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ABSTRACT

Films of dipolar molecules formed by physical vapor deposition are, in general, spontaneously polarized, with implications ranging from electron transfer in molecular optoelectronic devices to the properties of astrochemical ices in the interstellar medium. Polarization arises from dipole orientation, which should intuitively decrease with increasing deposition temperature, T . However, it is experimentally found that minimum or maximum values in polarization vs T may be observed for *cis*-methyl formate, 1-propanol, and ammonia. A continuous analytic form of polarization vs T is developed, which has the property that it is not differentiable at all T . The minima and maxima in polarization vs T are marked by singularities in the differential of this analytic form. This exotic behavior is presently unique to films of dipolar species and has not been reported, for example, in the related magnetic phases of spin glasses.

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INTRODUCTION

The presence of both short range interactions and an effectively infinite range mean field is well known to lead to complex behaviors in ordered or disordered solids. Examples include proton disorder in hexagonal water ice,^{1–3} quantum superfluids,⁴ and magnetic phases in spin glasses.⁵ The cooperative effect of interactions on the sub-nanometer scale and a permeating mean field can result in emergent properties, including non-ergodic phases of matter, spontaneous order, and unusual aging behaviors.^{4,6,7} Understanding non-ergodic behavior is a fundamental aim of statistical mechanics, and many mathematical models of such physical and theoretical systems have been presented to understand the interplay between long-range and short-range forces. The most well-known case is the one encountered in the much studied magnetic spin glasses.⁵

In the present work, we consider an electrostatic system of molecular dipoles embedded in a solid through which a static electric field permeates. The significant difference between the materials studied here and other such solids is that the static electric field is self-generated by the spontaneous orientation of molecular dipoles upon growth of the solid. These spontaneously electric—or spontelectric—materials have been extensively studied experimentally in our own group, and recently, others have reported experimental results showing similar phenomena. These materials,

prepared as thin films, are non-ergodic systems exhibiting spontaneous polarization. A mean-field model has been constructed to understand the temperature dependence of the strength of the spontaneously generated electric field and the ensuing reliance on the degree of dipole orientation. The Hamiltonian for this spontelectric model bears formal similarity to that of spin glasses.

Intuitively, one would assume that as the growth temperature increases, the degree of dipole orientation and so the strength of the spontaneously generated electric field should decrease. However, this is not always the case and several published reports demonstrate experimental systems where the degree of dipole orientation increases with increasing temperature; that is, spontelectrics may show the property that polarization vs temperature passes through a minimum or maximum with temperature.

With this report, we aim to show analytically that the experimentally observed maximum or minimum values of polarization with temperature are recreated by the Hamiltonian describing the spontelectric mean-field model. Furthermore, this is achieved in a novel manner that the model function describing polarization vs temperature of deposition is continuous but yet cannot be differentiated at every temperature, with the differential of the function passing through a singularity at a specific temperature. We find here that the temperature associated with the maximum or minimum

polarization is the one that gives rise to the singularity in the differential of the model function. Thus, the observed counter-intuitive behavior is associated with this singular behavior. This description, where the total differential of a continuous function cannot be regarded as its slope, is well-known to pure mathematicians⁸ but has not previously been encountered in a physical system.

THE MODEL BASED ON MEAN-FIELD THEORY

The spontelectric effect emerges in thin films formed by the condensation of dipolar molecules from the gas phase, on a sufficiently low temperature surface. The effect results from the collective dipole orientation throughout the film of the material, with the average dipole poised at a non-zero angle with the plane of the film.^{9–13} Components, in the x - y plane of the film, average to zero. Our focus here is on the functional relationship between the degree of polarization of these films and their temperature of deposition, T . We use a mean-field model to describe the interactions experienced by the average molecular dipole, embedded in a matrix of interacting dipoles. In the standard manner, the mean-field theory approach¹⁴ transforms a many-body problem into a one-body problem. Thus, inherently, any inhomogeneity and any fluctuations in the system are ignored since we only consider an average molecular dipole. Molecules are treated as dipoles, and we ignore much weaker multipole effects, which are effectively lumped into the model parameters described below.

In a spontelectric solid, molecular dipoles are subject to an effectively infinite range mean field, E_z , whose value may be expressed through three terms: first, a term defining the interactions that bind layers together, associated with polarization, dispersion, and covalent interactions; second, a term explicitly involving the dipole–dipole interaction, proportional to the square of the degree of dipole orientation;² and third, a term representing the spontelectric field itself and proportional to the degree of dipole orientation. Thus, the mean-field Hamiltonian for the system, \mathcal{E} , is given by the energy of interaction of the dipole in this infinite range field, E_z .

Thermal agitation affects the degree of polarization, represented, through the Langevin function, by $\text{Coth}(\mathcal{E}/T) - (\mathcal{E}/T)^{-1}$, using atomic units.¹⁵ Note that the field with which the average dipole interacts is itself a function of the degree of polarization, as we describe below. We find that the differential of the continuous function, $\text{Coth}(\mathcal{E}/T) - (\mathcal{E}/T)^{-1}$, may not describe its slope and minimum and maximum values are no longer marked by setting differentials to zero.

The mean field Hamiltonian for the system, \mathcal{E} , is given by the energy of interaction of the dipole, μ , in the mean effective field, E_z , expressed as

$$\mathcal{E} = \mu E_z = \mu \left[E_s \left[1 + \zeta \left(\frac{\langle \mu_z \rangle}{\mu} \right)^2 \right] - E_A \frac{\langle \mu_z \rangle}{\mu} \right], \quad (1)$$

where $\langle \mu_z \rangle / \mu$ marks the degree of orientation, defined as the average component of the dipole moment in the z -direction, normal to the plane of the film, divided by the total dipole moment of the species in the solid state [see the “supplementary material” S(i)]. The

temperature dependence of $\langle \mu_z \rangle / \mu$ is given by the Langevin function; see above.¹⁵ E_s , ζ , and E_A are three parameters to be determined by fitting to experimental data, where μE_s defines the symmetric interactions that bind dipoles together, associated with polarization, dispersion, and covalent interactions; $\mu E_s [\zeta (\langle \mu_z \rangle / \mu)^2]$ describes the dipole–dipole interactions, proportional to $(\langle \mu_z \rangle / \mu)^2$; and the third term $E_A \langle \mu_z \rangle / \mu$ represents the spontelectric field, itself represented as proportional to the degree of orientation. Thus, E_A in conjunction with orientation defines the backward–forward asymmetric field created by the average dipole and experienced by the average dipole. The value of E_A can be constrained by appeal to theory [see the “supplementary material” S(i)]. The system finds a configuration corresponding to a balance between thermal agitation, and the short-range and long (or infinite) range terms in the mean-field Hamiltonian in Eq. (1). The governing equation, therefore, has the form $f(T, \langle \mu_z \rangle / \mu) = \langle \mu_z \rangle / \mu$, an implicit equation containing feedback, through which the behavior of orientation with deposition temperature, T , depends on the degree of orientation itself.

The mean-field Hamiltonian in Eq. (1) is essentially very similar to that governing spin glasses, for example in Ref. 16, with the latter involving magnetic dipoles. Energetically, a similar competition between short-range interactions and a longer-range mean field is present in both spontelectrics and spin glasses. A key difference, however, is the spontaneous development of the electric field in a spontelectric material, as represented by the third term in Eq. (1), and the feedback between this term and that represented by $\zeta (\langle \mu_z \rangle / \mu)^2$.

Earlier work, involving the films of *cis*-methyl formate (*cis*-MF) revealed the singular behavior of the differential of the Hamiltonian in Eq. (1),^{10,17} but, for some years, remained the only such case observed experimentally. An additional set of experimental data has been acquired for 1-pentanol in the work of Athens’ group,¹² which displays the phenomenon discussed here and also new results that point very clearly to the same phenomenon in thin films of ammonia (NH_3).¹⁸

Three different measurement techniques were used to collect the experimental data that have been reported elsewhere for *cis*-methyl formate, ammonia, and 1-pentanol. In each case, molecular films, tens of nanometers thick, were prepared by condensing the particular species on a cold finger at a given deposition temperature, by background gas deposition under ultra-high vacuum conditions. The degree of spontaneous polarization was determined for *cis*-methyl formate by measuring the polarization charge at the surface of the film, as a function of deposition temperature and film thickness, using an electron irradiation technique.¹⁷ A similar approach was used for 1-pentanol, but polarization charge was measured using a Kelvin probe.¹² For ammonia, the strength of the spontaneously generated electric fields was determined by measuring Stark shifts induced in the position of absorption peaks assigned to Wannier–Mott excitons, in vacuum ultraviolet absorption spectroscopy.¹⁸

RESULTS

The degree of orientation is dictated by the competition between intermolecular interactions and interactions of the

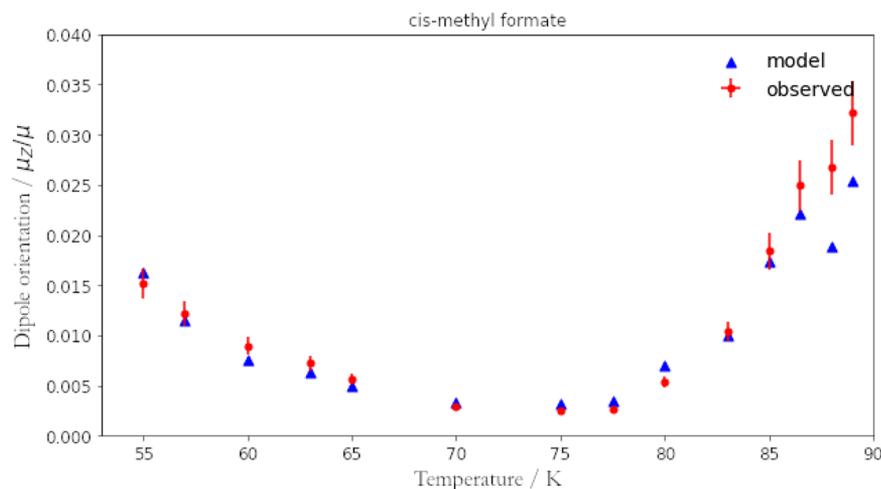


FIG. 1. Variation of the degree of dipole orientation, $\langle\mu_z\rangle/\mu$, as a function of deposition temperature for *cis*-methyl formate. Experimental data are shown as red points, derived from the direct measurement of film surface potentials.¹⁷ Fits to experiment, see the [supplementary material](#) Secs. S(iv) and S(v), are shown in blue. The values of fitting parameters are given in [Table I](#). Note that experimental values $\langle\mu_z\rangle/\mu$ are unstable for deposition temperatures ≥ 80 K, decaying by $\sim 50\%$ on a timescale of an hour, after an initial period of stability of ~ 2000 s.^{10,19} Where experimental error bars are not visible, they are smaller than the data point. Errors in temperature are ± 0.5 K.

molecular dipole with the self-generated spontelectric field, plus the disorder engendered through temperature. However, the experiment unexpectedly demonstrates that the degree of dipole orientation does not monotonically decrease with increasing deposition temperature. This is shown in [Fig. 1](#) for the case of *cis*-methyl formate, which shows a minimum value at 75–77.5 K. 1-pentanol also exhibits counter-intuitive properties, exhibiting a weak maximum in orientation in the 30–40 K deposition temperature range; see [Fig. 2](#).¹² Data for NH_3 are included in [Fig. 3](#), where the observed data do not show extrema but the model predicts extrema slightly above the desorption temperature for NH_3 . This is discussed in more detail below.

The polarization electric field, E_{spont} , the “spontelectric field,” equal to the macroscopic polarization divided by $\epsilon_0 = (4\pi)^{-1}$, arises from the voltage on the surface of the film. This voltage is generated by the dipoles protruding into free space at the film/vacuum interface. The voltage may be either positive, as in *cis*-MF, [Fig. 1](#), or negative, as in 1-pentanol, [Fig. 2](#), corresponding to the positive or

negative values of $\langle\mu_z\rangle/\mu$. For example, with reference to *cis*-MF, the δ -positive methyl group of methyl formate, $(\text{HC}=\text{O})-\text{O}-\text{CH}_3$, has a greater probability to extend from the surface into vacuum, compared with the δ -minus $(\text{HC}=\text{O})-\text{O}$ moiety. There is no free charge in the system, and therefore, E_{spont} is constant and is given by the surface voltage divided by the thickness of the film.¹⁰

The spontelectric model, outlined in Eq. (1), has proven successful in analyzing data for the variation of spontelectric fields with deposition temperature,²⁰ Stark shifts in reflection-absorption infrared spectroscopy (RAIRS),²¹ vacuum ultraviolet spectroscopy of films of NH_3 ¹⁸ and secondary relaxation in glassy *cis*-MF.²² RAIRS experiments have confirmed, through the vibrational Stark effect, the increase in dipole orientation in *cis*-MF for deposition temperatures ≥ 80 K, shown in [Fig. 1](#).²³ Here, we explicitly demonstrate that the singularity in the differential of Eq. (1) mirrors the counter-intuitive behavior of some spontelectric materials, namely those that demonstrate a maximum or minimum value of polarization at some temperature.

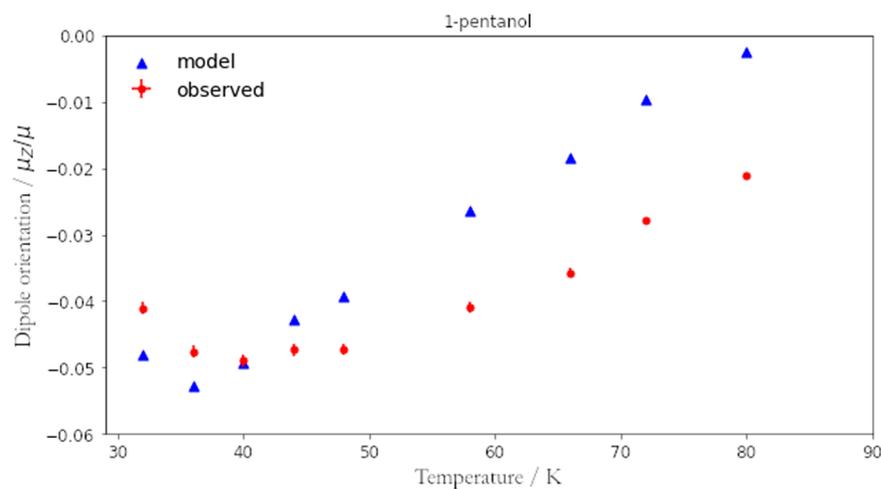


FIG. 2. Variation of the degree of dipole orientation, $\langle\mu_z\rangle/\mu$, as a function of deposition temperature for 1-pentanol. Experimental data are shown as red points, derived from the measurement of film surface potentials using a Kelvin probe.¹² Fits to experiment using the model outlined here, see the [supplementary material](#) Sec. S(iv), are shown in blue. The values of fitting parameters are given in [Table I](#).

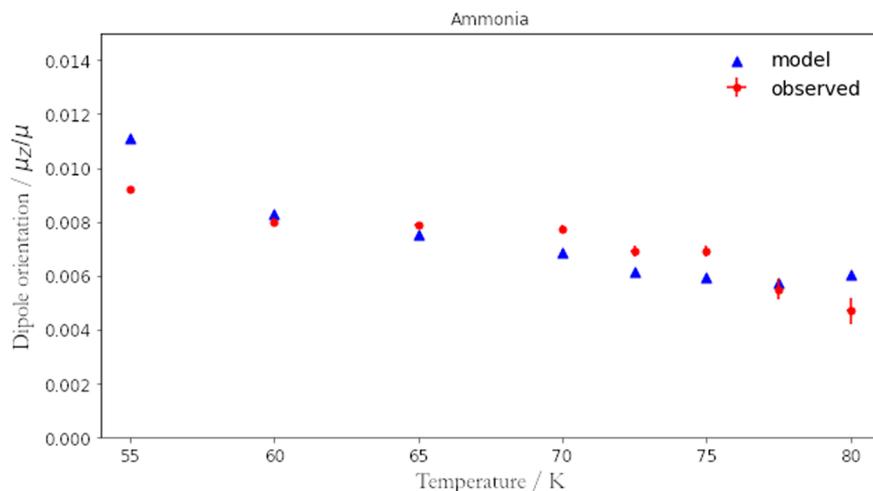


FIG. 3. Data for the degree of orientation, $\langle \mu_z \rangle / \mu$, in solid ammonia films, taken from experimental results in Ref. 18 (red points). The blue points show the fit obtained using the technique described in the [supplementary material](#) Sec. S(iv), yielding $E_S = 2.58 \times 10^7 \text{ V m}^{-1}$, $E_A = 5.49 \times 10^9 \text{ V m}^{-1}$, and $\zeta = 1.76 \times 10^4$ in [Table I](#), weighting the value at 55 K of orientation to 0.5 and all others to unity.

Analysis

An explicit expression for $f(T, \langle \mu_z \rangle / \mu)$ is obtained directly by substitution of E_z , from Eq. (1), into the Langevin function: see the [supplementary material](#) Sec. S(ii). We seek the differential of $f(T, \langle \mu_z \rangle / \mu)$ with respect to T , and this yields

$$\frac{d\left(\frac{\langle \mu_z \rangle}{\mu}\right)}{dT} = \frac{\left[-\frac{\mu E_z}{T^2} \operatorname{cosech}^2\left(\frac{\mu E_z}{T}\right) + (\mu E_z)^{-1}\right]}{\Phi} \quad (2)$$

and

$$\Phi = \frac{T \left[2\zeta \left(\frac{\langle \mu_z \rangle}{\mu}\right) E_S - E_A \right]}{\mu E_z^2} - \frac{\mu}{T} \left[2\zeta \left(\frac{\langle \mu_z \rangle}{\mu}\right) E_S - E_A \right] \operatorname{cosech}^2\left(\frac{\mu E_z}{T}\right) - 1. \quad (3)$$

We show in Sec. S(iii) of the [supplementary material](#) that the nominator in Eq. (2) cannot equal zero, for any combination of non-zero T and $\langle \mu_z \rangle / \mu$, or real values of parameters E_S , E_A , or ζ . Thus, we are faced with the property that [Fig. 1](#) shows that $\langle \mu_z \rangle / \mu$ vs T displays a minimum value, or equally a maximum absolute value in data for 1-pentanol, [Fig. 2](#), but that $d(\langle \mu_z \rangle / \mu) / dT$ cannot equal zero. The form of Eq. (2) is such that the differential tends to infinity as Φ tends to zero. Referring, for example, to *cis*-MF, to the low temperature side of the condition that Φ tends to zero, $d(\langle \mu_z \rangle / \mu) / dT$ is negative and, to the high temperature side, $d(\langle \mu_z \rangle / \mu) / dT$ is positive. This generates a minimum value in $\langle \mu_z \rangle / \mu$ vs T . The signs of $d(\langle \mu_z \rangle / \mu) / dT$ are reversed for 1-pentanol, which shows a maximum (negative) value of $\langle \mu_z \rangle / \mu$.

We obtain the values of parameters E_S , E_A , and ζ by fitting to experimental data vs deposition temperature for *cis*-MF,¹⁷ 1-pentanol,¹² ammonia,¹⁸ and, for comparison, nitrous oxide.²⁰ Details on the least squares fitting procedure are provided in the [supplementary material](#), Sec. S(iv), and we have produced an executable version of this paper to allow the reader to experiment with the fit, explained in the [supplementary material](#) Sec. S(v). For 1-pentanol, ammonia, and nitrous oxide, all three parameters are

treated as temperature independent, where we include for ammonia only the higher temperature phase formed at $T > 50 \text{ K}$, the phase of interest here.¹⁸ For *cis*-MF, ζ is allowed to vary with temperature, as discussed in the [supplementary material](#), Sec. S(vi).

We now seek to identify the temperature of deposition and associated degree of orientation that lead to singularities in $d(\langle \mu_z \rangle / \mu) / dT$, subject to $\Phi = 0$ and $f(T, \langle \mu_z \rangle / \mu) = \langle \mu_z \rangle / \mu$. Turning first to *cis*-MF, using a single set of values of parameters, E_S , E_A , and ζ , we reproduce the general experimental form of $\langle \mu_z \rangle / \mu$ vs T ([Fig. 1](#)) for the full range of deposition temperature between 55 and 89 K. This is shown in [Fig. S1](#) in the [supplementary material](#). Furthermore, if we restrict our determination of temperature independent values of E_S , E_A , and ζ to those based upon values of orientation measured below 75 K, that is, below the minimum value of $\langle \mu_z \rangle / \mu$, then the rapid rise in orientation at $T \geq 80 \text{ K}$ follows directly.¹⁰

We can create a more quantitative fit to data for *cis*-MF than that shown in the [supplementary material](#) [Fig. S1](#), by allowing ζ to vary with deposition temperature. This fit is shown in [Fig. 1](#). In support of the introduction of a temperature dependence of ζ , experimental data demonstrate the decay of dipole orientation with time in *cis*-MF.¹⁹ These show that the extent to which molecules are restricted in their angular motion, represented by the term involving $\zeta (\langle \mu_z \rangle / \mu)^2$ in Eq. (1), is deposition temperature dependent and that this dependence may be wholly represented by a temperature dependence of ζ ;²² see the [supplementary material](#), Sec. (vi).

We now turn to 1-pentanol,¹² between 32 and 48 K, the range for which maximum negative values of orientation were observed. The results, based on Kelvin probe measurements, may be expressed as electric fields. For example, the value of the spontelectric field, E_{spont} , is estimated to be $1.75 \times 10^8 \text{ V m}^{-1}$ for 1-pentanol at 40 K.²⁵ We use $E_A = 4\pi\mu/\Omega$, in atomic units, as derived in Ref. 10, rather than fitting, where μ is the solid state dipole and Ω is the molecular volume, itself related to the polarizability, α ;²⁶ see the [supplementary material](#) Sec. S(i). We find that $E_A = -5.61 \times 10^9 \text{ V m}^{-1}$ for 1-pentanol. Since $E_{\text{spont}} = E_A \langle \mu_z \rangle / \mu$, this allows the evaluation of $\langle \mu_z \rangle / \mu$ vs T for 1-pentanol shown in [Fig. 2](#).

The hypothesis is that the maximum negative value should occur at a point $(T, \langle \mu_z \rangle / \mu)$ such that $f(T, \langle \mu_z \rangle / \mu) = \langle \mu_z \rangle / \mu$ and $\Phi = 0$

TABLE I. Column 2: dipole moments, μ , of molecules in the solid. Columns 3, 4, and 5: values of parameters, in the Hamiltonian in Eq. (1), defining the mean field in solid films of *cis*-methyl formate (MF),²³ 1-pentanol,¹² and ammonia (NH₃),¹⁸ the latter for the higher temperature phase formed at $T > 50$ K. Parameters for nitrous oxide for $T \geq 48$ K are included for comparison.²⁴ Errors in the values of parameters leading to corresponding errors in the values of the degree of dipole orientation, $\langle \mu_z \rangle / \mu$, are ± 10 – 15% for *cis*-MF (see Fig. 1) and $\pm 5\%$ for NH₃. There are systematic errors associated with 1-pentanol, which cannot be readily assessed since these depend on quantities such as molecular spacing, which are not accurately known; see the [supplementary material](#) Sec. S(i). Errors shown for 1-pentanol are random errors associated with fitting.

Molecule	Dipole moment in solid, μ/D	$E_S/V \text{ m}^{-1}$	$E_A/V \text{ m}^{-1}$	ζ
<i>Cis</i> -methyl formate	0.354	$0.84 \pm 0.37 \times 10^7$	$1.23 \pm 0.27 \times 10^9$	See text and S(v)
1-pentanol	0.426	$4.65 \pm 0.42 \times 10^7$	$-2.75 \pm 1 \times 10^9$	275.7 ± 5.4
Ammonia (NH ₃)	0.577	$2.58 \pm 0.03 \times 10^7$	$5.49 \pm 0.06 \times 10^9$	$1.76 \pm 0.05 \times 10^4$
Nitrous oxide	0.0669	$48.54 \pm 0.22 \times 10^8$	$7.45 \pm 0.57 \times 10^8$	70.6 ± 3.1

are simultaneously satisfied. Holding E_S and ζ constant with temperature, we find that the presence of a maximum negative value, satisfying these constraints, is a direct consequence of our theoretical model. The least-squares best-fit variation of $\langle \mu_z \rangle / \mu$ vs T to observed values is shown in Fig. 2. We estimate $T = 36$ K for 1-pentanol for the maximum negative value, with an accompanying value $\langle \mu_z \rangle / \mu = -0.047$. The observed values are 40 K, with $\langle \mu_z \rangle / \mu = -0.046$, respectively.

The results for the films of NH₃ are shown in Fig. 3. Data have been measured only up to 80 K.¹⁸ We were unable to perform experiments at higher deposition temperatures since NH₃ does not “stick” at $T > 80$ K under our experimental conditions of base pressure of $< 10^{-9}$ mbar. Data for NH₃ are shown in red, and a fit to these values is in blue, using parameters in Table I. The results for NH₃ are similar in characteristics to those for *cis*-MF, in the range of temperature of deposition approaching that associated with the minimum value of $\langle \mu_z \rangle / \mu$ for *cis*-MF, from the low T side. However, for NH₃, access to values of high enough T , for which a minimum value of $\langle \mu_z \rangle / \mu$ might, in principle, be found, is not feasible. Thus, experimentally, T can never be such that $\Phi = 0$ [Eq. (3)] and $f(T, \langle \mu_z \rangle / \mu) = \langle \mu_z \rangle / \mu$ are simultaneously satisfied. We suggest, from the appearance of the data in Fig. 3, that 80 K is nevertheless close to the temperature for which the switch from negative to positive slope occurs in $d(\langle \mu_z \rangle / \mu) / dT$. The presence of a putative minimum value of $\langle \mu_z \rangle / \mu$, at sufficiently high T , may be inferred from the property of NH₃, shared with *cis*-MF and 1-pentanol that $E_S \ll E_A$ and ζ is large. A comparison of parameters for N₂O is shown in Table I, for which E_S and E_A are comparable in magnitude and no such minimum value in $\langle \mu_z \rangle / \mu$ vs T can be identified.^{10,24}

DISCUSSION

The feedback via dipole–dipole interactions in the Hamiltonian, specifically through the term $\mu E_S \zeta (\langle \mu_z \rangle / \mu)^2$, is an essential element in creating the non-monotonic behavior of $\langle \mu_z \rangle / \mu$ with increasing deposition temperature. Thus, the removal of feedback, writing $\zeta = 0$, entirely eliminates the non-monotonic behavior. The relative importance of terms in the Hamiltonian in Eq. (1) gives some insight into the analytic difference between *cis*-MF or 1-pentanol and spontelectric materials, such as nitrous oxide, which shows a monotonic decrease in $\langle \mu_z \rangle / \mu$ with increasing deposition

temperature. The ratio, r , of the third and first two terms, that is $\mu(E_A \langle \mu_z \rangle / \mu)$ and $\mu E_S [1 + \zeta (\langle \mu_z \rangle / \mu)^2]$, in the Hamiltonian, Eq. (1), is significantly greater in systems that display a minimum or maximum value in orientation vs deposition temperature. Thus, using the values in Table I, the value of r for *cis*-MF lies between 0.2 and 0.3 in the range $T = 55$ – 89 K and between 1.5 and 2.1 for 1-pentanol in the range $T = 32$ – 48 K. By comparison, for nitrous oxide, $r \sim 0.06$, in the range $T = 52$ – 60 K. This suggests that a stronger relative influence of the term associated with the spontelectric field, $\mu(E_A \langle \mu_z \rangle / \mu)$, introduces singularities into the differential of the governing function $f(T, \langle \mu_z \rangle / \mu)$, by causing Φ , Eq. (3), to pass through zero. For ammonia, in the range $T = 55$ – 80 K, $r \sim 0.7$ – 0.8 , lying between values for *cis*-MF and 1-pentanol.

It is also apparent that spontelectric materials are non-ergodic systems. Thus, the same film may be prepared through two different routes and yet have different properties. Hence, the measured properties of the film are not independent of the route by which it was formed, violating a fundamental tenet of a thermodynamic system. By way of example, a film of nitrous oxide formed by deposition at 40 K yields material with a spontelectric field of $1.09 \times 10^8 \text{ V m}^{-1}$. If you ostensibly prepare the same film by deposition at a higher temperature, say, 60 K, and cooling to 40 K, the spontelectric field is ~ 2.66 times lower. Thus, annealing and cooling do not achieve the same degree of polarization as achieved through direct growth. In this connection, the complex aging behavior of spontaneously polarized *cis*-methyl formate and alcohols shows that molecular dipoles are able to fluctuate and explore the potential energy landscape but only incompletely.^{12,19,22,27} The film may be trapped in a local minimum even in the absence of any glassy character. Thus, some degree of frustration may be preserved, similar to that encountered by magnetic moments in a spin glass.²⁸ The equivalent non-thermodynamic aspect of spin glasses, as evidenced by the distinction between zero-field-cooling and the thermoremanent magnetization, has most recently been studied in crystalline CuMn.²⁹ Our model of spontelectrics, however, implicitly assumes that films are governed by thermodynamics, since the Langevin expression is based on Boltzmann statistics. For the present, we assert that films formed by direct deposition at a specific temperature can be treated as thermodynamic systems, since the model provides a useful description of spontelectric properties in a wide variety of contexts.

The observation of spontaneous polarization in materials discussed here, methyl formate, 1-propanol, ammonia, and nitrous oxide, is not immediately of technological application. We note, however, that ices of ammonia have been observed on several bodies in our own solar system.^{30,31} Some of the implications for polarized carbon monoxide ices in the interstellar medium have been considered elsewhere and can have a profound influence on the efficiency of star formation.³² Spontaneous polarization has also been reported in thin glassy films of materials commonly used to produce optoelectrically active materials.³³ To our knowledge, the pathological behavior reported here in the temperature dependence of dipole orientation has not been reported for films used to produce optoelectronic devices. We note that models that account for dipole orientation in optoelectronic devices fail to take into account any role for the permeating static electric field and, therefore, ignore any of the feedback highlighted in the present work.^{34,35} Nonetheless, the properties described in these reports is similar to that reported for spontelectric materials.

An important advance has recently been made in understanding the mechanism for the spontaneous development of dipole order in films deposited from the gas phase.³⁶ Large-scale simulations of *cis*-methyl formate films showed that thermal fluctuations can lead the system down a non-ergodic branch into the spontelectric state. Strikingly, this molecular dynamics simulation reproduced the minimum value in net orientation in *cis*-MF vs T , giving a value of deposition temperature of ~ 70 K, close to that observed of 77.5 K. These calculations reinforced the earlier qualitative suggestion that librational fluctuations are an underlying feature in establishing the spontelectric state.³⁷

The physics of the model presented here is rather straightforward. It involves no more than very familiar electrostatics and statistical arguments, to yield general agreement with the experiment. The enhanced molecular mobility, that is, enhanced diffusion at higher T ,¹⁹ can be added as described elsewhere for *cis*-methyl formate,¹⁹ to achieve better agreement between the model and experiment. However, this is only a supplement and is inessential to the reversal of the slope of molecular orientation vs deposition temperature and the accompanying infinities in the differential of the governing function $f(T, (\mu_z)/\mu)$. For the present, we note only that nothing more is required than the mathematical structure of the model and its peculiar singular properties. The distinctive processes that act in the vicinity of the singularity in the differential remain intangible.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for appendixes describing (i) the derivation of dipole moments in the solid state, (ii) the derivation of Eq. (2), (iii) proof that the nominator in Eq. (2) cannot be zero, (iv) the least-squares procedure used to fit the model to the experimental data, (v) an executable version of this paper, and (vi) the temperature dependence of ζ .

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Andrew Cassidy: Conceptualization (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). **Frank P. Pijpers:** Conceptualization (equal); Formal analysis (equal); Methodology (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **David Field:** Conceptualization (equal); Formal analysis (equal); Methodology (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The authors have made an executable version of this paper with data and data analysis methods openly available in GitHub at <https://github.com/cassidy-andrew/Hidden-Singularities>. The data are archived on Zenodo with DOI: <https://doi.org/10.5281/zenodo.7785804>.

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