1. Appendix

It is straightforward to compute the configurational entropy of the tethered nanoparticle exactly. The number of unique ways one can arrange N_{AVE} ligands of type A onto $N_{VE} = N_V + N_E$ sites is given by,

$$\Omega_{VE} = \frac{N_{VE}!}{N_{AVE}!\left(N_{VE} - N_{AVE}\right)!} . \quad (1.)$$

Likewise, the number of ways of arranging N_{AF} ligands of type A onto N_F sites is given by,

$$\Omega_F = \frac{N_F!}{N_{AF}!\left(N_F - N_{AF}\right)!} = \frac{N_F!}{\left(N_A - N_{AVE}\right)!\left(N_F - N_A + N_{AVE}\right)!} . \quad (2.)$$

The configurational entropy for a system with N_{AVE} ligands of type A bonded along the edges and vertices is then,

$$S_{config}\left(N_{AVE}\right) = k_B \ln\left[\Omega_{VE} \cdot \Omega_F\right], \quad (3.)$$

where k_B is Boltzmann's constant. For a macrostate that is defined for multiple values of N_{AVE}, the total entropy can be computed by summing $S_{config}\left(N_{AVE}\right)$ over all N_{AVE} consistent with the macrostate.

To compute the conformational entropy of a tether, we used Monte Carlo integration to calculate the fraction of tether conformations that fit inside a Voronoi cell. This calculation was done off-lattice in the following way. First, we constructed Voronoi cells for each type of lattice site for each of the polyhedron lattices described above. Next, we placed the first tether bead at a random point on a sphere of radius $\sigma_L + d/2$ centered on the binding site. Here, $d = 0.5$ is the separation between adjacent tether beads. Additional tether beads were added to the sequence by placing them at a random point on a sphere of radius d centered on the previous bead. Each tether contained $L_i = 3$ beads. All tether conformations in which beads overlap (i.e. the separation between beads was less than *d*) were rejected since these are not self-avoiding. We used the above procedure to generate 10^9 unique self-avoiding tether conformations. Using the bead positions from these conformations, we then varied the bead radius σ_{Ti} and computed the fraction of tether conformations that remain inside the Voronoi cell as a function of σ_{Ti}.

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