53.

P. N. LEBEDEV'S IDEAS ON THE NATURE OF MOLECULAR FORCES

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THE strictest and fairest judge of scientific accomplishments is undisputedly time. And now, some 70 years after P. N. Lebedev's basic work on the measurement of the pressure exerted by light on solids and gases, we not only can see much more clearly the historical significance of this work against the background of development of science at that time, but also fully appreciate their fundamental and ever expanding influence on modern physics and astrophysics. It suffices to indicate that light pressure is the most direct experimental basis of Einstein's equivalence principle as applied to photons. The significance of light pressure in astrophysics increases approximately exponentially. And all this is not an accident, for nowhere does a scientist's intuition come into play more than in the choice of a topic or field of research capable of exerting a powerful influence on the development of science.

But Lebedev's intuition is manifest not only in the choice of a research trend. No less striking is his experimental physicist's intuition in the understanding of the nature and mutual connection of phenomena.

Among the most striking examples are those ideas concerning the nature of molecular forces, which were developed by him with particular detail in his Russian doctoral dissertation.

The very fact that Lebedev has considered in parallel astrophysical problems and the forces acting on molecules sounds quite modern and physically rigorously founded. Indeed, for comet gas tails and for gas stars, light pressure is the result of the action of waves on individual molecules. But if molecules can be excited, like resonators, by incident waves, then they can also emit them. From this it is but one step to a consideration of the interaction between molecule pairs via emitted and absorbed electromagnetic waves, and only a second step to identification of this interaction with molecular forces. However, only a scientist with a physical logic developed to the utmost and with the courage of a true discoverer, such as Lebedev dreamt to be in his youth and actually became, could make these two steps.

To gain a clear idea and to verify the extent to which Lebedev's ideas were in advance of his time and close to modern concepts, it is sufficient to cite the following items from his doctoral dissertation, published in Wiedemann Annalen in 1894 [1]. Considering the question of the ponderomotive action of waves on resonators, he wrote: "Hidden in Herz's research,

in the interpretation of light oscillations as electromagnetic processes, is still another as yet undealt with question, that of the sources of light emission, of the processes which take place in the molecular vibrator at the time when it gives up light energy to the surrounding space; such a problem leads us, on the one hand, into the region of spectral analysis, and on the other hand, quite unexpectedly as it were, to one of the most complicated problems of modern physics – the study of molecular forces. The latter circumstance follows from the following considerations: Adopting the point of view of the electromagnetic theory of light, we must state that between two radiating molecules, just as between two vibrators in which electromagnetic oscillations are excited, there exist ponderomotive forces: They are due to the electrodynamic interaction between the alternating electric current in the molecules (in accord with Ampere's laws) or the alternating charges in them (in accord with Coulomb's laws); we must therefore state that there exist between the molecules in such a case molecular forces whose cause is inseparably linked with the radiation processes..."

"... Of greatest interest and of greatest difficulty is the case of a physical body in which many molecules act simultaneously on one another, the vibrations of the latter not being independent, owing to their close proximity. If this question is ever solved completely, then, by using spectral-analysis data, we shall be able to calculate beforehand the magnitudes of the intermolecular forces due to the mutual radiation of molecules, to determine the laws governing their temperature dependence, and by comparing these calculated quantities with experiment answer the basic problem of molecular physics: Do all the so-called "molecular forces" reduce to an a priori known ponderomotive action of the radiation, as indicated above, to the electromagnetic forces, or do they include also other forces of still unknown origin"?

"... We have before us a large task – to study more complicated problems on the basis of the obtained results and, using direct experiments, to verify our concepts with their aid, or to investigate new, perhaps unexpected, peculiarities of the ponderomotive forces of interest to us; moving carefully and assuredly along this path, we can obtain also the solution of our main problem, that of calculating from spectral-analysis data the absolute magnitude of the interaction forces, due to mutual radiation, between

molecules of any body."

What Lebedev wrote approximately 70 years ago is not only a striking prediction of modern notions concerning the mechanism of molecular forces, and not molecular alone, but is at the same time essentially a clear cut and broadly conceived program for research on molecular and atomic interactions. What was lacking most for its realization at that time, however, was quantum mechanics and knowledge of atomic and molecular structure. Therefore the problem of constructing a quantitative theory of molecular forces was insoluble at that time. It was solved in first approximation only in the thirties, by London. However, compared with Lebedev's concepts, this was a backward step: the calculation was carried out in the electrostatic approximation and the molecular forces were attributed a quantum-electrostatic nature.

The first to use quantum electrodynamics for the calculation of forces between molecules (and also metals) was the Dutch theoretician Casimir[2] (together with Polder). He took into account the electromagnetic retardation in the propagation of electromagnetic oscillations from one molecule to another, which in the limit of large distances transforms the r^{-7} law into an r^{-8} law. Thus, the best confirmation of the electromagnetic nature of molecular forces was an investigation of the forces between molecules at large distances. With this, the transition between the two laws takes place at distances on the order of hundreds of Angstrom units (corresponding to a certain fraction of the characteristic wavelengths of the absorption spectrum of the bodies). However, the solution of this problem is hindered by the fact that, in all the previously investigated effects, the main contribution is made by interactions between nearest-neighbor molecules. Thus, for example, the heat of wetting is determined primarily by the interaction between the wetted surface and the liquid molecules which come in direct contact with it, and the contribution of the molecules located at distances larger than several hundred Å is too small to be detected. The most accurate information on molecular forces is given by calculation of the virial coefficients of gases. But even in gases, in spite of the appreciable mean distances between neighboring molecules, the main contribution is made by molecules which are closely located, for example, at the instant of collision or near this instant.

The problem of directly measuring molecular attraction as a function of the distance, including large distances (on the order of 10^{-5} cm), was first formulated by myself, initially in conjunction with F. B. Leïb[3]. The final development of the procedure and the measurements were made in conjunction with I. I. Abrikosova[4]. The procedure developed has made it possible to measure attraction forces between a number of pairs of solids (quartz-quartz, thallium halide -

thallium halide, quartz - chromium), separated by a vacuum or air gap of width 700—4000 Å. We show in the figure the dependence of the attraction force F of a quartz segment of 11-cm radius to a quartz plate, as a function of the gap width H. We shall not describe the procedure or present all the measurement results, referring the reader to the corresponding publications. We note only that the procedure was based on stabilization and regulation of the gap between the bodies with the aid of negative feedback. The negative feedback was produced with the aid of a raster-type photoelectronic relay and made it possible to measure by a null method the attraction force at any distance.

It should be noted that simultaneously with our measurements, Overbeck and Sparnaay reported measurements (by another method) of the molecular attraction of glass plates[5]. These measurements, however, were crudely in error because insufficient measures were taken to eliminate surface charges, and the results were overestimated by 3—4 orders of magnitude (!). The results of our measurements were subsequently duplicated, first by Kitchener[6] in London, and later by many others, including Overbeck and Sparnaay. After the very first results were obtained (for the quartz - quartz pair), it was necessary to compare them with the theory, in order to check on the latter. However, comparison with the formulas of Casimir's theory encountered difficulties connected essentially with the non-additivity of the molecular interactions between the condensed phases, a non-additivity which as a rule is forgotten, for example, when the methods for calculating dispersion forces, which are valid for gases (for which additivity of the forces holds) are used for solids or liquids.

Yet, non-additivity of molecular forces, connected with the mutual influence of neighboring molecules, was clearly indicated by Lebedev in the statements cited above.

Incidentally, the order of magnitude and the law governing the decrease of the forces with distance are not distorted by non-additivity, and approximate agreement was observed between our data and the theory of Casimir and Polder.

A more accurate comparison with theory was made possible after E. M. Lifshitz[7] developed the macroscopic theory of molecular attraction of macroscopic objects. This theory is based on the presence in all bodies, even at absolute zero temperature, of quantum fluctuations of the electromagnetic field. The propagation of these fluctuations in the form of waves produces in the gap between the surfaces an electromagnetic field, whose ponderomotive action (using the terminology prevailing in Lebedev's time) in the gap between the two bodies leads to their mutual attraction. For gaps whose width is much larger than the wavelengths characteristic of the given bodies, the formula for the attraction force f
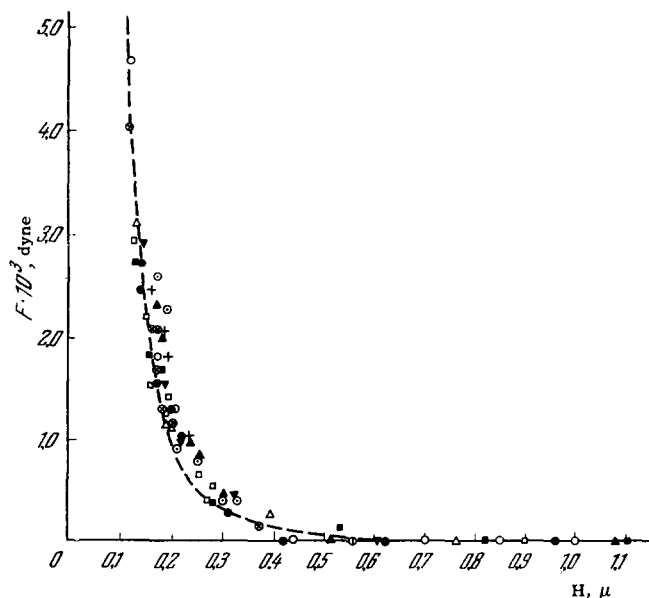
FIG. 1.

simplifies and assumes, for two identical bodies, the form

$$f = \frac{\hbar c}{l^4} \frac{\pi^2}{240} \left(\frac{\varepsilon_0 - 1}{\varepsilon_0 + 1}\right)^2 \varphi(\varepsilon_0), \qquad (1)$$

where $\hbar$ and c are Planck's constant and the velocity of light in vacuum, ε_0 is the static value of the dielectric constant, and $\varphi(\varepsilon_0)$ is a function obtained as a result of numerical integration.

Comparison with the previously performed experiments for glass and quartz has proved that formula (1) is valid within the limits of the measurement errors (the solid line in Fig. 1 represents the theoretical data calculated by means of formula (1) with allowance for the radius of curvature of the segment). Agreement was also observed for the quartz - chromium pair and for a pair of plates made of the mixed crystal BrTl-ITl.

Confirmation of the formula for the molecular interaction for large distances, at which the finite propagation velocity of the electromagnetic waves (which is taken into account by this formula) comes noticeably into play, is a decisive proof of the electromagnetic nature of molecular forces. It can be stated that the answer to the question posed by Lebedev 75 years ago is that molecular attraction does indeed "reduce to electromagnetic forces" and does not contain "other forces of still unknown origin."

At the same time, Lebedev's prediction that the molecular forces are connected with the spectrum of a body was also confirmed. This connection is directly expressed in E. M. Lifshitz's formulas for medium and small gap widths between bodies [7]. We note also that Lebedev's indication of a temperature dependence of the molecular forces, a dependence

missing in London's formulas but included in Lifshitz's, is also justified, since the absorption spectrum of condensed bodies varies with temperature. The next important problem was to verify quantitatively the electromagnetic nature of molecular attraction for the case when it is produced not through a vacuum gap but through a film of liquid. By way of a very typical situation in which molecular long-range forces in liquids play the decisive role, we can take the interaction between any two phases, 1 and 2, which are situated in a liquid medium 3 and are close to each other (Fig. 2). If the liquid film separating the bodies is plane-parallel, then in order to maintain equilibrium it is necessary to apply to its surfaces an excess pressure $\Pi = \Pi(h)$. called the wedging pressure [8]. When effective attraction exists between the two phases, the wedging pressure is negative. This case is always realized when both phases are identical. The excess pressure can be the result of the curvature of the surfaces of both phases beyond the limits of the film separating them. We have previously used [9] the equilibrium observed in this case to determine the $\Pi(h)$ dependence. In [10] there was observed an equilibrium state of plane-parallel film between two gas bubbles, and the values of $\Pi(h)$ were thus determined. Equilibrium could be observed only when $\Pi(h) > 0$, and then the molecular attraction should be overlapped by repulsion forces of a different nature (in particular, repulsion forces arising when two ionic double layers overlap).

For the case when only molecular attraction forces act and the film does not change its properties when it becomes thinner, so that we always have $\Pi(h) < 0$, it is possible to determine this function, using an idea of A. D. Scheludko, by observing the reduction in film thickness under the joint influence of the effective attraction $[-\Pi(h)]$ and the capillary pressure $2\sigma/r$. To obtain correct results it is essential that the film thickness remain uniform while it becomes thinner, and that its viscosity remain constant.

This method yielded [11] the values of $\Pi(h)$ for films of benzene and chlorobenzene in the interval 300—600 Å. The experimental data were compared both with formulas obtained from Casimir's microscopic theory,,and from the more rigorous macroscopic theory of Dzyaloshinskiĭ, Litshitz, and Pitaevskiĭ [12], which generalized Lifshitz's formulas to include the case when the interacting bodies are immersed in a liquid.

Within the limits of a sufficiently large scatter, the experimental data agree with both formulas. By the same token, these experiments confirm the electromagnetic nature of the molecular forces.

FIG. 2.
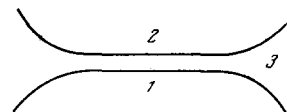
It may still be unclear why the net resultant of the molecular forces in a thin film, which tends to reduce its thickness, depends only on the action of the molecular forces at large distances. This, however, can be readily understood by recognizing that when the liquid flows out from the film into the surrounding liquid phase, the short-range molecular forces perform no work.

P. N. Lebedev's interests were not confined to the nature of molecular forces, but touched upon other fundamental problems of molecular physics. At his advice, his closest assistant and student, P. P. Lazarev, carried out an experimental investigation of the temperature jump on the boundary between a gas and a solid wall; V. Ya. Al'tberg investigated the attenuation of short acoustic waves. If we trace the sources of modern development of molecular physics research in our country, then most of them lead to Lebedev and his students. In this field, Lebedev's role as a teacher and a creator of a school is even larger than his role as a researcher. It is appropriate to mention in this connection that Lebedev's influence on this students was particularly strong because of his characteristic passion and lack of compromise in science.

Lebedev's high emotionality and his special relation to science remain in my memory from my school days, when I did not even plan to become a physicist. However, his emotional influence still retains its hold on me, and undoubtedly contributed greatly in work on difficult problems. To formulate difficult problems this perhaps is one of Lebedev's principal precepts. Lebedev's personal influence undoubtedly was transmitted to his students, primarily P. P. Lazarev and S. I. Vavilov, and is present in one form or another in our science even now, through the intermediacy of their students.

However, Lebedev himself succeeded in seeing only the first fruits of his influence. In Russia of that time there occurred for him a tragic discord between his desire and subjective ability of creating a school and the conditions for realizing this cherished goal.

His bitterness and personal tragedy permeate most clearly his article on Lomonosov and his similar tragedy. On Lebedev's 100th birthday we can, however, note with satisfaction that, unlike Lomonosov, we see not only the blossoming of his ideas, but also a school of physicists, the birth of which we owe P. N. Lebedev, a blossoming which became possible after the Great October Socialist Revolution.

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