Nanoparticle wrapping at small non-spherical vesicles: curvatures at play
Supplementary Information

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This supporting information discusses wrapping energies for spherical nanoparticles at spherical vesicles without volume constraint for various spontaneous curvatures. Furthermore, we discuss calculational details for the energy minimisation for non-spherical vesicles including volume and area constraints, and the equations for calculating reduced volumes prior to and after wrapping. We plot spinodals for out-to-in and in-to-out wrapping for reduced particle size $\tilde{R}_\mathrm{p} = 0.2$, reduced volume $v = 0.7$, and reduced spontaneous curvature $\tilde{c}_0 = -0.063$. Furthermore, we present the energy barriers $\Delta\tilde{E}$ that correspond to the in-to-out wrapping transitions shown Fig. 4 of the main text.

I. WRAPPING ENERGIES AT SPHERICAL VESICLES

Vesicles that are not subject to a volume constraint are spherical both before and after wrapping. Figure S1 shows wrapping energies for two different particle sizes and various spontaneous curvatures. For vesicle sizes of the order of 100 nm and typical spontaneous curvatures, our calculations show that membrane curvature prior to wrapping dominates over spontaneous curvature.

II. VOLUME AND AREA CONSTRAINTS

Both vesicle volume and total membrane area have target values during the energy minimisation. For each minimization step, Surface Evolver attempts to achieve these values by additional vertex moves. The procedure works analogously for both volume and area constraints and is described in the following exemplarily for a volume constraint [1].

As part of the energy minimization, a first step corrects for the deviation of the actual volume from the target volume. Assuming that the actual volume V of the vesicle deviates from the targed volume by $\delta V = \mid V - V_\mathrm{tar} \mid$, the vertices are moved by

$$\mathbf{R}_i = c_\mathrm{V}\, \mathbf{g}_{\mathrm{V}i} \;\text{ for each vertex}\, i\,, \tag{S1}$$

where $\mathbf{g}_{\mathrm{V}i}$ is the gradient of the volume for the coordinates of each vertex i of the triangular membrane. Here, the desired volume correction $\delta V = -\sum_i (c_\mathrm{V}\, \mathbf{g}_{\mathrm{V}i}) \cdot \mathbf{g}_{\mathrm{V}_{\mathrm{tar},i}}$ determines

$$c_\mathrm{V} = -\frac{\delta V}{\sum_i \mathbf{g}_{\mathrm{V}i} \cdot \mathbf{g}_{\mathrm{V}_{\mathrm{tar},i}}}\,. \tag{S2}$$

In a second step, the positions of the vertices are optimised in while preserving the vesicle volume. For a total force F_i on the vertex i, the projection of this force on the subspace of volume-preserving motions is

$$\mathbf{F}_{\mathrm{i,proj}} = F_\mathrm{i} - \sum_i p\, \mathbf{g}_{\mathrm{V}i} \;\text{ for each vertex}\, i\,. \tag{S3}$$

The condition $\sum_i \mathbf{F}_{\mathrm{i,proj}} \cdot \mathbf{g}_{\mathrm{V}i} = 0$ is used to determine the excess pressure

$$p = \frac{\sum_i \mathbf{F}_{\mathrm{i,proj}} \cdot \mathbf{g}_{\mathrm{V}i}}{\sum_i \mathbf{g}_{\mathrm{V}i} \cdot \mathbf{g}_{\mathrm{V}_{\mathrm{tar}}i}}\,. \tag{S4}$$

in the vesicle at equilibrium.

III. REDUCED VOLUMES AFTER COMPLETE WRAPPING

For a vesicle prior to wrapping a particle, the reduced volume is given by Eq. (5). When a particle enters the vesicle completely, the vesicle volume $V = 4/3\pi R_\mathrm{V}^3$ effectively increases by the particle volume V_p while its membrane area A decreases by the surface area of the particle A_p. The effective reduced volume after wrapping,

$$v_2 = \frac{6\sqrt{\pi}\,(V + V_\mathrm{p})}{(A - A_\mathrm{p})^{3/2}} = \frac{v + (R_\mathrm{p}/R_\mathrm{v})^3}{[1 - (R_\mathrm{p}/R_\mathrm{v})^2]^{3/2}}\,, \tag{S5}$$

has therefore increased compared with the reduced volume prior to wrapping, see also Ref. [2]. When a particle exits a vesicle completely, the reduced volume after wrapping,

$$v_2 = \frac{6\sqrt{\pi}\,(V - V_\mathrm{p})}{(A - A_\mathrm{p})^{3/2}} = \frac{v - (R_\mathrm{p}/R_\mathrm{v})^3}{[1 - (R_\mathrm{p}/R_\mathrm{v})^2]^{3/2}}\,, \tag{S6}$$

can both decrease and increase, see Fig. 6.

IV. SPINODALS FOR WRAPPING TRANSITIONS

Figure S2 shows, in addition to the data shown in Fig. 3 in the main text, regimes for metastable non-wrapped, partial-wrapped, and complete-wrapped states. For discontinuous transitions spinodals indicate the adhesion strengths at that wrapping and unwrapping transitions take place spontaneously. For $\tilde{R}_\mathrm{p} = 0.2$, $v = 0.7$, and out-to-in wrapping, see Fig. S2(a), for negative $\tilde{c}_0$ continuous binding and envelopment transitions occur, followed by discontinuous binding and envelopment transitions, and finally discontinous combined binding-envelopment transitions with increasing $\tilde{c}_0$. For $\tilde{R}_\mathrm{p} = 0.2$, $v = 0.7$, and in-to-out wrapping, see Fig. S2(b), separate binding and envelopment transitions occur for all values of $\tilde{c}_0$; they are discontinous only for combined wrapping and shape transitions. Also for $\tilde{R}_\mathrm{p} = 0.2$ and $\tilde{c}_0 = -0.063$, see Figs. S2(c, d), we find separate binding and envelopment transitions for all reduced volumes that are only discontinous if they are combined with shape transitions.

V. ENERGY BARRIERS FOR IN-TO-OUT WRAPPING

For in-to-out wrapping, energy barriers are only found along lines in the $\tilde{c}_0$-v-plane that correspond to the boundaries where shape changes of the vesicles occur, see Fig. S3 and Fig. 8 in the main text. These energy barriers are only about 1/4 as high as those for out-to-in wrapping.

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[2] A. H. Bahrami, M. Raatz, J. Agudo-Canalejo, R. Michel, E. M. Curtis, C. K. Hall, M. Gradzielski, R. Lipowsky, and T. R. Weikl, Adv. Coll. Interface Sci. **208**, 214 (2014).

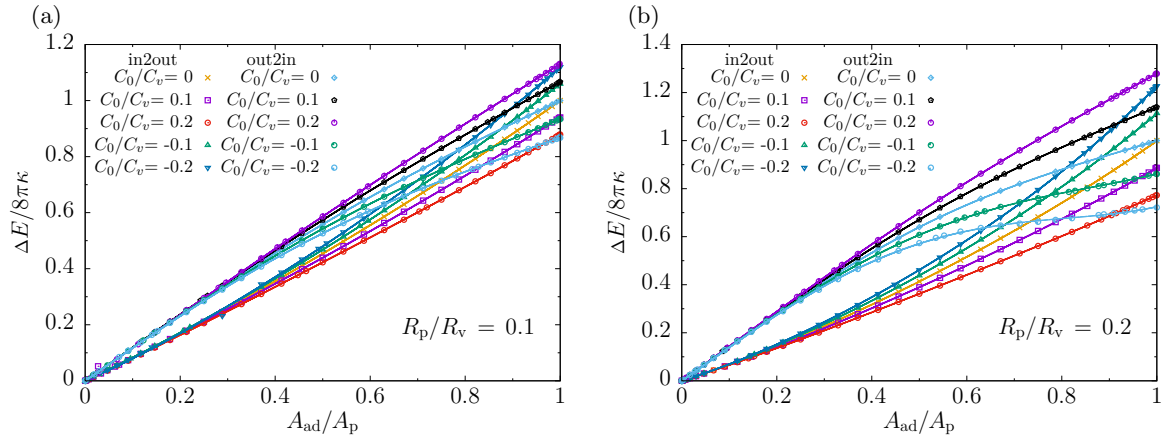

FIG. S1. Reduced wrapping energies $\Delta\tilde{E}$ as function of the wrapping fraction for particles at spherical vesicles for both, out-to-in and in-to-out wrapping. Data is shown for two different reduced particle sizes, (a) $\tilde{R}_p = 0.1$ and (b) $\tilde{R}_p = 0.2$ and various spontaneous curvatures.

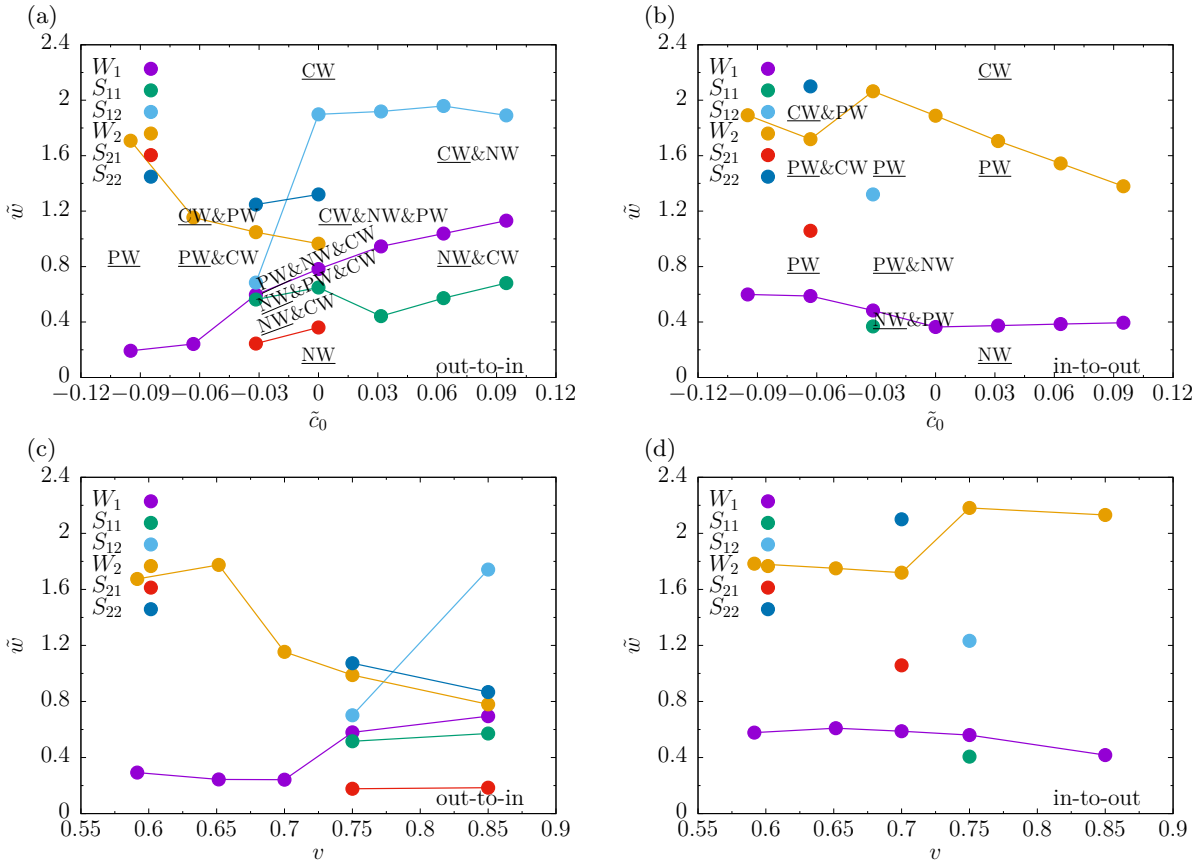

FIG. S2. Reduced adhesion strengths $\tilde{w}$ for reduced particle size $\tilde{R}_p = 0.2$, (a, b) for $v = 0.7$, as function of the reduced spontaneous curvature $\tilde{c}_0$, (c, d) for $\tilde{c}_0 = -0.063$ as function of the reduced volume v for out-to-in and in-to-out wrapping. In addition to the adhesion strengths for the transitions shown in Fig. 3 of the main text, also the spinodals S_{11} and S_{12} for W_1 and S_{21} and S_{22} for W_2 are shown. S_{11} and S_{21} denote unwrapping spinodals, S_{12} and S_{22} wrapping spinodals. Complete-wrapped (CW), partial-wrapped (PW), and non-wrapped (NW) states are indicated. Globally stable states are underlined in order to distinguish them from metastable states.

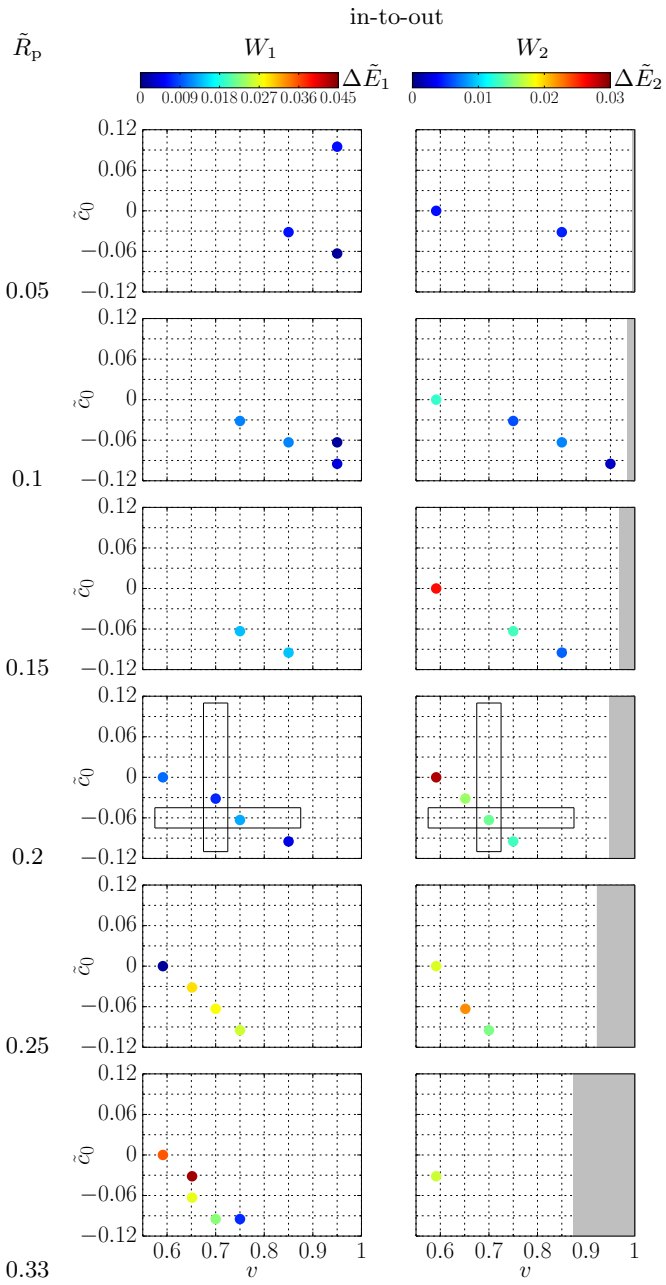

FIG. S3. Energy barriers $\Delta\tilde{E}_1$ and $\Delta\tilde{E}_2$ for the wrapping transitions W_1 and W_2, respectively. Data is shown for in-to-out wrapping for various reduced particle sizes $\tilde{R}_\mathrm{p}$, reduced volumes v, and reduced spontaneous curvatures $\tilde{c}_0$. Data for out-to-in wrapping is shown in Fig. 5 in the main text. Complete-wrapped states are not accessible in the grey-shaded areas due to lack of membrane area. The wrapping transitions for $\tilde{R}_\mathrm{p} = 0.2$ and $v = 0.7$ shown in Fig. 3(b) of the main text, and for $\tilde{c}_0 = -0.063$ shown in Fig. 3(d) of the main text, are marked.