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Solidity of viscous liquids. II. Anisotropic flow events

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Recent findings on displacements in the surroundings of isotropic flow events in viscous liquids [Phys. Rev. E **59**, 2458 (1999)] are generalized to the anisotropic case. Also, it is shown that a flow event is characterized by a dimensionless number reflecting the degree of anisotropy. [S1063-651X(99)00406-7]

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In a previous paper, henceforth referred to as (I) [1], it was argued that viscous liquids close to the glass transition [2–11]—where viscosity is roughly 10^{15} times larger than that of, e.g., room temperature water—are more like solids than like the less viscous liquids studied in standard liquid theory [12,13]. The idea [5] that viscous liquids are qualitatively different from less-viscous liquids is, of course, not new. It is a rather obvious idea, given the following fact. While ''ordinary'' less-viscous liquids have relaxation times in the picosecond range, i.e., comparable to typical phonon times, viscous liquids have much longer average relaxation times (roughly given by Maxwell's expression $\tau=\eta/G_\infty$, where η is the viscosity and G_∞ the instantaneous shear modulus). This decoupling of relaxation times from phonon times is also reflected in a decoupling of diffusion constants [14]: For less-viscous liquids the molecular diffusion constant D is of the same order of magnitude as the transverse momentum diffusion constant, the dynamic viscosity of the Navier-Stokes equation $\nu\propto\eta$. However, with increasing viscosity, D decreases (roughly as η^{-1} from a simple Stokes-Einstein type argument) while ν increases. At the glass transition ν is about 10^{30} times larger than D.

The average relaxation time increases dramatically upon cooling. Goldstein argued [15] that when τ becomes longer than about 1 ns there is a gradual onset of typical viscous-liquid behavior. As noted first by Angell [6], this is roughly at the temperature below which ideal mode-coupling theory [16] breaks down. It is generally believed that in viscous liquids ''real'' molecular motion beyond pure vibration takes place on the time scale defined by τ, although inhomogeneities are likely to give rise to faster relaxations in some parts of the liquid [17–22]. ''Real'' motion is rare because it involves overcoming energy barriers large compared to k_BT [2,15]. The transition itself is a jump between two potential energy minima, a process that lasts just a few picoseconds. One thus arrives at the following picture: Most molecular motion in a viscous liquid is purely vibrational; real motion is rare and takes place via sudden molecular rearrangements. It is interesting to note that this old picture [2,23] has never really been challenged (while the nature of the energy barrier to be overcome in the transition is still being debated [24]). In fact, extensive computer simulations have now definitively confirmed the picture [25].

The sudden molecular rearrangements [2,5,15,26–31] are referred to below as ''flow events.'' It is generally believed that flow events are localized in the sense that only a few molecules experience large displacements, while all other molecules are only slightly displaced; the large-displacement molecules involved in a flow event thus define a ''region'' of the liquid. Because flow events are rare and molecules most of the time just vibrate, a viscous liquid looks much like a solid. In (I) the small displacements in the surroundings of a flow event were calculated from solid elasticity theory, assuming spherical symmetry. It was shown that the displacement u in the surroundings of a region is given by (where r is the distance to the region)

$$u\propto\frac{1}{r^2}. \tag{1}$$

The displacement is purely radial. However, assuming spherical symmetry of flow events is not realistic; when molecules move from one potential energy minimum to another there must be some violation of spherical symmetry, even if the molecules have only radially dependent interactions. One is thus led to ask whether Eq. (1) and its consequences remain valid in the anisotropic case.

As in (I) the starting point is the solidity of viscous liquids as reflected in the slow ''real'' motion of the molecules. This fact implies that the average force on any molecule is extremely close to zero. In a continuum description, the average force per unit volume is the divergence of the stress tensor σ_{ij}, where $i,j=1,2,3$ are spatial indices. The condition of average zero force—elastic equilibrium—is (where $\partial_i=\partial/\partial x_i$ and one sums over repeated indices)

$$\partial_i\sigma_{ij}=0. \tag{2}$$

Linear elasticity theory [32] may be applied to the region surroundings, because the molecular displacements in these surroundings are small and because there is elastic equilibrium in the liquid before as well as after a flow event. Most likely, there are large ''frozen-in'' stresses in the liquid, but the *change* in the stress tensor induced by one flow event is small, except in the region itself. Now we define a sphere centered at the region, large enough that outside the sphere the flow event induced displacements and stress tensor changes are so small that linear elasticity theory applies for the changes. Image all molecules within the sphere being removed, and the forces from these molecules acting on the molecules outside the sphere being replaced by external forces applied to the surface of the sphere. This is done before as well as after the flow event. The flow event induced displacements of the surroundings can then be calculated from the change of these external forces. To do this we first consider the distance dependence of displacements in an elastic solid when an external force is applied to just one point. There is then a continuous flow of momentum into the solid at that point. The stress tensor is the momentum current, and the mechanical equilibrium condition [Eq. (2)] is the zero-divergence equation reflecting momentum conservation. By considering Gauss surfaces at various distances from the point, one concludes from Eq. (2) that the stress tensor decays as r^{-2}, where r is the distance to the point. Since the stress tensor is formed from first order spatial derivatives of the displacement u, we conclude that $u \propto r^{-1}$ [33]. This result also applies when several external forces are applied locally to the solid, as long as these forces do not sum to zero. In our case, however, the external forces replacing the forces from the molecules within the sphere do sum to zero: The forces from the molecules outside the sphere on those inside must sum to zero—otherwise the latter molecules would start to move. By Newton's third law, the sum of the forces acting from the molecules inside the sphere on those outside—the forces that are replaced by external forces—must therefore also sum to zero. When the external forces sum to zero, the stress tensor does not decay as r^{-2} but as r^{-3} (the mathematics behind this fact is the same as that implying that the electric field from a charge distribution with zero total charge decays as r^{-3} and not as r^{-2}). Consequently, since the stress tensor is given as first order derivatives of the displacement vector, we arrive at Eq. (1), which is now to be understood as valid for each of the three components of the displacement vector. In particular, we note that the predictions of (I) for the displacement and rotation angle distributions in the surroundings of a flow event [$P(u) \propto u^{-5/2}$ and $P(\phi) \propto \phi^{-2}$] are also valid in the anisotropic case. The first prediction has recently been confirmed in computer simulations of a binary Lennard-Jones mixture [34], and the second is consistent with the small rotation angle distribution tentatively inferred from NMR experiments on glycerol by Böhmer and Hinze: $P(\phi) \propto 1/\sin^2(\phi)$ [35].

We now show that it is possible to characterize flow events according to their anisotropy. The elastic equilibrium in the surroundings of a flow event before as well as after the flow event implies that the stress tensor change $\Delta\sigma_{ij}$ has zero divergence [i.e., obeys Eq. (2)]. Since $\mathbf{u}$ and $\Delta\sigma_{ij}$ are linked by linear elasticity theory, one has [32]

$$\nabla^2(\nabla \cdot \mathbf{u}) = 0. \tag{3}$$

This equation can be solved asymptotically for $r \to \infty$: Equation (1) implies $\nabla \cdot \mathbf{u} \propto r^{-3}$. Any real solution to the Laplace equation decaying as r^{-3} can be written [36] as $\alpha P_2(\theta,\phi)/r^3$, where $\alpha \geqslant 0$ is a constant and P_2 is a normalized linear combination of second order spherical harmonics: $P_2 = \Sigma_{m=-2}^{m=2} c_m Y_{2m}$, where $c_m^* = c_{-m}$ and $\Sigma_{m=-2}^{m=2} |c_m|^2 = 1$. This expression applies far away from the flow event: $r \gg r_0$, where r_0 is the region size. On the other hand, the expression does not apply beyond the ''solidity length'' l discussed in (I), where essentially no flow event induced displacements are expected. Since $\nabla \cdot \mathbf{u}$ is dimensionless, α has dimension (length)^3. Writing $\alpha = a/\rho_0$, where ρ_0 is the average (number) density and a is dimensionless, we have

$$\nabla \cdot \mathbf{u} = a \frac{P_2(\theta,\phi)}{\rho_0 r^3} \quad (r_0 \ll r \ll l). \tag{4}$$

The parameter a is a measure of the flow event anisotropy, the case $a=0$ corresponding to isotropic flow events.

In a homogeneous system described by linear elasticity theory, the density change following an elastic displacement is equal to $-\rho_0 \nabla \cdot \mathbf{u}$ [32]. Thus, if a viscous liquid were homogeneous, the density change in the surroundings of a flow event would be given by Eq. (4) (looking like an electronic *d*-orbital). However, the density of a viscous liquid is not quite spatially constant, and the density change induced by a flow event has an extra term, $-\mathbf{u} \cdot \nabla \rho$, coming from the fact that the whole density profile is displaced. Far away from the flow event this extra term dominates over the ($\nabla \cdot \mathbf{u}$) term.

The flow event induced changes given by Eqs. (1) and (4) were calculated from the fact that there is a linear relation between displacement and stress tensor change. These results are valid independent of the chemical nature of the liquid. One possible objection to these results is that dynamic inhomogeneities most likely give rise to spatially varying elastic constants. However, being mainly interested in the high viscosity limit where the solidity length is large, these inhomogeneities are not expected to have any significant effect on the average displacements in the surroundings of a flow event (the ''long wavelength'' limit). Finally, we note that the sharp distinction between ''real'' motion and vibration is somewhat blurred by the fact that real motion takes place not only in the region itself in the form of large jumps, but also in the surroundings in the form of small jumps.

To summarize, arguing from the ''solidity'' of viscous liquids, the flow induced displacement in the surroundings have been calculated for the general, anisotropic case. It has been shown that the r dependence of these displacements is the same that induced by isotropic flow events. A dimensionless number a has been introduced as a measure of the degree of anisotropy of a flow event.

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[1] J. C. Dyre, Phys. Rev. E **59**, 2458 (1999).
[2] W. Kauzmann, Chem. Rev. **43**, 219 (1948).
[3] G. Harrison, *The Dynamic Properties of Supercooled Liquids* (Academic, New York, 1976).
[4] S. Brawer, *Relaxation in Viscous Liquids and Glasses* (American Ceramic Society, Columbus, OH, 1985).
[5] J. C. Dyre, Phys. Rev. Lett. **58**, 792 (1987).
[6] C. A. Angell, J. Phys. Chem. Solids **49**, 863 (1988).

[7] C. A. Angell, J. Non-Cryst. Solids **131-133**, 13 (1991).
[8] U. Mohanty, Adv. Chem. Phys. **89**, 89 (1995).
[9] S. V. Nemilov, *Thermodynamic and Kinetic Aspects of the Vitreous State* (CRC, Boca Raton, FL, 1995).
[10] C. A. Angell, Curr. Opin. Solid State Mater. Sci. **1**, 578 (1996).
[11] C. A. Angell, in *The Physics of Complex Systems*, edited by F. Mallamace and H. E. Stanley (IOS, Amsterdam, 1997), p. 571.
[12] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986).
[13] J.-P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).
[14] C. K. Majumdar, in *Non-Debye Relaxation in Condensed Matter*, edited by T. V. Ramakrishnan and M. R. Lakshmi (World Scientific, Singapore, 1987), p. 351.
[15] M. Goldstein, J. Chem. Phys. **51**, 3728 (1969).
[16] W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).
[17] D. N. Perera and P. Harrowell, J. Chem. Phys. **104**, 2369 (1996).
[18] C. T. Moynihan and J. Schroeder, J. Non-Cryst. Solids **160**, 52 (1993).
[19] C. H. Wang and E. W. Fischer, J. Chem. Phys. **105**, 7316 (1996).
[20] R. Böhmer, G. Hinze, G. Diezemann, B. Geil, and H. Sillescu, Europhys. Lett. **36**, 55 (1996).
[21] M. T. Cicerone, F. R. Blackburn, and M. D. Ediger, J. Chem. Phys. **102**, 471 (1995).
[22] M. M. Hurley and P. Harrowell, Phys. Rev. E **52**, 1694 (1995).
[23] H. Eyring, J. Chem. Phys. **4**, 283 (1936).
[24] J. C. Dyre, J. Non-Cryst. Solids **235**, 142 (1998).
[25] T. B. Schrøder, S. Sastry, J. C. Dyre, and S. C. Glotzer, e-print cond-mat/9901271 (unpublished).
[26] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).
[27] M. Goldstein, Faraday Symp. Chem. Soc. **6**, 7 (1972).
[28] E. Donth, J. Non-Cryst. Solids **53**, 325 (1982).
[29] F. H. Stillinger, J. Chem. Phys. **89**, 6461 (1988).
[30] G. W. Scherer, J. Non-Cryst. Solids **123**, 75 (1990).
[31] R. V. Chamberlin, Phys. Rev. B **48**, 15 638 (1993).
[32] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, Oxford, 1970).
[33] In general, if a force field F is applied to a solid, the displacement is given by a standard Green's function expression, $u_i(\mathbf{r}) = \int d\mathbf{r}' G_{ij}(\mathbf{r}-\mathbf{r}') F_j(\mathbf{r}')$, where $G_{ij} \propto r^{-1}$ (the precise G_{ij} is given in the above reference). This only applies for tranlationally invariant solids and not for our case, where the solid has a ''hole'' in it, but far away from the hole our case is also translationally invariant.
[34] T. B. Schrødder (unpublished).
[35] R. Böhmer and G. Hinze, J. Chem. Phys. **109**, 241 (1998).
[36] G. Arfken, *Mathematical Methods for Physicists*, 3rd ed. (Academic, Boston, 1985).