Rheology of Complex Fluid-fluid Interfaces: A Unified Approach Based on Nonequilibrium Thermodynamics

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Abstract:
Surface rheological properties affect the dynamics of vesicles, nanoparticles, emulsion droplets, foam bubbles, polymer microcapsules, liquid jets, living cells, lung avioli, thin liquid films, and many other multiphase systems. Surface rheology is therefore relevant for a wide range of disciplines in the areas of physics, chemistry, engineering, biology, and medicine. Currently used descriptions of surface rheology have a number of limitations, and in particular are hard to generalize to the large deformation regime. Data are often analyzed with constitutive equations based on straightforward generalizations of models developed for describing bulk phase rheology. Since the latter are in general designed to describe incompressible materials, they are not guaranteed to describe highly compressible interfaces correctly. Here we discuss a unified approach to surface rheology based on nonequilibrium thermodynamics (NET) that provides a consistent set of balance and constitutive equations for the unambiguous determination of surface rheological parameters, both near and far beyond equilibrium. A closer integration of experimental surface rheology and multiphase nonequilibrium thermodynamics would clearly be beneficial for both disciplines.

Zusammenfassung:
Die rheologischen Eigenschaften von Oberflächen beeinflussen die Dynamik von Vesikeln, Nanopartikeln, Emulsionstropfen, Schaumzellen, polymeren Mikrokapseln, Flüssigkeitsstrahlen, lebenden Zellen, Lungenaviolen, dünnen Flüssigkeitsfilmen und vielen anderen mehrphasigen Systemen. Daher ist die Rheologie von Oberflächen für viele Disziplinen der Physik, Chemie, Ingenieurwissenschaft, Biologie und Medizin von Bedeutung. Viele der gegenwärtig angewandten Beschreibungsweisen für die Oberflächenrheologie weisen mehrere Grenzen auf. Insbesondere ist es schwierig, diese Methoden auf große Deformationen zu verallgemeinern. Daten werden oft mit Hilfe von Konstitutivgleichungen analysiert, die auf einer Verallgemeinerung von Modellen für „Bulk Phase"-Rheologie basiert. Da diese aber entwickelt wurden, um inkompressible Materialien zu beschreiben, sind sie nicht automatisch geeignet, um hochkompressible Grenzflächen korrekt zu modellieren. In dieser Arbeit betrachten wir einen vereinheitlichenden Ansatz für die Oberflächenrheologie basierend auf der Nichtgleichgewichtsthermodynamik. Dieses Vorgehen führt zu einem konsistenten System von Bilanz- und Konstitutivgleichungen für die eindeutige Bestimmung der rheologischen Parameter der Oberfläche, sowohl nahe als auch weit vom Gleichgewichtszustand. Eine tiefere Integration von experimenteller Oberflächenrheologie und Nichtgleichgewichtsthermodynamik von Multiphasensystemen würde für beide Disziplinen gewinnbringend sein.

Résumé:
Les propriétés rhéologiques surfaciques affectent la dynamique des vésicules, des nanoparticules, des gouttelettes d'émulsion, des bulles de mousse, des microcapsules polymériques, des jets de liquide, des cellules vivantes, des alvéoles des poumons, des films liquides minces, et de bien d'autres systèmes multiphasiques. La rhéologie surfacique est donc pertinente pour une gamme élargie de disciplines dans des domaines comme la physique, la chimie, l'ingénierie, la biologie et la médecine. Les descriptions actuelles de la rhéologie surfacique présentent un certain nombre de limitations, et en particulier, sont difficile à généraliser pour le régime des grandes déformations. Les expériences sont souvent analysées avec des équations constitutives basées sur des généralisations triviales de modèles développés pour décrire la rhéologie de volumes. Puisque ces derniers sont en général faits pour décrire des matériaux incompressibles, il n'est pas garanti qu'ils décrivent correctement des interfaces largement compressibles. Ici nous discutons une approche unifiée de la rhéologie surfacique basée sur la thermodynamique hors équilibre (NET) qui fournit un ensemble cohérent d'équations d'équilibre et constitutives, afin de déterminer de manière non ambiguë les paramètres de rhéologie surfacique aussi bien près que loin de l'équilibre. Une intégration plus rigoureuse de la rhéologie surfacique expérimentale dans la thermodynamique multiphasique et hors équilibre serait clairement bénéfique pour ces deux disciplines.

Key words: surface rheology, fluid-fluid interface, nonequilibrium thermodynamics

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surface rheological parameters, and a consistent set of balance equations and (nonlinear) constitutive equations to analyze surface rheological experiments. These constitutive equations eliminate the need to use straightforward generalizations of bulk constitutive equations to model interfacial behavior. We have shown that such generalizations have only limited validity, and should in general not be used to analyze surface rheological data. A closer integration of experimental surface rheology and multiphase nonequilibrium thermodynamics would clearly be beneficial for both disciplines.

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