Reply to "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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Our research group has been working on vapor-deposited films that are found to be electrically polarized for several years.[1,2] One of the interesting features seen is the variation in the measured film voltage as a function of the deposition temperature. The simplest form is a reduction of the voltage absolute value with increasing temperature, yet several compounds show nonmonotonic variations, with preservation of the voltage sign, whereas in more complicated cases, a voltage sign change is observed with deposition temperature. One of the very few groups around the world working on similar experiments is at Aarhus University in Denmark. In their publications,[3,4] they have proposed a model to explain the variations in film voltages with temperature. The model is based on concepts of condensed-phase electrostatics and is summarized in a set of two equations

$$g = \coth\left(\frac{E_z\mu}{T}\right) - \left(\frac{E_z\mu}{T}\right)^{-1} \tag{1}$$

and

$$E_z = E_s[1 + \xi g^2] - E_a g \tag{2}$$

g is the film voltage scaled to the surface number density of the deposited molecules and expresses the fraction of molecules with their dipole moment vector aligned perpendicularly to the plane of the substrate; T is the film temperature; E_z is the total electric field intensity in the film; and E_s, E_a, ξ, and μ are model parameters. Because of the complexity of the coupled equations, it is not possible to write an analytical expression for g as a function of T.

The claim[4] that this model can describe the variations in g with T encouraged us to try the model on our data. We did not succeed, and in the process, we realized that there were problems with the form of the model and with its use in deriving the parameters. In our recent publication,[2] we made a comment in passing with a brief explanation of the shortcomings of the model. Private communication has not convinced either side of the other's point of view, and we need to explain all details in a public forum.

We argued[2] that the set of eqs 1 and 2 can yield g as a function of T if a certain condition is met that allows simplification.

Furthermore, we found that this function is monotonic, and hence it could not have a minimum or maximum.

If we substitute

$$x = \frac{E_z\mu}{T} \tag{3}$$

then eq 1 becomes

$$g = \coth x - x^{-1} \tag{4}$$

The approximation

$$\coth x - x^{-1} = \frac{x}{3} - \frac{x^3}{45} + \ldots \approx \frac{x}{3} \tag{5}$$

brought to our attention by the authors in a 2017 paper,[5] simplifies eq 4. I will prove the validity of the approximation shortly. Equation 4 becomes

$$g \approx \frac{x}{3} = \frac{E_z\mu}{3T} \Rightarrow E_z = \frac{3Tg}{\mu} \tag{6}$$

By equating the right-hand sides of eqs 2 and 6, we get

$$\frac{3Tg}{\mu} = E_s(1 + \xi g^2) - E_a g \tag{7}$$

or

$$(E_s\xi\mu)g^2 - (E_a\mu + 3T)g + E_s\mu = 0 \tag{8}$$

Hence

$$g = \frac{E_a\mu + 3T \pm [(E_a\mu + 3T)^2 - 4E_s^2\mu^2\xi]^{1/2}}{2E_s\xi\mu} \tag{9}$$

It is clear that there may be two values of g for some T. In mathematics, that is equivalent to saying that a function for g

depending on T does not exist because it is not single-valued. It is possible to make a plot of the relation between g and T by expressing T as a function of g. From eq 7, we get

$$T = \frac{\mu}{3g}[E_s(1 + \xi g^2) - E_a g] \qquad (10)$$

Figure 1 shows the relationship between T and g based on the parameter values selected by the authors.[4] (See Table 1.) The
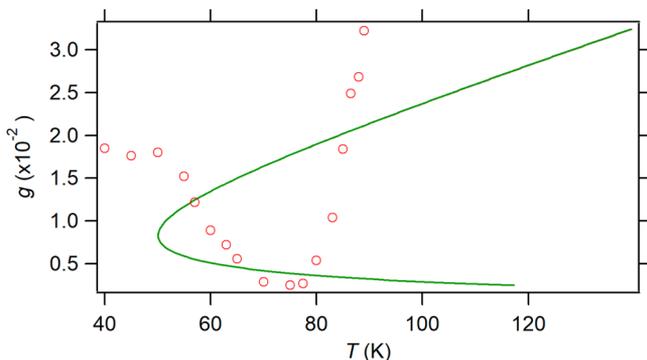

Figure 1. Comparison between experimental (open circles) and calculated (solid lines) values for methyl formate data. The green line is based on eq 10 derived after using the approximation of eq 3, whereas the red line is based on an iterative numerical calculation using the exact expressions of eqs 1 and 2.

Table 1. Parameter Values Proposed in Ref 6

parameter	methyl formate	1-pentanol
E_a	1.2064×10^7	1.2064×10^7
E_s	1.148×10^9	-4×10^9
ξ	14 500	1080
μ	0.354	0.61

original experimental data, on which the determination of the parameters was based, are also included in Figure 1. A third line drawn represents the numerical solution of eqs 1 and 2 without relying on the approximation of eq 5. It is not visible because it lies exactly under the curve calculated via eq 10, which is based on the approximation of eq 5.

The authors of the Comment[6] implemented their fitting procedure on our 1-pentanol data and concluded that the best parameter values for this set of data are as shown in Table 1. Figure 2 has been drawn in the same way as Figure 1 using these parameter values. This time, the approximation of eq 5 is not as good as that in the case of methyl formate because the red line appears under the green one, but the approximation is clearly adequate.

Both examples show that the approximation given by eq 5 is valid for the parameter values proposed. It is also seen that the proposed model does not describe the experimental data.

The contrast between simulated lines and the experimental data raises concerns about the correctness of the fitting procedure. Similar concerns had been expressed in our 2019 paper,[2] but we had refrained from making such direct comparisons. One might be able to trace the problems with the fitting procedure in the proof given in the Comment regarding the existence of a minimum in g as given by eq 1. The quantity E_z, given by eq 2 and needed in eq 1, requires the value of g. It is stated[6] that in this calculation, the experimental values
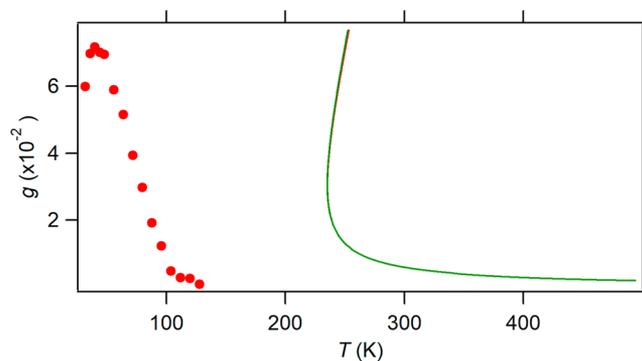

Figure 2. Absolute value of the degree of polarization for 1-pentanol films (solid circles) and the simulation based on the parameter values found in ref 6. (Solid lines are as described in Figure 1.)

of g and T were used. It comes as no surprise that the "calculated" g value varies with the experimental one because it depends on it and appears to go through a minimum.

In short, the concerns raised in the second paragraph of the Comment are unfounded. Point (i) is disproven graphically because the red and green lines coincide in Figures 1 and 2. Point (ii), besides trying to make a distinction between mathematical predictions and numerical calculations, is shown in both figures to be inaccurate because no maximum or minimum can be seen in the simulated curves.

Finally, I would like to point out that figure 1 in ref 6 indicates something rather unexpected. The derivative of g with respect to T is depicted as a function of both g and T, when it is clear from the data that g and T depend on one another. One may use a 3D picture to display dg/dT, but it will be a line in space not a surface. The shape of the green lines in Figures 1 and 2 shows that not all temperature values are available for T. Indeed, for $T < T_{lim}$, where T_{lim} is ~50.1 K for methyl formate and ~235.3 K for 1-pentanol, no value can be calculated for g based on the "Aarhus" model.

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Notes
The author declares no competing financial interest.

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