Counterion Density Wave Melting on Biopolymer Surfaces

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Introduction

It has been shown that multivalent counterion correlations can mediate like-charged attractions between polyelectrolytes. F-actin is an exemplary polyelectrolyte for investigating the spatial correlations of such multivalent counterions, since it is a stiff, helical, rodlike biopolymer with a large persistence length of ~10 μm, a large diameter of 80 Å, and a large linear charge density of ≈ −1e/2.5 Å. Recently, we found that the distribution of divalent counterions in a bundled phase of F-actin forms a 1-D counterion density wave (CDW) that is parallel to the actin filaments and does not follow the helical twist of F-actin. In fact, the periodic distribution of ions in the bundle causes a conformational change in the twist of the F-actin to optimize charge alignment [1] in a way analogous to polarons in ionic solids.

How is the behavior of this system changed if we use a mixture of ions of different sizes and valences? Lysozyme is a globular antibacterial protein that functions as an enzyme in cell-wall hydrolysis and has been shown to bind to actin in cystic fibrosis mucus. It has an approximate size of 25 x 25 x 45 Å and a total charge of +9e at neutral pH, so it is a model multivalent macroion that is significantly larger than typical hydrated ions. We find that the presence of lysozyme will melt the divalent CDW state. The system forms a CDW state at low lysozyme/divalent-ion ratios. As the lysozyme/ divalent-ion ratio increases, the columnar actin lattice expands, and the CDW state melts. This progression is directed and monitored by using synchrotron small-angle x-ray diffraction, as shown in Figs. 1 and 2.

Methods and Materials

F-actin was prepared according to Ref. 1. The samples were condensed with varying concentrations of lysozyme and $BaCl_2$ and sealed in 1.5-mm-diameter quartz capillaries. The small-angle x-ray scattering experiments were conducted at the UNI-CAT 34-ID beamline at the APS. The x-ray energy was 10 keV. The powder-averaged diffraction patterns were integrated by using the program Fit2D, producing a 1-D diffraction pattern.

Results

Experimental evidence for a CDW in electrostatically bundled F-actin is discussed in Ref. 1. Divalent ions in the bundle form a sinusoidal distribution along the length of the filament. The periodicity of the distribution causes the appearance of a sharp peak in a diffraction pattern. An example of a 1-D small-angle x-ray spectroscopy (SAXS) diffraction pattern of F-actin bundles is provided in Fig. 1. The signature of divalent-ion condensed F-actin is the CDW peak [Fig. 2, (a)] at q = 1.06 nm^{-1}. When the $BaCl_2$ concentration is fixed at 30 mM, the CDW peak appears strong in low lysozyme (1.23 mg/g) samples. The peak weakens as the lysozyme concentration increases, until it is indiscernible at a high lysozyme concentration (12.3 mg/g).

Discussion

From the preliminary 30 mM $BaCl_2$ data, it appears that lysozyme expands the columnar lattice of F-actin and melts the CDW. At present, we are trying to determine whether lysozyme replaces the divalent ions progressively or collectively.

Acknowledgments

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Reference

[1] T.E. Angelini, H. Liang, W. Wriggers, and G.C.L. Wong, Proc. Natl. Acad. Sci. U.S.A. **100**, 8634 (2003).

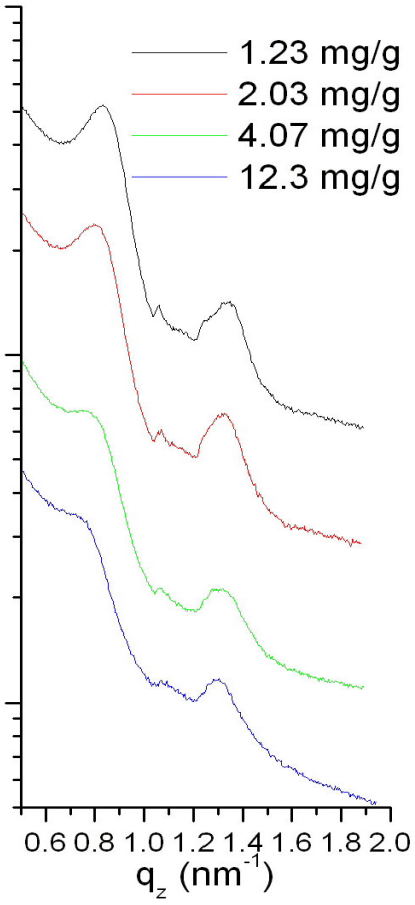

FIG. 1. SAXS diffraction pattern from F-actin bundles condensed by 30 mM $BaCl^2$, with varying lysozyme concentrations (in milligrams per grams of solution).

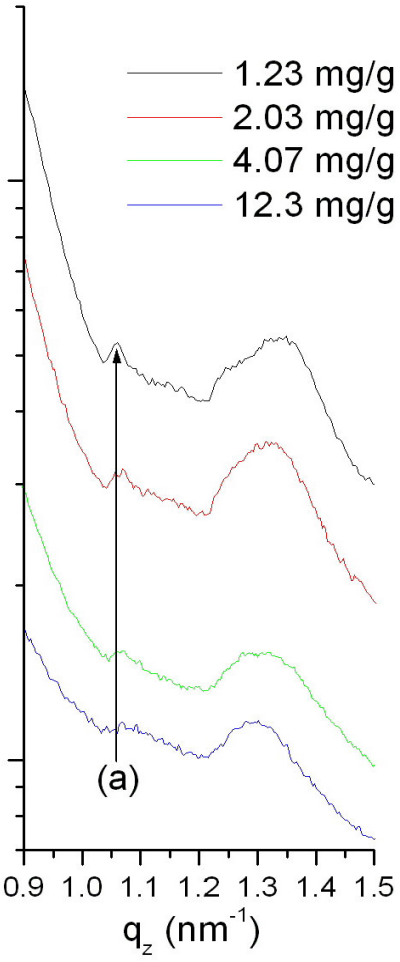

FIG. 2. SAXS pattern in FIG. 1 zoomed in to better demonstrate the charge density wave (a). The amplitude of this peak diminishes as lysozyme concentration increases, which indicates that the distribution of counterions is disrupted by lysozyme in the bundle.