



First-Principles Constitutive Equation for Suspension Rheology

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Using mode-coupling theory, we derive a constitutive equation for the nonlinear rheology of dense colloidal suspensions under arbitrary time-dependent homogeneous flow. Generalizing previous results for simple shear, this allows the full tensorial structure of the theory to be identified. Macroscopic deformation measures, such as the Cauchy-Green tensors, thereby emerge. So does a direct relation between the stress and the distorted microstructure, illuminating the interplay of slow structural relaxation and arbitrary imposed flow. We present flow curves for steady planar and uniaxial elongation and compare these to simple shear. The resulting nonlinear Trouton ratios point to a tensorially nontrivial dynamic yield condition for colloidal glasses.

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The imposition of flow can drive a fluid far from equilibrium. Because of the occurrence of long relaxation times, this effect is ubiquitous in complex fluids (colloids, polymers, etc.) whose rheology is of significant technological interest, and also represents an important challenge in nonequilibrium statistical physics. Continuum approaches have provided important insights, using symmetry and other principles to construct or constrain phenomenological constitutive relations. While the constitutive equations of Newtonian fluids and Hookian solids are derivable from fundamental starting points (the theory of linear response based on Onsager's regression hypothesis), there has been less progress with their nonlinear generalizations for viscoelastic fluids, plastic solids and other strongly deforming soft materials.

A central aim of theoretical rheology is thus to derive from the underlying microscopic interactions the constitutive equations that relate the stress tensor to the macroscopic deformation history of a material. For entangled polymer melts, the constitutive equation of Doi and Edwards [1] has enjoyed considerable success. An analogously general microscopic constitutive equation for colloidal dispersions remains conspicuously lacking [2]. Even the simplest hard-sphere colloids in concentrated suspension exhibit a broad range of viscoelastic behavior; alongside to flow-thinning [3] and thickening [4], slow structural relaxation leads to glasses showing a solidlike response, strain hardening or softening, and plastic flow [5].

But, while the linear viscoelastic spectra of colloidal suspensions are fairly well understood [6], only recently has progress been made in nonlinear flow predictions for simple shear [7,8]. Shear represents a relatively weak flow in which material lines grow linearly with time, while in elongational flows such growth is exponential, creating much more severe deformations of material elements. Thus, a description capable of handling arbitrary deformation histories is highly desirable. In the continuum approaches, invariance arguments strongly restrict the

deformation measures that can appear. A good microscopic theory (e.g., [1]) should implicitly respect such invariances so that a tensorially admissible constitutive structure emerges from a first-principles starting point.

In this Letter, we develop such a theory for dense suspensions of spherical colloidal particles under imposed time-dependent flow. Our approach, which considerably generalizes [7,8], is nonlinear in the velocity gradient tensor and, in the absence of flow, features a transition to a glassy solid as a function of the thermodynamic control parameters, allowing the delicate interaction between glass formation and (time-dependent) external deformation to be investigated. Our treatment assumes incompressible homogeneous flow, neglecting fluctuations of the solvent velocity field and thus hydrodynamic interactions [7]. These assumptions may break down at high flow rates and/or densities where lubrication forces drive cluster formation and shear thickening [4].

We consider a system of N spherical Brownian particles dispersed in a solvent with a specified velocity profile $\mathbf{v}(\mathbf{r}, t) = \boldsymbol{\kappa}(t) \cdot \mathbf{r}$. The time-dependent velocity gradient tensor $\boldsymbol{\kappa}(t)$ is assumed spatially constant, thus excluding the inhomogeneous flows which occur in shear-banded and shear-localized states. Incompressibility implies that $\text{Tr}\boldsymbol{\kappa}(t) = 0$. The distribution function evolves according to a Smoluchowski equation $\partial_t \Psi(t) = -\sum_i \boldsymbol{\partial}_i \cdot \mathbf{j}_i$ (where \mathbf{j}_i is the probability current of particle i) [1,9]:

$$\begin{aligned} \partial_t \Psi(t) &= \Omega(t) \Psi(t) \\ \Omega(t) &= \sum_i \boldsymbol{\partial}_i \cdot [\boldsymbol{\partial}_i - \mathbf{F}_i - \boldsymbol{\kappa}(t) \cdot \mathbf{r}_i]. \end{aligned} \quad (1)$$

\mathbf{F}_i is the force acting on particle i due to the other particles. The thermal energy and bare diffusivity are set to unity. Equilibrium and nonequilibrium solutions to (1) are distinguished by the existence of a finite probability current. Its existence rules out the possibility of a distribution function of Gibbs-Boltzmann form.

When constructing constitutive equations based on a given microscopic dynamics it is important to first identify the relevant affine deformation measures. We achieve this by considering the translational invariance of the two-time correlation functions. The first step is to show that a translationally invariant initial distribution function can lead to a *translationally invariant*, but anisotropic, distribution function $\Psi(t)$, despite the fact that the Smoluchowski operator is itself not translationally invariant. This follows from the formal solution

$$\Psi(\Gamma, t) = e^{\int_0^t ds \Omega(\Gamma, s)} \Psi_e(\Gamma), \quad (2)$$

where we assume an equilibrium Gibbs-Boltzmann distribution $\Psi_e(\Gamma)$ at $t = 0$, $\Gamma \equiv \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ and e_+ is a time-ordered exponential [10]. We now consider shifting the particle coordinates by a constant vector $\mathbf{r}'_i = \mathbf{r}_i + \mathbf{a}$. This leads to $\Omega(\Gamma', t) = \Omega(\Gamma, t) - \sum_i \partial_i \cdot \boldsymbol{\kappa}(t) \cdot \mathbf{a} \equiv \Omega(\Gamma, t) + A(t)$ and hence the shifted distribution function

$$\Psi(\Gamma', t) = e^{\int_0^t ds [\Omega(\Gamma, s) + A(s)]} \Psi_e(\Gamma), \quad (3)$$

where $\Psi_e(\Gamma') = \Psi_e(\Gamma)$. The time-ordered exponential can be rewritten using an operator identity

$$\begin{aligned} \Psi(\Gamma', t) &= \exp_+ \left(\int_0^t ds e^{\int_s^t ds' A(s')} \Omega(\Gamma, s) e^{-\int_s^t ds' A(s')} \right) \\ &\times e^{\int_0^t ds A(s)} \Psi_e(\Gamma). \end{aligned} \quad (4)$$

Using $A(t)\Psi_e(\Gamma) = 0$ and applying the commutator $[\Omega(\Gamma, s), A(s')] = -\mathbf{a} \cdot \boldsymbol{\kappa}^T(s) \cdot \boldsymbol{\kappa}^T(s') \cdot \sum_i \partial_i$ yields

$$\Psi(\Gamma', t) = \Psi(\Gamma, t), \quad (5)$$

as desired. We now use this result to study the invariance properties of the correlation functions. The correlation of two wave-vector-dependent fluctuations is given by $C_{f_{\mathbf{q}g\mathbf{k}}}(t, t') \equiv \langle \delta f_{\mathbf{q}}(t) \delta g_{\mathbf{k}}(t') \rangle_{\boldsymbol{\kappa}(t)}$, where $\langle \cdot \rangle_{\boldsymbol{\kappa}(t)}$ indicates an average over the distribution (2). Translating the particles by a constant vector \mathbf{a} and using (5) yields

$$C_{f_{\mathbf{q}g\mathbf{k}}}(t, t') = e^{-i[\bar{\mathbf{q}}(t, t') - \mathbf{k}] \cdot \mathbf{a}} C_{f_{\mathbf{q}g\mathbf{k}}}(t, t'). \quad (6)$$

Translational invariance requires that the correlation function is unaffected by the shift with \mathbf{a} . This leads to the requirement that a fluctuation at wave vector $\mathbf{k} = \bar{\mathbf{q}}(t, t')$ at time t' is correlated with a fluctuation with wave vector \mathbf{q} at time t as a result of the affine solvent flow, where

$$\bar{\mathbf{q}}(t, t') = \mathbf{q} \cdot e^{-\int_t^{t'} ds \boldsymbol{\kappa}(s)}. \quad (7)$$

For shear, (7) recovers the familiar shear-advection [8], while for an extensional flow, (7) describes the exponential deformation of material lines. The tensorial exponential function in (7) may appear unfamiliar, but is simply the inverse of the deformation gradient tensor $\mathbf{F}(t, t') \equiv \partial \mathbf{r}(t) / \partial \mathbf{r}(t')$, a standard quantity in elasticity theory used to connect initial (t') and final (t) coordinates following homogeneous deformation, $\mathbf{r}(t) = \mathbf{F}(t, t') \cdot \mathbf{r}(t')$. The de-

formation gradient is related to the velocity gradient tensor via $\partial_t \mathbf{F}(t, t') = \boldsymbol{\kappa}(t) \mathbf{F}(t, t')$. We can thus define the forward and reverse-advected wave vectors $\bar{\mathbf{q}}(t, t')$ and $\mathbf{q}(t, t')$ using the deformation gradient

$$\bar{\mathbf{q}}(t, t') = \mathbf{q} \cdot \mathbf{F}^{-1}(t, t'), \quad \mathbf{q}(t, t') = \mathbf{q} \cdot \mathbf{F}(t, t'). \quad (8)$$

The magnitudes of the advected wave vectors are thus related to the left and right Cauchy-Green tensors, given by $\mathbf{B}(t, t') = \mathbf{F}(t, t') \mathbf{F}^T(t, t')$ and $\mathbf{C}^{-1}(t, t') = \mathbf{F}^{-1}(t, t') \times [\mathbf{F}^{-1}(t, t')]^T$, respectively [11]:

$$\begin{aligned} \bar{q}^2(t, t') &= \mathbf{q} \cdot \mathbf{B}(t, t') \cdot \mathbf{q}, \\ q^2(t, t') &= \mathbf{q} \cdot \mathbf{C}^{-1}(t, t') \cdot \mathbf{q}. \end{aligned} \quad (9)$$

By considering the translational invariance of solutions to (1), we have thus identified the appropriate deformation measures for describing the affine deformation in our Brownian system. This enables us to formulate a theory obeying the principle of material objectivity [10], see below.

Integration through the transient flow history [7,8] yields an alternative solution of (1), formally equivalent to (2) but more suitable for approximation.

$$\Psi(t) = \Psi_e + \int_{-\infty}^t dt' \Psi_e \text{Tr} \{ \boldsymbol{\kappa}(t') \hat{\boldsymbol{\sigma}} \} e^{\int_{t'}^t ds \Omega^\dagger(s)}, \quad (10)$$

where $\hat{\sigma}_{\alpha\beta} \equiv -\sum_i F_i^\alpha r_i^\beta$ is the potential part of the microscopic stress tensor, and the adjoint Smoluchowski operator is $\Omega^\dagger(t) = \sum_i [\partial_i + \mathbf{F}_i + \mathbf{r}_i \cdot \boldsymbol{\kappa}^T(t)] \cdot \partial_i$. We take the system to be in quiescent equilibrium in the infinite past and thus neglect possible nonergodicity in the initial state and related ageing phenomena. The validity of this assumption will be dependent upon both the specific system and flow history under consideration [8]. By using (10) to calculate the average of $\rho_k^* \rho_k / N$ and, in the spirit of mode-coupling theory, approximating by projecting onto density fluctuations [7,12], we obtain an expression for the distorted structure factor $S_{\mathbf{k}}(t; \boldsymbol{\kappa}) = \langle \rho_k^* \rho_k \rangle_{\boldsymbol{\kappa}(t)}$

$$S_{\mathbf{k}}(t; \boldsymbol{\kappa}) = S_k - \int_{-\infty}^t dt' \frac{\partial S_{\mathbf{k}(t, t')}}{\partial t'} \Phi_{\mathbf{k}(t, t')}^2(t, t'), \quad (11)$$

where an isotropic term has been suppressed, n is the number density, and S_k is the equilibrium structure factor used to proxy the colloidal interactions [10]. Equation (11) describes the flow induced microstructural distortion which becomes appreciable when the flow interferes with slow cooperative structural relaxation [13]. Flow enters the description via the advected wave vector, both explicitly through $S_{\mathbf{k}(t, t')}$ and implicitly through its effect on the transient correlator. The second term in (11) is anisotropic, whereas the third term is purely isotropic.

Equation (10) also can be employed to directly approximate the stress tensor. Projection operator approximation of the resulting generalized Green-Kubo relation provides an explicit approximation for $\boldsymbol{\sigma}(t)$. This we find to be related directly to $S_{\mathbf{k}}(t; \boldsymbol{\kappa})$ by

$$\boldsymbol{\sigma}(t) = -\Pi\mathbf{1} - \int \frac{d\mathbf{k}\rho}{16\pi^3} \frac{\mathbf{k}\mathbf{k}}{k} c'_k \delta S_{\mathbf{k}}(t; \boldsymbol{\kappa}), \quad (12)$$

where c_k is the direct correlation function, $c'_k = dc_k/dk$, $\delta S_{\mathbf{k}}(t; \boldsymbol{\kappa}) = S_{\mathbf{k}}(t; \boldsymbol{\kappa}) - S_k$, and Π is an osmotic pressure contribution. For shear flow, $\sigma_{xy}(t)$ from (12) coincides with a result of Fredrickson and Larson [14] for sheared copolymers, reflecting the Gaussian statistics underlying both their approach and our own. Stresses are thus connected to microstructural distortions, which build up over time via the affine stretching of density fluctuations competing with structural rearrangements encoded in $\Phi_{\mathbf{k}}(t, t')$.

In order to close our theory, we require the transient correlator $\Phi_{\mathbf{k}}(t, t') = \langle \rho_{\mathbf{k}}^* \exp[-\int_{t'}^t ds \Omega^\dagger(s)] \rho_{\bar{\mathbf{k}}}(t, t') \rangle / NS_k$ describing the decay under flow of thermal density fluctuations, where $\langle \cdot \rangle$ denotes an equilibrium average. Time-dependent projection operator manipulations yield exact results for the equation of motion of the transient density correlator containing a generalized friction kernel which is amenable to mode-coupling approximations [7,8]. Applying these to our formal results yields

$$\begin{aligned} & \frac{\partial}{\partial t} \Phi_{\mathbf{q}}(t, t_0) \\ & + \Gamma_{\mathbf{q}}(t, t_0) \left(\Phi_{\mathbf{q}}(t, t_0) + \int_{t_0}^t dt' m_{\mathbf{q}}(t, t', t_0) \frac{\partial}{\partial t'} \Phi_{\mathbf{q}}(t', t_0) \right) = 0 \end{aligned} \quad (13)$$

where $\Gamma_{\mathbf{q}}(t, t_0) = \bar{q}^2(t, t_0) / S_{\bar{q}(t, t_0)}$. The friction kernel $m_{\mathbf{q}}(t, s, t_0)$ is the autocorrelation function of fluctuating stresses, which in mode coupling are connected to structural relaxation as described by the density correlator. In the present approximation, it is given by

$$\begin{aligned} m_{\mathbf{q}}(t, t', t_0) &= \frac{\rho}{16\pi^3} \int d\mathbf{k} \frac{S_{\bar{q}(t, t_0)} S_{\bar{k}(t', t_0)} S_{\bar{p}(t', t_0)}}{\bar{q}^2(t', t_0) \bar{q}^2(t, t_0)} \\ & \quad \times V_{\mathbf{q}\mathbf{k}\mathbf{p}}(t', t_0) V_{\mathbf{q}\mathbf{k}\mathbf{p}}(t, t_0) \\ & \quad \times \Phi_{\bar{\mathbf{k}}(t', t_0)}(t, t') \Phi_{\bar{\mathbf{p}}(t', t_0)}(t, t'), \end{aligned} \quad (14)$$

$$V_{\mathbf{q}\mathbf{k}\mathbf{p}}(t, t_0) = \bar{\mathbf{q}}(t, t_0) \cdot (\bar{\mathbf{k}}(t, t_0) c_{\bar{k}(t, t_0)} + \bar{\mathbf{p}}(t, t_0) c_{\bar{p}(t, t_0)}), \quad (15)$$

where $\mathbf{p} = \mathbf{q} - \mathbf{k}$. Equations (11)–(15) form a closed constitutive theory for the microstructure and stress response of Brownian particles under external flow, requiring only S_k and $\boldsymbol{\kappa}(t)$ as input [10].

We next consider our theory from the standpoint of continuum ‘‘rational mechanics’’ approaches [11], showing that (in common with [1]), it complies with their invariance requirements but avoids their oversimplifying assumptions. Such approaches often express $\boldsymbol{\sigma}(t)$ as a functional of a suitable deformation measure, weighted by a fading memory; an example is the integral form of the upper-convected Maxwell equation (Lodge equation) with the memory taken as a known sum of decaying exponentials [15]. In the present treatment, the memory is instead given by $\Phi_{\mathbf{k}}^2(t, t')$ which for general flows is both

anisotropic and a function of two times rather than a simple time difference. In the absence of flow, $\phi_{\mathbf{k}}(t)$ exhibits nonexponential decay and, in the glass, arrests to a finite plateau value leading to solidlike response [12].

An important symmetry consideration is the *principle of material objectivity* (or frame indifference) [11,15,16]. This asserts that the relationship between $\boldsymbol{\sigma}$ and $\boldsymbol{\kappa}$ should be invariant with respect to time-dependent rotation of either the material sample or the observer. Although this is only an approximate symmetry, based on the neglect of inertial effects at the microscopic level [16], many soft materials display this invariance to a good level of approximation. The overdamped Smoluchowski dynamics (1) underlying our treatment excludes inertial effects from the outset, so that our set of Eqs. (11)–(15) are material objective, so long as this is preserved by our approximations. This can be explicitly confirmed by using (8) and (9) to eliminate the advected wave vectors from (11)–(15) in favor of the deformation tensors [10].

Next, we address the comparison between elongational (planar or uniaxial) flow, and shear. Starting with the limit of small strain, we obtain the linear response result

$$\begin{aligned} \boldsymbol{\sigma}^l(t) &= \int_{-\infty}^t dt' \int \frac{d\mathbf{k}}{16\pi^3} \{ [\mathbf{k} \cdot \bar{\boldsymbol{\kappa}}(t') \cdot \mathbf{k}] \mathbf{k}\mathbf{k} \} \\ & \quad \times \left(\frac{S'_k \Phi_k(t-t')}{k S_k} \right)^2 \end{aligned} \quad (16)$$

where linearity enables us to introduce the symmetrized tensor $\bar{\boldsymbol{\kappa}}(t) = [\boldsymbol{\kappa}(t) + \boldsymbol{\kappa}^T(t)]/2$, and $\Phi_k(t)$ is the quiescent correlator. As all anisotropy in (16) is contained within the factor $\{ \cdot \}$, the angular integrals may be easily evaluated for a given $\boldsymbol{\kappa}(t)$. It follows that the planar-extensional and shear viscosities are related by $\eta_e/\eta_s = 4$, in compliance with one of *Trouton’s rules*. In the glass phase, the transient correlator does not relax to zero. Partial integration of (16), followed by taking the small-strain limit, leads to $\boldsymbol{\sigma}(t) = 2G\boldsymbol{\epsilon}(t)$, where $\boldsymbol{\epsilon}(t)$ is the infinitesimal strain tensor [$\text{Tr}\boldsymbol{\epsilon}(t) = 0$], $G = \rho^2 \int_0^\infty d\mathbf{k} k^4 [c'_k \phi_k(\infty)]^2 / (60\pi^2)$ is a known approximation for the linear modulus [6,12].

Taking this comparison beyond linear response requires numerical solution of (11)–(15). For simplicity, we perform calculations for a one-component system of hard spheres [17]. In Fig. 1, we show σ_{xy} under shear and $(\sigma_{xx} - \sigma_{yy})$ under planar elongation as a function of Peclet number, $\text{Pe}_0 = \dot{\gamma} d^2 / D_0$, where $\dot{\gamma}$ is the strain rate, for various packing fractions around the glass transition ϕ_c . A detailed comparison of theoretical shear flow curves with experiment can be found in [3]; we do not know of similar experimental data on elongational flows but hope our work may stimulate future studies. The lower left panel shows the Trouton ratio $(\sigma_{xx} - \sigma_{yy})/\sigma_{xy}$ as a function of Pe_0 . Upon entering the nonlinear (shear thinning) regime, this ratio is significantly reduced below the linear response value, indicating enhanced strain thinning under elongational flow relative to shear. Moreover, as ϕ_c is approached from below, the linear response regime moves to lower

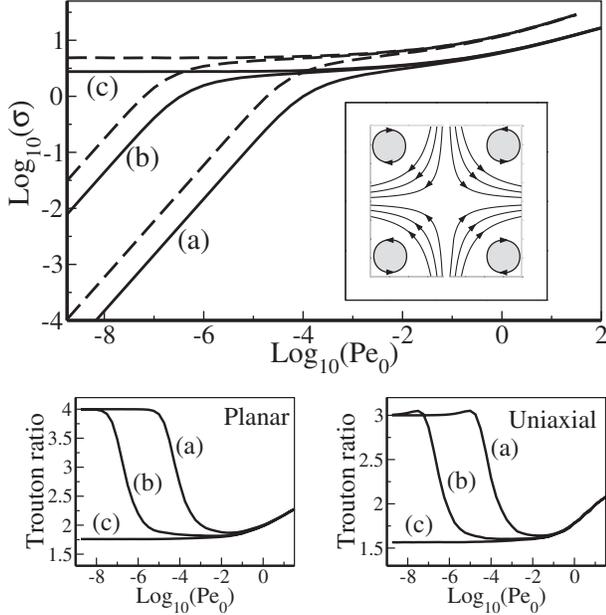


FIG. 1. Steady state stress $\sigma = \sigma_{xy}$ under shear (full lines, $\kappa_{ij} = \dot{\gamma}\delta_{xi}\delta_{yj}$) and stress difference $\sigma = \sigma_{xx} - \sigma_{yy}$ under planar elongation [broken lines, $\kappa_{ij} = \dot{\gamma}(\delta_{xi}\delta_{xj} - \delta_{yi}\delta_{yj})$] as a function of $Pe_0 = \dot{\gamma}d^2/D_0$, where d is the sphere diameter. Each curve is labeled according to the distance from the glass transition $\phi - \phi_c$, (a) 10^{-4} , (b) 10^{-3} , and (c) 10^{-2} . The inset shows a possible realization of planar elongational flow. The lower left panel shows the Trouton ratio for such flow while the lower right panel shows the ratio for uniaxial elongation [$\kappa_{ij} = \dot{\gamma}(\delta_{xi}\delta_{xj} - \delta_{yi}\delta_{yj}/2 - \delta_{zi}\delta_{zj}/2)$].

values of Pe_0 and disappears entirely on crossing the glass transition. The resulting plateau in the flow curve identifies a dynamical yield stress. The Trouton ratio displays an approximately constant (noninteger) value over the entire plateau: its low Pe_0 limit furnishes a nontrivial yield condition for the ratio between normal and shear stresses. In the lower right panel of Fig. 1, we show in addition the Trouton ratio for uniaxial elongational flow. We again obtain a nontrivial yield stress ratio, distinct from that found under planar elongation. Our results for uniaxial and planar extension, alongside those for shear [7], thus predict by first-principles theory three parameters of a dynamic yield surface for glasses. The limiting stress at zero flow rate for a fixed flow geometry identifies a point on a dynamic yield manifold. In a system where (as here) isotropic pressure is irrelevant, this manifold resides in the space of deviatoric (i.e., traceless) stress tensors, and in the principal stress frame (with stress eigenvalues $s_{1,2,3}$) can be represented, for instance, as a closed curve, $f(s_1 - s_3, s_2 - s_3) = 0$. Our new results for uniaxial and planar extension, alongside those for shear [7], predict from first-principles three parameters of the dynamic yield manifold for a glass.

In conclusion, we have derived from first principles a constitutive equation for dense colloidal suspensions subjected to an arbitrary time-dependent (but homogeneous)

deformation. Appeal to translational invariance identifies appropriate deformation measures for an approximate description of the system in terms of density fluctuations. Within our treatment, macroscopic stress is directly connected with structural distortion at the microstructural level. The inclusion of nonexponential slow relaxation arising from interactions leads to a unified description of fluid and glassy states. For steady shear, planar and uniaxial elongational flows, we find strong nonlinearities in the Trouton ratio as a function of strain rate. For colloidal glasses, we predict nontrivial relations between dynamic yield stresses in different flow geometries.

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