PCCP

PAPER

Spontaneous electric fields in films of *cis*-methyl formate

Oksana Plekan,[a] **Andrew Cassidy,**[a] **Richard Balog,**[a] **Nykola C. Jones**[b] **and David Field***[a]

A recent publication described a new group of spontaneously polarized materials in which electric fields in excess of 10^8 V m^{-1} may be present. This phenomenon arises through dipole alignment in solid films formed by straightforward deposition from vapour and characterises a novel class of materials. Here we present further results for the properties of these materials, focusing on films of *cis*-methyl formate. These films are shown to display some notable new chemical physics. We find the novel result that the degree of dipole alignment and the corresponding electric field in films of *cis*-methyl formate can have a counter-intuitive temperature dependence, *increasing* six-fold between 80 K and 89 K, in sharp contrast to the pronounced and expected fall with deposition temperature seen both here between 50 K and 75 K and in numerous other species. A theoretical model demonstrates that the switch of gradient with rising temperature should be a general phenomenon and is associated with crossing of a singularity in the gradient occurring at a set of critical values of temperature and alignment.

1 Introduction

Dipole alignment in solids presents major challenges both from the perspective of fundamental understanding of disordered solids and through the desire to create and manipulate systems with a view to nano-device fabrication. There exist numerous classes of both organic and inorganic ferroelectric materials, subjected to detailed study, which exhibit spontaneous polarization through aligned dipoles.[1] The structures of these widely ranging materials (*e.g.* ref. 2) are however determined by factors other than dipole–dipole interactions and all spontaneous polarization in solids, save in the present materials (which we have named 'spontelectrics'), is therefore extrinsic to the dipolar nature of the constituents of the material.

By contrast, spontelectric behaviour, as observed here in *cis*-methyl formate, is intrinsic to the dipolar nature of the constituent molecules. Dipole–dipole interactions play a central role and infinite range order is spontaneously generated through an interplay between dipole alignment, the electric field and the thermal motion associated with the temperature at which the solid is deposited, as well as inherent structural interactions.[3–5] The dependence of electric field, or the related degree of dipole alignment, on deposition temperature departs strongly from linear with powerful feedback mechanisms at play. In these, dipole alignment creates the electric field and the electric field creates dipole alignment, much as in any dielectric

the local field determines the molecular polarization and the local field is regulated by the polarization. Here, however, the field to which we refer is macroscopic, permeating the entire film and providing a constant presence throughout the film. Such intrinsically dipolar systems have long been sought through theoretical models,[6] culminating in some sophisticated but still inconclusive molecular dynamics simulations which suggested the existence of structures resembling that of the spontelectric state.[7] In addition aligned intrinsically dipolar structures have also been found in short chain oligomers of HCN in liquid helium droplets.[8]

Spontelectric materials have been found to form stable and metastable structures with properties governed to a very large degree by the bulk of the material rather than by the interfaces.[3] The feedback between electric field and dipole alignment in the bulk, which tends to create an ordered structure, is tempered by thermal disorder, determined by the temperature of film deposition. Since the degree of alignment is dictated by competition between order and disorder, for each higher deposition temperature a more disordered structure is expected and indeed can generally be inferred from experimental data. Here, however, we find the reverse behaviour at deposition temperatures greater than a critical value of 78 K–80 K, with significantly greater dipole alignment at temperatures above this critical temperature.

2 Experimental method and results

2.1 Method

The electric field within a film manifests itself by the presence of a voltage on the film surface. These are typically a few volts, depending on the temperature of deposition, the nature of the

a Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark. E-mail: dfield@phys.au.dk
b Department of Physics and Astronomy and Institute for Storage Ring Facilities (ISA), Aarhus University, DK-8000 Aarhus C, Denmark

molecule and in proportion to the film thickness, but have been measured as high as 38 volts.[3] A technique, described in more detail in ref. 3 and 4, has been developed which enables us to record these voltages to within 2–3 mV without perturbing the voltages. The method employs high resolution, low current density electron beams using a synchrotron photoionization source located on the ASTRID storage ring at Aarhus University where all experiments described here were performed.[9] The potentials on film surfaces are measured by interrogating the surface with electron beams of lowest energy of 2–3 meV and maximum current typically of 200 fA. Electron beams are generated in a cell at a nominal zero potential through photoionization of Ar within $\sim$5 meV of threshold (78.67 nm or 15.764 eV) at the $3p^5(^2P_{3/2})9d$ resonance (78.675 nm; $\sim$15.759 eV). This creates photoelectrons with an energy resolution corresponding to that of the photon beam of $\sim$1.5 meV. The photon beam waist is a few tens of microns and electrons are expelled from the region of photoionization in a 0.4 V cm^{-1} electric field without significant loss of energy resolution. The beam of electrons so formed is transported through a 4-element electrostatic lens and impinges on the film surface.

Since electrons are formed at nominally zero volts with an energy of $\sim$5 meV, the beam should therefore just be able to reach a target when the target is itself at this same nominal zero. Measurement of the bias required to locate the onset of a measurable current of 1 to 2 femtoamps therefore gives the potential on the surface of the film. A small correction[4] is necessary to establish a true difference between the clean gold substrate and the potential of formation of the electrons due to differing work functions of the gold substrate and the graphite walls of the photoionization chamber in which electrons are formed. We note that irradiation of the film surface, of area $\sim$0.28 cm^2, is not uniform. In the absence of measurable charging, as here under conditions of low current, this does not affect the accuracy of the technique of measurement of surface potential.

The target films are laid down on amorphous Au in an ultra-high vacuum system using standard surface science techniques. The substrate is cooled with a He cryo-cooler to temperatures in the range of 38 K upwards and cleaned by heating to 750 K. Standard dosing techniques from the background gas allow the deposition of uniform films of a known number of monolayers (ML) using temperature programmed desorption (TPD). The deposition rate is expressed as the number of monolayers deposited per second, typically 0.18 ML s^{-1}. The electric field is established from the linear slope of voltage vs. film thickness. Film uniformity is inferred from the fact that the films were laid down from background gas. Moreover, non-uniformity of films would cause increasingly broad onsets of the current vs. electron energy as increasingly thick films were laid down. This was not observed. Methyl formate is chemically stable on the amorphous gold surface at the temperatures employed. TPD data show no trace of any species other than the pure gas with which the surface was dosed.

2.2 Results

Results for methyl formate films for electric field, E_{obs}, and degree of dipole alignment, $\langle \mu_z \rangle/\mu$, defined below, are shown in Table 1 and in the two upper panels of Fig. 1 for films deposited

Table 1 Observed electric fields, expressed as mV per ML added, for layers of methyl formate deposited between 40 K and 89 K. A value of the layer spacing, s, of 0.244 nm was used in deriving the data for dipole alignment

Temperature/K	mV per ML	Degree of dipole alignment ($\langle \mu_z \rangle/\mu$)
40	5.78	0.0185
45	5.51	0.0176
50	5.65	0.0180
55	4.77	0.0152
57	3.82	0.0122
60	2.79	0.0089
63	2.26	0.0072
65	1.76	0.0056
70	0.923	0.0029
75	0.769	0.0025
77.5	0.834	0.0027
80	1.69	0.0054
83	3.26	0.0104
85	5.76	0.0184
86.5	7.81	0.0249
88	8.38	0.0268
89	10.1	0.0322

on polycrystalline gold at 17 different deposition temperatures between 40 K and 89 K. In order to create a homogeneous set of data, all films have been laid down under the same dosing conditions giving the same number of monolayers deposited per second from background gas. We have found that potentials on the surface of methyl formate films formed at $T > 77.5$ K tend to decay by typically a few per cent within ten minutes and can drop by a factor of two in four hours. Thus the higher temperature films are metastable on this time scale. In the present work we report only the initial electric field, on the minutes time scale, which is spontaneously created in films prepared at different deposition temperatures. In this connection it is known that between 90 K to 100 K methyl formate undergoes a phase change which has been attributed to crystallization.[10] We find that at 90 K and above, films are initially polarised but that the polarization decays too rapidly to establish an initial field from our experiments. This decay, though not explored here, is in itself interesting because it may allow one to follow the kinetics of this phase change in a critical temperature region.

Values of the degree of dipole alignment are estimated using $\langle \mu_z \rangle/\mu = \varepsilon_0 E_{obs}\Omega/\mu$, where $\langle \mu_z \rangle$ is the average component of the dipole in the z-direction, μ is the value of the full dipole of the molecule in the solid state and Ω is the effective volume of the molecule (0.103 nm^3). The value of μ is given[11,12] by $\mu = \mu_0/(1 + \alpha k/s^3)$ where α is the molecular polarizability of methyl formate (5.25 $\times$ 10^{-30} m^3), s is the spacing between successive layers (0.244 nm), $k = 11.034$ and μ_0 is the gas phase dipole moment of cis-methyl formate (0.6949 au, 1.766 D).

A mean-field model, originally introduced in ref. 3, is used here and is based on the concept that the net z-component of the electric field within the film, E_z, is composed of a local symmetrical part, defining the electrostatic interactions which bind layers to one another, and an asymmetrical part due to the infinite range field which permeates the film. The symmetrical part is expressed as a constant term plus a dipole–dipole term, proportional to $(\langle \mu_z \rangle/\mu)^2$. The form of the latter term reflects the fact that all dipole–dipole interactions, involving dipole-image charge, extended dipoles and arrays of dipoles, follow this squared relation.[13–15]
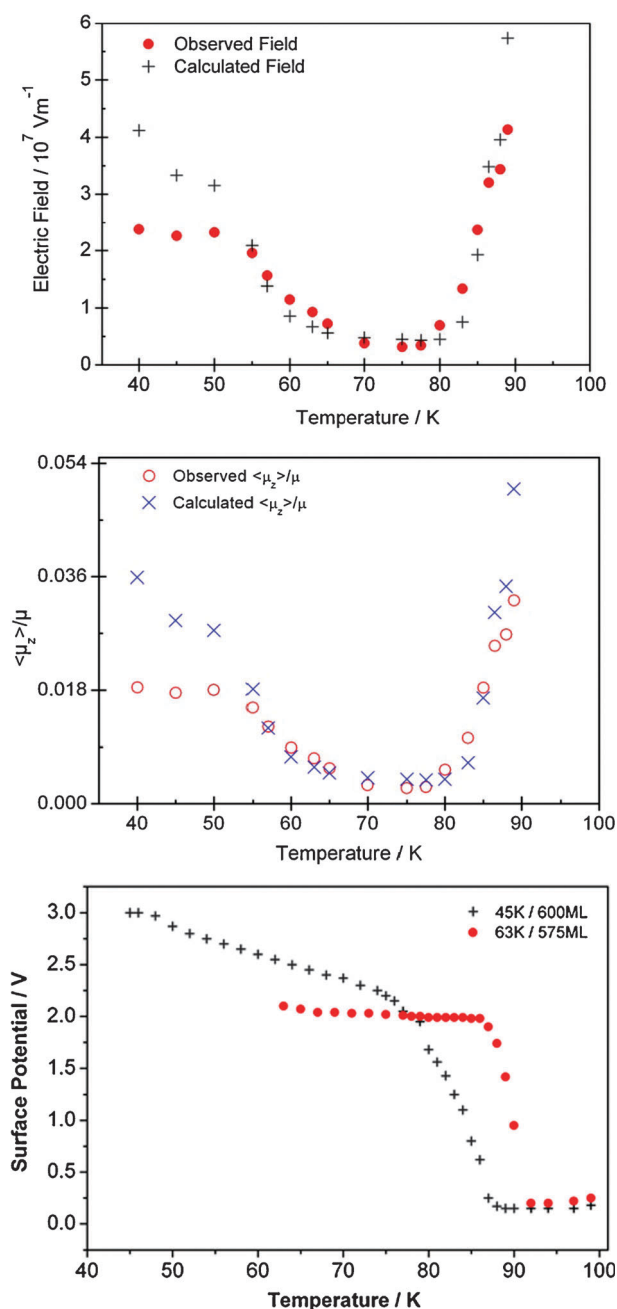
Fig. 1 Data for methyl formate. (Top) The variation of the observed electric field, E_{obs}, as a function of deposition temperature. (Middle) The variation of the degree of dipole alignment, $\langle\mu_z\rangle/\mu$, as a function of deposition temperature. Fits in the top panel are '+' symbols and in the middle panel are crosses. Fitting parameters are $\langle E_{sym}\rangle = 1.206 \times 10^7$ V m^{-1}, $\langle E_{asym}\rangle = 1.148 \times 10^9$ V m^{-1} and $\zeta = 1.45 \times 10^4$ (see eqn (1) and (2)). Systematic errors due to uncertainties in film thickness may yield errors of up to 30% in absolute values of electric fields. Random errors in electric fields vary from 1% at low temperature to 5% at the highest temperatures. (Bottom) Values of the surface potential as the temperature of films deposited at 45 K (crosses) and 63 K (filled points) is slowly raised, showing different Curie temperatures (see text). Errors in experimental values of voltages in Fig. 1c are 2–3 mV and of the temperature are ±1 K.

The $\zeta(\langle\mu_z\rangle/\mu)^2$ term in eqn (1) below essentially represents the tendency to hinder relative intermolecular rotational motion.

The symmetrical part of the contribution to E_z is related to the 'local field' at any molecular site as defined in standard texts.[16] The asymmetrical part, $\langle E_{asym}\rangle\langle\mu_z\rangle/\mu$, which has no direct counterpart in any previous description, save ref. 3, acts in opposition to the symmetrical part and represents the infinite range field created by the average dipoles and experienced by an average dipole. Hence, using atomic units throughout,

$$E_z = \langle E_{sym}\rangle\left[1 + \zeta\left(\frac{\langle\mu_z\rangle}{\mu}\right)^2\right] - \langle E_{asym}\rangle\frac{\langle\mu_z\rangle}{\mu} \qquad (1)$$

where $\langle E_{sym}\rangle$, $\langle E_{asym}\rangle$ and ζ are taken to be temperature independent parameters. Mean field theory gives an implicit expression for $\langle\mu_z\rangle/\mu$ yielding the familiar Langevin function for orientational interactions:[16]

$$\frac{\langle\mu_z\rangle}{\mu} = \coth\left(\frac{E_z\mu}{T}\right) - \left(\frac{E_z\mu}{T}\right)^{-1} \qquad (2)$$

In combination with eqn (1) this allows best fit values of $\langle\mu_z\rangle/\mu$ and the observed field, $E_{obs} = \langle E_{asym}\rangle\langle\mu_z\rangle/\mu$, to be obtained, using $\langle E_{sym}\rangle$, $\langle E_{asym}\rangle$ and ζ as fitting parameters. The non-linear dependence of E_z on $\langle\mu_z\rangle/\mu$ in eqn (1) and the feedback introduced through eqn (2), in which $\langle\mu_z\rangle/\mu$ is related through the Langevin function to E_z for a given temperature, illustrate the non-linearity of the system.

Fits to experiment, using values of parameters recorded in the caption, are shown in the upper two panels of Fig. 1 for the electric field and for $\langle\mu_z\rangle/\mu$ respectively. These fits reproduce with reasonable fidelity the variation of the electric field and dipole alignment with deposition temperature between 55 K and 89 K and, of particular interest, the rapid rise in field and alignment above 78 K–80 K. With regard to these fits, numerical tests demonstrate that in practice a problem of uniqueness does not arise. Further, given that the layer spacing, s, is poorly known, this was also adjusted to improve the fits, for which $s = 0.244$ nm. Data between 40 K and 50 K are not included in the fits. Films deposited at these temperatures show a Curie point at 82 K whereas films for higher temperatures show 90 K. This is illustrated in the lowest panel of Fig. 1. This indicates that films deposited at <50 K correspond to solid methyl formate of a different structure and thus different $\langle E_{sym}\rangle$, $\langle E_{asym}\rangle$ and ζ.

Note the fall of potential of ~ 1 V in Fig. 1 (bottom) over the duration of the experiment involving heating from 45 K to 80 K. This arises because films laid down at 45 K, and indeed for all deposition temperatures between 40 K and 50 K, show metastable behaviour on the time scale of hours. Films deposited between 55 K and 77.5 K are stable on the many hours time scale or more but observable metastability sets in once more at >77.5 K as mentioned above.

The parameters $\langle E_{sym}\rangle$, $\langle E_{asym}\rangle$ and ζ crudely define the potential energy landscape of the film. The agreement between observation and model with temperature independent values of $\langle E_{sym}\rangle$, $\langle E_{asym}\rangle$ and ζ implies that the potential energy landscape is largely unchanged for all deposition temperatures >50 K. Seemingly in contradiction, films have a different structure for each deposition temperature, represented by different values of $\langle\mu_z\rangle/\mu$. This contradiction may to some extent be resolved if we recognise that molecules can sample

more of the landscape at higher temperatures. This concept, exemplified by enhanced mobility of species condensing from the gas phase at and within the surface layers, has recently been developed in relation to glass formation through gas phase deposition.[17,18]

In the present case, more extensive sampling of the potential landscape will also modify feedback between bulk electric field and dipole orientation, itself modulated in a temperature dependent manner through the values of the three parameters. Following deposition, the system assumes some value of $\langle\mu_z\rangle/\mu$ and a corresponding structure characteristic of the substrate temperature. This structure in general represents a local rather than a global minimum (see below). The system can be dislodged from this configuration by heating above a characteristic Curie point: see bottom panel of Fig. 1.

The theory represented by eqn (1) and (2) remains a 'first order' description; as we have noted, different values of $\langle\mu_z\rangle/\mu$ represent different structures and imply different values of the symmetric part of the potential. This feedback has been ignored. Moreover the slow temporal decay of structures formed at 80 K and above suggests that systems initially enter metastable states in the energy landscape which then slowly percolate through a multiple minimum landscape towards ever more stable configurations, which may also involve crystallization.[10] This is analogous to the behaviour described in ref. 17, in which a figure of merit is introduced to gauge the extent to which a glass formed from gas phase deposition has relaxed towards the global minimum energy structure.

We focus now upon the change of slope from negative to positive at a critical temperature of 78 K–80 K and associated $\langle\mu_z\rangle/\mu \sim 0.003$. An obvious tactic is to obtain the total differential $d\langle\mu_z\rangle/\mu/dT$, but caution is necessary. Inserting eqn (1) into eqn (2) we obtain an implicit equation of the form $\langle\mu_z\rangle/\mu = f(\langle\mu_z\rangle/\mu,T)$. Implicit differentiation may be carried out using standard forms but these require that $\langle\mu_z\rangle/\mu = f(\langle\mu_z\rangle/\mu,T)$ is satisfied exactly. From a practical standpoint, high accuracy in the implicit equation is necessary in order to give quantitative results for the differential. The fit shown in Fig. 1 is found to be inadequate to yield quantitative agreement between experimental values of $d\langle\mu_z\rangle/\mu/dT$, obtained by interpolation from the data in Fig. 1, and those computed from the analytic form of the differential. Computed values of the gradient obtained by inserting derived values of $\langle E_{sym}\rangle$, $\langle E_{asym}\rangle$ and ζ into the differential function lie generally within a factor of 4 to 5 of observed values, but can be an order of magnitude in error. The switch from negative to positive slope appears at 83 K–85 K, rather than at the observed value of 78 K–80 K.

This quantitative breakdown may be ascribed to the 'first order' assumption, mentioned above, that $\langle E_{sym}\rangle$, $\langle E_{asym}\rangle$ and ζ are temperature independent and by implication $\langle\mu_z\rangle/\mu$ independent. Agreement between experimental and computed values of $d\langle\mu_z\rangle/\mu/dT$ can be greatly improved over a temperature range of a few degrees K by relaxing this assumption and adjusting $\langle E_{sym}\rangle$, $\langle E_{asym}\rangle$ and ζ locally over this range. We do not pursue this *ad hoc* approach further here. The qualitative behaviour described by the analytical form of $d\langle\mu_z\rangle/\mu/dT$ remains descriptive of the physics.
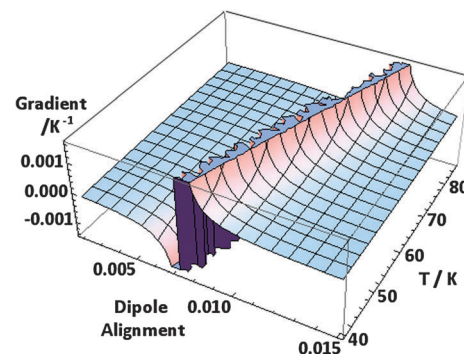

Fig. 2 The variation of the gradient $d\langle\mu_z\rangle/\mu/dT$, evaluated using eqn (3), as a function of the temperature, T, and the degree of dipole alignment $\langle\mu_z\rangle/\mu$, for $\langle E_{sym}\rangle = 1.206 \times 10^7$ V m^{-1}, $\langle E_{asym}\rangle = 1.148 \times 10^9$ V m^{-1} and $\zeta = 1.45 \times 10^4$, values obtained from fitting to data in Fig. 1a and b. The gradient is expressed in units of change in alignment per degree K.

The total differential of $\langle\mu_z/\mu\rangle = f(\langle\mu_z\rangle/\mu,T)$ is given by

$$\frac{d\langle\mu_z/\mu\rangle}{dT} = \frac{1/\mu E_z - (\mu E_z/T^2)\text{cosech}^2(\mu E_z/T)}{(\mu E'/T)\text{cosech}^2(\mu E_z/T) - E'T/\mu E_z^2 - 1} \quad (3)$$

where $E' = \langle E_{asym}\rangle - 2\zeta\langle E_{sym}\rangle\langle\mu_z/\mu\rangle$ and E_z is defined by eqn (1). A significant property of eqn (3) is the presence of a singular cut in $\langle\mu_z\rangle/\mu,T$ space for values which satisfy

$$(\mu E'/T)\text{cosech}^2(\mu E_z/T) - E'T/\mu E_z^2 - 1 = 0 \quad (4)$$

A representation of $d\langle\mu_z\rangle/\mu/dT$ as a function of temperature and $\langle\mu_z\rangle/\mu$ is shown in Fig. 2 using the fitted values of $\langle E_{sym}\rangle$, $\langle E_{asym}\rangle$ and ζ derived using eqn (1) and (2). Fig. 2 illustrates the set of singularities represented by eqn (4). Immediately to lower $\langle\mu_z\rangle/\mu$, T of this set, $d\langle\mu_z\rangle/\mu/dT$ is negative but is positive for higher $\langle\mu_z\rangle/\mu$, T on the other side of the singularity. Thus 'normal' and 'anomalous' behaviours are separated by the singular cut in Fig. 2. Note that for the values of $\langle E_{sym}\rangle$, $\langle E_{asym}\rangle$ and ζ used here, the nominator in eqn (3) is positive for the entire range of $\langle\mu_z\rangle/\mu$ and T. Thus it is the sign change in the denominator which wholly governs the change of sign in $d\langle\mu_z\rangle/\mu/dT$.

Given that eqn (1) and (2) are of general (approximate) validity, it follows that all spontelectric materials may in principle share the common feature of a decreasing and then increasing degree of dipole alignment with increasing deposition temperature, separated by a singular cut. Thus the anomalous behaviour reported for methyl formate is a general characteristic of this new class of materials. In this connection the condition expressed in eqn (4) cannot be accessed in the case of N$_2$O since the material cannot be deposited at sufficiently high temperature.[3] There is an analogy between the case of N$_2$O and those ferroelectric crystals which melt before leaving the ferroelectric phase.

The quantities which govern the sign of the denominator of eqn (3) are $\langle E_{sym}\rangle$, $\langle E_{asym}\rangle$ and ζ. We set out to investigate the sensitivity of the denominator to small variations of these parameters. Using $T = 77.5$ K (see Table 1) in the critical region and taking the partial derivatives of the function $(\mu E'/T)\text{cosech}^2(\mu E_z/T) - E'T/\mu E_z^2 - 1$ with respect to $\langle E_{sym}\rangle$, $\langle E_{asym}\rangle$ and ζ around the point at which this function is

close to zero, that is, where eqn (4) is approximately satisfied, we find that the sensitivities of the function to $\langle E_{sym} \rangle$ and ζ are very similar and that for $\langle E_{asym} \rangle$ is of opposite sign and 3.6 times smaller in absolute value. We therefore conclude that the factors which tip the slope from negative to positive are those associated with the symmetrical part of the potential and to a markedly lesser extent with the feedback parameter $\langle E_{asym} \rangle$. In addition we see that approaching from the negative side of the function, that is, from lower temperature, feedback tends to oppose the tendency to flip the system into the anomalous regime of positive $d\langle \mu_z \rangle/\mu/dT$. At this stage it is not possible to state if the greater influence of the symmetrical part of the potential is a general result or one specific to methyl formate.

The above analysis leads to a qualitative description of the events which may cause the increase of $\langle \mu_z \rangle/\mu$ with T for a set of critical combinations of T, $\langle \mu_z \rangle/\mu$. Species as they attach from the gas phase to the surface evidently find it favourable at all temperatures to form a dipole oriented structure. The formation of an energetically favourable, that is, oriented system, is enhanced by weakly hindered diffusion (greater mobility) and associated molecular motion. According to results in ref. 17–19, these are the conditions which are found as gas phase species condense to form solid material to a depth of a few nanometers, that is, 10–20 monolayers and, additionally, effects are likely to be enhanced very close to the surface. Greater thermal diffusion in higher temperature films implies that species are able to explore a greater volume of phase space, overcoming barriers imposed by $\langle E_{sym} \rangle$ and ζ between metastable states. We suggest that this in turn may increase the degree of dipole alignment that can be formed in the system overcoming the tendency to greater disorder associated with higher temperature. Molecular dynamics simulations would be valuable to test the validity of this conjecture. We also note that the local heat of adsorption makes a contribution to the dynamics, a factor which would be included in any molecular dynamics model.

An intriguing possibility arising from the present work is that it may be feasible to cause the system to switch the gradient, $d\langle \mu_z \rangle/\mu/dT$, abruptly by provision of an external stimulus of an electric field. A trivial extension of the theory may be made by adding an arbitrary electric field, E_{ex}, to the expression for E_z in eqn (1), yielding a new eqn (3) in which in each case where E_z appears, $E_z + E_{ex}$ would now be found. Evidently, if a layer is laid down which corresponds to a point in $\langle \mu_z \rangle/\mu$, T space close to the singular cut in Fig. 2, application of an appropriate external field could cause the system to hover extremely close to the singularity or to flip from, say, a negative $d\langle \mu_z \rangle/\mu/dT$ to a positive $d\langle \mu_z \rangle/\mu/dT$. If we consider a deposition temperature of 85 K and use the observed gradient of $+4.5 \times 10^{-3}$ per K, then in order to induce a sign change in the gradient and create, for example, a value of -0.09 per K, an applied field, E_x, of 760 V mm^{-1}, opposing E_z, would be required. This represents only a small perturbation to the system since the value of E_z in the unperturbed state is 50 times larger than this value of E_{ex}.

In conclusion, the current work has revealed some of the remarkably rich physics governing this new class of solid behaviour characterised by spontaneous dipole alignment. The condition for the onset of the counterintuitive property of methyl formate films, with $d\langle \mu_z \rangle/\mu/dT$ positive, may in fact be expressed rather simply. To first order in cosech^2 in eqn (4), the condition for singular behaviour is that the degree of dipole alignment be given by the ratio of the asymmetric parameter divided by twice the product of the symmetric and locking parameters, $\langle E_{asym} \rangle/2\zeta\langle E_{sym} \rangle$, yielding a figure of $\langle \mu_z \rangle/\mu \sim 0.003$ (see Table 1). As the degree of dipole alignment falls towards this value with increasing deposition temperature, the system will tend to cross the singular cut in Fig. 2 and move from one regime into the other, just as we observe in Table 1 or Fig. 1. A choice of species to examine the generality of our conclusions may be the homologous series methyl, ethyl, propyl formate *etc.* In this connection experiments have already shown that ethyl formate displays dipole alignment.

Notes and references

1 S. Horuchi and Y. Tokura, *Nat. Mater.*, 2008, **7**, 357.
2 J. Kroupa, P. Vanek, R. Krupkova and Z. Zikmund, *Ferroelectrics*, 1997, **202**, 229.
3 O. Plekan, A. Cassidy, R. Balog, N. C. Jones and D. Field, *Phys. Chem. Chem. Phys.*, 2011, **13**, 21035–21044.
4 R. Balog, P. Cicman, N. C. Jones and D. Field, *Phys. Rev. Lett.*, 2009, **102**, 073003.
5 D. Field, O. Plekan, A. Cassidy, R. Balog and N. C. Jones, *Europhys. News*, 2011, **42**, 32.
6 M. W. Klein, C. Held and E. Zuroff, *Phys. Rev. B: Solid State*, 1976, **13**, 3576.
7 S. H. L. Klapp and G. N. Patey, *J. Chem. Phys.*, 2001, **115**, 4718.
8 K. Nauta and R. E. Miller, *Science*, 1999, **283**, 1895.
9 S. V. Hoffmann, S. L. Lunt, N. C. Jones, D. Field and J.-P. Ziesel, *Rev. Sci. Instrum.*, 2002, **73**, 4157.
10 P. Modica and M. E. Palumbo, *Astron. Astrophys.*, 2010, **519**, A22.
11 A. Natan, L. Kronik, H. Haick and R. T. Tung, *Adv. Mater.*, 2007, **19**, 4103.
12 J. Topping, *Proc. R. Soc. London, Ser. A*, 1927, **114**, 67.
13 E. Cohen de Lara and J. Vincent-Geisse, *J. Phys. Chem.*, 1976, **80**, 1922.
14 B. L. Maschhoff and J. P. Cowin, *J. Chem. Phys.*, 1994, **101**, 8138.
15 D. Fernandez-Torre, O. Kupiainen, P. Pyykkö and L. Halonen, *Chem. Phys. Lett.*, 2009, **471**, 239.
16 C. Kittel, *Introduction to Solid State Physics*, John Wiley and Sons Inc., 3rd edn, 1968.
17 S. F. Swallen, K. L. Kearns and M. K. Mapes, *et al.*, *Science*, 2007, **315**, 353.
18 S. Singh and J. J. de Pablo, *J. Chem. Phys.*, 2011, **134**, 194903.
19 A. Sepulveda, *et al.*, *Phys. Rev. Lett.*, 2011, **107**, 025901.