



Analogy, extension, and novelty: Young Schrödinger on electric phenomena in solids[☆]

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ARTICLE INFO

Article history:

Received 15 December 2009

Received in revised form

14 July 2010

Accepted 31 December 2010

Keywords:

Schrödinger, E.

Dielectrics

Physical realism

Wave mechanics

ABSTRACT

The analysis of Erwin Schrödinger's first major theoretical work demonstrates his early commitment to Boltzmann's statistical–mechanical tradition, which also influenced his later contributions to quantum theory. It further reveals two central elements of his research style: The extension and modification of works by others, and the extensive use of analogies. Schrödinger extended Debye's theory of liquid dielectrics using Langevin's and Weiss's theories of magnetism, taking a formal analogy between mathematical laws of two separate phenomena as an indication for a physical analogy between them. His approach followed his commitment to “scientific realism”. Schrödinger attributed “reality” to the basic assumptions of a theory and therefore explored their consequences in various domains. For him, accordance with experimental findings proved the correctness of his assumptions. Following this methodology, Schrödinger advanced a kinetic (i.e., statistical) theory of solid dielectrics. His 1912 theory explained the behavior of solid dielectrics in an external electric field, piezoelectricity, pyroelectricity, and the change of melting temperature with pressure. It even provided a microphysical explanation for solidification itself. These explanations, however, required several rather speculative and doubtful assumptions, stemming from Schrödinger's reliance on analogy. This illustrates one of the pitfalls of the use of analogies.

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When citing this paper, please use the full journal title *Studies in History and Philosophy of Modern Physics*

1. Introduction

Historians and philosophers of science have spent considerable effort on studying Erwin Schrödinger's contribution to quantum mechanics, his disagreements with colleagues about its interpretation, and his later struggles in search of a unified field theory.¹ Yet, little has been written about Schrödinger's early

work. This is surprising in view of the role of early works in shaping scientific methodologies,² and even more so since historians have seen in Schrödinger's methodological and philosophical position a key to the special character of his contribution to quantum theory (wave mechanics). Moreover, Wessels (1983, p. 272) claimed that “Schrödinger's commitment to finding a coherent description of microsystems,” which guided his work on wave mechanics was rooted in his formative years in Boltzmann's institute in Vienna, and that his early papers were written under that influence. However, neither Wessels nor others have analyzed Schrödinger's methodology in his early papers. Among Schrödinger's early theories, the 1912 “Studies on the kinetics of dielectrics, their melting point, and their piezo- and pyroelectricity,” is the most extensive and elaborated (Schrödinger, 1912b, page numbers in parentheses refer to this paper). In this paper, he proposed a statistical microphysical theory of solid insulators, displaying an ambition similar to that of his later contributions to

[☆]The authors are members of the *Project on the History and Foundations of Quantum Physics*, a collaboration of the Max Planck Institute for the History of Science and the Fritz Haber Institute of the Max Planck Society in Berlin. The authors are grateful to Massimiliano Badino for many interesting discussions and helpful remarks. We would like to thank the participants of the Quantum History Reading Group at the Max Planck Institute for the History of Science for their comments on our presentation of this work; and Dieter Hoffmann, Christoph Lehner, Arne Schirmacher, Skúli Sigurdsson for comments on earlier versions of this manuscript.

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¹ E.g., Gerber (1969), Wessels (1979), Kragh (1982), Mehra and Rechenberg (1987), Beller (1999), Bertotti (1985), Bitbol (1996).

² See, e.g., Cassidy (1979) for a discussion of the impact of Werner Heisenberg's early work on his later professional style.

quantum theory. The present article analyzes this paper in its context, exploring young Schrödinger's methodology and style of research, and going beyond earlier studies in establishing Schrödinger's actual commitment to Boltzmann's approach.

Schrödinger considered himself a follower of Ludwig Boltzmann through his teachers Franz Exner and, foremost, Fritz (Friedrich) Hasenöhl. Both were students of Boltzmann. In his early theoretical work, Schrödinger followed Boltzmann's tradition of statistical atomistic explanations. His intention to extend the explanatory range of statistical theory guided his choice of topics. On a deeper level, the same tradition shaped his methodology and his understanding of the aim of physical theory. The summary of Schrödinger's paper (p. 1972) echoes Boltzmann's claim that "[i]t is precisely the main task of science to fashion the pictures [*Bilder*] that serve to represent a range of facts in such a way that we can predict from them the course of other similar facts" (Boltzmann, 1897, p. 242).³ This sentence resembles Newton's famous *dictum*: "The basic problem of philosophy seems to be to discover the forces of nature from the phenomena of motions and then to demonstrate the other phenomena from these forces" (Newton, 1999, p. 382). Yet, the differences between the two statements reveal more about the characteristics of Boltzmann and his followers than the similarities. Boltzmann did not claim that the suggested pictures are induced from phenomena. Unlike Newton, he and Schrödinger developed theories from hypotheses about unobserved entities (atoms, dipoles) and relations between them. They believed that by ascribing reality to these hypotheses, and by following their consequences for other phenomena, they would be able to "learn something new" about the hypothetical entities (Boltzmann, 1897, p. 242).

In his methodology of "scientific realism," Schrödinger treated theoretical entities like atoms, dipoles and waves, "as if" they were real. As Michel Bitbol claimed on the basis of Schrödinger's later writings, this kind of scientific realism agrees well with Schrödinger's metaphysical anti-realism, i.e., the view that the notion of a reality independent from human perception is meaningless. Bitbol characterizes the "two faces of Schrödinger's attitude towards the concept of 'reality'" as follows: "Fully recognize that the 'real objects which surround us' are nothing else than constructs, but take these constructs *very* seriously, since they are a precondition for our life. And conversely, when you have found a clear and adequate theoretical construct, do not diminish its significance by calling it *just a product of our minds, or a mere symbolic pattern*; think it is exactly the same type of structure as the one you are accustomed to call 'a real object.'"⁴ Thus, if our sense of reality is not rooted in an outside world independent of our mind, but only in our thought, as the metaphysical anti-realist holds, one is justified to ascribe the same kind of "reality" to theoretical entities as to observable bodies. The available evidence does not allow a reconstruction of Schrödinger's metaphysical stance in the early stages of his career.⁵ It does, however, allow conclusions about his realist methodology. While young Schrödinger was impressed and influenced by the philosophy and methodology of Ernst Mach (Moore, 1989, pp. 41–46), his theory of dielectrics does not display Mach's influence. Schrödinger's commitment to the

tradition of Boltzmann continued to shape his scientific work throughout his life, including his contributions to quantum mechanics.

Beyond his interests and commitments, Schrödinger's early work reveals two chief characteristics of his research strategy. In his 1933 Nobel lecture, Schrödinger characterized his work as follows:

Although I can work only very poorly in collaboration, and unfortunately also not with students, my work is never *entirely* independent as my interest in a question always rests on the interest of others in that same question. My word is seldom the first, but often the second, and is inspired by the desire to contradict or to rectify, even though in the end, the consequent extension might prove much more substantial than the initial contradiction that only served as the point of departure (Schrödinger, 1935, pp. 362–363, emphasis in the original).⁶

This strategy is apparent in Schrödinger's 1912 paper whose "point of departure" was a modification of a claim made by Debye and whose content was an "extension" of Debye's theory of dielectrics. Schrödinger "rectified" Debye's theory assuming, unlike Debye, that the basic assumptions of the theory are not restricted to liquids but valid also for solids. Schrödinger's paper not only exemplifies the fertility of extension and the novelty that can emerge when transferring ideas from one realm to another, but also the often speculative character of such an extension.

In developing his theory, Schrödinger followed an analogy between dielectrics and magnetism. He noticed a resemblance between the mathematical descriptions of the two phenomena. Following this formal analogy, he assumed a "physical analogy," to employ Maxwell's term, i.e., that the physical processes which lead to similar laws be similar (Maxwell, 1890, pp. 155–159). He thus supposed that the process leading to electric polarization in dielectrics resembles the one responsible for magnetic polarization (i.e., magnetization) in magnets. The analogy enabled him to employ not only mathematical results but also physical concepts from Paul Langevin's and Pierre Weiss's studies of magnetism within the new context of dielectrics. Adding a hypothesis of his own about the existence of permanent inner electric polarization in all solid insulators, Schrödinger transferred their hypotheses from para- and ferromagnetism to dielectrics.⁷ The extensive use of physical analogies is the second important characteristic of Schrödinger's research style. Analogy also played an important role in his later development of wave mechanics (see, e.g., Joas & Lehner, 2009). By closely examining Schrödinger's theory of dielectrics, we show how the use of analogy facilitated theory construction, yet, at the same time, concealed the introduction of problematic assumptions.

Schrödinger presented his theory of solid dielectrics when new information about the structure of solids became available through the new X-ray diffraction experiments. Within a few years, the results of these experiments would render Schrödinger's assumptions doubtful. Thus, the date of Schrödinger's publication enables the historian to identify some of the possible notions about the structure of crystals that the new X-ray crystallography would exclude. The limited knowledge about the microstructure of solids allowed Schrödinger a considerable freedom in his assumptions and thus in elaborating his theory. This freedom, however, was a dubious advantage, as it left

³ Quoted after Boltzmann (1974, p. 47).

⁴ Bitbol (1996, pp. 13–14) (emphasis in the original); see also: pp. viii–ix, 34–41; Wessels (1979).

⁵ To our knowledge, Schrödinger's private notes from the late 1910s provide the earliest evidence for such a position. He noted that fluctuation phenomena could provide "a new proof of the relative validity of Boltzmann's conception as opposed to [general] thermodynamics. *Absolutely valid theories do not exist.*" (transcribed in Hanle, 1975, p. 268).

⁶ Pagination according to the reprint in the collected papers. See also Darrigol (1992).

⁷ As explained in Section 3, Weiss's (1907) theory of ferromagnetism drew heavily on prior work on paramagnetism by Langevin (1905). It is therefore often referred to as the Langevin–Weiss theory, even though it is not a product of collaboration. We follow this convention in the present paper.

Schrödinger with too many possible hypotheses and too few restrictions on the theory. Schrödinger followed his theoretical convictions as well as the initial inspiration by Debye's theory in choosing among these hypotheses. Along the way, Schrödinger adopted assumptions that had already been advanced earlier in explaining piezoelectricity and pyroelectricity, namely the existence of permanent electric dipoles and of a permanent inner polarization in crystals.

Although a number of authors discuss Schrödinger's theory of dielectrics to some extent, they do not adequately describe its dependence on earlier works, and do not put it in its context. In particular, the important role of the theories of Langevin and Weiss has been overlooked so far. Consequently, the significance of these theories for Schrödinger's intellectual development and his scientific style has not been recognized.⁸

In Section 2, we discuss Schrödinger's motivation for developing a theory of dielectrics within his scientific context. Section 3 describes the theories by Langevin, Weiss, and Debye, upon which Schrödinger built his theory. Section 4 deals with Schrödinger's extension of Debye's theory, and the hypotheses explicitly and implicitly introduced in this process. Section 5 focuses on the role of the analogy to magnetism and its bearing on the basic ideas and assumptions of the theory. Section 6 follows Schrödinger's development of the theory to describe several, previously unconnected, phenomena, e.g., by using macrophysical knowledge, and the way he related his results to empirical data. Section 7 builds on the analysis of the previous sections to discuss the accomplishments, the plausible and less plausible consequences, and the limitations of Schrödinger's theory. This analysis allows for a reconstruction of Schrödinger's aims and the reasons for the limited reception of his theory. A brief conclusion evaluates the roles of analogy and "realist" methodology in Schrödinger's work.

2. The origins and context of the theory

"The following," Schrödinger wrote in the introduction to his 1912 paper, "merely consists of several not uninteresting consequences of a simple remark that I would like to add to the beautiful work of Mr. Debye, 'Some Results of a Kinetic Theory of Insulators.'" (p. 1938). Indeed, Debye's paper on liquid dielectrics, published eight months before the presentation of Schrödinger's work, appears to be the direct inspiration for Schrödinger's theory of solid dielectrics (Debye, 1912a). If Schrödinger later often built on the work of others, he was especially open to external stimulation in 1912. The then 25-year-old assistant at the Institute of Physics of the University of Vienna aspired to a career in theoretical physics, but still had no accomplishments in the field. He was looking for proper subjects to display his physical and mathematical abilities.

Paul Ehrenfest, rather than one of the Schrödinger's teachers, introduced him to the subject of his first theoretical paper. In February 1912, Ehrenfest visited Vienna and, rather accidentally, had a long meeting with the young assistant. Over lunch and in a café, Schrödinger learned about Langevin's and Weiss's theories of magnetism. "Schrödinger was so swept up by Ehrenfest's enthusiasm [for these theories] that he went on to study the subject thoroughly, give some seminars on it, and then write a paper of his own on diamagnetism." (Klein, 1970, p. 175).⁹ Beyond

Ehrenfest's enthusiasm, Langevin and Weiss offered an extension of Boltzmann's approach of statistical physics, well-fitting the inclination of the young Viennese. In elaborating on Langevin's theory, Schrödinger (1912a) acquired an expertise in Langevin-Weiss theory that facilitated its use in other contexts. He therefore had a clear interest in papers that used it, like Debye's. Moreover, Debye presented his work as a defense of statistical mechanics, which must have appealed to Schrödinger.¹⁰

Debye's starting point had been a discrepancy between the theoretical predictions and the observed electric behavior of liquid insulators. According to Debye, this discrepancy left two choices: One either had to abandon the equipartition theorem that lies at the heart of statistical mechanics or one had to "modify or improve the basic hypothesis concerning the structure of insulators" (Debye, 1912a, p. 97). The first choice would have added to the rising skepticism about the validity of the equipartition theorem. In another place, Debye (1912b) explicitly connected this skepticism to the introduction of quantum hypotheses in theories of black-body radiation and of the specific heats of solids. For dielectrics, Debye preferred the second alternative, favoring statistical mechanics over a quantum hypothesis. He provided a statistical-molecular account for the behavior of liquid dielectrics by adding an assumption about their structure. By following Debye, also Schrödinger implicitly preferred statistical mechanics over a quantum hypothesis. This was common. At the time, virtually nobody advanced quantum hypotheses for the phenomena studied by Schrödinger.¹¹ Still, such a preference should not be seen as a dogmatic rejection of quantum hypotheses. Debye's publication of a quantum theory of specific heat only a month after the appearance of his paper on dielectrics illustrates his pragmatic attitude towards the use of quantum hypotheses. In the latter paper, Debye rejected the validity of the equipartition theorem for the energy distribution in solids. Already two years earlier, he had published a quantum theory of black-body radiation (Debye, 1910, 1912b, c).

In applying different assumptions to resolve quantitative discrepancies with experiments, Debye's theories of specific heat and of insulators exemplify the problem-oriented physics characteristic of his teacher Arnold Sommerfeld. Recently, Suman Seth has called Sommerfeld's engagement with concrete questions and puzzles "physics of problems," and contrasted it with a search for general principles, which characterized the work of scientists like Planck and Einstein. Einstein put the emphasis somewhat differently: He saw Debye as a virtuoso, in contrast to a "Prinzipienfuchser," i.e., someone who is concerned with fundamental questions and principles, such as Ehrenfest, Bohr and himself (Seth, 2010). In concentrating on the extension of Boltzmannian principles of statistical physics, rather than on solving problems like Debye did, Schrödinger showed the characteristics of a "Prinzipienfuchser."¹² This early interest in basic laws and processes constitutes another persistent element of his scientific style.

Schrödinger seized the opportunity to extend the explanatory range of the molecular kinetic view of physics by accounting for phenomena hitherto beyond its reach, like the change in melting

(footnote continued)

In other words, his choice of research topics was apparently quite independent already at an early stage. See also Meyenn (1992).

¹⁰ Another reason for Schrödinger's interest in Debye's paper might have been the coincidence between Debye's topic and former research of Schrödinger's teacher Hasenöhr (Mayerhöfer, 1980). See also Moore (1989, pp. 37–41, 49–53, 75–78) and Scott (1967, p. 17).

¹¹ The one exception we are aware of is Boguslawski (1914).

¹² The separation between virtuoso and "Prinzipienfuchser" is not equivalent to that between theories of principle and theories of construction. In statistical mechanics, a "Prinzipienfuchser" (like Ehrenfest or Schrödinger) often constructs a theory in order to show the usefulness of Boltzmann's fundamental principles.

⁸ The two extensive biographical studies of Schrödinger by Moore (1989, pp. 59–62) and Mehra and Rechenberg (1987, pp. 113–118) discuss Schrödinger's 1912 paper on dielectrics. Moore did not only neglect the role of Langevin's work but also failed to notice the statistical basis of Schrödinger's theory. Hanle (1975) does not discuss Schrödinger's theory of dielectrics, in spite of its statistical basis. Brief discussions of the paper can be found in Scott (1967) and Darrigol (1992).

⁹ Thus, unlike Darrigol (1992, p. 240) claims, not all of "Schrödinger's early works derived from activities developed in the Viennese physicists' community."

temperature with pressure, and piezo- and pyroelectricity. He argued that statistical mechanics explained well the thermodynamic properties of gases and liquids, but not those of solids (pp. 1937–1938). In this vein, extending the methods of statistical mechanics to solids and solidification appears as a natural direction of development. Towards the end of the nineteenth century, Maxwell–Boltzmann statistics, originating from the thermodynamics of gases, was spread into the study of liquids (osmotic pressure, electrochemical concentration cells). During the first decade of the 20th century it was further applied to solids. In 1905, Hendrik Lorentz used the Boltzmann distribution in his study of the electron gas in electric conductors, and Langevin used it for magnetically polarized molecules in his theory of magnetism. Since the statistical theorems had been deduced for gas molecules, both Lorentz and Langevin (1905, pp. 115–116) had to justify their use for electrons or molecules in solids (Kaiser, 2001, pp. 262–263). Seven years later, Debye and Schrödinger adopted Langevin’s reasoning without expressing any need to justify the use of methods originally conceived for the statistics of gas molecules.

The particular phenomena that Schrödinger examined seem rather incidental to his aim to extend the molecular-kinetic explanation into solids. The one exception was the change of melting temperature with pressure, which was related to the general thermodynamical concept of phase transition. The general behavior of solid dielectrics was well explained by the electron theory. Piezo- and pyroelectricity, on the other hand, lacked an accepted explanation (Katzir, 2003). Piezoelectricity—the generation of electric voltage differences by pressure in specific directions in crystals—was discovered by the brothers Jacques and Pierre Curie in 1880.¹³ Already the Curies had connected piezoelectricity to pyroelectricity—the generation of electric polarization by heat in some crystals, a phenomenon known since the 18th century. Although several molecular explanations had been suggested for these phenomena, beginning with the Curie brothers, no model gained considerable acceptance. The earlier models could not account for all phenomena at the same time. The later models were speculative and rather arbitrary, and at best could regain the results of the phenomenological theory suggested in 1890 by Woldemar Voigt. Voigt’s theory, which was widely accepted, accounted for the experimental data, even if it said nothing about the absolute magnitudes of the effect. Since ca. 1895, the study of piezo- and pyroelectricity was a quiet field, which posed no serious challenge to Voigt’s phenomenological theory. Only one attempt at a novel explanation of the phenomena was advanced in that period: In 1901, Lord Kelvin (William Thomson) explained the effect on the grounds of a novel model of the atom. Like Kelvin’s theory, Schrödinger’s explanation of piezoelectricity followed from a new model—in this case of solids—rather than from a development within the field of piezoelectricity.

3. The theories of Debye, Langevin and Weiss

To facilitate the understanding of Schrödinger’s theory—his adoption, adaptation, and extension of previous results—we briefly describe the theories of Debye, Langevin and Weiss, as far as they are relevant to Schrödinger’s theory of solid dielectrics. Debye based his 1912 kinetic theory of liquid dielectrics on the assumption that “the interior of [liquid] dielectrics contains not only elastically bound electrons, but also permanent dipoles of constant electric moment” (Debye, 1912a, p. 97). Assuming that

the orientations of the molecular dipoles in an external field obey the laws of statistical mechanics, Debye derived their contribution to the electric polarization of the liquid. He found that for weak external fields E this contribution “has the Curie–Langevin form $E \cdot a/T$, where a is a constant, T the absolute temperature” (Debye, 1912a, p. 98).¹⁴ In addition to the external field, Debye considered the field induced by the molecules (E_i), using Lorentz’s result that $E_i = P/3$ (where P is the electric polarization) and generalizing it to apply not only to the elastically bound electrons (considered by Lorentz) but also to the permanent dipoles. This enabled him to derive an expression for the dielectric constant as a function of the temperature and two characteristic constants of the material. Debye’s new expression resolved the discrepancy between the results of statistical mechanics and the observed behavior of liquid dielectrics.

Langevin had derived an equation in the form used by Debye seven years earlier. Arguing by an analogy to gas molecules under the influence of gravity, he claimed that the energies of the magnetic dipoles also obey a Boltzmann distribution (Langevin, 1905).¹⁵ Assuming a uniform external field H penetrating the material and neglecting interactions between the dipoles, Langevin had derived an expression for the total magnetization per unit volume (I) of a paramagnetic material (in Schrödinger’s notation):

$$I = Nm \left(\coth \alpha - \frac{1}{\alpha} \right). \quad (1)$$

Here, Nm is the maximum polarization per unit volume (created by N dipolar molecules of magnetic moment m), and $\alpha = mH/kT$ (with k “Boltzmann’s” constant and T absolute temperature). In his 1912 theory, Debye only used an approximate form of Langevin’s expression.¹⁶

Two years later, Weiss extended Langevin’s theory to derive the spontaneous magnetization in ferromagnets. While Langevin’s theory explained paramagnetism, i.e., the induced magnetization in the presence of an external magnetic field, Weiss explained ferromagnetism, i.e., the presence of a finite magnetization even in the absence of an external field. The magnetization in Langevin’s theory is dependent on the presence of an external magnetic field, as can be seen from Eq. (1) for $H=0$. Weiss had to find a substitute for the external field in the case of ferromagnets. He replaced it by what he called the molecular field: “I assume,” he wrote, “that each molecule feels an action equal to that of a uniform field [...] proportional to its own intensity of magnetization and in the same direction, from the ensemble of surrounding molecules” (Weiss, 1907, p. 662, emphasis in the original).¹⁷

The molecular field was closely connected to Weiss’s concept of elementary crystals, a concept which would become central in Schrödinger’s theory. Already in 1905, Weiss had introduced this concept in an explanation of magnetism that relied on structure, without any use of statistics. He conceived the concept in his effort to understand the complex behavior of pyrrhotite (pyrrhotite), a magnetic crystal with which he had experimented:

We will thus assume that the complex structure of the crystal results from the juxtaposition of elementary crystals [...]

¹⁴ This expression actually is an approximate form of Langevin’s expression in the limit of weak external fields.

¹⁵ The energy of a dipolar moment \mathbf{m} in a field \mathbf{F} is given by $W = -\mathbf{m} \cdot \mathbf{F} = -mF \cos \vartheta$, where ϑ is the angle between field and dipole. The same relation holds regardless whether field and dipoles are magnetic or electric.

¹⁶ He used the weak-field limit of Eq. (1), i.e., $I = mN\alpha/3$ (valid for $mH \ll kT$). See Section 5. For a history of Langevin’s theory, see Navarro and Olivella (1997).

¹⁷ See also Langevin (1905, pp. 115–117). The assumption that all the molecules are subject to the same field was an essential condition in Langevin’s derivation.

¹³ A year later, they discovered the converse effect (which Schrödinger did not treat in his 1912 paper).

which each on their own possess a maximum and a minimum in their rectangular magnetization [i.e., an easy and a hard axis of magnetization]. These crystals are arranged in the magnetic plane at angles of 60° or, which amounts to the same, 120° (Weiss, 1905, p. 482).

Weiss believed that he had demonstrated experimentally that “the existence of the simple material [i.e., the elementary crystals] is certain” (Weiss, 1905, p. 483). Although he was unable to isolate an elementary crystal, he believed that this was possible in principle, and that he had managed to measure the inner magnetization of these elementary crystals. In his 1907 elaboration of Langevin’s theory, he extended his assumption from pyrrhotine to other crystals, assuming “that the crystals studied so far were formed by juxtaposition or interpenetration [*pénétration*] of simpler [elementary] crystals of various orientations.” Although Weiss mentioned a possible interpenetration of the elementary crystals, references to them in his paper suggest that he thought of them as spatially separated structures.¹⁸

Before working on solid dielectrics, Schrödinger (1912a) extended the treatment of diamagnetism in Langevin’s theory to resolve a discrepancy in the diamagnetic behavior of metals: In contrast to Curie’s expectation and Langevin’s (1905, p. 70) derivation, the magnetic susceptibility of metals was found to depend on temperature.¹⁹ Langevin had treated the diamagnetic contributions of the bound electrons in the molecules in detail and had only sketched how the conduction electrons in a metal might contribute to the magnetic susceptibility, following a suggestion by J. J. Thomson (Langevin, 1905, pp. 89–90). Schrödinger analyzed their contribution to the magnetic susceptibility, finding that they lead to a diamagnetic contribution which depended on temperature. For the case of Bismuth, Schrödinger found a reasonable quantitative agreement with experiment, while for all other metals he studied, the predictions of his new theory were far off. He explained this apparent contradiction by suggesting that the diamagnetism of the conduction electrons predicted by his theory was partly compensated by the paramagnetism discussed by Langevin (Eq. (1)).

4. The extension of Debye’s theory

In his very next paper, on dielectrics, Schrödinger (1912b), as mentioned, used Debye’s theory of liquid dielectrics as the starting point, extending it into solids. Debye (1912a, p. 99) had claimed that in solids “the molecules are no longer free to rotate” and therefore his statistical calculation is no longer valid, as it hinges on rotational freedom of the dipolar molecules. Schrödinger, on the other hand, assumed that the polar molecules could rotate also in the solid state, like the magnetic dipoles in theory of ferromagnetism (p. 1943). Debye had already pointed to a possible analogy. He had shown that at a certain “critical” temperature, his theory led to an infinity in the dielectric constant. He had inferred that below this critical temperature “polarization in the substance may occur without an external field,” so that “the critical temperature T_k plays a part analogous to the so-called Curie point for ferromagnetic substances” below which spontaneous magnetization appears (Debye, 1912a, p. 99). Debye, however, did not worry about the implications of this

result since already above the critical temperature, the dielectric would solidify and his theory could not be applied.

Schrödinger “rectified” (to use his words quoted in the introduction) Debye by identifying the dielectric critical temperature T_k with the melting temperature. For him, “the solid bodies owe the cohesion of their parts to that same intense self-electricization [*Selbstelektrisierung*].” (p. 7) In other words, solidification is due to the electrostatic forces arising from a “spontaneous” self-polarization: Below the critical temperature, the electric dipoles point approximately in the same direction (or directions, see below) and thus generate a strong polarization within the solid.

Schrödinger’s identification of the melting temperature with Debye’s critical temperature depended on viewing solid dielectrics as crystals. Since he assumed that the electric dipoles are arranged according to the structure of the material, and that they point along a preferred axis, the underpinning material structure should also be anisotropic (e.g., it cannot be amorphous). Here, Schrödinger’s dependence on recent developments in physics and chemistry becomes apparent. The view that all solids are crystals, while amorphous bodies are in fact liquids with high viscosity entered into textbooks only a decade earlier.²⁰ Schrödinger’s explanation of solidification as a result of electric interactions also fitted well the *Zeitgeist*: At the beginning of the century, many physicists assumed that electromagnetism would help unify larger portions of physics, even if they did not believe in the possible reduction of all phenomena to electromagnetic interactions, as proposed by advocates of the “electromagnetic view of nature” (Jungnickel & McCormach, 1986; McCormach, 1970; Katzir, 2005).

The identification of solidification with electrification followed theoretical reasoning rather than inference from experimental data. Nevertheless, a number of empirical findings supported this identification. First, it was able to explain the sharpness of the liquid-to-solid transition, i.e., the sudden change in the properties of substances at the melting point. Second, it qualitatively agreed with observed jumps in the magnitude of the dielectric coefficient that occur with the transition from solid to liquid.²¹ Third, Schrödinger could have found support in the discovery of a discontinuity in the specific heat near the Curie point in ferromagnets by Weiss and Beck (1908). The discontinuity suggested a close connection between magnetic and thermodynamical properties of matter. The analogy between magnets and dielectrics suggested a similar link between the dielectric and the thermodynamical properties.

However, empirical data contradicted a straightforward identification of the critical temperature with the melting point. As mentioned, the dielectric critical temperature T_k , calculated from Debye’s theory using data for liquids, was lower than the melting temperature of these substances. To resolve this discrepancy, Schrödinger argued that in solids, due to their anisotropy, the electric field produced by the molecules themselves (i.e., without external field) is no longer $E_i = P/3$, as Debye assumed following Lorentz. Schrödinger, however, argued that Lorentz’s derivation is invalid for the anisotropic case.²² This replacement, he claimed

¹⁸ For instance, Weiss (1907, p. 669) assumed that, unlike other kinds of iron which possess a single preferred direction, industrial iron is composed of tiny elementary crystals that make the “substance isotropic in appearance.”

¹⁹ Curie (1895, p. 289) already knew that his expectation did not hold for Bismuth. Honda (1910) and Owen (1912) demonstrated a temperature dependence for most diamagnetic elements experimentally.

²⁰ Schrödinger refers to (Nernst, 1909, p. 98). The idea that all solids are crystals appeared for the first time in the 4th edition, signed November 1903 (English translation of the 4th edition). It does not appear in earlier editions (e.g., 3rd edition from 1900).

²¹ In the case of benzophenone, for instance, the dielectric coefficient jumps from about 13 to about 3 at roughly the same temperature (Schrödinger, 1918, pp. 222–223).

²² For solids, he claimed, one is no longer allowed to assume spherical cavities, as Lorentz had done, but needs to replace them by ellipsoidal cavities. Schrödinger did not mention the Dutch physicist by name, but clearly referred to Lorentz (1909, pp. 132–139, 303–306), which is mentioned by Debye.

without a proof, leads to a new relation for the total electric field

$$E_t = E + E_i:$$

$$E_t = \frac{\mu}{3} P, \quad (2)$$

where μ is a material parameter, larger than one, characteristic of a given solid.²³ The new parameter led to a higher dielectric critical temperature T_k . By calculating the appropriate value of μ for several substances by assuming that T_k is equal to the melting temperature, Schrödinger resolved the discrepancy (pp. 1943–1944). Schrödinger's argument, however, holds only for the transition from solid to liquid but not for the reverse transition, since the liquid is isotropic and thus Lorentz's derivation remains valid. Schrödinger only hinted at this deficiency in his argument, by claiming that in cooling $\mu = 1$ can hold also for temperatures below the melting point. Yet, he did not provide any argument how in the process of cooling a liquid, μ can be higher than 1 above the critical temperature provided by Debye's expression.²⁴ The analogy between dielectrics and ferromagnets most probably inspired Schrödinger to devise this argument. He mentioned, but did not rely on, a similar argument by Weiss for the relations between the "molecular fields" and the intensities of magnetization along the three axes, the counterparts of the electric field and the polarization (pp. 1940–1943).²⁵ As we show below, in other cases Weiss was not only an inspiration but also a direct, yet at times problematic, source for Schrödinger.

5. The analogy to magnetism

"I believe," Schrödinger explained in a letter to Ehrenfest, "that the electric analogue of Curie's point of which Debye talks, is the melting point, so that solid (crystallized) dielectrics possess a (very high) permanent electric moment."²⁶ Schrödinger indeed extended the analogy between the magnetization in ferromagnets and the electric polarization in dielectrics by attributing physical meaning to a result regarded only as a formal peculiarity by Debye. Thus, he turned a formal analogy physical, or "material" in Mary Hesse's terms (Hesse, 1963).²⁷ While Debye had assumed electric dipoles, which can be seen as analogous to magnetic dipoles, Schrödinger assumed that the electric dipoles in solids are ordered to produce a finite electric moment (polarization) in analogy to the ordering of the magnetic dipoles that leads to finite magnetic moment in Langevin–Weiss theory. Note that the formal similarity between the two critical temperatures originated from the fact that both theories explained polarization in terms of hypothetical magnetic and dielectric dipoles. Of the six components of the analogy (magnetic dipoles–magnetic

polarization–critical temperature: Electric dipoles–electric polarization–critical temperature) only two (magnetic polarization and its critical temperature [the Curie temperature]) were observable.²⁸ The success of the molecular theories to account for phenomena of magnetism and liquid dielectrics supported the dipole hypothesis, the basis of the analogy. The more general analogy between the phenomena of magnetism and electric polarization, known since the eighteenth century, likely encouraged Schrödinger to assume an analogous mechanism for both cases. Still, at the bottom, the analogy was between theoretical entities rather than between observable effects. Schrödinger's endorsement of the analogy reveals his high trust in hypothetical entities, in agreement with his "scientific realism."

Subscribing to a physical reading of the analogy between magnets and dielectrics, Schrödinger returned to Langevin's full expression (Eq. (1)) instead of the approximate form used by Debye. Adding the contribution of bound electrons, which does not have a counterpart in magnets, he obtained for the electric polarization (p. 1941)

$$P = 3bE_t + Nm \left(\coth \alpha - \frac{1}{\alpha} \right), \quad (3)$$

where b is a constant stemming from the contribution of the elastically bound electrons, and in this case m is the electric moment of a molecule, and

$$\alpha = \frac{mE_t}{kT}. \quad (4)$$

Combining Eqs. (3) and (4) with Eq. (2) for the case without external field, Schrödinger found that only one specific nonzero polarization $P = P_s$ inside the crystal "is stable and must therefore always occur spontaneously" (p. 1942).

In explaining the origin of Langevin's expression, Schrödinger referred only to the assumption of electric dipoles that are free to rotate. Thereby, he incorrectly implied that the spontaneous polarization is due to this assumption alone. However, in transferring Langevin's expression, Schrödinger carried with it the assumptions made by Weiss in his treatment of ferromagnetism, the closer counterpart to Schrödinger's case. Although he mentioned Weiss's discussion, he did not mention that Weiss's derivation was based on the assumption of a uniform "molecular field". This assumption by itself already presupposes that the dipoles align along a single (preferred) axis and therefore the emergence of spontaneous polarization. Following Weiss, Schrödinger thus assumed order (uniform field) to explain an ordered phenomenon (polarization). It is unclear whether Schrödinger was aware of this. Relying on the analogy instead of deriving the expressions for the case of dielectrics, Schrödinger left this significant assumption unacknowledged. In this sense, analogies may not only reveal, but also conceal.

Schrödinger was more cautious in pointing out that the microphysical analogy between dielectrics and ferromagnets breaks down when it comes to their *macroscopic* behavior. Due to reasons explained below, dielectrics in general do not possess permanent macroscopic electric polarization as opposed to the permanent macroscopic magnetization of ferromagnets. According to Schrödinger, the analogy extends to the macroscopic behavior only in the case of piezo- and pyroelectric materials, which can show polarization without an external field.²⁹ Even in

²³ In general, μ has different values for each of the three axes, so Schrödinger introduced two additional parameters, λ and λ' .

²⁴ Since $\mu = 1$ in liquids, T_k gets its value from Debye's expression and is lower than the melting temperature (T_m). In solids, $\mu > 1$ and $T_k = T_m$. Thus, the temperature of solidification (i.e., a transition from liquid to solid) should be lower than the melting temperature (i.e., a transition from solid to liquid). So there is a temperature region in which a substance is either liquid or solid depending on its history, i.e., a hysteresis. Schrödinger claimed that the phenomenon of supercooling agrees with the two values that he ascribed to μ . However, following his theory rigorously, supercooling must exist for every liquid dielectric and extend over a considerably wider range of temperatures than observed.

²⁵ See Debye (1912a, p. 98) and Weiss (1907, pp. 667–668).

²⁶ Schrödinger to Ehrenfest, November 2, 1912, Archives for the History of Quantum Physics (the letter is misdated in the AHQP).

²⁷ This change in the role of the analogy finds an interesting parallel in Schrödinger's development of wave mechanics. Louis de Broglie had discussed an analogy between mechanics and optics in his wave theory of matter without further elaborating on it. Schrödinger realized the full potential of the optical-mechanical analogy by transforming it into a guiding principle for the construction of wave mechanics (Joas & Lehner, 2009).

²⁸ In the case of dielectrics, one cannot observe the appearance of electric polarization below the critical temperature, as one can in magnetism.

²⁹ Schrödinger (p. 1945) even called these materials "ferroelectric" (if you will) [*ferroelektrisch* (s.v.v.)] (quotation marks in original). He did not "anticipate ferroelectricity" as Busch (1987, pp. 274–275) claims, as he did not consider the effect of an electric field on the spontaneous polarization, a phenomenon for which the name "ferroelectricity" was coined in the 1920s.

piezo- and pyroelectric crystals, the analogy to ferromagnetism is incomplete, as an external electric field is unable to induce a polarization that persists after removing the external field. Still, the presence of a spontaneous polarization in these materials might have encouraged Schrödinger to assume inner permanent polarization in *all* dielectrics. For the case of pyroelectricity, an analogy between magnetism and electric polarization had already been suggested several times since the middle of the 18th century and, after the discovery of piezoelectricity in 1880, was extended to that phenomenon. Among other consequences, the analogy had led to the idea of permanent inner polarization in pyroelectric crystals (Katzir, 2006, pp. 27–29).

Probably the most curious concept that Schrödinger adopted through the analogy to magnetism was that of Weiss's "elementary crystal." He chose the "elementary crystal," instead of a real crystal, as the basic entity for his theoretical analysis. Following Weiss's 1907 definition, Schrödinger explained:

We therefore have to assume at least some types of crystals to consist of *interpenetrations* [*Durchdringungen*] of elementary crystals so that, in a physically finite volume, matter is evenly divided into two or more elementary crystals (or directions of polarization), while only physically infinitesimal or, let us say, very small volumes are built like an elementary crystal (p. 1958, emphasis in the original, see also pp. 1948–1949).

He thus suggested that each observable volume of the crystal consists of small and interpenetrating elementary crystals that could not be isolated experimentally but still contained a large enough number of molecular dipoles to allow for the application of statistics. Since the elementary crystals were not observed in experiment, they had to be smaller than experimentally detectable. It was quite common among contemporary authors to assume a small volume that is still large enough for statistical considerations, e.g., Lorentz in *The Theory of Electrons* (Lorentz, 1909). Schrödinger did not elaborate on the way the elementary crystals form a macroscopic crystal. Apparently, he pictured a crystal as a three-dimensional ordered "mosaic" of tiny elementary crystals with a simple lattice structure, each polarized into a certain direction and surrounded, at least partly, by surface charges which compensate its inner polarization.³⁰

In general, the arrangement of the elementary crystals follows the macroscopic symmetries of the crystal as a whole. In particular, Schrödinger detailed the structure of quartz, for which he adopted the arrangement of elementary crystals suggested by Weiss for pyrrhotite in 1905. The arrangement of several elementary crystals yields zero net polarization of the composite crystal, despite the nonzero polarization of each of its elementary constituents. Similar arrangements in which the polarizations of elementary crystals in different directions compensate each other are able to explain why most classes of crystals do not display a spontaneous polarization. Even if most crystals are not polarized as a whole, Schrödinger's view of solidification depends on the assumption that every elementary crystal develops spontaneous polarization. The polarization determines the electric properties of solids and thereby their cohesion and their melting temperature. Formally, the polarization of the elementary crystals only was able to play this important role because Schrödinger treated each elementary crystal independently. He derived the physical relations for each phenomenon (dielectrics, piezoelectricity,

pyroelectricity, changes in melting temperature with pressure) first for an elementary crystal, and then summed the effects of the individual elementary crystals. Only the sum of the *induced* polarizations for each elementary crystal were then added up to yield the total induced polarization for the real crystal as a whole.

Like Langevin's equations, the assumption of elementary crystals and its interpretation carried with them their history, even though it was left unacknowledged by Schrödinger. Weiss's 1905 theory did not aim at establishing a kinetic basis for magnetism. For Weiss, although he did not elaborate on this, the magnetization of an elementary crystal seems to originate from the material structure of the crystal, whose details he left unspecified. Two years later, when combining his earlier ideas with Langevin's statistical treatment, the directions of the dipoles could not be fixed in space and the elementary crystal became a domain in which the inner "molecular field" is uniform. Yet neither Weiss nor Schrödinger, who tacitly adopted Weiss's view, explained or even hinted at the reason why this uniform field is formed. To Weiss's assumption, Schrödinger added the hypothesis of surface charges on the circumference of the elementary crystals that would screen their internal electric fields. Weiss did not need this hypothesis since he neither assumed unobservable polarization (necessary for example for Schrödinger's account of piezoelectricity) nor did he explain phenomena as a result of processes within isolated elementary crystals. Thus, the picture of solids that followed from Schrödinger's assumptions was more complex and therefore less plausible than the already questionable one suggested by Weiss. It was certainly more hypothetical as it referred to the whole class of solid insulators, while Weiss discussed only specific ferromagnets. Moreover, Weiss could relate the assumed magnetic polarization to experimental observations while Schrödinger's analogous electric polarization remained entirely hypothetical.³¹

6. The elaboration of the theory

Equipped with his basic equations and the concept of elementary crystals, Schrödinger explained several phenomena. First, he derived the dependence of the polarization induced in an elementary crystal by an external electric field \mathbf{E} . The derivation was considerably simplified by the anisotropy of the elementary crystal, i.e., by the existence of a preferred axis of polarization, and by the limit of weak external fields.³² Relying on Eq. (2) between polarization and total electric field and using an expansion of the total polarization \mathbf{P} around \mathbf{P}_s ,³³ he found

$$P_x - P_s = \frac{3b}{1 - \mu b} + \frac{9T_k f'(\alpha_s)}{\mu T} E_x$$

$$P_y = \frac{3}{\mu(1 - \lambda)} E_y$$

$$P_z = \frac{3}{\mu(1 - \lambda')} E_z \quad (5)$$

where $f'(\alpha)$ is the derivative with respect to α of Langevin's function

$$f(\alpha) = \coth(\alpha) - 1/\alpha$$

³¹ The magnetization has a direct external manifestation, while the electric polarization is assumed to be screened by surface charges.

³² The preferred axis allowed Schrödinger to assume that for fields $E \ll P_s$, the direction of the total polarization does not deviate much from that of the spontaneous polarization P_s without field.

³³ Schrödinger employs a suitable coordinate system where the direction of spontaneous polarization coincides with the x -axis, $\mathbf{P}_s = (P_s, 0, 0)$, i.e., there are no cross-terms relating, say, P_y with E_x .

³⁰ The surface charges would explain why the inner polarization of piezoelectric crystals could not be observed (p. 1957). They are also needed to explain why the polarization of a given elementary crystal does not influence the electric dipoles of the other elementary crystals and therefore also not their polarization. This is a necessary assumption for Schrödinger's theory to hold, even though Schrödinger did not state it explicitly.

and α_s is the value of the auxiliary variable α without external field (i.e., for $P=P_s$). α_s is still a function of temperature.

Eqs. (5) recover the well-confirmed linear relationship between the components of the observed polarization and the components of the external electric field ($P_i = \varepsilon_i E_i$, where ε_i is the dielectric coefficient in direction i). The recovery of this basic relation (which had already been accounted for by Lorentz's electron theory) was a necessary condition for any new theory of dielectrics to be accepted. In principle, Schrödinger also provided an expression for the value of the dielectric coefficient, but since Eqs. (5) are for an *elementary crystal*, they could not be used directly to calculate observed values, and Schrödinger did not provide an estimate of the magnitude of the dielectric coefficients (pp. 9–14).

The restriction of Schrödinger's derivation to external fields considerably smaller than the spontaneous polarization ($E \ll P_s$) was not a real limitation of his theory, since the inner polarization predicted by his theory was large with respect to the electric fields used in the laboratory. Schrödinger estimated the magnitude of the inner polarization from the values of the maximum polarization P_0 in liquid dielectrics as calculated with the help of Debye's theory (p. 1962). Eqs. (5) are not valid for temperatures close to the critical temperature. Schrödinger considered this a merit of his theory, since it suggested anomalies in the behavior of dielectrics slightly below the melting point.³⁴

Since, for Schrödinger, a real crystal is made of elementary crystals with different axes of polarization, the resulting polarization in each direction is a complicated arithmetic mean of nonlinear functions of temperature. This, in a sense, helped Schrödinger, because the temperature-dependence that he found for elementary crystals contradicted experimental results for most materials. Schrödinger's dielectric coefficient (i.e., the relation between polarization and field) decreases with increasing temperature, while experiments showed an opposite tendency in most materials (Schrödinger, 1918, pp. 214–216). The contributions of different elementary crystals may compensate each other's dependence on temperature, but it is difficult to see how adding contributions that decrease with temperature would lead to an increase of the total dielectric coefficient. Schrödinger pointed at a possible extension of his theory that would be able to provide an effect in the correct direction. The extension would take into account that the bound electrons of the molecules are likely to have "different directions of easy polarizability." He justified this extension by pointing to the inner structure of the molecules (pp. 1962, 1970–1971). The theory in his paper, however, assumed unchangeable dipoles and he did not elaborate on an extension in this direction.

After showing how his assumptions account for the relation between electric field and observed polarization, Schrödinger turned to piezoelectricity. He assumed that a small mechanical deformation of the elementary crystal induces an electric field that depends on the spontaneous polarization. This assumption followed naturally, although not necessarily, from the presence of spontaneous polarization. Since the polarization results from the molecular dipoles, it was plausible that deformation, which changes the place and orientation of the molecules, modifies the total polarization. In addition, one also had to take into account that deformation changes the surface charge density of the elementary crystals. It is important to note that Schrödinger did not assume a change in the magnitude of the electric moment of the dipoles, but only a change in the total polarization. Employing

³⁴ In his review article on dielectrics, Schrödinger (1918) does not mention any measurements of the dielectric constant of solids near the melting point. Still, the drastic difference between the dielectric constants of many materials above and below the solid–liquid transition suggests such anomalies (see footnote 21 for an example).

a method similar to the one used for dielectrics, Schrödinger derived an expression for the electric polarization in an elementary crystal induced through deformation.³⁵ The expression is similar in structure to the expressions for the polarization due to an external field, even if the equations for the piezoelectric case are more complicated. By collecting the quite convoluted expressions for the coefficients that multiply each component of the strain, Schrödinger presented the equations in a simpler form, resembling that of Voigt's phenomenological theory (pp. 1953–1957). However, he did not recover the full form of Voigt's equations, since he did not include a general treatment of shear strains, but discussed them only for the special case of quartz (p. 1960). Schrödinger's equations assume a linear relation between the components of the electric field and the components of the deformation.³⁶ With the earlier assumed linear relation between the components of field and polarization, it is no wonder that Schrödinger recovered the "linear" relation between observed polarization and deformation.

The disagreement between the behavior of an elementary crystal and a real crystal became even more conspicuous in the case of piezoelectricity than in the case of dielectrics. In Schrödinger's theory, every elementary crystal is piezoelectric, while most real crystals are not, due to the arrangement of the elementary crystals. The specific arrangement determines which type of deformation induces electric effects in which direction. The arrangement itself follows the structure of the crystal, which was known from the observed, i.e., macrophysical, properties of particular species. In accounts of real crystals, like those he suggested for quartz and tourmaline, Schrödinger thus had to rely on macroscopic considerations. Thus, despite the microscopic basis of Schrödinger's theory, it could not rely exclusively on microscopic assumptions. Moreover, in order to account for the changes in polarization induced by shear strains, Schrödinger had to rely on Voigt's phenomenological theory. Voigt's theory also guided him in assuming a "linear" relation between deformation and polarization. His reliance on the phenomenological theory was similar to that of the earlier attempts by Riecke, Voigt, and Kelvin at formulating molecular theories of piezoelectricity (Katzir, 2003).

In one significant aspect, Schrödinger surpassed his predecessors. He succeeded to provide an estimate of the order of magnitude of the piezoelectric coefficients, in accordance with observed values. He showed that the piezoelectric coefficients are of the order of magnitude of the spontaneous polarization which, as mentioned, he calculated using Debye's theory. Schrödinger stressed his achievement (p. 27):

I believe that it is the first time that a theory accounts for the order of magnitude of the piezoelectric effect without making any assumption about the absolute magnitude of the electric moments of the molecules, about the number of electrons [*Elementarquanten*] that they contain, or any similar assumption.³⁷

³⁵ His derivation is valid for small deformations (a common assumption in the study of piezoelectricity), for temperatures far away from the melting point, and for zero external field. However, it also holds to good approximation for weak external fields.

³⁶ More precisely, the components of the electric field are linear combinations of the components of the polarization with coefficients that are "homogenous linear functions of the deformations" (p. 1954).

³⁷ This passage makes clear that Schrödinger did not show "a cautious attitude with respect to the still unsettled question—at least in Vienna—about the elementary charge," as Mehra and Rechenberg (1987, p. 116) claim. He was cautious about the nature of the molecules and their total charge and electric moment, which, of course, were unknown at the time. Contrary to the two historians' claim, Schrödinger's refusal to work from specific assumptions does not seem to reflect any particular Viennese background.

Yet, Schrödinger's estimate was not entirely microphysical because Debye's theory included a constant whose magnitude did not follow from microscopic considerations.³⁸

The assumption of unchangeable, permanently polarized molecules had already been suggested by Riecke in his 1891–1892 molecular theory of piezoelectricity. Like Schrödinger, he explained the total polarization of the crystal as stemming from polarized molecules.³⁹ Other theories had assumed that the inner polarization of most piezoelectric materials is only induced by the deformation (e.g., the theories of Voigt and Kelvin) and that undeformed crystals contain neither polarized molecules nor a permanent inner polarization. While Riecke postulated the existence of permanently polarized molecules in order to account for piezoelectricity, Schrödinger adopted the dipoles and polarization on theoretical grounds to explain a range of phenomena of solid dielectrics. In this respect, Schrödinger's assumptions were less *ad hoc* than Riecke's.⁴⁰

Schrödinger further explored the consequences of the spontaneous polarization for pyroelectricity. Since the polarization depends on the temperature, the explanation of pyroelectricity did not require further assumptions, only proper approximations. Limiting the discussion to tourmaline, the only substance for which quantitative data was available, he could use an approximation valid far below the melting temperature, which is high in this crystal. He derived the change in spontaneous polarization to second order in the variation of the temperature for an elementary crystal. Estimating the size of the effect for the specific arrangement of elementary crystals in tourmaline, he found reasonable agreement between his theory and Riecke's experimental measurements of the effect (pp. 1967–1970).⁴¹

The last phenomenon discussed by Schrödinger was the change in melting temperature under pressure. Through the piezoelectric effect, pressure induces a change in the dielectric coefficient of the elementary crystal. At the same time, pressure reduces the volume of the system and thereby increases the maximum polarization density P_0 that can possibly be reached in the system. Both effects together change the critical temperature T_k , i.e., the melting point. This argument rests on the assumption that *all* dielectric solids are composed of piezoelectric elementary crystals, which is far from a trivial assumption.⁴² In this case,

³⁸ This constant is Debye's b , reflecting the contribution to the dielectric constant induced by the displacement of the bound electrons, as opposed to the contribution a of the permanent dipoles.

³⁹ The two theories, however, are quite different both in their scope and in the kind of permanently polarized molecules that they assumed. Riecke, for instance, assumed multipolar molecules. It seems that Schrödinger, when writing his paper, was unaware of the details of Riecke's (1892) theory. He only referred to Riecke (1912) in a note added in proof (p. 1972).

⁴⁰ Both Riecke and Schrödinger had to assume a strong inner polarization in the crystal. However, Voigt (1897) challenged the assumption of strong inner polarization on experimental grounds (Katzir, 2006, pp. 207–209). In 1896, he had measured the voltage on the surface of fracture of tourmaline bars immediately after their breaking and had only found a weak surface charge. This hinted at the presence of only a weak permanent polarization before the breaking. Voigt's result, Schrödinger claimed (and Voigt also admitted, as acknowledged by Schrödinger), was not conclusive evidence against the presence of strong inner polarization. Schrödinger argued that the enormous surface charge density at the fracture would be compensated through the air before it could be measured (p. 1967).

⁴¹ While Schrödinger's theory predicts the "true" pyroelectric effect, in experiment one measures the combined effect of pyroelectricity and secondary piezoelectric contributions stemming from the thermal expansion of the crystal. Schrödinger calculated the magnitude of the latter from experimental measurements of the piezoelectric and thermal coefficients of tourmaline. He found that this secondary piezoelectric term contributes considerably more to the polarization than the "true" pyroelectric effect (Katzir, 2006, pp. 197–198, 205–207).

⁴² Technically speaking, the fact that every elementary crystal is piezoelectric follows from the presence of permanent polarization, which itself follows from the assumption that Eqs. (3) hold for the elementary crystal. As discussed above,

there are no contradictory contributions of the different elementary crystals, so Schrödinger could immediately generalize the results from one elementary crystal to the crystal as a whole. He recovered the qualitative dependence of the melting temperature on pressure, known from general thermodynamics: When the volume increases with solidification, the melting temperature decreases under pressure, while the opposite holds for substances whose volume decreases with solidification. Moreover, Schrödinger showed quantitatively that "the relative change in the melting temperature [under pressure] has to be of approximately the same order of magnitude as the change in volume brought about by that pressure in the solid phase" (p. 1969) and found a rough agreement with the experimental data for ice, for which data was available.⁴³ To improve the quantitative agreement between his theory and experiment, Schrödinger advanced an assumption about the dielectric properties of water.⁴⁴ In passing, Schrödinger noted that an extension of Debye's kinetic theory to what he called the "non-stationary states," i.e., to the response of matter to electric waves, would be of "utmost interest" (p. 1970). He followed up on this in a paper on anomalous dispersion one year later (Schrödinger, 1913).⁴⁵ Interestingly, in that paper, Schrödinger realized that dipoles alone could not account for anomalous dispersion in liquids. Instead, the permanent dipoles had to be supplemented (or even replaced) by the contribution of electrons in the material (which are bound to the atoms and aperiodically damped).

7. The character and aim of the theory

Schrödinger's theory of dielectrics did not predict any relations that did not follow from phenomenological theories. No new findings in the field prompted an extension or revision of these theories. Instead, the novelty of Schrödinger's theory lay in providing an explanation for—rather than a mere description of—the phenomena that it treated. Schrödinger did not attempt to resolve a discrepancy between theory and experiment as Debye had done for liquid dielectrics. His assumption about the microphysics of solids originated from the theoretical aim to advance a kinetic microphysical theory of solids. He supported his assumptions by the theory's ability to account for dielectrics and to explain several phenomena for which satisfactory microphysical explanations did not exist. In particular, the explanation of the change in the melting temperature with pressure supported Schrödinger's belief in the ability of providing "an atomistic answer to this question [of solidification]" (p. 1938). That pressure changes the melting point had been a surprising consequence of Carnot's principle, and its consequent experimental discovery a celebrated triumph of general thermodynamics (Smith & Wise, 1989, pp. 298–299). Schrödinger managed to recover the same result from microscopic considerations without invoking the second law of thermodynamics, which despite many efforts could not be rigorously reduced to statistical mechanics, and even surpassing it by providing a quantitative estimate.

(footnote continued)

Eqs. (3) are derived under the assumption of the existence of a uniform electric field in each individual elementary crystal.

⁴³ Ice is the only example treated in Planck's textbook on thermodynamics that Schrödinger relied upon (Planck, 1911, p. 151). Apparently, it was still unclear whether substances primarily contract or expand with solidification. Experiments were inconclusive (Brush, 1983, pp. 234–235).

⁴⁴ Schrödinger found that for water, the contribution μb of the bound electrons to the dielectric coefficient is slightly below one. He proposed that this might explain why water is a very good solvent.

⁴⁵ See also Scott (1967).

Quantitative estimates were also the advantage of his proposal over the phenomenological and the earlier explanatory theories of piezo- and pyroelectricity. The prediction of the order of magnitude of the piezoelectric coefficients was of particular importance since Schrödinger had to make the same assumptions as Voigt in his phenomenological theory, namely that the effect is “linear” and governed by the symmetry principle (the Neumann Principle stating that the symmetry of an effect cannot be lower than the symmetry of its causes).⁴⁶ In the spirit of Boltzmann’s words quoted in the introduction, Schrödinger emphasized that the quantitative predictions followed from the basic assumptions of the theory, without invoking any special assumptions, i.e., without arbitrariness, and thereby they corroborated the theory. In this context, one misses a similar quantitative estimate of the dielectric coefficients. Moreover, one could expect that a theory based on thermal rotations would show the dependence of these coefficients on temperature. However, as discussed, despite the dependence of the spontaneous polarization on temperature, Schrödinger did not provide any expression for the dependence of an observable quantity on temperature, and it is unclear whether the theory did not even contradict data for known dielectric coefficients of solids.

The accomplishments of Schrödinger’s theory were based on its speculative nature. The theory suggested a rather peculiar structure of solids—an arranged mosaic of tiny unobservable simple “elementary” crystals each consisting of many dipolar molecules (and possibly also electrically neutral molecules). The dipoles produce a very strong internal electric polarization which is compensated by surface charge for each elementary crystal individually. The inner polarization and the surface charge were neither observable, nor directly supported by experiment. Moreover, no explanation was provided for the uniformity of the electric field that characterizes the elementary crystal. Schrödinger further assumed that the magnitude of the molecular dipole moments is invariant. Thus the molecules are non-deformable (or at least their deformation negligible). In other words their structure is not altered with that of the crystal. In agreement with the contemporary view, he assumed that the elementary crystal is a lattice, and he was therefore led to assume that the polar molecules form the points of the lattice (p. 1953). These fixed molecules were somewhat at variance with contemporary notions of molecules, rooted in the kinetic theory of gases, according to which a molecule had inner degrees of freedom. Such a notion, of course, does not contradict the use of practically non-deformable molecules in solids. Yet, its view of molecules did not add to the attraction of Schrödinger’s kinetic theory of solids. Schrödinger was probably criticized about this assumption when he presented his work, since in a note added in proof he pointed to “some more recent work, particularly in the kinetic theory of gases, in which the forces of electrical dipoles of constant moment are introduced in order to account for molecular forces” (pp. 1971–1972).

However, non-deformable molecules became a problematic assumption a few years later. X-ray diffraction experiments and in particular those performed by William. H. and W. Lawrence Bragg in 1913 suggested that single atoms (or ions) occupy the lattice points, not composite polar molecules of the type suggested by Schrödinger. This means that, under deformation, single atoms move relative to each other, so that a dipolar molecule (which consists of at least two atoms) cannot be non-deformable. The Braggs examined a handful of dielectric crystals, but that alone would have sufficed to put Schrödinger’s theory under doubt, since it advanced an explanation for solidification of *all* insulators.⁴⁷ This case illustrates how the Braggs’ findings (if not already those of Friedrich, Knipping, and von Laue) changed the

way one could conceive the microphysical structure at least of some crystals, showing the need to account for the microphysical structure of crystals on an atomic rather than a molecular level.

That Schrödinger’s theory was incompatible with later developments, that it did not answer any immediate question in physics, and its speculative view of solids likely explain why it was not given much attention by other physicists.⁴⁸ The fate of Schrödinger’s theory differed much from the analogous theory of ferromagnetism, which continued to be used and developed. Weiss’s theory also was speculative. Yet its author supported the assumption of inner magnetization by indirect experimental evidence, and the crystal structure suggested by Weiss’s theory agreed better with the contemporary view of matter than the one suggested by Schrödinger. Probably more important for the reception of the two theories is the fact that Weiss, unlike Schrödinger, explained several empirical results previously unaccounted for, and suggested further experimental research related to his theory.⁴⁹

8. Conclusion

The accomplishments and limitations of Schrödinger’s theory of solids display advantages and drawbacks of the use of analogy. The analogy between dielectrics and magnetism, on the one hand, provided Schrödinger with means to build a statistical, microphysical theory of dielectrics that agreed with the central observations in the field. On the other hand, this physical analogy exposed Schrödinger to the risk of transferring more assumptions than warranted by the similarity between the phenomena. Schrödinger indeed did not carefully examine the implications of the analogy, but instead advanced a speculative theory, whose assumptions did not enjoy the same kind of empirical support as enjoyed by Weiss’s theory of magnetism. Following the analogy, he overlooked a central hypothesis of the theory, i.e., the assumption of order implicitly introduced with the “molecular field.” Already Weiss’s extension of Langevin’s theory had helped hiding this implicit assumption, as Langevin’s theory described ordered phenomena. Of course, the speculative character of Schrödinger’s theory followed also from his extension of Debye’s theory through the bold hypothesis that solidification is electrification. Extension and analogy led Schrödinger to a new theory of solids compatible with empirical data. They, however, also led to a more hypothetical, and eventually less successful theory than the theories he extended or used as a model.

The way Schrödinger regarded the analogy as a guide to physical processes that take place at the microphysical level displays his “scientific realism.” According to this methodology the phenomena should be explained by microphysical processes and structure, whose consequences for other phenomena should be studied as if the assumptions were real. Thus he developed the theory for several hitherto disconnected phenomena in which the assumptions seemed relevant and followed the details of these theories for a few prominent cases. Both the treatment of these phenomena and their detailed discussion provided predictions, with which he could corroborate the physical picture that he proposed. Both were not the obvious way to construct a theory.⁵⁰ When one regards hypotheses merely as instruments for

⁴⁸ Röntgen (1914) did not even refer to Schrödinger’s theory when he claimed on experimental grounds that pyroelectricity is only a secondary effect of piezoelectricity, a claim that contradicted Schrödinger’s theory.

⁴⁹ Auerbach (1920, pp. 923–927). See also: Keith and Quédec (1992, p. 375).

⁵⁰ The earlier history of piezoelectricity provides good examples for the preference of other ways to construct explanatory theories. The consequences of none of the early models were followed beyond piezoelectricity. The only exception was Kelvin’s 1901 theory, where piezoelectricity was one among a few phenomena explained by a model of the atom. Voigt did not detail his suggested molecular explanation for any crystal (Katzir, 2003).

⁴⁶ See Katzir (2003) and Riecke (1912).

⁴⁷ Jenkin (2008, pp. 337–339), Forman (1969), and Ewald (1969).

explaining specific phenomena, one should not worry if a particular hypothesis fails to explain an apparently related phenomenon. However, if the hypothesis is taken as real, one worries about such a failure, which suggests that the hypothesis is wrong, or should be modified. This is exactly what Schrödinger did a year later, when he considered abandoning the assumption of permanent dipoles due to their inability to explain anomalous dispersion (Schrödinger, 1913).

Looking back, Schrödinger's "scientific realism" connects his early theory of dielectrics to Boltzmann's tradition, and, looking ahead, to his later contributions to quantum mechanics. The way in which Schrödinger invented a physical process that justified the use of the analogy between the laws of dielectrics and magnetism, can also be found in his search for a "natural statistics" that would replace the "unnatural" Bose–Einstein statistics: On his way to wave mechanics, Schrödinger accepted de Broglie's hypothesis of matter waves and made it the physical basis of his theory (Joas & Lehner, 2009).

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