Excess wing physics and nearly constant loss in glasses

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Abstract. Excess wings and nearly constant loss are almost universal nonequilibrium phenomena in glass formers. Both lack an accepted theoretical foundation. A model-free and unified theoretical description for these phenomena is presented that encompasses also fast β-processes, emergent Debye peaks, and the relaxation strength of the boson peak. The theory is model-free in the same way as the classical Debye relaxation equation for orientational polarisation. It is based on generalizing time flow from translation semigroups to composite time translation-convolution semigroups. Composite translation-convolution fits have less parameters than traditional fits. They need only one dynamic scaling exponent, while four are needed in Havriliak–Negami fits. For glycerol the single dynamic exponent in the translation-convolution fit is found to be temperature-independent.

Keywords: glasses, excess wing, dynamical processes, slow relaxation, glassy dynamics, aging

Although Anderson in 1995 [1] expected a breakthrough by the year 2005 and despite intense worldwide activity ever since, *'the deepest and most interesting problem in solid state theory'* [1], as he labeled the glass transition, remains as puzzling as ever [2]. Different and often controversial views [3] (see below) on experimental observations and phenomena near the glass transition continue to compete [2], and Anderson's expectation has not been fulfilled, because universally applied phenomenological fits to glassy relaxation data have still not found a convincing model-free theoretical foundation.

Multiscale non-exponential relaxation phenomena are paradigmatic for glasses and to a large extent material-independent [2, 4, 5]. Almost all polymers [6], polyalcohols [7], plastic crystals [8], or water saturated porous silica [9] are but a few examples. In many materials the α-process is coupled to stress relaxation and solidification [7, figure 7]. Other commonalities of glassy relaxation such as the asymmetry of the α-peak [10], its temperature dependence [11], the nature of the excess wing [12, 13], the physics of the fast β-process [14], the constant loss phenomenon [15, 16], or the boson peak have remained obscure. Researchers still search for their microscopic origin. Excess wings and nearly constant loss phenomena could thus turn out to be the missing key for unlocking the secrets of the glass transition. My earlier results seem to indicate that excess wings emanate from the α-peak [17–19] instead of being directly identifiable with slow β-processes [7, pp 53–5].

Dielectric spectroscopy gives information about the collective orientational motion of dipolar molecules and molecular moieties. Experiments nowadays cover up to 20 decades in time [3, 20]. It is this huge breadth that makes dielectric spectroscopy an ideal tool to study temporal coarse graining in non-equilibrium statistical physics experimentally.

Given that excess wings are material- and observable-independent [21], theories should be model-free. Limited predictivity of two popular model-free approaches, namely (idealized A_2-type) mode coupling theory [22] and dielectric scaling theory [23], seems to have stifled interest in model-free approaches on the experimental side [3]. On the other hand model-free excess wings were obtained from coarse graining time flow in [17–19]. Recall that convolutional time flow integrates past and present to become future [24]. In translational time flow the present shifts into a future without past. A central objective of this work is to show that composite translation-convolution theory [17–19] unifies a model-free approach to excess wings with predictions for the asymmetric α-peak and nearly constant loss. More specifically, some predictions implicit in [18], will be made explicit.

Before turning to equations and results some terminology and some controversial viewpoints are discussed briefly. The term 'α-relaxation' refers to the dominant relaxation peak in the dielectric susceptibility at low frequencies. It is commonly attributed to the orientational polarization resulting from the translational degrees of freedom of dipolar molecules and molecular moieties. Upon lowering the temperature it moves towards lower frequencies and out of the accessible frequency window.

The term 'β-relaxation' means secondary processes at frequencies above the α-peak. Their physical origin is controversial. The β-relaxations are some times subdivided into slow resp. fast processes depending on whether they appear at lower resp. higher frequencies. The term 'excess wing' refers to a power law behaviour on the high frequency side of the α-peak [8]. Figure 1 in [25, figure 1] shows schematically the main features: α-process, slow and fast β-processes and the excess wing.

While the α-peak is widely agreed to be caused by structural relaxations, controversial views persist for the interpretation and molecular origin of the excess wing and those secondary β-processes, that seem to be intimately linked to the α-process. Such secondary processes must be distinguished from secondary relaxations that arise as intramolecular modes. Examples for intramolecular modes are side-chain motions in polymers. They are not the bone of contention. Instead, controversial views persist for secondary β-processes that are intimately linked to the α-process. They are thought to be generic and inherent to the glassy state of matter [20]. Sometimes these secondary processes appear as distinct relaxation peaks (in so called type B glass formers), sometimes they appear as a change of slope on the high-frequency side of the α-peak (excess wing in type A glass formers). There is no consensus concerning the microscopic origin or interpretation. They could be interpreted as transitions between minima in a complex energy landscape, as local small-angle librations of molecules or molecular moieties, or as local processes in regions of lower density interspersed with frozen heterogeneities.

The objective of this work is to corroborate the macroscopic interpretation from [17–19] that links the excess wing intimately to the α-peak. The advance achieved here allows to fit the experimental observations with a single dynamical exponent instead of four exponents traditionally used in the literature for more than 50 years. The results reported here may be called a breakthrough, because, at least for glycerol, these fewer parameters seem to be temperature independent. They admit a direct interpretation as parameters in an initial value problem. The traditional fit parameters for glycerol are temperature dependent and have remained without theoretical interpretation.

Let $\phi(s)$ be the dielectric polarization as a function of time $s > 0$ (in seconds) and let $\phi(u) = \int_0^\infty \phi(s) \exp(-us) \mathrm{d}s$ with $u = -\mathrm{i}\omega$ denote its (Fourier-)Laplace transform as a function of circular frequency ω. Define dimensionless time $t \in (0, \infty)$ by $s = t\tau$ where τ is the time scale in seconds, and the dimensionless dielectric relaxation function $\varphi : (0, \infty) \to \mathbb{R}$ by $\phi(s) = \phi_0 \varphi(s)$, where $\phi_0 = \lim_{s \to 0^+} \phi(s)$ is the initial value at $s = 0$ if it exists. The dielectric response function (or susceptibility) is $\epsilon(s) = -\mathrm{d}\phi(s)/\mathrm{d}s$. Its Laplace transform is normalized as $\varepsilon(u) = (\epsilon(u) - \epsilon_\infty)/\phi_0$ where $\phi_0 = \epsilon_0 - \epsilon_\infty$ is the dielectric strength with $\epsilon_\infty = \lim_{\omega \to \infty} \epsilon(-\mathrm{i}\omega)$ and $\epsilon_0 = \lim_{\omega \to 0} \epsilon(-\mathrm{i}\omega)$ if the limits exist. The normalized frequency dependent dielectric function $\varepsilon : (0, -\mathrm{i}\infty) \to \mathbb{C}$ is related to the Laplace transformed normalized relaxation function $\varphi(u)$ as $\varepsilon(u) = 1 - u\varphi(u)$.

The most widely used family of fit functions for the normalized dielectric function ε is the three-parameter Havriliak–Negami (HN) family [3, 9, 20, 26]

$$\varepsilon_{\mathsf{HN}}(u) = \frac{1}{[1 + (\tau u)^\eta]^\gamma} \tag{1}$$

with $u = -\mathrm{i}\omega$, a relaxation time parameter τ and two exponents $\eta \geqslant 0$, $\gamma \geqslant 0$. For $\gamma = 1, \eta = 1$ it becomes the classical Debye function. Contrary to the Debye function the Havriliak–Negami family of fit functions is usually postulated phenomenologically without derivation from an underlying microscopic model. For $\gamma = 1, \eta \neq 1$ (Cole–Cole) the loss peak is broader than in the Debye case, but remains symmetric. For $\gamma \neq 1, \eta = 1$ (Cole–Davidson) the loss peak is broadened and asymmetric. To fit also an excess wing requires a linear superposition of two HN-functions (where $\varepsilon_{\mathsf{HN}i}$ is ε from equation (1) with $\eta = \eta_i$, $\gamma = \gamma_i$ and $\tau = \tau_i$ for $i = 1, 2$)
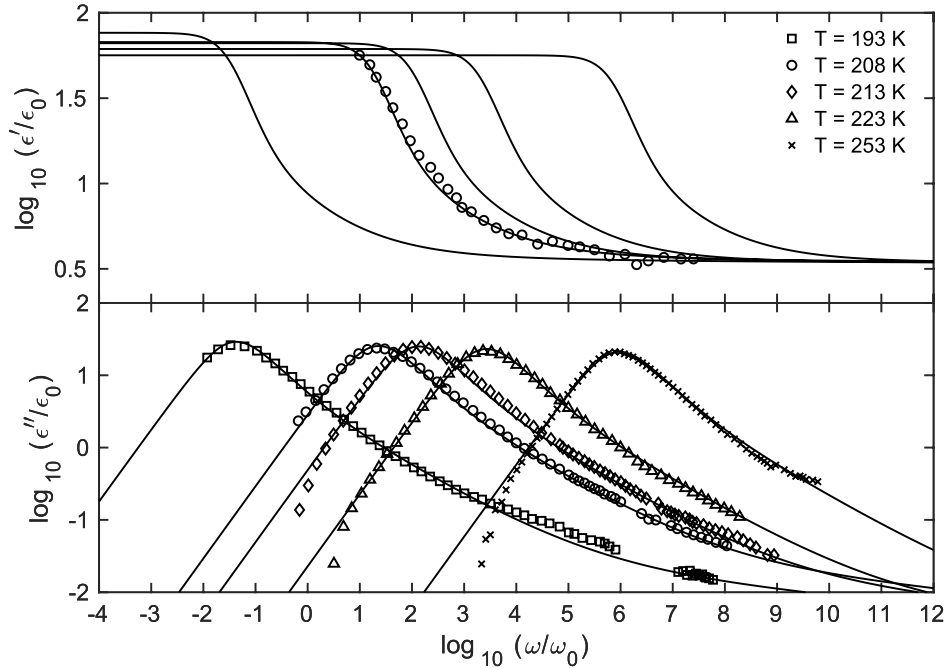
Figure 1. Transvolution fit, equation (3), for glycerol with parameters in table 1. The imaginary parts were extracted from [3, figure 4.11, p 118],[3, figure 3.5, p 66] and [3, figure 4.11, p 118]. The real part for $T = 208.3$ K was extracted from [27, figure 1(a)]. The units are $\omega_0 = 2\pi$ Hz and $\epsilon_0 = 10^7/(4\pi c^2)$ As Vm^{-1}.

$$\varepsilon(u) = w\, \varepsilon_{\mathsf{HN1}}(u) + (1 - w)\, \varepsilon_{\mathsf{HN2}}(u) \tag{2}$$

which has a total of 7 fit parameters. Note that $\varepsilon(0) = 1$, $\varepsilon_{\mathsf{HN}}(0) = 1$, $\varepsilon(-\mathrm{i}\infty) = 0$ and $\varepsilon_{\mathsf{HN}}(-\mathrm{i}\infty) = 0$. There is no model-free derivation known for equation (2).

The main result of this work is a model-free and unified theory for excess wings, nearly constant loss and emergent Debye peaks, that is based on composite translation-convolution semigroups of time flow [17, 18]. It results in a new composite translation-convolution family of fit functions ('transvolution' family for short)

$$\varepsilon(u) = \frac{1 + (\tau_\alpha u)^\alpha + (\tau_{\mathrm{ab}} u)^{1+\beta(\alpha-1)}}{1 + (\tau_\alpha u)^\alpha + \tau_1 u} \tag{3}$$

where $u = -\mathrm{i}\omega$, $0 < \alpha \leqslant 1$, $0 \leqslant \beta \leqslant 1$, τ_1 is the translational, τ_α the convolutional, and τ_{ab} the initial time scale. Equation (3) has only five parameters, two less than equation (2). Note that $\varepsilon(0) = 1$, but $\varepsilon(-\mathrm{i}\infty)$ does not need to vanish, contrary to equations (1) and (2).

The five-parameter family (3) is the result of coarse graining time as in [24, 28]. The coarse graining gives rise to a family of convolution semigroups $T_\alpha(t/\tau_\alpha)$ with parameter $0 < \alpha \leqslant 1$. For $\alpha = 1$ this becomes the translation semigroup $T_1(t/\tau_1)$. Equation (3) is derived in several steps. First one computes the infinitesimal generator of the composite semigroup $T_1(t/\tau_1)\, T_\alpha(t/\tau_\alpha)$ which governs the rate of change of the relaxation function φ. If the rate of change of the relaxation function φ is proportional to φ itself, as in the well known model-free Debye theory, a fractional differential equation can be established with generalized Riemann–Liouville derivatives of order α as originally

Table 1. Transvolution fit parameters (equation (3)) for glycerol at temperatures $T = 193, 208, 213, 223, 253$ K. The fits are displayed in figure 1.

	193 K	208.3 K	213 K	223 K	253 K
α	0.58	0.58	0.58	0.58	0.58
β	0.18	0.18	0.18	0.18	0.18
τ_α (s)	$10^{-0.26}$	$10^{-2.99}$	$10^{-3.76}$	$10^{-5.06}$	$10^{-7.61}$
τ_{ab} (s)	$10^{-1.7}$	$10^{-4.33}$	$10^{-5.28}$	$10^{-6.75}$	$10^{-9.35}$
τ_1 (s)	$10^{0.86}\tau_\alpha$	$10^{0.86}\tau_\alpha$	$10^{0.86}\tau_\alpha$	$10^{0.86}\tau_\alpha$	$10^{0.86}\tau_\alpha$

Table 2. Published traditional HN-parameters (equation (2)) for glycerol at temperatures $T = 193, 208, 223$ K from [3, p 118] and [3, p 67]. Note that $1 - w \approx 0.01$ is small.

	193 K	208.3 K	223 K
η_1	0.91	0.945	0.96
γ_1	0.62	0.6	0.62
τ_1 (s)	8.5	$10^{-1.98}$	$1.1 \cdot 10^{-4}$
η_2	0.8	1.0	0.8
γ_2	0.3	0.208	0.3
τ_2 (s)	$8.5 \cdot 10^{-4}$	$10^{-4.82}$	$2.8 \cdot 10^{-8}$
w	0.9895	0.9868	0.9924

suggested in [18]. Solving the resulting fractional Cauchy problem and taking equation (10) from [18] into consideration yields equation (3). Equation (3) generalizes equation (12) in [17] (or equation (36) in [18]) to which it reduces for $\tau_{\mathrm{ab}} = 0$.

The extra term $(\tau_{\mathrm{ab}}u)^{1+\beta(\alpha-1)}$ in equation (3) was absent in equation (36) in [18]. It arises from allowing for an initial instantaneous transvolution loss. The parameter α depends on the underlying microscopic dynamics as explained in detail in [24]. The dynamical exponent α characterizes recurrence times into subsets of measure zero in state space. Mathematical theorems restrict its range to $0 < \alpha \leqslant 1$. The parameter $0 \leqslant \beta \leqslant 1$ is the type of generalized Riemann–Liouville derivative used as the infinitesimal generator of transvolutional time flow. It classifies the type of convolutional initial data, but is not another exponent.

Figure 1 shows a fit for glycerol $C_3H_5(OH)_3$ using equation (3). The fit parameters are listed in table 1. The data points shown in figure 1 were extracted from [3, figure 3.5, p 66, [3, figure 4.11, p 118], and [3, figure 4.12, p 119]. The real part was extracted from [27, figure 1(a)]. Note that $\alpha = 0.58$, $\beta = 0.18$ and the ratio $\tau_1/\tau_\alpha = 7.244\,36$ are independent of temperature. This fixes three out of five parameters in table 1 and leaves two parameters temperature dependent. If four parameters were fixed, perfect data collapse under rescaling would be expected. The fact that only three parameters are fixed suggests partial and imperfect data collapse under rescaling. Figure 2 confirms this expectation. It shows the master curve for glycerol obtained from rescaling the curves in figure 1 to $\tau_1 = 1$ s, $\epsilon_0 = 1$ and $\epsilon_\infty = 0$.

Figure 3 shows traditional seven-parameter fits for glycerol from the literature based on equation (2) at three different temperatures. The seven parameters from [3] are reproduced in table 2 for convenient comparison with table 1.
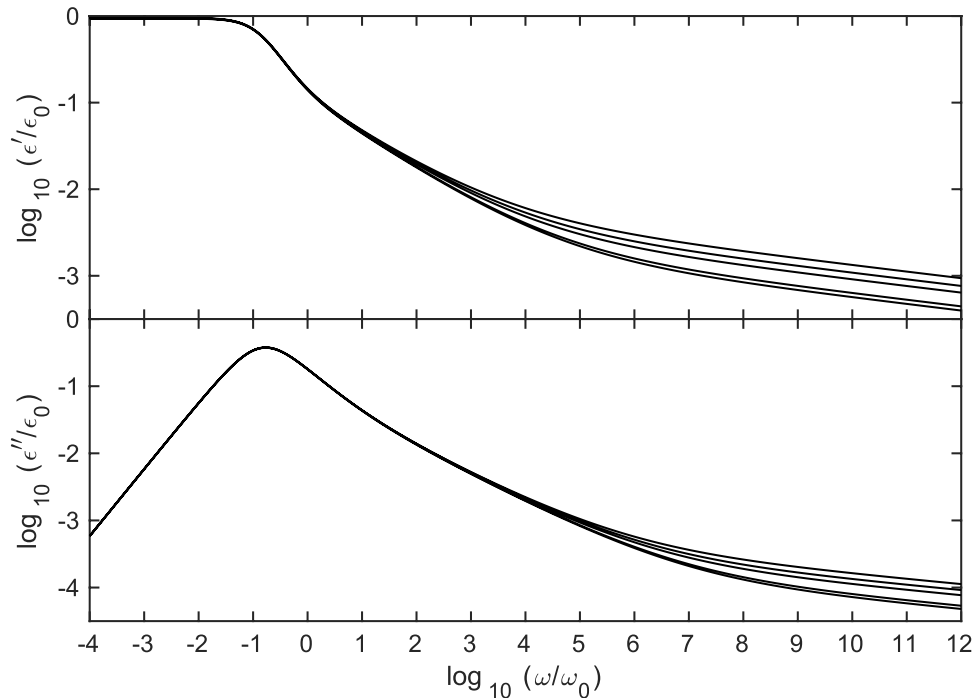
Figure 2. Data collapse for glycerol in the temperature range from $T = 193$ K to $T = 253$ K. The solid lines are those from figure 1 rescaled to $\tau_1 = 1$ s, $\epsilon_0 = 1$ and $\epsilon_\infty = 0$. The remaining parameters are from table 1. The units are $\omega_0 = 2\pi$ Hz and $\epsilon_0 = 10^7/(4\pi c^2)$ As Vm^{-1}.

The fit quality in figures 1 and 3 is comparable. Both fits capture asymmetry and broadening of the α-peak plus the excess wing. While the HN-fit (2) requires four exponents and seven parameters, the transvolution fit (3) needs one scaling exponent and five parameters. For the HN-family all seven parameters in table 2 depend on temperature. For transvolution (table 1) three parameters, namely α, β and the ratio τ_1/τ_α, are fixed and temperature independent. This seems to mark a significant breakthrough, because there does not seem to exist any other fit of the glycerol data over 12 decades in ω and 60 K in T with a single scaling exponent.

The parameter β in equation (3) classifies initial losses preceding the transvolutional α-relaxation process. For $\beta \approx 0$ equation (3) predicts nearly constant loss. This marks a second significant result. Nearly constant loss can account for the relaxation strength of fast β-processes [3]. A notorious problem of traditional fit functions, such as equation (2), is that they decay too rapidly. This rapid decay is the rationale behind postulating fast β-processes. Ad hoc modifications of the imaginary part ε'' of equation (2), such as equations (5.2) and (5.3) in [4], would violate Kramers–Kronig relations.

Figure 4 illustrates the emergence of nearly constant loss with $\beta \approx 0$ from a broad and asymmetric α-peak. Figure 4 also shows a symmetric Debye peak emerging from an asymmetric non-Debye peak. Debye peaks are often observed in monohydroxy alcohols [20]. Note that all four curves in figure 4 have fixed and constant $\alpha = 0.58$ and $\beta = 0.007$. No other family of fit functions is known to reproduce the behaviour seen in figure 4 with only one fixed exponent.
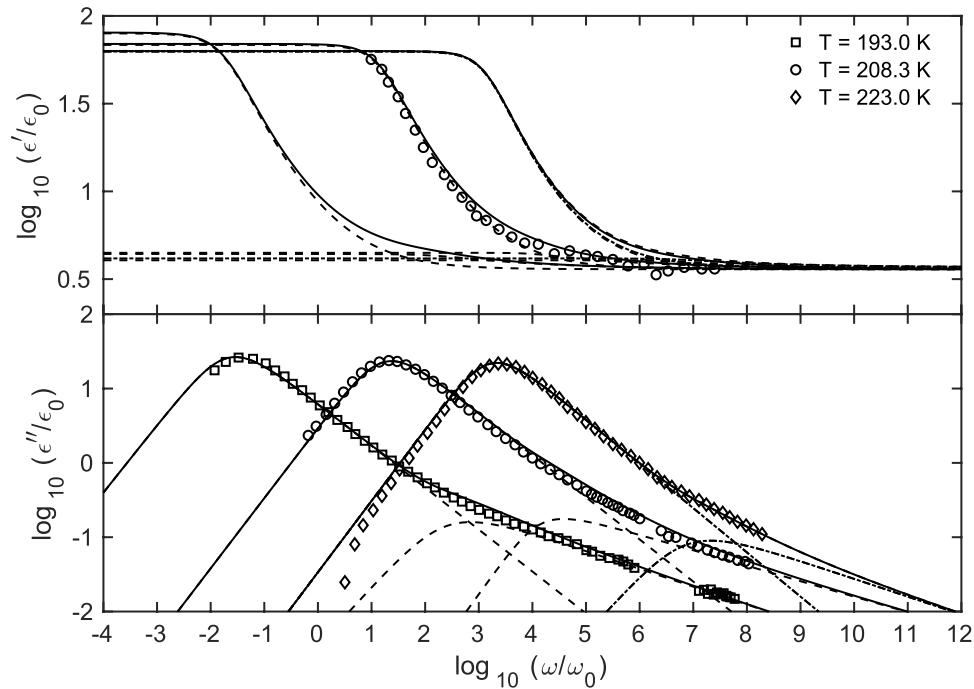
Figure 3. Traditional fits for glycerol using equation (2) with fit parameters from table 2. The units are $\omega_0 = 2\pi$ Hz and $\epsilon_0 = 10^7/(4\pi c^2)$ As Vm^{-1} the electric field constant.

Next, it is gratifying to observe that the transvolution fit for $T = 193$ K in figure 1 reveals a small maximum sitting on top of the excess wing. If confirmed, this could reconcile the view [23] that excess wings emanate from the α-peak, with the view [25] that excess wings are weak β-processes. Indeed the small maximum in figure 1 suggest that already at temperature $T = 193$ K above the glass transition $T_g \approx 185$ K a weak β-process can be detected on top of an excess wing that emanates superuniversally from the dominant α-peak.

Attention is drawn to an unusual 'defect wing' at low frequencies in the data for $T = 213, 223, 253$ K. The defect wing might be due to subtracting the measured d.c.-conductivity. The values of d.c.-conductivities were not published. Measuring them is difficult, because glycerol, due to its high hygroscopicity, will gain moisture until the glycerol-water mixture reaches equilibrium with the moisture in the air. Irrespective of whether a 'defect wing' represents a true, and hitherto overlooked, feature of the α-peak, it provides a splendid opportunity to highlight the flexibility of the transvolution fit formula. Figure 5 shows fits of the defect wing, the asymmetric and broad α-peak, and the excess wing in glycerol. No other family of fit functions seems to allow slopes larger than unity at low frequencies. Remarkably, the parameters $\alpha = 0.22$ and $\beta = 0.4$ in figure 5 are again temperature independent, albeit over a somewhat smaller range.

Table 3 summarizes the comparison between equations (2) and (3). The line labeled 'Boson peak' indicates, that the relaxation strength of the Boson peak is among the factors determining the initial time scale τ_{ab}. The table indicates also that equation (3) has a general and model-free theoretical background while equation (2) does not.
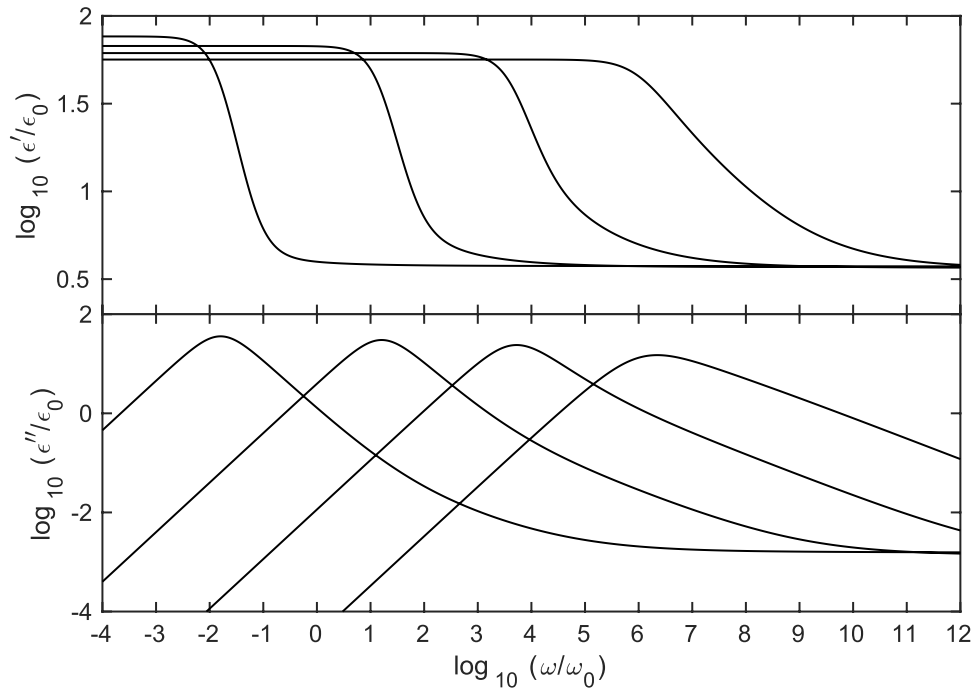
Figure 4. Symmetric Debye peak with excess wing and nearly constant loss emerging from a typical asymmetric α-peak (with $\eta = 1$ in equation (1)). In all curves $\alpha = 0.58$ and $\beta = 0.007$.
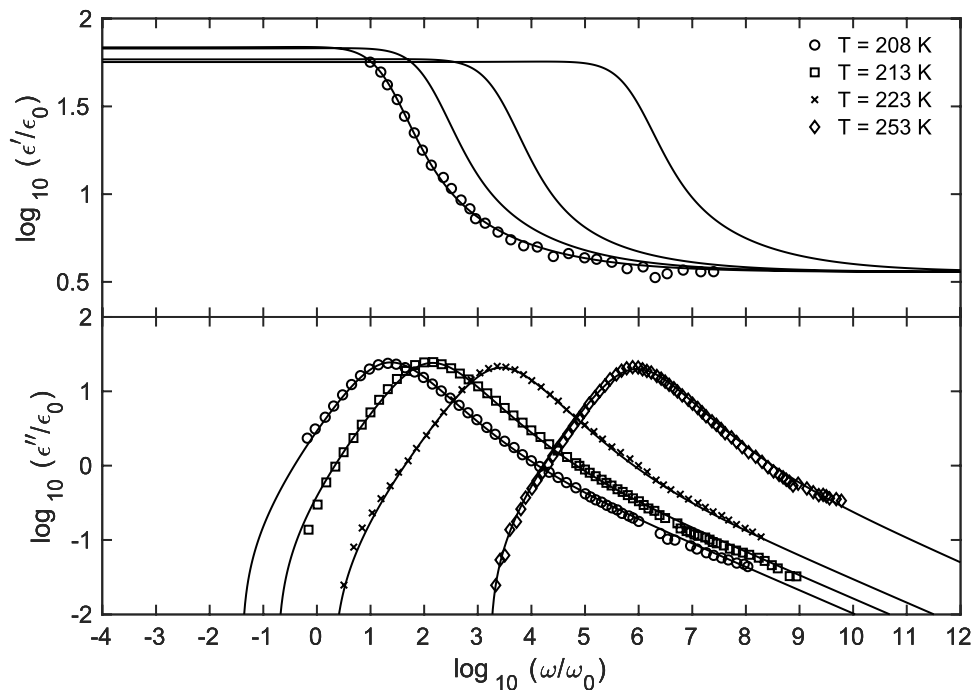

Figure 5. Second transvolution fit for glycerol with $\alpha = 0.22$, $\beta = 0.4$, in the range $T = 208$–253 K.

Table 3. Summary of comparison between composite translation-convolution fit (3) and traditional HN-fit (2).

	Equation (2)	Equation (3)
Number of fit parameters	7	5
T-dependent parameters in glycerol	7	2
Number of exponents	4	1
α-peak asymmetry	Yes	Yes
Excess wing possible	Yes	Yes
Defect wing possible	No	Yes
Constant loss possible	No	Yes
Fast β-process	No	Yes
Slow β-process	No	No
Emergent Debye peak	No	Yes
Model-free theory	No	Yes
Boson peak	No	Strength
Time-temperature scaling	No	Sometimes

In conclusion, this work reports a breaktrough in dielectric spectroscopy near the glass transition. Composite translation-convolution time flow is more flexible and has fewer parameters than previous phenomenological approaches rooted in translational flow of time. Equation (3) unifies asymmetry of the α-peak, excess wing physics, nearly constant loss, and emergent Debye peaks. In all cases investigated here the unification requires only one temperature independent exponent.

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