Designing and transforming yield-stress fluids

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Abstract

We review progress in designing and transforming multi-functional yield-stress fluids and give a perspective on the current state of knowledge that supports each step in the design process. We focus mainly on the rheological properties that make yield-stress fluids so useful and the trade-offs which need to be considered when working with these materials. Thinking in terms of "design with" and "design of" yield-stress fluids motivates how we can organize our scientific understanding of this field. "Design with" involves identification of rheological property requirements independent of the chemical formulation, e.g. for 3D direct-write printing which needs to accommodate a wide range of chemistry and material structures. "Design of" includes microstructural considerations: conceptual models relating formulation to properties, quantitative models of formulation-structure-property relations, and chemical transformation strategies for converting effective yield-stress fluids to be more useful solid engineering materials. Future research directions are suggested at the intersection of chemistry, soft-matter physics, and material science in the context of our desire to design useful rheologically-complex functional materials.

Keywords: soft matter, yield-stress fluid, design, engineering, extension, thixotropy, elasticity, colloids, emulsions, polymers, 3D printing, chemistry, physics, rheology, complex fluids

1. Introduction

Yield-stress fluids are perhaps the most utilized rheologically-complex soft materials in our world today. These materials reversibly transition from solid-like to fluid-like at a critical applied stress. At stresses above the yield stress these fluids flow readily, facilitating deposition or distribution; below the yield stress, shapes or suspended components are held in place. Designing *with* this solid elasto-plastic behavior enables applications ranging from the everyday to the extraordinary including drug delivery, food products, batteries, painting, surface coatings, biomaterials, concrete, and other scenarios depicted in Fig. 1[1].

There is a large space of many different chemistries and material structures that can be used for the design *of* yield-stress fluid behavior. 3D printing will be used as a motivating example through this review; Fig. 2 shows multiple microstructure formulations all used for this application: foams, polymer networks, microgel-particle suspensions, colloidal gels, and emulsions. In the simplest terms, two microstructure categories are involved, often called "glasses" and "gels". The glass category includes crowded elementary objects interacting repulsively with several nearest neighbors at high volume fraction (e.g. foams, microgel-particle suspensions, emulsions, pastes, and granular suspensions). The gel category involves attractive interactions between components and may appear at low volume fractions with percolated long-lifetime bonds (e.g. polymer networks, colloidal gels, capillary suspensions, and magnetorheological fluids). This categorization can become blurry as combinations of repulsive and attractive interactions are possible in the design space, e.g. as with "attractive glasses" created by locally crowded attractive colloidal particles.

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[1] A historical example comes from 17th century Flemish painters using yield-stress fluids to speed up the production of paintings[144,145]. Previously, layers of color and shade were superimposed only after lengthy drying. Rubens is claimed to be the first to have used a yield-stress fluid enabling him to speed up painting. The painting "La Kermesse" (now in the Louvre) could be produced in 24 hours, rather than weeks without these yield-stress fluids. Modern painters still use these types of Flemish medium paints, easily spreadable, but recovering quickly, yet easily modifiable; these functional traits are predominantly rheological in nature.
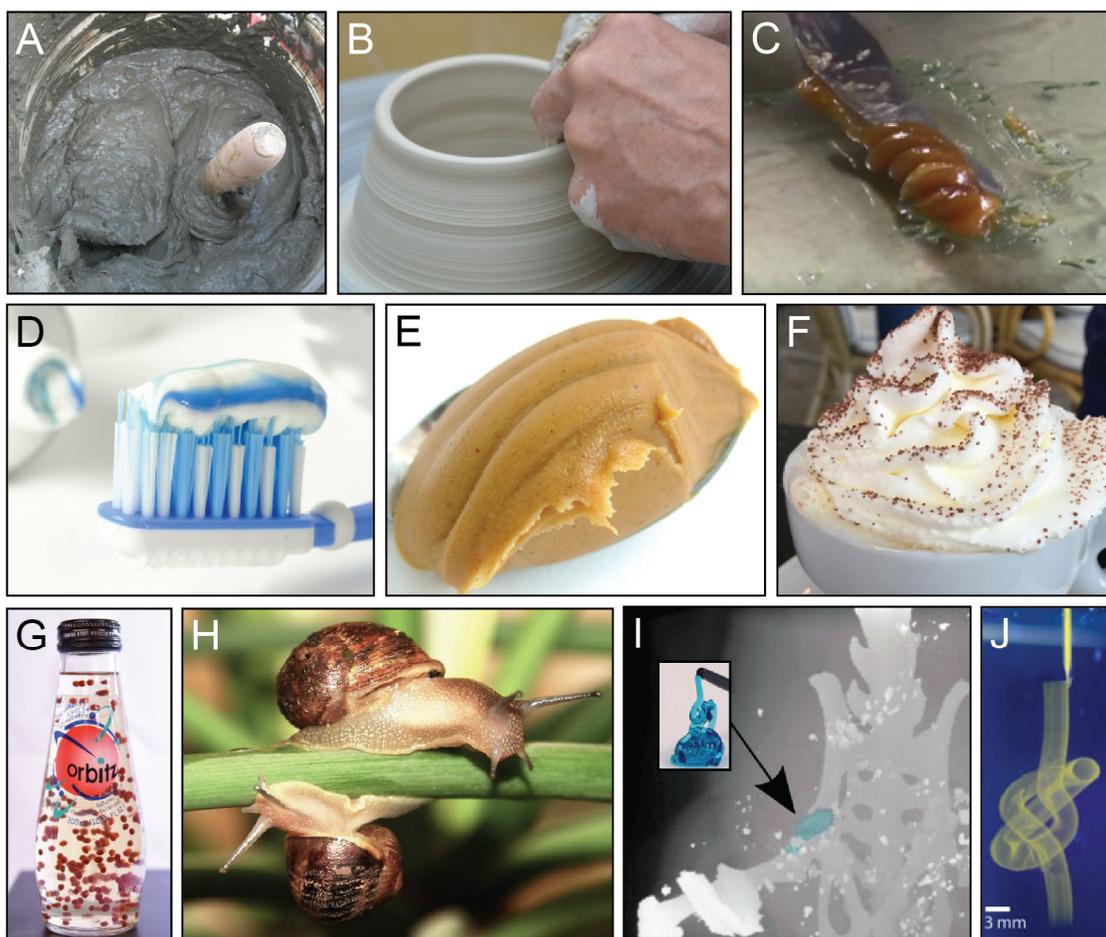
Fig 1. Yield-stress fluid engineering applications are diverse and important. A) building mortar with immobilized trowel, B) modeling clay, C) Flemish paint medium [1], D) toothpaste, E) peanut butter, F) whipped cream, G) Orbitz drink with suspended particles. Photograph courtesy A.Z.N., H) snails with slime adhesive. Photograph courtesy R.H.E., I) shear-thinning biomaterial and microCT image of injected mouse hindleg (image adapted from [2]), J) 3D printing in a sacrificial bath of yield-stress fluid (image adapted from [3]). Images A, B, D, E, and F are public domain under CC0.

The goal of this perspective is to review tools and information available to help make design decisions with yield-stress fluids and to describe areas in need of further research for this purpose. For in-depth reviews of general concepts of yield-stress fluids, property measurements, and fluid mechanics modeling, we refer the reader to existing literature[4–6]. In our work here, design thinking motivates how we organize knowledge. Fig. 3 outlines our vision of a design hierarchy[7] which contrasts design *with* and design *of* soft materials. Designing *with* these materials poses the question "What rheology is needed?" Whereas design *of* these materials asks, "How can it be achieved?"
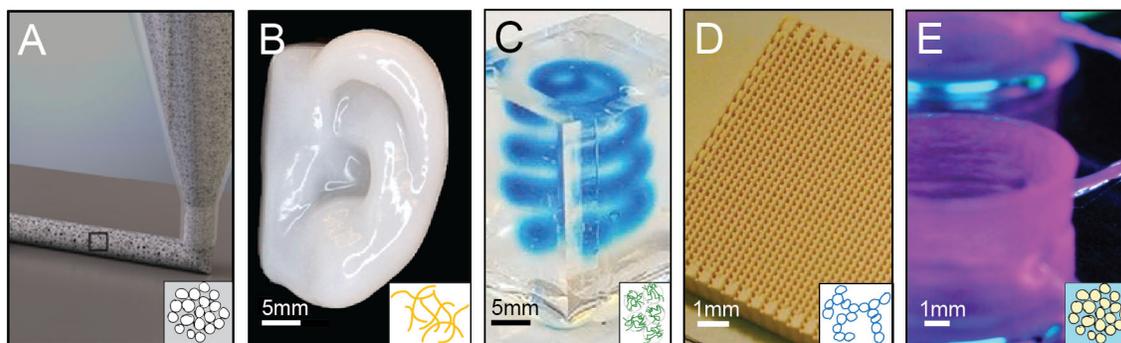
Fig 2. There are many ways to engineer different yield-stress fluids that will all fulfill a similar performance function. Though these yield-stress materials belong to completely different microstructural classes (inset schematics), they are all used for direct-write 3D printing applications including (images adapted from original sources with permission) A) foams for porous ceramics [8], B) fibrillar networks for bioprinting [9], C) crowded microgels (blue) in a supporting hydrogel (transparent) [10], D) colloidal particulate gel networks [11], and E) crowded emulsions (false color) [12]. Image B adapted with permission from Markstedt et al. [9]. Copyright 2015 American Chemical Society.

1.1 Caveats and controversy

There are numerous technical details which are constantly being refined that complicate precise definition and characterization of yield-stress fluids. Naturally, these unresolved complexities are problematic for the reorganization of knowledge according to design principles which benefits greatly from very clear mathematical and conceptual models. Here we recognize the most significant technical issues with yield-stress fluids as caveats to keep in mind when designing them. Despite these issues, we will demonstrate that relevant and meaningful design decisions can still be made with these materials.

We do not concern ourselves here with defining a *precise* yield stress since the yield transition is typically not sharp and multiple definitions are possible [6,13,14]. For our purposes, we consider yield-stress fluids to be materials that reversibly transition from effectively solid to effectively fluid and back again as a consequence of applied mechanical stress. Yielding may be gradual across a range of stress magnitudes and may occur as localized brittle cracking, shear-banding, or system-spanning diffuse failure [15]. An important distinction is that of the 'static' yield stress (for the transition from solid to liquid, e.g. start-up shear tests) versus the 'dynamic' yield stress (for transition from liquid to solid, e.g. steady flow tests of decreasing shear rate). These can be very different; when they are, the static yield stress is typically larger.
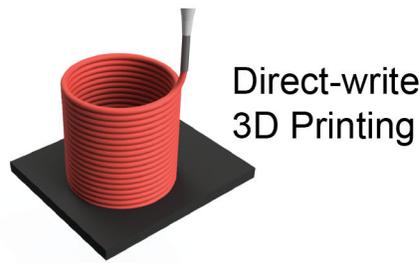
Furthermore, the forward and reverse transitions between solid-like and liquid-like are not instantaneous; the microstructural units require time to return to an arrested state. This reversible time-dependence is known as *thixotropy* and it is intimately linked with yielding in these materials, often complicating their characterization [13]. The term "thixotropic fluid" has unfortunately entered the nomenclature of several application areas as a surrogate for "yield-stress fluid", which does not acknowledge that the thixotropic timescale may or may not be very short, creating—from the engineering point of view—two extreme categories of yield-stress fluids known as "simple" and "thixotropic", respectively [16]. For practical purposes, simple yield-stress fluids are those for

which thixotropic timescales are too short to observe with available techniques or too short to matter for timescales of interest to the end user.
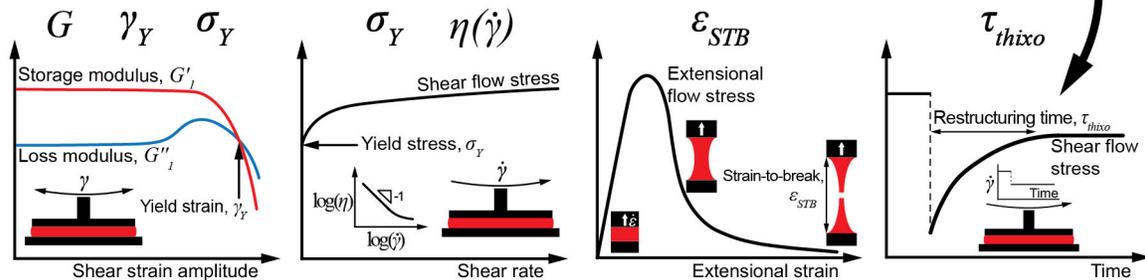
Yield-stress fluids are generally considered non-equilibrium systems both in their solid-like state and their tendency to age and flow over long time scales. To understand the solid-like response one must often consider the thermal motion and dynamics of the elementary objects (with the exception of athermal systems such as granular matter and some capillary suspensions, pastes, and emulsions); this requires statistical mechanics, not just continuum mechanics. To be predictive one needs to ultimately understand the elementary objects (colloids, nanoparticles, molecules, polymers), the inter-particle forces, the assembled structure of these objects, and how dynamic constraints emerge from all the former aspects as a function of thermodynamic state (temperature, concentration, pressure, etc.). This differs from a traditional understanding of "hard" materials, in which the solidity in crystals can be understood from symmetry, equilibrium phases, and thermodynamics.

With these caveats of definition and understanding in mind, we note that an effective or approximate yield stress is often sufficient for understanding a given material—though clarity in the definition is important for experimental reports and theoretical structure-property predictions [17,18]. To a certain degree, this leaves the definition to the user: effectively solid, effectively fluid, and the yielding transition depend on the end-use and timescales of interest which must be specified. Thus, for engineering purposes, describing materials as yield-stress fluids may be a matter of choice, as even a material with a very high "pre-yield" viscosity may be considered not to flow on practical time scales.
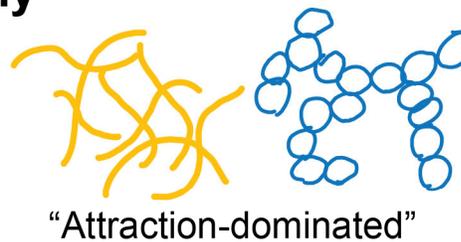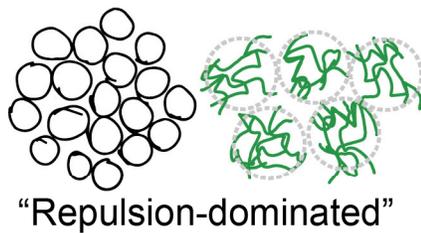
Performance

Direct-write
3D Printing

Design with Materials

Properties

$G \quad \gamma_Y \quad \sigma_Y$

Storage modulus, G'_1

Loss modulus, G''_1

γ

Yield strain, γ_Y

Shear strain amplitude

$\sigma_Y \quad \eta(\dot{\gamma})$

Shear flow stress

Yield stress, σ_Y

$\log(\eta)$

$\dot{\gamma}$

$\log(\dot{\gamma})$

Shear rate

ε_{STB}

Extensional flow stress

Strain-to-break, ε_{STB}

Extensional strain

τ_{thixo}

Restructuring time, τ_{thixo}

Shear flow stress

$\dot{\gamma}$

Time

Time

Design of Materials

Microstructure & Assembly

"Repulsion-dominated"   "Attraction-dominated"

Material Building Blocks

Fig. 3. Materials design encompasses design *with* a material (performance-to-properties), and design *of* a material (properties-to-structure). As an example, for designing *with* a direct-write 3D printing material, *performance* specifications require determination of relevant rheological *properties*. Depicted schematically from left to right, the key rheological properties include: viscoelastic moduli, yield strain, and yield stress from an oscillatory amplitude ramp experiment; yield stress and viscous effects from a steady shear flow experiment; extensional strain-to-break from a filament stretching experiment; and thixotropic restructuring time from a step-down shear flow experiment. Design *of* such a material requires determining *microstructures* that achieve those properties with the corresponding *material building blocks*.

1.2 Organization of this work

With this perspective, we demonstrate how design thinking motivates how we organize our scientific understanding of yield-stress fluids. We describe how we envision "design" applied to this area (Section 2) and give our opinion on the current state of designing *with* yield-stress fluids. That is, dealing with material properties independent of the building blocks, understanding inherent trade-offs between different properties, and generating lists of prioritized rheological properties of these complex fluids. We then review three key questions for design *of* yield-stress fluids in more detail: conceptual models for formulation (Section 3), quantitative models for structure-property prediction (Section 4), and chemical transformation routes to change yield-stress fluids into more useful multi-functional engineering materials (Section 5). As an example of how to utilize the presented design thinking process, we walk through our recent work on direct-write 3D printing (Section 6). Throughout, future research directions are suggested at the intersection of chemistry, soft-matter physics, and material science in the context of our desire to design and engineer these rheologically-complex functional materials.

2. Design-thinking motivates organization of knowledge

2.1 Design versus analysis

To design is to make decisions about what should be. Fig. 4 shows one visualization (of the many available [19]) for the design process which starts with an objective and ends with a final material for the purpose of direct-write 3D printing. Here the vertical width of the yellow path represents the number of ideas or concepts being considered at any given stage.

The work that we will describe in Section 6 is organized according to the design process depicted in Fig 4. If the reader is involved in research they call "design," then they might consider how it fits into the overall design process. For example, does it include planning and specifying material property targets? Concept generation and down-selection? Predictive capabilities that support detailed design with a particular concept? Optimization techniques? Something else?

Multiple concepts may achieve an objective, constituting an inverse problem, which we will call a problem of *design* (or engineering). This is a well-established problem that is different than *analysis*, a forward problem starting from specific, determined circumstances. Most academic literature in the field of rheology, complex fluids, non-Newtonian fluid mechanics, and soft matter, is often framed in terms of analyzing and understanding how materials or systems will behave. Design builds upon the knowledge from analysis, but frames problems differently and requires organizing the available information in different ways, e.g. to contrast how different concepts could achieve a specific desired outcome. Engineering design research has a strong community with broad interests ranging from design theory, to design methodologies, to optimization techniques, and beyond, and there are great opportunities for engineering design researchers to apply tools to rheology generally, and to yield-stress fluids specifically.
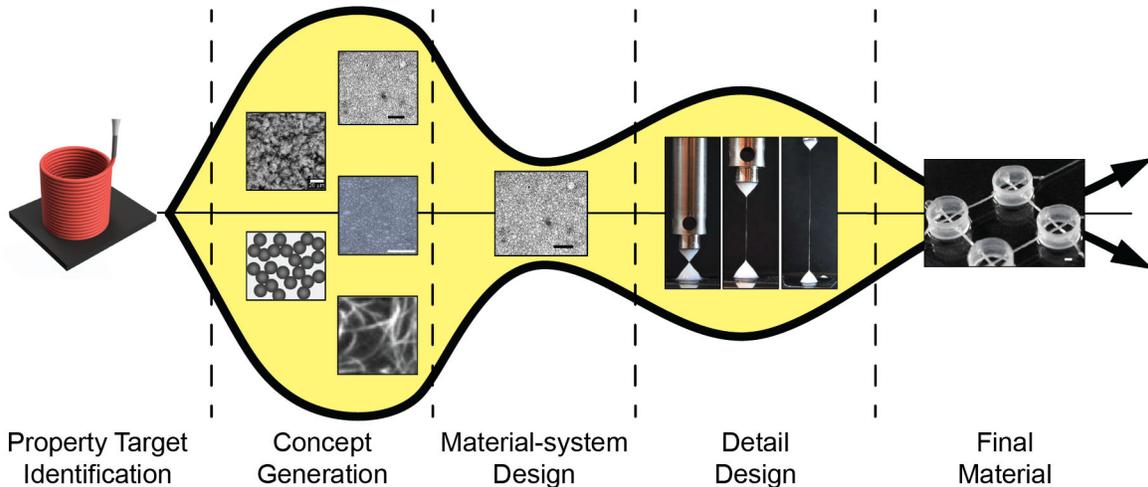
Fig. 4. Materials design process illustrated using some of our work in direct-write 3D printing [20]. Compare to Fig. 3: here the process focuses on design *of* the complex fluid, although design *with* the complex fluid identifies properties during the planning stage as an input to the remaining steps. Design process visualization adapted from [21], Concept generation images adapted from [3,8,11,22].

2.2 Design **with** materials

Design *with* yield-stress fluids occurs at the system level (Fig. 3), often approached from a continuum mechanics perspective dealing with complex properties, but not necessarily considering the microstructural cause of the rheological complexity. It asks, "What properties are important, or optimal?" and involves selection of already known materials based on their properties.

Key rheological experiments and the properties of yield-stress fluids they characterize are shown schematically in Fig. 3 ("Properties"); these and other engineering properties likely to be of interest include the following (with units):

- yield stress, σ_Y (Pa)
- elastic modulus pre-yield, G (Pa)
- yield strain, γ_Y (%)
- thixotropic restructuring time, τ_{thixo} (s)
- post-yield viscosity (Pa.s) or viscous effects, $\eta(\dot{\gamma})$ e.g. Herschel-Bulkley parameters: critical shear rate, flow index [14]
- uniaxial strain at break, ε_{STB} (%)
- density, ρ (kg/m^3)
- homogeneity of the material (particle, building block, or aggregate size) (μm)
- surface energy and wetting
- optical properties, e.g. maintain light transmittance for photo-chemical responsiveness
- transformation requirements, e.g. chemical or thermal, see Section 5

The precise target values for these properties will obviously depend on one's specific performance objective. Application areas where yield-stress fluid property targets have been considered, and published in the public domain, include: direct-write 3D printing of soft matter with and without sacrificial materials [23–25], injectable hydrogels for drug and cell delivery[26–30], field-activated fluids for car systems [31], concrete application and printing [32,33], and robotic adhesive locomotion [34]. These property targets often illuminate the limitations and trade-offs that must be considered or cleverly overcome, such as the difficulty in increasing the yield stress without increasing the post-yield viscosity [34].

As an inverse problem, the determination of these targets is non-trivial; for achieving a given functionality, it is highly likely that several different combinations of properties will satisfy the performance objective, and many properties may be irrelevant or interfere with the performance in unexpected ways. In the area of interfacial rheology, the design of a 2D yield-stress material was recently used to design bubbles where the surface rheology was engineered to arrest dissolution, in addition to classically used parameters such as bubble size distribution or solubility of gases [35]. Recent work by some of us clearly demonstrated the importance of a direct-write material's extensibility [20], a property that is often neglected with yield-stress fluids in general. Non-negligible thixotropic restructuring times also receive comparatively little attention as a target property in many applications, though recently have been used for 3D cell culturing [36].

There is an enormous and rich variety in the material properties of yield-stress fluids, giving us a wonderful toolbox to design with, but we need good toolbox organizers. Material property databases are in-progress for yield-stress fluids [14,37]. Visualization is complicated by function-valued rather than simple scalar properties, e.g. the shape of steady shear flow curves, not to mention viscoelastic and thixotropic response curves. These complex material responses must be reduced to simplified scalar quantities to make Ashby-style property charts [38], which are well-known and incredibly useful design tools for material selection for design. Fig. 5 is one example of an Ashby-style material property co-plot of yield stress and extensional strain-to-break for select yield-stress fluids. These plots reveal trade-offs and "white-space" for design needs[39]. More work should be done in this area to map out and make publicly accessible rheological property databases and visualizations if these materials are to be truly integrated into the engineering design toolbox.

2.3 Design *of* materials

When a new yield-stress fluid must be formulated to achieve an objective, e.g. to populate a new region within an Ashby-style property map, we consider this design *of* a material. Three important challenges arise: (1) selecting one of the many microstructures/formulations/additives to create a yield-stress in the fluid, (2) detail formulation decisions, which may or may not have predictive models available for guidance, and (3) engineering the material to transform into a more useful material (e.g. a strong structural solid). These three aspects are covered in more detail in each of the following sections.
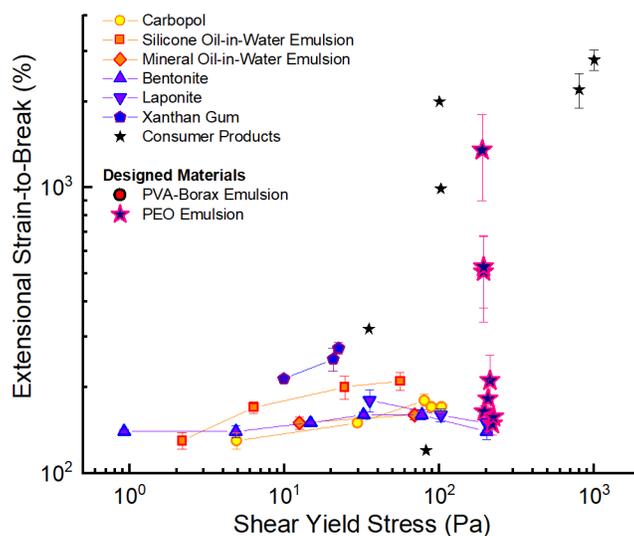
Fig. 5. Ashby-style co-plot showing measurements of extension properties of several yield-stress fluids and the ability to engineer new designed materials that achieve desired properties. The PEO Emulsion system is used for 3D printing shown in the inset of Fig. 4. (Image adapted from Nelson et al.[40] adding data from Rauzan et al.[41].)

3. How many ways to get a yield-stress fluid?

Not all complex fluid microstructures are capable of producing a yield-stress fluid. Non-associating polymer solutions, entangled polymer melts, dilute colloidal dispersions and other materials either lack a sample-spanning reversible mechanical connectivity that can bear a static load at sufficiently long timescales, or do not "flow" as a fluid above a yield point. Fluids that undergo modest shear-thinning and solids that strain-soften should not be considered to have undergone a yielding transition. However, many other microstructures do produce yield-stress fluids [14] which typically fall into the categories of "glass" or "gel" as noted in Section 1. Fig. 6 maps out these two categories, which may also be described as "repulsion-dominated" and "attraction-dominated", respectively. This morphological framework underlies much of the conceptual justification for expected yield-stress fluid properties.

Classes of repulsion-dominated systems include high volume fraction suspensions of hard or soft particles, concentrated emulsions and foams, and concentrated micellar or vesicular solutions. The concept of maximum packing, and distance to maximum packing, is often relevant in these crowded or glassy systems. On the other hand, lower volume fraction networked system classes include particulate gels, electro- and magneto-rheological fluids, and associating polymeric or fibrillar networks.

Most of these material classes have been demonstrated to be capable of producing materials with a yield stress in the range of 1 Pa to at least a few hundred Pa. For context, a liquid laundry detergent required a yield stress of only 0.15 Pa to suspend enzyme particles (diameter ~20 μm or more with relatively small density differences) while still being pourable [42]. Towards the other end of the spectrum, "smooth" commercial peanut butter has a yield stress of approximately 400 Pa [43]. Thus, unless an application demands a very large yield stress, there is significant design

freedom in one's choice of microstructure at this stage, and down-selection will nearly always be driven by chemical compatibility, secondary mechanical properties of importance, or other functionality. Such trade-offs will be part of the example discussed in Section 6 on designing a new direct-write 3D printing ink.

There is not yet a rigorous quantitative method for choosing which of the many material classes should be investigated as candidate solutions to one's design problem. Multiple material classes (and multiple structures and formulations within each class) can achieve the same properties, but for every satisfactory solution there are countless unsatisfactory ones and as a research community we continue to seek a rational design approach rather than costly guess-and-check methods.
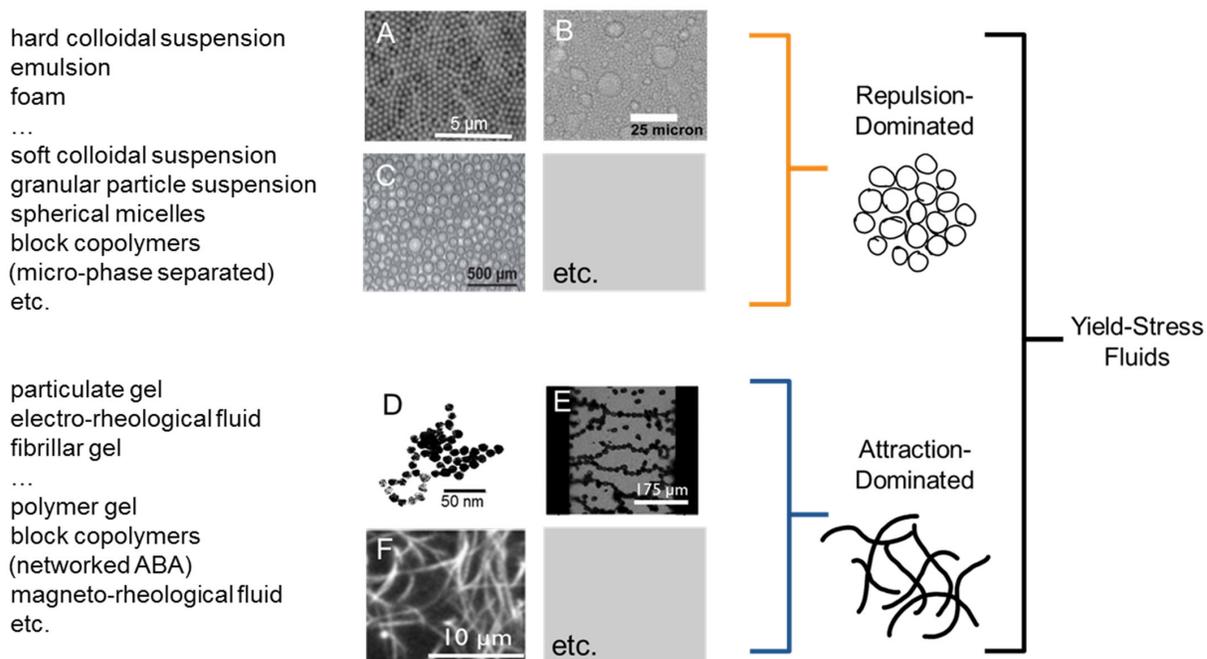

Fig. 6. The many strategies for achieving a yield-stress fluid. Combinations do of course exist. Example images are: A) microgel suspension [44], B) emulsion [45], C) foam [46], D) particulate gel [47], E) electrorheological fluid [48], F) fiber gel [22]. Adapted from [14].

Table 1 gives some specific examples of formulations that—for all practical purposes—produce yield-stress fluids, along with reported ranges of yield stress and general design guidelines (or heuristics) as applicable. This information and these insights are provided to assist readers in making engineering decisions to impart an existing material with a yield stress (e.g. adding particles or polymers or air bubbles) or to create new yield-stress fluids from scratch. The provided design heuristics are general guidelines for what is currently expected for each material class and should not be taken as absolutes. Indeed, clever circumventions of some of these guidelines are opportunities for innovative yield-stress fluid research directions.

Existing textbook and rheological modifier handbooks do not (yet) organize information like Table 1. Rather, different "additives" may each get their own entry, and it can be difficult to identify which microstructures and formulations might achieve a yield-stress fluid. Furthermore,

it is possible for the same additive to exist in multiple microstructural classes depending on concentration or properties of the surrounding medium, which may invalidate heuristics in Table 1. Clear examples are many of the additives in the particulate gel category which at low-to-moderate concentration have a high thixotropic restructuring time but at higher concentrations, as the material approaches the category of "attractive glasses", this thixotropic recovery time may become smaller or negligible as different physical mechanisms (crowding) take effect.

Of course, many systems have multiple components and may be literal or conceptual combinations of items listed in Table 1. Examples of these include gelled emulsions/foams (Ramsden-Pickering [8] and particle-free [49]), capillary suspensions [50], bimodal suspensions of particulates and emulsified droplets [51], and field-responsive microgels [52]. Though we have listed some key model systems and rheological modifiers that have been used to engineer yield-stress fluids, when designing new multi-functional materials it is necessary to keep in mind the microrheological framework of yielding and any available deterministic structure-to-rheology models that may greatly facilitate achieving one's specific performance goals, as discussed in the next section.

Table 1. An incomplete list of the many ways to engineer an effective yield-stress fluid

Material Class	Material System Details/Additive	Reported Yield Stress Range	Design Guidelines
Crowded hard particles	Brownian: PMMA spheres[53], silica sphere mixtures[54,55], anisotropic polystyrene[56] non-Brownian: polystyrene beads[57], glass beads[58], sand[58]	1-500 Pa 1-1000 Pa	High moduli Low yield strain Low thixotropic time High volume fraction
Effectively-crowded charged particles	Laponite in water (also reported as a gel)[59,60]	10-500 Pa	Low volume fractions Few practical examples
Crowded soft particles	Carbopol microgels in water[61,62] poly-NIPAM microgels in water[63,64] polybutadiene stars[65] dendrimers[66] diblock, triblock copolymer mixture in oil[67]	0.1 – 200 Pa	Low-moderate moduli, critical shear rate, and thixotropic time Low weight fractions with microgels Can be transparent
Crowded micelles and vesicles	Pluronic F127 in water[68,69] poly(oxyethylene-oxybutylene) in water[70] Triton X-100 in water[71]	0.1 – 500 Pa	Low thixotropic time Surface active additives
Crowded emulsions	silicone oil-in-water stabilized with SDS[72] water-in-mineral oil stabilized with Span-Tween[14]	0.03 – 1000 Pa	Low critical shear rate Low thixotropic time High volume fraction dispersed phase Allows encapsulation Robust in confinement Can be transparent
Foams	nitrogen in microgel solution[73] nitrogen in water/glycerol stabilized with TTAB, dodecanol[74]	0.1 – 20 Pa	Low moduli Often need supplementary stabilizing structure
Particulate gels	bentonite in water[14] silica in organic solvents[75,76] titanium dioxide in water [77] carbon black in oil[78] metal oxide nanoparticles in water[79] rod-shaped virus particles in water[80]	0.06 -500 Pa	High critical shear rate High thixotropic time (except high aspect-ratio particles) Low volume fraction Often highly tunable properties
Electrorheological fluids	titanium dioxide in silicone oil[81] silica spheres in corn oil[82]	0 (no applied field) – 120 kPa	High yield stress Active control
Magnetorheological fluids	carbonyl iron in mineral oil[83] carbonyl iron in grease[84]	0 (no applied field) – 80 kPa	High yield stress Active control Commercially available
Associating polymers or fibrils	nanofibrillated cellulose in water[9] xanthan gum in water[14]	1 – 500 Pa	High thixotropic time (at low concentrations) High yield strain Low volume fraction Very few predictive models

4. Can we predict properties from formulation and structure?

Quantitative property prediction *a priori* is rarely possible. To really predict properties, one must integrate chemistry and physics. That is, one must know how one goes from the shape, size, and size dispersity of the elementary objects, how they interact (repulsions, attraction potentials), the consequences of the interactions on a wide range of structural length scales including very local scales, and how structure and interactions conspire to define dynamical constraints (including thermally-induced activated barrier hopping[2]) on the different length scales, and thus the mechanical properties such as yielding, etc.

Theoretical estimates and scaling relations are available for some common classes of yield-stress fluids (see Table 1 in Nelson & Ewoldt [14]), including glasses (of hard spheres, charged particles, soft particles, emulsions, and foams) and gels (particulate gels, electrorheological fluids, and magnetorheological fluids). The estimates and scaling laws often omit numerical front factors but describe how yield stress changes with respect to design-relevant parameters such as volume fraction, interaction potential strength, size of building block (e.g. particle size), surface tension for emulsions and foams, and external field strength. Much work is still needed to be quantitatively predictive, and this is where more detailed modeling and simulation will have their place in the toolbox of the future.

Although huge gaps in our knowledge remain, great progress has been made in the development of theoretical and computational methods for predicting the rheology of certain structures, and potentially solving the rheology-to-structure problem for a number of material classes such as hard and soft colloidal glassy systems including emulsions [85–92], athermal granular materials [93], and dense colloidal gels [94–98]. Some of the persistent challenges in these efforts include potentially huge parameter spaces (e.g. shape and structural dispersity of particles), and the determination of appropriate boundary conditions. Microstructural parameters will almost certainly be coupled to multiple performance objectives.

Over the past decade, many different theoretical and simulation approaches have been carried out aimed at developing a physics-based understanding of diverse yield-stress materials. The efforts can be roughly organized into three broad aims. (i) What is the fundamental origin of solidity and how does an amorphous solid transform to a flowing fluid under deformation? (ii) What is the influence of repulsive forces which usually dominate at high volume fractions per a glass, versus strong short-range attractive forces which can result in long-lived physical bonds and a dynamic gel network at much lower volume fractions? (iii) What is the influence of elementary object shape and single particle rigidity on nonlinear mechanical response and yielding?

Below we describe recent progress in these three broad areas. Most of the success has come with amorphous repulsion-dominated material structures, but progress with attractive gels is also described. Materials such as polymeric glasses are not discussed below; although they yield and may have plasticity, they do not typically "flow" as a fluid above the yield stress and thus fall outside our scope here.

Theories and simulations for aim (i) typically adopt an effectively zero temperature perspective (infinite Deborah number, no thermal relaxation or activated processes) where flow is entirely driven mechanically a la granular materials. The main goal is then to understand the physical

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[2] The term "dynamic yielding" can be used to describe yielding when thermal motion is involved. Note this is a different concept from the "dynamic yield stress" observed in steady flow tests mentioned in Section 1.1.

mechanisms of the yielding transition on a large or coarse-grained scale using very simple particle models. Complementary efforts address aims (ii) and (iii) by including more microscopic detail with a strong focus on spatially local processes, including how deformation modifies structure and can assist thermally activated transport as an explicitly dynamical route to yielding.

4.1 Fundamental physical mechanism of yielding in amorphous systems

The yield transition can occur in two qualitatively distinct ways for amorphous materials, depending on the system preparation protocol, as shown by Berthier and coworkers with a simple spherical particle generic glass former for which they analytically solved a mean-field elasto-plastic model in combination with molecular dynamics (MD) simulations [99]. Well-annealed systems yield in a discontinuous brittle manner per a first-order nonequilibrium phase transition. For poorly annealed or quenched systems, yielding is a smooth continuous crossover, per ductile rheological behavior observed in foams, emulsions and colloidal glasses. For nonlinear oscillatory shear, a simultaneous simulation analysis of global mechanical response and particle-scale motion demonstrates that when macroscopic yielding occurs in a mechanically continuous manner the microscopic particle dynamics also strongly changes [99,100].

Rate-dependent effects have been recently refined by Wyart and coworkers [87], who have analyzed the flow curve of a model athermal glass of soft particles as the strain rate vanishes, which can be characterized by the so-called Herschel-Bulkley exponent $n = 1/\beta$. Based on an improved mean field model where thermomechanical noise has so-called non-Gaussian fat tails, this exponent was shown to be essentially unity. Even in the absence of a microscopic description of the yield process, in the simplest situation where there are no flow inhomogeneities, a scaling description of the yielding transition of soft particle solids at zero temperature can be still constructed, and qualitative connections to critical phenomena made [88]. In terms of design and engineering to control the exponent n, the range of possible values and mapping to different microstructure features is yet to be explored.

4.2 Microscopic theories for athermal amorphous mechanically-driven yielding

Theoretical progress for aims (ii) and (iii) has been made for dense repulsive particles under conditions where thermally-induced activated barrier hopping is ignored. Here we mention two specific, very different approaches.

Fuchs, Cates, and coworkers have employed ideal mode coupling theory (MCT) to address the yielding of mainly hard sphere colloidal glasses [85,101]. MCT is a force level, dynamically self-consistent, microscopic approach formulated in the liquid phase which relates particle interactions, local structure, and slow dynamics, and can predict the emergence and disappearance of rigidity. Since ergodicity-restoring thermally activated hopping processes are not included, ideal MCT predicts strict kinetic arrest (infinite viscosity) as a system is cooled or densified in equilibrium. Yielding then occurs in an "absolute" (purely mechanically-driven) sense beyond a threshold applied-stress where the rigid confining cage is destroyed. The lack of activated processes implies some connection of MCT with low temperature granular approaches. Many predictions have been made for various nonlinear rheological properties, and also the yield stress as a function of colloid volume fraction. For example, the latter emerges discontinuously above a critical volume fraction $\phi_{crit} \approx 0.515$ where $\sigma_Y = \sigma_{crit} + 112\sqrt{\phi - \phi_{Crit}}$ for $\phi > \phi_{crit}$ [102].

Berthier et al. [86] have tested aspects of MCT using simulation. They found it qualitatively captures the emergence and rapid growth of a yield stress in entropy-controlled hard-sphere glasses

as random close packing (RCP) is approached. But the emergence of solid behavior in glasses induced by *soft* repulsive interactions (e.g. as expected for emulsions, foams, and soft microgel particle suspensions) is not well described. The limitations were suggested to be related to the shortcomings of ideal MCT for caging dynamics in the equilibrium dense fluid.

A second major body of work by Bonnecaze, Cloitre, and coworkers [89,103], who use the word "design" to frame and motivate their work, has addressed the yielding and nonlinear rheological behavior of soft repulsive particles with an emphasis on deformable microgel suspensions and pastes. Beyond a soft jamming threshold volume fraction, these particles are in literal contact and interact roughly via elastic Hertzian contact repulsions. A sophisticated and quantitative 3D micromechanical model was constructed. Predicted properties include the linear elastic modulus, shear yield stress, and steady shear flow curves (which are well-described by a Herschel-Bulkley model). The shear stress depends primarily on the elastic contact modulus of the particles, E^*, as well as the dynamic pair distribution function and the solvent-mediated elasto-hydrodynamic interactions among deformed particles. Thus, the yield stress depends on multiple controllable parameters such as single particle elastic modulus (tunable via chemistry and degree of internal crosslinking), microgel size, and concentration.

The results are a real step toward design, providing a predictive simulation framework (with some experimental validation) for designing new soft additives with a desired rheological response. However, many design questions remain. For example, yield-stress fluid behavior can appear at lower volume fractions in an entropic glass regime below the soft-jamming threshold, where particles are "caged" but literal particle contacts are not required to generate the yield-stress, and this is not part of the modeling framework. Even in the "jammed" regime, the properties depend on the particle elastic modulus but this may be difficult to measure or predict *a priori*, and is unlikely to be part of technical specifications from a product supplier. The amount of design freedom, in terms of the range of available Herschel-Bulkley parameters, is also unclear. For example, the power-law exponent is always $n \approx 0.5$ from the simulations, but this is not universally the case experimentally even for systems of soft repulsive particles [14]. There is also no direct algebraic equation given for predicting the yield-stress, and thus full simulations would be required to predict this and other properties.

4.3 Microscopic theories for absolute and dynamic yielding in diverse soft matter systems

The MCT approach has been qualitatively extended by Schweizer and coworkers to construct the full local dynamic trapping potential experienced by a particle – the so-called nonlinear Langevin equation (NLE) theory which can treat both quiescent and mechanically-driven dynamics and rheology of *glass* and *gel* forming systems [90,91,94,95,104–109]. The theory works at the elementary object level and has been implemented for hard [90,91] and soft spheres [106], many arm stars [105], rigid rods and uniaxial hard objects [104,107], microgel particle suspensions [109], and polymer-colloid suspensions [94,95]. As in the MCT approach, liquid state theory is employed to predict local structural correlations, and from this local descriptor dynamical constraints are quantified, leading to the prediction of the conditions (in a high dimensional parameter space relevant to engineering design) for the emergence and degree of transient dynamic localization (caging, physical bond formation). But NLE theory also uniquely predicts the finite activation barrier for relaxation and flow, in the quiescent state and under external deformation. The linear elastic modulus, absolute and stress-assisted dynamic yielding,

flow curves, etc. can be approximately determined in a manner that in principle relates these quantities to the chemical and materials aspects.

At zeroth order, the numerical NLE theory can be simplified to provide an intuitive physical picture and allow useful analytic relations to be derived that encode how microscopic interactions, thermodynamic state, and local structure conspire to determine dynamical constraints, and thus slow activated dynamics, and nonlinear rheology. The key theoretical parameter is the strength of the mean square force, $\langle f^2 \rangle$, exerted on a particle by its surroundings. For particles that interact via pair decomposable harsh repulsive or hard-core potentials (with or without short range attractions), in dimensionless units this mean square force is proportional to a "coupling constant", v_∞. Specifically, $\langle f^2 \rangle \propto v_\infty \propto \phi g_d^2$, where ϕ is the suspension volume fraction and g_d is the intermolecular pair correlation function between two spherical particles or two interaction sites of a molecular-like object *at contact* [90,104,106]. For particles that interact via continuous repulsive forces (e.g., soft microgels), g_d is (to leading order) the amplitude of the first caging peak of the interparticle pair correlation function, $g(r)$ The chemistry aspects are all contained in g_d which is the most local measure of packing correlations, and which depends on everything – thermodynamic state, particle shape and softness, and intermolecular interactions. Future research opportunities exist here to quantitatively relate g_d to these design parameters for a range of different material systems.

To leading order, one can derive interconnections and scaling behavior between v_∞ and physical properties such as the yield stress. For the simplest case of spherical particles of diameter d, the coupling constant $v_\infty \propto \phi g_d^2$ grows strongly with volume fraction and strength of short range interparticle attractions. For hard spheres it diverges only as RCP is approached, while for soft particles it never diverges. The transient particle localization length (in a cage or in a physical bond) is given by $r_{loc} \propto d \cdot v_\infty^{-1}$, the activation barrier for hopping transport is $\beta F_B \propto v_\infty^{-1} \propto \left(d / r_{loc} \right)$, the dynamic shear modulus (in the absence of relaxation) is $G' \propto \phi k_B T / \left(d\, r_{loc}^2 \right)$ (a microrheology-like formula), and the maximum force confining a particle in a cage or in a physical bond is $f_{max} \propto k_B T\, r_{loc}^{-1}$. These formulas also apply under deformation but the dynamic localization length is predicted to change with applied stress or strain. At a critical degree of deformation, dynamic localization is destroyed corresponding to a particle-level solid-to-liquid transition at an "absolute yield stress" $\sigma_Y \propto f_{max} d^{-2} \propto \left(k_B T / d^3 \right) \sqrt{\beta d^3 G' / \phi} \propto k_B T / \left(d^2 r_{loc} \right)$. However, before this condition is reached, deformation can lower the activation barrier sufficiently that on the experimental time scale particles escape their dynamical constraints via thermally-induced activated hopping and thereby flow, a process called dynamic yielding. Other quantities such as the yield strain, pre-yield elastic modulus softening, and flow curves can also be determined.

The NLE theory has had significant successes for hard [90,91] and soft [105,106,109] repulsive force glass forming colloidal suspensions, polymer-colloid depletion gel forming suspensions [94,95], mixtures of spheres and rods [108], plastic glasses, attractive glasses, and gels of weakly nonspherical colloids [107], double yielding in dense suspensions of attractive nonspherical colloids [107], and other systems. We note in passing the NLE theory of dynamics, nonlinear rheology, and yielding has also been extended to treat polymer glasses [110,111] and

topologically entangled polymer liquids [112]. However, the NLE approach for colloidal matter only describes the local physics of caging and thermos-reversible physical bond formation, and does not capture longer range many-particle cooperative re-arrangements which can be important for yielding and rheological properties. A major generalization of NLE theory been recently formulated which does include many particle collective elastic effects that serve to facilitate local activated re-arrangements, the so-called Elastically Collective NLE (ECNLE) theory [113]. Extensive application of ECNLE theory to hard and soft colloids, and molecular and polymer glass formers has been carried out [109,113].

As also true of MCT, the NLE and ECNLE approaches do not capture some key physics that emerges beyond the soft jamming threshold, nor elasto-hydrodynamic effects important in overcompressed emulsions and microgel systems [89,103]. More generally, these microscopic approaches aim to treat thermalized Brownian suspensions, not athermal granular systems, although there may be some connections. As mentioned above, the lack of thermally activated processes in ideal MCT implies what it calls "yielding" is an abrupt solid-to-liquid transition driven entirely by external deformation, which seems in the qualitative spirit of yielding in granular systems. For NLE theory which does include thermally activated processes, in the absence of deformation it predicts for hard sphere fluids that the relaxation time and viscosity diverge, and the diffusion constant vanishes, only as the random close packing (RCP) volume fraction is approached. This follows from the idea discussed above that $\left\langle f^2 \right\rangle \propto \nu_\infty \propto \phi g_d^2$, which diverges only because the contact value of $g(r)$ diverges upon strict jamming. NLE theory also contains the concept of "absolute yield stress" which corresponds to an idealized solid-to-liquid transition driven solely by external stress (as signaled by the dynamic free energy changing from a localized to delocalized form) *if* the thermal fluctuations that allow activated barrier hopping are ignored. Other issues germane to granular systems remain to be carefully studied within the NLE theory framework, and its local nature implies fundamental physical effects such as the emergence of percolated force chains as jamming is approached are not accounted for.

Another interesting recent approach with microscopic elements considers the specific case of soft microgels using ideas of polymer physics [114]. It has been shown that aspects of the rheology of putatively jammed microgels at very high volume fractions composed of relatively small particles can be captured with such an approach if the system is modeled as a continuous polymer gel [114]. Commonalities between the mechanics of smaller microgel suspensions and the analogous large particle granular systems were identified. In both systems, with increasing volume fraction the particles can deform, and they transition from an ultra-dense particle suspension to something more akin to a continuous polymer network. However, under large deformations that mechanically force flow, the yielding behavior is very different since the smaller particles are influenced by Brownian fluctuations even in the soft jammed state, in contrast to the very large particle granular systems where dissipative interparticle friction effects are important. Thus the flow curves of the colloidal and granular particle systems of the same chemistry display some qualitatively different behaviors. Very recently [115,116], the polymer physics based perspective [114] has been employed to analyze lower volume fraction suspensions of commercial carbopols and charged microgels. This work suggests basic polymer physics ideas are useful for understanding aspects of a rather broad class of yield stress fluids where the elementary colloid is a soft polymeric object.

4.4 Simulation insights for yielding of gels

Scaling theories are available for weakly flocculated dispersions based on breaking bonds between particles [117], such as the relation $\sigma_Y \sim W'_{max} a^{-2} \phi^2$ with volume fraction ϕ, sphere radius a, and maximum force in terms of spatial gradient of interaction potential W'_{max}. Although instructive for making design decisions, these expressions serve more as a guide for making dimensionless plots to check results rather than predicting properties *a priori*. Strongly flocculated systems are more complex[118], with evidence that the yield stress is determined by nonlinear microscopic bending mechanics of colloidal aggregates and a critical bending moment M_c for failure [119–121], resulting in the expression $\sigma_Y \sim M_c a^{-3} \left(\phi/\phi_e\right)^{3/(3-d_f)}$ where ϕ_e is the effective cluster volume fraction and d_f is the fractal dimension of the network (e.g. $d_f = 1.8$ is expected from DLCA aggregation kinetics). While difficult to predict M_c a priori, examples exist for measuring M_c directly for individual aggregates and then successfully predicting the bulk rheology response [122].

Recent collaborative work on strongly aggregated depletion gels[123] focused on predicting the linear elastic shear modulus (but not yielding). They demonstrated with theory, Brownian Dynamics simulation, and experimental measurement of network structure, that the elastic modulus is primarily determined from the weakest elastic links between locally dense clusters, with each cluster acting as a rigid mechanical unit[124]. A theoretic approach based on cluster size and cluster-cluster contact number density, combined with classic Cauchy-Born theory of solid deformation, reasonably predicted the linear elastic modulus increase with concentration. What is still unknown, and important for true design, is a theory to readily predict cluster structures from formulation and building block properties, as well as a prediction for the yielding properties of these systems.

For better prediction and understanding of yielding, simulation has been used by multiple workers to investigate the yielding and microstructural behavior of gel-forming thermoreversible sticky spherical colloids. Zia and coworkers found that nonlinear mechanics is strongly influenced by bond strength, with bond rupture and re-formation triggering aging which further enhances kinetic arrest [125]. Under deformation, stress accumulates in stretched and oriented bonds until the yield point, beyond which energy is released. Although very few bonds are broken, they trigger the relaxation of many others which induces fluidity [97]. del Gado and coworkers [98] used simulations under effectively zero temperature conditions (an athermal quasistatic shear protocol) to investigate yielding of a model colloidal gel. A spatially-resolved analysis revealed the nature of stress localization and that yielding occurs by breaking a small fraction of the network connections. Stiffening can also occur due to stretching of the physically-bonded network chains of colloids aligned along the direction of maximum extension. Strong localization of tensile stresses was observed which triggers the breaking of a few network nodes at around 30% strain. At higher strains a large-scale reorganization of the gel structure occurs at the yield point.

A huge design space exists beyond what has been simulated, from changing particle shapes to more complex interaction potentials, e.g. electrostatic charge interactions with discotic clays (e.g. Laponite) having oppositely charged faces and edges. Not to mention the wide range of other attraction-dominated structures that can produce a yield-stress fluid (Fig. 6).

Modeling and simulation tools that enable design exploration through this space will be valuable, first to predict important properties such as the yield stress (quantitatively), as well as

other important properties listed in Section 2.2. Moreover, we encourage the community developing modeling and simulation tools to consider how their results can impact the wide range of ways to achieve a yield-stress fluid (Fig. 2, Fig.6, Table 1), in terms of the rheology-to-structure inverse problem[14]. Their impact will be magnified by publishing their code and creating user interfaces that are ready for the inverse problem to help make engineering decisions about what building blocks to use to achieve the desired properties. As a community, good progress has been made at determining design principles for the magnitude of the yield stress and post-yield viscous behavior of colloidal gel systems, but the ability to be predictive of thixotropic time effects is still elusive.

5. How to transform a yield-stress fluid to be more useful?

5.1 Designing chemistry of yield-stress fluids in parallel with design for rheology

Chemical processes for transforming composition and strength are key to increasing the functionality of yield-stress fluids; here we discuss notable transformations in the context of 3D printing. We focus on cases that envision their ultimate use as structural engineering materials, for which transformation processes are often required as the yield-stresses cited in Table 1 are orders of magnitude lower than those of engineering metals and ceramics. For multi-functional performance objectives, there are the two interrelated considerations of form and function as might be developed using materials that are rheologically optimized for 3D printing processes. The rheology here most directly interacts with the dynamics of a printing process to determine form for the structure. The rheology also has to embrace the materials compositions that can deliver the chemistry that in the end establishes functional performance. In this section we briefly review recent progress in research to develop chemistry and chemical processes that can transform the physiochemical properties of yield-stress fluid inks to achieve greater functionality within 3D printing applications.

5.2 Chemical methods for transforming

When developing new materials chemistry, it is useful to consider the question that asks, "What types of multi-functional programming/transformation are possible?" More importantly, the processing methods must make it possible to morph the physicochemical properties of a yield-stress fluid into those required by a functional structure or device. The majority of physiochemical transformations reported to date rely on relatively simple, well-known chemistries such as particle sintering [8,126], thermal cross linking/polymerization (e.g. of epoxy and silicone resins) [20,127,128], photo-crosslinking [129–131], frontal polymerization [132], and ion-crosslinking [133] as specific examples. For these cases, it is not the complexity of the chemistry that has been considered to matter most, but rather how its incorporation within the ink impacts its rheology and the dynamics of a 3D printing process. In a recent report [20], this potential impact for progress of this sort was illustrated with the printing-based fabrication of complex 3D elastomeric structures using a rheologically optimized particle-free emulsion as the precursor ink. The ink in this case actually embedded a composition far removed from the final elastomeric material structures themselves. Specific chemical processing steps in this case—conformal chemically directed encapsulation of the emulsion-derived structures in a nanoscale silica shell—stabilized the net printed form and made possible thermal annealing steps to both crosslink the silicone pre-polymers and drive out the water content carried by the original ink emulsion. There exists a significant

opportunity in research to provide new chemistries that can more broadly impact physiochemical properties to realize higher levels of structural complexity or application specific functionality.

The recent literature provides further notable examples of progress made to raise compositional and structural outcomes beyond those defined by both the structure and compositions of the initial printed forms. Exemplars of this progress are shape transformations, such as the demonstration of materials origami as a means to extend the complexity of 3D printed structures [134] to the programmed temporal transformation of structural forms via biomimetic 4D printing [129] as shown in Fig. 7. The nature of the materials chemistry that underpins each of these cases differs in significant ways, though each proceeds through the transformation of a structure printed initially as a sheet-like form.

The origami crane (Fig. 7A) shows an interesting example of titanium hydride yield-stress fluid ink that was used to print a sheet comprised of a periodic filamentary array with different lattice geometries. This ink was rheologically engineered as a high volume fraction particle paste (typically a simple, i.e. non-thixotropic, yield-stress fluid from the toolbox) to provide durable printed sheets that could be removed from the substrate and subsequently rolled, twisted, and folded to create the complex origami shapes. The high mass fraction of titanium in the yield-stress fluid ink makes it possible to sinter and oxidize the particles to form the mechanically stable titanium oxide origami crane shown. This chemistry, when combined with post-printing physical manipulation, provides a simple and more generalizable method of assembly [134]. In the second example, the folding flower shown in Fig. 7B, the physical bases of the folding transformation are directly embedded in the 2D preform at the time of printing. Here, a composite hydrogel yield-stress-fluid ink (cellulose nanofibril suspension) is used to print bimorphs that encode a nascent 3D shape. The assembly process exploits osmotic forces to drive a complex, temporally prescribed 3D morphological transformation in the bimorph. A post-printing physicochemical transformation, the photo polymerization of the N-isopropylacrylamide monomers in the ink, is required to produce a hydrogel composite that is not only stable in water but swells and folds to form the 3D flower shape. A swelling anisotropy in this case occurs as a consequence of the alignment induced by shear of cellulose nanofibrils present in the composite ink when the yield-stress fluid is extruded through the nozzle during printing. The morphology of the shape transformation is directed by the relative overlay of filaments in the bimorph. Theoretical mechanics models make it possible to construct predictive designs for 4D printing of complex shape evolving structures of the type illustrated by the example presented in Fig. 7B [129]. This evolution again illustrates elements of structural form that far exceed the attributes initially present in the printed yield-stress fluid.

In both cases described above, the rheological design of the yield-stress fluid ink serves as a means to embed printed structures with chemistries that can support useful property-selecting transformations, with directed 4D folding and modifications of mechanics/composition through chemical modification. It is interesting to note that the processing needed to make such modifications can be integrated directly on the fly using appropriately designed inks and sophisticated engineering of the robotic printer. Such methods greatly extend the prospective design rules that can be accommodated with rheologically optimized ink. In Fig. 8A a yield-stress fluid loaded with silver was used to print complex, curvilinear structures, ones whose printed 3D forms were promptly consolidated and annealed using focused laser irradiation programmed to follow filament extrusion in specific registry. This enables the fabrication of freestanding,

conductive, and ductile structures as are shown[135]. Fugitive media can also be used to great benefit in stabilizing 3D printed ink structures. A stunning example of this type of processing is shown in Fig. 8B, which shows images of a printed elastomeric chemomechanical actuator—a soft octobot. The fabrication in this case uses a catalytically curable silicone yield-stress fluid, a material that can be used to print and subsequently cure (in supported form) the complex hierarchy of reaction chambers required for this soft, autonomous robot [136]. When taken together, these notable works illustrate the rich landscape that exists for further advances in both chemistry and processes for the transformation of 3D printed structures fabricated using yield-stress fluid inks with engendered uses in electronics, sensors, actuators, and soft robotics.
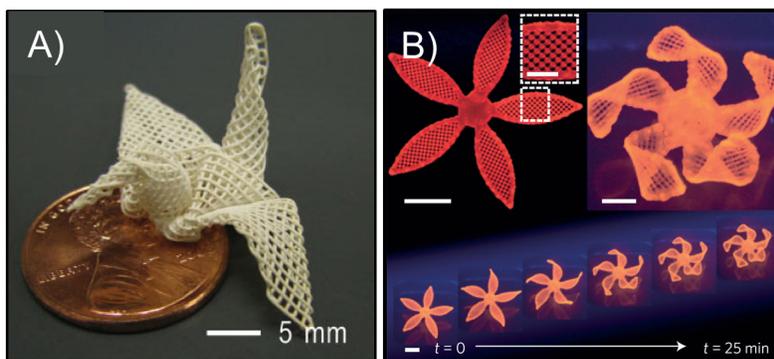

Fig. 7. A) Titanium oxide crane reprinted with permission from [134], B) Printed and resulting swollen flower (scale bar is 5 mm, inset is 2.5 mm) reprinted with permission from [129].
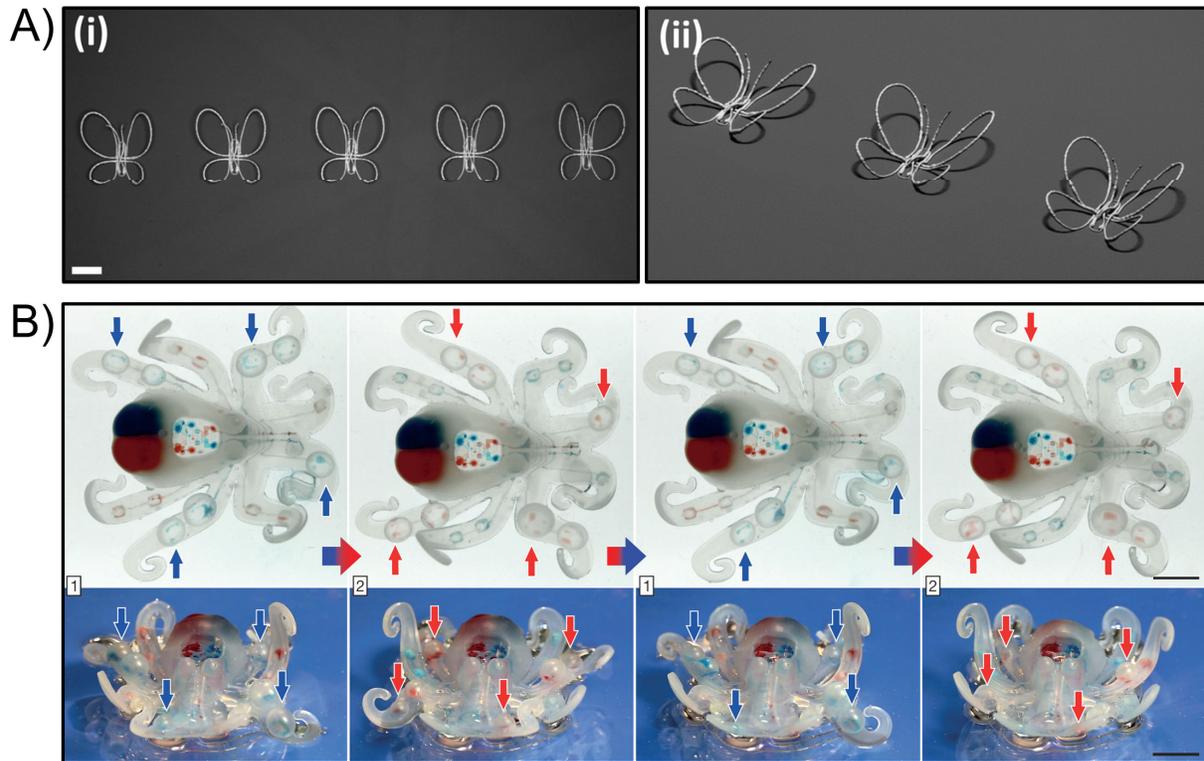
Fig. 8. A) Freestanding silver butterflies (scale bar is 1 mm) reprinted with permission from [135], B) Top-down and face-on actuation of octobot (scale bar is 10 mm) reprinted with permission from [136].

6. Example: design process applied to yield-stress fluid ink

The full design process integrates all the preceding content. Here we frame some of our recent contributions as an example of how the reader may be able to frame their own work by understanding this vision of the design process (Fig. 4), make use of the previous sections, and highlight needs for future research. Specifically, we focus on a new paradigm of *extensible* yield-stress fluids [137] which motivated formulation and study of a new multi-functional 3D printing ink [20]. The rheological requirements described for this application will be similar to many other applications, e.g. in Fig. 1, and we hope that the reader can see how the process generalizes.

6.1 Planning: property targets

In this stage, we broadly considered "what properties are important for direct-write 3D printing?" (Section 2), before narrowing our focus to a subset of performance criteria. Importantly, this question is independent of the material microstructures that will achieve those properties and we do not yet consider any optimization of the values of these properties. Several studies have been performed on design criteria of some of the relevant properties for this application (See Section 2.2), relating maximum build height to yield stress [25] and gap-spanning performance to linear modulus [23], but prior to our work the importance of high extensibility in direct-write 3D printing had only been conjectured [138].

The performance criteria that we chose to investigate were buildability, gap spanning, print speed, and printing diameter. The yield-stress fluid also had to be transformed post-printing to be

relevant as an engineering material. These targets were motivated in-part by the reported challenge of material clogging with small diameter nozzles, limiting feature sizes. The major properties we considered in the design of our material were the yield stress (Pa), pre-yield linear modulus (Pa), thixotropic restructuring time (s), homogeneity of the material (particle size nm), and uniaxial strain at break (%) (c.f. Fig. 3 for rheological measurement schematics). For better buildability and shape-retention of printed filaments, a sufficient yield stress, high pre-yield modulus, and low thixotropic restructuring time are needed. When spanning a gap, a high pre-yield modulus reduces filament sag. The post-yield viscous effects and yield strain were of secondary importance in our study, though we note here that there is a lack of correlative work between these properties and printing performance, e.g. printing resolution. We were interested in building structures relevant for biological or actuation applications and targeted a build height on the order of 1 cm. Comparing gravitational stresses to the yield stress for this height ($h = \sigma_Y^{\text{Target}} / \rho g$) results in a target yield stress of at least 100 Pa.

6.2 Concept generation: many structures give a yield stress

Next, we considered how to achieve the qualitative property targets. What material structures can satisfy our requirements? It is important to consider all possible materials, without prematurely down-selecting. This stage consisted of both surveying existing yield-stress fluid concepts and conceptually synthesizing new materials, i.e. organizing our toolbox (Section 3). A wide range of materials was considered (e.g. Fig.6, Table 1), which required down-selection.

6.3 Material-system design: property databases and models for formulation-structure-property relations

Down-selection was guided by conceptual models, chemical compatibility, the heuristics in Table 1, and scaling concepts (Table 1 of Nelson & Ewoldt [14]). The desire for a short thixotropic restructuring time eliminated attraction-based yield-stress fluid materials (Fig. 6, lower half) since they tend to have sparse networks of particles or polymeric molecules that can take a significant time to reform (i.e. we preferred here "simple" (negligible thixotropic time) rather than "thixotropic" yield-stress fluids—see Section 1.1.). Considering the remaining repulsion-dominated materials (Fig. 6, upper half: crowded particle suspensions, emulsions, foams etc.), in order to satisfy our target of very small printed filament diameters, we sought a particle-free yield-stress fluid since even sub-micron particles can form clogging aggregates [8]. This eliminated suspensions of hard or soft particles, as well as electro- and magneto-rheological materials (attraction-based materials but with short restructuring times). Foams were also eliminated since it is a significant engineering challenge to engineer a printable foam with suitably high stability, yield-stress, and linear modulus that is not particle-stabilized. Of our initial list, this left emulsions and micellar solutions, both of which have been experimentally demonstrated to be capable of achieving sufficiently high yield stresses and moduli for self-supporting structures.

Finally, we considered extensibility; because the paradigm of extensible yield-stress fluids was underdeveloped, we generated a property space of the extensibility of common model yield-stress fluids (Fig. 5). Here it is worth emphasizing that though the design process is depicted as linear, at any step iteration and revisiting of a previous step may be necessary. If none of the generated concepts satisfy one's property targets, down-selecting decisions may need to be relaxed or new concepts may need to be invented. Such was our case; finding the surveyed model fluids to be unsuitable for studying high extensibility, we created a new material concept based on juxtaposing

[14] a high volume fraction emulsion (yield-stress-providing microstructure) with a polymer network (extensibility-providing microstructure) in the continuous phase. Our down-selection process emphasizes our opinion that property databases for rheologically complex materials are greatly needed. Additionally, we note that down-selection to a single microstructure class will rarely be possible and one may have several candidate classes to evaluate and attempt to optimize in the detail design phase.

6.4. Detail design & final material

It is in this downstream step of the design process that optimization should occur, either by predictive equations or experimental iteration. For complex fluids we are still lacking validated comprehensive predictive capabilities to relate formulation to complex rheological properties, but there have been many theoretical and computational advances (Section 4).

The final material for an improved 3D printing ink was arrived at using experimental iteration with readily available materials (silicone oil, sodium dodecyl sulfate surfactant, and polyethylene oxide (PEO) of different molecular weights). The volume fraction of the dispersed silicone oil phase and the speed of homogenization were controlled to obtain a sufficiently high yield stress and linear modulus for building self-supporting structures and spanning gaps. The molecular weight of PEO in the continuous water phase was varied to control the extensibility of the material. Extensibility remains to be predicted from microstructural modeling and simulation and so we used an experimental approach to explore what was possible. Since the shear response was dominated by the high volume fraction of the dispersed phase, the PEO molecular weight had no functional influence on the shear yield stress or pre-yield modulus but a large influence on extensibility as shown in Fig. 5. With this model fluid, we were able to show that the higher extensibility, induced by the high molecular weight polymer, eliminated filament breakup when printing at high speeds. The filament stretching that occurred at high print speeds was important to mitigate die swell on extrusion, allowing for printing of filaments with diameters smaller than 10 microns.

Until this point, design of our material focused on the rheology and structure that matter for good 3D printing, not what matters to be useful as an engineering material. Though our printing material was designed to have a sufficient yield stress (~200 Pa) to build open 3D structures of our length scale of interest, this is insufficient for a structural sound engineering material. Iterating on the formulation of the emulsion, we chose to improve the structural properties of the material through polymerization of the oil phase into a robust continuous elastomer, thus intimately tying the transformation method to the microstructure design for printing (Section 5). Our choice of an emulsion material would allow for compartmentalization of functional components within hydrophilic or hydrophobic phases to be used in transformation or to modify structural or flow properties, encapsulation, etc.

7. Conclusions

The knowledge needed to design the functionalities of yield-stress fluids is at the intersection of chemistry, soft-matter physics, and material science. Our vision is for the community to continue to work toward design tools that will eventually mature to the point of textbooks and handbooks, which has occurred for other fields of engineering (such as machine design[139–141], material selection for design[38], and high-level aspects of chemical product design[142]). Yield-stress fluid behavior is perhaps the most commonly used rheological complexity, but many other rheological phenomena

exist that are critical for functionality in engineered systems, including linear viscoelasticity, shear-thickening, thixotropy, and extensional viscosity, to name a few. The design framework described here, especially Figs. 3 and 4, can be generalized to these other rheological phenomena [143]. We anticipate progress in the areas of design *with* complex fluids (methods to identify property targets, material selection databases) and design *of* complex fluids (structure-property predictions), integrated with other tools needed for design including uncertainty quantification, optimization techniques, and surrogate modeling to more completely develop the full design toolbox for rheologically complex fluids.

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Declarations of interest

The authors declare no competing interests.

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