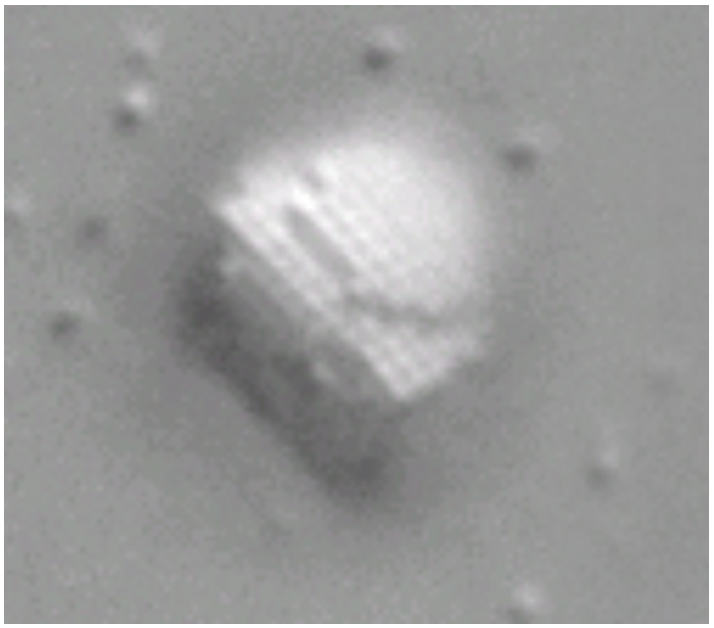
Binary Colloidal Crystals Using DNA Handshaking Interactions

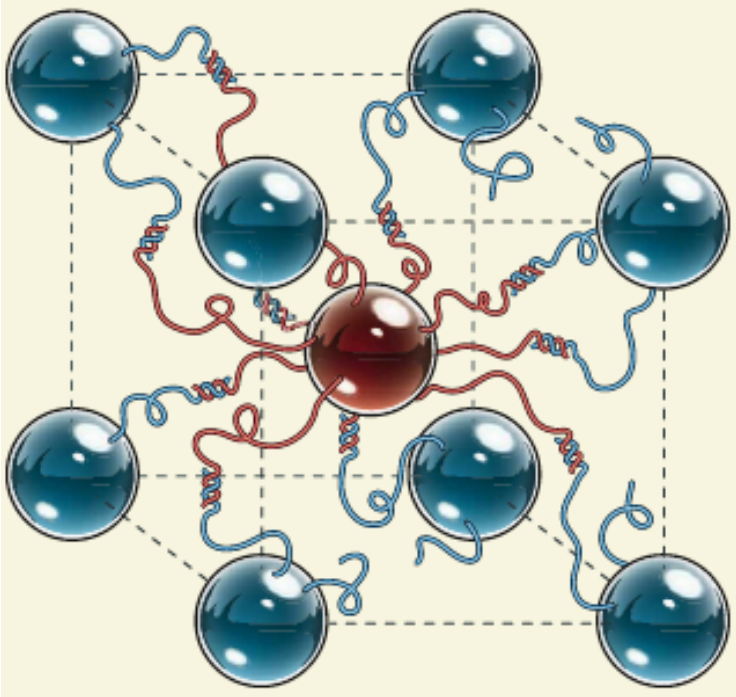
John C. Crocker

Chemical and Biomolecular Engineering



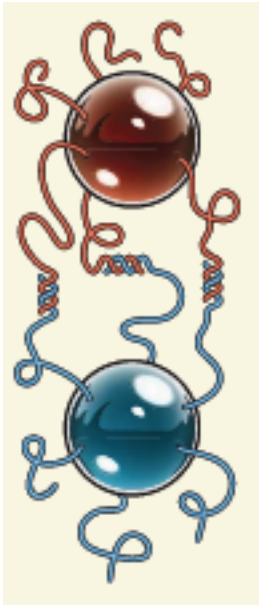
KITP
Santa Barbara
6.7.2012

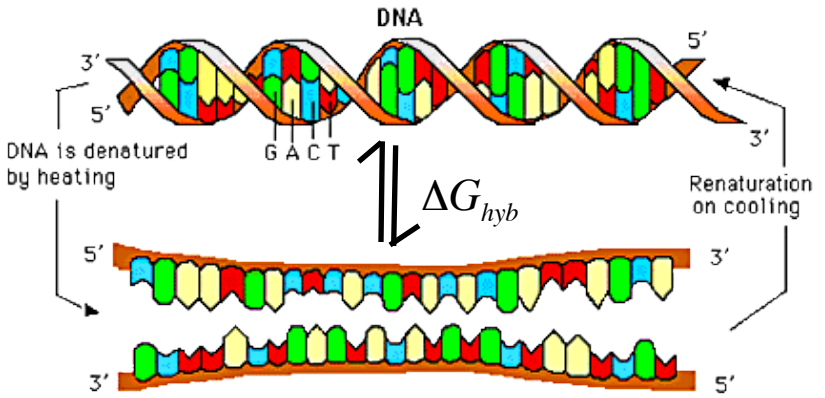
Use DNA to assemble particles



— *graft single-stranded DNAs to particles*
— *DNAs with complementary sequences will bridge particles together*
— *dynamic bridge formation: 'handshaking' allows structural annealing*

Use DNA to assemble particles





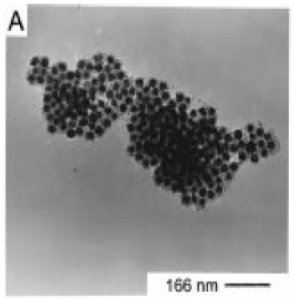
Features....

$$\Delta G_{hyb}(T) = \Delta G^{init}_{hyb}(T) + \sum_{i=1}^{10} n_i \Delta G^{i}_{hyb}(T)$$

- ***'hybridization' is a reversible two-state chemical reaction (ΔG)***
- ***temp dependent (ΔG) known a priori!***
- ***a 'library' of specific interacting pairs***
- ***chemistry is 'easy'***

Use DNA to assemble particles

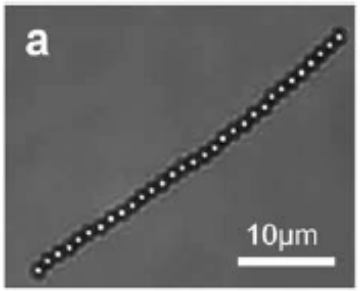
First Au nanoparticle assemblies (Mirkin 1996)



Mirkin et. al., *Nature*, (1996)

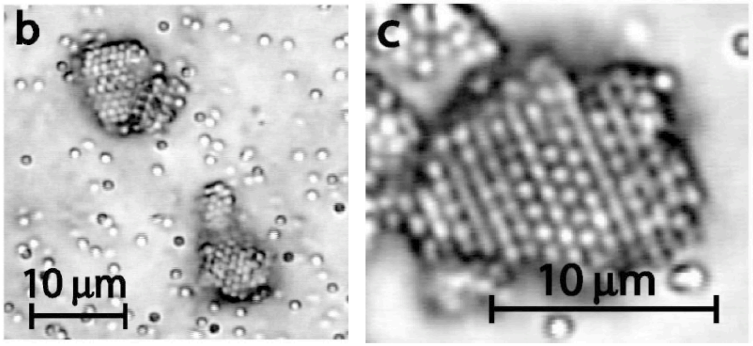
Alivisatos et. al., *Nature*, (1996)

Polymers (Biswal 2010)



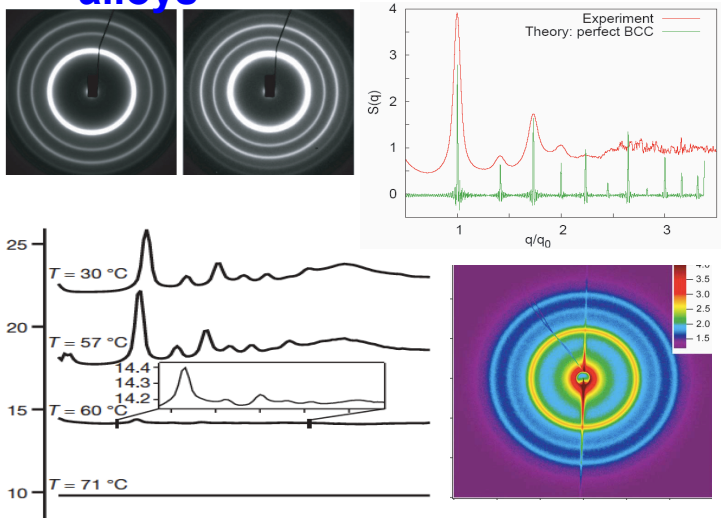
Li, Dichaun, *et al. Soft Matter.* 6, 4197 -4204 (2010)

Colloidal crystal (Crocker 2005)



Biancaniello, P.L. et al. *PRL.* 94, 058302 (2005).

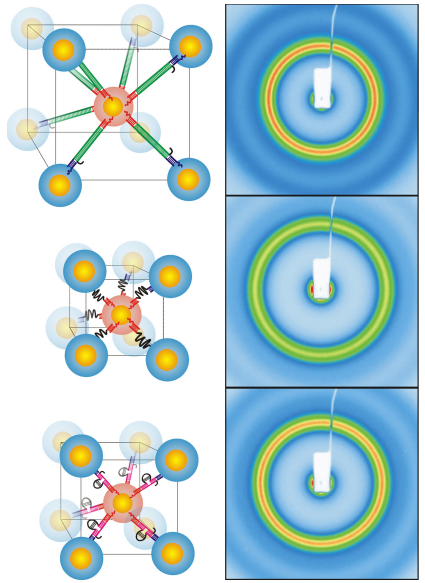
Nanoparticle (Gang and Mirkin 2008) alloys



Nykypanchuk, D. *et al. Nature.* 451, 549-552 (2008).

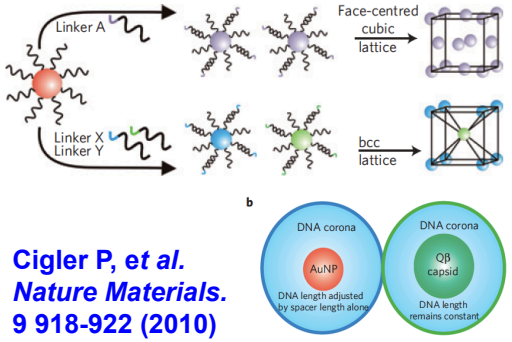
Park, S.Y. *et al. Nature.* 451, 553-556 (2008).

Reconfigure (Gang 2010)



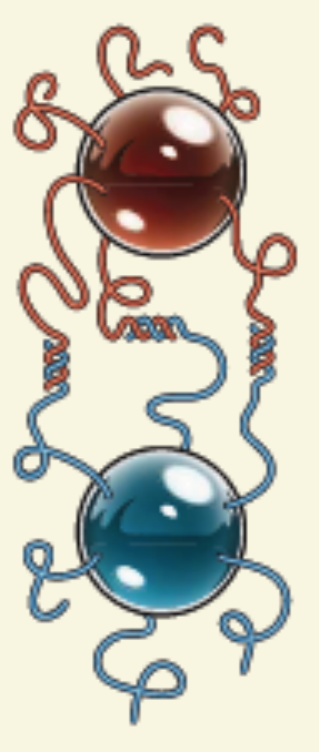
Maye MM, *et al. Nature Nanotechnology.* 5, 116-120 (2010)

Hybrids (Park 2010)



Cigler P, *et al. Nature Materials.* 9 918-922 (2010)

Use DNA to make crystals

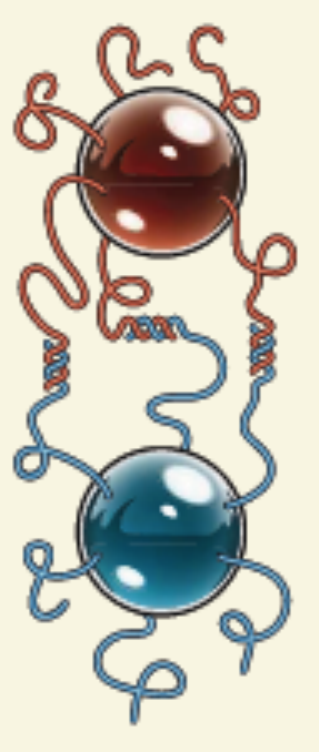


We seek a model soft material that has interesting crystalline phases and transformations, like real materials.

DNA assembly features:

—Interactions are 'specific', reversible, temperature tunable, can use DNA tech, etc.

Use DNA to make crystals



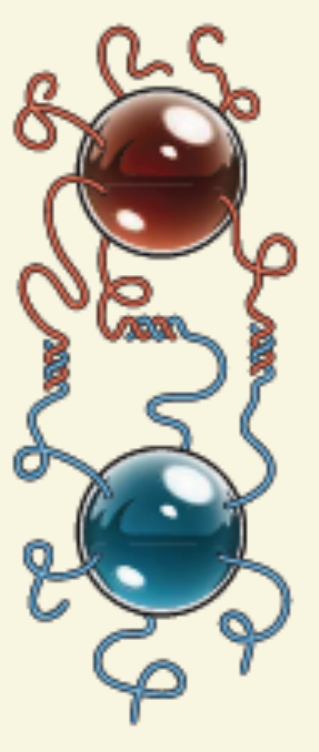
We seek a model soft material that has interesting crystalline phases and transformations, like real materials.

DNA assembly features:

—Interactions are 'specific', reversible, temperature tunable, can use DNA tech, etc.

—N-species have a symmetric NxN interaction matrix.

Use DNA to make crystals



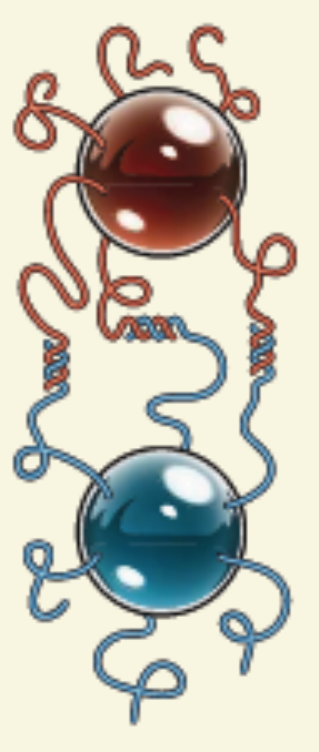
To be a good model system we need:

— A reliable empirical potential model (for simulations)

—Fast assembly kinetics

—Easy imaging and crystallography

Use DNA to make crystals



To be a good model system we need:

— A reliable empirical potential model (for simulations)

—Fast assembly kinetics

—Easy imaging and crystallography

Expt and simulation should agree!

Outline....

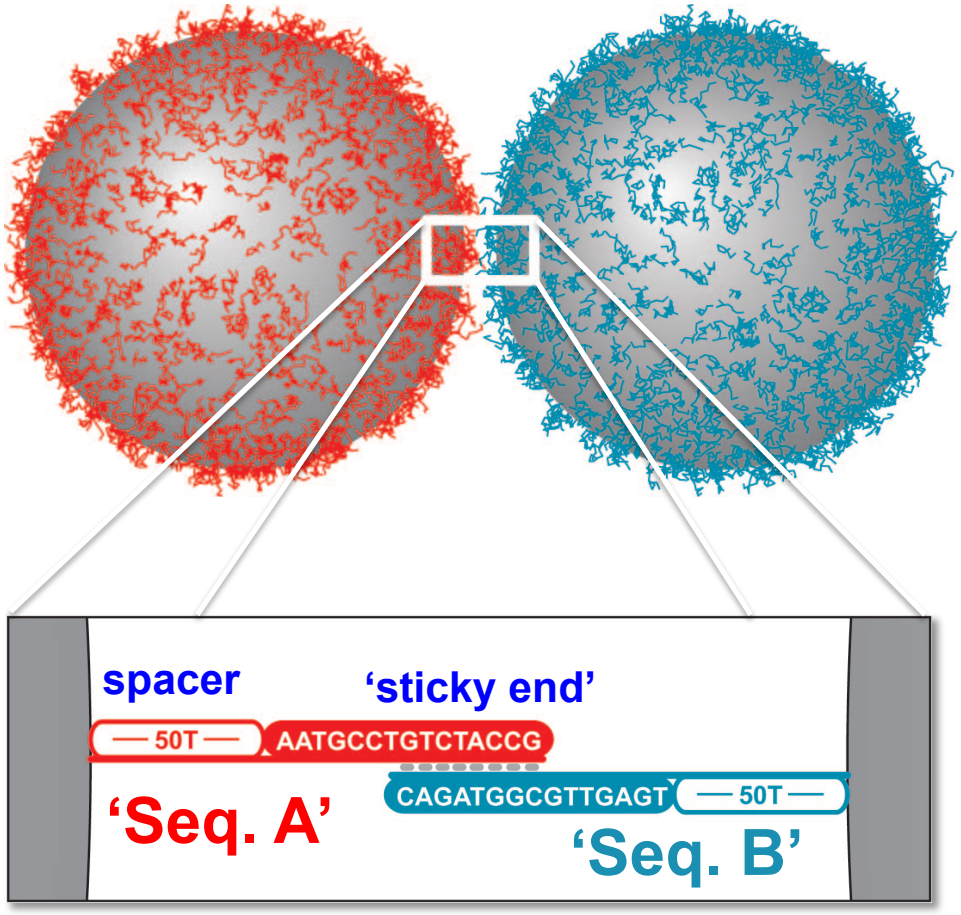
Ben Rogers

Marie Ung

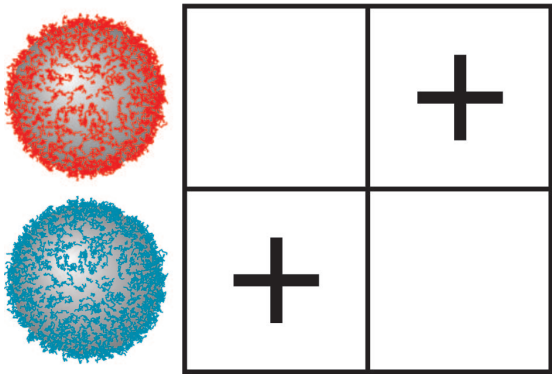
1. DNA interactions and dynamics
2. Simple crystals and real space crystallography
3. New phases and transformations

The experimental system

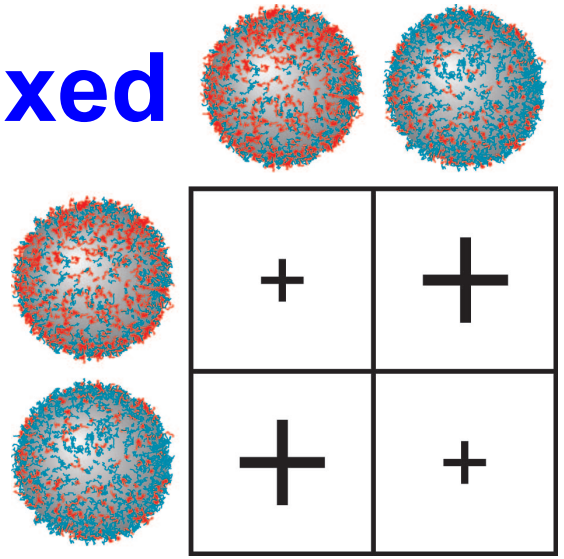
The binary system:
Two different particle species



Unmixed

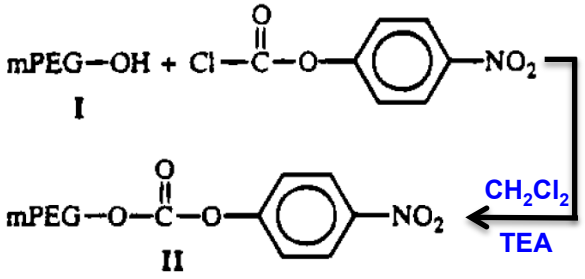


Mixed

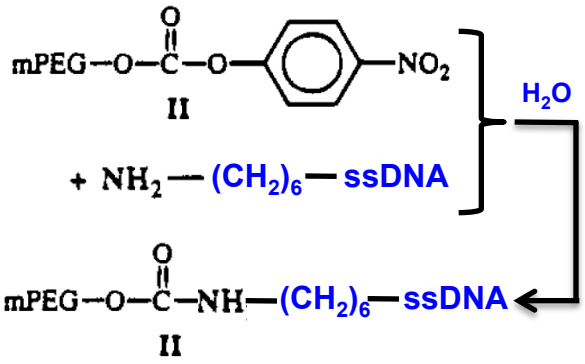


DNA labeling: physical grafting

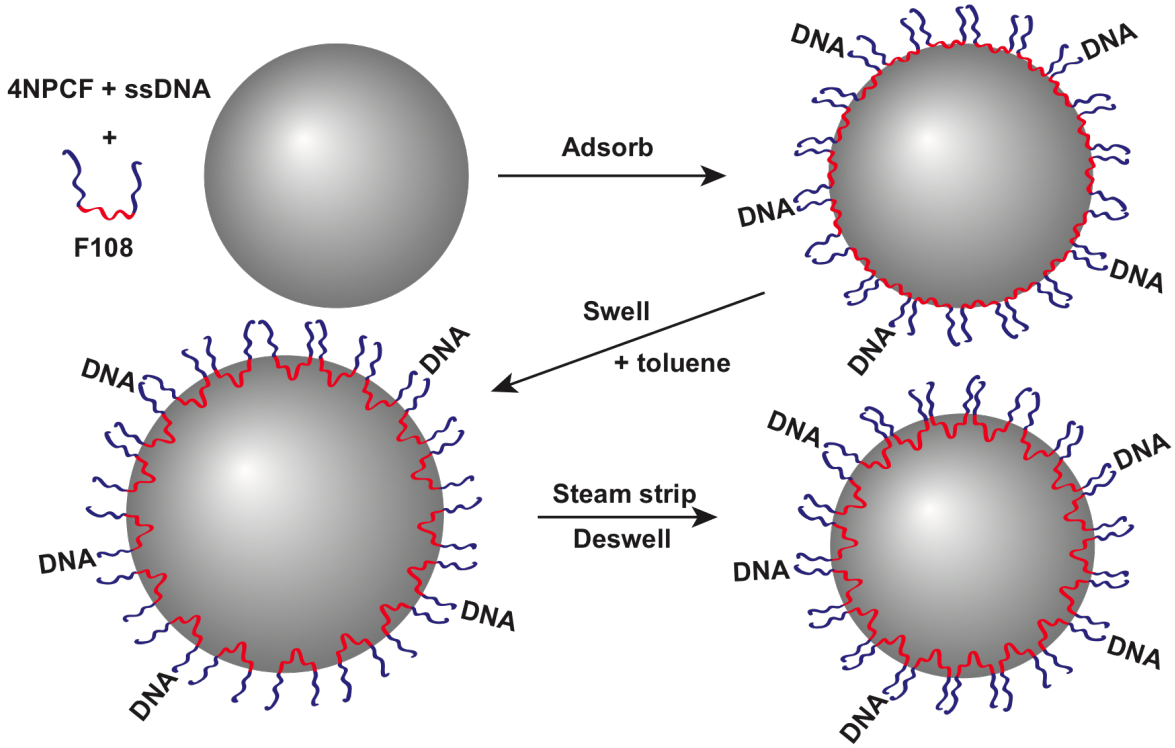
i. activation



ii. reaction



*Adapted from:
Monfardini, C., Schiavon, O., Caliceti, P., Morpurgo, M., Harris, J.M., Veronese, F.M. *Bioconjugate Chem*. 6, 62-69 (1995)



Densely PEGylated surface

Very Low Non-specific binding

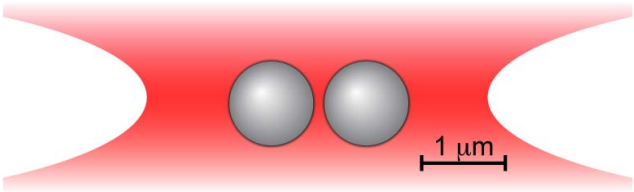
Protein-free: Long 'shelf life'

*Adapted from: Kim, A.J., Manoharan, V.N., Crocker, J.C. *JACS*. 127, 1592-1593 (2005)

Measure Interactions....

1. Resonant scanning mirror

Generate extended optical trap

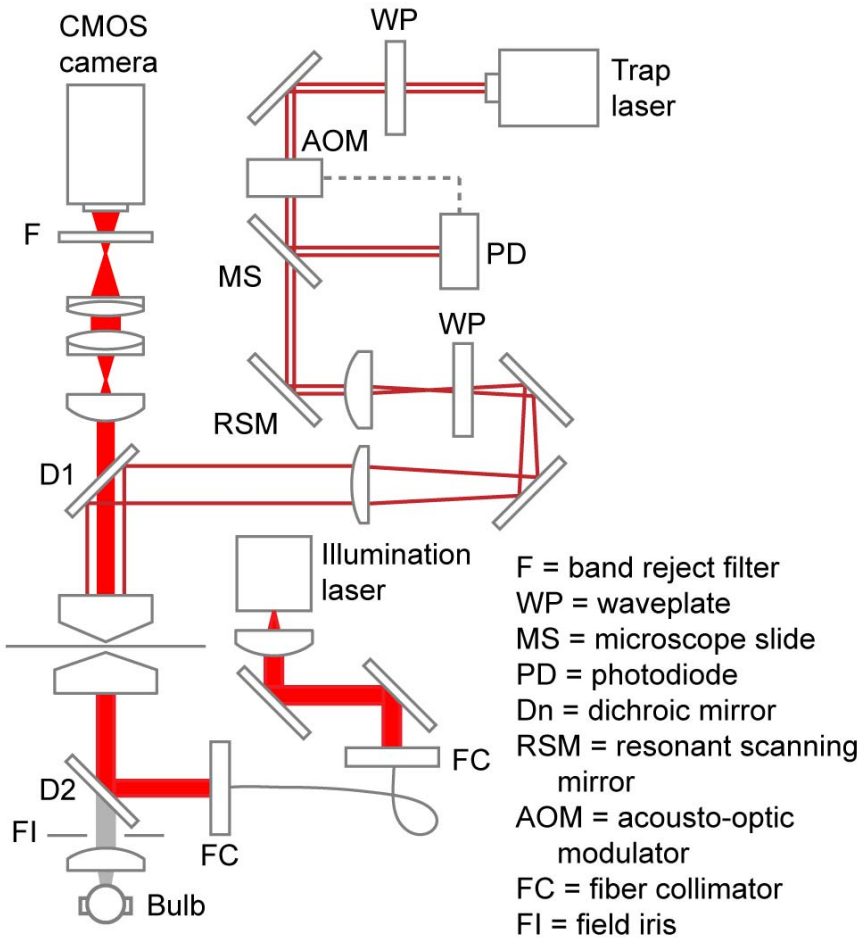


2. Acousto-optic modulator

Tailor the one-dimensional intensity profile

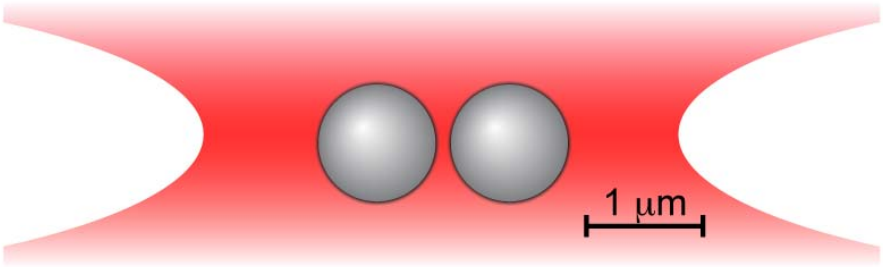
3. High-speed CMOS camera

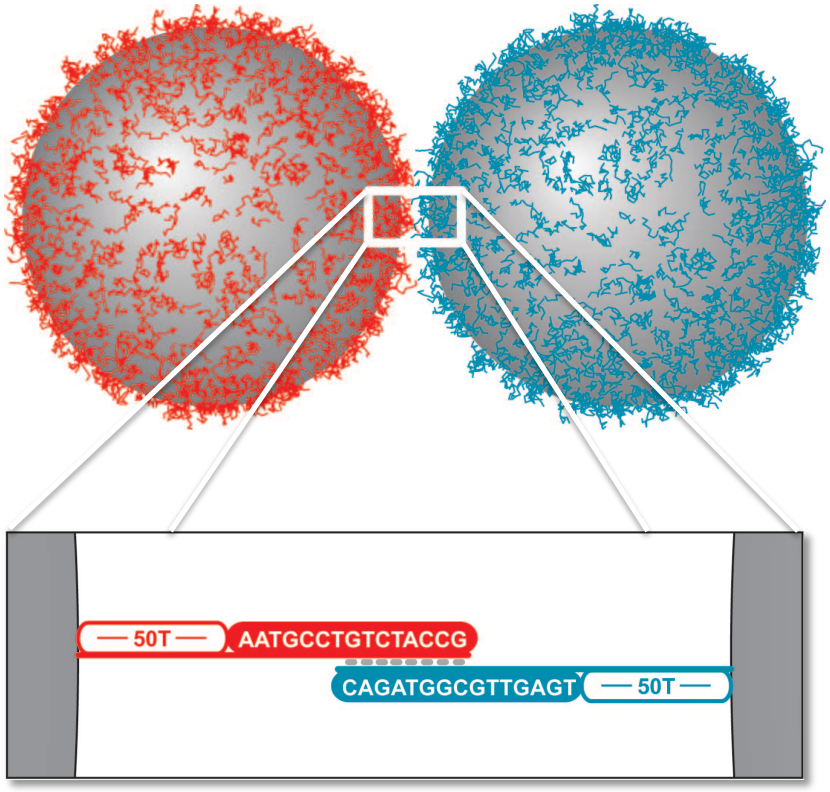
Image interacting particles

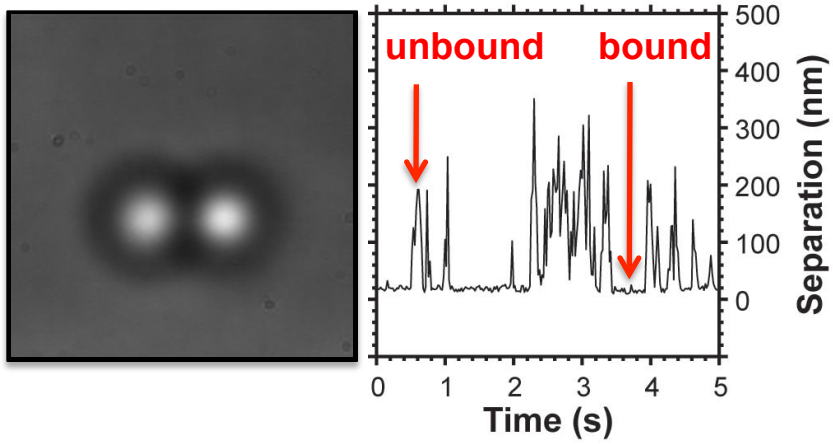


$$g(r) = e^{-V(r)/k_B T} \Rightarrow \frac{V(r)}{k_B T} = -\ln[g(r)]$$

Measuring DNA-induced interactions

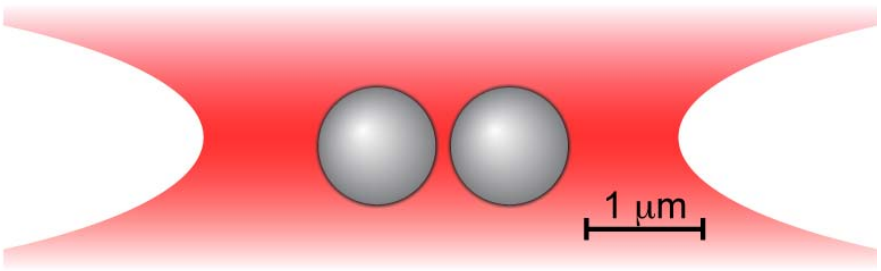


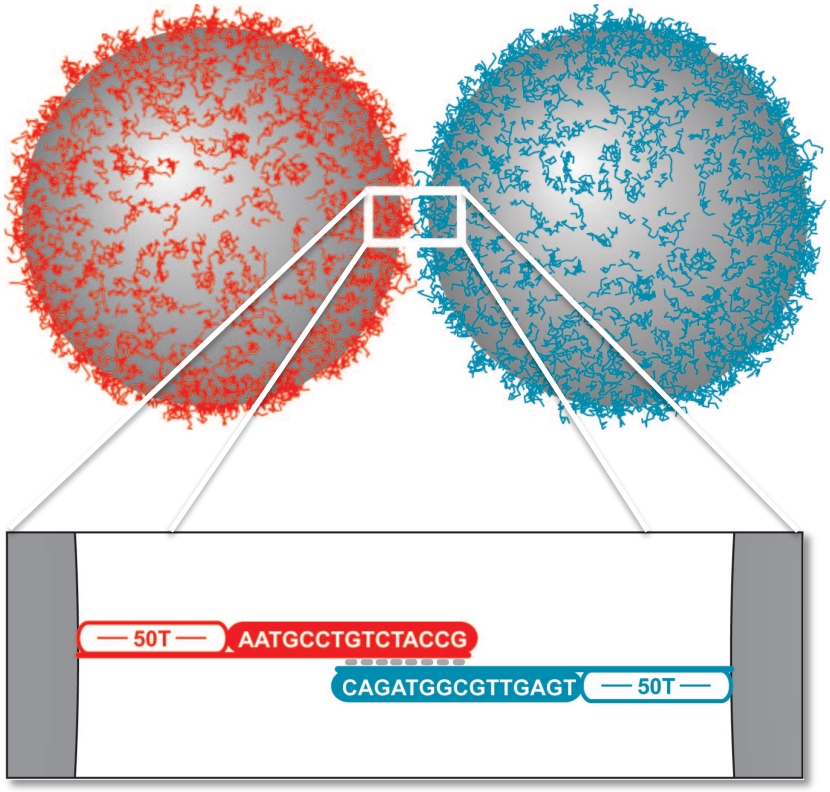


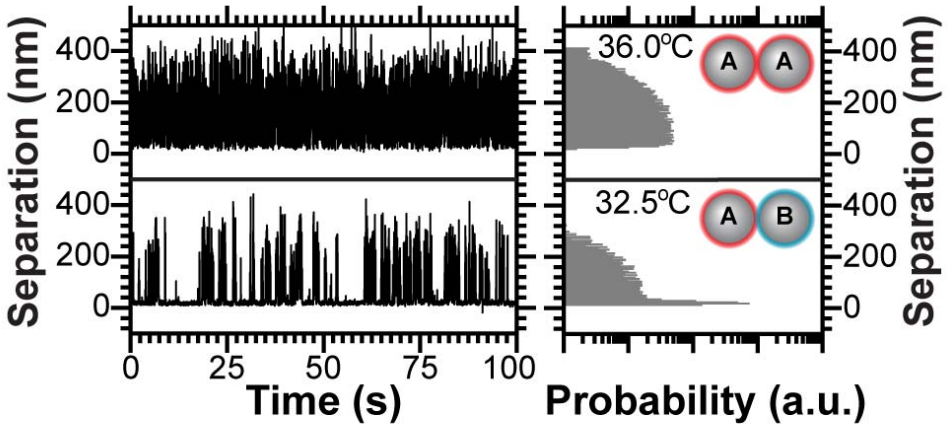


***particles bind and unbind as DNA bridges form and rupture**

Measuring DNA-induced interactions







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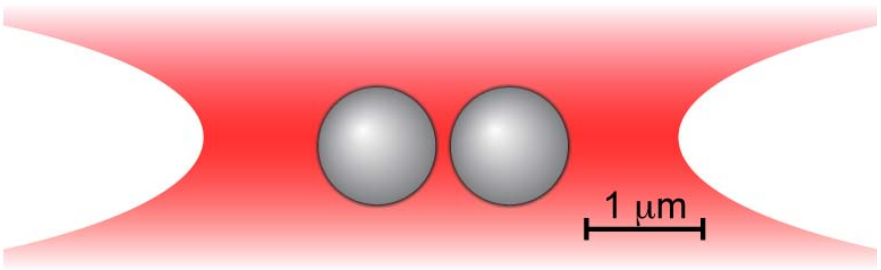
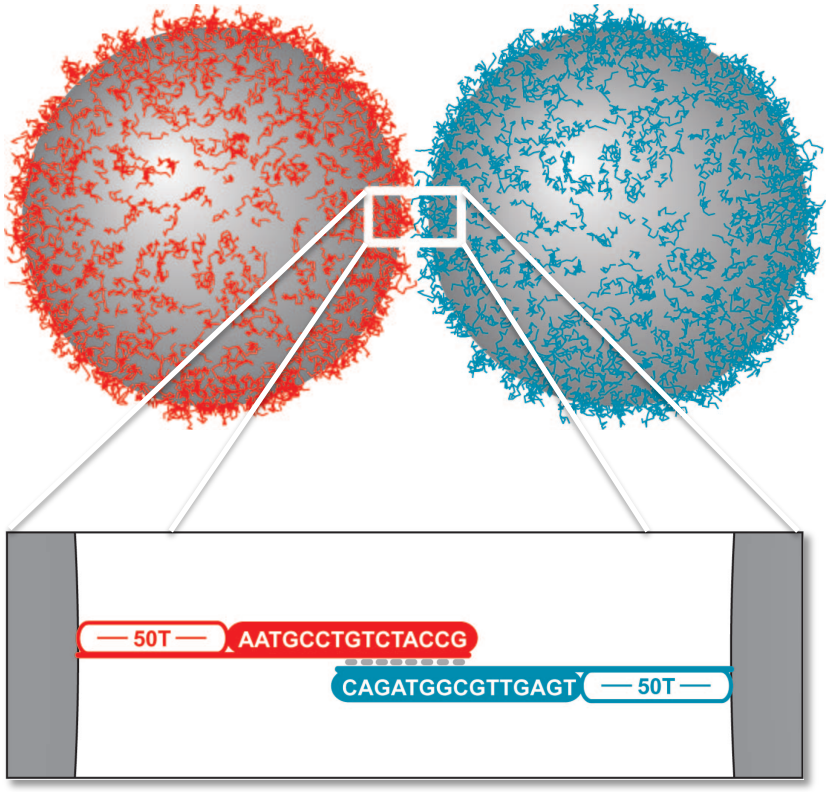
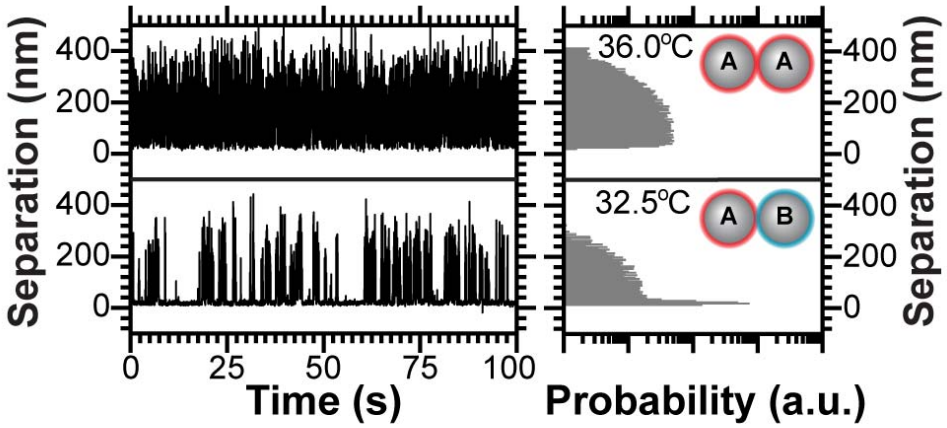
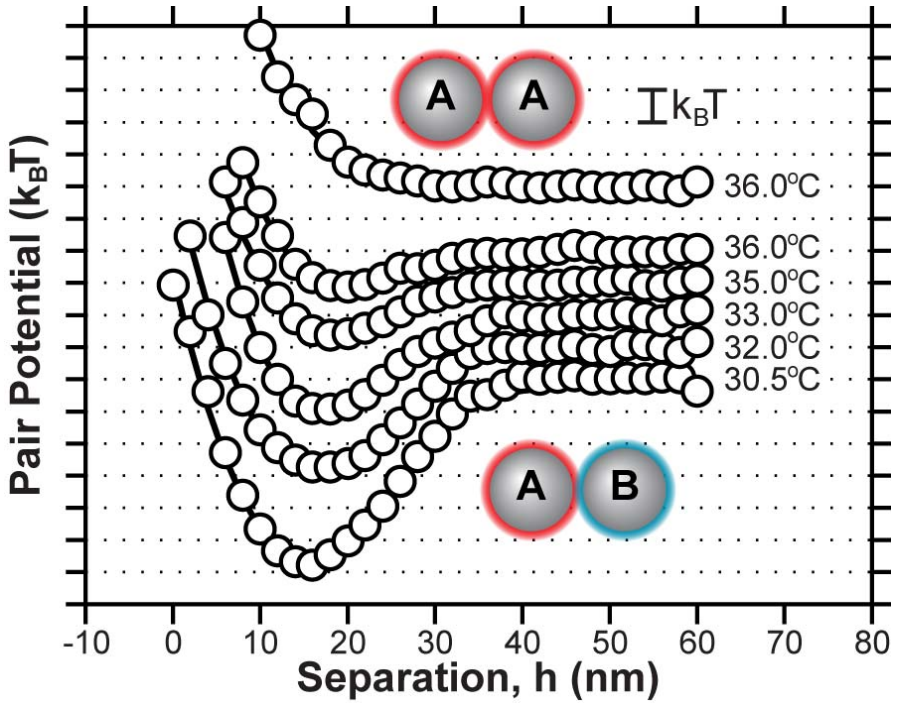


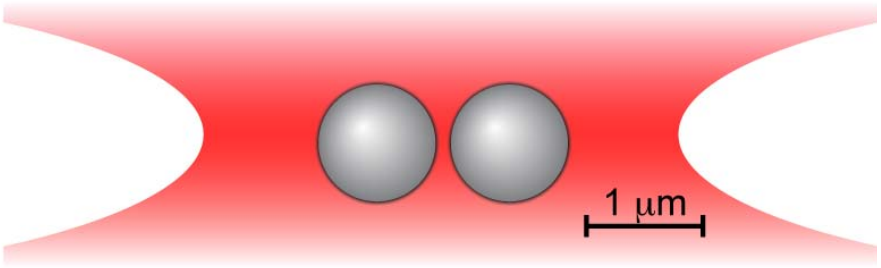






Rogers W.B., Crocker J.C., *PNAS*. 108, 15687-15692 (2011)

Measuring DNA-induced interactions

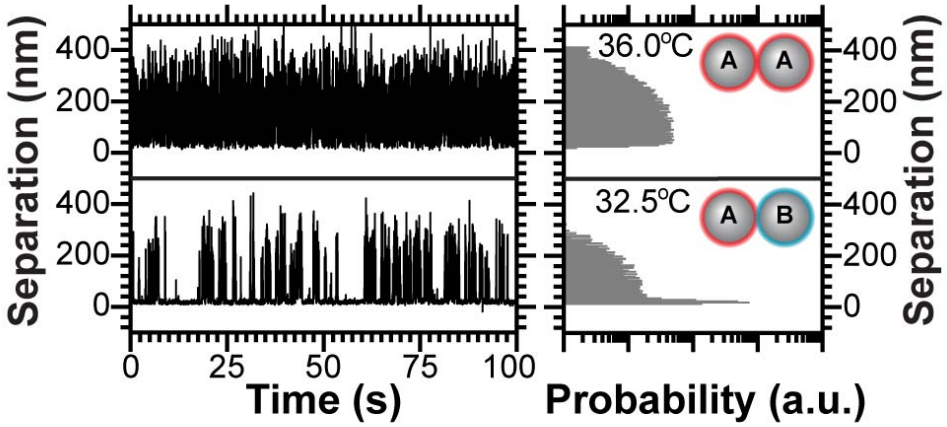


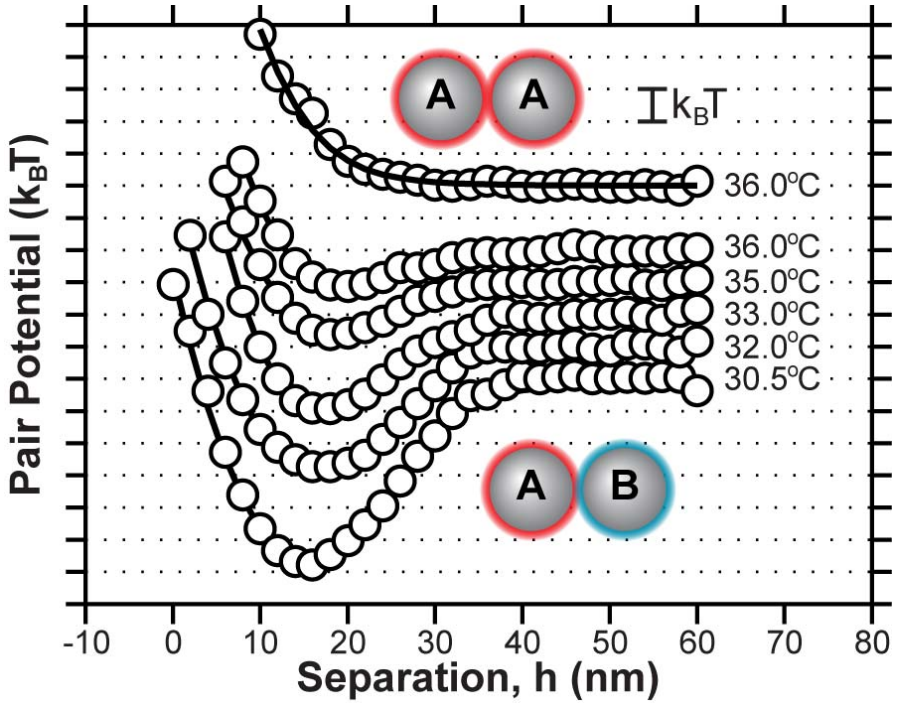
Attraction:

'DNA handshaking'

Repulsion:

DNA brush compression





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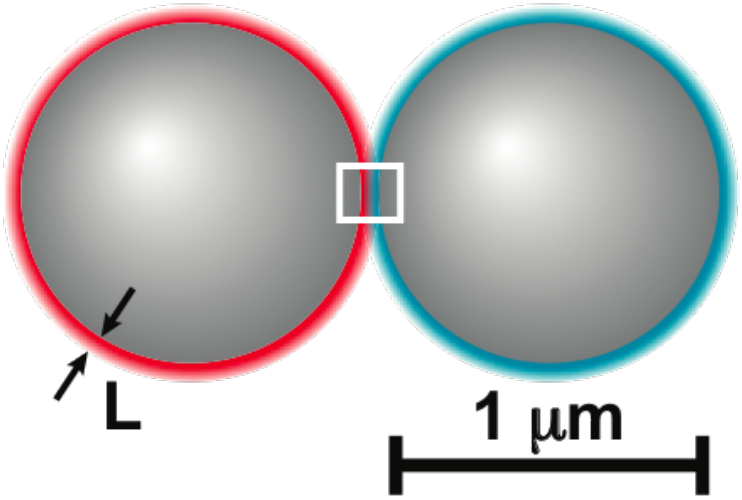
Handshaking attraction

The system:



Attraction:

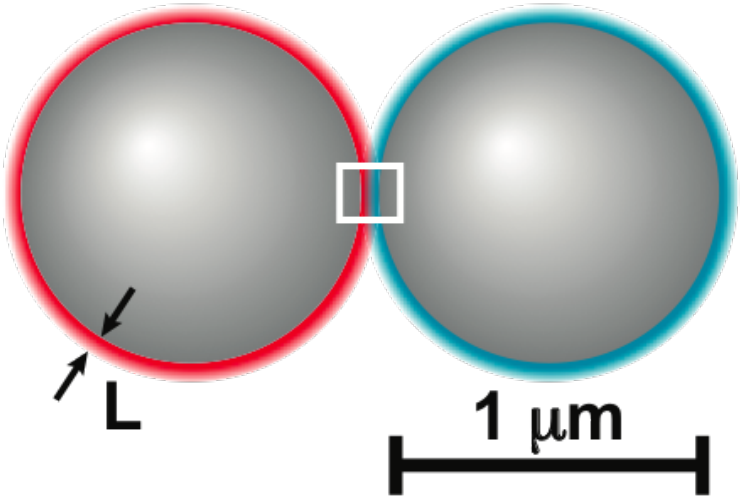
$$\frac{\Delta F_a}{k_B T} = -\ln(g(r))$$

The observed g(r) is just the Boltzmann distribution of the pair interaction

The $\Delta F=0$ reference state is the unbridged configuration

Handshaking attraction

The system:



Attraction:

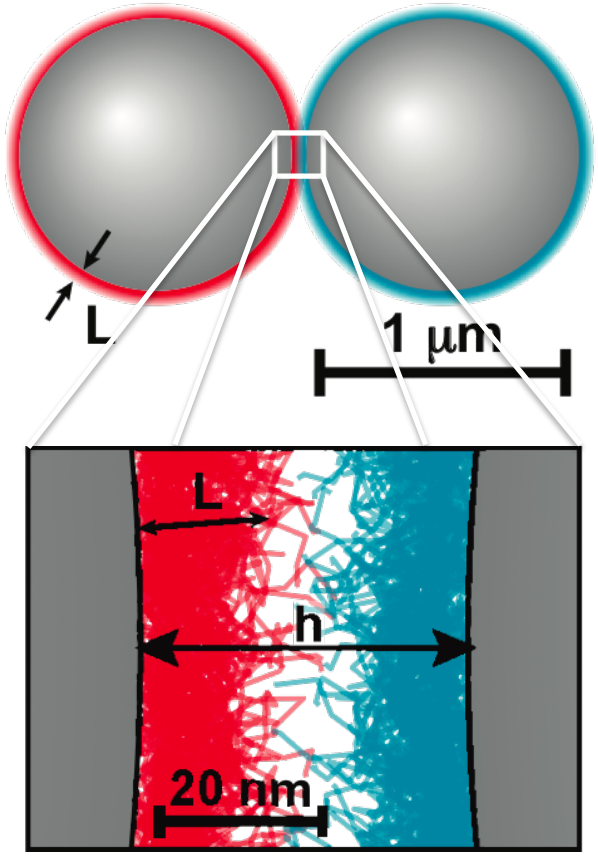
$$\frac{\Delta F_a(h)}{k_B T} = \ln(p_0(h))$$

The observed g(r) is just the Boltzmann distribution of the pair interaction

The $\Delta F=0$ reference state is the unbridged configuration

The observed g(r) is inversely proportional to the probability there are no bridges, at each separation.

Handshaking attraction



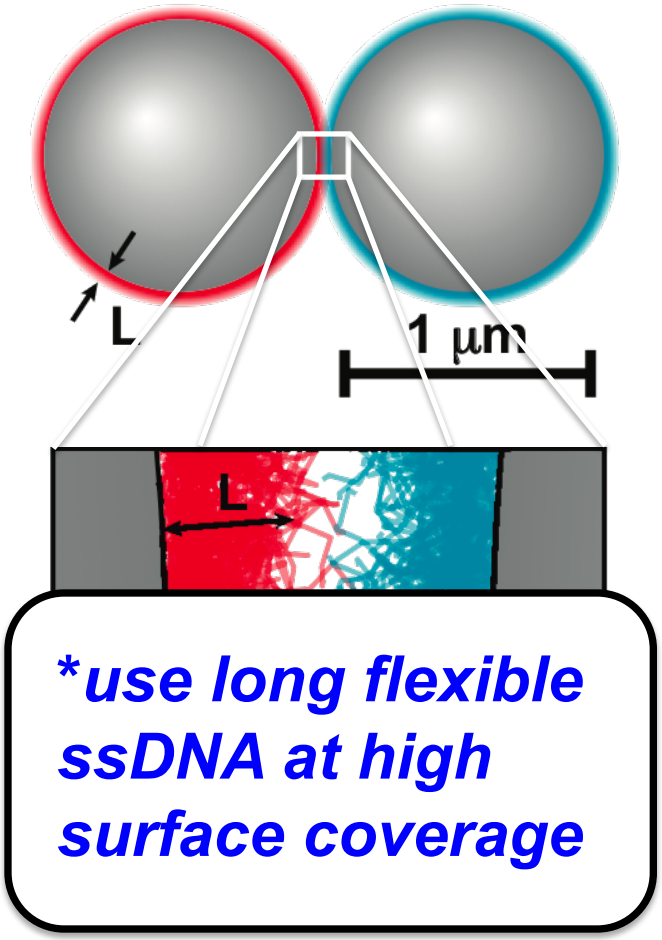
$$\frac{\Delta F_a(h)}{k_B T} = \ln(p_0(h))$$

Complexities

- ***Spatial nonuniformity***
- ***Vectorial nature of hybridization***
- ***Force sensitivity***
- ***Stochasticity***

1. Biancaniello PL, Kim AJ, Crocker JC (2005) *PRL* 94:058302, 2. Licata NA, Tkachenko AV (2006) *PRE* 74:041408
3. Dreyfus R, *et al.* (2009) *PRL* 102:048301, 4. Leunissen ME, Frenkel D (2011) *Journal of Chemical Physics* 134:084702

Handshaking attraction



*use long flexible ssDNA at high surface coverage

$$\frac{\Delta F_a(h)}{k_B T} = \ln(p_0(h))$$

Complexities

- *Spatial nonuniformity*
- ~~*Vectorial nature of hybridization*~~
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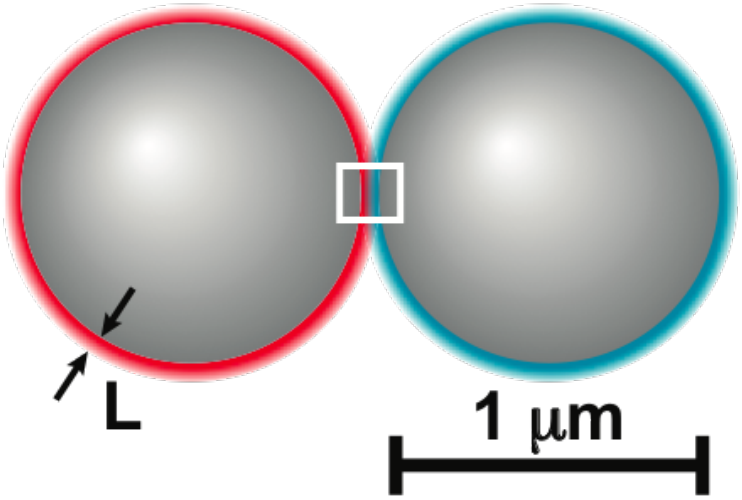
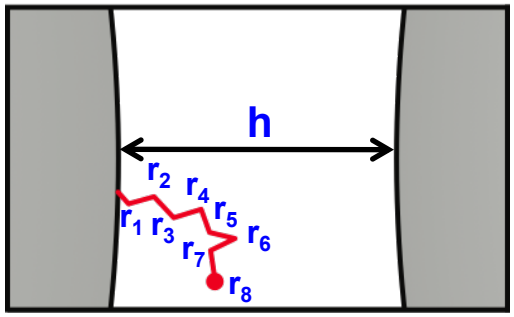


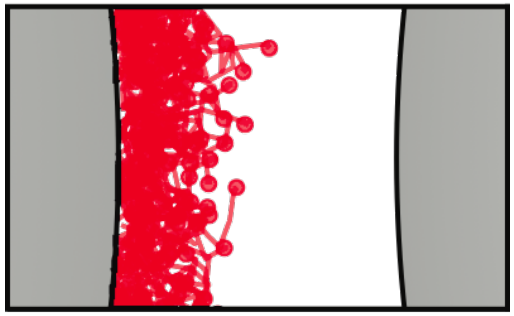
Step 1



Model as tethered Gaussian coil

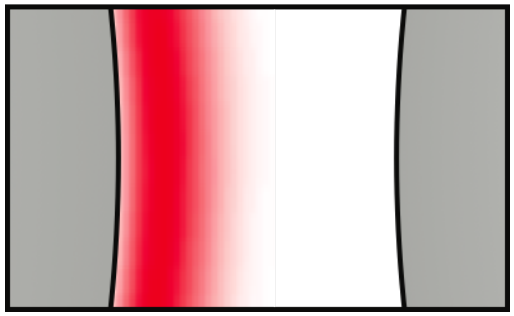
$$\sum_i \left[\left(\vec{r}_p - \vec{r}_i \right)^2 \le a^2 \right] = 0$$

Step 2



Generate >10^6 equilibrium configurations

Step 3

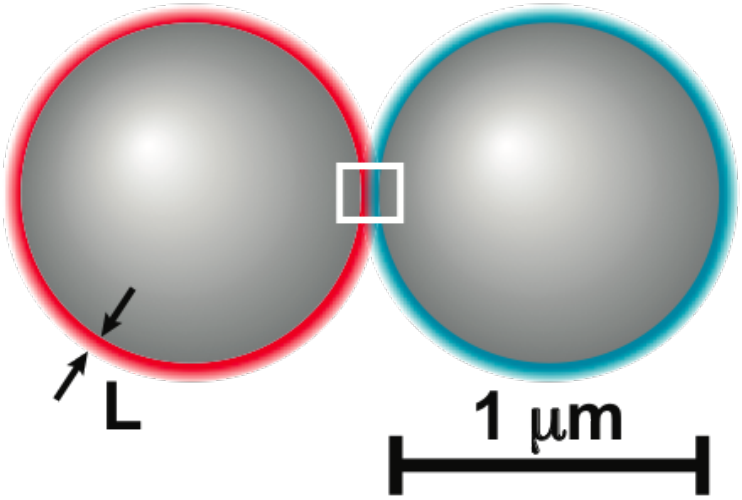


Construct 3D conc. field, C_A^0

$$N_{Av} \int C_A^0(\vec{r}) d^3\vec{r} = N_A$$

Handshaking attraction

The system:



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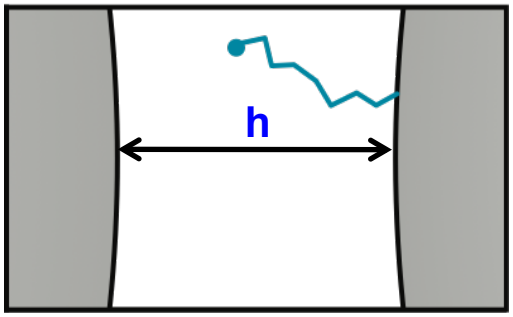

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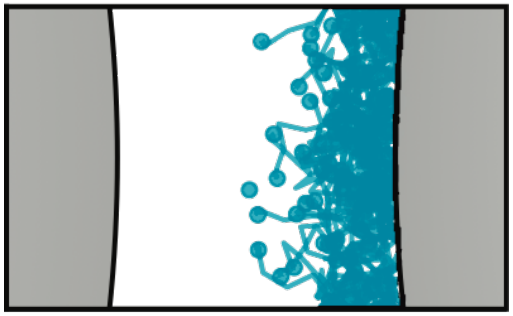

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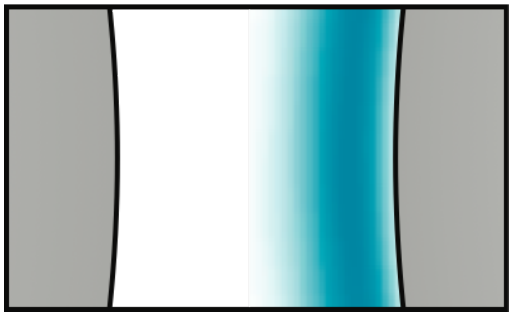
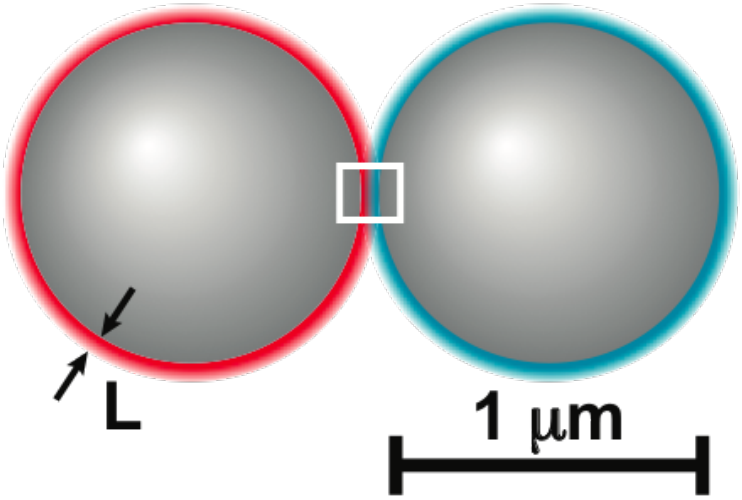


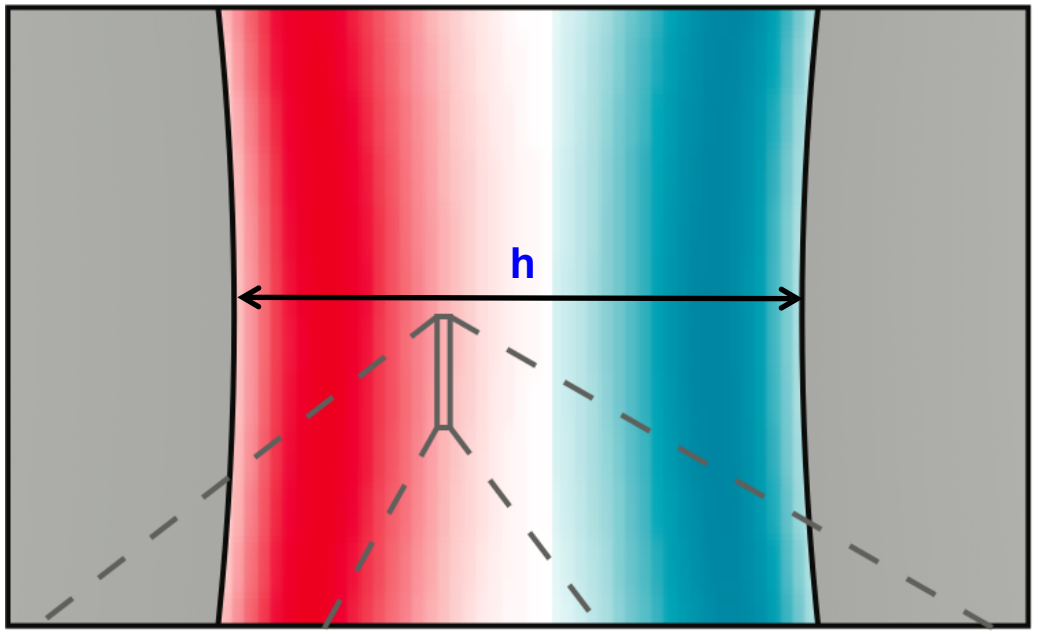
Construct 3D conc. field, C_B^0

$$N_{Av} \int C_B^0(\vec{r}) d^3\vec{r} = N_B$$

Local Chemical Equilibrium (LCE)

The system:





Attraction:

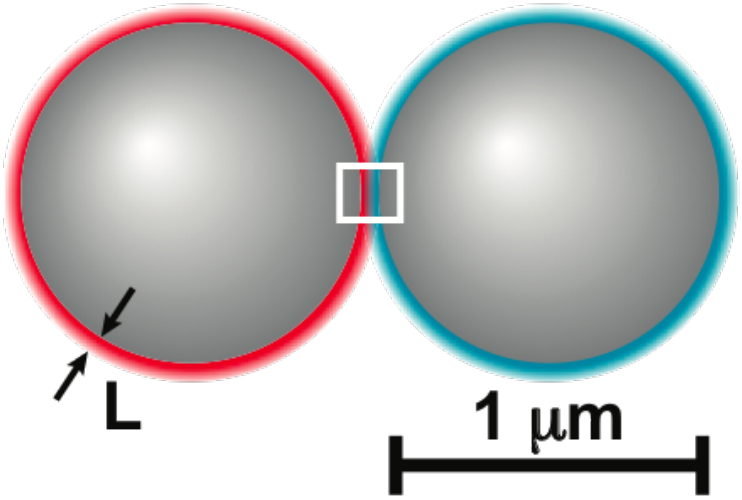
$$\frac{\Delta F_a}{k_B T} = \ln(p_0)$$

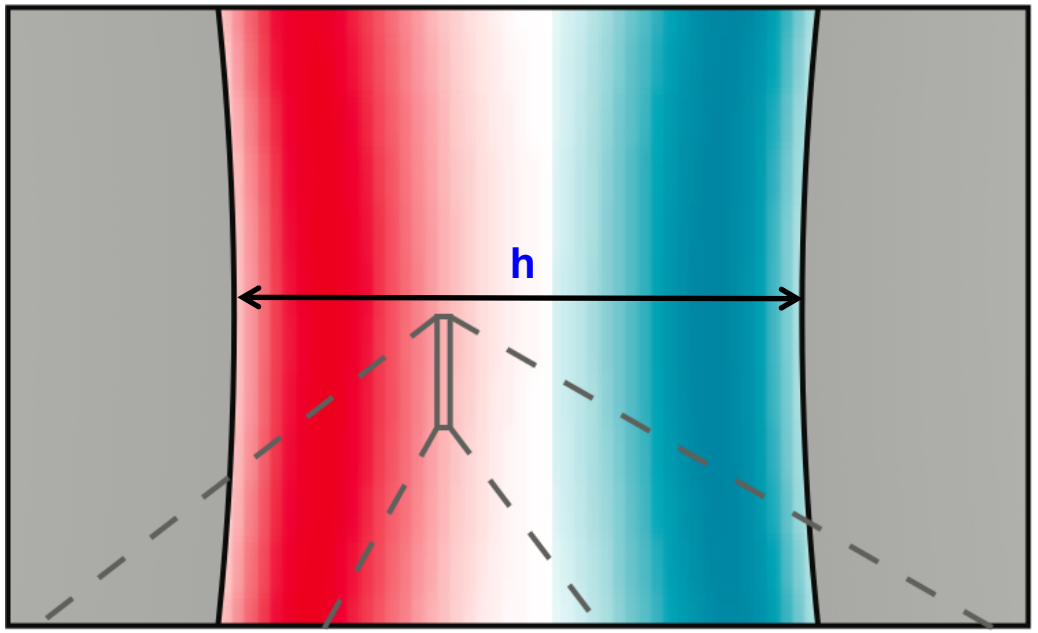
$$A + B \leftrightarrow AB$$

$$C_{AB} = \frac{C_A C_B}{C_0} \exp \frac{-\Delta G_{hyb}}{RT}$$

Local Chemical Equilibrium (LCE)

The system:





Attraction:

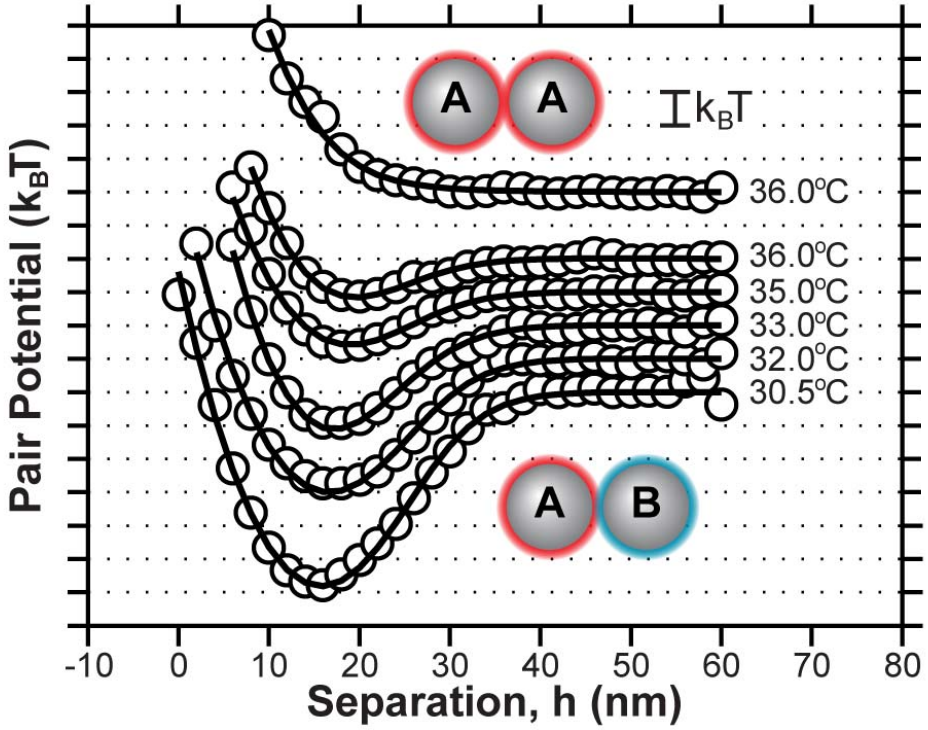
$$\frac{\Delta F_a}{k_B T} = \ln(p_0)$$

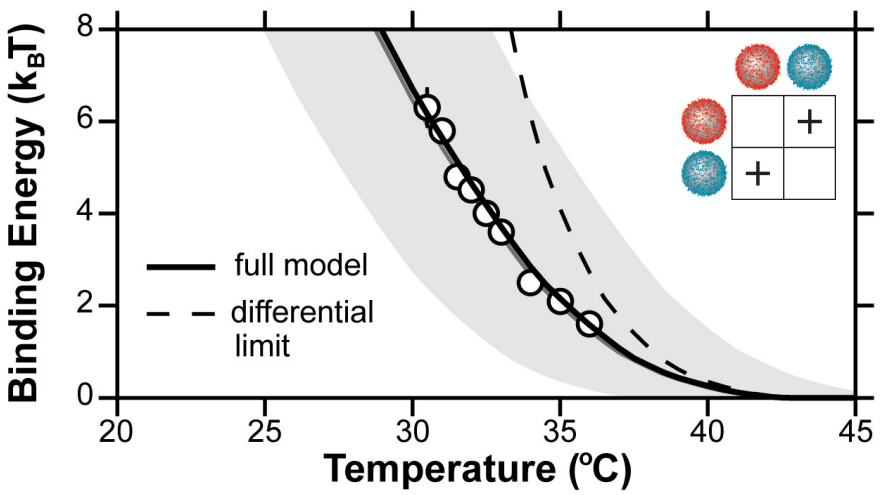
$$A + B \leftrightarrow AB$$

$$C_{AB} \rightarrow N_{AB}(box) \rightarrow p_0(box)$$

$$p_0 = \prod_i p_0(box_i)$$

Model validation





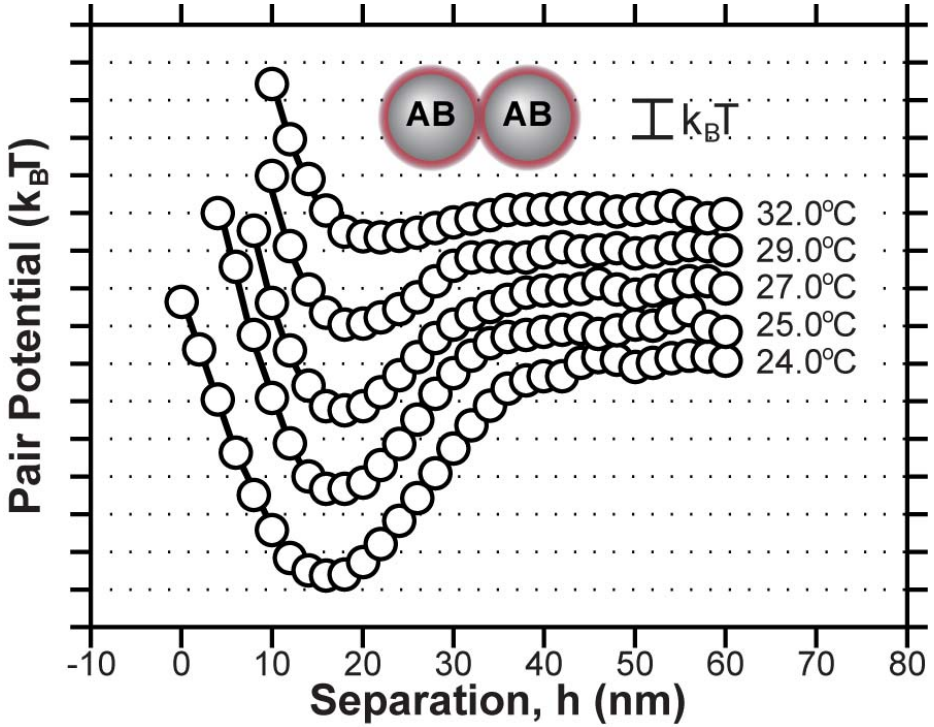
***Gray band shows predictions using NN model +/- uncertainty**

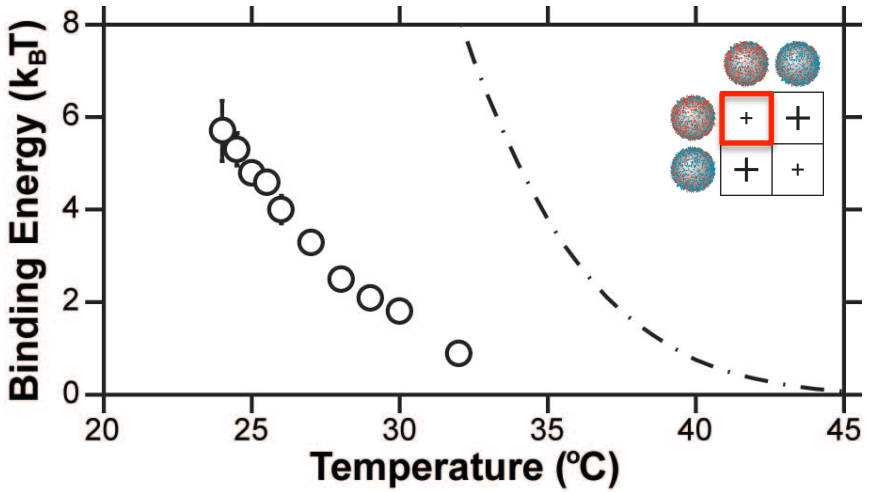
quantitative, without empirical corrections

Rogers W.B., Crocker J.C., *PNAS*. 108, 15687-15692 (2011)

Mixed DNA interactions

***Make same measurements for particles with a 50:50 mixture of two complementary DNA strands on their surface**



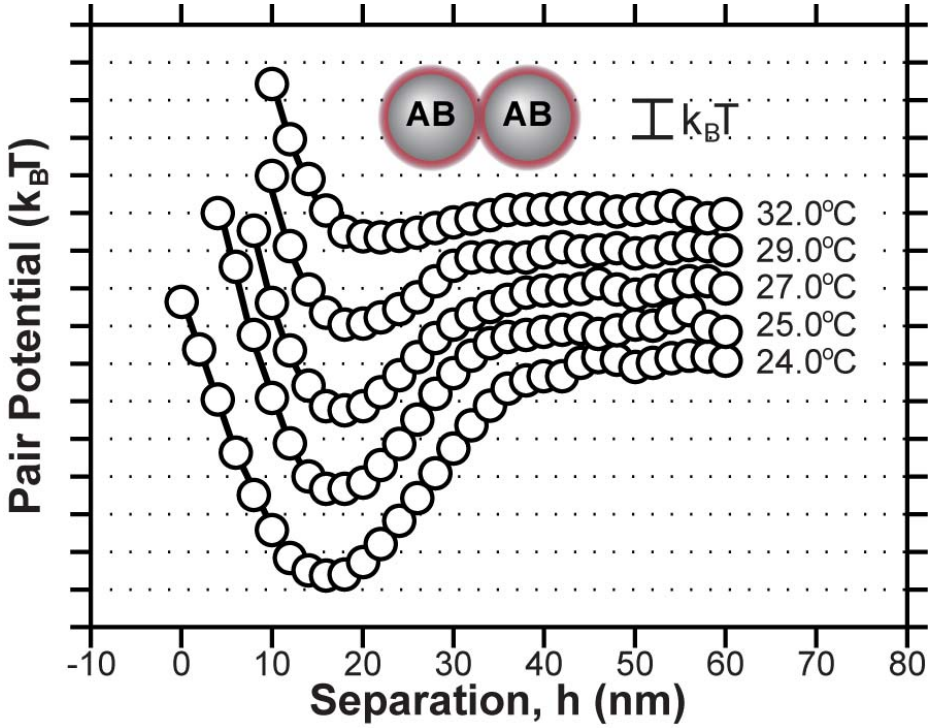


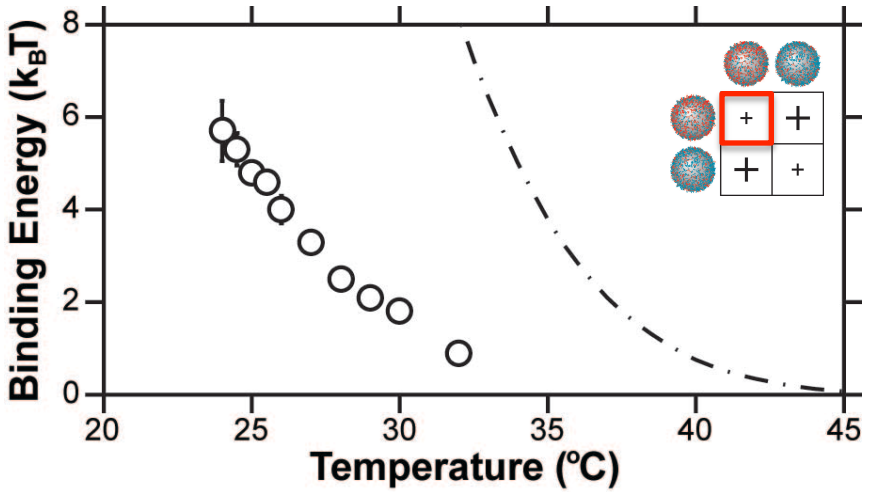
***Naive expectation is significantly off in magnitude and temp. dep.**

Rogers W.B., Crocker J.C., *PNAS*. 108, 15687-15692 (2011)

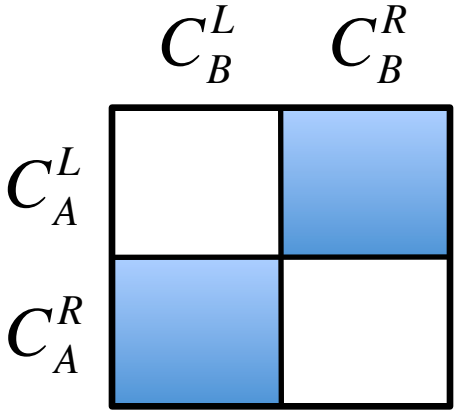
Looping vs. bridging

***Make same measurements for particles with a 50:50 mixture of two complementary DNA strands on their surface**





Complementary DNAs on a single particle surface can hybridize to form loops

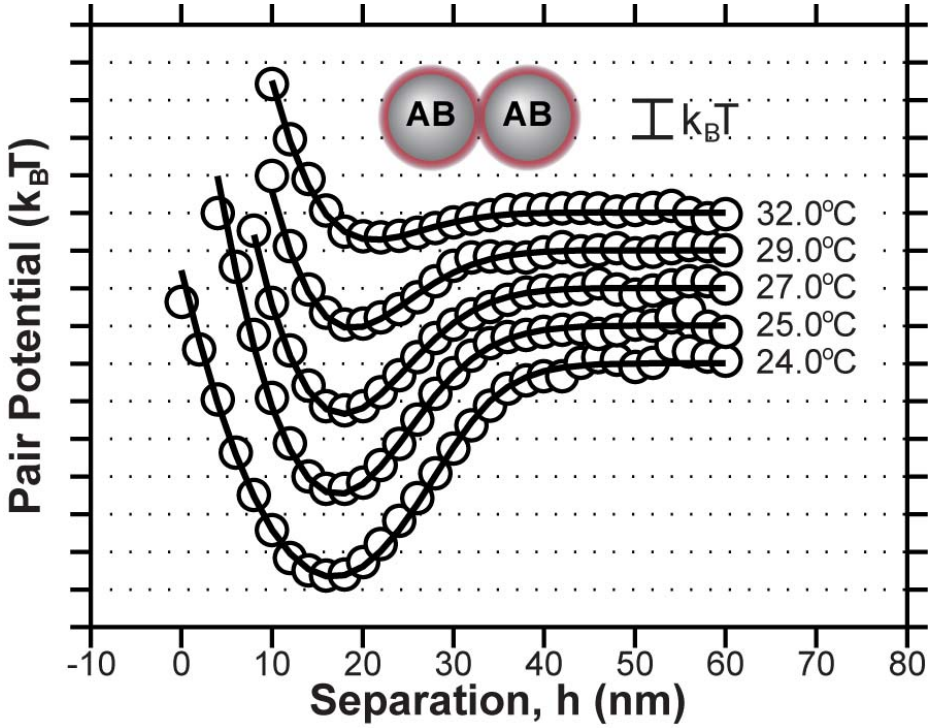


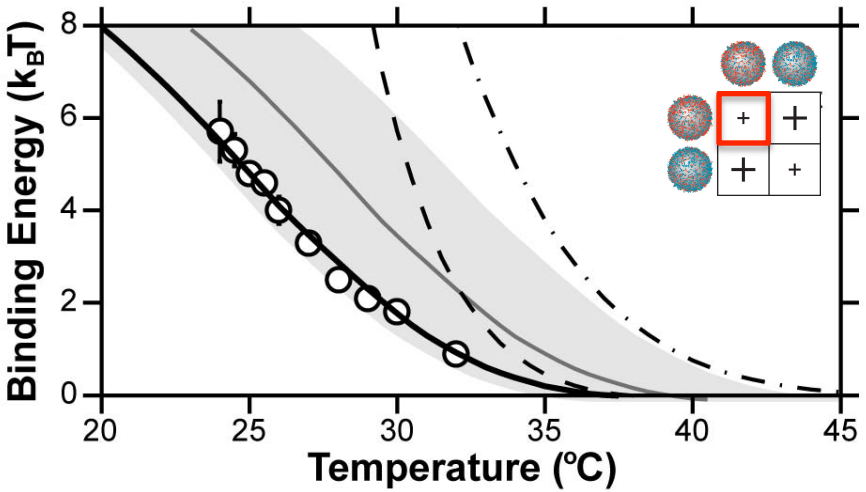
$$C_i = C_i^L + C_i^R$$

$$f_{bridge} = \frac{C_A^L C_B^R + C_A^R C_B^L}{C_A C_B}$$

Model validation

***Make same measurements for particles with a 50:50 mixture of two complementary DNA strands on their surface**



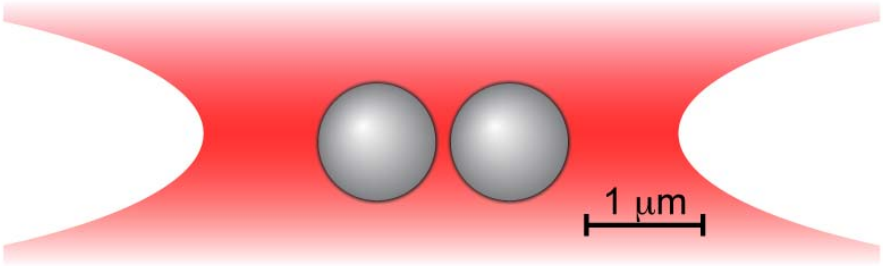


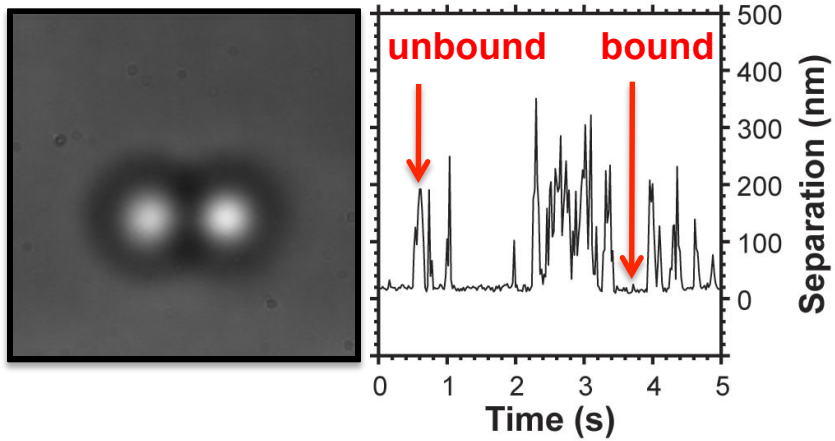
***Gray band shows predictions using NN model +/- uncertainty**

quantitative, without empirical corrections

Rogers W.B., Crocker J.C., *PNAS*. 108, 15687-15692 (2011)

Dynamics of adhesion



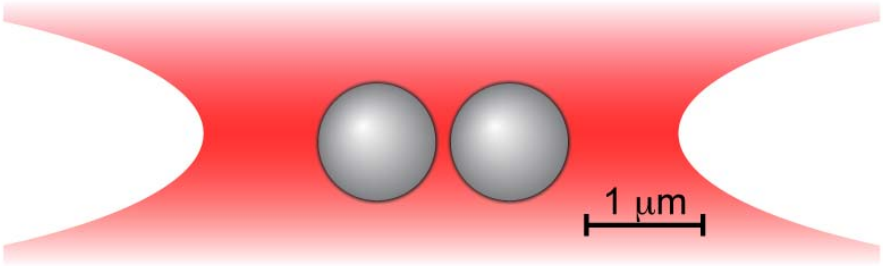


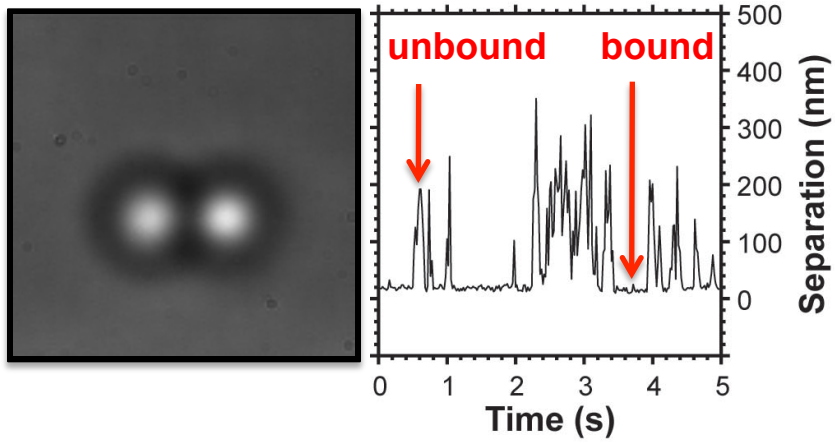
Model trajectory using Hidden Markov Model and Viterbi algorithm to determine most likely state trajectory

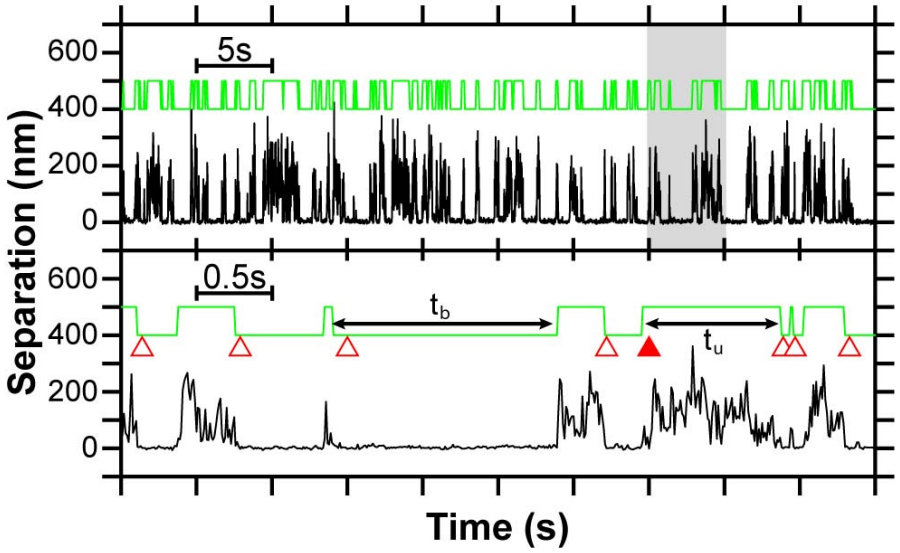
Emission distributions: $P_b(h), P_u(h)$

Transition probability: $k_u \Delta t, k_b \Delta t$

Dynamics of adhesion







△ **stick** ▲ **bounce**

***Model trajectory using Hidden Markov Model and Viterbi algorithm to determine most likely state trajectory**

Emission distributions: $P_b(h), P_u(h)$

Transition probability: $k_u \Delta t, k_b \Delta t$

$$Da = \frac{k_f N_b^2}{k_d} = \frac{\text{reaction rate}}{\text{diffusion rate}}$$

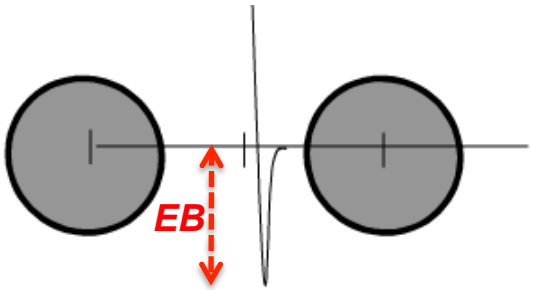
$$P_{bounce} = \frac{k_d^{well}}{N_b^2 k_f + k_d^{well}} \qquad Da = \frac{1}{P_{bounce}} - 1$$

Rogers W.B., Crocker J.C. *In preparation*

Dynamics of adhesion

Diffusion-limited (Da ~ 50)

***particles diffusing in an effective potential**

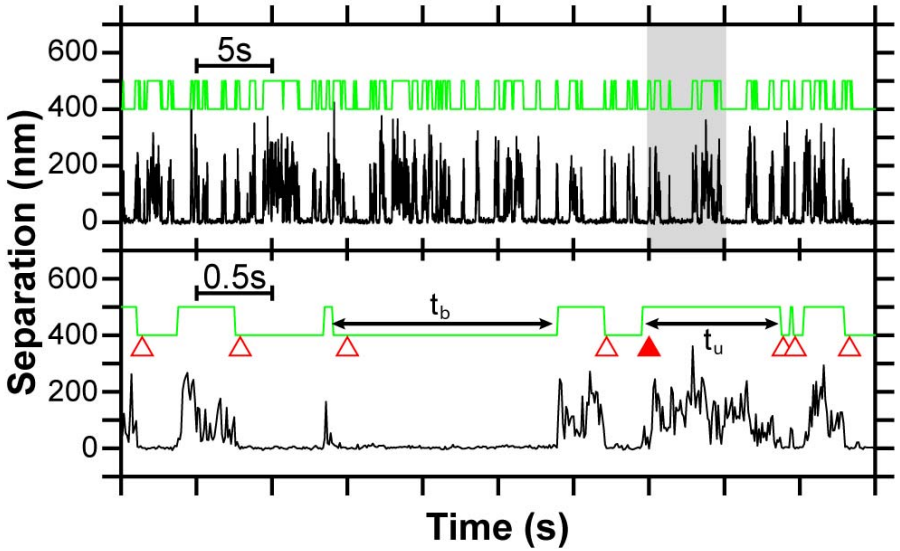


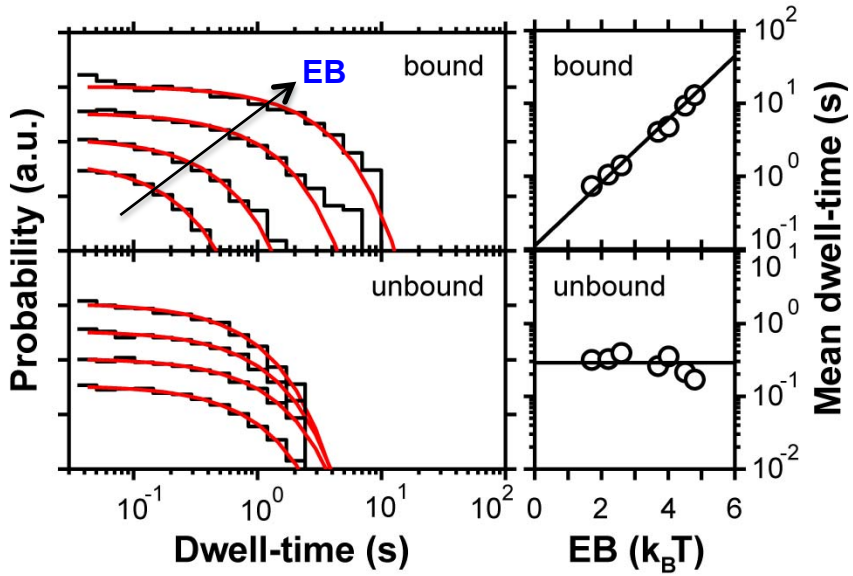
***exponential dwell-time distributions**

bound: $\langle t_b \rangle = \frac{1}{k_d^{well}} \exp \frac{EB}{k_B T}$

unbound: $\langle t_u \rangle = \frac{1}{k_d^{trap}}$

$k_d^{well} \sim 0.01s \qquad k_d^{trap} \sim 0.25s$





Rogers W.B., Crocker J.C. *In preparation*

Dynamics of adhesion

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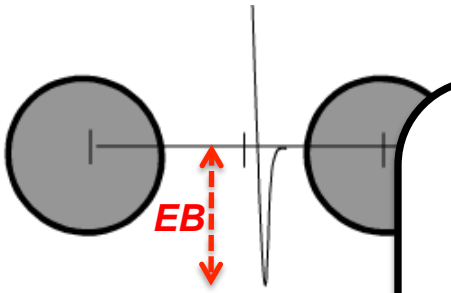


**exponential dwell-time*

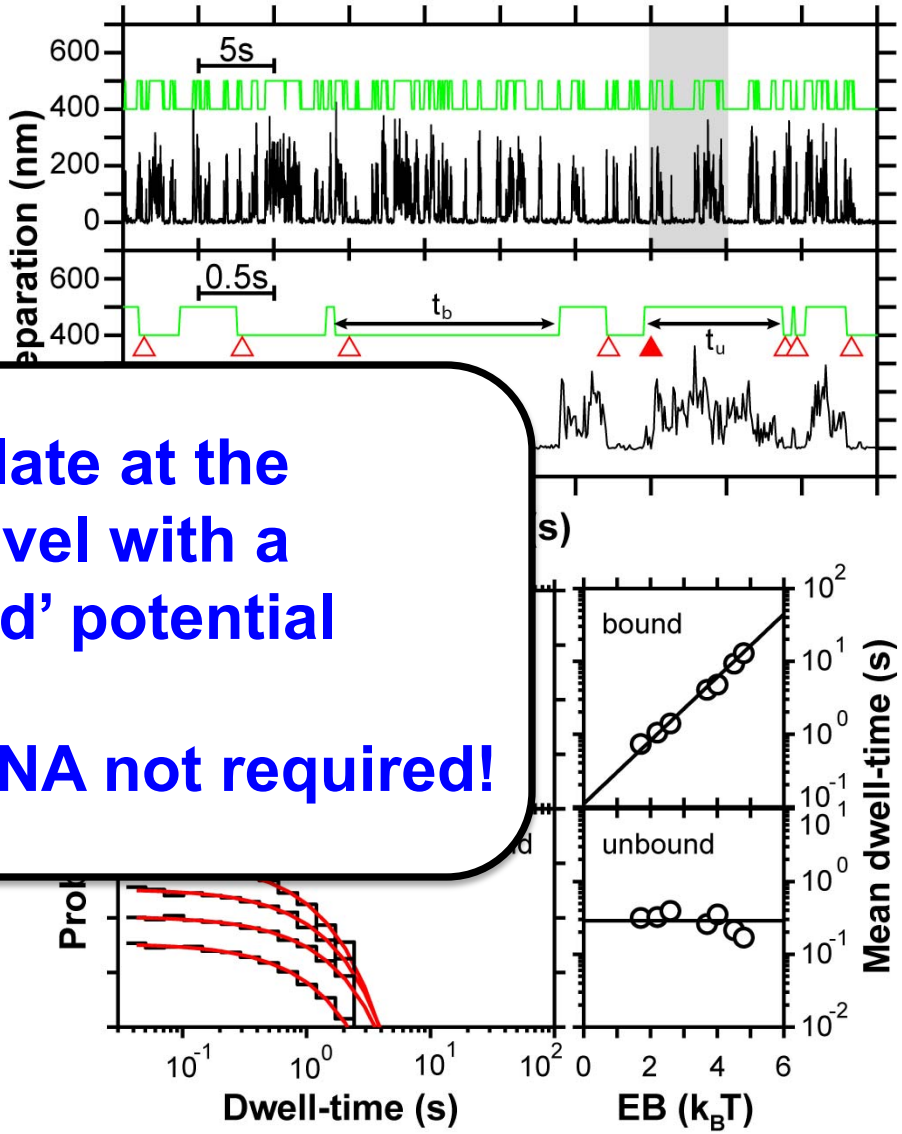
bound: $\langle t_b \rangle = \frac{1}{k_d^{well}} \exp$

unbound: $\langle t_u \rangle = \frac{1}{k_d^{trap}}$

$k_d^{well} \sim 0.01s \qquad k_d^{trap} \sim 0.25s$

Can simulate at the particle level with a 'mean field' potential

Explicit DNA not required!



Rogers W.B., Crocker J.C. *In preparation*

Outline....

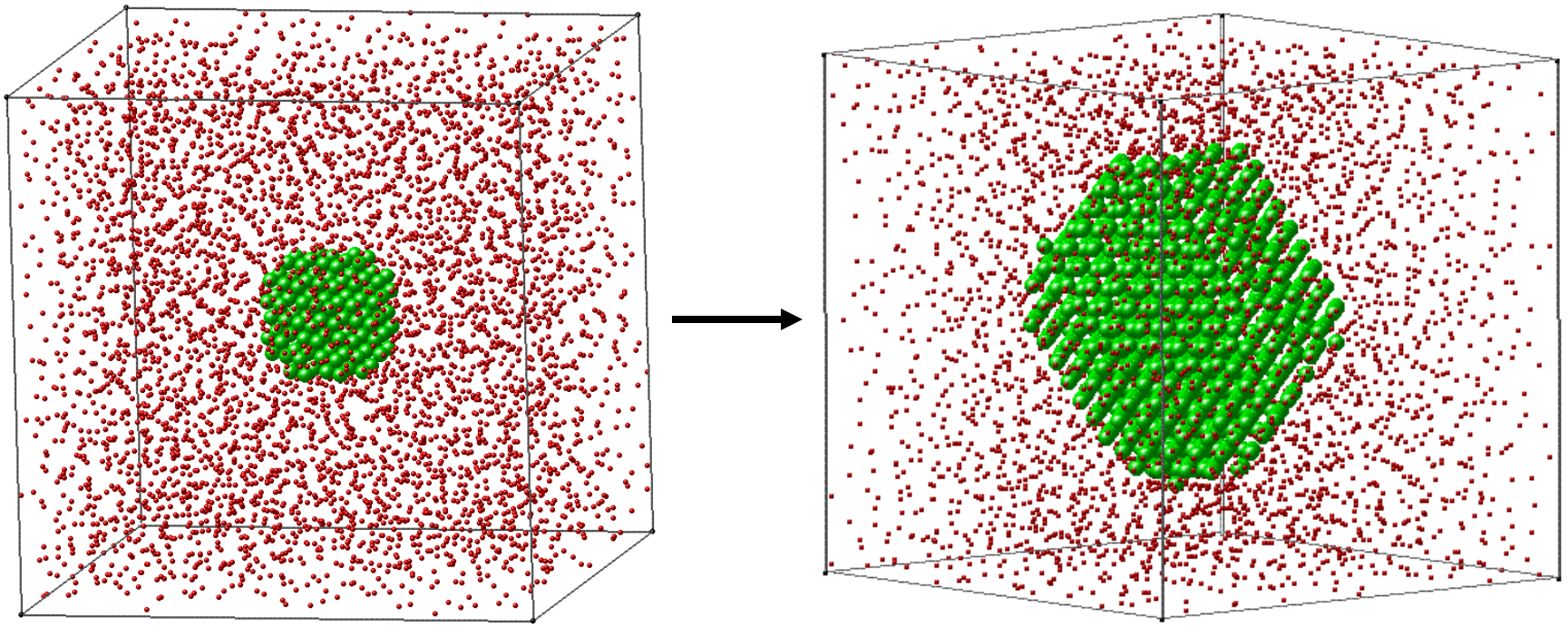
Ben Rogers

1. DNA interactions and dynamics
2. Simple crystals and real space crystallography
3. New phases and transformations

Marie Ung

Start simple: a ‘one component’ system.

Simulate with realistic potential



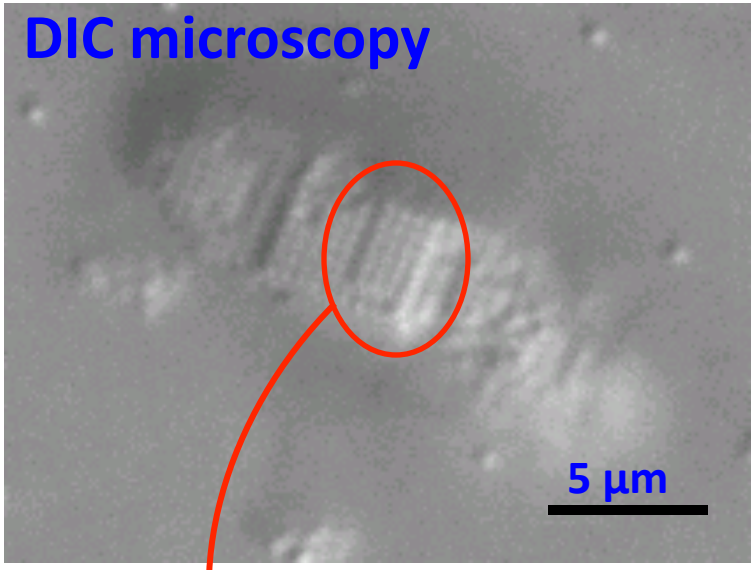
MMC and Brownian Dynamics both show rapid growth and homogeneous nucleation for 400 nm particles, form is RHCP

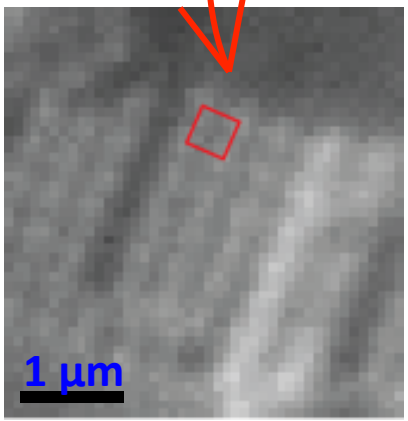
Talid Sinno

Scarlett, Crocker, Sinno, *J Chem Phys*. 132, 234705 (2010)

One component ‘check’

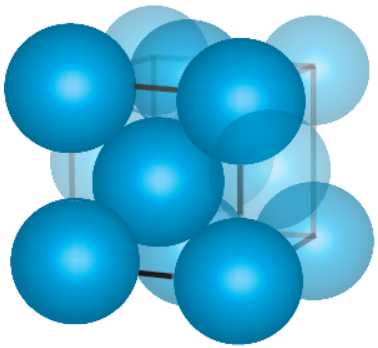
400 nm, ~5000 DNAs/bead



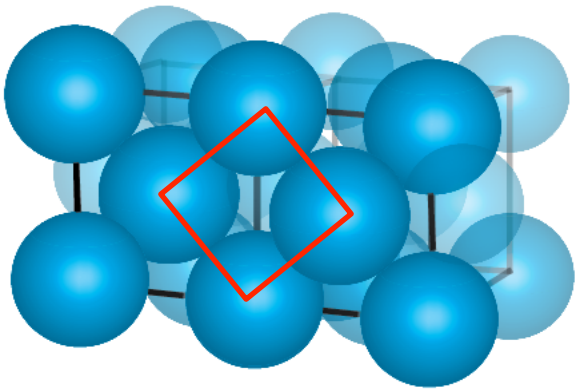


Benchtop thermal quenching
Passive cooling in water bath
~ 2°C/hr

- Colloidal xtals form in minutes
- Nucleation & growth kinetics similar to depletion interaction

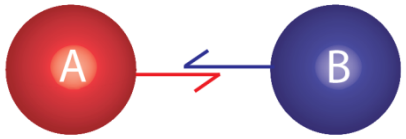


Face-Centered Cubic
(1 0 0)

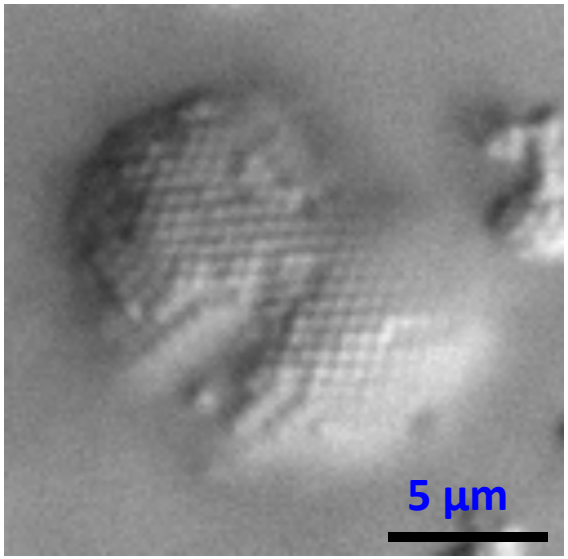


But can we make binary alloy crystals?

Binary crystals are easy

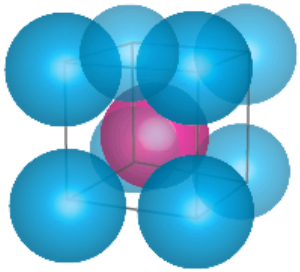


400 nm, ~5000 DNAs/bead
DIC microscopy

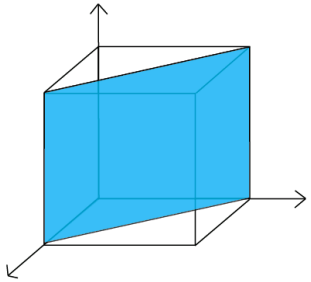


- **Binary xtals can form in minutes**

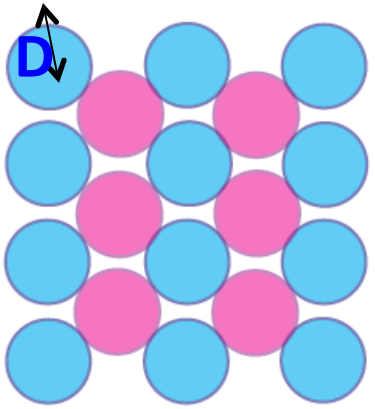
Simple binary crystals are bcc

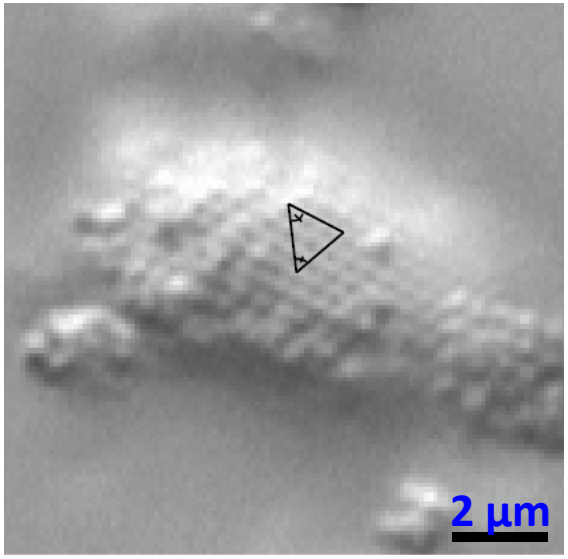


Body-Centered Cubic or CsCl

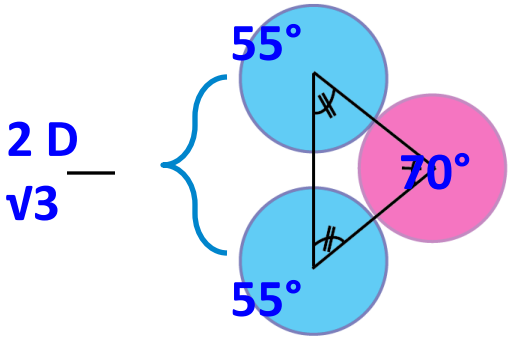


(1 1 0) plane



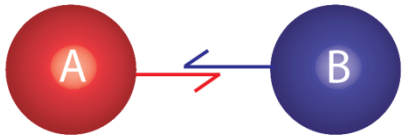


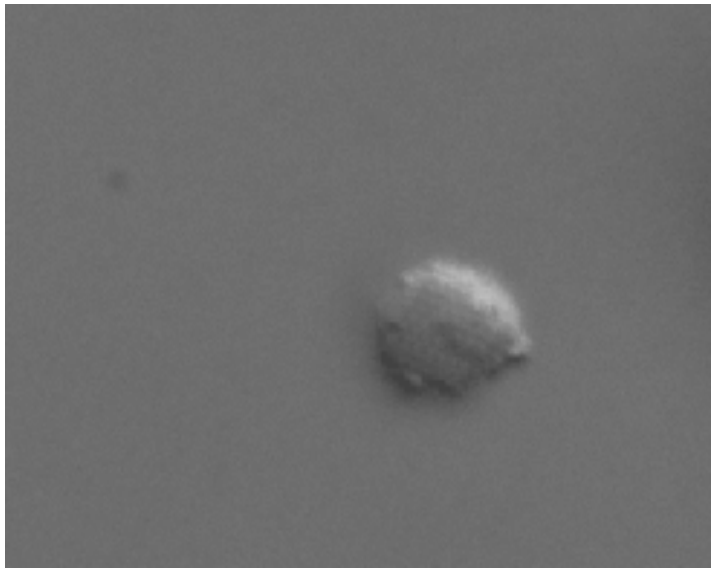
Indicates a (1 1 0) face of BCC

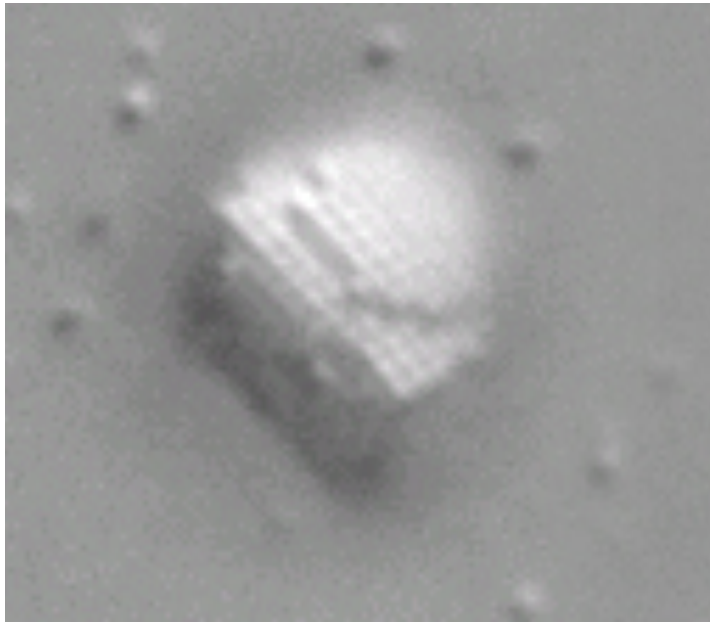


Binary crystals are easy

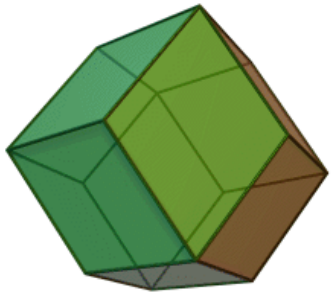
400 nm, ~5000 DNAs/bead
DIC microscopy







Predominant 110 facets give
Rhombic Dodecahedron

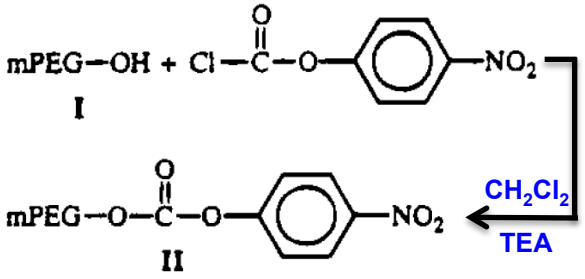


Compositional (AB) order not seen....

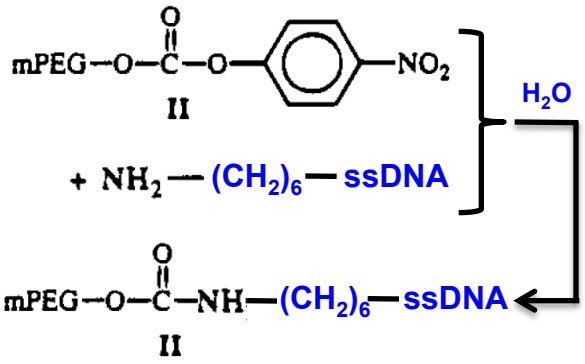
Can we do real space crystallography with confocal?

DNA labeling: physical grafting

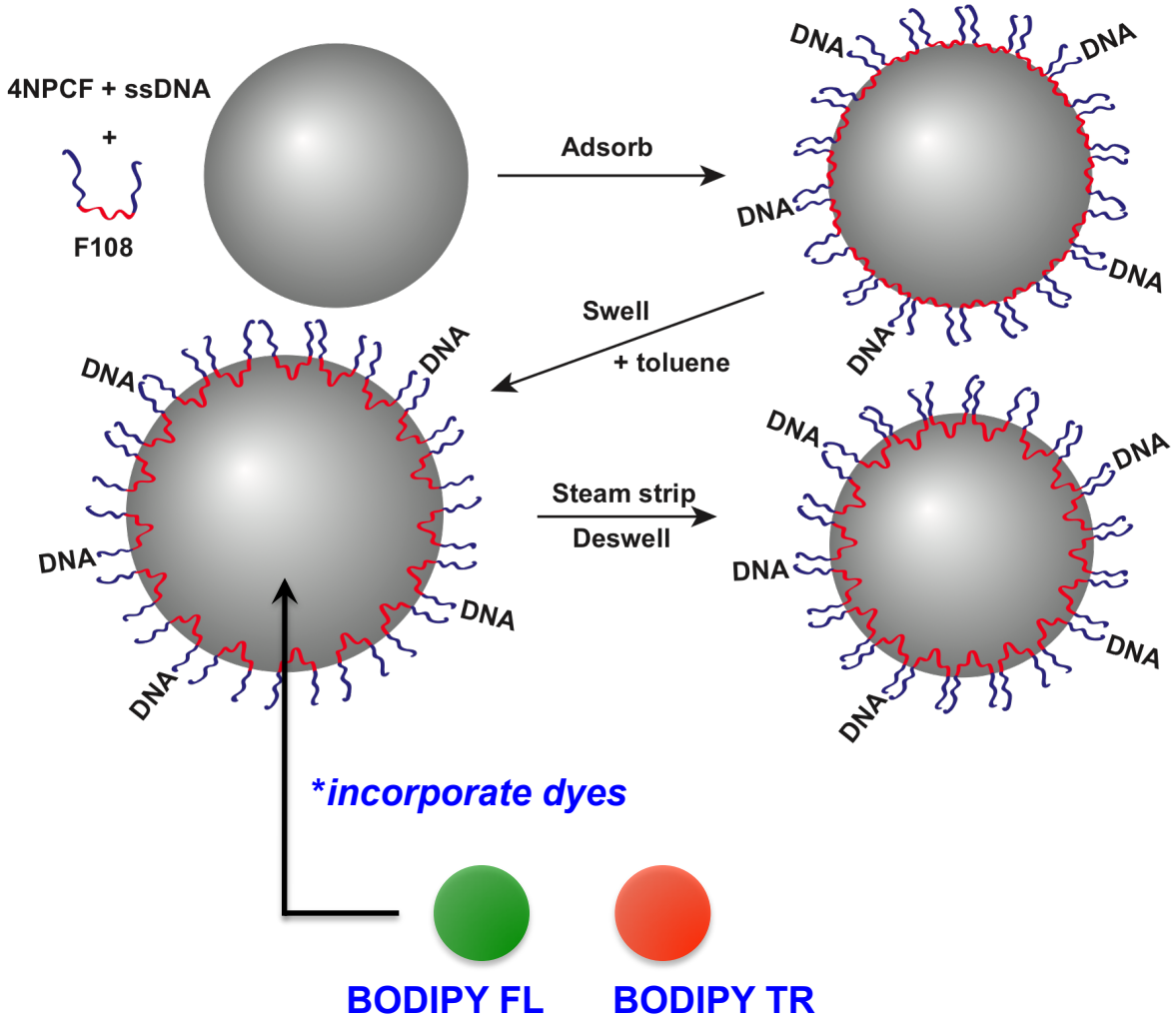
i. activation



ii. reaction

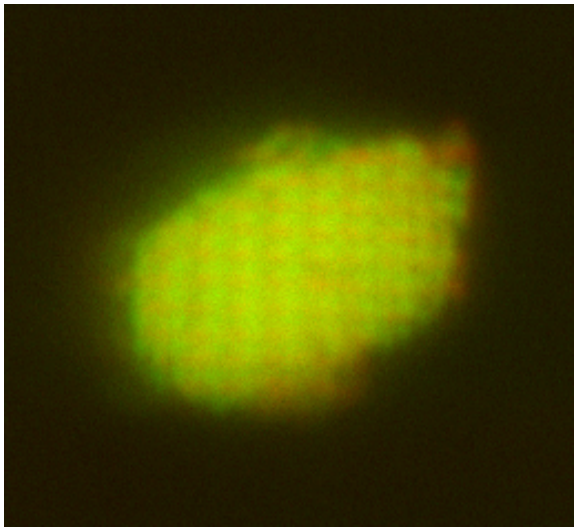


*Adapted from:
Monfardini, C., Schiavon, O., Caliceti, P., Morpurgo, M., Harris, J.M., Veronese, F.M. *Bioconjugate Chem*. 6, 62-69 (1995)



*Adapted from: Kim, A.J., Manoharan, V.N., Crocker, J.C. *JACS*. 127, 1592-1593 (2005)

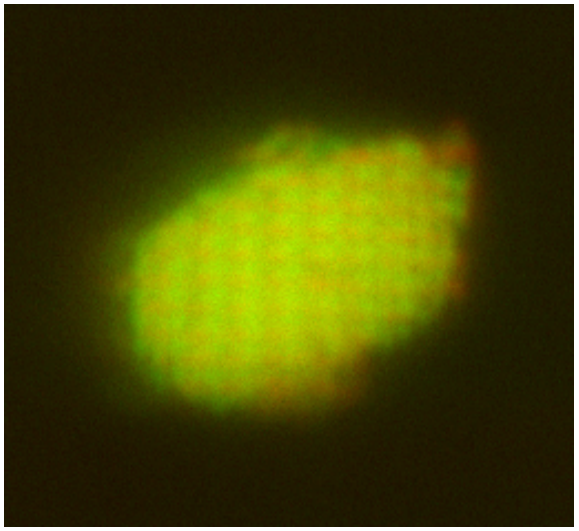
Confocal imaging

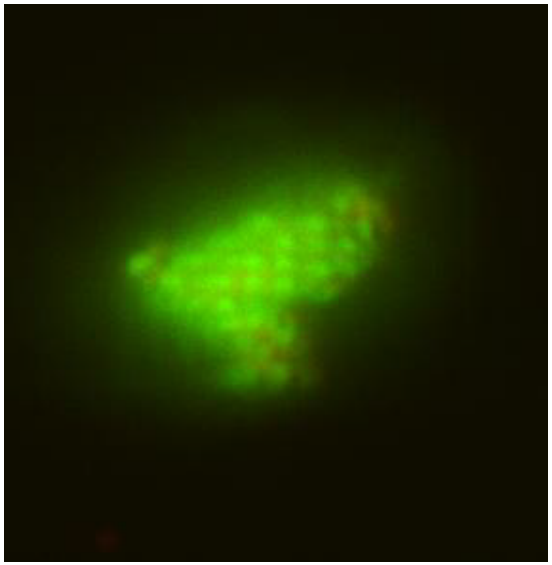


In-plane lattice spacing matches CsCl 110 plane

Can detect vacancies in the interior.

Confocal imaging





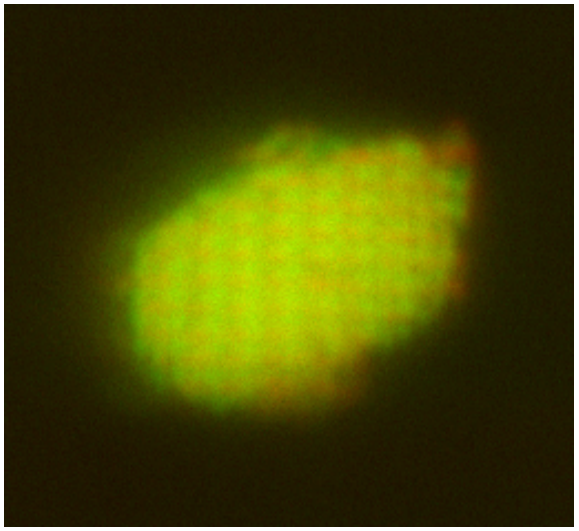
In-plane lattice spacing matches CsCl 110 plane

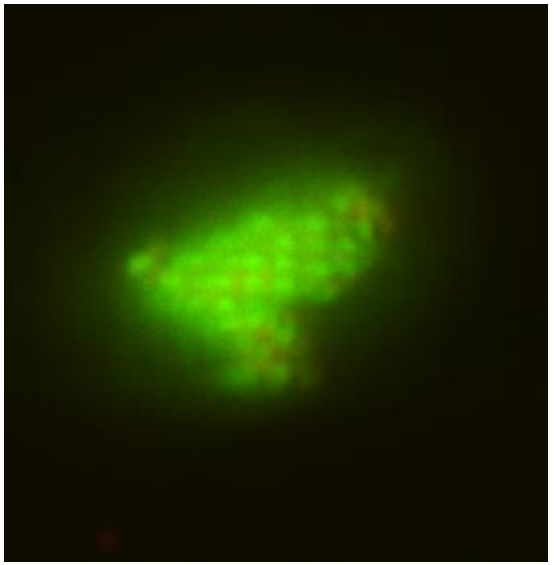
Can detect vacancies in the interior.

z-direction is normal to 110: xtal settles onto a facet

‘columns’ of intensity make Imaging easier

Confocal imaging





NOTE:

--particles are NOT index-matched.

--only works because particles are small -> low scattering

--crystals are effectively transparent

'Goldilocks' confocal imaging

Outline....

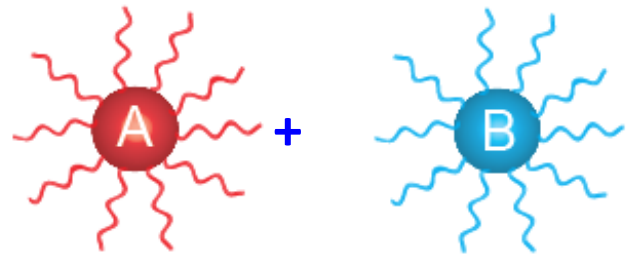
Ben Rogers

1. DNA interactions and dynamics
2. Simple crystals and real space crystallography
3. New phases and transformations

Marie Ung

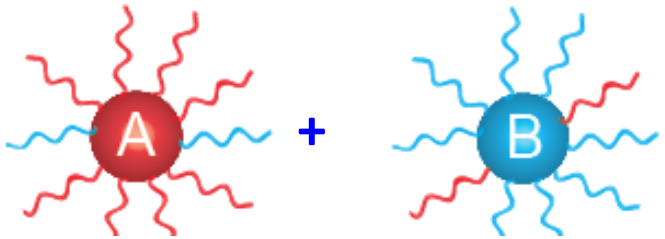
What does adding 'like' interactions do?

How to explore the phase diagram

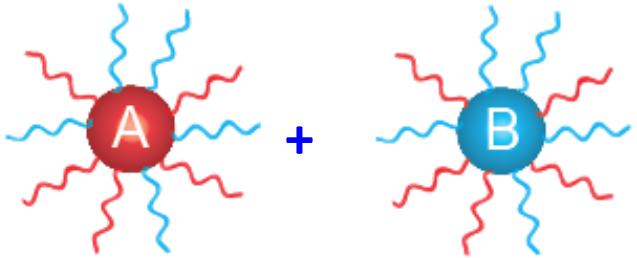


Mix the interacting strands on the beads...

$\alpha = 0 \quad E_{AB} > E_{AA} = E_{BB} = 0$



$\alpha = 0.1 \quad E_{AB} > E_{AA} = E_{BB} > 0$



$\alpha = 0.5 \quad E_{AB} = E_{AA} = E_{BB} > 0$

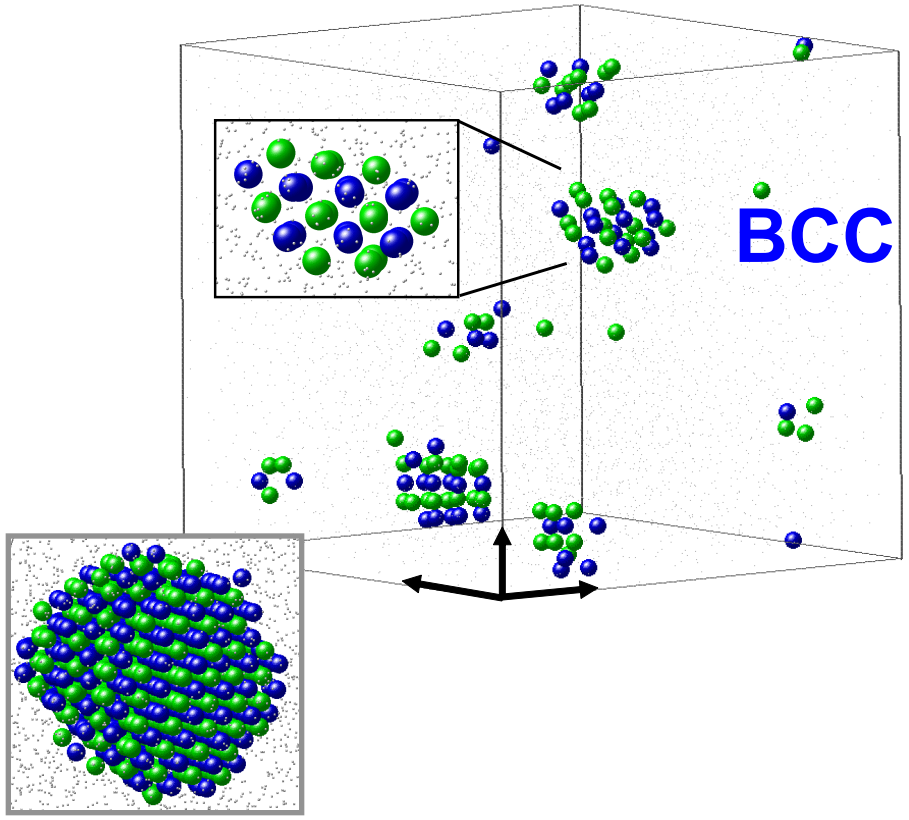
Features:

—Only 'one' hybridization reaction present, simple temperature dep.

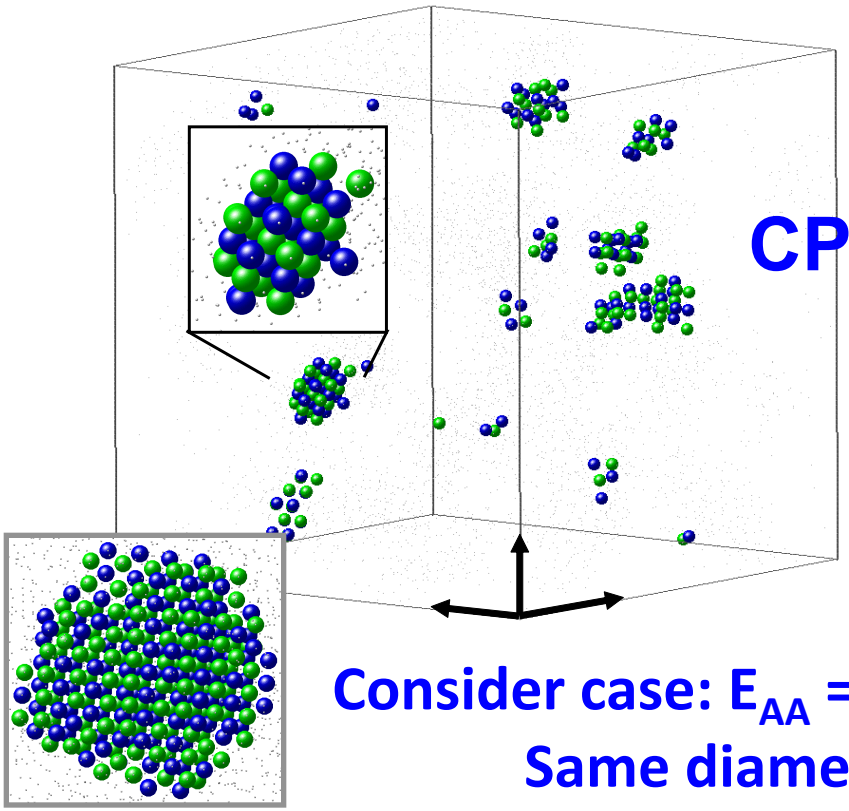
—Straightforward to calculate interaction matrix....

Spontaneous nucleation

Small 'like' interactions



Larger 'like' interactions



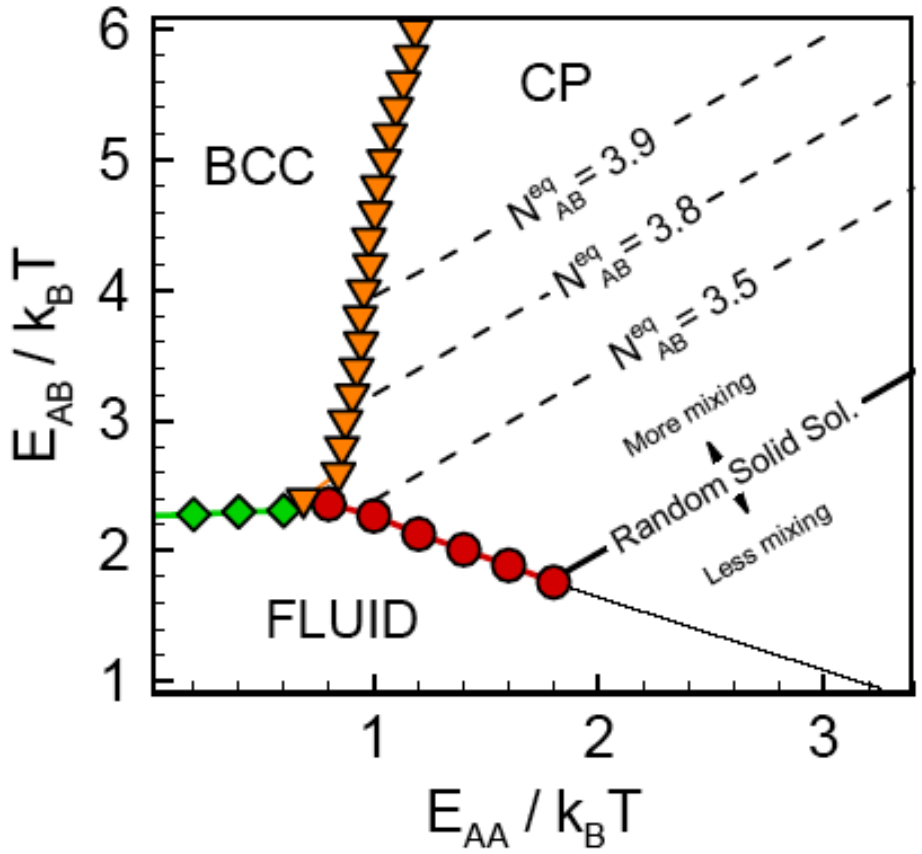
Consider case: $E_{AA} = E_{BB}$
Same diameter

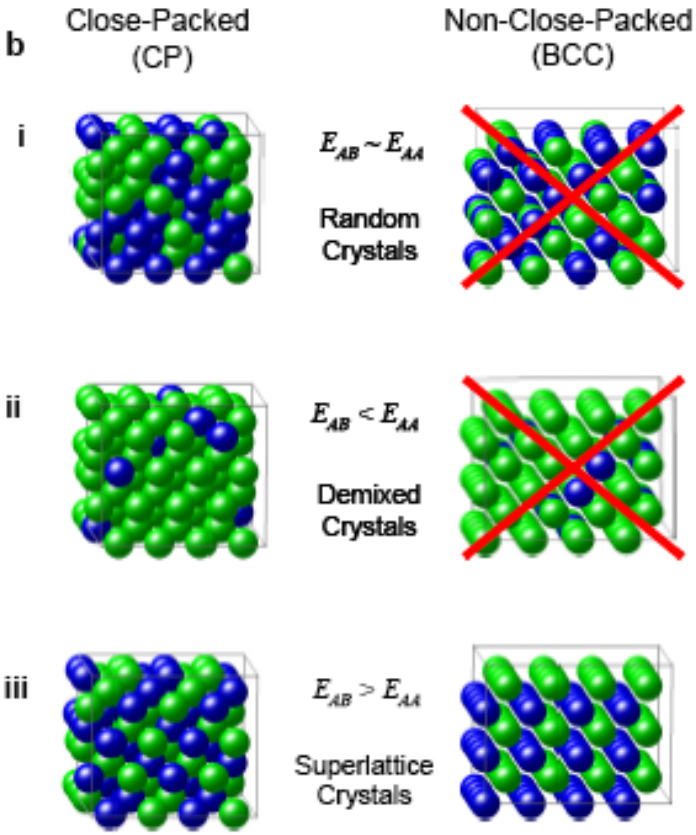
CP phase grows with compositional disorder: 'anti-site' growth sites on interface

Talid Sinno

Scarlett, Ung, Crocker, Sinno *Soft Matter*. 7, 1912-1925 (2011)

MMC Simulations





Many parameters...

Consider case: $E_{AA} = E_{BB}$

Same diameter

BCC superlattice = CsCl crystal

CP superlattice = Solid Solution

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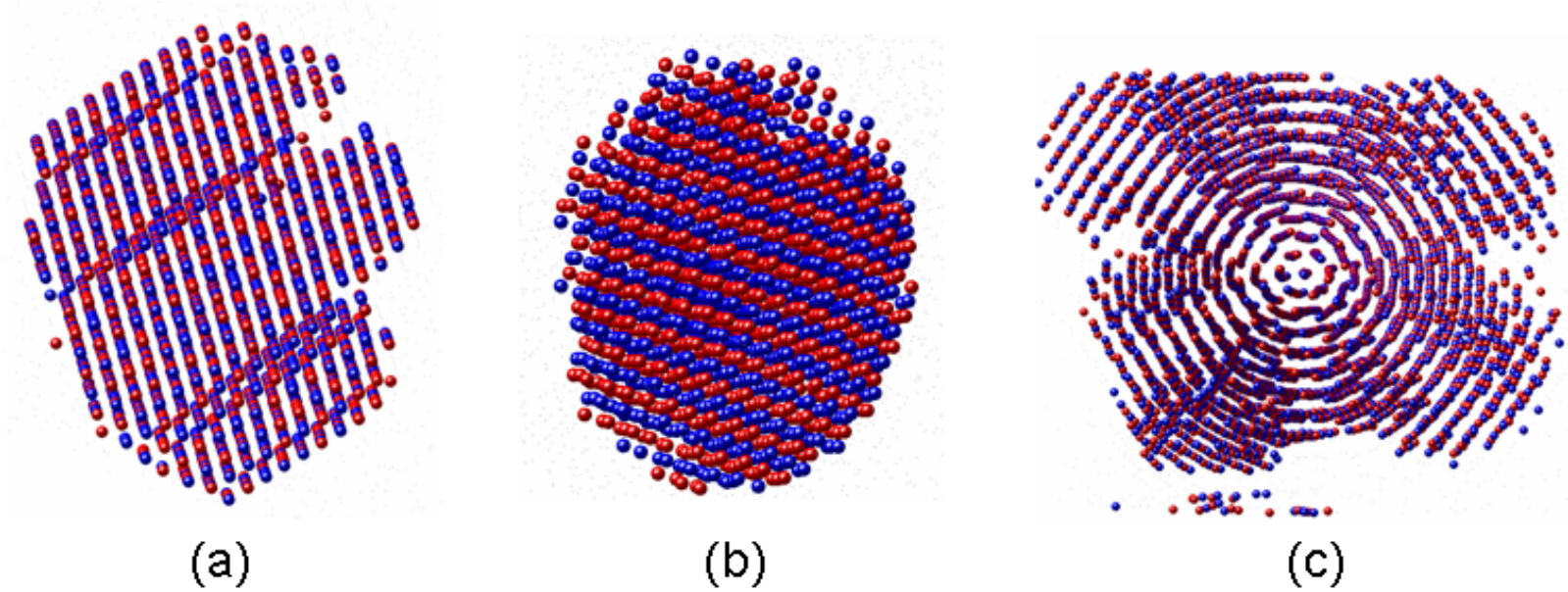
Scarlett, Ung, Crocker, Sinno *Soft Matter*. 7, 1912-1925 (2011)

Simulated binary phases

Two component system w/ experimental interaction



(a) (b) (c)

Crystallites display:

(a) Partially ordered FCC solid-solution phase with a high degree of compositional defects and a few stacking faults

(b) CsCl phases are perfectly ordered, but have...

(c) soft modes that can be 'quenched' by surface defects or grain boundaries.

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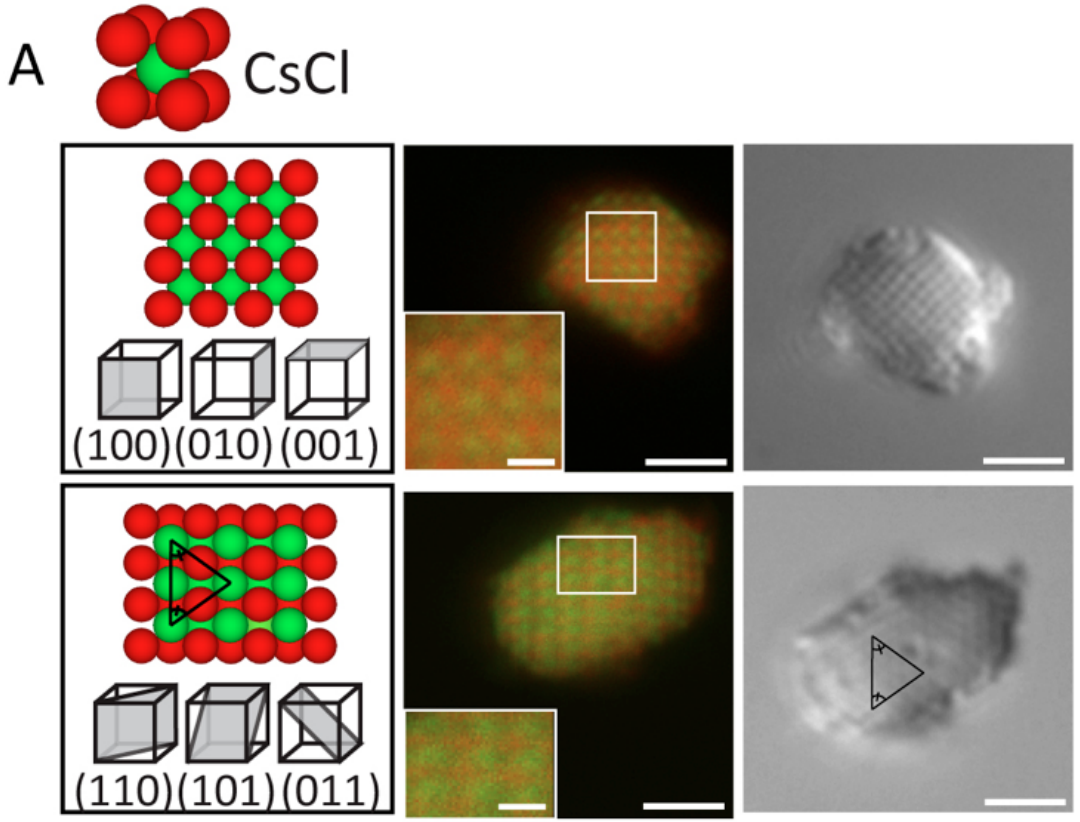
Weak ‘like’ interactions



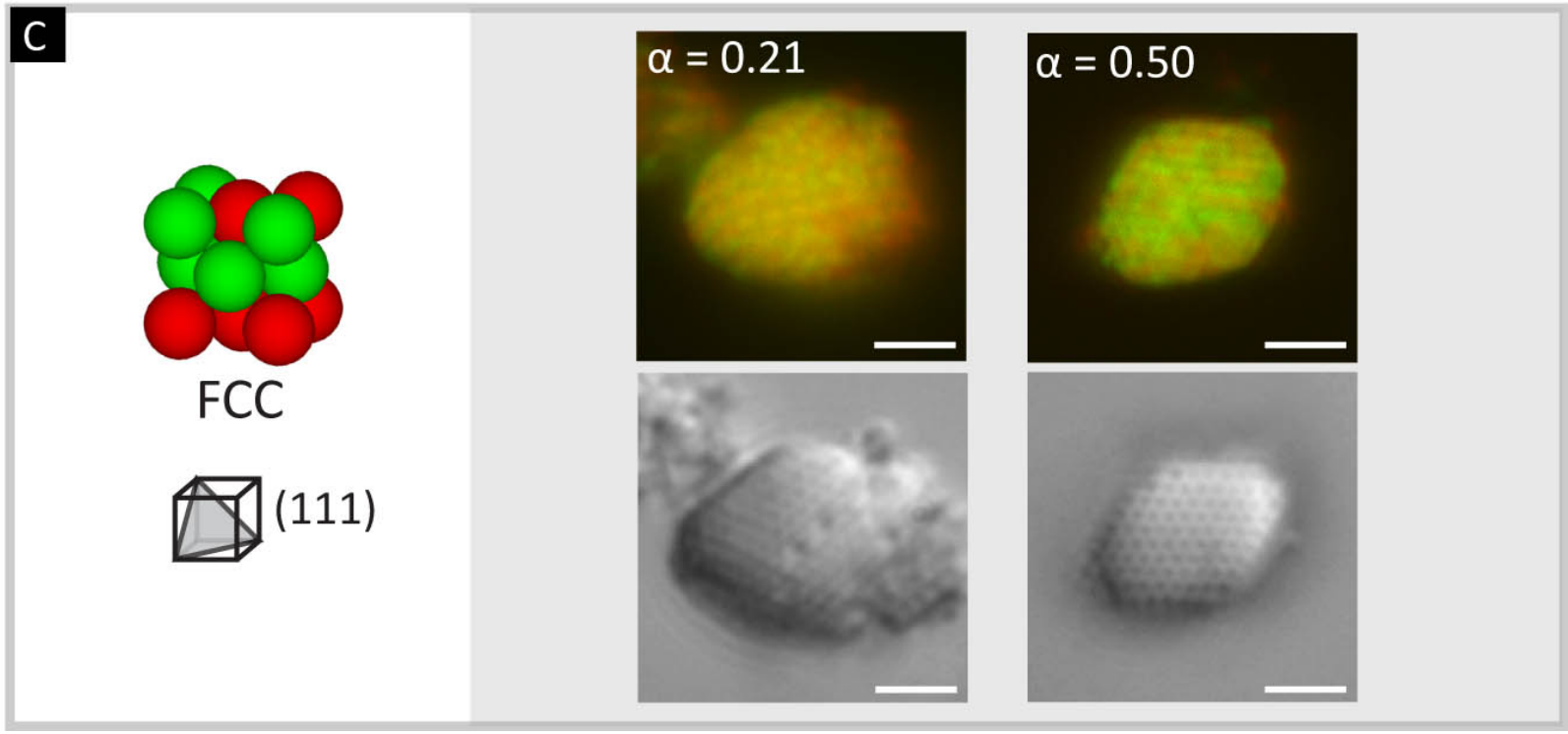
Expected features:

α = 0.0, 0.06

—Matches simulation expectations

—Crystals present ‘dense’, slow growing faces

Strongest ‘like’ interactions



Expected features:

—Well ordered FCC lattice (white light)

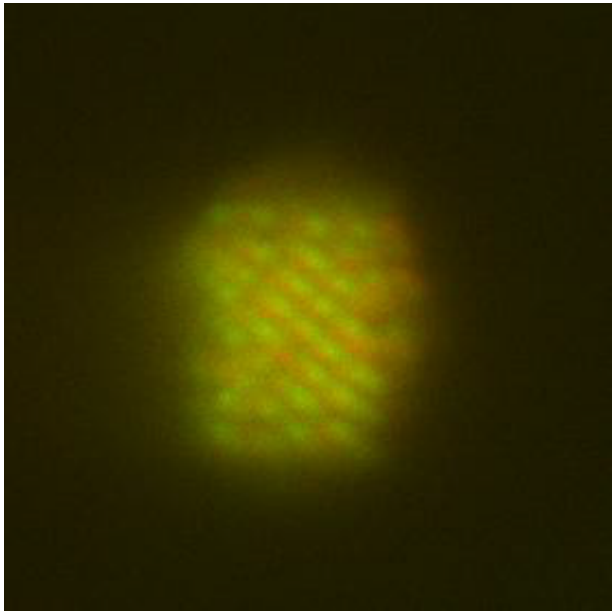
—Random solid solution matches simulations

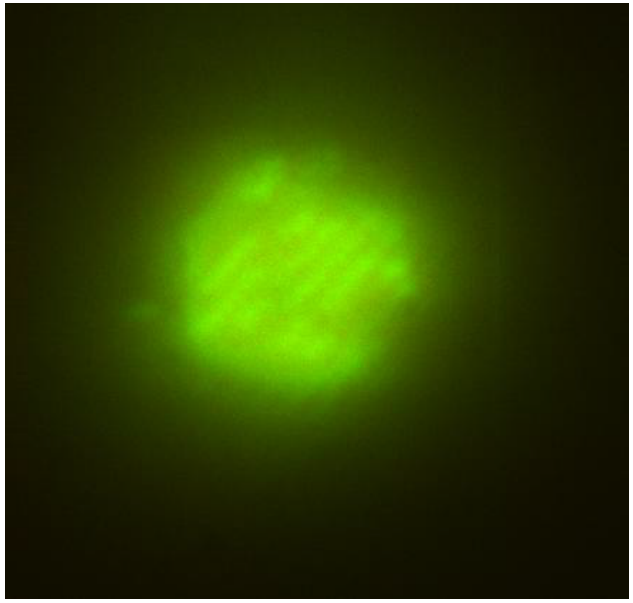
—lower contrast at α = 0.21 indicates partial anti-correlation

Intermediate 'like' interactions

α = 0.10, 0.13, 0.16

A surprise....

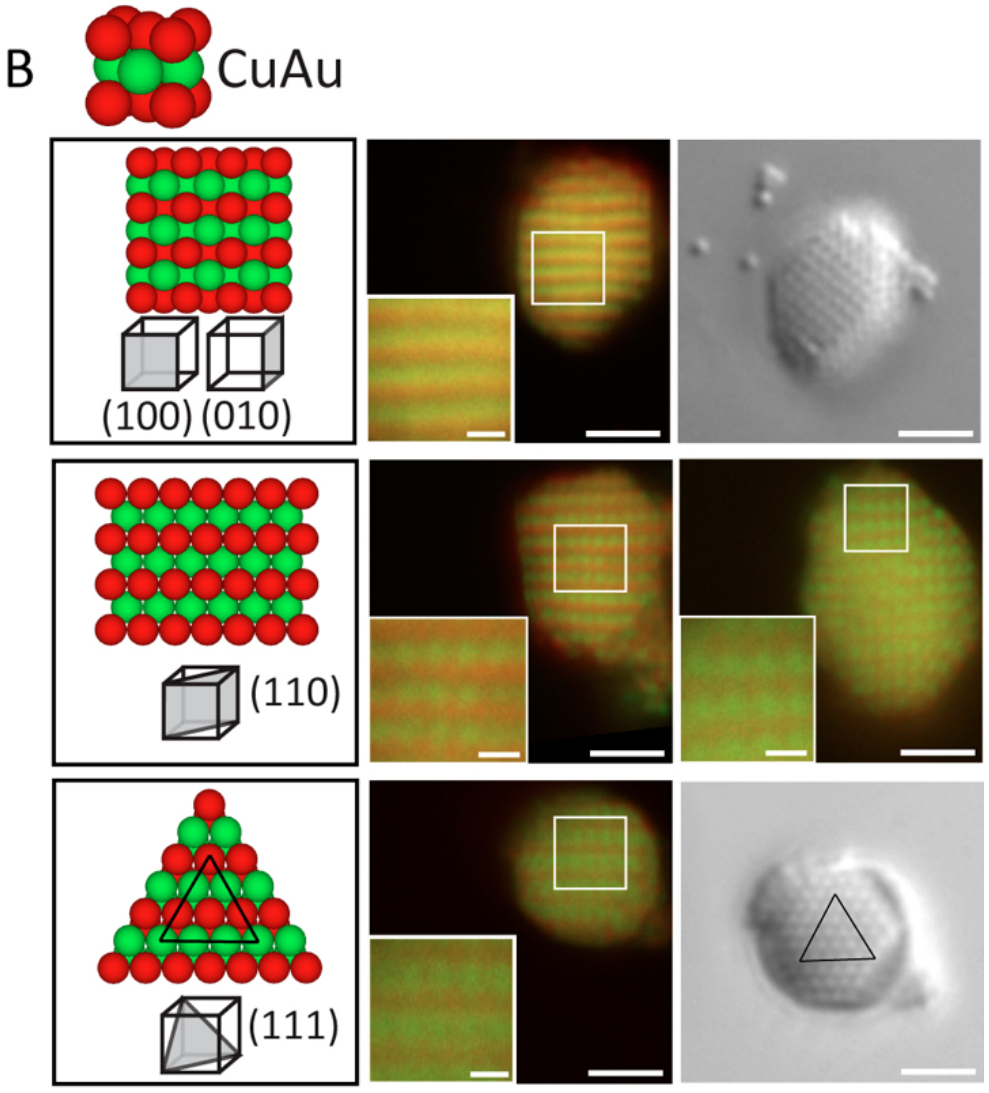




Highly ordered crystals that are NOT CsCl

3 different 2-d symmetries

Intermediate 'like' interactions



α = 0.10, 0.13, 0.16

Features:

—CuAu-FCC with low density of stacking faults

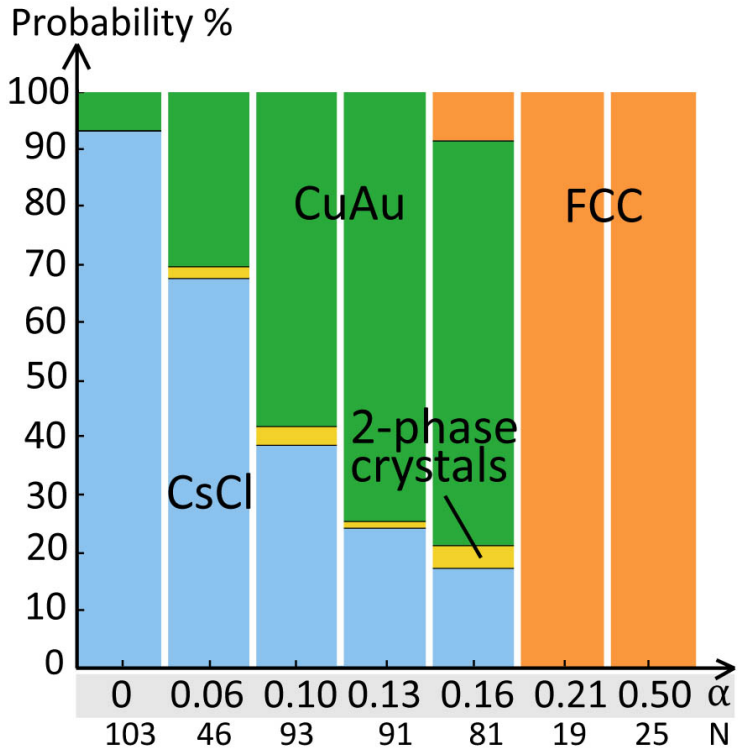
—'Coexists' with CsCl

Oddities:

—CsCl/CuAu xtal sizes match from sample to sample

—Many facets are not expected 'dense planes'

Crystal populations

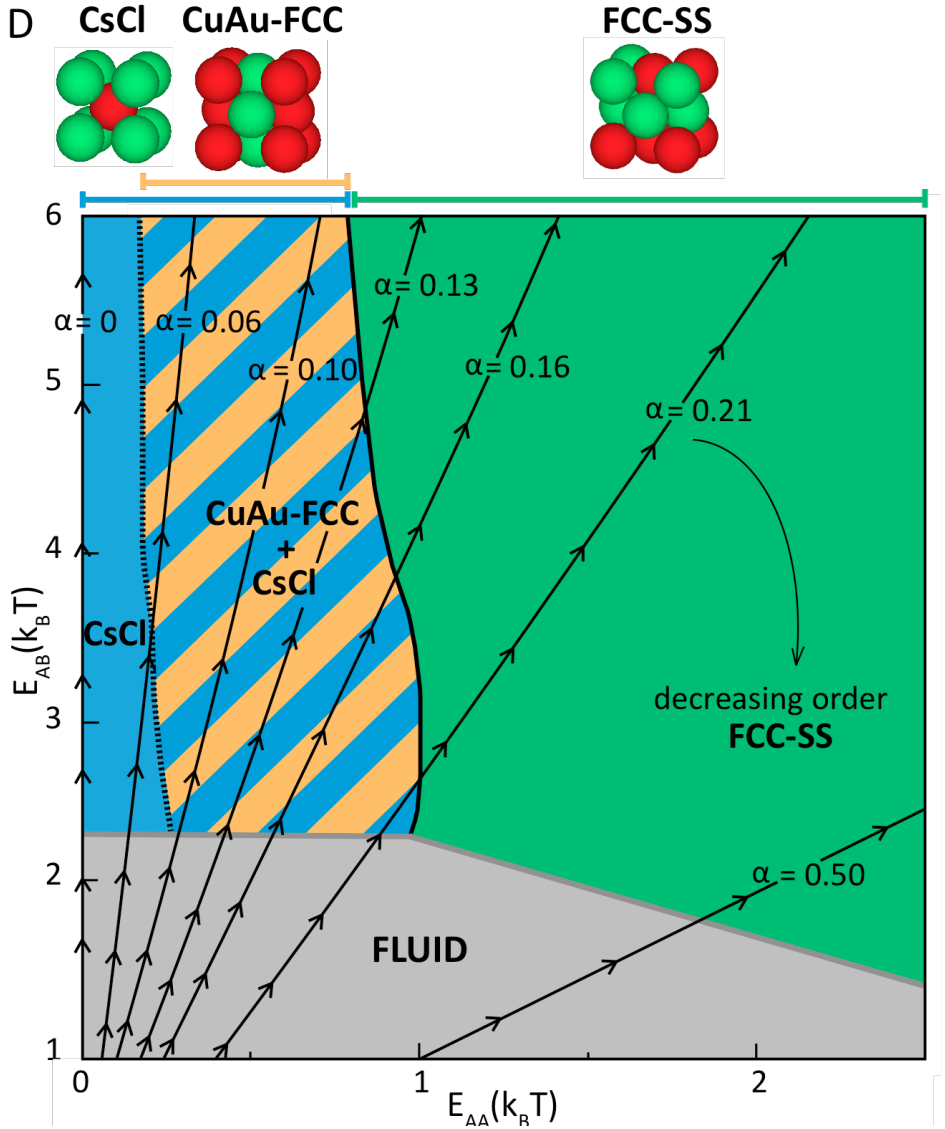


Scanned and 'solved' over 400 crystals with confocal

—CuAu is well ordered, present at low mixing, $\alpha < 0.1$

—Equilibrium coexistence or kinetic phase?

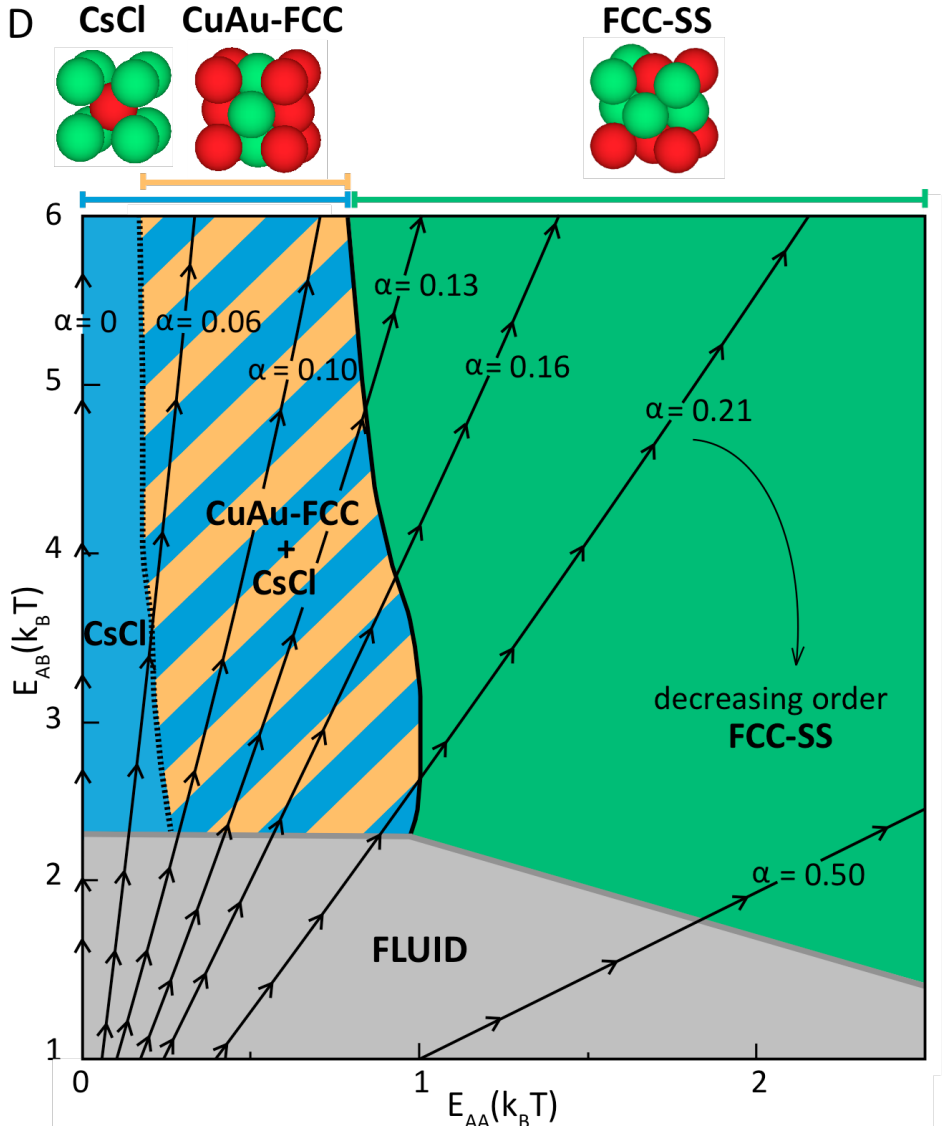
Computed phase trajectories

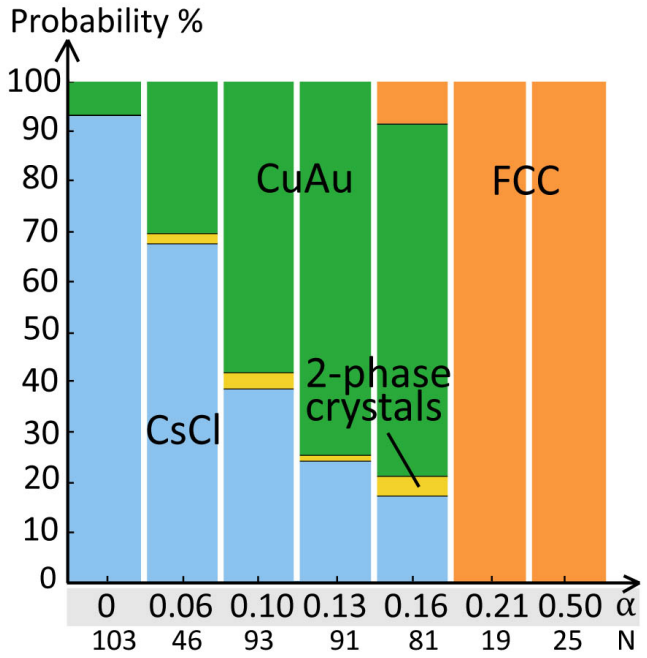


—Thermal quenching leads to interactions increasing proportionally in time, forming 'rays' across phase diagram

—CuAu-FCC does have lowest free energy over most of plane; Not kinetically accessible from fluid!

Computed phase trajectories

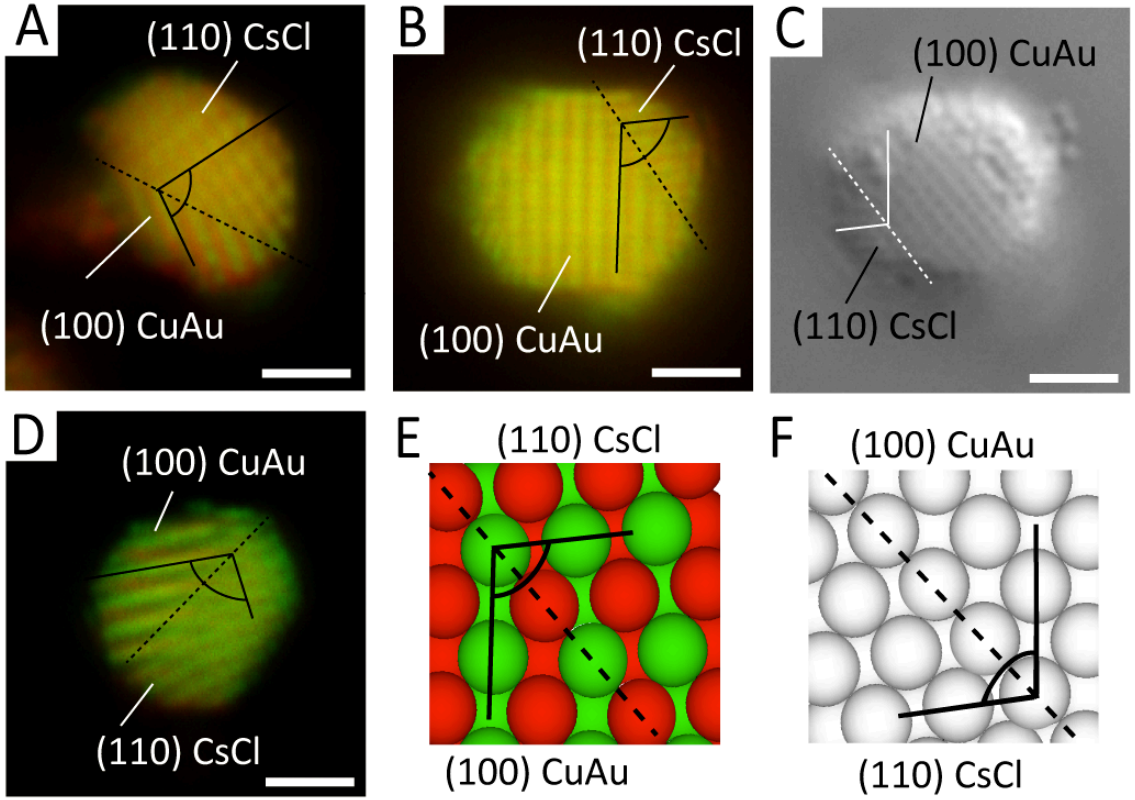




—All CuAu-FCC samples form CsCl first.....

solid-solid transformation?

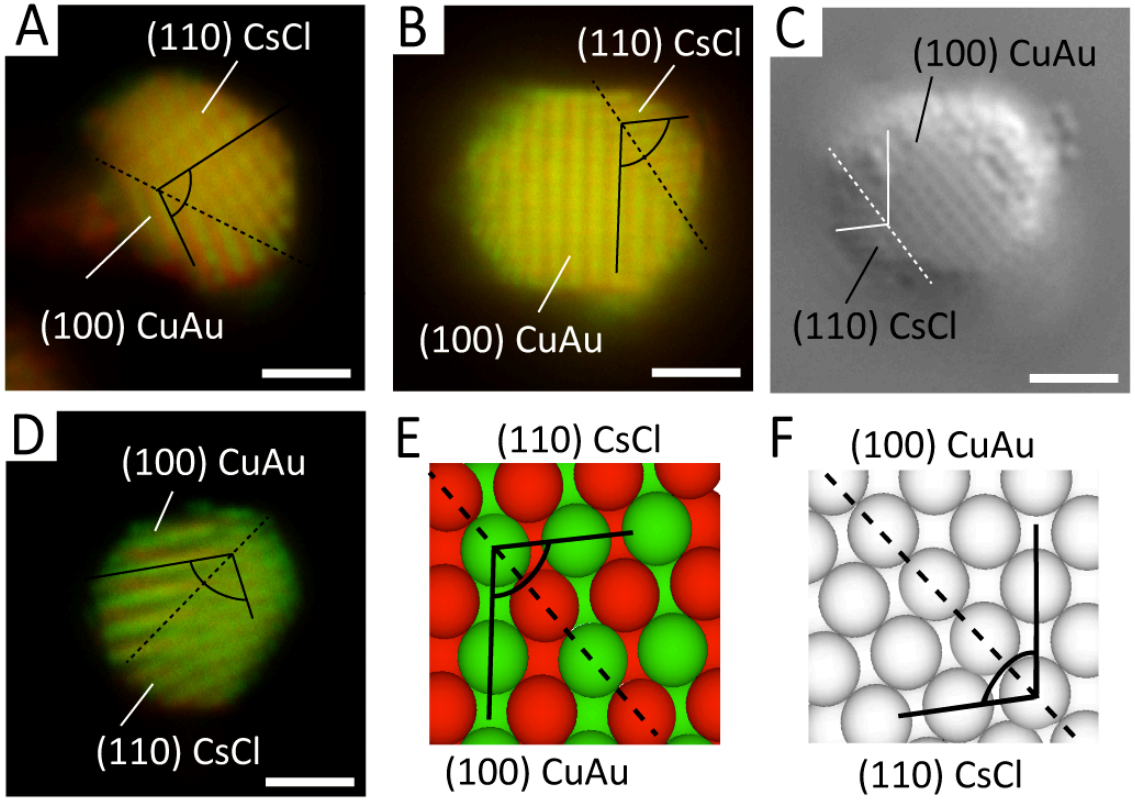
Diffusionless transformation

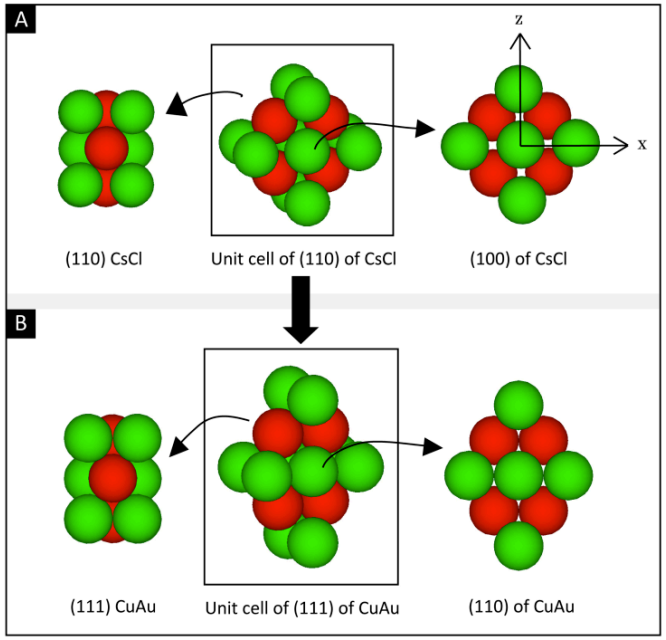


'Two phase' crystals observed:

—Interface and lattice orientations consistent over ~7 xtals: 'habit plane'

Diffusionless transformation





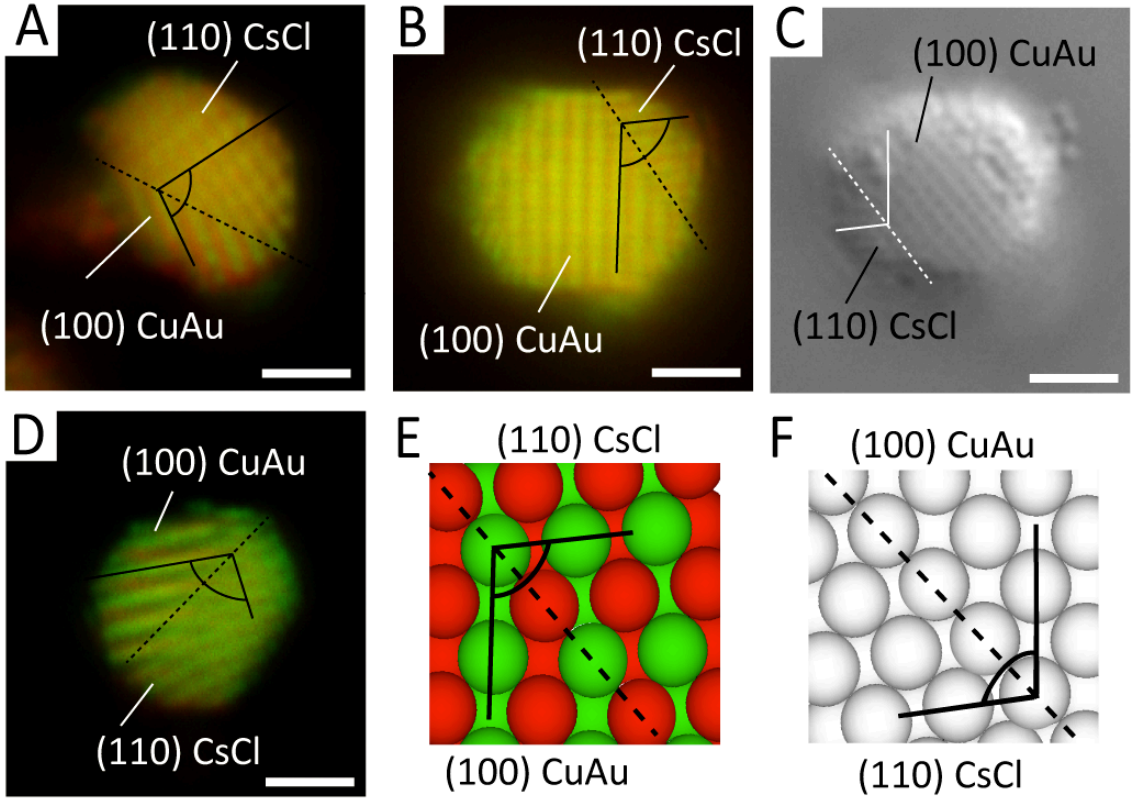
'Two phase' crystals observed:

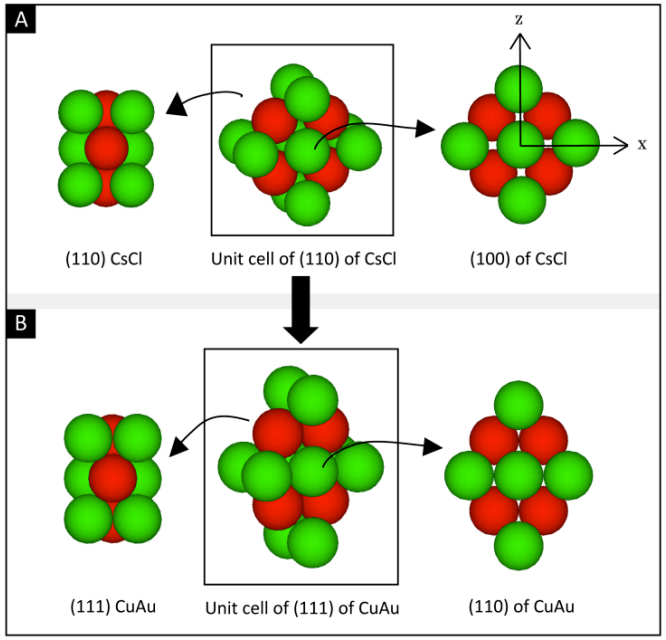
—Interface and lattice orientations consistent over ~7 xtals: 'habit plane'

—Consistent with classical BCC-FCC Martensitic transition mechanism

—Observed CuAu 'child' facets are CsCl 'parent' facets

Diffusionless transformation





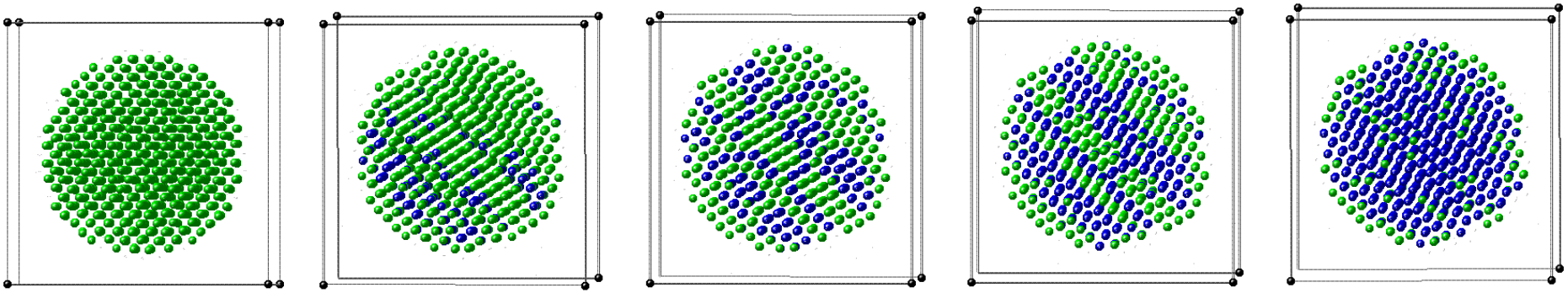
'Two phase' crystals observed:

—Single child domain and coherent interface resembles shape memory alloys.

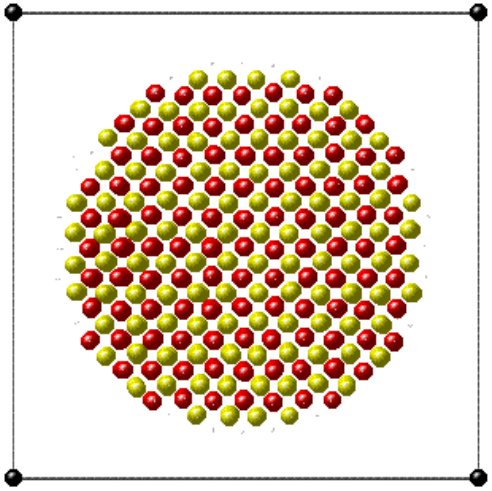
—Crystals are 'plastic' under shear

May have novel mechanical properties.

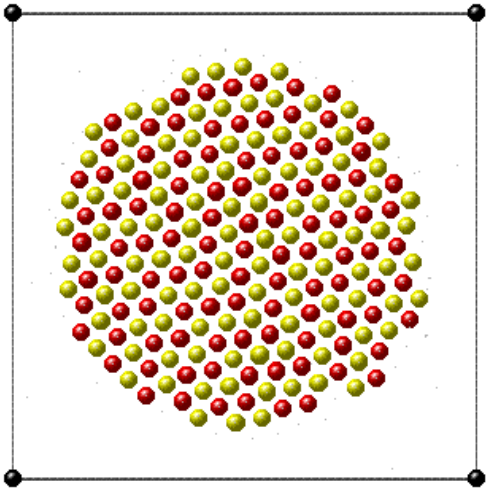
Diffusionless Transformation



BCC



CP



Child phase is RHCP (!)

—stacking faults have no energy penalty

—final phase selection is kinetic

—how to integrate a transition path in configuration space?

Summary

DNA-induced colloidal interactions are:

- versatile and specific
- well-understood for modeling
- fast and easy route to complex ordered particle structures
- Yields 'real' materials with rich behavior

Ben Rogers

Marie Ung

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NYU: Marie-Pierre Valignat, Remi Dreyfus, Paul Chaikin

Penn
University of Pennsylvania

NSF

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