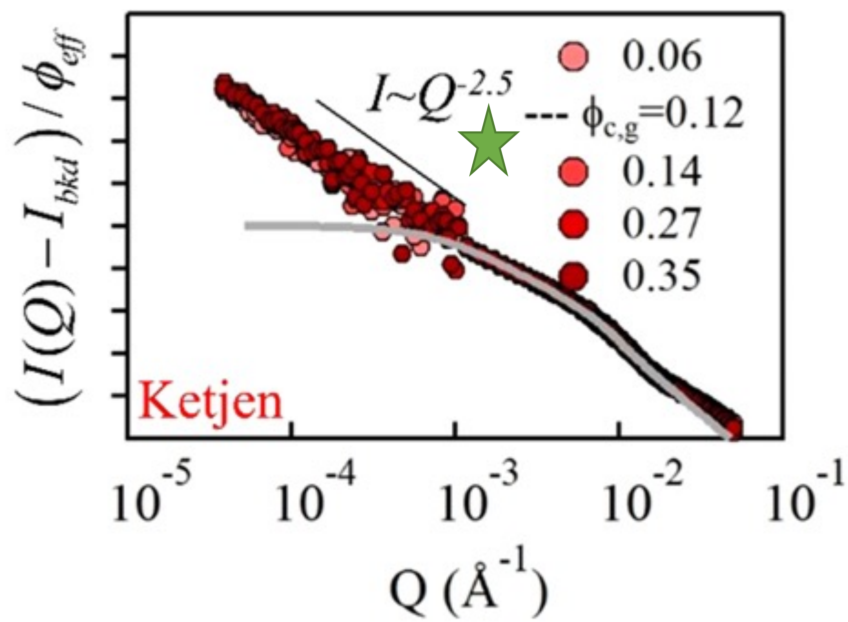
Multiscale Hierarchical Structures



Baeza, G.P., Genix, A.C., Degrandcourt, C., Petitjean, L., Gummel, J., Couty, M. and Oberdisse, J., **2013**. Multiscale filler structure in simplified industrial nanocomposite silica/SBR systems studied by SAXS and TEM. *Macromolecules*, *46*(1), pp.317-329.

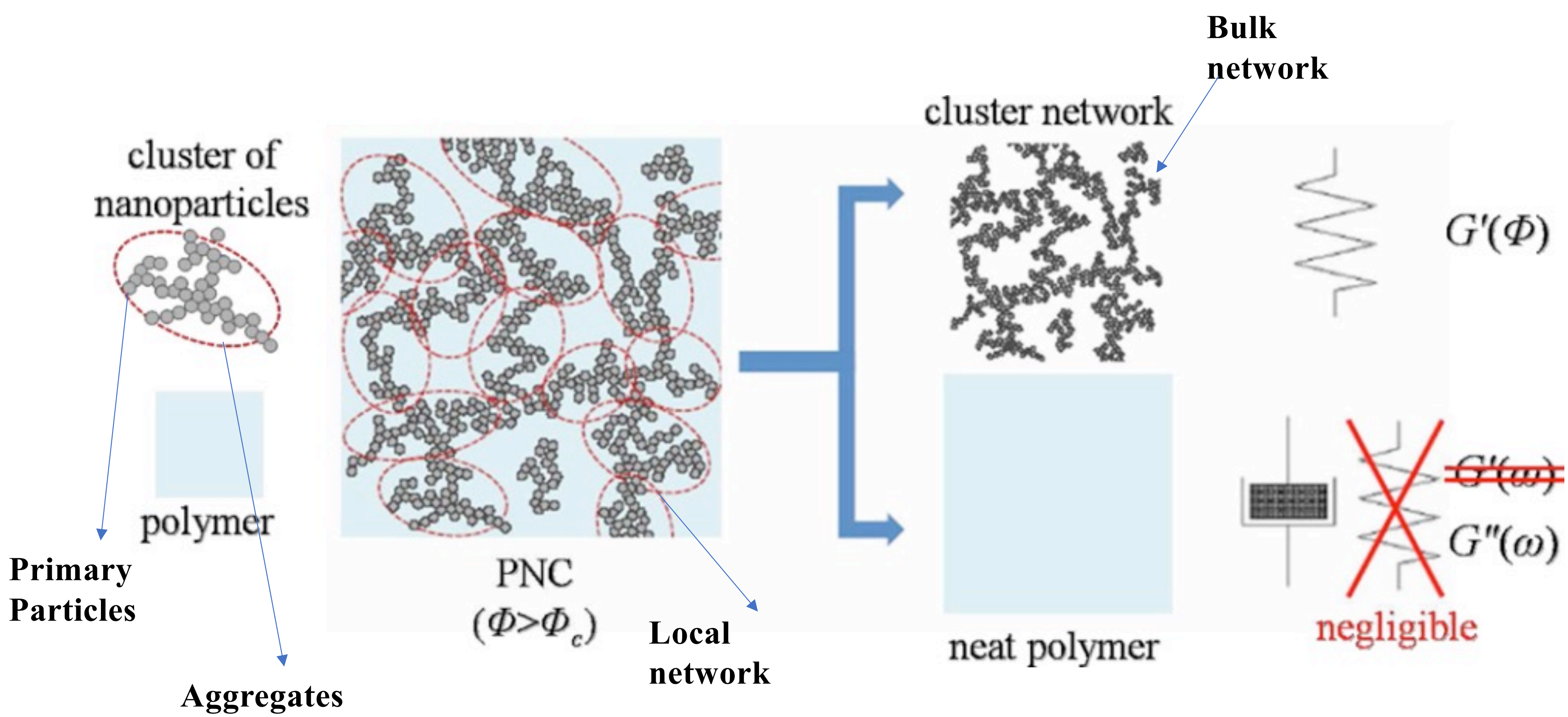
Multiscale Hierarchical Structures





Richards, J.J., Hipp, J.B., Riley, J.K., Wagner, N.J. and Butler, P.D., **2017**. Clustering and percolation in suspensions of carbon black. *Langmuir*, *33*(43), pp.12260-12266.

Multiscale Hierarchical Structures



Filippone, G., Romeo, G. and Acierno, D., **2010**. Viscoelasticity and structure of polystyrene/fumed silica nanocomposites: filler network and hydrodynamic contributions. *Langmuir*, *26*(4), pp.2714-2720.
Filippone, G. and Salzano de Luna, M., **2012**. A unifying approach for the linear viscoelasticity of polymer nanocomposites. *Macromolecules*, *45*(21), pp.8853-8860.

van der Waals model for incompatible polymer nanocomposites

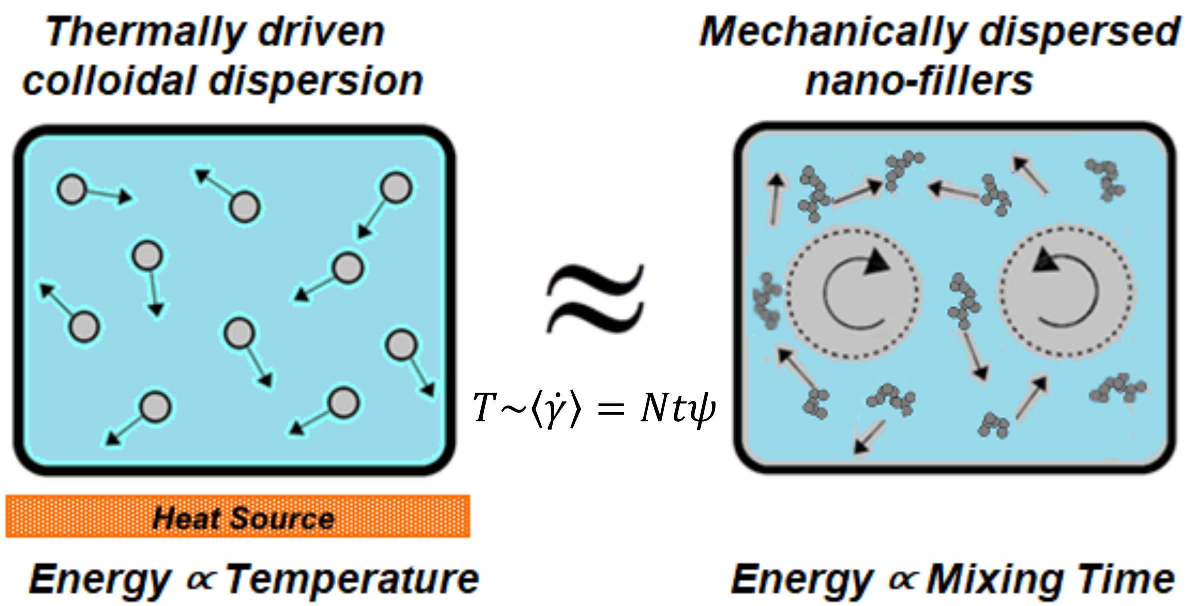
a reflects the attractive energy of interaction between aggregates.

$$\Pi = \frac{kT}{(V+b)} - \frac{a}{V^2}$$

b is the excluded volume

a is the attractive enthalpic interaction leading to phase separation

$$\Pi = kT\left(\frac{1}{V} + \frac{B_2}{V^2} + \cdots\right)$$

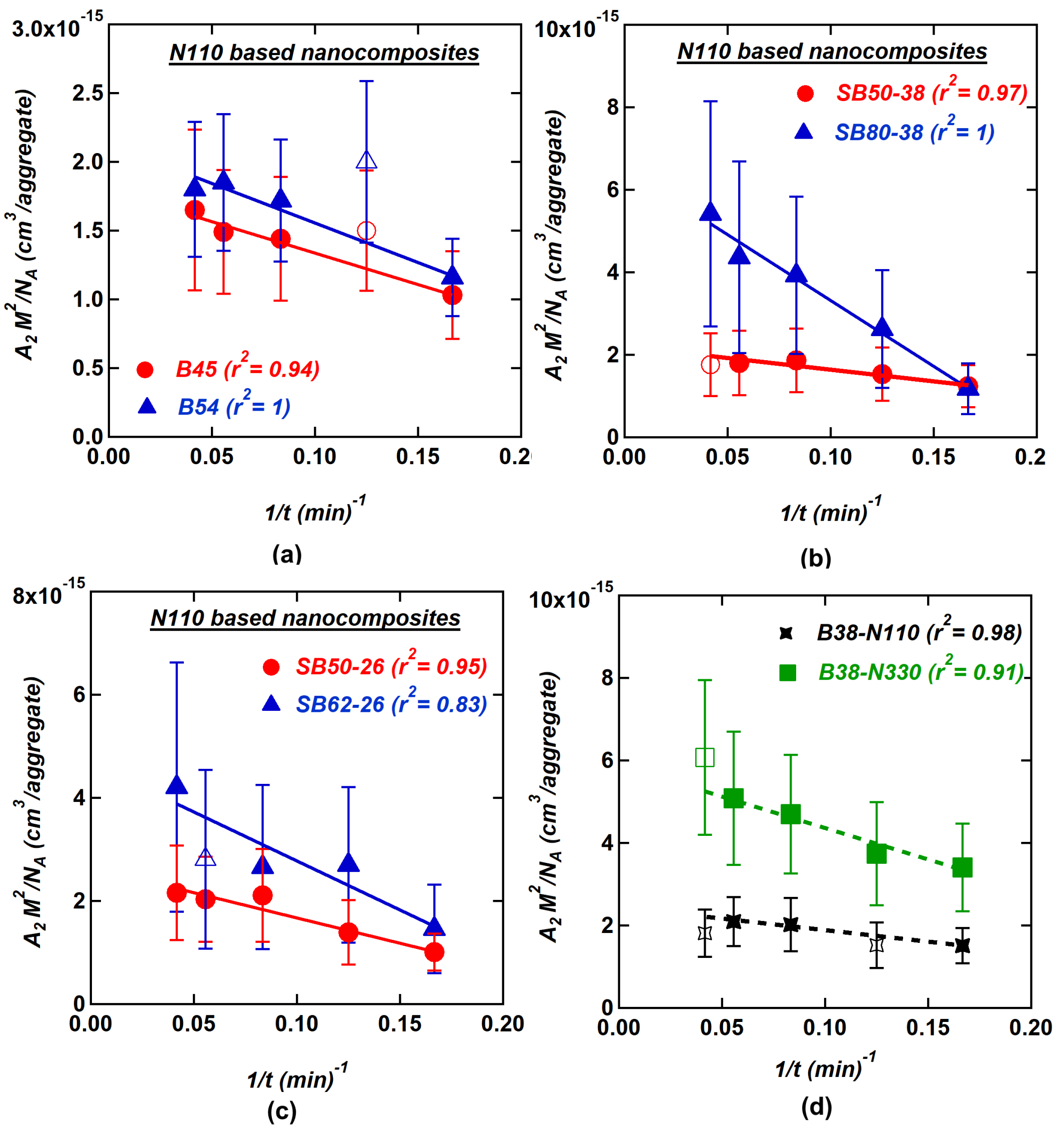


$$T \sim \langle \dot{\gamma} \rangle = Nt\psi$$

$$B_2(T) = b - \frac{a}{kT}$$

$$B_2(t) = b^* - \frac{a^*}{t}$$

Rishi, K.; Narayanan, V.; Beaucage, G.; McGlasson, A.; Kuppa, V.; Ilavsky, J.; Rackaitis, M. A Thermal Model to Describe Kinetic Dispersion in Rubber Nanocomposites: The Effect of Mixing Time on Dispersion. Polymer (Guildf). **2019**, 175, 272–282.

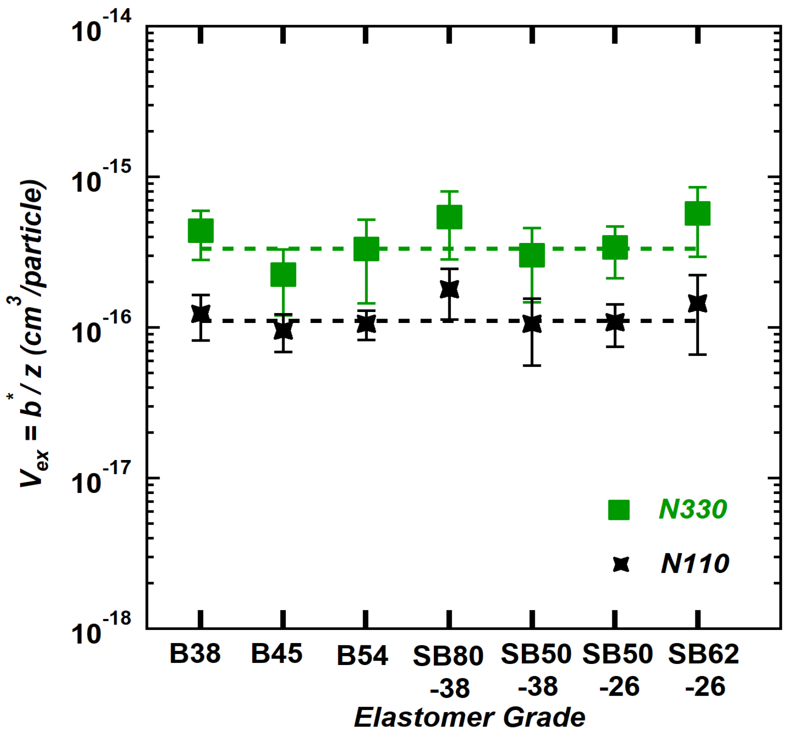


Van der Waals approach seems viable

$$B_2(t) = \frac{A_2(t)M^2}{N_A} = b^* - \frac{a^*}{t}$$

Rishi, K.; Narayanan, V.; Beaucage, G.; McGlasson, A.; Kuppa, V.; Ilavsky, J.; Rackaitis, M. A Thermal Model to Describe Kinetic Dispersion in Rubber Nanocomposites: The Effect of Mixing Time on Dispersion. Polymer (Guildf). 2019, 175, 272–282.

Excluded volume is associated with the occupied volume of an aggregate.
$(d_{p,N330}/d_{p,N110})^3 = 4.2$



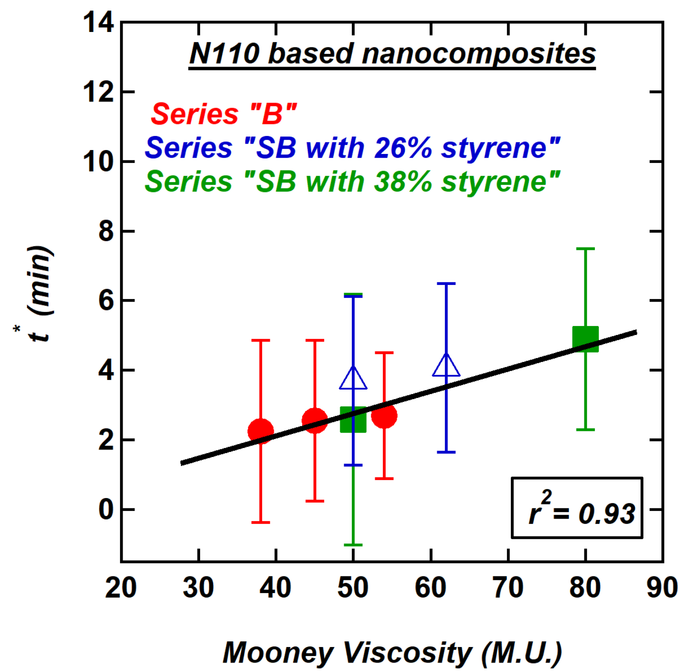
N110	Vulcan 8 (Cabot)	123 m^2/g	25.7 nm
N330	Vulcan 3 (Cabot)	76 m^2/g	41.6 nm

$$B_2(t) = b^* - \frac{a^*}{t}$$

Wetting time depends on **viscosity** and **primary particle size**

x-intercept reflects "wetting time"

$$B_2 = 0, \quad t^* = a^*/b^*$$



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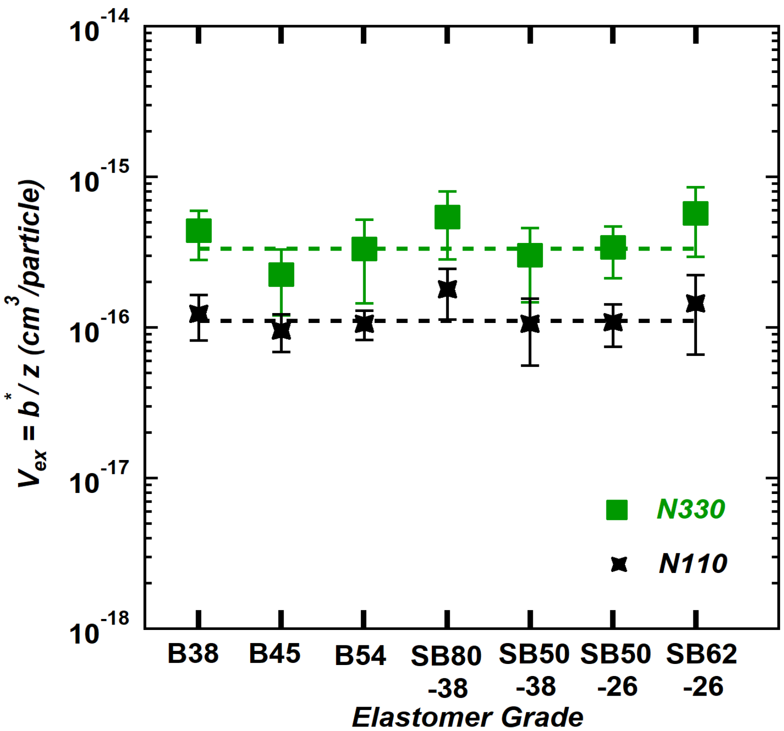


N110	Vulcan 8 (Cabot)	123 m^2/g	25.7 nm
N330	Vulcan 3 (Cabot)	76 m^2/g	41.6 nm

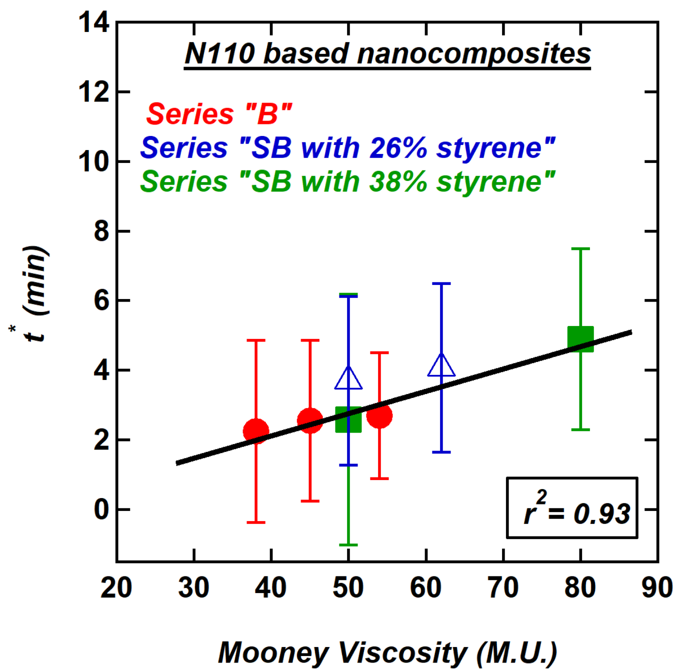
$$B_2(t) = b^* - \frac{a^*}{t}$$

Note: if a^*/b^* increases, B_2 decreases with viscosity

Wetting time depends on **viscosity** and **primary particle size**

x-intercept reflects "wetting time"

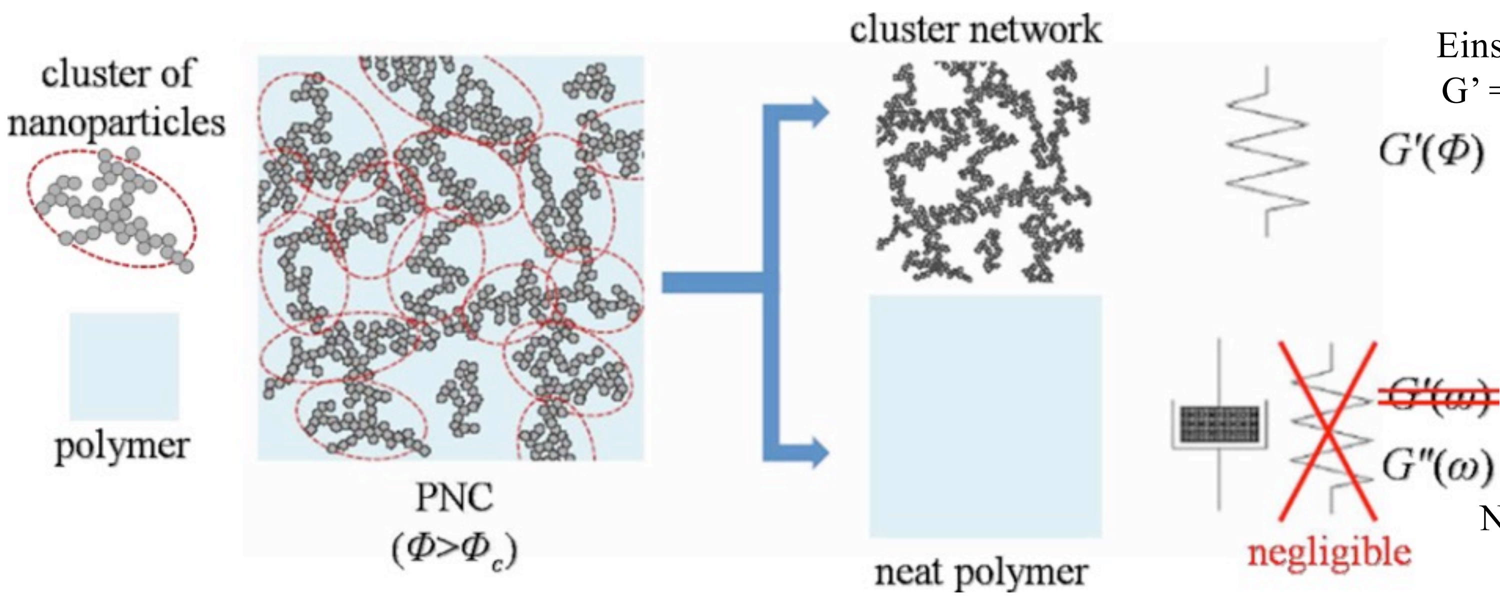
$$B_2 = 0, \quad t^* = a^*/b^*$$



Rishi, K.; Narayanan, V.; Beaucage, G.; McGlasson, A.; Kuppa, V.; Ilavsky, J.; Rackaitis, M. A Thermal Model to Describe Kinetic Dispersion in Rubber Nanocomposites: The Effect of Mixing Time on Dispersion. Polymer (Guildf). 2019, 175, 272–282. 4

Morphology from rheology

- How does this multi-hierarchical model relate to oscillatory rheometry?



Einstein/Guth-Gold:
$G' = G'_0 (1 + 2.5\ \phi_f)$

Network/Winter:
$G' \sim G'' \sim \omega^{\alpha}$

Filippone, G., Romeo, G. and Acierno, D., 2010. Viscoelasticity and structure of polystyrene/fumed silica nanocomposites: filler network and hydrodynamic contributions. *Langmuir*, *26*(4), pp.2714-2720.
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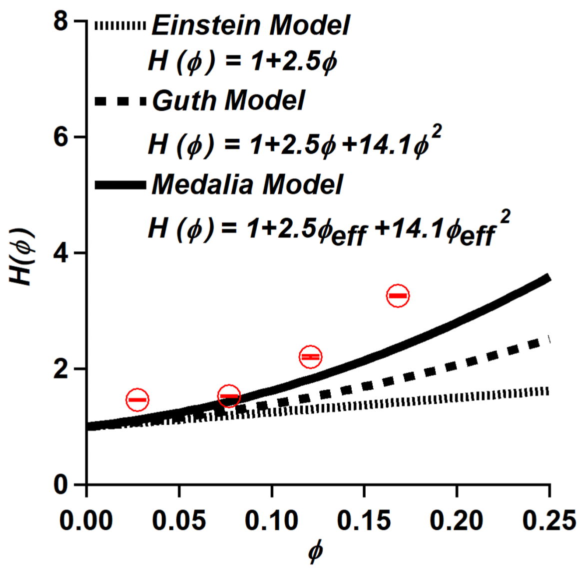
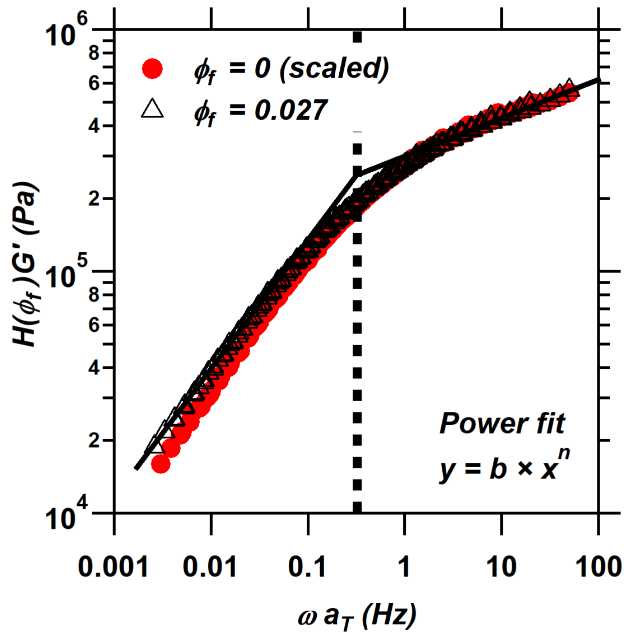
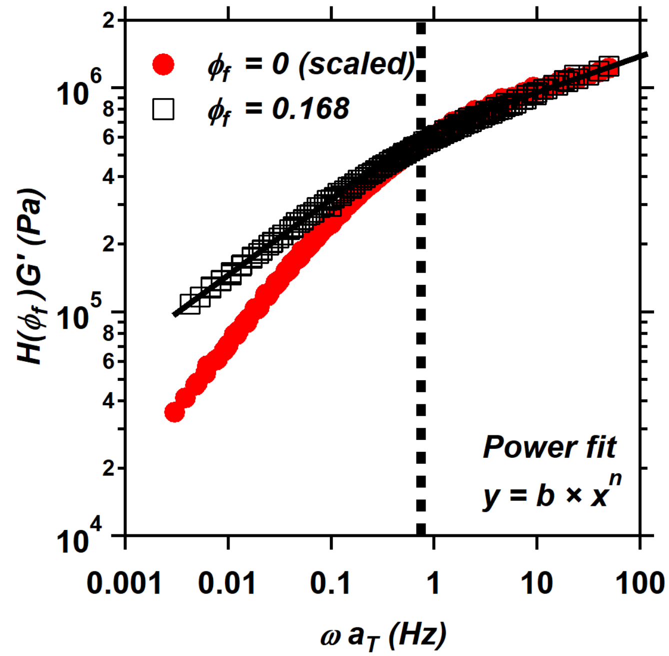




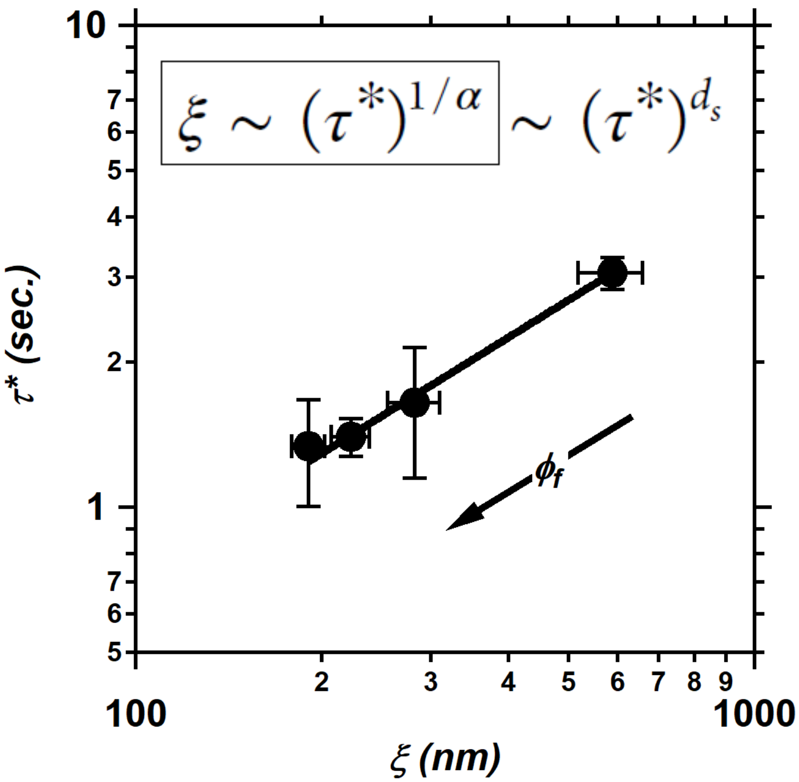


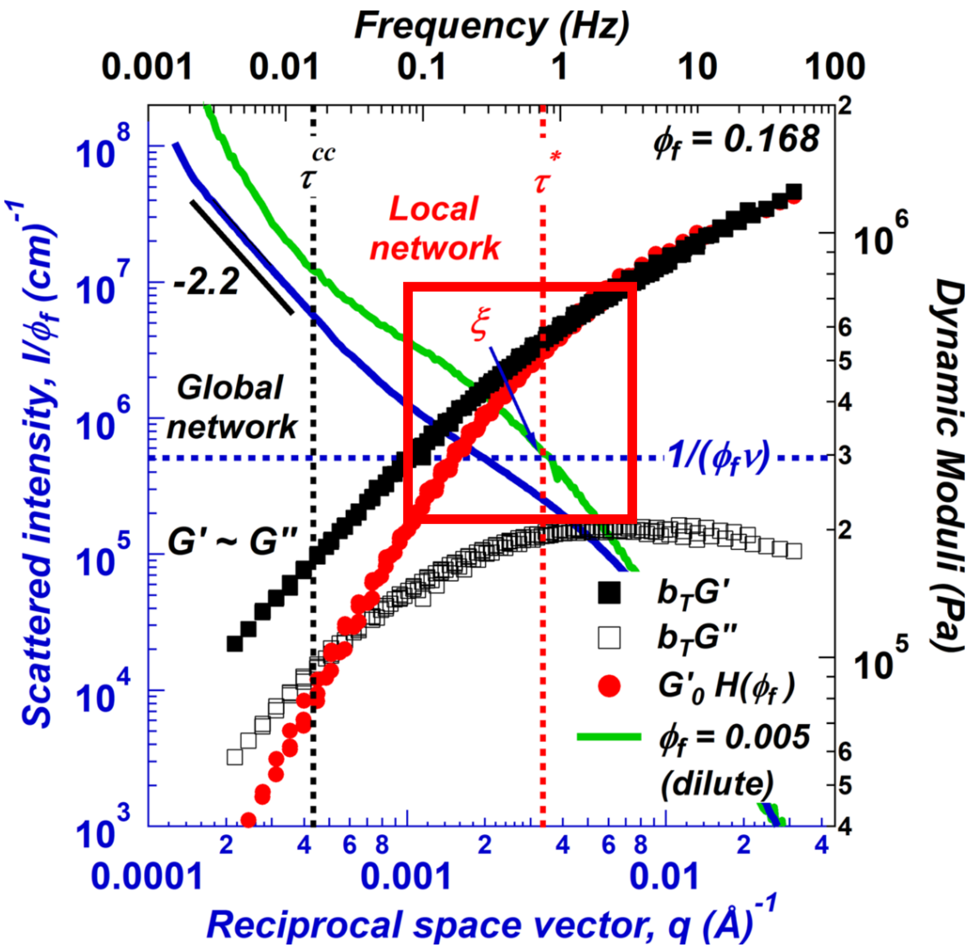
$$G = G_0(1 + K\phi)$$

$$G = G_0(1 + K\phi + K'\phi^2)$$

$$\phi_{\mathrm{eff}}/\phi = \beta = (1+e)/(1+\varepsilon) = (1+\rho DBPA)/(1+\varepsilon)$$

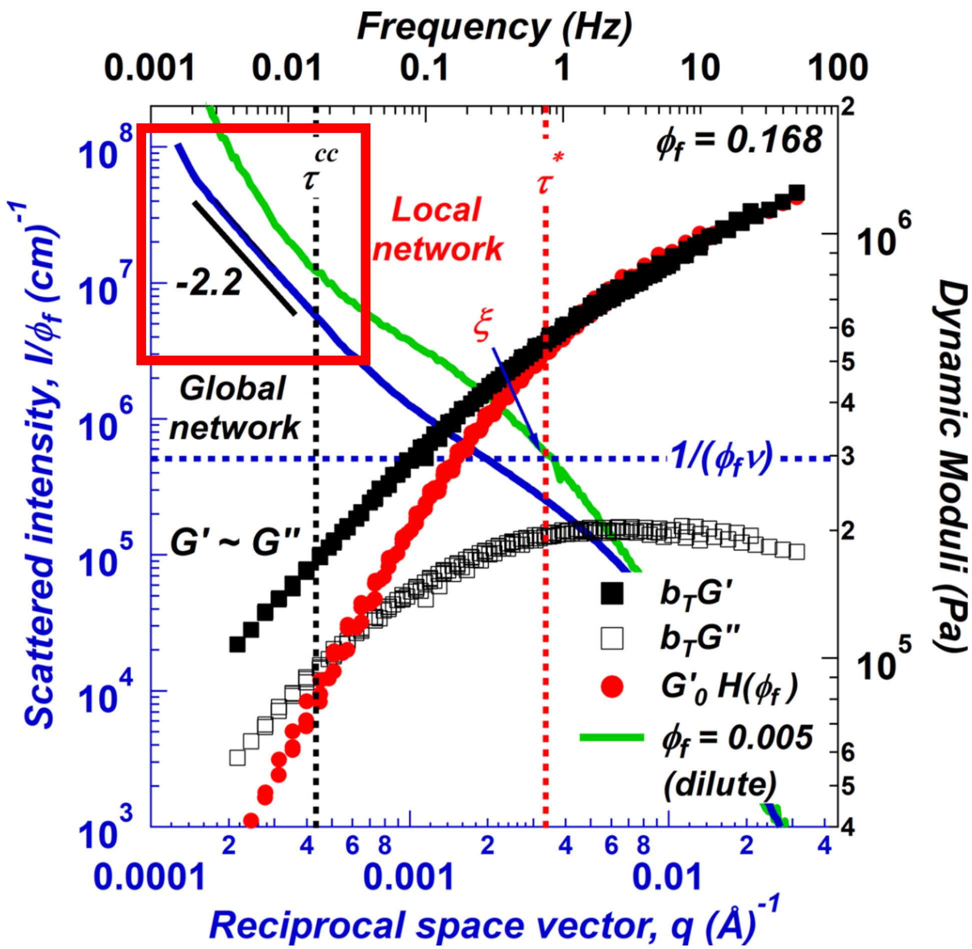
Einstein, 1909 (add Einstein reference here)
H. M. Smallwood, *J. Appl. Phys.* **1944**, *15*, 758.
E. Guth, *J. Appl. Phys.* **1945**, *16*, 20.
S. Wolff, M.-J. Wang, *Rubber Chem. Technol.* **1992**, *65*, 329.
G. Huber, T. A. Vilgis, *Kgk Kautschuk Gummi Kunststoffe* **1999**, *52*, 102.
G. Huber, T. A. Vilgis, *Macromolecules* **2002**, *35*, 9204.

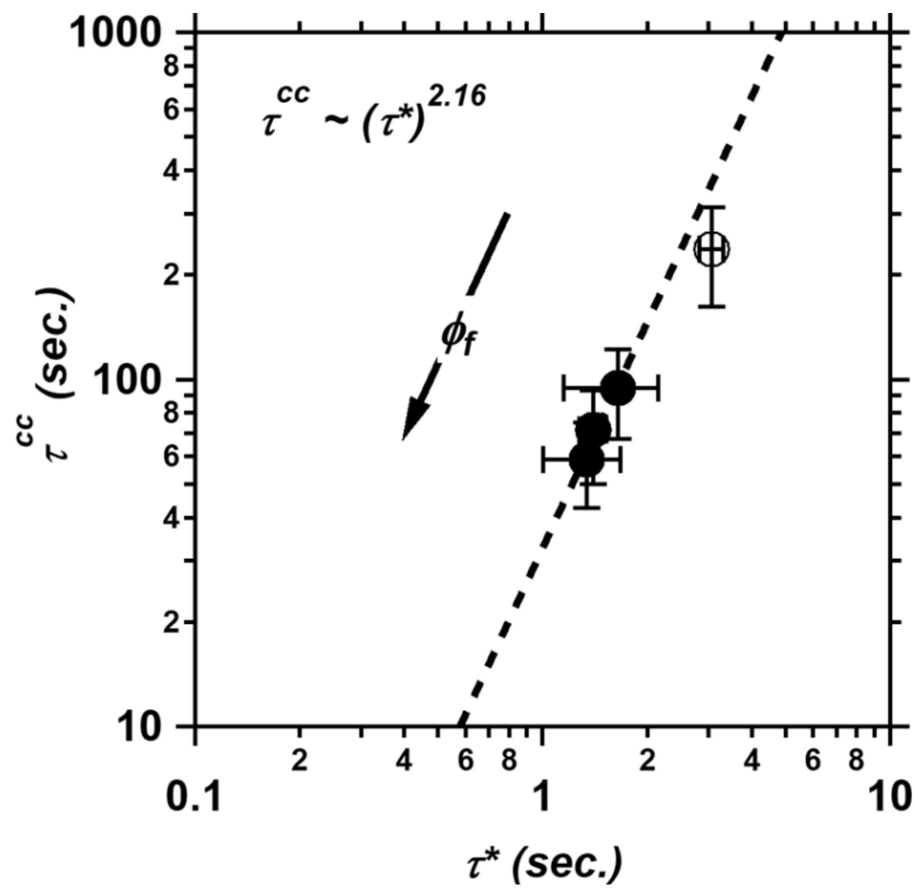




Rishi, K., Beaucage, G., Kuppa, V., Mulderig, A., Narayanan, V., McGlasson, A., Rackaitis, M. and Ilavsky, J., 2018. Impact of an emergent hierarchical filler network on nanocomposite dynamics. *Macromolecules*, *51*(20), pp.7893-7904.

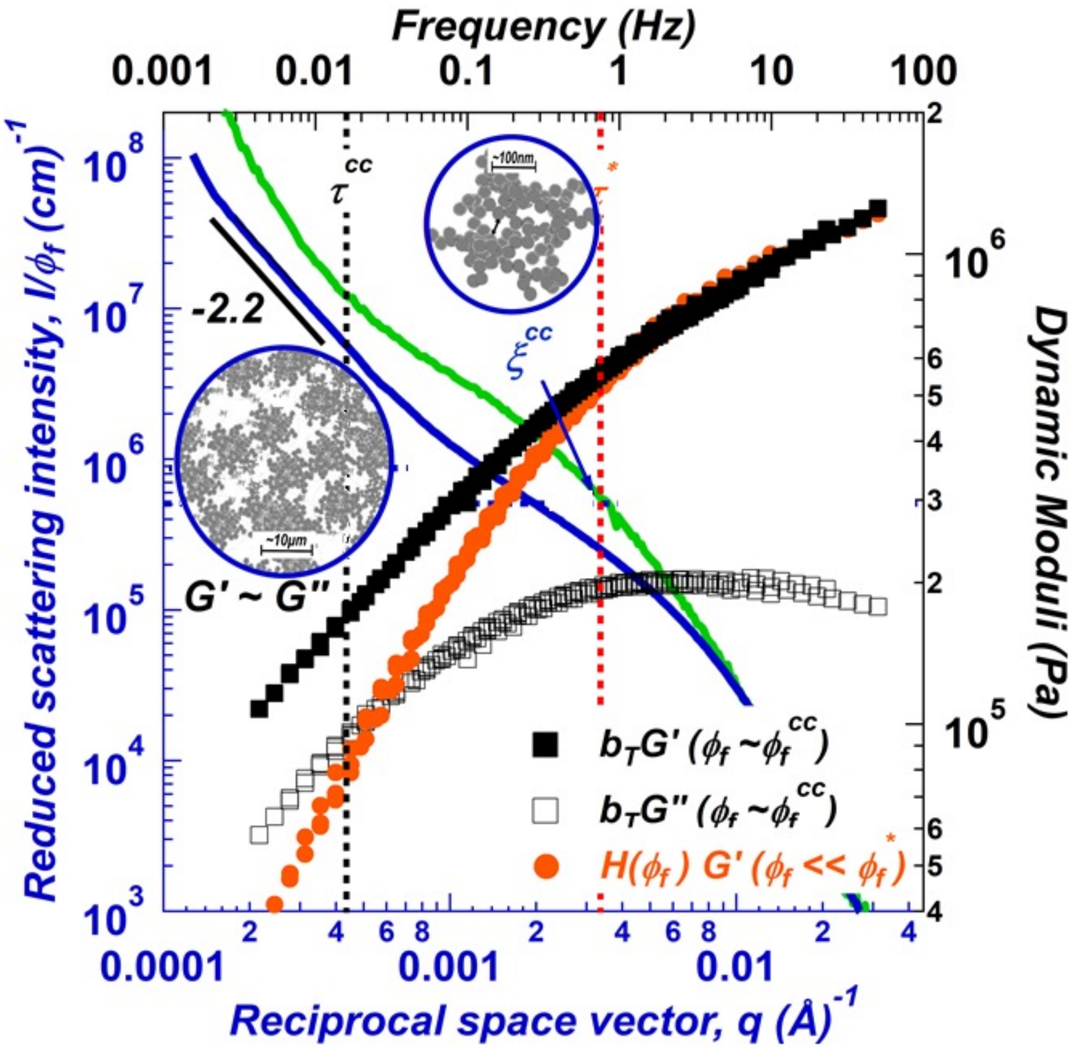
Vilgis, T.A. and Winter, H.H., 1988. Mechanical self similarity of polymers during chemical gelation. *Colloid and Polymer Science*, *266*(6), pp.494-500.





Macroscopic network dynamics is related to nanoscale clusters through the network d_f

Rishi, K., Beaucage, G., Kuppa, V., Mulderig, A., Narayanan, V., McGlasson, A., Rackaitis, M. and Ilavsky, J., 2018. Impact of an emergent hierarchical filler network on nanocomposite dynamics. *Macromolecules*, *51*(20), pp.7893-7904.

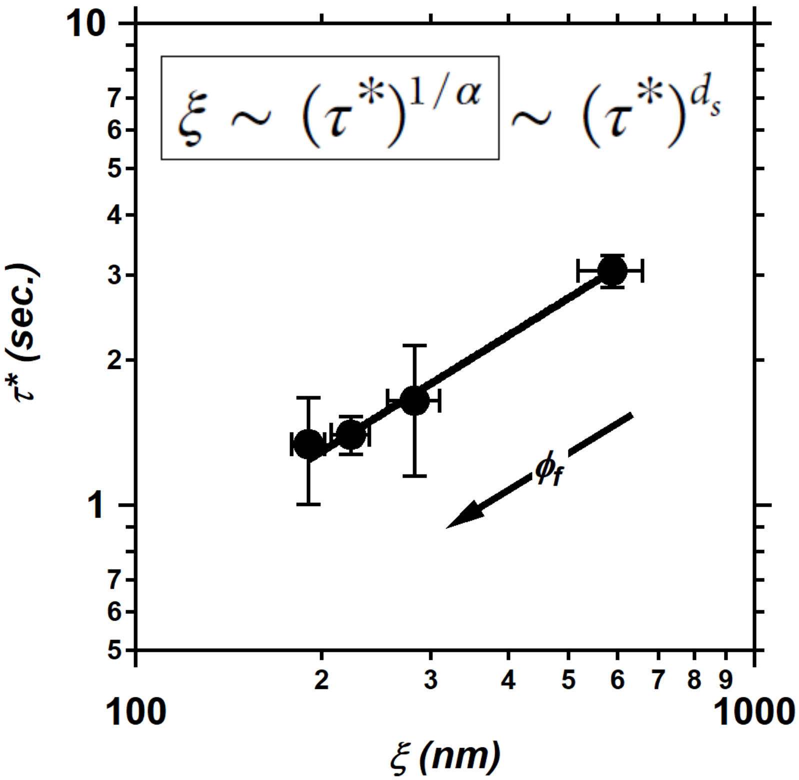


Einstein/Guth-Gold: $G' = G'_0 (1 + 2.5\ \phi_f)$

- At intermediate frequencies, deviation of semi-dilute rheology from dilute under same shear conditions ascertained by scaling dilute sample by Einstein-Smallwood factor
- At low oscillation frequencies, G'~G" indicates gel-like behavior*

Network/Winter
$G' \sim G'' \sim \omega^{\alpha}$

Rishi, K., Beaucage, G., Kuppa, V., Mulderig, A., Narayanan, V., McGlasson, A., Rackaitis, M. and Ilavsky, J., 2018. Impact of an emergent hierarchical filler network on nanocomposite dynamics. *Macromolecules*, *51*(20), pp.7893-7904.



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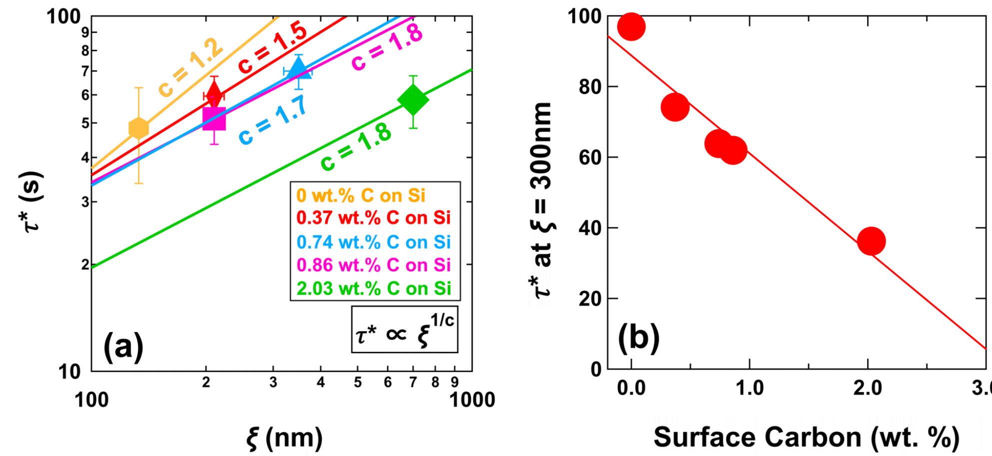
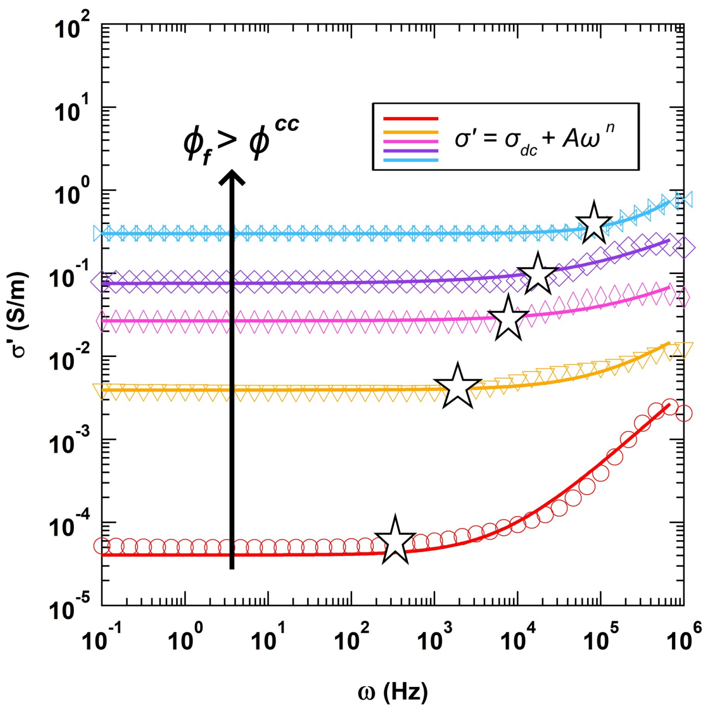
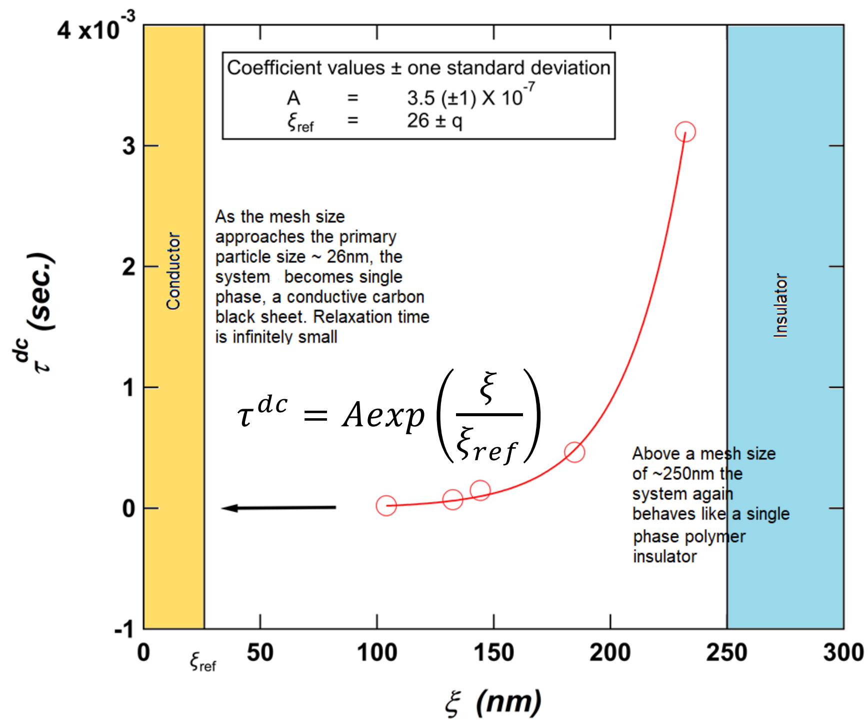


Okoli, U.; Rishi, K.; Beaucage, G.; Kammler, H. K.; McGlasson, A.; Michael, C.; Narayanan, V.; Grammens, J. *Dispersion and Dynamic Response for Flame-Synthesized and Chemically Modified Pyrogenic Silica in Rubber Nanocomposites*; in press 2022. *Polymer.*

Nanoscale control over hierarchical response

The impact of the local filler network on conductivity





Rishi, K., Gogia, A., Cui, X., Beaucage, G., Tang, A., Kumar, J., Kuppa, V. Structure-conductivity relationships in carbon black rubber nanocomposites. In preparation

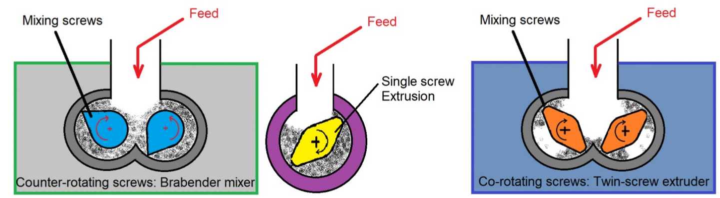
University of Dayton Research Institute

Greg Beaucage, University of Cincinnati gbeaucage@gmail.com

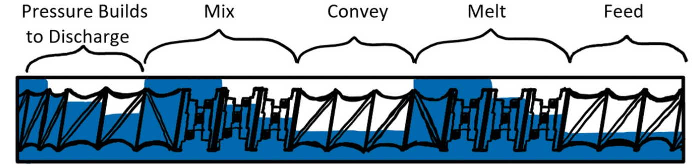
Mixing Geometry: Dispersive (Breakup) versus Distributive (Arrangement) Mixing

N110 Carbon Black in Polystyrene

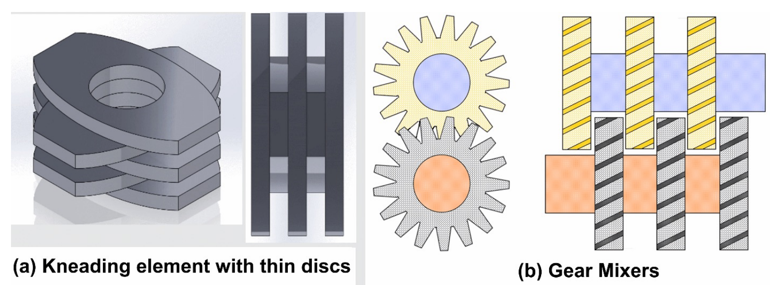
Sample Name	Processing equipment	Screw Speed, $\dot{N}$ (rpm)	Accumulated Strain, γ_{acc}
GM-300	Twin Screw Extruder utilizing Gear Mixers (TSE - GM)	300	2,000
GM-400	Twin Screw Extruder utilizing Gear Mixers (TSE - GM)	400	2,500
KB-300	Twin Screw Extruder utilizing Kneading Blocks (TSE - KB)	300	2,700
KB-400	Twin Screw Extruder utilizing Kneading Blocks (TSE - KB)	400	3,510
SSE	Single Screw Extruder	30	2,020
Mixer	Brabender Mixer with Banbury blades	60	1,575



(a) (b) (c)



(d)


(a) Kneading element with thin discs
(b) Gear Mixers

Veigel D, Rishi K, BeaucageG, Galloway J, Campanelli1 H, Ilavsky J, Kuzmenko I, Fickenscher M, Okoli U *Nanocomposite dispersion and distribution in melt mixers* Submitted *Polymer* (2022).

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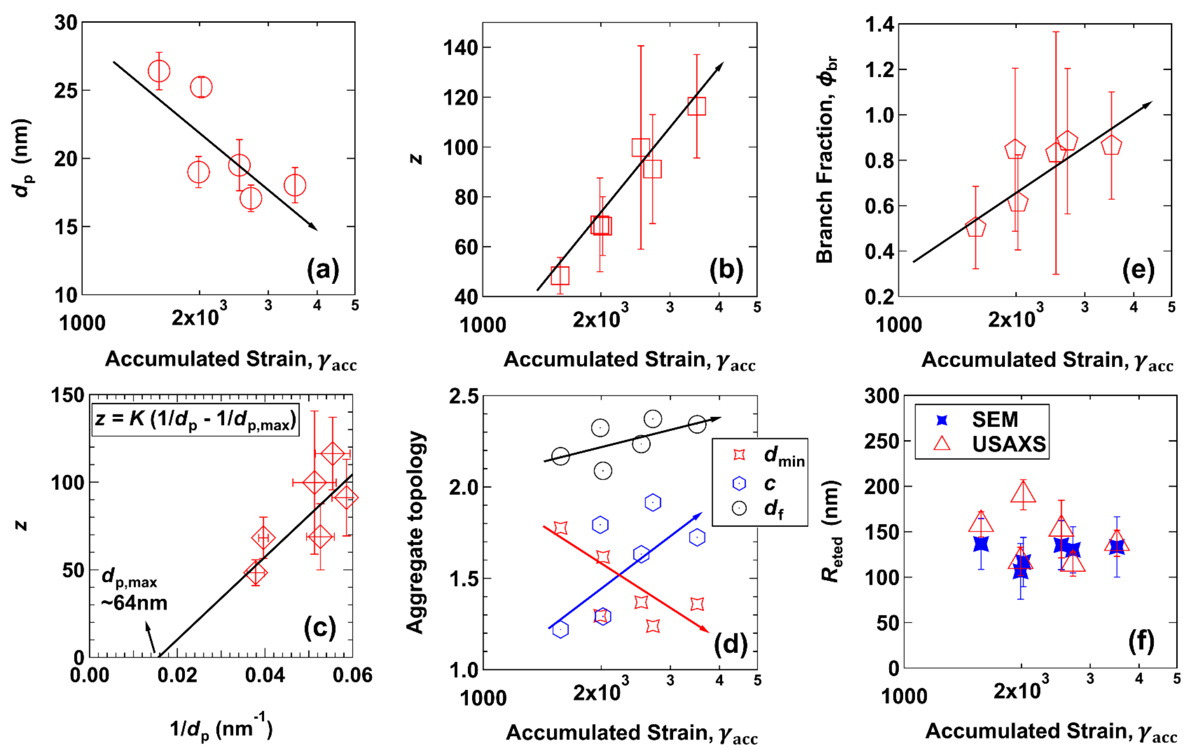
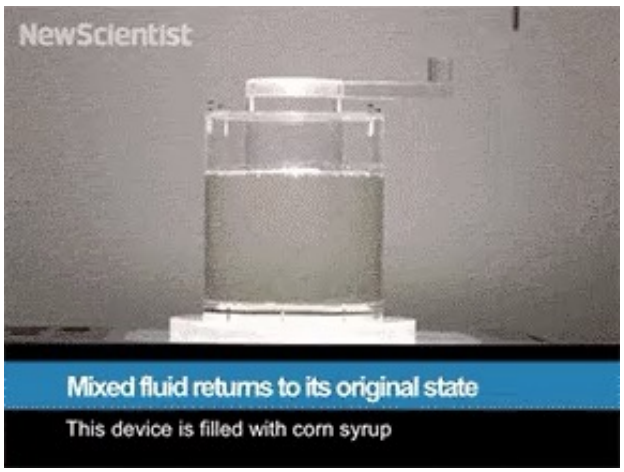
Distributive Mixing ≡ Structural breakup and changes

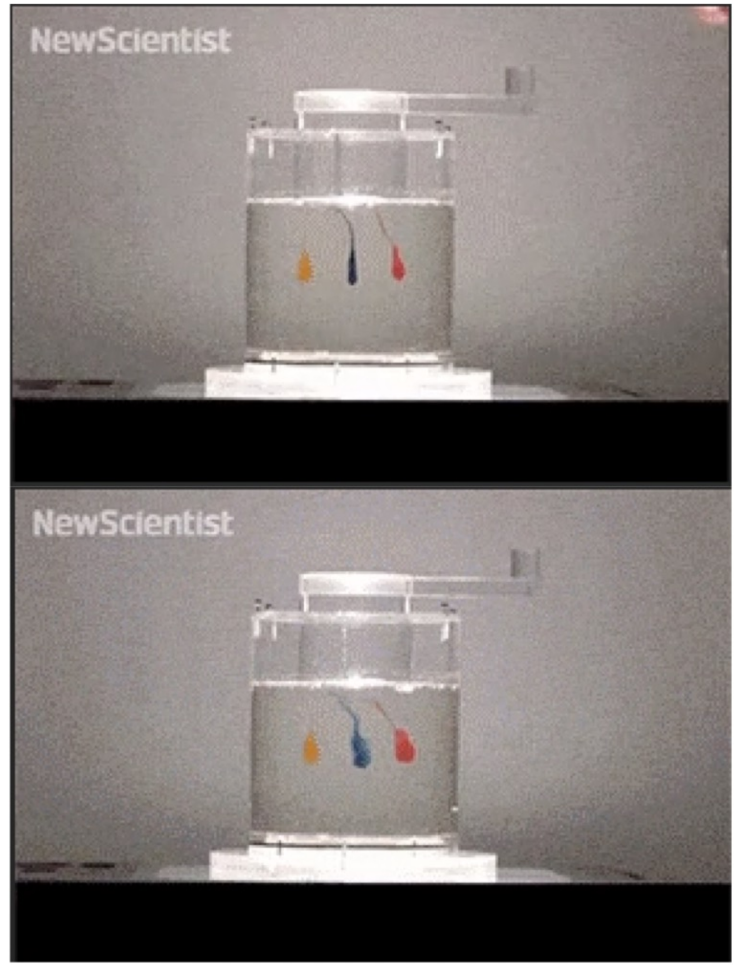


Veigel D, Rishi K, BeaucageG, Galloway J, Campanelli1 H, Ilavsky J, Kuzmenko I, Fickenscher M, Okoli U *Nanocomposite dispersion and distribution in melt mixers* Submitted *Polymer* (2022).

Distributive Mixing doesn't occur in laminar flow (*Re* << 2000 even at high strain rate) (Dispersive breakup can still occur if the particles are large enough)



$$Re = \frac{\rho v G}{\eta}$$



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Mixing Geometry and Shear Rate => Hierarchical Emergence

$$B_2(t) = b^* - \frac{a^*}{\gamma_{acc}}$$

$$\gamma_{acc} = \frac{vt}{G}$$

Smaller gap (G) :: Larger γ_{acc}
Better mixing (Larger B_2)

$$Re = \frac{\rho v G}{\eta}$$

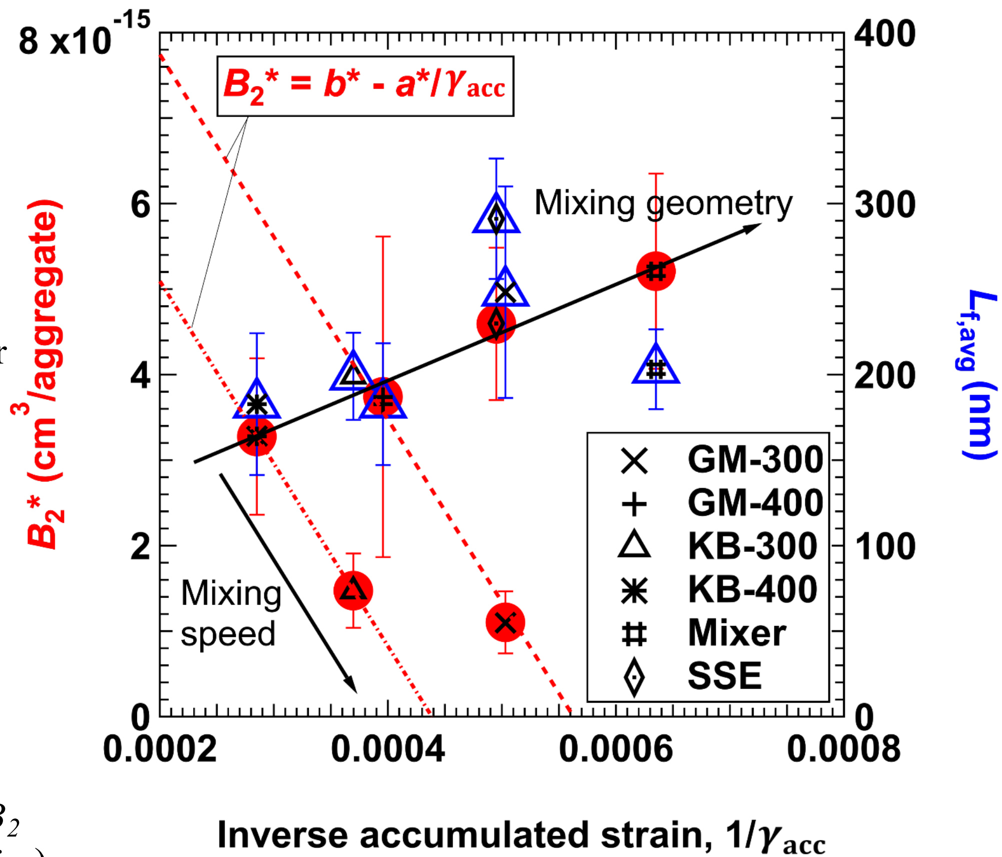
Re small (< 2000) => Laminar Flow
(no distributive mixing but particle breakup or dispersive mixing)

Re large (> 2000) => Turbulent Flow
(distributive and dispersive mixing)

Smaller gap (G) :: Smaller *Re*
Worse mixing (Smaller B_2)

$$B_2(t) = b^* - \frac{a^*}{t\,Re} = b^* - \frac{a^*\eta}{\rho G^2 \gamma_{acc}}$$

(*Viscosity dependence of B_2 was shown earlier*)



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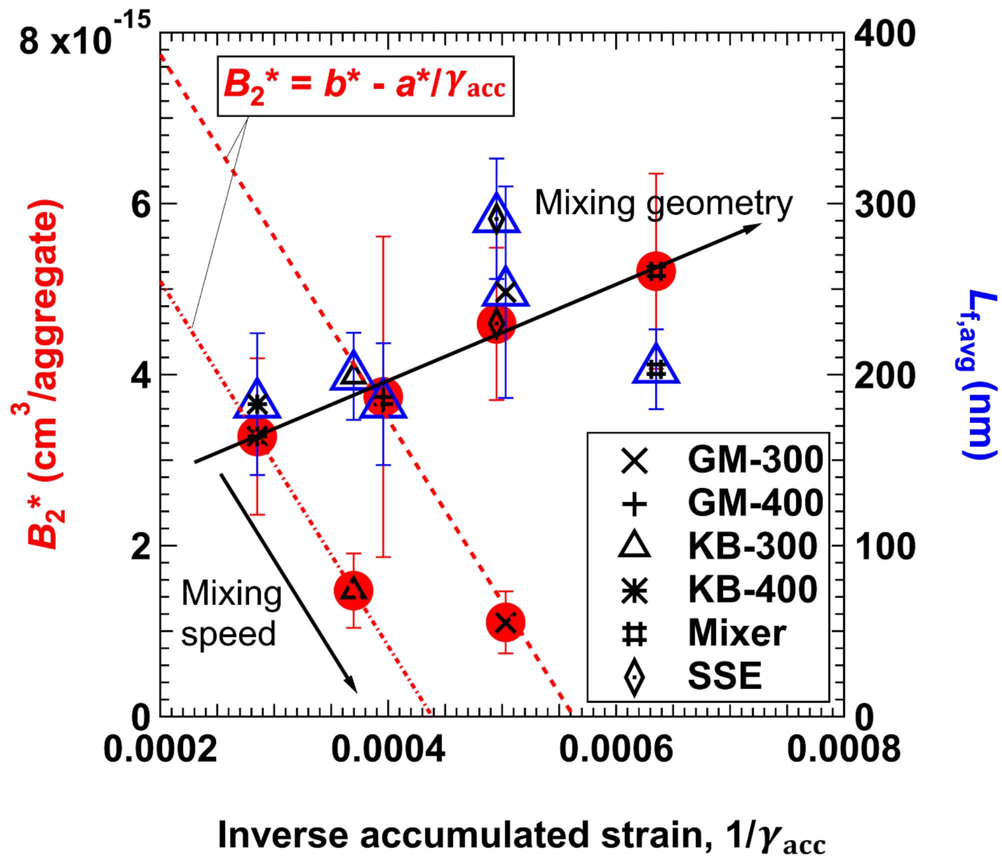
Mixing Geometry and Shear Rate => Hierarchical Emergence

B_2 measures the effective volume per aggregate which increases with breakup (dispersion) and better distribution

$L_{f,avg}$ seems to be most sensitive to distributive mixing and not sensitive to breakup/dispersion of nanoparticles



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Nanoparticle Dispersion in Nanocomposites

Greg Beaucage, Professor of Chemical and Materials Engineering, Cincinnati
Kabir Rishi, PhD NIOSH/CDC Cincinnati Research Laboratory

- There are multiple levels and not 1 that assemble from small to large sizes
- Dispersion has a size-scale dependence
- Large-scale network morphology relies on immiscible nanoscale clustering governed by a balance of thermodynamics and kinetics.
- This constitutes a multiscale physics approach
- The point of compatibilization is to control immiscibility that leads to hierarchical structures not to produce miscibility on the nano-scale
- Hierarchical dynamics can be directly linked to hierarchical structure
- We hope to couple structural measures of thermodynamics and MD modeling to predict structural emergence in complex hierarchical materials

Acknowledgements

lyondellbasell

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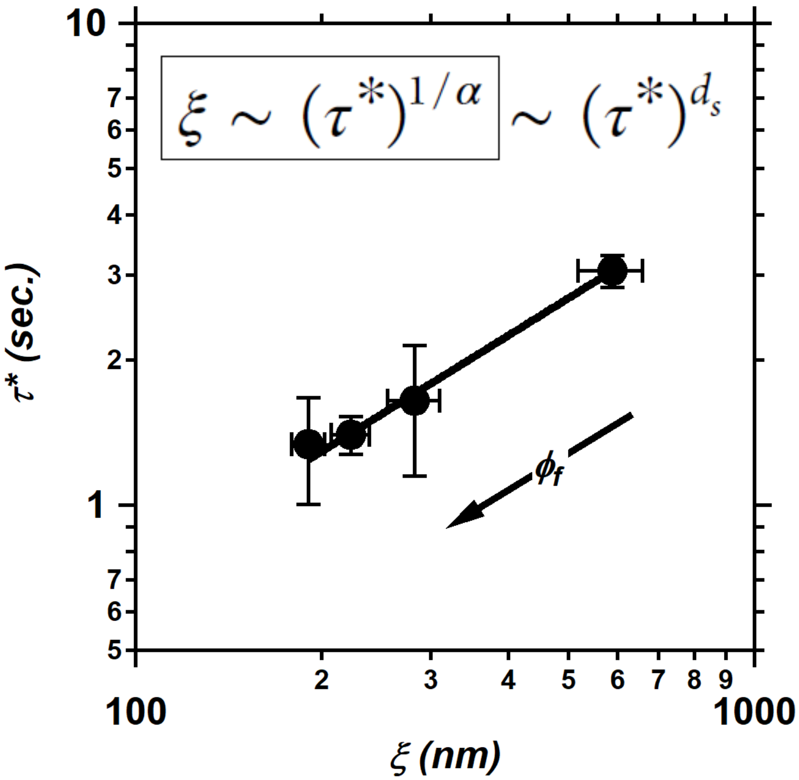

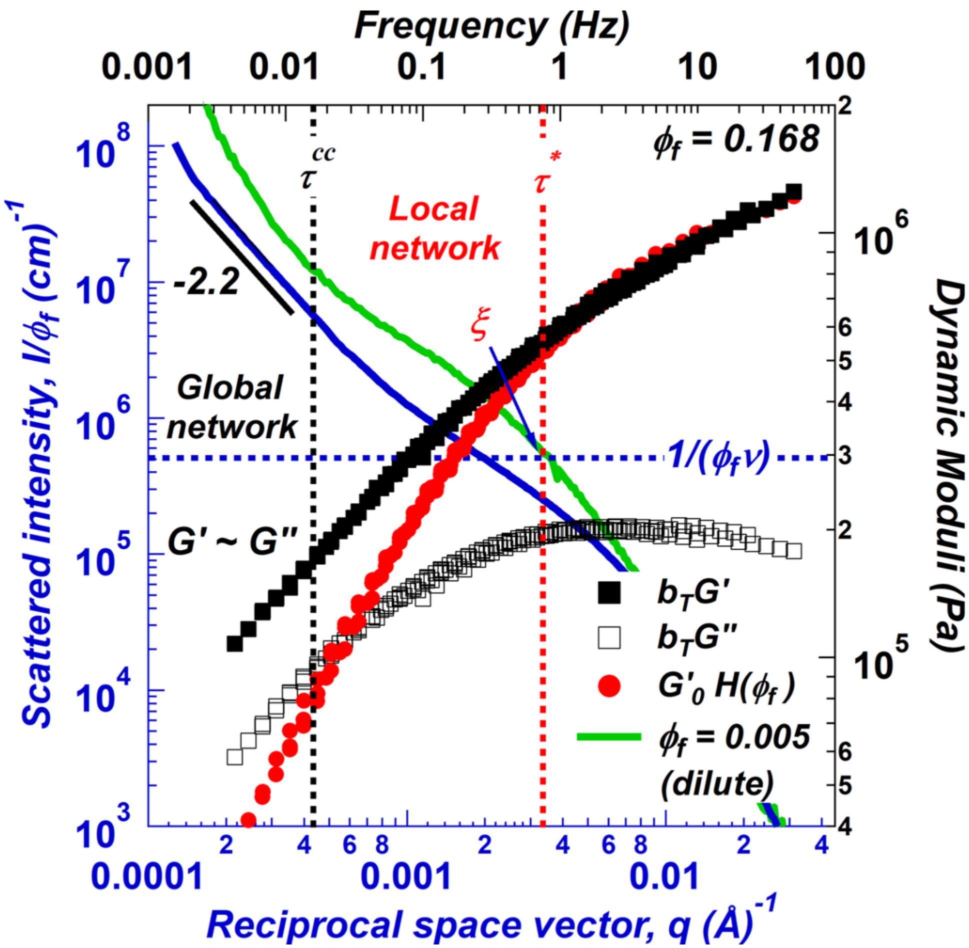

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Modeling of Multi-Hierarchical Emergence

A model for equilibrium clustering and its application to multi-hierarchical growth.

Greg Beaucage, Kabir Rishi, Andrew J Mulderig, **Karsten Vogtt**
University of Cincinnati

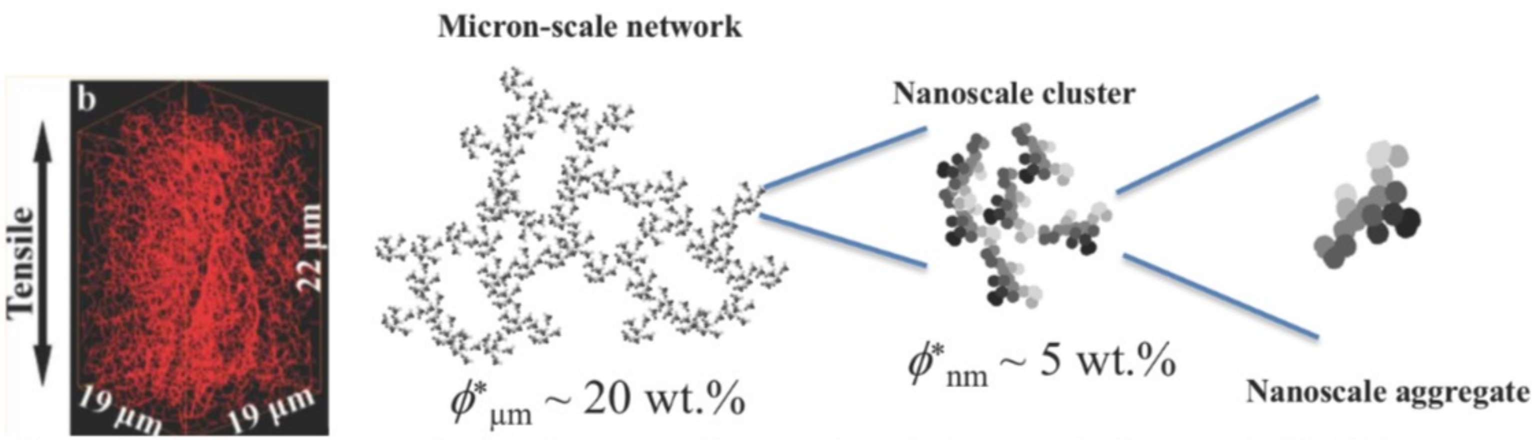

***Figure 1.** a) X-ray tomograph of carbon network in reinforced elastomer by Song et al. [3] b) Illustration of four structural levels in a carbon black/elastomer nanocomposite: micron-scale network; nano- to colloidal-scale cluster; nanoscale aggregate; primary particles. Percolation of the aggregates occurs at about 5 weight percent and leads to enhanced dynamic mechanical properties, while percolation of the clusters into a micron-scale network occurs at about 20 weight percent and leads to bulk conductivity and tear resistance.*

3. Song, L; Wang, Z; Tang, X.; Chen, L.; Chen, P.; Yuan, Q.; Li, L. *Visualizing the Toughening Mechanism of Nanofiller with 3D Xray Nano-CT: Stress-Induced Phase Separation of Silica Nanofiller and Silicone Polymer Double Networks* Macromolecules **50** 7249-7257 (2017).

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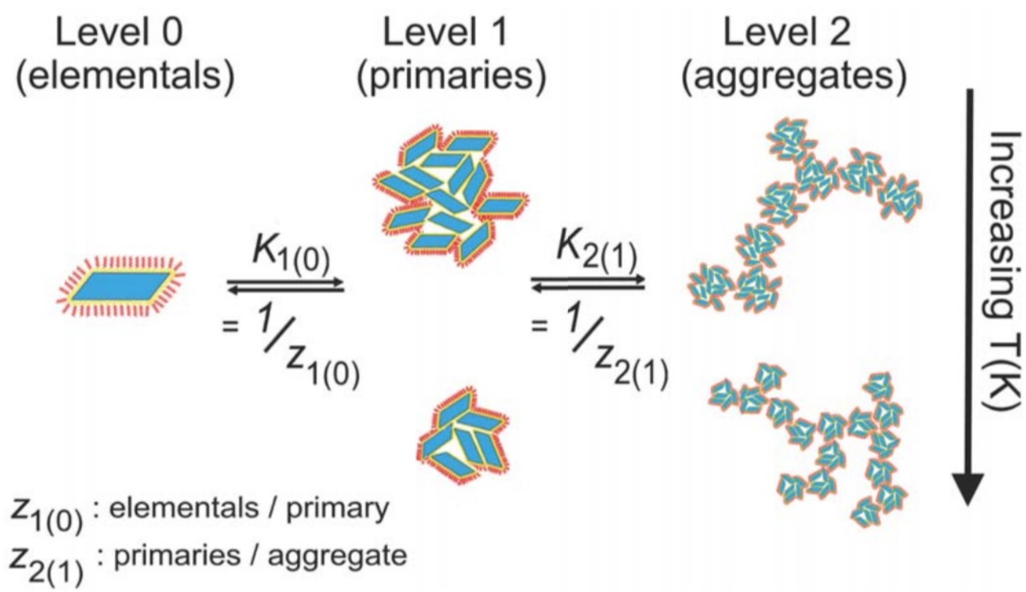

Figure 2. *Pigment nano-crystals (blue parallelogram) can exist as elemental particles or as clusters. Clusters of nano-crystals form primary particles depending on the solubility of the non-ionic surfactant (red hydrophilic/yellow oleophilic surfactant segments). The primary particles can exist as independent clusters at low temperatures near T_{CA}, or as ramified aggregates, above T_{CA} but below T_{LCST} for the surfactant. Aggregation is controlled by the nan-crystal cluster size, temperature, and bond enthalpy. [1]*

1. Rishi K; Mulderig A; Beaucage G; Vogtt K; Jiang H *Thermodynamics of Hierarchical Aggregation in Pigment Dispersions* Langmuir **35** 13100-13109 (2019).
2. Vogtt K; Beaucage G; Rishi K; Jiang H; Mulderig *A Hierarchical approach to aggregate equilibria* Phys. Rev. Res. **1** 033081 (2019).

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$$\Delta G_{2(1)} = RT \ln\left({N_1}^T / {N_2}^T\right) = -RT \ln\left(1 / z_{2(1)}\right) = -RT \ln\left(K_{2(1)}\right)$$ **Vogtt Equation (1,2)**

The number distribution of primary clusters, $N_1(n_0)$, consisting of n_0 elemental crystals and the number distribution of aggregates of these primary clusters, $N_2(n_1)$, comprising n_1 primary particles

${N_1}^{\mathrm{T}}$ is the total number of primary particles and
$N_2^T = \int_0^\infty N_2(n_1) \mathrm{d}n_1$ is the total number of aggregates at a given temperature
${N_1}^{\mathrm{T}}/{N_2}^{\mathrm{T}}$ = number average degree of aggregation
$K_{2(1)}$ is the dissociation constant

1. Rishi K; Mulderig A; Beaucage G; Vogtt K; Jiang H *Thermodynamics of Hierarchical Aggregation in Pigment Dispersions* Langmuir **35** 13100-13109 (2019).
2. Vogtt K; Beaucage G; Rishi K; Jiang H; Mulderig *A Hierarchical approach to aggregate equilibria* Phys. Rev. Res. **1** 033081 (2019).

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University of Cincinnati

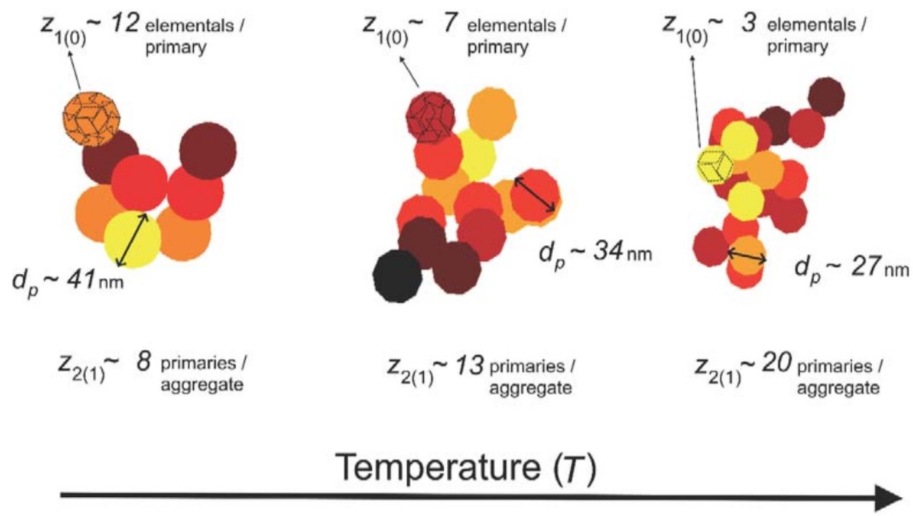
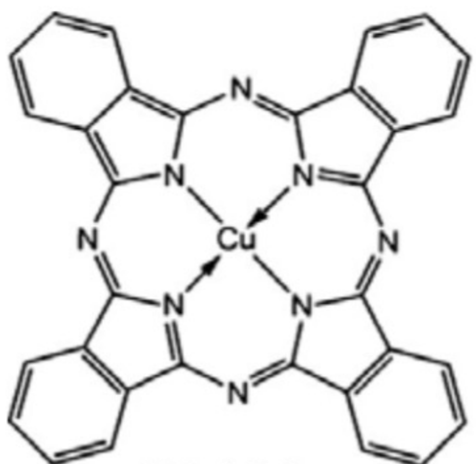


Figure 5. *Rearrangement of simulated[26] nanoparticle pigment PY14 aggregates with increasing temperature. (Simulated structures are based on USAXS data. [17]) At higher temperatures, the overall change in free energy to remove an elemental crystallite from a primary particle is decreased. Simultaneously, the overall change in free energy to remove a primary particle from an aggregate is increased across the temperature series. The total aggregate mass (proportional to the number of elemental particles in an aggregate) is observed to reduce with temperature as the aggregates rearrange to form new equilibrium fractal structures. [2]*

2. Vogtt K; Beaucage G; Rishi K; Jiang H; Mulderig *A Hierarchical approach to aggregate equilibria* Phys. Rev. Res. **1** 033081 (2019).
17. Mulderig, A; Beaucage, G; Vogtt, K; Jiang H; Kuppa V *Quantification of branching in fumed silica* J. Aerosol Sci. **109** 28-37 (2017).

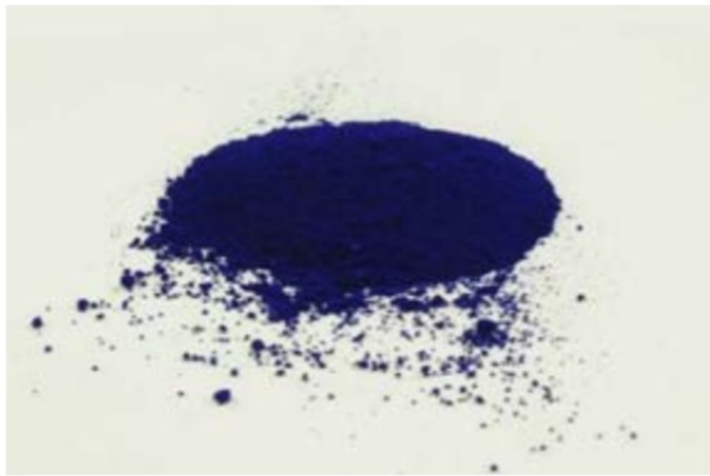
A model for equilibrium clustering and its application to multi-hierarchical growth.

Greg Beaucage, Kabir Rishi, Andrew J Mulderig, **Karsten Vogtt**
University of Cincinnati



PB 15:3

a



b

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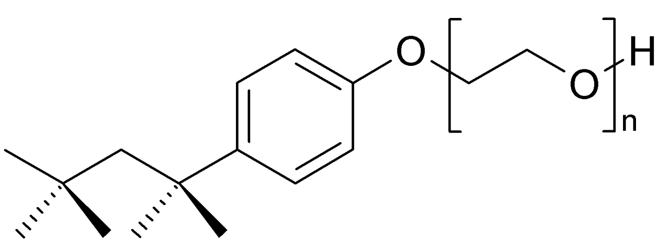

Figure 4. Pigment blue 15:3 (beta copper phthalocyanine).

Triton X-100 surfactant (PEO, hydroxyl and aromatic/alkane end groups.)

A model for equilibrium clustering and its application to multi-hierarchical growth.

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University of Cincinnati

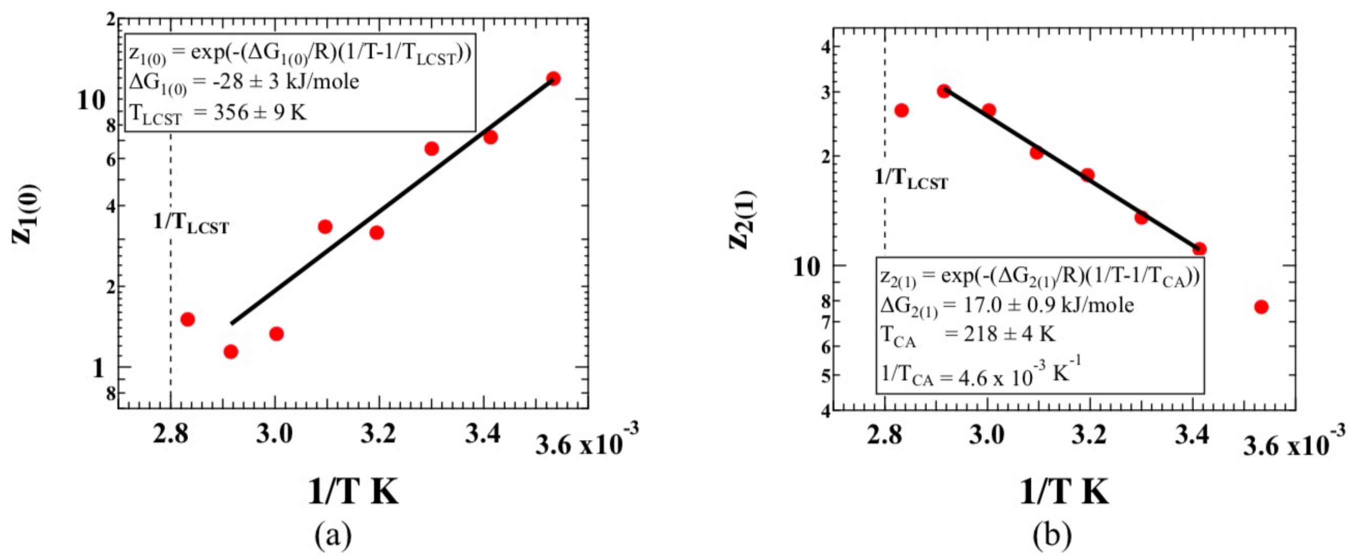

Figure 3. *Thermal behavior for aqueous pigment yellow 14/Triton™ X-100 showing Boltzmann dependence predicted by the Vogtt model [1,2] for reversible equilibria in multi-hierarchical structures. a) Primary nano-crystal cluster degree of aggregation, $z_{1(0)}$, as a function of inverse temperature. The critical temperature is close to the LCST temperature for Triton™ X-100. b) Aggregate degree of aggregation, $z_{2(1)}$, as a function of inverse temperature. The critical aggregation temperature, T_{CA}, is related to the reduction in surface to volume ratio for large primary particles. (T_{CA} is below the freezing point of water.)*

1. Rishi K; Mulderig A; Beaucage G; Vogtt K; Jiang H *Thermodynamics of Hierarchical Aggregation in Pigment Dispersions* Langmuir **35** 13100-13109 (2019).
2. Vogtt K; Beaucage G; Rishi K; Jiang H; Mulderig *A Hierarchical approach to aggregate equilibria* Phys. Rev. Res. **1** 033081 (2019).

A model for equilibrium clustering and its application to multi-hierarchical growth.

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University of Cincinnati

Work in Progress

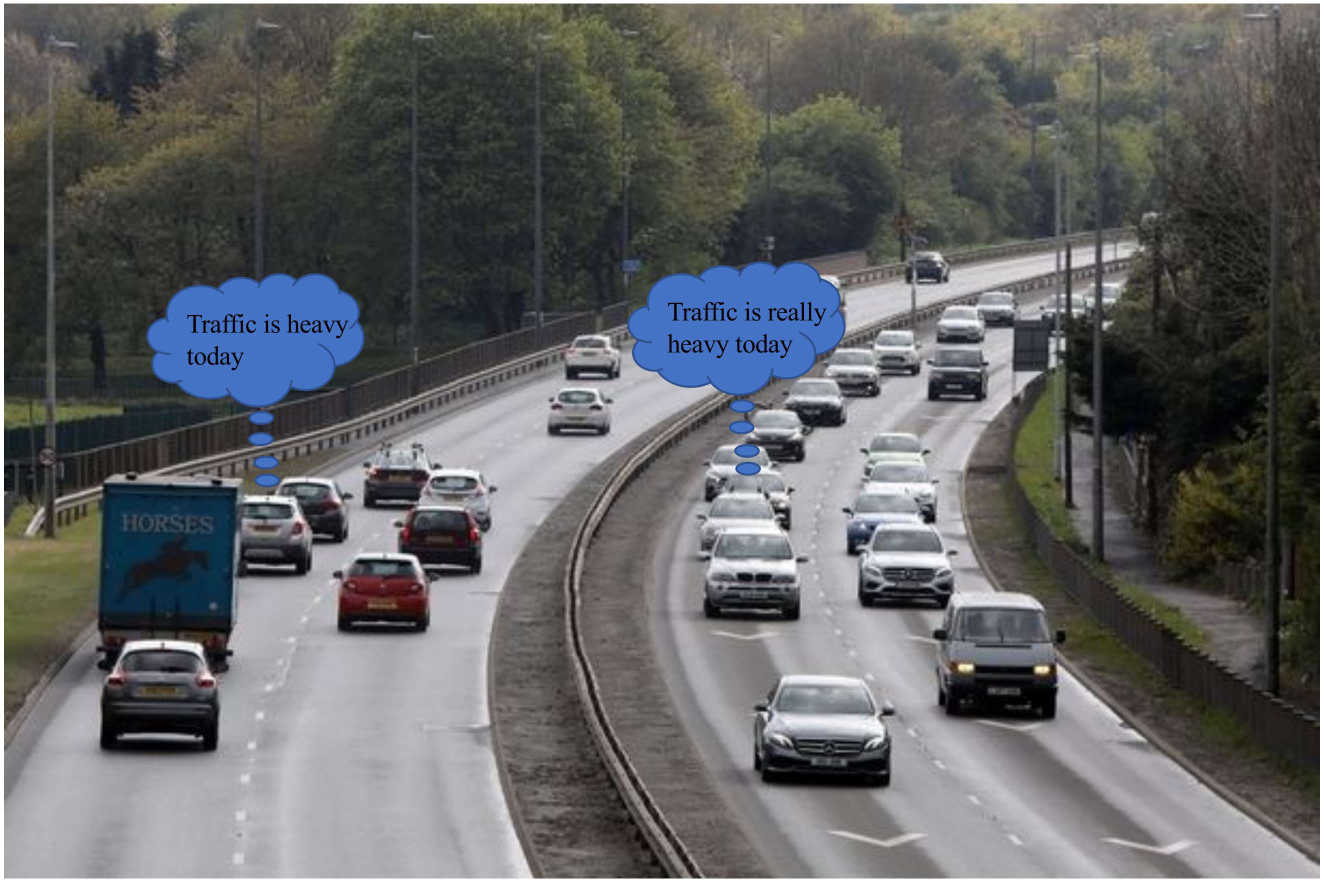
We can measure $z_{3(2)}$, $z_{2(1)}$, and $z_{1(0)}$ in USAXS which yields dissociation free energies $\Delta G_{3(2)}$, $\Delta G_{2(1)}$, $\Delta G_{1(0)}$
These can be used in a simulation of aggregate growth.
But this doesn't yield the topology, only the mass of the different structural levels.

Topology comes from the transport kinetics (reaction limited growth/diffusion limited growth).

1) Specify the particle concentration and size.
2) Distribute the particles allowing for excluded volume.
3) Use LAMMPS MD environment with experimental free energies of aggregation and structural sizes and Langevin dynamics

Thermodynamics: $z_{agglomerate}$; $z_{aggregate}$ (degree of aggregation), d_p, Sauter mean diameter of primary particles
Kinetics: topology, d_f, d_{min}, c, number of branches, branch length

Clustering can lead to locally higher concentrations

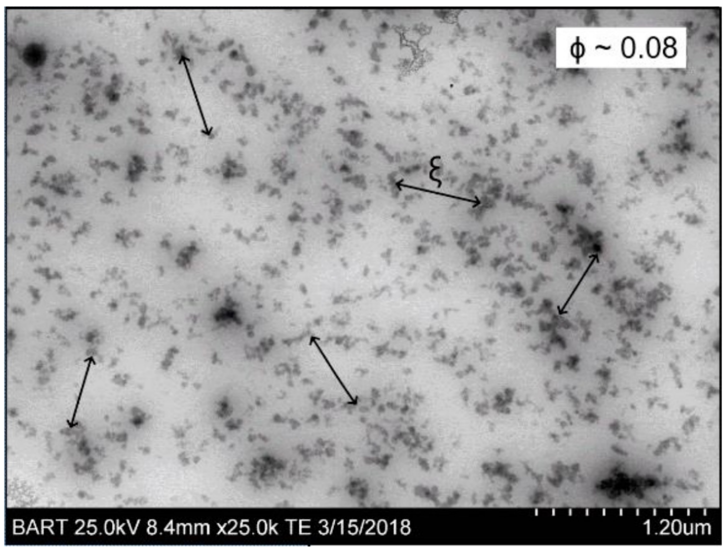


Greg Beaucage, University of Cincinnati gbeaucage@gmail.com

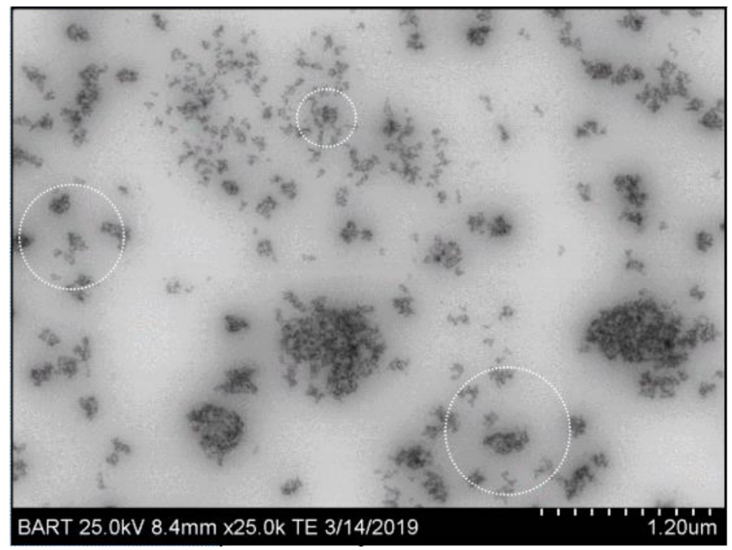
Clustering due to immiscibility

Kinetically dispersed systems

Mean field



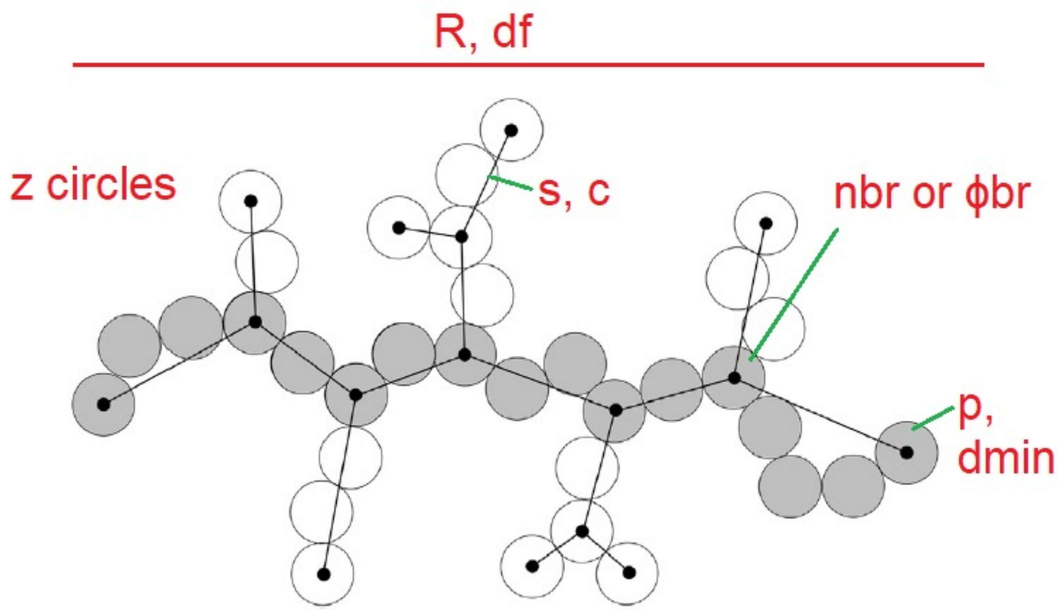
Specific interactions



Greg Beaucage, University of Cincinnati gbeaucage@gmail.com

Descriptors

Aggregate size, R
Primary particle size, d_p
Degree of aggregation, z
Short-circuit path length, p
Connective path length, s
Fractal dimension, d_f
Tortuosity, d_{min}
Connectivity, c
Branch fraction, ϕ_{br}
Branch number, n_{br}



Beaucage, G. Determination of branch fraction and minimum dimension of mass-fractal aggregates. ***Physical Review E – Statistical, Nonlinear, and Soft Matter Physics* 2004**, 70, 031401-1–031401-10.
Rai, D., Beaucage, G., Jonah, E. O., Britton, D. T., Sukumaran, S., & Härting, M. Quantitative investigations of aggregate systems. ***J. Chem. Phys.* 2012**, 137, 044311–1–044311-6.
Ramachandran, R., Beaucage, G., Kulkarni, A. S., McFaddin, D., Merrick-Mack, J., & Galiatsatos, V. Branch content of metallocene polyethylene. ***Macromolecules* 2009**, 42, 4746–4750.

Scattering

Unified Fit : $I(q) = \sum_{i=1}^{n} \left\{ G_i e^{-\frac{q^2 R_{g,i}^2}{3}} + e^{-\frac{q^2 R_{g,i+1}^2}{3}} B_i {q^*}^{-P_i} \right\};$ $q^* = \frac{q}{\mathrm{erf}\left(\frac{1.06 q R_{g,i}}{\sqrt{3}}\right)^3}$ $q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$

Parameters from Unified Fit used to determine topological parameters:

$$d_f = P_2; \quad z = \frac{G_1}{G_2} + 1; \quad d_{min} = \frac{B_2 R_{g,2}^{d_f}}{C_p \Gamma(d_f/2) G_2}; \quad C_p = \text{polydispersity factor}$$

$$R = \frac{R_g}{d_p} = z^{1/d_f} = p^{1/d_{min}} = s^{1/c} \qquad \phi_{br} = \frac{z - p}{p} \qquad n_{br} = \frac{z^{\left[\left(\frac{9}{4d_f} - \frac{5}{4c}\right) + \left(1 - \frac{1}{c}\right)\right]} - 1}{2}$$

Beaucage, G. Approximations Leading to a Unified Exponential/Power-Law Approach to Small-Angle Scattering ***J. Appl. Cryst.*** **1995**, *28* (6), 717–728.

Herrmann, H. J., & Stanley, H. E. The fractal dimension of the minimum path in two- and three-dimensional percolation. ***Journal of Physics A: Mathematical and General*** **1988**, 21, L829–L833.

Meakin, P., Majid, I., Havlin, S., & Stanley, H. E. Topological properties of diffusion limited aggregation and cluster-cluster aggregation. ***Journal of Physics A: Mathematical and General*** **1984**, 17, L975–L981.

Witten, T. A., & Sander, L. M. Diffusion-limited aggregation. ***Physical Review B*** **1983**, 27, 5686–5697.

Sorensen, C. M. Light scattering by fractal aggregates: A review. ***Aerosol Sci. Tech.*** **2001**, 35, 648–687.

Algorithm:

Input z and a sticking probability
Randomly grow aggregates
Compute the scattering parameters, p, R, n_{Br} etc.
Iterate by varying sticking probability until computed matches experimental

A. Mulderig, G. Beaucage, K. Vogtt, H. Jiang and V. Kuppa, Quantification of branching in fumed silica, **J. Aerosol Sci. 2017**, 109, 28–37.

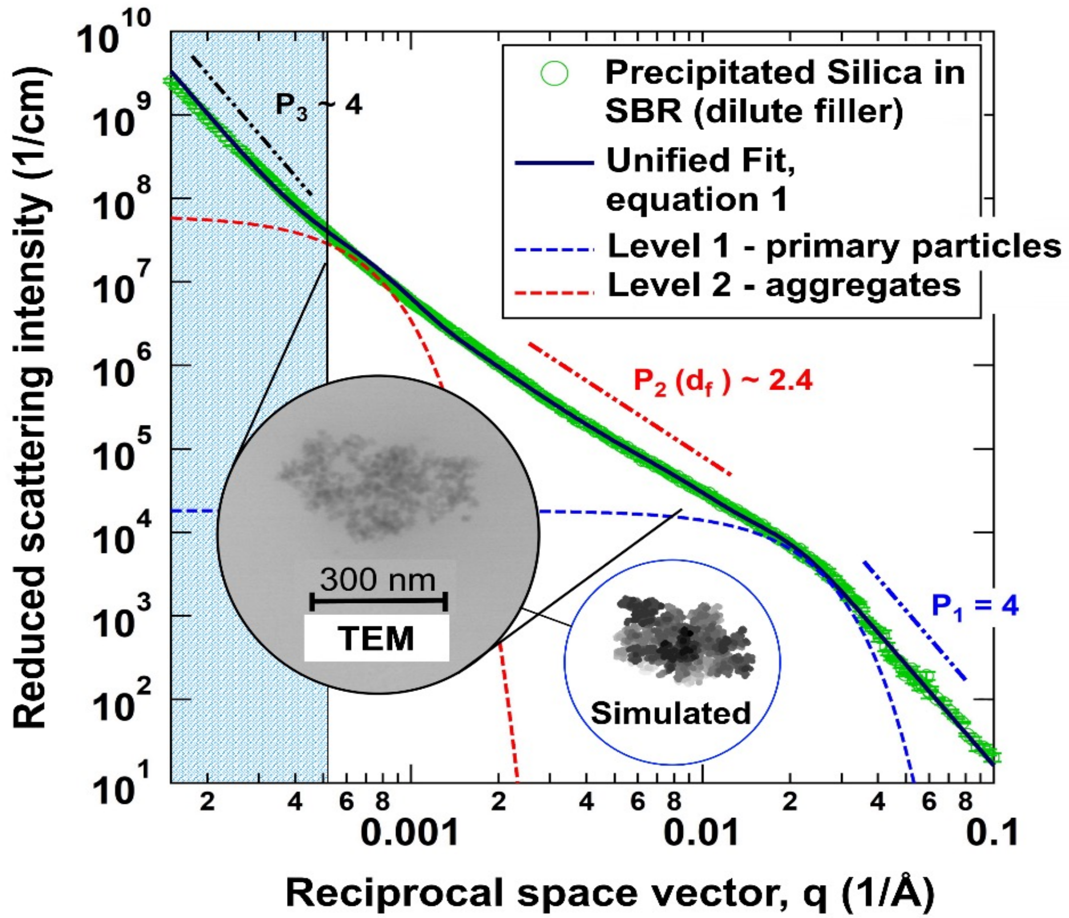
Experimental

Sample	A	B	C	D	E	F
R	19	19	26	24	37	91
d_p (nm)	36	21	17	14	12	10
C_p	1.54	1.53	1.51	1.50	1.52	1.51
z	157	177	483	567	819	6430
p	36	35	46	38	37	91
s	66	75	195	265	819	6430
d_{min}	1.21	1.20	1.17	1.14	1.00	1.00
c	1.41	1.46	1.62	1.75	1.86	1.95
d_f	1.70	1.75	1.90	1.98	1.86	1.95
n_{br} ($f = 3$)	19	23	68	106	409	3215
ϕ_{br}, %	77	80	91	93	95	99

Simulation

z	157	177	483	567	819	6430
Sticking probability	0.40	0.37	0.11	0.23	0.82	1.00
R	18	19	26	29	40	93
p	31	33	45	42	40	93
s	68	75	191	298	819	6430
d_{min}	1.2	1.2	1.17	1.11	1	1
c	1.47	1.48	1.62	1.7	1.82	1.93
d_f	1.76	1.75	1.9	1.89	1.82	1.93
n_{br}	21	26	68	121	409	3215
ϕ_{br}, %	80%	81%	91%	93%	95%	99%

A. Mulderig, G. Beaucage, K. Vogtt, H. Jiang and V. Kuppa, Quantification of branching in fumed silica, **J. Aerosol Sci. 2017**, 109, 28–37.



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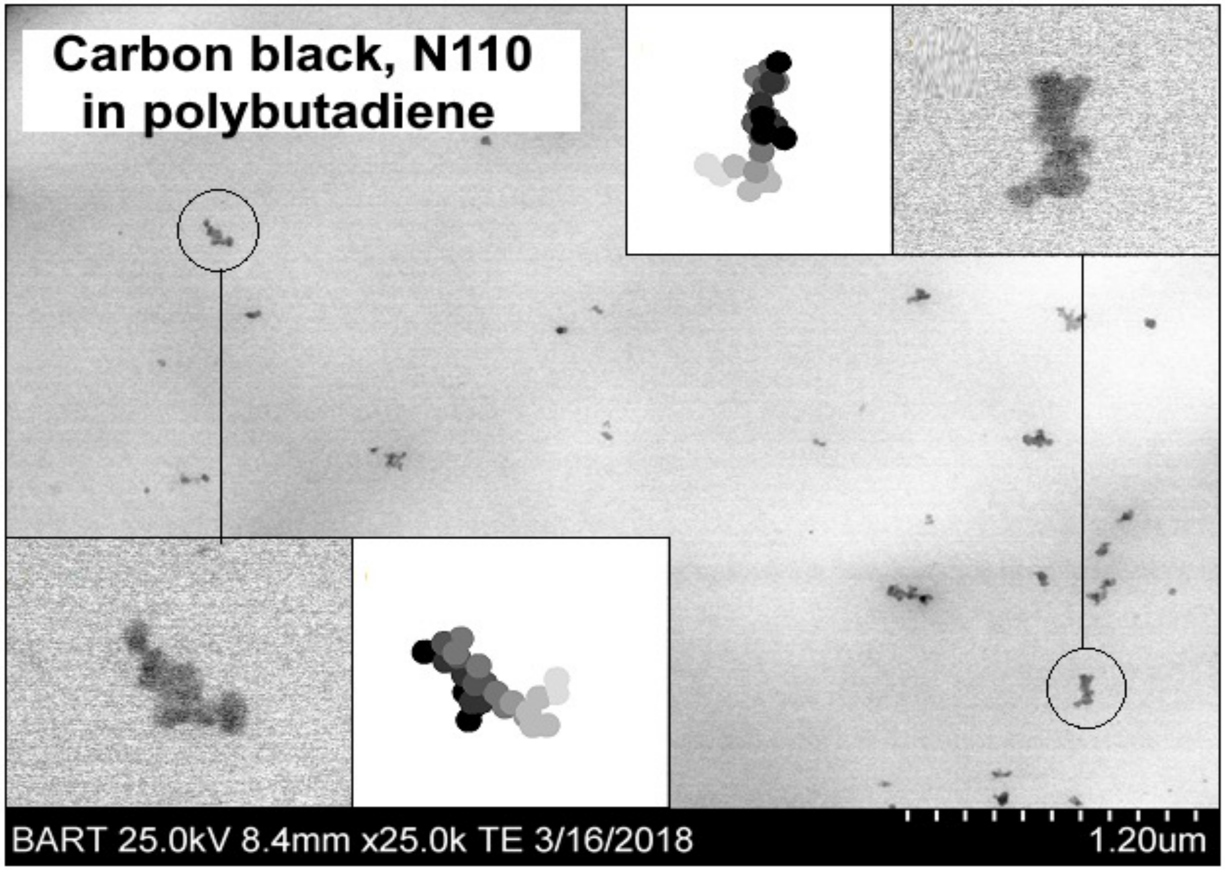
A. Mulderig, G. Beaucage, K. Vogtt, H. Jiang and V. Kuppa, Quantification of branching in fumed silica, **J. Aerosol Sci. 2017**, 109, 28–37.



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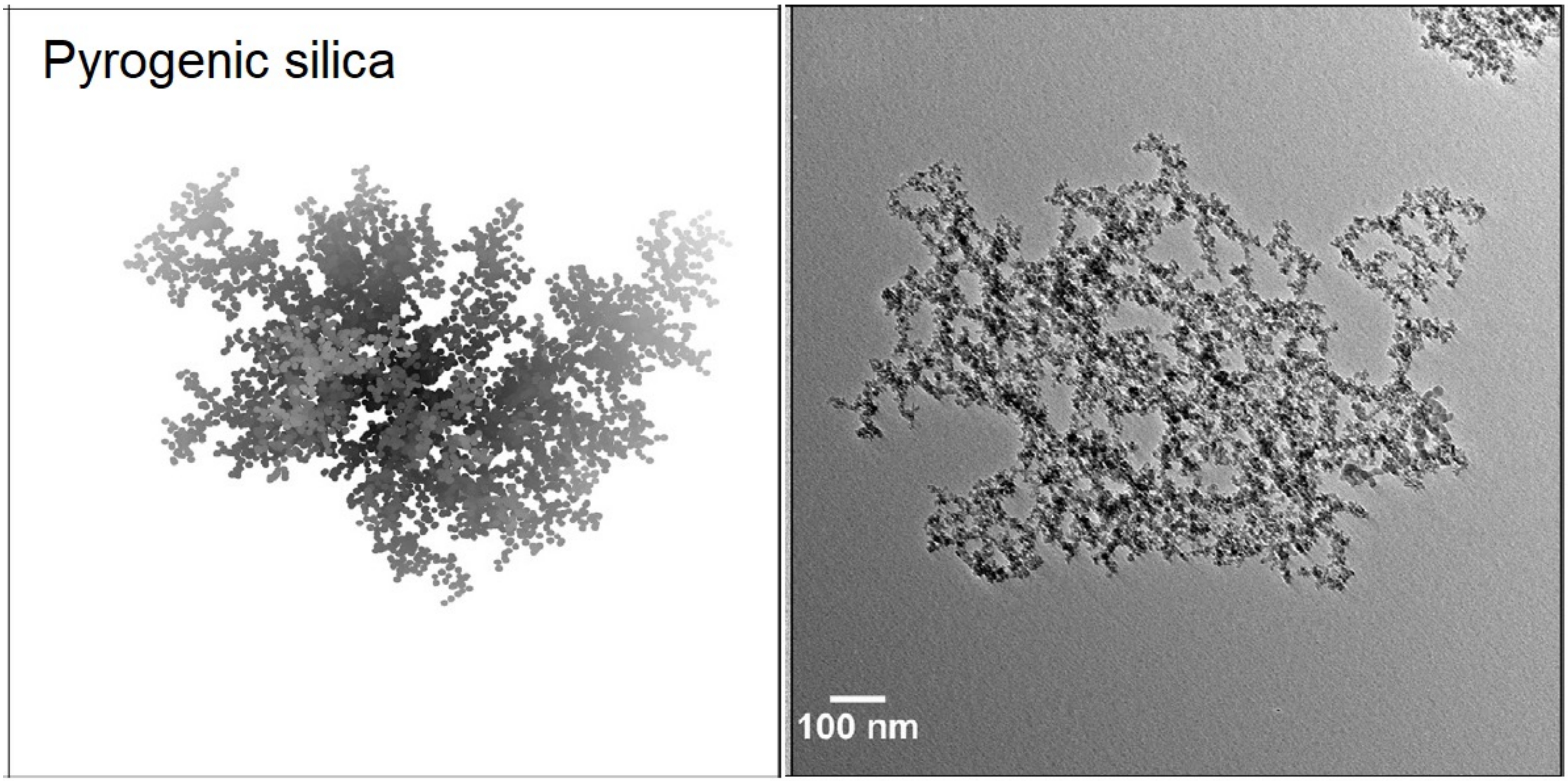
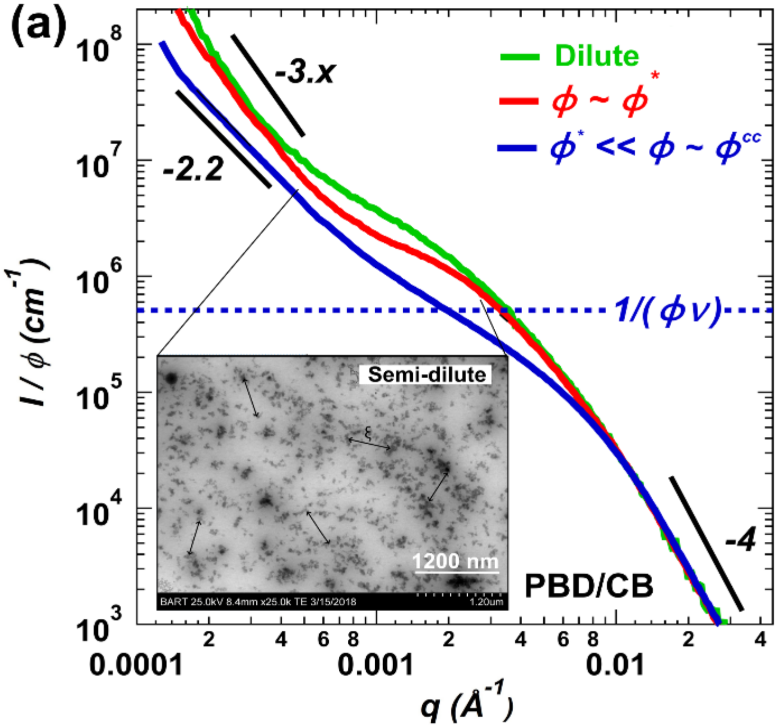
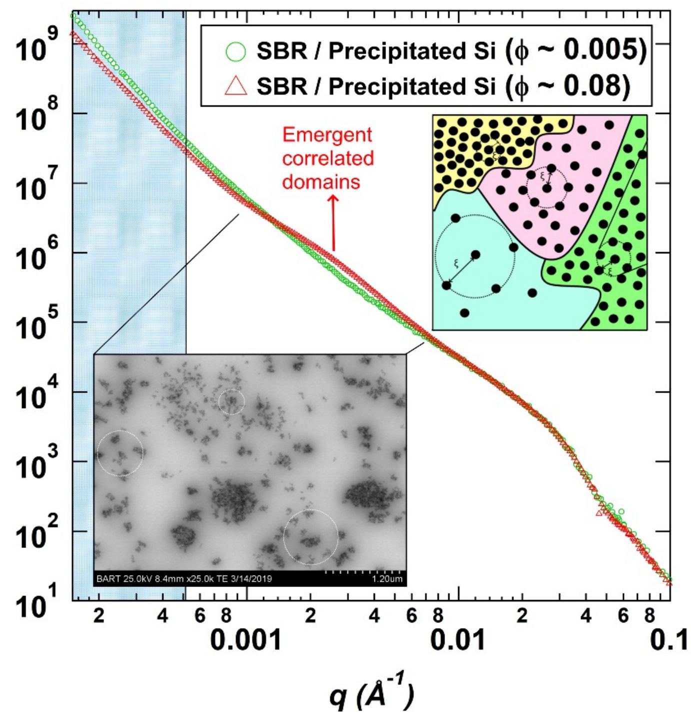
A. Mulderig, G. Beaucage, K. Vogtt, H. Jiang and V. Kuppa, Quantification of branching in fumed silica, **J. Aerosol Sci. 2017**, 109, 28–37.

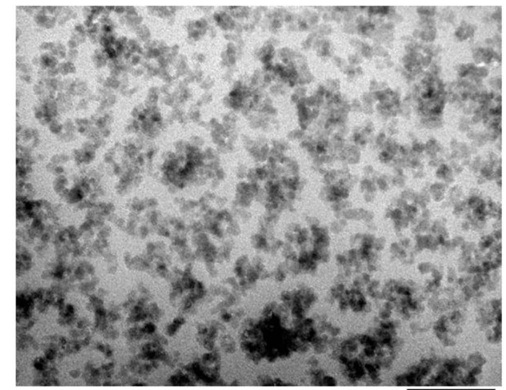


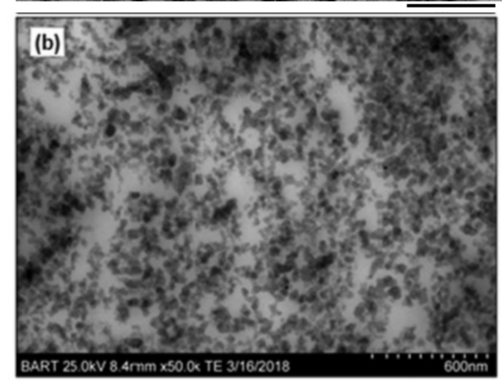
A. Mulderig, G. Beaucage, K. Vogtt, H. Jiang and V. Kuppa, Quantification of branching in fumed silica, **J. Aerosol Sci. 2017**, 109, 28–37.

Mean field (CB) and specific interactions (Silica)





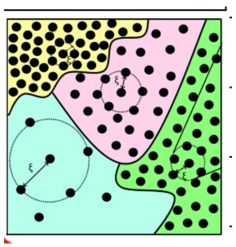


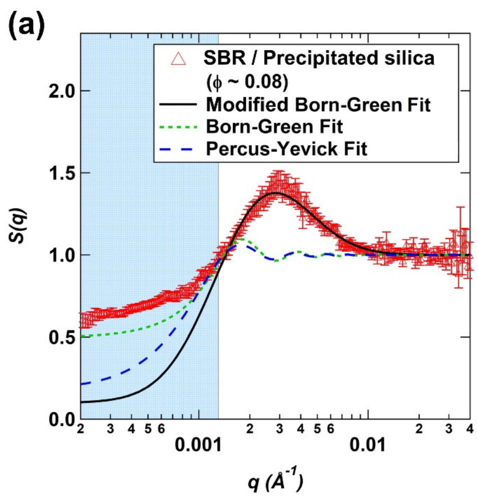


McGlasson, A., Rishi, K., Beaucage, G., Chauby, M., Kuppa, V., Ilavsky, J. and Rackaitis, M., 2020. Quantification of dispersion for weakly and strongly correlated nanofillers in polymer nanocomposites. *Macromolecules*, *53*(6), pp.2235-2248.
Rishi, K., Beaucage, G., Kuppa, V., Mulderig, A., Narayanan, V., McGlasson, A., Rackaitis, M. and Ilavsky, J., 2018. Impact of an emergent hierarchical filler network on nanocomposite dynamics. *Macromolecules*, *51*(20), pp.7893-7904.
Rishi, K.; Pallerla, L.; Beaucage, G.; Tang, A. Dispersion of Surface-Modified, Aggregated, Fumed Silica in Polymer Nanocomposites. J. Appl. Phys. 2020, 127 (17), 174702.

Specific interactions (Silica)

Positive a^* can lead to correlated silica aggregates, New scattering function to fit these curves (solves an impossible task)





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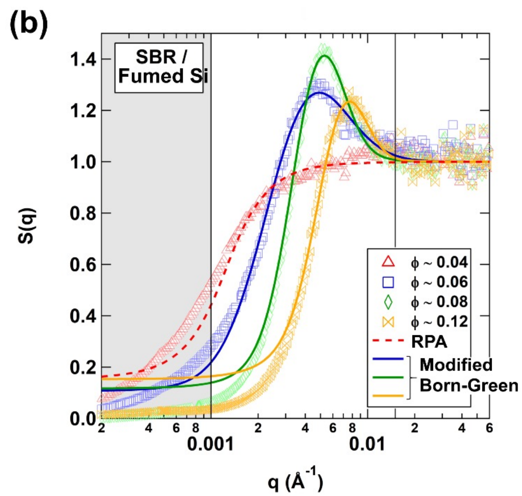

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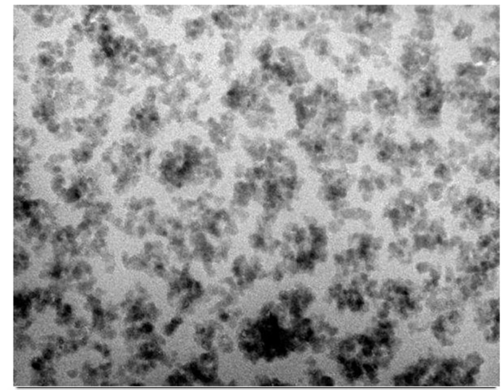

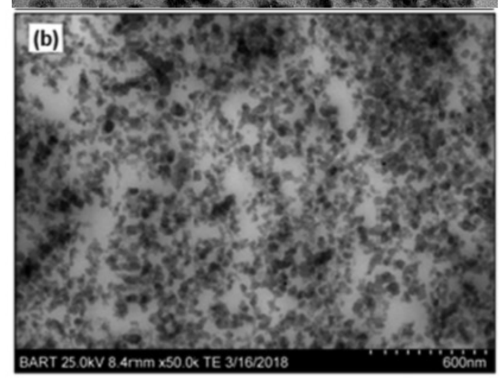

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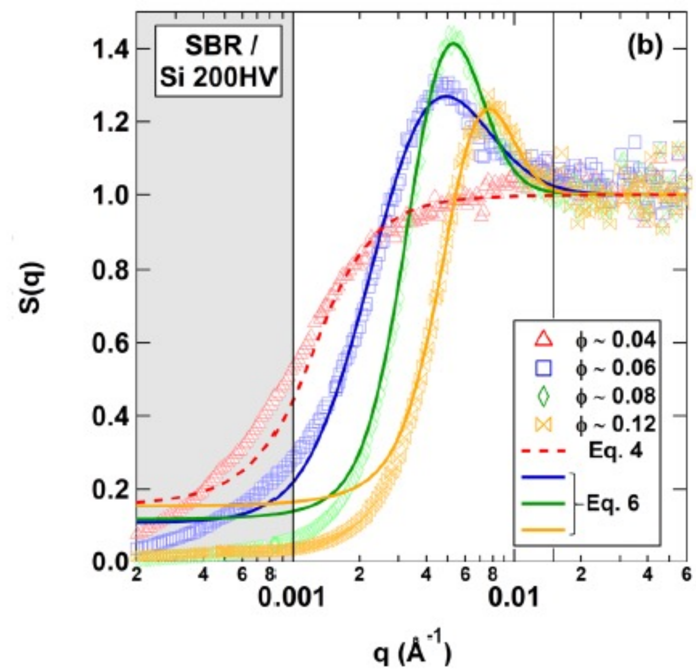
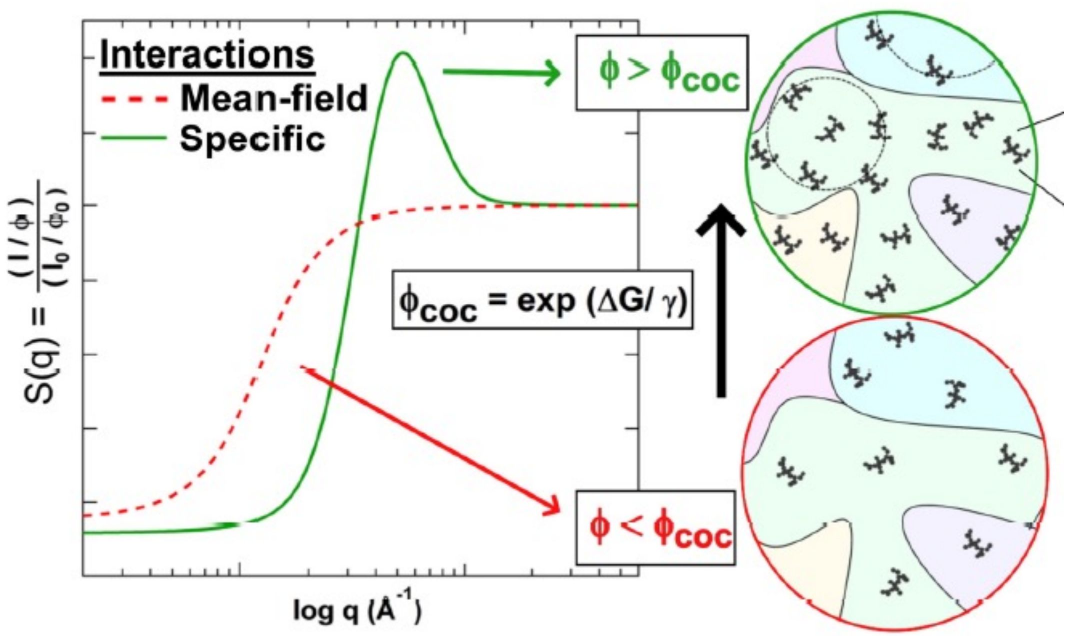
Rishi, K.; Pallerla, L.; Beaucage, G.; Tang, A. Dispersion of Surface-Modified, Aggregated, Fumed Silica in Polymer Nanocomposites. J. Appl. Phys. 2020, 127 (17), 174702.

Critical ordering concentration

Structural ordering is related to the Debye screening length and the dielectric constant of the polymer

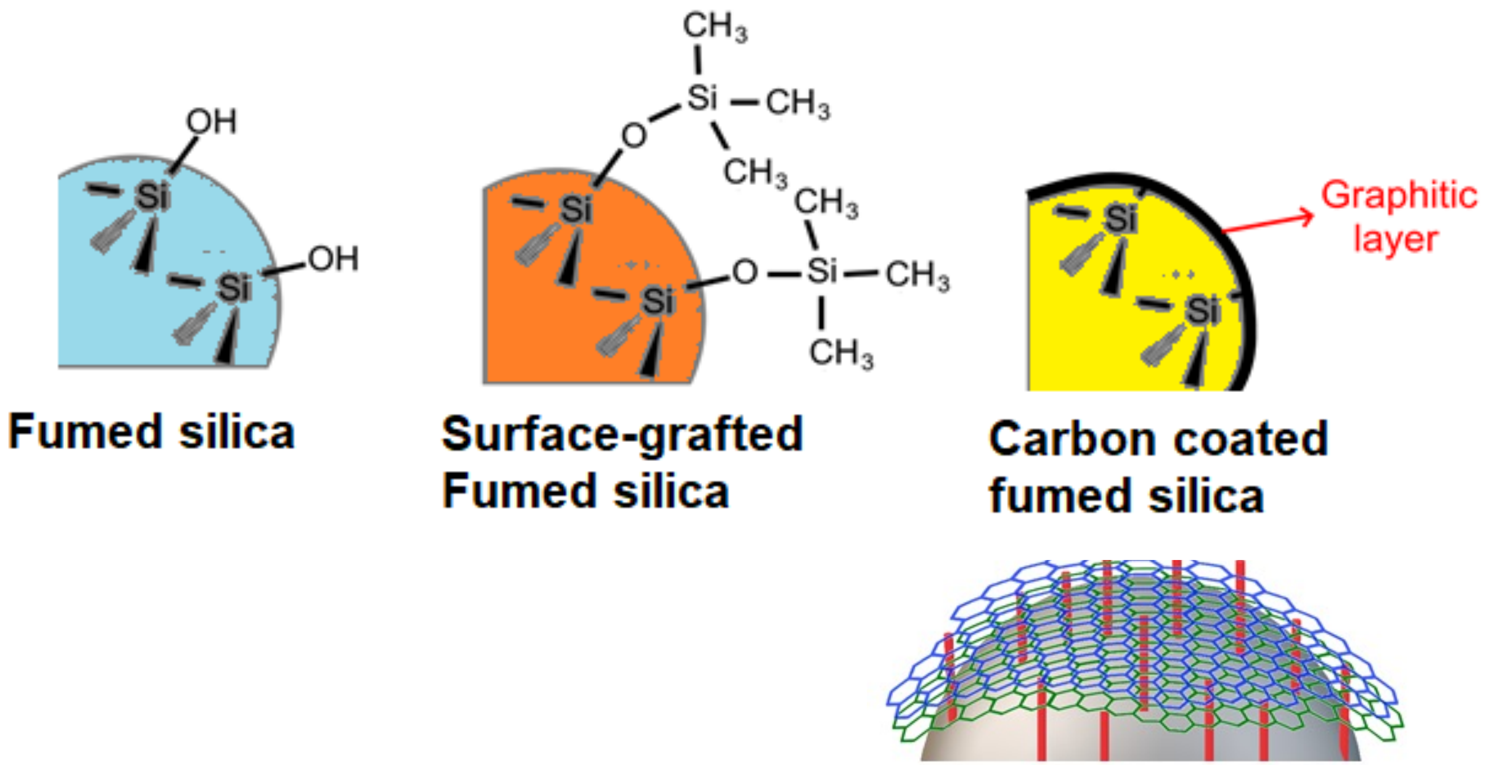




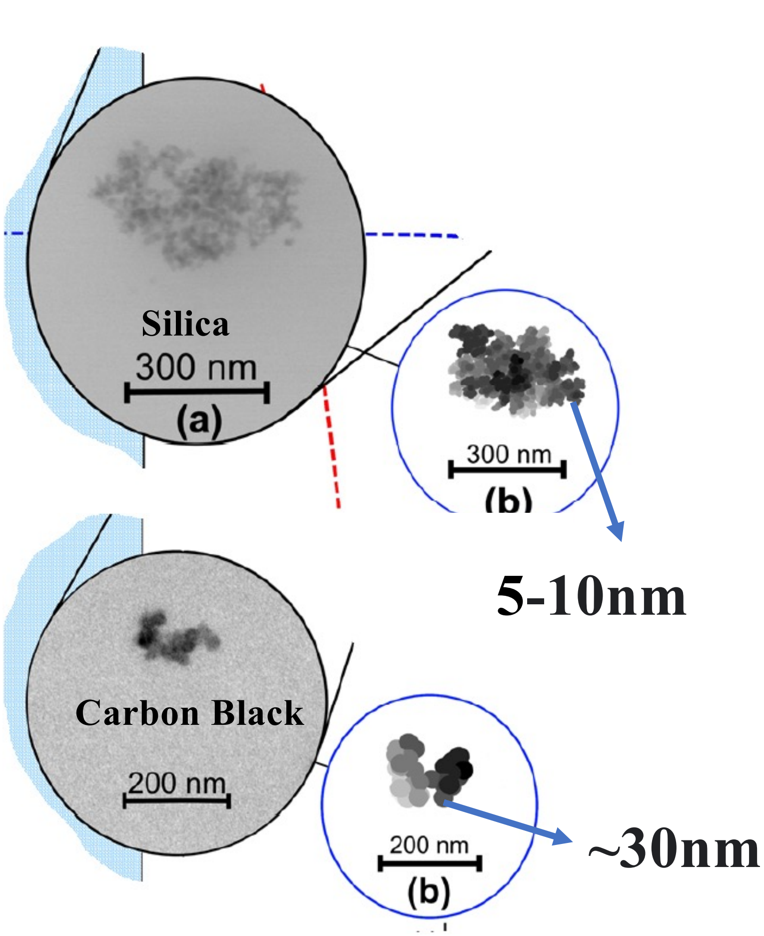
Rishi, K.; Pallerla, L.; Beaucage, G.; Tang, A. Dispersion of Surface-Modified, Aggregated, Fumed Silica in Polymer Nanocomposites. J. Appl. Phys. 2020, 127 (17), 174702.

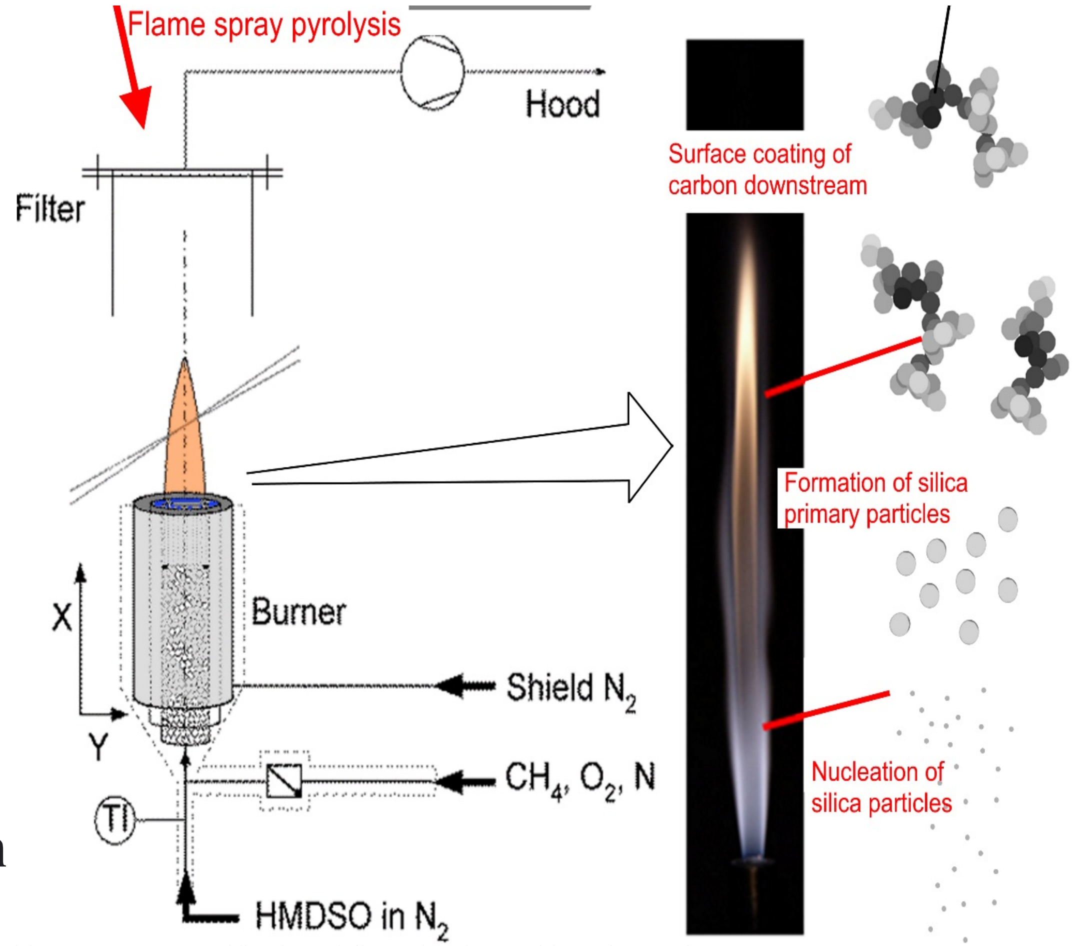
Aggregates to Clusters

Control <u>immiscibility</u> through surface modification



Okoli, U.; Rishi, K.; Beaucage, G.; Kammler, H. K.; McGlasson, A.; Michael, C.; Narayanan, V.; Grammens, J. *Dispersion and Dynamic Response for Flame-Synthesized and Chemically Modified Pyrogenic Silica in Rubber Nanocomposites*; 2022. Submitted to *Composites Sci. & Tech.*.





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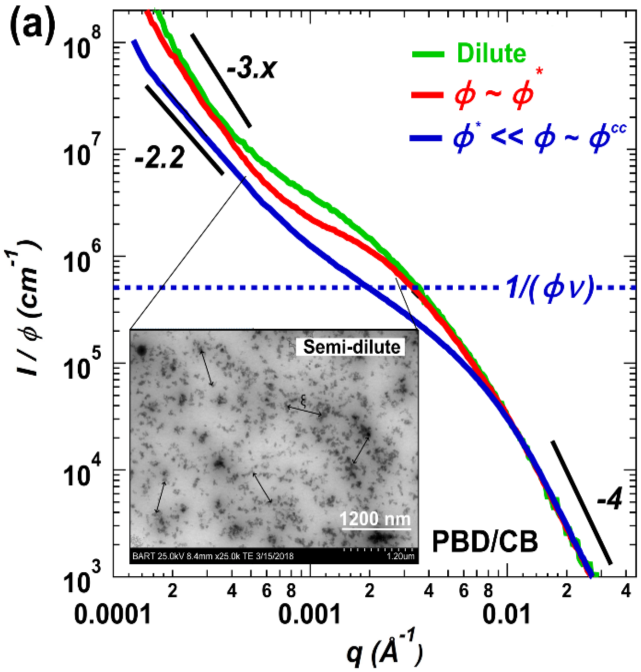
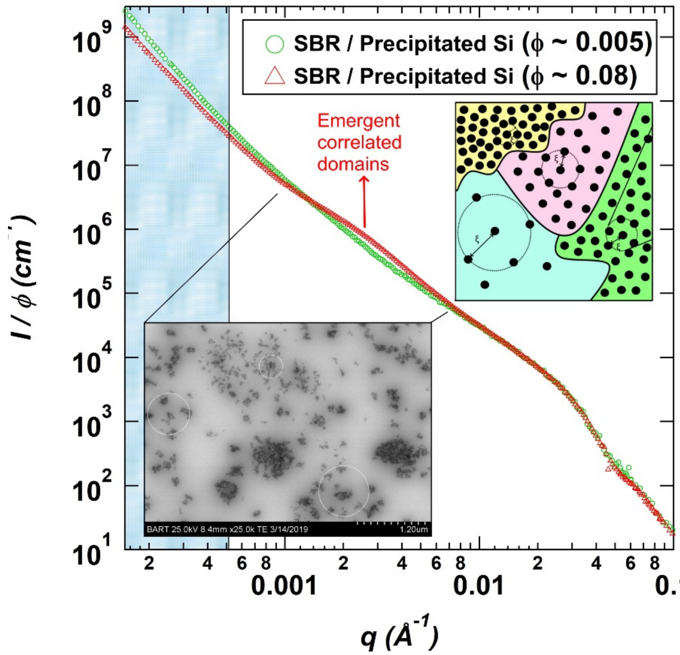
Clustered aggregates to bulk network

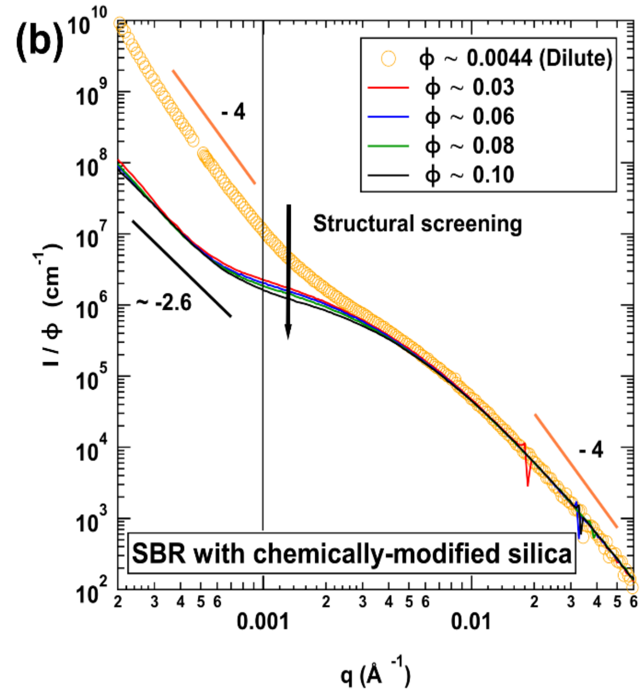
Carbon Black/Mean Field



Silica/Specific Interactions



Carbon Coated Silica/Mean Field



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Rishi, K.; Pallerla, L.; Beaucage, G.; Tang, A. Dispersion of Surface-Modified, Aggregated, Fumed Silica in Polymer Nanocomposites. J. Appl. Phys. 2020, 127 (17), 174702.

Method –
Si190 Precipitated silica, 3 grades of Aerosil® fumed silica, 6 grades of surface modified fumed silica, 4 grades of carbon coated silica

SBR, PDMS and Polystyrene

Mixing in a Brabender Plasticorder, Single screw extruder and vortex mixing

Matrix / Processing Technique	Processing specs.	Equipment specifications	Geometry Constant, Ψ	Total Accumulated strain, $\gamma = Nt\Psi$
SB80-38 / Brabender Mixing	N = 60 rpm t = 12 min	d_{wall} = 40 mm d_{rotor} = 35 mm $\mathfrak{H} = \frac{d_{wall}}{d_{rotor}}$ = 1.14 n = 1 [a]	$\frac{4\pi(\mathfrak{H})^{2/n}}{n\{(\mathfrak{H})^{2/n}-1\}}$ = 53.6 [b]	38600
PS / Single screw Extrusion	N = 5 rpm t = 12 min	d_{screw} = 11.7 mm L = 343 mm $H(343)$ = 1 mm	$\frac{\pi\{d_{screw}-2H(L)\}}{H(L)}$ = 33.6 [c]	2020
PDMS / Vortex Mixing	N = 3200 rpm t = 0.5 min	$R \gg r$	$\frac{2\pi(2R^2)}{(R^2-r^2)}$ = 12.6 [d]	20100

[a] power law index for styrene butadiene rubber
[b] Couette flow equation from Bousmina et al.
[c] equation from Hassinger et al.
[d] equation from Mezger

Rishi K, Pallerla L, Beaucage G, Tang A *Dispersion of surface-modified, aggregated, fumed silica in polymer nanocomposites* J. Appl. Phys. **127** 174702 (2020).

Surface Modification for Controlled Immiscibility

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

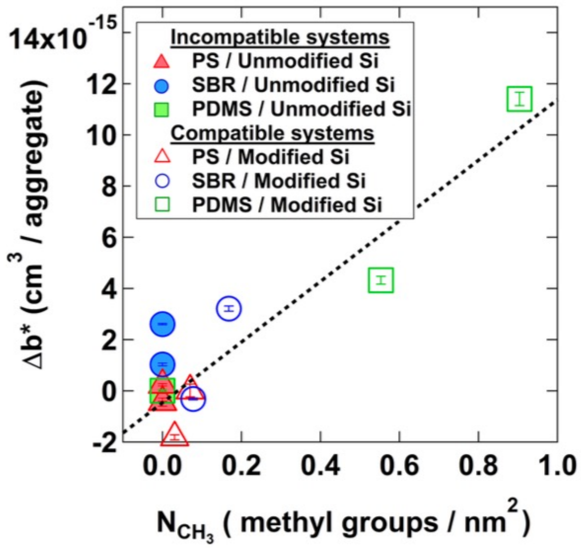
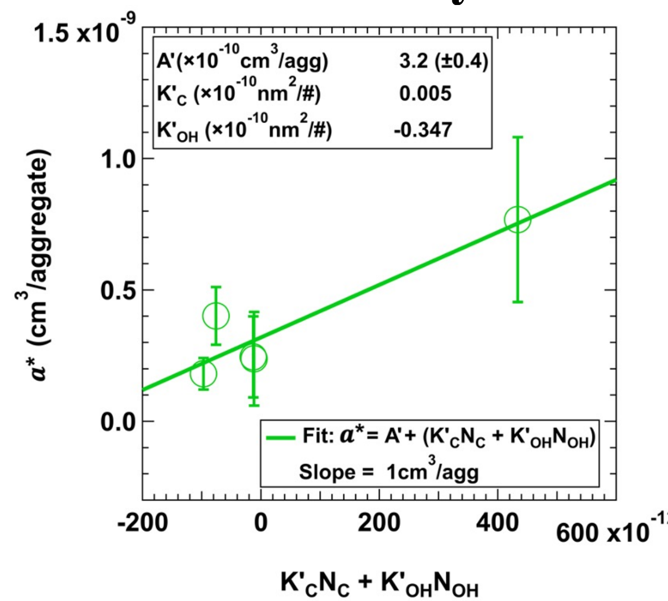


FIG. 11. A plot showing the bound polymer content (Δb^*) determined from the excluded volumes of the filler aggregates before and after dispersion as a function of surface methyl content (N_{CH_3}). The dashed line indicates that Δb^* is proportional to N_{CH_3} determined from FTIR.



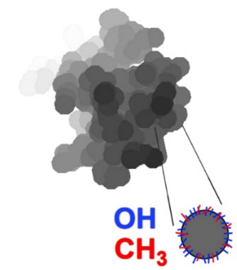


Figure 9. Plot of the particle interaction parameter, a^*, expressed in cm³/aggregate as a function of the linear sum of the surface carbon content (N_C) and surface hydroxyl content (N_{OH}) weighted differently. a^* is an attractive potential so negative values indicate relative repulsion between aggregates that increases with surface carbon content. That is, surface carbon enhances aggregate/polymer attraction relative to aggregate/aggregate attraction. The fit parameters, A', K'_C, and K'_{OH} were obtained through least squares minimization.

b^* can be calculated as the excluded volume for an aggregate, zV_0, without bound rubber

b^* increases with bound rubber.

a^* reflects the attractive energy of interaction between aggregates. $\Pi = \frac{RT}{(V+b)} - \frac{a}{V^2}$, attractive potential

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Greg Beaucage, University of Cincinnati gbeaucage@gmail.com