Critical Size for Bulk-to-Discrete Transition in 2D Layers: Abrupt Size Effect Observed via Calorimetry and Solid-State NMR

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Abstract:

Anomalous changes of physical properties are observed in an abrupt bulk-to-discrete transition in layered silver alkanethiolate (AgSCn, n = 1-16). A critical chain length of ncr = 7 marks the sharp boundary between the bulk (uniform, n ≥ 7) and discrete (individualistic, n ≤ 6) forms of AgSCn. Solid-state 13C NMR analysis reveals that none of the carbons share identical chemical environment in the discrete range, making each AgSCn with n = 2-6 uniquely different material, even though the crystal structure is preserved throughout. Extraordinary changes of thermodynamic properties appearing at this bulk-to-discrete transition include ~ 500% increases of melting enthalpy (ΔHm), ~ 50°C increases of melting point (Tm), and an atypical transition between size-dependent Tm depression and Tm enhancement.

We develop a new comprehensive Gibbs-Thomson model with piecewise excess free energy (ΔGexcess) to predict the nature of the abrupt size effect melting. A new 3D spatial model is constructed to divide the aliphatic chains of AgSCn into three bulk or discrete segments: (a) tail segment containing three carbons, (b) head segment containing two carbons, and (c) bulk mid-chain segment containing (n - 5) carbons. Odd/even effect of Tm and ΔHm is described by a constant ΔGexcess over the entire chain length range of AgSCn and is exclusively attributed to the localized tail segment. Bulk-to-discrete transition occurs when material properties are dominated by the discrete head and tail segments at n < ncr. Values of ncr are independently measured by both calorimetry and 13C NMR. This analysis is generalized to other aliphatic layers including n-alkanes with ncr ≈ 11.

This work is seminal to the design of novel aliphatic layers with tailorable properties (e.g., Tm) and has applications in molecular electronics and biophysics.

Summary of Research:

We observed an abrupt bulk-to-discrete transition occurring at a critical chain length of ncr = 7 in AgSCn (n = 1-16) layers, with extraordinary changes of chain melting properties, chemical environment, and relaxation time. Calorimetry and solid-state 13C NMR are coupled to probe the global and local characteristics of atoms within the discrete regions of aliphatic lamellae. Bulk (long chain) AgSCn (n ≥ 7) exhibits fixed NMR chemical shift and T1 values, and size-dependent melting predictable by the classical GT model. In contrast, discrete (short chain) AgSCn (n = 2-6) presents a short-chain effect, with completely different values of these parameters for every single change of chain length. None of the carbons share an identical chemical environment. The anomalous melting is well predicted by a new comprehensive GT model with variable ΔGexcess. AgSC1 is an outlier with a different crystal structure. A new 3D spatial model is constructed to divide the alkyl chains of AgSCn into two discrete (head, tail) and one bulk (midchain) segments. The discrete segments dominate the material at n < ncr.

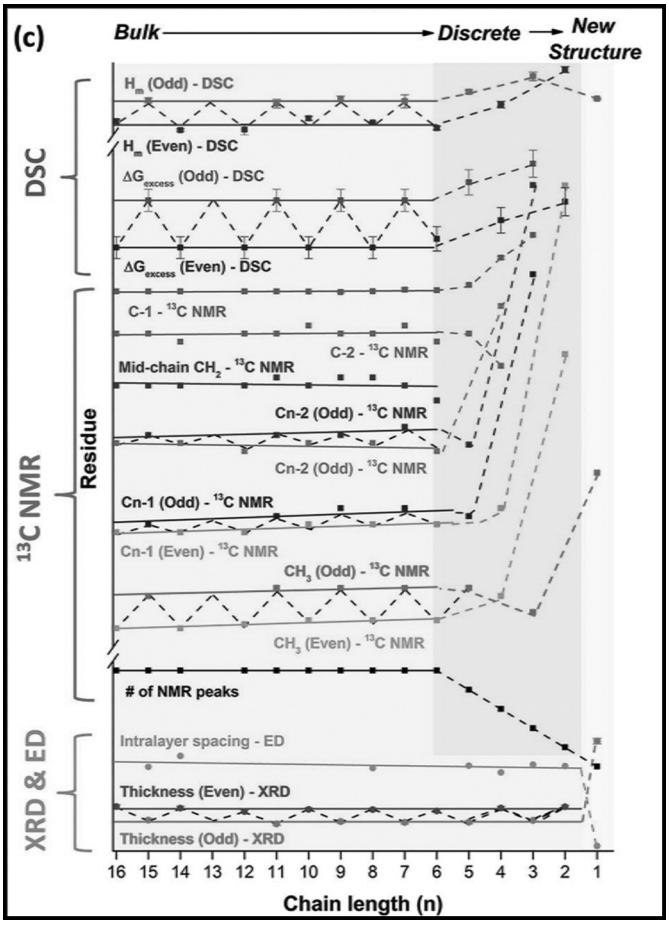

Figure 1: Plot summarizes the structural and property parameters (by DSC, 13C NMR, XRD, and electron diffraction) of AgSCn (n = 1-16) as the change of chain length. Each parameter is plotted as residue with regard to its linear fitting of certain bulk AgSCn. The thickness and intralayer spacing data are replotted from our prior paper and are preserved all through n = 2-16.

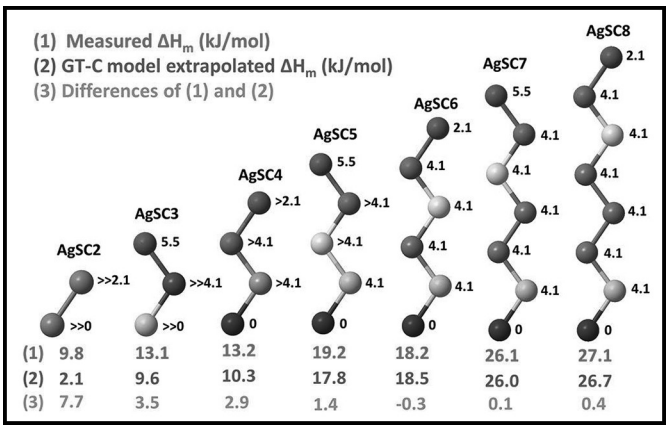

Figure 2: Cartoon shows the deconvolution of ΔHm of AgSCn (n =2-8) into contributions from each carbon (values beside carbons). The three rows of values represent (1) measured ΔHm, (2) ΔHm extrapolated from GT-C linear fitting, and (3) differences of (1) and (2).

An odd/even effect is detected in both the melting and NMR chemical shift of AgSCn and is exclusively attributed to the nature of the tail segment. This analysis is generalized to other extremely small aliphatic layers with discrete regions, including n-alkanes with ncr ≈ 11. This finding is instructive to the design of novel alkyl-based layers with controllable properties (e.g., Tm), through the manipulation of molecular segments (e.g., interfacial groups). Potential applications include the optimization of molecular electronics and the study of biological membranes.

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