Building colloidal crystals under microgravity

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NASA Advanced Colloids Experiments (ACE) Program on ISS:

Results of experiments:

ACE –T11: **Colloids of spherical particles, Nov 2020 - Jun 2021**
ACE-TR Ellipsoids: **Colloids of ellipsoidal particles, Sept 2021 - Feb 2021**

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MOTIVATION

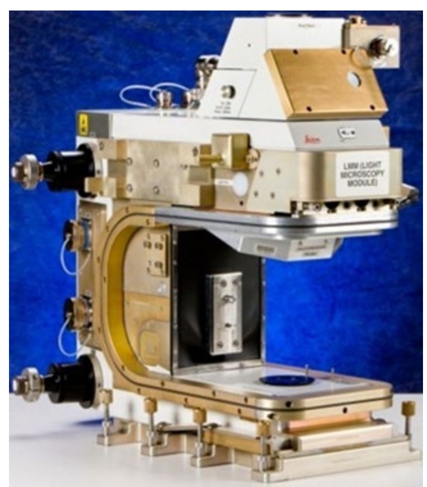
Why study colloids in microgravity?

- On Earth gravitational sedimentation confirms most colloidal systems to 2D with numerous artifacts due to floors and boundaries.
- Long-duration microgravity on the ISS literally adds another dimension to the problem making available 3D motion, 3D processing, 3D fundamental science, 3D protocols and 3D materials and devices

Light Microscopy Module (LMM)

Approach: Use high-resolution confocal (3D) microscopy in long-duration microgravity on the ISS to investigate the colloidal structure at the particle level.

Sample Module

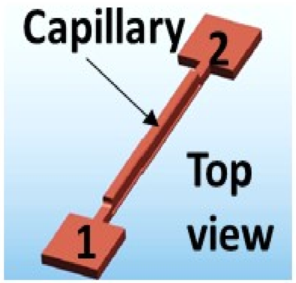


3D Microscope

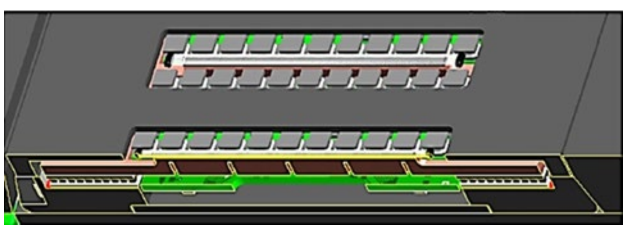
Fluids Integrated Rack

ACE SAMPLE MODULE

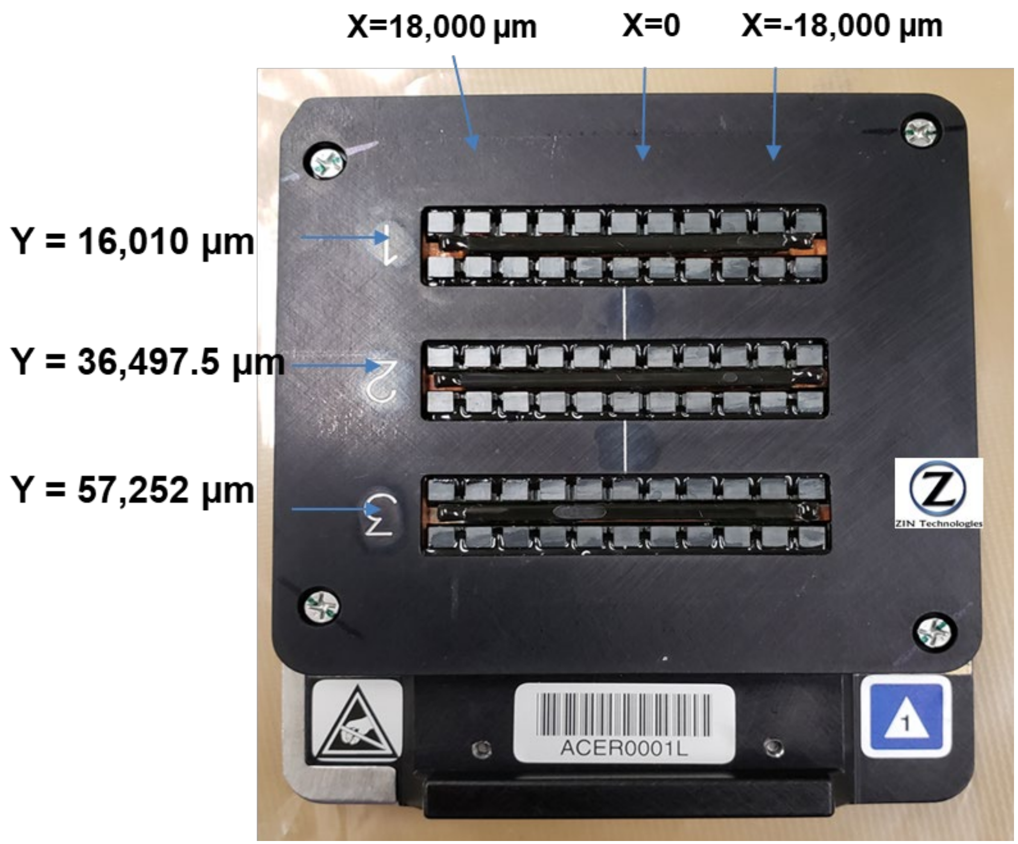
NASA GRC & ZIN Tech images



The capillary of diameter 0.140 mm is mounted between hot and cold thermistors 1 and 2.



Capillary sample cells surrounded by inductors that are used for walking a turning stirring bar for mixing a sample.

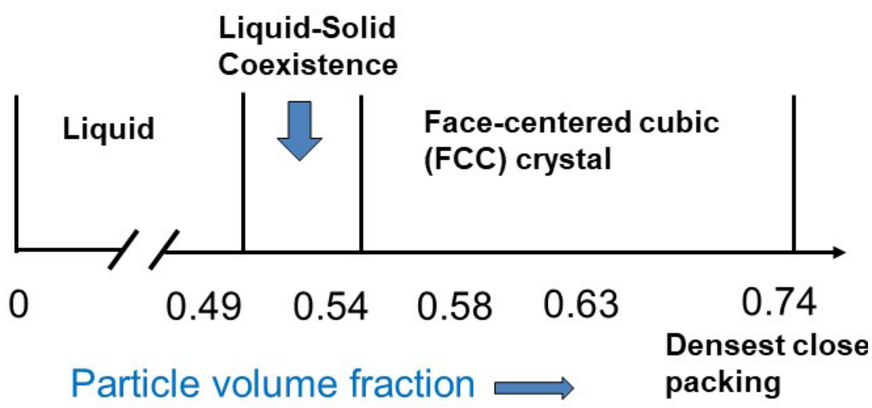


HARD SPHERES

- Hard spheres is the basic model of particles in the statistical mechanical theory of fluids and solids. Defined as impenetrable spheres that cannot overlap in space, they mimic the extremely strong repulsion that atoms and spherical molecules experience at very close distances. The hard-sphere colloid provides a generic model that explains the quasi-universal structure and dynamics of simple liquids.

- **The hard-sphere model is the cornerstone of our understanding of liquid crystallization!**

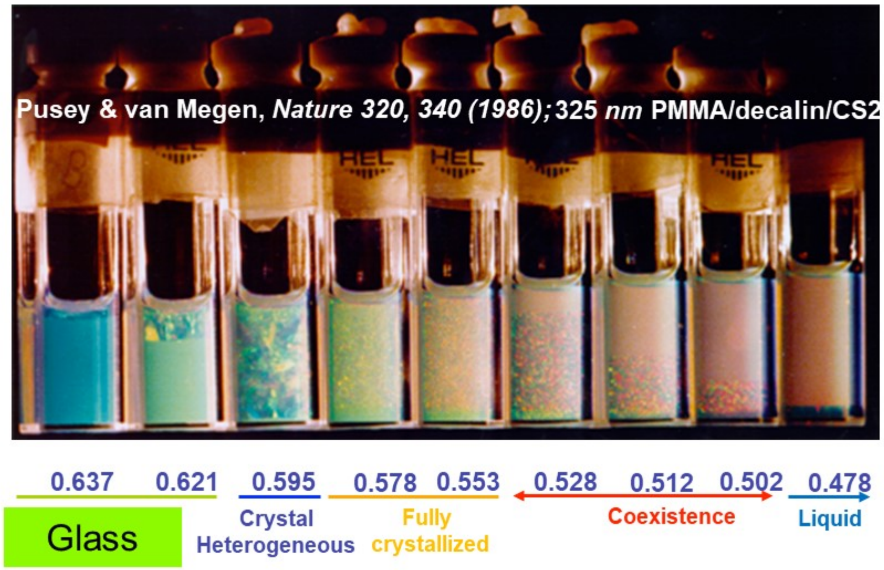
Most recent computer simulations predict the following equilibrium phase diagram for hard spheres



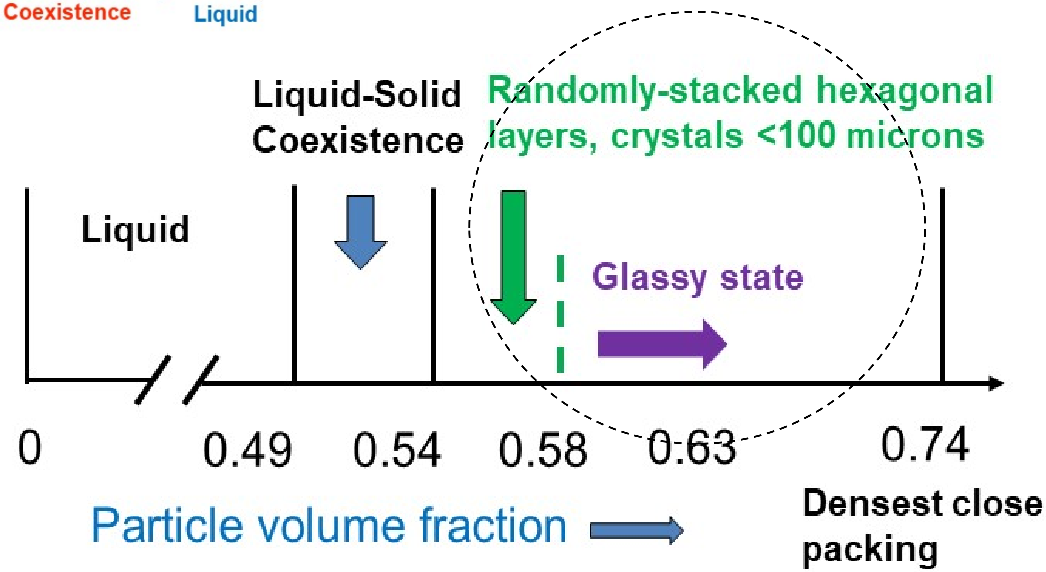
- **In terrestrial experiments heterogeneous polycrystalline materials with crystallites < $100\ \mu m$ form in sediments as the density increases toward the bottom of the samples.**

- **Due to gravitational settling of particles, terrestrial experiments fail to confirm the crystalline phases predicted.**

Experimental phase diagram of hard spheres



Crystallization for densities beyond 0.57 − 0.58 did not occur! Interpreted as the glassy state

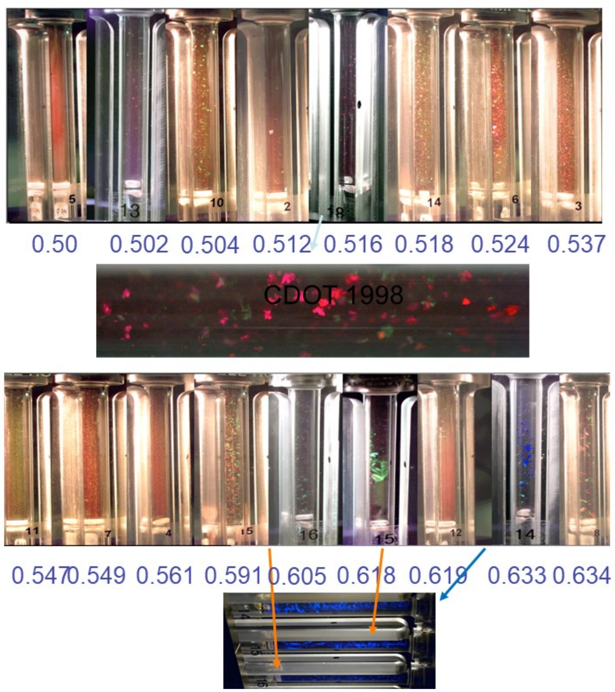


SPACE SHUTTLE EXPERIMENTS

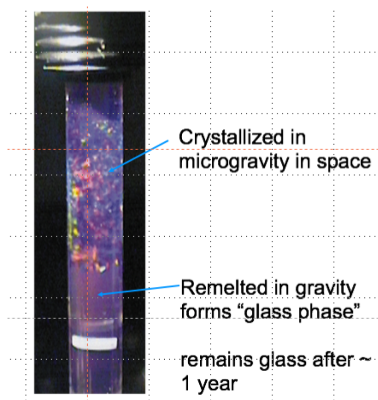
Colloidal Disorder-Order Transitions (CDOT) experiments:
First: STS-73, Nov 1995. Second: STS-95, Oct 1998.

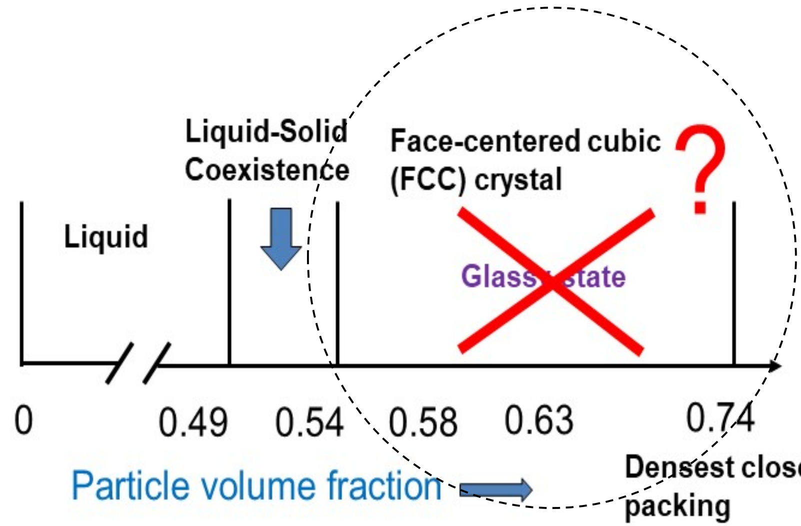
Theory revised maybe works???

CDOT 1998: Chaikin et al, Nature, 387, 883 (1997)



Volume fraction 60%





ACE-T11 Experiments 2021

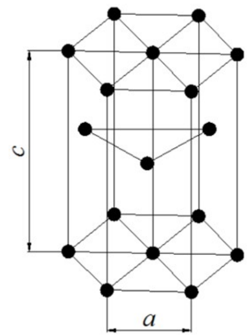
Equilibrium Crystal Structure

Most metals adopt hexagonal close packed (HCP) and face-centered cubic (FCC) structures

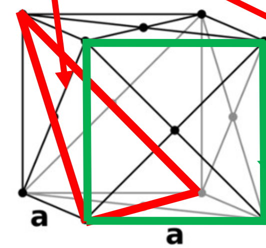
https://en.wikipedia.org/wiki/Periodic_table_(crystal_structure)

1 H HEX																		2 He HCP
3 Li BCC	4 Be HCP												5 B RHO	6 C HEX	7 N HEX	8 O SC	9 F SC	10 Ne FCC
11 Na BCC	12 Mg HCP												13 Al FCC	14 Si DC	15 P ORTH	16 S ORTH	17 Cl ORTH	18 Ar FCC
19 K BCC	20 Ca FCC		21 Sc HCP	22 Ti HCP	23 V BCC	24 Cr BCC	25 Mn BCC	26 Fe BCC	27 Co HCP	28 Ni FCC	29 Cu FCC	30 Zn HCP	31 Ga ORTH	32 Ge DC	33 As RHO	34 Se HEX	35 Br ORTH	36 Kr FCC
37 Rb BCC	38 Sr FCC		39 Y HCP	40 Zr HCP	41 Nb BCC	42 Mo BCC	43 Tc HCP	44 Ru HCP	45 Rh FCC	46 Pd FCC	47 Ag FCC	48 Cd HCP	49 In TETR	50 Sn TETR	51 Sb RHO	52 Te HEX	53 I ORTH	54 Xe FCC
55 Cs BCC	56 Ba BCC	*	71 Lu HCP	72 Hf HCP	73 Ta BCC/TETR	74 W BCC	75 Re HCP	76 Os HCP	77 Ir FCC	78 Pt FCC	79 Au FCC	80 Hg RHO	81 Tl HCP	82 Pb FCC	83 Bi RHO	84 Po SC/RHO	85 At	86 Rn FCC
87 Fr	88 Ra BCC	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
		*	57 La DHCP	58 Ce DHCP/FCC	59 Pr DHCP	60 Nd DHCP	61 Pm DHCP	62 Sm RHO	63 Eu BCC	64 Gd HCP	65 Tb HCP	66 Dy HCP	67 Ho HCP	68 Er HCP	69 Tm HCP	70 Yb FCC		
		**	89 Ac FCC	90 Th FCC	91 Pa TETR	92 U ORTH	93 Np ORTH	94 Pu MON	95 Am DHCP	96 Cm DHCP	97 Bk DHCP	98 Cf DHCP	99 Es FCC	100 Fm	101 Md	102 No		

Hexagonal array



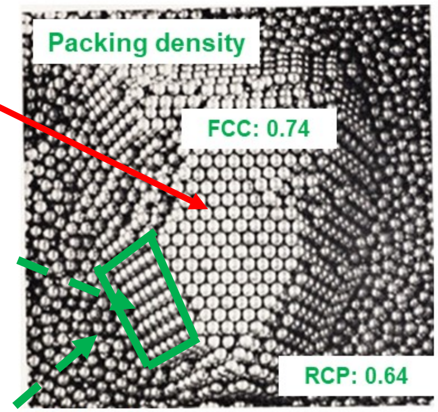
HCP



FCC

Packing Factor of HCP and FCC: 0.74
Random close packing (RCP): 0.64

Bernal, Proc R Soc A 280, 299 (1964)

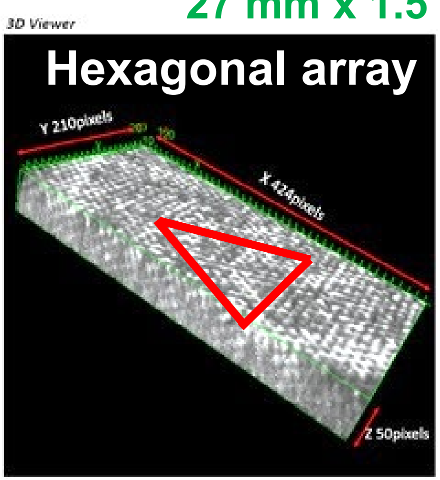


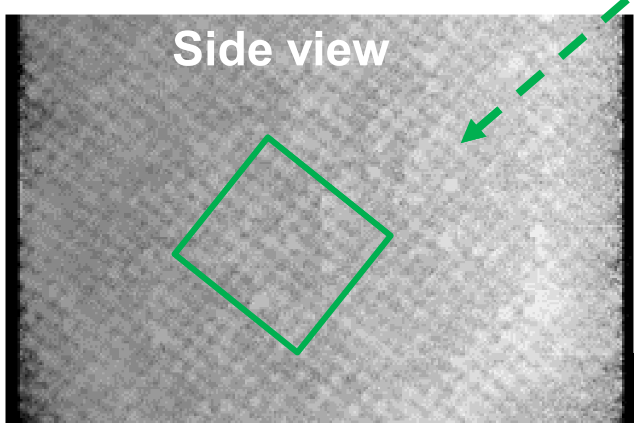
Ball bearings. FCC crystal surrounded by 'liquid' formed by shearing.

Theory does work!!!

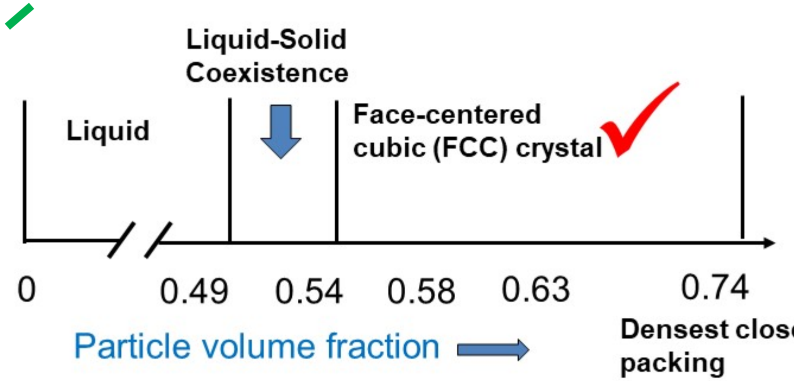
~100 Gb confocal images and videos

FCC crystal is of the size of the capillary
27 mm x 1.5 mm x 0.15 mm





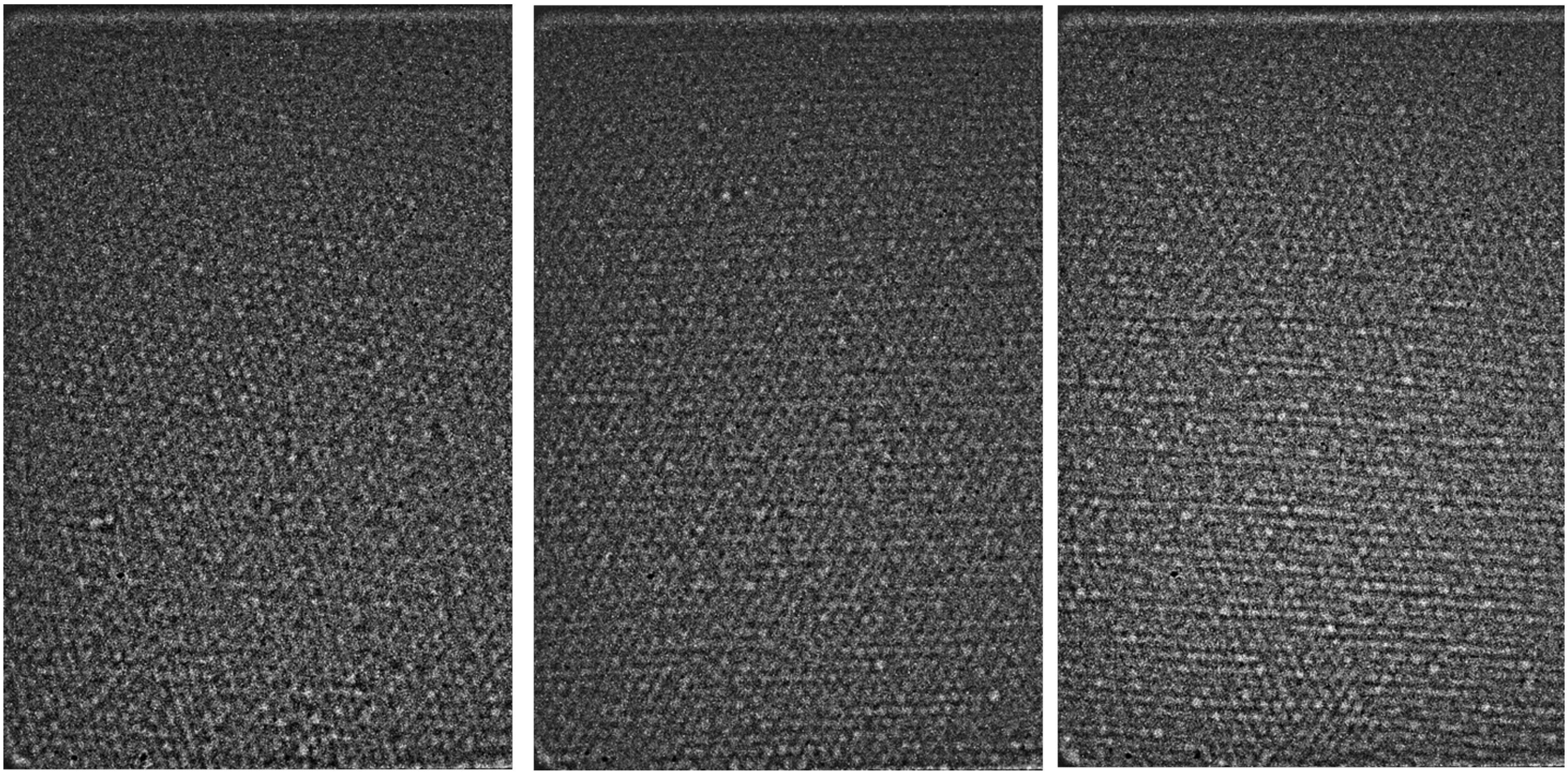
First confirmation of theory



Monodisperse fluorescent polymethyl methacrylate (PMMA) particles $1.29 \pm 0.02\ \mu m$

Crystallization of spherical particles on ISS

Confocal microscopy: Magnification 100 X, oil immersion objective



X= -10.885 mm

X= -2.836 mm

X= +16.921 mm

27 mm across the capillary

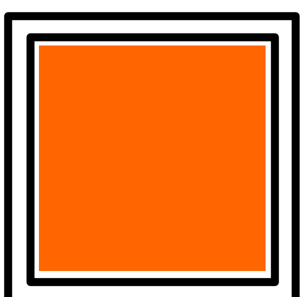
Parallel crystalline lines in every portion of the images across the entire sample capillary.

ACE-TR ELLIPSOIDS

The colloid of hard ellipsoids provides a generic model that explains the quasi-universal structure and dynamics of liquid crystals. Compared to molecules in liquid crystals which are too small to be seen with an optical microscope, the colloidal particles are huge in size and can be used to test predictions of computer simulations. .

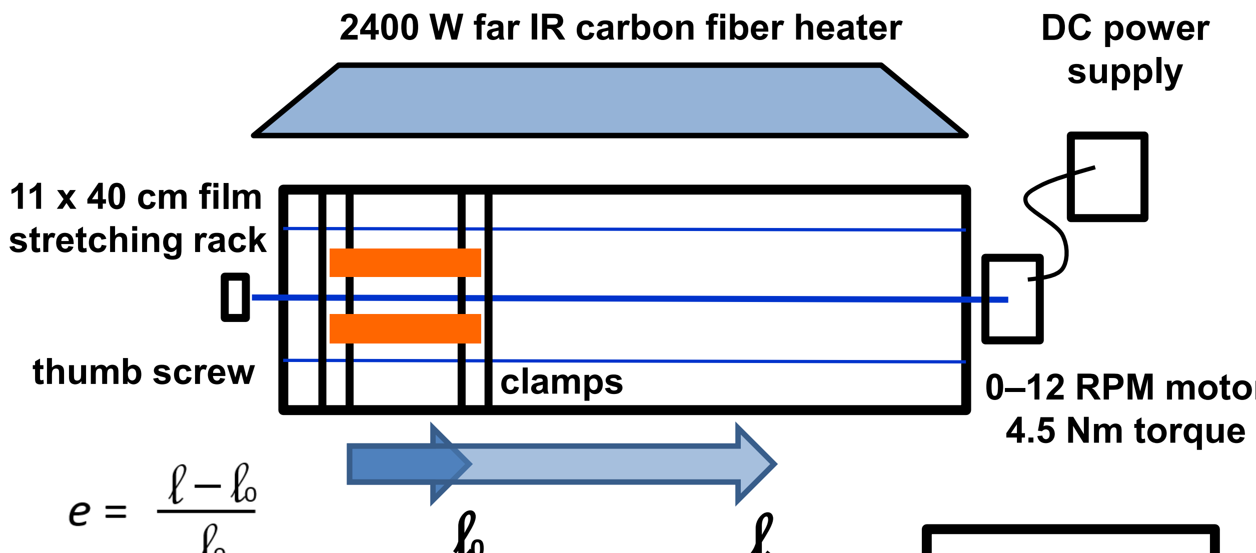
Synthesis of ellipsoids: Andrew D. Hollingsworth, NYU

- 1 to 2 micron dia. stabilized with poly(12-hydroxylstearic acid) PMMA spheres
- flurorescent labeling
- disperse PMMA spheres in PDMS prepolymer
- cast/cure PDMS film
- thermomechanical stretching / T soak / quench
- harvest ellipsoids
- photocrosslinking
- post-processing



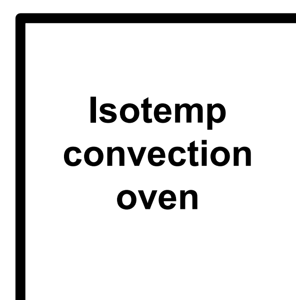
22 x 22 cm plexi mold (1.27 cm sheet)

Thermomechanical stretching PDMS film

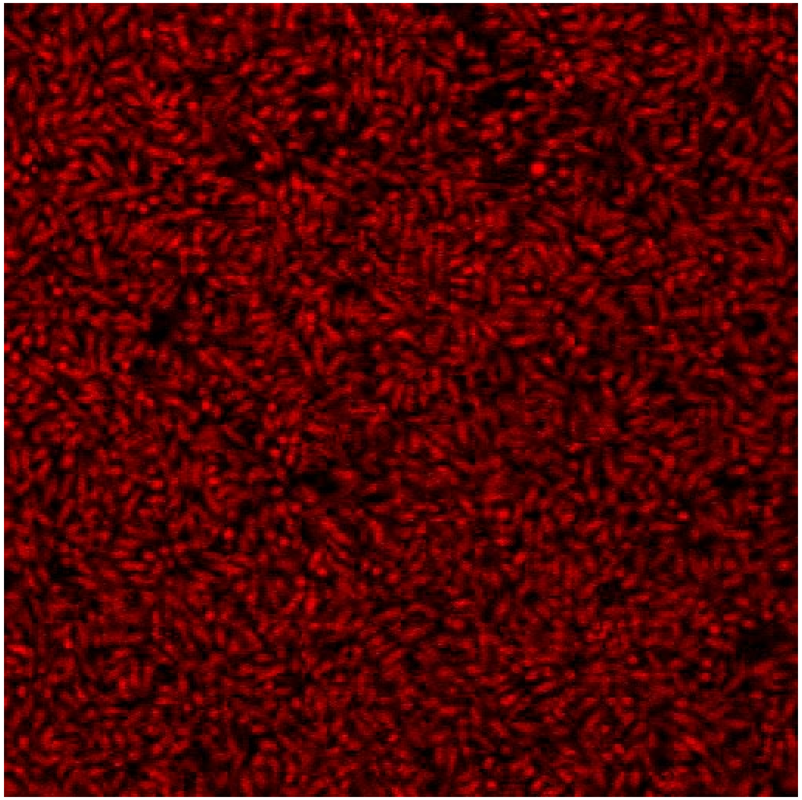


$$e = \frac{\ell - \ell_0}{\ell_0}$$

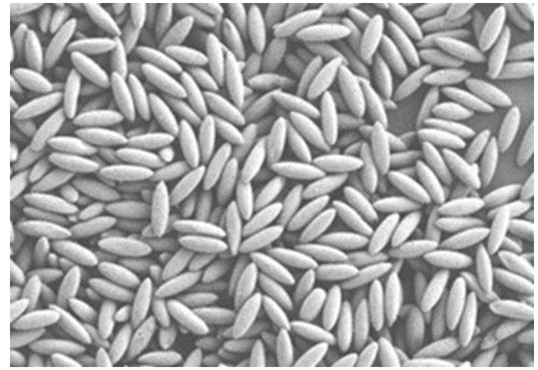
Film thickness: 0.15 cm
Particle density: 10^{10} /cm^3
Pull velocity: 0.5 cm/min
Film cure T: 60 h at RT; 3 h at 120°C
Annealing T: 30 min at 170°C



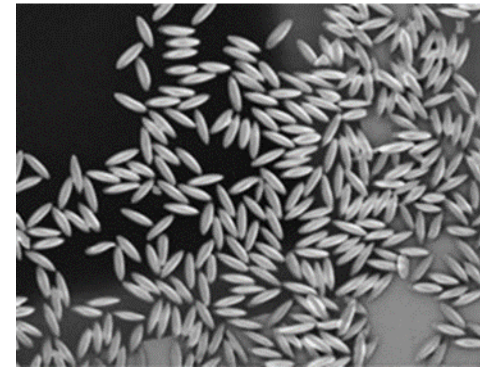
ELLIPSOIDAL COLLOIDS



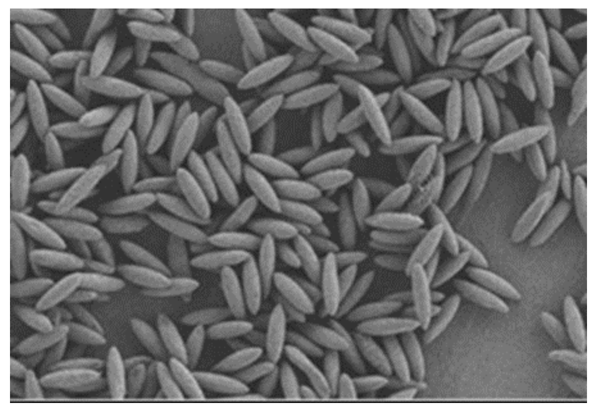
Leica SP5 confocal
63 X glycerol, 543 nm HeNe



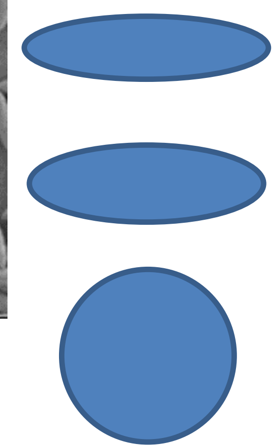
CSF-02-139A pulls 5 6b 7 8 9
$\alpha \approx 3.0$



CSF-02-139B pull 1
$\alpha \approx 3.7$



CSF-02-139C pull 10
$\alpha \approx 3.8$



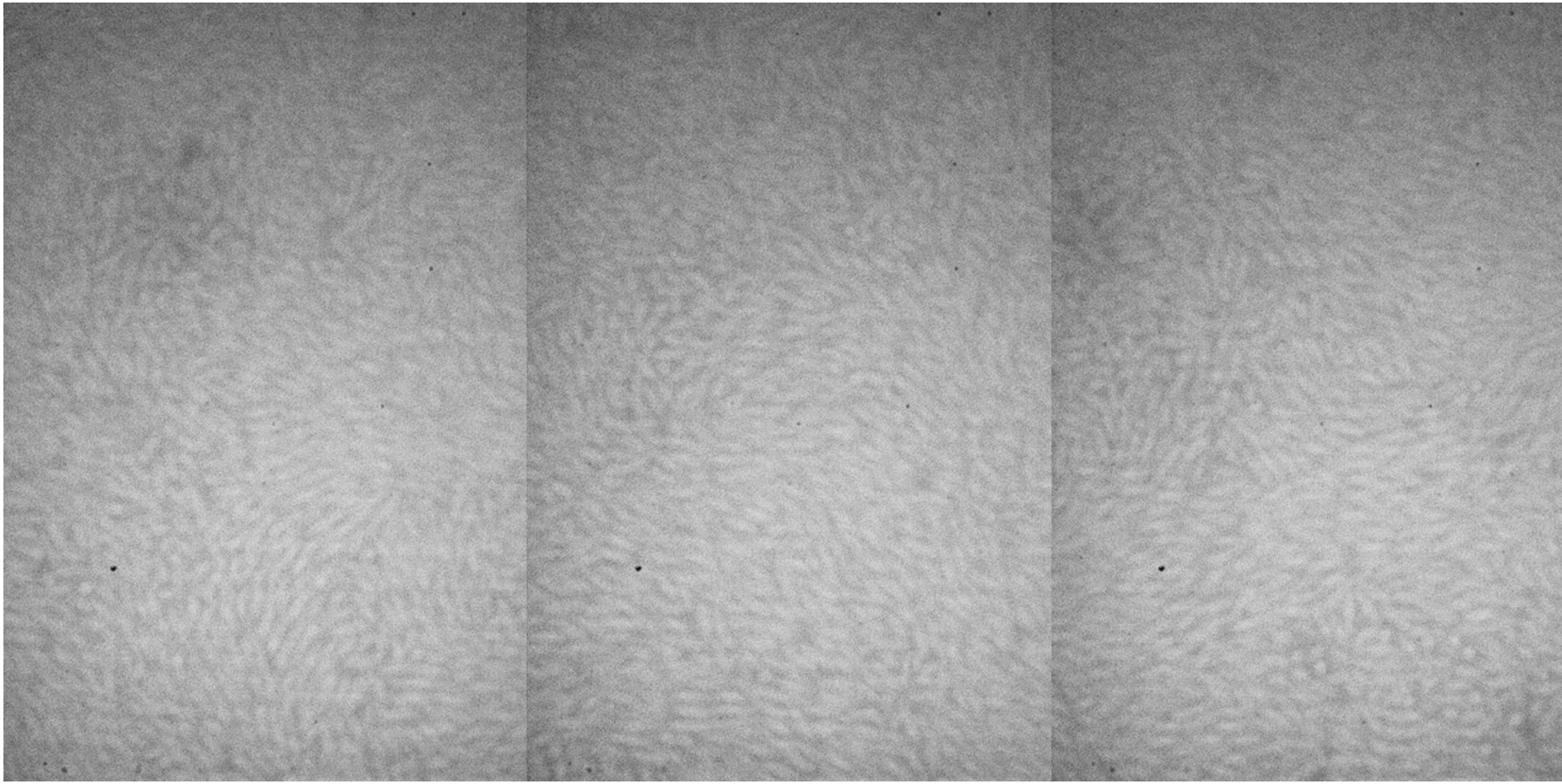
$\alpha = 3.8$

$\alpha = 3.0$

$\alpha = 1.0$

ACE-TR ELLIPSOIDS

Large nematic domains in scanning along the capillary axis on ISS



2020/10/05, 17:21:25.535, CnFcl, ACETR, S3001, C3, X100, X-16674, Z0+15, P4, E458961, 00945

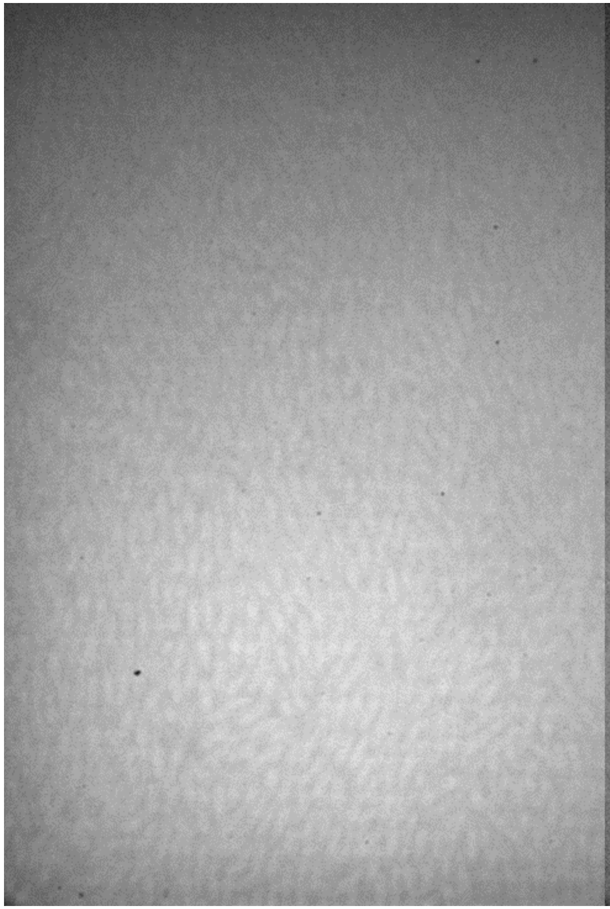
2020/10/05, 17:21:29.535, CnFcl, ACETR, S3001, C3, X100, X-16566, Z0+15, P5, E458961, 00946

2020/10/05, 17:21:33.535, CnFcl, ACETR, S3001, C3_X100, X-16457, Z0+15, P6, E458961, 00947

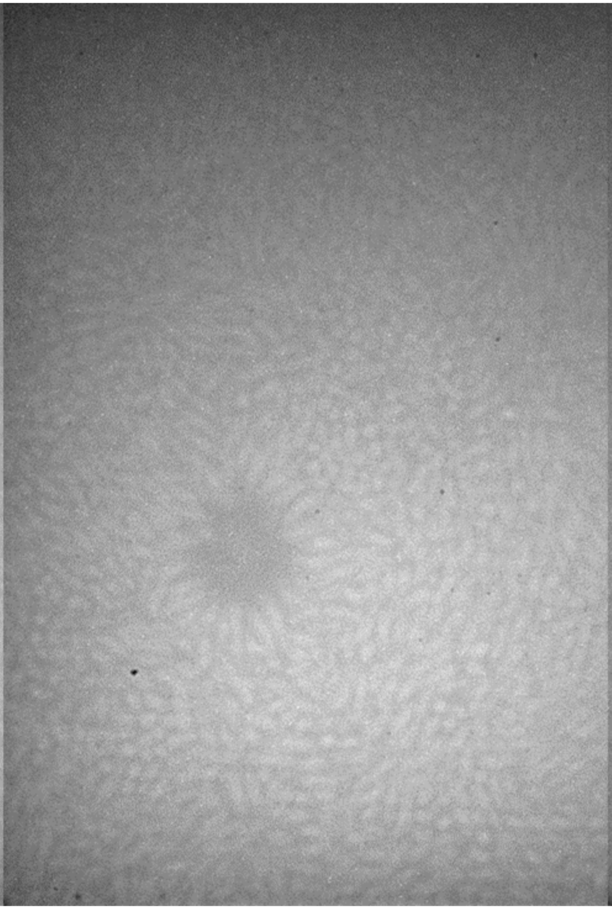
ACE-TR ELLIPSOIDS

Finding that microscopic colloidal ellipsoids mimic the molecular-sized structures, along with their defects, commonly called 'hedgehogs' in the liquid crystal community provides an important support for theoretical predictions.

Nematic domains and associated "hedgehog" defects on ISS



2020/09/24, 22:14:56.768, CnFcl, ACETR, S3001, C3, X100, X-13964, P29, E443412, 00250



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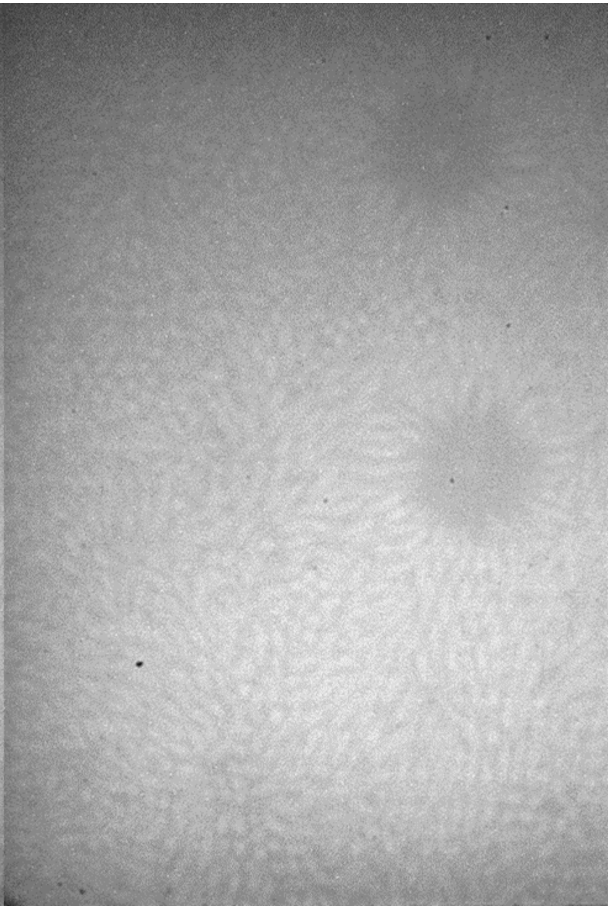

2020/09/24, 22:15:40.701, CnFcl, ACETR, S3001, C3, X100, X-12771, P40, E443412, 00261

CONCLUSIONS

Up until now theories for the simplest, most common, most fundamental Crystallization Transition from Liquid to FCC Crystal had not been confirmed.

Now it is!

- **Large FCC crystals observed on spherical colloids on ISS**
- **Large nematic domains observed in ellipsoidal colloids on ISS**

Simulations of equilibrium* work only when gravitational effects are unimportant

Build for the Future†

Use simulation/computation for equilibrium* materials processing in μg

Develop non-equilibrium** processing and dynamic materials/devices in μg

Proceed to understand effects of 1g in materials processing and design

In μg manufacture better materials for ceramics, paints, photonics, pastes for additive manufacturing for industry on Earth and for space exploration

* ***Equilibrium*** *– no net flows of matter or energy*

** ***Non-equilibrium*** *– forces, stresses, activity, energy conversion*

† ***See Grand Challenges in Soft Matter Science: Prospects for Microgravity Research - NASA/CP-20205010493***

Thank you!

Questions

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