

Viscosity Dependence on Particle Population

Brent Allen May Jarvis

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1 Introduction

Understanding colloidal dispersions is of great importance. These systems occur in many natural and man-made settings; glues containing clay particulate, crude and refined oil, silt held within rivers and many more systems can be modeled as colloidal dispersions. This study focuses on two distinct particle sizes, three high shear regimes, two low shear regimes, with the particle concentration ranging from 0% to 60%.

The relationship between particle concentration and viscosity has never been fully understood, and to date three theories are employed to model this relationship. These three theories are the Einstein, Mooney and Krieger-Dougherty formulas. One issue undertaken in examination of these theories was whether or not the jamming point occurs at one specific concentration regardless of particle size and rotation rate. Another issue encountered while conducting experiments was hysteresis. The solution seemed to age as experiments were carried out as well as exhibit behavior that implied that it "remembered" past events. One problem with these theories is that they are only good for low shear regimes, the limits of which are not thoroughly defined. High shear regimes have not been study very thoroughly in the past and so not much is known about their behavior. Because of this lack of attention to the high shear regimes the models set forth by Einstein, Mooney, and Krieger and Dougherty may not accurately predict the viscosity of a colloidal dispersion within the high shear regimes. This lack of attention to the high shear regime cannot be overlooked. The high shear regime needs as much focus as the low if a complete model is to be created.

The other main focus of this project is jamming. Jamming occurs when the solution has such a high concentration of particulate that the solution can no longer flow, however the concentration is not yet great enough to be close packing. Flow is defined as a fluid having a velocity gradient. The fluid has the greatest velocity near the driving force, and little or no velocity along the wall. Close packing occurs when there are so many particles that the shielding effect is overcome.

2 Theory

Viscosity is represents a fluids resistance to flow or being deformed by the tangential, shear stress. The equation given by Newton to find the viscosity

is

$$\frac{F}{A} = \eta \frac{\partial u}{\partial y} \quad (1)$$

where $\frac{F}{A}$ is the force per area, η is the viscosity, also known as the dynamic viscosity, and $\frac{\partial u}{\partial y}$ is the velocity gradient.

The relative viscosity of a solution is given by

$$\eta_r = \frac{\eta}{\eta_o} \quad (2)$$

where η_r is the relative viscosity, η is the viscosity of the solution at some concentration, and η_o is the viscosity of the pure solution. The relative viscosity is used in all plots for this paper.

Einstein derived the an equation for the relative viscosity of colloidal dispersion of hard spheres using Stokes law for fluids. The result is

$$\eta_r = 1 + 2.5\phi \quad (3)$$

where Φ is the concentration of hard spheres. The above equation is an approximation of the actual result which has the form. [1]

$$\eta_r = \frac{1 + 0.5\phi}{(1 - \phi)^2} \quad (4)$$

Einstein predicted that these equations would be useful only within the dilute limit. The exact specification of dilute has not been stated, it is believed to lie at 30%.

The next model to be developed was the Mooney equation. This equation models the increase of relative viscosity as an exponential relationship. This equation has the form

$$\eta_r = \exp \frac{S\phi}{1 - k\phi} \quad (5)$$

where S is a parameter that depends on particle shape, for hard spheres the Einsteinian value of 2.5 is used, k is another parameter that was suggested by Mooney to equal 1.25 for hard spheres dispersions. [3]

Finally Krieger and Dougherty suggested another equation for the relative viscosity of concentrated suspensions.

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-S\phi_m} \quad (6)$$

where S is as defined above, ϕ_m is the maximum volume fraction that dispersed particles can have. S is supposed to take on the value 2.5 in this equation as well. Beyond this value close packing occurs and viscosity by definition is undefined. The suggested value for this maximum concentration is roughly 494%. [2]

3 Experiment

The procedure to run this experiment is fairly straight forward. To calculate the mass of silica glass spheres, hereafter referred to as beads, to make a solution of some concentration, ϕ , the following equation was solved numerically

$$\phi = \frac{M_b \rho_b}{M_b \rho_b + V_g} \quad (7)$$

where M_b is the mass of the beads, ρ_b is the density of the beads, and V_g is the volume of glycerin. Silica glass spheres were used to ensure the hard sphere ideal assumed within each of the three models. The bead sizes were determined using a 100/120 mesh and 140/170 mesh, or approximately 71μ and 46μ . The beads were then examined using an microscope equipped with an edge detection program which determined that the spheres had a roundness ratio of 1.138 and 1.001 respectively.

The density was calculated in the lab using water displacement and a known mass of beads. An excel spreadsheet was created to calculate the concentration given the mass of beads and volume of glycerin using the above equation. Once the spreadsheet was set up mixing the different concentrations became a simple step. A rheometer was employed to measure the viscosity of the different concentrations. A rheometer is a machine that uses the stress on a rotating head to measure the shear resistance of a fluid. Free rotation of the head is ensured by an air bearing kept spinning by filtered air at a pressure of 30psi. A custom 38mm cylindrical head was designed to stir the glycerin within a sunken cup, also in the shape of a cylinder. This cup, as it will be referred to, resides in the center of a Plexiglas cube that contains a water bath kept at $20.0^\circ C$. The viscosity of glycerin has an exponential relationship with temperature, thus it is extremely important to keep the solution at some constant temperature. This relationship is modeled by

$$\eta = A \exp^{B/T} \quad (8)$$

where η is the viscosity of the fluid, A and B are constants that depend on the inherent properties of the fluid, and T is the temperature in Kelvin. The beads and glycerin were mixed directly within the cup. In order to accurately measure the volume of glycerin delivered pipets delineated with .1 mL markings were used. The beads were massed using the mass by difference method. The particles were then added in small amounts and slowly stirred in by hand. A metal spatula was used for this purpose. The mixing was done slowly to ensure that air bubbles would not form within the glycerin due to the stirring or air trapped between the particles when they became submerged. Air bubbles are notoriously difficult to remove from glycerin because of its viscousness. In other words the buoyant force in the air bubbles cannot overcome the weight of the glycerin and so the bubbles remain stationary within the fluid. The presence of air bubbles causes large errors when measuring viscosity, volume or mass.

The basic procedure that was programmed into the rheometer in order to measure viscosity begins with an hour pre-shear. During this step no data is taken and the geometry is rotating at 0.1000rad/s . During this hour any bubbles still left in the solution will be eradicated and the solution will have reached thermal equilibrium. The rotating geometry ensures that the temperature distribution is uniform. Following the pre-shear viscosity data is taken for two minutes at a sampling rate of 5/s while the geometry continues to rotate at 0.1000rad/s . Once this two minute sampling period is ended a short pre-shear begins while the geometry is sped up to the next rotation rate. Data was taken at $.1000\text{rad/s}$, 0.5000rad/s , 1.0000rad/s , 2.0000rad/s , and 4.0000rad/s for both particle sizes.

4 Results and Discussion

The Einstein equation does not fit the data well at all after the "dilute" limit. This limit appears to be around 25%. This can be seen in Figure 1, which extends only to 35%. Both the Mooney and Krieger-Dougherty functions did not work well when constraining the parameters in equations [5] and [6] to their suggested values indicated above. Table 1 illustrates that these values are not only different than the suggest values, but also indicates that they depend on particle size as well as possible shear rate. All fits were done with the data truncated at the graphical jamming points. As no graphical jamming point could be interpreted for the low shear regime, the

low shear data was truncated at one half of a percent higher than the high shear data. This follows the expected trend of jamming points encountered during experimentation. Table 2 gives the jamming concentrations. Figure 2 shows the data fitted with both the Mooney and Krieger-Dougherty formulas. It can be seen that both equations work fairly well. Figure 3 shows that the high shear viscosity plummets at about 52.3%. This could indicate the actual jamming point. There are no graphical jamming concentrations for $0.1000rad/s$, $0.5000rad/s$, and $1.0000rad/s$ because the viscosity within these shear regimes continues to increase exponentially. The observed jamming points were determined by attempting to identify whether the solution was flowing or moving en masse. Another interesting comparison to be made is the rate at which viscosity increases for each particle size. As can be seen in Figure 4 the larger the particle the smaller increase in viscosity. This effect is practically nonexistent until high concentrations are reached. Then the 46μ beads begin to cause a steeper increase in the viscosity than the 71μ beads.

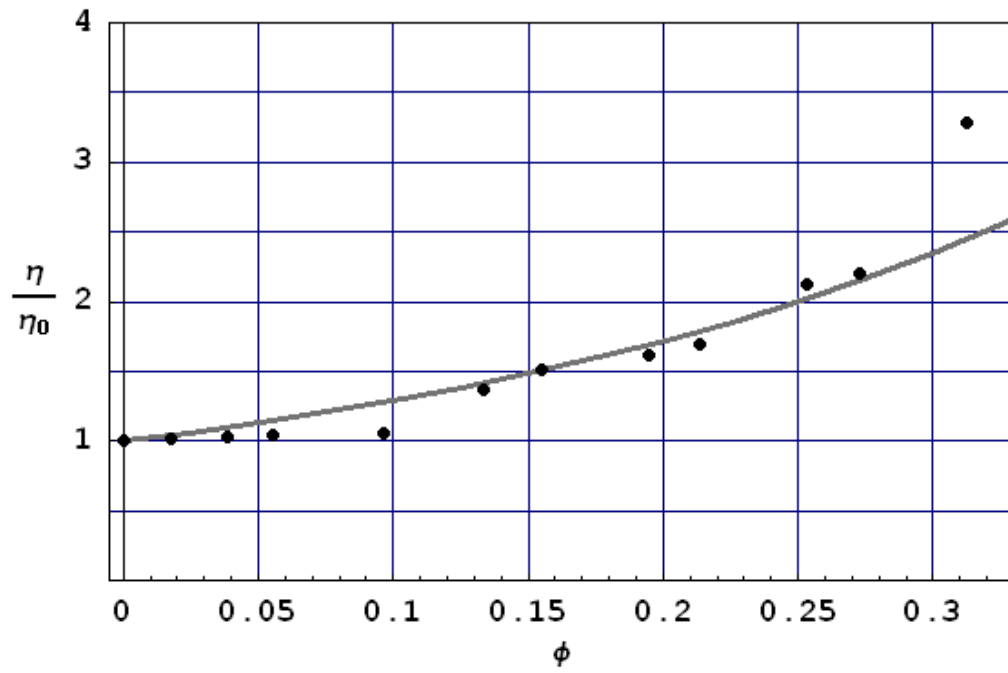


Figure 1: The line can be seen deviating more and more from the data as concentration increases past 25%. The data used is from the 71μ beads sheared at 0.1000 rad/s.

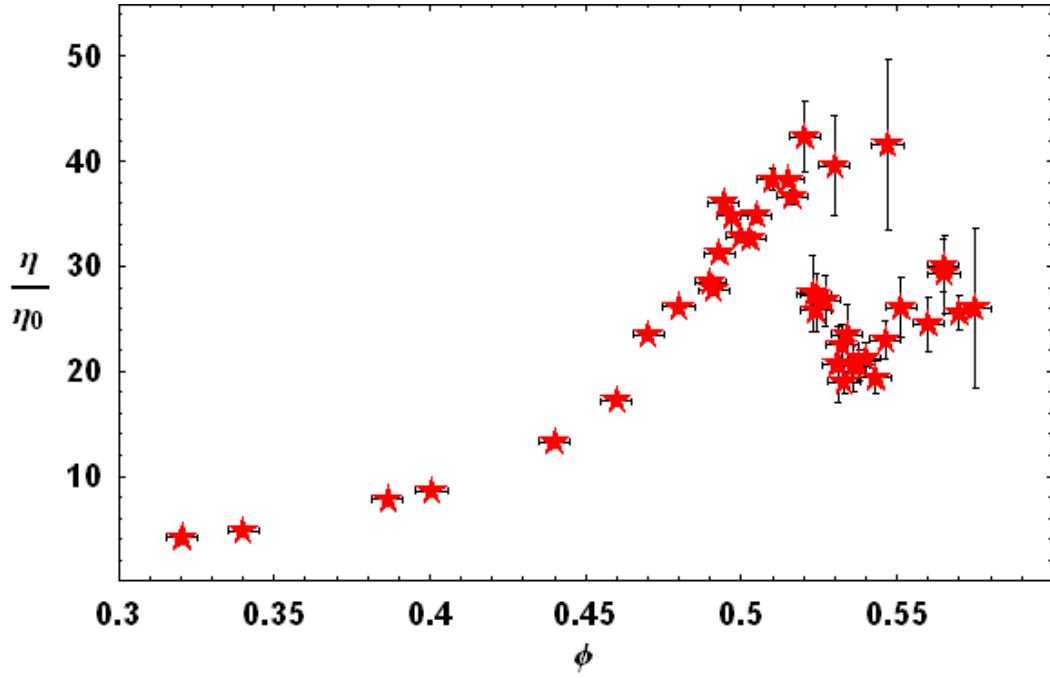


Figure 2: The grid line indicates the interpreted jamming point for the high shear regime. Data set is from the 46μ beads sheared at 0.1000rad/s .

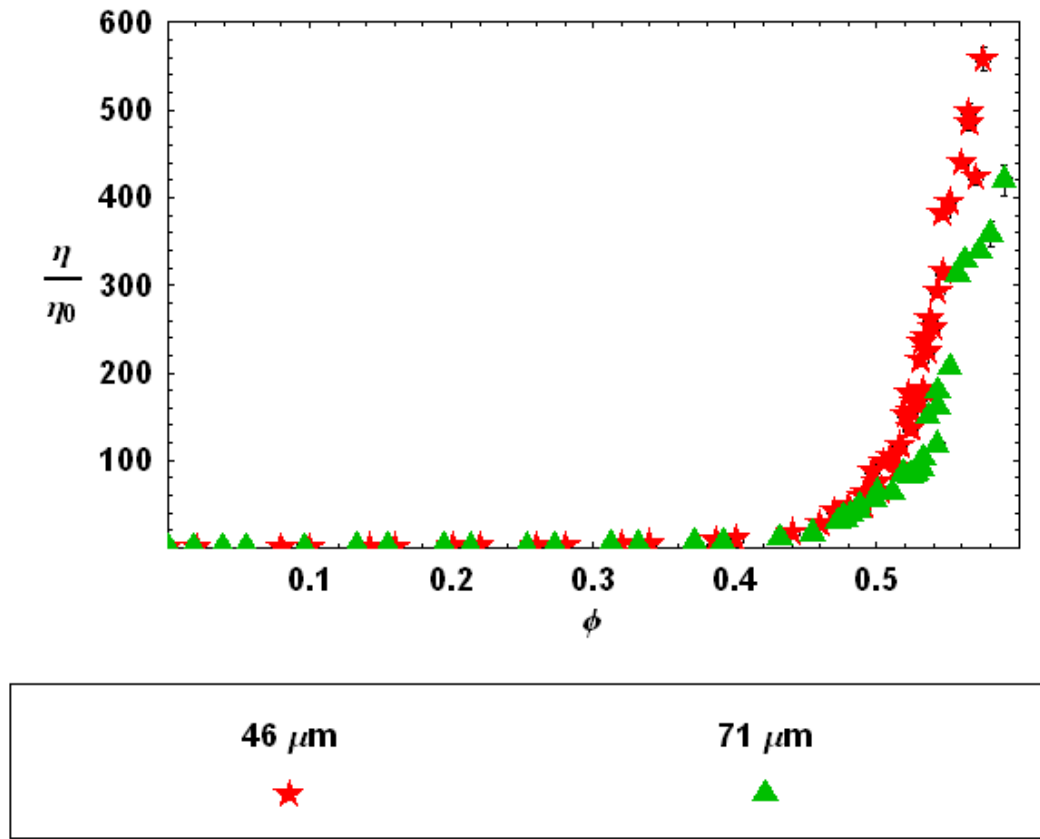


Figure 3: The 46 μ beads cause a larger effect than the 71 μ , especially at high concentrations.

1. Kuntiz *Rockefeller Inst. for Medical Research* (1926)
2. Meeker et al *Physical Review* **V.55, 5** (1996)
3. Simah *Journal of Applied Physics* **V.23, 9** (1952)
4. Dr. Matson—General Advising and Assistance with Paper