Shear Thickening in Electrically Stabilized Non-aqueous Colloidal Suspensions

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Abstract:
The authors previously introduced an activation model for the onset of shear thickening in electrically stabilized colloidal suspensions. It predicts that shear thickening occurs, when particles arranged along the compression axis in a sheared suspension do overcome the electrostatic repulsion at a critical shear stress, and are captured in the primary minimum of the DLVO interaction potential. A comparison with an experimental investigation on non-aqueous silica suspensions, carried out by Maranzano and Wagner, is performed. For particle systems that fall into the applicability range of the theory, a good coincidence between the experimental data and the model predictions can be found.

Zusammenfassung:
Die Autoren haben kürzlich ein Aktivierungsmodell für Scherverdickung in elektrisch stabilisierten kolloidalen Suspensionen vorgestellt. Es basiert auf der Idee, dass der kritische Stress der Scherverdickung erreicht ist, wenn Teilchen, die sich entlang der Kompressionsachse einer gescherten Suspension nähern, die elektrostatische Abstoßung überwinden und durch die van der Waals Anziehung des DLVO-Potentials eingefangen werden. Die Vorhersagen des Modells werden mit einer ausführlichen experimentellen Untersuchung an nicht-wässrigen Suspensionen, durchgeführt von Maranzano und Wagner, verglichen. Für die Teilchensysteme, die in den Anwendungsbereich der Theorie fallen, zeigen die theoretischen Vorhersagen eine sehr gute Übereinstimmung mit den experimentellen Werten.

Résumé:
Les auteurs ont précédemment introduit un modèle d'activation pour décrire l'émergence du comportement rhéo-épaississant dans les suspensions colloïdales électriquement stabilisées. Il prédit que le comportement rhéo-épaississant apparaît à une contrainte de cisaillement critique lorsque les particules, arrangées le long de l'axe de compression dans une suspension cisaillée, surmontent la répulsion électrostatique, et sont emprisonnée dans le minimum primaire du potentiel d'interaction de la théorie DLVO. Une comparaison avec une étude expérimentale menée avec des suspensions non aqueuses de silices par Maranzano et Wagner, est effectuée. Pour les systèmes de particules qui entrent dans le régime d'application de la théorie, une bonne coïncidence entre les données expérimentales et les prédictions du modèle peut être trouvée.

Key words: colloidal suspensions, shear thickening

1 INTRODUCTION

A number of theoretical attempts were made in the past to explain shear thickening in electrically stabilized colloidal suspensions. There are four main research directions. One is to neglect Van der Waals attraction between colloidal particles and consider them as effective hard spheres. For this type of interaction substantial progress in the understanding of shear thickening has been achieved by applying computer simulations. The idea is that short-range lubrication forces are responsible for the formation of large shear induced density fluctuations, known as hydroclusters [1 – 3]. A second approach is to relate shear thickening to an order-disorder transition, where an ordered, layered structure becomes unstable above a critical shear rate [4 – 6]. A third direction is based on a mode-coupling model, where the memory term takes into account the density, the shear stress and the shear rate. It was

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HS150 together with the theoretically expected critical shear stresses (σ_C^{CP}, σ_C^{CC}) for the onset of shear thickening (solid lines). The error bars indicate the uncertainty of the experimental data due to the finite resolution of the measurement. Also displayed is the critical stress σ_C^* which represents the border between the regimes of constant potential and constant charge. While for $\sigma_C < \sigma_C^*$, the onset of shear thickening can be expected to take place at CP particle interaction, for $\sigma_C > \sigma_C^*$ the model suggests that onset to occur at CC conditions. Note that it cannot be determined a priori whether $\sigma_C <> \sigma_C^*$.

For the HS1000 samples the experimental critical stresses fulfill the condition $\sigma_C < \sigma_C^*$, and are therefore expected to be given by σ_C^{CP}. Although not all data points match the predicted critical stress they are arranged close to σ_C^{CP}. On the other hand, the experimental data of the HS600 and HS150 system match the critical shear stress predictions σ_C^{CC}, in accordance with the fact that $\sigma_C > \sigma_C^*$. The data point of sample HS150 at Φ = 0.44 cannot be explained by the present model. We interpret it as an outlier. For comparison the predictions of the critical stress σ_C^{MW} for the onset of shear thickening as based on an effective hard sphere model by Maranzano and Wagner, which neglects Van der Waals attraction, are evaluated according to [14, 18]:

$$\sigma_C^{MW} = 0.096 \frac{\pi K \epsilon_0 \epsilon_r \Psi_0^2}{a} \tag{21}$$

In Figures 2 – 4 the critical stresses σ_C^{MW} are displayed, indicated by a dotted line. The effective hard sphere model appears usually to overestimate the critical stresses, by up to a factor 20 (with system HS1000), and demonstrates that ignoring the Van der Waals attraction is not justified. We want to emphasize that the experimental determination of the critical stresses is difficult, in particular when the transition into shear thickening occurs smoothly. Although not all experimental data points could be predicted by the present version of the theory, it gives a qualitative better picture of the shear thickening instability than the effective hard sphere model by Maranzano and Wagner.

CONCLUSIONS

The present investigation reveals that, within the applicability range, the activation model of shear thickening is in good agreement with experimental data of the critical stress obtained from electrically stabilized non-aqueous suspensions. This result is more satisfactory than what was previously found for aqueous suspensions where only the proper order of magnitude of the critical stress could be given. For practical applications, the present model delivers a good indication of the critical shear stresses for the onset of shear thickening in electrically stabilized non-aqueous suspensions.

As shown in Table 1 the maximum of the interaction potential, h_{max}, is at distances of a few hundred pm from the surface. Since a silicon atomic diameter is ~ 200 pm, the roughness of the particle surface prohibits a direct contact between the particles beyond the maximum of the interaction potential. We therefore suggest that the transition between reversible shear thickening and irreversible orthokinetic coagulation is smooth, and essentially determined by the distance of the maximum of the interaction potential to the surface and by the surface roughness of the particles. It is quite surprising that the presented continuum model gives that good predictions of the critical stress.

A shortcoming of the presented version of the model is that it is unable to predict shear thickening in sterically stabilized suspensions. Unlike the interaction potential predicted by the DLVO-theory, which shows two minima and one maximum (Figure 1), sterically stabilized systems exhibit a potential, which consists only of a shallow attractive minimum followed by a rapid increase as the surfaces of the colloidal particles approach each other closely. These particles systems cannot be treated with the present version of the activation model, while the effective hard sphere model should rather be applicable.

We have to emphasize that present computer simulations on electrically stabilized suspensions usually ignore the double layer dynamics and the surface roughness of the particles. Therefore these simulations are not accurate enough to be comparable with real systems. Simulations taking into account both effects are necessary in order to improve our understanding of the shear thickening phenomenon.

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