

On alpha relaxation in viscous liquids

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It is suggested that the generic $\omega^{-1/2}$ high-frequency decay of alpha relaxation may be the manifestation of a negative long time tail as typically encountered in stochastic dynamics.

The primary relaxation process in viscous liquids is termed alpha relaxation. This is the dominant and the slowest relaxation process. The alpha process is responsible for the glass transition - the kinetic falling out of equilibrium taking place basically when the cooling rate $d \ln T / dt$ exceeds the alpha relaxation rate [1, 2, 3, 4, 5]. Alpha relaxation is observable in dielectric relaxation experiments and in measurements of the frequency-dependent shear and bulk moduli [2, 6] and, e.g., of the frequency-dependent specific heat. The loss peaks obtained by measuring these linear response properties are of similar shape, but not identical. The loss peak frequencies are also similar, but not identical, and their temperature dependencies are usually quite similar. In the following we shall not dwell on the dissimilarities. We focus on the shear modulus, taking the viewpoint that this is the primary response function while, e.g., the dielectric loss is determined by the coupling of molecular rotation to shear flow [7, 8, 9, 10].

The features of alpha response functions $\chi(\omega)$, as typically reported in the literature, are: 1) The loss peak frequency ω_m is non-Arrhenius with an activation energy which increases as temperature decreases, the well-known fragility property of most viscous liquids; 2) On the low-frequency side of the loss peak the loss is virtually Debye like; 3) On the high-frequency side there are significant deviations from Debye behavior - here $\chi''(\omega)$ decays following an approximate power law. Summarizing points 2) and 3), alpha relaxation is reported to be characterized by

$$\chi''(\omega) \propto \begin{cases} \omega & , \omega \ll \omega_m \\ \omega^{-n} & , \omega \gg \omega_m \end{cases} . \quad (1)$$

In many cases a “wing” is observed where the exponent n changes to a lower value a few decades above the alpha loss peak frequency.

The vast majority of experiments report values of n between 0.35 and 0.65 [11] where n is often slightly temperature dependent; the latter implies violation of time-temperature superposition (the existence of a master curve to which measurements at differing temperatures may be scaled). At the 1997 Vigo meeting it was suggested by Olsen that beta relaxation processes may play a role at much lower frequencies than previously expected, and that these could explain the “wing” [12]. Lunkenheimer and coworkers subsequently found that upon long-time annealing the wing indeed develops into a separate relaxation process [13]. The picture which now emerges [14] is the following: Once effects of beta processes are eliminated at sufficiently low temperatures, the “generic” features of alpha relaxation come to light: Generic alpha relaxation obeys time-temperature superposition, and for the asymptotic behaviors the generic alpha process is characterized by

$$\chi''(\omega) \propto \begin{cases} \omega & , \omega \ll \omega_m \\ \omega^{-1/2} & , \omega \gg \omega_m \end{cases} . \quad (2)$$

Finally and notably, generic alpha relaxation is characterized by non-universal loss peak widths. This conclusion was reached based on dielectric relaxation measurements on several molecular liquids, but it applies also for the shear modulus $G(\omega)$ [14, 15, 16]. Curiously enough, the finding that $n = 1/2$ plays the role of a “fixed point” for the equilibrium liquid at low temperatures represents a step backwards in time: Around 1970 it was the prevailing opinion that $n = 1/2$ is the high-frequency exponent of alpha relaxation and that deviations from $n = 1/2$ are caused by interference from beta processes.

Excluding polymers, below follows a list of models which have been suggested in various contexts to explain $n = 1/2$: In 1948 Zener in his theory of “relaxation by thermal diffusion” for ultrasonic loss in metals predicted that the internal friction at high frequencies varies as $\omega^{-1/2}$ [17]. Glarum (1960), Doremus (1970), Phillips, Barlow, and Lamb (1972), Bordewijk (1975), Kimmich and Voigt (1978), Wyllie (1979), and Condat (1989) all arrived at the $\omega^{-1/2}$ -tail from essentially one-dimensional diffusion models [18, 19, 20, 21, 22, 23, 24]. Isakovitch and Chaban in 1966 predicted a limiting high frequency sound absorption per wavelength in highly viscous liquids varying as $\omega^{-1/2}$ from a model regarding the liquid as a microinhomogeneous medium [25] (see also Ref. [26]). Barlow, Erginsav, and Lamb, in 1967 in what is now known as the BEL model, regarded the shear mechanical impedance of a viscous liquid as a “parallel combination” of a Newtonian liquid and a Hookean solid, implying an $\omega^{-1/2}$ -tail for the high frequency shear modulus

[2, 27]. Montrose and Litovitz in 1970 derived the $\omega^{-1/2}$ -tail in a model invoking diffusion and relaxation of some unspecified order [28]. Majumdar, working in the time domain, arrived at the short time equivalent of the high-frequency tail in 1971 from the assumption that diffusive modes exist with amplitude $\propto k^{-2}$ [29]. Cunat in 1988 arrived at a distribution of relaxation times τ proportional to $\sqrt{\tau}$ for $\tau \rightarrow 0$ (which implies the $\omega^{-1/2}$ high-frequency tail) from a purely thermodynamic treatment [30]. Sjögren in 1990 showed that Eq. (2) arises in mode-coupling theory under certain conditions [31]. – Several of these models involve the diffusion equation which is assumed to apply even at times shorter than the alpha relaxation time. This nontrivial assumption is central also for the long time tail mechanism proposed below.

The BEL model focuses on the shear compliance $J(\omega)$ [= $1/G(\omega)$]. In dimensionless units the BEL model has a definite prediction for $J(\omega)$, implying universal loss peak width. Because this does not fit experiment the BEL expression for the shear compliance was soon formally generalized by the same authors [32] to (where all constants are real and $s \equiv i\omega$ is the Laplace frequency)

$$J(s) = a + b s^{-1/2} + c s^{-1}. \quad (3)$$

We shall refer to this as the “generalized BEL expression.” The original BEL model corresponds to $b^2/ac = 4$. Note that Eq. (3) implies Eq. (1) for the shear modulus loss $G''(\omega)$. In dimensionless units the generalized BEL expression has one free parameter and thus non-universal width of the loss peak.

Consider a shear flow in the x -direction where the velocity depends only on z . According to the fluctuation-dissipation theorem, if Q is the x -direction displacement of the top of the liquid (area L^2 in the x - y -plane, height h in the z -direction), the shear compliance is given by

$$J(s) = \frac{s}{2 k_B T} \frac{L^2}{h} \int_0^\infty \langle \Delta Q^2(t) \rangle e^{-st} dt. \quad (4)$$

Here $\langle \Delta Q^2(t) \rangle$ is the equilibrium mean-square displacement of the Q coordinate in time t , i.e., the zero shear stress thermal average of the square of $\Delta Q(t) \equiv Q(t) - Q(0)$.

Via Eq. (4) the generalized BEL expression translates into

$$\langle \Delta Q^2(t) \rangle = A + B t^{1/2} + C t. \quad (5)$$

In terms of the Q mean-square displacement the velocity-velocity autocorrelation function is given by

$$\langle \dot{Q}(0) \dot{Q}(t) \rangle = \frac{1}{2} \frac{d^2}{dt^2} \langle \Delta Q^2(t) \rangle. \quad (6)$$

Thus the generalized BEL expression implies

$$\langle \dot{Q}(0) \dot{Q}(t) \rangle \propto -t^{-3/2}. \quad (7)$$

Conversely, Eq. (7) implies the generalized BEL expression – except for the nontrivial requirement that AC/B^2 is not too far from one, a constraint which is necessary to fit data.

Equation (7) immediately brings to mind the long-time tails discovered in 1967 by Alder and Wainwright in early computer simulations of liquids [33]. These authors showed that the velocity-velocity autocorrelation function for a single molecule does not decay exponentially to zero at long times as previously expected, but as a power law with exponent $-3/2$:

$$\langle \dot{x}(0) \dot{x}(t) \rangle \propto +t^{-3/2}. \quad (8)$$

The explanation is the following. According to statistical mechanics at any given time molecular velocities are uncorrelated. Consider a particular molecule at time $t = 0$. It has a certain momentum while the surrounding molecules have on average zero momentum. As time passes the momentum of the molecule in question diffuses to the surrounding molecules (recall that the Navier-Stokes equation is basically a transverse momentum diffusion equation). At time t the momentum has diffused the distance $\sim t^{1/2}$ away, thus spread among $\sim t^{3/2}$ molecules. If the initial momentum of the molecule in question is more or less equally shared among these, every molecule on average has

momentum $\sim t^{-3/2}$. This includes the particular molecule in focus, thus explaining Eq. (8). – An excellent recent review of long time tails from a more sophisticated and general viewpoint has been given by Kirkpatrick and coworkers [34].

Central to the above argument are *momentum conservation* and the *diffusion equation*. If Eq. (7) were to reflect a long time tail two questions arises: 1) What is the role of momentum conservation in viscous liquids? 2) How does one explain a *negative* long-time tail [35]? The first question arises because viscous liquids close to the calorimetric glass transition have viscosities typically 10^{14} times larger than that of ordinary liquids like ambient water. Since the kinematic viscosity is the transverse momentum diffusion constant, these liquids have extremely large momentum diffusion constants. Consequently, just as momentum conservation does not play any role for the description of point defect motion in crystals, momentum conservation is *irrelevant* for the description of viscous liquid dynamics. This is one of the reasons that a description of viscous liquids by Langevin dynamics makes good sense.

It is possible to show that velocity-velocity autocorrelation functions are negative for any stochastic dynamics (i.e., dynamics described by a master equation). In particular, Langevin dynamics predict negative long-time tails of the required form, as shown below. First, however, we ask: What is the required conserved variable once momentum conservation is deemed irrelevant? Angular momentum conservation is irrelevant for the same reason that momentum conservation is. Energy conservation could be relevant because heat conduction is rather slow, but this process is almost temperature independent and thus unable to give alpha relaxation times which depend dramatically on temperature. The only alternative left is *particle number conservation*.

We proceed to recall how long-time tails typically arise from particle number conservation, working in real space instead of the usual k -space. By “long time” is here meant times long enough that density fluctuations decay following the diffusion equation. As a simple case, consider a variable F which is a sum of pair-wise contributions, $F = \sum_{ij} \phi(\mathbf{r}_i - \mathbf{r}_j)$. In terms of the density $\rho(\mathbf{r}) \equiv \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$ we have

$$F = \int d\mathbf{r}d\mathbf{r}' \phi(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r})\rho(\mathbf{r}'). \quad (9)$$

If the deviation from average density is denoted by $\Delta\rho \equiv \rho - \langle\rho\rangle$, F is given as

$$F = \text{Const.} + \int d\mathbf{r}d\mathbf{r}' \phi(\mathbf{r} - \mathbf{r}') \Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r}'). \quad (10)$$

The F -autocorrelation function is given by

$$\langle F(0)F(t) \rangle = \text{Const.} + \int d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3d\mathbf{r}_4 \phi(\mathbf{r}_1 - \mathbf{r}_2)\phi(\mathbf{r}_3 - \mathbf{r}_4) \langle \Delta\rho(\mathbf{r}_1, 0)\Delta\rho(\mathbf{r}_2, 0)\Delta\rho(\mathbf{r}_3, t)\Delta\rho(\mathbf{r}_4, t) \rangle. \quad (11)$$

In the Gaussian approximation the average of a product of four variables by Wick’s theorem is a sum of three terms, each a product of two pair correlation functions. One of the three terms is time-independent and we get [assuming $\phi(\mathbf{r}) = \phi(-\mathbf{r})$]

$$\langle F(0)F(t) \rangle = \text{Const.} + 2 \int d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3d\mathbf{r}_4 \phi(\mathbf{r}_1 - \mathbf{r}_2)\phi(\mathbf{r}_3 - \mathbf{r}_4) \langle \Delta\rho(\mathbf{r}_1, 0)\Delta\rho(\mathbf{r}_3, t) \rangle \langle \Delta\rho(\mathbf{r}_2, 0)\Delta\rho(\mathbf{r}_4, t) \rangle. \quad (12)$$

Letting $t \rightarrow \infty$ we find $\langle F \rangle^2 = \text{Const.}$ so, if $\Delta F \equiv F - \langle F \rangle$, Eq. (12) implies

$$\langle \Delta F(0)\Delta F(t) \rangle = 2 \int d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3d\mathbf{r}_4 \phi(\mathbf{r}_1 - \mathbf{r}_2)\phi(\mathbf{r}_3 - \mathbf{r}_4) \langle \Delta\rho(\mathbf{r}_1, 0)\Delta\rho(\mathbf{r}_3, t) \rangle \langle \Delta\rho(\mathbf{r}_2, 0)\Delta\rho(\mathbf{r}_4, t) \rangle. \quad (13)$$

A standard assumption in liquid theory is that the density correlation function $\langle \Delta\rho(\mathbf{r}, 0)\Delta\rho(\mathbf{r}', t) \rangle$ regarded as a function of \mathbf{r}' and t obeys the diffusion equation at long times. Since the density correlation function goes to zero as $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$ and $t \rightarrow \infty$, we have where D is the diffusion constant

$$\langle \Delta\rho(\mathbf{r}, 0)\Delta\rho(\mathbf{r}', t) \rangle \propto t^{-3/2} \exp\left(-\frac{(\mathbf{r} - \mathbf{r}')^2}{4Dt}\right). \quad (14)$$

When this is substituted into Eq. (13) one finds at long times, if ϕ is reasonably short ranged, $I \equiv \int d\mathbf{r}\phi(\mathbf{r})$, and $V = L^2h$ is the volume:

$$\langle \Delta F(0) \Delta F(t) \rangle \propto + V I^2 t^{-3/2}. \quad (15)$$

Next, we proceed to establish an expression for the Q velocity-velocity autocorrelation function in stochastic dynamics. To be specific, the liquid is modeled via standard Langevin dynamics. Given the irrelevance of momentum conservation for viscous liquids, this is a reasonable description of viscous liquid dynamics on the time scale of the alpha relaxation. Indeed, computer simulations have shown that Langevin dynamics is equivalent to classical mechanics on this time scale [36].

Denoting the degrees of freedom individually by X_j , collectively by X , and the Hamiltonian by $H(X)$, the Langevin equation of motion is:

$$\dot{X}_j = -\alpha \frac{\partial H}{\partial X_j} + \xi_j(t). \quad (16)$$

Here α sets the time scale and $\xi_j(t)$ is the standard Gaussian white noise term, the magnitude of which depends on temperature. If β is inverse temperature and $P(X, t)$ is the probability, the Smoluchowskii equation corresponding to Eq. (16) is

$$\frac{\partial P(X, t)}{\partial t} = \alpha \sum_j \frac{\partial}{\partial X_j} \left[e^{-\beta H(X)} \frac{\partial}{\partial X_j} \left(e^{\beta H(X)} P(X, t) \right) \right]. \quad (17)$$

To simplify notation we shall sum over repeated indices and abbreviate: $\partial_j \equiv \partial/\partial X_j$. Then Eq. (17) becomes

$$\dot{P} = \alpha \partial_j e^{-\beta H} \partial_j e^{\beta H} P. \quad (18)$$

We proceed to express the mean-square displacement of Q as a double integral over two full set of coordinates, X_1 and X_2 . It is convenient to let, e.g., $Q(X_1)$ be written simply as Q_1 . With this convention, Z the partition function, DX_1 the product of all dX_{1j} 's, and $P_{1 \rightarrow 2}(t)$ the Green's function, i.e., the probability to find the system at position X_2 at time t given it was at position X_1 at $t = 0$, we have

$$\langle \Delta Q^2(t) \rangle = \int DX_1 DX_2 (Q_2 - Q_1)^2 \frac{e^{-\beta H_1}}{Z} P_{1 \rightarrow 2}(t). \quad (19)$$

Utilizing detailed balance in the form $\exp(-\beta H_1) P_{1 \rightarrow 2}(t) = \exp(-\beta H_2) P_{2 \rightarrow 1}(t)$ and the fact that $P_{1 \rightarrow 2}$ obeys Eq. (18) as function of X_2 , Eq. (6) becomes after several partial integrations

$$\begin{aligned} \langle \dot{Q}(0) \dot{Q}(t) \rangle &= \frac{1}{2} \frac{d^2}{dt^2} \int DX_1 DX_2 (Q_2 - Q_1)^2 \frac{e^{-\beta H_1}}{Z} P_{1 \rightarrow 2}(t) \\ &= \frac{1}{2} \frac{d}{dt} \int DX_1 DX_2 (Q_2 - Q_1)^2 \frac{e^{-\beta H_1}}{Z} \dot{P}_{1 \rightarrow 2}(t) \\ &= \frac{\alpha}{2} \frac{d}{dt} \int DX_1 DX_2 (Q_2 - Q_1)^2 \frac{e^{-\beta H_1}}{Z} \partial_{2n} e^{-\beta H_2} \partial_{2n} e^{\beta H_2} P_{1 \rightarrow 2}(t) \\ &= -\alpha \frac{d}{dt} \int DX_1 DX_2 (Q_2 - Q_1) (\partial_{2n} Q_2) \frac{e^{-\beta H_2}}{Z} \partial_{2n} e^{-\beta H_1} e^{\beta H_2} P_{1 \rightarrow 2}(t) \\ &= -\alpha \int DX_1 DX_2 (Q_2 - Q_1) (\partial_{2n} Q_2) \frac{e^{-\beta H_2}}{Z} \partial_{2n} \dot{P}_{2 \rightarrow 1}(t) \\ &= -\alpha^2 \int DX_1 DX_2 (Q_2 - Q_1) (\partial_{2n} Q_2) \frac{e^{-\beta H_2}}{Z} \partial_{2n} \partial_{1j} e^{-\beta H_1} \partial_{1j} e^{\beta H_1} P_{2 \rightarrow 1}(t) \\ &= -\alpha^2 \int DX_1 DX_2 (\partial_{1j} Q_1) (\partial_{2n} Q_2) e^{-\beta H_1} e^{-\beta H_2} \partial_{2n} \partial_{1j} \frac{e^{\beta H_1}}{Z} P_{2 \rightarrow 1}(t) \\ &= -\alpha^2 \int DX_1 DX_2 (e^{\beta H_1} \partial_{1j} e^{-\beta H_1} \partial_{1j} Q_1) (e^{\beta H_2} \partial_{2n} e^{-\beta H_2} \partial_{2n} Q_2) \frac{e^{-\beta H_2}}{Z} P_{2 \rightarrow 1}(t) \end{aligned} \quad (20)$$

Thus in terms of the variable

$$F_Q \equiv e^{\beta H} \partial_j e^{-\beta H} \partial_j Q \quad (21)$$

we find because $\langle F_Q \rangle = 0$

$$\langle \dot{Q}(0)\dot{Q}(t) \rangle = -\alpha^2 \langle \Delta F_Q(0)\Delta F_Q(t) \rangle. \quad (22)$$

This indicates that Langevin dynamics in combination with the long-time behavior described by the diffusion equation resulting in Eq. (15) is able generate the extended BEL expression. To make this mechanism work properly, however, three questions must be answered:

1. How to express the degree of freedom coupling to a shear stress field in terms of microscopic coordinates?
2. How to justify the use of the diffusion equation at times shorter than the inverse alpha loss peak frequency?
3. How to ensure that the constants of Eq. (5) obey the requirement that AC/B^2 is not too far from one?

Regarding the first problem we need to identify the degrees of freedom coupling to a stress field. For a continuous displacement field $\delta u_m(\mathbf{r})$ [$m = 1, 2, 3$], if σ_{mn} is the stress tensor and $\delta u_{mn} \equiv (\partial_m \delta u_n + \partial_n \delta u_m)/2$ is the strain tensor, the work done on volume dV is $\delta W = dV \sigma_{mn} \delta u_{mn}$ [37], implying a change in free energy given by $\delta F = \int d\mathbf{r} \sigma_{mn}(\mathbf{r}) \delta u_{mn}(\mathbf{r})$. Assuming finite volume V with periodic boundary conditions this translates into $\delta F/V = \sum_{\mathbf{k}} \sigma_{mn}(-\mathbf{k}) \delta u_{mn}(\mathbf{k})$. Consequently, if the degree of freedom conjugate to $\sigma_{mn}(-\mathbf{k})$ is denoted by $Q_{\mathbf{k},mn}$, we have $\delta Q_{\mathbf{k},mn} = V \delta u_{mn}(\mathbf{k}) = \int d\mathbf{r} \exp(-i\mathbf{k} \cdot \mathbf{r}) [\partial_x \delta u_z + \partial_z \delta u_x]/2$. Specializing to the case where $\mathbf{k} = (0, 0, k)$, if the degree of freedom coupling to σ_{xz} is denoted simply Q_k , partial integrations leads to $\delta Q_k = ik \int (d\mathbf{r}/V) \exp(-ikz) \delta u_x/2$ which in terms of particle positions via the identification $\delta u_x(\mathbf{r}) = V/N \sum_j \delta x_j \delta(\mathbf{r} - \mathbf{r}_j)$ translates into

$$\delta Q_k = \frac{ik}{2N} \sum_j e^{-ikz_j} \delta x_j. \quad (23)$$

From this we would like to conclude that

$$Q_k = \frac{ik}{2N} \sum_j e^{-ikz_j} x_j. \quad (24)$$

The variation of Eq. (24), however, has an extra term besides Eq. (23). Although this term is $O(k^2)$ and thus apparently small at small k 's, to ensure that this is the case we must assume that the length of the system in the z -direction is much larger than in the x -direction: $h \gg L$. Under this condition, for small k the variation of Q_k defined in Eq. (24) is to a high accuracy given by Eq. (23). From here on we use Eqs. (15) and (22) to arrive at the required Eq. (7).

Regarding problem 2) it is not at all obvious that density fluctuations at times shorter than the alpha relaxation time are described by the diffusion equation. As mentioned, the present approach has this assumption in common with several previous models. The difference is that we do not need extra assumptions like the existence of defects [17, 18, 21, 22, 23, 24] or sharp edges [25, 26, 38].

It may be argued that problem 3) is solved if it is assumed that the rate constant α of the Langevin equation Eq. (16) is the *alpha relaxation rate* itself. How could this be justified? The obvious answer is that the Langevin equation is a course-grained description (thus the Hamiltonian is a free energy function): If the orientational degrees of freedom are eliminated, the resulting Langevin description deals exclusively with the motion of the centers of mass of the molecules. This approach might seem inconsistent in view of the fact that rotational motion is often slower than translations [39], but this is not so: The free energy as function of the centers of mass is found by integrating out the orientational degrees of freedom, and the assumption of Langevin dynamics ensures consistency with statistical mechanics. To have the relaxation time scale given (roughly) by $1/\alpha$ it is necessary, however, that the resulting description of the center of mass dynamics does not involve barriers much larger than $k_B T$. In other words, the large barriers which definitely exist in viscous liquids should exclusively be related to changes of orientation. This is probably not an unrealistic assumption, but more works remains to be done to show whether it is correct.

Whether or not the Langevin approach is useful for explaining Eq. (7) remains to be seen. We took Langevin dynamics just as an example of one possible stochastic dynamics. An obvious alternative, where the problem of time-scale does not seem to arise, is “inherent dynamics” – the master equation describing transitions between minima of the potential energy landscape. This approach effectively regards the liquid as a defective solid with infinitely fast transitions between states of mechanical equilibria. In future work we intend to consider this alternative to Langevin dynamics for explaining the generic features of alpha relaxation via the long-time tail mechanism.

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