

Tutorial 2: Core-corona colloidal particles in 2D.

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1 Introduction

A core-corona particle is a system made of a core of diameter D covered by a corona of length λ , (formed by grafted soft molecules or ligands such as linear, circular or branched polymers), interacting to another cores through repulsive hard interactions while the coronas interact to another coronas via a purely repulsive soft interactions [1, 2]. The self-assembly of designed colloids and coated nanoparticles is an ubiquitous phenomenon where the particles self-organize or "self-assemble" creating different fluid and crystalline ordered structures without any external chemical or physical field. Self-assembled materials are of great importance in the development of nanoscience and nanotechnology in fields such as photonics, drug delivery and oil recovery science [1, 2, 3].

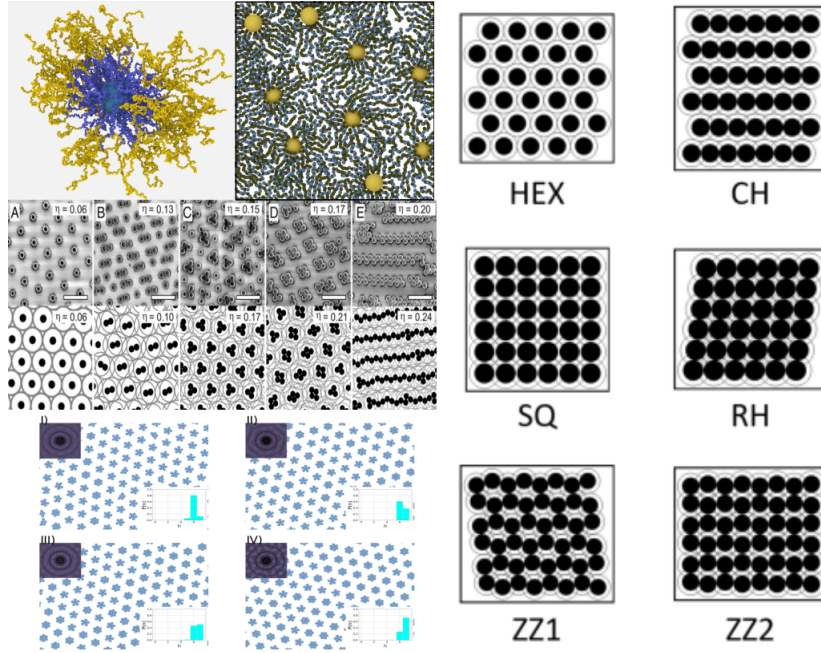


Figure 1: Core corona particles: self-assembled mesophases from experiments and computer simulations.

2 Self-assembling of core-corona particles

The absence of attractive interactions among core-corona particles makes the Free energy a function only of the Entropy and the Temperature, thus the effective interactions among core-corona particles are entropic in nature. The thermodynamical properties turn to be quite different with respect those modeled by using attractive-repulsive pair potentials. Due to the intrinsic interplay between the two scales defined by the core diameter D and the corona length δ , (the competition between the hard-core and the soft-shoulder interactions), the system minimizes the Free energy F by avoiding corona overlapping leading to the alignment of contiguous particle hard cores being responsible for the self-assembling of different fluid and crystalline mesophases [4, 5]. Experiments and computer simulations, have revealed the existence of different thermodynamic stable mesophases including isotropic and low dense hexagonal fluid phases, stripes, kagome, medium hexagonal fluid, honeycomb-like solid, square and high dense hexagonal crystalline solid mesophases (see figure 1). Another self-assembled colloidal such as cluster have been observed as well.

3 The Hard Core Square Shoulder model

The core-corona self-assembling phenomenon has been studied theoretically by means of the Hard Core Square Shoulder (HCSS) model mostly in two dimensions. Here the particles interact through a potential composed of an infinite Hard wall plus a "shoulder" of height ϵ . The hardcore wall is placed at a distance δ (the particle diameter) while the shoulder have a characteristic length δ (corona length) of height ϵ , (see figure 2) [2]. By using Monte Carlo simulations is possible to observe a broad sequence of different

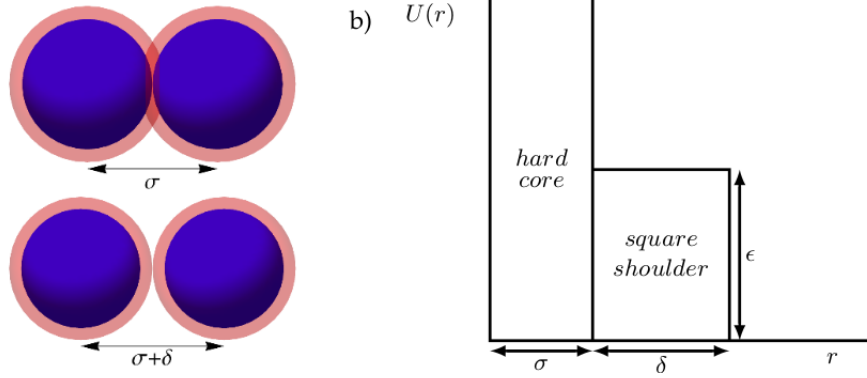


Figure 2: Ideal HCSS model using a hard wall plus a square shoulder.)

self-assembled networks.

4 The Lennard-Jones-Gauss model

In this tutorial, we use LAMMPS package to address the self-assembling of colloidal particles. We use Molecular Dynamics using a force continuous potential that mimicks the HCSS ideal model namely the Lennard-Jones-Gauss potential, this has an effective core diameter of $\sigma = 1.2$ and a corona $\delta = 1.2$ [4]:

$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} \right] + u_o \exp(-A_k(r_{ij} - r_k)^2) \quad (1)$$

where r_{ij} is the distance between particle i and j , σ is the particle diameter and ϵ is the well potential, here u_o is a constant and A is related to the variance of the Gaussian component and $r_o = 0.7\sigma$.

This potential is setup by using a tabulated potential in LAMMPS. For this, the potential and the force

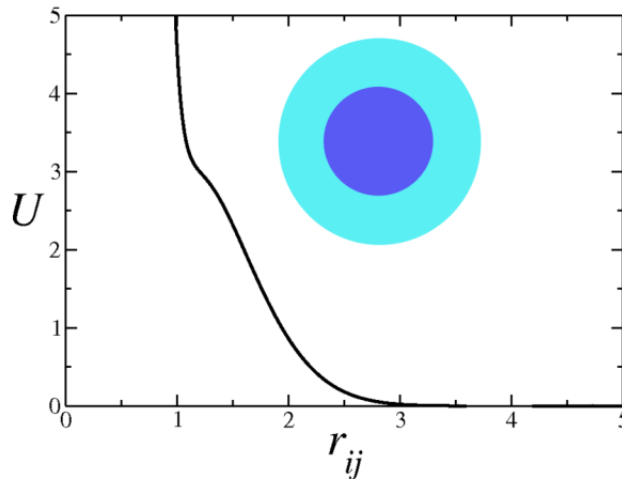


Figure 3: Simplified potential using a force continuous potential.

are both functions of the relative position and are numerically implemented. The code for studying the core-corona self-assembling is quite similar to the one used in the Lennard-Jones fluid case addressed in tutorial 1. The structural properties of the clusters at zero temperature to be calculated. To characterize the structure of the fluid, we compute the Radial Distribution Function (RDF) given by:

$$g(r) = \left\langle \frac{1}{\rho^2} \sum_{i=1}^N \sum_{j \neq i}^N \delta(r - r_i) \delta(r' - r_j) \right\rangle \quad (2)$$

where r is the particle position, N is the number of particles, ρ is the density and δ is the Dirac δ . In addition, the Static Structure Factor is computed as:

$$S(k) = \left\langle \frac{1}{N} \sum_{i=1}^N \sum_{j \neq i}^N \exp(-ik(r_i - r_j)) \right\rangle \quad (3)$$

the Diffraction Patterns (DP) are obtained by means of the Fourier Transform of $S(k)$ being of visual aid to recognizing specific mesophases. For instance, the DP of a perfect Superlattice cluster should present self-similar bright spots with hexagonal symmetry, while isotropic non-structured fluid mesophases show patterns of non-bright circular fringes. These two parameters are calculated from the trajectory files by means of the Freud package [?]. The formation of local crystal regions inside order and disordered clusters is inherent in the formation of dense mesophases such as complex stripes and networks. To characterize this feature, the average Bond Orientational parameter (BOO) is calculated to assess the hexatic or non-hexatic order observed inside dense structures, this is defined as:

$$\Psi_n = \left\langle \frac{1}{N} \sum_{i=1}^N |\exp(in\theta(r_{ij}))|^2 \right\rangle \quad (4)$$

where ν is an integer related to the symmetry to be investigated r_{ij} is the vector interconnecting the particles i and j , θ is the angle between the vector and arbitrary axis and N is the number of neighbours. It is worth to remark that the sole amount in the brackets, is the local m -fold BOO parameter useful to visualize the symmetries across the system, this amount is noted by ϕ_n ,

4.1 Task no. 1

Run the program using $n_{part} = 2500$ setting the temperature to $T = 0.1$. Vary the density using the following values: $\rho : [0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0]$.

- a) Save a snapshot to record the equilibrium self-assembly mesophase by using the Ovito or VMD visualizer generating a screenshot sequence of all densities.
- b) Write a python code to compute the thermodynamical properties using data obtained in the simulation.
- c) Compute the RDF.
- d) Compute the BOO.
- f) Compute the Diffraction Pattern.
- g) By using the Ovito software, make a short videoclip using the dump file.

4.2 Questions:

- 1.-What mesophases do you find using this model?.
 - 2.-How is the shape of the Diffraction Pattern in the colloidal mesophases.
 - 3.-From the Radial distribution Function, what can you conclude about the type of mesophases obtained, are these liquids or solid crystals?
 - 4.-Why the core-corona system self-assembles in non-square 2D crystalline lattices?.
 - 5.-How does the total energy depend on the core particle density?.
 - 6.- When using the GPU acceleration feature, how good the gpu package improves the time calculation?.
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References

- [1] E. A. Jagla, *Phys. Rev. E Stat. Phys. Plasmas Fluids Relat. Interdiscip. Topics*, 58, 1478, (1998).
- [2] G. Malescio and G. Pellicane, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 70, 021202, (2004).
- [3] J. Menath, J. Eatson, R. Brilmayer, A. Andrieu-Brunsen, D. M. Buzza and N. Vogel, *Proc. Natl. Acad. Sci.*, 118, 2113394118, (2021).

- [4] A. B. de Oliveira, P. A. Netz, T. Colla, and M. C. Barbosa, *J. Chem. Phys.*, 124, 084505, (2006).
- [5] Hans-Jörg Limbach, Axel Arnold, Bernward A. Mann and Christian Holm. "*ESPResSo - An Extensible Simulation Package for Research on Soft Matter Systems*". *Comput. Phys. Commun.*, 174(9) (704), (2006).
- [6] D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithm to Applications* (Academic Press, 1996),
- [7] A. Stukowski, *Mod. Sim. Matt. Sci. Eng.*, 18, 015012, (2010).
- [8] V. Ramasubramani, B. D. Dice, E. S. Harper, M. P. Spellings, J. A. Anderson and S. C. Glotzer, *Data. Comp. Phys. Comm.*, 254, 107275, (2020).