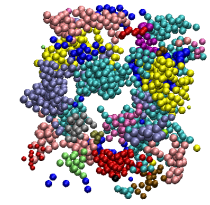


Living clusters and crystals from low-density suspensions of active colloids



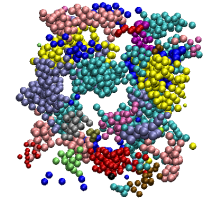
Chantal Valeriani



Universidad Complutense de Madrid

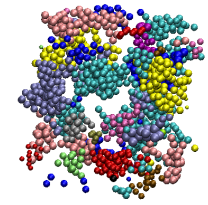
KITP, 13Th of February 2014

Outline



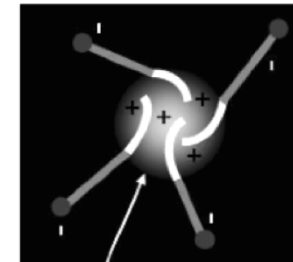
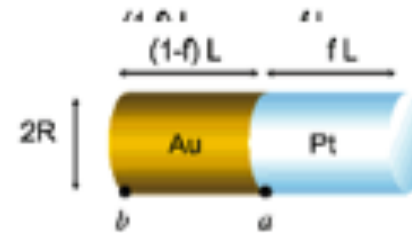
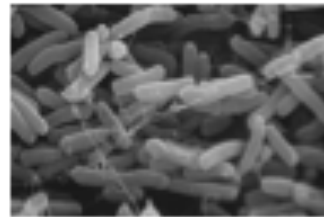
- ✓ Active colloids
- ✓ Self-assembly of active colloids
- ✓ What happens in a bacteria & polymer mixture?
- ✓ Can we make living clusters of active colloids in low concentrated suspensions?

Active colloids



active colloids: absorb energy from their surroundings or from an internal fuel and dissipate it while moving around

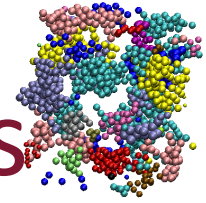
examples: living bacteria,
self-propelled colloids,
synthetic centrosomes



Ramaswamy (2004) & Marchetti (2013)

a suspension of active colloids is driven
out of equilibrium by its active nature

Self-assembly of active colloids

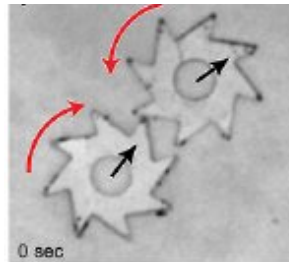


Why?

Technologically relevant

active colloids can be used to **self-assemble** novel smart materials, that could perform tasks such as

produce energy



perform directional motion

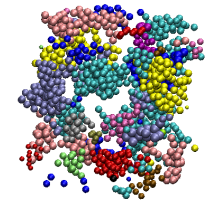
Di Leonardo PNAS (2009)

Sokolov PNAS (2009)

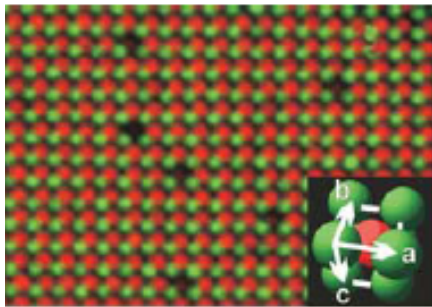
“Fundamentally” relevant

the Physics of a suspension of **intrinsically out of equilibrium** systems still needs to be fully understood

Self-assembly in Soft Matter (passive colloids)



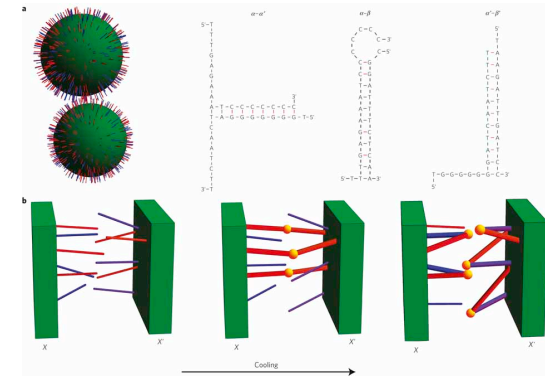
Oppositely charged colloids



Leunissen, Dijkstra,
van Blaaderen

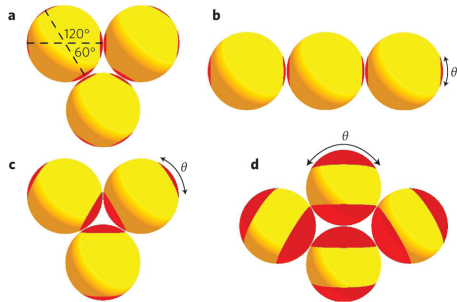
DNA-coated
colloids

Frenkel&Eiser
Pine&Chaikin

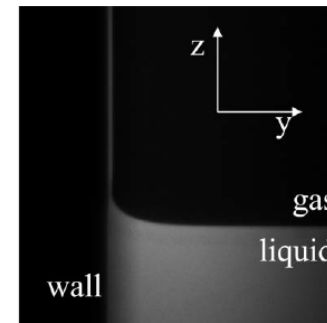


Colloid&Polymer mixture

Patchy colloids



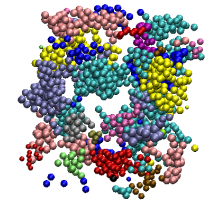
Sciortino
Delgado
Granick
Glotzer



Aarts & Lekkerkerker

What happens in a suspension of active colloids?

What happens in a bacteria & polymer mixture?



The team:

University of Edinburgh



Wilson Poon



Mike Cates



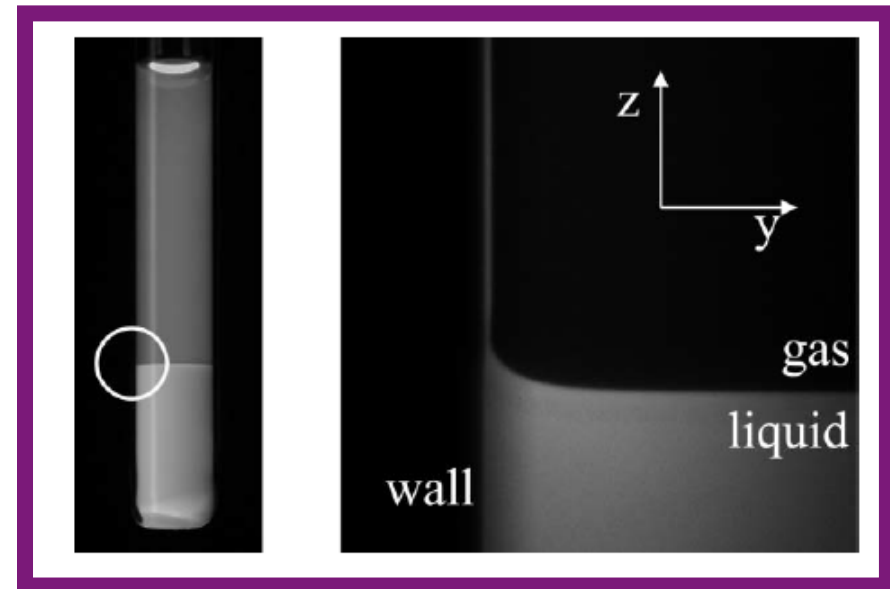
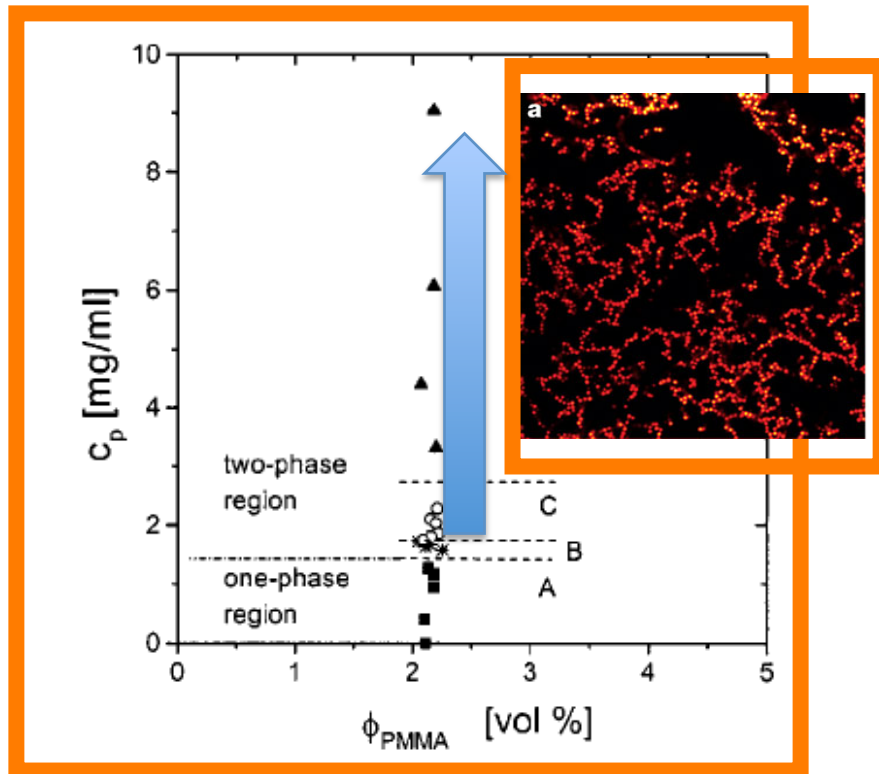
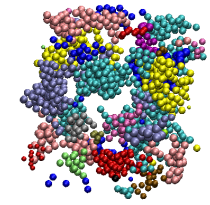
Davide Marenduzzo



Columbia University

Angelo Cacciuto

Colloid & Polymer mixture



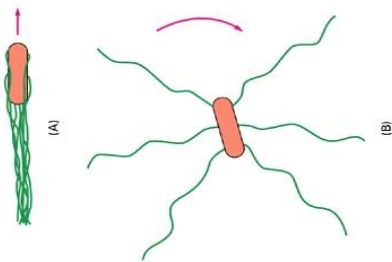
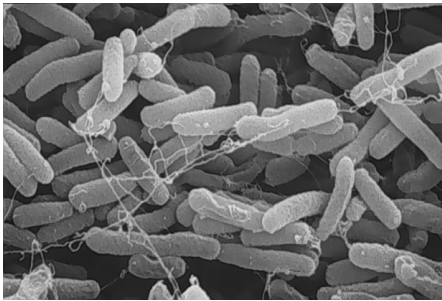
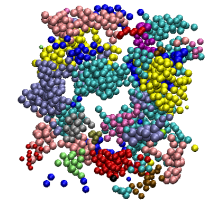
Asakura, Oosawa, Vrij (1954, 1976)

Lekkerkerker (1992, 2002)

Dijkstra (1999)

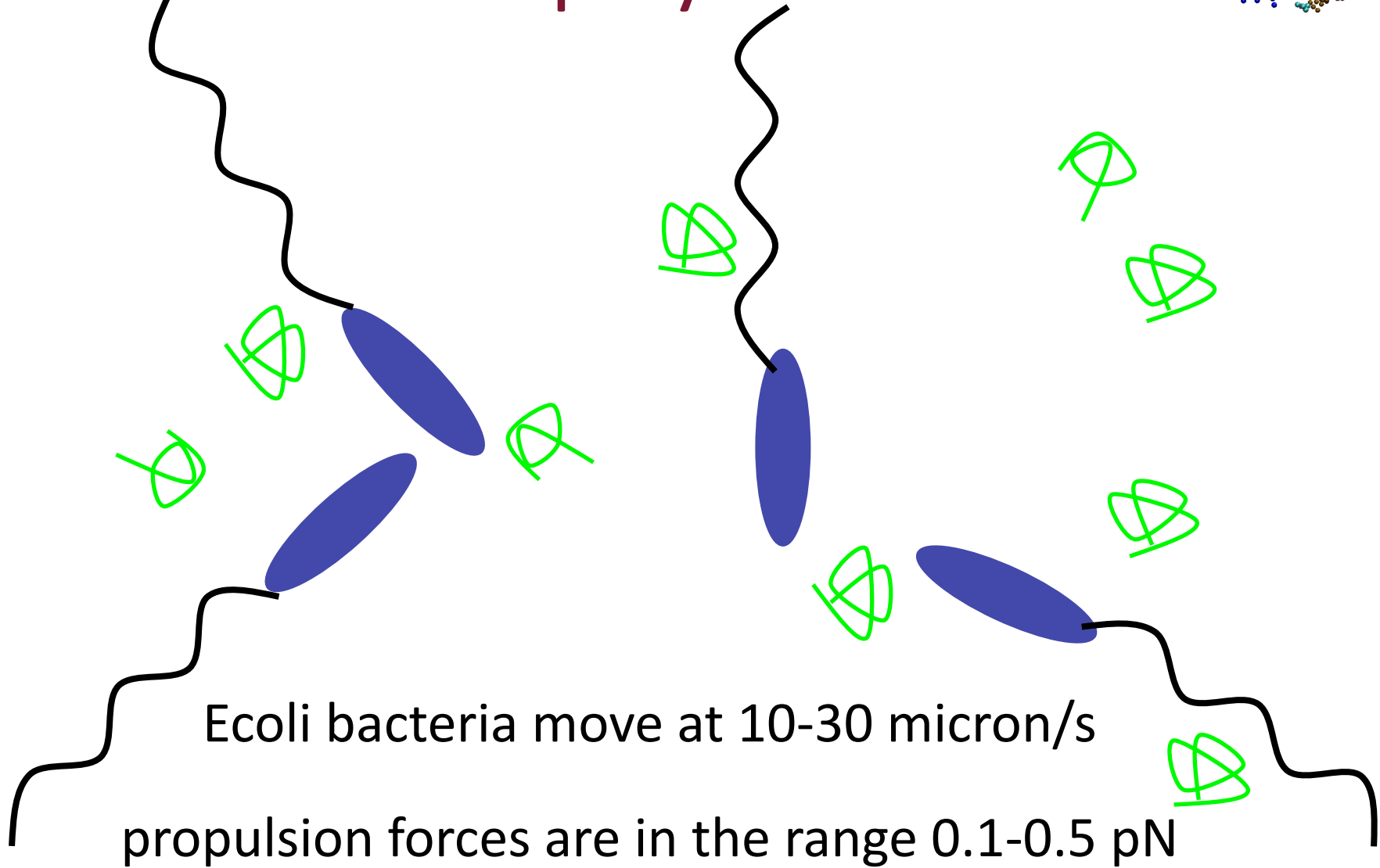
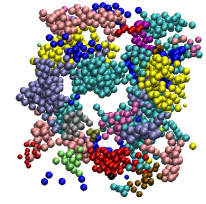
Aarts (2006)

Bacteria & polymer mixture

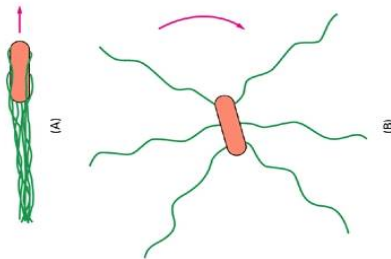
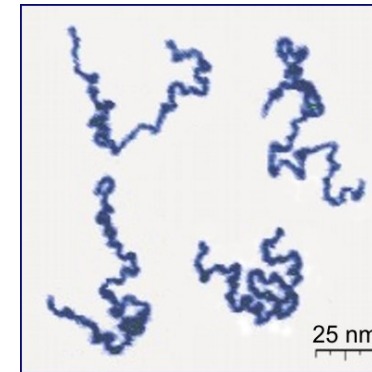
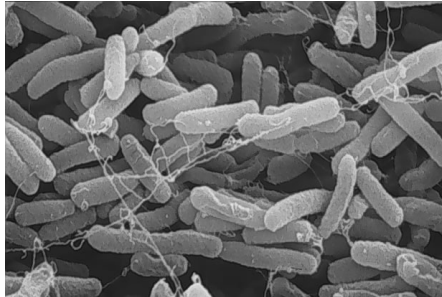
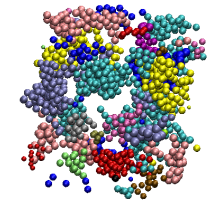


Bacteria swim (self-propel)
due to the presence of flagella

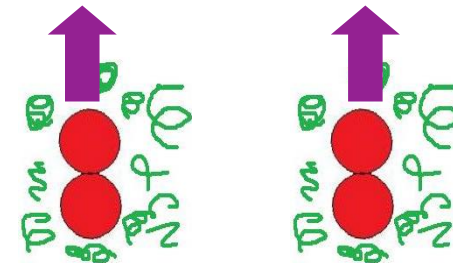
Bacteria & polymer mixture



Bacteria & polymer mixture



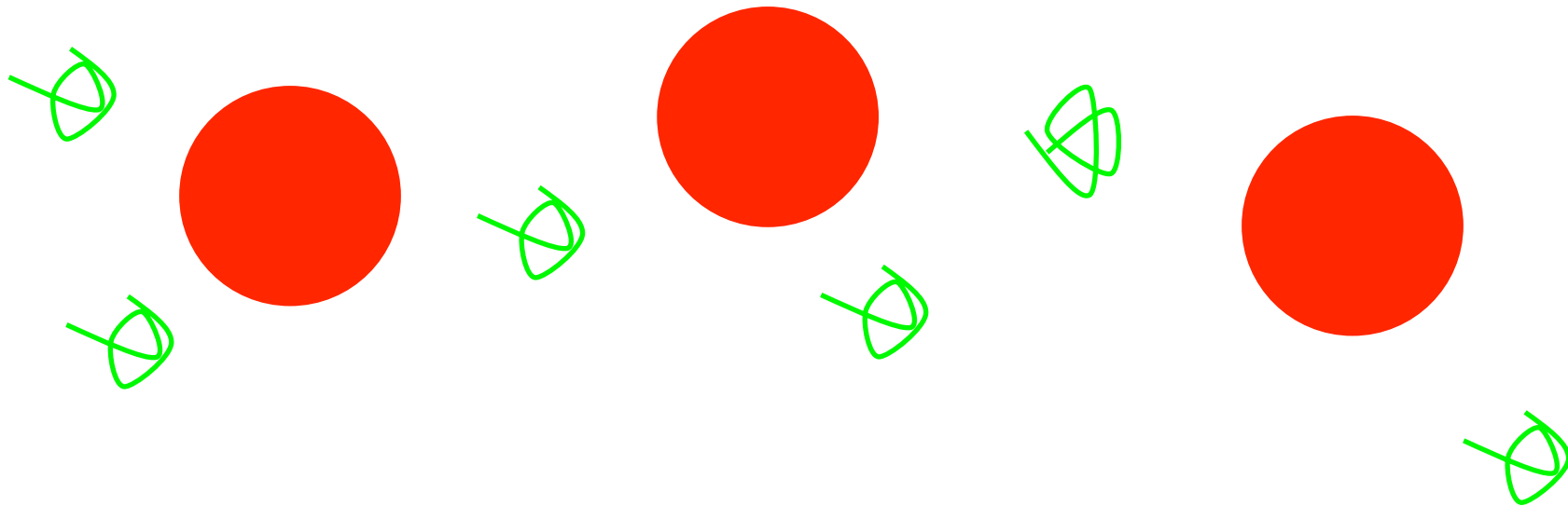
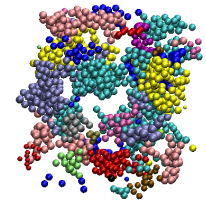
bacteria swim (**self-propel**)
due to the presence of flagella



polymers lead to depletion
attraction between
non-motile bacteria

Schwarz-Linek, Soft Matter(2010)

Bacteria & polymer mixture

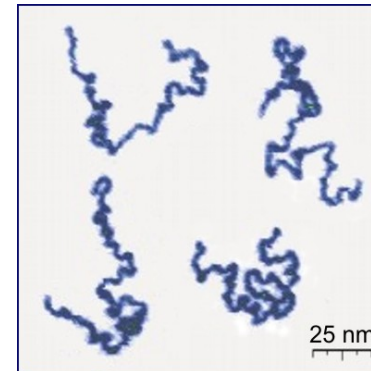
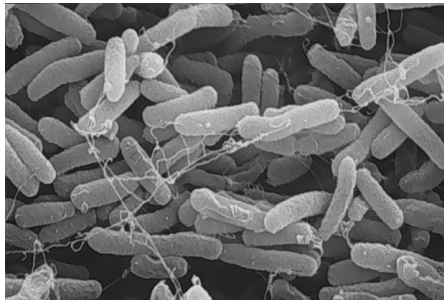
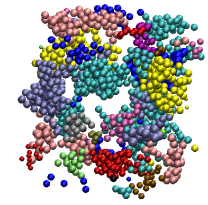


in a colloid-polymer mixture

depletion forces are $\sim k_B T / \text{giration radius}$ ($\sim 10\text{-}100$ nm)

so in the range of 0.05-0.5 pN

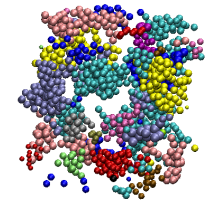
Bacteria & polymer mixture



competition between
propulsion and attraction

Bacteria & polymer mixture

experiments



Ecoli



NaPSS

simulations

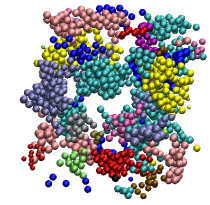
self-propelled
hard dumbbells



short-range
attractions

competition between
propulsion and attraction

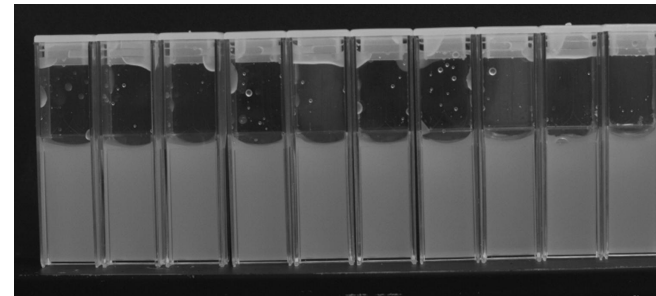
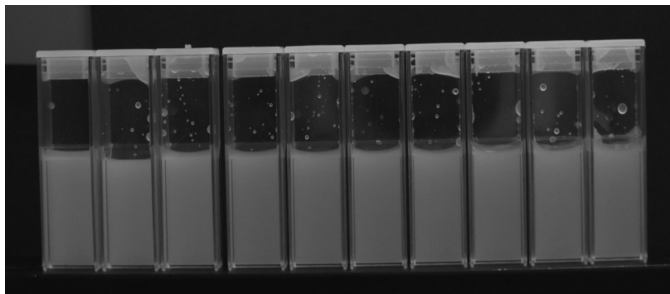
Phase separation



experiments

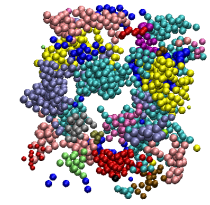
Non-motile Ecoli (alive, no flagella)

Motile Ecoli (alive, swimming)



→
increasing polymer (NaPSS)
concentration

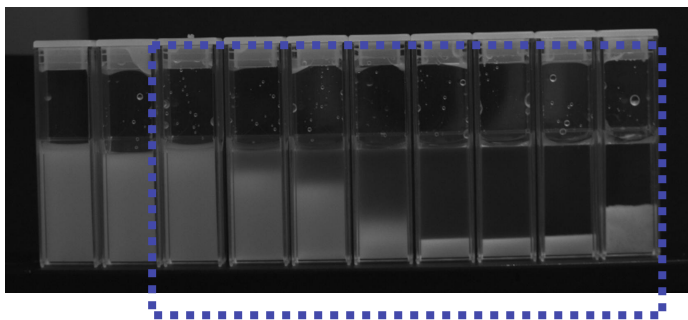
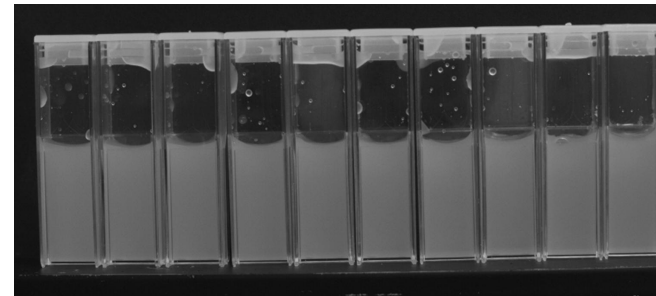
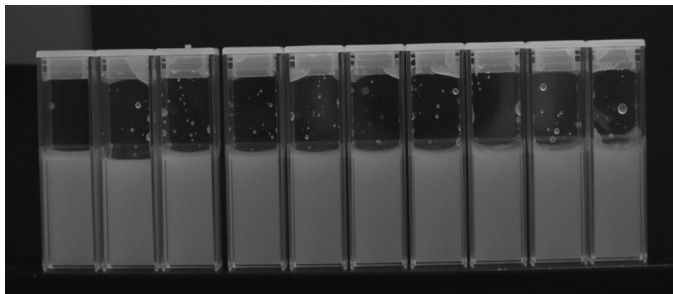
→
increasing polymer (NaPSS)
concentration



Phase separation experiments

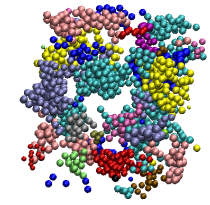
Non-motile Ecoli (alive, no
flagella)

Motile Ecoli (alive,
swimming)



2 hours: phase separation

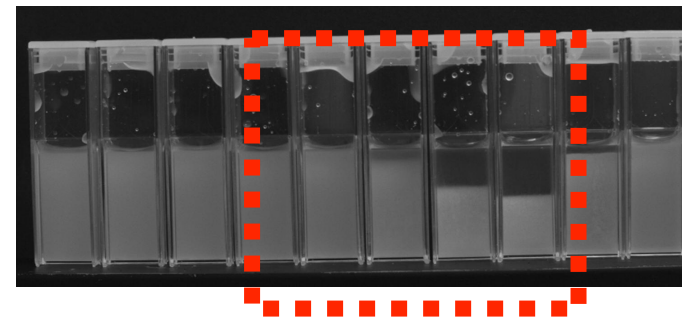
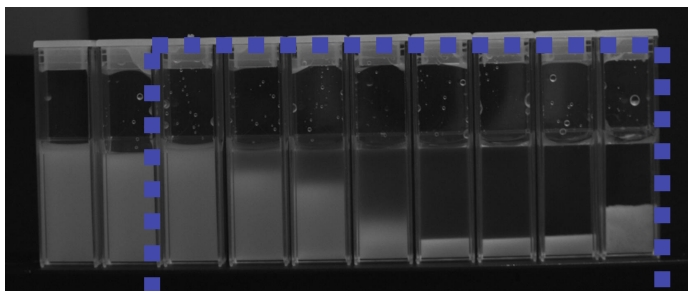
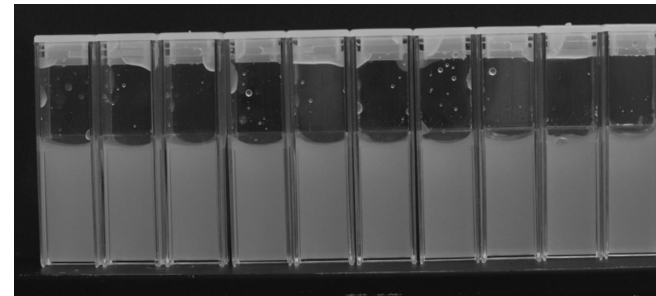
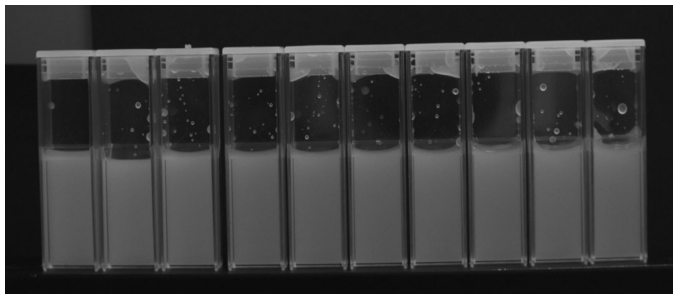
if NaPSS > 0.2 wt %



Phase separation experiments

Non-motile Ecoli (alive, no
flagella)

Motile Ecoli (alive,
swimming)

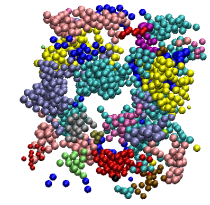


2 hours: phase separation

if NaPSS > 0.2 wt %

2 hours: phase separation

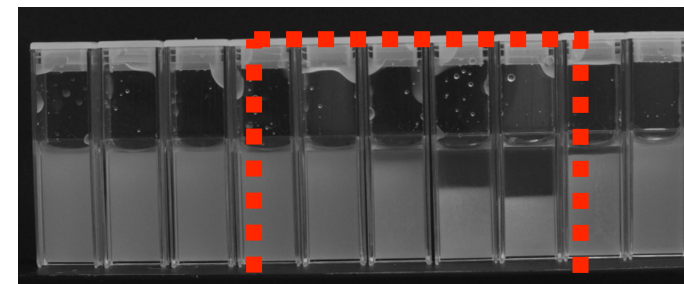
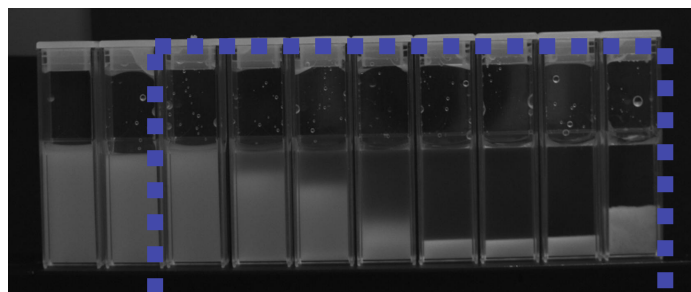
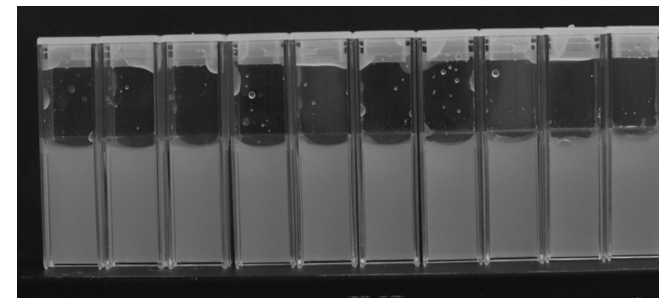
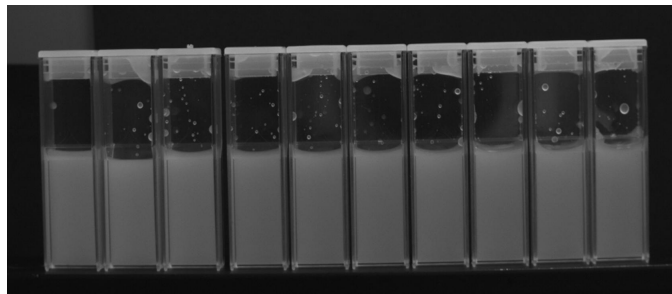
if NaPSS > 0.4 wt %



Phase separation experiments

Non-motile Ecoli (alive, no
flagella)

Motile Ecoli (alive,
swimming)

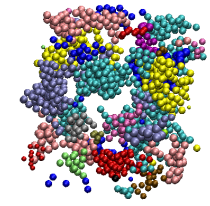


2 hours: phase separation

if NaPSS > 0.2 wt %

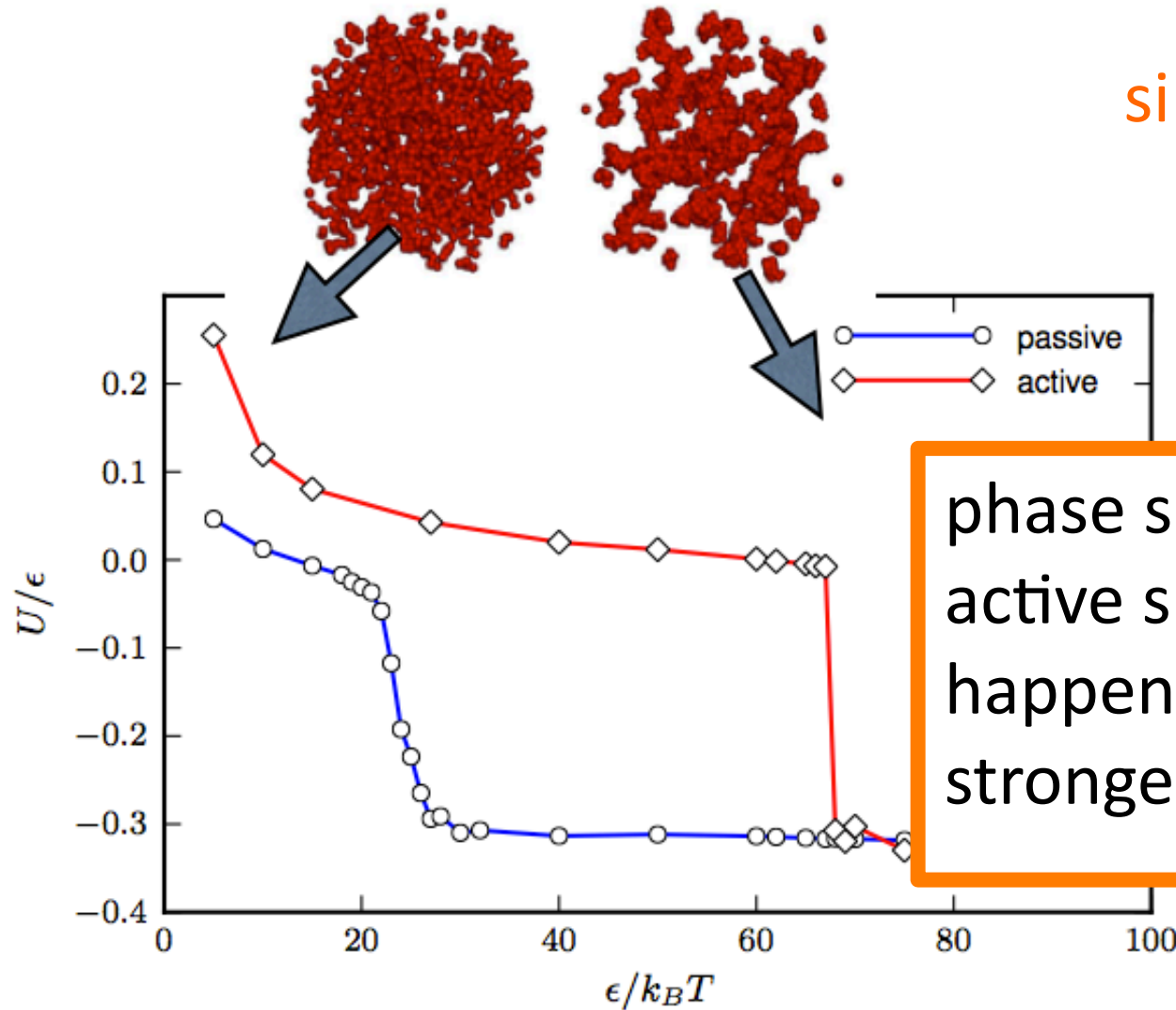
this corresponds to a

stronger depletion attraction

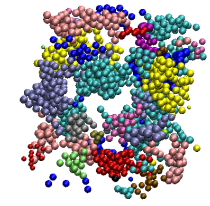


Phase separation

simulations

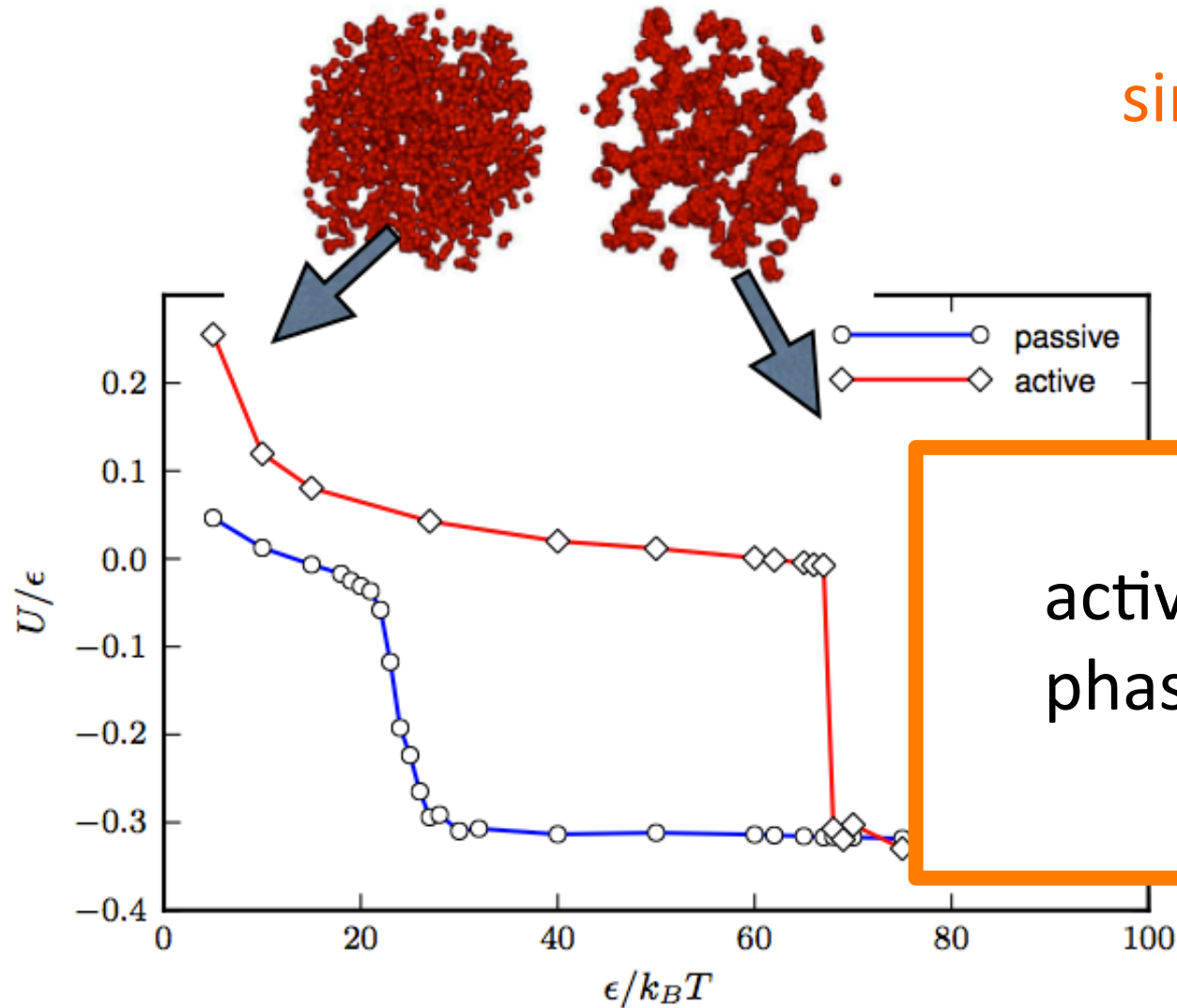


phase separation in an active suspension happens for stronger attraction



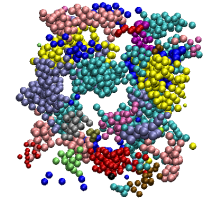
Phase separation

simulations

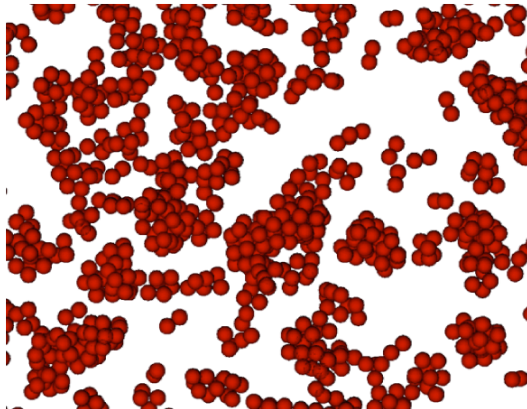


activity suppresses
phase separation

What happens just before phase separation takes place?



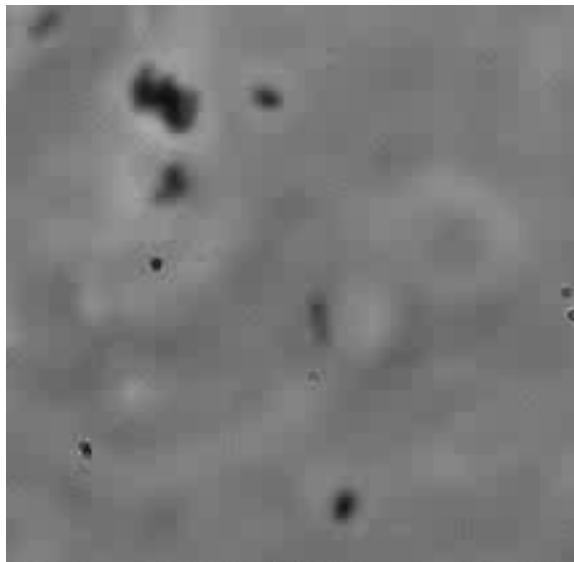
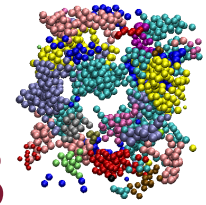
transient clusters



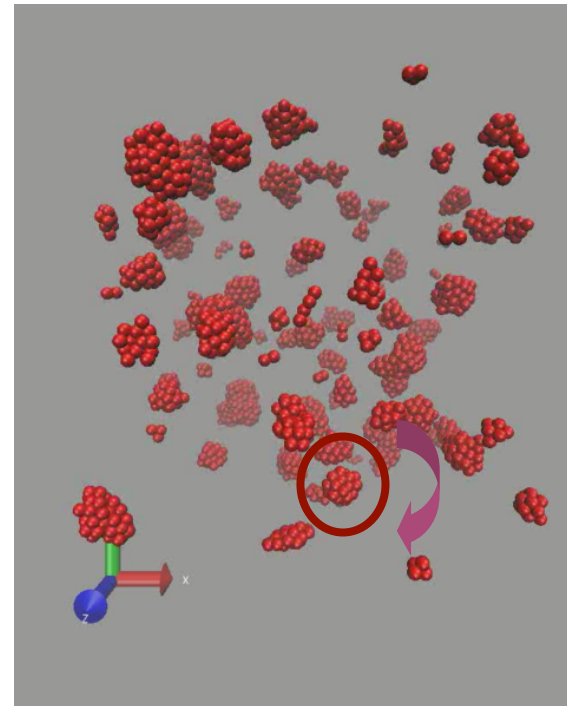
finite-size clusters of variable size (simulations)

small clusters (flagella of external bacteria may screen interactions) (experiments)

Self-assembly of nano-rotors



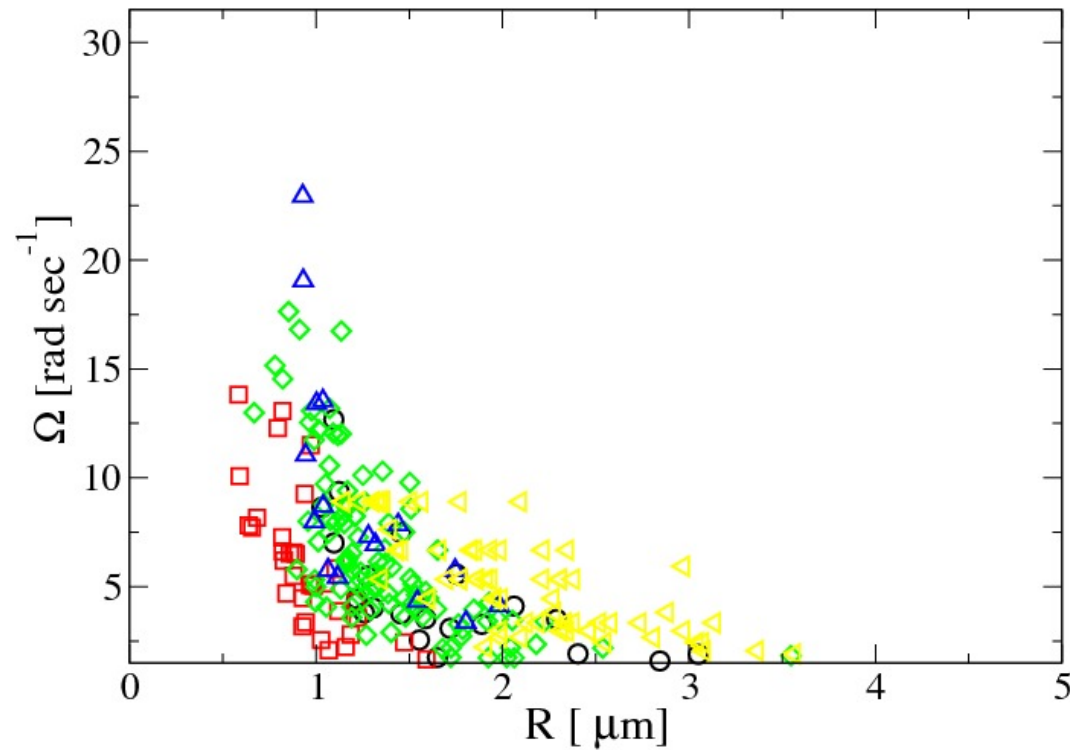
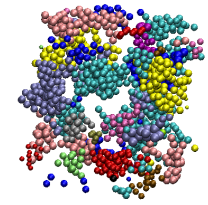
experiments



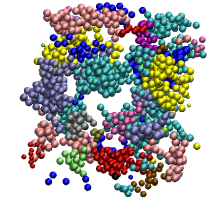
simulations

persistent clusters rotate unidirectionally

Clusters' angular velocity is a function of their size



angular velocity of a cluster decreases with its size

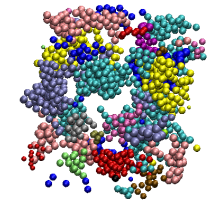


Conclusions

- ✓ Activity suppresses phase separation
- ✓ At lower polymer concentrations, formation of self-propelled and unidirectionally rotating clusters
- ✓ **Activity & propulsion** are the ingredients to self-assemble functional clusters

PNAS 106 4052 (2012)

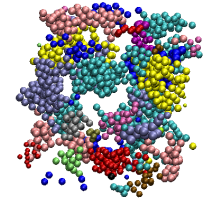
Research highlight in
Nature Materials/Nature Physics (2012)



However...

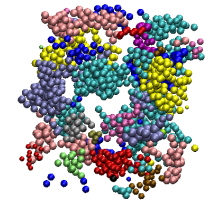
- ✓ in the bacteria & polymer mixture, we changed the attraction strength (polymer concentration) between active colloids
- ✓ but we did not modify their speed...
- ✓ therefore clusters were just transient and would aggregate at long times

Outline



- ✓ Active colloids
- ✓ Self-assembly of active colloids
- ✓ What happens in a bacteria & polymer mixture?
- ✓ Can we make living clusters of active colloids in low concentrated suspensions

Living clusters



Daan Frenkel



Stefano Angioletti Uberti



Bortolo Mognetti

The team:

Cambridge University

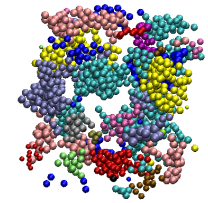
Columbia University



Angelo Cacciuto

Andela Sairc

Phase separation/clusters in 2 dim self-propelled systems



2 dim rod-shaped (at low/high concentrations) steric/ideal

Peruani, Deutsch, Bar (2006)

Yan, Marceau, Gompper (2010)

Ginelli, Peruani, Bar, Chate(2006)

or 2dim spherical shaped interacting via a repulsive potential
(at high concentration)

Redner, Hagan, Baskaran (2013)

Stenhammar, Tirabocchi, Allen,
Marenduzzo, Cates (2011)

Tailleur, Cates (2013)

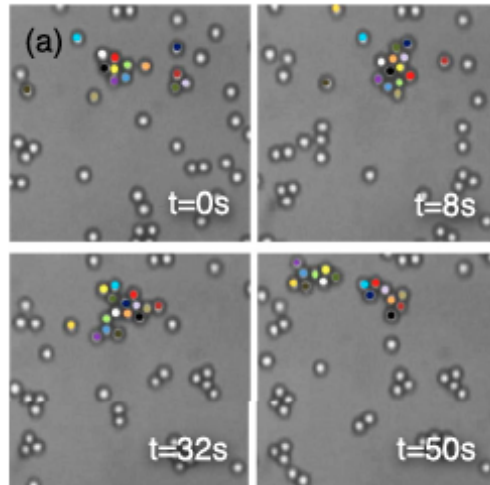
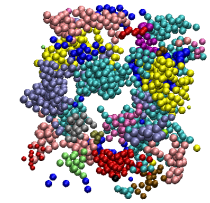
Henke, Fily, Marchetti (2011)

or 2dim spherical shaped interacting via an attractive potential
(at high concentration)

Redner, Baskaran, Hagan (2013)

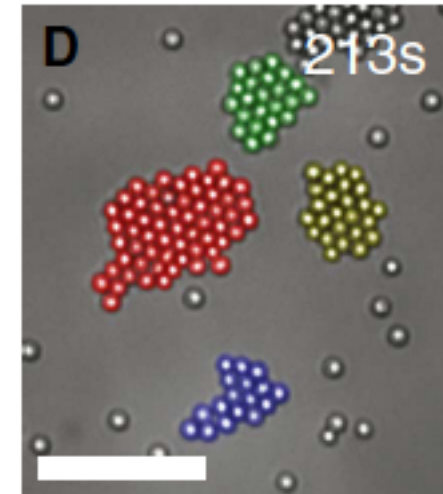
**What happens for attractive self-propelled
spheres at low concentrations?**

Experimental evidences for living clusters in 2 dim



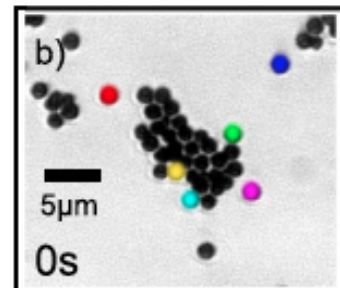
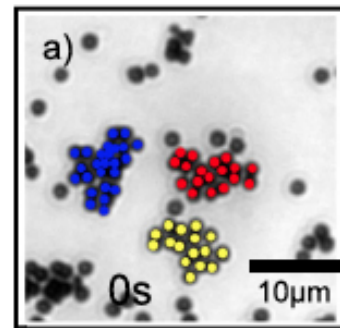
Theurkauff, Cottin-Bizonne,
Palacci, Ybert, Bocquet (2012)

cluster phase at
intermediate densities



Buttinoni, Bialke, Kummel,
Lowen, Bechinger, Speck (2013)

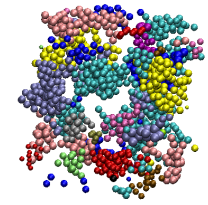
dynamic clusters at low densities
in a 2dim suspension of SP
purely repulsive colloids



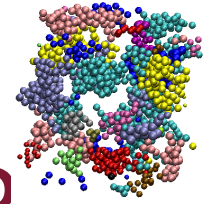
Palacci, Sacanna,
Steinberg, Pine, Chaikin (2013)

living clusters and crystals

Experimental evidences for living clusters in 2 dim

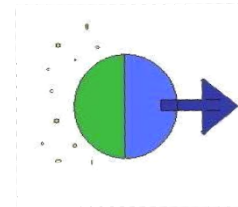


Which low concentrated suspensions of active colloids?



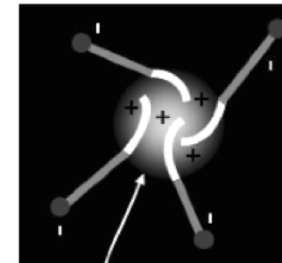
✓ Self-propelled colloids (SP)

to mimic reactive colloids



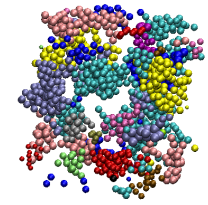
✓ Self-displaced colloids (SD)

to mimic synthetic centrosomes
(colloids & microtubules)



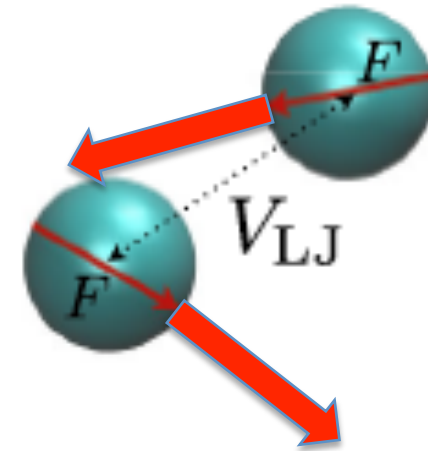
(Spoerke Langmuir (2008))

Self-propelled colloids



$$m\ddot{\mathbf{r}}_i = -\sum_{j \neq i} \frac{\partial V(r_{ij})}{\partial \mathbf{r}_i} - \zeta \dot{\mathbf{r}}_i + \mathbf{F}_i + \mathbf{F}_{R,i}$$

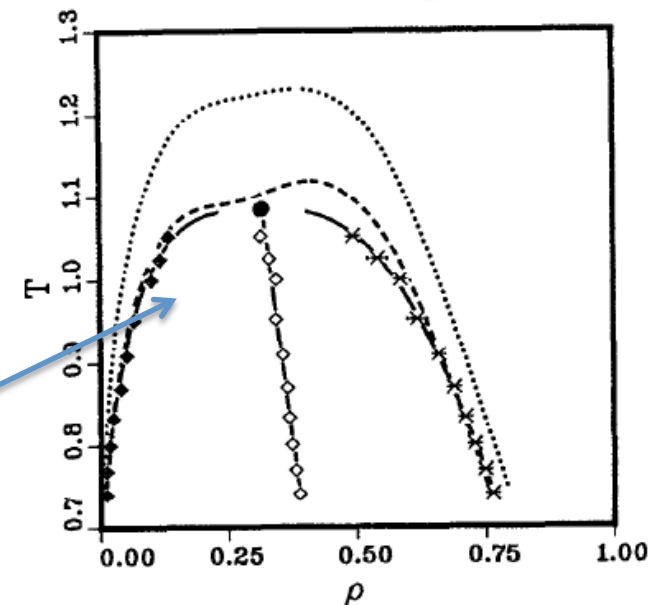
$$V(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma_p}{r_{ij}} \right)^{12} - \left(\frac{\sigma_p}{r_{ij}} \right)^6 \right]$$



truncated and shifted
Lennard-Jones interaction

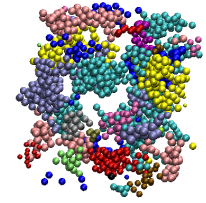
at low concentrations ($\phi=0.01-0.1$)

LAMMPS

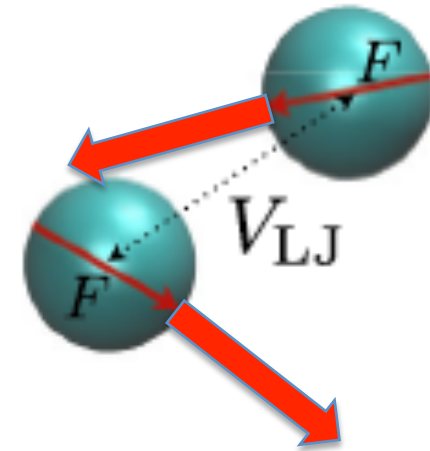


Smit (1992)

Self-propelled colloids



$$m\ddot{\mathbf{r}}_i = -\sum_{j \neq i} \frac{\partial V(r_{ij})}{\partial \mathbf{r}_i} - \zeta \dot{\mathbf{r}}_i + \mathbf{F}_i + \mathbf{F}_{R,i}$$

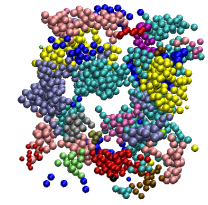


equilibrium: Lennard-Jones attraction

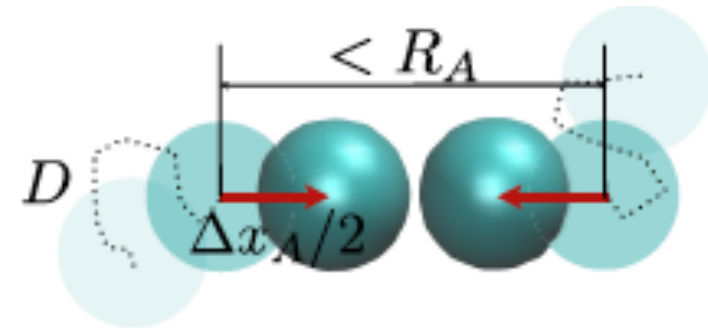
non-equilibrium: self-propulsion

Active versus **equilibrium** force

Self-displaced colloids

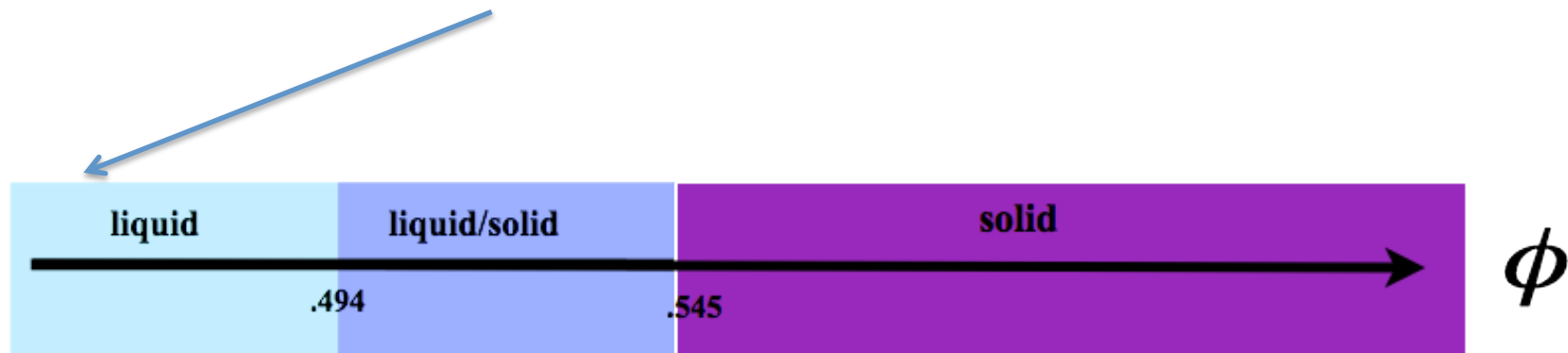


In the presence of ATP
two centrosomes are cross-linked
by molecular motors
and displaced towards each others



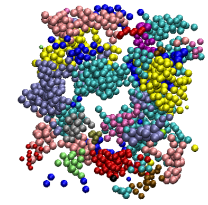
Monte Carlo

at low concentrations ($\phi=0.01-0.1$)

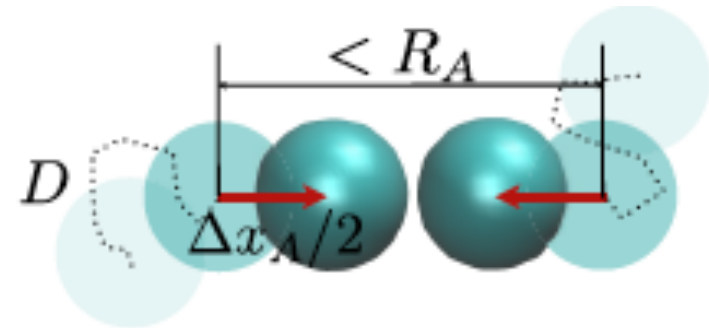


Alder&Wainwrigth (1957), Pusey&van Megen (1986)

Self-displaced colloids



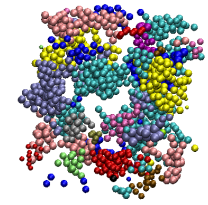
equilibrium: Brownian motion of hard-spheres with diffusion D



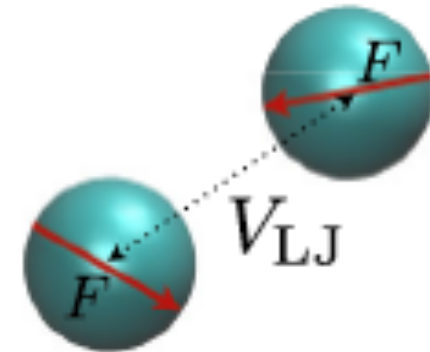
non-equilibrium: two colloids are displaced toward each other by molecular motors with a pulling rate v

Active versus **equilibrium** force

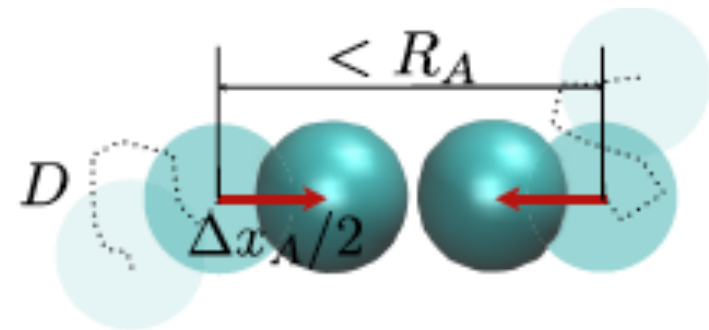
Is there a propensity for aggregation?



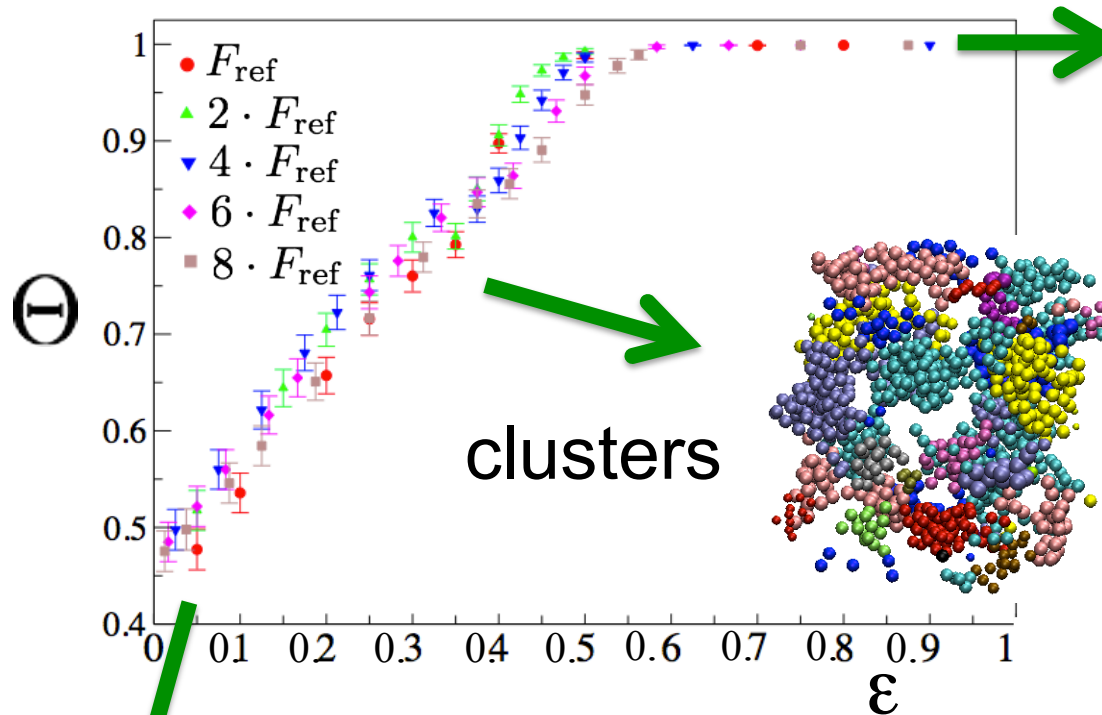
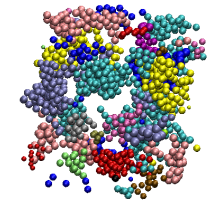
$$P_{\text{agg}}(\text{SP}) = \frac{\varepsilon}{F\sigma}$$



$$P_{\text{agg}}(\text{SD}) = \frac{\nu}{D/(R_A - \sigma)^2}$$

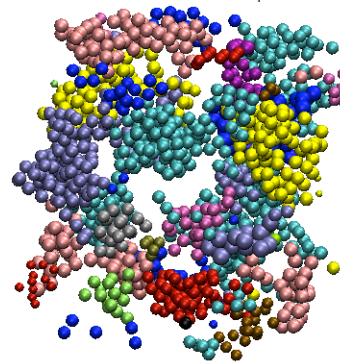


Is there a propensity for aggregation?



one large aggregate (liquid&gas)

clusters

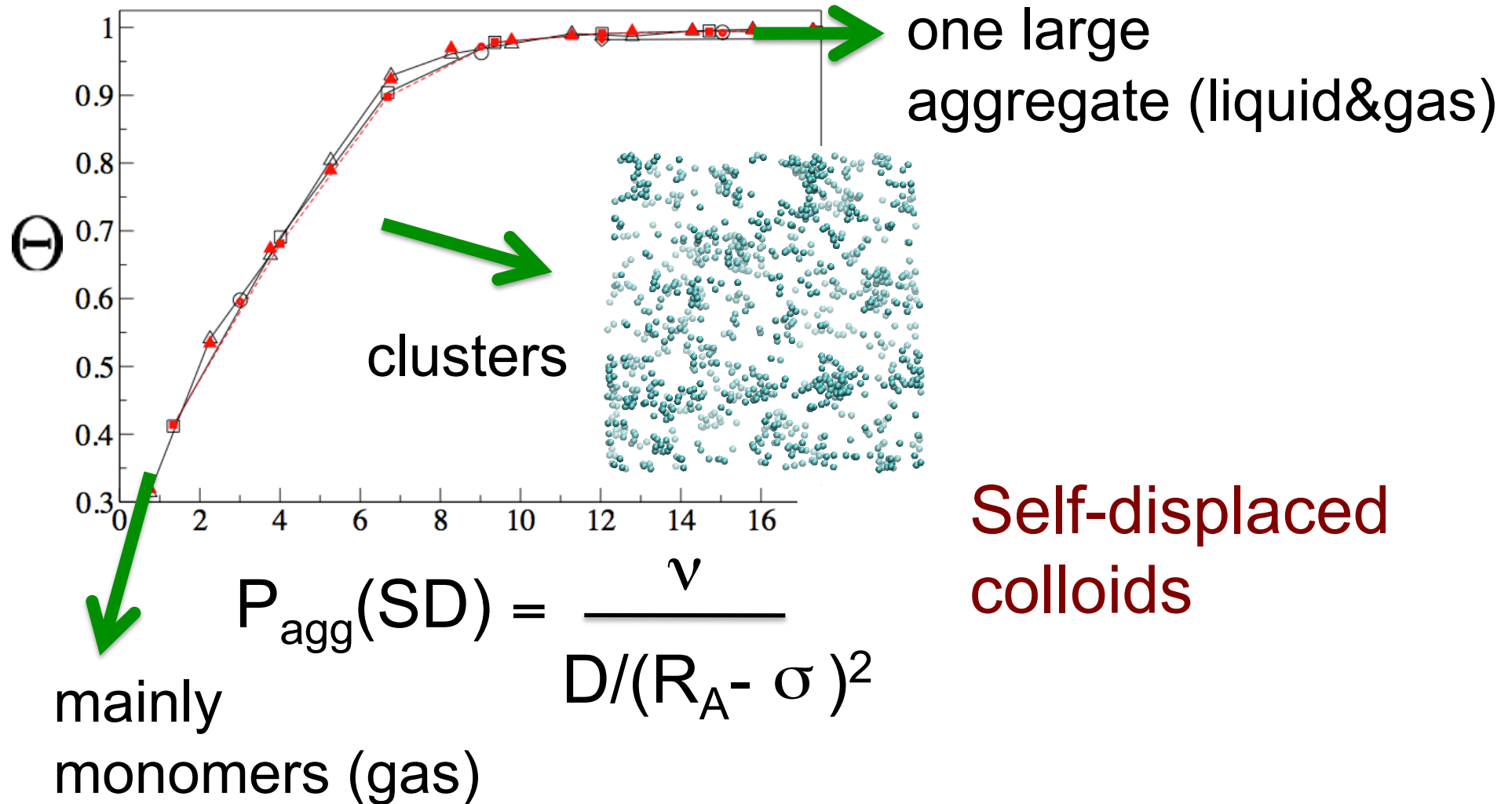
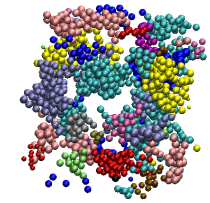


Self-propelled
colloids

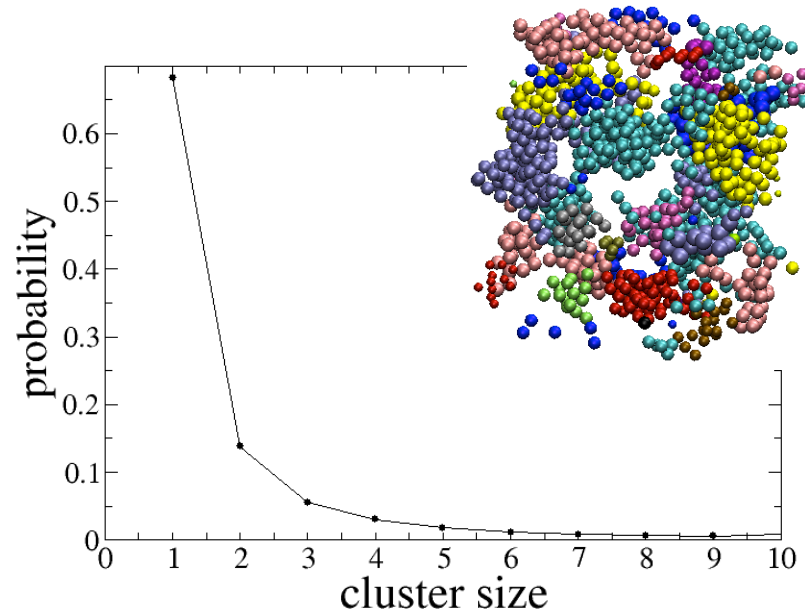
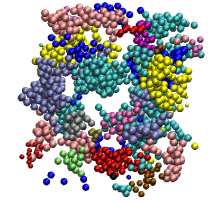
$$P_{\text{agg}}(\text{SP}) = \frac{\varepsilon}{F \sigma}$$

mainly
monomers (gas)

Is there a propensity for aggregation?

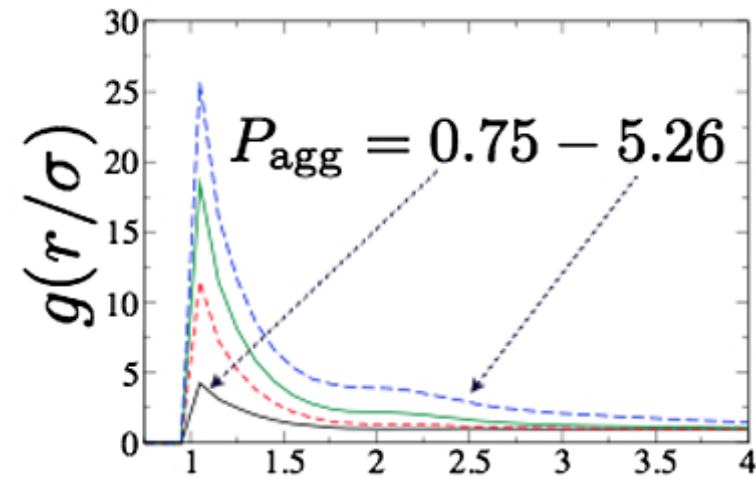


Preliminary characterization of the clusters



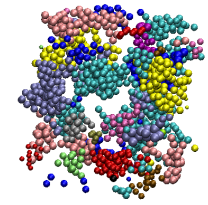
cluster-size distribution
seems power-law

clusters grow and shrink dynamically

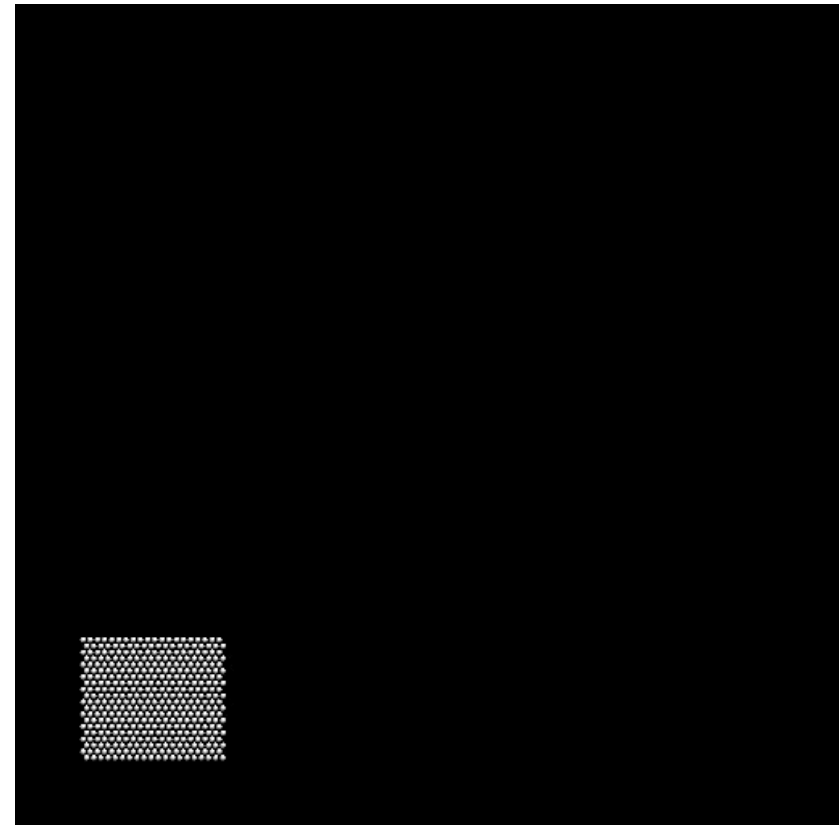


clusters are amorphous

Preliminary characterization of the clusters



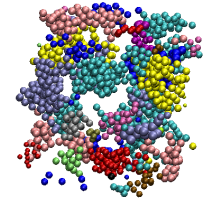
initial configuration: gas



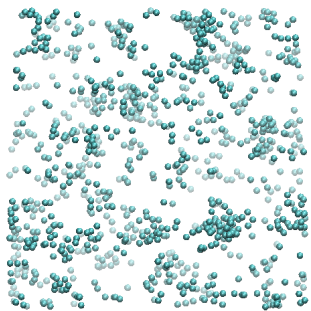
initial configuration: crystal

we observe them for different initial conditions

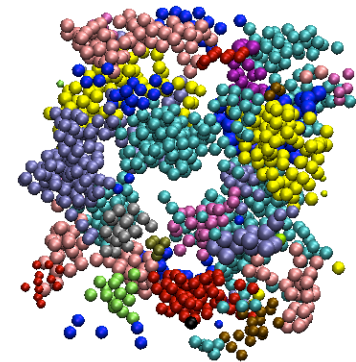
Therefore



the formation of living clusters at low concentrations is independent on the active suspension under study

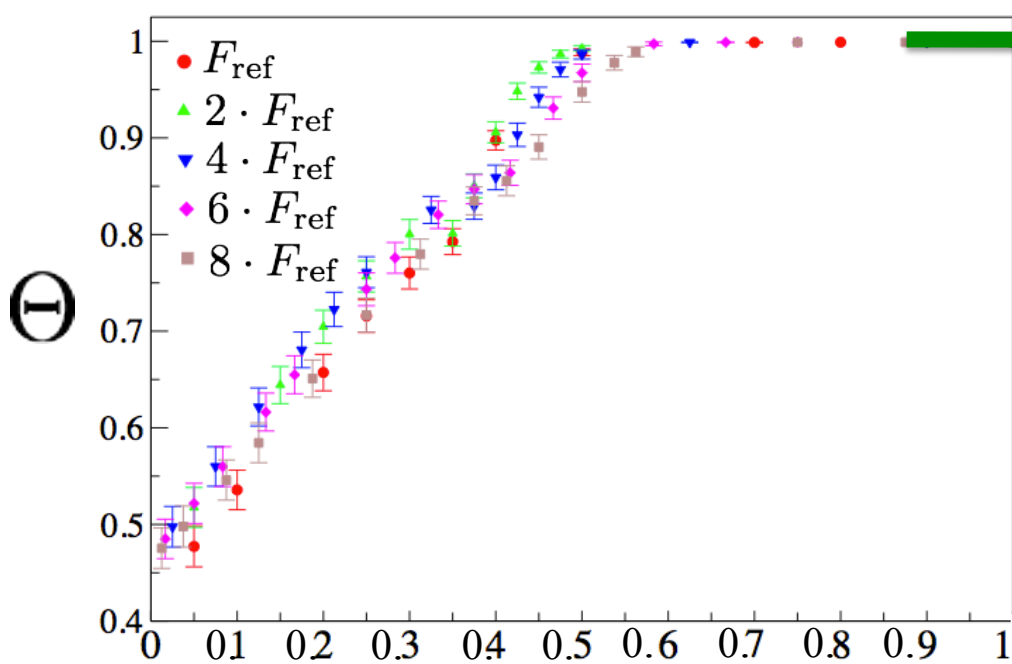
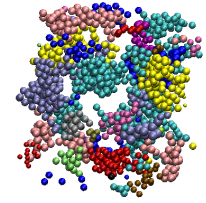


whether self-displaced or self-propelled



as long as there is a competition between **equilibrium** and **active** force

Is there anything special in the structure formed at large P_{agg} ?



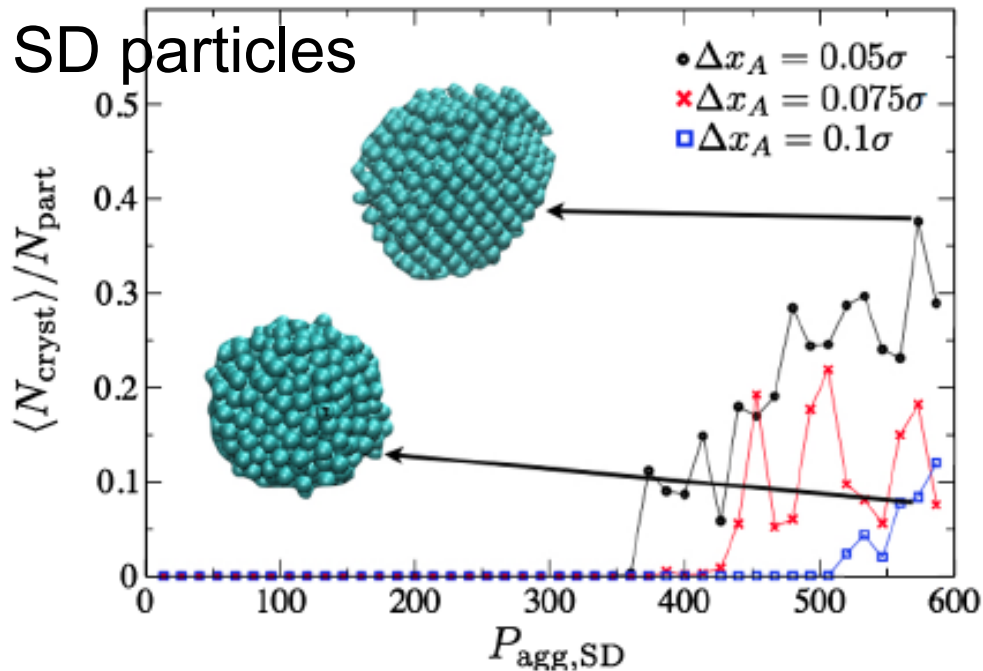
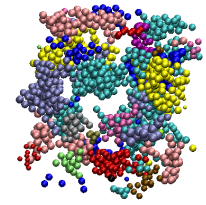
the system forms one large amorphous aggregate that **crystallizes** thanks to the activity

$P_{\text{agg}}(\text{SP})$

activity helps annealing defects!

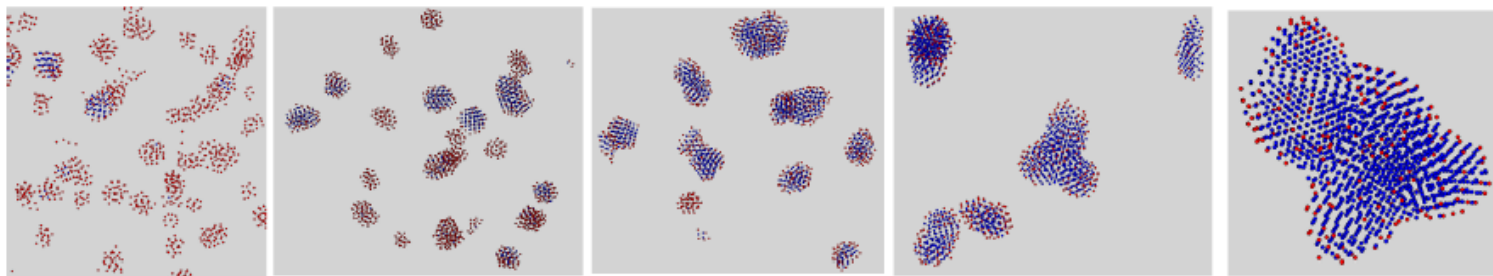
irreversible crystallization, not living crystals

Is there anything special in the structure formed at large P_{agg} ?

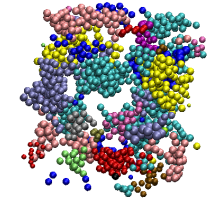


the system forms one large amorphous aggregate that **crystallizes** thanks to the activity

SP particles



t

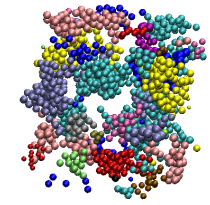


Conclusions

- ✓ In a **diluted suspension** of active colloids where an **active force competes with an equilibrium** one, the system can aggregate into **living clusters**
- ✓ When attraction dominates, the clusters can irreversibly **crystallize**

Physical Review Letter, 111 245702 (2013)

Focus article: Physics, 6 134 (2013)



Take-home message

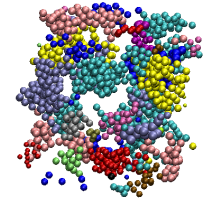
- ✓ Activity suppresses phase separation
- ✓ **Activity & propulsion** are the ingredients to self-assemble functional clusters
- ✓ In a **diluted suspension** of active colloids where an **active force competes with an equilibrium** one, the system can aggregate into **living clusters**

Physical Review Letter, 111 245702 (2013) Focus article: Physics, 6 134 (2013)

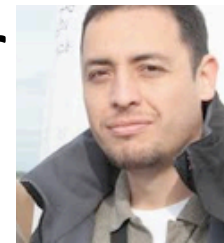
PNAS 106 4052 (2012)

Research highlight in
Nature Materials/Nature Physics (2012)

Questions and ongoing work



- ✓ Can we better characterize the clusters?
- ✓ What is the effect of hydrodynamic interactions?
- ✓ What is the effect of particles' shape in the process of self-assembly?
- ✓ What if we make the attraction anisotropic?
- ✓ What happens if we consider active and passive colloids?

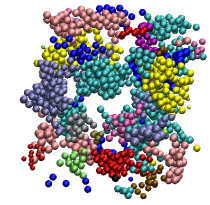


University of Barcelona

Paco Alarcon

Ignacio Pagonabarraga

Living clusters and crystals from low-density suspensions of active colloids



Muchas gracias!



Physical Review Letter, 111 245702 (2013)

Living clusters

Focus article: Physics, 6 134 (2013)

Bacteria & Polymers

PNAS 106 4052 (2012)

Research highlight in
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