Enrico Fermi Summer School

"Soft Matter Self-Assembly"

Varenna, June 28 - July 7 2015



Basic Concepts in Self Assembly

Francesco Sciortino

http://glass.phys.uniroma1.it/sciortino/





Search Topic SELF ASSEMBLY (WOS)

Results: 93,481

1821967-19805251981-19908,0821991-200045,0882001-2010

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First article containing the word "self-assembly" **A study of the self-assembly process in a small spherical virus formation of organized structures from protein subunits** *in vitro* By: Bancroft, J B; Hills, G J; Markham, R Virology Volume: 31 Issue: 2 Pages: 354-79

Published: 1967-Feb





What is self assembly:

The tendency of a system of particles to *spontaneously* form a well defined structure

(virus capsides, micelles, vescicles, tubes, sheets, crystals)

LAG PHASE

Amyloidogenic

von-specific

lative-state

Partial denaturatio

Complete denaturation

In brief: the approach to the free-energy minimum

Bilayer sheet

Liposome

Micelle





GROWTH PHASE

Protofibril

Bundling

Filamen

lymerizatio

Bundling

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Some examples of soft-matter self-assembly

Surface roughness directed self-assembly of patchy particles into colloidal micelles

Daniela J. Kraft^{a,1}, Ran Ni^b, Frank Smallenburg^b, Michiel Hermes^b, Kisun Yoon^c, David A. Weitz^c, Alfons van Blaaderen^b, Jan Groenewold^a, Marjolein Dijkstra^b, and Willem K. Kegel^a





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Colloids with valence and specific directional bonding

Yufeng Wang¹, Yu Wang¹, Dana R. Breed², Vinothan N. Manoharan^{3,4}, Lang Feng⁵, Andrew D. Hollingsworth⁵, Marcus Weck¹ & David J. Pine⁵





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AAAS

Science











DNA Origami



Some considerations on self-assembly (into finite size structures)

Self-assembly requires small (compared to the binding energy) temperatures to take place

The need to study the collective behavior of systems at low T (competition with crystallization and phase separation)

The need of directional (patchy) interactions

Basic thermodynamic description of self-assembly





Self-assembly requires small (compared to the binding energy) temperatures to take place



Rough estimate: bond breaks every 100 attempts....





The need to study the collective behavior of systems at low T (competition with crystallization and phase separation)







Università di Roma

The vanishing limit of the square-well fluid: The adhesive hard-sphere model as a reference system

J. Largo,^{1,a)} M. A. Miller,^{3,b)} and F. Sciortino^{1,2,c)}

The need of directional interactions

(cut the spherical square-well in a cone-well)



Figure 1. (a) Schematic representation of the patchy particles and their interactions; (b) a single patchy particle (red) with depicted Kern–Frenkel bonding volume (blue) for $\cos(\theta) = 0.4$ (corresponding to a patch coverage fraction $\chi = 0.3$ and range $\Delta = 0.5\sigma$).





The need of directional interactions



 $e^{\epsilon/k_B T} \approx 10^5$





Two "good" consequences of directional interactions...

(i) Limited valence suppresses the gas-liquid phase separation



Two "good" consequences of directional interactions...

II) Directional interactions allow for formation of non-interacting (a part from the excluded volume) aggregates, making it possible to suppress the driving force toward condensing a liquid phase







Phase Diagram of Janus Particles

PHYSICAL REVIEW LETTERS

week ending

4 DECEMBER 2009

Francesco Sciortino,¹ Achille Giacometti,² and Giorgio Pastore³

How to model "cluster" formation ?

$$Q = \prod_{n=1}^{\infty} \frac{Q_n^{N_n}}{N_n!}$$

$$Q_n = \frac{1}{n!\lambda^{3n}} \int d\vec{r_1} d\vec{r_n} d\Omega_1 ... d\Omega_n e^{-\beta V(\vec{r_1}...\vec{r_n},\Omega_1,...\Omega_n)}$$

(see lecture notes for the details)

$$N_n = Q_n \frac{N_1^n}{Q_1^n} = Q_n (\rho_1 \lambda^3)^n \qquad Q_1 = \frac{V}{\lambda^3}$$





Dimer partition function

Translational com entropy Bonding volume (entropy) Bonding energy



$$Q_{2} = \frac{1}{2!\lambda^{6}} \int' d\vec{r_{1}} d\vec{r_{2}} d\Omega_{1} d\Omega_{2} e^{-\beta V(\vec{r_{1}},\vec{r_{2}},\Omega_{1},\Omega_{2})}$$

$$Q_{2} = \frac{V}{2\lambda^{6}} \frac{4}{3} \pi [(\sigma + \Delta)^{3} - \sigma^{3})] \frac{[1 - \cos(\theta)^{2}]}{4} e^{\beta \epsilon}$$

















A unified view of polymer, dumbbell, and oligonucleotide DNA nearestneighbor thermodynamics J SantaLucia - Proceedings of the National Academy of Science 1998



Analogies with "chemical reaction" languages

$$\begin{split} N_1 + N_1 &<=> N_2 \\ K \text{ is a volume} \\ \frac{[N_2]}{[N_1]^2} = K \\ Q_2 &= \frac{VV_b}{2\lambda^6} e^{\beta\epsilon} = \frac{V}{\lambda^3} Q_{bond} \\ Q_{bond} &= \frac{V_b}{2\lambda^3} e^{\beta\epsilon} \end{split}$$



K contains only information related to the bonding





The most elementary self-assembly process: Equilibrium polymerization



1 NOVEMBER 2012 | VOL 491 | NATURE | 51



Colloids with valence and specific directional bonding

– Yufeng Wang¹, Yu Wang¹, Dana R. Breed², Vinothan N. Manoharan^{3,4}, Lang Feng⁵, Andrew D. Hollingsworth⁵, Marcus Weck¹ & David J. Pine⁵



For persistent chains....

$$Q_n^{f=2} = \frac{1}{n!\lambda^{3n}} \frac{\int d\vec{r}_1 d\vec{r}_n d\Omega_1 d\Omega_n \exp{-\beta V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_n, \Omega_1, ...\Omega_m)}}{\int d\Omega_1 d\Omega_n}$$
$$Q_n^{f=2} = 2^{n-1} \frac{V}{\lambda^3} \left[\frac{V_b}{\lambda^3} \exp{(\beta \epsilon)} \right]^{n-1} = \frac{V}{\lambda^3} \left[2\frac{V_b}{\lambda^3} \exp{(\beta \epsilon)} \right]^{n-1} = \frac{V}{\lambda^3} Q_{bond}^{n-1}$$

$$N_{n} = \frac{N_{1}^{n}}{Q_{1}^{n}}Q_{n} = \left(\frac{N_{1}\lambda^{3}}{V}\right)^{n} \frac{V}{\lambda^{3}}Q_{bond}^{n-1} = \rho_{1}V\left(\rho_{1}\lambda^{3}Q_{bond}\right)^{n-1} = N_{1}\left(\rho_{1}\lambda^{3}Q_{bond}\right)^{n-1}$$

$$= N_1 e^{(n-1)\ln(\rho_1 \lambda^3 Q_{bond})}$$















A schematic model for micelle formation

Two states: Monomer (size 1) and Micelle (size M)



ητ M

$$N = N_1 + MN_M = N_1 + MQ_M \frac{N_1^M}{Q_1^M}$$

$$Q_M = \frac{V}{\lambda^3} \left(\frac{V_b}{\lambda^3}\right)^{M-1} \exp(-\beta E_M)$$

$$\frac{N_1}{N} = 1 - M \left(\frac{N_1}{N}\right)^M \left(\frac{NV_b}{V}\right)^{M-1} \exp(-\beta E_M)$$

$$\bigotimes \text{SAPIENZA} \quad x = 1 - x^M A \quad \text{Colors with defined response}$$









A last example... cooperative polymerization

$$N_{1} + N_{1} <=> N_{2} \qquad \frac{[N_{2}]}{[N_{1}]^{2}} = K_{2}$$

$$N_{2} + N_{1} <=> N_{3} \qquad \frac{[N_{3}]}{[N_{1}][N_{2}]} = K_{3}$$

$$N_{n-1} + N_{1} <=> N_{n} \qquad \frac{[N_{n}]}{[N_{n-1}][N_{1}]} = K_{3}, \qquad n \ge 3$$

$$\rho = \sum_{1}^{\infty} n[N_{n}] = [N_{1}] + 2K_{2}[N_{1}]^{2} + \sum_{3}^{\infty} nK_{2}K_{3}^{n-2}[N_{1}]^{n} = [N_{1}] + \sum_{2}^{\infty} nK_{2}K_{3}^{n-2}[N_{1}]^{n}$$





$$K_3 \rho = K_3 [N_1] + \frac{K_2}{K_3} \frac{(2 - K_3 [N_1]) K_3^2 [N_1]^2}{(1 - K_3 [N_1])^2}$$





THE JOURNAL OF CHEMICAL PHYSICS 140, 144902 (2014)

Cooperative polymerization of one-patch colloids

Teun Vissers,^{a)} Frank Smallenburg,^{a)} Gianmarco Munaò, Zdeněk Preisler, and Francesco Sciortino *Sapienza, Università di Roma, Piazzale Aldo Moro 2, 00185, Roma, Italy*

$$T/\epsilon = 0.145$$
 $T/\epsilon = 0.140$ $T/\epsilon = 0.130$



FIG. 1. Snapshots of constant *NVT* simulations, for $k_{\rm B}T/\epsilon = 0.145$ (a), $k_{\rm B}T/\epsilon = 0.14$ (b), and $k_{\rm B}T/\epsilon = 0.13$ (c), all at density $\rho\sigma^3 = 0.05$. The attractive hemispheres are depicted in orange. Particles in a tube-like environment, according to the order parameter in Eqs. (5) and (6), are labeled black/orange. Other particles are blue/orange.

How do we calculate numerically cluster partition functions?

$$Q_n = \frac{1}{n!\lambda^{3n}} \int d\vec{r_1} d\vec{r_n} d\Omega_1 ... d\Omega_n e^{-\beta V(\vec{r_1}...\vec{r_n},\Omega_1,...\Omega_n)}$$

R. Pool and P. G. Bolhuis, The Journal of Physical Chemistry B 109, 6650 (2005),http://pubs.acs.org/doi/pdf/10.1021/jp045

R. Fantoni, A. Giacometti, F. Sciortino, and G. Pastore, Soft Matter 7, 2419 (2011).[576f.

D. J. Kraft, R. Ni, F. Smallenburg, M. Hermes, K. Yoon, D. A. Weitz, A. van Blaaderen, J. Groenewold, M. Dijkstra, and W. K. Kegel, Proc Natl Acad Sci U S A 109, 10787 (2012).[20] T. Vissers, Z.

Preisler, F. Smallenburg, M. Dijkstra, and F. Sciortino, J. Chem. Phys. 138, 164505 (2013).





GC MC in cluster space – (requires a definition of cluster)

$$P(n, z, T) = \frac{z^n Q_n}{\sum_n z^n Q_n}$$
$$\frac{P(n, z, T)}{P(1, z, T)} = \frac{z^{n-1} Q_n}{Q_1}$$

$$Q_n = V \frac{P(n, z, T)}{z^{n-1}P(1, z, T)}$$











Summary

The need of operating at low T (compared to ε)
The need of directional attractive interactions (or alternatively of highly non-monotonic interaction potentials
The need to suppress collective phenomena (competition with crystallization and phase separation)
How to develop a thermodynamic description of the clustering process, highlighting the role of the ratio between the bonding volume and the volume per perticle and the bonding volume and the perticute.

volume per particle and the bonding energy, the microscopic expression of the competition between the entropic driving force disfavoring self-assembly and the energetic driving force favoring the formation of low energy aggregates

How to predict the structure of the aggregate from the knowledge of the interaction potential (direct) or how to design the interaction potential to spontaneously assemble a desired structure (inverse).

How *external fields* and *interfaces* can be exploited to modify the routes toward the assembly of ordered structures



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Enjoy the school !!!









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