1. What is the definition and meaning of the Péclet number?
2. Estimate the number of neighboring particles in a hard sphere colloidal dispersion at Φ=0.40.
3. The intrinsic viscosity of a dilute colloidal suspension is equal to that of a dilute, non-colloidal suspension. Why do the Brownian forces acting on the colloid not contribute to the viscosity?
4. Describe the physical origins of shear thinning in semi-dilute suspensions of Brownian hard spheres.
5. Figure 3.21 shows a Stokesian dynamics simulation of how $\langle g(2a) \rangle$ varies as a function of Pe for a ϕ=.45 colloidal dispersion. How do these results relate to the onset of shear thickening?
6. Discuss the effect of Brownian motion on the dynamic moduli.
7. Explain the concepts underlying “caging” in a concentrated suspension. What is the effect on viscosity?
8. What is short time self-diffusivity? What force(s) play a part in its determination?
9. What are some of the issues surrounding measuring the viscosity near the hard sphere glass transition, φ=0.58?
10. Discuss the normal stress difference for concentrated hard sphere suspension as a function of shear rates. Compare them with the normal stress difference for non-colloidal suspension.
11. What information can we get from mode-coupling theory (MCT)?

1. The Péclet number is the ratio of the characteristic rate for advection to that for diffusion. This is relevant for colloidal suspensions as Brownian motion provides a natural relaxation mechanism that tends to drive the microstructure towards its equilibrium. The characteristic time for Brownian motion is a^2/D_o for dilute systems, which is the time required for a Brownian particle to diffuse an average distance equal to its radius. The corresponding time scale for shear flow (advective motion) is $\dot{\gamma}^{-1}$ Using the Stokes-Einstein-Southerland equation (1.5), the Péclet number is $Pe = 6\pi\eta\dot{\gamma}a^3/k_BT$. Hence, it characterizes a shear rate as high or low compared to the natural relaxation rate due to Brownian motion. For low shear rates Brownian motion is faster than rate of advection and the structure is near to equilibrium during flow. At high shear rates the microstructure will be distorted by flow. Finally, the rate of diffusion is hindered at higher particle concentrations and so a dressed Pe*can be used where the suspension viscosity is used instead of the medium viscosity. This can also be expressed as a ratio of stresses.
2. The number of neighboring particles is given in terms of the radial distribution function g(r). The probability of finding a particle at a distance r is given by $ng(r)$, where n is the particle number density. The calculation proceeds by integration over a distance corresponding to the first peak in the radial distribution function as:

   $N_{nn} = \int_{2a}^{2a+\delta} 4\pi n g(r) r^2 \, dr$, where δ is the distance of the first neighbor shell. Figure 3.7 suggests this range is approximately of order ½*a. A simple approximation can be made using the Carnahan-Starling approximation for the value of the pair distribution function at contact":

   g(2a) = [1-(ϕ/2)] / [1-ϕ]^3

   g(2a) = [1-(.4/2)] / [1-.4]^3

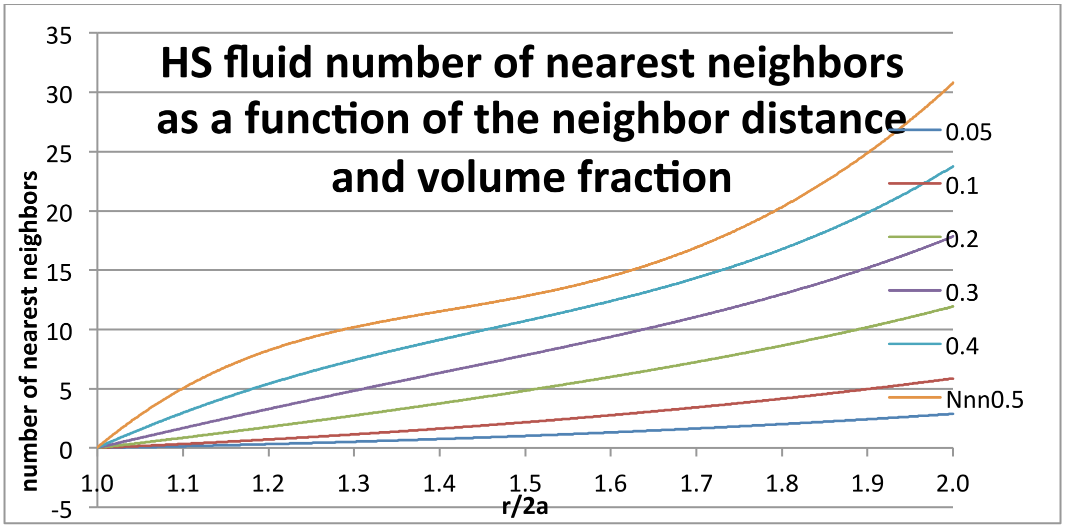
   g(2a) = 3.7

   Using an average value of (3.7+1)/2=2.35 for the pair probability in the nearest neighbor shell, an rough estimate for the number of nearest neighbors becomes:

   $$N_{nn} \approx \frac{4\pi}{3} a^3 n * (2.35) * \left(2.5^3 - 2^3\right)$$
   $$\approx \phi * (2.35) * (7.625) \approx 7$$

   Note that an FCC lattice has 12 nearest neighbors and a simple cubic lattice has 8. Thus, the hard sphere liquid is densely packed.

   Using the structures shown in Figure 3.7, the number of nearest neighbors for the hard sphere fluid have been calculated for various values of the nearest neighbor distance and the results are shown below:



3. Brownian motion is due to thermal fluctuations in the suspending medium that leads to a diffusive like motion of the colloid on time scales long relative to the molecular motion in the suspending medium and on length scales larger than the molecular size. The energy imparted by these thermal fluctuations to the colloid is dissipated by the friction of the colloidal motion against the suspending medium. This is known as the *fluctuation-dissipation theorem* and it means that there is no net energy transfer between the colloid and the suspending medium. Thus, at equilibrium there is no additional energy dissipation in the fluid due to Brownian motion that would contribute to the viscosity at the level of a single spherical particle. Note that we will see an interesting effect when the particles are asymmetric (Chapter 5). Energy is still dissipated by the presence of a particle in the shear flow according to the calculation presented in Chapter 2 and so the Einstein viscosity is observed for colloidal particles in the dilute limit.
4. The Brownian stress contribution is due to the forces acting between the particles Eqn. (3.10) and the spatial arrangement of the particles, i.e., the microstructure. Upon shearing, Figure 3.11 shows that the microstructure changes significantly due to the applied shear rate. Figure 3.11b shows how the Brownian forces contribute to the shear stress. At low shear rates the distortion of the microstructure is linear in shear rate and hence, so is the Brownian stress component, giving a constant contribution to the viscosity and hence, a zero shear rate viscosity. The hydrodynamic viscosity component is hardly affected by these changes in microstructure and remains essentially constant. At higher shear rates the distortion of the microstructure is significantly different and it saturates, such that the Brownian component to the viscosity decreases with shear rate. As the hydrodynamic contribution to the stress is still relatively constant the total viscosity drops and shear thinning is observed. At higher shear rates shear thickening is observed and this is discussed in Chapter 8 as a consequence of lubrication hydrodynamics.

5. <g(2a)> is related to the probability of finding a neighboring particle. At Pe below 1, <g(2a)> is relatively constant, but beyond Pe=1, <g(2a)> increases dramatically as the

shear flow drives particles closer together and increases the number of particles at close contact. Hydrodynamic interactions begin to grow as a result of the close particle proximity and these forces are exclusively dissipative. Thus, the suspension viscosity increases. More discussion of this effect is found in Chapter 8.

6. Brownian forces are at the root of elasticity in colloidal hard sphere suspensions. Figure 3.16 shows the magnitude of the elasticity and how it scales with the Brownian stresses introduced in Chapter 1. Increasing the particle concentration significantly increases the Brownian forces acting between particles and the observed high frequency elastic modulus. The frequency dependence of the moduli is shown in Figure 3.5, where for the colloidal liquid state, the viscous modulus is greater than the elastic modulus at all frequencies. Note that in the colloidal glassy state, as shown in Figure 3.24, for a range of frequencies the opposite is true. For colloidal suspensions in the fluid state the terminal regime is observed at low frequencies, as described in Figure 1.19, where the viscous modulus dominates. Figure 3.17 shows that frequency thinning is observed for the viscosity. The frequency at which this occurs is related to the time associated with Brownian motion. Frequency thinning should be evident when the characteristic time for oscillatory motion ω^{-1} becomes comparable with that of Brownian motion, a^2/D . At low frequencies the microstructure can relax during the oscillatory flow and there will be more viscous dissipation that at high frequencies where it cannot. The elasticity at high frequencies reflects that fact that the microstructure cannot relax on the time scale of the deformation as so for small amplitudes of deformation, the microstructure distortion is more close to affine deformation. This leads to energy storage and a high frequency plateau for *G'*. Thus, the frequency necessary for the appearance of a significant elasticity in a colloidal liquid is determined by a balance between the two time constants $\omega a^2/\mathcal{D} \simeq 1.1$.
7. Caging occurs at high volume fractions and refers to the presence of many neighboring particles in the colloidal liquid. In caging, particle motion becomes retarded because particles are surrounded by many neighbors. Viscosity greatly increases as caging becomes significant. The crowding at high volume fractions becomes sufficient enough to limit the particle's motion beyond its local position, leading to dynamic arrest. If all particles are "caged" by their nearest neighbor particles, then they cannot diffuse and the suspension will exhibit solid like behavior.
8. At high volume fractions, particles can become "caged" in by neighboring particles thus limiting their motion. Short time self-diffusivity is the rate of particle motion within the cage. The rate of diffusion is calculated purely by hydrodynamic particle interactions.
9. As the glass transition is approached the Brownian relaxation time becomes very long due to particle caging. Hence, very low shear rates or very low frequencies are required to study the equilibrium state. At the glass transition, the sample will exhibit an apparent yield stress. Slip can also occur at these high packing fractions. Measurements of monodisperse systems can also be hindered due to slow crystallization.
10. The shear rate behavior of the first normal stress difference is non-monotonic, owing to the competing effects of hydrodynamic and Brownian forces. The first normal stress

difference is positive at low shear rates for concentrated hard sphere suspension. The positive value reflects the contribution from Brownian forces. With increasing shear rates, the first normal stress difference becomes negative, a consequence of the growing contribution of hydrodynamic interactions. The normalized second normal stress difference is negative and remains negative for low and high shear rates. For non-colloidal suspensions the first and second normal stress differences are both negative and of comparable magnitude because they arise solely from hydrodynamic interactions.

11. MCT predicts the existence of an ideal glass transition, whereby particle motion at high volume fraction is very localized as a result of crowding by neighboring particles (caging). MCT also makes predictions for the contribution of Brownian forces to the stresses. The theory predicts that the zero shear viscosity should diverge at the ideal glass transition with a specific power law behavior.