Topological dereliction in liquid crystal-mediated particle assembly

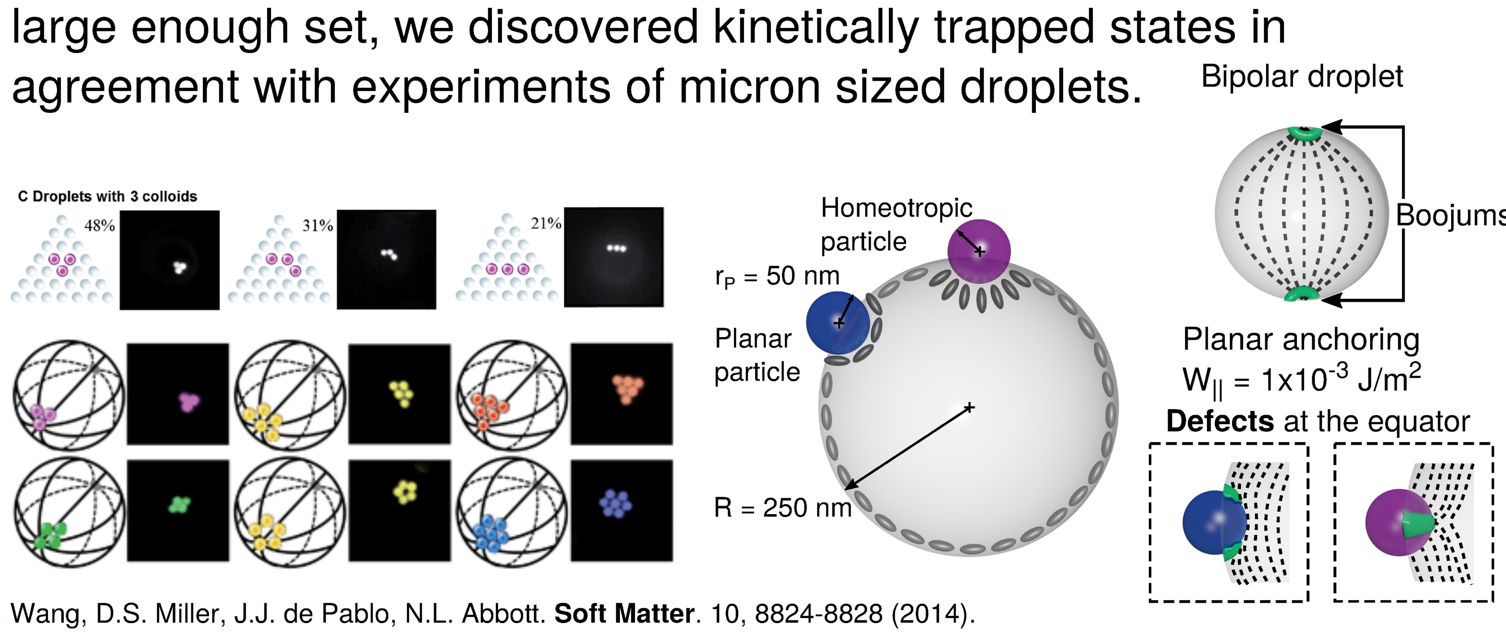
Viviana Palacio-Betancur[1], Julio C. Armas-Pérez[2], Juan P. Hernández-Ortiz[3,4], and Juan J. de Pablo[1,5]

[1] Pritzker School of Molecular Engineering, University of Chicago. Chicago, IL 60637, USA. [2] División de Ciencias e Ingenierías, Campus León, Universidad de Guanajuato, , León (Gto.) 37150, México.
[3] Departamento de Materiales y Minerales, Universidad Nacional de Colombia Sede Medellín. Medellín, Colombia. [4] Biotechnology Center, University of Wisconsin–Madison, Madison, WI 53706-1691, USA
[5] Materials Science Division, Argonne National Laboratory. Lemont, IL 60439, USA.

PRITZKER SCHOOL OF MOLECULAR ENGINEERING
THE UNIVERSITY OF CHICAGO

Abstract

Liquid crystal-mediated assembly of nanoparticles is driven by the elasticity of the anisotropic media. In the bulk, nanoparticles join through the liquid crystal (LC) defect and form lattices with crystalline order. In this work we study the behavior of adsorbed particles on the surface of a LC bipolar droplet. The free energy of the LC is described through the Landau-de Gennes formalism. A novel Metropolis sampling algorithm is used to minimize the free energy functional in function of the alignment tensor and the position of the particles. We observe that homeotropic particles annihilate the boojums, similarly to weakly planar anchored particles. These rules for particle assembly are conserved for small sets of particles. For a large enough set, we discovered kinetically trapped states in agreement with experiments of micron sized droplets.



X. Wang, D.S. Miller, J.J. de Pablo, N.L. Abbott. **Soft Matter**. 10, 8824-8828 (2014).
M. Rahimi, T.F. Roberts, J.C. Armas-Pérez, X. Wang, E. Bukusoglu, N.L. Abbott, J.J. de Pablo. **PNAS**. 112, 5297-5302 (2015).
A. Londoño-Hurtado, J.C. Armas-Pérez, J.P. Hernández-Ortiz, J.J. de Pablo. **Soft Matter**. 11, 5067-5076 (2015).

Theoretical description

We characterize the degree of ordering in terms of the tensor order parameter **Q**, which contains all the information for an accurate thermodynamic description of the system.

$$\mathbf{Q} = \left\langle \mathbf{uu} - \frac{\delta}{3} \right\rangle = S\left(\mathbf{nn} - \frac{\delta}{3}\right)$$

Free energy relaxation

$$F(\mathbf{Q}) = \int \mathrm{d}^3\mathbf{x}\left[f_L(A, U, \mathbf{Q}) + f_E(L_i, \mathbf{Q}, \nabla\mathbf{Q})\right] + \oint \mathrm{d}^2\mathbf{x} f_S(W, \mathbf{Q})$$

A theoretically-informed Monte Carlo method generates a Markov chain-of-states by randomly updating the **Q**-field and nanoparticle position. Stable configurations are found by following a Metropolis critera: $P_{acc}(o \rightarrow n) = \min\left[1, \exp(-\beta \Delta F)\right]$

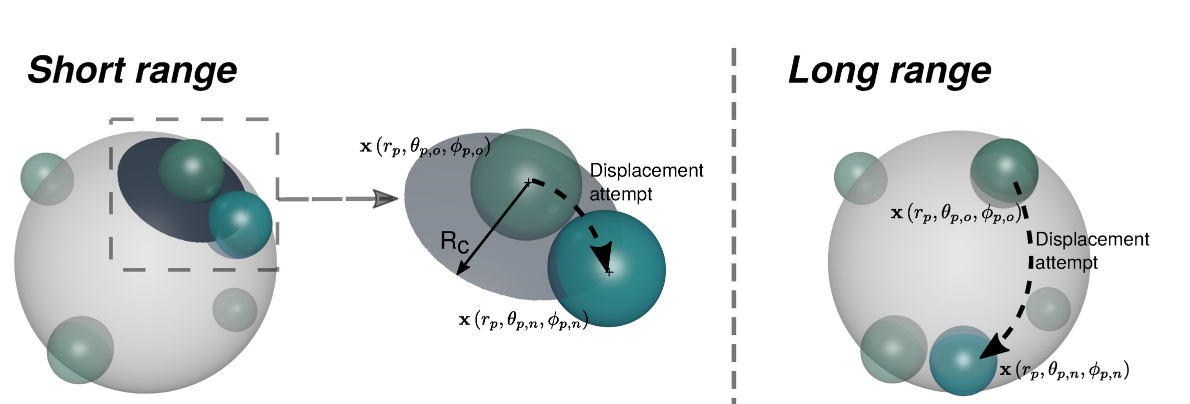
Q-field relaxation

Trial moves are performed on the coefficients of the projection:

$$a_{\mu,n}(\mathbf{x}) = a_{\mu,o}(\mathbf{x}) + \bar{\delta}_\mu (\lambda - 0.5)$$

NP relocation

Two pathways for NP moves: short and long range.



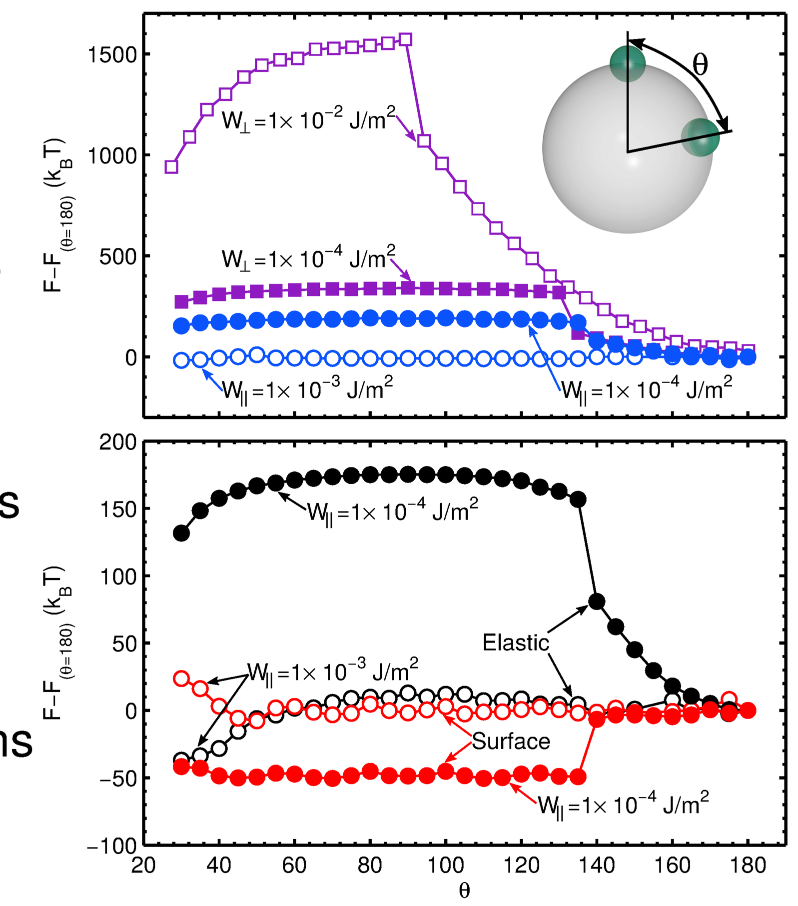
J.C. Armas-Pérez, A. Londoño-Hurtado, O. Guzmán, J.P. Hernández-Ortiz, J. J. de Pablo. **JCP**. 143, 44107 (2015)
J.C. Armas-Pérez, J.P. Hernández-Ortiz, J. J. de Pablo. **JCP**. 143, 243157 (2015).

Energetic exploration

We first perform GL relaxations with fixed particle positions: one particle is arrested at a boojum, the traveling particle approaches longitudinally.

For homeotropic particles, annihilation of the boojums drives the assembly.

Planar particles merge with the boojum instead. Elastic distortions are compensated by surface relaxation.

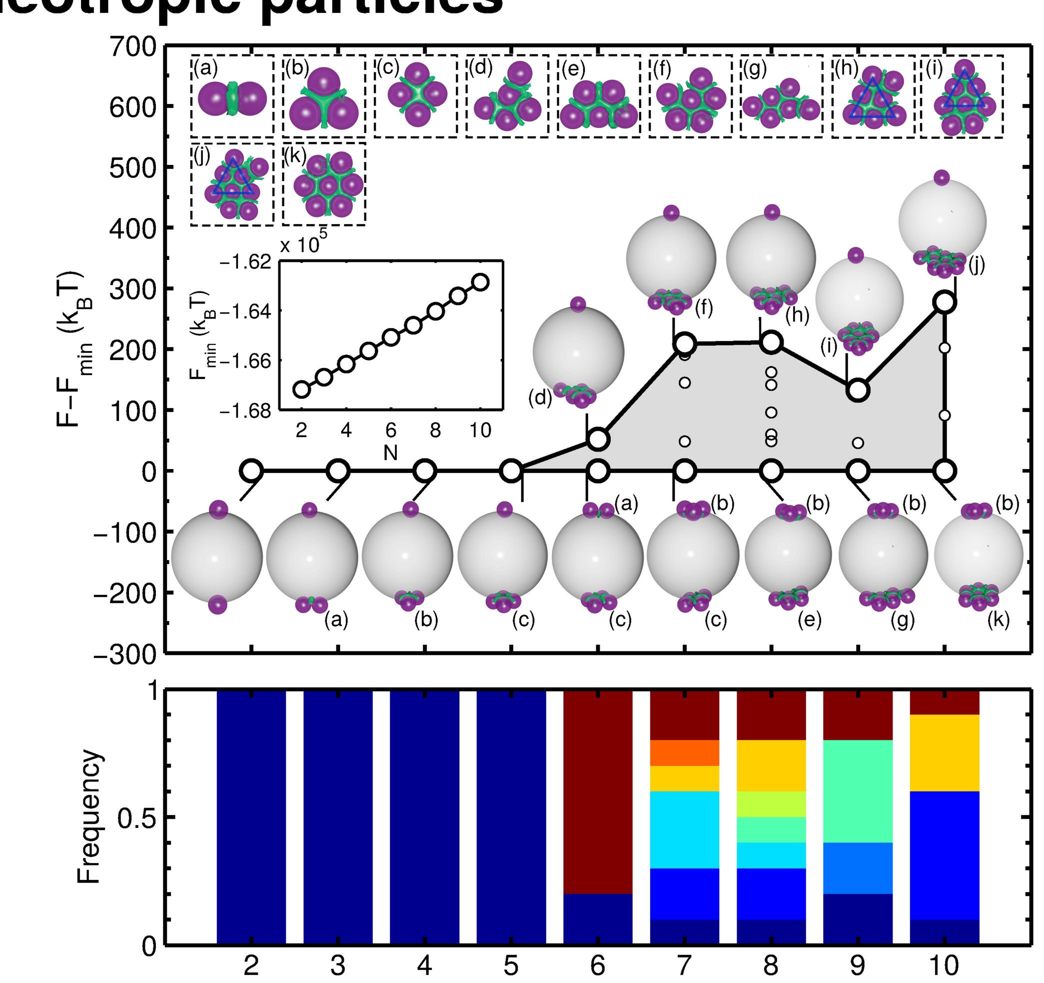


Homogeneous set

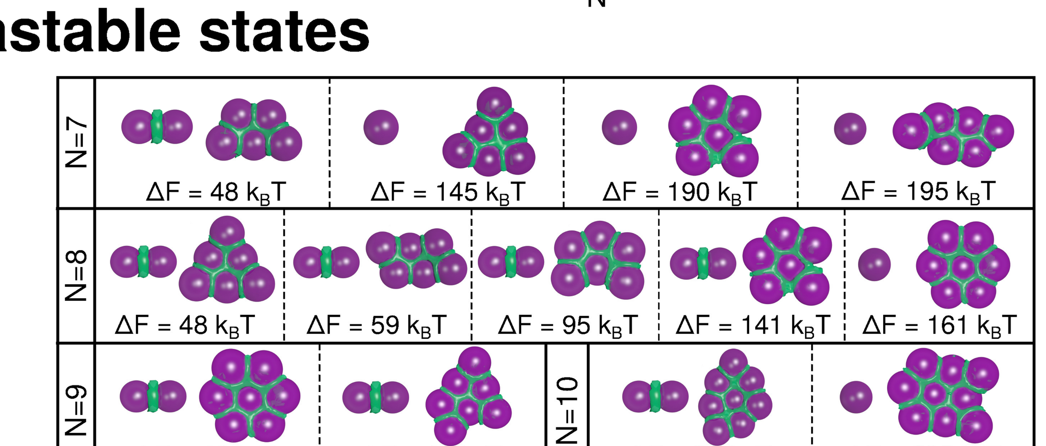
The anchoring type and strength serves as a control parameter to avoid metastable states, and guide the assembly towards the droplet boojums.

Small sets of particles follow the energetic minimization rational. For larger sets, elastic distortions are no longer the controlling mechanism. The system experiences **entropic frustration** caused by the multitude of possible assemblies.

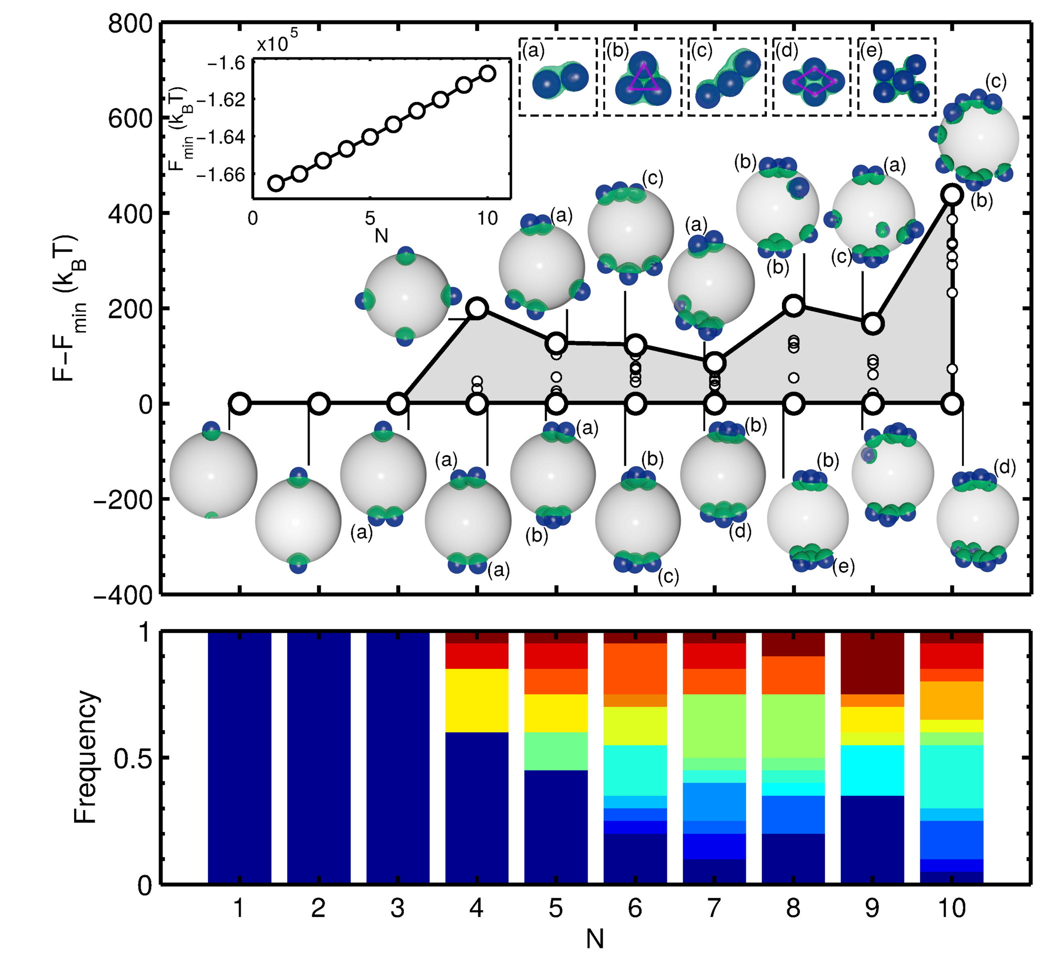
Homeotropic particles



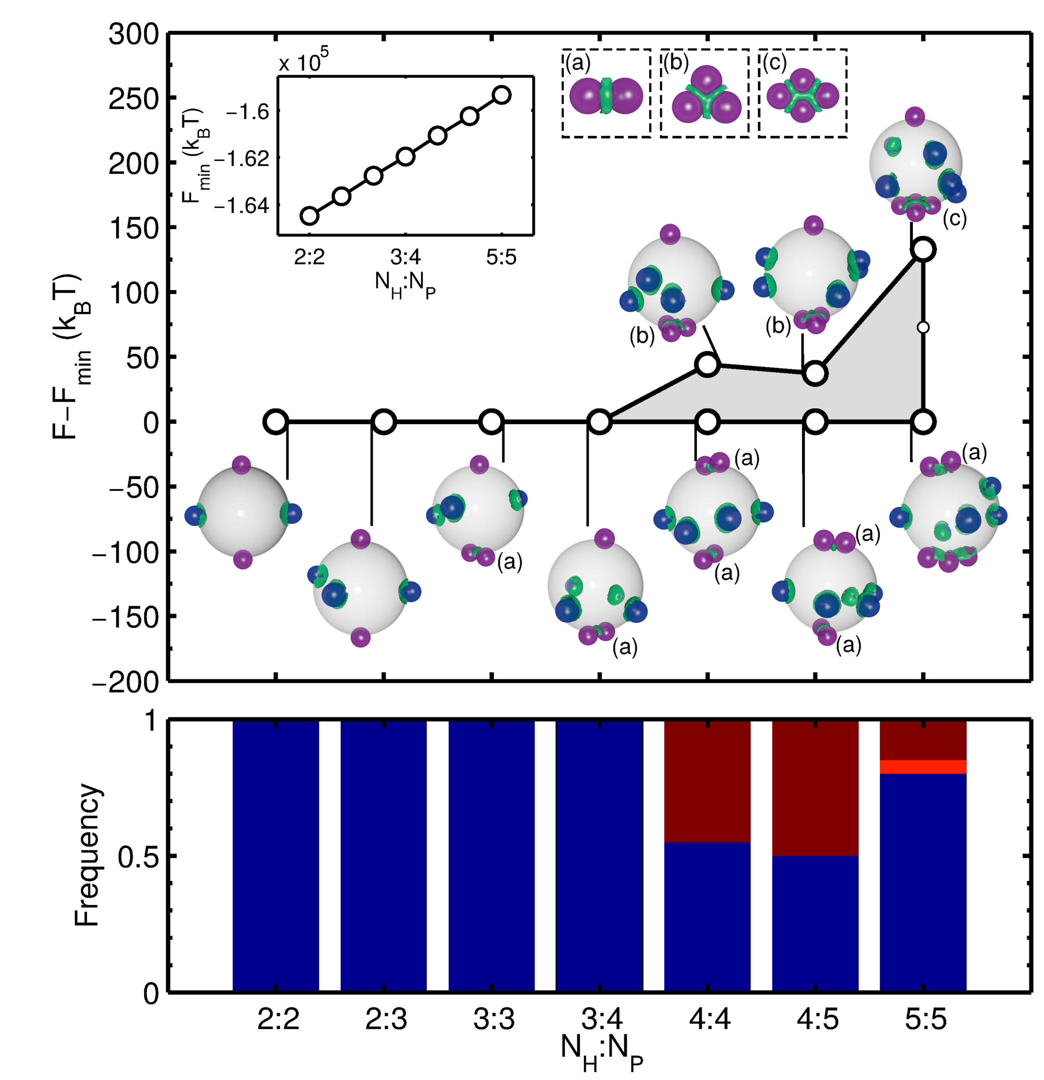
Metastable states



Planar particles



Heterogeneous set



Conclusions

- A novel algorithm allows us to explore the variety of assemblies of sets of particles adsorbed on the surface of a bipolar droplet.
- Homeotropic and planar particles assemble into closed-packed structures, and frustrate into various geometric arrays as the number of particles increases.
- The trapped configurations are caused by entropic frustration, when energetically is more favorable to form different arrays than to balance the number of particles at the boojums.

FULBRIGHT COLOMBIA
NSF
THE UNIVERSITY OF CHICAGO RESEARCH COMPUTING CENTER