

Polymer Physics
HW 9
March 11, 2022 (Due March 22)

This week we looked at the impact of interactions on low-angle scattering and we started to look at the hydrodynamic radius and methods to measure it. One method to determine the hydrodynamic radius is intrinsic viscosity. Barré L, Jestin J, Morisset A, Palermo T, Simon S *Relation between Nanoscale Structure of Asphaltene Aggregates and their Macroscopic Solution Properties* Oil & Gas Sci. Tech. Rev. IFP **64** 617-628 (2009) investigate the structure of mass-fractal asphaltene aggregates and solution properties using intrinsic viscosity and neutron scattering. Asphaltene is a polydisperse mixture of polyaromatic hydrocarbons that are slightly polar. These planar molecules are known to stack and the stacks form monomers in aggregates which further cluster. These network clusters hinder flow of crude oil under certain conditions of pressure, temperature and solvent quality.

- a) Equation 6 is the basis for the Zimm plot. Explain the origin of the concentration dependence for the zero-angle scattering shown by equation 7.
- b) The intrinsic viscosity is defined by the first term of a Taylor series expansion in concentration from the solvent viscosity, $\eta = \eta_0(1 + [\eta]\phi)$. For spheres the Einstein equation gives $[\eta] = 2.5$ or $5/2$. From this equation show how equations 15, 17 and 18 are obtained. (For equation 18 you can take the low concentration limit of the equation and use the exponential expansion first two terms, $\exp(x) = 1 + x + x^2/2! + \dots$ for the Taylor series and for equation 18 to get a relationship between $[\eta]$ and ϕ_m . Also, $(\exp(x))^2 = \exp(2x)$.) How is ϕ_m related to the overlap concentration c^* ?
- c) Explain the origin of equation 16.
- d) Explain the power-laws observed in equations 19, 20, and 21. For equation 21 derive the functional relationship between A_2 and M . You will need to refer to Reference 29 Burchard W. (1999) Solution properties of branched macromolecules, Adv. Polym. Sci. 143, 113-194. Burchard is the 81-page chapter that starts on page 113. There are two expressions that are used for the second virial coefficient, B_2 has units of volume and is the excluded volume for a fractal aggregate or polymer chain including enthalpic interactions and steric exclusion. B_2 is used with the volume fraction in the virial expansion. A_2 has more complicated units and is used with mass concentration, g/cc. On page 134 Burchard defines A_2 . He explains the relationship with the mass fractal dimension on page 151. The McLeish and Milner chapter at the end is worth glancing at as well. McLeish is the top polymer rheologist in the UK dealing with simulations of reptation and tube renewal (McLeish is now at U. Durham (Harry Potter set for the school scenes is the U Durham Cathedral), previously McLeish was at Leeds and some other UK school. He is somewhat of a rock star polymer rheologist. Coincidentally “Live at Leeds”, supposedly the best rock concert of all time, was on the Leeds campus, there is a plaque...
https://commons.wikimedia.org/wiki/File:The_Who_Plaque_at_University_Leeds.jpg
Milner is a top theoretician from Exxon.
- e) The main problem with asphaltenes is surface deposition and formation of a complex network that reduces pipe flow and inhibits oil extraction from sands (Canadian Tar Sands) and porous rocks. Barré studied this by adsorbing asphaltene to silica spheres and

measuring the plateau adsorption after a long time, Γ_{pl} in mg of asphaltene per m^2 of sphere surface area. If a monolayer of aggregates is considered, how would Γ_{pl} depend on the mass if the aggregates are mass fractals of mass-fractal dimension, d_f , for a surface of fixed surface area S ?