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Arkady P. Levanyuk, I. Burc Misirlioglu & M. Baris Okatan


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Landau, Ginzburg, Devonshire and others

Arkady P. Levanyuk^a, I. Burc Misirlioglu^{b,c}, and M. Baris Okatan^d

^aDepartment of Physics, University of Washington, Seattle, WA, USA; ^bFaculty of Engineering and Natural Sciences, Sabanci University, Istanbul, Turkey; ^cSabanci University Nanotechnology Research and Application Center, Istanbul, Turkey; ^dDepartment of Materials Science and Engineering, Izmir Institute of Technology, Izmir, Turkey

ABSTRACT

Macroscopic modeling of ferroelectric properties refers usually to Landau-Ginzburg-Devonshire theory. This paper questions the meaningfulness of this term, discussing contributions of the three authors in the title to what is supposed to be a theory. The limitations of every contribution are analysed. In the main text and, to more extent in the [Supplementary Material](#), the Landau theory is presented from an unusual perspective starting from simple mechanical models of spontaneous symmetry breaking and finishing by the Ising model. The aim of the presentation is to emphasize along with the qualitative breakthroughs the approximate character of macroscopic modeling associated with the above three authors.

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1. Introduction

The names of Landau and Devonshire are often mentioned in papers on ferroelectrics. Quite often one also mentions Landau-Ginzburg-Devonshire (LGD) which is more correct: it was Ginzburg [1] who, in 1945, first applied the Landau theory [2, 3] to ferroelectrics.¹ But how has this group formed? Were they doing the same though at different times? This is not a question from the point of science history only. There are conceptional differences between the approaches by Landau and Devonshire [4] which are useful to recall when both approaches are referred to in attempts to explain or describe experimental data. It is helpful to realize their limitations in order to not to be taken by surprise when the observed disagreements between the experiment and theory has a natural explanation: that the experimental conditions are beyond what the theory was designed for and not due to some imperfections in either the experiment or the theory.

An illustrative example is provided by the history of the findings by Minaeva et al. [5] in their study of sound propagation in uniaxial ferroelectric triglycinsulfate. The authors, inspired by theoretical results of Ref. [6], were investigating dependence of sound attenuation on the angle between the polar axis and the sound propagation

CONTACT Arkady P. Levanyuk  levanyuk@uw.edu

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¹We realize that usually when people mention LGD, they mean considering of gradients of polarization. This is unfortunate because Ginzburg was far from being the first to take into account this gradient term.

direction. They found that the predictions made with the use of Landau theory were qualitatively correct but in strong quantitative disagreement with the experiment. Within this paper the explanation is simple: an account for a nearly homogeneous depolarizing field excited by the acoustic wave, which was predicted to be the reason of angular dependence of the attenuation is beyond the Landau theory. This was overlooked both by the authoritative authors of Ref. [6] and by their readers. This was seemingly also the case of the author of a proposal to explain this disagreement [7]. Being both qualitatively meaningful and pioneering, such an attempt was equivalent to moving beyond the Landau theory while neither acknowledging the move nor analyzing such an important consequence that the theory stopped to be consistent [8]. As a result, a presumably new material constant has been introduced, the so-called ‘base dielectric constant’ which produced a lot of confusion including addition of this constant to the tables of material constants of ferroelectric materials. In effect, this ‘constant’ is nothing more than a parameter of a qualitative phenomenological model [8]. This parameter has a diffuse physical meaning and should be used with reservations and care though its order of magnitude can be, probably, realistically guessed. Anyway, it is not a material constant with a measurable numerical value as many people erroneously believed.

This unfortunate story shows that old theories, because of being old and, therefore, respected and convenient, are often used almost automatically without understanding their limitations. For this very reason, it is useful to reconsider such theories along with their conceptualities. In the same context, proposing new ways to teach them is certainly helpful for a sound development of science. The golden anniversary of the Ferroelectrics seems to be an appropriate occasion for such an undertaking, which is mainly pedagogical but also historical and methodological.

In the next section, the Landau theory is exposed from a different angle than by Landau himself. It is argued that, conceptually, this theory is closer to classical mechanics than to thermodynamics. This section is the longest in the paper and could be even longer if not being accompanied by the [Supplementary Material](#). It is recommended to be read before and to be consulted during the reading of the main text if some of its statements look non-evident. All the figures are in the [Supplementary Material](#) where they are numerated from 1 to 16. Reference (Sn) is to Section n of the [Supplementary Material](#). In [Sections 3](#) and [4](#), Ginzburg’s and Devonshire’s approaches are critically presented. In [Section 5](#), we comment on the role of the Landau theory in the macroscopic modeling of properties of ferroelectrics.

2. Landau

The Landau theory has been shown to be wrong in 1944 when Onsager published his exact solution of two-dimensional Ising model (see, e.g., [3]). A legend says that Landau spent a whole week trying hard to understand the Onsager paper and to check it, but the Onsager treatment was so complicated that he failed and stopped trying. During many years the contradiction between Onsager and Landau was a mystery for many scientists and motivation for others to understand its reason and to put forward a new theory equally general as the Landau one but without contradictions. Landau participated in these efforts since 1958 (see Ref. [3], Sec. 147) though he published nothing.

Huge collective efforts resulted about 1970 in construction of a modern theory of second order phase transitions (key words: critical indices, renormalization) which had some features common with the original Landau theory (see, e.g., [9]). They are: (i) to relate the second order phase transitions to spontaneous symmetry breaking with soft stability loss, (ii) to go beyond the standard thermodynamics by introducing what is called now the order parameter, (iii) to reveal universality of asymptotic behavior of a system close to the second order transition: this behavior is governed by the symmetry only, not by the physical meaning of the quantities involved. The modern theory of second order transitions is, practically, not referred to in the present-day ferroelectric studies. What people mean when mentioning Landau's name is his original, old theory. This is natural and we will comment in a proper place why it is so. Here we only mention that it is this theory which is of main interest in this paper. The main difficulty in exposing it is that, as it became clear as a result of development of the modern theory [9], the old one is not valid at the point of second order phase transition due to some thermal or quantum fluctuations. At the same time, this point is a reference point in the logic of the Landau theory. So that, to discuss its logic, it is better to begin with second order phase transitions without any fluctuations. Such transitions are possible in classical systems at zero temperature. For ferroelectric and other non-diffusional transitions this is a convenient starting point. To be illustrative we will consider mechanical models of crystals of the type often presented in textbooks: balls for atoms/ions connected by springs with whatever else that mimics interatomic/interionic forces. Since we will consider equilibrium structures only, the only branch of classical mechanics which we will refer to is statics. We will also emphasize the same Landau's achievements which were appreciated by the modern theory people. It will be argued that they are worth to be remembered in the studies on ferroelectric crystals also.

2.1. Spontaneous symmetry breaking

A symmetry 'breaks' when the structure loses some of its symmetry elements (operations) and converts into a structure with a smaller set of the symmetry elements (non-symmetrical structure, to be short). This is the so-called 'group-subgroup' transitions, meaning the groups of the symmetry elements. In mechanics this may happen even in a system with one degree of freedom (S1, Fig. 1). The term 'spontaneous' means that the loss of symmetry elements occurs due to change of a symmetry conserving *control parameter*, e.g., pressure or whatever else whose application conserves the symmetry properties of the system energy landscape² which are the reason of any symmetrical structure (The reader might find this expression vague and we refer the reader to the example below). That a symmetrical form of the energy landscape exists does not mean the system will also remain symmetrical. The loss of symmetry elements occurs because despite the symmetrical energy, the symmetrical structure becomes unstable. This happens because a minimum in the energy landscape which defined the symmetrical configuration can become a maximum or a saddle point without violating the symmetry of the energy landscape. The value of the control parameter when this happens is called its

²We mean energy landscape in the space of $N+1$ dimensions where N is the number of degrees of freedom of the system.

critical value. In the context of classical mechanical models what changes after crossing this point is the form of potential energy of the system (S1,2, Figs. 3,4,7). According to statics, referring to the balls & spring models considered in the [Supplementary Material](#), the potential energy is minimum when the balls are in their equilibrium positions, i.e., any set of displacements of the balls from these equilibrium positions lead to increase of the potential energy. But after crossing the critical point the symmetrical configuration corresponds not to minimum but to a saddle point (S2). This occurs without violating the symmetry of the potential energy (symmetry conserving control parameter) but the system obtains at least two equivalent directions for the most effective manner of diminishing of the potential energy and, of course, it does not miss the opportunity to go along in one of these directions. As a result, the system turns into one of two or more ‘less symmetrical’ equilibrium configurations which are equivalent with respect to the lost symmetry element(s) of the former equilibrium configuration.

2.2. Order parameter

The initial directions of the most effective diminishing of the potential energy or the directions of the fastest decent from the saddle point are straight lines in the N -dimensional (N is the number of the degrees of freedom) space of displacements of the balls from their positions in the symmetrical configuration of the system. For $N=2$ this is illustrated in S2. These directions present patterns of the ball displacements with respect to which the stability of the symmetrical structure is lost at the critical point (S2, S3). Note that all the directions appear simultaneously, i.e., they are all equivalent and transform one into another at symmetry operations of the symmetrical phase. The simplest case is when there are two patterns which differ whereby the same ball displaces in opposite directions. The amplitude of the pattern shows how far the breaking of the symmetry has gone. Reinterpreting the Landau theory, we are forced to call it order parameter. This is unfortunate and paradoxical: at spontaneous breaking of symmetry in classical systems at zero temperature, i.e., in the only dominion where the Landau theory is uncontested, there is no ordering but just displacements. It would be much better to call it in another way, e.g., as ‘symmetry breaking parameter’. But we will use the usual terminology believing that the reader’s confusion will still be less than with a consistent but unfamiliar terminology.

In the simplest case which we will discuss in the paper we have one-component order parameter (η). The two patterns correspond to different signs of η . All the symmetry operations of the symmetrical phase either do not change η or transform it to $-\eta$. Mathematically, this means that the order parameter transforms according to one-dimensional irreducible representation of symmetry group of the symmetrical structure. We emphasize that an exact knowledge of the pattern is not needed for the Landau theory. Its results are independent of the physical meaning of the order parameter. Nevertheless, this meaning is well defined for any specific case. Keep in mind that it treats about the amplitude of pattern of displacements (and its symmetrical equivalents) with respect to which the symmetrical structure loses its stability at the critical point. The Landau theory needs not to know this pattern to obtain its results. It needs only its transformational properties with respect to symmetry elements of the symmetrical

structure. But it is well understood that this pattern is unique for every system (model). The matter is that the loss of stability occurs always with respect to a single degree of freedom. Indeed, it treats about loss of stability with respect to any, even arbitrary small perturbations, so that this loss occurs immediately when such possibility arises for a set of symmetrically equivalent degrees of freedom without waiting for arising of instability conditions for another set at a further change of the control parameter. Importantly, by defining the order parameter through the pattern of displacements with respect to which the symmetrical phase loses its stability we must acknowledge that the order parameter has a *well-defined meaning close to the critical point only*. Indeed, the pattern of structural changes resulting from the stability loss is, naturally, close to the pattern with respect to which the stability loss occurs if the control parameter is close to its critical value and the two patterns coincide when the control parameter is at its critical value, i.e., just before disappearing. This is what is called the *soft stability loss*. But if we move away from the critical point further into the nonsymmetrical state, the structural pattern changes, there is no reason for it to remain rigid (See S3 in Suppl. Mat.).

2.3. Universality

In the above arguments we did not mention any specific model so that these arguments were *model-independent, universal*. Appearance of a saddle point instead of minimum of the potential energy with respect to any set of displacements of the classical bodies (balls in our story) from their positions in the symmetrical phase is what the spontaneous symmetry breaking consist of for the considered class of systems. In the simplest case this means existence of a degree of freedom (η) such that the potential energy as a function of η is minimum at $\eta = 0$ for the symmetrical structure but becomes maximum when the changing control parameter (p) crosses the critical point (p_c). The symmetrical structure becomes unstable but there appears the possibility of two nonsymmetrical equilibrium structures whose difference with the disappeared symmetrical one smoothly increases as the control parameter continues to change after crossing the critical point. The law governing this increase should become universal as $p \rightarrow p_c$. Landau had obtained this law: $\eta_e \propto \pm \sqrt{|p - p_c|}$, the subscript 'e' means 'equilibrium'. The law was found by minimizing the universal form of the potential energy which was derived expanding the potential energy $U(\eta, p)$ into Taylor series centered at $\eta = 0$ and keeping the minimum number of the terms. The potential energies of specific systems with soft spontaneous symmetry breaking are the closer to this form the closer is p to p_c . This form is:

$$U(\eta, p) = U_0(p) + a(p - p_c)\eta^2 + b\eta^4, \quad (1)$$

where $U_0(p)$ is unknown function and a, b are unknown constants. For the spontaneous breaking of symmetry to be soft the constant b should be positive.

Other universal laws can be obtained if we introduce the force h conjugated to η . This means that the term $-h\eta$ should be added to the right-hand side of Eq. (1). It is evident, both physically and formally, that when $h \neq 0$ then $\eta_e \neq 0$ at any value of p , i.e., the spontaneous symmetry breaking no more exists.

The function $\eta_e(h)$ is universal at $p = p_c$ and when $h \rightarrow 0$. The latter restriction is because the universal form of the potential energy at $p = p_c$ becomes exact for $\eta \rightarrow 0$ only (the Taylor expansion!). This law is $|\eta_e| \propto |h|^{\frac{1}{3}}$. One sees that $\frac{|\eta_e|}{|h|} \propto |h|^{-\frac{2}{3}} \rightarrow \infty$, as $h \rightarrow 0$, i.e., in the universality region

$$|\eta_e| \gg |h|, \quad (2)$$

when expressed in the same dimensions. One more universal result is:

$$\frac{d\eta_e(0)}{dh} \propto |p - p_c|^{-1} \text{ as } p \rightarrow p_c. \quad (3)$$

We see that the Landau theory is *predictive*. Remarkably, its predictions are relevant for a broad class of systems. This is because of the universality: all the patterns of the same symmetry properties exhibit the same behavior. Consider, for example, ferroelectric transition in BaTiO₃ and suppose, for simplicity, that only displacements of rigid Ti- and O-ions occur at the spontaneous symmetry breaking. The ‘pattern of displacements’, which lead to the change of symmetry at the spontaneous symmetry breaking, is the ratio of the displacements of the two ions, or the ratio of the polarizations due to these displacements, P_{Ti} and P_O . When studying the asymptotic behavior at $p \rightarrow p_c$ we can fix this ratio and concentrate on the behavior of the amplitude of the pattern. Changes in the form of the pattern, i.e., changes in the ratio are irrelevant to the asymptotic, they provide next order corrections. As we know from what is discussed above, the amplitude of the pattern, i.e., the order parameter is proportional to $\sqrt{|p - p_c|}$. Since the pattern can be considered as rigid, both P_{Ti} and P_O are proportional to $\sqrt{|p - p_c|}$. The same is valid for the full polarization $P = P_{Ti} + P_O$ and any other combination. That is why, referring to the universality region, one can identify the order parameter with the full polarization ignoring the real pattern with respect to which the symmetrical phase loses its stability at the spontaneous symmetry breaking. Once again, it is possible in the universality region only, not beyond it.

We have seen that the Landau theory provides several important universal results. Another matter is that, as we understand now, specific form of the universal dependencies ($\sqrt{|p - p_c|}$, $|p - p_c|^{-1}$, $|h|^{\frac{1}{3}}$) are valid for spontaneous symmetry breaking in classical systems at zero temperature only. But the revolutionary ideas of spontaneous symmetry breaking, order parameter and universality form an important part of modern theory of second order phase transitions.

The difficulties that the Landau theory experiences for non-zero temperatures, which were later overcome by the modern theory, are shortly mentioned in the [Supplementary Material](#). We have limited ourselves by outlining how they appear when one moves from spontaneous symmetry breaking in classical mechanical systems with a few degrees of freedom and without thermal motion (zero temperature) to more realistic systems with arbitrary large number of degrees of freedom exhibiting thermal motion (non-zero temperature). First, the same models which were discussed for zero temperature are considered for non-zero temperature. For systems with finite number degrees of freedom the idea of equilibrium loses its strict meaning and what has been called the spontaneous symmetry breaking at zero temperature converts into another phenomenon: splitting of peak in probability density of the order parameter. Instead of the potential energy for zero temperature this phenomenon can be described by what can be called

the Landau effective potential energy whose behavior is like that of the potential energy at zero temperature but with temperature entering the model as an additional control parameter. Transition to infinite systems converts the probability densities into a single or a pair of delta-functions, which, in the case of one degree of freedom, occurs at the limit of zero temperature only. For systems with infinite number of degrees of freedom this recovery is possible also for non-zero temperature though not for any infinite system but for those of 2D or 3D. The Landau effective potential energy acquires the meaning of the Landau free energy but, according to the modern theory, it proves to be a singular function of all its variables at the point of spontaneous symmetry breaking, making the Taylor expansion impossible and rendering the Landau theory inapplicable. It was already mentioned that finding of the new asymptotic behavior was a feat with participation of many scientists and a Nobel Prize for one of them [9]. But this new asymptotic behavior proved to be almost of no interest for the studies of ferroelectricity. This is a separate question which we will discuss in [Sec. 5](#).

Originally Landau did not start with zero-temperature classical system or non-diffusional transitions. Just the opposite: he begins with describing a crystalline structure in a way which considers the thermal motion. His main example of the control parameter was temperature. His first example was the atomic ordering in binary alloys, i.e., a diffusional transition. Also, he mentioned an ordering of NH_4 radicals in NH_4Cl where a huge λ -type anomaly of specific heat has been observed and then explained by Landau two years before compiling his famous paper [2]. Unfortunately, he paid no attention to the α - β transition in quartz which was interpreted as displacive (in modern terminology) about 10 years before [10]. He could not preview, of course, that his theory would have problems just with ordering which occurs due to change in temperature and will be ideally applicable to displacive transitions in classical models at zero temperature, which he did not even mention. The only term which can be found in his paper for what we call (unfortunately) the order parameter is 'degree of ordering'. Not an impressive difference.

It is probable that the first displacive phase transition which Landau became aware of was ferroelectric transition in BaTiO_3 (see the next Section). It was the BaTiO_3 structure which was used as an illustration of a second order transition in Sec.142 of Ref. [3]. However, this did not substantially influence the definition of the order parameter. Here is a quotation from the second and last Landau intravital edition of the *Statistical Physics*.

To give a mathematical description of a phase transition of the second kind, we define a quantity η which represents the extent to which the configuration of atoms in the less symmetrical phase differs from that in the more symmetrical phase, in the latter phase $\eta = 0$ and in the less symmetrical phase η has positive and negative values. For example, in a transition where there is a movement of atoms (as in BaTiO_3) η may be taken as the amount of displacement [11].

Well, the displacement of what? Of Ti or of O? Or, instead, maybe some deformation of the electronic clouds? In view of the above discussion the answer is: does not matter asymptotically or while we are in the universality region where the deviations from the asymptotical behavior are acceptable within our precision. Unfortunately, such a clarification is absent in this, otherwise magnificent, book. It sounds paradoxical but to our

knowledge there is no textbook with a consistent definition of the order parameter. This inevitably led to another difficulty. Instead of the potential energy used in the above zero-T version Landau introduced what was later called ‘constrained’ [12] or ‘incomplete’ [13, 14] thermodynamic potential. It treats about thermodynamic potential of a conditionally equilibrium system. According to Landau’s and Lifshitz’s Statistical Physics ([3], Sec.143) they mean thermodynamic potential ‘at fixed deviations from the symmetrical state, i.e., at fixed values of the order parameter’. This ‘i.e.’ is dubious. Given the universality, i.e., the irrelevance of the physical meaning of the order parameter to the asymptotic behaviors which results in infinite number of variants of physical meaning of the order parameter it remains unclear what to fix. It becomes meaningful if the order parameter is defined as the pattern of displacements with respect to which the more symmetrical structure loses its stability. This pattern of displacements is unique for every specific system and there is no doubt about what to fix though, within the universality region, one need to know nothing more than its symmetry properties. Beyond this region (whose boundary, recall, depends on our accepted precision) the structural changes brought to life by the stability loss cannot be characterized by a single variable except qualitatively within a model which does not claim to be exact, unlike Landau theory for zero-T classical models, which claim to be asymptotically exact.

3. Ginzburg

Ginzburg wrote in his memories [15] that he was impressed by the Landau theory since the pre-war times, in the very beginning of his scientific carrier. He dreamed to apply it to superfluidity and superconductivity. The obstacle was to guess what the order parameter was. It was several years after the end of the war that his idea about some wave function as the order parameter was assumed and justified by Landau. It resulted in Ginzburg’s Nobel Prize more than 50 years after the idea. It is hard to imagine a person who could estimate the importance of correct choice of the order parameter better than Ginzburg. But we go now to the time well before the idea and even before the end of the war when Ginzburg became aware of ferroelectric properties of BaTiO₃ discovered in a neighboring laboratory. Expectably, he applied the Landau theory to understand what ferroelectrics are and to explain the observations. He believed that the phase transition in BaTiO₃ was of the second order. The data were for polycrystalline samples and did not allow to establish the real order of the transition.

In 1970s, when commenting at his seminar on a talk about improper ferroelectrics where the order parameter is not polarization even in the symmetry aspect, Ginzburg remembered how in 1944 he discussed with Landau what the order parameter was for BaTiO₃. It was something like: ‘Displacements of some ions? And then we agreed that the polarization was also valid’. We do not know why they agreed and if they considered the universality. We have already argued that within a simple model, where the total polarization of BaTiO₃ has two additive contributions, P_{Ti} and P_O , due to the shifts of the corresponding ions, Ginzburg’s choice of the order parameter as $P = P_{Ti} + P_O$ is valid. He could also say that, since the order parameter had the same transformational properties as polarization, why not to use the polarization itself. Moreover, it should be introduced anyways to calculate observable quantities. So, Ginzburg’s

choice was natural but valid for the vicinity of phase transition only. He did not make a reservation which was natural: neither Landau made it.

Ginzburg justified the choice of polarization for the role of the order parameter in the manner frequently used until now: it is something which is absent in the non-ferroelectric phase but is present in the ferroelectric one. Excessive freedom given by this criterium was not mentioned. But the next step was consistent with the Landau theory. He wrote the ‘constrained’ free energy as

$$\Phi = \Phi_0 + \alpha P^2 + \frac{\beta}{2} P^4 - EP, \quad (4)$$

where E is the electric field, Φ_0 , α and β are functions of temperature and pressure. The Landau spirit is in use of a thermodynamic potential as a function of P and E simultaneously. In conventional equilibrium or ‘unconstrained’ thermodynamics one uses thermodynamic functions of external parameters whose fixation defines the equilibrium state and they are either E or P (another pair preferred by other authors is E and D , we will not discuss this question that is irrelevant to this paper). Let us discuss the meaning of Eq. (4) following the previous Section, i.e., starting with zero temperature ferroelectric transition in a system governed by classical mechanics. We have a slab of the ferroelectric material with ideal electrodes connected to an exceptionally large capacitance which fixes the voltage, i.e., the electric field in the slab. Then Φ is the potential energy of this two-part system. The first three terms constitute the potential energy when the electrodes are short-circuited, so that there is no electric field and we have a transition in a mechanical system with pressure as the control parameter, i.e., what we considered in the previous Section. The entirety of Eq. (4) is the potential energy of the system when the electrodes are connected to the capacitor (for more detail see Ref. [16]). Its minimum provides the equilibrium, i.e., the observable, value of P (P_e):

$$2\alpha P_e + 2\beta P_e^3 = E \quad (5)$$

Thus, Ginzburg derived the electrical equation of state with the use of which he explained the main properties of ferroelectrics. Of course, he did not consider zero temperature transitions. Like Landau did, he considered temperature as one more control parameter which is rightful to the same extent as pressure. Anyway, Ginzburg works was a breakthrough. Using a simple mathematics, he explained the main properties of ferroelectrics. It was the beginning of what an immense number of papers was later devoted to. Now, 75 years after his first work it might be easy, as well as useful and instructive, to criticize him (together with Landau) but he was a pioneer and it is unfortunate that his name is sometimes excluded from the ‘troika’ by those who naively believe that his contribution is only the account for gradients of the order parameter (in the latter, by the way, he was far from being the first).

4. Devonshire

Devonshire studied BaTiO_3 to far more detail than Ginzburg. He had more experimental data to explain: monocrystals of BaTiO_3 were already available in the West. In particular, he considered not one- but three-component polarization vector. But we are interested in his differences with Ginzburg of other nature and will imagine that

Devonshire considered one-component polarization and second order transition as well. He mentioned neither Landau theory nor Ginzburg's paper. It is unclear if he was aware of them. In principle, he could. The first Ginzburg's paper was published in English before development of the cold war with all its disastrous consequences for the exchange of scientific information between the Soviet Union and the West. But Devonshire's omission is not surprising anyway given that the Landau theory was basically neither accepted nor understood in the West until a decade later when the famous Ginzburg-Landau paper on superconductivity became known. It surprised the western scientific community by the abundance of results 'obtained from nothing', i.e., from the Landau theory applied to superconductors.

Devonshire followed the line which was begun by Mueller and Cady for Rochelle salt (see a good review by Kanzig [17]). They remained within the framework of usual thermodynamics and used conventional, not 'constrained', thermodynamic functions among whose variables were either P or E , not both at the same time. The Mueller-Cady theory was based on an important assumption that the same expressions for the thermodynamic potentials are valid for both paraelectric and ferroelectric phases. This was a deviation from the Gibbs theory of phase equilibrium. In his theory the two phases, A and B, coexist in equilibrium if their thermodynamic potentials, $G_A(p, T)$ and $G_B(p, T)$, are equal and, importantly, $G_A(p, T)$ and $G_B(p, T)$ are considered as independent functions. The possibility to describe the properties of the both phases by a single $G(p, T, P)$ or by a more complicated, e.g., with components of the strain tensor σ_{ik} instead of p , but still a single function is not evident though may seem natural. The argument [17] is that unlike Gibbs who referred to so different phases as liquid water and ice, we deal with the case where one phase is, in effect, a distortion of the other. The electric equation of state was obtained from a thermodynamic relation

$$E = \frac{\partial G}{\partial P} \quad (6)$$

where $G(T, P)$ is a thermodynamic potential whose Taylor expansion can be written down using symmetry arguments. In the simplest case $G(T, P)$ is given by the first three terms of Eq. (4). Then using the thermodynamic formula, one obtains Eq. (5). The subscript 'e' is not needed now because only equilibrium quantities are considered to be physical so that the thermodynamic potential for the values of P other than the equilibrium ones, i.e., obtained from Eq. (6) is virtually considered as a mathematical tool whose physical meaning is not specified in contrast to the Landau theory and the line followed in the [Supplementary Material](#). The temperature dependences of coefficients α and β which were taken from the Landau theory by Ginzburg, in the Mueller-Cady-Devonshire case had to be taken from the experimental data for the two phases. The form of $G(T, P)$ as a function of P at different temperatures was similar to that of Figs. 3,4 or to the form of Ginzburg's free energy for $E = 0$. But unlike the latter it was for any value of E . When referred to the paraelectric phase (Fig. 3) all the points of the curve correspond to equilibrium states for different values of E . But when it treats about the ferroelectric phase (Fig. 4) Eq. (6) provides equilibrium (stable), metastable and unstable solutions for P corresponding to a hysteresis loop for homogeneous polarization unrealizable in experiment but conceptually important.

The Mueller-Cady-Devonshire approach has left many questions unanswered. One can agree that a ferroelectric phase is a distortion of the paraelectric one. But why one uses the thermodynamic variables only to describe the distortion? The changes in structure can be tricky. Does the value of ratio of displacements of O and Ti ions in BaTiO₃ influence the energy? Evidently, yes. Then why only the thermodynamic, total polarization was enough for Devonshire? Yes, he was successful to fit experimental data available to him for all three ferroelectric phases of BaTiO₃. But what about new data? Given that he used data for small electric field, $\varepsilon_0 E \ll P$, can we expect that his thermodynamic potential would be valid for studies such as, e.g., electrocaloric effect in very thin films or effects of homogeneous depolarizing fields mentioned in the Introduction? Since in both mentioned cases the electric field is strong, $\varepsilon_0 E \sim P$, the expectations lack a foundation. Attempts to answer, within microscopic theory, the question why Devonshire was successful [18, 19, 20] has revealed that the success was not guaranteed.

5. Is it the Landau theory which is popular in ferroelectric community?

Recall once more that the Landau theory does not claim more than an asymptotic exactness. If we add that for many-body systems it can rightfully claim this for spontaneous symmetry breaking with soft stability loss in zero-temperature classical models only one may wonder why it is so popular in the ferroelectric community. Indeed, all the ferroelectric phase transitions in perovskites are due to change in temperature and they are of the first order, i.e., they are with a hard stability loss. Nevertheless, people fit experimental data within what they call LGD theory without any care for the universality region and become surprised when the fitting is not good. Often, there will be good agreement with experiment, what is not trivial and is worth discussing.

We will discuss this question after but now consider zero-temperature first order phase transition in a classical system. Let the system be driven to the stability loss from the symmetrical phase. What happens next is a jump wise change in the system structure unlike that we considered in Sec. 2 where we put the coefficient b in Eq. (1) positive. Now we should put it negative but Eq. (1) becomes physically meaningless with no finite minima, i.e., with no finite equilibrium value of η . To go back to physics, we must add the next term in the η expansion, that of the sixth order to have:

$$U(\eta, p) = U_0(p) + a(p - p_c)\eta^2 + b\eta^4 + c\eta^6 \quad (7)$$

with $c > 0$. Have we generalized the Landau theory to first order transitions (something he never did)? No, this is not the Landau theory anymore. As it was emphasized earlier, the Landau theory is asymptotically exact when p tends to p_c . It was so because $\eta_e(p)$ went to zero at $p \rightarrow p_c$ so that the first terms of the Taylor series become sufficient to represent the whole function (for the η values of interest, i.e., for η close to η_e) more and more exactly. But this is impossible for the first order transitions because $\eta_e(p_c) \neq 0$. What Eq. (6) represents is not the Landau theory. This is something superficially similar but lacking the main achievement of the Landau theory, i.e., its exactness although at the asymptotic limit and in special conditions only. Eq. (6) is useful but not as Landau theory but as a phenomenological model which provides important

qualitative and reasonable quantitative results with an appropriate choice of the coefficients but it cannot claim asymptotic exactness anywhere, unlike the Landau theory. So, what is used in the ferroelectric community should be properly called as, say, Landau-like phenomenological models meaning that they use idea of order parameter (not strictly defined unlike the Landau theory), respect the symmetry in the same way as Landau did, consider temperature as a control parameter and pay no attention to inapplicability of the Landau theory to a soft spontaneous symmetry breaking in many-body systems at finite temperatures (S6).

But why are these models so successful? Why did Devonshire manage to describe so well temperature-driven transitions in BaTiO_3 in a wide temperature range? This question is asked since long ago [18, 20] and an exhaustive answer is lacking. Some general ideas can be formulated, however. We should ask ourselves what ‘a wide temperature range’ means? Wide comparing with what? An answer clearly formulated in Ref. [19] but going down to several previous authors is that this ‘what’ is the so-called, ‘atomic temperature’, i.e., $10^4 - 10^5$ K. This is a natural scale of temperature dependence of crystal where there are no semi-independent, i.e., weakly coupled with the rest, ions or radicals which are ordered at zero temperature and become disordered at relatively low temperatures about the energy of this weak coupling. So how the phase transitions occur at much lower temperatures as it happens in perovskites? The answer is by chance or due to mutual canceling of two large (atomic!) contributions specific to the perovskite structure. This idea was virtually put forward by Slater in 1950 [21] and was supported repeatedly including recent observations [22] of BaTiO_3 films on substrate providing misfit strain about 1% and leading to an increase in the temperature of the ferroelectric phase transition by about 500 K. This is naturally explainable by the strain-modified cancelation of the above mentioned ‘atomic’ contributions. So that the temperatures of order of $10^2 - 10^3$ K are relatively low and not far from 0 K where the Landau theory is uncontested though not for a hard but for a soft spontaneous symmetry breaking. However, if the ‘hard’ is not too hard but is not extremely far from being soft then reality might be also not too far from what Landau predicted. This argument has been voiced by Ginzburg in 1949 [23] and is valid now also.

From another side, Devonshire’s success should not be overestimated. It was impressive, of course, that all three ferroelectric phases came out from temperature dependence of a single coefficient. But trying to achieve not only qualitative but also quantitative agreement, he was forced to suppose a temperature dependence of another coefficient with the scale of this temperature dependence being much smaller than the atomic temperature. This has incited suspicion of Vaks [20] who tried to explain this temperature dependence by the failure of Landau theory close to the point of spontaneous symmetry breaking at non-zero temperature. However, in Ref. [24] it was proposed to conserve terms up to eighth order in polarization instead of sixth order as in the original Devonshire expansion. It was found that the temperature dependence of the coefficient which Vaks was worried about was unnecessary to assume. Then additional experimental data were analyzed in Ref. [25] to conclude that both eighth power terms and the temperature dependence of the famous coefficient should be considered. This process seems unlimited. The Devonshire thermodynamic potential will change unlike the Landau theory which can be rethought and taught in different ways but will explain and predict the same basic things which it did in 1937.

6. Conclusion

One of the widespread ways to answer the question what the Landau theory consists in is saying that it is the mean field approximation for the Ising model. This paper is a protest against this saying. It is correct that the mean field approximation for the Ising model results in the Landau theory but it is not correct that this theory consists in this approximation. The Ising model whose role in the development of theory of phase transitions cannot be overestimated is a model of order-disorder phase transitions, i.e., the transitions which are driven by changes in temperature only. We argued that the most appropriate way to present the Landau theory is not from the order-disorder but from the displacive perspective. Unlike the order-disorder transitions the displacive ones are possible at zero temperature when they are driven by change in pressure of another non-thermal control parameter. When they are of the second order and are considered for classical models the Landau theory is correct without any reservation. Thus, discussion of such transitions is the most natural starting point for teaching the Landau theory. They are also natural starting point to understand the essence of the Landau-like modeling of the ferroelectric properties. Indeed, nowadays almost all the ferroelectric studies are concentrated on perovskites or similar materials. These transitions are mainly displacive (no transition is purely displacive if occurs at non-zero temperature) and their temperatures are low comparing with the natural scale of temperature dependences in this type of materials which is the so-called ‘atomic temperature’ (10^4 –105 K). Thus, the displacive perspective is much closer to the reality for the perovskite modeling than the order-disorder one.

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References

- [1] V. L. Ginzburg, On the dielectric properties of ferroelectric crystals and of barium titanate, *Zh. Eksp. Teor. Fiz.* 15, 739 (1945) [*J. Phys. USSR* 10, 107 (1946)].
- [2] L. D. Landau, On the Theory of Phase Transitions, 193–216, *Collected Papers of L.D. Landau* ed. by D. Ter Haar, (Pergamon, Oxford, 1965) [I: *Phys. Z. Sowjetunion* 11, 26, 1937; *Zh.Eksp.Teor Fiz.* 7, 19, 627 (1937). II: *Phys. Z. Sowjetunion* 11, 26, 545, (1937); *Zh.Eksp.Teor Fiz.* 7, 627 (1937)]
- [3] L. D. Landau, and E. M. Lifshitz, *Statistical Physics*, 3rd ed., part 1 (Elsevier, Oxford, 1980).
- [4] A. F. Devonshire, Theory of barium titanate - Part1, *Philos. Mag.* 40 (309), 1040 (1949). DOI: [10.1080/14786444908561372](https://doi.org/10.1080/14786444908561372); Theory of barium titanate - Part2, *Philos. Mag.* 42 (333), 1065 (1951). DOI: [10.1080/14786445108561354](https://doi.org/10.1080/14786445108561354); Theory of ferroelectrics, *Adv. Phys.* 3, 85–130 (1954). DOI: [10.1080/00018735400101173](https://doi.org/10.1080/00018735400101173).
- [5] K. A. Minaeva, B. A. Strukov, and K. Varnstorff, Anisotropy of Sound Absorption in Triglycine Sulfate Single Crystals, *Sov. Phys. Solid State* 10, 1665 (1969).

- [6] S. Y. Geguzina, and M. A. Krivoglaz, Influence of Long Range Dipole Dipole Forces on Attenuation and Velocity of Ultrasound in Ferroelectrics Near Second Order Transition Point, *Sov. Phys. Solid State* 9, 2441 (1968).
- [7] A. K. Tagantsev, The role of the background dielectric susceptibility in uniaxial ferroelectrics, *Ferroelectrics* 69 (1), 321 (1986) DOI: [10.1080/00150198608008205](https://doi.org/10.1080/00150198608008205); Landau Expansion for Ferroelectrics: Which Variable to Use?, *Ferroelectrics* 375, 19 (2008). DOI: [10.1080/00150190802437746](https://doi.org/10.1080/00150190802437746).
- [8] A. P. Levanyuk, B. A. Strukov, and A. Cano, Background dielectric permittivity: material constant or fitting parameter?, *Ferroelectrics* 503 (1), 94 (2016). DOI: [10.1080/00150193.2016.1218245](https://doi.org/10.1080/00150193.2016.1218245).
- [9] L. P. Kadanoff, Theories of Matter: Infinities and Renormalization in The Oxford Handbook of Philosophy of Physics, ed by Robert Batterman (Oxford University Press, New York, 2013)
- [10] R. E. Gibbs, Structure of a quartz, *Proc. Roy. Soc. A* 110, 443 (1926). DOI: [10.1098/rspa.1926.0025](https://doi.org/10.1098/rspa.1926.0025).
- [11] L. D. Landau, and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Oxford, 1969), p. 429. We refer to this edition because the wording was changed in the 3rd edition and BaTiO₃ was no more mentioned. The meaning of the quotation remained the same.
- [12] R. Alben, An exactly solvable model exhibiting a Landau phase transition, *Am. J. Phys.* 40 (1), 3 (1972). DOI: [10.1119/1.1986433](https://doi.org/10.1119/1.1986433).
- [13] A. P. Levanyuk, Contribution to the Theory of Phenomena Near Second Order Phase Transition Points, *Sov. Phys. Solid State* 5, 1294 (1963) [*Fiz. Tverd. Tela* 5, 1776 (1963)]
- [14] B. A. Strukov, and A. P. Levanyuk, *Ferroelectric Phenomena in Crystals* (Springer, Berlin, 1998).
- [15] V. L. Ginzburg, *About Science, Myself and Others* (IOP Publishing, Bristol, 2005).
- [16] A. P. Levanyuk, and B. A. Strukov, Ferroelectricity 192-201 in: *Encyclopedia of Condensed Matter Physics*, ed by F. Bassani, G.L. Liedl, P. Wyder (Academic Press, 2005). DOI: [10.1016/B0-12-369401-9/00435-6](https://doi.org/10.1016/B0-12-369401-9/00435-6).
- [17] W. Känzig, *Ferroelectrics and Antiferroelectrics* (Solid State Reprints, Academic, New York, 1957).
- [18] P. C. Kwok, and P. B. Miller, Free energy of displacive ferroelectrics, *Phys. Rev.* 151 (2), 387 (1966). DOI: [10.1103/PhysRev.151.387](https://doi.org/10.1103/PhysRev.151.387).
- [19] V. G. Vaks, Phase Transitions of the Displacement Type Ferroelectrics, *Sov. Phys. JETP* 27 (3) 486 (1968) [*Zh. Eksp. Teor. Fiz.* 54, 910 (1968)]
- [20] V. G. Vaks, Correlation Effects in Displacement Phase Transitions in Ferroelectrics, *Sov. Phys. JETP* 31, 161-167 (1970) [*Zh. Eksp. Teor. Fiz.* 58, 296 (1970)].
- [21] J. C. Slater, The Lorentz correction in barium titanate, *Phys. Rev.* 78 (6), 748 (1950). DOI: [10.1103/PhysRev.78.748](https://doi.org/10.1103/PhysRev.78.748).
- [22] K. J. Choi *et al.*, Enhancement of ferroelectricity in strained BaTiO₃ thin films, *Science* 306 (5698), 1005 (2004). DOI: [10.1126/science.1103218](https://doi.org/10.1126/science.1103218).
- [23] V. L. Ginzburg, Theory of ferroelectric phenomena, *Usp. Fiz. Nauk*, 38 (8), 490 (1949) (in Russian). DOI: [10.3367/UFNr.0038.194908b.0490](https://doi.org/10.3367/UFNr.0038.194908b.0490).
- [24] Y. L. Li, L. E. Cross, and L. Q. Chen, A phenomenological thermodynamic potential for BaTiO₃ single crystals, *J. Appl. Phys.* 98 (6), 064101 (2005). DOI: [10.1063/1.2042528](https://doi.org/10.1063/1.2042528).
- [25] Y. L. Wang *et al.*, Landau thermodynamic potential for BaTiO₃, *J. Appl. Phys.* 101 (10), 104115 (2007). DOI: [10.1063/1.2733744](https://doi.org/10.1063/1.2733744).