Generic Primary Mechanical Response of Viscous Liquids

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Four decades ago a seminal review by Jonscher [Nature (London) **267**, 673 (1977)] revealed that the dielectric response of conducting materials is characterized by a "remarkable universality". Demonstrating that the same response pattern is exhibited also by shear rheological spectra of nonpolymeric viscous liquids, the present contribution connects two branches of condensed matter physics: Concepts developed for charge transport can be employed for the description of mass flow and vice versa. Based on the virtual equivalence of the two dynamics a connection is established between microscopic and macroscopic viscoelastic characteristics of liquids, resembling the Barton-Nakajima-Namikawa relation for conductivity.

Uncovering the rules governing the dynamics in disordered materials has always been considered a search for the holy grail in condensed matter physics. In the literature several surveys report on relaxation patterns which are common to a large variety of amorphous materials [1–4]. Among them, Jonscher's "universal dielectric response" of solids [5] was hailed as a milestone for the understanding of the dominant role of many-body interactions in disordered materials [6]. These pioneering studies gained wide recognition by revealing that the conductivity spectra of a large variety of materials exhibit a rather simple shape which is practically insensitive to the microscopic structural details [7,8].

The discovery of a general character for the underlying mechanisms governing the dynamics of charged particles triggered an intensive research activity. Several theoretical approaches have been developed to explain this universal conductivity behavior [9,10], including Dyre's Random Barrier Model (RBM) [7,11]. In simple terms, this model considers that at short times the charge carriers are hopping over spatially randomly varying energy barriers, while at longer times, as soon as the carriers are able to overcome a certain energy threshold they perform Fickian diffusion. In the spirit of prior scaling approaches [12], the RBM relies on only two parameters. Although its premises were critically discussed [7,13], it has been successfully applied to describe the conductivity spectra of many ionic materials [14,15].

A seemingly disjointed situation of structural disorder in which the dynamics is also attributed to a broad distribution of activation energies is the one of molecular flow in viscous liquids. Often the reorganization of the microscopic liquid structure, the so-called structural (α-) relaxation process, is considered to take place on the time scale on which molecules are "escaping" from their local coordination cages [16]. This simplistic picture also implies a subdiffusive to diffusive dynamical transition similar to the situation of charge transport in conducting materials, although the characteristic barriers for the structural relaxation are, in general, not of Coulombic origin.

Molecular flow (probed via shear rheology) and charge transport (probed via dielectric spectroscopy) both share several fundamental characteristics. As conductivity σ connects the charge velocity to the applied electric field, fluidity F (the inverse of viscosity η) relates the deformation rate to the applied mechanical stress. Both σ and F provide access to the self-diffusion coefficient of migrating particles, via the Nernst-Einstein and the Stokes-Einstein relations, respectively [17]. Previously, the ionic conductivity was traced back to the time-dependent mean square displacement of the mobile charge carriers [18]. Exploiting the same formalism, the fluidity response of any liquid can analogously be expressed in terms of the mean square displacement of the constituent molecules.

As an example, consider ionic liquids, i.e., binary mixtures of anions and cations, where every charge hopping is also a rheological event [19]. Here, linear dielectric and mechanical responses should, in principle, both reflect the same underlying relaxation mechanism. In other words, for strongly polarization-flow coupled systems the "universal" rules governing charge dynamics should apply for the molecular transport as well. Are the ionic liquids unique in this respect?

In the present Letter we analyze the mechanical signature of the structural relaxation process for various viscous liquids, including van der Waals, ionic, and hydrogen-bonded fluids. In particular, we show (i) that in the fluidity representation the spectral shape of the shear responses [20] of the studied systems display the general "universal" relaxation behavior previously unraveled for conductivity [5], and (ii) that the applicability range of theoretical concepts previously introduced for the description of conductivity mechanisms can be extended to molecular flow. As a convenient means to capture the shape of liquids' shear response the RBM [7,11] turns out to be useful. As a practical example for the transfer of physical concepts, we
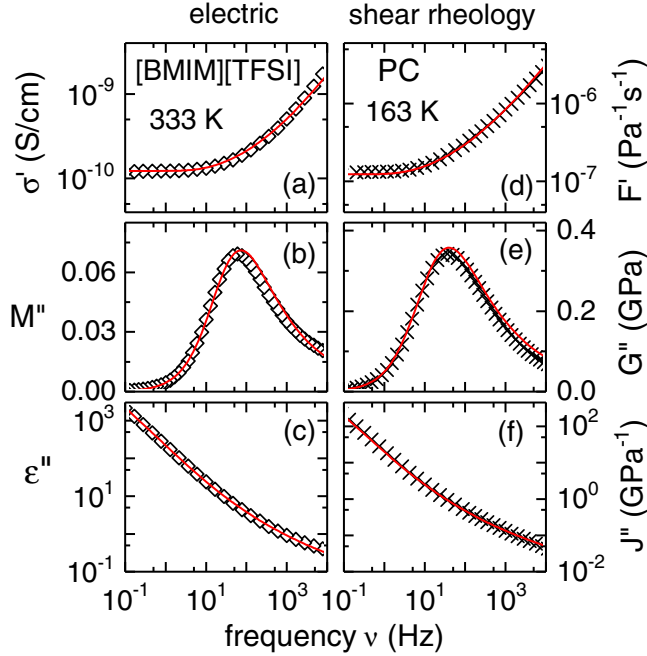
FIG. 1. Different representations of the charge transport data (empty diamonds) of the ionic liquid [BMIM][TFSI] at 333 K are given in the form of (a) conductivity, (b) electrical modulus loss, and (c) dielectric loss. The mechanical counterparts of these quantities, measured for PC at 163 K (crosses), are shown as (d) fluidity, (e) shear modulus loss, and (f) shear compliance loss. The red solid lines are fits using the RBM.

show that the Barton-Nakajima-Namikawa (BNN) relation holds for the complementary viscoelastic parameters of the studied liquids as well. These results open new exciting venues for the understanding of molecular dynamics in liquids and the physics of disorder in general.

Let us start by comparing typical results for the two types of dynamics observed by means of conductivity and shear mechanical spectroscopies. Figure 1 shows electrical data for the paradigmatic ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][TFSI]) obtained earlier [15]. The results are plotted on the left side of Fig. 1, using three common representations: (a) conductivity $\sigma' = \text{Re}[\sigma^*]$ (i.e., the real part of the complex quantity); (b) electric modulus loss $M'' = \text{Im}[(i\omega\varepsilon_0)/\sigma^*]$, and (c) dielectric loss $\varepsilon'' = \text{Im}[\sigma^*/(i\omega\varepsilon_0)]$. Here, $\omega = 2\pi\nu$ is the angular frequency and ε_0 the vacuum permittivity. Let us point out that irrespective of whether flow of charges or of molecules is probed, similar shapes are obtained even when considering a different glass formers. To underscore this statement, in Figs. 1(d)–1(f) we add shear mechanical data reported for the van der Waals liquid propylene carbonate (PC) [21,22]. The rheological counterparts of the electrical responses are fluidity $F' = \text{Re}[F^*]$, shear modulus loss $G'' = \text{Im}[(i\omega)/F^*]$, and shear compliance loss $J'' = \text{Im}[F^*/(i\omega)]$, respectively. Despite the differences in material, method, temperature (or time scale),

etc., the *spectral shapes* of the corresponding quantities displayed in Fig. 1 reveal a high degree of resemblance. It should be kept in mind though that in one case they reflect electric charge dynamics and mechanical flow events in the other. When comparing mechanical with electrical spectra or with other quantities in one and the same material, a decoupling of time scales may or may not occur in certain temperature ranges. As these effects have been discussed in detail in the literature [17,24], here we focus on the spectral shapes of the various response functions.

To further highlight the similarities between charge transport and rheological dynamics with respect to their overall frequency-dependent shape, we demonstrate next that the electric *and* the mechanical spectra can be described by the same theoretical concepts. For the present analysis, we found it convenient to exploit the RBM which has been used in the past to model the frequency-dependent conductivity response of numerous ionic conductors. The two adjustable parameters required in this approach are the steady-state conductivity σ_0 and the characteristic time $\tau_{\text{RBM}} = 1/(2\pi\nu_{\text{RBM}})$. As in related approaches [25] the latter marks a dynamical crossover from the subdiffusive to the diffusive ionic regime. According to this model these two parameters, determined from the spectra at relatively low frequencies, are governing the high-frequency conductivity response as well.

The lines in Figs. 1(a)–1(c), derived from the RBM expression [11]

$$\ln\frac{\sigma^*(\nu)}{\sigma_0} = \frac{i2\pi\nu\tau_{\text{RBM}}\sigma_0}{\sigma^*(\nu)}\left(1 + \frac{8}{3}\frac{i2\pi\nu\tau_{\text{RBM}}\sigma_0}{\sigma^*(\nu)}\right)^{-1/3} \quad (1)$$

describe the electrical results for the ionic liquid very well. This finding is consistent with reports that Eq. (1) provides a good description of the electrical response for a host of ion conductors. This is a remarkable observation considering the fact that the shape of the frequency-dependent electrical conductivity implied by Eq. (1) is unique (i.e., it cannot be adjusted and the two parameters σ_0 and τ_{RBM} are serving only as vertical and horizontal shift factors). More interesting in the current context is that the same expression (with σ^* replaced by F^* and σ_0 by the static fluidity F_0) yields an almost perfect description of the shear response of PC, see the lines in Figs. 1(d)–1(f). It is interesting to note that none among the premises leading to Eq. (1) is explicitly relying on the Coulombic origin of the underlying energy landscape. Could this theoretical concept therefore be more generally adopted to capture *structural relaxation processes* in liquids as well?

The shear spectra shown in Fig. 2 unveil the temperature evolution of the structural relaxation process for highly viscous ortho-terphenyl (OTP). These frequency-dependent moduli were recorded using an Anton-Paar MCR 502 spectrometer and complement previous time-domain rheological investigations of OTP [26]. The data are plotted using the modulus loss G'' and in the (less
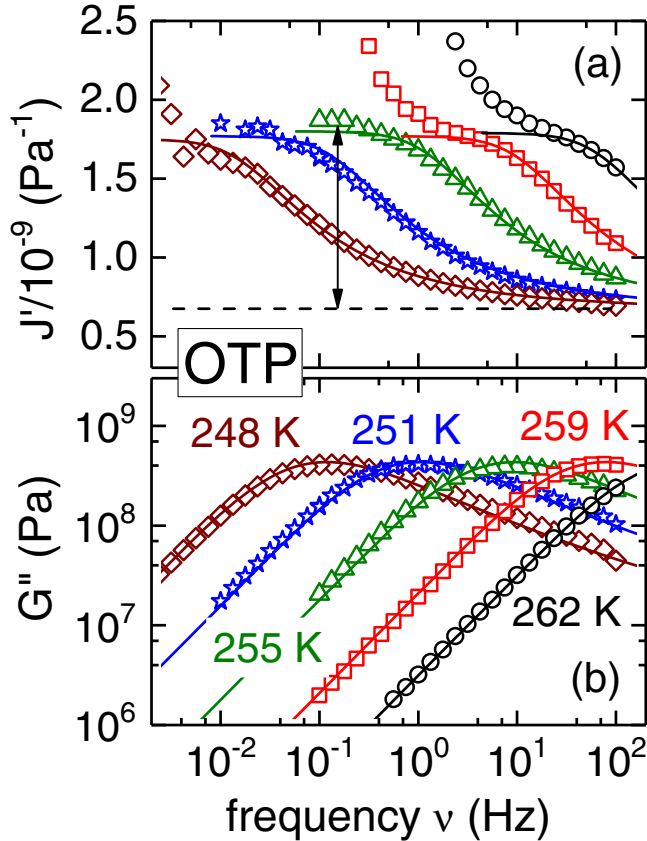
FIG. 2.   Frequency-dependent (a) shear compliance storage and
(b) shear modulus loss for OTP measured in this work. The solid
lines are fits with the RBM. In (a) the arrow corresponds to the ΔJ
value indicated in Fig. 4 for OTP (see text for details). The
increase of the signal at low frequencies is an artifact caused by
the low-torque limit of the rheometer.

common) compliance storage J' representations. The latter,
like the dielectric storage $\varepsilon' = \mathrm{Re}[\varepsilon^*]$, reveals the relaxation
contributions without interference by viscous flow or elec-
trical dc conductivity, respectively [15]. The analysis of
several representations of modulus *and* compliance data is
essential when checking the mutual agreement of exper-
imental features and theoretical approaches. For example,
the original solution proposed for the RBM [7] was able to
capture the salient features of the conductivity σ', but
not those of the ionic relaxation process in the dielectric
compliance spectra [27]. This issue is fixed in the largely
overlooked revised RBM equation [11], see Eq. (1).

As demonstrated by the fits included in Fig. 2, Eq. (1)
describes the overall structural relaxation response of OTP
at different temperatures reasonably well. For the following
discussion it is important to recall that the presently chosen
description of the *shear relaxation* features is also based on
two parameters, only. Clearly, for a comprehensive char-
acterization of the electrical *and* mechanical response
functions also the high-frequency compliance limits, albeit
not relaxational in character, are required. With respect to

Fig. 2(a), this implies that the instantaneous shear compli-
ance J_∞ needs to be taken into account, see the dashed line
for the spectrum at 248 K. This static quantity, however,
does not affect the F' response; In the same way the
instantaneous dielectric constant ε_∞ has no impact on σ'.

Let us now check whether the viscoelastic responses of
PC and OTP should be considered peculiar or whether
instead they reflect a spectral pattern common to structural
rearrangements of liquids in general. In other words, does
the "universality" previously revealed for the conductivity
have a counterpart in the mechanical signature of molecular
flow? To address this question we included in our analysis
the shear spectra probed in this Letter for tris-naphthyl-
benzene (TNB) and calcium nitrate-potassium nitrate
(CKN), and the literature data for pentaphenyltrimethyl-
trisiloxane (DC704), dibutyl phthalate (DBP), diethyl
phthalate (DEP), propylene glycol (PG), and m-toluidine
(mTOL) [28].

Constructing master curves (see also the Supplemental
Material [23]) as for the literature data in Ref. [28], we
confirmed first that the structural responses of all inves-
tigated systems obey time-temperature superposition. In a
second step, the master curves of all materials were
converted to fluidity which allows for a direct comparison
with the conductivity behavior. Figure 3 collects these
model-independent results on a reduced frequency scale: It
is clearly revealed that the primary mechanical responses of
all liquids considered in this Letter are very similar, in spite
of the large differences in the chemistry and in the nature of
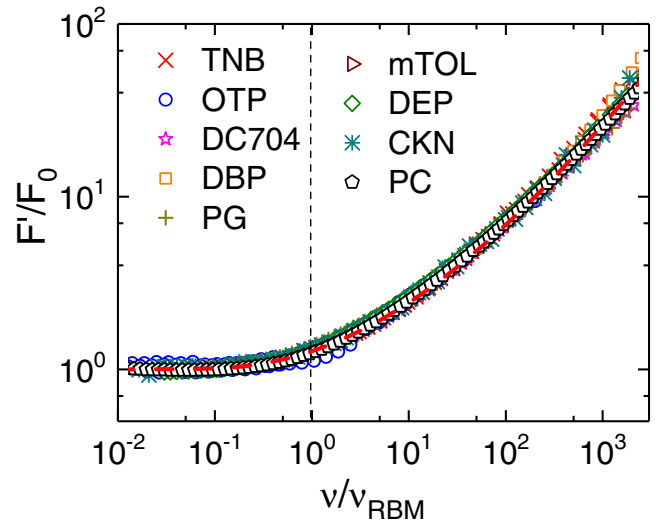the relevant microscopic interactions. The good common

FIG. 3.   Fluidity master curves constructed for the liquids
investigated in this Letter (TNB, CKN, and OTP) and using
literature data for the other liquids from Refs. [21,28]. All liquids
display a common behavior. The dashed red line is calculated
using Eq. (1). Details regarding the construction of the master
curves and their separate representation for each glass former are
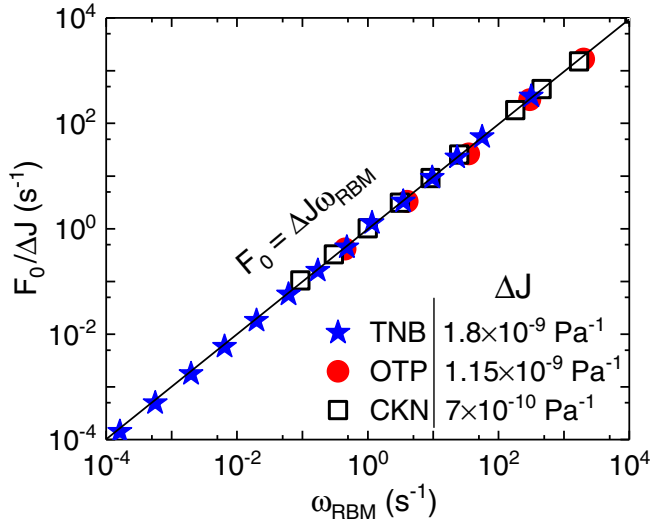given as Supplemental Material [23].

FIG. 4.   The connection between steady-state fluidity, compliance relaxation strength, and structural relaxation time is tested for TNB, OTP, and CKN in terms of the rheological BNN relation, Eq. (2).

description of all spectra collected in Fig. 3 strengthens this finding and demonstrates that liquid fluidities and charge conductivities display common generic spectral shapes. While this experimental finding does not rely on the validity of the RBM, the latter provides a possible rationale for its microscopic understanding. Also important would be to check whether Eq. (1) holds as well for materials exhibiting a significant degree of decoupling between macroscopic fluidity (viscosity) and microscopic mechanical relaxation times [13].

Why was such a remarkable simplicity not reported on before? One possible answer is that comparative dielectric and mechanical studies are usually performed for the α peak with the shear modulus loss function in mind [28]. Both the position and the shape of the modulus response depend on the ratio of the static and the instantaneous (unrelated to relaxation) compliances [29], which for nonpolymeric liquids is not at all negligible. To reflect the genuine relaxation behavior associated with liquid dynamics, we suggest to present mechanical results in the fluidity representation, similar to Jonscher's choice of conductivity to highlight the *relaxational* features of charge dynamics. Another factor which can impede the identification of the generic structural relaxation features is the presence of strong (high-frequency) secondary processes and, in polymers and related materials, of (low-frequency) normal modes. We note that models such as the RBM do not account for such features and that the shear responses of none of the liquids discussed in this Letter is significantly affected by them.

In the final part of this article we focus on a practical implication of the newly revealed possibility of knowledge transfer from the electrical to the mechanical field of

research. One reference expression for conductivity phenomena is the BNN relation [12,30]. Developed on empirical grounds, this relation has been demonstrated to hold for a large number of conductors. It connects the dc conductivity σ_0 with the ionic relaxation strength $\Delta\varepsilon$ and the characteristic frequency of the onset for ac conductivity ω_c, according to $\sigma_0 = p\varepsilon_0\Delta\varepsilon\,\omega_c$, with p a material constant close to 1. The rheological BNN equivalent should read

$$F_0 = \Delta J\omega_c. \tag{2}$$

Here, ΔJ denotes the compliance relaxation strength and the characteristic frequency $\omega_c = \omega_{RBM}$ can be estimated via Eq. (1) or, in a model independent way, for example, from the position of the inflection point in $J'(\omega)$.

In Fig. 4 we plot the results obtained for $F_0/\Delta J$ as a function of ω_{RBM} for the three systems measured in this Letter. From literature data [28], measured with a different rheological technique, we were not able to estimate the static compliance plateau (the so-called recoverable compliance) which is crucial for the present BNN type of analysis. Anyway, for the three liquids CKN, TNB, and OTP the data closely follow the solid line which corresponds to Eq. (2). For each liquid a single, temperature independent ΔJ was chosen, as indicated in Fig. 4. In Fig. 2(a) the arrow indicates the corresponding ΔJ for OTP, demonstrating good applicability of the BNN concept to experimental shear data.

One may note that Eq. (2) can be considered an alternative for the Maxwell relation ($\eta_0 = G_\infty\tau$, with the structural relaxation time $\tau \approx 1/\omega_c$ and $G_\infty = 1/J_\infty$), the latter being obtained by replacing ΔJ with J_∞. A glance at Fig. 2(a) reveals that, e.g., for OTP $\Delta J \approx 2J_\infty$ and for CKN $\Delta J \approx 3J_\infty$. Thus, for these glass formers the Maxwell relation with τ here identified with $1/\omega_{RBM}$, overestimates the viscosity by a factor of about 2–3. To address the question whether the newly introduced Eq. (2) may remove the inconsistencies usually noticed between experimental results and the Maxwell relation [28] certainly requires the analysis of far more systems than the ones considered in this Letter.

To summarize, we demonstrate that the translational molecular dynamics at least in the considered class of viscous liquids exhibit generic mechanical spectra, *qualitatively and quantitatively* similar to the ones characterizing the charge transport in ionically conducting materials. Based on the similarity of the two phenomena, our analysis reveals that a BNN-like relation can be established by connecting the static and dynamic viscoelastic parameters of simple (nonassociated and nonpolymeric) liquids. The major implication of this extended universality is that phenomenological and theoretical approaches developed for the description of dynamics in conducting materials can be adapted for the molecular flow. This broadens significantly the array of concepts which can be further developed for the understanding of molecular dynamics in viscous

liquids and its relation with the overarching features of the glass transition phenomenon.

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[23] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.119.248001 for regarding the construction of the master curves, a comparison of the fluidity master curves for the different liquids, and some limitations of the present approach.

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