Why do peptide amphiphiles form fibers?

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A computation multiscale effort capable of predicting the structure of self-assembled nanofibers and properties of Peptide Amphiphile (PA) gels is not trivial. The assembly into thermodynamically stable structures is dictated by the interplay of many non-covalent interactions. The basic model of peptide-amphiphiles demonstrates the importance of hydrogen bonding and hydrophobic interactions for self-assembly. For the purposes of the coarse-grained model (Figure 1), the PA is divided into three distinct units: hydrophobic (H), peptide (P), and epitope headgroup (E). Each peptide P is capable of forming two sets hydrogen bonds (i.e., to each of the P subunits of adjacent monomer).

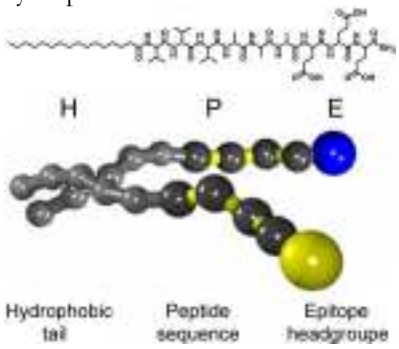

Figure 1. The chemical structure and united atom model of peptide-amphiphile molecule.

The composition of the PA molecules and the competition between different forces guide aggregation into the observed cylindrical assemblies. The path to this structure has proven difficult to determine experimentally, but the above simulations give some insight into the processes. Two mechanisms are possible: initial hydrogen bond formation into β-sheets and eventual reorganization into the cylinder or initial micelle formation by hydrophobic collapse followed by β-sheet formation then elongation into the cylinder (Figure 2). The simulations show that the path of the self-assembly taken in a particular instance is highly dependent on the initial conditions. In both cases, the nucleation depends on the interplay between the entropy change upon aggregation and the dominant attractive forces, i.e. hydrogen bonding or hydrophobic.

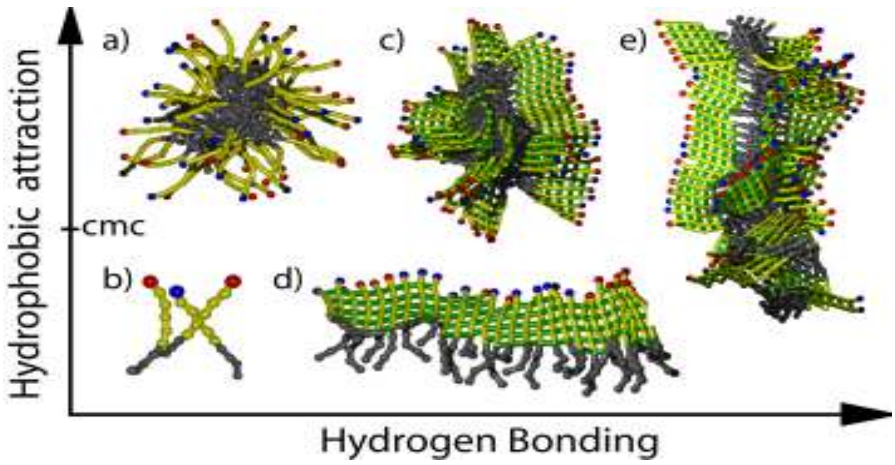

Figure 2. Snapshot of self-assembled peptide amphiphiles at different values of hydrogen bonding energy (a, b) $\varepsilon_A=0$, (c, d) $\varepsilon_A=2$ and (e) $\varepsilon_A=3$ in k_BT units. The hydrophobic groups are colored grey, β-sheet forming peptides in yellow, the terminal epitopes are blue or red, and hydrogen bonds are green.

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