Self-assembly and dynamics in nanoparticle superlattices

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CONTRACT DE-AC02-07CH11358

DMR-CMMT (1606336) New!!!

Also: D. Talapin and M. Boles (U Chicago & Stanford)
O. Gang (Columbia/Brookhaven)
**Programmable (Self)assembly?**

Assembling *ordered* materials, phases, structures from basic *components*, precisely.

Successful self-assembly

Failed self-assembly
**Nanoparticles Assembly**

Components: Nanoparticles.
Materials: Crystals (Supercrystals).

**How to control super-crystals structure?**

- **Proper Interactions:**
  - Capping ligands:
    - Functionalization, passivation

- **Control relaxation times**
  - Temperature cycling, annealing..

\[ \frac{\varepsilon_F}{k_B T} \]

SUCCESS?

Very narrow success range: Relaxation times grow very fast with characteristic energy.

**Proper Interactions: Assembling Nanoparticle Superlattices**

Spherical Nanoparticles functionalized with:

- **DNA (water)**

- **Hydrocarbons (oil)**
  - Shevchenko, Talapin et al. (Nature 2006)

- **New!!! Water soluble polymer:**
  - Polyethylene glycol (water)

- **New!!!**
  - DNA (water)

- **Hydrocarbons (oil)**

- **New!!! Water soluble polymer:**
  - Polyethylene glycol (water)

- **New!!!**

- **New!!!**

- **New!!!**

- **New!!!**

- **New!!!**
DNA Nanoparticles superlattices
**DNA Superlattices**

Solution of both A and B

Nykypanchuck, Maye, Van der lelie and Gang, Nature (2008)

(bcc)

General strategy for programmed self-assembly!

C. Knorowski and A. T., COSSMS (2011)
Hydrogen bond is between complementary base pairs and directional

CT beads=
C-G T-A short-range attraction (HB)
FL, CT beads= hard-core repulsion

PARAMETERS:
R=NP radius (6nm)
r=number of ssDNA strands per NP
\( \eta \)=NP density
T=Temperature


C. Knorowski, S. Burleigh and A. T., PRL (2011)
T. Li, R. Sknepnek, R. Macfarlane, C. Mirkin, M. Olvera de la Cruz, Nano. (2012)
HOOMD-blue is a general-purpose particle simulation toolkit. It scales from a single CPU core to thousands of GPUs.

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Want to run a Molecular Dynamics simulation using a custom force field? Or maybe you are
Phase Diagram of DNA (from theory)

- η = 1
- CsCl-bcc
- D-bcc
- Test case: No hydrogen bonds ($\epsilon_{bp}=0$)
- f-star polymer

- Xiong, Van der Lelie, Gang PRL (2009)
- C. Knorowski, S. Burleigh and A. T., PRL (2011)
Classical Nucleation Theory, defects

Defect Free  Substitutional  A-Vacancy  A-Interstitial

Internal energy constant during nucleation  Crystallization is entropically driven

DEFECT ANNHIILATION

Follows the following elimination reaction:

**Hydrophobicity and DNA**

Solution of monodisperse identical DNA-Au Nanoparticles (no hybridization), increase salt concentration.

Spontaneous Crystallization (Gibbs monolayer) at the air-water interface.

Bragg peaks

Gibbs monolayer implies **hydrophobicity**.

Capping ligand does have **hydrophobic blocks**.

<table>
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<th>Type</th>
<th>Sequence (5’ to 3’)</th>
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<tr>
<td>Thiol modified DNA – A</td>
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<td>TAA CCT AAC CTT CAT</td>
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<td>ATG AAG GTT AGG TTA</td>
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</table>

**Hydrophobicity** is an additional element to consider in the programmable self-assembly of DNA ...

What about (mildly) **Hydrophilic** ligands: PEG ?


Electrostatic induced superlattices

Water soluble polymer: Polyethylene glycol (water)

Zhang, Wang, Mallapragada, A.T, Vaknin (2017)
Zhang, Wang, Akinc, Mallapragada, A.T, Vaknin (2017)
**Electrostatic induced superlattices**


Phase diagram of PEG+salt +water

Salt Concentration (K$_2$CO$_3$)

PEG concentration

Low salt + PEG

High salt + No PEG

Nanoparticle

Salt ejected from PEG: Osmotic pressure leads to surface tension

Trading surface tension for polymer stretching

High quality crystals at the air-water interface: ex. DNA
**Induced forces**

INSIDE: A spherical brush at theta-point

OUTSIDE: high salt, poor solvent

Polymer stretching at the interface

\[
\frac{F}{k_B T} \approx \left( \frac{R}{b} \right)^3 \left( \sigma b^2 \right)^{3/2} (2w_0)^{1/4} \quad H(y) \sim 100 H(y)
\]

surface tension increases with high salt solution

\[
\frac{F}{k_B T} = 4\pi \gamma_{AB} R_h^2 \approx 0 - 200 \\
\gamma_{AB} \approx k_B T / b^2 \log([\text{salt}])
\]

Lattice constant: Balance between surface tension and stretching: may be tuned by salt.

\[
y = \frac{a_L}{2R_h}
\]

\[
H(y) \sim (1 - y)^3
\]

\[a_L\] Lattice constant
Lattice constant can be tuned over a very large range:

Two phase region: colloidal destabilization: 3D crystals

The softer the shell the more crystals!

3D Au-PEG supercrystals presents intriguing properties.

Superlattices of Hydrocarbon capped ligands
**Binary Superlattices by Solvent evaporation**

Solution of both A and B and solvent is evaporated

Nanoparticle A

Nanoparticle B

Capping ligand (hydrocarbon)

Soluble in organic solvent
Solvent evaporation produces a myriad of super-lattices!!!
These lattices are known from their atomic analogues..

NaCl  
CuAu  
AlB₂  
MgZn₂  
MgNi₂  
AuCu₃  
CFe₄  
CaCu₅  
CaB₆  
NaZn₁₃  
CubAB₁₃

Can we predict the structure of these supercrystals?
How many parameters are needed to characterize the phase diagram?

Shevchenko, Talapin, Kotov, O’Brien, Murray (Nature 2006)
**Packing fraction**

\[ \text{PF} = \frac{\text{Volume occupied by hard sphere}}{\text{Total Volume}} \]

**Total area** = \((2R)^2\)

**Occupied area** = \(\pi R^2\)

\[ \text{PF} = \frac{\pi}{4} = 0.7853 \]

In Binary systems packing fraction can be made larger by filling interstitials.

In 3D:

- \(\text{PF} = \frac{\pi}{18^{1/2}} = 0.740\)
- \(\text{PF} = \frac{\pi}{3^{1/2}/8} = 0.680\)
- \(\text{PF} = \frac{\pi}{6} = 0.524\)

The PF depends on the ratio of the two radii, \(\gamma = \frac{R_B}{R_A}\).

In Binary systems:

- Minimizing VdW forces by maximizing packing fraction?

---

**International Travel Planning: PACKING HACKS**
### Packing fraction of binary lattices, 3D case:

**PF does exceeds the fcc/hcp case**

\[
\gamma = \frac{r_B}{r_A}
\]

Model the nanoparticles as hard spheres

Radius of nanoparticle = half lattice constant of the two-dimensional hexagonal lattice.

\[
\gamma = \frac{r_B}{r_A}
\]

Strong Correlation between PF and experiment!
Minimal models

Simplest models whose **equilibrium phases** correlated with **maximum of packing fraction**?

Potential must be short-ranged:

Inverse power law:

\[ V_{hf}(r) = \varepsilon_{hf} \varepsilon \left( \frac{\sigma_{hf}}{r} \right)^p \]

If \( p \) goes to infinity is the **hard sphere model**:

At \( p \) finite is a softer potential:
Inverse power law:

\[ V_{hf}(r) = \varepsilon_{hf} \varepsilon \left( \frac{\sigma_{hf}}{r} \right)^p \]

There are 8 parameters:

\[
\begin{align*}
\varepsilon & \quad \sigma_A \\
\frac{T}{\varepsilon} & \quad \frac{V}{\sigma_A^3} \\
\varepsilon_{AB} & \quad \varepsilon_{BB} \\
\sigma_B & \quad x_B
\end{align*}
\]

Defines units of Length and energy.

Scale invariance:

\[
\xi_p = \frac{1}{\hat{T}^{3/p}} \frac{N}{\hat{V}}
\]

\[
\gamma = \frac{\sigma_B}{\sigma_A}
\]

There are 8 parameters:

- \(\varepsilon\)
- \(\sigma_A\)
- \(\frac{T}{\varepsilon}\)
- \(\frac{V}{\sigma_A^3}\)
- \(\varepsilon_{AB}\)
- \(\varepsilon_{BB}\)
- \(\sigma_B\)
- \(x_B\)

The phase diagram is a function of 4 parameters!

1 more parameter \((\varepsilon_{AB})\) than the hard sphere model.
Data that is not within \( +/− 0.2 \) in \( \gamma \) or \( \varepsilon_{AB} \) is marked with a black dot (those are points where the theoretical prediction is off)

Example \( \text{AlB}_2 \):

Experiment:

Theory:

No binary phases here:

Similar correlation is found with \( p=6 \)

\( p = 12 \)

Cannot account for low packing fraction phases (eg: \( \text{Li}_3\text{Bi} \)), \( \text{AuCu} \) does not appear, etc...

Broad features OK, predictions not specific enough....
The OXM Models ($X=P$)

$L = \text{maximum hydrocarbon extent}$

Dimensionless thermodynamics

$$\lambda = \frac{L}{R_A} \quad \text{Dimensionless hydrocarbon extent}$$

$$\tau = \frac{r_A}{R_A} \quad \text{Dimensionless radius (lattice constant)}$$

Assume that the shaded chain is space filling:

$$\tau^{OPM} = (1 + 3\lambda)^{1/3}$$

$$s_{AA} = 2R_A \tau^{OPM}$$

This is the OPM formula.

The OPM formula for a binary system is:

$$s_{AB}^{OPM} = \tau_A^{OPM} R_A + \tau_B^{OPM} R_B$$

The OXM Models ($X=C$)

\[ \lambda = \frac{L}{R_A} \]  Dimensionless hydrocarbon extent.

\[ \tau = \frac{r_A}{R_A} \]  Dimensionless lattice constant.

Assume that the OVERLAP cone is space filling:

\[ \tau^{OCM} = \eta_{HS}^{1/3} (1 + 3\lambda)^{1/3} \]

\[ s_{AA} = 2\tau^{OCM} R_A \]

\[ PF = \eta_{HS} \]

This is the OCM formula.

The OCM formula for a binary system is:

\[ s^{OCM}_{AB} = R_A \tau^{OCM}_A + R_B \tau^{OCM}_B \]

Experimentally: simple lattices: depends on NC coordination number q

\[ \tau^{OPM} = (1 + 3\lambda)^{1/3} \]

\[ \tau^{OCM} = \eta_{HS} \left(1 + 3\lambda\right)^{1/3} \]

q = 3 OCM

q \geq 6 OPM

\( r_A \)


Boles, Talapin JACS (2015)

The OPM-FE model

The OPM-model provides selection rules (no free energy).

A free energy (OPM-FE) is constructed by:

- OPM-Spheres of radius \( r_A = \tau^{OPM} R_A \)
- NCs in contact interact with VdW potential: \( V(i, j) = -\frac{A_B}{6D} \frac{r_i r_j}{r_i + r_j} = -\chi \frac{r_i r_j}{r_i + r_j} \equiv -\chi f(i, j) \)
- Free energy is:

\[
F = -\frac{\chi}{2} \sum_{i=1}^{N} \sum_{j \in N(i)} f(i, j)
\]

Minimum of OPM-FE = Minimum of VdW energy + chain entropy.

bcc to fcc transition in single component systems.

**Results for OPM-FE**

Model: OPM-FE

Bar = 1 (equilibrium) if < 1 how far is from equilibrium.

Binary systems: OPM-FE sometimes predicts the right phase, usually with the wrong lattice constant! OPM–FE = same phases as inverse power law, and with same discrepancies! OCM not in agreement!

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**Vortices and Neutral lines**

Imagine a mix of OPM and OCM.

This is a vortex on the surface of the sphere.

**Topology (Gauss-Bonnet theorem):** There can only be 2 ! (no-anti vortices)

However, vortex = projection of the 3-dimensional hydrocarbon orientation.

Vortices can “escape through the third dimension....”

NCs as SKYRMIONS WITH topological charge -1:


Neutral lines are generated!
The OTM model

Topological charge $q_T$: number of vortices.

What neutral lines look like when $q_T > 1$?
A) vortices

OTM HYPOTHESIS: Neutral lines are costly, need to be MINIMIZED:
- $q_T = 1, 2$ One or two vortices (no neutral lines).
- $q_T = 3$ Two vortices and one $\frac{1}{2}$ disclination or 3 vortices.
- $q_T = 4$ Four $\frac{1}{2}$ disclinations or 4 vortices with neutral lines.
- $q_T \geq 6$ neutral lines too costly, topological charge is trivial.

(Currently testing this hypothesis with explicit simulations!)

Ratio of nanoparticle radius (hexagonal lattice) is:

$$\gamma \equiv \frac{T_B^{\text{OTM}}(q_T=0)}{T_A^{\text{OTM}}(q_T=0)} = \frac{T_B^{\text{OPM}}}{T_A^{\text{OPM}}}$$
**Prediction of lattice structure within OTM:**

Example: MgZn₂
Space Group: P6₃mmc
Unit cell: 4A 8B

Wyckoff positions: 4f (A) Hex diamond
2a, 6h (B) Pyrochlore

\[ \tau_B \frac{\tau_{OPM}}{\tau_A} \]

\( \gamma \)

OTM: B-particles can only have \( q_T = 0 \)

A-A contacts (q=4)
B-B contacts (q=6)

\( \gamma > \gamma_c = \sqrt{\frac{2}{3}} \)

**Prediction of lattice structure within OTM:**

Example: MgZn$_2$

Space Group: P6$_3$mmc

Unit cell: 4A 8B

Wyckoff positions: 4f (A) Hex diamond

2a, 6h (B) Pyrochlore

\[ \gamma \equiv \frac{T_B}{T_A} \]

OPM: \( q_T = 0: \gamma = \gamma_c = \sqrt{\frac{2}{3}} \)

A-A contacts (q=4)

B-B contacts (q=6)

OTM: B-particles can only have \( q_T = 0 \) \( \gamma > \gamma_c = \sqrt{\frac{2}{3}} \)

\[ \frac{r_{OPM}}{r_A} = \gamma_c = \frac{r_B}{r_A} \]

Prediction

Computed from L, R

Measured experimentally

\[ a = 13.9 \text{ nm} \]

\[ c = 22.4 \text{ nm} \]
Within OTM PF widely exceeds the HS prediction for values $\gamma < \gamma_c$.

MgZn$_2$ is an example of a low HS PF that becomes High PF within OTM.
Prediction of Binary Packing density
OTM and experiment

Prediction of lattice structure

Uncertainty in Normalized separation is high ...

Boles, Talapin JACS (2015)
There is almost perfect agreement with experiments for all lattices studied in the experiments!

Prediction of ligand loss↓

<table>
<thead>
<tr>
<th></th>
<th>$\eta_u$</th>
<th>$d_{ij}$</th>
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<td>NaZn$_{13}$</td>
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<td>0.74</td>
</tr>
<tr>
<td>AuCu</td>
<td>0.05†</td>
<td>0.02</td>
</tr>
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</table>
**Ligand loss: The case of AuCu**

**OPM:** $q_T = 0$: $\gamma = \gamma_c = \sqrt{3} - 1 \approx 0.73$
- A-A contacts ($q=4$)
- A-B contacts ($q=8$)

**OTM:** B-particles can only have $q_T = 0$
- A-particles can have $q_T = 4$

The solution only reaches up to

$$\gamma = \gamma_{c,2} = 1/\sqrt{2} \approx 0.707$$

Experiments report $\gamma_{c,2} \leq 0.57$

Within **OTM**, experimental results are consistent only if ligands are lost and raw (PbS) are in contact along the (1 0 0) faces.

Experimental evidence in complete agreement with **OTM** prediction. Ligand loss seems a general feature in PbS, includes quasicrystals.

*Boles, Engel, Talapin, Chem. Rev. (on-line September 2016)*
**Conclusion**

*Superlattices: where topology meets geometry meets physics meets chemistry meets materials science!*

Superlattice structure prediction for 3 different assembly strategies:

1. DNA-water driven by hybridizations.
2. Hydrocarbons-Organic solvent driven by VdW forces.
3. PEG water driven by electrostatic segregation, and ultimately, by VdW forces.

DNA: Hydrophobicity in linkers influence the resulting phase diagram

Polymers (PEG): crystallization of spherical polymer brushes in 2D and 3D: Controlled lattice constant by salt concentration. Softer ligands (longer polymers) make more mesophases.

Hydrocarbon ligands: skyrmions (hedgehogs) with “non-topological” defects

OTM model explains structure and stability of super-crystal phases

GRAND CHALLENGE to Supercrystal prediction: Understand/Control relaxation times (DYNAMICS): Microfluidics?
Dynamical Lattice Theory

This is the harmonic approximation: Write the coordinates of every particle as

\[ \vec{R}_a = \vec{R}_a^0 + \vec{u}_a \]

Position of the particle in the lattice \hspace{1cm} Displacement from the lattice

The potential energy is:

\[ U = \frac{1}{2} \sum_{a,b} V(\vec{R}_a - \vec{R}_b) = \frac{1}{2} \sum_{a,b} V(\vec{R}_a^0 - \vec{R}_b^0) + \frac{1}{2} \sum_{a,b} u_i^0 D_{(a,i),(b,j)} u_j^b \]

\[ = U_0 + \frac{1}{2} \sum_{a,b} u_a D_{a,b} u_b \]

The free energy is:

\[ F^{harm} = U_0 + k_B T \log \det D \]

DLT is an approximation because we are neglecting higher order terms...

DLT becomes exact in the limit of very low temperatures!
**Computational tools**

**Calculation of free energies**

**Self-assembly simulations**

**MD DYNAMICS**

**HOODLT**

**HOOMD**


**+ GENETIC ALGORITHMS**

K. Ho Group collaboration (2016)
The known phase diagram is given by

At $T=0$, the equilibrium phase is hcp for $P < 878.49$

DLT calculation

hcp is the low temperature solid phase!!!

DLT is actually quite accurate!

How results are modified once anharmonic terms are included?
The anharmonic contribution is calculated in all these many points...

The difference in chemical potential is very small!

The free energy difference is a very subtle balance

Entropy favors fcc

Energy favors hcp
Model the nanoparticles as hard spheres of the respective diameters

\[ \gamma = \frac{d_A}{d_B} \]

\[ \gamma = 0.58 \]

NaCl
CuAu
AlB\textsubscript{2}
MgZn\textsubscript{2}
MgNi\textsubscript{2}
AuCu\textsubscript{3}
CFe\textsubscript{4}
CaCu\textsubscript{5}
CaB\textsubscript{6}
NaZn\textsubscript{13}
CubAB\textsubscript{13} + more

Eldridge, Madden, Frenkel (Nature 1993)
Assembly, when energies $\gg k_B T$ does not happen (within available time!)

- CATALYST, enzyme, etc…

$\frac{\varepsilon_F}{k_B T}$
We compute the free energy for the following 24 lattices:

> Stability (D-matrix positive definite) occurs only for a range of \( \gamma \)

<table>
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<th>SG</th>
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<td>P6/mmm</td>
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<td>hP2</td>
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<table>
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<th>( \gamma + 0.08 )</th>
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\( p = 12 \) \hspace{1cm} \( p = 6 \)