

Theory of heterogeneous viscoelasticity

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We review a new theory of viscoelasticity of a glass-forming viscous liquid near and below the glass transition. In our model we assume that each point in the material has a specific viscosity, which varies randomly in space according to a fluctuating activation free energy. We include a Maxwellian elastic term and assume that the corresponding shear modulus fluctuates as well with the same distribution as that of the activation barriers. The model is solved in coherent-potential approximation (CPA), for which a derivation is given. The theory predicts an Arrhenius-type temperature dependence of the viscosity in the vanishing-frequency limit, independent of the distribution of the activation barriers. The theory implies that this activation energy is generally different from that of a diffusing particle with the same barrier-height distribution. If the distribution of activation barriers is assumed to have Gaussian form, the finite-frequency version of the theory describes well the typical low-temperature alpha relaxation peak of glasses. Beta relaxation can be included by adding another Gaussian with center at much lower energies than that responsible for the alpha relaxation. At high frequencies our theory reduces to the description of an elastic medium with spatially fluctuating elastic moduli (heterogeneous elasticity theory), which explains the occurrence of the boson-peak-related vibrational anomalies of glasses.

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I. INTRODUCTION

It has been shown by Maxwell [1] that in materials with high viscosity the elastic response becomes as important as the viscosity. He suggested that the shear rate of such materials is given by the sum of a viscous term σ/η (where σ is the applied stress and η the viscosity) and an elastic term $\frac{d}{dt}\sigma/G_\infty$ (where G_∞ is the high-frequency elastic modulus). This suggestion implies - in agreement with experimental findings - that a high-viscosity material acts as an elastic material if an alternating stress with high enough frequency $\nu = \omega/2\pi$ is applied. As shown by Maxwell [1] such a material tends exponentially to thermal equilibrium after an external shear perturbation with a relaxation time

$$\tau = \eta/G_\infty. \quad (1)$$

If the time scale of external forces is smaller than τ the material acts like a solid, if it is larger than τ like a liquid. Therefore one defines the glass-transition temperature T_g to be that temperature at which τ is larger than a typical time scale of a glass blower’s manipulation, which corresponds to a viscosity of $\sim 10^{12}$ Pa s.

In glass-forming materials η varies exponentially with the inverse temperature as $\eta(T) \propto \exp\{E_A(T)/k_B T\}$. If the differential activation energy $E_A(T)$ does not depend on temperature, the material is called *strong*, if it does, *fragile* [2–4]. In fragile materials E_A is often parametrized with the Vogel-Fulcher equation $E_A/k_B T = B/(T - T_0)$, which would lead to a divergence at T_0 . Before reaching this value, however, $E_A(T)$ becomes constant in most substances.

The value of this low-temperature activation energy

of the viscosity does not agree to that of the diffusivity (*Stokes-Einstein violation*) [5–7]. We shall give an explanation for this anomaly below.

It has also been noticed, that the activation energy $E_A(T)$ has a similar temperature dependence as the high-frequency shear modulus $G_\infty(T)$ [8–13]. This has been rationalized by observing that the activation barrier, which has to be overcome during an activated relaxation step, comprises essentially elastic energy, which only involves the shear degrees of freedom [9], and one writes (“shoving model” [8–13])

$$E_A = V G_\infty. \quad (2)$$

The proportionality factor V is the volume of the material region, which participates in the relaxation step (activation volume). This relation will be of significance for our model of heterogeneous viscoelasticity to be described below.

Following Maxwell [1] one can define a frequency-dependent effective viscosity as

$$\frac{1}{\eta_{\text{eff}}(T, \omega)} = \frac{1}{\eta(T)} + \frac{s}{G_\infty}, \quad (3)$$

where $s = -i\omega + \epsilon$ is the Laplace frequency parameter (with $\epsilon \rightarrow +0$). This quantity is related to an effective frequency-dependent shear modulus $G_{\text{eff}}(\omega) = s\eta_{\text{eff}}(\omega) = G'(\omega) - iG''(\omega)$. Using Eqs. (1) and (3) one obtains for the mechanical loss modulus the Debye-shaped function

$$G''(\omega) = G_\infty \frac{\omega\tau}{1 + (\omega\tau)^2} \quad (4)$$

The maximum of the loss function, which is due to the structural relaxation - characterized by Maxwell's relaxation time τ - has been called α maximum and the process α (primary) relaxation. The maximum of dielectric loss function, which is coupled to the mechanical relaxation [14–16], shows also the temperature variation of $\eta(T)^{-1}$, but the shape of the dielectric spectrum is different from that of the mechanical spectrum [16, 17].

However, in all glass-forming materials the α maximum of mechanic and dielectric loss peaks deviates strongly from the Debye shape, i.e. it is much broader (*stretching*). Furthermore, on the high-frequency (or low-temperature) side of the alpha peak there is a second feature, which in some materials is a peak, in others only a shoulder: the secondary or beta relaxation peak [18–20]. It is commonly believed that, while the alpha peak describes viscous structural relaxation, the beta peak is due to residual motions within the already frozen glassy material [19, 20].

Above T_g many features of the glass transition, in particular the associated non-trivial fractal time dependence of the relaxation functions - including the stretching of the α relaxation peak - are captured by the mode-coupling theory (MCT) [21–23]. This theory - in its original version - describes a sharp transition towards a non-ergodic state, in which the relaxation function does not fully decay, but tends to a finite value f , the non-ergodicity parameter. This transition appears at a transition temperature T_c , which is higher than T_g .

It has become clear in the meantime that the critical temperature of the MCT denotes not a sharp transition, but rather a crossover in the liquid dynamics from a fluid regime to an activated regime [24, 25]. The activated dynamics is missing in the original MCT.

In order to take the activated dynamics into account MCT has therefore been generalized [26–29]. In this version MCT does not only treat momentum relaxation, which can be visualized by a succession of scattering events but also density relaxation, which is a succession of hopping events (relaxation steps). Such a distinction is also important in the theory of high-resistivity metals [30], where it leads to a cross-over in the temperature coefficient of the electronic resistivity.

Within such a treatment [26–30] the resistive transport coefficient - in our case the effective viscosity - is given by

$$\frac{1}{\eta_{\text{eff}}}(s) \propto \delta(T) + \frac{1}{m(s)}, \quad (5)$$

where $\delta(T) \propto \exp\{-E_A/k_B T\}$ describes the activated viscous motion and $m(z)$ is the MCT memory function, which generalizes the scattering and contains the mechanism of structural arrest. If one replaces the memory function by the result for the ideal-glass regime of the original MCT, namely $m(z) = m_f/s$, where m_f is the long-time limit of the memory function, which can be identified with the shear modulus of the glass [31, 32], one arrives at Maxwell's conjecture (3).

On the other hand, there is nowadays ample evidence, in particular from molecular-dynamics simulations, that near T_g the local re-arrangements exhibits a strong spatial heterogeneity [25, 33, 34]. (*dynamical heterogeneity*).

There are presently continuous efforts to formulate a theory of the glass transition which combines dynamical heterogeneity and the mode-coupling scenario [24, 25, 35–40]. These theories make contact to former spin-glass theories and the related replica formalism. In particular aspects of dynamical heterogeneity have been recently attempted to be incorporated into MCT by treating it as a Landau-type mean-field approximation within the replica approach and introducing the Gaussian fluctuations beyond the mean-field saddle point [41–44].

The idea of heterogeneity of relaxation processes has been also developed together with the concept of a very ragged free-energy landscape in configuration space, in which the glassy relaxation is considered to take place [18, 45–47].

In many publications dealing with dielectric and mechanic loss measurements [48–51] one quantifies the ideas of dynamic heterogeneity and ragged free-energy landscape to assume that the Maxwell-type relaxation processes may take place independently and one would be allowed to take the average over a distribution of relaxation barriers E_i or relaxation times $\tau = \tau_0 e^{E_i/k_B T}$,

$$G''(\omega) = G_\infty \int d\tau g(\tau) \frac{\omega\tau}{1 + (\omega\tau)^2}. \quad (6)$$

Many authors, e. g. Goldstein [45] and Palmer et al. [52], however, point out that near the glass transition relaxation processes are highly cooperative and are likely to involve more events that occur in series than in parallel. In fact, it is known [53], that spatially heterogeneous transport is neither well described by a parallel nor serial equivalent circuit. This is so, because the currents seek the path of least resistance, which, in the strong-disorder limit, amounts to a percolation problem, which is well described by coherent-potential and effective medium approximations [53–56].

The phenomenon of dynamic heterogeneity in glass-forming materials is paralleled by the observation that in the high-viscosity/glassy regime the local elastic moduli also exhibit spatial heterogeneities [57–64] (*elastic heterogeneity*). These, in turn, can be shown to be responsible for vibrational anomalies, which trade under the name “boson peak” [56, 60, 65–70]. Quite recently, the present authors have demonstrated [71], that the two types of dynamic heterogeneities can be reconciled within the same theoretical framework, namely the coherent-potential approximation (CPA) [56], applied to spatially inhomogeneous viscoelasticity. In the present contribution we review this theory and, in particular, show, how it can be generalized to include also secondary relaxation.

In the next section a derivation of the CPA for a spatially fluctuating viscosity is derived. In section III. the heterogeneous model is introduced and solved. The consequences for the alpha and beta relaxation and the $\omega = 0$

viscosity are demonstrated and discussed. The paper is finished by some conclusions.

II. DERIVATION OF A CPA FOR A SPATIALLY FLUCTUATING VISCOSITY

This derivation follows closely the derivation of the CPA for heterogeneous-elasticity theory, i.e. elasticity theory with spatially fluctuating elastic coefficients [56].

We consider a heterogeneous viscous liquid in which the viscosity has different values at different locations in space, $\eta \rightarrow \eta(\mathbf{r})$ which are assumed to fluctuate according to a given distribution $P[\eta(\mathbf{r})]$. Representing the pressure term as usual in terms of the compressibility K , the linearized Navier-Stokes equations in frequency space take the form [72, 73] ($s = -i\omega + \epsilon$):

$$s\rho_m v_\ell(\mathbf{r}, s) = \sum_m \left(\frac{K}{s} \partial_\ell \partial_m v_m(\mathbf{r}, s) + 2\partial_m \eta(\mathbf{r}) \hat{V}_{\ell m}(\mathbf{r}, s) \right) \quad (7)$$

where ρ_m is the mass density and $\partial_\ell \equiv \partial/\partial x_\ell$. $v_\ell(\mathbf{r}, s)$ are the Cartesian coefficients of the Eulerian velocity field, and \hat{V} is the traceless shear strain rate tensor $\hat{V}_{\ell m} = \mathcal{V}_{\ell m} - \frac{1}{3} \text{tr}\{\mathcal{V}\delta_{\ell m}\}$ with $\mathcal{V}_{\ell m} = \frac{1}{2}(\partial_\ell v_m + \partial_m v_\ell)$.

We can cast this set of equations into the form

$$0 = \sum_m A_{\ell m}[\eta] \quad (8)$$

where the linear operator $A[\eta]$ has the matrix elements

$$\langle \mathbf{r} | A[\eta] | \mathbf{r}' \rangle_{\ell m} = A_{\ell m}[\eta] \delta(\mathbf{r} - \mathbf{r}') \quad (9)$$

with

$$A_{\ell m} = s\delta_{\ell m} - \frac{1}{\rho_m} \left(\frac{K}{s} \partial_\ell \partial_m - \frac{2}{3} \partial_\ell \eta(\mathbf{r}) \partial_m + \partial_m \eta(\mathbf{r}) \partial_\ell + \delta_{\ell m} \sum_n \partial_n \eta(\mathbf{r}) \partial_n \right) \quad (10)$$

A is the inverse of the resolvent operator of the linear stochastic equations (7). Correspondingly, the matrix of Green's function [87] is given by

$$\mathbf{G}(\mathbf{r}, \mathbf{r}')_{\ell m} = \langle \mathbf{r} | A^{-1}[\eta] | \mathbf{r}' \rangle_{\ell m} \quad (11)$$

This matrix can be represented as a functional integral over mutually complex-conjugate vector fields [56, 74] $v_\ell^\alpha(\mathbf{r})$, $\bar{v}_m^\alpha(\mathbf{r})$ in n replicas of the system [88] ($\alpha = 1, \dots, n$) as

$$\mathbf{G}(\mathbf{r}, \mathbf{r}')_{\ell m} = \prod_{\alpha=1}^n \prod_{\mu\nu} \int \mathcal{D}[\bar{v}_\mu^\alpha(\mathbf{r}), v_\nu^\alpha(\mathbf{r})] \bar{v}_\ell^1(\mathbf{r}) v_m^1(\mathbf{r}') - \sum_{\mathbf{e}} \langle \mathbf{v}^\alpha | A | \mathbf{v}^\alpha \rangle \quad (12)$$

$$= \frac{\delta}{\delta J_{\ell m}^{(1)}(\mathbf{r}, \mathbf{r}')} \mathcal{Z}[J(\mathbf{r}, \mathbf{r}')] \Big|_{J=0} \quad (13)$$

Here we have defined a generating functional

$$\mathcal{Z}[J(\mathbf{r}, \mathbf{r}')] = \prod_{\alpha=1}^n \prod_{\ell m} \int \mathcal{D}[\bar{v}_\ell^\alpha(\mathbf{r}), v_m^\alpha(\mathbf{r})] - \sum_{\mathbf{e}} \langle \mathbf{v}^\alpha | A | \mathbf{v}^\alpha \rangle - \sum_{\mathbf{e}} \langle \mathbf{v}^\alpha | J^\alpha | \mathbf{v}^\alpha \rangle \quad (14)$$

with source-field matrices $J_{\ell m}^\alpha(\mathbf{r}, \mathbf{r}')$. The operator A can now be identified as the action of a Gaussian field theory. Its matrix element can be cast into the form

$$\langle \mathbf{v}^\alpha | A | \mathbf{v}^\alpha \rangle = \int d^3 \mathbf{r} \frac{1}{\rho_m} \left(s \sum_\ell |v_\ell^\alpha(\mathbf{r})|^2 + \frac{1}{2s} K \text{tr}\{\mathcal{V}^\alpha(\mathbf{r})\}^2 + \eta(\mathbf{r}) \sum_{\ell m} |\hat{V}_{\ell m}^\alpha(\mathbf{r})|^2 \right) \quad (15)$$

where the trace tr runs over the Cartesian indices. We now apply a procedure common in deriving effective field theories (Fadeev-Popov method [75]). First we replace the fluctuating viscosity $\eta(\mathbf{r})$ by a "place-holder" field $Q^{(\alpha)}(\mathbf{r}, s)$ with the help of a functional delta function. The latter is then, in turn, expressed as a functional integral over a second auxiliary field $\Lambda^{(\alpha)}(\mathbf{r}, s)$:

$$\begin{aligned} \mathcal{Z}[J] &= \int \mathcal{D}[\mathbf{v}, \bar{\mathbf{v}}] \int \mathcal{D}[Q] e^{-\langle \mathbf{v} | A[Q] - J | \mathbf{v} \rangle} \delta[\eta - Q] \\ &= \int \mathcal{D}[\mathbf{v}, \bar{\mathbf{v}}] \mathcal{D}[Q, \Lambda] e^{-\langle \mathbf{v} | A[Q] - J | \mathbf{v} \rangle} e^{\langle \Lambda | \eta - Q \rangle} \\ &= \int \mathcal{D}[Q, \Lambda] e^{-\text{Tr}\{\ln[\mathcal{A}[Q] - J]\}} e^{\langle \Lambda | \eta - Q \rangle} \end{aligned} \quad (16)$$

In this expression we have suppressed the replica indices for brevity. In the third line of Eq. (16) we have integrated out the original velocity fields $\bar{\mathbf{v}}^\alpha$ and \mathbf{v}^α . This can be done, because the functional integral in the second line is just a Gaussian. The trace Tr has to be taken over the continuous spatial variables, the Cartesian indices and the replica indices.

We now follow Köhler et al. [56] in coarse-graining our system of volume V into $N_c = V/V_c$ cells of diameter ξ and volume $V_c = \xi^3$, which is the correlation length of the fluctuations $\Delta\eta(\mathbf{r}) = \eta(\mathbf{r}) - \langle \eta \rangle$, defined by

$$\xi^3 = \frac{1}{\langle \eta^2 \rangle} \int d^3 \mathbf{r} \langle \Delta\eta(\mathbf{r} + \mathbf{r}_0) \Delta\eta(\mathbf{r}_0) \rangle \quad (17)$$

The fluctuating field $\eta(\mathbf{r})$ is then averaged over a given cell with label i , which gives a value η_i , which still fluctuates from cell to cell. The statistical fluctuations of these values can now be assumed to be uncorrelated, i.e.

$$P(\eta_1 \dots \eta_i \dots \eta_{N_c}) = \prod_{i=1}^{N_c} p(\eta_i) \quad (18)$$

We now associate with all fields discretized numbers corresponding to the center vectors \mathbf{r}_i of the cells: $\Lambda^{(\alpha)}(\mathbf{r}) \rightarrow$

$\Lambda_i^{(\alpha)}$ and $Q^{(\alpha)}(\mathbf{r}) \rightarrow Q_i^{(\alpha)}$. Using this the scalar product, which appears in the exponential in Eq. (16), can be written as:

$$\langle e^{\Lambda|\eta-Q} \rangle = \frac{V_c}{V} \sum_{\alpha} \sum_i \Lambda_i^{(\alpha)}(\mathbf{r}) \left(\eta_i^{(\alpha)} - Q_i^{(\alpha)} \right) \quad (19)$$

We now start to evaluate the configurational average. Due to the Fadeev-Popov transformation the only term to be averaged over is the term $e^{\langle \Lambda|\eta-Q \rangle}$.

Assuming that all the N_c coarse-graining cubes behave the same on average and using that the individual cubes are not correlated, we can write

$$\begin{aligned} \langle e^{\langle \Lambda|\eta-Q \rangle} \rangle &= \prod_{\alpha} \prod_i \left\langle e^{\frac{V_c}{V} \Lambda_i^{(\alpha)} (\eta_i^{(\alpha)} - Q_i^{(\alpha)})} \right\rangle_i \\ &= e^{\sum_{\alpha} \frac{V_c}{V} \ln \left(\left\langle \exp \left[-\frac{V_c}{V} \Lambda_i^{(\alpha)} (\eta_i^{(\alpha)} - Q_i^{(\alpha)}) \right] \right\rangle_i \right)} \quad (20) \end{aligned}$$

Note that the two occurring volume ratios do not cancel each other due to the average inside the logarithm. Using (20) the generating functional (16) can be written as

$$\mathcal{Z}[\tilde{J}] = \int \mathcal{D}[Q, \Lambda] e^{-S_{\text{eff}}[Q, \Lambda, \tilde{J}]} \quad (21)$$

where we have now replaced the source field matrix $J^{\alpha}(\mathbf{r}, \mathbf{r}')$ by translational-invariant one $\tilde{J}(\mathbf{r} - \mathbf{r}')$, which is not supposed to depend on the replica index α . The effective action takes the form

$$\begin{aligned} S_{\text{eff}}[Q, \Lambda, \tilde{J}] &= \text{Tr} \{ \ln (\mathcal{A}[Q] - \tilde{J}) \} \\ &\quad - \sum_{\alpha=1}^n \frac{V}{V_c} \ln \left(\left\langle e^{-\frac{V_c}{V} \Lambda_i^{(\alpha)} (\eta_i^{(\alpha)} - Q_i^{(\alpha)})} \right\rangle_i \right) \quad (22) \end{aligned}$$

Since the factor $\frac{V}{V_c}$ in the effective action (22) is much larger than unity a saddle point approximation can be employed to evaluate the integral in (21).

We now assume the ‘‘fields $Q_i^{(\alpha)}$ and $\Lambda_i^{(\alpha)}$ to be the same in all replicas. Varying the effective action with respect to the fields $Q_{i,s}$ and $\Lambda_{i,s}$ yields the following equation for the saddle-point quantities $Q_{i,s}^{(\alpha)}$ and $\Lambda_{i,s}^{(\alpha)}$:

$$0 = \frac{\left\langle -\frac{V_c}{V} \Lambda_{i,s}^{(\alpha)} (\eta_i - Q_{i,s}) e^{-\frac{V_c}{V} \Lambda_{i,s} (\eta_i - Q_{i,s})} \right\rangle_i}{\left\langle e^{-\frac{V_c}{V} \Lambda_{i,s} (\eta_i - Q_{i,s})} \right\rangle_i},$$

from which follows

$$0 = \left\langle \frac{\eta_i - Q_{i,s}}{\exp \left[\frac{V_c}{V} \Lambda_{i,s} (\eta_i - Q_{i,s}) \right]} \right\rangle_i \quad (23)$$

Since $\frac{V_c}{V} \ll 1$ the exponential in the denominator can be expanded to first order:

$$0 = \left\langle \frac{\eta_i - Q_{i,s}}{1 + \frac{V_c}{V} (\eta_i - Q_{i,s}) \Lambda_{i,s}} \right\rangle_i \quad (24a)$$

The second saddle point equation gives

$$\begin{aligned} \frac{\partial \text{tr} \{ \ln [\mathcal{A}(Q)] \}}{\partial Q_i} \Big|_{Q_i=Q_{i,s}} &= \frac{\frac{V_c}{V} \Lambda_{i,s} \left\langle e^{-\frac{V_c}{V} \Lambda_{i,s} (\eta_i - Q_{i,s})} \right\rangle_i}{\left\langle e^{-\frac{V_c}{V} \Lambda_{i,s} (\eta_i - Q_{i,s})} \right\rangle_i} \\ &= \frac{V_c}{V} \Lambda_{i,s} \quad (24b) \end{aligned}$$

The left-hand side can be evaluated under the assumption that the saddle point field Q_s is constant in space, i.e. $Q_{i,s} \equiv Q$ for all i . This corresponds to the introduction of an effective homogeneous medium in which

$$Q(s) = \eta(s) = G(s)/s \quad (25)$$

As in all effective-medium theories the effective medium is identified with the real medium, in which $\eta(s)$ is the macroscopic frequency-dependent viscosity and $G(s)$ the corresponding macroscopic shear modulus.

The homogeneous Matrix $A[Q]$ is both diagonal in the Cartesian indices and with respect to the \mathbf{k} vectors in \mathbf{k} space. The three diagonal elements (in Cartesian space) are the inverse longitudinal and transverse Green’s functions of the effective medium $1/G_L(\mathbf{k}, s)$ and (two entries) $1/G_T(\mathbf{k}, s)$, which are given by

$$1/G_L(\mathbf{k}, s) = s + \frac{1}{\rho_m} k^2 \left(\frac{K}{s} + \frac{4}{3} Q(s) \right) \quad (26a)$$

$$1/G_T(\mathbf{k}, s) = s + \frac{1}{\rho_m} k^2 Q(s) \quad (26b)$$

Defining a new field (‘‘susceptibility function’’) $\tilde{\Lambda}(s) = 3V_c/\tilde{\nu}V\Lambda(s)$ with $\tilde{\nu} = \nu^3/2\pi^2$ the CPA equations (24a) and (24b) become:

$$0 = \left\langle \frac{\eta_i - Q(s)}{1 + \frac{\tilde{\nu}}{3} (\eta_i - Q(s)) \tilde{\Lambda}(s)} \right\rangle_i \quad (27a)$$

$$\tilde{\Lambda}(s) = \frac{3}{k_{\xi}^3} \int_0^{k_{\xi}} dk k^4 \frac{1}{\rho_m} \left(\frac{4}{3} G_L(k, s) + 2G_T(k, s) \right) \quad (27b)$$

It is easily shown that the CPA equation (27a) is equivalent to the following equations

$$Q(s) = \left\langle \frac{\eta_i}{1 + \frac{\tilde{\nu}}{3} (\eta_i - Q(s)) \tilde{\Lambda}(s)} \right\rangle_i \quad (28a)$$

$$1 = \left\langle \frac{1}{1 + \frac{\tilde{\nu}}{3} (\eta_i - Q(s)) \tilde{\Lambda}(s)} \right\rangle_i \quad (28b)$$

For frequencies, which are much smaller than those, in which the inertial term in the Navier-Stokes equation (7) is important (at GHz frequencies and above) the susceptibility function $\tilde{\Lambda}(s)$ can be replaced by its low-frequency limit

$$\tilde{\Lambda}(s) \xrightarrow{s \rightarrow 0} \frac{2}{Q(s)} \quad (29)$$

III. HETEROGENEOUS-VISCOELASTICITY THEORY

A. Model

We now consider a heterogeneous viscoelastic model, in which equation (3) holds locally with both spatially fluctuating viscosity and shear modulus

$$\frac{1}{\eta_{\text{eff}}(\mathbf{r}, s)} = \frac{1}{\eta(\mathbf{r})} + \frac{s}{G(\mathbf{r})} \quad (30)$$

The local viscosity is assumed to be governed by a local free energy $\ln[\eta(\mathbf{r})/\eta_0] = F(\mathbf{r})/k_B T$ with $F(\mathbf{r}) = E(\mathbf{r}) - TS(\mathbf{r})$. E is the local energy barrier and S is a multi-excitation entropy [76, 77], which is related to E by a compensation (Meyer-Neldel) rule [76–79] $S(\mathbf{r})/k_B = \alpha E(\mathbf{r})$, so that we have $\eta(\mathbf{r}) = \eta_0 e^{\beta_{\text{eff}} E(\mathbf{r})}$ with $\beta_{\text{eff}} = [k_B T]^{-1} - \alpha$. The activation barrier, in turn, is assumed [10, 13] to be related by $E(\mathbf{r}) = VG(\mathbf{r})$ to the local high-frequency shear modulus, where V is an activation volume.

Taking (29) into account the CPA equation (28a) becomes

$$Q(s) \equiv \eta(s) = \left\langle \frac{\eta_{\text{eff}}^{(i)}}{1 - \frac{2\tilde{\nu}}{3} + \frac{2\tilde{\nu}}{3} \eta_{\text{eff}}^{(i)}/\eta(s)} \right\rangle_{P(E)} \quad (31)$$

where $\langle \dots \rangle_{P(E)}$ denotes an average over the distribution $P(E)$ of activation energies E . The explicit form of the local Maxwellian viscosity is

$$\frac{1}{\eta_{\text{eff}}^{(i)}(s)} = \frac{1}{\eta_{\text{eff}}(E, s)} = \frac{1}{\eta_0} e^{-\beta_{\text{eff}} E} + \frac{sV}{E} \quad (32)$$

In contrast to the local viscosity, which is, together with the distribution $P(E)$ the *input* to the CPA calculation, $Q(s) \equiv \eta(s)$ is the macroscopic frequency-dependent viscosity, which is the *output* of the calculation. The macroscopic viscosity is related to the macroscopic frequency-dependent shear modulus by

$$s\eta(s) = G(s) = G'(\omega) - iG''(\omega) \quad (33)$$

where $G''(\omega)$ is the mechanical loss function.

In the present treatment we use for $P(E)$ a single Gaussian (α relaxation) and a superposition of two Gaussians (β relaxation). We cut off $P(E)$ at $E = 0$, i.e. $P(E) = 0$ for $E < 0$.

We emphasize that in the very high frequency regime, where the full susceptibility function $\tilde{\Lambda}(s)$, Eq. (27b) has to be taken and where viscous effects become irrelevant, our theory reduces to heterogeneous elasticity theory, which describes the high-frequency anomalies associated with the boson peak [56, 60, 65–70]. This means that the present theory describes both dynamical and vibrational heterogeneities.

B. The case $\omega = 0$ and the Stokes-Einstein violation

As we want to compare in the following the behavior of the heterogeneous viscosity with diffusive single-particle motion in the same energy landscape, (heterogeneous diffusivity) in the $\omega = 0$ limit, we quote the CPA equations for this problem from Köhler et al. [56]:

$$D(s) = \left\langle \frac{D^{(i)}}{1 + \frac{\tilde{\nu}}{3} (D^{(i)}(s) - D(s)) \Lambda_D(s)} \right\rangle_i \quad (34)$$

with $\Lambda_D(s) = \frac{3}{k_B^2} \int_0^{k_B s} dk k^4 [s + D(s)k^2]^{-1}$. Here $D(s)$ is the dynamic diffusivity and $D^{(i)} = D_0 e^{-\beta_{\text{eff}, D} E^{(i)}}$ are the local diffusivities with $\beta_{\text{eff}, D} = [k_B T]^{-1} - \alpha_D$ [89]

In the $s = 0$ limit $\Lambda_D \rightarrow 1/D(s=0) \equiv 1/D$, and we obtain for the $\omega = 0$ diffusivity the CPA equation

$$\frac{\tilde{\nu}}{3} = \int_0^\infty dEP(E) \frac{1}{\left(\frac{3}{\tilde{\nu}} - 1\right) \frac{D}{D^{(i)}} + 1} \quad (35a)$$

For the viscosity $\eta = Q(0)$, on the other hand, we obtain from (31)

$$\frac{2\tilde{\nu}}{3} = \int_0^\infty dEP(E) \frac{1}{\left(\frac{3}{2\tilde{\nu}} - 1\right) \frac{\eta}{\eta^{(i)}} + 1} \quad (35b)$$

If the macroscopic viscosity and diffusivity are parametrized as $\eta \propto e^{\beta_{\text{eff}} E_A}$, $D \propto e^{-\beta_{\text{eff}, D} E_{A, D}}$, the integrands in Eqs. (35a) and (35b) become step functions $\theta(E - E_A)$ and $\theta(E_{A, D} - E)$, resp. in the low-temperature limit, and we arrive at

$$1 - \frac{2\tilde{\nu}}{3} = \int_0^{E_A} dEP(E) \quad \frac{\tilde{\nu}}{3} = \int_0^{E_{A, D}} dEP(E) \quad (36)$$

This means that (within CPA) both the diffusivity and viscosity with spatially fluctuating activation energies acquire an Arrhenius behavior, independently of the details of $P(E)$. This result is well known for the diffusivity and (for charged carries) conductivity in disordered materials [56, 80]. It reflects the fact that the carrier look for a path of minimum resistance through the material, which is a percolation path. In the percolation theory of hopping conduction [80] the number $\tilde{\nu}/3$ is the continuum percolation threshold, which we now call p_D . The analogous quantity for the viscosity is $p_\eta = 1 - 2p_D$, where the factor 2 can be traced back to the two transverse cartesian

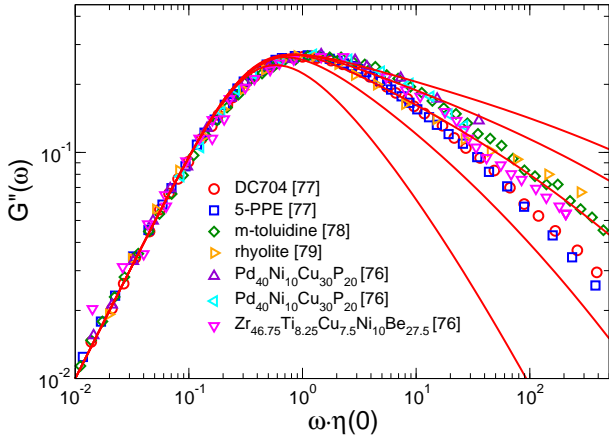


FIG. 1: Mechanical loss curves $G''(\omega) = \omega\eta'(\omega)$ vs. $\omega\eta(0)$ for fixed inverse temperature $\beta_{\text{eff}}E_1 = 26$, calculated in CPA according to Eq. (37) with a single Gaussian distribution with widths σ varied from 0.1 to 0.3 in steps of 0.05. The experimental data (symbols) are from metallic, organic and inorganic glasses [81–84].

degrees of freedom of the shear motion [56]. So we note the result that except for the special case $p_D = 1/3$ the activation energy for diffusion and viscosity should be different. The explanation is that the percolation process for a single-particle and cooperative motion in three dimension is different. If we take for $p_D = \tilde{\nu}/3$ the three-dimensional continuum percolation threshold ≈ 0.3 we arrive at $p_\eta = 1 - 2p_D = 0.4$. Using Eqs. (36) we arrive for a Gaussian distribution centered at E_1 with width parameter $\sigma/E_1 = 0.3$ at $E_{A,D}/E_1 = 0.843$ and $E_A/E_1 = 0.925$, i.e. the ratio is $E_{A,D}/E_A = 0.91$. This ratio (Einstein-violation parameter) depends on dimensionality through p_D , but it is non-universal, as it depends on (and becomes smaller with) the shape of the distribution.

All the above considerations assume that the energy distribution for the local diffusion coefficient is the same as that for the local viscosity, i.e. that locally the Einstein relation holds. Especially in materials consisting of several diffusing species - like metallic and ionic glasses - this assumption is certainly unjustified. It would be much more plausible to take the small-energy Gaussian, responsible for the beta relaxation, as that distribution for the diffusion. This would be in agreement with experimental findings relating the beta energy scale with that of the diffusion in metallic glasses [20].

C. Alpha relaxation

We turn now to the frequency dependence of the viscosity, as predicted by our theory of heterogeneous viscoelasticity. We can reformulate the CPA equation (31) in terms of the dimensionless viscosity $\eta(s)/\eta(0)$

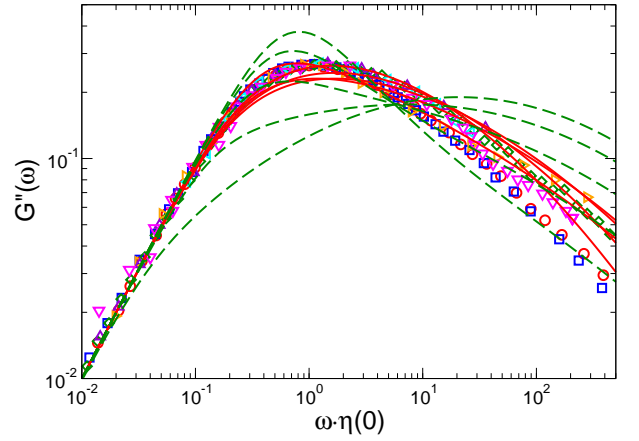


FIG. 2: Mechanical loss curves $G''(\omega) = \omega\eta'(\omega)$ vs. $\omega\eta(0)$ for inverse effective temperatures $\beta_{\text{eff}}E_1 = 16, 18, 20, 22, 24$, calculated in CPA, Eq. (37) for a Gaussian distribution of width $\sigma = 0.25$, (straight lines) and in VCA, Eq. (38), (dashed lines). The symbols denote the same experimental data as in Fig. 1.

as follows:

$$\frac{\eta(s)}{\eta(0)} = \left\langle \frac{1}{q_\eta \left(e^{\beta_{\text{eff}}(E_A - E)} + \frac{sV\eta(0)}{E} \right) + p_\eta \frac{\eta(0)}{\eta(s)} } \right\rangle_{P(E)} \quad (37)$$

with $p_\eta = \frac{2\tilde{\nu}}{3}$ and $q_\eta = 1 - p_\eta$. It can be seen from this representation that the strongest contribution to the integral comes from the energy $E \approx E_A$, so that effectively the function $\eta(s)/\eta(0)$ is approximately a universal function of the scaled frequency parameter $sV\eta(0)/E_A \approx sV\eta(0)/E_1$, where E_1 is the peak energy of the principal Gaussian (for $E_A \approx E_1$ see section E). This quasi-universality is inherited by the loss function $G''(\omega) \propto \omega\eta(0) \cdot \eta'(\omega)/\eta(0) = \omega\eta'(\omega)$. In all our calculations we measure viscosities in units of η_0 , mechanical loss functions in units of E_1/η_0 and frequencies in units of $E_1/V\eta_0$. The activation volume obviously enters only into the frequency scale.

In Fig. 1 we show the result of CPA calculations for a Gaussian distribution of activation energies with varying width σ together with a number of measured mechanical-loss spectra. [81–84][90]. A very important point is that the left wing of the alpha relaxation spectra is given by $G''(\omega) = \omega\eta(0)$. Because previously there was no proper theory for calculating the $\omega = 0$ value of the viscosity, efforts to describe the alpha maximum in terms of a distribution of activation energies have rested on shaky grounds.

Near the alpha peak the frequency dependence of $\eta(s)$ starts to be effective, which causes the strong asymmetry of the alpha relaxation spectrum. We see from Fig. 1 that for the chosen value of the inverse effective temperature $\beta_{\text{eff}}E_1 = 24$ the CPA curves for a width parameter $\sigma/E_1 = 0.2$ fits the data best.

It is of interest to compare our CPA calculation with

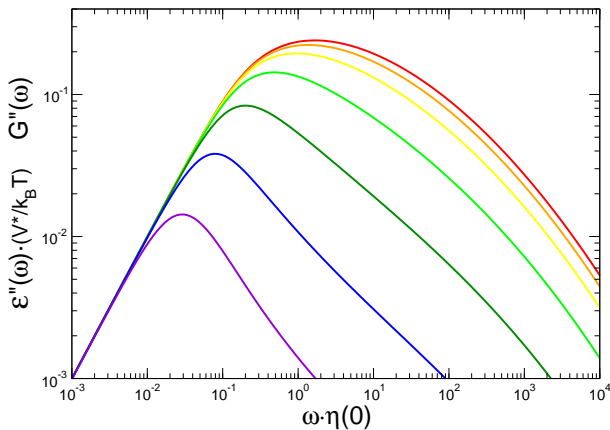


FIG. 3: Dielectric loss spectra calculated by means of the Gemant-DiMarzio formula (39) from $\eta(s)$ data calculated in CPA with $\beta_{\text{eff}} E_1 = 15$ and $\sigma/E_1 = 0.25$ and the Gemant-DiMarzio parameter $V^*/k_B T$ varied by decades (top to bottom) from 10^{-1} to 10^5 . The very top (red) line is the mechanical loss function $G''(\omega)$.

the previously used procedure (Eq. (6)) of averaging the local viscosities. In the theory of disordered systems this amounts to averaging over the Hamiltonian and has been called virtual-crystal approximation (VCA). If the self-consistent term in the denominator of (31) is omitted, one obtains

$$Q(s) = \left\langle \eta_{\text{eff}}^{(i)}(s) \right\rangle, \quad (38)$$

which is just the same as (6), except for the fact that in our model G_∞ is also assumed to fluctuate.

In Fig. 2 we compare the CPA calculations for different inverse effective temperatures with VCA calculations using (38). It is clearly seen that the approximate time-temperature scaling of the alpha peak, which is obeyed in CPA, is not reproduced in VCA. This can be traced again to the fact that the $\omega = 0$ value of the viscosity in VCA, which corresponds to a parallel-circuit formula is not correct, because it does not recognize the percolation aspects of the viscous currents. On the other hand, at frequencies much higher than that of the alpha relaxation peak, the percolation aspects lose their importance, because at these frequencies the viscous flow is an alternating one, probing only relaxational transitions to adjacent free-energy minima. In this frequency regime - as we will see in the paragraph on beta relaxation - the CPA approximately becomes equalent to the VCA, which means that the VCA and the corresponding expressions (6), (38) are justified in the high-frequency/low-temperature regime.

D. Dielectric relaxation

As noted in the introduction the peaks of dielectric loss data in glass-forming materials follow precisely the

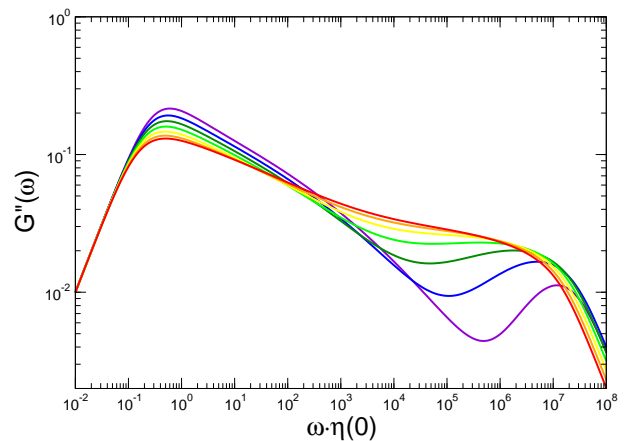


FIG. 4: Mechanical loss spectra for a distribution $P(E)$ with two Gaussians of weight $x_1 = 0.8$ and $x_2 = 0.2$ centered at $E_1 \equiv 1$ and $E_2/E_1 = 0.1$. The width of the high-energy peak is $\sigma_1/E_1 = 0.25$. The widths σ_2/E_1 of the second, low-energy peak is varied (from bottom to top) from 0.05 to 0.35 in equal steps of 0.05. The effective inverse temperature is set $\beta_{\text{eff}} E_1 = 25$.

inverse viscosity, and hence the peaks of the mechanical loss data. It has been noted, however that the shape of the loss curves are not the same [16, 17]. However, according to Gemant [14], DiMarzio and Bishop [15] and Niss et al. [16] they can be related to each other by

$$\epsilon''(\omega) = \text{Im} \left\{ \frac{1}{1 + \frac{V^*}{k_B T} G(s)} \right\}, \quad (39)$$

where V^* is a microscopic volume. A very similar formula can also be obtained within the mode-coupling formalism, applied to the coupling of special degrees of freedom (in this case the local dipoles) to the bulk relaxing dynamic variables [27, 85, 86], assuming that the bulk density fluctuations are essentially frozen.

In Fig. 3 we show the result for the dielectric loss for different values of the coefficient $V^*/k_B T$. It is seen that with increasing $V^*/k_B T$ the peak is shifted to the left and the stretching of the alpha peak becomes less pronounced. A detailed discussion of (39) can be found in the paper by Niss et al. [16].

E. Beta relaxation

As noted by Johari and Goldstein [18] and many authors later [19, 20] there exists a relaxation regime at the high-frequency and low-temperature side of the alpha-relaxation peak, which is sometime a peak, sometime a shoulder and sometime just a wing. This part of the energy spectrum has been reported [20] to be related to the glassy, i.e. solid-like yield dynamics.

We attempted to include this by adding a second Gaussian to the primary Gaussian, which describes the alpha

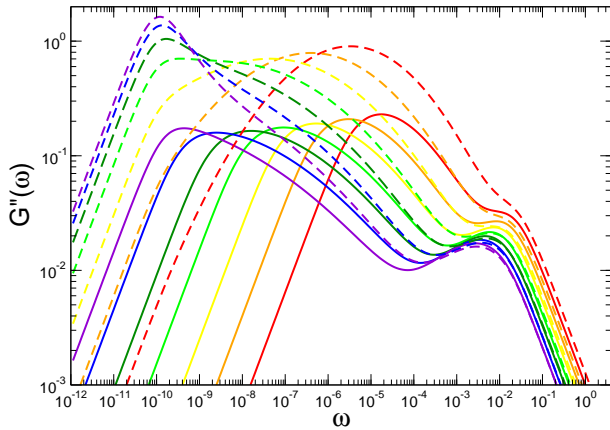


FIG. 5: Mechanical loss spectra for a two-Gaussian distribution $P(E)$ as in Fig. 4 calculated in CPA (31) and VCA (38). The parameters are the same as in Fig. 4 except that the inverse effective temperature is varied between $\beta_{\text{eff}}E_1 = 12$ and 24, and the width of the low-energy Gaussian is fixed to be $\sigma_2/E_1 = 0.1$. Note that the frequency axis is *not* scaled with the $\omega = 0$ viscosity.

relaxation, but with much lower center. The distribution is truncated at $E = 0$. Therefore with increasing width of the second Gaussian the latter becomes an almost constant wing on the low-energy side of the primary Gaussian. From Fig. 4, where we have varied the width of the secondary Gaussian, we see that by doing this we can describe the transition from a beta wing to a beta maximum.

As the beta relaxation is probed at frequencies much higher than the principal alpha peak it is worth while to check, whether in this regime the VCA gives similar results as the CPA. In Fig. 5 we show calculations with two Gaussians in CPA (Eq. (31)) and VCA (Eq. (38))

) for different temperatures and a fixed small width of the low-energy Gaussian. It can be seen that at high frequency the beta peak is reproduced in the VCA, which demonstrates that in the regime much above the alpha peak the VCA indeed agrees to the CPA. It can be shown that in VCA the temperature and/or frequency dependence reflects the underlying barrier distribution $P(E)$ with $E \propto -T \ln \omega$. So the peak at high omega reflects the low-energy peak of $P(E)$. On the other hand, the alpha peak - as discussed above - differs appreciably from the principal maximum of $P(E)$.

IV. CONCLUSION

In conclusion we can state that we have established a theory, which combines a theory for the DC viscosity, low-temperature α and β relaxation and the high-frequency vibrational anomalies within a unified framework. This has been achieved by assuming that the viscous and elastic coefficients of Maxwell's theory of viscoelasticity fluctuate in space according to a frozen distribution of activation barriers. We have found an explanation of the discrepancy of the activation energies for diffusion and viscosity in terms of the different percolative properties of the two heterogeneous transport problems and a theory for the joint alpha and beta relaxation below the glass transition.

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