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Differentiability breaking and Schwarz theorem violation in an aging material

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Dielectric constant measurements are performed in the frequency range from 1 kHz to 1 MHz on a disordered material with ferroelectric properties ($KTa_{1-x}Nb_xO_3$ crystals) after isothermal aging at the plateau temperature $T_{pl} \cong 10$ K. They show that the derivatives of the complex capacitance with respect to temperature and time present two very peculiar behaviors. The first point is that the first and second derivatives against temperature are not equal on the two sides of T_{pl}; this is differentiability breaking. The second point is that the two crossed second derivatives against temperature and time are not equal (indeed they have opposite signs); this is a violation of Schwarz theorem. These results are obtained on both the real part and the imaginary part of the capacitance. A model, initially imagined for aging and memory of aging, attributes the time-dependent properties to the evolution (growth and reconformations) of the polarization domain walls. It is shown that it can also explain the observed differentiability breaking (and in particular its logarithmic increase with the plateau duration t_{pl}) and the violation of Schwarz theorem.

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I. INTRODUCTION

Aging is said to occur if the evolution of a system, measured through some susceptibility or some extensive parameter, is nonstationary and depends on the thermal history. It is a consequence of disorder and frustration. Aging was noticed on the elastic compliance s of polymers a long time ago;[1] it has also been observed in many solids: on the magnetic susceptibility χ of spin glasses,[2–5] on the elastic constant c and on the dielectric constant ε of disordered dielectrics[6–8] and of structural glasses.[9]

Associated with aging, rejuvenation (evolution opposite to aging observed when temperature is lowered) and memory (sequel of aging seen after a back and forth temperature sweep) are also present in disordered and frustrated materials.[10–15]

Recently, differentiability breaking has been put in evidence in $KTa_{1-x}Nb_xO_3$ (KTN) crystals.[16] If after an isothermal plateau at temperature T_{pl} held during the lapse of time t_{pl}, a small temperature change dT is imposed, it induces a small capacitance change from which the partial derivative $\partial C/\partial T$ can be deduced. The point is that the derivative is not the same for $dT>0$ and $dT<0$ (except if $t_{pl}=0$). Therefore, the left-hand derivative and the right-hand derivative must be distinguished and, strictly speaking, the function $C(t_{pl},T)$ is not differentiable with respect to T since the value of $\partial C/\partial T$ is not unique at the point $(t=t_{pl},T=T_{pl})$. In other words, the function $C(t_{pl},T)$ has a cusp in $T=T_{pl}$. This is differentiability breaking; it is related to rejuvenation.

In the present paper we report on new results concerning some among the derivatives of $C(T,t)$ with respect to temperature and time. More precisely, we have found that

(i) As the first derivative $\partial C/\partial T$ does, the second derivatives $\partial^2 C/\partial T^2$, $\partial^2 C/\partial T\partial t$, and $\partial^2 C/\partial t\partial T$ also show differentiability breaking;

(ii) Moreover, the second crossed derivatives $\partial^2 C/\partial T\partial t$ and $\partial^2 C/\partial t\partial T$ are not equal (violation of Schwarz theorem). Indeed, the capacitance is a complex quantity and the quoted properties are valid for both its real part and its imaginary part.

We have performed a large number of experiments, with various plateau durations and several measuring frequencies. However, we present in great detail only one complete set of data with the idea that a unique counterexample is sufficient to rule out a theorem (indeed to invalidate the underlying hypotheses).

II. EXPERIMENTS

The pure potassium tantalate $KTaO_3$ crystal belongs to the cubic perovskite family. If a fraction x of tantalum ions is randomly substituted by isoelectronic niobium ions, the $KTa_{1-x}Nb_xO_3$ crystal thus obtained is ferroelectric if the niobium concentration x is superior to $x_c \cong 0.008$. For the two samples used in the preliminary study of differentiability breaking[16] we have observed broad transitions at the temperatures $T_{tr}=31$ and 38 K, defined by the maxima of the real part ε' and the imaginary part ε'' of the dielectric constant, which are almost independent of the measuring frequency f. From the phase diagram[17] we inferred that the niobium concentrations are $x=0.022$ (sample A) and $x=0.027$ (sample B), respectively. The experiments reported below are new; moreover, detailed experiments performed on sample B in its ferroelectric phase are analyzed following a modified method.

Using a Hewlett-Packard 4192A impedance analyzer, we have measured the electric capacitance and the dielectric loss at frequencies f, ranging from 1 kHz to 1 MHz. They can easily be transformed into the real part ε' and the imaginary part ε'' of the complex dielectric constant. Practically, the data are given in terms of the complex capacitance $C=C'-iC''$, proportional to $\varepsilon=\varepsilon'-i\varepsilon''$ (the rule is that $C=1$ pF corresponds to $\varepsilon \cong 16$ for sample B), which was measured as a function of time while the sample temperature $T(t)$ was a controlled function of time.

The following procedure was systematically used. After annealing near 55 K and initial rapid cooling across the transition temperature T_{tr} down to $T \cong 22$ K, cooling is continued at the cooling rate $r = -5.9\ \mathrm{mK\,s^{-1}}$, down to the plateau temperature T_{pl}. The duration of the plateau is t_{pl}. All steps before the plateau constitute what is called the thermal history of the sample.

III. METHOD AND PREVIOUS RESULTS

The original principle of our method has been described elsewhere.[18] It consisted in the study of small variations of the complex capacitance as responses to small temperature and time variations. We have measured the response in the vicinity of some remarkable point (T_0, t_0) in the (T, t) space. Taking $C(T_0, t_0)$ as reference, the deviation from this value is $dC = C(T_0 + dT, t_0 + dt) - C(T_0, t_0)$. For infinitesimal changes, dC is the sum of an instantaneous change proportional to dT and of a decrease due to aging, proportional to dt. This reads

$$dC = P(T_{pl},\ t_{pl})dT + Q(T_{pl},\ t_{pl})dt,$$

where it is explicitly put that T_0 is the plateau temperature T_{pl} and that the plateau duration is t_{pl} (the origin of time is chosen at the instant when T_{pl} is reached). The complex coefficients $P(T_{pl}, t_{pl})$ and $Q(T_{pl}, t_{pl})$ are the partial derivatives of $C(T,t)$ with respect to T and t calculated at (T_{pl}, t_{pl}). The coefficient P depends on temperature and time. The real and imaginary parts of the coefficient Q, which measure the effect of isothermal aging, are negative.

In a recent study[16] the method was applied to KTN crystals in the following way. Let there be two experiments, labeled 1 and 2, corresponding to two small temperature steps dT_1 and dT_2 (both positive or both negative) performed during the same time interval dt following the plateau. If the steps are supposed to be infinitesimal, they induce the following two complex capacitance changes

$$dC_1 = P dT_1 + Q dt \quad \text{and} \quad dC_2 = P dT_2 + Q dt,$$

with a unique coefficient Q. Then the complex coefficient $P = P' - iP''$ is easily deduced as

$$P = \frac{dC_2 - dC_1}{dT_2 - dT_1}.$$

For a given temperature step dT_1 different temperature steps dT_2 were used. Our experimental errors are $\Delta P' = \pm 0.2\ \mathrm{pF\,K^{-1}}$ and $\Delta P'' = \pm 0.1\ \mathrm{pF\,K^{-1}}$. Using these different steps we obtained, with errors smaller than $2\Delta P'$ and $2\Delta P''$, the same values for the real part P' and the imaginary part P'', respectively. This result is a good check of the validity of our method. In all our experiments we used the time interval $dt = 20$ s while the temperature steps were such that $|dT_1| \cong 0.125$ K and $dT_2 = 4dT_1$ which provide us with a good accuracy.

The main result was different values for both P' and P'' on the two sides of the plateau: they are larger for positive temperature jumps than for negative temperature jumps. This means that the derivatives of C' and C'' with respect to T are not the same on the left-hand side and on the right-hand side. This is differentiability breaking.

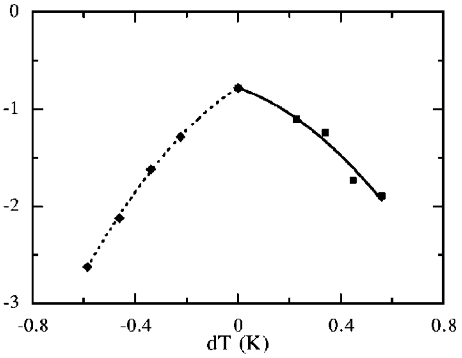

FIG. 1. Plot of the real part Q' of the capacitance time derivative $Q(T_{pl} + dT,\ t_{pl})$ after the temperature jump $T_{pl} \Rightarrow T_{pl} + dT$ occurring at the end of the aging plateau (at $t = t_{pl}$) as a function of the jump magnitude dT. The lines represent the fits with two different second degree polynomials: one for the data recorded with $dT > 0$ (squares), the other for those recorded with $dT < 0$ (diamonds). The experimental conditions were $f = 10$ kHz, $t_{pl} = 500$ s, and $T_{pl} = 10.1$ K.

Indeed, this calculation was crucially based on the hypothesis that the coefficient Q has the same value whatever the temperature increments are: this means that $Q(dT_1) = Q(dT_2)$. In other words, it was assumed that the temperature increments are sufficiently small to be considered as infinitesimal. The validity of this assumption is now questioned. Therefore, while keeping for the time interval the same very small value dt, hereafter the temperature increment dT is supposed to be small but finite and we push the analysis up to second order. The results reported below show that the systematic error introduced by this assumption is of the same magnitude that the experimental error; therefore, it does not invalidate our previous conclusions.

IV. NEW ANALYSIS AND PRELIMINARY RESULTS

We have determined by direct measurements how the coefficient $Q(T_{pl} + dT,\ t_{pl})$ depends on dT. After the plateau lasting t_{pl} at T_{pl}, the temperature is suddenly changed to $T_{pl} + dT$, with $|dT| \leqslant 0.6$ K, and a second plateau is started at this temperature. Then, by means of a least square method, we determine the best fit for the time variation of the capacitance $C(T_{pl} + dT,\ t)$ with the data recorded for $t \geqslant t_{pl} + dt$ and we extrapolate it to $t = t_{pl}$. The fit function is a stretched exponential. Once the free parameters of the fit function are known, we are able to obtain $C(T_{pl} + dT,\ t_{pl})$, the capacitance time derivative at $T_{pl} + dT$, and the capacitance jump between T_{pl} and $T_{pl} + dT$, which respectively read

$$Q(T_{pl} + dT,\ t_{pl}) = \left.\frac{\partial C}{\partial t}\right)_{T_{pl}+dT}$$

and

$$dC(T_{pl} + dT,\ t_{pl}) = C(T_{pl} + dT,\ t_{pl}) - C(T_{pl},\ t_{pl}).$$

The data for $Q(T_{pl} + dT,\ t_{pl})$ are shown in Fig. 1 (real part)

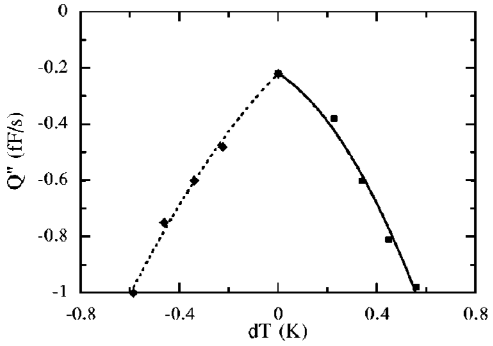

FIG. 2. Plot of the imaginary part Q'' of the capacitance time derivative $Q(T_{\rm pl}+dT,\ t_{\rm pl})$ after the temperature jump $T_{\rm pl}\Rightarrow T_{\rm pl}+dT$ occurring at the end of the aging plateau (at $t=t_{\rm pl}$) as a function of the jump magnitude *dT*. The lines represent the fits with two different second degree polynomials: one for the data recorded with $dT>0$ (squares), the other for those recorded with $dT<0$ (diamonds). The experimental conditions were $f=10$ kHz, $t_{\rm pl}=500$ s, and $T_{\rm pl}=10.1$ K.

and Fig. 2 (imaginary part); those for $dC(T_{\rm pl}+dT,\ t_{\rm pl})$ are displayed in Fig. 3 (real part) and Fig. 4 (imaginary part).

We must underline the differences between the two forms of the method. In the initial form[16,18] the studied capacitance change is from the point $(T_{\rm pl},\ t_{\rm pl})$ to the point $(T_{\rm pl}+dT, t_{\rm pl}+dt)$. In the form used here, the change is from $(T_{\rm pl},\ t_{\rm pl})$ to $(T_{\rm pl}+dT,\ t_{\rm pl})$. The variation during the lapse *dt* is eliminated by extrapolation from the data for $t\geqslant t_{\rm pl}+dt$.

As a first result, the data of Fig. 1 and 2 provide an upper limit of the bias introduced in Ref. 16 when assuming $Q(dT_1)=Q(dT_2)$: we know now that the deviations were smaller than $[Q'(0)-Q'(\pm 0.5\ {\rm K})]dt \cong 0.015$ pF and $[Q''(0)-Q''(\pm 0.5\ {\rm K})]dt \cong 0.01$ pF for $dt=20$ s; this was close to the experimental errors. Our previous data were practically correct.

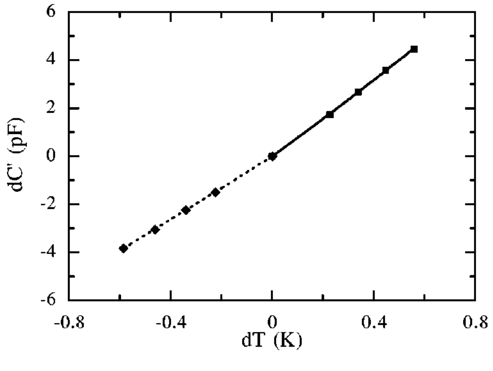

FIG. 3. Plot of the real part dC' of the capacitance change $dC(T_{\rm pl}+dT,\ t_{\rm pl})$ after the temperature jump $T_{\rm pl}\Rightarrow T_{\rm pl}+dT$ occurring at the end of the aging plateau (at $t=t_{\rm pl}$) as a function of the jump magnitude *dT*. The lines represent the fits with two different second degree polynomials: one for the data recorded with $dT>0$ (squares), the other for those recorded with $dT<0$ (diamonds). The experimental conditions were $f=10$ kHz, $t_{\rm pl}=500$ s and $T_{\rm pl}=10.1$ K.

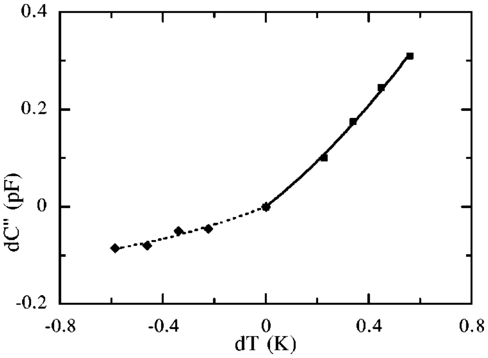

FIG. 4. Plot of the imaginary part dC'' of the capacitance change $dC(T_{\rm pl}+dT,\ t_{\rm pl})$ after the temperature jump $T_{\rm pl}\Rightarrow T_{\rm pl}+dT$ occurring at the end of the aging plateau (at $t=t_{\rm pl}$) as a function of the jump magnitude *dT*. The lines represent the fits with two different second degree polynomials: one for the data recorded with $dT>0$ (squares), the other for those recorded with $dT<0$ (diamonds). The experimental conditions were $f=10$ kHz, $t_{\rm pl}=500$ s, and $T_{\rm pl}=10.1$ K.

V. AN IMPORTANT QUALITATIVE RESULT

Before we turn to give quantitative results, we show now that we can infer an interesting property only from a qualitative result.

On the one hand, the (negative) coefficients $Q'(T_{\rm pl}+dT,\ t_{\rm pl})$ and $Q''(T_{\rm pl}+dT,\ t_{\rm pl})$ decrease from the values $Q'(T_{\rm pl},\ t_{\rm pl})$ and $Q''(T_{\rm pl},\ t_{\rm pl})$ for both $dT>0$ and $dT<0$ (see Figs. 1 and 2). This means that

$$\left.\frac{\partial Q'}{\partial T}\right)_{T_{\rm pl},t_{\rm pl}}=\left.\frac{\partial^2 C'}{\partial T\partial t}\right)_{T_{\rm pl},t_{\rm pl}} \quad \text{and} \quad \left.\frac{\partial Q''}{\partial T}\right)_{T_{\rm pl},t_{\rm pl}}=\left.\frac{\partial^2 C''}{\partial T\partial t}\right)_{T_{\rm pl},t_{\rm pl}}$$

have their sign opposite to the sign of *dT*.

On the other hand, we know from previous experiments[16] and from the analysis done below that the isothermal capacitance jump can be written in first approximation,

$$dC(T_{\rm pl}+dT,\ \ t_{\rm pl})\cong P\ dT,$$

where the coefficient P depends on $t_{\rm pl}$. Its time variation is $P(T_{\rm pl},t_{\rm pl})\cong P_0+M\ \ln(t_{\rm pl})$ for $t_{\rm pl}>200$ s where the coefficients M' and M'' have the sign of *dT*. It follows that

$$\left.\frac{\partial P'}{\partial t}\right)_{T_{\rm pl},t_{\rm pl}}=\left.\frac{\partial^2 C'}{\partial t\partial T}\right)_{T_{\rm pl},t_{\rm pl}}=\frac{M'}{t_{\rm pl}} \quad \text{and} \quad \left.\frac{\partial P''}{\partial t}\right)_{T_{\rm pl},t_{\rm pl}}=\left.\frac{\partial^2 C''}{\partial t\partial T}\right)_{T_{\rm pl},t_{\rm pl}}=\frac{M''}{t_{\rm pl}},$$

where the sign of these derivatives is that of *dT*.

Consequently, the two pairs of derivatives

$$\left.\frac{\partial^2 C'}{\partial T\partial t}\right)_{T_{\rm pl},t_{\rm pl}},\quad \left.\frac{\partial^2 C'}{\partial t\partial T}\right)_{T_{\rm pl},t_{\rm pl}}$$

on the one hand, and

$$\left.\frac{\partial^2 C''}{\partial T \partial t}\right)_{T_{\rm pl},t_{\rm pl}},\quad \left.\frac{\partial^2 C''}{\partial t \partial T}\right)_{T_{\rm pl},t_{\rm pl}}$$

on the other hand, have opposite signs.

Only from these qualitative results we are allowed to claim that Schwarz theorem (equality of the two crossed derivatives) is violated when applied to the capacitance after aging.

VI. MATHEMATICAL ANALYSIS AND RESULTS

We turn now to the numerical results of our measurements. They were performed with different plateau durations $t_{\rm pl} = 100$, 500, and 2000 s at the temperature $T_{\rm pl} = 10.1$ K. The data were recorded at $f = 10$ kHz.

In order to gather and classify the whole set of our results, we write down the Taylor expansion of the complex capacitance after the end of the isothermal aging (during the time $t_{\rm pl}$ at the temperature $T_{\rm pl}$):

$$\begin{aligned}
&C(T_{\rm pl}+dT, t_{\rm pl}+dt)\\
&\quad = C)_{\rm eop} + \left\{ \left.\frac{\partial C}{\partial T}\right)_{\rm eop} dT + \left.\frac{\partial C}{\partial t}\right)_{\rm eop} dt \right\} + \frac{1}{2}\left\{ \left.\frac{\partial^2 C}{\partial T^2}\right)_{\rm eop} dT^2 \right.\\
&\qquad \left. + \left.\frac{\partial^2 C}{\partial t \partial T}\right)_{\rm eop} dT\, dt + \left.\frac{\partial^2 C}{\partial T \partial t}\right)_{\rm eop} dt\, dT + \left.\frac{\partial^2 C}{\partial t^2}\right)_{\rm eop} dt^2 \right\}\\
&\qquad + \frac{1}{6}\left\{ 2 \left.\frac{\partial^3 C}{\partial T^2 \partial t}\right)_{\rm eop} dt\, dT^2 + \text{other third order terms} \right\},
\end{aligned}$$

where the lower index "eop," which stands for $(T_{\rm pl}, t_{\rm pl})$, means "end of plateau." In this expansion we have shown only the measured coefficients and we have assumed that the Schwarz theorem (equality of the two crossed second derivatives) could possibly not hold.

The three sets of data show differentiability breaking of $C(T,t)$ and confirm the violation of the Schwarz theorem. However, it would be tedious and unsurprising to reproduce all of them. Therefore, only one set of data is reported in detail in the Appendix.

VII. MODEL

Nonergodic isothermal aging (evolution at constant temperature towards a limit that depends on thermal history), rejuvenation (evolution opposite to aging after a temperature jump) and memory (sequel of aging after a back-and-forth journey to lower temperatures) can be explained in the frame of a model that attributes the time-dependent effects to reconformation and growth of the walls of the polarization domains.[19–21] Here we scrutinize the appropriateness of the model to explain the main two features reported in the present paper:

(i) The second derivative $\partial/\partial t(\partial C/\partial T) = \partial P/\partial t$ has the same sign that $dT = T - T_{\rm pl}$;
(ii) The second derivative $\partial/\partial T(\partial C/\partial t) = \partial Q/\partial T$ has its sign opposite to that of $dT = T - T_{\rm pl}$.

A. Isothermal aging

In the model, aging properties are attributed to the slow evolution of the area of domain walls. The average domain size R always increases in a ferroelectric phase. If we assume that the time t necessary to a domain wall of size R, in a crystal lattice of parameter a, to overcome a barrier energy scale Γ at temperature T is

$$t = \tau_\infty \exp[\Gamma (R/a)^\theta / (k_{\rm B} T)],$$

with $\theta \cong 1$, we deduce that after a plateau duration $t_{\rm pl}$ the domain has reached the size

$$\begin{aligned}
R(t_{\rm pl}) &= R_0 \left\{ 1 + \frac{a}{R_0} \frac{k_{\rm B} T_{\rm pl}}{\Gamma} \ln\left(1 + \frac{t_{\rm pl}}{\tau(R_0, T_{\rm pl})} \right) \right\}\\
&\approx R_0 \left\{ 1 + \frac{a}{R_0} \frac{k_{\rm B} T_{\rm pl}}{\Gamma} \ln\left(\frac{t_{\rm pl}}{\tau(R_0, T_{\rm pl})} \right) \right\},
\end{aligned}$$

where the characteristic time is $\tau(R_0, T_{\rm pl}) = \tau_\infty \exp[\Gamma(R_0/a)/(k_{\rm B} T_{\rm pl})]$.

The wall area contribution to the capacitance is proportional to the total wall area multiplied by the density of domains. Therefore, domain growth induces a decrease $\Delta C \propto R^2/R^3 \cong 1/R$ of the susceptibility because the total wall area decreases (the area of a domain increases but the number of domains decreases more strongly). Neglecting the distribution of size, the aging part reads

$$\Delta C = \frac{K}{R(t_{\rm pl})} \cong \frac{K}{R_0} \left\{ 1 - \frac{a}{R_0} \frac{T_{\rm pl}}{T_b} \ln\left(\frac{t_{\rm pl}}{\tau(R_0, T_{\rm pl})} \right) \right\}.$$

The coefficient K is a constant with the needed dimensions. Therefore, the time-dependent part of the capacitance is

$$\Delta C(t_{\rm pl}) = \frac{K}{R(t_{\rm pl})} \cong - \frac{K a}{R_0^2} \frac{T_{\rm pl}}{T_b} \ln\left(\frac{t_{\rm pl}}{\tau(R_0, T_{\rm pl})} \right).$$

It decreases as the logarithm of the plateau duration if $t_{\rm pl} \gg \tau(R_0, T_{\rm pl})$.

Growth is not the only possible motion of the domain wall; rearrangements (reconformation modes) of some parts of the wall also play a role.[22] The characteristic time $\tau(l,T)$ of the domain wall motion is a rapidly increasing function of the size of the displaced portion of area $A = l \times l$ of wall, according to $\tau(l,T) = \tau_\infty \exp[\Gamma(l/a)/(k_{\rm B}T)]$. The length l is necessarily smaller than the domain size R. Small-size motions are fast; they correspond to reconformations of parts of domain walls. Large-size motions (where $l \cong R$) are slow; they correspond to increases of the domain size. Indeed, there is a continuous distribution of the moving portion sizes and a correlative distribution of their characteristic times:

$$\begin{aligned}
\tau_{\rm min} &= \tau_\infty \exp[\Gamma/(k_{\rm B} T)]\\
&\leqslant \tau(l,\ T)\\
&\leqslant \tau_\infty \exp[\Gamma (R/a)/(k_{\rm B} T)] = \tau_{\rm max}.
\end{aligned}$$

This real-space language can be translated into terms of travel of a representative point over energy barriers $k_{\rm B} T_b$

$=\Gamma(l/a)$ in the phase space. Small-size motions correspond to jumps over low barriers and large-size motions to jumps over high barriers.

To simplify, reconformation of the area $A=l\times l$ means the equilibration between two possible configurations of this part of the wall. This occurs according to $x(t)=x_{\mathrm{eq}}+(x_0-x_{\mathrm{eq}})\exp[-t/\tau(l,T_{\mathrm{pl}})]$, where $x(t)$ is the difference of the probabilities to find the domain wall either in a configuration or in the other and x_0 is the initial value. The equilibrium value is $x_{\mathrm{eq}}(T_{\mathrm{pl}})=\tanh(T_\Delta/T_{\mathrm{pl}})$, where $2k_{\mathrm{B}}T_\Delta=2\Delta$ is the free-energy difference between the two minima of the double well associated with the two configurations. The characteristic time of the evolution is $\tau(l,\ T_{\mathrm{pl}})$. During domain growth, with the typical time $\tau_{\max}=\tau_\infty\exp[\Gamma(R/a)/(k_{\mathrm{B}}T)]$, all the reconformations are achieved in times $\tau(l,\ T_{\mathrm{pl}})\leqslant\tau_{\max}$. Therefore, except at the very beginning, during isothermal aging the reconformations of the wall are permanently in quasiequilibrium with the size R: the bottleneck (the slowest mode) of isothermal aging is due to domain growth. In other words, the wall reconformations only play a minor role during isothermal aging. On the contrary, their role is essential after temperature changes.

B. Rejuvenation upon cooling

We first examine the case when the sample is pushed out of its quasiequilibrium because the temperature is suddenly lowered to $T_{\mathrm{pl}}-dT$ in the short lapse δt. The configurations that were equilibrated at T_{pl} must evolve, starting from the initial value $x_0=x_{\mathrm{eq}}(T_{\mathrm{pl}})=\tanh(T_\Delta/T_{\mathrm{pl}})$ towards the new equilibrium value $x_{\mathrm{eq}}=x_{\mathrm{eq}}(T_{\mathrm{pl}}-dT)=\tanh[T_\Delta/(T_{\mathrm{pl}}-dT)]$. The corresponding possible evolution magnitude is

$$x_{\mathrm{eq}}-x_0\cong(T_\Delta/T_{\mathrm{pl}})\mathrm{sech}^2(T_\Delta/T_{\mathrm{pl}})(dT/T_{\mathrm{pl}})$$

while the kinetics of the evolution is governed by

$$\begin{aligned}x(t)-x_0={}&(T_\Delta/T_{\mathrm{pl}})\mathrm{sech}^2(T_\Delta/T_{\mathrm{pl}})(dT/T_{\mathrm{pl}})\\&\times[1-\exp\{-t/\tau(l,T_{\mathrm{pl}})\}].\end{aligned}$$

Very schematically, the reconformations that have enough time to achieve this evolution during δt are those with $\tau_{\min}\leqslant\tau(l,T_{\mathrm{pl}})\leqslant\delta t$, or equivalently $a\leqslant l\leqslant l(\delta t,\ T_{\mathrm{pl}})$, where $l(\delta t,\ T_{\mathrm{pl}})=a(k_{\mathrm{B}}T_{\mathrm{pl}}/\Gamma)\ln(\delta t/\tau_\infty)$. This leads to an "immediate" response that reads

$$x(\delta t)-x_0\cong(T_\Delta/T_{\mathrm{pl}})\mathrm{sech}^2(T_\Delta/T_{\mathrm{pl}})(dT/T_{\mathrm{pl}}).$$

Those with $l(\delta t,\ T_{\mathrm{pl}})\leqslant l\leqslant R(t_{\mathrm{pl}})$ are frozen in during the time δt. This leads to

$$x(\delta t)-x_0\cong 0.$$

A portion of wall bears the average dipolar moment $m_A(l,\ t)=\mu(l/a)^2x(t)$, where μ is the elementary moment of an off-center tantalum ion. The moment is coupled with the oscillating electric field $E(\omega)$. The corresponding contribution to the dielectric constant of a domain of size R due to the reconformations of size l is obtained when adding the effects of all the reconformations of this size. This provides a contribution of the Langevin-Debye type to the capacitance, with the form

$$dC(\omega,\ \ \delta t,\ \ l)\propto\frac{G(l)}{1+i\omega\tau(l,\ \ T_{\mathrm{pl}})}.$$

Then the contributions of all the reconformation lengths on a given domain wall have to be added. Indeed, as it was shown above, the sum is practically limited to those with $\tau_{\min}\leqslant\tau(l,\ T_{\mathrm{pl}})\leqslant\delta t$ or $a\leqslant l\leqslant l(\delta t,\ T_{\mathrm{pl}})$. Finally, the summation over all the domains gives the total effect $\Delta C(\omega,\ \delta t)$.

A rigorous calculation is out of the scope of the present paper. However, according to the previous discussion one can guess that $\Delta C(\omega,\ \delta t)$ is proportional to $\mathrm{sech}^2(T_\Delta/T_{\mathrm{pl}})\times(dT/T_{\mathrm{pl}})$. It is positive because $dT>0$.

Since the material is disordered, one may expect a distribution of the parameters T_Δ and T_b. However, most of the contributed domains are such that $T_\Delta<T_{\mathrm{pl}}$ and $T_b<T_{\mathrm{pl}}$. Otherwise, the occupation function $\tanh(T_\Delta/T_{\mathrm{pl}})\cong 1$ would be insensitive to temperature changes and the relaxation time $\tau(R_0,\ T_{\mathrm{pl}})=\tau_\infty\exp[\Gamma(R_0/a)/(k_{\mathrm{B}}T_{\mathrm{pl}})]$ would be too long.

Moreover, an important point to emphasize is that the number of reconformations increases as the area $A(t_{\mathrm{pl}})$ of the domain wall at the end of the plateau. Since

$$A(t_{\mathrm{pl}})\propto R^2(t_{\mathrm{pl}})\cong R_0^2\left\{1+2\,\frac{a}{R_0}\,\frac{T_{\mathrm{pl}}}{T_b}\ln\!\left(\frac{t_{\mathrm{pl}}}{\tau(R_0,\ \ T_{\mathrm{pl}})}\right)\right\},$$

it is expected that the time-dependent part of ΔC is proportional to $\ln[t_{\mathrm{pl}}/\tau(R_0,T_{\mathrm{pl}})]$ for long enough t_{pl}. This is actually observed. Finally, we get

$$P=\frac{\partial C}{\partial T}\approx P_0-M\ln[t_{\mathrm{pl}}/\tau(R_0,\ \ T_{\mathrm{pl}})].$$

The coefficient M is positive. The term P_0 is the volume contribution, due to the variation of the coherence length $\xi(T)$ with temperature that increases when approaching T_{tr}. The derivative is

$$\partial P/\partial t)_{\mathrm{eop}}=\partial^2C/\partial t\partial T)_{\mathrm{eop}}\approx -M/t_{\mathrm{pl}}<0\quad\text{for}\ \ T=T_{\mathrm{pl}}-dT.$$

C. Relaunching of isothermal aging

The coefficient $Q(T_{\mathrm{pl}},\ t_{\mathrm{pl}})$ is the measure of aging velocity. During isothermal aging at temperature T_{pl} the evolution slows down as time elapses, according to

$$Q(t_{\mathrm{pl}})=\frac{\partial C}{\partial t}=-K\,\frac{a}{R_0{}^2}\,\frac{T_{\mathrm{pl}}}{T_b}\,\frac{1}{t_{\mathrm{pl}}}.$$

After a long aging, the system is old, as shown by $C_{\mathrm{eop}}<C_0$ and $-Q_{\mathrm{eop}}<-Q_0$ (the inequalities on complex quantities must be understood as valid for their two parts, separately), because the capacitance decrease is governed by growth of large domains with the characteristic time t_{pl}. However, it seems younger immediately after the temperature jump since an initial enhancement of the aging velocity (sometimes called relaunching) is observed. This is also seen in negative temperature cycle experiments performed on KTN (Ref. 8) and on spin-glasses too.[3,4] This feature can be explained by the model.

Indeed, the system that begins to evolve at $t=t_{\rm pl}+\delta t$ and $T=T_{\rm pl}-dT$ is in a mixed state since short conformation modes are in equilibrium while long modes are not. In this picture, the wall is seen as wearing small crenels or capes that are the fastest forerunners of the domain growth. In other words, the wall is already prepared to grow because many dipoles already have the right orientation and the ferroelectric interactions can more easily align the other dipoles. This explain why the domain size growth is now unexpectedly fast. Consequently, after the temperature jump $-dT$ the initial decay $Q(T_{\rm pl}-dT,\ t_{\rm pl})$ is rapid. This is the meaning of the observed feature $Q(T_{\rm pl}-dT,\ t_{\rm pl})<Q(T_{\rm pl},\ t_{\rm pl})=Q_{\rm eop}$ from which it is deduced that $\partial Q/\partial T)_{\rm eop}=\partial^2C/\partial T\partial t)_{\rm eop}>0$.

The comparison between the two crossed second derivatives

$$\partial^2C/\partial t\partial T)_{\rm eop}<0 \quad \text{and} \quad \partial^2C/\partial T\partial t)_{\rm eop}>0$$

shows that the model qualitatively explains the Schwarz theorem violation (here, for the left-hand-side temperature derivatives). Moreover, the logarithmic variation of the coefficient $P=\partial C/\partial T$ with the plateau duration $t_{\rm pl}$ (due to the role of the domain size) is also contained in the model.

D. Behavior upon heating

Now we compare the two thermal ways of pushing the sample out of equilibrium, either by a negative temperature jump from $T_{\rm pl}$ to $T_{\rm pl}-dT$ (as seen above) or by a positive temperature jump from $T_{\rm pl}$ to $T_{\rm pl}+dT$. Indeed, what is expected is both symmetry and asymmetry. The symmetry comes from the ferroelectric nature of the phase. As a useful comparison, we first recall what happens in a paraelectric phase as in $\mathrm{K}_{1-y}\mathrm{Li}_y\mathrm{TaO}_3$, where the domain size is limited by the coherence length $\xi(T)$ that is a decreasing function of temperature. In such a material, after a long enough isothermal aging at $T_{\rm pl}$ many domains have reached their limit size $\xi(T_{\rm pl})$; then upon cooling at $T_{\rm pl}-dT$ or heating at $T_{\rm pl}+dT$ two antisymmetric (or opposite) behaviors are observed: initial increase for cooling and decrease for heating. On the contrary, in the ferroelectric phase of KTN the domain size may, in principle, go to infinity (or practically, to the sample size). Then upon cooling or heating, increase of the the domain size is expected in both cases. Therefore, the forerunners (the fastest reconformations modes) must act in the same way: rejuvenation is also expected when heating from $T_{\rm pl}$ to $T_{\rm pl}+dT$. Indeed, this is not totally true because things do not change at the same rate at $T_{\rm pl}-dT$ and at $T_{\rm pl}+dT$ and this difference introduces asymmetry. A more precise examination shows that the length of the reconformations becoming equilibrated during the lapse δt are limited by

$$l(\delta t,\ T_{\rm pl}-dT)=l(\delta t,\ T_{\rm pl})\left(1-\frac{dT}{T_{\rm pl}}\right)$$

and

$$l(\delta t,\ T_{\rm pl}+dT)=l(\delta t,\ T_{\rm pl})\left(1+\frac{dT}{T_{\rm pl}}\right).$$

Consequently, there are more reconformations implied in positive jumps than in negative ones in the ‘‘immediate’’ response. This lack of symmetry may explain differentiability breaking.[16] From this analysis we are led to assume that the small size reconformations responsible for the ‘‘immediate’’ response are not the same (if they were the same, a decrease of the capacitance would be observed, in contradiction with experiments). This point needs a deeper examination.

E. A comparison with phase transitions

The semimicroscopic model described above is not fully satisfying since the growing trend of the domains is introduced as an *ad hoc* hypothesis. Indeed, the features that have to be explained are reminiscent of phase transitions where the temperature behaviors are generally different above and below the transition temperature $T_{\rm tr}$. For instance, Landau theory predicts (and experiments confirm) that the temperature variations of the susceptibility do not have the same critical exponent on the two sides of $T_{\rm tr}$. The reason is simple: for $T>T_{\rm tr}$ and $T<T_{\rm tr}$, the landscapes of the phase space are different and, consequently, the equilibrium positions correspond to minima of the free energy with different curvatures. The analogy between aging and a phase transition has been already pointed out for the case of spin glasses[4,23] with the very puzzling circumstances that rejuvenation (and differentiability breaking in the case of KTN) occurs at any aging temperature $T_{\rm pl}$ and not at a single and well defined temperature $T_{\rm tr}$. However, this similarity could be a path to explore. Along this line, one may assume that a temperature change, either positive or negative, modifies the landscape in the phase space in such a way that the natural evolution is in both cases towards larger polarization domains. Following this view, the forerunners (the small size reconformations) quoted above would correspond to the creation of daughter valleys (separated by low barriers easy to jump over) inside mother valleys, as proposed for spin glasses.[3,4,23,24]

F. Comparisons

Several phenomena observed in KTN present some analogies (but also differences) with those observed in ferromagnetic or ferroelectric materials such as cusps at the end of the hysteresis cycle. This feature, which corresponds to differentiability breaking, is discussed in this section. However, to the best of our knowledge, there is no equivalent of the explicit violation of Schwarz theorem in these experiments.

Ferromagnetic materials and ferroelectric materials exhibit hysteresis cycles: when an alternative field (magnetic $\mathbf{H}$ or electric $\mathbf{E}$) is applied the magnetization $M(\mathbf{H})$ or polarization $P(\mathbf{E})$ curves are loops. If the amplitude of the applied field $\mathbf{H}_0$ or $\mathbf{E}_0$ is not too strong in order that the saturation is not reached, there is a cusp at each end of the cycle. This means that the derivatives dM/dH at $\mathbf{H}_0$ or dP/dE at $\mathbf{E}_0$ are not the same according to the direction of variation of the field. This is nothing else but differentiability breaking.

Hysteresis cycles are explained as the motion of (ferromagnetic or ferroelectric) domain walls under the action of the applied field. Similarly, the current model of aging in KTN also attributes the observed evolution to the displacement of polarization domain walls. However, in cycle experiments in the vicinity of the cusps the derivatives with respect to the field are both positive, for increasing or decreasing field. On the contrary, in our experiments (reported in the present paper and in Ref. 16) the derivatives with respect to temperature may have opposite signs for increasing or decreasing temperature. This rejuvenation effect is attributed to supplementary degrees of freedom (reconformations of the walls) which do not appear in cycle experiments.

But an important point has to be underlined. The symmetry of the differential parameter is quite different in the two cases: the temperature T is a scalar while the fields ($\mathbf{H}$ or $\mathbf{E}$) are vectors.

VIII. MATHEMATICAL COMMENT

The existence of the two second derivatives $\partial^2 f/\partial x^2$ and $\partial^2 f/\partial y^2$ of the function $f(x,y)$ is a sufficient condition for the equality $\partial^2 f/\partial y \partial x = \partial^2 f/\partial x \partial y$ (Schwarz theorem). We have shown that the second derivative $\partial^2 C/\partial t^2$ of the function $C(T,t)$ exists on the point $(T_{\mathrm{pl}}, t_{\mathrm{pl}})$. Consequently, if the second derivative $\partial^2 C/\partial T^2$ would exist too, the equality $\partial^2 C/\partial T \partial t = \partial^2 C/\partial t \partial T$ should be fulfilled. Indeed, we have found that, on the one hand, $\partial^2 C/\partial T^2$ does not exist on the point $(T_{\mathrm{pl}}, t_{\mathrm{pl}})$ and that, on the other hand, $\partial^2 C/\partial T \partial t \neq \partial^2 C/\partial t \partial T$ on the same point. These two features are in mutual agreement.

IX. CONCLUSION

We have put in evidence two properties of the derivatives of the complex capacitance (or of the complex dielectric constant) after aging. They are: on the one hand, the second derivatives $\partial^2 C/\partial T^2$, $\partial^2 C/\partial T \partial t$, and $\partial^2 C/\partial t \partial T$ show differentiability breaking (the left-hand and the right-hand derivatives are different), as it was already observed for the first derivative $\partial C/\partial T$;[16] on the other hand, the second crossed derivatives $\partial^2 C/\partial T \partial t$ and $\partial^2 C/\partial t \partial T$ are not equal (violation of Schwarz theorem). These features are qualitatively explained in the framework of a model that attributes the sample evolution to polarization domain dynamics by means of their wall reconformation and growth.

The nonequality $\partial^2 C/\partial T \partial t \neq \partial^2 C/\partial t \partial T$ is a remarkable result. However, it would be also very interesting to look for a possible violation of Schwarz theorem when the two variables are both relevant intensive parameters, such as temperature and biasing electric field, for instance. In that case, Schwarz equality corresponds to one of the Maxwell relations, well kwown in thermodynamics. Experiments aimed at checking or invalidating such a relation are now in progress. These experiments and those reported in the present paper enter the debate on appropriateness of standard thermodynamics to aging systems, a debate recently illustrated by the violation of the fluctuation-dissipation theorem.[25–27]

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APPENDIX

For the measurements reported here the index ''eop'' corresponds to $t_{\mathrm{pl}} = 500$ s and $T_{\mathrm{pl}} = 10.1$ K. The measuring frequency was $f = 10$ kHz. In addition to the numerical values for the real part and the imaginary part, we briefly indicate how the data are obtained.

1. The coefficient Q_{eop} and its derivatives

The two time derivatives are measured during isothermal aging at T_{pl}, hence for $dT = 0$. Here too, the aging function is determined by means of a least square method and, once the free parameters are known, the derivatives may be numerically calculated. This leads to

$$Q)_{\mathrm{eop}} = \left.\frac{\partial C}{\partial t}\right)_{\mathrm{eop}} = \{(-0.78 \mp 0.03) - i(-0.22 \mp 0.03)\}\ \mathrm{fF\,s^{-1}},$$

$$\left.\frac{\partial Q}{\partial t}\right)_{\mathrm{eop}} = \left.\frac{\partial^2 C}{\partial t^2}\right)_{\mathrm{eop}} = \{(+1.5 \pm 0.1) - i(+0.4 \pm 0.1)\}\ \mathrm{aF\,s^{-2}}.$$

The coefficient Q_{eop} depends on the plateau duration; it also depends on the measuring frequency: $|Q_{\mathrm{eop}}|$ and $|Q'_{\mathrm{eop}}|$ are larger for lower frequencies.

The temperature derivatives are calculated starting from the data of Figs. 1 and 2. Indeed, it is clear from the curves that the functions are not analytic. Consequently, we have to consider $Q(dT)$ as a piecewise function made of two pieces: one for $dT > 0$ and another for $dT < 0$. Then we write down two expansions,

$$Q^{\pm}(T_{\mathrm{pl}} + dT,\ t_{\mathrm{pl}}) = Q(T_{\mathrm{pl}},\ t_{\mathrm{pl}}) + \left.\frac{\partial Q}{\partial T}\right)^{\pm}_{\mathrm{eop}} dT + \frac{1}{2}\left.\frac{\partial^2 Q}{\partial T^2}\right)^{\pm}_{\mathrm{eop}} (dT)^2 + \cdots .$$

We obtain

$$\left\{\begin{aligned}\left.\frac{\partial Q}{\partial T}\right)_{\rm eop}&=\left.\frac{\partial^2 C}{\partial T\partial t}\right)_{\rm eop}=\{(-0.9\pm0.3)-i(-0.55\pm0.15)\}\ \text{fF s}^{-1}\,\text{K}^{-1}\\ \left.\frac{\partial^2 Q}{\partial T^2}\right)_{\rm eop}&=\left.\frac{\partial^3 C}{\partial T^2\partial t}\right)_{\rm eop}=\{(-4.0\pm1.5)-i(-3.0\pm0.6)\}\,\text{fF s}^{-1}\,\text{K}^{-2}\end{aligned}\right.\qquad \text{for } dT>0.$$

$$\left\{\begin{aligned}\left.\frac{\partial Q}{\partial T}\right)_{\rm eop}&=\left.\frac{\partial^2 C}{\partial T\partial t}\right)_{\rm eop}=\{(+1.65\pm0.1)-i(+0.9\pm0.1)\}\ \text{fF s}^{-1}\,\text{K}^{-1}\\ \left.\frac{\partial^2 Q}{\partial T^2}\right)_{\rm eop}&=\left.\frac{\partial^3 C}{\partial T^2\partial t}\right)_{\rm eop}=\{(-5.0\pm0.4)-i(-1.4\pm0.3)\}\ \text{fF s}^{-1}\,\text{K}^{-2}\end{aligned}\right.\qquad \text{for } dT<0.$$

The data clearly show that the left-hand derivatives and the right-hand derivatives are not equal: there is differentiability breaking.

2. The coefficient $P_{\rm eop}$ and its derivatives

For the temperature derivatives, we easily see that the curve of $dC(T_{\rm pl}+dT,t_{\rm pl})$ as a function of dT is not analytic (see Figs. 3 and 4). Here too, we have to consider $dC(T_{\rm pl}+dT,t_{\rm pl})$ as a piecewise function made of two pieces: one for $dT>0$ and another for $dT<0$. Then we write down the two following expansions:

$$P^{\pm}(T_{\rm pl}+dT,\ t_{\rm pl})=P^{\pm}(T_{\rm pl},\ t_{\rm pl})+\left.\frac{\partial P}{\partial T}\right)_{\rm eop}^{\pm}dT+\cdots.$$

We obtain

$$\left.\begin{aligned}P)_{\rm eop}&=\left.\frac{\partial C}{\partial T}\right)_{\rm eop}=\{(+7.6\pm0.1)-i(+0.4\pm0.1)\}\ \text{pF K}^{-1}\\ \left.\frac{\partial P}{\partial T}\right)_{\rm eop}&=\left.\frac{\partial^2 C}{\partial T^2}\right)_{\rm eop}=\{(+1.6\pm0.5)-i(+0.5\pm0.2)\}\ \text{pF K}^{-2}\end{aligned}\right.\qquad \text{for } dT>0,$$

$$\left.\begin{aligned}P)_{\rm eop}&=\left.\frac{\partial C}{\partial T}\right)_{\rm eop}=\{(+6.7\pm0.1)-i(+0.2\pm0.05)\}\ \text{pF K}^{-1}\\ \left.\frac{\partial P}{\partial T}\right)_{\rm eop}&=\left.\frac{\partial^2 C}{\partial T^2}\right)_{\rm eop}=\{(+0.6\pm0.2)-i(+0.2\pm0.1)\}\ \text{pF K}^{-2}\end{aligned}\right.\qquad \text{for } dT<0.$$

All the data clearly show that the left-hand derivatives and the right-hand derivatives are not equal: there is differentiability breaking.

The time derivative of the first term of the expansions is $\partial P/\partial t)_{\rm eop}\cong M/t_{\rm pl}$. From the preceding experiments we obtain

$$M'_{+}\cong+0.1\ \ \text{pF K}^{-1},$$

$$M''_{+}=(+0.01\pm0.02)\ \ \text{pF K}^{-1}\quad \text{for } dT>0$$

and

$$M'_{-}\cong-0.05\ \ \text{pF K}^{-1},\quad M''_{-}\cong-0.03\ \ \text{pF K}^{-1}\quad \text{for } dT<0.$$

These values have to be compared with those of $t_{\rm pl}(\partial Q/\partial T))_{\rm eop}$ which read

$$t_{\rm pl}\left.\frac{\partial Q}{\partial T}\right)_{\rm eop}=\{(-0.45\pm0.15)-i(-0.28\pm0.08)\}\ \ \text{pF K}^{-1}\quad \text{if } dT>0,$$

$$t_{\rm pl}\left.\frac{\partial Q}{\partial T}\right)_{\rm eop}=\{(+0.2\pm0.05)-i(+0.45\pm0.05)\}\ \ \text{pF K}^{-1}\quad \text{if } dT<0.$$

The Schwarz equality is strongly violated because the signs are not as they should be. Besides the signs, if the equality was valid here, we would have $t_{\rm pl}(\partial Q/\partial T)_{\rm eop}=M=\text{const}$ for long enough $t_{\rm pl}$; obviously, this is not true since our data show that the value of the left-hand side depends on $t_{\rm pl}$.

3. The Schwarz theorem violation

Beyond the numerical values these results put in evidence the following qualitative features:

(i) the function Q_{eop} is continuous but its first and second derivatives (at least) with respect to temperature are not continuous (therefore, Q_{eop} is not differentiable);

(ii) the function P_{eop} is discontinuous and its first derivative (at least) with respect to temperature and time are discontinuous (therefore, P_{eop} is not differentiable);

(iii) the crossed second derivatives of C with respect to temperature and time are such that

$$\left.\frac{\partial P}{\partial t}\right)_{\mathrm{eop}}=\left.\frac{\partial^2 C}{\partial t\partial T}\right)_{\mathrm{eop}}\neq\left.\frac{\partial^2 C}{\partial T\partial t}\right)_{\mathrm{eop}}=\left.\frac{\partial Q}{\partial T}\right)_{\mathrm{eop}};$$

this means violation of Schwarz equality.

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