Order and Disorder in Soft Materials

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Disorder & Entropy
Tiny (micron-size) Particles in Water

73 μm
Mixtures of tiny ‘pool balls’ & ‘marbles’
S = ENTROPY
W = Number of states (configurations) Accessible to Thermodynamic System with Energy E
Entropy, N Gas Particles in Box

Number of Configurations that fill entire box, far exceeds number of configurations that fill one quarter of the box.

System evolves to maximize entropy (i.e. become more disordered in absence of external influences).

Maximum Entropy Maximizes Free Volume per Particle
More Disorder, Greater Entropy

- Ordered Arrangement (Small Entropy)
- Disordered Mixture (Large Entropy)

System evolves to disordered mixture.
Free Energy \((F)\)

\[
F = U - TS
\]

internal energy associated with particle positions

tendency to disorder

Phases of Matter (solid, liquid, gas) minimize free energy
Conventional Solids & Liquids/Gases

As temperature increases:

- **Solid**: U large & negative, TS small. U dominates S.
- **Gas**: U ~ 0, TS large. S dominates U.

F = U - TS
Hard Sphere Systems

No attractive energy from $U$!

$F = -TS$ (only depends on entropy)

Hard Sphere phases maximize entropy!
Entropy Depends on Free Volume per Particle

More room to move $\Rightarrow$ Larger Entropy, Lower Free Energy
Hard Sphere Crystallization

Phase diagram

Ordered Crystal Maximizes Free Volume per Particle (Entropy)!

Binary Systems

$\phi_S, \phi_L, a_L/a_S$
Entropic Forces: Binary Particle Mixtures

Moving 2 large spheres together increases volume accessible to small spheres


Free energy, $F$

Free-energy gradient $\rightarrow$ Force

Free energy $F = -\frac{3}{2} \alpha \phi S k_B T$

$\Delta F = -T \Delta S$
Entropic Attraction Between Large Spheres

Crocker, Matteo, Dinsmore, Yodh,
Physical Review Letters v. 82, 4352 (1999)
Effect of Adding Small Particles to Suspension

click to play

2μm

150nm
Fluid Phase  Wall Crystalline Phase


Increasing $\Phi_s$
“Order” from More “Disorder”
RODS: Packing and Orientational Entropy

900 nm

• *fd* virus: 900 nm length 7 nm diameter

J. D. Bernal (1936), L. Onsager (1949)

Orientational Entropy ↔ Packing Entropy

Ratio: L/πD
Excluded Volume Depends on Rod Orientation

isotropic-nematic phase coexistence

isotropic

nematic

crossed polarizers

Dogic and Fraden, PRL 1997
Summary

• Entropy, Volume ‘maximization’ dominate Self-Assembly of Soft Matter
• More “Disorder” can lead to “Ordered” Soft Matter Structures.