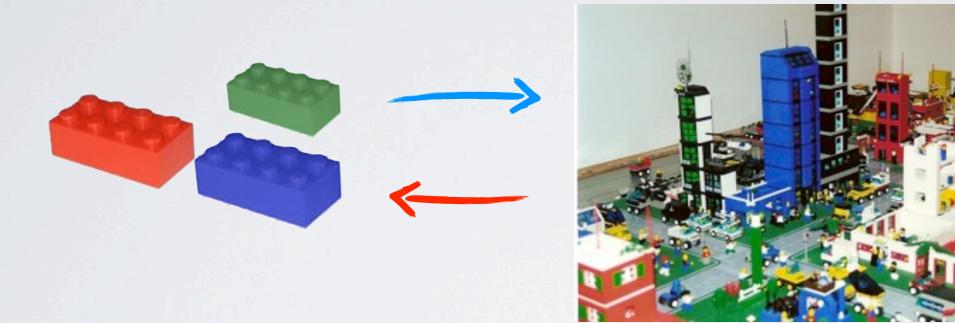
#### SELF-ASSEMBLY AND DIFFUSION OF ANISOTROPIC PARTICLES

Daniela J. Kraft



COST workshop, Lagrangian transport: from complex flows to complex fluids Soft Matter Physics, LION, Leiden University, The Netherlands March 7 2016



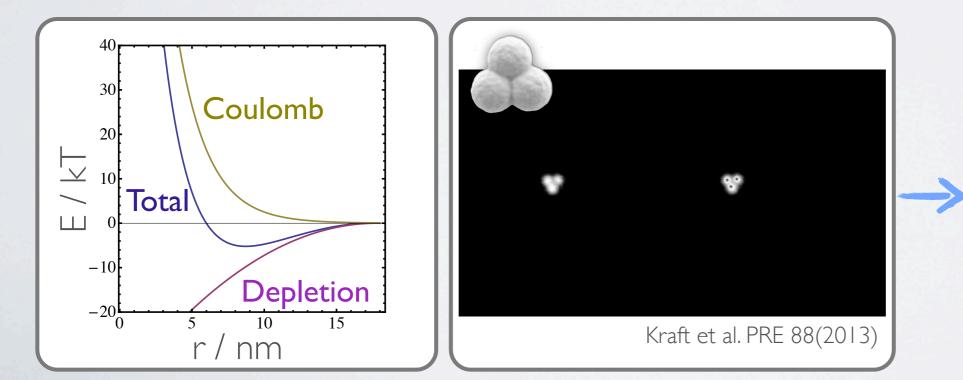


#### "What I cannot create, I do not understand." **R. Feynman**

## WHY COLLOIDAL PARTICLES?



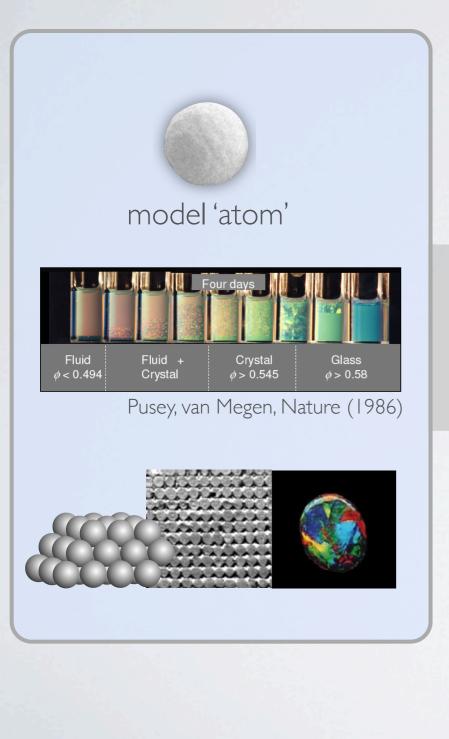
SOFT, SLOW, SEEABLE

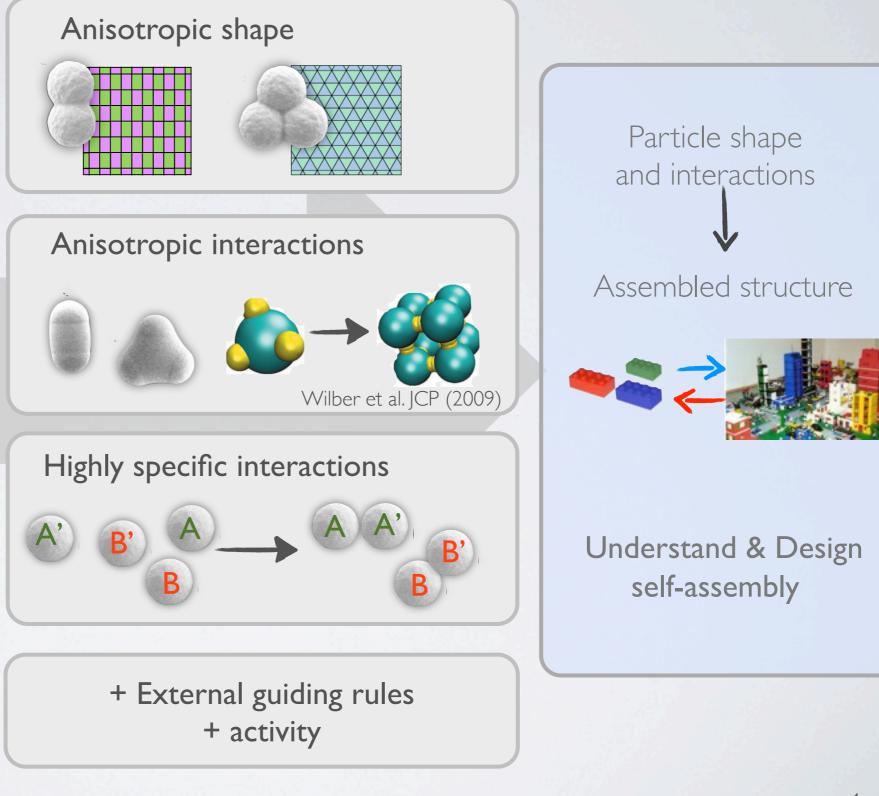


Ideal Model System For Doing Fundamental Physics

Applications

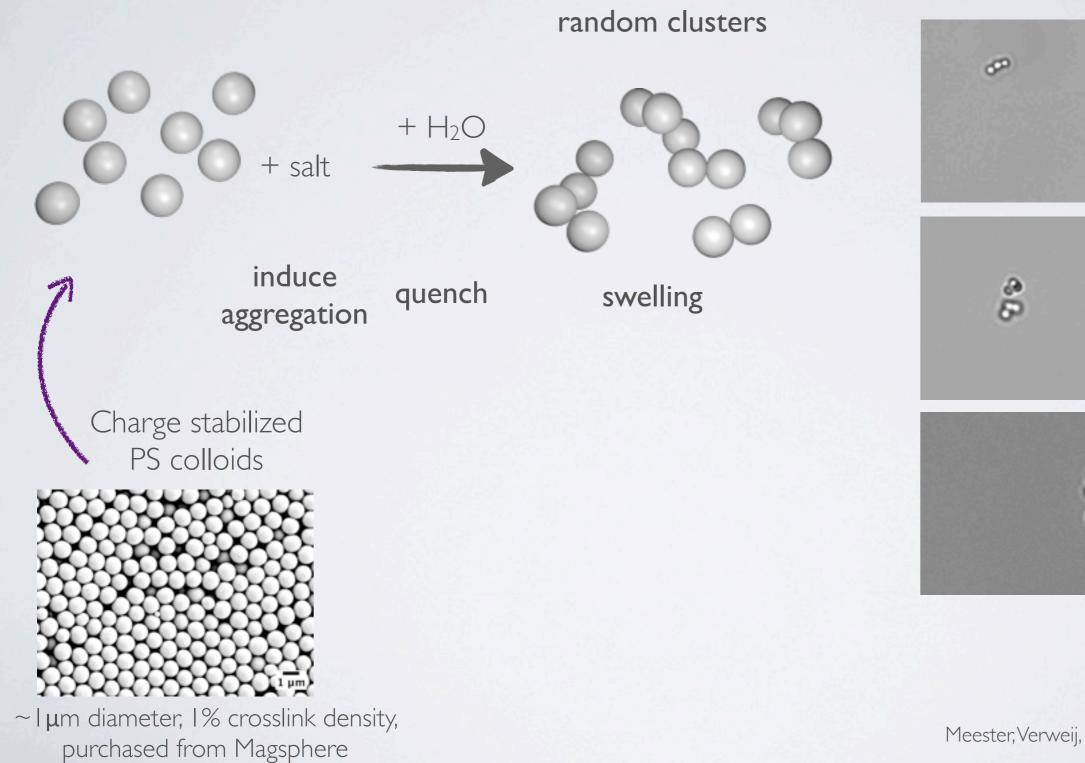
## FROM SPHERES TO COMPLEX PARTICLES





## Colloidal Recycling: Synthesis of Complex Colloidal Particles

### RESHAPING RANDOM COLLOIDAL CLUSTERS



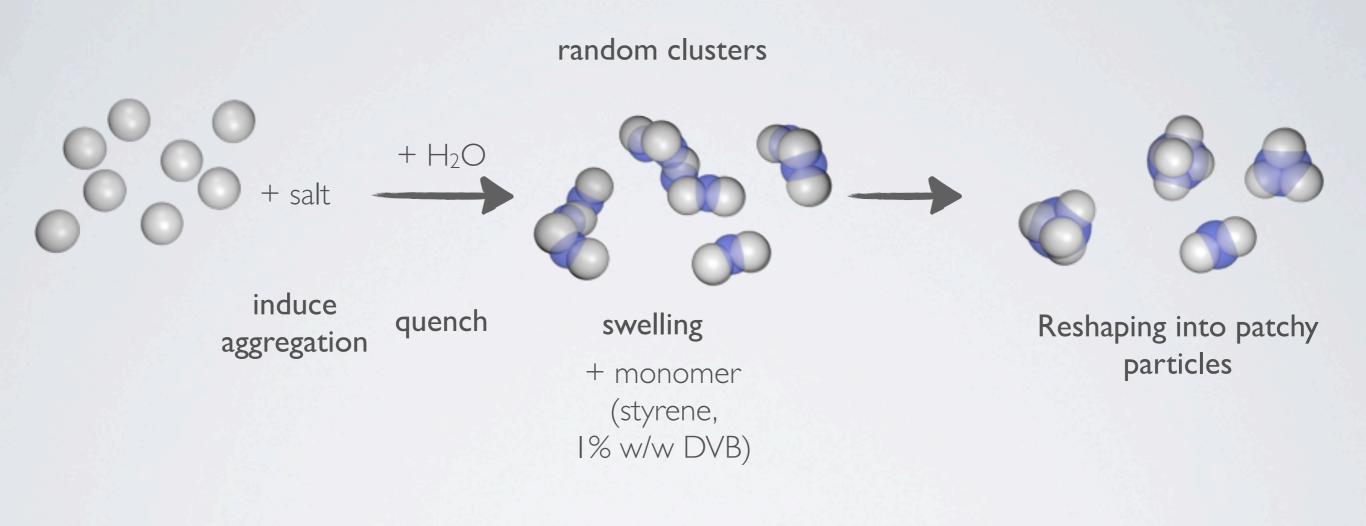
Meester, Verweij, vd Wel, Kraft, ACSNano (2016)

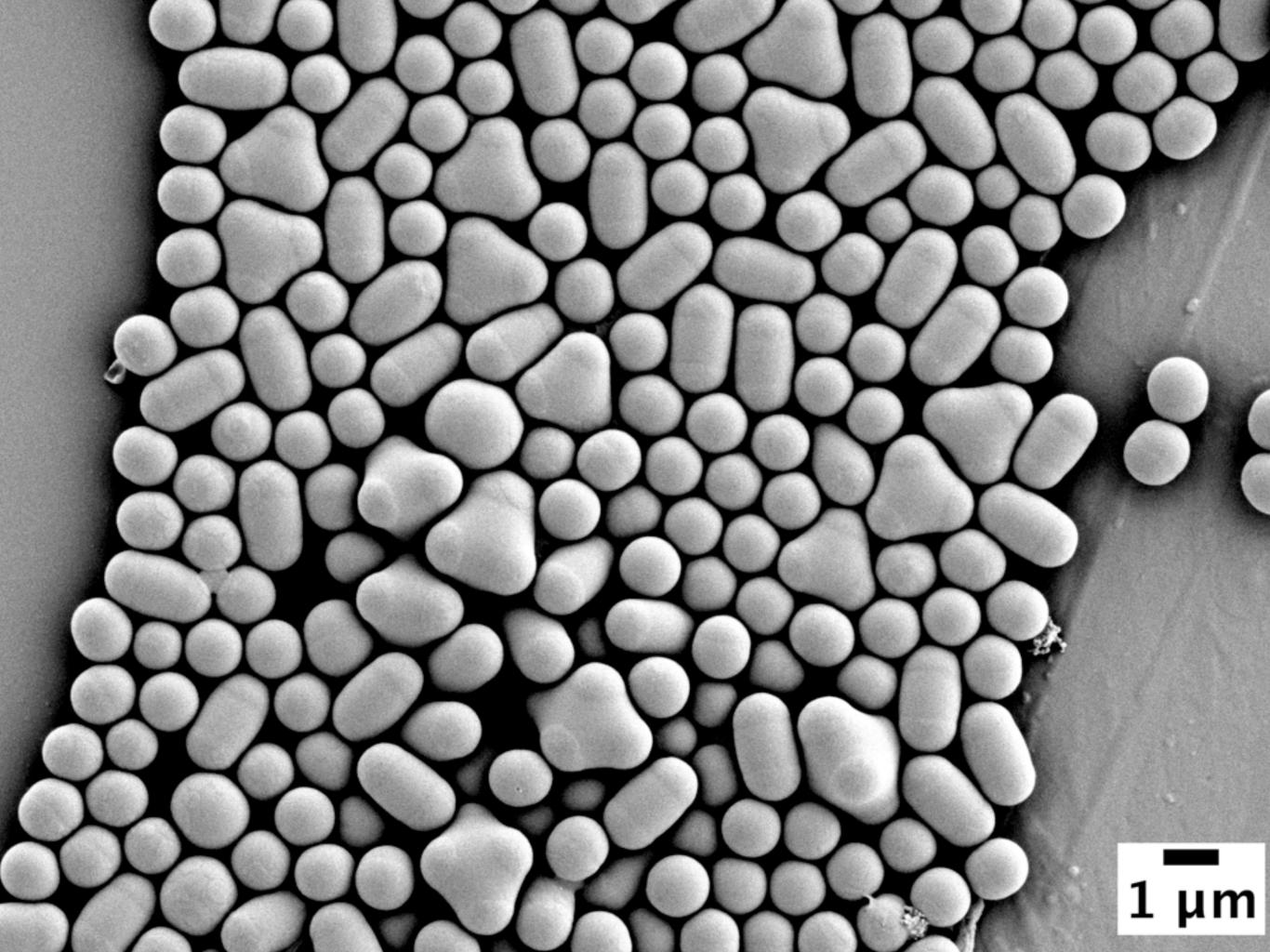
8

3

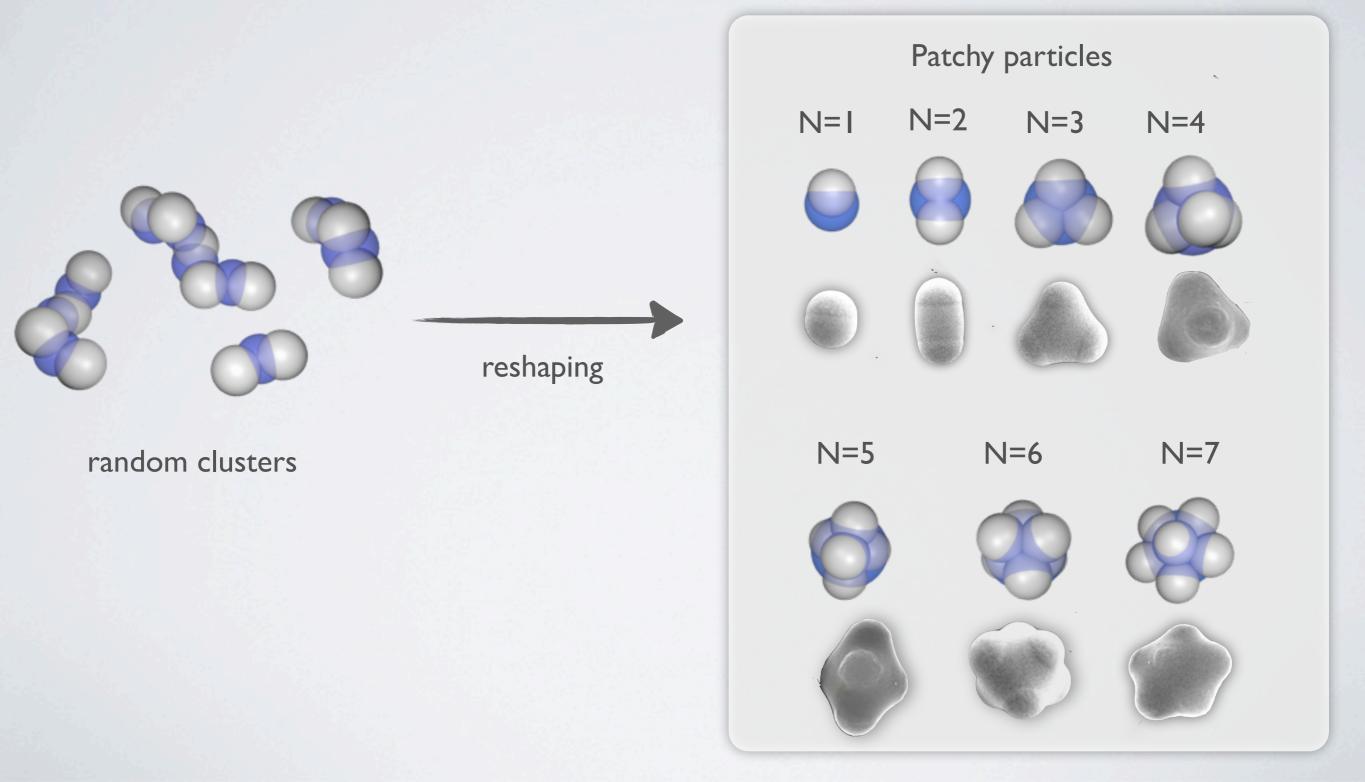
87

#### RESHAPING RANDOM COLLOIDAL CLUSTERS



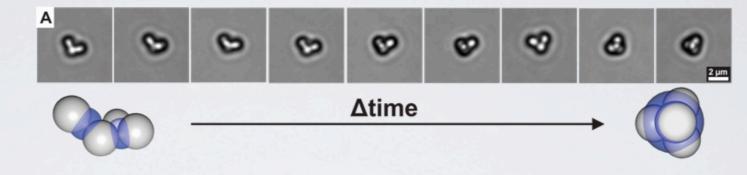


## PARTICLE SWELLING RECONFIGURES THE RANDOM CLUSTERS INTO UNIFORM PATCHY PARTICLES

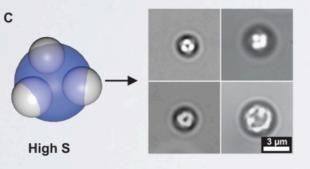


### **COALESCENCE DRIVEN RECONFIGURATION**

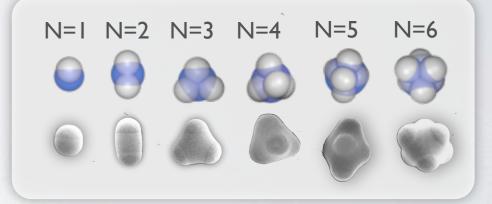
Liquid droplet coalescence drive rearrangement



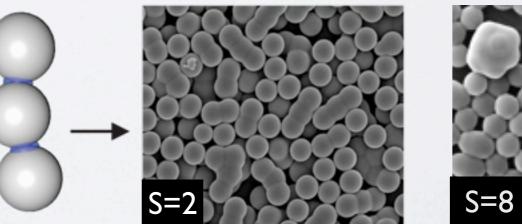
Liquid droplet confines the spheres

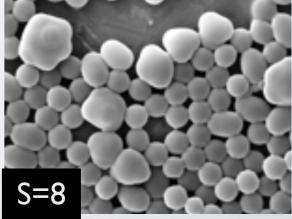


Cluster minimize the second moment of the mass distribution



Insufficient swelling
→ no / small liquid bridges
→ no reconfiguration!





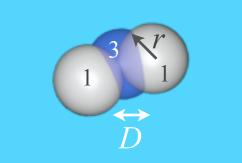
#### WHAT ENABLES RECONFIGURATION?

 $\begin{array}{c} 3 \\ 1 \\ D \end{array} \begin{array}{c} \gamma \\ 1 \\ D \end{array} \begin{array}{c} \gamma \\ 1 \\ 1 \end{array}$ 

Van der Waals interaction energy  $W(D) = -\frac{Ar}{12D}$ with the Hamaker constant A (Lifshitz theory)  $A = \frac{3}{4}k_BT\left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3}\right)^2 + \frac{3h\nu_e}{16\sqrt{2}}\frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}}$ 

polystyrene spheres:  $\epsilon_{PS} = 2.55$   $n_{PS} = 1.557$ 

polystyrene spheres in water:  $\epsilon_w = 80$   $n_w = 1.333$   $A_{PS-w} = 1.5 \cdot 10^{-20} J$ 

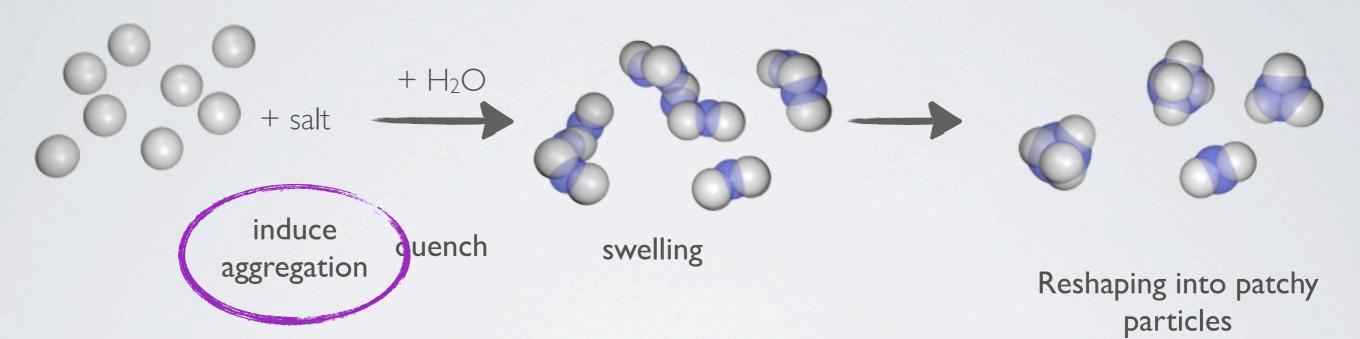


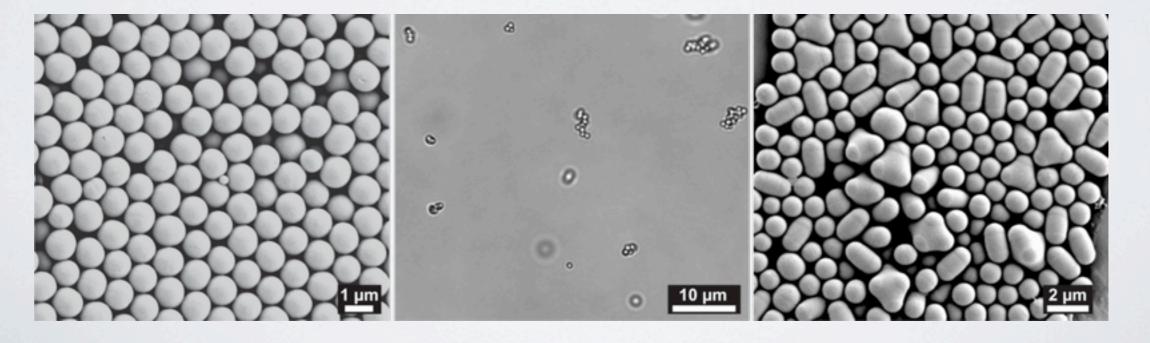
$$\epsilon_{st} = 2.47$$
  $n_{st} = 1.547$   $A_{PS-st} = 2.5 \cdot 10^{-23} J$ 

600x reduction of van der Waals attraction due to liquid bridges!

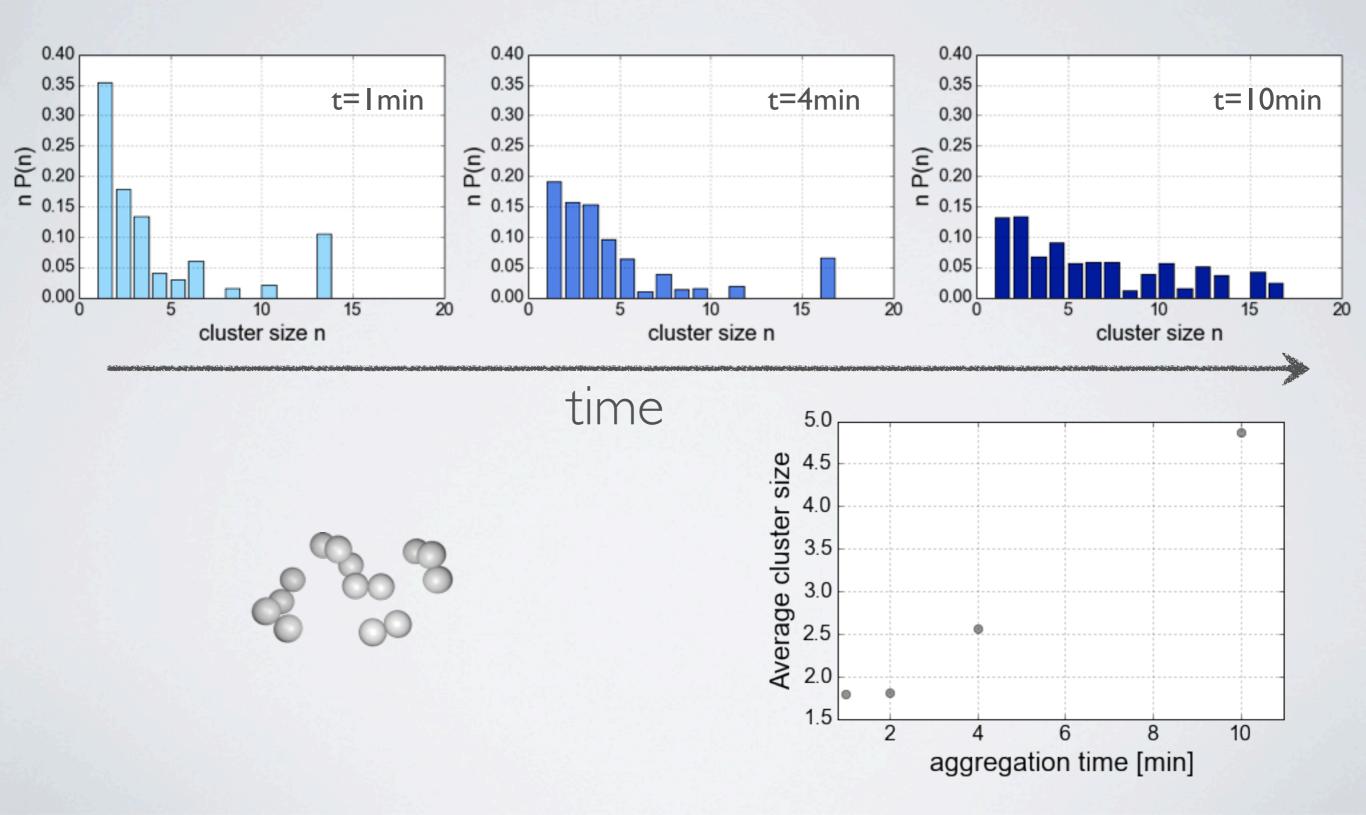
#### COLLOIDAL RECYCLING

random clusters

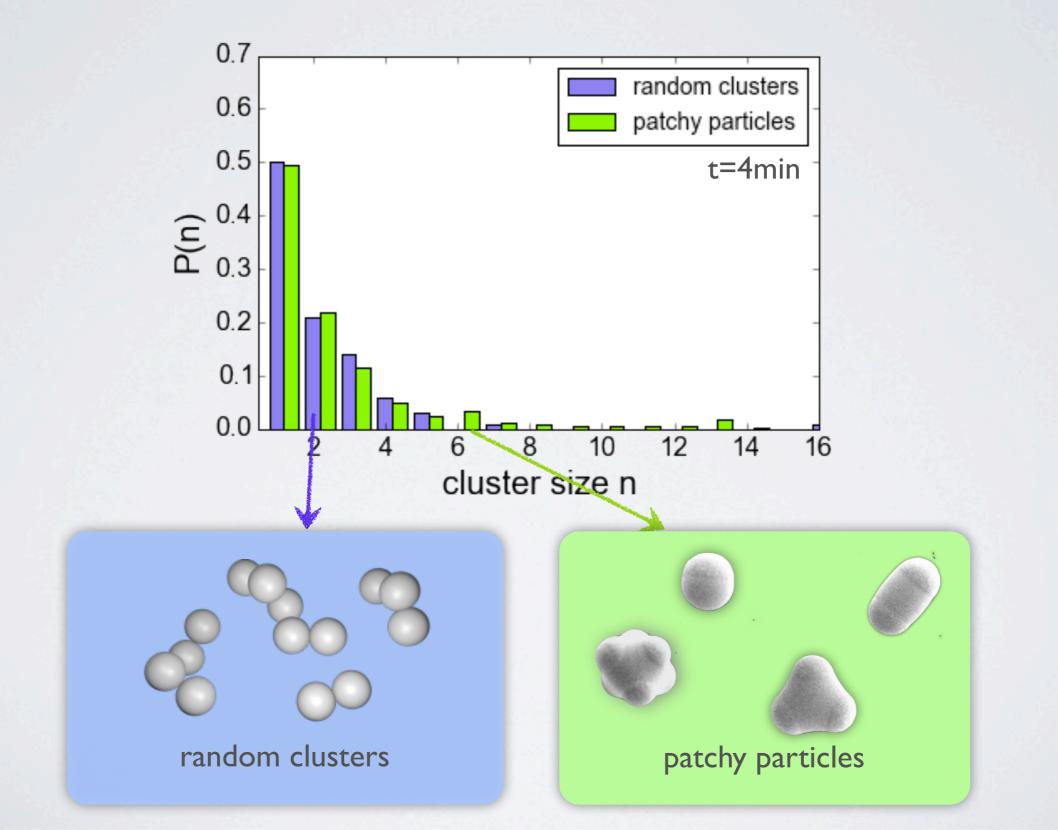




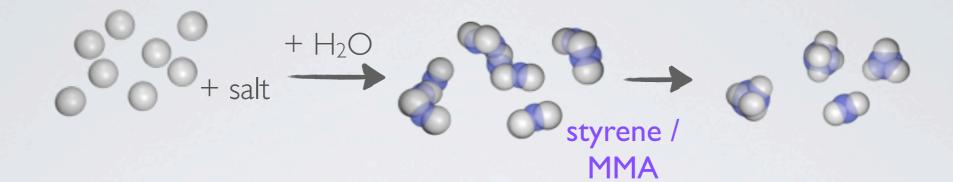
#### **CLUSTER SIZE IS TUNABLE BY AGGREGATION TIME**



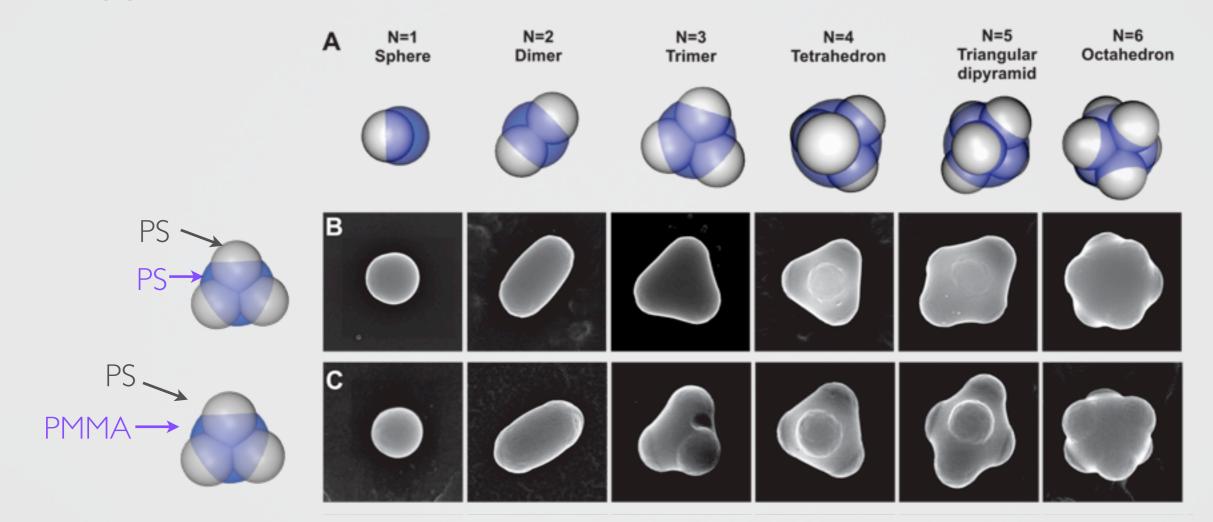
### ONLY RESHAPING DURING SWELLING, NO FURTHER AGGREGATION



### COMPOSITE PS / PMMA COLLOIDAL MOLECULES



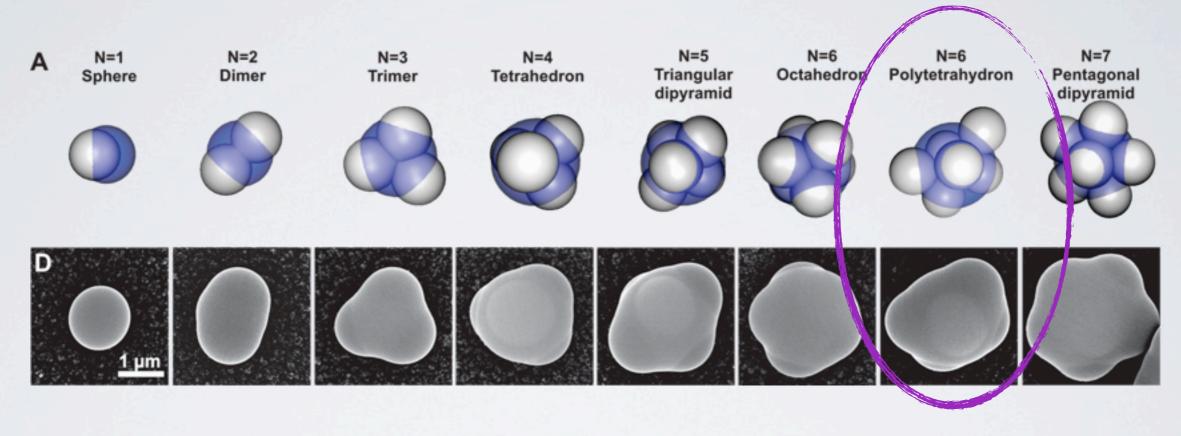
Patchy particles



Meester, Verweij, vd Wel, Kraft, ACSNano (2016)

### BEYOND DROPLET CONFINED CLUSTERS

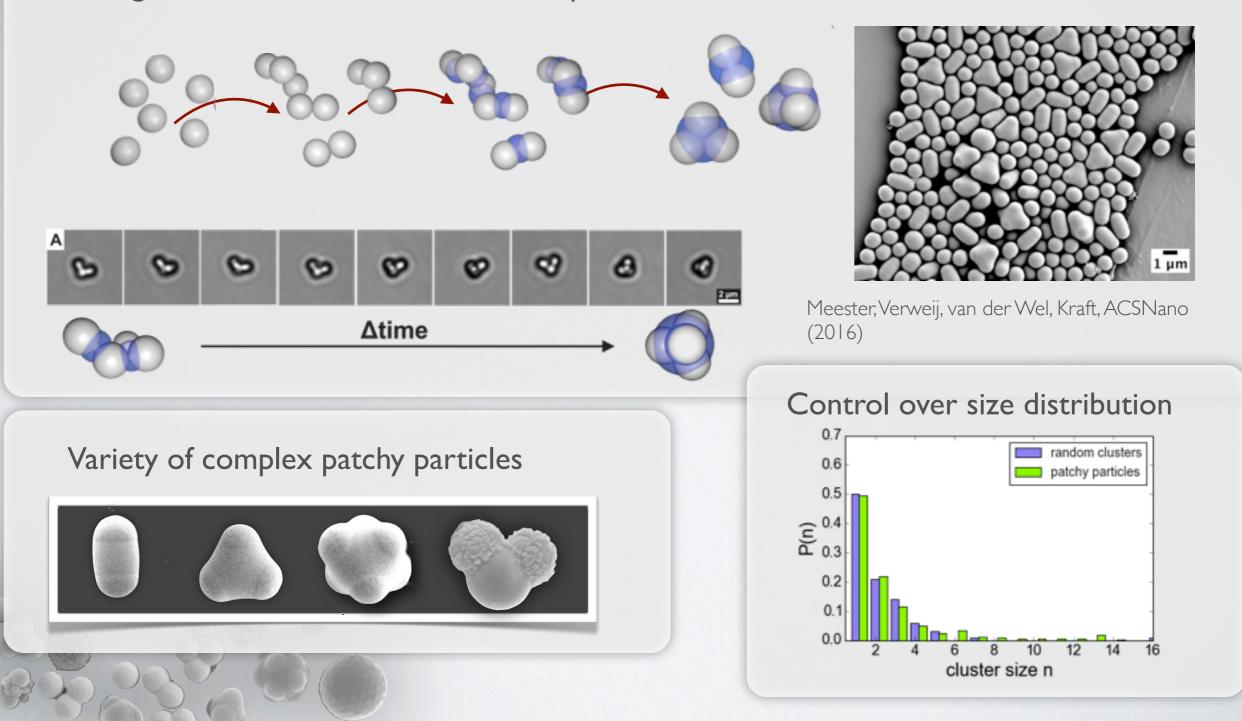
"homemade" soft PS swollen with toluene



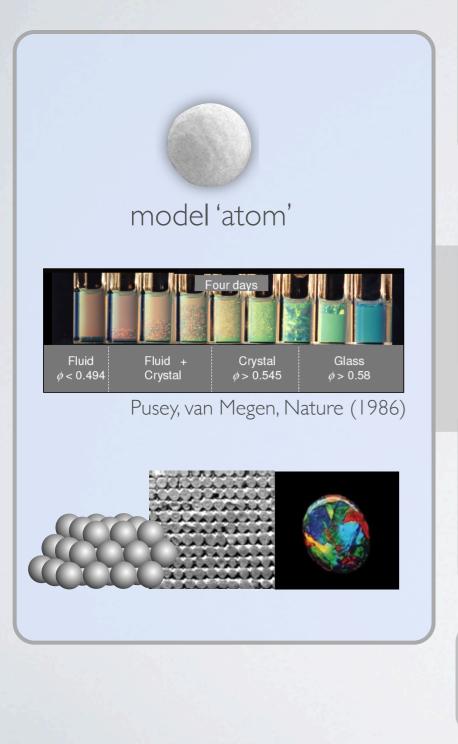
In clusters made up of softer particles and in the absence of cluster spanning droplets, **entropy** becomes important in determining the cluster shape!

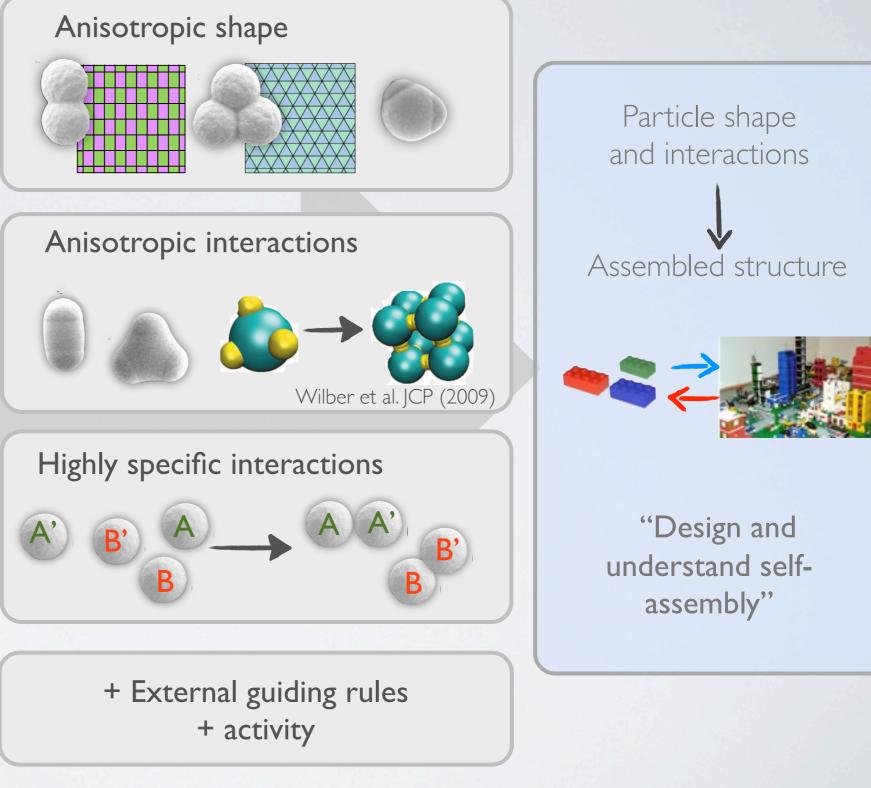
# SUMMARY - RECYCLING COLLOIDAL AGGREGATES INTO PATCHY PARTICLES

Reorganization of random clusters of spheres



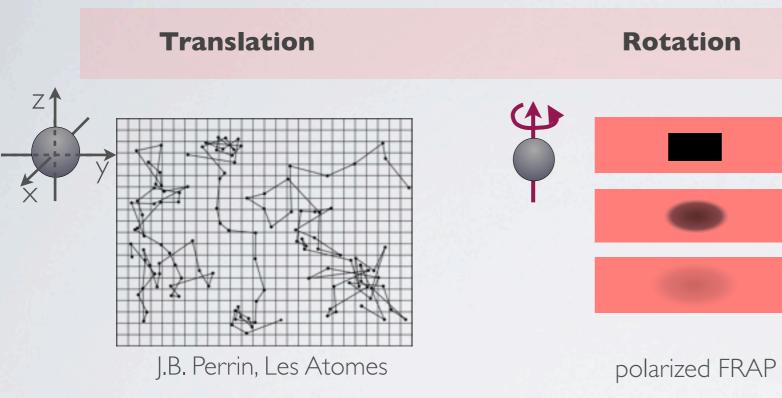
## FROM SPHERES TO COMPLEX PARTICLES





### BROWNIAN MOTION OF ANISOTROPIC COLLOIDAL PARTICLES

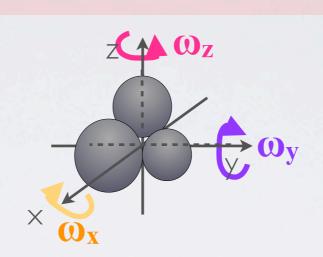
### **BROWNIAN MOTION OF ANISOTROPIC PARTICLES**



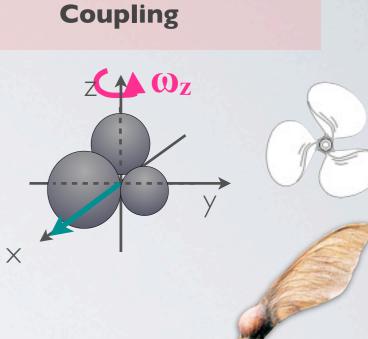
### **BROWNIAN MOTION OF ANISOTROPIC PARTICLES**

**Translation** 

Origin of coordinate system determines 'meaning' of diffusion coefficients



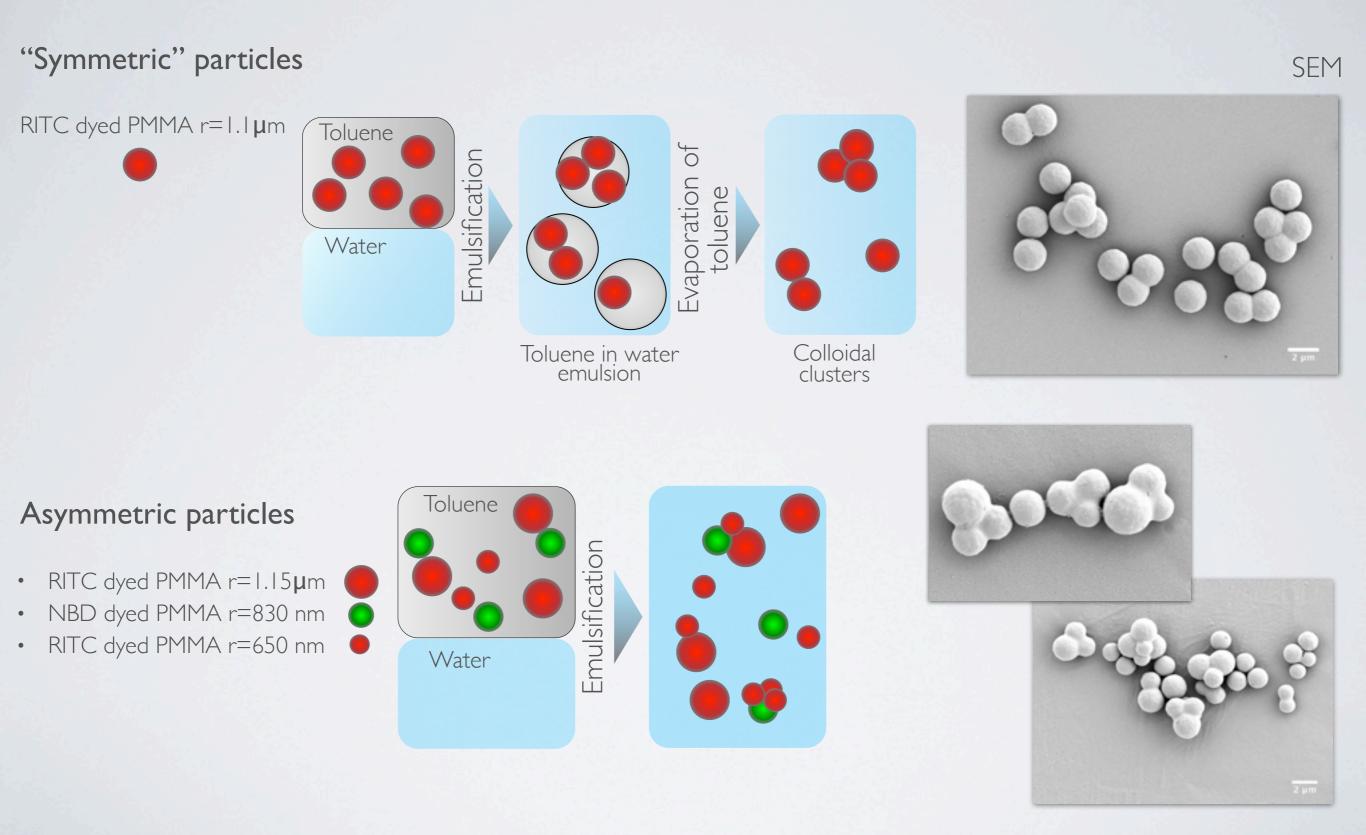
Rotation



Can we measure the shape-dependent diffusion coefficients?

http://de.wikipedia.org/wiki/Ahorne http://www.pt-boat.com/propeller/propeller.html

### SYNTHESIS OF ANISOTROPIC PARTICLES

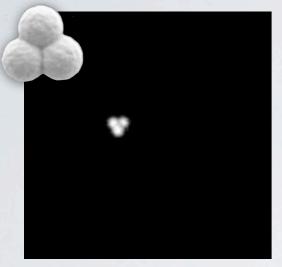


# DETERMINATION OF THE DIFFUSION CONSTANT MATRIX FROM 3D CONFOCAL MICROSCOPY

14

10

Confocal microscopy of fluorescent PMMA particles Track particle positions using IDL or Trackpy



•

10x real speed

- 0
- center of mass position

 $\Delta \vec{x}(t) = \vec{x}(t) - \vec{x}(0)$ 

• orthonormal orientation vectors  $\hat{u}_i(t)$  $\Delta \hat{u}(t) = \frac{1}{2} \sum_{i=1}^{3} \hat{u}_i(0) \times \hat{u}_i(t)$ 

 $\vec{\xi}(t) = (\Delta \vec{x}(t), \Delta \hat{u}(t))$ 

Calculate diffusion constant matrix from cross-correlations

Center of mass motion

 $\vec{x} = (x, y, z)$ 

$$\mathcal{D} = \frac{1}{2} \lim_{t \to 0} \frac{\partial}{\partial t} \left\langle \vec{\xi}(t) \otimes \vec{\xi}(t) \right\rangle$$

or  
$$\mathcal{D}_{i,j} = \frac{1}{2} \lim_{t \to 0} \frac{\partial}{\partial t} \left\langle \xi_i(t) \xi_j(t) \right\rangle$$

Change in body fixed axes t t+dt  $z' \uparrow \hat{u}_i(t)$   $y' \downarrow y'$   $x' \downarrow \hat{u}_i(t)$   $y' \downarrow \hat{u}_i(t)$  $y' \downarrow \hat{u}_i(t)$ 

Analyze trajectory and rotations using IDL

Tra	nel	atic		CO	upi	ing	trar	
Ira	.11510	alic	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	& rotation				
	$\Delta x$	$\Delta y$	$\Delta z$	$\Delta u_x$	$\Delta u_y$	$\Delta u_z$	;	
$\Delta x$	(*	*	*	*	*	*		
$\Delta y$	*	*	*	*	*	*	24	
$\mathcal{D}^{\Delta z}$	*	*	*	*	*	*	2	
$\mathcal{D}\overline{\Delta u}_x$	*	*	*	*	*	*		
$\Delta u_y$		*	*	*	*	*		
$\Delta u_z$	*	*	*	*	*	*		

S.

Coupling Rotation trans. & rot.

## THE HYDRODYNAMIC FRICTION MATRIX

Diffusion constant matrix still depends on temperature and viscosity

 $\mathcal{D}_0 = \frac{1}{2} \lim_{t \to 0} \frac{\partial}{\partial t} \left\langle \vec{\xi}(t) \otimes \vec{\xi}(t) \right\rangle$ 

Hydrodynamic friction matrix

 $\mathcal{H} = \frac{1}{\beta\eta} \, \mathcal{D}_0^{-1}$ 

Translation	(*	*	*	*	*	*)	Coupling trans.
	*	*	*	*	*	*	& rotation
H —	*	*	*	*	*	*	
n =	*	*	*	*	*	*	
Coupling		*	*	*	*	*	
Coupling trans. & rot.	*	*	*	*	*	*	Rotation

Only particle **shape and size** define the hydrodynamic friction matrix

eta inverse thermal energy

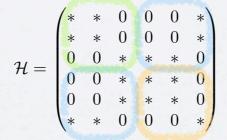
 $\eta$  viscosity

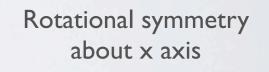
 $k_B$  Boltzmann constant

**Symmetries** in the particle shape reduce the complexity of the matrix

 $\mathcal{H}(\text{iso}) = \begin{pmatrix} * & 0 & 0 & 0 & 0 & 0 \\ 0 & * & 0 & 0 & 0 & 0 \\ 0 & * & 0 & 0 & 0 & 0 \\ 0 & 0 & * & 0 & 0 & 0 \\ 0 & 0 & 0 & * & 0 & 0 \\ 0 & 0 & 0 & 0 & * & 0 \end{pmatrix}$ 

One plane of symmetry (x-y plane)





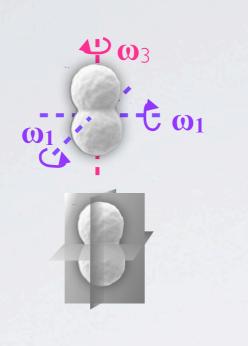
	$\mathcal{H}_{11}$	0	0	0	0	0
	0	$\mathcal{H}_{22}$	0	0	0	$-\mathcal{H}_{53}$
บ _	0	0	$\mathcal{H}_{22}$	0	$\mathcal{H}_{53}$	0
π –	0	0	0	$\mathcal{H}_{44}$	0	0
	0	0	$\mathcal{H}_{53}$	0	$\mathcal{H}_{55}$	0
	0	$-\mathcal{H}_{53}$	0	0	0	$\mathcal{H}_{55}$

<sup>1</sup>Happel and Brenner, Low Reynolds Number Hydrodynamics, Prentice Hall

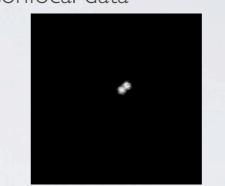
# DIMERS: UNIAXIAL PARTICLES

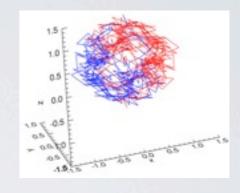
#### **Symmetries**

- Rotational symmetry and discrete rotational symmetry
  - Mirror symmetries for three perpendicular planes (orthotropic shape)



**Experiments** Confocal data

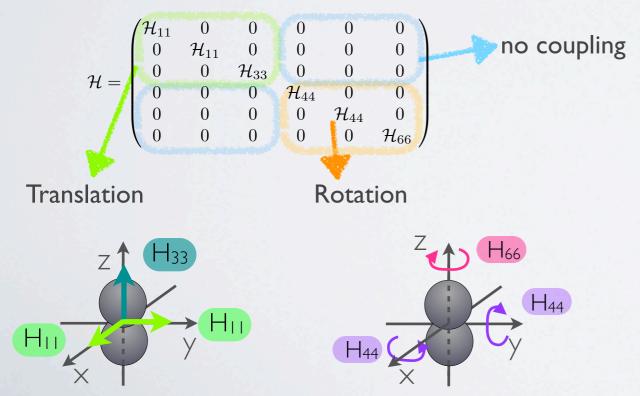




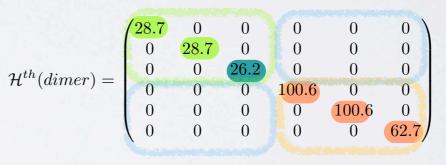
10x real speed

$\mathcal{H}^{exp}(dimer) =$	(25.2)	0.8	-1.2	-0.4	-1.8
	0.8	25.7	0.7	-5.6	-1.1
$\mathcal{U}^{exp}(dimor) =$	-1.2	0.7	19.7	-1.5	-0.2
$\pi$ (unner) –	-0.4	-5.6	-1.5	128.8	1.7
	-1.8	-1.1	-0.2	1.7	114.5
	( –				

#### Hydrodynamic friction matrix



#### Numerical calculation (Hydrosub code)



Shape symmetries are well represented in the hydrodynamic friction matrix!

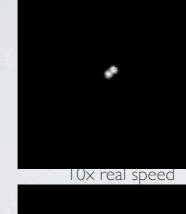
de la Torre and Carasco, Biopolymers 63, 163 (2002)

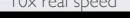
### UNIAXIAL PARTICLES - DIMERSWITH LONGER BOND LENGTH

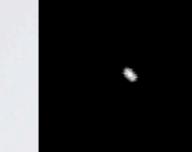
#### **Particles**

#### **Experiments**









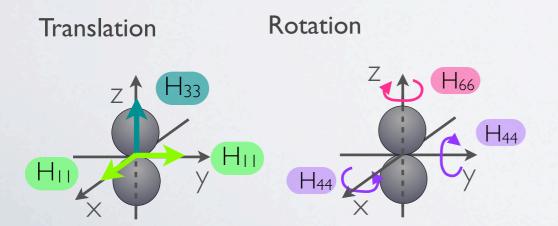
	(25.2)	0.8	-1.2	-0.4	-1.8	_/
	0.8	25.7	0.7	-5.6	-1.8 -1.1 -0.2 1.7 114.5	_
$\mathcal{H}^{exp}(dimer) =$	-1.2	0.7	19.7	-1.5	-0.2	_
$\pi$ (unner) –	-0.4	-5.6	-1.5	128.8	1.7	_
	-1.8	-1.1	-0.2	1.7	114.5	_
		—	and the second second	a stranger to state		_/

	(25.4)	0.5	-0.7	-1.4	-1.	-)
	0.5	26.1	0.1	0.	1.	-
$\mathcal{H}^{exp}(\text{dimer},2) =$	-0.7	0.1	22.3 0.6	0.6	3.8	_
$\pi$ (unner,2) –	-1.4	0.	0.6	180.3	-1.5	-
	-1.	1.	3.8	-1.5	186.	_
	/ -		- /	_		_/

 $D_{t,\parallel} = 0.073 \mu \mathrm{m}^2 / \mathrm{s}$  $D_{t,\perp} = 0.093 \mu \mathrm{m}^2 / \mathrm{s}$  $D_{t,\parallel}/D_{t,\perp}=1.28$  $D_r = 0.016 \text{ rad}^2/s$ 

$D_{t,\parallel}=0.071\mu\mathrm{m}^2/\mathrm{s}$
$D_{t,\perp}=0.082\mu\mathrm{m}^2/\mathrm{s}$
$D_{t,\parallel}/D_{t,\perp} = 1.15$
$D_r = 0.010 \text{ rad}^2/s$

Larger aspect ratio yields slower rotational diffusion constant

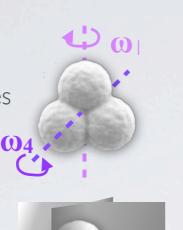


### **BIAXIAL PARTICLES**

#### **Symmetries**

Translation

Discrete rotational symmetries •



 Mirror symmetries for two perpendicular planes



Rotation

no coupling

#### **Hydrodynamic friction matrix**

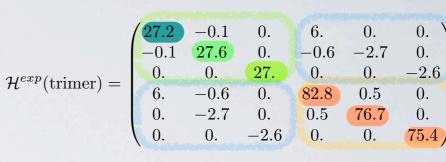
Z

 $\mathcal{H} = \begin{pmatrix} \mathcal{H}_{11} & 0 & 0 & 0 & 0 & 0 \\ 0 & \mathcal{H}_{22} & 0 & 0 & 0 & 0 \\ 0 & 0 & \mathcal{H}_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathcal{H}_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \mathcal{H}_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & \mathcal{H}_{66} \end{pmatrix}$ 

Ηეე

#### **Experiments**

Confocal data

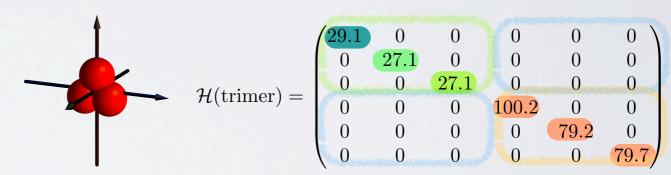


10x real speed

 $D_{t,z} = 0.068 \mu \mathrm{m}^2/\mathrm{s}$ 

 $D_{t,y} = 0.0685 \mu \text{m}^2/\text{s}$   $D_{r,x,y} = 0.023 \text{ rad}^2/\text{s}$  $D_{t,y} = 0.0665 \mu \text{m}^2/\text{s}$   $D_{r,z} = 0.024 \text{ rad}^2/\text{s}$ 

#### **Numerical calculations**

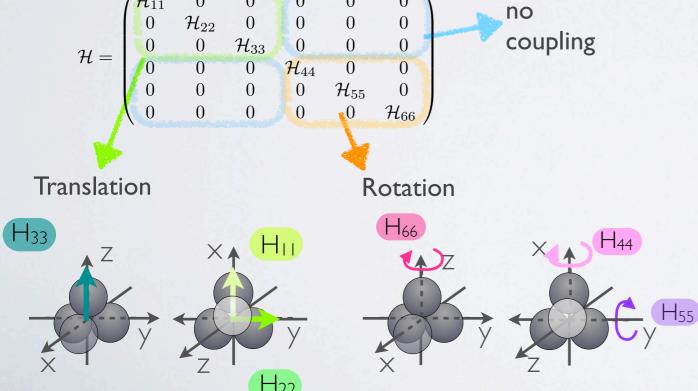


Shape symmetries are well represented in the hydrodynamic friction matrix

Kraft et al. PRE 88 (2013)

#### BIAXIAL PARTICLES WITH DISCRETE ROTATIONAL SYMMETRY

#### **Symmetries Experiments** Confocal data Discrete, helicoidal rotational • symmetries ( $\phi \rightarrow \phi + \Delta \phi$ , with -0.9 $0 < \Delta \phi < \pi$ ) $\mathcal{H}^{exp}(\text{tetramer}) = \begin{pmatrix} 0 & 42.6 & 0 & 1.6 & -0.5 \\ 0 & 42.6 & 0 & 1.6 & -0.5 \\ 0 & 0 & 43.1 & 0 & 0 & - \\ -0.9 & 1.6 & 0 & 212.6 & 0 \\ -1.5 & -0.5 & 0 & 0 & 212.2 \\ 0 & 0 & -0.6 & 0 & 0 & 21 \end{pmatrix}$ 0 -0.60 0 • Mirror symmetry 10x real speed $D_t = 0.043 \mu {\rm m}^2 / {\rm s}$ Translational diffusion: Rotational diffusion: $D_r = 8.7 \cdot 10^{-3} \text{rad}^2/\text{s}$ • **Hydrodynamic friction matrix Numerical calculations** no

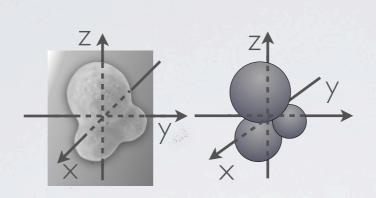




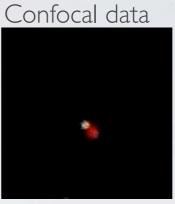
# ASYMMETRIC PARTICLES

#### **Symmetries**

- No rotational symmetries
- Mirror symmetry only



#### Experiments



5x real speed

#### **Hydrodynamic friction matrix** $\mathcal{H}_{51}$ $\mathcal{H}_{61}$ coupling $\mathcal{H}_{65}$ $\mathcal{H}_{51}$ $\mathcal{H}_{66}$ 0 $\mathcal{H}_{65}$ $\mathcal{H}_{61}$ 0 Translation Rotation H<sub>66</sub> H33 H<sub>55</sub> H<sub>44</sub> H

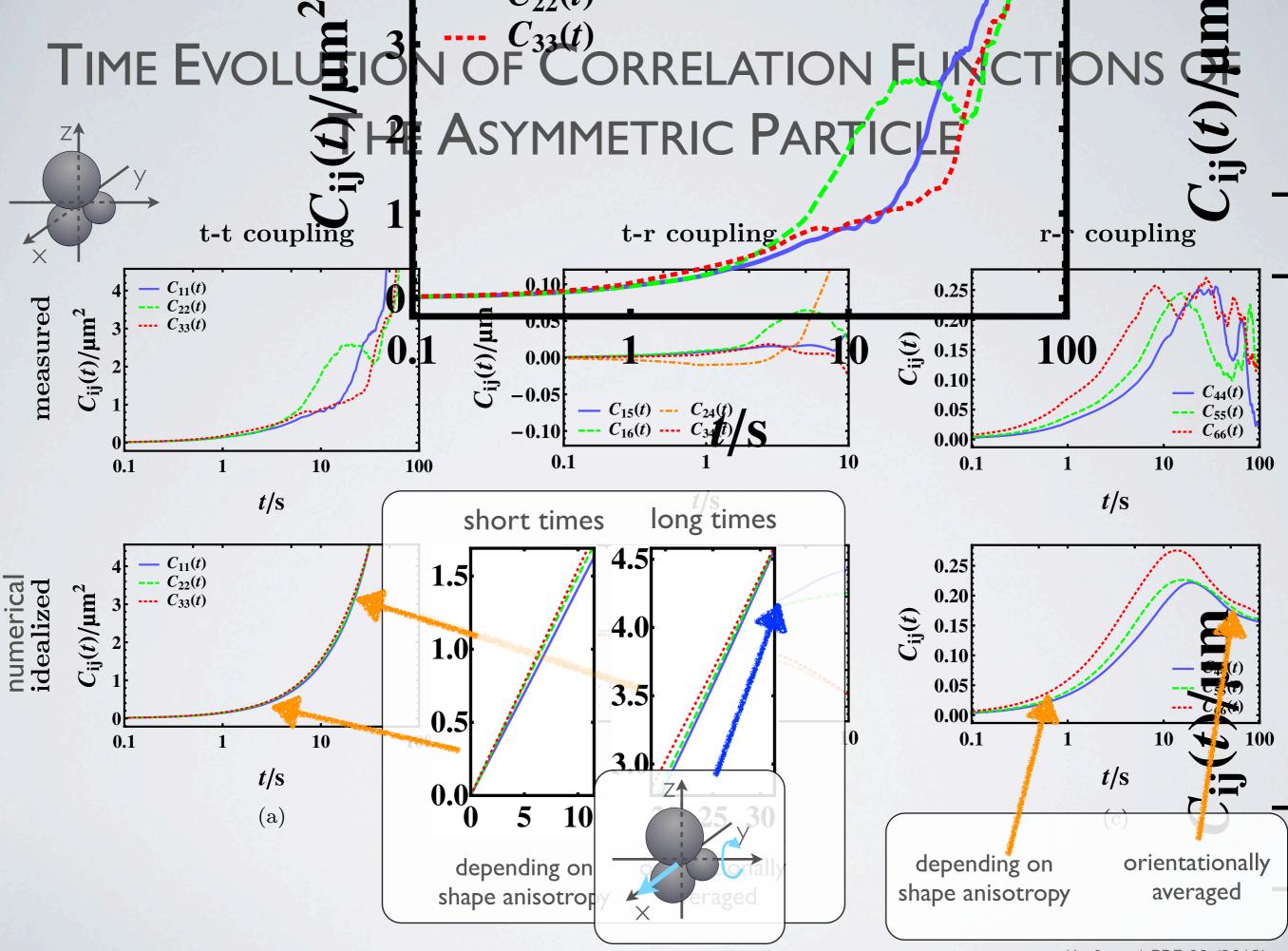
	(27.2)	3.9	0.7	6.0	-7.2	-6.1
Contraction of the second	3.9	29.2	-2.4	9.9	0.8	-9.7
1(exp(innex)) =	0.7	-2.4	21.7	-4.1	4.0	0.6
$\mathcal{H}^{ourp}(\text{irreg.}) =$	6.0	9.9	-4.1	137.0	-4.8	8.9
	-7.2	0.8	4.0	-4.8	102.4	19.5
$\mathcal{H}^{exp}(\text{irreg.}) =$	(-6.1)	-9.7	0.6	8.9	19.5	61.2

#### **Numerical calculations**

	27.9	0			-12.6	-7.2
	0	26.1	0.3	11.0	0	0
11	0	0.3	24.8	6.0	0	0
$\pi =$	0	11.0	6.0	104.4	0	0
	-12.6	0	0	0	90.2	11.2
	(-7.2)	0	0	0	11.2	58.9

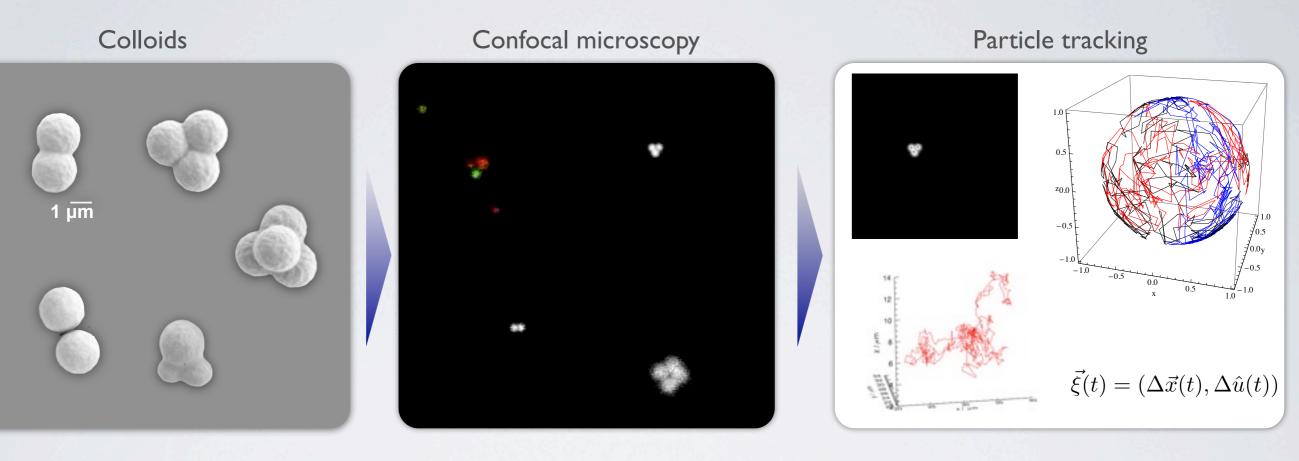
- Coupling between translation and rotation
- Coupling between rotational diffusion directions
- Particle shape is reflected in the hydrodynamic friction matrix

Kraft et al. PRE 88 (2013)



Kraft et al. PRE 88 (2013)

# EXPERIMENTAL DETERMINATION OF THE HYDRODYNAMIC FRICTION MATRIX



#### Hydrodynamic friction matrix

Translation	*	* *	* *	*	* *	*	Coupling trans. & rotation
2/	10		*		*	*	
n -	*	*	*	*	*	*	
Coupling trans. & rot.	*	*	*	*	*	*	
trans. & rot.	(*	*	*	*	*	*	Rotation

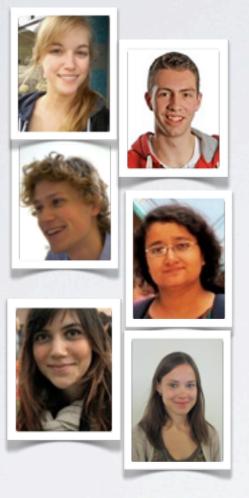
Depends only particle shape and size

- ✓ First\* 3D measurement of the full
   hydrodynamic friction matrix and diffusion
   matrix of anisotropic particles with different
   symmetries
- ✓ Particle symmetries determine symmetries in hydrodynamic friction matrix
- ✓ Good agreement between experiments and numerical predictions

### THANK YOU ....

#### Leiden University

Vera Meester Ruben Verweij Casper van der Wel Indrani Chakraborty Hans Frijters Sabine Matysik Melissa Rinaldin



#### Simulations

**University of Düsseldorf** Raphael Wittkowski Borge ten Hage Hartmut Löwen

#### Experiments

#### NYU

David Pine Andrew Hollingsworth Kazem Edmond

**Funding** Rubicon fellowship VENI grant Sectorplan Nanofront Gravity grants DAAD Rise fellowship

#### **Publications**

Meester, Verweij, van der Wel, Kraft, ACSNano (2016) Kraft et al. PRE 88 (2013)



