

Supporting Information: Cluster-driven dynamical arrest in concentrated lysozyme solutions

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SAXS measurements

We measured the static properties of aqueous solutions of lysozyme obtained under conditions of weak electrostatic screening.¹⁻³ They are determined experimentally by means of small-angle X-ray (SAXS) scattering measurements (see Materials and Methods). To extract the static structure

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factor $S_{eff}(q)$ from the measured intensity one has to divide with the form factor of the lysozyme monomer. The resulting $S_{eff}(q)$ contains information on the correlations between monomers on all length scales, including information on the aggregates formed by the monomers and their spatial correlation.

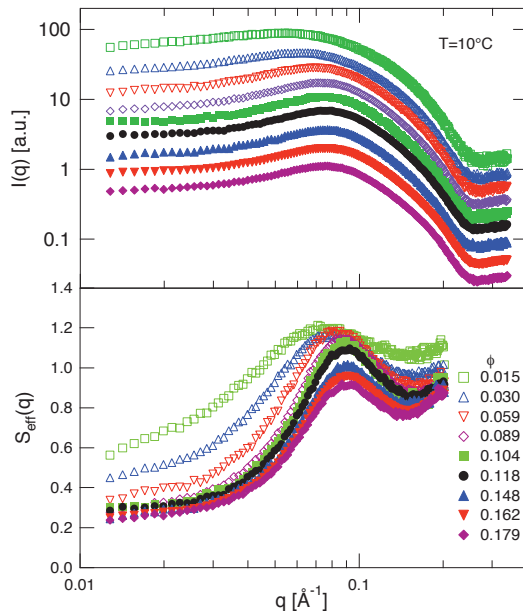


Figure 1: Top: Scattering intensity $I(q)/\phi$ versus scattering vector q obtained from a systematic SAXS investigation of the concentration dependence of lysozyme solutions at $T = 10^\circ \text{C}$ in H_2O and no added salt. The data has been shifted on the y-axis for better visibility. Bottom: Effective static structure factors $S_{eff}(q)$ obtained from the data shown in Top.

To highlight the dependence of the cluster peak position on concentration, we conducted additional experiments under conditions (10°C) where cluster growth is less pronounced. Figure 1 summarizes the results for $S_{eff}(q)$ obtained by SAXS experiments with lysozyme solutions at 10°C in the low salt limit for several values of lysozyme volume fractions. Qualitatively, we observe a systematic decrease of $S_{eff}(q \rightarrow 0)$ as ϕ increases, as well as the development of a low q peak in $S_{eff}(q)$ that we refer to as the cluster peak (q_c). This is followed at larger q by the so-called monomer peak (q_m), which is however outside of the q -range covered by our current SAXS measurements.^{1,2} The position of q_c moves to higher q with increasing ϕ up to $\phi \approx 0.08$, above which it remains almost constant while its amplitude continuously decreases. Simultaneously, the

amplitude of q_m increases with ϕ while its position at $q_m \approx 0.225 \text{ \AA}^{-1}$ was found to be insensitive to ϕ over the entire range investigated.¹

The qualitative behavior of $S_{eff}(q)$ provides insight into the type of interactions present among lysozyme particles. First, the decrease of $S_{eff}(0)$ with increasing ϕ is qualitatively consistent with that of a repulsive system. However, the fact that for intermediate and high ϕ we observe an almost constant peak position q_c contradicts the $q \propto n^{1/3}$ scaling expected for charged systems, where n is the particle number density. Note that here temperature plays an important role in the modulation of $S_{eff}(q)$.² Typically, an increase in temperature shifts q_c to lower values while q_m remains the same but with a slightly smaller amplitude of $S_{eff}(q_m)$. Finally, the high q peak at $q_m \approx 0.225 \text{ \AA}^{-1}$ suggests strong monomer-monomer correlations at contact resulting from the presence of attractive forces between the particles.

Viscosity measurements

The results for the flow curves on selected samples are shown in the inset of Figure 2. Surprisingly, a shear thinning region is visible for all flow curves and is particularly marked for the lowest measured volume fraction. This effect can be explained with the ability of proteins to unfold and expose their hydrophobic patches at air/water interface and subsequently form weak elastic networks.⁴ To test this hypothesis, we measured the flow curves of a low viscosity oil where a thin film of the lysozyme solution has been added on the border of our measuring tool. A strong increase of the viscosity at low shear rate is indeed observed and reported in Figure 2. This result demonstrates how this peculiar property of lysozyme at interfaces generates an additional effect for a purely viscous liquid of known viscosity. Figure 2 also shows that the actual zero shear viscosity of the oil can be recovered by an extrapolation of the flow curve at high strain rates. The accuracy of such a procedure strongly depends on the absolute value of the viscosity. We estimate that η_0 can be obtained within 25% at lowest ϕ , whereas an uncertainty of 4% or less can be reached for viscosities about ten times that of the solvent. However, it is important to point out that this procedure is only valid if the non-linear contribution arising from the interfacial network formed

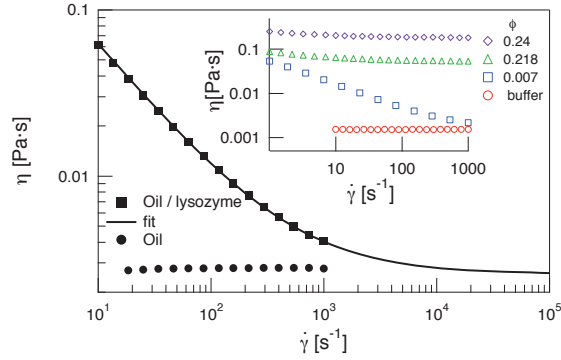


Figure 2: Illustration of the effect produced by the air/solution interface on the measured flow curves of a low viscosity oil with and without a thin layer of lysozyme solution added on the border of the measuring tool. The solid line is a fit to the data that allows to extrapolate the solution zero shear viscosity. Inset: Flow curves measured for lysozyme solutions at $T = 5C$ for various volume fractions.

by lysozyme decays for shear rates clearly separated from the onset of the non-linear behavior of the bulk solution, which we estimate to occur at much higher values of $\dot{\gamma}$ for lysozyme solutions under the current conditions.

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