

# BIOGRAPHICAL MEMOIRS

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## **Peter Joseph Wilhelm Debye, 1884-1966**

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*Biogr. Mem. Fell. R. Soc.* 1970 **16**, 175-232, published 1 November 1970

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P. Levy

## PETER JOSEPH WILHELM DEBYE

1884-1966

Elected For. Mem. R.S. 1933

PETRUS JOSEPHUS WILHELMUS DEBIJE (PETER DEBYE) was born on 24 March 1884 at Maastricht in the Limburg province of the Netherlands, a town bearing witness to much in the history and culture of at least three of Europe's present national groups. Some other notable physical scientists who share the same birthday are Georg Bauer Agricola (O.S. 1494: *De re metallica*), Joseph Priestley (1733), Josef Stefan (1835), and Adolf Butenandt (1903), another Nobel prizewinner in Chemistry. Debye died at Ithaca, the city where Cornell University is located in upper New York State, on 2 November 1966. In the three years that have since elapsed, a number of brief obituary notices have appeared: these and an earlier article by the writer have been used in preparing the following account. The sequence is essentially chronological with the subdivisions indicating Debye's academic location.

### EARLY YEARS

The burgomaster of Maastricht has made available a genealogy which is essentially complete to the fourth generation. One of the eight great-great-grandfathers is given as Joannes Debeij, born in 1752, the great-grandfather (1783-1854) being Pieter Eoduryk Debije. The whole family tree is firmly planted in Maastricht: three of the scientist's grandparents were born in and died at Maastricht, as did his parents. They were all also Roman Catholics. His parents, Joannes Wilhelmus Debije (1859-1937) and Maria Anna Barbara Ruemkens (1859-1940) were married on 23 May 1883, his father's twenty-fourth birthday. Records describe his father as a smith or foreman (smid: Werkmeister) in a metal-ware manufacturer's (J. G. Lambriex) at Maastricht which made items (including tinned-ware) for general use, from gates to kettles: he was well respected by his fellow-workmen and by the other citizens of Maastricht. The Sommerfelds met the parents at Aachen and Frau Sommerfeld carried a memory of the father's bright eyes. There was only one other child, a sister four years younger than the scientist. The mother was a dominant character with a keenness in money matters. She was for many years the cashier of the theatre which was an important centre in the life of Maastricht. Amongst Debye's most cherished memories (and he had a very retentive memory) were those of the opera music he heard as a youngster in Maastricht. He could recall and whistle many of the tunes even from works which have long since ceased to be performed.



Debye himself made it known that until he was five or six years old, and therefore regularly attending school, he very little knew or used the Dutch language: his medium was the Maastricht patois. This he fully retained throughout his life and not only spoke but corresponded in it with his Maastricht friends—the patois being appreciably different from Dutch. This serves to illustrate a significant aspect of Debye's character. There is no doubt but that he thought of himself as a Maastricht man, and Maastricht has, as the centre of the province of Limburg, some considerable independence of character in the Netherlands. Before the liberation from Spanish hegemony it was ruled jointly by the Duke of Brabant and the Archbishop of Liège. It has remained firmly Roman Catholic and its citizens still retain a feeling of some independence with respect to Holland in particular and the Netherlands in general. This lack of a firm national attachment added to the fact that his parents were fond of making family excursions at short notice to other, often distant, European cities, undoubtedly contributed to Debye's independence from national concerns and national politics.

Debye attended the Hoogere Burger School at Maastricht for five years from the age of twelve. His record in the school-leaving examination, which involved both written and oral tests in most subjects, can be summarized: algebra (8), geometry (10), trigonometry (8), projective drawing and geometry (8), mechanics (10), physics (10), chemistry (9), natural history (10), cosmography (10), history (6), geography (8), government and public administration (7), economics (6), Dutch (9), French (8), German (8), English (5). This record, achieved without any particular effort on his part, put him at the head of the Limburg list. It is impressive also for the range of subjects studied which, however, did not include Greek and Latin. This meant Debye could not then have entered a Dutch university. But it had been decided that he would take the job he had secured with Jurgens, the fats and margarine firm which later formed part of Unilever. Between leaving school and starting work the possibility of further education arose. Seventy years ago a fully-developed secondary education was itself by no means common for boys of such modest homes as Debye's: it implies unusual enlightenment on the part of his parents. The father, it seems, now averred that he 'would work night and day' were it necessary in paying for the further education out of his weekly earnings. The choice was between the Technical University at Delft and the Technische Hochschule at Aachen. Cost and the possibility of living at home made Aachen the choice and so Debye for some years left his bed soon after five to catch the early morning train to Aachen. In so doing he had already taken the most critical step of his whole career.

Aachen was thirty kilometres away and across the border in Germany. This transfer may have led to the restyling of his surname. The original form is Debije, variously pronounced in the Netherlands but often as Deb-ay: outside Dutch sources he almost invariably used Debye which, in English, had always been pronounced Deb-eye: on his birthplace (rebuilt as a shopping centre) he is Pie Debye, with the Maastricht familiar form of Peter



by which he was known there. This diversity of name-forms in part reflects the diversity of languages which is almost the birth-right of a Netherlander and which he early acquired and which (with Italian) he used to excellent effect in promoting (and translating) exchanges at conferences. But it was at Aachen that Debye first acquired full facility in the most powerful language at his command.

He was fortunate to have amongst his teachers at Aachen, Max Wien (experimental physics) and Arnold Sommerfeld (theoretical physics). His initial course was for the diploma in electrotechnology. In view of his life-long mastery in theoretical developments, it is relevant to note he can have devoted no great time to learning mathematics as such, but he did have an immediate immersion in its applications. Later he was to comment (in comparing matrix- and wave-mechanics) that he was far more familiar with differential equations than with matrices. His diploma work included a theoretical treatment of Foucault currents in a rectangular conductor and presented a mathematically elegant solution based on Green's theorem. This became his first published work. He was not, however, interested in electrical technology but rather in physical theory. Sommerfeld, who was later to describe the young student as 'a charming boy who looked out on the world and on life with intelligence and curiosity', had immediately recognized his ability. 'When I had the first possibility to appoint an assistant, there was no doubt in the choice. He went with me as an assistant to Munich in 1906. From here he set out on his victorious progress through Physics and Chemistry.' (1)\*

#### MUNICH, 1906-1911

Debye's doctoral thesis was completed at Munich (July 1908). He had at Aachen already studied the diffraction of light by cylindrical and spherical particles and the original title of the thesis was 'Über den Regenbogen (Concerning the rainbow)'. It dealt with the radiation pressure experienced by spherical particles of varied refractive properties. Not only did it include further evidence of mathematical ability of a high order in its original and extended treatment of Hankel functions and the asymptotic representation of Bessel functions, but it also gave Debye a grasp of what became a continually recurring theme in his career, the refinements of the interaction of radiation with matter. Another publication of this early period with Hondros (1910) was far ahead of its time in its practical value: it dealt with propagation problems of significance to radar and waveguide systems. In much of his later work Debye was often concerned with physically significant treatments and especially with deriving adequately sound and immediately usable relations which allowed of the quantitative evaluation of molecular

\* A reference given as a running number relates to the list of References: given as a year it relates to the Debye paper of that date, the titles of which appear in the Bibliography: if the year carries an asterisk, it means that the quotation given from the paper is taken, with the publishers' permission, from its translation in *P. J. W. Debye, Collected Papers*, Interscience Publ., N.Y. 1954. Other references (Book) are to Debye's volumes of which a separate list is given.



systems. In these treatments mathematical elegance and rigour could take second place, but few will doubt Debye's ability as a mathematician. David Hilbert was certain of it.

The five years at Munich (1906-1911) probably had a determinative role in orientating Debye towards his life-long interest in diffraction and the interaction of radiation with atomic and molecular systems. Röntgen was professor of experimental physics and, with selected students (e.g. Joffé, Pringsheim) continued careful studies of X-rays. In this environment and almost as a sequel to Debye's thesis, Sommerfeld suggested the problem of finding 'the optical properties of an anisotropic arrangement of isotropic resonators'. This was Paul Ewald's topic and the conclusions in his thesis led Laue, who had joined Sommerfeld as his second assistant, to suggest the experiment which settled the nature of X-rays. Sommerfeld was professor of theoretical physics but had insisted on having laboratory facilities: the dramatic success of this combination might well have influenced Debye but his predilection towards the experimental control of theory could already be seen in his favourite reading: Rayleigh, Maxwell, Boltzmann, Riemann, Drude. 'Debye was an avid reader of classical mathematics and physics, and in particular of Lord Rayleigh's papers and his *Theory of Sound*. Proper modes of vibration had a high priority in his mind . . . Especially the English masters keep the two parts (theory and experiment) of Physics together.' (2) On the status acquired by Debye in these early years at Munich, Ewald must again be quoted (3): 'Needless to say to those who know of his later development, Debye was, even then, an outstanding physicist, mathematician, and helpful friend. He was, not less than Sommerfeld himself, a centre for the senior students and graduates frequenting the Institute and the Physics Colloquium.'

Two of Debye's other publications from Munich must be mentioned. The first was a review article instigated by Sommerfeld: 'Stationary and quasi-stationary [electric] fields' (1910). Kramers has described this as a very beautiful and mathematically very elaborate ninety-page article, and other senior physicists have commented how they wish younger writers on this theme would first study Debye's article. The second was much briefer but, even in 1950, earned the special commendation of his teacher when, appropriately, presenting him with the Max Planck medal of the German Physical Society: in it Debye provided one of the first coherent deductions of Planck's radiation formula. It is entitled, 'The concept of probability in the theory of radiation' (1910).

In deducing his radiation formula (4) Planck assumed firstly that the energy can be absorbed and emitted in infinitesimal amounts. From this he found the connexion between the energy of a linear resonator and the energy density of the radiation field. In the second part of the argument, in order to establish the connexion between the equilibrium energy and the temperature, the assumption is made that the energy can be dealt with in finite energy-quanta. If this seems a remarkable procedure it must be remembered



that eight weeks before presenting his deduction of the formula, Planck had advanced it on an essentially empirical basis. Debye corrected this situation.

Debye considers the Rayleigh-Jeans radiation cube and enumerates the totality of the proper modes of the electromagnetic vibrations by the usual subdivision of the cube edge. Debye ascribes  $h\nu$  as the energy to each of these proper modes. Accordingly, his quantum is not restricted to atomic or molecular features as with Planck but is associated with proper modes which are distributed over the whole cube. He finds the probability for the quantal distribution as does Planck and likewise the most probable state by the usual variation method. The temperature accordingly enters via the entropy. The distribution function so obtained is Planck's radiation law. In the fourth edition of his monograph [*Die Theorie der Wärmestrahlung*] Planck himself adopted Debye's method which he characterized 'as an extremely simple deduction' of his radiation law.

#### ZÜRICH, 1911-1912

Debye left Munich in 1911 before Friedrich and Knipping had performed their experiment (May 1912). He was chosen as Einstein's successor in the chair of theoretical physics at Zürich University (a cantonal, not federal, institute). Einstein had published three papers on the specific heats of solids: the first (1907) was one of the apparently immediately successful applications of Planck's quantum hypothesis, as it gave a good representation of the specific heat of diamond and other elements over a wide temperature range. He assumed the atoms in the lattice had a single vibrational frequency: the specific heat was deduced as the temperature derivative of Planck's energy formula. But in his third paper on specific heats, published from Prague (May 1911), Einstein showed that the single-frequency model was quite unacceptable—individual atoms would lose their vibrational energy far too rapidly and, apart from that, the thermal conductivity of the lattice would be impossibly small. He concluded the paper thus: 'The theoretical problem is so to modify the molecular mechanics as to give not only the specific heat law but also the likelihood of accounting for the simple relation for the thermal conductivity.' Debye has himself described (1964) how he proceeded: 'I considered that Planck's formula should be applicable to any kind of vibrating system. Such was in my opinion a solid or a lattice of atoms, since by using the proper coordinates, this mechanical system could be described as an agglomeration of a number of independent vibrating systems, each with its own proper frequency. The only question was to find the spectrum of frequencies. I knew about the one dimensional case of a string of atoms which had been treated by Rayleigh and started to formulate the mathematical problem for a three-dimensional cubic arrangement . . . This turned out to be rather complicated. Soon I realized that for my immediate purpose it would not be necessary to know too much about the details of the spectrum. At high temperatures the frequency distribution is immaterial. One has only to know the number of degrees of freedom: each gets  $kT$ . On the other hand,

at low temperatures according to Planck's formula the high frequencies are going to carry less and less energy. So I decided to find out the density of distribution of proper frequencies in the limit . . .'

'In order to calculate the density distribution in the ionic spectrum I calculated the spectrum for a sphere of isotropic elastic material. This was a *tour de force* but I enjoyed it because at that time I knew so much about spherical harmonics and cylinder functions. As a matter of fact the method can be described as clumsy. Anyway, I got the right result.'

Two of the assumptions introduced in Debye's treatment were described by Sommerfeld in 1950 as 'bold'. Not only did he evaluate the total spectral distribution of the elastic modes but he equated the total number of degrees of freedom to the number of permitted proper vibrations. Secondly, he assigned to each of these an energy  $h\nu$ . The evaluation of the totality of elastic modes he undertook for the form of a sphere: whilst this had the advantage of a strain-free boundary, it led to difficult limiting values of the Bessel functions which Debye was only able to handle thanks to his previous work on this subject. Debye's paper on specific heats was received by the *Annalen der Physik* on 24 July 1912. On 12 March 1912, the *Physikalische Zeitschrift* received the first of two papers by Born and Kármán, the second being received on 30 November 1912 (5). The treatments were entirely independent and remarkably different in character. Born and Kármán accepted the point-mass structure of the crystal lattice and evaluated the vibrational spectrum by a detailed consideration of the coupled oscillations in the three-dimensional structure. This was closer to reality than the Debye model but even more intricate a problem. However, Debye himself used the Born-Kármán model in his major paper on the scattering of X-rays by a crystal lattice (10 October 1913). It is interesting and perhaps significant, that in the volume of fifty papers published with Debye's help to celebrate his seventieth birthday, the specific heat paper is the last but one in the volume in a group labelled 'Miscellaneous' (1954).

The relation he deduced for the specific heat per g atom at constant volume is historically the first of those to be described as the *Debye equation*:

$$C_v = \frac{9Nk}{\nu_D^3} \int_0^{\nu_D} \frac{e^x}{(e^x - 1)^2} x^2 \nu^2 d\nu$$

$x = (h\nu/kT)$ :  $\nu_D$  is the maximum frequency in the lattice.

It gives an excellent representation of the specific heat for a wide range of solids. Two features are especially noteworthy. The specific heat is a function of  $x_D = \theta/T$ , where  $\theta$  is a temperature (the Debye temperature) characteristic of the lattice,  $h\nu_D/k$ . And, secondly, at the lowest temperatures  $C_v$  becomes simply proportional to  $T^3$ , a most valuable guide in approaches to absolute zero of temperature.

The year 1912, when Debye was twenty-eight, also saw the publication of another major contribution. This was a four-page paper bearing the date



1 February (1912\*): *Some results of a kinetic theory of insulators*. 'The assumption that the interior of dielectrics contains not only elastically bound electrons but also permanent dipoles of constant electric moment enables us to explain in a completely satisfactory way the temperature dependence of the dielectric constant' [of polar compounds]. This is the scientific birthplace of molecular electric dipoles. However, the delivery process in this instance is not impressive. Rather than an *a-priori* deduction of the means for evaluating the molecular moments an essentially *ex-cathedra* statement is made: 'If the polarization,  $P$ , produced by an electric field of strength,  $E$ , is calculated, an expression with two additive terms is found. The first term of this expression measures the effect of the displaced electrons and is independent of temperature. We represent it by  $(\epsilon_0 - 1)E$ . The second term has the Curie-Langevin form  $E(a/T)$ , where  $a$  is a constant and  $T$  the absolute temperature. For gases we then obtain:

$$P = E(\epsilon_0 - 1) + E(a/T).$$

Later, the result  $a = N\mu^2/9k$  is quoted: here  $\mu$  is the dipole moment. This perfunctory character may well have been the result of Debye's unquestioned recognition that he was following the Langevin calculation of the mean magnetic moment of gas molecules carrying a permanent magnetic moment, although the Langevin paper (6) is not explicitly referred to and  $k$ , Boltzmann's constant, is introduced as 'the universal constant with which the natural logarithm of the probability is to be multiplied to obtain the entropy. Its value is according to Planck,  $1.346 \times 10^{-16}$  erg.' This is clearly an echo from the paper in which he deduces the Planck radiation formula.

The relation which has served to evaluate the electric moments ( $\mu$ ) of gaseous molecules and which again is always called the Debye equation is

$$P = \frac{4\pi}{3} N \left( \alpha_0 + \frac{\mu^2}{3kT} \right)$$

$P$  is evaluated from experiment via the Mossotti-Clausius factor:

$$P = \left( \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \right) V,$$

where  $V$  is the molar volume. Debye has called  $P$ , the molar *polarization*, although it differs from the net molecular *polarizability* only by the universal factor  $(4\pi/3)N$ . This is an unfortunate misnomer but it has in no way limited the effective use of  $P$  to determine the dipole moments and thence valuable information on the stereochemical structure and bonding characteristics of many hundreds of molecules. The practical e.s.u. (c.g.s.) unit of dipole moment,  $1 \times 10^{-18}$  e.s.u., has universally been known as the debye (D).

In his original account Debye was obliged to forgo the application of his equation to data for gases—scarcely any existed of sufficient precision. He was obliged to test his relation on data for liquid alcohols, water and some other polar solvents. In this way he derived the first values for the molecular electric moments. The 1912 values may be quoted in debyes together with

presently accepted ones: diethyl ether 1.18 (1.16): toluene 0.51 (0.34): water 0.57 (1.82): methyl alcohol 0.34 (1.71). It has long been appreciated that the simple Debye equation for  $P$  and  $\mu$  is quantitatively applicable only in the molecularly dilute gaseous state. Without correction it will not give a molecularly significant  $\mu$  value from data for pure liquids. Debye realized this limitation in the original paper (1912\*), even to the extent of indicating that the relation predicted a critical temperature below which spontaneous polarization would appear. 'As far as I know', he wrote, 'this has not been achieved in practice.' In fact, ferroelectricity was first observed by Valasek in 1921 in crystals of Rochelle salt, and only more recently has an analogous state been surmised in ice and something similar achieved in polar liquid phases (11).

An account has been given (7) of a Debye lecture in 1912 at the University of Leiden when he presented his treatment of the electric permittivity of gases and liquids. Everyone, including the young Debye, was anxious to see how Lorentz, who was present, would take this account: it seems he somewhat drowsily nodded approval, as if in answer to the presentation directed almost personally to him.

#### UTRECHT, 1912-1914

Historically, it is significant that a considerable delay occurred in the development of dipole moment studies. At this early stage Debye does not appear to have initiated any measurements himself, although there are indications that his intention to do so was one reason for his leaving Zürich in 1912, where his chair was in theoretical physics: he had hopes that at Utrecht he would be able to undertake experimental dipole moment studies. However, the appointment at Utrecht was again to a professorship of mathematical physics and theoretical mechanics. His inaugural lecture was on the kinetic theory of matter and its modern development (1913). In it he expressed the opinion that 'mathematical physics is in the first place physics and it could not exist without experimental investigations'. Moreover, he was glad to express his agreement on this with his senior colleague, W. H. Julius, the professor of experimental physics. Certainly Debye developed no experimental work there. This is not surprising as during the year or so actually at Utrecht he was occupied with two major theoretical developments: the entirely new representation of dielectric dispersion and the equally far-sighted treatment of the influence of lattice vibrations upon X-ray diffraction intensities. Perhaps the somewhat sketchy nature of the 1912 dipole moment paper contributed to the delay before other scientists pursued dipole moment measurements. Debye himself promised a fuller treatment—'A comprehensive paper regarding the relation between the deviations from the law of Clausius-Mossotti and the hypothesis of fixed moments is in preparation' (1913\*). Despite this 1913 statement Debye does not appear to have published such a comprehensive account before the *Handbuch der Radiologie* article (1925).



Again, it must be remembered that the valve, as an electrical oscillator, did not come into general laboratory use until after the 1914-1918 war. Then, a number of physicists and some chemists (Jona, Sanger, Weigt, Zahn, Smyth) made a start on measurements in gases: these were not easy. Although measurements of the permittivities of solutions had been made many years earlier, their use in evaluating dipole moments appears first to have been explored in a thesis done under Debye's direction at Gottingen by Fraulein L. Lange in 1918. When this was published in 1925, a spate of work was initiated, and was accelerated by a discussion organized by Debye at Leipzig in 1928 (Book, Ed. 1929) and by his publication of the volume *Polar Molecules* in 1929 (Book). By 1935 a list of dipole moments for 1100 compounds could be compiled (8).

Doubtless many reasons contributed to the brevity of the basic electric dipole moment paper. It appears probable that Debye had immediately become engaged on a considerable extension of the molecular model for dielectrics. In 1913 a masterly paper full of new insights appeared: *The theory of anomalous dispersion in the region of long-wave electromagnetic radiation*. This took the appreciation of electric permittivities (i.e. 'dielectric constants') in molecular terms from the equilibrium state, delineated by means of  $P$ , to the dynamic representation in which the rate of the dipole reorientation in the electric field is determinative. The simplicity and effectiveness of the treatment he advanced shows Debye's keen physical insight and his exceptional ability in constructing a quantitative appraisal leading to direct experimental control.

He starts from the realization that on the application (or disappearance) of an electric field the molecular dipoles will take a brief but finite time to attain their equilibrium orientation. For small molecules he estimates the time to be of the order of 10 picoseconds. This he does by applying Stokes's factor for the viscous drag on a rotating sphere to one of radius  $10^{-8}$  cm. He thus defines the time-scale of the orientation and the frequency range where the permittivity would pass from its value  $\epsilon_0$ , characteristic of static fields, to  $\epsilon_\infty$ , the value when the applied field oscillates so rapidly as not to allow any motion of the dipole: at such frequencies the material fails to show its polar character and the permittivity reverts to that of a non-polar medium. Debye evaluates the dynamics of the molecular orientation and displacement in the field by using a generalization of Einstein's equation for determining the mean square displacement of a particle having Brownian motion. This leads to an expression for the decay of polarization on removal of the orienting field which is simply exponential:

$$P(t) = P(0) e^{-kt} = P(0) e^{-t/\tau}.$$

$\tau$  is the relaxation time, i.e. the reciprocal of the first-order rate coefficient for the polarization time dependence. For spherical particles of radius  $r$  Debye originally gave

$$\tau = \frac{8\pi\eta r^3}{kT}$$

where  $\eta$  is the viscosity of the medium. In deducing this he restricted the rotation to a plane: the general rotation leads to a factor 4 in place of 8.

This work provided an entirely new appreciation of the frequency dependence of dielectric properties. Debye himself emphasized this: 'The hypothesis that molecules contain permanent dipole moments is the essential basis of the theory'—and that hypothesis was only a year old. Even so its most important aspect was its clear analysis of a typical molecular relaxation process, in which respect it has been a model for many later representations of rapid molecular changes. The frequency dependence of the permittivity ( $\epsilon'$ ) was necessarily accompanied by an electrical energy absorption factor ( $\epsilon''$ ), these being the two experimental observables associated with the time-dependence of the polarization. Debye gave effectively the relations:

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + \omega^2 \tau^2}$$

$$\epsilon'' = (\epsilon_0 - \epsilon_{\infty}) \frac{\omega \tau}{1 + \omega^2 \tau^2}$$

Here  $\omega$  is the angular frequency ( $2\pi\nu$  radian  $\text{s}^{-1}$ ).

That a maximum in  $\epsilon''$  is reached for  $\omega\tau = 1$  provides a very direct means of evaluating  $\tau$ . Using relations equivalent to these, Debye drew a dispersion and absorption curve for water: he took  $\epsilon_0 = 80$ :  $\epsilon_{\infty} = 2$ : and  $\lambda(\epsilon''_{\text{max}}) = 1$  cm. This was very good guesswork: at 20 °C acceptable values now are  $\epsilon_0 = 80.2$ :  $\epsilon_{\infty} = 4.5$ :  $\lambda(\epsilon''_{\text{max}}) = 1.7_4$  cm, and until 1947 (9) it could be said that no published data on the dielectric dispersion of water were certainly nearer to the correct values than Debye's guess of 1913. In the original paper he quotes no general numerical data but gives a reference to a recent summary (10): much of the best experimental work at that date was still due to Drude. In view of the complexity of the molecular interactions in water it is a surprising fact that the simple Debye relations, based on a single relaxation time, do fit the data almost as accurately as they can be determined. The same is true for many of the crystalline forms of ice. Although very many systems do show deviations from these Debye equations, in the sense of providing a flatter and wider absorption curve ( $\epsilon'' = f(\omega)$ ) than he predicted, the general character of these deviations is well understood. One way of expressing this extension of his treatment is to envisage a finite number or a continuous range of contiguous relaxation times to be present in a single molecular system.

In the original paper Debye acknowledges the cooperation of an assistant (R. Ortvy). Boltzmann's constant is now described simply and directly as such. And there is specific reference to one other aspect of molecular behaviour whose time-dependence can be treated in the same way. This is the Kerr effect, i.e. electrically induced double refraction. The general exploration of dielectric dispersion had to wait until the klystron and other v.h.f. sources became generally available, i.e. until after 1945. Debye





DEBYE AND HIS CONTEMPORARIES AT THE SOLVAY CONFERENCE IN BRUSSELS, 1927.

|             |            |            |              |              |               |                |                 |          |               |                 |              |
|-------------|------------|------------|--------------|--------------|---------------|----------------|-----------------|----------|---------------|-----------------|--------------|
| P. DEBYE    | A. PICCARD | E. HENRIOT | P. EHRENFEST | EG. HERZEN   | TH. DE DONDER | E. SCHRÖDINGER | E. VERSCHAFFELT | W. PAULI | W. HEISENBERG | R.H. FOWLER     | L. BRILLOUIN |
| I. LANGMUIR | M. KNUDSEN | W.L. BRAGG | H.A. KRAMERS | P.A.M. DIRAC | A.H. COMPTON  | L. de BROGLIE  | M. BORN         | N. BOHR  | C.T.R. WILSON | O.W. RICHARDSON |              |
|             | M. PLANCK  | Mme CURIE  | H.A. LORENTZ | A. EINSTEIN  | P. LANGEVIN   | Ch.E. GUYE     |                 |          |               |                 |              |

Absents: Sir W.H. BRAGG, H. DESLANDRES et E. VAN AUBEL

Photograph by courtesy of *Instituts Internationaux de Physique et de Chimie Solvay*.



did himself provide an introduction to experimental studies in this area in a paper at a Faraday Society Discussion (1934). The thermal assessment of the electrical loss factor  $\epsilon''$  which he described there was pursued by some of his associates, but it did not offer more than preliminary quantitative data.\* Especially in relation to its important molecular structural aspects much of the later v.h.f. work on dielectric dispersion was developed by C. P. Smyth at Princeton: von Hippel at M.I.T. organized solid state studies and a group of French physicists at the Sorbonne also took up these problems (11). The effective examination of the frequency dispersion of the Kerr constant was not undertaken until appropriate pulsed-field methods became available in the later 1950s. For small molecules the direct observation in real time of these dipole relaxation processes is only now being achieved.

Whilst professor at Utrecht, Debye married in Munich, Matilde Alberer, a Bavarian lady, three years his junior. She was one of three daughters of the boarding house he had stayed at in Munich. On marriage she acquired Dutch nationality and at present still resides at Ithaca. There were two children of the marriage, a son and a daughter. The former is now a senior industrial physicist in the U.S.A.: for several years, both at Berlin and at Ithaca, he very substantially assisted in his father's work, making notable contributions on the experimental side. The daughter and her two sons now also live in the U.S.A.

Debye's sojourn at Utrecht was only for two years. It seems that before he had been made a member of the senate there he was probably already committed to moving to Göttingen. Certainly one reason for this move was the poor immediate prospect at Utrecht for the laboratory facilities he desired. Nevertheless, the Utrecht period was a very fruitful one as, in addition to the treatment of dielectric dispersion, it embraced his work on lattice vibrations and X-ray diffraction intensities. Three brief reports, followed by a major paper dated 10 October 1913 (1914\*) originated at Utrecht: in the brief items (1913: *Verh. d. Phys. Gesell.*) his name appears as Debye.

The discovery of X-ray diffraction was made at Munich in May 1912 and Laue had immediately presented his theoretical interpretation of it (12). Debye was in the closest contact with developments at Munich. His own work there, the whole corpus of his interests in radiation problems and, most particularly, his recent treatment of lattice specific heats provided him with the clearest insight into the character and some of the refinements of X-ray diffraction. The paper which resulted is one of the great achievements in crystal physics. That its content should have been developed within months of the discovery of X-ray diffraction must remain for ever astonishing. It is difficult to convey briefly the depth and clarity of the approach, the

\* Professor Sack [Cornell] recalls the important contributions of J. Errera [Brussels], a close colleague of Debye's. In the stereochemical implications of molecular dipole moments (1925), in the study of dipole rotation and dispersion in solids (e.g. ice, 1924), and in dispersion measurements of the Kerr effect (1935), Errera contributed much to substantiate the Debye model of dielectric behaviour. A similar position, and friendship, was attained by S. Mizushima [Tokyo].



coherence of the presentation, and the degree of conviction achieved by the evaluation of numerical conclusions discriminating between two models differing only in one simple but fundamentally important assumption: but some points from the various sections may be quoted.

The introduction mentions the preliminary results already published (1914\*): 'The summation of the effects on the incident beam due to the atomic structure, no longer rigid as assumed by Laue, resulted in the absence of an effect on the sharpness of the interference maxima and in the existence of an intensity effect. An explanation was also found for the appearance of noticeable intensities mostly in those directions that deviate only by small angles from the direction of the incident beam, and at the same time for the fact that the so-called reflection of X-rays is observed under ordinary circumstances only if the incidence is not too steep. The computation further shows that, as a consequence of the thermal movement, the interference intensity must always be accompanied by a scattered radiation which has its maximum where the interference intensity is weakest . . .

'Firstly we have dropped the assumption of the mutual independence of the atoms. In this paper their movement is composed of superposed elastic waves whose wave numbers assume all values in the elastic spectrum of the body, a method that has proved successful in the theory of specific heats.

'Secondly, we thus created the opportunity to apply the quantum hypothesis in a definite manner to our case. We have not decided for or against the existence of zero-point energy . . . though different new articles by A. Einstein and O. Stern, H. Kamerling Onnes, W. H. Keesom, E. Oosterhuis present weighty reasons for the assumption of a zero-point energy . . . In fact it is clear from the very beginning that, if the fundamental concepts of the theory are correct, the mean square of the amplitude of the atomic movements itself and not its differential coefficient with respect to temperature (as in the case of specific heats) will be decisive. In view of this decision, to be made on the basis of experiments, we have developed the theory to a point where a formula is available which can be used numerically, and have appended numerical and graphical discussions.'

The subsequent sections are:

'I. Mathematical formulation of the principal problem . . . We therefore must establish the average of [the diffraction intensity] with respect to the displacements  $u$ ,  $v$ ,  $w$ , . . . If the probability of an arbitrary arrangement is known the mean value of this factor can be computed . . . this mean value constitutes the principal problem . . .

'II. Introducing normal coordinates. Just as in the case of the calculation of specific heats, the introduction of normal coordinates is also of great value for the representation of the atomic movement. For this purpose we might proceed from the conventional elastic differential equations for the condition of a continuously occupied space, and would thus be in a position to develop an approximate theory, as has been done for the computation of the mean heat energy. [Debye's treatment, 1912.] Instead we will here introduce the

atomic structure of the body from the beginning, and therefore define our new coordinates following the exposition by Born and v. Kármán (5) . . . We will attempt to exploit the advantages of both methods as much as possible.

'III. Computation of the desired mean value for the case of vanishing zero-point energy.

'IV. Computation of the required mean value with the assumption of zero-point energy.

'V. General results regarding the effect of the thermal movement.

'VI. The effect of heat at low temperatures.

'VII. Approximate formula for the temperature function valid at all temperatures.

'VIII. Numerical discussion and graphical presentation.

'Summary: . . .

'(4) The exponent in the function just mentioned vanishes at  $T = 0$  in the absence of zero-point energy: it remains finite and assumes a substantial value if zero-point energy exists . . .

'(8) . . . as for the specific heat of monatomic bodies . . . the temperature dependence is a function only of the ratio of the characteristic temperature  $\theta$  to the temperature of observation.'

An addendum, added in the proofs, incorporates valuable suggestions sent to the author by Sommerfeld and Lorentz. Debye's quantitative treatment needed correction in some respects. These corrections were provided by Waller who was also one of the authors with R. W. James and D. R. Hartree of a paper which (among others) clearly established the existence of zero-point energy by a careful evaluation of the X-ray diffraction intensities in rock-salt (13).

#### GÖTTINGEN, 1914-1920

Both Gerlach and Debye have sketched the circumstances in which Debye was invited to Göttingen. Significantly, David Hilbert took an active part, although the two established physics professorships were then occupied by Riecke and Voigt. They had been greatly impressed by Debye's contribution at a Wolskehl discussion devoted to the kinetic theory of matter at Göttingen from 21 to 26 April 1913. The speakers at this conference and their themes were: M. Planck, 'The significance of the quantum hypothesis for the theory of gases'; P. Debye, 'The equation of state on the basis of the quantum hypothesis'; W. Nernst, 'The kinetic theory of solids'; M. v. Smoluchowski, 'The limits of validity of the second law of thermodynamics'; A. Sommerfeld, 'Problems of free path lengths'; H. A. Lorentz, 'The application of kinetic methods to the motion of electrons'. Debye's paper dealt with several basic aspects of the quantum theory as seen at that date, including his representation of the general relation for imposing quantization in terms of the momentum: the character of this relation he said was based 'on a remark of Einstein' (1913). When Debye's contribution was published in the volume



of the conference papers it had an addendum which included two further original developments. The first treated the anharmonic terms in lattice vibrations, which provided the explanation of the expansion coefficient in solids: the second was a treatment of heat conduction in terms of the scattering and decay of sonic (phonon) waves. On this new basis Peierls systematized heat conduction in crystals sixteen years later. Undoubtedly it was this whole chapter in the volume which he edited that so impressed David Hilbert. Advantage was taken of the fact that Voigt was prepared to relinquish responsibilities on the experimental side and it was arranged to make part of the institute available for Debye—'a very unusual thing' (Gerlach).

Manneback (13a) has pointed out another profoundly significant remark of Debye's which much preceded his transfer to Göttingen. It appears as a note on a paper by Sommerfeld and Runge (*Ann. Physik*, **35**, 290 (1912)). Debye draws attention to the relations between the Jacobian equation of motion with partial derivatives of the first order and of second degree and the equation for linear waves of the second order. A transformation analogous to that of Riccati allows a passage from the one to the other and establishes a possible physical connexion between the two: this connexion is illustrated by the relations existing in the limit between the geometrical optics of Huygens and classical wave optics. The use that Schrödinger made of such ideas is well known.

The Göttingen appointment was to a professorship of theoretical and experimental physics and it offered definite prospects for experimental work as new laboratories had recently been completed there. An invitation to Göttingen at this date must, in any case, have been well-nigh irresistible to a mathematically inclined physicist. It is evidence of Debye's status to recall the extraordinary brilliance of the faculty he was asked to join as a senior member. In mathematics the head of the school was Felix Klein, and associated with him were David Hilbert, Carathéodory, Landau, Toeplitz, Weil, Runge and Courant. In physics there were Voigt, Wiechert, Madelung, Prandtl, Riecke, Born, von Kármán, Tamman and Simon.

Debye must have been contemplating his move to Göttingen almost simultaneously with the publication (July 1913) of Bohr's first paper on atomic structure (14). In that paper the quantization of the energy is introduced in what now appears a remarkable way and the result is subsequently shown to be equivalent to the assumption 'that the angular momentum of the electron round the nucleus in a stationary state of the system is equal to an entire multiple of a universal value' [ $h/2\pi$ ]. Bohr's further papers of 1913 are based on the relation  $mva = h/2\pi$ , as an *ad hoc* condition. Within the same year Debye presented a rationalized and more general version of the quantization condition, i.e.  $\oint p.dq = nh$  where  $p$  is the generalized momentum and  $q$  the associated coordinate, the integral extending over a complete period of the motion (15). It is worth noting that



Debye's statement of this condition (Utrecht, 10 February 1913) certainly preceded the availability to him of Bohr's first paper. This relation, introduced independently in 1915 and often associated with W. Wilson and Sommerfeld, became the accepted version of applying the quantization condition until wave-mechanics provided a more satisfactory basis in 1926. It immediately led, in Sommerfeld's model, to the introduction of the azimuthal quantum number and to the elliptic electron orbits in all atoms beyond beryllium. Such was his interest in the Bohr theory that Debye must have abandoned his intention of studying dipole moments experimentally. His first experimental work combined two other interests.

Debye took up X-ray diffraction in the hope that it might provide evidence for the electron orbits envisaged in the Bohr atomic model. A medical-type X-ray tube with a platinum anticathode was used and (hopefully) a sheet of paper taken as diffracting material. Not surprisingly, the photographs showed nothing of any hoped-for pattern: the source was capable of producing only continuous radiation. Fortunately his assistant, Paul Scherrer, was a young Swiss graduate so that the outbreak of war in 1914 caused a minimum disturbance to the work, as neither of them was of German nationality. The next step was the construction of a metal X-ray tube (in the first instance, copying the design of other workers) with a water-cooled copper target and an aluminium foil window for the escape of the rays. This copper 'home-made' type of continuously evacuated tube or, rather, modifications of it, remained in use in some laboratories until the end of the Second World War. With this new source and a cylindrical camera, Scherrer took a photograph of finely powdered lithium fluoride. In one sense the success was complete. The sharp rings of a typical powder diffraction photograph was obtained, and explained as formed by the intersection of conical beams from the randomly oriented crystals with the photographic plate. In their original paper Friedrich, Knipping and von Laue had failed to detect diffraction from a powdered crystal specimen, but later Friedrich found rings around the primary beam without appreciating their significance. The powder method was independently discovered by A. W. Hull at the General Electric Schenectady Laboratories: his account in 1917 appeared a year after the Debye-Scherrer paper which had not reached the U.S. owing to war conditions.

The powder method was for many years a much used means of crystal analysis and although for detailed structural analysis it has long been replaced by single crystal methods, it still retains its great value in the identification of any crystalline material, be it of natural or artificial origin, of chemical, biological, mineralogical or metallurgical character. As one of its first applications, Scherrer revealed the nature of metallic colloidal solutions and showed how to determine the sizes and structures of particles far below the resolving power of the light microscope. Gerlach has described how Debye and Scherrer enjoyed showing him their laboratory in 1916. The burnt-out (Ruhmkorff) induction coils of the X-ray set showed huge



swellings where the paraffin wax had come through the windings: Debye and Scherrer's amusement at their sight 'made a strange impression' on an experimental physicist trained by Paschen.

The structures of some cubic crystals were soon determined by the powder method, thanks to the clear understanding of those lattices from the early work of the Braggs. Even some crystals with complex ions, e.g.  $K_2PtCl_6$ , proved amenable to evaluation and, in this instance, provided important confirmation of the octahedral anionic structure arrived at chemically by Alfred Werner. Other lattices such as elementary boron proved too recondite for the powder method but graphite with its especially interesting layer structure was partly unravelled by Debye and Scherrer (1917). As had been realized from the sharpness of the powder photograph rings for lithium fluoride, the component ions were responsible for the diffraction and it was anticipated each ion would contribute intensity in relation to its total number of electrons. An evaluation of the lithium fluoride intensities led to the welcome conclusion that their total electrons were in the ratio 2 : 10. This appeared to be important confirmation for well-established anticipations but the quantitative significance of this early deduction was later criticized (16): it was obtained by a plausible but not a reliable extrapolation. The unquestioned importance of this evaluation was its indication that significant calculations could be made from X-ray intensities.

Systematic efforts were also made to detect 'structure' in liquids by X-ray diffraction. Narrow jets of benzene and cyclohexane were used, but only diffuse interference rings were recorded: these provided at best an indication of the average separation of the molecules in the liquid. However, the problem represented by these studies recurs in various forms throughout Debye's subsequent work. For disordered condensed phases (such as a liquid) the essential feature is to define the molecular radial distribution function, whilst for the dilute gaseous state it becomes the assessment of the molecular structure from the diffraction of randomly oriented molecules. These themes grew from the early Göttingen studies and related ones were amongst the most prominent interests of Debye's last years.

At Göttingen Debye also published theoretical treatments of hydrogen-like atomic spectra. One of them gave a presentation more systematic than that achieved by Sommerfeld and was based on the Hamiltonian (1916). This method was subsequently used by Bohr in his major paper (15) in the *Proceedings of the Copenhagen Academy* for 1918. Another stimulating theoretical investigation was Debye's account of the Zeeman effect in terms of the quantum hypothesis (1916). He deduced the discontinuous value of the angle between the electron orbit and the direction of the magnetic field, i.e. the space quantization of the orbits which had been introduced by Sommerfeld almost simultaneously.\* It is clear from the papers that

\* Bohr wrote (1918): 'Subsequently Sommerfeld himself and Debye have on the same lines indicated an interpretation of the effect of a magnetic field on the hydrogen spectrum which . . . undoubtedly represents an important step towards a detailed understanding of this phenomenon.'



Sommerfeld was the more convinced that the electron orbits were 'real' and oriented at fixed angles in the magnetic field. It was these accounts which led to the Stern–Gerlach experiment (1922). Gerlach recalls that when Otto Stern and he were telling Debye in 1921 of the difficulties and lack of success in their experiment at that date, Debye was quite explicit in his comments: they should not think that the details of the electron orbits had any physical reality, they merely arose from the mathematical model. They belonged to what Debye was accustomed to call the zoology of the quantum rules or the railway-guide for the electrons. This emphasizes the limited validity he ascribed to mathematical representation: but his quantization process was more intimately correct than he was prepared to allow. The success of the Stern–Gerlach experiment undoubtedly made a great impact on quantum-theoretical thinking: Born was to characterize it as 'perhaps the most impressive evidence we have of the fundamental difference between classical and quantum mechanics' (15). In view of Born's status in that field and of the fact that Debye is not always thought of as one of the architects of atomic physics, it is significant that in Born's volume of that title the only authors named more frequently than Debye are Bohr, Dirac, Heisenberg, Planck, Rutherford, Schrödinger and Zeeman.

In molecular physics, a theoretical paper of this period was that evaluating the van der Waals cohesive forces (1920\*). Keesom had emphasized that dipole-dipole interactions contributed significantly to gas molecular interactions. Debye proceeds: '[In the limit of high temperatures] it can be easily shown that two rigid electrical systems do not, in the mean, exert a force on one another . . . The situation is immediately and essentially changed if we consider molecules that are not completely rigid. The fact that each gas has a refractive index different from unity is proof of the mobility of the charges in the molecule. Taking this into consideration, it will be clear that a given molecule assumes an electric moment in the field  $F$  of another molecule, which moment is proportional to the field  $F$ . Thereby a mutual energy arises between two molecules which is proportional to the product of the field strength times moment, i.e. proportional to the square of  $F$ . Thus the average of the corresponding force cannot vanish. Further, it will be readily seen that the force is always one of attraction. Hence we may conclude that we have found in this force the origin of van der Waals's universal attraction.' Debye then writes the potential in the neighbourhood of any molecule consisting of a distribution of electric charges as

$$\phi = \frac{a}{r} + \frac{b}{r^2} + \frac{c}{r^3} + \dots$$

where  $a$  arises from the net charge;  $b$  from the dipole;  $c$  from the quadrupole, etc. He determines the interaction for quadrupole (i.e. non-dipolar) molecules and evaluates it, using the molar refraction as a measure of the polarizability.

In invoking the quadrupole field Debye provides one of the first convincing



statements to account for the attractive forces experienced by non-dipolar molecules, although the quadrupole field (which does not exist for the noble gas atoms) lacks the universal character of the dispersion interaction first revealed by London (1926). In a later paper (1921) Debye shows how, with a magic cross, zero field can be created along an axis about which the field's spatial variation is as large as possible. This is his suggested means of differentiation in an optical method between orientation due to a quadrupole moment interaction and that due to an induced moment (Kerr effect). The method has since been frequently used. He also offers an explanation of the universal repulsion between molecules: based on classical electrostatics only, it is not acceptable for molecular fields.

#### ZÜRICH, 1920-1927

Debye remained until 1920 at Göttingen: his six to seven-year stay there was the first of four such periods in European institutes. There followed Zürich (1920-1927), Leipzig (1927-1934), Berlin (1934-1940). Conditions must still have been very depressed in Germany when Debye accepted the directorship of the Physical Institute at the (Federal) Technische Hochschule in Zürich. He was now also editor of the *Physikalische Zeitschrift*. Rarely has an editor contributed so much of outstanding significance to his journal. Volume 24 (1923) contains from Debye:

pp. 161-166: a paper 'X-ray scattering and quantum theory'—received on 14 March 1923.

pp. 185-206: a paper 'On the theory of electrolytes. I. The freezing-point depression and related phenomena'—submitted on 27 February 1923.

pp. 305-325: a paper 'On the theory of electrolytes. II. The limiting law for electric conductivity'—received on 19 July 1923.

The first gives an original fully quantitative account of what became known as the Compton effect, i.e. the change in X-ray wavelength on scattering by an electron. The other two, in which his assistant Dr Erich Hückel was a joint author, created a new epoch in the study of electrolytes.

The paper on X-ray scattering is a masterpiece of presentation in its conciseness, in its clarity, and in the completeness with which it covers a new discovery of major physical significance. Debye based this paper on a report by A. H. Compton of his experimental data published as a bulletin of the National Research Council (Washington) in October 1922. *The Physical Review* on p. 267 of Vol. 19 (1922) carried a brief account of the results and a qualitative statement of their probable significance in an undated note from Compton. On 13 December 1922, Compton's major paper, replete with quantitative theoretical appraisal, was received by the *Physical Review* and it appeared in the May 1923 issue. Accordingly, the simultaneity of the two independent interpretations of the Compton effect is as close as could be wished. Some quotation may succeed in suggesting the quality of the Debye paper (1923\*).

'It is known that scattered X-ray radiation is polarized and varies in intensity with the direction of scattering . . . If  $\theta$  is the angle between the primary and the secondary beam the formula  $i_s \propto \frac{1 + \cos^2 \theta}{2}$  follows for the dependence of the scattered intensity  $i_s$  on the angle. At comparatively long wavelengths of the primary radiation, however, a substantial discrepancy exists . . . this effect is caused by the fact that the distances between the electrons in the atom are of the same order of magnitude as the wavelengths of the X-rays used for these experiments. Consequently the secondary rays originating at the different electrons of one single atom interfere with one another, and the scattered intensity at average wavelength is computed to be proportional to  $Z^2$  for  $\theta = 0$ , and proportional to  $Z$  for  $\theta = \pi$ , where  $Z$  is the number of electrons in the atom.\*

'If we now proceed to very short waves, the interference effect should, according to the calculations, contract to a progressively smaller angular region surrounding  $\theta = 0$ , and the intensity outside this region should be represented by Thomson's formula. All experimental evidence with short waves is contrary to this assumption. In the following I wish to present some thoughts referring exclusively to the short wave region.

'Four points seem to me to deserve particular attention:

1. The intensity of the scattered radiation is considerably higher in the direction of the primary radiation ( $\theta = 0$ ) than in the opposite direction ( $\theta = \pi$ ) in contradiction to the mathematically derived proportionality to  $(1 + \cos^2 \theta)$ .

2. It now appears to be certain that the radiation scattered in the direction of the primary beam is harder than that scattered in the opposite direction. Thus the wavelength is changed, again in contradiction to the above-mentioned computation.

3. The total energy of the scattered radiation sinks below the limiting value corresponding to Thomson's calculation . . .

4. Each scattering is accompanied by electron emission. The shorter the wavelength, the more the electrons appear to be ejected in the direction of the primary beam.

'Not all the experimental results are so unequivocal that the assertions 1 to 4 can be regarded as absolutely confirmed by experiments. However, I recently gained the impression from a survey by A. H. Compton (*Bull. Nat. Res. Council*, 4, No. 20, October 1922: *Nat. Acad. Sc.*, Washington, D.C.) that it is highly probable that they are correct. I will therefore hesitate no longer to present for discussion an explanation of these effects based on quantum theory which occurred to me as a possibility quite some time ago.

'Let us assume that classical electrodynamics fails also in the computation of the energy scattered by a free electron excited by primary radiation, and must be replaced by

\* It should be noted that precisely similar considerations were invoked in 1945 by Debye in treating light scattering by large polymer molecules: from these considerations he determined the effective length of the molecules.



a quantum concept.\* In particular the following picture holds. The primary X-ray radiation of frequency  $\nu_0$  transfers to a free electron in an elementary process the energy  $h\nu_0$ . This energy is transformed quantitatively, serving, first, to generate a secondary ray of frequency  $\nu$  and energy  $h\nu$  and, second, to impart a velocity  $v$  to the electron.

'The secondary radiation may be considered as "needle radiation" in Einstein's interpretation. On the basis of these premises, a highly detailed picture of the processes can be secured, provided it is assumed that (a) the law of conservation of energy and (b) the principle of conservation of momentum hold also in this instance. The two theorems are sufficient without any additional hypothesis.

'The velocities of the electrons will be of the order of the velocity of light,  $c$ ; we therefore use the relativistic formulae . . .'

Then follows a beautifully succinct deduction of (i) the frequency of the secondary ray; (ii) the velocity of the secondary electron; (iii) the direction in which the latter is ejected. The now well-known results are summarized diagrammatically for an incident X-ray of energy  $h\nu_0$  equal to the rest energy of the electron,  $mc^2$ : i.e.  $\nu_0 = 1.23 \times 10^{20} \text{ s}^{-1}$ , or  $\lambda_0 = 0.0243 \times 10^{-8} \text{ cm}$  (Debye's values).

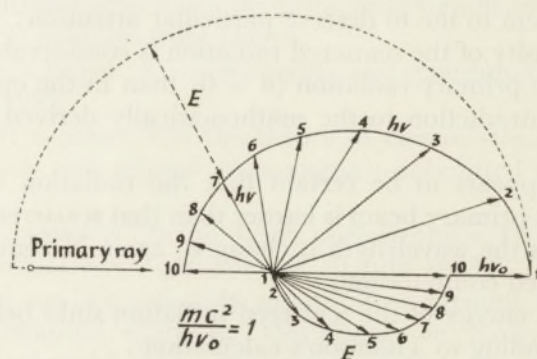


FIGURE 1

'The upper part of the figure shows a half-circle indicated by a dashed line with radius  $h\nu_0$ ; further, a series of arrows bounded by a full-line curve is drawn. Their lengths indicate the magnitude of the secondary radiation quanta  $h\nu$  in accordance with equation (5). The section of the radius extending between this curve and the circle measures the respective absolute value of the energy  $E$  of the electron, since it is required by the law of the conservation of energy that  $h\nu$  and  $E$  add up to  $h\nu_0$  (cf. eq.(6)). The lower part of the figure shows a series of arrows also bounded by a full-line curve. The length of these arrows represents the amount of the electron energy  $E$ , and they point in the direction of the electron velocity. The arrows for the radiation quanta  $h\nu$  as well as the arrows for  $E$  are numbered in such a manner that those belonging together have the same number. Their

\* Italics, M.D.

directions have been calculated from equation (7). It will be seen that the lower arrows are confined to an angular region of  $90^\circ$ , whereas the directions of the secondary radiation quanta cover a range of  $180^\circ$  . . . The third of the experimental results mentioned in the beginning has not as yet been discussed . . .

'Relying on the correspondence principle . . . the theory in fact demands that the scattering decrease below the electrodynamic limiting value to zero. It should be noted, however, that the reduction in scattering in this representation is associated with a simultaneously occurring increase in electron energy by such an amount that, as regards energy, the two effects together correspond to the electrodynamic limiting value at any wavelength . . . By means of experiments which reveal characteristic deviations from this scheme, we may hope to secure deeper insight into the laws of quantum theory, particularly as regards their relation to physical optics.'

This effect in X-ray scattering was of great significance in the development of atomic physics. It emphasized the wave-particle character of the photon, i.e. the duality which also appeared in the wave nature of the electron. As A. H. Compton's experimental assessment was basic to this appreciation and as he, independently of Debye, also evaluated it theoretically, he received the Nobel Prize for Physics in 1927.

The interest in electrolytes so fully developed in the papers with Hückel was an entirely new one for Debye. He himself explained (1923\*): 'The present considerations were stimulated by a lecture by E. Bauer on Ghosh's publications, held at the Physikalische Gesellschaft (Zürich). The general viewpoints taken as the basis for the computation of the freezing point depression as well as of the conductivity led me, among other things, to the limiting law involving the square root of the concentration. I could have reported on this during the winter of 1921 at the Kolloquium. With the active help of my assistant, Dr E. Hückel, a comprehensive discussion of the results and their collection took place during the winter of 1922.' This substantial period of gestation helps to explain the comprehensive nature of the two papers in 1923. In taking up the electrolyte problem Debye might be described as entering for the first time the area largely occupied by physical chemists. No one would now maintain that a border can be defined between it and physics: Debye himself is perhaps more responsible than any other single individual for its disappearance. The one functional difference involved is that a knowledge of chemical facts is needed adequately to experiment with the systems he now commenced studying.

The first paper carries a concise review of the approaches to understanding ionic solutions already taken. Arrhenius, van't Hoff, Nernst, W. Sutherland, P. Hertz, Milner, Bjerrum and Ghosh figure in this. The basic problem was that the simple laws established by van't Hoff for osmotic pressure and related equilibrium properties for solutes were seriously in error for strong electrolytes, i.e. for conventional salts and strong acids (HCl,  $\text{H}_2\text{SO}_4$ , etc.). Arrhenius's account of solution conductivities and ionic equilibria which



was adequate for weak electrolytes (acetic acid, ammonia, etc.) was equally inapplicable.

'Recently, under the influence of Bjerrum, the impression gained strength that consideration of the electrostatic forces, exerted by the ions on one another—and of considerable importance because of the comparatively enormous size of the elementary electric charge—must supply the desired explanation. Classical theory does not discuss these forces, rather, it treats the ions as entirely independent units. A new interaction theory has to be analogous in some respects to van der Waals's generalization of the law of ideal gases to the case of real gases. However, it will have to resort to entirely different expedients, since the electrostatic forces between ions decrease only as the square of the distance and thus are essentially different from the intermolecular forces which decline much more rapidly with an increase in distance.

'Milner [in 1912 and 1913] computed the osmotic coefficient along such lines. His computation cannot be objected to as regards its outline, but it leads to mathematical difficulties which are not entirely overcome, and the final result can only be expressed in the form of a graphically determined curve for the relation between  $(1-f_o)$  and the concentration  $[f_o$  is the "osmotic coefficient"]'. From the following it will further emerge that the comparison with experiment carried through by Milner, supposes the admission of his approximations for concentrations which are much too high and for which, in fact, the individual properties of the ions, not taken into account by Milner, already play an important part. In spite of this, it would be unjust to discard Milner's computation in favour of the more recent computations by Ghosh [1918, 1921] on the same subject. We shall have to revert, in the following, to the reason why we cannot agree to Ghosh's calculations, neither in their application to the conductivity nor in their more straightforward application to the osmotic pressure.'

That Debye was familiar with Milner's treatment when he came to write this paper is not always remembered. His electrolyte model was essentially identical with Milner's and they agreed even to the extent of concurrence on a number of basic relations. However, the mathematical manipulation was markedly different in the two cases and, most significantly, Debye reduced his conclusions to quantitative forms which could be applied directly to the physicochemical data. An all-important section was the calculation of the resultant electric potential ( $\psi$ ) in the neighbourhood of a positive ion in a uni-univalent salt solution (e.g. KCl): 'Direct calculation, as attempted by Milner, who considers each possible arrangement of ions and lets it enter into the computation with the probability corresponding to Boltzmann's principle, proved too difficult mathematically. We therefore replace it by another consideration, where the computation is, from the beginning, directed towards the average of the electric potential generated by the ions.' In a volume element  $dV$  where the potential is  $\psi$ , the average number of positive ions is  $ne^{-\epsilon\psi/kT}dV$  and of negative ions  $ne^{+\epsilon\psi/kT}dV$ :  $\epsilon$  is the

electronic charge and  $n$  the average number of each kind of ion per unit volume. The net charge density is  $\rho$ :

$$\rho = n\epsilon(e^{-\epsilon\psi/kT} - e^{+\epsilon\psi/kT}) = -2n\epsilon \cdot \sinh \frac{\epsilon\psi}{kT}$$

But Poisson's equation gives

$$\Delta\psi = -\frac{4\pi}{D}\rho$$

where  $D$  is the electric permittivity of the medium.

Except very close to the ion,  $\epsilon\psi/kT \ll 1$  and then

$$\Delta\psi = \frac{8\pi n\epsilon^2}{DkT}\psi = \kappa^2\psi$$

where

$$1/\kappa = \sqrt{\frac{DkT}{8\pi n\epsilon^2}}$$

The length  $(1/\kappa)$  introduced in this way is the basic parameter in the treatment: it replaces the average distance between ions in Ghosh's considerations. It represents the length over which the net charge density in the neighbourhood of one ion falls by a factor  $(1/e)$  and so measures the extent of the ion's 'atmosphere'. If  $(1/\kappa) \gg a$ , where  $a$  is the mean radius of the ions in solution, the potential energy of the single positive ion with respect to its surroundings is  $u = -\epsilon^2/D\kappa$ . When the ionic radii are not negligible, a factor  $(1/1 + \kappa a)$  appears in this relation.

From these factors the calculation proceeded to evaluate the osmotic pressure, vapour pressure lowering, freezing point depression and boiling point elevation for the solutions. All these aspects are directly interrelated. As the most precise and the greatest body of data was in the form of freezing point depressions, these were calculated for typical aqueous salt solutions:  $\text{KCl} : \text{K}_2\text{SO}_4 : \text{MgSO}_4 : \text{La}(\text{NO}_3)_3$ . As  $\kappa$  was simply proportional to (concentration) $^{1/2}$ , the already well-established fact that deviations from the simplest conditions in salt solutions increased as (concentration) $^{1/2}$  was immediately accounted for. The freezing point values were reproduced to within an accuracy of a few per cent up to concentrations of the order  $1 \times 10^{-2}$  gmol/litre—at which the deviations from the van't Hoff relations could already be more than 100 per cent. Using adjusted but plausibly acceptable mean ionic radii, Debye and Hückel extended their agreement up to concentrations approaching 0.1 gmol/litre. However, many other features apart from the ionic radius factor are now known to cause significant deviations from their original treatment. R. H. Fowler characterized the ionic radius term as an 'omnium gatherum' correction term best regarded as an empirical means of extending the fitment of experimental data to higher concentrations. Even so, the treatment was an instant success and for twenty years appraisals and refinements of it were made so that today it stands as an accepted major chapter in physical chemistry.

An appreciably more difficult task was undertaken in the second paper



with Hückel: that of evaluating the concentration dependence of the ion mobilities in solution. It must be noted that the absolute values of these mobilities were not considered, merely their progressive decrease (again proportionately to [concentration]<sup>1</sup>) from experimentally deduced values at 'infinite dilution'. As each ion moves under the applied electric field, the surrounding ions will also be constantly reforming the ion atmospheres. The important new feature is the relaxation time characterizing the rate of formation of the ionic atmosphere. With the ions in motion the ionic atmosphere will not attain its equilibrium distribution and the Boltzmann factor cannot now be applied to define it. Debye proceeded, not for the first nor by any means the last time, to use the equations for Brownian motion to provide a representation of the ionic distributions. For any one ion in motion its associated atmosphere will be more fully developed behind it than in the direction it moves. This provides a braking force which will increase with concentration. Another factor is the inevitable counter-movement of oppositely charged ions: as they all effectively carry some of the solvent in their immediate environs with them, any one ion will be moving through a solvent in some degree of motion in the opposite direction. This was assessed by the methods used by Helmholtz for the treatment of electrophoresis.

It will readily be appreciated that the theoretical treatment of ionic mobilities is very significantly more recondite a problem than treating the equilibrium features, and the paper presenting this material is far more impressive than the first. The evaluation of the retardation by the ion atmosphere is presented in five steps, the last representing the field and charge distribution around a moving ion. The electrophoretic forces generated by the counter-movement of the ions are treated in three stages. The evaluation of the resultant conductivity and its general numerical computation for aqueous solutions form the next two sections. Then comes a detailed consideration of the available experimental data and their conformity with the theory. There is some case for suggesting that this last section is the most impressive in an impressively powerful and original paper. Debye was well versed in the variety of mathematical methods that had gone to make the theory. To find the considerable body of experimental data handled with the clarity, thoroughness, and relevance they receive, when he had done no experimental work in this field, is evidence of mastery which all can appreciate. Aqueous solutions are treated systematically in two sections, and non-aqueous solutions in a further section illustrating the roles of the permittivity and viscosity factors. Whilst most physical chemists have never seen this paper, its main features have been built into their textbooks for forty years.

Of course the Debye-Hückel papers were only the first efforts at a quantitative treatment of strong electrolytes. Much further refinement and extension has been given these considerations. Debye recurred to both aspects—equilibrium and mobility features—in a number of other papers.



Especially there must be mentioned three major contributions in which H. Falkenhagen is a co-author. These treat of the frequency dependence of the conduction, an aspect clearly capable of giving critical information on the relaxation times of the ionic atmospheres, and other time dependent features in the mobility. Comparatively little has yet been done to explore these features experimentally. In the original treatment of mobilities Debye did not fully take into account the Brownian motion of the ions. This, however, initially escaped perhaps everyone's attention. He was, it seems, somewhat fond of telling the story of how, in 1925, there came uninvited to his director's office at Zürich, a timid young man smiling very nervously. Bowing to Debye over his desk he finally came out with: 'Wissen Sie dass Ihre Elektrolyt-theorie falsch ist?' It was Onsager. If this version (20) is correct, the youth of the visitor must be allowed to excuse the unqualified 'falsch'. It is always presumed that the immediate response was the offer to the visitor of a cigar, a chair and a writing pad: certainly for the first, there is a high probability.

Another item familiar to physical chemists has its origin in a Dutch paper (1923). This is an exposition by Debye of the influence of other electrolytes upon the solubility of sparingly soluble salts. No new theory is involved. The osmotic coefficient (i.e. one form of a thermodynamic activity coefficient) of the Debye-Hückel paper is used to give a quantitative account of the interionic effects. Using the data for silver sulphate as the insoluble salt, the various characteristic solubility influences are calculated and compared with experiment. This type of solubility study has proved to be a flexible and penetrating probe for many chemical equilibria. It was an unfortunate coincidence that Debye's electrolyte theory only became known in the same year as G. N. Lewis and H. M. Randall published their classic volume of chemical thermodynamics. That volume summarized with masterly clarity the experimental study over a period of thirty years of ionic and other equilibria, but it lacked the further insight made available by Debye's new treatment of electrolytes.

At Zürich, Debye's laboratory now attracted scientists from outside Europe: at the same time Debye himself spent time out of Europe. One product was a brief paper jointly with the young Linus Pauling, published from Pasadena (1925). It dealt with the electric permittivity factor in the electrolyte problem and confirmed Debye's earlier assumption of the macroscopic value for this in evaluating interionic potentials. A product of a winter term's stay at the Physics Department of M.I.T. was a more important paper (1925\*) entitled *Note on the scattering of X-rays*. It reveals very clearly a formative phase in Debye's thinking on diffraction by liquids and by single molecules and it is both physically and mathematically a gem of great clarity. As these two problems justifiably occupied a great deal of Debye's later efforts let us attempt again to follow him.

'There can be no question that not only in crystals, but also in the molecules of substances in the liquid or gaseous state, the atoms occupy



definite places . . . Therefore it should be possible to detect interference effects corresponding to the geometrical arrangement of the atoms in the molecule.

'If, for instance, the scattering of a liquid has been measured, one might possibly think that the properties of the scattering function, i.e. the scattered intensity plotted as a function of the angle between the secondary and primary X-ray, only depends on the dimensions and the form of the atomic frame constituting the molecule. From this point of view P. Debye and P. Scherrer in 1916 discussed the scattering of [liquid] benzene. In the meantime it became evident, however, that a very large number of different liquids yield diffraction-patterns which show only slight differences. Therefore, at the meeting of the German Physical Society in 1920 at Jena, Debye stated that the principal maximum of the scattering function must be due to interferences between the different molecules of the liquid . . . The theory of this effect seems to be as difficult as the theory of the correction for the dimensions of the molecules in the equation of state. Nevertheless, I believe that a first approximation . . . may be of some interest. It will be shown that even if the molecules are comparable with hard spheres and do not interact in any way . . . this alone is sufficient to cause a scattering function exhibiting a maximum.

'In this way it seems proved, both experimentally and theoretically, that it will only be possible, even in the case of liquids, to arrive at the scattering function characteristic of the molecule and its atomic frame, if we succeed in freeing the primary experimental result of the undesired intermolecular interferences. Further, it seems improbable that it will be possible to perform theoretical calculations which will give a reliable formula for this process in the case of dense liquids. Therefore, the only possible way to find the interferences due to the interaction of the atoms constituting the molecule, seems to be the performance of scattering experiments with gases of different densities . . . it should be possible to arrive at direct measurement of the atomic distances in the molecule.'

Debye then proceeds to calculate from first principles, and in the clearest possible fashion, the general form of the resultant scattering function for  $N$  structureless particles (e.g. spheres or small cubes) scattered through a volume  $V$ . With  $\psi$  = amplitude of the wave scattered by one particle :  $v_o$  = total volume of the particles :  $2a$  = diameter of the particles (there is confusion in the paper on this factor) :  $R$  the distance from the localized collection of particles at which the intensity ( $I_m$ ) is observed:  $\theta$  the angle between the secondary and primary ray, then

$$I_m = N \psi^2 / R^2 \left[ 1 - \frac{8v_o}{V} \phi \left( 8 \frac{\pi a}{\lambda} \sin \frac{\theta}{2} \right) \right]$$

$$\phi(u) = \frac{3}{u^3} (\sin u - u \cos u) \quad [\phi(0) = 1].$$

If the scattering of each particle were the same as the scattering of a single

resonator,  $\psi^2$  would be proportional to  $\frac{1}{2}(1 + \cos^2\theta)$  as the primary radiation is assumed unpolarized and the scattering yields a polarization which is complete for an angle  $\theta = 90^\circ$ . To visualize the effect of the scattering Debye draws the curve for the function

$$\left(\frac{1 + \cos^2\theta}{2}\right) \left[1 - \frac{1}{2}\phi\left(12\pi \sin \frac{\theta}{2}\right)\right]$$

This corresponds to  $(2a/\lambda) = 3$ . Under these assumptions, a ring would be observed with a maximum intensity at an angle of about  $\theta = 16^\circ$ .

'In general, the molecule will not act as a single resonator, but it is to be expected that there will exist an interference effect corresponding to the shape of the atomic frame. The whole scattering curve must now show a superposition of the two kinds of interference effects which may briefly be called the "inner" and the "outer" effect. Now the outer effect will always be proportional to  $v_0/V$ . It should therefore be possible to eliminate the outer effect which tends to vanish with decreasing density . . . then we may, in the case of nitrogen, for instance, expect as a result the direct measurement of the distance of the two N-atoms.'

Again, from the first principles, Debye modifies his previous calculation for structureless particles to one for molecules of radius  $a$  each containing two scattering centres distance  $l$  apart. He arrives at

$$I_m = 4N \frac{\psi^2}{R^2} \left\{ \frac{1}{2} \left[ 1 + \frac{\sin x}{x} \right] - \frac{8v_0}{V} \left( \frac{\sin x/2}{x/2} \right)^2 \phi(y) \right\}$$

$$x = 4\pi (l/\lambda) \sin \frac{\theta}{2}$$

$$y = 8\pi (a/\lambda) \sin \frac{\theta}{2}.$$

With decreasing density the influence of the second term in the curly bracket vanishes and the scattering function finally assumes the limiting form:

$$I_m = 4N \frac{\psi^2}{R^2} \frac{1}{2} \left[ 1 + \frac{\sin x}{x} \right]$$

agreeing with a general formula previously calculated (Debye 1915). Debye again takes  $(2a/\lambda) = 3$ , and  $l = a$ ; here  $\lambda$  might reasonably be  $1.0 \times 10^{-8}$  cm. Retaining both terms in  $I_m$  (total), he 'shows how the first maximum, occurring at about  $\theta = 12^\circ$  and corresponding to intermolecular interference, disappears with decreasing density, leaving only a second maximum at  $\theta = 45^\circ$  undisturbed, because this maximum corresponds to the interatomic interference of the two atoms constituting the molecule'.

This model calculation must have given Debye great confidence in his persistent and, later, successful efforts to evaluate the diffraction patterns of both liquids and gases.

The list of titles of his published papers (the total exceeds two hundred—see Bibliography) emphasizes the sustained wide range of his contributions.



In this account comment is restricted to the main or outstandingly original themes. It is noticeable, too, that the great majority of the papers carry only his own name: this probably results from their being still very largely theoretical and referring only to experimental data already published by other authors. Of his major interests, new aspects of electric dipole moments were delineated at Zürich. An especially valuable article appeared in the *Handbuch der Radiologie*, Vol. VI, 1925. In addition to a full exposition of the elements of dipole moment theory (promised in 1913), it includes an account of the Kerr effect in which Langevin's treatment is extended. This electro-optical effect is shown to offer information on the anisotropy of the polarizability of molecules—both polar and non-polar. The measurements are not easy and for forty years the systematic study of this effect has been in relatively very few hands. Laser sources and pulsed fields offer much improved sensitivity. Valuable deductions on many interesting aspects of molecular structure have been made from the Kerr effect starting from Debye's analysis (17). It was not until 1926 that Debye presented the definitive treatment of dipole-induced dipole interactions as a contributing feature in molecular cohesion. In the gas phase this is never comparable with the dipole-dipole or the dispersion force interaction, but in condensed phases it can become significant owing to the much closer proximity of the molecules and their assumption of orientations where the term may be at a maximum.

Perhaps the most original contribution published during this second period at Zürich was a brief but quite conclusive statement entitled: *Some remarks on magnetization at low temperatures* (1926\*). This in itself would have created an international reputation for a lesser scientist. In it Debye expounds the principle of adiabatic demagnetization as a means of cooling at the lowest temperatures. It may be recalled that Langevin pointed out in his initial 1904 treatment of paramagnetism that the sudden (or, strictly, adiabatic) demagnetization of oxygen gas would necessarily lead to a cooling effect and that an observation of this kind had been made experimentally in ferromagnetic nickel (Weiss & Picard 1921). However, no serious consideration appears to have been given to its use in achieving the lowest temperatures. Debye's interest seems to have stemmed from an experimental study of gadolinium sulphate by Kamerlingh Onnes but he was also himself Weiss's successor at Zürich. He presented in quantitative form an assessment of the prospects for cooling on adiabatic demagnetization. There were two obstacles to an accurate prediction: firstly, the specific heat of gadolinium sulphate was not known at the relevant low temperatures—but he made a plausible order-of-magnitude estimate for this: secondly, the indications were that if the Langevin function for the paramagnetism held, it would result in the absolute zero being attained. 'Naturally, this does not mean that there is a possibility of reaching absolute zero with such an adiabatic magnetic process. Rather it must be concluded the Langevin function is not correct. However, the facts that on the one hand the Langevin formula is verified by experiments at 1.3° absolute and on the other that a large



difference was found (above) between the possible magnetic and caloric entropy changes make it very probable that cooling considerably beyond the region of validity of the formula can be achieved. Therefore, it may be of interest to make measurements at low temperatures on the adiabatic cooling of gadolinium sulphate which can be expected when the magnetic field is switched off suddenly. *Footnote in the paper:* In addition, note that the specific heat measured at constant magnetic field  $C_H$  should differ noticeably from the specific heat at zero field,  $C_O$ , for from (8) it follows immediately that  $(C_H - C_O) \dots$  is already  $0.15 nk$ . We do not dare to venture a prediction of the magnitude of the cooling which can be realized: however, it appears not to be excluded that this can be large. Only experiments can decide, and the above analysis should stimulate the carrying out of these.'

Debye's statement appeared in 1926. In 1927, quite independently, Giauque at Berkeley published a similar proposal. This proposal was certainly a stimulating one but the experiment was not then readily attempted in many laboratories. Giauque eventually reported (19 March 1933) cooling from 1.5 to 0.25 K; a group of Leiden workers achieved a very similar result almost simultaneously (6 April 1933). Subsequently, temperatures below  $10^{-3}$  K have been attained by this method.\* For this and related work Giauque was awarded the 1949 Nobel Prize in Chemistry.

#### LEIPZIG, 1927-1934

In 1927 Debye left Zürich to become professor of experimental physics and director of the Physical Institute at Leipzig University: at the same time Heisenberg was appointed to the professorship in theoretical physics. (Some of Professor Heisenberg's impressions of Debye at Leipzig are given in a letter: Appendix A). It was during his period here that Debye's orientation to chemical physics became almost complete. One characteristic feature was the organization, with the help of the Ministry of Education for Saxony, of 'small and intimate' conferences in Leipzig on specialized topics. In 1928 the subject title was Quantum Theory and Chemistry; in 1929, Dipole Moments and Electromagnetic Radiation; in 1930, Electron Diffraction; in 1931, Molecular Structure; and in 1933, Magnetism. At these symposia, leading active contributors presented up-to-date statements on the topics discussed: these were published (as five monographs) by Hirzel of Leipzig and, in English translation, by Blackie in the U.K. The volumes (edited by Debye) were highly valued additions to the scientific literature and the discussions set a pattern much copied since.

Leipzig became a Mecca for physical chemists and molecular physicists. The translation from Zürich was accompanied by a change in direction in Debye's work. The electrolyte studies were phased out and there was a resurgence of developments in the diffraction studies of molecular structure.

\* Professor Bauer [Cornell] writes that in seminars (*ca.* 1940) Debye discussed the possibility of using nuclear spin demagnetization: this has led to temperatures of  $10^{-6}$  K. He also emphasizes how, throughout Debye's work, one continually encounters his profound grasp and masterly deployment of classical physics.



Firstly, however, the molecular aspects of dielectric behaviour, more particularly of gases and liquids, were given a systematic presentation in what has become a *locus classicus*: the volume *Polar Molecules* also appeared in a somewhat more extended version in German: *Polare Molekeln* (Books). Largely owing to the stimulus provided by this monograph, chemists now took a lively interest in molecular dipole moments. The topic received considerable attention in the 1930s and aspects outlined by Debye, especially those dealing with dipole relaxations, are still being actively pursued.

It was at Leipzig that Debye was able to achieve for the first time clear X-ray diffraction by isolated molecules. This was an advance of major significance in the work already started with Scherrer: the possibilities in this area had been considered even before their joint paper of 1916. A notably successful experiment was made with carbon tetrachloride vapour and interference rings were photometered and evaluated to give a chlorine-chlorine intramolecular distance of 3.1 Å (1929). This value was quickly improved 'to an accuracy of about 1 per cent' as 2.99 Å: the later, better, value is 2.89 Å.

There are two footnotes of particular interest in the definitive account of this new method (1930\*): an account, incidentally, which carries no acknowledgement of the fact that the experimental work was due to L. Bewilogua and F. Ehrhardt, although this had been made clear in an earlier note (1929). The first footnote reads: 'The investigations reported on here began in 1915 in a note entitled "Scattering of X-rays" (P. Debye, *Ann. Physik*, **46**, 809, 1915). This note contained the basic formulae used here, to demonstrate the essential point that random orientation cannot destroy the appearance of interference maxima. It is dated 15 February 1915 and is marked by the editors as "received 27 February 1915". By a strange coincidence, a paper on the same subject by P. Ehrenfest presented by H. A. Lorentz and H. Kammerlingh Onnes (*Amst. Akad.* **23**, 1132, 1915) was given at the meeting of the Amsterdam Academy on Saturday, 27 February 1915. The title of that paper is: "Concerning interference phenomena to be expected when X-rays pass through a diatomic gas." The two atoms are considered as two scattering points with a fixed distance between them, and it is shown that for this special case, also, interference effects should be observable in spite of random orientation.'

A second footnote reads: 'In the meantime Messrs Mark and Wierl have succeeded in performing a beautiful experiment (*Naturwiss.* **18**, 205, 1930) in which the interferences here discussed are obtained with cathode rays, the de Broglie wavelength of which is about thirty times as small as the wavelength of the X-rays we used. They give as a result of their measurements on CCl<sub>4</sub> the distance (Cl-Cl) as 3.14 Å. This value, however, should be corrected as we did our earlier value of 3.1 Å, with regard to the angular decrease in intensity which occurs with  $\beta$ -rays just as with X-rays. Based on the Schrödinger equation, this correction can be calculated, at least for



sufficiently fast electrons, in a similar manner using the Fermi distribution.

'Herr Mark mentions that Herr Bothe suggested the possibility of using  $\beta$ -rays instead of X-rays at the occasion of a lecture I gave at Zürich. I may add to this that Herr Pringsheim made a similar remark after an earlier lecture which I gave at the Berliner Physikalische Gesellschaft.'

There followed a succession of important molecular structural studies by X-ray diffraction in gases. After some simpler structures ( $\text{Cl}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{CS}_2$ ) the halogenated methanes and ethanes were examined, with notable extensions of the details of their structure and the appreciation of the limited rotational freedom in 1,2 dichloroethane,  $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ , with its 'cis', 'trans' and 'gauche' forms. Ethylenic isomerism and benzene were successfully evaluated by 1932. In the meantime, Mark and Wierl's electron diffraction method had also developed strongly, and as the intensities were such that satisfactory diffraction patterns could be obtained with electrons in seconds where the X-rays required hours, it was the electron diffraction method which took over this aspect of molecular structural studies.

Other developments at Leipzig included the X-ray diffraction study of liquids. Following Zernicke and Prins, Debye explained how the angular dependence of the scattered intensity could be inverted, using Fourier's theorem, to give the distribution function representing the probability of finding the molecules in the liquid at particular separations. With Menke, experimental data were first obtained for mercury for which 'The curve thus shows that even in the liquid state there exists a quasi-crystalline structure which is defined quantitatively in terms of the probability curve' (1930\*). Debye repeatedly approached liquid phase structure in terms of the concept of short-range order. The frequency dispersion of electrolytic conductivity and the influence of high-fields on ion mobility were also considered. For dielectric media Debye appears to have treated the non-linear field effect only in the *Handbuch der Radiologie* (1925; 2nd Ed., 1934). This is surprising, as that effect in polar liquids can be larger, more readily observed and more revealing than in electrolyte solutions. Its exploration is largely due to Piekara (18).

The dominating theme in Debye's scientific interests, the interaction of radiation with molecular systems, acquires another notable illustration in the study of the scattering and diffraction of light by ultrasonic waves. The clarity of Debye's statement again demands quotation: it is based upon his discussion in 1914 on the thermal conductivity of insulators, which marked the birth of phonon theory: developments in relation to electron conduction in metals (Bloch 1928) and thermal conductivity (Peierls 1929) had come later.

In the 1932 account with F. W. Sears, he wrote:

'In a paper published in 1922 Leon Brillouin treated the problem of light scattering. In accordance with the fact that for low temperatures Einstein's theory of specific heat has to be abandoned for Debye's theory, Brillouin attributes the thermal density fluctuations in the body (which, in his theory, as in a previous theory of Einstein's are responsible for the scattering) to a



superposition of sound waves. He tries to apply his theoretical results to the explanation of X-ray scattering. We know now that this application is far from correct, as for such short waves the electron density changes due to the atomic or molecular structure are much more important than the thermal fluctuations. For light waves, however, with a wavelength much longer than molecular distances, Brillouin's analysis leads to some remarkable results. They can be stated in the following manner. Suppose the primary light travels in Fig. 1 in a direction characterized by a vector  $\mathbf{S}_0$  of length unity in this direction. Let it be assumed that of the scattered light a part is observed travelling in another direction characterized by a unit vector,  $\mathbf{S}$ . Then firstly, of the sound waves of all possible directions, only those are important for the scattering which are travelling in or opposite to the direction of the vector  $\mathbf{s} = \mathbf{S} - \mathbf{S}_0$ . This can also be expressed by saying that the planes of the sound waves have to be situated such that the scattered light can be considered as optically reflected by these planes. But there is a second limitation. Of all the sound waves of direction  $\pm \mathbf{s}$ , only those of a definite wavelength  $\Lambda$  are effective. This wavelength is  $\Lambda = \lambda/s$  where  $\lambda$  is the wavelength of the light and  $s$  is the length of the vector  $\mathbf{s}$ , which is  $2 \sin \frac{\theta}{2}$ ,

calling  $\theta$  the angle between the primary and the secondary ray. This last condition can be expressed by saying that the consecutive planes of maximum density in the sound wave must be separated by a distance  $\Lambda$  such that the well-known relation of Bragg holds. In this case the light rays reflected by the consecutive planes will have path differences of one wavelength (of light) each and therefore the reflections will be strong. So we are left with only two sound waves, travelling with the velocity of sound  $q$ , one in the direction of  $+\mathbf{s}$  and the other in the direction of  $-\mathbf{s}$ . The frequency of the reflected light, according to Doppler's principle, will be changed, and instead of the primary frequency  $\nu_0$ , we shall find in the scattered light the two frequencies:

$$\nu = \nu_0 \left[ 1 \pm \frac{2nq}{c} \sin \frac{\theta}{2} \right]$$

where  $c$  is the velocity of light and  $n$  is the index of refraction of the medium.'

Debye points out that this effect had very probably been seen by Gross in 1930 and by Meyer and Ramm in 1932, but there were some divergencies in the echelon examination of the scattered light. He then describes the experiment done by Sears at his suggestion during a visit to M.I.T. in April 1932. A delightfully simple arrangement revealed many significant aspects of the interaction of the two wave-trains not covered by the simple statement already quoted. 'The original purpose was to demonstrate Bragg reflection by sound waves by adjusting the reflection angle. However, another phenomenon appeared immediately. As long as the quartz crystal (generating sound waves of length a few tenths of a millimetre) did not vibrate, only the image of the slit (illuminated, e.g. by a mercury arc lamp) was visible in the focal plane of the second lens. However, as soon as the quartz crystal was activated,



diffraction images appeared to the left and right of the central image. They were completely analogous to the grating spectra of an ordinary grating. Each spectrum shows colours which appear in the usual order; the spectra are equidistant. The number of visible orders depends on the intensity of the sound vibrations. It was possible to make more than twenty orders visible to the left and right of the central image. The phenomenon is very brilliant and the images can be directly projected and demonstrated in a large auditorium . . . The phenomenon therefore gives a very simple method for determining the speed of sound, since a simple measurement of the diffraction angle yields the ratio of the wavelength of the light to the wavelength of the sound.' Sears has commented on Debye's immediate reaction to the unexpected features in the observations: 'One thing impressed me greatly. When I had called Debye into the laboratory and showed him the experiment, he rushed back to his office and began a theoretical explanation by first writing down Maxwell's equations.' It is best, again, briefly to quote Debye.

' . . . a theory has been developed based on the assumption of a volume scattering, in which every volume of the liquid contributes to the total scattering in accordance with Maxwell's equations. In this way, it seems at first that one would expect only one reflection for a definite angle of incidence . . . Taking into account, however, that the dimensions of the illuminated volume of the liquid are finite, it can easily be shown that in our case Bragg's reflexion angle is not sharply defined and that reflexion should occur over a rather appreciable angular range. If  $l$  is the length of the path of light in the liquid,  $A$  the wavelength of the supersonic waves and  $\lambda$  the wavelength of the light, then two quantities are of importance: namely, the quotients  $l/A$  and  $A/\lambda$ . Only if  $l/A$  is large compared with  $A/\lambda$  does a sharp definition of Bragg's angle exist. Working with a frequency of  $10^7$  cycles,  $A$  is about 0.1 mm,  $l$  is of the order 10 mm and  $\lambda$  is about  $0.5 \times 10^{-3}$  mm. In this case, therefore,  $l/A = 100$  and  $A/\lambda = 200$ , the quotient of these two quantities is  $\frac{1}{2}$  and cannot be considered as large. A detailed analysis shows that in such a case reflection will occur over a range of angles left and right of the critical angle which follows from Bragg's relation. Moreover, the intensity variations predicted by the theory in varying the angle continuously are just the same as described in the rather peculiar experimental results on this point.

'We are, however, still left with another difficulty. The theory predicts only the first order spectrum . . . but it has assumed that the variations of the refractive index are of purely harmonic character. If they are not, then we can consider the disturbances as a superposition of frequencies  $\nu$ ,  $2\nu$ ,  $3\nu$ , etc., with the corresponding wavelengths  $A$ ,  $A/2$ ,  $A/3$ , etc., . . . This departure may be due to the non-sinusoidal character of the crystal vibrations, although higher harmonics may be produced by the scattering itself, if the intensity of the supersonic waves is high enough.'

It is difficult to imagine a simpler example which would reveal so many aspects of diffraction theory. In view of his obvious appreciation of the



numerous possibilities for studying liquid behaviour which this experiment provides, it is, perhaps, surprising that Debye scarcely pursued the method further.

#### BERLIN, 1934-1940

In 1934, it seems, Debye already found he could not fully isolate his work and the Physical Institute at Leipzig from undesirable political interference. In 1935 he moved to the directorship of the Physics Institute of the Kaiser-Wilhelm-Gesellschaft at Berlin-Dahlem. This had previously been headed by Einstein and von Laue but, then, as an institute for theoretical physics. Now, thanks to generous grants from the Rockefeller Foundation, magnificently equipped laboratories for experimental research were also available: the equipment included a very-low-temperature laboratory; high-voltage (3 MV); high magnetic fields; all chemical facilities; and excellent workshops. He caused the name to be changed to that of the Max-Planck Institute, a title ultimately taken over by the Gesellschaft as a whole. Simultaneously, Debye became professor of physics at the University of Berlin. These were State appointments in Germany, and as Debye had retained his Dutch nationality they necessitated his obtaining permission to accept the positions from his sovereign, Queen Wilhelmina. He quickly experienced police-state interference in the Berlin Institute, but up until his leaving, he also appears to have been treated with some deference by the Nazi authorities.

No major new themes appear in his own work at Berlin. Nevertheless, there were significant developments in many interests such as the dielectric properties and quasi-crystalline structure of liquids; paramagnetic relaxation; the achievement of the lowest temperatures by adiabatic demagnetization. These are recognizable extensions of earlier work. The application of the method of Fourier analysis to the evaluation of electron diffraction data notably extended the power of that method, as did the testing by his son, P. P. Debye, of the sector method on the experimental side (19). Debye also provided a theoretical treatment of the Clusius thermal diffusion method for isotope separation (1939).

With the arrival of war in 1939, Debye was soon confronted with unacceptable alternatives in the Institute. The authorities decided, without his knowledge, that the Institute should be used to explore the development of a uranium reactor; this was planned as a secret operation. Debye's account in the introduction to the volume entitled *Collected papers* (1954\*) is:

'At the time I accepted to go to Berlin I was still a Dutch citizen . . . At the same time the German government conceded in a letter signed by the Minister of Education, Dr Rust, that in accepting the positions offered, I did not become and would not be asked to become a German citizen. The positions, as usual, were lifetime positions. During the time the laboratory was still under construction, I received an offer from Harvard University, which I declined because I did not feel free to quit before having finished



what I had undertaken to do . . . The war broke out and one day without previous warning I was informed by Dr Telschow from the Kaiser-Wilhelm-Gesellschaft that I could no longer enter the laboratory except by becoming a German citizen. I refused. I was advised by the Minister of Education to stay at home and occupy myself by writing a book. Instead, I was able to overcome the difficulties put in my way by different German authorities and to leave for the U.S.A., by way of Italy, in order to give the Baker Lectures at Cornell University, to which I had been invited.'

Except by omission, this statement does not tell us anything of Debye's assessment of the Nazi régime. A Dutch colleague has commented: 'Debye's strong tie to Germany and perhaps even more his notable lack of political interests, was almost fatal for him. After 1933, the year in which Niels Bohr travelled to the German universities to see what he could do for the threatened (Jewish) physicists, Debye who, as a faithful Roman Catholic and as an honest Limburger, could have nothing to do with National-Socialism, did not immediately realize that there was no further place for him in German physics' (20). Certainly for Debye to have imagined in 1940 that his position had not been radically altered by the arrival of war: to have earlier thought, if only in view of what had happened in Einstein's case, that he should not leave Nazi Germany 'before having finished what I had undertaken to do', all indicates a considerable indifference to the political situation. It is probable that he had many offers of posts in the U.S.A. As early as 1915 G. N. Lewis, head of the Chemistry School at Berkeley, had written to Rutherford on behalf of colleagues in the Physics Department requesting his opinion on two promising young scientists: Peter Debye and Niels Bohr. The reply has been published (Appendix B). By the mid-thirties Debye's status was such that his assistants claimed their salaries could best be quoted in milli-debyes. One invitation to leave Berlin for Harvard is well-established: but a variety of reasons—scientific, financial, historical attachments and family affiliations—help to explain the late date at which he left the Nazi capital. However, Debye eventually arrived in the United States for what was to be his last appointment.

Having expressed his unpreparedness to accept the German Government's wishes, in leaving Berlin in January 1940, Debye was obliged to abandon his home and all his possessions there. His son had gone to the U.S. in the summer of 1939 but his wife remained in the German capital when Debye left Berlin, ostensibly to lecture in Zürich. From there he moved to Milan and telegraphed the family in Maastricht to send him money. With that help he was quickly able to reach New York. His wife joined him later, but his daughter and her two sons did not do so until after the war.

In 1936 Debye had been awarded a Nobel Prize in Chemistry 'for his contributions to the study of molecular structure through his investigations on dipole moments and on the diffraction of X-rays and electrons in gases'. The citation provides ample grounds for the award even if it is no more inclusive of Debye's overall contributions than was Einstein's (1921, in



Physics, 'for services to theoretical physics and the law of the photoelectric effect'). At this stage Debye's whole career had been as a professor of physics, but he was not the first physicist to be awarded a Chemistry prize. Rutherford was the first (1908); Marie Curie's second prize (1911) and that shared by Frédéric Joliot and Irène Joliot-Curie (1935) were other instances. Debye appears to have had no regrets in this choice. As much as anyone's, his work had served to close the gap between chemistry and physics and later he enjoyed a double status. Writing (28 December 1964) of the Lindau (Bodensee) meetings of Nobel prizewinners, he explained: 'These meetings are biennial, one year for physicists, one year for chemists. I always get invitations to both, probably because I belong to the status in between. I have only been there once as a chemist. I decided to attend a second time as a physicist' (21).

#### CORNELL UNIVERSITY, 1940-1966

Debye had an invitation to give the George Fischer Baker lectures in the Chemistry Department at Cornell University in 1940. These were immediately followed by his acceptance of the chairmanship of the Department. And in the charming surroundings of the Cornell campus he spent far the longest of his university stays. From 1952 he was Professor Emeritus but his work continued with unabated energy until 1966: there are some thirty-three publications between 1940-1952, and fifty after that date. In 1946 he became a citizen of the U.S.A.

The disruption of war and the possibility of the U.S.A. becoming involved in it were already clear when Debye arrived in Cornell. Whilst his status as a Dutch citizen may have kept him out of some projects, he was quickly brought in as a consultant on others. The dependence of the U.S.A., as of much of the rest of the world, upon Malayan rubber had led to an intensive programme of studies for substitutes. These were necessarily polymeric materials and this determined Debye's principal new interest. Basic to the evaluation of polymer properties is the knowledge of an appropriate mean molecular weight value and, in solutions, information on the configuration of the particles and their interaction as the concentration increases. For these features Debye developed the powerful light-scattering method. He himself explained the basis of this new technique (1947): 'The problem can be approached either by making a detailed calculation of the electromagnetic field surrounding a particle in order to derive the loss of primary light energy due to its radiation (Rayleigh, 1871) or by treating the effect of the molecular inhomogeneities on the light in a second approximation as due to spontaneous fluctuations of the density and the concentration in a medium which in a first approximation is considered to be perfectly homogeneous (Einstein, 1910).' The detailed information he was able to derive from the study of light scattering provided the most practical proof of his unique grasp of the possibilities.

In 1935 two French workers, Putzeys and Brosteaux, had successfully



applied Rayleigh's relations to spherical protein molecules in solution (22), but the method had not been generalized. Debye refers to this work. In one of his original presentations (1947) he deduces the turbidity of the solution ( $\tau$ ) using electromagnetic theory and the time average of Poynting's vector. If  $I$  is the light-beam intensity and  $x$  the direction of propagation,

$$-\frac{dI}{dx} = \tau I = \left( \frac{128\pi^5}{3} \frac{n}{\lambda^4} \frac{m^2}{F^2} \right) I$$

... 'the difference in dielectric constant between the solvent and the solution is proportional to  $n$ , the number of particles per cubic centimetre, and to  $m/F$ , the electric moment characterizing the particle in a field of unit intensity. The turbidity, according to equation 2 (above) is also proportional to  $n$ , but, unlike the dielectric constant, proportional to the square of  $m/F$ '.

His working relation for small particles took the simple form:

$$H \frac{c}{\tau} = \frac{1}{M} + 2Bc.$$

$H$  is a constant dependent upon  $1/\lambda^4$  and the refractive index (substituted in practice for the electric permittivity) of the solution:  $c$  is the concentration ( $\text{g cm}^{-3}$ ) and  $M$  the desired molecular weight.  $B$  is a factor expressing the interaction of the solute molecules in the solution and it is closely analogous to the second-virial coefficient of a gas in the form  $(B/V^2)$ . These are the simple essentials of the analysis. Considerable further detail can be deduced from the angular dependence of the scattered intensity, an aspect which only becomes significant when the particle (i.e. molecular) size approaches the same order of magnitude as the wavelength of the light, i.e. for particle dimensions of 1000 Å or more. The theoretical analysis and experimental study of these systems was the subject of about twenty papers (1944-1964). Some interesting practical problems associated with the small refractive index changes and the small scattered light intensities which had to be measured led to simple, novel and effective experimental methods: of these he was clearly pleased to write: 'Most of the instruments have been designed by P. P. Debye'—his son, who worked with him for a number of years.

The light scattering method is not a simple procedure for molecular weight determinations: it requires careful control in the preparation of the solutions and in the physical measurements. Its accuracy rarely exceeds a few per cent but that is ample for the polymer specimens usually measured. Most of the classical methods have to be abandoned at molecular weights above  $10^4$  and it is for such higher values that the light scattering method is readily applicable. The upper limit approaches  $10^7$  and it has been taken in special cases down to molecular weights below  $10^2$ . This gives it a wider range than any other single method.

In 1939 Debye gave a theoretical treatment of the Clusius-Dickel thermal diffusion method of isotope separation: but in Debye's model the diffusion took place in solution. The major aspects of his analysis were confirmed experimentally. This led, in 1945-1946, to a systematic study of



thermal diffusion and fractionation in solution, not only of essentially simple, medium-size molecules (e.g. toluene-chlorobenzene) but also of dissolved polymer molecules. Some striking results were achieved, supporting the general analysis. Initially, the theory did not directly relate the thermal diffusion to the molecular weight so that that aspect was of a purely experimental character.

Not surprisingly, Debye also became interested in other aspects of polymer molecule behaviour. He treated theoretically the viscosity of their solutions and produced an interpretation of the important empirical method of evaluating the molecular weights of polymers from these viscosities. This method, first introduced by Staudinger in 1926, had been the subject of much discussion and disagreement. Another aspect of such solutions to which Debye became attached was micelle formation. As the concentration is increased in solutions of many medium molecular weight compounds, it can happen that there is a rapid, but reversible, agglomeration of the molecules to large clusters termed micelles. This process depends upon inter-molecular interactions of an attractive character and were it to continue to the level of macroscopic particles it would be an example of phase separation. These features, both micelle formation and the critical conditions reached in the separation of a new phase, now received Debye's attention. They were admirably suited for light scattering studies, but other techniques including X-ray scattering, ultra-sonic measurements and high-frequency electric methods were also used. These studies were being actively pursued up to the last weeks of his never less than extremely busy life. Even after his eightieth birthday he refused to contemplate the possibility that a just normally active schedule of scientific activity would be acceptable.

A single instance of his latter-day vigour must suffice as evidence of its unusually high level. The National Bureau of Standards held a conference in Washington in the spring of 1965: the subject was 'Critical phenomena'. Over eighty years of age, Debye made a great impression on an international audience of younger scientific leaders, many of whom had not previously experienced him in action at such a meeting. Despite the intensive modern developments in the subject he was able frequently to add important and illuminating comments to the discussions; those at the end of one session led the colleagues who heard them to insist on his writing them up separately. They are, accordingly, on record (23), as are the impromptu remarks (24) he made as chairman of one session where the first speaker was unable to present a contribution so that Debye took the opportunity 'to speak two minutes to give you my conception of what he would have said. I think he would have said that if you want to look at what radiation is going to do when it falls on a medium with irregular fluctuations, you have to characterize these fluctuations first in a phenomenological way . . . characterizing these fluctuations by a correlation function . . . this correlation function has to be a correlation function in space as well as in time . . . from this correlation function you can calculate the intensity of the scattered radiation directly by



a simple Fourier transformation . . . you have to look at two things in the intensity distribution. First, how is the intensity distributed over the angles? This geometrical feature gives you an opportunity to characterize a length . . . you can also make a spectral investigation of the scattered light, which would be characteristic for time correlations . . . this is characterized by a correlation time or by a relaxation time, if you want to call it that way, depending on the circumstances. This would be completely phenomenological.

'I was prepared to tell him that this is a linear theory, which you generally call a Born approximation. If you come to the neighbourhood of the critical point, the correlations become bigger and bigger and bigger, so that probably your linear theory will not work any more. If you want to tell something about the angular distribution of the frequency distribution of the scattered radiation derived from actual observations, you have to introduce the right theory. The linear theory may not be correct at the critical point, because you get such big fluctuations. So I had hoped to induce him to say something about the second approximation and about what we are going to see there.'

Professor Widom has summarized his later research activities at Cornell (25): 'The major thrust of his work at Cornell was certainly scattering from amorphous media, mostly light-scattering, applied to the determination of the sizes and shapes of the scattering centres . . . With his 1959 paper on critical opalescence Debye started to apply his light-scattering ideas and techniques to the study of critical phenomena, especially to critical mixing points in solutions, where from the intensity and angular dissymmetry of scattered light one obtains a measure of the magnitude of the huge concentration fluctuations that characterize a critical point and a measure of their spatial extent, or of the distance over which they are correlated. In his theoretical work on this subject he essentially re-derived (without fully realizing it) the Ornstein-Zernike theory of critical opalescence . . .

'Debye interpreted the earlier light-scattering measurements of Zimm in terms of this theory, showing that they fit in their major features, and he went on to make measurements of his own. He really initiated the systematic measurement, by light-scattering, of correlation lengths near critical points, now a very active and important subject. Besides studying the critical mixing point of solutions of "small" molecules, he made analogous measurements near the critical solution point of polystyrene solutions, thus making contact with his earlier polymer work. Also, he managed to make contact with his early love, electrical forces, by predicting, and then measuring, the effect of an electric field on the critical solution point and on the associated critical opalescence. Indeed, he saw in this effect the possibility of determining the relaxation time of the concentration fluctuations, which was his last pre-occupation before his death (Bibliography, 1967). He hoped also to see the space-and-time dependence of critical concentration fluctuations by direct visual observation (not the electric field effect): this was the subject of the



last, posthumous paper (1968). The whole question of the space-and-time dependence of fluctuations, the relation between them and their manifestation in the spectral width and shape of scattered light was the central issue in the remarks he made at the Critical Phenomena conference.'

Debye's 'retirement' from the active headship of the Department at Cornell University had included a heavy programme of lecturing and consulting up and down the U.S.A. and usually two trips per annum to Europe, on one of which he would visit his sister in Maastricht. One such trip was to be in June-July 1965 when he planned to attend meetings in Germany and the U.K. and to visit Maastricht: he was busily engaged on the details of a study week he was organizing for the Pontifical Academy of Sciences at the Vatican City on the subject of Molecular Forces, and he was due to address the IUPAC Polymer Conference at Prague. These were merely his European plans at the age of eighty-one. Most of them, however, were abandoned. He wrote in February 1965: 'A medical check-up which I had a few days ago has disturbed all that. My doctor declares that I am carrying much too heavy a load, which according to him and in his words is "killing me" . . . I am not an invalid by any means and may still have a birthday or two in conformity with your good wishes.' This appraisal could be taken to suggest that his judgement on personal affairs was as sound as on scientific matters. He attended the Prague meeting in September 1965 but suffered a heart attack in April 1966 at Kennedy Airport when leaving on another European trip. Even then it is recorded that within a month he had resumed activities, including travelling to lectures and consultations. Certainly he returned to active participation in his group's work at the Cornell laboratories and when finally obliged to take to hospital he at first successfully insisted on having the use of a telephone to the laboratory in his oxygen tent. 'Where your treasure is, there will your heart be also.'

#### HIS SCIENTIFIC STATUS

Debye's work embraces so many major contributions to present-day chemical physics that it would be a most difficult task fully to appraise it. Fortunately a detailed appraisal is unnecessary as the student of that area in science needs no more than the reminder: *Si monumentum vis, circumspice*. Were an adequate assessment to be attempted it would require a careful evaluation of what precisely had preceded Debye's work on a variety of topics and (an even larger task) what were the developments directly attributable to his contributions: only then would the true extent of its value be established. For the present a summary list of only the major items need be attempted. With an indication of any earlier contribution of significance this might be:

Specific heats of crystalline solids (Einstein).

Electric dipole moments (Langevin).

The dielectric medium and molecular dipole relaxations.

Lattice vibrations and X-ray diffraction.



The rule for quantization in terms of classical mechanics.

X-ray diffraction by powders: amorphous materials: liquids: and gaseous molecules.

The space-quantization of electron orbits (Sommerfeld).

The electron-atom energy exchange (Compton).

Equilibrium properties of strong electrolyte solutions (Milner): their conductance and its frequency and field dependence.

Adiabatic demagnetization.

Phonon theory and the diffraction of light by sound waves.

Light scattering by solutions (Rayleigh, Einstein): the weights and shapes of polymer molecules.

The question can at least be asked whether, in the broad area of molecular physics, any single individual since Faraday has contributed so much.

Perhaps one spot-check on the magnitude and quality of Debye's gifts may be proffered the reader. In the volume *Chemistry at the Centenary (1931) Meeting of the British Association for the Advancement of Science* there are three brief reports by Debye of his contributions at the London meeting (1932). Each was on a different topic of major interest; each was being pursued in his own laboratory; and each was the result of his own original contributions to molecular science. Scarcely anything in these statements needs to be modified today: more than that, within their brief compass and at their level, it would be difficult, even forty years later, to give more clearly or more correctly a better synopsis of these three topics. They provide examples for all to study of that power of insight and mastery of expression which characterized the genius that was Peter Debye.

Debye's career was of a piece with the quality of his mind and his energy. There was a frequent change of location, as of interest, and a measured description of it has the same limitations as those of a kaleidoscope: the clarity and brilliance are accompanied by repeated changes of pattern and significance. Thanks to their fundamental character and their very high degree of originality it is possible that his pre-1920 contributions outweigh in significance even the totality of his many subsequent achievements. The decade 1910-1920 provided the foundations of a new molecular physics on which we are still building. The last decades, spent essentially in physical chemistry, cannot compare with his European period in physics. Whilst it needed a Debye to evolve the light-scattering method in its powerfully complete theoretical and experimental form, it is certain that some of his many interests in polymers could equally well have been developed by others. The chemical physicist is thus left with the still profitable exercise of considering what further branches of molecular behaviour Debye might have pursued had he remained in closer contact with physics after 1945.

Debye's status was acknowledged, apart from his Nobel Prize, by the conferment of honorary degrees by sixteen universities (including Oxford) and by his election to twenty or more national or regional scientific academies. A list of the major medals presented him suggests a roll-call of the



pioneers on whose work he built: with the countries making the award, these included the honours associated with Lorentz (Netherlands), Rumford and Faraday (the Royal Society and the Chemical Society, U.K.), Max Planck (Germany), Joseph Priestley, Benjamin Franklin and Willard Gibbs (U.S.A.). One distinction which pleased Debye perhaps before all others was the unveiling in 1939, in the Town Hall of his native Maastricht, of a shoulder-length bust. It is, in any case, certain that Debye never placed himself on a pedestal and there is likewise no chance that his place in molecular science will diminish with his passing. He belonged to a generation of academic scientists who rated themselves on the quality and continuity of their contributions to their chosen field, criteria now often diluted with other more general activities.

#### PERSONAL QUALITIES

It remains only to attempt a picture of the man, Peter Debye. This can fortunately be done with far greater conviction than a single individual could achieve by reference to the numerous appreciations written of him by colleagues and friends, some of whose close relations with him extended over several decades. A reader who did not himself know Debye will thus become convinced that he was an extremely pleasant, lively character who was fully as able to contribute pleasure to his friends and associates as to add to their insight on scientific matters: and that not only was he able to do this, but that he constantly enjoyed doing so.

His teacher, Arnold Sommerfeld, has already been quoted on Debye's prowess as a theoretical physicist. Forty-five years after first meeting his pupil he was to say (1): 'His motto in science and in life I would give as "It's all terribly simple"—("Das ist alles furchtbar einfach")'. I have recently heard this from his lips as he retailed his present work on the long, coiling, molecular chains of fibrous materials.'

Professor R. M. Fuoss, an associate of many years in the U.S., wrote in 1954 (26): 'Debye is known to his colleagues through his published work, but better by his active participation in meetings and by the lectures he delivers on various occasions . . . And to hear a Debye lecture is a real treat: he has an uncanny skill in presenting seemingly complicated subjects in a fashion which gets to the nub of the problem with a penetrating clarity. Best of all, though, Debye is known as one to whom we can go for research advice. As described in the citation from Harvard when he was made an honorary alumnus, Debye is "a large-hearted physicist who gladly lends to the chemist a helping hand".'

Debye's immediate colleagues at Cornell University (Professors Sack, Widom and Bauer) have characterized his *modus cogitandi* (27): 'In science, as in art, there is style. Debye's theories, his ways of looking at physical phenomena and of expressing his understanding of them, were as uniquely Debye's as a painting is unmistakably an El Greco or a van Gogh. The essential element of his style was simplicity, which for Debye was not merely



a technique: it was an earnest conviction. He knew that physical phenomena must have simple explanations; he took complexity to be lack of understanding. If a theory was not yet simple then it was not yet right—it was unfinished and imperfect. To achieve simplicity one must identify the essentials and isolate them from the irrelevancies. To recognize the essentials, to express them clearly and pictorially, and then to pursue their consequences with superb technical facility was Debye's style.

'... Though he had mathematical abilities of the highest level (one of his earliest papers contained the independent discovery of the method of steepest descents, and its application to the asymptotic behaviour of Bessel functions), he had a deep distrust of overly mathematical theories, and dismissed as "mere mathematics" any explanation of a physical phenomenon that lacked a concrete, visualizable basis.

'... Almost unique among theoreticians, he was not only vitally interested in explaining experimental results and suggesting new experiments to test a theory, but he participated actively by giving practical advice, designing new laboratory techniques, and following the day-to-day progress of his experimental co-workers... A number of his investigations actually started from industrial problems that came to his attention. It is thus not surprising that he was much sought after as a consultant.'

Reference has already been made to Debye's exceptional effectiveness as a lecturer. He possessed great facility of expression in the major European languages. His powers of clarification were a consequence of his own understanding. His mind penetrated farther than most and, equally remarkably, it seemed to possess a highly discriminating mechanism which almost automatically focused on the principal features in a hitherto unknown area. His own account of a colleague's book provides an indication of much more than the virtues he wished to praise in another's writing (28).

'The development, after the introduction of any new subject, is never presented as an example of strictly logical deduction from experimental evidence, carefully arranged *post factum*. Nor is it derived as a logical sequence of a mathematical formulation, appearing seemingly from nowhere at the very beginning of the argument.

'The sequence is described as it really happened, with historical truthfulness, and the idea is developed from its inception concurrently with its mathematical formulation from its starting point to the end. This, it seems to me, is the way to convey to the uninitiated reader that our science is essentially an art which could not live without the occasional flash of genius in the mind of some sensitive man, who, alive to the smallest of indications, knows the truth before he has the proof.'

The interplay of experiment with theory was never far from peak intensity in Debye's scientific thought. Professor Sack writes (21):

'What impressed me especially was his knack for making order of magnitude calculations that allowed a judgement of the feasibility of the experiment, his perseverance once he was convinced that meaningful results



would be obtained, and his attention to details, once the design was agreed upon. Just as he was an unsurpassed master in choosing the most appropriate mathematical techniques to solve a theoretical problem, he was very ingenious in choosing or inventing the most appropriate experimental techniques too . . . His abilities as lecturer and teacher were particularly evident in his big introductory physics courses (e.g. to *ca.* 400 students in Leipzig) which he gave from 1920 to 1934 in Zürich and in Leipzig . . . Debye gave great attention to keeping the lecture demonstrations meaningful and up to date. Only a few months after the first observation of electron diffraction, such an experiment was shown in his lecture (using an old-fashioned CRT that had to be constantly pumped and a Wimshurst-type electrostatic generator for voltage supply, which would barely work on a hot and humid day).'

Not only did Debye successfully explain scientific ideas and principles to audiences as diverse as school children, research specialists and business executives but his presentation also communicated his own enthusiasm for yet further exploration of the subject. Naturally, his Dutch colleagues have particular memories of his ability as a lecturer. They comment approvingly on the quite unspoilt retention of his native accent and of characteristic Limburg diction. His presentation of the Hustinx Prizes in 1962 was the reason for a popular lecture at Maastricht on 'The measurement of molecules'. On this singular occasion (he was lecturing in the theatre where his mother had been employed) he gave the largely lay audience a clear insight into quantitative aspects of the molecular world. He was able to show not only his own attachment to Maastricht and its people but to share with them his enthusiasm for exploring the physical world. Some of his introductory remarks (they were in Dutch) may be quoted:

'Ladies and Gentlemen,

'I have peculiar feelings while I stand here today.

'Firstly, I am thinking back to the day when as a youth of sixteen years, I experienced paradise in this building. That was when I attended my first opera performance—Gounod's *Faust* it was.

'I also recollect the occasion of thirty years ago when I had the opportunity to deliver an address in this building. Today, however, I have to think of the part I am playing in a very important occasion. This occasion is the handing over of the Hustinx Prizes.

'Finally I must also think of Maastricht. This town is well known for its hospitality, which would imply that the visitor must be treated in such a way that he feels completely at home. This would certainly mean that he must be addressed in such a way that he can understand everything. Therefore, as many of the visitors and acquaintances here today are Germans, I have decided to deliver my address in German.'

It was typical of Debye that when he attended a conference he participated fully. He would normally listen to all the contributions. Professor Long has written (29): 'At a recent conference, after he had just given his own talk in



the morning session and was returning to listen to the afternoon session, one of his friends suggested that, given his eighty years and the 9000 feet altitude, he might preferably rest. Debye's reply was characteristic: 'No, no, no; if I listen to the talks I may get some new ideas.' '

All who knew Debye will instantly recall what a readily approachable and particularly friendly person he was. His research associates all emphasize how he insisted on enjoyment as an essential element in one's work. Professor Nauman recalls his initial instructions (30): 'Work when you wish: there is no eight to five schedule. Come when you want to come, leave when you want to leave: just get something done but most of all have fun in your work.' Despite this completely relaxed approach on detail it should not be thought that Debye could suffer fools or fooling-about gladly. He had a keen appreciation of the value of time, especially his own time. This can be illustrated by Professor Nauman's memory of a telephone conversation of Debye's with a firm for which he had done some consulting: 'Yes, I would be pleased to visit your laboratories again . . . Yes, I received your cheque for expenses and honorarium . . . No, it was not satisfactory. I would rather visit your laboratories for nothing than be insulted by being offered such a small honorarium as that you sent last time. I find your problems interesting, but your policies are insulting . . . Yes, I will come.'

'He was an avid trout fisherman. He caught trout in the streams near Cornell where there were few. First he stalked the fish by walking and watching the stream without his rod. Later he sought the trout whose habits he had observed. After catching them, he released them, to be caught another day' (30). This interest and ability derived from his earliest days in Maastricht when his grandfather would take him fishing. And catching a fine fish was not an acceptable reason for going home—the young boy of ten protested strongly against a halt being called.

'Debye was an affectionate husband, father and grandfather. His principal hobbies were gardening and fishing and both were done with the steady participation of his wife. In 1948, when the Debyes were well over 60, they took over the principal upbringing of two of their young grandsons, and it was a matter of great pleasure to Debye that, by the time of his death, both of the boys were successful graduate students' (29).

And finally we may quote from some remarks made at Cornell University by Professor Henri Sack, a close colleague of Professor Debye's for over forty years (31): 'I have tried to find a simple attribute—if this is possible—with which to characterize Professor Debye's multifaceted personality, and feel that I come nearest to my personal image of him by saying that he was a truly happy or lucky man. He was not only endowed with a most powerful and penetrating intellect and an unmatched ability for presenting his ideas in a most lucid way, but he also knew the art of living a full life. He greatly enjoyed his scientific endeavours, he had a deep love for his family and home life, and he had an eye for the beauties of nature and a taste for the pleasures of the out-of-doors as manifested by his hobbies such as fishing, collecting



cacti, and gardening, mostly in the company of Mrs Debye. He enjoyed a good cigar and a good table, and he had affections for his students and associates and liked their company . . .

'At several occasions Professor Debye remarked that he did only those things he liked to do . . . he never was envious of other people's success; to him his own pastures were always the greenest and his greatest ambition was to do a perfect job of whatever problem he tackled. He did not worry whether he was called a physicist or a chemist . . . I am sure his greatest satisfaction came from the knowledge of having discovered something new, enhanced the understanding of a known phenomenon, or succeeded in communicating his ideas to others.

' . . . His eagerness to do any job well if it was worth doing at all was also reflected in his private life. In gardening he became a real expert, and his parties were always something special.

'His frequent comment in colloquia and meetings "Aber das ist ja so einfach" ("Look here, this is really *so* simple") has already become a Debye legend . . . For him the physical sciences were not a series of narrow specialities, but a coherent body of knowledge, where a few basic principles weaved like a red thread through the whole field. He was helped in his constant endeavour to correlate phenomena from different areas by his phenomenal memory. He may have forgotten the exact name of the author or the exact place of the publication, but he never forgot the essence of what he had read in a paper or heard at a meeting.

'At times Professor Debye could also be a stern task master. His criticism could be very articulate, especially in the early years. There could be no compromise when scientific truth was involved . . .

'And thus, I believe I can speak in the name of all those who had the privilege of having been closely associated with Professor Debye, in saying that we are grateful for all he has given us and that he will live in our memory as a brilliant scientist, a great teacher, a fatherly and helpful adviser, and, above all, as a happy man.'

A number of Professor Debye's colleagues and others have helped by providing information, references or permission to quote their own statements. Thanks are especially due and are gratefully offered to Professors S. H. Bauer, P. P. Ewald, F.R.S., R. M. Fuoss, W. Heisenberg, For. Mem. R.S., F. Hund, H. S. Johnston, F. A. Long, C. Manneback, R. V. Nauman, L. C. Pauling, For. Mem. R.S., A. J. Rutgers, H. S. Sack, E. J. W. Verwey and B. Widom (who also provided reprints). The Burgemeester of Maastricht, Dr A. M. I. H. Baeten and his secretary, Mr Minnis, generously provided photostats of local records and other publications, as did also Dr J. A. Poulis (Eindhoven) and Professor Debye's friend, Mr Edmond Hustinx of Maastricht, sent further material. Professor Hooykaas, Mrs Schotman and Dr Verwey helped at Utrecht, and Mrs M. H. J. Niël, Professor Debye's niece, contributed details of the family.

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thanked for allowing quotations from *The Collected Papers of Peter J. W. Debye*. The photograph of the 1927 Solvay Conference facing p. 184 is reproduced by courtesy of the Instituts Internationaux de Physique et de Chimie Solvay. The portrait is by W. Mantz, Maastricht, Netherlands.

Miss Glenys Owen is largely responsible for the bibliography; Mr Philip Davies sought literature; and other Aberystwyth colleagues, Mr Arnold Baise and Dr William Engelbrecht, helped with the Dutch sources; and Mr Huw Ceredig with proof-reading.

MANSEL DAVIES

#### APPENDIX A

Institut für Physik

8 München 23,  
Föhringer Ring 6  
16th January, 1970

Dear Professor Davies,

You ask me about the time when I worked together with Professor Debye in Leipzig some forty years ago. At that time Debye was mostly interested in X-ray measurements of the structure of molecules, and frequently discussed his problems with me. He had a strong interest in the theoretical side of these problems, and occasionally he asked me to work out details for him. For instance, for the calculations of X-ray scattering by atoms he used the Thomas-Fermi model as an approximation, and he urged me to evaluate the incoherent part of X-ray scattering from this model. Occasionally he took part in our theoretical seminars, e.g. when we discussed the quantum theory of ferromagnetism. Debye had not much interest for political questions and therefore he preferred to disregard as much as possible the political riots on the streets of Leipzig. He hoped—as many Germans did—that the extreme tendencies in the national-socialistic revolution would die down, so that Germany could return to a more or less normal state of political life. As a Dutchman he did not feel responsible for what happened in our country. Debye had a certain tendency to take things easy. He did not belong to that class of scientists who come to the laboratory very early in the morning and leave it not before midnight. From my room in the institute I could frequently see him walking around in his garden and watering the roses even during duty hours of the institute. But the centre of his interest was undoubt(ed)ly his science. When he saw with the beginning of war that he could not continue this quiet life of a scientist, he decided to leave Germany. He would not have been obliged to leave Germany according to German laws or to the tendency of the university or government officials. In 1936 or 1937 Debye had moved from Leipzig to Berlin, where the Kaiser Wilhelm Society had built a new institute for him. During the war some members of his family have lived in the house connected with the institute still a few years, but—if I remember correctly—they all left not later than 1942.

With best regards,

Yours, W. HEISENBERG.



College of Chemistry Newsletter, University of California, Berkeley.  
September 1969.

Letter from Professor E. Rutherford to Professor G. N. Lewis:  
December 1915.

Dear Lewis,

I have received your letter of November 19th asking me my opinion about Debye and Bohr, from the point of view of lecturers in Mathematical Physics.

I do not know Debye personally but I believe he is regarded as one of the best mathematicians of the day, and was recently appointed Professor in Göttingen in succession to Professor Voigt. As you know, he is a Dutchman by birth, and is undoubtedly a man of great ability both on the Mathematical and Physical side. I am unable to express any opinion about his lecturing qualifications etc. but my experience is that most Dutchmen speak English quite well.

Bohr, as you know, holds the position of Reader in Mathematical Physics in my Laboratory. I regard Bohr as one of the coming men in Mathematical Physics, and I think he has a better grip of Physics than any of the Mathematical people I have come across. He is a man of great originality, and, as you know, his work has already attracted wide attention, and I am confident will do so even more in the future. As a matter of fact, I think Bohr is just the type of man that would fill your bill. He is thoroughly *au courant* of all the modern physical problems, and has an extraordinarily wide knowledge of experimental as well as of theoretical Physics. He is a pleasant fellow, speaks English quite well, and is quite a clear and interesting lecturer.

I do not, of course, know how he would regard a visit to California, especially in war time. As you probably know, he is a Dane, the son of the late Professor of Pathology in the University of Copenhagen, and I believe he is likely soon to be given a Professorship in that University. He has a very charming wife.

I am at present very much occupied with Admiralty work, and have practically no time for my own investigations. My Research School has vanished to Flanders or to the Dardenelles, but we still have a good number of women students, and men physically unfit and under age, so we have to keep all our classes going.

Yours sincerely,  
E. RUTHERFORD.

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