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A Note on a Distribution of Relaxation Time in Ferroelectrics near the Curie Temperature

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Recently refined experimental results[1] on the relaxation process in ferroelectrics near the Curie temperature suggest that some of the so-called polydispersive ferroelectrics seem to exhibit monodispersive properties when the temperature homogeneity in the sample is well recovered. Previously, assuming a distribution of relaxation time, two of us presented a phenomenological theory[2] of the anomalous dielectric relaxation in ferroelectrics of the order-disorder type near the Curie point. The aim of this note is to point out the possibility that even a monodispersive substance with a single relaxation time might exhibit polydispersive properties near the Curie point when the temperature fluctuation in the substance is taken into consideration.

We take, as is well known, the substance as polydispersive when its complex dielectric constant $\varepsilon(\omega)$ is expressed as

$$\frac{\varepsilon(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty}=\int_0^\infty\frac{G(\tau)\,d\tau}{1+i\omega\tau}, \tag{1}$$

where ε_0 and ε_∞ are respectively the static and the electronic contribution to the dielectric constant, and $G(\tau)$ is a distribution function of relaxation time. For the special distribution of the Cole-Cole law which explains well the dielectric behaviours of many of the ferroelectrics,

$$\int_0^\infty\frac{G(\tau)\,d\tau}{1+i\omega\tau}=\frac{1}{1+(i\omega\tau_c)^\beta} \tag{2}$$

with the distribution function

$$F(s)=\frac{1}{2\pi}\cdot\frac{\sin\beta\pi}{\cosh\beta s+\cos\beta\pi},$$
$$-\infty<s<\infty, \tag{3}$$

where

$$s=\log(\tau/\tau_c),$$
$$G(\tau)\,d\tau=F(s)\,ds \tag{4}$$

and τ_c is a characteristic time and β gives a measure for the distribution of relaxation time.[2] The full width Γ in s at half maximum of this symmetrical distribution $F(s)$ is given by

$$\Gamma=\frac{2}{\beta}\cosh^{-1}(2+\cos\beta\pi) \tag{5}$$

and is illustrated in Fig. 1 as a function of β.

We consider a system of dipoles immers-

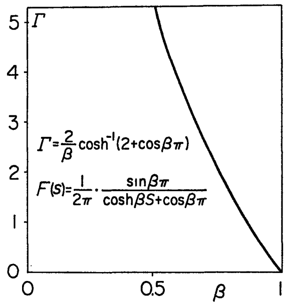

Fig. 1. The full width at half maximum of the distribution function $F(s)$.

ed in a monodispersive medium and subject to a molecular field. Owing to the critical slowing down of the relaxation of polarization in this system, the relaxation time τ is given as[2)]

$$\tau=\tau_0 X\simeq\frac{1}{\alpha(T-T_c)} \quad \text{near above } T_c,$$

$$X=\frac{\varepsilon_0+2}{\varepsilon_\infty+2}. \tag{6}$$

If there exists the average fluctuation of temperature $\varDelta T$ in the system, the subsequent fluctuation of the relaxation time is given by

$$\frac{\varDelta(1/\tau)}{1/\tau}=\frac{\varDelta T}{T-T_c}. \tag{7}$$

On the other hand, from Eq. (4), we have

$$\varDelta s=\frac{\varDelta\tau}{\tau}=-\frac{\varDelta(1/\tau)}{1/\tau}. \tag{8}$$

Assuming that the distribution of relaxation time due to the temperature fluctuation is of the Cole-Cole law type, we are led, from Eqs. (5), (7) and (8), to the possibility of measuring polydispersive properties corresponding to the width

$$\Gamma\simeq|\varDelta S|=\frac{\varDelta T}{T-T_c}. \tag{9}$$

If $\varDelta T$ is fixed as in the usual experimental condition, Γ is negligible at a high enough temperature from T_c. In the vicinity of T_c, however, the apparent distribution of relaxation time is very important. In any case, temperature fluctuation in the substance is inevitably accompanied by the apparent distribution of relaxation time. The above feature seems to appear in the case of $NaNO_2$.[1)~3)] According to the recent experimental results,[1)] this substance is monodispersive with $\beta=1.00$ and Γ calculated with Eq. (9) for $\varDelta T=1$°C varies from about 0.40 to 0.10 as $T-T_N$ changes from about 1°C to 10°C, corresponding approximately to $\beta=0.94$ and 0.98, respectively (see Fig. 1). These values are reasonable compared with the experimental value $\beta=0.94$ and the width of temperature fluctuation $\varDelta T\simeq 1$°C in a previous experiment.[3)] No appearance of the temperature dependence of β in the previous experiment[3)] except at a high enongh temperature seems to be due to rather rough temperature controll at a high temperature from T_N. In Rochelle salt the early measurement by Akao and Sasaki[4)] shows that the width of the distribution of relaxation time becomes broader as temperature approaches the upper Curie point, while the recent measurement by Sandy and Jones[1)] shows a rather monodispersive behaviour. This difference seems to be understood from our point of view. In TGS there also seem to exist the same circumstances in the differences between the measurement by Luther et al.[1)] and that by Hill et al.[5)]

In conclusion we emphasize the importance of temperature controll near T_c in order to distinguish between mono- and polydispersive behaviours.

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