070313 Quiz 4 Nanopowders

1) A nano-particle in the presence of ions reaches a "saturation charge". Explain why a saturation charge is reached in the presence of a corona discharge and an applied electric field and in the presence of an ion cloud. How does the saturation charge, n_e, depend on particle size for these two cases.

2) In the presence of a field, E, write an expression for the electrostatic force in terms of the ion charge and the field and use this expression to calculate the electrostatic mobility, $z = c_e/E$, assuming Stokes Law for the friction factor.

3) Thermophoresis is used for sampling of nanoparticles from a hot vapor stream. What is the size dependence of particles sampled using a room temperature TEM grid in a hot vapor stream of nanoparticles? Obtain this size dependence by considering 1) the ideal gas law (Pressure scales with temperature); 2) Force is pressure times area and for a nano-particle area scales with d_p^2; 3) Use the friction factor for the free molecular regime to demonstrate no size dependence to thermal motion.

4) Consider a fractal aggregate of z primary particles of size d_1 and overall aggregate size of d_{agg} such that $z = \alpha\left(\frac{d_{agg}}{d_1}\right)^{d_f}$. If the aggregate is a linear chain aggregate (draining/Rouse limit) the friction factor $f_{agg,draining} = z\, f_1$, but if the aggregate is fully branched (non-draining limit) such as a disk aggregate, $f_{agg,non\text{-}draining} = z^{1/df} f_1$. Obtain a general expression for $f_{agg} = \phi_{Br}(f_{agg,non\text{-}draining}) + (1-\phi_{Br})f_{agg,draining}$ by deriving the branch fraction, ϕ_{Br}, using the connectivity dimension, c.

A minimum path (shortcut) through the aggregate of p primary particles has a dimension d_{min} such that $p = \alpha\left(\frac{d_{agg}}{d_1}\right)^{d_{\min}}$ and $z^{1/df} = p^{1/dmin}$ so $z = p^{df/dmin} = p^c$. We define the branch fraction as the number of primary particles not in the minimum path, (z-p) divided by the total number of primary particles, z.

5) Write the Smoluchowski equation (two terms) using the collision frequency function β_{ij} and explain the relevance of the two terms (i.e. where do they come from). Why is there no break-up term in this equation? How is β_{ij} related to the diffusion coefficient? What is a self-preserving distribution?

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1) The ions impact the particle and impart charge on the particle. As charge builds up the ions are repulsed from the charged particle so that an equilibrium charge is reached. This occurs both in an electric field and in an ion cloud. In a field $n_e \sim Ed_p^2/e$, where e is the ion charge. In an ion cloud $n_e \sim kTd_p/e^2$.

2) $F = n_e e E \sim E^2 d_p^2 = f c_e$. Using $f = 3\pi d_p \eta$, $c_e \sim E^2 d_p/(3\pi \eta)$, and the mobility $z = Ed_p/(3\pi \eta)$. In the free molecular regime there is no size dependence to the mobility.

3) Thermophoretic sampling does not select by size. This can be shown by considering the free molecular regime where $f \sim d_p^2$. $PA = F \sim \rho\ kT\ d_p^2 = fc_T \sim d_p^2\ c_T$. So the thermophoretic velocity, c_T, does not depend on particle size in the free molecular regime.

4) $\phi_{Br} = \dfrac{z-p}{z} = 1 - \dfrac{p}{z} = 1 - z^{\frac{1}{c}-1}$ and

$$f_{agg} = f_1\left(\phi_{Br} z^{\frac{1}{d_f}} + \left(1-\phi_{Br}\right)z\right) = f_1\left(\left(1 - z^{\frac{1}{c}-1}\right) z^{\frac{1}{d_f}} + z^{\frac{1}{c}+1}\right)$$
$$= f_1\left(z - z^{d_{\min}-d_f+1} + z^{d_{\min}+d_f}\right)^{1/d_f}$$

5) $\dfrac{dn_k}{dt} = \dfrac{1}{2}\displaystyle\sum_{i+j=k}\beta_{i,j} n_i n_j - n_k \sum_{i=1}^{\infty}\beta_{i,k} n_i$ The equation explains the growth rate of or particles of mass k primary units. the first term is growth from lower masses and the second term is growth from mass k to larger masses. There is no break-up term because van der Waals interactions are fairly strong for nano-particles and an assumption of the Smoluchowski equation is that there is no breakup, once particles approach each other they bond premanently. β_{ij} is directly related to the diffusion coefficients of the two particles through, $\beta_{i,j} = 4\pi\left(D_i + D_j\right)\left(a_i + a_j\right)$ where a_i is the radius of the particle of mass i. After time the total number of particles decay and the number of primary particles of mass 1 decay but all other particles reach a maximum in number in time since they are created and then grow on to larger particles. The nature of the expression for the collision kernel is that a maximum for a given resulting volume occurs when one of the two particles is larger. This doesn't result in much growth of the large particle but a large loss for the small particle. Then the Smoluchowski equation describes the large eating preferentially the small so the population distribution reaches a kind of dynamic equilibrium where the relative width of the distribution and its shape remain constant at the mean grows. This is called a self-preserving distribution and is a direct consequence of the Smoluchowski approach and has been widely seen in nature. The self-preserving distribution is generally of the log-normal type.