VISCOELASTIC BEHAVIOR OF ULTRA-FINE PARTICLE SUSPENSIONS

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Introduction  Recently we found a quite useful system to investigate viscoelastic behavior of monodisperse spherical suspensions with hard-core like inter-particle potential.\(^1,\text{2}\)  Viscoelasticity of such a system was precisely measured in wide concentration range and also in wide frequency range with variety of particle size and, characteristic features were summarized as follows.\(^1\)

i) The zero-shear viscosity, \(\eta_0\), and also the high frequency limiting viscosity, \(\eta_{\infty}\), are obviously observed, and their reduced values with medium viscosity, \(\eta_m\), become functions of only volume fraction, \(\phi\), of suspended particles not of a particle radius, \(a\).

ii) The average relaxation time, \(\tau_w\), is about a half of (Peclet) time, \(\tau_p\), which could be defined as eq 1.

\[
\tau_p = \frac{a^2}{6D_s} \quad (1) \quad \tau_w = \frac{\pi a^3 \eta_m}{k_B T} \quad (2)
\]

where \(D_s\) is \(\phi\) dependent local (or short time) diffusion coefficient. The equation could be rewritten in eq 2 with an empirical relationship (modified Stokes-Einstein law)\(^1\) of \(D_s = k_B T/(6\pi a \eta_m)\), where \(k_B T\) is product of Boltzmann's constant and the absolute temperature.

iii) The high frequency limiting modulus, \(G_{\infty}\), was observed, and the reduced form, \(G_{\infty} a^3/k_B T\), is a function of \(\phi\) again.

iv) Distribution of relaxation time in the suspensions is not sharp but rather broad. The features of ii) and also of iii) imply that the origin of viscoelasticity in the suspensions are Brownian diffusive motion of suspended particles.

In this study, linear viscoelastic behavior was examined for suspensions of an ultra-fine silica particle with a radius of 7.5 nm dispersed in highly viscous medium consisting of ethylene glycol and glycerin, and was compared with that of previously examined suspensions with much larger radii of 60, 125, and 225 nm and with the hard-core like inter-particle potential. The size of the particle is so small, that the contribution of interface layer formed by medium molecules interacting with the surface of the particle to the whole rheological features becomes important in contrast with the larger particle systems in which particle radii would be much larger than thickness of the interface layer and the contribution of the layer to the rheological features would be negligibly small.

Experimental  Used silica particle (S7.5) had an average radius of 7.5 nm and was kindly supplied by Nissan Chemical Inc. Suspending medium was consisting of ethylene glycol and glycerin, and the weight ratio between them was 0.29:0.71. Concentration of the S7.5 varied from 0.09 to 1.2 g cm\(^{-3}\). Refractive index of the S7.5 particle is so close to that of
the suspending medium, that inter-particle potential would be effectively reduced.1

We carried out a dynamic viscoelastic measurement at various temperature from -50 to 20°C. The time-temperature superposition technique could be successfully employed, and we got viscoelastic functions; the storage, $G'$, and the loss, $G''$, moduli, of a wide frequency range.

**Results and Discussion**

**Effective Volume Fraction and Medium Viscosity:** The S7.5 system exhibited remarkable viscoelasticity as well as systems with larger radii as shown in Fig. 1. Important rheological parameters such as $\eta_0$, $\eta_m$, $G_m$, and $\tau_w$ could be easily and precisely evaluated. However, the dependence of $\eta_0/\eta_m$ and $\eta_m/\eta_m$ on $\phi$ for the S7.5 system was completely different from the relationship which holds in larger particle suspensions independently of the particle radius as seen in Fig. 2. This difference would result from contribution of the special interface layer on the surface of the S7.5 particle. It is likely that the S7.5 has cloth with some thickness and is dispersed in effective medium with different viscosity from the original bulk medium.

Here, we estimate effective volume fraction, $\phi_{\text{eff}}$, of the S7.5 including the thickness of the interface layer cloth and the effective viscosity, $\eta_m^+$, of surrounding medium through universal function between $\eta_0/\eta_m^+$ and $\phi_{\text{eff}}$. Because both $\eta_0/\eta_m$ and $\eta_m/\eta_m$ are universal functions of $\phi$ in the larger particle systems as seen in Fig. 2, $\eta_0/\eta_m^+$ must be a different universal one of only $\phi$ which could be evaluated from experimental data for larger particle systems. Then, the relationship between $\eta_0/\eta_m^+$ and $\phi$ valid in the larger particle systems1 is extended to the S7.5 system as the relationship between $\eta_0/\eta_m^+$ and $\phi_{\text{eff}}$. $\phi_{\text{eff}}$ and $\eta_m^+$ for the S7.5 system was estimated by rescaling the system to an equivalent hard-core suspension with $\phi_{\text{eff}}$ and $\eta_m^+$. The estimated $\eta_m^+$ had lower value than $\eta_m$ of the pure bulk medium in a wide concentration range. This suggests that
interface layer around the surface of the S7.5 possesses lower viscosity than \( \eta_m \), and the layer would overlap in the concentration range examined to form new environment with different rheological features from the pure medium.

**Relaxation Time:** The relationship between the average relaxation time, \( \tau_w \), and \( \phi \) for the S7.5 system was also badly deviated from that for the larger particle systems. In the S7.5 system, the particle would migrate wearing certain cloth thicker than the original radius of 7.5 nm in the effective medium with \( \eta_m \), therefore, the Peclet time, \( \tau_p \) for this system should not be estimated through the eq 1. Thus, we assumed a modified equation below for the effective Peclet time, \( \tau_{p\text{eff}} \), simply taking account of change of effective volume or an effective radius of the particle by the cloth. The effective volume of the S7.5 particle could be simply estimated at \( a^3(\phi_{\text{eff}}/\phi) \) as the first order approximation.

\[
\tau_{p\text{eff}} = \frac{\pi a^2 \eta_m \phi_{\text{eff}}}{k_B T \phi}
\]

(3)

Fig. 3 shows the dependence of \( \tau_w/\tau_{p\text{eff}} \) on \( \phi_{\text{eff}} \) for the S7.5 system. The relationship between \( \tau_w/\tau_p \) and \( \phi \) for the larger particle systems is also plotted in the same figure. Agreement between them is not so bad, and the idea of rescaling looks like consistent. From these, the average relaxation time for the S7.5 system was regulated by Brownian motion of the particle wearing the cloth.

**Reduced Modulus:** The reduced modulus, \( G_w a^3/k_B T \), for the S7.5 system is plotted in fig. 4 as a function of \( \phi \). In contrast with the feature in the average relaxation time, \( G_w a^3/k_B T \) for the S7.5 is smoothly merges into data for the larger particle systems, therefore, it is likely that \( G_w a^3/k_B T \) simply governed by the original \( \phi \) not by \( \phi_{\text{eff}} \) as found in the larger particle systems with the hard-core potential. This suggest that time scale of the Brownian motion of the S7.5 particle is controlled by a size which could be estimated from \( \phi_{\text{eff}} \) but \( G_w a^3/k_B T \) should be a function of only the number density of the suspended particle because the time scale of the Brownian motion of the particle could never affect magnitude of the high
frequency limiting modulus. Thus, \( \phi \) should be a unique controlling parameter for \( G_a^* a^3 k_B T \) even in the S7.5 system.

By the way, we can also check the idea of rescaling to the equivalent suspension in behavior of \( G_a^* a^3 k_B T \). According to the same simple idea of rescaling employed in the average relaxation time, the magnitude of \( G_a^* a^3 k_B T \) would be altered to \( G_a^* a^3 \phi_{\text{eff}} (k_B T \phi) \) and would be a function of \( \phi_{\text{eff}} \) as well as observed in the average relaxation time. The relationship between \( G_a^* a^3 \phi_{\text{eff}} (k_B T \phi) \) and \( \phi_{\text{eff}} \) is also plotted in the same figure. Although \( \phi_{\text{eff}} \) dependence of \( G_a^* a^3 \phi_{\text{eff}} (k_B T \phi) \) looks similar to that in larger particle systems, magnitude of \( G_a^* a^3 \phi_{\text{eff}} (k_B T \phi) \) for the S7.5 is about a quarter of \( G_a^* a^3 k_B T \) for the larger particle systems. The rescaling to the equivalent suspension does not work so well in the behavior of \( G_a^* a^3 k_B T \).

The solid line in Fig 4 represents theoretical prediction by Russell and Lionberger\(^4\) for Brownian monodisperse suspension with hard-core inter-particle potential. The line coincides with the data for both S7.5 and larger particle systems in the high \( \phi \) side, but deviated from them in the low \( \phi \) side. In Russell and Lionberger's theory, linear term of \( \phi \) was not considered because they paid attention only to behavior of concentrated suspensions, but Wagner\(^5\) pointed out necessarily of the linear term as in the equation of state of the ideal gas even in suspensions with hard-core inter-particle potential.

**Molecular Motion in the Interface layer:** The fact \( \eta_m^+ \) of the effective medium is lower than \( \eta_m \) in wide concentration range suggests that molecular motion of medium, ethylene glycol and glycerin, becomes faster by interacting with surface of the silica particle.

The reason for very high viscosities of ethylene glycol and glycerin is hydrogen bonding network among themselves. If there is certain factors to reduce density of hydrogen bonding, viscosity decreases with the efficiency of the factors. The surface of silica particle have a lot of silanol groups, and ethylene glycol and/or glycerine molecules would make strong hydrogen bonding to form the first adsorbed layer. Density of hydrogen bonding among the molecules would alter with distance from the surface of the particle. At places just out side of the first adsorbed layer, the density of hydrogen bonding among the medium molecules must be reduced because the interaction between the medium molecules and the first adsorbed layer would be stronger than that among the medium molecules. Viscosity of the medium at places enough far from the surface must become the same to \( \eta_m \) of bulk value.

Relaxation time of molecular motion of the medium glycerin could be monitored with a dielectric measurement since motion of the silica particle is inactive to dielectric response. A slight shift of relaxation frequency of the glycerin toward the high frequency side was observed in the S7.5 system at the concentration range where \( \eta_m^+ \) showed lower value than \( \eta_m \). This supports that existence of the interface layer which has lower viscosity than that of bulk state and validity of procedure we employed above based on the idea of rescaling the S7.5 system to the equivalent monodisperse suspension with hard-core inter-particle potential.

**References**