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PRE-VITRIFICATION VISCOSITY ENHANCEMENT BY LONGITUDINAL MODE COUPLING

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Résumé. - On propose un mécanisme par lequel la viscosité d'un liquide simple s'accroît suivant $\eta \propto (T - T_0)^{-1}$ près d'une valeur finie de $T_0$. Ce mécanisme comprend deux étapes: 1) un ralentissement de la relaxation structurelle contrôlée par la diffusion, au cas de $\eta \rightarrow \infty$; 2) une amplification de la viscosité par suite du couplage mode-mode aux modes longitudinaux qui relaxent lentement à cause de 1).

Abstract. - A mechanism is described for the viscosity of a simple liquid to grow as $\eta \propto (T - T_0)^{-1}$ at some finite $T_0$. It consists of two main steps: 1) a slowing-down of diffusion-controlled structural relaxation of density fluctuations as $\eta \rightarrow \infty$; 2) an enhancement of viscosity by mode-mode coupling to longitudinal modes which are slowly relaxing in view of 1).

Current theoretical descriptions of the liquid-glass transition [1-5] seem to agree that close to the glassy state flow is controlled by the motion of localized defects against an essentially solid background. On the other hand it is rather common view that a low-viscosity dense fluid flows just like a dense gas [6] in which no defects are needed for atomic layers to slip past each other. In trying to understand vitrification it is therefore a relevant question to ask why on cooling close to some finite limiting temperature the viscosity of a liquid begins to strongly rise, before any defects might be localized and long-living.

Thinking in terms of Maxwell viscoelasticity or a Green-Kubo formula the viscosity can be written as a product $\eta = G \tau$ where $G$ is the instantaneous shear modulus or the initial value of the Kubo integrand, and $\tau$ is the relaxation time of shear stresses of the Kubo integrand. Since in the soft-core system $G$ remains regular on solidification, a diverging viscosity must be connected to a diverging relaxation time.

The only mechanism known to systematically produce slowly-decaying Kubo integrands is mode-mode coupling to pairs, triads etc. of slow collective modes of motion. Which modes are expected to be slow close to vitrification? Not the transverse ones: they become infinitely fastly relaxing as $\eta \rightarrow \infty$.

For longitudinal modes /density fluctuations/ however we have good reason to expect slowing-down with increasing rigidity. As a matter of fact, in a glass the density-density correlation function does not decay to zero at all: for $F(q, t) = \langle \rho(-q, t) \rho(q) \rangle / N$ in a glass we have $F(q, t) \rightarrow R(q)$ for $t \rightarrow \infty$, with

$$R(q) = \left\langle \rho(-q) \rho(q) \right\rangle / N = \exp(-2W)S_p(q)$$

where \{\ldots\} means configurational averaging, $S_p(q)$ is the structure factor of equilibrium positions [9] and $\exp(-2W)$ is the Debye-Waller factor characterizing the fast vibrational relaxation of density.
fluctuations. \( R(q) \) is a direct analogue of the Edwards-Anderson order parameter of spin glasses [10].

With the above formulas we left the realm of genuine glass formers. Our derivation refers rather to computer glasses [11].

For finite but large \( \eta \) one expects that the plateau \( R(q) \) would slowly relax in time:

\[
F(q,t) \approx R(q) \exp(-\gamma(q)t) \quad \text{for } t \gg t^*,
\]

\( t^* \) being the relaxation time of fast vibrational transients. Implying that the slow structural relaxation is controlled in some way by the viscosity, we expect that

\[
\gamma(q) \equiv \gamma(q,\eta,T) \rightarrow 0 \quad \text{for } \eta \rightarrow \infty.
\]

Leaving aside the question about the law of the \( \eta \)-dependence of \( \gamma \), we turn to investigate the consequences of \([2]/, [3]/\) in calculating the viscosity itself. Motivated by the above reasoning, we evaluate the contribution of the emission of two /slow/ longitudinal modes to liquid viscosity. The calculation, details of which will be published elsewhere, applies the formalism of Bosse et al. [12], although the mode-mode coupling expansion is carried out already at the level of the Green-Kubo formula for viscosity. The result is

\[
\eta_u = \frac{k_B T}{6 \pi \eta v} \int dq \frac{q^4 [S'(q)]^2}{[S(q)]^4} \int_0^\infty dt F(q,t)^2.
\]

If \([1]/\) and \([2]/\) are introduced into \([4]/\), one finally obtains a formula for the full viscosity of the form

\[
\eta = \eta_u (\eta,T) + \eta_0 (T),
\]

where \( \eta_0 (T) \) is a "bare" viscosity containing all non-mode-coupling as well as non-slow-mode contributions, whereas \( \eta_u \) is a functional of \( \gamma(q,\eta,T) \). We notice the tendency of \( \eta_u \) to grow with decreasing temperature in view of the factor \( [S'(q)]^2 \) in \([4]/\) which increases as the features of \( S(q) \) get sharper. In evaluating \([4]/\) the integration over \( q \) must be restricted to values for which an exponential relaxation of the form \([2]/\) can be expected, viz. to values of \( q \) close to \( q_o = 2\pi/a \) where \( a \) is the atomic spacing.

Eq. \([5]/\) is an implicit equation to determine \( \eta \) for a given \( T \). It reveals an important feedback mechanism: changes in \( \eta \) are amplified by the mode-mode coupling term \( \eta_u \), the amplification being the stronger the lower is \( T \). Depending on the functional form of \( \eta_u (\eta,T) \) the feedback may give rise to an instability at some finite \( T=T_0 \), where \( \eta(T) \rightarrow \infty \). We propose this instability as a possible mechanism of vitrification.

To make things more concrete, one has to specify \( \gamma(q,\eta,T) \). A very crude approximation, which is our best for the moment, is obtained by the following steps:

- Vineyard's convolution approximation for \( F(q,t) \);
- macroscopic diffusion approximation for the self-density correlation function \( F_s(q,t) \);
- Stokes-Einstein relation for the diffusion constant.

These give

\[
\gamma(q,\eta,T) = q^2 k_B T / 4 \pi \eta v.
\]

Although the approximations leading to \([6]/\) can be argued to have a chance to accuracy at long times to which \([2]/\) is restricted anyway, the analytic form obtained is undoubtedly a very crude one. Nevertheless a more realistic theory may bear out its physical content: diffusion control of the structural relaxation of density fluctuations; viscosity control of the diffusion.

Using \([6]/\), we have a result of the simple form

\[
\eta_u = I(T) \eta,
\]
I(T) being an integral containing the factors $[S'(q)]^2$ inherited from \( \int q \) which make $I(T)$ increase with decreasing $T$.

With [7/7] it is trivial to solve [5/5]:

\[ \eta = \eta_0(T)/(1-I(T)) , \]

where the enhancement factor $[1-I(T)]^{-1}$ expresses the mechanism of viscosity feedback mentioned above. If $I(T_0) = 1$ is reached for some $T=T_0$, there $\eta$ diverges as

\[ \eta \approx A/(T-T_0) \]

which is of the form of a Batchinski-Hildebrand law [13,14]. Such a law is experimentally [11] found correct in a previtrification region, rather far from the actual glass transition.

That is not surprising, after all. Technically, the decoupling of four-particle correlation functions inherent in a mode-mode coupling calculation [12] classifies our approximation as a mean field one. Physically, previtrification is the mean-field region of the glass transition, in which the system obtains sufficient rigidity to develop its soliton-like critical fluctuations: the defects which control the flow in the true glass-transition region.

We close by remarking that [9/9], via [6/6] and [2/2], implies a narrowing of the quasi-elastic peak of neutron inelastic scattering about $q_0$, proportional to $T-T_0$. This is just the phenomenology observed by Bosio and Windsor [15] in liquid gallium about $T_0 = 157$ K. Vitrification is not observed, clearly in view of concurrent crystallization. However, an accompanying slowing-down of diffusion is observed [16]. This is, in our view, no evidence for the proposed mechanism of viscosity feedback. It is, however, evidence in favour of one facet of the story: the significance of longitudinal-mode-coupling contributions to viscosity.

References