Calculation of surface tension in a confined hard cut spheres liquid crystal using Monte Carlo simulation

Martín Pérez-Rodríguez, Manuel M. Piñeiro*
Departamento de Física Aplicada, Universidade de Vigo

Introduction. Monte Carlo simulations of slab confined hard cut spheres (HCS) have been performed to investigate the liquid crystal structure behavior and the confinement influence, by means of order parameter (OP), radial distribution function (RDF) and surface tension (γ).

The system definition was inspired by a previous work[1], and consisted of hard cut spheres of aspect ratio $L/D = 0.1$ (being $D = 1$ the particle diameter, considered as length scaling unit). The particles were confined between two fixed parallel walls separated by 6 length units in the z direction. In addition, two types of confining walls were considered: hard walls, which exclude the particle completely and adsorbent walls, which exclude only the center of mass. $6 \cdot 10^6$ cycles were considered for final simulations, after testing pressure and density results from $2 \cdot 10^6$ to $8 \cdot 10^6$, being the first half of the simulation considered as stabilization and the remaining as production steps. Simulations were performed first in the NPT ensemble, at pressures in the range $[0.5 - 9.0] \cdot 10^{-19}$ (reduced units) in steps of $0.5 \cdot 10^{-19}$ to asses the transition regions. Further simulations were performed from $1.5 \cdot 10^{-19}$ to $6.0 \cdot 10^{-19}$ in steps of $0.1 \cdot 10^{-19}$ to better determine the system behavior. To quantitatively characterize the system structure, the usual[2] order parameters were calculated in each simulation. Confinement effects were investigated by means of surface tension, which was calculated using the classical mechanical route, by determining the components of the pressure tensor, and in this case a recent method to compute either expansive and contractive contributions was applied[3]. When the expansion term is considered separately, an interesting result emerges: in a non confined system, an isotropic expansion produces some overlap only in concave particles; but in a confined one, a planar surface can effectively produce overlap, resulting in a non negligible contribution that may even change the surface tension sign.

Results. Expected isotropic (I) and nematic (N), and three additional higher pressure mesophases[4], disordered columnar (C_D), ordered hexatic columnar (C_H), and columnar solid (C_S), have been identified in the pressure range under consideration. Different order parameters account for the corresponding transitions, being the nematic order parameter main probe for $I - N$ transition, while the transitions between the columnar phases are determined by the appearance of order in the plane xy, parallel to the confining walls. $P^*(\rho^*)$ trend was useful to register the existence of all transitions. However it was not useful to asses neither the type of phase nor the internal structure of the system. The nonlinearity at higher pressures gave us a clue about the possibility of the last phase to be (almost) solid. Interestingly enough, surface tension expansion contribution has been observed to be a good descriptor of all the transitions in the bulk. Moreover, this capability of the expansion term could be easily generalized to non confined systems through the use of anisotropic expansions, considering the expansion in a z confined slab to be equivalent to an anisotropic expansion limited to the plane (x, z).

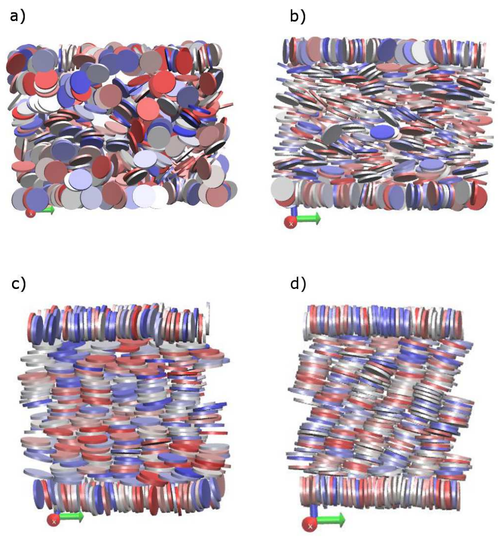

FIG. 1. Illustrative examples of observed mesophases in the adsorbent walls case. a) Isotropic ($P^* = 2.0 \cdot 10^{-19}$), b) Nematic ($P^* = 3.0 \cdot 10^{-19}$), c) Columnar hexatic ($P^* = 5.0 \cdot 10^{-19}$), d) Columnar solid ($P^* = 6.0 \cdot 10^{-19}$). Note that in d) the columns are tilted, arguably due to the effect of spherical surface on the particle rim, which causes the contact angle between a pair of particles to be greater than 0 at such high pressures. This effect was observed in all simulations above the $C_H - C_S$ transition.

---

* mmpineiro@uvigo.es

[1] M. M. Piñeiro, A. Galindo, A. O. Parry, *Soft Matter*, **3**, 768, (2007).

[2] E. M. del Río, E. de Miguel, *Phys. Rev. E*, **55**, 2916 (1997).

[3] P.E. Brumby, A. J. Haslam, E. de Miguel, G. Jackson, *Mol. Phys.*, **1**, (2010).

[4] Comparable but not equivalent structures to previously reported for unconfined hard cut spheres in: A. Cuetos, B. Martínez-Haya, *J Chem. Phys.*, **1**29, 214706, (2009).