Out-of-equilibrium relaxation of a time-dependent effective temperature

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Constitutive equations are proposed for the relaxation of a glassy material in contact with a thermal reservoir. The dynamics of a single state variable, identified as an effective temperature accounts for the emergence of glassy behavior at low bath temperature. Memory effect in cooling/reheating experiments are discussed along with several aspects of the response to shear: aging of the response to step strains, response to oscillatory forcing, and steady rheology.

The purpose of the present work is to introduce a limited set of kinetic equations which describe the out-of-equilibrium relaxation of a structural glass and its response to shear deformation. It was originally motivated by recent theories for the plasticity of amorphous solids, in an attempt to incorporate glassy relaxation at an elementary level. A quite simple picture emerges, which accounts for important properties of glassy materials, while its premises may hold for general classes of complex fluids. It echoes early theories of structural relaxation in a much more systematic framework, and provides theoretical grounding for phenomenological rate-and-state equations.

We consider, in this study, a piece of material at pressure $P$, in contact with a thermal reservoir at temperature $T$. We sort the material into subsystems (or zones) of, say, $z$ molecules, and characterize structural disorder by the distribution $\rho$ of volumes, $v_i \in [v_0, \infty]$, or enthalpies ($h_i = P v_i$) of these molecular configurations. ($v_0$ is a lower bound imposed by excluded volume effects.) At low $T$, the distribution $\rho$ evolves slowly, as opposed to the vibrations of the molecular structure which quickly equilibrate with the thermal bath. The evolution of $\rho$ is expected to result from transitions between metastable basins in phase space, and these transitions are supposed to be triggered by conformational changes of molecular subsystems (rearrangements). The typical size of a rearranging zones fixes $z$, which is here supposed to be independent of $T$ and $P$. At all times, molecular subsystems are in mechanical contact with neighboring subsystems, hence likely to exchange energy among themselves: very small displacements of the average positions of the molecules are sufficient to ensure these volume (or enthalpy) transfers. Mediated by acoustic modes (phonons), these transfers are thus expected to be fast, collective, processes, in contrast with rearrangements which, at low $T$, are expected to be rare, space-localized events.

This observation in the basis of the present work: it permits to separate these two thermodynamic processes (equilibration with the bath v.s. transfers between subsystems) and assume that spatial enthalpy fluctuations equilibrate on timescales at which the system is not in contact with the thermal reservoir. At all times, approximation is made that spatial fluctuations are in “adiabatic equilibrium”, characterized by a $(P, H)$-ensemble: the distribution $\rho$ is determined by statistical inference: it maximizes entropy under the single constraint that $H = \int dh \rho(h) h$ is known, whence $\rho(h) = \frac{1}{\lambda} \exp(-\lambda h)$, with the partition function $Z = \int_{h_0}^{\infty} d h \exp(-\lambda h) = (1/\lambda) \exp(-\lambda h_0)$, and where $\lambda$ is the Lagrange multiplier that enforces adiabaticity. $\Theta = 1/(k\lambda)$ is an effective temperature, but differs from the temperature of the thermal reservoir, unless the system has reached thermal equilibrium. This effective temperature is a generalization of Edwards’:

I made no assumption here that the system is exploring all configurations of some ergodic component at any relevant timescale but, rather, that, by being very large, it samples, at any single time, all possible configurations allowed by macroscopic constraints. At all time, $k \Theta(t) = H(t) - P v_0$. The previous Ansatz for $\rho$ serves here as a basis to investigate the relaxation of the system towards equilibrium. At any time, $H$ (or $\Theta$) suffice to characterize the internal state of the material. Their dynamics is specified by energy conservation: it results from the balance between thermal exchanges with the reservoir (heat) and the work of external forces. Estimating the rate of thermal exchanges with the bath is a difficult task; it requires, in principle, to determine all probabilities $p(h \rightarrow h')$ for the reconformations of molecular subsystems, leading to:

$$\frac{dH}{dt} = \int dh dh' p(h \rightarrow h') \rho(h) (h' - h) + W_{\text{ext}} \ . \ (1)$$

I argue that a generic form of this equation arises from the study of dominant contributions to the integral term. Then, I show that the resulting equation accounts for the emergence of slow relaxation and glassy behavior at low $T$, with a marked cooling rate dependence of the glass transition point. A study of the response to shear in various experimental set-up completes my presentation.

Rearrangements correspond to elementary contacts with the thermal reservoir: a fluctuation $\delta h$ of enthalpy requires a transfer of heat $\delta q = -\delta h$ from the thermal reservoir, hence occurs with probability $\exp(\delta S/k) = \exp(-\delta h/(kT))$. These thermally activated processes are very sensitive to the external constraints imposed on a
molecular subsystem by its surroundings: for low $v$, the reconformation of the molecules may require to deform their “cage” and pay a consequent price in elastic energy; for large $v$, molecules may move freely. Suppose, for the sake of simplicity, that the transitions $h \rightarrow h'$ are controlled by some energy barrier $h_b$ which is a simple function of the volume $v$. Obviously, $h_b(v)$ must be non-increasing, hence there exist an activation volume $v_a$, such that $h_b(v_a) = P v_a \equiv h_a$; beyond this point ($v > v_a$) the notion of barrier breaks down. Two different families of reactional pathways must be identified: when $h, h' < h_b$, transitions are activated, and transition state theory indicates that the rates must be written: $p(h \rightarrow h') = \nu \exp((h_b - h)/(kT))$; otherwise, there is no barrier per se and Monte-Carlo weights read: $p(h \rightarrow h') = \nu \min(1, \exp((h' - h)/(kT)))$. These transition probabilities verify detailed balance and are continuous functions of either $h$ or $h'$ when they cross $h_a$. $\nu$ is an update frequency, the temperature dependence of which might be neglected as it brings only minimal corrections. The calculation of the rhs of equation \ref{eq:2} is further simplified by allowing only transitions such that $h - h' = \pm \delta q$: the integral is separated into the sum $I_1$ over $h, h' \in [h_0, h_a]$, and $I_2$ over the complementary domain of integration. It appears that $I_1$ (resp. $I_2$) is of order $O((\Theta - T)^2)$ (resp. $O(\Theta - T)$) close to equilibrium, and is proportional to a factor of the form $\exp(-A/(kT))$ (resp. $\exp(-A'/(k\Theta))$) when $\Theta \gg T$. In both these limits, $I_1$ is dominated by $I_2$: the dynamics of $\Theta$ is controlled by the transition pathways (found with a frequency $\exp(-P(v_a - v_0)/(kT))$) which do not involve the crossing of energy barriers. It is therefore sufficient to restrict our discussion to the situation in which $I_1 \rightarrow 0$. To fix ideas, I assume that $h_b(v) \rightarrow \infty$ below $v_a$ and drops sharply at that point. (Such steep decay of $h_b$ is expected, for example, in the case of hard-sphere materials.)

After integration one gets from equation \ref{eq:1}:

$$k \dot{\Theta} = E_1 \exp\left[\frac{-\Delta h}{k \Theta}\right] \left(\exp\left(\frac{\delta q}{k\Theta} - \frac{\delta q}{kT}\right) - 1\right) + \sigma \dot{\gamma} ,$$

with $E_1 = \nu \delta q$ and $\Delta h = P(v_a - v_0)$. I anticipate here on the second part of this paper where the deformation of a material in a pure shear geometry will be considered: $\sigma$ is the (deviatoric) shear stress, $\dot{\gamma}$ the plastic strain rate, whence $W^{\text{ext}} = \sigma \dot{\gamma}$.

The results presented here do not depend qualitatively on further dependencies of $E_1$ on $T$ or $\Theta$, which may, however, bring logarithmic corrections.

In the absence of external stress ($\sigma = 0$), equation \ref{eq:2} admits thermodynamic equilibrium, $\Theta = T$, as its single fixed point. The timescale of the relaxation towards equilibrium increases with decreasing $T$, and at low $T$ the system may remain out-of-equilibrium on any observable timescale by the mere fact that $\Theta$ is small (or tries to).

When $\Theta \gg T$, equation \ref{eq:2} is dominated by:

$$k \dot{\Theta} = -E_1 \exp\left[\frac{-\Delta h}{k \Theta}\right] + \sigma \dot{\gamma} .$$

In this limit, the long-time relaxation of the variable $\Theta$ is easily obtained by integrating \ref{eq:3} (with $\dot{\gamma} = 0$): $\int_{\Theta_0}^{\Theta(t)} \exp[\Delta h/(k\Theta)] \, k \, d\Theta = -E_1 t$, and keeping only the dominant contribution: $k \Theta(t) \simeq \frac{\Delta h}{\log(E_1 t/\Delta h)}$. For finite $T$, this process dominates so long as $t << \tau_T = \Delta h \exp(\Delta h/(kT))/E_1$: $\tau_T$ diverges in the limit $T \rightarrow 0$.

An important property of the glass transition is that the observed transition point depends on the cooling rate. \ref{fig:1} Consider the following experiment: enthalpy is monitored during a steady cooling from an initial temperature $T_{\text{max}}$; after reaching $T_{\text{min}}$, the temperature is increased at the same rate back to $T_{\text{max}}$. This procedure is reproduced here by integrating equation \ref{eq:2} for different cooling/reheating rates. The resulting dynamics are portrayed figure \ref{fig:1} (left), where energy is shown as a function of $T$. Slowing down is seen as energy does not reach equilibrium at low temperature; upon reheating, energy does not go back along the same curve. As in the experiments, heat capacity is then extracted from this data according to the formula, $C_T = dH/dT$; the result is displayed figure \ref{fig:1} (right). The large increase of $C_T$ observed upon reheating marks a fictive glass transition point, which clearly depends on the cooling rate.

The rest of this paper is devoted to the study of a material under shear. Like thermal equilibration, the deformation of a material under an applied shear stress is expected to proceed by space-localized rearrangements. \ref{fig:1} However, the transition pathways that contributes respectively to elementary shear and elementary thermal

\begin{figure}[!h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Energy (left) and calorific capacity (right) as a function of temperature during cooling and reheating protocol, between $kT_{\text{max}} = 0.5$ and $kT_{\text{min}} = 0.001$, for cooling rates, $10^{-3}/k$ (solid line), $10^{-4}/k$ (dashed line), $10^{-5}/k$ (dotted line).}
\end{figure}
equilibration processes, are not necessarily identical at the molecular level. Therefore they may, in general, display different activation enthalpies. Without more knowledge, we can expect the response to small shear stresses to be of the form: \[ \dot{\gamma} = E_0 \exp \left( -\frac{\Delta h'}{kT} \right) \sigma \ . \] (4)

The update frequency $E_0$ normalizes the frequency of elementary vibrations, and incorporates corrections specific to this mode of deformation. Any dependency of $E_0$ on $\Theta$ or $T$ is neglected. ($E_0/E_1$ and $\Delta h/\Delta h'$ are expected to be of order 1.)

With equations (4) and (2) in hands I now study three experimental protocols: aging in the stress-linear region: this typical pattern emerges here solely from a change in the dynamical regime of $\Theta$. Relaxation curves for different ages $t_w$ are shown figure 3 (bottom). A plateau appears in the crossover region: this typical pattern emerges here solely from a change in the dynamical regime of $\Theta$. Relaxation curves for different ages $t_w$ are shown figure 3 (top). If fitted by $\exp(-t^{\beta}/\tau(t_w))$, it is easy to check that the apparent relaxation timescale $\tau(t_w)$ grows like $t_w^\alpha$, with $\alpha = 1 - \beta$: this phenomenon, usually referred as sub-aging is here a mere artifact of the lin-log representation: this type of scaling – which are very often used to treat experimental data – may be very misleading and hide, as it does here, the true aging behavior. If $\Delta h = \Delta h'$, $\beta = 0$, we find $G(t) \approx 1/t$. If $\Delta h < \Delta h'$, $\beta < 0$ and stress assumes a non-vanishing asymptotic value after relaxation, which increases with the age of the sample: $G(t \to \infty) \approx \exp \left( -|\alpha| t_w^{|\beta|} \right)$.

Another important experimental protocol consist in measuring the in-phase and out-of-phase moduli, $G'$ and $G''$, when the material is forced at time $t_w$ by an oscillatory shear, $\gamma(t) = \gamma_0 \sin(\omega(t - t_w))$. In practice, the measurement is performed by integrating the response a fixed number of periods $n$, for each frequency $\omega$. Since the material ages, every point on the spectrum depends on the whole history of the sample prior to its measurement. The resulting $G'$ and $G''$ are shown figure 2 (bottom). They clearly show an $\alpha$ relaxation peak which, here is solely the signature of the slow evolution of $\Theta$. This peak is obtained for large intervals of the parameters, under the conditions that $\mu$ is somewhat large (which, indeed, is reasonable, given the usual values of elastic constants); it weakens with the increasing age of the material.

To conclude this study, let me consider the regime of stationary deformation of the material, at temperature $T$, under a constant shear rate $\dot{\gamma}$. The steady state value of the variable $\Theta$ is the solution of:

$$\dot{\gamma} = E_0 \exp \left( -\frac{\Delta h + \Delta h'}{kT} \right) \left( 1 - \exp \left( \frac{\delta q}{kT} - \frac{\delta q}{kT} \right) \right) .$$

For $\Delta h = \Delta h'$, one finds, $\eta \dot{\gamma} = \sigma(1 + \frac{\delta q}{E_1^2} \sigma^2) - \frac{\delta q}{E_1^2}$. For $\Delta h \neq \Delta h'$, and $kT/\Delta h' >> \Delta h + \Delta h'$, this solution is dominated by the contribution, $\Theta = kT/(1 + \ldots$
a viscosity, \(h\), indicates that the system behaves as a Newtonian liquid with a constant shear rate: \(\dot{\gamma} = 1\), \(\Delta h = 1\), \(\Delta h' = 1\), \(\Theta(0) = 10\), and \(t_\omega = 10, 10^2, 10^3, 10^4, 10^5, 10^6, 10^7\). Bottom: Normalized frequency spectra for \(\mu = 100\), \(E_0 = E_1 = 0.01\), \(\Delta h = 1.5\), \(\Delta h' = 1\), \(t_\omega = 10\), \(\Theta(0) = 10\).

\[(kT/\delta q) \log \left(1 - \dot{\gamma}^2/(E_1 E_0)\right)\] which, for small \(\dot{\gamma}\), indicates that the system behaves as a Newtonian liquid with a viscosity, \(\eta\), with \(\eta = \exp[\Delta h'/kT]/E_0\). For \(kT \neq k\Theta \ll \Delta h + \Delta h'\), the solution is dominated by its \(T \to 0\) value, which leads to a power relation between stress and strain rate: \(\sigma \sim \dot{\gamma}^n\), with \(n = \frac{\Delta h - \Delta h'}{\Delta h + \Delta h'}\).

This study suggests, in the low temperature regime, there exists a direct relation between the exponent \(\beta\) (and \(\alpha\)) of the KWW relaxation, and the power law rheology displayed in steady shear. It establishes a relation between two highly dissimilar experimental situations – linear response in the aging regime, and steady shear deformation – in direct relation to the ratio \(\kappa = \Delta h/\Delta h'\) between activation barriers associated respectively to shear and energy relaxation processes. \(\kappa\) is expected to depend solely on geometrical aspect of the material: shape of the molecules or polydispersity of colloidal particles. The existence of such a relation can thus be tested experimentally by considering families of closely related materials in order to allow some variation of the exponents.

The equations proposed here are exaggerately simple. Their interest lies in the possibility to account for a whole set of properties commonly associated with the glass transition, in a over-simplified framework, in comparison to other studies of rheology. Various aspects of these questions certainly deserve further studies. In particular, a derivation of the transformation rates would bring out much needed information. One may, however, hope that out-of-equilibrium thermodynamics can be defined for structural glasses in terms of a few rate equations for the appropriate set of thermodynamic quantities.

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[15] \(k \Theta(t) = P(V - v_0)\) is proportional to a Van der Walls’ free-volume in light of the following discussion, free-volume activation appears to be closely related concepts.
[16] The limit we consider is in some sense, “opposite” to the mean-field approximation, in which case every variable \(v_i\) is directly coupled with the average \(\bar{v}\), whence the full distribution \(\rho(v_i - \bar{v})\) becomes the dynamical variable. We see that the mechanical contacts between subsystems may (below some critical dimension) drastically reduce the dimensionality of the relevant dynamics.
[17] I do not consider, in this work, dynamics of shear transformation zones.