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DIELECTRIC RESPONSE AND A PHENOMENON OF A NARROW BAND ABSORPTION FOR A CLASSICAL ROTOR IN A DOUBLE WELL POTENTIAL

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The theory of dielectric relaxation in a planar ensemble of polar molecules is presented for a model where dipoles rotate in an intermolecular conservative double well potential, having a profile $U = U_0 \sin^2\theta$. The evolution of wide band dielectric spectra is demonstrated when the potential depth U_0 is varied; an isotropic and anisotropic medium being taken as examples. The spectra comprise the Debye relaxation and the quasi-resonant Poley absorption region. The rigorous theory is compared with a simplified one which was called the hybrid quasi-elastic bond / extended diffusion model. This approximation is valid for a qualitative description and also for the quantitative one at the large field parameter $p = \left[U_0/(k_B T)\right]^{1/2}$.

For $p \gg 1$ the spectrum comprises one narrow absorption band and one Debye relaxation region considerably shifted to low frequencies. It is shown that in the long lifetime limit τ there exists a minimum absorption band $\Delta\nu_0(p)$. The quantity $\Delta\nu_0$ becomes small if the parameter $p \gg 1$. The dielectric relaxation in ice 1 is discussed with regards to this phenomenon.

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1. The Problem of Narrow Lines in a Classical Ensemble of Polar Molecules

During the last few years considerable attention has been paid to elaboration of molecular models of dielectric relaxation in strong absorbing polar liquids. A possibility was demonstrated[1-6] to describe by using such models the evolution of the spectrum of the orientational relaxation due to temperature change. A low frequency wing of this spectrum falls usually into the microwave region while the quasi-resonance Poley absorption falls into the FIR spectral region.

Let us list the typical dielectric properties of polar liquids:

a) a considerable (several times or in an order of magnitude) rise of the frequency ω_L of a maximum absorption comparing frequency ω_{gas}. The latter refers to the maximum rotational spectrum absorption due to the same (as in a liquid) polar molecules;

b) The frequency ω_D of maximum dielectric loss, $\varepsilon''_D = \max[\varepsilon''(\omega)]$, is one or two orders of magnitude less than the frequency ω_L, the Debye relaxation time $\tau_D = \omega_D^{-1}$ being a characteristic parameter of a liquid;

c) the wide band $\Delta\omega_L$ of the absorption spectrum is commensurable with the frequency ω_L of the absorption peak. Thus, in "simple" polar liquids

$$\omega_L > \omega_{gas} \; ; \; \omega_D << \omega_L \; ; \; \Delta\omega_L \sim \omega_L . \qquad (1.1)$$

The analytic theory[1-6] ignores quantum effects and so it is based on classical descriptions. This assumption is also made in our calculations These are valid not because of limitations imposed on a maximum radiation frequency ω (as one sometimes considers) but because the time τ, during which the local liquid structure exists, is small: τ^{-1} is usually not less than ω_L ,the frequency of maximum absorption:

$$\tau << \tau_D \; , \; \tau \sim \omega_L^{-1} . \qquad (1.2)$$

Simplifying the situation, one may "justify" the applicability of classic description by the following argument. Because of frequent collision in liquids the superposition of individual

rotational lines occurs and consequently the discrete rotational spectrum does not appear as a rule. In strongly absorbing liquids, unlike polar gas, the time τ between collisions is less than the collision time τ_c :

$$\{\text{liquid}\}: \quad \tau < \tau_c; \qquad \{\text{gas}\}: \tau \gg \tau_c. \tag{1.3}$$

It is because of this reason, the term "collision time", having a definite meaning in case of a gas, becomes vague in case of a liquid. Apart from this, quantum rotational lines characterizing a gas of weak interacting polar molecules shift considerably due to the strong intermolecular field.

p. We shall prove in the present investigation that in classical theory a new property of narrow absorption band is attributed to the effect of a strong conservative field on librating dipoles.

A dipole is a classical rotor (for simplicity we assume that it has a form of a linear molecule) which is characterized by a moment of inertia I and by a dipole moment μ. Note that *in a strong intermolecular field one narrow absorption band arises as if an envelope of a quantum spectrum were compressed into a narrow classical band and were shifted to higher frequencies.*

The Debye relaxation time increases substantially in this case as compared with a typical liquid:

$$\left\{\begin{array}{l}\text{state of substance,}\\ \text{characterized by a}\\ \text{narrow absorption line}\end{array}\right\}: \begin{array}{l}\tau \ll \tau_D\ ;\ \tau \gg \omega_L^{-1};\\ U_o/(k_B T) \gg 1;\ \Delta\omega_L \ll \omega_L\ .\end{array} \tag{1.4}$$

The following question arises. Does there exist a molecular system in which a considerable narrowing of an absorption band may be interpreted as an influence on a classical dipole of an effective intermolecular field? One example is more or less evident. It is ice 1 where the resonant absorption bands are several times narrower than in water, while the shift of the centres of absorption peaks to higher frequencies is about ten per cent[7-10]. On the other hand, in the case of ice the relaxation time is many orders of magnitude greater than in water.

It should be noted right away that both in ice and in liquid water *two* quasi-resonant absorption band are characteristic. This situation is more intricate than that in simple liquids. This fact complicates the interpretation but has no great significance since when water freezes both the absorption bands in the spectrum of of orientational relaxation becomes narrower and both shift.

For the study of the dielectric relaxation characterized by the properties (1.4), we use an approximation of plane trajectories (a planar ensemble). We chose the potential profile

$$U(\vartheta) = U_0(1 - \cos^2\vartheta), \tag{1.5}$$

where ϑ is an angular shift of a dipole relative to the symmetry axis of a potential U. This profile is called the double well potential (DWP).

In an introductory section 2 the basic relations needed for further consideration are presented. In Sec. 3 taking an example of an isotropic polar medium we shall discuss the results of rigorous calculations for the DWP model with the profile (1.5). In section 4 we shall show that a hybrid quasi-elastic bond / extended diffusion (QEB/ED) model is also applicable and that approximate analytical expressions are much simpler than in the strict DWP model. In Sec.5 on an example of an anisotropic medium we shall turn to the main effect of this work - to the narrowing of absorption lines due to action of a strong potential (1.5). In the final section 6 the relation of the field models of molecular rotation / dielectric relaxation to ice I is investigated.

2. The Approximation of Instantaneous Collision: General Expressions

The dielectric response of an *isotropic* medium to reorientations of dipoles is characterized by the complex susceptibility $\chi(\omega) = \chi' - i\,\chi''$. The complex propagation constant $k^* = k' + ik''$ and dielectric permittivity $\varepsilon^* = \varepsilon' + i\,\varepsilon''$ of a plane electromagnetic wave are related one to another by the equation

$$k^* = \frac{\omega}{c}\sqrt{\varepsilon^*} = \frac{\omega}{c}(n + i\varkappa), \tag{2.1}$$

where the star $*$ denotes complex conjugation. Let n_∞ be an

optical refractive index. If one ignores the difference between an internal and macroscopic electromagnetic field in a medium, then ϵ is related to χ by

$$\varepsilon^*(\omega) = n_\infty^2 + 4\pi\chi^*(\omega). \tag{2.2}$$

Thus the constant k is related to the complex susceptibility by the equation

$$k^{*2} = \frac{\omega^2}{c^2}\left[4\pi\chi^* + n_\infty^2\right]. \tag{2.3}$$

Equation (2.2) may be replaced by

$$\frac{\varepsilon^* - n_\infty^2}{4\pi}\,\frac{2\varepsilon^* + n_\infty^2}{3\varepsilon^*} = \chi^*(\nu) \tag{2.4}$$

when the difference between internal and macroscopic fields is approximately taken into consideration[2], eq. (2.3) being retained.

In an *anisotropic polar medium* the dielectric susceptibility χ is a tensor. *In this work we shall calculate right away the scalar quantity k*, the real part k' of which determines the phase velocity of an electromagnetic wave in a medium, while the imaginary part k" determines the absorption coefficient α:

$$\alpha = 2k'' = 2\,\frac{\omega}{c}\,\varkappa = \frac{\omega\varepsilon''(\omega)}{c\,n(\omega)}. \tag{2.5}$$

ANISOTROPIC MEDIUM. We introduce an *effective complex susceptibility* χ of an anisotropic medium[11], which is related to the propagation constant k (2.3), the relation ε to χ again being taken in the form (2.2) or (2.4). The cause of an anisotropy is an existence of an uniaxial intermolecular potential $U(\vartheta)$, ϑ being the angle between the the symmetry axis Z of the potential U and the dipole moment vector $\vec{\mu}(t)$ of a reorientating linear molecule. Note that if the directions of the local symmetry axes are random then in various points of the a dielectric sample the medium becomes isotropic.

We assume that the linearly polarized electric field $\mathbf{E}(t)$ varies harmonically in any point of a medium:

$$\mathbf{E}(t) = \mathbf{E}_m \sin(\omega t + \gamma). \tag{2.6}$$

We denote parallel and orthogonal directions of the amplitude vector $\mathbf{E}_m$ to the symmetry axis, by symbols $\parallel$ and $\perp$. The problem is

solved, if the frequency dependences $\chi_{\parallel}(\omega)$ and $\chi_{\perp}(\omega)$ are found for two crossed orientations since for an arbitrary angle Φ between Z and E_m the susceptibility χ is a known rational function of $\chi_{\parallel}(\omega)$ and $\chi_{\perp}(\omega)$.

When investigating the dependence of χ on ω we distinguish two mechanisms of the wave - medium interaction $\longmapsto$ for molecular rotation at equilibrium due to: a) the *periodic* rotation of a dipole in a potential well of a prescribed profile; and b) the stochastic (Brownian) reorientation of molecules. With regard to a) we calculate the spectral function (SF) and denote it K(z). It should be noted that K(z) differs from the SF L(z) introduced in work[11] by the multiplier $3\langle q^2\rangle$, which is not dependent on the radiation frequency ω and which will be difined later. The frequency dependence of K(z) describes the dielectric response in the FIR spectral range. Here z defined by $z = x + i\,y$ is the normalized complex frequency, $x = \eta\omega$ and $y = \eta/\tau$ being respectively the normalized radiation frequency and the frequency of "strong" collisions, $\eta = [I / (2k_B T)]^{1/2}$ is a normalizing parameter, k_B is a Boltzmann constant, T is absolute temperature and I is the moment of inertia. The K(z) function is proportional [11] to the spectrum of the autocorrelation function of the electric moment vector $\underset{\sim}{\mu}(t)$, which is performing undamped (periodic) rotation in a potential $U(\vartheta)$:

$$K(z) = 3\, iz\left\langle q_0 \int_0^{\infty} (q-q_0)\, e^{iz\varphi} d\varphi \right\rangle. \qquad (2.7)$$

Here the following dimensionless variables are used: the time $\varphi = t / \eta$, $q = q(\varphi) = \mu_E / \mu$, where μ_E is the projection of the electric moment vector $\vec{\mu}$ on the direction of the amplitude field vector E_m, $\mu = |\vec{\mu}|$, q_0 is the value of $q(\varphi)$ at the moment $\varphi = 0$ of a "strong collision". The q_0 coordinate is regarded as a point in a phase space Γ, and averaging over Γ is denoted by brackets $\langle\cdots\rangle$.

The second factor b) is determined by a collision model and plays an important role only in the low-frequency (Debye) spectral region. For definiteness we take the modified Gross collision model [1,11] in which χ is related to K by the equation

$$\chi^* = g\, G\, z\, K(z) \left[gx + \frac{iy}{\sigma} K(z) \right]^{-1}, \qquad (2.8)$$

where $G = \mu^2 N / (3\, k_B T)$, N is a concentration of polar molecules, g is a Kirkwood correlation factor and

$$\sigma = 3 \left[\langle q^2 \rangle - \langle q \rangle^2 \right] \qquad (2.9)$$

where $(1/3)\sigma$ is a dispersion of a q . In all equations below except Sec.6 we take g = 1 , while in Sec.6 a more realistic version of the Gross collision model in which g differs from 1 will be introduced.

For two cross orientations we write $\chi_\parallel$, $\langle\sigma_\parallel\rangle$, $K_\parallel$ or $\chi_\perp$, $\langle\sigma_\perp\rangle$, $K_\perp$, while at the "inclined" propagation of a wave

$$K(z) = K_\parallel(z) \cos^2\Phi + K_\perp(z) \sin^2\Phi. \qquad (2.10)$$

We repeat that Φ is the angle between $\mathbf{E}_m$ and Z.

ISOTROPIC MEDIUM. Now we dwell upon an important case of a macroscopic isotropic polar medium. We suppose that only a local anisotropy exists, and that in a macroscopic volume of a dielectric sample the complex susceptibility is found by averaging eq.(2.10) over all angles Ψ . We shall consider 4 cases:

a) *planar ensemble:*

$$\langle q \rangle = 0,\ \langle q^2 \rangle = 1/2;\ \sigma = 3/2,\ K(z) \equiv (1/2)(K_\parallel + K_\perp); \qquad (2.11)$$

b) *quasi-space ensemble.* In order to draw near real situation without substantial mathematical complication due to the calculation of trajectories in space we may obtain $K_\parallel(z)$ and $K_\perp(z)$ functions for planar trajectories while all averages are found for the "space" statistics:

$$\langle q \rangle = 0,\ \langle q^2 \rangle = 1/3,\ \sigma = 1,\ K(z) \equiv (1/3)(K_\parallel + K_\perp). \qquad (2.12)$$

Notwithstanding these "tricks", the integrated absorption is only the half of a strict value because the number of degrees of freedom is actually reduced in this approximation:

$$\int_{\infty}^{\infty} \omega\, \chi''(\omega)\, d\omega = \left\{ \begin{matrix} 1 \\ 2 \end{matrix} \right\} \pi\mu^2 N/(3I) \text{ for } \left\{ \begin{matrix} \text{quasi-space} \\ \text{space} \end{matrix} \right\} \text{ ensemble.} \qquad (2.13)$$

c) For better agreement with experiment in the FIR spectral region we may eliminate the last drawback, doubling the value $K(z)$ found above for a quasi-space ensemble

$$\sigma = 1;\ K(z) \equiv (2/3)(K_{\parallel} + K_{\perp});\ \left\{ \begin{array}{c} \text{corrected} \\ \text{quasi-space} \\ \text{ensemble} \end{array} \right\}. \tag{2.14}$$

d) space ensemble in which the following relations hold

$$\langle q \rangle = 0,\ \langle q^2 \rangle = 1/3,\ \sigma = 1,\ K(z) \equiv (1/3)(K_{\parallel} + 2K_{\perp}). \tag{2.15}$$

and the true integrated absorption corresponds. $K_{\parallel}$ and $K_{\perp}$ must be found by studying rotations in space.

In the three last cases b, c, d eq.(2.8) reduces to the following formula

$$\chi^* = g\ G\ z\ L(z) \left[gx + iy\ L(z) \right]^{-1}, \tag{2.16a}$$

which was widely used[1,2,6,11]. Here the spectral function

$$L(z) = \left\{ \begin{array}{l} L_{\text{planar}} \\ 2\ L_{\text{planar}} \\ L_{\text{space}} \end{array} \right\} \text{ for } \left\{ \begin{array}{l} \text{quasi-space} \\ \text{quasi-space with doubling of SF} \\ \text{space} \end{array} \right\} \text{ ensemble,} \begin{array}{l} (2.16b) \\ (2.16c) \\ (2.16d) \end{array}$$

$$L_{\text{plan.}} = (1/3)(K_{\parallel} + K_{\perp});\quad L_{\text{space}} = (1/3)(K_{\parallel} + 2K_{\perp}). \tag{2.16e}$$

DEBYE RELAXATION. "Static" (at $x = 0$) value of $K \equiv K_0 = K(iy)$ determines the parameters of the Debye relaxation, i.e. the static susceptibility χ_s, the relaxation time τ_D and susceptibility at the end of the Debye relaxation region (K_0 is real). The Debye frequency dependence has the form

$$\chi^*(x) = \chi_\infty + \left[\chi_s - \chi_\infty\right]\left[1 - ix\tau_D / \eta\right]^{-1}, \tag{2.17a}$$

and so

$$\max_x \{\chi''(x)\} = \chi''_D = \tfrac{1}{2}\left[\chi_s - \chi_\infty\right] \quad \text{at} \quad x = x_D = \eta/\tau_D, \tag{2.18a}$$

and

$$\chi_s = \chi^*(x)\Big|_{x=0},\quad \chi_\infty = \chi^*(x)\Big|_{x\to\infty},\quad \tau_D = \frac{\eta}{\chi_s - \chi_\infty} \lim_{x\to 0} \frac{\chi''(x)}{x}. \tag{2.18b}$$

For the Gross collision model, generalized to the case when $g \neq 1$, the above mentioned parameters are related to the spectral function K_0 as follows

$$\chi_s = g\sigma G;\quad \chi_\infty = GK_0;\quad \chi''_D = \tfrac{1}{2}G\left[g\sigma - K_0\right];\ \tau_D = g\tau\sigma / K_0. \tag{2.19}$$

Thus the Debye relaxation time is proportional to σ and to K_0^{-1}. In our impact theory approximation the life time τ is a free model

parameter. The experimentally determined relaxation time τ_D strongly depends on temperature and still more strongly on a phase state of a dielectric sample. The value of τ may be found by taking the prescribed value of τ_D if one finds the solution (relative to τ) of the equation

$$\sigma\,\tau \,/\, K(i\eta/\tau) = \tau_D \,/\, g \qquad \left\{ \begin{array}{c} \text{anisotropic} \\ \text{medium} \end{array} \right\}, \qquad (2.20)$$

or

$$[\langle q^2\rangle - \langle q\rangle^2]\,\tau \,/\, L(i\eta/\tau_D) = \tau_D \,/\, g \qquad \left\{ \begin{array}{c} \text{isotropic} \\ \text{medium} \end{array} \right\}. \qquad (2.21)$$

Here the r.h.s. is given by the experimental data. To the prescribed change of τ_D may correspond some change of the potential well depth U_0 accompanied by the change of the potential profile $U(\vartheta)$ and the lifetime τ.

The increase of the well depth U_0 greatly influences the "static" response K_0 and the dispersion σ, these values being different for the parallel and orthogonal susceptibilities. Examples of τ_D dependence on U_0 and τ are given in Sec.4.

In order to interpret experimental dielectric spectra one must describe the frequency dependence $\varepsilon(\omega)$ of the complex dielectric permittivity. We employ eq. (2.8) with g given by

$$g = \frac{\varepsilon_s - n_\infty^2}{4\pi}\,\frac{2\varepsilon_s + n_\infty^2}{3\varepsilon_s}\,\left[G\sigma\right]^{-1}. \qquad (2.22)$$

For g so defined eq.(2.4) and (2.8) give for $\omega = 0$ the permittivity $\varepsilon(\omega)$ which is equal to its experimental value ε_s.

3. The Rigorous Theory of Orientational Relaxation for the Double Well Potential

THE STEADY STATE PARAMETERS.

For simplicity we consider rotational motion in a plane, taking the dependence of the static field $E_o(\vartheta)$ on the angular shift ϑ as $\cos\vartheta$. Then we come to the double well potential (DWP) in the form $U(\vartheta) = \mathrm{const}(\vartheta) - \vec{\mu}\,/\vec{E}_o(\vartheta)$:

$$\left.\begin{array}{l}\text{Double well}\\ \text{potential}\\ \text{(DWP)}\end{array}\right\} U(\vartheta) = U_o(1 - \cos^2\vartheta), \quad E_o(\vartheta) = (U_o/\mu)\cos\vartheta. \qquad (3.1a)$$

In this formula we chose the arbitrary constant so that at the bottom of the well $U = 0$. Thus U_o is the well depth. The $U(\vartheta)$ function has two minima, the dipoles in neighboring wells have opposite orientations and so the average dipole moment $\langle\vec{\mu}\rangle$ of the dielectric sample is zero. In such a field model

$$\langle q_\parallel\rangle = \langle q_\perp\rangle = 0, \qquad \sigma_\parallel = 3\langle q_\parallel^2\rangle \text{ and } \sigma_\perp = 3\langle q_\perp^2\rangle. \qquad (3.1b)$$

We introduce the static field parameter p by

$$p \equiv \sqrt{U_o/(k_B T)} \qquad (3.1c)$$

and the normalized Hamiltonian of a dipole h = (the total energy of a dipole) / $(k_B T)$. Denoting by a dot the differentiating over of the time $\varphi = t/\eta$ we have

$$h = \dot{\vartheta}^2 + p^2\sin^2\vartheta, \qquad (3.2)$$

The integral

$$(\varphi + \varphi_o)p = \int_{\vartheta_o}^{\vartheta} \frac{d\vartheta}{\sqrt{h/p^2 - \sin^2\vartheta}} \qquad (3.3)$$

is obtained for the law of motion from (3.2). Putting in (3.2) $\dot{\vartheta} = 0$, we may relate the maximum angular shift $\beta \equiv |\vartheta|_{max}$ with the energy of a dipole h and the static field parameter p:

$$\beta \cong \left\{\begin{array}{l}\arcsin\sqrt{h/p^2}\\ \pi\end{array}\right\} \text{ for } \left\{\begin{array}{l}h\,/\,p^2 \leqslant 1\\ h\,/\,p^2 \geqslant 1\end{array}\right\}. \qquad (3.4)$$

Thus two sub-ensembles of librators and hindered rotators exist, the value $h = p^2$ being the threshold energy. We distinguish these sub-ensembles by indexes $\vee$ and $\circ$, respectively.

The quadrature (3.3) can be expressed in terms of elliptic

functions. It may be shown that the period $\check{\Phi}$ of the function $\check{q}_{\parallel}(\varphi)$ is determined by the equation $p\,\check{\Phi} = 2\mathbf{K}(k)$, where $\mathbf{K}$ is the complete elliptic integral of the first kind and $k = \sqrt{h}/p$ is its modulus [the reader should not confuse the latter with the propagation constant k in (2.1),(2.3),(2.5)]. Accordingly the normalized libration frequency is given by

$$\check{p} = \frac{\pi}{\check{\Phi}} = \frac{\pi p}{2\mathbf{K}(\sqrt{h}/p)} \quad . \tag{3.5}$$

The second group of particles performs a hindered rotation, the normalized period of which satisfies the equation

$$\overset{\circ}{\Phi} = 4h^{-1/2}\mathbf{K}(k), \quad \text{where} \quad k = p\,/\,\sqrt{h}. \tag{3.6a}$$

Thus the normalized rotational frequency is equal to

$$\overset{\circ}{p} = 2\pi\left[\overset{\circ}{\Phi}\right]^{-1} = (\pi/2)\sqrt{h}\left[\mathbf{K}(p/\sqrt{h})\right]^{-1}. \tag{3.6b}$$

Omitting calculations (see details in the review[11]), we present here the expressions for the steady state distribution function $W(h)$ and for the averaged values of q^2:

$$W(h) = \left\{2\pi^{3/2}I_0(p^2/2)\right\}^{-1}\exp\left[(p^2/2)-h\right], \tag{3.7a}$$

$$\begin{Bmatrix}\langle q^2_{\parallel}\rangle \\ \langle q^2_{\perp}\rangle\end{Bmatrix} = \frac{I_0(p^2/2)\pm I_1(p^2/2)}{2I_0(p^2/2)} = \frac{1}{3}\begin{Bmatrix}\langle\sigma_{\parallel}\rangle \\ \langle\sigma_{\perp}\rangle\end{Bmatrix}. \tag{3.7b}$$

The mean potential energy can be found from (3.7) and (3.1):

$$\langle U(\vartheta)\rangle = \begin{Bmatrix} \frac{1}{2}U_0\left[1-I_1\left(p^2/2\right)/I_0\left(p^2/2\right)\right] \\ (1/2)k_BT \\ (1/2)\,U_0 \end{Bmatrix} \quad \begin{Bmatrix} \text{general case} \\ \text{for } p \geqslant 1 \\ \text{for } p \ll 1 \end{Bmatrix} \tag{3.8}$$

Thus, in the case of a deep potential well the quantity $\langle U(\vartheta)\rangle$ is about $\frac{1}{2}(k_BT)$ and does not depend on U_0, while for a shallow well this average is about half depth.

In Table 1 rigorous and asymptotic values are presented for: the proportion $\check{r}$ of rotors, the mean libration amplitude $\langle\beta\rangle$, the normalized frequencies of libration and hindered rotation, $\langle\check{p}\rangle$ and

$\langle \overset{\circ}{p} \rangle$, the distribution functions $\check{f}(\check{p})$ and $\overset{\circ}{f}(\overset{\circ}{p})$ over these frequencies and the parameter y_c, viz.

$$\tau_c = \eta/y_c \approx \frac{1}{2} \left\langle \begin{matrix}\text{period of librational/} \\ \text{rotational motion}\end{matrix} \right\rangle = \eta\pi/\langle p \rangle. \qquad (3.9a)$$

The time τ_c means the average half period of reorientations and may serve as a measure of collision time[6] of particles, effected by the conservative potential U. The p - dependence of the steady state parameters and the distribution functions $\check{f}(\check{p})$ and $\overset{\circ}{f}(\overset{\circ}{p})$ are illustrated by Table 1 and Fig.1. The non-zero distribution $\check{f}(\check{p})$ appears only at sufficiently large field parameter p, it falls abruptly to zero at the maximum libration frequency $\check{p}$, equal to

$$\max \{\check{p}\} = p. \qquad (3.9b)$$

For a deeper well the distribution $\check{f}(\check{p})$ becomes narrower, while the peak of the distribution $\overset{o}{f}(\overset{o}{p})$ shifts to greater frequencies $\overset{\circ}{p}$. If p is sufficiently large ($p \geqslant 2$), almost all dipoles are librators: in this case the function $\overset{\circ}{f}(\overset{\circ}{p})$ press itself to the abscissa axis and the square beneath it becomes small. The mean libration amplitude $\langle \check{p} \rangle$ decreases when p rises, while the generalized parameter y_c (which is proportional to the reciprocal value of the collision time) increases. Thus the mean period of rotational motion decreases when the well depth increases.

SPECTRAL FUNCTIONS. Now let us consider dielectric relaxation due to reorientation of molecules in the double well potential. We represent the spectral function as a sum

$$K = \check{K} + \overset{\circ}{K}. \qquad (3.10)$$

Integrating (2.7) over time φ and steady state ensemble, we take into account (3.7) and the representation of (3.3) in terms of elliptic functions. Then the spectral function $K(z)$ is represented by a series, in which terms are quadratures over the modulus k of complete elliptic integrals. For the sub-ensemble of librators we take as a variable of integration $m = k^2$, so that

$$\mathbf{K} \equiv \mathbf{K}(k) \equiv \mathbf{K}(m^{1/2}); \qquad (3.11)$$

as a result we have

$$\begin{Bmatrix} \check{K}_{\parallel} \\ \check{K}_{\perp} \end{Bmatrix} = \frac{3\pi^{5/2}\, p^{3}\, e^{p^2/2}}{I_0(p^2/2)} \int_0^1 dm \frac{e^{-p^2 m}}{\mathbf{K}^3} \sum_{n=1}^{\infty} \frac{\left\{ \dfrac{4n^2 Q^{2n}}{(1+Q^{2n})^2 \left[\left(\dfrac{\pi n}{\mathbf{K}} \right)^2 p^2 - z^2 \right]} \; \dfrac{(2n-1)^2 Q^{2n-1}}{(1-Q^{2n-1})^2 \left[\left(\dfrac{\pi (2n-1)}{2\mathbf{K}} \right)^2 p^2 - z^2 \right]} \right\}}{} , \tag{3.12}$$

where

$$Q = \exp\,(-\pi \mathbf{K}'/\mathbf{K}), \quad \mathbf{K}' \equiv \mathbf{K}(\sqrt{1-m}), \tag{3.13}$$

and $\mathbf{K}$ is found from (3.11)

In the subensemble of hindered rotors the variable of integration k is substituted by $t = p/k$ (t is not the time here!), and we can obtain

$$\begin{Bmatrix} \overset{\circ}{K}_{\parallel} \\ \overset{\circ}{K}_{\perp} \end{Bmatrix} = \frac{6\pi^{5/2}\, e^{p^2/2}}{I_0\left(\frac{p^2}{2}\right) p^2} \int_p^{\infty} dt \frac{e^{-t^2} t^4}{\mathbf{K}^3} \sum_{n=1}^{\infty} \frac{Q^{2n-1} (2n-1)^2}{\left[(\pi t/2\mathbf{K}p)^2 (2n-1)^2 p^2 - z^2 \right] \left[1 \pm Q^{2n-1} \right]^2} , \tag{3.14}$$

where $\mathbf{K} \equiv \mathbf{K}(p/t)$ and Q is determined from (3.13) at $m = p^2 t^{-2}$.

For the first time this model was considered in work[12], where the solution of the problem was given for a planar dipole, rotating in a periodic potential $U_0 \cos M\theta$ (M = 1,2,3...). A more general consideration was given later[13-14] both for planar and space systems. Here we have followed another derivation for a planar system which was given in the review.[11]

Evolution of the dielectric spectra of an isotropic medium with the change of an intermolecular field is shown in Fig. 2. When the potential well depth increases, the local anisotropy rises and this leads to an appearance of the region of the low frequency (Debye) relaxation. The Debye frequency x_D of the maximum loss χ''_D is much lower than the frequency x_L of the absorption maximum. With the increase of the field parameter p the frequency x_L also rises, and the absorption curve $x\chi''(x)$ is localized near the peak frequency x_L.

Fig.2a, 2b are calculated for a some "boundary" lifetime τ, which is equal to the collision time[6] τ_c ⟶ ; in

other terms $\longmapsto$ $y = y_c$. It should be noted that at $y < y_c$. one can regard molecular reorientation in a state of a local order to be sufficiently prolonged, while at $y > y_c$ the reorientations are so short lived that librations actually degenerate, become damped. The last situation ($y > y_c$) is illustrated in Fig.4 for $p = 3$. Dielectric spectra qualitatively resemble typical spectra of strong absorbing liquids. It is especially true (see Fig. b) for a quasi-space calculation scheme (1.16c) with the doubled spectral function. Note that Fig.4a, as well as Fig.2-3, are drawn according to eq.(1.16d), that is for the quasi-space isotropic ensemble but without doubling of $K(z)$.

4. Hybrid Quasi Elastic Bond / Extended Diffusion Model

In this section we use the approximate representation of the spectral function $K_{\parallel}(z)$ and $K_{\perp}(z)$ by the following integrals[11]

$$\check{K}_{\parallel} = \frac{3\,\exp\left(p^2/2\right)}{8\,\pi^{1/2}\,p^3\,I_0\left(p^2/2\right)} \int_0^{p^2} \frac{\exp(-h)\,h^2\,dh}{\gamma\left[4p^2-\gamma^2 z^2\right]}\ ;\ \gamma \equiv \gamma(h) = \left(1 + \frac{h}{4p^2}\right)\ ; \tag{4.1a}$$

$$\check{K}_{\perp} = \frac{3\,\exp\left(p^2/2\right)}{2\,\pi^{1/2}\,p\,I_0\left(p^2/2\right)} \int_0^{p^2} \frac{\exp(-h)\,h\,dh}{\gamma\left[p^2-\gamma^2 z^2\right]}\ ; \tag{4.1b}$$

$$\overset{o}{K}_{\parallel} = \overset{o}{K}_{\perp} = \frac{3\,\exp\left(p^2/2\right)}{2I_0\left(p^2/2\right)}\,L_F;\quad L_F(z,p) \equiv \frac{2}{\sqrt{\pi}} \int_p^{\infty} \frac{\exp\left(-s^2\right)s^2 ds}{s^2 - z^2}, \tag{4.2}$$

which are obtained after a number of simplifications of the $\longmapsto$ series (3.12) and (3.14). Let us consider this approximation in more detail.

Eq.(4.1) correspond to the quasi-`elastic bond (QEB) approximation. In the latter we retain in the hamiltonian h only two first terms of the Taylor series for the potential $U_o \sin^2\theta$:

$$h = \underbrace{\dot{\vartheta}^2}_{\text{the normalized kinetic energy}} + \underbrace{p^2\vartheta^2}_{\text{the main term, responsible for harmonic librations}} - \underbrace{(p^2/2)\vartheta^4}_{\text{the term, responsible for an anharmonicity}} \quad .(4.3)$$

The last term takes into account the dependence of the libration frequency of a molecule on the energy h . The greater is h, the less is the frequency of the periodic motion. If e.g. the libration frequency $\check{\Omega}$ of a dipole is equal to the field $\mathbf{E}(t)$ frequency ω, then for a dipole of greater energy its libration frequency $\check{\Omega} < \omega$, the detuning $|\check{\Omega} - \omega|$ being greater for greater anharmonicity. This property leads to the widening of the absorption line and to the decrease of its peak value.

In the hybrid QEB/ED model we take into account also the contribution $\overset{\circ}{K}$ of hindered rotors to the spectral function. This contribution is found at $h \geqslant p^2$ on assuming that in the interval τ between strong collisions the dipoles of the second subensemble rotate freely just as in the extended diffusion model[1] , i.e. in the absence of the static potential U. For this reason the longitudinal and orthogonal spectral functions in (4.2) are equal, the anisotropy of the dielectric response bein due only to the libration subensemble. Thus the QEB/ED model behaves as if comprising two important particular cases.

At p>>1 one can put ∞ in the upper limit of (4.1) and take $K = 0$. Then we get the QEB approximation[11] .

On the contrary, *at a weak intermolecular field (p<<1)* we put $\check{K} = 0$, and take the the range of integration in (4.2) to be $[0, \infty]$.

Then we get the spectral function of the planar extended diffusion model:

$$L(z) = 1 + \sqrt{\pi}\, z\, w(z); \quad w(z) \equiv \frac{i}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-s^2)\,ds}{z - s}. \qquad (4.4)$$

Thus we may suppose that this hybrid model is applicable (at leas for a qualitative description) *for any field parameter p*.

In order to be convinced of the validity of this statement, we compared the approximate and rigorous descriptions (cf. Fig.2b and 3), see also Fig.4. At $p \geqslant 2$ the difference

between both approaches becomes small (curves 4 in Fig. 2б and 3; see also Fig. 4). At small p the above mentioned difference is greater. It is seen from the comparison of curves 1, 2 in Fig. 2б and 3, as well as from Fig. 5. Thus, the simple QEB/ED model is applicable for a qualitative description of dielectric spectra at any p values and is sufficiently true at $p \geqslant 2$ (of course, in the frames of applicability of the DWP model under consideration). This conclusion permits us to substantially simplify the consideration of the central idea of this investigation (see Sec.5).

An unusual property of a microscopic model was found when calculations were made for a small values of y (y = 0.005) and a moderate values of the field parameter p (p about 1), for which the contributions of both subensembles are commensurable. We mean the existence of two absorption maxima (curve 3), one due to the contribution of librators (curve 1) and other (curve 2) due to that of rotors. At a greater but still small value of y (y = 0.005) these maxima appear less distinctly. The principal significance of this result consists in that only one absorption maximum is usually characteristic for simple microscopic models, that is for models with simple $U(\vartheta)$ functions[1, 11]. The existence of a two-humped absorption curve, shown above, fascilitates the development of new models capable of describing similar frequency dependences, observed experimentally. We shall return to this point at the end of the article.

5. Phenomenon of the Narrow Band Absorption in an Anisotropic Polar Medium

RESONANCE REGION. We have found above that when the potential well is deep ($p > 2$) the FIR absorption band is narrower. Fig.6 shows a more detailed picture regarding an evolution of a dielectric loss spectrum due to the field parameter p or the life-time τ. The two values of p and y are taken ($p = 3.5$ and 4.5; $y = 0.1$ and 0.3). The second parameter y is chosen sufficiently small since at greater values of y a strong widening of an absorption band occurs . In Fig.6 only the part of a loss spectrum is presented related to the FIR region, In this region one may deduce the SF frequency dependence $K''(x)$ since $\chi''(x) \approx GK''(x)$.

Let Δx be the width of the resonance curve $K''(x)$ at the level 1/2 and Δx_o be the same quantity at $y = 0$. The latter (Δx_o) may be called the *minimum bandwidth* (in units $\eta\Delta\omega$) since at the infinite increase of life-time τ (as $y \to 0$) the parameter Δx_o remains non-zero, yet sufficiently low at large p. Correspondingly the term "*limiting line*" (for $y = 0$) is a characteristic of a classical ensemble of dipoles. In the present investigation we disregard quantum effects. When the field parameter p rises, the minimum line width Δx_o decreases and the normalized frequency x_m of a loss peak approaches the values

$$\left\{ \begin{array}{l} x_m \approx p \\ x_m \approx 2\,p \end{array} \right\} \text{ for the } \left\{ \begin{array}{l} \text{orthogonal} \\ \text{parallel} \end{array} \right\} \begin{array}{l} \text{orientation of a} \\ \text{radiation} \\ \text{field .} \end{array} \qquad (5.1)$$

Thus the loss line for a parallel orientation may be regarded as a second harmonic while the first harmonic corresponds to the orthogonal orientation. At $y = 0.1$ the lines, shown in Fig.6, are close to the limiting lines, while curves $\chi''(x)$ are considerably wider at $y = 0.3$. It is also seen from Fig.6

that in the case of narrow lines the approximate and rigorous theories agree well with one another.

The values of parameters Δx, K''_{max} and x_m of resonance lines are presented in Table 3 for the three y values 0.05, 0.1 and 0.3 in a wide range of the field parameter p. If $p \gg 1$ then at the orthogonal ($\perp$) orientation the loss line is much more intense than that at the parallel ($\parallel$) orientation. This property may be explained by the fact that at $\perp$ orientation molecular charges move almost along electromagnetic field lines and so radiation spends more power than at $\parallel$ orientation. In the last case charges move almost normal to the $\mathbf{E}(t)$ field lines and consequently a small torque $\vec{\mu} \times \mathbf{E}(t)$ results.

These considerations are confirmed formally by the Gordon's sum rule

$$\Pi = \int_{-\infty}^{\infty} \omega\chi''(\omega)\, d\omega = \frac{\pi\mu^2 N}{I}\,(1 - \langle q^2 \rangle), \qquad (5.2)$$

where Π denotes the integrated absorption. Indeed, if $p \gg 1$, then $\langle q_{\parallel}^2 \rangle \gg \langle q_{\perp}^2 \rangle$ and $\Pi_{\perp} \gg \Pi_{\parallel}$, the relevant statement in the previous paragraph is established.

We see also from Table 3 that

a) the relative width $\gamma = \Delta x / x_m$ of a resonance line decreases when p rises: at $p = 0$ we have $\gamma_{min} \approx 1.67$ while at $p = 5$ $\longleftarrow\!\!|$ $\gamma^{\parallel}_{min} \approx 0.09$ and $\gamma^{\perp}_{min} \approx 0.13$;

b) the maximum absorption, which is proportional to the product $x_m K''$, increases for $\perp$ orientation with the field parameter p; for $\parallel$ orientation this product goes through a maximum and then, at large p, quickly approaches zero because this type of interaction vanishes;

c) when p rises, the resonance loss or absorption line width $\Delta x = \eta\Delta\omega$ goes through its minimum value while the relative line width, we repeat, decreases with p;

d) the loss peak K''_{max} goes through its maximum value, if p rises.

In Fig. 6 d,e the frequency dependence of the real part of the spectral function is shown. If p is large, the region where $K'(x)$ substantially changes is concentrated near the centre x_m of a

line. For the main loss mechanism (at the orthogonal orientation) the amplitude of a change $K'_{\perp}$ in a resonance region is much greater than the value $K^{\perp}_{o}$, corresponding to $x = 0$.

DEBYE RELAXATION. For the same example as in Fig. 6 (p = 3.5; 4.5; y = 0.1; 0.3) the low frequency loss spectrum is shown in Fig. 7. Solid lines refer to the complex susceptibility obtained from eq.(1.8) for the hybrid QEB/ED model; dashed lines refer to the same quantity obtained for the fixed (x = 0) spectral function, that is, for $K'_{\perp}(iy)$, $K'_{\parallel}(iy)$ or $L''(iy)$, the last being required for an isotropic ensemble). If y decreases, the relaxation time τ_D increases, since the Debye loss maximum shifts to lower frequencies. For a parallel orientation the time τ_D is much greater than for an orthogonal one:

$$\tau^{\parallel}_D \gg \tau^{\perp}_D \text{ , if } \quad p \geqslant 2. \qquad (5.3)$$

This property may be explained by the following way. At a *parallel orientation* in one or the other well there will appear some excess concentration δN of dipoles orienting along electromagnetic field $\mathbf{E}(t)$, if the field frequency is not too great . This excess δN is due to stochastic forces which disturb the thermal equilibrium. It may be noted that regular torques due to a potential $U(\theta)$ cannot throw particles over their potential wells . When the field $\mathbf{E}(t)$ is switched off, the concentration of dipoles will approach the equilibrium in all wells. In order to reach the steady state distribution the "excess" particles must turn through a considerable angle $\theta \sim \pi$, and so the relaxation time $\tau^{\parallel}_D$ may be great. From the mathematical point of view this fact is due to the great value of the dispersion $\sigma_{\parallel}=3\langle q^2_{\parallel}\rangle$, since the mean direction cosine $\langle q_{\parallel}\rangle$ vanishes.

For a deep well with U_o large and K_o small the transfer of dipoles from one well to another is not easy. What results is an increase of the time $\tau^{\parallel}_D$. Note, this $\tau^{\parallel}_D$ rises abruptly with p, if $p \gg 1$.

At the *orthogonal orientation* the relaxation time $\tau^{\perp}_D$ is less than $\tau^{\parallel}_D$ since dipoles are to turn on less angle in order to resolve the excess concentration of dipoles appeared in the direction of the field $\mathbf{E}(t)$. The value of this excess is small since $\mathbf{E} \perp Z$.

It should be noted that the properties (5.2) and (5.3) were taken into consideration previously[13,14] for an example of wider lines of resonance absorption.

In isotropic media a dipole interact simultaneously with both

field components, $\mathbf{E}_{\perp}(t)$ and $\mathbf{E}_{\parallel}(t)$, since the symmetry axis is inclined at different angles to the direction of electromagnetic field. As a result at $p \gg 1$ the relaxation time τ_D is less than at $\parallel$ - orientation but greater than at $\perp$ - orientation.

It is also seen from Fig. 7 that for sufficiently frequent collisions, or equivalently for sufficiently large values of y the Debye loss maximum at $\perp$ orientation may almost reach the resonance absorption region. Because of this the approximation of fixed spectral function ($K \equiv K(iy)$, or $K \equiv L(iy)$ in an isotropic medium) may not be valid. However in our examples the substitution of K(z) by K(iy) and L(z) by L(iy) is admissible, as we may see from the solid and dashed lines in Fig. 7.

Thus, if the lifetime τ is great, or equivalently if $y \ll 1$, the agreement between the theory and experiment may be obtained, if:

a) the chosen value of the field parameter p permits us to obtain the correct position x_m of the resonance loss peak and simultaneously the line width. We may note that for small y the linewidth is close to the minimum width Δx_o);

b) the lifetime τ chosen or the corresponding value of y allows agreement between the theoretical low frequency spectrum and the experimental one.

The a) criterion demands the agreement of the theory and experiment for two parameters K''_{max} and Δx by fitting the only free model parameter p. Indeed, if we want to describe also the low frequency spectrum we need to fit lifetime τ or y for a prescribed value τ_D. As a result, the applicability of this DWP model to concrete molecular systems is restricted. We shall turn to this question in the next section.

In Fig. 8 we have a graph of the τ - dependence on the relaxation time τ_D or more precisely the dependence of τ_D/η on τ/η. The graph has a minimum at some critical value y_{crit} which divides two regions of low frequency relaxation. Note that y_{crit} is of the order of unity and depends on the value of p. Thus we have:

I. The region where collisions are not extremely frequent and $y < y_{crit}$; the relaxation time τ_D decreases along with the decrease of lifetime τ;

II. the region of very frequent collisions ($y > y_{crit}$), in which the relaxation time τ_D increases if the lifetime τ

decreases. In the limit $\tau \to 0$ the Hubbard relation is satisfied

$$\tau_D \tau = I / (2k_B T) \qquad \text{at} \quad y \gg 1. \tag{5.4}$$

An analysis shows[11] that in liquids only the first region may agree with experimental data and the most frequent collisions (near the point y_{crit}) approximately correspond to the temperature near boiling point / the most shallow potential well. In the QEB/ED model we have the similar dependence of τ_D on τ in the region **I** (see Fig.8b). But in this model the curve $\tau_D(\tau)$ has no point of minimum, so, the QEB/ED model is not applicable at very large y.

More detailed data, related to low frequency spectra (see Table 4) where all calculation are given for the rigorous theory (but in the approximation $K \equiv K(iy)$ for anisotropic medium and $L \equiv L(iy)$ for isotropic one). Using the formulae of Sec. 2 and Table 4 one can estimate, in particular, the static susceptibility χ_s and the quantity χ_∞.

6. On the Applicability of the Model to Calculation of Dielectric Spectra of Ice 1

In Table 5 the formulae are given in the quasi-elastic bond approximation, which permits to estimate specific parameters of low frequency (at $x \leqslant x_D$) and of high frequency (at $x \approx p$) dielectric spectra. These formulae were obtained[11] ⟶ for the QEB approximation where it was assumed that: a) the field parameter $p \gg 1$; b) the minimum resonance line width Δx and the peak position x_m are found for the limit $\tau \to \infty$, that is, for the limiting line; c) the parameters of low frequency (Debye) spectra are found for finite but large life-time τ (at $y \lll 1$).

Let us chose the temperature equal to 0°C, that is $T = 273.15K$. We take molecular constants of isolated molecule $\mu_o = 1.84$ D, optic (in the IR region) refractive index $n_\infty = 1.32$, the density $\rho = 1$ g·cm^{-3}, molecular mass $M = 18$. Then the normalizing parameter $\eta = [I/(2k_B T)]^{1/2} = 4.43 \cdot 10^{-14}$ s, the dipole moment μ in polar fluid is taken in the form $\mu = \mu_o(n_\infty^2 + 2)/3$. Then $G = \mu^2 N_A \rho/(3k_B TM) = 1.56$ (N_A - is the Avogadro number). In Table 6 the approximate

experimental[8,10] values of parameter for ice 1 are presented; the band near 830 cm^{-1} is denoted as $\mathcal{L}$ and the band near 226 cm^{-1} as $\mathcal{R}$ (the splitting of the second band is ignored; index "m"refers to centres of both bands and subscripts "min", "max" refer to the quantities, related to on the level 1/2 regarding the peak loss value ε''_m in these bands. Using experimental data [8] and the equation $\varepsilon^* = n^2 - æ^2 + 2inæ$, we may find the band width $\Delta\nu$ from the frequency dependence $\varepsilon''(\nu) = 2\, n(\nu)æ(\nu)$.

Using these data, we find:

At $\mathcal{L}$: $\chi_m = 0.05$, $x_m = 6.68$, $\Delta x_{exp} = 2.13$; (6.1)

At $\mathcal{R}$: $\chi_m = 0.058$, $x_m = 1.89$, $\Delta x_{exp} = 1$. (6.2)

For the description of the dielectric behavior of ice 1 we introduce two subensembles of molecules, like in case of liquid water[1,14] : [L], with less, and [R], with greater rotational mobility, to which $\mathcal{R}$ – and $\mathcal{L}$ – bands correspond in the FIR spectrum. As in the work[1] we suppose, that [L]-molecules are responsible for the Debye relaxation of polar medium. The above theory is applied *separately* to $\mathcal{L}$- and $\mathcal{R}$- regions of the FIR spectrum of ice 1.

Using the formulae of Table 5 we get the following estimations of the field parameter p and minimum line band Δx_o:

At $\mathcal{L}$: $p = 6.7$, $\Delta x_o = 0.074$; (6.3)

At $\mathcal{R}$: $p = 2$, $\Delta x_o = 0.235$. (6.4)

Thus the estimated minimum width of the $\mathcal{L}$-band is approximately 30 times less than the experimental value Δx_{exp}. The question arises, whether the loss curve can be widened due to the finiteness of the life time τ so that it may cancel this drawback. The life time τ we may estimate using Tables 5 and 6. Calculating the Kirkwood correlation factor $g = \frac{\varepsilon_s - n_\infty^2}{4\pi G}\,\frac{2\varepsilon_s + n_\infty^2}{3\varepsilon_s} = 2.21$, we find that the normalized collision frequency y is extremely low ($y \approx 4.1\cdot 10^{-7}$). Hence the theoretical width Δx practically coincides with the minimal one (Δx_o). So, if the DWP model with the profile $\cos^2\theta$ were employed it would seem impossible to remove the difference between the theoretical and experimental line widths Δx and Δx_{exp}. A possible way to improve the theory is to change the profile of the intermolecular potential.

The situation is different for R-band. The estimated value of

the p-parameter is about 2, and the minimum line width Δx_0 is several times less than the experimental value Δx_{exp}. Using data of Table 3 we find that the theoretical R-band may be widened by taking $y \simeq 0.3$. Then according to Table 4 the relaxation time will be in the order of picoseconds. Indeed, we have $\eta \simeq 0.038$ ps; so, putting from Table 4 the value $\tau_D/\eta = 21$, which corresponds to p =2 and y = 0.3, and multiplying the result by g = 2.21, we obtain: $\tau_D \simeq 21 g \eta \simeq 1.8$ ps. Consequently the corresponding wave length $\lambda_D = (2\pi c \tau_D)^{-1} \simeq 0.34$ cm. The relaxation time for R-molecules is thus several times less than its value for liquid water but it is many orders of magnitude less than the value of τ_D for the main relaxation region in ice 1.

At last, let us estimate the proportion r of molecules responsible for the R-band. Noting that at $p = 3$ and $y = 0.3$ the Table 3 gives $L''_{max} \approx (1/3)K''_{max} = 0.816/3$. Doubling this value in order to account approximately for the space statistics we obtain

$$r \approx \frac{\chi''_m(\text{experiment in } R)}{2\,\chi''_m\,(p=2,\ y = 0.3)} = \frac{0.058}{2GL''_{max}(p = 2,\ y = 0.3)} = 6.8\%. \qquad (6.5)$$

An important result of these estimations is to set oneself thinking that the proportion of H_2O molecules with greater rotational mobility has in ice the same order of magnitude as in liquid water in spite of more regular structure of ice and consequently the less proportion of "defects" of structure than in water. Indeed, the proportion of [R] - molecules in water is about 10%[1,4]. Indirectly this conclusion can be confirmed by the following experimental fact[8]: intensities of R - bands are nearly equal in ice 1 and liquid water. The obtained result can be reformulated as follows. The rotational / translational motion contributing to the R - band in FIR spectral region, actually is not frozen at water - ice transition in spite of the substantial (by many orders of magnitude) increase of viscosity and the Debye relaxation time. Hence, most probably, [R] - molecules present the inherent property of H-bond itself and have no direct relation to the "defects" of H - bond net.

Conclusion

1. A simple hybrid quasi-elastic bond / extended diffusion

model may be applied for a qualitative analysis of a dielectric relaxation described by a rigorous planar double well potential model with a profile $U_0\cos^2\vartheta$.

2. When a conservative field parameter $p = (U_0/k_BT)^{1/2}$ exceeds 4, the FIR absorption spectrum results in a narrow line and a great Debye relaxation time τ_D. In this work the notion of *limiting absorption line* is introduced, which has the minimum width and corresponds to the limit $\tau \to \infty$. If τ_D is very large, it is the limiting line that practically describes the FIR absorption spectrum.

3. The field DWP model can be applied for the description of the dielectric loss spectrum in the translational (near 200 cm^{-1}) band of hydrogen-bonded systems. The comparison of ice 1 and water spectra set oneself thinking that the very existence of [*R*]-molecules with greater mobility is due to the hydrogen bond itself, and not to the "defects" of H-bond net.

4. The field DWP model with a profile $U_0\cos^2\vartheta$ is not applicable to the description of a librational (near $\nu \simeq 800$ cm^{-1}) band of ice 1, since the theoretical absorption line is too narrow in this case. Comparison with the confined rotator model[4] implies the idea that both librational and translational bands may be described in frames of a new field model in which the potential profile $U(\vartheta)$ has the form of a "hat": flat bottom, abruptly elevating walls and flat edges where U depends weakly on the angle ϑ. The explanation of this idea was given recently[15,16]. The existence of a two-humped absorption curve, which was shown (Fig. 5c) for a cosine squared profile $U(\vartheta)$, supports the idea that both absorption peaks, α_L and α_R, can agree with experimental data for a suitable[15,16] potential form $U(\vartheta)$.

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CAPTIONS FOR FIGURES

Fig.1. Distribution functions of dipoles over frequencies of orientational motion of librators (a) and hindered rotators (b).

a: the field parameter p = 0.5 (1), 1(2), 2(3); dotted line - the asymptotic dependence.

b: p = 0.05 (1), 0.1 (2), 0.5(3) and 1(4); curve 5 - the Maxwellian distribution.

Fig.2. The frequency dependences of the imaginary part of the susceptibility (a) and the normalized absorption (b). The field parameter p = 0.5 (1), 1(2), 1.75 (3) and 3(4). Isotropic medium.

Fig.3. The frequency dependence of the normalized absorption coefficient. The QEB/ED model. All denotations as in Fig.2.

Fig.4. The loss susceptibility (1) and normalized absorption (2) as functions of frequency: the rigorous theory (solid lines) and QEB/ED model (dashed lines). a - for quasi-space ensemble; b - the same but with doubled spectral function. p = 3, y = 2, isotropic medium.

Fig.5. (a, b): ~~The~~ evolution of a dielectric loss spectrum due to the field parameter p for a relatively shallow potential well: p = 0.01 (1); p = 0.1 (2); p = 0.2 (3); p = 0.3 (4); p = 0.4 (5). a - rigorous theory, b - QEB/ED model; $y = y_2$.

(c): the plot $x\chi''(x)$, calculated for y = 0.005, p = 0.75 (curve 3) and y = 0.05, p =0.85 (curve 4). Curves 1 and 2 show the contributions of librators and hindered rotors to curve 3. Rigorous theory.

Fig.6. The evolution of a narrow loss line $K''(x)$ due to the field parameter p and to the strong collision frequency y: a, b - for the parallel orientation; c, d - for the orthogonal orientation.

QEB/ED model: solid lines for y = 0.1, dots for y = 0.3;

rigorous theory: dots for y = 0.1 and triangles for y = 0.3.

The field parameter p = 3.5 (a, c) and 4.5 (b, d).

d, e: the real part of the spectral function $K'(x)$ at p = 4.5 for y = 0.1 (solid line) and y = 0.3 (dashed line) at parallel (e) and orthogonal (f) orientations in frames of the QEB/ED model.

Fig.7. The frequency dependence of the loss susceptibility for parallel orientation (1), isotropic ensemble (2) and orthogonal orientation (3). Solid lines - for the spectral functions $K(z)$, $L(z)$; dashed lines - for the spectral functions $K(iy)$, $L(iy)$. The field parameter p = 4.5; at y = 0.1 (a) and 0.3 (b). The QEB/ED model.

Fig.8. The dependence of the relaxation time τ_D on the life time τ for isotropic dipolar ensemble. The field parameter p = 5 (solid line) and p = 2 (dashed line). a: rigorous theory; b: QEB/ED model.

Table 1. The parameters $\check{r}$, $\langle\beta\rangle$, $\langle\check{p}\rangle$, $\langle\overset{\circ}{p}\rangle$, y_c and distributions $\check{f}(\check{p})$ and $\overset{\circ}{f}(\overset{\circ}{p})$

Parameter	General case	For $p \gg 1$	For $p \to 0$
$\check{r}$	$\dfrac{2p\,\exp(p^2/2)}{\pi^{3/2} I_0(p^2/2)} \int_0^1 \mathcal{L}\,\mathbf{K}\,dm$	$\simeq 1$	$\dfrac{4p}{\pi^{3/2}}$
$\langle\beta\rangle$	$\dfrac{2}{\check{r}} \dfrac{p\,\exp(p^2/2)}{\pi^{3/2} I_0(p^2/2)} \int_0^1 \mathcal{L}\,\mathbf{K}\,\arcsin(\sqrt{m})\,dm$	$\dfrac{\pi^{1/2}}{2p}$	
$\langle\check{p}\rangle$	$2\mathrm{sh}\left(p^2/2\right)\left\{\check{r}\sqrt{\pi}\,I_0\left(p^2/2\right)\right\}^{-1}$	p	$\pi p/4$
$\langle\overset{\circ}{p}\rangle$	$\exp\left(-p^2/2\right)\left[\overset{\circ}{r}\,\pi^{1/2} I_0\left(p^2/2\right)\right]^{-1}$	$\simeq 0$	$\pi^{-1/2}$
y_c	$\exp(p^2/2)\left\{(\pi)^{3/2} I_0\left(p^2/2\right)\right\}^{-1}$		
$\check{f}(\check{p})$	$\dfrac{\pi^{1/2}\,\check{\gamma}^3}{I_0(p^2/2)} \dfrac{m\,m'}{\mathbf{E}-m'\mathbf{K}} \exp\left[\dfrac{p^2(1-2m)}{2}\right]$ where $\check{m}(p)$ is found from the equation $\check{p} = \pi p\,/\,(2\mathbf{K})$	$4p\,\gamma^3 e^{4p^2} \times \exp\left[-4p^2\gamma\right]$	$\simeq 0$
$\overset{\circ}{f}(\overset{\circ}{p})$	$\dfrac{\pi^{1/2}\,\overset{\circ}{\gamma}{}^3}{I_0(p^2/2)} \dfrac{m' m^{-3/2}}{\mathbf{E}(\sqrt{m})} \exp\left[\dfrac{p^2}{2}\left(1-\dfrac{2}{m}\right)\right]$ where $\overset{\circ}{m}(p)$ is found from the equation $\overset{\circ}{p} = \pi\,p\,/(2\sqrt{m}\,\mathbf{K}(\sqrt{m})$	$\simeq 0$	$\dfrac{2}{\sqrt{\pi}}\,e^{-\overset{\circ}{p}{}^2/2}$
Denotations	$\mathcal{L} = \exp(-p^2 m)$; $\mathcal{R} = \exp(-p^2 m^{-1})$; $m = k^2$; $m' = 1 - m$; $p = \sqrt{U_0/(k_B T)}$; $\check{\gamma} = p\,/\,\check{p}$, $\overset{\circ}{\gamma} = p/\overset{\circ}{p}$		

Table 2. The estimation of the steady state parameters. In the brackets [···] the asymptotic estimations are given.

The parameters of a medium	The conservative field parameter p						
	0	0.1	0.2	0.5	1	2	5
$\langle\beta\rangle$	0.868	0.867	0.864	0.841	0.759 [0.886]	0.493 [0.443]	0.179 [0.177]
$\check{r}$	0	0.0733 [0.072]	0.146 [0.144]	0.361 [0.359]	0.676 [0.718]	0.977	0.998
$\overset{\circ}{r}$	1	0.927	0.860	0.653	0.341	0.0266	0.000
y	0.180	0.180	0.183	0.203	0.278	0.582	1.575
$\langle\check{p}\rangle$	[0]	0.0769 [0.079]	0.154 [0.157]	0.391 [0.393]	0.817	1.838 [2]	4.96 [5]
$\langle\overset{\circ}{p}\rangle$	[0.564]	0.606	0.643	0.760	0.943	1.26	

Table 3. The parameters of a resonance loss line at $\begin{cases} y = 0.05 \\ y = 0.1 \\ y = 0.3 \end{cases}$

The field param. p	parallel orientation					Ortogonal orientation				
	0.1	0.5	1	2	5	0.1	0.5	1	2	5
K''_{max}	1.173 0.96 0.68	1.29 1.05 0.70	1.11 0.89 0.55	0.171 0.131 0.069	0.0046 0.0044 0.0032	1.173 0.96 0.68	1.305 1.06 0.728	1.79 1.31 0.774	2.14 1.67 0.816	0.827 0.769 0.415
x_m	0.66 0.79 0.79	0.724 0.87 0.871	1.2 1.2 1.26	2.09 2.09 2.18	9.55 9.55 9.55	0.66 0.79 0.79	0.724 0.724 0.832	0.87 0.87 1.05	1.82 1.82 1.82	5.01 5.01 5.01
Δx	1.10 1.21 1.33	0.88 0.97 1.24	0.63 0.78 1.07	0.493 0.61 1.01	0.88 1.35 1.35	1.10 1.21 1.33	1.0 1.07 1.31	0.56 0.79 1.11	0.336 0.5 0.85	0.677 0.677 1.113
$\frac{\Delta x}{x_m}$	1.67 1.53 1.68	1.22 1.12 1.42	0.53 0.65 0.85	0.24 0.29 0.46	0.092 0.141 0.141	1.67 1.53 1.68	1.38 1.49 1.58	0.64 0.91 1.06	0.19 0.28 0.47	0.135 0.135 0.222
$x_m K''_{max}$	0.774 0.758 0.537	0.934 0.914 0.610	1.33 1.07 0.69	0.36 0.27 0.15	0.044 0.042 0.031	0.774 0.758 0.537	0.945 0.767 0.606	1.56 1.14 0.81	3.90 3.04 1.49	4.14 3.85 2.08

Table 4. The dependence of the Debye relaxation parameters on the field parameter p (the rigorous theory).

$$\left\{\begin{array}{l}\text{apper}\\ \text{middle}\\ \text{lower}\end{array}\right\}\ \text{line} \rightarrow \text{at } y = \left\{\begin{array}{l}0.05\\ 0.1\\ 0.3\end{array}\right\}$$

parameter	Field parameter p						
	0.011	0.I	0.2	0.5	I	2	5
$\sigma_{\parallel}$	1.5	1.504	1.515	1.59	1.86	2.55	2.94
$\sigma_{\perp}$	1.5	1.496	1.485	1.41	1.14	0.453	0.061
	A: anisotropic medium						
$K_c^{\parallel}$	1.373 1.259 0.914	1.323 1.233 0.906	1.215 1.162 0.882	0.887 0.869 0.731	0.444 0.440 0.402	0.436 0.159 0.0422	0.0003 0.0003 $3\cdot10^{-4}$
$K^{\perp}$	1.374 1.26 0.914	1.404 1.289 0.922	1.422 1.320 0.944	1.373 1.322 1.023	1.113 1.098 0.964	0.450 0.448 0.434	0.0613 0.0613 0.0611
$\chi''_{D_{\parallel}}/G$	0.0637 0.120 0.293	0.0901 0.135 0.299	0.150 0.177 0.317	0.354 0.362 0.431	0.710 0.712 0.731	1.251 1.252 1.252	1.47 1.47 1.47
$\chi''_{D_{\perp}}/G$	0.0629 0.120 0.293	0.0463 0.104 0.287	0.0316 0.0823 0.270	0.01689 0.0422 0.191	0.0115 0.0190 0.0863	0.0019 0.0026 0.0098	$6\cdot10^{-7}$ 10^{-5} 10^{-4}
$\tau_D^{\parallel}/\eta$	21.86 11.9 5.47	22.72 12.2 5.54	24.95 13.04 5.73	35.95 18.34 7.23	84.0 42.4 15.5	1168 585.9 201.3	179448 89731 29936
$\tau_D^{\perp}/\eta$	21.83 11.9 5.47	21.32 11.60 5.41	20.89 11.25 5.24	20.5 10.64 4.58	20.4 10.35 3.93	20.2 10.12 3.48	20 10.00 3.35
	B: isotropic medium ($\sigma = 1$)						
L_o	0.916 0.840 0.609	0.909 0.841 0.609	0.879 0.827 0.609	0.753 0.730 0.585	0.519 0.513 0.455	0.164 0.164 0.159	0.0205 0.0205 0.0205
χ''_D/G	0.0422 0.080 0.195	0.0455 0.0796 0.195	0.0606 0.0863 0.196	0.123 0.135 0.208	0.240 0.244 0.272	0.418 0.418 0.421	0.49 0.49 0.49
τ_D/η	21.84 11.9 5.47	22.00 11.9 5.47	22.76 12.09 5.48	26.6 13.7 5.7	38.5 19.5 7.33	121.7 61.0 21.0	973.5 487 163

Table 5. Estimation of the parameters of dielectric spectra: QEB model

A. The resonance spectrum	B. The Debye relaxation region
$\begin{Bmatrix} (K''_{max})_{\parallel} \\ (K''_{max})_{\perp} \\ L''_{max} \end{Bmatrix} = \frac{\pi}{e} \begin{Bmatrix} 3/(4p^2 e) \\ 3 \\ 1 \end{Bmatrix}$	$\eta^{-1} \begin{Bmatrix} \tau_D^{\parallel} \\ \tau_D^{\perp} \\ \tau_D \end{Bmatrix} = (g/y) \begin{Bmatrix} 16p^4 \\ 1 \\ 8p^2 \dfrac{1+2p^2}{1+8p^2} \end{Bmatrix}$
$\begin{Bmatrix} (K'_{min})_{\parallel} \\ (K'_{min})_{\perp} \\ L'_{min} \end{Bmatrix} = - \begin{Bmatrix} 3/(16p^2) \\ 3 \\ 1 \end{Bmatrix}$	$\frac{1}{Gg} \begin{Bmatrix} \chi_s^{\parallel} \\ \chi_s^{\perp} \\ \chi_s \end{Bmatrix} = \begin{Bmatrix} 3 \\ 3/(2p^2) \\ 1+1/(2p^2) \end{Bmatrix}$
$(x_m)_{\parallel} = \frac{4p^3}{2p^2+1}$	$2G^{-1} \begin{Bmatrix} (\chi''_D)_{\parallel} \\ (\chi''_D)_{\perp} \\ \chi''_D \end{Bmatrix} = \begin{Bmatrix} 3(g - \frac{3}{2p^2}) \\ [3/(2p^2)](g-1) \\ g - \frac{3}{2p^2} \end{Bmatrix}$
$\begin{Bmatrix} (x_m)_{\perp} \\ x_m \end{Bmatrix} = \frac{4p^3}{4p^2+1}$	
$\begin{Bmatrix} \Delta x_o^{\perp} \\ \Delta x_o \end{Bmatrix} = \frac{2p}{4p^2+1}$	$G^{-1} \begin{Bmatrix} (\chi_\infty)_{\parallel} \\ (\chi_\infty)_{\perp} \\ \chi_\infty \end{Bmatrix} = \frac{1}{2p^2} \begin{Bmatrix} 3/(8p^2) \\ 3 \\ 1 \end{Bmatrix}$

Table 6. Dielectric constant of ice 1, used for estimation of free parameters of the DWF model.

$\mathcal{L}$ - band [8]	$\mathcal{R}$ - band [8]	Debye spectrum [10]
$\varepsilon''_m = 0.63$	$\varepsilon''_m = 0.73$	$\theta = \frac{200}{T} - 1 = 0.098$
$\nu_m = 800$ см$^{-1}$	$\nu_m = 226$ см$^{-1}$	$\tau_D = [2\pi\ 64.1 * 10^3 \times$
$\nu_{min} = 630$ см$^{-1}$	$\nu_{min} = 130$ см$^{-1}$	$\times \exp(-22.1\theta)] = 2.18 * 10^{-5}$ с
$\nu_{max} = 885$ см$^{-1}$	$\nu_{max} = 248$ см$^{-1}$	$\varepsilon_s = 81.8 + 96\theta = 91.24$
$\Delta\nu = 255$ см$^{-1}$	$\Delta\nu = 118$ см$^{-1}$	$\varepsilon_\infty = 3.15$

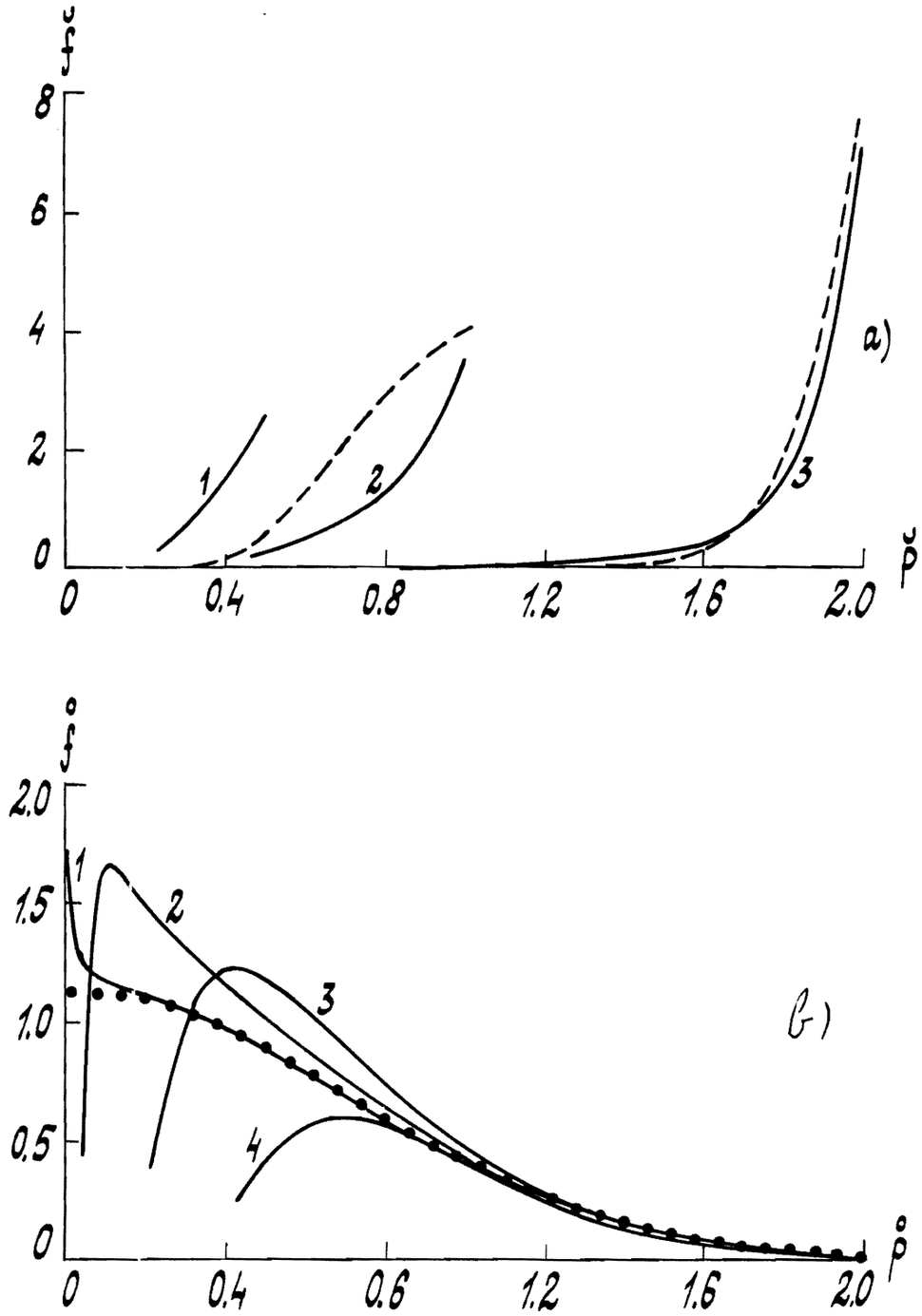


Fig. 1

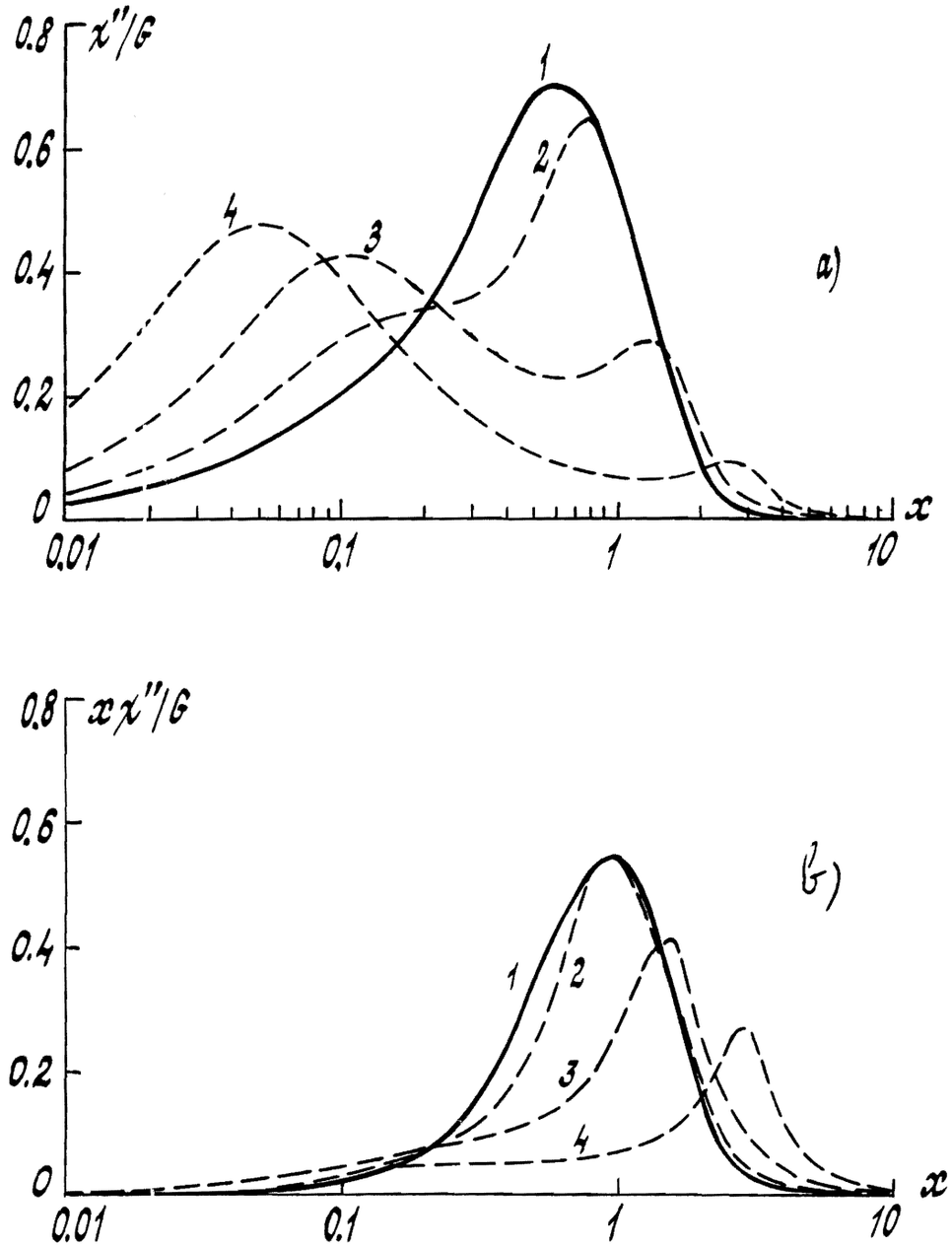

0.8
0.6
0.4
0.2
0
χ''/G
1
2
3
4
a)
x
0.01
0.1
1
10
0.8
0.6
0.4
0.2
0
xχ''/G
b)
1
2
3
4
x
0.01
0.1
1
10

Fig. 2

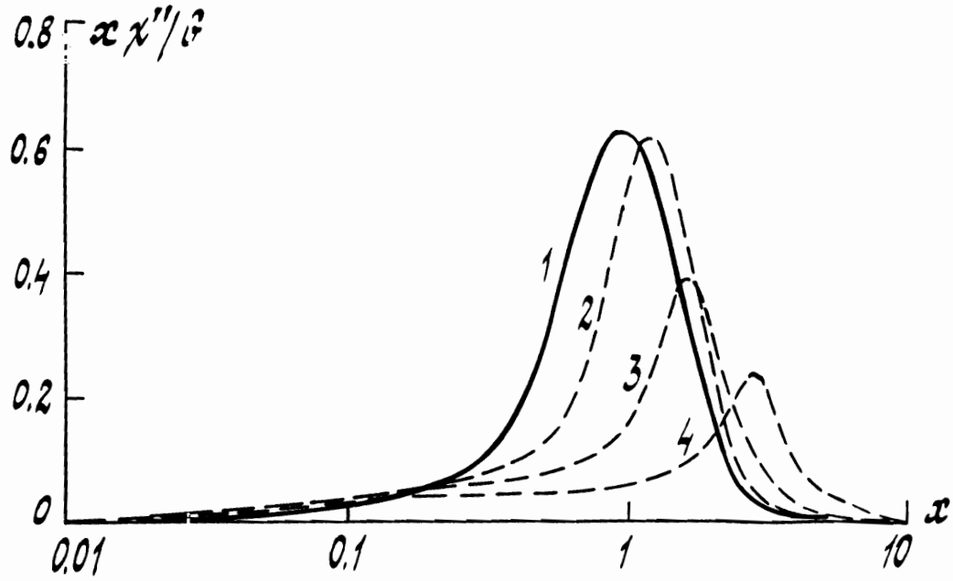


Fig. 3

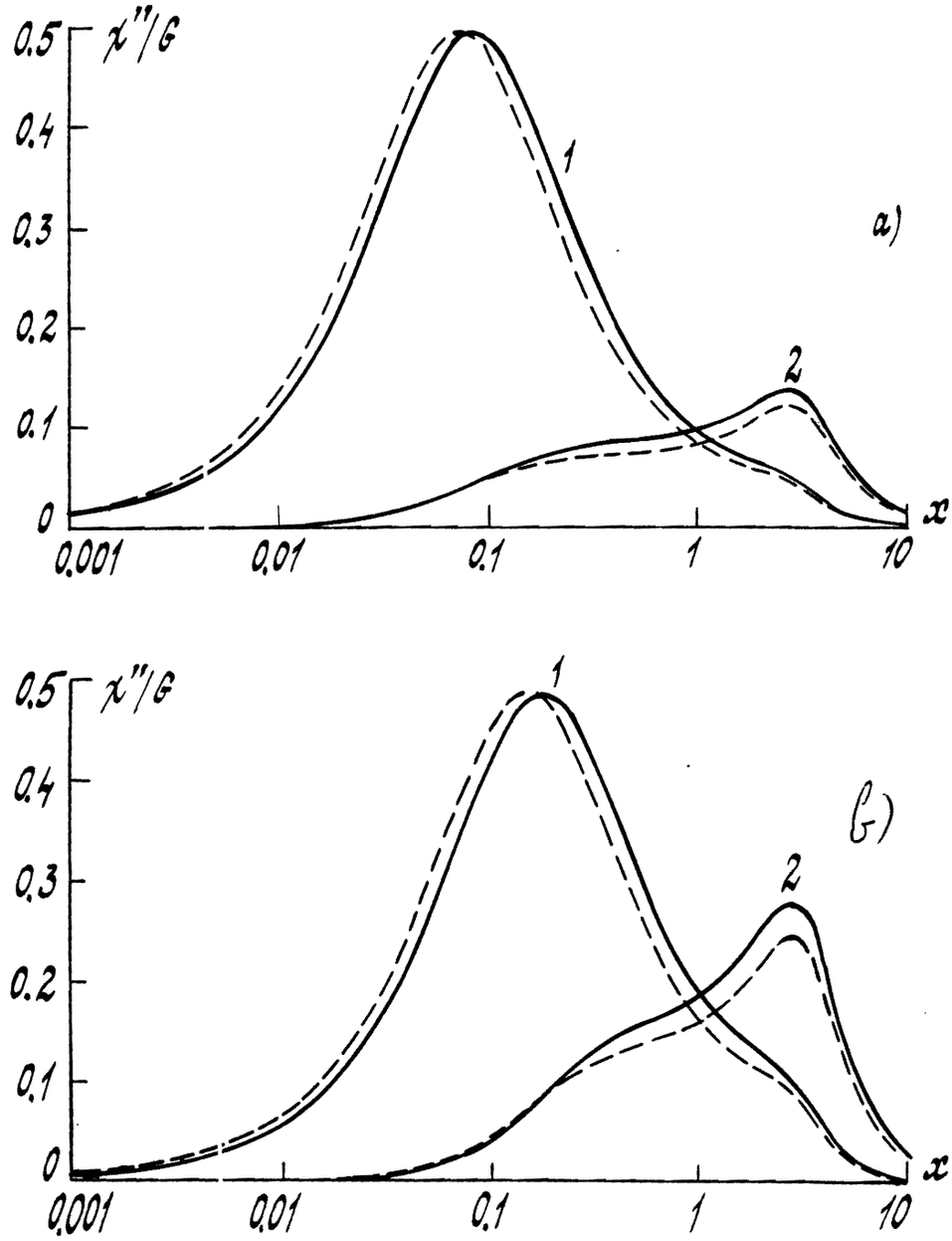
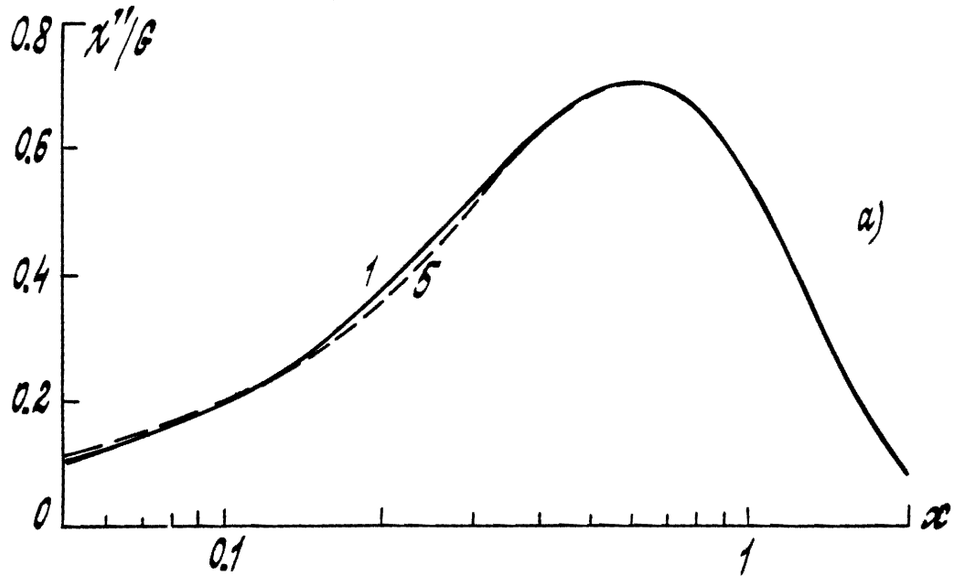

0.5
0.4
0.3
0.2
0.1
0
χ''/G
1
2
a)
x
0.001
0.01
0.1
1
10
0.5
0.4
0.3
0.2
0.1
0
χ''/G
1
2
б)
x
0.001
0.01
0.1
1
10

Fig. 4



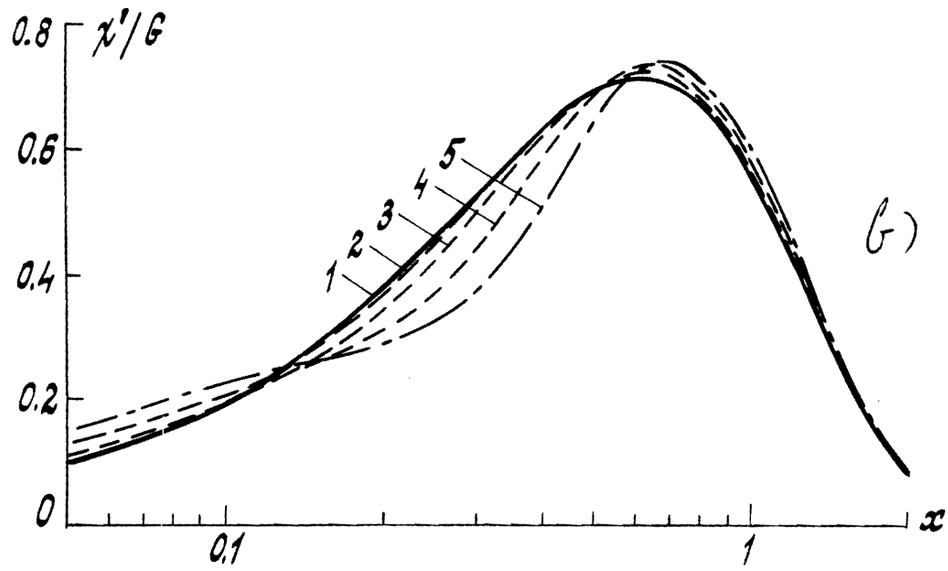


Fig. 5 a, б

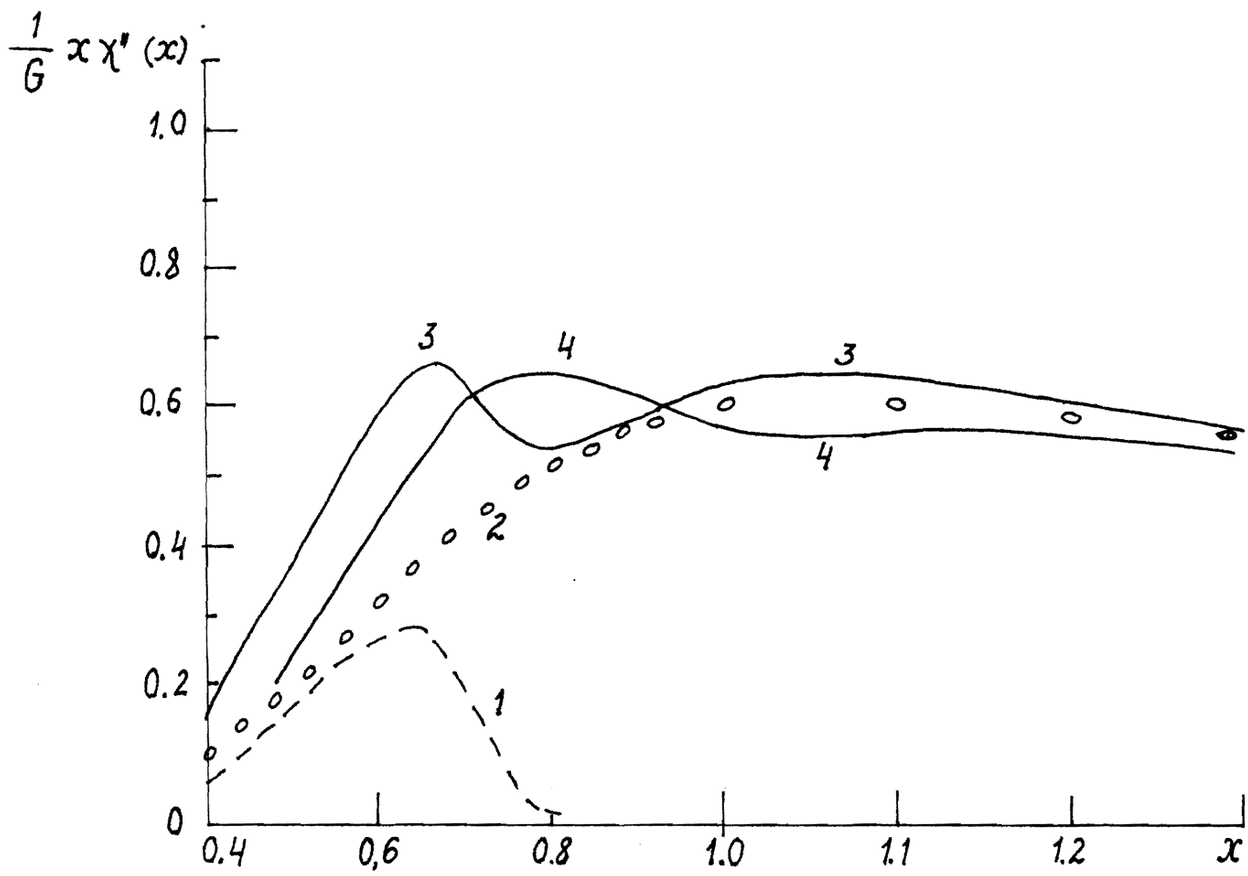
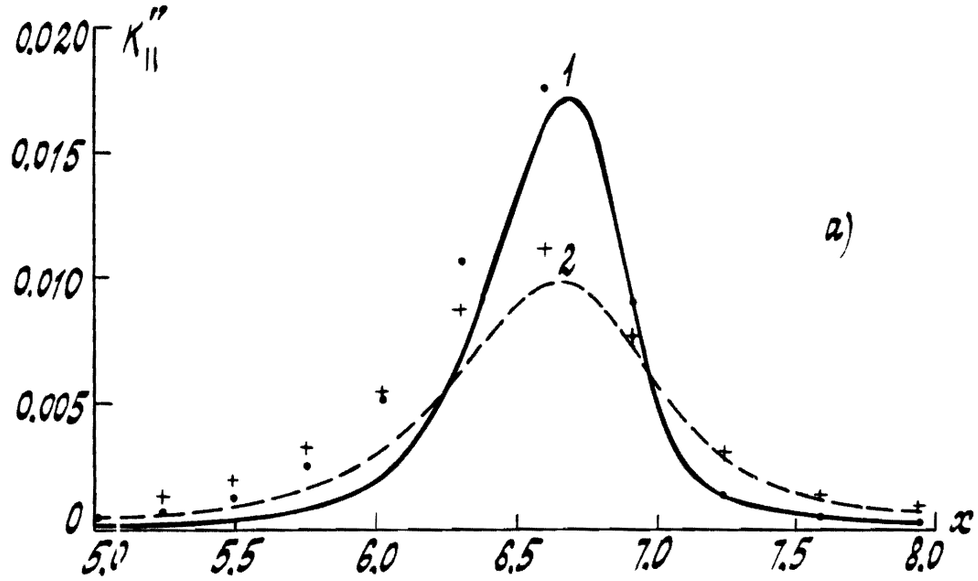


Fig. 5c


0.020
0.015
0.010
0.005
0
K''_{11}
1
2
a)
x
5.0
5.5
6.0
6.5
7.0
7.5
8.0

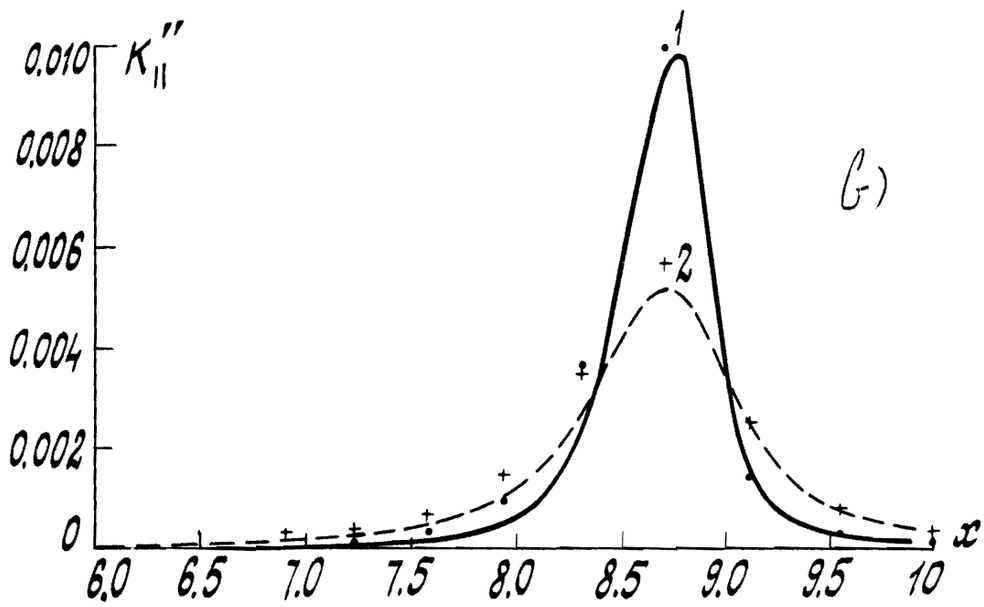
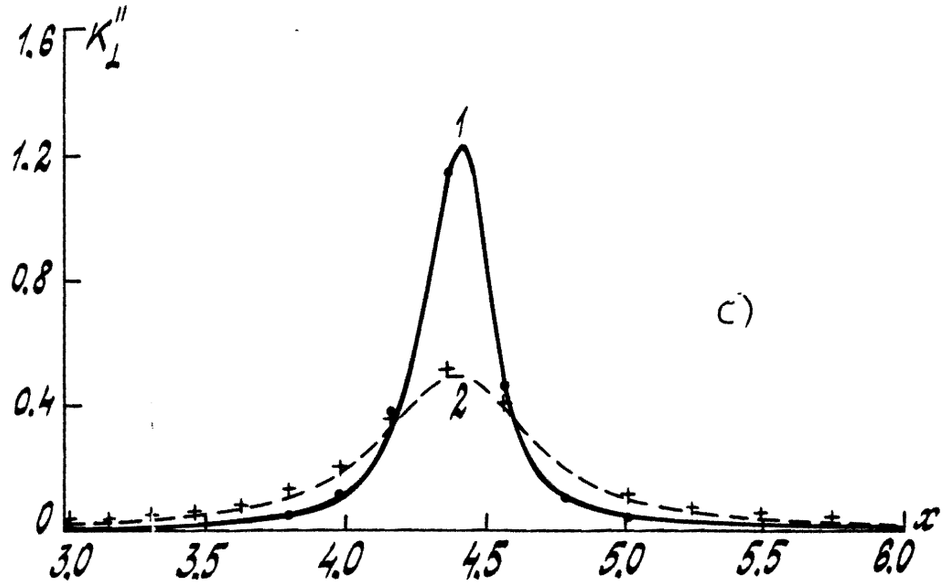

0.010
0.008
0.006
0.004
0.002
0
K''_{11}
1
2
б)
x
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10

Fig. 6 a, б


1.6
1.2
0.8
0.4
0
$K_\perp''$
1
2
c)
x
3.0
3.5
4.0
4.5
5.0
5.5
6.0

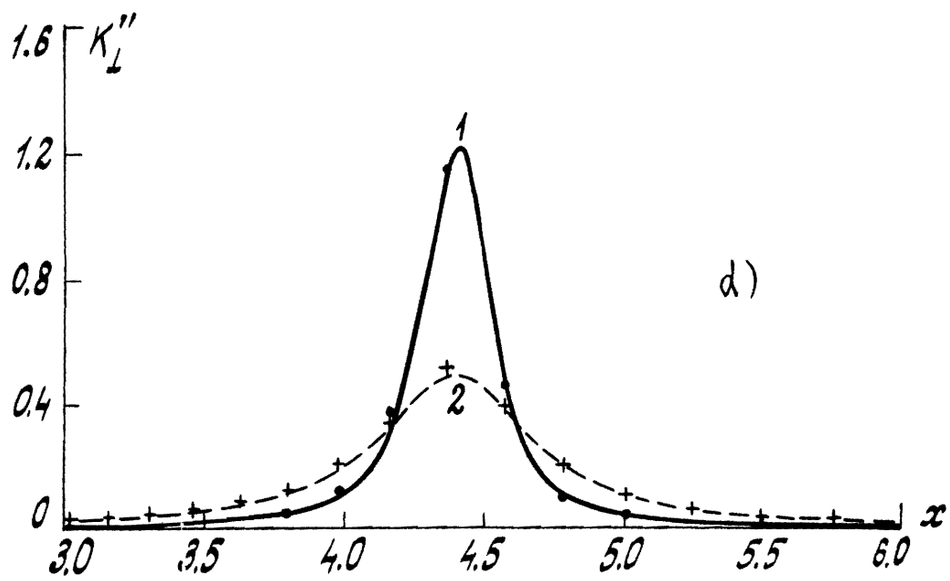
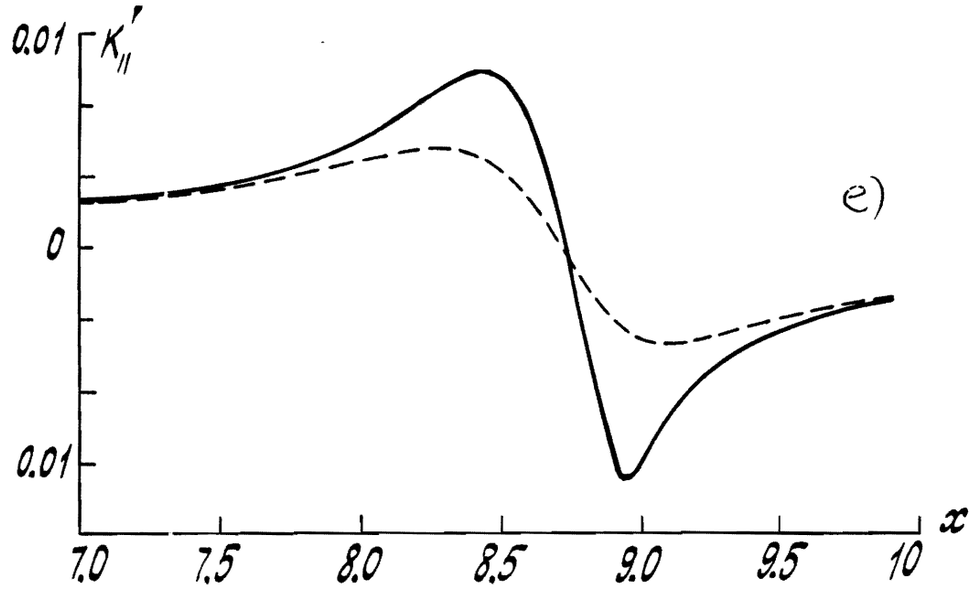

1.6
1.2
0.8
0.4
0
$K_\perp''$
1
2
d)
x
3.0
3.5
4.0
4.5
5.0
5.5
6.0

Fig. 6 c, d


0.01
$K_{\parallel}'$
0
0.01
e)
x
7.0
7.5
8.0
8.5
9.0
9.5
10

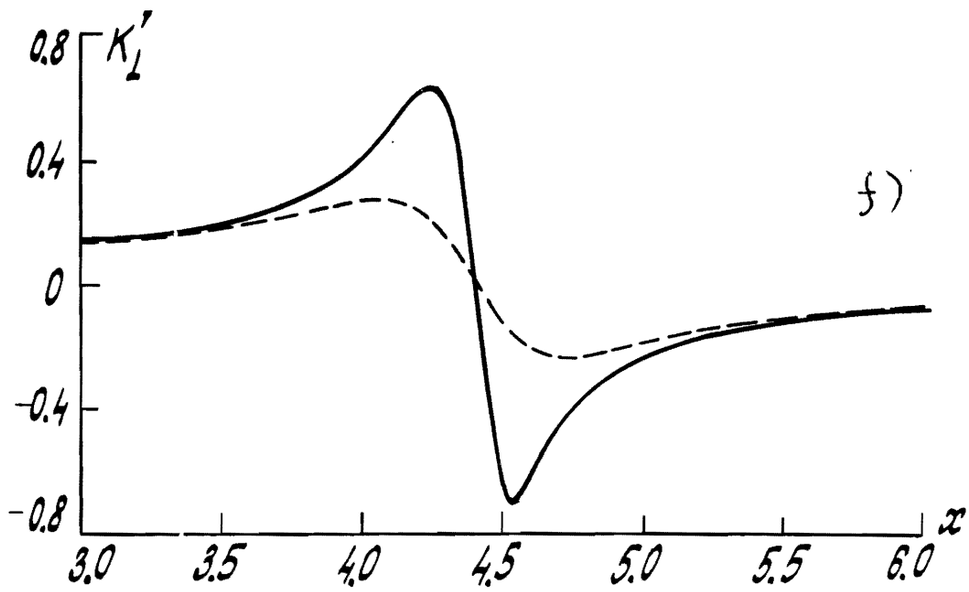
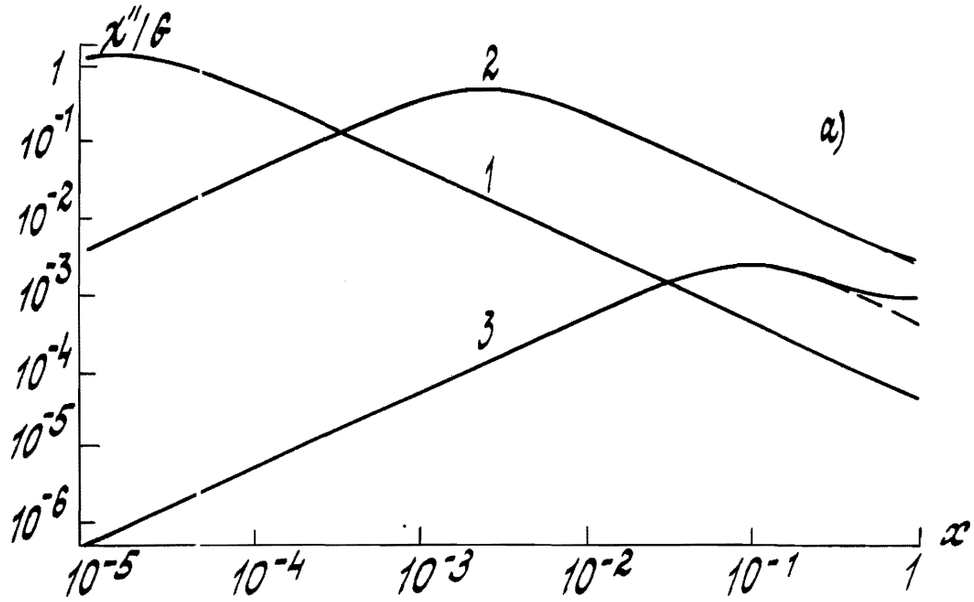

0.8
$K_{\perp}'$
0.4
0
-0.4
-0.8
f)
x
3.0
3.5
4.0
4.5
5.0
5.5
6.0

Fig. 6 e, f


χ''/G
1
10^-1
10^-2
10^-3
10^-4
10^-5
10^-6
2
1
3
a)
x
10^-5
10^-4
10^-3
10^-2
10^-1
1

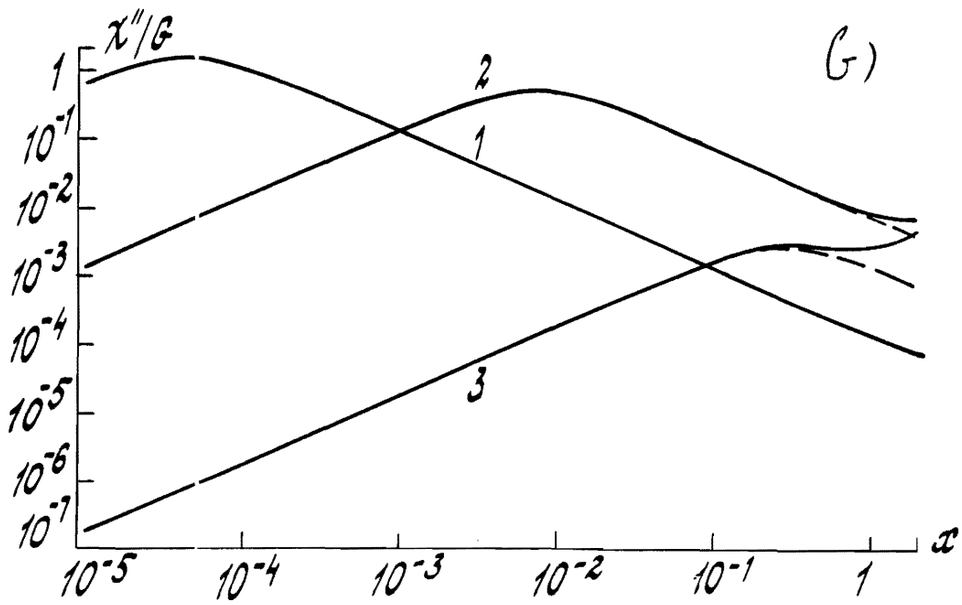
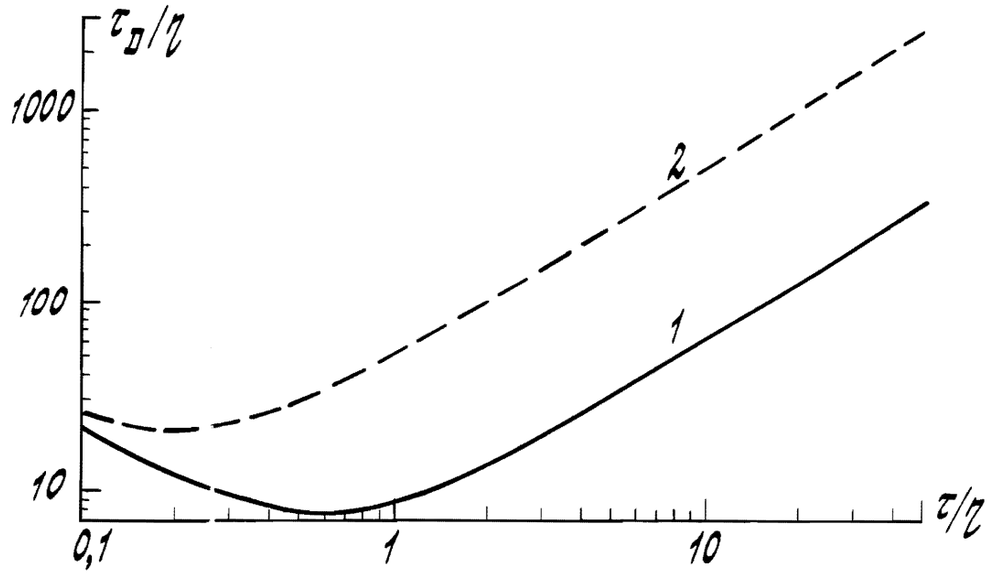

χ''/G
1
10^-1
10^-2
10^-3
10^-4
10^-5
10^-6
10^-7
2
1
3
б)
x
10^-5
10^-4
10^-3
10^-2
10^-1
1

Fig. 7


τ_D/τ
1000
100
10
2
1
0,1
1
10
τ/τ

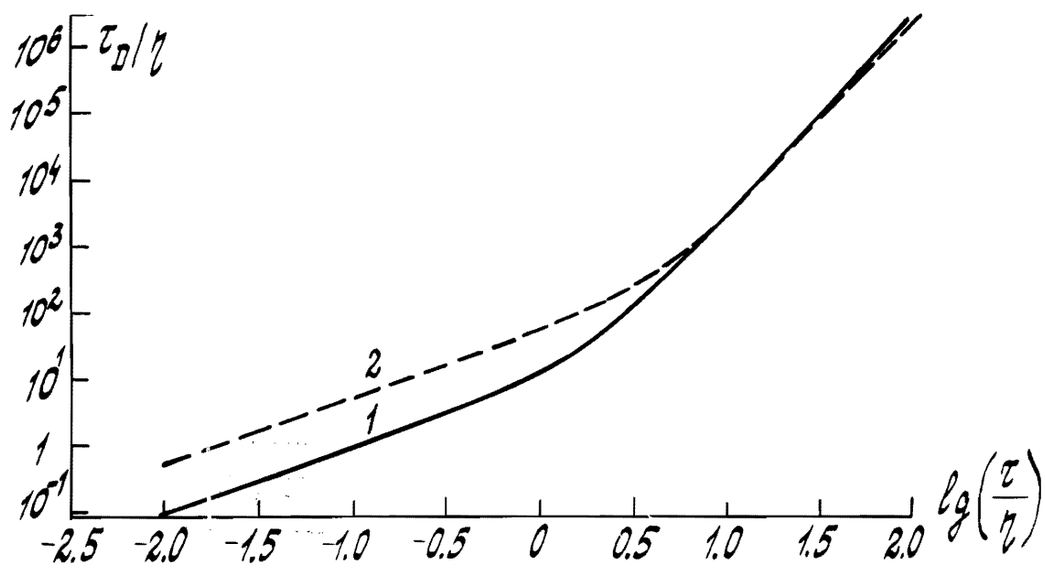

τ_D/τ
10^6
10^5
10^4
10^3
10^2
10^1
1
10^{-1}
2
1
-2.5
-2.0
-1.5
-1.0
-0.5
0
0.5
1.0
1.5
2.0
$lg\left(\frac{\tau}{\tau}\right)$

Fig. 8

NAME	I D No.

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