Overcoming Kinetic Barriers to Self-Assembly: Field-directed Colloidal Phase Transitions

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E. R. Dufresne, *Yale*—P. E. Hopkins, *Virginia*—A. M. Grillet, *Sandia*

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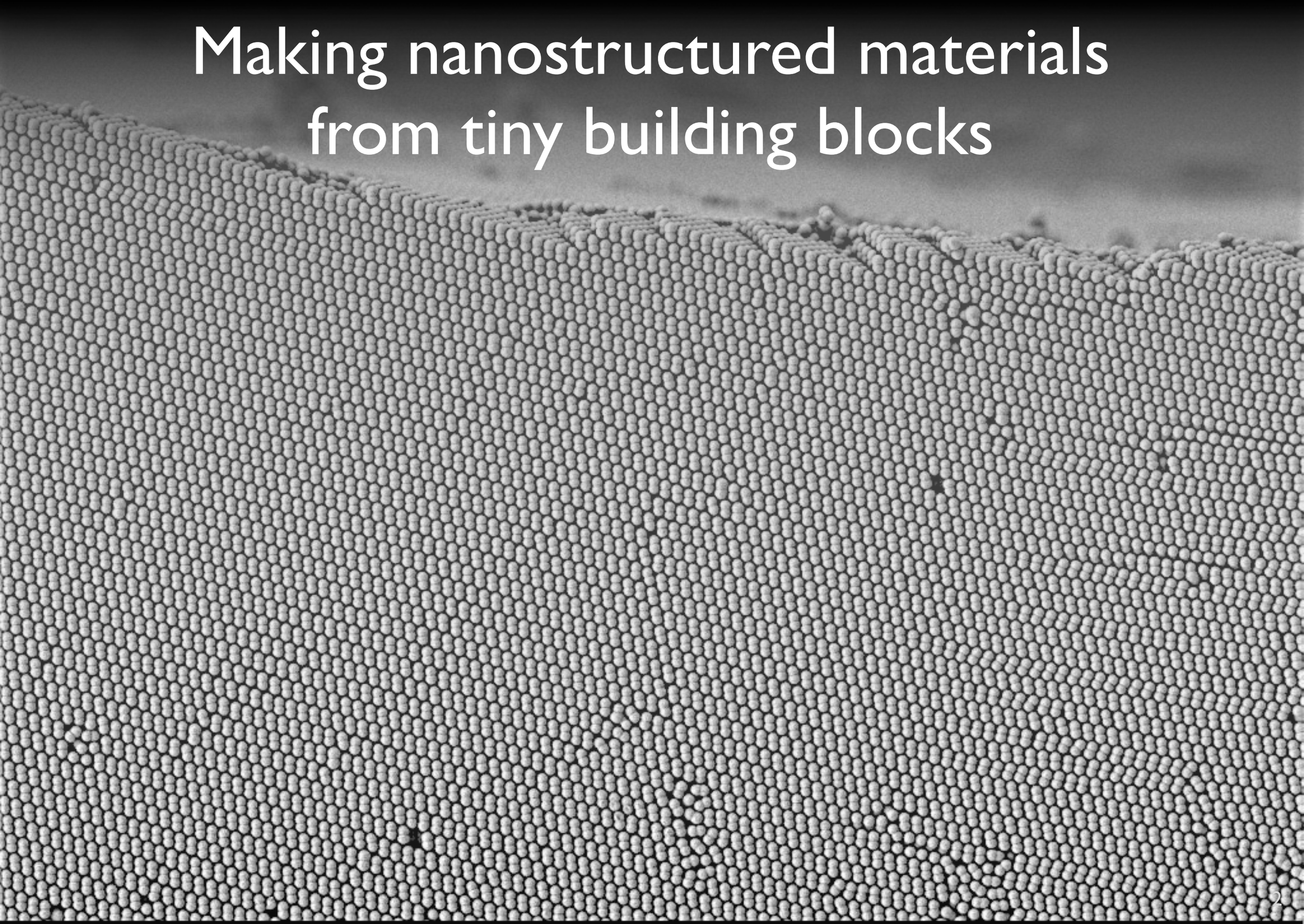
Division of Materials Sciences and Engineering award no. DE-FG02-09ER46626
National Science Foundation award no. CBET–0930549

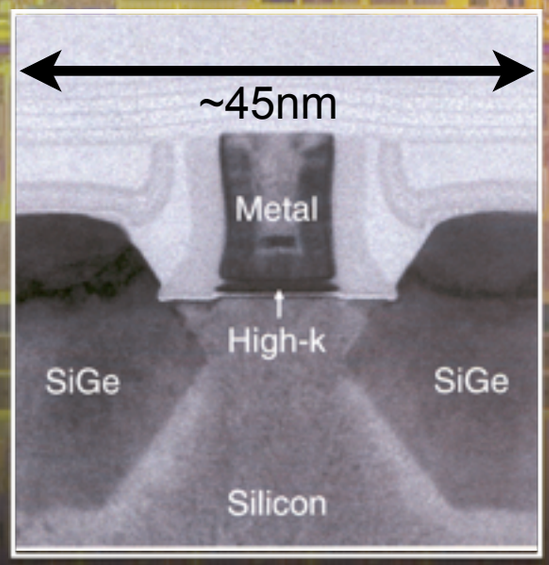
Making nanostructured materials from tiny building blocks



Nanostructures

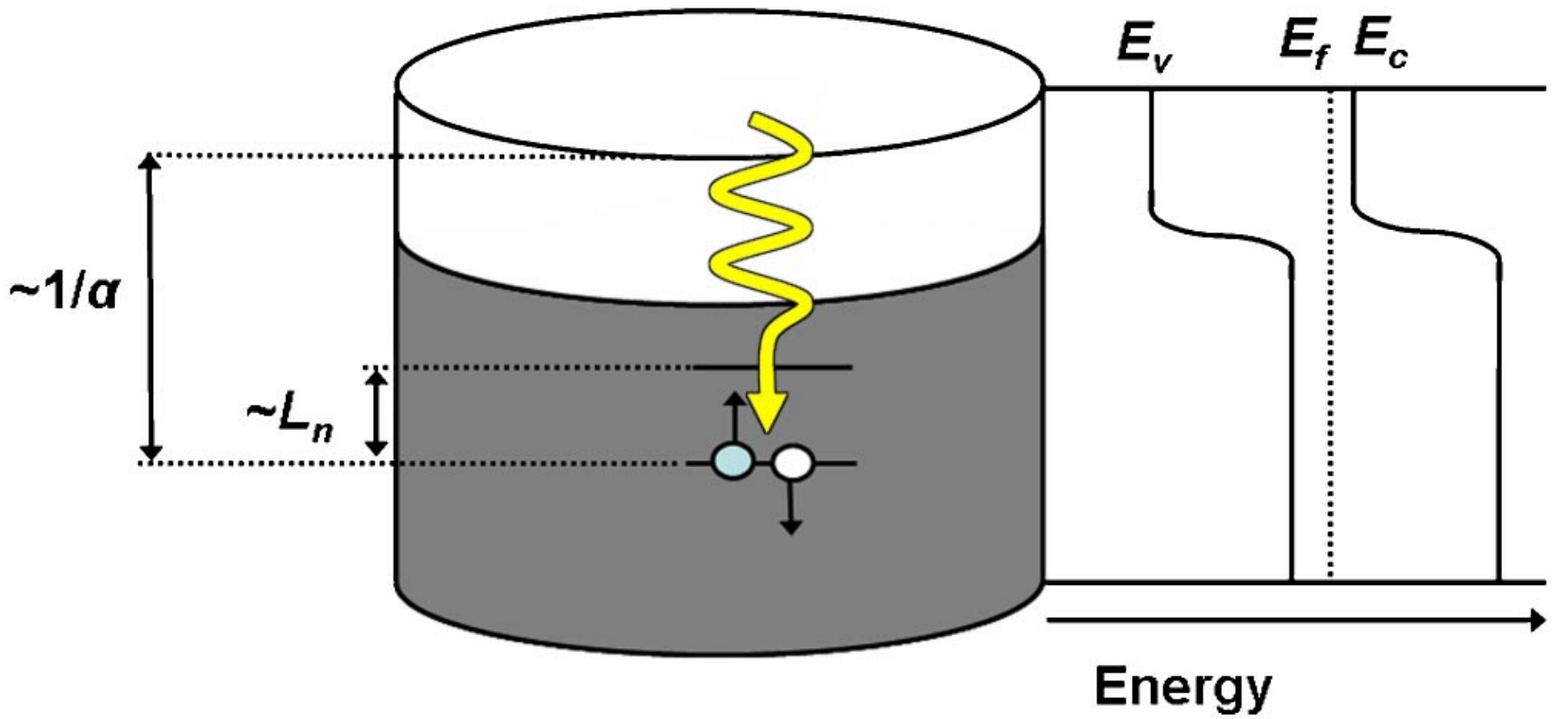
react to and guide
the transport of
heat, light, charge, molecular species...

Transistor



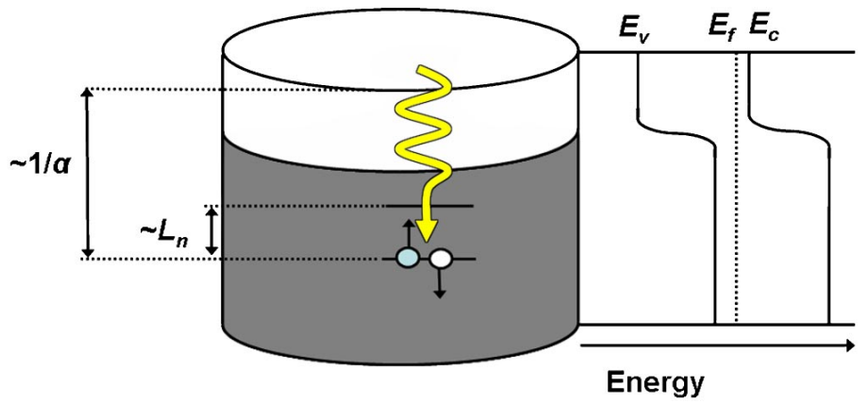
Nanostructured materials

Photovoltaic homojunction

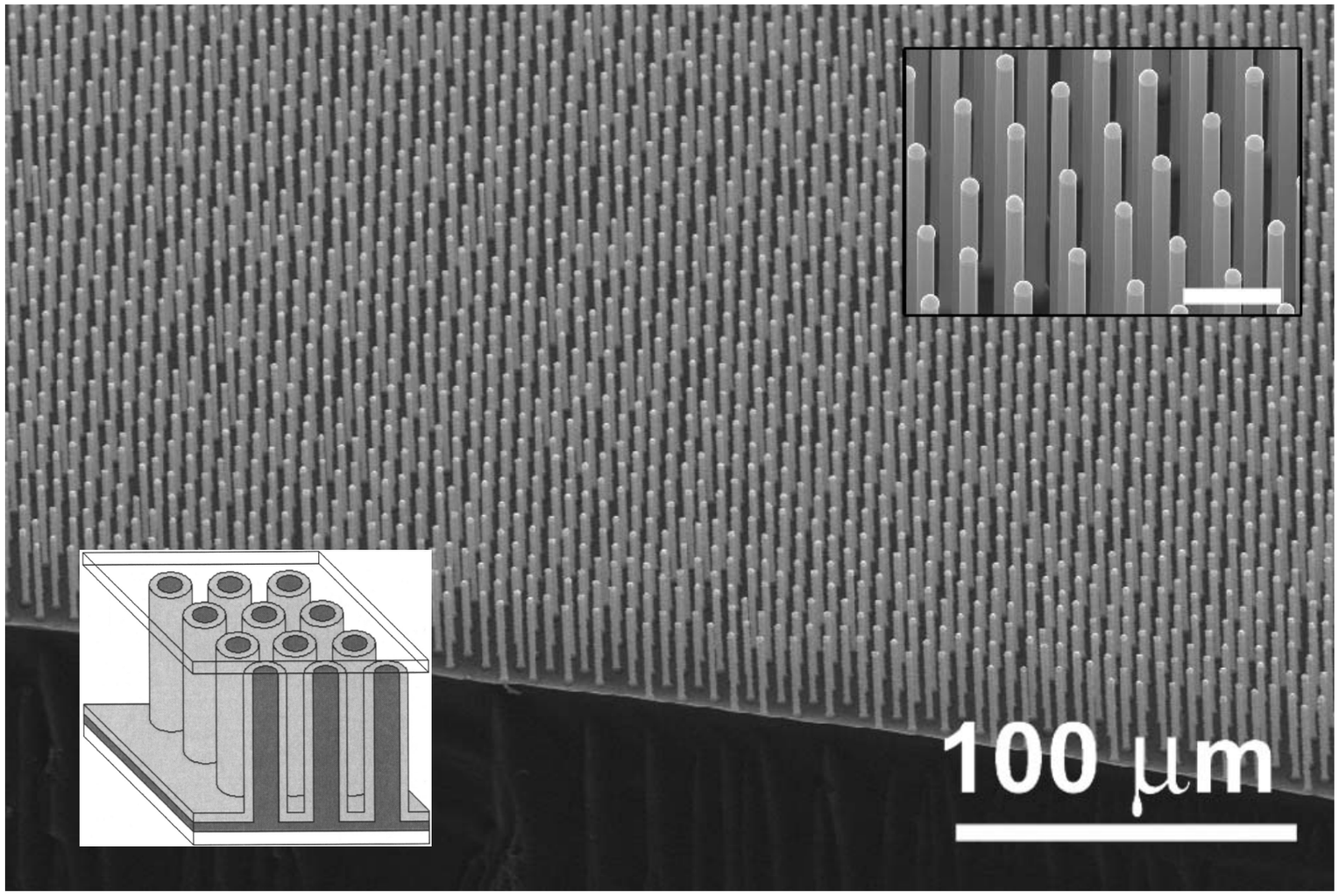


Nanostructured materials

Photovoltaic homojunction



Heterojunction photovoltaic

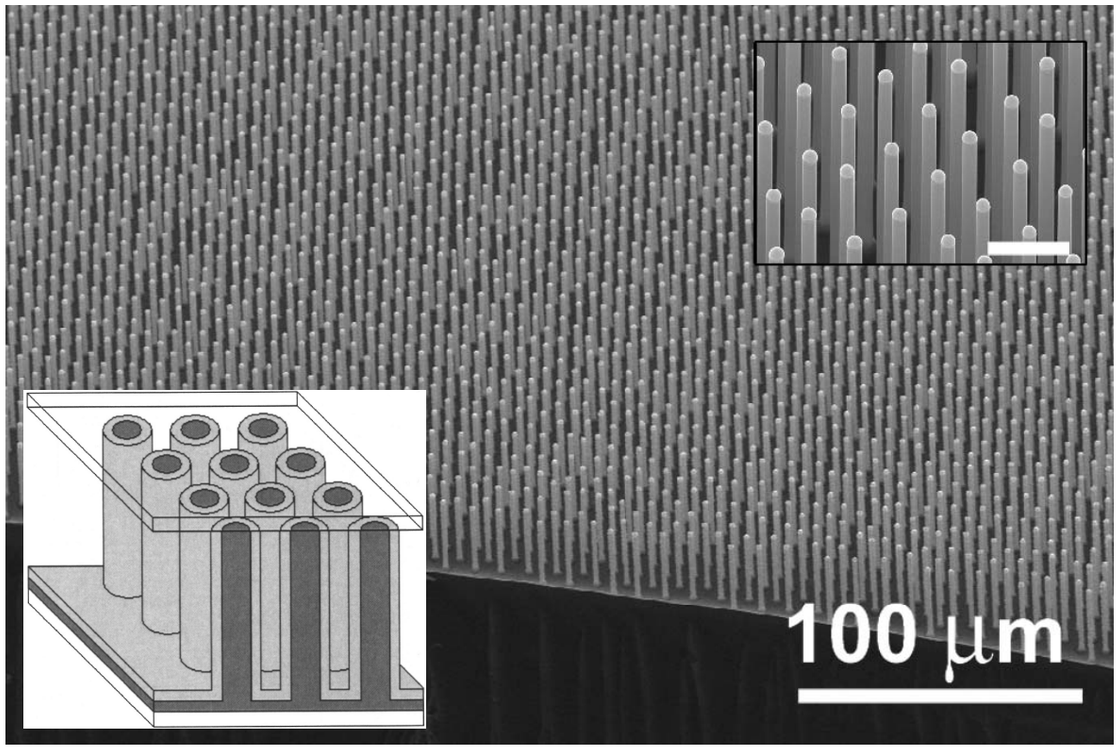


Kayes, B. M. *et al. Appl. Phys. Lett.* 91, 103110–103110–3 (2007).

Kayes et al., *J. Appl. Phys.* 97, 114302–114302–11 (2005).

Nanostructured materials

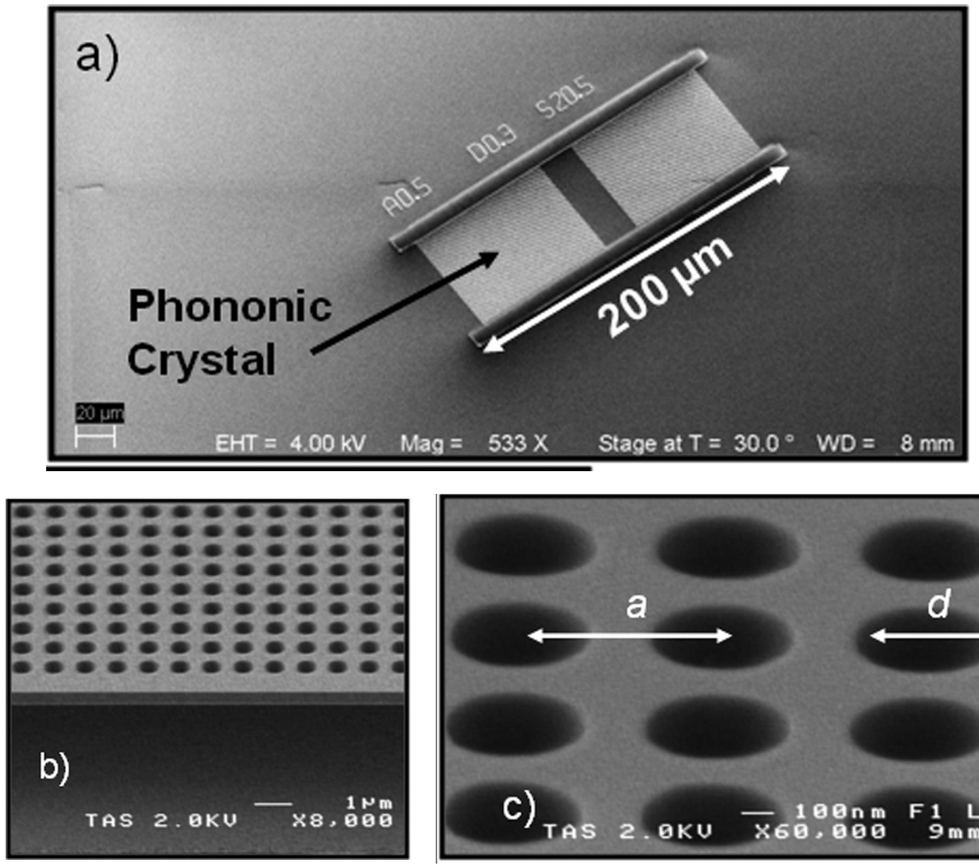
Heterojunction photovoltaic



Kayes, B. M. *et al. Appl. Phys. Lett.* 91, 103110–103110–3 (2007).

Kayes et al., *J. Appl. Phys.* 97, 114302–114302–11 (2005).

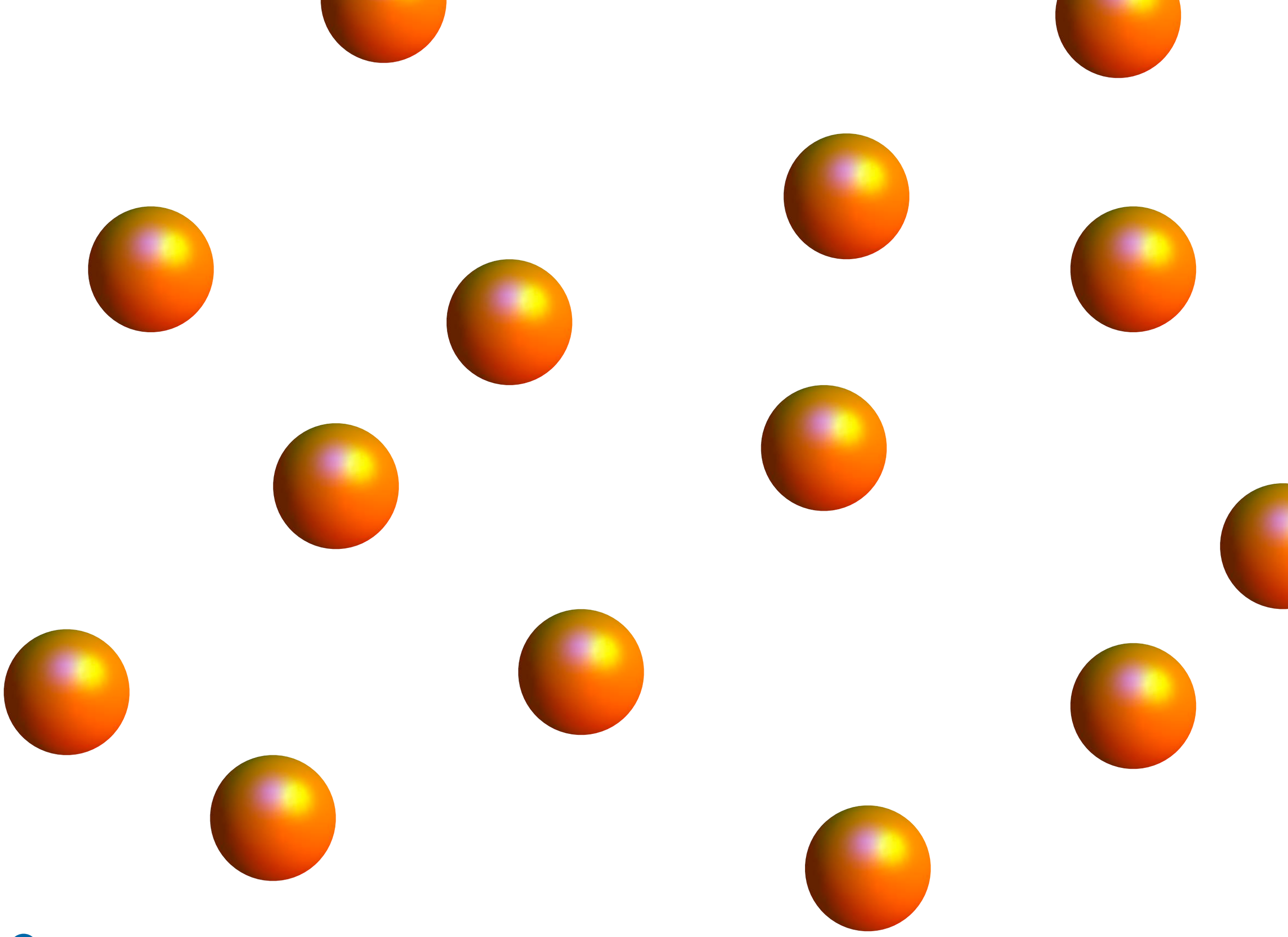
Thermal barrier material

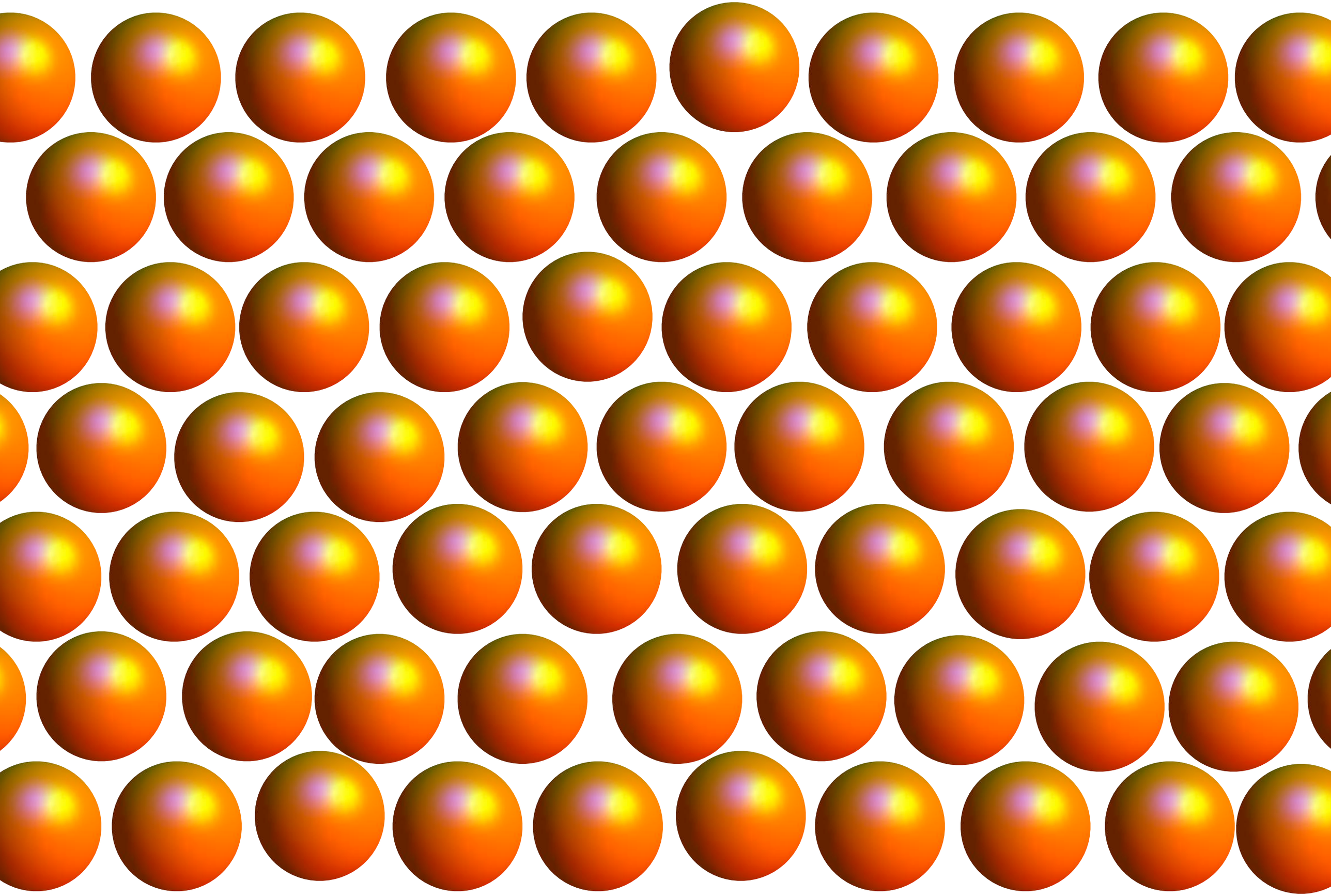


Silicon fabricated phononic crystal

Controls phonon propagation and scattering

Hopkins, P. E. et al. *Nano Lett* 11, 107 (2011).





Self-assembled nanostructures

Mittal, M. & Furst, E. M. *Adv. Funct. Mater.* 19, 3271–3278 (2009).
Hopkins, et al. *Appl. Phys. Lett.* 2011, 99, 133106.

atomic nano ⟷ *meso* ⟷ *macro*

macroscale
thermal transport
coatings and systems

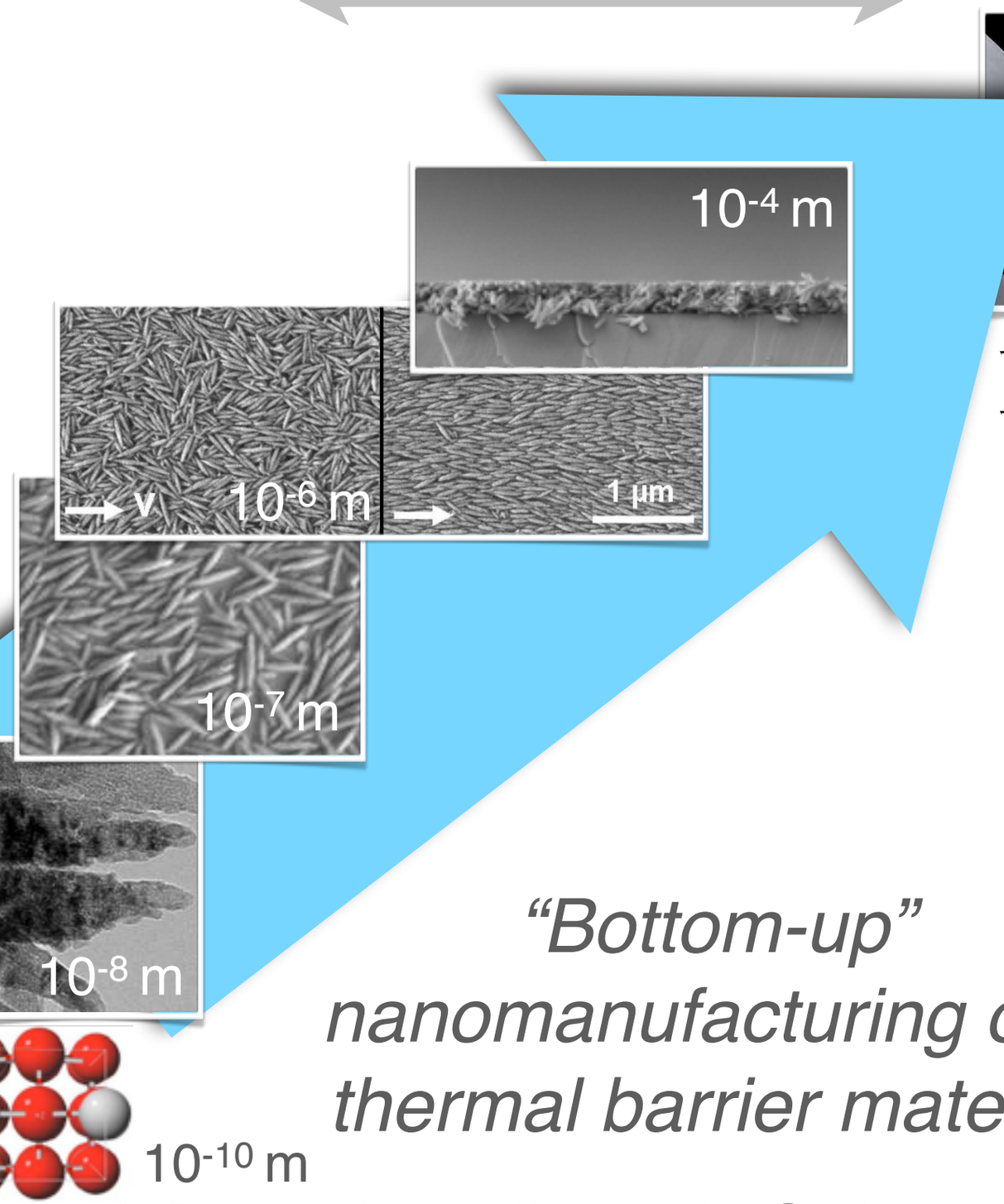
thin film deposition
–micro patterning

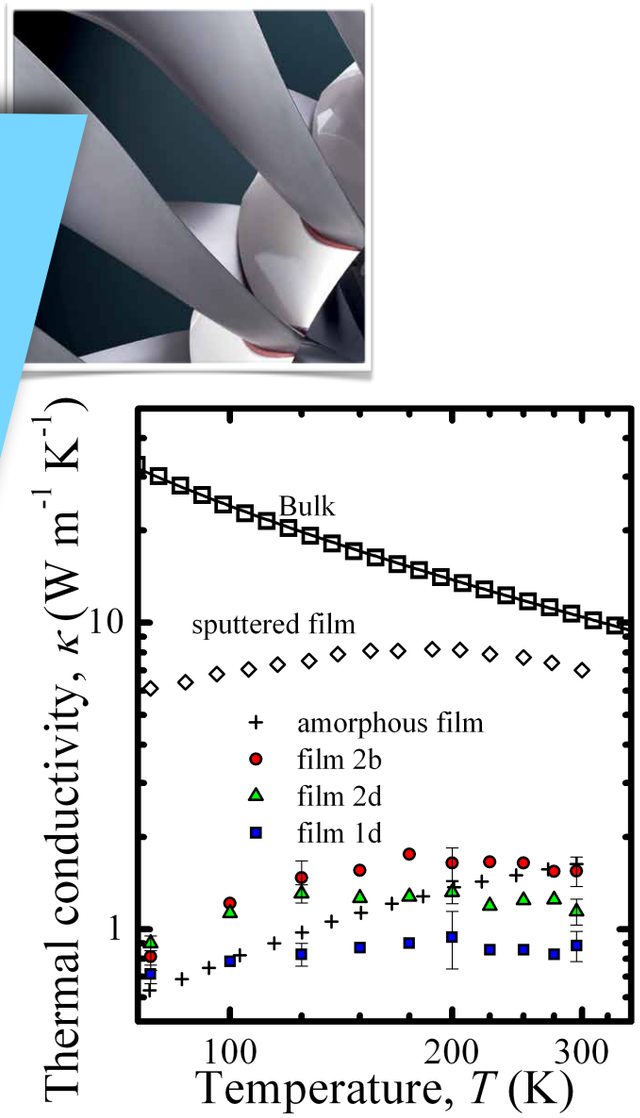
nanoparticle
directed organization
–contact resistance

anisotropic
nanoparticles
–boundary scattering

Anatase
nanocrystals
–phonon scattering

TiO_2
–phonons





"Bottom-up" nanomanufacturing of a thermal barrier material

Nanoparticle self-assembly will enable...

New nanomanufacturing processes

high rate, large scale, low cost

Applications, materials, and devices:

Energy (heterojunction photovoltaics, battery electrodes, ...)

Advanced coatings (thermal barriers, separation membranes)

Photonic, phononic, phoxonic (e-ink, optical switches, ...)

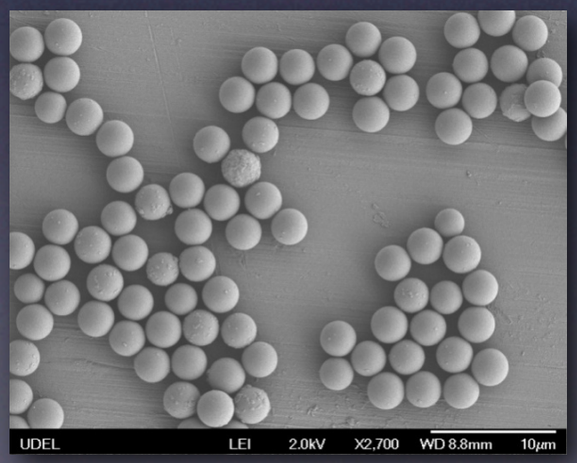
Microlens arrays (efficient lighting)

"Bottom-up" *versus* "Top-down"

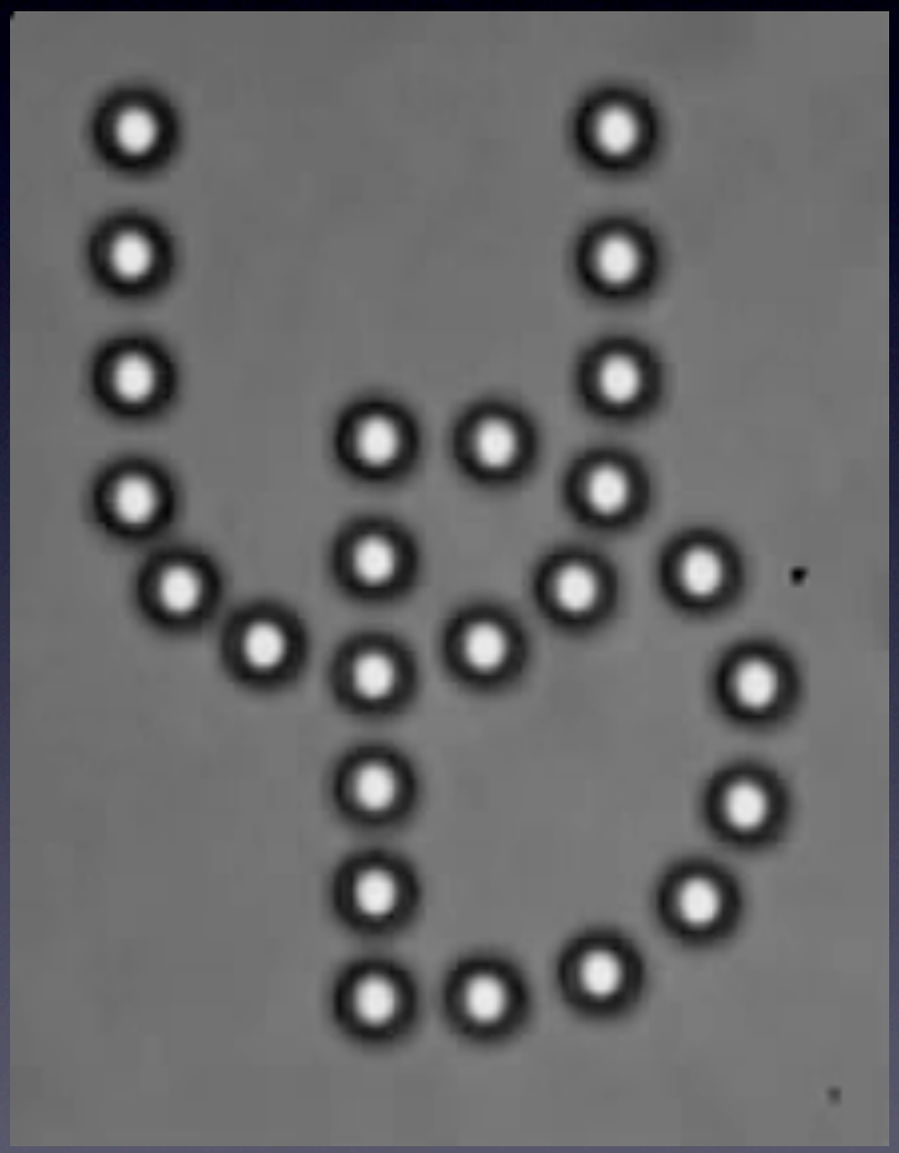
Colloids—*Κόλλα*

Thomas Graham, 1805–1869

A unique division of matter

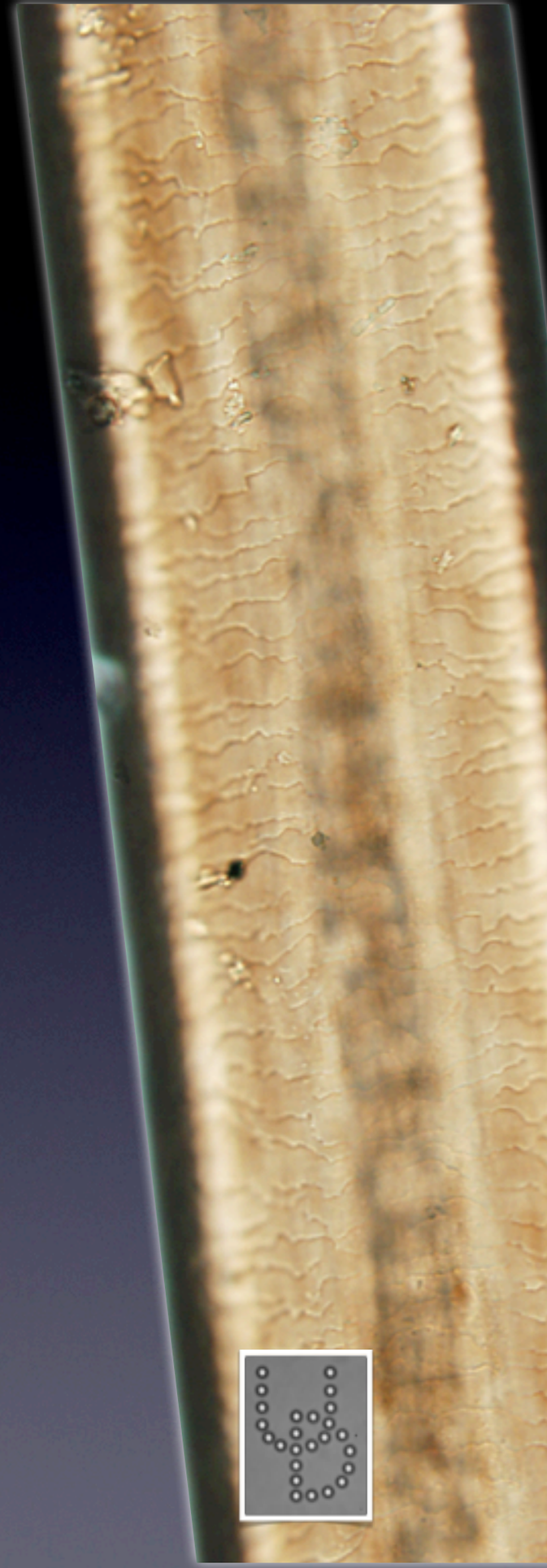


Polystyrene latex



Optically trapped colloids

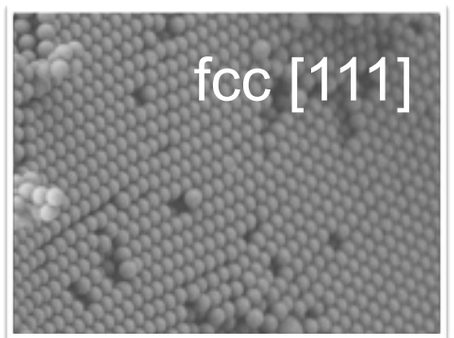
10µm

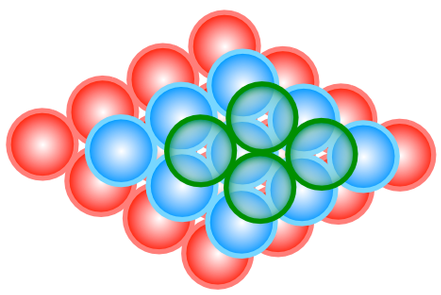


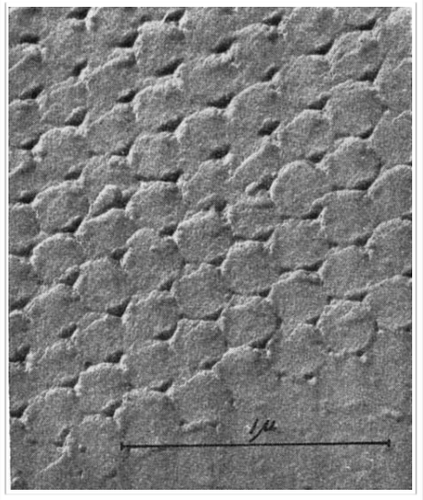
Self-assembly—colloids spontaneously form ordered structures

Hard sphere colloidal crystals

Pusey, P. & Van Megen, W. Nature 320, 340–342 (1986).
Sanders, J.V. Nature 204, 1151–1153 (1964).

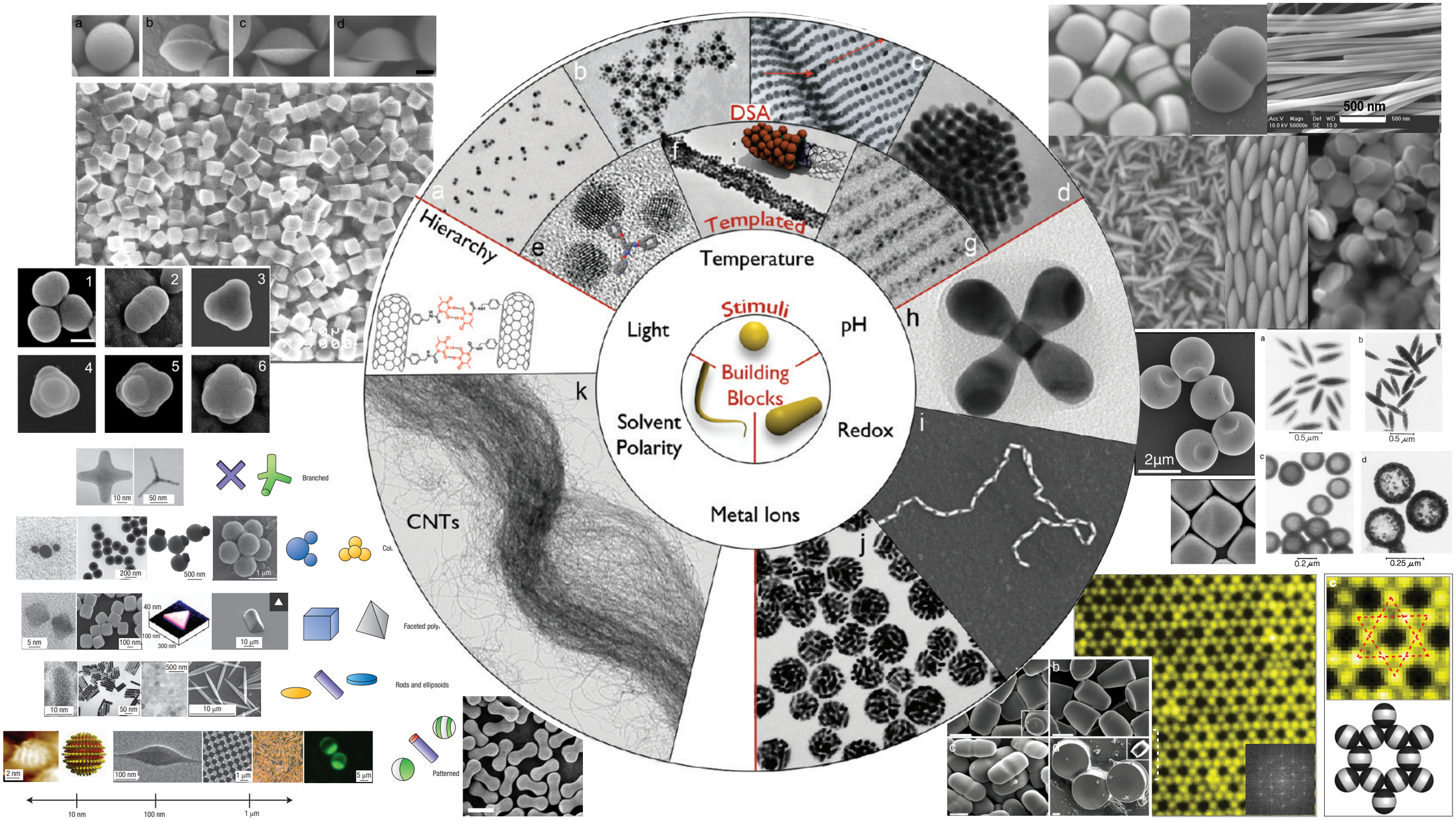






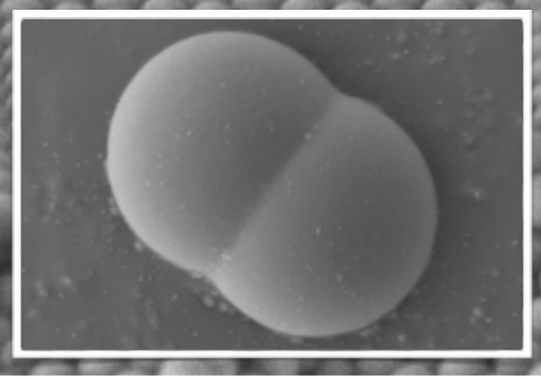
Colloidal and nanoparticle building blocks

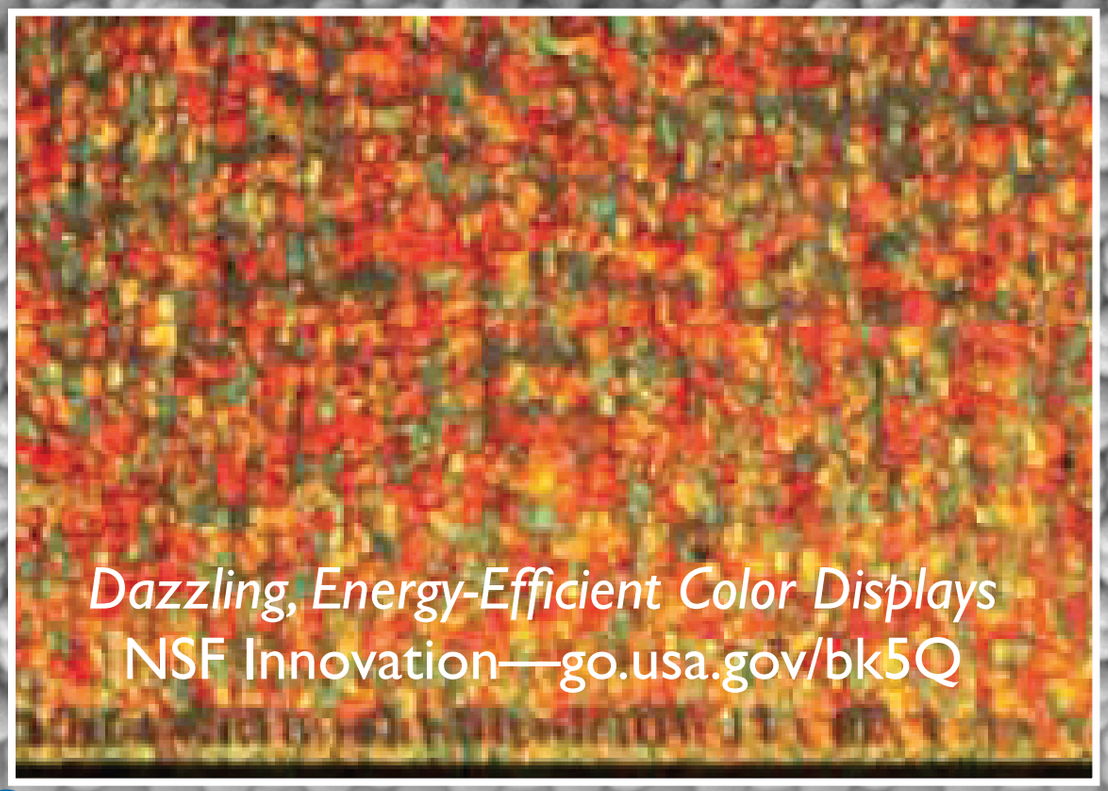
Grzelczak, Vermant, Furst, & Liz-Marzan, ACS Nano 4, 3591–3605 (2010).
Glotzer & Solomon, *Nature Mater.* 6, 557–562 (2007).
Solomon, *Curr. Opin. Coll. Int. Sci.* 16, 158–167 (2011).
Sacanna & Pine, *Curr. Opin. Coll. Int. Sci.* 16, 96–105 (2011).



Shape, interactions encode self-assembly

Simple monoclinic crystals formed from colloidal dumbbell particles
Forster, J. D. et al. *ACS Nano* 2011, 8, 6695–6700.



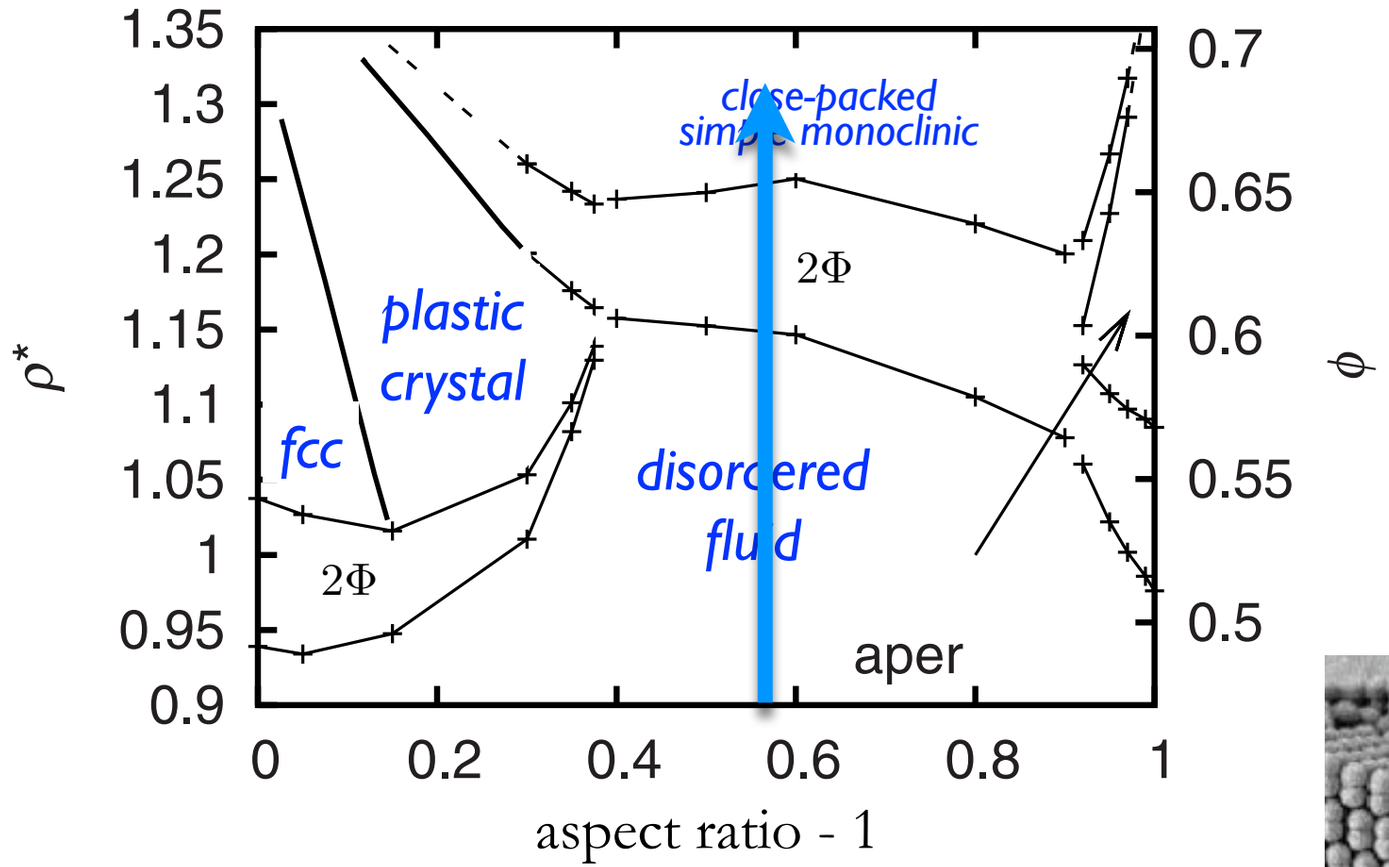


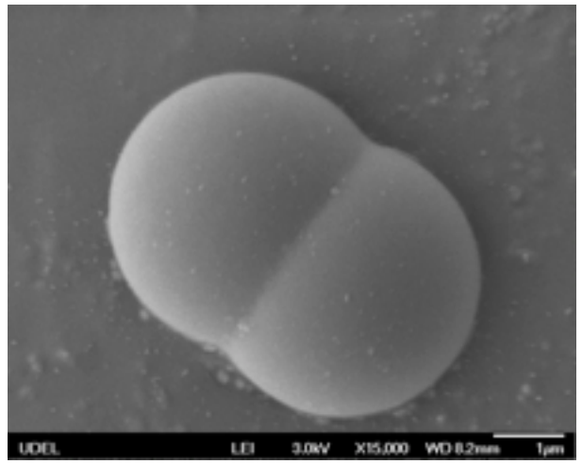
Dazzling, Energy-Efficient Color Displays
NSF Innovation—go.usa.gov/bk5Q

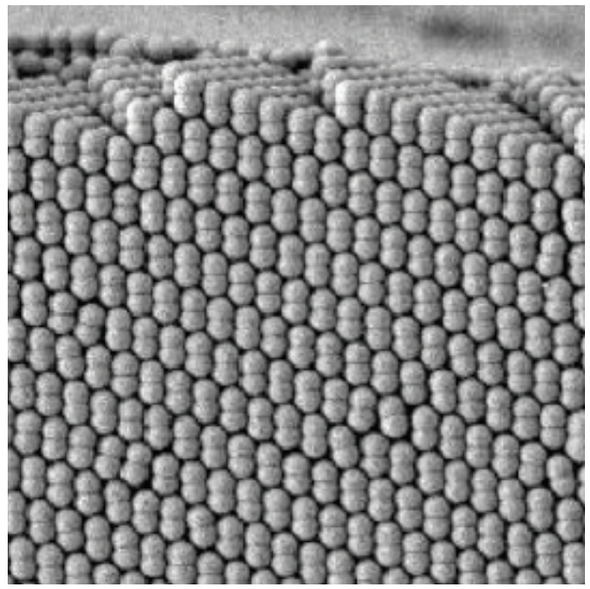
1 μm

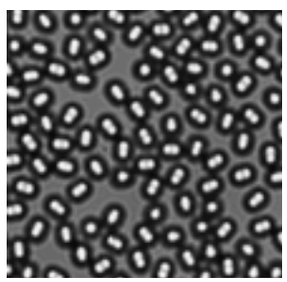
E. M. Furst—*CMET/Chemical & Biomolecular Engineering, University of Delaware*—furst@udel.edu

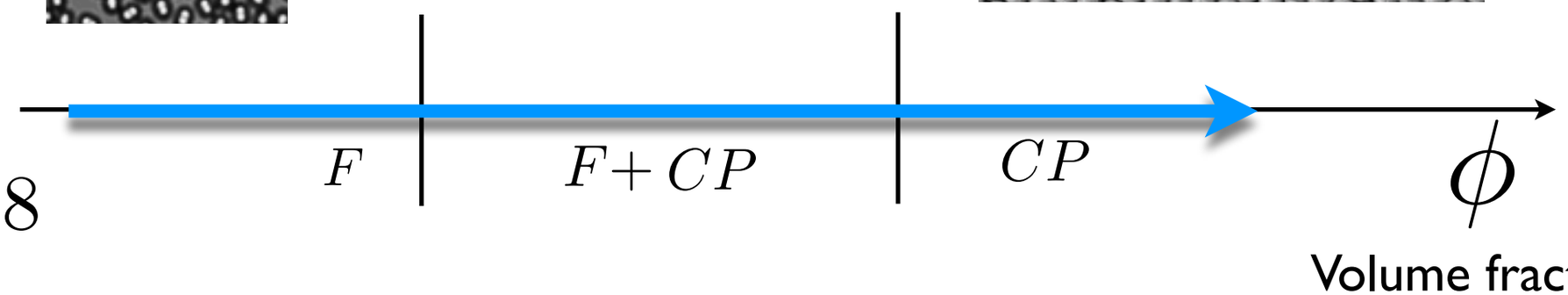
Dumbbell particle self-assembly







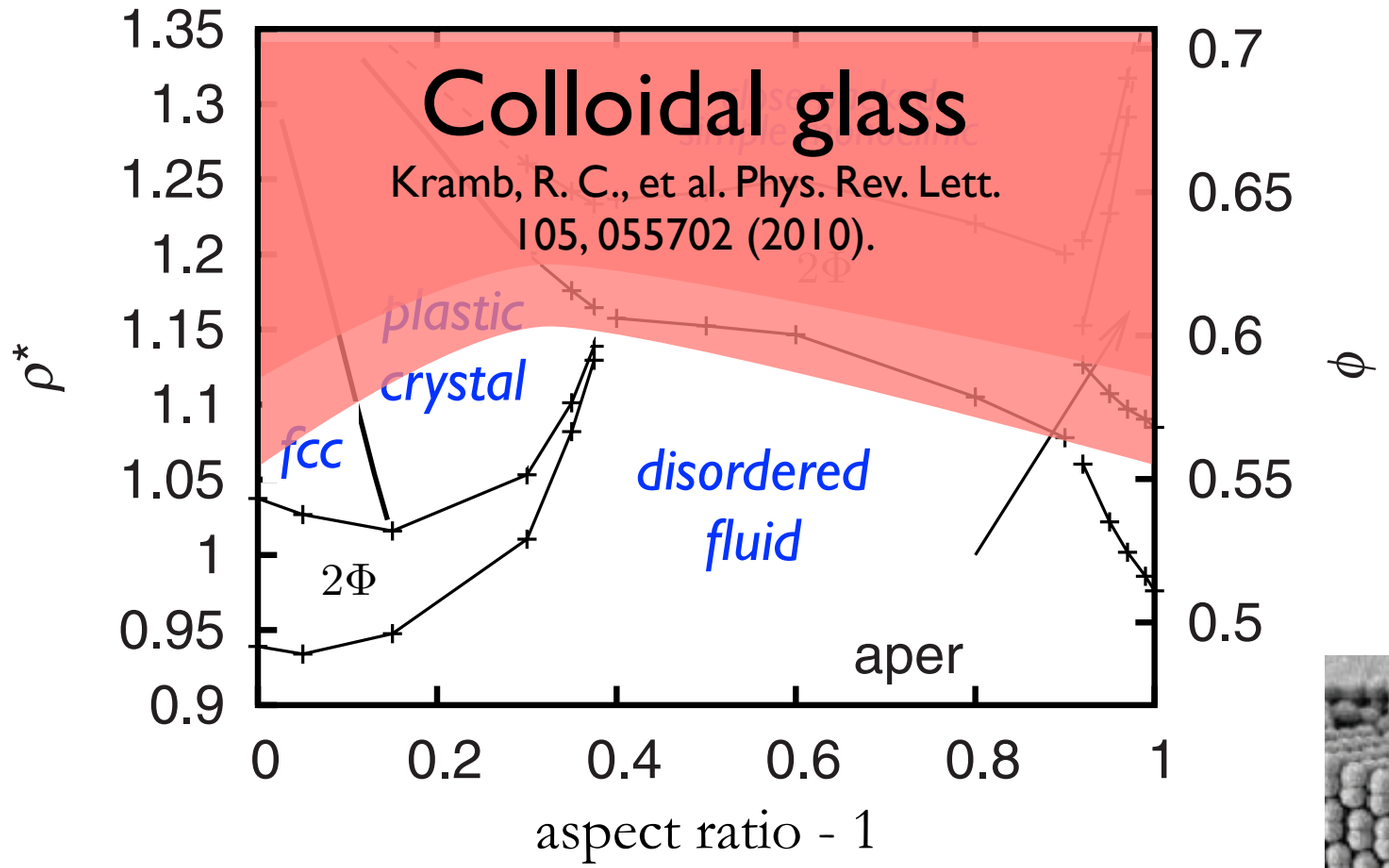


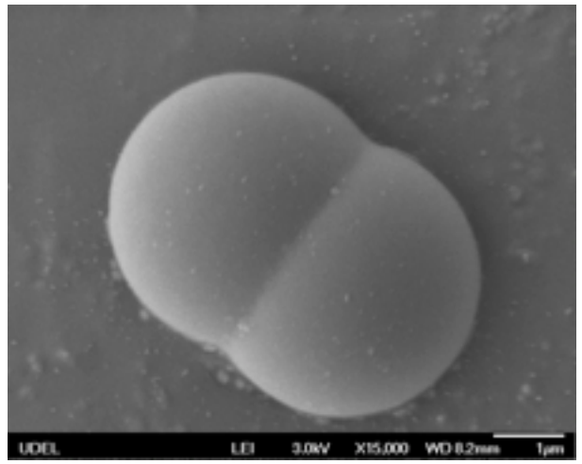


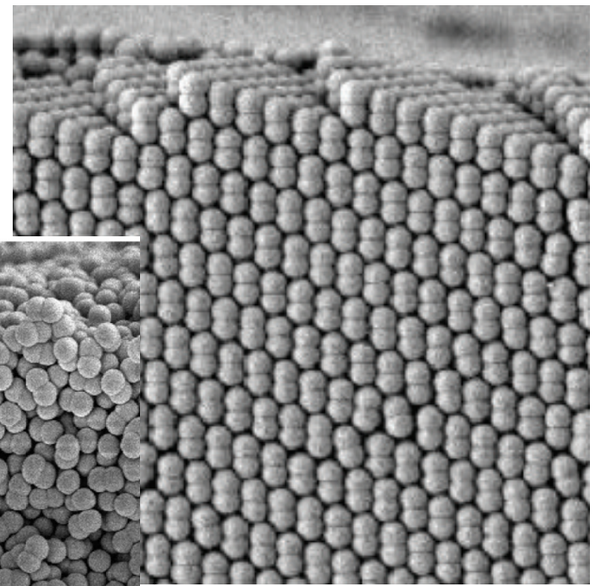
Kinetic traps and bottlenecks hinder crystal formation

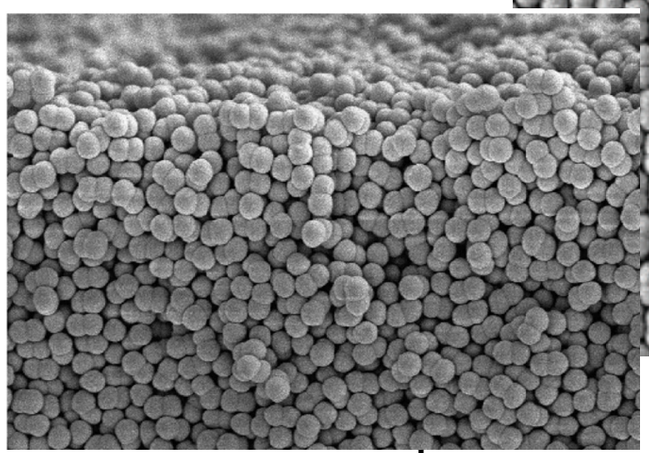
Non-equilibrium glass

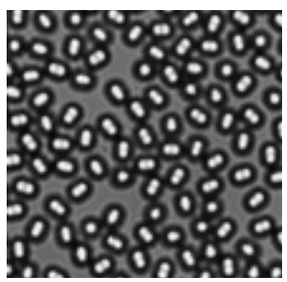
Self-assembly blocked by kinetic traps





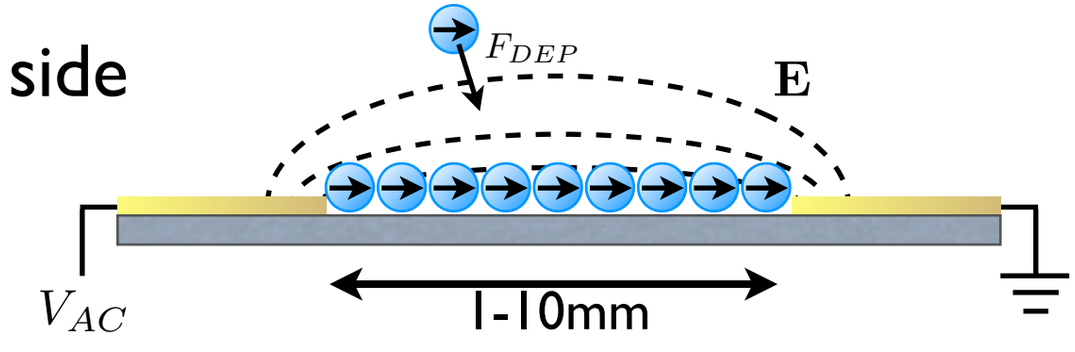




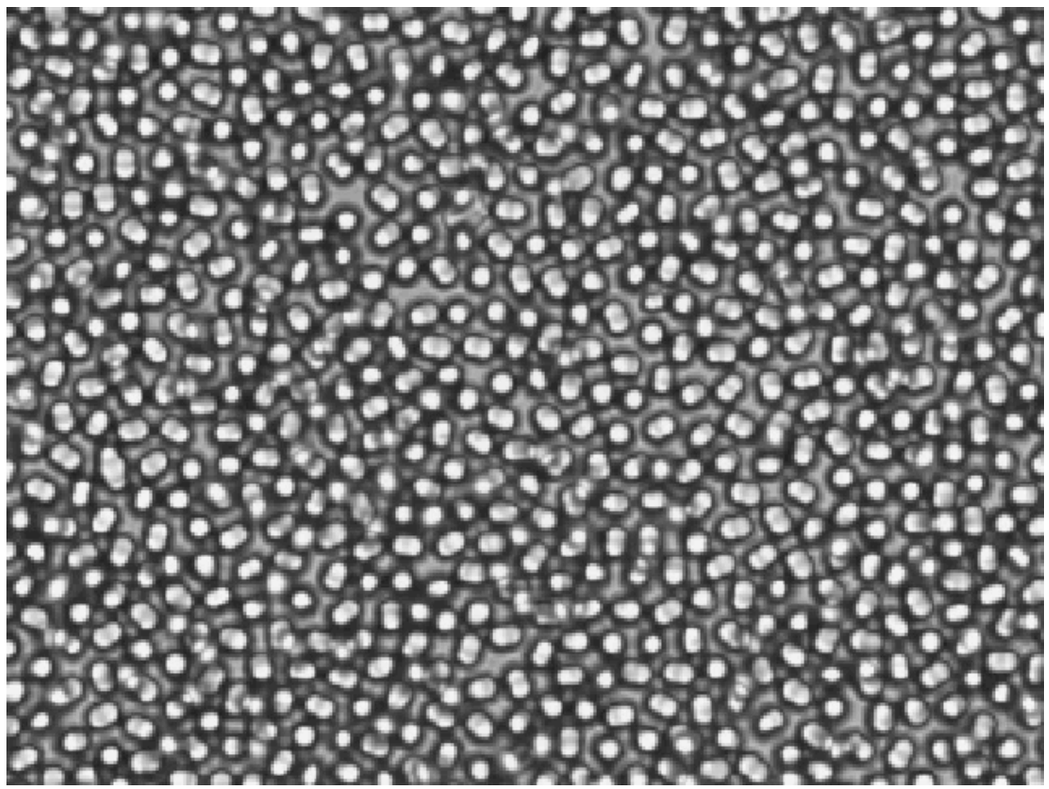


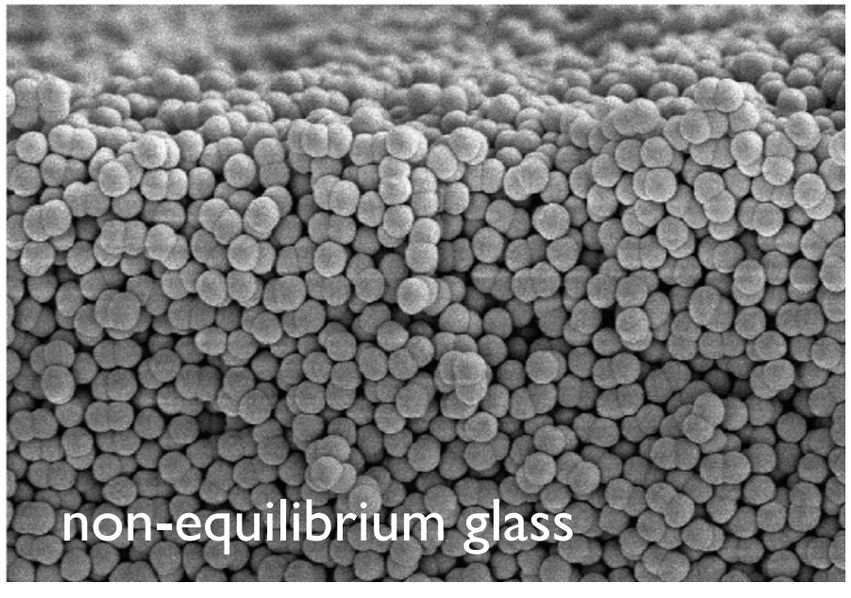
Self-assembly requires directing fields

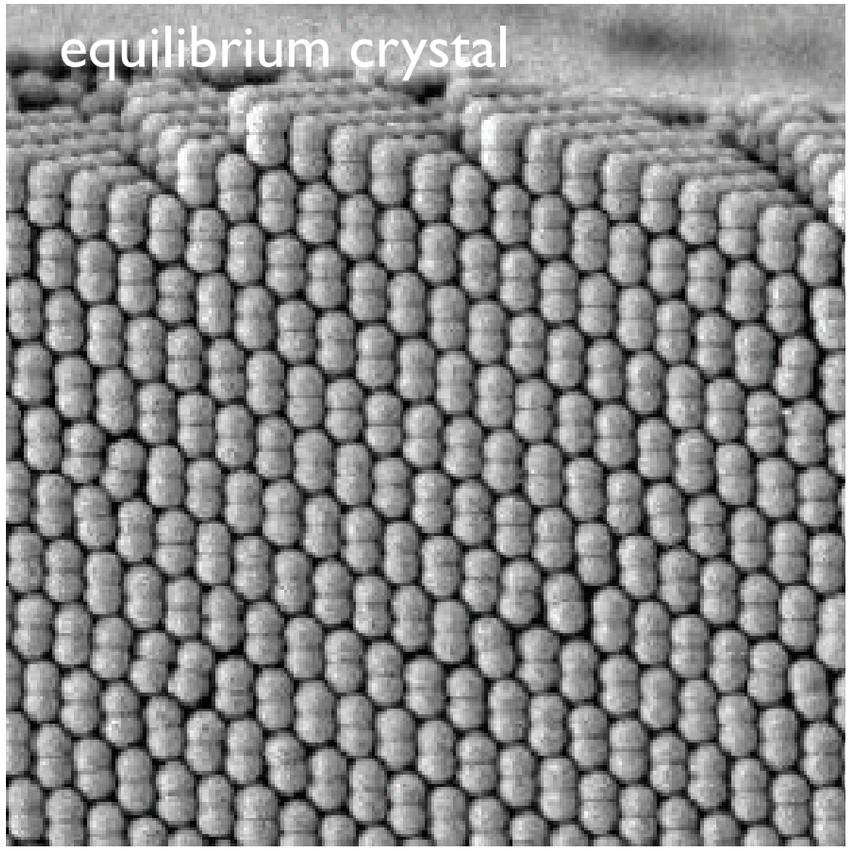
AC electric fields



Dumbbell colloids orienting in AC field



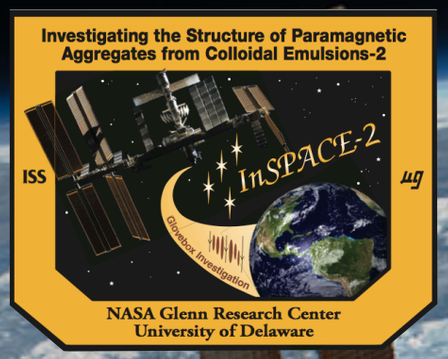




InSPACE-2

International Space Station (ISS)
Expeditions 16, 18, 19 and 20

James W. Swan, *et al. Proceedings of the National Academy of Sciences USA* 109, 16023–16028 (2012).



ISS astronauts:

Peggy Whitson
E. Michael Fincke
Koichi Wakata
Sandra H. Magnus
Frank De Winne
Michael R. Barratt

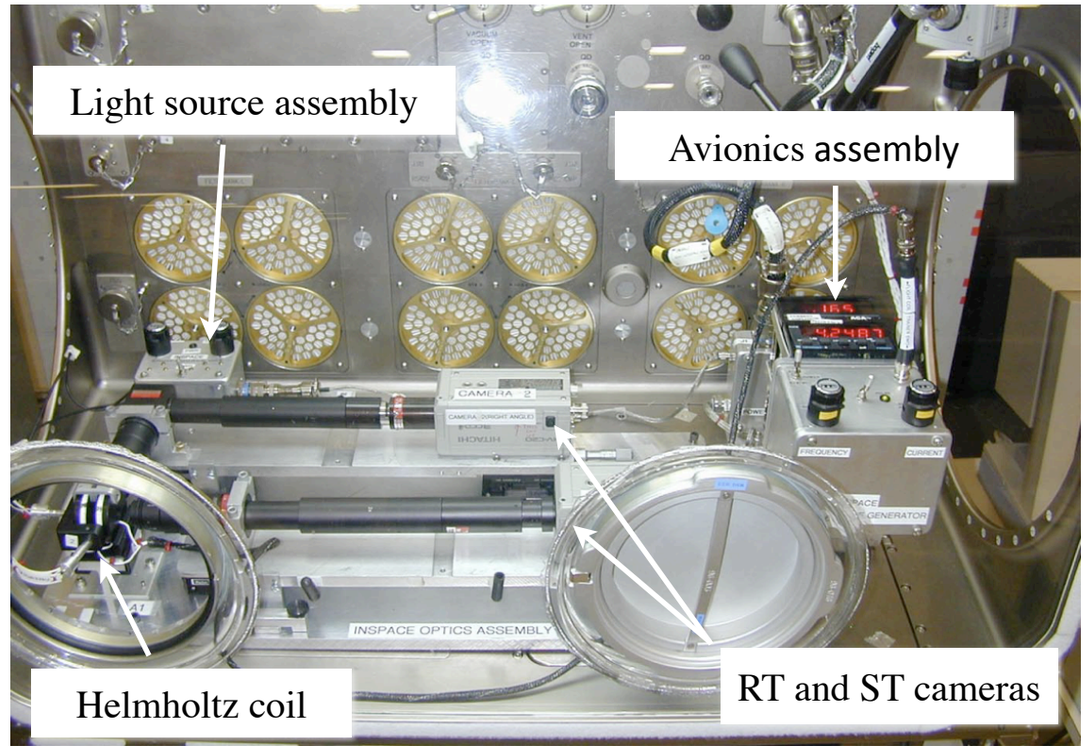
Model magnetorheological fluid:

paramagnetic latex spheres

1 µm diameter

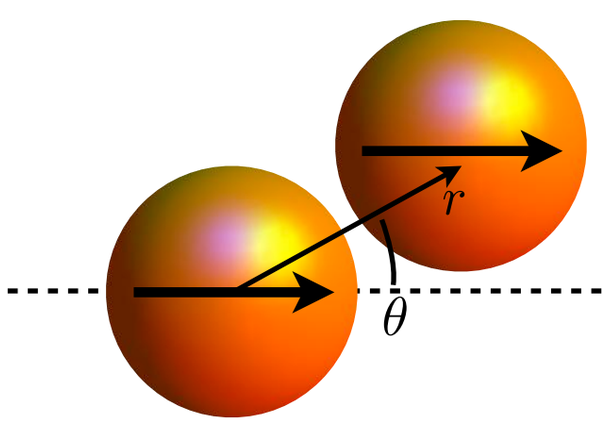
in water

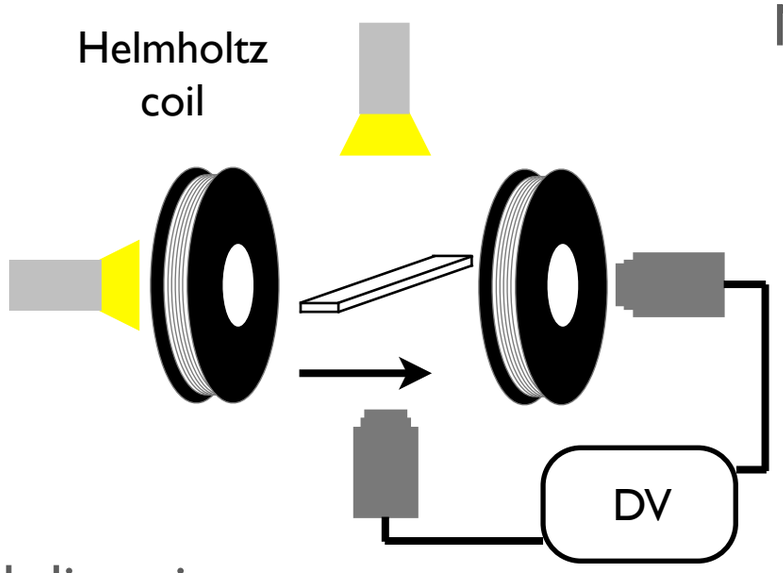
<1% particles by volume

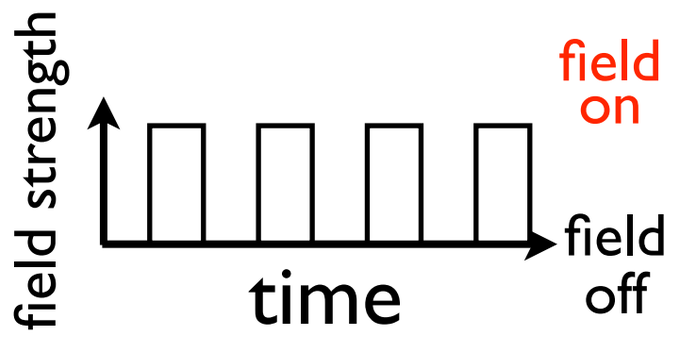


Microgravity Science Glovebox

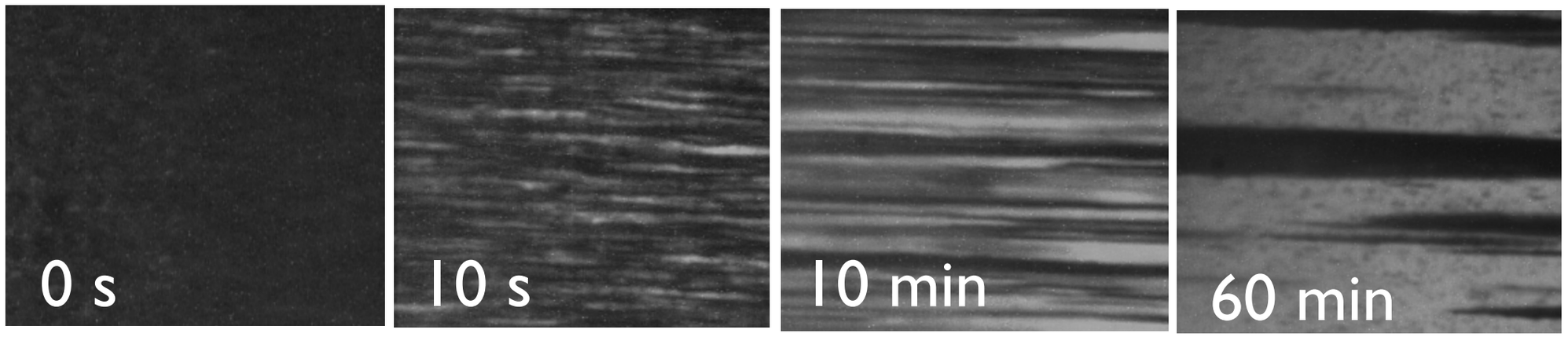
magnetic field



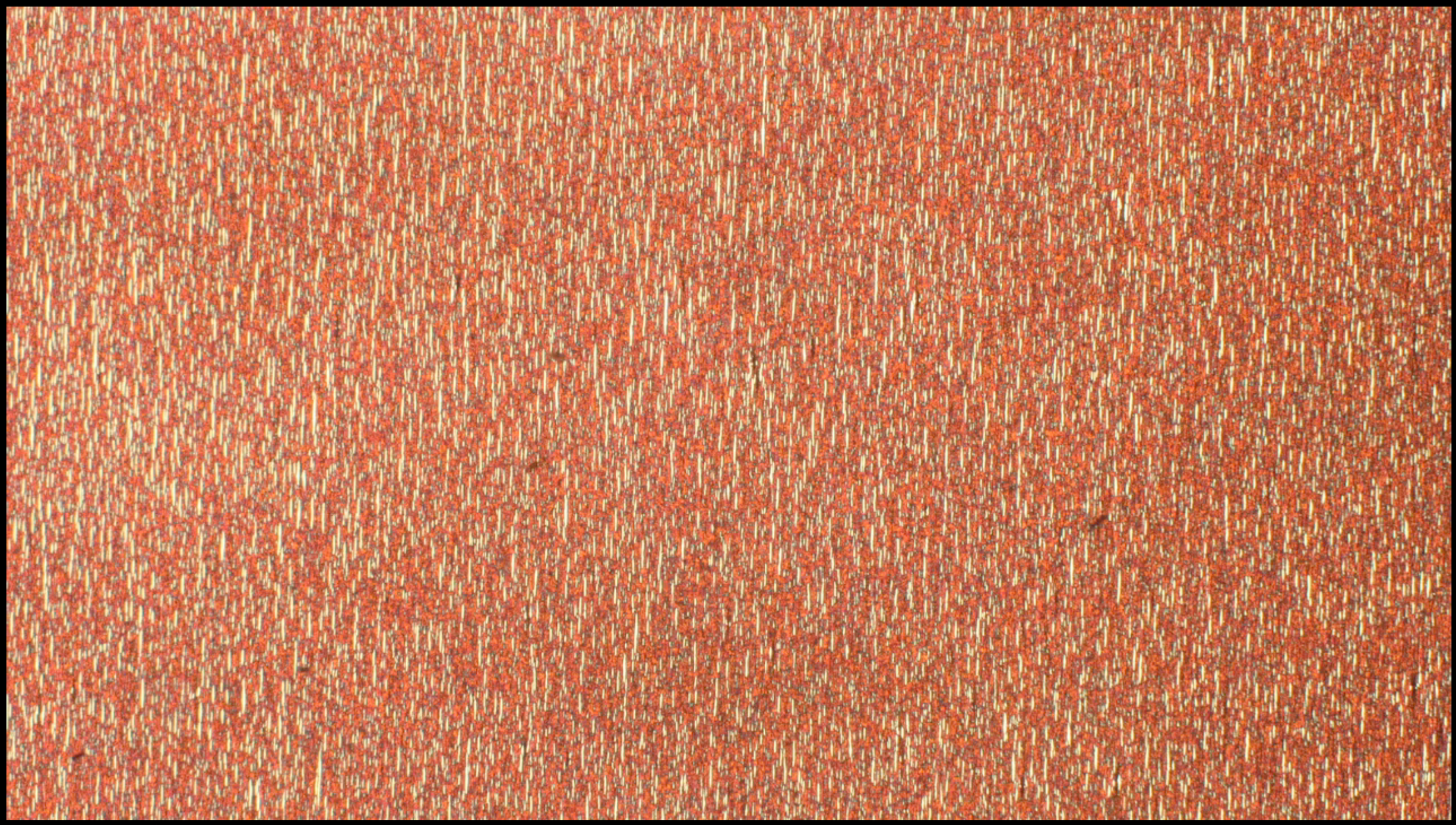




Suspension view across field direction



Arrested magnetic colloids in a magnetic field



H-field
0.9A, 10Hz

$\otimes\, g$

1.71×1.14 mm

Elapsed time: 1hr

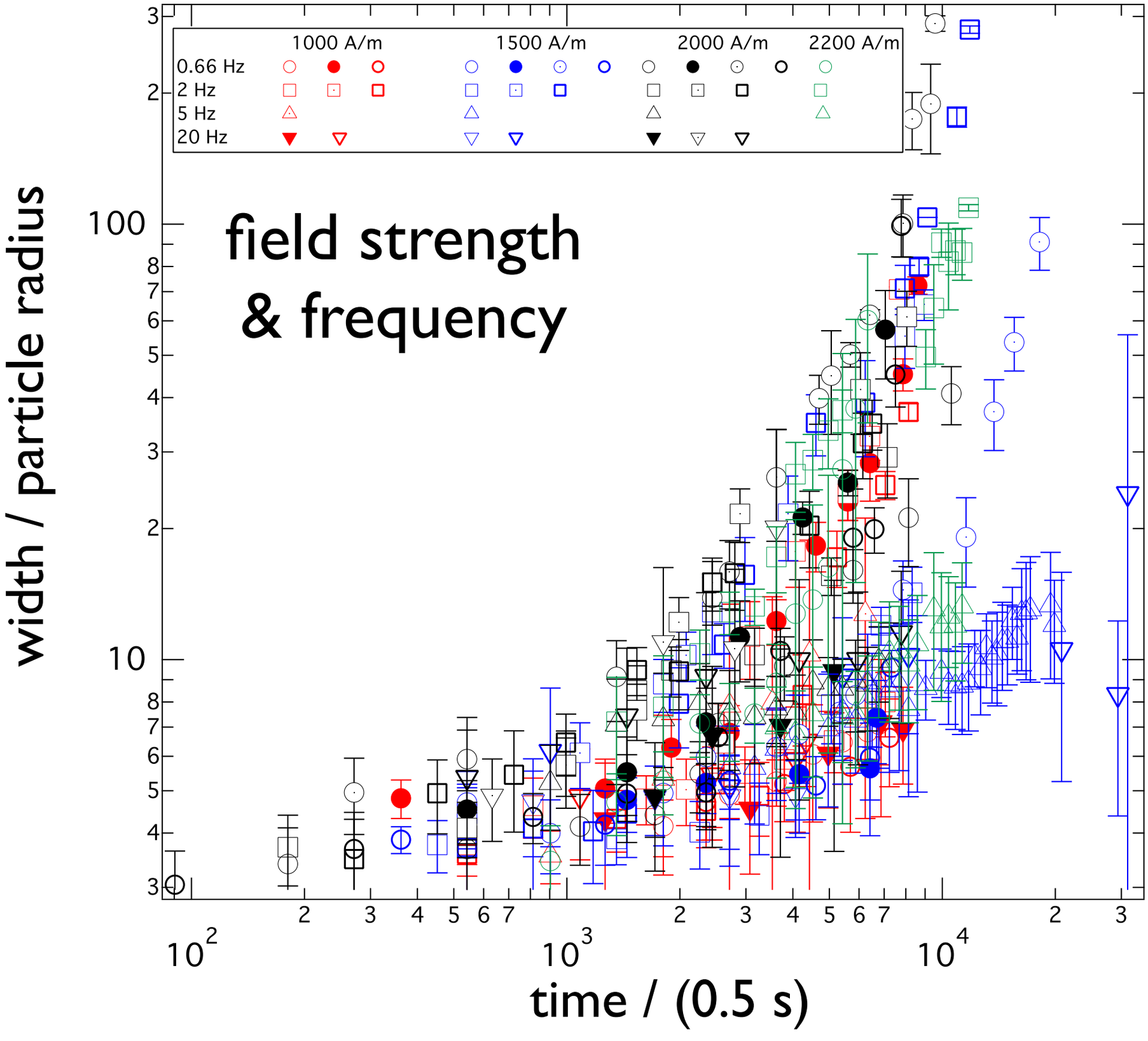
InSPACE suspension evolution

H-field ⟷

0.9A, 10Hz

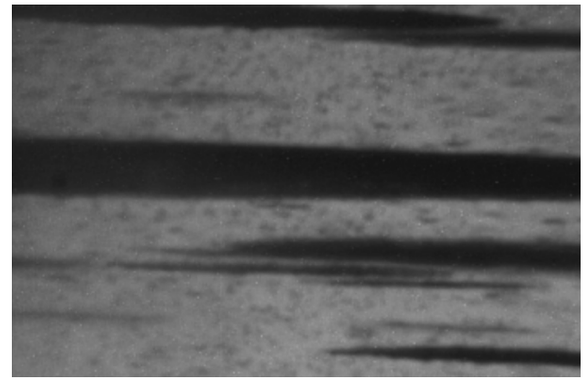
Time lapse

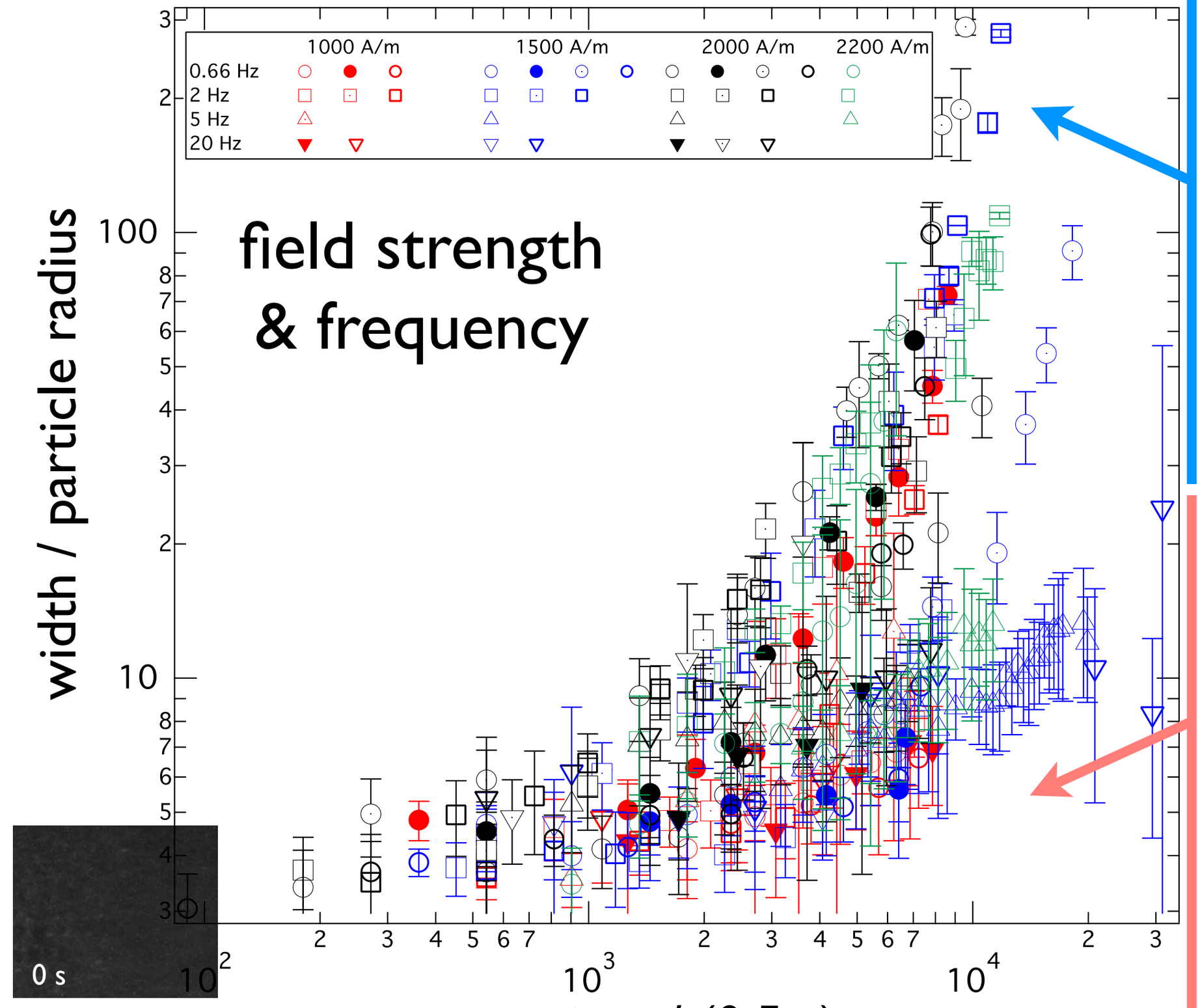
James W. Swan, *et al. PNAS* 109, 16023–16028 (2012).

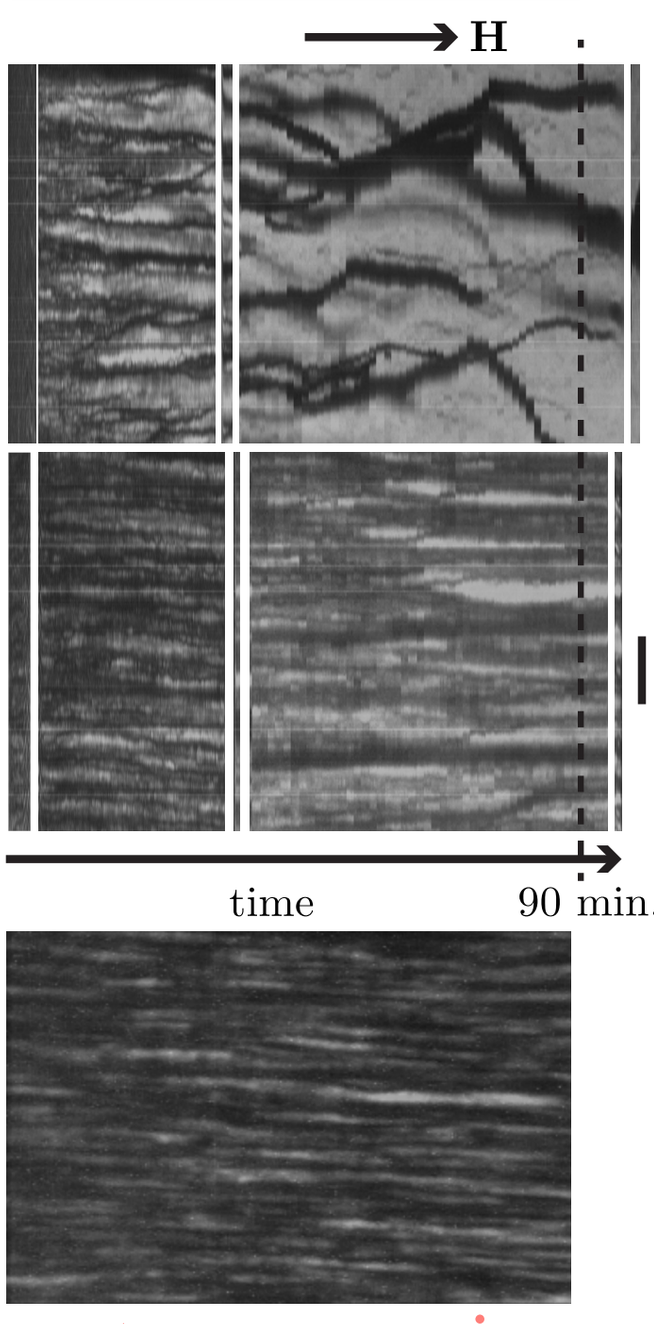


James W. Swan, *et al. PNAS* 109, 16023–16028 (2012).

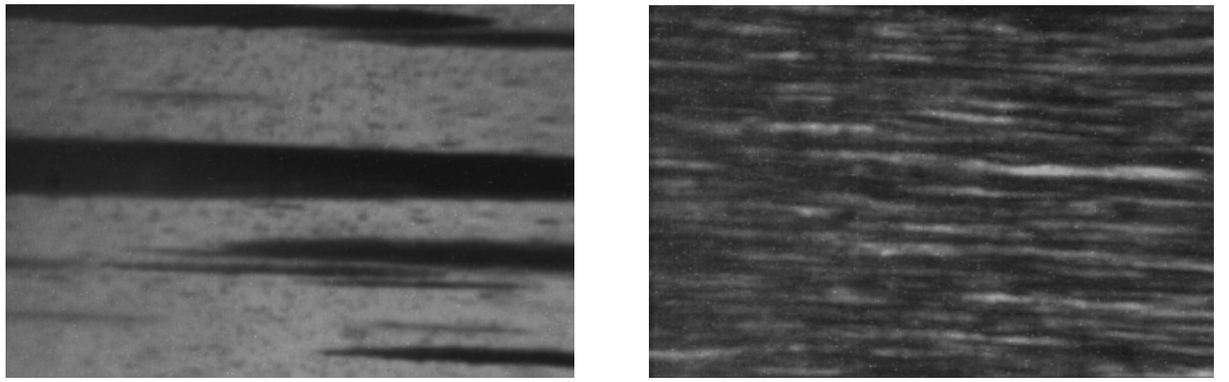
collapsed

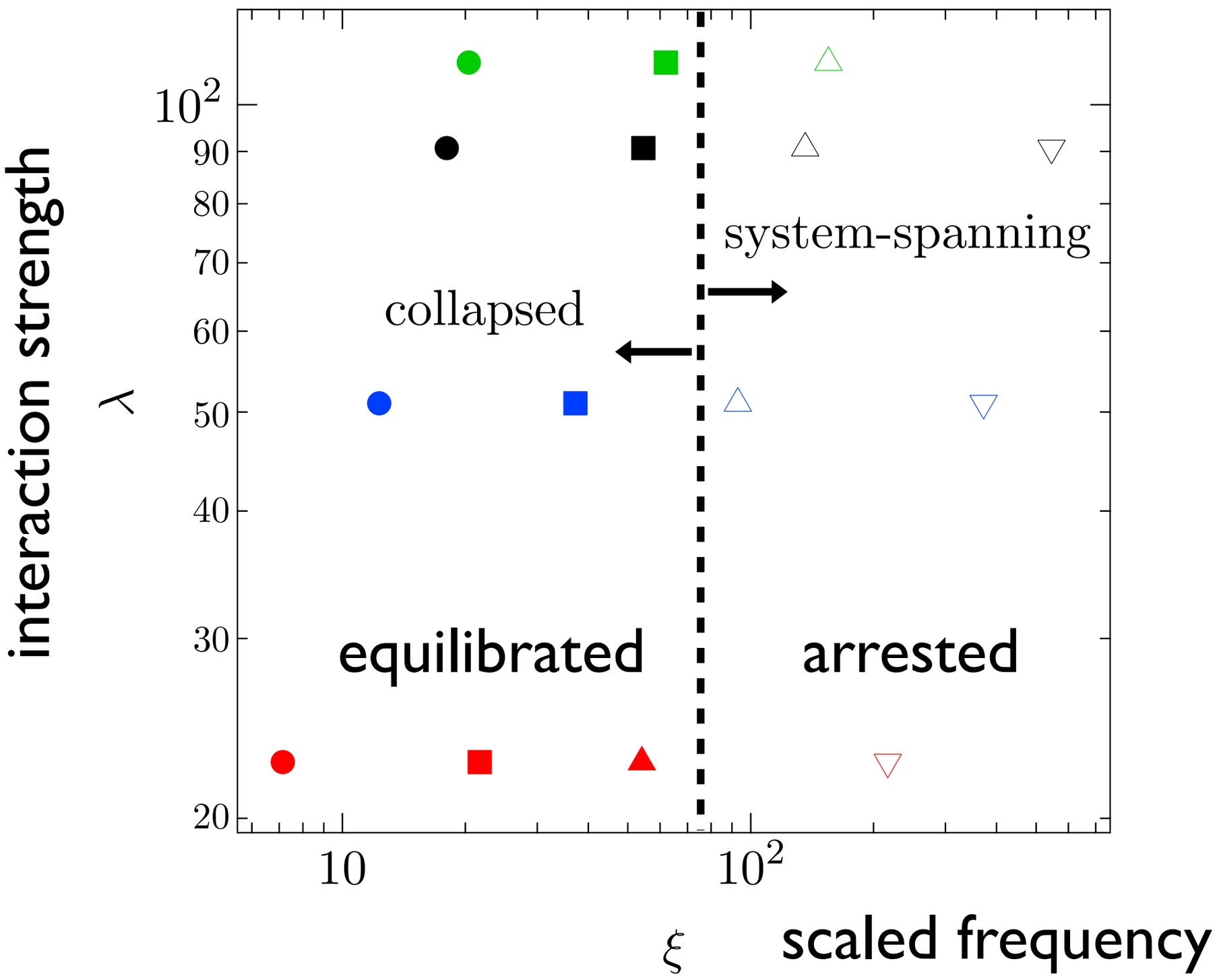




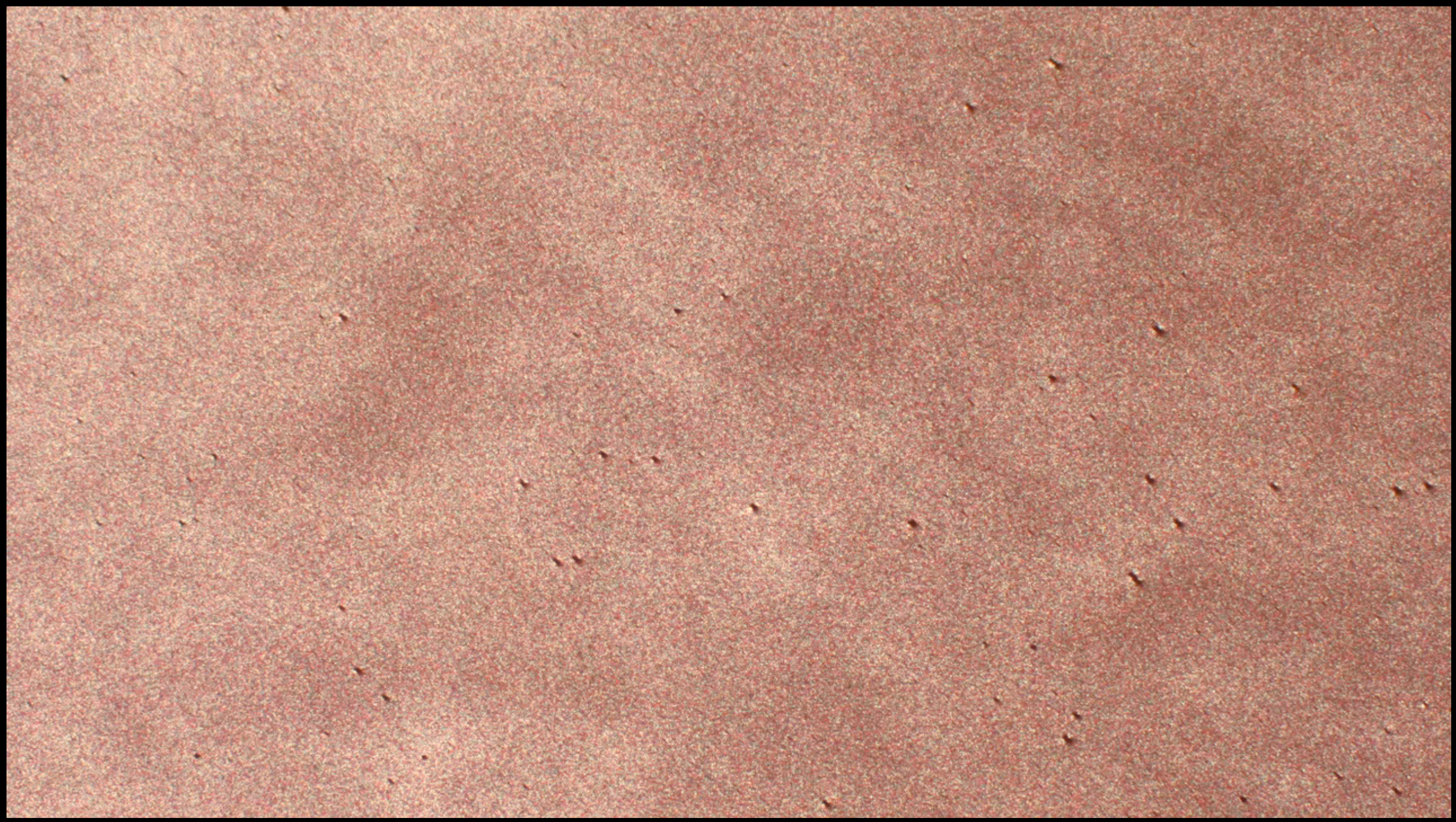


system-spanning




10^2
90
80
70
60
50
40
30
20
10
10^2
interaction strength
λ
scaled frequency
ξ
collapsed
system-spanning
equilibrated
arrested

Phase separating magnetic colloids in a 0.66 Hz H–field



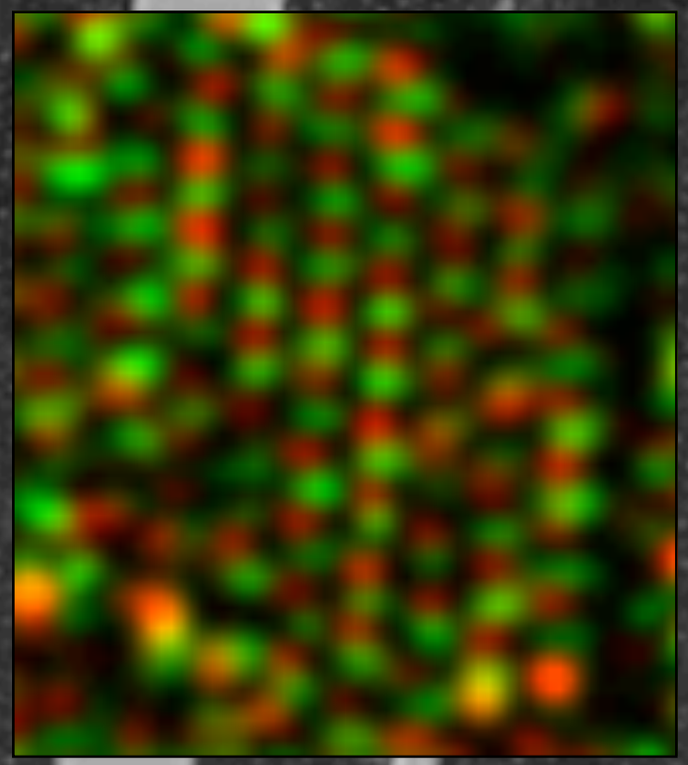
H-field
0.9A, 0.66 Hz

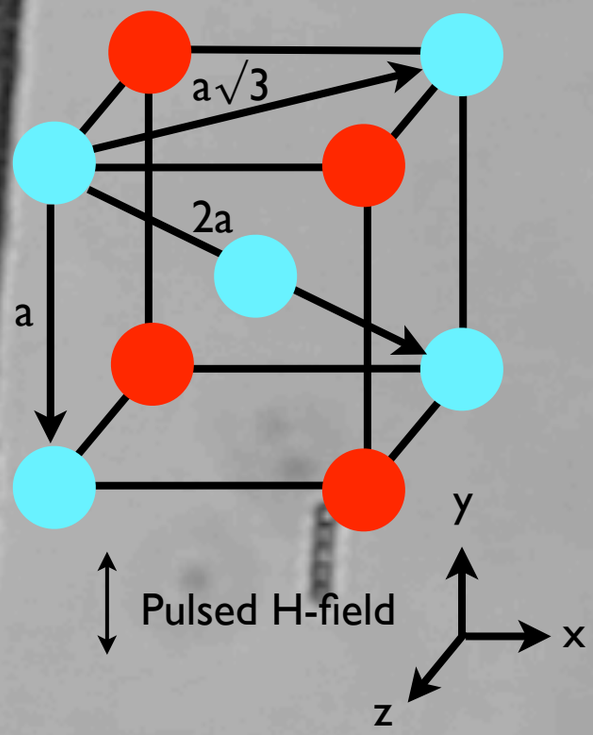
$\otimes\, g$

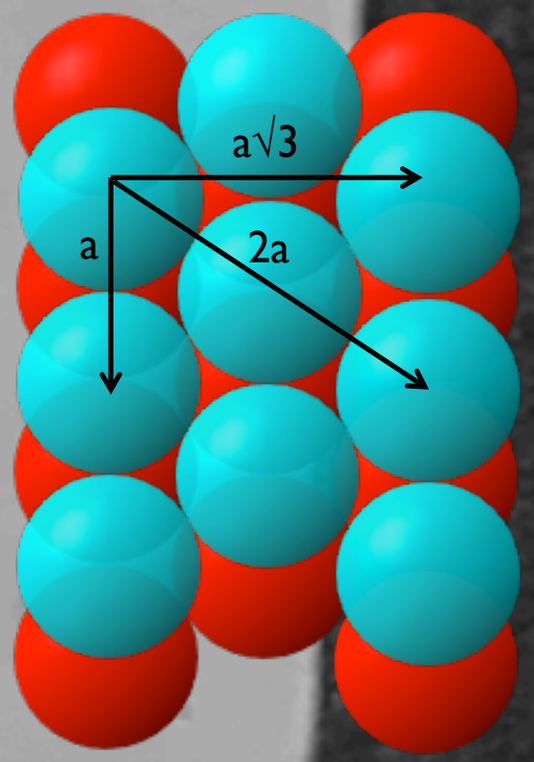
1.71×1.14 mm

Elapsed time: 1hr

Self-assembled crystal microstructure







Body Centered Tetragonal (BCT) 110

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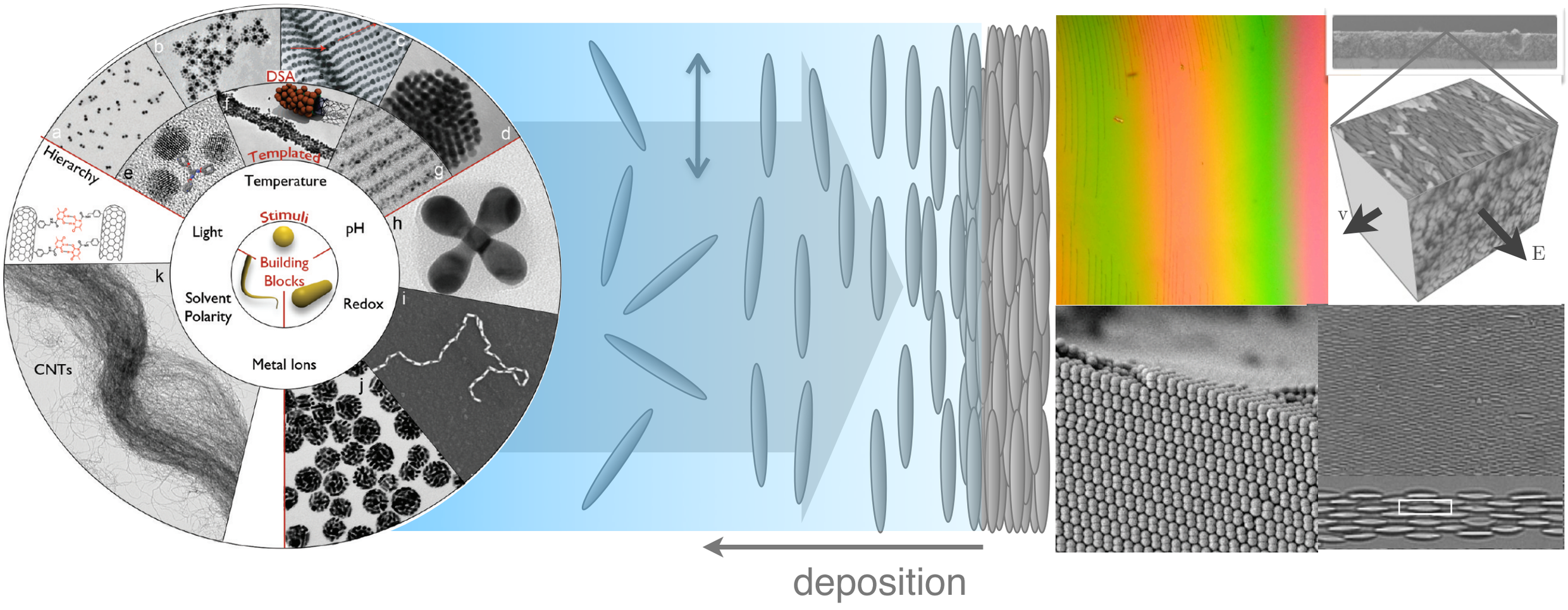
Directed Self-Assembly of Nanoparticles

Marek Grzelczak,[†,‡] Jan Vermant,[§,*] Eric M. Furst,[⊥,*] and Luis M. Liz-Marzán[†,*]

Nanoparticle building blocks → *Self-assembly with directing fields* → *Nano-structured materials*



"Bottom-up," low cost, large scale processing and manufacturing of nano-structured materials

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Photo credit ISS Expedition 30, NASA

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