

Determination of Charge or Polarization Distribution across Polymer Electrets by the Thermal Pulse Method and Fourier Analysis

A. S. DeReggi, C. M. Guttman, F. I. Mopsik, G. T. Davis, and M. G. Broadhurst
National Bureau of Standards, Washington, D. C. 20234
 (Received 20 September 1977)

Fourier analysis applied to the recently introduced thermal pulse method yields new and unique relations between the time-dependent pyroelectric response of a thin specimen and the Fourier coefficients of the charge or polarization distribution across its thickness. The new analysis is applied illustratively to thermal pulse data for a vinylidene fluoride copolymer electret.

Several new experimental methods have been proposed in recent Letters¹⁻³ to probe the spatial distribution of charge and/or polarization across the thickness of thin (thickness of order 10 μm) dielectric samples. These methods are currently of interest as means for studying piezoelectric and pyroelectric polymers. The electron-beam method of Sessler *et al.*¹ has a resolution of $\sim 1 \mu\text{m}$, but is destructive in the sense that the measuring process irreversibly changes the quantities measured. Acoustical methods of generating a propagating pressure step² across a sample in order to measure its inhomogeneous piezoelectric response are nondestructive; but the step rise-time requirements become severe if a resolution of 1 μm is desired (a resolution of 1 μm requires a step rise time of ≤ 0.5 ns assuming a sound velocity of 2000 m/s). Thermal methods for producing a transient inhomogeneous strain across a sample, in order to measure its inhomogeneous pyroelectric response, as, for example in Collins's thermal pulse method,^{3,5} are both nondestructive and comparatively easy to implement experimentally (thermal-equilibration times are ~ 1 ms). However, because the thermal equilibration process is diffusive rather than propagative (wavelike), information contained in the experimental data about charge and/or polarization distributions is convoluted with a time-dependent temperature distribution and somehow must be deconvoluted. The major and often-quoted¹⁻⁵ objection to the Collins thermal pulse method has been that the deconvolution procedure³⁻⁵ yields *nonunique* charge and/or polarization distributions.

In this Letter, we show that the Collins experiment yields the first few Fourier coefficients of the charge or polarization distribution, not the charge or polarization distribution itself as may be supposed from Collins's papers.^{1,2,3} Further, we present expressions for the response which allow the Fourier coefficients to be determined

from the experimental data by numerical or graphical analysis. We apply the new expressions to thermal pulse data for a copolymer of vinylidene fluoride with tetrafluoroethylene. This example illustrates both the power and the limitations of the thermal pulse method.

Consider, first, the temperature $T(x, t)$ at time t across a sample regarded as a slab of infinite extent and of thickness d (see inset in Fig. 1) after a radiant heat pulse of duration t_p has been applied to the surface $x = 0$. Assume that (1) the aluminum electrodes have negligible optical transmission and negligible thermal mass; (2) heat flows in the x direction only; and (3) the sample does not lose heat to the surroundings. The *initial* temperature $T(x, 0)$ taken at the *end* of the thermal pulse is written

$$T(x, 0) = T_1 + \Delta T(x, 0), \quad (1)$$

where T_1 is the uniform temperature of the sample prior to the pulse, and $\Delta T(x, 0)$ is the deviation from T_1 . In practice, $\Delta T(x, 0)$ is a sharply localized function extending from $x = 0$ with a width $\xi \ll d$. The temperature at $t > 0$ is $T(x, t) = T_1 + \Delta T(x, t)$, where⁶

$$\Delta T(x, t) = a_0 + \sum_{n=1}^{\infty} a_n \cos\left(\frac{n\pi x}{d}\right) \exp\left(-\frac{n^2 t}{\tau_1}\right), \quad (2)$$

where $\tau_1 = d^2/\pi^2 k$ with k the thermal diffusivity, and where

$$a_0 = d^{-1} \int_0^d \Delta T(x, 0) dx = \lim_{t \rightarrow \infty} \Delta T(x, t) \quad (3)$$

and

$$a_n = \frac{2}{d} \int_0^d \Delta T(x, 0) \cos\left(\frac{n\pi x}{d}\right) dx, \quad n = 1, 2, \dots \quad (4)$$

In the limiting case where $\Delta T(x, 0) \rightarrow \delta(x)$, all a_n 's are

$$a_n = 2a_0, \quad n = 1, 2, \dots \quad (5)$$

However, for a general $\Delta T(x, 0)$, the tempera-

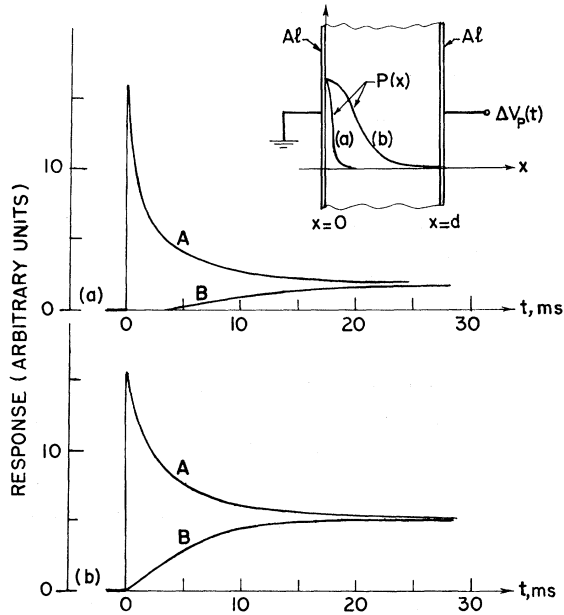


FIG. 1. Inhomogeneous pyroelectric response of two copolymer samples: (a) sample with pyroelectric activity concentrated towards surface $x=0$ and (b) sample with distributed pyroelectric activity. Signals marked A are for thermal pulse applied to surface $x=0$ and those marked B are for thermal pulse applied to surface $x=d$. Inset shows thermal pulse arrangement. Polymer samples have vacuum-deposited, reflecting (partially absorbing, nontransmitting) electrodes. Polarizations a and b shown in the inset are obtained from the first few Fourier moments of corresponding signals.

ture at the surfaces is described by

$$\Delta T(0,t) = a_0 + \sum_{n=1}^{\infty} a_n \exp(-n^2 t / \tau_1) \quad (6)$$

and

$$\Delta T(d,t) = a_0 + \sum_{n=1}^{\infty} (-1)^n a_n \exp(-n^2 t / \tau_1). \quad (7)$$

Expressions (6) and (7) have been used previously as the basis for thermal diffusivity measurements.⁷ In the present case, the dimensionless quantities $\Delta T(0,t)/a_0$ and $\Delta T(d,t)/a_0$ can be obtained by measuring the transient resistance of one or both electrodes as done by Collins.⁴ Then the a_n/a_0 and τ_1 can be determined without knowing the detailed shape of the light pulse.

Consider, now, the inhomogeneous pyroelectric response. Assume that real charge of volume density $\rho(x)$ and elementary dipoles responsible for polarization $\vec{P}(x) = \hat{x}P(x)$ move reversibly when the sample thermally expands or contracts. Following Collins,⁵ the open-circuit voltage due

to charge, ΔV_ρ , and that due to polarization, ΔV_p , are

$$\Delta V_\rho(t) = \frac{\alpha_x - \alpha_\epsilon}{\epsilon \epsilon_0} \int_0^d \rho(x) \int_0^x \Delta T(x',t) dx' dx, \quad (8)$$

and

$$\Delta V_p(t) = \frac{\alpha_p + \alpha_x - \alpha_\epsilon}{\epsilon \epsilon_0} \int_0^d P(x) \Delta T(x,t) dx, \quad (9)$$

where α_x , α_ϵ , and α_p are temperature coefficients $(1/x)dx/dT$, $(1/\epsilon)d\epsilon/dT$, and $(1/P)dP/dT$, respectively, ϵ is the relative permittivity, and ϵ_0 is the permittivity of vacuum. Substitution of (2) into the above equations gives

$$\Delta V_\rho(t) = \frac{\alpha_x - \alpha_\epsilon}{\epsilon \epsilon_0} \times \left[a_0 A_0 + \frac{d}{\pi} \sum_{n=1}^{\infty} \frac{a_n A_n}{n} \exp\left(\frac{-n^2 t}{\tau_1}\right) \right], \quad (10)$$

where

$$A_0 = \int_0^d x \rho(x) dx, \quad (11)$$

$$A_n = \int_0^d \rho(x) \sin(n\pi x/d) dx, \quad n=1,2,\dots, \quad (12)$$

and

$$\Delta V_p(t) = \frac{\alpha_p + \alpha_x - \alpha_\epsilon}{\epsilon \epsilon_0} \times \left[a_0 B_0 + \sum_{n=1}^{\infty} a_n B_n \exp\left(\frac{-n^2 t}{\tau_1}\right) \right], \quad (13)$$

where

$$B_0 = \int_0^d P(x) dx \quad (14)$$

and

$$B_n = \int_0^d P(x) \cos(n\pi x/d) dx, \quad n=1,2,\dots \quad (15)$$

It should now be noted that a_n , A_n , and B_n are coefficients of Fourier series expansions for $\Delta T(x,0)$, $\rho(x)$, and $P(x)$, respectively, if these are expanded as cosine, sine, and cosine series, respectively.

The foregoing analysis shows that the inhomogeneous pyroelectric response consists of exponentially decaying components with relaxation times τ_1/n^2 . Measurement of this response yields Fourier coefficient combinations $(a_n/a_0)(A_n/A_0)(d/\pi)$ in the charge case, or $(a_n/a_0)(B_n/B_0)$ in the polarization case (or a linear combination of these in the mixed case). For sufficiently short pulse duration ($t_r \ll \tau_1/n^2$ up to the highest n of

interest), the approximation $a_n/a_0 \approx 2$ can be made. Otherwise, a_n/a_0 can be obtained from a separate measurement of the transient resistance of the electrodes. Thus, Fourier coefficients of the charge or polarization distribution, A_n/A_0 or B_n/B_0 , can be determined up to terms with n of order $N = (\tau_1/t_r)^{1/2}$. The spatial resolution of the thermal pulse experiment is roughly d/N .

Limiting cases of charge and polarization distributions are of interest. Note that if $\rho(x) \rightarrow \delta(x)$, then $\Delta V_p(t) \rightarrow 0$ [i.e., charge on surface $x=0$ does not contribute to $\Delta V_p(t)$], while if $\rho(x) \rightarrow \delta(x-d)$, $\Delta V_p(t)$ becomes indistinguishable from $\Delta V_p(t)$ for uniform polarization. This is a manifestation of the electrostatic equivalence of $\rho(x)$ and $-dP/dx$. Note also that if $P(x) \rightarrow \delta(x)$, then $\Delta V_p(t)$ becomes proportional to $\Delta T(0, t)$ in (7), while if $P(x) \rightarrow \delta(x-d)$, then $\Delta V_p(t)$ becomes proportional to $\Delta T(d, t)$ in (8). This is a consequence of the symmetrical roles played by a_n and B_n .

Figure 1 shows signals proportional to open-circuit voltages for two copolymer samples 50 μm thick (vinylidene fluoride with 27% by weight of tetrafluoroethylene). For each sample, curve A is for light pulsed at $x=0$ and curve B is for light pulsed at $x=d$. The difference in the samples is in the poling treatment. Both samples were stored for long periods under short-circuit conditions after poling. Sample (a) was poled at room temperature by corona charging⁸ with a bias voltage of -2000 V. Curve A, shown in Fig. 1(a), is nearly proportional to the $\Delta T(0, t)$ signal (not shown) at times $t \gg t_r$ where $t_r \approx 20$ μs while curve B is nearly proportional to $\Delta T(d, t)$. These observations indicate (assuming that all $B_n = 0$ for $n > N$) a sample with strong localization of polarization towards $x=0$ as shown qualitatively by (a) in the inset (or a sample with a charge layer imbedded just inside the sample close to $x=0$). Sample (b) was poled during crystallization by maintaining 300 V across the sample as it was cooled from 130°C and crystallized for 6 h at 118.5°C before cooling further to 100°C (0.3 K/min) followed by quenching to room temperature. The signals for this case, shown in Fig. 1(b), indicate a distributed asymmetric pyroelectric activity.

Note that series (10) and (13) acquire alternating signs if the direction of irradiation is changed [in which case a_n changes to $(-1)^n a_n$] or if the sample is reversed [in which case A_n and B_n change to $-(-1)^n A_n$ and $-(-1)^n B_n$]. Thus, if separate response signals are obtained by thermally pulsing opposite surfaces in turn, the even

and odd Fourier coefficients can be obtained separately from the sum and the difference of the two signals. Visual comparison of the two signals also reveals whether the distribution of pyroelectric responsivity is symmetric or asymmetric.

Figure 2 shows semilog plots of the curves A and B from Fig. 1(b) together with $A+B$ containing only even terms of the response and $A-B$ containing only odd terms of the response. Assume that the responses are associated with polarization. Graphical analysis of the linear part of the odd response gives $\tau_1 = 4.8$ ms (in good agreement with the value expected from the thermal properties and the thickness of the film) and $2a_1B_1 = 14$. Removal of this linear part gives a remainder (curve D) with a slope $9/\tau_1$ indicating that $2a_3B_3 \approx 1.5$ and that $2a_5B_5 \approx 0$. Similar analysis of the even response gives $2a_0B_0 = 10.2$, $2a_2B_2 \approx 5$ (from curve C), and $2a_4B_4 \approx 0$. Since the pulse duration of $t_r \approx 20$ μs should allow about ten terms to be observed [$N = (\tau_1/t_r)^{1/2} > 10$], and terms for $n \geq 4$ do not appear in the pyroelectric response (though they appear in the $x=0$ resistance signal), it is concluded that the B_n for $n \geq 4$ are negligible compared to the four leading coefficients. The values of a_2B_2 and a_3B_3 are then corrected to the values 2.675 and 0.775, respectively.

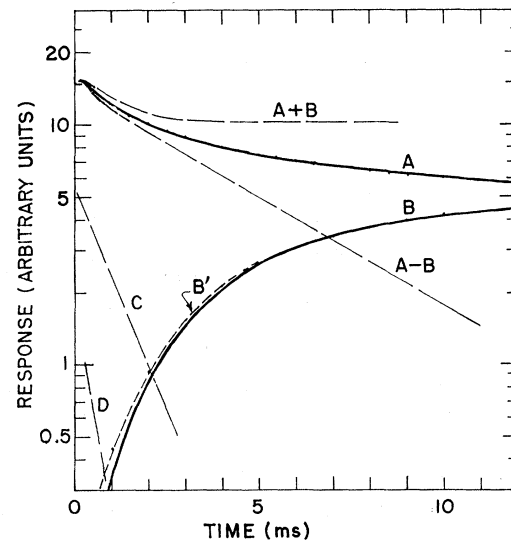


FIG. 2. Graphical analysis of response of Fig. 1(b). A and B, experimental data; $A+B$ and $A-B$ are even and odd response (see text). The relaxation time $\tau_1 = 4.18$ ms; coefficients $a_0B_0 = 5.1$, $a_1B_1 = 7$, $a_2B_2 = 2.675$, $a_3B_3 = 0.775$, and $a_nB_n = 0$ for $n \geq 4$ are determined as explained in text. B' is a plot of Eq. (13) with a_n replaced by $(-1)^n a_n$ using these a_nB_n . C and D represent the $n=2$ and $n=3$ terms, respectively.

tively, by forcing coefficients a_0B_0 , $-a_1B_1$, a_2B_2 , and $-a_3B_3$ when inserted into (13) to yield a curve B' in Fig. 2 within experimental uncertainty of measured curve B . The polarization distribution obtained from the determined coefficients, assuming $a_1 = a_2 = a_3 = 2a_0$, is the distribution b in the inset of Fig. 1.

The samples discussed in this Letter were chosen to illustrate the theory. Other copolymer samples and homopolymer (polyvinylidene fluoride) samples under different poling conditions can exhibit nearly uniform polarization.⁹ In such cases, the response is nearly steplike and $B_n/B_0 = 0$ for all n .

The present work indicates the source of ambiguity in the Collins's deconvolution procedure. The thermal pulse data (under conditions similar to those in Collins's experiments) yield no more than ten or fifteen coefficients [based on $N = (\tau_1/t_r)^{1/2}$]. Collins's electrical analog sought to obtain discrete distributions characterized by twenty adjustable parameters. Any discrete distribution (of which there are many) consistent with the determinable Fourier coefficients would

reproduce the measured transients within the noise in the data.

Partial support of this work by the U. S. Office of Naval Research is gratefully acknowledged.

¹G. M. Sessler, J. E. West, D. A. Berkley, and G. Morgenstern, *Phys. Rev. Lett.* **38**, 368 (1977).

²P. Laurenceau, G. Dreyfus, and J. Lewiner, *Phys. Rev. Lett.* **38**, 46 (1977).

³R. E. Collins, *Appl. Phys. Lett.* **26**, 675 (1975).

⁴R. E. Collins, *Rev. Sci. Instrum.* **48**, 83 (1977).

⁵R. E. Collins, *J. Appl. Phys.* **47**, 4804 (1976).

⁶See, for instance, R. V. Churchill, *Fourier Series and Boundary Value Problems* (McGraw Hill, New York, 1941), p. 109.

⁷W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbott, *J. Appl. Phys.* **32**, 1679 (1961).

⁸A. D. Southgate, *Appl. Phys. Lett.* **28**, 250 (1976).

⁹M. G. Broadhurst, G. T. Davis, S. C. Roth, and R. E. Collins, in *Proceedings of the 45th Annual Conference on Electrical Insulation and Dielectric Phenomena*, Buck Hill Falls, Pennsylvania, October 1976 (to be published).

Scaling Theory of the Asymmetric Anderson Model

F. D. M. Haldane^(a)

Bell Laboratories, Murray Hill, New Jersey 07974, and Physics Department, Princeton University, Princeton, New Jersey 08540

(Received 9 September 1977; revised manuscript received 30 November 1977)

A scaling theory is used to show that for temperatures $T \ll U$, the properties of the asymmetric Anderson model ($U \gg |E_d|, \Delta$) are universal functions of the scaling invariants Δ and $E_d^* = E_d + (\Delta/\pi) \ln(W_0/\Delta)$, where W_0 is the conduction electron bandwidth or U , whichever is smaller. Crossovers between various regimes of simple behavior as the temperature changes are described. $|E_d^*| \lesssim \Delta$ is identified as the criterion for a "mixed-valence" ground state, where the susceptibility $\approx \Delta^{-1}$. For $-E_d^* \gg \Delta$, there is a local-moment regime with a Kondo temperature $T_K \approx \Delta \exp(\pi E_d^*/2\Delta)$.

There has been recent interest in the asymmetric Anderson model¹ ($U \gg |E_d|, \Delta$) in connection with the theory of "mixed-valence" rare-earth materials.²⁻⁴ The numerical renormalization-group technique pioneered by Wilson⁵ allows the thermodynamic properties to be calculated,³ but the parameter space is large. Analytic results can clarify the dependence of physical properties on the model parameters, and provide a framework for the numerical exploration of the "crossovers" between limits describable by a simple effective Hamiltonian. This Letter reports a *scaling property* of the asymmetric Anderson

model; that is, universality of model properties as functions of the scaling invariants Δ and $E_d^* = E_d + (\Delta/\pi) \ln(W_0/\Delta)$, where $W_0 \approx U$ or the conduction electron bandwidth, whichever is smaller. The scaling equations also allow a simple description of the temperature dependence of physical properties.

The (nondegenerate) Anderson model is characterized by the parameters E_d , U , and $\Delta(\omega)$, and is

$$H = H^0 + E_d \sum_{\sigma} n_{d\sigma} + U n_d \dagger n_d \dagger + \sum_{k\sigma} V_{kd} c_{k\sigma} \dagger c_{d\sigma} + \text{H.c.},$$

$$H^0 = \sum_{k\sigma} \epsilon_k n_{k\sigma}; \quad \Delta(\omega) = \sum_k |V_{kd}|^2 \delta(\omega - \epsilon_k). \quad (1)$$