

Homework 9 Advanced Thermodynamics
Due Tuesday October 27, 2020

- a) Li C; Li Q; Kaneti YV; Hou D; Yamauchi Y; Mai Y *Self-assembly of block copolymers towards mesoporous materials for energy storage and conversion systems* Chem. Soc. Rev. **49** 4681-4736 (2020) review the use of block copolymer (BCP) templated ceramics in batteries. The TOC graphic (first page) shows three BCP structures, cylinders, spheres and double diamond. Sketch a microphase separation diagram of temperature versus block composition and show where these structures might be expected to form. What is the difference between this diagram and a normal phase diagram for two partially miscible materials such as the same two polymers not connected as a BCP? Do you expect to see a spinodal region for BCPs? Why or why not?
- b) We discussed the thermodynamics of lamellar phase equilibrium size in BCPs in class. Explain how the size of the interfacial region (thickness and area) impacts the spacing of lamellar domains. What assumptions are involved in the analysis presented in class?
- c) Obtain an expression for the spacing of cylindrical domains using the same approach presented in class. How does this differ from the equation for lamellar domains?
- d) Figure 3 of Li et al. Shows a plot of the BET pore size versus the block length, N . How does this plot compare with your prediction from part b and from the class for lamellae? Explain how the BET pore size is obtained and why it might differ from the direct measurement using scattering (SAXS on the right axis).
- e) Consider two applications of these templating methods in batteries, A) the production of a 100-micron thick porous lithium salt separator membrane through which diffusion of lithium ions is required and B) the production of a 1 mm thick porous graphite electrode into which lithium ions would intercalate. Chose a synthetic method from the paper by Li et al. for each material and roughly explain how you would go about producing these two materials.