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Shear, dilation, and swap: Mixing in the limit of fast diffusion

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ABSTRACT

Molecules of different species mix by local rearrangement and long-range migration. Under certain conditions, the molecules are partially jammed: they rearrange slowly, but migrate fast. Here we formulate a theory of mixing when the long-range migration of molecules is fast, and the local rearrangement of molecules sets the time needed for mixing. In this limit, the time needed for mixing is independent of the length scale of inhomogeneity. We identify three modes of local rearrangement: shear, dilation, and swap. All three modes break and form intermolecular bonds. We place the three modes on equal footing, as distinct, concurrent, nonequilibrium processes. Our theory thus removes the bias that assumes local chemical equilibrium but allows the nonequilibrium process of shear. We propose a kinetic model of four independent viscosity-like coefficients, and a thermodynamic model of ideal mixing of molecules of unequal sizes and nonzero volume of mixing. We illustrate the theory with several examples, including the development of growth stress, the homogenization of a bilayer, and the disappearance of an inclusion in a matrix.

1. Introduction

In liquids and solids, molecules touch one another, but can change neighbors. This change manifests itself in experiments of two types—creep and diffusion. In creep, external forces cause a piece of material to change shape, and the resistance to the change is characterized by viscosity. In diffusion, thermal agitation causes molecules to migrate, and the rate of migration is characterized by diffusivity. In many liquids, creep and diffusion originate from the same molecular process: breaking and forming intermolecular bonds. This notion is embodied in the Stokes-Einstein relation:

$$\frac{D\eta}{kT} = \frac{1}{Cb}, \tag{1}$$

where D is the diffusivity of a molecule migrating in a liquid, η is the viscosity of the liquid, kT is the temperature in the unit of energy, b is a length characteristic of the size of the molecule, and C is a dimensionless number depending on the shape of the molecule. As the temperature drops, the diffusivity decreases and the viscosity increases, but the Stokes-Einstein relation predicts that the quantity. $D\eta kT$ is a constant independent of temperature. Although Einstein (1905) derived (1) for micron-sized particles diffusing in pure liquids, the relation has been confirmed experimentally for particles as small as

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individual molecules diffusing in many liquids (Edward, 1970). Even in crystalline solids, the quantity $D\eta/kT$ can be temperature-independent, provided creep and diffusion originate from the same molecular process. Examples include creep in polycrystalline solids due to self-diffusion in grains (Nabarro, 1948; Herring, 1950) or along grain boundaries (Coble, 1963). In these cases the right-hand side of (1) is replaced by a constant depending on the size of the grains. In general, a material is said to obey the Stokes-Einstein relation if $D\eta/kT$ is independent of temperature.

The Stokes-Einstein relation fails, of course, whenever creep and diffusion in a material originate from different molecular processes. For example, in a crystalline solid, when creep is mediated by the gliding of dislocations, and diffusion is mediated by the hopping of vacancies, the viscosity and diffusivity disobey the Stokes-Einstein relation (Frost and Ashby, 1982; Needleman and Rice, 1980). As a second example, experiments in recent decades have shown that, in some supercooled liquids, as the temperature falls toward the glass-transition point, creep slows down steeply, but diffusion does not slow down as much, so that the quantity $D\eta/kT$ increases by orders of magnitude (Angell et al., 2000; Debenedetti and Stillinger, 2001; Faupel et al., 2003; Ediger and Harrowell, 2012). Such a supercooled liquid may form a dynamically heterogeneous structure that nearly jams creep, but still allows diffusion (Berthier, 2011; Ediger and Harrowell, 2012). As a third example, in a physical gel, polymer chains crosslink by physical bonds that reversibly break and form, and the molecules of the solvent migrate through the network of polymers. Under certain conditions, the time needed for the mixing of the polymers and the solvent is set by the breaking and forming of the physical crosslinks, not by the migration of solvent (Zhao et al., 2010; Hu and Suo, 2012).

Whereas the microscopic mechanisms that break the Stokes-Einstein relation are material-specific, macroscopic behavior can be described, independent of microscopic mechanisms, by a continuum theory that regards creep and diffusion as distinct processes. Analogous to poroelasticity that studies concurrent diffusion and elastic deformation, poroviscosity studies concurrent diffusion and creep. We have formulated a poroviscous theory of concurrent self-diffusion and creep in pure substances (Suo, 2004; Pharr et al., 2011; Li et al., 2014). Here we turn to mixtures of molecules of different species. Mixtures often separate into phases, but this paper will focus on solutions of single phases.

Consider a solution of two species of molecules. The binary solution is initially inhomogeneous over some length L, and evolves toward a homogeneous state. The time needed to homogenize the solution by diffusion scales as $\tau_D \sim L^2/D$. The time needed to homogenize the solution by creep scales as $\tau_C \sim \eta\Omega/kT$, where Ω is the mean volume per molecule (Section 2.5). When $\tau_D \ll \tau_C$, the rate of mixing is limited not by diffusion, but by creep. Thus, creep-limited mixing prevails over diffusion-limited mixing when

$$L \ll \sqrt{\frac{D\eta\Omega}{kT}}. \tag{2}$$

The quantity on right side is a material-specific length, $\sqrt{D\eta\Omega/kT}$, which we call the poroviscous length. For a material that violates the Stokes-Einstein relation, the poroviscous length changes with temperature, and can be much larger than the size of individual molecules. The poroviscous length has also appeared in the theory of concurrent creep and self-diffusion in pure substances (Suo, 2004; Pharr et al., 2011; Li et al., 2014), as well as in a theory of Brownian motion of molecular probes in supercooled liquids (Liu et al., 2015).

As noted above, when the length scale of inhomogeneity in a solution is small compared to the poroviscous length, the time needed for mixing is set by creep, not by diffusion. This paper devotes to viscous mixing in the limit of fast diffusion. In this limit, the time needed for mixing is independent of the length scale of inhomogeneity. To focus on viscous mixing, we neglect elasticity, and assume that diffusion is so fast that chemical potentials of the two species of molecules in the solution are uniform. We will discuss viscoelastic mixing and poroviscous mixing elsewhere. Viscous mixing studied here differs greatly from that commonly studied in hydrodynamics, where the Stokes-Einstein relation holds, molecules diffuse slowly, and stirring accelerates mixing.

1.1. *Link with theories of coupled deformation and diffusion*

Our work relates to a number of problems in materials that couple deformation and diffusion. Continuum theories have been proposed for a large number of systems, including crystals (Svoboda et al., 2006; Mishin et al., 2013), glasses (Stephenson, 1988), oxides (Suo et al., 2003; Loeffel and Anand, 2011), polymers (Govindjee and Simo, 1993), and soils and partially molten rocks (McKenzie, 1984; Viesca et al., 2008). Recent impetus comes from the fast development of high-capacity electrodes for lithium-ion batteries (Bower et al., 2011, Cui et al. 2012, Brassart et al., 2013; Drozdov, 2014; Di Leo et al., 2015). Another growing field to which our work is closely related addresses the coupling between deformation and diffusion in soft materials such as hydrogels (Zhao et al., 2010; Chester, 2012; Hu and Suo, 2012; Wang and Hong, 2012; Strange et al., 2013).

Most of the existing formulations—including the ones listed above—rely on the assumption of local chemical equilibrium. This corresponds to the approach of the classical thermodynamics of irreversible processes (De Groot and Mazur, 1984). The concentration of a mobile species at a given macroscopic point is determined by the equation of state. This approach allows the local non-equilibrium process of shear deformation by creep. The fundamentally different treatment of mixing and creep cannot be justified when both processes are mediated by similar molecular rearrangements. Such a theory cannot describe mixing in the limit of fast diffusion.