## Hard sphere 서스펜션의 LAOS유동하에서 비선형 거동에 대한 연구

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# Non-linear response of high concentration hard sphere suspensions under LAOS

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## Introduction

Suspensions or "dispersions" of particles in a liquid medium are ubiquitous. Blood, paint, ink, and cement are examples that hint at the diversity and technological importance of suspensions. Suspensions include drilling muds, foodstuffs, pharmaceuticals, ointments and cremes, and abrasive cleansers and are precursors of many manufactured goods, such as composites and ceramics. Control of the structure and flow properties of such suspensions is often vital to the commercial success of the product or of its manufacture[1]. Therefore rheological properties are needed to understand the phenomena encountered and changes occurring during processing. Rheological data are also needed to assess constitutive equations required for designing equipment and predicting changes under processing. Finally, rheological methods could be powerful tools to establish relationships between structure, formulation, processing and properties[2].

From the processing side, it is important to predict the rheological properties as a function of various parameters, including volume fraction, particle shape and size distribution, specific surface area of the particles and fluid properties, as well. Specially, volume fraction( $\phi$ ) is very important parameter. Under dilute conditions, the rheological properties of such hard sphere suspensions are simple and well understood[3]. The main features are a viscosity that increases linearly with the volume fraction of particles and that is independent of shear rate. The behavior of nondilute suspensions, however, is considerably more complicated. A detailed rheological classification of concentrated suspensions can be found in a recent review by Coussot and Ancey[4]. And under large strain/flow, the behavior of concentrated suspensions become more and more complicated and exhibit highly nonlinear responses. Specifically, the shear-thinning/thickening of the steady state viscosity and underlying structural changes have been extensively studied [5,6,7,8]. The objective of this study is to investigate the nonlinear response of concentrated suspension under large amplitude oscillatory shear (LAOS). Recently, we investigated that LAOS is very sensitive to the interactions or the shear-induced formation of microstructure [9]. When large strain amplitude is imposed, stress curve becomes no longer sinusoidal curve. Thus, we also investigate stress curve using high performance ADC (Analog digital converting) card.

## Experimental Methods

Materials and sample preparation. In this study, the suspensions consisted of monodisperse spherical particles dispersed in a Newtonian continuos phase. The matrix fluid was a Newtonian low-molecular-weight Poly(propylene glycol) (Sigma-Aldrich) with a dynamic viscosity  $n_D=300\,\text{mPas}$  and a density of  $\rho_D=1005\,\text{kg/m}^3$ . An evaporation of the matrix fluid at room temperature was not observed. Chemical reactions between the continuous and the disperse phase can be excluded. As the disperse phase, polymethylmethacylate (PMMA) sphere with diameters  $10\,\mu\text{m}$  was used. The density of the PMMA was  $\rho_S=1190\,\text{kg/m}^3$ . The volume fraction( $\phi$ ) was 54%.

Rheometry. Rheological measurements were carried out on strain controlled rheometer (RMS800) and stress controlled rheometer (Bohlin) using a parallel plate fixture with a diameter of 50mm (RMS 800) and 35mm (Bohlin). For the raw data acquisition, a 16bit ADC card (PCI-6052E; National Instruments, Austin, USA) with a sampling rate up to 333kHz was used. This ADC card was plugged into a stand-alone PC equipped with LabView software (National Instruments).

## Results and Discussion

Frequency sweep test. Fig. 1 shows the results of frequency sweep test for  $\phi$ =54% suspension at 25°C. Frequency sweep test was carried out in the frequency range from 0.01 to 100Hz using stress controlled rheometer (Bohlin ) at a fixed stress. From Fig. 1 the bending of G' and G" is appeared at low frequency region. This frequency sweep result is found at many references. The bending shape of in Fig. 1 seems to be a characteristic feature of a heterogeneous two-phase system [5,10,11]. For immiscible polymer blends with a high viscosity ration of the two phases, the bending of G' is appeared. As can be seen from Fig.1 the suspension approximately shows the behaviour of a Newtonian fluid ( $G' \propto \omega^2$ ;  $G'' \propto \omega$ ) at higher frequencies. The observed dependency of G' and G" on the frequency  $\omega$  in the high frequency range obeys the usual behaviour of Newtonian fluids. Namely, frequency sweep result show the combination of a Newtonian matrix and a high volume concentration of spherical particles.

Time sweep test. Time sweep test was conducted using strain controlled rheometer (RMS 800). Time sweep test is need to stress curve data using high performance ADC card. Suspension is affected preshear conditions[11], so we conducted two step time sweep test. At first step, time sweep test is conducted during 1800s at fixed strain and frequency (1Hz). At second step, time sweep test is imposed during 300s at same strain and frequency which is used at first step. We obtained stress curve from second time sweep test. Fig. 2 shows first time sweep test at fixed strain amplitude (70%) and frequency (1Hz). G' and G" is decreasing until asymptotic value. During preshearing, the microstructure of particles was approached equilibrium state.

Fig. 3 shows second time sweep test. G' and G" show constant value. Fig. 4 shows G' and G" as a function of strain amplitude from time sweep results. G' and G" shows strain thinning and strain thickening. The LAOS type is combination of type I (strain thinning) and type IV (G', G" increasing followed by decreasing). The stress curve as a function of time with different strain amplitude is shown Fig. 5.

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## References

- [1] R. G. Larson, The Structure and Rheology of complex fluids, Oxford University Press, Oxford, 1999.
- [2] P.J. Carreau, P.A. Lavoie, F. Yziquel, Rheological properties of concentrated suspensions, in: D.A. Siginer, D. De Kee, R.P. Chhabra (Eds.), Advances in the flow and rheology of Non-Newtonian fluids, Rheology Series 8, Elsevier, Amsterdam, 1999, pp. 1299-1345.
- [3] W.B. Russel, D.A. Saville, and W.R. Schowalter, Colloidal Dispersions, Cambridge University, London, 1989, Chap. 14.
- [4] P. Coussot and C. Ancey, Rheophysical classification of concentrated suspensions and granular pastes, Phy. Rev. E, 59(1999) 4445.
- [5] H. Watanabe, M.L. Yao, A. Yamagishi, K. Osaki, T. Shitata, H. Niwa, and Y. Morishima, Nonlinear rheological behavior of a concentrated spherical silica suspension, Rheol. Acta, 35(1996) 433.
- [6] H. Watanabe, M.L. Yao, K. Osaki, T. Shitata, H. Niwa, and Y. Morishima, Nonlinear rheological behavior of a concentrated spherical silica suspension: 2. Role of strain in shear-thickening, Rheol. Acta, 36(1997) 524.
- [7] H. Watanabe, M.L. Yao, K. Osaki, T. Shitata, H. Niwa, Y. Morishima, N.P. Balsara, and H. Wang, Nonlinear rheology and flow-induced structure in a concentrated spherical silica suspension, Rheol. Acta, 37(1998) 1.
- [8] H. Watanabe, M.L. Yao, K. Osaki, T. Shitata, H. Niwa, and Y. Morishima, Nonlinear rheological behavior of a concentrated spherical silica suspension: 3. Concentration dependence, Rheol. Acta, 38(1999) 2.
- [9] K. Hyun, S.H. Kim, K. H. Ahn, and S.J. Lee, Rheological properties of some complex fluids: A guideline for classification, J. Non-Newtonian Fluid Mech. 107(2002) 51.
- [10] T. Shikata and D.S. Pearson, Viscoelastic behaviour of concentrated spherical suspensions, J. Rheol., 38(1994) 601.
- [11] M. Schmidt and H. Munstedt, Rheological behaviour of concentrated monodisperse suspensions as function of preshear conditions and temperature: and experimental study, Rheol. Acta, 41(2002) 193.

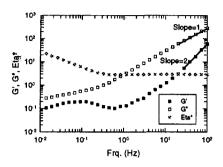


Fig. 1 G',G", and Eta\* as a function of frequency.

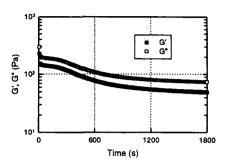


Fig. 2 G' and G" as a function of time at strain amplitude 70% and 1Hz at first time sweep.

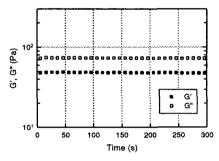


Fig. 3 G' and G" as a function of time at strain amplitude 70% and 1Hz at second time sweep.

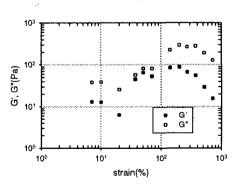


Fig. 4 G' and G'' as a function of strain amplitude from time sweep results.

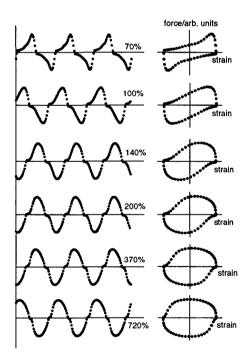


Fig. 5 Stress curve as a function of time at different strain.