

## FRactal Approach to Description of Viscoelastic Properties of Liquids in the Region of Transition to the Glassy State

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*Based on the notion of the multifractal nature of liquids in the region of their transition to the glassy state we give a description of viscoelastic properties of the media studied in terms of the dynamic shear modulus and modulus of losses and the coefficient of shear viscosity whose estimate ( $10^{13}$  P) corresponds to a value typical of glass. The relation between the memory function and the Kohlrausch function is found.*

Glass has found wide long-standing use in different branches of technology and science. Much of a substance is capable of being in the glassy state, the transition to which occurs with rather quick cooling of it to a temperature below the temperature of crystallization [1–3]. Due to the relative slowness of the process of crystallization, a liquid does not succeed in crystallization with a sharp decrease in temperature and as a result it passes to the glassy state. The temperature of vitrification depends on the rate of cooling and is a nonequilibrium parameter of a substance. In this state, the medium is an amorphous solid body with a nonequilibrium disordered structure where a long-range order is absent. The medium is capable of elastic reaction to slow shear deformation and thus possesses a nonzero shear modulus which is typical of solids [1, 4].

In the glassy state of substances, the density profile in the bulk phase is not plane, as in liquids, but has a certain number of peaks. In contrast to crystals, these peaks are not localized at the nodes of a certain periodic or quasiperiodic lattice but are randomly distributed. Relaxation to uniform density distribution occurs so slowly that it becomes unobservable. Transition to the crystalline state is also a rather lengthy process [5].

A strict theory of the glassy state has not been developed as yet, and it is doubtful whether it can be constructed in future [5].

The presented characteristics of the glassy state of a substance have a qualitative character; quantitative determination of it is introduced by agreement. The glassy state of a substance is said to be the state for which viscosity is of the order of  $10^{13}$  P or the characteristic time of relaxation reaches  $10^3$  sec [1, 4].

Since the glassy state is nonequilibrium, employment of equilibrium thermodynamics for describing it faces serious problems, and here the questions are greater in number than the answers to them (see, e.g., [6]).

The nonuniform density distribution in the form of random position of points of localization of particles and the appearance of clusters and fluctuating microvoids indicate that glass has a complex fractal structure. Glass is most likely a multifractal which is characterized by many fractal dimensions rather than one.

The objective of the paper is to describe viscoelastic properties of substances in the region of their transition to the glassy state on the basis of notions about the fractal structure of glass.

Since the glassy state of a substance is nonequilibrium, to describe it we shall use the notions and terms of nonequilibrium thermodynamics. In what follows, we study the viscoelastic properties of substances, which are characterized by the dynamic shear modulus and the modulus of losses at a certain frequency  $\omega$ . By virtue of the fact that glass has a fractal structure, in description of nonequilibrium processes in it it is natural to use a mathematical apparatus of fractional derivatives and integrals [7, 8].

Unlike the known works (see, e.g., [9]) where fractional derivatives with a fixed exponent of the fraction are used, in our work, to interpret the experimental data on the dependence of the dynamic shear modulus and the modu-

lus of losses on frequency we employed the notion of the multifractal structure of glass using two fractional exponents of fractal dimensions for different ranges of frequency as an example.

To describe the viscoelastic properties of glass we use the generalized Maxwell model. First, we consider the initial Maxwell model [1], which is represented by an equation which relates the shear stress and shear deformation of the medium:

$$\frac{d\sigma}{dt} + \frac{1}{\tau_0} \sigma = G \frac{d\varepsilon}{dt}. \quad (1)$$

In this case, it is taken into account that in the liquid state the equilibrium shear modulus is zero. The Maxwellian time of relaxation is expressed in terms of low-frequency shear viscosity and high-frequency (instantaneous) shear modulus:

$$\tau_0 = \eta / G. \quad (2)$$

We note that the Maxwell model is equivalent to the exponential representation of the transfer kernel (memory function) in the linear constitutive integral relation which connects stress and deformation:

$$\sigma(t) = \int_{-\infty}^t L(t-t') \frac{d\varepsilon(t')}{dt'} dt', \quad (3)$$

$$L(t-t') = G \exp(t-t')/\tau_0. \quad (4)$$

The memory function  $L(t)$  describes relaxation of shear stresses in fixed deformation  $\varepsilon_0 = \text{const}$  ( $d\varepsilon/dt' = \varepsilon_0 \delta(t')$ ). According to (3), in this case,

$$\sigma(t)/\varepsilon_0 = GL(t). \quad (5)$$

Thus, the memory function can be found from the experiments on relaxation of stresses.

To pass over to the equation of the generalized Maxwell model, we substitute ordinary derivatives in (1) by the fractional derivatives  $v(0 \leq v \leq 1)$ . As a result, we find the equation of the generalized Maxwell model

$$\frac{d^v \sigma}{dt^v} + \frac{1}{\tau_0^v} \sigma = G \frac{d^v \varepsilon}{dt^v}. \quad (6)$$

After the Fourier transformation  $\sigma(t) = \int_{-\infty}^{\infty} \sigma(\omega) \exp(i\omega t) dt$ , we find the algebraic equation for the Fourier transforms

$$(i\omega\tau_0)^v \sigma(\omega) + \sigma(\omega) = G (i\omega\tau_0)^v \varepsilon(\omega), \quad (7)$$

which allows one to obtain the following expression for the complex shear modulus:

$$G(\omega) = G \frac{(i\omega\tau_0)^v}{1 + (i\omega\tau_0)^v}. \quad (8)$$

At  $v = 1$ , using (8) as a basis, we find the expression for the shear modulus of the classical Maxwell model.

Having separated the real and imaginary parts in Eq. (8), we find expressions for the dynamic shear modulus and the modulus of losses:

$$G_1(\omega) = G \frac{(\omega\tau_0)^{\nu} \left( \cos \frac{\pi}{2} \nu + (\omega\tau_0)^{\nu} \right)}{1 + (\omega\tau_0)^{2\nu} + 2 (\omega\tau_0)^{\nu} \cos \frac{\pi}{2} \nu}, \quad (9)$$

$$G_2(\omega) = G \frac{(\omega\tau_0)^{\nu} \sin \frac{\pi}{2} \nu}{1 + (\omega\tau_0)^{2\nu} + 2 (\omega\tau_0)^{\nu} \cos \frac{\pi}{2} \nu}. \quad (10)$$

In turn, the dynamic shear viscosity  $\eta(\omega) = G_2(\omega)/\omega$  is determined by the equation

$$\eta(\omega) = \frac{G\tau_0 (\omega\tau_0)^{\nu-1} \sin \frac{\pi}{2} \nu}{1 + (\omega\tau_0)^{2\nu} + 2 (\omega\tau_0)^{\nu} \cos \frac{\pi}{2} \nu}. \quad (11)$$

Based on (9), we determine  $(\omega\tau_0)^{\nu}$  as a function of  $b = G_1(\omega)/G$ , i.e.,

$$(\omega\tau_0)^{\nu} = \frac{c}{2} \left( \frac{b}{1-b} - 1 \right) + \sqrt{\frac{c^2}{4} \left( \frac{b}{1-b} - 1 \right)^2 + \frac{b}{1-b}}, \quad c = \cos \frac{\pi}{2} \nu. \quad (12)$$

The time of relaxation (for a fixed frequency  $\omega$ ) increases sharply in transition to the glassy state. Thus, for relatively low frequencies glass reveals an instantaneous shear elasticity, since, in this case, the inequality  $\omega\tau_0 > 1$  is satisfied at frequencies which are much smaller than the corresponding frequencies for liquids with  $\tau_0 \approx (10^{-10} - 10^{-13})$  sec. Estimates of the time  $\tau_0$  for different types of glass will be given below. Therefore, we can note that instantaneous (high-frequency) shear elasticity for glass manifests itself in the region of low frequencies.

According to experimental data of [1], in the region of transition to the glassy state the value of  $\ln(G_1(\omega)/G)$  increases with a decrease in temperature; therefore, according to (12), in the mentioned region of transition to the glassy state we observe an increase in  $\tau_0$  with a decrease in temperature.

It is of interest to elucidate the physical meaning of the exponent of the fraction  $\nu$ . According to [10], it corresponds to the fraction of the remaining states in the processes of nonequilibrium evolution of the physical system and, thus, is the memory characteristic of the system. Thus, a value of  $\nu = 1$  corresponds to the exponential memory and  $\nu = 0$  describes the Markovian process. It is also of interest that the exponent of the fraction  $\nu$  is closely related to Cantor fractal set, which is determined on the axis of time, and is a fractal dimension of it.

We find the expression for the memory function. For this purpose we rewrite the constitutive equation (3) in the form

$$\sigma(t) = \int_0^{\infty} L(\tau) \frac{d\varepsilon(t-\tau)}{d\tau} d\tau. \quad (13)$$

Assuming  $\varepsilon = \varepsilon_0 \exp(i\omega t)$  and taking into account that  $d\varepsilon/dt = i\omega\varepsilon_0 \exp(i\omega t)$ , based on (13) we find a general expression for the complex shear modulus:

$$G(\omega) = i\omega \int_0^{\infty} d\tau L(\tau) \exp(-i\omega\tau). \quad (14)$$

According to the generalized Maxwell model with a fractional derivative, the shear modulus is determined by relation (8). Equating (14) and (8), we obtain the integral equation for the function of memory

$$i\omega \int_0^{\infty} d\tau L(\tau) \exp(-i\omega\tau) = G (i\omega\tau_0)^{\nu} / (1 + (i\omega\tau_0)^{\nu}). \quad (15)$$

Taking  $i\omega = p$ , we find the expression for the Laplace transform of the function of memory

$$pL(p) = G (p\tau_0)^{\nu} / (1 + (p\tau_0)^{\nu}).$$

Taking into account that

$$1/(1 + (p\tau_0)^{\nu}) = \sum_{n=0}^{\infty} (-1)^n (p\tau_0)^{-(n+1)\nu},$$

we write the expression for the Laplace transform of the sought-for function of memory:

$$L(p) = G\tau_0 \sum_{n=0}^{\infty} (-1)^n (p\tau_0)^{-n\nu-1}.$$

Taking into account that the original  $\Gamma^{-1}(\gamma)r^{\gamma-1}$  corresponds to the Laplace transform  $p^{-\gamma}$ , we find the expression for the function of memory

$$L(t/\tau_0) = G \sum_{n=0}^{\infty} (-1)^n (t/\tau_0)^{n\nu} \Gamma^{-1}(n\nu + 1). \quad (16)$$

Function (16) is known in the literature as the Mittag-Leffler function (see, e.g., [11]). We note that at  $\nu = 1$  expression (16) is reduced to the exponential function of the memory (4).

The Kohlrausch function, which is called the deformed exponent, is used in describing relaxation of stresses in glass and other non-Debye processes of relaxation [1, 12]. It has the following form:

$$K(t/\tau_0) = G \exp(-(t/\tau_0)^{\nu}), \quad 0 \leq \nu \leq 1. \quad (17)$$

If we represent the Kohlrausch function as a series

$$K(t/\tau_0) = G \sum_{n=0}^{\infty} (-1)^n (t/\tau_0)^{n\nu} \Gamma^{-1}(n + 1), \quad (18)$$

we can easily find the relation between the Mittag-Leffler function (16) and the Kohlrausch function (18):

$$L(t/\tau_0) = GK(t/\tau_0) + G \sum_{n=0}^{\infty} (-1)^n (t/\tau_0)^{n\nu} \alpha_{n\nu}, \quad (19)$$

where the quantity  $\alpha_{n\nu} = \Gamma^{-1}(n\nu + 1) - \Gamma^{-1}(n + 1)$  is the difference of the Weierstrass functions, which sharply decreases with an increase in  $n$ . Therefore, an infinite series on the right-hand side of (19) is a rapidly convergent series, i.e., on transition from (16) to (19) the convergence of series (16), which describes the memory function, is improved.

TABLE 1. Viscoelastic Properties of Quartz Glass at  $T = 1449$  K ( $G = 31 \cdot 10^9$  Pa) and Sodium Silicate at  $T = 728$  ( $G = 19 \cdot 10^9$  Pa)

Frequency $\omega$ , $\text{sec}^{-1}$	Quartz glass ( $\text{SiO}_2$ ), $\tau = 51.0$ sec, $\eta = 1.581 \cdot 10^{13}$ Pa·sec			Sodium silicate ( $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ ), $\tau_0 = 14.37$ sec, $\eta = 0.273 \cdot 10^{13}$ Pa·sec		
	$\nu$	$G_1 \cdot 10^{-9}$ , Pa		$\nu$	$G_1 \cdot 10^{-9}$ , Pa	
		experiment	calculation		experiment	calculation
$10^2$	0.3804	28.95	30.00	0.1884	14.11	15.14
10		28.08	28.71		13.89	13.64
1		26.81	26.97		13.33	12.94
1	0.5082	26.81	26.97	0.3616	13.33	12.94
$10^{-1}$		23.40	22.48		11.78	10.18
$10^{-2}$		11.92	12.43		5.56	6.06

In a number of studies [13, 14], attempts were undertaken to physically validate the Kohlrausch function. In our work, based on the fractal approach, we give one more interpretation of the function under consideration as a part of the Mittag-Leffler function of memory which describes retarded non-Debye relaxation.

We note that the process of relaxation in the medium on its approaching the glassy state is not only described by the time of relaxation but is characterized by a certain spectrum of relaxation times [9], whose distribution function, which corresponds to (8), has the form

$$H(\tau/\tau_0) = G \sin \nu\pi / (2\pi [\cosh(\nu \ln(\tau/\tau_0) + \cos \nu\pi)]). \quad (20)$$

On the basis of this formula, the dispersion of  $\ln(\tau/\tau_0)$  is determined as

$$\delta = \pi/\nu \sqrt{(1-\nu^2)/3}, \quad (21)$$

which allows one to estimate the maximum time of relaxation by the relation

$$\tau_{\max} = \tau_0 \exp\left(\frac{\pi}{\nu} \sqrt{(1-\nu^2)/3}\right). \quad (22)$$

We consider the possibility of interpreting experimental data by the frequency dependence of the dynamic shear modulus on the basis of formula (9) for quartz glass (silicon dioxide) and sodium silicate ( $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ ).

In [12], experimental data are given for the frequency range  $10^{-2}$ – $10^2$   $\text{sec}^{-1}$ . In interpreting these data we divide the range into two parts:  $10^{-2}$ – $1$   $\text{sec}^{-1}$  and  $1$ – $10^2$   $\text{sec}^{-1}$ . Using the least-squares method and formula (9), we find  $\nu$  for each of these parts, then we calculate the dynamic shear modulus as a function of frequency. Here,  $\tau_0$  is determined for the entire range of frequencies. Moreover, using the relation  $\eta = G\tau_0$  (see (2)), we estimate the order of magnitude of low-frequency shear viscosity. In Table 1, results of the calculation are compared with experimental data.

In principle, determination of the dependence of the fractal dimension of  $\nu$  on the frequency  $\omega$  allows one to accurately describe the viscoelastic properties of a substance which experiences transition to the glassy state. However, the determination of the dependence mentioned is not an easy task.

The results obtained on viscoelastic properties of liquids is only the first stage of using the notion of the multifractal nature of liquids in the region of their transition to the glassy state. One might expect that the approach suggested can give good results in the theory of other properties of substances which are in the glassy state or experience transition to the state considered.

## NOTATION

$\sigma$ , shear stress, Pa;  $\epsilon$ , shear deformation;  $\epsilon_0$ , amplitude of shear deformation;  $t$ , time, sec;  $G$ , high-frequency (instantaneous) shear modulus, Pa;  $\eta$ , low-frequency value of shear viscosity, Pa·sec;  $\tau_0$ , Maxwellian time of relaxation

(constant of time), sec;  $L$ , kernel of transfer (memory function);  $\nu$ , order of the fractional derivative;  $\omega$ , frequency, 1/sec;  $\delta(t)$ , delta function;  $G(\omega)$ , complex shear modulus, Pa;  $G_1(\omega)$ , dynamic shear modulus, Pa;  $G_2(\omega)$ , modulus of losses, Pa;  $\eta(\omega)$ , dynamic shear viscosity, Pa·sec;  $p$ , parameter of the Laplace transform;  $\Gamma(x)$ , gamma function;  $K(t/\tau_0)$ , Kohlrausch function;  $H(\tau/\tau_0)$ , distribution function of relaxation times;  $\delta$ , dispersion of the quantity  $\ln(\tau/\tau_0)$ ;  $\tau$ , relaxation time, sec;  $i$ , imaginary unit;  $\gamma$ , exponent;  $n$ , number of the term in the series.

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