An Invariance in the Kronig-Kramers' Relation

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I. Introduction

Given a pair of functions which satisfy the Kronig and Kramers' (K.K.) relation,[1,2] when the variables of these functions are transformed to new variables, we found that the requirement of the invariance of the K.K. relation provides a connection between the original and the transformed variables. This connection will be given in Part II. In Parts III and IV, we will utilize the result to establish a mathematical foundation of two graphical representations in the analysis of relaxation dispersions. We will prove the almost completeness of the representation in the sense that the graphs determine almost completely the dispersion functions.

II. An Invariance Relation

In the notation of paramagnetic relaxation, the K.K. relation of a pair of functions, the dispersion, $\chi'(\omega)$ and the absorption, $\chi''(\omega)$ are,

$$\chi'(\omega) - \chi_\infty = \int_0^\infty \frac{\omega\chi''(\omega)}{\omega^2 - \omega'^2}\, d\omega \qquad (1a)$$

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Abstract

From the restriction of the integration variable in the Kronig-Kramers' relation, an invariance property is established. This invariance relation is applied to establish the completeness of some representations used in the analysis of the relaxation dispersions.

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$$\chi''(\omega) = \int_0^\infty \frac{\omega'\left[\chi'(\omega) - \chi_\infty\right]}{\omega^2 - \omega'^2}\, d\omega' . \tag{1b}$$

We are interested in the possibility of changing ω to another variable h which is a function of ω, such that the K.K. relation remains unchanged after this variable transformation. Since the K.K. relation can be considered as a functional, our requirement is that the expressions,

$$\frac{\omega d\omega'}{\omega^2 - \omega'^2} \text{ and } \frac{\omega' d\omega'}{\omega^2 - \omega'^2} \tag{2}$$

in (1a,b) be form-invariant.

The restrictions on h are, from (1a,b),

$$h = 0 \text{ at } \omega = 0, \tag{3a}$$

$$h \to \infty \text{ as } \omega \to \infty \tag{3b}$$

$$h > 0, \text{ and} \tag{3c}$$

$$\frac{dh}{d\omega} > 0. \tag{3d}$$

Condition (3d) guarantees that h is a single valued function of ω. From the conditions of (3), we have,

$$h(\omega) = \alpha_0 + \alpha_1 \omega + \alpha_2 \omega^2 + \ldots , \tag{4}$$

with $\alpha_0 = 0$ from (3a) and $\alpha_i \geq 0$ from (3c,d). Substituting (4) into the first expression of (2)—the same result also follows from the other expression – we have,

$$\frac{hdh'}{h^2 - h'^2} = \frac{\omega d\omega'}{\omega^2 - \omega'^2} \left\{1 + \frac{\alpha_2}{\alpha_1}(\omega + 2\omega') + \ldots\right\}$$

$$\left\{1 + \frac{\alpha_2}{\alpha_1}\left[(\omega + \omega') + \frac{\omega^2 + \omega'^2}{\omega + \omega'}\right] + \ldots\right\}^{-1} . \qquad (5)$$

From the form invariance condition, therefore, we have, $\alpha_i = 0$ for $i \neq 1$. The coefficient α_1 is non-zero and positive, otherwise unrestricted.

From the above result, we conclude that the only permissible variable transformation is

$$\omega \rightarrow \alpha_1 \omega . \qquad (6)$$

We have, instead of (1a,b), the more general relations,

$$\chi'(\alpha\omega) - \chi_\infty = \int_0^\infty \frac{\omega\chi''(\alpha\omega)}{\omega^2 - \omega'^2} \, d\omega' , \qquad (7a)$$

$$\chi''(\alpha\omega) = \int_0^\infty \frac{\omega' \left[\chi'(\alpha\omega) - \chi_\infty\right]}{\omega^2 - \omega'^2} \, d\omega' . \qquad (7b)$$

III. Spectral Representation of Relaxation Dispersions

By spectral representation we mean the plot of the dispersion functions, $\chi'(\omega)$ and $\chi''(\omega)$ as a function of ω (Spectral representation I) or as a function of $\log\omega$ (Spectral representation II). Here and in the following our discussion will be confined to $\chi''(\omega)$, but a parallel development based on $\chi'(\omega)$ is trivial.[3]

Using the Casimir and DuPré absorption function in the spin-lattice relaxation[4] as an illustration,

$$\chi''(\omega) = (\chi_0 - \chi_\infty)\,\frac{\omega\tau_0}{1+\omega^2\tau_0^2}, \tag{8}$$

where τ_0 is the relaxation time. We have, for χ''_{max},[3]

$$\omega_m = \tau_0^{-1} \tag{9}$$

and the breadth of the half-width is,

$$\Delta\omega_{1/2} = 2\sqrt{3}\,\tau_0^{-1}. \tag{10}$$

Now we take a hypothetical absorption function, obtained from Eq. (8) by an α-transformation of Eq. (6)

$$\chi''(\omega) = (\chi_0 - \chi_\infty)\,\frac{\alpha\omega\tau_0}{1+\alpha^2\omega^2\tau_0^2} \tag{11}$$

In this case,

$$\omega_m = \alpha^{-1}\,\tau_0^{-1} \tag{13}$$

and

$$\Delta\omega_{1/2} = 2\sqrt{3}\,\alpha^{-1}\,\tau_0^{-1} \tag{14}$$

In the spectral representation I, a variation of α will be reflected in the change of the positions of ω_m and the breadth $\Delta\omega_{1/2}$. Therefore, it appears as if the line shape is effected by the α-transformation, that is, if there is an independent method to determine τ_0. However, we have investigated the mathematical formulation of the dispersion function and we found that the transformation

$$\omega \rightarrow \alpha\omega$$

is accompanied simultaneously by the transformation

$$\tau_0 \to \alpha^{-1} \tau_0 \tag{15}$$

and, indeed, τ_0 and α cannot be independently determined.

In the spectral representation II, the position of $\log \omega_m$ is shifted by the α-transformation, but from the same argument as in representation I, this shift is not determinable. For the half width, independent of Eq. (10) or (14),

$$\Delta \log \omega_{1/2} = \log (7 + 4\sqrt{3}). \tag{16}$$

Therefore, in representation II, the line shape is independent of α. In other words, it is an invariant of the α-transformation.

IV. Argand Diagram Representations

The Argand diagram is a frequency trace in the plane formed by $\chi'(\omega)$ and $\chi''(\omega)$ as coordinates, that is, a parametric representation of plotting $\chi'(\omega)$ against $\chi''(\omega)$ with ω as a parameter. This representation has been introduced in the analysis of many relaxation dispersion phenomena,[4,5] especially in the case of dielectric relaxation.[6] From the general property of the parametric representation, it might seem that the Argand diagram does not suffice to describe the dispersion functions $\chi'(\omega)$ and $\chi''(\omega)$ completely. What we mean here is the following: If experimental data fit the Argand diagram of a particular dispersion function pair, ignoring the match of the frequency parameter, does it confirm the theoretical dispersion function. The answer is yes, from the requirement of the K. K. relation, the only invariance of a parametric representation is a simultaneous change of the parameter ω to a new variable $h(\omega)$ in both $\chi'(\omega)$ and $\chi''(\omega)$. Equation (7) restricts this transformation to a linear one: $h = \alpha\omega$. Therefore we conclude that,

With the exception of an arbitrary linear transformation of frequency which leaves zero and infinity invariant, the Argand diagram characterizes the dispersion functions uniquely.

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