Theory of the highly viscous flow

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In an undercooled liquid close to the glass transition, the flow begins by many thermally activated back-and-forth jumps, structural Eshelby rearrangements of strained regions. Together, they lead at short times to the Kohlrausch shear relaxation, with β around 1/2, before the jumps become irreversible and the viscous flow begins. The Kohlrausch behavior is not yet well understood. Here, a theoretical explanation is given, starting from an exact result for the irreversible jumps, the lifetime distribution of the critical Eshelby region. A new close-packing picture is proposed for the numerically found string motion in soft vibrations and low-barrier relaxations in glasses. It enables a quantitative understanding of the Kohlrausch behavior. A continuity relation between the irreversible and the reversible Kohlrausch relaxation time distribution is derived. The full spectrum can be used in many ways, not only to describe shear relaxation data, but also to relate shear relaxation data to dielectric and bulk relaxation spectra, and to predict aging from shear relaxation data, as demonstrated for a very recent aging experiment.

The present paper devises the beginnings of a theory, starting from a previous exact result (Paper I) on irreversible jumps between stable structural regions equally distributed in the five-dimensional shear space. It is reasonable to define a dimensionless shear misfit e of a region in such a way that e^2 is the elastic misfit energy in units of k_B T. In thermal equilibrium, the states e in the five-dimensional shear misfit space have an average energy of 5/2 k_B T in the normalized distribution

\[ p(e) = \frac{1}{\pi^{3/2}} e^4 \exp(-e^2). \]  

(1)

The prefactor corrects the one of eq. (3) in Paper I, a mistake which does not invalidate the results of Paper I.

As shown in Paper I, the jump rate from e_0 to e gets a factor \exp((e_0^2 - e^2)/2) from the difference in the shear misfits. With this, the state e_0 has the escape rate

\[ r_0 = N_s \tau V \frac{8\pi^2}{3} \int_0^\infty \exp((e_0^2 - e^2)/2)e^4de \]

\[ = 4\sqrt{2}\pi^{3/2}N_s \tau V \exp(e_0^2/2), \]  

(2)

where \( N_s \) is the density of stable structural alternatives to the initial state in the five-dimensional e-space and \( \tau V \) is the jump rate for the barrier height V between two states with the same elastic misfit energy. \( N_s \) increases with the size of the region, because an additional particle adds structural excess entropy.

Averaging the escape rate of eq. (2) over all occupied states of eq. (1), one finds the average escape rate

\[ \tau = 32\pi^{5/2}\tau V N_s. \]  

(3)

This average escape rate equals the single jump rate \( \tau V \) already at the relatively low density

\[ N_s = \frac{1}{32\pi^{5/2}}, \]  

(4)

where the jumps become irreversible.

Paper I shows that for the critical region size, the average escape rate is

\[ r_c = \frac{1}{\tau_c} = \frac{G}{8\eta}, \]  

(5)

where G is the high frequency shear modulus and η is the viscosity.

The normalized decay time distribution in the barrier variable \( v = \ln(\tau/\tau_c) \) is

\[ l_{irre}(v) = \frac{1}{3\sqrt{2}\pi} \exp(v^2) \left( \ln(4\sqrt{2}) - v \right)^{3/2}. \]  

(6)

In this picture, the last regions to relax are the unstrained ones with the relaxation time \( 4\sqrt{2}\tau_c \), a factor of forty five longer than the Maxwell time \( \tau_M = \eta/G \).

Eq. (6) for the relaxation time distribution of the irreversible processes turned out to be able to describe dynamic heat capacity data with the Maxwell time from shear data for four different glass formers, among them two hydrogen bonded substances.

The Kohlrausch \( \beta \) for the reversible processes can be understood on the basis of the numerical finding of the

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motion of a string of neighboring atoms, first found in soft vibrations and low temperature relaxations in glasses [6] and later also seen at the glass transition [9, 21]. The numerous recent numerical investigations [11–15] of soft vibrations in glasses have not changed this string picture for the soft atomic motion.

But one cannot help wondering how the string motion changes the local shear strain. A plausible answer is provided in Fig. 1: there is a solid block of seven close-packed particles, against which a single particle moves between two close-packed positions. One needs this specific structure of the solid block, a combination of an octahedron and a tetrahedron, to define the close-packed positions for the moving particle unambiguously. In terms of close-packed crystalline substances, the moving particle changes from an hexagonal to a cubic position.

The energy barrier \( V_s \) for the jump is one third of the one estimated for a gliding atom triangle [16]

\[
V_s = \frac{GV_a}{2\pi^2}, \tag{7}
\]

where \( V_a \) is the particle volume.

Naturally, the elastic resistance of the surroundings reduces the barrier, sometimes even down close to zero, creating a tunneling state [17] or a soft vibrational mode [18, 19]. For the Kohlrausch \( \beta \), one has to reckon with a whole distribution of possible single-particle jump barriers between zero and \( V_s \). Let us assume \( V_\beta = V_s/2 \) and an entropy contribution of \( S_\beta = k_B \ln 2 \).

The displacement of the seven-particle unit will be small, so the outer particle has to move parallel to its surface (for \( V_\beta = V_s/2 \) about one quarter of the nearest neighbor distance), pushing and pulling its two neighbors along the line of motion with it. This explains not only the string motion [6, 10], but also its strong coupling to an external shear strain.

In this picture, the strain relaxation of an Eshelby domain happens by a simultaneous jump of \( N_\beta \) particles, surrounded by seven-particle blocks outside the Eshelby domain, with a total energy barrier \( V = N_\beta V_\beta \). In this situation, the Kohlrausch \( \beta \) is given by [3]

\[
\beta = \frac{S_\beta T}{V_\beta} = \frac{4\pi^2 \ln 2k_BT}{GV_a}. \tag{8}
\]

The ratio \( GV_a/k_BT \) at the glass transition has been estimated [16] to be 17.6 from a data collection [20] for many metallic glasses. This estimate contains an error which is corrected here: the average ratio is 65.6. Inserting this value into eq. (8), one finds \( \beta = 0.42 \) for the choice \( V_\beta = V_s/2 \), in excellent agreement with many measurements in metallic glass formers [21].

The value \( V_\beta = V_s/2 = 1.66k_BT \) agrees also reasonably well with the value 1.38\( k_BT \) deduced from periodic wiggles in the long time shear relaxation of a metallic glass at room temperature [22], with a period corresponding to a barrier difference \( \Delta V = 0.063 \) eV (in the present interpretation due to the addition of another single-atom jump) and a glass temperature of 529 K [23].

The soft vibrations in glasses are at present intensely studied numerically. From the point of view developed here, one should look for a neighboring close packed seven-atom unit, with a surface parallel to the strongest displacement as in Fig. 1, in these studies. The picture does also explain the finding of tunneling states in polycrystalline metals [24] in terms of single-atom jumps along the grain boundaries.

Note that the shear modulus entering eq. (8) is the one for short wavelengths, much less temperature-dependent than the one of macroscopic measurements, which is strongly influenced by fast relaxations [25]. Otherwise one could never explain the weak temperature dependence of \( \beta \) [21]. These considerations throw some doubt on the explanation of the fragility in terms of the elastic models [1, 20].

The alternative is the Adam-Gibbs picture [2]. With decreasing temperature, the density of stable states in shear space decreases with the decreasing excess structural entropy \( S_I \) per particle, forcing the critical region size to increase in order to fulfill eq. (1). Thus, the critical region size (and with it the barrier \( V \) for structural rearrangements) must diverge at the Kauzmann temperature, where the excess entropy extrapolates to zero.

This theoretical argument provides the explanation for the close equality, found experimentally in many glass formers [27, 28], of the Vogel-Fulcher temperature, where the viscosity extrapolates to infinity, and the Kauzmann temperature. But one must be aware that one only explains the parallel, not the Kauzmann paradoxon itself.

The cutoff of the reversible Kohlrausch relaxations at \( \tau_c \) can be calculated by integrating the decay function of the irreversible states up to the relaxation time \( \tau \) of a given relaxation in the Kohlrausch tail. One finds that the cutoff is well approximated by the Fermi function \( \tilde{F}(v) = 1/(1 + \exp(1.19e)) \) in the variable \( v = \ln(\tau/\tau_c) \). It follows that the complex shear compliance \( J(\omega) \) is

\[
GJ(\omega) = 1 + \int_0^\infty \frac{l_K(v)dv}{1 + i\omega\tau(v)} = \frac{i}{\omega\tau_M}. \tag{9}
\]
with the barrier density $l_K(v)$ of the reversible Kohlrausch processes

$$l_K(v) = (1 + 0.115\beta - 1.18\beta^2)F(v)\exp(\beta v). \quad (10)$$

The factor in the first parenthesis on the right side of eq. (10) results from the normalization condition \cite{3, 9} for the viscous decay, which requires that the sample has the viscous shear compliance $8/G$ within the terminal relaxation time $\tau_c = 8\eta/G$. One must have enough irreversible decay states below the longest decay time $4\sqrt{2}\tau_c$ to achieve this, taking into account that the average irreversible decay of a state yields a factor $2/0.4409$ more compliance response than the average reversible back-and-forth jump \cite{9}.

Fig. 2 (a) shows the fit of the very accurate $G(\omega)$-data \cite{29} for the vacuum pump oil DC704, a molecular glass former, in terms of these equations. If one calculates $GV_a/k_B T_g$ for this molecule, one gets 251, nearly a factor of four larger than expected from eq. \cite{8}. But this is understandable; the molecule has two flexible Si-O-Si connections and four soft rotational degrees of freedom at its benzene rings, enough flexibility to be considered to consist out of four independent rigid subunits, at least as long as only packing matters.

The successful quantitative connection between reversible and irreversible processes can be exploited further. This is shown in Fig. 2 (b), which displays dielectric and bulk relaxation data taken on the same sample in the same cryostat \cite{29} described with the same parameters as the shear data in Fig. 2 (a) plus one additional relaxation time.

The idea behind these additional fits is the following: The normalized barrier density of the irreversible processes is given in eq. \cite{10}. The total barrier density of reversible and irreversible processes is given

$$l_{tot}(v) = l_0(8l_{irrev} + l_K(v)), \quad (11)$$

where $l_K(v)$ is the Kohlrausch tail of eq. \cite{10} and the normalization factor $l_0 \approx 0.085$ depends on $\beta$, though not much.

If irreversible and reversible processes are both of the same kind, the total barrier density in dielectric, adiabatic density and shear relaxation should be the same.

As can be seen in Fig. 2 (b), this assumption holds in DC704, but both the molecular reorientation and the adiabatic density relaxation terminate before $4\sqrt{2}\tau_c$, both at approximately the same terminal relaxation time $\tau_t = 0.72\tau_c$. The total barrier density of eq. \cite{11} has to be multiplied with $\exp(-\tau(v)/\tau_t)$ and the normalization factor $l_0$ has to be recalculated.

The two peaks in Fig. 2 (b) happen to lie close together, but this is mere coincidence. In our next example, another vacuum pump oil, PPE, a chain of five connected phenyl rings, the dielectric peak lies lower and the adiabatic compressibility lies higher, independent of the temperature \cite{29}, so they no longer coincide. Also, the physical reasons behind their terminal relaxation times are quite different.

The adiabatic compressibility is not symmetric in the sense of the dielectric susceptibility, because strongly strained Eshelby regions tend to have a lower density than unstrained ones. Thus within the linear response there is a temperature oscillation on the same frequency, leading to a calculable compensation effect at low frequency.

In contrast, the dielectric response is completely symmetric, so there is no temperature oscillation at the same frequency. If the process stops before the shear fluctuations end, it must be because the faster part of the shear fluctuations have already managed to rotate every molecule.

Whatever the reason, the scheme provides a very convincing fit. This is also demonstrated by comparing to the dashed line in Fig. 2 (b), obtained by taking only the reversible part $l(v)$ of eq. \cite{10} into account. This gives a peak which is approximately at the same place, but which is much too broad.

Fig. 3 (a) shows the theory for the $G(\omega)$-data \cite{29} of PPE. Again, the agreement is excellent. $GV_a/k_B T_g$ is again 235, but considering the five phenyl rings of a single PPE molecule as independent packing units, one is again down to a reasonable $\beta$-value from eq. \cite{8}.

Fig. 3 (b) displays a fit of dielectric data from the same sample in the same cryostat with the same parameters and a cutoff at $\tau_t = 0.89\tau_c$. The dielectric data show a clear excess wing over the Kohlrausch tail, which is not contained in the theory.

If one forces the excess wing of the dielectric data on a fit of the shear data, the quality of the description deteriorates considerably. In fact, the logarithmic curvature
of the Kohlrausch tail of the shear data averages to zero within an error bar which is a factor two smaller than the logarithmic curvature of the dielectric data. The result indicates that the excess wing in PPE is due to processes which, unlike the Kohlrausch processes, do not couple strongly to the shear.

In another example, propylene carbonate, the Kohlrausch tails of both the shear and the dielectric data have a visible logarithmic curvature. But the logarithmic curvature of the shear data is again more than a factor of two smaller than the one of the dielectric data.

Propylene carbonate and glycerol are examples where the theoretical shear description of the present paper is not perfect: One has to shift the cutoff for the reversible states to $3\tau_c$, to considerably longer times, thus introducing an additional parameter. Then one retrieves a good fit of the shear data.

This indicates that propylene carbonate and glycerol belong to those glass formers where some memory remains after the thermal equilibration time $\tau_c$, though on a much smaller scale than in polymers and monomers, where one finds marked peaks at times much longer than $\tau_c$.

On the other hand, one finds a multitude of examples where the present theory of the shear relaxation works very well. Among them is the ionic glass former CKN and many molecular glass formers.

One can also include a secondary relaxation peak, adding three free parameters for its description. This is shown in the last example, squalane, in Fig. 4 (a), for the $G(\omega)$-data at 172 K. Since there are also data at 174, 176 and 178 K, one can make a Vogel-Fulcher extrapolation to $\tau_c = 188.7$ s at 167.73 K, the temperature of a very recent aging experiment. Then one can compare the measured equilibration with the prediction derived from eq. (11). This is shown in Fig. 4 (b).

To conclude, the previous quantitative analysis of the irreversible shear relaxation processes is extended to a full theoretical description of reversible and irreversible shear relaxation in liquids. The Kohlrausch behavior is explained in terms of a new close packing picture for the string motion of the soft modes responsible for the low temperature glass anomalies.

The theory works in network, ionic, metallic and molecular glass formers. The description not only gives the right Kohlrausch $\beta$ in metallic glass formers and provides a connection between glass transition and low temperature glass anomalies, but also has a well-defined terminal relaxation time in good agreement with a recent aging experiment. It is able to explain the equality of Vogel-Fulcher and Kauzmann temperatures in the extrapolation of the experimental data of many glass formers.

With these achievements, it can be considered as a solid basis to attack many of the numerous remaining unsolved questions in the dynamics of disordered matter.
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