Homework 2
January 27, 2025
Polymer Physics

Diffusion is based on Brownian motion which was first described in 1827. In 1905, 78 years later, a mathematical basis for Brownian motion was given by Einstein in one of his four "Annus Mirabilis" (remarkable year) papers. In this paper, the Stokes-Einstein (SE) equation was proposed for the diffusion coefficient relating bulk viscosity with molecular motion, kT, in the fluctuation dissipation theorem. Diffusion in polymers and in polymer composites follows some unique behavior depending on the molecular weight. For low molecular weight, oligomers, diffusion follows Rouse behavior where chains diffuse as individual molecules. For high-molecular weight polymers the chains diffuse under the strong influence of entanglements which form a mesh, and chains diffuse through a convoluted tube path in reptation. When particles are added to a polymer melt their diffusion is influenced by their size relative to the tube diameter and the interaction between the polymer and the particles. Large particles follow SE diffusion. Recently, Schweitzer proposed two modes of diffusion for nanoparticles with strong attractive interaction with a polymer melt, core-shell and vehicular diffusion. Core-shell follows SE with slight modifications for bound polymer and the matrix viscosity. Vehicular diffusion relies on desorption of the bound polymer. If the desorption time is longer than the entanglement relaxation time Schweitzer predicted two regimes II and III where regime III displays a polymer molecular weight dependence while regime II doesn't. By measurement of the diffusion coefficient, it is possible to distinguish these diffusive mechanisms and thereby verify Schweitzer's proposition. Wang K, Winey KI *Vehicular and Core-Shell Nanoparticle Diffusion in Attractive Entangled Polymer Melts* Macromolecules **57** 67889-6795 (2024) used time-of-flight secondary ion mass spectroscopy (ToF-SIMS) which is a technique to determine composition profiles normal to a surface by ablating a surface with Cs or Ga ions and collecting the ablated materials in mass spectroscopy to determine molecular weight (by time of flight) and concentration. A concentration profile by composition can be produced, Figure 1 c and d. From annealed samples the diffusion coefficient can be determined using Fick's law, equation 6.

a) Show (derive) a Gaussian profile for Brownian diffusion like that seen in Figure 1 c and d? How is this related to the random walk polymer, $<R^2> = nl^2$?

b) Derive the Stoke-Einstein law for diffusion. Under what conditions is this observed for particles in polymer composites? Wang, Schweitzer A and B study monodisperse single spherical particles, while most polymer fillers are aggregated polydisperse particles like carbon black and silica. Would this structure impact the SE behavior for diffusion? (Where does SE assume spherical monodisperse particles?) How would the structure of carbon black impact the vehicular, stick-slip, and modified Stokes-Einstein diffusion models?
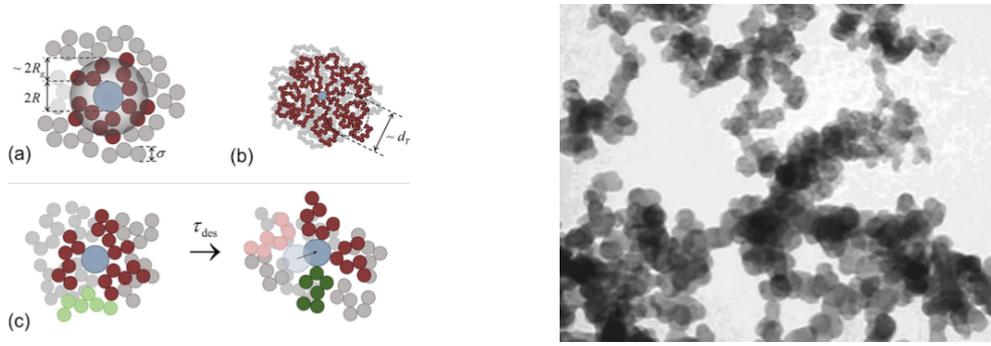
Figure 1. Left: Schweitzer A blue sphere is the nanparticle embedded in very short chain polymers, $Z_P = 20$ grey, red, or green balls.Right: typical TEM of a carbon black sample, primary particles are 5 nm in diameter, polymer would be 20 nm in diameter with $Z_P = 10,000$ Kuhn steps and a tube diameter of about 2.5nm.

c) Equation 8 is due to Einstein. When asked what work he wishes he had not done he mentioned this equation. Show that the first two terms in equation 8 are due to a displacement of the liquid with a non-flowing solid. Don't worry about the factor of 2.5 which can be calculated for a sphere.

d) Explain the modification of the SE equation to yield equation 2? Does it make sense to substitute equation 8 for the polymer viscosity to describe the diffusion of the particles that are increasing the viscosity? Consider the size of the spherical particles and the tube/chain size for the polymers.

e) SiO_2 has anionic surface charge while Al_2O_3 has no surface charge or a weak positive surface charge? P2VP has charged groups, positive, C, and negative, N. Can this explain the behavior seen in Figure 3? The Al_2O_3 particles are also much smaller than the SiO_2 particles. How does this impact the behavior of Figure 3?