Materials 218/UCSB: Assignment VII

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1. How would you describe the following phase transitions in crystal-chemical terms:
   (a) The complete slowing down of reorientation in solid C₆₀ at low temperatures.
   (b) The transition from cubic perovskite to tetragonal perovskite in PbTiO₃.
   (c) The change on going from the perovskite structure to the tetragonal tungsten bronze (ttb) structure.

2. Sketch isotherms of the van der Waals equation of state:

   \[ p = \frac{RT}{V_M} - \frac{a}{V_M^2} - b \]

   Show that for some of the isotherms, there are regions that are unstable. How is this corrected? Explain the nature of flat regions in the \( p - V_M \) isotherms of the corrected plot.

3. Use the perovskite tolerance factor (which you must calculate) to explain why CaTiO₃ and SrTiO₃ are different from BaTiO₃ in that the first two compounds do not display ferroelectricity.

   Radii for calculating \( t \) can be obtained from:

   [http://www.mrl.ucsb.edu/ seshadri/Periodic/index.html](http://www.mrl.ucsb.edu/ seshadri/Periodic/index.html)

4. BaMO₃ (M = Ti, Zr, Hf) display the following trend in the paraelectric-ferroelectric \( T_C \)'s: BaTiO₃ > BaZrO₃ ∼ BaHfO₃. Calculate the perovskite tolerance factors for these three compounds, and use these to explain the trend.

5. BaTiO₃ is a ferroelectric but BaSnO₃ is not. Can tolerance explain this (calculate \( t \))? If it cannot, provide an alternate suggestion.