Effective model for grafted polymer nanoparticles in two dimensions

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Introduction

Experimental and simulational studies have show that spherical colloids with tunable competitive interactions (as core-softened potentials) can be used to represent Polymer-Grafted Nanoparticles (GNPs):

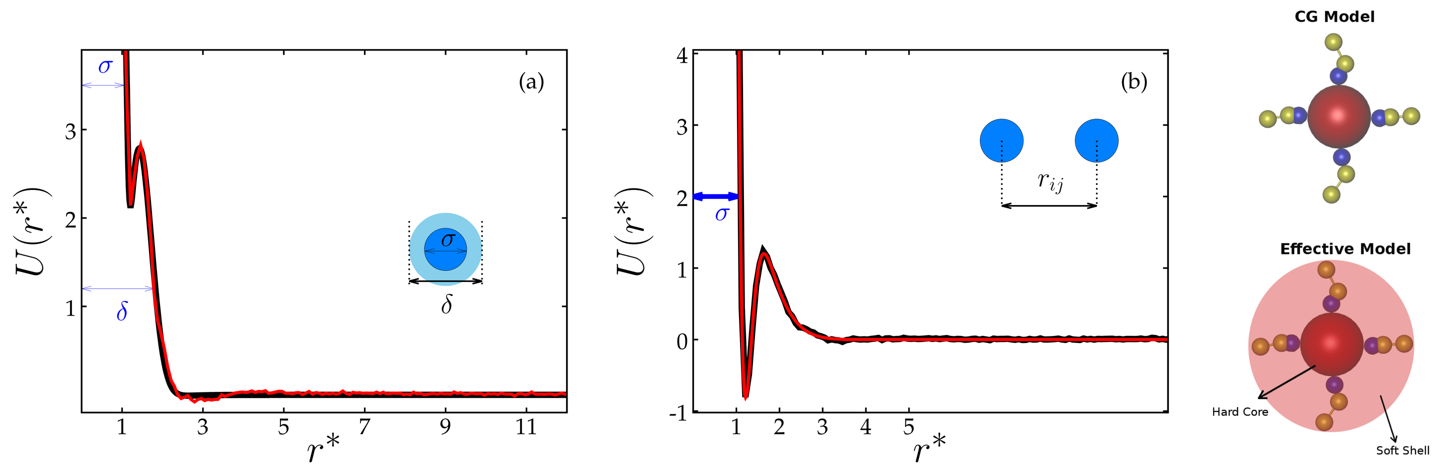

Figure 1: Core-softened potential for grafted nanoparticles polymers with four monomers (a) fixed and (b) free to rotate around nanoparticle core. Right: Effective model for grafted nanoparticles in 2D.

Data and Methods

Our system consists of 800 disks with diameter σ and mass m which interact via core-softened potentials obtained from the OZ equation for two cases: one where the polymers are free to rotate around the nanoparticle core and a second where the polymers are fixed, with a 45° angle among them:

$$U(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \sum_{j=1}^{3} h_j exp\left[-\left(\frac{r-c_j}{w_j}\right)^{2}\right], \qquad (1)$$

where $r_{ij} = |r_i - r_j|$ is the distance between two disks i and j.

Uno potential		Uyes potential	
Parameter	**Value**	**Parameter**	**Value**
h_1	3.50803	h_1	-3.80084
c_1	1.05317	c_1	1.11192
w_1	0.0887196	w_1	0.313324
h_2	3.2397	h_2	46.1324
c_2	1.37689	c_2	0.774361
w_2	0.468399	w_2	0.191852
		h_3	6.37621
		w_3	0.192937
		c_3	1.23615

Simulation details: Molecular Dynamics with temperature range from 0.05 to 1.00 and pressure range from 0.10 to 5.00, $\delta t = 0.001$, and PBC. We performed 5×10^5 steps to equilibrate and 2×10^6 steps for the results production stage.

Results

The PT phase diagram were constructed by analyzing behavior of Cp (T), msd's, rdf's and snapshots (Fig. 2):

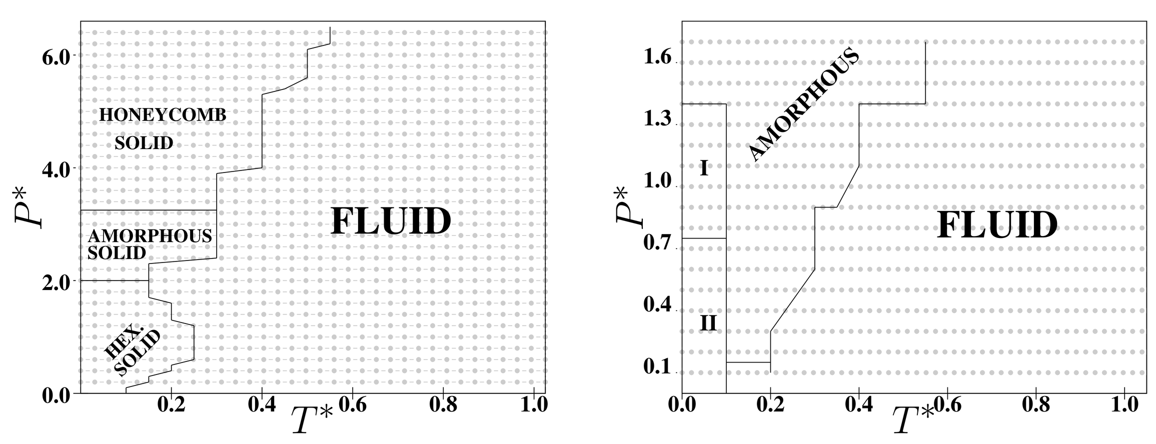

Figure 2: PT diagrams for two potentials.

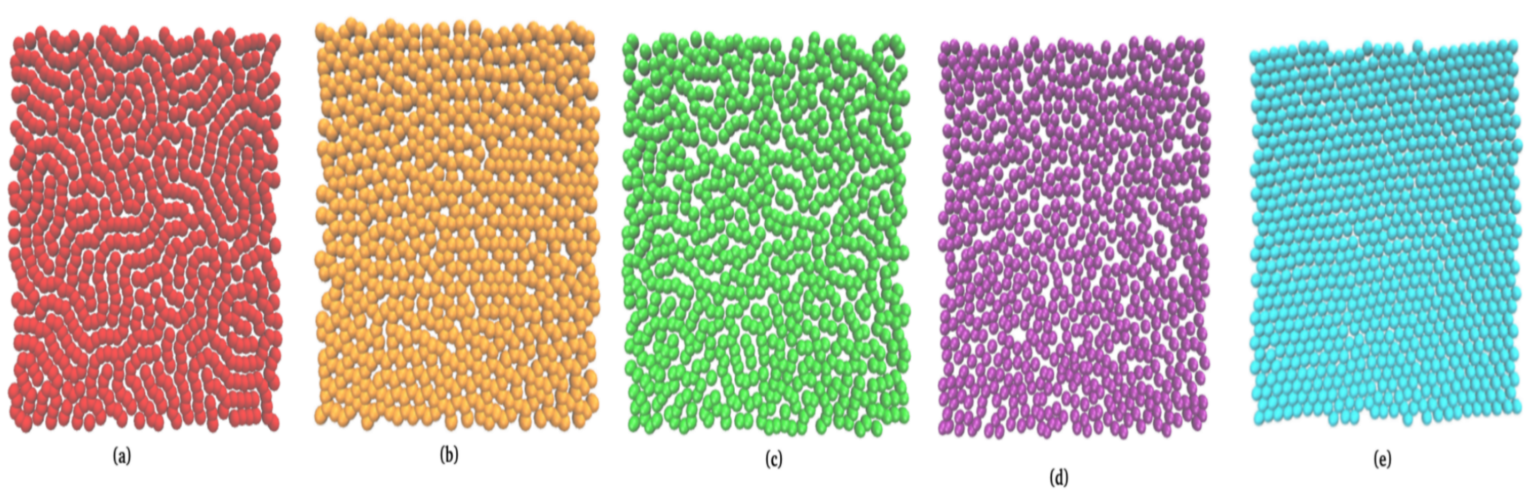

Figure 3: Snapshots from structures observed.

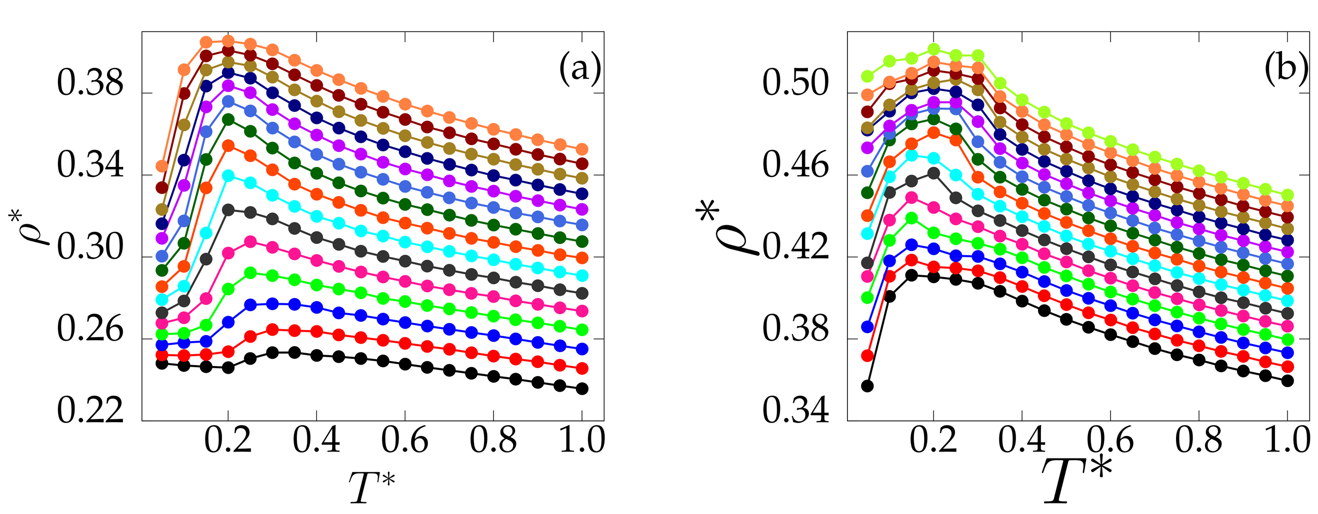

Figure 4: Density-temperature phase diagrams (two pressure intervals)

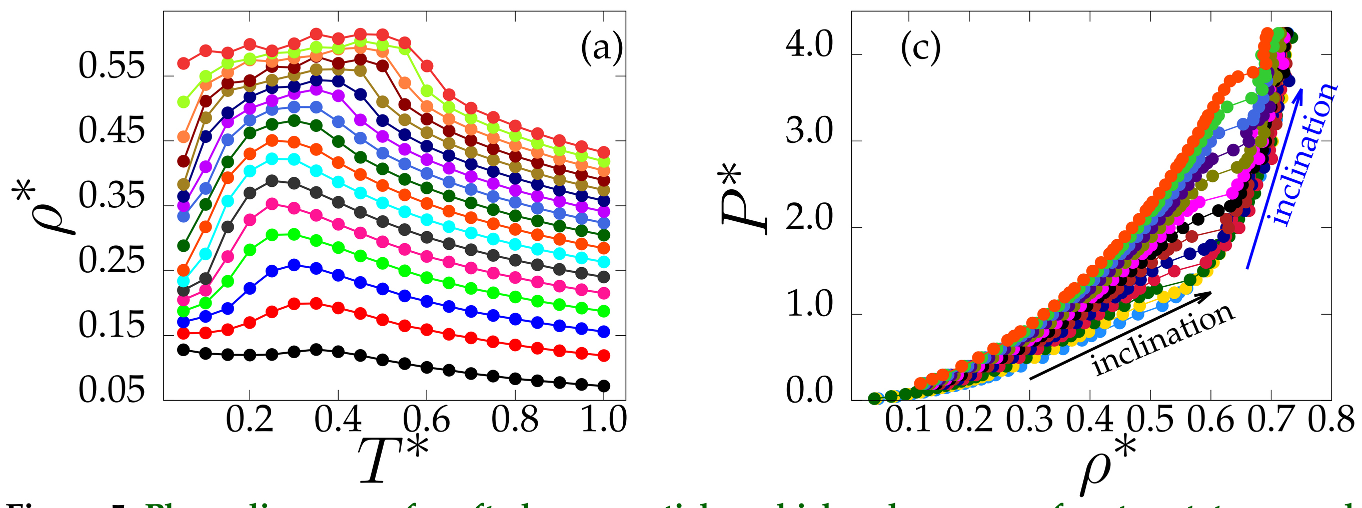

Figure 5: Phase diagrams of grafted nanoparticles which polymers are free to rotate around.

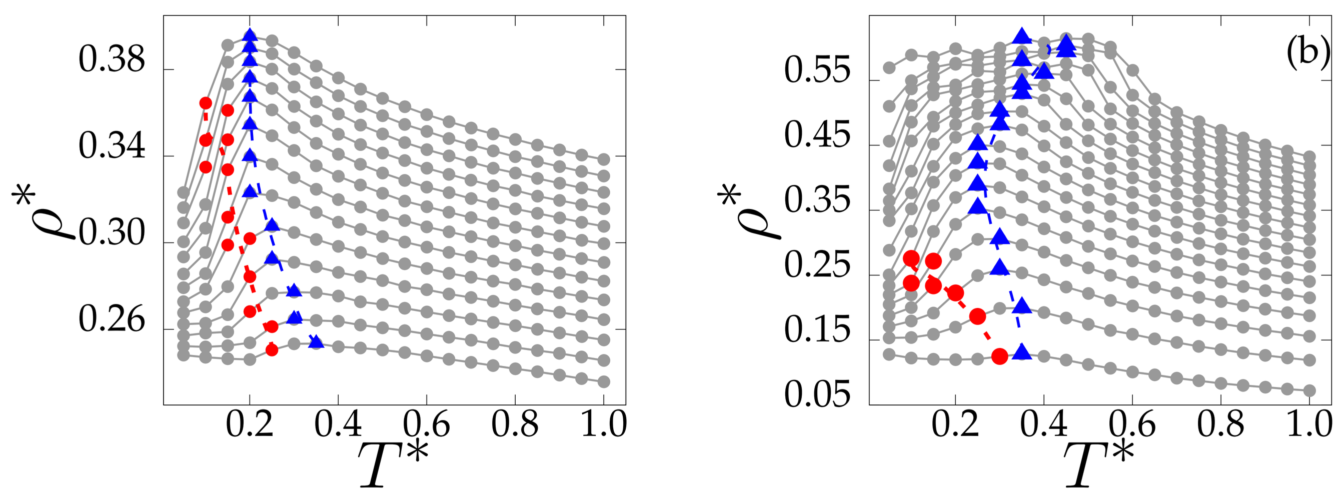

Figure 6: peaks in specific heat at constante pressure (Widom Line).

The density anomaly can be related to the system structure by analyzing the behavior of its radial distribution function:

$$\Pi_{12} = \frac{\partial g(r)}{\partial \rho}\,|_{\rho_1} \times \frac{\partial g(r)}{\partial \rho}\,|_{\rho_2} < 0. \qquad (2)$$

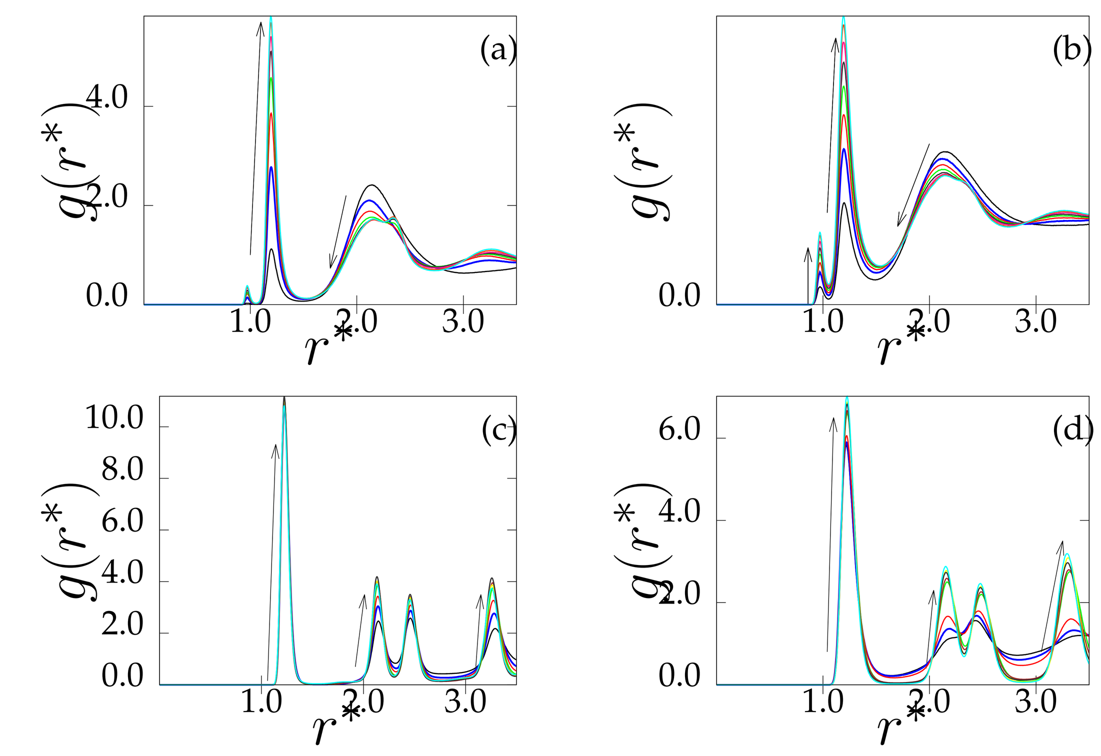

Figure 7: rdf's showing competition between thermals and pressure effects.

The regions identified by the radial distribution function as fulfilling the condition Eq.2 are illustrated as opened circles in figure 8. The solid curve shows the TMD line.

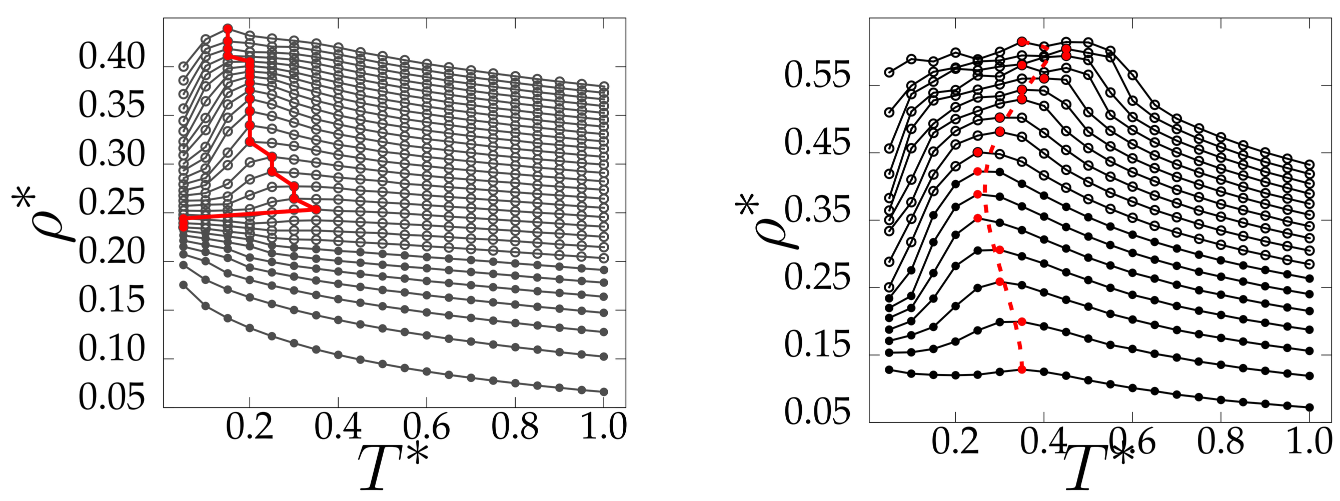

Figure 8: relation between competition between scales and structure(RDF).

The figure is the diffusion dependence with the pressure for each isotermal, showing the anomalous increment in D as we increase the fluid density for low temperatures:

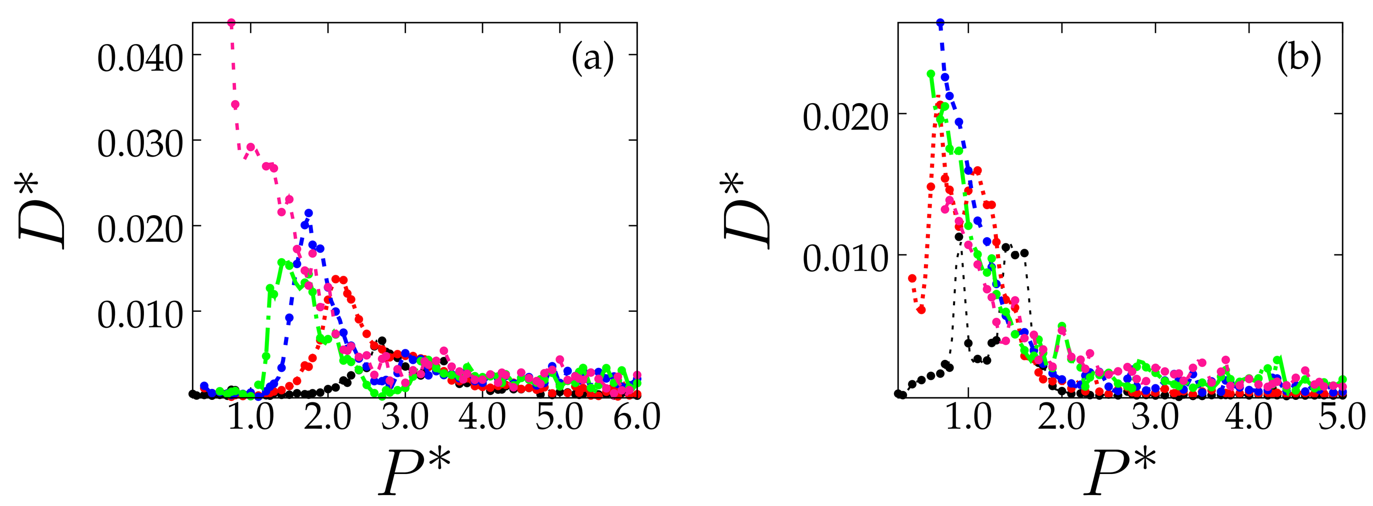

Figure 9: diffusion coefficient pressure relation.

Final Remarks

Due the competition in the system, we have observed the presence of water-like anomalies; it was observed different structural morphologies (worms, stripes, amorphous) for each nanoparticle case. For the fixed polymers case the waterlike anomalies are originated by the competition between the length scales, while for the free to rotate case the anomalies arises due a smaller region of stability in the phase diagram.