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ON DIFFUSIONAL MECHANISMS OF RELAXATION. PURE DIFFUSION AND DRIFT

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Abstract. - Diffusional drift model of relaxation is considered for translational and rotational diffusion. Expressions for complex compliance and dielectric constant are obtained. Results are visualized as complex diagrams and absorption spectra.

1. Introduction. - Relaxations are readily visualized as Cole-Cole complex diagrams \([1]\). These diagrams, half-circle for the classical Debye model, are sensitive to details of a relaxational process and often are complicated and asymmetrical \([2]\). Physical models suitable to describe asymmetrical diagrams were offered in \([3-5]\). Based on diffusional mechanisms, these models explain the asymmetry of Cole-Cole diagrams as a result of a transition from diffusional drift to pure diffusion at high frequencies and with properties of a pure diffusion mechanism. It was supposed, that at high frequency the diffusional drift did not contribute significantly. These models demand some structural elements existing, and boundary conditions at these elements are supposed to create the inhomogeneity of the distribution function, necessary for a pure diffusion process.

This point of view does not explain the asymmetry of complex diagrams in cases, where diffusional drift is to contribute also at high frequencies. That is, relaxation in liquids \([2]\), where it is difficult to suppose any structural elements; dielectric relaxation in polar polymers \([6]\), where forces are applied to single molecules at any frequency, etc. Therefore, this work continues the study begun at \([5]\) and is aimed at high-frequency drift-diffusion processes.

2. Translational diffusion. - As it was done before, some non-interacting diffusing kinetic elements are considered, for simplicity, in a one-dimensional model. It is shown in \([5]\), that the distribution function \(c(t, x)\) of these elements in a uniform field of the force \(F(t)\) is described with the generalized Fokker-Planck equation:

\[
\sum_{n=1}^{\infty} \frac{1}{n!} \frac{d^n}{d(i\omega)^n} \left. \frac{\partial^n}{\partial t^n} \right|_{\omega=0} c = \exp \frac{F_x}{T} \sum_{n=1}^{\infty} M_{2n} \frac{\partial^{2n}}{\partial x^{2n}} \left[ c \exp(-\frac{F_x}{T}) \right],
\]
where
\[ M_{2n} = \frac{1}{(2\pi)!} \int_{-\infty}^{\infty} 2n K(x) \, dx. \]  

Here \( w(t) \, dt \) is the probability of an element jumping in an infinitesimal time interval \( dt \) following time \( t \) from its position at \( t-0 \); \( w^*(i\omega) \) is the Fourier-transform of the function \( w(t) \); \( K(x_1-x) \, dx \) is the probability of this element arriving in an interval \( dx \) at a position \( x \) from a position \( x_1 \) in the absence of the force \( F \); \( T \) is the absolute temperature.

Let the equation (1) be solved in the interval \(-L < x < L\). Boundary conditions there will be accepted in the classical form for not transparent boundaries:

\[ \left( \frac{\partial c}{\partial x} - \frac{Fc}{T} \right)_{x=\pm L} = 0. \]  

The problem will be solved for little oscillating forces. In linear approximation by force

\[ c = c_0 + s \sin kx, \]  

where \( c_0 \) is the equilibrium density of kinetic elements. Then out of (3) we obtain:

\[ s = \frac{Fc_0}{kT \cos kL}. \]  

The resulted effect of relaxation, that is, the strain or the polar dielectric moment, is

\[ \varepsilon = \frac{\text{const}}{k^3} \int_{-L}^{L} (c - c_0) \, dx = \text{const} \frac{2Fc_0}{T(kL)^2} \left( \tan kL - 1 \right) a - \text{const} \frac{2Fc_0}{T(kL)^2}, \]

since we can assume \( |kL| \gg 1 \), and for complex values of \( k \), \( \tan kL \approx 1 \). In previous works \([3,5]\) expressions analogous (5) did not contain the multiplier \( x \) in the integrand, but it does not change the qualitative result. The principal difference of the result (6) from the solution for pure diffusion is the square power of \( kL \) in the denominator.

The expression (6), being used in a three-link rheological model for description of the unelastic link, yields the solution for the compliance \( J \) (see \([5]\)):

\[ (J - J_u)/(J_r - J_u) = (1 + \text{const} \frac{F_r}{F_D})^{-1} = \left[ 1 - B(ka)^2 \right]^{-1}, \]  

where \( J_u \) and \( J_r \) are unrelaxed and relaxed values of the compliance, \( a \) is a characteristic parameter of a diffusional model, and \( B=\text{const} \). This expression permits to compare results for different diffusional models, considered in \([5]\), in the case of drift.

For a uniform field, in linear approximation, the derivatives of \( F \) in (1) vanish, and we arrive at the equation of pure diffusion. Hence, this solution differs from the solution
in [5] only with boundary conditions. Thus, the eq. (1) yields the previously obtained result:

\[ \frac{1}{w^*}(i\omega) = K^*(ik), \]

where \( K^*(ik) \) is the Fourier transform of the function \( K(x) \). If the time dependance of individual diffusional jumps probability is simple exponential and all jumps cover equal distance \( a \) with equal likelihood of positive and negative senses, the equation (8) yields the expression

\[ 1 + \frac{i\omega}{\nu} = \cos ka, \]

where \( \nu \) is a multiplier in the exponent (see [5]). The complex Cole-Cole diagrams for the compliance \( J \) in this case are shown at the Fig. 1(curves a and b). These curves are nearer to experimental results, for example, [6], than the curves obtained for pure diffusion models in [5].

The finite propagation rate of a diffusional process can be taken into account with the help of an exponential correction multiplier in the time member of (8) (see [5]):

\[ (1 + \frac{i\omega}{\nu}) \exp(i\omega \tau) = \cos ka, \]

where \( \tau \) is a time constant. The diagram for (7) and (10) is also plotted at the Fig. 1(curve c). It differs from the curves for (9) qualitatively with the angle of approaching the origin.

It behooves to compare these results for diffusional drift with the Cole-Cole diagram for pure diffusion, described with the equation (see [5])

\[ (J - J_u)/(J - J_u) = (1 - Aika)^{-1}, \]

where \( A = \text{const} \) (see Fig. 2). These curves differ from Fig. 1 not only with the mode of approaching the origin, but yield also for the model (10) the double maximum of internal
friction.

Fig. 2: Cole-Cole diagrams for complex compliance. Pure diffusion. 
A-0.1; values of \( \nu \tau \) in (10):

- \( a = 10^{-2} \),
- \( b = 10^{-5} \),
- \( c = 10^{-20} \)

3. Rotational diffusion. - Rotational diffusion of non-interacting kinetic elements is considered in a uniform external field. It is supposed, that the rotational energy of an element in this field is

\[
U = - M(t) \cos \theta ,
\]

where \( \theta \) is a spherical coordinate angle. The generalized Fokker-Planck equation for rotational diffusion obtained in [5] reads:

\[
\sum_{n=1}^{\infty} \frac{1}{n!} \frac{d^n (1/w^*)}{d(i\omega)^n} \bigg|_{\omega=0} \frac{\partial^2 c}{\partial t^n} = \exp \frac{M \cos \theta}{T} \sum_{n=1}^{\infty} x_n \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) \right]^n (c \exp \frac{-M \cos \theta}{T}).
\]

The constants \( x_n \) are expressed through the Legendre transform \( K^*(\eta) \) of the density of probability \( K(\cos \psi) \), where \( \eta \) is a degree of the Legendre polynomial.

The equation for the Fourier and Legendre transforms, analogous to (8), is

\[
1/w^*(i\omega) = K^*(\eta) .
\]

If all diffusional jumps cover equal angles \( \psi_0 \) in arbitrary directions,

\[
K(\cos \psi) = \frac{1}{2\pi} \delta(\cos \psi - \cos \psi_0) ; \quad K^*(\eta) = \frac{\eta}{\eta} P(\cos \psi_0) ,
\]

where \( P_\eta \) is a Legendre polynomial.

Other particular cases can be considered with the help of the series expansion:

\[
P(\cos \psi) = 1 - \frac{N}{12} q + \frac{N(N-1,2)}{(21)^2} q^2 - \frac{N(N-1,2)(N-2,3)}{(31)^2} q^3 + \ldots ,
\]

where \( q = \sin^2 \frac{\theta}{2} \) and \( N = \eta(\eta+1) \). For example, if the angles of diffusional jumps are distributed exponentially, the use of (16) yields:

\[
K(\cos \psi) = \frac{\lambda}{4\pi} \exp (-\lambda q) , \quad \lambda \gg 1 ,
\]

\[
K^*(\eta) = \int_0^1 \exp (-\lambda q) P(\cos \psi) d(\lambda q) =
\]

\[
= 1 - \frac{N}{1!} \frac{1}{\lambda^1} + \frac{N(N-1,2)}{2!} \frac{1}{\lambda^2} - \frac{N(N-1,2)(N-2,3)}{3!} \frac{1}{\lambda^3} + \ldots
\]

\[
= \frac{1}{1+q} \sum_{n=1}^{\infty} \frac{(-1)^n q^n}{n!} .
\]
These results are applicable to the Drude's equation for the dielectric constant $\varepsilon$ \[7\], with substitution $\eta(\eta+1)$ for the expression $4i\omega/(\nu\langle\Delta^2\rangle)$:

$$\frac{\varepsilon - \varepsilon_u}{\varepsilon_r - \varepsilon_u} = \left[1 - \frac{\varepsilon_r + 2}{\varepsilon_u + 2} \eta(\eta+1)\right]^{-1} = (1 - CN)^{-1}. \quad (18)$$

Here $\varepsilon_u$ is the unrelaxed and $\varepsilon_r$ is the relaxed dielectric constant. The formula (18) resembles the eq. (7) for translational diffusion, hence, qualitative results are similar.

It is of interest to calculate the optical absorption coefficient $\alpha$ in accordance with this theory. The absolute values of wave velocity and refractivity are of no interest, thus $\alpha$ is calculated, upon the eq. (18), as

$$\alpha = \omega \frac{\text{Im} \varepsilon}{\varepsilon_r - \varepsilon_u} = \omega \frac{C \text{Im} N}{(1 - C \text{Re} N)^2 + (C \text{Im} N)^2}. \quad (19)$$

The calculations were fulfilled for the model of the determined jumps angle (15) at $C = 2$, $q = 10^{-3}$. The results are plotted at the Fig. 3.

**Fig. 3**: Coefficient of absorption for rotational diffusion. $K^*(\eta)$ - by (15); laws for $1/w^k(i\omega)$:

- $a = 1 + i\omega / \nu$,
- $b = \exp(i\omega / \nu)$,
- $c = (1 + i\omega / \nu) \exp(i\omega / \nu)$,
- $d = (1 + i\omega / \nu) \exp(0.1 i\omega / \nu)$

It is seen, that all the models yield $\alpha \sim \text{const}$ at $\omega / \nu \in [q, 1]$. This is due to validity of the classical approximation $i\omega / \nu \approx -qN$, when $\omega / \nu < 1$. At frequencies higher than the individual jumps frequency different models yield different results. For the model of the exponential dependence of $w(t)$, without an account of the finite diffusion process...
propagation velocity, \( a \to \infty \), when \( \omega \to \infty \). Vlasov's model of jumps over equal definite intervals \( 1/\nu \) yields the return to transparency (curve b) fit to qualitative description of experimental data. The law (10) yields curves of different shape (c, d), in accordance with the values of the product \( \nu \tau \).

Of course, rotational diffusion is also describable in the frames of Cole–Cole diagrams formalism. Also the absorption spectra due to translational diffusion are similar to the spectra for rotational diffusion. Nevertheless, when applying the stated results to experimental data, it should be remembered, that this theory does not yet take into account many physical effects: change of the angular momentum of the kinetic elements (J-diffusion), inertial and memory effects etc.

References
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