Electronic Supplementary Material (ESI) for Soft Matter.

A minimal representation of the self-assembly of virus capsids

Supplementary Information

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Uniqueness of the two simplest anisotropic multipolar terms of the capsomer-capsomer interaction

An important mathematical result has guided us in the construction of our capsomer-capsomer interaction model: the anisotropic terms (those depending on the angular orientation) of the standard multipolar expansion of the interaction between two charge distributions form a complete basis set to expand the angular dependence of the interaction between any two bodies (two capsomers in our case). This basis set is the direct product of two Wigner matrix basis sets $D^j_{mm'}(\phi_i, \theta_i, \chi_i)$ (see Ref. 42 in the Article), one for each of the two bodies ($i = 1, 2$). The angles ϕ_i, θ_i and χ_i give the angular orientation of each capsomer with respect to a reference frame whose z-axis is chosen along the intercapsomer unitary vector $\boldsymbol{n}_{12} = \boldsymbol{r}_{12}/r_{12}$, and j, m, m' are angular momentum quantum numbers with j belonging to the set $\{0, 1, 2, \ldots\}$ and, for a given j, the values of m and m' ranging from $-j$ to j. The monopole term corresponds to $j = 0$, dipole terms have $j = 1$ while quadrupole terms have $j = 2$. If the capsomers have axial symmetry with respect to rotations around the corresponding unitary vectors $\boldsymbol{v}_i$, introduced in Section 2 of the Article, then the capsomer-capsomer interaction will not depend on the rotation angles χ_i and thus one must have $m' = 0$. Note that ϕ_i and θ_i are the polar coordinates of $\boldsymbol{v}_i$ in the chosen reference frame. Besides, since the interaction must be invariant against arbitrary rotations of the complete two-body system it can only depend on the angles ϕ_i through the combination $\phi_1 - \phi_2$. As a consequence of these two symmetries the expansion of the capsomer-capsomer interaction will only contain terms of the form $D^{j'}_{-m0}(1)D^j_{m0}(2)$, where $(1) \equiv (\phi_1, \theta_1)$ and similarly for (2).

Let us find first the dipole-dipole terms satisfying the additional geometrical constraints of the capsomer-capsomer interaction. This dipole-dipole interaction, $V_{\rm dd}$, is a linear combination of the three terms $D^1_{00}(1)D^1_{00}(2)$, $D^1_{-10}(1)D^1_{10}(2)$ and $D^1_{10}(1)D^1_{-10}(2)$. From the form of the Wigner matrices and the real character of the interaction we arrive at the general linear combination

$$V_{\rm dd} = a\cos\theta_1\cos\theta_2 + b\sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2) + c\sin\theta_1\sin\theta_2\sin(\phi_1-\phi_2) \quad \text{(S-1)}$$

As discussed in Section 2 of the Article, we must have at equilibrium $\phi_1 - \phi_2 = 0$ and $\theta_1 + \theta_2 = \pi$, thus these values must correspond to an extremum (namely a minimum) of $V_{\rm dd}$. The first condition (for $\phi_1 - \phi_2$) requires $c = 0$ and $b < 0$. With these values, $\phi_1 = \phi_2$, and after scaling, Eq. 1 reduces to

$$V_{\rm dd} = \frac{a+1}{2}\cos(\theta_1+\theta_2) + \frac{a-1}{2}\cos(\theta_1-\theta_2) \quad \text{(S-2)}$$

A necessary condition for this equation to have a minimum at $\theta_1 + \theta_2 = \pi$ is $a > -1$. Then for $-1 < a < 1$ the minimum occurs at $\theta_1 = \theta_2 = \pi/2$, while for $a > 1$ it occurs at $\theta_1 - \theta_2 = \pm\pi$. Interestingly, for $a = 1$ we have a minimum independently of the value of the angle $\theta_1 - \theta_2$. Therefore the unique scaled dipole-dipole interaction satisfying the geometrical constraints of the capsomer-capsomer interaction for generic values of the dihedral angle $\Theta = \pi - (\theta_1 - \theta_2)$ is

$$V_{\rm dd} = \cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2) \quad \text{(S-3)}$$

In terms of the unitary vectors $\boldsymbol{v}_i$, Eq. S-3 reads

$$V_{\rm dd} = -\boldsymbol{v}_1\cdot\boldsymbol{v}_2 + 2\big(\boldsymbol{v}_1\cdot\boldsymbol{n}_{12}\big)\big(\boldsymbol{v}_2\cdot\boldsymbol{n}_{12}\big) \quad \text{(S-4)}$$

Let us find now the linear combination of monopole-dipole and monopole quadrupole angular terms required to fix the dihedral angle of the capsomer-capsomer interaction at equilibrium. We will start by assigning the monopole to capsomer 1 and the dipole and quadrupole to capsomer 2. Then this interaction ($V_{\rm mdq}$) can include only the terms $D^0_{00}(1)D^1_{00}(2)$ and $D^0_{00}(1)D^2_{00}(2)$, where D^0_{00} is independent of the angular variables. From the form of the Wigner matrices we obtain, except for an irrelevant additive constant term,

$$V_{\rm mdq} = a\cos\theta_2 + b\cos^2\theta_2 \quad \text{(S-5)}$$

The above expression must have a extremum (namely a minimum) at a given value $\theta_2 = \Theta/2$, where Θ is the required dihedral angle. Therefore we obtain $a/(2b) = -\cos(\Theta/2)$ and $b > 0$. In terms of the unitary vector $\boldsymbol{v}_2$ the scaled expression S-5 then reads

$$V_{\rm mdq} = (\boldsymbol{v}_2\cdot\boldsymbol{n}_{12})^2 - 2\cos(\Theta/2)\boldsymbol{v}_2\cdot\boldsymbol{n}_{12} \quad \text{(S-6)}$$

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By adding a symmetrical contribution from capsomer 1 we obtain finally

$$\begin{aligned} V_{\mathrm{mdq}} &= (\boldsymbol{v}_1 \cdot \boldsymbol{n}_{12})^2 + (\boldsymbol{v}_2 \cdot \boldsymbol{n}_{12})^2 \\ &+ 2\cos(\Theta/2)\big(\boldsymbol{v}_1 \cdot \boldsymbol{n}_{12} - \boldsymbol{v}_2 \cdot \boldsymbol{n}_{12}\big) \end{aligned} \tag{S-7}$$

Since the equilibrium configurations provided by Eq. S-7 satisfy $\theta_1 + \theta_2 = \pi$ and do not depend on ϕ_i, these are entirely compatible with those provided by Eq. S-4, and no frustration appears when adding the two contributions.