

# Comment on “Spontaneous Polarization of Cryo-Deposited Films for Five Normal Saturated Monohydroxy Alcohols, $C_nH_{2n+1}OH$ , $n = 1-5$ ”

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The authors of this Comment and others have been working for more than 10 years on the nature of solid films of dipolar molecules. These films can show spontaneous polarization following formation through gas-phase deposition. Much of the work on this so-called “spontelectric effect”<sup>1,2</sup> is underpinned by a mean-field model, outlined in ref 2. Because this model is a common thread running through the subject, we felt that it was necessary to clarify statements about the model in Piliđi et al.<sup>3</sup> The degree of dipole orientation is defined as the average component of the molecular dipole in the  $z$  direction perpendicular to the film surface,  $\langle \mu_z \rangle$ , divided by the total molecular dipole,  $\mu$ , for the species in the solid state, where this ratio  $\langle \mu_z \rangle / \mu$  is termed “ $g$ ” in ref 3. To quote ref 3, “...we are led to the conclusion that in the proposed model,  $g$  has no extremum for any nonzero parameter value. Consequently, it cannot describe data that exhibit a maximum or minimum”, referring to values of  $g$  versus the temperature of film deposition,  $T$ . The authors go on to conclude that the “Aarhus model” (the model developed by the authors of this Comment) is fundamentally flawed because maximum or a minimum numerical values of  $g$  versus  $T$  are observed in the data.

There are two substantive issues in the description of the model in ref 3: (i) the linearization of the Langevin function such that  $\coth x - x^{-1}$  is set equal to  $x/3$  and (ii) the lack of discrimination between an extreme value<sup>4</sup> and a maximum or a minimum numerical value of  $g$ . An extreme value is a maximum or minimum value found through setting the differentials of a function to be equal to zero, in the familiar manner, saddle points apart. We show below that maximum or minimum numerical values may be encountered in the absence of differentials being zero. They are, in fact, characterized by differentials becoming singular.

(i) Linearization: In the spontelectric model,<sup>3</sup> the “Aarhus model”,  $g = \coth x - x^{-1}$ , the Langevin function,<sup>5</sup> where  $x = E_z \mu / T$  and  $E_z = E_S [1 + \xi g^2] - E_a g$ ,<sup>2,6</sup> where  $E_S$ ,  $E_a$ , and  $\xi$  are  $T$ -independent parameters.  $E_S \xi$  relates to the strength of dipole–dipole coupling in the solid, and  $E_a g$  gives the value of the spontelectric field. Thus, using atomic units, we write

$$F(T, g) = \coth\{[\mu E_S(1 + \xi g^2) - E_a g]/T\} - \{[\mu E_S(1 + \xi g^2) - E_a g]/T\}^{-1} - g = 0 \quad (1)$$

Piliđi et al., p 8509,<sup>3</sup> linearize eq 1, appealing to a small  $x$ . In so doing, they implicitly lose the nonlinearity of the physics and thus a key feature of the spontelectric state. They then go on to claim, incorrectly, as we have mentioned above, that it is essential that  $dg/dT = 0$  to reproduce the maximum or minimum values in the experimental data of  $g$  versus  $T$ , and they move to show that this condition would entail  $4\mu^2 E_S^2 \xi = 0$ , with its attendant unphysical ramifications. We note that the expression for  $g$  given in ref 3 causes  $dg/dT$  to become imaginary for  $T \leq 56.8$  K for *cis*-methyl formate and  $\leq 40.2$  K for 1-pentanol, using the values of  $E_S$ ,  $E_a$ , and  $\xi$  given below.

(ii) The observed maximum or minimum numerical values in the data of  $g$  versus  $T$  result from the singular behavior of the differential  $dg/dT$ ,<sup>2</sup> whereas  $dg/dT = 0$ , in (i) above, is the condition for an extreme value, as defined above. Note also that the existence of eq 1 does not imply that  $g = f(T)$  exists.<sup>4</sup> Equation 1 is of the form  $g = f(T, g)$ . This is a continuous function with a discontinuity in the derivative. Such behavior is very well known in mathematics but is not so familiar in physics, in which, to the best of the authors’ knowledge, this form of discontinuity has not been shown to reproduce observable physical phenomena, save in the present case of spontelectrics. This is therefore the first such example for a real physical system, in which it is essential to invoke this mathematical property to reproduce experimental data.

In the absence of approximation, eq 1 cannot be solved algebraically for  $g$ . It may, however, be rigorously shown that  $dg/dT$  cannot be zero for any real or nonzero values of parameters. We obtain the total differential  $dg/dT$  through the implicit function theorem.<sup>4</sup> This may be expressed as  $dg/dT = -F_T/F_g$ , where  $F_T = \partial F(T, g)/\partial T$  and  $F_g = \partial F(T, g)/\partial g$ . For *cis*-methyl formate,  $E_S = 1.304 \pm 0.048 \times 10^7$  V m<sup>-1</sup>,  $\mu = 0.354$  D,  $E_a = 1.149 \pm 0.044 \times 10^9$  V m<sup>-1</sup>, and  $\xi = 14\,500 \pm 990$ , obtained by fitting to experimental data for  $g$  versus  $T$ . Note that the dipole moment,  $\mu$ , has been reduced from the gas-

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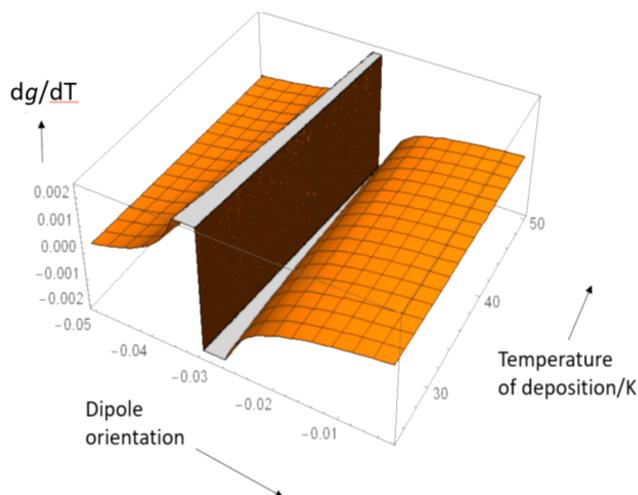
phase value to take account the depolarization in the solid-state environment,<sup>2</sup> the mention of which is omitted in ref 3. Measured values of  $g$  are, for example, 0.0089 at 60 K, 0.0025 at 75 K, and 0.0184 at 85 K, passing through a minimum numerical value at 75 K. Inserting these values of  $g$ ,  $\coth x - x^{-1}$  returns values of 0.0085, 0.0043, and 0.0187, replicating the feature that  $g$  passes through a minimum numerical value at  $\sim 75$  K.<sup>2,7</sup> We have used the same model to fit data for 1-pentanol, yielding  $E_s = 4.84 \times 10^7$  V m<sup>-1</sup>,  $E_a = -4.00 \times 10^9$  V m<sup>-1</sup>, and  $\xi = 1080$ , with  $\mu = 0.61$  D, using data kindly supplied by Pilidi et al. The dipole in the solid state has been reduced from the gas-phase value of 1.65 D using imperfectly known values of the lattice spacing and the polarizability of 1-pentanol.<sup>3,8</sup> The experiment shows a maximum  $|g|$  at 40 K of 0.030, and the model gives 38.6 K and  $|g| = 0.031$ . Values for available temperatures are shown in Table 1.

**Table 1. 1-Pentanol**

$T_d$ (K) <sup>a</sup>	observed values of $\langle \mu_z \rangle / \mu^b$	calculated values of $\langle \mu_z \rangle / \mu^c$
32	-0.0250	-0.0278
36	-0.0292	-0.0313
40	-0.0300	-0.0291
44	-0.0293	-0.0257
48	-0.0291	-0.0234

<sup>a</sup>Temperature of deposition. <sup>b</sup>Observed values of degree of orientation. <sup>c</sup>Calculated values, using parameters given in the text and obtained through inserting the observed value of  $g$  on the right hand side of eq 1 and checking for self-consistency.

Temperatures of 75 and 38.6 K for *cis*-methyl formate and 1-pentanol, respectively, are derived by solving for  $F_g = 0$ . Thus, as maintained above, minimum or maximum values of  $g$  are marked by singularities in  $dg/dT$ . This is shown in Figure 1 for 1-pentanol. Similar figures may be presented for *cis*-methyl formate<sup>2</sup> and solid ammonia films. The singularity is associated



**Figure 1.** Solid films of 1-pentanol. The variation of the gradient  $dg/dT$ , evaluated from the ratio  $F_T(T, g)/F_g(T, g)$ , as a function of the temperature,  $T$ , and the degree of dipole orientation,  $g$ , for values of  $E_s$ ,  $E_a$ , and  $\xi$  given in the text. Strictly every point on the surface shown should satisfy eq 1. This condition is only accurately fulfilled for the values of  $T$  and  $g$  given in Table 1. Errors arising for other pairs of values of  $T$  and  $g$  are, however, negligibly small on the scale of this figure.

with a change in sign of  $dg/dT$ , leading to the observed maximum in the numerical value of  $|g|$ . Note that the agreement with experiment described here is altogether lacking in the linearized form of eq 1.<sup>7</sup>

We mention that the “Aarhus” model described in ref 2 has proved remarkably successful in reproducing the deposition temperature dependence of spontaneous electric fields. This covers a variety of contexts involving surface potential measurements using electron beams,<sup>2</sup> Kelvin probes,<sup>3,9</sup> and vibrational and electronic Stark effects,<sup>10–12</sup> to name but a few references.

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### Notes

The authors declare no competing financial interest.

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- Note the error in ref 3. Their subsequent analysis is nevertheless correct.
- For example, use of the linearized expression for  $g$  in ref 3 yields  $g = 0.0064$ , 0.0044, and 0.0038 at 60, 75, and 85 K, respectively, for *cis*-methyl formate.
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