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**From explanation to description: Molecular and phenomenological theories of piezoelectricity**

THE SECOND HALF of the 19th century saw the rise of new corpuscular theories in physics. A reinterpretation of heat as a kind of motion by the kinetic theory of gases and subsequently by statistical mechanics is probably the most famous example of this development. The ion and the electron in electromagnetism, and developments in spectral analysis and the theory of anomalous dispersion, provide further examples. The success of corpuscular theories was only partial, however. Even the famous achievement of reducing heat to motion encountered difficulties, most famously in attempted explanation of the second law of thermodynamics.

Nonetheless, contemporaries regarded the theories of discrete matter as successful. Most physicists at the end of the century believed in a molecular-atomistic structure of matter, even if they interpreted it in different ways. The critical response to the opposition well demonstrates the view of the majority. In 1895 the German scientific society invited Georg Helm to present his criticism of the mechanical-atomistic view at its annual meeting. "The meeting was an unmitigated disaster" for the opposition. Eminent scientists attacked the speaker. Most physicists in the audience conceived the assumption of atoms or molecules as indis-

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The following abbreviations are used: *AHES*, *Archive for history of the exact sciences*; *AP*, *Annalen der Physik*; *OPC*, *Œuvres de Pierre Curie* (Paris, 1908); *GA*, *Akademie der Wissenschaften, Göttingen, Abhandlungen*; *GN*, *Akademie der Wissenschaften, Göttingen, mathematisch-Physikalische Klasse, Nachrichten*; *TMPP*, William Thomson, *Mathematical and physical papers* (6 vols., Cambridge, 1882-1911).

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pensable. Shortly after, Wilhelm Ostwald, the leading German antagonist to atomistic-mechanical explanation, regrettably observed: "Repeatedly one hears and reads that no other understanding of the physical world is possible except that based on the 'mechanics of atoms;' matter and motion seem the final concepts to which the manifold of natural phenomena must be reduced."<sup>1</sup> Still, some physicists preferred to base their accounts on overall principles, occasionally on those of thermodynamics and others did not regard the mechanical concepts as final. A few physicists, especially in Britain, favored reduction of atoms and molecules to singularities in a continuous medium. Another small group considered an electromagnetic reduction of physics; yet that did not deny the centrality of corpuscles.<sup>2</sup> Nevertheless, as the response to Helm's address displays, the growing explanatory power of corpuscular theories was generally recognized.

Piezoelectricity, discovered in 1880, underwent a development reverse to that of most fields of physics. The first molecular theories were soon replaced by a continuum theory, which guided most research in the field, while, at the same time, physicists continued to propose molecular models. Piezoelectricity concerns two basic effects of energy conversion in crystals: induction of electricity by pressure and the converse generation of elastic strain by an electric field. It is a macroscopic phenomenon of what is now called condensed matter. In this it differed from phenomena successfully explained by corpuscular assumptions. Unlike other electrical phenomena, piezoelectricity was closely linked to the structure of matter and did not reveal any direct relation to micro-physical processes. Ignorance of the micro-structure of solids favored continuum theories for the description of condensed matter.

In 1890 the early molecular model of piezoelectricity was superseded by what contemporaries called a phenomenological theory. According to Woldemar Voigt, who developed it, in such theory, "a small number of principles, i.e., rules derived from experience and ascribed hypothetical general validity, support an edifice of mathematical conclusions that yields the laws of the phenomena in the field concerned."<sup>3</sup> Phenomenological theories aimed at describing the phenomena and their relations as found empirically by using a minimal number of laws. They did not aim at explaining the relations between the phenomena on the basis of another effect or process (hence regarded as more basic) but only at describing them. Molecular theories or continuum models like the vortex atom, in contrast, aimed pre-

1. J.L. Heilbron, *A history of the problem of atomic structure from the discovery of the electron to the beginning of quantum mechanics* (Ph.D. dissertation, University of California, Berkeley, 1964), 16-24, 41-43, on 42. Later evidence convinced Ostwald by 1909 that "we have experimental proof for the discrete or grainy nature of matter" (*ibid.*, 44).

2. Olivier Darrigol, *Electrodynamics from Ampère to Einstein* (Oxford, 2000), 360-361; Russel McCormach, "H.A. Lorentz and the electromagnetic view of nature," *Isis*, 61 (1970), 459-497.

3. Woldemar Voigt, "Phänomenologische und atomistische Betrachtungsweise," in E. Warburg, ed., *Die Kultur der Gegenwart*, 3:3, vol. 1, *Physik* (Berlin, 1915), 714-731, on 716.



cisely at such explanation by invoking various hypotheses that could not be derived from empirical knowledge. The phenomenological approach accepted only hypotheses grounded on empirical results, either of the particular phenomena examined or of a larger field.<sup>4</sup> In the later part of the 19th century, the laws of elasticity and the basic laws of electrostatics (i.e., Coulomb's law in its various forms and the relationships between electric charge, voltage, force and moment) were conceived as expressing true verified relations. Therefore, physicists employed these laws in elaborating phenomenological theories for particular branches like piezoelectricity.

This paper studies the reasons for the peculiar development of piezoelectric theory. Why did the phenomenological become the dominant theory of the field? Why was none of the molecular models proposed after the introduction of Voigt's theory accepted? On the other hand, why did physicists continue to propose molecular explanations? Many protagonists did not view these different approaches as contradictory. The relinquishing of the molecular models of piezoelectricity did not originate in a rejection of molecularism. Nor were the later attempts at a molecular theory derived from a realist rejection of continuum theory. To answer the questions posed above requires a close look at the particular developments in the field.

## 1. FIRST MOLECULAR THEORIES

### The Curies'

The Curie brothers, Jacques and Pierre, found certain crystals compressed along specific (hemihedral) axes electrically polarized. A similar phenomenon owing to change in temperature, pyroelectricity, had been known since 1756. The Curies looked for analogous behavior with pressure. They probably reasoned from a molecular theory of pyroelectricity that implied an electric effect also for pressure.<sup>5</sup> Their theory, or perhaps model, followed William Thomson's notion that pyroelectric bodies possess permanent "bodily electro-polarization." This polarization is usually hidden since it "induces a superficial electrification which perfectly balances its electric force on all points in the external matter. . . . When the temperature of the substance is changed, its electro-polarization changes simultaneously, while the masking superficial electrification follows the change only by slow degrees."<sup>6</sup>

4. Here the term phenomenological is not restricted to laws but is employed also for theories, and is therefore more general than the usage in Nancy Cartwright, *How the laws of physics lie* (Oxford, 1983, 1-3). Also, phenomenological theories can be based on various assumptions and principles that are not derived from the empirical data of a specific theory, like the principle of energy conservation and considerations of symmetry.

5. Jacques and Pierre Curie, "Développement par compression de l'électricité polaire dans les cristaux hémihédres à faces inclinées," Société Minéralogique de France, *Bulletin*, 3 (1880), 90-93; Shaul Katzir, "The discovery of the piezoelectric effect," *AHES*, 57 (2003), 61-91.

6. William Thomson, "On the thermoelectric, thermomagnetic and pyroelectric properties of matter," *TMPP*, 1, 315-316.





The Curies suggested in 1881 that tourmaline, a paradigmatic pyroelectric crystal, is composed of polarized molecules oriented in parallel layers perpendicular to the direction of a polar axis. “Between the two opposite sides of successive layers of molecules exists a constant difference of [electric] tension, which brings about a condensation of electricity that depends on the distance between two layers; if this distance is changed (by variation of pressure or of temperature), the condensed quantity [of electricity on the layers and consequently on the bases] will change.” Following Thomson, they assumed that an inverse electric charge on the crystals’ surface neutralizes the exterior manifestation of “the condensed electricity” before the change. They conceived this arrangement in analogy to a zinc-copper dry battery. The development of charge by pressure according to this model agreed with their earlier empirical findings.<sup>7</sup>

The Curies regarded their model as plausible not only because of its agreement with experiment but also because they based it on a model of crystal structure. According to their view, the hemihedral (half symmetric) form of crystalline molecules, could support an electric tension between their opposing ends. The Curies had found empirically that in all crystals “the end corresponding to the more acute solid angle becomes negative by expansion. This constant relation is probably not accidental. If the molecular form is supposed analogous to the hemihedral crystal form, the acute end of a given molecule plays the same part in relation to the opposite base of the successive molecule as zinc does to copper in the [battery], namely it is constantly charged with positive electricity.”<sup>8</sup> These molecules are the crystallographic discrete building blocks of the crystal, not just arbitrary elements of volume. Yet, like crystallographers and other physicists and chemists, they identified neither these crystalline molecules nor their parts with the atoms or molecules of physics and chemistry, although they shared the standard assumption, that crystal molecules are composed of more elementary particles.

Since (according to the Curies) both pyro- and piezoelectricity are caused by mechanical changes of distance between polarized molecules, cooling and compressing should always have the same effect, while heating and decompressing should have the opposite effect. They had confirmed this inference in their initial experiments. Wilhelm Gottlieb Hankel challenged these findings on empirical grounds. He claimed that in some crystals like quartz, the effects of cooling ran counter to those of pressure. Hankel argued from the lack of a general correlation between pressure and cooling that pyro- and piezoelectricity are two distinct processes. He further supposed that heat radiation generates a third distinct phenomenon, “actinoelectricity,” which behaved inversely to pyroelectricity.<sup>9</sup>

7. Jacques and Pierre Curie, “Sur les phénomènes électriques de la tourmaline des cristaux hémihédres à faces inclinées,” *OPC*, 18-21, on 20.

8. *Ibid.*, 21.

9. Hankel also had theoretical grounds to suppose the existence of a special effect of radiation in his peculiar conception of molecules. Wilhelm Gottlieb Hankel, “Ueber die





In 1883 W.C. Röntgen, Charles Friedel, and Jacques Curie turned to the laboratory to refute Hankel's claims and to reinterpret his findings in accordance with the molecular theory. They claimed that the results that Hankel explained by distinct pyro- and actinoelectricity actually arise from contraction and expansion caused by inner temperature differences inside the crystals. In repeating an experiment of Hankel, Friedel and Jacques Curie measured the heat released from the crystal and found that its inner temperature during the process was not uniform. Cooling the same quartz uniformly, they did not observe actinoelectricity.<sup>10</sup>

In a compelling experiment Röntgen compared the effects of heating and cooling from the center of a circular quartz disc with the effects of heating and cooling from the circumference. He drilled a hole at the center of the disc, creating a wide ring. Heating from the center, he found the same electric effect as that of cooling from the circumference (which is the same as that of external pressure) and cooling from the center the same as heating from the circumference. All this agreed with his theory that cooling from the circumference and heating from the center cause radial tension towards the center. The electric effect of this tension causes the observed behavior. The results showed that the electric effect of a temperature change depends only on the direction of the temperature gradient inside the crystal. In Röntgen's model, uniform heating of quartz would not create an electric effect.<sup>11</sup>

Röntgen had assumed that polarized molecules were the source of piezo- and pyroelectricity.<sup>12</sup> He ascribed piezo- and pyroelectricity in quartz to changes of elastic tension induced by thermal expansion or pressure. This claim follows from the Curies' molecular theory, but can be held independently. Jacques Curie and Friedel were more explicit about their molecular assumptions. "For Mr. Röntgen the common cause [of piezo-, and pyroelectricity] is a change in the internal tension of the crystal. For us, it is more simply a change in the molecular distances."<sup>13</sup> Thus they maintained the interpretation that Jacques and Pierre Curie had suggested two years before.

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Entwicklung polarer Elektrizität in hemimorphen Krystallen durch Aenderung des Druckes in der Richtung der asymmetrisch ausgebildeten Axen," der Wissenschaften, Leipzig, *Berichte*, 1880, 144-147; "Über die Aktino- und Piezoelektrischen Eigenschaften des Bergkrystalles und ihre Beziehung zu den Thermoelektrischen," Akademie der Wissenschaften, Leipzig, Mathematisch-Physischen Classe, *Abhandlungen*, 12 (1881), 459-547; Shaul Katzir, *A history of piezoelectricity: The first two decades* (Ph.D. dissertation, Tel Aviv University, 2001), 45-47.

10. Jacques Curie and Charles Friedel, "Sur la pyro-électricité du quartz," *Comptes rendus*, 96 (1883), 1262-1269, 1390-1395, on 1390-1391, 1393-1394; Wilhelm Röntgen, "Ueber die thermo-, actino- und piezoelektrischen Eigenschaften des Quarzes," *AP*, 19 (1883), 513-518.

11. Röntgen (*ibid.*), 515-517; Katzir (ref. 9), 55-57.

12. He reported on his molecular assumption seven years later. Wilhelm Röntgen, "Electrische Eigenschaften des Quarzes," *AP*, 93 (1890) 16-24, on 23; Röntgen (ref. 10), 513.

13. Curie and Friedel (ref. 10). Their hypothesis does not seem simpler than Röntgen's.



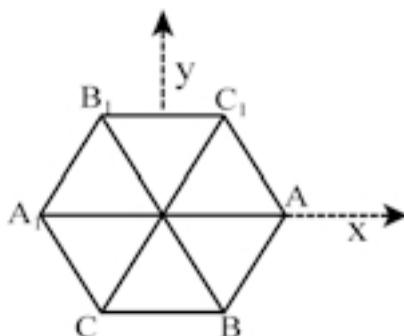


FIG.1 Quartz cut perpendicular to the principle axis ( $xy$  cut).  $AA_1$   $BB_1$   $CC_1$  are its electric axes.

On the hypothesis that pyroelectricity in quartz is induced only by expansion and contraction along polar axes, Friedel and Curie demonstrated mathematically that its uniform heating does not generate any electric effect. In this demonstration they assumed that the electric effects induced by expansion in the three non-orthogonal hemihedral (polar) axes of quartz, which form angles of  $60^\circ$  between them, are independent (figure 1). The effect in a particular direction is the sum of their projections in that direction. Generally, effects in non-orthogonal axes are not independent. In terms of the Curies' molecular assumption, an expansion along an axis changes the distances between polar molecules. The expansion should induce an electric effect independent from that induced in another direction. Hence, the assumption of independent effects is a consequence of their molecular model. Yet the Curies' original model explains the phenomena in a crystal with one polar axis, not in a crystal with a few non-orthogonal polar axes like quartz, whose three axes lie in the same plane. The model assumed parallel layers of molecules perpendicular to the polar axis: how three sets of such layers could be arranged on the same plane is not clear. Friedel and Curie discussed neither this question nor the molecular structure of quartz.<sup>14</sup>

The analysis of piezoelectricity through the supposition of independent electric effects in quartz's three polar axes was tacitly adopted by Paul Czermak in developing a mathematical theory of the crystal four years later. Czermak claimed to refrain from "any particular hypothesis" like the molecular theory.<sup>15</sup> However his tacit supposition of independent effects—unjustified by general notions—be-

14. Curie and Friedel (ref. 10), 1393-1394. On the basis of similar assumptions they demonstrated that uniform heating does not induce an electric effect on additional crystals previously regarded as pyroelectric. "Sur la pyro-électricité dans la blend, le chlorate de sodium et la boracite," *Comptes rendus*, 97 (1883), 61-66.

15. Paul Czermak, "Über der elektrische Verhalten des Quarzes," *Mathematisch-Naturwissenschaftlichen Classe, Akademie der Wissenschaften, Vienna, Sitzungsberichte*, 96 (1887), 1217-1244; 97 (1888), 301-324, on 1227; Katzir (ref. 9), 64-66.





trayed assumptions conforming only to the molecular model; apparently he thought along the lines of the Curies' hypothetical molecular theory, which he knew well.<sup>16</sup> As a former student of Boltzmann, Czermak's inclination towards a molecular assumption is hardly surprising.

Czermak's theory accounted quantitatively for electric effects caused by arbitrary unidirectional pressures. In addition to the independence of the three polar axes, he assumed that the electric effect (in charge or electric tension for the same arrangement) along such axes depends linearly on the pressure. This relation had been found empirically by the Curies and Hankel, and Czermak confirmed it in his own experiments. Czermak's examination gave a rough confirmation of his theory. But he measured only the electric effect in the direction of pressure, while his expression for the electric effect in one direction due to pressure in another deviated from former observations of the Curies by more than 40 percent. Czermak, however, did not refer to the Curies' observation.<sup>17</sup> Other physicists were likely to notice the failure of the theory on this point. They would have seen the origin of this failure in Czermak's dubious supposition that the effects in the three axes are independent.<sup>18</sup> Since this supposition follows from a molecular model like the Curies', a discerning observer at the time could have concluded that the current molecular assumption in the way it was employed by Jacques Curie and Friedel was insufficient to account for piezoelectricity.

### Others'

In his comprehensive book on electricity published in 1883, Gustav Wiedemann rejected Thomson's hypothesis of permanent polarization and therefore the hypothesis of polar molecules on which the Curies' model stood. He still suggested a molecular explanation, but his molecules became polar only by and during the physical process. Whereas the Curies saw the basic effect to be mechanical, Wiedemann took it to be thermal. Pressure generated heat that caused the crystal's electrification.<sup>19</sup> Pierre Duhem agreed that the effect was thermal but rejected any

16. Perhaps Czermak thought that the assumption was independent of a molecular hypothesis, since it does not require one; the logical derivation runs from the molecular hypothesis to his assumptions and not the other way around. Any mechanical assumption that assumes that the electric effect is owing to tension along and only along polar axes would lead to the same result. Nonetheless, historically such an assumption was suggested only with a molecular hypothesis. Röntgen, who referred the effect to inner elastic tension, did not relate it to the polar axes.

17. Czermak (ref. 15), 1218-1234; Jacques and Pierre Curie, "Déformations électriques du quartz," *OPC*, 30-32, on 31. This paper is the only one of those published in the *Comptes rendus* that Czermak did not mention.

18. The expression for the electric effect in the direction of pressure that follows from Czermak's assumption is close to the expression that follows from valid consideration of symmetry. Here Czermak could find rough confirmation.

19. Wiedemann claimed, without evidence, that pyroelectric crystals cut into two parts do



molecular explanation. In 1886 he published a theory of piezoelectricity as a secondary phenomenon of pyroelectricity, itself a special case of thermoelectricity—the generation of electric current by temperature differences and of temperature differences by electric current. He understood piezoelectricity as an epiphenomenon of a thermal effect.<sup>20</sup>

According to Duhem, in “natural” pyroelectric crystals, those electrified by uniform heating like tourmaline, pressure generates heat that creates the pyroelectric effect. In non-pyroelectric crystals, crystals that do not become electric due to uniform heating like quartz, pressure has an additional effect of deforming the material and thus breaking its symmetry. The break of symmetry enables the induction of pyroelectricity in such crystals just as in “natural” pyroelectrics. On this theory pyroelectricity was a kind of thermoelectricity. The approach had problems: thermoelectricity concerns closed circuits of conductors, but pyroelectric materials are poor conductors and the phenomenon appears without observable current; further, it was observed in crystals unconnected to an electric circuit, and was usually considered to induce only a static effect. Yet Duhem explained it by the theory of thermoelectricity and concluded that pyroelectricity arises from inner differences of temperature while most researchers attributed it to changes in the temperature of the whole crystal.

These peculiar assumptions attracted criticism from Pierre Curie and Aimé Vaschy in a discussion at the French Society of Physics in 1887. Curie had two additional objections: first, that the thermal effect of compression, suggested as an explanation by Duhem, is too small to explain the observed electric effect, and second, that Duhem’s mechanism could not explain the instantaneousness of the electric effect of pressure.<sup>21</sup> In 1887, Duhem did not accept the criticism, but in 1892 he realized that he had been mistaken. He thereupon proposed a phenomenological theory that agreed better with both the empirical data and the famous characteristics of his mature physics. In his earlier theory he tried to embrace piezoelectricity in thermodynamics by claiming that it has thermal origins. In the later theory he derived it from general thermodynamic potential functions, refraining from any hypothesis about the source and causes of the phenomenon.<sup>22</sup> The

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not display electric polarization. Gustav Heinrich Wiedemann, *Die Lehre von der Elektrizität* (2 vols., Braunschweig, 1883), 2, 336-337. The volume went to press before the appearance of Röntgen’s, and Curie and Friedel’s papers. Still Wiedemann maintained his explanation in the second edition a decade later, 2nd. edn. (1894), 2, 427-429.

20. Pierre Duhem, “Applications de la thermodynamique aux phénomènes thermo-électriques et pyro-électriques,” *École normale supérieure, Annales scientifiques*, 2 (1885), 405-424; 3 (1886), 263-302; Katzir (ref. 9), 97-108.

21. “Sur les phénomènes piézo-électriques,” *OPC*, 33-34.

22. Pierre Duhem, *Leçons sur l’électricité et le magnétisme* (3 vols., Paris 1892), 2, 391. The different character of Duhem’s two accounts of piezoelectricity points to a development in his view of the aim of scientific theory during the late 1880s to early 1890; Katzir (ref. 9), 106-108, 156-171.



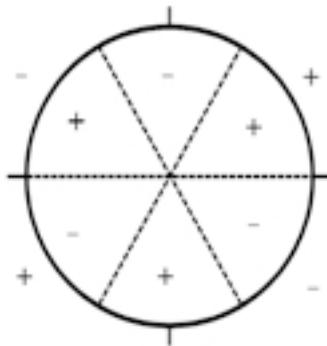


FIG. 2 Distribution of electricity by radial pressure (inside the circle) and by torsion (outside the circle) as observed by Röntgen.

two thermal explanations of piezoelectricity failed to offer a real alternative to the Curies' molecular theory. In his *Traité de cristallographie* (1884) Ernest Mallard concluded that in piezo- and pyroelectricity the development of electricity is done in the same manner as if it were simply linked to the variation of the distance that separates the molecules.<sup>23</sup>

The Curies' molecular explanation of piezoelectricity could have continued to dominate theoretical thinking on the subject had Röntgen not returned to its empirical study in 1889. In his earlier experiments Röntgen had examined the electric effect of mechanical pressure and the mechanical effect of electricity in quartz in various directions. Now he examined the electricity induced under torsion. He applied shear stress in a tangential direction to the circumference of a quartz cylinder, perpendicular to the crystal's principal axis (an axis known to have no electric activity). He measured qualitatively the distribution of electricity on the circular surface, and compared it with the known distribution of electricity due to radial pressure (identical to that of non-uniform heating). To Röntgen's surprise these distributions did not coincide. Moreover, the circumference of the cylinder divided into four electric zones of alternate positive and negative charge, in contrast to the six zones obtained by radial pressure (figure 2). Thus the phenomena showed a symmetry of the second order, rather than the known third order symmetry of the principal axis of quartz.

The division of electricity did not coincide with the known three (hemihedral) polar axes. Electric effects of contraction (or expansion) perpendicular to these axes should have had a symmetry of the third order rather than of the second. Furthermore, torsion included effects neither of pressure nor of contraction (or

23. Ernest Mallard, *Traité de cristallographie géométrique et physique* (2 vols., Paris, 1884), 2, 571.





expansion), but only of shearing stress and deformation. The observed phenomenon of torsion could not be explained by tension or contraction along the polar axes. The effect could still be connected to deformation but could not merely to expansion and contraction, as in the hypothesis of polarized molecules. As Röntgen put it: “How torsion-electricity...comes into being, I still have not been able to form an adequate idea; the assumption of polarized molecules, on which I initially based my electro-optic and piezoelectric researches, does not lead to the goal.” Unable to suggest an alternative explanation, Röntgen left the challenge to others.<sup>24</sup>

## 2. VOIGT'S GENERAL THEORY

An account of the way in which torsion induces electricity in quartz appeared as part of a general theory formulated by Woldemar Voigt as early as August 1890, seven months after the publication of Röntgen's results.<sup>25</sup> He wrote:<sup>26</sup>

The long series of observed analogies between the electric excitation of crystals by external forces, on the one hand, and by change of temperature on the other, has already led several researchers to the opinion that in both processes the deformation of the volume element, no matter whether it is caused by pressure or heating, forms the direct precondition for the electric phenomena. A universal and satisfactory proof of this view could not be possible as long as it was not made the basis of a rigorous theory—a theory that reduces all related phenomena to the least number of constants possible and that after their experimental determination enables physicists to calculate the resultant excitation both qualitatively and quantitatively.

His theory embraced all phenomena of electrification by pressure and change of temperature. No such rigorous and general mathematical theory, based on a few sound assumptions, had been suggested before. The few earlier theoretical accounts were not comprehensive, lacked rigor and did not account for the observed phenomena. Czermak's mathematical theory suffered not only from lack of rigor but also from contradictions with the experiments.

Voigt made two objections to the assumption, basic to the molecular explanations that all the phenomena of pyro- and piezoelectricity originate in contraction and expansion along specific polarized axes. Some crystal species, including quartz, cannot be electrically polarized under uniform pressure, but only under non-uniform pressure. The fact, which had been known since 1883, showed that these crystals cannot be permanently polarized as required by the molecular hypoth-

24. Röntgen (ref. 12), 23; Katzir (ref. 9), 73-76.

25. Woldemar Voigt, “Allgemeine Theorie der piëzo- und pyroelectrischen Erscheinungen an Krystallen,” *GA*, 36 (1890), 1-99.

26. *Ibid.*, 1.



esis.<sup>27</sup> The second objection concerned Röntgen's experiment, which showed that a deformation like torsion, which does not cause contraction or expansion, generated electricity in quartz. Thus Voigt suggested that any deformation can induce polarization.<sup>28</sup>

Voigt's theory of piezo- and pyroelectricity rests on two assumptions: that the induced electric moment (electric polarization in modern terminology) is proportional to the deformation, and that the symmetry of the piezoelectric effect is not lower than the symmetry of the crystals in which it occurs. The linear ratio had been verified for a few crystals by the Curie brothers and later by Hankel and Czermak.<sup>29</sup> The second assumption applied a general principle derived from many physical phenomena in crystals, which Voigt later called the "Neumann Principle." In addition to these two assumptions, Voigt supposed that deformations are the only causes of pyroelectricity, which thus became a secondary phenomenon to piezoelectricity. Unlike the two basic hypotheses, this assumption was not grounded in any experiment on natural pyroelectrics. Four years later he admitted the possibility of a direct effect of temperature change on natural pyroelectrics.<sup>30</sup>

The basic and general equation of piezoelectricity, which relates the three components of electric moments  $a$ ,  $b$ , and  $c$  to the six components of deformation (or strain)  $x_x$  in a differential volume element, follows from the theory's first assumption:

$$\left. \begin{aligned} a &= \varepsilon_{11}x_x + \varepsilon_{12}y_y + \varepsilon_{13}z_z + \varepsilon_{14}y_z + \varepsilon_{15}z_x + \varepsilon_{16}x_y \\ b &= \varepsilon_{21}x_x + \varepsilon_{22}y_y + \varepsilon_{23}z_z + \varepsilon_{24}y_z + \varepsilon_{25}z_x + \varepsilon_{26}x_y \\ c &= \varepsilon_{31}x_x + \varepsilon_{32}y_y + \varepsilon_{33}z_z + \varepsilon_{34}y_z + \varepsilon_{35}z_x + \varepsilon_{36}x_y \end{aligned} \right\} \quad (1)$$

where "the eighteen piezoelectric constants  $\varepsilon_{hk}$  are dependent on the character of the crystals and the location of the coordinate system  $x, y, z$ ."<sup>31</sup> Written for a small

27. Voigt did not refer to Friedel and Curie's demonstration that uniform pressure does not generate electric effect in crystals like quartz, which they based on the assumption that the effect originates from changes of distance along polar axes. Voigt probably considered their argument invalid since it assumes an independency of the effects in the three non-orthogonal axes. Furthermore, the same kind of assumption led to Czermak's incorrect results.

28. Voigt (ref. 25), 5-6.

29. Voigt was aware that the few examined cases did not prove the universal validity of linearity, and therefore left open the possibility of adding corrections of higher orders if needed. On the verifications see Jacques Pierre and Pierre Curie, "Lois du dégagement de l'électricité par pression dans la tourmaline," *OPC*, 15-17; Czermak (ref. 15), 1230-1232; Hankel, "Aktino" (ref. 9), 542.

30. Woldemar Voigt, "Piezo- und Pyroelectricität, diélectrische Influenz und Electrostriction bei Krystallen ohne symmetriecentrum," *GN* (1894), 343-372.

31. Voigt (ref. 25), 3-4. Since the crystal strain tensor is symmetrical ( $y_x = x_y$ ), only six (rather than nine) components of strain are needed.





volume element, the basic equation enabled Voigt to avoid any supposition about the fundamental structure of crystals. The equation agrees with a continuum picture of matter, but since the volume element can still be finite, the equation can be consistent with molecular or other structures.

The basic equation of the theory does not relate to any specific crystal. In order to derive the special relations of each of the 32 crystal classes, Voigt employed the second hypothesis of the theory, according to which any strain generates polarization in any crystal in every direction, unless the generation violates the symmetry of the crystal. For each class of crystals he found the coefficients identical to zero and those equal to each other; for quartz, the most studied crystal, he found,

$$\left. \begin{aligned} a &= \varepsilon_{11}(x_x - y_y) + \varepsilon_{14}y_x \\ b &= -\varepsilon_{14}z_x + \varepsilon_{11}x_y \\ c &= 0. \end{aligned} \right\} (2)$$

Unlike Czermak and previous researchers, Voigt did not study a particular crystal but all crystals in general. Moreover his derivation was not based on the crystal's polar axes, but directly on its symmetry as stated in orthogonal Cartesian coordinates.

Voigt's theory succeeded in accounting for the electric behavior of all crystals under changes of stress and temperature and in describing a few prominent cases in detail. In a comprehensive memoir he showed how the results of previous experiments fit the theory and predicted many effects then not yet observed. Voigt's approach is still the ground for current theory. The success of the theory demonstrated the power of a general analytical method, in the tradition of rational mechanics, to account for complicated phenomena. Where molecular theory failed to explain the known phenomena, the phenomenological theory successfully accounted for them and correctly predict more besides.

Voigt's phenomenology was typical of the approach of Franz Neumann's famous seminar in Königsberg, where Voigt studied.<sup>32</sup> Although by taste and training Voigt was not inclined to employ any hypotheses concerning the ontological structure of matter, he did not reject the molecular explanation of piezoelectricity for being speculative, but for being inadequate. Supporters of the molecular theory like Röntgen took to the same position; Pierre Curie, who had originally suggested the molecular model, was satisfied with Voigt's theory.<sup>33</sup> Support of a phenomeno-

32. K. Försterling, "Woldemar Voigt zum hundertsten Geburtstage," *Die Naturwissenschaften*, 38 (1951), 217-221, on 217; Kathryn M. Olesko, *Physics as a calling: Discipline and practice in the Königsberg seminar for physics* (Ithaca, 1991), 387-388. Olesko's claim, "the problem with this way of thinking was that it inhibited the kinds of thinking needed to achieve theoretical results," does not seem to fit Voigt's theoretical achievement in piezoelectricity.

33. According to Marie Curie, following the publication of Voigt's theory Pierre Curie suspended his plan to publish an analogous theory; Marie Curie, "Préface," *OPC*, v-xxi, on xiv.



logical theory was independent of a belief in the molecular constitution of matter.<sup>34</sup>

Voigt himself had developed molecular theories, for example of elasticity. To improve agreement with experiment he modified the previous molecular hypotheses in an attempt towards a “general and consequential theory of matter.” And he came to propose a molecular explanation for the general phenomenological theory of piezoelectricity.<sup>35</sup> Whether or not Voigt preferred a phenomenological to a molecular theory depended on the specific situation in the field and his particular goal.

That Voigt developed molecular theories for macroscopic phenomena suggests that he accepted the molecular structure of matter. From this point of view his general theory of 1890 was an intermediate, temporary step on the road to a molecular theory of piezoelectricity. Yet in practice it was more than a temporary step. In 1915, after the accumulation of compelling evidence for the atomic constitution of matter, Voigt wrote:<sup>36</sup>

Once the molecular constitution of matter and electricity is regarded as proven, physicists will be inclined to regard the molecular view as the only proper one and a phenomenological approach as something at best temporarily tolerable. In principle there is certainly no objection to this point of view. However, at least for the present and perhaps for some time, it does not do justice to actual circumstances. Things are not so simple. There is not a free choice between phenomenological and molecular views; in many areas there are very great, even insuperable, difficulties in following the latter way.

According to Voigt, these difficulties originated in direct knowledge of the molecular and inner molecular behavior, failure of most molecular accounts to provide more than a crude picture of reality. It followed that molecular explanations could be constructed only by assuming laws, principles, and considerations of symmetry justified from the phenomenological rather than the molecular point of view. Phenomenological theory was not only a temporary scaffold, but also an engine for further work even after construction of an edifice of molecular theory.<sup>37</sup>

34. British physicists continued to think about molecules and probably also to believe in their existence while preferring phenomenological theories that assumed continuous matter in hydrodynamics. This is another example that the support of analytical theory did not mean a denial of the molecular constitution of matter. Maria Yamalidou, “Molecular ideas in hydrodynamics,” *Annals of science*, 55 (1998), 369-400.

35. Woldemar Voigt, “Theoretische Studien über die Elasticitätsverhältnisse der Krystalle.” *GA* (1887), 1-52, and “L’état actuel de nos connaissances sur l’élasticité des cristaux,” C.L. Guillaume and L. Poincaré, eds., *Rapports présentés au congrès international de physique* (Paris, 1900) 1, 277-318, on 289.

36. Voigt (ref. 3), 722-723.

37. *Ibid.*, 723, 728. Voigt’s argument against the reduction of the physical theory to atoms is very close to the argument of solid state physicists concerning their inability to construct



The subsequent history of piezoelectricity well exemplified this dual role. Voigt's theory continued to shape further theoretical developments and experiments in the field after molecular models that agreed with it had been proposed.

### 3. LATER MOLECULAR THEORIES

#### **Riecke's**

Voigt's colleague in Göttingen, Eduard Riecke, devised the first such model. Riecke had studied pyroelectricity in tourmaline from a molecular perspective, assuming polarized molecules, and he had employed hypotheses of charged molecules in explaining electric phenomena of bulk matter since 1874, two years after earning his doctor's degree. His doctorrater, Wilhelm Weber, a leading adherent of the particulate charges in electromagnetic theories, was the major influence on Riecke's physics. Though Riecke adopted newer treatments of electrodynamics, he remained an active supporter of the hypothesis of a corpuscular carrier of discrete charge.<sup>38</sup> Discrete polarized molecules, or "systems of poles," formed the basis of his theory of piezo- and pyroelectrics. He accepted Voigt's account but searched for a more fundamental level that would explain the continuum theory. "It is not without interest," he wrote, "to ask further, how a simple elastic or thermal displacement of the molecules can give rise to the creation of electric moments, or electric displacements."<sup>39</sup> His theory would thus demonstrate the possibility of a mechanical-molecular explanation, but not the truth of his particular suggestion.

The theory that he presented in 1891 and 1892 aimed at deriving the piezoelectric equations of Voigt's theory from molecular displacements inside the crystal. By molecule Riecke understood not the elementary building blocks of nature, but rather combinations of atoms that determined their behavior. He did not think that phenomena should always be reduced to the most fundamental level. A reduction to a simpler level or even to simpler assumptions was for him the common irrefragable practice of physics.<sup>40</sup>

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their theories from the behavior of elementary particles. The controversy between "fundamental" physics and the physics of more complex phenomena did not begin with Philip W. Anderson's famous article "More is different: Broken symmetry and the nature of hierarchical structure of science," *Science*, 177 (1972), 393-396.

38. Eduard Riecke, "Ueber die Pyroelectricität des Turmalins," *AP*, 28 (1886), 43-80; "Zwei Fundamentalversuche zur Lehre von der Pyroelectricität," *AP*, 31 (1887), 889-912; Emil Wiechert, "Eduard Riecke," *GN* (1916), 45-56, on 48; Woldemar Voigt, "Eduard Riecke als Physiker," *Physikalische Zeitschrift*, 16 (1915), 219-221; Stanley Goldberg, "Riecke, Eduard," *DSB*, 11, 445-447; Katzir (ref. 9), 108-112.

39. Eduard Riecke, "Zur Moleculartheorie der piëzoëlectrischen und pyroëlectrischen Erscheinungen," *GN* (1891), 191-202, on 193; "Molekulartheorie der piëzoëlectrischen und pyroëlectrischen Erscheinungen," *GA*, 28 (1892), 1-52.

40. Eduard Riecke, "Thermodynamik des Turmalins und mechanische Theorie der Muskelkontraktion," *GN* (1893), 19-45, on 32.



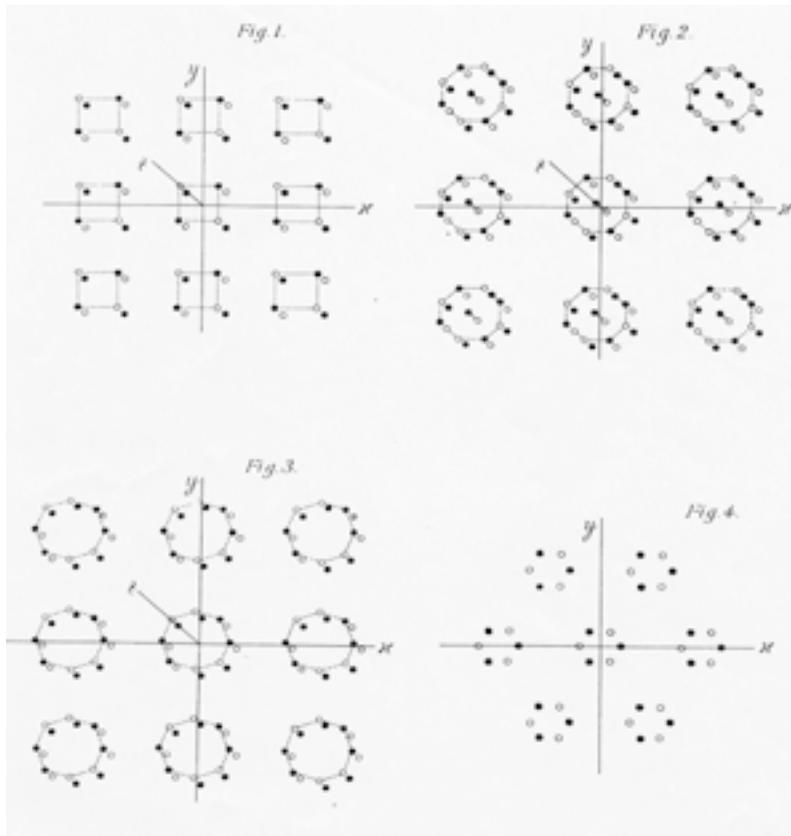


FIG. 3 Systems of molecules according to Riecke's theory. Figures 1, 2, 3 are projections of two layers on the plane of the paper. They show different classes of the quadratic system each based on another poles-system (molecule). In figure 4, which show a class of hexagonal system, all poles are in the plane of the paper, from. Source: Riecke (ref. 39).

In order that a simple displacement of molecules could elucidate the phenomena described in the phenomenological theory, the distribution of electricity in the molecules had to be more complex than previously assumed. In addition to bipolar molecules Riecke assumed more complex polar systems containing up to 24 poles. Implicitly he identified the polar system with the molecule and the poles as atoms or groups of atoms.<sup>41</sup> Following then current theories of crystal structure, each molecule had a symmetry corresponding to that of the lattice, equal to that of the system (figure 3). The theory presumed a different binding inside the molecules (or the polar systems) from that between them. The distances between the molecules varied, the distances within the polar systems were fixed. Consequently

41. These molecules are not necessarily identical with the chemical molecules. Riecke, *GA* (ref. 39), 5.





each molecule had a fixed polarity. Changes in the polarization of the crystal arose only through change in the relative position of the molecules. In 1915 Voigt would observe that the latest x-ray observations on the structure of crystals indicated that a molecular explanation of piezoelectricity should be sought in another direction.<sup>42</sup> In the 1890s, however, the arrangement of “the chemical atoms or molecules... within the unit cells formed by the space lattice remained a matter of speculation.”<sup>43</sup> Riecke justly stated that his picture of crystals agreed with accepted crystallographic and physical theories of crystalline structure.

Since according to the theory all molecules are polarized, they constantly exert electric force on one another. A permanent electric field and polarization, the resultants of all these forces, exist in all piezoelectric crystals and not only in pyroelectrics. As assumed by Thomson, superficial charge balances this polarization. According to Riecke’s theory, the piezoelectric effect derives from the sum of all the changes in the fields of the molecules, caused by relative displacements between them. To find this magnitude, Riecke employed both molecular and macroscopical (symmetry) considerations. For each class of crystals he obtained equations of the electric polarization in each direction as a function of the locations of the molecules, a constant, and the strains. Since the piezoelectric coefficients of Voigt’s general theory are, by definition, the coefficients of the strains in these equations, Riecke could identify them with the expressions that multiply the strains.<sup>44</sup> Thus, he found which coefficients differed from zero and which have the same value for each crystal class. His findings agreed with Voigt’s. Hence, he deduced the equations of the general theory for all classes from molecular assumptions. Yet in applying considerations of symmetry his derivation closely followed Voigt.

Although the expressions for the coefficients in the molecular theory contained many unknowns (through a constant that depends on the magnitude of the electric poles, the size of the molecules, their density and distances), in one case they supplied a basis for quantitative comparison between different coefficients of the same crystal. The phenomenological theory gave no guidance on this question. Riecke pointed out an agreement between the order of magnitude of the coefficients of tourmaline and their expressions in the molecular theory. He explained: “the constant  $\epsilon_{22}$  is relatively small [0.49, in comparison with  $-3$ ,  $-7.28$  and  $-9.35$  of the three others, all in units of  $10^{-4}$ ] because of its dependence on a polar system of a higher order, whose potential is given by a spherical function of the  $-4$ th

42. Voigt (ref. 38), 220.

43. John G. Burke, *Origins of the science of crystals* (Berkeley, 1966), 171; Arthur Birembaut, “Bravias, Auguste,” *DSB*, 2, 430-432; Marjorie Senechal, “Brief history of geometrical crystallography,” J. Lima-de-Faria, ed., *Historical atlas of crystallography* (Dordrecht, 1990), 43-59; Paul Forman, “The discovery of the diffraction of x-rays by crystals: A critique of myths,” *AHES*, 6 (1969), 38-71; P.P. Ewald, “The myth of myths: Comments on P. Forman’s paper on ‘The discovery of the diffraction of x-rays by crystals,’” *ibid.*, 72-83.

44. Riecke, *GA* (ref. 39), 27-43, Katzir (ref. 12), 115-118.





order. Against that the constants  $\epsilon_{15}$ ,  $\epsilon_{31}$  and  $\epsilon_{33}$  depend on a uniaxial system whose potential is of the  $-2$ nd order.<sup>45</sup>

It appears that, by explaining relative magnitudes of piezoelectric coefficients in the same crystal, Riecke's theory succeeded in accounting for phenomena beyond those assumed in its formulation, in a manner similar to the prediction of an unobserved phenomenon. Elsewhere Riecke claimed that "[t]he discovery of new phenomena on the basis of such a forecast [by a theoretical model] forms the true touchstone for the correctness of the underlying hypotheses, [and] for the usefulness of the models constructed with their help."<sup>46</sup> Riecke did not elaborate on the significance of the explanation of the relative magnitudes of the piezoelectric coefficients. He did not refer to any species but tourmaline in this context, despite the availability of relevant data for quartz through Riecke's own experiment in collaboration with Voigt.<sup>47</sup> In fact, the theoretical argument that works for tourmaline fails for quartz.<sup>48</sup> No relation exists between the order of the spherical function and the magnitudes of quartz coefficients. This failure does not refute the argument, since the magnitudes of the coefficients do depend on the spherical function of the potential, but also on unknown characteristics of the polar system. Since the expressions for the coefficients of tourmaline involve similar complications, Riecke's success with tourmaline was coincidental and not a demonstration of the theory's general explanatory power beyond the reach of the phenomenological account.

Riecke's alleged explanation of the coefficients' relative magnitudes was not even mentioned, let alone discussed or criticised, in publications of his contemporaries. Nor did he mention it in later publications. Describing his theory again in 1905 and 1912, he did not refer to his previous argument even when discussing the exact expressions for the piezoelectric coefficients of tourmaline.<sup>49</sup> In 1910 Voigt claimed that no molecular theory had yet predicted "specific results, such as numeric relations between the parameters" of the basic piezoelectric equations.<sup>50</sup> Since Voigt knew Riecke's theory well, he apparently did not accept Riecke's argument. The daily working connections between the two and the fact that Riecke did not repeat his claim suggest that Voigt may have expressed the objections to it to him privately.<sup>51</sup>

45. Riecke, *GA* (ref. 39), 43-52, on 50.

46. Eduard Riecke, *Lehrbuch der Physik* (3rd. edn, Leipzig, 1905), 4.

47. Eduard Riecke and Woldemar Voigt, "Die Piezoelectrischen Constanten des Quarzes und Turmalines," *AP*, 45 (1892), 523-552.

48. Katzir (ref. 9), 119.

49. Riecke (ref. 46), 145-155; "Zur Molekularen Theorie der Piezoelektrizität des Tourmalins," *Physikalische Zeitschrift*, 13 (1912), 409-415, on 411; and "Pyroelektrizität und Piezoelektrizität," L. Graetz, ed., *Handbuch der Elektrizität und des Magnetismus* (Leipzig, 1912), 1, 342-420.

50. Woldemar Voigt, *Lehrbuch der Kristallphysik* (Leipzig, 1910), 846-847.

51. In the first shorter communication on his molecular theory, Riecke did not mention the





## Voigt's

In 1893 Voigt described a generalization of Riecke's theory. He adopted the premises of unchangeable molecules whose centres coincide with centres of multipoles that occupy the lattice points. But he went beyond Riecke in allowing the symmetry of the pole system to be higher than that of the crystal. Whereas Riecke considered only five particular and relatively simple systems of poles, which have the same order of symmetry as the crystal, Voigt studied an arbitrary system of  $2^n$  poles. Instead of deriving the behavior of the crystal from its hypothetical structure, as Riecke had, he derived a possible structure of the crystal from its behavior.<sup>52</sup> In that he applied considerations of symmetry directly to functions of arbitrary potentials. His method resembled that used in elaborating his phenomenological theory three years earlier.

Voigt's mathematical treatment restricted polar systems to those with powers of two poles. Although convenient mathematically, it excluded likely polar systems including three out of the five that Riecke had suggested. The multipoles that Voigt found for the various crystal classes were physically less plausible than those that he rejected. In general each of his polar systems has  $2^{3+n}$  poles, where  $n$  is the crystal's order of symmetry. The number of poles in these systems can be smaller in some cases, but in most cases it reaches this limit. Voigt's polar systems ran from 8 to 8192 poles. These numbers are too high for geometrical visualization. They made any identification of the poles with the chemical atoms implausible.

Voigt himself did not regard this model as physically plausible.<sup>53</sup>

Another way of interpreting the piezoelectric phenomena seems to me to have the advantage of greater simplicity over Riecke's in many respects. Mr. Riecke represented molecules as dielectric polarized bodies, around which an invariable system of electric poles forms a group; on the other hand, I consider molecules that cannot be dielectrically polarized, but which contain poles, attached to individual atoms, that are *movable in respect to each other*. The phenomena in electric fields, like [those] effected by deformations, are then only a result and an expression of inner molecular rearrangements.

Voigt noted that his hypothesis would allow construction of a theory that would account for the symmetry of the crystal from the geometry of the atoms, without a need to use the potential function. The symmetry of the atoms in the molecules would be similar to that of the crystal as a whole and not much higher, as in his elaboration on Riecke's model.<sup>54</sup>

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argument about the relative magnitudes of the coefficients (he did not write the expressions for tourmaline coefficients there).

52. Woldemar Voigt, "Beiträge zur molekularen Theorie der Piezoelectricität," *GN* (1893), 649-671, 649-651; Katzir (ref. 9), 121-123.

53. Voigt (ref. 52).

54. *Ibid.*, 669-671.





Voigt seems to embody more surely than Riecke a new microphysical thinking, ascribing different properties to microscopic than to macroscopic objects; the molecule is no longer a dielectric like the crystal (it cannot possess polarization). His idea agreed well with the chemical concept of atoms inside the molecule and the physical consideration of internal molecular degrees of freedom, as attributed to molecules in the kinetic theory of gases.<sup>55</sup> Yet, crystals are very different from simple gases. A stereometric structure of a tourmaline molecule (chemical formula  $\text{NaMg}_3\text{Al}_6(\text{OH})_4(\text{BO}_3)_3\text{Si}_6\text{O}_{18}$ ) has many more possible configurations and degrees of freedom than a diatomic gas molecule. The problem becomes even more complicated when the relative positions of atoms in several such molecules in a crystal are considered. One can understand why Riecke preferred to deal with separate molecules with constant polarity. Voigt himself did not pursue his own hypothesis. He did not suggest any geometrical structure for any crystal.

In contrast to Riecke's theory, Voigt's sketchy suggestion assumes no permanent electric polarization in crystals that are not electrified by uniform pressure (like quartz). A change in the locations of atoms in the molecule can create an electric field where it did not exist before. The dismissal of permanent polarization left the molecular hypothesis in better agreement with the experimentally verified phenomenological theory. Moreover, Riecke's theory required the assumption of strong internal polarization (much stronger than that observed for piezo- and pyroelectricity), while no such assumption is needed in Voigt's theory. A few years later Voigt remarked that this assumption of "exorbitant large permanent specific moments [polarization]" adds theoretical complications that have no justification in the observations, and, moreover, is "unpleasant."<sup>56</sup>

In 1896 Voigt measured the permanent polarization of tourmaline at 33.4 statcoulomb/cm<sup>2</sup> at 24°C. Compared with a pyroelectric effect of 1.23 statcoulomb/cm<sup>2</sup>/°C this is not very large. Moreover, the pyroelectric effect of heating is in the opposite direction to that of the natural polarization. Therefore at about 50°C the internal electric moment of tourmaline should equal zero and at higher temperatures should have an opposite direction. These results contradicted the assumptions of Riecke's molecular theory and agreed with Voigt's atomistic hypotheses. Voigt, however, left this conclusion to the reader.<sup>57</sup>

Voigt examined empirically another consequence of his molecular suggestion. According to his model, a change of temperature should induce electricity in two ways: one by the piezoelectric effect due to thermal displacement, the other by the thermal movement of the electric poles inside the molecules. The latter possibility

55. The kinetic theory does not agree so well with Voigt's own molecular theory of elasticity, suggested six years earlier. It assumed discrete molecules with a fixed polarity. The internal motion of the atoms in the molecules could be assumed to have only a negligible influence on the molecules. Voigt, "Theoretische" (ref. 35).

56. Woldemar Voigt, "Versuch zur Bestimmung des wahren spezifischen electricische Momentes eines Turmalins," *AP*, 60 (1897), 368-375, on 370.

57. *Ibid.*





led him to account for the possible existence of a direct pyroelectric effect (not a secondary effect of piezoelectricity).<sup>58</sup> In an 1894 study he extended the general theory to account for secondary phenomena owing to electrical and mechanical changes induced by the piezoelectric effect.<sup>59</sup> In contrast, Riecke's theory does not predict any electrical effect from thermal movements. These only cause fluctuations in the separations of the molecules, which cause fluctuations in the electric fields, but not a net effect since they do not change the average distances. To distinguish between the possible separate effects Voigt carried out exact measurements of the pyro- and piezoelectric effects and thermal expansion in tourmaline in 1898. He found that about 20 percent of the total electric effect is not accounted for by the combined effect of thermal expansion and piezoelectricity and, hence, must be a genuine direct pyroelectric effect. Again he left to the reader the conclusion that the existence of such an effect agreed with his molecular model.<sup>60</sup>

Considerations of the molecular theory were a major motivation for both experiments, but not their sole motivation. The general phenomenological theory also supplied reasons for them. In measuring internal polarization, Voigt verified Thomson's hypothesis, which is also a consequence of the general theory, for the first time. Unlike permanent polarization, the existence of a direct pyroelectric effect was not a consequence of the general theory (neither is it a rigorous deduction from the molecular theory). Still, the inclusion of this effect in the mathematical theory of the subject followed from a cautious phenomenological approach. In 1893 Thomson, by then Lord Kelvin, noted that in considering only the indirect effect one makes "a hypothetical assumption unduly limiting the pyro-electric property to identify with the piezo-electric effect."<sup>61</sup> A year later Voigt accepted Kelvin's criticism and considered the possibility of direct pyroelectricity. The theory became more general and less hypothetical, in other words more truly phenomenological. In 1890, Voigt's student Friedrich Pockels generalized the theory of electro-optics (the effect of the electric field on double refraction) in a similar way by considering a direct effect without any assumption concerning the mechanism behind it.<sup>62</sup>

58. Woldemar Voigt, "Lässt sich die Pyroelectricität der Krystalle vollständig auf piëzoelctrische Wirkungen zurückführen?," *AP*, 66 (1898), 1030-1060, on 1034.

59. Voigt (ref. 30); Katzir (ref. 9), 179-187.

60. Voigt (ref. 58).

61. Lord Kelvin, "On the theory of pyro-electricity and piezo-electricity of crystals," *TMPP*, 5, 325-332, on 329.

62. Friedrich Pockels, "Ueber die Aenderungen des optischen Verhaltens und die elastischen Deformationen dielektrischer Krystalle im elektrischen Felde," *Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie, Beilage-band*, 7 (1891), 201-231.





## Kelvin's

Simultaneously with Voigt Lord Kelvin suggested a model of piezoelectricity based on displacements of atoms inside the molecules.<sup>63</sup> Unlike Voigt, Kelvin was not interested in introducing general principles for a future theory, but in finding a specific illustration for particular phenomena in quartz. His model did lead to the observed electrification by pressure in quartz. The model did not explain the electric effect of torsion.<sup>64</sup> Although his discussion was qualitative, Kelvin made a quantitative estimate of the effect by modeling quartz as a cluster of zinc and copper balls. These metals had already been mentioned for the same purpose by the Curies in their uniaxial molecular theory. Kelvin actually built his "realizable model."

Equal pressures along the polar axes of quartz (longitudinal) and perpendicular to them (transverse) induce effects of equal magnitude and inverse signs. The explanation of this relation in the model is so immediate that Kelvin did not even bother to state it.<sup>65</sup> Moreover, he was not satisfied with this kind of molecular explanation but sought to "prove, without any hypothetical assumption," the inverse behavior of strains in perpendicular directions. His proof was based on empirical findings, without reference to any molecular model.<sup>66</sup> Thus, Kelvin recognized the fragility of arguments based on plausible but hypothetical explanatory models. When available, he preferred macroscopic, non-hypothetical arguments.

A few weeks after presenting his model for quartz, Kelvin suggested one for any piezoelectric crystal. He thought that by comparing piezo- and pyroelectric crystals to an electrochemical cell, the Curies had supplied "the true matter-of-fact theory of a crystalline molecule." He conceived the molecule as a microscopic cell compounded of material with different electrochemical potentials. Variations in pressure or temperature change the distances between the molecules and thus the electric polarization of the assemblage. In contrast to Kelvin's model of quartz, his battery analogy assumed that the molecules themselves are not altered by pressure.<sup>67</sup> With a few simplifications Kelvin derived a solvable but very complex mathematical problem from the analogy and sketched its solution. Yet he preferred an experimental solution to the mathematical problem. Such an experiment had already been performed by the Curies. One can doubt the fertility of a model that

63. Lord Kelvin, "On the piezo-electric property of quartz," *TMPP*, 5, 311-322. The paper appeared originally in *Philosophical magazine* of October 1893. It is highly unlikely that Thomson had heard about Voigt's talk.

64. He referred to Voigt's theory in a general lecture in May 1893, "On the molecular tactics of crystal," *Baltimore lectures on molecular dynamics and the wave theory of light* (London, 1904), Appendix H, 602-642, on 639.

65. Ernest Mallard had suggested nine years earlier a similar explanation based on hypothetical polar molecules, like those assumed by the Curies; Mallard (ref. 23), 559-560.

66. Kelvin (ref. 63), 317-318.

67. Kelvin (ref. 61), 325-326.



predicted results only by measuring the phenomena that it was to elucidate.

Kelvin added instructions for constructing a concrete model, based on the same principles as the intellectual model, that might be more useful. This complex construction was to yield 21 piezo- and pyroelectric coefficients: Voigt's 18 and 3 independent pyroelectric coefficients. It would have consisted of an assemblage of molecules, each made up of 22 parts, one of zinc and 21 of copper. Twenty-one changes in the location of the zinc (located in identical places in all molecules) led to 21 equations, which with 21 measurements of the electric effect in each case sufficed to yield all the coefficients. It was a kind of analogue calculating machine. Unfortunately, it yielded only the coefficients of the model, not of a real crystal. The complicated construction that Kelvin had suggested and the limited knowledge obtainable from it perhaps explain why no one tried to build one.<sup>68</sup> That the model had a limited practical value did not seem to bother Kelvin. Its aim was to supply a visualization of piezoelectric phenomena and so a way to understand them. For him the models did not picture inner physical reality. He therefore felt free to use incompatible models for the same phenomena, like viewing the molecule as a continuous metallic-like surface in the general model and as made of movable separate balls in the model for quartz. Kelvin did not see in the model a justification for a theory or a demonstration of any truth about nature.<sup>69</sup>

In 1901 Kelvin advanced yet another explanatory model for piezo- and pyroelectricity. Unlike his former creations, this one was based on atomic rather than molecular considerations. It followed developments in atomic theory during the late 1890s, especially J.J. Thomson's discovery of the corpuscle-electron in 1897. Two years later J.J. Thomson advanced a model of the atom as an agglomeration of many small negative corpuscles in a sphere that acted as though it possessed a positive charge. Based on these general ideas, Kelvin suggested an atomic theory. He assumed that in crystals, in which all the atoms are oriented in the same direction, the distribution of the negative corpuscles inside the atoms can cause a net polarization. Movement of the atoms, caused by pressure or variation of temperature, changes the net polarization or even induces polarization in assemblages that were previously neutral. As in his earlier models of piezoelectricity, Kelvin does not aim here to propose the true mechanism of the phenomena, but to illustrate a way of understanding the phenomena. He also wanted to demonstrate the explanatory power of atomic theory. In suggesting specific models Kelvin preferred the simplicity of the explanation to the plausibility of its hypotheses.

#### 4. THE STATUS OF THE MOLECULAR EXPLANATION

Elaborating the phenomenological theory in 1894, Voigt did not even mention the molecular suggestion, which he himself had treated and advanced a year ear-

68. *Ibid.*, 327-333; Katzir (ref. 9), 134-135.

69. Crosbie Smith and M. Norton Wise, *Energy and empire: A biographical study of Lord Kelvin* (Cambridge, 1989), 463-471.





lier.<sup>70</sup> Except in pointing to the possibility of a direct pyroelectricity (which had additional sources), the molecular theories had no influence on the further development of the phenomenological theory of piezoelectricity. Extending the scope of the phenomenological theory both to other kinds of effects and to secondary influences and exploring the interrelations between its various manifestations and its relations to other phenomena were Voigt's central concerns in elaborating his general theory. Formulating that theory by thermodynamic potential functions was a parallel and connected effort in which both Riecke and Voigt participated.<sup>71</sup> Although handbook articles on piezoelectricity described one or more explanatory theories, Voigt's influential textbook of 1910 discussed them only briefly. Experimental accounts also gave them scant attention. As pointed out above, only two experiments were related to these theories. Thus, most involved in the research usually expressed indifference to molecular theories of piezoelectricity. Their shaky and controversial basis and their inability to predict further relations did not recommend them.

Kelvin's atomic explanation depended on his atomic model. The rejection of the model entailed the rejection of the explanation. No reference to the latter occurs in the literature on piezoelectricity.<sup>72</sup> The binding of the fate of explanatory theories with ideas of the structure of matter is most conspicuous in this example, but characterizes all mechanisms suggested for the source of piezoelectricity. All the mechanisms contained arbitrary elements constantly under threat of incompatibility with new views and findings on the physical structure of crystals. That was true for Riecke's theory as well as for Kelvin's atomic theory.<sup>73</sup>

The molecular theories of piezoelectricity well illustrate Voigt's claim that successful ones could only be constructed with reference to the phenomenological theory.<sup>74</sup> Examples are the principles of symmetry used by Riecke and Voigt. Kelvin, too, relied on Voigt's phenomenological theory to determine the number of parts in his model molecule and the number of measurements to obtain them. This property of the molecular theories made them appear ad hoc and arbitrary. Their failure to provide any unknown or unexplained relation made them also unfruitful. Riecke observed that "the true touchstone for the truth of the underlying hypotheses" is "the discovery of new phenomena."<sup>75</sup> Where molecular theories managed to reveal new relations, they were generally accepted.

70. Voigt (ref. 30).

71. On the theoretical elaboration of the phenomenological theory see Katzir (ref. 9), 144-193.

72. None of the essays on pyro- and piezoelectricity in the handbooks mentioned it: Riecke (ref. 49); Friedrich Pockels, "Pyro- and Piezoelectrizität," Adolf Winkelmann ed., *Handbuch der Physik* (Leipzig, 1905), 4:1, 766-791.

73. Voigt (ref. 38), 220.

74. Voigt (ref. 3), 723.

75. Riecke (ref. 46), 4.





In explaining the success of the corpuscular-hypothetical theory of electrons H.A. Lorentz wrote:<sup>76</sup>

[T]he theory of electrons is to be regarded as an extension to the domain of electricity of the molecular and atomistic theories that have proved of so much use in many branches of physics and chemistry. Like these, it is apt to be viewed unfavourably by some physicists, who prefer to push their way into new and unexplored regions by following those great highways of science which we possess in the laws of thermodynamics, or who arrive at important and beautiful results, simply by describing the phenomena and their mutual relations by means of a system of suitable equations. No one can deny that these methods have a charm of their own, and that, in following them, we have the feeling of treading on firm ground, whereas in the molecular theories the too adventurous physicist often runs the risk of losing his way and of being deluded by some false prospect of success. We must not forget, however, that *these molecular hypotheses can boast of some results that could never have been attained by pure thermodynamics, or by means of the equations of the electromagnetic field in their most general form*, results that are well known to all who have studied the kinetic theory of gases, the theories of dilute solutions, of electrolysis and of the genesis of electric currents by the motion of ions.

The molecular and phenomenological studies seem to be two parallel realms: one hypothetical, whose relation to reality is unknown, the other rigorous and firmly based on observations. J.L. Heilbron claimed that “in order to recapture the spirit of fin-de-siècle physics it will be necessary to admit a sort of professional schizophrenia, whose two personalities correspond to the physicist as practicing scientist and the physicist as philosopher of science.” As a physicist one believed in the existence of entities like atoms and molecules, which he doubted as a philosopher. Physicists’ cautious, sceptical philosophical claims about the reality of physical concepts, Heilbron showed, contradicted their practice and comments in scientific papers.<sup>77</sup> Notwithstanding the usefulness of this picture to the historical understanding of fin-de-siècle physics, it fails to consider differences between various practices. In phenomenological-thermodynamical research the physicists seem closer to their “philosophical persona” than to their “scientific” one. In this research physicists refrained from the speculative assumptions of molecular theories. The separation between the two realms of research resembles the two personalities discussed by Heilbron, but indicates that the division between the physicist *qua* philosopher and the physicist *qua* scientist is problematic. Was Voigt’s theory of secondary phenomena a work of a physicist *qua* philosopher and his molecular theories those of a physicist *qua* scientist?

76. Hendrik A. Lorentz, *The theory of electrons and its applications to the phenomena of light and radiant heat* (2nd ed., New York, 1952), 10-11 (text of 1909, italics in the original).

77. Heilbron (ref. 1), 26-27 and the following discussion.





The contribution of Voigt's molecular view to his decision to consider direct pyroelectricity reveals the significance of the molecular for the phenomenological theory. The two theoretical efforts were not independent of one another.<sup>78</sup> Voigt was well aware of the hypothetical nature of the atoms and molecules of his explanatory theory, but that did not vitiate this theory for his phenomenological approach, which he considered a true and valid description of relations between phenomena.

Since both molecular and phenomenological realms had potential benefits, advancing simultaneously in both was a reasonable strategy as long as one recognized the hypothetical character of the molecular against the firmer ground of the phenomenological. Investigators of piezoelectricity did not seek immediately the ultimate structure and mechanism of nature but a better knowledge of behavior that would enable description and, if possible, fundamental understanding.

**Table 1: Explanatory models, theories and suggestions of Piezoelectricity**

Theory	Compatibility with Voigt's theory	Mechanical <sup>1</sup>	Molecular/Atomistic	Thermo-electric	Elaborated explicitly <sup>2</sup>
The Curies'	-	+	+	-	+
Wiedemann's	-	-	+	+	-
Duhem's (1886)	-	-	-	+	+

Theories suggested after the introduction of Voigt's theory

Riecke's	+	+	+	-	+
Voigt's elaboration of Riecke's	+	+	+	-	+
Voigt's own	+	+	+	-	-
Kelvin's for quartz	partial	+	+	-	+
Kelvin's general	+	+	+	-	-
Kelvin's atomistic	+	+	+	-	-

1. A theory in which the electric effect is due to a mechanical process of pressure and/or a variation of temperature, such as a change of distance between charged corpuscles.

2. A theory explicitly elaborated mathematically or otherwise to attain relations that can be empirically examined.

+ indicates that the theory possesses the property mentioned in the column, while - signifies that it does not.

78. Olivier Darrigol shows that physicists moved with ease from one kind of argument to another in their theories of hydrodynamics and elasticity. Those who preferred continuum-phenomenological theory continued to believe in the molecular structure of matter and to consider it in their arguments. Olivier Darrigol, "Between hydrodynamics and elasticity theory: The first five births of the Navier-Stokes equation," *AHES*, 56 (2002), 95-150.





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**From explanation to description: Molecular and phenomenological theories of piezoelectricity**

ABSTRACT:

The second half of the 19th century saw the rise of new corpuscular theories in physics. Piezoelectricity, discovered in 1880, underwent a development reverse to that of most fields of physics. The first molecular theories were soon replaced by a continuum-phenomenological theory, which guided most research in the field, while, at the same time, physicists continued to propose molecular models. This article studies the reasons for the peculiar development of piezoelectric theory, through a close look at the models suggested and the developments in the field. It argues that the transition originated in a failure of the molecular model to account for new experimental results. Furthermore, later explanatory theories remained speculations, since they failed to derive any relations left unaccounted for by the phenomenological theory and since their basic premises were doubtful. Protagonists also raised general claims about the necessity of a phenomenological theory. Yet they did not derive their position from a doctrinal antagonism to molecular explanation. The same physicists studied both the secure phenomenological theory and speculative explanation simultaneously. They advanced in two mostly separated kinds of researches: molecular-atomistic and phenomenological-positivistic. Nevertheless, the separation between these approaches was not complete. This suggests that physicists embodied the same persona in elaborating “positivistic” theory as in elaborating “realistic” molecular theory.

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