## SELF-ASSEMBLY AND DIFFUSION OF ANISOTROPIC PARTICLES

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

## Why Colloidal Particles?



Size:
$\sim 10 \mathrm{~nm}$ - $10 \mu \mathrm{~m}$

## Soft, Slow, Seeable




Ideal Model System<br>For Doing<br>Fundamental Physics<br>Applications

## From Spheres to Complex Particles



## COLLOIDAL RECYCLING: SYNTHESIS OF COMPLEX COlLOIDAL PARTICLES

## Reshaping Random Colloidal Clusters



## Reshaping Random Colloidal Clusters

random clusters




Particle SWelling Reconfigures the Random Clusters into Uniform Patchy Particles


## Coalescence driven Reconfiguration

 Liquid dropletcoalescence drive rearrangement


Liquid droplet confines the spheres


Insufficient swelling

- no / small liquid bridges
$\Rightarrow$ no reconfiguration!



## What enables Reconfiguration?



$$
\text { Van der Waals interaction energy } W(D)=-\frac{A r}{12 D}
$$

with the Hamaker constant A (Lifshitz theory)

$$
A=\frac{3}{4} k_{B} T\left(\frac{\epsilon_{1}-\epsilon_{3}}{\epsilon_{1}+\epsilon_{3}}\right)^{2}+\frac{3 h \nu_{e}}{16 \sqrt{2}} \frac{\left(n_{1}^{2}-n_{3}^{2}\right)^{2}}{\left(n_{1}^{2}+n_{3}^{2}\right)^{3 / 2}}
$$

polystyrene spheres: $\quad \epsilon_{P S}=2.55 \quad n_{P S}=1.557$
polystyrene spheres in water: $\quad \epsilon_{w}=80 \quad n_{w}=1.333 \quad A_{P S-w}=1.5 \cdot 10^{-20} \mathrm{~J}$

polystyrene spheres in styrene:

$$
\epsilon_{s t}=2.47 \quad n_{s t}=1.547
$$

$$
A_{P S-s t}=2.5 \cdot 10^{-23} \mathrm{~J}
$$

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

## COLLOIDAL Recycling

random clusters


## Cluster Size is Tunable by Aggregation Time




time


## Only Reshaping During Swelling, no further AgGREGATION



## Composite PS / PMMA Colloidal Molecules



Patchy particles


## 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



Particle shape and interactions

$$
\downarrow
$$

Assembled structure

"Design and understand selfassembly"

## 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


Coupling


Can we measure the shape-dependent diffusion coefficients?

## SyNTHESIS OF ANISOTROPIC Particles



## Determination ofthe Diffusion Constant Matrix from 3D Confocal Microscopy

Confocal microscopy of fluorescent PMMA particles

Track particle positions using IDL or Trackpy

Analyze trajectory and rotations using IDL
Center of mass motion
$\vec{x}=(x, y, z)$


IOx real speed

- 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

$$
\mathcal{D}=\frac{1}{2} \lim _{t \rightarrow 0} \frac{\partial}{\partial t}\langle\vec{\xi}(t) \otimes \vec{\xi}(t)\rangle
$$

or
$\mathcal{D}_{i, j}=\frac{1}{2} \lim _{t \rightarrow 0} \frac{\partial}{\partial t}\left\langle\xi_{i}(t) \xi_{j}(t)\right\rangle$

Change in body fixed axes


## The Hydrodynamic Friction Matrix

Diffusion constant matrix still depends on temperature and viscosity

$$
\mathcal{D}_{0}=\frac{1}{2} \lim _{t \rightarrow 0} \frac{\partial}{\partial t}\langle\vec{\xi}(t) \otimes \vec{\xi}(t)\rangle
$$

Hydrodynamic friction matrix

$$
\mathcal{H}=\frac{1}{\beta \eta} \mathcal{D}_{0}^{-1}
$$

Only particle shape and size define the hydrodynamic friction matrix

| $\beta$ | inverse thermal energy |
| :--- | :--- |
| $\eta$ | viscosity |
| $k_{B}$ | Boltzmann constant |

Translation $\left(\begin{array}{cccccc}* & * & * & * & * & * \\ * & * & * & * & * & * \\ * & * & * & * & * & * \\ * & * & * & * & * & * \\ \text { Coupling } \\ * & * & * & * & * & * \\ * & * & * & * & * & *\end{array}\right)$ Rotation $\quad$ rotation
trans. \& rot.

Symmetries in the particle shape reduce the complexity of the matrix

$$
\begin{array}{cc}
\begin{array}{c}
\text { Orthotropic particle } \\
\text { (3 planes of symmetry) }
\end{array} & \begin{array}{c}
\text { One plane of symmetry } \\
\text { ( } x-y \text { plane) }
\end{array} \\
\mathcal{H}(\text { iso }) & =\left(\begin{array}{llllllll}
* & 0 & 0 & 0 & 0 & 0 \\
0 & * & 0 & 0 & 0 & 0 \\
0 & 0 & * & 0 & 0 & 0 \\
0 & 0 & 0 & * & 0 & 0 \\
0 & 0 & 0 & 0 & * & 0 \\
0 & 0 & 0 & 0 & 0 & *
\end{array}\right) \\
\mathcal{H}=\left(\begin{array}{cccccc}
* & * & 0 & 0 & 0 & * \\
* & * & 0 & 0 & 0 & * \\
0 & 0 & * & * & * & 0 \\
0 & 0 & * & * & * & 0 \\
0 & 0 & * & * & * & 0 \\
* & * & 0 & 0 & 0 & *
\end{array}\right)
\end{array}
$$

Rotational symmetry about x axis

$$
\mathcal{H}=\left(\begin{array}{cccccc}
\mathcal{H}_{11} & 0 & 0 & 0 & 0 & 0 \\
0 & \mathcal{H}_{22} & 0 & 0 & 0 & -\mathcal{H}_{53} \\
0 & 0 & \mathcal{H}_{22} & 0 & \mathcal{H}_{53} & 0 \\
0 & 0 & 0 & \mathcal{H}_{44} & 0 & 0 \\
0 & 0 & \mathcal{H}_{53} & 0 & \mathcal{H}_{55} & 0 \\
0 & -\mathcal{H}_{53} & 0 & 0 & 0 & \mathcal{H}_{55}
\end{array}\right)
$$

## DIMERS: UNIAXIAL PARTICLES

## Symmetries

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



## Hydrodynamic friction matrix



## Experiments

Confocal data


10x real speed

$$
\mathcal{H}^{e x p}(\text { dimer })=\left(\begin{array}{cccccc}
25.2 & 0.8 & -1.2 & -0.4 & -1.8 & - \\
0.8 & 25.7 & 0.7 & -5.6 & -1.1 & - \\
-1.2 & 0.7 & 19.7 & -1.5 & -0.2 & - \\
-0.4 & -5.6 & -1.5 & 128.8 & 1.7 & - \\
-1.8 & -1.1 & -0.2 & 1.7 & 114.5 & - \\
- & - & - & - & - & -
\end{array}\right) \quad \begin{aligned}
& D_{t, \perp}=0.073 \mu \mathrm{~m}^{2} / \mathrm{s} \\
& D_{t, \|}=0.093 \mu \mathrm{~m}^{2} / \mathrm{s} \\
& D_{t, \|} / D_{t, \perp}=1.28 \\
& D_{r}=0.016 \mathrm{rad}^{2} / \mathrm{s}
\end{aligned}
$$

Numerical calculation (Hydrosub code)

$$
\mathcal{H}^{\text {th }}(\text { dimer })=\left(\begin{array}{cccccc}
28.7 & 0 & 0 & 0 & 0 & 0 \\
0 & 28.7 & 0 & 0 & 0 & 0 \\
0 & 0 & 26.2 & 0 & 0 & 0 \\
0 & 0 & 0 & 100.6 & 0 & 0 \\
0 & 0 & 0 & 0 & 100.6 & 0 \\
0 & 0 & 0 & 0 & 0 & 62.7
\end{array}\right)
$$

Shape symmetries are well represented in the hydrodynamic friction matrix!

## UNIAXIAL PARTICLES - DIMERS WITH LONGER BOND LENGTH



$$
\begin{aligned}
& \mathcal{H}^{e x p}(\text { dimer })=\left(\begin{array}{cccccc}
25.2 & 0.8 & -1.2 & -0.4 & -1.8 & - \\
0.8 & 25.7 & 0.7 & -5.6 & -1.1 & - \\
-1.2 & 0.7 & 19.7 & -1.5 & -0.2 & - \\
-0.4 & -5.6 & -1.5 & 128.8 & 1.7 & - \\
-1.8 & -1.1 & -0.2 & 1.7 & 114.5 & - \\
- & - & - & - & - & -
\end{array}\right) \quad \begin{array}{l}
D_{t, \|}=0.073 \mu \mathrm{~m}^{2} / \mathrm{s} \\
D_{t, \perp}=0.093 \mu \mathrm{~m}^{2} / \mathrm{s} \\
D_{t, \|} / D_{t, \perp}=1.28 \\
D_{r}=0.016 \mathrm{rad}^{2} / \mathrm{s} \\
\mathcal{H}^{e x p}(\text { dimer }, 2)
\end{array} \\
& \\
&\left.\begin{array}{cccccc}
25.4 & 0.5 & -0.7 & -1.4 & -1 . & - \\
0.5 & 26.1 & 0.1 & 0 . & 1 . & - \\
-0.7 & 0.1 & 22.3 & 0.6 & 3.8 & - \\
-1.4 & 0 . & 0.6 & 180.3 & -1.5 & - \\
-1 . & 1 . & 3.8 & -1.5 & 186 . & - \\
- & - & - & - & - & -
\end{array}\right) \begin{array}{l}
D_{t, \|}=0.071 \mu \mathrm{~m}^{2} / \mathrm{s} \\
D_{t, \perp}=0.082 \mu \mathrm{~m}^{2} / \mathrm{s} \\
D_{t, \|} / D_{t, \perp}=1.15 \\
D_{r}=0.010 \mathrm{rad}^{2} / \mathrm{s}
\end{array}
\end{aligned}
$$

Larger aspect ratio yields slower rotational diffusion constant

## Translation

Rotation


## BIAXIAL PARTICLES

## Symmetries

- Discrete rotational symmetries

- Mirror symmetries for two perpendicular planes



## Hydrodynamic friction matrix

Translation
Rotation


## Numerical calculations



Shape symmetries are well represented in the hydrodynamic friction matrix

## BIAXIAL PARTICLES WITH DISCRETE ROTATIONAL SYMMETRY

## Symmetries

- Discrete, helicoidal rotational symmetries $(\varphi \rightarrow \varphi+\Delta \varphi$, with $0<\Delta \varphi<\pi)$
- Mirror symmetry



## Hydrodynamic friction matrix



Translation
Rotation

## Experiments

Confocal data


IOx real speed

$$
\mathcal{H}^{e x p}(\text { tetramer })=\left(\begin{array}{cccccc}
41.8 & 0 & 0 & -0.9 & -1.5 & 0 \\
0 & 42.6 & 0 & 1.6 & -0.5 & 0 \\
0 & 0 & 43.1 & 0 & 0 & -0.6 \\
-0.9 & 1.6 & 0 & 212.6 & 0 & 0 \\
-1.5 & -0.5 & 0 & 0 & 212.2 & 0 \\
0 & 0 & -0.6 & 0 & 0 & 210.4
\end{array}\right)
$$

$$
\text { - Translational diffusion: } \quad D_{t}=0.043 \mu \mathrm{~m}^{2} / \mathrm{s}
$$

- Rotational diffusion:

$$
D_{r}=8.7 \cdot 10^{-3} \mathrm{rad}^{2} / \mathrm{s}
$$

## Numerical calculations




## AsYmmetric Particles

## Symmetries

- No rotational symmetries
- Mirror symmetry only



## Experiments

Confocal data

## Hydrodynamic friction matrix



$5 \times$ real speed
$\mathcal{H}^{e x p}$ (irreg.) $=\left(\begin{array}{cccccc}27.2 & 3.9 & 0.7 & 6.0 & -7.2 & -6.1 \\ 3.9 & 29.2 & -2.4 & 9.9 & 0.8 & -9.7 \\ 0.7 & -2.4 & 21.7 & -4.1 & 4.0 & 0.6 \\ 6.0 & 9.9 & -4.1 & 137.0 & -4.8 & 8.9 \\ -7.2 & 0.8 & 4.0 & -4.8 & 102.4 & 19.5 \\ -6.1 & -9.7 & 0.6 & 8.9 & 19.5 & 61.2\end{array}\right)$

## Numerical calculations

$$
\mathcal{H}=\left(\begin{array}{cccccc}
27.9 & 0 & 0 & 0 & -12.6 & -7.2 \\
0 & 26.1 & 0.3 & 11.0 & 0 & 0 \\
0 & 0.3 & 24.8 & 6.0 & 0 & 0 \\
0 & 11.0 & 6.0 & 104.4 & 0 & 0 \\
-12.6 & 0 & 0 & 0 & 90.2 & 11.2 \\
-7.2 & 0 & 0 & 0 & 11.2 & 58.9
\end{array}\right)
$$

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


## Time Evolution of Correlation Functions of The Asymmetric Particle


r-r coupling



## Experimental Determination ofthe Hydrodynamic Friction Matrix



Hydrodynamic friction matrix

Translation $\left(\begin{array}{cccccc}* & * & * & * & * & * \\ * & * & * & * & * & * \\ * & * & * & * & * & * \\ * & * & * & * & * & * \\ * & * & * & * & * & * \\ * & * & * & * & * & *\end{array}\right)$ Rotation rotation
Coupling
trans. \& rot.
Depends only particle shape and size
$\sqrt{ }$ First* 3D measurement of the full hydrodynamic friction matrix and diffusion matrix of anisotropic particles with different symmetries
$\sqrt{ }$ Particle symmetries determine symmetries in hydrodynamic friction matrix
$\checkmark$ Good agreement between experiments and numerical predictions

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