

## Supporting Information (Manuscript # B903103K, A. Shukla *et al.*):

### 1. Scattering from casein micelles suspensions as a function of concentration

Figure S1 shows the typical SAXS patterns from casein micelles as a function of volume fraction from 0.003 to 0.1 (batch 1). The scattering features are identical for the volume fraction range of 0.01 – 0.1. This shows that the influence of the structure factor of interparticle interactions is not significant, presumably due to the large polydispersity of the micelles<sup>1</sup>. Therefore, the structure factor term was omitted in the SAXS analysis. Below 0.003, micelles tend to become unstable with gradual weakening of the globular part.

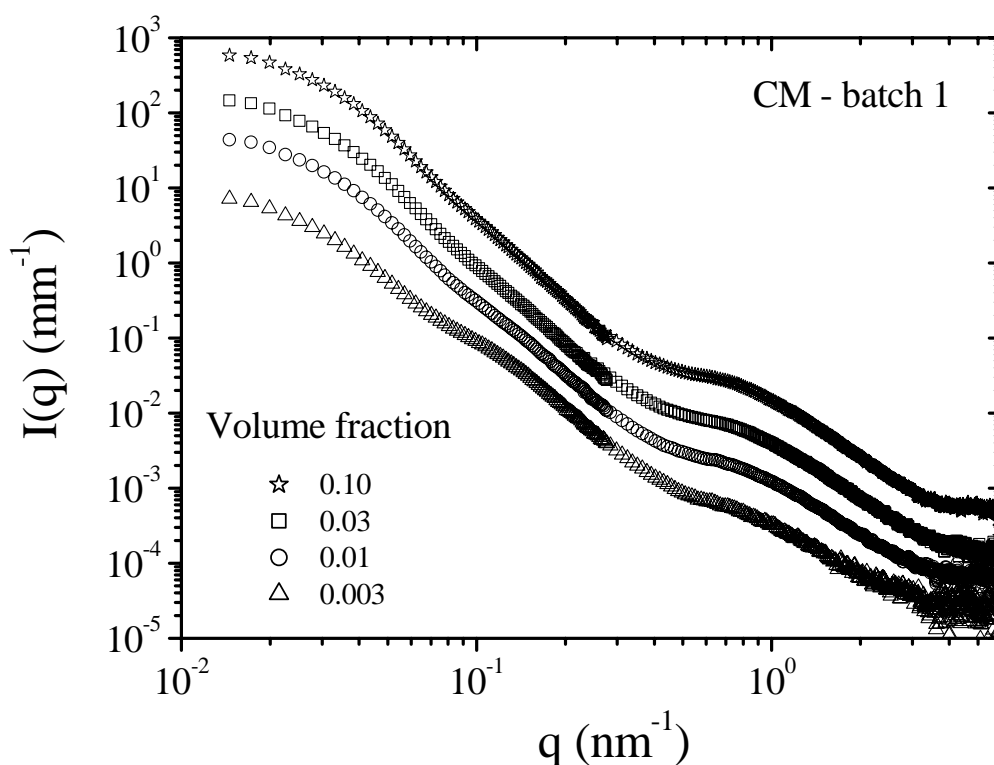


Figure S1: SAXS intensities from casein micelle suspensions as a function of the volume fraction. The shape of scattering curves superimpose over the range of volume fraction 0.01 – 0.1.

## 2. Modeling of SAXS data

From Figs. 1 and S1, it is evident that the total scattered intensity,  $I(q)$ , from casein micelles can be decomposed into a globular core-shell structure  $I_{CS}(q)$  and a non-globular internal structure  $I_{IS}(q)$ .

$$I(q) = I_{CS}(q) + I_{IS}(q) \quad (S1)$$

Neglecting the influence of the structure factor of interactions,  $I_{CS}(q)$ , has the general form,

$$I_{CS}(q) = N(\Delta\rho^* V_P)^2 P_{CS}(q) \quad (S2)$$

where  $N$  is the number density of particles,  $\Delta\rho^*$  is the difference between the radial X-ray scattering length densities for the particle and the buffer ( $\Delta\rho^* = r_e \Delta\rho$ , with  $r_e$  the electronic scattering length  $= 2.82 \times 10^{-15}$  m and  $\Delta\rho$  the electron density difference),  $V_P$  is the average volume of particles, and  $P_{CS}(q)$  is the form factor of the particles which depends on their size and shape<sup>1</sup>. However, casein micelles have a large distribution in their sizes. To treat this size polydispersity, Eq. (S2) needs to be averaged over the particle size distribution. Here, the size distribution was considered only in the core radius while the shell thickness,  $t$ , is assumed to be uniform. In this case,  $I_{CS}(q)$  is replaced by the size averaged quantity,

$$\langle I_{CS}(q, R) \rangle = \int_0^{\infty} I_{CS}(q, R) W(R, R_C, \sigma) dR \quad (S3)$$

where  $W(R, R_C, \sigma)$  is the normalized probability of finding a particle with a core radius between  $R$ , and  $R + dR$ , and  $R_C$  is the mean core radius. Here, the core polydispersity can be represented by the Schulz distribution<sup>2</sup>, which is both physically realistic as well as mathematically tractable. The normalized form of this distribution is given by

$$W(R, R_C, \sigma) = \frac{R^Z}{\Gamma(Z+1)} \left( \frac{Z+1}{R_C} \right)^{Z+1} \times \exp \left[ -\frac{R}{R_C} (Z+1) \right] \quad (S4)$$

where  $Z$  is related to the normalized second moment (or polydispersity)  $\sigma$  of the particle core radius distribution by the expression,

$$\sigma = \left( \frac{\overline{R^2}}{R_C^2} - 1 \right) = \frac{1}{Z + 1} \quad (\text{S5})$$

For finite  $Z$ , the Schulz distribution has the realistic feature that it is skewed towards large sizes. With increasing  $Z$ , Eq. (S4) asymptotically approaches a Gaussian and, in the limit of  $Z \rightarrow \infty$ , tends to a delta function at  $R_C$ . In addition, a Weibull distribution was also tried but the Schulze function was found to be sufficient.

For spherically symmetric core-shell particles with a radial electron density gradient,  $I_{CS}(q)$  is given by,

$$I_{CS}(q) = N (A_{CS}(q))^2 \quad (\text{S6})$$

where  $A_{CS}(q)$  is the complex scattering amplitude given by the Fourier transform of the radial scattering length density difference from the solvent<sup>1</sup>,  $\Delta\rho^*(r)$ , and

$$A_{CS}(q) = 4\pi \int_0^R \Delta\rho^*(r) \frac{\sin(qr)}{qr} r^2 dr \quad (\text{S7})$$

The  $\Delta\rho^*(r)$  of core is assumed to be independent of radius,  $\Delta\rho_C^*$ , and the shell  $\Delta\rho^*(r)$  has a smooth profile either Gaussian or exponential. For the Gaussian diffuse shell,

$$\Delta\rho^*(r) = \Delta\rho_S^* \frac{1}{\sqrt{2\pi t}} \exp\left(-\frac{(r-R)^2}{2t^2}\right) \quad (\text{S8})$$

where  $t$  is the thickness of the shell. In this case,  $A_{CS}(q)$  can be decomposed into the core and shell terms,  $A_C$  and  $A_S$ , respectively<sup>3</sup>.

$$A_C = \Delta\rho_C^* \frac{4\pi}{q^3} \{\sin(qR) - qR \cos(qR)\} \quad (\text{S9})$$

$$A_S = \Delta\rho_S^* \frac{4\pi\sqrt{2\pi t}}{q} \exp\left\{-\frac{q^2 t^2}{2}\right\} \{qt^2 \cos(qR) + R \sin(qR)\} \quad (\text{S10})$$

Then

$$I_{CS}(q) = N (A_C(q) + A_S(q))^2 \quad (\text{S11})$$

For the exponential diffuse shell,  $\Delta\rho^*(r)$  has the form,

$$\Delta\rho^*(r) = \Delta\rho_C^* \exp\left(-\frac{(r-R)}{t}\right) \quad (\text{S12})$$

In this case,  $P_{CS}(q)$  in Eq. (S2) has the following analytical form,<sup>4</sup>

$$P_{CS}(q) = \frac{4\pi}{q^3(q^2 t^2 + 1)} \left\{ qR(qt \sin(qR) - \cos(qR)) + \frac{(1 + 3q^2 t^2) \sin(qR) + 2q^3 t^3 \cos(qR)}{(q^2 t^2 + 1)} \right\} \quad (\text{S13})$$

With the exponential diffuse shell function in Eq. (S2), it was necessary to include an additive Debye-Bueche term<sup>1</sup> of the following form in the  $I_{CS}(q)$ ,

$$I_{DB}(q) = \frac{I_{DB}}{(1 + q^2 \xi_{DB}^2)^2} \quad (\text{S14})$$

For the internal structure with reticulated calcium phosphate nanoparticles,  $I_{IS}(q)$  was obtained using an identical equation as Eq. (S2) with the form factor of an oblate ellipsoid<sup>5</sup> with major and minor radii of  $r_a$  and  $r_b$ , respectively and the corresponding volume of the ellipsoid,  $V_E = \frac{4}{3} \pi (r_a r_b^2)$ .

For the internal structure of disintegrated calcium phosphate nanoparticles,  $I_{IS}(q)$  was given by the Debye function of random coil polymer chains.<sup>5</sup>

Table S1: Fit parameters for the globular core-shell structure of casein micelles using the electron density profiles [ $\Delta\rho(r)$ ] in Fig. 2.

		$R_C$ [nm]	$t$ [nm]	$\sigma$	$I_{DB}$	$\xi_{DB}$ [nm]
Batch1	Gaussian diffuse shell	33.9	11.5	0.49	Not applied	
	Exponential diffuse shell	34.4	11.0	0.49	2.5	14.4
Batch2	Gaussian diffuse shell	54.7	11.8	0.49	Not applied	
	Exponential diffuse shell	58.3	11.0	0.49	2.5	16.5
Batch2+EGCG	Gaussian diffuse shell	54.7	11.8	0.45	Not applied	
	Exponential diffuse shell	58.3	11.0	0.45	10	16.5

Table S2: Fit parameters for the internal structure using either the form factor of oblate ellipsoidal nanoparticles or the Debye function for random coil polymer chains.

	$r_a$ [nm]	$r_b$ [nm]	$I_D$	$R_G$ [nm]
Batch1	0.71	2.5	Not applied	
Batch2	0.78	2.5	Not applied	
Batch2+EGCG	Not applied		0.0024	1.8

## References

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