Symmetry Relation in Relaxation Dispersions

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A theorem on the relation between the symmetry of the dispersion function of the frequency variable and the distribution function of the relaxation time variable is proved. Some applications of this theorem are discussed.

I. INTRODUCTION

IN this paper, we discuss a theory on which we can base an evaluation of the characteristic relaxation time for a dispersive system with a distribution of relaxation times. The relaxation under consideration is manifested in many physical processes, which could vary widely from the point of view of the physical quantities and mechanism concerned, but a unified discussion which is quite independent of specific physical models is possible through a general mathematical approach.

To present the problem, we start in a formal way from the following equation[1]:

$$A^*(\omega)=A_\infty+(A_0-A_\infty)\int_{-\infty}^{\infty}\frac{G(\tau)}{1+i\omega\tau}d\ln\tau. \quad (1)$$

Here $A^*(\omega)$ is a complex quantity and depends on ω, the frequency. This quantity usually can be measured experimentally; it may denote dielectric permittivity, magnetic susceptibility, semiconductor conductivity, mechanical compliance, scattering amplitude of elementary particles, etc. The subscripts of A are to be identified with the value of ω. $G(\tau)$ is a dimensionless probability function of τ, with τ as the relaxation time variable. The special value of τ, which gives the maximum of $G(\tau)$, will be called the relaxation time and is denoted by τ_0. In the case of a single relaxation time dispersion such as Debye dispersion,[2] $G(\tau)$ is represented by

$$G(\tau)=\tau_0\delta(\tau-\tau_0), \quad (2)$$

where δ is the Dirac δ function.

We separate $A^*(\omega)$ into its real and imaginary part,

$$A^*(\omega)=A'(\omega)-iA''(\omega). \quad (3)$$

Two other relaxation times have been used,[3]

(1) $\tau_1=(\omega_1)^{-1}$, where ω_1 is determined from

$$A'(\omega_1)=\tfrac{1}{2}\cdot[A'(0)+A'(\infty)]. \quad (4)$$

(2) $\tau_2=(\omega_2)^{-1}$, where ω_2 has the property

$$A''(\omega_2)=\mathrm{Max}A''(\omega). \quad (5)$$

[1] J. Ross Macdonald and Malcolm K. Brachman, Rev. Mod. Phys. **28**, 393 (1956).
[2] P. Debye, *Polar Molecules* (Dover Publications Inc., New York, 1929), p. 102.
[3] L. C. Van der Marel, J. Van den Broek, and C. J. Gorter, Physica **24**, 93 (1958).

The values of τ_1, τ_2, and τ_0 are, in general, not equal. If the specific forms of $A'(\omega)$, $A''(\omega)$, and $G(\tau)$ are known, one can calculate them immediately. However, for a class of dispersion functions, even without knowing the specific forms, one can prove that

$$\tau_0=\tau_1=\tau_2. \quad (6)$$

This proof is the purpose of the present note.

II. SYMMETRY RELATION

We call a function $F(x)$ symmetrical about $x=x_0$ in the domain $(-\infty, \infty)$ of the real variable x, if one of the following two conditions is fulfilled:

$$(1)\ F(x-x_0)=F(x_0-x), \quad (7)$$

this is the case of ordinary line symmetry about $x=x_0$;

$$(2)\ F(x-x_0)+F(x_0-x)=2F(0), \quad (8)$$

this is a case of a point symmetry about the point $x=0$. The connection between the function $F(x)$ and the dispersion function $A(\omega)$ is that

$$A(\omega)=F(x) \quad (9)$$

with $x=\ln\omega$. Thus, $F(x-x_0)=A[\ln(\omega/\omega_0)]$. In order to avoid the use of an extraneous symbol, we shall write $A[\ln(\omega/\omega_0)]$ simply as $A(\omega/\omega_0)$. A similar remark applies to $G(\tau/\tau_0)$. Since physically both ω and τ are real and positive, the domain of these independent variables is $(0,\infty)$. In this respect, $A(\omega)$ or $G(\tau)$ cannot have symmetry in ω or τ space, respectively. It is only permissible to have a symmetry in $\log\omega$ or $\log\tau$ space.[4] A misunderstanding of this concept has appeared, for example, in the discussion of the Fröhlich distribution function[5] by Higasi.[6]

Now, we will establish the following theorems:

Theorem 1. $A'(\omega)$ and $A''(\omega)$ are symmetric functions of $\log\omega$ if, and only if, $G(\tau)$ is a symmetric function of $\log\tau$.

Theorem 2. The relation of Eq. (6) is satisfied if, and only if, the dispersion function is symmetric.

[4] To make this statement complete, we should add that δ function, as an improper function, forms the unique exception, that is, $\delta(\tau-\tau_0)$ appears as symmetrical with respect to τ_0 in τ space as τ spans from 0 to ∞.
[5] H. Fröhlich, *Theory of Dielectrics* (Oxford University Press, New York, 1949), p. 91; see also, T. Satoh, J. Phys. Soc. Japan **17**, 279 (1962).
[6] K. Higasi, *Dielectric Relaxation and Molecular Structure*, Monograph Ser. Res. Inst. Appl. Elec. Hokkaido Univ., **9** (1961).

The proof of these theorems, which is elementary, but involves some lengthy formulas and transformations, will be given in the Appendix.

We will call a dispersion which satisfies any conditions of the theorems a symmetrical dispersion. One important implication of these theorems is that if a dispersion is symmetric, τ_0 can be determined from $G(\tau)$, $A'(\omega)$, or $A''(\omega)$, irrespective of the exact forms of these functions.

The converse of the theorems is that if the dispersion is not symmetric, Eq. (6) is no longer true, and one has to know the specific form of dispersion functions in order to determine the relaxation time. In particular, it is necessary to know the function $G(\tau)$ because the idea of continuous relaxation is based on the concept of a statistical distribution of the relaxation times.

A nonsymmetrical dispersion shows itself in a most obvious way in the work of Davidson and Cole,[7] but this type of dispersion has been discussed much earlier; for example, in the work of Karapetoff.[8] Recently, this kind of dispersion has been observed in various relaxation phenomena, such as the magnetic susceptibilities of some paramagnetic salts,[3,9] the dielectric permittivity of alkali-halide crystals,[10] and some polar liquids,[11] the microwave conductivity of plasmas[12] and semiconductors,[13] etc. The fact that, for this class of dispersion, the equality of Eq. (6) is not true, seems not to have been recognized or discussed explicitly.[14]

We compiled in Table I a list of dispersion functions under symmetric and nonsymmetric classifications.

TABLE I. Some dispersion functions.

Symmetrical	Ref.	Nonsymmetrical	Ref.
Debye	a	Karapetoff	h
Cole and Cole	b	Davidson and Cole	i
Weichert, Wagner	c,d	Fang	j
Fröhlich	e	Glarum	k
Fuoss and Kirkwood	f	Margenau	l
Fuoss and Kirkwood	g	Stolz	m

[a] See Ref. 2.
[b] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).
[c] E. Wiechert, Wied. Ann. Phys. Lpz. **50**, 546 (1893).
[d] K. W. Wagner, Ann. Physik **40**, 817 (1913).
[e] See Ref. 5.
[f] R. M. Fuoss and J. G. Kirkwood, J. Chem. Phys. **23**, 1743 (1955).
[g] R. M. Fuoss and J. G. Kirkwood, J. Am. Chem. Soc. **63**, 385 (1941).
[h] See Ref. 8.
[i] See Ref. 7.
[j] See Ref. 9.
[k] See Ref. 11.
[l] See Ref. 12.
[m] See Ref. 13.

[7] D. W. Davidson and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).
[8] V. Karapetoff, Trans. AIEE **45**, 236 (1926).
[9] P. H. Fang, Physica **24**, 970 (1958); **27**, 681 (1961).
[10] J. R. Macdonald, J. Chem. Phys. **23**, 275 (1955).
[11] S. H. Glarum, J. Chem. Phys. **33**, 1371 (1960).
[12] H. Margenau, Phys. Rev. **109**, 6 (1958).
[13] H. Stolz, Ann. Physik **19**, 394 (1957); 334 (1958).
[14] P. H. Fang, Phys. Rev. **113**, 13 (1959); Ann. Physik **7**, 115 (1960); Appl. Sci. Res. Sect. B **9**, 51 (1961).

III. AN EXTENSION TO THE TEMPERATURE DOMAIN

In the relaxation system where the relaxation time satisfies Arrhenius relation

$$\tau=\tau_a \exp(E/kT) \tag{10}$$

with activation energy E, and reciprocal attempted frequency[15] τ_a, we can introduce a temperature T_0 such that

$$\frac{\tau}{\tau_0}=\exp\frac{E}{k}\left(\frac{1}{T}-\frac{1}{T_0}\right). \tag{11}$$

In this case, we can immediately extend the preceding theorems about symmetry in $\ln(\tau/\tau_0)$ space into $1/T$ space. This result has been found useful in the analysis of some dislocation relaxation data of the Bordoni peak.[16,17]

IV. CONCLUSION

The results of this note establish some general criteria which are useful in the analysis of relaxation dispersion data. Furthermore, in most dispersions, $A^*(\omega)$ is established in closed form, but sometimes $G(\tau)$ is more simple and in fact, only for some special parameters, its corresponding $A^*(\omega)$ can be represented in the closed form in terms of some special function.[18,19] Therefore, these theorems may be found helpful in the theoretical investigation of dispersion functions.

APPENDIX

Proof of Theorem 1. From Eq. (1), with the following notations for abbreviations:

$$a'(\omega,\tau_0)=\frac{A'(\omega,\tau_0)-A(\infty)}{A(0)-A(\infty)}, \quad a^*=\int_{-\infty}^{\infty}\frac{G(\tau,\tau_0)}{1+i\omega\tau}d\ln\tau, \tag{A1}$$

it follows that

$$a'(\omega,\tau_0)=\int\frac{G(\tau,\tau_0)}{1+\omega^2\tau^2}d\ln\tau, \tag{A2}$$

In the first part, we will prove that *the symmetry of $G(\tau,\tau_0)$ is a necessary and sufficient condition for the symmetry of $a'(\omega,\tau_0)$*. The method to prove the relation between $G(\tau,\tau_0)$ and $a''(\omega,\tau_0)$ is very similar. Therefore, we will not present it.

(1) Sufficient condition: From the symmetry of $G(\tau,\tau_0)$, we have

$$1.\ G(\tau,\tau_0)=G(\tau/\tau_0), \qquad 2.\ G(\tau/\tau_0)=G(\tau_0/\tau). \tag{A3}$$

The following relation which is the equivalent definition

[15] D. H. Niblett and J. Wilks, Advan. Phys. **9**, 1 (1960).
[16] P. H. Fang, Nuovo Cimento (to be published).
[17] P. G. Bordoni, Nuovo Cimento Suppl. **17**, 43 (1960).
[18] J. Ross Macdonald, J. Chem. Phys. **20**, 1107 (1952).
[19] P. H. Fang, Appl. Sci. Res. (to be published).

of the symmetry of $a'(\omega,\tau_0)$,

$$a'(\omega,\tau_0)+a'(1/\omega,\tau_0)=1\,, \tag{A4}$$

in particular, therefore, $a'(1)=\frac{1}{2}$ when $w\tau_0=1$ is to be proved. Writing $\tau=\tau_0 x$, from (A2),

$$a'(\omega,\tau_0)=\int_0^\infty \frac{G(x)}{1+\omega^2\tau_0{}^2x^2}\frac{dx}{x}. \tag{A5}$$

Since ω and τ_0 occur only in the product form $\omega\tau_0$, therefore, $a'(\omega,\tau_0)=a'(\omega\tau_0)$. By a further substitution of $y=x^{-1}$, remembering the normalization condition

$$\int_{-\infty}^{\infty} G(\tau,\tau_0)d\ln\tau=1\,, \tag{A6}$$

one finds

$$\begin{aligned}a'(\omega\tau_0)&=\int_0^\infty \frac{G(1/y)y^2}{\omega^2\tau_0{}^2[(y/\omega\tau_0)^2+1]}\frac{dy}{y}\\ &=\int_0^\infty G(y)\left[1-\frac{1}{1+(y/\omega\tau_0)^2}\right]\frac{dy}{y}\\ &=1-a'(1/\omega\tau_0)\,,\end{aligned} \tag{A7}$$

which was to be proved.

(2) Necessary condition: $a'(\omega\tau_0)$ can also be expressed as follows:

$$a'(\omega\tau_0)=\frac{1}{\omega^2}\int_0^\infty \frac{G(\tau)/\tau^2}{1/\omega^2+\tau^2}\tau d\tau. \tag{A8}$$

Set $\tau^2=u$, $\tau_0{}^2=u_0$ and $\omega^2=v^{-1}$,

$$v^{-1}a'[(u_0/v)^{1/2}]=\int \frac{1}{2}\frac{G(u)/u}{v+u}du. \tag{A9}$$

The right side is Stieltjes' integral,[20] therefore,

$$\frac{G(\tau)}{\tau^2}=\frac{i}{2\pi}\left\{2u^{-1}e^{-i\pi}a'\left[\left(\frac{u_0}{u}\right)^{1/2}e^{i\pi/2}\right]-2u^{-1}e^{i\pi}a'\left[\left(\frac{u_0}{u}\right)^{1/2}e^{-i\pi/2}\right]\right\}.$$

[20] E. C. Titchmarsh, *Fourier Integrals* (Oxford University Press, New York, 1949), 2nd ed., p. 317.

Returning to the original notations, one obtains,

$$G(\tau)=\frac{i}{\pi}\left[-a'\left(i\frac{\tau_0}{\tau}\right)+a'\left(-i\frac{\tau_0}{\tau}\right)\right]. \tag{A10}$$

However, from symmetry of $a'(\omega\tau_0)$, we have another relation,

$$\begin{aligned}1-a'\left(\frac{1}{\omega\tau_0}\right)&=\int_0^\infty G(\tau)\left[1-\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\right]\frac{d\tau}{\tau}\\ &=1-\int_0^\infty \frac{G(\tau)}{1/\omega^2+\tau^2}\tau d\tau,\end{aligned} \tag{A11}$$

With the notations of (A8),

$$a'\left[\left(\frac{v}{u_0}\right)^{1/2}\right]=\frac{1}{2}\int_0^\infty \frac{G(\tau)}{v+u}du. \tag{A12}$$

From the Stieltjes transform, we obtain

$$G(\tau)=\frac{i}{\pi}\left[-a'\left(i\frac{\tau}{\tau_0}\right)+a'\left(-i\frac{\tau}{\tau_0}\right)\right]. \tag{A13}$$

Comparing expressions (A8) and (A10) of G, we have proved

$$G(\tau/\tau_0)=G(\tau_0/\tau)\,. \tag{A14}$$

Proof of Theorem 2. To prove Theorem 2, we have only to repeat the proofs of Theorem 1. We proved both necessary and sufficient conditions, and τ_0 is implicitly identified as τ_1 in the proof for the part of $a'(\omega,\tau_1)$, and as τ_2 in $a''(\omega,\tau_2)$.

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