Distinguishing thixotropy, plasticity and viscoelasticity in complex fluids using parallel superposition Gaborheometry

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Abstract

There has been a resurgence of interest over the past decade in the class of fluids known broadly as *Thixotropic Elastoviscoplastic (TEVP)* Fluids which exhibit a wide range of rheologically challenging phenomena including thixotropy, elastoplastic creep below yield and an age-dependent yield stress. We illustrate how modern oscillatory rheometric techniques can be used to help distinguish the distinct contributions to what may be referred to broadly as *mutating materials* with rheological properties that are typically both time– and rate–dependent. The relative importance of these effects can be quantified by three distinct dimensionless parameters; a mutation number, a Weissenberg number and a *Mnemosyne number* that quantifies the importance of thixotropic effects in a fluid. The typical rheologist's approach of using Fourier transforms for analyzing oscillatory data implicitly assumes the signals are *time-translation invariant*, which constrains the mutation number of a sample to be extremely small. This constraint makes it difficult to quantify shear-induced rheological changes in thixotropic and aging materials. We use the *Gabor transform* (a Short Time Fourier Transform (STFT) that utilizes a Gaussian window) to provide optimal time-frequency resolution of the local viscoelastic properties of mutating materials. Finally, we also illustrate how parallel superposition flows can be combined with Gaborheometry to arrest aging of colloidal systems and simultaneously monitor the temporal evolution in the elastoviscoplastic response. By varying the relative strengths of the steady shearing component that "shear-melts" the microstructure and the superimposed oscillatory probe we show how one can unambiguously distinguish time-dependent thixotropic aging from local viscoelastic responses.

From plastocapillarity to elastocapillarity and anything in between

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Abstract

Many problems in engineering and geophysics feature the free surface flow of a viscoplastic fluid. Although negligible at large scales (*e.g.* lava flows and landslides), capillary forces may become significant at small scales (*e.g.* coating polymeric materials and 3D printing). The effect of yield stress on spreading droplets is considered. Experiments, asymptotic solutions, and numerical simulations are used to explain the droplets' dynamics and their final shape. Finally, the effect of elasticity on the spreading of yield stress fluids is explored and a computational framework is presented to study a full spectrum of capillary driven flows, from Plastocapillarity to Elastocapillarity and anything in between.

Topology, geometry, and fracture in networked materials: a tale of Scales

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Abstract

The skeleton of many natural and artificial structures may be abstracted as networks of nonlinearly interacting visco-elatic, and potentially visco-elasto-plastic, elements. Examples include rubber, gels, and soft tissues. Understanding the multiscale nature of deformation and failure of networked structures hold key for uncovering origins of fragility in many complex systems including biological tissues and enables designing novel materials. However, these processes are intrinsically multiscale and for large scale structures it is computationally prohibitive to adopt a full discrete approach. Here, we introduce an adaptive numerical algorithm for solving polymer networks, the building blocks in many biological and engineering systems, using an extended version of the Quasi-Continuum (QC) method. In regions of high interest, for example near defects or cracks, each polymer chain is idealized using the worm like chain model. Away from these imperfections, the network structure is computationally homogenized to yield an anisotropic material tensor consistent with the underlying network structure. Dynamic adaptivity provides a seamless transition across the two models. Overall, the proposed method provides a multi-resolution capability by retaining explicit representation of small-scale heterogeneities and topological features while still accurately accounting for bulk elasticity and loading. We illustrate the efficiency of the method by applying it to study the fracture of large-scale polymer network problems as realized in experiments on hydrogels. We further apply the method to test the influence of network topology on its fracture resistance and energy dissipation and emphasize the role of linear and nonlinear rate effects in controlling crack geometry. We discuss the implications of our findings for the analysis and design of tough networks.

Strain shift measured from stress-controlled oscillatory shear: evidence for a continuous yielding transition, and new techniques to determine recovery rheology measures

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Abstract

Understanding the yielding of complex fluids is an important rheological challenge that affects our ability to engineer and process materials for a wide variety of applications. Common theoretical understandings of yield stress fluids follow the Oldroyd-Prager formalism in which the material behavior below the yield stress is treated as solid-like, and above the yield stress as liquid-like, with an instantaneous transition between the two states. This formalism was built on a quasi-static approach to the yield stress, while most applications, ranging from material processing to end user applications, involve a transient approach to yielding over a finite timescale. Using stress-controlled oscillatory shear experiments we show that yield stress fluids flow below their yield stresses. This is quantified through measuring the strain shift, which is the value about which the strain oscillates during a stress-controlled test and is a function of only the unrecoverable strain. Measurements of the strain shift are therefore measurements of flow having taken place. These experimental results are compared to the Herschel-Bulkley form of the Saramito model, which utilizes the Oldroyd-Prager formalism, and the recently published Kamani-Donley-Rogers (KDR) model, in which one constitutive equation represents the entire range of material responses. Scaling relationships are derived, which allow us to show why yield stress fluids will flow across all stresses, above and below their yield stress. Finally, derivations are presented that show strain shift can be used to determine average metrics previously attainable only through recovery rheology, and these are experimentally verified.

Molecular scale insights into the rheology of thermally activated amorphous materials

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Abstract

Amorphous materials can be either athermal (e.g., foams and emulsions) or thermal (e.g., colloidal glasses and metallic glasses). These materials exhibit yield stresses above which they flow. They have microstructural elements with associated local energy barriers. Under deformation, elastic energy accumulates in local elements and pushes the configuration over the maximum energy, leading to plastic deformation (yielding transition). Although deformation of athermal materials has been studied by elastoplastic models, the combined effect of thermal fluctuations and mechanical loading on the yielding transition remains unclear. Furthermore, current elastoplastic models disregard molecular-scale information and only connect the mesoscopic properties to bulk behavior. As a model system for thermal materials, we study nanoparticle-organic hybrid materials (NOHMs), composed of inorganic nanocores densely grafted with polymer chains. Even without solvents, NOHMs can flow since the grafted polymers fill the space between the cores like an incompressible fluid. By formulating the free energy evolution in a deforming periodic array of solvent-free polymer-grafted nanoparticles, we estimate the energy barrier to nanostructure relaxation as a function of core volume fraction, polymer molecular weight, and grafting density. We propose a thermally activated elastoplastic model which uses the energy barrier to predict the material's rheological response via a Fokker-Planck equation. Surprisingly, the apparent yield stress is found to increase with decreasing core volume fraction or polymer molecular weight both of which make it more difficult for polymers to stretch and fill the void space. Our start-up shear predictions display a stress overshoot due to synchronized nanostructure relaxations.

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Systematic manipulation of disorder for extraordinary functionality in materials

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Abstract

Much of materials science deals with ordered crystalline or polycrystalline materials that are designed and delicately fabricated to have specific desired properties. However, *disordered* materials, such as glasses or granular media, have an untapped potential: they can exist in a multitude of metastable states that are distinguished by their microstructure. While the vast majority of these states have similar (boring!) bulk properties, there are a few rare cases that have spectacular behavior. The challenge, of course, is to direct the flow of material from its ordinary state to such targeted useful states that would never be discovered by chance alone. Inspired by biology, we meet this challenge by introducing material training protocols that allow evolution toward those desired states. In these protocols, the possible modes of relaxation are augmented by introducing extra transient degrees of freedom, such as particle radii, that allow an easier pathway to the target. Once that desired state is reached, the additional degrees of freedom are removed. In this talk, I will explore how different transient degrees of freedom lead to different behaviors such as enhanced stability. The framework I present provides a systematic approach to create novel materials by using disorder as a core feature of the design.

Obtaining test-independent values of the dynamic and static yield stresses for time-dependent materials

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Abstract

When it comes to the measurement of yield stress, the experimental procedure appears to play a significant role. Using a series of experiments, in which the effects of time dependence and shear banding were identified and taken into account, we determined the dynamic and static yield stresses of the materials as unique, test-independent properties. We studied the shear rheological properties of an aqueous suspension of Laponite® which is a highly time-dependent (thixotropic) material. To minimize the irreversible effect of aging on its material properties, the Laponite® dispersion was aged for 347 days under a controlled environment. For comparison, an aqueous solution of Carbopol®–a slightly time-dependent material–was also investigated. The peak values of the shear stress evolution in constant shear rate tests were compared with the static and dynamic yield stress values. We noticed that, as the shear rate is reduced the peak stress value tends asymptotically to the dynamic yield stress for the slightly time-dependent material, but to slightly above the static yield stress for the thixotropic material. For the Laponite® suspension, at relatively low shear rates, we observed that peak stresses are influenced by shear banding. By simulating stress evolution curves using stress step-changes, we eliminated the influence of shear banding and discovered that the lowest yielding point coincides with the static yield stress. In addition, we provided the complete flow curve for the Laponite® suspension, showing the role of the static and dynamic yield stresses, and the unattainable zone which is closely related to steady shear banding effects.

Rheology of bubbly elastoviscoplastic suspensions through direct numerical simulation

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Abstract

Elastoviscoplastic (EVP) fluids are ubiquitous in many industrial applications; in particular, bubbles suspensions in EVP fluids arise in dairy processing to impart favourable textural properties onto the final product, and in the construction of aerated concrete for superior thermal and acoustic insulative properties, to name a few. This motivates us to study the rheology of bubbles suspended in an EVP fluid, which we do through direct numerical simulation. The Saramito constitutive equation [1] is used to model the elastoviscoplasticity of the matrix fluid. An extensively validated, in-house Navier-Stokes solver [2] is used to perform the simulations: the level-set method is used for the interface capturing, and a direct, fast solver is used for the Poisson equation of the velocity-pressure coupling. We study both steady and oscillatory shear of the suspension and focus on the effects of the bubble volume fraction and the Capillary number on the bulk rheological properties. In the oscillatory shear rheology, we employ a hardening mechanism to better model the linear viscoelastic regime. Our results are in good qualitative agreement with results in the literature; stiffer bubbles are seen to behave similar to particles and harden the material, whereas deformable bubbles soften the material, leading to a decrease in the steady shear viscosities and the dynamic moduli.

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Transient structure-property-process relation of yield stress bottlebrush systems

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Abstract

Direct ink writing is a 3-D printing technology that has received increasing attention recently due to its low cost, energy efficiency, and design freedom. However, detailed rheological characterizations of the yielding transition the ink undergoes, and the deformation-induced structural changes that the ink exhibits are still being developed. In the present work, we use two yield stress materials formed by bottlebrush block copolymers (bBCPs) suspended in toluene and a mixture of toluene and m-xylene as model DIW ink formulations. We perform oscillatory recovery measurements over a wide range of deformations, closely resembling the printing conditions, to map out the transient responses of recoverable and unrecoverable contributions. Rheo-microscopy is utilized to identify and monitor the deformation-induced structural colors of the two systems while undergoing oscillatory tests. The decomposed moduli that are determined by the recoverable and unrecoverable contributions capture the yielding transitions favorably. The vibrant color induced by highly nonlinear deformations is correlated with the unrecoverable contributions. The trajectory of color changes over time is mapped out using the traditional and new Lissajous curves. The present findings provide new insights into understanding the rheological phenomena involved in the DIW printing process and tuning ink properties to achieve desirable features of the post-printing product.

Extraction of particle-scale cohesion parameters from bulk measurements on an air-bearing rheometer?

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Abstract

Granular media which includes cohesive powders and bulk solids have to be handled on a regular basis in a variety of industrial applications. Inter-particle cohesion significantly affects the flow behavior of these particulate and multiphase systems. Therefore, accurate prediction of inter-particle cohesion is of paramount importance when it comes to designing and optimizing various industrial unit operations. However, predicting particle-level cohesion is non-trivial at best. The state-of-the-art methods to develop cohesion models rely on atomic force microscopy analysis of individual particle surface under specific humidity conditions, which are time consuming, expensive and require specialized training. These methods are not conducive to an industrial setting where feedstock and ambient conditions change frequently. Therefore, exploring possible methods to extract inter-particle cohesion from straightforward bulk measurements is desired. In recent work carried out by Liu et al. [1], defluidization is identified as one example of a bulk behavior that can provide particle-level cohesion. In their work, a simplified square-force cohesion model is proposed, and with the help of discrete element method (DEM) simulations, it is demonstrated that the parameters for the square-force model can be extracted from the defluidization (pressure drop) curve. This defluidization-based approach is restricted to lightly cohesive particles. However, as the level of particle cohesion increases, standard defluidization curves cannot be obtained. In the present work, an air bearing rheometer coupled with a powder flow cell is used to carry out a careful exploration of defluidization behavior of particles with a range of cohesion levels. By adding energy through a rotating impeller, the rheometer is able to fluidize cohesive particles without channeling, which is not possible in conventional fluidized beds. Both pressure drop and torque are measured during defluidization. We also show that the results obtained on the rheometer are system size independent, thereby ensuring the feasibility of direct-coupling of the experiments with smaller DEM simulations. Furthermore, we show that the torque required to rotate the impeller may provide an alternative to the pressure-drop to characterize particle defluidization. We also show that the extracted characteristic-velocities from these

experiments may provide a relative-gauge for particle-level cohesion [2]. To accurately extract the inter-particle cohesion parameters, the measured values of the other particle-scale properties (e.g., coefficient of friction, coefficient of restitution) were used as inputs to the DEM simulations. Finally, the same particles were used in a separate experimental system in order to test the validity of square-force model parameters outside of the system from which they were extracted [3].

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Bubbles

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Abstract

Bubbles arise in a variety of contexts interesting for yield stress fluid mechanics. Here we address questions of the static limit for single and multiple bubbles which can be important for applications to greenhouse gas emission mitigation. We then examine the interaction of bubbles with interfaces, both clearing up an old problem and introducing a new problem.

Fluid microstructure to understand rheology

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Abstract

Understanding the microstructure of a complex fluid is important to better describe its rheology. A technique that can be employed to obtain the fluid microstructure is to use Scanning Electron Microscopy with a CRYO system to prepare liquid samples. We must consider two crucial steps in this preparation: freezing and sublimation. A quick freeze and adequate time/temperature slush guarantee the fluid structure without damage or modification. This work shows some examples of how Cryo-Scanning Electron Microscopy (cryo-SEM) can be used to observing and investigating the microstructure of complex fluids. We analyze the breakage and rebuilding process of a Laponite suspension. The interaction of nanoparticles with polymeric suspensions is also analyzed. We investigated a carbopol solution with varying pH and different concentration of graphene oxide nanosheets, a carbopol suspension with TiO_2 and SiO_2 nanoparticles, and a xanthan gum suspension with oxidized hexagonal boron nitride (h-BN-Oxi) nanoparticles. Finally, we observed the development of the microstructure of a cement paste during the hydration process. In all cases we present rheological data of the samples to observe how the rheology relates to the fluid microstructure.

Hidden hierarchy in dense suspension rheology: mysteries and latest results

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Abstract

Dense suspensions of fine particles are significant in numerous biological, industrial, and natural phenomena. They are often out-of-equilibrium and display various rheological features including liquid–solid phase transition under external deformation being one of the most interesting one. Developing an understanding of the mechanisms that drive these phenomena has over the last several years led to a surge in research activity at the intersection of fluid mechanics, granular materials, driven disordered systems, tribology, and soft condensed matter physics. One central aspect that emerged is that these phenomena occur due to a shear-activated or deactivated network of contacts between particles. I will briefly present the current state of understanding and challenges associated with relating the flow of material at the bulk scale with the microscopic physics at the particle scale. I will also show that in some cases, it is possible to skip some steps in the hierarchy but leads to an incomplete understanding. Finally, open challenges, avenues towards viscoplastic flow behavior connections between polymer rheology, colloids, and granular materials will be discussed.