

Dense suspensions and supercooled liquids: Dynamic similarities

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Dense suspensions and supercooled, glass-forming, fragile Lennard-Jones liquids near T_g should display similar relaxational and rheological behavior based on dynamical heterogeneities (actually, clusters of correlated, mobile particles embedded among the ordinary, bulk particles). Near structural arrest, we expect the shear-thinning onset to vanish as the inverse bulk- β relaxation time. Connection to mechanical properties of granular media near random loose packing is briefly considered. [S1063-651X(99)08108-8]

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The rheology of dense suspensions remains a largely empirical field of investigation. For example, there is at present no really convincing justification of Krieger's law [1]:

$$\eta = \eta_0 \left(1 - \frac{\phi}{\phi_c} \right)^{-k}, \quad (1)$$

relating viscosity η and solid fraction ϕ in the suspension. In Eq. (1), the exponent k is often close to 2, and the limiting solid fraction ϕ_c , where η diverges, is of order 60% in general. Nor do we quantitatively understand non-Newtonian behavior, that is, the dependence of effective viscosity on shear rate $\dot{\gamma}$ (in most cases of interest, shear thinning, i.e., a reduction of η as $\dot{\gamma}$ increases past some threshold $\dot{\gamma}_c$).

It is instructive, however, to think about analogies which might be drawn between dense suspensions and supercooled fragile [2] liquids: both exhibit non-Newtonian effects and a rapidly diverging viscosity (in the second class of materials, at or close to the glass temperature T_g). In the following we shall be interested mainly in the simplest class of systems: monodisperse spheres, either hard core or interacting via simple Lennard-Jones potentials. Deviation from spherical shape is not a critical parameter in practice. We do not consider colloidlike aggregation effects, which may lead to spectacularly large viscosities. Our aim is very limited indeed: we shall argue that, as the system approaches structural arrest (as ϕ approaches ϕ_c from below in one case, or T approaches T_g from above in the other), the shear-rate threshold $\dot{\gamma}_c$ goes down to zero and that $\dot{\gamma}_c$ is in fact simply related to the relaxational properties of the systems.

The crucial point is to realize that the physics here is dominated by *steric* considerations: the paucity of free volume, or equivalently the poor accessibility of available states in phase space, leads to caging (in the Frenkel [3] and Bernal [4] sense) and to backflow effects (in the Feynman [5] sense)—and therefore to cooperative particle motion and transiently correlated structures in the system. These are now referred to as *dynamical heterogeneities*. Extensive three-dimensional (3D) molecular dynamics simulations, recently performed on supercooled, glass-forming Lennard-Jones systems [6], have revealed that a sizable fraction ($\sim 5\%$) of the spherical particles are more *mobile* than the others and are

also better *correlated*, forming stringlike clusters whose sizes grow with decreasing temperature (the Lennard-Jones characteristic energy sets the scale for T_g , and T —or rather T_g/T —provides the natural control parameter). These “strings” are relatively long-lived, with lifetimes that are on the order of τ_β , the end of the β relaxation of the main (“bulk”) particles, as can be seen by comparing Figs. 1 and 4 in Ref. [6(a)]. (The α , β nonexponential dynamics are described by mode-coupling theory [7] and are related to backflow collective particle motion. The β step is the intermediate-time “shoulderlike” relaxation that precedes the long-time final α step). All time scales grow rapidly as T goes down towards T_g , but the α scale does so faster [6]. At that point we want to make two qualitative remarks. First, energetically favorable, that is, denser, packings will naturally reduce the local mobility. We thus expect the bulk, less mobile, particles to gather in clusters that are denser than average and are so to speak wet by an interstitial “liquid” of mobile particles with smaller-than-average density. This coarse-grained structural arrangement is of course just a transient one, but it could nevertheless be regarded instantaneously as some sort of “supersuspension.” Any control parameter that tends to break off this “microstructure” will necessarily impart greater free volume to the bulk particles. As these represent, by far [6], the dominant population of particles, their degree of packing will govern the activation energy for rearrangements in glass-forming liquids as well as the effective, “arrest,” limiting volume fraction ϕ_c in suspensions. Increasing the temperature, for instance, reduces the correlation between mobile particles [6]—which gives slightly more room to bulk particles thereby reducing the effective glass temperature or, equivalently, the characteristic activation energy, and therefore decreasing the viscosity. This may provide part of the explanation for the non-Arrhenius [2] behavior of viscosity in glass-forming, supercooled fragile simple liquids (see Fig. 1).

Similarly, and this brings us to our second point, subjecting the liquid to sufficient shear should also lead to microstructure breaking—both in supercooled liquids and in dense suspensions. In the latter case, for example, where temperature is less relevant, the control parameter is the relative solid fraction ϕ/ϕ_c [see Eq. (1)]. Shear-induced structure (or cor-

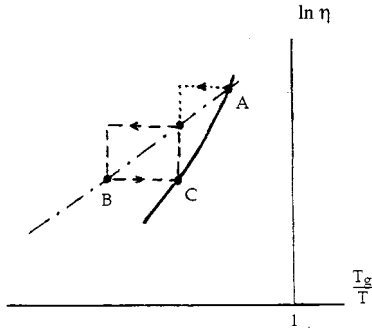


FIG. 1. Viscosity η vs T_g/T . Increasing the temperature not only allows activated jumps over higher energy barriers; it also results in a reduction in effective glass temperature T_g . In fragile glass-forming liquids close to T_g , this will bring about a faster-than-Arrhenius temperature dependence of viscosity. *AB*, Arrhenius; *AC*, fragile response.

relation) breaking amounts to slightly increasing the average free volume and therefore the effective ϕ_c . This, according to Krieger's law, leads to a reduction in apparent viscosity, which in effect is the shear-thinning effect. We shall not attempt to elaborate on these simple and crude considerations. It is perhaps more appropriate to suggest an order-of-magnitude argument for the shear-rate threshold $\dot{\gamma}_c$. Subjecting the system to shear flow will not affect the "microstructure" before the applied shear rate $\dot{\gamma}$ reaches the characteristic internal-shear scale of the mobile-particle clusters. So

$$\dot{\gamma}_c = \left. \frac{dv}{dr} \right|_{\text{mob}} \approx \frac{V}{R}, \quad (2)$$

where R is the typical cluster size, and

$$V = \frac{2a}{t^*} \quad (3)$$

is the characteristic correlated-motion velocity along the string (see Fig. 2). On "opposite" sides of the cluster, the local velocities are, crudely, $+\vec{V}$ and $-\vec{V}$; hence Eq. (2). From the simulations of Kob and co-workers [6], we may roughly identify $2a$ to be the particle diameter and R to be of order $10a$, t^* being a correlation time which rapidly grows as $T \rightarrow T_g$ or $\phi \rightarrow \phi_c$ and is of the same order of magnitude as the cluster lifetime [6] (i.e., as τ_β , as noted above). Thus

$$\dot{\gamma}_c = \left(\frac{2a}{R} \right) \frac{1}{\tau_\beta}. \quad (4)$$

In other words, the shear-thinning onset scales as, and is somewhat smaller than, the *inverse* bulk- β relaxation time. In particular, it vanishes at structural arrest.

Sheared-suspension flows confined in pipes may display plug formation, a dynamical segregation between less dense, highly sheared, domains close to the walls and denser, modestly sheared domains away from the walls. This lubrication effect results in a lower apparent viscosity, even for perfectly

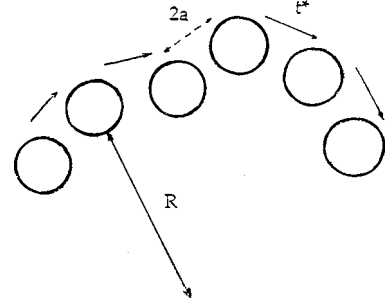


FIG. 2. Schematics of correlated motion on a string of mobile particles. After a "renewal" time t^* , every particle on the string occupies a new position that is close to the initial position of its neighbor particle. R is the local radius of curvature of the string.

Newtonian liquids. In the simplest case (Couette flow: uniform initial shear), plug sets in for shear rates greater than $\dot{\gamma}_*$ given by [8]

$$\dot{\gamma}_*^2 = \text{const} \times \frac{\eta}{(d\eta/d\phi)} = \text{const} \times \left[\frac{d \ln \eta}{d\phi} \right]^{-1}, \quad (5)$$

where the proportionality constant is material dependent. Substituting Krieger's law, Eq. (1), in this expression yields

$$\dot{\gamma}_*^2 = \text{const} \times \frac{\phi_c}{k} \left(1 - \frac{\phi}{\phi_c} \right). \quad (6)$$

[Note that this linear functional dependence is not affected by the actual value of Krieger's exponent k . But of course the simplifying Newtonian-flow assumption, in the derivation of Eqs. (5) and (6), is questionable in very dense suspensions, even at very low shear rates.] Thus, plug onset $\dot{\gamma}_*$ vanishes at structural arrest ($\phi \rightarrow \phi_c$), just as shear-thinning onset $\dot{\gamma}_c$ does. Which does so first remains to be seen.

For noninteracting hard spheres, Krieger's limiting solid fraction ϕ_c should lie somewhere between 0.555 and 0.635 (at vanishing shear and provided gravity-induced sedimentation effects are avoided): these are the random loose packing (RLP) and random close packing (RCP) densities [9], respectively, and a glass transition is expected in between. As shown by Onoda and Liniger [9], the RLP limit also marks the rigidity-percolation threshold and, simultaneously, the dilatancy onset—a basic concept in granular materials and soil mechanics. In plug flow, if the denser domain has local density above RLP, dilatancy will act *against* the drag force [8] that drives particles towards regions of low shear. Therefore, at a given overall density ϕ , it will tend to *enhance* somewhat the plug-flow threshold $\dot{\gamma}_*$ itself.

Random loose packing probably also represents the threshold for *force-chain* [10,11] formation and marginal mechanical stability, in dry sand, for example. The random network of force-sustaining chains of particles is locally oriented in response to the applied external stress, and rearranges in response to stress increments. These force chains are known [11] to carry most of the deviatoric stress (i.e., the effective "pressure anisotropy") in such "soft solids." This

is one further example of dynamical heterogeneities and therefore suggests, in agreement with observations, roughly similar anomalous rheology for a wide range of soft materials.

A model for such generic scaling of stress σ with shear rate $\dot{\gamma}$ was proposed in Ref. [12]. It is based on a mean-field noise parameter x that describes the coupling between local structural rearrangements and results in “activated” yield processes. x is taken to obey marginal dynamics and therefore to stay comparable to the “glass” transition value x_g (in our notations this amounts to taking $\phi \approx \phi_c$ or $T \approx T_g$). Depending on $(x - x_g)$, various rheological scaling regimes show up. In particular, for $x < x_g$, a Herschel-Bulkeley scenario is met: $\sigma = A + B \dot{\gamma}^n$, with a finite yield stress A and a non-Newtonian exponent n that depends on x and is small near x_g . (Interestingly, these considerations do not bring

about any shear-thickening regime, whereas some degree of shear thickening is reported in [9] beyond dilatancy onset.)

In conclusion, soft materials—whether dense suspensions, fragile supercooled liquids near T_g , slurries, or dry granular media—should generally display grossly similar complex rheological behavior. This is due to interactions and correlations between local rearrangement events, and is characterized by strongly heterogeneous dynamics. In dense suspensions reaching structural arrest somewhere between loose and close random packing, relaxation times and viscosity diverge whereas the shear-rate range $\dot{\gamma}_c$ of Newtonian behavior shrinks to zero as we have shown. Beyond rigidity and dilatancy onset, strong nonlinearities will be met. These complex features will probably be favored by particle deformability, in colloidal suspensions or the semisolid state (e.g., the mushy zone) in alloys. It is clear that the presently available overall picture of the problem requires many more refinements and experimental tests.

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