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New approach in the description of dielectric relaxation phenomenon: correct deduction and interpretation of the Vogel–Fulcher–Tamman equation

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Abstract

Based on the relationship between the power-law exponent and relaxation time $\nu(\tau)$ recently established in Ryabov *et al* (2002 *J. Chem. Phys.* **116** 8610) for non-exponential relaxation in disordered systems and conventional Arrhenius temperature dependence for relaxation time, it becomes possible to derive the empirical *Vogel–Fulcher–Tamman* (VFT) equation $\omega_p(T) = \omega_0 \exp[-DT_{VF}/(T - T_{VF})]$, connecting the maximum of the loss peak with temperature. The fitting parameters D and T_{VF} of this equation are related accordingly with parameters $(\nu_0, \tau_s\tau_0)$, entering to $\nu(\tau) = \nu_0[\ln(\tau/\tau_s)/\ln(\tau/\tau_0)]$ and (τ_A, E) figuring in the Arrhenius formula $\tau(T) = \tau_A \exp(E/T)$. It has been shown that, in order to establish the loss peak VFT dependence, a complex permittivity function should contain at least two relaxation times obeying the Arrhenius formula with two different set of parameters $\tau_{A1,A2}$ and $E_{1,2}$. It has been shown that (1) at a certain combination of initial parameters the parameter T_{VF} can be *negative* or even accept *complex* valued (2). The temperature dependence of the *minimum* frequency formed by the two nearest peaks also obeys the VFT equation with another set of fitting parameters. The available experimental data obtained for different substances confirm the validity and specific 'universality' of the VFT equation. It has been shown that the empirical VFT equation is *approximate* and possible corrections to this equation are found. As a *main* consequence, which follows from the correct 'reading' of the VFT equation and interpretation of complex permittivity functions with two or more characteristic relaxation times, we suggest a new type of kinetic equation containing non-integer (fractional) integrals and derivatives. We suppose that this kinetic equation describes a wide class of dielectric relaxation phenomena taking place in heterogeneous substances.

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1. Introduction and the formulation of the problem

In recent years, dielectric relaxation phenomena in glass-forming systems and similar hydrogen-bonded molecular materials received a lot of attention in both experimental and theoretical aspects [2–9]. The loss-peak angular frequency ω_p is generally temperature-dependent with either a simple activation law of the Arrhenius type or, as is supposed, with some more complicated relationship depending on the type and structural aspects of the dielectric material in question. In glass-forming materials, the loss-peak frequency of the α relaxation process does not follow the classical Arrhenius thermally activated temperature dependence but can be described by the empirical Vogel–Fulcher–Tamman (VFT) equation [6, 7, 8, 10a–10c, 11]. In the literature there are several attempts to explain this. One of the explanations is based on the Adam–Gibbs model of glass transition that assumes the existence of cooperatively rearranging regions. This model was developed in two subsequent papers. The first one, written by Gibbs and DiMarsio [12], considers the glass transition as a reflection of an underlying thermodynamics phase transition. The second one, developed by Adam and Gibbs [13], gives an expression for the relaxation time that contains the excess configurational entropy S_c in the denominator of an exponent:

See endnote 1

$$\tau(T) = \tau_\infty \exp(C/TS_c). \tag{1}$$

The temperature dependence of the configurational entropy, S_c, is calculated from the difference between the heat capacities of the liquid and crystalline states. If the temperature dependence of the configurational entropy, S_c is *assumed* to have the form [14–16]

$$S_c(T) = S_\infty(1 - T_K/T), \tag{2}$$

where the constant S_∞ is the limiting value of $S_c(T \to \infty)$ and T_K is the Kauzmann temperature defined in [17] (T_K is determined by extrapolation of the temperature dependence of excess configurational entropy S_c below T_g and gives the temperature where the configurational entropy would be equal to zero), then inserting this equation (2) into (1) with the assumption $T_K = T_{VF}$ yields the well-known VFT equation. But there are several problems:

(i) Adam–Gibbs theory with assumption (2) can explain the VFT equation only for the range of temperatures $T_g < T < T_B$ which depends on the fragility of the liquid and on the presence of a β relaxation [16] (T_B is defined as an empirical temperature above which the VFT law fails in a description of the experimental data);

(ii) there are some glassy substances for which T_K considerably differs from T_{VF} measured values [14];

(iii) in the Adam–Gibbs theory all cooperative rearrangements are assumed to be *identical* to each other with the same relaxation time. On the other hand, recent experiments have found that the relaxation of the molecules is dynamically heterogeneous [18–21], i.e. *there are fast and slow relaxing molecules and they can reverse their roles*;

(iv) in the Adam–Gibbs theory it was assumed that vibrational entropy of a glass is the *same* as the entropy of its crystalline phase, but, as has been pointed out in [22], it is *not* true.

So there is a problem in overcoming the basic drawbacks of the previous Adam–Gibbs theory or in developing an alternative approach for explanation of the empirical VFT equation. In this paper we give another explanation of the VFT equation and show that this equation, together with its generalized forms, has wider limits of applicability than were expected previously.

As is well known [10a–10c, 23] most of the experimental studies show that the dielectric *ac* response in many glass-forming materials can hardly be explained by the 'classical' Debye dielectric function that gives the complex permittivity $\varepsilon(j\omega)$:

$$\varepsilon(j\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon(0) - \varepsilon_\infty}{1 + j\omega/\omega_p}. \tag{3}$$

Generally, the experimentally observed non-Debye *ac* response of glass-forming hydrogen-bonded substances, as well as that of a variety of solid dielectric materials in a remarkably wide range of frequencies, have been found to exhibit much more broadening in their loss curves and in many cases they suffer from asymmetry. This non-Debye *ac* response can be classically correlated with some distribution of relaxation times quantifiable in terms of purely empirical parameters entering into the phenomenological dielectric functions being proposed to describe such behaviour [10a–10d, 23]. The most conventional empirical analytical dielectric expression that is often used to describe the generalized broadened asymmetric relaxation loss peak observed in many dielectric materials over a wide frequency range is the Havriliak–Negami (HN) equation [10a–10c, 11, 23]:

$$\chi_{HN}(j\omega) = \chi'(\omega) - j\chi''(\omega) = (\varepsilon(j\omega) - \varepsilon_\infty)/\varepsilon_0 = \frac{\varepsilon(0) - \varepsilon_\infty}{[1 + (j\omega/\omega_p)^\nu]^\beta}, \tag{4}$$

where $\chi_{HN}(j\omega)$ is the HN complex susceptibility with the real and imaginary components $\chi(j\omega)$ and $\chi''(j\omega)$, respectively, and $\varepsilon_0 = 8.854 \times 10^{-12}$ F m^{-1} is the permittivity of free space. The parameter ν ($0 < \nu \leqslant 1$) is a measure of the broadness of a symmetric dielectric relaxation curve and β ($0 < \beta \leqslant 1$) is the shape parameter of an asymmetric relaxation curve. The relaxation curve with $\beta = \nu = 1$ corresponds to the 'ideal' Debye-type ac response. When $\beta = 1$, the HN equation reduces to the well-known Cole–Cole (CC) empirical dielectric function. Another non-Debye dielectric behaviour is obtained from the HN expression for $\nu = 1$, which is known as the Cole–Davidson (CD) empirical function. Here, this type of behaviour will be collectively termed the *Debye-type* response [24].

Traditionally, the measured *ac* permittivity-frequency data is interpreted and analysed quantitatively by the use of Debye-type expressions or their linear combinations. To achieve such quantitative permittivity data analysis, some sort of non-linear curve-fitting programs [25] to the model chosen are usually employed. Usually, the use of empirical dielectric expressions is often criticized for they often involve adjustable parameters that are sometimes difficult to justify and understand their physical significance. Moreover, a conventional non-linear curve-fitting method usually results in a best curve fit to the experimental data with a number quantifying how good the fit is and yields a set of values for the adjustable parameters involved, which are always presumed to represent the behaviour of such data. However, such fitting programs can fit, given enough adjustable variables, almost any theoretical/empirical model, but they cannot tell you which theory/model should apply. Consequently, the deduced fitting parameters might be *illusive* or *misleading*, as one often obtains different sets of values for them, corresponding to different 'local' minima in the statistical function used in the minimization procedure, which give best fits to the same model chosen. Only when a 'global' minimum is arrived at through the minimization procedure can the obtained set of fitting parameters be considered to be physically well behaved and reliable for further analysis. In general, it is rather difficult to develop some additional justified criteria which are helpful in differentiation of the conventional and *imposed* data curve-fitting (IDCF) approach from an approach which does not contain initially supposed empirical functions and corresponds to a 'true' chosen hypothesis. But fortunately, in dielectric spectroscopy some additional criteria can be found [26].

Recently, a new approach based on the so-called *eigencoordinates* (ECs) method, which appears to be very efficient and relatively simple to use in data curve-fitting analysis, has been developed by one of the authors (RRN) [26, 27]. The basic ideas and procedures for applying the ECs method for analysing data are detailed in [27, 28]. It has been applied efficiently to analyse the measured complex permittivity for semiconducting selenium films [26a] and glycerol [26b] and without imposing *a priori* any equivalent-circuit model as is usually done by many researchers in the field. New impedance functions have been *recognized* to be

responsible for the observed complex permittivity behaviour of these substances at different temperatures and for various heat-treatment conditions by the use of the ECs method. New complex identified dielectric functions can be expressed as [26]

$$\varepsilon(j\omega) = \varepsilon_\infty + \frac{\varepsilon(0) - \varepsilon_\infty}{1 + R(j\omega)}. \tag{5}$$

The complex function $R(j\omega)$ is determined by the following expressions:

(a) for the equivalent circuit with two recap elements connected in parallel [26a]:

$$R(j\omega) = (j\omega\tau_1)^{\nu_1} + (j\omega\tau_2)^{\nu_2}, \tag{6a}$$

(b) for the equivalent circuit with two recap elements connected in series [26b]:

$$R(j\omega) = [(j\omega\tau_1)^{-\nu_1} + (j\omega\tau_2)^{-\nu_2}]^{-1}. \tag{6b}$$

Here we want to stress one *principal feature* of these functions, namely expressions (6) contain *two* relaxation times, forming one loss (asymmetrical in most cases) peak belonging to one function (5). These two relaxation times are presented in one function and are formed *without* additive combinations of the two 'simple' functions similar to the HN (4) function containing only one relaxation parameter. A single *recap* (defined also as a 'universal' capacitor) element [10a] or a combination of several *recap* elements entering into the last expressions is considered to depict the *fractal* nature of a sample interior and/or interfacial/electrode phenomena [29] through a general impedance form having intermediate characteristics with a 'fractional' power-law frequency response of the type [30–33]

$$Z_\nu(j\omega) \equiv R(j\omega\tau)^{-\nu}. \tag{7}$$

Here τ can be considered as a *definition* of the relaxation time of a fractal subsystem while R is a dimensional parameter with power-law exponent located in the interval $0 \leqslant \nu \leqslant 1$ but, in some cases, having values that exceed unity [33]. Each *recap* element, besides its own exponent ν, is dominant in a certain frequency range $\omega_{min} \leqslant \omega \leqslant \omega_{max}$, which cannot sometimes be achieved by the experimental set-up used, over which such a recap element should reflect the existence of a fractal structure formed in some mesoscopic systems. Based on such a self-similar structure approach, it is always possible to analyse the observed *ac* response through a dielectric/impedance function that involves one single *recap* element or a superposition of two or more such elements [26] instead of using empirical dielectric expressions or models incorporating equivalent circuits *a priori*. Identification of the actual combination of physically meaningful *recap* elements can be achieved relatively easily by employing the ECs data curve-fitting method in conjunction with a separation procedure that helps to differentiate the contributions of the different *recap* elements to the total impedance/dielectric function describing the observed behaviour [26].

Preliminary analysis made on the glycerol data in the available frequency and temperature range showed that temperature dependence of the parameters $\tau_{1,2}$ entering to the identified formula (5) with the relaxation function (6*b*) obeys the Arrhenius dependence but the temperature of the loss peak follows the VFT equation. This initial evidence prompted us with a basic idea of the relatively intimate relationship between the Arrhenius temperature dependence of the two relaxation times entering into the complex expressions (6) with the empirical VFT equation.

But for the complete investigation of this possible relationship the temperature dependence of the power-law parameters $\nu_{1,2}(T)$ was necessary. Recently a possible dependence of such type has been found in [1] and confirmed experimentally. So the main problem can be formulated as follows:

(1) Is it possible to derive (at least approximately) the empirical VFT equation based on the Arrhenius temperature dependence of relaxation times $\tau_{1,2}(T) = \tau_{A1,A2}[\exp(E_{1,2}/T)]$ entering into complex permittivity functions (6*a*) and power-law exponents $\nu_{1,2}(\tau)$ with the dependence found in [1]?
(2) Can this empirical equation be referred only to glass-forming systems or not?
(3) Is it possible to find the limits of applicability of the VFT equation and show the true limits of the parameters, entering in this empirical formula?
(4) Is it possible to detect the VFT equation and calculate the true values of the fitting parameters corresponding to the global minimum?
(5) Is it possible 'to improve' the initial VFT empirical equation and find its 'true' corrections?
(6) What is the physical meaning of the VFT equation?

The main purpose of this paper is to find the answers to these questions posed and give the correct interpretation of the VFT equation as a consequence of a specific kinetic phenomena observed in many heterogeneous materials.

2. Approximate expressions for a loss frequency peak and deduction of the VFT equation

In order to 'feel' a possible dependence of the maximum loss peak versus temperature it is necessary to obtain the corresponding equation for ω_p from the complex dielectric functions containing at least two relaxation parameters. As possible 'candidates' we took for analysis the expressions (6) entering in the relationship (5) and the dielectric function formed by an additive combination of the two CC functions, where the complex permittivity is presented in the form

$$\varepsilon(j\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_1}{1 + (j\omega\tau_1)^{\nu_1}} + \frac{\Delta\varepsilon_2}{1 + (j\omega\tau_2)^{\nu_2}}. \tag{8}$$

Taking the first derivative from the imaginary part of the complex permittivity, which is determined by expressions (5) and (8) and equating the obtained expression to zero one can obtain the corresponding transcendental equation for the finding of extreme points of the function $\omega_p(\tau_1, \tau_2, \nu_1, \nu_2)$. The corresponding equations look very cumbersome and are given in table 1. In general, these transcendental equations determine at least three roots (two possible peaks with one minimum between them) and cannot be expressed analytically. But numerical and dimensional analysis show that the leading term corresponding to the desired root can be expressed in the form

$$\omega_p(T) = C(T)\min(\tau_1^{-1}(T), \tau_2^{-1}(T))\left(\frac{\tau_1(T)}{\tau_2(T)}\right)^{1/\nu(T)}. \tag{9}$$

Here C is a dimensionless constant determined by the largest relaxation time and ν is the leading power-law exponent providing the low-frequency loss peak.

Let us *suppose* that the temperature dependence of the relaxation parameters $\tau_{1,2}$ corresponds to the Arrhenius relationship

$$\tau_{1,2}(T) = \tau_{A1,A2}\exp(E_{1,2}/T). \tag{10}$$

Here the parameters $\tau_{A1,A2} = \tau_{1,2}(\infty)$ define the characteristic time of the Arrhenius relaxation and the values $E_{1,2}$ describe approximately the average energy of reorientation of the fractal subsystem considered.

The dependence of the power-law exponent with respect to relaxation time [1] can be presented in the form

$$\nu(\tau) = \nu_0\frac{\ln(\tau/\tau_s)}{\ln(\tau/\tau_0)}. \tag{11}$$

Table 1. The structure of transcendental equations obtained for extremal points ω_p from expressions (5), (6) and (8).

Original equation	Corresponding transcendental equation
Two recaps in parallel	$S_{1,2} = \tau_{1,2}^2 \sin\Big(\frac{\pi\nu_{1,2}}{2}\Big), \quad T_1 = \tau_1^{2\nu_1}, \quad T_2 = \tau_2^{2\nu_2},$
$\varepsilon(j\omega) = \varepsilon_\infty + \dfrac{\varepsilon(0) - \varepsilon_\infty}{1 + R(j\omega)}$	$C_{1,2} = 2\tau_{1,2}^2 \cos\Big(\frac{\pi\nu_{1,2}}{2}\Big),$
$R(j\omega) = (j\omega\tau_1)^{\nu_1} + (j\omega\tau_2)^{\nu_2}$	$C_{12} = 2\tau_1^{\nu_1}\tau_2^{\nu_2}\cos\Big[\dfrac{\pi(\nu_1 - \nu_2)}{2}\Big]$
	$S_1\nu_1\omega_p^{\nu_1} + S_2\nu_2\omega_p^{\nu_2} + [S_1C_2(\nu_1 - \nu_2) + S_2C_1(\nu_2 - \nu_1)]\omega_p^{\nu_1+\nu_2}$
	$+ [S_2T_1(\nu_2 - 2\nu_1) - S_1C_{12}\nu_2]\omega_p^{2\nu_1+\nu_2}$
	$+ [S_1T_2(\nu_1 - 2\nu_2) - S_2C_{12}\nu_1]\omega_p^{\nu_1+2\nu_2}$
	$- S_1T_1\nu_1\omega_p^{3\nu_1} - S_2T_2\nu_2\omega_p^{3\nu_2} = 0.$
Two recaps in series	$S_{1,2} = \tau_{1,2}^2 \sin\Big(\frac{\pi\nu_{1,2}}{2}\Big), C_{1,2} = \tau_{1,2}^2 \cos\Big(\frac{\pi\nu_{1,2}}{2}\Big),$
$\varepsilon(j\omega) = \varepsilon_\infty + \dfrac{\varepsilon(0) - \varepsilon_\infty}{1 + R(j\omega)}$	$C_3 = \tau_1^{\nu_1}\tau_2^{\nu_2}\cos\Big[\dfrac{\pi(\nu_1 + \nu_2)}{2}\Big],$
$R(j\omega) = \dfrac{1}{(j\omega\tau_1)^{-\nu_1} + (j\omega\tau_2)^{-\nu_2}}$	$S_3 = \tau_1^{\nu_1}\tau_2^{\nu_2}\sin\Big[\dfrac{\pi(\nu_1 + \nu_2)}{2}\Big],$
	$N_1 = C_3S_1 - C_1S_3, N_2 = C_3S_2 - C_2S_3,$
	$D_{1,2,3} = C_{1,2,3}^2 + S_{1,2,3}^2,$
	$D_4 = 2(C_1C_2 + S_1S_2), D_5 = 2(C_1C_3 + S_1S_3),$
	$D_4 = 2(C_2C_3 + S_2S_3)$
	$N_1D_1\nu_2\omega_p^{3\nu_1} + N_2D_2\nu_1\omega_p^{3\nu_2} + [N_1D_2(2\nu_1 - \nu_2) + N_2D_4\nu_2]\omega_p^{\nu_1+2\nu_2}$
	$+ [N_2D_1(2\nu_2 - \nu_1) + N_1D_4\nu_1]\omega_p^{2\nu_1+\nu_2}$
	$+ [N_1D_6(\nu_1 - \nu_2) + N_2D_5(\nu_2 - \nu_1)]\omega_p^{2\nu_1+2\nu_2}$
	$- N_2D_3\nu_1\omega_p^{2\nu_1+3\nu_2} - N_1D_3\nu_2\omega_p^{3\nu_1+2\nu_2} = 0$
Two CC terms in series	$S_{1,2} = \Delta\varepsilon_{1,2}\tau_{1,2}^{\nu_{1,2}}\sin\Big(\frac{\pi\nu_{1,2}}{2}\Big), \quad T_{1,2} = \tau_{1,2}^{2\nu_{1,2}},$
$\varepsilon(j\omega) = \varepsilon_\infty + \dfrac{\Delta\varepsilon_1}{1 + (j\omega\tau_1)^{\nu_1}}$	$C_{1,2} = 2\tau_{1,2}^{\nu_{1,2}}\cos\Big(\frac{\pi\nu_{1,2}}{2}\Big),$
$+ \dfrac{\Delta\varepsilon_2}{1 + (j\omega\tau_2)^{\nu_2}}$	$N_1 = C_2S_1 - C_1S_2$
	$S_1\nu_1\omega^{\nu_1} + 2(S_1\nu_1C_2 + S_2\nu_2C_1)\omega^{\nu_1+\nu_2}$
	$+ (2S_1\nu_1T_2 + \nu_1N_1C_2 - S_2\nu_2C_1C_2)\omega^{\nu_1+2\nu_2} - S_1\nu_1T_1\omega^{3\nu_1}$
	$+ (2S_2\nu_2T_1 + \nu_2N_1C_1 - S_1\nu_2C_1C_2)\omega^{2\nu_1+\nu_2}$
	$+ T_1C_2(S_1\nu_1 - S_2\nu_2)\omega^{2\nu_1+2\nu_2}$
	$- N_1\nu_1T_1\omega^{3\nu_1+\nu_2} + (S_2\nu_1T_1C_1C_2 - T_1N_1C_2$
	$- 2S_1\nu_1T_1T_2)\omega^{3\nu_1+2\nu_2} + S_2\nu_2\omega^{\nu_2} - S_2\nu_2T_2\omega^{3\nu_2}$
	$+ (T_2(\nu_1 - \nu_2)(S_1C_1 + N_1) + T_2(2\nu_2 + \nu_1)N_1)\omega^{\nu_1+3\nu_2}$
	$+ (\nu_1T_2(S_1T_1 - N_1C_1) + \nu_2T_2(S_1C_1C_2 - 3S_2T_1))\omega^{2\nu_1+3\nu_2}$
	$+ (T_2T_1S_1C_2(\nu_2 - \nu_1) + T_2T_1S_2C_1(\nu_1 - \nu_2)$
	$- T_1T_2(\nu_2 + \nu_1)N_1)\omega^{3\nu_1+3\nu_2}$
	$+ \nu_1S_1T_2^2\omega^{\nu_1+4\nu_2} - \nu_1S_1T_2^2T_1\omega^{3\nu_1+4\nu_2}$
	$+ \nu_2S_2T_1^2\omega^{4\nu_1+\nu_2} - \nu_2S_2T_1^2T_2\omega^{4\nu_1+3\nu_2}$

Here $\nu_0 = d_G/2$, τ_s is the characteristic time of the self-diffusion process and τ_0 determines the cut-off time of the scaling relaxation process in the time domain. The parameter d_G defines the fractal dimension of the point set, where relaxation units are interacting with the statistical reservoir. Verification of relationship (11) describing the process of non-exponential relaxation in disordered systems with statistically self-similar structures shows that the characteristic times

τ_s and τ_0 do *not* depend on temperature and characterize the substance considered. Taking into account the temperature dependence of the relationship (11), which implies the leading power-law exponent chosen from (10), the approximate expression for the minimal root (9) can be expressed in the form

$$\omega_p(T) = C\omega_0 \exp\left(\frac{\Delta E_{12}}{\nu_0 T} - \frac{B}{T - T_{VF}}\right). \tag{12}$$

Here the parameters entering in this expression are defined as follows:

$$\omega_0 = \min(\tau_{A1}^{-1}, \tau_{A2}^{-1}) \exp\left[\frac{1 - A}{\nu_0} \ln\left(\frac{\tau_{A1}}{\tau_{A2}}\right)\right], \qquad T_{VF} = \frac{E}{\ln(\tau_s/\tau_A)}. \tag{13a}$$

$$E_{12} = E_1 - E_2, \qquad A = 1 - \frac{\ln(\tau_0/\tau_A)}{\ln(\tau_s/\tau_A)}, \qquad B = \frac{A}{\nu_0}\left(\Delta E_{12} + T_{VF} \ln\left(\frac{\tau_{A1}}{\tau_{A2}}\right)\right). \tag{13b}$$

The values T_{VF} and A in expressions (13) are defined by the parameters entering into the leading power-law exponent $\nu(\tau)$ with minimal value of $\tau = \tau_A \exp(E/T)$ among relaxation times defined by (10). If $|\Delta E_{12}/T| \ll 1$, then from expression (12) we obtain the desired VFT equation with parameter B defined as

$$\omega_p(T) = C\omega_0 \exp\left(-\frac{B}{T - T_{VF}}\right), \qquad \text{with } B = \frac{A}{\nu_0} \ln\left(\frac{\tau_{A1}}{\tau_{A2}}\right) T_{VF}. \tag{14}$$

Preliminary analysis shows that the empirical Vogel–Fulcher temperature T_{VF} in (13*a*) is *not directly* related to the critical temperature defining the phase transition in glass-forming systems. It is related to the intermittent (fractal) character of relaxation in self-similar systems [1] and defined by the behaviour of the power-law exponent $\nu(\tau)$ by means of the Arrhenius temperature dependence. It can accept *negative* values and is generated by a 'specific competition' between the power-law exponents $\nu_1(\tau_1)$ and $\nu_2(\tau_2)$, forming the leading asymptotic term for the low-frequency peak. From this preliminary analysis it follows also that the complex dielectric functions should be defined at least by the two relaxation times $\tau_1(T)$, $\tau_2(T)$. The VFT equation is expected to be 'universal' and applicable not only to the glass-forming systems; other extremal points of the function $\varepsilon(j\omega)$ can also be related by the VFT equation but with *other* values of the fitting parameters B and T_{VF}. It is obvious that the VFT equation is *approximate* and the first correction is stipulated by the Arrhenius part in (12). It is instructive also to find possible corrections to the VFT equation in order to see the limits of its applicability. Numerical analysis of the complete transcendental equations given in tables 1 and 2 shows that the most general relationship for the leading extremal term which can be derived from the reduced form of the initial transcendental equation for ω_p:

$$A(\omega_p\tau_1)^\alpha - B(\omega_p\tau_2)^\beta = 0, \tag{15a}$$

can be expressed as

$$\omega_p = \left(\frac{B}{A}\right)^{1/(\alpha-\beta)} \tau_2^{-1} \left(\frac{\tau_2}{\tau_1}\right)^{\alpha/(\alpha-\beta)} \equiv C \min(\tau_1^{-1}, \tau_2^{-1}) \left(\frac{\tau_1}{\tau_2}\right)^{a/(\nu_1 + b\nu_2)}. \tag{15b}$$

In the last formula the values a and b in the complex exponent are expressed frequently by some integer numbers. C is a constant which weakly depends on the values of the corresponding power-law exponents. Taking into account expressions (10) and (11) one can find the temperature dependence of the combined exponent in (15*b*). It can be presented in the following equivalent forms:

$$\frac{a}{\nu_1 + b\nu_2} = \frac{a}{\nu_{01}\frac{\ln(\tau_1/\tau_{s1})}{\ln(\tau_1/\tau_{01})} + b\nu_{02}\frac{\ln(\tau_2/\tau_{s2})}{\ln(\tau_2/\tau_{02})}} = r\frac{T^2 + a_1 T + b_1}{T^2 + a_2 T + b_2} = r\left[1 + \frac{p_1}{T - T_1} + \frac{p_2}{T - T_2}\right]. \tag{16}$$

The last expression is useful for analysis if the roots of the square trinomial in the dominator are real. Here new parameters are related to initial expressions as follows:

$$r = a\frac{a_{10}a_{20}}{\nu_{01}a_{1s}a_{20} + b\nu_{02}a_{2s}a_{10}}, \qquad a_1 = \frac{E_1 + E_2}{a_{10}a_{20}}, \qquad b_1 = \frac{E_1E_2}{a_{10}a_{20}}, \tag{17a}$$

$$a_2 = \frac{(\nu_{01}a_{20} + b\nu_{02}a_{2s})E_1 + (\nu_{01}a_{1s} + b\nu_{02}a_{10})E_2}{\nu_{01}a_{1s}a_{20} + b\nu_{02}a_{2s}a_{10}}, \qquad b_2 = \frac{(\nu_{01} + b\nu_{02})E_1E_2}{\nu_{01}a_{1s}a_{20} + b\nu_{02}a_{2s}a_{10}}, \tag{17b}$$

$$T_{1,2} = -\frac{a_2}{2} \pm \sqrt{\frac{a_2^2}{4} - b_2}, \qquad p_1 = \frac{T_1(a_1 - a_2) - (b_1 - b_2)}{T_1 - T_2},$$

$$p_2 = -\frac{T_2(a_1 - a_2) + (b_1 - b_2)}{T_1 - T_2}, \tag{17c}$$

$$a_{is} = \ln\left(\frac{\tau_{Ai}}{\tau_{si}}\right), \qquad a_{i0} = \ln\left(\frac{\tau_{Ai}}{\tau_{0i}}\right), \qquad (i = 1, 2). \tag{17d}$$

Taking into account expression (16) one can write the temperature dependence of the loss peak in two equivalent forms:

$$\omega_p = C\min(\tau_1^{-1}, \tau_2^{-1})\exp\left[\frac{T^2 + a_1T + b_1}{T^2 + a_2T + b_2}\left(r\ln\left(\frac{\tau_{A1}}{\tau_{A2}}\right) + r\frac{\Delta E_{12}}{T}\right)\right]$$

$$= \tilde{\omega}_0\exp\left[\frac{\Delta E}{T} + \frac{B_1}{T - T_1} + \frac{B_2}{T - T_2}\right] \tag{18}$$

$$\tilde{\omega}_0 = C\min(\tau_{A1}^{-1}, \tau_{A2}^{-1})\exp\left[r\ln\left(\frac{\tau_{A1}}{\tau_{A2}}\right)\right], \qquad \Delta E = r\Delta E_{12}\left(1 - \frac{p_1}{T_1} - \frac{p_2}{T_2}\right),$$

$$B_{1,2} = rp_{1,2}\left[\ln\left(\frac{\tau_{A1}}{\tau_{A2}}\right) + \frac{\Delta E_{12}}{T_{1,2}}\right]. \tag{19}$$

The generalized VFT equation presented by expression (18) confirms again the tendency marked in the analysis of the simplified expression (9), namely

(a) a certain 'universality' and applicability to a wide class of dielectric spectra described by expressions (5), (6) or (8) with relaxation times belonging to possible fractal subsystems;
(b) the absence of a link with possible phase transition phenomena;
(c) the fitting parameters $T_{1,2}$ defined by expression (17*c*) can accept in principle arbitrary values including *negative* and even *complex-conjugated* ones (when $4b_2 > a_2^2$);
(d) applicability of the last expression for the analysis of temperature dependences of other extreme points identified for an imaginary part of the complex permittivity function.

Preliminary analysis shows that it is rather difficult to establish the relationship between the fitting parameters obtained from the initial VFT equation or its generalized form (19) with the initial set of parameters following from relationships (17). From our point of view it is much more informative to find possible corrections to the recently found formula (11) and analyse carefully the dependence of the power-law exponents $\nu(\tau)$ with respect to temperature. Supposing that the relaxation times follow the Arrhenius dependence one can obtain for analysis the following expression:

$$\nu(T) = \tilde{\nu}_0\left[1 - \frac{b}{T + T_0}\right]. \tag{20}$$

The fitting parameters entering into the last expression are defined as follows:

$$\tilde{\nu}_0 = \nu_0\frac{\ln(\tau_A/\tau_s)}{\ln(\tau_A/\tau_0)}, \qquad T_0 = \frac{E}{\ln(\tau_A/\tau_0)}, \qquad b = E\frac{\ln(\tau_0/\tau_s)}{\ln(\tau_A/\tau_0)\ln(\tau_A/\tau_s)}. \tag{21}$$

Table 2. The reduced (simplified) forms of the transcendental equations, which approximate the initial transcendental equations in the vicinity of a low-frequency minimum.

Case	Chosen fitting parameters and leading parts (reduced equation) for equivalent scheme with two recaps in parallel
Case 1 (when the times $\tau_{1,2}$ are differed considerably from each other: $\tau_2 \gg \tau_1$)	Values of parameters $\tau_1 = 9 \times 10^{-8}$, $\nu_1 = 0.99$, $\tau_2 = 9 \times 10^{-4}$, $\nu_2 = 0.5$ (the values of parameters are chosen occasionally) $S_{1,2} = \tau_{1,2}^2 \sin\left(\frac{\pi \nu_{1,2}}{2}\right), \quad T_2 = \tau_2^{2\nu_2}$ Leading parts solution of this reduced equation $S_2 \nu_2 \omega_p^{\nu_2} - S_2 \nu_2 T_2 \omega_p^{3\nu_2} = 0 \rightarrow \omega_p = 1/\tau_2$
Case 2 (when the characteristic relaxation times $\tau_{1,2}$ are close to each other: $\tau_2 \sim \tau_1$)	Values of parameters $\tau_1 = 9 \times 10^{-4}$, $\nu_1 = 0.1$, $\tau_2 = 9 \times 10^{-4}$, $\nu_2 = 0.4$ (the values of parameters are chosen occasionally) $S_{1,2} = \tau_{1,2}^2 \sin\left(\frac{\pi \nu_{1,2}}{2}\right), \quad T_2 = \tau_2^{2\nu_2},$ $C_{1,2} = 2\tau_{1,2}^2 \cos\left(\frac{\pi \nu_{1,2}}{2}\right)$ Leading parts $[S_1 C_2(\nu_1 - \nu_2) + S_2 C_1(\nu_2 - \nu_1)]\omega_p^{\nu_1+\nu_2} - S_2 T_2 \nu_2 \omega_p^{3\nu_2} = 0 \rightarrow$ Solution of this reduced equation $\omega_p = C \min(\tau_1^{-1}, \tau_2^{-1})\left(\frac{\tau_1}{\tau_2}\right)^{a\nu_2/(\nu_1+b\nu_2)}$ The values of a and b in the complex exponent are expressed frequently by some integer numbers. C is a constant, which weakly depends on the values of the corresponding power-law exponents.

These expressions show again that the 'Volger–Fulcher temperature' T_0 can accept *any* arbitrary value defined by the ratio τ_A/τ_0. Comparing formulae (9), (11) and (12) with expression (20) it is easy to note that the inverse power-law exponent $1/\nu(T)$ can also be presented in the form (20) with the replacement $\nu_0 \rightarrow 1/\nu_0$, $\tau_s \leftrightarrow \tau_0$ in the corresponding expressions (21). This invariance is conserved also for the ratio $(\nu_1 + c_1\nu_2)/(\nu_1 + c_2\nu_2)$ which is decomposed into two partial fractions by analogy, as has been done for expression (16).

3. The use of the ECs method for detection of the VFT equation

One of the basic features of the above-mentioned ECs method is the determination of a 'global' minimum in the realized fitting procedure. It becomes important when we do *not* know *a priori* initial values of the parameters, especially in cases when the number of fitting parameters is sufficiently large. Another important feature of the ECs method consists of the capability of detection of the most suitable analytical hypothesis among other proposed hypotheses chosen for the fitting of real experimental data.

In the ECs representation, the ECs plots corresponding to a 'true' function should give a set of sloping lines with fitting constants that enter into a basic relationship in a *linear* way. They are related algebraically to the initial set of fitting parameters of the original function considered.

In this section we do not intend to exhibit all details of the ECs procedure (they are given in [26–28]). It is necessary to obtain the basic linear relationships and to plot all sloping lines for the identification of the initial VFT equation and the generalized expressions (12) and (18) containing the necessary corrections. Here it is sufficient to give only the final basic linear relationships corresponding to the chosen functions.

Ordinary VFT equation $\omega_p(T) = \omega_0 \exp(-DT_{VF}/(T - T_{VF}))$

$$\begin{aligned}
&Y(T) = C_1X_1(T) + C_2X_2(T) + C_3X_3(T),\\
&Y(T) = \int_{T_m}^{T} u \ln[\omega_p(u)]\,\mathrm{d}u - \langle\cdots\rangle,\\
&X_1(T) = \int_{T_m}^{T} \ln[\omega_p(u)]\,\mathrm{d}u - \langle\cdots\rangle; \quad C_1 = T_{VF},\\
&X_2(T) = T^2 - \langle\cdots\rangle; \qquad C_2 = \frac{\ln[\omega_0]}{2},\\
&X_3(T) = T - \langle\cdots\rangle; \qquad C_3 = -T_{VF}(D + \ln[\omega_0]).
\end{aligned} \tag{22}$$

The VFT equation with the Arrhenius correction: $\omega_p(T) = \omega_0 \exp(A/T - B/(T - T_{VF}))$

$$\begin{aligned}
&Y(T) = C_1X_1(T) + C_2X_2(T) + C_3X_3(T) + C_4X_4(T),\\
&Y(T) = \int_{T_m}^{T} u^2 \ln[\omega_p(u)]\,\mathrm{d}u - \langle\cdots\rangle,\\
&X_1(T) = \int_{T_m}^{T} u \ln[\omega_p(u)]\,\mathrm{d}u - \langle\cdots\rangle; \qquad C_1 = T_{VF},\\
&X_2(T) = T^3 - \langle\cdots\rangle; \qquad C_2 = \frac{\ln[\omega_0]}{3},\\
&X_3(T) = T^2 - \langle\cdots\rangle; \qquad C_3 = \frac{A - \ln[\omega_0]T_{VF} - B}{2},\\
&X_4(T) = T - \langle\cdots\rangle; \qquad C_4 = -AT_{VF}.
\end{aligned} \tag{23}$$

The 'generalized' form of the VFT equation with two temperatures

$$\begin{aligned}
&\omega_p(T) = \omega_0 \exp\left(\frac{A}{T} - \frac{B}{T - T_1} - \frac{C}{T - T_2}\right).\\
&Y(T) = C_1X_1(T) + C_2X_2(T) + C_3X_3(T) + C_4X_4(T) + C_5X_5(T) + C_6X_6(T),\\
&Y(T) = \int_{T_m}^{T} u^3 \ln[\omega_p(u)]\,\mathrm{d}u - \langle\cdots\rangle,\\
&X_1(T) = \int_{T_m}^{T} u^2 \ln[\omega_p(u)]\,\mathrm{d}T - \langle\cdots\rangle; \qquad C_1 = T_1 + T_2,\\
&X_2(T) = \int_{T_m}^{T} u \ln[\omega_p(u)]\,\mathrm{d}u - \langle\cdots\rangle; \qquad C_2 = -T_1T_2,\\
&X_3(T) = T^4 - \langle\cdots\rangle; \qquad C_3 = \frac{\ln[\omega_0]}{4},
\end{aligned} \tag{24}$$

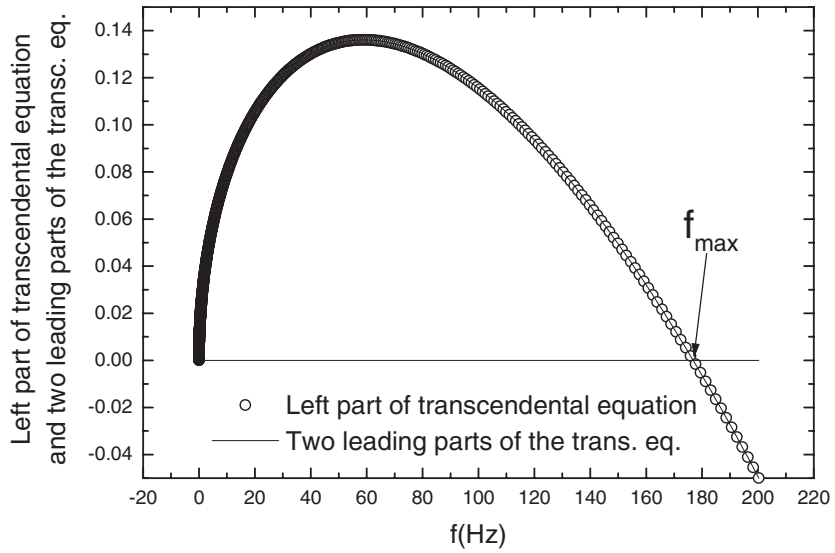

Figure 1. Open circles represent the left part of the transcendental equation (table 1, two recaps in parallel). The full line represents the sum of two leading parts of the transcendental equation for this case (see table 2, case 1). The parameters chosen for this case and the leading parts are shown in table 2 (case 1). The arrow shows the point at which the transcendental expression and the sum of two leading parts are equal to zero. This zero point determines the peak frequency of the imaginary part of complex susceptibility.

$$X_4(T) = T^3 - \langle\cdots\rangle; \qquad C_4 = \frac{A - B - C - \ln[\omega_0](T_1 + T_2)}{3},$$

$$X_5(T) = T^2 - \langle\cdots\rangle; \qquad C_5 = \frac{\ln[\omega_0]T_1T_2 - A(T_1 + T_2) + BT_2 + CT_1}{2},$$

$$X_6(T) = T - \langle\cdots\rangle; \qquad C_6 = AT_1T_2.$$

Here, the insertion of the operation $\langle\cdots\rangle$ means that the corresponding arithmetic mean value of the appropriate quantity should be subtracted [27]. This operation is necessary to eliminate possible constants from the corresponding equations and to provide the basic requirement for the *linear least square method* (LLSM), namely $\langle\varepsilon\rangle \equiv 0$ [34]. As has been mentioned above, the main elegant feature of the ECs method is its ability to differentiate the actual ('native') function from a spurious ('strange') function that does not satisfy this basic linear relationship. The basic linear relationship of a native function having s fitting parameters can be reduced to a set of $s2^{s-1}$ (here s is a dimension of the fitting vector [27]) self-verified sloping lines (ECs plots), which will be distorted by the strange function. Therefore, 'probing' of the validity/applicability of 'theoretical' models chosen to describe the experimental data under investigation by the ECs curve-fitting approach should be of general scientific interest [26–28].

The simulation experiment shows that not only the maximum point of the imaginary part of the complex susceptibility, but also the point of a *minimum* located between α and β peaks obeys the VFT equation with different values of corresponding fitting parameters. In this case the curves of temperature dependences of times τ_1 and τ_2 do not intersect with each other visually but have to be 'quasiparallel' in a semi-log scale picture. The VFT equation is stipulated by the temperature dependences of the power-law exponents $\nu_{1,2}$ described by equation (20). Another interesting feature that should be marked here is that, at some values

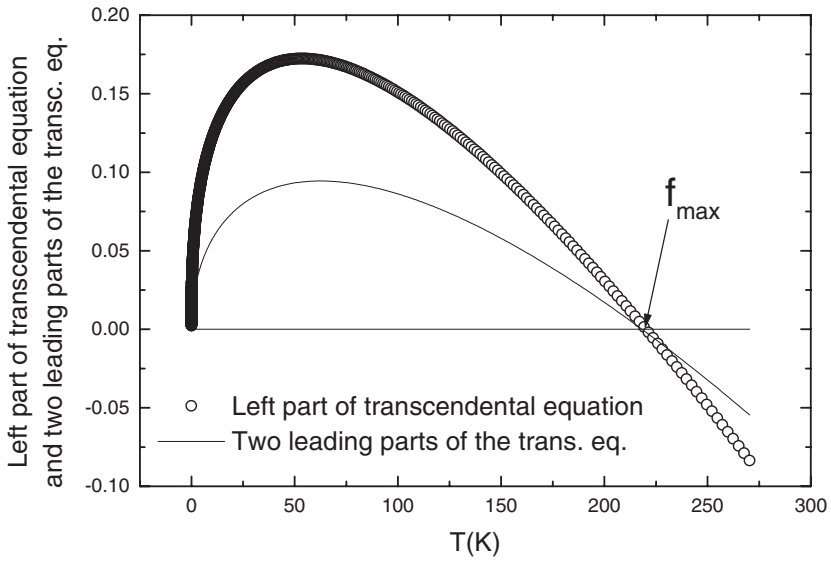

Figure 2. Open circles represent the left part of the transcendental equation (table 1, two recaps in parallel). The full curve represents the sum of two leading parts of the transcendental equation (table 2, case 2). The parameters chosen in this case and leading parts are shown in table 2 (case 2). The arrow shows the point at which the transcendental expression and the sum of two leading parts in this case are equal to zero.

of the fitting parameters realized with the help of the ECs method and corresponding to the *global* minimum, the parameters $T_{1,2}$ in the generalized equation (18) can accept *negative* or even *complex* conjugated values. Other details are illustrated by figures 1–5 together with their captions and do not need additional comments.

4. Analysis of available experimental data

The main conclusion, which follows from imitation experiments, is that the VFT equation is not *directly* related with critical phenomena taking place in glassy systems. It is a consequence of the basic relationships between the power-law exponent and relaxation time $\nu(\tau)$ recently established in [1] for non-exponential (scaling) relaxation in disordered systems and competition of the two processes with characteristic relaxation times $\tau_{1,2}$ (having an Arrhenius temperature dependence) expressed either in the form of equation (5) with $R(j\omega)$ from (6*a*) and (6*b*) or in the form of a linear combination of two CC type processes (8). In this section we shall try to analyse some real available experimental data in order to detect the VFT temperature dependence for peak frequency with the use of the ECs method. We want to stress here that the ECs method is more accurate in comparison with the method of transformation of initial data to a straight line (which incorporates the numerical differentiation operation) suggested by Stickel [35].

The first set of data which were analysed for verification of the VFT formula with possible corrections from the use of the ECs method (22)–(24) represent temperature dependences of the maximum loss peak frequency for $[(Ca(NO_3)_2]_{0.4}[KNO_3]_{0.6}$ (CKN) and $[(Ca(NO_3)_2]_{0.4}[RNO_3]_{0.6}$ (CRN) (strong ionic conductors) alongside glass-forming materials, such as glycerol and propylene carbonate (PC). We passed all these data related to the temperature dependence of the maximum loss peak frequency through the ECs 'tuned' for

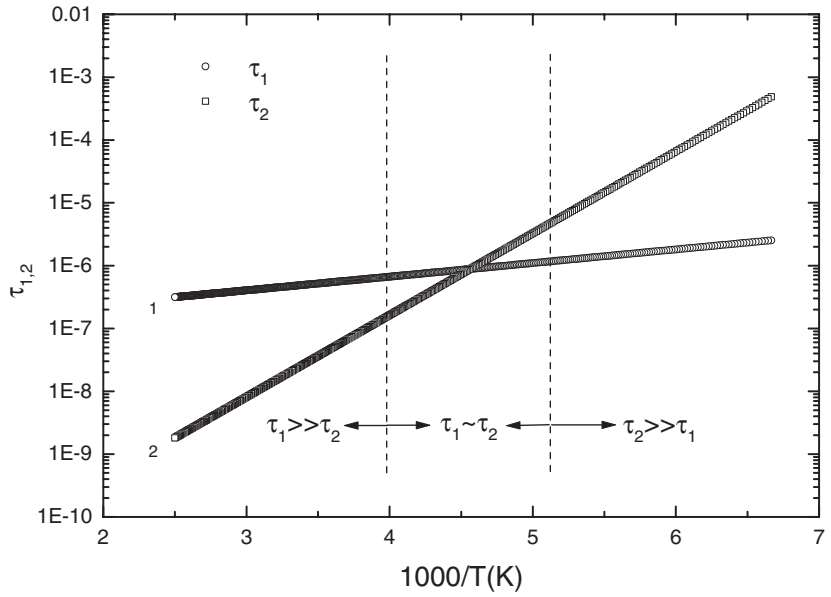

Figure 3. Open circles represent the temperature dependence of the relaxation time τ_1 ($\tau_1 = 9 \times 10^{-8} \times \exp(500/T)$). Open squares represent the temperature dependence of the relaxation time τ_2 ($\tau_2 = 1 \times 10^{-12} \times \exp(3000/T)$). Broken lines separate three regions: $\tau_1 \gg \tau_2$, $\tau_1 \sim \tau_2$ and $\tau_1 \ll \tau_2$.

the identification of three functions: a 'conventional' VFT function (12), VFT with Arrhenius correction (12) and the generalized VFT function expressed by equation (18). It has been found that the data for CKN and CRN are described by the generalized VFT law (18) with *complex*-conjugated values of temperatures T_1 and T_2. Open circles and full curves, respectively, in a semi-log scale show the CKN and CRN data and the corresponding fitting curves in figures 6 and 7. The temperature data for glass-forming glycerol and PC are described by the VFT equation with the Arrhenius correction (12). The data and corresponding fitting curves for glycerol and PC are shown in figures 8 and 9, respectively, by open geometrical figures and full lines, respectively, in a semi-log scale. The chosen fitting functions and the results of the fitting procedure (values of the fitting parameters) for this set of data are collected in table 3.

The second set of DS data for this analysis have been obtained from Professor Shin Yagihara and Dr Naoki Shinyashiki (Research Group of Molecular Complex System Physics Department, Tokai University, Japan). They represent temperature dependences of the maximum loss peak frequency for pure glycerol. We passed these data through the ECs 'tuned' for the identification of three functions: a 'conventional' VFT function (14), VFT with Arrhenius correction (12) and the generalized VFT function expressed by equation (18). It has been found that all these data are described by expression (14). The data and the corresponding fitting curves for these data are shown in figure 10 by open circles and full line, respectively, in a semi-log scale. The chosen fitting functions and the results of the fitting procedure (values of the fitting parameters) for these data are collected in table 3. Figure 11 demonstrates the 'German' and 'Japanese' frequency loss peaks combined together for comparison. These independent verifications reveal two important conclusions:

(a) independent verification of two types of glycerol exhibits almost the same temperature dependence;

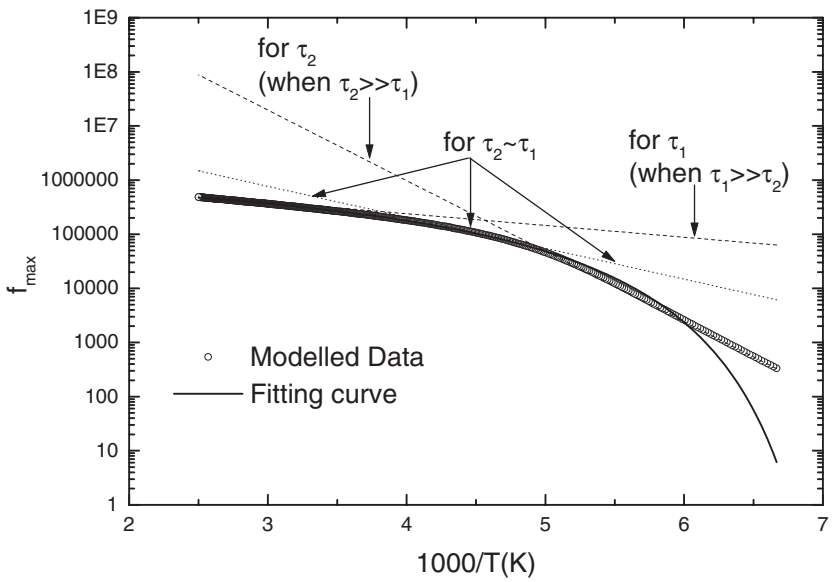

Figure 4. This figure demonstrates the temperature behaviour of the peak frequency marked by open circles. The temperature dependences of the parameters of relaxation times are shown in the caption to figure 3. The parameters for power-law exponents have some constant values: $\nu_1 = 0.9$ and $\nu_2 = 0.45$. The full line represents the fitting curve obtained with the use of the ECs method for an ordinary VFT law with fitting parameters: $T_{VF} = 132.98 \pm 0.18$, $D = 1.54 \pm 0.03$, $\omega_0/2\pi = 1.019 \times 10^6 \pm 3000$. Broken lines show the asymptotes for high- and low-temperature regions obtained from the original expression for the imaginary part of the complex susceptibility (table 1, two recaps in parallel) neglecting the smallest relaxation time. The parameters for these asymptotes coincide with the parameters that are shown in the caption to figure 3. The dotted line shows the result of the fitting procedure by the simple Arrhenius type equation for a narrow region where $\tau_1 \sim \tau_2$. The fitting parameters in this case are $\tau = 4 \times 10^{-9} \times \exp(1315/T)$. The resulting values of the fitting parameters of this Arrhenius equation for this small region occupy an intermediate position between that obtained for high- and low-temperature ranges and shown in the caption to figure 3.

(b) ECs methods without any initial guess gave fitting parameters which are *not* so close to each other (see table 3).

5. Summary and basic conclusions

In this paper it has been shown that:

(i) It is possible to derive the empirical VFT equation based on the Arrhenius temperature dependence of relaxation times $\tau_{1,2}(T) = \tau_{A1,A2}[\exp(E_{1,2}/T)]$ entering into complex permittivity functions (6), and with a dependence (11) for the power-law exponents $\nu_{1,2}(\tau)$ found in [1].

(ii) This empirical equation does not have any *direct* relation with the glass transition phenomena and so cannot be referred only to glass-forming systems. The verification of the VFT equation for ionic conductors and the validity of the VFT equation for minimal points following before/after a low-frequency peak confirms this *preliminary* statement.

(iii) There is a generalization of the VFT formula, i.e. equations (12) and (18), which can be used to describe the temperature dependence of the loss peak frequency below and above

Table 3. The fitting parameters of the VFT equation calculated for available substances. (The abbreviation GD means 'German' data obtained from Dr P Lunkenheimer, while J D means 'Japanese' data obtained from Professor Shin Yagihara.)

Data	Fitting function	Fitting parameters
Propylene carbonate (GD)	VFT with Arrhenius correction (12)	$T_{VF} = 132.6 \pm 1.9$ K $C\omega_0/2\pi = 1.6 \times 10^9$ $\Delta E_{12}/\nu_0 = 2051$ $B = 998.9$
Pure glycerol (GD)	VFT with Arrhenius correction (12)	$T_{VF} = 114.79 \pm 3.6$ K $C\omega_0/2\pi = 1.26 \times 10^{11}$ $\Delta E_{12}/\nu_0 = 5136$ $B = 4387$
CKN $[(Ca(NO_3)_2]_{0.4}[(K(NO_3)]_{0.6}$ (GD)	Generalized VFT function (18)	$T_1 = 340.322 - \mathrm{i} \times 52.61$ K $T_2 = 340.322 + \mathrm{i} \times 52.61$ K $\varpi_0/2\pi = 8.35 \times 10^{18}$ $\Delta E_{12} = -111\,67$ $B_1 = 299.47 - \mathrm{i} \times 144.104$ $B_2 = 299.47 + \mathrm{i} \times 144.104$
CRN $[(Ca(NO_3)_2]_{0.4}[(R(NO_3)]_{0.6}$ (GD)	Generalized VFT function (18)	$T_1 = 343.49 - \mathrm{i} \times 36.577$ K $T_2 = 343.49 + \mathrm{i} \times 36.577$ K $\varpi_0/2\pi = 3.6 \times 10^{24}$ $\Delta E_{12} = -15\,515.57$ $B_1 = 135.97 + \mathrm{i} \times 48.1$ $B_2 = 135.97 - \mathrm{i} \times 48.1$
Pure glycerol (JD)	VFT function (14)	$T_{VF} = 123.89 \pm 11.3$ K $\omega_0/2\pi = 2.42 \times 10^{14}$ $D = 20.2$

the glass-forming temperature T_g. As was shown by the treatment of CKN and CRN data the generalized VFT equation does not have a restriction on the temperature range below T_g (for CKN and CRN $T_g \approx 333$ K)

(iv) Previously the temperature dependence of the loss peak frequency was described by the VFT equation in quite a narrow temperature range $T_g < T < T_B$, which depends on the fragility of the liquid and on the presence of a β relaxation [16]. In our approach the VFT equation has wider limits of applicability. It follows from the existence of at least two relaxation processes in a fractal system studied and their specific temperature dependence.

Modelling experiments have shown that not only a maximum loss peak but also a *minimum* between two peaks obeys the conventional or generalized forms of the VFT equations. This behaviour cannot be explained by the Adam–Gibbs theory.

Also in this work we found relations (13*a*) and (17*c*) that connect the empirical T_{VF} temperature with characteristic times τ_A, τ_0 and τ_s and other relaxation parameters and so clarified a physical meaning for this empirical temperature.

This work gives the possibility to put forward some problems for experimentalists working in the field of dielectric spectroscopy.

They are:

(1) If the VFT temperature behaviour does not have a *direct* relation with the glass transition phenomena and is a consequence of the two or more relaxation processes, then this type of behaviour must be observed in non-glass-forming materials with two or more relaxation processes. This hypothesis needs further experimental verification.

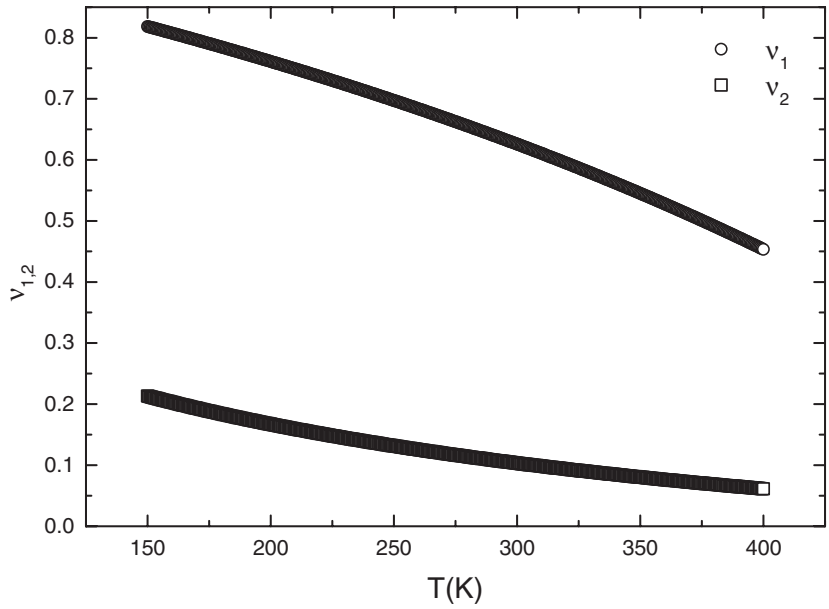

Figure 5. Typical temperature dependences of the power-law exponents $\nu_{1,2}$ that lead to VFT-like behaviour are shown here by open circles and squares. These temperature dependences were obtained with the help of parameters for the temperature dependences of relaxation times that coincide with those shown in the caption to figure 3 and with the parameters for equation (11): $\nu_1 = 0.96 \times \ln(\tau/1 \times 10^{-5})/\ln(\tau/1 \times 10^{-6})$, $\nu_2 = 0.5 \times \ln(\tau/1 \times 10^{-6})/\ln(\tau/1 \times 10^{-15})$.

(2) Do the generalized VFT equations expressed by formulae (12) and (18) have no restrictions in applicability for other glass-forming systems in the temperature range below the glass transition temperature T_g and also in the high-temperature range exceeding a temperature T_B, where the ordinary VFT equation fails in its description of the experimental data? This hypothesis also needs experimental verification for other glass-forming systems.

In this paper we tried to understand the basics of the VFT equation and find its true interpretation. It has been shown that the empirical VFT is generated by the scaling (non-exponential) character of relaxation taking place in a wide class of heterogeneous materials. In fact, *three* typical characteristic times should be used for the description of relaxation processes in heterogeneous materials. The characteristic time τ_s determines the duration of the self-diffusion process, while τ_0 defines the cut-off time of the scaling relaxation process in time domain. These two times figuring in expression (11) characterize the non-exponential part of the relaxation [1]. A possible individual reorientation of a dielectric dipole is characterized by the time τ_A. In reality one can expect that they obey the following relationship:

$$\tau_A \ll \tau_s \leqslant \tau_0. \tag{25}$$

(Here we should notice that in *model* experiments one can also obtain the VFT behaviour at 'nonphysical' conditions $\tau_A > \tau_s > \tau_0$.) The second part of this inequality is confirmed in [1] and by our calculations.

In conclusion, we should notice that relationship (11) obtained in [1] has an evaluative character. It is necessary to analyse more carefully a possible temperature dependence of the

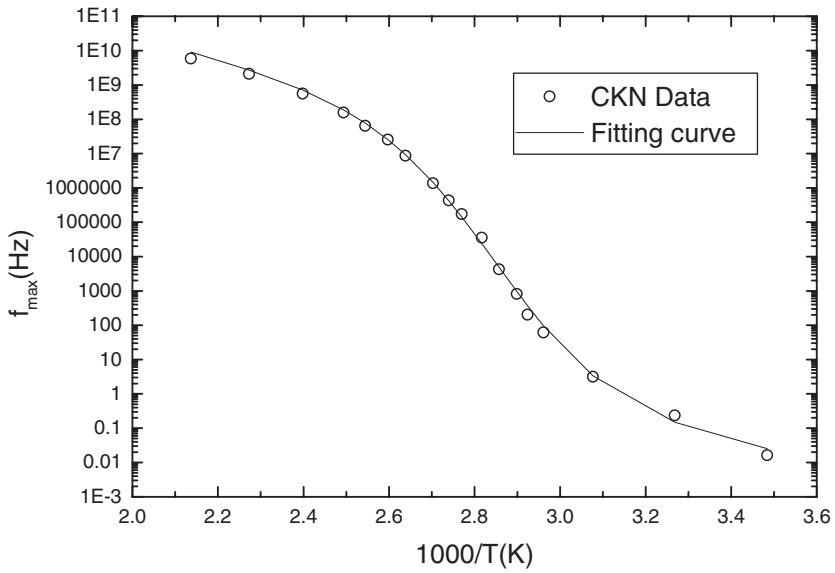

Figure 6. Open circles and full curve represent the temperature dependence of the maximum loss peak frequency for $[(Ca(NO_3)_2]_{0.4}[KNO_3]_{0.6}$(CKN) and the fitting curve obtained by the fitting procedure with the generalized VFT function (18). The chosen fitting function and the results of the fitting procedure (values of the fitting parameters) for these data are collected in table 3.

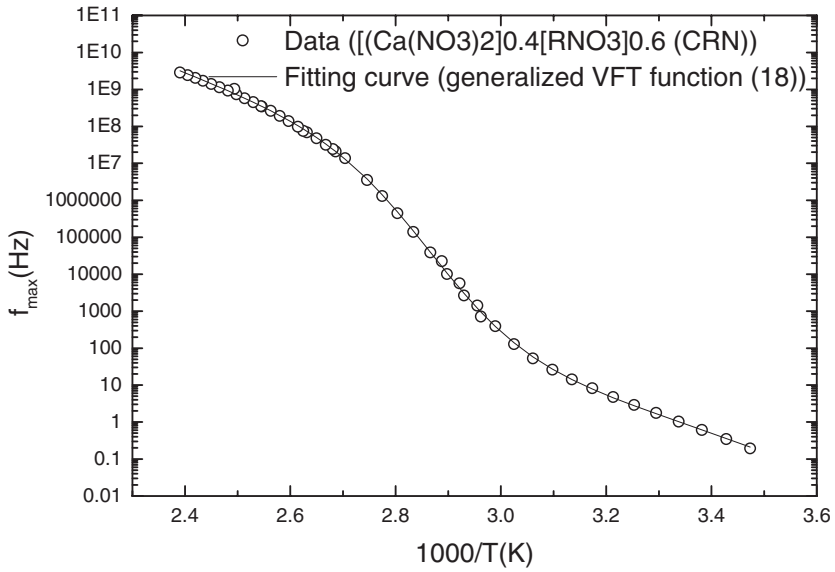

Figure 7. Open circles and full curve represent the temperature dependence of the maximum loss peak frequency for $[(Ca(NO_3)_2]_{0.4}[RNO_3]_{0.6}$ (CRN) and the fitting curve obtained by the fitting procedure with the generalized VFT function (18). The chosen fitting function and the results of the fitting procedure (values of the fitting parameters) for these data are collected in table 3.

parameters τ_s and τ_0 in order to increase the region of applicability of expression (11) for a deeper understanding of relaxation phenomena taking place in disordered materials with fractal structure.

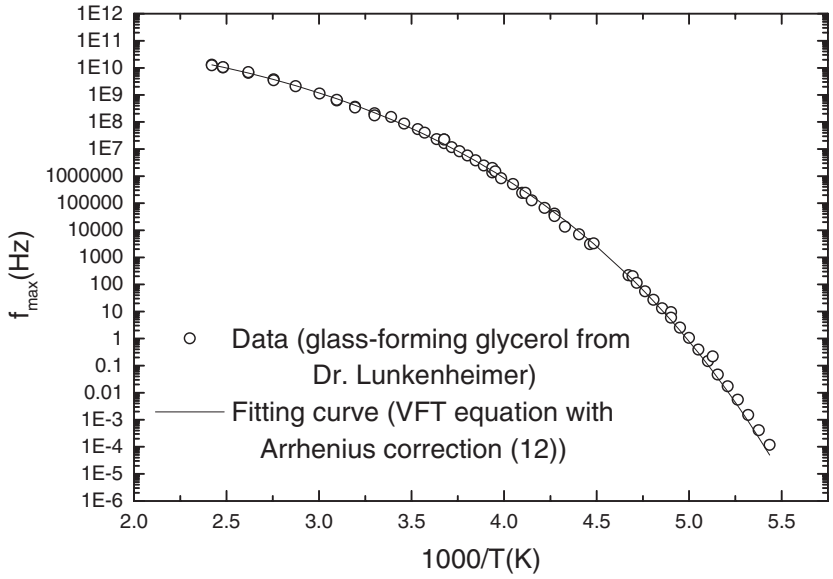

Figure 8. Open circles and full curve represent the temperature dependence of the maximum loss peak frequency for glass-forming glycerol and the fitting curve obtained by the fitting procedure using the VFT equation with the Arrhenius correction (12). The chosen fitting function and the results of the fitting procedure (values of the fitting parameters) for these data are collected in table 3.

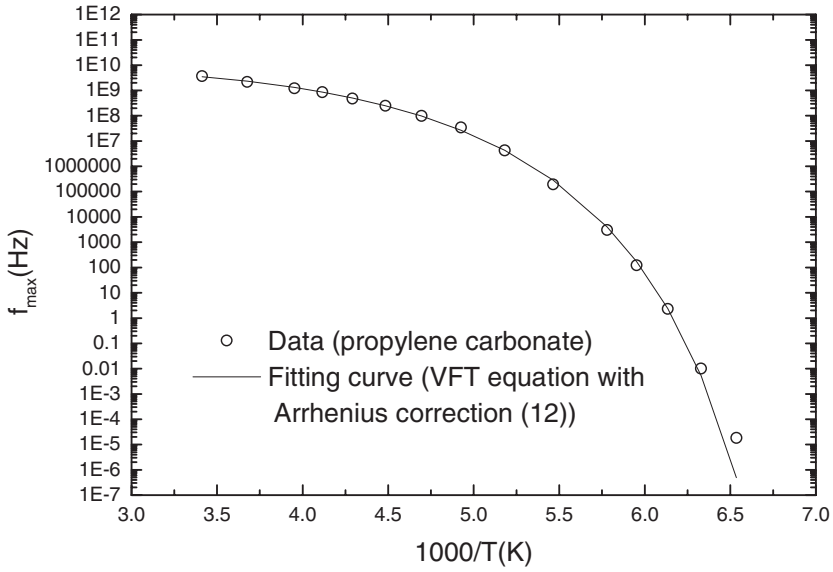

Figure 9. Open circles and full curve represent the temperature dependence of the maximum loss peak frequency for PC and the fitting curve obtained by the fitting procedure with the use of the VFT equation with the Arrhenius correction (12). The chosen fitting function and the results of the fitting procedure (values of the fitting parameters) for these data are collected in table 3.

Combining the investigations realized in this paper one can formulate the following important question:

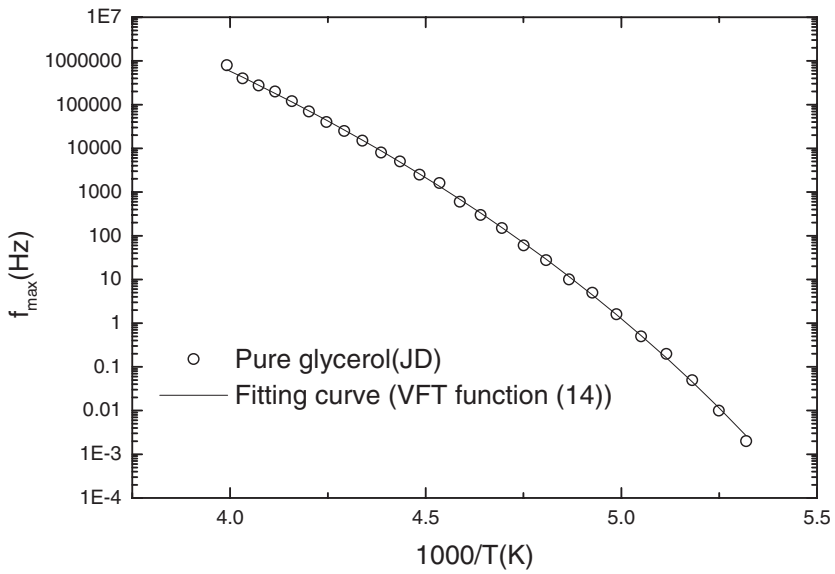

Figure 10. Open circles and full curve represent the temperature dependence of the maximum loss peak frequency for pure glycerol (Japanese data) obtained from Tokai University, Japan and the fitting curve obtained by the fitting procedure with the VFT equation (14), respectively. The chosen fitting function and the results of the fitting procedure (values of the fitting parameters) for these data are collected in table 3.

What kind of kinetic equation enables us to describe the relaxation phenomenon in a wide class of heterogeneous materials, where the identified complex permittivity function is described by equations (5) and (6) with a loss peak temperature dependence obeying the VFT equation?

After the detailed analysis realized in this paper the answer to this question can be found. Let us consider the kinetic equation in fractional derivatives of the following type:

$$[\tau_1^{\nu_1} D_{t_0}^{\nu_1} + \tau_2^{\nu_2} D_{t_0}^{\nu_2}](P(t) - P(t_0)) + P(t) = 0. \tag{26}$$

Here $P(t)$ is a value of the total polarization and the operator D_a^q $(0 \leqslant q \leqslant 1)$ defines the Riemann–Liouville non-integer differential operator [36]:

$$D_a^q f(x) = \frac{\mathrm{d}}{\mathrm{d}x}[D_a^{q-1} f(x)] = \frac{\mathrm{d}}{\mathrm{d}x}\left[\frac{1}{\Gamma(1-q)} \int_a^x (x-y)^{-q} f(y)\,\mathrm{d}y\right]. \tag{27}$$

The parameters $\tau_{1,2}$ determine some characteristic times, which provide the conservation of dimension in both parts of equation (26). It is easy to find the stationary solution of the kinetic equation (26). We present the solution in the form

$$P(t) = \chi(j\omega)\exp[j\omega t]. \tag{28}$$

Taking into account the value of the integral

$$D_{-\infty}^{\nu}[\exp(j\omega t)] = \frac{\mathrm{d}}{\mathrm{d}t}\left[\frac{1}{\Gamma(1-\nu)} \int_{-\infty}^{t} (t-u)^{-\nu} \mathrm{e}^{\mathrm{j}\omega u}\,\mathrm{d}u\right] = (j\omega)^{\nu}\exp(j\omega t) \tag{29}$$

and an initial condition $P(-\infty) = 0$ it is easy to find the expression for complex susceptibility:

$$\chi(j\omega) = \frac{\chi(0)}{1 + (j\omega\tau_1)^{\nu_1} + (j\omega\tau_2)^{\nu_2}}. \tag{30}$$

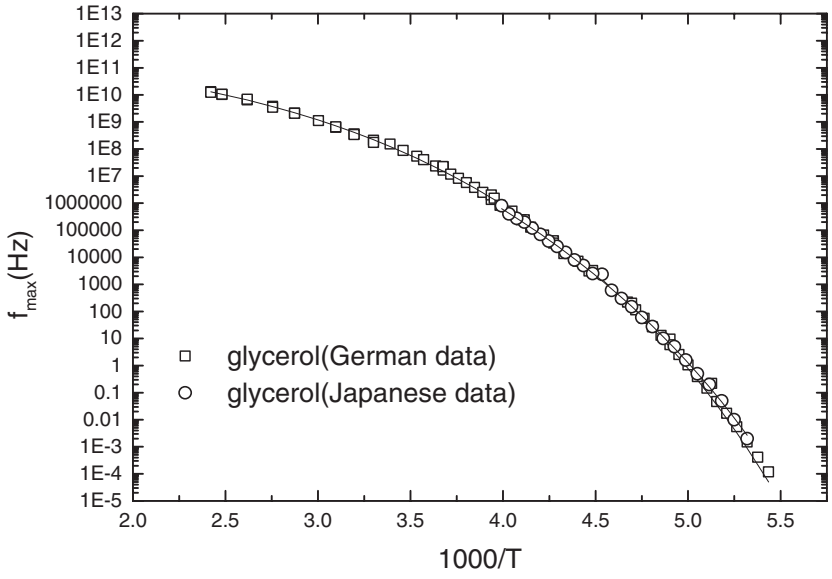

Figure 11. Open circles and squares and full curves represent together the temperature dependences of the maximum loss peak frequency and fitting curves for pure glycerol obtained from Tokai University, Japan, Japanese data and glycerol measured by Dr P Lunkenheimer (German data), respectively. The chosen fitting function and the results of the fitting procedure (values of the fitting parameters) for these data are collected in table 3.

This expression totally corresponds to the complex permittivity written in the form (5) with $R(j\omega)$ from (6*a*).

Let us consider another kinetic equation written in the form

$$[\tau_1^{-\nu_1} D_{t_0}^{-\nu_1} + \tau_2^{-\nu_2} D_{t_0}^{-\nu_2}](P(t) - P(t_0)) + P(t) = 0, \tag{31a}$$

or equivalently

$$[\tau_1^{-\nu_1} D_{t_0}^{-\nu_1} + \tau_2^{-\nu_2} D_{t_0}^{-\nu_2}]^{-1}(P(t) - P(t_0)) + P(t) = 0 \tag{31b}$$

where fractional exponents are supposed to be located in the interval $(0 \leqslant \nu_1, \nu_2 \leqslant 1)$. The stationary solution of these equations can be found by analogy with (26). At the initial condition $P(-\infty) = \chi(0)\exp[j(\omega - j\varepsilon)t](\varepsilon \to 0)$ (which corresponds to the adiabatic switching of the electric field at $t = -\infty$) it is easy to find the expression for complex susceptibility. It can be written as

$$\chi(j\omega) = \frac{[(j\omega\tau_1)^{-\nu_1} + (j\omega\tau_2)^{-\nu_2}]\chi(0)}{1 + [(j\omega\tau_1)^{-\nu_1} + (j\omega\tau_2)^{-\nu_2}]} = \frac{\chi(0)}{1 + [(j\omega\tau_1)^{-\nu_1} + (j\omega\tau_2)^{-\nu_2}]^{-1}} \tag{32}$$

and corresponds to the expression of the complex permittivity (5) with $R(j\omega)$ taken from (6*b*).

In such a way, we proved that the process of dielectric relaxation in a wide class of heterogeneous materials possessing a fractal structure is described by kinetic equations of the type (26) or (31). The special procedure developed in [26] for recognition of complex permittivity of the type (5) in the frequency domain and the validity of the VFT equation can be used as a *decisive* argument in proving that the real process of dielectric relaxation is described by kinetic equations containing a linear combination of fractional derivatives (26) or integrals (26). Generalizing these kinetic equations containing fractional derivatives one

can expect the following structure of kinetic equations describing the dielectric relaxation phenomenon in the time domain:

$$\sum_{k=1}^{n} \tau_k^{\nu_k} D_{t_0}^{\nu_k} [P(t) - P(t_0)] + P(t) = 0. \tag{33}$$

The physical meaning of the last kinetic equation is the following. We suppose that all relaxation systems, including a set of strongly correlated microdipoles, can be divided into n subsystems. It might be a set of dipole clusters or an ensemble of strongly correlated molecules. Each subsystem is interacting with a thermostat with the help of a collision mechanism, which is expressed by means of a fractional derivative (the physical meaning of the fractional integral is discussed in [36]). Each subsystem k ($k = 1, 2, \ldots, n$) is characterized by a relaxation time τ_k showing the contribution of the chosen relaxation unit to the general relaxation. The number of subsystems giving an additive contribution to the general picture of relaxation is defined by the structure of the concrete heterogeneous material considered. At an initial stage the kinetic equation (33) can be considered as a reasonable and phenomenological hypothesis, which is confirmed by experimental measurements. After identification of this type of kinetic equation on a wide class of heterogeneous materials further theoretical attempts should be undertaken in order to explain their microscopic origin.

In conclusion we want to stress that an attempt to represent a complex dielectric spectrum in the form of a linear combination of empirical functions of the type (3) or (4) can be considered only as an *approximation*. An additive combination of complex permittivity functions in the frequency domain can be justified only in the case when we deal with processes having *different* physical origins. It might be, for example, a relaxation process with a combination of electrode polarization effects or an independent LFD process related to the conductivity of a material with a bulk relaxation process, etc. From the picture of 'good fitting' obtained with the help of a linear combination of complex permittivity functions it becomes impossible to restore a 'true' kinetic equation for the total polarization, describing a 'true scenario' of the evolution of polarization in a time domain taking place for bulk material. The kinetic equation (33) for the total polarization giving a more consistent picture of dielectric relaxation for complex materials can serve as a reliable basis for the understanding of relaxation phenomena in a wide class of heterogeneous materials.

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