DYNAMIC PROPERTIES ON AN INTERMEDIATE RANGE SCALE IN GLASSFORMING MOLTEN SALTS

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ABSTRACT
A broad distribution of vibrational excitations is found in disordered solids in the frequency range around 1 THz, giving evidence for fluctuations of elastic properties over intermediate range (typically 20...30Å). In the glass-to-liquid transition the vibrational motions transform into relaxational motions on the same spatial scale. Coming from the liquid side, the transformation sets in at a temperature well above T\text{g}, and continues smoothly to T<T\text{g}. This decrease of relaxational motions explains the pronounced Vogel-Fulcher behaviour of viscosity of fragile glassforming melts, and perhaps also the suppression of crystallization.

1. INTRODUCTION: IRO IN GLASSES
Most non-crystalline materials including molten salts, show an almost crystal-like degree of order on a nearest-neighbour scale, and are homogeneous and isotropic on macroscopic scales. It is on the intermediate range scale, very roughly 10\textsuperscript{1}...10\textsuperscript{3} Å, where disorder can be detected most clearly, and its effects on transport and other properties are most pronounced. Here we want to address the question how important the atomic (molecular, ionic) dynamics, which happens on this range scale, is in glassforming salt melts. A characteristic feature which is caused by intermediate range order (IRO) is seen in the quasielastic scattering of light (or neutrons) from glasses, viz a typical broad peak in the 1 THz region, often called "boson peak" (bp). Examples can be seen in fig. 1 which shows new Raman data for B\textsubscript{2}O\textsubscript{3} and ZnCl\textsubscript{2}; for SiO\textsubscript{2} see (1), for neutron data on Ca\textsubscript{2}K\textsubscript{3}(NO\textsubscript{3})\textsubscript{7} (2). This spectral feature is also seen in amorphous semiconductors. It is scattering from (inhomogeneously distributed) vibrational excitations. They can be seen in light scattering basically due to loss of q-conservation (3).

An important information which one can derive from the bp is a measure of the spatial range of correlation of elastic properties in the glass, R\textsubscript{c}. Several derivations connecting the bp maximum \omega\textsubscript{bp} to R\textsubscript{c} have been given (4,5,6). The bp may be seen as caused by localization of strongly scattered acoustic phonons (wavevector k(\omega)). At \omega\textsubscript{bp}, the mean free path l(\omega) (7) fulfills the localization criterion l(\omega\textsubscript{bp})k(\omega\textsubscript{bp})\approx 1. With
\(<\Delta c^2>\) as the mean square fluctuation of sound velocity \(c\), and \(R_c\) the correlation length of that fluctuation, one gets
\[
R_c \approx \frac{1}{2 \langle \Delta c^2 \rangle / c^2} \frac{c}{\omega_{bp}}
\]

The alternative derivation given in (5), and used in (8), leads to \(R_c \approx 0.8 cT\Delta A/\omega_{bp}\). In a selection of glasses, we have found \(R_c\)-values of 20...30\(\AA\) (8). It may be important to point out that a parallel to this elastic IRO may be found in structural studies as well: In amorphous solids, a "first sharp diffraction peak" of the structure factor \(S(q)\) from neutron or X-ray measurements is ubiquitous. Its width \(\Delta Q\), which reflects the correlation length of some chemical ordering, yields an IRO parameter via \(2\pi/\Delta Q\). These values agree for quite a group of glasses with the \(R_c\) values obtained from the bp, within 20...50% (8,9). In view of the rough approximations involved, we consider this degree of agreement as an essential confirmation of the basic idea: In disordered solids IRO can be found on a scale of 20-30 \(\AA\).

2. THE MELT-GLASS-TRANSITION

In melts of normal (non glassforming) salts the characteristic feature seen in the quasielastic scattering of light or neutrons is the well known broad monotonous decay which happens in the same frequency range as the bp. Its width, which corresponds to the order of \(10^{-12}\)sec, and its intensity behave as a function of temperature as expected for a purely relaxational process.

But when we study glassforming salt melts, signs of the bp appear clearly at a temperature \(T^*\) well above the glass transition temperature \(T_g\): A hump develops close to where \(\omega_{bp}\) of the glass is. This may be seen for \(\text{ZnCl}_2\) and \(\text{B}_2\text{O}_3\) in fig. 1. As \(T\) is lowered towards \(T_g\), the bp vibrational (vib) feature grows at the expense of the relaxational spectral feature (rel); for more examples see (10,11,12,13). We will come back to the shape of the spectrum.

We now put up an hypothesis which, we believe, has important consequences for an understanding and for any formal treatment of the glass transition: Both, the vibrational motions seen in the boson peak (in light or neutron scattering), and the relaxational motions seen in the quasielastic spectrum (in roughly the same frequency range), are motions of essentially the same degrees of freedom.

In support of this hypothesis, we point to several experimental observations [and to possible explanations of these observations.]

1) Upon approaching \(T_g\) from above, there is a very smooth transition, which is very similar in all glassforming melts studied so far, between the "vib" spectral shape and the "rel" spectral shape. This transition continues below \(T_g\). Also the depolarization ratio is the same for both spectral features, and it is virtually independent of \(T\). [This suggests a conversion of the same atomic/ionic/molecular coordinates from relaxational to vibrational motion, like in a continuous freezing/melting process. If this process is quantified as a variation of coupling of the vibrations to a fast relaxing bath (14), then the full spectral shape can be very well described, see fig. 2 and (14,10,11,13)].
2) There is a striking parallel (15) between low-temperature specific heat $C_p(T)$ as a function of $T$ and the shape of the Raman-Spectrum in the corresponding frequency region, the rel-part corresponding to the two level system-contribution to $C_p$, and the vib-part corresponding to the excess vibrational density of states-contribution to $C_p$. The relative strength of the two contributions is systematically different in systems which are according to (16) strong or fragile glassformers. The point is that this systematics is the same for $C_p$ and for the Raman spectra (15). [A generalized coordinate, and strongly anharmonic potential curve for it, can explain both, the two level systems and the excess density of states, see e.g. (17) Anharmonic potentials induce relaxation, the bp is an excess density of vib states.]

3) The change from vib to rel motions is fully reversible upon T-cycling, as long as crystallization does not occur. [Glass and melt are in a thermodynamic quasi-equilibrium.]

4) Both, vib and rel Raman scattering are observed in disordered condensed matter. [Breakdown of momentum conservation law for light scattering (3) occurs in glass and melt, and thus is to be postulated for any "intermediate" state as well.]

Although the spectrum shape can reasonably well be described, as has often been done, by a sum of two terms, vib and rel spectrum (1,10,11), this should not be considered as counter-evidence to the above hypothesis. Also the treatment of bp explicitly as localized phonons, eq. [1], does not necessarily contradict (17) because in the model (17) one also arrives at $20...10^2$ atoms participating in the motion. - It will be interesting to see results from other spectroscopic techniques for which the relevant frequency range is accessible, like FIR. This will also be important for the question of the coupling coefficient (18).

On the theoretical side, mode coupling theory for the liquid-glass transition (MCT see e.g. (19)) has established in the last years as an important paradigm which allows quantitative analysis of spectral shapes. However, it does not include the bp explicitly, although the bp falls right into the frequency region of "the fast β relaxation" of MCT.

In what follows it will be assumed that the above hypothesis is basically correct, and further conclusions will be derived.

3. A CHARACTERISTIC TEMPERATURE ABOVE $T_g$

The bp "appears" at a rather sharply defined temperature $T^*$. In the model of Gochiyaev et al. (14) this is the temperature where the renormalized bp frequency $\omega_0^2 = \omega_{pp}^2 - \delta^2$ becomes zero; although no determination exists as yet for a molten salt, this temperature has been determined for molecular glassformers in (14) and recently in OTP, mTCP and glycerol (13). In fig. 3 we show the dependence of the parameter $\delta$ of the model (14) on $T$ around $T_g$ for the GeSBr$_2$ glassformer. This parameter $\delta$ will now be taken as a measure of the degree of transformation between liquid and glass. In a schematic separation of the spectrum into relaxational plus vibrational part, $\delta$ determines the real part. Thus upon cooling the melt from high $T$, the vib part starts to grow from zero and the real part starts to diminish, at $T^*$. Upon further cooling, the transition (i.e. $\delta(T)$) is smooth, apparently, without any divergence or further anomaly around $T_g$, see fig. 3.
The next point is that the temperature $T^*$ at which the bp "appears" upon cooling the melt, is at least close to (if not the same as) the temperature, at which the glassforming melt shows other changes of dynamical behaviour: Rotational and translational diffusion constants separate (20); the Debye-Waller factors indicate a break (21) in accord with MCT; viscosity shows the change in temperature dependence which is well known e.g. from the Angell-plot (16). Also in the MCT approach, a most important change of dynamics occurs at a temperature $T_c>T_g$ (19).

We quote from (13) the ratios $T^*/T_g$ and $T_c/T_g$ for three glassformers: 1.9 and 1.7 for glycerol, 1.3 and 1.2 for m-TCP, 1.2 and 1.2 for OTP. It appears to be very clear that these ratios correlate with the fragility. The main difference in dynamics between strong and fragile glassforming melts is the dominant type of motion: for strong systems it is vibrational, even at $T$ well above $T_{mel}$, while for fragile ones it is relaxational and the vibrational part comes in only shortly above $T_g$ (13). This is discussed in detail in ref. (15) and (13).

Connecting the results quoted for diffusion, Debye Waller factor, and viscosity with the hypothesis stated above, we are led to the conclusion that not only the spectral changes, but all the mentioned changes of dynamical properties have their major reason in processes occurring on the IRO spatial scale.

The smooth transition glass $\leftrightarrow$ liquid, seen in the smooth change of $\delta$ (fig. 3), is (dis-) appearance of relaxation on the time scale of $10^{-12}$ sec. Consequences of this change on other effects seen in the glass transition will be illustrated by showing the influence of "rel" and "vib" dynamics in two cases. The tremendous increase of viscosity $\eta$ towards $T_g+$ has been analyzed by Buchenau and Zorn (22) using an ansatz which reminds of the free-volume theory. Modifying it slightly, it reads

$$\eta = \eta_0 \exp \left( \frac{<u^2>_0}{<u^2>_{vib} + <u^2>_{rel}} \right)$$

Here $<u^2>_{vib}$ is the vibrational mean square displacement, and $<u^2>_{rel}$ its relaxational counterpart; $<u^2>_0$ is a fixed reference value. While Buchenau and Zorn took these values for liquid Se from neutron scattering, we may tentatively use Raman scattering data (using assumptions about the coupling coefficient $C(\omega)$ (18)). Such an analysis of the Raman spectra shows, as was just mentioned that in fragile systems $<u^2>_{rel}$ is large compared to $<u^2>_{vib}$, i.e. the rel part is large compared to the bp part. Also it is strongly temperature dependent (because $T^*/T_g$ is relatively small). Let us assume a linear decrease of $<u^2>_{rel}$ between $T^*$ and $T_g$:

$$<u^2>_{rel} = <u^2>_{rel_T} + \Delta u^2 \cdot \frac{T - T_g}{T^* - T_g}; T_g < T < T^*$$

$$\Delta u^2 = <u^2>_{rel_{Tg}} - <u^2>_{rel_T}$$

Here the indices liq and $T_g$ refer to $T>T^*$ and $T=T_g$, respectively. We use $<u^2>_{vib} = L \cdot T$ as a reasonable high $T$ assumption. Now $\Delta u^2/(T^*/T_g - 1)$ is large and

$$G = -<u^2>_{rel_T} + \Delta u^2 / (T^*/T_g - 1) > 0$$
Then one recovers a Vogel-Fulcher form for $\eta$: $\eta = \eta_0 \exp \left[ \frac{D}{T - T_0} \right]$ with

$$D = \frac{<u^2>_{vib}}{(L + H)\gamma}, T_0 = \frac{G}{(L + H)}, H = \Delta u^2 / (T^* - T_g) \quad [4]$$

In fragile systems, $G$ and $H$ are large, and the parameter $D$ becomes small, as is known. Above $T^*$, the contribution $<u^2>_{vib}$ is negligible.

It is thus seen how the smooth change from relaxational to vibrational motion between $T^*$ and $T_g$ induces the most prominent effect of the glass transition, viz. the extreme increase of $\eta$ (and thus of the slow or $\alpha$-relaxation time.) It is hoped that the ansatz eq. [2] can be derived from a feedback or percolation picture. In any case it removes the need for the unphysically large apparent activation energy which $\eta$ seems to display right above $T_g$, which is especially surprising since fragile systems usually have no strong inter-bonds.

As the second, short, discussion we would like to show how the vibrational motions stressed here (bp) may fit into the picture of the two-step relaxation (fast $\beta$-, followed by slow $\alpha$-relaxation). There is clear experimental evidence that the $\alpha$-relaxation splits off from the $\beta$-relaxation when the melt is cooled towards $T_g$; this becomes especially clear in MCT. It means that "part of those relaxations which used to be fast at high $T$" are becoming slow below some $T > T_g$ (viz at $T < T^*$ or $T_C$). The fact that the bp appears just where the slow relaxation splits off, does indeed suggest that groups of degrees of freedom couple, cooperate on an IRO scale in such a way that they relax slowly as a whole ($\alpha$ relaxation time) and therefore motions which are "internal" to that group become underdamped, so that one sees them in the boson peak.

4. CRYSTALLIZATION OR GLASS FORMATION?

Finally attention is drawn in fig. 4 to the low frequency Raman spectra of two mixed-cation nitrate melts. One of the melts is a good glass former (CKN), the other crystallizes. The first shows a reduced relaxational part at $T_m$, compared to the second, and also a very smooth development between $T_m$ and $T_g < T_m$. The comparatively large relaxational intensity in the second system disappears abruptly upon crystallization.

Generalizing this observation, we propose to assume the following reason for the inability to crystallize, which is constitutive for the glassforming melt: The relative lack of fast relaxational motions in the glassforming melt may be sufficient to suppress the reordering which would be required for the liquid-to-crystal transformation to take place.

5. SUMMARY

Evidence has been presented and discussed which shows 1) that an important process, or change occurring in the melt above the glass transition temperature $T_g$, is the transformation between relaxational and vibrational motions on the frequency scale of the order $1 \text{ THz}$; 2) that this transformation begins (upon cooling) at a temperature well above $T_g$, and continues through $T_g$ smoothly; 3) that this smooth transition is compatible with the Vogel-Fulcher temperature dependence of viscosity; 4) that the said relaxational and vibrational motions happen on an intermediate spatial scale of the order $10^4 \ldots 10^2 \text{ Å}$. 46
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Fig. 1: Low frequency Raman spectra of B₂O₃ and ZnCl₂. Curves for T > Tₖ ~ 525K and 400K, respectively, are for the (supercooled) melts. The factor n(v + 1, n(v)=[exp(hv/ kₖT)-1] , is the thermal normalisation for the Stokes side.

Fig. 2a: Normalized low frequency Raman spectra of glycerol, with spectral form given in (14) fitted to the points. T=0 curve is an extrapolation.

Fig. 2b: Renormalized bp frequency v₀^2=v₀^2-S². From (13).
Fig 3: Strength $\delta$ of the coupling between bp vibrational states and fast relaxing bath, derived according to (14), for glass former GeSBr$_2$, from (11).

Fig 4: Low frequency Raman spectra for two nitrates melts which do (Ca,K$_3$(NO$_3$)$_7$, top) or not do (KNa(NO$_3$)$_2$, bottom) form glasses. Tm of Ca$_3$K$_3$(NO$_3$)$_7$, was estimated.