Supporting information

Nonlinear dilatational rheology of different protein aggregates at the oil-water interface

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According to Rayner's study, it is known that the adsorption strength of particles to the oil-water interface can be described by the free energy of the particles adsorbed on the oil-water interface.[1] If a particle moves from an equilibrium position at an interface to any phase, a certain amount of energy is required. When it is completely out of the interface, the change of the surface free energy of the system can be easily calculated. By measuring the particle-oil, particle-water and oil-water interfacial tensions γ_{po}, γ_{pw}, γ_{ow}, the area of the oil-water interface A_{ow}, the area of the particle surface in contact with the water and oil phases A_{pw} and A_{po}, and the contact angle θ, the free energy of detach can be deduced and calculated, expressed as a function of the radius of the sphere and the contact angle of the oil-water particles as follows:

$$\Delta G_{detach} = \pi R^2 \gamma_{ow}(1-|cos\theta|)^2 \tag{1}$$

where ΔG_{detach} is the free energy of detach, R is the particle radius, γ_{ow} is the oil-water interfacial tension, and θ is the contact angle.

Assuming that the contact angles are all 90°, the equation for the free energy required to detach the protein and its aggregates from the oil-water interface can be simplified as:

$$\Delta G_{detach} = \gamma_{ow} \times A \tag{2}$$

In this paper γ_{ow} is 47 mN/m for pure decane-water interface and A is the cross-sectional area of the protein aggregates. Then the free energy of detach was calculated in Table S1.

Table S1 The free energy of detach of protein aggregates.

Interface type	Oil-water interfacial tension (γ_{ow}, mN/m)	Contact angle (θ)	Radius (R, nm)	Length (L, nm)	Cross-sectional area (A, nm^2)	Free energy of detach (ΔG_{detach}, kJ)
Long fibers	47.0	90.0	5-10.0	1000.0	10000.0-20000.0	470.0-940.0
Short fibers	47.0	90.0	5-10.0	100.0	1000.0-2000.0	47.0-94.0
Nanoparticles	47.0	90.0	90.0-175	--	25434.0-96162.5	1195.4-4519.6
βlg	47.0	90.0	2.5	--	19.6	9.2

Note: βlg represents "β-lactoglobulin".

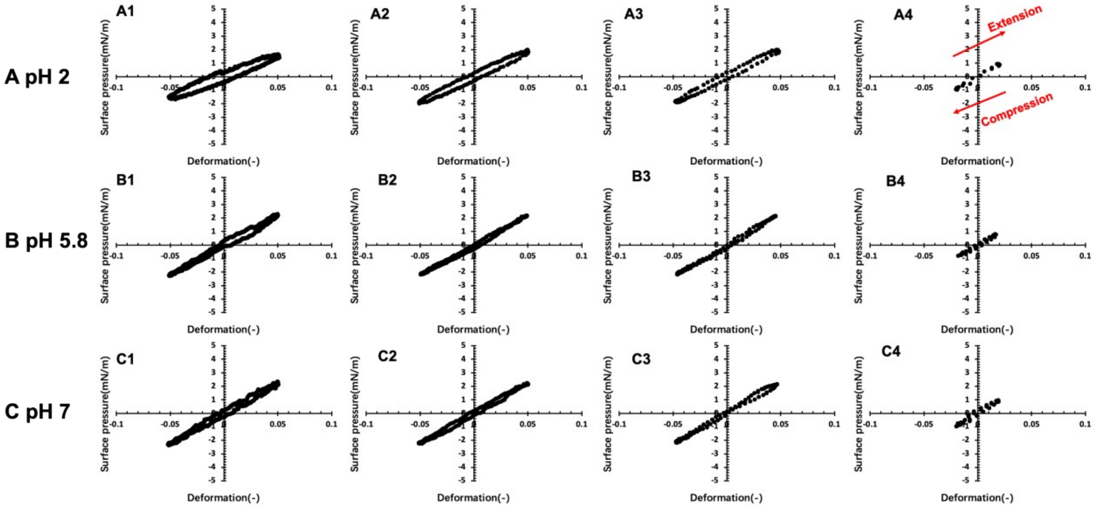

Fig. S1 Lissajous plots of protein fibril interface at (A) pH 2, (B) pH 5.8, and (C) pH 7 during dilatational oscillation with frequency of: A1-C1, 0.01 Hz; A2-C2, 0.05 Hz; A3-C3, 0.1 Hz; A4-C4, 0.4 Hz. The oscillation direction is indicated A4. The dilatational oscillation amplitude is controlled at 5%.

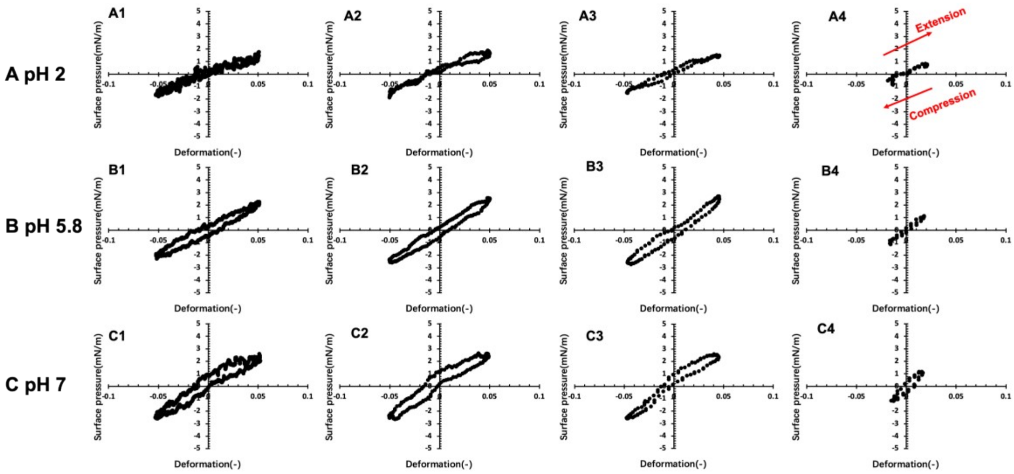

Fig. S2 Lissajous plots of protein nanoparticle interfaces at (A) pH 2, (B) pH 5.8, and (C) pH 7 during dilatational oscillation with frequency of: A1-C1, 0.01 Hz; A2-C2, 0.05 Hz; A3-C3, 0.1 Hz; A1-C1, 0.4 Hz. The oscillation direction is indicated A4. The dilatational oscillation amplitude is controlled at 5%.

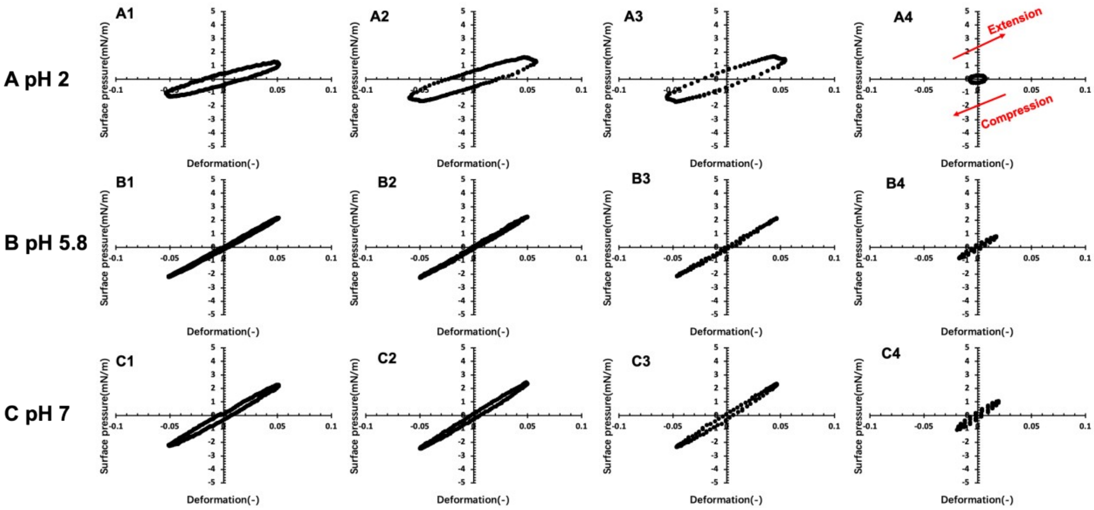

Fig. S3. Lissajous plots of β-lactoglobulin interfaces at (A) pH 2, (B) pH 5.8, and (C) pH 7 during dilatational oscillation with frequency of: A1-C1, 0.01 Hz; A2-C2, 0.05 Hz; A3-C3, 0.1 Hz; A1-C1, 0.4 Hz. The oscillation direction is indicated in A4. The dilatational oscillation amplitude is controlled at 5%.

References

1 M. Rayner, D. Marku, M. Eriksson, M. Sjöö, P. Dejmek and M. Wahlgren, *Colloids & Surfaces A Physicochemical & Engineering Aspects*, 2014, 458, 48-62.