“Entropy in Self-Assembly”

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Outline

• Entropy and Order, $\Omega$ (Hard-Sphere Crystallization, Onsager Theory, Entropy in the ground state (Networks, Crystal selection).

• Entropy attracts (Depletion Interactions, Safran, DNA functionalized Colloids)

• Self-Assembly

• When energy and entropy compete (DHS, Re-entrant gel)
Fig. 1 Examples of different manifestations of entropy. A two-component system in states with segregated components (a) has less entropy than in states where components are spatially intermixed (b). Particles crowding in random configurations (c) could avoid jamming by arranging into orderly patterns (d), thus allowing access to more free volume around each particle (dashed circles). Rod-like particles have more rotational entropy if allowed to have uncorrelated axial orientations (f), but may align and lose orientational entropy if this is compensated by gains in packing entropy (e). Whole polymer chains typically have negligible translational or rotational entropy but have significant conformational entropy; chains lose conformational entropy when forced to have too large end-to-end distances (g) as this reduces the number of conformations accessible when less constrained (h).
Phase Transition for a Hard Sphere System

B. J. Alder and T. E. Wainwright

University of California Radiation Laboratory, Livermore, California
(Received August 12, 1957)

J. Chem. Phys. 27, 1208 (1957)
Which one is more disordered?
**Hard Spheres (HS)**

Equilibrium properties

- Hard spheres present a fluid–solid phase separation due to entropic effects
Sterically stabilized PMMA particles (polydispersity 5-10 %)
Entropy in hard-spheres fluid

At constant $V$, we need to maximize the entropy

1) “Configurational” entropy (topological entropy)
2) Translational (Vibrational) Entropy (cage entropy)
A proxy to translational Entropy...

Fluid

FCC crystal

Mean Square Displacement ($\sigma_i^2$)

\[ \text{MSD} = |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \]
\(
\beta = 0.54
\)

\(\phi = 0.495\)

Stable Crystal

Coexistence

Stable Fluid

\(\text{Fluid Entropy (CS)}\)

\(\text{FCC Crystal Entropy (Hill)}\)

\(\beta P = \frac{dS}{dV}\)
Orientational Entropy

THE EFFECTS OF SHAPE ON THE INTERACTION OF COLLOIDAL PARTICLES

BY LARS ONSAGER
Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut

ANNALS NEW YORK ACADEMY OF SCIENCES 1949
Isotropic-Nematic Transition (Onsager Theory)

Isotropic

Nematic
Let’s assume that particles can be considered distinct according to the orientation of their principal axis \( a \). Then, the partition function of an ideal gas of these particles can be written as

\[
Z = \prod_i \frac{1}{\Delta N_i!} \left[ \int \int dr d\Omega \right]^{\Delta N_i}
\]

and the corresponding free-energy (defining \( \Delta \Omega_i = \sin \theta_i \Delta \theta_i \Delta \phi_i \)) as

\[
- \frac{S}{k_B} = \sum_i \Delta N_i \left[ 1 + \ln \left( \frac{V \Delta \Omega_i}{4\pi \Delta N_i} \right) \right]
\]

If we add the virial contribution, thus going beyond the ideal gas approximation, one obtains

\[
- \frac{S}{k_B} = \sum_i \Delta N_i \left[ 1 + \ln \left( \frac{V \Delta \Omega_i}{4\pi \Delta N_i} \right) \right] + \frac{1}{2V} \sum_{i,j} \beta(a_i, a_j) \Delta N_i \Delta N_j
\]

where \( \beta(a_i, a_j) \) is the virial coefficient (the excluded volume) between two particles oriented as \( a_i \) and \( a_j \).

For cylinders of length \( l \) and diameter \( d \), indicating with \( \gamma \) the angle between \( a_i \) and \( a_j \)

\[
- \beta(\gamma) = \frac{\pi}{2} d^3 \sin \gamma + \frac{\pi}{2} l^2 d + \frac{\pi}{2} ld^2 |\cos \gamma| + 2ld^2 E(\sin \gamma) + 2l^2 d |\sin \gamma|
\]

where

\[
E(\sin \gamma) = \int_0^{\frac{\pi}{2}} (1 - \sin^2 \gamma \sin^2 \phi)^{1/2} d\phi
\]

If \( L \gg d \),

\[
\beta(\gamma) = -2l^2 d |\sin \gamma|
\]
\[ \phi - I - N = 4 \]

\[ \frac{D}{L} = 90 \]

\[ \gamma = 90 \]

significant reduction of sampled phase space !!!!
It is convenient to normalize $\Delta N_i$ by $N$, such that $f(a_i)$ becomes the probability of observing a particle oriented in the solid angle $\Delta \Omega_i$. In this way

$$\Delta N_i = N f(a_i) \Delta \Omega_i \quad \text{with} \quad \int f(a_i) d\Omega = 1$$

In the isotropic case, all orientations are equally probable and $f(a_i) = \frac{1}{4\pi}$.

For the nematic case, we do not know a priori $f(a)$. Onsager postulated a functional form for $f(a)$ based on an additional parameter $\alpha$ that was then fixed by maximizing the nematic entropy. His choice was (calling $\theta$ the angle between $a$ and the nematic direction)

$$f(\theta) = \left( \frac{\alpha}{4\pi \sinh \alpha} \right) \cosh(\alpha \cos \theta)$$

Onsager shows how to calculate $\frac{1}{2V} \int \int \beta(\gamma) \frac{N^2}{(4\pi)^2} d\Omega d\Omega'$ when $\alpha \gg 1$ as well as how to maximize $S$ to evaluate $\alpha$.

Now let's compare the isotropic and the nematic case. First, let's highlight the orientational entropy:

$$-\frac{S}{k_B} = \sum_i \Delta N_i \left[ 1 + \ln \left( \frac{V \Delta \Omega_i}{4\pi \Delta N_i} \right) \right] =$$

$$\int N f(a_i) \Delta \Omega_i \left[ 1 + \ln \left( \frac{V}{4\pi N f(a_i)} \right) \right] = N \left[ 1 + \ln \left( \frac{V}{N} \right) \right] - N \int f(a_i) \ln \left( 4\pi f(a_i) \right)$$

The last contribution is the orientational entropy.
\[ \alpha = 10, \ f(\theta) \]
In the case of the nematic, there is an additional contribution equal to

$$\int f(a_i) \ln (4\pi f(a_i)) = \log \alpha - 1 + \frac{2}{3\alpha}$$

This contribution diverges to minus infinity with growing $\alpha$, as expected by localization in classical physics.

Let’s see now $\beta_2$. For the isotropic case, always in the limit $L \gg d$, (using $\int_0^\pi \sin^2 \gamma d\gamma = \pi/2$ and $\int_0^{2\pi} d\phi = 2\pi$)

$$\sum_{i,j} \beta(a_i, a_j) \Delta N_i \Delta N_j = 2l^2d \int \int \beta(\gamma) \frac{N^2}{(4\pi)^2} d\Omega d\Omega' = N^2 \frac{1}{4\pi} \int \beta(\gamma) \sin \gamma d\gamma d\phi = -2l^2dN^2 \frac{\pi}{4}$$

The corresponding expression for the nematic case (see Onsager article)

$$N^2 \int \beta(\gamma) f(\Omega) f(\Omega') \sin \gamma d\gamma d\phi \approx -2l^2dN^29\sqrt{2}\alpha^{-1/2}\pi^{-3/2}$$

which approaches zero for large values of $\alpha$. 
Nematic to...

- Smectic
- Chiral-Cholesteric
- Discotic
- Biaxial Nematic
- Twist-bend Nematic
How do we calculate the fluid entropy numerically

\[ F = U - TS \quad dF = dU - TdS - SdT = dU - dQ - SdT = -PdV - SdT \]

Along an isotherm (which does not cross a first-order line)

\[ dF = -PdV \quad F(V, T) = F_{\text{ideal-gas}}(V, T) - \int_{\infty}^{V} P_{\text{ex}}(V')dV' = F_{\text{ideal-gas}}(V, T) - \int_{0}^{N/V} \frac{P_{\text{ex}}(\rho)}{\rho^2}d\rho \]
How do we calculate the crystal entropy (free-energy) numerically

\[
H(\lambda) = (1 - \lambda)H_E + \lambda H_{\text{model}}
\]

\[
H(0) = H_E \quad H(1) = H_{\text{model}}
\]

\[
\beta F(\lambda) = -\ln \int e^{-\beta H(\lambda)} d\mathbf{r}^N \quad \frac{\partial \beta F(\lambda)}{\partial \lambda} = \frac{1}{\int e^{-\beta H(\lambda)} d\mathbf{r}^N} \frac{\partial}{\partial \lambda} \int e^{-\beta H(\lambda)} d\mathbf{r}^N =
\]

\[
= \frac{1}{\int e^{-\beta H(\lambda)} d\mathbf{r}^N} \int (H_{\text{model}} - H_E) e^{-\beta H(\lambda)} d\mathbf{r}^N = \langle H_{\text{model}} - H_E \rangle > \lambda
\]

Then

\[
\beta F(1) = \beta F(0) + \int_0^1 d\lambda \frac{\partial \beta F(\lambda)}{\partial \lambda} = \beta F(0) + \int_0^1 \langle H_{\text{model}} - H_E \rangle > \lambda d\lambda
\]
Entropy and flexibility
(translation+rotation)

(networks... limited valence... patchy particles)

if the liquid reaches a fully bonded state, then it has the same energy than the crystal!
Figure 1 | Colloidal kagome lattice after equilibration. a, Triblock Janus spheres hydrophobic on the poles (black, with an opening angle of 65°) and charged in the equator section (white), are allowed to sediment in deionized water. Then NaCl is added to screen electrostatic repulsion, allowing self-assembly by short-range hydrophobic attraction. b, Fluorescence image of a colloidal kagome lattice (main image) and its fast Fourier transform image (bottom right). Scale bar is 4 μm. The top panel in c shows an enlarged view of the dashed white rectangle in b. Dotted red lines in c highlight two staggered triangles. The bottom panel in c shows a schematic illustration of particle orientations.
DNA constructs: Limited-valence patchy particles
Figure 9. (a) Schematic diagram of seeded polymerization on tetrahedral colloidal clusters. (b) and (c) SEM image of colloidal clusters ($N = 1–7$) and their patchy particles. (Reprinted with permission from [10]. Copyright 2012 Nature Publishing Group.)
All particles are bonded with four neighbours.

There are loops of different length.

Particles “vibrate” around equilibrium positions.
How about (low density) crystals?

Entropy decides the most stable phase (exactly as in HS!)

Competition between:

- Number of microstates accessed at fixed bonding” (vibrational entropy) \( (S_{\text{vib}}) \)

- Number of different bonding topologies (configurational entropy) \( (S_{\text{conf}}) \)

\[ S_{\text{xt}} - S_{\text{fluid}} \]
Increasing the bond angle increases both entropies. Same rate?
On increasing flexibility: Ultrastable liquids!

Liquids more stable than crystals in particles with limited valence and flexible bonds

Frank Smallenburg* and Francesco Sciortino
Key elements for liquid stability at T=0 K: (ultrastable liquids!)

- Large flexibility of the angular interactions: (wide variety of networks, increasing $S_{\text{conf}}$)
- Low valence. Small density of the coexisting liquid phase

Thermodynamically stable!
Common Physical Framework Explains Phase Behavior and Dynamics of Atomic, Molecular, and Polymeric Network Formers

Stephen Whitelam, Isaac Tamblyn, Thomas K. Haxton, Maria B. Wieland, Neil R. Champness, Juan P. Garrahan, and Peter H. Beton
Crystal Selection by Entropy

Diamond

BCC
(2 interpenetrated diamond)

J. Chem. Phys 132, 184501 2010
Crystal Selection by Entropy

Figure 1 | Sketch of the phase diagram of triblock Janus particles. Self-assembly occurs when the strength of the interaction between patches (depicted in red) is large enough to overcome the random forces arising from the thermal jiggling of the particles. In this case they crystallize into a kagome lattice, or a closed-packed triangular lattice at higher density.
Crystal Selection by Entropy

\[ \theta = \pi/3 \]

\[ \theta > \pi/3 \]

\[ \Theta = 0 \]

\[ \Theta = 2\theta - \pi/3 \]

\[ \Theta < 2\theta - \pi/3 \]

\[ 2\theta = \text{patch width} \]

\[ \Theta = \text{free rotation angle} \]
Entropic disparity

\[ \zeta = \frac{L_1}{L_2} \]

Optimizing the formation of solid solutions with components of different shapes

Fernando A. Escobedo

Citation: The Journal of Chemical Physics 146, 134508 (2017); doi: 10.1063/1.4979091

FIG. 4. Pressure-composition phase diagram for the hard-core mixture of octahedra + spheres for size ratio \( \zeta = \sigma_{1} / \sigma_{2} = 0.836 \) (equal ODP \( \sim \) 7). Phase

FIG. 5. Pressure-composition phase diagrams for hard-core mixtures of octahedra + spheres for (a) \( \zeta = 0.955 \) and (b) \( \zeta = 1.0 \). Areas shaded in

Spheres (S)

Octahedra (M)

Mixed Spheres+Octahedra (R)
Predictive Self-Assembly of Polyhedra into Complex Structures

Dense Regular Packings of Irregular Nonconvex Particles

Joost de Graaf, René van Roij, and Marjolein Dijkstra
Phys. Rev. Lett. 107, 155501 – Published 3 October 2011

Fig. 1. Polyhedra are organized into four categories of organization as indicated by different colors.
Entropic Attraction
Large HS in a bath of small HS

Which distance is most probable?
Depletion interaction

\[ S \sim n_{\text{poly}} \ln V \]
\[ S \sim n_{\text{poly}} \ln V \]

\[ \Delta S \sim n_{\text{poly}} \frac{\Delta V}{V} \]

Let’s assume we have $N$ large HS and $M$ small HS. The partition function in the $NVT$ ensemble is

$$Q_{N+M} = \frac{1}{N!\lambda_N^{3N}} \frac{1}{M!\lambda_M^{3M}} \int d\vec{r}_1...d\vec{r}_N \int d\vec{s}_1...d\vec{s}_M e^{-\beta(V_{11}(\vec{r}^N) + V_{12}(\vec{r}^N,\vec{s}^M) + V_{22}(\vec{s}^M))}$$

and let’s define

$$e^{-\beta V_{eff}(\vec{r}^N)} \equiv \frac{1}{M!\lambda_M^{3M}} \int d\vec{s}_1...d\vec{s}_M e^{-\beta(V_{12}(\vec{r}^N,\vec{s}^M) + V_{22}(\vec{s}^M))}$$

such that

$$Q_{N+M} = \frac{1}{N!\lambda_N^{3N}} \int d\vec{r}_1...d\vec{r}_N e^{-\beta V_{11}(\vec{r}^N)} e^{-\beta V_{eff}(\vec{r}^N)}$$

The total interaction potential felt by the large HS is thus the sum of the direct interaction plus (a $T$ and $\rho$ dependent) effective potential.

$$V_{tot}(\vec{r}^N) = V_{11}(\vec{r}^N) + V_{eff}(\vec{r}^N)$$
1 Asakura-Oosawa for two colloids

If \( N = 2 \) and if we assume \( V_{22} = 0 \), but retaining the excluded volume interaction for \( V_{12} \)

\[
e^{-\beta V_{\text{eff}}(\vec{r}_1, \vec{r}_2)} = \frac{1}{M! \lambda^3 M} \int d\vec{s}_1 \ldots d\vec{s}_M e^{-\beta V_{12}(\vec{r}_1, \vec{r}_2, \vec{s}_M)}
\]

Since

\[
V_{12}(\vec{r}_1, \vec{r}_2, \vec{s}_M) = \sum_{j=1}^{M} v_{12}(\vec{r}_1, \vec{r}_2, \vec{s}_j)
\]

then

\[
e^{-\beta V_{\text{eff}}(\vec{r}_1, \vec{r}_2)} = \frac{1}{M! \lambda^3 M} \left[ \int d\vec{s}_1 e^{-\beta v_{12}(\vec{r}_1, \vec{r}_2, \vec{s}_1)} \right]^M
\]
\[ V_0 = \frac{4\pi}{3} \left( \frac{\sigma_c + \sigma_p}{2} \right)^3 \]

\[ \int d\vec{s}_1 e^{-\beta v_{12}(\vec{r}_1, \vec{r}_2, \vec{s}_1)} = V - 2V_0 + V_{\text{overlap}}(|\vec{r}_1 - \vec{r}_2|) \]
\[ e^{-\beta V_{\text{eff}}(R)} = \frac{1}{M! \lambda_{M}^{3M}} [V - 2V_{0} + V_{\text{overlap}}(R)]^{M} = \frac{(V - 2V_{0})^{M}}{M! \lambda_{M}^{3M}} \left[ 1 + \frac{V_{\text{overlap}}(R)}{V - 2V_{0}} \right]^{M} \approx \frac{(V - 2V_{0})^{M}}{M! \lambda_{M}^{3M}} \left( 1 + \frac{M}{V - 2V_{0}} V_{\text{overlap}}(R) \right) \]

where \( M/(V - 2V_{0}) \equiv \rho_{M} \) is the number density of small spheres. Hence

\[-\beta V_{\text{eff}}(R) = -M \left[ \ln(\rho_{M} \lambda_{M}^{3}) - 1 \right] + \ln(1 + \rho_{M} V_{\text{overlap}}(R)).\]

Expanding the logarithm (\( \ln(1 + x) \approx -x \))

\[ \beta V_{\text{eff}}(R) = V \rho_{M} \left[ \ln(\rho_{M} \lambda_{M}^{3}) - 1 \right] - \rho_{M} V_{\text{overlap}}(R) \]

Thus, beside a \( R \)-independent term, there is an entropic effective interaction which can be written (recognising \( k_{B}T \rho_{M} \) as the ideal gas pressure \( \Pi \) exerted by the small particles)

\[ V_{\text{eff}}(R) = -k_{B}T \rho_{M} V_{\text{overlap}}(R) = -\Pi V_{\text{overlap}}(R) \]
Sphere-Sphere Intersection

\[ u(r) = \begin{cases} \infty & 0 < r < \sigma \\ -\Pi V_{\text{overlap}} & \sigma < r < \sigma + \tau \\ 0 & r > \sigma + \tau \end{cases} \]

Letting \( R_1 = R \) and \( R_2 = r \) and summing the two caps gives

\[
V = V(R_1, h_1) + V(R_2, h_2) = \frac{\pi (R + r - d)^2 (d^2 + 2dr - 3r^2 + 2dR + 6rR - 3R^2)}{12d}.
\]

\[
V_{\text{overlap}} = \frac{\pi}{12} \left[ 2(\sigma + \tau) + r \right] \left[ (\sigma + \tau) - r \right]^2
\]

\[
\tau = 0.2\sigma
\]
Same story from a different perspective

\[
\frac{r}{2} = R_d \cos \theta_0 \quad \rightarrow \quad \cos \theta_0 = \frac{r}{2R_d}
\]

\[
d\vec{F} = -P \, d\vec{a} \quad \quad da = R_d^2 \sin \theta d\theta d\phi
\]

\[
dF_x = -|d\vec{F}| \cos \theta
\]

\[
F_x(r) = \int_{-\theta_0}^{\theta_0} dF_x = -P R_d^2 \int_0^{2\pi} \int_{-\theta_0}^{\theta_0} \cos \theta \sin \theta d\theta d\phi = -2\pi P R_d^2 [1 - \cos(\theta_0)^2] = -2\pi P R_d^2 \left[ 1 - \left( \frac{r}{2R_d} \right)^2 \right]
\]

\[
V(r) = -\int_{2R_d}^{r} F_x(r') dr'
\]
Figure 9. The effective depletion potential as a function of the density of small particles. This figure shows a comparison between MD data, the theory of Mao et al [2], and the superposition approximation using the RY pair distribution functions. In every case, the short-distance behaviour coincides with the perturbation theory of reference [2], and the long-range behaviour compares very well with the superposition approximation.
Visualizzazione of depletion forces

Phase separation of a bidisperse sphere mixture:

\[ r_b = 413\text{nm}, \quad r_s = 35\text{nm}, \]

Volume fraction: \( \Phi_b = 0.02 \) (visible), (not resolved)

Fig. 1. – Optical micrographs of polystyrene spheres \((r_1 = 0.413\ \mu\text{m}, \phi_1 = 0.02)\) at a flat, glass wall. (a) With no small spheres, a low area fraction of spheres \((\eta_1^{\text{wall}})\) is seen. The spheres remain in view for much less than a second before diffusing away into the bulk. (b) When small spheres are added \((r_2 = 0.035\ \mu\text{m}, \xi = .084, \phi_2 = 0.08)\), \(\eta_1^{\text{wall}}\) increases. The large spheres diffuse along the surface for an average of minutes before escaping to the bulk. The small spheres are invisible. (c) With \(\phi_2 = 0.16\), a crystallite made of the large spheres can be seen at the surface (after \(\approx 40\) h).

A.D. Dinsmore, P. B. Warren, W. C. K. Poon, and A. G. Yodh,
For depletion interactions, arrest at low $\phi$ (gelation) is the result of a phase separation process interrupted by the glass transition.
Depletion: shape and roughness

Fig. 1.28  Shape-selective separation induced by depletion forces
Osmotically driven shape-dependent colloidal separations

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FIG. 3. (Color) Schematic representations of the excluded volumes (yellow) between (a) two spheres of radius $a_s$; (b) two disks of radius $a_d$, oriented face-to-face; and (c) two disks oriented side by side with an edge overlap distance $z$. The small purple spheres represent micelles (not to scale).
Another example

Fig. 1.29 TEM images of a dispersion of rod-like and cube-like gold colloids. a Synthesized mixture, b sediment, c supernatant. Picture reprinted from K. Park, H. Koerner, and R. A. Vaia, Nano Lett., 10:1433, Copyright 2010, with permission from the American Chemical Society.
Fig. 1.30  A large colloidal sphere near a step edge in a sea of small spheres. The presence of the small spheres lead to depletion zones (*light grey regions*) near the walls of the container and around the big sphere. Overlap of depletion zones is indicated by the *hatched area*. This overlap volume increases the volume accessible to the small spheres, thereby increasing their entropy

**Entropic control of particle motion using passive surface microstructures**

A. D. Dinsmore*, A. G. Yodh* & D. J. Pine†
Fig. 1.31  a Colloidal ‘lock’ particles can be synthesized [284] containing a dimple into which ‘key’ particles, spherical colloids with appropriate size, can fit. b By adding depletants (polymer chains) a key can be pushed into a lock using the depletion force. Inspired by Solomon [285]
Lock and key colloids

S. Sacanna, W. T. M. Irvine, P. M. Chaikin & D. J. Pine

Figure 2 | Lock–key interactions. a, The depletion attraction potential between lock and key is proportional to the overlapping excluded volume $\Delta V$, which attains a maximum $\Delta V_{\text{max}}$ for the configuration in which the key particle, by virtue of its size and position, precisely fits into the spherical cavity of a lock particle. For all other configurations, $\Delta V < \Delta V_{\text{max}}$. Because the depletion interaction is also proportional to the density $n_p$ of the polymer depletant in solution, the interaction can be tuned by adjusting $n_p$ so that it is sufficiently strong to bind two particles only for the lock-and-key configuration. b, c, Snapshots from a movie showing an example of depletion-driven self-assembly of lock and key particles. The site-specificity of the interactions is captured in sequence b in which arrows indicate examples of successful (green) and unsuccessful (red) lock–key binding. Scale bars, 2 $\mu$m.

Figure 5 | Flexibility of the lock–key junctions in self-assembled colloidal molecules and polymers. Time-lapse optical microscopy images (left three columns), and schematics (rightmost column), show the flexibility of lock–key bonds in various assemblies (a–d), which are confined to two dimensions by being placed on a glass microscope slide. The absence of irreversible chemical bonds between the building blocks allows these ball-in-socket joints to move freely. Scale bars, 2 $\mu$m.
Surface roughness directed self-assembly of patchy particles into colloidal micelles

Playing with the properties of the co-solute

Depletant Shape...
Polymerizing solvent ...