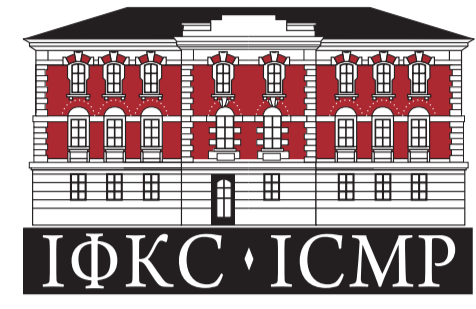


UNIVERSAL SHAPE PROPERTIES OF MESOSCOPIC POLYMER STARS AND THEIR AGGREGATES

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Application of star polymer

- Viscosity modifiers
- Micelle formation for target drug delivery
- Building blocks of polymer hydrogels

Polymer shape characteristics

- The gyration tensor \bar{Q} of the polymer chain :

$$Q_{ij} = \frac{1}{N} \sum_{n=1}^N N(x_n^i - x_{CM}^i)(x_n^j - x_{CM}^j) \quad i, j = 1, \dots, d. \quad (1)$$

Here x_n^i is i -th Cartesian coordinate of n -th monomer: $\bar{R}_n = (x_n^1, x_n^2, \dots, x_n^d)$, and $x_{CM}^i = \sum_{n=1}^N x_n^i / N$, $i = 1, \dots, d$ are the coordinates of the center of mass for the polymer chain.

- Radius of gyration:

$$R_g^2 = \text{Tr} \bar{Q}. \quad (2)$$

- Average center-end distance:

$$\langle R_{ce,f}^2 \rangle \equiv \langle r_{e,f}^2 \rangle = \left\langle \frac{1}{f} \sum_{k=1}^f [r_{k,N} - \bar{r}_c]^2 \right\rangle, \quad (3)$$

- The stretch ratio:

$$p_e(f) = \frac{\langle R_{ce,f}^2 \rangle}{\langle r_{e,1}^2 \rangle} \equiv \frac{\langle r_{e,f}^2 \rangle}{\langle r_{e,1}^2 \rangle}, \quad (4)$$

- Shape factor:

$$g(f) = \frac{\langle R_{g,f}^2 \rangle}{\langle R_{g,1}^2 \rangle}, \quad (5)$$

- The asphericity of the polymer chain is defined as:

$$A = \frac{d}{d-1} \frac{\text{Tr} \bar{Q}^2}{(\text{Tr} \bar{Q})^2}. \quad (6)$$

- The level of "spherization":

$$p_A(f) = \frac{\langle A_f \rangle}{\langle A_1 \rangle}, \quad (7)$$

Simulation approach

In our study we follow the mesoscopic method of dissipative particle dynamics (DPD) method. We follow the DPD approach as described in Ref. [5], the length is represented in units of the diameter of soft bead, and the energy scale is assumed to be $\epsilon^* = k_B T = 1$, where k_B is Boltzmann constant, T temperature, time is expressed in $t^* = 1$. The monomers are connected via harmonic springs, which results in the force:

$$\vec{F}_{ij}^B = -kr_{ij}\hat{r}_{ij}, \quad (8)$$

The non-bonded forces contain three contributions:

$$\vec{F}_{ij} = \vec{F}_{ij}^C + \vec{F}_{ij}^D + \vec{F}_{ij}^R, \quad (9)$$

The expressions for all these three contributions are given below [5]

$$\vec{F}_{ij}^C = \begin{cases} a(1-r_{ij})\hat{r}_{ij}, & r_{ij} < 1, \\ 0, & r_{ij} \geq 1, \end{cases} \quad (10)$$

$$\vec{F}_{ij}^D = -\gamma w^D(r_{ij})(\hat{r}_{ij} \cdot \vec{v}_{ij})\hat{r}_{ij}. \quad (11)$$

$$\vec{F}_{ij}^R = \sigma w^R(r_{ij})\theta_{ij}\delta t^{-1/2}\hat{r}_{ij}. \quad (12)$$

Where a is a repulsion coefficient a is the amplitude for the conservative repulsive force. The dissipative force has an amplitude γ and decays with the distance according to the weight function $w^D(x_{ij})$. The amplitude for the random force is σ and the respective weight function is $w^R(x_{ij})$. θ_{ij} is the Gaussian random variable.

Results

- **A Star polymer, the role of solvent quality:** we consider the star shaped polymers with the number of arms $f = 8$. The length of one arm is $N_f = 8$. We have studied two types of arms: f_1 arms with constant solubility and f_2 arms with variable solubility [3].

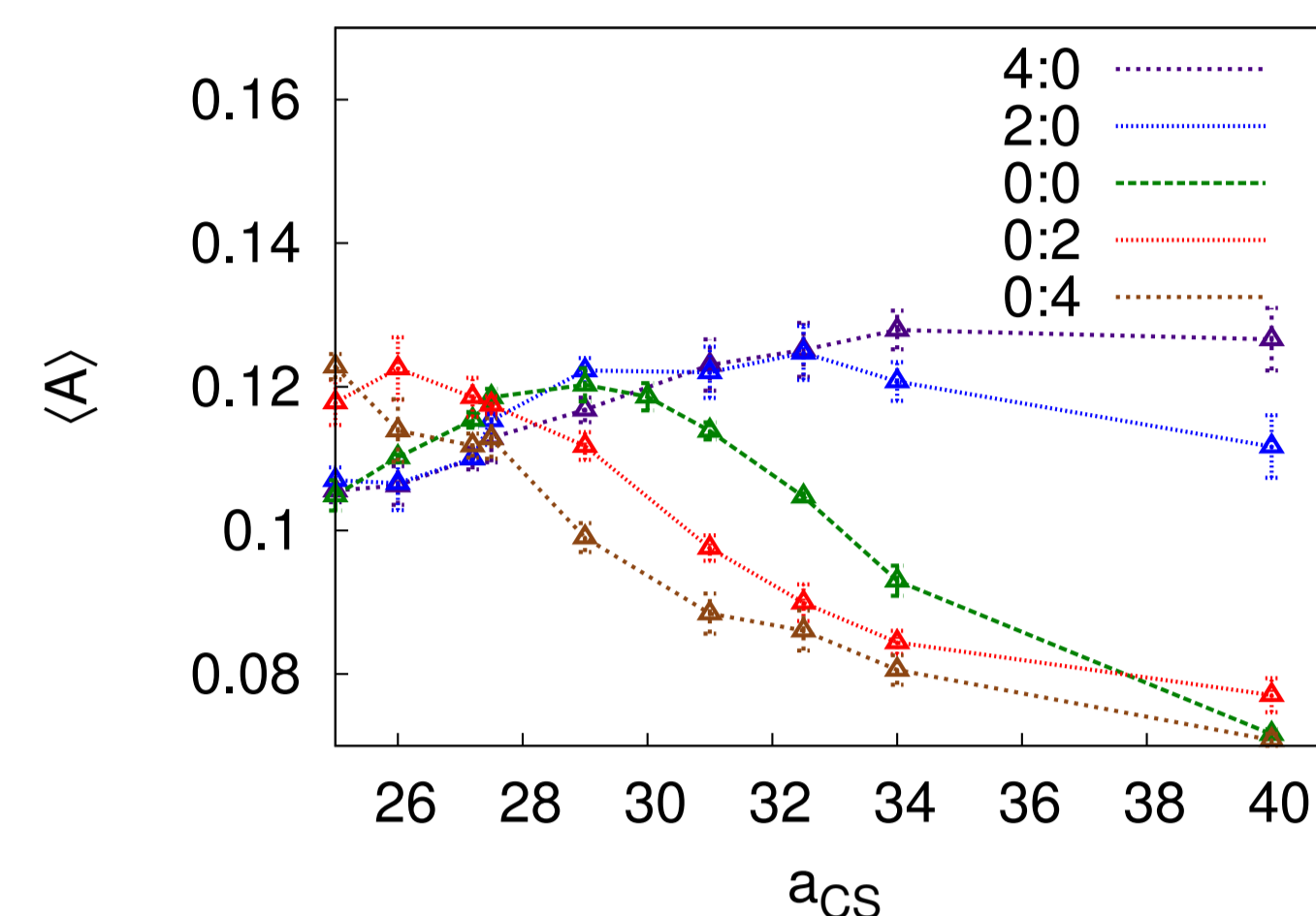


Figure 1: Asphericity A of the $(f_A : f_B)$ polymer star as a function of a_{CS} , the solvophobicity of the C beads. Here f_A is a number of solvophilic branches and f_B is a number of solvophobic branches. Factor a_{CS} discriminates between good ($a_{CS} = 25$) and bad ($a_{CS} = 40$) solvent quality. Green line corresponds to a homogeneous star with all branches of changing solubility (0 : 0).

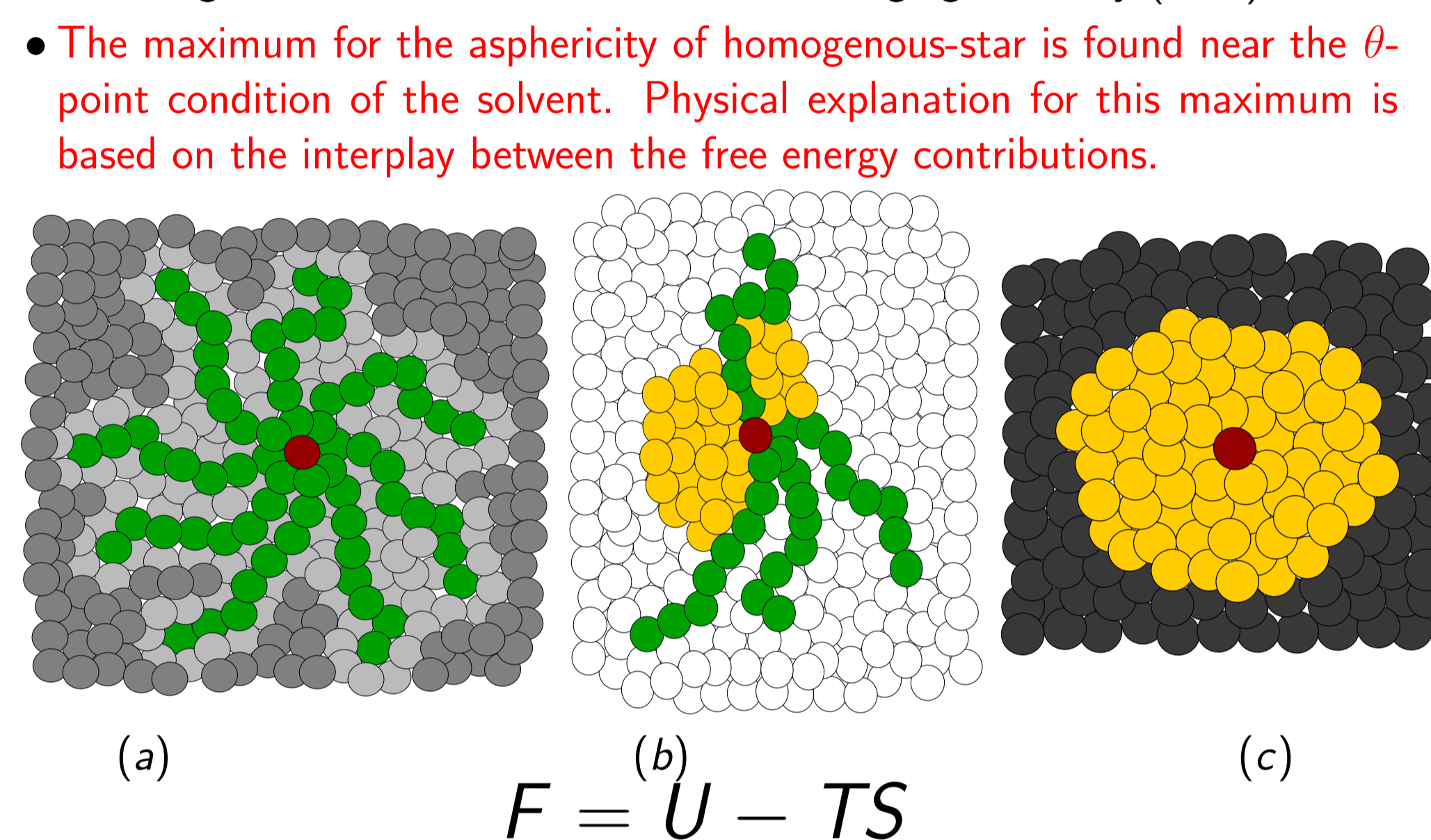


Figure 2: Schematic illustration for the conformation of individual branches of homogeneous star polymer (0 : 0) in various regimes. (a) good solvent, (b) θ -condition and (c) bad solvent.

- **B Star polymer, the role of the density of arms:** star polymer undergoes a transformation from a group of loosely coupled chains at low number of arms to a dense hairy colloid at their high number. We study the range of size and shape properties of the star molecule and of its individual arms upon this transformation [4].

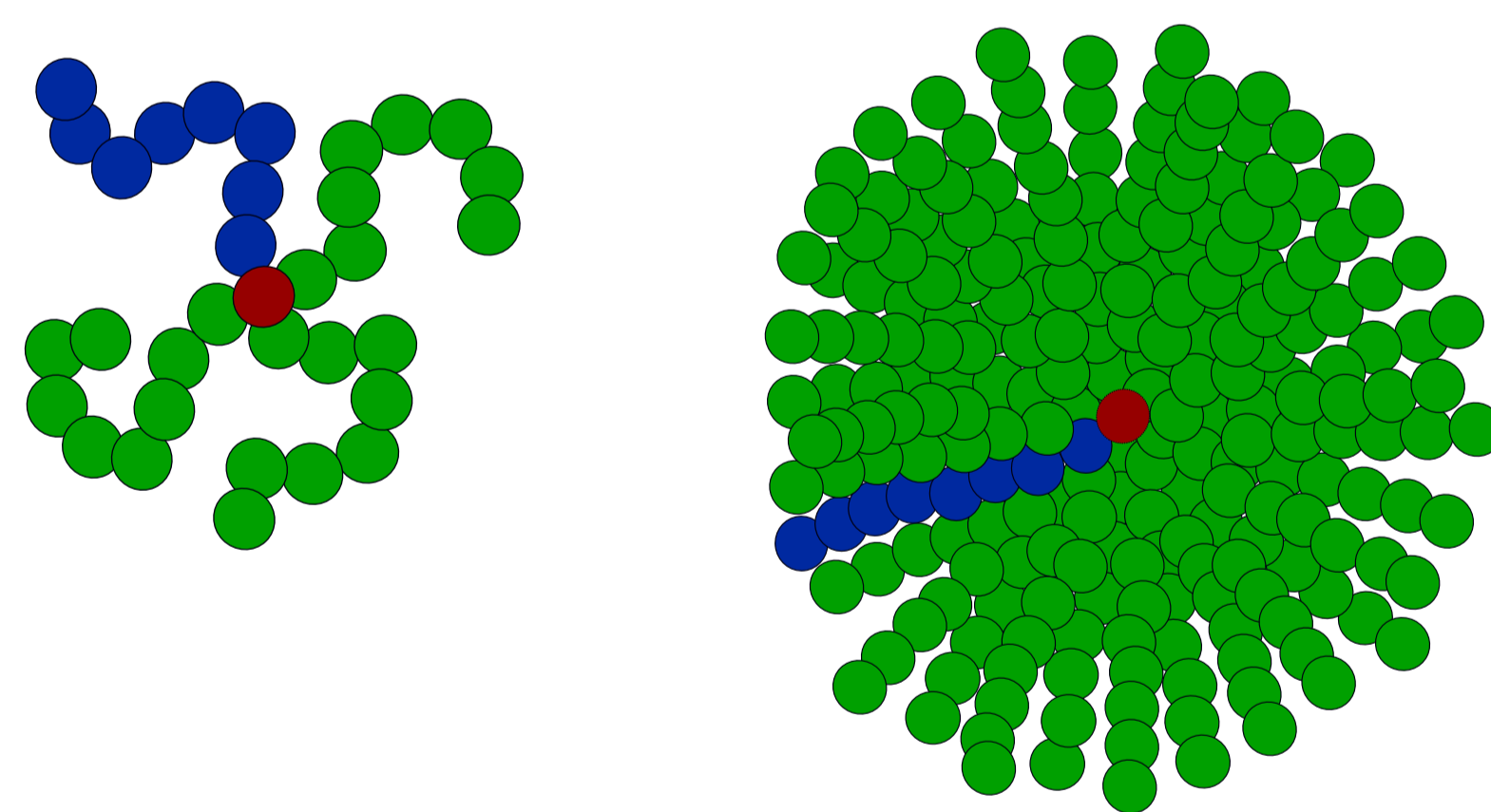


Figure 3: Schematic presentation of single arm conformation in branched f -arm polymer structure at polymeric (left) and colloidal (right) regimes.

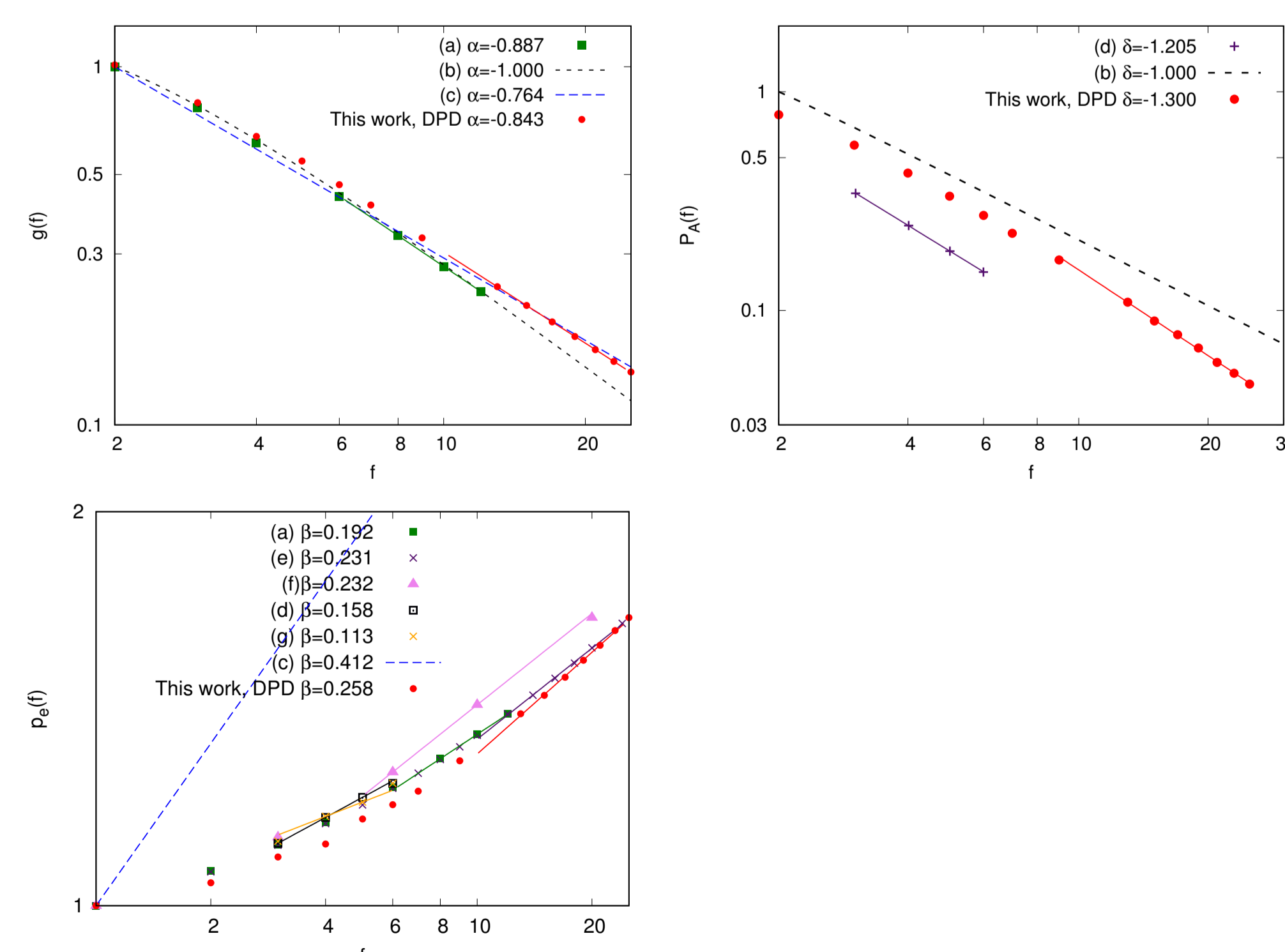


Figure 4: (a) Monte Carlo [6], (b) Gaussian, (c) Daoud-Cotton ansatz [7], (d) Monte Carlo [8], (e) Monte Carlo [9], (f) Molecular dynamics [10], (g) Monte Carlo [11].

- **Asymptotic behavior of our results show good agreement with Monte Carlo and molecular dynamics results, although the latter were obtained using substantially different potential. This demonstrates the universality of shape properties**

- **C Aggregates:** we study the effect of the molecular architecture of amphiphilic star polymers on the shape of aggregates they form in water. Four different architectures are considered (see Fig. 5). Four types of aggregate shape are observed: spherical, rod-like and disc-like micelle and a spherical vesicle [2].

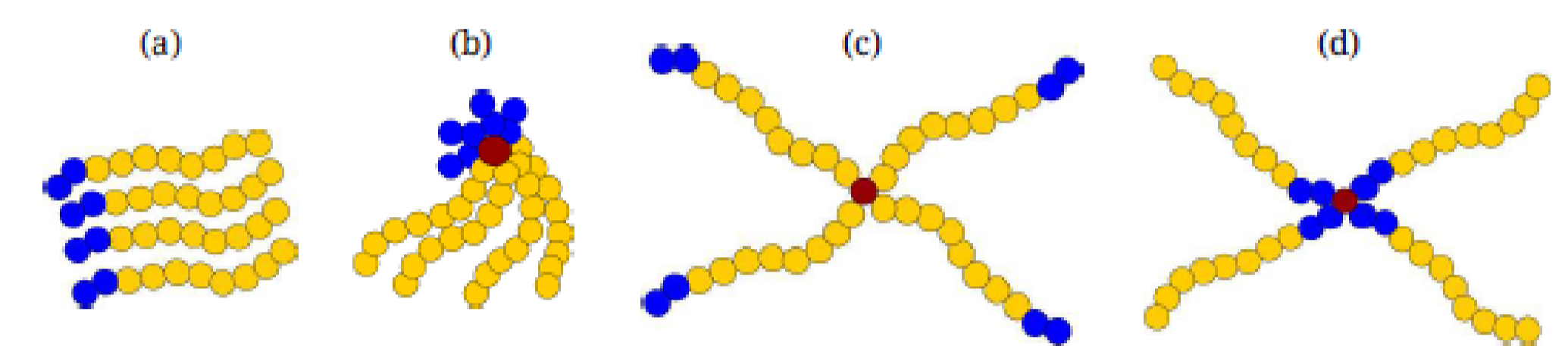


Figure 5: Molecular architectures used in this study: (a) linear diblock copolymers, (b) miktoarm star-polymer, (c) diblock 1 star-copolymer and (d) diblock 2 star-copolymer. Where hydrophilic beads (type A) are shown in blue, hydrophobic (type B) in yellow, central bead is shown in red

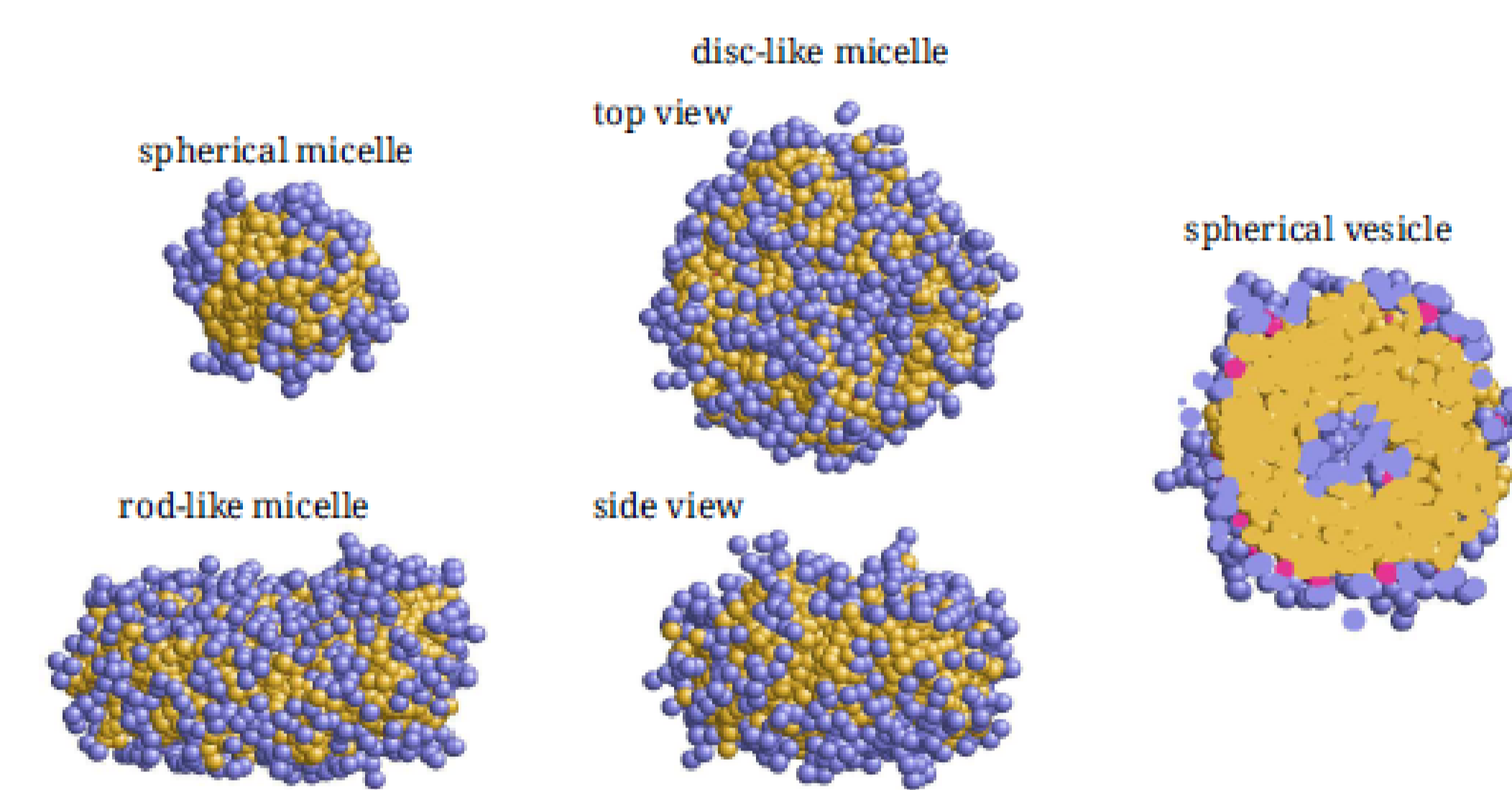


Figure 6: Basic shapes observed for aggregates of amphiphilic stars.

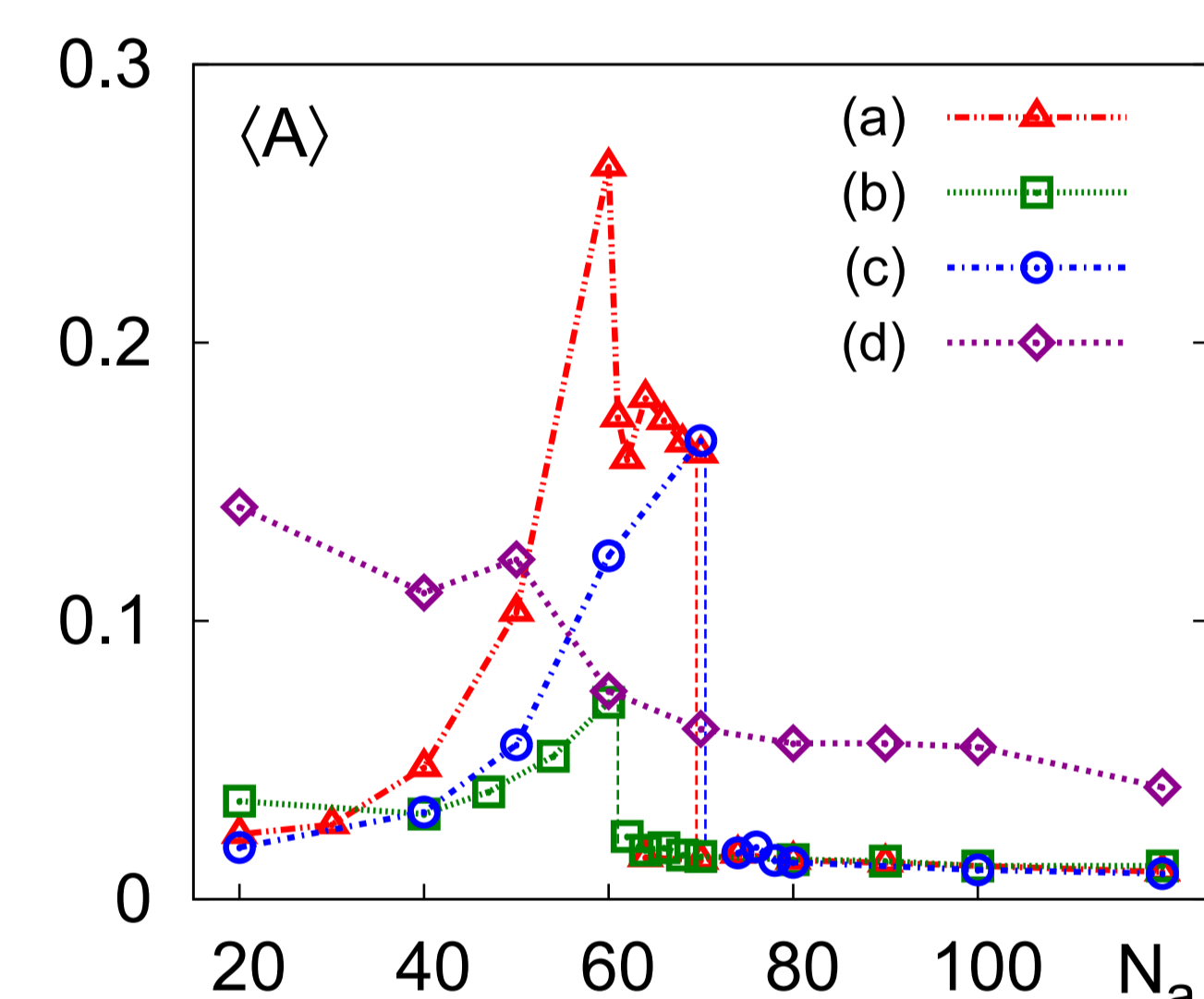


Figure 7: Asphericity A of the (a) linear diblock copolymers, (b) miktoarm star-polymer, (c) diblock 1 star-copolymer and (d) diblock 2 star-copolymer as a function of aggregate number N_a . Sharp transition from micellar shape to vesicle shape at $N_a = 65 - 70$.

- **Four molecular architectures have been examined see Fig. 5. For all cases, the same general sequence of shapes is found with an increase of the aggregation number, namely: spherical micelle, aspherical micelle and a spherical vesicle. The phase boundaries between these are found to depend on the details of the molecular architecture. For the case (a)(c), the transformation between a spherical and aspherical micelle occurs gradually, whereas the transition from an aspherical micelle into a spherical vesicle is in a form of a sharp transition. In the case (b), aspherical micelle is less stable and transition to a vesicle occurs at a lower aggregation number. The case (d) is characterised by gradual transitions between all the shapes.**

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