Soft Matter

ARTICLE TYPE

Cite this: DOI: 00.0000/xxxxxxxxxx

Electronic Supplementary Information—Casein micelles in milk as sticky spheres

Gregory N. Smith,*[a]§ Erik Brok,[a] Morten Vormsborg Christiansen,[b] and Lilia Ahrné[b]

S1 Modeling of literature USAXS data

To benchmark our model with other data in the literature, we applied our model to the only available USAXS data that we are aware of. The data were obtained from publications using the macOS application GraphClick,[1] which has been shown to be a reliable and viable method to extract data from images.

Compared to higher Q SAXS data, there are fewer examples of USAXS data over a broad Q range in the literature. In this section, we reinterpret two sets of literature data to show consistency with the sticky sphere model that we present in this study. These were both measured using Bonse–Hart cameras to access low Q.

S1.1 ESRF data

SAXS and USAXS data were measured on the X-ray scattering beamline ID02 at the ESRF (Grenoble, France).[2] Instrument configurations for SAXS (pinhole) and USAXS (Bonse–Hart) can be found in the literature.[3] The data that we discuss in this section are for fresh skim milk.[4] The literature data presented here was originally fitted by the authors using the Debye–Büche model, which treats as scattering objects as a random distribution of two phases with a smooth interface (Q^{-4} power law at the interface).

We fit the data to the same model proposed in this study, and we find excellent agreement over the whole Q range. All parameters are fixed to the values presented in the main study, except for the SLD differences and the $Q = 0$ intensity of the polymer chains. The best fit values for the SLD differences were $\Delta\rho_1 = (0.870 \pm 0.001) \times 10^{-6}$ Å^{-2}, $\Delta\rho_2 = (0.634 \pm 0.002) \times 10^{-6}$ Å^{-2}, and $\Delta\rho_3 = (3.79 \pm 0.02) \times 10^{-6}$ Å^{-2}. The best fit value of the intensity of the scattering from polymer chains was (0.775 ± 0.002) cm^{-1}. That good agreement between this model and the data can be obtained using an extremely constrained model (only scale factors varied and geometrical parameters varied) shows that the model that we are presenting is consistent with these literature data on milk.

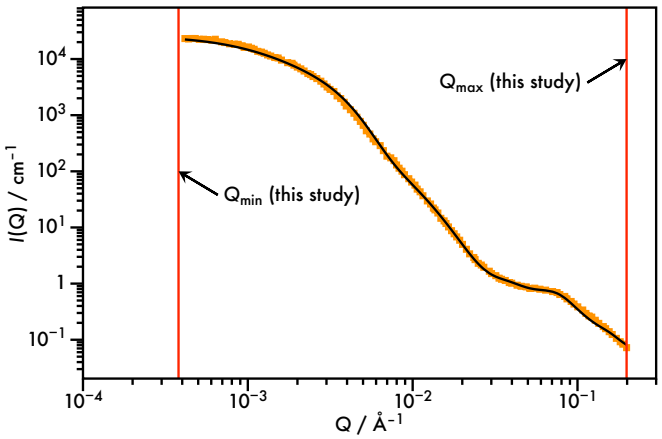

Fig. S1 SAXS and USAXS data from ID02 at the ESRF[3] on fresh skimmed milk.[4] The red lines show the Q range of the data presented in the main text of this study. The black line shows the best fit to the data obtained using the model presented in this study, with the number concentration of micelles and the $Q = 0$ intensity of the polymer chains as the only parameter that were varied.

S1.2 APS data

SAXS and USAXS data were measured using the USAXS facility, currently at APS 9ID USAXS/SAXS/WAXS at the APS (Argonne, USA).[5–7] The data from the APS were for skim milk at 7 °C,[8,9] and the specific data shown here taken from Peyronel *et al.*[9] The instrument configurations for SAXS (separate detector) and USAXS (Bonse–Hart) are provided in the literature in the same study.[9] The literature data presented here was originally fitted by the authors using the unified fit model of Beacauge, which treats the data as a series of connected power laws with smoothing parameters between each.

We fit the data to the same model proposed in this study, and we find excellent agreement over the whole Q range. Two modifications were required to preprocess the data before we attempted to fit it. Two backgrounds were fit and subtracted from the experimental data, a power law that dominated at low Q and a constant that dominated at high Q. The low Q power law was assumed to be the interface of a large object in the milk, giving rise to scattering consistent with the Porod law whereas the high Q constant was assumed to be incomplete subtraction of the instrument and sample background. The best fit values of the fit to the low Q power law were an exponent of $-(3.13 \pm 0.03)$ and scale of

[a] *Niels Bohr Institute, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen Ø, Denmark. E-mail: gregory.smith@nbi.ku.dk*
[b] *University of Copenhagen, Department of Food Science, 1958 Frederiksberg, Denmark.*
§ Present address: ISIS Neutron and Muon Source, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Didcot, OX11 0QX, United Kingdom. E-mail: gregory.smith@stfc.ac.uk

(1.0 ± 0.2). This would suggest the large objects are either aggregates (mass fractals) or rough interfaces (surface fractals). The best fit value of the fit to the high Q background was a constant of (0.19 ± 0.02).

Following this processing, the remaining parameters are fixed to the values presented in the main study, except for the SLD differences and the $Q = 0$ intensity of the polymer chains. The best fit values for the SLD differences were $\Delta\rho_1 = (0.656 \pm 0.002) \times 10^{-6}$ Å^{-2}, $\Delta\rho_2 = (0.411 \pm 0.007) \times 10^{-6}$ Å^{-2}, and $\Delta\rho_3 = (2.4 \pm 0.2) \times 10^{-6}$ Å^{-2}. The best fit value of the intensity of the scattering from polymer chains was (0.5 ± 0.1) cm^{-1}. Although additional backgrounds need to be incorporated, that good agreement between this model and the data can be obtained using an extremely constrained model (only scale factors varied and geometrical parameters varied) shows that the model that we are presenting is consistent with these literature data on milk.

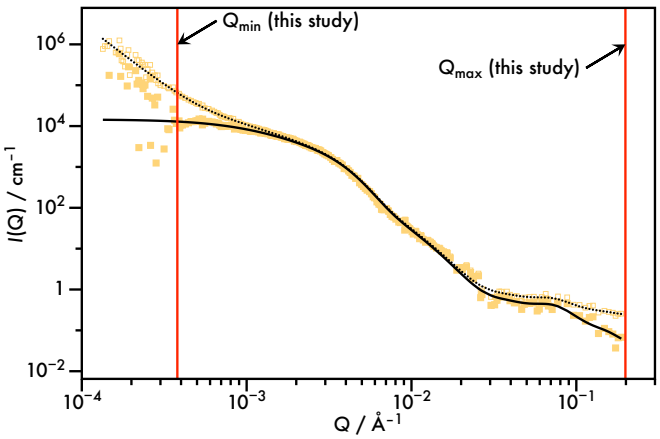

Fig. S2 SAXS and USAXS data from the USAXS facility at the APS on skim milk at 7 °C.[9] The red lines show the Q range of the data presented in the main text of this study. The filled squares and solid black lines show the data and fit after background subtraction, a power law ($I(Q) \propto Q^{-3.9}$) at low Q and a constant background at high Q. The empty symbols and dotted line, on the other hand, are the data and fit before background subtraction. The agreement between the best fit (solid line) and the data, obtained using the model presented in this study, is very good, with the number concentration of micelles and the $Q = 0$ intensity of the polymer chains as the only parameter that were varied.

Notes and references

1 M. A. Boyle, A. L. Samaha, A. M. Rodewald and A. N. Hoffmann, *Comput. Hum. Behav.*, 2013, **29**, 1023–1027.

2 T. Narayanan, M. Sztucki, P. Van Vaerenbergh, J. Léonardon, J. Gorini, L. Claustre, F. Sever, J. Morse and P. Boesecke, *J. Appl. Cryst.*, 2018, **51**, 1511–1524.

3 F. Pignon, G. Belina, T. Narayanan, X. Paubel, A. Magnin and G. Gésan-Guiziou, *J. Chem. Phys.*, 2004, **121**, 8138–8146.

4 F. Pignon, G. Belina, T. Narayanan, X. Paubel, A. Magnin and G. Gésan-Guiziou, *arXiv*, 2008, arXiv:0812.0879.

5 J. Ilavsky, P. R. Jemian, A. J. Allen, F. Zhang, L. E. Levine and G. G. Long, *J. Appl. Cryst.*, 2009, **42**, 469–479.

6 J. Ilavsky, F. Zhang, A. J. Allen, L. E. Levine, P. R. Jemian and G. G. Long, *Metall. Mater. Trans.A*, 2013, **44**, 68–76.

7 J. Ilavsky, F. Zhang, R. N. Andrews, I. Kuzmenko, P. R. Jemian, L. E. Levine and A. J. Allen, *J. Appl. Cryst.*, 2018, **51**, 867–882.

8 D. A. Pink, F. Peyronel, B. Quinn and A. G. Marangoni, *Phys. Fluids*, 2019, **31**, 077105.

9 F. Peyronel, A. G. Marangoni and D. A. Pink, *Food Res. Int.*, 2020, **129**, 108846.