

Supplementary material on the article:

**From sea-urchins to starfishes: controlling the adsorption of
star-branched polyelectrolytes on charged walls**

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As we are dealing with macromolecules with a *finite* number of degrees of freedom, the changes between states are not phase transitions but rather smooth crossovers. Nevertheless, an order parameter allowing an assignment of a phase to each orientational diagram can be defined. The set of points $y \equiv \langle \cos \theta_i \rangle$ seen as a function of $x \equiv i/(f-1)$ can be fitted for all states by a family of functions $h(x; x_0, y_0)$ of the form

$$h(x; x_0, y_0) = \begin{cases} (y_0 - 1) \frac{x}{x_0} + 1 & \text{for } 0 \leq x \leq x_0; \\ y_0 & \text{for } x_0 < x \leq 1, \end{cases}$$

with x_0 and y_0 being fit parameters (see inset of Fig. 1). These serve to define the two-dimensional order parameter $O = (O_1, O_2)$ as $O_1 = |y_0 - R_d/R_s|$ and $O_2 = 2x_0/(1 - y_0)$. O_1 is a measure of the distance of the star centre from the surface and O_2 of the sphericity of the nonadsorbed chains. The ideal values of O read as $(1, 1)$ for the sea-urchin, $(\beta, 1)$ for the jellyfish, $(0, 1)$ for the anemone, $(0, \gamma)$ for the antenna and $(0, 0)$ for the starfish, with $0 < \beta, \gamma < 1$.

The main plot of Fig. 1 shows the values (O_1, O_2) obtained for all parameters in the simulations of systems I and II. All data points follow, within small margins, a Γ -shaped line $(O_1 \cong 0, 0 \leq O_2 \leq 1) \cup (0 \leq O_1 \leq 1, O_2 \cong 1)$. In the absence of a horizontal segment of the $\langle \cos \theta_i \rangle$ -curves, we characterise the shape as spherical, since there is very weak adsorption of a few chains only. This explains the extension of the ‘sea-urchin’-symbols in Fig. 1 to values $O_1 < 1$.

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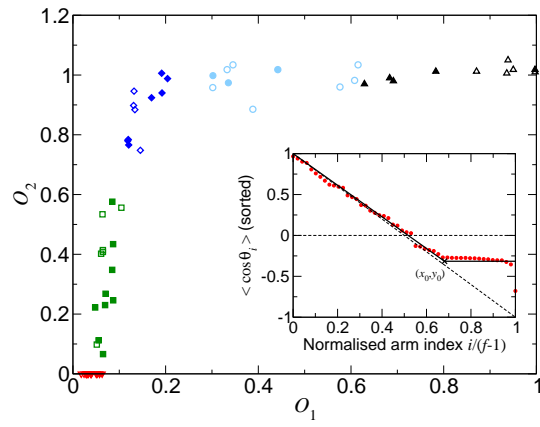


FIG. 1: Characterisation of the five shapes found, according to the value of the two-dimensional parameter defined in the text. Open symbols refer to system I and closed ones to system II. The symbols are colour-coded as in Fig. 3 of the main article. Black triangles up: sea-urchin; light blue circles: jellyfish; dark blue diamonds: anemone; green squares: antenna; red triangles down: starfish. The inset indicates the underlying procedure for the calculation of the order parameter.