A Microscopic Theory of Entropic Bonding

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Session: Faculty Candidates in CoMSEF/Area 1a

Q&A Session: Monday, November 16 (8:00 AM – 9:00 AM PST)
Entropy Maximization Drives Assembly

\[ F = U - TS \]

Low orientational entropy

Low translational entropy


Compression
Emergent Directional Entropic Force Drives Crystallization

Hard Sphere


Hard Polygon

Ye et al., PNAS, 2009

Hard Polyhedron

Hard Particle Monte Carlo

Damasceno et al., *Science*, 2012

Lee et al., *PNAS*, 2019

Schilling et al., *Phys. Rev. E*, 2005

Develop Theoretical Framework For \textit{a priori} Prediction of Entropic Crystallization
Thought Experiment

Increase Packing Fraction ($\eta$)

Maps out system free volume
Pseudoparticle ansatz

Increase Packing Fraction ($\eta$)

Maps out system free volume
Pseudoparticle ansatz

Incompressibility approximation

\[ N\langle \rho_p(l_m) \rangle + \langle \rho_q(l_m) \rangle = 1 \]

Mean-field Shape-Pseudoparticle Potential

\[ \beta U(\gamma, l_m) \sim \frac{1}{l_m^2(\Delta l_m)} \left\{ \ln[\rho_q(\gamma, l_m)] - \beta \mu_q(\gamma) \right\} \]
Pseudoparticle ansatz

Equilibrium Pseudoparticle Distribution

\[ \nabla^2 + \beta \nabla^2 U - (\beta \nabla U)^2 \rho_q = E \rho_q \]

Mean-field Shape-Pseudoparticle Potential

\[ \beta U(\gamma, l_m) \sim \frac{1}{l_m^2(\Delta l_m)} \left\{ \ln \left[ \rho_q(\gamma, l_m) \right] - \beta \mu_q(\gamma) \right\} \]
Converting to Shape Coordinates – Shape Orbitals

\[ \nabla^2 + \beta \nabla^2 U - (\beta \nabla U)^2 \] \[ \rho_q = E \rho_q \]
Crystalline Assemblies and Densest Packings of a Family of Truncated Tetrahedra and the Role of Directional Entropic Forces

Pablo F. Damasceno†, Michael Engel‡, and Sharon C. Glotzer†§†
Degenerate Quasicrystal of Hard Triangular Bipyramids

Amir Haji-Akbari, Michael Engel, and Sharon C. Glotzer

Density Dependent Lattice Transition
Entropic colloidal crystallization pathways via fluid–fluid transitions and multidimensional prenucleation motifs

Sangmin Lee, Erin G. Teich, Michael Engel, and Sharon C. Glotzer

PNAS July 23, 2019 116 (30) 14843-14851; first published July 8, 2019; https://doi.org/10.1073/pnas.1905929116
\[ \left[ -\nabla^2 + V \right] \Psi = E \Psi \]

Atomic

Entropic

\[ \left[ \nabla^2 + \nabla^2 U - (\nabla U)^2 \right] \rho_q = E \rho_q \]

Similarities to quantum motivates our introduction of the “entropic bond”
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Unused Slides
"Entropic Bond" now sounds counterintuitive.

Converting to Shape Coordinates – Shape Orbitals

“Orbital” Overlap Governs Assembly Behavior

\[ (\nabla^2 + \beta \nabla^2 U - (\beta \nabla U)^2) \rho_q = E \rho_q \]
Equilibrium Orientation and Distance – “Bonding” Orbitals

\[ \nabla^2 \psi + \beta \nabla^2 U - (\beta \nabla U)^2 \psi = E \rho_q \]
Degenerate Quasicrystal of Hard Triangular Bipyramids

Amir Haji-Akbari,1 Michael Engel,1 and Sharon C. Glotzer1,2,*

Density Dependent Lattice Transition
Simple Lattice Prediction
Emergent Directional Entropic Force Drives Crystallization

van Anders et al., *PNAS*, 2014

Ramasubramani et al., *Comp. Phys. Comm.*, 2020