Order and Disorder in Soft Materials

Arjun G. Yodh
Department of Physics & Astronomy
Laboratory for Research on the Structure of Matter
University of Pennsylvania, Philadelphia, PA

Acknowledgements:
Peter Yunker, Zexin Zhang, Piotr Habdas (Saint Joseph’s University)
National Science Foundation (MRSEC)
Disorder & Entropy
Tiny (micron-size) Particles in Water
Mixtures of tiny ‘pool balls’ & ‘marbles’

2µm
150nm
S = ENTROPY
W = Number of states (configurations) Accessible to Thermodynamic System with Energy E
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)

\[ F = U - TS \]

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

- **Solid**
  - $U$ is large and negative
  - $TS$ is small

- **Gas**
  - $U \approx 0$
  - $TS$ is large

- **Energy**
  - $U$ dominates $S$
  - $S$ dominates $U$

- **Free Energy**
  - $F = U - TS$
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

Cage Volume, $V^*$

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

Phase diagram

"Order" From More "Disorder"

Ordered Crystal Maximizes Free Volume per Particle (Entropy)!

Binary Systems

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

Excluded Volume

‘Recovered’ Excluded Volume

Moving 2 large spheres together increases volume accessible to small spheres

Entropic Attraction Between Large Spheres

Effect of Adding Small Particles to Suspension

2 μm

150 nm

click to play
Increasing $\Phi_s$

“Order” from More “Disorder”
RODS: Packing and Orientational Entropy

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

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

Orientational Entropy ↔ Packing Entropy
Excluded Volume Depends on Rod Orientation

isotropic-nematic phase coexistence

Dogic and Fraden, PRL 1997
Summary

• Entropy, Volume ‘maximization’ dominate Self-Assembly of Soft Matter

• More “Disorder” can lead to “Ordered” Soft Matter Structures.