Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

The shape equations and boundary conditions

Following ref[40], we switch from the Lagrange function (Eq. 9) to a Hamiltonian description of the energy in the free part of the membrane:

$$\begin{aligned}\mathscr{H} &= \dot{\psi} p_\psi + \dot{r} p_r + \dot{h} p_h - \mathscr{L} \\ &= \frac{p_\psi^2}{4r} - \frac{p_\psi \sin\psi}{r} - \frac{2\sigma r}{k_c}(1-\cos\psi) + p_r\cos\psi + p_h \sin\psi \ ,\end{aligned} \tag{12}$$

with the conjugate momenta in the following forms:

$$p_\psi = \frac{\partial L}{\partial \dot{\psi}} = 2r\left(\dot{\psi} + \frac{\sin\psi}{r}\right) \ , \tag{13a}$$

$$p_r = \frac{\partial L}{\partial \dot{r}} = \lambda_r \ , \tag{13b}$$

$$p_h = \frac{\partial L}{\partial \dot{h}} = \lambda_h \ . \tag{13c}$$

Applying the Hamilton's equations yields a set of 1st-order differential equations, *i.e.*, the shape equations:

$$\dot{\psi} = \frac{p_\psi}{2r} - \frac{\sin\psi}{r} \ , \tag{14a}$$

$$\dot{r} = \cos\psi \ , \tag{14b}$$

$$\dot{h} = \sin\psi \ , \tag{14c}$$

$$\dot{p}_\psi = \left(\frac{p_\psi}{r} - p_h\right)\cos\psi + \left(\frac{2\sigma r}{k_c} + p_r\right)\sin\psi \ , \tag{14d}$$

$$\dot{p}_r = \frac{p_\psi}{r}\left(\frac{p_\psi}{4r} - \frac{\sin\psi}{r}\right) + \frac{2\sigma}{k_c}(1-\cos\psi) \ , \tag{14e}$$

$$\dot{p}_h = 0 \ . \tag{14f}$$

The boundary conditions at large arc length are identical for both NP models studied here, since the membrane becomes flat at an infinite s. Hence,

$$\lim_{s\to\infty} \psi(s) = 0 \ , \tag{15a}$$

$$\lim_{s\to\infty} \dot{\psi}(s) = 0 \ . \tag{15b}$$

At the point where the membrane first detaches from the NP surface, the boundary conditions are, however, model specific. For the prolate spheroid, they are

$$r(0) = a\sin\alpha \ , \tag{16a}$$

$$h(0) = -c\cos\alpha \ , \tag{16b}$$

$$\psi(0) = \begin{cases} \arctan\left(\frac{c}{a}\tan\alpha\right) & \alpha \le \frac{\pi}{2} \\ \pi + \arctan\left(\frac{c}{a}\tan\alpha\right) & \alpha > \frac{\pi}{2} \end{cases} \tag{16c}$$

where again α denotes the polar angle of the point where the membrane detaches from the NP surface.

For the rounded cone model, the above boundary conditions are replaced by:

$$r(0) = R\sin\theta + L'\cos\theta \ , \tag{17a}$$

$$h(0) = -R\cos\theta + L'\sin\theta \ , \tag{17b}$$

$$\psi(0) = \theta \ . \tag{17c}$$

Note that if the membrane already detaches from the surface of the spherical tip (at a location with polar angle α), then $L' = 0$ and θ is replaced by α in the above equations.

As discussed in ref[40], the conjugate momenta p_h drops out of the above equations everywhere and $p_r(0)$ takes the following general form:

$$p_r(0) = \frac{1}{\cos\psi(0)}\left[\frac{p_\psi(0)\sin\psi(0)}{r(0)} + \frac{2\sigma r(0)}{k_c}(1-\cos\psi(0)) - \frac{p_\psi^2(0)}{4r(0)}\right] \ . \tag{18}$$

This leaves the only missing boundary condition being $p_\psi(0)$, which depends on $\dot{\psi}(0)$. The value of $\dot{\psi}(0)$ that fulfills Eq. 15 is found via the bisection method. Following the practice of ref[40], Eq. 15 is revised as $\psi(S) = 0$ and $\dot{\psi}(S) = 0$, where S is an arbitrarily large distance. In our calculations, we set $S = 200\,\text{nm}$. Different values of S were tested, which produced negligible differences in the resulting energy within our parameter space (data not shown).

Analysis of ΔE_{tot} for the rounded cone NP

The change in E_{tot} (ΔE_{tot}) upon pore formation is obtained by summing up the pore edge energy (E_{pore}), the contribution from Gaussian curvature (E_{gau}), and the released adhesion, bending and stretching energy due to the receding of the membrane. For the rounded cone NP model, when the pore is restricted to its tip,

$$\begin{aligned}\Delta E_{\text{tot\_RCtip}} &= \overbrace{\eta 2\pi R\sin\beta}^{E_{\text{pore}}} \overbrace{-2\pi k_g(1-\cos\beta)}^{E_{\text{gau}}} - E_{\text{RCtip}}(\alpha=\beta) \\ &= \eta 2\pi R\sin\beta - 2\pi k_g(1-\cos\beta) - [(4\pi k_c - 2\pi\omega R^2)(1-\cos\beta) \\ &\quad + \sigma\pi R^2(1-\cos\beta)^2] \ .\end{aligned} \tag{19}$$

From the above equation, it is straightforward to obtain:

$$\begin{aligned}\frac{\partial \Delta E_{\text{tot\_RCtip}}}{\partial\beta} &= \eta 2\pi R\cos\beta - 2\pi k_g\sin\beta - [(4\pi k_c - 2\pi\omega R^2)\sin\beta \\ &\quad + 2\sigma\pi R^2(1-\cos\beta)\sin\beta] \\ &= \frac{\sin\beta}{1-\cos\beta}\Delta E_{\text{tot\_RCtip}} - 2\pi R\eta - \sigma\pi R^2\sin\beta(1-\cos\beta) \ .\end{aligned} \tag{20}$$

With β restricted to the range of (0, θ] and $0 < \theta < \frac{\pi}{2}$, it is clear that when $\Delta E_{\text{tot\_RCtip}} < 0$, all three terms in the above equation are negative, resulting in $\frac{\partial \Delta E_{\text{tot\_RCtip}}}{\partial\beta} < 0$. For this reason, if a pore forms at all, it will at least grow to cover the entire spherical tip of the rounded cone. Setting $\Delta E_{\mathrm{tot\_RCtip}} = 0$, we further obtain the formula for ω_{PT} shown in the main text (Eq. 11).

When a pore continues to grow and spans a length L_p along the side of cone, the change in E_{tot} upon pore formation becomes

$$\begin{aligned}\Delta E_{\mathrm{tot\_RCside}} &= \overbrace{\eta 2\pi(R\sin\theta + L_p\cos\theta)}^{E_{\mathrm{pore}}} \overbrace{-2\pi k_g(1-\cos\theta)}^{E_{\mathrm{gau}}} - E_{\mathrm{RCside}}(L' = L_p) \\ &= AL_p^2 + B\,L_p + C\,\ln\left(1 + \frac{L_p}{R\tan\theta}\right) + D\ . \end{aligned} \tag{21}$$

where $A = \pi\cos\theta(\omega - \omega_{\mathrm{min}})$, $B = 2\pi[\eta\cos\theta + R\sin\theta(\omega - \omega_{\mathrm{min}})]$, $C = -k_c\pi\tan\theta\sin\theta$, and $D = 2\pi\eta R\sin\theta - 2\pi(1-\cos\theta)[k_g + 2k_c - (\omega - \omega_{\mathrm{min}})R^2]$, with $\omega_{\mathrm{min}} \equiv \sigma(1-\cos\theta)$.

Despite the complex form of $\Delta E_{\mathrm{tot\_RCside}}$, analysis of its differential shows that $\Delta E_{\mathrm{tot\_RCside}}$ achieves its minimum at a finite L_p under the condition that $\omega > \omega_{\mathrm{min}}$:

$$L_p = -R\tan\theta - \frac{\eta}{2(\omega - \omega_{\mathrm{min}})} + \frac{1}{2}\sqrt{\left(\frac{\eta}{\omega - \omega_{\mathrm{min}}}\right)^2 + \frac{2k_c\tan^2\theta}{\omega - \omega_{\mathrm{min}}}} \tag{22}$$

If $L_p > 0$, *i.e.*, when the pore grows onto the side of the rounded cone, its radius is $r_p = R\sin\theta + L_p\cos\theta$. Given the above expression of L_p, it becomes immediately clear that all R-dependent terms are canceled in r_p. As a result, when a pore grows onto the side of the rounded cone, its size becomes independent of the tip radius R. Similar as the derivation of ω_{PT}, setting $L_p = 0$ yields the formula for ω_{PbT}:

$$\omega_{\mathrm{PbT}} = \frac{k_c}{2R^2} - \frac{\eta}{R\tan\theta} + \sigma(1-\cos\theta)\ . \tag{23}$$

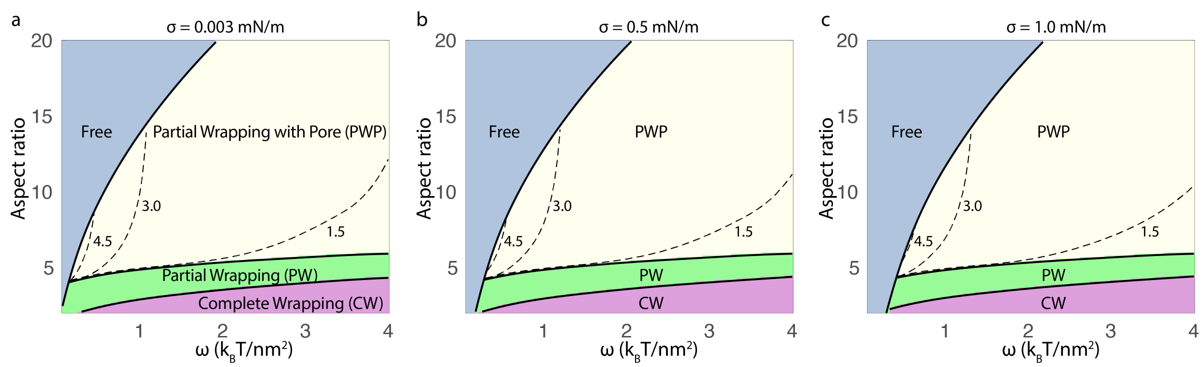

Fig. S1 Phase diagrams of the prolate spheroid NP with $c = 50\,\mathrm{nm}$ at $\sigma = 0.003\,\mathrm{mN/m}$ (a), $\sigma = 0.5\,\mathrm{mN/m}$ (b), and $\sigma = 1.0\,\mathrm{mN/m}$. Dashed curves represent contour lines of pore radius (unit: nm).

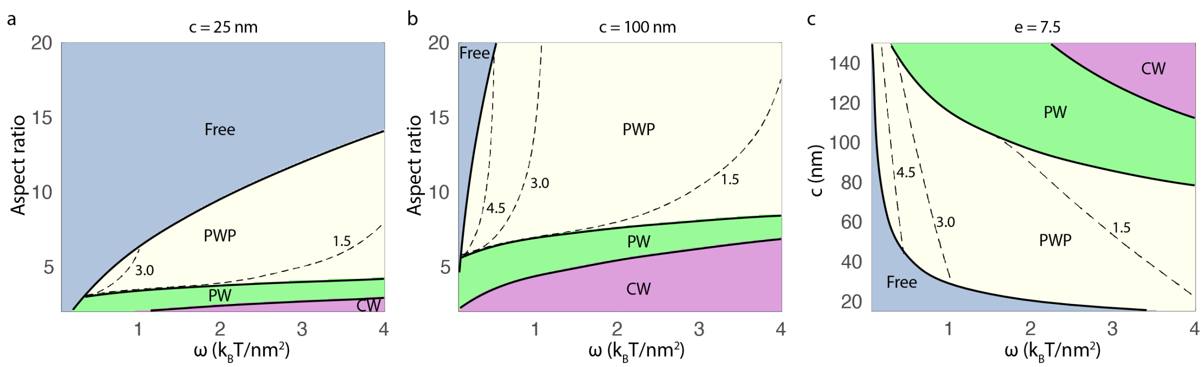

Fig. S2 **Phase diagrams of the prolate spheroid NP at $\sigma = 0.05\,\mathrm{mN/m}$ with $c = 25\,\mathrm{nm}$ (a), $c = 100\,\mathrm{nm}$ (b), or aspect ratio $e = 7.5$. Dashed curves represent contour lines of pore radius (unit: nm).**

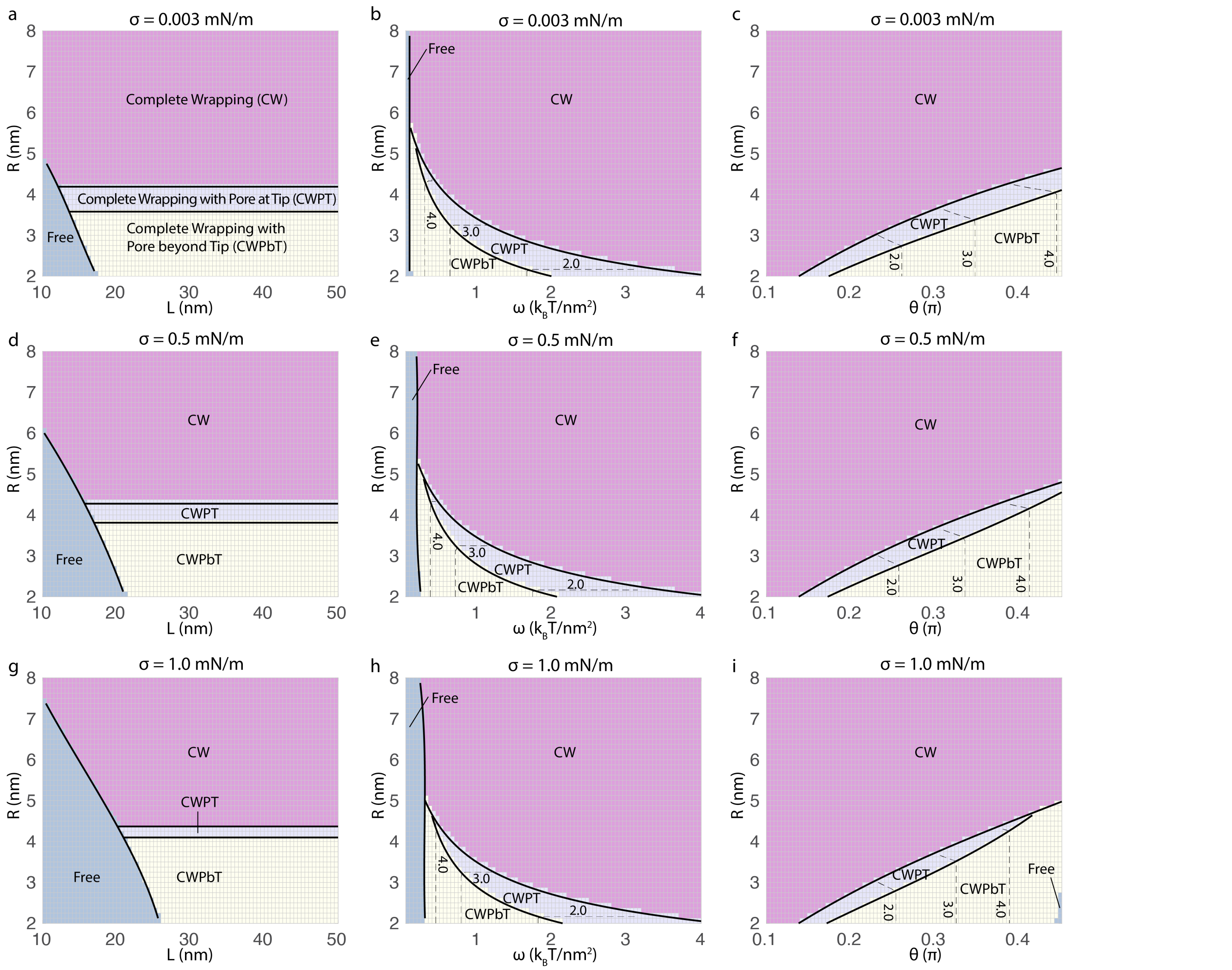

Fig. S3 Phase diagrams of the rounded cone NP at $\sigma = 0.003$ mN/m (a-c), $\sigma = 0.5$ mN/m (d-f) and $\sigma = 1.0$ mN/m (g-i), with (a, d, g) $\theta = 0.375\pi$ and $\omega = 0.5$ $k_B T/nm^2$, (b, e, h) $\theta = 0.375\pi$ and $L = 50$ nm, or (c, f, i) $L = 50$ nm and $\omega = 0.5$ $k_B T/nm^2$. Dashed curves represent contour lines of pore radius (unit: nm).

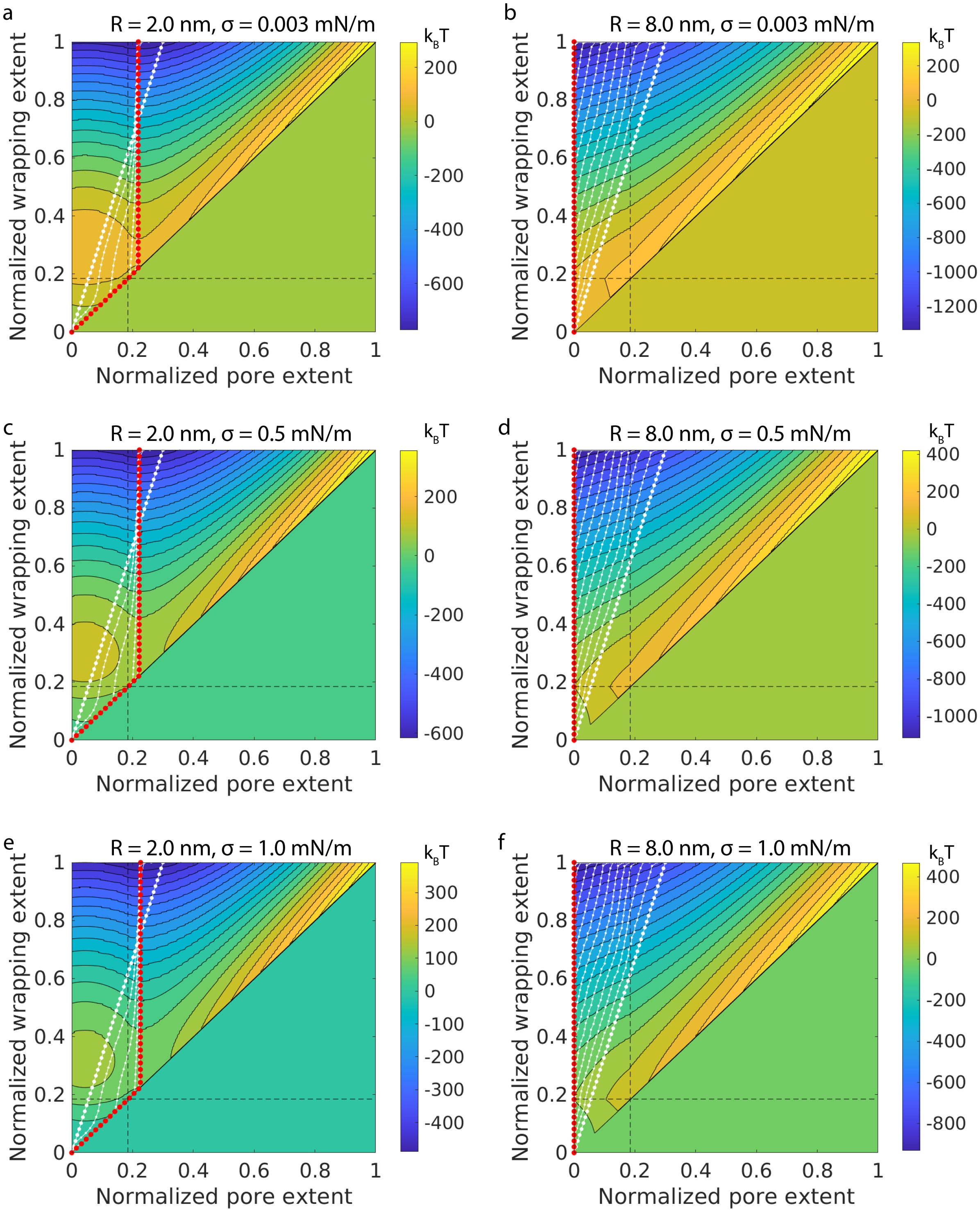

Fig. S4 Two-dimensional energy profiles of E_{tot} as a function of the normalized wrapping and pore extent with $\omega = 0.5$ k_BT/nm^2, $\theta = 0.295\pi$, $L = 30$ nm and (a) $\sigma = 0.003$ mN/m, $R = 2.0$ nm, (b) $\sigma = 0.003$ mN/m, $R = 8.0$ nm, (c) $\sigma = 0.5$ mN/m, $R = 2.0$ nm, (d) $\sigma = 0.5$ mN/m, $R = 8.0$ nm, (e) $\sigma = 1.0$ mN/m, $R = 2.0$ nm, or (f) $\sigma = 1.$ mN/m, $R = 8.0$ nm. The final MEPs determined by the string method are shown in red dots, while the initial strings are shown in big white dots, with small white dots representing the evolution of the strings. The boundary between the tip and the side of the rounded cone is marked by black dashed lines.